

Solutions Manual for
**Polymer Science and
Technology**
Third Edition

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**SOLUTIONS TO PROBLEMS IN POLYMER SCIENCE AND TECHNOLOGY,
3RD EDITION**

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CHAPTER 1

1-1 A polymer sample combines five different molecular-weight fractions, each of equal weight. The molecular weights of these fractions increase from 20,000 to 100,000 in increments of 20,000. Calculate \bar{M}_n , \bar{M}_w , and \bar{M}_z . Based upon these results, comment on whether this sample has a broad or narrow molecular-weight distribution compared to typical commercial polymer samples.

Solution

Fraction #	$M_i (\times 10^{-3})$	W_i	$N_i = W_i/M_i (\times 10^5)$
1	20	1	5.0
2	40	1	2.5
3	60	1	1.67
4	80	1	1.25
5	100	1	1.0
Σ	300	5	11.42

$$\bar{M}_n = \frac{\sum_{i=1}^5 W_i / N_i}{\sum_{i=1}^5 W_i / N_i} = \frac{5}{1.142 \times 10^{-4}} = 43,783$$

$$\bar{M}_w = \frac{\sum_{i=1}^5 W_i M_i}{\sum_{i=1}^5 W_i} = \frac{300,000}{5} = 60,000$$

$$\bar{M}_z = \frac{\sum_{i=1}^5 W_i M_i^2}{\sum_{i=1}^5 W_i M_i} = \frac{4 \times 10^8 + 16 \times 10^8 + 36 \times 10^8 + 64 \times 10^8 + 100 \times 10^8}{3 \times 10^5} = 73,333$$

$$\frac{\bar{M}_z}{\bar{M}_n} = \frac{60,000}{43,783} = 1.37 \text{ (narrow distribution)}$$

1-2 A 50-gm polymer sample was fractionated into six samples of different weights given in the table below. The viscosity-average molecular weight, \bar{M}_v , of each was determined and is included in the table. Estimate the number-average and weight-average molecular weights of the original sample. For these calculations, assume that the molecular-weight distribution of each fraction is extremely narrow and can

be considered to be *monodisperse*. Would you classify the molecular weight distribution of the original sample as narrow or broad?

Fraction	Weight (gm)	\bar{M}_v
1	1.0	1,500
2	5.0	35,000
3	21.0	75,000
4	15.0	150,000
5	6.5	400,000
6	1.5	850,000

Solution

Let $M_i \approx M_v$

Fraction	W_i	\bar{M}_i	$N_i = W_i/M_i$ ($\times 10^6$)	$W_i M_i$
1	1.0	1,500	667	1500
2	5.0	35,000	143	175,000
3	21.0	75,000	280	627,500
4	15.0	150,000	100.	2,250,000
5	6.5	400,000	16.3	2,600,000
6	1.5	850,000	1.76	1,275,000
Σ	50.0		1208	7,929,000

$$\bar{M}_n = \sum_{i=1}^6 W_i / N = \frac{50.0}{1.21 \times 10^{-3}} = 41,322$$

$$\bar{M}_w = \frac{\sum_{i=1}^6 W_i M_i}{\sum_{i=1}^6 W_i} = \frac{7,930,000}{50.0} = 158,600$$

$$\frac{\bar{M}_w}{\bar{M}_n} = \frac{158,600}{41,322} = 3.84 \text{ (broad distribution)}$$

1-3 The Schultz-Zimm [11] molecular-weight-distribution function can be written as

$$W(M) = \frac{a^{b+1}}{\Gamma(b+1)} M^b \exp(-aM)$$

where a and b are adjustable parameters (b is a positive real number) and Γ is the gamma function (see Appendix E) which is used to normalize the weight fraction.

(a) Using this relationship, obtain expressions for \bar{M}_n and \bar{M}_w in terms of a and b and an expression for M_{\max} , the molecular weight at the peak of the $W(M)$ curve, in terms of \bar{M}_n .

Solution

$$\bar{M}_n = \frac{\int_0^\infty W dM}{\int_0^\infty (W/M) dM}$$

let $t = aM$

$$\int_0^\infty W dM = \frac{a^{b+1}}{\Gamma(b+1)} \int_0^\infty (t/a)^b \exp(-t) d(t/a) = \frac{a^{b+1}}{\Gamma(b+1)} \frac{1}{a^{b+1}} \int_0^\infty t^b \exp(-t) dt = \frac{1}{\Gamma(b+1)} \Gamma(b+1) = 1$$

$$\int_0^\infty (W/M) dM = \frac{a^{b+1}}{\Gamma(b+1)} \int_0^\infty (t/a)^{b-1} \exp(-t) d(t/a) = \frac{a^{b+1}}{\Gamma(b+1)} \frac{1}{a^b} \int_0^\infty t^{b-1} \exp(-t) dt = \frac{a^{b+1}}{\Gamma(b+1)} \frac{1}{a^b} \Gamma(b) =$$

$$\frac{a}{b\Gamma(b)} \Gamma(b) = \frac{a}{b}$$

$$\bar{M}_n = \frac{1}{a/b} = \frac{b}{a}$$

$$\bar{M}_w = \frac{\int_0^\infty WM dM}{\int_0^\infty W dM} = \int_0^\infty WM dM = \frac{a^{b+1}}{\Gamma(b+1)} \int_0^\infty (t/a)^{b+1} \exp(-t) d(t/a) = \frac{a^{b+1}}{\Gamma(b+1)} \frac{\Gamma(b+2)}{a^{b+2}} =$$

$$\frac{(b+1)\Gamma(b+1)}{a\Gamma(b+1)} = \frac{b+1}{a}$$

(b) Derive an expression for M_{\max} , the molecular weight at the peak of the $W(M)$ curve, in terms of \bar{M}_n .

Solution

$$\frac{dW}{dM} = \frac{a^{b+1}}{\Gamma(b+1)} [bM^{b-1} \exp(-aM) + M^b (-a) \exp(-aM)] = 0$$

$$bM^{b-a} = aM^b$$

$$\frac{b}{a} = M^a = \bar{M}_n \quad (\text{i.e., the maximum occurs at } \bar{M}_n)$$

(c) Show how the value of b affects the molecular weight distribution by graphing $W(M)$ versus M on the same plot for $b = 0.1, 1,$ and 10 given that $\bar{M}_n = 10,000$ for the three distributions.

Solution

$$a = \frac{b}{10,000}$$

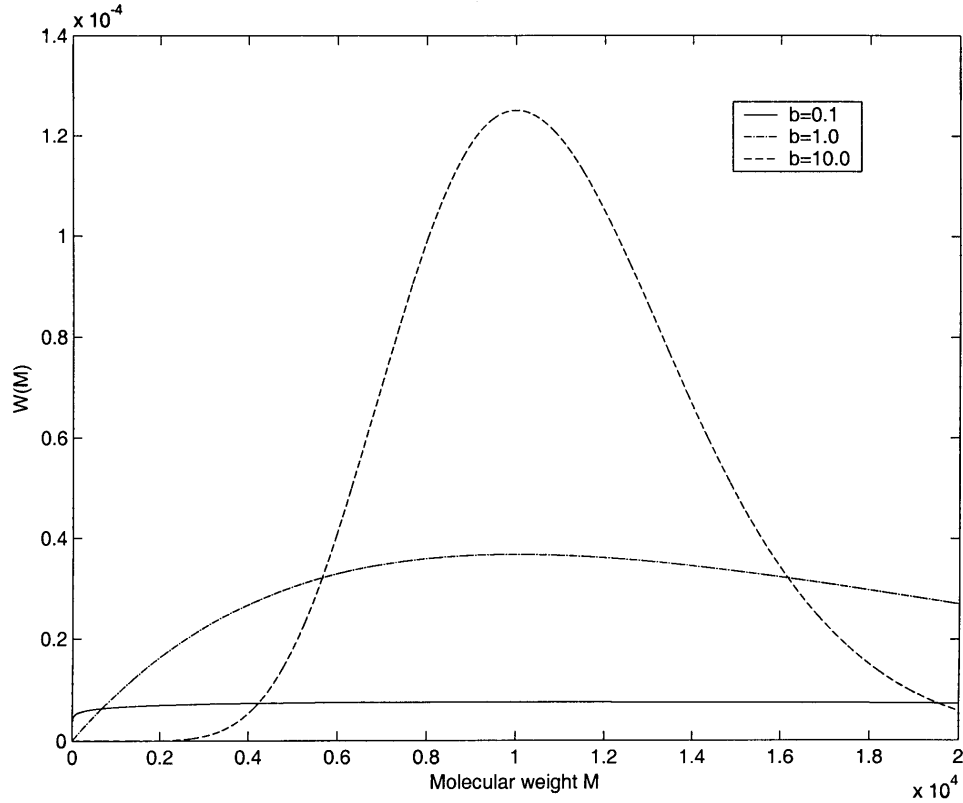
b	0.1	1	10
a	1×10^{-5}	1×10^{-4}	1×10^{-3}

$$W = \frac{a^{b+1}}{\Gamma(b+1)} M^b \exp(-aM) dM$$

where $\Gamma(b+1) = \int_0^\infty (aM)^b \exp(-aM) dM$.

Plot $W(M)$ versus M

Hint: $\int_0^\infty x^n \exp(-ax) dx = \Gamma(n+1)/a^{n+1} = n!/a^{n+1}$ (if n is a positive integer).



1-4 (a) Calculate the z -average molecular weight, \bar{M}_z , of the discrete molecular weight distribution described in Example Problem 1.1.

Solution

$$\bar{M}_z = \frac{\sum_{i=1}^3 W_i M_i^2}{\sum_{i=1}^3 W_i M_i} = \frac{1(10,000)^2 + 2(50,000)^2 + 2(100,000)^2}{1(10,000) + 2(50,000) + 2(100,000)} = 80,968$$

(b) Calculate the z -average molecular weight, \bar{M}_z , of the continuous molecular weight distribution shown in Example 1.2.

Solution

$$\bar{M}_z = \frac{\int_{10^3}^{10^5} M^2 dM}{\int_{10^3}^{10^5} M dM} = \frac{(M^3/3)_{10^3}^{10^5}}{(M^2/2)_{10^3}^{10^5}} = 66,673$$

(c) Obtain an expression for the z -average degree of polymerization, \bar{X}_z , for the Flory distribution described in Example 1.3.

Solution

$$\bar{X}_z = \frac{\sum_1^{\infty} X^2 W(X)}{\sum_1^{\infty} X W(X)} = \frac{\sum_1^{\infty} X^3 p^{x-1}}{\sum_1^{\infty} X^2 p^{x-1}}$$

Let

$$A = \sum_1^{\infty} X p^{x-1} = 1 + 2p + 3p^2 + \dots = \frac{1}{1-p} \quad (\text{geometric series})$$

$$B = \sum_1^{\infty} X^2 p^{x-1} = 1 + 2^2 p + 3^2 p^2 + \dots$$

$$C = \sum_1^{\infty} X^3 p^{x-1} = 1 + 2^3 p + 3^2 p^2 + \dots$$

Can show that $B(1-p) = A(1+p)$

$$\text{Therefore } B = \frac{1+p}{(1-p)^3}$$

$$\text{Write } C(1-p) = \sum_{x=1}^{\infty} 3X^2 p^{x-1} - \sum_{x=1}^{\infty} 3Xp^{x-1} + \sum_{x=1}^{\infty} p^{x-1} = 3B - 3A^2 + \frac{1}{1-p} = \frac{1+4p+p^2}{(1-p)^3}$$

$$\text{Therefore } C = \frac{1+4p+p^2}{(1-p)^4}$$

$$\text{and finally } \bar{X}_z = \frac{\sum_1^{\infty} X^3 p^{x-1}}{\sum_1^{\infty} X^2 p^{x-1}} = \frac{C}{B} = \frac{1+4p+p^2(1-p)^3}{(1-p)^4(1+p)} = \frac{1+4p+p^2}{(1-p)(1+p)} = \frac{1+4p+p^2}{1-p^2}$$

$$\bar{M}_z = M_o \bar{X}_z$$

CHAPTER 2

2.1 If the half-life time, $t_{1/2}$, of the initiator AIBN in an unknown solvent is 22.6 h at 60°C, calculate its dissociation rate constant, k_d , in units of reciprocal seconds.

Solution

$$[I] = [I]_o \exp(-k_d t)$$

$$\frac{[I]}{[I]_o} = \frac{1}{2} = \exp(-k_d t)$$

$$-k_d t = \ln(1/2) = -0.693$$

$$k_d = \frac{0.693}{t} = \frac{0.693}{22.6 \text{ h} \cdot 3600 \text{ s}} = 8.52 \times 10^{-5} \text{ s}^{-1}$$

2.2 Styrene is polymerized by free-radical mechanism in solution. The initial monomer and initiator concentrations are 1 M (molar) and 0.001 M, respectively. At the polymerization temperature of 60°C, the initiator efficiency is 0.30. The rate constants at the polymerization temperature are as follows:

$$k_d = 1.2 \times 10^{-5} \text{ s}^{-1}$$

$$k_p = 176 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_t = 7.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

Given this information, determine the following:

(a) Rate of initiation at 1 min and at 16.6 h

Solution

$$R_i = 2fk_d[I] = 2(0.30)(1.2 \times 10^{-5})[I] = 7.2 \times 10^{-6} [I]$$

$$[I] = [I_0] \exp(-k_d t)$$

at 1 min:

$$[I] = 0.001(0.9993) = 0.0009993 \text{ M}$$

$$R_i = (7.2 \times 10^{-6})(0.0009993) = 7.19 \times 10^{-9} \text{ M s}^{-1}$$

at 16.6 h:

$$[I] = 0.001(0.488) = 0.000488 \text{ M}$$

$$R_i = (7.2 \times 10^{-6})(0.000488) = 3.51 \times 10^{-9} \text{ M s}^{-1}$$

(b) Steady-state free-radical concentration at 1 min

Solution

$$[\text{IM}_x \cdot] = \left(\frac{fk_d}{k_t} \right)^{1/2} [I]^{1/2}$$

at 1 min:

$$[\text{IM}_x \cdot] = \left[\frac{(0.30)(1.2 \times 10^{-5})}{7.2 \times 10^7} \right]^{1/2} (0.0009993)^{1/2} = 7.08 \times 10^{-9} \text{ M}$$

(c) Rate of polymerization at 1 min

Solution

$$R_o = k_p [\text{IM}_x \cdot][M]$$

$$[M] = [M]_0 \exp(-k_p [\text{IM}_x \cdot] t) = (1) \exp[-176(7.08 \times 10^{-9})60] = 0.9999 \text{ M}$$

$$R_o = 176(7.08 \times 10^{-9})(0.9999) = 1.24 \times 10^{-6} \text{ M s}^{-1}$$

(d) Average free-radical lifetime, τ , at 1 min, where τ is defined as the radical concentration divided by the rate of termination

Solution

$$\tau = \frac{[\text{IM}_x \cdot]}{2k_t [\text{IM}_x \cdot]^2} = \frac{1}{2k_t [\text{IM}_x \cdot]} = \frac{1}{2(7.2 \times 10^7)(7.08 \times 10^{-9})} = 0.981 \text{ s}$$