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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	$N_i = W_i / M_i (\times 10^5)$
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

$$\overline{M}_{n} = \sum_{i=1}^{5} W_{i} / N = \frac{5}{1.142 \times 10^{-4}} = 43,783$$

$$\overline{M}_{w} = \frac{\sum_{i=1}^{5} W_{i} M_{i}}{\sum_{i=1}^{5} W_{i}} = \frac{300,000}{5} = 60,000$$

$$\overline{M}_{z} = \frac{\sum_{i=1}^{5} W_{i} M_{i}^{2}}{\sum_{i=1}^{5} W_{i} M_{i}} = \frac{4 \times 10^{8} + 16 \times 10^{8} + 36 \times 10^{8} + 64 \times 10^{8} + 100 \times 10^{8}}{3 \times 10^{5}} = 73,333$$

$$\frac{\overline{M}_{z}}{\overline{M}_{n}} = \frac{60,000}{43,783} = 1.37 \text{ (narrow distribution)}$$

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)	\overline{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 $M_i \approx M_y$

Fraction	W_i	\overline{M}_{i}	$N_i = W_i / M_i$	W_iM_i
		Ľ	(×10 ⁶)	
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

$$\overline{M}_{n} = \sum_{i=1}^{6} W_{i} / N = \frac{\overline{50.0}}{1.21 \times 10^{-3}} = 41,322$$
$$\overline{M}_{w} = \frac{\sum_{i=1}^{6} W_{i} M_{i}}{\sum_{i=1}^{6} W_{i}} = \frac{7,930,000}{50.0} = 158,600$$

 $\frac{M_{w}}{\overline{M}_{p}} = \frac{158,600}{41,322} = 3.84$ (broad distribution)



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

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 \overline{M}_n and \overline{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 \overline{M}_n .

Solution

$$\overline{M}_{n} = \frac{\int_{0}^{\infty} W dM}{\int_{0}^{\infty} (W/M) dM}$$

let $t = aM$

$$\int_{0}^{\infty} W dM = \frac{a^{b+1}}{\Gamma(b+1)} \int_{0}^{\infty} (t/a)^{b} \exp(-t) d(t/a) = \frac{a^{b+1}}{\Gamma(b+1)} \frac{1}{a^{b+1}} \int_{0}^{\infty} t^{b} \exp(-t) dt = \frac{1}{\Gamma(b+1)} \Gamma(b+1) = 1$$

$$\int_{0}^{\infty} (W/M) dM = \frac{a^{b+1}}{\Gamma(b+1)} \int_{0}^{\infty} (t/a)^{b-1} \exp(-t) d(t/a) = \frac{a^{b+1}}{\Gamma(b+1)} \frac{1}{a^{b}} \int_{0}^{\infty} t^{b-1} \exp(-t) dt = \frac{a^{b+1}}{\Gamma(b+1)} \frac{1}{a^{b}} \Gamma(b) = \frac{a}{D}$$

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

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

$$\overline{M}_{w} = \frac{\int_{0}^{\infty} WM dM}{\int_{0}^{\infty} W dM} = \int_{0}^{\infty} WM dM = \frac{a^{b+1}}{\Gamma(b+1)} \int_{0}^{\infty} (t/a)^{b+1} \exp(-t) d(t/a) = \frac{a^{b+1}}{\Gamma(b+1)} \frac{\Gamma(b+2)}{a^{b+2}} = \frac{(b+1)\Gamma(b+1)}{a\Gamma(b+1)} = \frac{b+1}{a}$$

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

Solution

$$\frac{dW}{dM} = \frac{a^{b+1}}{\Gamma(b+1)} \Big[bM^{b-1} \exp(-aM) + M^{b}(-a) \exp(-aM) \Big] = 0$$
$$bM^{b-a} = aM^{b}$$
$$\frac{b}{a} = M^{a} = \overline{M}_{n} \text{ (i.e., the maximum occurs at } \overline{M}_{n})$$

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

Solution

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

$$\frac{b}{a} \frac{0.1}{1 \times 10^{-5}} \frac{1}{1 \times 10^{-4}} \frac{10}{1 \times 10^{-3}}$$

$$W = \frac{a^{b+1}}{\Gamma(b+1)} M^{b} \exp(-aM) dM$$
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, \overline{M}_z , of the discrete molecular weight distribution described in Example Problem 1.1.

Solution

$$\overline{M}_{z} = \frac{\sum_{i=1}^{3} W_{i} M_{i}^{2}}{\sum_{i=1}^{3} W_{i} M_{i}} = \frac{1(10,000)^{2} + 2(50,000)^{2} + 2(100,000)^{2}}{1(10,000) + 2(50,000) + 2(100,000)} = 80,968$$

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

Solution

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

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

Solution

$$\overline{X}_{z} = \frac{\sum_{1}^{\infty} X^{2}W(X)}{\sum_{1}^{\infty} XW(X)} = \frac{\sum_{1}^{\infty} X^{3}p^{x-1}}{\sum_{1}^{\infty} X^{2}p^{x-1}}$$

Let

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

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

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

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

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

and finally $\overline{X}_{z} = \frac{\sum_{1}^{\infty} X^{3} p^{x-1}}{\sum_{1}^{\infty} X^{2} p^{x-1}} = \frac{C}{B} = \frac{1+4p+p^{2}(1-p)^{3}}{(1-p)^{4}(1+p)} = \frac{1+4p+p^{2}}{(1-p)(1+p)} = \frac{1+4p+p^{2}}{1-p^{2}}$

 $\overline{M}_{z} = M_{o}\overline{X}_{z}$

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

 $\begin{bmatrix} \mathbf{I} \end{bmatrix} = \begin{bmatrix} \mathbf{I} \end{bmatrix}_{o} \exp(-k_{d}t)$ $\frac{\begin{bmatrix} \mathbf{I} \end{bmatrix}}{\begin{bmatrix} \mathbf{I} \end{bmatrix}_{o}} = \frac{1}{2} = \exp(-k_{d}t)$

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$$-k_{\rm d}t = \ln(1/2) = -0.693$$
$$k_{\rm d} = \frac{0.693}{t} = \frac{0.693}{22.6 \text{ h}} \frac{\text{h}}{3600 \text{ s}} = 8.52 \times 10^{-5} \text{ s}^{-1}$$

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:

$$k_{\rm d} = 1.2 \times 10^{-5} \,{\rm s}^{-1}$$

 $k_{\rm p} = 176 \,M^{-1} \,{\rm s}^{-1}$
 $k_{\rm t} = 7.2 \times 10^7 \,M^{-1} \,{\rm s}^{-1}$

Given this information, determine the following:

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

Solution

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

 $[I] = [I_o] \exp(-k_d t)$
at 1 min:
 $[I] = 0.001(0.9993) = 0.0009993 M$
 $R_i = (7.2 \times 10^{-6})(0.0009993) = 7.19 \times 10^{-9} M \text{ s}^{-1}$
at 16.6 h:
 $[I] = 0.001(0.488) = 0.000488 M$
 $R_i = (7.2 \times 10^{-6})(0.000448) = 3.51 \times 10^{-9} M \text{ s}^{-1}$

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

Solution

$$\left[\mathbf{IM}_{x} \cdot \right] = \left(\frac{fk_{d}}{k_{t}}\right)^{1/2} \left[\mathbf{I}\right]^{1/2}$$

at 1 min:

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

(c) Rate of polymerization at 1 min

Solution

$$R_{o} = k_{p} [IM_{x} \cdot][M]$$

 $[M] = [M]_{o} \exp(-k_{p} [IM_{x} \cdot]t) = (1) \exp[-176(7.08 \times 10^{-9})60] = 0.9999 M$
 $R_{o} = 176(7.08 \times 10^{-9})(0.9999) = 1.24 \times 10^{-6} M s^{-1}$

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

Solution

$$\tau = \frac{\left[\mathrm{IM}_{x} \cdot\right]}{2k_{t}\left[\mathrm{IM}_{x} \cdot\right]^{2}} = \frac{1}{2k_{t}\left[\mathrm{IM}_{x} \cdot\right]} = \frac{1}{2\left(7.2 \times 10^{7}\right)\left(7.08 \times 10^{-9}\right)} = 0.981 \text{ s}$$

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