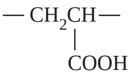
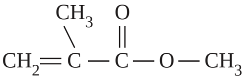
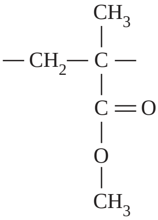
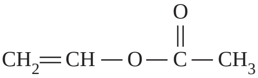
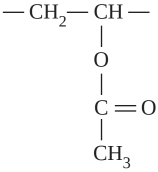
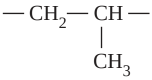
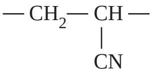
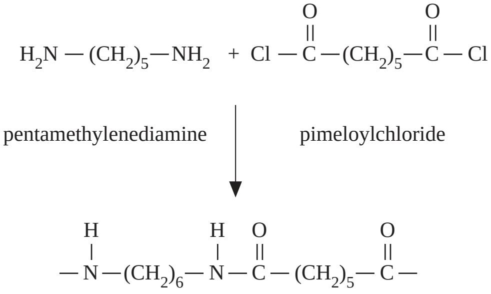
SOLUTIONS TO CHAPTER 1 PROBLEMS

1.1.

Monomer	Repeating Unit	Polymer Name
a. $CH_2{=}CH{-}COOH$	 $-CH_2CH(COOH)-$	Poly(acrylic acid)
b.  $CH_2{=}C(CH_3){-}C(=O){-}O{-}CH_3$	 $-CH_2{-}C(CH_3)(C(=O){-}O{-}CH_3){-}$	Poly(methyl methacrylate)
c.  $CH_2{=}CH{-}O{-}C(=O){-}CH_3$	 $-CH_2{-}CH(O{-}C(=O){-}CH_3){-}$	Poly(vinyl acetate)
d. $CH_2{=}CH{-}CH_3$	 $-CH_2{-}CH(CH_3){-}$	Polypropylene
e. $CH_2{=}CH{-}CN$	 $-CH_2{-}CH(CN){-}$	Polyacrylonitrile

1.2. a.

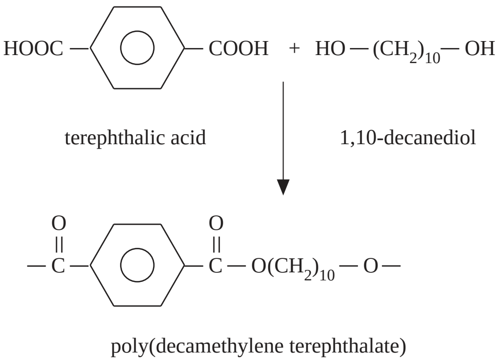


$$H_2N-(CH_2)_5-NH_2 + Cl-C(=O)-(CH_2)_5-C(=O)-Cl \longrightarrow -N(H)-(CH_2)_6-N(H)-C(=O)-(CH_2)_5-C(=O)-$$

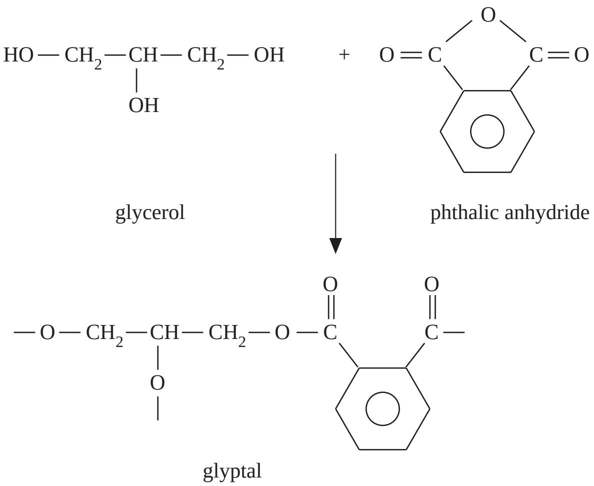
pentamethylenediamine

pimeloylchloride

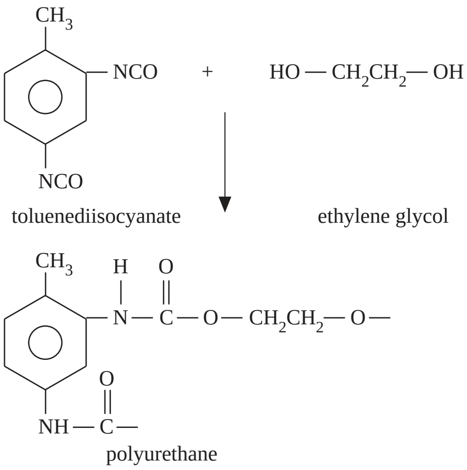
poly(pentamethylene pimelamide); nylon 5,7 b.


HOOC
COOH
+
HO — (CH2)10 — OH
terephthalic acid
1,10-decanediol
O
O
C
C — O(CH2)10 — O
poly(decamethylene terephthalate)

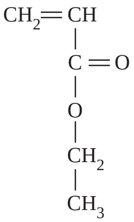
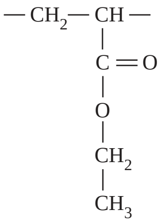
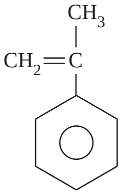
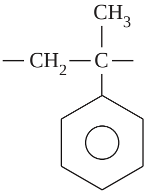
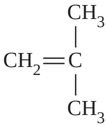
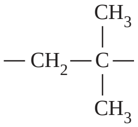
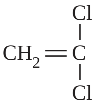
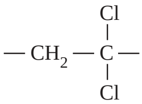
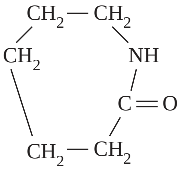
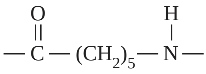
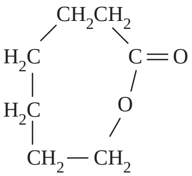
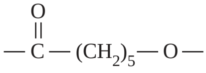
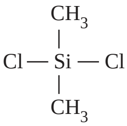
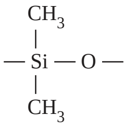
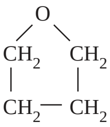
c.


HO — CH2 — CH — CH2 — OH
OH
+
O
O = C
C = O
glycerol
phthalic anhydride
O — CH2 — CH — CH2 — O — C
C
O
glyptal

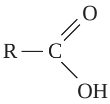
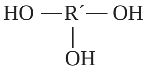
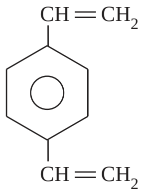
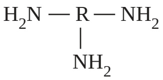
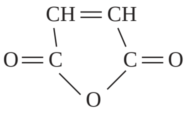
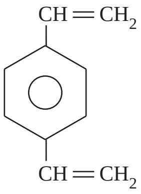
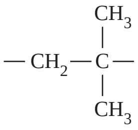
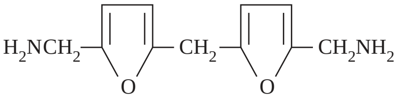
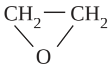
d.

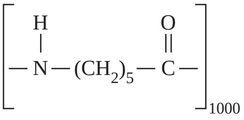

CH3
NCO
NCO
+
HO — CH2CH2 — OH
toluenediisocyanate
ethylene glycol
CH3
H
O
N — C — O — CH2CH2 — O
NH — C
polyurethane

1.3.

Monomer	Repeating Unit	Polymer
a.  $CH_2{=}CH-C({=}O)-O-CH_2-CH_3$	 $-CH_2-CH(-C({=}O)-O-CH_2-CH_3)-$	Poly(ethyl acrylate)
b. 		Poly(α-methyl styrene)
c.  $CH_2{=}\overset{CH_3}{\underset{CH_3}{C}}$	 $-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-$	Polyisobutylene
d.  $CH_2{=}\overset{Cl}{\underset{Cl}{C}}$	 $-CH_2-\overset{Cl}{\underset{Cl}{C}}-$	Poly(vinylidene chloride)
e. 	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{\mid}{N}}-$	Polycaprolactam (nylon 6)
f. 	 $-\overset{O}{\overset{\|}{C}}-(CH_2)_5-O-$	Polycaprolactone
g.  $Cl-\overset{CH_3}{\underset{CH_3}{Si}}-Cl$	 $-\overset{CH_3}{\underset{CH_3}{Si}}-O-$	Poly(dimethyl siloxane)
h. 	$-O-(CH_2)_4-$	Poly(tetramethylene oxide)

1.4.

		Polymer		
			Yes	
Monomer A	**Monomer B**	**No**	**Linear**	**Branched/ Cross-linked**
a. 	 $HO—R'(OH)—OH$	X		
b. $HOOC—R—COOH$	$HO—R'—OH$		X	
c. $HO—R—OH$	$R'—N{=}C{=}O$	X		
d. 				X
e. $HO—(CH_2)_5COOH$			X	
f.  $H_2N—R(NH_2)—NH_2$	$HOOC—R'—COOH$			X
g. 				X
h. $H_2N—R—NH_2$	$OCN—R'—NCO$		X	
i.  $—CH_2—C(CH_3)_2—$			X	
j. CH_2O				X
k. 			X	

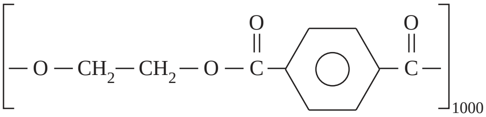
1.5. a. 

$$\left[-\overset{H}{\overset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}- \right]_{1000}$$

Molecular weight of repeat unit = 15 + (14 × 5) + 28 = 113

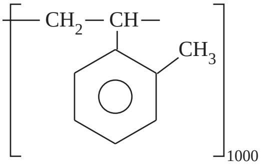
$$Mw_{polymer} = (MW_{repeat\ unit})(DP) = 113 \times 1000$$

$$= 1.13 \times 10^5$$

b. 

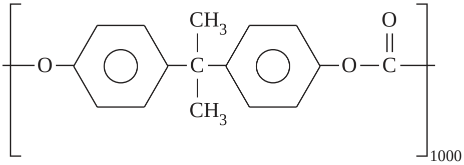
Molecular weight of repeating unit = 16 + (14 × 2) + 16 + 28 + (6 × 12) + 4 + 28

$$Mw_{polymer} = (MW_{repeat\ unit})(DP) = 192 \times 1000$$
$$= 1.92 \times 10^5$$

c. 

Molecular weight of repeat unit = 14 + 13 + (6 × 12) + 4 + 15 = 118

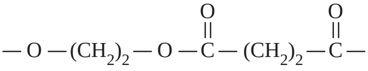
$$Mw_{polymer} = 118 \times 1000 = 1.18 \times 10^5$$

d. 

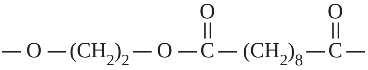
Molecular weight of repeat unit = 16 + (12 × 6) + 4 + 12 + (2 × 15) + (12 × 6) + 4 + 16 + 28

= 254

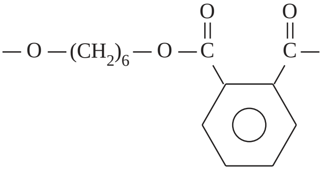
$$Mw_{polymer} = MW_{repeating\ unit} = 254 \times 1000$$
$$= 2.54 \times 10^5$$

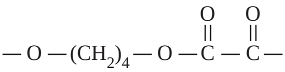
1.6. a. 

$$-O-(CH_2)_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_2-\overset{\displaystyle O}{\overset{\|}{C}}-$$

b. 

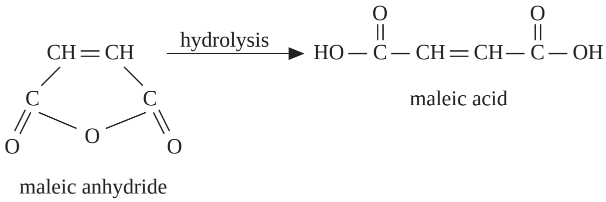
$$-O-(CH_2)_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_8-\overset{\displaystyle O}{\overset{\|}{C}}-$$

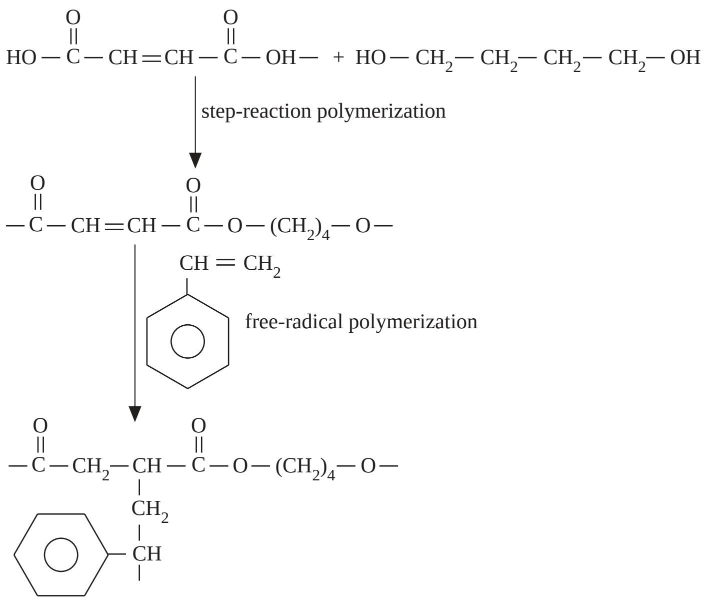
c. 

d. 

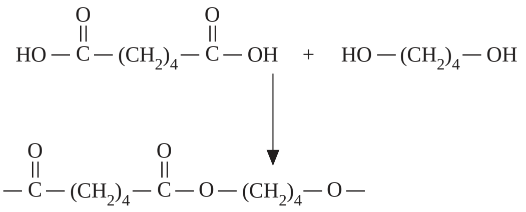
$$-O-(CH_2)_4-O-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-$$

1.7.





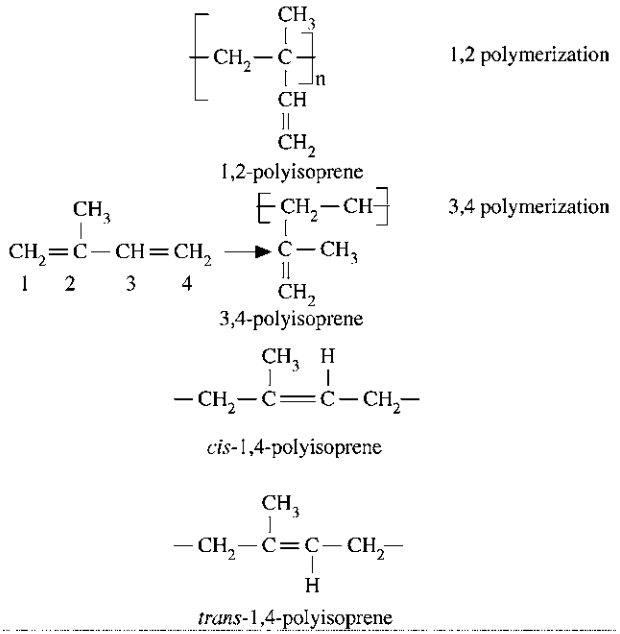
This is a polyester with polystyrene grafted onto the backbone.



$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \quad + \quad HO-(CH_2)_4-OH \longrightarrow -\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-O-$$

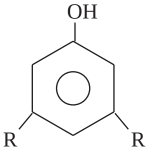
This is a polyester without a possibility of reaction with styrene since there are no residual double bonds in the main chain.

1.8.



This residual double bond in the main chain permits vulcanization.

1.9. To be a good adhesive, the reactants must be capable of forming a cross-linked structure. In this reaction, formaldehyde behaves as a glycol HO–CH_2–OH (its hydrated form). It is therefore bifunctional. To form a cross-linked structure with formaldehyde, therefore, the phenolic compound must be trifunctional. From elementary organic chemistry, only compound C is trifunctional and should therefore be chosen.



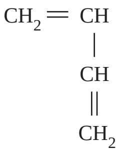
1.10.

n	Name of Amine	Functionality
1	Diethylenetriamine	5
2	Triethylenetetramine	6
3	Tetraethylenepentamine	7
4	Pentaethylenehexamine	8

SOLUTIONS TO CHAPTER 2 PROBLEMS

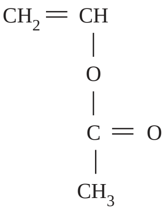
2.1. The ease of polymerization of a vinyl monomer depends on the reactivities of the monomer and the attacking radical. Substituents that stabilize the product radical tend also to stabilize the monomer but to a much smaller extent. Resonance stabilization depresses the reactivity of radicals. In contrast to vinyl acetate, butadiene has conjugated double bonds. Using 1,2 polymerization of butadiene as an example, it is apparent that the product radical from butadiene is much more resonance stabilized than that from vinyl acetate. In fact, the monomer–radical propagation rate constants at 60°C are 100 and 2300 l/mol-s for butadiene and vinyl acetate, respectively.

a.



$CH_2=CH-CH=CH_2$

butadiene



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

vinyl acetate

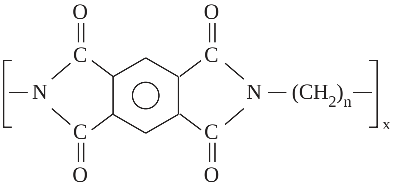
b. The higher the initiator concentration, the higher the number of chain radicals initiated. Therefore, for a fixed monomer concentration, the average number of monomers consumed by each chain radical will be reduced as the initiator concentration increases.

2.2. Phthalic anhydride is a saturated acid. Its incorporation into the resin mixture serves to decrease the overall cross-link density and, consequently, resin brittleness.

2.3. The melting point of the polymer decreases with increasing flexibility, i.e., increasing value of n.

$H_2N-(CH_2)_2-NH_2$
ethylenediamine

$H_2N-(CH_2)_{10}-NH_2$
dexcamethylenediamine

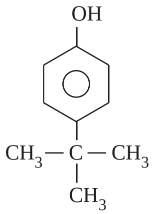


aromatic polyimide

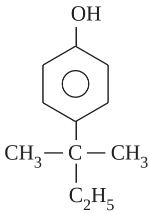
Poly(decamethylene pyromellitimide), n = 10, is more likely to form a useful polymer than poly(ethylene pyromellitimide), n = 2. In fact, diamines whose carbon chain contains less than seven carbon atoms form polymers that degrade at or below their melting points.

2.4. The polymers from the three compounds will have ladder-type structures. However, the polymers from compounds B and C will have at least one and two skeletal bond(s) per repeating unit while a double-cyclization polymer will result from compound A. The presence of one or two consecutive single bonds between aromatic units will enhance polymer susceptibility to thermal degradation. In principle, therefore, under identical conditions the thermal stability of the resulting polymers will be A more than B more than C.

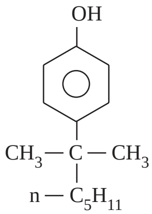
2.5. The presence of substituent alkyl groups on the phenolic ring renders the resulting phenolic resins oil-soluble.



p-tertiary butyl phenol

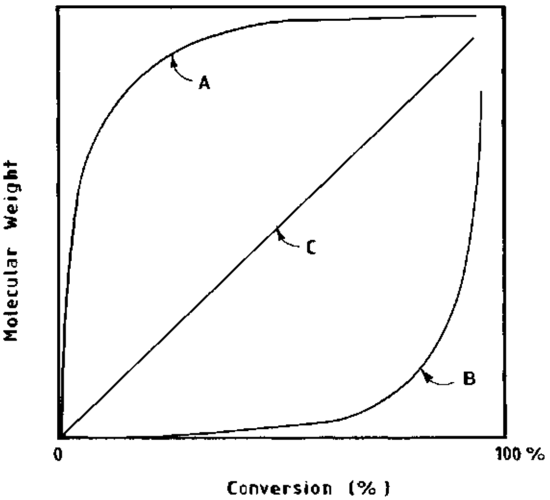


p-tertiary amyl phenol



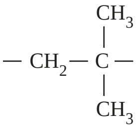
p-tertiary octyl phenol

2.6. In free-radical polymerization, high molecular weight is formed at a very early stage of polymerization (line A). In condensation polymerization, high-molecular-weight polymer is formed only toward the end of the reaction, i.e., conversion approaches 100% (line B). In living polymerization, the molecular weight is directly proportional to conversion.



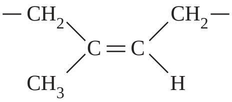
SOLUTIONS TO CHAPTER 3 PROBLEMS

3.1a.



$$-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-$$

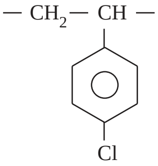
polyisobutylene
(PIB)



poly(1,4-*cis*-polyisoprene)
(natural rubber)

PIB is a saturated polymer. Natural rubber has a residual double bond on its main chain and this is susceptible to oxidative attack.

b. $-CH_2-CH_2-$ polyethylene (nonpolar)

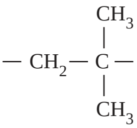


poly(*p*-chlorostyrene) (polar)

Poly(*p*-chlorostyrene) is polar and therefore is not suitable as an electrical insulator. Polyethylene, on the other hand, is nonpolar and will not conduct electricity.

c. PMMA is amorphous; there are therefore no regions of differing indices of refraction in the polymer. Hence, it is transparent. At room temperature, polyethylene is semicrystalline, having both crystalline and amorphous components that differ in their refractive indexes. Consequently, PE is translucent. At 135°C, PMMA is still amorphous, while polyethylene also becomes amorphous since its melting point is 135°C. Both polymers are then transparent.

d. $-CH_2-CH_2-$ polyethylene

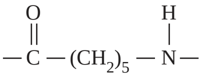


$$-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-$$

polyisobutylene

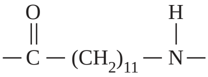
In contrast to polyethylene, it is impossible sterically to accommodate the two methyl groups in polyisobutylene in the planar zigzag conformation. However, a helical conformation can accommodate the pendant groups.

e.



$$-\overset{\overset{O}{\|}}{C}-(CH_2)_5-\overset{\overset{H}{|}}{N}-$$

nylon 6



$$-\overset{\overset{O}{\|}}{C}-(CH_2)_{11}-\overset{\overset{H}{|}}{N}-$$

nylon 12

For the same degree of polymerization, the density of the hydrophilic amide linkages –NHCO– is higher, while the length of the hydrophobic methylene ($-CH_2-$) group is smaller in nylon 6 than in nylon 12.

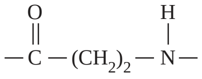
f. Small amounts of chlorine produce irregularities in the polymer structure. This reduces crystallinity and hence lowers the softening point. Large amounts of chlorine in the structure lead to resumed crystallinity in addition to higher polarity. Thus the softening point increases.

g. The addition of glass fibers increases the number of nucleation sites in semicrystalline polymers. This produces an increase in the degree of crystallinity and, consequently, an enhanced heat distortion temperature. By definition, amorphous polymers are noncrystalline and, as such, this mechanism is inoperable.

h. The high cohesive energy density of polyethylene makes it highly crystalline and insensitive to solvents except at temperatures close to its melting point (about 135°C). Thus, even though gasoline and PE are both hydrocarbons, gasoline will not dissolve PE when used in an automobile gasoline tank.

i. Teflon is nonpolar due to high degree of symmetry of the starting monomers, has an extremely high CED because the small size of the fluorine atom permits close packing of molecular chains, and is not attacked by chemicals.

j. $-CH_2-CH_2-$ polyethylene (nonpolar)



$$-\overset{\overset{O}{\|}}{C}-(CH_2)_2-\overset{\overset{H}{|}}{N}-$$

nylon 6 (polar)

The predominant intermolecular bonds in nylon 6 are hydrogen bonds resulting from the highly polar –NHCO– amide linkages. On the other hand, polyethylene is held together by van der Waals forces, which are much weaker than the polar hydrogen bonds in nylon 6.

3.2. Styrene is soluble in CH_3OH but not in H_2O. Precipitation with H_2O will consequently bring down both the unreacted styrene monomer and polystyrene. No, attempting to distill off the monomer would probably initiate thermal polymerization of styrene.

3.3.

$$\overline{M}_n = \frac{\sum W_i}{\sum W_i/M_i}$$

$$= \frac{200}{\dfrac{100}{2\times 10^3} + \dfrac{50}{2\times 10^4} + \dfrac{50}{1\times 10^5}}$$

$$= 3770 \text{ g/mol}$$

$$\overline{M}_w = \sum W_i M_i$$

$$= 100/200 \times 2 \times 10^3 + 50/200 \times 2 \times 10^4 + 50/200 \times 1 \times 10^5$$

$$= 31{,}000 \text{ g/mol}$$

$$\text{Polydispersity} = \frac{\overline{M}_w}{\overline{M}_n} = \frac{31{,}000}{3770} = 8.2$$

3.4.

$$\overline{M}_n = \frac{\sum W_i}{\sum W_i/M_i}$$

$$\overline{M}_n = \frac{200 + 200 + 100}{200/1.2 \times 10^5 + 100/5.6 \times 10^5 + 100/10.0 \times 10^5}$$

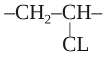
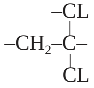
$$= 2.35 \times 10^5 \text{ g/mol}$$

$$\overline{M}_w = \sum W_i M_i = \frac{200}{500} \times 4.5 \times 10^5 + \frac{200}{500} \times 8.9 \times 10^5 + \frac{100}{500} \times 10^5$$

$$= 7.36 \times 10^5 \text{ g/mol}$$

3.5.

Polymer	$\bar{X}_n$	Assignment
P	1500	Poly(vinyl chloride)
V	2000	Poly(vinylidene chloride)

Polymer	Repeating Unit	Comment
Poly(vinyl chloride)	 $-CH_2-\underset{\displaystyle CL}{\underset{\vert}{CH}}-$	Polar
Poly(vinylidene chloride)	 $-CH_2-\overset{\displaystyle -CL}{\overset{\vert}{\underset{\displaystyle CL}{\underset{\vert}{C}}}}-$	Nonpolar

PVC is a polar polymer, whereas poly(vinylidene chloride), due to symmetry, is nonpolar. Its cohesive energy is derived essentially from van der Waals forces. This means that it will require a higher number of monomers strung together to develop good physical properties.

3.6. As a result of the reactions that occur during free-radical polymerization, the reacting monomer(s) may be arranged in different ways on the polymer chain. Consequently, most free-radical polymerizations yield atactic polymers, which are noncrystalline. However, in cases where the pendant group is small enough to fit into a crystalline lattice, crystalline polymers are formed — for example, poly(vinyl alcohol). Besides, if the monomer is symmetrical, free-radical polymerization may also yield crystalline polymers, e.g., polyethylene and polytetrafluoroethylene.

3.7.

$$\text{CED} = \frac{\Delta H_V - RT}{V_1}$$

$$RT = (1.98 \text{ cal/mol K})\,(273 + 25 \text{ K})$$

$$= 590 \text{ cal/mol}$$

$$\delta = \left(\text{CED cal/cm}^3\right)^{1/2}$$

Solvent	CED (cal/cm³)	δ (cal/cm³)$^{1/2}$
2,2,4-Trimethylpentane	47.0	6.90
n-Hexane	52.8	7.3
CCL_4	73.9	8.6
$CHCl_3$	85.8	9.3
Dioxane	94.8	9.7
CH_2Cl_2	99.4	10.0
$CHBr_3$	111.9	10.6

From graph, δ_2 (polymer) = 9.3

$$\mathrm{CED} = \delta^2 = 86.5\ \mathrm{cal/cm^3}$$

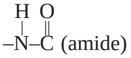
$$\Delta H_m = 1/2\,(1 - 1/2)\,(11.8 - 9.3)^2$$

$$= 1.56\ \mathrm{cal/cm^3}$$

3.8. a. The crystalline form of a polymer is always denser than the amorphous form because of more efficient molecular packing. In a semicrystalline polymer this difference in densities between the amorphous and crystalline regions of the polymer determines its transparency since the index of refraction is proportional to the density. Similarly, polymer rigidity depends on the degree of crystallinity. Polyethylene and polypropylene produced by stereospecific catalysts are semicrystalline. The polymers are translucent because of the difference in the refractive indices between the amorphous and crystalline components. With copolymerization, however, there is a mutual destruction of crystallinity. The copolymer is amorphous, soft, and transparent since there no longer exist regions of differing refractive indices.

b. In this case a block copolymer is produced. The sequences of ethylene and polypropylene units are long enough to crystallize independently. The individual properties of the separate polymers are retained by the block copolymer.

3.9.

Absorption	Responsible Structure	Comments
H_2O	 $-\overset{\mathrm{H}}{\overset{\vert}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}$ (amide)	As n increases, water absorption becomes low because the hydrocarbon nature of the polymer predominates. Consequently, hexane absorption increases with n. On the other hand, as n decreases, ability for hydrogen bonding through the amide linkages is enhanced. Water absorption increases while hexane absorption decreases.
Hexane	$-CH_2-$ (methylene)	

3.10. The copolymer may be regarded as having a structure in which glassy polystyrene acts as crosslinks for the rubbery polybutadiene. For such a lightly cross-linked polymer, solubility (swelling) is highest when the solubility parameter of the polymer δ_2 is equal to that of the solvent. The solubility parameter of a 1:1 mixture of pentane and ethyl acetate is given by:

$$\delta = 1/2\,(7.1) + 1/2\,(9.1) = 1/2\,(7.1 + 9.1)$$

$$= 8.1$$

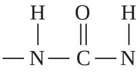
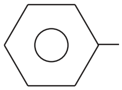
3.11.

Material (urea derivative)	Comments
(1) Hexamethylenediamine	Flexible but symmetrical molecules; –NH–CO–NH– group enhances CED and as such crystallizes readily and with high melting point.
(2) Tris(2-aminoethylamine)	Less flexible than (1), and branched but trifunctional. Crystallization tendency reduced, CED also reduced, hence relatively lower melting point.
(3) Triethyleneoxide diamine	Flexible ether, difunctional. Introduction of oxygen atom into the main chain reduces rotational energy barrier. Enhanced flexibility considerably reduces crystallization tendency and also crystalline melting point.
(4) Poly(oxypropylene triamine)	Polymeric and branched nature makes crystallization impossible. Reduced CED and hence a liquid at room temperature.

3.12. Proper molecular alignment is a requirement for crystallinity. A dilute solution allows sufficient molecular translation to meet this requirement. In contrast, given the extensive molecular entanglements in a polymer melt, enough molecular alignment is impossible, and hence crystal perfection is smaller than that from a dilute solution. However, at high temperature sufficient molecular mobility occurs for proper molecular alignment, and consequently, enhanced crystallinity is obtained.

SOLUTIONS TO CHAPTER 4 PROBLEMS

4.1. Increasing order of T_m: e < a < b < d < c.

Material	Comments
c	With linkages  $-\overset{H}{\overset{\mid}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{\mid}{N}}$, forms strong H-bonds; phenyl rings  are stiff and rigid. Both increase T_m
d	Urea linkages; high density of hydrogen bonding
b	Amide linkages; same density of hydrogen bonding as d but urea linkages generally stronger than amide linkages
a	Amide linkages but relatively smaller density of hydrogen bonding than b due to longer distances between amides; $(CH_2)_8$ vs. $(CH_2)_4$
e	Ester linkages enhance molecular rotation and hence reduce T_m

4.2. Since PVC and dibutyl sebacate have about the same value of solubility parameters, they are compatible and hence the following expression is applicable:

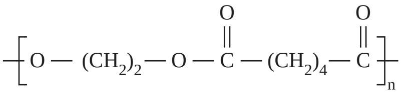
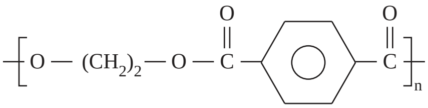
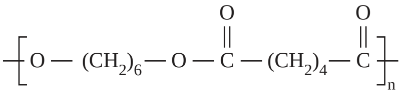
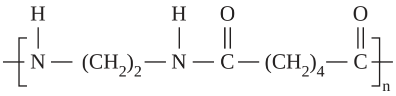
$$T_g = V_A T_{gA} + V_B T_{gB}$$

V_A and V_B are volume fractions of polymer and plasticizer, respectively.

$$25 = (1 - V_B)\,85 + V_B\,(-100)$$

$$V_B = \frac{60}{185} = 32.4\%$$

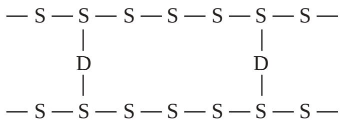
4.3.

Polymer	Structure
a. Poly(ethylene adipate)	 $\left[O-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}} \right]_n$
b. Poly(ethylene terephthalate)	
c. Poly(hexamethylene adipate)	 $\left[O-(CH_2)_6-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}} \right]_n$
d. Poly(ethylene adipamide)	 $\left[\overset{H}{\overset{\mid}{N}}-(CH_2)_2-\overset{H}{\overset{\mid}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}} \right]_n$

Order of decreasing melting point: b > d > a > c.

Polymer	Comments
b	Presence of phenyl rings stiffens backbone and increases T_m
d	Amide linkages form hydrogen bonds
a	Ester linkages more flexible than amide linkages in (d)
c	Ester linkages; and more flexible than (a); $(CH_2)_6$ vs. $(CH_2)_2$

4.4.



$$\begin{array}{ccccccccccccccc}
- & S & - & S & - & S & - & S & - & S & - & S & - & S & - \\
 & & & | & & & & & & & & | & & & \\
 & & & D & & & & & & & & D & & & \\
 & & & | & & & & & & & & | & & & \\
- & S & - & S & - & S & - & S & - & S & - & S & - & S & -
\end{array}$$

S = styrene residue, D = divinyl benzene residue

$$T_g^c - T_g = \frac{3.9 \times 10^4}{M_c}$$

$$T_g^c = T_g \text{ of cross-linked polymer}$$

$$T_g = T_g \text{ of uncross-linked polymer}$$

$$7.5 = \frac{3.9 \times 10^4}{M_c}$$

$$M_c = 5200$$

$$M_c = \overline{X}_n M_o$$

$$M_o = \text{molecular weight of styrene } \left(CH_2 - CH -\right) = 104$$

$$\overline{X}_n = \frac{M_c}{M_o} = \frac{5200}{104} = 50$$

4.5.

$$\frac{T_g}{T_m} = \frac{2}{3} \text{ for unsymmetrical polymers}$$

$$T_g = 100°C = 273 + 100 = 373 \text{ K}$$

$$T_m = \frac{3}{2} \times 373 = 559.5 \text{ K} = 286.5°C$$

4.6.

$$\frac{1}{T_m} = \frac{1}{T_m^\circ} - \frac{R}{\Delta H_m} \ln x$$

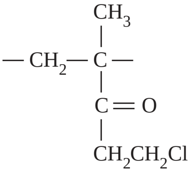
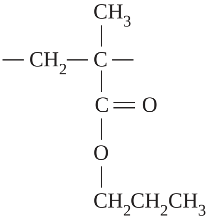
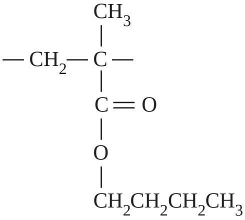
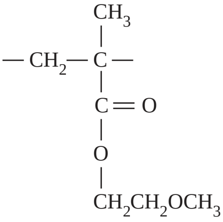
$$T_m = 250 + 273 = 423 \text{ K}$$

$$\frac{1}{T_m} = \frac{1}{423} - \frac{1.98\ (\text{cal/mol})}{2500 \text{ cal/mol}} \ln 0.75$$

$$= 0.0021$$

$$T_m = 467 \text{ K} = 194°C$$

4.7.

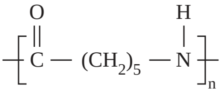
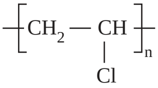
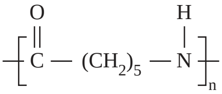
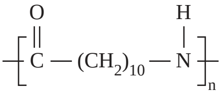
Polymer	**Structure**
Poly(2-chloroethyl methacrylate)	 $-CH_2-C(CH_3)(C(=O)CH_2CH_2Cl)-$ I
Poly(*n*-propyl methacrylate)	 $-CH_2-C(CH_3)(C(=O)OCH_2CH_2CH_3)-$ II
Poly(*n*-butyl methacrylate)	 $-CH_2-C(CH_3)(C(=O)OCH_2CH_2CH_2CH_3)-$ III
Poly(2-methoxyethyl methacrylate)	 $-CH_2-C(CH_3)(C(=O)OCH_2CH_2OCH_3)-$ IV

Poly(2-chloroethyl methacrylate) is more polar than poly(*n*-propyl methacrylate) due to the chlorine atom on the side of the chain. Similarly, poly(2-methoxyethyl methacrylate) is more polar than poly(*n*-butyl methacrylate). The glass transition temperatures of the more polar polymers are higher.

4.8. $$f = f_g + \alpha\left(T - T_g\right)$$

$$= 0.025 + 60.6 \times 10^{-6}\,(150 - 100) = 0.028$$

4.9.

Polymer 1	**Polymer 2**	**Comments on Relative T_m**
Polyethylene $[CH_2\ CH_2]_n$	Random copolymer of ethylene and propylene  $-\left[\overset{\overset{O}{\parallel}}{C}-(CH_2)_5-\overset{\overset{H}{\vert}}{N}\right]_n-$	T_m (polymer 1) > T_m (polymer 2). Polymer 1 is highly crystalline while copolymerization disturbs molecular order and hence reduces crystallinity of copolymer.
Poly(vinyl chloride) (PVC)  $-\left[CH_2-\underset{\underset{Cl}{\vert}}{CH}\right]_n-$	Polytetrafluoroethylene (Teflon) $-\left[CF_2-CF_2\right]_n-$	T_m (Teflon) > T_m (PVC) because of small size of fluorine atom; Teflon is highly symmetrical hence it has high CED.
Nylon 6  $-\left[\overset{\overset{O}{\parallel}}{C}-(CH_2)_5-\overset{\overset{H}{\vert}}{N}\right]_n-$	Nylon 11  $-\left[\overset{\overset{O}{\parallel}}{C}-(CH_2)_{10}-\overset{\overset{H}{\vert}}{N}\right]_n-$	T_m (1) > T_m (2). Density of amide linkages –(NHCO–) is higher in nylon 6 than nylon 11. Consequently, nylon 6 has higher CED resulting from H-bonding. Nylon 11 is more flexible than nylon 6 (longer $–CH_2–$ sequences).

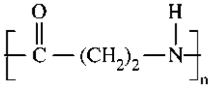
SOLUTIONS TO CHAPTER 5 PROBLEMS

5.1. The compatibilizing agent prevents the migration of the blended homopolymers. This restriction in mobility minimizes the volume occupied by each polymer in its environment within the material. Consequently, molecules of each polymer in the blend form higher coils compared with the respective homopolymers. In addition, to improve chemical and solvent resistance, a major consequence of such reduction in the number of entanglements is improved flow properties, i.e., a higher melt index. Recall that melt index is defined as the weight of polymer flowing through a given orifice under certain prescribed standard conditions.

5.2. In order to obtain adhesives of high solids content, the dextrin must be highly soluble in water. The starch degrative product with a lower degree of polymerization will be expected to be more soluble. Given the manufacturing conditions of white and yellow dextrins, canary dextrins will be expected to have a lower average degree of polymerization and, consequently, are more suitable as envelope seal adhesives.

5.3.

a. Structure of nylon 6:



$$\left[\overset{\overset{\displaystyle O}{\|}}{C} - (CH_2)_2 - \overset{\overset{\displaystyle H}{|}}{N} \right]_n$$

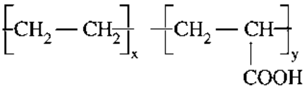
Presence of amide linkages favors hydrogen bonding and, consequently, water absorption. A decrease in the intensity of H-bonding and presence of hydrophobic groups should reduce water absorption. Copolymerize, for example, $H_2N(CH_2)_{10}$-NH_2.

b. A polymer that possesses the ability to flow is generally tough and capable of blunting crack propagation. The flow properties of PE can be increased by decreasing its crystallinity or density by:

1. Copolymerization of butene, hexene, or octene
2. Copolymerization of small quantities of acrylic acid
3. Copolymerization of acrylate (CH_2› CH–CO–O–R) where R is an alkyl group with molecular weight higher than CH_3

c. Copolymerization of rubber (butadiene) to generate a microstructure of dispersed rubber phase within a glassy styrene matrix. Rubbery phase helps to prevent propagation of microcracks and thus increase impact resistance.

5.4. Structure of copolymer

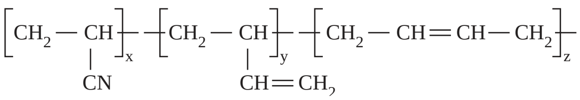


$$\left[CH_2 - CH_2 \right]_x \left[CH_2 - \underset{\underset{\displaystyle COOH}{|}}{CH} \right]_y$$

Recall that melt index, by definition, is amount of polymer flowing through a given orifice under some specified conditions. Introduction of the polar acrylic acid unit into the polymer structure increases its polarity while at the same time disrupting the interchain bonding and crystalline nature of PE. Initially, the disruption of the interchain interaction of PE predominates. Consequently, flow is enhanced and melt index increases. Further increase in acrylic acid content results in the predominance of chain polarity and hence intermolecular attraction. This leads to a decrease in the flow properties.

As the polarity of the copolymer increases with the increasing content of acrylic acid, the bonding with ionic groups on A1 increases. The peel strength therefore increases correspondingly.

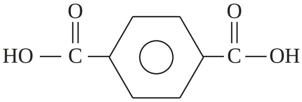
5.5. The structure of nitrile rubber:

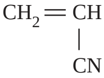


$$\left[CH_2 - \underset{\underset{\displaystyle CN}{|}}{CH} \right]_x \left[CH_2 - \underset{\underset{\displaystyle CH=CH_2}{|}}{CH} \right]_y \left[CH_2 - CH = CH - CH_2 \right]_z$$

Nitrile rubber is a copolymer of acrylonitrile and butadiene. The poor resistance to oil is due to the butadiene component. Acrylonitrile is highly polar, and its introduction into the structure therefore enhances the oil resistance of the copolymer, the extent of which depends on its content in the copolymer.

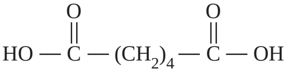
5.6. Copolymerization of the following monomers with the starting monomer(s) of the given homopolymer should, in principle, bring about the desired changes. The extent to which these changes are realized will, however, depend on the composition of the comonomers.

(ia)  Introduces rigid phenyl rings into polymer backbone

(ib) 

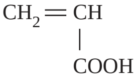
$CH_2=CH(CN)$

Polarity of monomer (due to presence of CN group) enhances intermolecular attraction and hence reduces the possibility of chemical attack

(ic) 

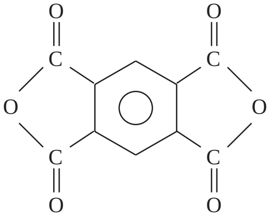
$HO-C(=O)-(CH_2)_4-C(=O)-OH$

Presence of $(CH_2)_4$ should enhance overall flexibility

(id) 

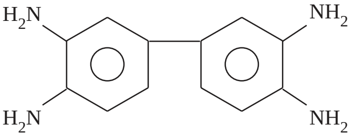
$CH_2=CH(COOH)$

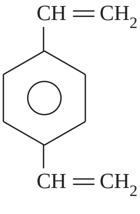
Increases polymer polarity

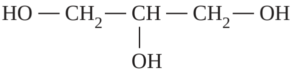
(ie) 

Introduces aromatic rings with imide or imidazole units into polymer structure

or



(iia)  Affects cross-linking due to increased functionality

(iib) 

$HO-CH_2-CH(OH)-CH_2-OH$

Trifunctionality of monomer results in cross-linking

5.7. The reactivity ratios of the components are

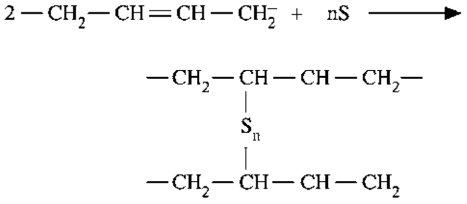
Maleic anhydride (1)	r_1	r_2	r_1r_2
Methyl methacrylate (2)	0.02	6.7	0.134
Vinyl acetate (2)	0.003	0.055	0.00017

Based on these reactivity ratios, the tendency toward alternation is much greater with vinyl acetate as the curing monomer. Thus the polymer resulting from cure of the polyester with vinyl acetate will consist of short but numerous cross-links, while that cured with methyl methacrylate will consist of long but relatively fewer cross-links. Good creep resistance demands high cross-link density; i.e., cure with vinyl acetate will be preferable for this application.

5.8. The brittleness of films from cured UF resins may be attributed to the strong hydrogen bonding of the urea (–NH–CO–NH) interunit linkages and the stiff methylene ($–CH_2–$) units. Any structure that will increase the flexibility of UF polymer chain will therefore reduce the brittleness of the cured UF resin. The phenyl rings will enhance stiffness, while long sequences of $(CH_2)_2$ will enhance flexibility. Consequently, the brittleness of cured UF films will be reduced in the order: b < c < d < a.

5.9. The introduction of flexibilizing molecular units into the polymide structure should produce a useful adhesive. Therefore, compound B would be preferable to compound A. The presence of the ––O– reduces molecular rotational energy and thus enhances flexibility. The resulting polymer structure has both imide and benzimidazole units, which are characterized by high aromatic and low hydrogen contents. The structure is very rigid and therefore should possess high temperature resistance.

5.10. Vulcanization reaction:



$$2\,-CH_2-CH{=}CH-CH_2- \;+\; nS \longrightarrow \begin{array}{c} -CH_2-\underset{|}{CH}-CH-CH_2- \\ S_n \\ -CH_2-\overset{|}{CH}-CH-CH_2 \end{array}$$

Basis: 100 g rubber. From stoichiometry therefore:

$$100\ \text{g rubber} \times \frac{1\ \text{g mol rubber}}{54\ \text{g rubber}} \times \frac{n\ \text{g mol S}}{2\ \text{g mol rubber}} \times \frac{32\ \text{g S}}{1\ \text{g mol S}}$$

$$= \frac{3200n}{108}\ \text{g S}$$

a. For disulfide cross-links, n = 2. Amount of sulfur = 59.26 phr.
b. For decasulfide cross-links, n = 10. Amount of sulfur = 296.30 phr.

5.11. UF resin stability to hydrolysis will be expected to increase in the order: monomer 3 > monomer 1 > monomer 2. UF resins as result of their urea linkages [HN –CO–NH] are capable of absorbing water through hydrogen bonds. Inclusion of these monomers into the resin structure will break the frequency of these linkages and therefore reduce the possibility of water absorption and, consequently, hydrolysis. The 12 and 6 methylene groups in monomers 3 and 1, respectively, will be expected to increase the hydrophobicity of the resins, with monomer 3 being more effective than monomer 1. On the other hand, monomer 2, while reducing overall water uptake, is still capable of encouraging water absorption because of the oxygen atoms.

5.12.

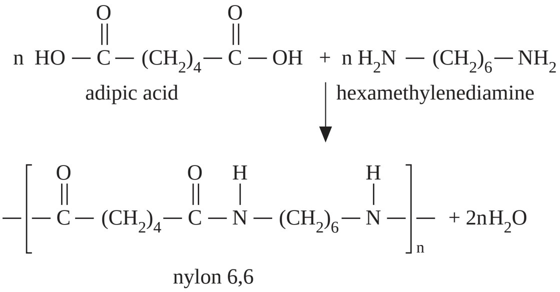
$$-\!\left[CH_2-CH_2\right]_n\!- \qquad \text{Polyethylene}$$

$$-\!\left[CH_2-CH_2-O\right]_n\!- \qquad \text{Poly(ethylene oxide)}$$

The presence of oxygen atoms in poly(ethylene oxide) would be expected to enhance its flexibility relative to polyethylene. Stiff main chains apparently permit more independent movement of side chains. Therefore, the number of methylene spacer groups required to eliminate interference on the reactivity

SOLUTIONS TO CHAPTER 6 PROBLEMS

6.1.



$$n\ HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH + n\ H_2N-(CH_2)_6-NH_2 \longrightarrow -\left[-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\right]_n- + 2nH_2O$$

a. $$\overline{X}_n = \frac{1}{1-p};\ M_0 = \frac{226}{2} = 113$$

$$\overline{M}_n = \frac{M_o}{1-p} = \frac{113}{1-0.98} = \frac{113}{0.02} = 5650$$

b. $$\overline{X}_n = \frac{1+r}{2r(1-p)+1-r}$$

$$r = \frac{100}{102} = 0.98$$

$$\overline{X}_n = \frac{1+0.98}{2(0.98)\,(1-0.98)+1-0.98} = \frac{1.98}{0.0592} = 30.45$$

$$\overline{M}_n = M_oX_n = 3779$$

c. $$M_n = 113 \times 100 = 11{,}300;\ X_n = \frac{1}{1-0.99} = 100$$

d. $$\overline{M}_n = \frac{\Sigma N_iM_i}{\Sigma N_i}$$

Consider 1 mol of usual product, i.e., $\Sigma N_i = 1$

$N_A + N_N = 1$, N_A = mol of afternoon shift

N_N = mol of night shift

N_A (3779) + (1 – N_A) (11,300) = 5650

N_A (3779 – 11,300) = 560 – 11,300

$$N_A = \frac{5650}{7521} = 0.75$$

$$N_B = 1-0.75 = 0.25$$

$$\overline{M}_n = \frac{\Sigma N_iM_i^2}{\Sigma N_iM_i} = \frac{0.75(3379)^2+0.25(11{,}300)^2}{0.75(3779)+0.25(11{,}300)} = 7533$$

6.2. Unfractionated system:

$$\overline{M}_w = 2,\ \text{to}\ \overline{M}_w = 12{,}000$$

Fractionated system: consider 1 mol of the system, then

$$\mathrm{Ni} + \mathrm{N2} = 1.$$

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \sum N_i M_i \text{ since } \sum N_i = 1$$

$$= N_i(2000) + N_2(10,000)$$

$$= 0.5(2000) + 0.5(10,000)$$

$$= 6000$$

Note that M_n is the same for both the fractionated and unfractionated systems.

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{0.5(2000)^2 + 0.5\left(10,000^2\right)}{6000} = 8667$$

Melt viscosity is proportional to $\overline{M}_w$. Since $\overline{M}_w$ (fractionated) < $\overline{M}_w$ (unfractionated), melt viscosity will decrease.

6.3a.

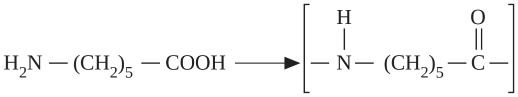
$$\overline{X}_n = \frac{1+r}{2r(1-p)+1-r}$$

$$r = \frac{100}{105} = 0.95$$

$$\overline{X}_n = \frac{1+0.95}{2(0.95)\,(1-0.98)+1-0.95}$$

$$= \frac{1.95}{0.088} = 22.16$$

$$M_n = \overline{X}_n M_0$$



$$H_2N-(CH_2)_5-COOH \longrightarrow \left[-\overset{\displaystyle H}{\overset{|}{N}}-(CH_2)_5-\overset{\displaystyle O}{\overset{\|}{C}}-\right]$$

$$M_o = 113$$

$$\overline{M}_o \equiv 22.13 \times 113 = 2504$$

b. For maximum degree of polymerization, P = 1

$$\overline{X}_n = \frac{1+r}{1-r} = \frac{1.95}{0.05} = 39$$

$$\overline{M}_n = 39 \times 113 = 4407$$

6.4a. $$\overline{X}_n = \frac{1}{1-P}$$

P	0.5	0.99	1
X_n	2	100	∞

b. $$r = \frac{100}{101} = 0.99$$

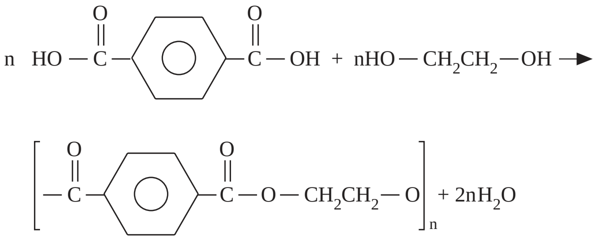
Maximum degree of polymerization

$$\overline{X}_n = \frac{1+r}{1-r} = \frac{1.99}{0.01} = 199$$

c. $$r = \frac{N_A}{N_B + 2N_{monoacid}} = \frac{100}{100 + 2 \times 2} = \frac{100}{104} = 0.96$$

$$\overline{X}_n = \frac{1+0.96}{1-0.96} = 49$$

6.5.



a. $$\overline{M}_n = \overline{X}_n M_o = \frac{M_o}{1+p}$$

$$M_o = \frac{192}{2} = 96$$

$$\overline{M}_n = \frac{96}{1-0.99} = 9600$$

b. $$\overline{M}_w = M_o\,\overline{X}_w = M_o\left(\frac{1+p}{1-p}\right)$$

$$= 96\left(\frac{1+0.99}{1-0.99}\right) = \frac{96 \times 1.99}{0.01}$$

$$= 19{,}104$$

c. $$P_x = p^{x-p}\left(1-p\right)$$

$$= \left(0.99\right)^{3-1}\left(1-0.99\right) = 9.80 \times 10^{-3}$$

d. $W_x = X\left(p^{x-1}\right)(1-p)^2$

$$= 3\left(0.99^{3-1}\right)(1-0.99)^2$$

$$= 2.94 \times 10^{-4}$$

6.6. $W_x = X\left(P^{x-1}\right)(1-p)^2$

	P		P	
	0.10	**0.90**	**0.10**	**0.90**
n	1	1	100	100
W_x	0.98	0.01	8.1×10^{-98}	2.95×10^{-5}

At low conversions, the fraction of monomer is high, while the fraction of higher molecular weight polymers is low. Conversely, at high conversions the fraction of monomers is low, whereas the fraction of high-molecular-weight polymers becomes much higher.

6.7. $\overline{M}_n = M_o \overline{X}_n = \dfrac{M_o}{1-p}$

For nylon 5,M_o = 113

For nylon 6,12 $M_o = \dfrac{324}{2} = 162$

Nylon 6, $\overline{M}_n = \dfrac{113}{1-0.95} = 3260$

Nylon 6,12, $M_n = \dfrac{162}{1-0.95} = 3240$

6.8. $N_x = P^{x-1}(1-P)^2 = (0.98)^{100-1}(1-0.98)^2 = 5.41 \times 10^{-5}$

$W_x = XP^{x-1}(1-P)^2 = 100(0.98)^{100-1}(1-0.98)^2 = 5.41 \times 10^{-3}$

Fraction of monomers= $1(0.98)^o\ (1-0.98)^2$

$= 4.0 \times 10^{-4}$

SOLUTIONS TO CHAPTER 7 PROBLEMS

7.1. Since f is independent of monomer concentration,

[M]	$[I]^{1/2}$	$R_p/[I]^{1/2}[M]$
9.04	0.485	0.044
8.63	0.454	0.043
7.19	0.0505	0.045
6.13	0.478	0.044
4.96	0.560	0.044
4.75	0.438	0.045
4.22	0.480	0.043
4.17	0.162	0.041
3.26	0.495	0.044
2.07	0.459	0.044

Since $R_p/[I]^{1/2}[M]$ is constant, data are consistent with rate of polymerization by free-radical mechanism.

7.2. a.

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}[M]$$

Assuming f is independent of [M] to keep R_p constant, [I] and [M] must be kept constant.

b.

$$\frac{d[M\cdot]}{dt} = 2f\,k_d[I]$$

$$= 2\,k_d[I] \text{ assume } f = 1$$

$$k_d = 3.25 \times 10^{-4}\,\text{min}^{-1}$$

$$= 5.42 \times 10^{-6}\,\text{s}^{-1}$$

$$I = 6.6 \times 10^{-6}\,\text{mol/ml}$$

$$R_i = \frac{d[M\cdot]}{dt} = 2\left(5.42\times10^{-6}\,\text{s}^{-1}\right)\left(6.6\times10^{-6}\,\text{mol/ml}\right)$$

$$= 7.5 \times 10^{-11}\,\text{mol/ml} - \text{s}$$

$$\overline{X}_n = \frac{R_p}{R_i}$$

$$R_p = 1.79 \times 10^{-3}\,\text{g/ml} - \text{min}$$

$$= \frac{1.79}{104} \times 10^{-3}\,\text{mol/ml} - \text{min}$$

$$= 1.72 \times 10^{-5}\,\text{mol/ml} - \text{min}$$

$$\overline{X}_n = \frac{1.72\times10^{-5}\,\text{mol/ml} - \text{min}}{4.29\times10^{-9}\,\text{mol/ml} - \text{min}}$$

$$= 4.01 \times 10^{3}$$

c.

$$\frac{-d[I]}{dt} = f\,k_d\,[I]$$

$$\frac{-d[I]}{[I]} = k_d\,dt;\ f = 1$$

$$[I] = e^{-k_d t}$$

$$= e^{-\left(3.25 \times 10^{-4} \times 60 \times 3\right)}$$

$$= 94.3\%$$

7.3. a. In general, for radical chain polymerization, polymerization rates are given by

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}[M]$$

$$I \xrightarrow{k_d} 2R\cdot$$

$$= d[I]/dt = fk_d[I]$$

$$\ln\frac{[I]}{[I_o]} = k_d\,t \quad \text{if } f = 1$$

$$k_d = \frac{\ln 2}{44} = 1.58 \times 10^{-2}\ h^{-1}$$

$$= 4.38 \times 10^{-6}\,s^{-1}$$

Substituting for the constants:

$$R_p = (145\ l/mol - s)\left(\frac{4.38 \times 10^{-6}\,s^{-1}}{0.180\ l/mol - s}\right)^{1/2}[I]^{1/2}[M]$$

$$= 0.715[I]^{1/2}[M]$$

b. Assume that at 50% conversion:

$$[I] = [I_o]$$

$$[M] = [M_o]/2$$

Total volume = 100 + 400 + 0.5 = 500 ml = 0.51 since density = 1

$$[I] = \frac{0.5\ g}{0.5\ l} \times \frac{1\ mol}{242\ gmol} = 4.13 \times 10^{-3}\,mol/l$$

$$[M] = \frac{50\ g}{0.5\ l} \times \frac{1\ mol}{104\ gmol} = 0.962\ mol/l$$

$$R_p = 0.715\left(4.13 \times 10^{-3}\right)^{1/2}(0.962)\ mol/l - s$$

$$= 0.044\ mol/l - s$$

c. $$R_p = -d[M]/dt = k_p\left(\frac{k_d}{k_t}\right)^{1/2}[I_o]^{1/2}[M]$$

$$\int\frac{d[M]}{[M]} = k_p\left(\frac{k_d\ I_o}{k_t}\right)^{1/2}\int dt$$

$$t = \frac{\ln[M]/[M_o]}{k_p\left[k_d[I_o]/k_t\right]^{1/2}} = \frac{\ln 2}{k_p\left(\frac{k_d[I_o]}{k_t}\right)^{1/2}} = 15.1\ \mathrm{s}$$

7.4. The general expression for X_n when there is transfer is given by Equation 7.39 (in text book).

For the polymerization of pure styrene, there is obviously no solvent, hence the second term on the right-hand side of the expression drops out.

a. Comparing the remaining expression with the given equation:

b. $$C_M = 0.60\times10^{-4}$$

$$\frac{1}{\overline{X}_n} = 0.60\times10^{-4} + 8.4\times10^2\frac{10^{-4}}{(8.35)^2} + 2.4\times10^7\frac{(10^{-4})^2}{(8.35)^3}$$

$$= 0.00166$$

$$\overline{X}_n = 602$$

c. For normal termination:

$$\frac{1}{\overline{X}_n} = 8.4\times10^2\frac{R_p}{[M]^2} = 8.4\times10^2\left[10^{-4}/(8.35)^2\right]$$

$$= 0.0012$$

$$\overline{X}_n = 833$$

d. Comparing the given expression with the general transfer equation:

$$\frac{k_t}{k_p^2} = 840\text{, i.e., }\frac{k_p^2}{2k_t} = \frac{1.19}{2}\times10^{-3} = 5.95\times10^{-4}$$

$$\nu = \frac{k_p^2}{2k_t}\frac{[M]^2}{R_p} = 5.95\times10^{-4}(8.35)^2/10^{-4} = 415$$

e. $$C_I\left(\frac{k_t}{k_p^2\, fk_d}\right)=2.4\times10^7$$

$$C_I=2.4\times10^7\,\frac{k_p^2\, fk_d}{k_t}=2.4\times10^7\times2.29\times10^{-9}$$

$$=0.055$$

f. $$k_t/k_p^2=840;\ f\,k_d\,k_p^2/k_t=2.29\times10^{-9}$$

$$\text{whence } f\,k_d=1.92\times10^{-6}$$

$$f=\frac{1.92\times10^{-6}}{3.2\times10^{-6}}=0.61$$

7.5. For transfer to solvent, the relevant equation is

$$1/X_n=\left(1/X_n\right)_o+C_s[S]/[M]$$

$$\left(1/X_n\right)_o=\text{reciprocal degree of polymerization in the absence of a solvent (bulk polymerization)}$$

$$M_{no}=M_m\ X_{no}$$

$$\text{where } M_m=\text{mol wt of repeat unit}$$

$$=104\text{ for PS}$$

$$4.16\times10^5=104\ X_{no}$$

$$\overline{X}_{no}=(4.16/104)\times10^5$$

$$\frac{1}{\overline{X}_{no}}=2.5\times10^{-4}$$

Dilution factor = 2, i.e., [S]/[M] = 2

$$1/\overline{X}_{no}=2.5\times10^{-4}+2C_s$$

Cyclohexane:

$$1/\overline{X}_n=2.5\times10^{-4}+2\times0.16\times10^{-4}$$

$$\overline{X}_n=3550$$

$$\overline{M}_n=3.69\times10^5$$

Carbon tetrachloride:

$$1/\overline{X}_n = 2.5 \times 10^{-4} + 2 \times 180 \times 10^{-4}$$

$$\overline{X}_n = 27.59$$

$$\overline{M}_n = 2.87 \times 10^3$$

7.6.

$$\overline{M}_n = \frac{1}{4}\overline{M}_{no}\text{, i.e., } \frac{1}{\overline{X}_n} = \frac{4}{\overline{X}_{no}} = \frac{1}{\overline{X}_{no}} + C_S[S]/[M]$$

$$C_S[S]/[M] = 6 \times 10^{-4}$$

Styrene: $[S]/[M] = 6 \times 10^{-4}/0.31 \times 10^{-4} = 19.35$
Methyl methacrylate: $[S]/[M] = 6 \times 10^{-4}/0.52 \times 10^{-4} = 11.54$
Vinyl acetate: = $[S]/[M] = 6/92 = 0.07$

7.7. We note first that high temperatures promote chain transfer and, consequently, a decrease in X_n. More fundamentally, however, if termination predominates over transfer, then,

$$\overline{X}_n \propto \frac{k_p}{k_t} \propto e^{-(E_p - E_t)/RT}$$

Now if $E_t > E_p$, then X_n should increase with decreasing temperature. In cationic polymerization, the propagation step involves the approach of an ion to a neutral monomer molecule in a medium of low dielectric constant. The activation energy required for this process is essentially zero. However, the termination step requires the combination of an ion pair — a process that involves a considerable activation energy. Thus in cationic polymerization, $E_t > E_p$.

7.8.

Impurity	**$X_n(R_p/R_t)$**
Water	0.1
Ethanol	40

Thus the molecular weight of polystyrene formed in the presence of ethanol is 400 times that formed in the presence of water. High polymer formation is more probable with ethanol impurity.

7.9. Sterically regular structures of polymers are generally obtained only in the absence of free ions. If anionic coordination is carried out in media of high solvating power like ethers or amines, the bond between the metal of the catalyst and the carbon atom of the growing polymer chain is substantially ionized. Consequently, the polymer anion behaves essentially as a free ion, and the positive counterion is unable to perform its function of coordinating, orienting, and inserting the incoming monomer in the polymer chain and therefore structural regularity cannot be assured. In effect, there is a change from an anionic coordination polymerization mechanism to an anionic polymerization.

7.10. a. Kinetic chain length ν = average number of monomers consumed by each primary radical. In this case ν is simply an equal distribution of available monomer among the initiators, that is,

$$\nu = \overline{X}_n = [M]/[I] = 1.0/1.0 \times 10^{-4}$$

$$= 10^4$$

$$\overline{M}_n = M_o\overline{X}_n = 104 \times 10^4$$

b. For termination by coupling

$$\overline{M}_n = 2\overline{X}_n\, M_o = 2\nu = 2.08 \times 10^6$$

c. In the presence of transfer agent, X_n is reduced

$$\overline{X}_n = \nu = [M]/([I]+[T])$$

$$= 1.0/(1.0 \times 10^{-4} + 6.0 \times 10^{-4})$$

$$= 1.43 \times 10^3$$

$$\overline{M}_n = M_o\, X_n = 1.43 \times 10^3 \times 104$$

$$= 1.49 \times 10^5$$

7.11. a.

$$R_p = -d[M]/dt = k_p \left(\frac{f\, k_d}{k_t} \right)^{1/2} [I]^{1/2} [M]$$

$$= K[I]^{1/2}[M]$$

$$\text{Run A, } R_p = \frac{1.0 \times 0.5}{500} \text{ mol/l} - \text{min} = 1.0 \times 10^{-3} \text{ mol/l} - \text{min}$$

$$K_A = \frac{R_p}{[I]^{1/2}[M]} = \frac{1.0 \times 10^{-3}}{(0.0025)^{1/2}(0.5 \times 1.0)} = 4.0 \times 10^{-2}$$

$$\text{Run C, } R_p = \frac{0.8 \times 0.40}{600} = 5.33 \times 10^{-4} \text{ mol/l} - \text{min}$$

$$K_c = \frac{5.33 \times 10^{-4}}{(0.001)^{1/2}(0.8 \times 0.6)} = 3.5 \times 10^{-2}$$

$$\text{Hence, } K_c \approx K_A = K = 4.0 \times 10^{-2}$$

$$\text{Run D, } R_p = 4.0 \times 10^{-2} (0.01)^{1/2} (0.25 \times 0.5)$$

$$= 5 \times 10^{-4} \text{ mol/l} - \text{min}$$

$$\text{Time for this conversion} = \frac{0.5 \times 0.25}{5 \times 10^{-4}}$$

$$= 250 \text{ min}$$

b.

$$\ln R_{p_{60}}/R_{p_{80}} = \frac{E}{R}\left(\frac{1}{T_{60}} - \frac{1}{T_{80}}\right)$$

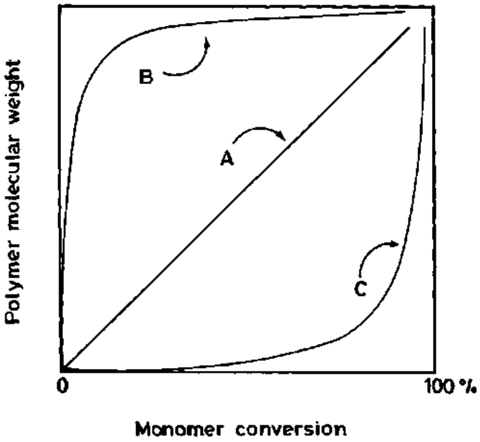
$$R_{p_{80}} = \frac{0.5 \times 0.75}{700} = 5.36 \times 10^{-4}$$

$$\ln \frac{1.0 \times 10^{-3}}{5.36 \times 10^{-4}} = \frac{E}{1.99}\left(\frac{1}{333} - \frac{1}{353}\right)$$

$$0.624 = E\left(8.55 \times 10^{-5}\right)$$

$$E = 7.3 \text{ kcal/mol}$$

7.12.



SOLUTIONS TO CHAPTER 8 PROBLEMS

8.1. From Table 8.1:

Monomer (1)	**Monomer (2)**	r_1	r_2
Methyl methacrylate	Styrene	0.46	0.52
Styrene	Vinyl chloride	17	0.02

Using the copolymer equation:

Feed Composition, f_1	**Methyl Methacrylate–Styrene**		**Styrene–Vinyl Chloride**	
	F_1	F_2	F_1	F_2
0.25	0.31	0.69	0.86	0.14
0.50	0.49	0.51	0.96	0.06
0.75	0.67	0.33	0.98	0.02

For styrene–vinyl chloride copolymer, because of the large difference in the reactivity ratios of the monomers, lowering the composition of styrene in the feed does not necessarily result in a reduction of the styrene content in the copolymer. On the other hand, because of the similarity in reactivity ratios in the styrene–methyl methacrylate system, the styrene content of the copolymer can be controlled by an adequate control of feed composition.

8.2.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

Hence, for $r_1 = 0.02$ and $r_2 = 0.3$, polymer composition is as follows:

f_1	F_1
0.25	0.34
0.50	0.44
0.75	0.49

$$r_1 = k_{11}/k_{12} = 0.02 \quad \text{or} \quad k_{11} = 0.02\ k_{12}$$

$$k_{22} = 0.3\ k_{21}$$

Each radical shows a greater preference for adding the other monomer. Consequently, each radical prefers to add the other monomer, and as such there is a tendency toward alternation.

8.3. For ideal copolymerization, the copolymer equation reduces to:

$$F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

$$r_1 = 1/r_2 = 0.1$$

$$F_1 = 10 \times 10.75/\left(10(0.75) + 0.25\right)$$

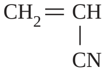
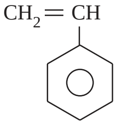
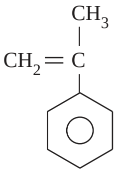
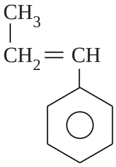
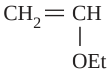
$$= 0.97$$

8.4. The possible monomer pairs and their corresponding r_1r_2 values are

Monomer Pair	r_1r_2
Butadiene–styrene	0.780
Butadiene–acrylonitrile	0.006
Butadiene–vinyl chloride	0.308
Styrene–acrylonitrile	0.016
Acrylonitrile–vinyl chloride	0.108

As the quantity r_1r_2 approaches zero, the tendency toward alternation increases. Therefore, butadiene–acrylonitrile will be the most suitable pair of monomers for the application under these conditions.

8.5.

Monomer	Structure
a. Acrylonitrile	 $CH_2{=}\underset{\displaystyle CN}{\underset{\mid}{CH}}$
b. Styrene	
c. α-Methyl styrene	
d. 2-Methyl styrene	
e. Vinyl ethyl ether	 $CH_2{=}\underset{\displaystyle OEt}{\underset{\mid}{CH}}$

Order of reactivity: c > b > a > d > e.

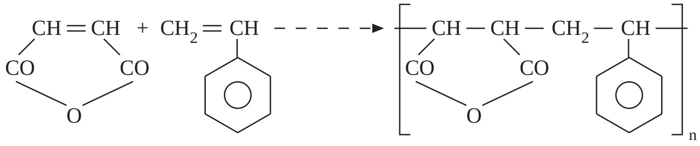
Basis:

1. General order of reactivity of monomers due to substituents:

$$-C_6H_5 > CN > OR$$

2. Additional substitution on the α-C is additive
3. 2- or β-substitution reduces reactivity of monomer

8.6.



The tendency for alternation increases as the difference in polarity between two monomers increases. Styrene is an electron donor monomer, while maleic anhydride is an electron acceptor. Consequently, alternating copolymerization between both monomers is facilitated. Notice that r_1r_2 for the monomers is 0.0006.

8.7.

$$r_1 = Q_1/Q_2 \exp\left[-e_1\left(e_1 - e_2\right)\right]$$

$$r_2 = Q_2/Q_1 \exp\left[-e_2\left(e_2 - e_1\right)\right]$$

Monomer					
1	**2**	r_1	r_2	r_1r_2	F_1
A	B	27.80	0.027	0.751	0.94
A	C	0.563	0.089	0.050	0.59
C	D	1.556	0.639	0.994	0.61

The copolymer from the polymerization of monomers A and C will show the highest alternation tendency.

8.8. Composition. From Equation 8.9:

Monomer Pair	F_1 **(%)**
a	50.00
b	61.88
c	50.00
d	49.26

Sequence:

$$r_1 = k_{11}/k_{12}; \; r_2 = k_{22}/k_{21}$$

a. $k_{11} = k_{12} = k_{22} = k_{21}$. The probability that monomer 1 will be next to monomer 2 in the chain is exactly the same as either of the monomers being next to itself, and consequently the resulting polymer is random. The composition of polymer formed later in the reaction remains unchanged.

b. $k_{11} = 1.89\ k_{12}$; $k_{22} = 0.78\ k_{11}$. In this case also, a random copolymer is formed, but there is a much greater tendency for monomer 1 to be next to itself in the polymer monomer formed at the beginning of the reaction. Later on in the polymerization, as a result of the depletion of monomer 1, the polymer formed has a greater tendency of having monomer 2 next to itself.

c. $k_{11} = 0.01\ k_{12}$; $k_{22} = 0.01\ k_{21}$. Each monomer radical prefers the second monomer, and polymer formed should be alternating. The composition and sequence of polymer at the initial and later stages of the reaction are identical.

d. $k_{11} = 0.002\ k_{12}$; $k_{22} = 0.032\ k_{21}$. There is a strong tendency toward alternation. Polymer formed at the later stages of reaction will be almost identical to that formed initially; however, polymer formed later will contain more of monomer 1, while that formed initially will contain more monomer 2.

SOLUTIONS TO CHAPTER 9 PROBLEMS

9.1. a. Better contact provides a better opportunity for electron transfer. Fast separation builds a high charge. Slow separation allows some of the electrons that would have remained on the surface of the acceptor to return to equilibrium, thus lowering the charge.

b. PVA/EVA offers a good balance of properties, including excellent outdoor weatherability, a complete absence of plasticizer migration (especially important for medical uses) and improved low-temperature capacity. These properties recommend PVA/EVA copolymer for outdoor and medical applications.

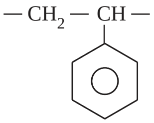
c. As long as the plasticizer is free of impurities, the choice of plasticizer has little or no effect on the electrical properties of the PVC compound. Plasticizer permanence for long service life of wire and cable formulations at increasingly high rating temperatures and flame retardancy are the most critical criteria in selecting a plasticizer system. DUP, DTDP, and UDP, which have much higher molecular weight, combined with the exceptionally high-temperature low volatility of trimellitates will more readily satisfy the above criteria than DOP and DINP with relatively low molecular weight and volatility.

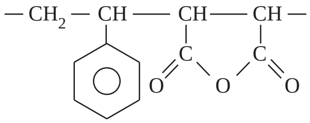
d. One of the most important demands placed on PVC compounds for interior automotive uses is low plasticizer volatility at high temperatures. A car interior can easily reach 82°C on a hot summer day with all windows closed. A plasticizer that is relatively volatile at such temperature will cause fogging of windshield and window surfaces. In such applications where nonfogging is important, the exceptionally low volatility of trimellitate plasticizers as well as their good processibility, compatibility, and low water extraction make these plasticizers better alternatives than phthalate esters.

e. Any ingredient of a food container that can migrate into the food is subject to regulation. Substances that are known to be carcinogenic or toxic are not sanctioned at all for food contact. Various regulations relate to extraction of plasticizers from a food container by dry, oily, or aqueous foods. Plasticizers from soya and linseed oil epoxides are derivatives from edible substances that are unlikely to be toxic. The primary reasons for the popularity of adipates over phthalates in food-wrap films are their better oxygen transmission, better resistance to water extraction, and better low-temperature flexibility.

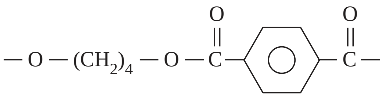
f. Extraction of plasticizers from PVC by coatings such as nitrocellulose or the migration of the plasticizers to the finishes soften the coatings making the surfaces unacceptable. The problem can be reduced by the use of plasticizers such as polymerics with little or no affinity for the coating to be encountered and the selection of a plasticizer with resistance to migration.

g. The polar nature of the C–Cl bonds promotes intermolecular interactions of the α-hydrogen of PVC with carbonyl groups in various polyesters and, hence, miscibility with these systems. Polystyrene, which has no carbonyl groups, is incapable of these interactions and is therefore completely immiscible with PVC. However, styrene–maleic anhydride copolymers contain both carbonyl groups and the electron-withdrawing oxygen in the five-membered ring. These in-chain functionalities promote intermolecular interactions that are responsible for the partial miscibility of PVC with SMA.

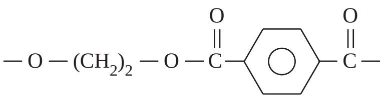




h.



poly(butylene terephthalate) (PBT)



poly(ethylene terephthalate) (PET)

Polycarbonate (PC), an amorphous polymer, provides the toughness for both blends. The crystallinity of PBT and PET contributes the chemical resistance. The shorter methylene groups in PET relative to PBT (2 vs. 4) enhance chain stiffness and hence high-temperature rigidity in PET.

i. Uninhibited ABS is subject to rapid deterioration of physical properties, which is characterized by yellowing and embrittlement from thermal oxidation and outdoor exposure. This is due mainly to the breakdown or oxidation of the unsaturated (double) bonds in the rubber (butadiene) phase. On the other hand, oxidation of polystyrene homopolymer is relatively slow.

j. PVC is susceptible to thermal and oxidative degradation during processing and in service. Consequently, the polymer requires stabilization against the deteriorating effects of heat, light, and/or oxygen. On the other hand, PVC has a high content of chlorine and therefore possesses inherently some level of flame retardance. PVC, therefore, does not require the addition of flame retardants.

k. Black colors result in excessive heat build-up and are therefore avoided in such housing applications as home siding and window profiles. Colorants containing heavy metals are avoided in toys and food wrapping because of possible toxicity.

$$E_L = E_m\left(1-\phi_f\right) + E_f\,\phi_f$$

$$E_f = 10.5\times10^6 \text{ psi} \quad (\text{for E - glass})$$

$$E_m = 2.0\times10^5 \text{ psi} \quad (\text{for polypropylene})$$

9.2. Basis: 100 g of composite

Fiber content = 50 wt% = 50 g

$$\text{Density of E-glass} = \left(0.092\ \frac{\text{lb}}{\text{in.}^3}\right)\left(\frac{454\text{ g}}{\text{lb}}\right)\left(\frac{1\text{ in.}}{2.54\text{ cm}}\right)^3$$

$$= 2.55\ \text{g/cm}^3$$

$$V_f = \frac{50}{2.55} = 19.61\ \text{cm}^3$$

$$V_m = \frac{50}{0.905} = 55.25\ \text{cm}^3$$

$$\phi_f = \frac{19.61}{19.61+55.25} = 0.26$$

$$E_L = 2.0\times10^5(1-0.26)+10.5\times10^6(0.26)$$

$$= 2.88\times10^6 \text{ psi}$$

SOLUTIONS TO CHAPTER 10 PROBLEMS

10.1. Both polyesters and nylon 6,6 are prepared by step-growth polymerizations. The activation energies for such reactions are of the order of 84 kJ/mol. It is therefore usual to employ elevated temperatures to accelerate these reactions. The step-growth polymerizations shown are characterized by polymerization–depolymerization equilibria, with equilibrium constants given by

$$\mathrm{K_e} = \frac{[E]\left[H_2O\right]}{[COOH]\,[OH]} \tag{1}$$

$$\mathrm{K_e} = \frac{[N]\left[H_2O\right]}{[COOH]\,[OH]} \tag{2}$$

where [E] = concentration of the polyester; and [N] = concentration of nylon 6,6. From the definition of the extent of reaction, p, and using Equation 3 for our discussion:

$$[\mathrm{E}] = \mathrm{pC_o} \text{ and } [\mathrm{COOH}] = [\mathrm{OH}] = \mathrm{C} = \mathrm{C_o}\ (1 - \mathrm{p})$$

It follows that the equilibrium constant becomes

$$\mathrm{K_e} = \frac{C_o p\left[H_2O\right]}{C_o^2(1-p)^2} = \frac{p\left[H_2O\right]}{C_o(1-p)^2} \tag{3}$$

That is,

$$(1-\mathrm{p})^2 = \frac{p\left[H_2O\right]}{C_o K_e} \tag{4}$$

To obtain a high-molecular-weight product, a high degree of conversion is imperative (i.e., p = 1). In this case Equation 6 reduces to

$$1-\mathrm{p} = \left(\frac{\left[H_2O\right]}{C_o K_e}\right)^{1/2} \tag{5}$$

Recall that the number average degree of polymerization is given by

$$\overline{X}_n = \frac{1}{1-p} = \left(\frac{C_o K_e}{\left[H_2O\right]}\right)^{1/2} \tag{6}$$

It is obvious from Equation 6 that for a high value of $\overline{X}_n$, the concentration of water in the reaction mixture must be minimized. Since $\mathrm{K_a}$ @ $\mathrm{K_e}$, the need to reduce the concentration of water in polyester manufacture is more important in the manufacture of nylon 6,6. Consequently, the final stages of polyester manufacture are carried out at reduced pressures.

10.2. For a first-order decay of the initiator,

$$[\mathrm{I}] = \left[\mathrm{I_o}\right] \mathrm{e}^{-\mathrm{k_d t}}$$

In this case, Equation 10.12 becomes

$$\ln\frac{[M]}{[M_o]} = \frac{2k_p}{k_d}\left(\frac{f\,k_d}{k_t}\right)^{1/2}[I_o]^{1/2}\left[e^{kdt/2}-1\right]$$

$$= \frac{2}{k_d}\,k\left[e^{-k_d t/2}-1\right]$$

where $k = k_p\left(\frac{f\,k_d}{k_t}\right)^{1/2}[I_o]^{1/2} = 2.70 \times 10^{-6}\ \text{s}^{-1}$ (Example 10.7).

$$\frac{2}{k_d} = \frac{2}{1.92 \times 10^{-6}}\ \text{s} = 1.04 \times 10^{6}\ \text{s}$$

$$\ln\frac{[M]}{[M_o]} = \left(1.04 \times 10^{6}\ \text{s}\right)\left(2.70 \times 10^{-6}\ \text{s}^{-1}\right)\left[\text{e}^{-0.96 \times 10^{-6}t}-1\right]$$

$$\frac{[M]}{[M_o]} = 0.9$$

$$\ln\ 0.9 = 2.8\left[e^{-0.96 \times 10^{-6}t}-1\right]$$

$$0.96 = e^{\left(-0.96 \times 10^{-6}t\right)}$$

$$3.84 \times 10^{-2} = 0.96 \times 10^{-6}\ \text{t}$$

$$\text{t} = 4.0 \times 10^{4}\ \text{s} = 11.1\ \text{h}$$

$$\ln\frac{[M]}{[M_o]} = -kt$$

$$\mathrm{k} = k_p\left(\frac{f\,k_d}{k_t}\right)^{1/2}[I]^{1/2}$$

$$\mathrm{k}^2 = \frac{k_p^2}{k_t}\left(f\,k_d\right)[I]$$

$$= \left(0.95\times10^{-3}\,\frac{l}{mol{-}\mathrm{s}}\right)\left(1.92\times10^{-6}\,\frac{1}{\mathrm{s}}\right)\left(4.0\times10^{-3}\,\frac{mol}{l}\right)$$

10.3.

$$= 7.30\times10^{-12}\,\mathrm{s}^{-2}$$

$$\mathrm{k} = 2.70\times10^{-6}\ \mathrm{s}^{-1}$$

$$\ln\frac{[M]}{[M]_o} = -2.70\times10^{-6}\,t$$

$$\frac{[M]_o - [M]}{[M_o]} = 0.8\text{, i.e., }\frac{[M]}{[M_o]} = 0.2$$

$$\ln\,0.2 = -2.70\times10^{-6}\,\mathrm{t}$$

$$\mathrm{t} = 5.96\times10^{5}\ \mathrm{s}$$

Time required for 80% conversion is certainly unrealistic. However, it should be noted that Equation 10.2 holds only for the initial few percentage points of polymerization. At high conversions substantial deviations occur — recall the Tromsdorff effect.

10.4. For a batch reactor

$$\mathrm{t} = -\int_{[M_o]}^{M}\frac{dM}{R_p} \tag{1}$$

For thermal polymerization:

$$\mathrm{R_p} = k_p\left(\frac{k_i}{k_t}\right)^{1/2}[\mathrm{M}]^2 = \mathrm{k}[\mathrm{M}]^2 \tag{2}$$

where $\mathrm{k} = k_p\left(\frac{k_i}{k_t}\right)^{1/2}$. Substituting Equation 1 into Equation 2 and integrating yields

$$k_t = \frac{1}{[M]} - \frac{1}{[M]_o}$$

$$k^2 = \frac{k_p^2}{k_t} \cdot k_i = \left(8.5 \times 10^{-3} \frac{l}{mol\text{–}s}\right)\left(4.2 \times 10^{-11} \frac{l}{mol\text{–}s}\right)$$

$$= 35.7 \times 10^{-14} \left(\frac{l}{mol\text{–}s}\right)^2$$

$$k = 5.97 \times 10^{-7} \text{ l/mol–s}$$

(3)

$$k_t = \left(2.5\, h \times 3600 \frac{s}{h}\right)\left(5.97 \times 10^{-7} \frac{l}{mol\text{–}s}\right)$$

$$= 0.0054 = \frac{1}{[M]} - \frac{1}{[M]_o}$$

$$\frac{1}{M} = 0.054 + \frac{1}{10} = \frac{1.054}{10}$$

$$\frac{[M]}{[M]_o} = \frac{9.49}{10} = 94.9\%$$

After 2.5 of thermal polymerization, residual monomer concentration is 94.9%, which means that the product polymer cannot be processed into drinking cups without further purifications.

10.5.

$$\Delta T = \left(18.2 \times 10^3 \frac{cal}{g\ mol}\right)\left(\frac{g\ mol\ °C}{29.5\ cal}\right)$$

$$= 617°C$$

10.6. The rate of polymerization for radical chain polymerization is given by the equation:

$$R_p = k_p \left(\frac{f\, k_i}{k_t}\right)^{1/2} [I]^{1/2}\ [M].$$

Assuming f is independent of both [I] and [M], then

$$R_p = R[I]^{1/2}\ [M]$$

$$k = \frac{R_p}{[I]^{1/2}\ [M]}$$

$$= \frac{\left(1.94 \times 10^{-4}\ mol/l\text{–}s\right)}{\left(2.35 \times 10^{-4}\ mol/l\right)^{1/2} \left(9\ mol/l\right)}$$

$$= 1.41 \times 10^{-3}\ (\text{l/mol})^{1/2}\ \left(s^{-1}\right)$$

$$k = \frac{R_p}{[I]^{1/2}\ [M]}$$

$$= \frac{\left(1.94 \times 10^{-4}\ mol/l\text{–s}\right)}{\left(2.35 \times 10^{-4}\ mol/l\right)^{1/2} (9\ mol}$$

$$= 1.41 \times 10^{-3}\ \left(l/\text{mol}\right)^{1/2}\ \left(\text{s}^{-1}\right)$$

For solution polymerization

$$[\text{M}] = \frac{9\ mol}{4.5\ l} = 2\ M$$

$$\text{R}_\text{p} = \left[1.41 \times 10^{-3}\left(\frac{l}{mol}\right)^{1/2} \text{s}^{-1}\right]\left[2.11 \times 10^{-4}\left(\frac{mol}{l}\right)\right]^{1/2}\left[2\frac{mol}{l}\right]$$

$$= 1.41 \times 1.45 \times 2 \times 10^{-5}\ \text{mol}/l\text{–s}$$

$$= 0.41 \times 10^{-4}\ \text{mol}/l\text{–s}$$

$$\text{Kinetic chain length } \upsilon = \frac{R_p}{R_t} = \frac{R_p}{R_i}$$

$$\text{For bulk polymerization } \upsilon_b = \frac{1.94 \times 10^{-4}}{4.0 \times 10^{-4}} = 4.85$$

$$\text{For solution polymerization } \upsilon_s = \frac{0.41 \times 10^{-4}}{4.0 \times 10^{-4}} = 1.02$$

$$\text{Ratio } \frac{\left(\overline{X}_n\right)_b}{\left(\overline{X}_n\right)_s} = \frac{4.85}{1.02} = 4.75$$

10.7. Bulk polymerization is attractive for the production of polymers that are free from impurities from other ingredients of the polymerization recipe. However, polymerization in batch reactors does not always lead to 100% conversions. Consequently, the product polymer in this case must necessarily contain unreacted monomers, which are normally difficult to remove. The use of a polymer with traces of a toxic monomer for food wrap is therefore a bad decision.

10.8. The concentrations of micelles and droplets are about 10^{18} and 10^{11}, respectively. In the recipe:

$$\text{Volume of soap} = \frac{5}{0.2} = 25\ \text{cm}^3$$

$$\text{Volume of monomer} = \frac{100}{0.8} = 125\ \text{cm}^3$$

$$\frac{Vmic}{Vdrop} = \frac{25}{125} = 0.2$$

The surface-to-volume ratio of a sphere is 3/R.

$$\left(\frac{S\ mic}{V\ mic}\right)\Big/\left(\frac{S\ drop}{V\ drop}\right)=\frac{R\ drop}{R\ mic}$$

$$\frac{S\ mic}{S\ drop}=\left(\frac{V\ mic}{V\ drop}\right)\left(\frac{R\ drop}{R\ mic}\right)$$

Average diameter of a micelle = 100 Å = 10^{-6} cm. Average diameter of a droplet = 10,000 Å = 10^{-4} cm.

$$\frac{S\ mic}{S\ drop}=0.2\times\frac{10^{-4}}{10^{-6}}=20$$

Ratio of total surface area of micelles to droplets:

$$\frac{N\ mic}{N\ drop}\cdot\frac{S\ mic}{S\ drop}=20\times\frac{10^{18}}{10^{11}}=20\times10^{7}$$

10.9a. $$\mathrm{R_p}=k_p\,\frac{N}{2}\,[M]$$

$$\mathrm{N}=\left(12.04\times10^{14}\ \frac{particles}{ml}\right)\left(\frac{1\ mol}{6.02\times10^{23}\ particles}\right)\left(\frac{1000\ ml}{1\ \mathrm{l}}\right)$$

$$=2.00\times10^{-6}\ \frac{mol}{\mathrm{l}}$$

$$\mathrm{R_p}=\frac{1}{2}\left(550\ \frac{\mathrm{l}}{mol\text{–s}}\right)\left(2.00\times10^{-6}\ \frac{mol}{\mathrm{l}}\right)\left(5\ \frac{mol}{\mathrm{l}}\right)$$

$$=2750\times10^{-6}\ \frac{mol}{\mathrm{l\text{-}s}}=2.75\times10^{-3}\ \mathrm{mol/ls}$$

$$\text{At 80\% conversion, monomer consumed}=0.8\times5M=4\ \frac{mol}{\mathrm{l}}$$

$$\text{Time required to achieve this}=\left(4\ \frac{mol}{\mathrm{l}}\right)\left(\frac{1}{2.75\times10^{-3}}\ \frac{\mathrm{l\text{–}s}}{mol}\right)$$

$$=1.45\times10^{3}\ \mathrm{s}$$

$$=0.40\ \mathrm{h}$$

$$\overline{X}_n = \frac{k_p\, N[M]}{R_i}$$

$$\mathrm{R_i} = \left(1.1\times 10^{12}\ \frac{radicals}{mol-\mathrm{s}}\right)\left(\frac{1\ mol}{6.02\times 10^{23}\ radicals}\right)\left(\frac{1000\ ml}{1\ \ell}\right)$$

$$= 0.183\times 10^{-8}\ \frac{mol}{\ell-\mathrm{s}} = 1.83\times 10^{-9}\ \frac{mol}{\ell-\mathrm{s}}$$

$$\overline{X}_n = \left(\frac{550\ \ell}{mol-\mathrm{s}}\right)\left(2.00\times 10^{-6}\ \frac{mol}{\ell}\right)\left(5\ \frac{mol}{\ell}\right)\left(\frac{1\ \ell-\mathrm{s}}{1.83\times 10^{-9}\ mol}\right)$$

$$= 3.01\times 10^{6}$$

b.

$$= 3.01\times 10^{6}\ \frac{monomers}{chain}$$

$$\text{No. of chains per particle} = \left(3.01\times 10^{6}\ \frac{monomer}{chain}\times 133\ \frac{chains}{particle}\right)$$

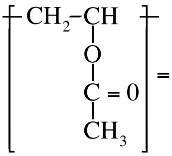
$$= 400\times 10^{6}\ \frac{monomers}{particle}$$

$$= \left(400\times 10^{6}\ \frac{monomers}{particle}\right)\left(\frac{g\ mol\ monomers}{6.02\times 10^{23}\ monomers}\right)$$

$$= 66.5\times 10^{-17}\ \frac{g\ mol\ monomers}{particle}$$

$$\left(66.50\times 10^{-17}\ \frac{g\ mol\ monomer}{particle}\right)\left(\frac{86\ g}{1.0\ g\ mol\ monomer}\right)$$

Molecular weight of vinyl acetate



$$\left[\!-\mathrm{CH_2-CH(-O-C(=O)-CH_3)}-\!\right] = 86$$

Therefore, on the average, each particle weighs 5.72 × 10^{-14} g. But the average density = 1.25 g/cm^3.

$$\text{Average volume of particle} = \left(5.72 \times 10^{-14}\ g\right)\left(\frac{1}{1.25}\ \frac{cm^3}{g}\right)$$

$$= 4.58 \times 10^{-14}\ \text{cm}^3$$

$$\text{Vol of a sphere} = \frac{4}{3}\pi R^3 = 4.58 \times 10^{-14}\ \text{cm}^3$$

$$\text{R}^3 = 4.58 \times 10^{-14} \times \frac{3}{4\pi}\ \text{cm}^3$$

$$\text{R}^3 = 1.09 \times 10^{-14}\ \text{cm}^3$$

$$\text{R} = 2.22\ \text{cm} \times 10^{-5}\ \text{cm}$$

$$\text{D} = 4.44 \times 10^{-5}\ \text{cm}$$

10.10. An energy balance for the isothermal reaction given:

$$\text{V}\left(-\Delta\text{H}_\text{p}\right)\text{R}_\text{p} = \text{UA}\left(\text{T}_\text{r} - \text{T}_\text{c}\right)$$

$$\text{V} = \pi\text{R}^2\text{L} = \pi\left(\frac{5.046}{2}\right)^2 \cdot 2.5 = 50\ \text{m}^3$$

V = reaction volume

U = overall heat transfer coefficient

A = wall heat transfer area

T = temperature of coolant

$$\text{R}_\text{p} = \left(\frac{10^{-4}\ mol}{\text{l-s}}\right)\left(\frac{1\ \text{l}}{1000\ cm^3}\right)\left(\frac{1\ cm^3}{\left(10^{-2}\ m\right)^3}\right) = \frac{10^{-1}\ mol}{m^3\text{–s}}$$

$$\text{V}\left(-\Delta\text{H}_\text{p}\right)\text{R}_\text{p} = 50\ \text{m}^3\left(21.3\frac{kcal}{mol}\right)\left(10^{-1}\ \frac{mol}{m^3\text{s}}\right)$$

$$= 106.49\ \text{kcal/s}$$

$$\text{A}_\text{w}\left(\text{T} - \text{T}_\text{c}\right) = 0.0135\ \frac{cal}{cm^2\,\text{s}\,K}\left(\pi \times 5.046\,m \times 2.5\,m \times 10^4\ \frac{cm^2}{m^2}\right)\left(T - T_c\right)$$

$$= 0.0135\ \frac{cal}{cm^2\text{s}\ K}\left(39.63 \times 10^4\ \text{cm}^2\right)\left(\text{T} - \text{T}_\text{c}\right)$$

$$= 5.35 \times 10^3\ \left(\text{T} - \text{T}_\text{c}\right)$$

$$\text{T} - \text{T}_\text{c} = \frac{1.065 \times 10^5}{5.35 \times 10^3} = 19.9$$

$$\text{T}_\text{c} = 50 - 19.9 = 30.1°\text{C}$$

10.11. Consider a monomer mass balance

$$\mathrm{v}[\mathrm{M}]_{\mathrm{o}} - \mathrm{v}[\mathrm{M}] = \mathrm{Rp} \cdot \mathrm{V}$$

$$\mathrm{v} = \text{volumetric flow rate}$$

$$[\mathrm{M}]_{\mathrm{o}},\ [\mathrm{M}] = \text{monomer concentration in the feed and effluent, respectively}$$

$$\mathrm{V} = \text{reactor volume}$$

$$\mathrm{R_p} = \text{rate of polymerization}$$

$$[\mathrm{M}]_{\mathrm{o}} - [\mathrm{M}] = \mathrm{R_p} \cdot \frac{V}{v} = \mathrm{R_p}\ \tau$$

$$\tau = \text{mean residence time}$$

$$\mathrm{R_p} = \mathrm{k_p}\ \frac{N}{2}\,[M]$$

$$\text{Conversion} = 75\% = \frac{[M]_o - [M]}{[M_o]} = 0.75$$

$$[\mathrm{M}] = 0.25\,[\mathrm{M_o}]$$

$$[\mathrm{M}]_{\mathrm{o}} - 0.25\ \mathrm{M_o} = \mathrm{k_p}\ \frac{N}{2}\left(0.25[M]_o\right) \cdot \tau$$

$$3 = \mathrm{k_p}\ \frac{N}{2} \cdot \tau$$

$$6 = \mathrm{k_p} \cdot \mathrm{N} \cdot \tau$$

$$\mathrm{k_p} = \left(2200\ \frac{\text{l}}{mol\text{–s}}\right)\left(\frac{10^{-3}\,m^3}{\text{l}}\right)$$

$$= 2.20\ \mathrm{m^3/mol{-}s}$$

$$\mathrm{N} = \left(1.8 \times 10^{14}\ \frac{particles}{cm^3}\right)\left(\frac{1\ mol}{6.02 \times 10^{23}\ particles}\right)\left(\frac{cm^3}{10^{-6}\ m^3}\right)$$

$$= 2.99 \times 10^{-4}\ \mathrm{mol/m^3}$$

$$\tau = \frac{6}{k_p \cdot N} = 6\left(\frac{1}{2.20}\ \frac{mol\text{–s}}{m^3}\right)\left(\frac{10^4}{2.99}\ \frac{m^3}{mol}\right)$$

$$= 9.12 \times 10^3\ \mathrm{s}$$

$$= 2.53\ \mathrm{h}$$

$$\text{Flow rate: } \frac{V}{\mathrm{v}} = \tau,\ \ \mathrm{V} = 50\ \mathrm{m^3}$$

$$\mathrm{v} = \frac{V}{\tau} = \frac{50\ m^3}{2.53\ h}$$

$$= 19.73\ \mathrm{m^3/h}$$

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10.12a. Assuming first-order kinetics, then

$$M = M_o\ e^{-k\tau}$$

$$\text{Conversion } p = \frac{M_o - M}{M_o} = \frac{M_o - M_o e^{-k\tau}}{M_o}$$

$$= 1 - e^{-k\tau}$$

$$\tau = \text{residence time}$$

$$p = 1 - e^{-(10^{-2})(10^{2})} = 1 - e^{-1} = 1 - 0.368$$

$$= 0.632$$

b.

$$\frac{V}{\tau} = \frac{\pi R^2 L}{t} = \frac{\pi D L}{4\tau} = \frac{\pi\left(2 \times 10^{-2}\right)^2 L}{4 \times 3.14 \times 10^{-4}} = 10^2$$

$$L = 100 \text{ m}$$

10.13. Adequate temperature control is a problem associated with bulk polymerization. This problem is accentuated by high media viscosity. Chain reaction polymerizations are more exothermic than step-growth polymerizations. Also, the media viscosity in chain reaction polymerizations increases very rapidly even at the early stage of the reaction. This contrasts sharply with step-growth polymerizations where viscosity builds up gradually in the course of reaction. Proper mixing is a problem encountered with the use of plug flow reactors and this can further enhance the problems of bulk polymerization. Given the lower viscosity and milder temperatures in polycondensations, plug flow reactors will be more favorable in the bulk polymerizations of poly(ethylene tetraphthalate) — a step-growth polymer — than polyisobutylene — a chain reaction polymer.

10.14. Nylon 6,6 is a polycondensation polymer. To develop polymeric properties, step-growth polymers require a high degree of conversion, which cannot be obtained in a CSTR. Putting a number of CSTRs in series makes high extents of reaction possible.

10.15. Given the relative heats of polymerization of both monomers, solution polymerization will be more appropriate for butene. This should permit a better temperature control, because the heat generated can easily be dissipated by the choice of an appropriate solvent.

10.16.

Basis: 100 lb of polymer solution

$$\text{Heat of polymerization} = (10 \text{ lb})(620 \text{ Btu/lb})$$

$$= 6200 \text{ Btu}$$

$$\text{Heat absorbed by solvent} = mC_p$$

$$= (90 \text{ lb})(0.96 \text{ Btu/lb°F})$$

$$\Delta T = \frac{6200}{90 \times 0.96} = 72°\text{F}$$

$$\text{Feed temperature} = 122 - 72 = 50°\text{F}$$

SOLUTIONS TO CHAPTER 11 PROBLEMS

11.1. Vol of PVC material extruded per year = $\pi(R_c^2 - R_I^2)L$.

$$L = \frac{20\text{ ft}}{\text{h}} \times \frac{16\text{ h}}{\text{day}} \times \frac{300\text{ day}}{\text{year}} \times \frac{12\text{ in.}}{\text{ft}}$$

$$= 1.152 \times 10^6 \text{ in./year}$$

$$\text{PVC vol/year} = \pi\left[(2.5)^2 - 2^2\right] \times 1.152 \times 10^6 \text{ in.}^3$$

$$= 8.143 \times 10^6 \text{ in.}^3$$

$$\text{Density} = 1.44 \text{ g/cm}^3 \left| \frac{1\text{ lb}}{454\text{ g}} \right| \frac{(2.54\text{ cm})^3}{1\text{ in.}^3} \right| = 0.052 \text{ lb/in.}^3$$

$$\text{PVC mass/year} = 8.143 \times 10^6 \text{ in.}^3 \times 0.052 \text{ lb/in.}^3$$

$$= 4.232 \times 10^5 \text{ lb}$$

$$\text{Working hour/year} = 16 \times 300 = 4800$$

$$\text{PVC extrusion rate} = 88 \text{ lb/h} = 90 \text{ lb/h}$$

$$\text{Motor power requirement} = 7 \text{ to } 18 \text{ hp since } 1 \text{ hp motor is required for } 5 \text{ to } 10 \text{ lb/h extruded material.}$$

11.2.

a. The process of crystallization involves an orderly arrangement of polymer molecules from a disordered polymer melt. Consequently, for a given mass of polymer, there is a decrease in volume as the polymer crystallizes from the melt, i.e., crystallization results in shrinkage. Thus when a crystalline polymer is extruded, the associated shrinkage as the polymer is cooled from the melt results in part distortion. Under other hand, amorphous polymer when cooled from the melt undergoes a gradual dimensional change and consequently it is easier to maintain the shape of the extruded part.

b. During melting of a crystalline polymer, additional heat is required to break up the intermolecular bonding forces at the polymer melting point. In general, therefore, more heat is required to extrude a crystalline polymer than an amorphous one. Therefore, if thermal conditions are comparable, the extrusion rate is higher for amorphous than crystalline polymers.

c. Many polymers, depending on their composition, absorb moisture from the air. This can result in steam formation and, consequently, frothing during extrusion. In some cases, the presence of water promotes polymer degradation. The attendant molecular weight reduction can potentially change a tough polymer into a brittle one. In either case, therefore, the presence of too much water in polymers can result in poor product quality. It is, therefore, essential to remove water and volatiles from the polymer before extrusion by installation of a hopper dehumidifier.

11.3.

$$\text{hp} = 0.0004\, C_p Q(T_m - T_f) + 0.0004\, QH_f$$

where H_f = latent heat of fusion.

a. Polystyrene

$$60 \times 0.75 = 0.0004 \times 0.45\,(500 - 77)\ Q$$

$$Q = \frac{60 \times 0.75}{0.0004 \times 0.45 \times 423}\ \text{lb/h} = 591\ \text{lb/h}$$

b. Polyethylene

$$0.75 \times 60 = 0.0004 \times 0.91\,(440 - 77)\ Q + 0.0004 \times 104\ Q$$

$$= 0.1321\ Q \times 0.0416\ Q$$

$$Q = 259\ \text{lb/h}$$

c. Nylon 6,6

$$0.75 \times 60 = 0.0004 \times 0.63\,(530 - 77)\ Q + 0.0004 \times 5$$

$$45 = 0.1142\ Q \times 0.0224\ Q$$

$$Q = 329\ \text{lb/h}$$

11.4.

$$\text{Input drive power (in hp)} = \frac{\text{Torque} \times \text{rpm}}{5252}$$

The torque a screw can safely carry is proportional to the cube of the root diameter. That is,

$$\tau = kd^3$$

For 2.5-in.-diameter screw,

$$\tau = K\,(2.5)^3 = 40 \times \frac{5252}{200}$$

$$K = \frac{5252}{50} \times \frac{(1)^3}{2.5}$$

For 4.5-in.-diameter screw,

$$150\ \text{rpm} \quad \tau = \frac{5252}{50} \times \frac{(4.5)^3}{2.5}$$

$$\text{hp} = \frac{5252}{50} \times \frac{(4.5)^3}{2.5} \times \frac{150}{5252} = 176$$

$$200\ \text{rpm} \quad \text{hp} = \frac{525^2}{50}\ \frac{(4.5)^3}{2.5} \times \frac{200}{5252} = 233$$

11.5. Volume of syringe = $\frac{\pi D_o^2 L}{4} = \frac{\pi(1)6}{4}$ = 4.71 in.^{3}.

$$\varepsilon = \frac{\sigma}{E}; \quad D = D_o(1+\varepsilon)$$

Volume of syringe due to dimensional change of material = $\pi D^2 L/4$.

Material	**Modulus (psi)**	**ΔV (in.^{3})**	**ΔV (%)**
Steel	30×10^6	4.77 – 4.71 = 0.06	1.3
Copper	18×10^6	4.81 – 4.71 = 0.10	2.1
Aluminum	10×10^6	4.88 – 4.71 = 0.17	3.6

11.6. High mold temperatures permit the polymer melt to cool more slowly and thus favor greater crystallinity. This means that, on the average, a greater number of primary bonds must be broken for failure to occur and therefore the molded part has a higher tensile strength. A higher degree of crystallinity also means an increase in the possible difference between the refractive indices of the amorphous and crystalline components (enhances optical anisotropy) of the molded part and consequently reduces part cavity.

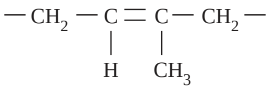
11.7.

Extrusion Blow Molding	**Polymer**
Continuous	Poly(vinyl chloride)
Intermittent	Polyethylene

Poly(vinyl chloride), unlike polyethylene, is a heat-sensitive polymer. If used in the intermittent process, it may suffer some degradation because polymer melt has to be kept hot in the extruder during the blowing, cooling, and removal of part from the mold.

SOLUTIONS TO CHAPTER 12 PROBLEMS

12.1. Natural rubber is poly(*cis*-1,4-isoprene):

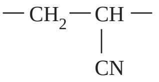


$$-CH_2-\underset{\displaystyle H}{\underset{|}{C}}=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2- ;\quad M = 68$$

$$\delta = \frac{\rho \Sigma E}{M} = 1.1\left[\frac{(2\times 131.5)+121.5+84.5+148}{68}\right]$$

$$= 10.0$$

Polyacrylonitrile:



$$-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}- ;\quad M = 53$$

$$\delta = 1.15\,\frac{[131.5+86+354.5]}{53}$$

$$= 12.4$$

From Table 12.1:

Polymer	Most Suitable Solvent
Natural rubber	Dichlorobenzene
Polyacrylonitrile	Nitromethane

12.2.

Polymer	$\delta(\text{cal/cm}^3)^{1/2}$	Solvent	$\delta(\text{cal/cm}^3)^{1/2}$
Poly(methyl methacrylate)	9.25	Methyl methacrylate	8.8
Poly(vinyl chloride)	9.9	Vinyl chloride	7.8
Polyacrylonitrile	12.35	Acrylonitrile	11.9
		Water	23.4
		Dimethylformamide	12.1

a. In bulk polymerization a soluble initiator is added to pure monomer in the liquid state to effect polymerization. In a homogeneous bulk polymerization system the resulting polymer is soluble in the monomer, whereas in heterogeneous systems the polymer precipitates from the molten monomer. The differences in solubility parameters between poly(methyl methacrylate) and methyl methacrylate (about 0.45) and between poly(vinyl chloride) and vinyl chloride (about 2.1) suggest that PMMA is soluble in its monomer whereas PVC is not.

b. In solution polymerization, both the starting monomer and resulting polymer are soluble in the solvent medium. On the other hand, in precipitation polymerization the monomer is soluble, whereas the polymer is insoluble in the solvent. Given the differences in their solubility parameters, both PAN and acrylonitrile will be soluble in dimethyl formamide but certainly not in water.

12.3. When there is restriction to bond angles,

$$\overline{r^2} = nl^2\ \frac{1-\cos\theta}{1+\cos\theta}$$

$$\theta = 109.5°; \quad \cos\theta = -0.334$$

$$\overline{r^2} = 2\ nl^2$$

$$\left(\overline{r^2}\right)^{1/2} = \sqrt{2n}\,l$$

12.4

a.

$$n = 2\,DP = 2\times 10^6/72 = 2.78\times 10^4$$

$$\overline{r_0^2} = \left(670\ \text{Å}\right)^2$$

$$C_\infty = (670)^2/\left(2.78\times 10^4\right)(1.53)^2$$

$$= 6.9$$

b.

$$\sigma = \left(\overline{r_0^2}/\overline{r_{0f}^2}\right)^{1/2}$$

$$\overline{r_0^2} = 670\ \text{Å}$$

$$\overline{r_{0f}^2} = nl^2\left(\frac{1-\cos\theta}{1+\cos\theta}\right)$$

$$= 2\ nl^2 \text{ since } \theta = 109.5°$$

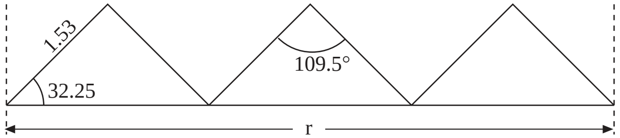
$$\left(\overline{r_{0f}^2}\right)^{1/2} = \sqrt{2n}\,l = \sqrt{72}/2\times 10^3\times 1.53$$

$$\sigma = \frac{670\sqrt{72}}{2\times 10^3\times 1.53} = 1.86$$

c.

$$a_p = \frac{l}{2}\left(C_\infty + 1\right) = \left(\frac{6.9+1}{2}\right)1.53 = 6.04$$

d.



$$r = nl\ \cos\cos 32.25 = \left(2\times 10^6/72\right)\times 1.53\ \cos 32.25$$

$$= 3.47\times 10^4\ \text{Å}$$

12.5a. At theta temperature

$$\overline{r_0^2} = nl^2\left(\frac{1-\cos\theta}{1+\cos\theta}\right)\left(\frac{1+\cos\theta}{1-\cos\theta}\right)$$

$$= \frac{2M}{M_0}\, l^2\left(\frac{1-\cos\theta}{1+\cos\theta}\right)\left(\frac{1+\cos\theta}{1-\cos\theta}\right)$$

where M is the molecular weight of the polymer, while M_0 is the molecular weight of the repeating unit. Assuming θ and ϕ are independent of molecular weight, which is generally true,

$$\left(\overline{r_0^2}\right)^{1/2} = k\,M^{1/2}$$

b. Since the T = θ varies for different solvents and since solvent power increases with increasing temperature $\left(\overline{r_0^2}\right)^{1/2}$ will generally increase with temperature.

c. $$\left(\overline{r^2}\right)^{1/2} = \alpha\left(\overline{r_0^2}\right)^{1/2} = \alpha\, k\ M^{1/2}$$

12.6. From Equation 12.51:

$$\Gamma = \frac{\bar{v}_2^2\ \overline{M}_n}{V_1}\left(1-\chi_1\right)$$

$$1-\chi_1 = \frac{\Gamma V_1}{\bar{v}_2^2\ \overline{M}_n} = \frac{\Gamma\ M_1/\rho_1}{\left(1/\rho_2\right)^2\ \overline{M}_n}$$

$$= \frac{\Gamma\ \rho_2^2\ M_1}{\rho_1\ \overline{M}_n}$$

$$= \frac{\left(79.2\ \text{cm}^3/\text{g}\right)\left(1.19\ \text{g}/\text{cm}^3\right)^2\left(72\ \text{g}/\text{mol}\right)}{\left(0.8\ \text{g}/\text{cm}^3\right)\left(1.63\times10^5\ \text{g}/\text{mol}\right)}$$

$$= 0.062$$

$$\chi_1 = 0.5 - 0.062$$

$$= 0.438$$

From Equation 12.30:

$$\ln a_1 = \ln \nu_1 + \left(1-\frac{1}{x}\right)\nu_2 + \chi_1\ \nu_2^2$$

$$x = \frac{V_2}{V_1} = \frac{M_2/\rho_2}{M_1/\rho_1} = \frac{1.63\times10^5/1.19}{72/0.8} = 1.52\times10$$

$$\ln a_1 = \ln 0.5 + \left(1 - 1/1.52 \times 10^3\right) 0.5 + 0.438\,(0.5)^2$$

$$a_1 = 0.92 = \rho_1 / \rho_1^0$$

$$\rho_1 = a_1 \rho_1^0 = 0.92 \times 100$$

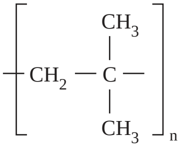
$$= 92 \text{ mm Hg}$$

12.7. Theoretically, for free rotation about valence bonds,

$$\left(\overline{r_0^2}\right)^{1/2} = \sqrt{2n}\,l$$

$$n = 2\text{ DP} = 2\text{ M/M}_o$$

where M_0 = molecular weight of the monomer.



$$\left[CH_2 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}} - \right]_n$$

Polyisobutylene: $M_o = 56$

$$M_o = 56$$

$$n = \frac{2\text{ M}}{56} = \frac{M}{28}$$

$$\left(\overline{r_0^2}\right)^{1/2} = \left(\frac{2\text{ M}}{28}\right)^{1/2} l$$

$$\left(\frac{\overline{r_0^2}}{M}\right)^{1/2}_{cal} = \frac{1.54}{\sqrt{14}} = 0.412$$

$$\frac{\left(\overline{r_0^2}/M\right)^{1/2}_{exp}}{\left(\overline{r_0^2}/M\right)^{1/2}_{cal}} = \frac{0.795}{0.412} = 1.93 \text{ at } 24°\text{C}$$

$$= \frac{0.757}{0.412} = 1.84 \text{ at } 95°\text{C}$$

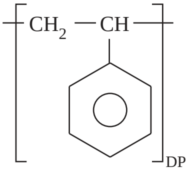
a. Experimental values correspond to the dimensions of a real polymer where completely free rotation about valence bonds is impossible due to steric hindrance.
b. As temperature increases, restrictions to free rotation decrease and, consequently, molecular size decreases.

$$\left(\frac{\overline{r^2}}{M}\right)^{1/2} = 0.795$$

$$M = \left(\frac{1000}{0.795}\right)^2 = 1.58 \times 10^6$$

12.8.

$$\overline{r_{0f}^2} = 2\,nl^2$$



$M_o = 104$

$$n = 2\ DP;\ \ DP = \frac{10^6}{104} = 9.62 \times 10^3,\ l - 1.54\ Å$$

$$\left(\overline{r_{0f}^2}\right)^{1/2} = \sqrt{2n}\,l$$

$$= \left(4 \times 9.62 \times 10^3\right)^{1/2} \times 1.54\ Å$$

$$= 302\ Å$$

12.9a.

$$\text{Contour length } L = n\,(1.54 \cos 35.25)$$

$$= 2\ DP\,(1.54 \cos 35.25)$$

$$= 2 \times \frac{8.85 \times 10^5}{56}\,(1.54 \cos 32.25)$$

$$= 3.98 \times 10^4\ Å$$

b.

$$\text{Volume of a molecule} = V_m = \frac{4}{3}\pi r^3 = \frac{M}{\rho N_{A_v}}$$

$$r^3 = \frac{3\,M}{4\pi\rho N_{Av}}$$

$$= \frac{3 \times 8.85 \times 10^5}{4\pi \times 0.8 \times 6.02 \times 10^{23}}$$

$$r = 76\,Å$$

c.

$$\left(\overline{r_0^2}/M\right)^{1/2} = 800 \times 10^{-11}$$

$$\left(\overline{r_0^2}\right)^{1/2} = \left(800 \times 10^{-11}\right)\left(8.85 \times 10^5\right)^{1/2}$$

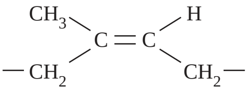
$$= 750\ Å$$

d.

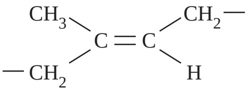
$$\frac{V_{rc}}{V_{cc}} = \left(\frac{750}{76}\right)^3 = 961;\quad \begin{array}{l} rc = \text{random coil} \\ cc = \text{compact coil} \end{array}$$

In the solid state if random coils exist, there is interpenetration of molecules.

12.10. natural rubber: *cis*-1,4-polyisoprene



gutta-percha: *trans*-1,4-polyisoprene



Repulsions between substituted groups are less in gutta-percha, where the isoprene units exist in *trans* configuration, than in natural rubber with units in the *cis* configuration. Consequently, the hindrance to coiled configurations as a result of steric interactions between near-neighboring units is less in gutta-percha than in natural rubber. Therefore gutta-percha chains have unperturbed dimensions, more nearly those which they would assume if all single-bond rotations were completely free.

12.11.

$$\eta_{sp} = \eta_r - 1$$

$$\eta_{sp}/c = (\eta_r - 1)/c = [\eta] + k'[\eta]^2 c$$

η_{sp}/C	C
0.618	0.275
0.625	0.344
0.702	0.896
0.744	1.199
0.829	1.604
0.946	2.108

Intercept of graph of η_{sp}/C vs. C from Figure S12.11A is 0.557 (dl/g). Therefore, [η] = 0.557 (dl/g).

$$\text{Slope of Figure 12.11A} = 0.174\left(\frac{\text{dl}}{\text{g}}\right)^2 = k'[\eta]^2$$

$$k' = \text{Huggins constant} = \frac{0.174}{(0.557)^2}$$

$$= 0.561$$

$$\text{From Figure 12.11B, intercept} = 1.482\left(\frac{\text{cm solvent}}{\text{g/dl}}\right)$$

$$\frac{RT}{\overline{M}_n} = \text{intercept}$$

$$\overline{M}_n = \frac{RT}{\text{intercept}}; \quad R = \frac{0.8205 \times 1033}{0.780}\left(\frac{\text{dl} - \text{cm solvent}}{\text{mol} \cdot \text{K}}\right)$$

$$\overline{M}_n = \frac{0.8205 \times 1033}{0.780}\left(\frac{\text{dl} - \text{cm} - \text{solvent}}{\text{mol} \cdot \text{K}}\right)(303\,\text{K})\left(\frac{1}{1.482 \text{ cm solvent}}\right)$$

$$= 2.22 \times 10^5 \text{ g/mol}$$

$$RTA_2 = \text{slope}$$

$$A_2 = \text{slope}/RT$$

$$= \left(0.636 \, \frac{\text{cm} - \text{solvent}}{(\text{g/dl})^2}\right)\left[\frac{0.780}{0.8205 \times 1033 \times 303} \, \frac{\text{mol}}{\text{dl} \cdot \text{cm solvent}}\right]$$

$$= 1.93 \times 10^{-6} \, \frac{\text{dl} - \text{mol}}{\text{g}^2}$$

12.12a. $$\frac{\pi}{c} = R_T\left[\frac{1}{\overline{M}_n} + A_2 c + A_3 c^2 + \ldots\right]$$

Solution A:

From Figure S12.12, $\frac{RT}{M_n}$ = intercept on $\frac{\pi}{c}$ as $c \rightarrow 0$

$$= 158.03 \, \frac{\text{cm solvent}}{\text{g/cm}^3}$$

$$\overline{M}_n = \left(\frac{82.06 \text{ cm}^3 \times 1033 \text{ cm } H_2O}{\text{mol}-\text{K}}\right)(300\,\text{K})\left(\frac{1}{158.03 \times 0.85 \, \frac{\text{cm } H_2}{\text{g/cm}^3}}\right)$$

Note: cm solution ≈ cm solvent

$= \text{cm } H_2O/\rho_s$

where r_s = density of solvent

$\overline{M}_n = 1.89 \times 10^5$ g/mol

Solution B:

$$\text{Intercept} = 296.77 \, \frac{\text{cm solution}}{\text{g/cm}^3}$$

$$M_n = \left(\frac{82.06 \text{ cm}^3 \times 1033 \text{ cm } H_2O}{\text{mol}-\text{K}}\right)(300\,\text{K})\left(\frac{1}{296.77 \times 0.85 \, \frac{\text{cm } H_2O}{\text{g/cm}^3}}\right)$$

$$= 1.01 \times 10^5 \text{ g/mol}$$

$$\text{Slope} = \text{RTA}_2$$

Solution A: slope = 17059 cm solution/(g/cm^3)

$$A_2 = \frac{1705 \text{ g cm solution/g/cm}^3}{\left(82.06 \text{ cm}^3\text{–atm/mol–K}\right)\left(300\,\text{K}\right)}$$

$$= 5.7 \times 10^{-4} \text{ mol–cm}^3/\text{g}^2$$

Solution B: slope = 2373/cm solution/(g/cm^3)

$$A_2 = \frac{23731 \times 0.85 \text{ cm H}_2\text{O}/\left(\text{g/cm}^3\right)}{82.06 \text{ cm}^3 \cdot \text{cm H}_2\text{O/mol–K} \times 1033\left(300\,\text{K}\right)}$$

$$= 7.10 \times 10^{-4} \text{ mol–cm}^3/\text{g}^2$$

b. Basis = 100 g mixture

$$\overline{M}_n = \frac{\Sigma w_i}{\Sigma w_i / M_i} = \frac{100}{\dfrac{25}{1.89 \times 10^5} + \dfrac{75}{1.01 \times 10^5}}$$

$$= 1.14 \times 10^5$$

c. Solution A:

$$\overline{M}_w = 2 \times 1.89 \times 10^5 = 3.78 \times 10^5$$

Solution B:

$$\overline{M}_w = 2 \times 1.01 \times 10^5 = 2.02 \times 10^5$$

$$\overline{M}_w = \sum w_i M_i = 0.25 \times 3.78 \times 10^5 + 0.75 \times 2.02 \times 10^5$$
$$= 2.46 \times 10^5$$

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{2.46 \times 10^5}{1.14 \times 10^5}$$

$$= 2.16$$

SOLUTIONS TO CHAPTER 13 PROBLEMS

13.1. Resilience is the area under the elastic portion of the stress–strain curve.

$$\text{Resilience} = \int_0^{\sigma_y} \sigma d\varepsilon$$

$$\sigma = E\varepsilon$$

$$\text{Resilience} = \int_0^{\varepsilon_y} E\varepsilon d\varepsilon = \frac{\left(E\varepsilon_y^2\right)}{2}$$

$$\varepsilon_y = \frac{\sigma_y}{E}$$

$$\text{Resilience} = \frac{E}{2}\left(\frac{\sigma_y}{E}\right)^2 = \frac{\sigma_y^2}{2E}$$

$$= \frac{\left(62.05 \times 10^6\right)^2 \left(N/m^2\right)}{2\left(24.13 \times 10^3\right)\left(N/m^2\right)} = 79.78 \times 10^4 \ \text{J/}$$

13.2.

Polymer	% Reduction of area
T	(2.0 – 1.0)/2.0 = 50
S	(20.0 – 18.0)/20 = 10

Children's toys need to withstand lots of abuse without breaking (i.e., should be tough). Therefore polymer T would be more suited for this application.

13.3. Nylon 6,6 with its strongly polar hydrogen bonding and polycarbonate with combined strong polar forces and rigid backbone show high rigidity and strength combined with a good measure of ductility.

13.4. At σ_N, the load is maximum.

$$F = \sigma A$$

$$dF = \sigma dA + A d\sigma = 0$$

i.e.,

$$d\sigma/\sigma = -dA/A$$

For uniform deformation, there is a constancy of the volume of the material being deformed, i.e.,

$$AL = A_0L_0$$

$$A = \left(A_0L_0\right)/L$$

$$dA = -A_0L_0 \ dL/L^2 = -AL \ dL/L^2 = -AdL/L$$

or

$$-dA/A = dL/L$$

but

$$d\varepsilon = dL/L$$

$$d\sigma/\sigma = -dA/A = dL/L = d\varepsilon$$

$$d\sigma/d\varepsilon = \sigma$$

For the relation

$$\sigma = K\varepsilon^{n}$$

$$d\sigma/d\varepsilon = n\,K\varepsilon^{n-1} = \sigma$$

i.e., $nK\varepsilon^{n-1} = K\varepsilon^{n}$. This can only be true if $\varepsilon = n$.

$$\begin{aligned} \sigma_n &= K\varepsilon^{n} \\ &= K\varepsilon^{\varepsilon} \\ &= 10^{6}(0.5)^{0.5}\ \mathrm{N/m^2} \\ &= 7.07 \times 10^{5}\ \mathrm{N/m^2} \end{aligned}$$

13.5.

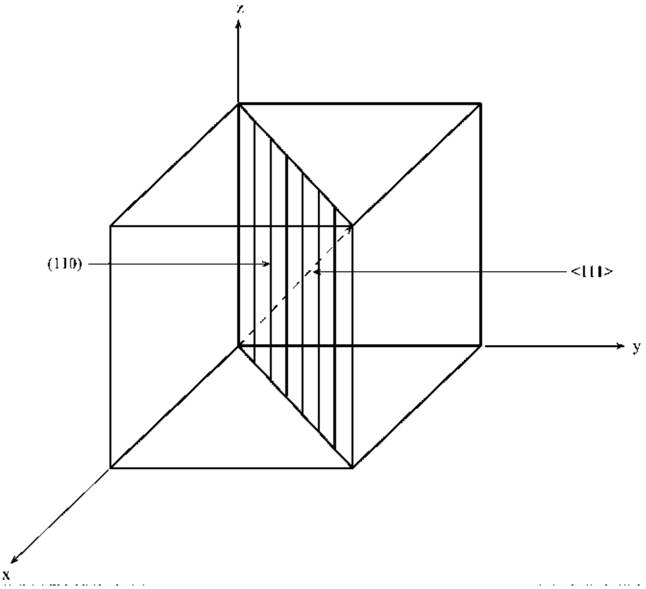
$$(\sigma_s)_{max} = \sigma/2$$

$$\sigma = 2(\sigma_s)_{max}$$

$$\sigma = P/A = 2(\sigma_s)_{max}$$

$$\begin{aligned} P &= 2A(\sigma_s)_{max} \\ &= \left(2 \times 10^{-4}\ \mathrm{m^2}\right)\left(10^{6}\,\mathrm{N/m^2}\right) \\ &= 2 \times 10^{2}\ \mathrm{N} \end{aligned}$$

13.6.



Slip plane = (110)
Normal to slip plane = [110]
Slip direction [111]
Tensile axis [100]
φ = angle between tensile axis and normal to the slip plane
θ = angle between tensile axis and slip direction
$\bar{a}$ = vector along tensile axis = i
$\bar{b}$ = vector along slip direction = i+j+k
$\bar{c}$ = vector normal to slip plane = i+j

$$\cos\theta = \frac{\vec{a}\cdot\vec{b}}{|\vec{d}|\,|\vec{b}|} = \frac{1}{\sqrt{3}}$$

$$\cos\theta = \frac{\vec{a}\cdot\vec{c}}{|\vec{d}|\,|\vec{c}|} = \frac{1}{\sqrt{2}}$$

$$(\sigma_s)_{max} = \sigma \cos\theta \cos\phi$$

$$= \sigma\left(1/\sqrt{3}\right)\left(1/\sqrt{2}\right)$$

$$\sigma = (\sigma_s)_{max}\ \sqrt{6}$$

$$= 27.58\times 10^6\ \sqrt{6}\ \mathrm{N/m^2}$$

$$= 67.55\times 10^6\ \mathrm{N/m^2}$$

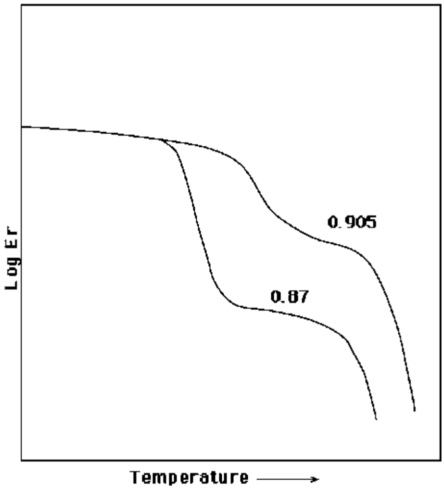
13.7. a. The fact that materials from the copolymer are transparent in spite of the differing refractive indices of the respective homopolymer suggests that the SBS polymer is a block copolymer existing in two separate phases. From Figure 13.25, room temperature lies between the glass transition temperatures of polybutadiene (–80°C) and polystyrene (110°C). At room temperature the rubbery polybutadiene domains are cross-linked by the hard and glossy polystyrene regions. Consequently, the tensile strength reflects the state of the polystyrene regions and remains high.

b. Natural rubber is soluble in hexane, while PMMA is soluble in ethyl acetate. Therefore, when the graft copolymer is isolated from ethyl acetate, the rubber chains assume coiled conformation or collapsed, while the PMMA chains are extended. The resulting physical properties of the copolymer resemble those of PMMA. On the other hand, when the copolymer is isolated from hexane, the PMMA chains are coiled while the rubber chains are extended. The properties in this case resemble those of rubber.

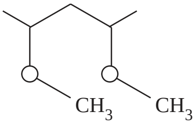
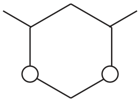
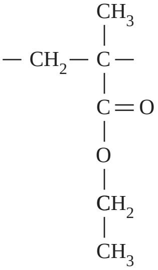
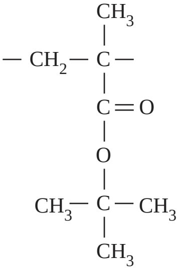
c. In water, the hydrophilic poly(vinyl alcohol) blocks are solubilized and extended holding the tightly coiled polystyrene segments in solution. In benzene, the opposite situation occurs, but in acetone, with intermediate properties between water and benzene, both blocks are relatively extended.

d. Copolymers of hexamethylene adipamide and hexamethylene terephthalamide are isomorphous, while copolymers of hexamethylene sebacamide and hexamethylene terephthalamide are nonisomorphous. The addition of a comonomer to a crystalline polymer results in a drastic loss in crystallinity and the attendant properties, except in cases where both comonomers form isomorphous copolymers.

13.8.



13.9.

Polymer	Structure	T_g °C
Poly(vinyl methyl ether)		-13
Poly(vinyl formal)		105
Poly(ethyl methacrylate)	 $-CH_2-C(CH_3)(C(=O)-O-CH_2-CH_3)-$	100
Poly(*t*-butyl methacrylate)	 $-CH_2-C(CH_3)(C(=O)-O-C(CH_3)_3)-$	135

In the first pair of polymers, the introduction of rings into the main chain of poly(vinyl formal) increases the T_g significantly compared with poly(vinyl methyl ether) with relatively flexible side chains. In the second pair of polymers, the presence of the much bulkier *t*-butyl group in the ester side group enhances chain stiffness and therefore raises the T_g.

13.10. As n increases, the side chain becomes flexible, and the overall stiffness of the polymer decreases.

13.11. a. Plane stress:

$$\sigma_f = \left(\frac{E\,G_c}{\pi a}\right)^{1/2}$$

b. Plane strain:

$$\sigma_f = \left[\frac{E\,G_c}{\pi a\left(1-\nu^2\right)}\right]^{1/2}$$

In this case, $\sigma_f = \sigma_u$, hence for plane stress for material H:

$$a = \frac{E\,G_c}{\pi \sigma_f^2} = \frac{\left(532 \times 10^6 \ \mathrm{N/m^2}\right)\left(0.06 \times 10^3 \ \dfrac{\mathrm{N\text{-}m}}{\mathrm{m^2}}\right)}{(3.14)\left(15.3 \times 10^6 \ \mathrm{N/m^2}\right)^2}$$

$$= 43.4 \times 10^{-6} \ \mathrm{m} = 43.4 \ \text{Å}$$

	a x 10^{-6} (m)	
Material	**Plane Stress**	**Plane Strain**
S	2136	213600
H	43	4340

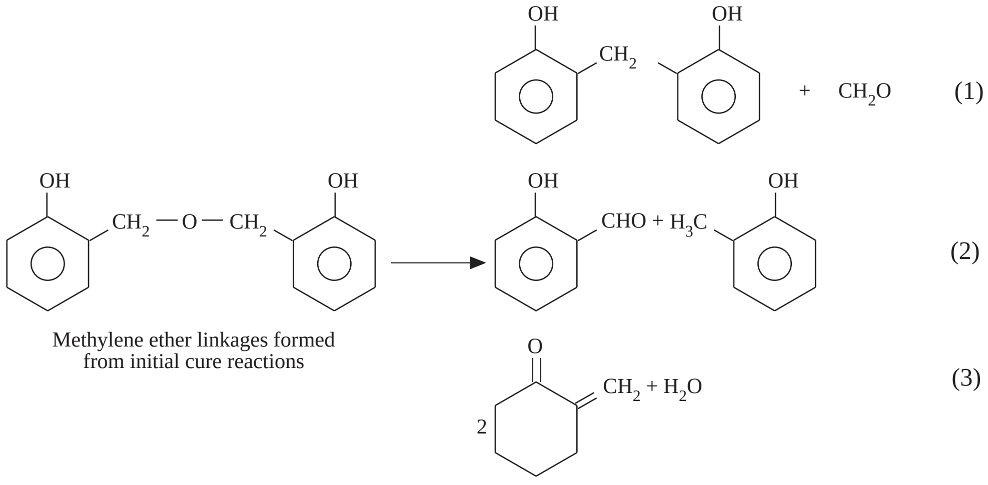
Material S, unlike H, is rubbery and therefore capable of extensive plastic deformation. Consequently, only very large cracks can cause rupture. Material S shows extensive deformation before fracture while H is relatively brittle. Thus S will be a preferable material in the application.

13.12. From the dynamic mechanical properties, resin D is evidently more flexible than resin A. As the resins are cured, the more flexible resin (D) develops less internal stress than the stiffer resin A due to greater molecular mobility. As wood absorbs and releases moisture during cyclic wet–dry treatment, the adhesive joint is subjected to cyclic stress. Resin D, due to its flexibility, is able to respond reversibly to the cyclic stress whereas the stiffer resins begin to degrade after five wet–dry cycles.

13.13. Chains containing either linkages are expected to be relatively flexible. As cure time increases the number of these chains formed apparently increases also, and consequently the fracture initiation energy increases due to increased ability for plastic deformation. However, at the onset of decomposition of these chains into the more rigid methylene bridges (1) or scission products (2 and 3), a drop in the fracture energy would be predicted.

The difference between the fracture initiation and arrest energies ($G_{Ic} - G_{Ia}$) is the energy released during crack propagation. If $G_{Ic} - G_{Ia}$ is small, it implies (in most cases) that the material in the immediate vicinity of the crack tip undergoes plastic deformation, blunts the crack, and arrests its propagation. In cases where G_{Ic} is large, a propagating crack travels long distances before being arrested. Therefore, the magnitude of $G_{Ic} - G_{Ia}$ is a measure of a materials resistance to catastrophic failure. Obviously, material B is more cured than material A; $G_{Ic} - G_{Ia}$ is considerably larger for material B than A and consequently, material B is more susceptible to catastrophic failure.

13.3.



Possible subsequent decomposition products on further cure

SOLUTIONS TO CHAPTER 14 PROBLEMS

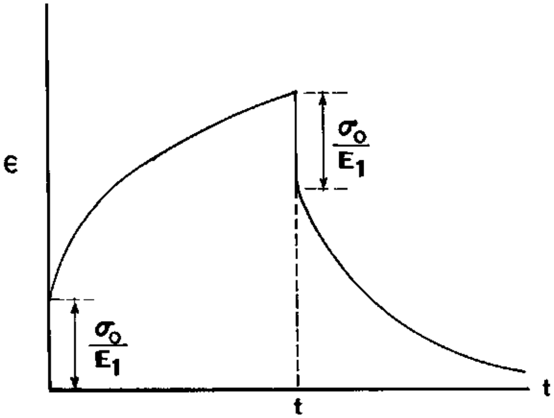
14.1. a. The strains of the spring and the Voigt element are additive. Therefore, the rheological equation for the model is

$$\varepsilon = \varepsilon_1 + \varepsilon_2$$

$$= \frac{\sigma_0}{E_1} + \frac{\sigma_0}{E_2}\left[1 - e^{-t/\tau_2}\right]$$

where $t_2 = \eta_2/E_2$.

b.



14.2. For the generalized Maxwell model, the relaxation modulus is given by

$$E_r(t) = \sum_{i=1}^{n} E_i e^{-t/\tau_i}$$

$$= 10^5\ e^{-10/10} + 10^6 e^{-10/20} + 10^7\ e^{-10/30}$$

$$= 78.04 \times 10^5\ \mathrm{N/m^2}$$

14.3.

$$J(t) = \frac{\varepsilon(t)}{\sigma_0} = \sum_{i=1}^{4} J_i\left(1 - e^{-t/\tau_i}\right)$$

Element No.	J_i(mN)	t_i (s)
1	0.2×10^{-8}	100
2	10^{-10}	5
3	0.2×10^{-8}	10
4	10^{-8}	500

$$J(t) = 0.2 \times 10^{-8}\left(1 - e^{-100/100}\right) + 10^{-10}\left(1 - e^{-100/5}\right) + 0.2 \times 10^{-8}\left(1 - e^{-100/10}\right) + 10^{-8}\left(1 - e^{100/50}\right)$$

$$= 0.126 \times 10^{-8} + 10^{-10} + 0.2 \times 10^{-8} + 10^{-8} \times 0.181$$

$$= 0.517 \times 10^{-8}$$

$$\varepsilon(t) = J(t) \times \sigma_0 = \left(0.517 \times 10^{-8}\right)\left(10^{8}\right)$$

$$\varepsilon(t) = 0.517$$

14.4. For this material the creep compliance from the Boltzmann superposition principle is

$$\varepsilon(t) = J(10,000)\sigma_0 + J(10,000 - 100)\ 10^7 + J(10,000 - 1000)\ 10^6$$

$$= 10^{-8}\left[1 - e^{-10^4\left(10^{-4}\right)}\right]10^8 + 10^{-8}\left[1 - e^{-10^{-4}\left(10^4 - 100\right)}\right]10^7 + 10^{-8}\left[1 - e^{-10^{-4}(10000-1000)}\right]$$

$$= 0.632 + 0.63 + 0.006$$

$$= 0.701$$

14.5. First, find the time at T_g:

$$\log_{10} a_t = \log\frac{t_T}{t_{Tg}} = \frac{-17.44\left[0 - (-70)\right]}{51.6 + T - T_g}$$

$$= \frac{-17.44 \times 70}{51.6 + 70} = +10.04$$

$$\frac{t_{0°C}}{t_{-70°C}} = 9.13 \times 10^{-11}\ \text{h}$$

$$\frac{10^4}{9.03 \times 10^{-11}} = t_{-70°C}$$

$$t_{-70°C} = 1.095 \times 10^{14}\ \text{h}$$

Now use this value to determine the T.

$$\log\frac{t_T}{t_{-70°C}} = \frac{-17.44(T + 70)}{51.6 + t_{-70°C} + 70}$$

$$\log\frac{10}{1.095 \times 10^{14}} = \log_{10}\ 9.13 \times 10^{-14} = \frac{-17.44\ (T + 70)}{51.6 + T + 70}$$

$$-13.04 = \frac{-17.44\ (T + 70)}{121.6 + T}$$

$$T = 83°C$$

14.6.

$$\log\frac{\tau_T}{\tau_{Tg}}=\frac{-17.44\left(T-T_g\right)}{51.6+T-T_g}$$

$$\log\frac{\tau_{o_c}}{\tau_{Tg}}=\frac{-17.44\left(O-T_g\right)}{51.6+O=T_g}$$

$$\log\frac{10^4}{10^{13}}=\frac{+17.44\,T_g}{51.6-T_g}$$

$$T_g=-55°C$$

$$\log\frac{\tau_{25}}{\tau_{-55}}=\frac{-17.44\times 80}{131.6}=-10.6$$

$$\tau_{25}=2.5\times 10^2\text{ s}$$

$$\log a_T=\log\frac{t_r}{t_{T_g}}=\log\frac{\omega_{Tg}}{\omega_T}=\frac{-17.44(130-150)}{51.6+130-150}$$

$$\log\frac{\omega_{T_g}}{\omega_T}=11.04$$

$$\omega_{Tg}=1.09\times 10^{11}\ \omega_T$$

$$=1.09\times 10^{11}\ \left(\omega_T=1\text{ cycle/s}\right)$$

14.7.

$$\log\frac{\omega_{T_g}}{\omega_T}=\frac{-17.44(T-150)}{T-98.4}$$

$$\log\frac{1.09\times 10^{11}}{10^3}=\frac{-17.44(T-150)}{T-98.4}$$

$$8.04=\frac{-17.44(T-150)}{T-98.4}$$

$$\tau=194°C$$

14.8.

$$\log a_T=\log\frac{\tau_T}{\tau_{T_g}}=\frac{-17.44(T-100)}{51.6+150-100}$$

For T = 150°C

$$\log\frac{\tau_{150}}{\tau_{100}}=\frac{-17.44\ (150-100)}{51.6+150-100}$$

$$=-8.58$$

$$\tau_{150}=2.61\times 10^{-9}\text{ s}\left(\tau_{Tg}\right)$$

For T = 125°C

$$\log \frac{\tau_{125}}{\tau_{100}} = \frac{-17.44\,(125-100)}{51.6+125-100}$$

$$= 5.69$$

$$\tau_{125} = 2.03 \times 10^{-6}$$

$$\frac{\tau_{150}}{\tau_{125}} = \frac{2.61 \times 10^{-9}}{2.03 \times 10^{6}}$$

$$= 1.29 \times 10^{-3}$$

SOLUTIONS FOR CHAPTER 15 PROBLEMS

15.1. a. Copolymerization with propylene helps to reduce the density of HDPE. HDPE is used for telephone cable insulation because of its greater toughness and because it experiences less absorption of petroleum jelly and other organic cable fillers that are placed into telephone cables to exclude water. Improved toughness helps to resist damage when individual insulated wires are assembled into cables using high-speed machinery. An extremely broad MWD is needed to achieve good extrusion characteristics at the high wire speeds involved.

b. The high crystalline melting point of polypropylene (T_m = 165 to 171°C) along with its high heat deflection temperature permits products made from polypropylene to be heat sterilized. On the other hand, the relatively low crystalline melting point of polyethylene and, particularly, the low heat deflection temperature of PE and PS limits the range of good mechanical properties and, as such, polyethylene and polystyrene products are susceptible to deterioration in quality due to heat sterilization.

c. Polypropylene is a nonpolar hydrocarbon polymer. It is therefore not affected by polar solvents like ethanol and acetone. However, it has a tendency to swell in nonpolar solvents such as benzene and carbon tetrachloride.

d. Since semicrystalline polymers are generally not 100% crystalline, they have regions of differing refractive indices; that is, they exhibit optical anisotropy. Consequently, semicrystalline polymers like polypropylene and polyethylene — particularly in thick sections — are translucent. On the other hand, amorphous polymers are optically isotropic and hence transparent. Random copolymerization of propylene and ethylene results in mutual destruction of crystallinity. The resulting random copolymer is therefore transparent. Polymers for film application must necessarily be tough and flexible. This is typical of random copolymers of propylene and ethylene. Filaments must have high modulus and tensile strength. These requirements are satisfied by polypropylene homopolymer.

e. Chlorinated PVC has a higher heat deflection temperature than pure PVC. Consequently, it is more suitable for use in piping for hot-water systems.

f. Manufacture of PVC involves predominantly suspension, emulsion, and, sometimes, bulk polymerization of vinyl chloride. In all cases, the reaction does not usually go to completion. Unreacted monomer must be removed from the final product. Commercial PVC may therefore be expected to contain a certain amount of vinyl chloride. Since vinyl chloride is a suspected carcinogen, its contact with food must generally be avoided. This limits the use of PVC in food packaging. Besides, PVC used for food packaging must meet stringent standards to prevent possible contact of food with any unreacted vinyl chloride, a potential carcinogen.

g. Cold temperature toughness, gloss, and chemical resistance permit general-purpose ABS to be used in applications requiring refrigeration. Appliance housings, business machines, television cabinets, and interior aircraft uses are applications that require increased resistance to ignition from minor flame sources, hence the use of fire-retardant ABS grade.

h. Because of the pressure of polar amide groups and the effect of absorbed moisture on dielectric properties, nylon insulation is restricted by low-frequency applications. Nylon toughness and abrasion resistance make it suitable as a protective covering for primary electrical insulation.

i. Compared with nylons 6 and 6,6, nylons 11, 12, 6,12 have much lower moisture absorption, possess increased flexibility at high and low temperatures, and have exceptional resistance to stress cracking.

j. PPS has excellent chemical resistance and thermal resistance and is inherently flame retardant. Its chemical resistance is exemplified by its extreme inertness to organic solvents and inorganic salts and bases. This, combined with its hardness and nonstick characteristics, makes PPS a corrosion-resistant material suitable for food contact and aggressive environments.

k. Poly(chlorotrifluoroethylene) chains have a much lower symmetry than polytetrafluoroethylene due to the presence of the relatively larger chlorine. Consequently, the degree of molecular order in poly(chlorotrifluoroethylene), and hence crystallinity, is relatively lower than in PTFE. This is reflected in the relative melting points. Similarly, the lower symmetry in the chlorine-containing polymer prevents crystallization when the polymer is quenched, thus resulting in a completely amorphous polymer that is generally optically clear. The presence of chlorine makes poly(chlorotrifluoroethylene) a polar polymer. This detracts from its electrical properties.

l. The presence of double bonds in the skeletal structure of a polymer makes it susceptible to oxidative degradation and attack by ozone. Unlike most elastomers, butyl rubber has virtually no unsaturation in its skeletal structure.