CHAPTER 5

POLYMER STRUCTURES

PROBLEM SOLUTIONS

5.4 (a) Compute the repeat unit molecular weight of polystyrene.

(b) Compute the number-average molecular weight for a polystyrene for which the degree of polymerization is 26,000.

Solution

(a) The repeat unit molecular weight of polystyrene is called for in this portion of the problem. For polystyrene, from Table 5.3, each repeat unit has eight carbons and eight hydrogens. Thus,

$$m = 8(A_C) + 8(A_H)$$

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

(b) We are now asked to compute the number-average molecular weight. Since the degree of polymerization is 26,000, using Equation 5.6

$$\overline{M}_n = (DP)m = (26{,}000)(104.14 \text{ g/mol}) = 2.70 \times 10^6 \text{ g/mol}$$

5.7 Is it possible to have a poly(methyl methacrylate) homopolymer with the following molecular weight data and a of polymerization of 530? Why or why not?

Molecular Weight Range (g/mol)	w_i	x_i
8,000–20,000	0.02	0.05
20,000–32,000	0.08	0.15
32,000–44,000	0.17	0.21
44,000–56,000	0.29	0.28
56,000–68,000	0.23	0.18
68,000–80,000	0.16	0.10
80,000–92,000	0.05	0.03

Solution

This problem asks if it is possible to have a poly(methyl methacrylate) homopolymer with the given molecular weight data and a degree of polymerization of 530. 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	7400
80,000–92,000	86,000	0.03	2580
		$\overline{M}_n = \sum x_i M_i = 47{,}720$ g/mol	

For PMMA, from Table 5.3, each repeat unit has five carbons, eight hydrogens, and two oxygens. Thus,

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

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

Now, we will compute the degree of polymerization using Equation 5.6 as

$$DP = \frac{\overline{M}_n}{m} = \frac{47{,}720 \text{ g/mol}}{100.11 \text{ g/mol}} = 477$$

Thus, such a homopolymer is *not possible* since the calculated degree of polymerization is 477 (and not 530).

5.9 For a linear freely rotating polymer molecule, the total extended chain length L depends on the bond length between chain atoms d, the total number of bonds in the molecule N, and the angle between adjacent backbone chain atoms θ, as follows:

$$L = Nd \sin\left(\frac{\theta}{2}\right) \qquad (5.8)$$

Furthermore, the average end-to-end distance r for a randomly winding polymer molecule in Figure 5.6 is equal to

$$r = d\sqrt{N} \qquad (5.9)$$

A linear polytetrafluoroethylene has a number-average molecular weight of 500,000 g/mol; compute average values of L and r for this material.

Solution

This problem first of all asks for us to calculate, using Equation 5.8, the average total chain length, L, for a linear polytetrafluoroethylene polymer having a number-average molecular weight of 500,000 g/mol. It is necessary to calculate the degree of polymerization, DP, using Equation 5.6. For polytetrafluoroethylene, from Table 5.3, each repeat unit has two carbons and four flourines. Thus,

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

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

and

$$DP = \frac{\overline{M}_n}{m} = \frac{500{,}000 \text{ g/mol}}{100.02 \text{ g/mol}} = 5000$$

which is the number of repeat units along an average chain. Since there are two carbon atoms per repeat unit, there are two C—C chain bonds per repeat unit, which means that the total number of chain bonds in the molecule, N, is just (2)(5000) = 10,000 bonds. Furthermore, assume that for single carbon-carbon bonds, d = 0.154 nm and θ = 109° (Section 5.4); therefore, from Equation 5.11

$$L = Nd \sin\left(\frac{\theta}{2}\right)$$

$$= (10{,}000)(0.154 \text{ nm}) \left[\sin\left(\frac{109°}{2}\right)\right] = 1254 \text{ nm}$$

It is now possible to calculate the average chain end-to-end distance, r, using Equation 5.9 as

$$r = d\sqrt{N} = (0.154 \text{ nm})\sqrt{10,000} = 15.4 \text{ nm}$$

5.10 Using the definitions for total chain molecule length L (Equation 5.8) and average chain end-to-end distance r (Equation 5.9), for a linear polyethylene determine the following:

(a) the number-average molecular weight for L = 2,600 nm;

(b) the number-average molecular weight for r = 30 nm.

Solution

(a) This portion of the problem asks for us to calculate the number-average molecular weight for a linear polyethylene for which L in Equation 5.8 is 2,600 nm. It is first necessary to compute the value of N using this equation, where, for the C—C chain bond, d = 0.154 nm, and θ = 109°. Thus

$$N = \frac{L}{d \sin\left(\frac{\theta}{2}\right)}$$

$$= \frac{2{,}600 \text{ nm}}{(0.154 \text{ nm}) \sin\left(\frac{109°}{2}\right)} = 20{,}738$$

Since there are two C—C bonds per polyethylene repeat unit, there is an average of N/2 or 20,738/2 = 10,369 repeat units per chain, which is also the degree of polymerization, DP. In order to compute the value of $\overline{M}_n$ using Equation 5.6, we must first determine m for polyethylene. Each polyethylene repeat unit consists of two carbon and four hydrogen atoms, thus

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

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

Therefore

$$\overline{M}_n = (DP)m = (10{,}369)(28.05 \text{ g/mol}) = 290{,}850 \text{ g/mol}$$

(b) Next, we are to determine the number-average molecular weight for r = 30 nm. Solving for N from Equation 5.9 leads to

$$N = \frac{r^2}{d^2} = \frac{(30 \text{ nm})^2}{(0.154 \text{ nm})^2} = 37{,}950$$

which is the total number of bonds per average molecule. Since there are two C—C bonds per repeat unit, then $DP = N/2$ = 37,950/2 = 18,975. Now, from Equation 5.6

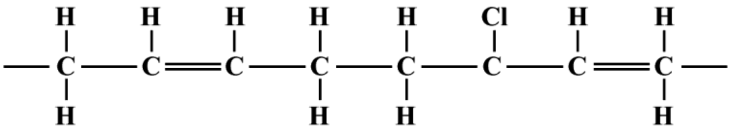
$$\overline{M}_n = (DP)m = (18{,}975)(28.05 \text{ g/mol}) = 532{,}249 \text{ g/mol}$$

5.15 Sketch the repeat structure for each of the following alternating copolymers: (a) poly(butadiene-chloroprene), (b) poly(styrene-methyl methacrylate), and (c) poly(acrylonitrile-vinyl chloride).

Solution

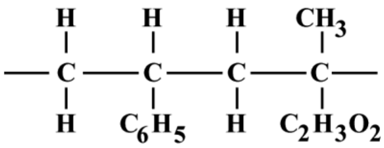
This problem asks for sketches of the repeat unit structures for several alternating copolymers.

(a) For poly(butadiene-chloroprene)

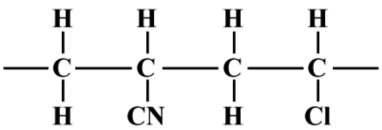


(NOTE THAT THIS DIAGRAM IS WRONG, AND THE SECOND DOUBLE BOND SHOULD BE SHIFTED TO THE LEFT)

(b) For poly(styrene-methyl methacrylate)



(c) For poly(acrylonitrile-vinyl chloride)



5.18 An alternating copolymer is known to have a number-average molecular weight of 250,000 g/mol and a degree of polymerization of 3500. If one of the repeat units is styrene, which of ethylene, propylene, tetrafluoroethylene, and vinyl chloride is the other repeat unit? Why?

Solution

For an alternating copolymer which has a number-average molecular weight of 250,000 g/mol and a degree of polymerization of 3500, we are to determine one of the repeat unit types if the other is styrene. It is first necessary to calculate $\bar{m}$ using Equation 5.6 as

$$\bar{m} = \frac{\overline{M}_n}{DP} = \frac{250{,}000 \text{ g/mol}}{3500} = 71.43 \text{ g/mol}$$

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

$$m_s = 8(A_{\text{C}}) + 8(A_{\text{H}})$$

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

Now, using Equation 5.7, it is possible to calculate the repeat unit weight of the unknown repeat unit type, m_x. Thus

$$m_x = \frac{\bar{m} - f_s m_s}{f_x}$$

$$= \frac{71.43 \text{ g/mol} - (0.5)(104.14 \text{ g/mol})}{0.5} = 38.72 \text{ g/mol}$$

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

$m_{\text{ethylene}} = 2(A_{\text{C}}) + 4(A_{\text{H}}) = 2(12.01 \text{ g/mol}) + 4(1.008 \text{ g/mol}) = 28.05 \text{ g/mol}$

$m_{\text{propylene}} = 3(A_{\text{C}}) + 6(A_{\text{H}}) = 3(12.01 \text{ g/mol}) + 6(1.008 \text{ g/mol}) = 42.08 \text{ g/mol}$

$m_{\text{TFE}} = 2(A_{\text{C}}) + 4(A_{\text{F}}) = 2(12.01 \text{ g/mol}) + 4(19.00 \text{ g/mol}) = 100.02 \text{ g/mol}$

$m_{\text{VC}} = 2(A_{\text{C}}) + 3(A_{\text{H}}) + (A_{\text{Cl}}) = 2(12.01 \text{ g/mol}) + 3(1.008 \text{ g/mol}) + 35.45 \text{ g/mol} = 62.49 \text{ g/mol}$

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

5.21 A random poly(isobutylene-isoprene) copolymer has a number-average molecular weight of 200,000 g/mol and a degree of polymerization of 3000. Compute the fraction of isobutylene and isoprene repeat units in this copolymer.

Solution

For a random poly(isobutylene-isoprene) copolymer in which $\overline{M}_n$ = 200,000 g/mol and *DP* = 3000, we are asked to compute the fractions of isobutylene and isoprene repeat units.

From Table 5.5, the isobutylene repeat unit has four carbon and eight hydrogen atoms. Thus,

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

Also, from Table 5.5, the isoprene repeat unit has five carbon and eight hydrogen atoms, and

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

From Equation 5.7

$$\overline{m} = f_{ib}m_{ib} + f_{ip}m_{ip}$$

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

$$\overline{m} = 56.10x + (68.11)(1 - x)$$

since $f_{ib} + f_{ip} = 1$. Also, from Equation 5.6

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

Or

$$3000 = \frac{200,000 \text{ g/mol}}{[56.10x + 68.11(1 - x)] \text{ g/mol}}$$

Solving for x leads to $x = f_{ib} = f(\text{isobutylene}) = 0.12$. Also,

$$f(\text{isoprene}) = 1 - x = 1 - 0.12 = 0.88$$