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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 $\bar{M}_{\mathrm{n}}$, $\bar{M}_{\mathrm{w}}$, and $\bar{M}_{\mathrm{z}}$. 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

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

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

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

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

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, $\bar{M}_{\mathrm{v}}$, 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 $t = aM$

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

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

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

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

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

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

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

Solution

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

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

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

(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 $\bar{M}_{\mathrm{n}}$ = 10,000 for the three distributions.

Solution

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

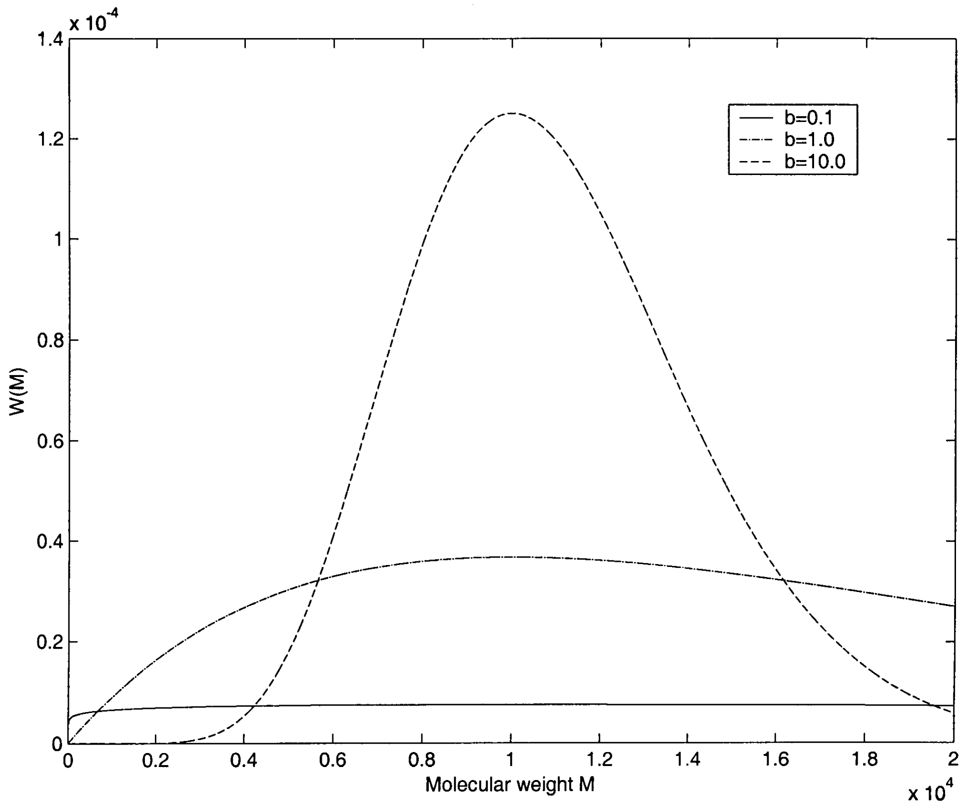
b	0.1	1	10
a	1×10^{-5}	1×10^{-4}	1×10^{-3}

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

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.