

HW 9

Problem 14.5

a. To Find:

- (a) The number-average molecular weight
- (b) The weight-average molecular weight
- (c) The degree of polymerization
for the given polypropylene material

b. Given:

<i>Molecular Weight Range (g/mol)</i>	x_i	w_i
8,000–16,000	0.05	0.02
16,000–24,000	0.16	0.10
24,000–32,000	0.24	0.20
32,000–40,000	0.28	0.30
40,000–48,000	0.20	0.27
48,000–56,000	0.07	0.11

c. Assumptions:

The given data is accurate; the material (polypropylene) is pure.

d. Solution:

- (a) Number-average molecular weight:

Molecular wt. Range	Mean M_i	x_i	$x_i M_i$
8,000-16,000	12,000	0.05	600
16,000-24,000	20,000	0.16	3200
24,000-32,000	28,000	0.24	6720
32,000-40,000	36,000	0.28	10,080
40,000-48,000	44,000	0.20	8800
48,000-56,000	52,000	0.07	3640

$$\bar{M}_n = \sum x_i M_i = 33,040 \text{ g/mol}$$

(b) Weight-average molecular weight:

Molecular wt. Range	Mean M_i	w_i	$w_i M_i$
8,000-16,000	12,000	0.02	240
16,000-24,000	20,000	0.10	2000
24,000-32,000	28,000	0.20	5600
32,000-40,000	36,000	0.30	10,800
40,000-48,000	44,000	0.27	11,880
48,000-56,000	52,000	0.11	5720

$$\overline{M}_w = \sum w_i M_i = 36,240 \text{ g/mol}$$

(c) Degree of polymerization:

For polypropylene, the repeat unit molecular weight, $m = 3(A_C) + 6(A_H) = (3)(12.01 \text{ g/mol}) + (6)(1.008 \text{ g/mol})$
 $= 42.08 \text{ g/mol}$

$$DP = \frac{\overline{M}_n}{m} = \frac{33,040 \text{ g/mol}}{42.08 \text{ g/mol}} = 785$$

(a) 33040 g/mol

**(b) 36240
g/mol**

(c) 785

Problem 14.8

a. To Find:

- (a) Wt% of Chlorine to be added
- (b) How this chlorinated poly-ethylene differs from PVC

b. Given:

High-density poly-ethylene is chlorinated such that Cl atoms replace 5% of the original H atoms.

c. Assumptions:

- (i) All the Chlorine added is utilized in replacing the existing H atoms – no Cl atom stays unutilized.
- (ii) Exactly 5 % of the original H atoms are replaced by Cl atoms.
- (iii) The original material is pure poly-ethylene.
- (iv) No other atom species (which could potentially replace H atoms) is added.

d. Solution:

(a) Consider 50 carbon atoms in the high density poly-ethylene. These correspond to 100 possible side-bonding sites. Initially, all 100 sites are occupied by H. Post-chlorination, 95 of these sites are occupied by hydrogen and 5 sites are occupied by Cl.

Mass of 50 carbon atoms, $m_C = 50(A_C) = (50)(12.01 \text{ g/mol}) = 600.5 \text{ g}$

Mass of 95 H atoms, $m_H = 95(A_H) = (95)(1.008 \text{ g/mol}) = 95.76 \text{ g}$

Mass of 5 Cl atoms, $m_{Cl} = 5(A_{Cl}) = (5)(35.45 \text{ g/mol}) = 177.25 \text{ g}$

Using a modified form of Equation 4.3, concentration of chlorine, C_{Cl} is:

$$C_{Cl} = \frac{m_{Cl}}{m_C + m_H + m_{Cl}} \times 100 = \frac{177.25 \text{ g}}{600.5 \text{ g} + 95.76 \text{ g} + 177.25 \text{ g}} \times 100 = 20.3 \text{ wt\%}$$

20.3 wt%

(b) Compared to chlorinated poly-ethylene, in poly(vinyl chloride):

- (1) 25% of the side-bonding sites are substituted with Cl
- (2) Substitution is probably less random

Problem 14.17

a. To Find:

The number-average molecular weight of a random nitrile rubber [poly(acrylonitrile-butadiene) copolymer].

b. Given:

1. Fraction of butadiene repeat units, $f_{\text{Bu}} = 0.30$ (\Rightarrow fraction of acrylonitrile repeat units, $f_{\text{Ac}} = 0.70$)
2. Degree of polymerization = 2000

c. Assumptions:

Given data is accurate; the material is pure.

d. Solution:

The two repeat units in this co-polymer are acrylonitrile and butadiene.

From Table 14.5, the **acrylonitrile repeat unit** contains 3 Carbon atoms, 1 Nitrogen atom and 3 Hydrogen atoms. Thus, the molecular weight of the acrylonitrile repeat unit is:

$$m_{\text{Ac}} = 3(A_{\text{C}}) + (A_{\text{N}}) + 3(A_{\text{H}}) = (3)(12.01 \text{ g/mol}) + 14.01 \text{ g/mol} + (3)(1.008 \text{ g/mol}) = \mathbf{53.06 \text{ g/mol}}$$

The **butadiene repeat unit** contains 4 Carbon atoms and 6 Hydrogen atoms. Thus, the molecular weight of the butadiene repeat unit is:

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

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

$$\bar{m} = f_{\text{Ac}}m_{\text{Ac}} + f_{\text{Bu}}m_{\text{Bu}} = (0.70)(53.06 \text{ g/mol}) + (0.30)(54.09 \text{ g/mol}) = 53.37 \text{ g/mol}$$

From Equation 14.6, the number-average molecular weight is:

$$\bar{M}_n = \bar{m} (DP) = (53.37 \text{ g/mol})(2000) = 106,740 \text{ g/mol}$$

106740 g/mol

Problem 14.19

a. To Find:

- (a) Ratio of butadiene to styrene repeat units in the given co-polymer
- (b) Type of co-polymer

b. Given:

- 1. Number-average molecular weight of copolymer = 350000 g/mol
- 2. Degree of polymerization = 4425

c. Assumptions:

- (i) Given data is accurate.
- (ii) The material is pure.

d. Solution:

(a) From Equation 14.6, the average repeat unit molecular weight of the copolymer, \bar{m} , is calculated as:

$$\bar{m} = \frac{\bar{M}_n}{DP} = \frac{350,000 \text{ g/mol}}{4425} = 79.10 \text{ g/mol}$$

From Table 14.5, the butadiene repeat unit contains 4 Carbon atoms and 6 Hydrogen atoms. Thus, the molecular weight of the butadiene repeat unit is :

$$m_b = 4(A_C) + 6(A_H) = 4(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) = 54.09 \text{ g/mol}$$

The styrene repeat unit contains 8 Carbon atoms and 8 Hydrogen atoms. Thus, the molecular weight of the styrene repeat unit is:

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

Let f_b be the chain fraction of butadiene repeat units. Since there are only two repeat unit types in the copolymer, the chain fraction of styrene repeat units f_s is $1 - f_b$. Equation 14.7 may be written as:

$$\bar{m} = f_b m_b + f_s m_s = f_b m_b + (1 - f_b) m_s$$

$$\Rightarrow f_b = \frac{\bar{m} - m_s}{m_b - m_s} = \frac{79.10 \text{ g/mol} - 104.14 \text{ g/mol}}{54.09 \text{ g/mol} - 104.14 \text{ g/mol}} = 0.50$$

$$\Rightarrow f_s = 1 - f_b = 1 - 0.50 = 0.50$$

Hence, the ratio of butadiene to styrene repeat units = $\frac{f_b}{f_s} = \frac{0.50}{0.50} = 1.0$ (or 1:1)

(b) The ratio of the the two units in the co-polymer is 1:1 in case of alternating co-polymers. There is no fixed ratio prescribed for random, graft and block co-polymers (1:1 could be a possible ratio for each of these types!)

Therefore, with the ratio of butadiene to styrene repeat units obtained in part (a), this co-polymer be of alternating, random, graft and block types.

(a) 1 (or 1:1)

**(b) Alternating, random, graft
and block types**

Problem 14.25

a. To Find:

- (a) Densities of totally crystalline and totally amorphous polytetrafluoroethylene (PTFE).
(b) % Crystallinity of a specimen having a density of 2.26 g/cm^3 .

b. Given:

$\rho \text{ (g/cm}^3\text{)}$	<i>crystallinity (%)</i>
2.144	51.3
2.215	74.2

c. Assumptions:

Given data is accurate; material is pure.

d. Solution:

(a) From Equation 14.8: $\%Crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} * 100 \quad \dots(1)$

Where ρ_c is the density of totally crystalline PTFE; ρ_a is the density of totally amorphous PTFE and ρ_s is the density of the given specimen.

We can obtain two equations from the two sets of data given and solve for ρ_a and ρ_c .

(A) For $\rho_s = 2.144$ and % crystallinity = 51.3

$$51.3 = \frac{\rho_c(2.144 - \rho_a)}{2.144(\rho_c - \rho_a)} * 100$$
$$\Rightarrow 51.3 * 2.144 / 100 = \frac{\rho_c(2.144 - \rho_a)}{(\rho_c - \rho_a)} \quad \dots(2)$$

(B) For $\rho_s = 2.215$ and % crystallinity = 74.2

$$74.2 = \frac{\rho_c(2.215 - \rho_a)}{2.215(\rho_c - \rho_a)} * 100$$
$$\Rightarrow 74.2 * 2.215 / 100 = \frac{\rho_c(2.215 - \rho_a)}{(\rho_c - \rho_a)} \quad \dots(3)$$

Dividing (2) by (3) :

$$51.3 \cdot 2.144 / (74.2 \cdot 2.215) = \frac{(2.144 - \rho_a)}{(2.215 - \rho_a)}$$

$$\Rightarrow 0.669 = \frac{(2.144 - \rho_a)}{(2.215 - \rho_a)} \Rightarrow 1.482 - 0.669\rho_a = 2.144 - \rho_a \Rightarrow 0.331 \rho_a = 0.662$$

$$\Rightarrow \rho_a = 2.000 \text{ g/cm}^3$$

Substituting the value of ρ_a in (2) :

$$51.3 \cdot 2.144 / 100 = \frac{\rho_c (2.144 - 2.000)}{(\rho_c - 2.000)}$$

$$\Rightarrow 1.1 = \frac{\rho_c (0.144)}{(\rho_c - 2.000)} \Rightarrow 1.1 \rho_c - 2.2 = 0.144 \rho_c \Rightarrow 0.956 \rho_c = 2.2$$

$$\Rightarrow \rho_c = 2.301 \text{ g/cm}^3$$

(b) Substituting the values of ρ_c and ρ_a in (1) for $\rho_s = 2.26 \text{ g/cm}^3$:

$$\% \text{ Crystallinity} = \frac{(2.301 \text{ g/cm}^3)(2.260 \text{ g/cm}^3 - 2.000 \text{ g/cm}^3)}{(2.260 \text{ g/cm}^3)(2.301 \text{ g/cm}^3 - 2.000 \text{ g/cm}^3)} \times 100 = 87.9$$

$$(a) \rho_a = 2.000 \text{ g/cm}^3 ; \rho_c = 2.301 \text{ g/cm}^3$$

$$(b) 87.9 \% \text{ Crystallinity}$$