Chem 466

lecture # 7

02/04/2014

Exam I, Thursday, Feb 6, 2014

- calculators + rulers allowed

- Adriana office hrs: 02/05 @ 3pm
  in 1423 or 1427

- exam material through 01/30 lecture
  sheet of equations will be provided at exam

Quiz #3  \( \bar{x} = 5.1, \text{ S.D.} = 4.0 \)
(D) Control over Macromolecular Architecture

1. Linear polys

2. X-linked networks (contd)
   - X-linked materials are also called thermosets, because often the x-linking is activated by heat
   - X-linking is called curing
   - Because $D_n \to \infty$, x-linked polys cannot be processed w/out breakage of covalent bonds

   - prepd/x-linked/cured once in final form, from:
     (i) mult-funct. monomers
     (ii) mult-funct. macromolecules/pre-pols (convenient Often because of relatively high viscosity for pre-forming/molding processes - e.g. silicone caulk)

     w/ x-linking through mixs of
     chain ends +/or stable
     chain groups w/ or w/out added x-linking agent(s)
Stoichiometry of the functional groups + conditions dict as the products

- Linear + Branched poly structure that can lead ultimately to a crosslinked network where $DP_n \to \infty$
  
  = "gel" = network polymer

- Links between the chains can be:
  - at chain ends (if pre-poly)
  - along backbone
  - both @ ends + along backbone

- Crosslinked polys become insoluble & infusible once gel point is reached, however, they can swell in solvents that are analogs for the non-crosslinked polymer
gel pt. occurs at the critical extent of monomers, \( p_a \)

\[
P_c = \frac{2}{f_{av}} \quad \text{(Carothers' eqn.)}
\]

for a stoichiometric balance of functionalities

where, \( f_{av} = \text{average functionality} \)

\[
f_{av} = \frac{\sum N_i f_i}{\sum N_i}
\]

- \( f_{av} > 2 \) gives x-linked network
- \( p_a \) increases as \( f_{av} \) increases
- \( f_{av} \) increases as monomer func. increases

Ex. for ABA:

\[
2 A - A + 3 B - B
\]

\[
f_{av} = \frac{2 \cdot 3 + 3 \cdot 2}{2 + 3} = 2.4
\]

\[
\Rightarrow P_c = \frac{2}{2.4} = 0.83
\]

\( @ 83\% \) conversion an insoluble gel will be obtained

\( A_3 + B_2 \) e.g. silicone, whereas if \( A_4 + 2B_2 \) \( \Rightarrow f_{av} = \frac{1.4 + 2 \cdot 2}{1 + 2} = 1.7 \)

e.g. epoxy \( \Rightarrow P_c = 0.74 \)
Examples:

- polysiloxane/silicone demo, e.g., bathroom caulk, sealant, adhesive, etc.
  - an example of chain-end x-linking upon a reagent from the atmosphere (H₂O) and then coupling of poly chain ends + x-linker

\[ \text{H}_2\text{O} \left( \text{Si} - \text{O} \right)_n \text{Si} - \text{OH} + \text{CH}_3 - \text{Si} - \text{O} - \text{X} \rightarrow 3\text{H}_2\text{O} \]

- pre-polymer:
  - viscous (low Tg ~ 130°C)
  - inactive x-linker

- catalytic:
  - in H₂O

- + A+A
- + B+B
- Xns possible

- loosely x-linked network

- 3 pt. x-link site
Example:

1. Epoxy resin, e.g., adhesives, coatings, paints, etc.

Tube 1

\[ \begin{align*}
\text{R-OH} & + \text{R'-CN} \rightarrow \text{R-O-R'} + \text{CN} \\
\end{align*} \]

- Short prepolymer
- N/Electrophilic epoxide
- Chain ends \( (A_n) \)
- Nucleophilic alcohol
- Side chain groups \( (A_{n-1}) \)

Mechanism:

- R-OH (epoxy opening)
- N/C attack
- R'-CN
- R-O-R' + CN
- H transfer
- R-O-NR'

Tube 2

\[ \begin{align*}
\text{NH}_2 \\
\text{CH}_2 \\
\text{NH}_2 \\
\text{(crosslinking agent)} \\
\text{NH}_2 \\
\text{CH}_2 \\
\text{NH}_2 \\
\text{(crosslinking agent)} \\
\end{align*} \]

- N/Electrophilic amines
- \( (B_4) \)

Reaction of 1 or 2 of A groups

Reactions of 1, 2, 3, or 4 of B groups
- Alternatively, if \( n \) is large, then x-linking is accomplished via react of side chain \(-\text{OH}^-\) groups (by epoxide chain ends in low conc.) by add of an electrophilic linking agent.

\[ \text{cat.} \quad \text{C} = \text{O} \]

\[ \text{OH} \]

\[ n-1 \]