CHAPTER 14

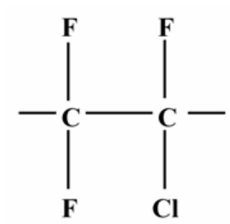
POLYMER STRUCTURES

PROBLEM SOLUTIONS

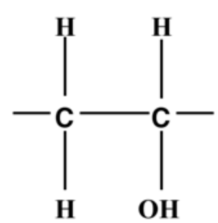
Hydrocarbon Molecules
Polymer Molecules
The Chemistry of Polymer Molecules

14.1 The repeat unit structures called for are sketched below.

(a) Polychlorotrifluoroethylene



(b) Poly(vinyl alcohol)



14.19 (a) This portion of the problem asks us to determine the ratio of butadiene to acrylonitrile repeat units in a copolymer having a weight-average molecular weight of 250,000 g/mol and a degree of polymerization of 4640. It first becomes necessary to calculate the average repeat unit molecular weight of the copolymer, $\overline{m}$, using Equation 14.6 as

$$\overline{m} = \frac{\overline{M}_n}{DP} = \frac{250,000 \text{ g/mol}}{4640} = 53.88 \text{ g/mol}$$

If we designate f_b as the chain fraction of butadiene repeat units, since the copolymer consists of only two repeat unit types, the chain fraction of acrylontrile repeat units f_a is just $1 - f_b$. Now, Equation 14.7 for this copolymer may be written in the form

$$\overline{m} = f_b m_b + f_a m_a = f_b m_b + (1 - f_b) m_a$$

in which m_b and m_a are the repeat unit molecular weights for butadiene and acrylontrile, respectively. These values are calculated as follows:

$$m_b = 4(A_{\text{C}}) + 6(A_{\text{H}}) = 4(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) = 54.09 \text{ g/mol}$$

$$m_a = 3(A_{\text{C}}) + 3(A_{\text{H}}) + (A_{\text{N}}) = 3(12.01 \text{ g/mol}) + 3(1.008 \text{ g/mol}) + (14.01 \text{ g/mol})$$

$$= 53.06 \text{ g/mol.}$$

Solving for f_b in the above expression yields

$$f_b = \frac{\overline{m} - m_a}{m_b - m_a} = \frac{53.88 \text{ g/mol} - 53.06 \text{ g/mol}}{54.09 \text{ g/mol} - 53.06 \text{ g/mol}} = 0.80$$

Furthermore, $f_a = 1 - f_b = 1 - 0.80 = 0.20$; or the ratio is just

$$\frac{f_b}{f_a} = \frac{0.80}{0.20} = 4.0$$

(b) Of the possible copolymers, the only one for which there is a restriction on the ratio of repeat unit types is alternating; the ratio must be 1:1. Therefore, on the basis of the result in part (a), the possibilities for this copolymer are random, graft, and block.

14.18 For an alternating copolymer that has a number-average molecular weight of 100,000 g/mol and a degree of polymerization of 2210, we are to determine one of the repeat unit types if the other type is ethylene. It is first necessary to calculate $\overline{m}$ using Equation 14.6 as

$$\overline{m} = \frac{\overline{M}_n}{DP} = \frac{100{,}000 \text{ g/mol}}{2210} = 42.25 \text{ g/mol}$$

Since this is an alternating copolymer we know that chain fraction of each repeat unit type is 0.5; that is $f_e = f_x$ = 0.5, f_e and f_x being, respectively, the chain fractions of the ethylene and unknown repeat units. Also, the repeat unit molecular weight for ethylene is

$$m_s = 2(A_\text{C}) + 4(A_\text{H})$$

$$= 2(12.01 \text{ g/mol}) + 4(1.008 \text{ g/mol}) = 28.05 \text{ g/mol}$$

Now, using Equation 14.7, it is possible to calculate the repeat unit weight of the unknown repeat unit type, m_x. Thus

$$m_x = \frac{\overline{m} - f_e m_e}{f_x}$$

$$= \frac{45.25 \text{ g/mol} - (0.5)(28.05 \text{ g/mol})}{0.5} = 62.45 \text{ g/mol}$$

Finally, it is necessary to calculate the repeat unit molecular weights for each of the possible other repeat unit types. These are calculated below:

$m_\text{styrene} = 8(A_\text{C}) + 8(A_\text{H}) = 8(12.01 \text{ g/mol}) + 8(1.008 \text{ g/mol}) = 104.16 \text{ g/mol}$
$m_\text{propylene} = 3(A_\text{C}) + 6(A_\text{H}) = 3(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) = 42.08 \text{ g/mol}$
$m_\text{TFE} = 2(A_\text{C}) + 4(A_\text{F}) = 2(12.01 \text{ g/mol}) + 4(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$
$m_\text{VC} = 2(A_\text{C}) + 3(A_\text{H}) + (A_\text{Cl}) = 2(12.01 \text{ g/mol}) + 3(1.008 \text{ g/mol}) + 35.45 \text{ g/mol} = 62.49 \text{ g/mol}$

Therefore, vinyl chloride is the other repeat unit type since its *m* value is almost the same as the calculated m_x.

14.17 This problem asks for us to calculate the number-average molecular weight of a random poly(isobutylene-isoprene) copolymer. For the isobutylene repeat unit there are four carbon and eight hydrogen atoms. Thus, its repeat unit molecular weight is

$$m_{\mathrm{Ib}} = 4(A_{\mathrm{C}}) + 8(A_{\mathrm{H}})$$

$$= (4)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 56.10 \text{ g/mol}$$

The isoprene repeat unit is composed of five carbon and eight hydrogen atoms. Thus, its repeat unit molecular weight is

$$m_{\mathrm{Ip}} = 5(A_{\mathrm{C}}) + 8(A_{\mathrm{H}})$$

$$= (5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 68.11 \text{ g/mol}$$

From Equation 14.7, the average repeat unit molecular weight is just

$$\overline{m} = f_{\mathrm{Ib}} m_{\mathrm{Ib}} + f_{\mathrm{Ip}} m_{\mathrm{Ip}}$$

$$= (0.25)(56.10 \text{ g/mol}) + (0.75)(68.11 \text{ g/mol}) = 65.11 \text{ g/mol}$$

Since DP = 1500 (as stated in the problem), $\overline{M}_n$ may be computed using Equation 14.6 as

$$\overline{M}_n = \overline{m}\,(DP) = (65.11 \text{ g/mol})(1500) = 97{,}700 \text{ g/mol}$$

14.16 For a poly(acrylonitrile-butadiene) alternating copolymer with a number-average molecular weight of 1,000,000 g/mol, we are asked to determine the average number of acrylonitrile and butadiene repeat units per molecule.

Since it is an alternating copolymer, the number of both types of repeat units will be the same. Therefore, consider them as a single repeat unit, and determine the number-average degree of polymerization. For the acrylonitrile repeat unit, there are three carbon atoms, three hydrogen atoms, and one nitrogen atom, while the butadiene repeat consists of four carbon atoms and six hydrogen atoms. Therefore, the acrylonitrile-butadiene combined repeat unit weight is just

$$m = 7(A_{\mathrm{C}}) + 9(A_{\mathrm{H}}) + 1(A_{\mathrm{N}})$$

$$= (7)(12.01 \text{ g/mol}) + (9)(1.008 \text{ g/mol}) + (14.01 \text{ g/mol}) = 107.15 \text{ g/mol}$$

From Equation 14.6, the degree of polymerization is just

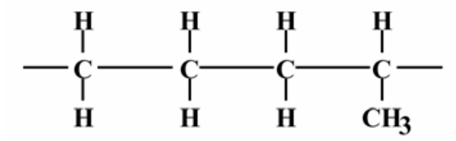
$$DP = \frac{\overline{M}_n}{m} = \frac{1{,}000{,}000 \text{ g/mol}}{107.15 \text{ g/mol}} = 9333$$

Thus, there is an average of 9333 of both repeat unit types per molecule.

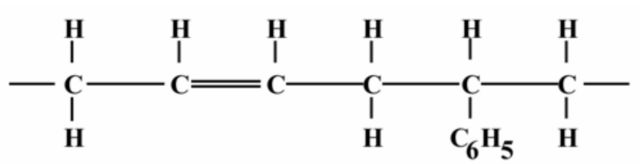
Copolymers

14.15 This problem asks for sketches of the repeat unit structures for several alternating copolymers.

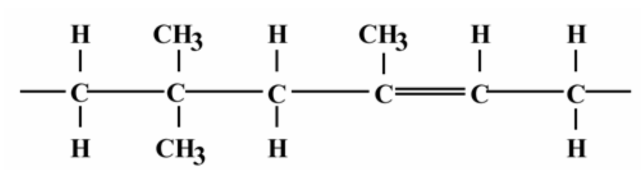
(a) For poly(ethylene-propylene)



(b) For poly(butadiene-styrene)



(c) For poly(isobutylene-isoprene)



14.14 (a) It is *not possible* to grind up and reuse phenol-formaldehyde because it is a network thermoset polymer and, therefore, is not amenable to remolding.

(b) Yes, it is *possible* to grind up and reuse polypropylene since it is a thermoplastic polymer, will soften when reheated, and, thus, may be remolded.

Thermoplastic and Thermosetting Polymers

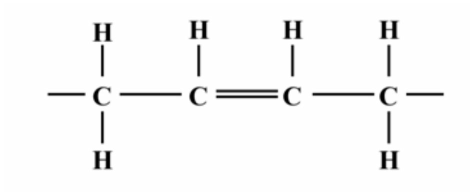
14.13 This question asks for comparisons of thermoplastic and thermosetting polymers.

(a) Thermoplastic polymers soften when heated and harden when cooled, whereas thermosetting polymers, harden upon heating, while further heating will not lead to softening.

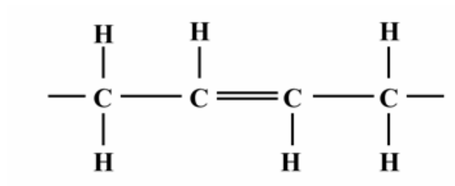
(b) Thermoplastic polymers have linear and branched structures, while for thermosetting polymers, the structures will normally be network or crosslinked.

14.12 This problem asks for us to sketch cis and trans structures for butadiene and chloroprene.

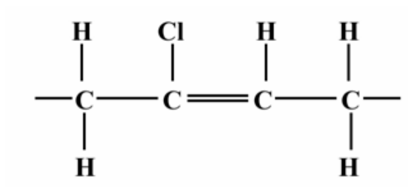
(a) The structure for *cis* polybutadiene (Table 14.5) is



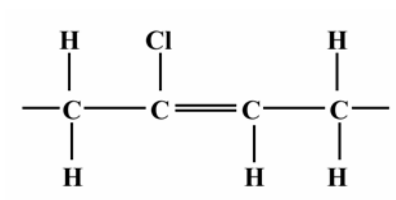
The structure of *trans* butadiene is



(b) The structure of *cis* chloroprene (Table 14.5) is



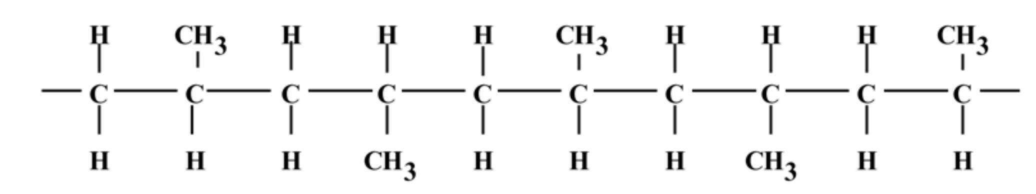
The structure of *trans* chloroprene is



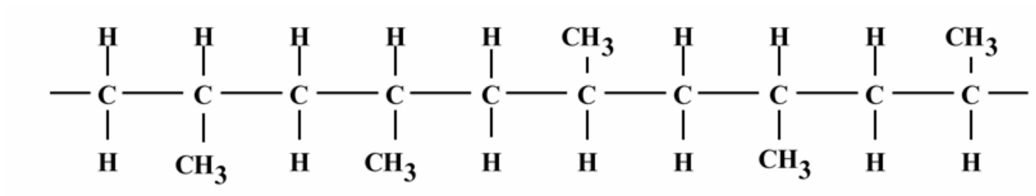
Molecular Configurations

14.11 We are asked to sketch portions of a linear polypropylene molecule for different configurations (using two-dimensional schematic sketches).

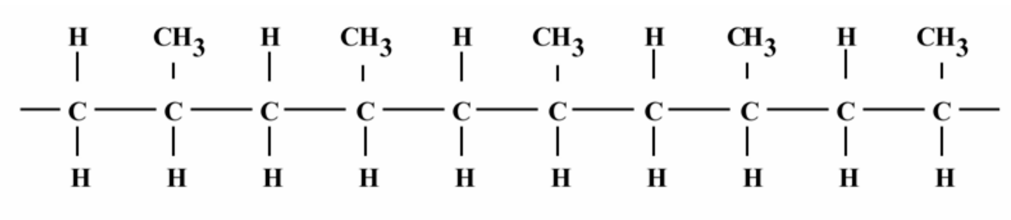
(a) Syndiotactic polypropylene



(b) Atactic polypropylene



(c) Isotactic polypropylene



14.8 (a) For chlorinated polyethylene, we are asked to determine the weight percent of chlorine added for 8% Cl substitution of all original hydrogen atoms. Consider 50 carbon atoms; there are 100 possible side-bonding sites. Ninety-two are occupied by hydrogen and eight are occupied by Cl. Thus, the mass of these 50 carbon atoms, m_C, is just

$$m_C = 50(A_C) = (50)(12.01 \text{ g/mol}) = 600.5 \text{ g}$$

Likewise, for hydrogen and chlorine,

$$m_H = 92(A_H) = (92)(1.008 \text{ g/mol}) = 92.74 \text{ g}$$

$$m_{Cl} = 8(A_{Cl}) = (8)(35.45 \text{ g/mol}) = 283.60 \text{ g}$$

Thus, the concentration of chlorine, C_{Cl}, is determined using a modified form of Equation 4.3 as

$$C_{Cl} = \frac{m_{Cl}}{m_C + m_H + m_{Cl}} \times 100$$

$$= \frac{283.60 \text{ g}}{600.5 \text{ g} + 92.74 \text{ g} + 283.60 \text{ g}} \times 100 = 29.0 \text{ wt\%}$$

(b) Chlorinated polyethylene differs from poly(vinyl chloride), in that, for PVC, (1) 25% of the side-bonding sites are substituted with Cl, and (2) the substitution is probably much less random.

14.7 This problem asks if it is possible to have a poly(vinyl chloride) homopolymer with the given molecular weight data and a degree of polymerization of 1120. The appropriate data are given below along with a computation of the number-average molecular weight.

Molecular wt. Range	Mean M_i	x_i	x_iM_i
8,000-20,000	14,000	0.05	700
20,000-32,000	26,000	0.15	3900
32,000-44,000	38,000	0.21	7980
44,000-56,000	50,000	0.28	14,000
56,000-68,000	62,000	0.18	11,160
68,000-80,000	74,000	0.10	7440
80,000-92,000	86,000	0.03	2580

$$\overline{M}_w = \sum x_i M_i = 47,720 \text{ g/mol}$$

For PVC, from Table 14.3, each repeat unit has two carbons, three hydrogens, and one chlorine. Thus,

$$m = 2(A_{\text{C}}) + 3(A_{\text{H}}) + (A_{\text{Cl}})$$

$$= (2)(12.01 \text{ g/mol}) + (3)(1.008 \text{ g/mol}) + (35.45 \text{ g/mol}) = 62.49 \text{ g/mol}$$

Now, we will compute the degree of polymerization using Equation 14.6 as

$$DP = \frac{\overline{M}_n}{m} = \frac{47,720 \text{ g/mol}}{62.49 \text{ g/mol}} = 764$$

Thus, such a homopolymer is *not possible* since the calculated degree of polymerization is 764 not 1120.

The repeat unit molecular weights of the polymers listed in Table 14.3 are as follows:

Polyethylene--28.05 g/mol

Poly(vinyl chloride)--62.49 g/mol

Polytetrafluoroethylene--100.02 g/mol

Polypropylene--42.08 g/mol

Polystyrene--104.14 g/mol

Poly(methyl methacrylate)--100.11 g/mol

Phenol-formaldehyde--133.16 g/mol

Nylon 6,6--226.32 g/mol

PET--192.16 g/mol

Polycarbonate--254.27 g/mol

Therefore, polytetrafluoroethylene is the material since its repeat unit molecular weight is closest to that calculated above.

14.6 (a) From the tabulated data, we are asked to compute $\overline{M}_n$, the number-average molecular weight. This is carried out below.

Molecular wt. Range	Mean M_i	x_i	$x_i M_i$
8,000-20,000	14,000	0.05	700
20,000-32,000	26,000	0.15	3900
32,000-44,000	38,000	0.21	7980
44,000-56,000	50,000	0.28	14,000
56,000-68,000	62,000	0.18	11,160
68,000-80,000	74,000	0.10	7400
80,000-92,000	86,000	0.03	2580

$$\overline{M}_n = \sum x_i M_i = 47{,}720 \text{ g/mol}$$

(b) From the tabulated data, we are asked to compute $\overline{M}_w$, the weight-average molecular weight. This determination is performed as follows:

Molecular wt. Range	Mean M_i	w_i	$w_i M_i$
8,000-20,000	14,000	0.02	280
20,000-32,000	26,000	0.08	2080
32,000-44,000	38,000	0.17	6460
44,000-56,000	50,000	0.29	14,500
56,000-68,000	62,000	0.23	14,260
68,000-80,000	74,000	0.16	11,840
80,000-92,000	86,000	0.05	4300

$$\overline{M}_w = \sum w_i M_i = 53{,}720 \text{ g/mol}$$

(c) We are now asked if the degree of polymerization is 477, which of the polymers in Table 14.3 is this material? It is necessary to compute *m* in Equation 14.6 as

$$m = \frac{\overline{M}_n}{DP} = \frac{47{,}720 \text{ g/mol}}{477} = 100.04 \text{ g/mol}$$

$$m = 2(A_{\mathrm{C}}) + 4(A_{\mathrm{F}})$$

$$= (2)(12.01 \text{ g/mol}) + (4)(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$$

And

$$DP = \frac{\overline{M}_n}{m} = \frac{49{,}800 \text{ g/mol}}{100.02 \text{ g/mol}} = 498$$

14.5 (a) From the tabulated data, we are asked to compute $\overline{M}_n$, the number-average molecular weight. This is carried out below.

Molecular wt Range	Mean M_i	x_i	x_iM_i
10,000-20,000	15,000	0.03	450
20,000-30,000	25,000	0.09	2250
30,000-40,000	35,000	0.15	5250
40,000-50,000	45,000	0.25	11,250
50,000-60,000	55,000	0.22	12,100
60,000-70,000	65,000	0.14	9100
70,000-80,000	75,000	0.08	6000
80,000-90,000	85,000	0.04	3400

$$\overline{M}_n = \sum x_i M_i = 49{,}800 \text{ g/mol}$$

(b) From the tabulated data, we are asked to compute $\overline{M}_w$, the weight-average molecular weight.

Molecular wt. Range	Mean M_i	w_i	w_iM_i
10,000-20,000	15,000	0.01	150
20,000-30,000	25,000	0.04	1000
30,000-40,000	35,000	0.11	3850
40,000-50,000	45,000	0.23	10,350
50,000-60,000	55,000	0.24	13,200
60,000-70,000	65,000	0.18	11,700
70,000-80,000	75,000	0.12	9000
80,000-90,000	85,000	0.07	5950

$$\overline{M}_w = \sum w_i M_i = 55{,}200 \text{ g/mol}$$

(c) Now we are asked to compute the degree of polymerization, which is possible using Equation 14.6. For polytetrafluoroethylene, the repeat unit molecular weight is just

14.4 (a) The repeat unit molecular weight of polypropylene is called for in this portion of the problem. For polypropylene, from Table 14.3, each repeat unit has three carbons and six hydrogens. Thus,

$$m = 3(A_{\mathrm{C}}) + 6(A_{\mathrm{H}})$$

$$= (3)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol}) = 42.08 \text{ g/mol}$$

(b) We are now asked to compute the number-average molecular weight. Since the degree of polymerization is 15,000, using Equation 14.6

$$\overline{M}_n = (DP)m = (15{,}000)(42.08 \text{ g/mol}) = 631{,}000 \text{ g/mol}$$

14.3 We are asked to compute the degree of polymerization for polystyrene, given that the number-average molecular weight is 500,000 g/mol. The repeat unit molecular weight of polystyrene is just

$$m = 8(A_{\mathrm{C}}) + 8(A_{\mathrm{H}})$$

$$= (8)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 104.14 \text{ g/mol}$$

Now it is possible to compute the degree of polymerization using Equation 14.6 as

$$DP = \frac{\overline{M}_n}{m} = \frac{500{,}000 \text{ g/mol}}{104.14 \text{ g/mol}} = 4800$$

Molecular Weight

14.2 Repeat unit weights for several polymers are asked for in this problem.

(a) For polytetrafluoroethylene, each repeat unit consists of two carbons and four fluorines (Table 14.3). If A_C and A_F represent the atomic weights of carbon and fluorine, respectively, then

$$m = 2(A_C) + 4(A_F)$$

$$= (2)(12.01 \text{ g/mol}) + (4)(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$$

(b) For poly(methyl methacrylate), from Table 14.3, each repeat unit has five carbons, eight hydrogens, and two oxygens. Thus,

$$m = 5(A_C) + 8(A_H) + 2(A_O)$$

$$= (5)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) + (2)(16.00 \text{ g/mol}) = 100.11 \text{ g/mol}$$

(c) For nylon 6,6, from Table 14.3, each repeat unit has twelve carbons, twenty-two hydrogens, two nitrogens, and two oxygens. Thus,

$$m = 12(A_C) + 22(A_H) + 2(A_N) + 2(A_O)$$

$$= (12)(12.01 \text{ g/mol}) + (22)(1.008 \text{ g/mol}) + (2)(14.01 \text{ g/mol}) + (2)(16.00 \text{ g/mol})$$

$$= 226.32 \text{ g/mol}$$

(d) For poly(ethylene terephthalate), from Table 14.3, each repeat unit has ten carbons, eight hydrogens, and four oxygens. Thus,

$$m = 10(A_C) + 8(A_H) + 4(A_O)$$

$$= (10)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) + (4)(16.00 \text{ g/mol}) = 192.16 \text{ g/mol}$$

14.29 This problem asks that we compute the diffusion flux at 350 K for water in polystyrene. It is first necessary to compute the value of the permeability coefficient at 350 K. The temperature dependence of P_M is given in the problem statement, as follows:

$$P_M = P_{M_0} \exp\left(-\frac{Q_p}{RT}\right)$$

And, incorporating values provided for the constants P_{M_0} and Q_p, we get

$$P_M = \left[9.0 \times 10^{-5} \ \frac{(\text{cm}^3\ \text{STP})(\text{cm})}{\text{cm}^2\text{-s-Pa}}\right] \exp\left[-\frac{42{,}300\ \text{J/mol}}{(8.314\ \text{J/mol-K})(350\ \text{K})}\right]$$

$$= 4.4 \times 10^{-11} \ \frac{(\text{cm}^3\ \text{STP})(\text{cm})}{\text{cm}^2\text{-s-Pa}}$$

And, using Equation 14.9, the diffusion flux is equal to

$$J = P_M \frac{\Delta P}{\Delta x} = P_M \frac{P_2 - P_1}{\Delta x}$$

$$= 4.4 \times 10^{-11} \frac{(\text{cm}^3\ \text{STP})(\text{cm})}{\text{cm}^2\text{-s-Pa}} \left(\frac{20{,}000\ \text{Pa} - 1{,}000\ \text{Pa}}{3.0\ \text{cm}}\right)$$

$$= 2.8 \times 10^{-7} \ \frac{(\text{cm}^3\ \text{STP})}{\text{cm}^2\text{-s}}$$

14.28 This problem asks us to compute the permeability coefficient for carbon dioxide through high density polyethylene at 325 K given a steady-state permeability situation. It is necessary for us to Equation 14.9 in order to solve this problem. Rearranging this expression and solving for the permeability coefficient gives

$$P_M = \frac{J\,\Delta x}{\Delta P} = \frac{J\,\Delta x}{P_2 - P_1}$$

Taking P_1 = 2500 kPa (2,500,000 Pa) and P_1 = 4000 kPa (4,000,000 Pa), the permeability coefficient of CO_2 through HDPE is equal to

$$P_M = \frac{\left[2.2 \text{ x } 10^{-8} \, \dfrac{(\text{cm}^3 \text{ STP})}{\text{cm}^2 \text{ - s}}\right](5 \text{ cm})}{(4{,}000{,}000 \text{ Pa - } 2{,}500{,}000 \text{ Pa})}$$

$$= 0.73 \text{ x } 10^{-13} \, \frac{(\text{cm}^3 \text{ STP})(\text{cm})}{\text{cm}^2 \text{ - s - Pa}}$$

Diffusion in Polymeric Materials

14.27 This is a permeability problem in which we are asked to compute the diffusion flux of oxygen through a 15-mm thick sheet of low density polyethylene. In order to solve this problem it is necessary to employ Equation 14.9. The permeability coefficient of O_2 through LDPE is given in Table 14.6 as 2.2×10^{-13} (cm^3 STP)-cm/cm^2-s-Pa. Thus, from Equation 14.9

$$J = P_M \frac{\Delta P}{\Delta x} = P_M \frac{P_2 - P_1}{\Delta x}$$

and taking P_1 = 150 kPa (150,000 Pa) and P_2 = 2000 kPa (2,000,000 Pa) we get

$$= \left[2.2 \times 10^{-13} \frac{(\mathrm{cm^3\ STP})(\mathrm{cm})}{\mathrm{cm^2 - s - Pa}}\right]\left(\frac{2{,}000{,}000\ \mathrm{Pa} - 150{,}000\ \mathrm{Pa}}{1.5\ \mathrm{cm}}\right)$$

$$= 2.7 \times 10^{-6} \frac{(\mathrm{cm^3\ STP})}{\mathrm{cm^2 - s}}$$

$$\rho_s = \frac{-\rho_c \rho_a}{C(\rho_c - \rho_a) - \rho_c}$$

$$= \frac{-(0.946 \text{ g/cm}^3)(0.841 \text{ g/cm}^3)}{(0.746)(0.946 \text{ g/cm}^3 - 0.841 \text{ g/cm}^3) - 0.946 \text{ g/cm}^3}$$

$$= 0.917 \text{ g/cm}^3$$

14.26 (a) We are asked to compute the densities of totally crystalline and totally amorphous polypropylene (ρ_c and ρ_a from Equation 14.8). From Equation 14.8 let $C = \frac{\text{\% crystallinity}}{100}$, such that

$$C = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)}$$

Rearrangement of this expression leads to

$$\rho_c(C\rho_s - \rho_s) + \rho_c\rho_a - C\rho_s\rho_a = 0$$

in which ρ_c and ρ_a are the variables for which solutions are to be found. Since two values of ρ_s and C are specified in the problem, two equations may be constructed as follows:

$$\rho_c(C_1\rho_{s1} - \rho_{s1}) + \rho_c\rho_a - C_1\rho_{s1}\rho_a = 0$$

$$\rho_c(C_2\rho_{s2} - \rho_{s2}) + \rho_c\rho_a - C_2\rho_{s2}\rho_a = 0$$

In which ρ_{s1} = 0.904 g/cm^3, ρ_{s2} = 0.895 g/cm^3, C_1 = 0.628, and C_2 = 0.544. Solving the above two equations for ρ_a and ρ_c leads to

$$\rho_a = \frac{\rho_{s1}\rho_{s2}(C_1 - C_2)}{C_1\rho_{s1} - C_2\rho_{s2}}$$

$$= \frac{(0.904\ \text{g/cm}^3)(0.895\ \text{g/cm}^3)(0.628 - 0.544)}{(0.628)(0.904\ \text{g/cm}^3) - (0.544)(0.895\ \text{g/cm}^3)} = 0.841\ \text{g/cm}^3$$

And

$$\rho_c = \frac{\rho_{s1}\rho_{s2}(C_2 - C_1)}{\rho_{s2}(C_2 - 1) - \rho_{s1}(C_1 - 1)}$$

$$= \frac{(0.904\ \text{g/cm}^3)(0.895\ \text{g/cm}^3)(0.544 - 0.628)}{(0.895\ \text{g/cm}^3)(0.544 - 1.0) - (0.904\ \text{g/cm}^3)(0.628 - 1.0)} = 0.946\ \text{g/cm}^3$$

(b) Now we are asked to determine the density of a specimen having 74.6% crystallinity. Solving for ρ_s from Equation 14.8 and substitution for ρ_a and ρ_c which were computed in part (a) yields

$$\% \text{ crystallinity } = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

$$= \frac{(1.450 \text{ g/cm}^3)(1.382 \text{ g/cm}^3 - 1.300 \text{ g/cm}^3)}{(1.382 \text{ g/cm}^3)(1.450 \text{ g/cm}^3 - 1.300 \text{ g/cm}^3)} \times 100$$

$$= 57.4\%$$

14.25 (a) We are asked to compute the densities of totally crystalline and totally amorphous poly(ethylene terephthalate) (ρ_c and ρ_a from Equation 14.8). From Equation 14.8 let $C = \dfrac{\%\ \text{crystallinity}}{100}$, such that

$$C = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)}$$

Rearrangement of this expression leads to

$$\rho_c(C\rho_s - \rho_s) + \rho_c\rho_a - C\rho_s\rho_a = 0$$

in which ρ_c and ρ_a are the variables for which solutions are to be found. Since two values of ρ_s and C are specified in the problem statement, two equations may be constructed as follows:

$$\rho_c(C_1\rho_{s1} - \rho_{s1}) + \rho_c\rho_a - C_1\rho_{s1}\rho_a = 0$$

$$\rho_c(C_2\rho_{s2} - \rho_{s2}) + \rho_c\rho_a - C_2\rho_{s2}\rho_a = 0$$

In which ρ_{s1} = 1.408 g/cm^3, ρ_{s2} = 1.343 g/cm^3, C_1 = 0.743, and C_2 = 0.312. Solving the above two equations for ρ_a and ρ_c leads to

$$\rho_a = \frac{\rho_{s1}\rho_{s2}(C_1 - C_2)}{C_1\rho_{s1} - C_2\rho_{s2}}$$

$$= \frac{(1.408\ \text{g/cm}^3)(1.343\ \text{g/cm}^3)(0.743 - 0.312)}{(0.743)(1.408\ \text{g/cm}^3) - (0.312)(1.343\ \text{g/cm}^3)} = 1.300\ \text{g/cm}^3$$

And

$$\rho_c = \frac{\rho_{s1}\rho_{s2}(C_2 - C_1)}{\rho_{s2}(C_2 - 1) - \rho_{s1}(C_1 - 1)}$$

$$= \frac{(1.408\ \text{g/cm}^3)(1.343\ \text{g/cm}^3)(0.312 - 0.743)}{(1.343\ \text{g/cm}^3)(0.312 - 1.0) - (1.408\ \text{g/cm}^3)(0.743 - 1.0)} = 1.450\ \text{g/cm}^3$$

(b) Now we are to determine the % crystallinity for ρ_s = 1.382 g/cm^3. Again, using Equation 14.8

14.24 For this problem we are given the density of nylon 6,6 (1.213 g/cm^3), an expression for the volume of its unit cell, and the lattice parameters, and are asked to determine the number of repeat units per unit cell. This computation necessitates the use of Equation 3.5, in which we solve for *n*. Before this can be carried out we must first calculate V_C, the unit cell volume, and *A* the repeat unit molecular weight. For V_C

$$V_C = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

$$= (0.497)(0.547)(1.729)\sqrt{1 - 0.441 - 0.054 - 0.213 + 2(0.664)(0.232)(0.462)}$$

$$= 0.3098 \text{ nm}^3 = 3.098 \times 10^{-22} \text{ cm}^3$$

The repeat unit for nylon 6,6 is shown in Table 14.3, from which the value of *A* may be determined as follows:

$$A = 12(A_{\mathrm{C}}) + 22(A_{\mathrm{H}}) + 2(A_{\mathrm{O}}) + 2(A_{\mathrm{N}})$$

$$= 12(12.01 \text{ g/mol}) + 22(1.008 \text{ g/mol}) + 2(16.00 \text{ g/mol}) + 2(14.01 \text{ g/mol})$$

$$= 226.32 \text{ g/mol}$$

Finally, solving for *n* from Equation 3.5 leads to

$$n = \frac{\rho V_C N_{\mathrm{A}}}{A}$$

$$= \frac{(1.213 \text{ g/cm}^3)(3.098 \times 10^{-22} \text{ cm}^3\text{/unit cell})(6.023 \times 10^{23} \text{ repeat units/mol})}{226.32 \text{ g/mol}}$$

$$= 1 \text{ repeat unit/unit cell}$$

14.23 For each of four pairs of polymers, we are asked to (1) state whether it is possible to decide which is more likely to crystallize; (2) if so, which is more likely and why; and (3) it is not possible to decide then why.

(a) No, it is not possible to decide for these two polymers. On the basis of tacticity, the isotactic PP is more likely to crystallize than the atactic PVC. On the other hand, with regard to side-group bulkiness, the PVC is more likely to crystallize.

(b) Yes, it is possible to decide for these two copolymers. The linear and syndiotactic polypropylene is more likely to crystallize than crosslinked cis-isoprene since linear polymers are more likely to crystallize than crosslinked ones.

(c) Yes, it is possible to decide for these two polymers. The linear and isotactic polystyrene is more likely to crystallize than network phenol-formaldehyde; network polymers rarely crystallize, whereas isotactic ones crystallize relatively easily.

(d) Yes, it is possible to decide for these two copolymers. The block poly(acrylonitrile-isoprene) copolymer is more likely to crystallize than the graft poly(chloroprene-isobutylene) copolymer. Block copolymers crystallize more easily than graft ones.

Polymer Crystallinity

14.22 The tendency of a polymer to crystallize decreases with increasing molecular weight because as the chains become longer it is more difficult for all regions along adjacent chains to align so as to produce the ordered atomic array.

14.21 For a random poly(styrene-butadiene) copolymer in which $\overline{M}_n$ = 350,000 g/mol and *DP* = 5000, we are asked to compute the fractions of styrene and butadiene repeat units.

From Table 14.5, the styrene repeat unit has eight carbon and eight hydrogen atoms. Thus,

$$m_{st} = (8)(12.01 \text{ g/mol}) + (8)(1.008 \text{ g/mol}) = 104.14 \text{ g/mol}$$

Also, from Table 14.5, the butadiene repeat unit has four carbon and six hydrogen atoms, and

$$m_{bu} = (4)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol}) = 54.09 \text{ g/mol}$$

From Equation 14.7

$$\overline{m} = f_{st}m_{st} + f_{bu}m_{bu}$$

Now, let $x = f_{st}$, such that

$$\overline{m} = 104.14x + (54.09)(1 - x)$$

since $f_{st} + f_{bu} = 1$. Also, from Equation 14.6

$$DP = \frac{\overline{M}_n}{\overline{m}}$$

Or

$$5000 = \frac{350{,}000 \text{ g/mol}}{[104.14x + 54.09(1 - x)] \text{ g/mol}}$$

Solving for x leads to $x = f_{st} = f(\text{styrene}) = 0.32$. Also,

$$f(\text{butadiene}) = 1 - x = 1 - 0.32 = 0.68$$

14.20 For a copolymer consisting of 35 wt% ethylene and 65 wt% propylene, we are asked to determine the fraction of both repeat unit types.

In 100 g of this material, there are 35 g of ethylene and 65 g of propylene. The ethylene (C_2H_4) molecular weight is

$$m(\text{ethylene}) = 2(A_C) + 4(A_H)$$

$$= (2)(12.01\text{ g/mol}) + (4)(1.008\text{ g/mol}) = 28.05\text{ g/mol}$$

The propylene (C_3H_6) molecular weight is

$$m(\text{propylene}) = 3(A_C) + 6(A_H)$$

$$= (3)(12.01\text{ g/mol}) + (6)(1.008\text{ g/mol}) = 42.08\text{ g/mol}$$

Therefore, in 100 g of this material, there are

$$\frac{35\text{ g}}{28.05\text{ g/mol}} = 1.25\text{ mol of ethylene}$$

and

$$\frac{65\text{ g}}{42.08\text{ g/mol}} = 1.54\text{ mol of propylene}$$

Thus, the fraction of the ethylene repeat unit, *f*(ethylene), is just

$$f\,(\text{ethylene}) = \frac{1.25\text{ mol}}{1.25\text{ mol} + 1.54\text{ mol}} = 0.45$$

Likewise,

$$f\,(\text{propylene}) = \frac{1.54\text{ mol}}{1.25\text{ mol} + 1.54\text{ mol}} = 0.55$$