

# 20

## Polymer Science\*

---

Historical Background  
Pharmaceutical Applications of Polymers  
Definitions  
Molecular Weight Averages  
Molecular Weight Determination from Solution  
Viscosity  
Conformation of Dissolved Linear  
Macromolecules  
Polymers as Thickening Agents  
Polymer Solutions—Overview  
Solvent Selection  
Preparing Polymer Solutions  
Thermodynamics of Polymer Solutions  
Phase Separation  
Gel Formation, Coacervation, and  
Microencapsulation

Polymers in the Solid State—Overview  
Mechanical Properties  
Interchain Cohesive Forces  
Crystallinity  
Tacticity  
Morphology  
Orientation  
Thermodynamics of Fusion and Crystallization  
Glass—Rubber Transition  
Plasticization  
Elastomers  
Fabrication Technology  
Future Trends in Pharmaceutical and Other  
Biomedical Uses of Polymers

---

### HISTORICAL BACKGROUND

High polymers found technologic applications many years before their nature was understood. Early practical applications included the mercerization of cotton (treatment of yarn with cold strong caustic to produce shrinkage and increase its strength and affinity for dyes) (John Mercer, 1844); the nitration of cellulose to Pyroxylin USP (Braconnot, 1833) and to guncotton (Schoenbein, 1847); the molding of nitrated cellulose plasticized with camphor, called *celluloid*, into billiard balls and detachable collars (Hyatt, 1868); the extrusion of collodion through spinnerettes followed by denitrication of the resulting filaments (Chardonnet, 1886); the acetylation of cellulose (Schuetzenberger, 1870); and the formation of the water-soluble cellulose derivatives xanthate (Cross and Bevan, 1893) and cuprammonium cellulose (Schweizer, 1857), eventually leading to the

production of regenerated cellulose fibers and films (viscose and Bemberg rayon, cellophane film).

Goodyear discovered the vulcanization of rubber by sulfur in 1839. Fully synthetic resins from phenol and formaldehyde, called *bakelite*, were manufactured by Baekeland beginning in 1910.

Recognition of the chemical nature of polymers began only in the early 1920s, when Staudinger concluded, from research on natural rubber, starch, and cellulose, that these compounds consisted of giant chains of carbon atoms (plus oxygen atoms in the case of the two polysaccharides) held together by covalent bonds. They were truly macromolecules. This notion was met with disbelief and even ridicule by many of his contemporaries. Not until the 1930s, when linear polymers were being synthesized, especially by W. H. Carothers in the Du Pont laboratories, did Staudinger's concept gain universal acceptance—a prime example of delayed recognition. The Nobel prize in chemistry was finally awarded to Staudinger in 1953.

Mark<sup>1</sup> and Flory,<sup>2</sup> pioneers in the physical chemistry of polymers in the solid state and in solution, were active until their recent deaths. The bulk of their work

---

\*This chapter was prepared by Dr. Hans Schott, Professor of Pharmaceutical and Colloid Chemistry, Temple University, School of Pharmacy, Philadelphia, PA.

was done in the last 45 years, and Flory received the Nobel prize in chemistry in 1974. Likewise, nearly all of the information in this chapter was developed after 1940.

### PHARMACEUTICAL APPLICATIONS OF POLYMERS

With the inclusion of tests and standards for high-density polyethylene and other plastics in the twentieth revision of the U.S. Pharmacopeia, polymers have officially entered the world of pharmacy. Actually, pharmacists have been employing polymers in every aspect of their work for many years. Typical examples are polyethylene and polyolefin bottles, polystyrene vials, rubber closures, rubber and plastic tubing for injection sets, and flexible bags of plasticized polyvinyl chloride to hold blood and intravenous solutions. Barrels and plungers of hypodermic syringes are made of polypropylene or, when optical clarity is required, of polycarbonate. Unit-dose packaging makes use of unplasticized polyvinyl chloride for cups and trays, laminates of polyethylene with aluminum or cellophane, and polyester film for strip-package or blister-package containers.

Among the water-soluble polymers used to coat tablets are hydroxypropyl methylcellulose and hydroxypropylcellulose, polyethylene glycol, povidone, and sodium carboxymethylcellulose. Some of these polymers are also used as binders for tableting granulations, as are acacia, gelatin, and sodium alginate. Ethylcellulose, being insoluble in water, is combined with water-soluble polymers to influence the dissolution rate of the coating film. Cellulose acetate phthalate, hydroxypropyl methylcellulose phthalate, and copolymers of methacrylic acid and its esters, Eudragit, are used for enteric coating of tablets. Starch as a tablet disintegrant has been joined recently by carboxymethyl starch of low substitution and by cross-linked povidone. All three polymers are insoluble but swell rapidly and extensively in water.

A wide variety of synthetic and natural polymers are used to thicken suspensions and ophthalmic solutions, as protective colloids to stabilize emulsions and suspensions and to form water-soluble jellies and ointment bases. Gelatin has the widest range of applications in the pharmaceutical field. It is the major constituent of hard and soft capsules, in addition to being used as a suppository base, as an emulsifying and suspending agent, for absorbable films, powders and sponges, as a boot in combination with zinc oxide, and for microencapsulation in combination with acacia.

Sustained-release dosage forms employ polymers as shells for microencapsulated drugs, as erodible and nonerodible matrices, as barrier membranes to regulate the release of drugs by diffusion, as ion-exchange resins, as reagents to form slightly soluble salts with basic drugs (tannic and polygalacturonic acids), and as

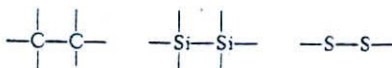
backbones for pendent drug molecules attached by labile bonds.

In addition to polymers being used as excipients, some drugs themselves are polymers, including insulin, heparin and its antagonist, protamine sulfate, the plasma expanders dextran and normal human serum albumin, and the bulk laxatives methylcellulose and sodium carboxymethylcellulose. In addition, there is polycarophil, which binds fecal water to decrease the fluidity of diarrheal stools. The anion-exchange resins colestipol hydrochloride and cholestyramine bind and increase the fecal excretion of bile salts to lower the blood cholesterol level.

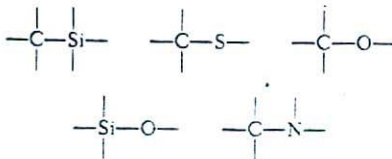
Thus, it is seen that polymers are essential to the dispensing pharmacist, to the manufacturing pharmacist, and to the research pharmacist.

### DEFINITIONS<sup>3-7</sup>

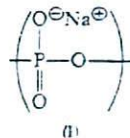
As Staudinger recognized, carbon atoms can bond to one another, forming the backbone of linear polymers via long chains of covalently bonded carbon atoms. Silicon and sulfur possess the same ability. Such *homochain* polymers have the following backbone structures:



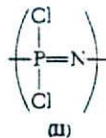
*Heterochain* polymers contain other atoms in the backbone. Examples include



and even purely inorganic polymers such as polymetaphosphate (Calgon)

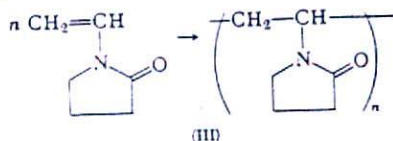


and polyphosphonitrilic chloride,



When vinylpyrrolidone, a *monomer*, is polymerized, it forms the *linear polymer* polyvinylpyrrolidone (Pov-

idone USP), a protective colloid capable of complexing iodine and whose aqueous solutions form strong films on drying.

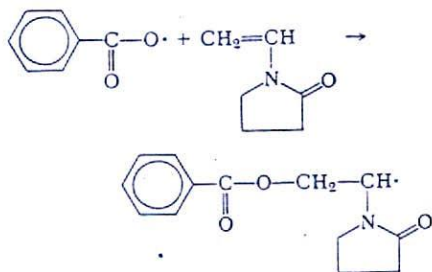


The structure between parentheses represents the *repeat unit* or *mer*. The number  $n$  of repeat units per macromolecule is called the *degree of polymerization* (DP).

The polymerization of such vinyl compounds is called an *addition* or *chain-reaction polymerization*. The process is most often started by a free radical formed by the thermal decomposition of an *initiator* such as benzoyl peroxide. Such a

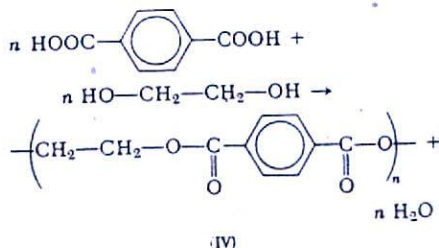


free radical adds to the double bond of a vinyl monomer, opening it and producing another compound with an unpaired electron:



The free radical propagates rapidly as  $n - 1$  other monomer molecules add successively to the growing chain, forming the polymer of Structure III.

*Condensation* or *stepwise polymerization* is illustrated by the formation of polyethylene terephthalate, a polyester used to form fibers and films:

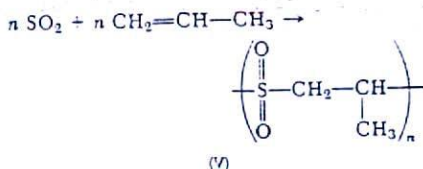


This polyesterification reaction proceeds stepwise, and the molecular weight of the polymer increases gradually as the steam formed is vented from the reactor.

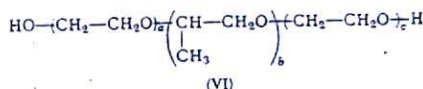
*Homopolymers* consist of a single monomer, such as Structures I to III; *copolymers* incorporate two or more monomers. Many naturally occurring polymers such as cellulose and natural rubber are homopolymers, but proteins are copolymers of different amino acids.

One of the many polyolefins is a resin for containers used to store parenteral solutions. It is a *random copolymer* of ethylene (*E*) and propylene (*P*): The two repeat units follow no particular sequence in the chain, for example,  $-\text{PPEPEPEPP}-$ .

In *alternating copolymers* such as polypropylene sulfone, made by the copolymerization of propylene and sulfur dioxide, the two mers alternate:



*Block copolymers* contain long sequences of the same mer. For instance, the fecal softener poloxalkol is a block copolymer of ethylene oxide and propylene oxide:



The *monomer functionality* determines whether a polymer is formed by a reaction and whether this polymer is linear, branched, or a network (or cross-linked) polymer. Acetic acid and ethanol are monofunctional, that is, each molecule possesses one reactive functional group. Their esterification produces only another monomer, ethyl acetate. Ethylene glycol and phthalic acid are bifunctional monomers, and their esterification produces the linear polymer IV. When ethylene glycol is partially or completely replaced by the trifunctional monomer glycerin, a cross-linked or network polymer is produced that is insoluble and infusible and is therefore called *thermosetting*. Small amounts of glycerin produce a branched structure.

Most linear and branched polymers are *thermoplastic*, that is, they can be softened or melted by heat and dissolved in appropriate solvents. Linear (a), branched (b), and network or cross-linked polymers (c) can be represented schematically as in Figure 20-1.

In network polymers, such as the polyesters produced by the condensation of *glycerin* (trifunctional) and *phthalic anhydride* (bifunctional), called *glyptals*, each macroscopic object consists of a single molecule because each atom in the object is bound to every other atom through covalent bonds.

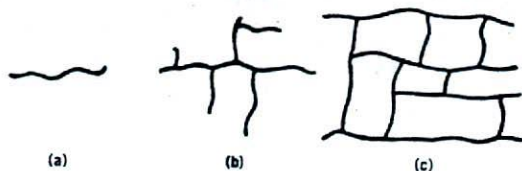
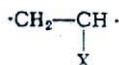
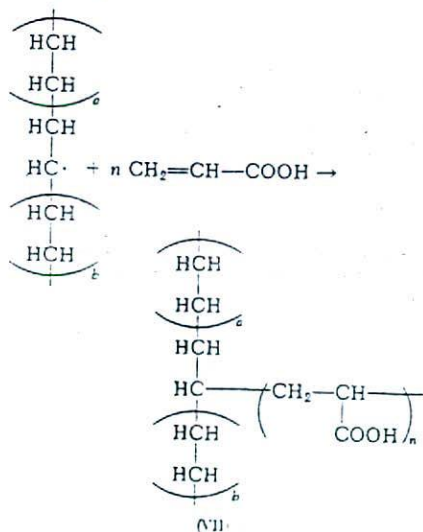


Fig. 20-1. Schematic illustration of branching and cross-linking.

Vinyl monomers are bifunctional since the carbon-carbon double bond can be considered to contain two unpaired electrons:



During free-radical chain polymerizations, a free radical can abstract a hydrogen atom from an existing chain, producing another free radical that can grow into a *branch* through the addition of monomer molecules. Ionizing radiation can also introduce such free radicals into a polymer, and a second monomer can be grafted onto a polymeric substrate after irradiation. For instance, irradiating polyethylene film or molded objects with gamma rays followed by exposure to acrylic acid results in the *grafting* of polyacrylic acid branches onto the polyethylene substrate, rendering the polyethylene surface hydrophilic:

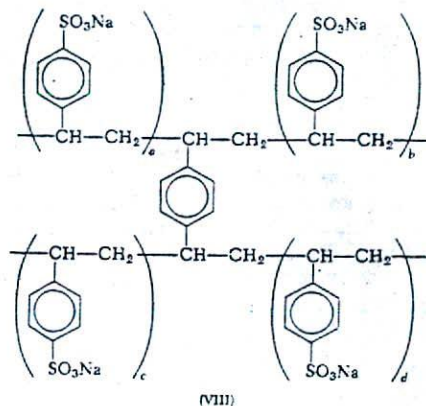


This structure represents a *graft copolymer*.

Network copolymers that are monographs in the USP/NF include the cation-exchange resin sodium polystyrene sulfonate, used to remove excess potassium ions and the anion-exchange resin cholest-

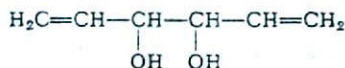
tyramine, used to remove bile salts, croscarmellose sodium, and crospovidone. The last two products are cross-linked carboxymethylcellulose sodium and povidone. Their linear analogs are water-soluble. The cross-linked polymers are insoluble but swell fast and extensively in aqueous media, including gastric juice. These powders, with average particle size of the order of 50  $\mu\text{m}$ , are incorporated into tablets at about 2% as disintegrants.

Sodium polystyrene sulfonate, a polyelectrolyte, is soluble in water. To make it insoluble in water, styrene (a bifunctional monomer) is copolymerized with a small percentage of divinylbenzene (a tetrafunctional monomer). After sulfonation and neutralization, the structure of the resin is



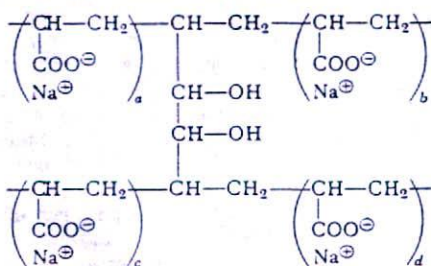
The two linear chains *ab* and *cd* are tied together by the phenylene cross-link. In a grain of ion-exchange resin, all polystyrene sulfonate chains are thus tied together into a single network. The influx of aqueous gastrointestinal fluid swells the grain until the phenylene cross-links are strained, so that the fluid freely permeates the swollen grain and exchanges its  $\text{K}^+$  with the  $\text{Na}^+$  of the resin. The grain does not dissolve because it consists of a network of covalent carbon-carbon bonds holding together all repeat units and chains.

Polycarbophil, a monograph (see calcium polycarbophil, in the U.S.P. XXII), is polyacrylic acid lightly cross-linked with divinyl glycol,



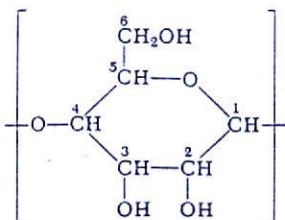
Each particle consists of a single molecule because of its network structure. Swelling in the acid gastric fluid is minimal because the carboxylic acid groups are not ionized. In the neutral to slightly alkaline intestinal fluids, particularly of the colon, the carboxylic acid groups become ionized, making the polymer a *polyelectrolyte*. The schematic structure of two chains of

polyacrylic acid in the ionized form, tied together by one divinyl glycol cross-link, is as shown:



The high concentration of ionic groups inside the carbophil particles causes a large influx of water by osmosis, swelling the particles until the cross-links are strained. The cross-links prevent the dissolution of the sodium polyacrylate chains, however. Each grain, when fully swollen, absorbs 50 to 65 times its weight in water, decreasing the fluidity of liquid stool in diarrheal disorders.

Two definitions pertain to cellulose and starch derivatives. The anhydroglucose repeat unit has three hydroxyl groups, namely, the primary hydroxyl on the Number 6 carbon atom, which is the first to react during substitution reactions, and two secondary hydroxyls on the Number 2 and 3 carbon atoms. Cellulose is a linear polymer consisting of D(+)-glucose residues,



that are linked by  $\beta$ -1,4 glycosidic bonds.

The *degree of substitution (DS)* represents the number of hydroxyl groups per anhydroglucose repeat unit that have been substituted, for example, methylated, carboxymethylated, oxyethylated, acetylated, and so on. *DS* values range from 0 to 3.00 and are usually not integer numbers because they represent average values over an entire sample.

*Molar substitution (MS)* in hydroxyethyl cellulose is the average number of ethylene oxide molecules that have reacted with one anhydroglucose repeat unit. After an ethylene oxide molecule has added onto one of the three hydroxyl groups, the resulting hydroxyethyl group can add more ethylene oxide molecules in competition with the remaining two glucose hydroxyls. While the *MS* is known from the weight increase of the cellulose sample or from the consumption of ethylene oxide, the *DS* of hydroxyethyl cellulose is usually not known. For commercial hydroxyethyl cellulose, the *MS*

is usually in the range of 1.8 to 2.3. This value may correspond to a *DS* of 0.9 to 1.0, indicating that most of the ethoxylation took place on one hydroxyl group, probably the primary hydroxyl group of the Number 6 carbon atom, each of which added two ethylene oxide molecules on the average.

Molar substitution is used instead of degree of substitution whenever the substitution reaction in cellulose produces hydroxylated derivatives. *MS* values can exceed 3.00. Some grades of hydroxypropyl cellulose, produced by the ring-opening addition of propylene oxide to alkali cellulose, have an *MS* of 4.0 and above.

### MOLECULAR WEIGHT-AVERAGES<sup>9,9</sup>

Small molecules and many biopolymers are *monodisperse*, that is, all molecules of a given pure compound have the same molecular weight. All sucrose molecules weigh 342.30 g divided by Avogadro's number; all molecules of human serum albumin weigh 69,000 g divided by Avogadro's number.

In synthetic polymerization reactions such as III to V, no two chains grow equally fast or for the same length of time. The resultant macromolecules are *heterodisperse*, that is, they have different chain lengths and a range of molecular weights, which can be described by an average molecular weight and by a molecular weight distribution.

The problem of choosing a meaningful average value for the molecular weight is identical to that encountered in micromeritics (Chapter 16). Take the simple example of a batch of polystyrene made up of two monodisperse or homogeneous fractions, Fraction A with a molecular weight of 1000 and Fraction B with a molecular weight of 100,000. The low-molecular-weight fraction A, with a *DP* of 9 to 10, is called an *oligomer*. Assuming that the batch contains an equal number of molecules *n* or an equal mole fraction *X* of the two polystyrene fractions:  $n_A = n_B$  and

$$X_A = \frac{n_A}{n_A + n_B} = X_B = \frac{n_B}{n_A + n_B} = 0.500$$

The average molecular weight  $\bar{M}$ , based on the number of molecules present, should be

$$\begin{aligned}
 \bar{M} &= (0.500)(1000) + (0.500)(100,000) \\
 &= \frac{1000 + 100,000}{2} = 50,500 \quad (20-1)
 \end{aligned}$$

One can argue, however, that this averaging procedure gives an unrealistic value because each small molecule A affects  $\bar{M}$  just as strongly as each large molecule B even though it weighs only 1% of B. Only 1% of the weight of the sample consists of molecules A with a molecular weight of 1000 while 99% of the weight consists of molecules B of molecular weight 100,000.

Therefore, based on the weight fraction  $w$  of  $A$  and  $B$  present, the average molecular weight should more realistically be expressed as

$$\bar{M} = (0.01)(1000) + (0.99)(100,000) = 99,010 \quad (20-2)$$

The former molecular weight average is called the *number-average* molecular weight,  $\bar{M}_n$ . It is obtained by adding the molecular weight of each molecule or mole in the sample and dividing by the total number of molecules or moles. The latter molecular weight average is called the *weight-average* molecular weight,  $\bar{M}_w$ . It is an average weighted according to the weight fraction  $w$  (or the  $w/v$  concentration in solution) of each molecule or mole.

Mathematically, the general expression is

$$\bar{M}_b = \frac{\sum w_i M_i^b}{\sum w_i M_i^{b-1}} = \frac{\sum N_i M_i^{b+1}}{\sum N_i M_i^b} \quad (20-3)$$

in which the weight fraction  $w_i$  of the  $i$ th monodisperse fraction, with the homogeneous molecular weight  $M_i$ , is equal to the number of molecules  $n_i$ , or of moles  $N_i$ , times  $M_i$ , divided by the total weight of the sample, namely, by  $\sum n_i M_i$  or  $\sum N_i M_i$ , respectively.  $b$  is an integer whose value specifies the particular average of  $M$ .

If  $b = 0$ , the number-average molecular weight results. Keeping in mind that  $\sum w_i = 1$  and  $\sum X_i = 1$ , equation (3) becomes

$$\bar{M}_n = \frac{1}{\sum w_i / M_i} = \frac{\sum N_i M_i}{\sum N_i} = \sum X_i M_i \quad (20-4)$$

This equation is comparable to the first equation in Table 16-3 and pertains to a number-average distribution.

To calculate  $\bar{M}_n$  for the bimodal polystyrene sample, the most convenient term in equation (20-4) is the expression in  $X_i$  that was already used in equation (20-1). To use the expression in  $w_i$ , one must calculate  $w_A$  and  $w_B$ . Assume that the sample consists of two molecules of  $A$  and two of  $B$ . Then

$$w_A = \frac{(2)(1000)}{(2)(1000) + (2)(100,000)} = 0.009901$$

and

$$w_B = \frac{(2)(100,000)}{(2)(1000) + (2)(100,000)} = 0.990099$$

As a check,  $w_A + w_B = 1.000000$ . Then, from the term containing  $w_i$  in equation (20-4):

$$\bar{M}_n = \frac{1}{\frac{0.009901}{1000} + \frac{0.990099}{100,000}} = 50,500$$

The number-average molecular weight is influenced especially by the low-molecular-weight fraction in a polymer. Experimentally, it is determined by end-group analysis and from the colligative properties, especially osmotic pressure (Chapter 5).

If  $b = 1$  in equation (20-3) the weight-average molecular weight results:

$$\bar{M}_w = \sum w_i M_i = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum X_i M_i^2}{\sum X_i M_i} \quad (20-5)$$

This equation is comparable to  $\sum nd^2/\sum nd$  in Table 16-3 and pertains to the weight-average distribution. For the polystyrene sample, using the term in  $X_i$  from equation (20-5) gives

$$\bar{M}_w = \frac{(0.500)(1000)^2 + (0.500)(100,000)^2}{(0.500)(1000) + (0.500)(100,000)} = 99,020$$

Using the term in  $w_i$  gives

$$\bar{M}_w = (0.009901)(1000) + (0.990099)(100,000) = 99,020$$

Since the molecules contribute to the weight-average molecular weight of a polymer in direct proportion to their weight in the sample, this average is especially sensitive to high-molecular-weight fractions, for example, to a lightly cross-linked fraction in an otherwise linear polymer.

Another molecular weight average, the  $z$ -average, is obtained by setting  $b = 2$  in equation (20-3):

$$\bar{M}_z = \frac{\sum w_i M_i^2}{\sum w_i M_i} = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum X_i M_i^3}{\sum X_i M_i^2} \quad (20-6)$$

$\bar{M}_z$  is obtained from sedimentation equilibrium measurements in the ultracentrifuge. For the bimodal polystyrene sample,  $\bar{M}_z = 99,990$ .

There are number-average and weight-average degrees of polymerization to match the number-average and weight-average molecular weights. For instance, if a povidone sample has  $\bar{M}_w = 70,000$ , then  $\bar{DP}_w = 70,000 \div 111.1 = 630$ . The molecular weight of the repeat unit, which is also the molecular weight of the vinylpyrrolidone monomer, is 111.1.

From their definitions, it follows that  $\bar{M}_z \geq \bar{M}_w \geq \bar{M}_n$ , and  $\bar{M}_w/\bar{M}_n = \gg 1$ . This ratio is a measure of the polydispersity of a polymer sample. Many biopolymers are monodisperse; for them, the ratio  $\bar{M}_w/\bar{M}_n$  is unity. For vinyl polymers made by solution polymerization to high conversion, the ratio is in the 2 to 5 range. For vinyl polymers made by bulk polymerization, the ratio is frequently about 10. Gel permeation chromatography is used for analytic and preparative polymer fractionation. Fractional precipitation, described in the following, is also used.

#### MOLECULAR WEIGHT DETERMINATION FROM SOLUTION VISCOSITY<sup>10,11</sup>

Staudinger predicted and found, with solutions of cellulose derivatives, that the reduced viscosity of a polymer is proportional to its molecular weight. Reduced viscosity is specific viscosity divided by concentration (equation (15-22)). His observations were modified by Mark and Houwink and by the theoretic

analysis of W. Kuhn. The reduced viscosity was replaced by the intrinsic viscosity or limiting viscosity number  $[\eta]$ , which is the reduced viscosity extrapolated to infinite dilution. The proportionality of  $[\eta]$  is to a power,  $\alpha$ , of the molecular weight usually between 0.5 and 1.1. The most common  $\alpha$  values are between 0.6 and 0.8.

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{12} - \eta_1}{c\eta_1} = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (20-7)$$

in which  $\eta_{12}$  is the viscosity of the solution of concentration  $c$ ,  $\eta_1$  is the viscosity of the solvent, and  $\eta_{sp}$  is the specific viscosity defined by equation (15-20). Since concentration in polymer viscometry is usually expressed in grams of polymer per deciliter of solution (1 dL = 0.1 liter = 100 mL or  $\text{cm}^3$ ), corresponding to % w/v,  $[\eta]$  is given in units of dL/g. In colloid chemistry,  $[\eta]$  is usually expressed in mL/g.

If Einstein's law of viscosity is obeyed,  $[\eta] = 0.025$  dL/g. This value is approximated by globular proteins at the isoelectric point and by polymer latexes. Most polymer molecules in solution, including denatured proteins, assume the shape of voluminous random coils. For them,  $[\eta]$  is one to four orders of magnitude larger.

The modified Staudinger equation, often called the Mark-Houwink equation (equation (15-24)) is

$$[\eta] = KM^a \quad (20-8)$$

The parameters  $K$  and  $a$  are constant for a given polymer-solvent combination at a given temperature. The exponent  $a$  usually has values between 0.5 and 0.8.  $K$  values are in the  $0.2 \times 10^{-4}$  to  $8 \times 10^{-4}$  dL/g range. For instance, for polyvinyl alcohol in water at 30° C,  $K = 4.28 \times 10^{-4}$  dL/g and  $a = 0.64$ . Extensive tabulations of  $K$  and  $a$  values for many polymers in different solvents at different temperatures have been published.<sup>12</sup>

The values of  $K$  and  $a$  are determined by calibration measurements, using polymer fractions of known molecular weight (see *Problem 20-6*). Thus, viscosity measurements do not afford absolute molecular weight determinations like osmometry, light scattering, or ultracentrifugation. Because of the simplicity of the equipment and speed and accuracy of the measurements,  $[\eta]$  determination is the method most widely and routinely used to determine polymer molecular weights.

The viscosity-average molecular weight,  $\bar{M}_v$ , lies between the weight-average and the number-average value. It is closer to the former, often being 10 to 20% below  $\bar{M}_w$ .

$$\bar{M}_v = (\sum w_i M_i^a)^{1/a} = \left( \frac{\sum N_i M_i^{a+1}}{\sum N_i M_i} \right)^{1/a} \quad (20-9)$$

For a polydisperse sample,  $M$  in the Mark-Houwink equation, equation (20-8), is replaced by  $\bar{M}_v$ . For  $\alpha = 1$ ,  $\bar{M}_v = \bar{M}_w$  as given by equation (20-5).

Viscosities of dilute solutions are measured in glass capillary viscometers. Experimental precautions include working in constant-temperature baths regulated to  $\pm 0.02^\circ$  C and using efflux times of at least 200 seconds. Slow flow rates obviate the kinetic energy correction, minimize end effects, and give essentially zero-shear viscosities, that is, the flow occurs in the lower Newtonian region, and the solution viscosity is independent of the efflux time  $t$ . A special glass capillary viscometer with a series of bulbs permits measurement of the apparent viscosity at a series of shear rates and extrapolation to zero shear.

For accurate extrapolation to zero concentration, solution concentrations are usually chosen to give relative viscosities between 1.1 and 1.5. Because the polymer solutions used are so dilute, their density is practically identical with that of the solvent, simplifying equation (17-12) to

$$\eta_{rel} = \frac{\eta_{12}}{\eta_1} \cong \frac{t_{12}}{t_1} \quad (20-10)$$

Extrapolation of reduced viscosities to zero concentration to obtain the intrinsic viscosity eliminates the effect of the buildup of the reduced viscosity due to intermolecular entanglements. The linear extrapolation is usually made by the Huggins equation:

$$\frac{\eta_{sp}}{c} = \eta_{red} = [\eta] + k_1[\eta]^2 c \quad (20-11)$$

An alternate definition of intrinsic viscosity makes use of the inherent viscosity, namely,  $\eta_{inh} = \ln \eta_{rel}/c$ . According to this definition,

$$[\eta] = \lim_{c \rightarrow 0} \frac{\ln \eta_{rel}}{c} \quad (20-12)$$

TABLE 20-1. Viscosity Measurements of Dilute Solutions of Polymethyl Methacrylate in Ethylene Chloride at 25° C<sup>13</sup>

$c_2$ (g/dL)	Efflux times (sec)	$\eta_{rel} = \frac{t_{12}}{t_1}$	$\eta_{inh} = \frac{\ln \eta_{rel}}{c_2}$	$\eta_{red} = \frac{\eta_{rel} - 1}{c_2}$
0	$t_1$ 235.6	1.000	—	—
0.125	246.2	1.045	0.352	0.360
0.250	257.0	1.091	0.348	0.364
0.500	279.6	1.187	0.342	0.374
1.000	328.6	1.395	0.333	0.295

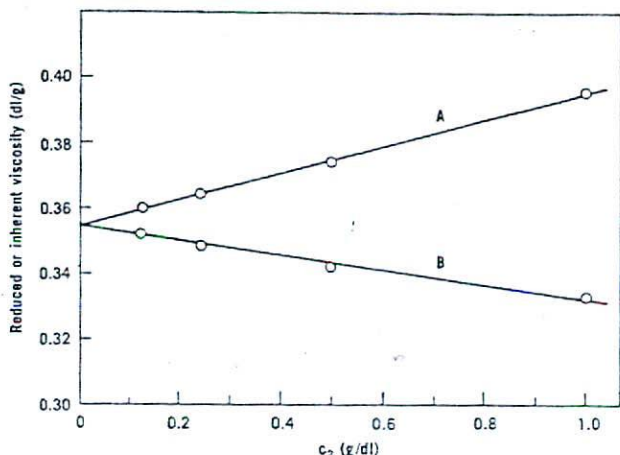


Fig. 20-2. Plots of reduced and inherent viscosity versus concentration for polymethyl methacrylate in ethyl chloride at 25°C for the determination of intrinsic viscosity. Line A represents reduced viscosity; line B represents inherent viscosity.

Another linear extrapolation to obtain  $[\eta]$ , using the inherent viscosity, is based on the Kraemer equation:

$$\eta_{\text{inh}} = \frac{\ln \eta_{\text{rel}}}{c} = [\eta] - k_2[\eta]^2 c \quad (20-13)$$

A set of experimental viscosity data illustrates the use of the Huggins and Kraemer equations to determine intrinsic viscosity from relative viscosities.

**Example 20-1.** From the data of Table 20-1, determine the intrinsic viscosity by means of the Huggins and Kraemer equations. Subscript 1 refers to the solvent, 2 to the polymer and 12 to the polymer solution. Efflux times are given with four significant figures because they are averages of four to five measurements. Linear regression analysis of the data plotted according to the Huggins equation (Fig. 20-2, line A), gives  $\eta_{\text{red}} = 0.354 + 0.0404c$ . Hence,  $[\eta] = 0.354 \text{ dl/g}$  and

$$k_1 = \text{slope}([\eta]^2) = 0.0404/(0.354)^2 = 0.322$$

Linear regression analysis according to the Kraemer equation (Fig. 20-2, line B) gives  $\eta_{\text{inh}} = 0.354 - 0.0212c$ . Hence,  $[\eta] = 0.354 \text{ dl/g}$  and

$$k_2 = -\text{slope}([\eta]^2) = -(-0.0212)/(0.354)^2 = 0.170$$

The two lines converge to their common intercept  $[\eta]$  at  $c = 0$ . Instead of using linear regression analysis, intercept and slopes of the two lines can be obtained from Figure 20-2. The sum of the Huggins and Kraemer slope constants,  $k_1 + k_2 = 0.322 + 0.170 = 0.492 = 0.500$ , as required by theory.

#### CONFORMATION OF DISSOLVED LINEAR MACROMOLECULES<sup>2,5,6,8,14,15</sup>

Because of a relatively large freedom of rotation around bonds between carbon and other atoms forming their backbone, polymer chains are quite flexible. This is illustrated in Figure 20-3 by depicting four successive carbon atoms in a chain, and fixing the bond (length = 1.54 Å) between carbon atoms 1 and 2 as reference in the plane of the paper.

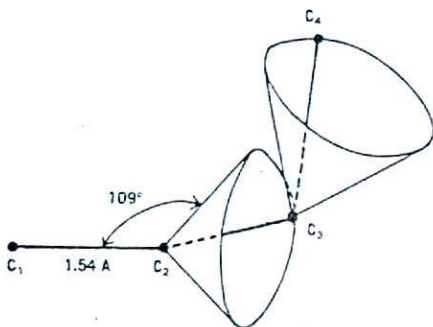


Fig. 20-3. Rotational freedom in a four-carbon atom chain sequence.

Atom Number 3 can be located anywhere on a circle around the base of a cone swept out by rotating the  $C_2-C_3$  bond at the fixed tetrahedral bond angle of  $109^\circ$  relative to the  $C_1-C_2$  bond. When locating  $C_4$ , every position of atom Number 3 on that circle gives rise to another cone with a circular base swept out by rotating the  $C_3-C_4$  bond at a  $109^\circ$  angle.  $C_4$  may be located on any point of any one of these many circles. This illustrates that the number of possible conformations\* of a polymer chain of many carbon atoms is enormous, resulting in a high flexibility for that chain.

Because they are buffeted by surrounding solvent molecules engaged in thermal agitation, polymer chains in solution adopt ever-changing shapes of random coils

\*Different geometric arrangements of polymer chains caused by rotation about single bonds in their backbone are designated as conformations. Different arrangements fixed by chemical bonding that involve isomerism are called configurations. Changes in configuration require breaking and reforming of primary valence bonds.<sup>4,5</sup>



in a writhing segmental Brownian motion. Most polymers have a bulk density of  $1 \text{ g/cm}^3$ , but in solution, the randomly coiled chains are permeated by solvent and occupy a volume many times larger than their bulk volume. The average density of polymer segments within a randomly coiled chain is of the order of  $10^{-5}$  to  $10^{-3} \text{ g/cm}^3$ .

The dimensions of the coiled chain depend on the polymer-solvent interaction, being larger in a thermodynamically good solvent that solvates the chains extensively but more shrunken in a poor solvent. Bulky substituents (e.g., the phenyl group in polystyrene), ionized groups (e.g., sodium carboxylate groups in neutralized Carbomer USP), rings in the backbone (such as those in polyethylene terephthalate or cellulose), or unsaturation (as the partial double bond in polypeptide chains introduced by resonance) reduce the flexibility of the polymer chain and result in more open or larger coils and hence in larger intrinsic viscosities.

The shape of a randomly coiled polymer chain changes continuously owing to the random bombardment by solvent molecules, and no two chains have the same shape at a given time. Therefore, the dimensions of a random coil are averaged over all polymer molecules and over long periods of time by statistical techniques. The problem of predicting the distance between the two ends of a coiled chain is analogous to calculating the distance traveled by a diffusing particle in random Brownian motion, which is treated as a *random flight* (Fig. 20-4). In the case of a polymer chain, each step corresponds to adding another carbon atom to the chain. Three restrictions prevent treatment of the *end-to-end distance*,  $R$ , as a completely random flight: Each step can only proceed by the distance of the carbon-carbon bond length of  $1.54 \text{ \AA}$ , the bond angle of  $109$  to  $110^\circ$  must be preserved, and there are steric hindrances.

The root-mean-square value of the end-to-end distance  $R$  is used for its average. For the four  $R$  values of 100, 200, 300, and  $400 \text{ \AA}$ , the root-mean-square average is

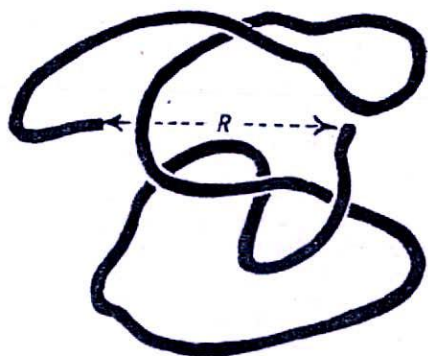


Fig. 20-4. Randomly coiled linear polymer chain showing end-to-end distance  $R$ .

$$\langle R^2 \rangle^{1/2} = \sqrt{\frac{100^2 + (2)(200)^2 + 300^2}{4}} = 212 \text{ \AA}$$

In addition to the end-to-end distance, the *radius of gyration*,  $S$ , is also used to describe the dimensions of the randomly coiled chain. It is the root-mean-square distance of the chain segments from the center of gravity of the coiled chain and is more meaningful than  $R$  for branched polymers, in which there are more than two chain ends. For linear polymers,  $\langle R^2 \rangle = 6\langle S^2 \rangle$ .

As W. Kuhn calculated in 1934 by the *random flight* method, if a polymer molecule consists of a chain of  $n$  identical segments of length  $L$  that are freely jointed, that is, with no restriction as to the bond angle  $\theta$  between segments,

$$\langle R^2 \rangle = nL^2 \quad (20-14)$$

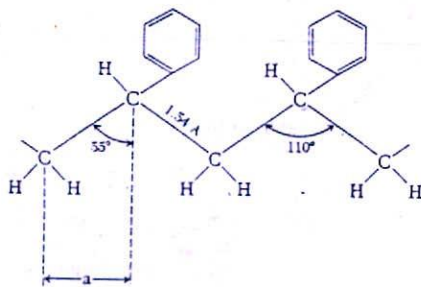
Thus,  $\langle R^2 \rangle$  is directly proportional to the molecular weight. Introducing the tetrahedral bond angle  $\theta = 110^\circ$ , with  $\cos \theta = -\frac{1}{3}$ , and assuming free rotation about that angle, the root-mean-square end-to-end distance is doubled:

$$\langle R^2 \rangle \cong \left( \frac{1 - \cos \theta}{1 + \cos \theta} \right) nL^2 = 2nL^2 \quad (20-15)$$

The following factors further expand the dimensions of real polymer molecules in solution, increasing the end-to-end distance beyond the value given by equation (20-15): short-range interactions, namely, steric hindrance to free rotation about carbon-carbon bonds in the backbone of the chain caused by bulky substituents or by rings, or unsaturation in the backbone producing rigid planar conformations; ionic groups; and long-range intramolecular interactions, namely, the excluded volume (chain segments have finite thickness, and no two segments can occupy the same volume at the same time).

**Example 20-2.** For a polystyrene molecule with a molecular weight of 1,000,000, calculate the length of the fully extended chain (called the *contour length*), the root-mean-square end-to-end distance assuming a freely jointed chain, and the root-mean-square end-to-end distance and the radius of gyration for a bond angle of  $110^\circ$ .

The molecular weight of styrene and of the repeat unit is 104.16; hence,  $DP = 1,000,000/104.16 = 9600$ . The fully extended chain, in a planar, all-*trans*, zig-zag conformation, has the following dimensions:



Projection of the  $1.54 \text{ \AA}$  carbon-carbon bond length on the chain axis makes the contribution  $a = (1.54 \text{ \AA}) \sin (110^\circ/2) = (1.54 \text{ \AA}) \sin 55^\circ =$

1.26 Å to the contour length of the chain. Each repeat unit adds  $1.26 \text{ \AA} \times 2 = 2.52 \text{ \AA}$  to that length; for 9600 repeat units, it is  $2.52 \text{ \AA} \times 9600 = 24,190 \text{ \AA}$ .

The polystyrene chain contains  $n = 2 DP = 2 \times 9600 = 19,200$  bonds in the backbone of the chain of  $L = 1.54 \text{ \AA}$ . According to equation (20-14), if it is freely jointed, its root-mean-square end-to-end distance is  $(R^2)^{1/2} = [(19,200)(1.54 \text{ \AA})^2]^{1/2} = 213 \text{ \AA}$ .

With the restriction of the tetrahedral bond angle but allowing free rotation, equation (20-15) gives  $(R^2)^{1/2} = [(2)(19,200)(1.54 \text{ \AA})^2]^{1/2} = 302 \text{ \AA}$ , corresponding to  $(S^2)^{1/2} = (R^2)^{1/2}/\sqrt{6} = 123 \text{ \AA}$ .

The actual  $(R^2)^{1/2}$  value for a polystyrene fraction with molecular weight of  $10^6$ , deduced from intrinsic viscosity measurements in good solvents, is at least three times larger.<sup>16</sup> This discrepancy is chiefly due to the greater stiffness of the polystyrene chain brought about by hindered rotation around the carbon-carbon chain bonds, which in turn is ascribed to the bulky phenyl side groups and to solvation of the macromolecule.

For comparison, a latex sphere consisting of a polystyrene molecule with a molecular weight of  $10^6$  and a density of  $1.06 \text{ g/cm}^3$  has a radius

$$R = \left[ \frac{\left( \frac{10^6 \text{ g}}{\text{mole}} \right) \left( \frac{\text{mole}}{6.023 \times 10^{23} \text{ molecules}} \right)}{\left( \frac{\text{cm}^3}{1.06 \text{ g}} \right) \left( \frac{10^{24} \text{ \AA}^3}{\text{cm}^3} \right) \left( \frac{3}{4\pi} \right)} \right]^{1/3} = 72 \text{ \AA}$$

The same molecule dissolved as a random coil, with a radius of about  $1100 \text{ \AA}$ , occupies a volume  $(1100/72)^3 = 3600$  times larger. The polymer segment density within the random coil is  $1.06 \text{ g/cm}^3/3600 = 2.9 \times 10^{-4} \text{ g/cm}^3$ . Thus, polymer molecules in solution spread throughout the solvent and occupy or fill the solution space effectively. Therefore, dissolved polymers are excellent thickening agents for solvents (see next section).

## POLYMERS AS THICKENING AGENTS<sup>1,2,17</sup>

The extraordinary ability of dissolved macromolecules to build up the relative viscosity of their solutions is illustrated with high-viscosity, USP-grade methylcellulose. An aqueous 2.00% (*w/v*) solution has an apparent viscosity at low shear and room temperature of 80 poise. Since water has a viscosity of 0.01 poise, the relative viscosity of that solution is 8000, that is, the 2% of dissolved polymer increases the viscosity of water 8000-fold!

At a polymer molecular weight of 300,000 and a molecular weight of 187 for a methylcellulose repeat unit with a degree of substitution of 1.8,  $DP = 300,000/187 = 1600$ . If each of the macromolecules were cut up by hydrolysis into its building blocks, namely, 1600 molecules of methylglucose, a 2.19% solution of methylglucose would result. While the viscosity of methylglucose solutions has not been reported, the viscosity of a 2.19% (*w/v*) solution of glucose in water, which is probably about the same, is a mere 1.05 centipoise, that is, only 5% higher than the viscosity of water. Splitting the polymer into its building blocks reduces the relative viscosity from 8000 to 1.05. Even a 34% (*w/v*) solution of glucose in water has a relative viscosity of only 2.99. By contrast, the viscosity of polymer solutions increases almost exponentially with concentration. (The reader will note that the viscosity values in Figure 20-5 are plotted on an eighth-root scale that is almost as compressed as a logarithmic

scale.) Solutions of high polymers frequently set to gels at concentrations of 5% or higher.

The factors responsible for the thickening action of dissolved polymers are discussed in the following paragraphs, starting with considerations of single polymer molecules in solution and then considering the effect of intermolecular entanglements. The reasons for the pseudoplastic or shear-thinning behavior of polymer solutions (defined on p. 456) are also discussed.

Each repeat unit of methylcellulose has three to four ether groups and one to two hydroxyl groups that are extensively hydrated in aqueous solution. An ether oxygen has two unshared electron pairs and can therefore bind two water molecules by hydrogen bonding. Each of these water molecules can hydrogen-bond additional water molecules, thus surrounding the polymer chain with a sheath of water of hydration. Likewise, a polystyrene molecule dissolved in benzene is extensively solvated by van der Waals forces. When the chains move, their solvation layers are dragged along. The resultant increase in the size of the flow units increases the resistance to flow or the viscosity of the solution.

Solvation cannot account for the considerable increase in viscosity due to the dissolved polymer, however, because the 1600 molecules of methylglucose are as extensively hydrated as is the methylcellulose macromolecule. The chief difference is the cooperative nature of the flow of the latter, in which all 1600 repeat units plus their water of hydration must move together, resulting in a very large flow unit.

A very large amount of solvent is located within a randomly coiled polymer molecule. As mentioned previously, a random coil consists of approximately 0.01% polymer and 99.99% solvent. Only a small portion of that solvent is attached to the polymer by secondary valence forces. The bulk of the solvent is "free."

According to the *free-draining coil* model, the randomly coiled polymer chain in translational motion leaves the free solvent within it largely unperturbed. For this freely permeable coiled chain, theoretic calculations predict that the intrinsic viscosity is proportional to the molecular weight, making the exponent  $a$  in the Mark-Houwink equation (equation (20-8)) unity. At the other extreme, if the random coil were completely impenetrable to external solvent attempting to flow through it and all solvent molecules within the coil moved with the same velocity as the coil itself,  $a$  would equal 0.5.

The viscosity observed for dilute polymer solutions is far greater than that calculated for free-draining coils, indicating that a portion of the free solvent molecules inside a coiled macromolecule is mechanically trapped and is dragged along when the macromolecule moves. Some of the nonsolvating solvent forms part of the flow unit, further increasing its size and frictional resistance.

Newton postulated that a solvent is made up of a stack of parallel, very thin layers. Laminar flow in pure

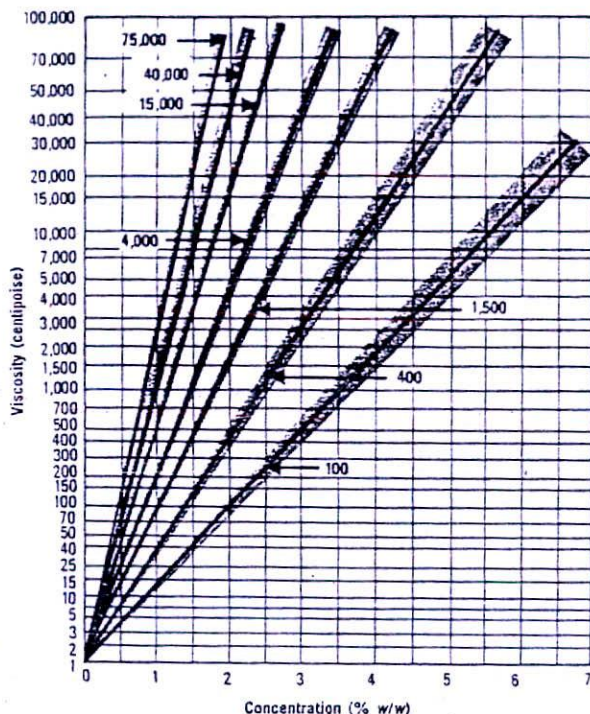


Fig. 20-5. Viscosity of aqueous solutions of different grades of Methocel, methylcellulose, at 20° C versus concentration. Numbers on the curves represent viscosities of 2% (*w/w*) solutions in centipoises. Representative number-average molecular weights corresponding to these numbers written in parentheses are: 26,000 (100 cps); 63,000 (1500 cps); 120,000 (15,000 cps). The vertical scale is eighth-root rather than logarithmic. (Reprinted with permission of The Dow Chemical Company.)

shear consists in the slippage of these layers past one another. Motion is transmitted by friction between adjacent layers. Layers near the source of the shear stress that promotes flow move faster than more distant layers or layers near a wall. There is a velocity gradient, shown by the difference in the length of the arrows representing the velocity of flow of individual layers in Figure 20-6. A randomly coiled macromolecule spans several adjacent solvent layers moving with different velocities. The upper portion of the random coil is subject to a greater shear stress than the lower portion because it is immersed in faster-moving layers. The resultant couple causes the random coil to rotate clockwise. This rotation further increases the frictional resistance of the solution.

The thermal agitation of the solvent molecules combined with the great chain flexibility causes dissolved linear macromolecules to become entangled even at moderate concentrations (Fig. 20-7A). Because each random coil extends through a relatively large volume of solution and because its segments are engaged in continuous Brownian motion, neighboring chains tend to interpenetrate and become entangled. During flow, chain entanglements act as temporary cross-links and pro-

mote the cooperative motion of adjacent, interpenetrating chains. The Huggins equation (equation (20-11)) is valid only for dilute solutions having relative viscosities of 2.0 or less, in which intermolecular entanglements are minimal. Chain entanglements cause the reduced

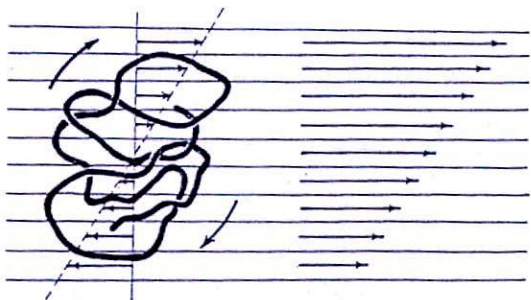


Fig. 20-6. A randomly coiled linear macromolecule in a laminar shear field exhibiting rotational motion. Arrows inside the coil indicate relative velocity of solvent layers. The solvent layer through the center of the coil is "stationary," i.e., moves with the same velocity as the coil. Arrows to the right of the coil indicate absolute velocity of solvent layers.

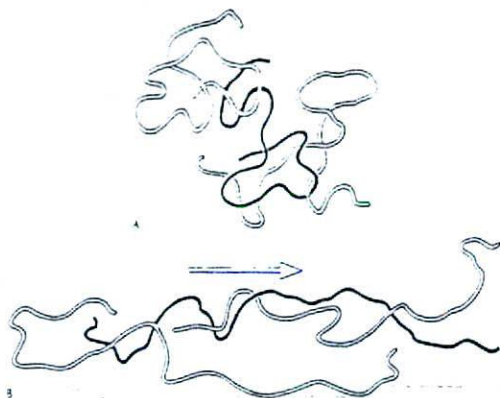


Fig. 20-7. Three randomly coiled linear polymer chains: (A) at rest; (B) in a shear field. (From H. Schott and A. Martin, *American Pharmacy*, 7th Edition, L. W. Dittert, Ed., Lippincott, Philadelphia, 1974.)

viscosity to increase faster with concentration than is predicted by equation (20-11). For the large thickening effects required in pharmaceutical formulations, semilogarithmic relationships between solution viscosity (or reduced viscosity) and concentration, such as those of Figure 20-5, are more representative.

The same factors that promote the unusually high viscosity of polymer solutions cause them to be pseudoplastic or shear-thinning, so that the apparent solution viscosity decreases continuously with increasing shear stress or rate of shear (see Chapter 17).

Under the influence of increasing shear, isolated randomly coiled polymer chains uncoil or unravel progressively, becoming more elongated and streamlined, and line up in the direction of flow. The reduced cross-sectional area of the coiled macromolecules in the flow direction causes smaller disturbances of fewer streamlines in the solvent, reducing the friction. The same coil deformation also reduces the amount of water trapped inside the chains that is dragged along as they move, reducing the size of the flow units and hence the frictional resistance or viscosity of the solution.

The tendency of the random coils to rotate in the shear field depicted in Figure 20-6 is reduced, because chains that are largely uncoiled and elongated in the direction of flow overlap fewer solvent layers, reducing the magnitude of the couple that produces rotation.

Interpenetrating polymer chains are gradually disentangled with increasing shear and tend to flow increasingly as separate units. Consequently, the size of the flow units drops as does the resistance to flow or viscosity. Figure 20-7B pictures the three previously interpenetrating chains largely disentangled, uncoiled, and lined up in the direction of flow.

Brownian motion of chain segments tends to produce roughly spherical random coils that interpenetrate one another and trap mechanically large amounts of sol-

vent. This effect is independent of the applied shear. The opposite effect of partial uncoiling, elongation, and alignment of the random coils, reduction in the amount of trapped solvent, and disentanglement in flow is proportional to the applied shear. Therefore, for each shear stress or rate of shear applied to a polymer solution, there is a corresponding average equilibrium degree of chain uncoiling, elongation, and disentanglement, resulting in a characteristic average size for the flow unit with a characteristic average amount of mechanically trapped solvent and, hence, a characteristic value for the apparent viscosity.

At low shear rates, the effects of Brownian motion prevail. The chains largely retain the conformation of random coils, trap large amounts of solvent, and remain extensively entangled, resulting in large flow units and high apparent viscosity. At high shear rates, the chains are largely uncoiled and elongated, trapping much less solvent, and are mostly disentangled, resulting in small flow units and low apparent viscosity.

Because the polymer chains are exceedingly thin and flexible, they adjust to changing shear rates almost instantaneously, that is, much faster than the response time of viscometers. These short relaxation times preclude hysteresis effects or thixotropy (see Chapter 17). The apparent viscosity of polymer solutions does not depend on the shear history (length of time and level of shear rate at which the polymer solution was stirred previously), but only on the current rate of shear (and on concentration and temperature, of course).

## POLYMER SOLUTIONS—OVERVIEW

Some of the problems and questions encountered in the preparation, characterization, and use of polymer solutions are: what solvent to use; how to mix polymer and solvent; at what concentration to work; how temperature and molecular weight affect this use; concentration; what thermodynamic factors govern dissolution, solution properties, and the solubility limit; how to prevent gelation or precipitation (or how to promote it if gels are desired). These and related topics are discussed in the following sections.

## SOLVENT SELECTION<sup>4,5a,18,19</sup>

Just as for small molecules, polymers dissolve best or most extensively in solvents having similar solubility parameters (defined by equation (10-21)). For a liquid to dissolve a polymer, the difference between their solubility parameters should be less than about 2 (cal/cm<sup>3</sup>)<sup>1/2</sup>.<sup>\*</sup> The heat of vaporization of polymers

\* 1 (cal/cm<sup>3</sup>)<sup>1/2</sup> = 2.046 (joule/cm<sup>3</sup>)<sup>1/2</sup>.

cannot be determined because attempts to evaporate them cause thermal decomposition into low-molecular-weight fragments. Thus, indirect methods are required to determine  $\delta_2$  values for polymers.

An obvious method is to measure the solubility limit of a given polymer fraction at a given temperature in a variety of solvents. Maximum solubility is observed in the solvent whose  $\delta_1$  best matches  $\delta_2$ . Alternatively, fixed amounts of a polymer sample are mixed with constant volumes of a series of solvents having gradually increasing  $\delta_1$  values to give final concentrations comparable to the intended use concentration. The polymer will be soluble at room temperature in a group of solvents covering a certain range of  $\delta_1$  values. Its  $\delta_2$  value is about midpoint in the range of  $\delta_1$  values of the solvents in which the polymer is completely soluble.<sup>12</sup> Polymers are most extensively solvated in solvents of the same  $\delta$  value, resulting in stiffer chains with greater radii of gyration. Hence, plots of intrinsic viscosity of linear polymers dissolved in a variety of solvents versus  $\delta_1$  reach maxima at  $\delta_1 = \delta_2$ .<sup>20</sup>

Cross-linked polymers, for example, rubber vulcanizates, cannot dissolve but swell most extensively in solvents having the same  $\delta$  value.<sup>21</sup> Plots of degree of swelling in different solvents ( $\text{cm}^3$  solvent uptake/g dry polymer) versus  $\delta_1$  reach maxima at  $\delta_1 = \delta_2$ .

Estimates of the solubility parameter of polymers can be made by treating it as an additive and constitutive property based on the molar attraction constants  $F$  of the groups that make up their repeat units:

$$\delta_2 = \frac{\sum F}{V} = \frac{\rho_2 \sum F}{M} \quad (20-16)$$

in which  $V$  and  $M$  are molar volume and molecular weight, respectively, of the repeat unit and  $\rho_2$  is the polymer density.<sup>22-24</sup> Group contributions to the molar attraction constant of a repeat unit are listed in Table 20-2.

**Example 20-3.** Using the data of Table 20-2, calculate the solubility parameter of polymethyl methacrylate. The polymer (Lucite, Plexiglas) has a density of 1.18  $\text{g/cm}^3$ .

$$\begin{aligned} & \left( \text{CH}_2 - \underset{\substack{| \\ \text{CO}-\text{CH}_3 \\ | \\ \text{O}}}{\text{C}} \right) \quad M = 100 \\ & \sum F = 2(-\text{CH}_2) + (-\text{CH}_2) + \left( \underset{\substack{| \\ \text{C}}{\text{---}} \right) + \\ & \left( \underset{\substack{| \\ \text{O}}}{\text{C}} - \text{O} \right) = 2(179) + 133 + 0 + 303 = 794 \\ & \delta_2 = \frac{(1.18)(794)}{100} = 9.4 \text{ (cal/cm}^3)^{1/2} \end{aligned}$$

This value agrees well with the experimentally determined value of  $9.3 \pm 0.2$ .

TABLE 20-2. Molar Attraction Constants  $F$  of Groups in  $(\text{cal/cm}^3)^{1/2}$ /mole repeat unit<sup>16a,22,23</sup>

Group	F	Group	F
$-\text{CH}_3$	179	$-\text{C}-\text{O}-$	303
$-\text{CH}_2-$	133	$\begin{array}{c}   \\ \text{O} \end{array}$	
$-\text{CH}$	67	$-\text{OH}$	240
$-\text{C}-$	0	$-\text{OH}$ aromatic	171
$-\text{CH}=\text{CH}-$	231	$-\text{NH}_2$	230
$-\text{CH}=\text{CH}-$ aromatic	237	$-\text{NH}-$	180
$-\text{O}-$ ether, acetal	108	$-\text{N}-$	61
$-\text{C}-$ $\begin{array}{c}   \\ \text{O} \end{array}$	284	$-\text{C}\equiv\text{N}$	400
		$-\text{Cl}$	206
		$-\text{Cl}$ aromatic	161

Table 20-3 lists solubility parameters for a variety of polymers. The value for a given polymer may vary, depending on the polarity and/or hydrogen-bonding capacity of the solvents used to determine  $\delta_2$ .

The methods outlined here for determining the solubility parameter of polymers fail when the predominant forces between solvent and polymer molecules are dipole forces or hydrogen bonds rather than London dispersion forces. In that case, a refinement consists in splitting the solubility parameter of the solvents into three partial parameters corresponding to the contribution of these three types of secondary valence forces, and plotting the component parameters in a three-dimensional system in which polymers are then located.<sup>12,24,25</sup>

TABLE 20-3. Solubility Parameters of Polymers in  $(\text{cal/cm}^3)^{1/2}$ <sup>12,21-24</sup>

Polymer	$\delta_2$
Polytetrafluoroethylene	6.2
Polydimethyl siloxane	7.6
Polyethylene	7.9
Polyisobutylene	8.0
Polyisoprene (natural rubber)	8.1
Polychloroprene	8.7
Polypropylene	8.7
Polystyrene	8.8-9.3
Polyethyl methacrylate	9.1-9.5
Polyvinyl chloride	9.4-9.8
Polyvinyl acetate	9.6
Polyethylene terephthalate	10.7
Cellulose diacetate	10.9
Polyvinylidene chloride	12.2
Polyvinyl alcohol	12.6-14.2
Polyhexamethylene adipamide (6,6 nylon)	13.6
Polyacrylonitrile	12.5-15.4
Cellulose	15.7

## PREPARING POLYMER SOLUTIONS

The dissolution of solid polymers in solvents occurs in two overlapping stages. Upon contact, the solvent molecules start diffusing immediately into the solid particles, gradually swell them, and transform them into gel particles. The solvated polymer molecules in the swollen particle surface gradually become disentangled from one another and slowly diffuse out into the solvent. The latter stage can be speeded up considerably by stirring, which disentangles matted polymer chains and reduces the thickness of the stagnant liquid layer surrounding each particle.

Most polymers are available as powders or grains. When these are added to a solvent with stirring, the mixing conditions must result in complete wetting and separation of the particles before they can swell and become sticky or gelatinize. Otherwise, the particles tend to aggregate into lumps, in which a swollen, translucent outer layer sometimes even encloses dry powder particles. Because of their large size or small surface areas, these lumps dissolve very slowly.

To cause dispersal of the powders and avoid lumping, the initial solvent temperatures should be conducive to limited swelling and poor dissolution. For instance, methylcellulose is more soluble in cold than in hot water. Therefore, its powder should be dispersed with high shear in about one fourth the total amount of water heated to 80° to 90° C. Because of the poor solvent power of hot water for methylcellulose, the particles are dispersed before their surface layer becomes swollen and tacky. Once the particles are thoroughly wetted and dispersed, the rest of the water is added cold or even as ice to cool the suspension to about 5° C, at which temperature water is an excellent solvent and swells and dissolves the dispersed particles fast with moderate shear. The procedure is similar for hydroxypropylcellulose and hydroxypropyl methylcellulose.

Most water-soluble polymers, such as polyvinyl alcohol and sodium carboxymethylcellulose, are more soluble in hot than in cold water. Therefore, their powders are wetted out and dispersed in ice-cold water, followed by dissolution at 90° C or above for the former and 60° to 65° C for the latter. An alternative procedure to prevent agglomeration of polymer powders into lumps during dissolution consists in prewetting the powders with a water-miscible liquid that does not swell the polymer. For methylcellulose and sodium carboxymethylcellulose, anhydrous alcohol or propylene glycol is recommended.

Some polymers are used in mixed solvents. To dissolve ethylcellulose in an 80% toluene/20% ethyl alcohol mixture, the powder is first slurried in toluene until a uniform dispersion is obtained. The development of surface stickiness, swelling, and dissolution is slow because toluene by itself is only a poor solvent. The alcohol is then added to effect prompt dissolution.

Aqueous polymer solutions, especially of cellulose derivatives, are stored for approximately 48 hours after dissolution to promote full hydration, maximum viscosity and clarity. If salts are to be incorporated, they are added at this point rather than dissolved in the water before adding the polymer; otherwise, the solutions may not reach their full viscosity and clarity.

## THERMODYNAMICS OF POLYMER SOLUTIONS<sup>1,2,8,9,18,25-29</sup>

For the dissolution of a polymer (subscript 2) in a solvent (subscript 1) at constant temperature  $T$ , the free energy of mixing or solution (see Chapter 10) is

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (20-17)$$

in which  $G$ ,  $H$ , and  $S$  represent free energy, enthalpy or heat, and entropy, respectively (defined in Chapters 3 and 10);  $\Delta$  indicates the changes in these parameters during mixing, that is, the differences between  $G$ ,  $H$ , and  $S$  of the solution and of the polymer plus solvent prior to dissolution.

For dissolution to occur spontaneously,  $\Delta G_m$  must be negative. This can be realized by a negative  $\Delta H_m$  (exothermic mixing) or by a positive  $\Delta S_m$  (increased randomness or disorder), preferably at a high temperature. Entropy effects are predominant in the dissolution of polymers at all temperatures.

To dissolve crystalline polymers, the secondary valence forces holding the chains together in the lattice, represented by the heat of fusion (see the following), must be overcome. Polyethylene, because of its high crystallinity, is soluble in solvents such as toluene only when heated within 25° C of its melting point. Cellulose is insoluble in water even though its monomer, dextrose, is very soluble. Attempts to dissolve cellulose in water by heating under pressure result instead in hydrolysis. The melting point of cellulose is so high that it undergoes thermal decomposition rather than melting when heated dry. The following discussion refers to the dissolution of polymers in the amorphous state.

Because the molecular weight and molar volume of polymers are so much greater than those of solvents, concentrations are expressed as volume fractions  $\phi$  (defined in chapter 10) rather than as mole fractions  $X$  as is customary for small solute molecules. In comparatively dilute polymer solutions,  $X_1$  is close to unity, whereas  $\phi_1$  is not.

**Example 20-4.** Calculate the mole fractions and volume fractions of the components in a 5% (w/w) solution of a polystyrene fraction ( $M_2 = 80,000$ ) in toluene ( $M_1 = 92$ ). The densities are: toluene,  $\rho_1 = 0.87$ ; polystyrene,  $\rho_2 = 1.08$ ; solution,  $\rho_{12} = 0.88$  g/cm<sup>3</sup>. Using 100 cm<sup>3</sup> solution as basis for the calculations.

$$(100 \text{ cm}^3 \text{ solution}) \left( \frac{0.88 \text{ g}}{\text{cm}^3} \right) = 88 \text{ g solution}$$

The number of moles is

$$n_1 = (88 - 5 \text{ g}) \left( \frac{\text{mole}}{92 \text{ g}} \right) = 0.902 \text{ mole}$$

and

$$n_2 = (5 \text{ g}) \left( \frac{\text{mole}}{80,000 \text{ g}} \right) = 0.0000625 \text{ mole}$$

The mole fractions are

$$X_1 = \frac{0.902}{0.902 + 0.0000625} = 0.99993 \approx 1.000$$

and

$$X_2 = \frac{0.0000625}{0.902 + 0.0000625} = \frac{0.0000625}{0.902} = 0.00007 \approx 0.000$$

The volumes are

$$V_1 = (88 - 5 \text{ g}) \left( \frac{\text{cm}^3}{0.87 \text{ g}} \right) = 95.4 \text{ cm}^3$$

and

$$V_2 = (5 \text{ g}) \left( \frac{\text{cm}^3}{1.08 \text{ g}} \right) = 4.63 \text{ cm}^3$$

The volume fractions are

$$\phi_1 = \frac{95.4}{95.4 + 4.63} = 0.954$$

$$\phi_2 = \frac{4.63}{95.4 + 4.63} = 0.046$$

As a check,  $0.954 + 0.046 = 1.000$ .

**Heat of Mixing.** The dissolution of polymers is frequently endothermic, with the heat of mixing  $\Delta H_m$  positive (which militates against dissolution because it tends to make  $\Delta G_m$  positive) but small. In terms of the solubility parameter<sup>18,19</sup>:

$$\Delta H_m \approx V_{12}(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (20-18)$$

in which  $V_{12}$  is the volume of the mixture.

In the *Flory-Huggins theory* of polymer solutions, published independently by these two polymer chemists between 1941 and 1944,  $\Delta H_m$  is assumed to be positive and is given by the van Laar expression:

$$\Delta H_m = \chi RT n_1 \phi_2 \quad (20-19)$$

in which  $\chi$  is the Flory-Huggins interaction parameter.

Deviations of polymer solutions from ideal behavior as represented by Raoult's law (see Chapters 5 and 10), for example, are ascribed mainly to the small entropies

\*This dimensionless parameter, sometimes represented by  $u$ , characterizes the interaction energy for a given polymer-solvent combination. It specifies, in multiples of  $RT$ , the excess free energy of transfer of a mole of solvent from the pure solvent to the pure polymer phase. Comparison of equations (20-18) and (20-19) gives

$$\chi = \left( \frac{V_1}{RT} \right) (\delta_1 - \delta_2)^2$$

in which  $V_1$  is the molar volume of the solvent. The interaction parameter  $\chi$  is related to the second virial coefficient  $A_2$  of polymer solutions, which in turn is connected with the coefficient  $B$  of equation (15-12) by the relation<sup>19</sup>  $B = RTA_2 = RT(\omega_2^2/V_1)(0.5 - \chi)$ ;  $\omega_2$  is the partial specific volume of the dissolved polymer.  $A_2$ ,  $B$ , and  $\chi$  can be calculated from osmotic pressure, light scattering, or vapor pressure data. Ideal behavior occurs when  $A_2 = B = 0$  or  $\chi = 0.5$ , making the plot of reduced osmotic pressure versus concentration a straight, horizontal line (Curve 1 of Figure 15-7).

of mixing, resulting from the enormous disparity in size of the molecules of the two components.

**Entropy of Mixing.** Flory and Huggins derived the entropy of mixing of polymer solutions from statistical calculations based on a pseudolattice model, depicted in two dimensions in Figure 20-8. Each lattice point or site can be occupied either by a solvent molecule or by a segment of the polymer chain. A linear polymer molecule is assumed to consist of a number of segments joined flexibly together, each having the same size as a solvent molecule. For polystyrene dissolved in toluene, a segment is identical with a repeat unit. The conformational entropy of mixing is calculated from Boltzmann's relationship  $\Delta S_m = R \ln W$ , in which  $W$  is the number of distinguishable arrangements of filling the lattice with polymer chains and solvent molecules. The result is

$$\Delta S_m = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad (20-20)$$

in which  $\phi_2 = \frac{Nn_2}{n_1 + Nn_2}$  for  $n_2$  moles of polymer molecules of  $N$  segments each, provided polymer and solvent have the same density, because each polymer segment occupies the same volume as one solvent molecule.  $N$  often represents  $DP$ . For polymer samples with a broad molecular weight distribution,  $n_2 \ln \phi_2$  is summed over all fractions, becoming  $\sum n_{2,i} \ln \phi_{2,i}$ . As before,  $\phi_1 + \sum \phi_{2,i} = 1.00$

Since both  $\phi_1$  and  $\phi_2$  are less than 1, their logarithms are negative and  $\Delta S_m$  is positive, as one would expect.

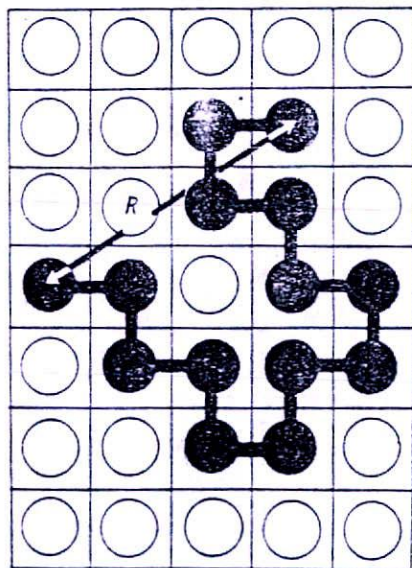


Fig. 20-8. Placement of a 14-segment, 13-link polymer chain occupying 14 lattice sites and of 21 solvent molecules on a  $5 \times 7$  two-dimensional lattice.  $\phi_1 = \frac{21}{35} = 0.60$ ;  $\phi_2 = \frac{14}{35} = 0.40$ .

because mixing causes an increase in disorder or randomness. A positive  $\Delta S_m$  makes a negative contribution toward  $\Delta G_m$  according to equation (20-17), promoting dissolution.

**Example 20-5.** Estimate the entropy change when dissolving 78 g of a polystyrene fraction with a molecular weight of 52,000 in 1090 cm<sup>3</sup> of toluene (molecular weight, 92 g/mole). Densities are 1.07 g/cm<sup>3</sup> for the polystyrene and 0.87 for toluene. The numbers of moles are

$$n_1 = (1090 \text{ cm}^3) \left( \frac{0.87 \text{ g}}{\text{cm}^3} \right) \left( \frac{\text{mole}}{92 \text{ g}} \right) = 10.3 \text{ mole}$$

and

$$n_2 = (78 \text{ g}) \left( \frac{\text{mole}}{52,000 \text{ g}} \right) = 0.0015 \text{ mole}$$

The polymer volume is

$$V_2 = (78 \text{ g}) \left( \frac{\text{cm}^3}{1.07 \text{ g}} \right) = 72.9 \text{ cm}^3$$

and the volume fractions are

$$\phi_1 = \frac{1090}{1090 + 72.9} = 0.9373$$

and

$$\phi_2 = \frac{72.9}{1090 + 72.9} = 0.0627$$

As a check,  $0.9373 + 0.0627 = 1.0000$ . The entropy of mixing is

$$\begin{aligned} \Delta S_m &= - \left( \frac{1.987 \text{ cal}}{\text{mole} \cdot \text{K}} \right) (2.303) [(10.3 \text{ mole}) \\ &\quad \times (\log 0.9373) + (0.0015 \text{ mole}) (\log 0.0627)] \\ &= 1.33 \text{ cal}^\circ\text{K} \end{aligned}$$

If the styrene had not been polymerized, the entropy change of mixing 78 g or 0.75 mole liquid styrene monomer with 1090 cm<sup>3</sup> or 948 g or 10.3 mole toluene can be calculated by equation (1) of chapter 2 in reference 18 for ideal solutions as

$$\begin{aligned} \Delta S_m &= -R(n_1 \ln X_1 + n_2 \ln X_2) \\ &= - \left( \frac{1.987 \text{ cal}}{\text{mole} \cdot \text{K}} \right) (2.303) \left[ (10.3 \text{ mole}) \right. \\ &\quad \times \log \left( \frac{10.3}{10.3 + 0.75} \right) + (0.75 \text{ mole}) \\ &\quad \left. \times \log \left( \frac{0.75}{10.3 + 0.75} \right) \right] \\ &= 5.45 \text{ cal}^\circ\text{K} \end{aligned}$$

This equation for  $\Delta S_m$  of two kinds of small molecules is quite similar to equation (20-20). The  $\Delta S_m$  value for dissolving the monomer is four times larger than that for dissolving the same amount of polymer.

**Free Energy of Mixing.** Combining equations (20-17), (20-19), and (20-20) gives the overall free energy of dissolution per mole of lattice sites or of solvent:

$$\Delta G_m = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_1 \phi_2) \quad (20-21)$$

The first two terms in the parentheses, representing entropy contributions, are negative. The third term, representing the enthalpy contribution, is positive and militates against dissolution.

This equation shows why two or more molten polymers are, as a rule, incompatible. When the solvent in a polymer solution is replaced by an equal volume of a

second liquid polymer,  $n_1$  decreases substantially at constant  $\phi_1$ , making the first term in the parentheses very small. The sum of the first two terms, which are negative, would then be smaller than the third term, which is positive, making  $\Delta G_m$  positive. The process occurring spontaneously, because its free energy change is negative, would be the opposite of mixing, namely, phase separation of the two liquid polymers. In fact, even dilute solutions of two different kinds of polymers in the same solvent frequently separate into two phases upon mixing, with each phase containing practically all of one of the polymers.

Differentiation of equation (20-21) with respect to  $n_1$  gives the partial molar free energy of mixing (defined on p. 67):

$$\frac{\Delta \bar{G}_1}{RT} = \ln a_1 = \ln \phi_1 + \left( 1 - \frac{1}{N} \right) \phi_2 - \chi \phi_2^2 \quad (20-22)$$

This is the basic equation of the Flory-Huggins theory. The activity of the solvent,  $a_1$ , is equal to  $p_1/p_1^\circ$  (see Raoult's law on pp. 107 and 218). Thus, equation (20-22) can be verified by measuring the vapor pressure of the solvent. The agreement between calculated and observed activities is generally fair to good. Alternative expressions are still being developed.

#### PHASE SEPARATION<sup>1,4,5,6a,9,28,29,30</sup>

Equation (20-22) predicts when phase separation will occur in a polymer solution: if  $\chi$  and, hence,  $\Delta H_m$ , is zero or negative,  $\Delta \bar{G}_1$  is negative, and mixing occurs, over the entire range of compositions or  $\phi$  values, helped by the mutual attraction between polymer and solvent. The interaction parameter  $\chi$  is actually composed not only of the temperature-dependent enthalpy term (equation (20-19)) but also of a temperature-independent, entropy-related term. For most polymer-solvent combinations,  $\chi$  is positive and increases with decreasing temperature as the solvent becomes progressively poorer, causing  $\Delta G_m$  and  $\Delta \bar{G}_1$  to become progressively less negative. When they change from negative to positive, at a critical value  $\chi_c$ , phase separation begins.

In binary solvent-polymer systems, equilibrium between two phases requires that  $\Delta \bar{G}_1$  be the same in both phases, which corresponds to the requirement that the first and second derivative of  $\Delta \bar{G}_1$  with respect to  $\phi_2$  be zero. Applying this requirement to equation (20-22) results in the three equations, (20-23), (20-24), and (20-25), relating the  $\chi_c$  and  $\phi_{2,c}$  values at the critical solution temperature  $T_c$ , and  $T_c$  itself, to the polymer molecular weight:

$$\chi_c = \frac{(1 + \sqrt{N})^2}{2N} \cong \frac{1}{2} + \frac{1}{\sqrt{N}} \quad (20-23)$$

$N$ , the number of polymer segments equivalent in size



to a solvent molecule, represents the ratio of the molar volumes of polymer to solvent and, frequently, the  $DP$ . The critical solution temperature (also called upper consolute temperature; cf. p. 40 and Figures 2-14 and 2-16) is the temperature above which complete solution occurs over the entire range of concentrations. Phase separation begins only below  $T_c$ . This equation indicates that, as the chain length  $N$  or  $DP$  increases,  $\chi_c$  falls, and the temperature at which a polymer fraction first becomes completely soluble increases. This effect is small, however, because the minimum value of  $\chi_c$  for very high molecular weights is 0.5.

The dependence of phase separation on molecular weight can be used for polymer fractionation. The temperature of a polymer solution at nearly critical conditions ( $\chi$  only slightly below 0.5) is lowered progressively. Alternatively, the polymer sample is dissolved in a good solvent, and a liquid miscible with the solvent that does not dissolve the polymer ( $\chi \gg 0.5$ ) is added in successive increments at constant temperature. Examples of polymer-solvent-precipitant systems are gelatin-water-ethanol and polystyrene-benzene-methanol.<sup>12</sup> Both processes render the solvent increasingly poorer and gradually increase the  $\chi$  value of the system. The solution exceeds the  $\chi_c$  value of the highest-molecular-weight fraction first, causing it to precipitate in a separate layer (see the following), which is removed from the main volume of the solution. With further cooling or nonsolvent addition, the  $\chi_c$  values of progressively lower-molecular-weight fractions are exceeded, causing them to precipitate in turn. The oligomer or low-molecular-weight tail, possessing the highest  $\chi_c$ , remains in solution the longest. Refractionation is usually used to obtain sharper fractions.

The critical volume fraction of the polymer is

$$\phi_{2,c} = \frac{1}{1 + \sqrt{N}} \approx \frac{1}{\sqrt{N}} \quad (20-24)$$

As  $N \approx DP \approx 10^3$  to  $10^4$  for typical polymers,  $\phi_{2,c} \approx 0.03$  to  $0.01$  or 3 to 1 volume percent. Polymer solubilities near the critical temperature generally amount to only a few percent ( $v/v$ ).

Typical phase diagrams for four polystyrene fractions in cyclohexane<sup>30</sup> are shown in Figure 20-9. They resemble binary phase diagrams of low-molecular-weight solutes (e.g., Fig. 2-14), except that the present curves are highly asymmetric and nearly coincide with the temperature axis for low  $\phi_2$  values. The areas above the curves are single-phase regions representing complete miscibility; those beneath the curves represent two-phase regions or partial miscibility. The fraction with a molecular weight of 43,600 has a critical solution temperature of 19° C. Above that temperature, there is complete miscibility; below it, phase separation occurs. The 15° tie line (defined on p. 40) indicates that at 15° C, solutions of that polystyrene

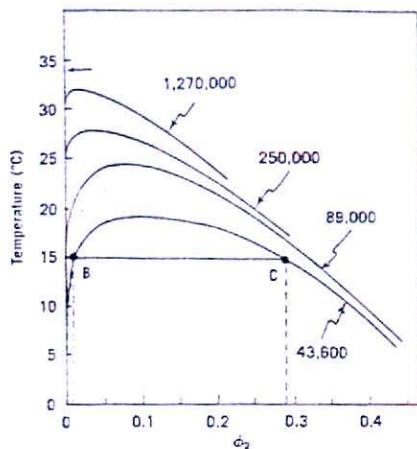


Fig. 20-9. Binary phase diagram of polystyrene-cyclohexane showing the precipitation temperature as a function of polymer concentration for four polystyrene fractions. Numbers represent viscosity-average molecular weights (From A. R. Shultz and P. J. Flory, *J. Am. Chem. Soc.* 74, 4762, 1952, reprinted with permission from the *Journal of the American Chemical Society*. Copyright 1952, American Chemical Society.)

fraction separate into two phases: The one represented by Point B, with  $\phi_2 = 0.007$ , is almost pure solvent. Even the polymer-rich phase represented by Point C has  $\phi_2 = 0.29$  only, that is, it contains 71% ( $v/v$ ) solvent. These facts indicate that the solvent is much more soluble in the polymer than the polymer is in the solvent.

The coexistence of two liquid phases, one the nearly pure solvent and the other a moderately concentrated polymer solution, is called *coacervation*. The polymer-rich phase, called a *coacervate*, is a viscous liquid or sometimes a gelatinous semisolid, depending on the polymer concentration and molecular weight.

The critical solution temperature  $T_c$  is related to the molecular weight by

$$\frac{1}{T_c} = \frac{1}{\theta} \left( 1 + \frac{D}{\sqrt{M}} \right) \quad (20-25)$$

in which  $D$  is a constant for the polymer-solvent combination. The Flory temperature  $\theta$  is the critical temperature,  $T_c$ , for a polymer of infinite molecular weight. The  $\theta$  temperatures for some polymer-solvent systems are found in Table 20-4. According to equation (20-25),  $T_c$  increases as the molecular weight of the polymer fraction increases. Qualitatively, this is corroborated by Figure 20-9.

**Example 20-6.** Using the data obtainable from Figure 20-9, show that equation (20-25) is correct and evaluate  $D$ . For polystyrene in cyclohexane  $\theta$  is 34.0° C (see Table 20-4). Rearranging equation (20-25) gives

TABLE 20-4. Theta Temperatures for Various Polymer-Solvent Systems for Polymers of Infinite Molecular Weight<sup>1,2,7</sup>

Polymer	Solvent	$\theta$ , °C
Polystyrene	Cyclohexane/toluene( $\frac{87}{13}$ )	15
	Cyclohexane	34.0
Polyethylene	Cyclohexanol	83.5
	n-Hexane	133
	n-Octanol	180
Polymethyl methacrylate	Toluene	-65
	Acetone	-55
	Methyl ethyl ketone/isopropanol( $\frac{50}{50}$ )	25.0
	n-Propanol	84.4
Polyvinyl alcohol	Water	-102
	Dioxane	-10
Povidone	Water/acetone( $\frac{23}{27}$ )	25
	Isopropanol	30
Polyoxyethylene	n-Hexane	-173
Polydimethyl siloxane	Toluene	-30
	Methyl ethyl ketone	20

$$D = \frac{(\theta - T_c) \sqrt{M}}{T_c}$$

The  $T_c$  values (highest temperatures reached by the curves) for the four polystyrene fractions listed in the following tabulation were read from Figure 20-9.  $D$  is then calculated for each of the fractions with this equation with  $T_c$  expressed in degrees Kelvin.

$M \times 10^{-3}$	$T_c$ , °C	$T_c$ , °K	$D$
$\infty$	34.0	307.2	—
1,270	31.1	304.3	10.7
250	27.6	300.8	10.6
89	23.6	296.8	10.5
43.6	19.2	292.4	10.6
			mean $10.6 \pm 0.1$

Since all four fractions give  $D$  values that are identical within  $\pm 1\%$ ,  $D$  is constant, corroborating equation (20-25).

Alternatively, the plot of the reciprocal of  $T_c$  in degrees absolute versus  $1/\sqrt{M}$  for the four polystyrene fractions is linear. Extrapolation to  $1/\sqrt{M} = 0$  (corresponding to  $M = \infty$ ) according to equation (20-25) gives  $T_c = \theta = 307.2^\circ \text{K} = 34.0^\circ \text{C}$ , in perfect agreement with the experimental value of  $\theta$ . The slope of that plot is 0.03429. According to equation (20-25), the slope equals  $D/\theta$ . Since  $\theta = 307.2$ ,  $D = (0.03429)(307.2) = 10.5$ , in agreement with the average  $D$  value calculated previously.

As the temperature of the polymer solutions is lowered, the solvent becomes progressively poorer until, at the Flory or  $\theta$ -temperature, the solvent becomes what is known as a  $\theta$ -solvent. At these conditions, the polymer-solvent interaction is so weak that it is balanced exactly by the polymer-polymer interaction, that is, by the attraction between polymer segments that are at some distance from one another along the chain but that approach each other during its writhing motion. The latter, long-range intramolecular interaction tends to contract the random coil while solvation tends to expand it, thereby increasing the end-to-end distance and radius of gyration. Because the two types of interactions are in exact balance at the

$\theta$ -temperature, polymer chains assume their unperturbed dimensions. The dimensions are governed only by bond lengths, bond angles, and the potential hindering bond rotation as caused, for instance, by bulky side groups, but not by segment-solvent nor by segment-segment attractions. The excluded volume vanishes at the  $\theta$ -temperature, and the chains interpenetrate one another freely with no net interaction, as they do in the molten state. At temperatures a few degrees below the  $\theta$ -temperature, the intermolecular attraction among polymer segments is sufficiently stronger than the attraction between polymer segments and solvent molecules to cause precipitation. Above the  $\theta$ -temperature, solvation predominates.

At the  $\theta$ -temperature, the partial molar free energy due to polymer-solvent interaction is zero, and the solution behaves ideally over a range of concentrations: The second virial coefficient becomes zero and  $\chi = 0.5$ . Hence, polymer solutions are often studied at the  $\theta$ -temperature.

Since the polymer chain is tightly coiled and compact in a  $\theta$ -solvent, the exponent  $a$  in the Mark-Houwink equation (equation (20-8)) becomes 0.5. The reason is as follows. At  $\theta$ -conditions, the chain behaves ideally, that is, as if it were freely jointed and perfectly flexible so that its shape is described by the random-flight model (see p. 564). The chain dimensions are unperturbed by polymer-solvent and intramolecular polymer-polymer interactions (excluded volume effect), and the square of the root-mean-square end-to-end distance,  $\langle R^2 \rangle$ , is proportional to the molecular weight  $M$  (see equation (20-14)). The hydrodynamic volume of a randomly coiled chain, comprising the volume of the random coil plus that of the solvent inside it, is always proportional to the cube of the end-to-end distance. For the ideal random coil, it is also proportional to  $M^{3/2}$  because  $\langle R^2 \rangle$  is proportional to  $M$ . The anhydrous volume is always proportional to  $M$ . The hydrodynamic volume thus increases faster with increasing chain length than the anhydrous volume by the solvation factor  $M^{3/2}/M = M^{1/2}$ . Since the intrinsic viscosity depends on the size of the flow unit or the solvation factor, it is proportional to  $M^{1/2}$  at  $\theta$ -conditions where the random coil behaves ideally, making  $a = 0.5$ . Equation (20-8) then becomes

$$[\eta]_{\theta} = k_{\theta} M^{0.5} \quad (20-8a)$$

If the random coil does not behave ideally because solvation and other factors that reduce chain flexibility expand it and increase  $\langle R^2 \rangle$  beyond the unperturbed value corresponding to the  $\theta$ -state,  $a$  will increase above 0.5.

$\theta$ -Temperatures for different polymer-solvent combinations extrapolated to infinite molecular weight are listed in Table 20-4. A more extensive list and a summary of the experimental methods used to determine  $\theta$ -solvents are given in reference 12.

## GEL FORMATION, COACERVATION, AND MICROENCAPSULATION<sup>31</sup>

Gels are semisolids characterized by relatively high yield values. Their plastic viscosity may be low, but they possess some elasticity. Gels consist of two interpenetrating continuous phases. One is solid, composed of highly asymmetric particles with a high surface area; the other is liquid. The solid phase extending throughout an aqueous gel may be a "house of cards" type built by bentonite clay platelets 10 to 50 Å thick whose positively charged edges attract their negatively charged faces, or it may consist of microscopic soap fibers produced by crystallization of soap molecules into ribbons. The liquid phase permeates the solid scaffolding, filling the voids.

Polymer solutions are prone to setting to gels because the solute consists of long and flexible chains of molecular thickness that tend to become entangled, attract each other by secondary valence forces, and even crystallize. When the three-dimensional polymerization of multifunctional monomers (functionality  $\geq 3$ ) reaches a given conversion, gelation occurs at a sharp "gel point." Cross-linking of dissolved polymer molecules also causes their solutions to gel. Both types of reaction produce permanent gels, held together by primary valence forces.

Reversible gel formation of polymer solutions, involving only secondary valence forces, occurs when the solvent becomes so poor that the polymer precipitates. Intermolecular contacts between polymer segments form in preference to contacts between polymer segments and solvent molecules, turning points of chain entanglements into physical cross-links. This kind of gel formation occurs when the temperature of the solution is lowered 10° C or more below the  $\theta$ -temperature. For instance, aqueous gelatin solutions set to gels when cooled to temperatures in the vicinity of 30° C (the gel melting point). These temperatures decrease somewhat as the concentration increases. Aqueous methylcellulose solutions gel when heated above ~50° C (thermal gelation) because the polymer is less soluble in hot water and precipitates.

Because of its pronounced tendency to crystallize, polyethylene separates from solutions in organic solvents as a crystalline solid. Since single polyethylene chains extend through several crystalline regions and connect them, gels are formed when the polyethylene concentration is high enough to fill the entire solution with a continuous network of interconnected chains, held together by shared crystallites (see the following). Polyethylene resins dissolved in hot mineral oil at a 5% concentration crystallize on cooling to form the hydrocarbon ointment base called Plastibase or Jelene (see p. 500). Hot aqueous solutions of pectin and agar containing only 2 to 5% of these polysaccharides set to gels on cooling, immobilizing 95 to 98% of interstitial water.

Other polymers require higher concentrations to gel or solidify their entire solutions.

Gels often contract on standing, and some of the interstitial liquid is squeezed out. This phenomenon, called *syneresis*, is due to additional crystallization or to the formation of additional contact points between polymer segments on aging. In the case of irreversible gels formed by three-dimensional polymerization, continuing cross-linking or polycondensation reactions tighten the polymer network and shrink the solid phase.

If not enough polymer is present to form a fibrous network extending throughout the entire solution when phase separation occurs, gelatinous precipitates containing typically about 10 to 20% polymer separate from almost pure solvent (see previous discussion). The compositions of these two phases are given by Points C and B in Figure 20-9. Such phase separations can be brought about not only by cooling the solutions below  $T_c$ , but also by adding a nonsolvent liquid and thereby raising  $x$  above  $x_c$ .

In the case of aqueous polymer solutions, the addition of salts can also cause phase separation, which is called *salting out*. Abstraction of water of hydration from polymers due to the addition of large amounts of salts (several molal), which require water for their own hydration, raises the effective  $\phi_2$  of polymer solutions above their critical value  $\phi_{2,c}$ . Polyelectrolytes are particularly prone to salting out. The electrostatic repulsion between approaching segments that, together with hydration, contributed to their solubility in water is swamped by the addition of large amounts of inorganic ions, further contributing to precipitation. Combinations of a water-miscible nonsolvent liquid and a salt produce synergistic salting-out effects.

The formation of such gels or gelatinous precipitates is reversible. Heating of gelatin gels or of Plastibase above their gel melting points, cooling of methylcellulose gels below the temperature of thermal gelation, and addition of more solvent after a nonsolvent liquid or a salt has produced phase separation, revert these two-phase systems to homogeneous solutions.

The same factors that bring about reversible gelation or separation of a gelatinous precipitate from polymer solutions may, under different conditions of composition and temperature, lead to *coacervation*, that is, the separation of small droplets of a polymer-rich, second liquid phase. On standing, these droplets eventually coalesce. This phenomenon has been studied extensively with gelatin by Bungenberg de Jong.<sup>31</sup> Maintaining a temperature of 50° C to avoid gel formation, the addition of alcohol or of sodium sulfate to isoelectric aqueous gelatin solutions produces coacervation. For instance, a system containing 13% gelatin, 38% water, and 49% alcohol separated a coacervate containing 27% gelatin, 37% water, and 36% alcohol. Another system with a composition of 9% gelatin, 80% water, and 11%

TABLE 20-4. Theta Temperatures for Various Polymer-Solvent Systems for Polymers of Infinite Molecular Weight<sup>1,2,7</sup>

Polymer	Solvent	$\theta$ , °C
Polystyrene	Cyclohexane/toluene( $\frac{47}{13}$ )	15
	Cyclohexane	34.0
	Cyclohexanol	83.5
Polyethylene	n-Hexane	133
	n-Octanol	180
Polymethyl methacrylate	Toluene	-65
	Acetone	-55
	Methyl ethyl ketone/isopropanol( $\frac{50}{50}$ )	25.0
	n-Propanol	34.4
Polyvinyl alcohol	Water	-102
	Dioxane	-10
Povidone	Water/acetone( $\frac{15}{87}$ )	25
	Isopropanol	30
Polyoxyethylene	n-Hexane	-173
Polydimethyl siloxane	Toluene	-30
	Methyl ethyl ketone	20

$$D = \frac{(\theta - T_c)\sqrt{M}}{T_c}$$

The  $T_c$  values (highest temperatures reached by the curves) for the four polystyrene fractions listed in the following tabulation were read from Figure 20-9.  $D$  is then calculated for each of the fractions with this equation with  $T_c$  expressed in degrees Kelvin.

$M \times 10^{-3}$	$T_c$ , °C	$T_c$ , °K	$D$
$\infty$	34.0	307.2	—
1,270	31.1	304.3	10.7
250	27.6	300.8	10.6
89	23.6	296.8	10.5
43.6	19.2	292.4	10.6
			mean 10.6 ± 0.1

Since all four fractions give  $D$  values that are identical within ±1%,  $D$  is constant, corroborating equation (20-25).

Alternatively, the plot of the reciprocal of  $T_c$  in degrees absolute versus  $1/\sqrt{M}$  for the four polystyrene fractions is linear. Extrapolation to  $1/\sqrt{M} = 0$  (corresponding to  $M = \infty$ ) according to equation (20-25) gives  $T_c = \theta = 307.2^\circ \text{K} = 34.0^\circ \text{C}$ , in perfect agreement with the experimental value of  $\theta$ . The slope of that plot is 0.03429. According to equation (20-25), the slope equals  $D/\theta$ . Since  $\theta = 307.2$ ,  $D = (0.03429)(307.2) = 10.5$ , in agreement with the average  $D$  value calculated previously.

As the temperature of the polymer solutions is lowered, the solvent becomes progressively poorer until, at the Flory or  $\theta$ -temperature, the solvent becomes what is known as a  $\theta$ -solvent. At these conditions, the polymer-solvent interaction is so weak that it is balanced exactly by the polymer-polymer interaction, that is, by the attraction between polymer segments that are at some distance from one another along the chain but that approach each other during its writhing motion. The latter, long-range intramolecular interaction tends to contract the random coil while solvation tends to expand it, thereby increasing the end-to-end distance and radius of gyration. Because the two types of interactions are in exact balance at the

$\theta$ -temperature, polymer chains assume their *unperturbed dimensions*: The dimensions are governed only by bond lengths, bond angles, and the potential hindering bond rotation as caused, for instance, by bulky side groups, but not by segment-solvent nor by segment-segment attractions. The excluded volume vanishes at the  $\theta$ -temperature, and the chains interpenetrate one another freely with no net interaction, as they do in the molten state. At temperatures a few degrees below the  $\theta$ -temperature, the intermolecular attraction among polymer segments is sufficiently stronger than the attraction between polymer segments and solvent molecules to cause precipitation. Above the  $\theta$ -temperature, solvation predominates.

At the  $\theta$ -temperature, the partial molar free energy due to polymer-solvent interaction is zero, and the solution behaves ideally over a range of concentrations: The second virial coefficient becomes zero and  $\chi = 0.5$ . Hence, polymer solutions are often studied at the  $\theta$ -temperature.

Since the polymer chain is tightly coiled and compact in a  $\theta$ -solvent, the exponent  $a$  in the Mark-Houwink equation (equation (20-8)) becomes 0.5. The reason is as follows. At  $\theta$ -conditions, the chain behaves ideally, that is, as if it were freely jointed and perfectly flexible so that its shape is described by the *random-flight model* (see p. 564). The chain dimensions are unperturbed by polymer-solvent and intramolecular polymer-polymer interactions (excluded volume effect), and the square of the root-mean-square end-to-end distance,  $\langle R^2 \rangle$ , is proportional to the molecular weight  $M$  (see equation (20-14)). The hydrodynamic volume of a randomly coiled chain, comprising the volume of the random coil plus that of the solvent inside it, is always proportional to the cube of the end-to-end distance. For the ideal random coil, it is also proportional to  $M^{3/2}$  because  $\langle R^2 \rangle$  is proportional to  $M$ . The anhydrous volume is always proportional to  $M$ . The hydrodynamic volume thus increases faster with increasing chain length than the anhydrous volume by the solvation factor  $M^{3/2}/M = M^{1/2}$ . Since the intrinsic viscosity depends on the size of the flow unit or the solvation factor, it is proportional to  $M^{1/2}$  at  $\theta$ -conditions where the random coil behaves ideally, making  $a = 0.5$ . Equation (20-8) then becomes

$$[\eta]_{\theta} = k_{\theta} M^{0.5} \quad (20-8a)$$

If the random coil does not behave ideally because solvation and other factors that reduce chain flexibility expand it and increase  $\langle R^2 \rangle$  beyond the unperturbed value corresponding to the  $\theta$ -state,  $a$  will increase above 0.5.

$\theta$ -Temperatures for different polymer-solvent combinations extrapolated to infinite molecular weight are listed in Table 20-4. A more extensive list and a summary of the experimental methods used to determine  $\theta$ -solvents are given in reference 12.

### GEL FORMATION, COACERVATION, AND MICROENCAPSULATION<sup>31</sup>

Gels are semisolids characterized by relatively high yield values. Their plastic viscosity may be low, but they possess some elasticity. Gels consist of two interpenetrating continuous phases. One is solid, composed of highly asymmetric particles with a high surface area; the other is liquid. The solid phase extending throughout an aqueous gel may be a "house of cards" type built by bentonite clay platelets 10 to 50 Å thick whose positively charged edges attract their negatively charged faces, or it may consist of microscopic soap fibers produced by crystallization of soap molecules into ribbons. The liquid phase permeates the solid scaffolding, filling the voids.

Polymer solutions are prone to setting to gels because the solute consists of long and flexible chains of molecular thickness that tend to become entangled, attract each other by secondary valence forces, and even crystallize. When the three-dimensional polymerization of multifunctional monomers (functionality  $\geq 3$ ) reaches a given conversion, gelation occurs at a sharp "gel point." Cross-linking of dissolved polymer molecules also causes their solutions to gel. Both types of reaction produce permanent gels, held together by primary valence forces.

Reversible gel formation of polymer solutions, involving only secondary valence forces, occurs when the solvent becomes so poor that the polymer precipitates: Intermolecular contacts between polymer segments form in preference to contacts between polymer segments and solvent molecules, turning points of chain entanglements into physical cross-links. This kind of gel formation occurs when the temperature of the solution is lowered 10° C or more below the  $\theta$ -temperature. For instance, aqueous gelatin solutions set to gels when cooled to temperatures in the vicinity of 30° C (the gel melting point). These temperatures decrease somewhat as the concentration increases. Aqueous methylcellulose solutions gel when heated above ~50° C (thermal gelation) because the polymer is less soluble in hot water and precipitates.

Because of its pronounced tendency to crystallize, polyethylene separates from solutions in organic solvents as a crystalline solid. Since single polyethylene chains extend through several crystalline regions and connect them, gels are formed when the polyethylene concentration is high enough to fill the entire solution with a continuous network of interconnected chains, held together by shared crystallites (see the following). Polyethylene resins dissolved in hot mineral oil at a 5% concentration crystallize on cooling to form the hydrocarbon ointment base called Plastibase or Jelene (see p. 500). Hot aqueous solutions of pectin and agar containing only 2 to 5% of these polysaccharides set to gels on cooling, immobilizing 95 to 98% of interstitial water.

Other polymers require higher concentrations to gel or solidify their entire solutions.

Gels often contract on standing, and some of the interstitial liquid is squeezed out. This phenomenon, called *syneresis*, is due to additional crystallization or to the formation of additional contact points between polymer segments on aging. In the case of irreversible gels formed by three-dimensional polymerization, continuing cross-linking or polycondensation reactions tighten the polymer network and shrink the solid phase.

If not enough polymer is present to form a fibrous network extending throughout the entire solution when phase separation occurs, gelatinous precipitates containing typically about 10 to 20% polymer separate from almost pure solvent (see previous discussion). The compositions of these two phases are given by Points C and B in Figure 20-9. Such phase separations can be brought about not only by cooling the solutions below  $T_c$  but also by adding a nonsolvent liquid and thereby raising  $\chi$  above  $\chi_c$ .

In the case of aqueous polymer solutions, the addition of salts can also cause phase separation, which is called *salting out*. Abstraction of water of hydration from polymers due to the addition of large amounts of salts (several molar), which require water for their own hydration, raises the effective  $\phi_2$  of polymer solutions above their critical value  $\phi_{2,c}$ . Polyelectrolytes are particularly prone to salting out. The electrostatic repulsion between approaching segments that, together with hydration, contributed to their solubility in water is swamped by the addition of large amounts of inorganic ions, further contributing to precipitation. Combinations of a water-miscible nonsolvent liquid and a salt produce synergistic salting-out effects.

The formation of such gels or gelatinous precipitates is reversible. Heating of gelatin gels or of Plastibase above their gel melting points, cooling of methylcellulose gels below the temperature of thermal gelation, and addition of more solvent after a nonsolvent liquid or a salt has produced phase separation, revert these two-phase systems to homogeneous solutions.

The same factors that bring about reversible gelation or separation of a gelatinous precipitate from polymer solutions may, under different conditions of composition and temperature, lead to *coacervation*, that is, the separation of small droplets of a polymer-rich, second liquid phase. On standing, these droplets eventually coalesce. This phenomenon has been studied extensively with gelatin by Bungenberg de Jong.<sup>31</sup> Maintaining a temperature of 50° C to avoid gel formation, the addition of alcohol or of sodium sulfate to isoelectric aqueous gelatin solutions produces coacervation. For instance, a system containing 13% gelatin, 33% water, and 49% alcohol separated a coacervate containing 27% gelatin, 37% water, and 36% alcohol. Another system with a composition of 9% gelatin, 80% water, and 11%

sodium sulfate separated a coacervate of 25% gelatin, 69% water, and 6% sodium sulfate.

Among the systems polymer-solvent-nonsolvent liquid capable of undergoing coacervation are natural rubber-benzene-methanol, polystyrene-xylene-petroleum ether, polyvinyl acetate-methyl ethyl ketone-*n*-hexane, polyvinyl acetate-chloroform-isopropanol, and ethylcellulose-dichloromethane-*n*-hexane. For instance, coacervation occurs when a 9% ethylcellulose solution in dichloromethane is combined with two to four times its volume of *n*-hexane.<sup>22</sup>

Coacervation is the basis for one method of *microencapsulation* of solid or liquid drugs that has wide commercial application, for instance, in the manufacture of sustained-release dosage forms.<sup>33,34</sup> The core material, that is, the drug to be encapsulated, must be available as a fine powder, preferably micronized, or as an immiscible liquid. It is dispersed (or, if it is a liquid, emulsified) in the polymer solution prior to coacervation and must therefore be insoluble in the liquid medium. The precipitant liquid or salting-out electrolyte is added with continuous stirring. The coacervate droplets form mainly around the core particles, which act as nuclei because, even prior to the addition of precipitants, the solid surfaces are coated with a layer of adsorbed polymer, albeit a very thin one. Stirring is maintained to prevent the coacervate droplets, which engulf the core particles, from coalescing. The coacervate phase must be fluid enough to wrap completely around the core particles but viscous enough to avoid being sheared off the surface of the particles during stirring. To transform the viscous liquid coacervate envelopes into solid, continuous polymer shells completely encasing the core particles, they must be dried and hardened. The first step usually consists in cooling the system, preferably to a temperature below the second-order transition temperature of the polymer (see the following). Cooling will concentrate, shrink, and harden the polymeric wall material. The polymer may also be cross-linked to shrink and harden the microcapsule shells further, causing them to tighten and collapse around the core particles. Gelatin walls are commonly cross-linked with formaldehyde, which forms intermolecular methylene bridges. The microencapsulated particles with their shells still swollen by solvents are washed by decantation and finally dried. Commercial microcapsules have diameters in the range between 5 and 500  $\mu\text{m}$ , and wall thicknesses between 1 and 10  $\mu\text{m}$ .

## POLYMERS IN THE SOLID STATE—OVERVIEW

Some polymers are useful as elastic closures, others as strong packaging films or fibers, and still others as tough plastic containers. The end uses of solid polymers depend on their mechanical, permeability, electric, thermal, and optical properties, which in turn are

governed by their chemical nature, processing variables, and morphologic characteristics.

Among the pertinent factors, besides molecular weight and molecular weight distribution, are the following. The chemical structure of the polymers depends on the nature of the atoms and bonds in the backbone, for example, the stereoregular configuration of chain atoms and the presence of rings or double bonds in the chain, and on the polarity, frequency, and size of the substituent or side groups. These factors determine the flexibility and symmetry of the chains, the closeness of chain packing in the solid state and, hence, the magnitude of the interchain attraction, cohesion, and strength of the polymers.

In addition to the factors just mentioned, the crystallinity of polymers depends on thermodynamic aspects. Crystallinity and orientation also depend on processing conditions such as the rate of extrusion or injection and especially on the rate of cooling when the polymer is processed in the molten state, and on drawing or other postextrusion treatment. Branching, especially short-chain branching, and random copolymerization interfere with crystallization. For amorphous polymers, cross-linking (vulcanization) or the use of fillers may be desirable. Polymer processing methods are described in the following section.

The chemical composition and processing variables together determine the molecular order and morphologic characteristics of polymeric objects, specifically, the degree of crystallinity, the degree of chain orientation or alignment, the number and size of crystallites and spherulites, and any preferred orientation of the crystallites, as well as the susceptibility to developing flaws (cracks, crazing). These and related topics are discussed in the following section.

## MECHANICAL PROPERTIES<sup>35-39</sup>

Solids can be deformed by tension, bending, shear, torsion, and compression. The following discussion is limited to tension, which is the mode most widely tested. The cause of deformation is stress, that is, the applied force  $F$  per unit area of cross-section  $A$ . Stress in tension is called *tensile stress*  $\sigma$ . The most widely used units of stress are: lb/in.<sup>2</sup> or psi, dyne/cm<sup>2</sup>, and newton/m<sup>2</sup> or N/m<sup>2</sup>. The conversion factors are 1 psi = 6.895  $\times 10^4$  dyne/cm<sup>2</sup> = 6895 N/m<sup>2</sup>. The effect of stress is deformation or strain. Strain in tension is called *elongation*  $\epsilon$ . It is the increase in length  $\Delta L = L - L_0$  relative to the original length  $L_0$ , that is,  $\epsilon = (L - L_0)/L_0 = \Delta L/L_0$ , in which  $L$  is the length under a given tensile stress. Elongation is dimensionless because it is expressed as a fraction of the original length. It can also be expressed as a percentage, 100  $\Delta L/L_0$ .

Ideal or elastic solids are deformed when subjected to stress but regain their original shape and dimensions

TABLE 20-5. Mechanical Properties of Some Solids<sup>25,27,38</sup>

Material	Young's Modulus (psi × 10 <sup>-3</sup> )	Tensile Strength (psi × 10 <sup>-3</sup> )	(Tensile Strength) Specific Gravity (psi × 10 <sup>-3</sup> )
Glass	87	10	4
Steel	320	60	7.6
Copper	174	39	4.3
Aluminum	100	9	3.3
Polystyrene	5	7	6.6
Polymethyl methacrylate	4.6	9	7.6
Polyvinyl chloride	4.7	7	5
6,6 Nylon	2.9	10	8.8
Cellulose acetate (secondary)	2.9	6.6	5.1
High-density polyethylene	1.7	5.3	5.5
Low-density polyethylene	0.36	2.2	2.4
Natural rubber (vulcanized, unfilled)	0.0019	2.9	3.1
Tendon	0.19	—	—
Gelatin gel, 30% solids	0.00022	—	—

when the stress is released. According to *Hooke's law*, the stress is directly proportional to the strain. In tension:

$$\frac{F}{A} = E \left( \frac{L - L_0}{L_0} \right) \quad (20-26)$$

The proportionality constant  $E$ , called *Young's modulus* or *modulus of elasticity*, is a measure of the hardness, stiffness, or rigidity (or softness, flexibility, or pliability) of the solid, that is, of its resistance to deformation:  $E = \Delta\sigma/\Delta\epsilon$ . Characteristic values are listed in Table 20-5, in which glass, metals, and tendon are included for comparison. Steel has an elastic modulus  $320/2.9 = 110$  times greater than 66 nylon, indicating that it is 110 times stiffer or harder and that the force required to stretch a steel wire by, say, 1% is 110 times greater than that required to stretch an equally thick nylon filament by the same amount. Nylon is 1500 times stiffer than pure gum rubber because the ratio of their moduli is  $2.9/0.0019 \approx 1500$ .

Representative stress-strain curves in tension or load-elongation curves are plotted in Figure 20-10 for steel, a typical tough plastic such as high-density polyethylene, a thermoplastic cellulose derivative or a nylon, and a typical elastomer. The curve for the plastic is discussed in detail. Along the linear portion  $LO$ , the elongation is directly proportional to the applied stress, following Hooke's law, equation (20-26). Young's modulus is the slope of  $LO$  or the tangent of the angle  $LOC$ . The linear portion of the curve for steel is about 100 times steeper than for the plastic while the one for the rubber is about 1000 times flatter, reflecting the magnitude of their moduli of elasticity. Beyond  $L$ , the plot curves and Hooke's law no longer applies.

Point  $R$  is the *yield point*, and the corresponding stress  $M$  is the *yield stress*. The plastic behaves elastically when subjected to stresses below  $M$ . When stresses up to the yield stress are applied and then removed, a plastic specimen that had stretched along  $OLR$  retracts along the same curve  $RLO$  and assumes

its original length. The curve shows no hysteresis, and the sample undergoes no permanent elongation. Beyond  $R$ , where the applied stresses exceed  $M$ , the specimen exhibits plasticity, becoming ductile and flowing or creeping under nearly constant stress, resembling a highly viscous liquid. The corresponding portion  $RAH$  of the stress-strain curve is nearly horizontal. This phenomenon is called *cold flow* or *creep*. If the stress is released at  $A$ , the sample retracts along  $AC$ . The nonrecoverable deformation  $OC$  is called *permanent set*. Cold flow causes a change in the structure of the plastic. Crystalline domains may melt and reform with an orientation parallel to the direction of flow. Disordered, randomly coiled chains lined up parallel to one another during cold flow may crystallize, and flaws may heal. Thus, the curve may turn up after  $H$  because the structural rearrangement stiffened the specimen, increasing its modulus and resistance to

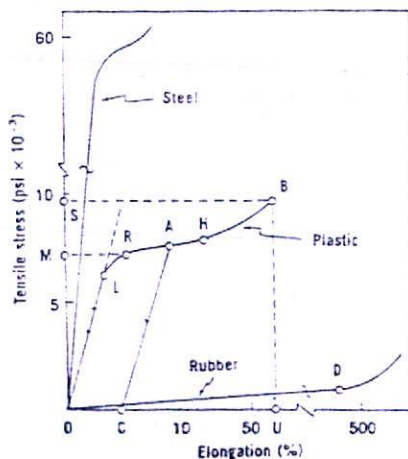


Fig. 20-10. Three stress-strain curves. Psi is an abbreviation of  $\text{lb/in}^2$ . See the text for discussion of the curves.

deformation. This phenomenon is called *strain hardening*. At *B*, the sample ruptures: *U* is the ultimate elongation or the *elongation to (or at) break*; *S* is the *tensile strength* or ultimate strength. See Table 20-5 for representative values.

Since tensile strength measures the ability of solids to withstand rupture, plastics are generally weaker than metals. Because plastics are also lighter, they have approximately the same tensile strength as metals when compared on an equal weight basis (as is done in the last column of Table 20-5, headed Tensile Strength/Specific Gravity) rather than on an equal volume basis (as is done in the third column, headed Tensile Strength). Even though elastomers are much softer than plastics, their tensile strength is not much lower.

The time during which solids are subjected to stress may affect their behavior. Stresses smaller than the yield stress, if applied for long periods of time, may produce creep (see p. 468 for creep of pharmaceutical solids). Faster testing speeds, that is, higher rates of elongation, result in higher tensile strength and lower elongation to break. Another related fact is that the tensile strength determined at low speeds, which is closest to an equilibrium value, is usually smaller by at least an order of magnitude than the tensile strength calculated from the cohesion of the polymer, using data such as those of Table 20-7. The explanation for these two facts is the existence of cracks, notches, or voids in the piece of plastic or strip of film being tested. These flaws represent weak spots where failure or rupture will occur. The cracks or voids grow and propagate under stress; if the specimen is stretched slowly, their rate of propagation keeps up with the rate of elongation of the entire specimen. Extensive propagation of cracks or voids lowers the tensile strength of the specimen because the intact material next to these flaws bears

the entire load distributed over a reduced area and ruptures.

Temperature has a profound effect on the mechanical properties of polymers. All data in this chapter refer to room temperature unless stated otherwise. Young's modulus and the tensile strength of plastics are reduced by raising the temperature, while their elongation to break is increased. Elastomers, on the other hand, become stiffer when the temperature is raised, that is, their modulus of elasticity increases. Joule observed in 1859 that a rubber band, stretched to a given length by a weight suspended from it, contracted upon heating and stretched upon cooling. The increase in tension of a stretched rubber band on heating resembles the increase in pressure of a gas with increasing temperature.

The areas under the stress-strain curves of Figure 20-10 represent the product, stress  $\times$  elongation, which is the energy or work necessary to break the polymeric material. It is equal to

$$\int_0^{\epsilon=B} \sigma \, d\epsilon$$

and constitutes a measure of its toughness or brittleness. In Table 20-6, polymers are divided into five categories according to a qualitative description of their mechanical behavior and the corresponding stress-strain characteristics. Hard or stiff polymers, as opposed to soft ones, are characterized by high moduli. Strong (as opposed to weak) polymers have high tensile strengths. Tough (as opposed to brittle) polymers have large areas under their stress-strain curves and require large amounts of energy to break under stress, combining high or at least moderate tensile strength with high elongation.

Stiff and brittle plastics such as polystyrene and

TABLE 20-6. Qualitative Description and Stress-Strain Characteristics of Various Polymers at Room Temperature<sup>37,40</sup>

Polymer Description	Characteristics of Stress-Strain Curve					Examples
	Young's Modulus	Yield Stress	Tensile Strength	Elongation to Break		
Soft, weak	Low	Low	Low	Low to moderate		Soft gels
Soft, tough	Low	Low	Moderate	Very high (20-1000%)		Elastomers, plasticized polyvinyl chloride
Hard, brittle	High	None (break around yield point)	Moderate to high	Very low (<2%)		Polystyrene, polymethyl methacrylate, phenol-formaldehyde resins
Hard, strong	High	High	High	Moderate (~5%)		Rigid polyvinyl chloride, impact-resistant polystyrene polyblends
Hard, tough	High	High	High	High (cold drawing or "necking")		Nyions, ethyl cellulose, cellulose nitrate, cellulose acetate



polymethyl methacrylate have high moduli and high tensile strength, that is, their stress-strain curves rise steeply. They break at elongations of only about 2%, however, undergoing little or no cold flow: their breaking point *B* occurs at about the same point at which other polymers of comparable modulus have a yield point *R*. Their stress-strain curves extend over narrow areas, indicating that the work required to break them is small and that they have low impact resistance. Some commercial grades of polystyrene are toughed considerably by incorporating 5 to 10% of an elastomer. Elastomers are soft, and their stress-strain curves are shallow at low elongations. The curves frequently turn up rather sharply at elongations of about 200 or 300%, however, and extend to ultimate elongations as high as 700% or more, so that the areas under the curves are large and the elastomers tough.

Most hard and tough polymers such as thermoplastic cellulose derivatives, nylons, and the engineering plastics acetal, polycarbonate, and polysulfone owe their high elongation to *cold drawing* or "necking": The specimens do not elongate uniformly but, after the yield point, develop a constricted region or neck that undergoes large, permanent elongation. As the stretching continues, the constricted region propagates in both directions toward the specimen clamps. The cross-sectional area of the drawn portion or neck remains constant during the stretching. Not all polymers fit into the five categories. For instance, low-density polyethylene (LDPE) has a moderate modulus, yield stress, and tensile strength and a high elongation. It is moderately hard and tough.

The end use of polymers is governed largely by their mechanical properties at room temperature. Elastomers fall into the "soft, tough" category, whereas plastics fall into one of the three "hard" categories (hard, brittle; hard, strong; hard, tough). Table 20-7 lists the distinctive mechanical properties of commercial elastomers, plastics, packaging films, and textile fibers. The latter two have similar properties and are grouped together. They are stronger and stiffer than plastics because, after extrusion, they are cold drawn, which brings their chains into alignment, promotes more extensive crystallization, and preferentially orients the crystallites (see the following sections).

The properties of plastics listed in Table 20-7 are those of thermoplastic resins that are processed in the molten state rather than those of highly cross-linked,

thermosetting resins such as melamine-formaldehyde. Plastics are generally intermediate in mechanical properties between the weaker and softer elastomers and the stronger and stiffer films or fibers, overlapping both groups. Some polymers such as 66 nylon and polypropylene can function both as plastics and as films or fibers. Cold drawing produces orientation and higher crystallinity, which increases their tensile strength about ten times and doubles or triples their modulus, bringing them from the plastics to the film/fiber range.

### INTERCHAIN COHESIVE FORCES

The forces responsible for the mechanical strength of packaging films and plastic containers are the secondary valence forces between adjacent polymer chains rather than the primary valence forces joining together the backbone atoms of single chains. This fact is corroborated by three observations. First, mechanical stresses causing failure are usually much smaller than the strength of covalent bonds. When a solid polymeric object is ruptured by an external stress, the weak secondary valence forces between chains are the ones to yield and break because they are the weakest links in the object; these weak forces cause chains to slip and move past one another and produce deformation, flow, and failure. Second, primary valence bonds are not generally broken when a packaging film tears or a plastic container ruptures, and the molecular weight of the polymer is not reduced. Thirdly, the energy or strength of the covalent bonds between carbon-carbon, carbon-oxygen, and carbon-nitrogen atoms forming the backbones of the chains of most commercial films, fibers, plastics, and elastomers are all in the 70 to 85 kcal/mole range. This range is much too narrow to account for the vast differences in mechanical strength of the four categories of polymeric objects shown in Table 20-7.

Two models showing the need for lateral attraction between chains are a parallel bundle of pencils and a bowl of cooked spaghetti, with the pencils and noodles representing polymer chains. The individual pencils are strong, and even the individual noodles are much stronger than the mass in the bowl. Without some glue or lateral adhesion, the bundle of pencils would fall apart and the mass of spaghetti could be pulled apart without breaking any noodles, that is, the assemblies

TABLE 20-7. Typical Mechanical Properties of Commercial Elastomers, Plastics, and Films/Fibers

End Use	Tensile Strength (psi $\times 10^{-3}$ )	Young's Modulus (psi)	Ultimate Elongation (%)
Elastomers	1-4	10-400	300-900
Plastics	2-12	$10^4-5 \times 10^5$	2-200
Films/Fibers	20-100	$10^5-10^6$	10-50

would have negligible mechanical strength and would be much weaker than the component elements or chains.

Table 20-8 lists individual polymers, the structure of their repeat units, and the magnitude of their interchain attraction energy or cohesion. The latter values were calculated by summing the attractive energies for all groups in 5-Å lengths of polymer chains, assuming that each chain is surrounded by four other chains. The polymers are listed in order of increasing polarity corresponding to increasing attraction between chains. They fall into three categories:

Cohesive energies between 1.0 and 2.0 kcal/mole are the lowest. These polymers are primarily hydrocarbons and only dispersion forces, the weakest of the secondary valence forces, are involved in interchain attraction. The solid polymers in this category are elastomers, with the lowest mechanical strength. Plastics are stronger. Their cohesive energies range from 2 to 5 kcal/mole and involve dipole-dipole attraction in addition to dispersion forces. The highest interchain attraction, above 5 kcal/mole, produces materials with the highest strength, suitable for use as films and fibers. The high cohesion is due to interchain attraction by

TABLE 20-8. Energy of Interchain Attraction or Cohesion for Different Polymers<sup>1</sup>

Polymer	Repeat Unit	Cohesion (kcal/mole)
Polyethylene	$\text{CH}_2\text{—CH}_2\text{—}$	1.0
Polysisobutylene	$\begin{array}{c} \text{CH}_3 \\   \\ \text{—CH}_2\text{—C—} \\   \\ \text{CH}_3 \end{array}$	1.2
cis-Polyisoprene (natural rubber)	$\begin{array}{c} \text{CH}_3 \\   \\ \text{—CH}_2\text{—C=CH—CH}_2\text{—} \end{array}$	1.3
Polychloroprene	$\begin{array}{c} \text{Cl} \\   \\ \text{—CH}_2\text{—C=CH—CH}_2\text{—} \end{array}$	1.8
Polyvinyl chloride	$\begin{array}{c} \text{—CH}_2\text{—CH—} \\   \\ \text{Cl} \end{array}$	2.6
Polyvinyl acetate	$\begin{array}{c} \text{—CH}_2\text{—CH—} \\   \\ \text{O—CO—CH}_3 \end{array}$	3.2
Polystyrene	$\begin{array}{c} \text{—CH}_2\text{—CH—} \\   \\ \text{C}_6\text{H}_5 \end{array}$	4.0
Polyvinyl alcohol	$\begin{array}{c} \text{—CH}_2\text{—CH—} \\   \\ \text{OH} \end{array}$	4.2
Cellulose acetate (secondary)	$\begin{array}{c} \text{CH}_2\text{O—CO—CH}_3 \\   \\ \text{—O—} \text{C}_5\text{H}_7\text{O—} \\   \\ \text{OH} \quad \text{O—CO—CH}_3 \end{array}$	4.8
Cellulose	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{—O—} \text{C}_5\text{H}_7\text{O—} \\   \\ \text{OH} \quad \text{OH} \end{array}$	6.2
6 Nylon	$\begin{array}{c} \text{—C—NH—(CH}_2\text{)}_5\text{—} \\    \\ \text{O} \end{array}$	5.6
Silk fibroin	$\begin{array}{c} \text{—C—NH—CH—} \\    \quad   \\ \text{O} \quad \text{R} \end{array}$	9.8

ELASTOMERS

PLASTICS

FILMS and FIBERS

hydrogen bonds, the strongest secondary valence forces, in addition to dispersion and dipole-dipole attractive forces.

Since the solubility parameter and the energy of interchain attraction are both a measure of the polarity of the polymers, they should be related. Comparison of the  $\delta_2$  values of Table 20-3 and the cohesion values of Table 20-8 gives the following linear regression,<sup>41</sup> with a correlation coefficient of 0.93:

$$\text{cohesion} = -3.90 + 0.676 \delta_2 \quad (20-27)$$

There are two exceptions in Table 20-8. Polyethylene, according to its calculated cohesion, belongs after the elastomers, but according to its actual mechanical strength belongs among the stronger plastics. Polyvinyl alcohol has the strength of fiber- or film-forming polymers even though its calculated cohesion places it among the plastics, which are weaker. The chains of these two polymers are smooth and symmetric, permitting them to pack or fit together closely.<sup>1</sup> Van der Waals intermolecular attraction forces fall off with the seventh power of the interchain distance. Interchain distances in angstroms for amorphous polymers at room temperature, obtained from the halos in their x-ray diffraction patterns, are as follows: polyethylene, 5.5; *cis*-polyisoprene, 5.9; polyisobutylene, 7.8. The kinky configuration of the natural rubber chain and the two bulky methyl side groups in polyisobutylene produce larger interchain distances and, hence, smaller interchain attraction and lower mechanical strength than those of polyethylene, which has a straight and smooth chain.

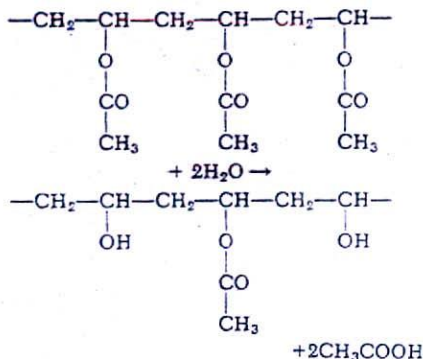
In summary, for polymers to be mechanically strong, they should have smooth and symmetric chains capable of fitting together closely, without bulky side groups, and a high concentration of polar functional groups.

### CRYSTALLINITY

Maximum interchain attraction, resulting in greatest mechanical strength, requires that the polymer chains be packed as densely as possible and that the polar groups of adjacent chains be in registry, so that there is an efficient geometric matching-up of interacting dipoles or hydrogen-bonding groups between chains. Thus, to be mechanically strong, a polymer should be highly crystalline. Conversely, a weaker and softer polymer for use as an elastomer can be obtained by preventing crystallization, for example, by random copolymerization.

Polyvinyl alcohol crystallizes in a fully extended zigzag conformation. The repeat distance along the chain axis, 2.52 Å, corresponds to layers of hydroxyl groups largely hydrogen bonded. This arrangement, plus the relatively small size of the hydroxyl groups resulting in smooth chains, produces a highly crystalline polymer.<sup>4</sup> Polyvinyl alcohol is manufactured by the

hydrolysis of polyvinyl acetate. Commercial products are available with varying degrees of hydrolysis and, hence, a wide range of solubilities and strengths. Hydrolysis is a random process, leaving residual acetyl groups randomly distributed along the polymer chains. A partially hydrolyzed product:



is in effect a random copolymer of polyvinyl alcohol and polyvinyl acetate. Residual acetyl groups, because of their bulk, keep adjacent chains apart and lower the density and crystallinity of the product. They reduce the interchain dispersion forces and interrupt the matching of hydrogen-bonding hydroxyl groups between adjacent chains, resulting in lower mechanical strength and higher gas permeability.

Polyethylene crystallizes with the chains in the fully extended planar zigzag conformation packed side by side with their axes parallel to one another. Isotactic polypropylene (see the following section) crystallizes with the chains in a helical conformation, three repeat units per turn. In random copolymers of ethylene and propylene in the 40/60 to 60/40 range, the chains can fit into neither the zigzag lattice of polyethylene nor the helical lattice of polypropylene. On cooling from the melt, the chains remain disordered and the copolymers, called *polyolefins*, are amorphous. In addition to being virtually free of extractables, they contain no spherulites (see under *Morphology*) because they lack crystallinity, which increases their translucency. Furthermore, their modulus or stiffness (see under *Mechanical Properties*) is low. The resultant higher impact resistance compared with that of the two crystalline homopolymer resins, combined with the low water vapor transmission rate common to all hydrocarbon plastics, makes the polyolefins useful as containers for purified water and parenteral solutions.

Short-chain branching disrupts the crystallinity of solid polymers and weakens them mechanically. Depending on the polymerization process, polyethylene can be mostly linear (high-density polyethylene, HDPE), producing a tough plastic that crystallizes well and is mechanically strong, or it can be branched, with *n*-butyl or pentyl side chains, which result in lower

TABLE 20-9. Effect of Short-Chain Branching on Crystallinity and Other Properties of Polyethylene<sup>1,2</sup>

Property	Polyethylene Resin of:		
	Low Density (LDPE)	Medium Density	High Density (HDPE)
Methyl groups per 1000 C atoms	83-16	46-8	0
Density (g/cm <sup>3</sup> )	0.910-0.925	0.925-0.940	0.941-0.965
Crystallinity (%)	37-50	50-62	62-75
Tensile modulus (psi × 10 <sup>-3</sup> )	3-25	25-55	60-150
Permeability* to:			
Oxygen	3.4-1.5	1.4-0.9	0.8-0.5
Carbon dioxide	12.5-5.4	5.1-3.0	2.3-1.0
Water vapor	65-42	39-29	5-15

\* Transmission rate,  $\frac{\text{cm}^3 \text{ gas, STPKcm thickness}}{(\text{cm}^2 \text{ area}) \text{ sec (cm Hg)} 10^{10}}$

crystallinity, lower density, and a weaker, softer, and more permeable plastic (low-density polyethylene, LDPE). HDPE is used in containers. LDPE in packaging films. There are also polyethylene resins of intermediate density. Table 20-9 shows the effect of branching in polyethylene resins on some of their properties. The extent of branching is measured by IR as the number of methyl groups per 1000 carbon atoms: each methyl group represents one branch. Since branching interferes with the close packing or crystallization of the chains, it results in polymers with fewer and smaller crystalline domains and a large fraction of amorphous or disordered domains having therefore lower density. The greater softness of LDPE compared with HDPE is reflected in a lower modulus. Diffusion through polymers occurs primarily in the amorphous regions, whereas the crystalline domains are comparatively impervious to penetrants. Thus, the permeability toward gases and vapors increases with decreasing crystallinity or density, being lowest for HDPE.

By measuring the density  $\rho_{\text{obs}}$  of a polymer sample or its reciprocal, the specific volume  $v_{\text{obs}}$ , one can calculate how crystalline it is, that is, the weight fraction  $\alpha$  of crystalline domains or  $1 - \alpha$  of amorphous domains;  $100\alpha$  represents percent crystallinity. Specific volumes are additive. If  $v_{\text{am}}$  is the specific volume of the completely amorphous polymer, extrapolated from the specific volume of the molten polymer at different temperatures above the melting point to room temperature, and  $v_{\text{cr}}$  is the specific volume of the perfectly crystalline polymer, calculated from its unit cell dimensions obtained from x-ray diffraction, then

$$v_{\text{obs}} = \alpha v_{\text{cr}} + (1 - \alpha)v_{\text{am}}$$

Hence,

$$\alpha = \frac{v_{\text{am}} - v_{\text{obs}}}{v_{\text{am}} - v_{\text{cr}}} \quad (20-28)$$

**Example 20-7.** For polyethylene,  $\rho_{\text{cr}} = 1.000$  and  $\rho_{\text{am}} = 0.861$  g/cm<sup>3</sup> at 25° C; hence  $v_{\text{cr}} = 1.000$  and  $v_{\text{am}} = 1.161$  cm<sup>3</sup>/g. Calculate the percent crystallinity for a low-density sample with  $\rho_{\text{obs}} = 0.912$  and a medium-density sample with  $\rho_{\text{obs}} = 0.933$  g/cm<sup>3</sup>. For LDPE.

$$\alpha = \frac{1.161 - 1.0912}{1.161 - 1.000} = 0.401$$

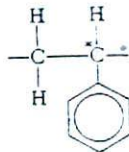
For the medium-density sample,

$$\alpha = \frac{1.161 - 1.0933}{1.161 - 1.000} = 0.554$$

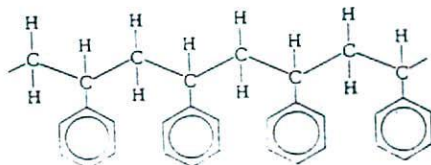
The LDPE is 40% crystalline and 60% amorphous; the medium-density sample is 55% crystalline and 45% amorphous.

### TACTICITY<sup>6a</sup>

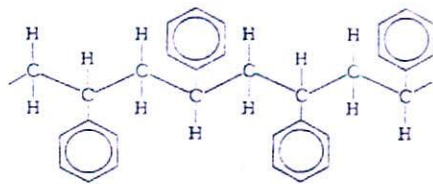
Commercial polystyrene used for manufacturing plastic vials and other vinyl homopolymers such as polymethyl methacrylate or polyvinyl acetate cannot crystallize, even though their chains have little or no branching. In vinyl polymers, every other chain carbon atom is essentially asymmetric without, however, producing optical activity.



Three different types of homopolymers with different configurations and different physical properties can be produced, depending on the method and conditions of polymerization. With the main chain of a polystyrene molecule in the planar zigzag conformation, the phenyl groups can all be on the same side of the main chain, that is, they are all either above or below the plane of the main chain:



In this arrangement, all tertiary carbon atoms have the same configuration, that is, all are *d*- (or *l*-):  $-ddddd-$ . This is the *isotactic* form. In the *syndiotactic* configuration, the phenyl groups lie alternatively above and below the plane of the backbone:



Syndiotactic polymers are alternating  $-dldld-$  copolymers. Both classes of polymers are produced through stereospecific, stereoregular, or coordination polymerization generally employing Ziegler-Natta catalysts, such as mixtures of an aluminum alkyl and a titanium chloride. Isotactic and syndiotactic polymers crystallize owing to their regular structures. Because of the theoretic importance of these structures and the commercial importance of the polymers, Ziegler and Natta were jointly awarded the 1963 Nobel prize in chemistry.

In *atactic* polymers, there is no regularity in the configuration of the asymmetric carbon atoms. The substituent groups lie randomly above and below the plane of the backbone. Atactic polymers are random  $-dlldldll-$  copolymers and, because of their lack of stereoregularity, cannot crystallize. Free-radical addition polymerization generally produces atactic polymers. The effect of stereoregularity on selected physical properties is shown in Table 20-10.

#### MORPHOLOGY<sup>64</sup>

Crystalline domains are called *crystallites*. They alternate with more disordered, "amorphous" regions. Single polymer chains often run through several contiguous crystallites and amorphous regions. When

TABLE 20-10. Effect of Stereoregularity on Some Polymer Properties

	Density (g/cm <sup>3</sup> )	Melting Point or Softening Temperature (°C)
Polypropylene		
Atactic, amorphous	0.85	75
Isotactic, crystalline	0.93	160
Syndiotactic, crystalline	0.90	138
Polystyrene		
Atactic, amorphous	1.06	100
Isotactic, crystalline	1.11	235

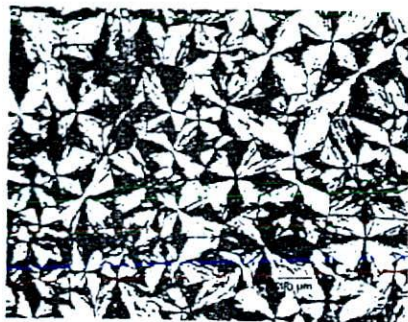
polymers are processed from the melt or from solution into films or molded objects, crystallization starts when nuclei develop here and there in the evaporating solution or in the cooling melt. The nuclei form as a few chain segments in the randomly coiled and entangled mass line up, and arrange themselves into an orderly lattice. Crystallization proceeds as these nuclei grow into crystallites until all the solvent has evaporated or all the melt has solidified.

When neighboring crystallites grow, quite a few segments of the chains forming these crystallites cannot be incorporated into them but remain outside in a disordered state. Being trapped between crystallites immobilizes such segments and prevents them from aligning and fitting into a lattice. When the mass cools, these segments are frozen into their disordered conformations as amorphous regions. If the molten polymer is cooled slowly or annealed, more chain segments have the opportunity to arrange or incorporate themselves into crystallites. Quenching freezes more segments into amorphous regions because the solidification is too sudden to permit extensive ordering and results in lower crystallinity. These considerations explain why even objects of HDPE, a polymer possessing smooth, symmetric chains without branches or side groups, are seldom more than 80% crystalline.

Single crystals of HDPE, visible in the electron microscope as thin, flat, rhombohedral platelets, form when very dilute solutions (~0.1%) of the polymer are slowly cooled. Electron diffraction measurements indicate that the polymer chains in single crystals of HDPE and other polymers are oriented perpendicularly to the faces of these lamellae. Since polymer molecules in extended conformation are at least 1000 Å long, whereas the platelets are only about 100 Å thick, the chains in these single crystals are folded and double back over themselves repeatedly. Chain folding occurs in the crystallites of many synthetic polymers.

**Spherulites.** Crystallization in synthetic polymers often produces polycrystalline aggregates called *spherulites*. These are spherical, radially symmetric arrays of fibrillar crystallites ranging in diameter from less than one micron to several millimeters. Microtome sections examined under the microscope show fibers or feathery radiating from the center of a spherulite like spokes of a wheel (see Fig. 20-11). Spherulites are quite common in plastics. It is not known exactly why they form, but they grow from their centers outward until they meet other growing spherulites. Individual polymer chains are folded and oriented perpendicularly to the fiber axes or spherulitic radii.

Slow cooling or annealing of molten plastics produces fewer but large spherulites; quenching or the addition of nucleating agents produces more and small spherulites. Because the boundaries between spherulites are weak regions prone to failure under stress, spherulites, especially large ones, reduce the strength and toughness of plastics and tend to make them brittle. Fortu-



(a)



(b)

Fig. 20-11. (a) Spherulites of polyethylene crystallized from a thin film of melt. Transmission photomicrograph between crossed polarizers showing characteristic extinction crosses. (b) Spherulites of isotactic polypropylene crystallized from a thin film of melt. Photomicrograph with oblique reflected light showing radiating fibrous texture. (Courtesy of Dr. H. D. Keith, Bell Laboratories.)

nately, there is some overlapping and interpenetration between fibers of adjacent spherulites across their boundaries, providing mechanical interlocking and reinforcing the boundaries. One visible effect of spherulites is the opacity of polyethylene bottles.

**Microcrystalline Cellulose.** This form of cellulose consists entirely of crystalline material. Its manufacture involves the following steps. Native cellulose is treated with dilute mineral acid, which penetrates the amorphous, disordered regions relatively fast because of their lower density and hydrolyzes the accessible cellulose chain segments located there into water-soluble fragments. The acid is washed out before it penetrates the ordered and dense crystalline regions appreciably, leaving the crystallites intact. Washing also removes the soluble degradation products of the cellulose that constituted the amorphous regions. The remaining mass consists of the "unhinged" crystallites, which are no longer connected by the chain segments from the amorphous regions. Wet milling of the mass of crystallites, followed by spray-drying of their aqueous suspension, results in spongy, porous aggregates of fibrillar bundles that are used as tablet additives.

Additional shear breaks up the aggregated bundles into the individual needle- or rod-shaped crystallites averaging  $0.3 \mu\text{m}$  in length and  $0.02 \mu\text{m}$  in width. These colloidal particles thicken water and other liquids to thixotropic vehicles and, at higher concentrations, to semisolids.

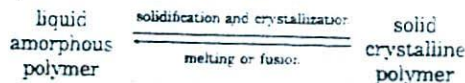
## ORIENTATION

Drawing fibers with or without the application of heat causes permanent elongation or cold flow and promotes the alignment or orientation of polymer chains and crystallites in the direction of stretch, that is, parallel to the fiber axis. This orientation process, called cold drawing, is carried out at a temperature below the melting point but above the glass transition temperature of the polymer (see the following). Cold drawing often causes crystallites to melt and to reform with parallel orientation. Even noncrystallizing polymers can be oriented by drawing. Polymers capable of crystallization crystallize more extensively when their chains are lined up parallel to each other. Drawing increases the strength and stiffness of fibers.

When films are extruded through a flat die and drawn in the direction of extrusion, alignment causes increased strength in that direction but reduced strength and the tendency to split in the transverse direction. Films are therefore oriented biaxially, that is, they are drawn simultaneously in the direction of extrusion and in the transverse direction. This is easily accomplished by extruding the film through a die with a circular slit and stretching the tubular film with air pressure applied from the inside to the zone where it is solidifying (cf. p. 591 and Fig. 20-15).

## THERMODYNAMICS OF FUSION AND CRYSTALLIZATION<sup>64</sup>

Equation (20-17), previously applied to the binary system solvent-polymer, is now applied to the one-component system consisting of the polymer alone, to describe the reversible process:



$$\Delta G_f = \Delta H_f - T \Delta S_f \quad (20-17a)$$

The subscripts are changed from  $m$  (for mixing) to  $f$  (fusion) or  $c$  (crystallization).

**Heats of Crystallization and Fusion.** The latent heat of crystallization or solidification,  $\Delta H_{c/f}$ , is negative because the process is exothermic. It represents the bond energies released during crystallization by the increased interchain attraction through secondary valence forces. When the polymer solidifies, the chains arrange themselves into an orderly lattice. The polar

groups of adjacent chains are matched and the inter-chain distances reduced (i.e., the density increases). Both factors maximize the formation of secondary valence bonds between adjacent chains by dispersion and dipole forces. Dipole forces depend on the presence of polar groups as measured, for instance, by the solubility parameter. Heat of fusion,  $\Delta H_f$ , represents the energy that must be supplied to break a large fraction of the secondary valence forces between neighboring chains as the polymer melts. High-density polyethylene has a heat of crystallization of  $-1850$  cal/mole mer and a heat of fusion of  $+1850$ . The corresponding values for low-density polyethylene are about one half of these because of its lower crystallinity.

For crystalline and semicrystalline polymers, the heats of fusion and crystallization have the same absolute values only if the solid sample whose  $\Delta H_f$  is being measured during melting and the solidifying sample whose  $\Delta H_{cr}$  is being measured during solidification and crystallization have the same degree of crystallinity. If either process involves a higher degree of crystallinity, the corresponding enthalpy change will have a higher absolute value. Most thermodynamic data reported for polymers refer to the fusion process rather than to crystallization.

Transition temperatures (temperature of solidification and melting, glass transition temperature, temperature of thermal degradation), specific heat and heat of fusion and, for crystalline polymers, heat of crystallization are measured by differential thermal analysis (DTA) or differential scanning calorimetry (DSC). In DTA, the sample and a thermally inert reference material are heated or cooled at a programmed rate. The temperature difference between the two materials is recorded as a function of temperature. In DSC, the amount of heat required to maintain the temperature of the sample at the value given by the temperature program is measured either as the power input or as the heat flow<sup>11</sup> (see pp. 46–49).

Additional  $\Delta H_f$  values are listed in Table 20–11. The

data are given in cal/g rather than in cal/mole repeat unit to be more closely comparable: The repeat units of polyethylene and polyethylene terephthalate have molecular weights of 28 and 192, respectively. Their heats of fusion in cal/g, relating approximately to equal volumes or chain lengths, are 66 and 30, that is, the  $\Delta H_f$  value for polyethylene is over twice that for polyethylene terephthalate. On a cal/mole repeat unit basis, the values are 1850 and 5760, with the latter having a  $\Delta H_f$  value over three times larger than the former.

Polyethylene has a high heat of fusion even though it lacks polar groups because its chains are smooth and symmetric and can pack together closely. Since van der Waals forces fall off with the seventh power of the distance, small interchain distances result in large interchain attraction and high  $\Delta H_{cr}$ .

**Entropies of Crystallization and Fusion.** The entropies of mixing and of fusion are quite similar if the former is considered only for the polymer. The Boltzmann relationship,  $S = R \ln W$ , applied to the fusion process, is

$$\begin{aligned}\Delta S_f &= S_l - S_s = R \ln W_l - R \ln W_s \\ &= R \ln \frac{W_l}{W_s} \approx R \ln W_l\end{aligned}\quad (20-29)$$

Subscript *l* refers to the liquid, molten, or amorphous polymer, and subscript *s* refers to the solid, crystalline polymer.  $W$ , the number of possible chain conformations, is unity for the crystalline polymer, which has only one stable lattice conformation. By contrast,  $W_l$  is enormously large because of the freedom of rotation about the bonds in the backbone of the chains of molten or liquid polymers, making  $W_l \gg W_s$ ,  $W_l/W_s \gg 1$ , and  $\Delta S_f$  positive. According to equation (20–17a), a positive entropy change contributes to making the free energy change for the process negative and thereby tends to make that process occur spontaneously. This is an example of the universal tendency toward randomization or disorder. The reverse process of ordering or

TABLE 20–11. Melting Points, Heats and Entropies of Fusion, and Glass Transition Temperatures for Various Polymers<sup>5,12,24</sup>

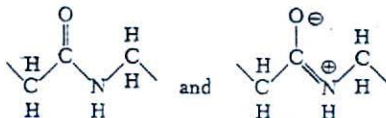
Polymer	$T_{MP}$ (°C)	$\Delta H_f$ (cal/g)	$\Delta S_f$ (cal/g °K)	$T_g$ (°C)	$\left(\frac{T_g}{T_{MP}}\right)$ (°K)
Polydimethyl siloxane (silicone rubber)	-40	4.3	0.02	-121	0.65
Polybutadiene (1,4- <i>cis</i> )	2	40.6	0.15	-95	0.65
Polyisoprene ( <i>cis</i> , natural rubber)	26	15	0.05	-68	0.68
Polyethylene (HDPE)	139	66	0.16	-70	0.49
Polypropylene (isotactic)	186	62	0.13	-18	0.55
Polystyrene (isotactic)	240	20.5	0.04	85	0.69
Polyethylene terephthalate	265	30	0.06	69	0.64
Polynexamethylene adipamide (66 nylon)	265	48	0.09	53	0.61
Polytetrafluoroethylene (Teflon)	325	13.7	0.023	126	0.67

crystallization is opposed by freedom of rotation through fusion and its increase in entropy. For polyethylene,

$$\Delta S_f = +4.5 \text{ cal/mole mer} \cdot ^\circ\text{K and}$$

$$\Delta S_{cr} = -4.5.$$

The magnitude of  $S_f$  and  $\Delta S_f$  depends on  $W_f$ , which in turn depends on the flexibility of the chains or the freedom of rotation around chain bonds within the constraint of the tetrahedral carbon-carbon bond angle. As is seen in Table 20-11,  $\Delta S_f$  is high for polyethylene. The methyl and especially the much larger phenyl side groups on every other carbon atom in the polypropylene and polystyrene chains hinder free rotation about the chain bonds and reduce the number of conformations that these chains can assume in the molten or liquid state. Therefore, the entropies of fusion of polypropylene and polystyrene are lower than that of polyethylene, by 19 and 75%, respectively. An olefinic double bond and a phenylene ring in the polymer backbone render the chains of polyisoprene and of polyethylene terephthalate relatively stiff, reducing  $W_f$  and  $\Delta S_f$  considerably. Resonance between



confers partial double bond character to the C—N bond and coplanarity to the amide group and the two carbon atoms, accounting for the stiffness and low  $\Delta S_f$  of polyamides, including polypeptides. The potential energy barrier hindering rotation about a  $F_2C—CF_2$  bond is more than an order of magnitude higher than that about a  $H_2C—CH_2$  bond, resulting in considerable chain stiffness and a low entropy of fusion for polytetrafluoroethylene.

**Melting Point.** The transition between solid, crystalline, and liquid, amorphous polymers occurs at their crystalline melting point. Two opposing factors affect the free energy change and the melting point, one favoring fusion and the other crystallization.

Fusion occurs spontaneously if  $\Delta G_f$  is negative. According to equation (20-17a)  $\Delta G_f$  depends on  $\Delta H_f$ ,  $\Delta S_f$ , and temperature. Since fusion is endothermic,  $\Delta H_f$  is positive, and a high heat of fusion tends to make  $\Delta G_f$  positive, opposing fusion and favoring crystallization.  $\Delta S_f$  is also positive but, since the product  $T \Delta S_f$  in equation (20-17a) is preceded by a minus sign, it makes a negative contribution to  $\Delta G_f$ . Thus, a high entropy of fusion and a high temperature tend to promote fusion and oppose crystallization.

Below the melting point, the absolute value of  $\Delta H_f$  (which is positive) is greater than the absolute value of  $T \Delta S_f$  (which is also positive but makes a negative

contribution to  $\Delta G_f$  because of the minus sign preceding it). On balance,  $\Delta G_f$  is positive, and fusion does not occur spontaneously. Solidification and crystallization of molten polymers occur spontaneously below their crystalline melting points, however, and the equilibrium state is the solid, crystalline state because  $\Delta G_{cr}$  is negative.

Neither the  $\Delta H_f$  nor the  $\Delta S_f$  values depend markedly on temperature. Thus, as  $T$  and  $T \Delta S_f$  increase,  $\Delta G_f$  becomes increasingly smaller. At the melting point,  $\Delta G_f = 0$ , and above the melting point, it becomes negative. Therefore, fusion occurs spontaneously above the melting point and the equilibrium state of the polymer is the molten, liquid, or amorphous state.

At the crystalline melting point, solid and liquid polymers are in equilibrium, and  $\Delta G_{cr} = \Delta G_f = 0$ . Hence, from equation (20-17a),

$$T_{MP} = \frac{\Delta H_f}{\Delta S_f} \quad (20-30)$$

High melting points in polymers can be achieved by high values of  $\Delta H_f$  and/or by low values of  $\Delta S_f$ . Polarity, indicated by a high solubility parameter, tends to increase  $\Delta H_f$  and the melting point by increasing the secondary valence forces between chains. Chain stiffness lowers  $\Delta S_f$  and raises the melting point.

**Example 20-8.** High-density polyethylene has a latent heat of fusion of 1850 cal/mole mer and a crystalline melting point of 139°C. Calculate its entropy of fusion.

$$T_{MP} = 139^\circ\text{C} + 273 = 412^\circ\text{K}$$

From equation (20-30),

$$\begin{aligned} \Delta S_f &= \Delta H_f / T_{MP} \\ &= \left( \frac{1850 \text{ cal}}{\text{mole mer}} \right) \left( \frac{1}{412^\circ\text{K}} \right) = 4.49 \text{ cal/mole mer} \cdot ^\circ\text{K} \end{aligned}$$

To compare this value with that of Table 20-11, note that the molecular weight of a mer or repeat unit,  $—CH_2—CH_2—$ , is 28. Therefore,

$$\Delta S_f = \left( \frac{4.49 \text{ cal}}{\text{mole mer} \cdot ^\circ\text{K}} \right) \left( \frac{\text{mole mer}}{28 \text{ g}} \right) = 0.16 \text{ cal/g} \cdot ^\circ\text{K}$$

Decreases in either the molecular weight or the size of the crystallites lower the melting point of a polymer somewhat. Since most commercial polymers have a range of molecular weights and crystallites of different sizes, their melting point is not as sharp as that of low-molecular-weight crystalline compounds.

Practical considerations often dictate the choice of polymers according to their melting point. Many resins are extruded in the molten state. Since thermal degradation is much more extensive at higher temperatures, low melting points and low processing temperatures are desirable from the fabricator's viewpoint. End-use preferences are for high melting points. For instance, steam sterilization carried out at 121°C and sterilization by dry heat at even higher temperatures would soften or melt polyethylene containers. Polypropylene containers, on the other hand, can be steam sterilized



since their melting point is 173° to 186° C and their heat distortion temperature is 145° C.

### GLASS-RUBBER TRANSITION<sup>6,6a</sup>

Neither atactic polystyrene nor SBR (styrene-butadiene rubber, a random copolymer of 76% butadiene/24% styrene) can crystallize. Yet, at room temperature, amorphous polystyrene is hard and brittle, whereas SBR is soft and extensible. The former is in the "glassy" state, the latter in the "rubbery" state. Upon lowering the temperature, SBR reversibly turns glassy (hard and brittle) over a narrow temperature range centered at -62° C. Upon heating, polystyrene reversibly turns rubbery (soft and extensible) over a narrow temperature range centered at 90° C. The temperature at which a glassy polymer becomes rubbery on heating and a rubbery polymer reverts to a glassy one on cooling is called the *glass transition temperature*,  $T_g$ .

The mechanical properties of SBR and polystyrene in their rubbery state (SBR above -62° C and polystyrene above 90° C) are rather similar. Their consistency is that of chewing gum. The major constituent of chewing gum, a gummy substance called chicle, is an impure form of *trans*-polyisoprene, another rubber. Both rubbery polymers have low tensile strength, low modulus of elasticity (ca.  $10^2$  psi, where psi represents lbs/in.<sup>2</sup>), and very high elongation. The mechanical properties of the two polymers in their glassy state (at temperatures below their respective glass transition temperatures) are also rather similar: Both have comparatively high tensile strength, high modulus of elasticity (ca.  $10^5$  psi), and very low elongation. The effect of temperature on the modulus of elasticity of the two polymers is illustrated in Figure 20-12. The values change little with temperature except near the glass transition temperature, where they change abruptly. A shift along the temperature axis by 152° C nearly superim-

poses the two curves.<sup>7</sup> The major difference between the two polymers is that, at room temperature, polystyrene, like most plastics, is below its  $T_g$  and is therefore in the glassy state, while SBR, like all elastomers, is above its  $T_g$  and is therefore in the rubbery state.

Polymers in the rubbery state are very viscous liquids, with relatively high freedom of rotation around the carbon-carbon bonds in the backbone within the constraint of the tetrahedral bond angle. The temperature is high enough so that most bonds can overcome the potential energy barrier against rotation. Rotational freedom results in very flexible chains, segmental or micro-Brownian motion, and changing chain conformations, as discussed for polymer solutions. Segmental mobility is considerably smaller in rubbery, liquid bulk polymers than in their solutions because of the much higher viscosity of the former.

As the temperature is lowered progressively, the number of bonds capable of overcoming the potential energy barrier to rotation diminishes, as does the segmental mobility. At the glass transition temperature, rotational or micro-Brownian motion ceases altogether, that is, the chain conformations are frozen in. Below  $T_g$ , the only motion left is the vibration of atoms about their equilibrium positions. When a polymer is stressed at temperatures below its  $T_g$ , the frozen, randomly coiled chains have largely lost their ability to slip past one another. Because rupture is not preceded by cold flow, elongations to break are small, and the polymer is brittle.

The amorphous domains in partly crystalline polymers undergo glass-rubber transitions just as purely amorphous polymers do. Many commercial grades of crystallizable polymers are about half crystalline and half amorphous. Two characteristic transition temperatures are associated with such semicrystalline polymers, the glass transition temperature with the amorphous portion, and the crystalline melting point with the crystalline portion.  $T_g$  is always lower than  $T_{MP}$ . Factors that restrict the rotation around carbon-carbon backbone bonds, such as the bulky phenyl side groups in polystyrene, render the chain stiffer. They raise the glass transition temperature by restricting the segmental mobility in the amorphous regions and increase the crystalline melting point by reducing the segmental mobility in the melt and, hence, the entropy of fusion (see previous discussion). Polar, especially hydrogen-bonding, groups that increase the interchain attraction or cohesion also raise  $T_g$  and  $T_{MP}$ , the latter by increasing the heat of fusion.

Since the two transition temperatures are affected by the same factors, their values are related. As is seen in Table 20-11, the ratio  $T_g/T_{MP}$  is equal to 1/2 for polymers with symmetric chains like polyethylene (also for polyvinylidene chloride and dimethylsilicones) and to 2/3 for polymers whose main-chain carbon atoms do not have two identical substituents, provided both

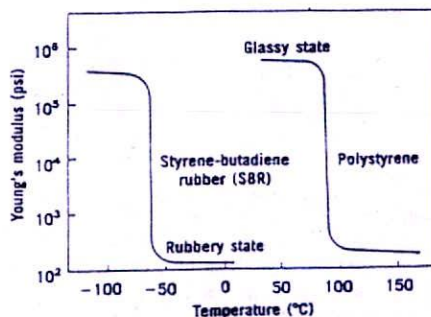


Fig. 20-12. Schematic plot of Young's modulus versus temperature for two amorphous polymers. Polystyrene is in the glassy state (brittle solid), while SBR is in the rubbery state (soft, very viscous semisolid) at room temperature.

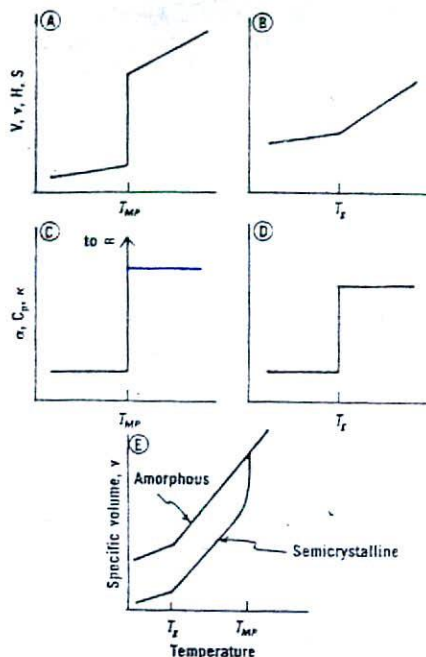


Fig. 20-13. Effect of melting point  $T_{MF}$  and glass transition temperature  $T_g$  on thermodynamic functions of crystalline, amorphous, and semicrystalline polymers. See text for definition of symbols.

temperatures are expressed on the absolute temperature scale.

From the thermodynamic viewpoint, melting as a phase change is a *first-order transition*:  $\Delta G_f = 0$  at the melting point. Primary thermodynamic functions, that is, properties such as volume  $V$  or density and its reciprocal, specific volume  $v$ , entropy, and enthalpy undergo a sharp discontinuity at the melting point of a crystalline polymer, which, in the case of enthalpy, is the latent heat of fusion (Fig. 20-13A). The glass transition is identified as a *second-order transition*. At the glass transition temperature of an amorphous polymer, the primary functions merely undergo a change in slope when plotted against temperature (Fig. 20-13B). The derived thermodynamic functions: heat capacity

$$C_p = \left( \frac{\partial H}{\partial T} \right)_P$$

cubic thermal expansion coefficient

$$\alpha_v = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$$

or

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

and isothermal compressibility

$$\kappa = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

go to infinity at a first-order transition such as occurs at the melting point of a crystalline polymer (Fig. 20-13C) and show a sharp discontinuity at a second-order transition such as occurs at the glass transition temperature of an amorphous polymer (Fig. 20-13D). Figure 20-13E shows the dependence on temperature of the specific volume of an amorphous and of a partly crystalline polymer. Both plots undergo a change in slope at  $T_g$  corresponding to the glass transition in the amorphous polymer and in the amorphous portion of the semicrystalline polymer. When the temperature is increased to the melting point, the crystalline portion of the semicrystalline polymer melts, resulting in an abrupt increase in the specific volume and a discontinuity in the specific volume-temperature plot as the compact crystallites suddenly change into the less dense melt.

The initial slope of the plot below  $T_g$ , which represents the thermal expansion coefficient of the solid polymer, is smaller than the slope above the melting point, which represents the thermal expansion coefficient of the molten polymeric liquid. For atactic polymethyl methacrylate and polystyrene, which are completely amorphous plastics, and for the elastomer SBR,  $\alpha = dv/dT$  at atmospheric pressure is 2.15, 2.5, and  $1.8 \times 10^{-4} \text{ cm}^3/\text{g} \cdot \text{K}$  in the glassy state and 4.6, 5.5, and  $6.6 \times 10^{-4} \text{ cm}^3/\text{g} \cdot \text{K}$  in the liquid-rubbery state, respectively.

From a kinetic viewpoint, the glass transition temperature is the temperature at which the relaxation time for segmental motion in the polymer backbone is comparable to, or at least of the same order of magnitude as, the time scale of the temperature change during the measurement. Therefore, the glass transition of a polymer is not as sharp and well defined as the melting point and depends much more on the method of measurement and on the rate of heating or cooling during the measurement. Thermal expansion coefficient, elastic modulus or hardness, heat capacity, thermal conductivity, isothermal compressibility, broad-line NMR, dielectric constant, and refractive index, which are used to measure the glass transition temperature, may give values that vary by as much as  $20^\circ \text{C}$  for a single sample. The experimentally measured  $T_g$  depends on the rate of heating or cooling. Fast cooling of a rubbery polymer during the measurement gives a higher value for the  $T_g$  than slow cooling, whereas fast heating of a glassy polymer gives a lower value than slow heating. These observations indicate that the glass transition is not a genuine thermodynamic transition but a kinetic phenomenon.

The glass transition temperature decreases somewhat with the molecular weight of a polymer. Many polymers have two or three glass transitions corre-

sponding to the freezing-in of the rotational motions that occur in the main chain and in side chains as well as those of entire side groups.

The glass-rubber transition occurs in amorphous polymers and in the amorphous domains of partly crystalline polymers. Therefore, the properties of highly crystalline polymers, with about 20% or less of amorphous regions, undergo little if any change at the  $T_g$ . The profound effect of the glass transition on the mechanical properties of amorphous polymers or polymers with low crystallinity (below 10%) is illustrated by Figure 20-12 for the elastic modulus. Within a temperature range of about 10° C, the modulus changes more than 1000-fold. Polymers of intermediate crystallinity (10 to 80%) are hornlike and tough in texture below their  $T_g$  and leathery and tough between their  $T_g$  and  $T_{MP}$ . They may retain their good impact resistance in part even below the  $T_g$ .

The diffusivity (see Chapter 13) of small molecules through amorphous or semicrystalline polymers is considerably lower below than above their glass transition temperatures. The segmental mobility in the amorphous regions above the  $T_g$  greatly facilitates the transport of penetrants.

### PLASTICIZATION

The glass transition temperature of a random copolymer on the Kelvin scale is frequently the weighted average of the glass transition temperatures of the two homopolymers on a weight (or, sometimes, volume) fraction basis.

**Example 20-3.** Polyvinyl chloride and polyvinyl acetate have  $T_g$  values of 81° and 29° C, respectively. Calculate the glass transition temperature of a random copolymer of 80% *w/w* vinyl chloride and 20% *w/w* vinyl acetate.

$$T_g = (0.8)(81 + 273) + (0.2)(29 + 273) = 344^\circ \text{K} = 71^\circ \text{C}$$

This process, by which  $T_g$  of rigid polyvinyl chloride is lowered through copolymerization, is called *internal plasticization*. It extends the lower end of the temperature range over which polyvinyl chloride is flexible. *External plasticizers* are high-boiling liquids that, at room temperature, have low vapor pressures and are not volatile. Their role is to lower the  $T_g$  of a polymer below room temperature, rendering it softer and more flexible. They must be soluble in the polymer. External

plasticizers act as lubricants between the polymer chains, facilitating the slippage of chain past chain under stress and extending the temperature range for segmental rotation to lower temperatures. If these liquids solvate the polymer extensively, they stiffen its chains and render them less flexible. Therefore, they should be poor solvents that are just compatible with the polymer. Plasticizers are liquids with low glass transition temperatures, in the range of -50° to -150° C, at which they freeze to glasses rather than crystallize on cooling. Their diffusion coefficients in the polymer should be comparatively low to minimize migration. Plasticizer migration from the walls of containers may contaminate the contents. Internal plasticizers do not migrate at all. External plasticizers are only effective with amorphous polymers or in the amorphous regions of semicrystalline polymers.

The effect of di-(2-ethylhexyl)phthalate, also called dioctyl phthalate, on the properties of polyvinyl chloride is shown in Table 20-12. The pure polymer is rigid at room temperature because it is in the glassy state. The plasticizer has a glass transition temperature of about -100° C and, at the 30% level, lowers that of the polymer to 5° C. At room temperature, plasticized polyvinyl chloride is therefore in the rubbery state. In the form of bags, it is used in containers for parenteral solutions and plasma because of its flexibility and transparency. A problem associated with the high level of di-(2-ethylhexyl)phthalate in flexible polyvinyl chloride bags containing intravenous solutions or plasma is the release of the liquid plasticizer, which exists in the infusion liquids as colloidal droplets,<sup>42</sup> especially upon agitation.<sup>43</sup> The released plasticizer may also become molecularly associated with lipid or protein components of stored plasma or whole blood.<sup>44</sup>

### ELASTOMERS<sup>45</sup>

Elastomers or rubbers are polymers characterized by low glass transition temperatures. Those that are homopolymers capable of crystallizing also have low melting temperatures, mostly below room temperature (see the first three entries in Table 20-11). Elastomers are characterized by low solubility parameters (see Table 20-3) and low interchain attractive forces (Table 20-8). Like most crystalline polymers at temperatures

TABLE 20-12. Effect of Plasticizer on Mechanical Properties of Polyvinyl Chloride

Property	Rigid Polyvinyl Chloride	Polyvinyl Chloride (70% w/w) + Dioctyl Phthalate (30%)
Tensile strength (psi)	8000	3600
Young's modulus (10 <sup>5</sup> psi)	4.6	0.2
Elongation to break (%)	30	200
Glass transition temperature (°C)	31	5

above their melting points and amorphous polymers above their glass transition temperatures, raw rubbers are viscous liquids of taffy-like consistency. They flow under stress, are tacky, and have little snap-back or elasticity. The appropriate model is a bowl of spaghetti.

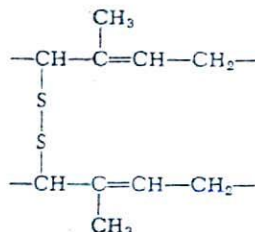
Moderate cross-linking, called *vulcanization*, ties the chains together by primary valence bonds at a few points, preventing slippage of chain past chain under stress. Mechanical stresses are generally too weak to break primary valence bonds. The randomly coiled, lightly cross-linked chains of vulcanized elastomers are uncoiled and extended by stress, but this elongation stops when cross-links and backbone bonds become strained. The extended chains resume their original random conformations rapidly when the stress is released, causing the object to snap back to its original shape. Thus, the cross-links impart elasticity, minimize creep and permanent set, and eliminate tackiness. The high segmental mobility or micro-Brownian motion at room temperature is preserved because vulcanization raises the glass transition temperature by only a few degrees.

The cross-links are spaced widely apart, on the average about 1 per 100 repeat units, and do not prevent the reversible crystallization of homopolymer elastomers when stretched to high elongations. Stresses producing high elongations forcibly line up the randomly coiled elastomer chains in spite of the resultant decrease in entropy. This chain alignment or orientation leads to crystallization in stretched homopolymer elastomers, which thereby lowers their free energy by an amount equal to the heat of crystallization.

The stress-strain curves turn up at these elongations (Point *D* in Figure 20-10) because crystallization increases the modulus of elasticity. Once the stress is released, the elastomers "melt" because the absolute value of the positive  $T \Delta S$  term is larger than the absolute value of the positive  $\Delta H_f$ . According to equation (20-17a),  $\Delta G_f$  is negative, and the elastomers that had crystallized under stress revert spontaneously to the more stable, contracted state in which the chains are randomly coiled. The latent heat of fusion or crystallization of elastomers is comparatively small because most elastomers are hydrocarbons, lacking polar groups. Furthermore, many have kinky chains owing to olefinic unsaturation in the *cis* configuration in their backbone and/or bulky side groups that prevent close packing and increase the distance between adjacent chains. These factors reduce the interchain cohesion and, hence,  $\Delta H_f$ . While solvents of low polarity dissolve raw gums, they merely swell vulcanized rubbers.

Vulcanization or curing of natural rubber and other polybutadiene-type elastomers is carried out by mixing 2 to 5% sulfur plus a vulcanization accelerator (a mercaptobenzothiazole, a thiuram sulfide or disulfide, or a dithiocarbamate) and an activator (a zinc, lead, or calcium soap) into the raw gum and heating to 130° to 150° C. The olefinic unsaturation activates the hydrogen

on the  $\alpha$ -carbon, and sulfide or disulfide cross-links are introduced:



Extensive cross-linking, using 30% or more of sulfur based on the weight of raw natural rubber, produces a hard plastic with an ultimate elongation of only about 4% called *ebonite*.

Elastomers without olefinic unsaturation may be vulcanized by added peroxides that, on heating, decompose and abstract protons from the chains, producing free radicals. The combination or coupling of free radicals from adjacent chains produces cross-links between them.

Even vulcanization does not improve the mechanical properties of most elastomers sufficiently for certain end uses. *Reinforcing fillers* are powders of small particle size, 200 to 500 Å, such as carbon blacks and colloidal silicon dioxide. They are incorporated into the raw rubber together with the vulcanizing ingredients by milling, at levels of 20 to 75% of the weight of raw gum. The small particle size produces a large rubber-filler interfacial area; the degree of reinforcement increases with decreasing particle size.<sup>35</sup>

Incorporation of reinforcing fillers into homopolymer elastomers capable of crystallizing on stretching, such as natural rubber, polychloroprene, and polyisobutylene, usually increases their tensile strength and reduces their elongation to break only moderately but may improve their tear and abrasion resistance greatly. On the other hand, elastomers that cannot crystallize on stretching, such as the random copolymers of styrene with butadiene, butadiene with acrylonitrile, and ethylene with propylene, must be compounded with reinforcing fillers to attain satisfactory tensile strength and Young's modulus as well as abrasion and tear resistance. Their pure-gum vulcanizates are weak and soft, but reinforcing fillers can raise the mechanical properties to the levels developed in homopolymers by crystallization on stretching.

The reinforcing particles must be well wetted by the rubber to promote intimate dispersion during milling and good adhesion after vulcanization. The elastomer chains are strongly adsorbed on the colloidal filler particles and adhere to them even at large deformations. The composite thus acquires some of the strength, stiffness, and abrasion resistance of the disperse phase because the solid particles are mechanically integrated with the rubber.

Inert fillers and pigments such as clay, calcium carbonate, and talc do not improve the mechanical properties but facilitate molding and extruding and lower the price.

### FABRICATION TECHNOLOGY<sup>38,46-49</sup>

Thermoplastic resins are fabricated in the molten state by extrusion into films or fibers and by molding into three-dimensional objects.

**Extrusion.**<sup>38,46,47</sup> A single-screw extruder is a conveyor similar to a meat grinder. It consists of a screw, driven by a motor connected to its shaft through a gear reducer, rotating inside a cylindrical barrel. The rotating screw moves the resin pellets forward and generates by shear most of the heat required to melt the pellets, as well as the hydrostatic pressure to force the molten plastic through the die (Fig. 20-14).

The size of the extruder is described by the inside diameter of the barrel, which ranges from 1 inch for extruders with a capacity of about 5 lb/hr to 8 inches for a capacity of about 1000 lb/hr. The length of the barrel is about 18 to 24 times its diameter for the extrusion of thermoplastics. Shorter barrels are used to extrude rubber.

The screw consists of three zones, namely, a feed section, a transition section, and a metering section. The screw usually has the same pitch or helical angle in the three sections but decreasing channel depth. The process variables—temperature and speed of revolution of the screw—do not afford a range of conditions wide enough for the effective extrusion of different polymers. For instance, polyamides have lower melt viscosities than polyethylene resins, while polyvinyl chloride resins degrade readily at high temperatures. Therefore, different screws are available for a single extruder, having different lengths for the three zones,

different channel depths, and different compression ratios (channel depth in the feed section to channel depth in the metering section, that is, volumetric displacement in the feed section to that in the metering section.)

Resin pellets, granules, or flakes are fed from the hopper into the feed section of the extruder, from where they are conveyed to the transition section. Here the pellets are compressed and melted. A large portion of the heat required to melt the resin is generated by viscous friction as the pellets are sheared between the rotating screw and the stationary wall of the barrel. Another portion of the heat is supplied externally through the barrel, usually by electric band heaters mounted on the barrel. As the resin advances through the transition zone, it is plasticated, melted, and mixed. By the time it reaches the metering section, it is a homogeneous, very viscous liquid. The metering section of the screw has the shallowest channel depth. It pumps the melt through a screen-pack filter into the die cavity. The filter removes solid impurities and lumps of unmelted resin. If the extruded film is to have uniform thickness, it is essential that the melt exits through the die slit at a constant flow rate, free of sudden surges. The metering section ensures a constant delivery rate.

Flat film is extruded downward through a die with a long slit for an opening onto highly polished chill rolls that are water-cooled. From there, the sheet is rolled up on a windup roll. *Tubular film* is produced by extruding the melt upward through an annular die around a mandrel (Fig. 20-15). As the tube is pulled upward, it is blown up to a bubble by air injected through the mandrel, stretched, and biaxially oriented. The hot tubular film is cooled by air issuing through the holes of a hollow ring surrounding the tube near the point where it leaves the die, below the zone where it is inflated to a bubble. As the inflated, solidifying film moves upward, it is gradually deformed into the layflat

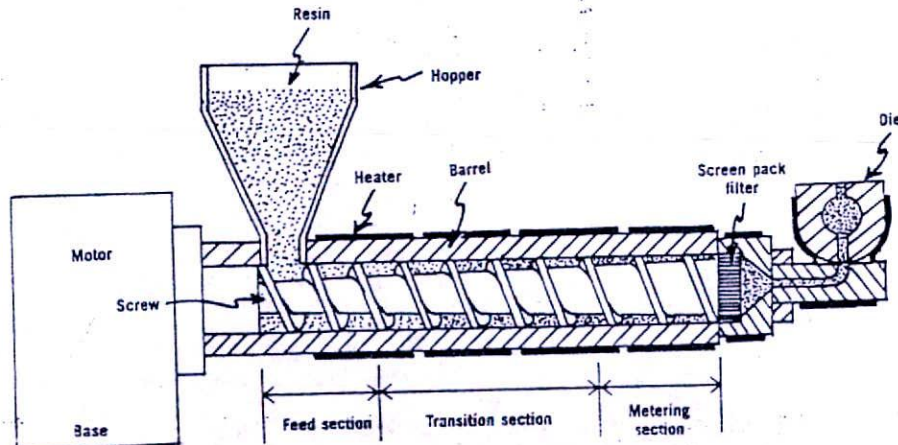


Fig. 20-14. Schematic drawing of a single-screw extruder.

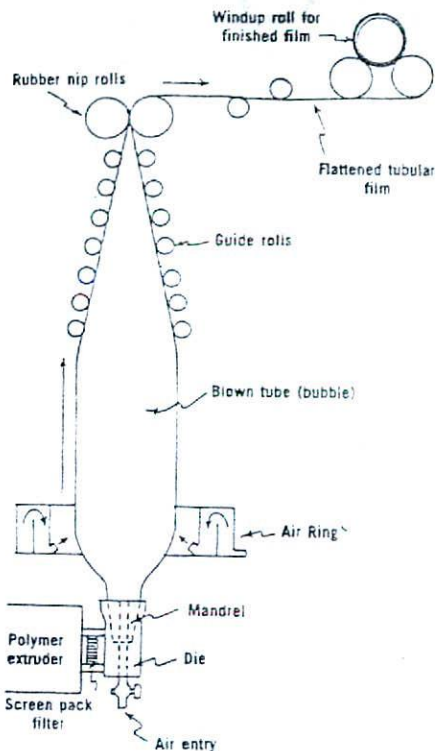


Fig. 20-15. Schematic drawing of tubular film extrusion, showing film being pulled upwards and expanded into a bubble.

form by the action of guide rolls. A pair of rubber-covered nip rolls collapses the film completely and thereby seals in the inflating air that expanded the molten film issuing from the die into a bubble. A windup roll then rolls the flattened film up, pulling it upward continuously away from the die.

**Injection molding.**<sup>38,46-49</sup> Of the various molding processes, injection molding is the most widely used. The following three operations are carried out successively. The thermoplastic resin, in the form of pellets, is heated, melted, and pushed into the die cavity, which is filled with the melt. The molten plastic cools and solidifies in the mold while under pressure. Finally, the mold is opened and the part is ejected. Molds may have several cavities for the simultaneous molding of several parts, or a single cavity.

Two types of machines are used to melt and inject the resin into the mold, a *plunger injection molding machine* and a *reciprocating screw injection molding machine*. The plunger molding machine is fitted with a hydraulic ram that compresses the resin pellets at the same time that they are heated and melted. The molten resin is pushed through a nozzle into the mold cavities and is cooled under pressure to below its melting or glass transition temperature. The molten resin shrinks

on cooling, the mold is opened, and the solidified plastic parts are ejected.

The second molding machine, consisting of a reciprocating screw, mixes and homogenizes the melting resin. The screw resembles that of the single screw extruder depicted in Figure 20-14, except that it is moved forward and backward in the barrel by a hydraulic mechanism. The resin is fed from a hopper into the barrel, plasticized and melted by the rotating screw. The screw, then acting as a plunger, forces the melt into the mold cavities, where the plastic cools and solidifies. The molded plastic is then ejected from the mold cavities.

The molten resin shrinks on cooling and solidifying because its density decreases with rising temperature. Amorphous plastics shrink far less on solidifying than semicrystalline plastics owing to crystallization of the latter (see equation (20-28) and (Fig. 20-13)). Molds are filled under high pressure. By compressing the melt, more material is made to flow into the mold cavity, reducing the *shrinkage on cooling*. The average linear shrinkage of polystyrene on cooling from 500° F to room temperature ranges from 3.5% at atmospheric pressure to 1.4% at 10,000 psi and 0.3% at 20,000 psi. Percent refers to the linear dimension at room temperature and atmospheric pressure. The corresponding linear shrinkage of polyethylene is 7.0%, 5.1%, and 3.6%, respectively. These values are higher because polyethylene is semicrystalline whereas polystyrene is amorphous. Mold pressures in commercial injection machines range from 6000 to 60,000 psi.

#### FUTURE TRENDS IN PHARMACEUTICAL AND OTHER BIOMEDICAL USES OF POLYMERS

This chapter illustrates some of the pharmaceutical applications of polymers. In the past, wider use of polymers in the health sciences field was limited by economic consideration: The pharmaceutical industry uses polymers in much smaller amounts than do other industries such as the textile, packaging, and tire industries. Therefore, the manufacturers of plastics and elastomers found no economic incentive to tailor-make polymers for the special needs of the pharmaceutical industry, or to seek clearance from the Food and Drug Administration for pharmaceutical applications of existing commercial polymers.

Presently, health scientists, commercial laboratories, and some pharmaceutical companies design, prepare, manufacture, and process or fabricate their own polymers in accordance with their specialized requirements. The following areas of polymer research and development are being actively pursued by academic and industrial investigators and health science practitioners. In addition to sutures, implants of plastics and elastomers in human and animal bodies are widely used for repair or replacement of tissues, organs, or parts of organs. Some of the problems encountered with im-

plants are degeneration of adjoining tissues and formation of blood clots and thrombi on the surfaces of implanted synthetic polymers; enlargement of implants through sorption of lipids or moisture, which constitutes a problem with precision parts; and corrosion and weakening of implants due to interaction with enzymes and other physiologic compounds and/or mechanical stresses. Considerable research is in progress to achieve biocompatibility of synthetic polymers through surface modification to prevent blood clotting, to make porous implants that permit ingrowth of adjoining tissue, and to search for stronger and more durable polymers.

A skin substitute to cover burns has been introduced. It is a composite made of an outer layer of silicone elastomer to protect the wound from infection and dehydration, bonded to a porous bottom layer that is adhesive and biodegradable consisting of cross-linked collagen combined with glycosaminoglycan. After the skin has grown back underneath this composite film, the bottom layer is biodegraded and the elastomeric top layer sloughed off.<sup>50</sup>

Sustained-release dosage forms are a fertile area for the application of plastics, elastomers, and film-forming polymers (see Chapters 13 and 19). The synthesis and evaluation of macromolecular prodrugs is in full swing. Medical and pharmaceutical journals publish increasing numbers of articles dealing with polymers, while polymer journals publish increasing numbers of articles dealing with pharmaceutical and biomedical uses of polymers. Three specialized publications, "Journal of Biomedical Materials Research," "Biomaterials, Medical Devices and Artificial Organs," and "Biomaterials," started in 1967, 1973, and 1980, respectively, cover polymeric as well as other biomaterials, for example, ceramics and metals.

#### References and Notes

- H. Mark and A. V. Tobolsky, *Physical Chemistry of High Polymeric Systems*, Interscience, New York, 1950.
- P. J. Flory, *Principles of Polymer Chemistry*, Cornell University, Ithaca, 1953.
- A. K. Schmidt and C. A. Martles, *Principles of High-Polymer Theory and Practice*, McGraw-Hill, New York, 1948.
- F. W. Billmeyer, *Textbook of Polymer Science*, 3rd Edition, Wiley, New York, 1984.
- H.-G. Elias, *Macromolecules I, Structure and Properties*, translated by J. W. Stafford, 2nd Edition Plenum, New York, 1984.
- P. C. Hiemenz, *Polymer Chemistry*, Dekker, New York, 1984.
- L. H. Sperling, *Introduction to Physical Polymer Science*, Wiley, New York, 1992.
- L. Mandelkern, *An Introduction to Macromolecules*, Springer-Verlag, New York, 1972.
- B. Vollmert, *Polymer Chemistry*, translated by E. H. Immergut, Springer-Verlag, New York, 1973.
- M. L. Miller, *The Structure of Polymers*, Reinhold, New York, 1966.
- P. W. Allen (Ed.), *Techniques of Polymer Characterization*, Butterworths, London, 1959.
- E. A. Collins, J. Bares and F. W. Billmeyer, *Experiments in Polymer Science*, Wiley, New York, 1973.
- J. Brandrup and E. H. Immergut (Eds.), *Polymer Handbook*, 3rd Edition, Wiley, New York, 1989.
- F. W. Billmeyer and C. B. de Than, *J. Am. Chem. Soc.* 77, 4763, 1955.
- C. Tanford, *Physical Chemistry of Macromolecules*, Wiley, New York, 1961.
- P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York, 1969.
- T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.* 73, 1915, 1951.
- F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962.
- J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, 3rd Edition, Dover, New York, 1964.
- J. H. Hildebrand, J. M. Prausnitz and R. L. Scott, *Regular and Related Solutions*, Van Nostrand Reinhold, New York, 1970.
- D. Mangaraj et al., *Makromol. Chem.* 65, 39, 1963; 67, 75, 34, 1963; 84, 225, 1965.
- G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.* 54, 1731, 1742, 1958.
- P. A. Small, *J. Appl. Chem.* 3, 71, 1953.
- K. L. Hoy, *J. Paint Technol.* 42, 76, 1970.
- D. W. van Krevelen, *Properties of Polymers, Their Estimation and Correlation with Chemical Structure*, 2nd Edition, Elsevier, New York, 1976.
- C. M. Hansen, *J. Paint Technol.* 39, 104, 505, 511, 1967; I & EC Prod. Res. Dev. 3(1), 2, 1969.
- E. M. Frith and R. F. Tuckett, *Linear Polymers*, Longmans, Green, London, 1951.
- H. Morawetz, *Macromolecules in Solution*, 2nd Edition, Wiley, New York, 1975.
- H. Tompa, *Polymer Solutions*, Butterworths, London, 1956.
- K. Shinoda, *Principles of Solution and Solubility*, Marcel Dekker, New York, 1978.
- A. R. Shultz and P. J. Flory, *J. Am. Chem. Soc.* 74, 4760, 1952; 75, 3888, 1953.
- H. R. Kruyt (Ed.), *Colloid Science II, Reversible Systems*, Elsevier, New York, 1949.
- S. Kasai and M. Koishi, *Chem. Pharm. Bull.* 25, 314, 1977.
- C. Thies, *Polymer-Plast. Technol. Eng.* 5(1), 1, 1975.
- P. L. Madan, *Drug Dev. Ind. Pharm.* 4, 95, 1978; *Asian J. Pharm. Sci.* 1, 1, 1979.
- R. Houwink, *Elasticity, Plasticity and Structure of Matter*, 2nd Edition, Warren Press, Washington, D.C., 1953.
- T. Alfrey, *Mechanical Behavior of High Polymers*, Interscience, New York, 1948.
- L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Reinhold, New York, 1974.
- F. Rodriguez, *Principles of Polymer Systems*, 2nd Edition, Hemisphere Publishing, Washington, D.C., 1982.
- H. Schott, in *Remington's Pharmaceutical Sciences*, 18th Edition, A. R. Gennaro (Ed.), Mack Publishing Co., Easton, Pa., 1990, Chapter 20.
- T. S. Carswell and H. K. Nason, *Modern Plastics*, 21, 121, June, 1944.
- H. Schott, *Biomaterials* 3, 195, 1982.
- J. H. Corley, T. E. Needham, E. D. Sumner and R. Mikeal, *Am. J. Hosp. Pharm.* 34, 259, 1977.
- M. Horioka, T. Aoyama and H. Karasawa, *Chem. Pharm. Bull.* 25, 1791, 1977.
- I. J. Stern, J. E. Miripol, R. S. Izzo and J. D. Lueck, *Toxicol. Appl. Pharmacol.* 41, 507, 1977.
- M. Morton (Ed.), *Rubber Technology*, 2nd Edition, Van Nostrand Reinhold, New York, 1973.
- E. C. Bernhardt (Ed.), *Processing of Thermoplastic Materials*, Reinhold, New York, 1969.
- J. M. McKelvey, *Polymer Processing*, Wiley, New York, 1962.
- I. I. Rubin, *Injection Molding—Theory and Practice*, Wiley, New York, 1972.
- H. S. Kaufman and J. J. Falcetta (Eds.), *Introduction to Polymer Science and Technology*, Wiley, New York, 1977.
- T. Jaksic and J. F. Burke, *Ann. Rev. Med.* 38, 107, 1987.

#### Problems

- 20-1. Consider the following three combinations of reagents:
  - (a)  $C_2H_5OH + HOOC-(CH_2)_4-COOH$ ;
  - (b)  $H_2N-(CH_2)_6-NH_2 + Cl-CO-(CH_2)_6-CO-Cl$  + enough  $Na_2CO_3$  to neutralize the hydrochloric acid formed;
  - (c) In a mixture of 50 mole-% propylene glycol + 50 mole-% phthalic anhydride, replace 20 mole-% of the propylene glycol with 10 mole-% pentaerythritol,  $C(CH_2O)_4$ .

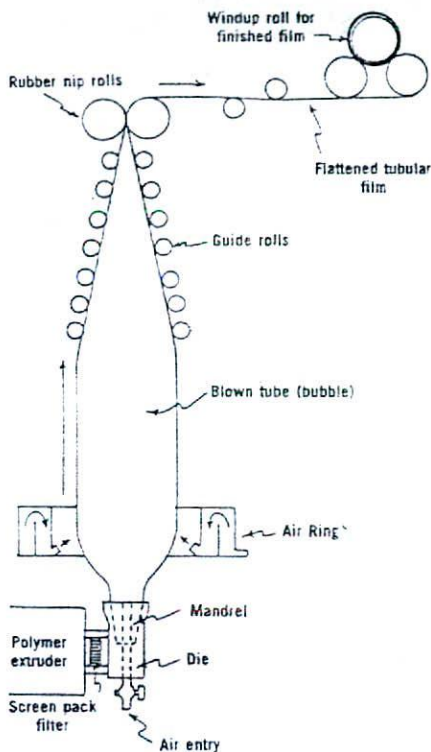


Fig. 20-15. Schematic drawing of tubular film extrusion, showing film being pulled upwards and expanded into a bubble.

form by the action of guide rolls. A pair of rubber-covered nip rolls collapses the film completely and thereby seals in the inflating air that expanded the molten film issuing from the die into a bubble. A windup roll then rolls the flattened film up, pulling it upward continuously away from the die.

**Injection molding.**<sup>38,46-49</sup> Of the various molding processes, injection molding is the most widely used. The following three operations are carried out successively. The thermoplastic resin, in the form of pellets, is heated, melted, and pushed into the die cavity, which is filled with the melt. The molten plastic cools and solidifies in the mold while under pressure. Finally, the mold is opened and the part is ejected. Molds may have several cavities for the simultaneous molding of several parts, or a single cavity.

Two types of machines are used to melt and inject the resin into the mold, a *plunger injection molding machine* and a *reciprocating screw injection molding machine*. The plunger molding machine is fitted with a hydraulic ram that compresses the resin pellets at the same time that they are heated and melted. The molten resin is pushed through a nozzle into the mold cavities and is cooled under pressure to below its melting or glass transition temperature. The molten resin shrinks

on cooling, the mold is opened, and the solidified plastic parts are ejected.

The second molding machine, consisting of a reciprocating screw, mixes and homogenizes the melting resin. The screw resembles that of the single screw extruder depicted in Figure 20-14, except that it is moved forward and backward in the barrel by a hydraulic mechanism. The resin is fed from a hopper into the barrel, plasticized and melted by the rotating screw. The screw, then acting as a plunger, forces the melt into the mold cavities, where the plastic cools and solidifies. The molded plastic is then ejected from the mold cavities.

The molten resin shrinks on cooling and solidifying because its density decreases with rising temperature. Amorphous plastics shrink far less on solidifying than semicrystalline plastics owing to crystallization of the latter (see equation (20-28) and (Fig. 20-13). Molds are filled under high pressure. By compressing the melt, more material is made to flow into the mold cavity, reducing the *shrinkage on cooling*. The average linear shrinkage of polystyrene on cooling from 500° F to room temperature ranges from 3.5% at atmospheric pressure to 1.4% at 10,000 psi and 0.3% at 20,000 psi. Percent refers to the linear dimension at room temperature and atmospheric pressure. The corresponding linear shrinkage of polyethylene is 7.0%, 5.1%, and 3.6%, respectively. These values are higher because polyethylene is semicrystalline whereas polystyrene is amorphous. Mold pressures in commercial injection machines range from 6000 to 60,000 psi.

#### FUTURE TRENDS IN PHARMACEUTICAL AND OTHER BIOMEDICAL USES OF POLYMERS

This chapter illustrates some of the pharmaceutical applications of polymers. In the past, wider use of polymers in the health sciences field was limited by economic consideration: The pharmaceutical industry uses polymers in much smaller amounts than do other industries such as the textile, packaging, and tire industries. Therefore, the manufacturers of plastics and elastomers found no economic incentive to tailor-make polymers for the special needs of the pharmaceutical industry, or to seek clearance from the Food and Drug Administration for pharmaceutical applications of existing commercial polymers.

Presently, health scientists, commercial laboratories, and some pharmaceutical companies design, prepare, manufacture, and process or fabricate their own polymers in accordance with their specialized requirements. The following areas of polymer research and development are being actively pursued by academic and industrial investigators and health science practitioners. In addition to sutures, implants of plastics and elastomers in human and animal bodies are widely used for repair or replacement of tissues, organs, or parts of organs. Some of the problems encountered with im-



plants are degeneration of adjoining tissues and formation of blood clots and thrombi on the surfaces of implanted synthetic polymers; enlargement of implants through sorption of lipids or moisture, which constitutes a problem with precision parts; and corrosion and weakening of implants due to interaction with enzymes and other physiologic compounds and/or mechanical stresses. Considerable research is in progress to achieve biocompatibility of synthetic polymers through surface modification to prevent blood clotting, to make porous implants that permit ingrowth of adjoining tissue, and to search for stronger and more durable polymers.

A skin substitute to cover burns has been introduced. It is a composite made of an outer layer of silicone elastomer to protect the wound from infection and dehydration, bonded to a porous bottom layer that is adhesive and biodegradable consisting of cross-linked collagen combined with glycosaminoglycan. After the skin has grown back underneath this composite film, the bottom layer is biodegraded and the elastomeric top layer sloughed off.<sup>50</sup>

Sustained-release dosage forms are a fertile area for the application of plastics, elastomers, and film-forming polymers (see Chapters 13 and 19). The synthesis and evaluation of macromolecular prodrugs is in full swing. Medical and pharmaceutical journals publish increasing numbers of articles dealing with polymers, while polymer journals publish increasing numbers of articles dealing with pharmaceutical and biomedical uses of polymers. Three specialized publications, "Journal of Biomedical Materials Research," "Biomaterials, Medical Devices and Artificial Organs," and "Biomaterials," started in 1967, 1973, and 1980, respectively, cover polymeric as well as other biomaterials, for example, ceramics and metals.

#### References and Notes

- H. Mark and A. V. Tobolsky, *Physical Chemistry of High Polymeric Systems*, Interscience, New York, 1950.
- P. J. Flory, *Principles of Polymer Chemistry*, Cornell University, Ithaca, 1953.
- A. X. Schmidt and C. A. Martles, *Principles of High-Polymer Theory and Practice*, McGraw-Hill, New York, 1948.
- F. W. Billmeyer, *Textbook of Polymer Science*, 3rd Edition, Wiley, New York, 1984.
- H.-G. Elias, *Macromolecules I, Structure and Properties*, translated by J. W. Stafford, 2nd Edition Plenum, New York, 1984.
- P. C. Hiemenz, *Polymer Chemistry*, Dekker, New York, 1984.
- L. H. Sperling, *Introduction to Physical Polymer Science*, Wiley, New York, 1992.
- M. Mandelkern, *An Introduction to Macromolecules*, Springer-Verlag, New York, 1972.
- B. Vollmert, *Polymer Chemistry*, translated by E. H. Immergut, Springer-Verlag, New York, 1973.
- M. L. Miller, *The Structure of Polymers*, Reinhold, New York, 1966.
- P. W. Allen (Ed.), *Techniques of Polymer Characterization*, Butterworths, London, 1959.
- E. A. Collins, J. Bares and F. W. Billmeyer, *Experiments in Polymer Science*, Wiley, New York, 1973.
- J. Brandrup and E. H. Immergut (Eds.), *Polymer Handbook*, 3rd Edition, Wiley, New York, 1989.
- F. W. Billmeyer and C. B. de Than, *J. Am. Chem. Soc.* 77, 4763, 1955.
- C. Tanford, *Physical Chemistry of Macromolecules*, Wiley, New York, 1961.
- P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York, 1969.
- T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.* 73, 1915, 1951.
- F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962.
- J. H. Hildebrand and R. L. Scott, *The Solubility of Nonelectrolytes*, 3rd Edition, Dover, New York, 1964.
- J. H. Hildebrand, J. M. Prausnitz and R. L. Scott, *Regular and Related Solutions*, Van Nostrand Reinhold, New York, 1970.
- D. Mangaraj et al., *Makromol. Chem.* 65, 39, 1963; 67, 75, 34, 1963; 84, 225, 1965.
- G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.* 54, 1731, 1742, 1958.
- P. A. Small, *J. Appl. Chem.* 3, 71, 1953.
- K. L. Hoy, *J. Paint Technol.* 42, 76, 1970.
- D. W. van Krevelen, *Properties of Polymers, Their Estimation and Correlation with Chemical Structure*, 2nd Edition, Elsevier, New York, 1976.
- C. M. Hansen, *J. Paint Technol.* 39, 104, 505, 511, 1967; I & EC Prod. Res. Dev. 3(1), 2, 1969.
- E. M. Frith and R. F. Tuckett, *Linear Polymers*, Longmans, Green, London, 1951.
- H. Morawetz, *Macromolecules in Solution*, 2nd Edition, Wiley, New York, 1975.
- H. Tompa, *Polymer Solutions*, Butterworths, London, 1956.
- K. Shinoda, *Principles of Solution and Solubility*, Marcel Dekker, New York, 1978.
- A. R. Shultz and P. J. Flory, *J. Am. Chem. Soc.* 74, 4760, 1952; 75, 2888, 1953.
- H. R. Kruyt (Ed.), *Colloid Science II, Reversible Systems*, Elsevier, New York, 1949.
- S. Kasai and M. Koishi, *Chem. Pharm. Bull.* 25, 314, 1977.
- C. Thies, *Polymer-Plast. Technol. Eng.* 5(1), 1, 1975.
- P. L. Madan, *Drug Dev. Ind. Pharm.* 4, 95, 1978; *Asian J. Pharm. Sci.* 1, 1, 1979.
- R. Houwink, *Elasticity, Plasticity and Structure of Matter*, 2nd Edition, Warren Press, Washington, D.C., 1953.
- T. Alfrey, *Mechanical Behavior of High Polymers*, Interscience, New York, 1948.
- L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Reinhold, New York, 1974.
- F. Rodriguez, *Principles of Polymer Systems*, 2nd Edition, Hemisphere Publishing, Washington, D.C., 1982.
- H. Schott, in *Remington's Pharmaceutical Sciences*, 18th Edition, A. R. Gennaro (Ed.), Mack Publishing Co., Easton, Pa., 1990, Chapter 20.
- T. S. Carswell and H. K. Nason, *Modern Plastics*, 21, 121, June, 1944.
- H. Schott, *Biomaterials* 3, 195, 1982.
- J. H. Corley, T. E. Needham, E. D. Sumner and R. Mikeal, *Am. J. Hosp. Pharm.* 24, 259, 1977.
- M. Horioka, T. Aoyama and H. Karasawa, *Chem. Pharm. Bull.* 25, 1721, 1977.
- I. J. Stern, J. E. Miripol, R. S. Izzo and J. D. Lueck, *Toxicol. Appl. Pharmacol.* 41, 507, 1977.
- M. Morton (Ed.), *Rubber Technology*, 2nd Edition, Van Nostrand Reinhold, New York, 1973.
- E. C. Bernhardt (Ed.), *Processing of Thermoplastic Materials*, Reinhold, New York, 1959.
- J. M. McKelvey, *Polymer Processing*, Wiley, New York, 1962.
- I. I. Ruben, *Injection Molding—Theory and Practice*, Wiley, New York, 1972.
- H. S. Kaufman and J. J. Falicetta (Eds.), *Introduction to Polymer Science and Technology*, Wiley, New York, 1977.
- T. Jaksic and J. F. Burke, *Ann. Rev. Med.* 38, 107, 1987.

#### Problems

- 20-1. Consider the following three combinations of reagents:
  - (a)  $C_2H_5OH + HOOC-(CH_2)_4-COOH$ ;
  - (b)  $H_2N-(CH_2)_6-NH_2 + Cl-CO-(CH_2)_9-CO-Cl + \text{enough } Na_2CO_3 \text{ to neutralize the hydrochloric acid formed}$ ;
  - (c) In a mixture of 50 mole-% propylene glycol + 50 mole-% phthalic anhydride, replace 20 mole-% of the propylene glycol with 10 mole-% pentaerythritol,  $C(C_2H_4)_3O$ .

What type of polymer will be formed by the three condensation reactions?

*Partial Answer:* (a) Diethyl adipate will be formed. Since one of the two monomers is monofunctional, no polymer results.

20-2. When  $a = 1$  in the Mark-Houwink equation, equation (20-8) becomes

$$\frac{\eta_{sp}}{c} = K M^a$$

the original Staudinger equation, for very dilute polymer solutions. The statement is made in the text that the molecular weight average obtained in that case is the weight-average molecular weight. Prove it.

20-3. When determining the molecular weight of a sample of 6-nylon or poly( $\epsilon$ -caprolactam),  $\text{H}[\text{NH}-(\text{CH}_2)_5-\text{CO}]_n\text{OH}$ , 2.500 g dry polymer consumed  $2.21 \text{ cm}^3$  of  $0.1 \text{ N NaOH}$ . What is the number-average degree of polymerization, i.e., the value of  $n$ ? Note that each polymer chain or molecule has one amine and one carboxylic acid end-group.

*Answer:*  $n = 100$

20-4. A polymer sample was fractionated into three homogeneous or monodisperse fractions as follows:

Data for Problem 20-4

Fraction	Weight, grams	Molecular weight
A	10	100,000
B	20	
C	100	10,000

Given that the weight-average molecular weight of the entire sample is 23,000, calculate the molecular weight of fraction B.

*Answer:* 50,000 (49,500 has three significant figures, which is more than the  $M$  values of the input).

20-5. A sample of polyvinyl chloride was fractionated from its solution in tetrahydrofuran. The weight-percent (based on the weight of the entire sample) and the molecular weight ( $g/\text{mole}$ ) of successive fractions were as follows:

Data for Problem 20-5

Fraction no.	Weight-%	Molecular weight
1	6	$7 \times 10^3$
2	9	$1.7 \times 10^4$
3	15	$3.8 \times 10^4$
4	20	$7.5 \times 10^4$
5	23	$1.4 \times 10^5$
6	16	$2.5 \times 10^5$
7	8	$4.5 \times 10^5$
8	3	$1.05 \times 10^6$

Assuming that the fractions are essentially monodisperse, calculate  $\bar{M}_w$ ,  $\bar{M}_n$ ,  $\bar{M}_z$ , and  $\bar{M}_w/\bar{M}_n$  of the polyvinyl chloride sample.

*Answer:*  $\bar{M}_w = 401,000$ ;  $\bar{M}_n = 162,000$ ;  $\bar{M}_z = 43,500$ ; and  $\bar{M}_w/\bar{M}_n = 2.73$

20-6. The polymethyl methacrylate sample of Table 20-1 was one of four fractions of very narrow molecular weight distribution, essentially monodisperse, that had been studied by light scattering and by viscosity in ethylene chloride solution at  $25^\circ \text{C}$ .<sup>13</sup> The molecular weights and intrinsic viscosities of these fractions are as follows:

Data for Problem 20-6

Fraction no.	Molecular weight	Intrinsic viscosity (dL/g)
1	393,000	1.084
2	168,000	0.571
3	117,000	0.430
4	91,000	0.354

Determine the values of  $K$  and  $a$  in the Mark-Houwink equation, (20-8), for polymethyl methacrylate in ethylene chloride at  $25^\circ \text{C}$ .

*Answer:* Linear regression analysis of equation (20-8) gives  $a = 0.765$ ,  $K = 5.74 \times 10^{-5} \text{ dL/g}$

20-7. Calculate the solubility parameter of polyvinyl chloride. The unplasticized polymer has a density of  $1.42 \text{ g/cm}^3$ .

*Answer:*  $\delta = 9.2 \text{ (cal/cm}^3)^{1/2}$

20-8. Pyroxylin USP (cellulose dinitrate) has a solubility parameter of  $10.8 \text{ (cal/cm}^3)^{1/2}$ . It is insoluble in ethyl alcohol ( $\delta = 12.7 \text{ (cal/cm}^3)^{1/2}$ ) and in ethyl ether ( $\delta = 7.4 \text{ (cal/cm}^3)^{1/2}$ ), but it is soluble in a mixture of these two solvents. Explain briefly.

20-9. Will the intrinsic viscosity of polyethylene oxide increase, decrease, or remain unaffected as the temperature of its aqueous solution is increased?

*Hint:* Express your answer in terms of hydration.

20-10. Which solution of polyethylene oxide has the higher reduced viscosity in water at  $25^\circ \text{C}$ , one of  $0.001\%$  (w/v) or one of  $1.00\%$ ? Explain your answer in terms of the Huggins equation.

20-11. Consider the crystalline melting points of the following polymers:

Polymer	Melting point, $^\circ \text{C}$
A $\text{+O-(CH}_2\text{)}_2\text{-O-CO-(CH}_2\text{)}_6\text{-CO+}$	45
B $\text{+O-(CH}_2\text{)}_2\text{-O-CO-}\bigcirc\text{-CO+}$	265
C $\text{+CH}_2\text{-CH}_2\text{+}$	135
D $\text{+CH}_2\text{-}\bigcirc\text{-CH}_2\text{+}$	380

(a) Explain the increased melting point in going from A to B.

(b) Explain the increased melting point in going from C to D.

20-12. The melting points of some isotactic polyolefins  $\text{+CH}_2\text{-CH+}$  are as follows:

R	Melting point, $^\circ \text{C}$
E $\text{-CH}_3$	165
F $\text{-C}_2\text{H}_5$	125
G $\text{-CH}_2\text{-CH}_2\text{-CH}_3$	75

Explain the trend in melting point when going from E to F to G.

20-13. The glass transition temperatures of polyacrylonitrile, polybutadiene, and of a nitrile rubber (a copolymer of butadiene and acrylonitrile) are  $104^\circ$ ,  $-95^\circ$ , and  $-25^\circ \text{C}$ , respectively. Estimate the composition of the nitrile rubber.

*Answer:* 37% (w/w) acrylonitrile and 63% (w/w) butadiene. *Note:* The solvent resistance increases in proportion with the acrylonitrile content; 40% acrylonitrile is about the upper limit in nitrile rubbers.

20-14. Load-elongation data for a fiber of secondary cellulose acetate, obtained with a tensile tester at 25° C, are given below.

Data for Problem 20-14

Stress (pound/square inch, psi)	Strain or elongation (%)
2000	0.94
4000	1.88
5000	2.35
5630	2.80
6000	3.13
6360	4.22
6200	5.00
6000	6.88
5580	10.0
5880	15.0
5880	20.0
5880	22.0 (rupture)

(a) Plot the strain-stress curve. (b) Calculate Young's modulus from the slope of the initial linear portion of the plot (which includes the origin). *Note:* To obtain the modulus in psi, the strain or elongation should have no units. Therefore, the percent elongation must be changed into fractional values. For instance, use 0.0188 instead of 1.88%. (c) What is the yield stress and the tensile strength? (d) What is the permanent deformation at 20% elongation, and what is the elongation to break?

*Answers:* (b) 213,000 psi; (c) 6360 psi and 5580 psi; (d) 20% - 4.22% = 15.78%, and the elongation to break is 22%.

20-15. The load-elongation data below were obtained by stretching a specimen of vulcanized natural rubber without filler (pure gum) in a tensile tester until it ruptured.

Data for Problem 20-15

Stress (psi)	Elongation (in./in.)
26.3	0.15
49.0	0.28
80	0.60
90	0.75
116	1.00
142	2.00
178	3.0
263	4.0
410	5.0
660	6.0
1120	7.0
2010	8.0

(a) Plot the stress-strain curve. (b) Calculate the (initial) Young's modulus. *Note:* that only the initial two points are on a straight line with the origin and give the same initial modulus. *Note:* At elongations > 0.23 or 23%, the plot tends to level off and the modulus decreases. At elongations  $\geq 2.00$  or 200%, the curve turns up, which corresponds to an increase in modulus.

*Answer:* (b) 175 psi

20-16. (a) Using the data of Problem 20-15, calculate the tensile strength and the elongation to break. (b) The stress-strain curve is sigma-shaped. What causes the upturn at strains  $\geq 2.0$ , which corresponds to an increase in modulus?

*Answer:* (a) 2010 psi and 8.0 (i.e., 300%). In the previous problem, the elongation was expressed in percent because it was quite low, less than 1.0 in./in. or 100%. The tensile strength is given in pounds per square inch of original cross-section of the tensile specimen. Since the specimen is stretched to 9 times its original length, the cross-sectional area decreases considerably in the course of the extension. The true tensile strength would be the load to break the specimen divided by the cross-sectional area at the elongation to break. It is approximately 10 times greater than the apparent value calculated above. Tensile strength and Young's modulus, calculated in Problems 20-15 and 20-16, are somewhat lower than the corresponding values in Table 20-5, indicating that the specimen of Problems 20-15 and 20-16 was somewhat less vulcanized or cross-linked than the specimen of Table 20-5. The latter sample was presumably compounded with more sulfur.

(b) The rubber crystallizes at extensions  $\geq 2.0$ , as the extended chains are progressively lined up parallel to one another. Crystallization causes the specimen to stiffen.

20-17. A filament of HDPE has a diameter of 2 mm. By how many percent will a 30-kg weight stretch it reversibly? Use Table 20-5 for Young's modulus.

*Answer:* 3.0%

20-18. The specific volume of molten polypropylene, in  $\text{cm}^3/\text{g}$ , is a linear function of the temperature  $T$  (in degrees centigrade) according to the following equation:

$$v_{\text{m}} = 1.156 + 0.000841 T$$

The density of completely crystalline polypropylene at 25° C, as calculated from x-ray diffraction data, is  $0.936 \text{ g/cm}^3$ . Estimate the density at 25° C of a sample of solid polypropylene that is two-thirds crystalline.

*Answer:*  $0.907 \text{ g/cm}^3$

20-19. Hydroxypropyl methylcellulose, type 2190, USP contains (on a dry basis) 7 to 12% (w/w) hydroxypropyl groups,  $\text{OH}-\text{CH}-\text{CH}_2-\text{O}-$ , and 28 to 30% (w/w) methoxy groups,

$\begin{array}{c} | \\ \text{CH}_3 \\ | \\ \text{CH}_2-\text{O}- \end{array}$

Using the average values of 9.5% and 29% for the weight percentages of the two substituent groups, calculate the degree of substitution (DS) for hydroxypropoxy and methoxy, by means of algebra.

*Answer:* DS for hydroxypropoxy = 0.33; DS for methoxy = 2.42

20-20. A polypeptide containing lysine and benzyl glutamate as the sole monomers has been synthesized. The following data were obtained by analysis: 4.632 g polymer consumes 1.65 mL of 0.10 *N* NaOH when titrated against thymol blue, and 2.087 g polymer generates 183.3 mL nitrogen STP when analyzed according to the Van Slyke method (treatment with  $\text{NaNO}_2$  + acetic acid produces 1 molecule  $\text{N}_2$  for each  $\text{NH}_2$  group by diazotization). STP means standard temperature (273.15°K or 0°C) and pressure (1 atmosphere or 76 cm Hg). Calculate the average molecular weight. What type of average is it? Calculate the mole-% lysine and benzyl glutamate.

*Answer:*  $\bar{M}_n = 28,070$ ; mole-% lysine = 62.9, mole-% benzyl glutamate = 37.1