"You have two choices", jamf cried, his last lecture of the year ... "stay behind with carbon and hydrogen, take your lunch-bucket in to the works every morning with the faceless droves who can't wait to get in out of the sunlight or move beyond. Silicon, boron, phosphorus -- these can replace carbon, and can bond to nitrogen, instead of hydrogen -- move beyond life, toward the inorganic. Here is no frailty, no mortality -- here is Strength, and the Timeless." Then his well-known finale, as he wiped away the scrawled C-H on his chalkboard and wrote, in enormous letters, Si-N.

The wave of the future.

from Gravity's Rainbow by Thomas Pynchon

\[
M_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \quad M_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}
\]

\[
\frac{\pi}{c} = \frac{RT}{M} (1 + Ac)
\]

\[
\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2c \quad \quad [\eta] = KM^n
\]

\[
\log ([\eta_x] M_x) = \log ([\eta_y] M_y)
\]

Average  67.6
Median  65
High    83

\[\begin{array}{cc}
80 & 2 \\
70 & 3 \\
60 & 6 \\
50 & 2 \end{array}\]

\[\overline{72 + \text{SBK}}\]
1. (9) For each of the following, name the polymer, and name and give structure(s) for monomer(s).

   a) \([\text{CH}_2-\text{CH-O}]\)  
      \[\text{CH}_3\]
      poly (propylene glycol)  
      \(\text{HO-CH}_2-\text{CH-OH}\)  
      \(\text{CH}_2\)  
      poly (propylene oxide)  
      \(\text{CH}_2-\text{CH-CH}_3\)  
      propylene oxide

   b) \([\text{CH}_2-\text{C}=\text{CH-CH}_2-\text{CH}_2-\text{CH}_2]\)
      \[\text{CH}_3\]
      poly (isoprene-co-ethylene)  
      \(\text{CH}_2\)  
      isoprene  
      \(\text{CH}_2=\text{C-CH=CH}_2 + \text{CH}_2=\text{CH}_2\)  
      ethylene

   c) \([\text{C-CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}]\)
      \(\text{O}\)
      nylon 6 or poly caprolactam  
      \(\text{NH}\)  
      caprolactam

2. (9) Give the structure and name of monomers which could be used to produce each of the following. Also show the repeat unit — show stereochemistry clearly, if necessary.

   a) cis-1,4-polyisoprene
      \(\text{CH}_3\)
      \(\text{CH}_2\)  
      \(\text{CH}_2\)
      \(\text{CH}_2\)
      \(\text{CH}_2\)
      \(\text{H}\)
      \(\text{CH}_2\)  
      \(\text{CH}_2\)
      \(\text{CH}_2\)
      \(\text{CH}_2\)
      \(\text{CH}_2\)

   b) isotactic poly(vinyl chloride)
      \(\text{CH}_2\)  
      \(\text{CH}_2\)
      \(\text{CH}_2\)
      \(\text{CH}_2\)
      \(\text{CH}_2\)
      \(\text{Cl}\)
      \(\text{Cl}\)
      \(\text{Cl}\)

   c) a polyurethane
      \(\text{CH}_3\)
      \(\text{N}\)
      \(\text{C} =\text{O}\)
      \(\text{N}\)
      \(\text{C} =\text{O}\)
      \(\text{HO-CH}_2-\text{CH}_2-\text{OH}\)
      \(\text{CH}_2\)  
      \(\text{CH}_2\)
      \(\text{CH}_2\)
      \(\text{O}\)
      \(\text{H}\)  
      \(\text{CH}_3\)
      \(\text{CH}_2\)
      \(\text{CH}_2\)
      \(\text{CH}_2\)
      \(\text{O}\)
3. (10) A sample of poly(ethylene terephthalate) was fractioned with the following results:

<table>
<thead>
<tr>
<th>molecular weight (g/mol)</th>
<th>mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0x10^4</td>
<td>10.0 g</td>
</tr>
<tr>
<td>2.5x10^4</td>
<td>25.0 g</td>
</tr>
<tr>
<td>5.0x10^4</td>
<td>20.0 g</td>
</tr>
<tr>
<td>1.0x10^5</td>
<td>5.0 g</td>
</tr>
</tbody>
</table>

Determine $M_n$, $M_w$, $DP_n$, and the polydispersity.

<table>
<thead>
<tr>
<th>$M_n$</th>
<th>$g$</th>
<th>$n$</th>
<th>$nM$</th>
<th>$nM^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10000</td>
<td>10</td>
<td>0.001</td>
<td>10</td>
<td>10000</td>
</tr>
<tr>
<td>25000</td>
<td>25</td>
<td>0.001</td>
<td>25</td>
<td>625000</td>
</tr>
<tr>
<td>50000</td>
<td>20</td>
<td>0.0004</td>
<td>20</td>
<td>1000000</td>
</tr>
<tr>
<td>100000</td>
<td>5</td>
<td>0.00005</td>
<td>5</td>
<td>500000</td>
</tr>
<tr>
<td>185000</td>
<td>60</td>
<td>0.00245</td>
<td>60</td>
<td>2225000</td>
</tr>
</tbody>
</table>

$M_n = 2.4E+04$

$M_w = 3.7E+04$

4. (10) Compare and contrast step growth and chain growth polymerizations. For each, list type of monomer(s), constituents of reacting mixture, relative speed of reaction, requirements for high polymer.

<table>
<thead>
<tr>
<th>Step growth</th>
<th>Monomer type (give example)</th>
<th>Reaction mixture</th>
<th>Relative speed</th>
<th>Requirements for high polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>14O - C =&gt; C - O - C - O</td>
<td>di-functional</td>
<td>all sizes under control</td>
<td>slow</td>
<td>1:1 stoichiometric, no byproducts</td>
</tr>
<tr>
<td>Chain growth</td>
<td>monomer + growing chains</td>
<td>fast</td>
<td>no chain transfer, initiator</td>
<td></td>
</tr>
</tbody>
</table>
5. (12) Discuss the importance of polymer solutions.

a) Are polymers generally easier or more difficult to get into solution than small molecules? Why?

\[ \Delta G = \Delta H - T \Delta S < 0 \]

\[ \Delta S \text{ not as large - polymer restricts state} \]

\[ \Delta H \text{ usually > 0; polymers have high Tf.} \]

b) How do you choose a solvent for a particular polymer?

want similar Tf - use solubility parameters - get similar solubility parameters for solvent & polymer

c) What is the difference between a good solvent and a poor solvent?

Good: strong solute-solvent force - polymer will expand

Poor: weak Tf, polymer contracted

d) Describe the "solution process", that is, what happens when the polymer and solvent are mixed, on a molecular level.

1st polymer absorbs solvent & swells, then, if solvent can overcome all interactions, polymer-polymer forces, it dewets.

e) Discuss the change in enthalpy, entropy, and free energy when forming a polymer solution. Compare signs and magnitudes to those for "simple" solutions of small molecules.

\[ \Delta G \text{ must be < 0 for both:} \]

- for same monomer & polymer in same solvent

\[ \Delta G \text{ is more negative than for monomer} \]

\[ \Delta G \text{ solution} \]

\[ \Delta S \text{ small > 0} \]

\[ \Delta H \text{ usually > 0} \]

\[ \text{can be > 0, < 0 or = 0} \]
6. (12) a) What common features do viscosity and osmotic pressure have in common as techniques for polymer molecular weight determination?

b) What are the principal differences?

- Absolute, \( M_n \) is more consistent.  
- Relative - mod. \( M_n \) & \( M_w \), quicker \( M_w \)

c) Why do we extrapolate the data to zero concentration in each case (give a molecular description)?

- Want ideal polymer solution - no polymer-polymer IF

- \( \frac{1}{\eta} = \frac{1}{\eta} \) vs C int. = \[ M_w \]
- \( \eta \) vs C int. = \[ M_n \]

7. (6) A sample of a polymer molecule with acid groups (-COOH) at each end (and no other free acid groups) was analyzed and the acid groups made up 0.01270% of the mass of the polymer. What is its molecular weight? Which molecular weight average is this?

- \( 2 \text{ (COOH)} = 90 \text{ g/mol} \)
- In one gram polymer \( \frac{0.000129}{90 \text{ g/mol}} = 1.3 \times 10^{-6} \text{ mol} \)
- \( \frac{1.09}{1.3 \times 10^{-6} \text{ mol}} = 8.5 \times 10^5 \text{ g/mol} \)
b) What is in the column (assume using a solvent-based system, not water)?

- gel PS-divinyl benzene

3. c) How is a GPC instrument "calibrated"?

- mono disperse PS stds.

4. d) What is a "universal calibration curve"? How is it used?

- \[ \text{log MW} \]

\[ \text{CN} \]

5. e) What limitations does GPC have?

- must be in solution (TDHF)
- need K&G calibration
- costly

6. f) What is the primary advantage of GPC over other molecular weight determination techniques?

- get entire MW dist.
9. (12) a) List the steps involved in free radical chain growth polymerization. Name each step and show the basic reaction(s) for each step. Show a possible initiator (name and structure):

\[ \text{Initiation: } I \rightarrow \text{C} = \text{O} - \text{O} - \text{C} - \text{O} \]

for example

\[ \text{Propagation: } M_n + M \rightarrow M_{n+1} \]

\[ \text{Coupling: } M_n + M_m \rightarrow M_{n+m} \]

\[ \text{Termination: } M_n + M_n \rightarrow M_{n+m} \]

\[ \text{Deproportionation: } M_n + M_m \rightarrow M_n + M_m \]

\[ \text{Chain transfer: } M_n + X \rightarrow M_n + X \]

\[ X = \text{solvent, monomer, other} \]

b) How would this differ if an anion was used rather than a free radical? What would be a possible initiator? What are the advantages of this over free radical polymerization?

no termination, "living" polymer, make block copolymers, narrow MW distribution

Na\(\text{CO}_3\) sodium carbonate

10. (8) What is meant by "growing plastics"? What are examples of two polymers that can be "grown"? What are the basic advantages and disadvantages of this idea?

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