Chem 466

Lecture #2

01/16/2014

Quiz #1  $\bar{x} = 9.6$

$\text{S.D.} = 1.7$

Monday, January 20 is MLK holiday

\(\Rightarrow\) no office hours
## General Introduction to Polymers

### Structural Features

1. **Repeat units** (which include side chain functionalities)
2. Bonding between repeat units and connectivity to chain ends
3. Chain ends (may be same or different)

**All structural components must always be shown**

- Repeat units (which include side chain functionalities)
- Bonding between repeat units and connectivity to chain ends
- Chain ends (may be same or different)

### Properties

- **Depend on**:
  - Composition of monomer
  - Polym. chem.
  - Post-polym. chemical modification reactions

- **Can be same along backbone (homopolymers)** or different (copolymers — statistical (random), alternating, block, gradient, etc.)
  - The sequence is important & is controlled during polym. and/or via post-polym. chem. transformations

- **# repeat units, \( n = DP \), degree of polym. = \( N \)**
  - Poly for \( n \geq 10 \)
  - Since mol. wt. of monomer is typically \( \approx 100 \text{ Da} \)
  - Polym. mol. wt. typically \( \geq 1000 \text{ Da} \) (text p. 7)
bonding between repeat units + connectivity to chain ends

- depends upon:
  - polymer chem.
  - monomer structure
  - initiator + terminator structures (if employed for polymer)
  - post-polymer chem. transformations

- repeat units can be connected through 2 sites (linear poly) or more (branched or x-linked poly, etc.)

chain ends

- depend upon chem. used for polymer
  - monomer structure
  - step-growth, condensation polymer vs. chain-growth addition polymer mechanisms
  - initiator
  - terminator

- can influence the poly properties
- must always be drawn
(B) Properties

- For polymers, as for small molecules, the properties (physical, chemical, mechanical, optical, etc.) depend upon:
  - composition
  - stereochemistry
  - topology/bonding sequence (architecture, regiochemistry, structural isomerism)
  - chain length (degree of polymerization vs. mol. wt.)

**General trends**
- As degree of polymerization (n) increases, solubility, viscosity, thermal transition temperature increase.

\[
\text{monomer} \rightarrow \text{oligomer} \rightarrow \text{polymer}
\]

- \( n = 1 \)
- \( n \leq 10 \)
- \( n > 10 \)
- Mw \( \leq 500 \text{ Da} \)
- Mw \( \leq 1000 \text{ Da} \)
- Mw \( \geq 1000 \text{ Da} \)

(Other words, macro-monomer)

E.g., as seen for PS standards (Slide #7 of Lecture #1)

\[
\text{cis} \quad \text{vs.} \quad \text{trans}
\]

- Trans: \( T_m = -31 \text{°C} \)
- Cis: \( b.p. = 145-146 \text{°C} \)

- Loss of x-stacking
  - As \( n \uparrow \)
  - \( b.p. \uparrow, T_g \uparrow \)
  - No \( T_m \)
  - No b.p. (before decomposition)

- \( T_g \geq 100 \text{°C} \)
for synthetic polymers, sizes are not homogeneous
- distributions of degrees of polymerization
- distributions of mol. wt.
  => average values are det'd.

polydispersity
- a measure of the breadth of the mol. wt. distribution
- polydispersity index = PDI ≥ 1

mol. wt. distributions can be determined experimentally by separation and analysis of polymers having diff. DP/MW/size

mol. wt. distribution is controlled synthetically (to some extent) and also can be altered by fractionation or degradation

experimentally, important to report % conversion of monomers during polymerization and yield of isolated poly, to indicate whether fractionation occurred during work-up of run + purification
\[ PDI = \frac{\overline{M}_w}{\overline{M}_n} = \frac{\text{wt. ave. } \overline{M}_w}{\text{# ave. } \overline{M}_w} \]

where, \( \overline{M}_w = \sum w_x M_x = \sum N_x M_x^2 \)

\[ \sum N_x M_x \]

\[ w = \frac{N_x M_x}{(\text{mol})(g/(\text{mol}))} \]

- Experimentally, \( \overline{M}_w \) is determined from light scattering in solution. Scattering intensity is greater for larger molecules, biased by large molecules.

\[ \text{and, } \overline{M}_n = \frac{\text{total wt. of molecules}}{\text{total # moles}} = \frac{\sum N_x M_x}{\sum N_x} \]

- Experimentally, \( \overline{M}_n \) is determined from methods that count molecules (colligative properties), e.g., osmometry, freezing pt. depression, etc., and also by end group analysis, e.g., titration, NMR spectroscopy, etc.

* The full distribution of molecule vs. mol. wt. is observed by size exclusion chromatography or MALDI-TOF mass spectrometry experimentally.
**I. General Introduction to Polymers (cont'd)**

**D) Overview of Polym. Mechanisms**

Condensation, step-growth vs. addition, chain-growth polymerizations?

1. **Condensation vs. Addition Polymers - slide**

Example chemistry: Poly (bisphenol A carbonate) via an A + B B condensation polym of bisphenol A + phosgene

\[
\begin{align*}
\text{Addn:} & \quad \overline{\text{H}} \quad \overline{\text{O}} \quad \overline{\text{H}} + n \text{ HCl} \\
\text{Elim:} & \quad \overline{\text{H}} \quad \overline{\text{O}} \quad \overline{\text{H}} + n \text{ HCl} \\
\text{Deprot.} & \quad \overline{\text{H}} \quad \overline{\text{O}} \quad \overline{\text{H}} + n \text{ HCl} \\
\text{Base:} & \quad \sqrt[\text{H}]{\text{H}^+} + \text{EtNH}_2^+ \\
\text{Base H Cl} & \quad \text{e.g. EtNH} \cdot \text{Cl} \quad \text{or} \quad \text{CONH}_2 \text{Cl} \\
\end{align*}
\]
Condensation step-growth polymers are recognized by the functional groups along the polymer backbone that can be produced by coupling of functionalities, e.g., condensation.

However, there are many exceptions, especially as possibilities for ring-opening chain-growth polymers do alternatives (a poly may appear to originate from step-growth polybutadiene but may actually be from chain-growth polybutadiene).

Example chemistry: Polystyrene via a traditional, non-controlled radical chain addition polymer using AIBN (azo-bisisobutyronitrile) as the initiator.

Three mechanistic steps are involved:

1) Initiation (places initiator on the chain end)
2) Propagation
3) Termination (places terminator on the chain end)
The image contains a chemical reaction and notes on polymerization:

**Initiation**

\[ \text{N} = \text{N} \xrightarrow{\Delta} 2 \text{Y} + \text{N}_2 \]

AIBN

**Propagation**

Initiating radical

Radical Add’n

Radical Add’n

Termination

(highly reactive radicals can undergo several types of termination: irreversible or reversible (basis of controlled radical polymerization))

**Addition**

- Chain growth polymers are recognized typically by E-E bonds along the backbone—however, there are many exceptions, e.g., by possibilities for polym through other types of multiple bonds of polymer by ring-opening reactions