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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
$\Sigma$	300	5	11.42

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

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

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

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

**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
$\Sigma$	50.0		1208	7,929,000

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

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

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

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  $\Gamma$  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**

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

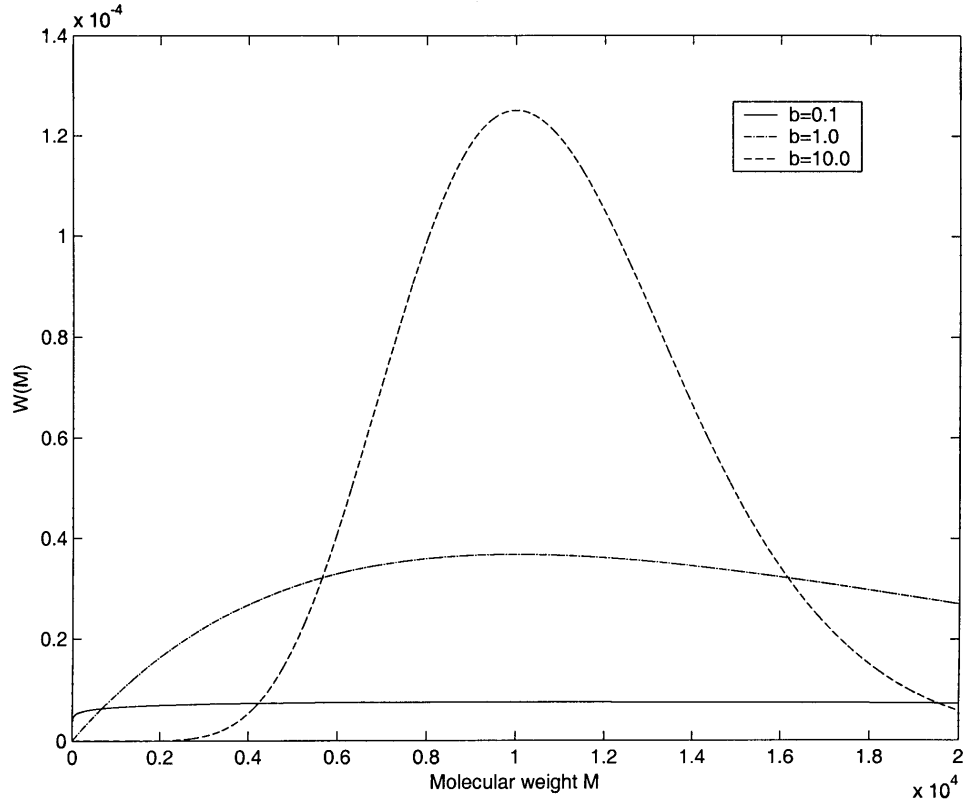
<b>b</b>	0.1	1	10
<b>a</b>	$1 \times 10^{-5}$	$1 \times 10^{-4}$	$1 \times 10^{-3}$

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

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 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.