CHAPTER 7

Densities, Coefficients of Thermal Expansion, and Compressibilities of Amorphous Polymers

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Tables in this chapter contain published pressure-volume-temperature data for amorphous homopolymers. Measurements below the melting temperatures for semi-crystalline materials are not included because of the potentially large variance among samples with differing degrees of crystallinity. Rogers [1] and Zoller [2] have also compiled equation-of-state data for amorphous polymers.

7.1 DENSITIES AS A FUNCTION OF TEMPERATURE

The temperature dependence of polymer densities at atmospheric pressure is given in Tables 7.1 and 7.2. Table 7.1 gives densities measured above the glass transition temperature T_g and, for semi-crystalline polymers, above the melting temperature. Table 7.2 lists densities of amorphous polymers below T_g. Volumetric data are presented here in terms of the density ρ rather than the more commonly reported specific volume $v_{sp} = 1/\rho$ because, for most systems, ρ is a more linear function of temperature than is v_{sp}. For most entries, the densities have been fitted to a power series

$$\rho(t) = a_0 + a_1 t + a_2 t^2 + \ldots, \tag{7.1}$$

with t representing the centigrade temperature. In the other cases, the polymer density is written as an exponential function of the centigrade temperature t

$$\rho(t) = \rho(0) e^{-\alpha_0 t}. \tag{7.2}$$

This latter form is for measurements in which the thermal expansion coefficient

$$\alpha = \frac{1}{v_{sp}} \left(\frac{\partial v_{sp}}{\partial t} \right)_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial t} \right)_P, \tag{7.3}$$

was found to be independent of temperature; i.e., $\alpha = \alpha_0$. Additional density data can be found in Chapter 29.

Tables 7.3 and 7.4 are compilations of densities and thermal expansion coefficients at one atmosphere tabulated at 20 °C intervals. Measurements below T_g are indicated by a *g* preceding the value. Some of the entries in these tables are taken directly from the published reports; consequently, there are occasional small variations between these values and those computed from the smoothing expressions in Tables 7.1 and 7.2. Densities judged to be more accurate than $\pm 0.001 \text{g/cm}^3$ are recorded in Table 7.3 with an additional digit. Thermal expansion coefficients can also be determined from the power series expressions in Tables 7.1 and 7.2 using

$$\alpha = -\frac{a_1 + 2a_2 t + \ldots}{a_0 + a_1 t + a_2 t^2 + \ldots}, \tag{7.4}$$

which follows from Eqs. (7.1) and (7.3).

TABLE 7.1. *Densities, measured above T_g, as a function of temperature.*

Polymer	ρ, g/cm^3, (t in °C)	Temp. range, °C	Ref.
Natural Rubber, unvulcanized	$0.9283 - 6.10 \times 10^{-4}t$	0–25	[3]
Natural Rubber, cured	$0.9210 - 5.86 \times 10^{-4}t$	0–25	[3]
Polyamide, Nylon 6	$1.316 \exp(-4.70 \times 10^{-4}t)$	236–295	[4]
Polyamide, Nylon 6,6	$1.306 \exp(-6.60 \times 10^{-4}t)$	245–297	[4]
	$1.145 - 6.47 \times 10^{-4}t$	270–285	[5]
Poly (butene-1), isotactic	$0.876 \exp(-6.75 \times 10^{-4}t)$	133–246	[6]
Poly(*n*-butyl methacrylate)	$1.0695 - 5.82 \times 10^{-4}t - 0.98 \times 10^{-6}t^2 + 0.241 \times 10^{-8}t^3$	34–200	[7]
	$1.070 - 6.95 \times 10^{-4}t + 0.40 \times 10^{-6}t^2$	20–120	[8]
Poly(ε-caprolactone)	$1.110 - 7.81 \times 10^{-4}t + 0.519 \times 10^{-6}t^2$	101–148	[1]
Polycarbonate, (with Bisphenol *A*)	$1.254 - 6.35 \times 10^{-4}t - 0.116 \times 10^{-6}t^2$	151–340	[9]
	$1.2739 \exp(-6.21 \times 10^{-4}t)$	171–330	[38]
Poly(cyclohexyl methacrylate)	$1.1394 - 5.90 \times 10^{-4}t - 0.163 \times 10^{-6}t^2$	110–199	[7]
Poly(2,6-dimethylphenylene ether)	$1.168 - 6.95 \times 10^{-4}t - 0.070 \times 10^{-6}t^2$	203–320	[10]
Poly(dimethyl siloxane)	$0.9919 - 8.925 \times 10^{-4}t + 0.265 \times 10^{-6}t^2 - 0.0030 \times 10^{-8}t^3$	20–207	[11]
	$0.994 - 9.76 \times 10^{-4}t + 0.904 \times 10^{-6}t^2$	25–70	[12]
	$0.990 - 8.59 \times 10^{-4}t + 0.23 \times 10^{-6}t^2$	16–145	[49]
Poly(1,3-dioxepane)	$1.064 - 3.5 \times 10^{-4}t$	6–16	[43]
Poly(1,3-dioxolane)	$1.254 - 10.9 \times 10^{-4}t$	25–80	[44]
Polyetheretherketone	$1.397 \exp(-6.69 \times 10^{-4}t)$	338–400	[13]
Polyethylene, branched	$0.868 \exp(-6.73 \times 10^{-4}t)$	112–225	[14]
	$0.882 - 7.97 \times 10^{-4}t + 0.74 \times 10^{-6}t^2$	135–198	[7]
Polyethylene, linear	$0.8674 - 6.313 \times 10^{-4}t + 0.367 \times 10^{-6}t^2 - 0.055 \times 10^{-8}t^3$	130–207	[15]
	$0.863 - 4.73 \times 10^{-4}t - 0.38 \times 10^{-6}t^2$	142–200	[7]
Poly(ethylene terephthalate)	$1.390 - 7.82 \times 10^{-4}t$	274–342	[16]
Poly(ethyl methacrylate)	$1.156 - 6.59 \times 10^{-4}t$	65–95	[8]
Polyisobutylene	$0.9297 - 5.123 \times 10^{-4}t + 0.0615 \times 10^{-6}t^2$	0–150	[17]
Poly(methyl methacrylate)	$1.223 - 5.29 \times 10^{-4}t - 0.507 \times 10^{-6}t^2$	120–270	[18]
	$1.2135 - 4.64 \times 10^{-4}t - 0.648 \times 10^{-6}t^2$	114–159	[7]
	$1.228 \exp(-5.23 \times 10^{-4}t)$	115–230	[4]
	$1.211 - 5.96 \times 10^{-4}t$	105–150	[8]
	$1.229 - 7.12 \times 10^{-4}t$	110–194	[48]
Poly(methyl methacrylate), isotactic	$1.252 - 8.40 \times 10^{-4}t + 0.56 \times 10^{-6}t^2$	55–190	[19]
Poly(4-methyl pentene-1)	$0.843 - 5.11 \times 10^{-4}t$	240–319	[45]
Poly(*o*-methyl styrene)	$1.064 - 5.58 \times 10^{-4}t + 0.125 \times 10^{-6}t^2$	139–198	[20]
Polyoxybutylene	$0.985 - 6.82 \times 10^{-4}t$	30–90	[42]
Polyoxyethylene	$1.142 \exp(-7.09 \times 10^{-4}t)$	88–224	[1,21]
	$1.140 - 8.08 \times 10^{-4}t$	30–90	[42]
	$1.139 - 7.31 \times 10^{-4}t$	75–136	[47]
Polyoxymethylene	$1.336 \exp(-6.77 \times 10^{-4}t)$	183–220	[22]
Polypropylene, atactic	$0.848 - 0.19 \times 10^{-4}t - 3.05 \times 10^{-6}t^2$	80–120	[1]
Polypropylene, isotactic	$0.859 \exp(-6.60 \times 10^{-4}t)$	175–230	[4]
	$0.862 \exp(-6.70 \times 10^{-4}t)$	170–300	[6]
	$0.8414 - 3.79 \times 10^{-4}t - 0.316 \times 10^{-6}t^2$	180–300	[38]
Polystyrene	$1.0865 - 6.19 \times 10^{-4}t + 0.136 \times 10^{-6}t^2$	100–222	[23]
	$1.077 - 5.49 \times 10^{-4}t + 0.124 \times 10^{-6}t^2$	115–196	[20]
	$1.067 - 5.02 \times 10^{-4}t - 0.135 \times 10^{-6}t^2$	79–320	[10]
Polysulfone, (with Bisphenol *A*)	$1.314 - 6.49 \times 10^{-4}t - 0.018 \times 10^{-6}t^2$	185–371	[24]
Polytetrafluoroethylene	$2.340 - 24.33 \times 10^{-4}t + 0.309 \times 10^{-6}t^2$	330–372	[25]
Polytetrahydrofuran	$0.996 \exp(-6.691 \times 10^{-4}t)$	62–166	[1,21]
Poly(vinyl acetate)	$1.2124 - 8.62 \times 10^{-4}t + 0.223 \times 10^{-6}t^2$	35–100	[26]
Poly(vinyl chloride)	$1.394 - 2.03 \times 10^{-4}t - 2.19 \times 10^{-6}t^2$	100–150	[1]
Poly(vinylidene fluoride)	$1.816 - 26.77 \times 10^{-4}t + 4.75 \times 10^{-6}t^2$	180–220	[40]
Poly(vinyl methyl ether)	$1.0725 - 7.259 \times 10^{-4}t + 0.116 \times 10^{-6}t^2$	25–120	[27]

TABLE 7.2. *Densities of polymer glasses as a function of temperature.*

Glassy polymer	T_g, °C	ρ, g/cm^3, (t in °C)	Temp. range, °C	Ref.
Poly(*n*-butyl methacrylate)	20	$1.063 - 4.01 \times 10^{-4}t$	−30–20	[8]
Polycarbonate, (with Bisphenol *A*)	151	$1.204 - 3.05 \times 10^{-4}t$	30–151	[9]
	142	$1.2044 \exp(-2.21 \times 10^{-4}t)$	40–121	[38]
Poly(cyclohexyl methacrylate)	107	$1.106 - 2.69 \times 10^{-4}t$	19–85	[7]
Poly(2,6-dimethylphenylene ether)	203	$1.070 \exp(-2.09 \times 10^{-4}t)$	30–203	[10]
Poly(ethyl methacrylate)	65	$1.131 - 3.06 \times 10^{-4}t$	−35–65	[8]
Poly(methyl methacrylate)	100	$1.188 - 1.34 \times 10^{-4}t - 0.91 \times 10^{-6}t^2$	30–100	[18]
	105	$1.188 - 1.72 \times 10^{-4}t - 1.04 \times 10^{-6}t^2$	17–80	[7]
	105	$1.175 - 2.47 \times 10^{-4}t$	−30–105	[8]
	105	$1.187 - 2.35 \times 10^{-4}t - 0.67 \times 10^{-6}t^2$	20–95	[48]
Poly(methyl methacrylate), isotactic	47	$1.225 - 2.65 \times 10^{-4}t$	9–26	[19]
Poly(*o*-methyl styrene)	131	$1.027 - 2.64 \times 10^{-4}t$	29–82	[20]
Polystyrene	92	$1.048 - 1.88 \times 10^{-4}t - 0.608 \times 10^{-6}t^2$	8–75	[20]
	79	$1.052 \exp(-2.86 \times 10^{-4}t)$	30–79	[10]
Polysulfone, (with Bisphenol *A*)	186	$1.242 - 2.59 \times 10^{-4}t$	30–186	[24]
Poly(vinyl acetate)	31	$1.196 - 3.37 \times 10^{-4}t$	−30–20	[26]

7.2 DENSITIES AS A FUNCTION OF PRESSURE

Pressure-volume data have been reported for many polymers. In most cases the Tait equation

$$\rho(P,t) = \frac{\rho(0,t)}{1 - C\ln\left[1 + \frac{P}{B(t)}\right]}, \qquad (7.5)$$

accurately represents the relationship between ρ and the pressure P. In it, the unitless parameter C is usually equated to 0.0894, while the temperature-dependent parameter $B(t)$ is written as a function of two other empirical parameters b_0 and b_1:

$$B(t) = b_0 e^{-b_1 t}. \qquad (7.6)$$

As above, t is the centigrade temperature. Literature values for C, b_0, and b_1 are collected in Tables 7.5 (above T_g) and 7.6 (below T_g). The zero-pressure density ρ(0,t), which is virtually the same as the density at atmospheric pressure, can be computed from expressions in Tables 7.1 and 7.2.

Table 7.7 lists equations for the temperature dependence of thermal pressure coefficients $\gamma = (\partial p/\partial t)_v$ that have been directly determined.

Isothermal compressibilities

$$\kappa_T = -\frac{1}{v_{sp}}\left(\frac{\partial v_{sp}}{\partial P}\right)_t = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_t, \qquad (7.7)$$

at atmospheric pressure are summarized in Table 7.8. Most are derived from the Tait equation with parameters from Tables 7.5 and 7.6:

$$\kappa_T = \frac{C}{b_0} e^{b_1 t} (\text{at zero pressure}). \qquad (7.8)$$

Others are obtained from thermal pressure and expansion coefficients through the relation

$$\kappa_T = \frac{\alpha}{\gamma}. \qquad (7.9)$$

In most instances the latter values of κ_T have smaller uncertainties because of the greater accuracy that usually accompanies direct measurements of γ and α. Values of κ_T for glasses are preceded with a g in Table 7.8.

Related information can be found in Chapter 29.

TABLE 7.3. *Densities* (g/cm^3).

Temperature (deg C)	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340	360	380	Ref.
Natural rubber, unvulcanized	0.9283	0.9162																			[3]
Natural rubber, cured	0.9211	0.9093																			[3]
Polyamide, Nylon 6													1.176	1.165	1.154	1.143					[4]
Polyamide, Nylon 6,6															0.963						[5]
														1.100	1.086	1.071					[4]
Poly(butene-1), isotactic								0.797	0.786	0.776	0.765	0.755	0.745								[6]
Poly(*n*-butyl methacrylate)			1.045	1.032	1.018	1.004	0.990	0.975	0.961	0.947	0.933										[7]
	*g*1.063[a]	1.057	1.043	1.030	1.017	1.005	0.993														[8]
Poly(*ε*-caprolactone)						1.037	1.023	1.010													[1]
Polycarbonate, (with Bisphenol *A*)			*g*1.192	*g*1.186	*g*1.180	*g*1.174	*g*1.167	*g*1.161	1.150	1.136	1.123	1.109	1.095	1.081	1.067	1.053	1.039	1.025			[9]
			*g*1.194	*g*1.188	*g*1.183	*g*1.178	*g*1.173			1.139	1.125	1.111	1.097	1.084	1.070	1.057	1.044				[38]
Poly(cyclohexyl methacrylate)		*g*1.101	*g*1.095	*g*1.090	*g*1.084		1.066	1.054	1.041	1.028	1.015										[7]
Poly (2,6-dimethylphenylene ether)			*g*1.061	*g*1.057	*g*1.052	*g*1.048	*g*1.043	*g*1.039	*g*1.035	*g*1.030	*g*1.026	1.012	0.997	0.983	0.968	0.953	0.939				[10]
Poly(dimethyl siloxane)		0.9742	0.9566	0.9393	0.9222	0.9053	0.8887	0.8722	0.8560	0.8400	0.8242										[11]
			0.9566	0.9389																	[12]
		0.974	0.956	0.939	0.922	0.905	0.889	0.873	0.857												[41]
		0.973	0.956	0.939	0.923	0.906	0.890	0.874													[49]
Poly(1,3-dioxolane)			1.210	1.188	1.167																[44]
Polyetheretherketone																		1.113	1.098	1.084	[13]
Polyethylene, branched							0.801	0.790	0.780	0.769	0.759	0.749									[14]
								0.785	0.774	0.763	0.752										[7]
Polyethylene, linear								0.7847	0.7735	0.7624	0.7514										[15]
								0.789	0.778	0.766	0.753										[7]
								0.784	0.774	0.763											[41]
Poly(ethylene terephthalate)															1.172	1.156	1.140	1.125			[16]
Poly(ethyl methacrylate)	*g*1.131	*g*1.125	*g*1.119	*g*1.113	1.103																[8]
Poly(hydroxybutyrate)		1.177																			[46]
Polyisobutylene	0.9297	0.9195	0.9093	0.8992	0.8891	0.8791	0.8691	0.8592													[17]
		0.912	0.901	0.890	0.880	0.870	0.861	0.851	0.842												[41]
Poly(methyl methacrylate)			*g*1.181	*g*1.177	*g*1.171	*g*1.166	1.153	1.139	1.126	1.112	1.097	1.082	1.067	1.052							[18]
		*g*1.184	*g*1.179	*g*1.174	*g*1.168		1.148	1.136	1.123												[7]
							1.153	1.141	1.129	1.117	1.106	1.094									[4]
	*g*1.175	*g*1.170	*g*1.165	*g*1.160	*g*1.155	*g*1.150	1.140	1.128													[8]
		*g*1.182	*g*1.177	*g*1.171	*g*1.164		1.144	1.129	1.115	1.101											[48]
Poly(methyl methacrylate), isotactic		*g*1.220		1.204	1.189	1.174	1.160	1.146	1.132	1.119											[19]
Poly(4-methyl pentene-1)													0.720	0.710	0.700	0.690	0.679				[45]
Poly(*o*-methyl styrene)			*g*1.016	*g*1.011	*g*1.006			0.9881	0.9777	0.9674	0.9571										[20]
Polyoxybutylene			0.958	0.944	0.931																[42]
					0.944	0.931	0.919	0.907	0.895												[1,21]
Polyoxyethylene					1.086	1.070	1.053	1.037	1.022	1.007	0.992										[41]
			1.107	1.091	1.075																[42]
						1.063	1.048	1.033	1.018	1.004	0.990	0.976									[1,21]
					1.081	1.066	1.051														[47]
Polyoxymethylene											1.167	1.151									[22]
Polypropylene, atactic					0.827	0.816	0.802														[1]
									0.773	0.762	0.752										[41]
Polypropylene, isotactic										0.764	0.754	0.744	0.734	0.724	0.714	0.705					[6]
										0.763	0.753	0.743	0.732	0.721	0.711	0.699					[38]
										0.763	0.753	0.743									[4]
Polystyrene						1.0260	1.0142	1.0025	0.9909	0.9795	0.9681	0.9569									[23]
		*g*1.044	*g*1.040	*g*1.035			1.0125	1.0021	0.9919	0.9818	0.9717										[20]
			*g*1.040	*g*1.034	1.026	1.016	1.005	0.994	0.984	0.973	0.961	0.950	0.939	0.928	0.916	0.905	0.893				[10]
Polysulfone, (with Bisphenol *A*)			*g*1.232	*g*1.226	*g*1.221	*g*1.216	*g*1.211	*g*1.206	*g*1.201	*g*1.195	1.183	1.170	1.157	1.144	1.130	1.117	1.104	1.091	1.078		[24]
Polytetrafluoroethylene																		1.548	1.504		[25]
Poly(vinyl acetate)	*g*1.196	*g*1.189	1.1783	1.1615	1.1449	1.1285															[26]
Poly(vinyl chloride)						1.352	1.338	1.322													[1]
Poly(vinylidene fluoride)										1.488	1.471	1.457									[40]
Poly(vinyl methyl ether)		1.0580	1.0436	1.0294	1.0152	1.0011	0.9871														[27]

[a] *g* = glass.

TABLE 7.4. *Thermal expansion coefficients* ($\times 10^{-4} K^{-1}$).

Temperature (deg C)	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340	360	380	Ref.
Natural Rubber, unvulcanized	6.6	6.6																			[3]
Natural Rubber, cured	6.5	6.4																			[3]
		6.7																			[28]
Polyamide, Nylon 6													4.7	4.7	4.7						[4]
Polyamide, Nylon 6.6														6.6	6.6						[4]
															6.8						[5]
Poly(butene-1), isotactic								6.7	6.7	6.7	6.7	6.7	6.7								[6]
Poly(*n*-butyl methacrylate)			6.2	6.5	6.8	7.0	7.2	7.3	7.4	7.4	7.4										[7]
	*g*3.8[a]	6.4	6.4	6.3	6.2	6.1	6.1														[8]
Poly(ε-caprolactone)							6.4	6.3													[1]
Polycarbonate, (with Bisphenol *A*)			*g*2.6	*g*2.6	*g*2.6	*g*2.6	*g*2.6	*g*2.6	5.8	5.9	6.1	6.2	6.3	6.4	6.6	6.7	6.8	6.9			[9]
			*g*2.2	*g*2.2	*g*2.2	*g*2.2	*g*2.2			6.2	6.2	6.2	6.2	6.2	6.2	6.2					[38]
Poly(cyclohexyl methacrylate)		*g*2.4	*g*2.5	*g*2.5	*g*2.5		5.9	6.0	6.2	6.3	6.4										[7]
Poly(2,6-dimethylphenylene ether)			*g*2.1	*g*2.1	*g*2.1	*g*2.1	*g*2.1	*g*2.1	*g*2.1	*g*2.1	*g*2.1	7.1	7.3	7.4	7.6	7.7	7.8				[10]
Poly(dimethyl siloxane)		9.06	9.11	9.17	9.23	9.29	9.35	9.41	9.47	9.53	9.59										[11]
		9.0																			[28]
			9.4	9.2																	[12]
Poly(1,3-dioxolane)			9.0	9.2																	[44]
Polyetheretherketone							6.7	6.7	6.7	6.7	6.7	6.7						6.7	6.7	6.7	[13]
Polyethylene, branched							6.7	6.7	6.7	6.7	6.7	6.7									[14]
								7.5	7.2	6.9											[7]
									7.5	7.7	7.8	8.0									[39]
Polyethylene, linear								7.14	7.18	7.24	7.32										[15]
									7.3	7.4	7.5	7.6									[39]
										7.0	7.0										[29]
									7.6	7.9											[7]
Poly(ethylene terephthalate)															6.8	6.8	6.8	6.8			[16]
Poly(ethyl methacrylate)	*g*2.7	*g*2.7	*g*2.7	*g*2.7	6.0																[8]
Polyisobutylene	5.51	5.54	5.58	5.61	5.65	5.68	5.72	5.75													[17]
Poly(methyl methacrylate)			*g*1.8	*g*2.1	*g*2.4	*g*2.7	5.5	5.8	6.1	6.4	6.7	7.0	7.2	7.5							[18]
		*g*1.8	*g*2.2	*g*2.5	*g*2.9		5.4	5.7	6.0												[7]
							5.2	5.2	5.2	5.2	5.2	5.2									[4]
	*g*2.1	*g*2.1	*g*2.1	*g*2.1	*g*2.1	*g*2.1	5.2	5.2													[8]
			*g*2.5	*g*2.7	*g*2.9																[48]
Poly(methyl methacrylate), isotactic		*g*2.2		6.4	6.3	6.2	6.1	5.9	5.8	5.7											[19]
Poly(4-methyl pentene-1)												7.1	7.2	7.3	7.4	7.5					[45]
Poly(*o*-methyl styrene)			*g*2.6	*g*2.6	*g*2.6			5.3	5.3	5.3											[20]
Polyoxybutylene			7.1	7.2	7.3																[42]
					6.7	6.7	6.7	6.7	6.7												[1,21]
Polyoxyethylene						7.1	7.1	7.1	7.1	7.1	7.1	7.1									[1,21]
			7.3	7.4	7.5																[42]
					6.7	6.8	7.0														[47]
Polyoxymethylene										7.9											[29]
											6.8	6.8									[22]
Polypropylene, atactic					6.1	7.7	9.3														[1]
Polypropylene, isotactic										6.6	6.6	6.6									[4]
											6.9	7.1	7.3	7.5	7.7	8.0					[38]
										6.7	6.7	6.7	6.7	6.7	6.7	6.7					[6]
										6.7	6.7										[29]
Polystyrene						5.78	5.79	5.81	5.82	5.84	5.85	5.87									[23]
		*g*2.0	*g*2.3	*g*2.5			5.1	5.1	5.1	5.1	5.1										[20]
			*g*2.9	*g*2.9	5.0	5.2	5.3	5.4	5.6	5.7	5.8	5.9	6.0	6.2	6.3	6.4	6.5				[10]
Polysulfone, (with Bisphenol *A*)			*g*2.1	*g*2.1	*g*2.1	*g*2.1	*g*2.1	*g*2.1	*g*2.2	*g*2.2	5.5	5.6	5.7	5.8	5.9	6.0	6.1	6.1			[24]
Polytetrafluoroethylene																		14.4	14.7		[25]
Poly(vinyl acetate)	*g*2.8	*g*2.8	7.13	7.17	7.20	7.23															[26]
Poly(vinyl chloride)						4.7	5.5	6.2													[1]
Poly(vinylidene fluoride)											5										[40]
Poly(vinyl methyl ether)			6.87	6.92	6.96	7.01	7.06														[27]

[a] g = glass.

TABLE 7.5. *Parameters for the Tait equation, Eqs. (7.5) and (7.6), for amorphous polymers above T_g.*

Polymer	C	b_0, bar	b_1, deg C^{-1}	Temp. range, deg C	Pressure range, bar	Ref.
Natural Rubber, cured	0.0894	1916	0.00425	0–25	0–500	[3]
Natural Rubber, unvulcanized	0.0894	1937	0.00517	0–25	0–500	[3]
Polyamide, Nylon 6	0.0894	3767	0.00466	236–295	0–2000	[4]
Polyamide, Nylon 6,6	0.0894	3538	0.00376	270–285	0–600	[5]
	0.0894	3164	0.00504	245–297	0–2000	[4]
Poly(butene-1), isotactic	0.0894	1675	0.00453	133–246	0–2000	[6]
Poly(*n*-butyl methacrylate)	0.0894	2267	0.00534	34–200	0–2000	[7]
Poly(ε-caprolactone)	0.0894	1890	0.00393	100–148	0–2000	[1]
Polycarbonate, (with Bisphenol *A*)	0.0894	3100	0.00408	151–340	0–1800	[9]
	0.0894	2803	0.00387	171–330	100–2000	[38]
Poly(cyclohexyl methacrylate)	0.0894	2952	0.00522	123–200	0–2000	[7]
Poly(2,6-dimethylphenylene ether)	0.0894	2278	0.00429	203–320	0–1800	[10]
Poly(dimethyl siloxane)	0.1009	1041	0.00585	25–70	0–1000	[30]
	0.0988	960	0.00604	29–60	0–800	[31]
	0.0894	885	0.00610	25–70	0–900	[12]
	0.0894	915	0.00609	18–150	0–2200	[49]
Polyetheretherketone	0.0894	3880	0.00412	338–400	0–2000	[13]
Polyethylene, branched	0.0894	1867	0.00439	112–225	0–2000	[14]
	0.0970	1987	0.00510	140–200	0–1000	[30]
	0.0894	1771	0.00470	130–200	0–2000	[7]
	0.0894	1884	0.00488	140–203	0–2000	[32,33]
Polyethylene, linear	0.0894	1767	0.00466	142–200	0–2000	[7]
	0.0894	1683	0.00429	140–200	0–2000	[7]
Poly(ethylene terephthalate)	0.0894	3697	0.00415	274–342	0–2000	[16]
Polyisobutylene	0.0871	1907	0.00415	53–110	0–1000	[30]
Poly(methyl methacrylate)	0.0894	3000	0.00508	105–255	0–1800	[18]
	0.0894	2875	0.00415	114–160	0–2000	[7]
	0.0894	3850	0.00672	120–139	0–2000	[33,34]
	0.0894	4278	0.00369	115–230	0–2000	[4]
	0.0894	3006	0.00426	110–194	0–2000	[48]
Poly(methyl methacrylate), isotactic	0.0894	2992	0.00456	55–190	0–2000	[19]
Poly(*o*-methyl styrene)	0.0894	2619	0.00411	139–198	0–2000	[20]
Polyoxybutylene	0.0894	1786	0.00422	62–166	0–700	[1,21]
Polyoxyethylene	0.0894	2077	0.00395	88–224	0–700	[1,21]
	0.0894	2870	0.00473	75–136	0–2000	[47]
Polyoxymethylene	0.0894	3058	0.00433	183–220	0–2000	[22]
Polypropylene, atactic	0.0894	1621	0.00660	80–120	0–1000	[1]
Polypropylene, isotactic	0.0894	1491	0.00418	170–300	0–2000	[6]
	0.0894	1475	0.00413	175–230	0–2000	[4]
	0.0894	1705	0.00498	180–300	100–2000	[38]
Polystyrene	0.0894	2169	0.00332	115–196	0–2000	[20]
	0.0894	2521	0.00408	79–320	0–1800	[10]
	0.0894	2435	0.00414	115–249	0–2000	[33,34]
Polysulfone, (with Bisphenol *A*)	0.0894	3659	0.00376	186–370	0–2000	[24]
Polytetrafluoroethylene	0.0894	4252	0.00938	343–372	0–2000	[25]
Poly(vinyl acetate)	0.1046	2231	0.00343	64–120	0–1000	[30]
	0.0894	2035	0.00426	35–100	0–800	[26,35]
Poly(vinyl chloride)	0.0894	3522	0.00565	82–97	0–2000	[33,34]
	0.0894	2942	0.00532	100–150	0–2000	[1]
Poly(vinylidene fluoride)	0.0894	1066	0.00042	180–220	0–1200	[40]

TABLE 7.6. *Parameters for the Tait equation, Eqs. (7.5) and (7.6), for polymer glasses.*

Glassy polymer	C	b_0, bar	b_1,deg C^{-1}	T_g, deg C	Temp. range, deg C	Pressure range, bar	Ref.
Polycarbonate, (with Bisphenol *A*)	0.0894	3878	0.00261	151	30–151	0–1800	[9]
	0.0894	3251	0.00133	142	40–141	100–1500	[38]
Poly(cyclohexyl methacrylate)	0.0894	3762	0.00298	107	19–74	0–2000	[7]
Poly(2,6-dimethylphenylene ether)	0.0894	3314	0.00200	203	30–203	0–1800	[10]
Poly(methyl methacrylate)	0.0894	3767	0.00470	100	30–100	0–1800	[18]
	0.0894	3564	0.00323	105	17–91	0–2000	[7]
	0.0894	3717	0.00396	111	20–100	0–2000	[33]
	0.0894	4296	0.00416	105	20–95	0–2000	[48]
Poly(methyl methacrylate), isotactic	0.0894	4968	0.00670	47	9–26	0–2000	[19]
Poly(*o*-methyl styrene)	0.0894	3596	0.00355	131	29–82	0–2000	[20]
Polystyrene	0.0894	3449	0.00271	92	8–75	0–2000	[20]
	0.0894	3917	0.00431	79	30–79	0–1800	[10]
	0.0894	3337	0.00330	88	20–61	0–2000	[33,34]
Polysulfone, (with Bisphenol *A*)	0.0894	4323	0.00154	186	30–186	0–2000	[24]
Poly(vinyl acetate)	0.0894	3079	0.00097	31	−30–20	0–800	[26,35]
Poly(vinyl chloride)	0.0894	3751	0.00241	75	20–51	0–2000	[33,34]

TABLE 7.7. *Thermal pressure coefficients as a function of temperature.*

Polymer	$(\partial P/\partial t)_v$, bar/K, (t in °C)	Temp. range, °C	Ref.
Natural Rubber, cured	$13.75 - 0.0545t - 0.481 \times 10^{-4}t^2$	20–50	[28]
Poly(dimethyl siloxane)	$8.71 - 0.0474t + 0.93 \times 10^{-4}t^2$	25–162	[11]
	$9.00 - 0.0538t + 1.54 \times 10^{-4}t^2$	−20–50	[28]
Polyethylene, high density	$13.22 - 0.0558t + 0.896 \times 10^{-4}t^2$	139–192	[15]
Polyisobutylene	$12.66 - 0.0545t + 1.02 \times 10^{-4}t^2$	10–172	[17]
Polyoxyethylene	$15.79 - 0.0250t + 1.532 \times 10^{-4}t^2$	50–103	[36]
Polypropylene, isotactic	$23.19 - 0.1757t + 4.22 \times 10^{-4}t^2$	158–195	[37]
Polystyrene	$15.81 - 0.0859t + 2.70 \times 10^{-4}t^2$	27–100	[23]
Poly(vinyl methyl ether)	$13.81 - 0.0514t + 0.005 \times 10^{-4}t^2$	20–120	[27]

TABLE 7.8. *Isothermal compressibilities (× 10^{-5} bar^{-1}) at atmospheric pressure.*

Temperature (deg C)	0	20	40	60	80	100	120	140	160	180	200	220	240	260	280	300	320	340	360	380	Ref.
Natural Rubber, cured		5.3																			[28]
	4.6	5.0																			[3]
Natural Rubber, unvulcanized	4.6	5.0																			[3]
Polyamide, Nylon 6													7.3	8.0	8.8						[4]
Polyamide, Nylon 6,6															7.2						[5]
														10.5	11.6						[4]
Poly(butene-1), isotactic								10.1	11.0	12.1	13.2	14.5	15.8								[6]
Poly(*n*-butyl methacrylate)			4.9	5.4	6.0	6.7	7.5	8.3	9.3	10.3	11.5										[7]
Poly(ε-caprolactone)						7.0	7.6	8.2													[1]
Polycarbonate, (with Bisphenol *A*)			*g*2.6[a]	*g*2.7	*g*2.8	*g*3.0	*g*3.2	*g*3.3	5.5	6.0	6.5	7.1	7.7	8.3	9.0	9.8	10.6	11.5			[9]
			*g*2.9	*g*3.0	*g*3.1	*g*3.1	*g*3.2	*g*3.3		6.4	6.9	7.5	8.1	8.7	9.4	10.2	11.0				[38]
Poly(cyclohexyl methacrylate)		*g*2.5	*g*2.7	*g*2.8					6.3	7.0	7.7	8.6									[7]
Poly(2,6-dimethylphenylene ether)			*g*2.9	*g*3.0	*g*3.2	*g*3.3	*g*3.4	*g*3.6	*g*3.7	*g*3.9	*g*4.0	10.1	11.0	12.0	13.0	14.2	15.5				[10]
Poly(dimethyl siloxane)			13.1	14.8	16.7	19.0	21.4	24.1	27.0												[11]
	10.0	11.3	12.8																		[28]
			12.3	13.8																	[30]
			13.1	14.8																	[31]
			12.9	14.6																	[12]
		11.0	12.5	14.1	15.9	18.0	20.3	22.9													[49]
Polyetheretherketone																		9.4	10.2	11.0	[13]
Polyethylene, branched							8.1	8.9	9.7	10.6	11.5	12.6									[14]
								10.0	11.0	12.2	13.5										[30]
								9.7	10.7	11.8	12.9										[7]
								9.4	10.4	11.4	12.6										[32,33]
Polyethylene, linear								10.0	11.0	12.1											[15]
									10.7	11.7	12.9										[7]
								9.7	10.6	11.5	12.5										[7]
Poly(ethylene terephthalate)															7.7	8.4	9.1	9.9			[16]
Polyisobutylene		4.8	5.2	5.8	6.3	6.9	7.5	8.2													[17]
				5.9	6.4	6.9															[30]
Poly(methyl methacrylate)			*g*2.9	*g*3.1	*g*3.5	*g*3.8	5.5	6.1	6.7	7.4	8.2	9.1	10.1								[18]
		*g*2.7	*g*2.9	*g*3.0	*g*3.2		5.1	5.6	6.0												[7]
		*g*2.6	*g*2.8	*g*3.1	*g*3.3	*g*3.6	5.2	5.9													[33,34]
		*g*2.3	*g*2.5	*g*2.7	*g*2.9		5.0	5.4	5.9	6.4											[48]
Poly(methyl methacrylate), isotactic		*g*2.1		3.9	4.3	4.7	5.2	5.7	6.2	6.8											[19]
Poly(4-methyl pentene-1)													19	20	22	24	27				[45]
Poly(*o*-methyl styrene)			*g*2.9	*g*3.1	*g*3.3			6.1	6.6	7.2											[20]
Polyoxymethylene											6.9	7.6									[22]
Polyoxyethylene						6.4	6.9	7.5	8.1	8.8	9.5	10.3									[1,21]
				5.2	5.5	6.0															[36]
					4.5	5.0	5.5														[47]
Polypropylene, atactic					9.4	10.7	12.2														[1]
Polypropylene, isotactic										12.7	13.8	15.0	16.3	17.8	19.3	21.0					[6]
										12.7	13.8	15.0									[4]
									11.2	12.8											[4,6,37]
										13	14	16	17	19	21	23					[38]
Polystyrene			4.5	5.0	5.5	6.0															[23]
		*g*2.7	*g*2.9	*g*3.1			6.1	6.6	7.0	7.5											[20]
			*g*2.7	*g*3.0	4.9	5.3	5.8	6.3	6.8	7.4	8.0	8.7	9.4	10.2	11.1	12.1	13.1				[10]
		*g*2.9	*g*3.1	*g*3.3			6.0	6.6	7.1	7.7	8.4	9.1	9.9								[33,34]
Polysulfone, (with Bisphenol *A*)			*g*2.2	*g*2.3	*g*2.3	*g*2.4	*g*2.5	*g*2.6	*g*2.6	*g*2.7	5.2	5.6	6.0	6.5	7.0	7.5	8.1	8.8	9.4		[24]
Polytetrafluoroethylene																			61.6		[25]
Polytetrahydrofuran					7.0	7.6	8.3	9.0	9.8												[1,21]
Poly(vinyl acetate)					6.2	6.6	7.1														[30]
	*g*2.9	*g*3.0	5.2	5.7	6.2	6.7															[26,35]
Poly(vinyl chloride)		*g*2.5	*g*2.6		4.0	4.5															[33,34]
						5.2	5.8	6.4													[1]
Poly(vinylidene fluoride)										8.9	9.0	9.0									[40]
Poly(vinyl methyl ether)		5.3	5.8	6.4	7.2	8.1	9.2														[27]

[a] *g* = glass.

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CHAPTER 8

Thermodynamic Properties of Proteins

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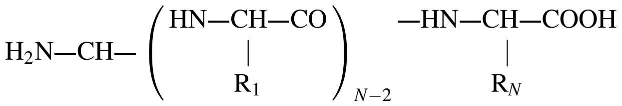
Proteins are heteropolymers consisting of 20 different type of amino acid residues. They all share a common backbone

$$\begin{array}{c} H_2N\text{—}CH\text{—}COOH \\ | \\ R \end{array}$$

and differ by the side chain radical, R. Amino acid residues are arranged into a polypeptide chain through formation of peptide bonds



$$H_2N\text{—}CH\text{—}\left(\begin{array}{c} HN\text{—}CH\text{—}CO \\ | \\ R_1 \end{array}\right)_{N-2}\begin{array}{c} \text{—}HN\text{—}CH\text{—}COOH \\ | \\ R_N \end{array}$$

The side chains, R_N, vary in size and chemical nature (Table 8.1), allowing a great variety of properties. Naturally occurring polypeptides adopt a unique three dimensional conformation in solution. The structures of many of them have been solved by X-ray crystallography and 2D-NMR.

8.1 HEAT CAPACITY

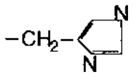
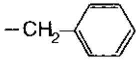
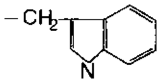
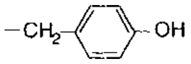
Tables 8.2 and 8.3 present molar heat capacities of solid amino acids and polyamino acids. Table 8.4 presents specific heat capacities of anhydrous and hydrated proteins. All of the measurements were done by using adiabatic absolute calorimetry and their accuracy is better than 1–2%. Heat capacity of anhydrous proteins can be predicted using empirical approach developed by Wunderlich (see e.g., [1]).

In the presence of the solvent water, the heat capacity of proteins increases. The partial molar heat capacity of proteins in the native state, $C_p^N(T)$, appears to be a linear function of temperature [2–5]. The $C_p^N(T)$ increases with the increase of temperature with a slope from 0.005 to 0.008 $J\,K^{-2}\,g^{-1}$ for small globular proteins depending on the protein [6]. The absolute value of $C_p^N(T)$ at 25 °C ranges between 1.25 and 1.80 $J\,K^{-1}\,g^{-1}$, depending on the proteins [6]. The heat capacity of the denatured state, $C_p^D(T)$, for small globular proteins is always larger than the heat capacity of the native state, and depends on temperature in a more complicated way. The temperature dependence is nonlinear at low temperatures (0–75 °C). At temperatures above 75 °C the heat capacity function appears to be almost independent of temperature. At 25 °C, $C_p^D(T)$ values for different proteins range from 1.85 to 2.20 $J\,K^{-1}\,g^{-1}$, while at 100 °C they are higher, 2.1–2.4 $J\,K^{-1}\,g^{-1}$. A nonlinear dependence of the heat capacity of denatured protein is in agreement (within 5%) with what one can expect for the heat capacity of an unfolded polypeptide chain, $C_p^U(T)$, of the same amino acid composition [7–10]. The latter can be calculated as a sum of contributions from side chains and from the peptide unit:

$$C_{p,2}^U = (N-1)\cdot C_{p,2}(\text{—CHCONH—}) + \sum_{i=1}^{N} C_{p,2}(-R_i), \tag{8.1}$$

where $C_{p,2}$(—CHCONH—) is the heat capacity of the peptide unit, $C_{p,2}(-R_i)$ is the heat capacity contribution of the side-chain of the *i*th amino acid residue, and *N* is the number of amino acid residues in the polypeptide chain. These contributions, for the temperature range 5–125 °C are listed in Table 8.5. The agreement is observed not only in the temperature dependence of these two functions ($C_p^D(T)$ and $C_p^U(T)$) but in majority of cases in the absolute values as well [7–10]. The close correspondence between the measured

TABLE 8.1a. *Properties of 20 naturally occurring amino acids.*

Name	Three letter code	One letter code	Side Chains (–**R**) **R**–CH(NH_2)COOH	Mol Mass Da	pK_a	ΔH_{ion} kJ mol^{-1}	Volume Å^3	ASA_{mc} Å^2	ASA_{sc}^{npl} Å^2	ASA_{sc}^{pol} Å^2
Alanine	Ala	A	$-CH_3$	71.08			88.6	46	67	
Arginine	Arg	R	$-(CH_2)_3-CNH(=NH)NH_3$	156.20	12	44.9	173.4	45	89	107
Asparagine	Asn	N	$-CH_2-CONH_2$	114.11			117.7	45	44	69
Aspartic acid	Asp	D	$-CH_2-COOH$	115.09	4.5	4.6	111.1	45	48	58
Cystein	Cys	C	$-CH_2-SH$	103.14	9.1–9.5	36.0	108.5	36	35	69
Glutamine	Gln	Q	$-(CH_2)_2-CONH_2$	128.14			143.9	45	53	91
Glutamic acid	Glu	E	$-(CH_2)_2-COOH$	129.12	4.6	1.6	138.4	45	61	77
Glycine	Gly	G	$-H$	57.06			60.1	85		
Histidine	His	H		137.15	6.2	43.6	153.2	43	102	49
Isoleucine	Ile	I	$-CH(CH_3)-C_2H_5$	113.17			166.7	42	140	
Leucine	Leu	L	$-CH(CH_3)_2-CH_2$	113.17			166.7	43	137	
Lysine	Lys	K	$-(CH_2)_4-NH_2$	128.18	10.4	53.6	168.6	44	119	48
Methionine	Met	M	$-(CH_2)_2-S-CH_3$	131.21			162.9	44	117	43
Phenylalanine	Phe	F		147.18			189.9	43	175	
Proline	Pro	P	*	97.12			122.7	38	105	
Serine	Ser	S	$-CH_2-OH$	87.08			89.0	42	44	36
Threonine	Thr	T	$-CH_2-(CH_3)-OH$	101.11			116.1	44	74	28
Tryptophane	Trp	W		186.21			227.8	42	190	27
Tyrosine	Tyr	Y		163.18	9.7	25.1	193.6	42	144	43
Valine	Val	V	$-CH-(CH_3)_2$	99.14			140	43	117	
			α-amino		6.8–7.9					
			α-carboxyl		3.5–4.3					

*Proline is an imono acid; Enthalpies of ionization of side chains at 25 °C, ΔH_{ion}, are from [19]; van der Waals volume from [20]; ASA_{mc}, surface area of the backbone, ASA_{sc}^{npl}, nonpolar surface area of the side chains, and, ASA_{sc}^{pol}, polar surface area of the side chains are from [14].

TABLE 8.1b. *Heat capacities (J K^{-1}mol^{-1}) of solid amino acids.*

T/K	C_p	T/K	C_p	T/K	C_p
L-Alanine (89.1 Da) [21]					
10	0.494	90	47.87	220	96.23
15	1.674	100	52.55	230	99.58
20	3.849	110	56.94	240	102.93
25	6.724	120	61.09	250	106.32
30	10.09	130	65.10	260	111.55
35	13.75	140	68.99	270	113.05
40	17.37	150	72.72	280	116.40
45	20.91	160	76.32	290	119.66
50	24.40	170	79.83	300	122.84
55	27.78	180	83.22	310	125.98
60	31.02	190	86.53	273.15	114.10
70	37.03	200	89.79	298.15	122.26
80	42.64	210	93.01	310.15	126.02
L-Arginine·HCl (210.7 Da) [22]					
10	2.326	90	105.52	220	205.10
15	6.481	100	114.68	230	212.21
20	12.25	110	123.26	240	219.37
25	19.21	120	131.46	250	226.52
30	26.91	130	139.37	260	233.72
35	34.91	140	147.15	270	241.00
40	42.93	150	154.72	280	248.20
45	50.71	160	162.09	290	255.27
50	58.16	170	169.41	300	262.25
55	65.27	180	176.65	310	269.16
60	72.05	190	183.76	273.15	243.26
70	84.43	200	190.87	298.15	260.96
80	95.48	210	197.90	310.15	269.28
L-Aspartic acid (134.1 Da) [23]					
10	0.732	90	64.02	220	122.51
15	2.686	100	69.45	230	126.69
20	6.033	110	74.64	240	130.88
25	10.31	120	79.54	250	134.98
30	15.14	130	84.27	260	139.03
35	20.09	140	88.83	270	143.14
40	25.18	150	93.26	280	147.32
45	30.06	160	97.57	290	151.63
50	34.70	170	101.80	300	155.98
55	39.10	180	106.06	310	160.37
60	43.30	190	110.21	273.15	144.47
70	50.88	200	114.31	298.15	155.19
80	57.70	210	118.41	310.15	160.42

TABLE 8.1b. *Continued.*

T/K	C_p	T/K	C_p	T/K	C_p
L-Asparagine · H_2O (150.1 Da) [23]					
10	0.686	90	76.48	220	161.21
15	2.343	100	83.93	230	167.28
20	5.376	110	91.13	240	173.34
25	9.531	120	98.07	250	179.41
30	14.63	130	104.85	260	185.44
35	20.29	140	111.46	270	191.38
40	26.18	150	117.95	280	197.28
45	32.13	160	124.35	290	203.18
50	37.95	170	130.71	300	208.99
55	43.56	180	136.94	310	214.81
60	48.95	190	143.09	273.15	193.26
70	58.99	200	149.12	298.15	207.90
80	68.12	210	155.19	310.15	214.89
L-Cystine (240.3 Da) [24]					
10	1.644	90	102.13	220	206.98
15	5.284	100	111.13	230	214.18
20	15.25	110	120.00	240	221.33
25	18.03	120	128.66	250	228.49
30	25.49	130	137.24	260	235.60
35	33.14	140	145.52	270	242.59
40	40.63	150	153.64	280	249.53
45	47.87	160	161.59	290	256.40
50	54.85	170	169.54	300	263.17
55	61.51	180	177.23	310	269.91
60	67.91	190	184.81	273.15	244.81
70	79.87	200	192.30	298.15	261.92
80	91.21	210	199.70	310.15	269.99
L-Glutamic acid (147.1 Da) [23]					
10	0.276	90	70.17	220	137.24
15	2.782	100	76.53	230	142.01
20	6.259	110	82.34	240	146.78
25	10.86	120	87.95	250	151.54
30	16.12	130	93.22	260	156.31
35	21.69	140	98.37	270	161.17
40	27.18	150	103.39	280	166.11
45	32.59	160	108.41	290	171.08
50	37.80	170	113.39	300	175.98
55	42.68	180	118.24	310	180.79
60	47.28	190	122.93	273.15	162.72
70	55.65	200	127.70	298.15	175.06
80	63.18	210	132.47	310.15	180.87

TABLE 8.1b. *Continued.*

T/K	C_p	*T*/K	C_p	*T*/K	C_p
L-Glutamine (146.2 Da) [23]					
10	0.728	90	72.55	220	144.06
15	2.460	100	78.99	230	149.45
20	5.791	110	84.94	240	154.72
25	10.48	120	90.67	250	159.91
30	15.91	130	196.23	260	165.02
35	21.80	140	101.76	270	170.04
40	27.72	150	107.28	280	175.10
45	33.46	160	112.63	290	180.12
50	38.93	170	117.95	300	185.10
55	44.06	180	123.18	310	189.83
60	48.87	190	128.37	273.15	171.63
70	57.66	200	133.60	298.15	184.18
80	65.48	210	138.74	310.15	189.91
Glycine (75.1 Da) [21]					
10	0.255	90	39.53	220	77.49
15	0.967	100	43.26	230	80.08
20	2.393	110	46.69	240	82.84
25	4.464	120	50.00	250	85.60
30	7.037	130	53.09	260	88.45
35	9.933	140	56.07	270	91.25
40	13.00	150	58.91	280	94.06
45	16.12	160	61.67	290	96.90
50	19.25	170	64.39	300	99.75
55	22.26	180	67.03	310	102.63
60	25.15	190	69.66	273.15	92.13
70	30.49	200	72.30	298.15	99.20
80	35.26	210	74.89	310.15	102.68
Glycylglycine (132.1 Da) [25]					
10	0.707	90	67.86	220	130.12
15	2.607	100	73.85	230	134.35
20	6.071	110	79.50	240	138.62
25	10.70	120	84.89	250	142.84
30	15.87	130	89.87	260	147.19
35	21.23	140	94.81	270	151.50
40	26.56	150	99.58	280	155.85
45	31.65	160	104.27	290	160.29
50	36.58	170	108.74	300	164.81
55	41.21	180	113.09	310	169.45
60	45.61	190	117.40	273.15	152.88
70	53.81	200	121.71	298.15	163.97
80	61.21	210	125.90	310.15	169.54

TABLE 8.1b. *Continued.*

T/K	C_p	*T*/K	C_p	*T*/K	C_p
L-Histidine·HCl (191.6 Da) [22]					
10	1.711	90	102.63	220	195.39
15	5.690	100	111.09	230	202.13
20	11.93	110	119.04	240	208.91
25	19.33	120	126.57	250	215.81
30	27.29	130	133.85	260	222.80
35	35.38	140	140.96	270	229.87
40	43.26	150	147.90	280	236.90
45	50.88	160	154.81	290	243.89
50	58.12	170	161.63	300	250.79
55	64.81	180	168.36	310	257.65
60	71.17	190	175.14	273.15	232.09
70	82.80	200	181.92	298.15	249.53
80	93.22	210	188.66	310.15	257.73
L-Isoleucine (131.2 Da) [26]					
10	2.741	90	74.89	220	147.53
15	6.343	100	81.80	230	152.59
20	10.80	110	88.41	240	157.74
25	15.82	120	94.68	250	162.97
30	20.93	130	100.63	260	168.16
35	26.12	140	106.36	270	173.26
40	31.22	150	111.88	280	178.53
45	36.22	160	117.24	290	183.76
50	41.08	170	122.55	300	189.28
55	45.82	180	127.70	310	194.89
60	50.38	190	132.72	273.15	174.93
70	58.95	200	137.65	298.15	188.28
80	67.15	210	142.59	310.15	194.97
L-Leucine (131.2 Da) [26]					
10	2.452	90	75.44	220	148.91
15	6.468	100	82.22	230	154.60
20	11.50	110	88.53	240	160.46
25	16.93	120	94.64	250	166.52
30	22.53	130	100.50	260	172.93
35	28.08	140	106.15	270	179.70
40	33.32	150	111.63	280	186.77
45	38.40	160	117.03	290	194.31
50	43.26	170	122.38	300	202.51
55	47.82	180	127.70	310	211.38
60	52.17	190	132.93	273.15	181.88
70	60.42	200	138.11	298.15	200.96
80	68.20	210	143.43	310.15	211.50

TABLE 8.1b. *Continued.*

T/K	C_p	T/K	C_p	T/K	C_p
L-Lysine·HCl (182.7 Da) [22]					
10	2.460	90	97.74	220	186.61
15	6.594	100	106.36	230	192.92
20	12.23	110	114.47	240	199.33
25	18.82	120	122.22	250	205.81
30	25.89	130	129.54	260	212.42
35	33.08	140	136.40	270	219.16
40	40.11	150	143.05	280	225.94
45	46.94	160	149.58	290	232.97
50	53.64	170	155.94	300	240.25
55	60.12	180	162.09	310	247.86
60	66.32	190	168.16	273.15	221.25
70	77.70	200	174.26	298.15	238.91
80	88.12	210	180.41	310.15	247.99
L-Methionine (149.2 Da) [24]					
10	2.017	90	82.68	220	157.28
15	5.883	100	89.50	230	164.14
20	11.48	110	95.90	240	172.05
25	17.79	120	101.96	250	181.13
30	24.23	130	107.70	260	192.67
35	30.65	140	113.26	270	208.28
40	36.70	150	118.66	280	229.79
45	42.43	160	124.01	290	259.20
50	47.87	170	129.24	300	298.28
55	53.01	180	134.47	310	298.19
60	57.91	190	139.70	273.15	214.30
70	66.99	200	145.19	298.15	290.04
80	75.19	210	151.04	310.15	296.85
L-Phenylalanine (165.2 Da) [27]					
10	2.594	90	74.73	220	152.05
15	6.682	100	80.96	230	158.49
20	11.87	110	86.94	240	165.02
25	17.36	120	92.72	250	171.54
30	23.16	130	98.49	260	178.07
35	28.93	140	104.31	270	184.60
40	34.36	150	110.17	280	191.13
45	39.44	160	116.11	290	197.69
50	44.23	170	122.01	300	204.22
55	48.74	180	127.95	310	210.71
60	53.01	190	133.93	273.15	186.65
70	60.79	200	139.87	298.15	203.01
80	67.99	210	145.85	310.15	210.79

TABLE 8.1b. *Continued.*

T/K	C_p	T/K	C_p	T/K	C_p
L-Proline (115.1 Da) [27]					
10	1.301	90	59.08	220	116.06
15	4.105	100	63.60	230	120.50
20	8.314	110	67.91	240	124.93
25	13.01	120	72.17	250	129.33
30	17.85	130	76.36	260	133.85
35	22.65	140	80.63	270	138.16
40	27.17	150	84.98	280	142.67
45	31.42	160	89.45	290	147.28
50	35.38	170	93.93	300	152.09
55	39.02	180	98.41	310	156.98
60	42.43	190	102.84	273.15	141.00
70	48.62	200	107.24	298.15	151.17
80	54.10	210	111.63	310.15	157.07
L-Serine (105.1 Da) [28]					
10	0.816	90	55.90	220	107.78
15	2.703	100	61.09	230	111.25
20	5.556	110	65.73	240	114.77
25	9.063	120	70.12	250	118.28
30	13.03	130	74.35	260	121.84
35	17.21	140	78.41	270	125.39
40	21.46	150	82.34	280	128.99
45	25.63	160	86.11	290	132.59
50	29.69	170	89.83	300	136.23
55	33.59	180	93.47	310	139.91
60	37.31	190	97.11	273.15	126.52
70	44.18	200	100.67	298.15	135.56
80	50.33	210	104.22	310.15	140.00
L-Tryptophane (204.2 Da) [27]					
10	4.393	90	84.56	220	178.20
15	10.02	100	91.92	230	185.69
20	16.51	110	99.04	240	193.34
25	23.04	120	106.06	250	201.08
30	29.35	130	113.18	260	208.87
35	35.28	140	120.33	270	216.52
40	40.78	150	127.45	280	224.22
45	45.61	160	134.64	290	231.92
50	51.00	170	141.80	300	239.58
55	55.73	180	148.99	310	247.32
60	60.17	190	156.27	273.15	218.95
70	68.70	200	163.59	298.15	238.15
80	76.86	210	170.88	310.15	247.44

TABLE 8.1b. *Continued.*

T/K	C_p	*T*/K	C_p	*T*/K	C_p
L-Tyrosine (181.2 Da) [27]					
10	1.389	90	75.06	220	162.72
15	3.908	100	82.05	230	169.45
20	7.724	110	88.83	240	176.23
25	12.57	120	95.56	250	183.05
30	18.07	130	102.26	260	189.91
35	23.91	140	108.87	270	196.86
40	29.62	150	115.52	280	203.84
45	35.24	160	122.26	290	210.79
50	40.59	170	128.99	300	217.74
55	45.56	180	135.77	310	224.60
60	50.29	190	142.38	273.15	199.08
70	59.20	200	149.12	298.15	216.44
80	67.49	210	155.81	310.15	224.72
L-Valine (117.2 Da) [24]					
10	1.100	90	64.73	220	133.01
15	3.192	100	71.34	230	137.57
20	6.615	110	77.57	240	142.05
25	10.69	120	83.55	250	146.61
30	15.18	130	89.16	260	151.17
35	19.86	140	94.56	270	155.85
40	24.46	150	99.83	280	160.50
45	29.04	160	104.98	290	165.06
50	33.50	170	109.91	300	169.70
55	37.87	180	114.73	310	174.31
60	42.09	190	119.37	273.15	157.28
70	50.04	200	123.89	298.15	168.82
80	57.61	210	128.41	310.15	174.39

heat capacity of the denatured protein and the calculated one for the unfolded polypeptide chain is a strong argument that heat denatured proteins are indistinguishable thermodynamically from fully unfolded (D ≈ U).

8.2 PARTIAL VOLUME

The partial specific volume of proteins can be measured experimentally [11,12] or can be estimated from the amino acid composition of the protein using equation

$$V_2 = (N - 1) \cdot V_2(\text{—CHCONH—}) + \sum_{i=1}^{N} V_2(\text{—}R_i), \quad (8.2)$$

where N is number of amino acid residues in the protein sequence, $V_2(\text{—CHCONH—})$ is the contribution of a peptide unit, and $V_2(\text{—}R_i)$ is the contribution of the ith amino acid side chain. These contributions are listed in Table 8.6. For more details, compilation of the experimental data on the partial volume of proteins is recommended [12].

8.3 THERMODYNAMIC FUNCTIONS

Because the absolute value of the heat capacity of the native state is always larger than the heat capacity of the unfolded state, and because they have different temperature dependencies, the heat capacity change upon unfolding is positive and temperature dependent itself:

$$\Delta_{\mathrm{N}}^{\mathrm{U}} C_{\mathrm{p}}(T) = C_{\mathrm{p}}^{\mathrm{U}}(T) - C_{\mathrm{p}}^{\mathrm{N}}(T), \quad (8.3)$$

where $\Delta_{\mathrm{N}}^{\mathrm{U}} C_{\mathrm{p}}(T)$ is a nonlinear function of temperature. It has maximum at around 50 °C, decreases at high temperatures and appears to reach zero at ~140 °C). The heat capacities of proteins in the native and unfolded states and the heat capacity change upon unfolding are presented in Table 8.7.

TABLE 8.2. *Temperature dependence of the partial molar volumes (cm^3 mol^{-1}) of the peptide unit and of the side chains of amino acid residues for the temperature range 5–125 °C [11].*

	Temperature (°C)					
	5	25	50	75	100	125
–CHCONH–	28.3	28.0	28.6	28.9	29.0	29.4
–R$_i$						
Ala	24.8	27.2	30.1	33.1	36.3	39.4
Arg	81.2	85.7	88.4	90.4	92.1	93.5
Asn	44.1	45.7	47.8	49.3	50.8	52.4
Asp	39.0	41.5	44.5	47.3	49.9	52.6
Cys	40.5	40.5	40.5	40.5	40.5	40.5
Gln	58.4	61.0	63.2	66.0	68.5	69.7
Glu	54.9	57.5	60.7	63.6	66.3	69.3
Gly	10.9	10.3	9.6	9.2	8.9	8.5
His	65.1	64.0	63.1	62.4	61.8	61.1
Ile	64.5	66.1	67.7	69.8	71.8	74.0
Leu	75.0	77.6	80.2	82.9	86.5	89.4
Lys	72.4	73.5	75.8	78.5	81.3	84.8
Met	73.3	72.1	70.2	69.0	67.9	66.7
Phe	82.0	86.3	92.0	97.9	102.6	107.9
Pro	36.0	35.8	34.1	33.7	33.5	33.2
Ser	27.1	27.8	28.8	29.7	30.7	32.0
Thr	44.2	44.7	45.9	47.6	50.9	54.6
Trp	110.9	110.9	110.9	110.9	110.9	110.9
Tyr	88.2	90.0	92.2	94.1	95.9	97.8
Val	60.7	63.0	65.7	68.5	71.7	74.5

The non-zero heat capacity change upon protein unfolding means that all other thermodynamic functions are also temperature dependent:

$$\Delta_{\mathrm{N}}^{\mathrm{U}}H(T) = \Delta_{\mathrm{N}}^{\mathrm{U}}H(T_0) + \int_{T_0}^{T} \Delta_{\mathrm{N}}^{\mathrm{U}}C_{\mathrm{p}}(T)\mathrm{d}T \qquad (8.4)$$

$$\Delta_{\mathrm{N}}^{\mathrm{U}}S(T) = \Delta_{\mathrm{N}}^{\mathrm{U}}S(T_0) + \int_{T_0}^{T} \Delta_{\mathrm{N}}^{\mathrm{U}}C_{\mathrm{p}}(T)\mathrm{d}\ln T \qquad (8.5)$$

$$\Delta_{\mathrm{N}}^{\mathrm{U}}G = \Delta_{\mathrm{N}}^{\mathrm{U}}H - \mathrm{T}\Delta_{\mathrm{N}}^{\mathrm{U}}\mathrm{S} \qquad (8.6)$$

These functions are presented in Table 8.7 for a selected set of 20 proteins, for which the thermodynamics of unfolding have been measured with highest accuracy.

8.4 HYDRATION EFFECTS

The contribution of solvent (water) to the observed changes of the thermodynamic parameters of proteins can be assumed to be proportional to the changes in water accessible surface area of the protein groups. The water accessible surface area can be calculated from the X-ray or NMR structure of the native protein by computing the surface formed by the center of a spherical probe rolling on the surface of the protein (see e.g., [13,14]). As was shown earlier, the hydration effects of protein groups exposed to water upon unfolding [15–18] can be expressed as follows:

$$\Delta C_{p,k}^{\mathrm{hyd}}(T) = \sum_i \Delta_{\mathrm{N}}^{\mathrm{U}}\mathrm{ASA}_{k,i} \times \Delta\hat{C}_{p,k,i}^{\mathrm{hyd}}(T) \qquad (8.7)$$

$$\Delta H_k^{\mathrm{hyd}}(T) = \sum_i \Delta_{\mathrm{N}}^{\mathrm{U}}\mathrm{ASA}_{k,i} \times \Delta\hat{H}_{k,i}^{\mathrm{hyd}}(T) \qquad (8.8)$$

$$\Delta S_k^{\mathrm{hyd}}(T) = \sum_i \Delta_{\mathrm{N}}^{\mathrm{U}}\mathrm{ASA}_{k,i} \times \Delta\hat{S}_{k,i}^{\mathrm{hyd}}(T) \qquad (8.9)$$

$$\Delta G_k^{\mathrm{hyd}}(T) = \sum_i \Delta_{\mathrm{N}}^{\mathrm{U}}\mathrm{ASA}_{k,i} \times \Delta\hat{G}_{k,i}^{\mathrm{hyd}}(T), \qquad (8.10)$$

where $\Delta_{\mathrm{N}}^{\mathrm{U}}\mathrm{ASA}_{k,i}$ is the change of water accessible surface area of protein group i of type k upon unfolding and $\Delta\hat{C}_{p,k,i}^{\mathrm{hyd}}(T)$, $\Delta\hat{S}_{k,i}^{\mathrm{hyd}}(T)$, $\Delta\hat{G}_{k,i}^{\mathrm{hyd}}(T)$, and $\Delta\hat{H}_{k,i}^{\mathrm{hyd}}(T)$ are the hydration heat capacity change, enthalpy, entropy, and Gibbs energy change of this type of group the normalized per square angstrom. These normalized hydration effects were determined by the transfer of model compounds from the gaseous phase to water and their values are listed in Table 8.8.

TABLE 8.3. *Heat capacities (J K^{-1} mol^{-1}) of solid poly (amino acids).*

Poly-L-Alanine (m.w 15,000 Da) [29]					
T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	42.65	590	120.06
0.2	0.00	200	44.96	600	121.57
0.3	0.00	210	47.19	610	123.07
0.4	0.00	220	49.46	620	124.55
0.5	0.00	230	51.71	630	126.02
0.6	0.00	240	53.93	640	127.47
0.7	0.00	250	56.18	650	128.91
0.8	0.00	260	58.39	660	130.34
0.9	0.00	270	60.61	670	131.76
1.0	0.00	273.15	61.30	680	133.16
1.2	0.00	280	62.79	690	134.56
1.4	0.00	290	64.97	700	135.95
1.6	0.00	298.15	66.76	710	137.32
1.8	0.00	300	67.17	720	138.69
2	0.01	310	69.30	730	140.05
3	0.02	320	71.40	740	141.40
4	0.05	330	73.54	750	142.75
5	0.10	340	75.60	760	144.08
6	0.17	350	77.64	770	145.41
7	0.27	360	79.65	780	146.74
8	0.40	370	81.64	790	148.06
9	0.56	380	83.72	800	149.38
10	0.75	390	85.66	810	150.70
15	1.95	400	87.58	820	152.01
20	3.31	410	89.47	830	153.32
25	4.66	420	91.35	840	154.63
30	5.95	430	93.31	850	155.94
40	8.40	440	95.13	860	157.25
50	10.75	450	96.93	870	158.55
60	13.06	460	98.72	880	159.86
70	15.35	470	100.48	890	161.16
80	17.63	480	102.22	900	162.47
90	19.89	490	103.94	910	163.78
100	22.15	500	105.64	920	165.10
110	24.43	510	107.32	930	166.41
120	26.70	520	108.98	940	167.74
130	28.99	530	110.62	950	169.06
140	31.25	540	112.24	960	170.39
150	33.52	550	113.84	970	171.73
160	35.78	560	115.42	980	173.09
170	38.05	570	116.98	990	174.44
180	40.37	580	118.53	1000	175.80

TABLE 8.3. *Continued.*

Poly-L-Arginine·HCl (m.w 132,000 Da) [30]					
T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	168.39	590	410.48
0.2	0.00	200	174.72	600	415.75
0.3	0.00	210	180.99	610	420.90
0.4	0.00	220	187.37	620	426.02
0.5	0.00	230	193.59	630	431.08
0.6	0.00	240	199.90	640	436.12
0.7	0.00	250	206.23	650	441.09
0.8	0.00	260	212.56	660	446.07
0.9	0.00	270	218.86	670	451.00
1.0	0.01	273.15	220.85	680	455.91
1.2	0.01	280	225.21	690	460.79
1.4	0.01	290	231.62	700	465.91
1.6	0.02	298.15	236.88	710	470.48
1.8	0.03	300	237.99	720	475.28
2	0.04	310	244.49	730	480.05
3	0.14	320	250.83	740	484.81
4	0.34	330	257.21	750	489.54
5	0.66	340	263.60	760	494.23
6	1.13	350	269.96	770	498.98
7	1.77	360	276.31	780	503.65
8	2.57	370	282.71	790	508.31
9	3.51	380	289.10	800	512.93
10	4.58	390	295.25	810	517.55
15	10.76	400	301.53	820	522.18
20	17.16	410	307.69	830	526.80
25	23.29	420	313.80	840	531.38
30	29.14	430	319.89	850	535.98
40	40.34	440	325.97	860	540.57
50	51.21	450	332.02	870	545.16
60	61.91	460	338.03	880	549.75
70	72.42	470	343.99	890	554.32
80	82.61	480	349.82	900	558.90
90	92.43	490	355.58	910	563.48
100	101.85	500	361.27	920	568.07
110	110.73	510	366.89	930	572.67
120	119.11	520	372.45	940	577.26
130	127.01	530	377.96	950	581.87
140	134.57	540	383.44	960	586.49
150	141.75	550	388.86	970	591.12
160	148.67	560	394.31	980	595.77
170	155.41	570	399.73	990	600.42
180	161.97	580	405.15	1000	605.07

TABLE 8.3. *Continued.*

Poly-L-Aspartic acid·Na (m.w 42,500 Da) [30]					
T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	105.03	590	249.25
0.2	0.00	200	109.57	600	252.01
0.3	0.00	210	114.02	610	254.74
0.4	0.00	220	118.55	620	257.41
0.5	0.00	230	122.86	630	260.03
0.6	0.00	240	127.19	640	262.63
0.7	0.00	250	131.48	650	265.19
0.8	0.00	260	135.71	660	267.74
0.9	0.00	270	139.84	670	270.26
1.0	0.00	273.15	141.14	680	272.77
1.2	0.01	280	143.96	690	275.25
1.4	0.01	290	148.05	700	278.00
1.6	0.01	298.15	151.40	710	280.19
1.8	0.02	300	152.07	720	282.63
2	0.02	310	156.17	730	285.05
3	0.08	320	160.08	740	287.47
4	0.19	330	164.01	750	289.86
5	0.38	340	167.90	760	292.22
6	0.65	350	171.71	770	294.65
7	1.01	360	175.46	780	297.02
8	1.47	370	179.27	790	299.37
9	2.01	380	182.83	800	301.65
10	2.62	390	186.42	810	303.98
15	6.16	400	190.09	820	306.30
20	9.83	410	193.59	830	308.62
25	13.34	420	197.03	840	310.94
30	16.69	430	200.44	850	313.25
40	23.10	440	203.81	860	315.55
50	29.33	450	207.18	870	317.85
60	35.48	460	210.50	880	320.15
70	41.58	470	213.78	890	322.43
80	47.59	480	216.97	900	324.72
90	53.48	490	220.11	910	327.02
100	59.27	500	223.19	920	329.32
110	64.90	510	226.23	930	331.62
120	70.40	520	229.22	940	333.93
130	75.70	530	232.18	950	336.24
140	80.90	540	235.10	960	338.55
150	85.89	550	237.99	970	340.87
160	90.88	560	240.94	980	343.21
170	95.65	570	243.74	990	345.55
180	100.39	580	246.51	1000	347.89

TABLE 8.3. *Continued.*

Poly-L-Asparagine (m.w 10,400 Da) [30]					
T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	97	590	235.78
0.2	0.00	200	100.96	600	238.61
0.3	0.00	210	104.88	610	241.40
0.4	0.00	220	108.90	620	244.14
0.5	0.00	230	112.73	630	246.84
0.6	0.00	240	116.63	640	249.51
0.7	0.00	250	120.52	650	252.16
0.8	0.00	260	124.40	660	254.80
0.9	0.00	270	128.19	670	257.41
1.0	0.00	273.15	129.40	680	260.00
1.2	0.01	280	132.02	690	262.58
1.4	0.01	290	135.84	700	265.41
1.6	0.01	298.15	138.99	710	267.70
1.8	0.02	300	139.62	720	270.23
2	0.03	310	143.51	730	272.75
3	0.09	320	147.23	740	275.27
4	0.22	330	150.98	750	277.77
5	0.43	340	154.71	760	280.23
6	0.74	350	158.39	770	282.77
7	1.14	360	162.02	780	285.24
8	1.64	370	165.73	790	287.71
9	2.22	380	169.20	800	290.09
10	2.85	390	172.73	810	292.54
15	6.39	400	176.35	820	294.98
20	9.92	410	179.79	830	297.41
25	13.29	420	183.19	840	299.85
30	16.50	430	186.56	850	302.27
40	22.69	440	189.91	860	304.69
50	28.72	450	193.27	870	307.11
60	34.66	460	196.59	880	309.52
70	40.49	470	199.87	890	311.93
80	46.16	480	203.07	900	314.34
90	51.66	490	206.22	910	316.76
100	56.96	500	209.32	920	319.18
110	62.02	510	212.39	930	321.61
120	66.88	520	215.42	940	324.04
130	71.54	530	218.41	950	326.47
140	76.09	540	221.37	960	328.91
150	80.41	550	224.31	970	331.36
160	84.70	560	227.30	980	333.82
170	88.84	570	230.15	990	336.28
180	92.96	580	232.98	1000	338.75

TABLE 8.3. *Continued.*

Poly-L-Glutamic Acid·Na (m.w 74,000 Da) [30]					
T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	100.57	590	282.92
0.2	0.00	200	106.20	600	286.38
0.3	0.00	210	111.79	610	289.78
0.4	0.00	220	117.49	620	293.13
0.5	0.00	230	122.98	630	296.42
0.6	0.00	240	128.45	640	299.68
0.7	0.00	250	133.90	650	302.91
0.8	0.00	260	139.28	660	306.11
0.9	0.00	270	144.57	670	309.28
1.0	0.00	273.15	146.23	680	312.42
1.2	0.00	280	149.83	690	315.54
1.4	0.01	290	155.07	700	318.90
1.6	0.01	298.15	159.33	710	321.72
1.8	0.01	300	160.21	720	324.77
2	0.02	310	165.42	730	327.80
3	0.07	320	170.42	740	330.83
4	0.16	330	175.41	750	333.82
5	0.31	340	180.36	760	336.78
6	0.53	350	185.21	770	339.80
7	0.83	360	189.98	780	342.76
8	1.20	370	194.80	790	345.70
9	1.64	380	199.34	800	348.55
10	2.14	390	203.89	810	351.47
15	5.03	400	208.50	820	354.37
20	8.02	410	212.91	830	357.26
25	10.89	420	217.26	840	360.15
30	13.62	430	221.56	850	363.03
40	18.86	440	225.83	860	365.90
50	23.96	450	230.06	870	368.76
60	28.99	460	234.25	880	371.62
70	34.05	470	238.38	890	374.46
80	39.17	480	242.39	900	377.32
90	44.38	490	246.33	910	380.15
100	49.71	500	250.21	920	383.01
110	55.12	510	254.02	930	385.88
120	60.64	520	257.79	940	388.74
130	66.24	530	261.50	950	391.60
140	71.96	540	265.17	960	394.47
150	77.65	550	268.80	970	397.35
160	83.41	560	272.47	980	400.25
170	89.13	570	276.00	990	403.15
180	94.87	580	279.48	1000	406.04

TABLE 8.3. *Continued.*

Poly-Glycine II (m.w 15,000 Da) [29]					
T / K	C_p	*T* / K	C_p	*T* / K	C_p
0.1	0.00	190	64.83	590	163.11
0.2	0.00	200	67.40	600	165.32
0.3	0.00	210	69.93	610	167.40
0.4	0.00	220	72.48	620	169.46
0.5	0.00	230	75.06	630	171.51
0.6	0.00	240	77.62	640	173.53
0.7	0.00	250	80.17	650	175.55
0.8	0.00	260	82.75	660	177.56
0.9	0.00	270	85.25	670	179.55
1.0	0.00	273.15	86.07	680	181.53
1.2	0.00	280	87.91	690	183.50
1.4	0.01	290	90.45	700	185.46
1.6	0.01	298.15	92.53	710	187.40
1.8	0.02	300	93.01	720	189.34
2	0.02	310	95.58	730	191.26
3	0.07	320	98.42	740	193.17
4	0.17	330	100.85	750	195.07
5	0.34	340	103.43	760	196.97
6	0.58	350	105.99	770	198.85
7	0.88	360	108.61	780	200.73
8	1.25	370	112.07	790	202.60
9	1.67	380	113.75	800	204.47
10	2.11	390	116.28	810	206.33
15	4.52	400	118.87	820	208.18
20	6.87	410	121.42	830	210.03
25	9.09	420	123.91	840	211.88
30	11.22	430	126.39	850	213.72
40	15.34	440	128.84	860	215.57
50	19.38	450	131.26	870	217.41
60	23.38	460	133.69	880	219.26
70	27.32	470	136.15	890	221.10
80	31.17	480	138.47	900	222.93
90	34.86	490	140.93	910	224.74
100	38.46	500	143.23	920	226.58
110	41.89	510	145.51	930	228.42
120	45.16	520	147.77	940	230.26
130	48.25	530	150.01	950	232.13
140	51.22	540	152.23	960	233.99
150	54.11	550	154.43	970	235.84
160	56.91	560	156.72	980	237.71
170	59.56	570	158.86	990	239.56
180	62.21	580	161.00	1000	241.44

TABLE 8.3. *Continued.*

Poly-L-Histidine (m.w 49,000 Da) [30]					
T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	113.43	590	322.88
0.2	0.00	200	119.22	600	327.05
0.3	0.00	210	124.97	610	331.18
0.4	0.00	220	131.00	620	335.25
0.5	0.00	230	136.77	630	339.26
0.6	0.00	240	142.71	640	343.24
0.7	0.00	250	148.55	650	347.16
0.8	0.00	260	154.44	660	351.08
0.9	0.00	270	160.16	670	354.96
1.0	0.00	273.15	161.98	680	358.80
1.2	0.01	280	165.99	690	362.62
1.4	0.01	290	171.78	700	366.68
1.6	0.01	298.15	176.53	710	370.18
1.8	0.02	300	177.51	720	373.92
2	0.02	310	183.37	730	377.62
3	0.08	320	188.85	740	381.32
4	0.19	330	194.70	750	385.35
5	0.38	340	200.39	760	388.63
6	0.65	350	206.06	770	392.33
7	1.01	360	211.37	780	395.95
8	1.46	370	217.02	790	399.55
9	2.00	380	222.34	800	403.07
10	2.61	390	227.64	810	406.63
15	6.13	400	233.12	820	410.19
20	9.77	410	238.35	830	413.74
25	13.26	420	243.62	840	417.29
30	16.60	430	248.73	850	420.81
40	22.98	440	253.79	860	424.33
50	29.18	450	258.82	870	427.83
60	35.30	460	263.82	880	431.33
70	41.45	470	268.78	890	434.81
80	47.55	480	273.62	900	438.34
90	53.66	490	278.34	910	441.82
100	59.79	500	282.98	920	445.31
110	65.84	510	287.56	930	448.80
120	71.95	520	292.09	940	452.29
130	77.90	530	296.63	950	455.74
140	83.91	540	301.19	960	459.24
150	89.79	550	305.55	970	462.75
160	95.72	560	309.97	980	466.26
170	101.66	570	314.36	990	469.77
180	107.57	580	318.66	1000	473.28

TABLE 8.3. *Continued.*

Poly-L-Leucine (m.w 150,000 Da) [30]					
T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	116.64	590	300.37
0.2	0.00	200	121.12	600	304.48
0.3	0.00	210	125.58	610	308.56
0.4	0.00	220	130.13	620	312.57
0.5	0.00	230	134.68	630	316.52
0.6	0.00	240	139.08	640	320.46
0.7	0.00	250	143.73	650	324.36
0.8	0.00	260	148.34	660	328.25
0.9	0.00	270	152.93	670	332.10
1.0	0.00	273.15	154.40	680	335.93
1.2	0.01	280	157.73	690	339.73
1.4	0.01	290	162.40	700	343.79
1.6	0.01	298.15	166.35	710	347.30
1.8	0.02	300	167.14	720	351.05
2	0.03	310	172.11	730	354.77
3	0.10	320	176.90	740	358.49
4	0.23	330	181.86	750	362.18
5	0.45	340	186.62	760	365.84
6	0.77	350	191.58	770	369.57
7	1.20	360	196.37	780	373.22
8	1.74	370	201.29	790	376.87
9	2.39	380	206.03	800	380.43
10	3.11	390	210.82	810	384.04
15	7.31	400	215.77	820	387.65
20	11.65	410	220.55	830	391.24
25	15.81	420	225.28	840	394.84
30	19.78	430	230.00	850	398.43
40	27.39	440	234.67	860	402.00
50	34.77	450	239.32	870	405.57
60	42.05	460	243.94	880	409.14
70	49.23	470	248.57	890	412.70
80	56.23	480	253.07	900	416.26
90	63.02	490	257.58	910	419.83
100	69.61	500	262.12	920	423.39
110	75.80	510	266.50	930	426.97
120	81.73	520	270.85	940	430.55
130	87.31	530	275.16	950	434.13
140	92.66	540	279.43	960	437.72
150	97.73	550	283.68	970	441.32
160	102.69	560	287.99	980	444.93
170	107.40	570	292.15	990	448.55
180	112.07	580	296.28	1000	452.17

TABLE 8.3. *Continued.*

Poly-L-Lysine·HBr (m.w 560,000 Da) [30]					
T / K	C_p	*T* / K	C_p	*T* / K	C_p
0.1	0.00	190	145.15	590	369.70
0.2	0.00	200	150.98	600	374.53
0.3	0.00	210	156.76	610	379.32
0.4	0.00	220	162.67	620	384.05
0.5	0.00	230	168.43	630	388.73
0.6	0.00	240	174.25	640	393.34
0.7	0.00	250	180.11	650	397.95
0.8	0.00	260	185.97	660	402.53
0.9	0.00	270	191.81	670	407.07
1.0	0.00	273.15	193.66	680	411.59
1.2	0.01	280	197.69	690	416.07
1.4	0.01	290	203.67	700	420.81
1.6	0.02	298.15	208.57	710	424.99
1.8	0.03	300	209.60	720	429.41
2	0.04	310	215.67	730	433.88
3	0.12	320	221.57	740	438.27
4	0.28	330	227.54	750	442.64
5	0.55	340	233.53	760	446.93
6	0.95	350	239.48	770	451.33
7	1.47	360	245.45	780	455.65
8	2.14	370	251.45	790	459.97
9	2.93	380	257.16	800	464.20
10	3.81	390	262.98	810	468.44
15	8.97	400	268.86	820	472.72
20	14.30	410	274.58	830	476.98
25	19.40	420	280.24	840	481.25
30	24.27	430	285.88	850	485.49
40	33.60	440	291.53	860	489.73
50	42.66	450	297.16	870	493.97
60	51.59	460	302.74	880	498.20
70	60.41	470	308.28	890	502.42
80	69.03	480	313.68	900	506.65
90	77.39	490	319.02	910	510.88
100	85.48	500	324.29	920	515.12
110	93.23	510	329.49	930	519.36
120	100.61	520	334.64	940	523.61
130	107.63	530	339.75	950	527.86
140	114.40	540	344.82	960	532.12
150	120.83	550	349.88	970	536.39
160	127.20	560	354.99	980	540.68
170	133.25	570	359.90	990	544.98
180	139.25	580	364.88	1000	549.28

TABLE 8.3. *Continued.*

Poly-L-Methionine (m.w 160,000 Da) [30]					
T / K	C_p	*T* / K	C_p	*T* / K	C_p
0.1	0.00	190	108.51	590	281.22
0.2	0.00	200	113.39	600	284.80
0.3	0.00	210	118.22	610	288.35
0.4	0.00	220	123.15	620	291.84
0.5	0.00	230	127.96	630	295.28
0.6	0.00	240	132.69	640	298.70
0.7	0.00	250	137.51	650	302.09
0.8	0.00	260	142.24	660	305.45
0.9	0.00	270	146.91	670	308.80
1.0	0.00	273.15	148.39	680	312.12
1.2	0.01	280	151.59	690	315.42
1.4	0.01	290	156.30	700	318.96
1.6	0.01	298.15	160.16	710	321.96
1.8	0.02	300	160.95	720	325.21
2	0.02	310	165.71	730	328.44
3	0.08	320	170.29	740	331.66
4	0.19	330	174.90	750	334.86
5	0.38	340	179.52	760	338.03
6	0.65	350	184.14	770	341.27
7	1.02	360	188.63	780	344.44
8	1.48	370	193.22	790	347.60
9	2.02	380	197.58	800	350.67
10	2.63	390	201.95	810	353.81
15	6.19	400	206.41	820	356.94
20	9.87	410	210.69	830	360.07
25	13.39	420	214.94	840	363.19
30	16.76	430	219.15	850	366.30
40	23.20	440	223.35	860	369.41
50	29.47	450	227.55	870	372.51
60	35.63	460	231.71	880	375.61
70	41.81	470	235.82	890	378.69
80	47.91	480	239.84	900	381.79
90	53.95	490	243.80	910	384.89
100	59.95	500	247.75	920	387.99
110	65.83	510	251.60	930	391.10
120	71.58	520	255.42	940	394.21
130	77.17	530	259.20	950	397.33
140	82.68	540	262.94	960	400.45
150	87.98	550	266.66	970	403.59
160	93.28	560	270.43	980	406.73
170	98.43	570	274.06	990	409.89
180	103.53	580	277.65	1000	413.04

TABLE 8.3. *Continued.*

Poly-L-Phenylalanine (m.w 23,000 Da) [30]					
T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	105.52	590	320.05
0.2	0.00	200	111.58	600	324.19
0.3	0.00	210	117.56	610	328.26
0.4	0.00	220	123.77	620	332.27
0.5	0.00	230	129.77	630	336.22
0.6	0.00	240	135.84	640	340.12
0.7	0.00	250	141.94	650	343.98
0.8	0.00	260	148.03	660	347.80
0.9	0.00	270	154.06	670	351.58
1.0	0.00	273.15	155.97	680	355.33
1.2	0.00	280	160.10	690	359.04
1.4	0.01	290	166.22	700	362.99
1.6	0.01	298.15	171.17	710	366.38
1.8	0.01	300	172.21	720	370.01
2	0.02	310	178.30	730	373.60
3	0.07	320	184.21	740	377.19
4	0.16	330	190.14	750	380.73
5	0.32	340	196.03	760	384.24
6	0.54	350	201.84	770	387.81
7	0.85	360	207.56	780	391.32
8	1.23	370	213.32	790	394.79
9	1.68	380	218.82	800	398.15
10	2.19	390	224.34	810	401.59
15	5.15	400	229.91	820	405.01
20	8.21	410	235.28	830	408.42
25	11.14	420	240.58	840	411.82
30	13.93	430	245.81	850	415.23
40	19.30	440	250.98	860	418.69
50	24.54	450	256.11	870	421.97
60	29.82	460	261.18	880	425.33
70	35.20	470	266.17	890	428.68
80	40.69	480	271.04	900	432.03
90	46.37	490	275.83	910	435.38
100	52.17	500	280.53	920	438.73
110	57.97	510	285.16	930	442.10
120	63.85	520	289.73	940	445.46
130	69.77	530	294.23	950	448.82
140	75.67	540	298.67	960	452.19
150	81.61	550	303.05	970	455.57
160	87.59	560	307.46	980	458.96
170	93.53	570	311.71	990	462.36
180	99.53	580	315.91	1000	465.75

TABLE 8.3. *Continued.*

Poly-L-Proline (m.w 44,000 Da) [30]

T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	75.68	590	224.54
0.2	0.00	200	79.12	600	227.75
0.3	0.00	210	82.65	610	230.92
0.4	0.00	220	86.17	620	234.04
0.5	0.00	230	89.84	630	237.11
0.6	0.00	240	93.57	640	240.14
0.7	0.00	250	97.35	650	243.15
0.8	0.00	260	101.24	660	246.14
0.9	0.00	270	105.05	670	249.09
1.0	0.00	273.15	106.28	680	252.02
1.2	0.00	280	108.98	690	254.93
1.4	0.01	290	112.99	700	258.08
1.6	0.01	298.15	116.23	710	260.69
1.8	0.01	300	116.90	720	263.54
2	0.02	310	120.99	730	266.37
3	0.06	320	125.05	740	269.19
4	0.14	330	129.05	750	271.98
5	0.28	340	133.07	760	274.76
6	0.48	350	137.11	770	277.52
7	0.75	360	141.16	780	280.27
8	1.08	370	145.18	790	283.00
9	1.48	380	149.17	800	285.72
10	1.93	390	153.17	810	288.43
15	4.54	400	157.15	820	291.13
20	7.25	410	160.94	830	293.81
25	9.83	420	164.77	840	296.49
30	12.30	430	168.58	850	299.16
40	17.03	440	172.40	860	301.82
50	21.63	450	176.17	870	304.48
60	26.15	460	179.91	880	307.13
70	30.64	470	183.62	890	309.78
80	35.04	480	187.24	900	312.42
90	39.31	490	190.88	910	315.06
100	43.46	500	194.46	920	317.70
110	47.45	510	197.95	930	320.34
120	51.27	520	201.40	940	322.98
130	54.95	530	204.81	950	325.63
140	58.51	540	208.19	960	328.28
150	62.00	550	211.54	970	330.93
160	65.43	560	214.84	980	333.59
170	68.84	570	218.11	990	336.26
180	72.27	580	221.35	1000	338.94

TABLE 8.3. *Continued.*

Poly-L-Serine (m.w 6,000 Da) [30]					
T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	73.88	590	188.29
0.2	0.00	200	77.23	600	190.62
0.3	0.00	210	80.53	610	192.92
0.4	0.00	220	83.94	620	195.17
0.5	0.00	230	87.14	630	197.39
0.6	0.00	240	90.38	640	199.59
0.7	0.00	250	93.62	650	201.77
0.8	0.00	260	96.82	660	203.93
0.9	0.00	270	99.94	670	206.07
1.0	0.00	273.15	100.94	680	208.20
1.2	0.00	280	103.08	690	210.31
1.4	0.01	290	106.22	700	212.68
1.6	0.01	298.15	108.82	710	214.51
1.8	0.01	300	109.32	720	216.60
2	0.02	310	112.52	730	218.67
3	0.06	320	115.57	740	220.74
4	0.13	330	118.65	750	222.79
5	0.26	340	121.72	760	224.81
6	0.44	350	124.74	770	226.90
7	0.68	360	127.71	780	228.93
8	0.99	370	130.76	790	230.95
9	1.36	380	133.58	800	232.90
10	1.77	390	136.46	810	234.90
15	4.16	400	139.44	820	236.90
20	6.64	410	142.26	830	238.89
25	9.01	420	145.06	840	240.89
30	11.27	430	147.83	850	242.88
40	15.60	440	150.58	860	244.86
50	19.82	450	153.34	870	246.83
60	23.96	460	156.08	880	248.81
70	28.13	470	158.79	890	250.77
80	32.26	480	161.41	900	252.74
90	36.36	490	164.00	910	254.72
100	40.44	500	166.55	920	256.69
110	44.46	510	169.06	930	258.68
120	48.42	520	171.54	940	260.66
130	52.29	530	174.00	950	262.64
140	56.10	540	176.43	960	264.63
150	59.75	550	178.84	970	266.62
160	63.42	560	181.32	980	268.63
170	66.95	570	183.67	990	270.64
180	70.46	580	185.99	1000	272.64

TABLE 8.3. *Continued.*

Poly-L-Tryptophane (m.w 160,000 Da) [30]

T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	110.46	590	392.95
0.2	0.00	200	117.96	600	398.53
0.3	0.00	210	125.38	610	404.03
0.4	0.00	220	133.19	620	409.44
0.5	0.00	230	140.76	630	414.76
0.6	0.00	240	148.48	640	420.03
0.7	0.00	250	156.27	650	425.24
0.8	0.00	260	164.15	660	430.40
0.9	0.00	270	171.89	670	435.50
1.0	0.00	273.15	174.37	680	440.57
1.2	0.00	280	179.76	690	445.58
1.4	0.01	290	187.75	700	450.81
1.6	0.01	298.15	194.19	710	455.48
1.8	0.01	300	195.57	720	460.36
2	0.02	310	203.53	730	465.21
3	0.06	320	211.25	740	470.03
4	0.15	330	219.15	750	474.98
5	0.29	340	226.94	760	479.53
6	0.49	350	234.59	770	484.32
7	0.77	360	242.15	780	489.05
8	1.12	370	249.75	790	493.72
9	1.53	380	257.06	800	498.26
10	1.99	390	264.45	810	502.88
15	4.67	400	271.85	820	507.48
20	7.45	410	279.00	830	512.06
25	10.12	420	286.06	840	516.63
30	12.66	430	293.07	850	521.19
40	17.53	440	300.03	860	525.81
50	22.31	450	306.93	870	530.23
60	27.14	460	313.70	880	534.73
70	32.15	470	320.37	890	539.22
80	37.44	480	326.92	900	543.70
90	43.07	490	333.34	910	548.18
100	48.96	500	339.67	920	552.66
110	55.06	510	345.91	930	557.14
120	61.47	520	352.06	940	561.62
130	68.11	530	358.13	950	566.10
140	74.83	540	364.12	960	570.59
150	81.71	550	370.03	970	575.08
160	88.75	560	375.95	980	579.59
170	95.85	570	381.69	990	584.11
180	103.12	580	387.36	1000	588.62

TABLE 8.3. *Continued.*

Poly-L-Tyrosine (m.w 125,000 Da) [30]					
T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	112.30	590	351.96
0.2	0.00	200	119.12	600	356.61
0.3	0.00	210	125.88	610	361.20
0.4	0.00	220	132.86	620	365.71
0.5	0.00	230	139.62	630	370.15
0.6	0.00	240	146.44	640	374.54
0.7	0.00	250	153.27	650	378.89
0.8	0.00	260	160.08	660	383.20
0.9	0.00	270	166.81	670	387.46
1.0	0.00	273.15	168.94	680	391.68
1.2	0.00	280	173.55	690	395.86
1.4	0.01	290	180.35	700	400.28
1.6	0.01	298.15	185.86	710	404.13
1.8	0.01	300	187.02	720	408.22
2	0.02	310	193.78	730	412.26
3	0.07	320	200.35	740	416.30
4	0.16	330	206.93	750	420.29
5	0.31	340	213.47	760	424.24
6	0.54	350	219.92	770	428.26
7	0.84	360	226.28	780	432.22
8	1.22	370	232.68	790	436.13
9	1.66	380	238.80	800	439.92
10	2.16	390	244.94	810	443.79
15	5.09	400	251.13	820	447.65
20	8.12	410	257.11	830	451.49
25	11.01	420	263.01	840	455.32
30	13.78	430	268.84	850	459.15
40	19.09	440	274.61	860	463.04
50	24.28	450	280.34	870	466.74
60	29.52	460	285.98	880	470.53
70	34.92	470	291.55	890	474.29
80	40.53	480	297.00	900	478.07
90	46.43	490	302.35	910	481.84
100	52.53	500	307.62	920	485.61
110	58.80	510	312.81	930	489.39
120	65.28	520	317.93	940	493.17
130	71.86	530	322.97	950	496.95
140	78.48	540	327.95	960	500.74
150	85.16	550	332.87	970	504.54
160	91.94	560	337.81	980	508.35
170	98.69	570	342.59	990	512.17
180	105.51	580	347.30	1000	515.98

TABLE 8.3. *Continued.*

Poly-L-Valine (m.w 7,230 Da) [29]

T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	100.26	590	255.89
0.2	0.00	200	104.36	600	259.29
0.3	0.00	210	108.39	610	262.65
0.4	0.00	220	112.55	620	265.96
0.5	0.00	230	116.53	630	269.23
0.6	0.00	240	120.58	640	272.47
0.7	0.00	250	124.67	650	275.70
0.8	0.00	260	128.75	660	278.90
0.9	0.00	270	132.79	670	282.06
1.0	0.00	273.15	134.07	680	285.22
1.2	0.01	280	136.83	690	288.36
1.4	0.01	290	140.90	700	291.75
1.6	0.01	298.15	144.29	710	294.60
1.8	0.02	300	144.98	720	297.70
2	0.03	310	149.19	730	300.78
3	0.09	320	153.30	740	303.85
4	0.21	330	157.63	750	306.90
5	0.41	340	161.52	760	309.92
6	0.70	350	165.61	770	313.02
7	1.09	360	169.67	780	316.04
8	1.57	370	173.83	790	319.05
9	2.13	380	177.77	800	321.99
10	2.75	390	181.78	810	324.98
15	6.26	400	185.90	820	327.97
20	9.82	410	189.87	830	330.94
25	13.20	420	193.83	840	333.93
30	16.43	430	197.71	850	336.89
40	22.65	440	201.57	860	339.86
50	28.70	450	205.43	870	342.82
60	34.68	460	209.28	880	345.77
70	40.64	470	213.09	890	348.72
80	46.51	480	216.82	900	351.67
90	52.26	490	220.56	910	354.63
100	57.88	500	224.34	920	357.59
110	63.32	510	227.95	930	360.56
120	68.54	520	231.54	940	363.52
130	73.53	530	235.10	950	366.49
140	78.37	540	238.62	960	369.47
150	82.98	550	242.13	970	372.46
160	87.52	560	245.69	980	375.46
170	91.86	570	249.12	990	378.47
180	96.11	580	252.52	1000	381.47

TABLE 8.3. *Continued.*

Poly(L-Lysine·HBr-Alanine) (molar ratio 46 / 54, m.w 37,000 Da) [31]

T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	206.38	590	506.35
0.2	0.00	200	214.69	600	512.75
0.3	0.00	210	222.88	610	518.97
0.4	0.00	220	231.18	620	525.12
0.5	0.00	230	239.30	630	531.21
0.6	0.00	240	247.45	640	537.26
0.7	0.00	250	255.56	650	543.26
0.8	0.00	260	263.67	660	549.20
0.9	0.01	270	271.64	670	555.12
1.0	0.01	273.15	274.17	680	561.01
1.2	0.01	280	279.76	690	566.87
1.4	0.02	290	287.85	700	572.96
1.6	0.03	298.15	294.45	710	578.50
1.8	0.04	300	295.86	720	584.27
2	0.06	310	304	730	590.01
3	0.20	320	312.22	740	595.73
4	0.48	330	320.06	750	601.42
5	0.93	340	328.04	760	607.07
6	1.58	350	335.95	770	612.79
7	2.45	360	343.82	780	618.42
8	3.51	370	352.64	790	624.04
9	4.73	380	359.42	800	629.57
10	6.07	390	367.07	810	635.16
15	13.49	400	374.86	820	640.74
20	20.89	410	382.42	830	646.30
25	27.91	420	389.84	840	651.87
30	34.62	430	397.23	850	657.42
40	47.57	440	404.59	860	662.97
50	60.21	450	411.91	870	668.51
60	72.70	460	419.19	880	674.07
70	85.10	470	426.46	890	679.59
80	97.26	480	433.46	900	685.14
90	109.08	490	440.54	910	690.66
100	120.58	500	447.40	920	696.22
110	131.63	510	454.17	930	701.79
120	142.27	520	460.88	940	707.36
130	152.37	530	467.53	950	712.98
140	162.12	540	474.12	960	718.58
150	171.43	550	480.65	970	724.21
160	180.55	560	487.33	980	729.85
170	189.29	570	493.72	990	735.51
180	197.91	580	500.06	1000	741.19

TABLE 8.3. *Continued.*

Poly (L-Lysine·HBr-Phenylalanine) (molar ratio 51/49, m.w 49,700 Da) [31]

T / K	C_p	*T* / K	C_p	*T* / K	C_p
0.1	0.00	190	231.52	590	695.94
0.2	0.00	200	244.11	600	705.37
0.3	0.00	210	256.66	610	714.69
0.4	0.00	220	269.59	620	723.87
0.5	0.00	230	282.20	630	732.92
0.6	0.00	240	294.93	640	741.90
0.7	0.00	250	307.72	650	750.80
0.8	0.00	260	320.48	660	759.62
0.9	0.00	270	333.16	670	768.37
1.0	0.01	273.15	337.16	680	777.05
1.2	0.01	280	345.88	690	785.66
1.4	0.02	290	358.75	700	794.76
1.6	0.02	298.15	369.22	710	802.74
1.8	0.03	300	371.42	720	811.20
2	0.05	310	384.33	730	819.67
3	0.16	320	396.86	740	828.05
4	0.37	330	409.47	750	836.36
5	0.72	340	422.04	760	844.52
6	1.23	350	434.47	770	852.88
7	1.92	360	446.82	780	861.11
8	2.79	370	459.25	790	869.28
9	3.81	380	471.09	800	877.26
10	4.97	390	483.04	810	885.32
15	11.68	400	495.11	820	893.40
20	18.63	410	506.80	830	901.45
25	25.28	420	518.34	840	909.50
30	31.63	430	529.79	850	917.53
40	43.79	440	541.18	860	925.61
50	55.66	450	552.50	870	933.49
60	67.48	460	563.70	880	941.46
70	79.47	470	574.76	890	949.39
80	91.68	480	585.56	900	957.34
90	104.15	490	596.21	910	965.29
100	116.76	500	606.70	920	973.24
110	129.47	510	617.04	930	981.21
120	142.32	520	627.25	940	989.18
130	155.16	530	637.35	950	997.16
140	168.01	540	647.34	960	1005.15
150	180.69	550	657.26	970	1013.16
160	193.48	560	667.26	980	1021.20
170	206.10	570	676.89	990	1029.26
180	218.82	580	686.52	1000	1037.32

TABLE 8.3. *Continued.*

Poly(L-Glutamic Acid·Na-Tyrosine) (molar ratio 50/50, m.w 30,000 Da) [31]

T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	223.26	590	637.55
0.2	0.00	200	235.44	600	645.58
0.3	0.00	210	247.51	610	653.52
0.4	0.00	220	259.88	620	661.31
0.5	0.00	230	271.82	630	668.98
0.6	0.00	240	283.82	640	676.57
0.7	0.00	250	295.79	650	684.09
0.8	0.00	260	307.68	660	691.54
0.9	0.00	270	319.39	670	698.92
1.0	0.01	273.15	323.08	680	706.23
1.2	0.01	280	331.08	690	713.48
1.4	0.01	290	342.82	700	721.21
1.6	0.02	298.15	352.36	710	727.84
1.8	0.03	300	354.34	720	734.93
2	0.04	310	366.04	730	741.98
3	0.15	320	377.35	740	748.99
4	0.35	330	388.67	750	755.91
5	0.68	340	399.92	760	762.78
6	1.17	350	410.98	770	769.79
7	1.83	360	421.89	780	776.66
8	2.65	370	432.89	790	783.48
9	3.63	380	443.36	800	790.10
10	4.73	390	453.86	810	796.85
15	11.12	400	464.48	820	803.57
20	17.73	410	474.70	830	810.27
25	24.06	420	484.79	840	816.97
30	30.10	430	494.76	850	823.65
40	41.68	440	504.65	860	830.37
50	52.98	450	514.47	870	836.91
60	64.23	460	524.18	880	843.53
70	75.67	470	533.74	890	850.11
80	87.33	480	543.08	900	856.72
90	99.27	490	552.26	910	863.31
100	111.42	500	561.30	920	869.92
110	123.70	510	570.19	930	876.55
120	136.19	520	578.97	940	883.16
130	148.71	530	587.64	950	889.79
140	161.26	540	596.19	960	896.43
150	173.67	550	604.65	970	903.08
160	186.19	560	613.19	980	909.77
170	198.54	570	621.40	990	916.47
180	210.96	580	629.53	1000	923.16

TABLE 8.3. *Continued.*

Poly(L-Proline-Glycine-Proline) (molar ratio 66/34, m.w 5,300 Da) [31]					
T / K	C_p	T / K	C_p	T / K	C_p
0.1	0.00	190	194.56	590	568.71
0.2	0.00	200	203.74	600	576.61
0.3	0.00	210	213	610	584.43
0.4	0.00	220	222.29	620	592.12
0.5	0.00	230	231.85	630	599.69
0.6	0.00	240	241.51	640	607.20
0.7	0.00	250	251.27	650	614.63
0.8	0.00	260	261.23	660	621.99
0.9	0.00	270	271.04	670	629.29
1.0	0.01	273.15	274.20	680	636.53
1.2	0.01	280	281.05	690	643.71
1.4	0.02	290	291.24	700	651.36
1.6	0.03	298.15	299.50	710	657.92
1.8	0.04	300	301.22	720	664.96
2	0.05	310	311.51	730	671.95
3	0.18	320	321.71	740	678.90
4	0.43	330	331.81	750	685.80
5	0.84	340	341.90	760	692.66
6	1.44	350	351.99	770	699.48
7	2.22	360	362.07	780	706.27
8	3.19	370	372.08	790	713.02
9	4.29	380	382.11	800	719.74
10	5.50	390	392.03	810	726.43
15	12.24	400	401.90	820	733.10
20	18.95	410	411.35	830	739.74
25	25.31	420	420.84	840	746.36
30	31.40	430	430.41	850	752.96
40	43.14	440	439.84	860	759.54
50	54.63	450	449.18	870	766.11
60	65.95	460	458.42	880	772.67
70	77.21	470	467.57	890	779.22
80	88.32	480	476.53	900	785.77
90	99.14	490	485.51	910	792.31
100	109.70	500	494.35	920	798.85
110	119.99	510	502.98	930	805.39
120	129.90	520	511.52	940	811.94
130	139.55	530	519.96	950	818.49
140	148.95	540	528.32	960	825.06
150	158.18	550	536.58	970	831.64
160	167.27	560	544.75	980	838.25
170	176.34	570	552.83	990	844.87
180	185.52	580	560.81	1000	851.51

TABLE 8.4. *Heat capacities ($J\,K^{-1}\,g^{-1}$) of anhydrous and hydrated proteins.*

Anhydrous bovine zinc insulin (5,665 Da) [32]

T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$
10	1.987	90	45.56	220	94.73
15	4.427	100	49.87	230	98.58
20	7.305	110	53.93	240	102.42
25	10.42	120	57.78	250	106.32
30	13.64	130	61.51	260	110.21
35	16.86	140	65.27	270	114.14
40	19.95	150	69.04	280	118.03
45	22.90	160	72.80	290	122.05
50	25.74	170	76.53	300	126.11
55	28.48	180	80.21	310	130.25
60	31.14	190	83.81	273.15	115.35
70	36.21	200	87.40	298.15	125.35
80	41.00	210	91.04	310.15	130.29

Hydrated (4.0% H_2O) bovine zinc insulin (5,665 Da) [32]

T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$
10	1.933	90	46.94	220	98.95
15	4.339	100	51.25	230	103.01
20	7.284	110	55.40	240	107.07
25	10.49	120	59.41	250	111.21
30	13.89	130	63.39	260	115.44
35	17.23	140	67.32	270	119.75
40	20.46	150	71.30	280	124.10
45	23.56	160	75.23	290	128.45
50	26.55	170	79.20	300	132.84
55	29.43	180	83.14	310	137.24
60	32.20	190	87.03	273.15	121.13
70	37.46	200	90.96	298.15	132.01
80	42.38	210	94.94	310.15	137.28

Anhydrous bovine chymotrypsinogen (25,666 Da) [32]

T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$
10	1.874	90	46.86	220	97.82
15	4.343	100	51.09	230	101.67
20	7.297	110	55.31	240	105.56
25	10.53	120	59.33	250	109.50
30	13.87	130	63.26	260	113.55
35	17.15	140	67.15	270	117.57
40	20.33	150	70.96	280	121.67
45	23.38	160	74.77	290	125.86
50	26.39	170	78.58	300	130.08
55	29.34	180	82.43	310	134.27
60	32.19	190	86.23	273.15	118.87
70	37.48	200	90.08	298.15	129.29
80	42.26	210	93.97	310.15	134.35

TABLE 8.4. *Continued.*

Hydrated (10.7% H_2O) bovine chymotrypsinogen (25,666 Da) [32]					
T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$
10	1.778	90	51.13	220	114.56
15	4.184	100	55.98	230	120.16
20	7.309	110	60.71	240	125.86
25	10.84	120	65.44	250	131.59
30	14.43	130	70.12	260	137.40
35	18.06	140	74.81	270	143.30
40	21.61	150	79.50	280	149.24
45	25.03	160	84.22	290	155.23
50	28.28	170	88.95	300	161.34
55	31.45	180	93.76	310	167.11
60	34.55	190	98.70	273.15	145.35
70	40.45	200	103.85	298.15	160.42
80	45.94	210	109.12	310.15	167.40

Anhydrous native bovine serum albumin (66,433 Da) [33]					
T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$
10	1.854	90	46.23	220	96.48
15	4.234	100	50.54	230	100.25
20	7.058	110	54.69	240	104.01
25	10.14	120	58.74	250	107.91
30	13.36	130	62.63	260	111.88
35	16.60	140	66.44	270	115.90
40	19.72	150	70.25	280	119.96
45	22.71	160	74.06	290	124.14
50	25.71	170	77.82	300	128.32
55	28.61	180	81.59	310	132.55
60	31.37	190	85.31		
70	36.62	200	89.08		
80	41.59	210	92.80		

Anhydrous denatured bovine serum albumin (66,433 Da) [33]					
T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$
10	1.866	90	46.44	220	97.15
15	4.272	100	50.79	230	101.04
20	7.176	110	54.94	240	105.02
25	10.36	120	58.99	250	109.08
30	13.62	130	62.93	260	113.22
35	16.87	140	66.78	270	117.45
40	20.00	150	70.63	280	121.71
45	23.05	160	74.43	290	126.02
50	26.08	170	78.20	300	130.37
55	29.06	180	81.92	310	134.77
60	31.92	190	85.69	273.15	118.78
70	37.10	200	89.50	298.15	129.54
80	41.88	210	93.30	310.15	134.81

TABLE 8.4. *Continued.*

Hydrated (2.14% H_2O) bovine serum albumin (66,433 Da) [33]

T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$
10	1.678	90	47.07	220	99.75
15	4.038	100	51.46	230	103.81
20	7.079	110	55.65	240	107.86
25	10.54	120	59.75	250	111.92
30	13.70	130	63.68	260	116.06
35	16.96	140	67.66	270	120.33
40	20.11	150	71.67	280	124.52
45	23.18	160	75.73	290	128.78
50	26.20	170	79.75	300	133.05
55	29.09	180	84.31	310	137.28
60	31.90	190	87.70		
70	37.29	200	91.71		
80	42.34	210	95.73		

Anhydrous bovine serosal collagen (280,950 Da) [33]

T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$
10	1.774	90	45.10	220	93.09
15	4.105	100	49.20	230	96.65
20	6.891	110	53.22	240	100.25
25	10.00	120	57.11	250	103.93
30	13.18	130	60.88	260	107.70
35	16.33	140	64.56	270	111.46
40	19.42	150	68.16	280	115.31
45	22.37	160	71.71	290	119.12
50	25.28	170	75.23	300	122.93
55	28.07	180	78.83	310	126.73
60	30.77	190	82.43	273.15	112.68
70	35.94	200	86.02	298.15	122.22
80	40.71	210	89.58	310.15	126.78

Hydrated (13.53% H_2O) bovine serosal collagen (280,950 Da) [33]

T/K	$C_p \times 10^2$	T / K	$C_p \times 10^2$	T / K	$C_p \times 10^2$
10	1.536	90	50.63	220	113.60
15	3.895	100	55.52	230	118.95
20	6.945	110	60.25	240	124.52
25	10.41	120	64.94	250	130.29
30	14.00	130	69.58	260	136.23
35	17.68	140	74.35	270	142.34
40	21.26	150	78.87	280	148.57
45	24.53	160	83.55	290	155.02
50	27.86	170	88.28	300	161.63
55	31.10	180	93.09	310	168.41
60	34.16	190	98.07	273.15	144.31
70	39.95	200	103.14	298.15	160.42
80	45.44	210	108.32	310.15	168.49

TABLE 8.4. *Continued.*

Rat tail tendon collagen at different water content, R (grams of water per gram of protein) [34]

R (g/g)	Temperature (°C)				
	−60	−40	−20	0	20
			Before denaturation		
1.44	1.582	1.778	2.343	3.033	3.117
1.01	1.548	1.849	2.469	2.816	2.908
0.93	1.598	1.891	2.510	2.812	2.900
0.79	1.582	1.862	2.594	2.669	2.812
0.65	1.556	1.841	2.803	2.481	2.586
0.527	1.577	1.883	2.761	2.339	2.435
0.468	1.498	1.799	2.803	2.259	2.335
0.428	1.494	1.757	2.469	2.176	2.247
0.376	1.381	1.715	1.925	2.000	2.155
			After denaturation		
1.44	1.674	1.904	2.929	3.293	3.548
1.02	1.686	1.946	3.347	3.138	3.439
0.93	1.695	1.950	3.766	2.966	3.314
0.79	1.715	2.029	3.347	2.862	3.264
0.651	1.715	2.050	3.347	2.715	3.130
0.524	1.766	2.121	3.347	2.607	2.853
0.468	1.674	2.033	3.347	2.552	2.778
0.428	1.582	1.941	2.510	2.481	2.653
0.375	1.464	1.799	2.929	2.393	2.569

Keratin (merino wool) [35]

	Water content (% of weight of keratin)									
T / °C	0	2.8	7.6	10.4	16.9	20.9	24.8	28.4	30.7	33.9
−70	0.887	0.925	1.004	1.013	1.088	1.176	1.230	1.247	1.264	1.230
−60	0.929	0.971	1.059	1.067	1.159	1.255	1.322	1.351	1.364	1.343
−50	0.971	1.013	1.109	1.121	1.234	1.335	1.414	1.456	1.464	1.460
−40	1.008	1.054	1.159	1.176	1.305	1.414	1.506	1.561	1.565	1.573
−30	1.046	1.096	1.213	1.230	1.377	1.494	1.607	1.665	1.682	1.674
−20	1.088	1.142	1.264	1.280	1.448	1.577	1.715	–	–	–
−10	1.125	1.184	1.318	1.335	1.519	1.657	1.787	–	–	–
0	1.167	1.226	1.368	1.393	1.590	1.745	1.883	1.992	2.063	2.079
10	1.205	1.272	1.423	1.452	1.665	1.837	1.975	2.079	2.146	2.159
20	1.243	1.314	1.473	1.523	1.745	1.933	2.067	2.167	2.230	2.234
30	1.284	1.356	1.527	1.594	1.837	2.050	2.197	2.255	2.310	2.318
40	1.322	1.402	1.582	1.665	1.933	2.142	2.255	2.330	–	2.356
50	1.364	1.443	1.636	1.732	2.025	2.201	2.310	2.372	–	2.393
60	1.402	1.494	1.695	1.803	2.105	2.255	2.356	2.402	2.460	2.439
70	1.443	1.540	1.757	1.879	2.180	2.314	2.402	2.439	2.494	2.481
80	1.481	1.590	1.820	1.962	2.238	2.360	2.448	2.494	2.540	2.519
90	1.523	1.640	1.887	2.054	2.293	2.406	2.494	2.540	–	2.556
100	1.561	1.690	1.950	2.151	2.330	2.448	2.536	2.586	–	2.602

TABLE 8.5. *Temperature dependence of the partial molar heat capacities ($J\ K^{-1}\ mol^{-1}$) of the peptide unit and of the side chains of amino acid residues for the temperature range 5–125 °C [18].*

	Temperature (°C)					
	5	25	50	75	100	125
–CHCONH–	3.7	15.2	26.2	29.8	33.7	33.7
$-R_i$						
Ala	175.7	166.7	156.2	144.7	134.6	124.1
Arg	204.6	273.4	305.8	315.1	318.7	318.5
Asn	72.9	88.8	109.8	125.2	140.5	154.2
Asp	72.8	89	106.2	124.5	140.7	154.3
Cys	225.4	237.6	250.8	260.7	268.2	276.1
Gln	168	180.2	193.4	203.3	210.8	218.7
Glu	168.3	179	192	203.7	211.4	217.8
Gly	82.3	78	71.7	66.4	59.7	53.9
His	205.7	179.6	177.2	179.6	187.1	196.8
Ile	406.8	402.3	397.1	390.8	386	380.8
Leu	385.9	381.7	377.8	372.9	369.4	365.5
Lys	215.1	249.8	266.9	274.4	278.1	274.4
Met	197.1	175.9	158.1	150.3	148.1	143.9
Phe	395.7	383	370.3	358.4	348.3	339.6
Pro	214.6	177.7	152.3	142.8	135.6	130.1
Ser	75.6	81.2	85.7	91.4	97.3	102.1
Thr	194.2	184.5	182.2	186.5	199	216.2
Trp	471.2	458.5	445.8	433.9	423.8	415.1
Tyr	310.6	301.7	295.2	294.5	300.1	304
Val	324.6	314.4	305	294.7	285.7	269.6

TABLE 8.6. *Temperature dependence of the partial molar volumes ($cm^3\ mol^{-1}$) of the peptide unit and of the side chains of amino acid residues for the temperature range 5–125 °C [11].*

	Temperature (°C)					
	5	25	50	75	100	125
–CHCONH–	28.3	28.0	28.6	28.9	29.0	29.4
$-R_i$						
Ala	24.8	27.2	30.1	33.1	36.3	39.4
Arg	81.2	85.7	88.4	90.4	92.1	93.5
Asn	44.1	45.7	47.8	49.3	50.8	52.4
Asp	39.0	41.5	44.5	47.3	49.9	52.6
Cys	40.5	40.5	40.5	40.5	40.5	40.5
Gln	58.4	61.0	63.2	66.0	68.5	69.7
Glu	54.9	57.5	60.7	63.6	66.3	69.3
Gly	10.9	10.3	9.6	9.2	8.9	8.5
His	65.1	64.0	63.1	62.4	61.8	61.1
Ile	64.5	66.1	67.7	69.8	71.8	74.0
Leu	75.0	77.6	80.2	82.9	86.5	89.4
Lys	72.4	73.5	75.8	78.5	81.3	84.8
Met	73.3	72.1	70.2	69.0	67.9	66.7
Phe	82.0	86.3	92.0	97.9	102.6	107.9
Pro	36.0	35.8	34.1	33.7	33.5	33.2
Ser	27.1	27.8	28.8	29.7	30.7	32.0
Thr	44.2	44.7	45.9	47.6	50.9	54.6
Trp	110.9	110.9	110.9	110.9	110.9	110.9
Tyr	88.2	90.0	92.2	94.1	95.9	97.8
Val	60.7	63.0	65.7	68.5	71.7	74.5

TABLE 8.7. *Thermodynamics characteristics of the proteins (partial molar heat capacity of the native, C_p^N(kJ K^{-1} mol^{-1}), and unfolded state, C_p^U(kJ K^{-1} mol^{-1}), and the heat capacity, $\Delta_N^U C_p$(kJ K^{-1} mol^{-1}), enthalpy, $\Delta_N^U H$(kJ mol^{-1}), entropy, $\Delta_N^U S$(J K^{-1} mol^{-1}), and Gibbs energy changes upon unfolding, $\Delta_N^U G$(kJ · mol^{-1}))*.*

Protein		Temperature (°C)					
		5	25	50	75	100	125
ROP[1]	C_p^N	7.9	9.0	10.4	11.7	13.1	14.4
	C_p^U	11.9	12.9	13.9	14.2	14.5	14.6
	$\Delta_N^U C_p$	7.9	7.9	7.0	5.0	2.9	0.4
	$\Delta_N^U H$	107	265	451	580	601	700
SH3 domain[2]	C_p^N	9.7	10.6	11.7	12.8	13.9	15.0
	C_p^U	14.7	15.4	16	16.4	16.6	16.6
	$\Delta_N^U C_p$	5.0	4.8	4.3	3.6	2.7	1.6
	$\Delta_N^U H$	−32	52	146	222	274	296
	$\Delta_N^U S$	−166	126	428	653	797	856
	$\Delta_N^U G$	14.1	14.5	7.8	−5.2	−23.3	−44.7
BPTI[3]	C_p^N	8.7	9.5	10.5	11.4	12.4	13.4
	C_p^U	11.5	12.5	13.1	13.5	13.7	13.7
	$\Delta_N^U C_p$	2.8	3.0	2.6	2.1	1.3	0.3
	$\Delta_N^U H$	72	130	200	259	303	323
	$\Delta_N^U S$	87	288	514	690	809	864
	$\Delta_N^U G$	47.8	44.2	34.0	18.9	1.2	−20.9
CI2[4]	C_p^N	12.4	13.3	14.5	15.6	16.7	17.8
	C_p^U	15.8	16.9	17.8	18.0	18.2	18.0
	$\Delta_N^U C_p$	3.4	3.6	3.3	2.4	1.5	0.2
	$\Delta_N^U H$	66	135	221	292	341	362
	$\Delta_N^U S$	119	360	636	850	986	1041
	$\Delta_N^U G$	32.9	27.7	15.6	−3.8	−26.8	−52.3
Eglin-c[5]	C_p^N	11.9	12.9	14.1	15.4	16.6	17.9
	C_p^U	16.1	16.8	17.6	17.9	18.2	18.1
	$\Delta_N^U C_p$	4.2	3.9	3.5	2.5	1.6	0.2
	$\Delta_N^U H$	33	115	208	283	335	358
	$\Delta_N^U S$	−22	262	561	786	929	989
	$\Delta_N^U G$	39.1	36.9	26.8	9.5	−11.5	−35.6
Protein G[6]	C_p^N	8.1	8.9	9.9	10.9	11.9	12.9
	C_p^U	11.7	12.5	13.2	13.5	13.9	13.9
	$\Delta_N^U C_p$	3.6	3.6	3.3	2.6	2.0	1.0
	$\Delta_N^U H$	−4	67	153	227	283	320
	$\Delta_N^U S$	−103	145	422	643	801	897
	$\Delta_N^U G$	24.6	23.8	16.7	3.2	−15.8	−37.0
Tendamistat[7]	C_p^N	11.4	12.1	13.0	13.9	14.8	15.7
	C_p^U	14.9	15.7	16.6	16.8	17.1	17.1
	$\Delta_N^U C_p$	3.5	3.6	3.6	2.9	2.3	1.4
	$\Delta_N^U H$	−22	70	176	262	321	351
	$\Delta_N^U S$	−213	109	452	711	877	955
	$\Delta_N^U G$	37.2	37.5	30.0	14.6	−6.1	−29.1

TABLE 8.7. *Continued.*

Protein		Temperature (°C)					
		5	25	50	75	100	125
Ubiquitin[8]	C_p^N	11.2	12.6	14.3	16.0	17.7	19.4
	C_p^U	17.0	18.3	19.4	19.8	20.2	20.2
	$\Delta_N^U C_p$	5.8	5.7	5.1	3.8	2.5	0.8
	$\Delta_N^U H$	– 88	27	162	273	351	393
	$\Delta_N^U S$	– 444	– 44	393	727	959	1068
	$\Delta_N^U G$	35.4	40.1	35.1	20.0	– 6.7	– 32.1
RNase T1[9]	C_p^N	14.6	16.1	17.8	19.7	21.9	24.3
	C_p^U	20.1	21.4	22.8	24.0	24.9	25.1
	$\Delta_N^U C_p$	5.5	5.3	5.0	4.3	3.0	0.8
	$\Delta_N^U H$	173	281	410	528	621	672
	$\Delta_N^U S$	444	817	1233	1584	1845	1976
	$\Delta_N^U G$	49.6	37.5	11.7	– 23.2	– 67.2	– 114.4
Met-J[10]	C_p^N	37.8	40.2	43.2	46.2	49.2	52.2
	C_p^U	45.8	49.2	52.1	53.2	54.3	54.3
	$\Delta_N^U C_p$	8.0	9.0	8.9	7.0	5.1	2.1
	$\Delta_N^U H$	92	270	498	692	832	902
Cytochrome c[11]	C_p^N	15.8	17.5	19.7	21.9	24.0	26.2
	C_p^U	22.7	24.3	25.8	26.3	26.8	26.8
	$\Delta_N^U C_p$	6.9	6.8	6.1	4.4	2.8	0.6
	$\Delta_N^U H$	– 53	89	268	421	532	593
	$\Delta_N^U S$	– 319	174	752	1210	1520	1681
	$\Delta_N^U G$	35.7	37.1	25.1	– 1.1	– 35.0	– 76.0
Barnase[12]	C_p^N	16.5	18.5	21.0	23.5	26.0	28.5
	C_p^U	23.6	25.4	26.9	27.4	28.0	28.1
	$\Delta_N^U C_p$	7.1	6.9	5.9	3.9	2.0	0.1
	$\Delta_N^U H$	167	307	467	590	664	690
	$\Delta_N^U S$	379	866	1384	1752	1959	2029
	$\Delta_N^U G$	61.6	48.9	20.0	– 19.7	– 66.7	– 117.5
RNase A[11]	C_p^N	19.5	20.8	22.5	24.2	25.8	27.5
	C_p^U	24.1	26.0	27.8	28.5	29.3	29.5
	$\Delta_N^U C_p$	4.6	5.2	5.3	4.3	3.5	2.0
	$\Delta_N^U H$	220	294	405	512	603	664
	$\Delta_N^U S$	641	896	1254	1574	1826	1989
	$\Delta_N^U G$	41.8	27.0	– 0.0	– 35.8	– 78.1	– 127.6
Lysozyme[11]	C_p^N	18.2	20.0	22.2	24.4	26.7	28.9
	C_p^U	26.7	29.1	31.1	31.8	32.4	32.5
	$\Delta_N^U C_p$	8.5	9.1	8.9	7.4	5.7	3.6
	$\Delta_N^U H$	111	242	408	562	683	753

TABLE 8.7. *Continued.*

Protein		Temperature (°C)					
		5	25	50	75	100	125
	$\Delta_N^U S$	164	618	1153	1615	1954	2138
	$\Delta_N^U G$	65.4	57.8	35.6	− 0.0	− 45.8	− 97.9
Interleukin 1β[13]	C_p^N	26.4	28.1	30.1	32.2	34.3	36.4
	C_p^U	33.3	35.6	37.6	38.4	39.2	39.2
	$\Delta_N^U C_p$	6.9	7.5	7.5	6.2	4.9	2.8
	$\Delta_N^U H$	7	151	330	501	640	736
	$\Delta_N^U S$	− 99	401	1006	1516	1903	2155
	$\Delta_N^U G$	34.5	31.5	5.1	− 26.6	− 69.8	− 121.7
Myoglobin[11]	C_p^N	21.8	24.2	27.3	30.3	33.4	36.5
	C_p^U	35.6	37.6	39.5	40.0	40.5	40.3
	$\Delta_N^U C_p$	14.4	14.0	12.8	10.3	7.7	4.4
	$\Delta_N^U H$	− 231	6	291	555	774	920
	$\Delta_N^U S$	− 919	− 116	805	1595	2207	2588
	$\Delta_N^U G$	24.5	40.6	31.0	− 0.1	− 49.2	− 110.0
T4-Lyz[14]	C_p^N	25.2	28.1	31.8	35.5	39.1	42.8
	C_p^U	36.2	39.1	41.5	42.2	43.1	43.0
	$\Delta_N^U C_p$	11.0	11.0	9.7	6.7	4.0	0.2
	$\Delta_N^U H$	20	240	499	671	805	856
	$\Delta_N^U S$	− 190	576	1413	1928	2302	2439
	$\Delta_N^U G$	72.8	68.4	42.6	0.1	− 53.6	− 114.7
Papain[15]	C_p^N	28.1	32.0	36.8	41.7	46.5	51.4
	C_p^U	45.0	48.0	50.5	51.3	52.1	51.9
	$\Delta_N^U C_p$	16.9	16.0	13.7	9.6	5.6	0.5
	$\Delta_N^U H$	− 166	164	535	826	1015	1091
	$\Delta_N^U S$	− 911	236	1438	2312	2840	3042
Chymotrypsin[15]	C_p^N	34.3	37.7	42.0	46.3	50.6	54.8
	C_p^U	49.2	51.8	54.3	55.1	56.0	55.8
	$\Delta_N^U C_p$	14.9	14.1	12.3	8.8	5.4	1.0
	$\Delta_N^U H$	− 21	268	598	862	1039	1119
	$\Delta_N^U S$	− 260	746	1813	2602	3099	3312
	$\Delta_N^U G$	51.3	45.7	12.4	− 43.5	− 116.9	− 199.2
Pepsinogen[15]	C_p^N	44.2	51.7	61.1	70.4	79.8	89.2
	C_p^U	78.4	82.3	86.3	87.7	89.6	89.7
	$\Delta_N^U C_p$	34.2	30.6	25.2	17.3	9.8	0.5
	$\Delta_N^U H$	− 577	72	770	1301	1639	1767
	$\Delta_N^U S$	− 2279	− 19	2242	3739	4687	5030

[1] ROP[36]; [2] SH3[37]; [3] BPTI[5]; [4] CI-2[38]; [5] Eglin-c[39]; [6] protein G[40]; [7] Tendamistat[41]; [8] Ubiquitin[42]; [9] RNase T1[43]; [10] Met-J[44]; [11] Cytochrome c, RNase A, Lysozyme, Myoglobin[45,46]; [12] Barnase[47]; [13] Interleukin-1β[48]; [14] T4-Lyz[49]; [15] Papain, Chymotrypsin, Pepsinogen[50].

*Reported entropies and Gibbs energies are for the conditions of maximal stability [17]. The entropies and Gibbs energy of unfolding for rop and met-J are not available since the unfolding represents a bimolecular two-state process.

TABLE 8.8. *Normalized values of the heat capacities ($\Delta\hat{C}_p^{hyd}$ in J K^{-1} mol^{-1} Å^{-2}), enthalpies ($\Delta\hat{H}^{hyd}$ in J mol^{-1} Å^{-2}), entropies ($\Delta\hat{S}^{hyd}$ in 10^{-3} J K^{-1} mol^{-1} Å^{-2}), and Gibbs energies ($\Delta\hat{G}_p^{hyd}$ in J K^{-1} mol^{-1} Å^{-2}) of hydration of various surfaces [17].*

		Temperature (°C)					
		5	25	50	75	100	125
		Nonpolar surfaces					
Aliphatic	$\Delta\hat{C}_p^{hyd}$	2.24	2.14	2.03	1.91	1.80	1.66
	$\Delta\hat{H}^{hyd}$	−166	−122	−70	−21	26	69
	$\Delta\hat{S}^{hyd}$	−730	−578	−409	−263	−134	−22
	$\Delta\hat{G}^{hyd}$	37	50	62	71	75	77
Aromatic	$\Delta\hat{C}_p^{hyd}$	1.65	1.55	1.41	1.29	1.19	1.09
	$\Delta\hat{H}^{hyd}$	−180	−148	−111	−77	−46	−18
	$\Delta\hat{S}^{hyd}$	−430	−319	−199	−98	−12	62
	$\Delta\hat{G}^{hyd}$	−61	−53	−47	−43	−42	−43
		Polar surfaces of:					
Arg	$\Delta\hat{C}_p^{hyd}$	−0.38	−0.20	−0.12	−0.04	0.01	0.08
	$\Delta\hat{H}^{hyd}$	−821	−827	−831	−833	−834	−833
	$\Delta\hat{S}^{hyd}$	−458	−478	−492	−497	−498	−495
	$\Delta\hat{G}^{hyd}$	−694	−685	−672	−660	−647	−635
Asn	$\Delta\hat{C}_p^{hyd}$	−1.27	−1.01	−0.67	−0.41	−0.16	0.09
	$\Delta\hat{H}^{hyd}$	−871	−894	−915	−928	−936	−936
	$\Delta\hat{S}^{hyd}$	−575	−654	−723	−763	−783	−785
	$\Delta\hat{G}^{hyd}$	−711	−699	−681	−663	−643	−623
Asp	$\Delta\hat{C}_p^{hyd}$	−1.72	−1.40	−1.07	−0.71	−0.40	−0.11
	$\Delta\hat{H}^{hyd}$	−684	−715	−746	−768	−782	−788
	$\Delta\hat{S}^{hyd}$	−360	−469	−569	−636	−675	−691
	$\Delta\hat{G}^{hyd}$	−584	−575	−562	−547	−530	−513
Cys	$\Delta\hat{C}_p^{hyd}$	1.80	2.01	2.23	2.42	2.54	2.70
	$\Delta\hat{H}^{hyd}$	−309	−271	−218	−160	−98	−32
	$\Delta\hat{S}^{hyd}$	−535	−402	−232	−59	113	283
	$\Delta\hat{G}^{hyd}$	−160	−151	−143	−139	−140	−145
Gln	$\Delta\hat{C}_p^{hyd}$	−0.38	−0.22	−0.06	0.07	0.17	0.30
	$\Delta\hat{H}^{hyd}$	−697	−703	−706	−706	−703	−697
	$\Delta\hat{S}^{hyd}$	−571	−591	−604	−603	−594	−579
	$\Delta\hat{G}^{hyd}$	−538	−527	−511	−497	−481	−467
Glu	$\Delta\hat{C}_p^{hyd}$	−0.71	−0.55	−0.35	−0.17	−0.05	0.09
	$\Delta\hat{H}^{hyd}$	−549	−562	−573	−580	−583	−582
	$\Delta\hat{S}^{hyd}$	−392	−436	−473	−492	−500	−498
	$\Delta\hat{G}^{hyd}$	−440	−432	−420	−409	−396	−383

TABLE 8.8. *Continued.*

		Temperature (°C)					
		5	25	50	75	100	125
His	$\Delta\hat{C}_p^{hyd}$	– 1.96	– 2.43	– 2.38	– 2.26	– 2.07	– 1.82
	$\Delta\hat{H}^{hyd}$	– 1,084	– 1,128	– 1,188	– 1,247	– 1,301	– 1,349
	$\Delta\hat{S}^{hyd}$	– 542	– 693	– 888	– 1060	– 1211	– 1337
	$\Delta\hat{G}^{hyd}$	– 933	– 922	– 901	– 878	– 848	– 816
Lys	$\Delta\hat{C}_p^{hyd}$	– 1.31	– 1.53	– 1.59	– 1.36	– 1.15	– 0.94
	$\Delta\hat{H}^{hyd}$	– 685	– 714	– 753	– 789	– 821	– 847
	$\Delta\hat{S}^{hyd}$	– 384	– 482	– 609	– 716	– 804	– 870
	$\Delta\hat{G}^{hyd}$	– 578	– 570	– 556	– 540	– 519	– 498
Met	$\Delta\hat{C}_p^{hyd}$	– 3.51	– 3.83	– 4.07	– 4.04	– 3.91	– 3.75
	$\Delta\hat{H}^{hyd}$	– 399	– 473	– 572	– 672	– 774	– 869
	$\Delta\hat{S}^{hyd}$	– 158	– 412	– 732	– 1031	– 1308	– 1555
	$\Delta\hat{G}^{hyd}$	– 356	– 350	– 335	– 315	– 283	– 247
Ser	$\Delta\hat{C}_p^{hyd}$	– 1.62	– 1.40	– 1.20	– 0.96	– 0.72	– 0.48
	$\Delta\hat{H}^{hyd}$	– 1015	– 1045	– 1078	– 1104	– 1126	– 1140
	$\Delta\hat{S}^{hyd}$	– 878	– 983	– 1089	– 1168	– 1227	– 1265
	$\Delta\hat{G}^{hyd}$	– 771	– 752	– 726	– 698	– 667	– 636
Thr	$\Delta\hat{C}_p^{hyd}$	– 1.09	– 1.29	– 1.22	– 0.89	– 0.29	0.55
	$\Delta\hat{H}^{hyd}$	– 1262	– 1287	– 1318	– 1343	– 1359	– 1356
	$\Delta\hat{S}^{hyd}$	– 971	– 1053	– 1156	– 1232	– 1274	– 1265
	$\Delta\hat{G}^{hyd}$	– 992	– 972	– 944	– 916	– 881	– 850
Trp	$\Delta\hat{C}_p^{hyd}$	1.05	0.96	1.07	1.08	1.03	1.05
	$\Delta\hat{H}^{hyd}$	– 1,181	– 1,161	– 1,135	– 1,110	– 1,084	– 1,055
	$\Delta\hat{S}^{hyd}$	– 766	– 693	– 615	– 534	– 460	– 392
	$\Delta\hat{G}^{hyd}$	– 968	– 954	– 936	– 924	– 912	– 899
Tyr	$\Delta\hat{C}_p^{hyd}$	– 1.46	– 1.48	– 1.36	– 1.15	– 0.86	– 0.59
	$\Delta\hat{H}^{hyd}$	– 824	– 854	– 889	– 921	– 946	– 963
	$\Delta\hat{S}^{hyd}$	– 314	– 415	– 531	– 625	– 695	– 742
	$\Delta\hat{G}^{hyd}$	– 735	– 730	– 717	– 703	– 686	– 667
CONH	$\Delta\hat{C}_p^{hyd}$	– 2.08	– 1.81	– 1.56	– 1.53	– 1.49	– 1.55
	$\Delta\hat{H}^{hyd}$	– 1662	– 1702	– 1745	– 1785	– 1823	– 1862
	$\Delta\hat{S}^{hyd}$	– 890	– 1026	– 1162	– 1278	– 1383	– 1481
	$\Delta\hat{G}^{hyd}$	– 1415	– 1396	– 1370	– 1340	– 1307	– 1272

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CHAPTER 9

Heat Capacities of Polymers

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9.1 INTRODUCTION

The heat capacity of a substance can be defined as the amount of heat required to change its temperature by one degree. A more useful quantity is specific heat capacity, which is the amount of heat required to change the temperature of one unit mass of a material by one degree. Heat capacity is a fundamental property of any material. It is a macroscopic parameter that can be linked to molecular structure and vibrational motions at microscopic level [1].

Heat capacity under constant pressure (C_p) is defined as the heat quantity which is required to increase the temperature of the unit mass of a material by 1 K or 1°C under constant pressure. It is given by the following equation:

$$C_p = \Delta Q/m\Delta T \quad (\text{unit: J/(g K)}), \tag{9.1}$$

where ΔQ is the required heat quantity (in Joules), m is the mass of the sample (in grams or kilograms), ΔT is the temperature increase from T_1 to T_2 (in degrees Celsius or Kelvins). The molar heat capacity under constant pressure is defined as that heat quantity which is required to heat the unit mole of a material through 1 K or 1°C under constant pressure (in J/(mol K)). The experimental heat capacities are measured at constant pressure. However, in order to link heat capacity with the vibrational spectrum, C_p must first be converted to the heat capacity at constant volume.

At constant volume, heat capacity can be defined as follows;

$$C_v = \Delta Q/m\Delta T \quad (\text{unit: J/(g K)}). \tag{9.2}$$

The relationship between two heat capacities is

$$C_p - C_v = V\alpha^2 T/K_T \tag{9.3}$$

where α is the thermal expansion coefficient and K_T is the isothermal bulk modulus.

Heat capacity is a fundamental property of any material. It can be measured by adiabatic calorimetry (0–100 K), differential scanning calorimetry (DSC) (above 100 K), and some other techniques [2–4]. Theoretical interpretation of heat capacity has been carried out by various researchers through analysis based on the separation of the vibrational spectrum into group and skeletal vibrations as well as normal mode and their dispersion analysis [5–8]. The table in this chapter contains the heat capacity data in the literature for selected polymers. The heat capacity for any given polymer is a temperature-dependent quantity. Due to the space limitations, the heat capacity values at selected temperatures are listed in this table for the selected polymers. Temperatures are chosen such that at least two data points are included in both the glassy and rubbery regions. A crude extrapolation could be used to compare experimental data at other temperatures. The specific heat increment at T_g, ΔC_p, is also given for the selected polymers. Readers can find more detailed information about ΔC_p from the original references. Since heat capacity also depends on the state of the polymer, the state of the polymer is specified by the following abbreviations whenever possible:

a = amorphous; c = crystalline; s = solid;
m = melt; sc = semicrystalline; g = glassy.

The description of the theory of heat capacity and the application of heat capacity measurements have been given by Wunderlich and other researchers [2,3–17]. The most comprehensive and updated heat capacity data are collected in the ATHAS data bank (Advanced THermal AnalysiS) which has been developed over the last 25 years by Wunderlich (Chemistry Department, The University of Tennessee), and coworkers.

TABLE 9.1. *Heat capacities of selected polymers.*

					$C_p{}^b$			
Polymer	Abbreviations	Molecular^a weight (g/mol)	T_g (K)	Temperature (K)	(kJ/(kg K))	(J/(mol K))	$\Delta C_p{}^c$ (J/(mol K))	Ref.
1. Main-chain carbon polymers								
Poly(acrylics)								
Poly(*iso*-butyl acrylate)	PiBA	128.17	249	220	1.2156	155.80	36.60	[18]
				240	1.3365	171.30		
				300	1.8108	232.09		
				500	2.3388	299.77		
Poly(*n*-butyl acrylate)	PnBA	128.17	218	80	0.5598	71.75	45.40	[18]
				180	1.0632	136.27		
				300	1.8201	233.28		
				440	2.1803	279.45		
Poly(ethyl acrylate)	PEA	100.12	249	90	0.5792	57.99	45.60	[18]
				200	1.0301	103.13		
				300	1.7867	178.88		
				500	2.2189	222.16		
Poly(methyl acrylate)	PMA	86.09	279	100	0.6154	52.98	42.30	[18]
				200	0.9816	84.51		
				300	1.765	151.99		
				500	2.143	184.49		
Poly(dienes)								
1,4-Poly(butadiene)	PBD	54.09						
cis-			171	50	0.3694	19.98	29.10	[19,20]
				150	0.8967	48.50		
				300	1.960	106.00		
				350	2.214	114.90		
trans-			180	50	0.3465	18.74	28.20	[19,20]
				150	0.9057	48.99		
				300	NA	NA		
				500	2.616	141.50		
Poly(1-butene)	PB	56.11	249	100	0.6733	37.78	23.06	[19]
				200	1.2190	68.40		
				300	2.086	117.02		
				600	3.071	172.31		
Poly(1-butenylene)	PBUT	55.10						
cis-			171	30	0.2140	11.79	28.91	[3,19,20]
				130	0.7775	42.838		
				300	1.924	106.03		
				450	2.409	132.73		
trans-			190	30	0.1761	9.704	26.48	[3,19,20]
				130	0.7898	43.516		
				300	1.924	106.03		
				450	2.409	132.73		
Poly(alkenes)								
Poly(ethylene)	PE	14.03	252	100	0.674	9.45 (c)	10.1	[21]
				200	1.110	15.57		
				300	1.555	21.81 (s)		
					2.202	30.89 (m)		
				600	3.127	43.87		
Poly(1-hexene)	PHE	84.16	223	100	0.7020	59.08 (a)	25.1	[19]
				200	1.3319	112.09		
				250	1.903	160.18 (a)		
				290	2.079	174.98 (a)		

TABLE 9.1. *Continued.*

Polymer	Abbreviations	Molecular[a] weight (g/mol)	T_g (K)	Temperature (K)	C_p[b]		ΔC_p[c] (J/(mol K))	Ref.
					(kJ/(kg K))	(J/(mol K))		
Poly(isobutene)	PiB	56.11	200	50	0.2440	13.69 (a)	22.29	[19]
				150	0.8660	48.59		
				300	1.962	110.09 (a)		
				380	2.311	129.66		
Poly(2-methylbutadiene)	PMBD	68.12						
cis-			200	50	0.3573	24.34	30.87 (a)	[19]
				150	0.9025	61.48		
				300	1.911	130.20		
				360	2.216	144.80		
Poly(4-methyl-1-pentene)	P4MPE	84.16	303	80	0.5610	47.21	33.7 (a)	[19]
				180	1.090	91.75		
				250	1.4449	121.60		
				300	1.728	145.40		
Poly(1-pentene)	PPE	70.14	233	200	1.253	87.90	27.03 (a)	[19]
				220	1.338	93.82		
				300	2.058	144.34		
				470	2.770	194.32		
Poly(propylene)	PP	42.08	260	100	0.6238	26.25 (c)	17.37	[22]
				200	1.132	47.63 (c)		
				300	1.622	68.24 (s)		
					2.099	88.34 (m)		
				600	3.178	133.73 (a)		
			Poly(methacrylics)					
Poly(*n*-butyl methacrylate)	PnBMA	142.20	293	80	0.5472	77.81	29.70	[18]
				200	1.1557	164.34		
				300	1.8524	263.41		
				450	2.3673	336.63		
Poly(*i*-butyl methacrylate)	PiBMA	142.20	326	230	1.2229	173.90	39.00	[18]
				300	1.5710	223.40		
				350	2.0190	287.10		
				400	2.1127	300.43		
Poly(ethyl methacrylate)	PEMA	114.15	338	80	0.5155	58.84	31.70	[18]
				300	1.4666	167.42		
				350	1.9489	222.47		
				380	2.0462	233.57		
Poly(hexyl methacrylate)	PHMA	170.25	268	270	1.8264	310.77	—	[18]
				300	1.9091	324.83		
				420	2.2396	381.06		
Poly(methacrylic acid)	PMAA	86.09	—	100	0.5248	45.18	—	[18]
				200	0.9456	81.41		
				300	1.307	112.50		
Poly(methacrylamide)	PMAM	85.11	—	100	0.5904	50.25	—	[18]
				200	1.032	87.81		
				300	1.395	118.70		
Poly(methyl methacrylate)	PMMA	100.12	378	100	0.5742	57.49	33.5	[18]
				300	1.3755	137.72		
				400	2.0766	207.91		
				550	2.4323	243.52		
			Poly(styrenes)					
Poly(styrene)	PS	104.15	373	100	0.4548	47.37 (g)	30.7 (a)	[23]
				300	1.2230	127.38		
					1.2730	132.58		[4]

TABLE 9.1. *Continued.*

					$C_p{}^b$			
Polymer	Abbreviations	Molecular[a] weight (g/mol)	T_g (K)	Temperature (K)	(kJ/(kg K))	(J/(mol K))	$\Delta C_p{}^c$ (J/(mol K))	Ref.
				400	1.9322	201.24		
				600	2.4417	254.30		
—, α-methyl	PαMS	118.18	441	100	0.4712	55.69	25.3	[19]
				300	1.2752	150.70 (g)		
				460	2.1868	258.44		
				490	2.3331	275.72		
—, *p*-bromo-	PBS	183.05	410	300	0.79650	145.800	31.9	[3,24]
				350	0.92349	169.045		
				420	1.2651	231.582		
				550	1.4641	267.995		
—, *p*-chloro-	PCS	138.60	406	300	1.0229	141.780	31.1	[3,24]
				350	1.19848	166.110		
				410	1.6331	226.345		
				550	1.9134	265.195		
—, *p*-fluoro-	PFS	122.14	384	130	0.47611	58.152	33.3	[3,24]
				200	0.62048	75.786		
				300	0.93079	113.687		
				380	1.2672	154.773		
—, *p*-iodo-	PIS	230.05	424	300	0.67607	155.53	37.9	[3,24]
				400	0.89102	204.980		
				430	1.1145	256.41		
				550	1.2570	289.17		
—, *p*-methyl-	PMS	118.18	380	300	1.2743	150.600	34.6	[3,24]
				350	1.4917	176.290		
				390	1.9449	229.846		
				500	2.2766	269.05		
		Poly(vinyl halides) and poly(vinyl nitriles)						
Poly(acrylonitrile)	PAN	53.06	378	100	0.5695	30.22	—	[18]
				200	0.9286	49.27		
				300	1.297	68.83		
				370	1.624	86.16		
Poly(chlorotrifluoroethylene)	PC3FE	116.47	325	80	0.2787	32.46	—	[19]
				200	0.6257	72.87		
				300	0.85945	100.10		
				320	0.90667	105.60		
Poly(tetrafluoroethylene)	PTFE	50.01	240	100	0.3873	19.37	7.82	[3,19,25]
				200	0.6893	34.47		
				300	0.9016	45.09 (s)		
					1.028	51.42 (m)		
				700	1.454	72.69		
Poly(trifluoroethylene)	P3FE	82.02	304	100	0.4049	33.21	21.00	[19]
				200	0.7128	58.46		
				300	1.078	88.40		
Poly(vinyl chloride)	PVC	62.50	354	100	0.4291	26.82 (g)	19.37 (a)	[19]
				300	0.9496	59.35 (g)		
				360	1.457	91.08		
				380	1.569	98.05		
Poly(vinylidene chloride)	PVC2	96.95	255	100	0.3745	36.31	70.26	[19]
				200	0.5932	57.51		
				250	0.7115	68.98		
				300	NA	NA		
Poly(vinylidene fluoride)	PVF2	64.03	233	100	0.4435	28.40	22.80	[19]

TABLE 9.1. *Continued.*

Polymer	Abbreviations	Molecular[a] weight (g/mol)	T_g (K)	Temperature (K)	C_p[b]		ΔC_p[c] (J/(mol K))	Ref.
					(kJ/(kg K))	(J/(mol K))		
				150	0.6185	39.60		
				230	0.8918	57.10		
				250	0.7856	50.30		
				300	NA	NA		
Poly(vinyl fluoride)	PVF	46.04	314	100	0.5204	23.96	17.80 (a)	[19]
				200	0.8692	40.02		
				300	1.301	59.91		
				310	1.353	62.29		
			Others					
Poly(*p*-phenylene)	PPP	76.10	—	80	0.3708	28.22 (sc)	—	[26,27]
				150	0.58135	44.241 (sc)		
				250	0.92926	70.717 (sc)		
				300	1.117	85.040 (sc)		
Poly(vinyl acetate)	PVAc	86.09	304	80	0.3230	27.81	53.7	[19]
				300	1.183	101.86		
				320	1.8409	158.48		
				370	1.898	163.37		
Poly(vinyl alcohol)	PVA	44.05	358	60	0.2674	11.78	—	[19]
				150	0.7187	31.66		
				250	1.185	52.21		
				300	1.546	68.11		
Poly(vinyl benzoate)	PVBZ	148.16	347	190	0.71808	106.39	69.5	[19]
				300	1.1025	163.35		
				400	1.8390	272.47		
				500	2.0333	301.25		
Poly(*p*-xylylene)	PPX	104.15	286	220	0.91445	95.241 (sc)	37.6 (a)	[3,28]
				250	1.0576	110.149 (sc)		
				300	1.3022	135.622 (sc)		
				410	1.8686	194.619 (sc)		
		2. Main-chain heteroatom polymers						
			Poly(amides)					
Poly(iminoadipoyliminododecamethylene)	Nylon 612	310.48	319	230	1.2296	381.78	214.8 (a)	[3,29,30]
				300	1.5926	494.48		
				400	2.4842	771.30		
				600	3.1596	980.986		
Poly(iminoadipoyliminohexamethylene)	Nylon 66	226.32	323	230	1.1139	252.10	145.0 (a)	[31]
				300	1.4638	331.30		
				400	2.3794	538.50		
				600	2.793	632.1		
Poly(iminohexamethylene-iminoazelaoyl)	Nylon 69	268.40	331	230	1.1980	321.53	—	[3,29,30]
				300	1.5204	408.080		
				400	2.3840	639.874		
				600	3.0720	824.534		
Poly(iminohexamethylene-iminosebacoyl)	Nylon 610	282.43	323	230	1.2069	340.870	—	[3,29,30]
				300	1.5644	441.820		
				400	2.3975	677.125		
				600	3.1041	876.685		

TABLE 9.1. *Continued.*

Polymer	Abbreviations	Molecular[a] weight (g/mol)	T_g (K)	Temperature (K)	C_p[b]		ΔC_p[c] (J/(mol K))	Ref.
					(kJ/(kg K))	(J/(mol K))		
Poly(imino-(1-oxohexamethylene))	Nylon 6	113.16	313	70	0.4400	49.78	93.6 (a)	[31]
				300	1.5023	170.00		
				400	2.5186	285.00		
				600	2.7881	315.50		
Poly(imino-1-oxododecamethylene)	Nylon 12	197.32	314	230	1.2874	254.020	—	[3,29,30]
				300	1.6952	334.49		
				400	2.4709	487.565		
				600	3.2786	646.945		
Poly(imino-1-oxoundecamethylene)	Nylon 11	183.30	316	230	1.2996	238.21	—	[3,29,30]
				300	1.7507	320.91		
				400	2.4567	450.314		
				600	3.2449	594.794		
Poly(methacrylamide)	PMAM	85.11	—	100	0.5904	50.25	—	[18]
				200	1.032	87.81		
				250	1.214	103.30		
				300	1.395	118.70		
			Poly(amino acids)					
Poly(L-alanine)	PALA	71.08	—	230	1.102	78.33	—	[32]
				300	1.315	93.47		
				350	1.498	106.5		
				390	1.622	115.3		
Poly(L-asparagine)	PASN	114.10	—	230	0.958	109.3	—	[33]
				300	1.218	139.0		
				350	1.397	159.4		
				390	1.537	175.4		
Polyglycine	PGLY	57.05	—	230	0.929	53.00	—	[32]
				300	1.170	66.75		
				350	1.356	77.36		
				390	1.516	86.49		
Poly(L-methionine)	PMET	131.19	—	220	0.936	122.8	—	[33]
				300	1.347	176.7		
				350	1.595	209.3		
				390	1.768	232.0		
Poly(L-phenylalanine)	PPHE	147.18	—	220	0.830	122.1	—	[33]
				300	1.153	169.7		
				350	1.382	203.4		
				390	1.548	227.8		
Poly(L-serine)	PSER	87.08	—	220	0.959	83.50	—	[33]
				300	1.297	112.9		
				350	1.541	134.2		
				390	1.747	152.1		
Poly(L-valine)	PVAL	99.13	—	230	1.213	120.2	—	[32]
				300	1.455	144.2		
				350	1.647	163.3		
				390	1.802	178.6		
			Poly(esters)					
Poly(butylene adipate)	PBAD	200.24	199	80	0.54302	108.734	140.046	[26,27]
				150	0.87449	175.107		
				300	1.9706	394.595		
				450	2.2147	443.470		

TABLE 9.1. *Continued.*

					$C_p{}^b$			
Polymer	Abbreviations	Molecular^a weight (g/mol)	T_g (K)	Temperature (K)	(kJ/(kg K))	(J/(mol K))	$\Delta C_p{}^c$ (J/(mol K))	Ref.
Poly(butylene terephthalate)	PBT	220.23	248	150	0.61075	134.505 (sc)	106.77	[3]
			320	200	0.82262	181.166	77.812	
				300	1.6134	355.311		
				400	1.8187	400.532		
				570	2.1678	477.407		
Poly(ethylene terephthalate)	PET	192.16	342	100	0.4393	84.42	77.8 (a)	[3,34,31]
				300	1.172	225.2		
				400	1.8203	349.80		
				600	2.1136	406.15		
Poly(tridecanolactone)	PTDL	212.34	237	185	0.95	202	—	[35]
				260	1.45	308		
				300	1.79	380		
				395	2.15	457		
Poly(trimethylene adipate)	PTMA	186.21	—	300	NA	NA	—	[3,36]
				310	1.8710	348.401		
				330	1.9137	356.341		
				360	1.9776	368.252		
Poly(trimethylene terephthalate)	PTT	206.2	331	180	0.73	150.53	—	[37]
				250	0.97	201.29		
				350	1.54	318.41		
				400	1.79	368.75		
Poly(trimethylene succinate)	PTMS	158.15	—	300	NA	NA	—	[3,36]
				310	1.8401	291.014		
				330	1.8721	296.074		
				360	1.9201	303.664		
Poly(γ-butyrolactone)	PBL	86.09	214	100	0.6012	51.760	57.4	[3,31,38]
				210	1.024	88.170		
				300	1.810	155.858 (m)		
				350	1.870	161.031 (m)		
Poly(ε-caprolactone)	PCL	114.15	209	100	0.62322	71.140	59.5	[3,31,38,39]
				200	1.0243	116.923		
				300	1.4229	162.42		
					1.8138	207.04 (s)		
				350	1.9415	221.62 (m)		
Poly(glycolide)	PGL	58.04	318	100	0.5250	30.470	44.4	[3,31,38,39]
				300	1.127	65.42		
				400	1.999	116.039 (m)		
				550	2.098	121.75 (m)		
Poly(β-propiolactone)	PPL	72.07	249	100	0.5568	40.130	50.4	[3,31,38,39]
				240	1.044	75.220		
				300	1.878	135.354 (m)		
				400	2.081	149.994 (m)		
Poly(ethylene oxalate)	PEOL	116.07	306	100	0.49910	57.930	56.23	[3,40,41]
				300	1.1175	129.705		
				320	1.6395	190.295 (m)		
				360	1.7012	197.456 (m)		

TABLE 9.1. *Continued.*

Polymer	Abbreviations	Molecular[a] weight (g/mol)	T_g (K)	Temperature (K)	C_p[b]		ΔC_p[c] (J/(mol K))	Ref.
					(kJ/(kg K))	(J/(mol K))		
Poly(ethylene sebacate)	PES	228.29	245	120	0.66292	151.338 (s)	154.059	[3,31]
				200	0.95269	217.490 (sc)		
				300	1.9245	439.34 (m)		
				410	2.1923	500.500 (m)		
			Poly(oxides)					
Poly(oxy-2,6-dimethyl-1, 4-phenylene)	PPO	120.15	482	80	0.4418	53.08	31.9 (a)	[42]
				300	1.2459	149.70		
				500	2.1232	255.10		
				570	2.2555	271.00		
Poly(oxyethylene)	POE	44.05	206	100	0.6114	26.93 (s)	38.96	[42,43]
				200	0.9507	41.88 (s)		
				300	1.257	55.36 (s)		
					1.995	87.89 (m)		
				450	2.223	97.91		
Polyoxymethylene	POM	30.03	190	100	0.5554	16.68 (s)	27.47	[42,43]
				150	0.7266	21.82 (s)		
				300	1.283	38.52 (s)		
					1.920	57.67 (m)		
				600	2.292	68.83		
Poly(oxy-1,4-phenylene)	POPh	92.10	358	300	1.185	109.10 (s)	21.4 (a)	[42]
				350	1.367	125.90 (s)		
				400	1.694	156.00 (m)		
				600	2.003	184.50 (m)		
Poly(oxypropylene)	POPP	58.08	198	80	0.537	31.21 (s)	32.15	[42]
				180	1.014	58.89 (s)		
				300	1.915	111.23 (m)		
				370	2.105	122.27 (m)		
Poly(oxytetramethylene)	PO4M	72.11	189	80	0.5465	39.41 (s)	46.49	[42]
				180	1.033	74.52 (s)		
				300	1.985	143.15 (m)		
				340	2.081	150.04 (m)		
Poly(oxytrimethylene)	PO3M	58.08	195	80	0.5095	29.59 (s)	50.73	[42]
				180	0.9464	54.97 (s)		
				300	1.373	79.73 (s)		
					2.055	119.34 (m)		
				330	2.107	122.37		
			Others					
Poly(diethyl siloxane)	PDES	102.21	135	50	0.38820	39.678 (sc)	30.189	[3,44–47]
				100	0.73995	75.630 (sc)		
				300	1.6184	165.417 (m)		
				360	1.7525	179.125 (m)		
Poly(dimethyl itaconate)	PDMI	158.16	377	110	0.59700	94.419 (a)	54.23	[48]
				300	1.3183	208.507 (a)		
				400	1.9282	304.968 (m)		
				450	2.0009	316.463 (m)		
Poly(dimethyl siloxane)	PDMS	74.15	146	50	0.3672	27.23	27.7 (a)	[44,49,50]
				100	0.7131	52.88		
				300	1.591	118.0		
				340	1.657	122.9		
Poly(4-hydroxybenzoic acid)	PHBA	120.11	434	170	0.58914	70.762	34	[51]
				300	1.0207	122.60		
				400	1.3662	164.091		
				434	1.4686	176.399		

TABLE 9.1. *Continued.*

Polymer	Abbreviations	Molecular[a] weight (g/mol)	T_g (K)	Temperature (K)	C_p[b] (kJ/(kg K))	C_p[b] (J/(mol K))	ΔC_p[c] (J/(mol K))	Ref.
Poly(lactic acid)	PLA	72.07	332.5	200	0.97	69.75	—	[52]
				300	1.32	95.30		
				400	2.09	150.56		
				470	2.16	155.77		
Poly(4,4′-isopropylidene diphenylenecarbonate)	PC	254.27	418	100	0.43143	109.70 (s)	48.5	[44]
				300	1.207	306.8 (s)		
				450	1.9570	497.60 (m)		
				560	2.207	561.3 (m)		
Poly(oxy-1,4-phenylene-oxy-1, 4-phenylene-carbonyl-1, 4-phenylene)	PEEK	288.30	419	300	NA	NA	78.1	[53–55]
				419	1.789	515.8		
				500	1.928	555.9		
				750	2.358	679.8		
Poly(oxy-1,4-phenylene-sulphonyl-1, 4-phenylene-oxy-1,4-phenylene-(1-methylidene)-1, 4-phenylene)	PBISP	442.54	458.5	200	0.75870	335.754	102.482	[3,56,57]
				300	1.1161	493.934		
				500	1.9436	860.132		
				540	2.0251	896.19		
Poly(*p*-phenylenebenzobisoxazole)	PBO	234.21	—	10	0.01	2.69	—	[58]
				100	0.32	76.00		
				200	0.64	148.82		
				300	0.97	226.84		
Poly(1,4-phenylene sulphonyl)	PAS	140.16	492.6	150	0.597	83.7	—	[57]
				300	1.009	141.4		
				500	1.571	220.2		
				620	1.642	230.1		
Poly(1-propene sulphone)	P1PS	106.14	10	0.01580	1.677	—		[59]
				30	1.165	123.7		
Trigonal selenium	SEt	78.96	303.4	100	0.2304	18.19 (s)	13.29	[60]
				300	0.318	25.11		
				400	0.3338	26.36 (s)		
					0.4777	37.72 (m)		
				600	0.4343	34.29		

[a] This is the molecular weight of the repeat unit of the polymer.

[b] Except the data for PTDL and P1PS, C_p data reported in the unit of kJ/(kg K) were converted from the C_p data in J/(mol K) which were directly cited from the literature, using the molecular weight of the repeat unit.

[c] Specific heat increment at T_g.

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CHAPTER 10

Thermal Conductivity

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Thermal conductivity of polymers is an important thermal property for both polymer applications and processing. Polymers typically have intrinsic thermal conductivity much lower than those for metals or ceramic materials, and therefore are good thermal insulators. Further enhancement of this thermal insulating quality can be achieved by foaming polymers. In other applications which require higher thermal conductivity, such as in electronic packaging and encapsulations, satellite devices, and in areas where good heat dissipation, low thermal expansion and light weight are needed, polymers reinforced with fillers, organic or inorganic, are becoming more and more common in producing advanced polymer composites for these applications [1–8].

Most polymeric materials are processed and fabricated at elevated temperatures, often above their melting temperatures. This process may be long and expensive because of the low thermal conductivity of polymers. Subsequently, the cooling process or annealing may also be controlled by heat transport properties of polymers, which eventually affect the physical properties of the materials. One example is crystalline polymers, for which the structural and morphological features may be significantly changed with the speed of cooling. Careful consideration in designing polymer processing is vital to achieve desired properties.

Definition. For one-dimensional and rectilinear heat flow, the steady-state heat transfer in polymeric materials can be described by the Fourier's law of heat conduction:

$$q = -k\frac{\mathrm{d}T}{\mathrm{d}x}, \qquad (10.1)$$

where q is the heat flux (i.e., the heat transfer rate per unit area normal to the direction of flow), x is the thickness of the material, $\mathrm{d}T/\mathrm{d}x$ is the temperature gradient per unit length, and the proportionality constant k is known as the thermal conductivity.

The units for thermal conductivity k are expressed as W/(m K) in SI units, Btu in./(ft^2 h °F) in English units, and cal/(cm s °C) in cgs units. The corresponding units for heat flux are expressed as W/(m^2), Btu/(ft^2 h), and cal/(cm^2 s), respectively. The conversion factors of units transform for k in these systems are listed in Part XI, Chapter 63.

Polymers and foamed polymers. Temperature, pressure, density of polymer, orientation of chain segments, crystal structures, degree of crystallinity, and many other factors may significantly affect thermal conductivity of polymers [9–18]. Therefore the thermal conductivity values can be varied in literatures for same polymers. In addition, discrepancies also occur for thermal conductivity values obtained using different test methods [19]. The data in the tables in this chapter may be the representative values of thermal conductivity and are not necessarily the absolute ones.

Generally, pure polymers have low thermal conductivities, ranging from 0.1 το 0.6 W/(m K), as listed in Table 10.1. Foaming polymers may further enhance this low thermal conductivity. Polymer foams with lower density have more air and thus have lower thermal conductivity. The cell size of foamed polymers may also have an effect on thermal conductivity. Smaller foam cell size tends to yield lower thermal conductivity. Most foamed polymers have thermal conductivity values in the order of 10^{-2}W/(m K), which is about 10 times less than the same polymers. Table 10.2 is the list of thermal conductivities for common commercial foamed polymers.

The effect of temperature on polymers is of practical importance because most polymers are processed at relatively high temperature and have applications in a wide temperature range. The temperature dependence of thermal conductivity of polymers has been studied from extremely low temperatures at 0.1 K to above melting point [11,13–18,20]. Generally, with increase in temperature, thermal conductivity for amorphous polymers increases gradually

TABLE 10.1. *Thermal conductivity k of polymers.*

Polymer	Temperature (K)	*k* (W/m K)	Reference
Polyamides			
Polyauryllactam (nylon-12)		0.25	[21]
		0.19	[22]
Polycaprolactam (nylon-6)			
Moldings	293	0.24	[19]
Crystalline	303	0.43	[9]
Amorphous	303	0.36	[9]
Melt	523	0.21	[9]
Poly(hexamethylene adipamide) (nylon-6,6)			
Moldings	239	0.24	[19]
Crystalline	303	0.43	[9]
Amorphous	303	0.36	[9]
Melt	523	0.15	[23]
Poly(hexamethylene dodecanediamide)(nylon-6,12)		0.22	[24]
Poly(hexamethylene sebacamide) (nylon-6,10)		0.22	[19]
Polyundecanolactam (nylon-11)		0.23	[21]
Polycarbonates, polyesters, polyethers, and polyketones			
Polyacetal		0.3	[21]
		0.23	[19,24]
Polyaryletherketone	293	0.30	[24]
Poly(butylene terephthalate) (PBT)	293	0.29	[19]
		0.16	[9]
Polycarbonate (Bisphenol A)	293	0.20	[9,19]
Temperature dependence	300–573	*a*	[13]
	150–400	*a*	[14]
Poly(dially carbonate)		0.21	[19]
Poly(2,6-dimethyl-1,4-phenylene ether)		0.12	[22]
Polyester			
Cast, rigid		0.17	[19]
Chlorinated		0.33	[19]
Polyetheresteramide	303	0.24–0.34	[25]
	353	0.20–0.26	[25]
Polyetheretherketone (PEEK)		0.25	[22]
Poly(ethylene terephthalate) (PET)	293	0.15	[19]
Temperature dependence	200–350	*a*	[26,27]
Poly(oxymethylene)	293	0.292	[23]
	293	0.44	[26]
Temperature dependence	100–400	*a*	[26]
Poly(phenylene oxide)			
Molding grade		0.23	[21]
Epoxides			
Epoxy resin			
Casting grade	293	0.19	[19]
Temperature dependence	300–500	0.19–0.34	[28]
Halogenated olefin polymers			
Polychlorotrifluoroethylene	293	0.29	[19]
	311–460	0.146–0.248	[20]
Poly(ethylene–tetrafluoroethylene) copolymer		0.238	[22]
Polytetrafluoroethylene	293	0.25	[19]
	298	0.25	[29]
	345	0.34	[29]
Low temperature dependence	5–20.8	*a*	[20]
Poly(tetrafluoroethylene–hexafluoropropylene)			

TABLE 10.1. *Continued.*

Polymer	Temperature (K)	*k* (W/m K)	Reference
Copolymer(Teflon EEP)		0.202	[23]
Poly(vinyl chloride)			
Rigid	293	0.21	[19]
Flexible	293	0.17	[19]
Chlorinated	293	0.14	[19]
Temperature dependence	103	0.129	[23]
	273	0.158	[23]
	373	0.165	[23]
Poly(vinylidene chloride)	293	0.13	[23]
Poly(vinylidene fluoride)	293	0.13	[19,21]
	298–433	0.17–0.19	[22]
Hydrocarbon polymers			
Polybutene		0.22	[22]
Polybutadiene			
Extrusion grade	293	0.22	[19]
Poly(butadiene–styrene) copolymer (SBR)			
23.5% Styrene content			
Pure gum vulcanizate		0.190–0.250	[9]
Carbon black vulcanizate		0.300	[9]
Polychloroprene (Neoprene)			
Unvulcanized	293	0.19	[9,19]
Pure gun vculcanizate		0.192	[9]
Carbon black vulcanizate		0.210	[9]
Polycyclooctene			
80% *trans* content		0.27	[4]
Poly(1,3-cyclopentylenevinylene) [poly(2-norbornene)]		0.29	[9]
Polyethylene			
Low density		0.33	[19]
Medium density		0.42	[19]
High density		0.52	[19]
Temperature dependence	20–573	*a*	[9,13,20]
Molecular weight dependence		*a*	[20]
Poly(ethylene–propylene) copolymer		0.355	[9]
Polyisobutylene		0.13	[29]
Polyisoprene (natural rubber)			
Unvulcanized		0.13	[9,19]
Pure gum vulcanizate		0.15	[9]
Carbon black vulcanizate		0.28	[9]
Poly(4-methyl-1-pentene)	293	0.167	[22]
Polypropylene	293	0.12	[19]
		0.2	[9]
Temperature dependence		*a*	[15–17]
Polystyrene	273	0.105	[9]
	373	0.128	[9]
	473	0.13	[9]
	573	0.14	[9]
	673	0.160	[22]
Poly(*p*-xylylene) (PPX)		0.12	[22]
Polyimides			
Polyetherimide		0.07	[24]
Polyimide			
Thermoplastic	293	0.11	[19,24]
Thermoset		0.23–0.50	[24]
Temperature dependence	300–500	*a*	[14]

TABLE 10.1. *Continued.*

Polymer	Temperature (K)	k (W/m K)	Reference
Phenolic resins			
Poly(phenol–formaldehyde) resin			
Casting grade		0.15	[19]
Molding grade		0.25	[19]
Poly(phenol–furfural) resin			
Molding grade	293	0.25	[19]
Polysaccharides			
Cellulose			[23]
Cotton		0.071	[23]
Rayon		0.054–0.07	[23]
Sulphite pulp, wet		0.8	[23]
Sulphite pulp, dry		0.067	[23]
Laminated Kraft Paper		0.13	[23]
Alkali cellulose		0.046–0.067	
Different papers	303–333	0.029–0.17	[23]
Cellulose acetate	293	0.20	[19]
Cellulose acetate butyrate	293	0.33	[19]
Cellulose nitriate		0.23	[24]
Cellulose propionate		0.20	[21]
Ethylcellulose		0.21	[30]
Polysiloxanes			
Poly(dimethylsiloxane)	230	0.25	[31]
	290	0.20	[31]
	340	0.20	[31]
	410	0.17	[31]
Poly(methylphenylsiloxance)			
9.5% Phenyl, $d = 1{,}110\,\mathrm{kg/m^3}$	273	0.158	[32]
	323	0.150	[32]
	373	0.144	[32]
48% Phenyl, $d = 1{,}070\,\mathrm{kg/m^3}$	273	0.143	[32]
	323	0.136	[32]
	373	0.127	[32]
62% Phenyl, $d = 1{,}110\,\mathrm{kg/m3}$	273	0.141	[32]
	323	0.137	[32]
	373	0.132	[32]
Polysulfide and polysulfones			
Polyarylsulfone		0.18	[9]
Polyethersulfone		0.18	[9]
Poly(phenylene sulfide)	293	0.29	[21]
	240–310	0.288	[9]
Poly(phenylene sulfone)		0.18	[22]
Udel polysulfone		0.26	[9]
Polyurethanes			
Polyurethane			
Casting resin	293	0.21	[19]
Elastomer	293	0.31	[19]
Vinyl polymers			
Polyacrylonitrile	293	0.26	[19,24]
Poly(acrylonitrile–butadiene) copolymer (NBR)			
35% Acrylonitrile	333	0.251	[9]
	413	0.184	[9]
Poly(acrylonitrile–butadiene–styrene) copolymer (ABS)			
Injection molding grade		0.33	[19]
Poly(acrylonitrile–styrene) copolymer	293	0.18	[9]
Poly(*i*-butyl methacrylate)			
At 0.82 atm		0.13	[18]
Pressure and temperature dependence		*a*	[18]

TABLE 10.1. *Continued.*

Polymer	Temperature (K)	k (W/m K)	Reference
Poly(*n*-butyl methacrylate)			
At 0.82 atm		0.45	[18]
Pressure and temperature dependence		*a*	[18]
Poly(butyl methacrylate–triethylene glycol dimethacrylate) copolymer		0.15	[29]
Poly(chloroethylene–vinyl acetate) copolymer	293	0.134	[20]
	325	0.146	[20]
	375	0.218	[20]
Poly(dially phthalate)		0.21	[19]
Poly(ethyl acrylate)	310.9	0.213	[20]
	422.1	0.230	[20]
	533.2	0.213	[20]
Poly(ethyl methacrylate)m			
At 0.82 atm	273	0.175	[18]
Pressure and temperature dependence		*a*	[18]
Poly(ethylene vinyl acetate)		0.34	[33]
Poly(methyl methacrylate)	293	0.21	[19]
Temperature dependence		*a*	[20,34–37]
Poly(methyl methacrylate–acrylonitrile) copolymer		0.18	[21]
Polymer(methyl methacrylate–styrene) copolymer		0.12–0.21	[24]
Poly(vinyl acetate)		0.159	[9]
Poly(vinyl acetate–vinyl chloride) copolymer		0.167	[30]
Poly(vinyl alcohol)		0.2	[9]
Poly(*N*-vinyl carbozole)	293	0.126	[22]
	443	0.168	[22]
Poly(vinyl fluoride)	243	0.14	[9]
	333	0.17	[9]
Poly(vinyl formal)			
Molding grade	293	0.27	[19]

[a] See references citied in column 4.

in the glassy region and decreases slowly or remains constant in the rubbery region. For crystalline polymers, thermal conductivity decreases steadily with the increase in temperature below the melting point. At temperature above the melting point, it behaves in a similar way as amorphous polymers. Some of the values of polymer thermal conductivity measured at various temperatures are listed in Table 10.1. More results on temperature dependence can be found in the references cited.

Thermal conductivity of polymers is highly dependent on polymer chain segment orientation [10,12]. This is because thermal energy transports more efficiently along the polymer chain. Crystalline polymers have highly ordered chain segments, and therefore have higher thermal conductivity than amorphous polymers. Amorphous polymers may exhibit anisotropic thermal transport properties if polymer chains are partially oriented, with thermal conductivity along the chains higher than that perpendicular to the chains.

Reinforced polymers and thermally conductive polymer composites. Polymers are often reinforced with fillers to improve their mechanical, electrical, and thermal properties. The thermal conductivity of filled polymers is primarily determined by the type and amount of fillers used. The thermal properties of the filler, the size, shape, and orientation of filler particles or fibers in polymer matrix, and the percentage of fillers are all important factors that determine the thermal conductivity of reinforced polymers. As shown in Table 10. 3, polymers reinforced with inorganic fillers usually increase their thermal conductivities from a few percent to a few times. The filler percentages listed in Table 10.3 are weight percentages, unless otherwise indicated.

Highly thermal conductive polymer composites can be obtained by using fillers with high thermal conductivity and at high percentages. Thermally conductive polymer composites find wide applications in semiconductor industry such as electronic components encapsulation, in which the heat dissipation of circuit boards becomes more and more important as silicon chips get denser and faster. Other applications of thermally conductive polymer composites

TABLE 10.2. *Thermal conductivity k of foamed polymers.*

Polymer	k (W/m K)	Reference
Poly(acrylonitrile–butadiene) copolymer		
$d = 160\text{–}400\,\text{kg/m}^3$	0.036–0.043	[9]
Cellulose acetate		
$d = 96\text{–}128\,\text{kg/m}^3$	0.0450–0.45	[9]
Polychloroprene (neoprene)		
$d = 112\,\text{kg/m}^3$	0.040	[9]
$192\,\text{kg/m}^3$	0.065	[9]
Poly(dimethylsiloxane)		
Sheet, $d = 160\,\text{kg/m}^3$	0.086	[9]
Epoxy		
$d = 32\text{–}48\,\text{kg/m}^3$	0.016–0.022	[9]
$80\text{–}128\,\text{kg/m}^3$	0.035–0.040	[9]
Polyethylene		
Extruded plank		
$d = 35\,\text{kg/m}^3$	0.053	[9]
$64\,\text{kg/m}^3$	0.058	[9]
$96\,\text{kg/m}^3$	0.058	[9]
$144\,\text{kg/m}^3$	0.058	[9]
Sheet, extruded, $d = 43\,\text{kg/m}^3$	0.040–0.049	[9]
Sheet, crosslinked, $d = 26\text{–}38\,\text{kg/m}^3$	0.036–0.040	[9]
Polyisocyanurate		
$d = 24\text{–}56\,\text{kg/m}^3$	0.012–0.02	[9]
Polyisoprene (natural rubber)		
$d = 56\,\text{kg/m}^3$	0.036	[9]
$320\,\text{kg/m}^3$	0.043	[9]
Phenolic resin		
$d = 32\text{–}64\,\text{kg/m}^3$	0.029–0.032	[9]
$112\text{–}160\,\text{kg/m}^3$	0.035–0.040	[9]
Polypropylene		
$d = 54\text{–}96\,\text{kg/m}^3$	0.039	[9]
Polystyrene		
$d = 16\,\text{kg/m}^3$	0.040	[19]
$32\,\text{kg/m}^3$	0.036	[19]
$64\,\text{kg/m}^3$	0.033	[19]
$96\,\text{kg/m}^3$	0.036	[19]
$160\,\text{kg/m}^3$	0.039	[19]
Poly(styrene–butadiene) copolymer (SBR)		
$d = 72\ \text{kg/m}^3$	0.30	[9]
Poly(urea–formaldehyde) resin		
$d = 13\text{–}19\ \text{kg/m}^3$	0.026–0.030	[9]
Polyurethane		
Air blown, $d = 20\text{–}70\,\text{kg/m}^3$		
At 0°C	0.033	[38]
At 20°C	0.036	[38]
At 70°C	0.040	[38]
CO_2 blown, $d = 64\,\text{kg/m}^3$, at 20°C	0.016	[19]
20% closed cells, at 20°C	0.033	[19]
90% closed cells, at 20°C	0.016	[19]
500 μm cell size, at 20°C	0.024	[19]
100 μm cell size, at 20°C	0.016	[19]
Poly(vinyl chloride)		
$d = 56\,\text{kg/m}^3$	0.035	[9]
$d = 112\,\text{kg/m}^3$	0.040	[9]

TABLE 10.3. *Thermal conductivity k of reinforced polymers and thermally conductive polymer composites.*

Polymer	k (W/m K)	Reference
Polyacetal		
5–20% PTFE	0.20	[24]
Poly(acrylonitrile–butadiene–styrene) copolymer (ABS)		
20% Glass fiber	0.20	[19]
Polyaryletherketone		
40% Glass fiber	0.44	[24]
Polybenzoxazine (bisphenol A/methylamine/formaldehyde		
93% Aluminum nitride	7.4	[5]
94.1% Aluminum oxide	3.4	[5]
Polybenzoxazine (bisphenol A/methylamine/formaldehyde		
50–90% Boron nitride	1.7–37.5	[5]
Polybenzoxazine (bisphenol F/methylamine/formaldehyde)		
85% Boron nitride	20.9	[5]
Polybenzoxazine (bisphenol A/aniline)		
85% Boron nitride	19.8	[5]
Polybenzoxazine (bisphenol F/aniline)		
85% Boron nitride	10.6	[5]
Poly(butylenes terephthalate) (PBT)		
30% Glass	0.29	[19]
	0.20	[9]
40–50% Glass fiber	0.42	[24]
Polycarbonate		
10% Glass fiber	0.22	[19]
30% Glass fiber	0.32	[19]
Polychloroprene (neoprene)		
33% Carbon black	0.210	[9]
Polycyclooctene		
80% *trans* content, 20% boron oxide	0.41	[4]
Poly(dially phthalate)		
Glass fiber	0.21–0.62	[22]
Epoxy		
50% Aluminum	1.7–3.4	[39]
25% Al_2O_3	0.35–0.52	[39]
50% Al_2O_3	0.52–0.69	[39]
75% Al_2O_3	1.4–1.7	[39]
30% Mica	0.24	[19]
50% Mica	0.39	[19]
Silica	0.42–0.84	[19,39]
Epoxy (cresol–novolak)		
70% Boron nitride	6.07–11.6	[6]
Polyetheretherketone (PEEK)		
30% Glass fiber	0.21	[24]
30% Carbon fiber	0.21	[24]
Polyethylene		
5–25% (vol.) Al_2O_3	1–1.6	[2]
30% Glass fiber	0.36–0.46	[24]
Poly(ethylene terephthalate) (PET)		
30% Glass fiber	0.29	[9,19]
45% Glass fiber	0.31	[9]
30% Graphite fiber	0.71	[24]
40% PAN carbon fiber	0.72	[24]
Polyimide		
Thermoplastic, 15% graphite	0.87	[39]
40% graphite	1.73	[24,39]
Thermoset, 50% glass fiber	0.41	[24]

TABLE 10.3. *Continued.*

Polymer	k (W/m K)	Reference
Polyisoprene (natural rubber)		
33% carbon black	0.28	[9]
Poly(melamine–formaldehyde) resin		
Asbestor	0.544–0.73	[9]
Cellulose fiber	0.27–0.42	[24]
Glass fiber	0.42–0.48	[24]
Macerated fabric	0.443	[9]
Wood flour/cellulose	0.17–0.48	[24]
Poly(melamine–phenolic) resin		
Cellulose fiber	0.17–0.29	[39]
Wood flour	0.17–0.29	[39]
Nylon-6 (polycaprolactam)		
30–35% Glass fiber	0.24–0.28	[24]
Nylon-6,6 [poly(hexamethylene adipamide)]		
30–33% Glass fiber	0.21–0.49	[24]
40% Glass fiber and mineral	0.46	[24]
30% Graphite or PAN carbon fiber	1.0	[24]
Nylon-6,12 [poly(hexamethylene dodecanediamide)]		
30–35% Glass fiber	0.427	[24]
Poly(phenylene oxide)		
30% Glass fiber	0.16	[24]
Poly(phenylene sulfide)		
40% Glass fiber	0.288	[9]
30% Carbon fiber	0.28–0.75	[24]
Polypropylene		
40% Talc	0.32	[19]
40% CaCO3	0.29	[19]
40% Glass fiber	0.37	[19]
Polyurethane		
49% Boron nitride,1% silicon dioxide	0.55	[40]
Polystyrene		
20% Glass fiber	0.25	[26]
Poly(styrene–acrylonitrile) copolymer		
20% Glass fiber	0.28	[24]
Poly(styrene–butadiene) copolymer (SBR)		
33% Carbon black	0.300	[9]
Polytetrafluoroethylene		
25% Glass fiber	0.33–0.41	[24]
Poly(urea–formaldehyde) resin		
33% Alpha cellulose	0.423	[9]

include communication satellite device, structural components for spacecraft, computer cases, and many others that require light weight and good thermal conduction. Fillers used in thermally conductive polymers include metal and metal oxides, boron oxide, and graphitic carbon fibers. High thermalconductive polymer composites may have thermal conductivities 10 to over a 100 times higher than those of pure polymers, equal to or higher than thermal conductivities for some metals. Table 10.3 also includes some of those high thermal conductivity polymer composites.

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CHAPTER 11

Thermodynamic Quantities Governing Melting

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11.1 PREFATORY REMARKS

In this section a compilation and tabulation of the key thermodynamic parameters that govern the fusion of crystalline homopolymers is presented. The key parameters of interest are the equilibrium melting temperature, T_m^0, defined as the melting temperature of a large perfect crystal comprising infinite molecular weight chains, the enthalpy of fusion per chain repeating unit, ΔH_u, which is independent of the level of crystallinity, and the entropy of fusion, ΔS_u, which is obtained from the above quantities. The data listed in Tables 11.1–11.3 are limited to those homopolymers for which a complete set of thermodynamic parameters are available. Copolymers will not be included since this would involve specifying the sequence distribution of the comonomer. An exception will be made, however, for stereoregular polymers which, from the point of view of crystallization behavior, should be treated as copolymers [1]. Most polymers in this category are not completely stereoregular and cognizance must be taken of this fact when using the data assigned. We shall not be tabulating melting temperatures by themselves, without the auxiliary thermodynamic parameters. Before examining and using the data listed it is important to understand the theoretical and experimental foundations for the quantities that are given and the limitations that are imposed.

Although a collection of regularly structured, flexible chains will crystallize, they never do so completely. Depending on the molecular constitution, the chemical nature of the chain and the crystallization conditions the level of crystallinity attained can range from 90% to just a few percentage. In order for the crystallization of polymers from the melt to be carried out at finite rates, it must be conducted at temperatures well below the equilibrium melting temperature. Consequently, a polycrystalline, partially ordered, system is the one that actually develops. This crystalline system is well removed from equilibrium and can be considered to be in a metastable state. A structural and morphological complex system is thus developed that governs properties, including thermodynamic ones.

The kinetic restraints that are placed on the crystallization of polymers make it difficult, if not impossible to directly determine their equilibrium melting temperatures. The directly observed melting temperatures are primarily a reflection of the structure and morphology of the actual crystalline systems. The primary factors involved are the crystallite thickness, the interfacial free energy, and the influence, if any, of the noncrystalline region. There are, however, indirect methods by which to estimate the value of T_m^0. One of these is a theoretical method. The others are based on extrapolative procedures. To properly use the T_m^0 values that are tabulated, and to understand their limitations, the basic assumption involved and the problems in execution need to be recognized.

The theoretical method is based on the work of Flory and Vrij [2]. Here, the equilibrium melting temperatures of a series of oligomers (low molecular weight chains of uniform length) are analyzed. In this treatment an additional entropic term is added to the expression for the molar entropy of fusion of long-chain molecules in an ordered crystalline array. This term, which takes into account the disruption on fusion of the terminal groups of neighboring molecules, exerts an important influence in analyzing the experimental melting temperatures for *n*-paraffins and their convergence to the limit, T_m^0 for the infinite length chain. By analyzing the fusion of the *n*-alkanes, up to $C_{100}H_{202}$, the T_m^0 value for linear polyethylene was found to be 418.7±1 K. This is the only polymer to which this theoretical method has been applied. There are not enough data available for oligomers with other type repeating units to apply this method to other polymers. It is important in utilizing this method that all the molecules be of uniform chain length so that molecular crystals can be formed.

Both of the extrapolative methods are based on the Gibbs–Thomson equation for the melting of crystallites of finite size [3]. For a lamellar crystallite, whose length is very much greater than its thickness, this equation can be expressed as:

$$T_m = T_m^0\left(1 - \frac{2\sigma_{ec}}{\Delta H_u l}\right). \tag{11.1}$$

Here T_m is the experimentally observed melting temperature of a crystallite of thickness l and σ_{ec} is the interfacial free energy associated with the basal plane of the lamellar crystallite. Eq. (11.1) was developed to describe the melting of small crystals in equilibrium with the melt. Hence only two phases (or regions) are involved. The implicit assumption is made that the boundary between them is a sharp one. In general, long-chain molecules do not fulfill this condition. It is now well established, by theory and experiment, that there is a diffuse interfacial region, 10–30 Å thick, which connects the crystalline with the liquid-like region [4]. The analog to Eq. (11.1) to account for the melting of small crystallites, when equilibrium between three phases is involved, has yet to be developed.

Despite the problem described above, Eq. (11.1) has been used to determine T_m^0 by measuring the observed melting temperature, T_m, as a function of the crystallite thickness. Accordingly, a plot of T_m against $1/l$ should be linear and extrapolate to T_m^0. An example of this procedure is illustrated in Fig. 11.1 for poly(tetrafluoroethylene) [5]. A straight line clearly results in the plot of T_m against $1/l$. An extrapolated value of 335 °C is obtained for T_m^0. In this example the largest crystallite thickness that was generated was about 5,000 Å. Thus, the extrapolation was not unduly long. This method appears to be quite satisfactory for poly(tetrafluoroethylene). However, for many of the flexible chain-type polymers, such as linear polyethylene, poly(propylene), poly(hexamethylene adipamide), poly (pivalolactone), among others, the maximum thickness used in the extrapolation is usually less than 200 Å. In many cases it is less than 100 Å. Hence, most commonly there is a very long and treacherous extrapolation to $l = \infty$.

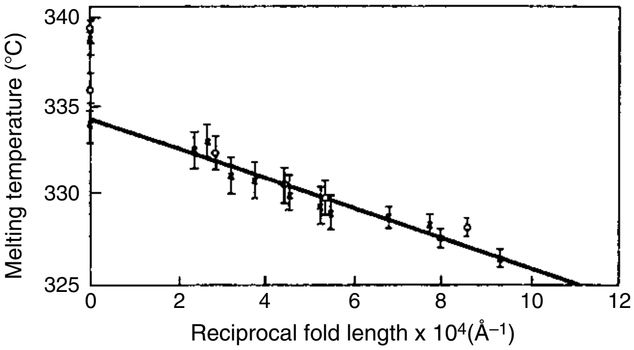


FIGURE 11.1. Melting temperature, in degrees Celsius, as a function of reciprocal crystallite thickness in Ångstroms for poly(tetrafluoroethylene) [5].

There are also other matters of concern that need to be taken into account when using this method. It is very rare to develop a uniform crystallite thickness distribution. In particular, the distribution becomes very broad after high-temperature crystallization. The question then arises as to what portion of the distribution curve corresponds to the observed melting temperature. Usually some average crystallite thickness is measured. The use of this method with polymer systems where a large proportion of the crystallinity develops during the quenching process, after isothermal crystallization, would introduce major uncertainties if the crystallite thickness (l) is measured at room temperature.

When linearly extrapolating Eq. (11.1) it is tacitly assumed that σ_{ec} is independent of the crystallite thickness. Crystallite thicknesses are usually controlled by varying the crystallization temperature. Theory has shown that, among other factors, σ_{ec} depends on the flux of chains emanating from the basal plane of the lamellar crystallite [4]. This flux will in term depend on the tilt angle of the chain, i.e., the angle between the chain axis and the normal to the basal plane [6]. For many polymers the tilt angle depends on the crystallization temperature. Consequently, a variation in σ_{ec} with crystallite thickness can be expected, for many systems. Whether using Eq. (11.1), or the appropriate equivalent equation (when available), the functionality between σ_{ec} and l is needed to properly estimate T_m^0.

Consideration should also be given to the meaning of the extrapolated value, obtained by measuring melting of folded chain crystallites, when the equilibrium state requires an almost completely extended state [7,8]. The interfacial free energies will be different in the two cases.

Small-angle x-ray scattering is one of the standard methods that are used to determine crystallite thickness. A crystalline system comprising a set of stacked lamellae gives a characteristic long period. The long period must then be corrected for the level of crystallinity to obtain the crystallite thickness. In many studies this correction has not been made. Consequently, in these cases there is an indeterminate error in the extrapolation to T_m^0.

For the reasons that have been cited above, it is not surprising that there are serious discrepancies in the T_m^0 values determined by different studies of the same polymer using this method. For example, linear polyethylene, T_m^0 values, which were obtained by this extrapolative method, vary from 411.3 to 419.0 K among different investigators [9]. Although the difference is not a large range on an absolute basis, it is crucially important in analyzing crystallization kinetics because the undercooling, $(T_m^0 - T_c)$ is involved.

The other extrapolative method that is used was also developed from the Gibbs–Thomson equation [10,11].

Here, l and σ_{ec} are related to the corresponding quantities that define a nucleus of critical size, namely, l^* and σ_{ec}. For a Gibbs type two-dimensional coherent nucleus $l^* = 2\sigma_{en}/\Delta G_u$, where $\Delta G_u = \Delta H_u \Delta T / T_m^0$ [12] and $\Delta T = T_m^0 - T_c$. The interfacial free energy σ_{en} now represents that of the critical size nucleus. If it is assumed that $l/l^* = m$ and $\beta = \sigma_{ec}/\sigma_{en}$ over the complete range of crystallization temperatures then

$$T_m = T_m^0\left(1 - \frac{\beta}{m}\right) + \frac{\beta}{m}T_c. \tag{11.2}$$

For a three-dimensional homogeneous nucleus, or for certain types of heterogeneous nuclei [13–15], under the same assumptions

$$T_m = T_m^0\left(1 - \frac{\beta}{2m}\right) + \frac{\beta}{2m}T_c. \tag{11.3}$$

The further assumption is commonly made that $\beta = 1$. In this case Eq. (11.2) becomes

$$T_m = \frac{(m-1)}{2m}T_m^0 + \frac{T_c}{2m} \tag{11.4}$$

and Eq. (11.3) becomes

$$T_m = \frac{(2m-1)}{2m}T_m^0 + \frac{T_c}{2m}. \tag{11.5}$$

For this type of extrapolation we need not concern ourselves with which type of nucleation is controlling the crystallization since the only interest is evaluating T_m^0. In either case, assuming that m is constant over the complete interval of crystallization temperatures, there is a linear relation between T_m and T_c. Thus, a linear extrapolation to the $T_m = T_c$ straight line should in principle lead to T_m^0. The concept, as outlined above, requires low levels of crystallinity so that the mature crystallite will resemble the critical nucleus as closely as possible. However, independent experiments have made clear that the quantity m, a measure of crystallite thickening, is strongly dependent on the crystallization temperature [16,17]. It is also dependent on molecular weight. In addition it is reasonable to expect that $\sigma_{ec} > \sigma_{en}$ so that β will not be constant.

With this theoretical background we can examine some of the experimental results typical of this popular extrapolative method that is used to obtain T_m^0. In brief summary, the results depend on the nature of the polymer, the level of crystallinity that is developed, and the range of crystallization temperatures that is used. A set of $T_m - T_c$ data for poly(ethylene oxide), $M_w = 6.1 \times 10^5$, are given in Fig. 11.2 [18]. At the low levels of crystallinity the data are represented by two intersecting straight lines. The line with the steeper slope extrapolates to a T_m^0 value of 349.2 K. When the crystallinity level is increased, the observed melting points are represented by a single straight line. The extrapolated T_m^0 value of 341.2 K is now much lower. The value obtained at the lower crystallinity level is preferred by theory. However, this quantity still does not represent the highest T_m^0 value that has been deduced for this polymer (see Table 11.1). It is important to note that the data obtained at the low crystallinity level can also be represented by a continuous curve.

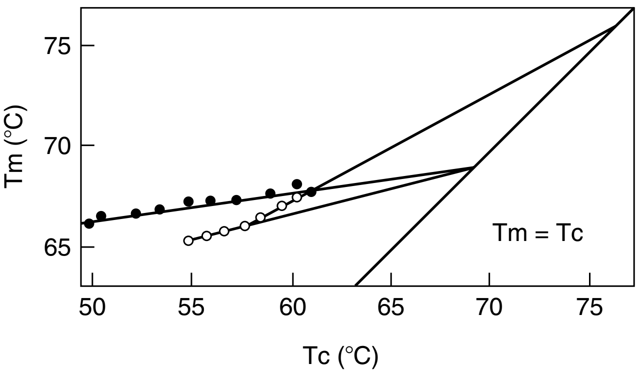


FIGURE 11.2. Plot of melting temperature against crystallization temperature for poly(ethylene oxide), (●) high crystallinity; ○ low crystallinity. Temperature in degrees Celsius [18].

The question arises as to what happens if the T_c range is extended to higher temperatures. An example is given in Fig. 11.3 for a linear polyethylene sample having a most probable molecular weight distribution, $M_w = 351,000$, that was crystallized to a crystallinity level of less than 10% [12]. For the range in crystallization temperatures shown the data are best represented by a curve. If, however, the measurements are restricted to 126 °C, or less, the data would be represented by two intersecting straight lines. Within this range the extrapolated $T_m^0 = 417\,\text{K} - 418$ is in agreement with theoretical expectations [2]. However, if the range of crystallization temperatures is increased to 131 °C (a high T_c for this polymer), then, the data points deviate from the straight line toward high values and a linear extrapolation is no longer operationally feasible. This behavior

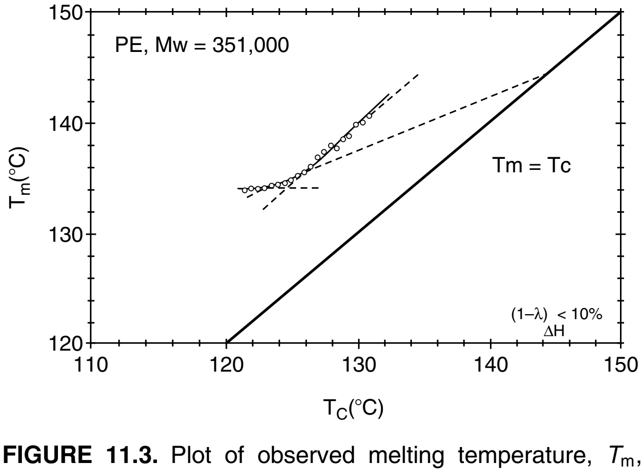


FIGURE 11.3. Plot of observed melting temperature, T_m, against crystallization temperature, T_m, for a linear polyethylene having a most probable molecular weight distribution, $M_w = 351{,}000$. Degree of crystallinity less than 10%. Temperature in degrees Celsius [12].

is not unique to linear polyethylene, it is also shown by many other polymers. There is, therefore, a serious dilemma in using this method. If T_c is too high then the extrapolation cannot be made. In order to carry out the extrapolation an arbitrary decision must be made as to the highest T_c value to be used. Thus the value obtained for T_m^0 will also involve an element of arbitrariness. The fact that the parameter m varies with the crystallization temperature is a major reason for the curvature that is observed. Several theoretical proposals have been made to improve the data analysis in order to obtain a more reliable extrapolated value of T_m^0 [19,20]. The validity and reliability of the proposed methods awaits further study.

There are obvious difficulties in obtaining T_m^0 by either of these extrapolative methods. Therefore, caution must be used in accepting, and using, the values so obtained. Equilibrium melting temperatures listed in Tables 11.1 and 11.3 have been obtained by one or the other of these methods, except for the theoretical value for linear polyethylene.

11.2 ENTHALPY OF FUSION PER REPEATING UNIT, ΔH_u

There are several experimental methods that allow ΔH_u to be determined. Two of these are based on direct thermodynamic methods. They do not involve knowledge of the crystallinity level of the polymer. A third method is an indirect one that does require such knowledge.

One of the thermodynamic methods involves the adaptation of the classical freezing point-composition relation to the melting of polymer-diluent mixtures. The most common situation encountered when a low molecular weight diluent is admixed with a polymer, is that the crystalline phase remains pure. Under these conditions, for polymers of high molecular weight, the melting temperature of a polymer-diluent mixture, T_m, can be expressed as [7,21]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}\left[(1 - v_2) - \chi_1(1 - v_2)^2\right]. \tag{11.6}$$

In deriving this equation, the chemical potentials in the melt of the two components are given by the Flory–Huggins theory [22]. In Eq. (11.6), V_u and V_1 are the molar volumes of the chain repeating unit and diluent, respectively; v_2 is the volume fraction of polymer in the mixture and χ_1 is the Flory–Huggins interaction parameter [22]. The implicit assumption is made in deriving Eq. (11.6) that σ_{ec} is independent of composition. The similarity of Eq. (11.6) to the classical expression for the freezing point depression is readily apparent. It has been found that, for a given polymer, the same value of ΔH_u is obtained irrespective of the diluent used, giving support to the validity of Eq. (11.6) [23]. Measurement of the melting point depression is a powerful method for determining ΔH_u. Enthalpies of fusion per repeating unit that were determined by this method are listed in Table 11.1.

The other thermodynamic method that can be used to determine ΔH_u involves the variation of the equilibrium melting temperature with applied hydrostatic pressure, p. The Clapeyron equation

$$\frac{dT_m^0}{dp} = T_m^0\frac{\Delta V_u}{\Delta H_u} \tag{11.7}$$

has been shown to apply to polymers [24], as it does to all substances. In this equation ΔV_u is the difference between the volume, per unit, of the pure melt and of the pure crystal. It is important, therefore, that these two quantities be known as a function of both temperature and pressure in order to properly apply Eq. (11.7). The ΔH_u values that have been obtained by this method are given in Table 11.2.

The ΔH_u values, obtained by indirect methods, of polymers that, except for minor exceptions, are not included in Table 11.1 or 11.2, are listed in Table 11.3. In general, the enthalpy of fusion is measured for a given sample and the level of crystallinity of the same specimen is determined, by one of the many methods that are available. The ΔH_u value can then be calculated from these measurements. One problem associated with this procedure is that not all methods of measuring the level of crystallinity give exactly the same value. Small but significant differences are found between different techniques that reflect different sensitivities to the elements of phase structure [25]. A corollary to this procedure is to determine the enthalpy of fusion as a function of density for a sample that is crystallized in different ways. The results are then extrapolated to the density of the unit cell in order to obtain ΔH_u. The density of the unit cell needs to be well established, and a long extrapolation is usually involved.

The purpose of these prefatory remarks has been to explain the underlying theoretical basis for the data that appear in the tables that follow and the experimental difficulties that are involved. Such tabulations must always be taken cautiously and critically. However, with proper care, and understanding, the data should be very useful.

Related information can be found in Chapters 30 and 31.

TABLE 11.1. *Thermodynamic quantities determined by use of diluent equation [Eq. (11.6)].*

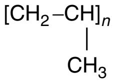
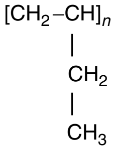
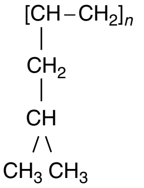
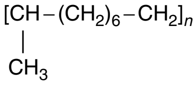
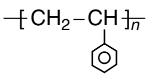
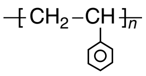
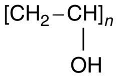
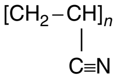
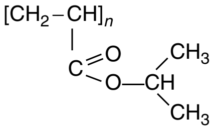
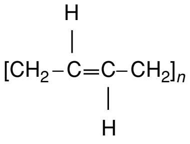
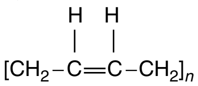
Polymer		T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	References
Ethylene $[CH_2]_n$		418.7	4,142	295.8	9.9	[26–28]
Isot.-propylene[a]  $[CH_2-CH(CH_3)]_n$	α	485.2	8,786	208.8	18.1	[29–36]
	β	465.2	8,201	194.9	17.6	
Isot.-butene-1  $[CH_2-CH(CH_2CH_3)]_n$	(I)	408.7	6,318	112.5	15.5	[37–38]
	(II)	397.2	6,276	111.9	15.8	
	(III)	379.7	6,485	115.6	17.1	
4-Methyl pentene-1  $[CH-CH_2]_n$ with $CH_2-CH(CH_3)_2$ side group		523.2	5,297	63.7	10.1	[39]
1-Methyl octamer  $[CH(CH_3)-(CH_2)_6-CH_2]_n$		268.2	10,857	86.2	40.5	[40]
Isot.-styrene 		>516.2[b]	8,682[c]	83.4	16.8	[41–44]
Synd.-styrene 		>560.5[d]	8,577	82.4	15.3	[45–47]
Vinyl alcohol  $[CH_2-CH(OH)]_n$		523.2	6,862	156.1	13.1	[48–50]
Acrylonitrile  $[CH_2-CH(C{\equiv}N)]_n$		593.2	5,021	94.7	8.5	[51,52]
Isot.-*iso*-propyl acrylate  $[CH_2-CH(COOCH(CH_3)_2)]_n$		450.2	5,857	51.4	13.0	[53]
trans-1,4 Butadiene  $[CH_2-CH{=}CH-CH_2]_n$	(I)	369.2	13,807	255.7	37.4	[54]
	(II)	421.2	4,602	85.2	10.9	
cis-1,4 Butadiene  $[CH_2-CH{=}CH-CH_2]_n$		273.2	9,205	170.4	33.7	[55]

TABLE 11.1. *Continued.*

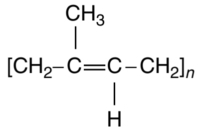
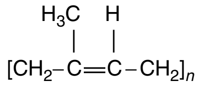
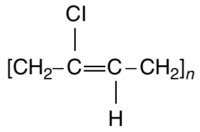
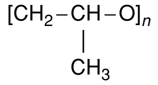
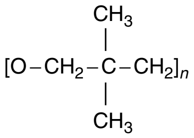
Polymer		T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	References
trans-1,4 Isoprene  $[CH_2-\overset{CH_3}{C}=\underset{H}{C}-CH_2]_n$	(α) (β)	360.2 354.2	12,719 10,544	187.0 155.1	35.3 29.8	[56–58]
cis-1,4 Isoprene  $[CH_2-\overset{H_3C}{C}=\overset{H}{C}-CH_2]_n$		308.7	4,393	64.6	14.2	[59,60]
trans-1,4 Chloroprene  $[CH_2-\overset{Cl}{C}=\underset{H}{C}-CH_2]_n$		380.2	8,368[e]	94.6	22.0	[61–63]
trans-Pentenamer $[CH{=}CH-CH_2-CH_2-CH_2]_n$		307.2	12,008	176.3	39.1	[64,65]
trans-Octenamer[e] $[CH{=}CH-(CH_2)_5-CH_2]_n$		350.2	23,765	215.7	67.9	[66]
cis-Octenamer $[CH{=}CH-(CH_2)_5-CH_2]_n$		311.2	21,000	190.9	67.5	[67]
trans-Decenamer[e] $[CH{=}CH-(CH_2)_7-CH_2]_n$		353.2	32,844	237.6	92.9	[66]
trans-Dodecenamer $[CH{=}CH-(CH_2)_9-CH_2]_n$		357.2	41,171	247.6	115.3	[66,68]
Methylene oxide $[CH_2-O)_n$		479.2	7,012	233.7	14.6	[69–72]
Ethylene oxide $[CH_2-CH_2-O]_n$		353.2	8,703	197.8	24.6	[73–75]
Isot.-propylene oxide  $[CH_2-\underset{CH_3}{CH}-O]_n$		355.2	7,531 8,368[f]	129.8	21.2	[76,77]
Trimethylene oxide $[(CH_2)_3-O]_n$		323.2	8,786	151.5	27.2	[78]
Tetramethylene oxide $[(CH_2)_4-O]_n$		330.2	15,899	220.8	48.2	[79]
Hexamethylene oxide $[(CH_2)_6-O]_n$		346.7	23,640	236.4	68.2	[80]
1,3 Dioxolane $[O-CH_2-O-(CH_2)_2]_n$		366.2	15,481	209.2	42.3	[81]
1,3 Dioxepane $[O-CH_2-O-(CH_2)_4]_n$		303.0	14,454	141.7	47.7	[82]
1,3 Dioxocane $[O-CH_2-O-(CH_2)_5]_n$		319.2	7,740	75.9	24.3	[83]
3,3 Dimethyl oxetane  $[O-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2]_n$	II III	349.2 329.2	9,205 7,448	107.0 86.6	26.3 22.6	[84]

TABLE 11.1. *Continued.*

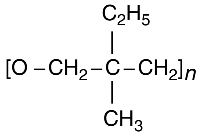
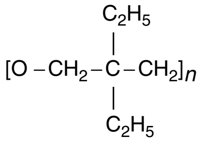
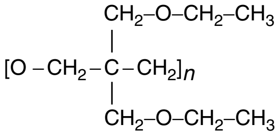
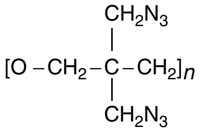
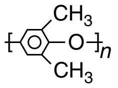
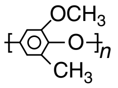
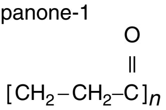
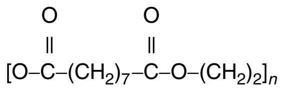
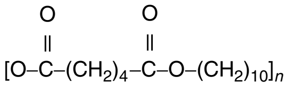
Polymer	T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	References
3-Ethyl 3-methyl oxetane  $[O-CH_2-\overset{C_2H_5}{\underset{CH_3}{C}}-CH_2]_n$	334.2	6,276	62.8	18.8	[85]
3,3 Diethyl oxetane Monoclinic	373.2	10,460	91.8	28.0	[86]
Orthorhombic  $[O-CH_2-\overset{C_2H_5}{\underset{C_2H_5}{C}}-CH_2]_n$	353.2	10,042	88.1	28.4	[86]
3,3-bis Ethoxy methyl Oxetane  $[O-CH_2-\overset{CH_2-O-CH_2-CH_3}{\underset{CH_2-O-CH_2-CH_3}{C}}-CH_2]_n$	398.2	9,414	54.1	23.6	[87]
3,3-bis Azido methyl Oxetane  $[O-CH_2-\overset{CH_2N_3}{\underset{CH_2N_3}{C}}-CH_2]_n$	401.2	53,555	318.8	133.5	[87]
2,6 Dimethyl,1,4 phenylene oxide 	548.2	5,230	43.6	9.5	[88,89]
2,6 Dimethoxy,1,4 phenylene oxide 	560.2	3,184	20.9	5.7	[90]
Trimethylene sulfide $[(CH_2)_3-S]_n$	363.2	10,460	141.4	28.8	[91]
Propanone-1  $[CH_2-CH_2-\overset{\overset{O}{\parallel}}{C}]_n$	>528.2	12,600	225.0	<23.8	[92]
Ethylene azelate  $[O-\overset{\overset{O}{\parallel}}{C}-(CH_2)_7-\overset{\overset{O}{\parallel}}{C}-O-(CH_2)_2]_n$	338.2	43,095	138.1	127.6	[93]
Decamethylene adipate  $[O-\overset{\overset{O}{\parallel}}{C}-(CH_2)_4-\overset{\overset{O}{\parallel}}{C}-O-(CH_2)_{10}]_n$	352.7	42,677	150.3	121.0	[94]

TABLE 11.1. *Continued.*

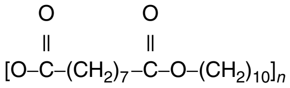
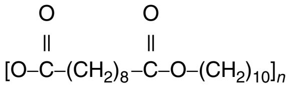
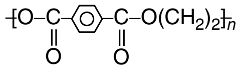
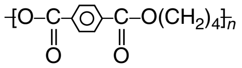
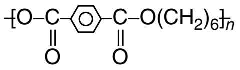
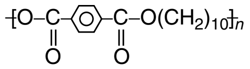
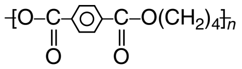
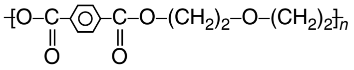
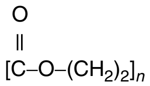
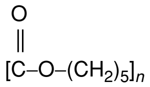
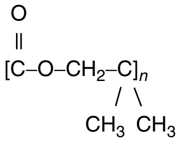
Polymer	T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	References
Decamethylene azelate  $[O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_7{-}\overset{O}{\overset{\|}{C}}{-}O{-}(CH_2)_{10}]_n$	342.2	41,840	129.7	121.3	[93]
Decamethylene sebacate  $[O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}{-}O{-}(CH_2)_{10}]_n$	353.2	50,208	147.7	142.2	[95]
Ethylene terephthalate 	613.2	23,430	122.0	38.2	[96–98]
Tetramethylene terephthalate 	503.2	31,798	144.5	63.2	[99]
Hexamethylene terephthalate 	433.7	35,564	143.4	82.0	[93]
Decamethylene terephthalate 	411.2	46,024	151.4	111.9	[93]
Tetramethylene isophthalate 	425.7	42,258	192.1	99.3	[99,100]
Diethylene glycol terephthalate 	373.2	39,748	168.4	106.5	[101]
β-propiolactone  $[\overset{O}{\overset{\|}{C}}{-}O{-}(CH_2)_2]_n$	357	8,577	119.1	24.0	[102]
ε-caprolactone  $[\overset{O}{\overset{\|}{C}}{-}O{-}(CH_2)_5]_n$	337	16,297	142.9	48.3	[102]
α,α' Dimethyl propiolactone  $[\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\underset{CH_3\ CH_3}{C}]_n$	542.2	14,853	148.5	27.4	[103–105]

TABLE 11.1. *Continued.*

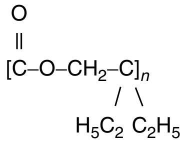
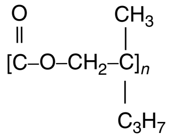
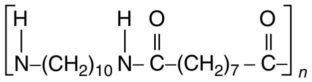
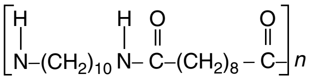
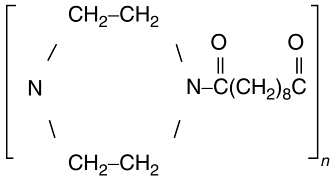
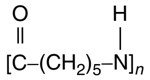
Polymer		T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	References
α,α' Dimethyl propiolactone  $[\overset{\overset{O}{\Vert}}{C}-O-CH_2-\underset{H_5C_2\;\;C_2H_5}{C}]_n$		531.2	20,920	163.4	39.4	[106]
α-Methyl, α- *N* propyl, β–propiolactone  $[\overset{\overset{O}{\Vert}}{C}-O-CH_2-\overset{\overset{CH_3}{\vert}}{\underset{\underset{C_3H_7}{\vert}}{C}}]_n$		425.2	14,602	114.1	34.3	[107]
Decamethylene azelamine  $\left[\overset{\overset{H}{\vert}}{N}-(CH_2)_{10}\overset{\overset{H}{\vert}}{N}-\overset{\overset{O}{\Vert}}{C}-(CH_2)_7-\overset{\overset{O}{\Vert}}{C}-\right]_n$		487.2	36,819	112.9	75.3	[93]
Decamethylene sebacamide  $\left[\overset{\overset{H}{\vert}}{N}-(CH_2)_{10}\overset{\overset{H}{\vert}}{N}-\overset{\overset{O}{\Vert}}{C}-(CH_2)_8-\overset{\overset{O}{\Vert}}{C}-\right]_n$		489.2	34,727	102.7	71.0	[93]
N,N' sebacoyl piperazine  $\left[N\langle\begin{smallmatrix}CH_2-CH_2\\CH_2-CH_2\end{smallmatrix}\rangle N-\overset{\overset{O}{\Vert}}{C}(CH_2)_8\overset{\overset{O}{\Vert}}{C}\right]_n$		453.2	25,941	102.9	57.2	[108]
Caprolactam  $[\overset{\overset{O}{\Vert}}{C}-(CH_2)_5-\overset{\overset{H}{\vert}}{N}]_n$	γ^g	502.2	17,949	158.8	35.7	[109]
Ester amide[h] 6-6		526	92,885	188.3	176.6	[110]
Ester amide[h] 12-2		517	102,522	194.6	198.3	[110]
Ester amide[h] 12-6		487	116,315	200.8	238.8	[110]
Ester amide[h] 12-12		470	140,164	211.3	298.2	[110]
Urethane[i]						
$n = 2$		440.2	44,267	192.5	100.6	[111]
$n = 5$		428.2	45,522	167.4	106.3	[111]
$n = 10$		427.2	61,505	179.8	144.0	[111]

TABLE 11.1. *Continued.*

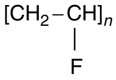
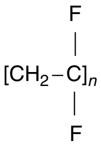
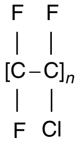
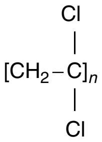
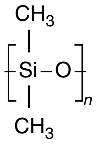
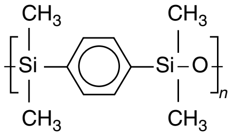
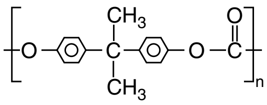
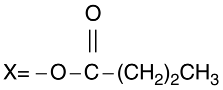
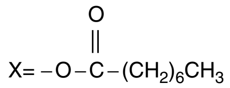
Polymer		T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	References
Urethane[j]						
$n = 5$		462.2	54,810	154.8	118.6	[111]
$n = 10$		465.2	70,961	167.4	152.5	[111]
Vinyl fluoride  $[CH_2-\underset{F}{\underset{\vert}{C}}H]_n$		470.2	7,531	163.7	16.0	[112]
Vinylidene fluoride  $[CH_2-\overset{F}{\overset{\vert}{\underset{F}{\underset{\vert}{C}}}}]_n$	(α)	532.2	6,694	104.6	12.6	[113–115]
Chloro trifluoro ethylene  $[\overset{F}{\overset{\vert}{\underset{F}{\underset{\vert}{C}}}}-\overset{F}{\overset{\vert}{\underset{Cl}{\underset{\vert}{C}}}}]_n$		483.2	5,021	43.1	10.4	[116]
Vinylidene chloride  $[CH_2-\overset{Cl}{\overset{\vert}{\underset{Cl}{\underset{\vert}{C}}}}]_n$		468.2	5,623	58.6	12.0	[117]
Dimethyl siloxane[k]  $\left[\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{Si}}}}-O\right]_n$		233	2,767	36.7	11.9	[118]
Tetramethyl-*p*-silphenylene siloxane 		433.2	11,340	54.4	26.2	[119]
2,2'-bis 4,4'(Oxyphenyl) propane carbonate 		590.2	34,008	133.9	57.6	[120,121]
Cellulose tributyrate[l]  $X= -O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_2CH_3$		480.2	12,552	33.7	26.1	[122]

TABLE 11.1. *Continued.*

Polymer	T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	References
Cellulose trinitrate[l] $X = -O-NO_2$	>973	3,765–6,276	12.6–21.1	3.9–6.4	[123]
Cellulose (2.44) nitrate[l] Cellulose $[O-NO_2]_{2.44}$	890.2	5,648	21.5	6.3	[124]
Cellulose tricaprylate[l]  $X = -O-\overset{\overset{O}{\parallel}}{C}-(CH_2)_6CH_3$	389.2	12,970	24.0	33.3	[125]
Collagen	418.2[m]	9,414	100.4	22.5	[126]

[a] The equilibrium melting temperature of isotactic polypropylene is still debated between values ranging from 458 to 493 K. See for example refs [200, 201, 202].

[b] 516.2 K is the highest T_m observed [44]. Therefore, T_m^0 should be greater.

[c] Average value of references cited.

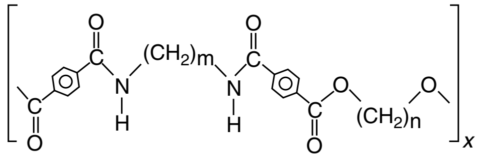
[d] Extrapolated equilibrium melting temperatures of the α and β forms are very close to one another. Depending on the method used they are close to 545 or 573 K [203].

[e] Extrapolated to all *trans*.

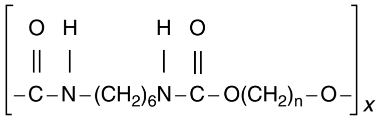
[f] Obtained by direct determination of activity coefficients in polymer-diluent mixtures.

[g] That these data belong to the γ form is deduced from the reported specific volumes (V_c^γ) and the heat of fusion data of Fig. 13 of von K-H Illers et al. ref [166].

[h] Ester-amide (n–m)

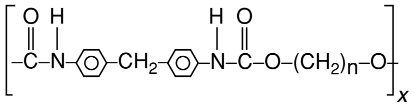


i



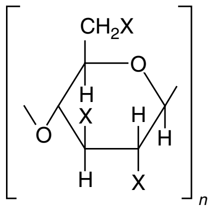
$$\left[-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_6\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\parallel}}{C}-O(CH_2)_n-O-\right]_x$$

j



[k] The value of ΔH_u was determined with only one diluent. It was originally reported in terms of calories per mole of chain atoms and misinterpreted. The value in joules per gram was subsequently clarified by M. I. Arangurem [204].

l



[m] Extrapolated from the melting point of glycol mixtures.

TABLE 11.2. *Thermodynamic quantities determined by the use of Clapeyron equation [Eq. (11.7)]*

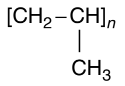
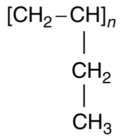
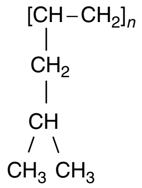
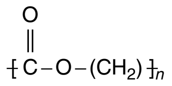
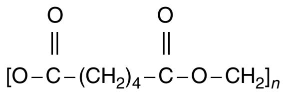
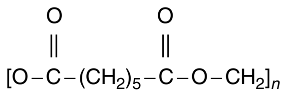
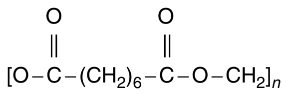
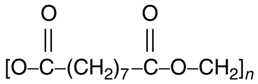
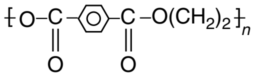
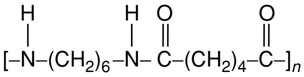
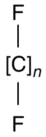
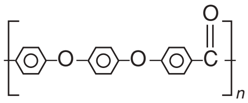
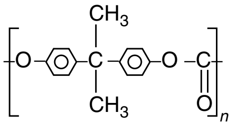
Polymer	$T_m^{0\,a}$ (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	References
Ethylene $[CH_2]_n$	414.6	4,059	289.9	9.8	[127]
Isot.-propylene (γ)  $[CH_2-\underset{CH_3}{\underset{\vert}{CH}}]_n$	460.2	$6{,}300^b$	150	13.7	[128]
		$7{,}980^b$	190	17.3	[128]
Isot.-butene-1 (I)	406.2	$7{,}782^c$	138.7	19.2	[129,130]
(II)  $[CH_2-\underset{\underset{\underset{CH_3}{\vert}}{CH_2}}{\underset{\vert}{CH}}]_n$	392.9	$7{,}531^c$	134.2	19.2	
4-Methyl pentene-1  $[\underset{\underset{\underset{CH_3\ CH_3}{CH}}{\vert}}{\underset{\underset{CH_2}{\vert}}{CH}}-CH_2]_n$	506.2	5,205	61.9	10.3	[131]
Methylene oxide $[CH_2-O]_n$	456.2	11,673	389.1	25.6	[132]
Ethylene oxide $[CH_2-CH_2-O]_n$	339.2	9,037	205.4	26.6	[133]
Tetramethylene oxide $[(CH_2)_4-O]_n$	315.9	14,728	204.6	46.6	[133]
Glycolic acid  $[\overset{O}{\overset{\Vert}{C}}-O-(CH_2)]_n$	504.6	10,626	183.2	21.1	[134]
Ethylene adipate  $[O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}-O-CH_2]_n$	326.2	20,150	127.5	61.8	[135]
Ethylene pimelate  $[O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_5-\overset{O}{\overset{\Vert}{C}}-O-CH_2]_n$	309.2	27,489	159.8	88.9	[135]
Ethylene suberate  $[O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_6-\overset{O}{\overset{\Vert}{C}}-O-CH_2]_n$	336.2	24,451	131.4	72.8	[135]

TABLE 11.2. *Continued.*

Polymer	T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	References
Ethylene azelate  $[O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_7-\overset{O}{\overset{\Vert}{C}}-O-CH_2]_n$	320.2	40,488	202.4	126.4	[135]
Ethylene terephthalate 	535.2	26,150	136.2	48.9	[136]
Hexamethylene Adipamide α_2  $[-\overset{H}{\overset{\vert}{N}}-(CH_2)_6-\overset{H}{\overset{\vert}{N}}-\overset{O}{\overset{\Vert}{C}}-(CH_2)_4-\overset{O}{\overset{\Vert}{C}}-]_n$	542.2	43,367	191.9	79.9	[137]
Tetrafluoro ethylene (virgin)	619.2	5,105	102.1	8.2	[138]
Tetrafluoro ethylene (melt cured)  $[\overset{F}{\overset{\vert}{\underset{\underset{F}{\vert}}{C}}}]_n$	601.2	4,632	92.6	7.7	[138]
aryl-ether–ether–ketone 	611.2	47,359	164.4	77.5	[139]
2,2'bis(4,4' Oxyphenyl) propane carbonate 	506.2	39,497	155.5	78.0	[140]

[a] Melting temperature actually used in calculation.

[b] Both values are quoted.

[c] Average values.

TABLE 11.3. *Unique values of thermodynamic parameters determined by indirect methods.*

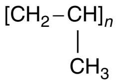
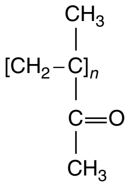
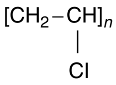
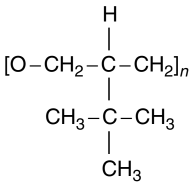
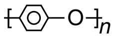
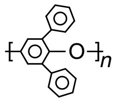
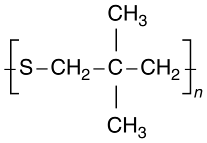
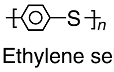
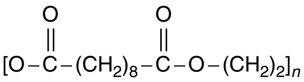
Polymer		T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	Method	References
Synd.-propylene  $[\mathrm{CH_2-\underset{CH_3}{CH}}]_n$		455.2[a]	8,274	196.7	18.2	DSC-x ray	[141,142]
Methyl methacrylate  $[\mathrm{CH_2-\overset{CH_3}{\underset{\underset{CH_3}{C=O}}{C}}}]_n$	Isot.	411.2	5,021	50.2	12.2	DSC-x ray	[143]
	Synd.	$>$397.5				DSC-Mn	[144]
Synd.-vinyl chloride  $[\mathrm{CH_2-\underset{Cl}{CH}}]_n$		538.2[b]	4,937	79.0	9.2	DSC-x ray	[145]
		658.2[c]	6,694	107.1	10.2	DSC-x ray	
Octamethylene oxide $[(\mathrm{CH_2})_8-\mathrm{O}]_n$		356.2	32,401	253.1	91.0	DSC-density	[146]
3-Tertbutyl oxetane  $[\mathrm{O-CH_2-\overset{H}{\underset{CH_3-\underset{CH_3}{C}-CH_3}{C}}-CH_2}]_n$		350.2	5,021	45.2	14.3	DSC-x ray	[147]
1,4 Phenylene ether 		535.2	7,824	85.0	14.6	DSC-x ray	[148]
2,6 diphenyl 1,4 phenylene ether 		757.2	12,201	50.0	16.1	DSC-x ray	[149]
Ethylene sulfide $[\mathrm{CH_2-CH_2-S}]_n$		489.2	14,226	237.1	29.1	(T_m-mol. wt)[d]	[150]
3,3'-Dimethyl thietane  $\left[\mathrm{S-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2}\right]_n$		286.2	5,442	56.7	19.0	DSC-x ray	[151]
p-Phenylene sulfide 		621.7	12,092	112.0	19.4	DSC-x ray	[152–154]
Ethylene sebacate  $[\mathrm{O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_8-\overset{O}{\overset{\Vert}{C}}-O-(CH_2)_2}]_n$		356.2	36,765	161.2	103.2	DSC-density	[155]

TABLE 11.3. *Continued.*

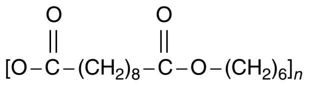
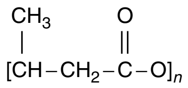
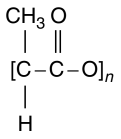
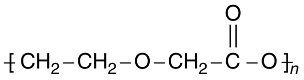
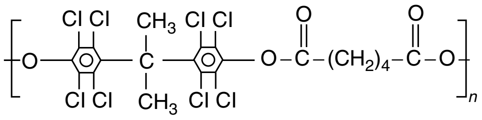
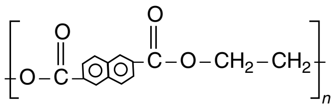
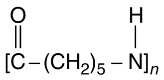
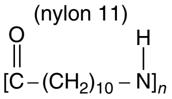
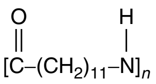
Polymer	T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	Method	References
Hexamethylene sebacate  $[O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_8-\overset{O}{\overset{\Vert}{C}}-O-(CH_2)_6]_n$	344.2	38,456	133.8	111.8	(T_m-mol. wt)[d]	[156]
3-Hydroxy butyrate  $[\overset{CH_3}{\overset{\vert}{C}H}-CH_2-\overset{O}{\overset{\Vert}{C}}-O]_n$	476.2[e]	13,286[f]	154.5	27.9	DSC-x ray density	[157–159]
L-Lactic acid  $[\underset{H}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-\overset{O}{\overset{\Vert}{C}}-O]_n$	480.2	5,858	81.2	12.2	DSC-x ray	[160,161]
	457	14,580[g]	202.5	31.9	DSC-Mn	[162]
P-Dioxanone  $[CH_2-CH_2-O-CH_2-\overset{O}{\overset{\Vert}{C}}-O]_n$	387	10,496	102.9	27.1	DSC-additive group	[163]
Tetrachloro bis phenol-A-adipate 	556.2	33,890	55.2	60.9	DSC-x ray	[164]
Ethylene 2,6-naphthalene dicarboxylate 	610.2	24,987	93.9	40.9	DSC-x ray density	[165]
Caprolactam (nylon 6) γ α  $[\overset{O}{\overset{\Vert}{C}}-(CH_2)_5-\overset{H}{\overset{\vert}{N}}]_n$	481 ± 2 551 ± 6	30,271[h]	267.9	56.8	DSC-specific volume	[166,167]
Undecane amide (nylon 11)  $[\overset{O}{\overset{\Vert}{C}}-(CH_2)_{10}-\overset{H}{\overset{\vert}{N}}]_n$	514.2	35,982	196.6	70.0	DSC-density	[168,169]
Laurolactam (nylon 12)  $[\overset{O}{\overset{\Vert}{C}}-(CH_2)_{11}-\overset{H}{\overset{\vert}{N}}]_n$	500	48,403	245.7	96.8	DSC-additive heat capacities	[170]

TABLE 11.3. *Continued.*

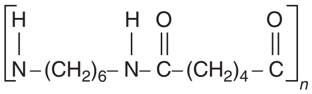
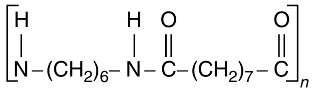
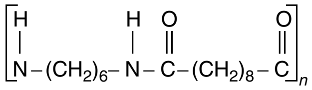
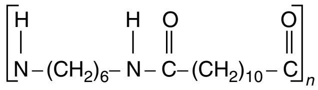
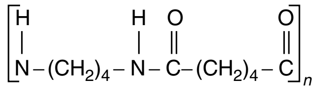
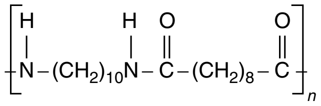
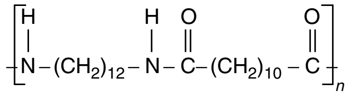
Polymer	T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	Method	References
Hexamethylene adipamide (nylon 6, 6)  $\left[\overset{\overset{H}{\mid}}{N}-(CH_2)_6-\overset{\overset{H}{\mid}}{N}-\overset{\overset{O}{\parallel}}{C}-(CH_2)_4-\overset{\overset{O}{\parallel}}{C}\right]_n$	545.7	42,556	188.3	78	DSC-specific volume	[171,172]
Hexamethylene azelamide (nylon 6, 9)  $\left[\overset{\overset{H}{\mid}}{N}-(CH_2)_6-\overset{\overset{H}{\mid}}{N}-\overset{\overset{O}{\parallel}}{C}-(CH_2)_7-\overset{\overset{O}{\parallel}}{C}\right]_n$	500	69,010	257.5	138	DSC-additive heat capacities	[170]
Hexamethylene sebacamide (nylon 6, 10)  $\left[\overset{\overset{H}{\mid}}{N}-(CH_2)_6-\overset{\overset{H}{\mid}}{N}-\overset{\overset{O}{\parallel}}{C}-(CH_2)_8-\overset{\overset{O}{\parallel}}{C}\right]_n$	511	59,699	211.7	116.8	DSC-specific volume	[173,174]
Hexamethylene decaneamide (nylon 6, 12)  $\left[\overset{\overset{H}{\mid}}{N}-(CH_2)_6-\overset{\overset{H}{\mid}}{N}-\overset{\overset{O}{\parallel}}{C}-(CH_2)_{10}-\overset{\overset{O}{\parallel}}{C}\right]_n$	520	80,100	258.4	154	DSC-additive heat capacities	[170]
Tetramethylene adipamide (nylon 4, 6)  $\left[\overset{\overset{H}{\mid}}{N}-(CH_2)_4-\overset{\overset{H}{\mid}}{N}-\overset{\overset{O}{\parallel}}{C}-(CH_2)_4-\overset{\overset{O}{\parallel}}{C}\right]_n$	623.2	41,618	210.2	66.8	DSC-x ray	[175]
Decamethylene sebacamide (nylon 10, 10)  $\left[\overset{\overset{H}{\mid}}{N}-(CH_2)_{10}\overset{\overset{H}{\mid}}{N}-\overset{\overset{O}{\parallel}}{C}-(CH_2)_8-\overset{\overset{O}{\parallel}}{C}\right]_n$	487	82,472	244.0	169.3	DSC-specific volume	[176]
Dodecamethylene decaneamide (nylon 12,12)  $\left[\overset{\overset{H}{\mid}}{N}-(CH_2)_{12}-\overset{\overset{H}{\mid}}{N}-\overset{\overset{O}{\parallel}}{C}-(CH_2)_{10}-\overset{\overset{O}{\parallel}}{C}\right]_n$	477.7	115,127	292.2	241.0	DSC-specific volume	[177]
Imide[i]						
n=1	613.2	72,467	143.8	118.2	DSC-x ray	[178]
n=2	577.2	80,165	146.3	138.9	DSC-x ray	[178]
n=3	541.2	87,956	148.6	162.5	DSC-x ray	[178]

TABLE 11.3. *Continued.*

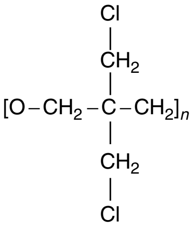
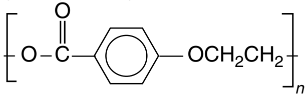
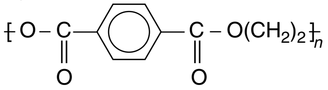
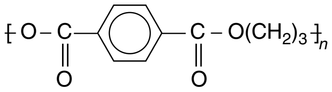
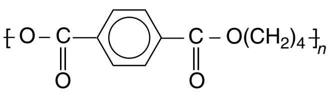
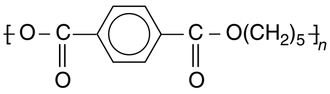
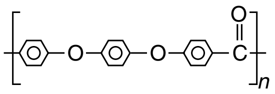
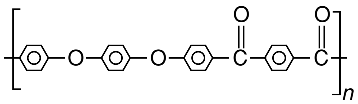
Polymer	T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	Method	References
3,3' bischloro Methyl Oxacyclobutane  $[O-CH_2-\underset{\underset{\underset{\text{Cl}}{\vert}}{CH_2}}{\overset{\overset{\overset{\text{Cl}}{\vert}}{CH_2}}{\overset{\vert}{\underset{\vert}{C}}}}-CH_2]_n$	476.2	19,456	126.3	40.9	DSC-density	[179]
2-Hydroxy ethoxy benzoate 	505	15,088 ± 656	92 ± 4	29.9	DSC-x ray	[180]
Ethylene terephthalate 	613	25,920	135	42.3	DSC-density-x-ray	[181]
Trimethylene terephthalate 	525	28,800	139.8	54.9	DSC-x ray	[182,183]
Butylene terephthalate 	509.2	31,240	142	61.4	DSC-x ray	[184]
Pentamethylene terephthalate 	422.6	39,944	170.7	94.5	DSC-x ray	[185]
Aryl-ether–ether ketone 	668.2	38,258	132.8	57.3	DSC-density-x ray	[181,186]
Aryl-ether–ether ketone–ketone 	660	48,608	124	73.6	DSC-x ray	[187,188]

TABLE 11.3. *Continued.*

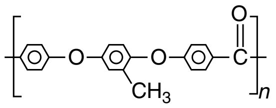
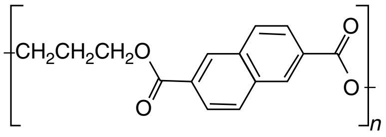
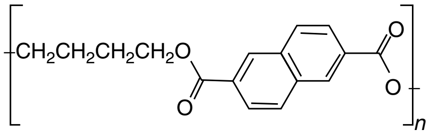
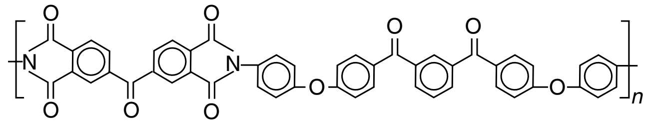
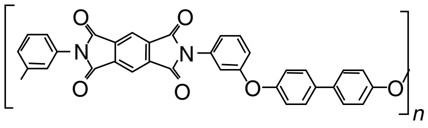
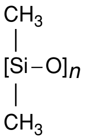
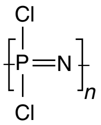
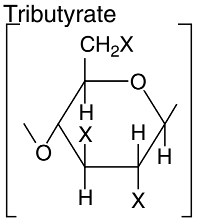
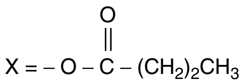
Polymer	T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	Method	References
Methyl-substituted aryl-ether–ether ketone 	> 513.2	22,348	74.0	< 43.5	DSC-x ray	[189]
Trimethylene 2,6 naphthalate β α 	496 470	26,051	101.8	52.5	DSC-x ray	[190]
Butylene 2,6 naphthalate 	567	32,940	122	58.1	DSC-x ray	[191,192]
LARC-CPI 	663.2	100,294	127.6	151.2	DSC-x ray	[193]
New-TPI 	679.2	63,800	116	93.9	DSC-density	[194]
Dimethylsiloxane [j]  $\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n$	235.2	4,619[k]	62.4	19.6	Calorimetry-DSC	[195–197]
Dichlorophosphazene  $\left[\underset{Cl}{\overset{Cl}{P}}=N\right]_n$	306.2	8,380	71.0	27.4	DSC-x ray	[198]
Urethane[l]						
$n = 2$	440.2	41,547	180.6	94.4	DSC-x ray	[111]
$n = 3$	434.2	41,840	171.5	96.4	DSC-x ray	[111]
$n = 4$	453.2	48,534	188.1	107.1	DSC-x ray	[111]
$n = 5$	428.2	41,463	152.4	96.8	DSC-x ray	[111]
$n = 6$	438.2	51,882	181.4	118.4	DSC-x ray	[111]
$n = 7$	419.2	58,534	161.8	115.8	DSC-x ray	[111]

TABLE 11.3. *Continued.*

Polymer	T_m^0 (K)	ΔH_u (J/mol)	$\Delta H_u/M_0$ (J/g)	ΔS_u (J/K mol)	Method	References
$n = 8$	430.2	55,229	175.9	128.4	DSC-x ray	[111]
$n = 9$	420.2	52,300	159.5	124.5	DSC-x ray	[111]
$n = 10$	427.2	56,484	165.2	132.2	DSC-x ray	[111]
Urethane[m]						
$n = 2$	510.2	48,534	155.6	95.1	DSC-x ray	[111]
$n = 3$	500.2	47,279	145.0	94.5	DSC-x ray	[111]
$n = 4$	505.2	52,718	155.1	104.4	DSC-x ray	[111]
$n = 5$	462.2	51,045	144.2	110.4	DSC-x ray	[111]
$n = 6$	470.2	51,882	141.0	110.3	DSC-x ray	[111]
$n = 7$	464.2	50,626	132.5	109.1	DSC-x ray	[111]
$n = 8$	469.2	59,413	150.0	126.6	DSC-x ray	[111]
$n = 9$	463.2	58,576	142.9	126.4	DSC-x ray	[111]
$n = 10$	465.2	69,036	162.8	148.4	DSC-x ray	[111]
Cellulose Tributyrate	465	12,851	34.5	27.6	DSC-heat capacity	[199]





$X = -O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_2CH_3$

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[a] For a sample 94% syndiotactic content (diads based analysis by ^{13}C NMR), $T_m = 160$ °C, $\Delta H_u = 1920$ cal/mol. Data from S. & D. Cheng et al [205].

[b] For 64% syndiotactic polymer.

[c] Calculated in Reference 145 for 100% syndiotactic material by modifying the data of D. Koekott, [206].

[d] Samples do not have most probable molecular weight distribution.

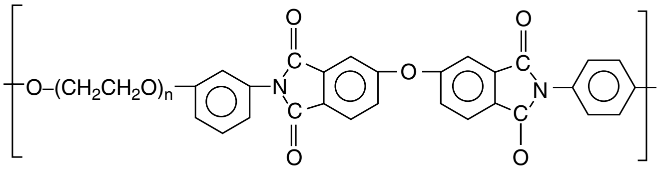
[e] Cited R. P. Pearce and R. H. Marchessault, [207].

[f] Average of literature values.

[g] The observed heat of fusion of a highly regular poly L-lactide (>99.9%) is 98.4 J/g (see E.J. Munson et al. [208]).

[h] Taking $V_c{}^\alpha = 0.814$ cm^3/g from D. R. Holmes, et al. [209]. If all literature values for $V_c{}^\alpha$ are considered, ΔH_u ranges from 6215 cal/mol to 7250 cal/mol (26000 J/mol–30334 J/mol).

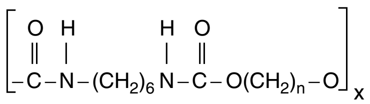
[i]



[j] Higher alkyl siloxanes are not included due to their liquid-crystal characteristics

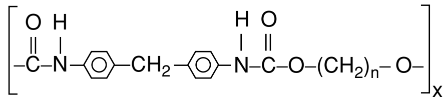
[k] Average value.

[l]



$\left[-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_6\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-O(CH_2)_n-O\right]_x$

[m]



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CHAPTER 12

The Glass Temperature

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12.1 INTRODUCTION

The equilibrium liquid state certainly is not as well understood as the crystalline state, and glasses which are nonequilibrium liquids are less well understood, but their unusual time-dependent properties have fascinated investigators for many years. There is no intention here to completely cover all the known properties of glasses or the ground covered by the numerous exhaustive reviews [1–10] and pertinent monographs, [11–34] but an attempt will be made to direct the reader to many of the significant observations, papers, theories, monographs, and review articles dealing with many of their interesting facets.

Many of the kinetic phenomena exhibited by glasses were described in the early monograph by G. O. Jones [12]. The so-called Kauzman Paradox or "catastrophe" drew attention to the precipitous decrease of the entropy of disordered glasses toward values which were less than that of the ordered crystalline state [1]. A second order thermodynamic transition appeared to be necessary to avert the "catastrophe." Kinetic phenomena were encountered that led to decades of controversy about the nature of the glass "transition" temperature. Nearly all of the manifestations of glassy behavior have been determined to be kinetic in nature. In fact, it will be seen below that glass formation and the associated time and rate dependent changes in properties are examples of volume viscoelasticity.

Any liquid which does not crystallize upon cooling is destined to become a glass. When a liquid is cooled continuously, the rate of diffusion decreases while the viscosity increases, reflecting a diminishing molecular mobility.

The enhanced sluggishness of molecular response is due to the increasing molecular crowding and the attendant cooperativity of the molecular motions. At relatively high temperatures the mobility of the molecules of a liquid is great enough to maintain an equilibrium density, reflecting the more efficient packing that occurs during cooling. Eventually the mobility decreases to the point where the molecular rearrangements, necessary to alter the liquid structure, cannot keep up with a given fixed rate of cooling. Subsequently the liquid's specific volume becomes increasingly greater than its equilibrium value at each lower temperature. At the same time, the liquid exhibits glassy properties, an extremely high viscosity, greater than 10^{12} poise (10^{11} P sec), and a low compliance, about $10^{-10}\mathrm{cm}^2/\mathrm{dyne}$ ($10^{-9}\mathrm{Pa}^{-1}$). Most significantly, at temperatures near the departure from an equilibrium density during cooling, any and all liquids are measurably, if not markedly, viscoelastic. The departure from equilibrium during cooling signals the glass temperature T_g. Note, we do not call it a glass "transition" temperature since no transition occurs in the liquid. It is still a liquid below T_g, albeit with an enormous, but measurable, viscosity. For T_g to be a material characterizing function, it must be defined in a cooling experiment, whether it be a quench or a constant rate of cooling, so that it emanates from a unique equilibrium condition. When determined from a cooling experiment, T_g is found to be a unique function of the cooling rate, q. This is because it is a manifestation of viscoelastic behavior. Viscoelastic behavior is a time-, rate-, and frequency-dependent behavior. T_g reflects a characteristic molecular mobility, virtually by the definition given above. When the rate of molecular rearrangement cannot keep up with the rate of cooling, equilibrium is lost.

While polymer glasses are of principal interest here, it must be kept in mind that qualitatively all glasses behave similarly whether they are organic, inorganic, or metallic.

The glass temperature T_g of a given polymer depends on the rate of cooling, q, the pressure, P, the number average molecular weight, M_n, and if in solution, its volume fraction, ϕ_2. In short, $T_g(q,P,M_n,\phi_2)$. For a polycrystalline polymer, changes of T_g occur with a variation of the degree of crystallinity and the nature of the morphology of the material. The effect of each of these experimental variables will be discussed below with minimal reference to model-dependent analyses. The emphasis will be on the phenomenology that has been observed. The free volume [36–38], entropy [39–42], coupling [43], and fictive temperature [44–46] models have all been used in analyzing the phenomena with conflicting results in many cases. In addition to the original presentations, the models have been outlined in the many review papers referred to above.

12.2 DEPENDENCE OF T_g ON THE RATE OF COOLING q

Although the rate dependence of T_g is constantly acknowledged, its direct observation has rarely been systematically observed. Fig. 12.1 shows the dilatometric results of Greiner and Schwarzl [5b] on a polystyrene covering 3 1/2 decades of cooling rate, q. The T_g, determined from the intersection of the equilibrium line with the varying glassy lines varies from 96 °C at the highest q of 2.0 °C/min down to 86 °C at the lowest rate of cooling employed which was 7×10^{-4} °C/min. Illustrative values of the thermal contraction coefficient, α, curves calculated from the curves of Fig. 12.1 are seen in Fig. 12.2

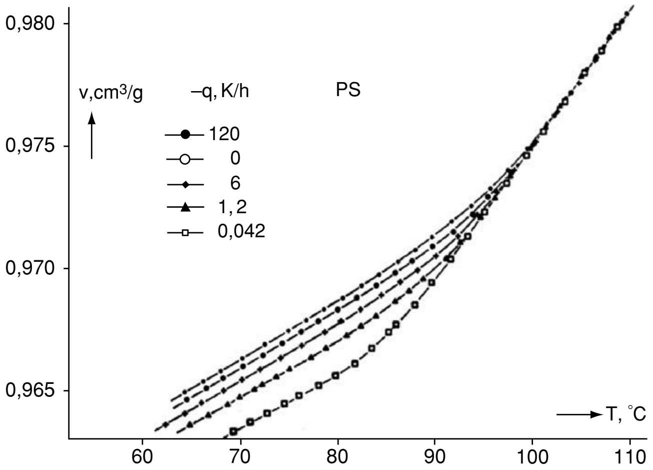

FIGURE 12.1. Volume-temperature curves of PS extending through the glass temperature under various rates of cooling, as indicated. (From Greiner and Schwarzl, by permission [5b].)

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

A slightly lower glassy α is found with decreasing q but the temperature span between the limiting equilibrium and glassy lines is found to significantly diminish with decreas-

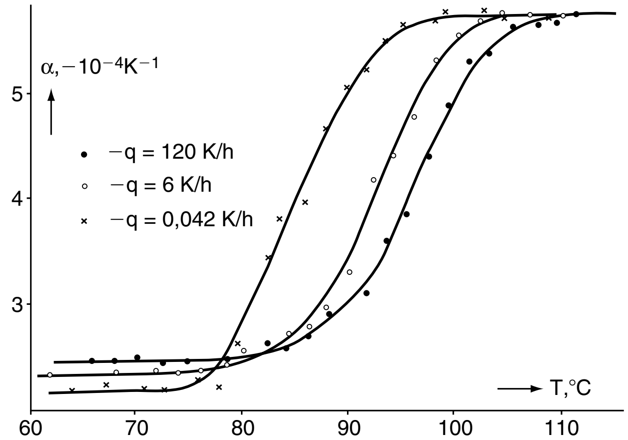

FIGURE 12.2 Thermal expansion coefficient, calculated from the data of Fig. 12.1, for PS under various rates of cooling. (From Greiner and Schwarzl, by permission [5b].)

ing q. This observation is in accord with that reported by Moynihan *et al.* [46,47] on several inorganic glasses. Using the Macedo-Litovitz hybrid equation, Rekhson and Scherer rationalized this broadening [48]. Bero and Plazek observed the same broadening on a fully cured epoxy resin which is a viscoelastic solid since it is comprised of a molecular network which precludes flow [49]. This is in contrast with the polystyrene of Greiner and Schwarzl which is a viscoelastic liquid, because it is constituted of linear molecules and it does flow. The specific volume-temperature cooling curves for the epoxy resin are shown in Fig. 12.3. The extent of the temperature range between equilibrium liquid-like and glassy contractions is shown in Fig. 12.4. The rate dependence of T_g is also presented by Greiner and Schwarzl [5b] for polymethyl-methacrylate, PMMA, polyvinylchloride, PVC, and polycarbonate, PC.

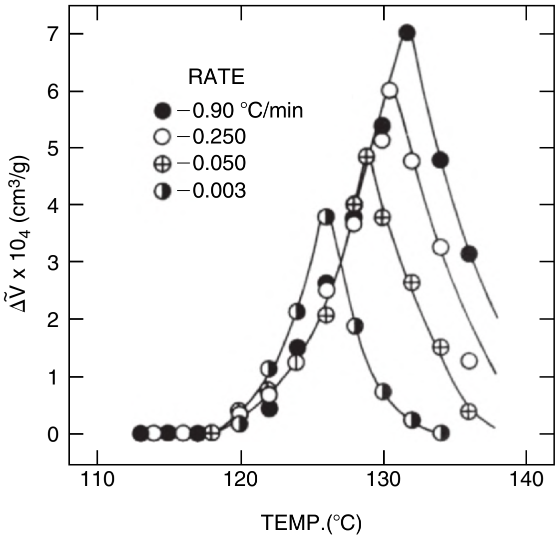

FIGURE 12.4. Deviation of measured specific volume points from the equilibrium and glass lines of Fig. 12.1 plotted as a function of temperature, showing the extent of the transformation range and its change with the rate of cooling.

12.3 VOLUME AND ENTHALPY VARIATIONS AND THE FICTIVE TEMPERATURE T_f

With great care and effort, Richardson and Savill [50] have succeeded in measuring the T_g of polystyrene in cooling as a function of rate in a differential scanning calorimeter, DSC, and have compared the results obtained dilatometrically. Their study covered the molecular weight range from 580 up to 2.0×10^6. The checks agreed within about 1 °C. The difficulty of the study was made clear. Most investigators do not have the opportunity to exercise the effort needed to obtain accurate T_gs from DSC measurements. Most DSC measurements are carried out as heating scans [51] which result in yielding something close to the fictive temperature T_f of Tool [44]. Investigators of inorganic glasses have long appreciated the distinction between T_g and T_f while polymer scientists in general are not aware of or ignore it. Figure 12.5 shows the glass temperature as the intersection point of the volume, v, or enthalpy, H, temperature lines of the equilibrium (or metastable equilibrium) liquid and the glass

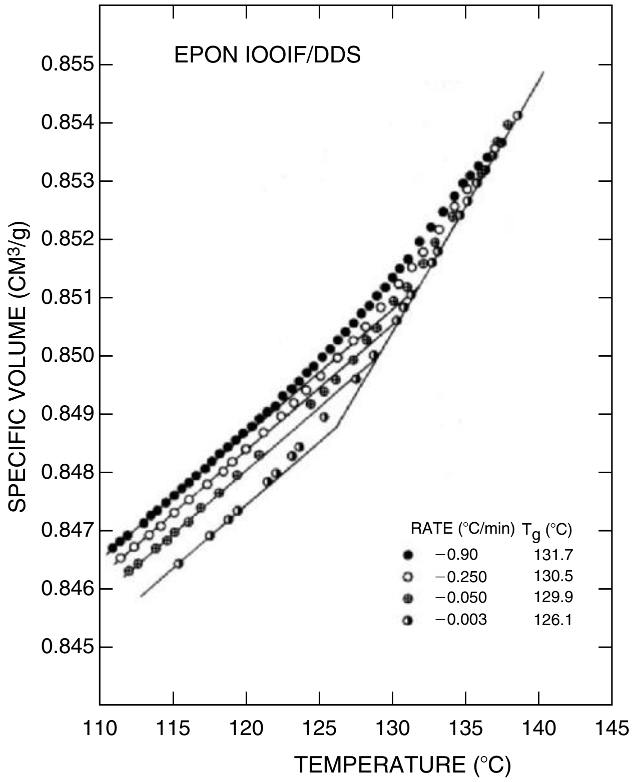

FIGURE 12.3 The specific volume $\bar{V}$(cm^3/g) of EPON 1001F fully cured with a stoichiometric amount of 4,4′–diamino diphenyl sulfone (DDS) shown as a function of temperature at four different rates of cooling 0.90, 0.25, 0.050, and 0.003 °C/min. Glass temperatures identified by the intersection point of the equilibrium and glass lines are listed.

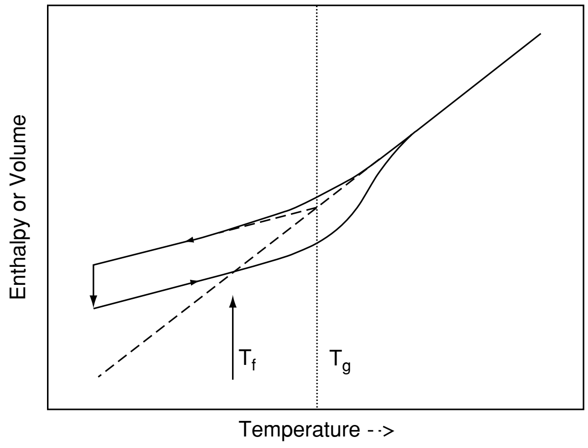

FIGURE 12.5. Schematic plot of the enthalpy or the volume as a function of temperature for glass-forming liquids. The fictive, T_f and glass, T_g, temperatures are indicated.

obtained in cooling. The intersection point is usually chosen as T_g. [3,23,34,49,50]. For a given substance this definition is a material characterizing function of the rate of cooling since it is the measure of the departure from a unique equilibrium. Figure 12.5 also shows how T_f which identifies the state of a specimen. T_f is the result of a simple geometric operation. The specific volume or enthalpy of a specimen must be known and a line having the slope of a glass line is drawn through it. The intersection of this glass line with the equilibrium line is T_f. Note that T_f is not a function of the heating rate. A fictive temperature measured by heating at the same rate as that of an immediately preceding cooling from above T_g approximates T_g and is called $T_{f,g}$.

In an actual heating curve, if it is slow enough, an appreciable spontaneous contraction or decrease in H can occur during the heating, which would yield an intersection point slightly below T_f. For equal cooling and heating rates, T_f is measurably lower than T_g. Without corrections for thermal lags, actual scans often show indicated temperatures where $T_f > T_g$. This is a clear indication of the error incurred. DSC measurements in the past have almost universally been carried out in the heating mode [51,52] because thermal lags can be corrected with melting point standards. Since freezing is a nucleated process, super cooling always occurs which prevents an accurate calibration during cooling. However, it has been observed that some liquid-crystal meso-phase transitions do not show super-cooling, thus making accurate calibrations during cooling a convenient possibility [53].

In addition, it should be noted that, while it is generally recognized that the dynamic loss tangent peaks are 15°–20 °C higher than $T_g(q = 1\ °/\text{min})$, [54,55a] the temperatures of these maxima continue to be reported as T_gs. Twenty degrees above T_g, the rate of molecular motion in many polymers is about a million times greater than that found at T_g. Therefore, predictions for rate processes based on such incorrect T_gs can be in error by six orders of magnitude. The uncertainty of many of the reported values, therefore, should not be taken lightly for practical purposes. In addition, serious differences of opinion exist concerning the molecular mobility at T_g. Such differences cannot be resolved until a better collection of T_gs is available. Even then, different analyses and models appear to lead to differing conclusions. Some discussion of these will be found below.

12.4 ISOTHERMAL CONTRACTION NEAR AND BELOW T_g

The kinetics of spontaneous time-dependent contraction of a glass following a quench from equilibrium above T_g is frequently studied. This kind of measurement is one of the experiments carried out by Kovacs [3] in his classical studies on the time-dependent variation of the specific volume of glasses. The most common study involves quenching from a fixed temperature above T_g down to different temperatures below T_g. At each chosen lower temperature, the spontaneous contraction is monitored as a function of time. The results of such quenches and annealing are illustrated in Fig. 12.6. A commercial polystyrene (Dylene 8; Arco Polymers, $M_n = 0.93 \times 10^5$, $M_w = 2.2 \times 10^5$) was studied [55b]. The fractional excess (above equilibrium) specific volume $(v(t)/v_{\text{inf}}) - 1$ is plotted as a function of the logarithmic annealing or aging time. $\bar{v}(t)$ is the time-dependent specific volume and $\bar{v}_{\text{inf}} = v(\infty)$ is the equilibrium value for the temperature at which the densification is occurring.

Measurements such as these can be used to define a T_g which would be a material-characterizing function of the time of annealing (or physical aging [31]). In spite of the acknowledged intrinsic nonlinearity of the contractions linear parallel segments of the response are observed which can be easily extrapolated to zero excess specific volume [3]. In Fig. 12.6, lines tangent at the points of inflection can be extrapolated to zero. This intersection with the logarithmic time axis yields the time-temperature relationship for this T_g. T_g would then be a function of the aging time. The advantage of this kind of T_g is the greater resolution that is possible relative to that available from a cooling curve. The intersection point of the equilibrium and glass lines yields a T_g value which is probably valid to within a degree. The rate of time-scale shifts with temperature in the quench experiments is equivalent to that of viscoelastic processes [49], which are large. An order of magnitude change in rate of transport processes near T_g requires a temperature change from 1.5° to 6 °C depending on the material.

12.5 THE CONCENTRATION DEPENDENCE OF THE GLASS TEMPERATURE, $T_g(\phi_2)$

Usually a diluent decreases the T_g of a polymer severely. Early measurements [56] indicated that solvents with lower T_gs of their own decreased the T_g of a polymer to a greater

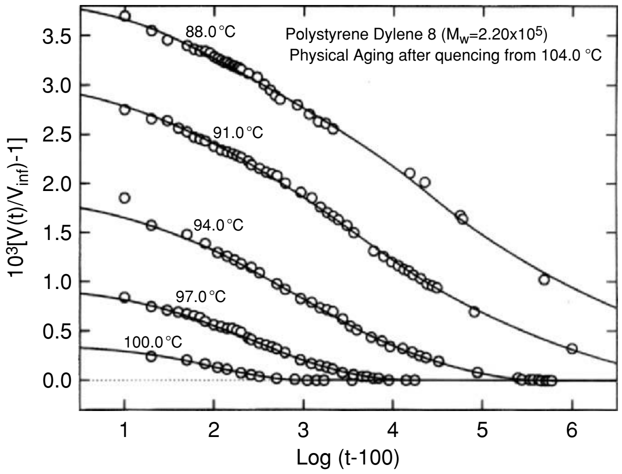

FIGURE 12.6. The fractional excess specific volume $[\bar{v}(t) - \bar{v}(\infty)]/\bar{v}(\infty)$ for a polystyrene at different temperatures shown as a function of the logarithmic time after quenching from $T = 104.0$ °C. (100 sec is subtracted as the approximate time to reach the temperature indicated.)

extent. This can be seen in Fig. 12.7 where the compositional variation of the T_g of polystyrene in a number of solvents is shown. Solutions of a polymer in solvents with T_gs higher than its own will usually have a greater value than that of the neat polymer [57].

The impression of a simple relationship given by Fig. 12.7 is misleading since a continuously decreasing negative slope is indicated. For polystyrene, PS, solutions in toluene [58] and *m*-tricresyl phosphate [59,60] this has been shown not to be the case. In 1964 Braun and Kovacs reported results on the polystyrene/toluene system which showed two descending curves which came together in a cusp [58] (see Fig. 12.8). The results were rationalized by fitting the Kelley–Bueche equation [61],

$$T_g = \frac{\phi_2 \alpha_2 T_{g2} + \phi_1 \alpha_1 T_{g1}}{\phi_2 \alpha_2 + \phi_1 \alpha_1},$$

to the data above the temperature of the cusp, T_c. This equation was derived assuming that the free volumes of the polymer and the solvent were additive and that T_g is an iso-free volume temperature.[a] ϕ is the volume faction; α is the cubical thermal expansion coefficient of the fractional free volume, $f = v_f/v$; subscripts 1 and 2 represent the solvent and polymer, respectively. v_f is the free volume and v the measured volume. Below T_c, Braun and Kovacs used the equation [58],

$$T_g = T_{g1} + \frac{f_{g2}}{\alpha_1}\left(\frac{\phi_2}{\phi_1}\right),$$

where f_{g2} is the fractional free volume of the polymer at its T_g.

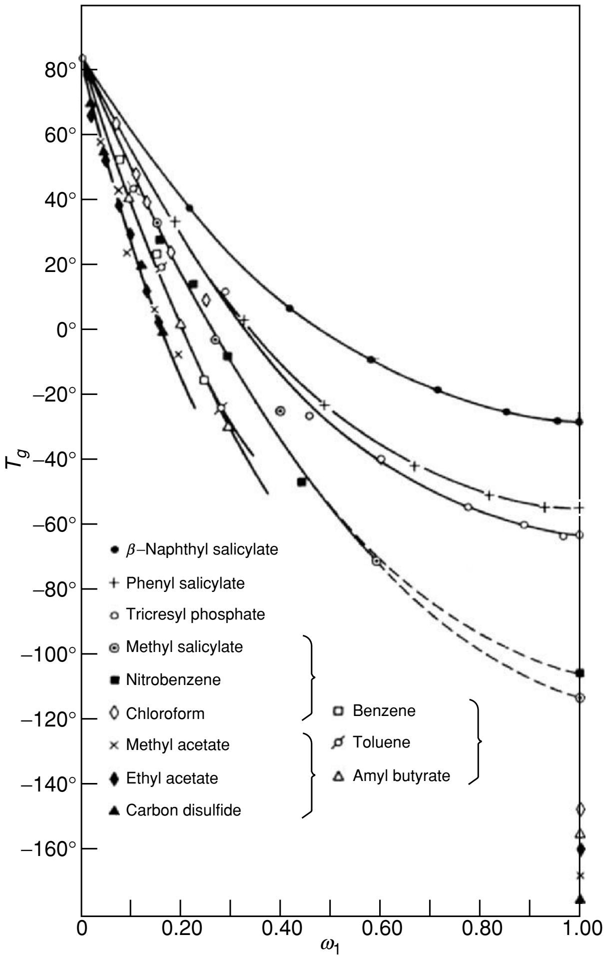

FIGURE 12.7. The compositional variation of the glass temperature T_g of polystyrene in 12 different solvents. W_1 is the weight fraction of solvent. (From Jenckel and Heusch, by permission, [56].)

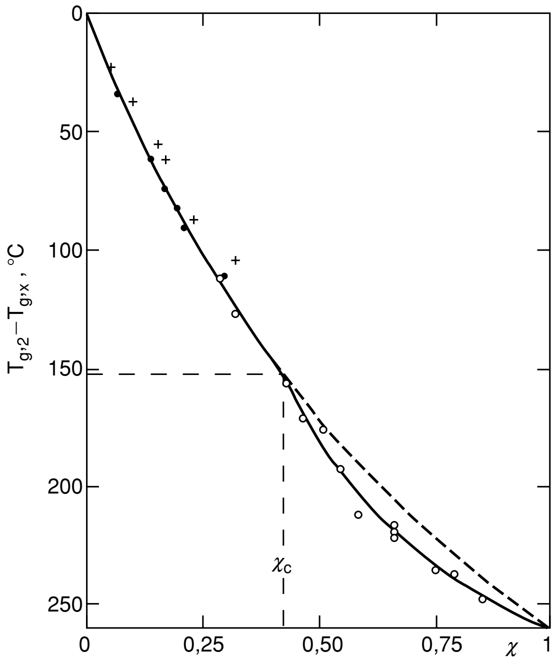

FIGURE 12.8. The depression of T_g of a polystyrene by dissolution in toluene. x is the weight fraction of toluene. Filled circles represent dilatometric determinations and unfilled circles were obtained by means of differential thermal analysis, DTA. The crosses represent the results of Jenckel and Heusch [56]. (From Braun and Kovacs by permission, [58].)

Pezzin *et al.* found the same kind of behavior exhibited by polyvinyl chloride PVC in two different plasticizers, dibutyl phthalate, DBP, and dicyclohexylphthalate, DCHP [62,63]. The same two equations provided excellent fits to the PVC solution data (see Fig. 12.9). For polystyrene dissolved in *m*-tricresyl phosphate, TCP, additional factors were noted.

Differential thermal analysis measurements indicated double T_gs for solutions with lower polymer concentrations beyond the depicted cusp in Fig. 12.10 [59]. Creep recovery measurements on this system showed that the solvent molecules in the solutions have higher mobilities than the polymer chain segments. A lower temperature and greater crowding is therefore necessary to force the solvent molecules from an equilibrium response. Therefore, it was

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[a] Other treatments are now available [137,138].

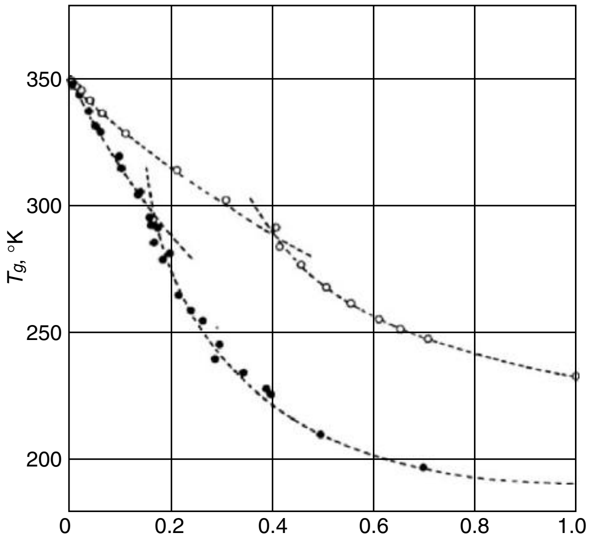


FIGURE 12.9. The T_g of a polyvinlychloride as a function of diluent concentration in two different solvents. Open circles-dicyclohexylplthate and filled circles-dibutylphthalate. W_1 is the weight fraction of diluent. (From Pezzin, Omacini, and Zilio-Grandi by permission [62].)

concluded that the higher T_gs reflected those of the polymer chain segments in a solvent-altered environment and the lower T_gs reflected the solvents mobility in the presence of the polymer chain segments [60]. For different bulk polymers, T_g local mode or short-range molecular motions are found within experimental uncertainty at the same place on the time or frequency scales of response [64–66]. For the solutions of PS in TCP, the T_gs from the lower "altered solvent" curve were necessary to bring the solvent contribution to the recoverable compliance into correspondence with other solutions. The higher T_gs were also needed to bring the contribution from polymer local modes into correspondence [60]. The mobility of solvent molecules and how it is influenced by the presence of polymer solute molecules has been investigated and documented by measurements of pulsed field-gradient NMR [67], oscillatory electric bire-fringence [68,69], ^{13}C NMR relaxation [70], photon correlation spectroscopy [71–73a], and dielectric dispersion [73b]. Solvent molecules generally have a decreased mobility in the presence of polymer molecules with greater T_gs.

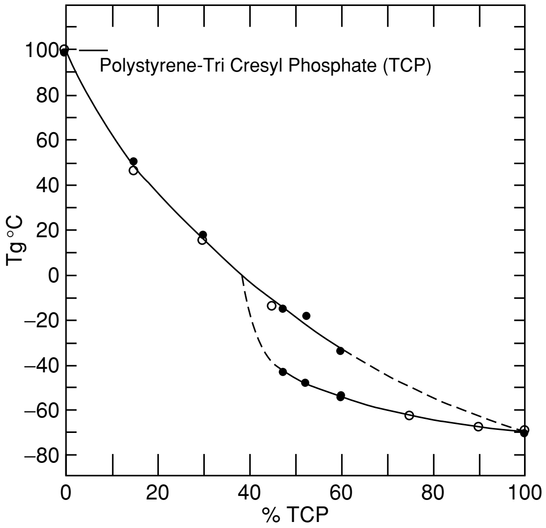


FIGURE 12.10. The T_gs of a polystyrene as a function of the weight percent of the solvent *m*-tricresyl phosphate.

In most cases, free volume concepts at least qualitatively predict the shift of solvent and polymer chain segment mobilities towards one another. The most frequently encountered case, where a polymer with a higher T_g than that of the solvent, brings to the solution a smaller contribution of free volume which decreases the solvent's mobility. At the same time the solvent, being far above its T_g, brings a large contribution of free volume to the solution which accelerates polymer segment motions. However, there are solutions where the solvent's mobility is *increased* by the presence of a polymer whose undiluted T_g is higher than that of the solvent. In this case, obviously, free volume concepts are inadequate. In these cases, the coupling model of Ngai has been able to attribute the unexpected solvent acceleration to a "primitive" or uncoupled relaxation time of the polymer which is smaller than that of the solvent [73].

12.6 DEPENDENCE OF T_g ON MOLECULAR WEIGHT AND CROSSLINKING

During the transformation of a monomer into a polymer, many atoms separated by van der Waals distances (~5 Å) participate in the formation of covalent bonds (1–3 Å). Therefore during polymerization, an increase in the macroscopic density ensues, while on the molecular level a decrease in free volume and entropy occurs while the cooperativity of motions increase. Concomitantly the glass temperature can increase by more than 100 °C. Several important adhesive systems are based on this increase. The cyanoacrylate "Super Glue" starts as a monomer with a $T_g < 0$ °C and it polymerizes to a linear soluble polymer with a T_g which is in the neighborhood of 100 °C upon application under anaerobic conditions. For linear polymers the simple equation [74]

$$T_g = T_g(\infty) - K/M_n,$$

which reflects the linear decrease in T_g with the increase in concentration of polymer chain ends does an adequate job of describing most existing data in the literature. Deviations may occur at very low molecular weight. The more elaborate Gibbs-Dimarzio theory [40,41] which concentrates on the conformational entropy can fit data to lower molecular weights.

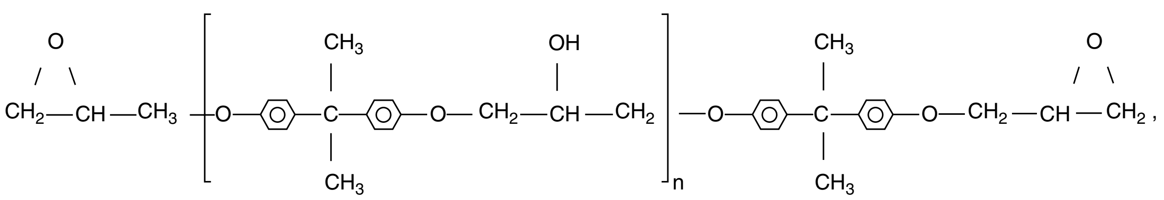
Uncatenated cyclic polydimethylsiloxane, PDMS, shows [75] a slight increase in T_g with decreasing molecular weight. This trend has been rationalized by Gutman and Dimarzio [76]. However, it was observed that the rate of creep at 120 °C for cyclic polystyrene, PS, with $M_w = 1.11 \times 10^4$ in the softening dispersion was the same within experimental uncertainty as a cyclic sample with a $M_w = 1.85 \times 10^5$. This indicates that the T_gs of the two samples had to be within one or two tenths of a degree of one another [77]. For their linear counterparts, the rate of creep of the lower molecular weights is about 100 times faster where the difference in T_gs is about 10 °C.

Crosslinking can increase the T_g above that of the infinite molecular weight linear polymer. This increase can be accounted for with the equation of Fox and Loshaek [74].

$$T_g \simeq T_g(\infty) - K/M_n + K_x \rho,$$

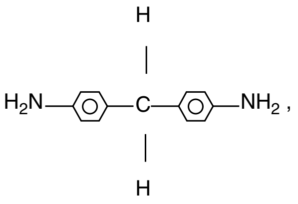
where ρ is the number of crosslinks/gram.

Epoxy resins based on the diglycidyl ether of bisphenol A, DGEBA, are the most widely produced and studied. Their chemical structure is represented by

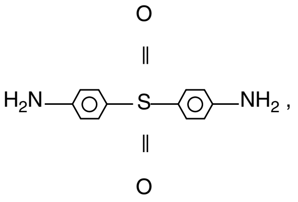


where (n+1) is the average number of repeat units in the epoxy resin molecule. Diamines are most often used in curing these resins. Two examples are:

4,4′-methylene dianiline, MDA,



whose molecular weight is 198.3 g/mol, melting point range 90–93 °C and density, $\rho(23\ ^\circ\mathrm{C}) = 1.16\,\mathrm{g/cm^3}$; and 4,4′ diamino diphenyl sulfone, DDS



MW 248.3 g/mol, Mp 175–178 °C, $\rho(23\ ^\circ\mathrm{C}) = 1.38\,\mathrm{g/cm^3}$.

The effect of the developing network during curing on T_g and the mechanical behavior is illustrated with an epoxy resin Epon[b] 1001F ($n = 2.3$) cured with DDS [81]. The degree of network development was determined by reacting the epoxy resins stoichiometrically with varying ratios of the tetrafunctional crosslinker DDS and the chain-stopping monofunctional methyl aniline. Some properties of the resin at different stages of network development are given in Table 12.1. Fictive temperatures $T_{f,g}$ [82–84] which approximate T_g are presented along with closely related temperatures. The $T_{f,g}$ (10°/min) for the neat unreacted epoxy resin was 31 °C. The short-term (0.1–10^2 sec) behavior at T_g can be described by a viscoelastic recoverable compliance which appears to be the same for all amorphous materials, without secondary viscoelastic dispersions contributions in this timescale range. A recoverable creep compliance is found that can be fitted to the Andrade equation [85–87].

$$J_r(t) = J_g + \beta t^{1/3},$$

where J_g is the glassy compliance which has a value in the neighborhood of $1 \times 10^{-9}\mathrm{Pa}^{-1}(1 \times 10^{-10}\,\mathrm{cm^2/dyne})$; t is the time; and β is a constant which depends on the choice of $T_g(q)$. For the choice of $q = 10\ ^\circ/\mathrm{min}$ it can be seen in Table 12.1 that $\beta(T_{f,g}) \simeq 2 \times 10^{-9}(\mathrm{Pa\ sec}^{1/3})^{-1}$. The first three levels of crosslinking yielded viscoelastic liquids (gel fraction=0) that flow and exhibit steady-state recoverable compliances [18]. A material which was extremely close to the incipient point of gelation was yielded by 45% DDS, where a macroscopic molecular network just appears. At this point the recoverable compliance at long times is immeasurably high; i.e., J_e^0 is operationally infinite. At higher crosslinker ratios, the equilibrium compliance J_e of the molecular network is readily measurable. At 50% crosslinking agent $J_e \simeq 1.0 \times 10^{-4}\mathrm{Pa}^{-1}$ (see Fig. 12.11).

T_gs of fully cured bisphenol-A-based epoxy resins with varying crosslink densities were measured during cooling (5°/min) in a pressurized bellows dilatometer (5 MPa). The crosslinking agent was DDS. The results are shown in Fig. 12.12. The molecular weights per crosslinked unit, M_x, were 420 for Epon 828; 910 for 1001F; 1520 for 1004F; and 2870 for 1007F. The T_gs obtained were 204°, 127°, 112°, and 101 °C, respectively. The loosest network epoxy, 1007F, has the highest specific volumes and the lowest T_g. The volume changes during the curing of Epon 1001F are shown in Figs. 12.13a and 12.13b. In Fig. 12.13a the temperature history of the cure is shown along with the volume changes due to heating, curing, and cooling as a

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[b] Shell Corp. trademark.

TABLE 12.1. *Characterizing parameters.*

DDS	$T_{f,g}$[a]	$T_{0,J}$[b]	$T_{0,a}$[c]	$J_g \times 10^{10}$[d] (cm^2/dyne)	$\beta \times 10^{10}$[d]	ρ(25 °C)[e] (g/cm^3)	log J_e[f] (cm^2/dyne)	M_x[g]
0.25	63.0	64.1	66.3	1.13	1.46	—	−5.53	—
0.35	65.0	66.0	65.0	0.685	1.43	1.188	−4.10	—
0.40	70.6	69.9	66.4	0.65	1.95	—	−3.60	—
0.45	72.5	72.5	69.9	1.45	2.06	1.189	—	—
0.50	73.4	75.4	73.7	1.06	1.19	1.191	−5.00	2.95×10^5
0.60	80.0	84.9	82.0	1.15	2.63	1.194	−5.98	3.10×10^4
0.70	86.4	89.2	88.7	1.24	1.78	1.218	−6.43	1.12×10^4
1.0	132.0	135.6	135.5	1.36	1.95	1.205	−7.04	680

[a] Measured using DSC; all heating rates were 10 °C/min, following cooling at a rate of 10 °C/min (20 °C/min rate of cooling for 0.35 and 0.45 DDS; and 80 °C/min for 1.0 DDS).

[b] Reference temperatures that match the softening region on the creep compliance reduced time scale. Reference system was 0.45 DDS.

[c] Reference temperatures obtained from the temperature shift factor, a_T, analysis (see Fig. 12 in Ref. 81).

[d] Andrade equation parameters for $T = T_{0,J}$.

[e] Density of fully cured samples measured by flotation; followed by pycnometry.

[f] For the viscoelastic liquids J_e is the steady-state recoverable compliance and for the viscoelastic solids, beyond the gel point it is the equilibrium compliance.

[g] Average molecular weight per crosslinked unit calculated from J_e: $M_x = \rho RTJ_e$.

function of time [82]. The volume changes are presented in Fig. 12.13b as a function of temperature, where the initial fictive temperature, T_f, of the reactant mixture and the glass temperature, T_g, of the fully cured resin can be seen.

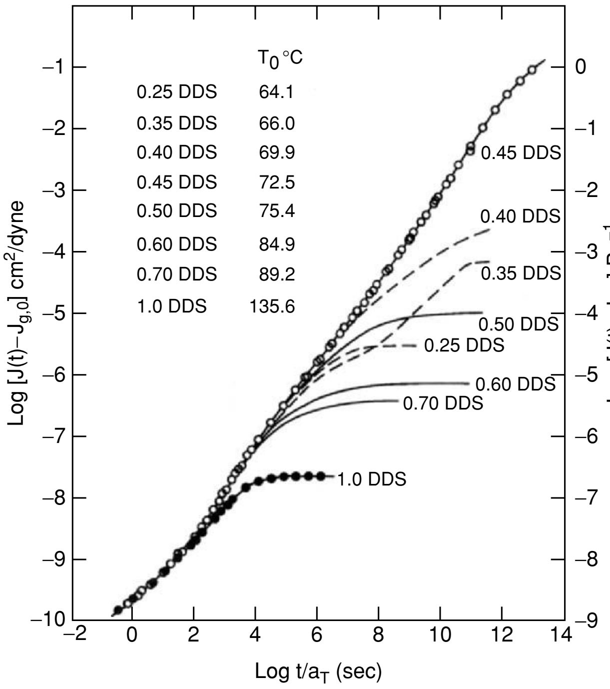


FIGURE 12.11. Comparison of all of the time-dependent reduced compliance $[J(t) - J_{g,0}]$ as logarithmic functions of $\log t/a_T$. Comparison temperatures are indicated above and in Table 12.1. $J_r(t) - J_{g,0}$ is shown for the viscoelastic liquids (dashed lines); i.e., specimens with no gel fraction.

The increase in $T_{f,g}$ during curing has been seen to track the degree of cure. This can be seen in Fig. 12.14 where five variables have been monitored during the curing of Epon 1001F at 142 °C which is about 10 °C above the T_g of the fully cured material. The degree of cure was monitored by the increase in density. The gel fraction became measurable after several hours signaling the presence of a macroscopic

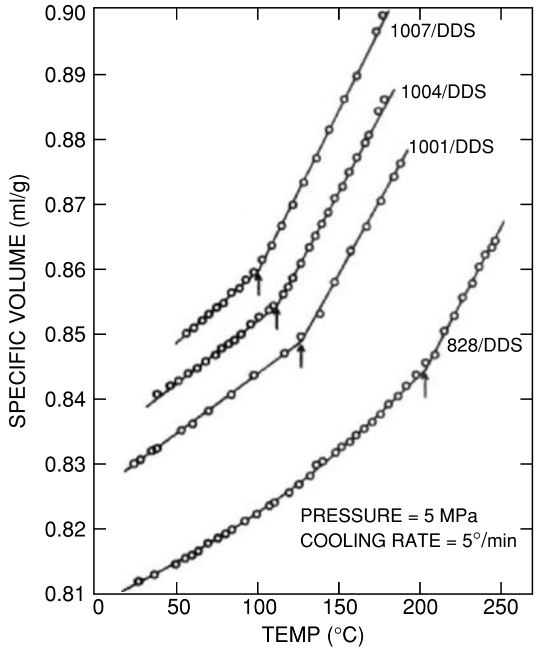


FIGURE 12.12. Specific volume - temperature curves for four epoxy resins with increasing crosslink density from 1007/DPS to 828/DPS. Measurements were made during cooling at 5°/min under a pressure of 5 MPa.

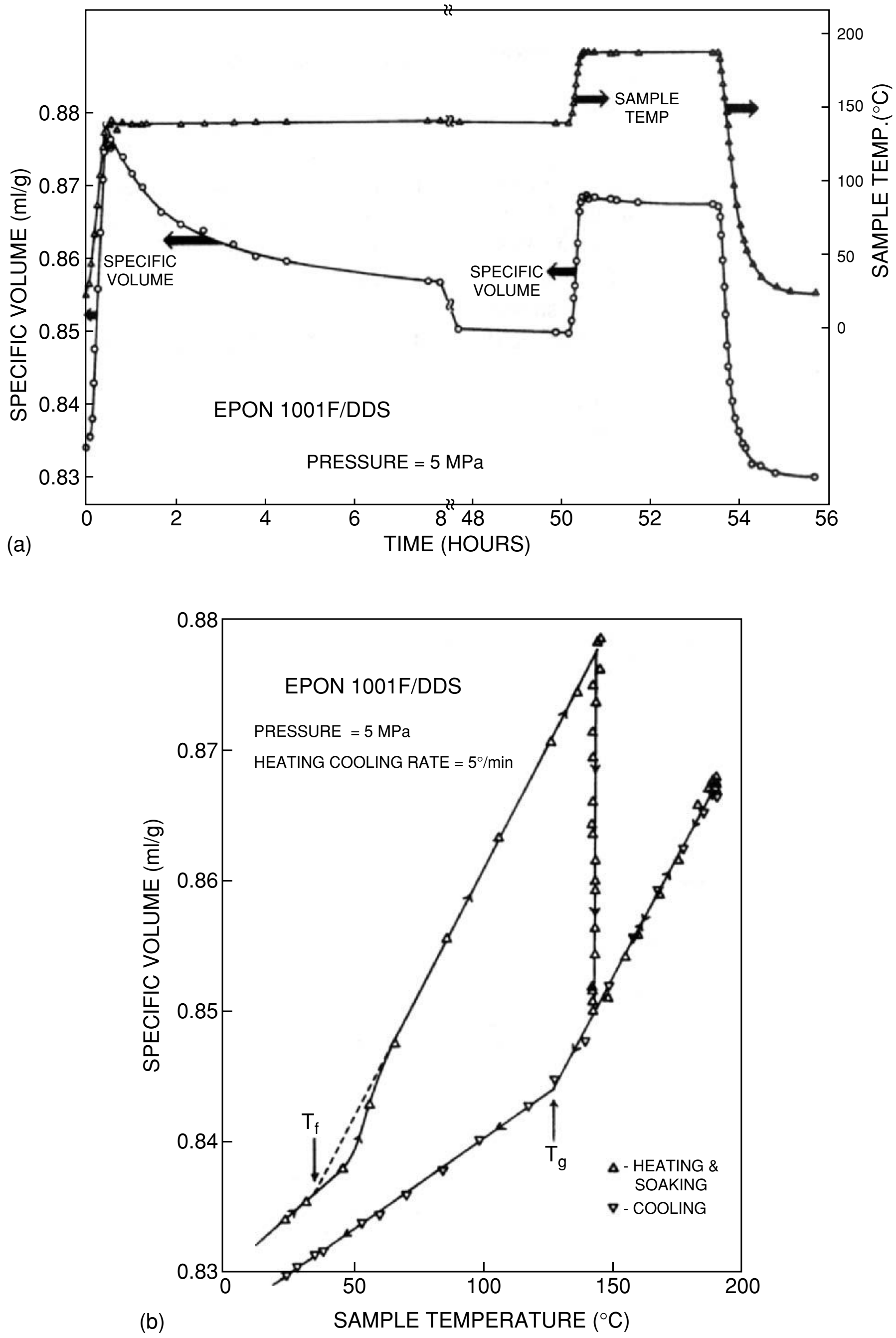


FIGURE 12.13 (a) Specific volume - temperature history of 1001F/DDS epoxy resin during curing under a pressure of 5 MPa. (b) Specific volume data from Fig. 12.13a plotted as a function of the temperature.

molecular network. Before the point of incipient gelation, the viscosity can be seen to climb toward infinity before gelation. After gelation, the precipitous drop in the equilibrium compliance of the developing network continues until a complete cure is achieved in about two days. Using the starting and final $T_{f,g}$s as limits it can be seen that they follow the degree of cure.

When an epoxy resin is cured at a temperature which is below its ultimate $T_g(\infty)$ at full cure, the $T_{f,g}$ will increase rapidly as the reaction proceeds until the T_g becomes equal and surpasses the temperature of cure T_c. The reaction then becomes diffusion-controlled and the rate of reaction and increase in $T_{f,g}$ decelerates to a much lower but still perceptible value as can be seen in Fig. 12.15 [82]. The curing reaction continues significantly even when T_c is 50 °C below T_g. Room temperature cures of epoxy resins can therefore be expected to continue for years.

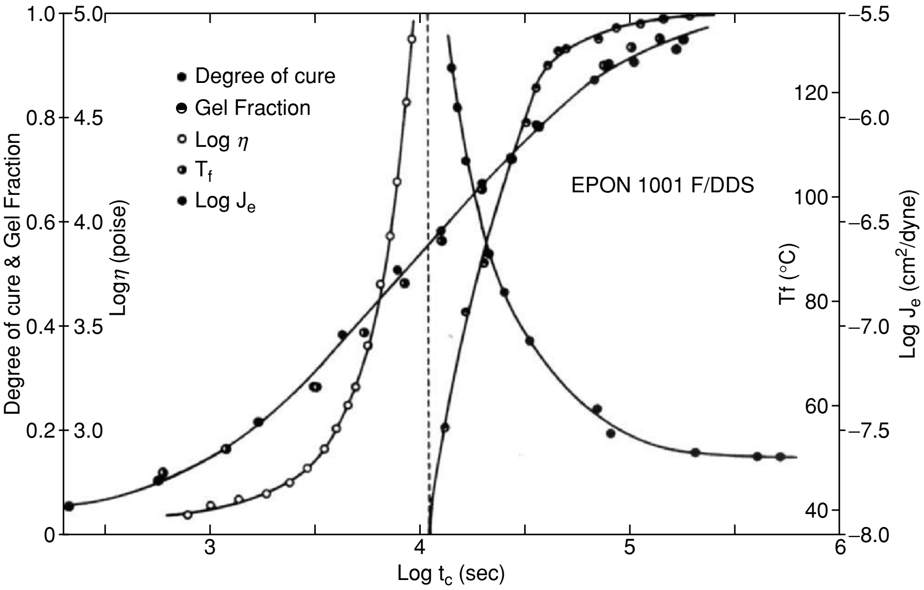


FIGURE 12.14. Comparison of changing parameters during the curing of 1001F/DDS at 142 °C. The logarithm of the viscosity $\eta(p)$ and the equilibrium compliance J_e(cm^2/dyn) as well as the fictive temperature T_f, the degree of cure, and the gel fraction are shown as functions of the logarithm of the time of curing $T_c(s)$.

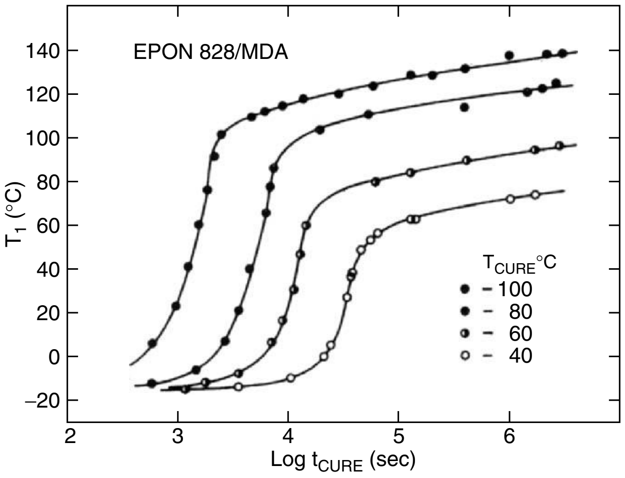


FIGURE 12.15 Fictive temperatures, T_f, observed during the curing of an epoxy resin at temperatures below the $T_g(\infty)$ of the fully cured state.

12.7 DEPENDENCE OF T_g ON THE DEGREE OF CRYSTALLINITY AND MORPHOLOGY

Nearly all crystalline polymers contain chain segments that do not reside in a crystalline lattice. Usually these noncrystalline segments can be considered to constitute an amorphous phase which therefore can become glassy. The T_g of this amorphous phase depends on the degree of crystallinity. T_g increases and decreases with the presence of crystallinity. It can increase or decrease with the degree of crystallinity depending on the relative density of the amorphous and crystalline states. Most often the more orderly crystalline state has the higher density at T_g and the noncrystalline molecular chains are constrained by being anchored to the immobile crystallites and T_g increases. On rare occasions the crystalline state has a lower density than the amorphous material [88]. In this case, less constraint on the noncrystalline chain segments increases the entropy causing T_g to decrease. T_g is not a unique function of the degree of crystallinity. At least in the usual case where the density of the crystalline state at T_g is higher than that of the amorphous state, the temperature at which the crystallites are formed plays a dominating role. At temperatures above the maximum in the crystal growth rate [89], and of course, below the melting temperature T_m, the rate of nucleation is low and therefore relatively few spherulites are formed and the tie molecules in between crystallites are relatively unconstrained. Hence the increase in T_g with increased crystallinity is relatively slight [89] as seen in Fig. 12.16. However, at temperatures below the maximum in crystal growth rate and near T_g, the rate of nucleation can be profuse. Many crystallites are formed and tie molecules are therefore shorter and more constrained. Therefore a given degree of crystallinity is more effective in raising T_g (see Fig. 12.17). The above conclusions are drawn from the mechanical results reported by Groeninckx *et al.* [89] where the onset of the steep decrease in $\log E_r(10)$ with temperature can be considered as a rough estimate of T_g. Direct confirmation with proper T_g measurements is desirable.

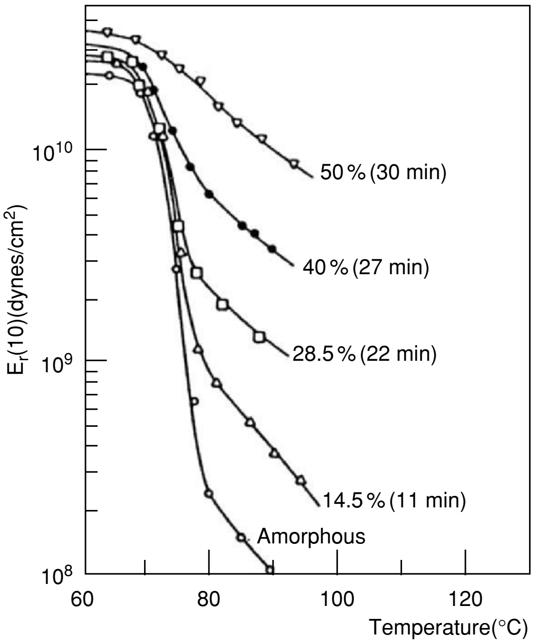


FIGURE 12.16. Ten-second stress relaxation moduli $E_r(10)$ of PET crystallized at 227°C to different degrees presented as a function of temperature. Crystallization times are also shown as well as the estimated degree of crystallinity from density measurements. (From Groeninckx, Berghmans, and Smets, by permission, [89].)

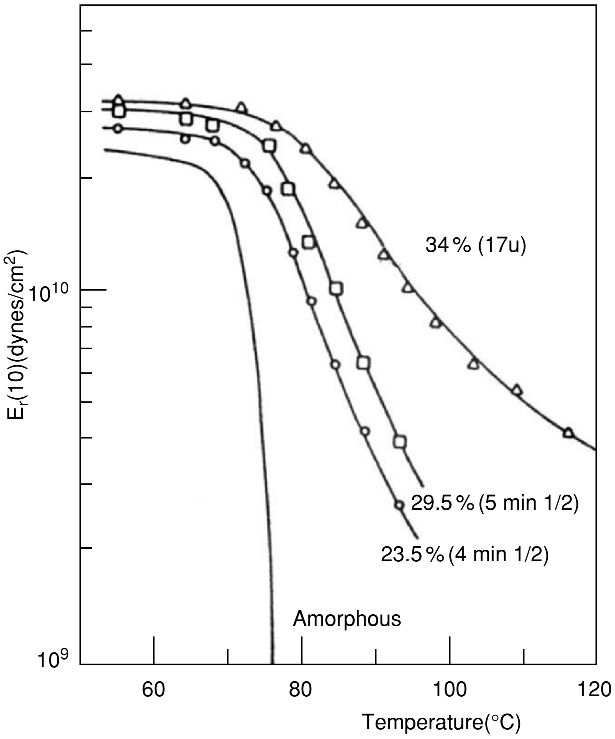


FIGURE 12.17. Ten second stress relaxation moduli $E_r(10)$ of PET crystallized at 120°C to different degrees presented as a function temperature. (From Groeninckx, Berghmans, and Smets, by permission, [89].)

12.8 DEPENDENCE OF T_g ON INTERMOLECULAR FORCES

The greater the intermolecular interaction, all other things being equal, the higher T_g will be. It has been proposed that T_g is a linear function of the cohesive energy density CED [90].

$$\mathrm{CED} = 0.5\mathrm{MRT_g} - 25\mathrm{M},$$

where R is the gas constant and M is a parameter analogous to the number of degrees of freedom of a molecule. Eisenberg has shown how T_g increases dramatically in a phosphate glass with the decrease in size of incorporated anions and with increases in their charge [91]. He has also shown how in ionomers (specifically ethyl acrylate-acrylic acid copolymers neutralized with various cations) T_g is a common smoothly increasing function of $c\ q/a$ as shown in Fig. 12.18. c is the cation concentration, q is its charge, and a is the distance between centers of charge, as shown in Fig. 12.18. The onset of the observed sigmoid coincides with the domination of a wide range of properties by ionic clusters.

12.9 THE EFFECT OF PRESSURE ON T_g

An increase in pressure on an amorphous material increases molecular crowding and interactions along with decreasing the entropy. Regardless of the variable which one looks upon as significant, an increase in T_g is expected. If a rapid pressure increase is incurred, a time-dependent decrease in volume will follow if the temperature is near or below T_g. This is indeed a simple voluminal viscoelastic creep process. The resultant behavior is quite analogous to that seen following a temperature quench as discussed above. The similar response to pressure jumps has been shown by Goldbach and Rehage [92]. The expected increase in T_g with increases in pressure has been documented by McKinney and M. Goldstein [93]. Discussions in the literature are confounded by not restricting the definition of T_g to cooling from an equilibrium state.

12.10 EFFECT OF MOLECULAR STRUCTURE ON T_g

12.10.1 Internal Plasticization and Chain Stiffness

If side chains on the polymer backbone are increased in length only, it is generally observed that T_g decreases, ostensively because the linear side chains increase the fractional free volume between the chains and any structural change which increases the diameter of the side chains reverses the tendency; i.e., T_g increases. This is a reflection of the following general principle.

Any structural feature which increases the size of the jumping unit of the molecular chain will increase T_g. An

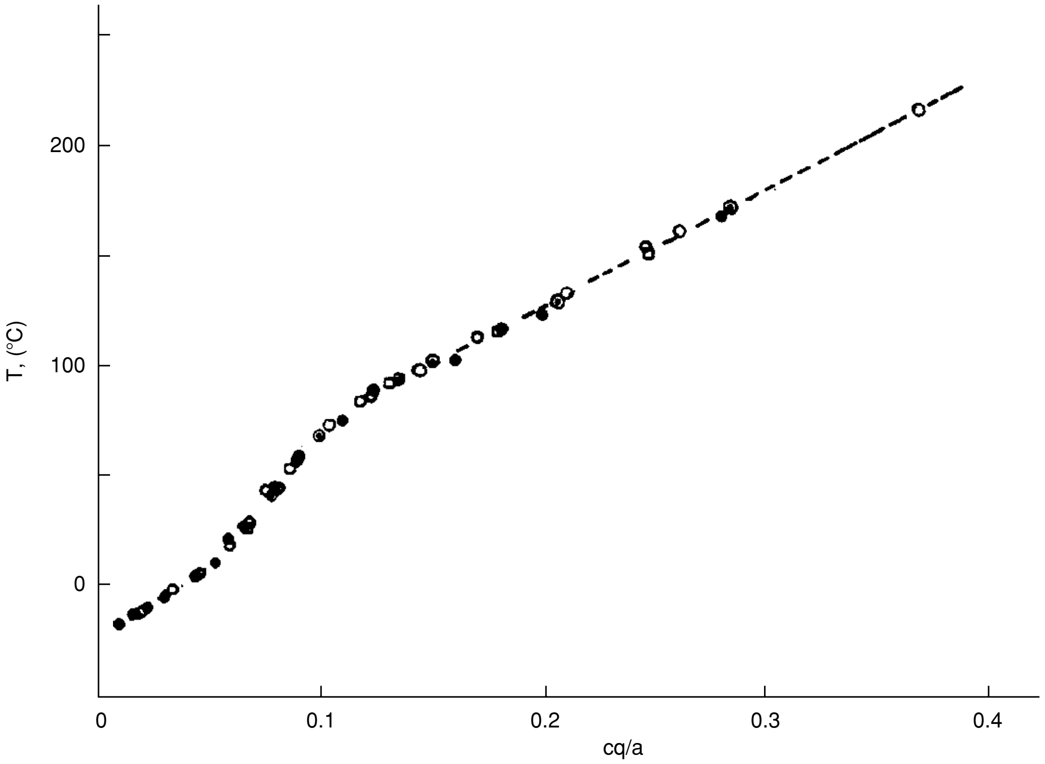


FIGURE 12.18. T_g of ethyl acrylate - acrylic acid copolymers neutralized with various cations shown as a function of *cq/a*, where *c* is the cation concentration, *q* is its charge, and *a* is the distance between centers of charge. (From Matsuura and Eisenberg, by permission, [91b].) Different symbols represent different cations.

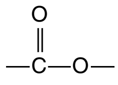
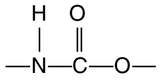
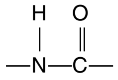
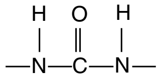
increase in chain stiffness resulting from longer rigid units in the chain backbone or more bulky side groups which drastically increase the potential barriers to rotation, cause substantial increases in T_g. Steric barriers to rotation are raised appreciably if a second side group is introduced on alternate chain backbone atoms. The pairs, polymethylmethacrylate PMMA ($T_g \simeq 115c$)-polymethylacrylate PMA (14 °C) and poly(α-methylstyrene) (~168 °C)-polystyrene (100 °C), illustrate the effect. Introducing paraphenyl rings into a chain backbone increases T_g since a longer portion of the chain has to be involved in a molecular segmental displacement. To the contrary introducing additional methylene (—CH_2—) groups or ether oxygens into the polymer chain backbone lowers T_g because of the increased chain flexibility. With no side atoms or groups and a wide open bond angle (> 111°) the ether oxygen is considered the premier flexibilizing unit.

12.10.2 Effect of Polarity

The stronger the interactions between neighboring polymer chain segments, the greater the thermal kinetic energy must be to create holes of sufficient size to allow a diffusive jump of a chain segment to occur. Therefore, the greater the polarity of a polymer, the higher the T_g will be. The greatest effect will be due to resultant components of dipole units which are perpendicular to the chain backbone. The greater T_g of polyacrylonitrile (~ 103 °C) relative to that of polypropylene (− 14 °C) must be due to the large electron affinity of the nitrile group (—C ≡ N).

Enhancing the flexibility of a polymer chain by introducing an ether oxygen into its backbone will lower T_g and the melting temperature, T_m. Increasing the polarity or the opportunity for hydrogen bonding between neighboring chain segments increases T_g and T_m. The effects of such variations are illustrated in Table 12.2 where the coupling units are varied in a family of otherwise similar polymers.

TABLE 12.2. *Effect of polarity and hydrogen bonding.*

Low T_gs and T_Ms ↓	—R—O—R′—	polyethers
	 $-\overset{O}{\overset{\|}{C}}-O-$	polyesters
	 $-\overset{H}{\overset{\|}{N}}-\overset{O}{\overset{\|}{C}}-O-$	polyurethanes
	 $-\overset{H}{\overset{\|}{N}}-\overset{O}{\overset{\|}{C}}-$	polyamides
High T_gs and T_Ms	 $-\overset{H}{\overset{\|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{\|}{N}}-$	polyureas

12.10.3 Influence of Symmetry

On the basis of some of the above comments it would be expected that the T_g of polyisobutylene PIB [CH_2—C $(CH_3)_2]_n$ would be higher than that of polypropylene PP [CH_2—C(H)$CH_3]_n$. The polarity of PIB is lower than that of PP because the opposing dipoles tend to cancel one another. However, the polarity is low in both cases and would not be expected to be a dominating factor. The two side groups on alternate carbon backbone atoms of the PIB certainly should present overall higher barriers to rotation than that present in the PP. Yet the T_g of PIB at -73 °C is some 59 ° lower than that of PP. Likewise, the T_g of polyvinylidene chloride [CH_2—$CCl_2]_n$ at -17 °C is 63° lower than that of polyvinylchloride [CH_2—CClH$]_n$. It was discovered by Boyd and Breitling [95] that whereas there are indeed higher barriers to rotation in the vinylidene polymers, there are adjacent potential energy wells with an extremely low barrier in between them, thus allowing for very free rotation over a limited angle of about 20° which permits liquid structures to adjust far more rapidly than expected.

12.10.4 Effects of Tacticity

It is surprising that stereochemical variations in tacticity [96] have no measurable effect on the T_g of polymethylacrylate PMA and polystyrene PS, but they have a substantial effect on that of polymethylmethacrylate PMMA and poly(α-methylstyrene) PαMS [97]. The explanation appears to lie in the added steric repulsion to rotation due to the presence of the asymmetric double side groups on alternate chain backbone atoms. Extended planar zig-zag configurations of the chains are not possible and it is clear that different helical forms of highly isotactic and syndiotactic chains obtain. The stiffness of the helices are obviously significantly different. A reflection of the differences in the helical character of the chain conformation is seen in the variation of the dielectric permittivity as a function of the tacticity [98]. Highly syndiotactic samples of PMMA have a dominant β loss peak reflecting independent motion of the carbonyl dipole in the ester side group. However, as the degree of istacticity is increased, the dipole activity is shifted to the α backbone loss peak. As the limit of total isotacticity is approached, the β loss peak virtually vanishes, indicating that the carbonyl dipole motion is locked in with the chain backbone motion. A consequence of the lack of independent side chain motion (β mechanism) in iso-PMMA is a much smaller glassy compliance, J_g [99]. Secondary (sub-t_g) loss mechanisms are listed in this handbook in the chapter authored by Fried.

12.11 DIFFERENCES OF OPINION CONCERNING T_g

Qualitatively free volume concepts usually provide a rationale for observed behavior [18], but clearly they do not provide a comprehensive understanding. Interactions and coupling also play a role. Occasionally, as mentioned above, a polymer with a T_g, which is higher than that of its solvent will increase the mobility of the solvent molecules. This is contrary to what is expected according to free volume concepts. Such acceleration can be understood if the uncoupled mobility of the polymer is greater than that of the solvent [73].

In addition to the free volume [36,37] and coupling [43] models, the Gibbs–Adams–DiMarzo [39–42], (GAD), entropy model and the Tool–Narayanaswamy–Moynihan [44–47], (TNM), model are used to analyze the history and time-dependent phenomena displayed by glassy supercooled liquids. Havlicek, Ilavsky, and Hrouz have successfully applied the GAD model to fit the concentration dependence of the viscoelastic response of amorphous polymers and the normal depression of T_g by dilution [100]. They have also used the model to describe the compositional variation of the viscoelastic shift factors and T_g of random Copolymers [101]. With Vojta they have calculated the model molecular parameters for 15 different polymers [102]. They furthermore fitted the effect of pressure on kinetic processes with this thermodynamic model [103]. Scherer has also applied the GAD model to the kinetics of structural relaxation of glasses [104]. The GAD model is based on the decrease of the conformational entropy of polymeric chains with a decrease in temperature. How or why it applies to nonpolymeric systems remains a question.

The TNM model has been used to describe structural relaxation during the heating and cooling of amorphous crowded liquids by O'Reilly [8] and by Hodge [10]. A disturbing result of the application of the TNM model is that the effective relaxation time, τ, is not constant at T_g but varies almost eight orders of magnitude when comparing values for different materials [8]. This variation is in serious conflict with the nearly constant rate of creep at T_g observed on a wide variety of amorphous materials [60,64–66]. The TNM model employs the stretched time-scale of the Kohlrausch [105]-William-Watt [106] function: i.e., relaxation which is proportional to $\exp[-(t/\tau)^m]$. The Kovacs, Aklonis, Hutchinson, and Ramos, KAHR, model employs a distribution function of retardation times to describe volume memory and other viscoelastic effects. In the KAHR model it is assumed that the retardation function shifts to longer times with decreasing temperature while its shape is conserved. This requires thermorheological simplicity[c] which does not always hold near and below T_g [78,107].

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[c] See the discussion on thermorheological simplicity in Chapter 26 on Viscoelastic Behavior.

The influence of rates on T_g and glass formation has recently been treated by Shi [108]. His results should be examined and tested. He predicts upper and lower bounds for T_g based on thermodynamic and kinetic factors.

12.12 SOME CORRESPONDING PROPERTIES AT T_g

In Table 12.3 a number of properties determined in the neighborhood of T_g are listed [109]. The T_gs were determined at or reduced to a rate of cooling of 0.2°/min. A wide variety of amorphous materials are represented. The first five materials tri-α-naphthylbenzene, Tri cresyl phosphate Aroclor 1248, 6 phenyl ether, and 1,2 diphenylbenzene (o-terphenyl) are nonpolymeric compounds; $Tl_2SeAs_2Te_3$ is an inorganic glass-former; selenium is a polymeric element; polystyrene, amorphous polypropylene, polyvinylacetate, and polyisobutylene are linear organic polymers; Epon 1004/DDS, Epon 1007/DDS, and Viton 10A are crosslinked organic polymers; and 20 PB/A1248 is a solution of a linear organic polymer, 1,2 polybutadiene in an organic solvent, Aroclor 1248. The T_∞ is the hypothetical temperature in the Vogel, Fulcher, Tamman, and Hesse (VFTH) equation [18] and the Williams, Landel, and Ferry (WLF) equation [18] where the viscosity becomes infinite. It is hypothetical because it is implicitly assumed that an equilibrium density persists. At an infinitely slow rate of cooling it appears by extrapolation that $T_g(q = -\infty) = T_\infty$ [49] which, in this limit, makes it a candidate for the second order thermodynamic transition of the GAD model. According to the "universal" form of the WLF equation $T_g - T_\infty \simeq 52$. In Table 12.3, the values vary from 29° to 175 °C. Logarithmic values of the glassy shear compliance J_g(cm^2/dyne) at T_g are given. Most values are close to − 10.0 as is often observed. Values as high as −9.4 have been reported [110] and the chalcogenide glass $Tl_2SeAs_2Te_3$ is the lowest at −11.1.

Logarithmic values for the steady-state recoverable shear compliance J_e^0(cm^2/dyne) are also shown. For the nonpolymer J_e^0 values are 2.5 to 3.0 times larger than J_g. For the linear polymers, since J_e^0 is a function of the molecular weight up to value 5 times that of the entanglement value, M_e, and its distribution, much larger ratios are seen. Of course, the network polymers exhibit equilibrium compliances that are determined by the level of crosslinking and are not steady-state values. Steepness indices, $S_{Tg}, = -T_g[d \log a_T/dT]_{Tg}$ which indicate the temperature sensitivity of viscoelastic processes at T_g are also listed. S_{Tg} correlates with the breadth of the effective viscoelastic spectrum; i.e., the higher S_{Tg} is, the broader the viscoelastic response is. Thus, the tempera-

TABLE 12.3. *Properties of amorphous materials near and below T_g.*

	T_∞	J_g	Log$J_e^0(T_g)$	T_g	S_{T_g}	Log$\eta(T_g)$	$\beta_{T_g} \times 10^{1}2$	$T_g^{1\ell}$	ΔT_g
Material	**°C**			**°C**		**poise**	**cm^2/dyne-s$^{1/3}$**	**°C**	**°C**
Tri-α-naphthylbenzene	−73.2	−10.022	−9.548	63.8[i]	74.8	12.445	16.67	60.8	3.0
Tri-cresyl phosphate	−116.7	−10.110	−9.586	−73.0[i]	80.5	12.905	10.09	−73.0	—
Aroclor 1248[a]	−181.1	−10.372	−9.987	−50.0[i]	62.0	12.746	6.146	−47.7	−2.3
6-Phenyl ether[b]	−99.8	−10.140	−9.766	−25.0[i]	84.6	12.677	7.700	−23.9	−1.1
1,2 Diphenylbenzene	−101.3	−10.347	−9.926	−32.4[i]	87.6	12.367	9.746	−31.3	−1.1
$Tl_2SeAs_2Te_3$	−113.2	−11.102	−10.64	67.4	60.5	12.246	3.980	69.9	−2.5
Se	10.5	−10.482	−8.480	32.0	155	12.67	7.590	32.8	−0.8
Polystyrene[c]	69.0	−10.022	−4.660	97.5[i]	137.4	13.74[h]	20.88	95.7	1.8
Polypropylene[d]	−46.4	−9.934	−4.820	−14.0	135.4	13.85[h]	15.80	−15.0	1.0
Polyvinylacetate[e]	6.0	−10.046	−4.650	34.8[i]	94.2	17.05[h]	16.95	36.4	−1.6
Polyisobutylene[f]	−135	−10.460	−5.715	−76.2[i]	45.1	15.23[h]	14.62	−77.4	1.2
EPON 1004/DDS[g]	60.8	−9.879	−7.390	107.7	147.8	—	9.816	107.5	0.2
EPON 1007/DDS[g]	50.7	−9.928	−7.100	97.3	144.0	—	7.590	98.1	−0.8
Viton 10A[j]	−54.0	−9.969	−5.940	−26.1	136.3	—	14.56	−26.9	0.8
20PB/A1248[k]	−163.6	−10.495	−4.750	−50.0[i]	61.7	17.0[h]	9.900	−49.8	−0.2

[a] Aroclor 1248 is a chlorinated biphenyl.

[b] 6-Phenyl ether is an abbreviation for bis(*m*-(*m*-phenoxy phenoxy)phenyl)ether.

[c] Commercial Polystyrene ($M_w = 2.20 \times 10^5$)

[d] Amorphous Polypropylene ($M_w = 2.05 \times 10^5$)

[e] Polyvinylacetate ($M_w = 6.50 \times 10^5$)

[f] Polyisobutylene ($M_w = 7.80 \times 10^4$)

[g] EPONs are epoxy resins consisting of a diglycidyl ether of bisphenol *A* cross-linked using diaminodiphenyl sulfone(DDS) as the curing agent. They are network polymers that do not flow.

[h] Viscosities were calculated using the Vogel, Fulcher, Tamman, and Hesse (VFTH) equation.

[i] Glass temperatures were measured at a cooling rate of 0.2 °C/min otherwise they were calculated using the shift factors.

[j] Viton 10A is a fluoroelastomer.

[k] 20PB/A1248 is a 20-wt % solution of a Polybutadiene ($M_w = 1.34 \times 10^5$) in Aroclor 1248.

[l] T_g' is the temperature at which $\beta = 10 \times 10^{-12}$cm^2/dyne-sec$^{1/3}$.

ture dependence of dissipative processes is related to their time and frequency dependence [139].

Although the viscosities of nonpolymeric liquids have close to the same viscosity at T_g of $\sim 3 \times 10^{12}$ poise ($\sim 3 \times 10^{11}$Pa sec), this value is smaller than the classically referred to value of 1.0×10^{13} poise in spite of the fact that most common T_gs have been determined at a rate of cooling of 1°/min. At the cooling rate of 0.2°/min the T_gs reported here would be several degrees lower and thus higher viscosities would be expected. The widely accepted value for $\eta(T_g) \simeq 10^{13}$ poise does not hold at all for linear polymers, as noted above, because of the dependence of η on the molecular weight [140], and for crosslinked polymers, which do not flow. The local segmental mobility is obviously the determining factor for the packing density of amorphous polymers, whether or not chain-like molecules are entangled or crosslinked. Local molecular packing and motions are believed to be the determining factors for the liquid structure. Long range motions cannot be influential in defining the density. Molecular packing beyond several nearest neighbors in an amorphous system such as a supercooled liquid cannot be coordinated because of the absence of long-range order. Evidence for this assertion can be seen by comparing the retardation spectra obtained from volume contraction with that obtained from shear creep.

The kinetics of isothermal volume contraction and expansion of a cured epoxy resin, which is completely amorphous, below its T_g has been followed [49]. Since the free volume determines the molecular mobility, contraction following a decrease in temperature is going to be faster than the expansion following an increase to the same temperature since its starting specific volume is larger. This is the reason for the well known asymmetry of approach toward an equilibrium density. To minimize the asymmetry a series of small temperature jumps of 2.5 °C were utilized in following the contraction and expansion kinetics. Figure 12.19 shows that the asymmetry is minimal with such temperature changes.

This study of physical aging was different from conventional studies in that each temperature increment was incurred after equilibrium was achieved. The results on an epoxy resin derived from a diglycidyl ether of bisphenyl A (Epon 1001), which was fully cured with DDS (4,4′-diamino diphenyl sulphone), are shown in Fig. 12.20, where $V(t)$ is the specific volume after the temperature step, and $V(\infty)$ is the equilibrium volume at the final temperature.

Since the thermal driving force was virtually the same with each step, simple temperature reduction could be attempted with horizontal time-scale shifts. The successful reduction is presented in Fig. 12.21.

It was assumed that the results were reasonably close to linear behavior and the more extensive curve obtained from the cooling steps was analyzed to obtain a normalized retardation spectrum $L(\tau)$.

$$\int L_0(\tau)\mathrm{d}\ln\tau = 1$$

then

$$\frac{V(0^+) - V(t)}{V(0^+) - V(\infty)} = \int_{-\infty}^{+\infty} \left(L_0(\tau)(1 - \mathrm{e}^{-\frac{t}{\tau}})\mathrm{d}\ln\tau\right).$$

The $L_0(\tau)$ that was obtained is shown in Fig. 12.22 with the retardation spectrum obtained from the shear creep compliance function, $J(t)$. The levels of the short time behavior are matched. Three features should be noted. The functionality at short times is the same within experimental uncertainty. The 1/3 slope of log $L(\tau)$ at short time indicates that the response is dominated by motions that contribute to Andrade creep. [66,85–87,141,142]

$$J_A(t) = J_A + \beta\ t^{1/3},$$

where t is the time of creep, and J_A and β are characterizing constants.

The positive curvature and the following maximum of the creep compliance $L(\tau)$ indicate the contribution of polymeric molecular modes of motion to the recoverable compliance. Since no positive curvature is seen in the volume contraction $L_0(\tau)$, no polymeric modes are present and no long range coordinated motions of any kind are detected.

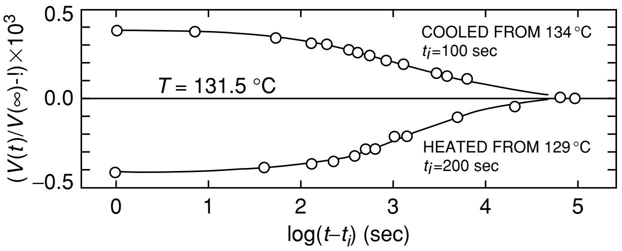


FIGURE 12.19. Fractional volume deviation from equilibrium as a function of time at 131.5 °C after cooling from 134 °C and after heating from 129 °C plotted versus the logarithm of the corrected aging time $t - t_i$ where t_i is the estimated time for the specimen to reach a uniform temperature. Reproduced from Donald J. Plazek and Craig A. Bero, Precise Glass Temperature, *J. Phys.: Condens. Matter.* **15** (2003) 5789–5802 with permission from Institute of Physics Publishing.

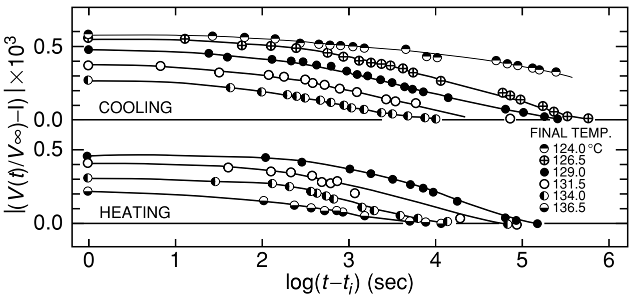


FIGURE 12.20. Absolute fractional volume deviation from equilibrium as a function of the logarithm of the corrected aging time for five temperature after cooling 2.5 °C from equilibrium and four temperatures after heating. Reproduced from Donald J. Plazek and Craig A. Bero, Precise Glass Temperature, *J. Phys.: Condens. Matter.* **15** (2003) 5789–5802 with permission from Institute of Physics Publishing.

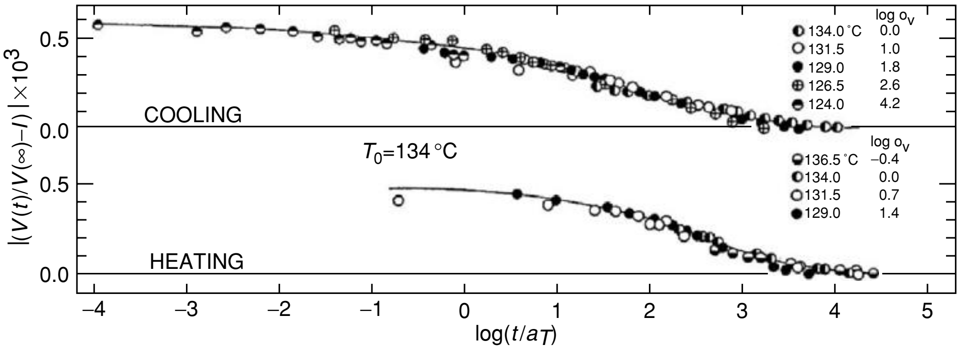


FIGURE 12.21. Volume contraction and expansion from Fig. 12.3 reduced by time-scale shifts to the chosen reference temperature $T_o = 134$ °C. The time t/a_T is the corrected reduced value. Reproduced from Donald J. Plazek and Craig A. Bero, Precise Glass Temperature, *J. Phys.: Condens. Matter.* **15** (2003) 5789–5802 with permission from Institute of Physics Publishing.

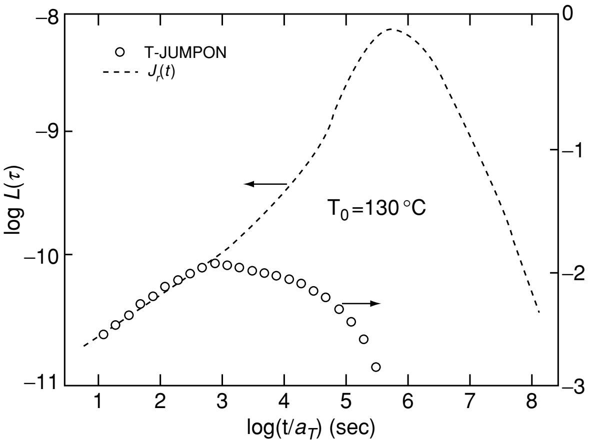


FIGURE 12.22. Comparison of retardation spectra for voluminal L_0 and shear deformation L_s. In this double logarithmic plot of the distribution functions of retardation times τ the ordinate scales have been adjusted to superpose the short-time results. τ/a_T is the reduced retardation time. Reproduced from Donald J. Plazek and Craig A. Bero, Precise Glass Temperature, *J. Phys.: Condens. Matter.* **15** (2003) 5789–5802 with permission from Institute of Physics Publishing.

Only local mode molecular motions contribute to changes in the local packing structure of a liquid and the mobility of those modes decrease rapidly with decreasing temperature. At some temperature, because of the diminishing rate of possible molecular rearrangements, the equilibrium liquid structure can no longer be maintained. Below this temperature the liquid is a glass. The average relaxation time for these motions should be same for all amorphous materials, since the local molecular rearrangement rate that is insufficient to keep up with a given rate of cooling is only a function of that rate of cooling.

12.13 VISCOELASTIC BEHAVIOR AT T_g

The viscoelastic behavior of an amorphous nonpolymeric dehydroabietic acid DHAA as seen at the glass temperature along with that of a low molecular weight unentangled polystyrene ($M = 1.64 \times 10^4$) and a high molecular weight entangled polystyrene ($M = 3.8 \times 10^6$) has been shown in the form of many of the commonly presented functions. They are shown as logarithmic functions of the reduced time t/a_T (sec) and/or frequency ωa_T (rad/sec), where a_T is the temperature shift factor [18]. The viscoelastic functions presented include:

1. The shear creep & recoverable (dashed line) compliance $J(t)$ & $J_r(t)$cm^2/dyne or Pa^{-1};
2. The stress relaxation modulus $G(t)$, dynes/cm^2 or Pa;
3. The dynamic storage $J'(\omega)$ and loss $J''(\omega)$ compliances;
4. The dynamic storage $G'(\omega)$ and loss $G''(\omega)$ moduli;
5. The loss tangent $\tan\delta = J''(\omega)/J'(\omega) = G''(\omega)/G'(\omega)$;
6. The real component of the dynamic viscosity $\eta'(\omega)$ and the imaginary component $\eta''(\omega)$;
7. The retardation function $L(\tau)$cm^2/dyne or Pa^{-1}; and
8. The relaxation spectrum $H(\tau)$dyne/cm^2 or Pa.

The systematic variation of the viscoelastic functions with molecular structure can clearly be seen. Because of the additivity of strains arising from different molecular mechanisms [143,144] it should be noted that the clearest picture is seen in the development of $L(\log\tau)$ with changes in molecular weight. Effects of branching and molecular weight distribution are not considered here. The simplest behavior is exhibited by the nonpolymeric DHAA (See Fig. 12.23 [115]). The logarithm of the retardation spectrum exhibits a linear increase with the logarithmic reduced time scale time scale at relatively short times up to a rather abrupt maximum value. The slope of the linear portion has a value of 1/3 within experimental uncertainty. This slope reflects the fact that the recoverable creep compliance appears to display Andrade creep with a proportionality to the cube root of time before the long-time limiting steady-state recoverable compliance is approached. Although the amorphous materials that have been examined can be fit to the Andrade $t^{1/3}$ linearity at short times near T_g there is the

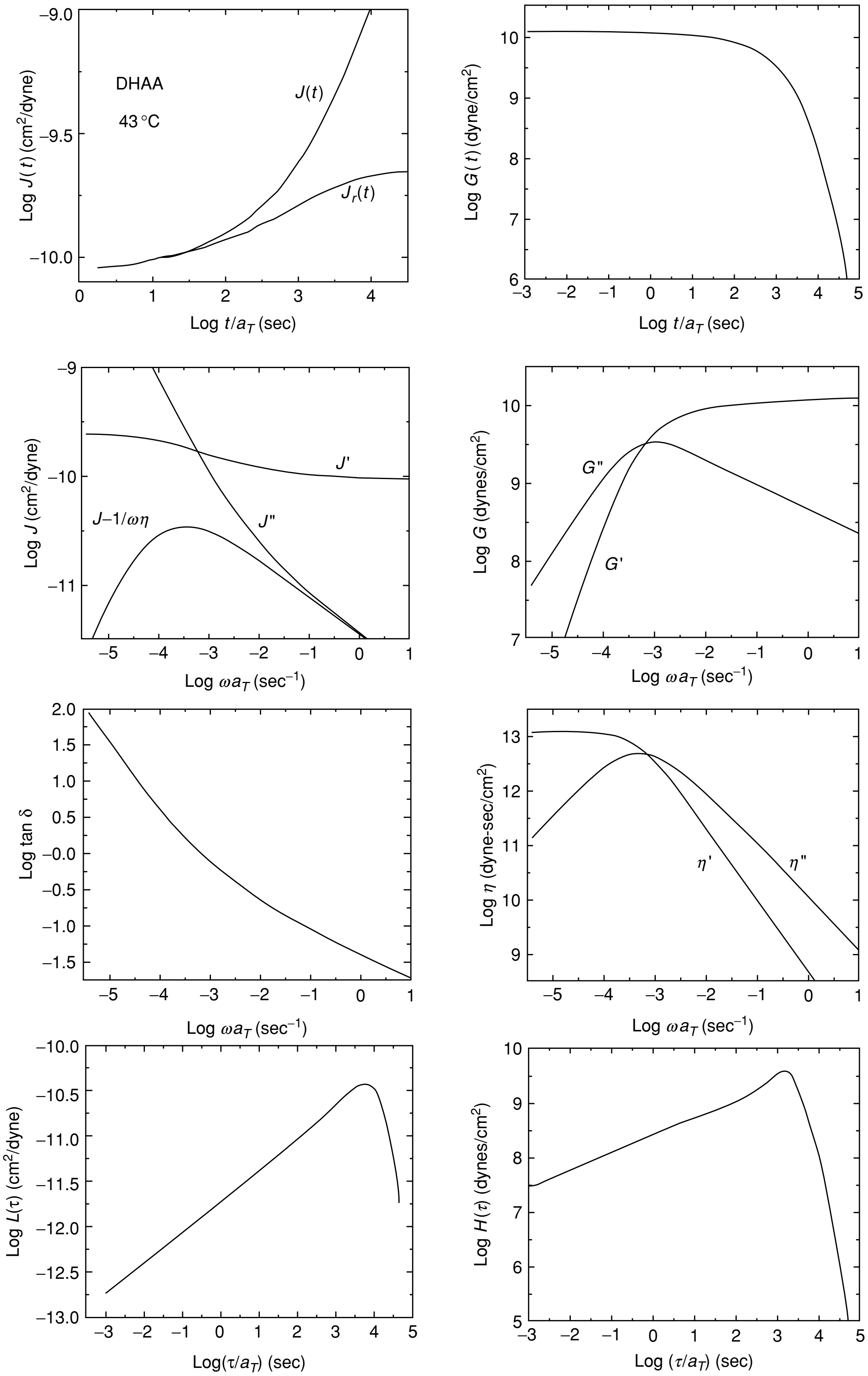


FIGURE 12.23. Viscoelastic functions of a nonpolymeric glass former (DHAA). Reproduced from Donald J. Plazek and Craig A. Bero, Precise Glass Temperature, *J. Phys.: Condens. Matter*. **15** (2003) 5789–5802 with permission from Institute of Physics Publishing.

possibility that such fits are an approximation to a functionality that varies from material to material. The functionality is the generalized Andrade creep t^{1-n} [145–155], where $(1-n)$ is the fractional exponent of the Kohlrausch relaxation function, $\exp[-(t/\tau)^{1-n}]$ [156]. The complement of the Kohlrausch exponent, n, is the coupling parameter of the Coupling Model [145–155]. To be able to utilize an operationally effective means to determine corresponding glass temperature we will assume that the Andrade creep observed is real. In any case the contributions to the recoverable deformation in this regime are identified as local mode intermolecular motions which are also seen in permittivity measurements and are referred to as the alpha mechanism.

The same behavior can be seen in low molecular weight polymers as is illustrated with the polystyrene PS A61 [3]. It's molecular weight is just below the molecular weight between entanglements, $M_e = 17{,}000$ for polystyrene. Hence there is no entanglement network. In fact the presence of entanglements is not seen until $M > M_c = 35{,}000$, for polystyrene. Above M_c the viscosity is proportional to $M^{3.4}$ and the entanglement plateau appears in the compliance and modulus functions. The additional feature seen in the $\log[L(\tau)]$ for this polystyrene in Fig. 12.24 as a function of the logarithmic reduced time is the pronounced peak seen at long-times [115]. The molecular motions contributing to the recoverable deformation at Logarithmic reduced times between 4 and 7 are believed to be the polymeric normal Rouse modes [18]. The most complicated viscoelastic response is exhibited by high molecular weight polymers with entangled linear molecular chains (Fig. 12.25 [115]). The data shown were obtained on a narrow distribution polystyrene PS F380 with a molecular weight of 3.8×10^6. At moderate long-times beyond the local mode and the Rouse normal mode motions a second Andrade $t^{1/3}$ region is seen in the entanglement rubbery region where polymeric chains with varying chain lengths are sequentially being partially oriented. At still longer times where the polymeric chains are disentangling permanent viscous flow deformation is accumulating linearly with time and the maximum orientation per unit stress is being approached, involving the molecular contortions with retardation times between $\mathrm{Log}(t/a_T) = 11$ and 14.

12.14 UNIVERSAL BEHAVIOR AT T_g

As mentioned above, if it is assumed that Andrade creep is the true functional form exhibited by amorphous materials at short times at T_g, a common behavior is operationally observed that can be used to determine corresponding T_g's for these materials. Since the mobility of the local mode motions determines the T_g, a kinetic characterizing variable, such as the Andrade coefficient β, which is determined by these motions, can be associated with T_g. If we examine the glassy Andrade regions of the retardation spectra for many amorphous materials at their respective T_g's we find that they are all close to one another as seen in Fig. 12.26. Fourteen amorphous materials including organic and inorganic polymers and nonpolymers are represented. They are identified in Table 12.3 [109].

In producing Fig. 12.26 the best T_g's that were available for a cooling rate $Q = 0.2$ °C/min were used to fix the time-scale. The variability relative to the average position is about one decade on the time-scale. Tricresyl phosphate (TCP) was chosen as the reference material; i.e., the position of it's log $L(\tau)$ was assumed to be correct for its T_g (0.2 °C/min cooling). The T_g's of the other glass-formers were adjusted to match the position of the glassy Andrade region to that of TCP. The required changes of the T_g's were about 2 °C or less. The T_g adjustments are listed in Table 12.3. Since glass temperatures are often in doubt by more than several degrees it is felt that the Andrade line seen in Fig. 12.27 represents all of the materials within experimental uncertainty and therefore the common curve can be used to determine relative T_g's with a precision that is not possible by any other means.

12.15 DETERMINATION OF T_g FROM THE COMPIANCE FUNCTIONS

From the common line in the retardation functions shown at T_g in Fig. 12.27 the Andrade coefficient β_{Tg} can be calculated. Smith showed [157] that when Andrade creep is observed

$$L(\tau) = 0.246\beta\tau^{1/3}.$$

Therefore since at T_g, $L(\tau) = 2.24 \times 10^{-12}$ at $\tau = 1\,sec$

$$\beta_{\mathrm{Tg}} = 9.11 \times 10^{-12}(\mathrm{cm}^2/\mathrm{dyne\ sec}^{1/3})$$

or

$$\beta_{\mathrm{Tg}} = 9.11 \times 10^{-11}\left(\mathrm{m}^2/\mathrm{N\ sec}^{1/3}\right),$$

one simply has to determine β as a function of temperature to find out where β has this value to determine T_g. The T_g defining β_{Tg} can be obtained from dynamic mechanical properties as well as from the recoverable creep compliance $J_r(t)$, since we showed [87] that

$$J'(\omega) = J_A + 0.773\beta\omega^{-1/3}$$

and

$$J''(\omega) = 0.446\beta\omega^{-1/3}$$

when $J'(\omega)$ and $J''(\omega)$ are the storage and loss components of the complex dynamic compliance

$$J^*(\omega) = J'(\omega) - iJ''(\omega)$$

and β is the same Andrade coefficient seen in $J_r(t)$.

At present, β_{Tg} seems to be the best indicator of the mobility at T_g. Some T_gs with the experimental conditions, where available, are given in Table 12.4. They appear to be

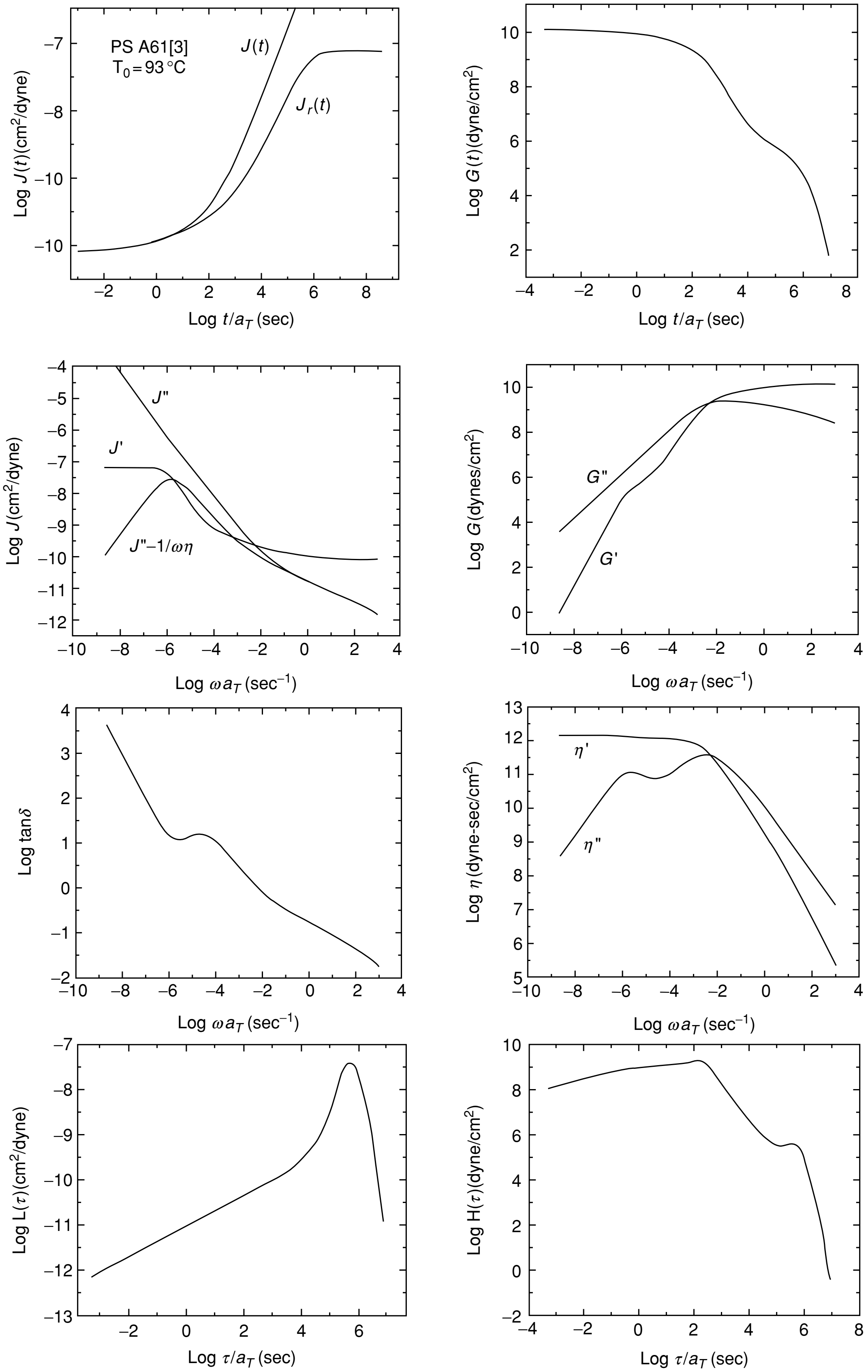


FIGURE 12.24. Viscoelastic functions of a low molecular weight polystyrene (16,400). Reproduced from Donald J. Plazek and Craig A. Bero, Precise Glass Temperature, *J. Phys.: Condens. Matter*. **15** (2003) 5789–5802 with permission from Institute of Physics Publishing.

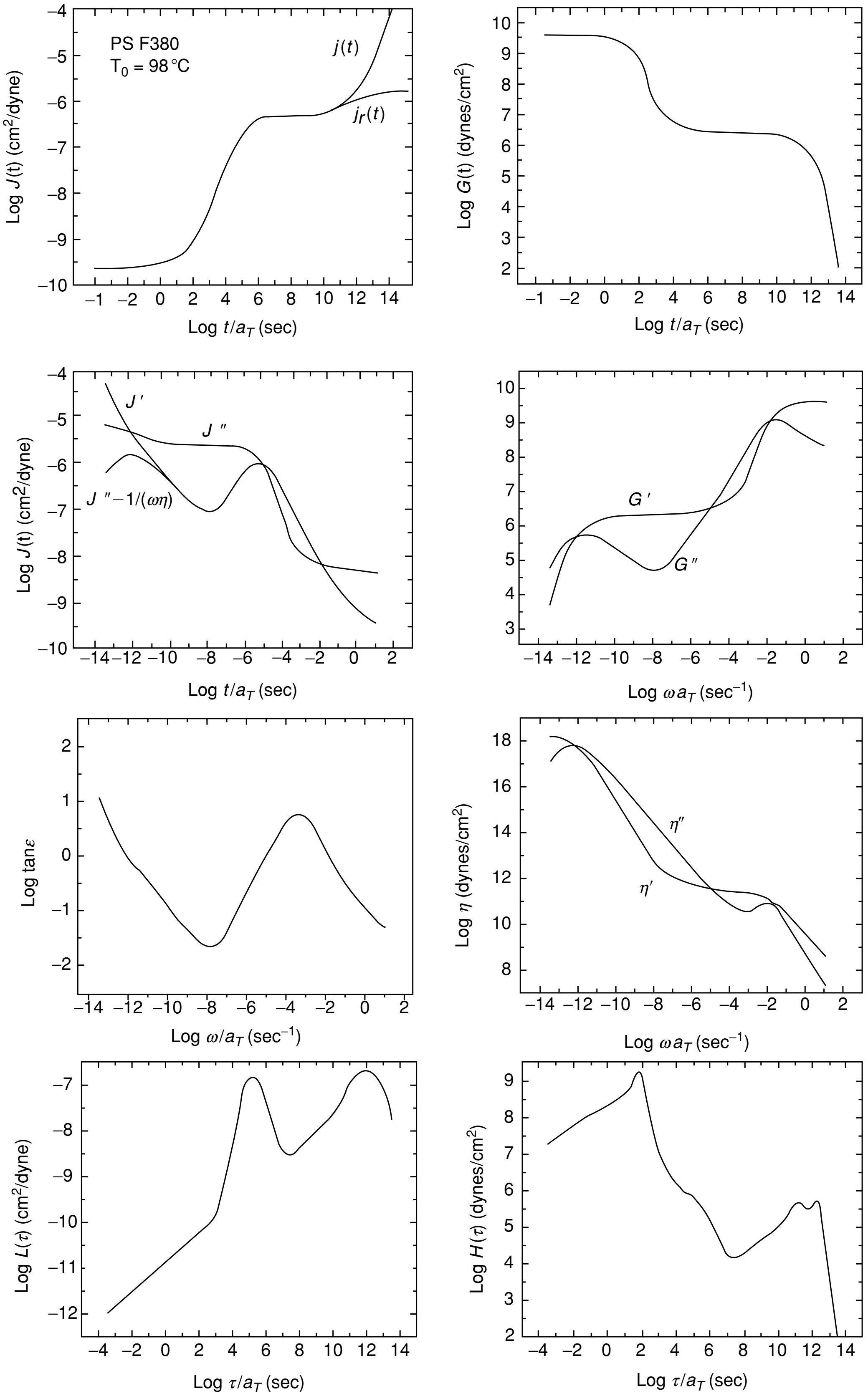


FIGURE 12.25. Viscoelastic functions of a high molecular weight polystyrene, 3.8×10^6. Reproduced from Donald J. Plazek and Craig A. Bero, Precise Glass Temperature, *J. Phys.: Condens. Matter.* **15** (2003) 5789–5802 with permission from Institute of Physics Publishing.

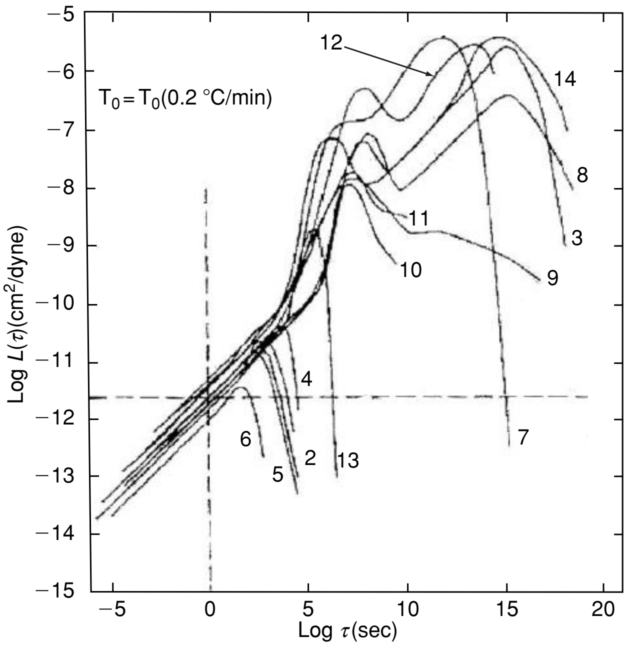


FIGURE 12.26. Comparison of the retardation spectra at $T_0 = T_g(0.2\ °C/min)$ for (1) 6PE, (2) Aroclor 1248, (3) polypropylene, (4) TCP, (5) OTP, (6) $Tl_2SeAs_2Te_3$, (7) PS Dylene 8, (8) PIB, (9) Viton 10A, (10)Epon 1004/DDS, (11) Epon 1007/DDS, (12)PB/Aroclor 1248 soln., (13) Se, (14) PVAc. Reproduced from Donald J. Plazek and Craig A. Bero, Precise Glass Temperature, *J. Phys.: Condens. Matter.* **15** (2003) 5789–5802 with permission from Institute of Physics Publishing.

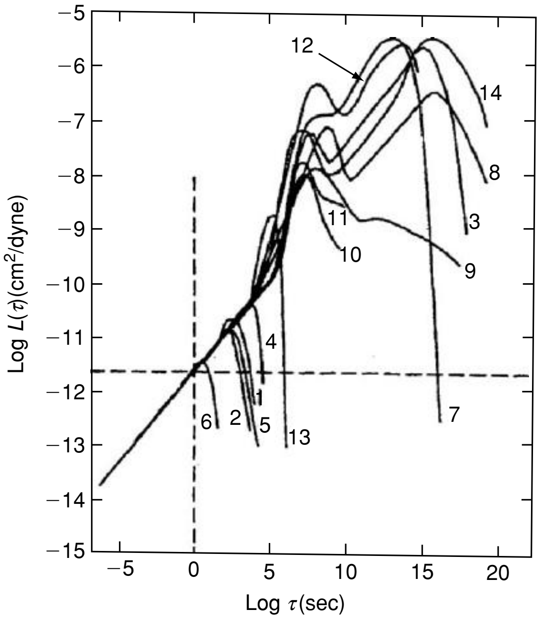


FIGURE 12.27. Superposition of the retardation spectra at short times for the glass-formers of Fig. 12.26. Reproduced from Donald J. Plazek and Craig A. Bero, Precise Glass Temperature, *J. Phys.: Condens. Matter.* **15** (2003) 5789–5802 with permission from Institute of Physics Publishing.

among the best published values. All of the above mentioned caveats should be noted when utilizing these literature values.

12.16 T_g OF POLYMER THIN FILMS AND POLYMER CONFINED IN NANOMETER SCALE DIMENSIONS

The change of the T_g of bulk polymers when reducing one or more of its dimensions to nanometer scale is of interest to workers in fundamental research as well as in applications to technology. The experimental activities in the last decade are mostly on measurements of T_g of nanoscale polymer thin films, and only in recent years some studies of polymers confined inside nanoporous host systems have been reported [158]. The results reported so far are confusing. The glass temperature of polymers subject to nanometer-scale confinement have been reported to increase, decrease, or not changed, depending on the polymer, the geometry and nature of the confinement, and the technique of measurement [159]. For example, the T_g of free-standing thin polystyrene films was reported to decrease continuously with thickness h by about 60 K when h is near 20 nm as measured by ellipsometry and Brillouin scattering [160]. On the other hand, much smaller reductions of T_g were reported for thin polymer films on substrates, and free-standing atactic poly(methyl methacrylate) thin films of comparable molecular weight and thickness as polystyrene [158]. While T_g of isotactic poly (methyl methacrylate) films on aluminum are lower than that of the bulk and decrease with film thickness, the opposite is found if the films are sandwiched between two polystyrene films [161]. The change of T_g thus depends on the nature of the interfaces of the polymer thin film. This dependence resembles that found by molecular dynamics simulations of thin films of binary Lennard-Jones particles nanoconfined by walls defined by a smooth repulsive potential or by frozen binary Lennard-Jones particles [162]. A plausible explanation of the observed dependence of change of T_g on interface was given by the Coupling Model [163]. Experimental techniques and computer simulations that probe the viscoelastic response from global chain dynamics do not find the reduction of T_g in nanometer thin films as deduced by the studies of the local segmental dynamics [164].

For studies of polymers confined inside nanoporous host systems, the most comprehensive study was reported for poly(dimethyl siloxane) and poly(methylphenyl siloxane) down to 5 nm by neutron scattering and dielectric and calorimetric measurements [165]. An increase of molecular mobility, implying a decrease of T_g, was observed on decreasing the pore size. The increment of the specific heat capacity at the glass transition normalized by the mass of confined polymers also decreases with pore size, indicating a concomitant decrease of the cooperative length scale with a decrease of T_g. An explanation has been offered [163].

Excluding some experimental results which may turn out to be artifacts, the majority of the data in the literature are real and worth consideration. The variability of the results, arising from dependence on polymer, nature and geometry of confinement, and experimental techniques, does not necessarily mean that the situation is unmanageable. It makes

TABLE 12.4. *Selected T_gs for some common polymers.*

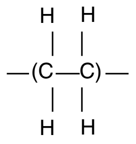
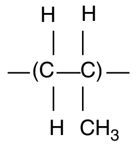
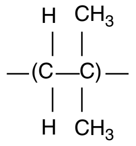
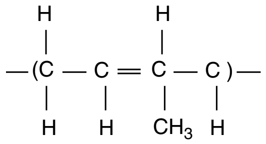
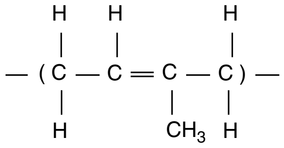
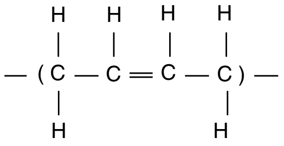
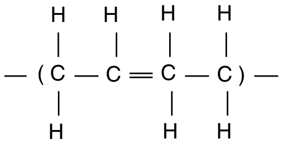
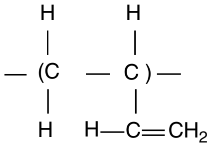
Name	Repeat unit	M_n	$T_g(q_c)$ °C(deg/ min.)	$T_{f,g}(q_c,q_h)$ °C	Method[a]	Reference
Nonaromatic hydrocarbon backbone polymers						
Polyethylene	 $-(\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}})-$	2×10^5		−26(−,2)	Lin. dil.	[112]
				−120	Lin. dil.	[122]
			−20,−130		Dil.	[135]
Polypropylene (amorphous)	 $-(\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}})-$	6×10^4		−10(10,10)	DSC	[113]
Polyisobutylene	 $-(\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{CH_3}{C}})-$	4.9×10^3	−76(0.017)		Dil.	[114]
		6.6×10^5	−76(0.2)		Dil.	[115]
Cis 1,4 polyisoprene	 $-(\overset{H}{\underset{H}{C}}-\underset{H}{C}=\overset{H}{\underset{CH_3}{C}}-\underset{H}{C})-$			−70	Lin. dil.	[122]
Trans 1,4 polyisoprene	 $-(\overset{H}{\underset{H}{C}}-\overset{H}{C}=\underset{CH_3}{C}-\overset{H}{\underset{H}{C}})-$		−58		Dil.	[132]
Cis 1,4 polybutadiene	 $-(\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}})-$		−105		Dil.	[121]
			−114		Dil.	[129]
Trans 1,4 polybutadiene	 $-(\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}})-$		−102		Dil.	[129]
1,2 Polybutadiene	 $-(\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H-C=CH_2}{C}})-$		−7		Dil.	[129]

TABLE 12.4. *Continued.*

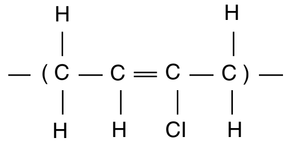
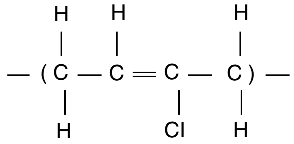
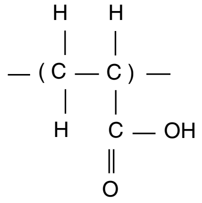
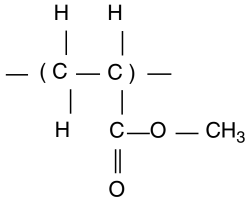
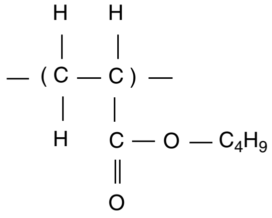
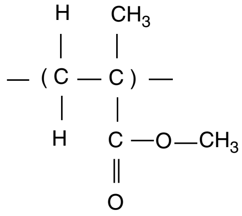
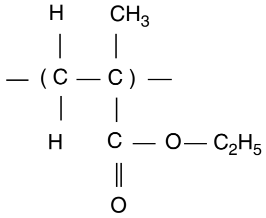
Name	Repeat unit	M_n	$T_g(q_c)$ °C(deg/min.)	$T_{f,g}(q_c,q_h)$ °C	Method[a]	Reference
Cis neoprene	 $-(CH_2-CH=CCl-CH_2)-$		−20		DTA	[130]
Trans neoprene	 $-(CH_2-CH=CCl-CH_2)-$		−45		DTA	[130]
		~ 10^5	−45 Lin. dil.	131		
			−40		Dil.	[132]
Polyacrylates						
Polylacrylic acid	 $-(CH_2-CH(COOH))-$		103		Lin. dil.	[127]
Polymethylacrylate	 $-(CH_2-CH(C(=O)-O-CH_3))-$	9 × 10^5	14(20)		DSC	[125]
			8		Dil.	[123]
Polybutylacrylate	 $-(CH_2-CH(C(=O)-O-C_4H_9))-$			−24	Dil.	[123]
Polymethyl-methacrylate	 $-(CH_2-C(CH_3)(C(=O)-O-CH_3))-$	~ $10^{5(b)}$	102.8(1)		Dil.	[5b]
		6.0 × $10^{4(c)}$		108(1)	DTA	[116]
		6.0 × $10^{4(c)}$		$110(1)^e$	DTA	[116]
		6.0 × $10^{4(c)}$	106(0.017)		Dil.	[116]
		~ 3 × 10^{5b}		120(−1)	DTA	[116]
		~ 3 × 10^{5b}		$122(-,1)^e$	DTA	[116]
		~ 3 × 10^{5b}	117(0.017)		Dil.	[116]
		~ 3 × 10^{5d}	43(0.5)		Dil.	[136]
Polyethyl-methacrylate	 $-(CH_2-C(CH_3)(C(=O)-O-C_2H_5))-$		66		Dil.	[123]
			65		Dil.	[126]
		~ 10^5				

TABLE 12.4. *Continued.*

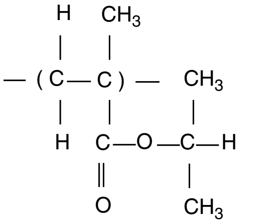
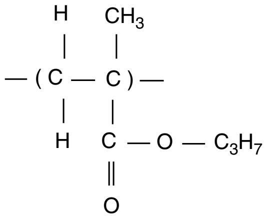
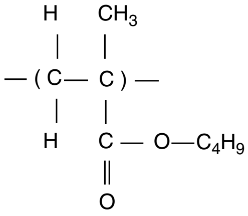
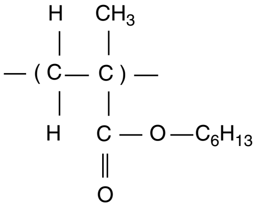
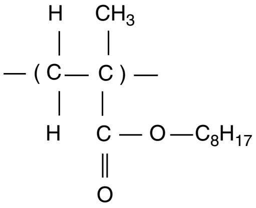
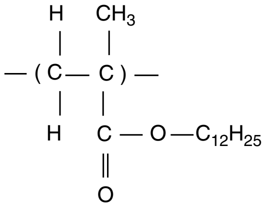
Name	Repeat unit	M_n	$T_g(q_c)$ °C(deg/ min.)	$T_{f,g}(q_c,q_h)$ °C	Method[a]	Reference
Poly-*i*-propylmethacrylate	 $-(\mathrm{CH_2}-\mathrm{C}(\mathrm{CH_3})(\mathrm{C(=O)-O-CH(CH_3)_2}))-$	$\sim 10^5$	81		Dil.	[123]
			88		Dil.	[126]
Poly-*n*-propylmethacrylate	 $-(\mathrm{CH_2}-\mathrm{C}(\mathrm{CH_3})(\mathrm{C(=O)-O-C_3H_7}))-$	$\sim 10^5$	35		Dil.	[124]
			43		Dil.	[126]
Poly-*n*-butylmethacrylate	 $-(\mathrm{CH_2}-\mathrm{C}(\mathrm{CH_3})(\mathrm{C(=O)-O-C_4H_9}))-$	$\sim 10^5$	19		Dil.	[123]
			20		Dil.	[124]
			23		Dil.	[126]
Poly-*n*-hexylmethacrylate	 $-(\mathrm{CH_2}-\mathrm{C}(\mathrm{CH_3})(\mathrm{C(=O)-O-C_6H_{13}}))-$		−5		Dil.	[124]
Poly-*n*-octylmethacrylate	 $-(\mathrm{CH_2}-\mathrm{C}(\mathrm{CH_3})(\mathrm{C(=O)-O-C_8H_{17}}))-$		−20		Dil.	[124]
Poly-*n*-dodecylmethacrylate	 $-(\mathrm{CH_2}-\mathrm{C}(\mathrm{CH_3})(\mathrm{C(=O)-O-C_{12}H_{25}}))-$		−65		Dil.	[124]

TABLE 12.4. *Continued.*

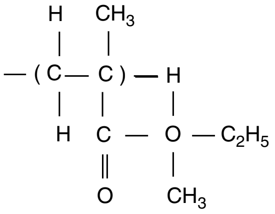
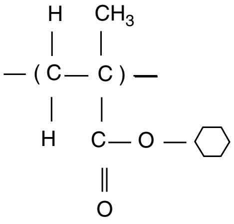
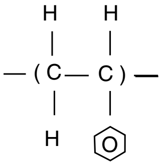
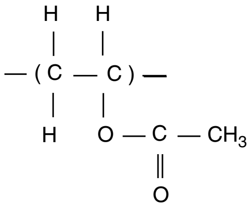
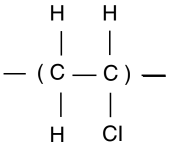
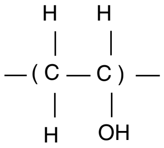
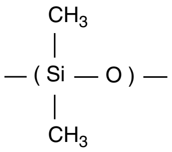
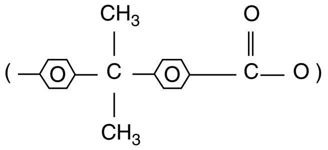
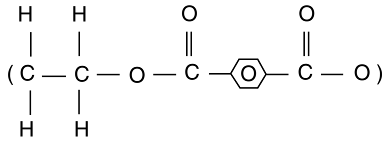
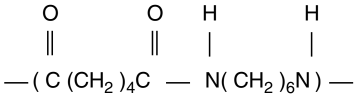
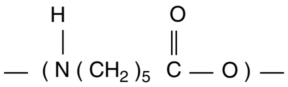
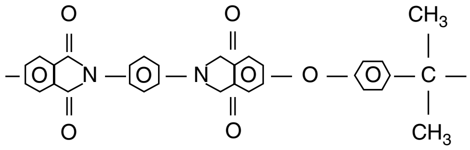
Name	Repeat unit	M_n	$T_g(q_c)$ °C(deg/ min .)	$T_{f,g}(q_c,q_h)$ °C	Method[a]	Reference
Poly-*i*-butylmethacrylate			53		Dil.	[124]
Poly-cyclo-hexylmethacrylate			66		Dil.	[123]
		$\sim 10^5$	62		Dil.	[126]
Vinyl polymers						
Polystyrene		2.1×10^5	94.8(1.0)		Dil.	[5b]
			92.1(0.1)		Dil.	[5b]
		9.2×10^4	97.5(0.2)		Dil.	[115]
Polyvinylacetate		$\sim 3 \times 10^5$	34.8(0.2)		Dil.	[115]
Polyvinylchloride		2.8×10^3	71.0(1.0)		Dil.	[5b]
Polyvinylalcohol				95	DTA	[128]
Heterogeneous backbone polymers						
Polydimethylsiloxane			−123(0.3)		Dil.	[117]

TABLE 12.4. *Continued.*

Name	Repeat unit	M_n	$T_g(q_c)$ °C(deg/ min .)	$T_{f,g}(q_c,q_h)$ °C	Method[a]	Reference
Bisphenol *A* polycarbonate			144		Lin. dil.	[118]
Polyethylene-terephthalate				70(10,10)	DSC	[119]
Nylon 66	 $-(\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{\|}{N}}(CH_2)_6\overset{H}{\overset{\|}{N}})-$	– –3 × 10^4	50(–,1)		DTA	[133]
			52		DTA	[134]
Nylon 6	 $-(\overset{H}{\overset{\|}{N}}(CH_2)_5\overset{O}{\overset{\|}{C}}-O)-$		40		DTA	[134]
Polyetherimide				213(80,10)	DSC	[120]

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[a] Dil. ≡ volume dialtometry; Lin dil. ≡linear dilatometry; DSC≡differential scanning calorimetry; DTA≡differential thermal analysis.

[b] ~75% syndiotactic.

[c] Ideally atactic.

[d] ~99% isotactic.

[e] Dried at 170 °C in vacuum for 68 h.

the problem more difficult, but more studies in the future should help to improve the understanding of the diverse experimental results.

12.17 WHEN DO VOLUME AND ENTROPY FIRST ENTER INTO DETERMINING MOLECULAR MOBILITY?

Conventional models or theories consider only the segmental relaxation of amorphous polymers and the primary relaxation of nonpolymeric glass-formers in the change of molecular mobility with temperature and pressure (and concomitant changes in free volume and/or configurational entropy) leading to vitrification. Here we wish to recognise two different kinds of secondary relaxation processes. There is one that precedes and leads *to* the primary relaxation and others that are not related such as side group motion which are independent of the chain backbone motion. The same can be said for secondary relaxations in nonpolymeric glass-formers that involve isolated intramolecular motion of a part of the basic unit. However, there are secondary relaxations which must involve the polymer backbone like polybutadiene (PB) and even polyisoprene (PI). The existence of a secondary relaxation in PB is well known [166], but in PI it was found only recently [167]. Equally intriguing is the appearance of secondary relaxations in rigid small molecule glass-formers such as toluene and chlorobenzene [168,169], where there are no internal degrees of freedom. Therefore these secondary relaxations must originate from some local intermolecular motion of the entire molecule. Such secondary relaxations are called the Johari–Goldstein (JG)

β-relaxation to honor their discovery of secondary relaxations even in totally rigid molecules. They are supposedly universal, existing in all glass-formers, and are considered to be the precursor of the primary structural relaxation. Some criteria for distinguishing JG β-relaxation from other garden variety of secondary relaxations have been established based on their properties that mimic the primary relaxation [170]. The relaxation time τ_β of JG β-relaxation has Arrhenius temperature dependence in the glassy state, but the actual temperature dependence of τ_β at temperatures above T_g is not a continuation of the Arrhenius temperature dependence below T_g. It is more like another VFTH temperature dependence that is weaker than that of τ_α [170–172]. Also τ_β is pressure dependent in the equilibrium liquid state ($T > T_g$) [170], and increases on physical aging in the glassy state [173]. Polymerization and cross-linking experiments on Epon 828 have shown that τ_β increases with the increase of covalent bonds formed during the process, which follows the trend of the primary relaxation [174–176]. In binary miscible mixtures of two glass-formers, the relation between τ_β and the primary relaxation time of a component changes systematically with the composition [177]. Although all the properties are less spectacular than that of the primary relaxation, they indicate that τ_β depends on volume and entropy. There is also good correspondence between τ_β and the primitive relaxation time τ_0 of the Coupling Model [170–171,173,178], the latter is definitely a precursor of the primary relaxation and is volume and entropy dependent.

The relaxation strength, $\Delta\varepsilon_\beta$, of the JG relaxation in all these glass-formers is found to change on heating through the glass temperature in a similar manner as the changes observed in the enthalpy H, entropy S, and volume V [179,180]. The derivative of $\Delta\varepsilon_\beta$ with respect to temperature, $\mathrm{d}\Delta\varepsilon_\beta/\mathrm{d}T$, increases from lower values at temperatures below T_g to higher values at temperatures above T_g, a mimicry of the same behavior of the specific heat C_p and the expansion coefficient, which are the derivatives $\mathrm{d}H/\mathrm{d}T$ and $\mathrm{d}V/\mathrm{d}T$, respectively.

Thus, volume and entropy have already entered into the determination of molecular mobility of the JG β-relaxation and τ_β, at times long before the emergence of the α-relaxation and τ_α in the equilibrium liquid state. Since time is the natural variable, the dependence of molecular mobility on temperature, pressure, volume, and entropy originate in τ_β or τ_0. The stronger dependences of the primary relaxation time on the same variables are the consequence of the many-molecule (cooperative and dynamically heterogeneous) dynamics that increase the magnitude of τ_β naturally. It is the involvement of an increasing number of molecules (proportional to the cooperative length-scale and the width of the dispersion) in the primary relaxation than that involved in the local JG β-relaxation. The results suggest models and theories of vitrification that address only the α-relaxation need a new paradigm [181].

Related information can be found in Chapter 13.

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CHAPTER 13

Sub-T_g Transitions

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There have been a number of good general reviews of relaxation processes that occur at temperatures below the glass-transition temperature (T_g) [1–6]. Early dynamic-mechanical studies were surveyed by Woodward and Sauer [7]. Although now outdated, the seminal work reviewing both dynamic-mechanical and dielectric data is still the excellent 1967 monograph by McCrum, Read, and Williams [8]. It is not the purpose of this review to approach the comprehensive coverage provided by McCrum et al. but to summarize important results for the major polymer groups and to include more recent studies, especially for engineering thermoplastics not available prior to 1967. Where appropriate, mention is made of recent efforts at molecular modeling that aid in understanding the nature of molecular processes that operate below T_g.

A variety of techniques can be used to detect relaxational processes occurring below T_g. These include dynamic-mechanical, dielectric, NMR (e.g., ^{1}H line width and pulsed ^{13}C NMR relaxation times), and thermally stimulated discharge current (TSC) measurements. Of these, dynamic-mechanical methods [9] have been the most widely used to study secondary-relaxation processes in polymers. These include free vibration methods, principally torsional pendulum [10,11] and torsional braid [12], and forced oscillation (FO) methods utilizing mechanically driven tensile, torsional, and flexural strains provided by a number of commercial instruments. The ability to vary oscillation frequency over a wide range makes FO (ca. 0.016–160 Hz) and dielectric techniques (ca. $10–10^6$ Hz) especially useful for the determination of activation energies. Early dynamic methods also included resonance electrostatic methods that provide dynamic data over a higher (acoustic) frequency range (ca. $10^3–10^4$ Hz) than is possible using FO dynamic mechanical methods. Basic principles and instrumentation for resonance electrostatic and other dynamic measurements are given by Ferry [13].

In the following sections, the results of dynamic-mechanical and dielectric measurements of important amorphous and semicrystalline polymers are summarized and conclusions regarding the origin of sub-T_g molecular motions are offered. As illustrated by Fig. 13.1, temperature assignments for principal relaxations are the temperatures at the maximum of the dynamic-mechanical or dielectric tan δ or loss modulus peaks at the reported frequencies. Values determined from tan γ data are slightly higher than those determined from loss modulus values, and temperature assignments increase with increasing frequency. Typically, peak assignments for T_g are slightly higher (ca. 15–20 °C) than obtained by dilatometry at low cooling rates. Where available, data for only dry, unconditioned samples are reported in this review.

13.1 AMORPHOUS POLYMERS

The prevailing view is that the glass transition (α relaxation in amorphous polymers) is associated with the coordinated motion of 50–100 carbon atoms and associated substituent groups about the chain axis, while secondary relaxations reflect the motions of smaller numbers (e.g., 4–8) of carbon atoms about the chain axis (e.g., crankshaft-type motions) or motions of substituent groups [1]. Sub-T_g relaxations occurring in the amorphous glass are labeled in order of decreasing temperature assignment as β, γ, and δ and reflect motions of progressively smaller molecular units with correspondingly lower activation energies.

The β relaxation in amorphous glasses has been assigned to the onset of motions which are precursors to

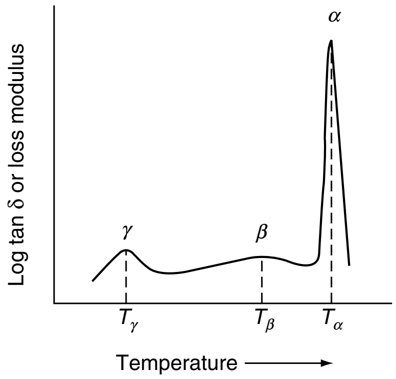


FIGURE 13.1. Idealized representation of the dynamic mechanical spectrum for an amorphous polymer illustrating temperature assignments for the $\alpha(T_g)$, β, and γ relaxations.

the long-range segmental motions occurring at T_g and, therefore, may be considered to be a general phenomenon of glassy materials, polymeric or otherwise [14–16]; however, the β relaxation is not always detectable and remains a somewhat controversial subject. In the case of a number of polymers such as polycarbonate [17], polysulfone [18,19], and polyarylates [20], the β relaxation has been attributed to defects in the glass and as such is affected by thermal treatment sometimes evident when the sample has been quenched from the melt but reduced or eliminated by annealing.

Several relationships have been proposed to relate the temperature assignment for the β transition to T_g. For example, Boyer [3] has suggested that (at 100 Hz)

$$T_\beta \approx 0.75T_g \tag{13.1}$$

for both amorphous and semicrystalline polymers, where temperature is in degrees Kelvin. Van Krevelen [21] has proposed that

$$T_\beta + T_g \approx 635 \tag{13.2}$$

for amorphous polymers and

$$T_\beta \approx 0.8T_g - 40 = 0.5T_m - 25 \tag{13.3}$$

for semicrystalline polymers, where T_m is the crystalline-melting temperature.

In general, secondary-relaxation processes are affected by sample history and the presence of diluents. For example, the method of film preparation (e.g., molding or casting), thermal history (annealed or quenched), and moisture absorption can affect the temperature range, activation energy, and magnitude of some sub-T_g transitions. The dynamic-mechanical and dielectric spectra of polyamides and related polymers such as poly(amide–imides) that are highly water absorbent are particularly sensitive to the presence of absorbed water. Thermal treatment (annealing or quenching) will affect the tail (onset) of the glass transition peak (β transition) but may have little affect on lower-temperature relaxations (i.e., γ peak) [22,23].

Secondary relaxation processes have been correlated with a number of physical and mechanical properties. For example, there is a good correlation between impact strength and the occurrence of main-chain secondary loss processes [24–26], especially for amorphous polymers [21]. There is also reasonable correlation between secondary loss processes and gas permeability [27–29].

Energies required for main-chain and side-group motions can be obtained by determining the effect of frequency on the maximum temperatures of the loss or tan δ peaks. The temperature at the peak maxima, T_{max}, increases with increasing frequency and the activation energy, E_a, of the relaxational process may be determined from the slope of a semilog plot of frequency (f) versus reciprocal peak-temperature ($1/T_{max}$) as

$$\ln f = -\left(\frac{E_a}{R}\right)\frac{1}{T_{max}} + \ln f_0, \tag{13.4}$$

where f_0 is a constant obtained from the intercept.

Typically, activation energies for low-temperature (i.e., γ) relaxations are small (ca. 10–80 kJ mol^{-1}). Heijboer [30] has suggested that for sub-T_g relaxations other than local main-chain motions

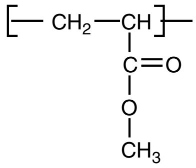
$$E_a = 0.060T_{max} \text{ (at 1 Hz)}, \tag{13.5}$$

where E_a is in kcal mol^{-1} and T_{max} is in degrees K. Activation energies are about 20% higher than given by Eq. (13.5) for main-chain motions. Corresponding activation energies for the glass transition, reflecting longer-range cooperative motions, are about an order of magnitude greater than those for sub-T_g relaxations.[†] High activation energies mean that the temperature location of the glass transition (i.e., the α relaxation in amorphous glasses) is relatively insensitive to a change in frequency compared to secondary-relaxation processes.

13.1.1 Poly(Alkyl Acrylates) and Poly(Alkyl Methacrylates)

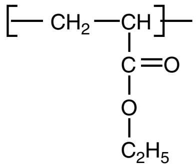
Dynamic-mechanical and dielectric data for several poly(alkyl acrylates) including poly(methyl acrylate) (PMA) (1), poly(ethyl acrylate) (PEA) (2), poly(n-butyl acrylate) (PBA) (3), and poly(cyclohexyl acrylate) (PCA) (4)

[†] In the case of the glass transition, the relationship between T_m and frequency is given by the WLF equation and not the Arrhenius relationship given by Eq. (13.4). Therefore, a semilog plot of f versus $1/T_{max}$ will appear curved over a sufficiently wide frequency range. An *apparent* activation energy for the glass (α_a) transition may be calculated from use of Eq. (13.4) over a more limited frequency range as is typical for most dynamic-mechanical measurements.



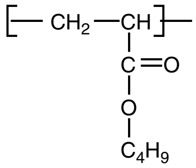
$-[CH_2-CH(C(=O)-O-CH_3)]-$

1



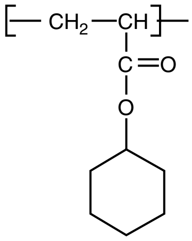
$-[CH_2-CH(C(=O)-O-C_2H_5)]-$

2



$-[CH_2-CH(C(=O)-O-C_4H_9)]-$

3



4

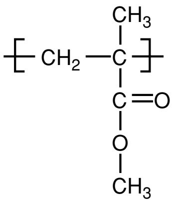
are given in Table 13.1. As shown by this data, the predominant (β) relaxation process in poly(alkyl acrylates) occurs at low temperatures (145–197 K) with an activation energy of ca. 30–60 kJ mol^{-1}. Both T_g and the β-relaxation temperature decrease with increasing length of the side chain in the case of linear alkane substitution (i.e., PMA>PEA>PBA) [31]. From ^{13}C NMR (spin-lattice relaxation time) measurements and molecular-dynamics simulations, Kikuchi et al. [32] have concluded that molecular motions in PEA and PBA consist of internal rotation or torsional oscillation of each functional group and a slower motion induced by backbone motion.

Also included in Table 13.1 are data for several poly(alkyl methacrylates) including poly(methyl methacrylate) (PMMA) (5), poly(ethyl methacrylate) (PEMA) (6), poly(2-hydroxyethyl methacrylate) (PHEMA) (7), poly(*n*-propyl methacrylate) (PnPMA) (8), poly(*n*-butyl methacrylate) (PnBMA) (9), and poly(isobutyl methacrylate) (PiBMA) (10).

The predominant sub-T_g process in poly(alkyl methacrylates) is the β relaxation (activation energy of 80–121 kJ mol^{-1}) appearing around 285–336 K and nearly independent of the length of the alkyl group (e.g., methyl, ethyl, propyl, and butyl) while T_g decreases with increasing side chain length (i.e., internal plasticization) [33]. In the case of PMMA, the intensity of the β relaxation of amorphous samples increases with increasing syndiotacticity but decreases with increasing isotacticity [34].^{13}C NMR studies have indicated that the nature of the β relaxation in PMMA may be a π (180°) flip of the OCO plane of the side group coupled to a random rotation (20° amplitude) of the main chain [35].

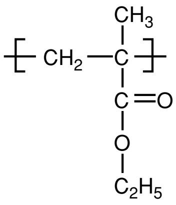
In the case of poly(methacrylates) with longer alkyl groups such as poly(isobutyl methacrylate) (PiBMA) and poly(*n*-butyl methacrylate) (PnBMA), a low-temperature (γ) relaxation is reported near 125–133 K due to side-chain motions involving the four-atom sequence —O—C—C—C or —C—C—C—C— [36]. Poly(isopropyl methacrylate) (PiPMA) which does not have this sequence does not exhibit a relaxation at 120 K but does show one at 50 K (1,000 Hz) similar to that reported for PEMA (see Table 13.1). In those two cases, the low-temperature (δ) relaxation is attributed to rotation of the isopropyl or ethyl group that is attached to the COO group [37]. Esteve-Marco et al. [38] have reported results of dielectric measurements and molecular mechanics calculations of poly(chloroethyl methacrylate) and poly(chloropropyl methacrylate).

Molecular-mechanics simulation has been used extensively to study molecular motions in poly(alkyl methacrylates). As an example, Cowie and Ferguson [33,39] have



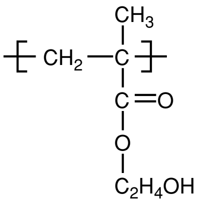
$-[CH_2-C(CH_3)(C(=O)-O-CH_3)]-$

5



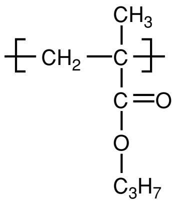
$-[CH_2-C(CH_3)(C(=O)-O-C_2H_5)]-$

6



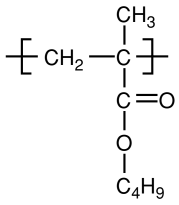
$-[CH_2-C(CH_3)(C(=O)-O-C_2H_4OH)]-$

7



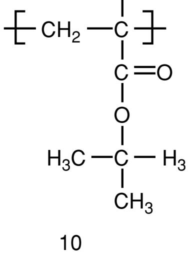
$-[CH_2-C(CH_3)(C(=O)-O-C_3H_7)]-$

8



$-[CH_2-C(CH_3)(C(=O)-O-C_4H_9)]-$

9



$-[CH_2-C(CH_3)(C(=O)-O-C(H_3C)(H_3)(CH_3))]-$

10

TABLE 13.1. *Glass-transition and secondary-relaxation temperatures of poly(alkyl acrylates) and poly(alkyl methacrylates).*

Polymer[a]	Technique[b]	f^c Hz	T_g (K)	$E_a{}^d$ kJ mol^{-1}	T_β (K)	E_a kJ mol^{-1}	T_γ (K)	E_a kJ mol^{-1}	T_δ (K)	E_a kJ mol^{-1}	Ref.
PMA	D	1,000	307		195	43					[31]
PEA	D	1,000	278		177	50					[31]
PBA	D	1,000	250		145	29					[31]
PCA	Dilatometry		290								[118]
	FO	1			197	60					
	D	1			192						
PMMA	TP	1			299						[24]
PMMA	FO	1	386	955	281	81					[119]
a-PMMA	TBA	1.24	388		297						[34]
s-PMMA	TBA	1.25	403		300						
i-PMMA	TBA	1.4	336		285						
PMMA	D					80					[120]
i-PMMA	FO										[121]
amorph.		3			336	105					
crystal.		3			311						
PEMA	D	110							50	9	[122]
PEMA	D	10			310	80					[120]
PHEMA	D	0.02			323	121					[120]
PnPMA	VR	40–600					123				[110]
PnBMA	VR	40–600					115				[110]
PnBMA	D	30					133	23			[37]
PnBMA						80					[110]
PiBMA	D	10					125	25			[37]

[a] PMA, poly(methyl acrylate); PEA, poly(ethyl acrylate); PBA, poly(*n*-butyl acrylate); PCA, poly(cyclohexyl acrylate); PMMA, poly(methyl methacrylate); PEMA, poly(ethyl methacrylate); PHEMA, poly(2-hydroxyethyl methacrylate); PnPMA, poly(*n*-propyl methacrylate); PnBMA, poly(*n*-butyl methacrylate); PiBMA, poly(isobutyl methacrylate).

[b] ES, resonance electrostatic method; FO, forced oscillation dynamic-mechanical analysis; FV, free vibration; TP, torsion pendulum; TSC, thermally stimulated discharge current measurement; D, dielectric; VR, vibrating reed.

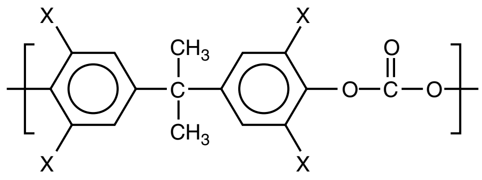
[c] $\omega = 2\pi f$ where ω is the angular frequency (rad s^{-1}) and f is frequency in units of Hz; 10 rad^{-1} = 1.5915 Hz.

[d] Apparent activation energy calculated from Eq. (13.4); 1 kJ mol^{-1} = 0.2387 kcal mol^{-1} = 0.0104 eV/molecule.

concluded that the β relaxation of PMMA is due to the rotation of the oxycarbonyl unit with an activation energy of 70–90 kJ mol^{-1}. Studies by Heijboer et al. [40] of (syndiotactic) PMMA indicate that the calculated barrier to alkoxycarbonyl group rotation is lower than experimentally observed for the β relaxation unless main-chain torsion angles are constrained. In the case of PnPMA, molecular-mechanics calculations suggest that the γ relaxation observed at about 90 K at 1 Hz (activation energy of 22 kJ mol^{-1}) could be attributed to hindered rotation around the O—CH_2—CH_2 bond of the propyl group; similar loss peaks have been observed in the case of poly(*n*-alkyl methacrylates) with longer alkyl groups (e.g., butyl, pentyl, and hexyl) [41]. Similar correlation of the δ relaxations of syndiotactic PEMA, PIPMA, and poly(cyclohexyl methacrylate) with limited rotations around the O-alkyl bond was made more recently by Heijboer et al. [42] through the use of molecular-mechanics calculations.

13.1.2 Polycarbonates

The most extensive studies of the dynamic-mechanical properties of polycarbonates have been reported by Yee et al. [17,43,44] and by Vardarajan and Boyer [45]. Some results of dynamic-mechanical and dielectric measurements of bisphenol-A polycarbonate (PC) and two tetrasubstituted bisphenol-A polycarbonates,



tetramethylbisphenol-A polycarbonate (TMPC, X = CH_3) and tetrachlorobisphenol-A polycarbonate (TCPC, X = Cl), are summarized in Table 13.2. Results for PC reveal a β relaxation in the range from 320 to 370 K and a γ relaxation in the range from 150 to 230 K. In addition, Varadarajan and Boyer [45] report a very low-temperature transition (δ) near 53 K. As appears to be the case of for several other thermoplastics such as poly(2,6-dimethyl-1, 4-phenylene oxide) and polysulfone, the β relaxation is affected by thermal history (i.e., observable in samples

TABLE 13.2. *Glass-transition and secondary-relaxation temperatures of polycarbonates.*

Polymer[a]	Technique[b]	f[c] Hz	T_g (K)	E_a[d] kJ mol^{-1}	T_β (K)	E_a kJ mol^{-1}	T_γ (K)	E_a kJ mol^{-1}	Ref.
PC	TP	0.5–1.2	423				164		[123]
PC	D	100	423				153		[124]
PC					373				[125]
PC	TP	1			340		183		[24]
PC	TP	1					173	36	[49]
PC	TP	1.24					165	44	[73]
PC	TSC	0.032					140	27	[46]
							219	50	
PC	FO	1	426	800			163	52	[119]
PC	D	10	423	800	>343 shoulder		173	10–45	[48]
PC	FO	1	423		353		173	54	[17]
PC	D	120	420	838			160		[47]
							220		
PC	FO	10–50			343	193	187		[45]
PC	TP	~1					173		[126]
PC	FO	1	411		343		178	59	[127]
PC	D	10^6					230	18	[128]
PC	D	100					188	48	[129]
	FO	90					222		
PC	FO	1	431		321		188		[130]
PC	FO	11					188	56	[43]
PC	FO	1	436						[131]
PC	NA						168		[106]
PC	TO	110	423		363		193		[78]
PC	FO	15.9					176	45	[132]
TMPC	FO	1	476				323	80	[133]
TMPC	FO	11					347	103	[43]
TMPC	NA						318		[106]
TCPC	TP	0.5–1.2					351		[123]

[a] Polymer abbreviations: PC, bisphenol-A polycarbonate; TMPC, tetramethylbisphenol-A polycarbonate; TCPC, tetrachlorobisphenol-A polycarbonate.
[b–d] Legend in Table 13.1.

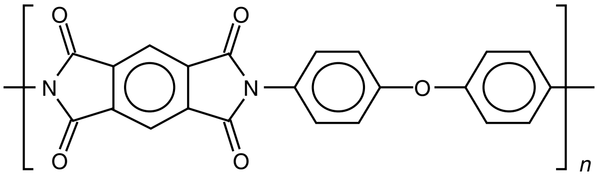
quenched from the melt but absent in annealed samples) [46,47]. There is evidence that the γ relaxation may consist of two [46–48] and possibly three [45] overlapping relaxations. The intensity of the γ relaxation peak has been reported to increase with increasing water content [49].

The molecular basis for sub-T_g molecular relaxations in the case of PC may include segmental motion and rotations of phenyl and methyl groups. The nature of these motions have been studied in detail by ^{13}C NMR spectroscopy and explored by semiempirical molecular-orbital (MO) calculations. Results of ^{13}C NMR measurements (spin–lattice relaxation times) by Jones and Bisceglia [50] indicate that several molecular processes may be coupled or synchronous. NMR studies by Schaefer et al. [51] have shown that the dominant motion in PC may be π flips of the phenylene ring about the main chain extending over a broad frequency range and superimposed on 30° ring oscillations; chlorine substitution of the rings eliminates both ring and main-chain motions. Activation energies of 37–50 kJ mol^{-1} for phenylene group motion have been obtained from NMR measurement [52,53]. Methyl-group substitution at the orthopositions (e.g., TMPC) shifts the onset of fast ring flips by about 180 K [54]. As indicated by the dynamic-mechanical data given in Table 13.2, the low-temperature relaxation (comparable to the γ relaxation in PC) reported for TMPC and TCPC occurs at substantially higher temperatures (ca. >320 K) than for PC in agreement with the NMR results. Comparison of the dynamic mechanical spectra of bisphenol-A PC with trimethylcyclohexylbisphenol PC and spirobisindane-PC for which phenylene ring motion is greatly restricted has led Wimberger-Friedl and Schoo [55] to conclude that the γ relaxation originates from motion of the carbonate group while phenylene group motion contributes as a separate mechanism to the high-temperature side of this relaxation.

Semiempirical MO calculations of model compounds suggest that the γ relaxation of PC may result from phenylene-ring flips (calculated activation energies of about 41 kJ mol^{-1}) as well as methyl-group rotation while the δ relaxation mentioned earlier may be due to *oscillations* of the phenylene ring and the methyl group as well as rocking motions of carbonyl groups [56,57]. In agreement with results from NMR studies, semiempirical MO calculations of TMPC indicate that phenylene rotation is restricted due to repulsion between the aromatic methyl group and the carbonyl oxygen atom [58].

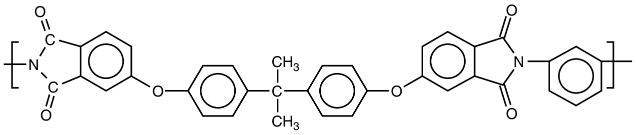
13.1.3 Polyimides and other Imide Polymers

Polyimides (PIs) represent a broad class of high-T_g polymers derived from the polycondensation of an aromatic dianhydride and diamine. The most widely investigated polyimide is polypyromellitimide or poly(4,4′-oxydiphenylenepyromellitimide) (Kapton®) whose repeat unit structure is given below

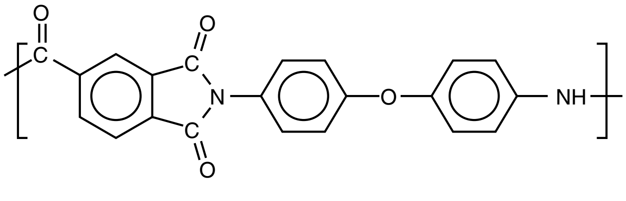


Very recently, Wang et al. [29] have reported dynamic mechanical data for a number of polyimides derived from 1,4-bis(4-aminophenoxy) 2-*tert*-butylbenzene (BATB) and 3,3′,5,5′-tetramethyl-bis[4-(4-aminophenoxy)-phenyl]sulfone (TMBPS). Temperatures for the γ relaxation (DMA, 1 Hz) ranged from 152 to 185 K for the BATB-based polyimides and 150–161 K for the TMBPS-based polyimides. In general, bulky groups in the dianhydride segment, such as the hexafluoroisopropylidene group of 6FDA, reduces polymer packing, increases fractional free volume, and consequently causes the γ relaxation to occur at lower temperature.

Other polymers that contain imide groups include polyetherimide (PEI) (e.g., Ultem®)



poly(amide-imide) (PAI) (e.g., Torlon®)



Representative dynamic-mechanical and dielectric data for Kapton PI, PEI, and PAI are given in Table 13.3. In general, an important sub-T_g relaxation for PIs is the β relaxation observed in the temperature range between 338 and 405 K and having an activation energy of about 84–117 kJ mol^{-1} [59]. In addition, PIs exhibit a γ relaxation in the range between 160 and 250 K that has been attributed to water absorption. For example, early dynamic-mechanical measurements of Kapton PI revealed two sub-T_g relaxations at 15,000 Hz—one at 400 K (β) attributed to torsional oscillations of the phenylene ring and another at 250 K identified here at the γ relaxation which was observed to increase in intensity with sorbed water [60]. Computer modeling suggests that the β relaxation is probably associated with the relatively noncooperative motion of the diamine unit which is suppressed by crystallinity or orientation [59]. Other molecular-dynamics simulations of Kapton PI reveal near out-of-phase torsional motions about the nitrogen–phenyl bonds that involve the whole chain and is not localized in one small region [61]. Molecular dynamics studies of a semicrystalline PI (PTDA–DMDA) by Natarajan and Mattice [62] suggest that π-flips of phenoxy rings in the amorphous phase covers a broad range of activation energies.

Dynamic-mechanical data for PEI given in Table 13.3 indicates a β relaxation at about 340–380 K and a γ relaxation at about 160–186 K. These relaxations are comparable to those cited above for Kapton although they occur at slightly lower temperatures. As in the case of Kapton, the γ-relaxational peak of PEI is reported to increase in intensity with sorbed water [63]. From comparison of the dielectric spectra of PEI, poly(ether sulfone) (PES) (see Section 13.1.6), and polyarylates with their corresponding low-molecular-weight compounds, Schartel and Wendorff [64] have concluded that both intrachain and interchain interactions contribute to the γ relaxation in these polymers.

Results of dynamic-mechanical measurements of a sample of PAI dried at 190°C are summarized in Table 13.3. The locations of the β- and γ-relaxational peaks at 338 and 204 K (at 1 Hz) are comparable to that of Kapton and PEI. As in the previous cases, sorbed water has been observed to increase the intensity and decrease slightly the temperature of the γ relaxation while the temperature and activation energy of the β relaxation increases with increasing water content [65].

13.1.4 Poly(phenylene oxides)

Dynamic-mechanical and dielectric properties of three poly(phenylene oxides)

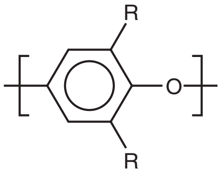


TABLE 13.3. *Glass-transition and secondary-relaxation temperatures of imide polymers.*

Polymer[a]	Technique[b]	f[c] Hz	T_g (K)	E_a[d] kJ mol^{-1}	T_β (K)	E_a Kj mol^{-1}	T_γ (K)	E_a kJ mol^{-1}	Ref.
PI	ES	15,000			400	84–105	250	66	[60]
PI	ES	14,000			405				[134]
PI	TP	1					185	44	[69]
PEI	TP	(~1)	485		343		168		[63]
PEI	FO	1	492		355		160 (shoulder)		[130]
PEI	FO	1	501	330–1,250					[135]
	D	1,000	513						
PEI	FO	35			379		186		[136]
PEI	D							43	[64]
PAI	FO	1	549		338	117	204		[65]

[a] PI, polypyromellitimide (Kapton polyimide) or poly(4,4'-oxydiphenylenepyromellitimide); PEI, poly(ether-imide); PAI, poly-(amide-imide).
[b–d] Legend given in Table 13.1.

poly(p-phenylene oxide) ($R = H$), poly(2,6-dimethyl-1,4-phenylene oxide) ($R = CH_3$), and poly(2,6-diphenyl-1,4-phenylene oxide) ($R = C_6H_5$), are summarized in Table 13.4. Dynamic measurements of poly(p-phenylene oxide) (H_2PPO) reveal a γ relaxation in the region of 120–160 K (1 Hz) having an activation energy of about 50 kJ mol^{-1}.

The majority of dynamic-mechanical studies for poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) provide evidence for only a weak shoulder (γ relaxation) in the vicinity of 125–160 K; however, a distinct peak has been observed by dielectric measurements [66,67]. In addition, there is evidence for a broad, low-intensity β peak in the range from 240 to 370 K. Sample preparation and impurities appear to have a significant effect on the appearance of the weak sub-T_g relaxational processes in PPO [68,69]. By comparison, dynamic-mechanical data for poly(2,6-diphenyl-1,4-phenylene oxide) (P_2PPO), a semicrystalline polymer ($T_m = 753$ K), suggests as many as three distinct sub-T_g relaxations [68,70].

In terms of intramolecular flexibility, the poly(2,6-disubstituted-1,4-phenylene oxides) are freely rotating chains [71]; however, intermolecular steric effects may limit phenylene rotation in the solid state and perhaps account for the absence of detectable sub-T_g relaxational processes. For example, results of ^{13}C NMR measurements indicate that the phenylene rings of PPO can execute only small amplitude motions due to the relative stiffness and dense packing of the PPO chain and blockage from rings on adjacent chains.

TABLE 13.4. *Glass-transition and secondary-relaxation temperatures of poly(phenylene oxides).*

Polymer[a]	Technique[b]	f[c] Hz	T_g(K)	E_a[d] kJ mol^{-1}	T_β(K)	E_a kJ mol^{-1}	T_γ(K)	E_a kJ mol^{-1}	Ref.
H_2PPO	ES	7,000	423				121 (shoulder)		[134]
H_2PPO	TP	1					160	50	[68]
H_2PPO	FO	110	363				155		[70]
PPO	ES	7,040			370	84	140 (shoulder)		[137]
PPO	TP	1			273		158		[24]
PPO	ES	7,000			370	84	140 (shoulder)		[134]
PPO	FO	110			240				[138]
PPO	D	100	512	628			158	36	[66]
PPO	D	100	517				157		[67]
PPO	TP	1					205	44	[49]
PPO	TP	~1.3			277	78	125 (shoulder)	40	[73]
PPO	TP	~1			286	67	135 (shoulder)	42	[68]
PPO	ES	9,640			373		126	29–34	[69]
P_2PPO	TP	~1			348	96	γ 238	50	[68]
							δ 83	17	
P_2PPO	FO	110	502		363		143		[70]

[a] H_2PPO, poly(p-phenylene oxide); PPO, poly(2,6-dimethyl-1,4-phenylene oxide); P_2PPO, poly(2,6-diphenyl-1,4-phenylene oxide).
[b–d] Legend given in Table 13.1.

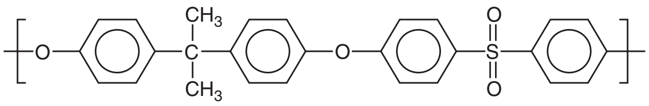
13.1.5 Polystyrenes

Molecular motions in polystyrene (PS) have been extensively reviewed by Boyer [72]. Results of dynamic-mechanical studies of polystyrene, poly(4-methylstyrene) (P4MS), poly(4-chlorostyrene) (P4CS), and poly(α-methylstyrene) (PAMS) are summarized in Table 13.5. These and other studies show evidence for three transitions for PS below T_g. These include β (ca. 325 K), γ (ca. 130–180 K), and δ (ca. 30–40 K) transitions with activation energies of about 147, 42, and 8–13 kJ mol^{-1}, respectively. The δ relaxation has been associated with hindered partial rotation and wagging of the phenyl group [73]. It decreases in intensity with crystallinity in isotactic PS [74]. The origin of the γ transition is less certain and may be due to motion of end groups.

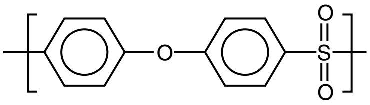
Results of molecular-dynamics simulations suggest that sub-T_g relaxations may include crankshaft-type motions of the PS backbone and librational motions of the pendant phenyl rings that depend upon the local environment [61]. NMR measurements indicate that the most prevalent molecular motion is restricted phenyl-group rotation with an average total displacement of ranging from 40° for *ortho*-substituted polystyrene to 70° for *para*-substituted polystyrenes having bulky nonpolar substituent groups [75]. Restrictions are due to intramolecular steric interactions and interchain packing (for unsubstituted PS). These conclusions are consistent with molecular mechanics studies reported by Khare and Paulaitis [76].

13.1.6 Polysulfones

Extensive studies of the dynamic-mechanical properties of a number of different polysulfones has been reported by Robeson et al. [77] and by Aitken et al. [78] Most of studies reported in the literature have focused on the two commercially important polysulfones — bisphenol-A polysulfone (PSF)



and polyethersulfone (PES)



Results of dynamic-mechanical and dielectric studies of PSF and PES are summarized in Table 13.6. Results for PSF indicate a well-defined γ relaxation located near 162–229 K. There is substantial evidence that the intensity of the γ-relaxational peak increases with sorbed water content [49,77,79]. Substitutions that hinder phenylene mobility increase the temperature of the γ relaxation [78]. There is controversy concerning the existence of a β relaxation located around 330–360 K that is sensitive to thermal history as has been reported for polycarbonate [18,19,80]. The dynamic-mechanical behavior of PES, which has a slightly lower T_g, is similar to that of PSF with a prominent γ relaxation that is also water sensitive [49] and is located in the region from 163 to 265 K.

Results of semiempirical molecular orbital (CNDO/2) calculations suggest that the γ relaxation is due to phenylene-group rotation of the isopropylidene moiety with a calculated activation energy of 42 kJ mol^{-1}, rotation of the methyl groups in the isopropylene group with an activation energy of 41 kJ mol^{-1}, and possibly the diphenyl sulfone rotation with an activation energy of 42 kJ mol^{-1} while the β relaxation is attributed to diphenyl ether rotation with an activation energy of 167 kJ mol^{-1} [18,19]. Molecular simulations have shown that the rotational barriers for C—O or C—C bonds are higher than those for C–S bonds in PSF and that the mechanism for relaxation in the bulk state may be due to cooperative ring-flip motions associated with rotations about the C—S linkage [81]. NMR studies have indicated that the β-relaxation is due to π flips of the aromatic rings that are unaffected by sorbed water but decrease in frequency in the presence of antiplasticizers [82]. Dynamic mechanical studies of PES by Shi et al. [83] indicated that the low-temperature (γ) transition (ca. 193 K) is associated

TABLE 13.5. *Glass-transition and secondary-relaxation temperatures of polystyrenes.*

Polymer[a]	Technique[b]	f[c] Hz	T_α(K)	T_β(K)	T_γ(K)	T_δ(K)	E_a kJ mol^{-1}	Ref.
PS	ES	5,590			185	38	8.4	[134]
PS	FO	110	379	325	133			[138]
PS	TP	1				38		[74]
PS	D	100	394		154			[67]
PS	TP	1.7				33		[73]
P4MS	ES	9,700				92	8.8	[134]
P4CS	ES	8,330				95	9.2	[134]
PAMS	ES	7,850				126	16	[134]

[a] PS, polystyrene; P4MS, poly(4-methylstyrene); P4CS, poly(4-chlorostyrene); PAMS, poly(α-methylstyrene).
[b–d] Legend given in Table 13.1.

TABLE 13.6. *Glass-transition and secondary-relaxation temperatures of bisphenol-A polysulfone and polyethersulfone.*

Polymer[a]	Technique[b]	f^c Hz	T_g(K)	$E_a{}^d$ kJ mol^{-1}	T_β(K)	E_a kJ mol^{-1}	T_γ(K)	E_a kJ mol^{-1}	Ref.
PSF	ES	6,088					229	50	[79]
PSF	TP	1	468				163		[139]
PSF	TP	1					206	70	[49]
	D	1,000					207		
PSF	TP	0.67					162		[73]
PSF	TP	1	448				183		[140]
PSF	FO	11			333		173		[80]
PSF	FO	1.59		920		282	173	45	[19]
PSF	FO	1	470				177		[130]
PSF	FO	110	459		358		193		[78]
PES	TP	1			273		163		[139]
PES	TP	1					226	55	[49]
PES	TP	1	476				183		[140]
PES	D	2.1×10^6					265	21	[128]
PES	TP	$\sim$1					178		[141]
PES	FO	35					170		[136]
PES							175		[106]
PES	FO	110	498				193		[78]
PES	D							45	[64]

[a] PSF, bisphenol-A polysulfone; PES, polyethersulfone.
[b–d] Legend given in Table 13.1.

with the rotation of phenylene rings. Recent quasielastic neutron scattering of PES [84] and PSF [85] have suggested that the γ and δ relaxations may be associated with π-flips and oscillations of phenyl rings, respectively.

13.1.7 Poly(vinyl chloride)

The dynamic spectrum of poly(vinyl chloride) (PVC) has been widely reported and reveals a major β relaxation located in the range from 195 to 273 K. Havriliak and Shortridge [86,87] have suggested that the molecular nature of the β relaxation in PVC is a hindered rotation of a segment about its main-chain axis. Results of dynamic-mechanical and dielectric studies of PVC are summarized in Table 13.7. PVC is weakly crystalline due to syndiotactic sequences of repeating units. Harrell and Chartoff [88] have shown that crystallinity shifts the α relaxation to slightly higher temperature, shifts the β relaxation to lower temperature, and reduces peak intensity. Kakutani et al. [89] have suggested that the β relaxation may be composed of two overlapping relaxational processes at 223 and 273 K due to motions in the amorphous and crystalline regions, respectively. Chlorination of PVC shifts the α relaxation to higher temperatures and broadens the β relaxation peak while plasticization decreases the β relaxation and shifts it to lower temperature (i.e., the high-temperature portion of the β peak is reduced) [90]. Molecular dynamics studies of torsional angles changes by Meier and Struik [91] suggest that a localized five-bond transition may result in activation energies responsible for the β relaxation and higher activation energies associated with the glass transition.

13.2 SEMICRYSTALLINE POLYMERS

Boyd has provided a detailed review of relaxational processes that occur in semicrystalline polymers [92] as well as a discussion of their molecular origins [93]. In general, the dynamic-mechanical and dielectric spectra of semicrystalline polymers are more complex than those of amorphous ones. This complexity results from the presence of additional transitions resulting from crystalline regions, varying degrees of crystallinity in different samples, and the possibility of different crystalline forms. While discussing the dynamic-mechanical and dielectric properties of semicrystalline polymers in this section, the usual convention will be used where the α peak is now associated with the crystalline–melting transition, the β peak is commonly identified with the glass-transition of the amorphous region, and sub-T_g relaxations are indicated as γ and δ [92].

13.2.1 Polyamides

Dynamic-mechanical and dielectric data have been widely reported for most aliphatic polyamides, especially poly(ε-caprolactam) (nylon-6 or PA-6; $T_g \approx 313$ K) and poly(hexamethylene adipamide) (nylon-6,6 or PA-6,6; $T_g \approx 323$ K). Results of dynamic-mechanical and dielectric measurements of PA-6 and PA-6,6 (Table 13.8) provide evidence for three relaxations (β, γ, and δ) in these polymers at temperatures below their crystalline–melting temperature T_m (487–506 K for PA-6 and 523–545 K for PA-6,6) [8]. The β relaxation (located at above 310–347 K for PA-6,6 and 357–370 K for PA-6,6) is associated with high

TABLE 13.7. *Glass-transition and secondary-relaxation temperatures of PVC.*

Technique[a]	f[b] Hz	T_g(K)	E_a[c] kJ mol^{-1}	T_β(K)	E_a kJ mol^{-1}	Ref.
D			364		63	[96]
TP	~2	358		223	63	[90]
D			524		63	[142]
TP	1			208–218	42–54	[143]
FO (D)	110			223 (β_2)	67	[89]
				273 (β_1)	45	
D					50–60	[144]
TP	~2			233		[145]
FO	3.5			239	65	[88]
FO		360	754	226	54	[119]
FO	11			235		[146]
TSC				195		[147]

[a] ES, resonance electrostatic method; FO, forced oscillation dynamic-mechanical analysis; FV, free vibration; TP, torsion pendulum; TSC, thermally stimulated discharge current measurement; D, dielectric; VR, vibrating reed.
[b] $\omega = 2\pi f$ where ω is the angular frequency (rad s^{-1}) and f is frequency in units of Hz; 10 rad^{-1} = 1.5915 Hz.
[c] Apparent activation energy calculated from Eq. (4); 1 kJ mol^{-1} = 0.2387 kcal mol^{-1} = 0.0104 eV/molecule.

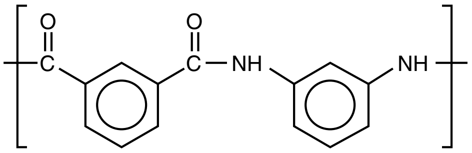
TABLE 13.8. *Secondary-relaxation temperatures of polyamides.*

Polymer[a]	Technique[b]	f[c] Hz	T_β (K)	E_a[d] kJ *mol*$^{-1}$	T_γ (K)	E_a kJ *mol*$^{-1}$	T_δ (K)	E_a kJ *mol*$^{-1}$	Ref.
PA-6	D					61			[96]
PA-6	ES	~10,000	310		241		156		[97]
PA-6	TP	~1	330		203		123		[94]
PA-6	FO	1	347						[131]
PA-6	FO	1	335		220		147		[148]
PA-66	VR	40–600			249		156		[110]
PA-66	FO	11	363						[149]
PA-66	FO		357		245		186		[95]
PA-66	FO	1	370						[131]
Nomex	ES	~10,000			291 (γ)				[97]
					442 (γ^*)				
Nomex	TP	~1	550	665	352	83	120	24	[98]
Kevlar	ES	~10,000			291 (γ)	63			[97]
					417 (γ^*)	92			
Kevlar	FO	110	733	767	333	204	243	52	[99]
Kevlar	TP	~1	816	813	235 (γ)	54	115	21	[98]
					440 (γ^*)	83			

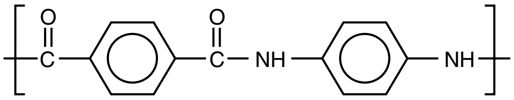
[a] Polymer abbreviations: PA-6,6, nylon-66; PA-6, nylon-6; Nomex, poly(*m*-phenylene isophthalamide); Kevlar, poly(*p*-phenylene terephthalamide).
[b–d] Legend given in Table 13.1.

activation-energy molecular motions occurring in the amorphous phase (i.e., glass transition) that are affected by the overall degree of crystallinity and crystalline morphology [94] as well as plasticization by sorbed water [95]. The γ relaxation (ca. 200–240 K for PA-6) is comparatively weak with an activation energy approximately 61 kJ mol^{-1} [96]. The γ relaxation increases in intensity with sorbed water suggesting motions involving (amide) carbonyl groups that are hydrogen bonded to water molecules. The intensity of the γ relaxation increases with the relative concentration of amide groups and shifts to lower temperatures in the presence of sorbed water [97]. The δ relaxation (activation energy of ca. 42 kJ mol^{-1} in the case of PA-6) occurs at ca. 120–160 K and is believed to be due to motions of the methylene groups [94]. Frosini and Butta [97] have suggested that the δ relaxation occurs at about the same temperature (160–180 K at $\sim 10^4$ Hz) for all aliphatic polyamides but increases in intensity with increasing number of methylene groups.

Two important aromatic polyamides (aramids) are poly(*m*-phenylene isophthalamide) (Nomex) ($T_g > 503$ K)



and poly(p-phenylene terephthalamide) (Kevlar) ($T_g \sim$ 618 K)



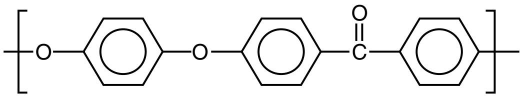
Unfortunately, the number of good dynamic mechanical and dielectric studies of well-characterized samples is limited. Some dynamic mechanical data for these two aramids are given in Table 13.8. A study by Badayev et al. [98] (Table 13.7) indicates that although the β and γ peaks of these aramids are located at temperatures higher than those for the aliphatic polyamides, their activation energies are comparable with those of the two aliphatic polyamides. Both aliphatic and aromatic polyamides display a low-temperature relaxation (δ) at ca. 115–190 K; however, a molecular mechanism other than methylene group motion suggested for aliphatic polyamides must exist for the aramids. Kunugi et al. [99] report three principle relaxations (β, γ, and δ) for Kevlar fiber where the δ relaxation was observed to be more prominent in the presence of sorbed water. The results of Kunugi et al. for annealed samples and those of several other investigations (Table 13.8) indicate that the γ peak of aramids may appear as two weak peaks – one in the region above and below room temperature (291–333 K) and one at 417–440 K (γ^*) with a slightly higher activation energy.

13.2.2 Poly(alkylene oxides)

Results of dielectric and dynamic-mechanical measurements of several poly(alkylene oxides) including poly(oxymethylene) (POM), poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), and poly(tetramethylene oxide) (PTMO) are summarized in Table 13.9. The sub-T_g γ-relaxation in PEO has been attributed to local twisting motion of main chains in both amorphous region and defective regions of the crystalline regions [100]. The γ relaxation (amorphous) has been reported to increase as the proportion of oxygen in the main chain increases (i.e., POM > PEO > PPO > PTMO).

13.2.3 Poly(aryl ether ether)

Results of dynamic-mechanical measurements of poly(aryl ether ether ketone) (PEEK) ($T_m = 613$–673 K)



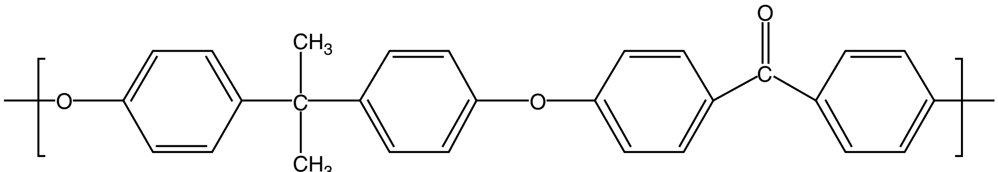
are summarized in Table 13.10. An β peak corresponding to the glass transition occurs at about 420 K and is sensitive to the crystalline morphology of the sample [101]. Candia et al. [102] report two β peaks at 423 and 488 K where the higher temperature peak represents reorganization following the crystallization process. In addition, there is evidence for a broad γ relaxation in the region between 170 and 213 K which may be due to contributions from two [103,104] or three [105] overlapping relaxations. This low-temperature sub-T_g relaxation has been attributed to localized wagging of the polar bridges within the amorphous regions while the high-temperature relaxation is attributed to a combination of wagging motions and phenylene flips and is affected by intermolecular interactions [101].

Sommer et al. [106] have looked at the effect of substituent group structure of the bisphenol groups on the T_g and the γ-relaxation temperature of the following four polyetherketones (PEKs):

TABLE 13.9. *Glass-transition and secondary-relaxation temperatures of poly(alkylene oxides).*

Polymer[a]	Technique[b]	f^c Hz	T_β(K)	$E_a{}^d$ kJ mol^{-1}	T_γ(K)	E_a kJ mol^{-1}	Ref.
POM	TP	1			203		[24]
POM	D	2.1×10^6			247	19	[128]
PEO	TP	1	206	126–147			[150]
PEO	D	12,800	236		198	38	[100]
PEO	D	20			140	33	[151]
PPO	VR		228		164		[110]
PPO	TP	1	211				[150]
PPO	D	2,000	208	130–155	150	25–30	[152]
PTMO	VR	40–600	221		164		[110]
PTMO	D	2,000	188–198	155–163		13–21	[152]

[a] POM, polyoxymethylene; PEO, poly(ethylene oxide); PPO, poly(propylene oxide); PTMO, poly(tetramethylene oxide).
[b–d] Legend given in Table 13.1.



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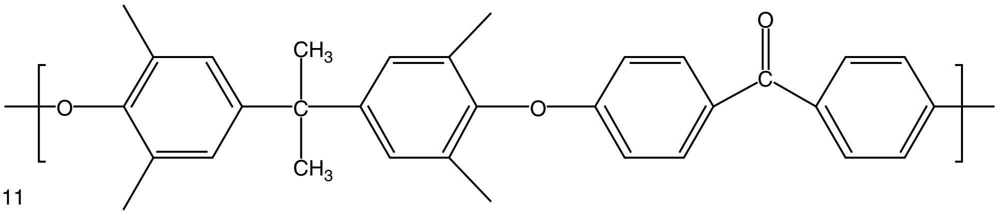

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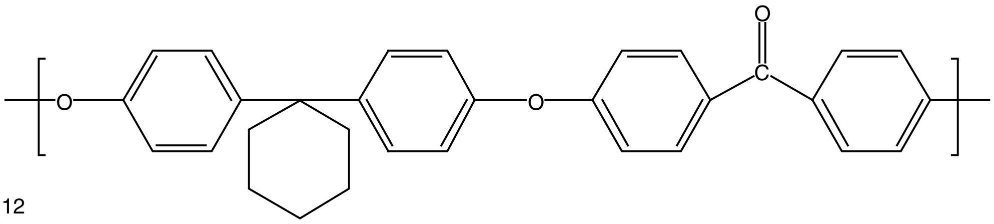

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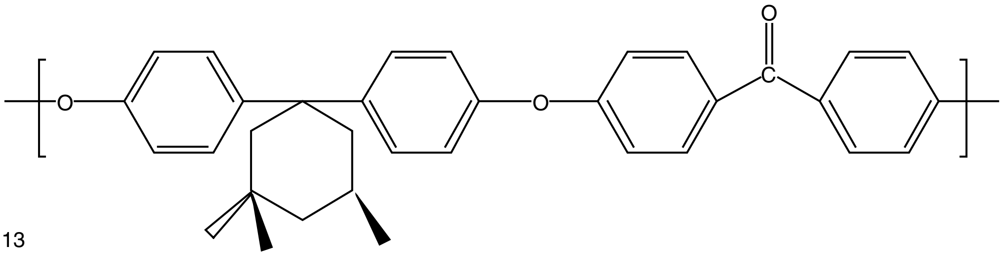

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As shown by the data in Table 13.10, the temperature for the γ relaxation increases with increasing steric hindrance to rotation of the bisphenol group in the order PEK(10) >*TMBPA-PEK*(11) > *BPZ-PEZ*(12). Methyl substitution of the cyclohexylidene ring in the case of TMC-PEK(13) lowers the γ temperature compared to PPZ-PEZ.

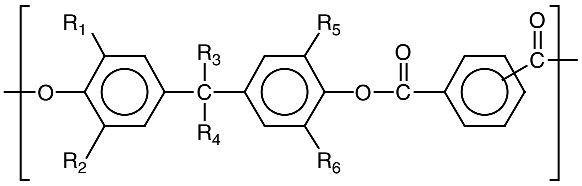
13.2.4 Polyesters

Dielectric and dynamic mechanical data for poly(ethylene terephthalate) (PET) ($T_m \approx 538$ K), poly(butylene terephthalate) (PBT) ($T_m \approx 493$ K), and several fully aromatic polyesters or polyarylates having the general structure shown below

TABLE 13.10. *Glass-transition and secondary-relaxation temperatures of poly(aryl ether ether).*

Polymer[a]	Technique[b]	f^c Hz	T_β (K)	$E_a{}^d$ kJ mol^{-1}	T_γ (K)	E_a kJ mol^{-1}	Ref.
PEEK	TP	~1	423		193		[105]
	TP	~1	416		176		[63]
	TP	~1			183	30–100	[103]
	FO	35			170		[136]
	FO	5		amorph. 1,250–1,900	213	80	[104]
	FO	110	423		208	31	[102]
PEK	NA				180		[106]
TMBPA-PEK					198		[106]
BPZ-PEK					209		[106]
TMC-PEK					191		[106]

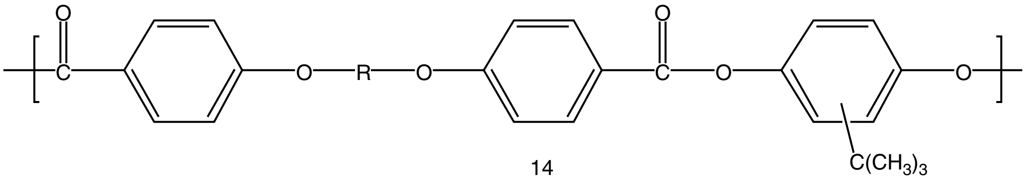
[a] PEEK, poly(aryl ether ether ketone); PEK, bisphenol-A polyetherketone; TMBPA-PEK, tetramethylbisphenol-A PEK; BPZ-PEK, PEK from cyclohexylidene; TMC-PEZ, PEK from trimethyl-cyclohexylidene PEK.
[b–d] Legend given in Table 13.1.



are summarized in Table 13.11. Results for both PET and PBT are comparable with a $\beta(T_g)$ relaxation observable in crystalline samples in the region from 344 to 366 K and a sub-T_g γ-relaxation in the region of 188–237 K. The β-relaxation temperature increases with crystallinity while the γ relaxation is relatively unaffected [107].

Charati et al. [20] have reported dynamic-mechanical data for a number of different polyarylates. They concluded that the γ relaxation originates from defects of the glass and is reduced through thermal annealing. A δ relaxation (water sensitive) was attributed to phenylene motion in the bisphenol moiety and is shifted to high temperatures with substitution of the bisphenol moiety. From molecular-mechanics calculation of conformational energies of three polyarylates derived from terephthalic acid, Charati et al. [108] have concluded that low-energy π phenyl-ring flips are possible through cooperative motions of both rings. From dielectric measurements of several polyarylates and related polymers, Schartel and Wendorff [64] concluded that the δ relaxation (activation energy of $\sim$ 46 kJ mol^{-1}) must involve both intrachain and interchain contributions with a correlation length of no greater than a single repeat unit.

del Campo et al. [109] have reported the dielectric spectra of a series of nematic polyesters following the form of structure 14 where R is a methylene chain of 4, 6, 8, 10, or 12 units. They attributed the β and γ relaxations to local reorganizations of the mesogenic units and the methylene units of the spacer groups, respectively. The characteristics of the molecular motions associated with the β relaxation are influenced by the conformation arrangement of chains in the nematic phase.



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13.2.5 Polyolefins

The presence of a varying numbers of side branches having different lengths and varying levels of crystallinity in different grades of polyethylene (PE), including low-density (LDPE), linear low-density (LLDPE), and high-density polyethylene (HDPE), complicate the interpretation of the dynamic-mechanical spectrum of this polymer. In addition, the nonpolar nature of polyethylene makes it unsuitable for dielectric analysis in its unmodified form although electrical properties can be enhanced by irradiation in air. In general, the relaxational processes in polyethylene may be characterized as α, β, and γ in order of decreasing temperature. The α process has been associated with the melting of PE crystallites of different sizes and decreases in intensity with decreasing crystallinity as may be achieved through irradiation [110] or chlorination as examples. The α-peak temperature is higher for high-density samples. There is evidence that the overall α process may result from two and possibly three different mechanisms [111]. Alberola et al. [112] report

TABLE 13.11. *Glass-transition and secondary-relaxation temperatures of polyesters.*

Polymer[a]	Technique[b]	f^c Hz	T_β (K)	$E_a{}^d$ kJ mol^{-1}	T_γ (K)	E_a kJ mol^{-1}	T_δ (K)	E_a kJ mol^{-1}	Ref.
PET	TP	1	292 (amorph.) 365 (cryst.)	770	208	52 (wet) 71 (dry)			[153]
PET	D								[142]
amorph.				829		63			
Crystal.				387		NA			
PET	D					50			[154]
PET	FO	1	366						[131]
PBT	D					50			[154]
PBT	D	10,000	344	281	237	55			[155]
	FV	10	334		188				
PBT	FO	1	353						[131]
PBT	D	1,600	355	483	198	27			[107]
PAR	FO	1.6	423–587	1,060–1,144	353–493	369	172–383		[20]

[a] PET, poly(ethylene terephthalate); PBT, poly(butylene terephthalate); PAR, various polyarylates.
[b–d] Legend given in Table 13.1.

TABLE 13.12. *Glass-transition and secondary-relaxation temperatures of polyolefins.*

Polymer[a]	Technique[b]	f^c Hz	T_α (K)	$E_a{}^d$ kJ mol^{-1}	T_β (K)	E_a kJ mol^{-1}	T_γ (K)	E_a kJ mol^{-1}	Ref.
LDPE	VR	40–600			265		159		[110]
LDPE	D	1,000					153 175	48	[113]
HDPE	TP	1					153		[24]
HDPE	TP	1					152		[114]
LLDPE	FV	1.59	297–303		256		149		[156]
i-PP	FV	1	325–400	110–170	275	380			[115]
i-PP	TP	1	343–359		279				[116]

[a] LDPE, low-density polyethylene; HDPE, high-density polyethylene; LLDPE, linear low-density polyethylene; *i*-PP, isotactic polypropylene.
[b–d] Legend given in Table 13.1.

two high-temperature (α) processes in the temperature range from 303 to 393 K with activation energies of 80–210 kJ mol^{-1}. The weak β relaxation, particularly evident in low-density samples, is typically observed between 220 and 280 K and is sometimes identified with motions in the interlaminar region (amorphous–crystalline interphase) and is observed to decrease in intensity upon annealing [113]. The γ relaxation typically lies in the temperature range from 123 to 153 K. Willbourn [110] has suggested that this transition is characteristic of coordinated motions of a minimum of three or four methylene groups (e.g., crankshaft-type mechanism). The γ relaxation is observed to increase in intensity as sample crystallinity increases and the α peak decreases. In the case of LDPE, as many as three low-temperature (γ) relaxations have been detected by TSC measurements [113]. Both the β and γ relaxations have characteristics that may be associated with the glass transition such as high activation energy (ca. 150–200 kJ mol^{-1}) and WLF dependence [112] although the β relaxation may be associated with side chain motions involving CH_3 groups [114]. It is also noted that polyethylene can achieve structural recovery by annealing at temperatures below the γ-relaxation temperature [112].

Some representative dynamic-mechanical data for isotactic polypropylene (*i*-PP) are given in Table 13.12. It is noted that the activation energy of the α relaxation is smaller than that of the β relaxation (glass transition of amorphous fraction) suggesting a less cooperative process attributed to the diffusion of defects in the crystalline phase [115]. Jawad and Alhaj-Mohammad [116] associated the β relaxation with the glass transition and report that the intensity of the β peak decreases with drawing suggesting that β relaxation depends on mobility of chains in the amorphous regions.

13.2.6 Poly(phenylene sulfide)

Poly(*p*-phenylene sulfide) (PPS) ($T_m \approx 558$ K) exhibits only weak sub-T_g relaxational processes. Dynamic-mechanical data [68,70] suggest a low-temperature (δ) relaxation in the region of 165–233 K with an activation energy of about 46 kJ mol^{-1} [68]. There may be a higher-temperature relaxation at 313 K (γ) and one at 361 K (β) [70]. Deuterium NMR studies of deuterated amorphous PPS by Henrichs et al. [117] suggest that PPS can undergo rapid π flips with a distribution of activation energies centered about 46 kJ mol^{-1}.

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CHAPTER 14

Polymer–Solvent Interaction Parameter χ

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Many thermodynamic properties of polymer solutions such as solubilities, swelling equilibria, and the colligative properties can be expressed in terms of the polymer-solvent interaction parameter χ. This unitless quantity was originally introduced by P. J. Flory [1] and M. L. Huggins [2] as an exchange interaction parameter in their lattice model of polymer solutions. In their definition, the quantity $kT\chi$ (k is the Boltzmann constant; T, the absolute temperature) is the average change in energy when a solvent molecule is transferred from pure solvent to pure, amorphous polymer. The reader is referred to Flory [3] for details. However, as explained in the following section, for this compilation χ is defined empirically, independent of the Flory–Huggins or any other model.

Values of χ have been collected in the table below for binary mixtures of homopolymers and low molecular weight liquids. Interaction parameters for systems with two polymeric components, i.e., polymer blends, can be found in Chapter 19. Other tabulations of χ are available [119,120,136].

14.1 DEFINITION

The change in the Gibbs free energy for mixing two components at constant temperature T and pressure P depends on the heat ΔH_{mix} and entropy ΔS_{mix} of mixing through the general thermodynamic relation

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}. \tag{14.1}$$

In the case of n_2 moles of an amorphous polymer dissolving in n_1 moles of solvent, the combinatorial contribution to the entropy of mixing [1–3] is

$$\Delta S_{\text{mix}}^{(\text{comb})} = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2). \tag{14.2}$$

Here, R is the gas constant and ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively, in the resulting solution. The volume fraction of polymer can be expressed in terms of the weight fraction w_2 of polymer and densities ρ_1 and ρ_2 of the pure components:

$$\phi_2 = 1 - \phi_1 = \frac{w_2\rho_1}{\rho_2 + w_2(\rho_1 - \rho_2)}. \tag{14.3}$$

That part of ΔG_{mix} that exceeds the contribution from the combinatorial entropy, namely,

$$\Delta G_{\text{mix}}^{\text{R}} = \Delta G_{\text{mix}} - (-T\Delta S_{\text{mix}}^{(\text{comb})}), \tag{14.4}$$

is the residual free energy [4].

Many thermodynamic properties of interest can be directly related to the change that the chemical potential of the solvent undergoes on mixing,

$$\mu_1 - \mu_1^0 = \left(\frac{\partial \Delta G_{\text{mix}}}{\partial n_1}\right)_{T,P,n_2} \tag{14.5}$$

Differentiation of Eq. (14.4) with respect to n_1 yields the residual chemical potential,

$$(\mu_1 - \mu_1^0)^R = (\mu_1 - \mu_1^0) - RT[\ln(1 - \phi_2) + \phi_2(1 - 1/x)], \tag{14.6}$$

where x is the ratio of the molar volume of polymer to that of solvent:

$$x = \frac{\rho_1 M_2}{\rho_2 M_1}. \tag{14.7}$$

M_1 and M_2 are the (number-average) molecular weights. The unitless interaction parameter χ is defined for this compilation as a reduced residual chemical potential using Eq. (14.6):

$$\chi = \frac{(\mu_1 - \mu_1^0)^R}{\phi_2^2 RT} = \frac{(\mu_1 - \mu_1^0)}{\phi_2^2 RT} - \frac{\ln(1-\phi_2) + \phi_2(1 - 1/x)}{\phi_2^2}. \qquad (14.8)$$

14.2 METHODS OF MEASUREMENT

Most of the entries in the table below were obtained from osmotic pressure, vapor sorption, or inverse gas chromatography measurements [5].

Osmotic pressure measurements can be used to evaluate χ at small volume fractions of polymer. The osmotic pressure Π of a solution relative to pure solvent is related to the chemical potential and, with Eq. (14.8), to χ through the thermodynamic expression

$$\mu_1 - \mu_1^0 = -\Pi V_1, \qquad (14.9)$$

where V_1 is the molar volume of solvent. The interaction parameter in the limit of infinite dilution can also be determined from the second virial coefficient A_2, i.e., the slope of a plot of Π/RTc_2 versus the concentration $c_2 = \rho_2\phi_2$ (i.e., mass of polymer per volume of solution) at $c_2 = 0$:

$$\chi = \frac{1}{2} - A_2 V_1 \rho_2^2. \qquad (14.10)$$

Vapor sorption studies yield values of χ for solutions at intermediate-to-high polymer concentrations. The vapor pressure P_1 of solvent above a polymer solution relative to that of pure solvent P_1^0 at the same temperature is

$$(\mu_1 - \mu_1^0) = RT \ln\frac{P_1}{P_1^0}. \qquad (14.11)$$

Substitution for $(\mu_1 - \mu_1^0)$ in Eq. 14.8 from Eq. 14.11 yields χ.

Inverse gas chromatography can be used to obtain the polymer-solvent interaction parameter in the limit of $\phi_2 = 1$. Here χ is found from the retention volume of the low molecular-weight component in the vapor phase as it is eluted over the polymer which is the stationary component in a gas-phase chromatography experiment.

The Flory Θ-temperature affords another means of determining the interaction parameter. The Θ-temperature is defined [3] such that at $T = \Theta$ and $\phi_2 = 0$, $\chi = 1/2$. Θ-temperatures are tabulated in Chapter 15.

14.3 GENERAL FEATURES AND SIGNIFICANCE

For many systems, χ has been found to increase with polymer concentration and decrease with temperature with a dependence that is approximately linear with, but in general not proportional to, $1/T$. According to Eqs. 14.5 and 14.8, for a given volume fraction ϕ_2 of polymer, the smaller the value of χ, the greater the rate at which the free energy of the solution decreases with the addition of solvent. Consequently, liquids with the smallest χ's are usually the best solvents for a polymer. Negative values of χ often indicate strong polar attractions between polymer and solvent. Solutions for which χ increases with increasing temperature at constant ϕ_2 have a negative partial molar heat of mixing, $(\partial \Delta H_{\mathrm{mix}}/\partial n_1)_{P,T,n_2} < 0$, i.e., the addition of a small quantity of solvent to a solution is exothermic. In the limit of infinite molecular-weight polymer, $\chi = 1/2$ at the critical solution temperature which occurs at $\phi_2 \to 0$ and $T = \Theta$.

The interaction parameters tabulated in Table 14.1 have been collected either directly from the sources cited or from an earlier compilation [5]. For some entries, a range of χ values is given, representing measurements made over a range of temperatures or concentrations. In these cases, the first value in the range of χ's corresponds to the first temperature or concentration in the range of temperatures or concentrations, with χ varying monotonically between the extremes. For example, in the system poly(dimethyl siloxane)+benzene at 20 °C [6], χ is reported as "0.64–0.85" for ϕ_2 between 0.4 and 1 to indicate that $\chi = 0.64$ at $\phi_2 = 0.4$ and $\chi = 0.85$ at $\phi_2 = 1$.

The polymer–solvent interaction parameter is only slightly sensitive to the molecular weight provided that the molecular weight is high. Thus, studies using only low molecular weight polymers have not been used for the table. In those cases in which measurements were made with polymers of different molecular weights, only the results for the highest molecular weight material are reported in Table 14.1.

Measurements on dilute solutions, especially osmotic pressure measurements, can yield unusually accurate values for χ. These entries are recorded to the thousandth place. At the other extreme, the experimental uncertainty in χ is large for the larger values of χ obtained, for example, in inverse gas chromatography at $\phi_2 \to 1$; these entries are written to the nearest tenth.

The values of χ found in Table 14.1 were obtained using the volume fraction ϕ_2 as the measure of polymer concentration, consistent with Eq. 14.8. However, instead of χ, many of the studies cited in the table reported χ_{wt} or χ^*, interaction parameters which are based on the weight fraction (particularly in connection with inverse gas chromatographic studies) or the segment fraction (using the model of Flory for polymer solutions [137]), respectively. Since both χ_{wt} and χ^* differ from the volume-fraction based χ, these interaction parameters have been recalculated using Eq. 14.8 for Table 14.1 to give χ. Thus, for example, in the case of inverse gas chromatography, $\chi = \chi_{\mathrm{wt}} + \ln(\rho_1/\rho_2)$ in the limit $\phi_2 \to 1$, where ρ_1/ρ_2 is the ratio of the density of the solvent and to that of the liquid (as opposed to glassy or crystalline) polymer.

Related information can be found in Chapters 15–17, and 19.

TABLE 14.1. *Interaction parameters.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
Cellulose acetate, 2.3 acetate groups per residue				
acetone	25 to 45	0	0.44	[7–9]
acetic acid	25 to 45	0	0.40	[9]
aniline	25 to 35	0	0.375 to 0.34	[7–9]
1,4-dioxane	25 to 45	0	0.38	[7–9]
methyl acetate	25 to 35	0	0.45	[7–9]
nitromethane	25 to 45	0	0.43	[7–9]
2-picoline	25	0	0.36	[7]
3-picoline	25	0	0.285	[7]
4-picoline	25	0	0.26	[7]
pyridine	25 to 45	0	0.28	[7–9]
Cellulose acetate, 2.5 acetate groups per residue				
acetone	30	0.2 to 0.4	0.30 to 0.51	[10]
1,4-dioxane	30	0.2 to 0.4	0.31 to 0.51	[10]
methyl acetate	30	0.2 to 0.4	0.43 to 0.59	[10]
pyridine	30	0.2 to 0.4	0.07 to 0.09	[10]
tetrahydrofuran	13	0	0.442	[11]
Cellulose acetate, 3.0 acetate groups per residue				
chloroform	25	0	0.34	[12]
	30	0.2 to 0.6	0.36 to 0.51	[13]
dichloromethane	25	0 to 0.6	0.3 to 0.49	[13]
Cellulose nitrate, 2.4 nitrate groups per residue				
acetone	25	0	0.27	[7]
	30	0 to 0.2	0.24 to 0.05	[10]
amyl acetate	25	0	0.02	[7]
2-butanone	25	0	0.21	[7]
butyl acetate	25	0	0.015	[7]
ethyl acetate	25	0	0.22	[7]
2-heptanone	25	0	0.02	[7]
2-hexanone	25	0	0.15	[7]
methyl acetate	25	0	0.30	[7]
	30	0 to 0.2	0.17 to −0.06	[10]
2-octanone	25	0	0.16	[7]
propyl acetate	25	0	0.13	[7]
Cellulose nitrate, 2.6 nitrate groups per residue				
acetone	20	0.2 to 0.8	0.14 to −1.24	[14]
acetonitrile	20	0.4 to 1	0.59 to −0.1	[14]
cyclopentanone	20	0.2 to 0.8	0.42 to −2.4	[14]
2,4-dimethyl-3-pentanone	20	0.2 to 0.6	0.62 to −1.7	[14]
1,4-dioxane	20	0.4 to 0.8	1.2 to −1.7	[14]
ethyl acetate	20	0.2 to 0.6	0.04 to −1.35	[15]
ethyl formate	20	0.2 to 0.8	−0.08 to −3.2	[15]
ethyl *n*-propyl ether	20	0.8	1.20	[14]
isoamyl acetate	20	0.2 to 0.6	−0.89 to −3.3	[15]
3-methylbutanone	20	0.2 to 0.6	−0.5 to −1.6	[14]
nitromethane	20	0.2 to 0.8	0.66 to 0.45	[14]
pinacolone	20	0.2 to 0.8	0.16 to −3.7	[14]
propyl acetate	20	0.2 to 0.8	−0.38 to −4.1	[15]
Ethyl cellulose, 2.3 ethyl groups per residue				
acetone	25	0	0.46	[7]
benzene	25	0	0.48	[7]
n-butyl acetate	25	0	0.24	[7]
carbon tetrachloride	25	0	0.46	[7]
chloroform	25	0	0.34	[7]
ethyl acetate	25	0	0.395	[7]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
2-heptanone	25	0	0.38	[7]
methyl acetate	25	0	0.41	[7]
2-pentanone	25	0	0.37	[7]
n-pentyl acetate	25	0	0.28	[7]
n-propyl acetate	25	0	0.33	[7]
toluene	25	0	0.47	[7]
Hydroxypropyl cellulose				
acetone	25	0.60 to 0.90	0.58 to 0.83	[124]
ethanol	25	0.61 to 0.90	0.57 to 0.55	[124]
tetrahyrofuran	25	0.52 to 0.90	0.34 to 0.48	[124]
water	25	0 to 0.13	0.480 to 0.52	[122]
	25	0.51 to 1	0.63 to 1.55	[123]
	40	0 to 0.13	0.499 to 0.54	[122]
Polyacrylamide				
water	3	0.10	0.51	[111]
	25	0	0.495	[104]
	25	0.06	0.53	[109]
	60	0.08	0.49	[111]
0.2N HCl	20 to 61	0	0.499 to 0.491	[105]
Polyacrylonitrile				
dimethylformamide	14	0	0.2	[16]
Poly(*N*-acryloylpyrrolidine)				
ethanol	10 to 60	0.08	0.45	[111]
water	3	0.07	0.49	[111]
	30	0.12	0.53	[111]
	60	0.35	0.66	[111]
Poly(*cis*-1,4-butadiene)				
benzene	35	0.06 to 0.10	0.28	[125]
carbon tetrachloride	23.5	0.62 to 0.85	0.11 to 0.02	[106]
chloroform	23.5	0.60 to 0.80	−0.06 to −0.20	[106]
dichloromethane	23.5	0.69 to 0.85	0.32 to 0.21	[106]
cyclohexane	23.5	0.65 to 0.83	0.46 to 0.34	[106]
n-decane	35	0.16 to 0.23	0.46	[125]
n-hexadecane	35	0.26 to 0.30	0.54	[125]
n-hexane	23.5	0.67 to 0.88	0.61 to 0.45	[106]
n-octane	*ca.* 50	0.38 to 0.42	0.31 to 0.27	[108]
Polybutadiene, 10% *cis*, 21% *trans*, 69% vinyl				
acetone	40 to 100	1	1.64 to 1.32	[126]
acetonitrile	40 to 100	1	2.86 to 2.36	[126]
benzene	40 to 100	1	0.26 to 0.19	[126]
1-butanol	40 to 100	1	2.76 to 1.64	[126]
2-butanone	40 to 100	1	1.19 to 0.97	[126]
butyl acetate	40 to 100	1	0.52 to 0.44	[126]
butyronitrile	40 to 100	1	1.90 to 1.57	[126]
carbon tetrachloride	40 to 100	1	0.10 to 0.15	[126]
chloroform	40 to 100	1	0.05 to 0.07	[126]
1-chlorobutane	40 to 100	1	0.33 to 0.25	[126]
1-chloropentane	40 to 100	1	0.37 to 0.32	[126]
1-chloropropane	40 to 100	1	0.36 to 0.30	[126]
cyclohexane	40 to 100	1	0.22 to 0.15	[126]
ethanol	40 to 100	1	3.41 to 2.30	[126]
ethyl acetate	40 to 100	1	0.86 to 0.69	[126]
ethylcyclohexane	40 to 100	1	0.08 to 0.04	[126]
ethyl ether	40 to 100	1	0.42 to 0.40	[126]
n-heptane	40 to 100	1	0.36 to 0.31	[126]
1-heptene	40 to 100	1	0.25 to 0.23	[126]
n-hexane	40 to 100	1	0.37	[126]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
1-hexene	40 to 100	1	0.32 to 0.28	[126]
methanol	40 to 100	1	3.85 to 2.70	[126]
methyl acetate	40 to 100	1	1.14 to 0.92	[126]
methylcyclohexane	40 to 100	1	0.17 to 0.13	[126]
methyl isobutyl ketone	40 to 100	1	0.95 to 0.72	[126]
n-octane	40 to 100	1	0.34 to 0.28	[126]
1-octene	40 to 100	1	0.23 to 0.21	[126]
n-pentane	40 to 100	1	0.44 to 0.36	[126]
3-pentanone	40 to 100	1	0.82 to 0.67	[126]
1-propanol	40 to 100	1	2.97 to 1.97	[126]
2-propanol	40 to 100	1	2.93 to 1.86	[126]
proprionitrile	40 to 100	1	2.25 to 1.82	[126]
n-propyl acetate	40 to 100	1	0.67 to 0.55	[126]
n-propyl ether	40 to 100	1	0.51 to 2.26	[126]
tetrahydrofuran	40 to 100	1	0.35 to 0.29	[126]
toluene	40 to 100	1	0.14 to 0.12	[126]
Poly(1-butene)				
benzene	135	1	0.49	[17]
cyclohexane	135	1	0.20	[17]
n-decane	115 to 135	1	0.30	[17]
2,5-dimethylhexane	115 to 135	1	0.36	[17]
2,4-dimethylpentane	115 to 135	1	0.40	[17]
2,3-dimethylpentane	115 to 135	1	0.35	[17]
3-ethylpentane	115 to 135	1	0.34	[17]
n-heptane	115 to 135	1	0.38	[17]
2-methylhexane	115 to 135	1	0.39	[17]
3-methylhexane	115 to 135	1	0.38	[17]
n-nonane	115 to 135	1	0.32	[17]
n-octane	115 to 135	1	0.36	[17]
toluene	135	1	0.47	[17]
2,2,4-trimethylpentane	115 to 135	1	0.35	[17]
Poly(butylene adipate)				
acetone	120	1	0.54	[18]
benzene	120	1	0.27	[18]
2-butanone	120	1	0.43	[18]
carbon tetrachloride	120	1	0.55	[18]
chloroform	120	1	−0.06	[18]
dichloromethane	120	1	0.70	[18]
ethyl acetate	120	1	0.43	[18]
n-heptane	120	1	1.5	[18]
n-hexane	120	1	1.4	[18]
n-pentane	120	1	1.3	[18]
Poly(*n*-butyl methacrylate)				
ethanol	27	0 to 1	0.492 to 1.29	[118]
	86	0 to 1	0.399 to 0.95	[118]
2-propanol	40	0 to 1	0.509 to 1.4	[118]
	80	0 to 1	0.477 to 1.0	[118]
Poly(ε-caprolactone)				
acetone	100 to 120	1	0.46 to 0.54	[18, 19]
benzene	100 to 120	1	0.06 to 0.11	[18, 19]
	70 to 140	1	−0.04 to 0.01	[114]
n-butane	100	1	1.22	[19]
1-butanol	100	1	0.59	[19]
2-butanone	100 to 120	1	0.36 to 0.45	[18, 19]
n-butyl acetate	70 to 140	1	0.21 to 0.26	[114]
	100	1	0.31	[19]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
carbon tetrachloride	100 to 120	1	0.25 to 0.37	[18, 19]
chlorobenzene	100	1	−0.08	[19]
	80 to 140	1	−0.18 to −0.06	[114]
1-chlorobutane	100	1	0.33	[19]
chloroform	100 to 120	1	−0.40 to −0.22	[18, 19]
chloromethane	100	1	0.16	[19]
1-chloropentane	100	1	0.33	[19]
cycloheptane	100	1	0.83	[19]
cyclohexane	100	1	0.88	[19]
cyclohexene	100	1	0.60	[19]
cyclooctane	100	1	0.83	[19]
cyclopentane	100	1	0.82	[19]
n-decane	100	1	1.44	[19]
1, 1-dichloroethane	100	1	−0.04	[19]
1,2-dichloroethane	100	1	−0.14	[19]
dichloromethane	100	1	−0.26	[19]
1,4-dioxane	100	1	0.13	[19]
ethanol	100	1	1.01	[19]
ethyl acetate	100 to 120	1	0.36 to 0.42	[18, 19]
	70 to 140	1	0.32 to 0.29	[114]
ethylbenzene	100	1	0.16	[19]
	70 to 140	1	0.10 to 0.14	[114]
n-heptane	100 to 120	1	1.2	[18, 19]
n-hexane	100 to 120	1	1.2	[18, 19]
methyl acetate	100	1	0.39	[19]
	70 to 140	1	0.35 to 0.32	[114]
n-nonane	100	1	1.37	[19]
n-octane	100	1	1.30	[19]
n-pentane	100 to 120	1	1.2	[18, 19]
1-pentanol	100	1	0.46	[19]
2-pentyl acetate	70 to 140	1	0.40 to 0.28	[114]
propane	100	1	1.21	[19]
1-propanol	100	1	0.72	[19]
propyl acetate	100	1	0.33	[19]
	70 to 140	1	0.29 to 0.24	[114]
n-propylbenzene	90 to 140	1	0.20 to 0.19	[114]
2-propylbenzene	80 to 140	1	0.10 to 0.13	[114]
tetrahydrofuran	100	1	0.13	[19]
toluene	100	1	0.08	[19]
	70 to 140	1	−0.01 to 0.07	[114]
1,1,1-trichloroethane	100	1	0.07	[19]
trichloroethylene	100	1	0.02	[19]
n-undecane	100	1	1.52	[19]
Polycarbonate				
benzene	179 to 253	1	0.49 to 0.39	[121]
cyclohexane	179 to 253	1	1.23 to 0.77	[121]
n-decane	179 to 253	1	1.67 to 1.52	[121]
n-dodecane	179 to 253	1	1.74 to 1.46	[121]
ethylbenzene	179 to 253	1	0.49 to 0.47	[121]
ethylcyclohexane	179 to 253	1	1.12 to 0.92	[121]
n-heptane	179 to 253	1	1.73 to 1.34	[121]
n-hexadecane	211 to 253	1	1.73 to 1.57	[121]
n-hexane	179 to 231	1	1.87 to 1.19	[121]
methylcyclohexane	179 to 253	1	1.19 to 0.82	[121]
n-nonane	179 to 253	1	1.69 to 1.43	[121]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
n-octane	179 to 253	1	1.60 to 1.45	[121]
n-tetradecane	179 to 253	1	1.82 to 1.54	[121]
toluene	179 to 253	1	0.46 to 0.37	[121]
n-undecane	179 to 253	1	1.73 to 1.53	[121]
Polychloroprene				
acetone	100	1	0.87	[19]
benzene	100	1	0.18	[19]
n-butane	100	1	0.99	[19]
1-butanol	100	1	1.61	[19]
2-butanone	100	1	0.61	[19]
butyl acetate	100	1	0.44	[19]
carbon tetrachloride	100	1	0.23	[19]
chlorobenzene	100	1	0.10	[19]
1-chlorobutane	100	1	0.39	[19]
chloroform	100	1	0.28	[19]
chloromethane	100	1	0.52	[19]
1-chloropentane	100	1	0.33	[19]
cycloheptane	100	1	0.45	[19]
cyclohexane	100	1	0.55	[19]
cyclohexene	100	1	0.38	[19]
cyclooctane	100	1	0.40	[19]
cyclopentane	100	1	0.55	[19]
n-decane	100	1	0.94	[19]
1,1-dichloroethane	100	1	0.37	[19]
1,2-dichloroethane	100	1	0.48	[19]
dichloromethane	100	1	0.43	[19]
1,4-dioxane	100	1	0.46	[19]
ethanol	100	1	2.27	[19]
ethyl acetate	100	1	0.64	[19]
ethylbenzene	100	1	0.16	[19]
n-heptane	100	1	0.88	[19]
n-hexane	100	1	0.91	[19]
methyl acetate	100	1	0.81	[19]
n-nonane	100	1	0.92	[19]
n-octane	100	1	0.90	[19]
n-pentane	100	1	0.96	[19]
1-pentanol	100	1	1.41	[19]
propane	100	1	1.36	[19]
1-propanol	100	1	1.83	[19]
propyl acetate	100	1	0.51	[19]
tetrahydrofuran	100	1	0.06	[19]
1,1,1-trichloroethane	100	1	0.21	[19]
trichloroethylene	100	1	0.24	[19]
toluene	100	1	0.14	[19]
n-undecane	100	1	0.96	[19]
Poly(*o*-chlorostyrene)				
butyl acetate	30	0	0.490	[20]
chlorobenzene	30	0	0.472	[20]
toluene	30	0	0.470	[20]
Poly(*p*-chlorostyrene)				
butyl acetate	30	0	0.448	[20]
chlorobenzene	30	0	0.465	[20]
toluene	22	0.2 to 0.6	0.55	[21]
	30	0	0.489	[20]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
Poly(*N*, *N*-diethylacrylamide)				
ethanol	10 to 60	0.08	0.47	[111]
water	3	0.07	0.50	[111]
	30	0.05	0.62	[111]
	60	0.85	1.16	[111]
Poly(*N*,*N*-dimethylacrylamide)				
ethanol	10 to 60	0.08	0.40 to 0.41	[111]
water	3	0.07	0.48	[111]
	60	0.10	0.52	[111]
Poly(dimethyl siloxane)				
acetone	100	1	1.33	[19]
benzene	20	0.4 to 1	0.64 to 0.85	[6]
	25	0.2 to 1	0.56 to 0.82	[22–25]
	30	0.08 to 0.47	0.50 to 0.36	[116]
	30	0.88 to 1	0.745 to 0.759	[135]
	25 to 70	1	0.80 to 0.74	[25,26]
	40 to 100	1	0.79 to 0.58	[19,25]
n-butane	100	1	0.25	[19]
1-butanol	100	1	1.91	[19]
2-butanone	20	0.08 to 0.30	0.52 to 0.61	[27]
	25	0	0.50	[28]
	30	0.35 to 0.66	0.44 to 0.66	[138]
	50	0.08 to 0.29	0.50 to 0.58	[27]
butyl acetate	100	1	0.68	[19]
carbon dioxide ($20 < P < 62$ bar)	35	0.78 to 0.94	0.75	[117]
carbon dioxide ($P = 300$ bar)	45	0.67	0.45	[115]
carbon tetrachloride	100	1	0.36	[19]
chlorobenzene	20	0 to 0.2	0.475 to 0.54	[29]
	60	0 to 0.2	0.455 to 0.52	[29]
	100	1	0.76	[19]
1-chlorobutane	100	1	0.49	[19]
chloroform	100	1	0.60	[19]
chloromethane	100	1	0.44	[19]
1-chloropentane	100	1	0.48	[19]
cycloheptane	25 to 70	1	0.56 to 0.53	[26]
	100	1	0.42	[19]
cyclohexane	20	0 to 0.2	0.409 to 0.44	[29]
	25	0.2 to 0.6	0.46 to 0.50	[23]
	25 to 70	1	0.48	[26]
	30	0.35 to 0.95	0.42	[22]
	100	1	0.35	[19]
cyclohexene	100	1	0.36	[19]
cyclooctane	25 to 70	1	0.66 to 0.61	[26]
	100	1	0.50	[19]
cyclopentane	25 to 70	1	0.42 to 0.46	[26]
	100	1	0.28	[19]
n-decane	100	1	0.51	[19]
1,1-dichloroethane	100	1	0.60	[19]
1,2-dichloroethane	100	1	0.96	[19]
dichloromethane	100	1	0.69	[19]
2,6-dimethyl-4-heptanone	35	0.08 to 0.22	0.45 to 0.49	[27]
1,4-dioxane	25 to 70	1	1.32 to 1.18	[26]
	100	1	1.06	[19]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
ethyl acetate	100	1	0.82	[19]
ethanol	100	1	2.6	[19]
ethylbenzene	24	0.4 to 1	0.54 to 0.77	[6]
	25 to 70	1	0.83 to 0.78	[25]
	25 to 70	1	0.77 to 0.73	[26]
	100	1	0.62	[19]
n-heptane	20	0.4 to 1	0.46	[6]
	35	0.06 to 0.19	0.42	[30]
	50	0.06 to 0.16	0.43	[30]
	25 to 70	1	0.49	[25,26]
	100	1	0.35	[19]
3-heptanone	35	0.08 to 0.29	0.48 to 0.56	[27]
	50	0.08 to 0.26	0.47 to 0.53	[27]
hexamethyldisiloxane	23	0.4 to 1	0.30 to 0.25	[6]
	25 to 70	1	0.28 to 0.34	[26]
n-hexane	20	0.03 to 0.17	0.39 to 0.37	[30]
	30	0.86 to 1	0.387 to 0.397	[135]
	50	0.06 to 0.11	0.41	[30]
	25 to 70	1	0.46	[25,26]
	100	1	0.30	[19]
mesitylene	25 to 70	1	0.95 to 0.86	[26]
methyl acetate	100	1	1.01	[19]
2-methylbutane	25	1	0.39	[25]
	100	1	1.10	[19]
2-methylheptane	25 to 70	1	0.50	[25,26]
2-methylhexane	25 to 70	1	0.45	[25,26]
3-methylhexane	25 to 70	1	0.44	[26]
2-methylpentane	25 to 70	1	0.44	[25]
4-methyl-2-pentanone	20	0.10 to 0.22	0.49 to 0.55	[27]
	35	0.09 to 0.24	0.48 to 0.53	[27]
n-nonane	20	0.07 to 0.21	0.48 to 0.49	[30]
	50	0.07 to 0.21	0.46 to 0.49	[30]
	100	1	0.45	[19]
octamethylcyclotetrasiloxane	25	0.10 to 0.17	0.31 to 0.37	[31]
octamethyltrisiloxane	23	0.4 to 1	0.22 to 0.14	[6]
n-octane	20	0.4 to 1	0.50	[6]
	20	0.05 to 0.21	0.45 to 0.46	[30]
	50	0.06 to 0.19	0.43 to 0.45	[30]
	25 to 100	1	0.56 to 0.40	[19,25]
n-pentane	20	0.4 to 1	0.43 to 0.40	[6]
	25 to 70	1	0.42	[25]
	25 to 70	1	0.45 to 0.49	[26]
	100	1	0.31	[19]
1-pentanol	100	1	1.75	[19]
propane	100	1	0.21	[19]
1-propanol	100	1	2.06	[19]
propyl acetate	100	1	0.72	[19]
tetrahydrofuran	100	1	0.48	[19]
toluene	20	0 to 1	0.445 to 0.82	[6,29]
	25 to 70	1	0.80 to 0.75	[25]
	25 to 70	1	0.75 to 0.71	[26]
	100	1	0.59	[19]
	30	0.07 to 0.45	0.47 to 0.57	[116]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
1,1,1-trichloroethane	100	1	0.37	[19]
trichloroethylene	100	1	0.53	[19]
2,2,4-trimethylpentane	25 to 70	1	0.44	[25,26]
n-undecane	100	1	0.58	[19]
m-xylene	25 to 70	1	0.82 to 0.76	[26]
o-xylene	25 to 70	1	0.86 to 0.80	[26]
p-xylene	25	0.6 to 1	0.58 to 0.78	[6]
	25 to 70	1	0.80 to 0.77	[25,26]
Poly(1,3-dioxocane)				
tetrahydrofuran	25	0	0.38	[128]
toluene	25	0	0.37	[112]
Polyepichlorohydrin				
acetone	100	1	0.28	[19]
benzene	100	1	0.25	[19]
n-butane	100	1	1.65	[19]
1-butanol	100	1	1.12	[19]
2-butanone	100	1	0.20	[19]
butyl acetate	100	1	0.36	[19]
carbon tetrachloride	100	1	0.69	[19]
chlorobenzene	100	1	0.24	[19]
1-chlorobutane	100	1	0.62	[19]
chloroform	100	1	0.25	[19]
chloromethane	100	1	0.36	[19]
1-chloropentane	100	1	0.65	[19]
cycloheptane	100	1	1.19	[19]
cyclohexane	100	1	1.25	[19]
cyclohexene	100	1	0.84	[19]
cyclooctane	100	1	1.20	[19]
cyclopentane	100	1	1.16	[19]
n-decane	100	1	2.12	[19]
1,1-dichloroethane	100	1	0.33	[19]
1,2,-dichloroethane	100	1	0.20	[19]
dichloromethane	100	1	0.18	[19]
1,4-dioxane	100	1	0.04	[19]
ethanol	100	1	1.58	[19]
ethyl acetate	100	1	0.35	[19]
ethylbenzene	100	1	0.44	[19]
n-heptane	100	1	1.79	[19]
n-hexane	100	1	1.72	[19]
methyl acetate	100	1	0.39	[19]
n-nonane	100	1	1.99	[19]
n-octane	100	1	1.89	[19]
n-pentane	100	1	1.64	[19]
1-pentanol	100	1	1.03	[19]
propane	100	1	1.71	[19]
1-propanol	100	1	1.22	[19]
propyl acetate	100	1	0.33	[19]
tetrahydrofuran	100	1	0.01	[19]
1, 1, 1-trichloroethane	100	1	0.46	[19]
trichloroethylene	100	1	0.53	[19]
toluene	100	1	0.31	[19]
n-undecane	100	1	2.24	[19]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
Poly(*N*-ethylacrylamide)				
ethanol	10 to 60	0.08	0.39 to 0.40	[111]
water	3	0.05	0.42	[111]
	30	0.06	0.46	[111]
	60	0.10	0.51	[111]
Polyethylene, low density				
benzene	125 to 135	1	0.43 to 0.36	[32,33]
1-butanol	135	1	1.38	[32]
carbon tetrachloride	135	1	0.24	[32]
chlorobenzene	135	1	0.34	[32]
1-chlorobutane	135	1	0.44	[32]
chloroform	135	1	0.41	[32]
cyclohexane	125 to 135	1	0.18	[32,33]
cyclohexanol	135	1	1.22	[32]
cis-decahydronaphthalene	120 to 145	1	0.03	[34]
trans-decahydronaphthalene	120 to 145	1	0.01	[34]
n-decane	120 to 145	1	0.25 to 0.29	[32,34]
2,4-dimethylhexane	120 to 145	1	0.33	[34]
2,5-dimethylhexane	120 to 145	1	0.35	[34]
3,4-dimethylhexane	120 to 145	1	0.25	[34]
n-dodecane	110 to 145	1	0.18	[35]
	120 to 145	1	0.24	[34]
ethylbenzene	120 to 145	1	0.33	[34]
n-heptane	109	0.2 to 0.6	0.29 to 0.34	[36]
mesitylene	120 to 145	1	0.24	[34]
3-methylheptane	120 to 145	1	0.30	[34]
3-methylhexane	120 to 145	1	0.34	[34]
n-nonane	120 to 145	1	0.28	[32,34]
n-octane	120 to 145	1	0.30	[34]
1-octene	135	1	0.31	[32]
2-pentanone	135	1	0.88	[32]
phenol	135	1	1.5	[32]
1,2,3,4-tetrahydronaphthalene	105	0	0.495	[37]
	120 to 145	1	0.28	[34]
toluene	120 to 145	1	0.34	[34]
2,2,4-trimethylhexane	120 to 145	1	0.28	[34]
2,2,4-trimethylpentane	120 to 145	1	0.34	[34]
m-xylene	120 to 145	1	0.29	[34]
p-xylene	81	0	0.45	[38]
	120 to 145	1	0.28	[34]
xylene	73 to 92	0	0.49	[39,40]
Polyethylene, high density				
cis-decahydronaphthalene	149	1	0.07	[34]
trans-decahydronapthalene	149	1	0.05	[34]
n-decane	145 to 190	1	0.18	[35]
	149	1	0.31	[34]
	185	1	0.12	[41]
2,4-dimethylhexane	149	1	0.38	[34]
2,5-dimethylhexane	149	1	0.40	[34]
3,4-dimethylhexane	149	1	0.31	[34]
n-dodecane	149	1	0.28	[34]
ethylbenzene	149	1	0.37	[34]
mesitylene	149	1	0.28	[34]
2-methylheptane	149	1	0.39	[34]
3-methylhexane	149	1	0.40	[34]
n-nonane	149	1	0.34	[34]
n-octane	149	1	0.36	[34]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
1,2,3,4-tetrahydronaphthalene	149	1	0.32	[34]
toluene	149	1	0.39	[34]
2,2,4-trimethylhexane	149	1	0.35	[34]
2,2,4-trimethylpentane	149	1	0.40	[34]
m-xylene	149	1	0.34	[34]
o-xylene	110	0	0.31	[37]
p-xylene	105	0	0.22	[37]
	149	1	0.32	[34]
xylene	85	0	0.34	[39]
Poly(ethylene adipate)				
acetone	120	1	0.53	[18]
benzene	120	1	0.58	[18]
2-butanone	120	1	0.88	[18]
carbon tetrachloride	120	1	0.88	[18]
chloroform	120	1	0.29	[18]
dichloromethane	120	1	0.96	[18]
ethyl acetate	120	1	0.55	[18]
n-heptane	120	1	2.1	[18]
n-hexane	120	1	2.0	[18]
n-pentane	120	1	1.8	[18]
Poly(ethylene oxide)				
acetone	100	1	0.47	[19]
benzene	50	0.2 to 0.6	0.18 to 0.10	[42]
	70	0.2 to 0.8	0.19 to 0.09	[42]
	100	1	0.13	[19]
n-butane	100	1	1.64	[19]
1-butanol	100	1	0.41	[19]
2-butanone	100	1	0.43	[19]
butyl acetate	100	1	0.48	[19]
carbon tetrachloride	100	1	0.38	[19]
chlorobenzene	100	1	−0.04	[19]
1-chlorobutane	100	1	0.57	[19]
chloroform	100	1	−0.55	[19]
chloromethane	100	1	0.12	[19]
1-chloropentane	100	1	0.63	[19]
cycloheptane	100	1	1.23	[19]
cyclohexane	100	1	1.23	[19]
cyclohexene	100	1	0.85	[19]
cyclooctane	100	1	1.26	[19]
cyclopentane	100	1	1.12	[19]
n-decane	100	1	2.10	[19]
1,1-dichloroethane	100	1	−0.04	[19]
1,2-dichloroethane	100	1	−0.31	[19]
dichloromethane	100	1	−0.51	[19]
1,4-dioxane	100	1	0.20	[19]
ethanol	100	1	0.70	[19]
ethyl acetate	100	1	0.39	[19]
ethylbenzene	100	1	0.40	[19]
n-heptane	100	1	1.75	[19]
n-hexane	100	1	1.70	[19]
methyl acetate	100	1	0.36	[19]
n-nonane	100	1	1.97	[19]
n-octane	100	1	1.85	[19]
n-pentane	100	1	1.66	[19]
1-pentanol	100	1	0.34	[19]
propane	100	1	2.17	[19]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
1-propanol	100	1	0.47	[19]
propyl acetate	100	1	0.43	[19]
tetrahydrofuran	100	1	0.30	[19]
1,1,1-trichloroethane	100	1	0.20	[19]
trichloroethylene	100	1	0.08	[19]
toluene	100	1	0.26	[19]
n-undecane	100	1	2.22	[19]
Poly(ethylene succinate)				
acetone	120	1	0.61	[18]
benzene	120	1	0.79	[18]
2-butanone	120	1	0.69	[18]
carbon tetrachloride	120	1	1.32	[18]
chloroform	120	1	0.49	[18]
dichloromethane	120	1	1.09	[18]
ethyl acetate	120	1	0.70	[18]
n-heptane	120	1	1.9	[18]
n-hexane	120	1	1.9	[18]
n-pentane	120	1	2.6	[18]
Poly(hexamethylene sebacate)				
acetone	120	1	0.82	[18]
benzene	120	1	0.21	[18]
2-butanone	120	1	0.58	[18]
carbon tetrachloride	120	1	0.37	[18]
chloroform	120	1	0.06	[18]
dichloromethane	120	1	0.81	[18]
ethyl acetate	120	1	0.57	[18]
n-heptane	120	1	1.0	[18]
n-hexane	120	1	1.2	[18]
n-pentane	120	1	1.1	[18]
Poly(2-hydroxyethyl methacrylate)				
di(ethylene glycol)	25	0 to 0.35	0.49 to 0.40	[43]
Poly(4-hydroxystyrene)				
acetone	170 to 190	1	0.25 to 0.58	[110]
2-butanone	170 to 190	1	0.52 to 0.62	[110]
n-butyl acetate	170 to 190	1	1.47 to 1.20	[110]
chlorobenzene	190	1	1.99	[110]
dioxane	190	1	−0.03	[110]
ethyl acetate	170 to 190	1	1.06 to 1.07	[110]
2-methyl-1-propanol	190	1	1.10	[110]
3-pentanone	170 to 190	1	1.08 to 0.76	[110]
1-propanol	190	1	1.01	[110]
2-propanol	170 to 190	1	0.96 to 0.84	[110]
n-propyl acetate	170 to 190	1	1.22 to 1.10	[110]
tetrahydrofuran	170 to 190	1	0.21 to 0.27	[110]
toluene	170 to 190	1	2.20 to 2.22	[110]
Polyisobutylene				
acetone	100	1	1.90	[44]
benzene	10	0.4 to 0.8	0.67 to 0.92	[45]
	25	0 to 1	0.498 to 1.06	[45–47]
	25 to 65	1	0.88 to 0.61	[48–51]
	27	0.6 to 1	0.73 to 1.07	[52]
	30	0	0.495	[53]
	40	0.6 to 0.8	0.70 to 0.80	[45]
	50	0 to 0.2	0.485 to 0.583	[47]
	100	1	0.70	[44]
	37 to 200	1	1.18 to 0.70	[107]
n-butane	25 to 46	1	0.66	[54]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
	100	1	0.65	[44]
1-butanol	100	1	2.45	[44]
2-butanone	100	1	1.55	[44]
butyl acetate	100	1	1.06	[44]
carbon tetrachloride	100	1	0.48	[44]
	23.5	0.76 to 0.87	0.54	[130]
chlorobenzene	100	1	0.70	[44]
1-chlorobutane	100	1	0.68	[44]
chloroform	100	1	0.78	[44]
	23.5	0.82 to 0.91	0.67	[130]
chloromethane	100	1	0.91	[44]
1-chloropentane	100	1	0.59	[44]
cycloheptane	100	1	0.29	[44]
cyclohexane	8	0.2	0.437	[47]
	25	0 to 1	0.43	[46,51,55]
	25 to 65	1	0.55 to 0.40	[48–51]
	30	0 to 0.2	0.44	[47,53]
	100	1	0.39	[44]
	23.5	0.75 to 0.86	0.38	[130]
cyclohexene	100	1	0.40	[44]
cyclooctane	100	1	0.24	[44]
cyclopentane	100	1	0.41	[44]
	23.5	0.79 to 0.86	0.32 to 0.27	[130]
n-decane	100	1	0.48	[44]
1,1-dichloroethane	100	1	0.87	[44]
1,2-dichloroethane	100	1	1.13	[44]
dichloromethane	100	1	1.00	[44]
2,2-dimethylbutane	23.5	0.71 to 0.85	0.49 to 0.46	[130]
2,2-dimethylpropane	25 to 46	1	0.82 to 0.87	[54]
	35	0.8	0.82	[54]
1,4-dioxane	100	1	1.26	[44]
ethanol	100	1	3.3	[44]
ethyl acetate	100	1	1.35	[44]
ethyl benzene	100	1	0.59	[44]
n-heptane	25 to 65	1	0.57 to 0.47	[48,49]
	100	1	0.53	[44]
	23.5	0.80 to 0.87	0.51	[130]
n-hexane	25 to 65	1	0.65 to 0.50	[48,49]
	100	1	0.56	[44]
methyl acetate	100	1	1.55	[44]
2-methylbutane	25 to 35	0.8	0.65	[54]
	35 to 46	1	0.65 to 0.68	[54]
2-methylpropane	25 to 46	1	0.78 to 0.70	[54]
n-nonane	25	1	0.49	[49]
	100	1	0.49	[44]
n-octane	25	0.2 to 0.4	0.44 to 0.48	[56]
	25 to 65	1	0.52 to 0.43	[48,49]
	100	1	0.50	[44]
n-pentane	25	0 to 1	0.48 to 0.75	[48,49,51,54,57,58]
	35	0.4 to 1	0.62	[54,57]
	40	0 to 0.4	0.49 to 0.57	[57]
	40 to 65	1	0.61 to 0.57	[48,51,54]
	55	0.6 to 0.8	0.63	[57]
	100	1	0.60	[44]
1-pentanol	100	1	2.20	[44]
propane	35	1	0.61	[54]
	100	1	0.79	[44]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
propyl acetate	100	1	1.19	[44]
tetrahydrofuran	100	1	0.68	[44]
toluene	100	1	0.60	[44]
1,1,1-trichloroethane	100	1	0.56	[44]
trichloroethylene	100	1	0.54	[44]
2,2,4-trimethylpentane	23.5	0.67 to 0.87	0.50 to 0.45	[130]
n-undecane	100	1	0.48	[44]
Poly(*cis*-isoprene)				
acetone	0	1	2.1	[59]
	25	0.8 to 1	1.27 to 1.8	[59]
benzene	10	0.6 to 0.8	0.42	[60]
	25	0 to 1	0.40 to 0.43	[60–62]
	25 to 55	1	0.46 to 0.43	[63]
	40	0.8	0.41	[60]
	23.5	0.69 to 0.86	0.33 to 0.28	[106]
2-butanone	25	0.6 to 1	0.86 to 1.43	[59]
	45	0.6 to 1	0.83 to 1.2	[59]
carbon tetrachloride	23.5	0.69 to 0.84	0.14 to 0.02	[106]
chloroform	23.5	0.66 to 0.85	0.19 to −0.01	[106]
cyclohexane	20	0 to 0.20	0.31	[113]
	23.5	0.64 to 0.84	0.29 to 0.21	[106]
dichloromethane	23.5	0.69 to 0.89	0.54 to 0.41	[106]
ethyl acetate	25	0.4 to 1	0.69 to 1.24	[59,64]
	50	0.4 to 1	0.68 to 1.0	[59,64]
ethylbenzene	25 to 55	1	0.34 to 0.30	[63]
n-heptane	25 to 55	1	0.50	[63]
	23.5	0.68 to 0.84	0.37 to 0.29	[106]
n-hexane	25 to 55	1	0.54 to 0.50	[63]
2-methylheptane	25 to 55	1	0.50 to 0.47	[63]
2-methylhexane	25 to 55	1	0.51	[63]
2-methylpentane	25 to 55	1	0.56 to 0.52	[63]
n-octane	25 to 55	1	0.49 to 0.46	[63]
n-pentane	25 to 55	1	0.61 to 0.53	[63]
toluene	25 to 55	1	0.36 to 0.32	[63]
2,2,4-trimethylpentane	25 to 55	1	0.49 to 0.46	[63]
p-xylene	25 to 55	1	0.27	[63]
Poly(*N*-isopropylacrylamide)				
ethanol	10 to 60	0.09	0.46 to 0.47	[111]
water	3	0.07	0.49	[111]
	30	0.14	0.55	[111]
	60	0.74	1.08	[111]
Poly(*DL*-lactide)				
acetone	120	1	0.56	[18]
benzene	120	1	0.52	[18]
2-butanone	120	1	0.53	[18]
carbon tetrachloride	120	1	0.89	[18]
chloroform	120	1	0.32	[18]
dichloromethane	120	1	0.99	[18]
ethyl acetate	120	1	0.46	[18]
n-heptane	120	1	2.0	[18]
n-hexane	120	1	2.0	[18]
n-pentane	120	1	1.6	[18]
Poly(methacrylamide)				
water	23 to 56	0	0.500 to 0.499	[105]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
Poly(methacrylic acid)				
0.02 N HCl	20 to 58	0	0.498 to 0.500	[105]
Poly(methyl acrylate)				
acetone	100	1	0.40	[19]
benzene	90 to 110	1	0.51 to 0.37	[19,65]
n-butane	100	1	1.86	[19]
1-butanol	100	1	0.79	[19]
2-butanone	100	1	0.40	[19]
butyl acetate	100	1	0.58	[19]
butylbenzene	90 to 110	1	1.14 to 1.05	[65]
tert-butylbenzene	90 to 110	1	1.03 to 0.95	[65]
butylcyclohexane	90 to 110	1	2.3 to 2.1	[65]
carbon tetrachloride	100	1	0.68	[19]
chlorobenzene	100	1	0.31	[19]
1-chlorobutane	100	1	0.74	[19]
chloroform	100	1	−0.10	[19]
chloromethane	100	1	0.34	[19]
1-chloropentane	100	1	0.84	[19]
cycloheptane	100	1	1.56	[19]
cyclohexane	90 to 110	1	1.7 to 1.5	[19,65]
cyclohexene	100	1	1.31	[19]
cyclooctane	100	1	1.61	[19]
cyclopentane	100	1	1.47	[19]
cis-decahydronaphthalene	90 to 110	1	2.1 to 1.8	[65]
trans-decahydronaphthalene	90 to 110	1	2.1 to 1.9	[65]
n-decane	88 to 100	1	2.7 to 2.4	[19,65]
1,1-dichloroethane	100	1	0.20	[19]
1,2-dichloroethane	100	1	0.02	[19]
dichloroethane	100	1	−0.09	[19]
1,4-dioxane	100	1	0.20	[19]
n-dodecane	90 to 110	1	3.0 to 2.7	[65]
ethanol	100	1	1.01	[19]
ethyl acetate	100	1	0.43	[19]
ethylbenzene	90 to 110	1	0.83 to 0.67	[19,65]
n-heptane	100	1	2.10	[19]
n-hexane	100	1	2.08	[19]
methyl acetate	100	1	0.38	[19]
naphthalene	100 to 110	1	0.48	[65]
n-nonane	100	1	2.4	[19]
n-octane	90 to 100	1	2.4 to 2.2	[19,65]
n-pentane	100	1	1.92	[19]
1-pentanol	100	1	0.76	[19]
propane	100	1	2.5	[19]
1-propanol	100	1	0.82	[19]
propyl acetate	100	1	0.49	[19]
n-tetradecane	90 to 110	1	3.4 to 3.1	[65]
tetrahydrofuran	100	1	0.34	[19]
1,2,3,4-tetrahydronaphthalene	90 to 110	1	1.04 to 0.95	[65]
3,3,4,4-tetramethylhexane	90 to 110	1	2.2 to 1.9	[65]
toluene	90 to 110	1	0.67 to 0.62	[65]
	100	1	0.53	[19]
1,1,1-trichloroethane	100	1	0.43	[19]
trichloroethylene	100	1	0.45	[19]
3,4,5-trimethylheptane	90 to 110	1	2.4 to 2.2	[65]
2,2,5-trimethylhexane	90 to 110	1	2.5 to 2.2	[65]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
2,2,4-trimethylpentane	90 to 110	1	2.4 to 2.1	[65]
n-undecane	100	1	2.7	[19]
Poly(methyl methacrylate)				
acetone	25 to 27	0	0.48	[66,67]
benzene	16 to 27	0	0.47 to 0.44	[16,67]
butyl acetate	2 to 60	0	0.496 to 0.487	[68]
1-chlorobutane	14 to 48	0	0.515 to 0.495	[68]
chloroform	27	0	0.44	[67]
1,4-dioxane	27	0	0.42	[67]
4-heptanone	16 to 62	0	0.515 to 0.490	[68]
isoamyl acetate	20 to 60	0	0.524 to 0.499	[68]
3-pentanone	27	0	0.49	[67]
tetrahydrofuran	25 to 27	0	0.494 to 0.46	[67,69]
toluene	27	0	0.45	[67]
m-xylene	27	0	0.50	[67]
Poly(α-methylstyrene)				
toluene	25	0.3 to 0.7	0.48 to 0.65	[70]
Polypropylene				
acetone	100	1	1.72	[44]
benezene	25	0	0.498	[71]
	100	1	0.51	[44]
butane	100	1	0.37	[44]
1-butanol	100	1	2.23	[44]
2-butanone	100	1	1.36	[44]
butyl acetate	100	1	0.84	[44]
carbon tetrachloride	100	1	0.29	[44]
chlorobenzene	100	1	0.54	[44]
1-chlorobutane	100	1	0.48	[44]
chloroform	100	1	0.61	[44]
chloromethane	100	1	0.76	[44]
1-chloropentane	100	1	0.39	[44]
cycloheptane	100	1	0.10	[44]
cyclohexane	25	0	0.42	[71]
	100	1	0.17	[44]
cyclohexene	100	1	0.22	[44]
cyclooctane	100	1	0.06	[44]
cyclopentane	100	1	0.21	[44]
1,1-dichloroethane	100	1	0.70	[44]
1,2-dichloroethane	100	1	0.97	[44]
dichloromethane	100	1	0.86	[44]
1,4-dioxane	100	1	1.15	[44]
ethanol	100	1	3.0	[44]
ethyl acetate	100	1	1.14	[44]
ethylbenzene	100	1	0.40	[44]
n-decane	100	1	0.18	[44]
n-heptane	100	1	0.24	[44]
n-hexane	80	1	0.18	[72]
	100	1	0.28	[44]
methyl acetate	100	1	1.37	[44]
n-nonane	100	1	0.20	[44]
n-octane	100	1	0.22	[44]
n-pentane	100	1	0.35	[44]
1-pentanol	100	1	1.99	[44]
propane	100	1	0.46	[44]
propyl acetate	100	1	0.96	[44]
tetrahydrofuran	100	1	0.55	[44]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
toluene	100	1	0.43	[44]
1,1,1-trichloroethane	100	1	0.37	[44]
trichloroethylene	100	1	0.39	[44]
n-undecane	100	1	0.17	[44]
Polystyrene				
acetic acid	162 to 229	1	3.0 to 2.1	[73]
acetone	25	0.6 to 1	0.81 to 1.1	[74]
	40	1	1.08	[75]
	50	0.6 to 0.8	0.80 to 0.92	[74]
	162 to 229	1	1.30 to 0.56	[73]
acetonitrile	162 to 229	1	2.02 to 0.93	[73]
aniline	162 to 229	1	1.11 to 0.68	[73]
benzaldehyde	162 to 229	1	1.22 to 0.80	[73]
benzene	15	0.3 to 0.8	0.40 to 0.26	[76]
	25 to 30	0	0.455 to 0.43	[77,78]
	30	0.3 to 0.8	0.40 to 0.26	[76]
	40	1	0.26	[75]
	45	0.3 to 0.8	0.40 to 0.26	[76]
	60	0.3 to 0.8	0.40 to 0.26	[76]
	120 to 200	1	0.32 to 0.39	[41,51]
	160 to 180	1	0.29 to 0.24	[65]
	162 to 229	1	0.66 to 0.13	[73]
	23.5	0.61 to 0.79	0.28 to 0.17	[129]
benzyl alcohol	162 to 229	1	1.42 to 0.65	[73]
1-butanol	162 to 229	1	1.47 to 0.82	[73]
2-butanone	10 to 50	0.2	0.547 to 0.542	[79]
	25	0.4 to 0.8	0.63 to 0.77	[80]
	27 to 52	0	0.490 to 0.474	[78,81–84]
	40	1	0.84	[75]
	70	0.6 to 0.8	0.63 to 0.72	[80]
	162 to 229	1	1.16 to 0.36	[73]
butyl acetate	30	0	0.466	[20]
	162 to 229	1	1.01 to 0.45	[73]
tert-butyl acetate	22 to 64	0	0.501 to 0.494	[132]
	64 to 111	0	0.494 to 0.501	[132]
	30 to 90	0.12 to 0.32	0.60 to 0.59	[133]
	143 to 183	1	0.39 to 0.1	[133]
butylbenzene	183 to 203	1	0.38 to 0.34	[65]
butylcyclohexane	160 to 180	1	0.77 to 0.71	[65]
carbon tetrachloride	40	1	0.29	[75]
	162 to 229	1	0.90 to 0.26	[73]
	23.5	0.71 to 0.81	0.22 to 0.24	[129]
chlorobenzene	30	0	0.454	[20]
	162 to 229	1	0.68 to 0.28	[73]
	137.6	1	0.30	[107]
chloroform	25	0.2 to 0.8	0.52 to 0.17	[74]
	40	1	0.13	[75]
	50	0.2 to 0.8	0.45 to 0.14	[74]
	162 to 229	1	0.43 to −0.01	[73]
	23.5	0.62 to 0.81	0.05 to −0.15	[129]
cumene	25	0	0.444	[77]
cyclohexane	15	0.5	0.77	[85]
	24	0 to 0.2	0.508 to 0.58	[86]
	30	0.3	0.62	[85]
	34	0 to 0.8	0.500 to 0.93	[86]
	35	0 to 0.3	0.50 to 0.57	[87]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
	40	1	0.64	[75]
	44	0 to 0.8	0.494 to 0.93	[86]
	45	0 to 0.3	0.49 to 0.56	[87]
	49 to 60	0	0.495 to 0.486	[84]
	50	0.1	0.51	[85]
	65	0 to 0.3	0.47 to 0.54	[87]
	160 to 180	1	0.62 to 0.53	[65]
	162 to 229	1	1.11 to 0.46	[73]
	23.5	0.78 to 0.84	0.79 to 0.81	[129]
	30 to 50	0	0.52 to 0.39	[134]
	35	0.28 to 0.94	0.61 to 1.08	[139]
	65	0.23 to 0.92	0.52 to 0.69	[139]
cyclohexanone	27 to 57	0	0.436	[81]
cyclopentane	40	1	0.64	[75]
cis-decahydronapthalene	183 to 203	1	0.47 to 0.42	[65]
trans-decahydronaphthalene	183 to 203	1	0.52 to 0.46	[65]
n-decane	183 to 203	1	1.01 to 0.94	[65]
	120 to 160	1	1.36 to 1.03	[107]
1,2-dichloroethane	162 to 229	1	0.85 to 0.22	[73]
dichloromethane	40	1	0.34	[75]
	162 to 229	1	0.62 to −0.21	[73]
	23.5	0.64 to 0.82	0.17 to 0.05	[129]
1,4-dioxane	40	1	0.43	[75]
	162 to 229	1	0.95 to 0.42	[73]
n-dodecane	183 to 203	1	1.09 to 1.00	[65]
ethanol	162 to 229	1	1.80 to 0.43	[73]
ethyl acetate	27 to 49	0	0.490	[84]
	162 to 229	1	1.14 to 0.35	[73]
ethylbenzene	10 to 60	0.2	0.44	[88]
	25	0	0.450	[77]
	120 to 185	1	0.22 to 0.14	[72]
ethylene glycol	162 to 229	1	3.8 to 2.2	[73]
ethyl ether	162 to 229	1	0.78 to 0.71	[73]
fluorobenzene	40	1	0.37	[75]
formamide	162 to 229	1	4.1 to 3.2	[73]
n-heptane	40	1	0.95	[75]
	162 to 229	1	1.33 to 0.25	[73]
n-hexane	40	1	0.97	[75]
	162 to 229	1	1.35 to −0.03	[73]
n-hexadecane	183 to 203	1	1.22 to 1.14	[65]
isopropyl ether	40	1	0.78	[75]
	162 to 229	1	1.42 to 0.41	[73]
methanol	162 to 229	1	2.19 to 0.44	[73]
methylcyclohexane	72	0 to 0.4	0.49 to 0.67	[89]
2-methyl-1-propanol	162 to 229	1	1.71 to 0.81	[73]
naphthalene	183 to 203	1	0.12	[65]
nitrobenzene	162 to 229	1	1.18 to 0.72	[73]
n-octane	40	1	0.95	[75]
	162 to 229	1	2.19 to 0.80	[73]
1-octanol	162 to 229	1	1.41 to 0.55	[73]
n-pentane	162 to 229	1	1.12 to 0.83	[73]
1-pentanol	162 to 229	1	1.75 to 0.86	[73]
1-propanol	162 to 229	1	1.71 to 0.27	[73]
2-propanol	40	1	2.6	[75]
	162 to 229	1	1.74 to −0.15	[73]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
propyl acetate	25	0.4 to 0.8	0.66	[74]
	40	1	0.52	[75]
	70	0.4 to 0.8	0.60	[74]
pyridine	162 to 229	1	1.02 to 0.23	[73]
tetrachloroethylene	40	1	0.36	[75]
n-tetradecane	183 to 203	1	1.14 to 1.08	[65]
tetrahydrofuran	162 to 229	1	0.70 to −0.16	[73]
1,2,3,4-tetrahydronaphthalene	183 to 203	1	0.20	[65]
3,3,4,4-tetramethylhexane	160 to 180	1	0.90 to 0.76	[65]
toluene	22	0.2 to 0.6	0.40	[21]
	25	0.4 to 0.8	0.42 to 0.31	[80,87]
	25	0.2 to 0.8	0.37 to 0.16	[76]
	27 to 40	0	0.437 to 0.482	[20,53,69,78,81,82,84]
	40	1	0.19	[75]
	45	0 to 0.3	0.41 to 0.37	[87]
	60	0.8	0.32	[80]
	65	0 to 0.3	0.40 to 0.37	[87]
	68	0	0.452	[81,84]
	80	0.4 to 0.6	0.40 to 0.35	[80]
	162 to 229	1	0.67 to 0.04	[73]
	23.5	0.66 to 0.83	0.34 to 0.22	[129]
	25	0.03 to 0.34	0.43 to 0.40	[127]
	25	0.07 to 0.20	0.40 to 0.39	[131]
	40	0.06 to 0.18	0.42	[131]
	137.6	1	0.32	[107]
trichloroethylene	40	1	0.19	[75]
	162 to 229	1	0.69 to 0.12	[73]
2,2,4-trimethylpentane	162 to 229	1	1.72 to 0.35	[73]
water	162 to 229	1	4.4 to 3.1	[73]
o-xylene	162 to 229	1	0.72 to 0.26	[73]
Poly(tetramethylene oxide)				
acetone	100	1	0.73	[19]
benzene	100	1	0.04	[19]
n-butane	100	1	0.76	[19]
1-butanol	100	1	0.54	[19]
2-butanone	100	1	0.53	[19]
butyl acetate	100	1	0.30	[19]
carbon tetrachloride	100	1	0.10	[19]
chlorobenzene	100	1	−0.09	[19]
1-chlorobutane	100	1	0.22	[19]
chloroform	100	1	−0.38	[19]
chloromethane	100	1	0.19	[19]
1-chloropentane	100	1	0.18	[19]
cycloheptane	100	1	0.41	[19]
cyclohexane	100	1	1.23	[19]
cyclohexene	100	1	0.28	[19]
cyclooctane	100	1	0.40	[19]
cyclopentane	100	1	0.45	[19]
n-decane	100	1	0.80	[19]
1,1-dichloroethane	100	1	0.00	[19]
1,2-dichloroethane	100	1	0.05	[19]
dichloromethane	100	1	−0.12	[19]
1,4-dioxane	100	1	0.39	[19]
ethanol	100	1	1.08	[19]
ethyl acetate	100	1	0.45	[19]
ethylbenzene	100	1	0.07	[19]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
n-heptane	100	1	0.73	[19]
n-hexane	100	1	0.74	[19]
methyl acetate	100	1	0.58	[19]
n-nonane	100	1	0.78	[19]
n-octane	100	1	0.75	[19]
n-pentane	100	1	0.76	[19]
1-pentanol	100	1	0.37	[19]
propane	100	1	0.90	[19]
1-propanol	100	1	0.71	[19]
propyl acetate	100	1	0.36	[19]
tetrahydrofuran	100	1	0.13	[19]
1,1,1-trichloroethane	100	1	−0.02	[19]
trichloroethylene	100	1	−0.06	[19]
toluene	100	1	0.04	[19]
n-undecane	100	1	0.83	[19]
Poly(ε-valerolactone)				
acetone	120	1	0.64	[18]
benzene	120	1	0.34	[18]
2-butanone	120	1	0.43	[18]
carbon tetrachloride	120	1	0.61	[18]
chloroform	120	1	−0.02	[18]
dichloromethane	120	1	0.86	[18]
ethyl acetate	120	1	0.54	[18]
n-heptane	120	1	1.6	[18]
n-hexane	120	1	1.6	[18]
n-pentane	120	1	1.5	[18]
Poly(vinyl acetate)				
acetaldehyde	125 to 140	1	0.35 to 0.32	[90]
acetone	25 to 29	0	0.40	[91–93]
	30 to 40	0.8	0.34	[94]
	30 to 50	1	0.31 to 0.39	[94]
	100 to 140	1	0.32 to 0.21	[19,90]
acetonitrile	125 to 140	1	0.54 to 0.49	[90]
allyl chloride	40	1	0.27	[94]
benzene	5	0.2	0.46	[95]
	20	0	0.42	[16]
	30	0.4 to 0.8	0.45 to 0.29	[96]
	35 to 62	0	0.51 to 0.42	[97]
	30 to 50	1	0.30 to 0.26	[94]
	80 to 140	1	0.44 to 0.25	[19,90,98]
	125 to 145	1	0.37 to 0.32	[32,99,100]
n-butane	100	1	1.97	[19]
1-butanol	100 to 135	1	0.62 to 0.38	[19,99]
2-butanol	135	1	0.31	[99]
2-butanone	10 to 45	0	0.43	[91]
	100 to 140	1	0.34 to 0.20	[19,90]
butyl acetate	100	1	0.51	[19]
butylbenzene	125 to 145	1	0.95 to 0.88	[100]
butylcyclohexane	125 to 145	1	1.90 to 1.75	[100]
carbon tetrachloride	90 to 135	1	0.85 to 0.63	[19,32,98]
chlorobenzene	100 to 135	1	0.28 to 0.33	[19,32]
1-chlorobutane	100 to 135	1	0.73 to 0.66	[19,32]
chloroform	80 to 135	1	−0.17 to −0.09	[19,32,98]
chloromethane	100	1	0.25	[19]
1-chloropentane	100	1	0.82	[19]
1-chloropropane	40	1	0.75	[94]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
cycloheptane	100	1	1.63	[19]
cyclohexane	100 to 140	1	1.65 to 1.16	[19,32,90,98,100]
cyclohexene	100	1	1.18	[19]
cyclohexanol	135	1	0.44	[32,99]
cyclooctane	100	1	1.67	[19]
cyclopentane	100	1	1.53	[19]
cis-decahydronaphthalene	125 to 145	1	1.65 to 1.50	[100]
n-decane	100 to 145	1	2.5 to 2.01	[19,32,99,100]
1-decanol	135	1	0.81	[99]
1,1-dichloroethane	100	1	0.19	[19]
1,2-dichloroethane	100 to 140	1	−0.04 to 0.00	[19,90]
dichloromethane	100	1	−0.14	[19]
dimethylphthalate	25	0	0.400	[91]
1,4-dioxane	25	0	0.407	[91]
	100 to 140	1	0.17 to 0.03	[19,90]
n-dodecane	125 to 145	1	2.48 to 2.27	[99,100]
ethanol	50	0	0.47	[97]
	100	1	0.80	[19]
ethyl acetate	20	0	0.415	[16]
	100	1	0.36	[19]
ethylbenzene	100 to 135	1	0.66 to 0.58	[19,99]
n-heptane	100 to 120	1	2.14 to 1.63	[19,90,98]
1-heptanol	135	1	0.55	[99]
n-hexadecane	135	1	2.99	[99]
n-hexane	100 to 120	1	2.06 to 1.71	[19,98]
1-hexanol	135	1	0.49	[99]
isopropylamine	40	1	0.66	[94]
methanol	125 to 140	1	0.77 to 0.73	[90]
methyl acetate	100	1	0.30	[19]
2-methyl-2-propanol	135	1	0.30	[99]
nitroethane	125 to 140	1	0.14 to 0.19	[90]
n-nonane	100 to 145	1	2.38 to 1.88	[19,32,99,100]
n-octane	90 to 120	1	2.3 to 1.94	[19,98]
1-octanol	135	1	0.65	[99]
1-octene	135	1	1.55	[32]
n-pentane	100	1	2.06	[19]
1-pentanol	100 to 135	1	0.59 to 0.41	[19,99]
2-pentanone	135	1	0.38	[32]
propane	100	1	3.2	[19]
1-propanol	30 to 50	1	1.3 to 1.0	[94]
	100 to 135	1	0.64 to 0.38	[19,99]
2-propanol	125 to 140	1	0.44 to 0.35	[90,99]
propyl acetate	100	1	0.42	[19]
propylamine	40	1	0.61	[94]
n-tetradecane	135	1	2.70	[99]
tetrahydrofuran	100 to 140	1	0.30 to 0.14	[19,90]
1,2,3,4-tetrahydronaphthalene	125 to 145	1	0.83 to 0.77	[100]
3,3,4,4-tetramethylhexane	125 to 145	1	1.72 to 1.56	[100]
toluene	80 to 140	1	0.56 to 0.40	[19,90,98,99]
1,1,1,-trichloroethane	100	1	0.49	[19]
trichloroethylene	100	1	0.40	[19]
1,2,3-trichloropropane	15 to 50	0	0.38	[91]
2,2,4-trimethylpentane	100 to 120	1	2.17 to 1.86	[98]
n-undecane	100 to 145	1	2.7 to 2.14	[19,99,100]
vinyl acetate	30	0.4 to 0.8	0.41 to 0.22	[96]
water	40	1	2.5	[101]

TABLE 14.1. *Continued.*

Solvent	Temperature (°C)	Volume fraction, ϕ_2	χ	References
Poly(vinyl alcohol)				
water	30	0	0.494	[102]
Poly(vinyl chloride)				
acetaldehyde	125 to 140	1	0.76 to 0.69	[90]
acetone	120 to 140	1	0.77 to 0.53	[18,90]
acetonitrile	125 to 140	1	0.98 to 0.92	[90]
benzene	120	1	0.75	[18]
	125 to 140	1	0.41 to 0.37	[90]
2-butanone	0 to 50	0	0.402 to 0.413	[103]
	120 to 140	1	0.72 to 0.46	[18,90]
carbon tetrachloride	120	1	1.14	[18]
chloroform	120	1	0.91	[18]
cyclohexane	125 to 140	1	1.21 to 1.09	[90]
cyclohexanone	30 to 69	0	0.240 to 0.264	[103]
1,2-dichloroethane	125 to 140	1	0.55 to 0.49	[90]
dichloromethane	120	1	1.63	[18]
1,4-dioxane	14 to 77	0	0.518 to 0.454	[103]
	125 to 140	1	0.18 to 0.13	[90]
ethyl acetate	120	1	0.94	[18]
n-heptane	120	1	2.0	[18]
	125 to 140	1	1.64 to 1.54	[90]
n-hexane	120	1	2.1	[18]
methanol	125 to 140	1	1.42 to 1.24	[90]
nitroethane	125 to 140	1	0.69 to 0.61	[90]
n-pentane	120	1	1.7	[18]
2-propanol	125 to 140	1	1.10 to 0.97	[90]
tetrahydrofuran	125 to 140	1	0.43 to 0.34	[90]
toluene	125 to 140	1	0.45 to 0.41	[90]
Poly(vinyl methyl ether)				
acetone	40	1	0.75	[75]
benzene	40	1	0.15	[75]
2-butanone	40	1	0.50	[75]
carbon tetrachloride	40	1	0.06	[75]
chloroform	40	1	−0.92	[75]
cyclohexane	40	1	1.16	[75]
cyclopentane	40	1	1.14	[75]
dichloromethane	40	1	−0.39	[75]
1,4-dioxane	40	1	0.20	[75]
ethylbenzene	25	0.06 to 0.16	0.29 to 0.27	[131]
fluorobenzene	40	1	0.00	[75]
n-heptane	40	1	1.15	[75]
n-hexane	40	1	1.16	[75]
isopropyl ether	40	1	0.76	[75]
n-octane	40	1	1.16	[75]
2-propanol	40	1	0.90	[75]
propyl acetate	40	1	0.25	[75]
tetrachloroethylene	40	1	0.34	[75]
toluene	40	1	0.14	[75]
	25	0.06 to 0.15	0.28 to 0.26	[131]
trichloroethylene	40	1	−0.26	[75]
Poly(*N*-vinyl pyrrolidone)				
water	25	0.06	0.48	[109]

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CHAPTER 15

Theta Temperatures

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15.1 INTRODUCTION

The statistically averaged configurations of polymers can conceptually be treated under the framework of a *freely jointed* chain, similar to that of a diffusing particle executing a random flight, with each of the skeletal bonds of the chain resembling a step in the random walk. Apart from the condition that each step size (or bond length) is fixed, there is no restriction on the spatial positions of successive steps in this model. However, the significant differences which set a real chain apart from a random flight model are that (1) the "cross over" of paths of any two bonds is prohibited resulting in *volume exclusion* and (2) the contiguous bonds are restricted to a narrow range of bond angles. These factors result in an expansion of the random coil compared to the ideal freely jointed chain. In addition, steric hindrance between atoms and groups limit the dihedral rotational range as well, limiting the scope of the *freely rotating* chain concept. In the latter, the bond length and bond angle are constrained but the dihedral angles may assume any value. Thus, the random coil of a real chain will be more expanded than predicted by the freely jointed or freely rotating chain models.

The concept of the excluded volume and the theta conditions have been explained eloquently by Flory [1,2]. The average configuration of a polymer chain in a dilute solution is dictated by short-range and long-range interactions. The former is determined by the geometrical constraints such as the bond length, bond angle, and the hindrance to dihedral rotations caused by steric interactions between the atoms or groups separated by a short sequence of bonds. The long-range effects are due to the interactions between units which are remote from one another in *sequence*, but close to each other in *space*. The configuration of the polymer chain must depend also on its environment. In a good solvent, the energy of interaction between a chain element and an adjacent solvent molecule would exceed the mean of the energies of interaction between the polymer-polymer and the solvent-solvent pairs. The chain will then tend to expand further, so as to reduce the frequency of contacts between pairs of polymer elements. In a poor solvent, however, where the energy of polymer-solvent interaction is unfavorable, more compact configurations, in which polymer-polymer contacts occur more often, will be preferred. If the solvent medium is sufficiently poor, i.e., the interaction energy with the polymer is sufficiently positive, the energy of interaction, at a certain temperature, may compensate exactly the influence of volume exclusion. When this condition, called the "Theta (Θ) condition" is achieved, the polymer chain will assume its so-called random flight configuration, its overall dimensions then being determined solely by short-range bond lengths, bond angles, and sterically favorable dihedral rotations. At this temperature an exact balance occurs between the effect of mutual volume exclusion of the segments, which tends to enlarge the molecule, and the effect of a positive energy of mixing, which encourages first neighbor contacts between polymer segments, and hence a more compact configuration for the molecule. The chain dimension will then be unperturbed by self-interaction of long range. The unperturbed dimensions thus obtained may then be interpreted in terms of the short-range features of the chain molecule.

In terms of the thermodynamics of mixing the polymer and the solvent, the Θ temperature is defined as that at which the excess chemical potential is zero. The latter ($\Delta\mu$) is given by Flory [1]

$$\Delta\mu = RT(\kappa_1 - \psi_1)(\upsilon_2)^2, \qquad (15.1)$$

where κ_1 and ψ_1 are the enthalpy and entropy parameters and υ_2 refers to the volume fraction of the polymer in a volume element. R and T are the gas constant and absolute temperature, respectively. Defining an ideal temperature (Θ) by

$$\Theta = \kappa_1 T/\psi_1, \tag{15.2}$$

such that

$$\psi_1 - \kappa_1 = \psi_1(1 - \Theta/T), \tag{15.3}$$

Eq. (1) transforms to

$$\Delta\mu = -RT\psi_1(1 - \Theta/T)(\upsilon_2)^2. \tag{15.4}$$

When the temperature $T = \Theta$, the excess chemical potential due to the polymer segment-solvent interaction reduces to zero. Thus at the theta temperature, the deviation from ideality vanishes. The system in this case can be binary, consisting of the solvent and the polymer or ternary, with a mixture of two solvents and the polymer.

In terms of the phase equilibrium of the poor-solvent/polymer mixture, the Θ temperature is identified with the critical miscibility temperature in the limit of infinite molecular weight. This then leads to the possibility of a Θ_l corresponding to the lower critical solution temperature (LCST) and Θ_u for the upper critical solution temperature (UCST) (see e.g., [3]). Although in most cases the LCST is inaccessible due to the boiling point of the solvent or the polymer degradation, both Θ_l and Θ_u have been determined in a few cases [4–6]. (In polymer science, the definitions of LCST and UCST are such that the lower critical solution temperature actually corresponds to the higher temperature in the phase diagram. In the tables which follow, notice that Θ_l is higher than Θ_u. This is in contrast to the case in colloid chemistry, where the lower critical flocculation temperature in indeed a lower temperature than the upper critical flocculation temperature.)

At the theta temperature, the intrinsic viscosity $[\eta]$ is related to the unperturbed dimension of the polymer and its molecular weight [1] by

$$[\eta]_\Theta = \Phi(\langle r^2\rangle_0/M)^{3/2}M^{1/2}, \tag{15.5}$$

or

$$[\eta]_\Theta = K_\Theta M^{1/2}, \tag{15.6}$$

where $\langle r^2\rangle_0$ is the unperturbed mean square end-to-end distance, Φ is the Flory universal constant and K_Θ is a constant defined by

$$(\langle r^2\rangle_0/M)_\infty = (K_\Theta/\Phi)^{2/3}. \tag{15.7}$$

Flory [2] recommended a value of 2.6×10^{21} for Φ, when r is expressed in centimeters and $[\eta]$, in deciliters per gram.

The "characteristic ratio" of the unperturbed end-to-end distance of a chain with n skeletal bonds is defined by

$$C_n = \langle r^2\rangle_0/nl^2 \tag{15.8}$$

where l is the average bond length per repeat unit. The denominator, nl^2, in Eq. 15.8 corresponds to the value of the mean square end-to-end distance if no correlations exist between bond directions, i.e., that of a freely jointed chain. Thus, the characteristic ratio represents the ratio between the actual unperturbed dimension of a real chain to that of a conceptual freely jointed chain. Hence, the more rigid and extended the chain is, the higher will be the value of C_n.

In the limit of infinite molecular weight, the characteristic ratio C_∞ can be calculated from K_Θ using the relationship [2]

$$C_\infty = (K_\Theta/\Phi)^{2/3}(M_0/l^2). \tag{15.9}$$

Here, M_0 is the mean molecular weight of the repeat unit of the chain (averaged over the skeletal bonds in the repeat unit) and l is the average bond length per skeletal bonds of the repeat unit. K_Θ in Eq. (15.9) is expressed in $\mathrm{dl.g^{-1}(g\ mol\ wt)^{-1/2}}$.

Let us illustrate the calculation of C_∞ from K_Θ, using Eq. 15.9 with two examples, one for a chain with two skeletal bonds in the repeat unit and the other with three skeletal bonds:

1. For poly(isobutylene), $[\text{—CH}_2\text{—C(CH}_3)_2\text{—}]_n$, $K_\Theta = 10.7 \times 10^{-4}$ [7] (see Table 15.1). Two skeletal bonds comprise the repeat unit, with a molecular weight of 56. Hence, $M_0 = 28$. With an average skeletal bond length of 1.53×10^{-8} cm,

$$M_0/l^2 = 11.96 \times 10^{16}.$$

With the value of Φ cited above, $(K_\Theta/\Phi)^{2/3} = 5.5328 \times 10^{-17}$. The value of C_∞ is then 6.6.

2. The repeat unit of poly(oxyethylene), $[\text{—O—CH}_2\text{—CH}_2\text{—}]_n$, consists of three skeletal bonds and hence $M_0 = 14.67$. With a value of 1.53×10^{-8} cm for the length of the C—C bond and 1.43×10^{-8} cm for the two C—O bonds, the average l is 1.46×10^{-8} cm. Using a value of 11×10^{-4} for K_Θ [8] (see Table 15.9), the value of C_∞ is 3.88.

Studies, experimental or theoretical, under the Θ condition allow probing of the influence of the chain structure, tacticity, nature of the side groups, and the composition of the polymers on the overall chain configuration in terms of the local interactions which are dictated by bond lengths, bond angles, and the distribution of torsion angles. This enables relating these molecular features to the ultimate functional properties of the polymers. For example, the entanglement molecular weight, distance between entanglements, and viscoelastic properties have been correlated with the characteristic ratio, C_∞, of the unperturbed end-to-end distance [9–13].

The determination of the theta temperature by several techniques, such as intrinsic viscosity, phase equilibria, osmometry, light scattering, sedimentation equilibrium, and cloud point titration has been discussed comprehensively in a number of sources [1,14–16]. The influence of tacticities of select polymers on their theta temperatures and the unperturbed dimensions has also been reviewed [15,16]. The differences in the θ temperatures of protiated and deuterated systems have been studied [16a,b].

This chapter presents a collection of theta temperatures reported for various polymers, in Tables 15.1–15.11. In cases where a number of authors have studied the same polymer, the results are given in chronological order. This, in a sense, serves to follow the progress in this area. The solvents and the corresponding theta temperatures are grouped together from the results of a particular author(s) so that these would correspond to samples with the same characteristics in terms of M_w and its distribution.

In these tables, the polymer name is given in the first column. The tacticities of the polymer studied, if reported by the authors, are given either in terms of the diad fraction (f_m or f_r), or triad fractions (f_{mm}, f_{mr+rm}, and f_{rr}). Here the subscripts m and r refer to meso and racemic diads, respectively (see Chapter 1 on Chain Structures for these definitions). In Table 15.11, which is devoted to copolymers, the

TABLE 15.1. *Poly(alkanes).*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(acenaphthalene)	3.3–170	1.2–1.5	ethylene dichloride	30.0	3.35	[20]
	7.3–231			35.0	4.56	[21]
Polybutene-1, isotactic	10.5–93.5	1–1.2	anisole	89.1		[22]
	12.8–94		cyclohexane/*n*-propanol (69/31)	35.0	24.7	[23]
	39–259		anisole	89.0	11.1	[24]
			phenylether	148.0	10.3	
			phenetole	64.5	11.3	
Polybutene-1, atactic	4.4–130		anisole	86.2		[22]
	11.8–290		anisole	83.0	10.8	[24,25]
			i-amylacetate	23.0	11.3	
			phenylether	141.0	10.4	
			phenetole	61.0	10.5	
			toluene	−46.0	13.3	
Polyethylene	34–149		bis (2-ethylhexyl)adipate	145 (low density) 170 (high density)		[26]
	8.2–16.5	11.3	biphenyl	125.0	-	[27]
			diphenylene oxide	118.0	-	
	and	and	dodecanol-1	138.0	31.6	
			2-ethylhexyl sebacate	150.0	-	
	31.7	1.6	2-ethylhexyl adipate	170.0	-	
	2.19–103.5		biphenyl	127.5	32.3	[28,29]
			decanol	153.3	30.2	
			diphenyl ether	161.4	29.5	
			diphenyl methane	142.2	31.5	
			dodecanol-1	137.3	30.7	
			octanol-1	180.1	28.6	
	4.5–39.3	1.65–3.34	biphenyl	125.0 (high density)	39.8	[30]
	$M_\eta = 1.4–44.2$		*p*-tert amyl phenol	199.2		[31,32]
			anisole	153.5		
			benzyl phenyl ether	191.5		
			biphenyl	127.5	33.0	
			n-decanol	153.3		
			diphenyl ether	163.9	30.9	
			diphenyl methane	142.2	32.2	
			n-lauryl alcohol	137.3		
			p-nonyl phenol	162.4		
			n-octanol	180.1		
	8.98–90.9	~1.3	dioctyl adipate	145	23.7	[33]
	4.1–15.1		*p*-xylene/*n*-hexanol (30:70)	155,160		[34,35]

TABLE 15.1. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
	0.49–44.0		*n*-pentane	80.0		[36]
			n-hexane	133.3		
			n-heptane	173.9		
			n-octane	210.0 (all LCST)		
	low density 0.87–699	low density 1.11–6.94	biphenyl	118 (low density)		[37]
	high density 5.73–27.1	high density 1.68–1.95		130 (high density)	30.2 at 130 °C	
	0.9–68.8	1.0–1.97	biphenyl	128.0	38.0	[38]
			dodecanol	143.4	32.8	
			3,5,5 trimethylhexylacetate	121.0	34.6	
Poly(hexene-1)	8.13–143		phenetole	61.3	9.57	[39]
Poly(hexene-1 sulphone)	10.9–69.5		*n*-hexyl chloride	13.0		[40]
			MEK/isopropanol (37/63)	24.0		
			MEK/isopropanol (41.5/58.5)	4.0		
	M_n = 7–88.6		*n*-hexyl chloride	13.0	5.3	[41]
			MEK/*n*-hexane (29.8/70.2)	8.0		
	9.2–107	1.13	dioxane/*n*-hexane (40/60)	20.5	6.5	[42]
Poly(isobutylene)	M_η = 18–188		benzene	24.0	10.7	[7,43]
	(Ref. 7) 0.5–131		ethylbenzene/phenyl ether (75/25)	26.8	10.8	
	(Ref. 43)		ethylbenzene/phenyl ether (50/50)	76.0	11.7	
			phenetole	86.0	9.1	
			anisole	105.5	9.1	
			toluene	−13.0		
			ethyl *n*-caprylate	22.0		[44]
	117.1		*n*-butanol/*n*-hexane (23.6/76.4)	25.0		[45]
			n-butanol/methylcyclohexane (29.2/70.8)			
			butanone/carbon tetrachloride (33.7/66.3)			
			butanone/cyclohexane (36.8/63.2)			
			butanone/*n*-hexane (36.6/63.4)			
			carbon tetrachloride/dioxane (63.8/36.2)			
			chlorobenzene/*n*-propanol (76/24)			
			chloroform/*n*-propanol (77.1/22.9)			
			cyclohexane/dioxane (45.1/54.9)			
			cyclohexanol/toluene (29.3/70.7)			
			n-decanol/*n*-hexane (41.1/58.9)			
			n-decanol/methylcyclohexane (47.5/52.5)			
			dioxane/*n*-hexane (48.2/51.8)			
			dioxane/methylcyclohexane (51/49)			
			n-heptanol/*n*-hexane (37.4/62.6)			
			n-heptanol/methylcylohexane (39.5/60.5)			
			n-hexane/*n*-hexanol (68.3/31.7)			
			n-hexane/3-methylbutanone (57.6/43.4)			
			n-hexane/*n*-octanol (63.7/36.3)			
			n-hexane/*n*-pentanol (71.7/28.3)			
			n-hexane/ *n*-propanol (80.3/19.7)			

TABLE 15.1. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temper-ature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
			methylcylohexane/*n*-octanol (56/44)			
			methylcyclohexane/*n*-pentanol (65.2/34.8)			
			methylcyclohexane/*n*-propanol (74.2/25.8)			
	900	1.3	benzene	24.5		[46]
			n-pentane	θ_1:76.0		
			dibutyl ether	θ_1:204.0		
	16–470	~1.1	*i*-amyl isovalerate	22.1	11.0	[47]
	15–71		*i*-amyl isovalerate	21.0		[48]
			i-amyl benzyl ether	23.7	10.8	
			i-amyl *n*-butyrate	28.0	11.4	
			n-amyl *n*-butyrate	22.0		
			benzene	22.8	11.5	
			n-butyl *n*-butyrate	46.2		
			3-methyl 5-heptanone	55.5	10.9	
	0.01–179		benzene	25.0		[49]
			i-amyl isovalerate	25.0		
	8–160		*i*-amyl isovalerate	27.0		[50]
Poly-((S)-4-methyl hexene-1) $f_m > 0.95$	13.6–1200	2–6.8	α-chloronaphthalene	165.0	8.88	[51]
			o-dichlorobenzene	133.0	11.5	
Poly(4-methylpentene-1), isotatic			biphenyl	194.6		[52]
			diphenyl ether	210.0		
			diphenyl methane	176.6		
Poly(2-methylpentene-1 sulphone)	$M_n = 4.7–56.3$		MEK/isopropanol (39.5/60.5)	22.5	9.1	[41]
			MEK/*n*-hexane (35.4/64.6)	11.5	9.1	
Poly(octene-1)	25–400		phenetole	50.4	6.55	[53]
Poly(pentene-1), isotactic	$M_n = 10.8$		phenetole	56.0		[54]
syndiotactic	$M_n = 2.8$		phenetole	48.5		
isotactic	$M_n = 13.2–42.7$		isoamyl acetate	31.0		[55]
isotactic	6.1–306		2-pentanol	64.0	12.1	[56]
isotactic, atactic	0.2–23.1 (isotactic)		anisole	85.0	*i*:10.6;*a*:9.9	[57]
			i-butylacetate	32.5	*i*:12.0;*a*:10.0	
	0.2–55 (atactic)		diphenylmethane	121.0	*i*:9.8	
			phenetole	64.0	*i*:11.3;*a*:9.8	
Poly(1-phenyl-1-propyne)	1.5–145	1.06–1.09	phenylether	149.0	*i*:9.8;*a*:9.4	
Poly(propylene) syndiotactic	11.7		cyclohexane	36.0		[58]
Poly(propylene), isotactic			isoamyl acetate	42.0	17.2	[59]
			phenyl ether	145.4		[60]
			isoamyl acetate	~70.0		[61]
	2.8–56.4		*p*-tert-amylphenol	140.8		[62,63]
			benzyl phenyl ether	181.8		
			benzyl propionate	157.5		
			n-butanol	147.2		
			p-tert-butyl phenol	166.0		
			dibenzyl ether	183.2	10.6	
			biphenyl	125.1	15.2	
			diphenyl ether	142.8	13.7	

TABLE 15.1. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
	$M_\eta = 5.0$–53.1		diphenyl	125.0	14.1	[64]
			phenylether	143.0	13.0	
Poly(propylene), atactic			phenyl ether	153.5		[60]
			1-chloronaphthalene	74.0		[65,66]
			cyclohexanone	92.0		
	$M_\eta = 4.3$–70.8		biphenyl	129.0	12.8	[64]
			diphenyl ether	146.0	12.5	
			isobutyl acetate	58.0	15.8	
			isoamylacetate	34.0	16.8	
	2.3–42.0	1.02–1.35	1-octanol	77.0	11.5	[67]
Poly(propylene), atactic [hydrogenated poly (2-methyl-1,3-pentadiene)] $f_m = 0.502$	3.91–37.1	1.04–1.12	2-octanol	37.6	13.2	[68]
Polypropylene (head-to-head)	$M_n = 0.22$–4.19		isoamylacetate	43.0	10.3	[69]
	1.64–43.3	1.0–1.07	isoamylacetate	56.8	12.6	[70]

TABLE 15.2. *Poly(alkenes).*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(butadiene), (*cis*: 0.98)	$M_n = 5.3$–48.9		isobutyl acetate	20.5	18.5	[71]
Poly(butadiene), *cis* (*cis*: 0.95; *trans*: 0.01; 1,2: 0.04)			diethyl ketone	10.3	18.1	[72]
			methylisoamyl ketone	12.6	17.8	
			methyl *n*-propyl ketone	59.7	15.7	
			methylisoamyl ketone/ methyl *n*-propyl ketone			
			(3/1)	22.3	17.5	
			(1/1)	32.7	17.1	
			(1/3)	46.2	16.7	
			diethyl ketone/methyl *n*-propyl ketone (3/2)	30.0	17.4	
Poly(butadiene), *cis*	5.0–110		*n*-heptane/*n*-hexane (50/50)	5.0		[73]
Poly(butadiene), *cis* (*cis*: 0.93; *trans*: 0.04; 1,2: 0.03)	$M_\eta = 10.8$–69.2		diethyl ketone	θ_u:14.0 θ_i:208.0		[4]
			ethyl propyl ketone	θ_u:-22.0 θ_i:237.0		
			propylene oxide	θ_u:35.0 θ_i:141.0		
Poly(butadiene) (*cis*:0.36; *trans*: 0.57; 1,2 *vinyl*: 0.07)	1.08–57.1	≤1.1	dioxane	26.5	17.8	[74]
Poly(butadiene), *trans* (*trans*: 0.94; 1,2: 0.06)	$M_\eta = 4.7$–19.3		diethyl ketone	213.0		[4]
			ethyl propyl ketone	240.0		
			propylene oxide	146.0		
Poly(butadiene), *cis*, cyclized Deg. Cycl.			cyclohexane/dioxane		K_θ as a function of cyclization is given in Figure 6 of this ref.	[75]

TABLE 15.2. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temper- ature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
9%	10.8–51.8		(12/88)	30.0		
31%	6.2–116		(17/83)	30.0		
46%	4.8–34.6		(21/79)	30.0		
63%	3.6–110		(30/70)	30.0		
81%	5.5–86		(39/61)	30.0		
1,4-poly(2,3-dimethyl butadiene) (>85% *trans*-1,4; 3% 1,2 *vinyl*)	$M_n = 5.01$ and 1.81		cyclohexane/*n*-propanol (81.3/18.7)	25.0	22.7	[76]
1,4-1,2-poly(dimethylbutadiene) (*trans* 1,4: 23%; *cis* 1,4: 32%; 3,4: 45%)	2.51–23.8	1.03–1.19	isoamylacetate	30.0	12.6	[70]
Poly(chloroprene)	5.6–79.4	1.22–1.5	MEK	25.0	11.6	[77]
			cyclohexane	45.5	10.7	
			cylopentane	56.3	-	
	15.1–304		MEK	25.0	11.3	[78]
	58.7–171		trans decalin	2.0		[79]
Poly(isoprene) (43% brominated)	380		cyclohexane	20.0		[80]
Poly(isoprene)			methyl isobutyl ketone	13.0		[81]
Poly(isoprene), *cis*	5–100		n-hexane/isopropanol (50/50)	21.0	16.6	[73]
Poly(isoprene), *cis* (96%)	6.9–75	1.29–1.98	dioxane	31.2	13.4	[82]
Poly(isoprene), *cis* (94%)	linear 9.4		methyl isobutyl ketone	16.5		[83]
			methyl propyl ketone	33.0		
3 branches	5.7; Br: 1.75		methyl propyl ketone	33.0		
11 branches	18; Br: 1.6		methyl propyl ketone	27.8		
22 branches	34.2; Br: 1.6		methyl propyl ketone	23.5		
			methyl isobutyl ketone	15.0		
Poly(isoprene), *trans* (96%)	$M_\eta = 9.2–27$		dioxane toluene/*n*-propanol	47.7	19.1	[82]
			(68.4/31.6)	25.0	22.2	
			(67.6/32.4)	30.0	21.9	
			(66.5/33.5)	35.0	21.7	
			(65.8/34.2)	40.0	21.4	
			(64.5/35.5)	45.0	21.3	
			(63.8/36.2)	50.0	21.1	
Poly(isoprene), *cis*: 0.70; *trans*: 0.23;						[74,84, 85]
3,4: 0.07, star linear	0.5–222.5	1.06–1.17	dioxane	34.1	11.5	
4-arm star	3.8–195	1.0–1.1	dioxane	33.4	8.9	
6-arm star	4.5–144.6	1.01–1.04	dioxane	33.5	7.2	
			methyl isobutyl ketone	12.2		
			methyl *n*-propyl ketone	25.4		
8-arm star	arm:0.51–75; star: 4.1–590		dioxane	32.8		
12-am star	arm:0.35–44.5; star: 4.1–526		dioxane	32.9		
Poly(isoprene) (1,2: 0.35; 3,4: 0.65)			benzene/isopropanol (55/45)	20.0		86
Poly(2-methyl-1,3-pentadiene) (*cis/trans*: 64/36)	4.45–37.7		2-octanol	28.9	11.2	[87]
Poly(methylbutylene) (hydrogenated 1,4 polyisoprene)	0.84–60.0	1.02–1.13	*n*-hexyl acetate	60.9	18.9	[88]
1,4 polymyrcene (1,4: 90%; 3,4: 10%)	6.66–58.3	≤1.07	2-octanol	35.9	6.28	[70]

TABLE 15.2. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	K_θ.10^4 [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(pentenamer) (80% *trans*)	3.6–63.5	1.0–1.22	isoamyl acetate	38.0	23.4	[89]
Poly(vinylethylene)	1.22–52.1	1.02–1.13	2-octanol	32.8	12.0	[90]
Poly(vinylethylene) (1,2: 98%; 1,4: 2%)	1.12–48.9	≤1.07	1-hexanol	66.0	11.8	[70]

TABLE 15.3. *Poly(vinyl)s.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	K_θ.10^4 [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(ethylethylene)	2.66–55	1.03–1.11	2-octanol	23.5	7.4	[90]
	5.2–54.5	1.03–1.11	2-octanol	21.0	8.22	[70]
			1-octanol	53.0	7.49	
Poly(vinyl acetate)	87–346		methyl isopropyl ketone/*n*-heptane (73.2/26.8)	25.0		[91]
	2.7–126.8	∼2.0	*n*-heptane/methyl isopropyl ketone (27.3/72.7)	30.0	9.2	[92]
	4.1–83		ethyl *n*-butyl ketone	29.0	9.29	[93]
			ethyl isoamyl ketone	66.0	8.20	
	0.35–150	1.02–1.05	methanol	6.0	10.1	[94]
	3.0–32		ethyl *n*-butyl ketone	29.0	9.55	[95]
			carbon tetrachloride	46.4		
			ethanol	19.0		[83]
			3-heptanone	29.0		
	0.8–130		cetyl alcohol	123.0	5.37	[96]
Branched			ethanol	12–15		[83]
			3-heptanone	26.0		
Poly(9-vinyladenine)	$M_n = 9.4$, 13, and 51		sodium cacodylate/water (0.1 m/L)	40.0	2.92	[[97]
Poly(vinyl alcohol)	1.35, 3.44, and 7.41		water	97.0		[98]
			t-butanol/water (32/68/w/w)	25.0		[99]
			ethanol/water (41.5/58.5 w/w)	25.0		
			methanol/water (41.7/58.3 w/w)	25.0		
			i-propanol/water (39.4/60.6 w/w)	25.0		
			n-propanol/water (35.1/6.49 w/w)	25.0		
Poly(vinyl alcohol), urethanized 4.9%; 8.1% or 11.5%	DP = 770–2040		*n*-propanol/water(30/40)	30.0		[100]
			n-propanol/water(40/50)	60.0		
			toluene	37.0	7.62	[101]
Poly (vinyl carbanilate)			cyclohexanol	55		[101a]
			diethyl ketone	35		

TABLE 15.3. *Poly(vinyl)s.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temper-ature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(*N*-vinylcarbazole)	34.6–229		chlorobenzene	−36.5		[102]
	7.6–56.4	1.2–1.3	nitrobenzene	−20.4		
			chlorobenzene/methanol (85.9/14.1)	25.0	7.38	[103]
		7.2–4.9	1,3-dichlorobenzene/ methanol(85/15)	25.0	8.77	
Poly(vinyl chloride)			benzyl alcohol	155.4	15.6	[104]
	4.3–48.7		THF/water (100/11.9); (100/9.5)	30.0		[105]
			n-butanol/cyclohexanone (15.8/100)	59.0		[106]
			n-butanol/cyclohexanone (41.5/100)	72.0		
			cyclohexane/DMF (100/12.8)	40.5		
			cyclohexanone	51.0		
			DMF	36.5		
			THF/water (100/5)	17.0		
	$M_n = 1.89$–10.2		methanol/THF (42/58)	22.0		[107]
$f_r = 0.53$–0.57	6.8 and 11.8		THF/water (91/9)	25.0		[108]
Poly(3-vinylpyrene)	3.5–48.7	∼1.1	chloroform	25.0	5.2	[109]
			methanol/THF (8/92)	25.0		
Poly(2-methyl-5-vinyl pyridine)	10.4–99		isoamyl acetate	53.2	8.4 (average)	[110]
			n-amyl acetate	48.2		
			isobutyl acetate	49.0		
			n-butyl acetate	21.8		
			ethyl *n*-butyrate	50.0		
			ethyl propionate	25.4		
			methyl isobutyl ketone	37.4		
			n-propyl acetate	19.3		
			n-propyl propionate	58.0		
			propionitrile	−3.6		
			tetrahydronaphthalene	49.5		
	6.7–120		*n*-amyl acetate	48.2	8.3	[111]
			n-butyl acetate	21.8	8.4	
			methyl isobutyl ketone	37.4	8.0	
Poly(2-vinylpyridine)	42–445		*n*-heptane/*n*-propanol (59.6/40.4 w/w)	25.0	12.0	[112]
	3.5–23.3	≤1.2	benzene	15.0	7.2	[113]
Poly(*N*-vinylpyrrolidone)	1.15		acetone/water (66.8/33.2)	25.0		[114]
	$M_n = 9.9$–45.7	≤1.4	acetone/water (66.8/33.2)	25.0	7.4	[115]
			Na_2SO_4/water (0.55 m/l)	28.0	5.8	
Poly(vinyl sulfonic acid)	DP=366–3640		KBr/water (0.347M)	5.7	7.72	[116]
			KCl/water (0.349M)	5.5	7.65	
			KCl/water (0.650M)	26.0	8.91	
			KCl/water (1.001M)	44.5	9.01	
			NaBr/water (0.346M)	−0.6	10.72	
			NaBr/water (1.008M)	40.1	10.6	
			NaCl/water (1.003M)	32.4	10.78	
Poly(vinyltriazole)	197		dimethyl formamide/dioxane (76.6/23.4)	25.0		[117]

TABLE 15.4. *Poly(styrenes).*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly (*p*-tert-butylstyrene) ($f_i = 0.15$, $f_s = 0.55$, $f_h = 0.30$)	1.8–640	1.02–1.22	1-nitropropane	31.0	6.1	[118,119]
Poly (*p*-tert-butylstyrene)	2.74–45.5 and 5.1–748	≤1.11 and 1.05–1.17	3-nonanol	10.9	5.95	[120–122]
			2-octanol	32.7	5.57	
			1-hexanol	65.0	5.11	
			1-nitropropane	31.0	6.00	
Poly(*p*-chlorostyrene)	20.1–125		ethyl benzene	−14.7	6.4	[123,124]
			ethyl carbitol	27.8	6.4	
			ethyl chloroacetate	−1.8	5.9	
			methyl chloroacetate	64.6	6.4	
			i-propyl acetate	75.7	6.4	
			i-propyl benzene	59.0	6.5	
			i-propyl chloroacetate	−8.2	5.6	
	M_η =34.1–1.79.9	1.37–1.79	benzene	8.0		[125]
			benzene/methanol			
			(5.5/1)	26.7		
			(5/1)	32.4		
			(4.5/1)	41.6	5.61	
Poly(*p*-decylstyrene)	21.3–57		MEK/butylethylketone (1/1.24)	21.2		[126]
Poly(3,4-dichlorostyrene)	35–540		butyl acetate/butyl alcohol (13/1 w/w)	32.9	5.6	[127]
Poly(*p*-hexylstyrene)	60–90		MEK	30.2		[126]
Poly(*p*-isopropylstyrene)			dioxane/isopropanol (35/65)	20.0		[86]
Poly(*p*-methoxystyrene)	8–150		*t*-butyl benzene	52.2	7.4	[128]
			isoamylacetate	75.0	6.9	
			dichlorodecane	92.6		
			methyl isobutylketone	23.4	6.4	
Poly(*p*-methoxystyrene)	$M_\eta = 7.6$–63.1		benzene/methanol (73.7/26.3)	25.0		[129]
			chloroform/methanol (66.5/33.5)	25.0		
			chloroform/cyclohexane (36.1/63.9)	25.0		
			MEK/*n*-heptane (80/20)	25.0		
			MEK/*n*-propanol (80.6/16.4)	25.0		
			toluene/cyclohexanol (62.8/37.2)	25.0		
Poly(α-methyl styrene)	29.4; 30.6; and 38.0		cyclohexane	36.2		[81]
Poly(α-methyl styrene)						[130,131]
f_{mm}: 0.08; f_{mr}: 0.48; f_{rr}: 0.44	9–400		cyclohexane	37.0	7.8	
f_{mr}: 0.10; f_{rr}: 0.90	2.7–367	1.8–2.8	cyclohexane	32.5	7.39	
f_{mr}: 0.19; f_{rr}: 0.81	2.6–17.5	1.11–1.60	cyclohexane	33.3	7.52	
f_{mm}: 0.03; f_{mr}: 0.29; f_{rr}: 0.68			cyclohexane	34.5		
f_{mm}: 0.06; f_{mr}: 0.40; f_{rr}: 0.55			cyclohexane	35.6		
f_{mm}: 0.11; f_{mr}: 0.45; f_{rr}: 0.44			cyclohexane	37.0	7.89	
Poly(α-methyl styrene)	20.4–747; also two samples with $M_n = 3.93$ and 8.01		cyclohexane	34.5	7.3	[132]
			trans-decalin	9.5	6.7	
	2.01–90.3	1.01–1.12	1-chloro-*n*-hexane	10.0	6.51	[133]
			cyclohexane	34.5	6.88	
			1-chloro-*n*-octane	53.0	6.31	

TABLE 15.4. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly (α-methyl styrene) 53% syndio; 41% hetero; 5% iso	5.9–341	1.03–1.15	cyclohexane	36.2		[133a]
Poly (α-methyl styrene) $f_r = 0.72$	0.053–322	1.01–1.05	cyclohexane	30.5		[133b]
Poly(*p*-methylstyrene)	16.3–197		diethyl succinate	16.4	7.0	[134]
Polystyrene	$M_\eta = 7.0$–127		cyclohexane	34.0	7.9	[135]
			ethylcyclohexane	70.0	7.3	
	$M_\eta = 0.4$–697		cyclohexane	34.0	8.2	[43]
	4–146		MEK/isopropanol (6/1)	23.0	7.30	[136]
	$M_\eta = 10.2$–53.2		toluene/methanol			[137]
			(76.9/23.1)	25.0	9.2	
			(75.2/24.8)	34.0	8.9	
			(72.8/27.2)	45.0	8.8	
	$M_\eta = 1.8$–271.6		decalin (23.1% *cis*)	19.3		[138]
	8.5–395		cyclohexane	35.0	8.0	[139]
	40.6	1.05	1-chloro-*n*-undecane	32.8	7.86	[140]
			diethyl malonate	35.9	7.69	
			cyclohexane	34.8	8.66	
	17		*n*-butyl formate	−9.0		[141]
			cyclohexane	34.0		
			cyclohexanol	83.5		
			decalin	29.5		
			diethyl malonate	31.0		
			diethyl oxalate	51.5		
			hexyl-*m*-xylene	12.5		
			methylcyclohexane	68.0		
	33.5		benzene/cyclohexanol (38.4/61.6)	25.0		[142]
			benzene/*n*-hexane (34.7/65.3)	25.0		
			benzene/methanol (77.8/22.3)	25.0		
			benzene/isopropanol (64.2/35.8)	25.0		
			butanone/methanol (88.7/11.3)	25.0		
			carbontetrachloride/methanol (81.7/28.3)	25.0		
			chlorobenzene/di-isopropyl ether (32/68)	25.0		
			chloroform/methanol (75.2/24.8)	25.0		
			dioxane/methanol (71.4/28.6)	25.0		
			methanol/tetrahydrofuran (28.7/71.3)	25.0		
	40.6		1-chloro-*n*-decane	6.6		[143]
			1-chloro-*n*-undecane	32.8		
			1-chloro-*n*-dodecane	58.6		
	$M_\eta = 1.04$– 123		benzene/isopropanol (66/34)	20.0		[86]
			dioxane/isopropanol (55/45)	20.0		
	$M_n = 0.054$– 0.72	≤ 1.1	cyclohexane	34.5	8.4	[144]
			n-hexane/3-methylbutanone (48/52)	20.0		[145]
			cyclohexane	34.5	7.8	[72]
			methyl cyclohexane	70.5	7.0	
			diethyl malonate	34.2	7.2	
			diethyl oxalate cyclohexane/ methylcyclohexane	55.8	7.3	
			(2/1)	43.0	7.8	
			(1/1)	48.0	7.5	
			(1/2)	54.0	7.3	

TABLE 15.4. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temper- ature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
			diethylmalonate/diethyl oxalate			
			(4/1)	40.0	7.1	
			(1/1)	47.4	7.1	
			(1/4)	52.6	7.1	
	5.8–200		trans decalin	23.8		[61]
			cyclohexanol	83.5		[146]
	4–440		decalin			[147]
			62% cis	15.2		
			100% cis	12.0		
	1.9–440		dioctyl phthalate	22.0		[148]
			trans decalin	23.5		[149]
	28 and 62	1.86 and 1.38	trans decalin	18.2		[150]
	220	≤1.1	benzene/*n*-butanol (58/42)	35.0		[151]
			benzene/heptane (44/56)	35.0		
			benzene/isopropanol (61/39)	35.0		
			benzene/methanol (74.7/25.3)	35.0		
			carbontetrachloride/heptane (53/47)	35.0		
			carbontetrachloride/*n*-butanol (65/35)	35.0		
			dioxane/heptane (41.5/58.5)	35.0		
			dioxane/isopropanol (51.5/48.5)	35.0		
			dioxane/methanol (66.5/33.5)	35.0		
			nitropropane/heptane (42/58)	35.0		
	7.0		cyclohexane	34.5		[152]
			methyl cyclohexane	60.0		
			d, l-terpineol	78.5	8.25 at 80 °C	
			cyclohexanol	83.5		
			3-methyl cyclohexanol	98.0		
			d, l-menthol	115.0		
	9–56	<1.2	dioxane/methanol (66.5/33.5)	35.0	8.2	[153]
	7.0; 16, and 800		benzene/methanol (78/22)	21.5, 23.5		[83]
			cyclohexane	34.5		
			decalin	14.5		
			diethyl malonate	35.6		
	2.2–137	1.19–2.8	cyclohexanol	86.0		[34,154]
	49–1340	<1.07	cyclohexane	34.5	8.77	[155]
			trans-decalin	20.4	8.05	
	3.7–270	<1.1	cyclopentane	θ_u:19.6	8.0	[156,157]
				θ_l:154.2	7.9	
	1–20;	<1.06	ethyl acetate	θ_u:−44.0		[5]
				θ_l:139.0		
	67; and 270	<1.15;	isoamyl acetate	θ_u:−49.0		
		and <1.1		θ_l:220.0		
			isobutyl acetate	θ_u:−46.0		
				θ_l:172.0		
			isopropyl acetate	θ_u:−27.0		
				θ_l:107.0		
			methyl acetate	θ_u:43.0		
				θ_l:114.0		
			n-propyl acetate	θ_u:−80.0		
				θ_l:178.0		
	21.5 and 250	<1.1 and ~2.0	dimethoxy methane/diethyl ether (330/70)	θ_u:−27.0 θ_l:−5.0		[6]
	11–270	1.15–1.94	1-chlorodecane	6.2	6.9	[158]
			trans decalin	22.8	6.7	

TABLE 15.4. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
			1-chlorodecane/3-methyl cyclohexanol (78/22)	22.8	7.5	
			cyclohexane	35.0	8.4	
			1-chlorodecane/3-methyl cyclohexanol (75/25)	35.0	7.4	
			diethyl oxalate	59.6	7.2	
			1-chlorodecane/3-methyl cyclohexanol (50/50)	59.6	7.2	
			cyclohexanol	87.8	7.1	
			1-chlorodecane/3-methyl cyclohexanol (10/90)	87.8	7.05	
			3-methyl cyclohexanol	98.4	6.5	
	3.7–200		Tetrahydrofuran/water (92.3/7.7)	25.0		[159]
	2.2–137	1.18–1.48	cyclohexanol	79.0		[160]
	10, 39, and 60	<1.1	1-phenyl decane	28.0		[161]
	10.6–96	<1.09	cyclohexane	34.5	8.59	[162]
			diethyl malonate	36.0	7.4	[163]
	10.6–77	<1.09	toluene/methanol (77/23)	25.1	9.0	[164]
Polystyrene, atactic	3.7–95	1.03–1.19	1-chloro-*n*-decane	8.5	8.01	[165]
			cycloheptane	19.0	8.09	
			cyclooctane	20.5	8.16	
			cyclopentane	20.5	8.40	
			1-chloro-*n*-undecane	32.8	7.74	
			cyclohexane	34.5	8.37	
			diethyl malonate	34.5	7.53	
			diethyl oxalate	58.2	7.35	
			1-chloro-*n*-dodecane	58.6	7.40	
			dimethyl succinate	67.6	7.30	
			methylcyclohexane	68.0	7.82	
			ethylcyclohexane	75.0	7.80	
Polystyrene atactic	0.047–347	1.00–1.05	methyl acetate	41.5		[165a]
Polystyrene, comb	M_n (backbone): 9.5–9.7 M_n (branch): 6.5–35.8		cyclohexane	31–33		[166]
	15–850		benzene/methanol (78/22)	16–24		[83]
			cyclohexane	18–33		
			decalin	4.5		
			diethyl malonate	22		
	backbone: 15.1–86; branch: 17.8–362		cyclohexane	25–33		[167]
Polystyrene, trifunctional star	34.8		cyclohexane	34.8		[168]
Polystyrene, four-arm star	8.5–311		cyclohexane	34.5	6.6	[168a]
Polystyrene, six-arm star	5.6–320		cyclohexane	34.5	5.5	[168b]
Polystyrene, star, 9.4 br/mol	47		cyclohexane	22.0		[169]
Polystyrene (head-to-head)	8.28	2.0	cyclohexane	19.0		[170]
Polystyrene, deuterated	7.3	2.08	cyclohexane	30.0		[170]
Polystyrene, deuterated	11.5		cyclohexane	30.0		[16a]
Polystyrene, deuterated	11.5		cyclohexane-D_{12}	35, 36		[16a]
Polystyrene	13.0		cyclohexane-D_{12}	38, 40		[16a]
Polystyrene	2.5–1320	1.06–1.3	cyclohexane-D_{12}	38		[16b]

Θ_u: theta temperature corresponding to the upper critical solution temperature; Θ_l: corresponding to lower critical solution temperature (see Introduction).

TABLE 15.5. *Poly(acrylics)/ poly(methacrylics).*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(acrylamide)	0.33–80		methanol/water (40/60)	20.0	12.7	[171]
	43–1000		methanol/water (41/59)	25.0	15.0	[172]
Poly(*N*-isopropylacrylamide)	13.8–910	1.2–1.4	water	30.6		[173]
Poly(2-acrylamido-2-methyl propane sulfonamide)	24.5–122.5		dioxane/water (18.5/81.5)	25.0	17.2	[174]
sodium poly(acrylate)	1.5–50		Aq. sodium bromide (1.504 m/L)	15.0	12.4	[175]
Poly(acrylonitrile), isotactic	$M_\eta =$ 4.6–20.6		ethylene-carbonate	60.0	29.5	[176]
Poly(acrylonitrile)	113–297		ethylene carbonate/ water (85/15)	44.0	29.8	[177]
Poly(methacrylonitrile)	0.54–8.0		dimethylformamide	29.2	30.6	[178]
Poly(cetyl acrylate)	4.7–14 000	1.18–1.47	butyl acetate	15.2		[179]
Poly(decyl acrylate)			*i*-amylalcohol	−8.5		[180]
			n-butylalcohol	−24.5		
			ethylacetate	9–11		
Poly(ethyl acrylate)	$M_\eta =$ 1.8–74		*n*-butanol	44.9		[181]
			ethanol	37.4		
			methanol	20.5		
			n-propanol	39.5		
	30–160	1.4	*n*-propanol	39.5	7.89	[182]
Poly(phenyl acrylate)	16–257	2.0	ethyl lactate	11.5	5.52	[183]
Poly(benzyl methacrylate)	19–170	1.4	cyclopentanol	73.2	2.8	[184]
Poly(*p*-biphenyl methacrylate)	8–108		benzene	11.0		[185]
Poly(*n*-butyl methacrylate)	30–260		isopropanol	21.5	2.95	[186]
	40–170		isopropanol	23.7	3.66	[187]
	11.7–64		isopropanol	25.0	4.2	[188]
		1.15	*n*-octane	68.9	3.81	[189]
			n-decane	84.8	4.07	
			n-dodecane	101.0	4.23	
			n-hexadecane	119.8	3.50	
			isopropanol	20.9	4.02	
			isobutanol	10.7	3.88	
Poly(tert-butyl methacrylate) (free radical, f_{mm}: 0.03; f_{mr+rm}: 0.38; f_{rr}: 0.59)	3.42–155	1.07–1.26	cyclohexane	10.0	4.89	[190]
			n-heptane	64.0	4.86	
Poly(tert-butyl methacrylate) (anionic, f_{mm}: 0.08; f_{mr+rm}: 0.47; f_{rr}: 0.45)	2.77–107	≤1.1	cyclohexane	10.0	6.08	[190,191]
Poly(4-*t*-butylcyclohexyl methacrylate)	23–110	1.4	*n*-butanol	25.0	3.1	[192]
Poly(*t*-butylcyclohexyl methacrylate)	15–193		*n*-butanol	40.0		[193]
Poly(2-*t*-butylphenyl methacrylate)	4.2–110	1.3	cyclohexane	18.4	3.5	[194]
Poly(4-*t*-butylphenyl methacrylate)	18–86	1.4	cyclohexane	25.0	4.4	[192]
Poly(*p*-*t*-butylphenyl methacrylate)	7–204	1.1–1.5	cyclohexane	25.0	4.5	[193a]
Poly(2-chloroethyl methacrylate) (f_{mm}: 0.07; f_{mr+rm}: 0.37; f_{rr}: 0.56)	3.2–54	1.2	*o*-dichlorobenzene	35.7	4.73	[194a]
Poly(cyclobutyl methacrylate) (f_{mm}: 0.03; f_{mr+rm}: 0.32; f_{rr}: 0.65)	4.83–31.1	∼1.1	*n*-butanol	37.5	4.8	[195]
Poly(cyclobutylmethyl methacrylate) (f_{mm}: 0.03; f_{mr+rm}: 0.30; f_{rr}: 0.65)	7.02–89.1	1.2–1.4	1-butanol	40.0	3.82	[196]
Poly(cyclododecyl methacrylate) (f_{mm}: 0.03; f_{mr+rm}: 0.34; f_{rr}: 0.63)	5.1–470	1.3	*n*-hexylacetate	35.0	3.3	[16,195]
Poly(cyclohexyl methacrylate) (f_{mm}: 0.13; f_{mr}: 0.36; f_{rr}: 0.51)	10–420	1.2	*n*-butanol	23.0	4.5	[197]

TABLE 15.5. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(cyclohexyl methacrylate)	10–125	~1.1	*n*-butanol	22.5	4.52	[198]
			octane	83.4	4.07	[199]
			decane	93.6	4.24	
			dodecane	97.5	4.29	
			propanol	39.5	4.90	
			butanol	22.5	4.58	
			hexanol	9.2	4.39	
			octanol	17.9	4.53	
			nonanol	20.2	4.55	
			decanol	23.0	4.64	
Poly(cyclohexylmethyl methacrylate) (f_{mm}: 0.03; f_{mr+rm}: 0.30; f_{rr}: 0.65)	5.59–81.5	1.2–1.4	1-butanol	45.0	4.23	[196]
Poly(cyclopentyl methacrylate) (f_{mm}: 0.02; f_{mr+rm}: 0.32; f_{rr}: 0.66)	2.9–358		cyclohexane	36.0	4.6	[195]
Poly(cyclooctyl methacrylate) (f_{mm}: 0.03; f_{mr+rm}: 0.34; f_{rr}: 0.63)	6.6–460	1.3	2-butanol	45.0	3.7	[16]
Poly(2-decahydronaphthyl methacrylate)	7–320	1.4	dipropyl ketone	25.0	4.2	[200]
Poly(decyl methacrylate)	25–73	1.14–1.6	1-pentanol	9.6		[201]
Poly(*n*-decyl methacrylate) (f_{mm}: 0.02; f_{mr}: 0.29; f_{rr}: 0.69)	3–90	1.4	ethyl acetate	11.0	3.5	[202]
Poly(2,6-diisopropylphenyl methacrylate)	5.1–40	1.2–1.24	THF/water (90.9/9.1)	25	9.4	[203]
Poly(2,6-dimethylphenyl methacrylate)	3.4–82.3	1.05–1.27	toluene	25.0	7.7	[204]
			THF/water (90.6/9.4)	25.0		
Poly(diphenylmethyl methacrylate) (f_{mm}: 0.25; f_{mr+rm}: 0.46; f_{rr}: 0.29)	8.7–574	1.1–1.26	3-heptanone	45.0	3.31	[205]
Poly(*n*-docosyl methacrylate) (f_{mm}: 0.04; f_{mr}: 0.33; f_{rr}: 0.63)	6–140	1.4	amyl acetate	31.0	3.7	[202]
Poly(*n*-dodecyl methacrylate)	26–360		*n*-amylalcohol	29.5	3.5	[206]
Poly(dodecyl methacrylate)	15–800		*n*-amylalcohol	29.5	2.85	[207]
	26–360		isopropyl acetate	13.0	3.2	[208]
Poly(ethyl methacrylate)	20–263		MEK/isopropanol (12.5/87.5)	23.0	4.73	[209]
	22–127		isopropanol	36.9	4.8	[187]
			MEK/isopropanol (1/7)	23.0	4.7	
	59.7–191		*n*-butyl chloride	−13.3		[210]
			methyl *n*-butyl bromide	0		
			methyl *n*-propyl ketone	−0.5		
			m-xylene	−2.7		
	22.0		isopropanol	36.9	5.91	[211]
Poly(2-ethylbutyl methacrylate)	50–330	1.3	isopropanol	27.4	3.4	[212]
Poly(n-hexyl methacrylate)	64–400		isopropanol	32.6	4.3	[213]
Poly(hexyleneoxy phenylenecarboxy phenyleneoxymethylene methacrtylate) (side chain LC polymer)	16.2–128		toluene	15.5		[214]
Poly (2-hydroxyethyl methacrylate)			isopropanol	37.0	6.0	[215]
	10–500		urea/water (mol/L)			[216]
			4	10.0	2.5	
			6	27.2	4.0	
			8	52.5	4.25	
Poly (2-hydroxyethyl methacrylate) f_m>0.85	M_η:3.9–81.6		water	15.3	2.15	[217]
			ethanol	15.8	6.23	
			1-propanol	32.1	6.10	
			2-propanol	14.0	6.45	
			2-butanol	3.7	6.50	

TABLE 15.5. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(*dl*-isobornyl methacrylate)	10–120	1.3	1-octanol	39.6	3.2	[218]
Poly(isobutyl methacrylate)	$M_n = 50.1$–115.9		2-hydroxy	19.5	2.65	[219]
Poly(isooctyl methacrylate)	84.7		acetone/*n*-heptane (64.1/35.9)	25.0		[220]
Poly(*n*-octyl methacrylate)	33–1300		*n*-butanol	16.8	2.7	[221]
Poly(*n*-lauryl methacrylate)	27–241		*n*-amyl alcohol	29.5	3.48	[208]
	M_n=16–122	1.63–1.69	*n*-amyl alcohol	29.5	3.48	[222]
Poly(5-*p*-methyl methacrylate) (f_m: 0.13)	13–230	1.5	methylpropyl ketone	25.0	4.4	[194]
Poly(1-{6-[4-(4-methoxyphenoxycarbonyl) phenoxy] hexyloxycarbonyl}-1-methylethylene)	8.9–107.6	1.22–1.56	toluene	17.0	2.69	[223]
Poly(methyl methacrylate)	30–284		MEK/isopropanol (50/50)	25.0	5.92	[223a]
	58–294		toluene/methanol (5/9)	26.2	5.59	[187]
	0.27–250	1.2–1.4	acetonitrile	30.0		[224]
	$M_\eta = 1$–260		acetonitrile	45.0	4.8 (average)	[225]
			diisopropyl ketone	46.0		
			2-ethyl butyraldehyde	22.0		
			4-heptanone	33.8		
			methyl neopentyl ketone	35.0		
			3-octanone	72.0		
	20, 130, and 650		*n*-butylchloride	35.0	5.3	[226]
			dioxane/*n*-hexane (59/41)	20.0		[86]
			n-hexane/3-methylbutanone (17/83)	20.0		[145]
	5.1 and 367	1.57 and 1.68	acetone/ethanol (47.7/52.3)	25.0	5.34	[227]
			acetone/methanol (78.1/21.9)	25.0	7.38	
			butanone/cyclohexane (59.5/40.5)	25.0	6.32	
			butanone/*n*-hexane (70.7/29.3)	25.0	7.61	
			butanone/isopropanol (58.2/41.8)	25.0	6.29	
			carbon tetrachloride/*n*-hexane (99.4/0.6)	25.0	7.21	
			carbon tetrachloride/methanol (53.3/46.7)	25.0	8.69	
			dioxan/cyclohexane (53.4/46.4)	25.0	7.70	
			cyclohexanol	77.6		[146]
			butanol	85.0		[181]
			propanol	83.2		
	M_η = 5– 110		cyclohexanone/isopropanol (51.6/48.4 w/w)	21–22	5.25	[228]
	3–30	<1.2	dioxane/cyclohexane (53/47)	20.0	6.4	[153]
			acetonitrile	38.0	5.25	[229]
	11–142	≤ 1.1	acetonitrile	32.3	4.0	[230]
			2-ethoxyethanol	37.8	5.6	
isotactic, $f_m = 0.9$	7.9–131.4		MEK/isopropanol (50/50)	30.3	9.0	[231]
			3-heptanone	40.0	8.7	
			n-propanol	75.9	7.61	
			p-cymene	152.1	5.66	
isotactic	M_η = 2.8– 52	1.0–1.5	acetonitrile	27.6	7.55	[232]
isotactic, $f_m = 0.94$	17.3		butanone/isopropanol (55/45)	25.0		[233]
			n-butyl chloride	26.5		

TABLE 15.5. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
syndiotactic	16.8		butanone/isopropanol (55/45)	8.0		
			n-butyl chloride	35.0		
$f_r = 0.8$	$M_\eta = 379$		nitrobenzene/isopropanol (42.9/57.1 w/w)	18.0		[149]
			m-xylene	24.0		
syndiotactic, $f_r = 0.78$	8.57–162	1.06–1.24	3-octanone	72.0	5.52	[233a]
			4-heptanone	33.8	5.00	
syndiotactic, $f_r = 0.92$	3.4	1.17	acetonitrile	44.0		[234]
PMMA $f_r = 0.79$	0.06–158	1.00–1.09	acetonitrile	44.0		[234a]
			n-butyl chloride	40.8		
atactic, $f_m = 0.07$	6.6–171		MEK/isopropanol (50/50)	25.0	5.92	
			3-heptanone	33.7	6.31	
			n-propanol	84.4	6.79	
			p-cymene	159.7	5.75	
f_{rr}: 0.60; f_{mr+rm}: 0.34; f_{mm}: 0.06	14–274	1.3–2.8	acetonitrile	28.0	4.30	[235]
			butyl chloride	35.0	5.15	
			m-xylene	25.0	5.15	
f_{rr}:0.43; f_{mr+rm}:0.51; f_{mm}:0.06	16.9	≤1.1	acetonitrile/butanol (93/7)	25.0		[236]
			acetonitrile/methanol (90/10)	25.0		
			acetonitrile/pentyl acetate (93/7)	25.0		
			acetonitrile/*n*-propanol (93/7)	25.0		
atactic, $f_r = 0.79$	0.03–283	≤1.07	acetonitrile	44.0		[237–240]
			n-butyl chloride	40.8		
Poly(β-naphthyl methacrylate)	21–290	1.6	benzene	25.0	5.4	[200]
	5.9–275	~1.5	tetralin	20.0	4.75	[241]
			toluene	55.0	3.9	
Poly(*n*-octadecyl methacrylate) (f_{mm}:0.02; f_{mr}:0.28; f_{rr}:0.70)	1.5–93	1.3	*n*-propyl acetate	36.0	3.7	[202]
Poly(octadecyl methacrylate)	62–320	1.7–2.2	butyl acetate	10.5		[242]
Poly(pentachlorophenyl methacrylate)	5.3–70	1.4	benzene	40.0	5.37	[243]
			ethylbenzene	25.0	5.37	
	$M_n = 1.6$, 14.4, and 23.9		benzene/toluene (10/90)	10.0		[244]
			benzene/toluene (50/50)	14.0		
			ethylbenzene	25.0		
			benzene/ethylbenzene (50/50)	30.0		
			chloroform	35.0		
			benzene	37.0		
	$M_n = 1.6$, 14.4, and 23.9		ethyl benzene	25.0		[193]
Poly(4-phenylbutyl-1-methacrylate) (f_{rr}:0.63; f_{mr+rm}:0.29; f_{mm}:0.08)	14.3–472	1.14–1.32	1-chloroundecane	23.0	3.37	[245]
Poly(2-phenylethyl-1-methacrylate) (f_{rr}:0.60; f_{mr+rm}:0.34; f_{mm}:0.06)	5.9–118	1.1–1.41	1-chloroheptane	27.5	3.67	[245]
Poly(phenylthiol methacrylate) (f_{mm}:0.16; f_{mr}:0.38; f_{rr}:0.46)	4.1–25	1.3	MEK	25.0	3.86	[246]
Poly(stearyl methacrylate) (f_{rr}:0.7; f_{mr+rm}:0.28; f_{mm}:0.02)	1.5–93.4	1.3	*n*-propyl acetate	36.0	3.71	[202]
Poly(tetrahydrofurfuryl methacrylate)	M_n = 16.9–61.3		2-hydroxymethyl tetrahydrofuran/methanol (80/20)	31.2	3.49	[247]

TABLE 15.5. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(tetrahydro-4 *H*-pyranyl-2-methacrylate) ($f_{rr} = 0.5$)	4.8–84	1.2	isobutanol	30.5	3.3	[248]
Poly(4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate) (f_{mm}:0.15; f_{mr}:0.4; f_{rr}:0.45)	M_n = 16–71		benzyl acetate	14.0	4.4	[249]
Poly(*n*-tridecyl methacrylate) (f_{mm}:0.02; f_{mr}:0.28; f_{rr}:0.70)	8–140	1.4	ethyl acetate	27.0	3.2	[202]

TABLE 15.6. *Other carbon chains.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(dibenzyl itaconate)	1.7–17	1.37	acetone	25.0	3.6	[250]
			THF/water (87.4/12.6)	25.0	5.02	
Poly (monobenzyl itaconate)	3.1–19.28		methanol	25.0		[251]
Poly(monocyclohexyl itaconate)	2.2–20.2	1.25–1.4	methanol	25.0	14.0	[251a]
Poly(monocyclopentyl itaconate)	2–21.5	1.1–1.4	methanol	25.0	12.0	[251a]
Poly(mono-methyl itaconate)	8.7–59.3	1.20–1.25	methanol	25.0	5.05	[252]
			2-ethoxyethanol	25.0	4.90	
Poly(mono-*n*-octyl itaconate)	7.8–110	1.25–1.30	2-propanol	30.0		[252a]
(di-methyl); (di-ethyl); (di-*n*-propyl); (di-*n*-butyl); (di-*n*-amyl); (di-*n*-hexyl); (di-*n*-heptyl); (di-*n*-octyl); (di-*n*-nonyl); (di-*n*-decyl); (di-*n*-undecyl) Polyitaconates	10–50		various common solvent mixtures	30.0		[253]
Poly[*N*-(*n*-octadecyl)maleimide]	$M_n = 0.12–19$		1-butanol	120.7	-	[254]
			1-decanol	39.5	18.2	
			1-hexanol	79.1	37.0	
			1-octanol	53.8	23.4	

TABLE 15.7. *Chains with silicon/oxygen/sulphur atoms.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(dimethylsiloxane)	55–120		MEK	20.0	7.8	[255]
			$C_8F_{18} + C_2Cl_4F_2$ (33.2/66.8)	22.5	10.6	[255]
	$M_n = 7.76$ and 10.7		benzene	−6.0		[256]
			bromobenzene	78.5		
			bromocyclohexane	28.0		
			n-butyl acetate	−38.0		
			chlorobenzene	−19.0		
			cyclohexane	−68.0		
			ethyl acetate	5.0		
			n-heptane	−173.0		
			n-hexane	−173.0		
			methylcyclohexane	−113.0		
			methylcyclopentane	−98.0		

TABLE 15.7. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
			methyl ethyl ketone	20.0		
			n-nonane	−113.0		
			n-octane	−143.0		
			phenetole	89.5		
			n-propyl acetate	−28.0		
			toluene	−33.0		
			xylene	−48.0		
	$M_\eta = 1.9–80$		*o*-dichlorobenzene	87.0	8.1	[257]
	1.7–88.6		bromocyclohexane	28.0	7.9	[258]
Poly(methylphenylsiloxane)	5–150	1.05–1.12	diisobutylamine	30.4	5.15	[259]
Poly(methyl-3,3,3-trifluoropropylsiloxamer)	6–550	1.2	cyclohexyl acetate	25.0	4.10	[260]
			methyl hexanoate	72.8	4.45	
Poly(phenylsilasesquioxane)	1–900		mesitylene/toluene (30/70)	25.0		[261]
Poly(propylene sulphide) ($f_m = 0.55$)	17–74	1.1–2.38	*n*-heptane/toluene (31.5/68.5)	25.0	9.42	[262]

TABLE 15.8. *Poly(esters).*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta.10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Polyarylate (terephthalic/isophthalic: 50/50)	$M_\eta = 1.45–6.84$		dioxane/cyclohexane (68/32)	25.0	27.1	[263]
Poly(arylate-arylenesulphonoxide)			dioxane	23.5		[264]
Poly(ethylene terephthalate)	2.7–15.2		dichloroacetic acid/cyclohexane (60/40)	25.0	22.0	[265]
Poly(ε-caprolactone)	1.38; 9.73 and 42.1		benzene/*n*-hexane (85.1/14.9)	25.0		[266]
			chlorobenzene/*n*-hexane (70.2/29.8)	25.0		
			n-hexane/nitrobenzene (33.0/67.0)	25.0		
Polycarbonate, bisphenol-*A*	0.5–76		*n*-butyl benzyl ether	170.0	21.0	[267]
			dioxane/cyclohexane (64/36)	25.0		
	2.76–8.8	1.07–1.3	cyclohexane/dioxane (36.1/63.9 w/w)	25.0	23.4	[268]
Poly(*D*,*L*-β-methyl-β-propiolactone)	1.96–15.0		*n*-butyl chloride	13.0	10.0	[269]
Poly(octamethylene sebacate)	4.5		benzene/*n*-hexane (48.3/51.7)	25.0		[266]
			bromobenzene/*n*-hexane (45.0/55.0)	25.0		
			chlorobenzene/*n*-hexane (37.5/62.5)	25.0		
Poly[2,2-propane-*bis*(4-phenylthiocarbonate)]	0.94–19	1.2–1.4	chloroform/cyclohexane (76.5/23.5)	25.0	19.0	[267a]
Poly(tetramethylene adipate)	2.29		benzene/*n*-hexane (83.3/16.7)	25.0		[266]
			chlorobenzene/*n*-hexane (75.9/24.1)	25.0		
			n-hexane/nitrobenzene (43.3/56.7)	25.0		

TABLE 15.9. *Poly(acetals) and poly(ethers).*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta \cdot 10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(2,6-dimethyl-1,4-phenylene oxide)	3.7	2.0	methylene chloride	69.0		[268a]
Poly(diphenylether sulfone)	6.3–14		DMF/methanol (83/17)	25.0	11.2	[269a]
			DMF/toluene (39/61)	30.0	12.4	
Poly(oxyethylene)	0.5–700		0.45M K_2SO_4/water	35	13.0	[8]
			0.39M $MgSO_4$/water	45	11.0	
	0.07–3.7		chloroform/*n*-hexane (47.4/52.6)	20.0		[114]
	0.4–3.8		acetonitrile/isopropyl ether (45/55)	20.0		[86]
			chloroform/*n*-hexane (54/46)	20.0		
			nitroethane/isopropyl ether (45/55)	20.0		
	0.16–103	1.05–1.25	methyl isobutyl ketone	50.0	12.0	[270]
			diethylene glycol diethyl ether	50.0	14.0	
	$M_n = 0.1$–0.6		water	5.0		[271]
	0.12–5.5	1.06–1.68	benzene/isooctane (100/48)	71.0		[272]
	2		water aqueous:	96.0		[273]
			2.4M NaCl	54.0	12.0	
			2.4M KCl	48.0	11.8	
			0.3M K_2CO3	56.0	14.6	
			0.3M Na_2SO_4	52.0	14.8	
			0.3M K_2SO_4	52.0	14.2	
			0.39M $MgSO_4$	43.0	17.8	
			0.45M $MgSO_4$	32.0	17.0	
			0.50$MgSO_4$	26.0	17.6	
	2	1.08	aqueous sodium acetate			[274]
			0.75M	75.0	-	
			1.50M	55.0	-	
			2.00M	45.0	-	
			3.00M	31.0	-	
			aqueous KF			
			0.30M	78.0	-	
			0.50M	66.0	-	
			0.80M	49.0	16.1	
			1.00M	38.0	-	
			aqueous $Na_2S_2O_3$			
			0.20M	74.0	-	
			0.30M	63.0	-	
			0.40M	52.0	-	
			0.50M	41.0	-	
			aqueous K_3PO_4			
			0.20M	63.0	-	
			0.30M	45.0	16.6	
			0.35M	38.0	-	
			0.40M	26.0	-	
			aqueous $ZnSO_4$			
			0.30M	54.0	16.8	
			0.35M	48.0	17.7	
			0.45M	35.0	18.7	
Poly(oxyethylethylene) (poly(1-butene oxide))	5.5–117	1.3–2.1	isopropanol	30.0	11.1	[275]
Poly(oxypropylene)	65–90		isooctane	50.0		[276]
Poly(oxytrimethylene)	$M_n = 6.5$–29.2		cyclohexane	27.0	8.89	[277]

TABLE 15.9. *Poly(acetals) and poly(ethers).*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta \cdot 10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(tetrahydrofuran)	$M_n = 3.2$–11.8		toluene	−28.0		[278]
	3.5–110	~1.04	ethyl acetate/*n*-hexane (22.7/77.3)	32–33		[279]
	$M_n = 3.8$–21		isopropanol	44.6	23.1	[280]
			diethyl malonate	33.5	24.3	
			ethyl acetate/*n*-hexane (22.7/77.3)	30.4	26.7	
	14		diethyl malonate	33.5		[281]

TABLE 15.10. *Poly(amides), poly(phosphates), poly(ureas), etc.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta \cdot 10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(*n*-*n*-hexyl isocyanate)	3.8–42.4		methanol/toluene (19.5/80.5)	25.0		[282]
			methanol/carbon tetrachloride (18.5/81.5)	25.0		
Nylon 6	15.1–19		*m*-cresol/decalin (25/75)	30.0		[281]
Nylon 66	3.2	1.88	KCl (2.3M) formic acid (90%)/water	25.0	19.2	[283, 284]
			KCl (2M)/formic acid (86.5%)/water	25.0		
	0.26–5.3		KCl (2.3M)/formic acid (90%)/water	25.0	25.3	[285]
	3.2	1.74	carbon tetra chloride/cyclohexane/*m*-cresol (0.55/0.40/0.05)	25.0		[286]
Poly(*N*-methyldodecane lactam)	0.5–8		1,4-dioxane	30.5	21.5	[287]
Poly(trimethyl hexamethylene terephthalamide) (poly(iminoterephthaloylimino-2,2,4/2,4,4-trimethylhexa-methylene)) (Trogamid T®)	1.16–27.6	1.3–2.0	aniline	142.0	14.8	[288]
			pyrroline	62.0	15.1	
Poly[ethylene methylene bis (4-phenyl carbamate)] (or poly(ethylene glycol co-4,4′-diphenylmethane diisocyanate))	0.33–4.2		acetone/dimethyl formamide (29/71)	25.0	30.0	[289]
Poly(heptamethylene urea)			dichloroacetic acid	46.0	35.4	[290]
			sulfuric acid (90%)	46.0	27.0	
Lithium polyphosphate	100		LiCl (0.4M)/water	20.0		[291]
Sodium polyphosphate	1.1–125		NaBr/water (0.415 mol/l)	25.0	4.94	[292]
Poly(diphenoxyphosphazene)	60	4.7	tetrahydrafuran	30		[292a]
Polyurethane (toluene-2,4-diisocyanate extended polypropylene glycol)	0.77–7.3		toluene/isooctane (1/1.4)	39.5	10.75	[293]

TABLE 15.11. *Copolymers.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temper-ature °C	$K_\theta \cdot 10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(acrylonitrile-*co*-butadiene) (26/74 w/w)	5–130		cyclohexane/MEK (64/36)	20.0		[73]
(40/60 w/w)	3–80		cyclohexane/MEK (52.5/47.5)	22.0		
Poly(1-butenylene-*co*-vinylethylene) (high 1,2 polybutadiene with 1,2 = 43%; *trans:cis*=2.3:1)	0.88–22	1.01–1.1	1,4 dioxane	15.7	17.3	[88]
Poly(*p*-chlorostyrene-*co*-methyl methacrylate) (52/48)	15–120		trans-decalin/trichloro ethylene (78/22)	22.3	6.4	[294]
Poly(divinyl ether-*co*-maleic anhydride methyl ester) (1:2)	1.5–54.3		tetrahydrofuran	30.0	4.89	[295]
Poly(ethylene-*co*-butene) (40 ethyl branches/100 backbone carbons)	1.95–53.6	≤1.07	3-octanol	5.0	9.36	[70]
			2-octanol	29.0	8.92	
			1-octanol	59.0	8.37	
Poly(ethylene-*co*-isopropylethylene); *ethylene-1-butene copolymer, hydrogenated 1,2 polybutadiene*	0.92–22.8	1.01–1.09	*n*-hexyl acetate	65.0	18.8	[88]
Poly(ethylene-*alt*-propylene)	2.45–39.1	1.03–1.07	benzene	19.0	20.6	[67]
Poly(isobutyl vinyl ether-*alt*-maleic anhydride)	15.1–56		acetone	30.0	12.5	[296]
			NaCl/water (1.0 m/L)	25.0	21.0	
Poly(isopropenylethylene- *co*-1-methyl-1-vinylethylene) (high vinyl content polyisoprene with 1,2= 20–25%; 3,4 = 70–75%; 1,4<5%)	1.34–27	1.0–1.22	2-octanol	30.5	10.2	[88]
Poly(isopropylethylene-*co*-1-methyl-1-ethylethylene) (hydrogenated high vinyl polyisoprene)	1.5–27.8	1.03–1.18	2-octanol	26.2	8.3	[88]
Poly(*p*-isopropylstyrene -*co*-styrene)			dioxane/isopropanol			[86]
88/12			(37/63)	20.0		
56/44			(44/56)	20.0		
33/67			(48/52)	20.0		
Poly(*p*-methoxystyrene -*co*-styrene)						[297, 298]
26.4/73.6	6.1–66.5		isoamyl formate	30.5	9.6	
53/47	6.6–178.3		isoamyl formate	22.8	8.7	
			isoamyl propionate	18.1	8.4	
			n-esyl methyl ketone	27.0	9.5	
75.6/24.4	7.9–171.7		isoamyl formate	37.0	8.1	
			t-butyl benzene	12.5	7.5	
Poly(1-methyl-1 -butylene-*co*-isopropenylethylene) [essentially polyisoprene, with 1,4 (mostly *trans*) = 51%; 3,4 = 49%]	1.07–41.1	≤1.07	2-octanol	41.3	9.6	[88]
Poly(1-methyl-butylene -*co*-isopropylethylene) (hydrogenated polyisoprene)	1.13–42.5	1.02–1.08	2-octanol	55.3	9.1	[88]
Poly(1-(4-methylpentyl) -1-butylene-*co* -1-(1,5-dimethylhexyl)ethylene) (hydrogenated 1,4-polymyrcene)	7.1–63.2	≤1.1	2-octanol	51.0	7.14	[70]
Poly(styrene-*co*-acrylonitrile) (49/51)	27–224		ethyl acetate	43.0		[299]
Poly(styrene-*co*-butadiene) (23.9/76.1 w/w)	$M_\eta = 15.2$ –86		methyl *n*-propyl ketone	21.0	22.0	[300]

TABLE 15.11. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta \cdot 10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
			methyl isobutyl ketone	46.0		
Poly(styrene-*co*-butadiene) (25/75 w/w)	4–80		*n*-octane	21.0	16.2	[73]
Poly(styrene-*co*-isooctyl methacrylate) (80/20)	$M_n = 46.9$		butanone/methanol (99.4/0.6)	25.0		[220]
Poly(styrene-*co*-methylmethacrylate)						[145]
(76.3/23.7)			benzene/*n*-hexane (44/56)	20.0		
			benzene/isopropanol (57/43)	20.0		
			n-hexane/3-methyl butanone (40/60)	20.0		
(58.1/41.9)			benzene/*n*-hexane (51/49)	20.0		
			benzene/isopropanol (51/49)	20.0		
			n-hexane/3-methyl butanone (34/66)	20.0		
(42.3/57.7)			benzene/*n*-hexane (59/41)	20.0		
			benzene/isopropanol (48/52)	20.0		
			n-hexane/3-methyl butanone (29/71)	20.0		
(26.1/73.9)			benzene/*n*-hexane (62/38)	20.0		
			benzene/*n*-propanol (41/59)	20.0		
			n-hexane/3-methyl butanone (24/76)	20.0		
Poly(styrene-*co*-methyl methacrylate)						[301]
(29.3/70.7)	$M_n = 4.7$–59.2		2-ethoxy ethanol	40.0		
			cyclohexanol	68.0		
(56.2/43.8)	$M_n = 3.4$–50		2-ethoxy ethanol	58.4		
			cyclohexanol	61.3		
(70.2/29.8)	$M_n = 4.0$–43		2-ethoxy ethanol	72.8		
			cyclohexanol	63.0	8.75	
Poly(styrene-*co*-methyl methacrylate) (50/50)			cyclohexanol	68.6		[146]
Poly(trifluoro nitrosomethane-*co*-tetrafluoroethylene) (50/50)	28.3–197		trichlorotrifluoroethane (Freon 113)	35.0	3.8	[302]
Poly(arylate-*b*-arylenesulphonoxide) (50/50)			dioxane	23.5		[264]
Poly(isoprene-*b*-styrene) (80% *cis* 1,4 isoprene; 11.8–52.2% styrene)	$M_n = 10.4$–49.7	≤1.14	methyl ethyl ketone	44.0	11.63	[303]
Poly(styrene-*b*-methyl methacrylate) (50/50)			cyclohexanol	81.6		[146]
Poly(styrene-*b*-methyl methacrylate)						[301, 304]
(36/64)			2-ethoxy ethanol	69.5		
			cyclohexanol	80.5		
(49.6/50.4)	$M_n = 31.7$		2-ethoxy ethanol	81.0		
			cyclohexanol	81.3		
(73.2/26.8)			cyclohexanol	84.0		
(85.1/14.9)			cyclohexanol	84.0		

TABLE 15.11. *Continued.*

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta \cdot 10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly(vinyl acetate-*g*-styrene)	copolymer: $M_n = 28.9$–60.3; backbone $M_n = 13.9$–29.2; vAc content 48.2–63.1%		diisobutyl ketone	136.5		[305]
			ethyl acetoacetate	108.5		

Starch and cellulose.

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Theta temperature °C	$K_\theta \cdot 10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Amylose	15–220		0.5N potassium chloride	25		[306]
			0.5N potassium hydroxide	25		
Amylose tricarbanilate			cyclohexanol	120		[101a]
			diethylene glycol–diethylether	90		
Dextran	2.9–19.1 (M_n)		dimethyl sulfoxide	50.4, 54.4		[307]
			water	43.6, 44.8		[308]
			ethylene glycol	55		[309]
			methoxy ethylene glycol	60		[310]
	8.0	1.5	ethylene glycol	8		[311]
	40			15		
	200			34		
Cellulose, regenerated	8.0		8 wt% aq NaOH	40		[312]
Cellulose diacetate	5.9, 9.8, and 14.2	1.21, 1.27, 1.20	2-butanone	50		[313]
Cellulose diacetate			2-butanone	$\theta_l = 160$ $\theta_u = 37$		[314]
Cellulose diacetate	3.76–17.5	1.23–1.38	acetone	$\theta_l = 155$		[315]
Cellulose triacetate			benzyl alcohol	$\theta_l = 140$ $\theta_u = 80$		[316]
Cellulose triacetate			methylene chloride	27		[317]
Cellulose triacetate	1.4–12.6		nitromethane	47		[318]
Cellulose triacetate, hydrolyzed			epichlorohydrin	24		[319]
Hydroxypropyl cellulose	7.3 ($M_{\mathrm{s,D}}$)	2		$\theta_l = 41$		[320]
Cellulose tributyrate	$M_n = 7.7 - 22.2$		dodecane/toluene: 75:25 (v/v)	122	8.4	[321]
Cellulose tricaproate	4.1–148	1.03–1.76	dimethyl formamide	41		[322]
			dioxane/water: 100/7 (v/v)	43		
Cellulose tricaprylate	$M_n = 8.1 - 35$		dimethyl formamide	140	11.3	[321]
			-phenylpropyl alcohol	48	12.9	
Cellulose tricarbanilate			anisole	94		[323]
			cyclohexanol	73		
Cellulose tricarbanilate			dibutyl ketone	45		[101a]
			diethylene glycol-dibutylether	45		
			cyclohexanol	80		
Pullulan	30	1.3–1.5	ethylene glycol	12		[311]
	51			16		
	100			24		

TABLE 15.11. *Continued.*

Effect of co-solutes.

Polymer	$M_w \times 10^{-4}$	Dispersity (M_w/M_n)	Solvent	Co-solute	Theta temperature °C	$K_\theta \cdot 10^4$ [dl.g^{-1} (g mol wt)$^{-1/2}$]	Refs.
Poly (*N*-vinyl pyrrolidone)	7.8	1.7	water	NaH_2PO_4			[324]
				0.8 m/L	77		
				1.2 m/L	35		
				KH_2PO_4			
				0.8 m/L	64		
				1.1 m/L	35		
				Na_2SO_4			
				0.35 m/L	73		
				0.5 m/L	36		
				Na_2CO_3			
				0.4 m/L	59		
				0.6 m/L	19		
				K_2CO_3			
				0.45 m/L	56		
				0.55 m/L	40		
				K_2HPO_4			
				0.4 m/L	55		
				0.5 m/L	33		
				Na_3PO_4			
				0.25 m/L	57		
				0.35 m/L	16		
				K_3PO_4			
				0.30 m/L	61		
				0.35 m/L	40		
Poly (*N*-vinyl-2-pyrrolidone)	7.8	1.7	water	benzoic acid 0.5×10^{-3}	73.8		[325]
				o-hydroxy benzoic acid 0.5×10^{-3}	72.5		
				p-hydroxy benzoic acid 0.5×10^{-3}	72		
				aniline 0.5×10^{-3}	77.8		
				o-hydroxy aniline 0.5×10^{-3}	73.4		
				p-hydroxy aniline 0.5×10^{-3}	73.2		
Poly (*N*-vinyl- 2-pyrrolidone)	7.8	1.7	water	hydroquinone			[326]
				1.0×10^{-2}M	54.5		
				1.5×10^{-2}M	35.3		
				catechol			
				1.0×10^{-2}M	66.4		
				3.0×10^{-2}M	27.3		
				phenol			
				1.0×10^{-2}M	69.5		
				2.0×10^{-2}M	55.5		
				resorcinol			
				4.0×10^{-3}	69.3		
				9.0×10^{-3}	45.4		
				phloroglucinol			
				1.5×10^{-3}	59.6		
				3.0×10^{-3}	42.4		
Cellulose I				Na Fe tartrate complex	20		[327]
Cellulose II				Na Fe tartrate complex	25		[327]

compositions of the monomers comprising the copolymer are given, where available. The range of molecular weight (M_w) of the samples used and the dispersity (M_w/M_n) are given in the second and third columns, respectively. In most of the cases, the value of M_w refers to the weight average molecular weight. In some papers, only the viscosity-average molecular weights (M_η) were specified, and in some others, only the number-average molecular weight (M_n) data have been reported. In these cases, it is so noted in the second column. In cases where the authors did not specify the molecular weight in tables or in the text, no attempt was made to read the molecular weight range from the figures in their papers. The solvent and the theta temperature are given in the fourth and fifth columns. In the case of mixed solvents, the composition is given in terms of the volume ratio (eg., v_1/v_2) of the two solvents. Occasionally, if an author had used weight fractions (w_1/w_2) of the two solvents, it is so indicated.

In addition, the values of K_Θ, corresponding to Eq. (15.6) above, are also given, if the authors had reported them. This would enable the reader to estimate the characteristic ratio C_∞ using Eq. (15.9), as shown in the examples above. It was felt that since a number of properties of polymers are being correlated to C_∞ as mentioned above, listing the values of K_Θ would be of value. Although under Θ conditions, the value of K_Θ should be the same at a given temperature irrespective of the solvent used, deviations have been discussed [15,17].

The value of K_Θ can also be deduced without resort to establishing Θ conditions, by measurements in good solvents and determining the expansion factor. Several methods have been used to this end [15,18,19]. These are dealt with in other chapters in this handbook.

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Related information can be found in Chapter 17.

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CHAPTER 16

Solubility Parameters

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Solubility parameters provide a simple method of correlating and predicting the cohesive and adhesive properties of materials from a knowledge of the properties of the components only. Particularly for polymers, applications include finding compatible solvents for coating resins, predicting the swelling of cured elastomers by solvents, estimating solvent pressure in devolatilization and reactor equipment [1] and predicting polymer–polymer [2], polymer–binary-solvent [3], random copolymer [4], and multi-component solvent equilibria [5–8].

16.1 COHESIVE ENERGY DENSITY AND SOLUBILITY (HILDEBRAND) PARAMETER

If U is defined as the molar internal energy (the molar potential energy of a material relative to the ideal vapor at the same temperature), then the molar cohesive energy (the energy associated with the net attractive interactions of the material) is defined as $-U$. As presented by Polak [9]:

$$-U = {}_l\Delta_g U + {}_g\Delta_\infty U, \qquad (16.1)$$

where ${}_l\Delta_g U$ is the molar vaporization energy and ${}_g\Delta_\infty U$ is the energy required to expand the saturated vapor to infinite volume at constant temperature, that is, the energy necessary to completely separate the molecules.

The stabilizing or cohesive effect in condensed phases can be expressed in terms of the cohesive energy density, defined as

$$c = -U/V, \qquad (16.2)$$

where V is the molar volume. Cohesive energy was the basis of the original definition by Hildebrand and Scott [10–12] of what is now generally called the solubility parameter or Hildebrand parameter:

$$\delta = c^{0.5} = (-U/V)^{0.5}. \qquad (16.3)$$

This parameter was intended for nonpolar, nonassociating systems in which ${}_g\Delta_\infty U = 0$ and $-U = {}_l\Delta_g U$, but the concept has been extended to all types of systems. The dimension of δ is $(\mathrm{cal/cm^3})^{0.5} = 2.046 \times 10^3 (\mathrm{J/m^3})^{0.5} = 2.046\,\mathrm{MPa}^{0.5}$. The solubility parameter can be considered as the ''internal pressure'' of the solvent [13–15].

Based on the pioneering work of van der Waals [16] and van Laar [17], the Hildebrand–Scatchard equation was derived on semitheoretical grounds by Scatchard [18,19] and Hildebrand [20–24] and popularized by Hildebrand, Scott, Prausnitz and others [25–37, 10–12]. For a binary mixture, the Hildebrand–Scatchard equation is expressed as

$$\Delta H_m/V_m = (\delta_1 - \delta_2)^2 \phi_1 \phi_2, \qquad (16.4)$$

where ΔH_m is the enthalpy change on mixing, V_m the volume of the mixture, ϕ_i the volume fraction of i in the mixture, and δ_i the solubility parameter of the ith component. In general, $(\delta_1 - \delta_2)^2$ must be small for the components to be miscible. Equation (16.4) gives the heat of mixing of regular solutions in which (a) the components mix with no volume change on mixing at constant pressure, (b) the interaction forces act between the center of the molecules and the interaction between a pair of molecules is not influenced by the presence of other molecules, (c) the mixing is random and the distribution is temperature independent, (d) no reaction occurs between the components, and (e) there is no complex formation or special association. These assumptions are not generally valid, but they produce an equation which has proven valuable both in its own right and as a starting point for other empirical expressions.

16.2 EXPANDED SOLUBILITY PARAMETERS

The solubility parameter describes the enthalpy change on mixing of nonpolar solvents well but does not give uniform results when extended to polar systems. Complete miscibility is expected to occur if the solubility parameters are similar and the degree of hydrogen bonding is similar between the components. Other investigators have decomposed the Hildebrand parameter into several terms, representing different contributions to the energy of mixing. van Arkel [38], Small [39], and Andersen, Prausnitz, and coworkers [12,40–45] divided the total solubility parameter into two main components, defining a nonpolar solubility (δ_λ) and a polar solubility parameter (δ_τ). Although this tends to neglect induction interactions, these may be taken care of by an additional parameter. Polar–nonpolar parameters are related to the Hildebrand parameter by

$$\delta^2 = \delta_\lambda^2 + \delta_\tau^2. \tag{16.5}$$

Here δ_λ can be identified with the dispersive term and δ_τ corresponds to the polar orientational term. This approach has been also applied to polymer solutions [41] and complex formation [46].

Hansen and co-workers [47–68] proposed a practical extension of the Hildebrand parameter method to polar and hydrogen-bonding systems, primarily for use in polymer–liquid interactions. It was assumed that dispersion, polar, and hydrogen-bonding parameters were valid simultaneously, related by Eq. (16.6), with the values of each component being determined empirically on the basis of many experimental observations:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2, \tag{16.6}$$

where δ_t is Hansen's total solubility parameter, δ_d the dispersive term, δ_p the polar term, and δ_h the hydrogen-bonding term. Hansen's total solubility parameter should be equal to the Hildebrand parameter, although the two quantities may differ for materials with specific interactions when they are determined by different methods. The three component parameters were plotted on a set of three mutually perpendicular axes. The Hansen parameters give improved agreement with data but are still not completely accurate in predicting solution thermodynamics for every system.

Parameters describing and correlating the solvent abilities of liquids have been based on a great variety of chemical and physical properties. Some are measures of solvent basicity, and others are obtained from direct determinations of the solubility of a representative solute in a range of liquids. For example, the solubility of hydrogen chloride in liquids at 10 °C was used in this way by Gerrard and co-workers [69,70] and the resulting solvent basicity scale was compared with other scales by Arnett [71] and by Dack [72]. More direct measures of liquid basicity include the enthalpy of mixing with trichloromethane and with other hologenated hydrogen-bond donors in basic solvents [72,71] and the enthalpy of coordination with antimony trichloride [71,73]. Most of the other numerous scales of "basicity" or "electron donating ability" are single-valued and even more difficult to correlate with each other or with solubility parameters. Although they agree in their general trends, the detailed orders of solvent basicity depend on the system from which the scale is derived [72,74].

16.3 CALCULATION AND CORRELATIONS FOR SOLUBILITY PARAMETERS

16.3.1 Solvents

Solubility parameters can be determined by direct measurement, correlations with other physical parameters, or indirect calculations. The solubility parameters of solvents usually can be determined directly. The following methods can be used to develop correlations between solubility parameters and other physical properties of solvents.

Vaporization Enthalpy

If the enthalpy of vaporization, ΔH, has been determined calorimetrically (or from the temperature dependence of the vapor pressure) at the required temperature, and if this is well below the boiling point of the liquid, the Hildebrand parameter may be evaluated with the assumption that the vapor is ideal:

$$\delta = (\Delta H - RT)^{0.5}/V^{0.5}. \tag{16.7}$$

When the value of the vaporization enthalpy is known at one temperature (commonly at normal boiling point), it is desirable to be able to evaluate it at another temperature. In such procedures for extrapolating volumes or enthalpies, a corresponding state procedure is often used. This is frequently based on the reduced temperature T_r, reduced vapor pressure P_r, and reduced molar volume V_r, defined by

$$T_r = T/T_c,\ P_r = P/P_c,\ V_r = V/V_c, \tag{16.8}$$

where the subscript c refers to the values at the critical point. For example, ΔH may be evaluated to within about 2% over a wide range of temperatures, even within a few degrees of T_c by means of the Watson empirical relationship [75–77]:

$$\begin{aligned}\Delta H_2/\Delta H_1 &= (T_c - T_2)^{0.38}/(T_c - T_1)^{0.38}\\ &= (1 - T_{r,2})^{0.38}/(1 - T_{r,1})^{0.38}.\end{aligned} \tag{16.9}$$

Solvent molar volume are often available or can be calculated by group molar volume methods at 25 °C [76]. The molar volume for solids at 25 °C can be extrapolated from liquid-state values (if the liquid is assumed to be subcooled).

Boiling Point

A simple, convenient method of estimating the vaporization enthalpy is the application of the Hildebrand and Scott equation [12,24,35], which expresses ΔH at 25 °C (ΔH^0) in terms of the normal boiling point T_b:

$$\Delta H^0(\mathrm{J\ mol^{-1}}) = -12\ 340 + 99.2[T_b(\mathrm{K})] + 0.084[T_b(\mathrm{K})]^2 \quad (16.10)$$

Van der Waals Gas Constant

Tables are available in many handbooks for the van der Waals correction constants to the ideal gas law, *a* and *b*. For some liquids, these values may be at hand when other data are not available. They can be used to check Hildebrand parameter values obtained from other sources:

$$\delta = 1.2\frac{a^{1/2}}{V}, \quad (16.11)$$

where a has units of 1^2 atm.

Surface Tension

Michaels [78] has shown that the surface tension can be related to the cohesive energy density

$$\frac{{}_l\Delta_g V}{V_i} = A\left(\frac{I}{V_i}\right)^{1/3}\gamma_L, \quad (16.12)$$

where γ_L is the surface tension, V_i is the molar volume of species i, and A is a constant. Koenhen and Smolders [79] correlated surface tension and two Hansen parameters:

$$\delta_d^2 + \delta_p^2 = 13.8\left(\frac{I}{V_i}\right)^{1/3}\gamma_L. \quad (16.13)$$

Equation (16.9) does not describe cyclic compounds, acetonitrile, carboxylic acids, polyfunctional alcohols, and other polar compounds as well. δ_h is probably not related to the liquid–vapor interfacial energy; these interactions do not involve breaking hydrogen bonds.

Internal Pressure

The internal pressure is defined as

$$\pi = (\partial U/\partial V)_T. \quad (16.14)$$

Bagley and co-workers [14,15,80,81] and Scigliano [82] utilized the chemical-bond-discriminating property of cohesive and internal pressures to subdivide the Hildebrand parameter in another way. One part corresponding to the physical or nonchemical effects is the volume-dependent Hildebrand parameter, defined by

$$\delta_v^2 = \pi. \quad (16.15)$$

The other component is a residual parameter, arising from chemical effects:

$$\delta_p^2 = (\Delta U - \pi V)/V, \quad (16.16)$$

$$\delta_p^2 \approx \delta_h^2,\ \delta_v^2 \approx \delta_d^2 + \delta_p^2. \quad (16.17)$$

One advantage of this approach for separation of the component parameters is that it makes use of the thermodynamic quantities π and ΔU, which are fairly readily available for most liquids, in contrast to other empirically determined component solubility parameters. The internal pressure can be measured experimentally by determining the thermal pressure coefficient or the coefficient of expansion and isothermal compressibility, it also can be calculated from other physical properties. Vavruch [83] developed and tested an expression for internal pressure in terms of critical temperature T_c,

$$\pi\ (\mathrm{MPa}) = 63.0(1.5T_c - T)/V, \quad (16.18)$$

where V is the molar volume. The mean percentage deviation was 3.8% for 25 selected liquids (excluding alkanes, alkenes, monohydric alcohols, carboxylic acids, water, liquid metals, and probably cryogenic fluids).

Index of Refraction

The dispersive Hansen parameter δ_d can be related to the index of refraction n_D [79,84]:

$$\delta_d = 9.55n_D - 5.55. \quad (16.19)$$

The interaction energy between nonpolar molecules should depend on the molar polarizability (London dispersion forces) and therefore the index of refraction.

Dipole Moment

Hansen and Skaarup [66] related the polar Hansen parameter to the dielectric constant ε and the dipole moment μ:

$$\delta_p^2 = \frac{12\ 108}{V^2}\frac{\varepsilon - 1}{2\varepsilon + n_D^2}\ (n_D^2 + 2)\mu^2. \quad (16.20)$$

Beerbower and Dicky [85] proposed an empirical relationship:

$$\delta_p^2 = 9.5\mu/V_i^{1/2}. \quad (16.21)$$

16.3.2 Polymers

Measurements

For polymers, solubility parameters cannot be calculated from heat of vaporization data because of their nonvolatility. Other methods of estimation must be used.

The Internal Pressure P_i

Olabisi and Simha [86] developed one approach to calculate the solubility parameter through the internal pressure, P_i:

$$\delta^2 = P_i = \left(\frac{\partial U}{\partial V}\right)_T \approx T\alpha/\beta, \qquad (16.22)$$

where α is the thermal expansion coefficient ($°C^{-1}$) and β is the compressibility (cm^3/cal).

Swelling Data

A method often used for slightly cross-linked polymers [87] and applicable to partially crystalline material such as polyvinyl chloride (PVC) is based on finding the maximum swelling using a series of solvents of varying and known solubility parameters. The assumption is that the interaction and the degree of swelling will be a maximum when the solubility parameter of the polymer matches that of the solvent. This may be inaccurate for systems having opposite polarities or interacting through hydrogen bonding for which the heat of mixing is negative.

Inverse Phase Gas Chromatography

A number of investigations have been performed to measure infinite dilution weight fraction activity coefficients by applying inverse phase gas chromatography [88–97]. These coefficients can be related to solubility parameters by using a thermodynamic theory for polymer solutions, such as Flory–Huggins theory. The polymer is the stationary phase in a gas-chromatography column. Both binary and multicomponent equilibra [98,99] can be studied using this technique. Values of the enthalpy of vaporization can be determined at the experimental temperature [93]. Chromatographic methods have the advantage of measurement of thermodynamic values once the columns have been made. Both V_1 and ΔH_1^v must be known at the temperature of the column. Molar volumes for the solvents can be determined by using literature density equations or generating equations from density data.

Refractive Index

Dispersive Hansen parameters can be predicted from refractive-index measurements of polymers [79]. Wu [100] has suggested an effective cross-sectional area to relate the cohesive energy density and surface tension.

$$\delta_d^2 = A\left(\frac{n_s}{V_{i,s}}\right)^{1/3} \gamma_s^d, \qquad (16.23)$$

where n_s is the number of atoms in a segment, $V_{i,s}$ is the molar volume of a segment, and γ_s^d is the dispersion contribution to the free surface energy.

Intrinsic Viscosity

Solubility parameters can also be estimated from intrinsic viscosity. Flory [101] related intrinsic viscosity to polymer molecular weight and the chain-expansion factor. The chain-expansion factor can, in turn, be related to the polymer-solvent interaction parameter using the Flory-Huggins theory. A variety of models can be used to relate the interaction parameter to solubility parameters [87,102,103]; these equations have the form

$$[\eta] = K_{\mathrm{I}} - K_{\mathrm{II}} V_i^n \Delta\delta^2, \qquad (16.24)$$

where $[\eta]$ is the intrinsic viscosity, K_i are constants, and n is either 1/2 or 1 [104].

Other Methods

The dipole moment has been successfully applied to measure δ_p by Koenhen and Smolders [79]. The dipole moments of polymers are between 70% and 90% of those of the corresponding monomer units. The Hansen hydrogen-bonding parameter δ_h is given by [63]

$$\delta_h^2 = E_h/V_i. \qquad (16.25)$$

The solubility parameter can also be calculated through the heat of solution directly [105,106], solution behavior [107,108], and by extrapolation [109].

Group Contribution Methods

Group contribution methods have been applied to the problem of estimating the solubility parameter without physical measurements [110–117,39,118,119]. Small [39] was one of the first to recognize the additive properties of the molar attraction constant F_i, which is defined by

$$F_i = (E_i V_i)^{1/2}, \qquad (16.26)$$

where E_i and V_i are the cohesion energy and molar volume of the group being considered. Values of F_i, in units of cal$^{1/2}$cm$^{3/2}$, were obtained by regression analysis for various common structural groups in low-molecular-weight compounds. From the additivity of the F_i values and Eq. (16.3) one obtains:

$$\delta = \rho \frac{\sum_i F_i}{M}, \qquad (16.27)$$

where ρ is the density of the polymer, M is the molar mass of the polymer, and the summation is carried over all structural features in the molecule.

The contributions of Hoy [116], Konstam and Feairlieller [120], and Van Krevelen [121] is summarized in Table 16.1. Some values of F_i, from which solubility parameters can be calculated with the aid of Eq. (16.27), are listed.

TABLE 16.1. *Group contributions to solubility parameter*[a].

Group	F_i		
	Small	van Krevelen	Hoy
–CH_3	437	420	303
=CH_2	272	280	269
=CH–	57	140	176
=C=	−190	0	65
=CH_2	388	—	259
=CH–	227	222	249
=C <	39	82	173
–CH=(aromatic)	—	—	240
–C=(aromatic)	—	—	201
–$CH(CH_3)$–	495	560	479
–$C(CH_3)_2$–	685	841	672
–CH=CH–	454	444	497
HC≡C–	583	—	—
–C≡C–	454	—	—
Cyclopentyl	—	1,380	1,300
Cyclohexyl	—	1,660	1,470
Phenyl	1,500	1,520	1,400
Phenylene	1,350	1,380	1,440
Naphthyl	2,340	—	—
–OH	—	754	462
–CO–	562	685	538
–CHO	—	—	599
–COO–	634	511	688
–COOH	—	651	998
–O–(C=O)–O–	—	767	904
–(C=O)–O–(C=O)–	—	767	1,160
–NH_2	—	—	464
–NH–	—	—	368
–N<	—	—	125
–CHCN	896	1,120	901
–CN	839	982	725
–(C=O)–NH–	—	1,290	906
–O–(C=O)–NH–	—	1,480	1,040
–N=C=O	—	—	734
–H	164–205	140	−103
–S–	460	460	428
–SH	644	—	—
–F	250	164	84
–C1(primary)	552	471	420
–Br(primary)	695	614	528
–I	870	—	—
–CF_2–	307	—	—
–CF_3	561	—	—
–O–N=O	900	—	—
–NO_2	900	—	—
–PO_4	1,020	—	—
–Si–	−77	—	—

[a] Adapted from D. W. van Krevelen, Properties of Polymers, 3rd edition (Elsevier, Amsterdam), p. 200 (1990).

16.4 POLYMER-SOLVENT INTERACTION PARAMETER

The enthalpic component of polymer–solvent interaction parameter χ_H can be related to the solubility parameters via

$$\chi_H = \frac{V_i}{RT}(\delta_i - \delta_j)^2. \tag{16.28}$$

This equation links the polymer–solvent interaction parameter with the solubility parameters of polymer and solvent. For nonpolar systems the entropic term χ_s is usually taken to be a constant between 0.3 and 0.4 ($\chi_s = 0.34$ is often used) [41,122]. Equation (16.33) can thus be rewritten as

$$\chi = 0.34 + \frac{V_i}{RT}(\delta_i - \delta_j)^2 \tag{16.29}$$

for nonpolar systems $\chi = \chi_H + \chi_s$ where Eq. (16.27) is a good description of the enthalpic portion of the interaction parameter. According to Flory [123,124] a polymer j and a solvent i are expected to be completely miscible through the entire composition range provided that

$$\chi < \frac{1}{2}\left[1 + \left(\frac{V_i}{V_j}\right)^{1/2}\right]^2. \tag{16.30}$$

There is thus a critical polymer–solvent interaction parameter value

$$\chi_c = \frac{1}{2}\left[1 + \left(\frac{V_i}{V_j}\right)^{1/2}\right]^2 \tag{16.31}$$

and for $(V_i/V_j) \to 0$,

$$\chi_c = 0.5. \tag{16.32}$$

If χ must be less than 0.5 for full polymer–solvent miscibility, and χ_s is about 0.3, it follows that χ_H must be very small to meet the miscibility criterion, and that δ_i and δ_j must have very similar values. Specific interactions (such as hydrogen bonding between molecules of type i and type j to a greater extent than i-i and j-j hydrogen bonding) can result in the lower χ_H and thus enhance the mutual solubility.

For real polymer–solvent systems the experimental χ values and their dependences on composition, temperature, and molar mass provide useful indications of the nature and extent of the polymer–solvent interaction. For a polymer to be soluble in a solvent at a particular temperature, χ must be below 0.5 at high levels of ϕ_j. If the χ value is only slightly larger than 0.5, the polymer is expected to be swollen by the solvent.

There exist a number of extensive published collections of solubility parameters for both low-molecular-weight compounds (e.g., organic solvents) and high polymers [121,125–127]. Our purpose is to give a select number of solubility parameters data in Tables 16.2–16.5 that are representatives for the solvents used in various polymer technologies and the more important representative classes of high polymers used in industry and academic investigations. For the latter we have followed the suggested classes in Billmeyers's text [128]. We have taken some pains to include more recent data not necessarily found in the more exhaustive collections.

TABLE 16.2. *Hildebrand parameters of representative solvents at 25 °C*[a]*.*

Solvent	$\delta[(MPa)^{1/2}]$	H-bonding tendency[b]
Acetaldehyde	21.1	m
Acetic acid	20.7	s
Acetic anhydride	21.1	s
Acetone	20.3	m
Acetonitrile	24.3	p
Acetophenone	21.7	m
Acetyl chloride	19.4	m
Acetylmorpholine (*N*)	23.7	m
Acetylpiperidine (*N*)	22.9	s
Acetylpyrrolidine (*N*)	23.3	s
Acrolein	20.1	s
Acrylic acid	24.6	s
Acrylonitridle	21.5	p
Allyl acetate	18.8	m
Allyl alcohol	24.1	s
Allyl chloride	18.0	m
Ammonia	33.4	s
Amyl acetate (normal)	17.4	m
Amyl alcohol	20.5	s
Amylamine (normal)	17.8	s
Amyl bromide (normal)	15.6	m
Amyl chloride	17.0	m
Amylene	14.1	p
Amyl ether (normal, di-)	14.9	m
Amry formate (normal)	17.4	m
Amyl iodide (normal)	17.2	m
Anethole (*para*)	17.2	m
Aniline	21.1	s
Anthracene	20.3	p
Apco#18 solvent	15.3	p
Apco thinner	16.0	p
Aroclor 1248	18.0	p
Benzaldehyde	19.2	m
Benzene	18.8	p
Benzonitrile	17.2	p
Benzyl alcohol	24.8	s
Bicyclohexyl	17.4	p
Bromobenzene	20.3	p
Bromonaphthalene	21.7	p
Bromostyrene (*ortho*)	20.1	p
Butadiene-1,3	14.5	p
Butane (normal)	13.9	p
Butanediol-1,3	23.7	s
Butanediol-1,4	24.8	s
Butanediol-2,3	22.7	s
Butyl acetate (*iso*)	17.0	m
Butyl acetate (normal)	17.4	m
Butyl acylate (*iso*)	17.4	m
Butyl acylate (normal)	18.0	m
Butyl alcohol (*iso*)	21.5	s
Butyl alcohol (normal)	23.3	s
Butylamine (mono, normal)	17.8	s
Butyl bromide (normal)	17.8	m
Butyl (iso) butyrate (normal)	16.0	m
Butyl (normal) butyrate (normal)	16.6	m
Butyl chloride (*iso*)	16.6	m
Butylene-2,3 carbonate	24.8	m
Butylene (*iso*)	13.7	p
Butyl ether	16.0	m
Butyl formate (*iso*)	16.8	m
Butyl formate (normal)	18.2	m
Butyl idoide (normal)	17.6	m
Butyl lactate (normal)	19.2	m
Butyl methacrylate	16.8	m
Butyl stearate	15.3	m
Butyl propionate	18.0	m
Butyraldehyde	18.4	m
Butyric acid (*iso*)	21.1	s
Butyric acid (normal)	21.5	s
Butyrolactone	25.8	m
Butyronitrile (*iso*)	20.1	p
Butyronitrile (normal)	21.5	p
Carprolactam	26.0	m
Caprolactone	20.7	m
Capronitrile	19.2	p
Carbon disulfide	20.5	p
Carbon tetrachloride	17.6	p
Celanese solvent 601	18.8	m
Chloroacetonitrile	25.8	p
Chlorobenzene	19.4	p
Chloroethyl acetate (beta)	19.8	m
Chloroform	19.0	p
Chlorostyrene (*ortho* or *para*)	19.4	p
Chlorotoluene (*para*)	18.0	p
Cresol (*meta*)	20.9	s
Cyclobutanedione	22.5	m
Cyclohexane	16.8	p
Cyclohexanol	23.3	s
Cyclohexanone	20.3	m
Cyclopentane	17.8	p
Cyclopentanone	21.3	m
Cymene (*para*)	16.8	p
Decahydronaphthalene	18.0	p
Decane (normal)	13.5	p
Decyl acrylate (*iso*)	16.8	m
Diacetone alcohol	18.8	m
Diacetone alcohol methyl ether	16.8	m
Diacetylpiperazine (*N,N*)	28.0	m
Diamyl phthalate	18.6	m
Dibenzyl ether	19.2	m
Dibromoethane-1,2	21.3	p
Dibromoethylene-1,2	20.7	p
Dibutoxyethyl phthalate (Kronisol)	16.4	m
Dibutylamine	16.6	s
Dibutyl fumarate	18.4	m
Dibutyl maleate	18.4	m
Dibutyl phenyl phosphate	17.8	m
Dibutyl phthalate	19.0	m

TABLE 16.2. *Continued.*

Solvent	$\delta[(MPa)^{1/2}]$	H-bonding tendency[b]
Dibutyl sebacate	18.8	m
Dichloroacetic acid	22.5	s
Dichlorobenzene (*ortho*)	20.5	p
Dichlorodifluoromethane (Feon 12)	11.3	p
Dichloroethyl ether	20.1	m
Dichloroethylene, *cis*-1,2	18.6	p
Dichloroethylene, *trans*-1,2	18.4	p
Dichlorofluoromethane (Freon 21)	17.0	p
Dichloropropane-1,2	18.4	p
Dichloropropane-2,2	16.8	p
Diethylacetamide (*N,N*)	20.3	m
Diethylamine	16.4	s
Diethyl carbonate	18.0	m
Diethylene glycol	24.8	s
Diethylene glycol monobutyl ether (normal)	19.4	m
Diethylene glycol monobutyl ether	20.9	m
Diethylene glycol monobutyl ether acetate	17.4	m
Diethylene glycol monolaurate	17.8	m
Diethyl ether	15.1	m
Diethylformamide (*N,N*)	21.7	m
Diethyl ketone	18.0	m
Diethyl maleate	20.3	m
Diethyl oxalate	17.6	m
Diethyl phathalate	20.5	m
Diethyl-2,2-propanediol-1,2 (heptylene glycol)	20.3	s
Diethyl sulfone	25.4	m
Difluoro-tetrachloroethane (Freon 112)	16.0	p
Diformylpiperazine (*N,N*)	31.5	m
Dihexyl ether	16.4	m
Epichlorohydrin	22.5	s
Ethane	12.3	p
Ethylacetamide (*N*)	25.2	s
Ethyl acetate	18.6	m
Ethyl acrylate	17.6	m
Ethyl alcohol	26.0	s
Ethylamine	20.5	s
Ethyl amyl ketone	16.8	m
Ethylbenzene	18.0	p
Ethyl benzoate	16.8	m
Ethyl bromide	19.6	m
Ethyl-2-butanol-1	21.5	s
Ethyl *n*-butyrate	17.4	m
Ethyl caprylate	14.9	m
Ethyl chloride	18.8	m
Ethyl cyanoacetate	22.5	m
Ethylene bromide	19.8	p
Ethylene carbonate	30.1	m
Ethylene chlorohydrin	25.0	s
Ethylene cyanohydrin	31.1	s
Ethylenediamine	25.2	s
Ethylene dichloride	20.1	p

TABLE 16.2. *Continued.*

Solvent	$\delta[(MPa)^{1/2}]$	H-bonding tendency[b]
Ethylene glycol	29.9	s
Ethylene glycol diacetate	20.5	m
Fluorocarbons, aliphatic	12.7	p
Fluorocarbons, aromatic	15.3	p
Formamide	39.3	s
Formic acid	24.8	s
Formylmorpholine (*N*)	26.6	m
Formylpiperidine (*N*)	23.5	m
Furane	19.2	m
Furfural	22.9	m
Furfuryl alcohol	25.6	s
Glycerol	33.8	s
Heptane (normal)	15.1	p
Heptyl alcohol (normal)	21.7	s
Hexamethylphosphoramide	21.5	s
Hexane (normal)	14.9	p
Hexanediaol-2,5	21.1	s
Hexene-1	15.1	p
Hexyl alcohol (normal)	21.9	s
Hydrazine	37.3	s
Hydrogen	6.9	p
Hydrogenated terphenyl	18.4	p
Hydrogen cyanide	24.8	s
Idobenzene	20.7	p
Isophorone	18.6	m
Isoprene	15.1	p
Lauryl alcohol	16.6	s
Low odor mineral spirits	14.1	p
Maleic anhydride	27.8	s
Malononitrile	30.9	p
Mesitylene	18.0	p
Mesityl oxide	18.4	m
Methacrylic acid	22.9	s
Methane	11.0	p
Methanol	29.7	s
Methylacetamide	29.9	s
Methyl acetate	19.6	m
Methyl acrylate	18.2	m
Methylamine	22.9	s
Methyl amyl acetate	16.4	m
Methyl amyl ketone	17.4	m
Methyl benzoate	21.5	m
Methyl bromide	19.6	m
Naphthalene	20.3	p
Neopentane	12.9	p
Neopentyl glycol	22.5	s
Nitrobenzene	20.5	p
Nitroethane	22.7	p
Nitromethane	26.0	p
Nitro-*n*-octane	14.3	p
Nitro-1-propane	21.1	p
Nitro-2-propane	20.3	p
Nonyl phenol	19.2	s
Octane (normal)	15.6	p
Octyl alcohol (normal)	21.1	s

TABLE 16.2. *Continued.*

Solvent	$\delta[(MPa)^{1/2}]$	H-bonding tendency[b]
Pentachloroethane	19.2	p
Pentane (normal)	14.3	p
Pentanediol-1,5	23.5	s
Pentanediol-2,4	22.1	s
Perchloroethylene	19.0	p
Perfluoroheptane	11.9	p
Perfluoromethylcyclohexane	12.3	p
Phenathrene	20.1	p
Phenylhydrazine	25.6	s
Pine oil	17.6	p
Piperdine	17.8	s
Piperidone	27.8	s
Propane	13.1	p
Propyl formate	18.8	m
Pyridine	21.9	s
Quinoline	22.1	s
Styrene	19.0	p
Styrene oxide	21.5	m
Succinic anhydride	31.5	s
Tetrachloroethane-1,1,2,2	19.8	p
Tetrachloroethylene	19.0	p
Tetraethylene glycol	20.3	s
Tetrahydrofuran	18.6	m
Tetrahydronaphthalene	19.4	p
Tetramethylene sulfone	27.4	m
Tetramethyloxamide	23.3	m
Thiophene	20.1	m
Toluene	18.2	p
Tolylenediisocyanate	23.7	s
Tributylamine	15.8	s
Trichloroethane-1,1,2	19.6	p
Trichloroethylene	18.8	p
Trichlorofluoromethane	15.5	p
Trichlorotrifluoroethane	14.9	p
Tricresyl phosphate	17.2	m
Triethylamine	15.1	s
Triethyleneglycol	21.9	s
Triethylenetetramine	22.7	s
Trimethyl-3,5,5-hexanol	17.2	s
Triphenyl phosphate	17.6	m
Triphenyl phosphite	19.0	m
Tripropylene glycol	18.8	s
Turpentine	16.6	p
Valeric acid (normal)	20.1	s
Valeronitrile (normal)	15.6	p
Varnolene (varsol #2)	19.6	p
Vinyel acetate	18.4	m
Vinyel chloride	16.0	m
Vinyel toluene	18.6	p
V M & P naphtha	15.6	p
Water	47.9	s
Xylene	18.0	p

[a] Adapted from J. Brandrup, E. H. Immergut, and E. A. Grulke, Polymer Handbook, 4th edition, John Wiley & Sons, New York (1999).

[b] p denotes poor; m, moderate; s, strong.

TABLE 16.3. *Hansen solubility parameters of representative liquids at 25 °C[a].*

Solvent	V (cm^3/mol)	Solubility parameter [(MPa)$^{1/2}$]			
		δ_d	δ_p	δ_h	δ_t
Acetaldehyde	57.1	14.7	8.0	11.3	20.3
Acetic acid	57.1	14.5	8.0	13.5	21.3
Acetic anhydride	94.5	16.0	11.7	10.2	22.3
Acetone	74.0	15.5	10.4	7.0	20.1
Acetonitrile	52.6	15.3	18.0	6.1	24.6
Acetophenone	117.4	19.6	8.6	3.7	21.7
Acetyl chloride	71.0	15.8	10.6	3.9	19.4
Acrylonitrile	67.1	16.4	17.4	6.8	24.8
Allyl alcohol	68.4	16.2	10.8	16.8	25.8
Amyl (i) acetate	148.8	15.3	3.1	7.0	17.2
Aniline	91.5	19.4	5.1	10.2	22.5
Anisole	119.1	17.8	4.1	6.8	19.4
Benzaldehyde	101.5	19.4	7.4	5.3	21.5
Benzene	89.4	18.4	0.0	2.0	18.6
Benzenediol-1,3	87.5	18.0	8.4	21.1	28.8
Benzoic acid	100.0	18.2	7.0	9.8	21.9
Benzonitrile	102.6	17.4	9.0	3.3	19.8
Benzyl alcohol	103.6	18.4	6.3	13.7	23.7

TABLE 16.3. *Continued.*

Solvent	V (cm^3/mol)	Solubility parameter [(MPa)$^{1/2}$]			
		δ_d	δ_p	δ_h	δ_t
Biphenyl	154.1	21.5	1.0	2.0	21.7
Bis(2-chloroethyl) ether	117.6	18.8	9.0	5.7	21.7
Bis-(*m*-phenoxyphenyl) ether	373.0	19.6	3.1	5.1	20.5
Bromobenzene	105.3	20.5	5.5	4.1	21.7
Bromochloromethane	65.0	17.4	5.7	3.5	18.6
Bromoform	87.5	21.5	4.1	6.1	22.7
Bromotrifluoromethane	97.0	9.6	2.5	0.0	10.0
Butanol-1	91.5	16.0	5.7	15.8	23.1
Butanol-2	92.0	15.8	5.7	14.5	22.1
Butyl (i) acetate	133.5	15.1	3.7	6.3	16.8
Butyl (*n*) acetate	132.5	15.8	3.7	6.3	17.4
Butyl (*n*) benzyl phthalate	306.0	19.0	11.3	3.1	22.3
Butylamine-*n*	99.0	16.2	4.5	8.0	18.6
Butylchloride (*n*)	104.9	16.4	5.5	2.0	17.4
Butyl-*n* lactate	149.0	15.8	6.5	10.2	19.8
Butyraldehyde	88.5	14.7	5.3	7.0	17.2
Butyric-*n* acid	110.0	14.9	4.1	10.6	18.8
Butyronitrile	87.0	15.3	12.5	5.1	20.5
Carbon disulfide	60.0	20.5	0.0	0.6	20.5
Carbon tetrachloride	97.1	17.8	0.0	0.6	17.8
Chloro-3-propanol	84.2	17.6	5.7	14.7	23.7
Chlorobenzene	102.1	19.0	4.3	2.0	19.6
Chlorodifluoromethane	72.9	12.3	6.3	5.7	14.9
Chloroform	80.7	17.8	3.1	5.7	19.0
Cyclohexanol	106.0	17.4	4.1	13.5	22.5
Cyclohexanone	104.0	17.8	6.3	5.1	19.6
Cyclohexylamine	115.2	17.4	3.1	6.5	18.8
Decanol-1	191.8	17.6	2.7	10.0	20.5
Di-(2-chloro-*i*-propyl) ether	146.0	19.0	8.2	5.1	21.3
Di-(2-methoxyethyl) ether	142.0	15.8	6.1	9.2	19.2
Di-(*i*-butyl) ketone	177.1	16.0	3.7	4.1	16.8
Diacetone alcohol	124.2	15.8	8.2	10.8	20.9
Dibenzyl ether	192.7	17.4	3.7	7.4	19.2
Di-butyl stearate	382.0	14.5	3.7	3.5	15.3
Dichlorobenzene (o)	112.8	19.2	6.3	3.3	20.5
Dichloroethane-1,1	84.8	16.6	8.2	0.4	18.4
Dichloroethylene-1,1	79.0	17.0	6.8	4.5	18.8
Dichlorofluoromethane	75.4	15.8	3.1	5.7	17.0
Dichlorofluoromethane	92.3	12.3	2.0	0.0	12.5
Diethyl carbonate	121.0	16.6	3.1	6.1	18.0
Diethyl ether	104.8	14.5	2.9	5.1	15.8
Diethyl ketone	106.4	15.8	7.6	4.7	18.2
Diethyl phthalate	198.0	17.6	9.6	4.5	20.5
Diethyl sulfate	131.5	15.8	14.7	7.2	22.7
Diethyl sulfide	108.2	17.0	3.1	2.0	17.4
Diethylamine	103.2	14.9	2.3	6.1	16.4
Diethylbenzene (*p*)	156.9	18.0	0.0	0.6	18.0
Diethylene glycol monobutyl-*n* ether	170.6	16.0	7.0	10.6	20.5
Diethylene glycol monoethyl ether	130.9	16.2	9.2	12.3	22.3
Diethylene glycol monomethyl ether	118.0	16.2	7.8	12.7	21.9
Diethylenetriamine	108.0	16.8	13.3	14.3	25.8
Dimethyl phthalate	163.0	18.6	10.8	4.9	22.1
Dimethyl sulfone	75.0	19.0	19.4	12.3	29.9

TABLE 16.3. *Continued.*

		Solubility parameter [(MPa)$^{1/2}$]			
Solvent	V (cm^3/mol)	δ_d	δ_p	δ_h	δ_t
Dimethyl sulfoxide	71.3	18.4	16.4	10.2	26.6
Dimethyl-1,3-butanol-1	127.2	15.3	3.3	12.3	19.8
Dimethylformamide	77.0	17.4	13.7	11.3	24.8
Dimethylformamide-*N,N*	92.5	16.8	11.5	10.2	22.7
Dimethylhydrazine-1,1	76.0	15.3	5.9	11.0	19.8
Di-*n*-butyl phthalate	266.0	17.8	8.6	4.1	20.3
Di-*n*-butyl sebacate	339.0	13.9	4.5	4.1	16.2
Di-*n*-propylamine	136.9	15.3	1.4	4.1	16.0
Dioctyl phthalate	277.0	16.6	7.0	3.1	18.2
Dioxane-1,4	85.7	19.0	1.8	7.4	20.5
Epichlorhydrin	79.9	19.0	10.2	3.7	21.9
Ethanethiol	74.3	15.8	6.5	7.2	18.4
Ethanolamine	60.2	17.2	15.5	21.3	31.5
Ethanolamine	58.5	15.8	8.8	19.4	26.6
Ethoxyethyl acetate-2	136.2	16.0	4.7	10.6	19.6
Ethyl acetate	98.5	15.8	5.3	7.2	18.2
Ethyl bromide	76.9	16.6	8.0	5.1	19.0
Ethyl chloroformate	95.6	15.5	10.0	6.8	19.6
Ethyl cinnamate	166.8	18.4	8.2	4.1	20.5
Ethyl formate	80.2	15.5	8.4	8.4	19.6
Ethyl lactate	115.0	16.0	7.6	12.5	21.7
Ethyl-1-butanol-1	123.2	15.8	4.3	13.5	21.3
Ethyl-2-hexanol-1	157.0	16.0	3.3	11.9	20.1
Ethylbenzene	123.1	17.8	0.6	1.4	17.8
Ethylene carbonate	66.0	19.4	21.7	5.1	29.5
Ethylene cyanohydrin	68.3	17.2	18.8	17.6	30.9
Ethylene diamine	67.3	16.6	8.8	17.0	25.4
Ethylene dibromide	87.0	19.6	6.8	12.1	23.9
Ethylene dichloride	79.4	19.0	7.4	4.1	20.9
Ethylene glycol monobutyl-*n* ether	131.6	16.0	5.1	12.3	20.9
Ethylene glycol monoethyl ether	97.8	16.2	9.2	14.3	23.5
Ethylene glycol monomethyl ether	79.1	16.2	9.2	16.4	24.8
Formamide	39.8	17.2	26.2	19.0	36.6
Formic acid	37.8	14.3	11.9	16.6	25.0
Furan	72.5	17.8	1.8	5.3	18.6
Furfuraldehyde	83.2	18.6	14.9	5.1	24.3
Furfuryl alcohol	86.5	17.4	7.6	15.1	24.3
Hexamethyl phosphoramide	175.7	18.4	8.6	11.3	23.3
Isophorone	150.5	16.6	8.2	7.4	19.8
Mesityl oxide	115.6	16.4	7.2	6.1	18.8
Mesitylene	139.8	18.0	0.0	0.6	18.0
Methanol	40.7	15.1	12.3	22.3	29.7
Methyl acetate	79.7	15.5	7.2	7.6	18.8
Methyl chloride	55.4	15.3	6.1	3.9	17.0
Methyl ethyl ketone	90.1	16.0	9.0	5.1	19.0
Methyl *i*-amyl ketone	142.8	16.0	5.7	4.1	17.4
Methyl *i*-butyl ketone	125.8	15.3	6.1	4.1	17.0
Methyl oleate	340.0	14.5	3.9	3.7	15.5
Methyl-2-propanol-1	92.8	15.1	5.7	16.0	22.7
Methylene dichloride	63.9	18.2	6.3	6.1	20.3
Methylene diiodide	80.5	17.8	3.9	5.5	19.0
Methylnaphthalene-1	138.8	20.6	0.8	4.7	21.2
Methyl-*N*-pyrrolidone-2	96.5	18.0	12.3	7.2	22.9

TABLE 16.3. *Continued.*

Solvent	V (cm^3/mol)	Solubility parameter [(MPa)$^{1/2}$]			
		δ_d	δ_p	δ_h	δ_t
Morpholine	87.1	18.8	4.9	9.2	21.5
Naphthalene	111.5	19.2	2.0	5.9	20.0
Nitrobenzene	102.7	20.1	8.6	4.1	22.1
Nitroethane	71.5	16.0	15.5	4.5	22.7
Nitromethane	54.3	15.8	18.8	5.1	25.0
Nitropropane-2	86.9	16.2	12.1	4.1	20.7
Nonyl phonoxyl ethanol	275.0	16.8	10.2	8.4	21.3
Octanol-1	157.7	17.0	3.3	11.9	20.9
Octanol-2	159.1	16.2	4.9	11.0	20.3
Octoic-*n* acid	159.0	15.1	3.3	8.2	17.6
Oleic acid	320.0	14.3	3.1	5.5	15.8
Oleyl alcohol	316.0	14.3	2.7	8.0	16.6
Pentanol-1	109.0	16.0	4.5	13.9	21.7
Perfluorodimethylcyclohexane	217.4	12.5	0.0	0.0	12.5
Perfluoromethylcyclohexane	196.0	12.5	0.0	0.0	12.5
Perfluoro-*n*-heptane	227.3	12.1	0.0	0.0	12.1
Phenol	87.5	18.0	5.9	14.9	24.1
Propanol-1	75.2	16.0	6.8	17.4	24.6
Propanol-2	76.8	15.8	6.1	16.4	23.5
Propionitrile	70.9	15.3	14.3	5.5	21.7
Propyl (*i*) palmitate	330.0	14.3	3.9	3.7	15.3
Propyl (*n*) chloride	88.1	16.0	7.8	2.0	17.8
Propylamine-*n*	83.0	17.0	4.9	8.6	19.6
Propylene carbonate	85.0	20.1	18.0	4.1	27.2
Pyridine	80.9	19.0	8.8	5.9	21.7
Pyrrolidone-2	76.0	19.4	17.4	11.3	28.4
Quinoline	118.0	19.4	7.0	7.6	22.1
Stearic acid	326.0	16.4	3.3	5.5	17.6
Styrene	115.6	18.6	1.0	4.1	19.0
Succinic anhydride	66.8	18.6	19.2	16.6	31.5
Tetrachloroethane-1,1,2,2	105.2	18.8	5.1	9.4	21.7
Tetrachloroethylene	101.1	19.0	6.5	2.9	20.3
Tetrahydrofuran	81.7	16.8	5.7	8.0	19.4
Tetrahydronaphthalene	136.0	19.6	2.0	2.9	20.0
Tetramethylurea	120.4	16.8	8.2	11.0	21.7
Toluene	106.8	18.0	1.4	2.0	18.2
Trichlorobiphenyl	187.0	19.2	5.3	4.1	20.5
Trichloroethane-1,1,1	100.4	17.0	4.3	2.0	17.6
Trichloroethylene	90.2	18.0	3.1	5.3	19.0
Trichlorofluoromethane	92.8	15.3	2.0	0.0	15.5
Tricresyl phosphate	613.0	19.0	12.3	4.5	23.1
Tridecyl alcohol	242.0	14.3	3.1	9.0	17.2
Triethyl phosphate	171.0	16.8	11.5	9.2	22.3
Triethylene glycol mono-oleyl ether	418.5	13.3	3.1	8.4	16.0
Trimethyl phosphate	99.9	16.8	16.0	10.2	25.4
Tri-*n*-butyl phosphate	345.0	16.4	6.3	4.3	18.0
Water	18.0	15.5	16.0	42.4	47.9
Xylene (*o*)	121.2	17.8	1.0	3.1	18.0

[a] Adapted from J. Brandrup, E. H. Immergut, and E. A. Grulke, Polymer Handbook, 4th edition, John Wiley & Sons, New York (1999).

TABLE 16.4. *Solubility parameters of representative polymers.*

Polymer	δ(MPa$^{1/2}$)	*T* (°C)	Method	Reference
Cellulose	32.02			[129]
Cellulose diacetate	23.22		Calc.	[39]
Cellulose nitrate (11.83% N)	21.44		Calc.	[39]
Epoxy resin	22.3			[130]
Natural rubber	16.2			[131]
	17.09			[132]
Poly(4-acetoxystyrene)	22.7	25	Visc.	[133]
Poly(acrylic acid)				
—, butyl ester	18.0	35		[134]
	18.52		Swelling	[134]
—, methyl ester	20.77		Swelling	[134]
	20.7		Swelling	[135]
Poly(acrylonitrile)	26.09	25	Calc.	[39]
Poly(butadiene)	16.2	75	IPGC	[136]
	17.15		Calc.	[39]
Poly(butadiene-co-acrylonitrile)				
BUNA N (72/25)	18.93	25	Calc.	[39]
(61/39)	20.5	75	IPGC	[136]
Poly(butadiene-co-styrene)				
BUNA S (85/15)	17.41		Calc.	[137]
	17.39		Obs.	[137]
Poly(butadiene-co-vinylpyridine)				
(72/25)	19.13			[132]
Poly(chloroprene)	18.42	25		[129]
	19.19		Calc.	[39]
	17.6		Swelling	[131]
Poly(dimethyl siloxane)	14.9	30	Calc.	[138]
Poly(ethylene)	16.6		Calc.	[39]
Poly(ethylene)	16.4		Calc.	[139]
	16.2		Obs.	[140]
Poly(ethylene-co-vinyl-acetate)	18.6	25	IPGC	[93]
	17.0	75	IPGC	[136]
Poly(*tetra*-fluoroethylene)	12.7		Calc.	[39]
Poly(heptamethylene *p,p′*-bibenzoate)	19.50	25	Visc.	[141]
Poly(4-hydroxystyrene)	23.9	25	Visc.	[133]
Poly(isobutene)	16.06	35	Av.	[142]
	16.47		Swelling	[142]
	16.06	25		[129]
Poly(isobutene-co-isoprene) butyl rubber	16.47			[122]
Poly(isoprene)	15.18	25	Calc.	[112]
1,4-*cis*	16.68	25		[142]
	16.57	35		[142]
	20.46	35	Swelling	[142]
	16.6		Swelling	[134]
	16.68	25	Calc.	[39]
Poly(methacrylic acid)				
—, isobutyl ester	14.7	140	IPGC	[91]
—, ethyl ester	18.31		Swelling	[135]
—, methyl ester	18.58	25		[87]
Poly(methacrylonitrile)	21.9		Calc.	[39]
Poly(methylene)	14.3	20	Extrap.	[143]
Poly(α-methyl styrene)	18.75	30	Visc.	[144]
Poly(σ-methylstyrene-co-acrylonitrile)	16.4	180	IPGC	[145]
Poly(oxyethylene)	20.2	25	IPGC	[91]
Poly(propylene)	18.8	25		[114]
Poly(styrene)	18.72	35		[142]
Poly(styrene-co-*n*-butyl-methacrylate)	15.1	140	IPGC	[91]
Poly(thioethylene)	19.19		Swelling	[131]

TABLE 16.4. *Continued.*

Polymer	δ(MPa$^{1/2}$)	T (°C)	Method	Reference
Poly(vinyl acetate)	19.62	25	Calc.	[112]
Poly(vinyl alcohol)	25.78			[129]
Poly(vinyl chloride)	19.28		Calc.	[112]
	19.8		Obs.	[94]
Poly(vinyl chloride), chlorinated	19.0	25	Visc.	[146]
Poly(vinyl propionate)	18.01	35		[147]

TABLE 16.5. *Hansen solubility parameters of representative polymers.*

Polymer (trade name, supplier)	Solubility parameter (MPa$^{1/2}$)				Reference
	δ_d	δ_p	δ_h	δ_t	
Acrylonitrile-butadiene elastomer (Hycar 1052, BF Goodrich)	18.6	8.8	4.2	21.0	[54]
Alcohol soluble resin (Pentalyn 255, Hercules)	17.5	9.3	14.3	24.4	[54]
Alcohol soluble resin (Pentalyn 830, Hercules)	20.5	5.8	10.9	23.5	[54]
Alkyd, long oil (66% oil length, Plexal P65, Polyplex)	20.42	3.44	4.56	21.20	[54]
Alkyd, short oil (Coconut oil 34% phthalic anhydride; Plexal C34)	18.50	9.21	4.91	21.24	[54]
Blocked isocyanate (Phenol, Suprasec F5100, ICI)	20.19	13.16	13.07	27.42	[54]
Cellulose acetate (Cellidore A, Bayer)	18.60	12.73	11.01	25.08	[54]
Cellulose nitrate (1/2 s; H-23, Hagedon)	15.41	14.73	8.84	23.08	[54]
Epoxy (Epikote 1001, Shell)	20.36	12.03	11.48	26.29	[54]
Ester gum (Ester gum BL, Hercules)	19.64	4.73	7.77	21.65	[54]
Furfuryl alcohol resin (Durez 14383, Hooker Chemical)	21.16	13.56	12.81	28.21	[54]
Hexamethoxymethyl melamine (Cymel 300 American Cyanimid)	20.36	8.53	10.64	24.51	[54]
Isoprene elastomer (Cariflex IR 305, Shell)	16.57	1.41	−0.82	16.65	[54]
Methacrylonitrile/methacrylic acid copolymer	17.39	14.32	12.28	25.78	[148]
Nylon 66	18.62	5.11	12.28	22.87	[6]
Nylon 66 (Zytel, DuPont)	18.62	0.00	14.12	23.37	[54]
Petroleum hydrocarbon resin (Piceopale 110, Penn. Ind. Chem.)	17.55	11.19	3.60	17.96	[54]
Phenolic resin (Resole, Phenodur 373 U Chemische Werke Albert)	19.74	11.62	14.59	27.15	[54]
Phenolic resin, pure (Super Beckacite 1001, Reichhold)	23.26	6.55	8.35	25.57	[54]
Poly(4-acetoxy, α-acetoxy styrene)	17.80	10.23	7.37	21.89	[149]
Poly(4-acetoxystyrene)	17.80	9.00	8.39	21.69	[133]
Poly (acrylonitrile)	18.21	16.16	6.75	25.27	[6]
Polyamid, thermoplastic (Versamid 930, General Mills)	17.43	−1.92	14.89	23.02	[54]
Poly(*p*-benzamide)	18.0	11.9	7.9	23.0	[150]
cis-Poly(butadiene)elastomer (Bunahuls CB10, Chemische Werke Huels)	17.53	2.25	3.42	18.00	[54]
Poly(isobutylene) (Lutonal IC/123, BASF)	14.53	2.52	4.66	15.47	[54]
Poly(ethyl methacrylate) (Lucite 2042, DuPont)	17.60	9.66	3.97	20.46	[54]
Poly(ethylene terephthalate)	19.44	3.48	8.59	21.54	[6]
Poly(4-hydroxystyrene)	17.60	10.03	13.71	24.55	[133]
Poly(methacrylic acid)	17.39	12.48	15.96	26.80	[148]
Poly(methacrylonitrile)	18.00	15.96	7.98	25.37	[148]
Poly(methyl methacrylate)					
Poly(sulfone), Bisphenol A (Polystyrene LG, BASF)	21.28	5.75	4.30	22.47	[54]
Poly(sulfone), Bisphenol A (Udel)	19.03	0.00	6.96	20.26	[151]
Poly(vinyl acetate) (Mowilith 50, Hoechst)	20.93	11.27	9.66	25.66	[54]
Poly(vinyl butyral) (Butvar B76, Shawinigan)	18.60	4.36	13.03	23.12	[54]
Poly(vinyl chloride) (Vipla KR $K = 50$, Montecatini)	18.23	7.53	8.35	21.42	[54]
Poly(vinyl chloride)	18.72	10.03	3.07	21.46	[113]
Poly(vinyl chloride)	18.82	10.03	3.07	21.54	[6]
Saturated polyester (Desmophen 850, Bayer)	21.54	14.94	12.28	28.95	[54]

TABLE 16.5. *Continued.*

Polymer (trade name, supplier)	Solubility parameter (MPa$^{1/2}$) δ_d	δ_p	δ_h	δ_t	Reference
Styrene-butadiene (SBR) raw elastomer (Polysar 5630, Polymer Corp.)	17.55	3.36	2.70	18.07	[54]
Terpene resin (Piccolyte S-1000, Penn. Ind. Chem.)	16.47	0.37	2.84	16.72	[54]
Urea-formaldehyde resin (Plastopal H, BASF)	20.81	8.29	12.71	25.74	[54]
Vinylidene cyanide/4-acetoxy, α-acetoxy styrene copolymer	21.48	11.25	7.16	21.89	[149]
Vinylidene cyanide/4-chloro-styrene copolymer (Rohm and Haas)	16.98	12.07	8.18	22.38	[149]
Poly(styrene)	18.64	10.52	7.51	22.69	[54]

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CHAPTER 17

Mark–Houwink–Staudinger–Sakurada Constants

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17.1 INTRODUCTION

The viscosity of a dilute polymer solution depends on the nature of polymer and solvent, the concentration of the polymer, its average molecular mass and molecular mass distribution, the temperature, and the shear rate. The most important characteristic quantity in a very dilute solution, at vanishing shear rate, is the limiting viscosity number, which is defined as [1]

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_s}{\eta_s c}, \qquad (17.1)$$

where η is the viscosity of the solution, η_s that of the pure solvent, and c the polymer concentration. The importance of this number is that it is the basis of a convenient, rapid relative determination of a certain average molar mass of a polymer sample. $[\eta]$ has the dimensions of a reciprocal concentration or a reciprocal density, for which ml/g is used here. The concentration is expressed in grams of solute per milliliter of solution, or more frequently, in grams of solute per 100 milliliters of solution. The quantity $[\eta]$ of a polymer solution is connected with the dimension of the isolated polymer molecule. Within a given series of polymer homologs, $[\eta]$ increases with the molar mass M; hence it is a measure of M. The limiting viscosity number $[\eta]$ for a series of homologous polymers under a fixed solvent condition (solvent species and temperature) follows the Mark–Houwink–Staudinger–Sakurada (MHSS) relation [2]:

$$[\eta] = K\overline{M}_v^{\,a} \qquad (17.2)$$

over an extended range of molar masses. Here K is the MHSS "constant," and a the MHSS "exponent"; $\overline{M}_v$ is called viscosity average molar mass, which is defined as

$$\overline{M}_v(a) = (\Sigma M_i^a w(M_i))^{1/a}, \qquad (17.3)$$

where $w(M_i)$ is the weight fraction of molecules of molar mass M_i. In a sample consisting of N_i molecules of molar mass M_i, the weight fraction $w(M_i) = M_iN_i/\Sigma M_iN_i$. Mathematically it follows that

$$\Sigma w(M_i) = 1, \qquad (17.4)$$

$$\overline{M}_v(a_1) > \overline{M}_v(a_2),\ a_1 > a_2. \qquad (17.5)$$

In the MHSS equation both the exponent a and the coefficient K depend on the polymer solvent pair and the temperature. Empirically the value of the exponent a is roughly characterized by the difference of the solubility parameters of polymer (δ_p) and solvent (δ_s) [3].

The parameters K and a are evaluated from the intercept and slope, respectively, of the double-logarithmic plots of $[\eta]$ against M_v determined for a series of samples that differ only in their molar mass. The main experimental facts that have to be explained theoretically are as follows [4]:

1. When $[\eta]$ of a sharp (i.e., essentially monodisperse) polymer fraction of molar mass M is plotted against M on a log–log graph paper, it gives a straight line over a wide range of M.
2. The slope a of the line for linear flexible polymers in non-θ solvents is in the range $0.5 < a < 0.8$; polymers having an a larger than 0.8 are suspected to be semiflexible.
3. In general, a is larger for a better solvent.
4. Under θ conditions (unperturbed random coil), for linear, flexible polymers, Eq. (17.2) becomes

$$[\eta]_\theta = K_\theta \overline{M}_v^{1/2}, \qquad (17.6)$$

and for a given polymer K_θ is nearly independent of the solvent species.

The ratio of $[\eta]/[\eta]_\theta$ is called the viscosity expansion factor α^3. The viscosity-averaged molar mass (M_v) obtained from the MHSS equation may also be used to get information about the degree of molar mass dispersion from the comparison of the $\overline{M}_v$ values of a polymer sample in two different solvents [5,6].

The prefactor K in Eq. (17.6) can be expressed in terms of the hydrodynamic factors Φ_θ, ρ_θ, and P_θ, which are defined as follows:

$$\Phi_\theta = [\eta]_\theta M/(6\langle s^2\rangle_\theta)^{1.5}, \tag{17.7}$$

$$\rho_\theta = \langle s^2\rangle_\theta^{0.5}/R_{H\theta}, \tag{17.8}$$

$$P_\theta = k_B\Theta/[(6\langle s^2\rangle_\theta)^{0.5}\eta_s D_0], \tag{17.9}$$

where Θ denotes the theta temperature in degrees Kelvin, $\langle s^2\rangle^{0.5}$ is the root-mean-square radius of gyration, k_B is Boltzmann's constant, η_s is the viscosity coefficient of the solvent, and R_H is the Stokes radius, the hydrodynamic size of the polymer coil. Θ_θ, ρ_θ, and P_θ are independent of molecular weight M; they were first introduced by Flory, Fox, and Mandelkern [7,8].

In the nondraining limit,

$$K_\theta = N_A(\pi/6)^{1.5}a^3 m^{-1.5}\Gamma, \tag{17.10}$$

$$\Phi_\theta = N_A(\pi/6)^{1.5}\Gamma, \tag{17.11}$$

$$\rho_\theta = 6^{0.5}\pi\Gamma', \tag{17.12}$$

where N_A is Avogadro's constant, a is the spring length defined by Eq. (17.17), m is the molar mass of one bead in the spring–bead polymer chain, and Γ and Γ' are dimensionless constants whose values depend on what theory is employed. According to the Krikwood–Riseman theory, we have $\Gamma = 1.259$ and $\Gamma' = 0.192$ [9], which yield $\Phi_\theta = 2.87 \times 10^{23}\,\mathrm{mol}^{-1}$ and $\rho_\theta = 1.48$.

Experimental values of Φ_θ and ρ_θ are considerably influenced by the polydispersity of polymer samples used; however, both Φ_θ and ρ_θ are universal to a first approximation, the former being mostly found to be in the range $(2.0 - 2.7) \times 10^{23}\mathrm{mol}^{-1}$ and the latter in the range 1.25–1.35 (6.15–5.70 for P_θ). Recently, Oono and Kohmoto [10,11] applied renormalization-group theory to the polymer hydrodynamics of the Krikwood–Riseman scheme and computed the values of $\Phi_\theta = 2.36 \times 10^{23}\mathrm{mol}^{-1}$ and $P_\theta = 6.20$, which compares rather favorably with experimental values.

After the Krikwood–Riseman theory [12], there are many theories that have been developed by other researchers, such as the dependence of intrinsic viscosity on molecular weight by Flory and Fox [13,7], and by Yu and Stockmayer [14], and others [15,16]; the effect of rate of shear by Kuhn [17], Cerf [18], and others [19–23]; Ham–Zimm theory of branched polymers [24,25]; Crothers and Zimm theory of wormlike chains [26]; theories for rigid rod molecules [17,27–30]; theories for rigid sphere molecules [28,31–33]; and theories for flexible ring molecules by Fukatusu and Kurata [34] and by Bloomfield and Zimm [35], etc. We will not go into details here.

The abbreviations of the methods for determining the molar mass of polymer samples are as follows:

1. Methods for the number-average molecular weight, M_n: CR, cryoscopy; EB, ebullioscopy; EG, end-group titration; OS, osmotic pressure; VOS, vapor pressure osmometry.
2. Methods for the weight-average molecular weight, M_w: LS, light scattering; SA, approach to the sedimentation equilibrium (Archibald's method).
3. Empirical or semiempirical methods: GPC, gel permeation chromatography; LV, limiting viscosity-number–molecular-weight relationship; SD, sedimentation diffusion.

Practically, the MHSS constants are obtained for the $[\eta]$–M relationships expressed in terms of number-average molar mass $\overline{M}_n$ or weight-average molar mass $\overline{M}_w$ determined by the above methods, i.e.,

$$[\eta] = K_n\overline{M}_n^a \tag{17.13}$$

or

$$[\eta] = K_w\overline{M}_w^a. \tag{17.14}$$

The values of K_n and K_w are influenced by the polydispersity of molar mass of the polymer samples. For the exponential polydispersity of molar mass,

$$K_n = K\Gamma(a + h + 1)/h^a\Gamma(h + 1), \tag{17.15}$$

$$K_w = K\Gamma(a + h + 1)/(h + 1)^a\Gamma(h + 1), \tag{17.16}$$

where h is a constant and Γ is the gamma function. For the log-normal polydispersity of molar mass,

$$K_n = K(\overline{M}_w/\overline{M}_n)^{0.5a(a+1)}, \tag{17.17}$$

$$K_w = K(\overline{M}_w/\overline{M}_n)^{0.5a(a-1)}. \tag{17.18}$$

Therefore, K_n is more sensitive to the polydispersity of molar mass.

Extensive tables of K and a values exist [36,37]. In Tables 17.1 and 17.2 we provide two tables of MHSS constants of commonly used polymer–solvent systems with original references.

TABLE 17.1. *Martk-Houwink constant-K values.*

Polymer	Solvent	Temperature (°C)	$K\times10^3$ (ml/g)	Range $M\times10^{-4}$	Method	Reference
Amylose	(aq)KCl (0.33M)	25	112	16–230	LS	[38]
Cellulose tricarbanilate	Anisole	94	130	31–220	LS	[39]
Cellulose trioctanoate	Dimethylformamide	140	113	10–32	OS	[40]
Poly(butadiene)						
98%-*cis*, 2%-1,2	Benzene	30	33.7	5–50	OS	[41]
	Toulene	20.5	185	5–50	OS	[41]
95%-*cis*, 1%-*trans*, 4%-1,2	Benzene	30	8.5	15–50	LS	[42]
	Toulene	30	33.9	10–65	OS	[43]
94%-*cis*, 4%-*trans*, 2%-1,2	Benzene	25	41.4	9–120	OS	[44]
	Dioxane	20.2	205	9–120	OS	[44]
92%-*cis*, 3%-*trans*, 6%-1,2	Benzene	32	10	10–160	LS	[45]
51%-*cis*, 43%-*trans*, 6%-1,2	Toluene	30	39	11–25	OS	[46]
Poly(butadiene-*co*-acrylonitrile)						
Buna-*N* rubber	Acetone	25	50	2.5–10	OS	[47]
	Benzene	25	13	2.5–10	OS	[47]
	Toulene	25	49	2.5–40	OS	[47]
Poly(butadiene-*co*-styrene)						
Buna-S, GR-S, or SBR rubber	Benzene	25	52.5	1–160	OS	[48]
	Toulene	25	52.5	2.5–50	OS	[47]
Poly(2-*tert*-butylbutadiene)	Benezene	21	4.2	6–90	SD	[49]
	Octane	21	4.2	6–35	SD	[49]
Poly(chloroprene)						
Neoprene CG	Benzene	25	2.02	6–150	OS	[50]
Neoprene GN	Benzene	25	14.6	2–96	OS	[51]
Neoprene W	Benzene	25	15.5	5–100	OS	[52]
Poly(isoprene)						
Natural rubber	Benzene	30	18.5	8–28	OS	[53]
	Toulene	25	50.2	7–100	OS	[54]
Synthetic *cis*	hexane	20	68.4	5–80	SD	[55]
	Toulene	30	8.51	20–100	LS	[56]
Synthetic *trans*	Benzene	32	43.7	8–140	LS	[57]
Poly(1,2-trichlorobutadiene)	Benzene	25	31.6	25–130	LS	[58]
Poly(alkene) C_{10}–C_{18}	Toluene	25	12.7	2–18	LS	[59]
Poly(alkene) C_{12}–C_{18}	Cetane	38	21	4–700	LS	[60]
Poly(1-butene)						
Atactic	Benzene	30	22.4	0.03–0.5	EG	[61]
Isotactic	Heptane	35	4.73	4.5–90	LS	[62]
Poly(ethylene)						
Low pressure	Bibhenyl	127.5	323	2–30	LV	[63]
	Octanol	180.1	286	2–105	LV	[63]
High pressure	Decalin	70	38.73	0.2–3.5	OS	[64]
Poly(isobutene)						
	Benzene	24	107	18–188	LV	[65]
	Carbon tetrachloride	30	29	0.05–126	OS, CR	[66]
	Toluene	0	40	1–146	LV	[66]
Poly(isobutene-*co*-isoprene), butyl rubber	Benzene	22.8	115	15–72	LS	[67]
	Toluene	25	66	15–30	OS	[68]
Poly(3-methyl-1-butene)	Diisobutylene	20	42	1–20	LS	[69]
Poly(4-methyl-1-butene)	Biphenpl	194.6	152	6–30	OS	[70]
Poly(1-octene)	Bromobenzene	25	2.9	25–400	LS	[71]
	Cyclohexane	30	5.75	25–400	LS	[71]
Poly(pentenamer)						
80 ~ 85%*trans*, 19 ~ 12%-*cis*	Cyclohexane	30	56.9	3.6–63	LS	[72]
	Toluene	30	52.1	3.6–63	LS	[72]

TABLE 17.1. *Continued.*

Polymer	Solvent	Temperature (°C)	$K\times10^3$ (ml/g)	Range $M\times10^{-4}$	Method	Reference
Poly(propylene)						
Atactic	Benzene	25	27	6–31	OS	[73]
	Toluene	30	21.8	2–34	OS	[74]
Isotactic	Biphenyl	125.1	152	5–42	LV	[75]
Syndiotactic	Heptane	30	31.2	9–45	LS	[76]
Poly(acrylamide)	Water	30	6.31	2–50	SD	[77]
Poly(butyl arylate)	Acetone	25	6.85	5–27	LS	[78]
Poly(*tert*-butyl arylate)	Acetone	25	4.7	7–31	LS	[79]
	Hexane	24.2	49	7–31	LS	[79]
	Methanol	25	16	7–31	LS	[79]
Poly(1, 1-dihydroperfluorobutyl acrylate)	Benzofluoride	26.6	13	20–200	LS	[80]
Poly(*N, N*-dimethylamide)	Methonal	25	17.5	5–122	LS	[81]
	Water	25	23.2	5–122	LS	[81]
Poly(ethyl scrylate)	Acetone	25	51	35–450	LS	[82]
	Benzene	30	27.7	5–67	OS	[83]
	Chloroform	30	31.4	9–54	OS	[83]
Poly(2-ferrocenylethyl acrylate)	Benzene	25	4.68	1.4–2.7	VOS, GPC	[84]
Poly(ferrocenylethly acrylate)	Benzene	25	6.84	0.7–2	VOS, GPC	[85]
Poly(hexadecyl acrylate)	Methanol	30	48.7	6–70	OS	[83]
	Heptane	20	1.74	1–10	LS	[86]
Poly(isopropyl acrylate)	Acetone	30	13	6–30	LS	[87]
	Benzene	25	14.9	7–70	OS	[88]
	Chloroform	30	14.1	7–30	LS	[89]
Poly(methyl acrylate)	Acetone	20	7.4	7–32	OS	[90]
	Benzene	25	2.58	20–130	OS	[91]
	Toluene	30	7.79	25–190	LS	[92]
Polt(1-methylphenyl acrylate)	Butyl acetate	25	14.7	2–110	SD	[93]
Poly(morpholinocarbonylethylene)	Dimethylformamide	25	18	?	LS	[94]
Poly(piperidinocarbonylethylene)	Dimethylformamide	25	32	?	LS	[94]
Poly(propyl acrylate)	Butanone	30	15	71–181	LS	[95]
Poly(benzyl methacrylate)	Benzene	30	1.03	17–120	LS	[96]
Poly(butyl methacrylate)	Acetone	25	18.4	100–600	LS	[97]
	Benzene	30	(4.0)	8–300	LS	[98]
	Butanone	23	1.56	25–260	LS	[99]
	Chloroform	20	0.78	4–800	LS	[100]
Poly(*tert*-butyl methacrylate)	Butyl acetate	25	22	46–870	LS	[101]
Poly(2-*tert*-butylphenyl methacrylate)	Benzene	25	7.8	4–113	LS	[102]
	Butanone	25	9.0	4–113	LS	[102]
	Cyclohexane	18.4	35.5	4–113	LS	[102]
Poly(4-*tert*-butylphenyl methacrylate)	Acetone	20	5.75	6–350	LS	[103]
	Bromobenzene	20	4.1	15–2,500	LS	[104]
	Chloroform	20	2.4	6–300	LS	[105]
	Cyclohexane	25	47	11–204	LS	[106]
	Tetrahydrofuran	25	9.4	7–88	LS	[106]
Poly(cyclohexyl methacrylate)	Benzene	30	8.4	80–200	LS	[107]
	Butanol	23	33.7	57–445	LS	[108]
	Cyclohexane	25	8.8	10–419	LS	[109]
Poly(cyclohexyl thiolmethacrylate)	Cyclohexane	25	8.65	4–60	LS	[110]
	Tetrahydrofuran	35	4.07	4–60	LS	[110]
Poly(dodecyl methacrylate)	Butyl acetate	23	8.64	26–360	LS	[111]
Poly(2-ethylbutyl methacrylate)	Butanone	25	2.21	48–332	LS	[112]
	2-propanol	27.4	33.7	48–332	LS	[112]
Poly(ethyl methacrylate)	Butanone	23	2.83	20–263	LS	[113]
	Ethyl acetate	35	8.6	65–1,200	LS	[114]
Poly(2-ferrocenylethyl methacrylate)	Benzene	N/A	3.12	2–9	VOS,GPC	[84]
Poly(ferrocenylmethyl methacrylate)	Benzene	25	27.8	0.6–3.6		[85]
Poly(hexadecyl methacrylate)	Benzene	21	5.9	130–440	SD	[115]
	Heptane	21	3.92	130–440	SD	[115]

TABLE 17.1. *Continued.*

Polymer	Solvent	Temperature (°C)	$K\times10^3$ (ml/g)	Range $M\times10^{-4}$	Method	Reference
Poly[4-(4- hexadecyloxy-benzoyloxy)-phenyl methacrylate]	Carbon tetrachloride	N/A	33.1	10–2,000	SD	[116]
Poly(hexyl methacrylate)	Butanone	23	2.12	6–41	LS	[117]
	2-propanol	32.6	43	6–41	LS	[117]
Poly(2-hydroxyethyl methacrylate)	Dimethylformamide	30	10.6	4–52	LS	[118]
	Methanol	30	52.4	4–52	LS	[118]
Poly(isobutyl methacrylate)	Acetone	25	0.199	300–1,100	LS	[119]
	Benzene	25	7.03	50–116	OS	[120]
	Butanone	20	5.56	300–1,100	LS	[119]
Poly(5-*p*-menthyl methacrylate)	Benzene	25	9.6	12–230	LS	[102]
	Cyclohexane	25	11.5	12–230	LS	[102]
	Tetrahydrofuran	25	11.5	12–230	LS	[102]
Poly(methacrolein)	Dimethylformamide	20	2.8	0.5–2	OS,CR	[121]
Poly(methacrylic acid)	Methanol	26	242	4–20	OS	[122]
Poly(methacrylonitrile)	Acetone	20	95.5	35–100	OS	[123]
	Dimethylformamide	29.2	306	0.6–8	LV	[124]
Poly(2-methoxyethyl methacrylate)	Butanone	25	7.34	4–220	LS	[125]
	Tetrahydrofuran	25	7.57	4–220	LS	[125]
Poly(methyl butacrylate)	Butanol	13	57	6–60	LS	[126]
	Butanone	30	5.43	7–430	LS	[126]
Poly(methyl *a*-chloroacrylate)	Chloroform	30	3.08	20–780	LS	[127]
Poly(methyl ethacrylate)	Benzene	30	2.35	16–110	LS	[126]
	Butanone	30	4.29	4–200	LS	[126]
Poly(methyl methacrylate)	Acetone	20	5.5	7–700	SD	[128]
	Acetonitrile	30	39.3	10–86	LV	[129]
	Benzene	20	8.35	7–700	SD	[128]
	Butanone	25	6.8	8–137	LS	[130]
Poly(octadecyl methacrylate)	Tetrahydrofuran	30	2.5	20–170	LS	[131]
Poly(octyl methacrylate)	Butanol	16.8	26.8	33–1,250	LS	[132]
	Butanone	23	4.47	33–1,250	LS	[132]
Poly(*N*-phenyl methacrylamide)	Acetone	20	28.2	10–320	LS	[133]
Poly(stearyl methacrylate)	Tetrahydrofuran	30	9	1.5–94	LS	[134,135]
Poly(tetrahydrofurfuryl methacrylate)	Acetone	30	24	16–62	OS	[136]
Poly[(hexadecyloxy)ethylene]	Heptane	21	70.8	0.5–3	SD	[137]
Poly(methoxyethylene)	Benzene	30	76	1–45	LS	[138]
	Butanone	30	137	1–45	LS	[138]
Poly[(octadecyloxy)ethylene]	Benzene	25	170	0.1–1.5	LS	[131]
	Tetrahydrofuran	30	224	9.4–11	LS	[131]
Poly(chlorotrifluoroethylene)	2,5-dichlorobenzotrifluoride	130	6.15	7–51	OS	[139]
Poly(vinyl alcohol)	Water	25	20	0.6–2.1	OS	[140]
Poly(vinyl bromide)	Cyclohexane	25	32.8	2–10	LS	[141]
	Tetrahydrofuran	25	15.9	2–10	LS	[141]
Poly(vinyl chloride)	Benzyl alcohol	155.4	156	4–35	LS	[142]
	Chlorobenzene	30	71.2	3–19	SA	[143]
	Cyclohexanone	20	11.6	2–10	OS	[144]
	Tetrahydrofuran	20	3.63	2–17	OS	[145]
Poly(vinyl flouride)	Dimethylformamide	90	6.42	14–66	SV	[146]
Poly(vinylidene chloride)	Hexamethylphosphoramide	25	25.8	0.8–12	LS	[147]
Poly(allyl acetate)	Benzene	27	66	0.1–0.3	CR	[148]
Poly(vinyl acetate)	Benzene	30	22	34–102	LS	[149]
	Butanone	25	13.4	25–346	LS	[150]
	Chlorobenzene	25	110	0.15–7	OS	[151]
	Chloroform	20	15.8	7–68	OS	[152]
	Dioxane	25	11.4	4–34	OS	[153]
	Ethanol	56.9	90	4–150	OS,LS	[154]
	Methanol	6	101	0.3–150	OS,LS, VOS	[154,155]
	Toluene	25	108	4–15	OS	[153]

TABLE 17.1. *Continued.*

Polymer	Solvent	Temperature (°C)	$K \times 10^3$ (ml/g)	Range $M \times 10^{-4}$	Method	Reference
Poly(vinyl benzoate)	Xylene	32.5	62	10–24	OS	[156]
Poly(vinyl butyrate)	Benzene	30	11.15	3–15	OS	[157]
Poly(vinyl caproate)	Benzene	30	15.47	3–126	OS	[157]
Poly(vinyl 4-chlorobenzoate)	Water	30	64	6–35	LV	[158]
Poly(vinyl formate)	Acetone	30	29.3	3–41	LV	[159]
	Acetonitrile	30	14.1	3–41	LV	[159]
	Dioxane	30	20.7	3–41	LV	[159]
	Methyl acetate	30	37.6	3–24	LV	[159]
Poly(vinyl isobutyrate)	Benzene	30	11.05	5–20	OS	[157]
Poly(vinyl isocaproate)	Benzene	30	51	3–17	OS	[157]
Poly(vinyl pivalate)	Acetone	25	2.88	40–217	LS	[160]
Poly(4-bromostyrene)	Benzene	20	95.5	3–30	OS	[161]
	Chlorobenzene	30	7.43	59–400	LS	[162]
	Toluene	30	18.2	63–400	LS	[163]
Poly(p-*tert*-butylstyrene)	Benzene	35	7.1	1.8–640	LS	[164]
	Cyclohexane	35	9.9	1.8–640	LS	[164]
	1-nitropropane	31	61	1.8–640	LS	[164]
Poly(2-chlorostyrene)	Toulene	25	11.5	14–101	LS	[165]
Poly(4-chlorostyrene)	Benzene	30	30.6	10–200	LS	[166]
	Butanone	25	29	3–140	LS	[167]
	Chloroform	30	14.8	10–200	LS	[166]
	Dioxane	30	17.6	10–200	LS	[166]
	Toluene	20	24.1	2–40	LS	[168]
Poly(4-cyclohexylstyrene)	Heptane	30	32.3	4–30	OS	[169]
	Toluene	30	10.6	2–30	OS	[169]
Poly(2,5-dichlorostyrene)	Toluene	21	12.6	7–66	LS	[170]
Poly(3,4-dichlorostyrene)	Chlorobenzene	30	4.39	8–51	OS	[169]
Poly(2,4-dimethylstyrene)	Benzene	20	3.8	3–22	LS	[171]
	Butyl acetate	20	10.2	3–22	LS	[171]
	Cyclohexane	20	14.8	3–22	LS	[171]
	Toluene	30	9.52	5–12	LS	[172]
Poly(3-fluorostyrene)	Benzene	25	15.3	N/A	LS	[173]
	Butanone	25	13.8	N/A	LS	[173]
	Chloroform	25	12.8	1–15	LS	[173]
Poly(4-fluorostyrene)	Benzene	25	40.8	N/A	LS	[173]
	Butanone	25	11.1	N/A	LS	[173]
	Chloroform	25	16.1	0.2–13	LS	[173]
Poly(4-iodostyrene)	Dioxane	20	33	10–118	LV	[174]
Poly(*p*-isopropylstyrene)	Toluene	25	12.3	14–75	LS	[175]
Poly(*o*-methoxystyrene)	Toluene	30	6.4	13–35	LS	[176]
Poly(*p*-methoxystyrene)	Butanone	30	3.75	13–75	LS	[176]
	Pentyl acetate	25	55	22–220	LS	[177]
	Toluene	25	10.5	22–220	LS	[177]
Poly(*m*-methylstyrene)	Benzene	30	7.36	8–115	OS	[178]
	Cyclohexane	30	11.76	15–83	OS	[178]
	Ethyl acetate	30	17.72	15–83	OS	[178]
Poly(*p*-methylstyrene)	Diethyl succinate	16.4	70	16–200	LS	[179]
	Toluene	30	8.86	19–180	LS	[179]
Poly[(2,3,4,5,6-pentafluorostyrene)]	4-methyl-2-pentanone	20	4.37	10–260	OS	[180]
Poly(styrene)						
Atactic	Benzene	30	6.3	1–300	SD	[181]
	Butanone	25	39	1–180	LS	[182]
	Butyl chloride	40.8	15.1	29–106	LS	[183]
	Chlorobenzene	25.7	7.4	62–424	LS	[183]
	Chloroform	25	7.16	12–280	LS	[184]
	Cyclohexane	28	108	0.6–69	OS	[185]
	Dichloroethane	25	21	1–180	LS	[182]

TABLE 17.1. *Continued.*

Polymer	Solvent	Temperature (°C)	$K\times10^3$ (ml/g)	Range $M\times10^{-4}$	Method	Reference
	Dimethylformamide	35	31.8	0.4–87	LS	[186]
	Dioxane	34	15	8–80	DV	[187]
	Ethylbenzene	25	17.6	7–150	OS	[188]
	Tetrahydrofuran	25	11	1–100	GPC	[189]
	Toluene	20	4.16	4–137	LS	[183]
Atactic, anionic	Benzene	25	100	0.04–1	VOS,EB	[190]
	Cyclohexane	34	74.5	N/A	LS	[191]
	Cyclohexene	25	16.3	20–107	LS	[192]
	Toluene	20	10.69	3–4,000	LS,OS,SD	[193]
Isotactic	Benzene	30	9.5	4–75	OS	[194]
	Chloroform	30	25.9	9–32	OS	[195]
	Toluene	30	11	3–37	OS	[196]
Poly(styrenesulfonic acid)	Aqueous HCl (0.52 M)	25	0.344	18–46	LV	[197]
	Aqueous HaCl (0.52 M)	25	0.312	18–46	LV	[197]
Poly[(biphenyl-4-yl)-ethylene]	Benzene	20	21.4	7–170	LS	[198]
Poly(*tert*-butyl crotonate)	Toluene	25	7.7	0.6–35	OS,GPC	[199]
Poly(vinyl carbanilate)	Dioxane	20	13.7	6–200	LS	[200]
Poly(dibutyl itaconate)	Toluene	25	5.7	20–105	LS	[201]
Poly(dicyclohexyl itaconate)	Toluene	25	13.1	5–56	LS	[202]
Poly(didecyl itaconate)	Toluene	25	8.01	13–82	LS	[201]
Poly(diethyl itaconate)	Toluene	25	1.48	5–61	LS	[201]
Poly(dihexyl itaconate)	Toluene	25	3.71	12–122	LS	[201]
Poly(dimethyl itaconate)	Benzene	25	5.18	4–120	LS	[201]
Poly(dioctyl itaconate)	Toluene	25	3.67	11–163	LS	[201]
Poly(dipropyl itaconate)	Toluene	25	1.62	13–109	LS	[201]
Poly(dipropylcyclohexyl itaconate)	Pentyl acetate	25	14	16–91	LS	[203]
	Toluene	25	2.23	16–91	LS	[203]
Poly(diundecyl itaconate)	Toluene	25	10.01	9–250	LS	[201]
Poly(vinylcarbazole)	Benzene	25	30.5	0.7–45	LS	[204]
	Bromobenzene	25	5.14	7–49	GPC	[205]
	Chlorobenzene	30	5.23	7–57	GPC	[206]
	Chloroform	25	5.93	7–49	GPC	[205]
	Cyclohexanone	25	20	2–45	LS	[204]
	1,2-dichlorobenzene	25	11	4–44	GPC	[207]
	1,3-dichlorobenzene	25	5.6	7–49	GPC	[207]
	Nitrobenzene	25	9.25	7–49	GPC	[205]
	Tetrachloroethane	25	12.9	2–45	LS	[204]
	Tetrahydrofuran	25	14.4	1–45	LS	[204]
	Toluene	37	76.2	4–107	OS	[208]
Poly(1-vinylimidazol)	Aqueous NaCl(0.1 M)	25	122	9–90	LS	[209]
	Aqueous NaCl(0.5 M)	25	121	9–90	LS	[209]
Poly(5-vinyl-2-methylpyridine)	Butanone	25	13.9	13–88	LS	[210]
	Dimethylformamide	25	13	4–40	OS	[211]
	Methanol	25	18	4–40	OS	[211]
Poly(1-vinynaphthalene)	Benzene	20	2.2	4–17	LS	[198]
Poly(2-vinynaphthalene)	Benzene	17	1.7	10–100	LS	[212]
Poly(3-vinylpyrene)	Chloroform	25	51	3–50	LS	[213]
	1,2-dichlorobenzene	25	11.7	3–50	LS	[213]
	Tetrahydrofuran	25	31.8	3–50	LS	[213]
Poly(2-vinylpyridine)	Benzene	25	6.6	3–11	LS	[214]
	Butanone	25	97.2	3–93	LS	[215]
	Dimethylformamide	25	14.7	3–93	LS	[216]
	Dioxane	25	30.9	3–93	LS	[216]
	Methonal	25	11.3	3–93	LS	[216]
	Pyridine	25	13.8	3–93	LS	[215]
Poly(4-vinylpyridine)	Ethanol	25	1.51	1–4	SD	[217]
	Water	25	22	10–185	LS	[218]

TABLE 17.1. *Continued.*

Polymer	Solvent	Temperature (°C)	$K\times10^3$ (ml/g)	Range $M\times10^{-4}$	Method	Reference
Poly(vinylpyrrolidone)	Chloroform	25	19.4	2–23	LS	[219]
	Methanol	30	23	2–23	LS	[219]
	Water	20	64	1–9	SD	[220]
Poly(vinyltrimethylsilane)	Cyclohexane	25	8.2	59–213	LS	[221]
Poly(acrylonitrile-*co*-styrene)						
38.3/61.7 mol. Azeotropic	Butanone	30	36	15–120	LS	[222]
	Tetrahydrofuran	25	21.5	10–78	LS	[223]
62.7/37.4 mol., random	Butanone	30	53	19–56	LS	[224]
	Dimethylformamide	30	12	19–56	LS	[224]
Poly(acrylonitrile-stat-styrene)						
27.4/72.6 mol	Dimethylformamide	30	12	14–58	LS	[225]
38.5/61.5 mol	Dimethylformamide	30	16.2	22–106	LS	[225]
47.5/52.5 mol	Dimethylformamide	30	17.2	14–78	LS	[225]
Poly(dimethyl itaconate-*co*-styrene)						
75/25 wt	Toulene	25	6.6	6–22	LS	[226]
67/33 wt	Toulene	25	9	4–19	LS	[226]
27/73 wt	Toulene	25	10.9	6–40	LS	[226]
0/100 wt	Toulene	25	11.45	3–58	LS	[226]

TABLE 17.2. *Mark–Houwink constants K and a values.*

Polymer	Solvent	T (°C)	$K\times10^2$(ml/g)	a	Range $M\times10^{-5}$	Method	Reference
Amylose	Dimethyl sulfoxide	20	0.397	0.82	0.2–21.7	LS	[227]
	Ethylenediamine	25	1.55	0.70	3.1–31.0	LS	[228]
	Water	20	1.32	0.68	3.6–21.7	LS	[227]
Cellulosetricarbanilate	Acetone	25	0.143	0.91	3.1–22.0	LS	[229]
	Dioxane	25	0.0813	0.97	3.1–22.0	LS	[229]
	Pyridine	20	0.346	0.86	0.7–27.0	LS	[230]
Cellulosetrioctanoate	Toluene	30	1.73	0.70	0.8–3.5	OS	[40]
Ethyl cellulose	Acetone	20	0.151	1.05	0.11–0.8	SD	[231]
	Benzene	25	2.92	0.81	0.4–1.4	OS	[232]
	Methanol	25	5.23	0.65	1.0–4.1	LS	[233]
Poly(acrylamide)	Water	30	0.631	0.80	0.2–5.0	SD	[234]
		30	0.65	0.82	0.4–12.7	OS	[235]
Poly(acrylic acid)							
—, sodium salt	(aq)NaBr (0.5 M)	15	5.27	0.62	0.1–5.0	LV	[236]
	(aq)NaOH (2 M)	25	4.22	0.64	0.4–5.0	OS	[237]
Poly(acrylonitrile-co-styrene) 38.3/61.7 mol, azeotropic	tetrahydrofuran	25	2.15	0.68	1.0–7.8	LS	[238]
Poly(butadiene)							
98% *cis*, 2% 1,2	Benzene	30	3.37	0.715	0.5–5.0	OS	[239]
	Toluene	30	3.05	0.725	0.5–5.0	OS	[240]
95% *cis*, 1% *trans*, 4%, 1,2	Cyclohexane	30	1.12	0.75	1.5–5.0	LS	[241]
ca. 100% *cis*	Benzene	32	1.45	0.76	0.8–1.8	LS	[242]
	Heptane/hexane (50/50 vol)	20	13.8	0.53	0.5–	SD	[243]
97% *trans*, 3% 1,2	Cyclohexane	40	2.82	0.70	0.4–1.7	LS	[244]
	Toluene	30	2.94	0.753	0.5–1.6	OS	[245]
Poly(butadiene-co-acrylonitrile)							
Buna-N rubber	Acetone	25	5.0	0.64	0.25–1.0	OS	[246]
	Benzene	25	1.3	0.55	0.25–1.0	OS	[246]
	Chloroform	25	5.4	0.68	0.25–1.0	OS	[246]

TABLE 17.2. *Continued.*

Polymer	Solvent	T (°C)	$K \times 10^2$ (ml/g)	a	Range $M \times 10^{-5}$	Method	Reference
Poly(butadiene-co-styrene)							
Buna-S, GR-S, or SBR rubber	Benzene	25	5.25	0.66	0.1–16.0	OS	[247]
	Cyclohexane	30	3.16	0.70	0.5–2.5	OS	[248]
	Toluene	25	5.25	0.667	0.25–5.0	OS	[246]
Poly(1-butene)							
Atactic	Benzene	30	2.24	0.72	0.003–0.05	EG	[249]
	Ethylcyclohexane	70	0.734	0.80	0.4–13.0	LS	[250]
Isotactic	Decalin	115	0.949	0.73	0.45–9.0	LS	[251]
	Ethylcyclohexane	70	0.734	0.80	0.8–9.4	LS	[250]
	1,2,4-trichlorobenzene	135	1.18	0.729		GPC	[252]
Poly(*tert*-butylacrylate)	Acetone	25	0.47	0.75	0.7–3.1	LS	[253]
	Methanol	25	1.60	0.61	0.7–3.1	LS	[253]
Poly(*N*-*n*-butylitaconimide)	Benzene	30	3.99	0.707	1.2–15.4	LS	[254]
	Tetrahydrofuran	30	2.57	0.790	1.2–15.4	LS	[254]
	Toluene	30	12.7	0.570	1.2–15.4	LS	[254]
Poly(chloroprene)							
Neoprene W	Benzene	25	1.55	0.72	0.5–8.0	LS	[255]
	Carbontetrachloride	25	2.21	0.69	1.5–30.0	LS	[256]
Poly(dihexoxyphosphazene)	Benzene	25	2.01	0.79	0.26–22.8	LS	[257]
Poly(ethylene)							
Low pressure	Decalin	135	6.2	0.70	0.2–10.5	LS	[258,259]
	1,2,4-trichlorobenzene	135	9.54	0.64	0.3–4.5	LS	[260]
		135	5.1	0.706	0.08–12.3	GPC,LS	[261]
		135	5.16	0.691		GPC	[252]
	p-Xylene	105	5.1	0.725	0.04–5.0	LV	[262]
High pressure	Decalin	70	3.873	0.738	0.02–0.4	OS	[263]
	p-Xylene	75	13.5	0.63	0.02–0.8	OS	[264]
Poly(ethyl acrylate)	Acetone	25	5.1	0.59	3.5–45.0	LS	[265]
	Benzene	30	2.77	0.67	0.5–6.7	OS	[266]
Poly(ethylmethacrylate)	Butanone	23	0.283	0.79	2.0–26.3	LS	[267]
	Ethyl acetate	35	0.86	0.71	6.5–120.0	LS	[268]
Poly(3-hexylthiophene)	Terahydrofuran	25	0.12	0.58	0.15–5.0	GPC,OS	[269]
	Toluene	25	1.312	0.77	0.4–2.2	GPC,LS	[270]
Poly(imionoadipoylimino-	*m*-cresol	25	24.0	0.61	0.14–0.5	LS,EG	[271]
hexamethylene) (nylon 66)	(aq)HCOOH (90 vol %)/ HCOOHa (0.1 *M*)	25	3.28	0.74	0.1–0.5	EG	[272]
Poly(isoprene)							
Natural rubber	Benzene	30	1.85	0.74	0.8–2.8	OS	[273]
	Cyclohexane	27	3.0	0.70	18.5–	LS,OS	[274]
	Toluene	25	5.02	0.667	0.7–10.0	OS	[275]
Synthetic *cis*	Hexane	20	6.84	0.58	0.5–8.0	SD	[276]
	Toluene	30	0.851	0.77	2.0–10.0	LS	[277]
Synthetic *cis*							
84% *cis*, 14% *trans*, 2%-1,2	Benzene	25	1.33	0.78	0.2–8.0	OS	[278]
		25	1.12	0.78	0.2–6.0	OS	[278]
Synthetic *trans*	Benzene	32	4.37	0.65	0.8–14.0	LS	[242]
Synthetic *trans* (98%)	Benzene	30	1.81	0.722	1.4–7.7	LS	[279]
	Cyclohexane	30	1.62	0.736	1.4–7.7	LS	[279]
Poly(methylacrylate)	Acetone	25	0.55	0.77	2.8–16.0	LS	[280]
	Benzene	25	0.258	0.85	2.0–13.0	OS	[281]
	Ethyl acetate	35	1.1	0.69	2.4–14.8	LS	[282]
Poly(methyl methacrylate)							
Atactic	Acetone	25	0.53	0.73	0.2–78.0	LS	[283]
	Benzene	25	0.55	0.76	0.2–74.0	LS	[283]
	Butanone	25	0.68	0.72	0.8–13.7	LS	[284]

TABLE 17.2. *Continued.*

Polymer	Solvent	T (°C)	$K \times 10^2$ (ml/g)	a	Range $M \times 10^{-5}$	Method	Reference
Isotactic	Acetone	30	2.30	0.63	0.5–12.8	LS	[285]
	Benzene	30	0.52	0.76	0.5–12.8	LS	[285]
	Acetonitrile	20	13.0	0.448	0.3–1.9	LV	[286]
Poly(methyl methacrylate)-block-poly(styrene), A_k–B_n, *k/n*, 54/46 wt.	Toluene	30	0.73	0.73	0.58–9.3	LS	[287]
Poly(oxy-2,6-dimethyl-1,4-phenylene)	Benzene	25	2.6	0.69	0.3–1.7	LS	[288]
Poly[oxy(dimethyl-silylene)]	Benzene	20	1.2	0.68	0.55–1.2	LV	[289]
	Toluene	20	2.0	0.66	0.03–2.0	LS,OS	[290]
	Cyclohexane	35	1.02	0.735	0.7–9.0	LS	[291]
Poly(oxy-1-oxo-3-methyltrimethylene) *D,L*	Chloroform	30	1.66	0.76	0.2–1.5	LS	[292]
D-Poly(propylene)	Trifluoro ethanol	25	2.22	0.76	0.2–1.5	LS	[292]
Atactic	Benzene	25	2.7	0.71	0.6–3.1	OS	[293]
	Cyclohexane	25	1.6	0.80	0.6–3.1	OS	[293]
	Toluene	30	2.18	0.725	0.2–3.4	OS	[294]
Isotactic	Decalin	135	1.10	0.80	0.2–6.2	LS	[293]
		135	1.00	0.80	1.0–10.0	LS	[295]
	p-Xylene	85	9.6	0.63		OS	[294]
Head to head 94% *trans*, 6% 1,2	Cyclohexane	30	0.416	0.86	0.21–0.4 1	VOS,OS	[296]
Syndiotactic	Heptane	30	3.12	0.71	0.9–4.5	LS	[297]
Poly(styrene)							
Atactic	Benzene	20	1.23	0.72	0.06–52.0	SD	[298]
	Butanone	25	3.9	0.58	0.1–18.0	LS	[299]
	Chloroform	25	0.716	0.76	1.2–28.0	LS	[300]
		25	1.12	0.73	0.7–15.0	OS	[301]
	Dichloroethane	25	2.10	0.66	0.1–18.0	LS	[299]
	N-methylpyrrolidone	30	4.92	0.577	0.3–4.0	GPC	[302]
	Tetrahydrofuran	25	1.10	0.725	0.1–10.0	GPC	[303]
	Toluene	25	1.05	0.73	1.6–10.0	LS	[304]
Atactic, anionic	Benzene	25	0.78	0.75	4.0–600.0	LS	[305]
	Toluene	25	0.977	0.73	0.1–10.4	SD	[306]
Isotactic	Benzene	30	1.06	0.735	0.4–3.7	OS	[307]
	Chloroform	30	2.59	0.734	0.9–3.2	OS	[308]
	o-Dichlorobenzene	25	1.79	0.677	0.2–10.0	LV	[309]
	Toluene	30	1.10	0.725	0.3–3.7	OS	[308]
Poly[sulfonyl-(butylethylene)]	Benzene	25	0.89	0.70	0.9–10.7	OS	[310]
	Chloroform	25	0.58	0.75	0.7–5.4	OS	[311]
	Dioxane	25	0.62	0.76	0.9–10.7	OS	[310]
Poly(vinyl acetate)	Acetone	25	2.14	0.68	0.4–3.4	OS	[312]
		25	1.46	0.72	0.07–0.13	EG	[313]
		25	1.08	0.72	0.09–0.25	EG	[313]
	Benzene	30	2.2	0.75	3.4–10.2	LS	[314]
		30	5.63	0.62	0.3–8.6	OS	[315]
		30	5.63	0.62	0.7–5.4	LS	[316]
	Chloroform	25	2.03	0.72	0.4–3.4	OS	[317]
	Methanol	25	3.80	0.59	0.4–2.2	OS	[312]
Poly(vinyl alcohol)	Water	30	4.53	0.64	0.1–8.0	LS	[318]
	Water	80	9.4	0.56	1.0–4.6	LS	[319]
Poly(vinyl chloride)	Chlorobenzene	30	7.12	0.59	0.3–1.9	SA	[320]
	Cyclohexane	25	1.38	0.78	0.1–1.2	OS	[321]
	Tetrahydrofuran	25	1.63	0.776	0.2–3.0	LS	[322]

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Related information can be found in Chapter 15.

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CHAPTER 18

Polymers and Supercritical Fluids

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Mixtures of polymers and supercritical fluids (SCFs) have many features in common with mixtures of polymers and conventional incompressible liquids. As a result, a variety of operations, such as polymerization, dissolution and precipitation, swelling, fractionation, plasticization, impregnation, and extraction, can be carried out on polymers using SCFs. Several monographs and review articles address these and other applications [1–13]. A supercritical fluid is a substance at conditions above its critical temperature (T_c) and critical pressure (P_c). Such compounds used with polymers are often gaseous at ambient or near-ambient conditions, and have critical temperatures which are low enough to prevent excessive thermal degradation of the polymer. When temperature or pressure conditions are below the critical point, the compound is not a true SCF, but such compressible fluids are also included here under the abbreviation SCF. Table 18.1 below lists the properties of some representative SCF compounds, most of which have been used with polymers. The low normal boiling points (T_b) of many of these materials insure that little or none of the SCF remains to contaminate the polymer after a mixture has been depressurized to atmospheric conditions.

Two significant features distinguish SCFs from conventional liquid solvents:

1. The SCF is compressible, so pressure can be adjusted as an independent variable. In liquid solvent systems, only temperature can be varied, and
2. SCFs often have lower density (or, equivalently, higher specific volume) than liquids. Hence, they can be more effective than liquids at increasing the polymer free volume and enhancing transport properties.

Additionally, pure SCFs have no interfacial tension (since no vapor–liquid interface exists), so penetration into and removal from solid porous structures is facilitated. Note, however, that an SCF-swollen polymeric fluid will exhibit an interfacial tension with an SCF phase.

Of these features, the pressure-dependence of SCF properties dominates or influences virtually every process conducted on polymers. Pressure governs such properties as density, solubility parameter, and dielectric constant; changes of more than an order of magnitude are common when pressure is sufficiently increased to transform a gas into a supercritical fluid. This chapter primarily compiles experimental data on the pressure dependence of physical properties of fluid phase polymer-SCF mixtures. Phase equilibria are addressed, including the solubility of polymers in SCFs, the solubility of SCFs in liquid polymers, and the three-phase solid–fluid–fluid equilibria of crystalline polymers saturated with SCFs. Additional thermodynamic properties include glass transition temperature depressions of polymers, and interfacial tension between SCF-swollen polymers and the SCF. The viscosity of fluid phase polymer-SCF mixtures is also treated.

TABLE 18.1. *Critical properties of some compounds.*

SCF	T_c(°C)	P_c(MPa)	T_b(°C)
Ethylene	9.3	5.06	−103.7
Fluoroform	26.0	4.82	−82
Chlorotrifluoromethane	28.9	3.92	−81.1
Carbon dioxide	31.0	7.38	−78.8[a]
Ethane	32.2	4.88	−88.6
Nitrous oxide	36.5	7.26	−88.5
Propylene	91.9	4.62	−47.4
Chlorodifluoromethane	96	4.91	−40.8
Propane	96.7	4.25	−42.1
1,1,1,2-tetrafluoroethane	101	4.06	−26.2
Dimethyl ether	127	5.33	−24.8
Ammonia	132.5	11.28	−33.35
1-chloro-1,1-difluoroethane	137	4.05	−10
n-Butane	152	3.80	−0.5
Dichlorofluoromethane	178.5	5.17	9
Dichlorotrifluoroethane	183	3.68	27.6
Ethylene oxide	195.6	7.19	10.6
n-Pentane	196.6	3.37	36.1
Trichlorofluoromethane	198.1	4.41	23.7
Trifluoroethanol	225.4	4.825	75
Acetone	235	4.8	56.2
Isopropanol	235.2	4.76	82.3
Methanol	240	7.95	64.6
Ethanol	243	6.38	78.5
Ethyl acetate	257	3.88	77
Chloroform	263	5.47	61.7
Isooctane	270.7	2.57	99.2
Cyclohexane	280.3	4.07	80.7
Benzene	318.6	4.90	80.0
Toluene	320.8	4.10	110.6
p-Xylene	343.1	3.52	138.4
Water	374.2	22.05	100.0

[a] Sublimation temperature.

18.1 SOLUBILITY OF POLYMERS IN SCFS

The heuristic rule for solubility in liquid solvents, "like dissolves like," applies similarly to polymers dissolving in SCFs. Thus, hydrocarbon polymers such as polyethylene are soluble in hydrocarbon SCFs such as the alkenes and *n*-alkanes, while polar polymers such as poly(methyl methacrylate) are soluble in polar SCFs such as chlorodifluoromethane. Carbon dioxide is generally a poor solvent for most high molecular weight polymers [14], but notable exceptions exist, such as siloxane polymers and fluorinated polymers. Solubility in CO_2 is also enhanced when CO_2-philic moieties are located in accessible side chains rather than in the less accessible main chain [15].

The solubility parameter for a compressible fluid increases from the gaseous state with increasing pressure (or density). Since solubility parameters for polymers, especially polar polymers, are relatively high, increasing pressure (or density) at constant temperature facilitates dissolution of polymers in SCFs. Conversely, decreasing the pressure at constant temperature causes the polymer to be rejected from solution.

The effect of temperature on polymer solubility in SCF solutions is more varied than the effect of pressure. Polymer solutions exhibit two different types of phase behavior: upper consolute solution temperature (UCST) or lower consolute solution temperature (LCST). In UCST behavior, two equilibrium liquid phases are converted to a single phase as the temperature is increased at constant pressure. In LCST behavior, a single liquid phase separates into two phases as the temperature is increased. U-L-CST behavior, where a two-phase solution becomes a single phase with increasing temperature, and, upon a further increase in temperature separates again into two phases, is also possible, but rarer. In conventional liquid solvents, LCST behavior is attributed to the difference in thermal expansion coefficients between the solvent and polymer, and to entropic effects as the solvent "condenses" around the polymer in order to solvate it. In polymer/SCF solutions, the mismatch in thermal expansion coefficients can be quite pronounced, since the solvent is highly compressible while the polymer is not. Also, "clustering" of SCF molecules around solute molecules is well-known in SCF solutions with low molecular weight solutes [16], so LCST phase behavior is common in polymer/SCF solutions.

Since both pressure and temperature are independent variables for controlling polymer/SCF phase behavior, it is informative to plot phase behavior in a P–T diagram, as shown schematically in Fig. 18.1. Coexistence curves separate regions where a single-phase solution exists from regions where two or more phases exist. If the coexistence curve exhibits a positive slope with temperature, the solution shows LCST behavior, while a negative slope is indicative of UCST behavior. Although curves for both types of behavior are shown in Fig. 18.1, for a given polymer/solvent system it may not be possible to see both branches, as solvent freezing or polymer degradation may occur at low and high temperatures, respectively. Increasing polymer molecular weight shifts the coexistence curves to higher pressures (i.e., decreased solubility), while improving the solubility parameter match (through changes in solvent type or composition, or changes in copolymer composition), shifts the P–T curves to lower pressures.

Polymer concentration also influences the location of the coexistence curves for polymer/SCF mixtures. Figure 18.2 shows a pressure-composition diagram for polycaprolactone ($M_w/M_n = 1.6$) in chlorodifluoromethane; this system exhibits LCST phase behavior. The curve shape is typical of that seen for most other polymer/SCF systems, including highly monodisperse polymers. The cloud point pressure increases steeply with increasing polymer concentration in very dilute solutions, reaches a somewhat broad maximum at intermediate concentrations ranging from about 2 to 10 wt %, and then decreases again in highly concentrated solutions. Increasing polymer molecular weight increases

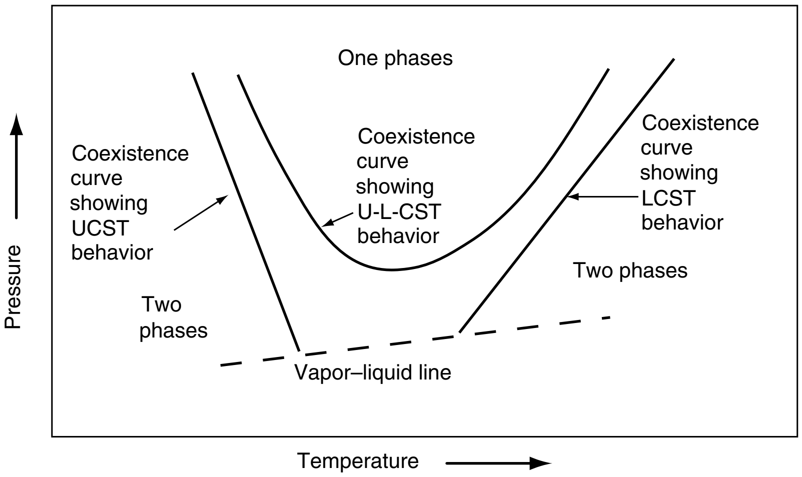

FIGURE 18.1. Schematic P–T diagram of polymer/SCF solutions.

the cloud point pressure, except at high polymer concentrations where molecular weight has little effect on the phase equilibrium.

The phase behavior of polymer/SCF mixtures can be described using versions of the lattice fluid (LF) model such as that developed by Sanchez and Lacombe [17]. The LF equation of state is relatively simple, and has been successfully used to describe either polymers dissolved in SCFs, or SCFs dissolved in polymers [18,19], including phenomena such as retrograde vitrification. The statistical associating fluid theory (SAFT) [20] can also describe the phase behavior of polymers dissolved in SCFs. The SAFT model, while somewhat more cumbersome to implement than the LF model, is especially well-suited for polymers with varying backbone architecture, such as branched polymers or copolymers. Both the Sanchez–Lacombe and SAFT models have been incorporated into commercially available modeling software [21].

Table 18.2 below lists polymer/SCF solutions which have been experimentally characterized for phase behavior.

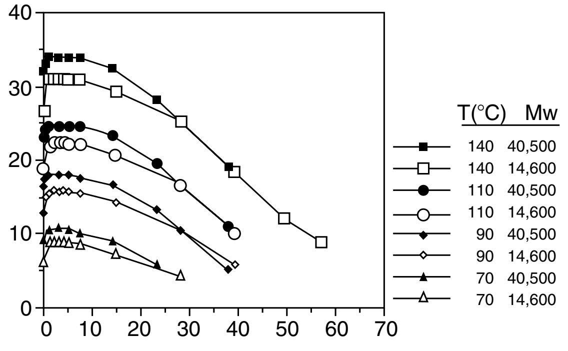

FIGURE 18.2. Phase behavior of polycaprolactone/$CHClF_2$ solutions.

Experimental techniques generally fall into one of two categories: optical measurements or sampling procedures. Optical techniques include qualitative visual observation of the cloud point, or quantitative determination of turbidity changes as pressure is lowered. Solution pressure may be lowered either by increasing the solution volume, usually by a movable piston, or else by venting off solution from a constant volume cell. Visual cloud points are difficult to distinguish accurately at extremely low or high concentrations, so much optical data center on the intermediate concentration regime where the P–x curve is flat. Sampling procedures involve analysis of the compositions of the two fluid phases in equilibrium with each other. These measurements are also difficult at extremely high concentrations because of the high viscosity of the polymer-rich phase. Alternately, only the solvent-rich phase may be sampled in a flow-through cell, provided that mass transfer does not limit the polymer concentration. Unless otherwise noted, the phase behavior results in Table 18.2 were acquired by visual observation of cloud points in a variable volume view cell. Equation of state models used to fit the experimental data are also noted in Table 18.2.

18.2 SOLUBILITY OF SCFS IN POLYMERS

Supercritical carbon dioxide is of special interest as an SCF for use with polymers, owing to its low critical point and nontoxic, nonflammable nature. However, as Table 18.2 demonstrates, the number of high molecular weight (>10 kDa) polymers which dissolve in supercritical CO_2 is relatively small. However, CO_2 and other SCFs are readily sorbed into a wide variety of polymers at elevated pressures. When the polymer in which the SCF dissolves is in the liquid or rubbery state, the sorption of SCF into the polymer generally follows Henry's law [77],

TABLE 18.2. *Solubility of polymers in supercritical fluids.*

Polymer	Mw (kDa)	Solvent	Temp. (°C)	Pressure (MPa)	Polym. Conc. (wt%)	Phase Behavior	Ref.	Technique	Modeling
Polyethylene									
Linear	4–118	Ethylene	130–170	155–190	2–24	UCST	[22]	Visual cloud point (CP)^a	
Linear	13–120	Propane	110–135	40–70	.25–24	Flat^b	[23]		
Linear	2–420	*n*-Butane	100–200	5–30	1–10	LCST	[24]		
	420	*n*-Butane/ 0–33% CO_2	100–200	25–80	5	Changes with % CO_2	[24]		
Linear	121	Cyclohexane/ 35–52% CO_2	160–210	27–55	3–20	LCST or Flat (high%CO_2)	[25]		
		Toluene/41–65% CO_2	160–210	38–70	3–12	UCST, ULCST	[25]		
		n-Pentane/ 30–40% CO_2	160–210	10–70	3–9	UCST, ULCST	[25]		
Linear	NR	CCl_3F	150–200	1.7–13.6	0.5–20	LCST	[26]		
Branched	315	Ethylene	105–140	140–200	0.33–30	UCST	[27]	Visual CP	
Branched	108	Ethane	95–130	120–130	5	Flat	[28]		SL^c with temperature-dependent mixing parameters
		Propane	100–130	55–60	5	Flat			
		Ethylene	115–135	160–180	5	UCST			
		Propylene	90–140	60	5	Flat			
Branched	65–113	Dimethyl ether	110–165	50–140	5	UCST	[29]		SAFT^d
Branched	NR	Ethylene	100–270	119–175	0.7–30	UCST	[30]	Visual CP with sampling	
Branched	46–108	Ethane	115–152	100–128	5.5	UCST	[31]		
	46–108	Propane	105–152	45–58	5.5	Flat	[31]		
Branched	17–246	Propane	110–150	40–60	0.15–29	Flat	[32]	Visual CP, constant vol.^{e}	
	246	Ethane	120–150	115–120	5	UCST	[32]		
	246	*n*-Butane			5	Flat	[32]		
	246	*n*-Pentane	90–160	0.5–11	5	LCST	[32]		
Branched	28^d	Ethylene	130	130–190	5–45	UCST	[33]	Visual CP	
Low density	45.3	Ethylene	130–248	120–164	5	UCST	[34]		PC-SAFT^f
Linear low density	52	Ethylene	122–167	140–175	0.5–18	UCST	[35]	1.08 PDI	SL
Polyethylene	121	*n*-pentane	97–167	8–50	5	LCST	[36]	Transmitted intensity	
Branched polyethylene	32–2,000	ethylene	117–172	90–200	0.2–20	UCST	[37]		
Polyethylene	0.5–5	ethylene	140–240	53–62	0.3–3.2 (mol%)	UCST	[38]		PRSV^2 with Wong–Sandler mixing rule

TABLE 18.2. *Continued.*

Polymer	Mw (kDa)	Solvent	Temp. (°C)	Pressure (MPa)	Polym. Conc. (wt%)	Phase Behavior	Ref.	Technique	Modeling
Ethylene copolymers									
Ethylene-*co*-propylene	0.8–96	Propylene	−10–200	30–46	15	ULCST, LCST	[39]		
						LCST	[39]		
	Butene/ Ethylene	−25–200	1.5–40	15		LCST	[39]		
	Hexene/ Ethylene	−25–200	1–27	15		UCST, LCST	[39]		
	0.8–96	Propylene	100, 150	18–42	0.8–33	LCST	[40]		SAFT
		Ethylene	20–200	57–172	3.8, 16	ULCST	[40]		SAFT
	5.9	Propylene	100, 150	18–30	1.8–33	LCST	[41]		
Ethylene-*co*-methyl acrylate	69–279	*n*-Butane	135–210	60–250	5	UCST	[29]		
Ethylene-*co*- methyl acrylate	75–99	Ethane	160–175	230–260	5	UCST	[28]		SL with temperature-dependent mixing parameters
		Propane	45–170	100–280	5	UCST			
		Ethylene	25–130	120–260	5	UCST			
		Propylene	25–135	40–140	5	UCST			
	99	*n*-Hexane Propane other	145–155	80–260	5	UCST	[42]		
		Propane	70–160	150–220	5	UCST	[42]		
		Propane / 10 %alcohol	70–160	80–240	5	UCST	[42]		
Ethylene-*co*-methyl acrylate	110–128	Ethylene	100–220	118–211	5	UCST	[34]		PC-SAFT
Ethylene-*co*-methyl acrylate	34–59	Propane	65–160	60–200	5	UCST	[43]		SL
		Propane / 0–9% Ethanol	65–160	45–200	5	UCST, Flat			
		Propane / 0–41% Acetone	40–140	25–175	5	UCST, Flat			SL
		$CHClF_2$	65–150	6–30	5	LCST			
		$CHClF_2$ / 0–39% Ethanol	65–150	3–20	5	LCST			
		$CHClF_2$ / 0–39% Acetone	65–150	3–25	5	LCST			
Ethylene-*co*-methyl acrylate	75–185	Ethylene	30–240	125–270	5	UCST	[44]		
Ethylene-*co*-ethyl acrylate	117–157	Ethylene	80–260	98–163	5	UCST	[34]		PC-SAFT
Ethylene-*co*-propyl acrylate	112–147	Ethylene	80–260	98–153	5	UCST	[34]		PC-SAFT
Ethylene-*co*-butyl acrylate	35–297	Ethylene	50–245	75–180	5	UCST	[44]		SAFT
Ethylene-*co*-acrylic acid	24–247	1-Butene	120–220	50–250	5	UCST	[29]		
Ethylene-*co*-methyl methacrylate	20–84	Ethylene	80–255	104–186	5	UCST	[34]		PC-SAFT

TABLE 18.2. *Continued.*

Polymer	Mw (kDa)	Solvent	Temp. (°C)	Pressure (MPa)	Polym. Conc. (wt%)	Phase Behavior	Ref.	Technique	Modeling
Polystyrene									
Polystyrene	20	Diethyl ether	−70–170	5–200	15.4	LCST	[45]	Turbidity	
Polystyrene	110	Diethyl ether/ Acetone	−100–200	0–31	10	UCST, LCST	[45]		
Polystyrene	4,9	*n*-Butane	120–200	4–65	0.5–80	LCST(high, low polymer concn) USCT(intermediate concn)	[46]	Laser turbidity CP, variable vol.	
	9	*n*-Pentane	130–220	4–35	5–80	LCST(high, low polymer concn) USCT(intermediate concn)	[46]		
	0.4–3	Ethane	40–60	8.5–34	0.001–20	LCST	[47]	Sampling	
	0.4–1.1	CO_2	40	25	0.01–1	NR	[47]	Sampling	
	0.4–1.6	Ethane / 13% Propane	40	25	1–10	NR	[47]	Sampling	
	1,9	Propane	50–180	25–67	0.2–4	UCST	[48]		
	114, 929	Dichloro-trifluoroethane	75–145	3–35	0.03–7.3	LCST	[49]		
Polystyrene	270	*trans*-decahydronaphthalene	1–16	10–90	4.2–21.6 (vol%)	UCST	[50]	Light Scattering	SL
Isotactic	22	*n*-Butane	155–201	9–13	13–26	LCST	[51]	Visual CP, constant vol.	
Other hydrocarbon polymers									
Polypropylene		CO_2	163–208	45–95	6.7–38	UCST	[52]	Laser CP, constant, vol.	
Atactic polypropylene	6 (M_v)	CO_2	25, 32	13.5	0.15–0.25	LCST	[53]		
Poly(1-butene)		*n*-Butane	167–190	12–17	5.5–21	LCST	[52]		
		CO_2	132–146	30–90	6.3–38	UCST	[52]		
Poly(1-butene) (atactic)	0.4–1.3 (M_v)	CO_2	30–33	17.9–23.4	0.6–1		[53]		
Polybutadiene	5(M_v)	CO_2	25	19.3	0.27		[53]		
Polyisobutylene	0.5(M_v)	CO_2	25	20.3	0.44	NR	[53]		
Polyisobutylene	50	*n*-Butane	155–200	7–10	18.8–31.4	LCST	[51]	Visual CP constant vol.	
Polyisobutylene (telechelic)	1–11	Propane	25–150	25–45	7	LCST, ULCST	[54]	Visual CP constant vol.	SAFT
	1–11	Dimethyl ether	75–150	45–65	5	ULCST, LCST	[54]		SAFT
	0.2–11	Ethane	25–150	2–120	9–43	LCST, UCST (high MW)	[54]		SAFT
	0.2–1	CO_2	50–180	4–200	5–52		[54]		SAFT
Polyisobutylene	1.25	Propane	90–113	4–7	27.1	LCST	[55]	Sampling	

TABLE 18.2. *Continued.*

Polymer	Mw (kDa)	Solvent	Temp. (°C)	Pressure (MPa)	Polym. Conc. (wt%)	Phase Behavior	Ref.	Technique	Modeling
Acrylate or Methacrylate Polymers									
Poly(methyl methacrylate)	10.6	$CHClF_2$/Acetone	65–155	2.5–25	5	LCST	[43]	Visual CP, variable vol.	
Poly(methyl methacrylate)	50	$CHClF_2$	75–150	3–30	0.08–0.26	LCST	[56]	Visual CP, variable vol.	
Poly(methyl methacrylate)	74	$CHClF_2$	65–140	3–29	0.03–15	LCST	[57]	Visual CP, variable vol.	SL-HB[h]
Poly(methyl methacrylate)	104.7	Propylene	154–259	108–270	5	UCST	[34]		PC-SAFT
Poly(ethyl methacrylate)	280	$CHClF_2$	75–140	3–25	0.08	LCST	[56]		
Poly(butyl methacrylate)	65.5	Ethylene	100–235	103–138	5	UCST	[34]		PC-SAFT
Poly(decyl methacrylate)	250–730	Isooctane	230–320	1.5–7.5	5–30	LCST	[58]		
Polystyrene-*b*-poly(methyl methacrylate)	70	$CHClF_2$	110	21	0.08		[56]		
Poly(methyl acrylate)	2.03	CO_2	25	22–54	1–6		[15]		
	2.85	CO_2	25–50	67–102	1–10	LCST	[15]		
Poly(methyl acrylate)	30.7	$CHClF_2$	64–136	2.5–22.5	5	LCST	[43]		
Poly(methyl acrylate)	186.9	Propylene	200–258	140–275	5	UCST	[34]		PC-SAFT
Poly(ethyl acrylate)	153.7	Ethylene	81–260	101–161	5	UCST	[34]		PC-SAFT
Poly(propyl acrylate)	108.3	Ethylene	80–258	87–109	5	UCST	[34]		PC-SAFT
Poly(*n*-butyl acrylate)	30–940	Nitrous oxide	75	10.3–51.7	0.006–0.03		[59]		
Aliphatic Polyesters									
Poly(ε-caprolactone)	14.6, 40.5	$CHClF_2$	55–145	3–35	0.03–19	LCST	[57]		SL-HB
Poly(L-lactic acid)	50	$CHClF_2$	55–150	3–28	0.08	LCST	[56]	Constant vol.	
Poly(L-lactic acid)	1–10	CO_2/10–40% $CHClF_2$	55–65	7–20	0.001–0.05	LCST	[60]	Flow cell sampling	
Poly(L-lactic acid)	1–2.1	CO_2/0–1% Acetone	55–65	7–20	0.001–0.05	LCST	[61]	Flow cell sampling	
Poly(L-lactic acid)	1–2.1	$CClF_3$	55	11–12	<0.5	NR[i]	[61]	Flow cell sampling	
Poly(D,L-lactic acid)	0.9	CO_2	55	20	<0.5	NR	[61]		
Poly(glycolic acid)	NR	CO_2	55	18–20	<0.5	NR	[61]		
Poly(lactic-*co*-glycolic acid)	70–149	CO_2	33–97	131–300	5	Nearly athermal	[62]		
Poly(lactic-*co*-glycolic acid)	128–130	CHF_3	27–81	54–147	5	LCST	[62]		
Poly(lactic-*co*-glycolic acid)	70–130	$CHClF_2$	36–72	1.5–24	5	LCST	[62]		
Poly(γ-hydroxybutyrate)	800	CO_2	35–75	12–35	0.05–1	LCST	[63]	Extraction	
Polyethers									
Polyethylene glycol	0.4–0.6	CO_2	40	20	0.25–1.25	NR	[64]		SL
Poly(ethylene glycol)	0.2–0.6	CO_2	40	20	0.05–4	NR	[65]	Sampling	
Poly(propylene glycol) (Low polydispersity)	0.45–2.16	Ethane	20–100	5–30	0.5–4	ULCST	[66]		SL-HB
Poly(propylene oxide)	3.5	CO_2	50–70	98–135	5	UCST	[15]		
PEG/nonylphenylether	2.5	CO_2	45;60	12–30	0.005–0.07	LCST	[67]	extraction	

TABLE 18.2. *Continued.*

Polymer	Mw (kDa)	Solvent	Temp. (°C)	Pressure (MPa)	Polym. Conc. (wt%)	Phase Behavior	Ref.	Technique	Modeling
Siloxane Polymers									
Poly(dimethyl siloxane)	135	CO_2	25, 52	19.3	0.3, 1	UCST	[53]		
Poly(dimethyl siloxane)	13	CO_2	22	25–32	1–10		[68]	Visual CP, constant vol.	
Poly(dimethyl siloxane-co-methylhydrosiloxan-g-propyl acetate); other side chains also reported	Degree of polymerization = 25	CO_2	22	12–35	0.4–5.5	NR	[69]	Transmitted light intensity	
Fluorinated Polymers									
Poly(hexafluoro-propylene oxide)	13.6	CO_2	22	6–15	1–10		[68]	Visual CP, constant vol.	
Poly(tetrahydroperfluoro-decylacrylate)		CO_2	10–70	5–25	0.087–7.32	LCST	[70]	Visual CP, variable vol.	
Poly(vinylidene fluoride)	180; 275	$CHClF_2$	120–180	71–73	5	UCST	[71]		
		$CHClF_2$	129–207	72–76	5				
Poly(vinylidene fluoride)	180; 275	CO_2	140–200	159–165; 158–170	5	UCST	[71]	Visual CP, variable vol.	
			125–220						
Poly(vinylidene fluoride)	180; 275	CHF_3	170–225	180–230	5	UCST	[71]		
Poly(vinylidene fluoride)		Dimethyl ether				LCST	[71]		
Poly(1,1-dihydroperfluorooctylacrylate)	1,400	CO_2	30–90	10–200	0.09–16	LCST	[72]		SAFT
Poly(tetrafluoroethylene-*co*-vinyl acetate)	140–180	CO_2	25; 75–128	50–56	1–10		[73]	Visual CP, variable vol.	
				74–90	5	LCST			
Methacrylate, perfluorinated propylene oxide graft copolymers	6.2–11	CO_2	40	16–42	1–28		[74]		
Other Polymers									
Cellulose triacetate	145.7	Ethyl acetate	185–235	3.5–8.5	0.5–5	LCST	[75]	Visual CP, variable vol.	
Poly(vinyl acetate)		CO_2	25	63–66	3–6	NR	[73]	Visual CP, variable vol.	
Poly(vinyl acetate)	0.98–585	CO_2	25	13.6–67.6	1–12	NR	[15]		
Poly(vinyl acetate)	585	CO_2	17–207	67–125	5	LCST	[15]		
Poly(ε-caprolactam)		Trifluoroethanol / 0–48% CO_2	25–100	13–35	3–14		[76]		SAFT, SL
Poly(ε-caprolactam)		CO_2	233–241	40–50	13.8–16.5	UCST	[52]		

[a] Cloud point determined by eye.
[b] Phase boundary nearly independent of temperature.
[c] Sanchez–Lacombe equation of state.
[d] Statistical associating fluid theory equation of state.
[d] Viscosity average molecular weight.
[e] Constant volume view cell.
[f] Perturbed chain SAFT model.
[g] Peng-Robinson-Stryjek-Vera equation of state.
[h] Sanchez–Lacombe hydrogen bond model.
[i] Not reported.

shown in Eq. (18.1), where the mass fraction of sorbed SCF (w_{SCF}) is proportional to the partial pressure of the SCF, P_{SCF}.

$$w_{\mathrm{SCF}} = k_{\mathrm{H}} P_{\mathrm{SCF}}. \tag{18.1}$$

The Henry's law constant, k_{H}, is independent of molecular weight except at extremely low molecular weight (< 1kDa), but is often a strong function of temperature, typically showing an Arrhenius-like dependence. The slope of the Arrhenius plot can be correlated with the enthalpy of dissolution of the SCF in the polymer [78]. An alternate correlation based on corresponding states suggests that k_{H} should scale with $(T_c/T)^2$, rather than with $1/T$ [79]. However, the proportionality constant for $(T_c/T)^2$ scaling is not a universal constant. Over the temperature range common for SCF-polymer mixtures, little difference is detectable between $1/T$ scaling and $1/T^2$ scaling, so data are presented here with the $1/T$ scaling. The solubility of the SCF in the polymer may either increase with temperature (for polymer-SCF pairs exhibiting UCST phase behavior), or solubility may decrease with increasing temperature (for polymer-SCF pairs exhibiting LCST phase behavior.) Hence, the Arrhenius coefficient for k_{H} may be either positive or negative. Table 18.3 lists Henry's law constants for rubbery and molten polymers. The temperature dependence of the Henry's law constants are correlated with absolute temperature via the Arrhenius expression:

$$\ln(k_{\mathrm{H}}) = \frac{A}{T} + B, \tag{18.2}$$

where k_{H} (from Eq. (18.1)) has units of mass fraction per MPa, and T has units of degrees Kelvin.

Care should always be exercised when using solubility data for glassy or crystalline polymers (not included here), because SCF sorption occurs preferentially in the amorphous phase, which may additionally experience swelling-related stress. Solubility data for CO_2 in solid polymers is compiled in [5]. Often, the pressure dependence of SCF sorption in glassy polymers follows a dual-mode sorption model, with substantial deviations from Henry's law.

Solubility of SCFs in polymers is determined experimentally by one of several general techniques. Gravimetric techniques monitor the in situ weight gain of a polymer sample exposed to a surrounding high pressure SCF. These techniques require the application of a buoyancy correction term to the raw data, since the polymer swells upon exposure to the SCF. The swollen volume may be measured experimentally, or it may be estimated using an equation of state, typically the Sanchez–Lacombe model. Another experimental technique measures mass gain of a polymer exposed to an SCF by monitoring the change in resonant frequency of an oscillating sensor, typically a quartz crystal. The amount of SCF sorbed in a polymer may also be determined by recording the pressure decay in a reservoir of SCF in contact with the polymer.

18.3 MELTING POINT DEPRESSIONS OF POLYMERS IN THE PRESENCE OF SCFS

The melting temperature (T_{m}) of a semicrystalline polymer is usually lower in the presence of a soluble SCF than it is in the pure polymer at ambient pressure. When a polymer crystallizes from an SCF-saturated solution, the resulting three-phase (S–L–G), two-component equilibrium is univariant, according to the phase rule, so T_{m} is only a function of pressure under these conditions. Experimental measurements of the polymer melting point in the presence of an excess of CO_2 typically exhibit the pressure dependence shown in Fig. 18.3. The melting temperature decreases approximately linearly with increasing pressure above ambient conditions, then it abruptly levels off to a near constant value. Occasionally, some deviations from this behavior are seen: (1) a small (1–2°C) increase is T_{m} is sometimes recorded at low pressure, before the linearly decreasing region occurs. This is attributed to annealing of small crystallites; (2) at very high pressure, following the plateau zone, T_{m} sometimes begins to increase with increasing pressure; and (3) the plateau zone where T_{m} is constant is sometimes missing, so that a region of linearly decreasing T_{m} is followed immediately by a region of linearly increasing T_{m}. The qualitative features of the SCF-saturated melting point curves are similar for polymers and for sparingly soluble low molecular weight crystalline compounds such as naphthalene and biphenyl [100].

The melting point of a polymer saturated with an SCF is determined experimentally either visually, or else by high pressure calorimetry, although the pressure range for the latter is often limited by instrument constraints to a few MPa. Table 18.4 presents values of $\mathrm{d}T_{\mathrm{m}}/\mathrm{d}P$ in the linear region (low pressure) for polymers saturated with an SCF. In cases where an increase in T_{m} occurred at very low pressure, as in Fig. 18.3, the lowest pressure points were not included in the linear least squares line fitting. When the experimental pressures were high enough so that the second (plateau) region could be seen, this has been noted in the Comments.

18.4 SCF-INDUCED T_g DEPRESSION

Sorption of an SCF in a polymer can lower its glass transition temperature (T_{g}) significantly below that seen at atmospheric pressure. For a given polymer, the glass transition temperature depression is found to increase as the amount of SCF sorbed increases [105]. Because CO_2 solubility usually decreases with increasing temperature, it is possible for a polymer/CO_2 mixture at elevated pressure to undergo a liquid-to-glass transition as the temperature is raised. This phenomenon, referred to as ''retrograde vitrification'' [18], has been observed for poly(methyl methacrylate) [105,106]. Table 18.5 reports the pressure dependence of T_{g} observed for polymers which have been exposed to a high pressure SCF. T_{g} depression curves look similar to

TABLE 18.3. *Henry's law constants of SCFs in Polymers.*

Polymer	Diluent	Temp. Range (C)	Pressure (MPa)	k_H (mass fraction/MPa)	A (Eq. (18.2))	B (Eq. (18.2))	Ref.	Technique	Comments
Polyethylene	CO_2	185–227	0.7–2.0		171	−4.87	[77] [80]	Pressure decay	
Polyethylene, branched	CO_2	125–250	NR		546	−6.235	[81]	Gas–liquid chromatography	
Polystyrene	CO_2	65–129	4–44				[82]	MSB[a] and pressure decay	
Polystyrene	CO_2	100–200	2–20		1080	−8.081	[83]	MSB	SL[b]
Polystyrene	*n*-Butane	75–200	0.1–3		2034	−8.231	[84]	Volumetric	Only mass fraction <0.05 used in fitting
Polystyrene	Isobutane	75–200	0.1–3		1846	−8.094	[84]	Volumetric	Only mass fraction <0.05 used in fitting
Polystyrene	HCF_2Cl	85	0–2.5	0.0539			[85]	QCM[c]	
Polypropylene	CO_2	160–200	5.4–17.5		760	−6.637	[86]	Pressure decay	SL used for swelling correction
Polypropylene	*n*-Butane	165–210	0.3–3.1		2366	−8.144	[84]	Volumetric	
Polypropylene	Isobutane	165–210	0.3–3		2025	−7.637	[84]	Volumetric	
Poly(methyl methacrylate)	HCF_2Cl	70	0–1	0.153			[85]	QCM	
Poly(ε-caprolactone)	CO_2	70–85	0.2–6.5		1131	−7.524	[87]	Quartz spring microbalance	SL
Poly(butylene succinate)	CO_2	50–180	1–20		1038	−7.528	[88]	MSB	SL used for swelling correction
Poly(lactic-*co*-glycolic acid) (48L/52G)	CO_2	40	1–3	0.0152			[89]	Gravimetric	
Poly(lactic-*co*-glycolic acid) (53L/47G)	CO_2	40	1–3	0.0162, 0.0164			[89]	Gravimetric	
Poly(lactic-*co*-glycolic acid) (54L/46G)	CO_2	40	1–3	0.0195			[89]	Gravimetric	
Polyethylene glycol	CO_2	65–100	4–14		1687	−8.807	[90]	Sampling	SAFT[d] modeling
Polyethylene glycol	CO_2	40	5–11	0.0198			[91]	NIR[e]	
Polypropylene glycol	CO_2	25	2–6	0.0294			[91]	NIR	
Polypropylene glycol	CO_2	35	2–6	0.0200			[91]	NIR	
Poly(phenylene oxide)	CO_2	150	2–20	0.00524			[92]	MSB	SL used for swelling correction
Poly(phenylene oxide)	CO_2	200	2–20	0.00405			[92]	MSB	SL used for swelling correction
Poly(vinyl acetate)	CO_2	40–100	0.2–17.4		1882	−9.344	[83]	MSB	SL used for swelling correction

[a] Magnetic suspension balance.

[b] Sanchez–Lacombe equation of state used.

[c] Quartz crystal microbalance.

[d] Statistical associating fluid theory.

[e] Near infrared spectroscopy.

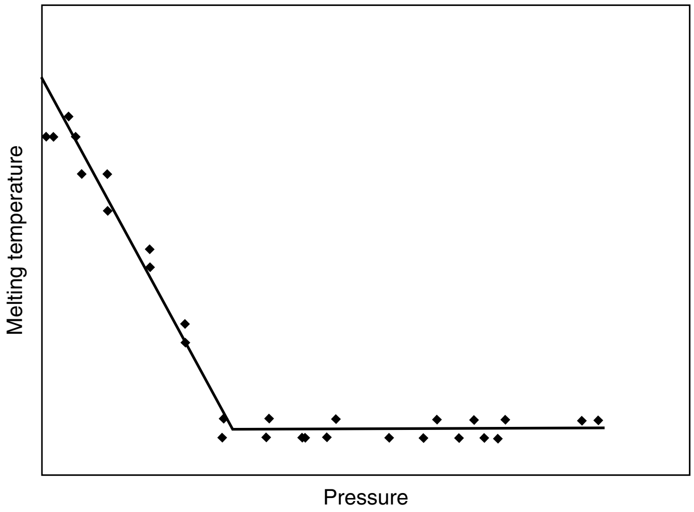

FIGURE 18.3. Representative plot of melting point depression of polymer exposed to CO_2. Lines are added as a guide to the eye.

melting point depression curves – a near linear decrease of T_g with increasing pressure is seen at low pressures. However, the typical magnitude of the slope of the T_g vs. P curve is considerably higher (about 5–10 times) than the typical magnitude of the T_m vs. P curve (e.g., from Table 18.4). An equation of state can be used to predict SCF-induced T_g depression, using either an isofree volume condition or the isoconfigurational entropy condition of the Gibbs-DiMarzio criterion.

18.5 INTERFACIAL TENSION BETWEEN SCF AND SCF-SWOLLEN POLYMER

The interfacial tension (IFT) between an SCF-swollen polymer and the saturating SCF decreases with pressure, as the solubility of the SCF in the polymer increases. For polymers which exhibit complete miscibility with the SCF at an experimentally achievable pressure, the IFT will vanish as the pressure approaches the apex of the P–x curve. Several comprehensive studies of the IFT of polymers swollen with CO_2 have been conducted; these are summarized in Table 18.6. These studies indicate that the molecular weight of the polymer does not influence IFT, probably because SCF solubility in the polymer is independent of molecular weight. For mixtures exhibiting LCST phase behavior, temperature has a minor effect on IFT, because the decrease in IFT associated with increasing temperature in pure polymers is largely offset by an increase in IFT due to decreased solubility of the SCF in the polymer. Plots of IFT vs. CO_2 pressure typically show a steep decreasing slope at lower pressure, followed by a more gradual decrease at higher pressure. The values of IFT in Table 18.6 were measured by analyzing the shape of a pendant drop.

18.6 VISCOSITY OF POLYMER/SCF MIXTURES

Because SCFs typically have lower density and higher compressibility than a pure polymer melt, dissolution of the SCF into the polymer melt results in swelling of the polymer. This in turn leads to an increase in free volume of the mixture, so transport properties such as viscosity and diffusion coefficient can be significantly enhanced. The semi-empirical Doolittle equation [128,129] predicts that the zero-shear rate viscosity, η_0, of a polymer is exponentially related to the fractional free volume, f, via:

$$\eta_0 = A \exp\left[B\left(\frac{1}{f} - 1\right)\right]. \qquad (18.3)$$

A viscoelastic shift factor, a_S, can be found from the ratio of the experimentally measured zero shear rate viscosity (at test conditions of P, T, and SCF concentration), to the experimentally measured zero shear rate viscosity (at some reference conditions of P_{ref}, T_{ref}, and reference SCF concentration). Once a_S is determined experimentally, a master curve can be constructed by plotting η/a_S vs. $a_S\dot{\gamma}$ where η is the measured viscosity and $\dot{\gamma}$ is the measured shear rate. If the fractional free volume, f, is estimated from an equation of state as $f = 1 - \rho/\rho^*$, where ρ is the mixture density and ρ^* is the mixture close-packed density, then the shift factor due to the presence of the SCF can be calculated from Eq. (18.3), provided the constant B is known. Experimentally, B for SCF-swollen polymers has been found to be near unity [130,131], in agreement the universal constants of the WLF equation [132] for the temperature dependence of pure polymers.

TABLE 18.4. *Melting point depressions of semicrystalline polymers saturated with* CO_2.

Polymer	M_w (kDa)	T_{m0} (°C)	$-dT_m/dP$ (°C/MPa)	Pressure range (MPa)	Minimum T_m (°C)	Ref.	Comments
Low density polyethylene		105.4	0.5	0.1–10.4	NS[a]	[93]	Monitored temperature of high pressure melt cooling.
Low density polyethylene		112	5	0.1–30	85.6	[94]	No region of $dT_m/dP = 0$. Slope changes sign abruptly
Syndiotactic polystyrene		277	1.71	0.1–7	NS	[95]	HP-DSC[b]
Isotactic polypropylene		147–154	1.24	0.1–4.5	NS	[96]	HP-DSC
Isotactic polypropylene	85	165	1.0	0.1–3	NS	[97,98]	HP-DSC
Isotactic polypropylene	133	180	1.18	0.1–10	NS	[98,99]	HP-DSC
Isotactic polypropylene		154,164	1.24	0.1–4.5	NS	[96]	HP-DSC
Poly(ε-caprolactone)	4	63	2.41	0.1–28	36	[100]	
Poly(butylene succinate)	140	118	1.14	0.1–20	102	[100]	
Poly(L-lactide)	180	160	2.2	0.5–2	NS	[98]	HP-DSC
Poly(ethylene terephthalate)	180	257	0.67	0.1–8.5	NS	[95]	HP-DSC
Poly(ethylene terephthalate)	50.7	253	0.42	1–3	NS	[101]	HP-DSC
Polyethylene glycol	1.5	45	2.6	0.1–30	29	[102]	
Polyethylene glycol	4	57	2.14	0.1–30	42	[102,103]	
Polyethylene glycol	12	62	1.55	0.1–31	47	[103]	
Polyethylene glycol	35	61	1.55	0.1–30	47	[102]	
Poly(vinylidene fluoride)	530	158	0.48	0.1–68	135	[104]	Dilation
Other Solvents							
Low density polyethylene/$CHClF_2$		105.4	1.38	0.1–6.9	NS	[93]	

[a] Not seen in the experimental pressure range.

[b] High pressure differential scanning calorimetry.

TABLE 18.5. *Glass transition temperature depressions of polymers in the presence of SCFs.*

Polymer	Diluent	T_{g0}(°C)	$-\mathrm{d}Tg/\mathrm{d}P$ (°C/MPa)	Wt%CO_2	P (MPa)	$T_{g,P}$ (°C)	Ref.	Technique
Polystyrene	CO_2	100			2.03	78	[107]	DSC[a]
Polystyrene	CO_2	100			6.08	35	[105]	CC[b]
Polystyrene	CO_2	100			8.0	40	[108]	High pressure partition chromatograpy
Polystyrene	CO_2	104	8.1		5.33	61	[109]	HP-DSC
Polystyrene	1,1,1,2-tetrafluoroethane	104	8.5		3.28	76	[109]	HP-DSC
Poly(4-methyl-1-pentene)	CO_2	40			1.5	20	[110]	Soprtion
Poly(methyl methacrylate)	CO_2	105			3.95	32.7	[105]	CC
Poly(methyl methacrylate)	CO_2	105			8.0	40	[108]	High pressure partition chromatograpy
Poly(methyl methacrylate)	CO_2	105			10.0	36	[108]	High pressure partition chromatograpy
Poly(methyl methacrylate)	CO_2	92	8.9		4.7	50	[111]	Molecular probe chromatography
Poly(methyl methacrylate)	CO_2	90.7	10.6		3.77	50.8	[112]	High pressure calorimetry
Poly(methyl methacrylate)	Methane	90.7			22	73.5	[112]	High pressure calorimetry
Poly(methyl methacrylate)	Ethylene	90.7			5.52	57.3	[112]	High pressure calorimetry
Poly(methyl methacrylate)	CO_2	105			3.95	58.5	[105]	CC
Poly(methyl methacrylate)	CO_2	105			3.95(rv)[c]	32.7(rv)	[105]	CC
Poly(methyl methacrylate)	CO_2	105			4.05	42	[105]	CC
Poly(methyl methacrylate)	CO_2	105			3.75	75	[106]	CC
Poly(methyl methacrylate)	CO_2				3.75(rv)	5(rv)	[106]	CC
Poly(methyl methacrylate)	CO_2				6.08	45	[106]	CC
Poly(ethyl methacrylate)	CO_2	61			2.13	24	[113]	Sorption
Poly(ethyl methacrylate)	CO_2	61			1.62	24	[113]	Dilation
Acrylonitrile/methyl acrylate terpolymer (Barex)	CO_2	85		6.7		54	[114]	Ambient pressure DSC
Poly(acrylic acid)	CO_2	100			8.0	48	[115]	IGC[d]
Poly(L-lactide)	CO_2	NR	3.5		2		[98]	
Poly(ethylene terephthalate)	CO_2	74			2.03	52	[107]	DSC
Poly(ethylene terephthalate)	CO_2	74			2.03	52	[107]	DSC
Poly(ethylene terephthalate)	CO_2	74			2.03	52	[107]	DSC
Poly(phenylene oxide)	CO_2	210			1.4	25	[116]	Sorption isotherm
Poly(phenylene oxide)	CO_2	216			6.20	184.4	[117]	DSC
Poly(phenylene oxide)	CO_2	219			4.46	55	[118]	DSC
Poly(phenylene oxide)	CO_2	209			8.0	156	[115]	IGC
						101 (rv)		
					10.0	126		
Polycarbonate	CO_2	148			2.03	97	[107]	DSC
Polycarbonate	CO_2	150			8.0	75	[108]	High pressure partition chromatograpy
Polycarbonate	CO_2	145	9.0		9.3	60	[109]	HP-DSC
Polycarbonate	CO_2	151			3.1	25	[116]	Sorption isotherm

TABLE 18.5. *Continued*

Polymer	Diluent	T_{g0}(°C)	$-dTg/dP$ (°C/MPa)	Wt%CO_2	P (MPa)	$T_{g,P}$ (°C)	Ref.	Technique
Polycarbonate	CO_2	156			1.11	138	[119]	HP-DSC
					3.4(rv)	0(rv)	[111]	
Polycarbonate	CO_2	148			2.03	97	[107]	DSC
Polycarbonate	CO_2	148			6.08	55	[118]	DSC
Tetramethyl polycarbonate	CO_2	195	6.6		5.62	160	[120]	High pressure scanning calorimetry
Polycarbonate	CO_2	150	7.1		5.62	109	[120]	High pressure scanning calorimetry
Tetrachloro polycarbonate	CO_2	233	4.74		5.62	206	[120]	High pressure scanning calorimetry
Tetrabromo polycarbonate	CO_2	267	3.65		5.62	247	[120]	High pressure scanning calorimetry
Poly(vinyl chloride)	CO_2	75			2.03	57	[107]	DSC
Poly(vinyl chloride)	CO_2	77	13.4		4.26	16	[109]	HP-DSC
Poly(vinyl pyrrolidone)	CO_2	165			8	120, 71(rv)	[115]	IGC
					10	106, 96(rv)	[115]	IGC
Poly(vinyl pyrrolidone)	CO_2	161			8	100.5, 81(rv)	[115]	IGC
Poly(vinyl pyrrolidone-co-vinyl acetate)	CO_2	96			8	36	[115]	IGC
Polysulfone	CO_2	182			3.4	23	[116]	Sorption isotherm
Poly(ether sulfone)	CO_2	222			2.7	21	[116]	Sorption isotherm
Poly(ether imide)	CO_2	199			2.8	21	[116]	Sorption isotherm
Cellulose acetate	CO_2	187			1.1	27	[116]	Sorption isotherm
Cellulose triacetate	CO_2	185			1.0	24	[116]	Sorption isotherm
Poly(vinylidene fluoride)	CO_2	105			2.53	60	[107]	DSC
Poly(amic acid)	CO_2	156			6.08	−8	[118]	DSC
Polyimide	CO_2	227			6.08	0	[118]	DSC
Poly(*p*-phenylene sulfide)	CO_2	85.5			2.03	75	[121]	Sorption isotherm
Poly(vinyl benzoate)	CO_2	65.5			3.39	25	[122]	Dilation
Poly(vinyl butyral)	CO_2	51			2.63	25	[122]	Dilation

[a] Differential scanning calorimetry.

[b] Creep compliance.

[c] Retrograde vitrification.

[d] Inverse gas chromatography.

TABLE 18.6. *Interfacial tension between polymers and carbon dioxide.*

Polymer	M_w (kDa)	Temp. (°C)	Pressure (MPa)	IFT (mN/m)	Ref.
Polystyrene	158	90	10	15.02	[123]
			25.4	9.38	
		140	3.9	37.61	
			20.2	12.41	
		160	5	24.54	
			17	13.91	
Polystyrene	309	100	8.2	20	[124]
			29	7.4	
		150	6.9	29	
			30	9.9	
Polystyrene	120	200	0.1	27.5	[125]
			10	17	
	NR	210–230	0.1	24	
			7	14	
Polypropylene	985	160–180	10.6	17	[124]
			25	7.3	
Poly(methyl methacrylate)	89.2	90	10	13	[124]
			33	4.5	
Poly(ethylene glycol)	0.6	45	8	10.5	[126]
			13	5	
			30	3.1	
Poly(ethylene glycol) nonylphenyl ether	2.5	50	9.9	22	[127]
			14.9	16	
			25.4	10	
		70	9.9	18	[127]
			14.9	11	
			25.4	9	
Poly(dimethyl siloxane)	*100 Pa s	40	1.7	16.4	[123]
			30.7	0.08	
	*1,000 Pa s	40	4.75	11.4	
			30	0.09	
	*15,000 Pa s	40	5.2	8.9	
			30.24	0.23	

*Viscosity at 25°C.

Table 18.7 lists viscosity reductions measured due to the presence of an SCF in the polymer. Because few researchers have reported the zero shear rate viscosity for both the pure polymer melt and the SCF-swollen melt, an experimental shift factor cannot usually be estimated from the data. Instead, Table 18.7 lists the ratio of viscosity measured in the presence of SCF diluent (η_{Dil}) to the viscosity measured in the absence of diluent (η), at some reference conditions. Unless otherwise specified, the reference state has no SCF, and has the same temperature as the experimental state. The pressure for the reference state, and dynamic characterization conditions (e.g., constant stress, σ, or constant $\dot{\gamma}$) are also specified in Table 18.7.

Experimental techniques for the characterization of SCF-diluted polymer viscosity generally fall into one of two categories – pressure-driven or drag-driven flow. Pressure-driven techniques include capillary flow and slit die extrusion, with viscosity calculated from the pressure drop vs. flow rate relation. Because viscosity is a function of pressure in these systems, the viscosity measured by pressure-driven techniques is an average quantity for the pressure range used in the experiment. Vibrating sensor surfaces or translating spheres are examples of drag-driven viscosity measurement devices. These avoid the difficulty of pressure variations, but usually lack the dynamic range of pressure-driven devices, i.e., are restricted to a limited range of $\dot{\gamma}$.

TABLE 18.7. *Viscosity reduction of polymer/SCF mixtures.*

Polymer	Diluent	Temp (°C)	Reference viscosity (Pa-s)	Reference Pressure (MPa)	Matching condition	η_{Dil}/η_{Ref}	P (MPa)	SCF Concn (wt%)	Ref.	Technique
High density polyethylene	CH_3CF_2Cl	200	NR	NR	$\sigma = 50\,kPa$	0.604	NR	8.96	[133]	Pressure-driven slit die rheometer
Low density polyethylene	CO_2	150	602	1.4	$\dot{\gamma} = 45\,s^{-1}$	0.71	4.7	7.8	[131]	Capillary rheometer
Low density polyethylene	CO_2	200	1.5×10^4	NR	$\dot{\gamma} = 10\,s^{-1}$	0.53	NR	4.0	[134]	Extrusion slit die
Low density polyethylene	CO_2	195	1,230	19.2	$\dot{\gamma} = 16\,s^{-1}$	0.759	19.2	7	[135]	Extrusion wedge die
Linear low density polyethylene	CH_3CF_2Cl	135	NR	NR	$\sigma = 50\,kPa$	0.475	NR	10.97	[133]	Pressure-driven slit die rheometer
Polystyrene	CO_2	195	3,900	19.2	$\dot{\gamma} = 13\,s^{-1}$	0.405	19.2	4	[135]	Extrusion wedge die
Polystyrene	CO_2	200	4,800	11.2	$\dot{\gamma} = 25\,s^{-1}$	0.389	9.3	4	[136]	Extrusion slit die
Polystyrene	CO_2	150	9,900	0.1	$\dot{\gamma} = 10\,s^{-1}$	0.187	12.18	5.2	[137]	Capillary
Polystyrene	CH_3CHF_2	150	5,600	0.1	$\dot{\gamma} = 21\,s^{-1}$	0.052	16.41	10.4	[137]	Capillary
Polypropylene	CH_3CF_2Cl	175	NR	NR	$\sigma = 50\,kPa$	0.438	NR	10	[133]	Pressure-driven slit die rheometer, constant stress
Polypropylene	*n*-pentane	200	2,200	NR	$\sigma = 50\,kPa$	0.413	NR	5.14	[133]	Pressure-driven slit die rheometer
Polypropylene	CO_2	175	NR	NR	$\sigma = 50\,kPa$	0.282	NR	4.9	[133]	Pressure-driven slit die rheometer
Polypropylene	CO_2	190	9,200	NR	$\dot{\gamma} = 10\,s^{-1}$	0.576	NR	6.0	[134]	Extrusion slit die
Poly(methyl methacrylate)	CO_2	210	1.1×10^4	6.89	$\dot{\gamma} = 10\,s^{-1}$	0.29	7.72	6.0	[134]	Extrusion slit die
Acrylonitrile/methyl acrylate terpolymer (Barex)	CO_2	180	10^5	NR	$\dot{\gamma} = 15\,s^{-1}$	0.395	17.2	6.7 Sat	[114]	Capillary rheometer
Poly(butylenes succinate)	CO_2	180	4,000	29.6	$\dot{\gamma} = 10\,s^{-1}$	0.625	31	6	[138]	Extrusion slit die
Poly(ethylene glycol)	CO_2	40	0.044	0.1		0.112	20	Sat	[139]	Vibrating Wire
Poly(ethylene glycol) 6,000	CO_2	80	0.83	0.1	$\dot{\gamma} = 10^5\,s^{-1}$	0.204	32.4	Sat	[103]	High frequency oscillatory shear
Poly(ethylene glycol) 6,000	CO_2	100	0.57	0.1	$\dot{\gamma} = 10^5\,s^{-1}$	0.309	29.8	Sat	[103]	High frequency oscillatory shear
Poly(ethylene glycol) 6,000	CO_2	120	0.39	0.1	$\dot{\gamma} = 10^5\,s^{-1}$	0.479	30.3	Sat	[103]	High frequency oscillatory shear
Poly(ethylene glycol) 20,000	CO_2	80	3.48	0.1	$\dot{\gamma} = 10^5\,s^{-1}$	0.358	31.9	Sat	[103]	High frequency oscillatory shear
Poly(ethylene glycol) 20,000	CO_2	100	3.10	0.1	$\dot{\gamma} = 10^5\,s^{-1}$	0.454	32.1	Sat	[103]	High frequency oscillatory shear
Poly(ethylene glycol) 20,000	CO_2	120	3.19	0.1	$\dot{\gamma} = 10^5\,s^{-1}$	0.476	33.6	Sat	[103]	High frequency oscillatory shear
Poly(propylene glycol) 2,700	CO_2	25	0.56	0.1	NR	0.111	4.0	20.7 Sat	[140]	Vane torque rheometer
Poly(propylene glycol) 2,700	CO_2	35	0.34	0.1	NR	0.186	4.0	17.3 Sat	[140]	Vane torque rheometer
Poly(ethylene glycol) nonylphenyl ether	CO_2	50	NR	NR	Bubble size	0.79 Pa s	10	Sat	[127]	Bubble rise
						0.56 Pa s	20	Sat		
Poly(dimethyl siloxane)	CO_2	30	65	0.1	Zero shear rate	0.036	20.7	29.32	[141]	Levitated sphere
Poly(dimethyl siloxane)	CO_2	50,80	248	NR	$\dot{\gamma} = 100\,s^{-1}$	0.366	9.1	20.7Sat	[142]	Capillary
		80	214			0.617	8.7	8.8 Sat		
Poly(vinylidene fluoride)	CO_2	210	10^4	NR	$\dot{\gamma} = 10\,s^{-1}$	0.5	NR	3.0	[134]	Extrusion slit die
Polyamide 11	CO_2	225	40	NR	$\dot{\gamma} = 100\,s^{-1}$	0.75	NR	3.0	[143]	Slit die rheometer

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CHAPTER 19

Thermodynamics of Polymer Blends

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19.1 INTRODUCTION

Polymer blends have found widespread uses in phase-separated as well as homogeneous states [1–4]. In some cases such as high impact polystyrene, a dispersed polymeric phase is introduced to improve the mechanical properties of the matrix. In other cases blends are created inadvertently due to side-reactions during polymerization. Low-density polyethylene, which is a mixture of several different kinds of linear and branched chains, is an example of such a blend. The physical properties of polymer blends depend crucially on morphology. The mechanical and optical properties of phase separated blends, for instance, are fundamentally different from those of homogeneous mixtures. The range of accessible morphologies is, to a large extent, determined by thermodynamic interactions.

There is considerable interest in organizing polymer domains on the nanometer length scale. Block copolymers comprising covalently bonded immiscible chains offer one avenue for creating such structures. These molecules are amphiphilic and thus organize into microphases that are similar to those found in systems containing surfactants. The main purpose of this paper is to provide a listing of the properties that enable the determination of the phase behavior of homopolymer blends as well as more complex periodic phases formed in the presence of block copolymers.

Current understanding of thermodynamic interactions and their effect on the phase behavior of polymer mixtures rests on three theoretical developments: (1) The derivation of an expression for the free energy of mixing in polymer systems by Huggins and Flory [5–7]. (2) The development of the random phase approximation (RPA) for characterizing concentration fluctuations in homogeneous polymer mixtures by de Gennes, Leibler, and others [8–12]. (3) The development of self-consistent field theory (SCFT) for characterizing microphase separated systems by Helfand and Edwards [13–15]. In the Flory–Huggins theory (FHT), the thermodynamics of mixing is dependent on a parameter, χ, which must be determined experimentally. The RPA was originally proposed by de Gennes to relate the scattering functions of single-phase homopolymer blends to the χ parameter and statistical segment lengths of the chains, l. In subsequent work the RPA has been extended to predict the scattering from homogeneous block copolymer melts [9] and complex multicomponent mixtures [11,12]. Experimentally measured scattering curves from homogeneous mixtures can thus be used to determine χ and l parameters. The properties of microphase separated mixtures can be predicted by SCFT if χ and l are known. The thermodynamic properties of systems that cannot exhibit macrophase separation such as diblock copolymer melts can be entirely described by a combination of RPA and SCFT. More complex mixtures of homopolymers and block copolymers can, however, exhibit both microphase and/or macrophase separation. In such cases, all three thermodynamic frameworks (RPA, SCFT, and FHT) are required for making predictions.

This chapter summarizes the available data (χ and l parameters) for polymer–polymer interactions in the melt state. The equations that are necessary to convert χ parameters into binary homopolymer blend phase diagrams are also provided. We also summarize methods for predicting the properties of nanostructures with interfaces that are stabilized by the presence of block copolymers.

19.2 DEFINITIONS AND THERMODYNAMIC THEORIES

The Flory–Huggins theory provides an expression for the free energy density of mixing of two homopolymers labeled A and B [5–7].

$$\frac{\Delta G_\mathrm{m}}{kT} = \frac{\phi_\mathrm{A}\ln\phi_\mathrm{A}}{v_\mathrm{A}\hat{N}_\mathrm{A}} + \frac{(1-\phi_\mathrm{A})\ln(1-\phi_\mathrm{A})}{v_\mathrm{B}\hat{N}_\mathrm{B}} + \frac{\chi\phi_\mathrm{A}(1-\phi_\mathrm{A})}{v}. \tag{19.1}$$

$\hat{N}_i$ is the number of monomers in chain i, and v_i is the volume of each monomer on chain i, ϕ_A is the volume fraction of component A in the mixture, v is an arbitrary reference volume, χ is the Flory–Huggins interaction parameter, ΔG_m is the free energy change on mixing per unit volume, k is the Boltzmann constant, and T is the absolute temperature. In this work the reference volume, v, is equal to $0.1\ \mathrm{nm}^3$.

The first two terms in the right hand side (RHS) of Eq. (19.1) represent the combinatorial contribution to ΔG_m which arises due to an increase in the number of possible chain configurations in the mixture relative to the pure components. The third term in the RHS of Eq. (19.1) represents noncombinatorial contributions to ΔG_m. If we assume that this contribution arises from random, pair-wise contact between monomers, then it is proportional to $\phi_\mathrm{A}(1-\phi_\mathrm{A})$ and the χ parameter is a measure of its strength. In this case χ would depend only on T and would be independent of $\hat{N}_i$ and ϕ_A. However, additional constraints due to monomer architecture and connectivity, specific interactions, and finite compressibility can also give rise to noncombinatorial contributions. If the χ parameter contains contributions from such effects then it may be a complicated function of $\hat{N}_i$, ϕ_A, and T. The expression for the combinatorial contribution was derived on the basis of several simplifications, and inadequacies of this expression are also lumped into χ.

It is convenient to rewrite Eq. (19.1) as

$$\frac{\Delta G_\mathrm{m} v}{kT} = \frac{\phi_\mathrm{A}\ln\phi_\mathrm{A}}{N_\mathrm{A}} + \frac{(1-\phi_\mathrm{A})\ln(1-\phi_\mathrm{A})}{N_\mathrm{B}} + \chi\phi_\mathrm{A}(1-\phi_\mathrm{A}), \tag{19.2}$$

where

$$N_i = \frac{\hat{N}_i v_i}{v}, \tag{19.3}$$

N_i, the number of monomers of volume v in a chain of type i, is a more convenient measure of chain length than $\hat{N}_i$. However, it is important to note that N_i depends weakly on temperature (because v_i depends on temperature) while $\hat{N}_i$ does not.

Classical thermodynamics can be used to predict phase diagrams in polymer blends on the basis of Eq. (19.2). We present the governing equations assuming that χ is only a function of T. The spinodal curve, i.e., the curve enclosing the region within which a homogeneous mixture is thermodynamically unstable, is given by

$$\chi(T) = \frac{1}{2}\left[\frac{1}{N_\mathrm{A}\phi_\mathrm{A}} + \frac{1}{N_\mathrm{B}\phi_\mathrm{B}}\right]. \tag{19.4}$$

The binodal curve, i.e., the locus of compositions of the two phases in thermodynamic equilibrium with each other, can be obtained by solving two simultaneous equations:

$$\ln\left[\frac{\phi_\mathrm{A}^\mathrm{I}}{\phi_\mathrm{A}^\mathrm{II}}\right] + (\phi_\mathrm{A}^\mathrm{II} - \phi_\mathrm{A}^\mathrm{I})(1 - N_\mathrm{A}/N_\mathrm{B}) + \chi(T)N_\mathrm{A}\left[(1-\phi_\mathrm{A}^\mathrm{I})^2 - (1-\phi_\mathrm{A}^\mathrm{II})^2\right] = 0, \tag{19.5a}$$

$$\ln\left[\frac{1-\phi_\mathrm{A}^\mathrm{I}}{1-\phi_\mathrm{A}^\mathrm{II}}\right] + (\phi_\mathrm{A}^\mathrm{I} - \phi_\mathrm{A}^\mathrm{II})(1 - N_\mathrm{B}/N_\mathrm{A}) + \chi(T)N_\mathrm{B}\left[(\phi_\mathrm{A}^\mathrm{I})^2 - (\phi_\mathrm{A}^\mathrm{II})^2\right] = 0, \tag{19.5b}$$

where $\phi_\mathrm{A}^\mathrm{I}$ and $\phi_\mathrm{A}^\mathrm{II}$ are the volume fractions of polymer A in the coexisting phases.

The binodal and spinodal curves meet at the critical point. The volume fraction of component A at the critical point is given by

$$\phi_\mathrm{A,c} = \frac{1}{1 + (N_\mathrm{A}/N_\mathrm{B})^{1/2}} \tag{19.6}$$

and the value of χ at the critical point is given by

$$\chi_\mathrm{A,c} = \frac{1}{2}\left[\frac{1}{N_\mathrm{A}^{1/2}} + \frac{1}{N_\mathrm{B}^{1/2}}\right]^2 = \frac{1}{2N_\mathrm{ave}}, \tag{19.7}$$

where

$$N_\mathrm{ave} = \left[\frac{1}{N_\mathrm{A}^{1/2}} + \frac{1}{N_\mathrm{B}^{1/2}}\right]^{-2}. \tag{19.8}$$

While the spinodal curve and the critical points can easily be calculated for polymer mixtures with arbitrary N_i, ϕ, and v_i the calculation of the binodal curve requires numerical methods [16]. However, for blends consisting of polymers with equal molecular volumes ($N = N_A = N_B$), the equations simplify considerably. The spinodal curve is given by

$$\chi(T) = \frac{1}{2N\phi_A(1 - \phi_A)}, \tag{19.9}$$

the binodal curve is given by an analytical expression,

$$\chi(T) = \frac{1}{N(1 - 2\phi_A)} \ln\left[\frac{1 - \phi_A}{\phi_A}\right] \tag{19.10}$$

and critical point is located at

$$\phi_{A,c} = 1/2 \quad \text{and} \quad \chi_c = 2/N. \tag{19.11}$$

The phase diagram of a polymer blend in $T - \phi$ space can thus be determined from Eqs. (19.1–19.11) if the temperature dependence of χ is known.

The χ parameters obtained from polymer blends are often linear functions of $1/T$.

$$\chi(T) = A + B/T. \tag{19.12}$$

However, in some cases a distinct nonlinearity is observed when χ is plotted versus $1/T$. In such cases the data can be fit to a quadratic function in $1/T$.

$$\chi(T) = A + B/T + C/T^2. \tag{19.13}$$

Predicting the phase behavior of a block copolymer composed of N_A monomers of type A and N_B monomers of type B requires knowledge of the size of the chains in addition to χ and N_i. The unperturbed radius of gyration of a polymer chain, $R_{g,i}$ is given by

$$R^2_{g,i} = \frac{1}{6}\hat{N}_i\hat{l}_i^2 = \frac{1}{6}\left[\frac{\hat{N}_i v_i}{v}\right] l_i^2 = \frac{1}{6}N_i l_i^2, \tag{19.14}$$

where $\hat{l}_i$ and l_i are statistical segment lengths of chains of type i based on monomer volumes v_i and v, respectively. Note that the value of l_i depends explicitly on our definition of v. To a good approximation $R_{g,i}$ is independent of temperature [17], which implies that $\hat{l}_i$ is independent of temperature. The temperature dependence of l_i arises due to the temperature dependence of v_i.

When polymers self-assemble to give periodic ordered phases, only a fraction of chain configurations that are available in homogeneous phases are permissible. SCFT provides a convenient framework for computing the reduction in entropy due to this effect. In this theory, individual chains are assumed to be affected by the presence of a spatially varying external field $w_m(z)$. For convenience, we restrict our attention to one-dimensional phases. The partition function of a chain of s monomers of type i constrained so that the sth monomer is held fixed at z, q_i, is given by

$$\frac{\partial q_i(z,s)}{\partial s} = \frac{l_i^2}{6}\frac{\mathrm{d}^2 q_i(z,s)}{\mathrm{d}z^2} - w_m(z)q_i(z,s). \tag{19.15}$$

The field $w_m(z)$ depends on the composition profiles, $\phi_i(z)$, and χ_{ij} between the different chains in the system. We use subscripts i and j for χ to acknowledge the fact that in many systems we will have more than two types of monomers. Since the composition of component i at z is proportional to the number of chain configurations reaching that point, there is a relationship between $\phi_i(z)$ and $q_i(z,s)$,

$$\phi_i(z) = C_i \int_{s=0}^{N_i} \mathrm{d}s\, q_i(z,s) q_i^*(z,s), \tag{19.16}$$

where C_i is a normalizing constant, and $q^*(z,s)$ obeys Eq. (19.15) with a minus sign in front of the right hand side. $q(z,s)$ and $q^*(z,s)$ are partition functions of subchains from 0 to s and from s to N, respectively.

To compute the composition profiles at equilibrium, one assumes a set of composition profiles, computes q_i using Eq. (19.15) and then computes new composition profiles using Eq. (19.16). This iterative procedure is repeated until the computed composition profiles converge. A more detailed description of SCFT is given in [15]. Details regarding SCFT computations used by our group are given in [17,18].

The simplest application of RPA and SCFT is for a symmetric diblock copolymer with $N = N_A = N_B$. The theoretically predicted order-to-disorder occurs when [9,15,19]

$$\chi(T)N = 5.268 - 0.134(l_B/l_A) + 0.114(l_B/l_A)^2, \tag{19.17}$$

where we have assumed that $1 \leq l_B/l_A \leq 2$, which covers the range of l values in this chapter. If the two statistical segment lengths are assumed to be equal, $l = l_A = l_B$, then Eq. (19.17) reduces to the more familiar result that $\chi N = 5.248$ at the order-disorder transition, and the repeat distance of the lamellar phase that forms when $\chi > 5.248/N$, $d = 1.865N^{1/2}l$. In the disordered state when $\chi < 5.248/N$, concentration fluctuations with length scale $= d$ form spontaneously and grow in amplitude as the order–disorder transition temperature is approached. This results in a scattering peak that can be detected by either SAXS or SANS, at scattering vector $q = 2\pi/d$. The scattering profiles obtained from weakly ordered block copolymers and disordered block copolymers are thus not very different.

It is important to recognize that Eqs. (19.1–19.17) can only be used if χ_{ij}, l_i, and ν_i, are known. For convenience, all three quantities are tabulated in this chapter.

19.3 EXPERIMENTAL METHODS FOR DETERMINING χ AND l

Most of the data presented in this chapter were obtained by applying RPA to small angle neutron scattering profiles from homogeneous homopolymer blends. This approach was pioneered by Herkt-Maetzky and Schelten, Murray *et al.*, and Hadziioannou and Stein [20–22]. The composition and molecular weight dependence of χ thus obtained has been studied in some systems. While χ is generally found to be independent of N_i, linear and quadratic dependences on ϕ_A have been reported in some cases [23,24]. Since relatively little is known about the ϕ_A dependence of χ at this stage, we do not consider such refinements. In this chapter we use values of χ obtained from $\phi_A \approx 1/2$ mixtures and ignore its dependence on ϕ_A and N_i. Statistical segment lengths of polymer chains are usually determined from SANS experiments on binary hydrogenous and deuterated versions of the same homopolymer. l_i has been found to vary by as much as 20% from sample to sample [25].

Experiments of Roe *et al.* [26] and Hashimoto *et al.* [27] demonstrated that scattering experiments on disordered block copolymers may also be used to determine χ and l parameters, using the RPA theory of Leibler [9]. In a subsequent paper, Fredrickson and Helfand showed that fluctuation corrections to the RPA are important in block copolymer melts [28]. When available, χ parameters obtained from block copolymer melts are reported after fluctuation corrections have been incorporated. l_i values obtained from block copolymers are often [29,30] but not always [31] larger than those obtained in homopolymer blends.

Aside from RPA based techniques, χ can also be estimated from experimentally determined binodal and spinodal curves, using Eqs. (19.4) and (19.5). Methods to obtain binodal and spinodal curves are summarized in [2].

19.4 OBSERVED TEMPERATURE DEPENDENCES OF χ AND BINARY PHASE DIAGRAMS

A variety of phase behaviors have been observed in binary homopolymer blends. Some blends phase separate on heating while others phase separate on cooling. This depends on whether χ increases or decreases with temperature. Blends in which χ changes nonmonotonically with temperature exhibit more complex phase diagrams. The temperature dependence of χ for 83 polymer blends is summarized in Table 19.1. The nomenclature is defined in a section just above Table 19.1 and chemical structures of the polymers are given in Table 19.2. Blends are classified into six types, based on the temperature dependence of χ. The properties of each blend type are illustrated with the help of an example extracted from Table 19.1. Binodal and spinodal curves (T versus ϕ_A) for a particular blend were calculated using Eqs. (19.9) and (19.10), respectively. The example calculations are restricted to blends with $N_1 = N_2$.

19.4.1 Type I. χ is Positive and Increases Linearly with $1/T$ ($B > 0$, $C = 0$)

The χ parameters of a large number of polymer blends exhibit this kind of temperature dependence. An example of this is the SPB(88)/*d*SPB(78) blend [system 27a], and the temperature dependence of χ is shown in Fig. 19.1(a). Increasing temperature in such blends leads to increased miscibility. This behavior is often referred to as upper critical solution temperature (UCST) behavior. A typical phase diagram obtained from such systems is shown in Fig. 19.1(b). The spinodal and binodal curves were calculated for a SPB(88)/*d*SPB(78) blend with $N = 2,000$. A 50/50 mixture of these polymers is predicted to be two phase at room temperature but single phase at temperatures above 105 °C. The qualitative features of the phase diagrams obtained from all type I blends will be similar to Fig. 19.1(b). Of course the locations of the phase boundaries will depend on A, B, and N.

19.4.2 Type II. χ is Negative and Decreases Linearly with $1/T$ ($B < 0$, $C = 0$)

These systems exhibit linear χ versus $1/T$ plots but with negative slopes. The role of temperature is thus reversed in

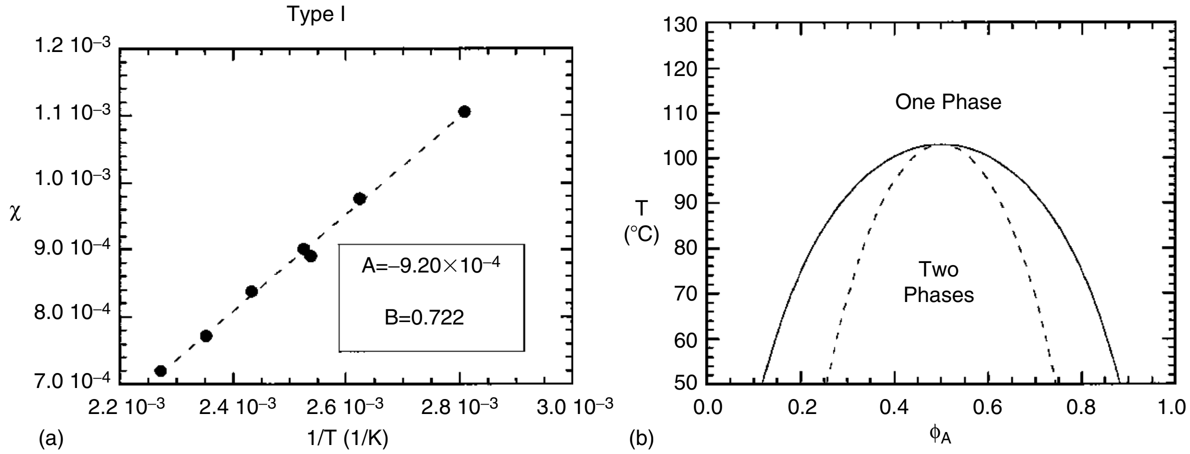

FIGURE 19.1. Example of a Type I blend [system 27a]. (a) A plot of χ versus $1/T$ for a SPB(88)/*d*SPB(78) blend. Symbols represent experimental data and the dashed line represents a least squares fit, using criteria described in Section 19.10. (b) Predicted binodal (solid curve) and spinodal (dashed curve) of a SPB(88)/*d*SPB(78) blend with $N = 2,000$.

such blends, relative to its role in type I blends. Increasing temperature leads to an increase in χ and hence, lower miscibility. Such behavior is referred to as lower critical solution temperature or LCST behavior. The PIB/*d*HHPP blend [system 62] is a typical example, and the temperature dependence of χ is shown in Fig. 19.2(a). The χ parameter is negative over most of the observable temperature window. Note that B is an order of magnitude larger than that obtained in the SPB(88)/*d*SPB(78) system (a typical type I blend). Several type II blends such as PS/PVME and PS/PXE exhibit similarly large B values. As a consequence, phase transition temperatures are remarkably insensitive to composition and component molecular weights. The phase diagram for a PIB/*d*HHPP blend with $N = 6{,}000$ is shown in Fig. 19.2(b). Note that the transition from single phase to two phase occurs at 170 ± 5 °C regardless of composition. If the molecular weight of the components is decreased by a factor of two, the resulting change in the critical temperature is only 7 °C—from 166 to 173 °C. In contrast, the phase diagram of most type I blends would be altered dramatically if N were decreased by a factor of two.

19.4.3 Type III. χ is Positive and Increases Nonlinearly with $1/T$ ($C \neq 0$, $d\chi/dT \neq 0$)

These systems are qualitatively similar to type I in that χ decreases with increasing temperature, and thus they also exhibit UCST behavior. The only difference is that the χ versus $1/T$ plots are nonlinear. An example of such behavior is PEB/*d*SPI(7) [system 41b], and the temperature dependence of χ is shown in Fig. 19.3(a). The calculated phase diagram for this blend with $N = 2{,}900$ is shown in Fig. 19.3(b). This phase diagram is qualitatively different

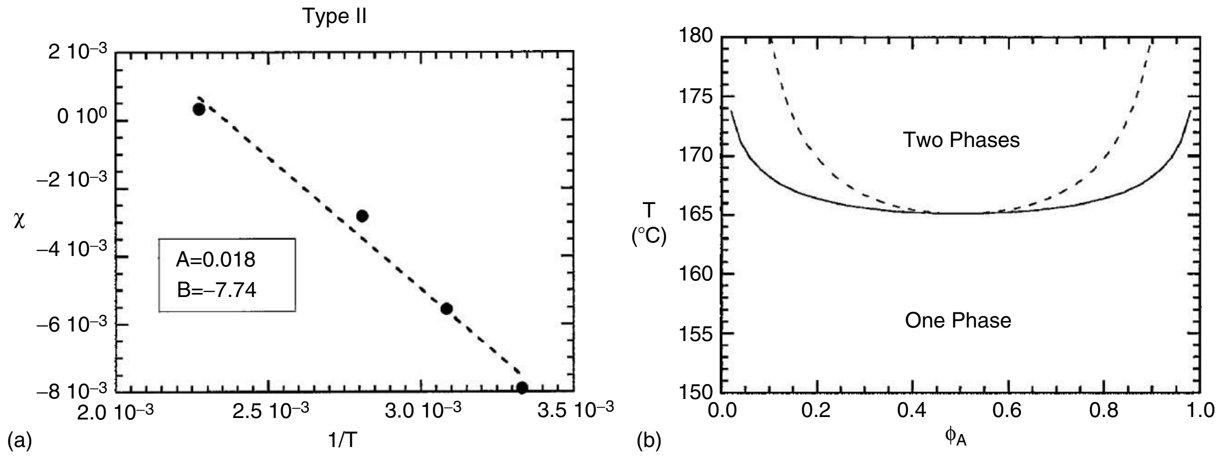

FIGURE 19.2. Example of a Type II blend [system 62]. (a) A plot of χ versus $1/T$ for a PIB/*d*HHPP blend. Symbols represent experimental data and the dashed line represents a least squares fit, using criteria described in Section 19.10. (b) Predicted binodal (solid curve) and spinodal (dashed curve) of a PIB/*d*HHPP blend with $N = 6{,}000$.

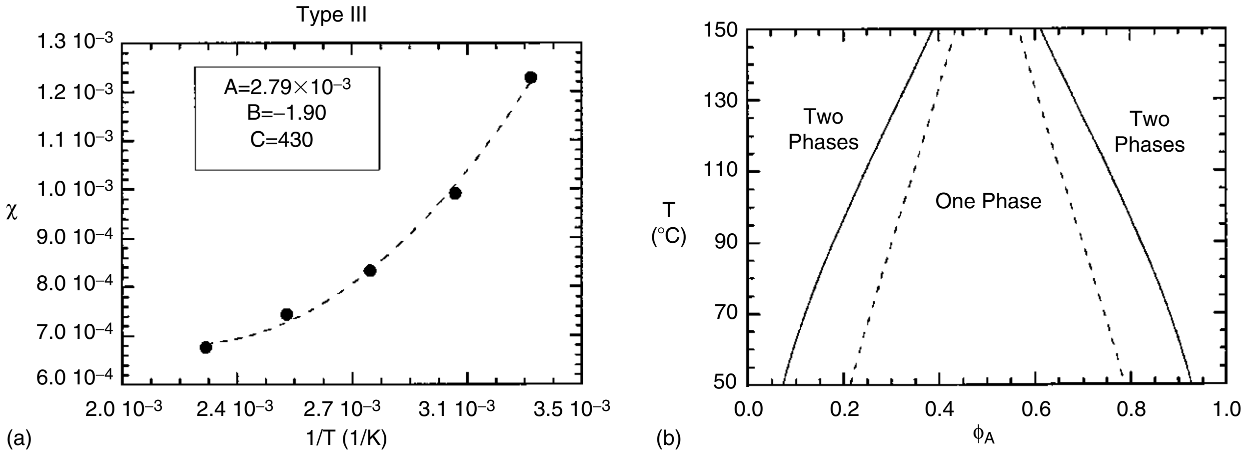

FIGURE 19.3. Example of a Type III blend [system 41b]. (a) A plot of χ versus $1/T$ for a PEB/*d*SPI(7) blend. Symbols represent experimental data and the dashed curve represents a least squares fit, using criteria described in Section 19.10. (b) Predicted binodal (solid curve) and spinodal (dashed curve) of a PEB/*d*SPI(7) blend with $N = 2{,}700$.

from type I because of the appearance of a "neck" at elevated temperatures. This is due to the fact that the gradient of the χ versus $1/T$ plot decreases with increasing temperature, i.e., C is positive. In other words, increasing temperature results in relatively little increase in miscibility at high temperatures. For blends that have positive C values, the phase diagram would abruptly "flatten out" at elevated temperatures instead of "necking". Unlike type I blends, the qualitative features of the type III phase diagrams are affected by component molecular weights. For example, the calculated phase diagram of a PEB/*d*SPI(7) blend with $N = 2{,}700$ does not show a neck, and is qualitatively similar to Fig. 19.1(b), i.e., a type I blend. This is due to the fact that the critical temperature of this blend is 100 °C, and over the limited temperature range between 27 and 100 °C, the nonlinearity of χ versus $1/T$ is relatively unimportant.

19.4.4 Type IV. χ is Positive and Nonmonotonic with Temperature, and $C > 0$

The χ parameter in these systems is also parabolic in $1/T$ and thus these systems are in many respects like type III blends. The difference is that the bottom of the parabola occurs at an experimentally accessible temperature. An example of such a system is HHPP/*d*SPI(7) [system 51] and the dependence of χ on $1/T$ is presented in Fig. 19.4(a). For a given ϕ_A, such behavior can lead to multiple solutions to Eqs. (19.9) and (19.10) that lie within the accessible temperature window. These systems can thus exhibit both LCST and UCST behavior. A HHPP/*d*SPI(7) blend with $N = 5{,}700$ is predicted to exhibit such behavior, and the calculated phase diagram is shown in Fig. 19.4(b). Single phase behavior is observed at intermediate temperatures and phase separation is observed toward the outer edges of the available temperature window. LCST behavior is predicted at high temperatures and UCST behavior is predicted at low temperatures.

19.4.5 Type V. χ is Positive and Nonmonotonic with Temperature, and $C < 0$

The χ versus $1/T$ plots from these systems also show an extremum as was the case with type IV blends; however the sign of the curvature (C) is negative. The SPI(7)/*d*PP [system 47b] blend exhibits such behavior as can be seen in Fig. 19.5(a). Like type IV blends, these systems can thus exhibit both LCST and UCST behavior. The difference is that UCST behavior is predicted at high temperatures and LCST behavior is predicted at low temperatures. The binodal and spinodal curves for such systems thus form closed loops and the two-phase region is restricted to the middle of the phase diagram. The calculated phase diagram for a SPI(7)/*d*PP blend with $N = 580$ has these characteristics and is shown in Fig. 19.5(b).

19.4.6 Type VI. Athermal Mixing, χ is Independent of T ($B = 0$ and $C = 0$)

In a few cases χ is, within experimental error, independent of temperature. Examples of such systems are SPI(7)/SPB(66) blend [system 39] and SPI(50)/SPB(78) blends [system 54]. The temperature dependence of χ for the SPB(66)/*d*SPI(7) blend is shown in Fig. 19.6(a). If A is finite, $B \equiv 0$, and $C \equiv 0$ then the phase diagram is composed of vertical lines. Blends that are single phase at room temperature will remain single phase at all temperatures, while blends that are phase separated at room temperature will remain phase separated at all temperatures. Figure 19.6(b) shows the predicted phase diagram for a SPB(66)/*d*SPI(7) blend with $N = 3{,}000$. The phase boundaries are not exactly vertical because the experimentally determined B is not identically zero.

It is obvious that measured values of B and C can never be identically equal to zero. Thus precise measurements on

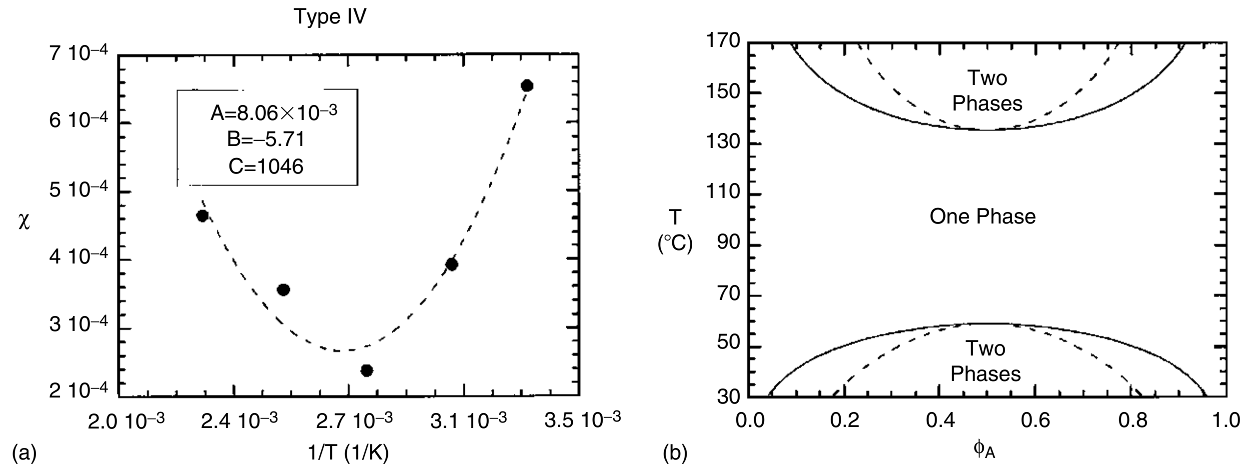

FIGURE 19.4. Example of a Type IV blend [system 51]. (a) A plot of χ versus $1/T$ for a HHPP/*d*SPI(7) blend. Symbols represent experimental data and the dashed curve represents a least squares fit, using criteria described in Section 19.10. (b) Predicted binodal (solid curves) and spinodal (dashed curves) of a HHPP/*d*SPI(7) blend with $N = 5{,}700$.

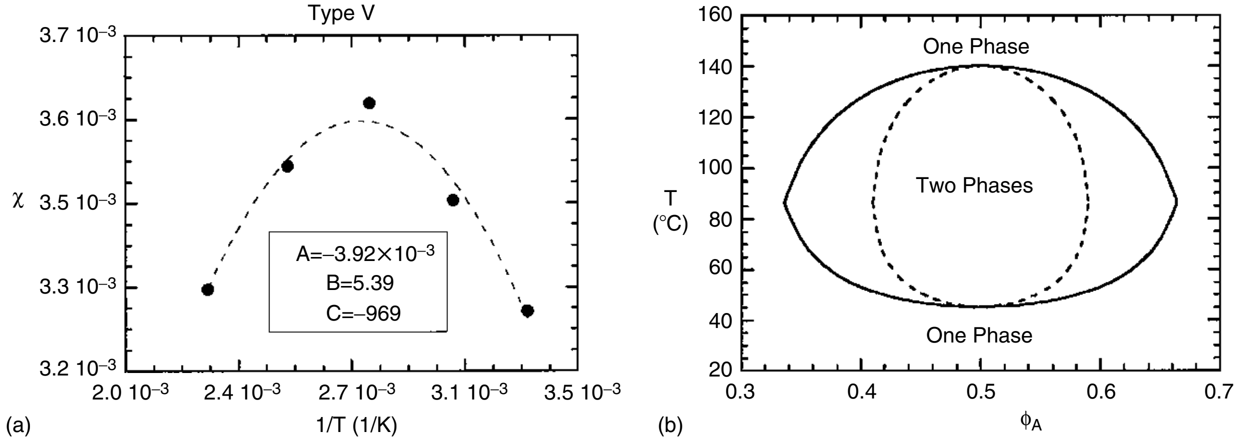

FIGURE 19.5. Example of a Type V blend [system 47b]. (a) A plot of χ versus 1/*T* for a SPI(7)/*d*PP blend. Symbols represent experimental data and the dashed curve represents a least squares fit, using criteria described in Section 19.10. (b) Predicted binodal (solid curves) and spinodal (dashed curves) of a SPI(7)/*d*PP blend with $N = 580$.

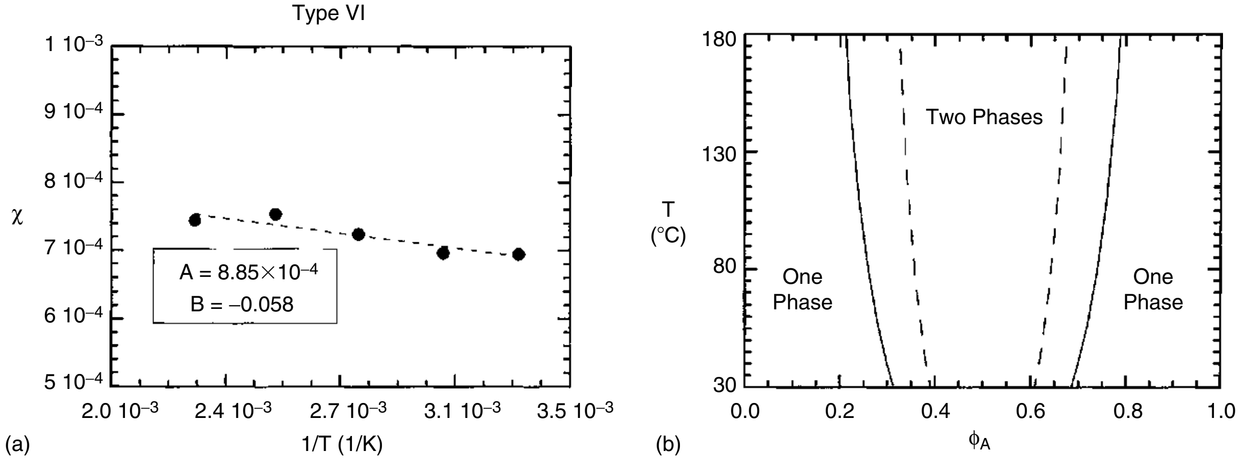

FIGURE 19.6. Example of a Type VI blend [system 39b]. (a) A plot of χ versus 1/*T* for a SPB(66)/*d*SPI(7) blend. Symbols represent experimental data and the dashed curve represents a least squares fit, using criteria described in Section 19.10. (b) Predicted binodal (solid curves) and spinodal (dashed curves) of a SPB(66)/*d*SPI(7) blend with $N = 3{,}000$.

Type VI systems will eventually lead to a reclassification. In fact, systems in this category have the potential to display extremely rich thermodynamics because χ could, in principle oscillate about a constant value. System 10 is an example of such behavior. In [32] it is shown that χ is an oscillatory function of T. In this case, the temperature dependence of χ cannot be described by Eq. (19.13). The parameters given for system 10 are thus valid over a restricted temperature window.

The smallest value of $|\chi|$ reported thus far in the polymer blend literature is obtained from the SPI(50)/SPB(78) system [system 54]. The χ parameter is nearly zero over the entire temperature window. Such a blend is unique because it is predicted to be single phase regardless of composition and temperature. The phase diagram of this system is predicted to be blank, regardless of component molecular weights.

19.5 SIMPLIFICATIONS

The phase diagrams presented above were calculated assuming that χ is independent of composition. Also, small changes in N with temperature were ignored. It may be of interest to note that all the examples chosen to illustrate the various types of blends were mixtures of polyolefins. The calculated binodal and spinodal curves represent extrapolations of χ parameters determined in the single-phase region. The composition dependence of χ in polyolefin blends is relatively weak in the mid-range of compositions $1/4 < \phi_A < 3/4$ [24,25]. Thus calculated phase boundaries in the examples are expected to be in agreement with experimental measurements. Direct measurements of the binodal and spinodal curves in some polyolefin blends were found to be consistent with χ parameters derived from SANS [33,34]. For other systems such as the PS/PVME system, χ exhibits a more pronounced composition dependence [23]. If $\chi(\phi_A)$ is known then the phase diagrams can be predicted using classical thermodynamics as demonstrated in [23]. In such cases, the experimentally determined phase diagram may differ significantly from predictions based on the χ parameters reported in this work.

The classification of blends into different types is based on current knowledge and may not be permanent. It is possible that future experiments on these mixtures may unravel new features in the temperature dependence of χ, due to widening of the temperature window, more detailed measurements, or better instrumentation. For instance, type II behavior cannot persist at arbitrarily high temperature because all blends must be single phase in the limit $T \to \infty$. Hence, the two-phase region must close to form a loop at higher temperatures. Type II blends may thus be considered to be type V blends which have only been explored over a limited temperature range. On the other hand, practical limitations such as chain degradation may prevent all type II blends from showing type V behavior.

19.6 PREDICTIONS OF THE χ PARAMETER

The solubility parameter formalism, introduced by Hildebrand and Scott [35], may be used to predict χ parameters. In this approach, χ parameters are estimated from differences in solubility parameters of the pure components, δ_i, which in turn are related to their cohesive energy densities.

$$\chi = \frac{v_{\mathrm{ref}}}{kT}(\delta_2 - \delta_1)^2 \qquad (19.17)$$

Graessley, Lohse, and coworkers have found that the data from several polyolefin blends were consistent with the solubility parameter approach [36]. They were thus able to estimate δ from χ parameters measured by SANS. Group contribution methods have been developed by Small [37], Hoy [38], and van Krevelen [39] for predicting cohesive energy densities. None of these methods are based on data obtained from polymer mixtures [40] and usually lead to large errors when applied to polymer blends.

19.7 EFFECT OF DEUTERIUM SUBSTITUTION ON χ

Most of the data given in Table 19.1 were obtained from mixtures in which one of the polymers was labeled with deuterium. Of course, the objective of these experiments is to obtain χ between undeuterated polymers because deuterated polymers are seldom used in practical applications. The effect of deuterium labeling on thermodynamics of chemically dissimilar polymers was studied by Rhee and Crist [41], and Graessley, Lohse, and coworkers [42]. It was found that χ in polyolefin blends could either increase or decrease depending upon which species was labeled. They also found that χ between unlabeled polymers was equal to the average of the χs obtained from the two labeled blends. Values of A, B, and C for unlabeled polyolefin mixtures in Table 19.1 were calculated on this basis. However, this rule is not universal and has only been verified in a few polyolefin blends [41,42]. Other systems such as PMMA/PS [system 1] do not obey this rule.

In the early years (prior to 1980), the effect of deuterium substitution on polymer blend thermodynamics was assumed to be negligible. In a pioneering publication, Buckingham and Hentschel [43] estimated χ between protonated and deuterated polymers that are otherwise identical (isotopic blends) to be about 10^{-3}. They thus came to the surprising conclusion that isotopic blends should be phase separated at modest molecular weights ($N \sim 10^3$). Elegant experimental proof for this effect was provided by Bates and coworkers [44].

19.8 COMPLEX PHASE BEHAVIOR IN MULTICOMPONENT MIXTURES

The Flory–Huggins theory, RPA, and SCFT, along with the information in Tables 19.1 and 19.2 enable prediction of the structure and phase behavior of complex polymer mixtures in the mean-field limit. We discuss two illustrative examples of such predictions. More details regarding these examples can be found in the original references [18,45,46].

19.8.1 Interfacial Adsorption in a Multicomponent Type I System

A–B diblock copolymers adsorb spontaneously at the interface between two immiscible A and B homopolymers. Our objective here is to make quantitative predictions of the nature of the adsorbed layer. In this case, the phase behavior depends on only one χ parameter, that between the A and B homopolymers, and the statistical segment lengths of the A and B chains. The specific example that we will study is the adsorption of a SPB(89)–SPB(63) diblock copolymer at the interface between SPB(89) and SPB(63) homopolymers at room temperature [A = SPB(89) and B = SPB(63)]. For this system, $\chi = 0.0064$ (system 33 in Table 19.1), $l_{\mathrm{A}} = 0.49\,\mathrm{nm}$, and $l_{\mathrm{B}} = 0.75\,\mathrm{nm}$. We consider the interface between SPB(89) and SPB(63) homopolymers with $N_{\mathrm{A}} = 4,230$ and $N_{\mathrm{B}} = 3,600$. It is straightforward to show that the two homopolymers are highly immiscible because $\chi N_{\mathrm{ave}} = 6.2$ which is much greater than 2 (see Eq. (19.8) for definition of N_{ave}). We consider the adsorption of a SPB(89)-SPB(63) diblock copolymer with $N_{\mathrm{Ab}} = 790$ and $N_{\mathrm{Bb}} = 730$ where the subscript "b" refers to the chains comprising the block copolymer. We consider two flat homopolymer-rich phases with the diblock copolymer adsorbed at the interface. The z-axis of our coordinate frame is perpendicular to the interface. The results of SCFT predictions for $\phi_{\mathrm{AB}}(z)$, the volume fraction of the A–B diblock copolymer across an interface between the homopolymers located at $z = 190\,\text{nm}$, is shown by the curve in Fig. 19.7(a). The average volume fraction of the diblock copolymer in the system was 0.07. The peak value of ϕ_{AB} is 0.43 which is substantially larger than 0.07. This indicates a strong tendency for the block copolymer to accumulate at the interface. The symbols in Fig. 19.7(a) are experimentally measured values of $\phi_{AB}(z)$ for the same system. While some discrepancies are evident, especially in predicting ϕ_{AB} far away from the interface, it is clear that our SCFT predictions of the nature of the adsorbed block copolymer layer are in excellent agreement with the measurements. The two quantities of importance in an adsorption experiment are Γ, the interfacial excess of diblock copolymer, and σ, the thickness of the adsorbed layer. The data in Fig. 19.7(a) are replotted on a linear scale in Fig. 19.7(b). The shaded region in Fig. 19.7(b) is Γ while the width of the peak is σ. In Fig. 19.7(c) we plot Γ as a function of $\phi_{AB,A}$, the concentration of the block copolymer in the A-rich phase. The

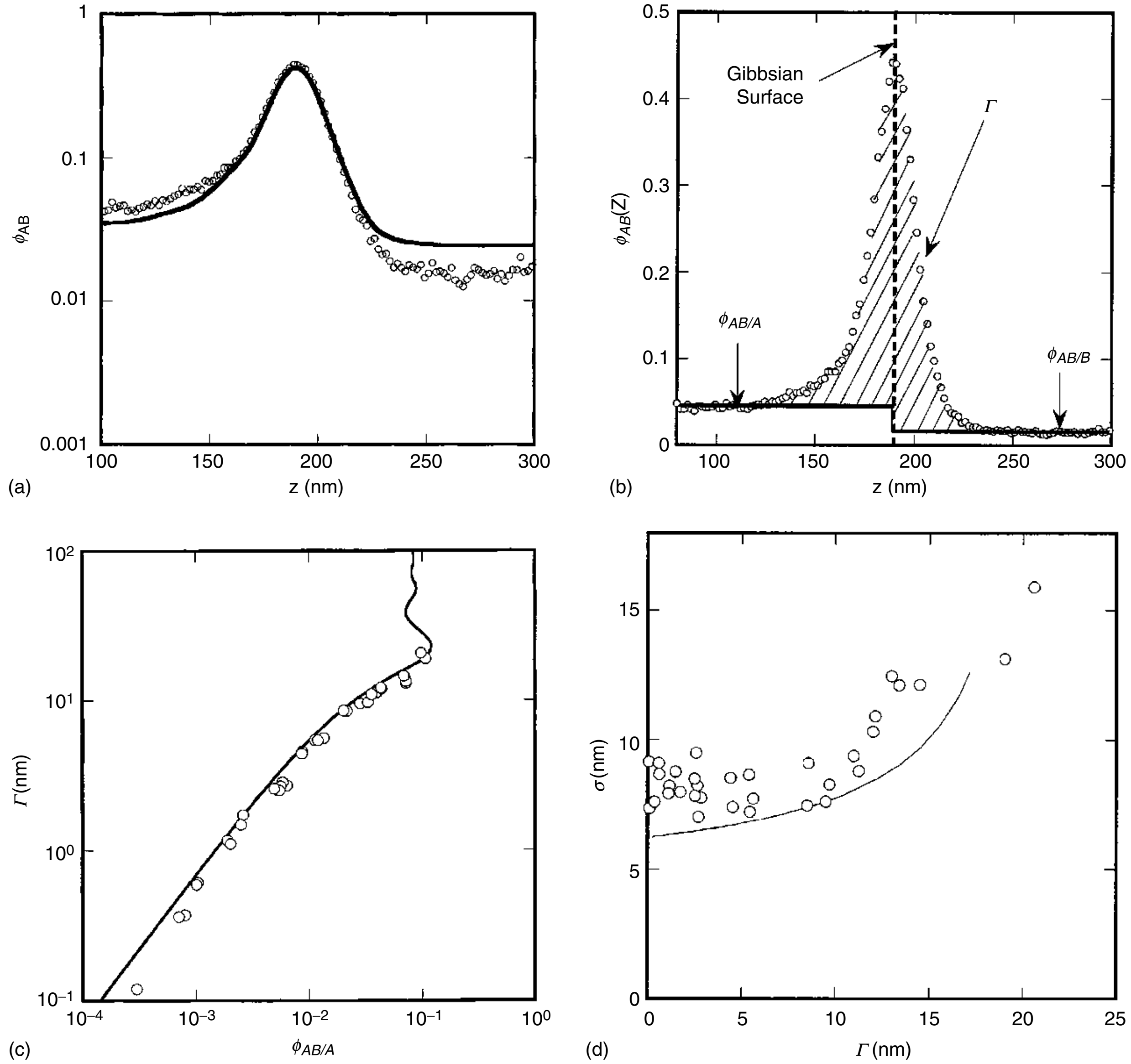

FIGURE 19.7. Interfacial activity in a Type I blend of an A–B diblock copolymer added to a blend of A and B homopolymers [A = SPB(89) and B = SPB(63)]. $N_A = 4{,}230$ and $N_B = 3{,}600$ for the homopolymers, while $N_{Ab} = 790$ and $N_{Bb} = 730$ for the block copolymer. Symbols show experimental measurements using secondary-ion mass spectrometry (SIMS), and curves show SCFT predictions using χ and l values from Tables 19.1 and 19.2. (a) Volume fraction profile in loglinear format of the diblock copolymer for a sample with 0.07 volume% block copolymer with an A/B interface at $z = 190$ nm. (b) Volume fraction profile in linear-linear format of the diblock copolymer for a sample with 0.07 volume% block copolymer with an A/B interface at $z = 190$ nm. The cross-hatched area represents the adsorbed amount, Γ. (c) Adsorption isotherm: the dependence of the adsorbed amount, Γ, on the copolymer volume fraction in the A-rich phase $\phi_{AB/A}$. (d) The thickness of the adsorbed layer (standard deviation of the volume fraction profile near the peak), σ, plotted versus the amount adsorbed, Γ.

symbols in Fig. 19.7(c) represent experimental measurements while the curve is the SCFT prediction. We find that the dependence of Γ on copolymer loading is also accurately captured by SCFT. In Fig. 19.7(d) we compare measurements of σ versus Γ with SCFT predictions. The increase in σ at high values of Γ indicates stretching of the copolymer brush due to molecular crowding at the interface. Both the value of Γ, where stretching is first observed, and the magnitude of chain stretching can be predicted entirely on the basis of unperturbed chain dimensions and the binary χ parameter.

19.8.2 Multicomponent Mixtures with Different Interaction Types

We now consider the behavior of multicomponent mixtures where we add an A–C copolymer to a blend of A and B homopolymers. Our objective was to study the effect of attractive interactions between B and C monomers (i.e., $\chi < 0$) on interfacial properties and microphase separation. The complexity in these mixtures is the fact that their phase behavior is governed by three χ parameters χ_{AB}, χ_{AC}, and χ_{BC} and three statistical segment lengths, l_{A}, l_{B}, and l_{C}. We consider the case where A = SPB(89), B = PIB, and C = SPB(63). The temperature dependence of χ_{AB} (system 61), χ_{AC} (system 33), and χ_{BC} (system 59) are shown in Fig. 19.8(a). Note that the three systems have very different temperature dependencies. χ_{AB} is a Type VI system, χ_{AC} is a Type I system, and χ_{BC} is a Type II system. Multicomponent A/B/A–C mixtures can thus exhibit unusual phase behavior. This is illustrated in a mixture with $N_{\mathrm{A}} = 464$, $N_{\mathrm{B}} = 437$, $N_{\mathrm{Ab}} = 1{,}510$, and $N_{\mathrm{Cb}} = 1{,}263$. In Fig. 19.8(b) we show the results of scattering studies on an A/B/A–C mixture with 25% A, 25% B, and 50% A–C by volume. This sample is microphase separated between room temperature and 140 °C, homogeneous at temperatures between 140 and 190 °C and phase separated at temperatures above 190 °C. It is not surprising that some systems macrophase separate upon heating. In fact, this is a characteristic of Type II systems. It is, however, unusual for a microphase separated system to become homogeneous at intermediate temperatures before exhibiting macrophase separation. In Fig. 19.8(b), we compare the characteristics of our A/B/A–C mixture measured by SANS (symbols) with theoretical predictions (curves). Between room temperature and 140 °C, the domain spacing of the microphase separated state d decreases with increasing temperature. The experimental data in this regime is in quantitative agreement with SCFT predictions (dashed curve). The SCFT analysis shows that the observed change in d is entirely due to the temperature dependence of the three χ_{ij} parameters and not a change in the size of the chains because $\hat{l}_i$ is constant. As the temperature approaches 140 °C, SCFT calculations, where we assume the presence of one-dimensional periodic concentration profiles, fail to converge. This implies that some other kind of phase is stable at temperatures ≥140 °C. RPA and FHT calculations indicate that the homogeneous phase is stable at temperatures between 140 and 190 °C. In this regime, the scattering profiles contain peaks due to the presence of concentration fluctuations with a well-defined length scale, and their length scale increases with increasing temperature. This trend is also captured

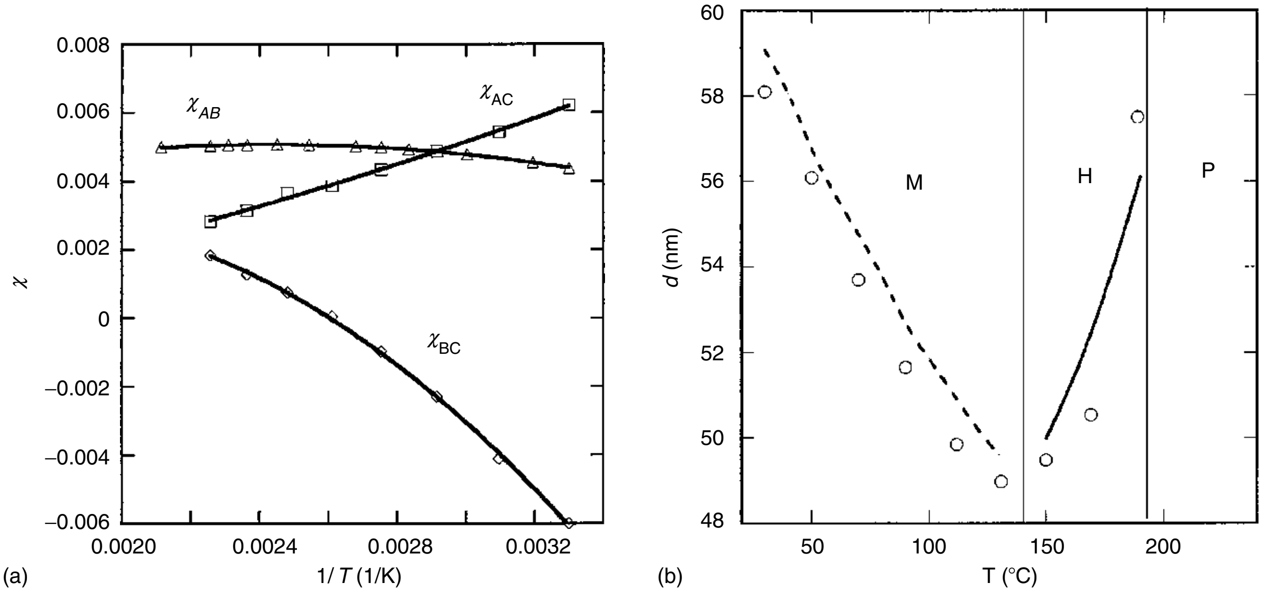

FIGURE 19.8. Phase behavior of a mixture of two homopolymers A and B in the presence of an A–C block copolymer [A = SPB(89), B = PIB, and C = SPB(63)]. (a) The temperature dependence of χ_{AB} (system 61, Type VI), χ_{AC} (system 33, Type I), and χ_{BC} (system 59, Type II). (b) The structure and phase behavior of a mixture containing 25% A, 25% B, and 50% A–C by volume. $N_{\mathrm{A}} = 464$ and $N_{\mathrm{B}} = 437$ for the homopolymers, while $N_{\mathrm{Ab}} = 1{,}510$, and $N_{\mathrm{Cb}} = 1{,}263$ for the block copolymer. Circles indicate the variation of domain spacing d with temperature measured by SANS. The dashed curve shows SCFT predictions while the solid curve shows RPA predictions. M≡microphase separation, H≡homogeneous, and P≡macrophase separation.

quantitatively by RPA (solid curve). Above 190 °C, the sample phase separates on macroscopic length scales (the SANS peak is lost and the sample turns cloudy). The theoretically predicted macrophase separation temperature, 205 °C, is in reasonable agreement with experiments.

19.9 ACKNOWLEDGMENT

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19.10 ORGANIZATION OF TABLES AND NOMENCLATURE

1. Table 19.1 gives values of A, B, and C for a given polymer pair. These parameters can be used to estimate χ parameters within the specified temperature range. In cases where χ was approximately a linear function of $1/T$, the parameters A and B represent best linear fits through the data and C was set to zero. The parameter C was only used in cases where the nonlinearity was evident. In border-line cases where the nonlinearity was not as pronounced, the results of both linear and nonlinear fits are tabulated. Only one set of A, B, and C values are reported for each system. Systems such as polystyrene/polyisoprene and polystyrene/poly(vinyl methyl ether) have been examined by several groups. In many instances, the values obtained were consistent with each other. In cases where inconsistencies were found, some personal judgment was exercised.
2. In Table 19.1 and in the text, polymers are referred to by their abbreviated names. The full names and chemical structures of the polymers are given in Table 19.2. Monomer volumes and statistical segment lengths, necessary for obtaining phase diagrams from χ, are also listed in Table 19.2.
3. The letter "*d*" in front of the polymer name indicates that it was labeled with deuterium. The number of H atoms substituted by D per monomer is indicated for each system within curly brackets—{*d*3} implies that 3 of the H atoms in the monomer (defined in Table 19.2) were replaced by D. If deuteration levels are not specified it indicates that the polymer was fully deuterated.
4. The letter "S" in front of a name indicates that the polymer was obtained by saturating the double bonds of a polymeric precursor. For example, SPS is the polymer obtained by saturating polystyrene (PS) and is often referred to in the literature as poly(vinyl cyclohexane).
5. Dienes such as butadiene (isoprene) usually polymerize by 1,4- or 1,2- (3,4-) addition. The number in parentheses at the end of a name refers to the percentage of 1,2- units in the polybutadiene chains and the percentage of 3,4- units in the polyisoprene chains.

These materials are, to a good approximation, random copolymers of 1,4- and 1,2- (or 3,4-) units.

TABLE 19.1. *The dependence of χ on temperature. $\chi = A + B/T + C/T^2$.*

	System	A^a	B (K)^a	C(K^2)^a	T Range (°C)	Type	Refs.
1a	PMMA/*d*PS	1.74×10^{-2}	2.39	—	120–180	I	[47]
1b	PS/*d*PMMA	1.80×10^{-2}	1.96	—	170–210	I	[47]
1c	PS/PMMA	1.29×10^{-2}	1.96	—	100–200	I	[48]
1d	*d*PS/*d*PMMA	1.54×10^{-2}	1.96	—	130–210	I	[47]
2a	PVME/*d*PS	9.73×10^{-2}	−41.6	—	60–150	II	[16,49]
2b	PS/PVME	1.03×10^{-1}	−43.0	—	60–150	II	[49]
3a	PS/*d*PXE	5.8×10^{-2}	−37.7	—	100–280	II	[50]
3b	PXE/*d*PS	5.9×10^{-2}	−32.5	—	180–330	II	[51]
4	PS/PI(7)	7.85×10^{-3}	17.6	—	100–180	I	[52]
5	PS/PB(95)	-1.57×10^{-2}	18.7	—	50–180	I	[53]
6	PS/SPB(95)	4.11×10^{-3}	15.2	—	50–180	I	[53]
7	TMPC/*d*PS	1.57×10^{-1}	−81.3	—	190–250	II	[54]
8	PCHA/*d*PS	6.7×10^{-2}	−35	—	120–155	II	[55]
9	PS/P2VP	-1.8×10^{-2}	35	—	155–230	I	[56]
10	PPMA/*d*PS	5.15×10^{-2}	−27.2	5,127	80–130	IV	[57]
11	PBMA/*d*PS	1.07×10^{-1}	−60.4	9,807	20–130	III	[58]
12	PB(7)/PαMS	-5.5×10^{-2}	38	—	130–190	I	[59]
13	PS/PαMS	-1.17×10^{-3}	1.9	—	170–200	VI	[59]
14	PMMA/PαMS	3.14×10^{-2}	−2.53	—	170–210	II	[60]

TABLE 19.1. *Continued.*

	System	A^a	B (K)^a	C(K^2)^a	T Range (°C)	Type	Refs.
15	P4MS/PαMS	2.3×10^{-2}	-1.30	—	140–170	VI	[61]
16	P4MS/PS	-4.6×10^{-3}	3.2	—	160–230	I	[62]
17	PI(7)/*d*PB(12)	4.20×10^{-3}	-0.906	—	20–130	II	[63]
18	PI(7)/*d*PB(97)	7.42×10^{-3}	-3.22	—	30–110	II	[64]
19	PB(68)/*d*PB(63)	-1.30×10^{-3}	0.411	—	20–180	I	[65]
20	PB(7)/*d*PB(63)	-5.64×10^{-4}	0.825	—	20–180	I	[65]
21	PB(97)/*d*PB(11)	6.79×10^{-3}	0.561	—	(-7)–90	I	[66]
22	SPS/SPI(7)	1.47×10^{-2}	7.48	—	30–180	I	[67]
23	SPS/SPI(5)	-3.1×10^{-3}	13.3	—	140–250	I	[68]
24	SPS/SPB(7)	-1.47×10^{-2}	24.9	—	160–280	I	[68]
25	SPS/SPB(90)	-7.4×10^{-3}	9.5	—	180–330	I	[68]
26a	SPB(97)/*d*SPB(88) {d3}	-6.26×10^{-4}	0.543	—	30–170	I	[24,25,36,69–73]
26b	SPB(88)/*d*SPB(97) {d3}	-8.70×10^{-4}	0.650	—	30–170	I	[24,25,36,69–73]
26c	SPB(97)/SPB(88)	-7.48×10^{-4}	0.597	—	30–170	I	[24,25,36,69–73]
27a	SPB(88)/*d*SPB(78) {d2}	-9.20×10^{-4}	0.722	—	30–170	I	[24,25,36,69–73]
27b	SPB(78)/*d*SPB(88) {d3}	-1.07×10^{-3}	0.889	—	30–170	I	[24,25,36,69–73]
27c	SPB(88)/SPB(78)	-9.95×10^{-4}	0.806	—	30–170	I	[24,25,36,69–73]
28a	SPB(78)/*d*SPB(66) {d3}	-6.67×10^{-4}	0.607	—	80–170	I	[24,25,36,69–73]
28b	SPB(66)/*d*SPB(78) {d3}	-6.51×10^{-4}	0.647	—	110–170	I	[24,25,36,69–73]
28c	SPB(78)/SPB(66)	-6.59×10^{-4}	0.627	—	110–170	I	[24,25,36,69–73]
29a	SPB(66)/*d*SPB(52) {d3}	-7.81×10^{-4}	0.653	—	110–170	I	[24,25,36,69–73]
29c	SPB(52)/*d*SPB(66) {d3}	-6.26×10^{-4}	0.751	—	140–170	I	[24,25,36,69–73]
29c	SPB(66)/SPB(52)	-7.04×10^{-4}	0.702	—	140–170	I	[24,25,36,69–73]
30a	SPB(52)/*d*SPB(38) {d3}	-9.65×10^{-4}	0.598	—	50–170	I,III	[24,25,36,69–73]
		(1.95×10^{-3})	(-1.607)	(412)	50–170		
30b	SPB(38)/*d*SPB(52) {d3}	-9.74×10^{-4}	0.707	—	110–170	I	[24,25,36,69–73]
30c	SPB(52)/SPB(38)	-9.70×10^{-4}	0.653	—	110–170	I	[24,25,36,69–73]
31a	SPB(38)/*d*SPB(32) {d3}	-4.26×10^{-4}	0.232	—	80–170	I	[24,25,36,69–73]
31b	SPB(32)/*d*SPB(38) {d3}	-5.90×10^{-4}	0.396	—	80–170	I	[24,25,36,69–73]
31c	SPB(38)/SPB(32)	-5.08×10^{-4}	0.314	—	80–170	I	[24,25,36,69–73]
32a	SPB(25)/*d*SPB(8) {d3}	-2.02×10^{-3}	1.10	—	120–170	I	[24,25,36,69–73]
32b	SPB(8)/*d*SPB(25) {d4}	-3.14×10^{-3}	1.68	—	120–170	I	[24,25,36,69–73]
32c	SPB(25)/SPB(8)	-2.58×10^{-3}	1.39	—	120–170	I	[24,25,36,69–73]
33	SPB(89)/*d*SPB(63) {d3}	-1.47×10^{-3}	1.32	300	30–250	III	[74]
34	SPB(7)/SPB(90)	-3.8×10^{-3}	10.2	—	110–280	I	[68]
35	PE/*d*SPB(32) {d3}	-3.46×10^{-3}	2.59	—	140–200	I	[24,25,36,69–73]
36	PE/*d*SPB(25) {d4}	-3.23×10^{-3}	2.09	—	140–200	I	[24,25,36,69–73]
37a	PEB/*d*SPB(78) {d2}	-2.53×10^{-3}	2.50	-383	30–170	III	[24,25,36,69–73]
37b	SPB(78)/*d*PEB {d3}	-2.17×10^{-3}	2.24	-382	30–170	III	[24,25,36,69–73]
37c	PEB/SPB(78)	-2.35×10^{-3}	2.37	-383	30–170	III	[24,25,36,69–73]
38a	PEB/*d*SPB(66) {d3}	1.41×10^{-3}	-1.17	291	30–170	III	[24,25,36,69–73]
38b	SPB(66)/*d*PEB {d3}	2.40×10^{-3}	-1.87	405	30–170	III	[24,25,36,69–73]
38c	PEB/SPB(66)	1.91×10^{-3}	-1.52	348	30–170	III	[24,25,36,69–73]
39a	SPI(7)/*d*SPB(66) {d3}	6.90×10^{-4}	0.119	—	30–170	I,VI	[24,25,36,69–73]
39b	SPB(66)/*d*SPI(7) {d5}	8.85×10^{-4}	-0.058	—	30–170	VI	[24,25,36,69–73]
39c	SPI(7)/SPB(66)	7.88×10^{-4}	0.03	—	30–170	VI	[24,25,36,69–73]
40a	SPI(7)/*d*SPB(52) {d3}	3.66×10^{-3}	-3.22	676	30–170	III	[24,25,36,69–73]
40b	SPB(52)/*d*SPI(7) {d5}	2.43×10^{-3}	-2.03	443	30–170	III	[24,25,36,69–73]
40c	SPI(7)/SPB(52)	3.05×10^{-3}	-2.63	560	30–170	III	[24,25,36,69–73]
41a	SPI(7)/*d*PEB {d3}	2.71×10^{-3}	-1.85	420	30–170	III	[24,25,36,69–73]
41b	PEB/*d*SPI(7) {d5}	2.79×10^{-3}	-1.90	430	30–170	III	[24,25,36,69–73]
41c	PEB/SPI(7)	2.75×10^{-3}	-1.88	425	30–170	III	[24,25,36,69–73]
42a	SPI(7)/*d*SPB(38) {d3}	-2.01×10^{-3}	0.940	—	110–170	I	[24,25,36,69–73]
42b	SPB(38)/*d*SPI(7) {d5}	-2.93×10^{-3}	1.56	—	110–170	I	[24,25,36,69–73]
42c	SPI(7)/SPB(38)	-2.47×10^{-3}	1.25	—	110–170	I	[24,25,36,69–73]
43	SPI(5)/SPB(90)	-4×10^{-4}	4.2	—	130–310	I	[68]
44	SPI(5)/SPB(7)	-1.37×10^{-2}	7.5	—	110–170	I	[68]
45a	PP/*d*SPB(97) {d3}	4.54×10^{-3}	-4.71	1,364	30–130	III	[24,25,36,69–73]
45b	SPB(97)/*d*PP {d4}	2.44×10^{-3}	-3.27	1,051	30–130	III	[24,25,36,69–73]

TABLE 19.1. *Continued.*

	System	A^a	B (K)^a	C(K^2)^a	T Range (°C)	Type	Refs.
45c	PP/SPB(97)	3.49×10^{-3}	-3.99	1,208	30–130	III	[24,25,36,69–73]
46a	PP/*d*SPB(78) {d3}	7.47×10^{-3}	-6.38	1,426	50–170	III	[24,25,36,69–73]
46b	SPB(78)/*d*PP {d4}	3.81×10^{-3}	-3.50	895	50–170	III	[24,25,36,69–73]
46c	PP/SPB(78)	5.64×10^{-3}	-4.94	1,161	50–170	III	[24,25,36,69–73]
47a	PP/*d*SPI(7) {d5}	-3.02×10^{-3}	4.59	-944	30–170	III	[24,25,36,69–73]
47b	SPI(7)/*d*PP {d4}	-3.92×10^{-3}	5.39	-969	30–170	V	[24,25,36,69–73]
47c	PP/SPI(7)	-3.47×10^{-3}	4.99	-957	30–170	V	[24,25,36,69–73]
48a	HHPP/*d*SPB(78) {d2}	-1.53×10^{-3}	1.24	—	110–170	I	[24,25,36,69–73]
48b	SPB(78)/*d*HHPP {d4}	-2.20×10^{-3}	1.40	—	30–170	I	[24,25,36,69–73]
48c	HHPP/SPB(78)	-1.87×10^{-3}	1.32	—	110–170	I	[24,25,36,69–73]
49a	HHPP/*d*SPB(66) {d3}	7.16×10^{-3}	-6.17	1,338	30–170	III	[24,25,36,69–73]
49b	SPB(66)/*d*HHPP {d4}	6.75×10^{-3}	-5.84	1,280	30–170	III	[24,25,36,69–73]
49c	HHPP/SPB(66)	6.96×10^{-3}	-6.01	1,309	30–170	III	[24,25,36,69–73]
50a	HHPP/*d*PEB {d3}	1.27×10^{-3}	-0.96	282	30–170	III	[24,25,36,69–73]
50b	PEB/*d*HHPP {d4}	2.43×10^{-3}	-1.86	457	30–170	III	[24,25,36,69–73]
50c	HHPP/PEB	1.85×10^{-3}	-1.41	370	30–170	III	[24,25,36,69–73]
51	HHPP/*d*SPI(7) {d5}	8.06×10^{-3}	-5.71	1,046	30–170	IV	[24,25,36,69–73]
52a	HHPP/*d*PP {d4}	-4.27×10^{-3}	2.13	—	30–130	I	[24,25,36,69–73]
52b	PP/*d*HHPP {d4}	-3.01×10^{-3}	1.54	—	30–130	I	[24,25,36,69–73]
52c	HHPP/PP	-3.64×10^{-3}	1.84	—	30–130	I	[24,25,36,69–73]
53a	SPI(50)/*d*HHPP {d4}	-2.20×10^{-3}	1.24	—	30–170	I,III	[24,25,36,69–73]
		(1.11×10^{-3})	(-1.17)	(430)	30–170		[24,25,36,69–73]
53b	HHPP/*d*SPI(50) {d5}	-1.74×10^{-3}	1.29	—	50–170	I	[24,25,36,69–73]
53c	SPI(50)/HHPP	-1.97×10^{-3}	1.27	—	50–170	I	[24,25,36,69–73]
54a	SPI(50)/*d*SPB(78) {d2}	-1.62×10^{-4}	-0.04	—	50–170	VI	[24,25,36,69–73]
54b	SPB(78)/*d*SPI(50) {d5}	-1.63×10^{-4}	$+0.02$	—	30–170	VI	[24,25,36,69–73]
54c	SPI(50)/SPB(78)	-1.63×10^{-4}	-0.01	—	50–170	VI	[24,25,36,69–73]
55a	SPI-3,4/*d*SPB(97) {d3}	-2.85×10^{-4}	0.297	—	30–170	I	[24,25,36,69–73]
55b	SPB(97)/*d*SPI-3,4 {d5}	-2.40×10^{-4}	0.298	—	30–140	I	[24,25,36,69–73]
55c	SPI-3,4/SPB(97)	-2.63×10^{-4}	0.298	—	30–140	I	[24,25,36,69–73]
56	PI-3,4/*d*PTMSS	1.40×10^{-2}	-4.9	—	140–200	II	[75]
57	PI-3,4/PαMS	3.3×10^{-2}	6.07	—	190–200	I	[76]
58	PIB/*d*SPB(66) {d3}	2.20×10^{-2}	-7.92	—	30–110	II	[77]
59	PIB/*d*SPB(63) {d3}	-5.27×10^{-3}	10.3	$-3,168$	30–250	II	[74]
60	PIB/*d*SPB(78) {d3}	1.30×10^{-2}	-4.37	—	30–110	II	[77]
61	PIB/*d*SPB(89) {d3}	-4.43×10^{-4}	4.52	-927	30–250	VI	[74]
62	PIB/*d*HHPP {d4}	1.80×10^{-2}	-7.74	—	30–170	II	[77]
63	SPI(7)/*d*SPB(97)	4.01×10^{-4}	3.79	—	130–190	I	[78]
64	PI(6)/SPB(99)	-2.13×10^{-2}	8.61	—	50–125	I	[79]
65	PI(7)/*d*SPI(7)	-2.38×10^{-2}	17.2	—	40–210	I	[80]
66	PB(7)/*d*PB(7)	-2.15×10^{-4}	0.305	—	(-23)–90	I	[81]
67	PB(97)/*d*PB(97)	1.04×10^{-4}	0.158	—	40–100	I	[82]
68	PS/*d*PS	-1.73×10^{-4}	0.117	—	150–220	I	[81]
69	SPB(97)/*d*SPB(97)	-0.37×10^{-4}	0.261	—	30–100	I	[82]
70	PEO/*d*PMMA	-2.1×10^{-3}	0	—	80–160	VI	[83]
71	PEO/PS	-1.73×10^{-2}	23.7	—	210–230	I	[84]
72	PEO/PI(7)	1.38×10^{-1}	72	—	80–130	I	[85]
73	PEO/PBO	-8.2×10^{-2}	74.5	—	60–300	I	[86]
74	PI(6)/PFDMS	2.5×10^{-2}	4.83	—	170–200	I	[87]
75	PS/PFDMS	2.3×10^{-2}	3.11	—	160–210	I	[88]
76	PS/PFI	-9.4×10^{-2}	92	—	130–180	I	[89]
77	PS/PFB	7.8×10^{-2}	192	—	120–195	I	[90]
78	PB(99)/PFB	1.7×10^{-1}	89	—	120–195	I	[90]
79	SPB(99)/PFI	-1.83×10^{-1}	231	—	50–125	I	[79]
80	PI(6)/PFI	7.77×10^{-2}	83.7	—	50–125	I	[79]
81	PDMS/PEMS	1.93×10^{-3}	2.15	—	60–150	I	[91]
82	PDMS/PS	3.1×10^{-2}	58	—	165–225	I	[92]
83	PDMS/PI(7)	-8.5×10^{-3}	25.3	—	165–225	I	[92]

[a] Parameters χ, A, B, and C are based on a reference volume, $v = 0.1\ \mathrm{nm}^3$.

TABLE 19.2. *Nomenclature, definitions, and monomer volumes.*

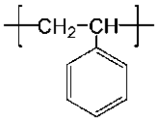
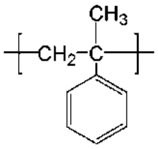
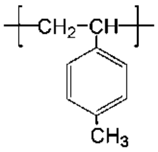
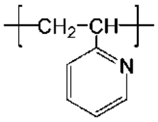
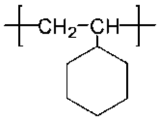
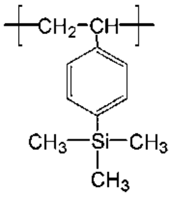
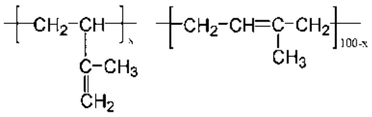
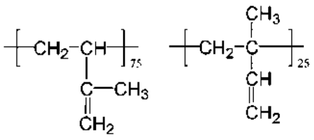
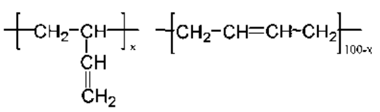
Polymer	Chain composition and definition of monomer[a]	Monomer volume[b] v_i(nm^3)	Statistical segment length[c] l_i (nm)	Temperature (°C)	Refs.
PS polystyrene		0.179	0.50	140	[30]
PαMS poly(α-methyl styrene)		0.185	0.53	140	[30,93]
P4MS poly(4-methyl styrene)		0.189	0.50	23	[62,94]
P2VP poly(2-vinyl pyridine)		0.179	0.50	140	[95]
SPS saturated polystyrene		0.199	0.42	140	[30]
PTMSS poly(4-trimethylsilyl styrene)		0.305	0.42	25	[75]
PI(x) polyisoprene		0.136	0.56 ($x = 5$)	140	[30]
PI-3,4 3,4-polyisoprene		0.127	0.55	25	[30]
PB(x) polybutadiene		0.111	0.66 ($x = 10$)	140	[30]

TABLE 19.2. *Continued.*

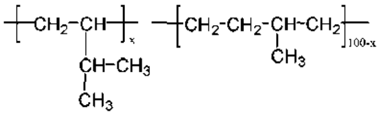
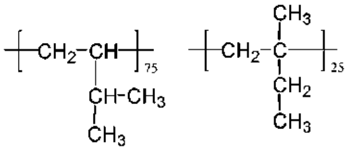
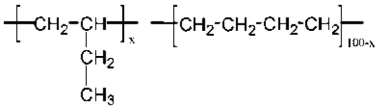
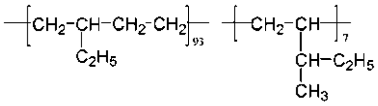
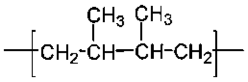
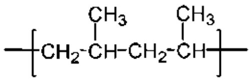
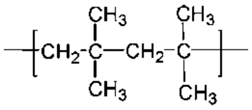
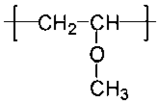
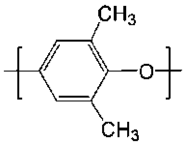
Polymer	Chain composition and definition of monomer[a]	Monomer volume[b] v_i(nm^3)	Statistical segment length[c] l_i (nm)	Temperature (°C)	Refs.
SPI(x) saturated polyisoprene	 $-[CH_2-CH(CH(CH_3)-CH_3)]_x-[CH_2-CH_2-CH(CH_3)-CH_2]_{100-x}-$	0.147	0.63 ($x = 5$)	140	[30]
SPI-3,4 saturated 3,4-polyisoprene	 $-[CH_2-CH(CH(CH_3)-CH_3)]_{75}-[CH_2-C(CH_3)(CH_2-CH_3)]_{25}-$	0.144	0.51	140	[30]
SPB(x) saturated polybutadiene	 $-[CH_2-CH(CH_2-CH_3)]_x-[CH_2-CH_2-CH_2-CH_2]_{100-x}-$	0.117	0.47 ($x = 89$) 0.72 ($x = 63$)	140	[74]
PEB poly(ethyl butylene)	 $-[CH_2-CH(C_2H_5)-CH_2-CH_2]_{93}-[CH_2-CH(CH(C_2H_5)-CH_3)]_7-$	0.174	0.62	140	[30]
HHPP head-to-head polypropylene	 $-[CH_2-CH(CH_3)-CH(CH_3)-CH_2]-$ + 3% other isomers	0.172	0.58	140	[30]
PP polypropylene	 $-[CH_2-CH(CH_3)-CH_2-CH(CH_3)]-$ + 3% other isomers	0.176	0.57	140	[30]
PE polyethylene	$-[CH_2-CH_2-CH_2-CH_2]-$	0.119	0.77	140	[30]
PIB polyisobutylene	 $-[CH_2-C(CH_3)_2-CH_2-C(CH_3)_2]-$	0.218	0.58	140	[74]
PEO poly(ethylene oxide)	$-[CH_2-CH_2-O]-$	0.069	0.72	140	[30]
PBO poly(butylene oxide)	$-[CH_2-CH_2-CH_2-CH_2-O]-$	0.134	0.57	140	[30,86]
PVME poly(vinyl methylether)	 $-[CH_2-CH(O-CH_3)]-$	0.094	0.62	140	[93,96]
PXE poly(2,6-dimethyl-1, 4-phenylene oxide)		0.204	0.88	173	[94]

TABLE 19.2. *Continued.*

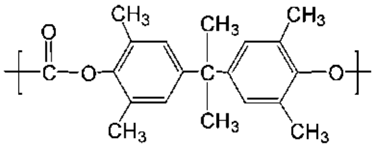
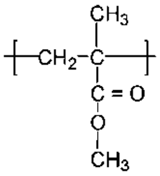
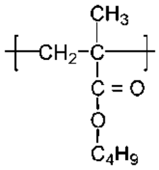
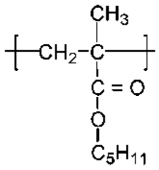
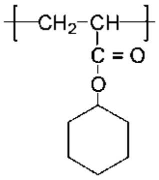
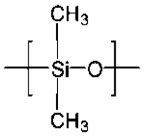
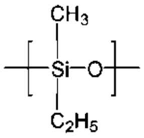
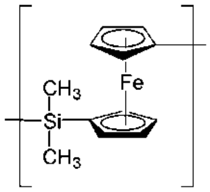
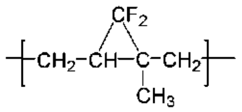
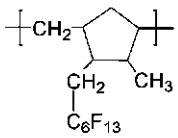
Polymer	Chain composition and definition of monomer[a]	Monomer volume[b] v_i(nm^3)	Statistical segment length[c] l_i (nm)	Temperature (°C)	Refs.
TMPC tetramethyl-bisphenol-A polycarbonate		0.470	0.48	140	[97]
PMMA poly(methyl methacrylate)		0.149	0.54	140	[30]
PBMA poly(*n*-butyl methacrylate)		0.220	0.49	25	[58,98]
PPMA poly(*n*-pentyl methacrylate)		0.252	0.45	25	[98]
PCHA poly(cyclohexyl acrylate)		0.237	N.A.	20	[55]
PDMS poly(dimethyl siloxane)		0.138	0.50	140	[92]
PEMS poly(ethylmethyl siloxane)		0.150	0.52	25	[91]
PFDMS Poly(ferrocenyl dimethylsilane)		0.340	0.82	140	[87,88]

TABLE 19.2. *Continued.*

Polymer	Chain composition and definition of monomer[a]	Monomer volume[b] v_i(nm^3)	Statistical segment length[c] l_i (nm)	Temperature (°C)	Refs.
PFI fluorinated polyisoprene		0.156	0.58	25	[89]
PFB fluorinated polybutadiene		N.A.	N.A.	N.A.	[90]

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[a] For random copolymers consisting of two kinds of repeat units, monomers are defined as either of the structures shown.

[b] Monomer volume (nm^3) = 1.66 × 10^{-3} × [molar mass of monomer (g/mol)]/density(g/cm^3)]. To obtain monomer volumes at other temperatures, the expansion coefficient d ln v_i/dT must be known. For many polymers the expansion coefficient is about (7 ± 1) × 10^{-4}(1/K).

[c] Statistical segment lengths are based on a reference volume of 0.1 nm^3 at the temperatures listed. Statistical segment lengths can be computed at other temperatures based on the assumption that Rg is independent of temperature. N.A. implies data not available. A useful summary of polymer properties is given by Fetters *et al.* [99].

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