Solutions to Problem Set 1

Star polymers are branched molecules with a controlled number of linear arms anchored to one central molecular unit acting as a branch point. Schaeften and Flory prepared poly (ε-caprolactam) four- and eight-arm stars using cyclohexanone tetrapropionic acid and dicyclohexanone octapropionic acid as branch points. The authors present the following stoichiometric definitions/relation to relate the molecular weight of the polymer to the concentration of unreacted acid groups in the product. Provide the information required for each of the following steps:

(a) The product has the formula \( R - \left[ \text{CO} - \text{NH} - \left( \text{CH}_2 \right)_5 \text{CO} - \right]_y - \text{OH} \). What is the significance of \( R \), \( y \), and \( b \)?

(b) If \( Q \) is the number of equivalents of multifunctional reactant which react per mole of monomer and \( L \) represents the number of equivalents of unreacted (end) groups per mole of monomer, then \( <y> = (1-L)(Q+L) \). Justify this relationship, assuming all functional groups are equal in reactivity.

(c) If \( M_0 \) is the molecular weight of the repeat unit and \( M_b \) is the molecular weight of the original branch molecule divided by \( b \), then the number-average molecular weight of the star polymer is

\[
M_n = b \left( M_0 \frac{1-L}{Q+L} + M_b \right)
\]

Justify this result and evaluate \( M_0 \) and \( M_b \) for the \( b = 4 \) and \( b = 8 \) stars.

(d) Evaluate \( M_n \) for the following molecules:

\[
\begin{array}{ccc}
b & Q & L \\
4 & 0.2169 & 0.0018 \\
8 & 0.134 & 0.00093 \\
\end{array}
\]

1.5 (a) \( R = \text{cyclohexanone} \) for \( b = 4 \) and \( \text{bicyclohexanone} \) for \( b = 8 \).

\( b \) = number of arms in star

\( y \) = degree of polymerization of each linear chain

(b) \( 1 - L \) = number of equivalents of reacted groups per mole monomer

\( Q + L \) = total number of equivalents of "ends" per mole monomer

\[ \therefore \text{ ratio } = \frac{\text{number of reacted groups}}{\text{number of ends}} = y \]

(c) For a molecule with \( b \) arms

\[
\bar{M}_n = bM_{n,arm} + M_{\text{central}}
\]

and \( M_{n,arm} = yM_0 = \frac{1-L}{Q+L} M_0 \)

\( M_b = \frac{M_{\text{central}}}{b} \)

\[ \therefore \bar{M}_n = b \left( M_0 \frac{1-L}{Q+L} + M_b \right) \]
Barzer reported the following data for a fractionated polyester made from sebacic acid and 1,6-hexanediol: evaluate $M_n$, $M_w$, and $M_x$.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Mass (g)</th>
<th>$M \times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.15</td>
<td>1.25</td>
</tr>
<tr>
<td>2</td>
<td>0.73</td>
<td>2.05</td>
</tr>
<tr>
<td>3</td>
<td>0.415</td>
<td>2.40</td>
</tr>
<tr>
<td>4</td>
<td>0.35</td>
<td>3.20</td>
</tr>
<tr>
<td>5</td>
<td>0.51</td>
<td>3.90</td>
</tr>
<tr>
<td>6</td>
<td>0.34</td>
<td>4.50</td>
</tr>
<tr>
<td>7</td>
<td>1.78</td>
<td>6.35</td>
</tr>
<tr>
<td>8</td>
<td>0.10</td>
<td>4.10</td>
</tr>
<tr>
<td>9</td>
<td>0.94</td>
<td>9.40</td>
</tr>
</tbody>
</table>

By dividing $m_i$ by $M_i$, we obtain the number of moles for each fraction, $n_i$. We then utilize the equations

$$M_n = \frac{\sum n_i M_i}{\sum n_i}, \quad M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}, \quad M_x = \frac{\sum n_i M_i^3}{\sum n_i M_i}$$

to obtain $M_n = 29.1$ kDa, $M_w = 46.1$ kDa and $M_x = 62.5$ kDa.

Consider a set consisting of 4-8 family members, friends, neighbors, etc. Try to select a variety of ages, genders, and other attributes. Take the mass of each individual (a rough estimate is probably wiser than asking directly) and calculate the number- and weight-average masses for this set. Does the resulting PDI indicate a rather "narrow" distribution? If you picture this group in your mind, do you imagine them all to be roughly the same size, as the PDI probably suggests?

Example solution (inspired by the characters of Marvel Comics):

<table>
<thead>
<tr>
<th>Character</th>
<th>Mass (kg)</th>
<th>$w_i$</th>
<th>$wM_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jean Gray</td>
<td>52</td>
<td>0.11</td>
<td>5.7</td>
</tr>
<tr>
<td>Rogue</td>
<td>54</td>
<td>0.11</td>
<td>6.2</td>
</tr>
<tr>
<td>Bruce Banner</td>
<td>58</td>
<td>0.12</td>
<td>7.1</td>
</tr>
<tr>
<td>Elektra</td>
<td>59</td>
<td>0.12</td>
<td>7.3</td>
</tr>
<tr>
<td>Spider-Man</td>
<td>75</td>
<td>0.16</td>
<td>11.8</td>
</tr>
<tr>
<td>Magneto</td>
<td>86</td>
<td>0.18</td>
<td>15.7</td>
</tr>
<tr>
<td>Wolverine</td>
<td>88</td>
<td>0.19</td>
<td>16.5</td>
</tr>
</tbody>
</table>

For the listed characters,

$$M_n = \frac{\sum M_i}{7} = 67.5 \text{ kg}$$

$$M_w = \sum w_i M_i = 70.6 \text{ kg}$$

$$\text{PDI} = \frac{M_w}{M_n} = 1.04$$

Based on PDI, the selected distribution is quite narrow.
Give the overall chemical reactions involved in the polymerization of these monomers, the resulting repeat unit structure, and an acceptable name for the polymer.

(a) \[ \text{Me} \quad \text{O} \quad \text{C} = \text{O} \quad \text{OH} \]

(b) \[ \text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 + \text{O} \quad \text{Cl} - \text{CH}_2 - \text{CH}_2 - \text{Cl} \]

(c) \[ \text{HO} \quad \text{C} = \text{O} \quad \text{OH} \]

(d) \[ \text{HO} \quad \text{C} = \text{O} \quad \text{OH} \]

(e) \[ \text{O} \quad \text{C} = \text{N} \quad \text{N} = \text{C} = \text{O} \quad \text{HO} - \text{CH}_2 - \text{OH} \]

(f) \[ \text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH} - \text{Me} \quad \text{O} \quad \text{O} \quad \text{C} = \text{O} \quad \text{OH} \]

(See corrected solutions at end of problem set)

1.12 (a) poly(methacrylic acid) (T) or poly[1-(carboxy)-1-methylethylene] (I)

\[ n \quad \text{H}_2\text{C} \quad \text{O} \quad \text{C} = \text{O} \quad \text{OH} \quad \xrightarrow{\text{Me}} \quad \text{Me} \quad \text{O} \quad \text{C} = \text{O} \quad \text{OH} \]

A chain growth process (free radical) through the carbon-carbon double bond; initiation and termination steps are not specified.

(b) poly(tetramethylene adipamide) (T) or poly(iminoadipoyliminobutane-1,4-diyl) (I)

\[ n \quad \text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 + n \quad \text{Cl} - \text{CH}_2 - \text{CH}_2 - \text{Cl} \quad \xrightarrow{\text{Me}} \quad \{ \text{HN} - \text{CH}_{2} \quad \text{O} \quad \text{C} = \text{O} \quad \text{HN} - \text{CH}_{2} \} + 2n \text{HCl} \]

A step growth (polycondensation) process between a diamine and a diacid chloride.
(c) poly(6-hydroxyhexanoic acid) (T) or poly(oxycarbonyl pentamethylene) (I)

\[
\begin{align*}
\text{n HO} & \quad \text{O} \\
\text{n} & \quad \text{O} \\
\text{H}_2\text{O}
\end{align*}
\]

A step growth (self-condensation) of an \(\alpha\)-hydroxy, \(\omega\)-carboxy alkane.

(d) same as (c) by mistake!

It was supposed to be poly(acrylonitrile) (T) or poly(1-cyanoethylene) (I)

\[
\begin{align*}
\text{n} & \quad \text{CN} \\
\text{n} & \quad \text{CN}
\end{align*}
\]

A chain growth process (free radical) through the carbon-carbon double bond; initiation and termination steps are not specified.

(e) poly(tetramethylene phenylethane) (T) or poly(oxytetramethyleneoxy carbonylimino-1,4-phenyleneimino carbonyl) (I)

\[
\begin{align*}
\text{n} & \quad \text{O} = \text{C} = \text{N} \\
\text{n} & \quad \text{N} = \text{C} = \text{O}
\end{align*}
\]

A step growth polymerization (strictly, not a condensation) between a diisocyanate and a diol. Note that in reality the NH groups can react with the NCO groups to produce some crosslinking.

(f) poly(alanine) (T) or poly[imino(1-methyl-2-oxo-ethylene)] (I)

\[
\begin{align*}
\text{n} & \quad \text{Me} \\
\text{n} & \quad \text{Me}
\end{align*}
\]

A step growth (self-condensation) of an amino acid.

15/ What would be \(M_w\) and \(M_n\) for a sample obtained by mixing 10 g of polystyrene \(M_w = 100,000, M_n = 70,000\) with 20 g of another polystyrene \(M_w = 60,000, M_n = 20,000\)?

1.15 The mole fractions can be obtained from the sample masses and \(M_n\) values:

\[
x_1 = \frac{10}{70,000 + 20/20,000} = \frac{1}{8}, \quad x_2 = \frac{7}{8}
\]

Therefore for the mixture

\[
M_n = \frac{70,000}{8} + \frac{7 \times 20,000}{8} = 26,250
\]

The weight fractions are easily seen to be 1/3 and 2/3, giving

\[
M_w = \frac{1}{3} \times 100,000 + \frac{2}{3} \times 60,000 = 73,333
\]
What would $M_w$ and $M_n$ be for an equimolar mixture of tetradecane and decane? (Ignore isotope effects.)

Tetradecane ($\text{C}_{14}\text{H}_{30}$) and decane ($\text{C}_{10}\text{H}_{22}$) have molecular weights of 198 and 142, respectively. For an equimolar mixture, $x_i = 0.5$, and therefore

$$M_n = \frac{1}{2} (198 + 142) = 170$$

The weight fractions are given by the proportion of mass, and therefore

$$M_w = \frac{198}{198 + 142} \times 198 + \frac{142}{198 + 142} \times 142 = 174.6$$

The polydispersity is 1.027.
Chem 466

Chapter 1 problem 12

(a) \[ n \overset{\text{AlBN}}{\xrightarrow{\Delta}} \overset{\text{poly (methacrylic acid)}}{\overset{\text{mechanism}}{\xrightarrow{\text{Initiation}}}} \overset{\text{Propagation}}{\xrightarrow{\text{Termination}} \text{rxn (to be discussed in Chapter 3)}} \]
(6) \[ nH_2N\text{--NH}_2 + n\text{--NH}_2\text{--CO} \rightarrow \]

\[ \text{xs Base} \downarrow \quad -2n-1\text{HCl} \]

\[ \text{hydrolytically unstable} \]

\[ \text{H}_2\text{O (upon isolation in air)} \]

Mechanism:

\[ \text{Nylon 4, 6} \]

\[ \text{or poly(tetramethylenediamine adipamide)} \]

\[ \text{Add'n} \uparrow \]

\[ \text{Elim} \]

\[ \text{deprotonation} \uparrow \]

\[ \text{repeats many times to produce the polymer} \]
\[ (C) \_n \ \text{HO-} \ \text{O-H} \ \xrightarrow{\Delta, \text{H}^+ \text{cat.}} \ \text{H(O-)} \ \text{O-H} \ \_n \ _{n-1} \ \text{H}_2\text{O} \]

poly (6-hydroxyhexanoic acid)

poly (6-hydroxycapric acid)

poly (\(\varepsilon\)-caprolactone)

Mechanism:

Add'\_n \ \text{H}^+ \ \text{O-H}

repeats many times to produce polymer

\[ \text{depot. H} \]

\[ \text{Elim.} \]

\[ \text{H}^+ \text{transfer} \]
(d) mistake in textbook; was supposed to be

\[ \text{AIBN} \quad \xrightarrow{\Delta} \quad \text{polyacylonitrile} \]

acylonitrile

the radical polym. mechanism is
the same as for (a)