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 $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$. 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 **(×10⁻³)**	W_i	$N_i = W_i/M_i$ **(×10⁵)**
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

$$\overline{M}_n = \sum_{i=1}^{5} W_i / N = \frac{5}{1.142\times10^{-4}} = 43,783$$

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

$$\overline{M}_z = \frac{\sum_{i=1}^{5} W_i M_i^2}{\sum_{i=1}^{5} W_i M_i} = \frac{4\times10^8 + 16\times10^8 + 36\times10^8 + 64\times10^8 + 100\times10^8}{3\times10^5} = 73,333$$

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

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, $\overline{M}_v$, 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_iM_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 $t = aM$

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

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

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

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

$$\overline{M}_w = \frac{\int_0^\infty WMdM}{\int_0^\infty WdM} = \int_0^\infty WMdM = \frac{a^{b+1}}{\Gamma(b+1)}\int_0^\infty (t/a)^{b+1} \exp(-t)\,d(t/a) = \frac{a^{b+1}}{\Gamma(b+1)}\frac{\Gamma(b+2)}{a^{b+2}} =$$

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

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

Solution

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

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

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

(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 $\overline{M}_n$ = 10,000 for the three distributions.

Solution

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

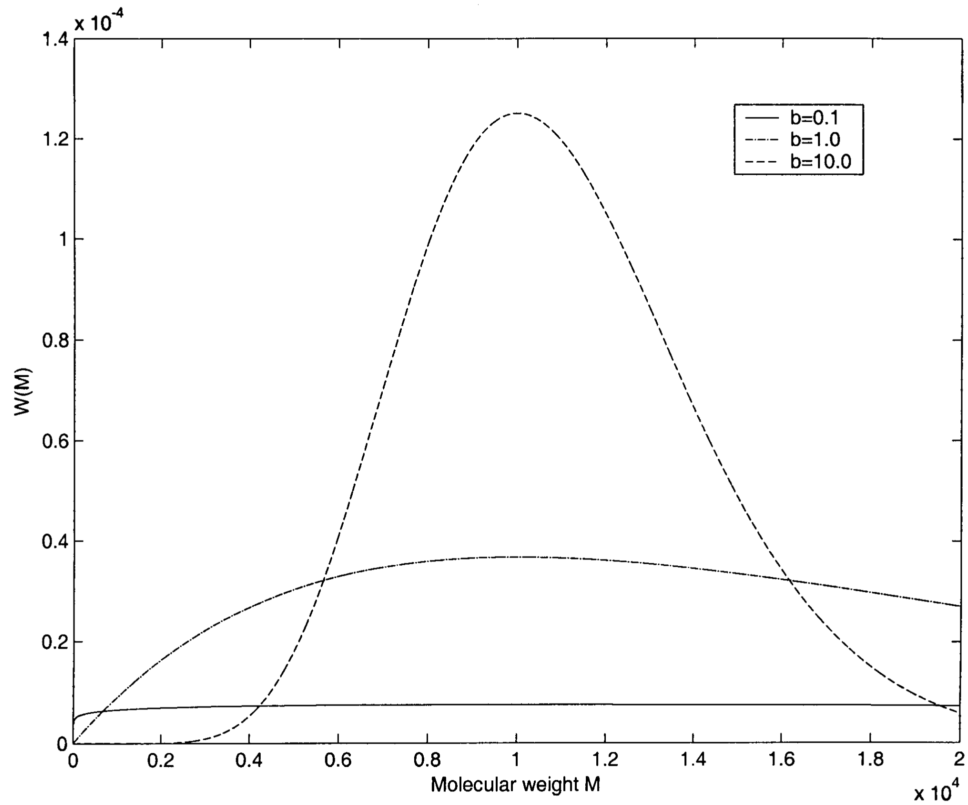
b	0.1	1	10
a	1×10^{-5}	1×10^{-4}	1×10^{-3}

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

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 interger).



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

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

(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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$k_d = \frac{0.693}{t} = \frac{0.693}{22.6\ \text{h}}\frac{\text{h}}{3600\ \text{s}} = 8.52\times10^{-5}\ \text{s}^{-1}$$

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:

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

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

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

Given this information, determine the following:

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

Solution

$$R_i = 2fk_d[\text{I}] = 2(0.30)(1.2\times10^{-5})[\text{I}] = 7.2\times10^{-6}[\text{I}]$$

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

at 1 min:

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

$$R_i = (7.2\times10^{-6})(0.0009993) = 7.19\times10^{-9}\,M\ \text{s}^{-1}$$

at 16.6 h:

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

$$R_i = (7.2\times10^{-6})(0.000448) = 3.51\times10^{-9}\,M\ \text{s}^{-1}$$

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

Solution

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

at 1 min:

$$[\text{IM}_x] = \left[\frac{(0.30)(1.2\times10^{-5})}{7.2\times10^{7}}\right]^{1/2}(0.0009993)^{1/2} = 7.08\times10^{-9}\,M$$

(**c**) Rate of polymerization at 1 min

Solution

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

$$[\text{M}] = [\text{M}]_o\exp(-k_p[\text{IM}_x\cdot]t) = (1)\exp\left[-176(7.08\times10^{-9})60\right] = 0.9999\ \text{M}$$

$$R_o = 176(7.08\times10^{-9})(0.9999) = 1.24\times10^{-6}\ M\ \text{s}^{-1}$$

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

Solution

$$\tau = \frac{[\text{IM}_x\cdot]}{2k_t[\text{IM}_x\cdot]^2} = \frac{1}{2k_t[\text{IM}_x\cdot]} = \frac{1}{2(7.2\times10^{7})(7.08\times10^{-9})} = 0.981\ \text{s}$$