Solutions Manual for
Polymer Science and Technology
Third Edition

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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 $n$, $M_w$, and $z$. Based upon these results, comment on whether this sample has a broad or narrow molecular-weight distribution compared to typical commercial polymer samples.

**Solution**

<table>
<thead>
<tr>
<th>Fraction #</th>
<th>$M_i \times 10^3$</th>
<th>$W_i$</th>
<th>$N_i = W_i/M_i \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>1</td>
<td>5.0</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>1</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>1</td>
<td>1.67</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>1</td>
<td>1.25</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>1</td>
<td>1.0</td>
</tr>
<tr>
<td>Σ</td>
<td>300</td>
<td>5</td>
<td>11.42</td>
</tr>
</tbody>
</table>

\[
\bar{M}_n = \frac{\sum_{i=1}^{5} W_i}{N} = \frac{300}{1.142 \times 10^{-5}} = 43,783
\]

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

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

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

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?

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight (gm)</th>
<th>$\bar{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>1,500</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>35,000</td>
</tr>
<tr>
<td>3</td>
<td>21.0</td>
<td>75,000</td>
</tr>
<tr>
<td>4</td>
<td>15.0</td>
<td>150,000</td>
</tr>
<tr>
<td>5</td>
<td>6.5</td>
<td>400,000</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>850,000</td>
</tr>
</tbody>
</table>

**Solution**

Let $M_i = M_n$

<table>
<thead>
<tr>
<th>Fraction</th>
<th>$W_i$</th>
<th>$\bar{M}_i$</th>
<th>$N_i = W_i/M_i$ (x10^6)</th>
<th>$W_iM_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>1,500</td>
<td>667</td>
<td>1500</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>35,000</td>
<td>143</td>
<td>175,000</td>
</tr>
<tr>
<td>3</td>
<td>21.0</td>
<td>75,000</td>
<td>280</td>
<td>627,500</td>
</tr>
<tr>
<td>4</td>
<td>15.0</td>
<td>150,000</td>
<td>100</td>
<td>2,250,000</td>
</tr>
<tr>
<td>5</td>
<td>6.5</td>
<td>400,000</td>
<td>16.3</td>
<td>2,600,000</td>
</tr>
<tr>
<td>6</td>
<td>1.5</td>
<td>850,000</td>
<td>1.76</td>
<td>1,275,000</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>50.0</td>
<td></td>
<td>1208</td>
<td>7,929,000</td>
</tr>
</tbody>
</table>

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

$$\bar{M}_w = \frac{\sum W_i M_i}{\sum W_i} = \frac{7,930,000}{50.0} = 158,600$$

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


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

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

**Solution**

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

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

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

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

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

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

**Solution**

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

\[ bM^{b-a} = aM^b \]

\[ \frac{b}{a} = M^a = \bar{M}_n \]

(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**

\[ a = \frac{b}{10,000} \]

<table>
<thead>
<tr>
<th>( b )</th>
<th>0.1</th>
<th>1</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>( 1 \times 10^{-5} )</td>
<td>( 1 \times 10^{-4} )</td>
<td>( 1 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

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

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**

$$
\bar{M}_z = \frac{\int_{10^6}^{10^9} M^2 dM}{\int_{10^6}^{10^9} M dM} = \frac{(M^3/3)_{10^9} - (M^3/3)_{10^6}}{(M^2/2)_{10^9} - (M^2/2)_{10^6}} = 66,673
$$

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

\[ \bar{X}_z = \frac{\sum_{i}^\infty X^i W(X)}{\sum_{i}^\infty X W(X)} = \frac{\sum_{i}^\infty X^i p^{r-i}}{\sum_{i}^\infty X^i p^{r-i}} \]

Let

\[ A = \sum_{i}^\infty X p^{r-i} = 1 + 2p + 3p^2 + \cdots = \frac{1}{1 - p} \quad \text{(geometric series)} \]

\[ B = \sum_{i}^\infty X^2 p^{r-i} = 1 + 2^2 p + 3^2 p^2 + \cdots \]

\[ C = \sum_{i}^\infty X^3 p^{r-i} = 1 + 2^3 p + 3^3 p^2 + \cdots \]

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

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

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

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

and finally \( \bar{X}_z = \frac{\sum_{i}^\infty X^3 p^{r-i}}{\sum_{i}^\infty X^2 p^{r-i}} = \frac{C}{B} = \frac{1 + 4p + p^2}{(1 - p)^4 (1 + p)} = \frac{1 + 4p + p^2}{(1 - p)(1 + p)} = \frac{1 + 4p + p^2}{1 - p^2} \)

\( \bar{M}_z = M_w \bar{X}_z \)

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

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

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