Figure 1: Processing and molecular structure of a polymer determines its function, structure, and morphology, which in turn determines its final properties.

**Diversity of Polymer Chains (two types):**

**A)** Low molar mass (small) molecules

Example:

![Molecule](http://example.com/molecule.png)

Synthesis determines molecular structure.

One goal of synthesis is to avoid side reactions and achieve a pure product.

**B)** Polymer

- Control molecular structure
- Control regularity of backbone
  - Ex: stereochemistry

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 course materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Ex: sequencing in copolymers

These three polymers are different even though they have the same number of monomers:

- abababab    regular copolymer
- abbaaaba    random copolymer
- aaaaabbb   block copolymer

- Control molecular weight

  - Impacts polydiversity:

    Polydisperse versus Monodisperse

  - Overall molecular weight (MW) or mass
    - If a polymer has low MW, it acts like a fluid above $T_g$
    - If a polymer has high MW, it acts like a rubber above $T_g$
    - MW also determines mechanical properties, viscosity, rheology

- Control architecture

  - linear chain polymer
  - lightly branched polymer
  - “combed” polymer
  - “star polymer”
Course Goals

Goal 1: Structural and architectural control

- To gain a sense of rational design and synthesis
- To develop an intuition about the impact of a structure on property
- The following two examples demonstrate how structure determines the polymer’s physical and chemical properties:
  - Ex 1: polyamides (Kevlar® by DuPont)
    - Kevlar®’s very low flexibility makes it a rigid structure
    - The hydrogen bonding enhances rigidity and makes it solvent-resistant
    - The long backbone gives it high mechanical strength
    - In fact, Kevlar® has a liquid crystalline structure
  - Ex 2: polydimethylsiloxane (PDMS)
    - The longer Si—O bond makes PDMS very flexible
    - CH₃ makes the polymer hydrophobic
    - Tg ≈ -100°C

Goal 2: Apply knowledge to processes in industrial and commercial settings

- Determine which process is best for certain applications (Ex: there are ways to synthesize PDMS)
- There are variables in polymer approach, synthetic route, starting materials and/or catalysts, and solvent conditions

Goal 3: Awareness of new tools and approaches to materials design

- Less traditional approaches
- Functionalization of polymers
- Self-assembly approaches
Description of Molecular Weight in Polymers

Each MW can be represented as $M_i$

$N_i = \text{number of molecules of MW}=M_i$

$w_i = \text{weight fraction of given system of chains with MW}=M_i$

$$w_i = \frac{N_i M_i}{\sum N_i M_i}$$

$\bar{M}_n = \text{number average MW} = \frac{\text{total weight}}{\text{total # molecules in sample}} = \frac{\sum N_i M_i}{\sum N_i}$

$\bar{M}_w = \text{weight average MW} = \frac{\sum (N_i M_i)^2}{\sum (N_i M_i)} = \frac{\sum N_i (M_i)^2}{\sum N_i M_i}$

The following graph shows the relationship between $w_i$ and $m_i$:

Polydispersity can be measured by PDI (polydispersity index): $z = \frac{\bar{M}_w}{\bar{M}_n} \geq 1.0$.

$z = 1.03$ or $1.05$ is considered close to monodisperse
Types of Polymerization

A) Chain growth

- In chain growth, a monomer is activated and polymerization propagates by activating neighboring monomers. The process is very rapid and high MW polymers are achieved quickly.
- The following describes the chain growth reaction in which $*$ represents the activated monomer $M$. This can be a free radical, negative charge, or positive charge:

1. $R^* + M \rightarrow RM^*$
2. $RM^* + M \rightarrow RMM^*$
   ...
3. $RM_n^* + M \rightarrow RM_{n+1}^*$

3. Event that terminates

B) Step growth

- In chain growth, bifunctional monomers are added systematically to form covalent bonds. It generally involves 2 (or more) functional groups: “a” and “b.” Molecular weight increases “slowly” as dimers become trimers, which in turn become tetramers.
- Examples of polymers formed by chain growth: nylons, polyesters, polypeptides (proteins)
- [Handout] These are typical a and b groups:

$$a + b \rightarrow c + d \quad \text{where} \quad c = \text{covalent link}$$
$$d = \text{byproduct}$$

1. $a—a + b—b \rightarrow a—c—b + d$

   $\text{HO—C—R—C—OH} + \text{HO—R}^1\text{OH} \rightarrow$

   $\text{HO—C—R—C—O—R}^1\text{OH}$

   ester link

   $\text{+ H}_2\text{O}$

2. $a—c—b + a—a \rightarrow a—c—c—a$

3. $a—c—c—a + b—c—c—c—a \rightarrow a(c)_a + d$
Step Growth Polymerization

2 functional groups: \( a,b \rightarrow \) form new link \( c \), may be a side product \( d \)

\[
a—a + b—b \rightarrow a—c—b + d
\]

For example, if \( a—a \) is a diacid and \( b—b \) is a diol:

\[
\begin{array}{c}
\text{from diacid} \\
\text{from diol}
\end{array}
\]

Polyester
(one repeat unit consists of 2 structural units)

Degree of polymerization
\[
\overline{M}_n = \frac{p_n \cdot M_u}{2}
\]
where \( M_u \) = molecular weight (MW) of individual repeat units

Can also have \( a—b \) monomers:

\[
\begin{array}{c}
\text{HO—CH}_2—\text{COH} \\
\rightarrow \text{OR”—C}
\end{array}
\]

In this case:
- \( R” = \text{CH}_2 \)
- The repeat unit is the structural unit

\[
\overline{M}_n = p_n \cdot M_u
\]
Determining MW as a Function of Conversion

How do you determine MW as a function of conversion?

\[ \bar{p}_n = \frac{\text{total initial # of monomer units}}{\text{total # of molecules remaining}} = \frac{N_o}{N_{total}} \]

Simple thought experiment:

<table>
<thead>
<tr>
<th>50 monomer units</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 a—a</td>
</tr>
<tr>
<td>25 b—b</td>
</tr>
</tbody>
</table>

If have 50% conversion ⇒ 25 a+b reactions
⇒ lose molecule w/each reaction (2 molecules become 1)

\[ \bar{p}_n = \frac{50}{50-25} = 2 \]

So \( \pi \) (conversion) can be related to \( \bar{p}_n \).

\( (Na)_o = \text{initial # of a reactive group} = 2 \) (# of a-a monomers)
\( (Nb)_o = \text{initial # of b reactive group} = 2 \) (# of b-b monomers)

\[ \pi_a = 1 - \frac{Na}{(Na)_o} \quad \pi_b = 1 - \frac{Nb}{(Nb)_o} \]

Define \( r = \frac{(Na)_o}{(Nb)_o} \leq 1 \) Define: a is minority functional group

Stoichiometric ratio

Total # of functional groups initially present

\[ N_o = (Na)_o + (Nb)_o = (Na)_o \left[ 1 + \frac{1}{r} \right] \]

At a given time \( t \), have conversion \( \pi_a \)

\[ N_t = \# \text{ of functional groups at time } t = (Na)_o \left( 1 - \pi_a \right) + (Nb)_o - (Na)_o \pi_a \]

Na Nb
\[ N_i = (Na)_o \left( 1 - 2\pi_a + \frac{1}{r} \right) \]

\[ \vdots \]

\[ p_n = \frac{N_o}{2} = \frac{N_o}{N_i} = \frac{1 + \frac{1}{r}}{1 - 2\pi_a + \frac{1}{r}} = \frac{1 + r}{1 - 2\pi r + r} \]

\[ \pi_a = \pi \text{ (assume referring to minority)} \]

Simple case: \( r = 1.0 \) (perfect stoichiometry)

<table>
<thead>
<tr>
<th>At</th>
<th>( \pi )</th>
<th>( p_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \pi = 0.995^* )→</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>( \pi = 0.99 ) →</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>( \pi = 0.98 ) →</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>( \pi = 0.90 ) →</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

*Can take a long time. First 95% takes same time as last 2-3%.

Must \( \uparrow \pi \) to get high MW \( \bar{p}_n = \frac{1}{1 - \pi} \) As \( \pi \uparrow \), \( \bar{p}_n \) explodes.

But, there is a problem:

**Control of MW**

How to control MW?

a) Control \( \pi \) (conversion)

Issue:

\[
\begin{align*}
\text{MW changes when you} \\
\text{ship it or store it.}
\end{align*}
\]

b) Control stoichiometry:

Assume: e.g. \( \pi = 1.0 \)

\[ p_n = \frac{1 + \frac{1}{r}}{1 - \frac{1}{r}} = \frac{1 + r}{1 - r} \]

Add excess of \( b-b \)
End up “capping” chains w/b groups
groups cannot react with each other

e.g. 1% excess of b-b
\[ \Rightarrow \max \ p_n = 199 \]

Can intentionally cap with alcohol or ester for certain applications.
Can use \( \pi, r \) to predict MW outcome of rxn.

Can also use monofunctional unit as an end capping agent:
\[ a-a \]
\[ b-b \]
\[ b-x \] where \( x \) is a desired final group that can’t react with \( a \) or \( b \)
e.g. phenol

• polyurethanes: longer chain molecules
• surface groups

Here we redefine the ratio \( r \):

\[
\begin{align*}
\text{Assume} & \\
\text{a—a} & \\
b—b & \\
b—x & \text{ where } x \text{ is a desired final group that can’t react with a or b} \\
e.g. \text{phenol} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Caveat: } (Na)_o \text{ and } (Nb)_o & \\
a—a & b—b \text{ for this to work.} \\
\end{align*}
\]

Same expression if you’re using \( a-b \) monomers.

**MW Distribution as a Function of Conversion:**

Assumptions:
1. Equal reactivities for all \( a, b \) functional groups.
   Reactivities are the same for short \( a—a \) and long polymer (length independence) in viscous fluid.
2. Perfect stoichiometry: \( r = 1 \)
3. For ease of explanation, use \( a-b \) monomer (\( \pi_a = \pi_0 \)).

At a given time \( t \), have conversion \( \pi \)

Probability that an \( a \) group has reacted: \( p = \pi \)
(will use p, π interchangeably)
Probability that a molecule has x structural units = \( \wp_x \)

<table>
<thead>
<tr>
<th>x structural units ( \Rightarrow )</th>
<th>(x-1)</th>
<th># of a groups reacted</th>
<th>Prob of this combination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a group unreacted</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Prob of x-1 a groups reacted: \( p^{x-1} \)
Prob of unreacted a: \( (1-\pi) \) or \( (1-p) \)

So, \( \wp_x = p^{x-1}(1-p) \)

\[ \wp_x = \text{number fraction of chains with degree of polymerization } x \]

\[ \wp_x = \frac{\text{# of x-length chains}}{\text{total # of chains}} = \frac{N_x}{N_{\text{total}}} = \frac{N_x}{N_o(1-p)} = \frac{N_x}{N_o - N_o p} \]

\[ N_x = \wp_x N_o(1-p) \]

Every time a molecule reacts lose \( N_o p \).

\[
\begin{align*}
\wp_x &= \frac{N_x}{N_{\text{total}}} \\
&= \frac{N_x}{N_o - N_o p}
\end{align*}
\]

increase conversion \( \rightarrow \) narrower and broader

**Flory-Shulz Distribution: Some Monomer Always Present**

\[ \bar{p}_n = \frac{\sum xN_x}{\sum N_x} = \sum x\wp_x = \sum xp^{x-1}(1-p) \]

\[ \sum p^{x-1} = \frac{1}{1-p} \]

\[ \sum xp^{x-1} = \frac{1}{(1-p)^2} \]

\[ \bar{p}_n \Rightarrow \frac{1}{(1-p)} \]
Weight fraction: \[ w_x = \frac{xN_x}{N_o} = x(1-p)^2 p^{x-1} \]

\[ \bar{p}_w = \frac{1+p}{1-p} \quad \text{or} \quad \frac{1+\pi}{1-\pi} \]

Result of using $\bar{p}_w$ expression and summations

\[ \text{PDI} = z = \frac{\bar{p}_w}{p_n} = 1 + p = 1 + \pi \]

As \[ \pi \to 1.0 \]
\[ z \to 2.0 \]
Kinetics of Step Growth Polymerization (Chapter 2)

\[ A + B \rightarrow \text{polymer} + \text{byproduct} \]

\[ R_p = \text{rate of polymerization} \]

\[ R_p = -\frac{d[M]}{dt} = -\frac{d[a]}{dt} = -\frac{d[b]}{dt} = k[a][b] \]

Assume \( r = 1 \), where \( r \) is the stoichiometric ratio. \( r = \frac{a}{b} \)

\[ [a] = [b] \]

Terminology \( \bar{p}_n \) varies with \( t \) → \( \bar{p}_n = \frac{[a][b]}{a} \)

\( (X_n) \) p. 50

\[ \frac{-d[a]}{dt} = k[a]^2 \]

\[ \frac{-d[a]}{[a]^2} = kt \]

\[ \frac{1}{[a]} - \frac{1}{[a]_b} = kt \]

\[ \frac{[a][b]}{[a]} - 1 = [a][b]kt \]

\[ \pi = 1 - \frac{[a]}{[a]_b} \]

in book, \( \pi = p \) (p. 46)

\[ \frac{[a][b]}{[a]} = \frac{1}{1 - \pi} \]

\[ \frac{[a][b]}{1 - \pi} - 1 = \bar{p}_n - 1 \]

Notes:

1. \( [M] \propto \frac{1}{t} \) as time ↑, concentration of monomer ↓
2. \( \bar{p}_n \) increases linearly with time

\[
\begin{array}{ccc}
a + b & \xrightleftharpoons[k_r]{k_r} & c + d \\
\text{LeChatlier’s Principle: remove water} & k_r >> k_r & \text{To drive reaction forward}
\end{array}
\]
Making esters:

$$\sim \text{COOH} + \sim \text{OH} \xleftrightarrow{K_{eq}} \sim \text{C} - \text{O}\sim + \text{H}_2\text{O}$$

Ester can hydrolyze with water and go backwards (reverse rxn) \rightarrow drug delivery

$$K_{eq} = \frac{[\text{COO}] [\text{H}_2\text{O}]}{[\text{COOH}] [\text{OH}]}$$

Assume at $$t = 0$$: $$[\text{M}] = [\text{M}]_b$$

Put in terms of $$\pi$$:

$$[\text{COOH}] = \pi [\text{COOH}]_b = \pi [\text{OH}]_b = \pi [\text{M}]_b$$

$$[\text{OH}] = \pi [\text{OH}]_b = [\text{OH}]_b = [\text{M}]_b (1 - \pi)$$

$$K = \frac{(\pi [\text{M}]_b)^2}{[\text{M}]_b (1 - \pi)^2}$$

$$K = \frac{\pi^2}{(1 - \pi)^2}$$

$$\pi = \frac{K^{\frac{1}{2}}}{1 + K^{\frac{1}{2}}}$$

In closed system, limited by $$K$$ (reaction constant).

That also means rxn and polymer limited by $$K$$.

$$\overline{p}_n = \frac{1}{1 - \pi} = 1 + K^{\frac{1}{2}}$$

where $$\overline{p}_n$$ is the # average degree of polymerization (# of units in polymer)

Polyesterification: $$K: 1 \sim 10$$

$$\overline{p}_n \sim 2 - 5$$ monomers

Polyamidation: $$K: 100 - 1000$$

$$\overline{p}_n : 10 - 40$$

In between: removing some of the water

**Open Driven System**

Removing byproduct

- $$\text{H}_2\text{O}$$ by temperature, low pressure, or $$\text{N}_2$$ blowing of water
- Acid like $$\text{HCl}$$, base neutralization

$$[\text{H}_2\text{O}] \leftrightarrow \text{MW} (\overline{p}_n)$$

How $$\text{H}_2\text{O}$$ affects $$\overline{p}_n$$
COH + OH $\rightleftharpoons$ C-O $+ H_2O$

$$K = \frac{[CO\Theta^+] [H_2O]}{[COOH] [OH]} = \frac{\pi[H_2O]}{[M_n] (1 - \pi)^2}$$

$$K = \frac{1}{1 - \pi} \cdot \frac{\pi}{1 - \pi} \cdot \frac{[H_2O]_{eq}}{[M_n]}$$

$$\overline{p_n} = \frac{1}{1 - \pi}$$

$$\frac{\pi}{1 - \pi} = \frac{1}{1 - \pi} - \frac{1 - \pi}{1 - \pi} = \frac{1}{1 - \pi} - 1 = \overline{p_n} - 1$$

$$K = \overline{p_n} \cdot (\overline{p_n} - 1) [H_2O]_{eq}$$

$$[H_2O]_{eq} = \frac{[M_n] K}{\overline{p_n} (\overline{p_n} - 1)}$$

only get down to a certain water concentration

$\rightarrow$ solve for best $p_n$ possible

**Polyesterification Using Acid Catalysis**

More active than COOH

Acid catalyst

$$K_{12} = \frac{k_1}{k_2} = \frac{[OH]}{[HA][COOH]}$$

$\rightarrow$ slow step (rate-determining step)
\[ R_p = \frac{-d[\text{COOH}]}{dt} \] Rate of disappearance of carboxylic monomer

\[
R_p = k_3 \left[ C^+ (OH)_2 \right] [\text{OH}] \quad \text{(from previous page)}
\]

\[
= k_3 K_{12} [HA][\text{COOH}] [OH]
\]

From equilibrium expression [HA] is constant because it's regenerated.

\[
R_p = \frac{-d[\text{COOH}]}{dt} = k' [\text{COOH}][\text{OH}] \quad \text{where } k' = k_3 K_{12} [HA] \text{ constant}
\]

Self-catalyzed: [HA] = [COOH]

\[
R_p = \frac{-d[\text{COOH}]}{dt} = k'' [\text{COOH}][\text{OH}] \quad \text{where } k'' = k_3 K_{12}
\]

\[
R_p = \frac{-d[M]}{dt} = k' [M]^3 \quad \text{separate and integrate}
\]

\[
2k't = \frac{1}{[M]^3} - \frac{1}{[M]_b^3}
\]

\[
[M] = [M]_b (1 - \pi)
\]

\[
\left( \frac{\bar{P}_n}{[M]_b} \right)^2 = \frac{1}{(1 - \pi)^2} = 2[M]_b^2 k't + 1
\]

Much slower because of time-dependence (\(\sqrt{t}\))
That's why people add acid to drive reaction.

High Temperature
- increase k
- remove byproduct (evaporate H\(_2\)O)

Bulk or mass conditions (no solvent)
- \([M]_o\) is maximum
- no need to separate product
- viscosity $\eta$ low until high $\pi$
- direct processing

Use solvent
- monomers are not miscible with each other but miscible with solvent
- allow high $T$
- dilute viscous media (carrier for viscous media)
  $\rightarrow$ improves processing
- improves heat and mass transfer
Acid catalyst [HA]

\[ [a] \cdot kt = \frac{1}{1 - \pi} - 1 = \overline{p_n} - 1 \]

\( \overline{p_n} \) linear ↑ with time

For self-catalyzed case:

\[ \frac{1}{(1 - \pi)^2} = \overline{p_n}^2 = 2M_1 \cdot kt + 1 \]

\( \Rightarrow \overline{p_n} \) ↑ with \( \sqrt{t} \)

Basic rate expression for acid catalyst:

\[ R_p = k_3k_{12}[HA][COOH][OH] \]

\( \downarrow \) decrease

Self-catalyzed:

\[ R_p = k_3k_{12,COOH}[COOH]^2[OH] \]

Slower reaction

Gets extremely slow at the end of the reaction

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{OH} + \text{COOH} \rightarrow \text{O} \quad \text{C} \quad \text{O} )</td>
<td>Polyester ((k \sim 1))</td>
</tr>
<tr>
<td>( \text{NH}_2 + \text{COOH} \rightarrow \text{O} \quad \text{H} \quad \text{C} \quad \text{N} )</td>
<td>Polyamide ((k \sim 10))</td>
</tr>
</tbody>
</table>

In some cases \(k \sim 100\) (hungry polymer)

Typical process conditions for near equilibrium step growth:

- High \(T\)
  - to increase \(k\) \((k↑ \text{ with } T↑)\)
  - to aid in byproduct removal
- Bulk or mass polymerization (no solvent)
  - if the reactants are miscible (forming 1 uniform, mixed phase), get highest concentrations possible
  - no need for separations step (remove solvent)
  - viscosity \(\eta\) low enough to process until high MW
  - product can be directly processed into final form
- Solvents
  - may be needed to solubilize two monomers (reactants)

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
- could allow higher T to be approached without scorching polymer
- carrier (dilutant) for viscous media (exp for high MW)

**Interchange Reactions in Near-Equilibrium Polymerization**

\( (k \sim 1-10) \)

Ex: polyamide (but same thing happens in polyester)

Illustration of shuffling of chain segments (redrawn below):

Continued on next page
• If no removal of byproduct (H₂O)  
  ⇒ No net change in MW 
• Only if H₂O is removed during interchange will MW change (increase)  
  ⇒ Can be used to increase MW in the final form of a product
Real Industrial Processes

\[
\text{Diacid + Diol} \rightarrow \text{low MW polymers \{Crosslinked networks\}} \quad \text{Less need for high } \pi
\]

Making polyethylene terephthalate (PET) (polyester)

Trade names: Mylar®, Dacron®, Terylene®

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{OCH}_2\text{CH}_2 & \quad \text{n}
\end{align*}
\]

\[T_m = 270^\circ C\]

<table>
<thead>
<tr>
<th>High mechanical strength (from aromatic group rigidity)</th>
<th>{Ideal material for carpet, clothing, photographic substrates, Boil-in-Bag meals, PET Coke bottles}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tough (flexibility in backbone)</td>
<td></td>
</tr>
<tr>
<td>Partially crystalline (adds to toughness)</td>
<td></td>
</tr>
<tr>
<td>[\Rightarrow$9.5\text{ billion/}year]</td>
<td></td>
</tr>
</tbody>
</table>

\[\text{O} \quad \text{O} \quad \text{H}_2\text{C} \quad \text{H}_2\text{C} \quad \text{OH}\]

\[\text{Need high MW} \quad \text{Very slow} \quad \text{Very expensive} \quad \text{Instead...}\]

2-Step Process

1. dimethyl terephthalate

\[
\begin{align*}
\text{H}_3\text{COC} & \quad \text{O} \quad \text{COCH}_3 + 2 \quad \text{H}_2\text{C} \quad \text{C} \quad \text{OH} \\
\text{easy to purify, cheap} & \quad \text{ethyleneglycol (EG)}
\end{align*}
\]

\[
\text{HO} \quad \text{CH}_2\text{CH}_2 \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{OH} + 2 \quad \text{H}_3\text{COH} \quad \text{Methanol} \quad \text{(collect as it is dripped off)}
\]
T ~ 150 – 210 °C
P ~ 1 atm
Done in “solvent” of excess ethylene glycol (increase rate of forward rxn)
Detailed mechanism for above reaction:

2. T = 270°C – 280°C (increase T)
   Drip stops
   P = 0.5 – 1 torr (create vacuum)
   Drive off EG

Advantages:
1. Stoichiometry balance not needed (only one monomer)
2. Dimethyl ester more easily purified
3. Ester interchange k (rate constant) is larger than k for acid + alcohol (better kinetics)
4. removal of ethylene glycol (EG) is cleaner than H₂O removal
**Practical Example #2: Polyester anhydrides for Biodegradable polymer systems**

1. diacid + diol $\rightarrow$ oligomeric polyester

   $\text{HO}_n\text{O}^\text{R}_{\text{excess}}\text{O}^\text{R}^\prime\text{O}$

   $\text{HO}_n\text{O}^\text{R}_{\text{excess}}\text{O}^\text{R}^\prime\text{O}$

   “macromer”

2. form ester macromer dianhydride

   $\text{H}_3\text{C}_\text{O}^\text{O}^\text{CH}_3_{\text{acetic anhydride}}$ $\rightarrow$ $\text{H}_3\text{C}_\text{O}^\text{OH}_{\text{acetic acid byproduct}}$

3. melt condensation

   add heat

   $\text{polyester}$

   - ester groups: relatively hydrolysable
   - anhydride groups: can be even more hydrolytically susceptible
   $\Rightarrow$ degradable polymer
   $\Rightarrow$ alkyl esters, acids
Biologically Relevant Polymer Presentation

Definitions of Biologically Relevant Polymers:

- **Enzymatically degradable** – Polymer degrades through enzymatic breakdown in a biological (or ecological) environment (hydrolysis or oxidation catalyzed by enzyme).

- **Hydrolytically degradable** – Polymer undergoes hydrolytic degradation without assistance from enzyme under biologic conditions – often accelerated by pH or pH/temperature.

- **Bioresorbable or absorbable or resorbable** – Polymer breaks down into remnants that are natural products readily absorbed into the body, resulting in complete loss of original mass.

- **Biocompatible** – Polymer (degradable or not) does not cause a negative reaction or induce toxicity in the presence of or in contact with tissue, blood or organs


Poly α-hydroxyacids are hydrolytically degradable (PLLA, PDLA, PGA, PLGA)

Poly(hydroxyalkanoates), poly(alkylene dicarboxylates) are enzymatically degradable

Polycondensation of traditional monomer yields low molecular weight oligomer

Polycondensation of cyclic monomer yields high molecular weight material

Hydrophobic, hydrophilic nature determined by R groups

For example, -CH₂- groups affect hydrophobicity and make the polymer more difficult to degrade in water

Stereochemistry affects crystallinity.

Enzymatic breakdown dependent on ability of enzyme to adsorb to the PE macromolecule at appropriate sites.

Aliphatic polyesters typically undergo enzymatic breakdown via esterases such as lipase (used in body to break down triacylglycerols to fatty acid and glycerol)

Aromatic polyesters are too hydrophobic and too rigid to allow binding by enzyme.
Lipases often ineffective on PEs with optically active center (PHB, PLLA, etc.) – PHA depolymerase effective in some cases, others require hydrolytic degradation or other enzymes.

Factors in degradation rate: hydrophobicity, stereochemistry, bulkiness of side groups, and crystallinity.

Manipulate with primary monomer structure, copolymerization.

PGA, PLLA, PDLLA, and PCL have moderate glass transition temperature.

Can create libraries of molecules:

**Polyamides (Nylons)**

- Most common nylons:
  Nylon 6,6:

- aliphatic polyamides
  \[ \text{diamines} + \text{diacids} \]

\[
\begin{align*}
\text{NH}_2 & + \text{HOC} \quad \left\{ \begin{array}{c}
\text{Keq} \sim 10 - 100 \text{ (high rate of rxn)}
\end{array} \right.
\end{align*}
\]

**Commercial Syntheses**

1)

\[
\begin{align*}
\text{n} \quad \text{H}_2\text{N}-\left(\text{C}^2\text{H}_4\right)_6\text{NH}_3 & + \quad \text{HOC}-\left(\text{C}^2\text{H}_4\right)_4\text{COH} \\
\quad \text{conc'd} \quad \text{H}_2\text{O} & \rightarrow \left\{ \begin{array}{c}
\text{O} \quad -\text{OC}-\left(\text{C}^2\text{H}_4\right)_4\text{CO}^- \\
\text{H}_3\text{N}^+ \quad -\text{OC}-\left(\text{C}^2\text{H}_4\right)_6\text{NH}_3
\end{array} \right.
\end{align*}
\]

pKa ~ 9.0 basic
pKa ~ 5.0 acidic

“Nylon Salt”
Not nylon but precursor
proton exchange $\rightarrow$ salt

- 50% wt concentration in $H_2O$
- Adjust pH of solution by titrating acid/base monomer
  $\Rightarrow$ pH = 7.0 $\rightarrow$ stoichiometry r = 1.0
- If MW control desired, add monofunctional acid or amine

2) Salt solution concentration to a slurry
   - a concentrated solution containing particles (concentrated suspension)

   Raise T to $\sim 210^oC$, P = 250 psi (steam)
   Rxn proceeds at moderate rates (water $\rightarrow$ steam $\rightarrow$ ...)

3) As $p_n$ $\uparrow$, go to next stage:
   $T \uparrow$ to 275$^oC$ (above $T_m$ of Nylons)
   P $\downarrow$ to 1 atm $\rightarrow$ reduces $H_2O$

$\Rightarrow$ High MW with time/conversion

** One way to make a polyamide

Nylon6,6
- 50% crystallinity
- form flexible fibers: crystalline structures are strong
good H-bonding
- solvent resistance (Patagonia – clothing, carpets)

Differences in Reactivity

1. 

\[
\begin{align*}
\text{HO} & \text{R} \text{O} \text{OH} < & \text{R} \text{O} \text{O} & < & \text{Cl} \text{R} \text{O} \text{Cl} < & \text{Cl} \text{Cl}
\end{align*}
\]

diacids          acid anhydride          diacid chlorides (very reactive)

2. Also very reactive
3.

\[
\text{HO-} \text{R-} \text{OH} \quad \text{HO-} \text{RCH}_{2} \text{OH} \quad \text{RHN-} \text{R-} \text{NHR} \quad \text{H}_2 \text{N-} \text{R-} \text{NH}_2
\]

\( R = \text{alkyl} \)

For highly reactive species:

Ex: diacid chloride + diamine + diol \quad K_{eq} = 10^5 \sim 10^8

\[
\begin{align*}
\text{can treat these as irreversible} \\
\rightarrow \text{different reaction profiles and times}
\end{align*}
\]

- Kinetics can become diffusion controlled (stirring becomes more important)
- Highly exothermic (high \(\Delta H\))
- Need to consider heat transfer
- Short reaction times (relative to diol + diacid)

Most common:

\[
\begin{align*}
\text{O} & \quad \text{C-Cl} \quad + \quad \text{H}_2\text{N-} \quad \rightarrow \quad \text{O} \quad \text{CNH-} \quad + \quad \text{HCl} \\
\text{O} & \quad \text{C-Cl} \quad + \quad \text{OH} \quad \rightarrow \quad \text{O} \quad \text{CO-} \quad + \quad \text{HCl} \\
\text{N} & \quad \text{C-} \quad + \quad \text{OH} \quad \rightarrow \quad \text{N} \quad \text{CO-} \quad \text{no byproduct}
\end{align*}
\]
Far from equilibrium polymerizations:

Processing: Bulk reactions much less desirable
- extremely reactive, exotherms huge
- high concentrations further increase $R_p$

Better to use solution polymerization:
- can control heat removal, viscosity
- controlled by solvent choice (high capacity or low capacity solvent)

Must consider solvent effects:
- solubility of both monomers
- solubility of high MW polymer
  → wrong (poor) solvent can lead to low MW product

  e.g. polyisocyanate

\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{H}_2 \\
\text{C} \\
\text{N} \\
\end{array}
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{H}_2 \\
\text{C} \\
\text{N} \\
\end{array}
\]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Polarity</th>
<th>$\eta_{inh}$ (relative to MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hazardous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td></td>
<td>0.17</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td></td>
<td>0.36</td>
</tr>
<tr>
<td>DMSO (used in many biological systems)</td>
<td></td>
<td>0.69</td>
</tr>
</tbody>
</table>

For specific case of fast polymerization:
- low temps are often desired
  -40°C ~ 80°C
- large $\Delta H_{exo}$ ⇒ $T \uparrow$ can lower $\pi \downarrow$
- at good conditions, it is very easy to get 100% $\pi$
- lower concentrations
- slow addition of monomer(s) ⇒ control exotherm, prevent clumping
Alternatives to Solution Polymerization

Two Phase Polymerization

\[
\begin{align*}
\text{H}_2\text{O} \text{ (aqueous phase)} & \quad \text{H}_2\text{N}-\text{R-NH}_2 + \text{Base} \\
\text{CH}_2\text{Cl} \text{ (organic phase)} & \quad \text{O} \quad \text{O} \\
& \quad \text{Cl-C-R'-CCl}
\end{align*}
\]

Draw polymer from interface

Interfacial Polymerization:
1. Reactants diffuse to interface
2. Immediate reaction \(\rightarrow\) perfect stoichiometry at interface
   Form high MW polymer
3. Remove polymer \(\rightarrow\) fresh interface
Polymerization continues until monomer is depleted in organic and/or H\(_2\)O phases.

Key Differences
- Diffusion controlled (not kinetically)
- Bulk stoichiometry is irrelevant
- Treat 2 phases as reservoirs
- Higher concentrations in phases \(\rightarrow\) higher mass transfer driving forces
- \% conversion is not a factor in final MW

Details:
- addition of the base, HCl is generated

\[
\begin{align*}
\text{H}_2\text{N}–\text{R}–\text{NH}_2 & \quad \text{HCl} \\
& \quad \text{H}_3\text{N}–\text{R}–\text{NH}_3
\end{align*}
\]

unprotected amine is very reactive

non-reactive

Nonreactive bases:

\[
\begin{align*}
\text{Pyridine} & \quad \text{Na}_2\text{CO}_3
\end{align*}
\]

weak base

10.569, Synthesis of Polymers, Fall 2006
Prof. Paula Hammond

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Avoid bases with HO⁻ (e.g. NaOH)
Because they can react with acid Cl groups:

\[
\begin{align*}
\text{ClC–R–CCl} & \rightarrow \text{O} \quad \text{O} \\
\text{HO} & \rightarrow \text{HOC–R–CCl}
\end{align*}
\]

- generally true that diamine has higher diffusion rate in organic phase than diacid chloride in \( H_2O \) phase

-crystalline phase?

\[
\text{H}_3\text{N}–\text{R}–\text{NH}_3 \quad \text{H}_2\text{O} \\
\text{film is generated at underside of interface}
\]

→ organic solvent ⇒ precipitant
must precipitate only high MW polymer

Advantages:
- No need for heavy refrigeration or cooling
  (have very little T-increase, phases absorb exotherm)
- Get high MW without perfect conversions or stoichiometry
  rate of withdrawal affects MW
  when rate – formation of chain formation
- Rates of withdrawal, organic solvent choice
- No high-η medium
- Polymer is readily separated from solvent and unreacted monomers

Products made this way:
- aliphatic polyamides
- aromatic polyamides
- polycarbonates
- polysulfides
Stirred Interfacial

![Diagram of organic phase dispersed in aqueous phase with drops ranging from ~μm to 1 mm in size.]

- Slow stir rate: generate bubble encapsulating products
- Fast stir rate (shear): continuous removal of polymer from droplet, fine particles of polymer, shear can remove polymer film, fresh interface
- Example: Carbon-less carbon epoxy

Polycarbonates:

\[ \left( R - O - C - O \right)_n \]

formed from diol + carbonic acid

e.g.

- Phosgene (very reactive)
- Or

Not as fast but much safer reaction

diphenyl carbonate (much safer)
formed via stirred interfacial process
- high $T_g \sim 150^\circ C$
- non-crystalline (bulky CH$_3$ groups to prevent crystalline phase the aromatic groups would try to form)
  $\Rightarrow$ fully amorphous $\rightarrow$ optical clarity
- tough material
- application: CDs, optical lenses, glasses, windshields
Polyimides

\[ H_2N-R-NH_2 + O\left(\begin{array}{c} \text{R} \\ \text{C} \end{array}\right)CO \rightarrow \left(\begin{array}{c} \text{R} \\ \text{C} \end{array}\right)CON \]

Staged formation of Polyimides

Stage 1: Formation of polyamic acid

\[ H_2N-\text{O-}NH_2 + \text{HO-C-CO} \rightarrow H_2N-\text{O-}NH-\text{C-CO} \rightarrow \left(\begin{array}{c} \text{O} \\ \text{O} \end{array}\right)\text{CON} \]

- T ~ 30°C - 50°C
- B/c anhydride is reactive
- No side product
- Can CAST polyamic acid or SPIN into final form
- Relatively soluble in many solvents

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Stage 2: Cyclization
- reaction takes place in solid state or near solid state
- H₂O removal

\[ \text{I} \xrightarrow{- \text{H}_2\text{O}} \text{II} \]

\[ \text{III} \]

\[ \begin{align*}
\text{rigid} & \quad \text{rigid} \\
\text{Kapton®} & \quad \text{Pyralin®} \\
\text{Vespel®} &
\end{align*} \]

T > 150°C
Low P (vacuum)
Final product is intractable

**Aromatic Polyamides**

"Wholly" aromatic

\[ \left( \begin{array}{c}
\text{H} \\
\text{N-Ar} \\
\text{H-C-Ar} \\
\text{C}
\end{array} \right) \]

\[ \left( \begin{array}{c}
\text{H} \\
\text{N-Ar} \\
\text{C}
\end{array} \right) \]

\[ \left( \begin{array}{c}
\text{H} \\
\text{N-Ar} \\
\text{H-C-Ar} \\
\text{C}
\end{array} \right) \]

- very high stiffness, modulus
- high mechanical strength
- solvent resistance
- "performance" polymers
- hydrogen bonding + regular structure
  \[ \Rightarrow \text{very stable crystallites} \]

Ar = \[ \text{p-phenylene} \]

\[ \text{m-phenylene} \]

biphenyl

or

"aramids"
H-bonding
β sheets
⇒ semicrystalline
very high melting points
rigid backbones
⇒ liquid crystal phases in soln

Example:

\[
\begin{array}{cccc}
\text{Kevlar® (Dupont)}
\end{array}
\]

Compare to: high tensile steel

<table>
<thead>
<tr>
<th></th>
<th>Ultimate TS</th>
<th>(\varepsilon) at break</th>
<th>Energy at break</th>
<th>Weakness: Low compressive strength. (analogy: broom straws)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar 49</td>
<td>3.6 GPa</td>
<td>2.7%</td>
<td>25 MJ/m(^3)</td>
<td></td>
</tr>
<tr>
<td>High tensile steel</td>
<td>1.5 GPa</td>
<td>0.8%</td>
<td>6 MJ/m(^3)</td>
<td></td>
</tr>
</tbody>
</table>

How to react? (making aramids)

- Bulk melt: \(T_m\) way too high!
- Interfacial polymerization: possible

Get product as precipitate at interface
Works for partially aromatic polyamides
Solvent: solvate low + mod MW’s
Remain phase separated from \(H_2O\)

- Solution polymerization:

\[
\begin{align*}
\text{Cl} &= \text{H}_2\text{N} \\
\text{O} + \text{reactive groups} &
\end{align*}
\]

highly reactive – allows dilution

Reaction conditions:
\(T \approx 25^\circ\text{C} - 50^\circ\text{C}\) or lower
Add \(Li_2CO_3, Na_2CO_3, CaOH\)
Solvents: must be very polar, H-binding groups
Advantageous if also sol basic
⇒ neutralize HCl
Often add LiCl or other Li salts to solvent

⇒ aid in H-bond break-up

<table>
<thead>
<tr>
<th>Common Solvents:</th>
<th>CHCl₃</th>
<th>CH₂Cl₂</th>
<th>CH₃CN</th>
<th>Cl-CH₂-Br</th>
<th>DMAc</th>
<th>NMP</th>
<th>DMSO</th>
<th>Less polar</th>
<th>More polar</th>
</tr>
</thead>
</table>

Kevlar®:

- $T_m = 570^\circ C$
- $T_g = ?$
- $T_{deg} = 550^\circ C$ in N₂
- $E_o = 6000 \sim 8000 \text{ kg/mm}^2$

Slight Change: go from p (para) to m (meta) linkages

Branching and Network Formation

- So far: difunctional monomers: $f = 2$
- When monomer functionality $f \geq 3 \Rightarrow$

Examples:

1. $a-b + a\frac{1}{a} \rightarrow \text{branches}$

2. $a-b + a_f + b\frac{1}{b} \rightarrow \text{branches, then crosslinks}$

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3. $a - a + b - b + b_f \rightarrow$ branches, then crosslinks

4. $a_f + b_f \rightarrow$ branches, crosslinked networks
Network formation

Consider first case:

\[ a-b + a-a \]

\[ [a_3] \]

monomers so far have been difunctional

\[
\begin{align*}
H_2N-R-COH & \\
\begin{array}{c}
O \\
\end{array} & \\
\begin{array}{c}
\| \\
\end{array} & \\
\begin{array}{c}
O \\
\end{array} & \\
\begin{array}{c}
\| \\
\end{array} & \\
\begin{array}{c}
HOC-R'-COH \\
\end{array} & \\
\begin{array}{c}
O \\
\end{array} & \\
\begin{array}{c}
\| \\
\end{array} & \\
\begin{array}{c}
HO-R''-OH \\
\end{array} & \\
\end{align*}
\]

difunctional = 2 groups that can react (participate in rxn)

trifunctional:

\[
\begin{align*}
HO-R''-OH & \\
\end{align*}
\]

Always end in ‘a’ group

Forms branches, not crosslinks

What is the molecular weight or MW distribution?
(Peebles, Schaefgen, Flory) for \( a-b + a_r \) systems

\[
f = \text{func of } a_r
\]

\[
\pi = \text{conversion of } b\text{-groups (b=minority)}
\]

\[
r = \left( \frac{N_B}{N_A} \right)_0 \leq 1.0
\]

\[
\frac{p_n}{p_w} = \frac{fr\pi + 1 - r\pi}{1 - r\pi}
\]

\[
\frac{p_w}{p_n} = \frac{(f - 1)^2 (r\pi)^2 + (3f - 2)r\pi + 1}{(fr\pi + 1 - r\pi)(1 - r\pi)}
\]
Consider limit as $r \to 1.0$

\[
\lim_{r \to 1.0} \frac{p_w}{p_n} = 1 + \frac{1}{f} \left( r \to 1.0 \right) \left( \pi = 1.0 \right)
\]

Specific cases:
Let $f = 1$ ⇒ $a\overset{—}{b} + a\overset{—}{x}$

end capper

same as $a\overset{—}{b} +$ end capper

⇒ $z = 2.0$ ⇒ same result discussed for general difunctional systems

let $f = 2$ ⇒ $a\overset{—}{b} + a\overset{—}{a}$

linear polymer

$z = 1 + \frac{1}{2} = 1.5 \to$ narrower MWD

does this make sense?

Recall: $a\overset{—}{b} + a\overset{—}{a}$ :

Join 2 chains together with $a\overset{—}{a}$

Get rid of extremeties of MWD.

Longer chains are joined together with short chain.

Long chains can join with long chains but much less likely.

Consider an example with $a_t$:

1 mol $a\overset{—}{b} + 10^{-2}$ mol $a_3$:

(0.01)

$f = 3$

1 b group to 1.03 a groups

Note: for $r = 0.97$ and typical $a\overset{—}{b}$ polymerization:

\[
\frac{p_n}{p_w} = 66 = \frac{1 + r}{1 - r}
\]
\[ r = \frac{1}{1.03} \approx 0.97 \]

\[ p_n = \frac{3(0.97) - 0.97 + 1}{1 - 0.97} \approx 99 \]

**Systems forming networks**

Soluble fraction → "sol"
Polymer chains, oligomers, monomers not connected to network

Gel fraction → insoluble, intractable
⇒ constitutes network

Gel point: \( \pi \) at which an infinite network is formed \( \Rightarrow \pi_c \)

Above gel point \( \pi_c \):
\[ \text{gel fraction} \uparrow \]
\[ \text{sol fraction} \downarrow \]

Determine \( \pi_c \) as:
\[ \frac{p_n}{p_w} \to \infty \]

Carothers \[ p_n \to \infty \]

Consider simplest case:
Equal # of a,b functional groups

Define \( f_{AVG} = \frac{\sum N_i f_i}{\sum N_i} \)

\[ f_i = \text{functionality of given monomer} \quad f_i \geq 1.0 \]

\[ N_i = \text{# of molecules with } f_i \]

\[ \begin{array}{c}
3 \quad \text{HO-}\text{C-}\
\text{OH} \\
1 \quad \text{HO-CH}_2\text{CH-CH}_2\text{OH} \\
1.5 \quad \text{HOCH}_2\text{CH}_2\text{OH}
\end{array} \]

\[ f_{AVG} = \frac{3(2)+1(3)+1.5(2)}{3+1+1.5} = \frac{12.0}{5.5} = 2.18 \]

Can define conversion

\[ N_o = \text{initial # of monomer molecules} \]
\[ N = \text{# of remaining molecules} \]

Initial # of functional groups = \( f_{AVG} N_o \)
r=1.0 ⇒ 6 HCOH
6 OH

# of functional groups reacted = 2(N_o−N)

For each a—b reaction, lose 1a, 1b ⇒ 2 functional groups
For each a—b reaction, decrease # of molecules by 1

\[ \pi = \frac{\text{# of functional groups reacted}}{\text{total # of functional groups}} = \frac{2(N_o - N)}{N_o f_{AVG}} \]

\[ p_n = \frac{N_o}{N} \] (see original definition)

# avg degree of polymerization

Rearrange \( \pi \):

\[ N_o f_{AVG} \pi = 2N_o - 2N \]

\[ N_o (\pi f_{AVG} - 2) = -2N \]

\[ \frac{-2}{N_o} \pi f_{AVG} = 2 \]

\[ p_n = \frac{N_o}{N} = \frac{2}{2 - \pi f_{AVG}} \]

Universal expression
Carothers Equation
Works for all the cases, but \( f_{AVG} \) must be adjusted when \( r \neq 1.0 \)

Rearrange Carothers:

\[ \pi = \frac{2}{f_{AVG} - \frac{2}{p_n f_{AVG}}} \]

Consider gel point:

\[ p_n \rightarrow \infty \]

\[ \Rightarrow \pi_c = \frac{2}{f_{AVG}} \] \{ general expression for Carothers \}

\[ \text{more functionality} \rightarrow \text{gel at lower conversion} \]

e.g. \( f_{AVG} = 2.18 \)

\[ \pi_c = \frac{2}{2.18} = 0.92 \]

Consider less perfect case:

\[ f_{AVG} = \sum \frac{N_i f_i}{N_i} \text{ only time for } r = \left( \frac{N_o}{N_b} \right) = 1.0 \]

If \( r \neq 1.0 \) ⇒ only gain in increased MW + crosslinking when using \( -a + -b \)
(i.e. deficient group quantity determines how many of these reactions take place)
Excess of b only decreases $p_n$ by end capping
Count only a groups + 2

$$f_{AVG} = \frac{2\left(\sum N_{ai}f_{ai}\right)}{\sum N_i}$$

$f_{Ai} =$ function in - a of monomer i
$N_{Ai} =$ # of molecules of monomer i

Example:

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>$f_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>HOCH$_2$CH$_2$OH</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>O</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HOC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>COH</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>HOCH$_2$CH$_2$CHCH$_2$OH</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Enter body copy in Verdana 10.

$8b,7a$ deficient where $a = \text{OH}$

$\begin{array}{c}
\text{O} \\
\text{b} = \text{COH}
\end{array}$

$$f_{AVG} = \frac{2(N_a f_a + N_c f_c)}{N_a + N_b + N_c} = \frac{2(2(2) + (1)(3))}{2 + 4 + 1} = 2.0$$

$$\pi_c = \frac{2}{2.0} = 1.0$$

Only at full conversion do you form network.

$\pi_c > 1.0 \Rightarrow$ physically impossible to create network

Case of exact stoichiometry: doesn’t matter which is deficient.

Let $N_b = 3.5$

$$\pi_c = \frac{2}{2.15} = 0.93$$

Other case:

Flory-Stockmayer

$$p_n \to \infty$$

Generalized cases:
\[\pi_c = \frac{1}{\sqrt{\left\{f_{w,A} - 1\right\}\left(f_{w,B} - 1\right)\}}\]

\[f_{w,A} = \frac{\sum_i f_{A,i}^2 N_{A,i}}{\sum_i f_{A,i} N_{A,i}}\]

where \(f_{w,i}\) can be \(\geq 1.0\)

\[f_{w,B} = \frac{\sum_i f_{B,i}^2 N_{B,i}}{\sum_i f_{B,i} N_{B,i}}\]

\[r = \frac{\sum_i f_{A,i} N_{A,i}}{\sum_i f_{B,i} N_{B,i}} \leq 1.0\]

For our earlier example, \(\pi_c = 0.90\) \((N_B = 3.5)\)

Carothers: \(\pi_c = 0.93\)

Lower \(\pi_c\) → longest chains form more of infinite network
Building Macromolecules Step by Step

Step growth advantages:
- systematically build well-defined structures
- two examples:

**Dendrimers: regularly multibranched polymers with a common core**

- grow with core + func ≥ 2
- each incremental increase yields an exponential increase in MW, # of end groups
  "generation" → increment

Two approaches to making dendrimers:
1. Convergent synthesis
2. Divergent synthesis

**Dendrimer Divergent Synthesis**

\[ \text{Functional group x must be made inert or protected} \]

\[ \text{denotes: inactive} \]
Polyamidoamine dendrimers:

1. Michael addition:

\[ R-\text{NH}_2 + \text{H}_2\text{C}=\text{CHCOCH}_3 \rightarrow R-\text{N}-\text{CH}_2\text{CH}_2-\text{COCH}_3 \]

2. Amidation:

\[ \text{H}_2\text{N}-\text{CH}_2\text{CH}_2-\text{NH}_2 \rightarrow (\text{amidation}) \rightarrow \text{R-N} \]

Repeat 1 and 2 for each new generation.

Need core molecule:

Tomalia:
- \( \text{NH}_3 \) (trifunctional core)
- or
- \( \text{NH}_2-\text{CH}_2\text{CH}_2\text{CH}_2 \) (tetrafunctional core)

- can convert end group to other group to suit application

Dendrimer Convergent Approach
Repeat 1 and 2 to build dendron (branch).

3 After reaching desired dendron generation:

Convergent
+ block copolymers easily
+ purify between steps more easily

Divergent
- difficulty in purification
- potential for more defects due to stoichiometry
+ more readily adapted to commercial batch process
Frednet, Hawker, Wooley

\[
\text{BnO} \quad \begin{array}{c}
\text{Br} \\
\text{BnO}
\end{array} + \begin{array}{c}
\text{OH} \\
\text{HO}\end{array} \xrightarrow{\text{Williamson Coupling}} \begin{array}{c}
\text{BnO} \\
\text{BnO} \\
\text{BnO}
\end{array}
\]

\[
\begin{array}{c}
\text{K}_2\text{CO}_3 \\
\text{Crown Ether}
\end{array} \xrightarrow{\text{K}_2\text{CO}_3} \text{Crown Ether}
\]

\[
\text{Generation 2 (G-2)}
\]

Applications:
- Can be made into fullerenes
- Use benzene groups → electronic properties
- Metal particles trapped in structure
- Microelectronics, nanoparticles

Polypeptides: one step at a time

Build specific sequence:

\[
\begin{array}{c}
\text{H}_2\text{N} - \text{C} - \text{COH} \\
\text{CH}_3
\end{array} + \begin{array}{c}
\text{H}_2\text{N} - \text{C} - \text{COH} \\
\text{CH(CH}_3\text{)}_2
\end{array}
\]

alanine

valine

Sequence order is important.

R.B. Merrifield:
- Use of a solid support + protection group
- Polymer solid support: polystyrene in latex bead form (PS)
Protection of amino terminus:

\[ \text{t-butoxy carbonyl (t-boc)} \]

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{C-O-C=O} & \quad \text{H}_2\text{N-CH-COOH} \\
\text{t-boc} & \quad \text{protected amine}
\end{align*}
\]

For deprotection:

Use 25-50% trifluoroacetic acid (TFA) in CH\(_2\)Cl.

Add first amino acid:
Needs coupling agent to speed process:
- facilitate -NH₂ + -COOH rxn by increasing reactivity of -COOH
- dicyclohexylcarbodiimide (DCC)
→ activates COOH
Segmented Copolymers

Segmented Polyurethanes (Prof. Hammond’s thesis)

1. “soft segment” → ends in –OH groups
   - oligomer
   - low $T_g$ (liquid-like at 25°C)

\[
\text{HO} \quad \text{OH} \quad \text{HO--(CH}_2\text{)\text{4} \cdot \text{O--H}}
\]

Oligomeric diols

\[
\text{HO--CH}_2\text{O--Si--O--CH}_2\text{OH}
\]

Simple polyether

\[
\text{MW:} \quad \sim 1000 - 10,000
\]

2. Diisocyanate: (-N=C=O)
   
   e.g.
   
   \[
   \text{OCN-} \cdot \text{CH}_2\text{)}\text{6-} \text{NCO}
   \]

3. Chain extender
   - Connector between different units
   - Almost always short diol
   
   ex:
   
   \[
   \text{HO-(CH}_2\text{)}\text{n-} \text{OH}
   \]

To get segmented polyurethane:
1. Endcap soft segment w/diisocyanate:

\[
2 \text{OCN-} \cdot \text{R-} \cdot \text{NCO} + \text{HO--OH} \rightarrow \text{OCN-} \cdot \text{R-} \cdot \text{NCO}
\]

No byproduct
2. or

\[
\begin{align*}
onC &= NCO\quad + \quad \text{OCN}\quad \rightarrow \quad \text{Hard Segment} \\
&= NCO\quad + \quad \text{HOR'}\quad \rightarrow \quad \text{soft isocyanate chain extender}
\end{align*}
\]

\[
\begin{array}{|c|c|c|c|}
\hline
\text{soft} & \text{isocyanate} & \text{chain extender} & \text{Hard Segment} \\
\hline
1 & 2 & 1 & \text{Can be made longer by adding diol and diisocyanate in equal proportions} \\
1 & 3 & 2 & \text{Can be made longer by adding diol and disocyanate in equal proportions} \\
1 & 4 & 3 & \text{Can be made longer by adding diol and disocyanate in equal proportions} \\
- & - & - & \text{Can be made longer by adding diol and disocyanate in equal proportions} \\
- & - & - & \text{Can be made longer by adding diol and disocyanate in equal proportions} \\
\hline
\end{array}
\]

- held together by hydrogen bonds
- some degree of crystallinity
- \( T_m \) (flow temp)

Step Growth Polymerization

- 2\textsuperscript{nd} order kinetics
- MW \( \uparrow \) linearly with time (\( \overline{\mu} = 1 + [\theta] kT \))
- MW \( \propto \frac{1}{1 - \pi} \)
- All species in rxn bath are reactive
- Need high \( \pi \) for high MW
- monomer activation required for polymerization
- only activated monomer/polymer growing chains are active in rxn (\( \rho \) small fraction at given time)
- growing chains get large rapidly then terminate, deactivates chain
- new monomer is activated

Chain Growth (Addition)
\[ R^* + M \rightarrow RM^* \]
\[ RM^* + M \rightarrow RMM^* \]

- have only monomer growing chains
- high MW polymer
- \( MW \neq f(\pi) \) unless “living” system

Addition monomers are:

- vinyl groups (C=C)
- ketones (C=O)
- aldehydes
- heterocyclic ring monomers (strained)

Propagating (active) species:

- anionic
- cationic
- free radical

Processes in Addition Polymerization:

1. Initiation
2. Propagation
3. Termination
4. Transfer of charge or active species from one chain to another
Free Radical Polymerization

Kinetics: \( I \rightarrow 2R^* \)

1. Initiation:

\[
R^* + H_2C=CH \rightarrow R^*H_2C\overset{H}{\underset{H}{\cdot}}C\overset{R'}{\underset{R'}{\cdot}} \quad \text{initiation fragment}
\]

2. Propagation Step:

\[
RM^* + M \rightarrow RM_2^*
\]

\[
RM_n^* + M \rightarrow RM_{n+1}^*
\]

\[
R\overset{H_2}{\underset{H}{\cdot}}C\overset{H}{\overset{R'}{\underset{R'}{\cdot}}C} + H_2C\overset{CHR'}{\underset{R'}{\cdot}} \rightarrow R\overset{H_2}{\underset{H}{\cdot}}C\overset{H_2}{\overset{R'}{\underset{R'}{\cdot}}C\overset{H}{\overset{R'}{\underset{R'}{\cdot}}C}}
\]

3. Termination:

Happens one of 2 ways:

a. coupling

\[
RM_n^* + RM_p^* \rightarrow RM_{n+p}^* \quad \text{R doubling size of polymer}
\]

b. disproportionation

\[
\overset{\text{ktd}}{\text{C}}\overset{\text{H}}{\underset{\text{H}}{\text{R'}}} + \overset{\text{C}}{\text{H}}\overset{\text{CH}}{\underset{\text{R'}}{\text{R'}}} \rightarrow \overset{\text{C}}{\text{H}}\overset{\text{CH}}{\underset{\text{R'}}{\text{R'}}} + \overset{\text{C}}{\text{H}}\overset{\text{CH}}{\underset{\text{R'}}{\text{R'}}}
\]

4. Chain Transfer:
Kinetic Rate Expression

Initiation:
\[ \text{I} \xrightarrow{k_d} 2 \text{R} \cdot \quad \text{dissociation (rate determining)} \]
\[ \text{R} \cdot + \text{M} \longrightarrow \text{RM} \cdot \]
\[ \frac{d[\text{RM} \cdot]}{dt} = \int \frac{d[\text{R} \cdot]}{dt} \]
\[ \text{efficiency factor} \]
\[ \frac{d[I]}{dt} = k_d[I] = \frac{1}{2} \frac{d[\text{R} \cdot]}{dt} \]
\[ \text{create 2 fragments} \]
\[ \frac{d[\text{RM} \cdot]}{dt} = f \int \frac{d[\text{R} \cdot]}{dt} = 2f k_d[I] k_d \sim 10^{-4} - 10^{-6} \frac{l}{\text{mol} \cdot \text{sec}} \]

Propagation
\[ \text{RM}_n \cdot + \text{M} \longrightarrow \text{RM}_{n+1} \cdot \]
\[ R_p = \frac{d[M]}{dt} = k_p[M \cdot][M] \]
\[ [M \cdot] = [M_n \cdot] \text{ any active monomer} \]
\[ \text{(assume equal reactivity for all M \cdot species)} \]
\[ k_p \sim 10^{2} - 10^{4} \frac{l}{\text{mol} \cdot \text{sec}} \]

Termination
\[ \text{M}_i \cdot + \text{M}_j \cdot \longrightarrow \text{M}_{i+j} \]
\[ R_i = -\frac{d[M\cdot]}{dt} = 2k[M\cdot]^2 \]

assume same disproportionation:

let \( k_i = k_{i_c} + k_{i_d} \)

\[ k_t \sim 10^6 - 10^8 \text{ mol}^{-1}\text{sec} \]

How fast are you creating polymer?

**Polymerization rate**

\[ -\frac{d[M\cdot]}{dt} = R_p = k_p[M\cdot][M] \]

Assume steady state free radical concentration \([M\cdot]\)

\[ \Rightarrow R_i = R_t \]

\[ 2k_i[M\cdot]^2 = 2k_{i_d}f[I] \]

Solve for \([M\cdot]:\)

\[ [M\cdot] = \left(\frac{k_{i_d}f[I]}{k_i}\right)^{\frac{1}{2}} \text{ plug into } R_p \text{ expression} \]

\[ R_p = k_p \left(\frac{k_{i_d}f[I]}{k_i}\right)^{\frac{1}{2}}[M] \]

Generic Form:

\[ R_p = \left(\frac{k_p^2}{2k_i}R_i\right)^{\frac{1}{2}}[M] \]
How to determine MW in free radical polymerization

**Kinetic Chain Length**

\[ \nu = \text{# of monomers added per effective free radical} \]

\[ \nu = \frac{\text{rate of chain growth}}{\text{rate of chain initiation}} = \frac{\text{rate of chain growth}}{\text{rate of chain termination}} \]

\[ \nu = \frac{R_p}{R_i} = \frac{k_i[M]}{2(fk_d k_i [I]/)^{1/2}} \]

\[ \bar{p}_n = \nu \text{ if termination is by disproportionation process} \]

\[ \bar{p}_n = 2\nu \text{ if termination is by coupling} \]

Generally, (if no chain transfer):

\[ \bar{p}_n = 2a\nu \text{ where } 1/2 \leq a \leq 1 \]

100% disproportionation

100% disproportionation

\[ \bar{M}_n = M_a \cdot \bar{p}_n \]

molecular weight of vinyl monomer unit

What happens more often?

- Coupling usually greater than disproportionation
- Percent of coupling increases if: steric factors prevent effective coupling:

![Steric factors diagram](image)

or if: \(\beta\)-hydrogens are more reactive:
Consider

\[ \nu = \frac{k_p [M]}{2(fk_d k_i [I]^2) \sigma} \]

\[ R_p = k_p \left( \frac{f k_p [I]}{k_i} \right)^{\frac{1}{2}} [M] \]

Increase \( R_p \) by: \([M]^\uparrow, [I]^\uparrow\)

But increase \( \nu \rightarrow [M]^\uparrow, [I]^\downarrow \)

Thus you want to increase \([M]\)

**Chain Transfer**

1. \( \text{Mn} \cdot + \text{X'} - Y \xrightarrow{k_{tr}} \text{Mn-X'} + Y \), \( k_{tr} = \text{transfer constant} \)

Chain transfer can occur when there are solvent impurities. But sometimes using chain transfer can be advantageous.

2. \( \text{Y} - + \text{M} \xrightarrow{k_a} \text{YM} \cdot \)

3. \( \text{YM} \cdot + \text{M} \xrightarrow{k_p} \text{YMn} \cdot \)

Chain transfer agent \( \rightarrow \text{CTA} \)

Used to decrease MW in polymerization

\( k_p \gg k_{tr} \) and \( k_p \approx k_a \Rightarrow R_p \) is the same \( \overline{P_n} \downarrow \)

slightly \( \rightarrow \) moderately

depending on CTA

\( k_p \ll k_{tr} \) and \( k_p \approx k_a \Rightarrow R_p \) same \( \overline{P_n} \downarrow \) dramatically

\( k_p \gg k_{tr} \) and \( k_a < k_p \Rightarrow R_p \downarrow \) slightly and \( \overline{P_n} \downarrow \) slightly

\( k_p \ll k_{tr} \) and \( k_a < k_p \Rightarrow R_p \downarrow \) drastically and \( \overline{P_n} \downarrow \) drastically

**Transfer Types:**

1. to monomer: \( k_{tr,m} \quad \text{Mn} \cdot + \text{M} \rightarrow \text{M}_n + \text{M} \).

2. to solvent or impurity \( k_{tr,s} \quad \text{Mn} \cdot + \text{S} \rightarrow \text{M}_n + \text{S} \).
or CTA

3. to initiator: \( k_{tr,I} \) \[ M_n + I \rightarrow M_n + I. \]

All act to decrease \( p_n \): (assume coupling)

\[
\frac{1}{p_n} = \frac{R_i}{2R_p} + \frac{R_{tr,m} + R_{tr,s} + R_{tr,I}}{R_p} = \frac{R_i}{2} + k_{tr,m}[M \cdot I] + k_{tr,s}[M \cdot S] + k_{tr,I}[M \cdot I]
\]

Use resistor analogy: (resistors in series)

\( C = \) transfer constant

\( C_m = \frac{k_{tr,m}}{k_p} \), \( C_s = \frac{k_{tr,s}}{k_p} \), \( C_I = \frac{k_{tr,I}}{k_p} \)

since \( R_p = k_p[M \cdot I][M] \)

\[
\frac{1}{p_n} = \frac{R_i}{2R_p} + C_m + C_s \left[ \frac{S}{M} \right] + C_I \left[ \frac{I}{M} \right]
\]

Additive effect of each constant

\[
\frac{R_i}{2R_p}
\]

\[
\left( \frac{1}{p_n} \right) \leftrightarrow \frac{1}{2v}
\]

Often only have transfer to CTA (or impurity)

\[
\frac{1}{p_n} = \frac{R_i}{2R_p} + C_s \left[ \frac{S}{M} \right]
\]

\[
\left( \frac{f_{tr,I}}{k_p[M]} \right)^{1/2} = \frac{1}{2v}
\]
For a given amount of initiator [I] and monomer [M]

\[ \frac{1}{P_n} = \frac{1}{P_{n0}} + C_s \frac{[S]}{[M]} \]

Useful to control MW is free radical with high \( k_p \) and/or really low \( k_t \)

C\(_s\) values for different compounds:
- alkanes (weakest)
- cyclic hydrocarbons
- benzenes, aromatics

Increasing radical stability

\[
\text{weakest} < \text{alkanes} < \text{cyclic hydrocarbons} < \text{benzenes, aromatics}
\]

High C\(_s\) values:
- weak C—H bonds
- stabilized by conjugation

- weak C—Cl, C—Br, C—I
\[
\begin{align*}
R-\overset{\Cl}{\underset{H}{C}} - \overset{R}{\underset{\cdot}{C}} & \quad \overset{R}{\underset{\cdot}{C}} \quad \overset{R}{\underset{\cdot}{C}} + \overset{R}{\underset{\cdot}{C}} \\
\text{weak S—S bonds, S—H} & \\
\text{weakest} & \\
\text{largest C}_5 & 
\end{align*}
\]

<table>
<thead>
<tr>
<th>CTA (chain-transfer-agents)</th>
<th>(C_S \times 10^4) for styrene</th>
<th>(C_S \times 10^4) for Vinyl acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.023</td>
<td>1.2</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.031</td>
<td>7.0</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.42</td>
<td>17.0</td>
</tr>
<tr>
<td>n-butyl alcohol</td>
<td>1.6</td>
<td>20.0</td>
</tr>
<tr>
<td>(\text{CHCl}_3) (chloroform)</td>
<td>3.4</td>
<td>150.0</td>
</tr>
<tr>
<td>Tri-methyl amine</td>
<td>7.1</td>
<td>370</td>
</tr>
<tr>
<td>n-butyl mercaptan</td>
<td>210,000</td>
<td>480,000</td>
</tr>
</tbody>
</table>

\[\overset{\text{SH}}{\underset{\text{SH}}{\text{SH}}}\]
Energetics

General Equation

\[ k = A e^{\frac{-E}{RT}} \]

\[ \ln k = \ln A - \frac{E}{RT} \]

For thermal decomposition of initiator

\[ R_p = k_p [M][M] = k_p \left( \frac{k_d}{k_t} \right)^{1\over2} f^{1\over2}[M][I]^{1\over2} \]

net rate "fudge factor"

Arrhenius expression:

\[ \ln \left[ k_p \left( \frac{k_d}{k_t} \right)^{1\over2} \right] = \ln \left[ A_p \left( \frac{A_d}{A_t} \right)^{1\over2} \right] = \ln \left[ \frac{E_p + E_d - E_t}{RT} \right] \]

constant w.r.t. Temp

\[ E_p = \text{activation energy for propag. step} \]

\[ \left[ E_p + \frac{E_d - E_t}{2} \right] \text{is activation energy for polymerization} \]

\[ E_R = E_p + \frac{E_d - E_t}{2} \]

Overall:

\[ \ln R_p = \ln \left[ A_p \left( \frac{A_d}{A_t} \right)^{1\over2} \right] + \ln \left[ f[I]^{1\over2}[M] \right] - \frac{E_R}{RT} \]
Sample Values of $E_p$ and $E_t$ in kJ/mol

<table>
<thead>
<tr>
<th>Monomers</th>
<th>$E_p$ (kJ/mol)</th>
<th>$E_t$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl chloride</td>
<td>16</td>
<td>17.6</td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>29.7</td>
<td>22.2</td>
</tr>
<tr>
<td>Methyl metacrylate</td>
<td>26.4</td>
<td>11.9</td>
</tr>
<tr>
<td>Styrene</td>
<td>26.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initiator</th>
<th>$E_d$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIBN</td>
<td>123.4</td>
</tr>
<tr>
<td>Acetyl Peroxide</td>
<td>136</td>
</tr>
<tr>
<td>Benzoyl Peroxide</td>
<td>124.3</td>
</tr>
</tbody>
</table>

On Average: $E_p \sim 20 - 30$  
$E_t \sim 10 - 15$  
$E_d \sim 100 - 150$  
$\Rightarrow E_R = E_p + E_d/2 - E_t/2$  
is dominated by $E_d$  
$E_R \sim 80 - 90$ kJ/mol

Because $R_p$ is a positive number $\rightarrow$ positive activation energy
If $T \uparrow$, $k \uparrow$

e.g. if $T \uparrow \sim 10^\circ C$, $R_p \uparrow$ by 2-3x  
(rate of polymerization increases by 2 or 3 times)

What about $\bar{p}_n$?  
(assume no chain transfer)

$$\bar{p}_n = 2a\nu$$

let $a = 1$ (coupling)

$$\bar{p}_n = 2\nu = \frac{k_p [M]}{(k_d k_i [I])^{\frac{1}{2}}}$$

$$\ln p_n = \ln \left[ \frac{A_p}{(A_d A_i)^\frac{1}{2}} \right] + \ln \left[ \frac{[M]}{([I])^{\frac{1}{2}}} \right] - \frac{E_p}{RT} \left[ \frac{E_d}{2} + \frac{E_t}{2} \right]$$

$\Rightarrow$ on average, get negative value for [ ] E term

$$\Rightarrow \left[ \frac{E_p}{RT} \right]$$ is negative
Thermodynamics

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

should be negative for polymerization to take place

1. \( \Delta H \) → strongly exothermic rxns
   \( \Delta H_p \) (enthalpy of propagation) → ~ -160 to -60 kJ/mol

2. \( \Delta S \) → lose entropy with polymerization
   \( \Delta S \) → ~ -90 to -120 J/(mol·K)

   or -0.09 to -0.12 kJ/(mol·K)

Usually \( \Delta H \) is much larger than \( T \Delta S \) term

\( \Rightarrow \) negative \( \Delta G \) (thermodynamically favorable to polymerize)

At certain Temp range, its possible for \( \Delta G \to 0 \)

\( \Rightarrow \) get near equilibria conditioning

\[ \underset{\text{M} \cdot}{\text{M}} + \text{M} \xrightleftharpoons[\text{k}_{d_p}]{\text{k}_p} \underset{\text{MM} \cdot}{\text{M}} \]

depropagation rate constant

At equilibrium (or near):

\[ - \frac{d[M]}{dt} = (k_p [M] - k_{d_p} )[M \cdot] \]

at equilibrium = 0

\[ K_{eq} = \frac{[M_{n+1} \cdot]}{[M_n \cdot][M]} \] and \([M_n \cdot]\) approx. equal

\[ \frac{1}{[M]} = \frac{k_p}{k_{d_p}} \]
\[
[M_{eq}] = \frac{k_{dp}}{k_p} = \frac{1}{K_{eq}}
\]

equilibrium monomer concentration at a given temp

Will always define with respect to monomer conc or temperature.

Standard States Defns:

\[\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq}\]
\[\Delta G = \Delta G^\circ + RT \ln K_{eq} = 0\]
\[\Delta H^\circ - T\Delta S^\circ = -RT_c \ln\left[\frac{M}{[M]_{eq}}\right] = RT_c \ln[\text{M}_{eq}]\]

Solve for T:

\[T_c = \frac{\Delta H^\circ}{\Delta S^\circ + R \ln[M]_{eq}}\]

"ceiling temp" \ [M]_{eq} defined as ratio: \ [\text{E}\] Equilibrium monomer conc \ [\text{S}] Standard state monomer conc

= highest T for polymerization to occur \ [\text{S}]= 1 M soln (or bulk conc’n)

\[\ln\left[\frac{[M]}{[M]_r}\right] = \ln[M]_{eq} = \frac{\Delta H^\circ}{RT_c} - \frac{\Delta S^\circ}{R}\]

determine \ [M]_e from T

ceiling temperature term when no monomer conc is specified, is usually assuming that \ [M]_e = [M]_{\text{bulk}}
<table>
<thead>
<tr>
<th>Examples</th>
<th>$[M]_c$ (M)</th>
<th>$T_c$ (assuming bulk monomer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl acetate</td>
<td>$1 \times 10^{-4}$</td>
<td>--</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>--</td>
<td>220°C</td>
</tr>
<tr>
<td>$\alpha$-methyl styrene</td>
<td>2.2</td>
<td>61°C</td>
</tr>
</tbody>
</table>
Thermodynamics (Continued)

\[ \Delta H^o - T \Delta S^o = \Delta G^o = -RT \ln K_{eq} \]

\[ \Delta G = \Delta G^o + RT \ln K_{eq} \quad \text{in general} \]

but at equilibrium:

\[ \Delta G = 0 = \Delta G^o + RT \ln K_{eq} \]

so \( \Delta H^o - T_c \Delta S^o = -RT_c \ln \left[ \frac{1}{[M]_c} \right] \) at equilibrium

where \([M]_c = \text{ceiling monomer con’c}\)

Solve for \(T_c\):

\[ T_c = \frac{\Delta H^o}{\Delta S^o + R \ln [M]_c} \]

\([M]_c = \frac{[M]_{eq}}{[M]^o} \quad \text{Equilibrium} \]

\([M]^o \Rightarrow \text{bulk concentration of monomer or 1 mol/L (depending on who’s defining it)} \]

We will use 1 mol/L

Susceptible polymers for “unzipping”

Carbonyl: \( CH_2=O \)

\( \text{e.g.} - (CH_2-O) \) unzips to form formaldehyde

\( CH_3-CH=O \)

\( CCl_3-CH=O \) \( \text{Other carbonyls} \)

Cyclics:

\( \text{THF} \)

\( \text{trioxane} \)

unzips via \( \left( C^2-O \right)_n \) as well
<table>
<thead>
<tr>
<th>Monomer</th>
<th>([M]_c ) @ 25°C (mol/L)</th>
<th>(T_c) (pure monomer) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl acetate</td>
<td>(\text{H} = \text{O} = \text{C})</td>
<td>(1 \times 10^{-9})</td>
</tr>
<tr>
<td>CH(<em>3)C(</em>=)O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl metacrylate (MMA)</td>
<td>(\text{H}_3\text{C} = \text{O})</td>
<td>(1 \times 10^{-3})</td>
</tr>
<tr>
<td>CH(<em>3)CH(</em>=)O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha)-methyl styrene</td>
<td>(\text{C} = \text{C})</td>
<td>(2.2)</td>
</tr>
</tbody>
</table>

### Polydispersity Index (PDI) for Free Radical Polymerization

\[
\nu = \frac{R_p}{R_t} = \frac{k_p[M]}{k_i[M]} = \frac{k_p[M]}{(2k_d f k_i[I])^{1/2}}
\]

\[
\overline{p}_n = 2a \nu
\]

#### Statistical Approach

- \(p\) = probability of growth of polymer chain  
  = "propagation probability"

\[
p = \frac{k_p[M]}{k_p[M] + 2k_i[M]} = \frac{R_p}{R_p + R_t(1 + R_p)}
\]

if needed (for chain transfer)

\(1-p\) = probability of chain termination

\[
1-p = \frac{2k_i[M]}{k_p[M] + 2k_i[M]}
\]

\(X_i\) = number fraction of radicals having reached degree of polymerization = \(i\)

\[
X_i = p^{(i-1)}(1-p)
\]

for chain end
\[
p_n = \frac{\sum_{i=1}^{\infty} iX_i}{\sum_{i=1}^{\infty} Xi} = \sum_{i=1}^{\infty} iX_i = (1 - p)\sum_{i=1}^{\infty} ip^{i-1} \quad \text{apply series definition}
\]

\[
\Rightarrow \quad p_n = \frac{1}{1 - p} \quad \left\{ \begin{array}{l}
\text{here } p \neq \pi \text{ as in step growth}
\end{array} \right.
\]

now \( p = \frac{R_p}{R_p + R_t} \)

\[
p_n = \frac{1}{1 - p} = \frac{R_p + R_t}{R_t}
\]
as \( p \to 1.0 \) (i.e. \( R_p \gg R_t \))

\[
\Rightarrow p_n \to \nu
\]

\[
\Rightarrow \quad p_n \to \frac{R_p}{R_t}
\]

\[
p_w = \sum iWi = \sum i^2X_i = \sum \frac{i^2X_i}{p_n} \quad \text{apply series defn}
\]

weight fraction

\[
\Rightarrow \quad p_w = \frac{1 + p}{1 - p}
\]

PDI: \( z = 1 + p \) \( \equiv \) disproportionation \( \quad \text{as } p \to 1.0 \)
\( z \to 2.0 \)

This all assumes termination by disproportionation
If we assume coupling, account for \(-X \cdot Y-\)

\[
\Rightarrow \quad p_n = \frac{2}{1 - p}
\]

\[
p_w = \frac{2 + p}{1 - p}
\]

\[
z = \frac{p_w}{p_n} = \frac{2 + p}{2} \quad \left\{ \begin{array}{l}
\text{as } p \to 1.0 \quad z \to 3/2
\end{array} \right.
\]
Instantaneous vs. Integrated Rate Expressions

\[ R_p = k_p \left( \frac{f_k d}{k_i} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} [M] = -\frac{d[M]}{dt} \]  
instantaneous expression

Express things in terms of \( \pi \) (monomer conversion)

\[ \pi = \frac{[M]_o - [M]}{[M]_o} = 1 - \frac{[M]}{[M]_o} \]

\[ \frac{d\pi}{dt} = -\frac{1}{[M]_o} \frac{d[M]}{dt} \]

\[ \frac{d\pi}{dt} = k_p \left( \frac{f_k d}{k_i} \right)^{\frac{1}{2}} [I]^{\frac{1}{2}} [1 - \pi] \]

integrate assuming a constant \( [I] = [I]_o \)

\[ \pi(t) = 1 - \exp \left[ -k_p \left( \frac{f_k d}{k_i} \right)^{\frac{1}{2}} [I]_o t \right] \]

so applies to batch polymer \( [M] \downarrow \)
but \( [I] \) constant \( \Rightarrow \) e.g. early stages of polymer

If \( [I] \) is not held constant:

\[ \frac{d[I]}{dt} = -k_d [I] \]

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

\[ \frac{d\pi}{dt} = k_p \left( \frac{f_k d}{k_i} \right)^{\frac{1}{2}} [I]_o \frac{1}{2} \exp\left( -\frac{k_d t}{2} \right)(1 - \pi) \]

Integrate from \( t=0 \) to \( t \):

\[ \pi_t = 1 - \exp \left\{ \left( \frac{2k_p}{k_d} \right) \left( \frac{f_k d}{k_i} \right)^{\frac{1}{2}} \left[ I \right]_o \frac{1}{2} \exp\left( -\frac{k_d t}{2} \right) - 1 \right\} \]

global expression: time of conv \( \rightarrow \) conv at that time
\([M], [I] \downarrow \Rightarrow R_p \downarrow\)

Max conversion is batch situation:

Let \(t \rightarrow \infty\)
So that all of I is consumed

\[
\pi_{\text{max}} = 1 - \exp\left\{-\left( \frac{2k_p}{k_d} \right) \left( \frac{f k_d}{k_t} \right)^{\frac{1}{2}} \right\} \left[ I \right]^{\frac{1}{2}}
\]

e.g. Polystyrene, 1 wt% AIBN

\(\Rightarrow \pi_{\text{max}} = 96.7\%\)

\(\overline{p_n} = f(t)\) \(\overline{p_n}\) becomes fxn of time

\[
\overline{p_n}(t) = \frac{R_p(t)}{R_i(t)} \quad \leftarrow [M] \quad \leftarrow [I]
\]

Time avg value:

\[
\langle \overline{p_n}(t) \rangle = \frac{\text{tot mol of monomer polym}}{\text{tot mol of "dead" chains (formed)}} = \frac{a[M]_o \pi(t)}{f[I]_o \left(1 - \exp(-k_d t)\right)}
\]

\(\langle \overline{p_n} \rangle\)

\(\pi \rightarrow\)
**Tromsdorff Effect (or Auto-acceleration)**

- Auto-acceleration usually occurs in radical chain polymerizations and normally in bulk polymerization.
- As conversion (\(\pi\)) increases, the viscosity (\(\eta\)) increases so much that the ends cannot find each other to terminate polymerization. This in turn lowers the effective termination rate (\(k_{t,\text{eff}}\)) and termination rate (\(R_t\)) and thus, the average number weight of polymerization \(\overline{P}_n\) increases. In other words:

  \[
  \pi \uparrow \rightarrow \eta \uparrow \rightarrow k_{t,\text{eff}} \downarrow \rightarrow R_t \downarrow \rightarrow \overline{P}_n \uparrow
  \]

- In auto-acceleration,
  - There is no change in \(k_d\) because there are small molecules
  - There is no change in \(k_p\) because of small molecules as well
  - But for \(k_t\), the rate of termination decreases because the two growing chain ends cannot find each other.

- We know from previous lecture that the rate of polymerization is:

  \[
  R_p = k_p \left( \frac{2k_d f[I]}{k_i} \right)^{1/2} [M]
  \]

  And the number average degree of polymerization is:

  \[
  \overline{P}_n = 2 a \nu \quad \text{where } \frac{1}{2} \leq a \leq 1
  \]

  \[
  a = 1 \text{ for coupling}
  \]

  \[
  a = \frac{1}{2} \text{ for disproportionation}
  \]

  Where \(\nu\) is the number of monomers added per effective free radical and given by:

  \[
  \nu = \frac{k_p[M]}{(2k_d f[I])^{1/2}}
  \]

- See Figure 3-15 in Odian for a plot that demonstrates autoacceleration.

**Emulsion Polymerization**

*(See handout: Ch. 12)*

- In emulsion polymerization there are some key "ingredients":
  - The monomer must be insoluble in water and polymerizable by free radicals
  - Water-soluble initiator
  - Water
  - Surfactant
**Formation of micelles**

In water, soap (e.g. sodium palmitate) is added to the aqueous phase. For example: \( \text{CH}_3(\text{CH}_2)_n\text{COO}^- \text{Na}^+ \)

The surfactant forms micelles at high concentrations:

**Add monomer and disperse as droplets**

- large monomer drops (~mm)
- micelle with monomer (1Å to 0.1μm) and initiator (I)
- empty micelle

- The initiator (I) can diffuse into the micelle particle and polymerize the monomer
- More monomer from the droplet diffuses over and polymerizes
- Thus the particle size increases
**The three stages of emulsion polymerization:**

**Stage I:**
- The monomer diffuses to the empty micelle from droplet
- Polymerization initiated in micelles to become polymer particles
- New particles are generated as micelles are consumed
- This stage lasts for conversion $\pi \sim 0\text{-}15\%$

**Stage II:**
- No more surfactant available to generate new particles
- Monomer diffuses into now a constant number of particles to maintain some equilibrium $[M]$ with the particle
- The monomer reservoir drops get slowly consumed
- An equilibrium between increasing interfacial tension within micelle and monomer/polymer dilution leads to a constant volume fraction where $\Phi_2$ is the volume fraction of the polymer and $\Phi_1$ is the volume fraction of the monomer

$$[M] = [M]_0(1 - \Phi_2)$$

**Stage III:**
- This stage occurs when conversion $\pi \sim 40\text{-}60\%$
- All the monomers exist in particles

---

10.569, Synthesis of Polymers, Fall 2006  
Prof. Paula Hammond  
Lecture 14  
Page 3 of 5  

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
The monomer droplets are exhausted
- [M] in particles continually decreasing as π increases
- Particle size is constant
- Conversion rate can reach up to 80-100%

**Smith-Ewart Model**
- The Smith-Ewart model states that one radical diffuses into a particle at a time and termination occurs when another radical R• diffuses in:

![Diagram of Smith-Ewart model](image)

- There is 1-100 seconds between radical entry events

Why does polymerization happen in the particle rather than the droplet? Answer: Large polymer particles have a much lower surface area to volume ratio than the small droplets. The probability of a free radical entering a droplet versus a micelle particle is very small.

**Kinetics:**
- Assumptions:
  - All radicals enter the micelle
  - When radical enters a particle, there is instant initiation if there are no other radicals present. If there is a radical already present, termination occurs
- The number of monomer molecules converted to polymer per second per particle is given by:

\[
- \frac{dm}{dt} = \frac{1}{2} k_p [M] = \frac{\text{monomers}}{\text{sec} \cdot \text{radical}}
\]

½ because the chain grows half the time (the other ½ is to terminate the polymer)

**Initiators**
- Rate of production of initiator radicals is given by:

(Ch. 12.1.3, p. 251 in handout)
\[ \rho = \frac{N_d}{10^4} (1 - \Phi) k_d \tau [X][Y] = \frac{\text{radicals}}{\text{cm}^3 \cdot \text{sec}} \]

Where \( \Phi \) is the organic (monomer) volume fraction

\( k_d \tau \) is the \( k_d \) for the radical

\([X]\) and \([Y]\) are the concentration of the redox initiators

- The number of particles in solution is given by:

\[ n = \left( \frac{\text{# of particles}}{\text{cm}^3} \right) \]

\[ n = (0.53)(c_s a_s)^{3/5} \rho^{2/5} \left( \frac{dv}{dt} \right)^{-2/5} \]

Where \( c_s \) is the concentration of the surfactant

\( a_s \) is the area of the surfactant head group

- Define \( \Delta t \) as the time between R\textsuperscript{•} entry:

\[ \Delta t = \frac{n}{\rho} \text{ is usually 1-100 sec} \]

\[ p_n = k_p [M] \Delta t = k_p [M] \frac{n}{\rho} \]
Lecture 15: Processing Approaches: Suspension (bead) Polymerization Processes, Polyvinyl Chloride via Precipitation Polymerization, Polyethylene via Radical Polymerization

Rate of conversion, emulsion polymerization

\[
\overline{p_n} = k_p [M] \Delta t = k_p [M] \frac{N}{\rho}
\]

In general,

\[
R_p = \frac{n}{2}
\]

\[
-\frac{dm}{dt} = \frac{1}{2} k_p [M]
\]

\[
R_p = \frac{n}{2} k_p [M]
\]

\[
\rho \text{ (radicals)}
\]

\[
\overline{p_n} = k_p [M] \Delta t = k_p [M] \frac{N}{\rho}
\]

Emulsion Polymerization: monomer → porous particles

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
introduce plasticizer
more readily processible, aerodyn. in powder form

Common emulsion polymers:
- styrene + copolymers
- vinyl chlorides  ex. Pleather
- butadiene
- vinylidene chloride
- vinyl acetate
- vinyl acrylates (acrylics)
- methyl acrylates

Advantages:
- low $\eta$ (viscosity)
- great $T$ control
- final product $\rightarrow$ fine powder
  or water form $\rightarrow$ coatings

Disadvantages:
- a lot of soap as impurity
  ex. In medical applications, can be irritant

Suspension Polymerization:
(Pearl of Bead)
"Ingredients"
- monomer – organic phase
- aqueous phase
- initiator (soluble in monomer phase)
- stabilizer, often a polymer, such as PVOH

```
  CH2CH
  OH
```

hydrophobic backbone

polar, hydrophilic sidegroup

```
OH
CH2CH
OH
```
much more soluble in water

PVOH is absorbed at interface of droplet

stirred

organic droplets
Organic droplets: ~ 1 μm – 1 cm
Drop size determined by impeller speed
Within each droplet, have
- initiator
- monomer
⇒ Batch reactor within droplet
   Kinetics are identical to typical large scale free radical polymerization
   • initiation
   • propagation
   • termination
   • steady state assumption

Concerned with avoiding drop coalescence
⇒ premix initiator + monomer
⇒ agitate H2O phase + add organic phase
   ~ 20 – 30 % vol
⇒ adjust impellar speed to get desired drop size
⇒ add stabilizer (PVOH)
⇒ continue stirring at more gentle speed and increase T to 40°C → 80°C depending on which
   initiator you’re using
⇒ initiator activation
⇒ go to near complete conversion
   (may need to increase T for final % π)

Products:
- glassy rigid beads often called “latex beads”
- very uniform
- nice spherical shapes

\[
\text{styrene} + \text{divinyl benzene (tetrafunctional)} \rightarrow \text{x-linked network}
\]
vary surface chain:

\[
\begin{align*}
\text{bead} & \quad \text{SnCl}_4 \quad \text{ClICH}_2\text{OCH}_3 \\
& \quad \text{CH}_2\text{Cl} \\
& \quad 1. \text{N(CH}_3)_3 \quad 2. \text{NaOH} \\
& \quad \text{CH}_2\text{N}^{+} \quad \Theta\text{OH}
\end{align*}
\]

or

\[
\begin{align*}
\text{bead} & \quad \text{H}_2\text{SO}_4 \\
& \quad \text{SO}_3^{\Theta} \\
& \quad \text{Na}^{\Theta}
\end{align*}
\]

cation exchange

Form Pores:
- add non-solvent + monomer w/organic phase

Form connected channels of non-solvent

→ go to high \(\pi\)

flash off non solvent

If monomer (e.g. styrene) is well-dissolved in solvent, but solvent is poor for high MW polymer (e.g. cyclohexane)

\[
\begin{align*}
\text{styrene} & \quad \text{cyclohexane} \\
20 \text{ – } 30 \% & \quad \text{PS, } T_g \sim 100^\circ\text{C}
\end{align*}
\]

pockets of cyclohexane

Increase T to 120\(^\circ\)C
⇒ expansion ~ foaming effect
⇒ very large increases in size and decreases in density (mostly air)
⇒ STYROFOAM®
The following figures are adapted from page 250 of Polymer Synthesis:¹

Fig 12.2. Diagrams showing the three stages of emulsion polymerization: (I) Micelles increasing; (II) micelles exhausted, droplet phase remains; (III) droplet phase exhausted.

- $n$ number of particles per unit volume
- $n^*$ number of micelles per unit volume
- $[M]$ monomer concentration in the droplets and in the particles
- $R_p$ overall rate of polymerization
- $\bar{p}_n$ instantaneous degree of polymerization

Rate of Conversion, Emulsion Polymerization

\[ \overline{p}_n = k_p [M] \Delta t = k_p [M]^n \]

rate of production of free radicals

\[ R_p = \frac{n}{2} k_p [M] = \text{monomer molecules per sec per cm}^3 \]

# particles per cm\(^3\) \(\text{l/mol-sec}\)

* (recall that the rate, \(-dm/dt\) of disappearance of monomer molecules per particle per second is \(\frac{1}{2} k_p [M]\))

In general, for conversion:

\[ \frac{d\pi}{dt} = \frac{n}{2} k_p [M] \cdot \frac{1}{C} = n \cdot \frac{-dm}{dt} \cdot \frac{1}{m_o} \]

\(=\text{monomers/sec-cm}^3\)

\[ C = \frac{\Theta N_A \rho_m}{M_u} = \text{initial # of monomers in total volume} \]

How much you’ve added

where \(\Theta = \text{cm}^3\) monomer charged/cm\(^3\) of total volume = volume fraction
\(\rho = \text{density of monomer (g/cm}^3\))
\(N_A = \text{Avogadro’s number} = 6.023 \times 10^{23} \text{ molecules/mole}\)
\(M_u = \text{MW of monomer (repeat) unit}\)

For Stage I:

\([M] \equiv [M]_{eq} = [M]_o (1 - \Theta_2)\)

where \([M]_o = \text{pure monomer}\)
\(\Theta_2 = \text{vol. Fraction of polymer in particles at equilibrium}\)
\(n = n(t) \text{ b/c number of particles}\)

\[ \Rightarrow \int^{\pi}_{\pi_0} d\pi = \frac{1}{C} \int_0^{n(t)} n(t) \frac{k_p [M]_o}{2} (1 - \Theta_2) dt \]
For Stage II:
Surfactant consumed, droplets still exist
Growing particles

\[
\left[ M \right] = \text{constant} = \left[ M \right]_0 \left(1 - \Theta_2 \right)
\]
\[n = \text{constant}\]
\[
\int_{t_i}^{t_f} d\pi = \frac{1}{C} \int_{t_i}^{t_f} \frac{n}{2} k_p \left[ M \right]_b (1 - \Theta_2) dt
\]
\[
\Rightarrow \pi_{II} - \pi_I = \frac{n k_p \left[ M \right]_b \left(1 - \Theta_2 \right)}{2C} (t_{II} - t_I)
\]

Stage III:
Droplets exhausted, only particles
On avg, particles all same size, grow at same rate

Here, monomer is consumed w/in particles, as monomer \(\rightarrow\) polymer, \([M] \downarrow\) w/in particle.

\[
\left[ M \right] = \left[ M \right]_b (1 - \pi)
\]
\[
\Rightarrow \int_{t_i}^{t_f} d\pi = \frac{1}{C} \int_{t_i}^{t_f} k_p \left[ M \right]_b (1 - \pi) \frac{n}{2} dt
\]
\[
\Rightarrow \frac{-\Delta \ln (1 - \pi)}{\Delta t} = \frac{k_p \left[ M \right]_b n}{2C}
\]
For Stage I:

\[ n = f \left( C_s, a_s, \rho, \nu_n, \frac{dm}{dt} \right) \]

where \( C_s \) = surfactant concentration  
\( a_s \) = area of surfactant molecule (of polar head)  
\( \rho \) = rate of radical production  
\( \nu_n \) = vol of a single repeat  
\( \frac{dm}{dt} \) = rate of monomer polym.

Empirical expression:

\[ n \approx 0.53 \left( C_s a_s \right)^{\frac{3}{2}} \rho^{\frac{2}{5}} \left( -\nu_n q \frac{dm}{dt} \right) \]

\[ q = \frac{\text{vol polymer} + \text{vol monomer}}{\text{vol polymer}} \]

inside the particle (related to [M])
“Precipitation Polymerization”

polymer:  
- semicrystalline
- semicrystalline polymer not soluble in monomer

⇒ crystalline regions insoluble
⇒ amorphous regions remain soluble

Polymerization in bulk monomer

As # of high MW chains ↑, precipitation occurs

Also:

- occur in polymer chains with enough irregularity to form short chains

- some active sites remain accessible via diffusion through pores

polymer flakes, particles, etc. are porous

monomer can still diffuse to active sites

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Kinetics
- ill-defined and complex
- similar to emulsion polymerization
- can have red light/green light effect with free radicals
⇒ gain advantages
  → more temp/heat control
  → low η (can dilute slurry)
  → no surfactant

<table>
<thead>
<tr>
<th>Common Monomers</th>
<th>$T_{m,crys}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl chloride</td>
<td>140 – 200°C</td>
</tr>
<tr>
<td>Vinyl fluoride</td>
<td>200 – 230°C</td>
</tr>
<tr>
<td>Vinylidene fluoride</td>
<td>200°C</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>317°C</td>
</tr>
<tr>
<td>Tetrafluoroethylene (Teflon)</td>
<td>327°C</td>
</tr>
</tbody>
</table>

Dispersion Polymerization
- monomer
- organic solvent (good for monomer, bad for polymer)
- initiator
  - particle stabilizer: repel sticky polymers, avoid coalescence

As polymerization occurs, form large solid/semisolid particles of polymer

Random copolymers
  Incorporating 2 or more different monomer units in chain growth process
  (radical, cationic, or anionic polymerizations)

Consider 2 different monomers: 1 and 2

\[
\begin{align*}
\{M_1^* + M_1 \rightarrow k_{11}\} & \rightarrow \{M_1^*\} \\
\{M_1^* + M_2 \rightarrow k_{12}\} & \rightarrow \{M_2^*\} \\
\{M_2^* + M_1 \rightarrow k_{21}\} & \rightarrow \{M_1^*\} \\
\{M_2^* + M_2 \rightarrow k_{22}\} & \rightarrow \{M_2^*\}
\end{align*}
\]

\[
\begin{align*}
-\frac{d[M_1]}{dt} &= k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \\
-\frac{d[M_2]}{dt} &= k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]
\end{align*}
\]

The ratio of rates of monomers entering polymer chains
\[
\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]} \text{ (relative rates)}
\]

Assume steady state concentration of both \([M_1^*]\) and \([M_2^*]\)

\[\rightarrow \text{Rate of } M_2^* \rightarrow M_1^* = \text{rate of } M_1^* \rightarrow M_2^*\]

\[k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2]\]

Simplify and combine with \(\frac{d[M_1]}{d[M_2]}\):

\[\frac{d[M_1]}{d[M_2]} = \frac{[M_1][r_1[M_1] + [M_2]]}{[M_2][r_1[M_1] + r_2[M_2]]}\]

where \(r_1 = \frac{k_{11}}{k_{12}}\) and \(r_2 = \frac{k_{22}}{k_{21}}\)

(reactivity rates)

\[
\begin{align*}
\text{reactivity of } M_1^* \text{ with } M_1 & \equiv r_1 \\
\text{versus } M_1^* \text{ with } M_2 & \\
\text{reactivity of } M_2^* \text{ with } M_2 & \equiv r_2 \\
\text{versus } M_2^* \text{ with } M_1 & \\
\end{align*}
\]

Fraction of each monomer:

\[f_1 = \frac{[M_1]}{[M_1] + [M_2]} \quad f_2 = \frac{[M_2]}{[M_1] + [M_2]} \]

\(\Rightarrow\) expressions for monomer composition

Define:

\[F_i = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \] instantaneous polymer composition

Combine expressions and definitions:

\[F_1 = \frac{n_1 f_1^2 + f_1 f_2}{n_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \] copolymer composition equation
Special Cases:

1. "Ideal" copolymerization:

\[ r_1 \cdot r_2 = 1.0 \]

\[ \Rightarrow \frac{k_{22}}{k_{21}} = \frac{k_{12}}{k_{11}} \]

\[ r_2 = \frac{1}{r_1} \]

probability of \( M_1^* \) or \( M_2^* \)

react with \( M_1 \) vs \( M_2 \) is equal

2. \( r_1 = r_2 = 0 \)

neither \( M_1 \) nor \( M_2 \) react with themselves

\[ \begin{align*}
M_1 &\rightarrow M_2^* \\
M_2 &\rightarrow M_1^*
\end{align*} \]

Perfectly alternating composition:

\( M_1,M_2,M_1,M_2,... \) (not random at all)

Regardless of \( f_1 \): \( F_1 = 0.5 \)
2 extremes:
- perfect Bernoullian (random) case: $r_1 = r_2 = 1$
  \[ r_1 r_2 = 1 \]
- perfect alternating case: $r_1 = r_2 = 0$
  \[ r_1 r_2 = 0 \]

As $r_1 r_2$ product goes from $0 \to 1.0$, move from random to alternating sequencing:

If $r_1 < 1.0$ and $r_2 < 1.0$
Then induce inflection $\Rightarrow$ form an azeotrope:

Find azeotrope condition:

\[
f_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)} \text{ azeotrope exists at this monomer composition}
\]

- Block polymer: If $r_1 > 1$, $r_2 > 1$
  \[ M_1M_1M_1M_1M_2M_2M_2M_2 \]
- Consecutive homopolymer if $r_1 >> r_2$

\[ M_1 \text{ homopolymerizes } r_1 >> 1 \]

Then

\[ M_2 \text{ homopolymerizes } r_2 << 1 \]
Final comments: copolymerization

Recall azeotrope: occurs $r_1, r_2 < 1$

$\Rightarrow f_1 = F_1$

monomer comp = final copolymer comp
- if you have no perturbations, can get same composition throughout full range of $\pi$
- if there is perturbation $\rightarrow$ move further and further away from $f_1 = F_1$

For all copolymerizations in which
- azeotrope comp
- perfectly alternating system ($f_1 = F_1$)
We have unchanged polymer composition

BUT for all other cases (most cases), monomer compositions are continually changing.
- must create different expressions and integrate to get polymer composition averaged over conversion

Skeist:

$$\pi = 1 - \frac{[M]}{[M]_0} = 1 - \left[ \frac{f_1}{(f_1)_0} \right]^{\alpha} \left[ \frac{f_2}{(f_2)_0} \right]^{\beta} \left[ \frac{(f_1)_0 - \delta}{(f_1 - \delta)} \right]^{\gamma}$$

where

$$\alpha = \frac{r_2}{1 - r_2}$$
$$\beta = \frac{\eta}{1 - r_1}$$
$$\gamma = \frac{1 - \eta r_2}{(1 - r_1)(1 - r_2)}$$
$$\delta = \frac{1 - r_2}{2 - \eta - r_2}$$

For $r_2 > r_1$ (M₂ consumed more rapidly)
**Stereochemistry of polymer chains**

- **Isotactic**: same side
  
- **Syndiotactic**: alternating
  
- **Atactic**: no sequence, random

**Dyad tacticity**

- Isodyad: \( m = \text{meso} \)
  
- Syndio: \( r = \text{racemic} \)
  
- Fraction \( m + r = 1.0 \)

**Triad tacticity**

- Iso: \( mm \) \( \% \)
  
- Syndio: \( rr \) \( \% \)
  
- Hetero: \( mr \) \( \% \)
  
- \( mm + rr + mr = 1 \)
  
- Use percentages = 100%
  
- (use NMR to determine percentage)

**CH\(_2\)=CHR**

**In “normal” solution/bulk free radical polymerization**

\[ \begin{array}{c}
\text{R} \quad \text{H} \\
+ \quad \text{H}_2\text{C}=\text{CHR} \\
\text{R} \quad \text{H} \\
\end{array} \quad \xrightarrow{k_r} \quad \begin{array}{c}
\text{R} \quad \text{R} \\
\quad \text{H} \\
\quad \text{C} \quad \text{R} \\
\end{array} \quad \xrightarrow{k_m} \quad \begin{array}{c}
\text{R} \quad \text{R} \\
\quad \text{H} \\
\quad \text{C} \quad \text{R} \\
\end{array} \]
\[ \frac{k_r}{k_m} \Rightarrow \text{determine tacticity} \]

\[ \frac{k_r}{k_m} \sim 1.0 \Rightarrow \text{atactic} \]

\[ \frac{k_r}{k_m} \ll 1.0 \Rightarrow \text{isotactic} \]

\[ \frac{k_r}{k_m} \gg 1.0 \Rightarrow \text{syndiotactic} \]

Sterics prefer syndiotactic addition.

\( E_a \) slightly higher for iso addition

\[ \text{As } T \uparrow \text{iso fractions } \uparrow \]
\[ T \downarrow \text{syndio fractions } \uparrow \]

e.g. PMMA:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H}_2 \text{C}-\text{C} \text{CH}_3 \\
\text{C} - \text{C} - \text{CH}_3
\end{array}
\]
\[ T_p = 100^\circ \text{C} \quad T_p = -78^\circ \text{C} \]
\[ r = 0.73 \quad r = 0.87 \]

e.g. PVC

\[
\begin{array}{c}
\text{Cl} \\
\text{H}_2 \text{C}-\text{C} \text{H} \\
\text{C} - \text{C} - \text{Cl}
\end{array}
\]
\[ T_p = 60^\circ \text{C} \quad T_p = -38^\circ \text{C} \]
\[ r = 0.5 \quad r = 0.6 \]

**Coordination Polymerization**

Coordinated catalyst: usually metal/metal halide or oxide complex:
- promote stereospecific + controlled addition of monomer

Ziegler and Natta Nobel Prize, 1963
(Germany) (Italy)

e.g.
\[ \text{Initiator: Group I-III metal (e.g. Al)} \]
\[ + \text{ transition metal (e.g. Ti)} \]

\[ \text{group metal} \quad \overset{\text{G}}{\longrightarrow} \quad \overset{\text{RHC} = \text{CH}_2}{\text{RHC} = \text{CH}} \quad \overset{\text{H}}{\longrightarrow} \quad \overset{\text{H}_2 \text{C} - \text{C}}{\text{H}_2 \text{G}} \quad \overset{\text{escape for}}{\text{insertion of new}} \quad \overset{\text{monomer}}{\text{monomer}} \]

\text{Ziegler-Natta Catalyst}

\text{Usually TiCl}_4 \text{ or TiCl}_3

\[ + \quad \text{AlR}_3 + \text{AlR}_2\text{Cl} \]
\[ \text{R=CH}_2\text{CH}_3 \text{ or } (\text{CH}_2)_n\text{CH}_3 \]

\text{“Escort” process guides stereochemistry}
\text{many of Z-N catalysts}
\text{(crys) ⇒ isotactic addition}
\text{(soluble) ⇒ syndiotactic}
Consider polypropylene

\[
\begin{array}{c}
\text{CH}_3 \\
\text{C} \quad \text{C} \\
\text{CH}_3
\end{array}
\]

Atactic PP: \( T_g \sim -70^\circ C \)
fully noncrystalline
liquid-like, paste

Isotactic PP: \( T_m = 170^\circ C \)
highly crystalline
amorphous region: \( T_g \sim -50^\circ C - -60^\circ C \)
insoluble

Syndiotactic PP: very crystalline \( T_m \sim 130^\circ C \)

\[
\begin{array}{c}
\text{CH}_2=\text{CH}_2 \\
\text{CH}_2=\text{CH}_2
\end{array}
\]

Regular structure

Traditional free radical polymerization

Tubular Reactors: 2-6 cm in diameter
0.5 – 1.5 km in length

\[
\begin{array}{c}
\text{CH}_2=\text{CH}_2 \\
\text{gas} \\
\text{add} \\
\text{initiator} \\
\text{O}_2, \text{H}_2\text{O}_2, \text{CTA}
\end{array}
\]

\[
\text{heat to} \\
175^\circ C
\]

\[
\text{peak T} \\
300^\circ C
\]

\[
\text{supercritical fluid}
\]

\[
\text{T} > T_{\text{crit}} \\
P > 200 \text{ MPa}
\]

\[
\pi = 20-30\%
\]

\[
\text{precipitate}
\]

\[
\text{T} = 25^\circ C
\]
Chain transfer to monomer and polymer:

\[ \sim \to \sim + \sim + \sim \to \text{Highly branched, Irregular length} \]

Branches hinder crystallinity
- Low density PE (LDPE)
  - \( \rho = 0.9 \, \text{g/cm}^3 \)
  - \( T_g = -120^\circ C \)
  - \( T_m = 105^\circ C \)
- Irregular length

Z-N catalyst: reduce transfer

\[ \text{minimal branching} \]

High density PE (HDPE)
- \% crystallinity: 80-90%
- \( \rho = 0.94 - 0.96 \)
- \( T_m > 130^\circ C \)
Recap from last lecture

Low Density Polyethylene (LDPE)
- Formed using traditional free radical polymerization
- It has 40-60% crystallinity
- Its density ($\rho$) is 0.91 g/cm$^3$
- Melting temperature: $T_m = 105$-$115^\circ$C
- Glass transition temperature: $T_g = -120^\circ$C

High Density Polyethylene (HDPE)
- Formed using a Ziegler-Natta (Z-N) catalyst
- Crystallinity is much higher: 70-90%
- Its density ($\rho$) is 0.94-0.96 g/cm$^3$

Additionally, the Z-N catalyst can be used to control branching easily to form:

Linear Low Density Polyethylene (LLDPE)

Metallocene Catalyst
- The metallocene catalyst is similar to the Z-N catalyst.
- It's composed of a group IV-B transition metal (e.g. Hf, Ti, Zr)
- It's used to obtain a narrow MW distribution (narrower than the Z-N catalyst), but because Z-N catalyst is much easier to use, it is often the preferred method of polymerization
- In addition, usage of metallocene catalyst can result in random distributions in copolymer. In contrast, Z-N catalyst results in clusters.
- Finally, the metallocene catalyst is less sensitive to functional groups in monomers.

Terminal Functionalization
- End capping only good for living system
- Functional initiation not good for Ziegler-Natta catalyst
- Chain transfer: $\beta$-hydrogen transfer to monomer

Handouts about metallocene catalysts:


Ionic Polymerization

1. Anionic
2. Cationic

**Anionic Polymerization**
- very aggressively charged negative group

\[
\text{C}_4\text{H}_9\text{Li} + \text{H}_2\text{C}==\text{CHY} \rightarrow \text{C}_4\text{H}_9\text{CH}_2\text{C}==\text{CHY} \text{ Li}^+ \]

n-butyl lithium

This is a form of \[
\text{Li}^+ \]

Also have negative charge on other atoms:
e.g. ring opening:

\[
\text{H} \text{C}==\text{O} + \text{H}_2\text{C}==\text{CHR} \rightarrow \text{H} \text{C}==\text{O} \text{ R} \text{ C}==\text{O} \text{ R} \]

ew bond formed

**Monomer Requirements**

In general, for vinyl monomers, need monomer that supports a stable carbanion

1.

\[
\text{CH}_2\text{C}==\text{CHY} \]

Y should be electron withdrawing
⇒ stabilizes $\Theta$ charge by sharing with C$\Theta$

Y can fit a range of electron-withdrawing groups
How withdrawing impacts monomer reactivity

2. (second requirement for monomer)

monomer should have no protic or acidic hydrogens
No: 
- COOH  carboxyl groups
- R-OH  alcohols
- NH2  amide groups
  (polyacrylimide in electrophoresis)
  for biological experiments

and more... basically if it gives a H away easily, it’ll be a problem

3. contains no electrophilic groups:
   Note: carbanion is a very strong nucleophile

   Avoid e.g.

   \[
   \begin{array}{c}
   \text{N}=\text{C}=\text{O} \\
   \text{R}
   \end{array}
   \rightarrow
   \begin{array}{c}
   \text{H} \\
   \text{N}=\text{C}=\text{R}
   \end{array}
   \]

   There are some exceptions: certain groups are electrophilic but less reactive to
   carbanion of interest:

   e.g.

   \[
   \begin{array}{c}
   \text{O} \\
   \text{C}=\text{OCH}_3
   \end{array}
   \]

   That’s why we have ranking of reactive groups

Finally

4. Carbanion generated must be able to attack its own monomer

Now, good monomers for anionic polymerizations:

Vinyl:
- styrenes:

- vinyl aromatics:

- vinyl pyridines:
Alkyl methacrylates:

\[ \text{CH}_3 + \text{longer alkyls} \]

NOT acrylates:

\[ \text{H} \]

Carbon that becomes anion is the one with the Y group.

Ex: methyl methacrylate

Ring Compounds:

- epoxides: \( \text{O} \) \quad \text{BUT not free radical versions of epoxy}

- lactones: \( \text{O} \) \quad \text{ex: get caprolactone}

- siloxanes: \( \text{Si} \text{O} \text{Si} \) \quad \text{ex: silly putty silicone oil}

**Anionic Polymerization Initiators**

What about initiators?

There are rules that govern good initiators as well:
must be reactive enough to attack monomer
i.e. stronger nucleophile
(more aggressive)

So this depends on the monomer to be initiated:
• If monomer substituent Y is strongly e- withdrawing;
  → then activated monomer is relatively stable
  → relatively weaker nucleophiles can initiate it
    ex: epoxy: ethoxyanion
    initiate ring polymerization with variety of initiators

• If substituent Y is weakly e- withdrawing:
  → need stronger nucleophile to initiate it:
  ⇒ need to know reactivity trends in monomers

Reactivity trends:

\[
\begin{align*}
\text{Increasing ease of initiation} \\
\text{Most difficult} & \quad \text{Easiest to initiate} \\
\text{usually don’t introduce protic systems to help propagation} & \quad \text{(use them to terminate reaction)}
\end{align*}
\]

Types of initiators and trends of reactivities

“mild” ———————————————————— “strong” reactivity
another useful initiator:

Aromatic radical anions:

\[
\text{Na}^0 + \text{Na napthalene} \rightarrow \left[ \begin{array}{c}
\cdot \cdot \\
\cdot \\
\end{array} \right] \text{Na}
\]

Na “gives” electron to Naphthalene reduction

\[
\text{YCH} = \text{CH}_2 + \text{YCH} = \text{CH}_2 \rightarrow \text{dianionic species propagate in both directions}
\]

\[
\Rightarrow \quad \begin{array}{c}
\cdot \cdot \\
\cdot \\
\end{array} \text{Na}
\]

CH\text{2} can pair with itself
dimerization of (lower) radical species
Choosing Initiators (for anionic polymerization)

(must be strong enough to initiate monomer)
→ should not attack any monomer side groups

e.g. styrene:

\[
\text{Readily initiated by any alkyl lithiuns (e.g. n-butyl Li, sec-butyl Li)}
\]

Cations: (Na) (Na)

CANNOT initiate with diphenyl methyl Na

\[
\text{Compare with:}
\]

\[
\text{e- withdrawing effect large due to inductance}
\]

MMA

\[
\text{resonance}
\]

→ easy to initiate
→ fluorenyl Na⁺, diphenyl methyl Na

But NOT:

\[
\text{side reactions with ester}
\]
Kinetics of anionic polymerization

In protic media:

\[
\text{Termination in ionic polymerization} \quad \Rightarrow \quad \text{only by transfer or side rxn} \quad \Rightarrow \quad \text{no coupling/disproportionation}
\]

IF transfer leads to anion that is reactive enough to initiate monomer \( \Rightarrow \) transfer

IF transfer leads to anion that won’t initiate monomer \( \Rightarrow \) termination

\[
\begin{align*}
\text{Initiation:} & \quad \text{NaNH}_2 \xrightleftharpoons[K]{K} \text{Na}^+ + \text{NH}_2^- \\
\text{Propagation:} & \quad \text{NH}_2^+ + \text{M} \xrightarrow{k_i} \text{NH}_2\text{M}^+ \\
\text{Transfer to solvent:} & \quad \text{NH}_2\text{M}_i^+ + \text{NH}_3 \xrightarrow{k_{\text{tr, NH}_3}} \text{NH}_2\text{M}_i + \text{NH}_2^- \\
\text{Transfer to water: (termination event)} & \quad \text{NH}_2\text{M}_i^+ + \text{H}_2\text{O} \xrightarrow{k_{\text{tr,H}_2\text{O}}} \text{NH}_2\text{M}_i + \text{OH}^-
\end{align*}
\]

relatively stable, will not initiate styrene

(only thing HO\(^-\) will initiate is epoxides)

\[
R_i = k_i [\text{NH}_2^-] [\text{M}] = k_i [M] [\text{NaNH}_2] / [\text{Na}^+] \]

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Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
\[ R_p = k_p [M^-] [M] \]
\[ R_{tr, NH_3} = k_{tr, NH_3} [M^-] [NH_3] \]
\[ R_{tr, H_2O} = k_{tr, H_2O} [M^-] [H_2O] \]

termination

Steady state assumption: \([M^-] = \text{constant}\)
\[ R_i = R_{tr, H_2O} \]
\[ \frac{k_i K [M] [NaNH_2]}{[Na^+]^2} = k_{tr, H_2O} [M^-] [H_2O] \]

rearrange to get expression for \([M^-]\)
\[ [M^-] = \frac{k_i K [M] [NaNH_2]}{k_{tr, H_2O} [H_2O] [Na^+]} \]

\[ R_p = \frac{K k_i k_p [M^2] [NaNH_2]}{k_{tr, H_2O} [Na^+] [H_2O]} \] 2nd order in \([M]\)

\[ R_p \propto [M]^2 \]
(b/c: \([M^-] \propto [M]\))

\[ \frac{1}{p_n} = \frac{C_{NH_3} [NH_3]}{[M]} + \frac{C_{H_2O} [H_2O]}{[M]} \]

transfer transfer
to solvent to \(H_2O\)

**Living Polymerizations**

1. No transfer
   - No termination events due to other side rxns that might occur due to impurities
   => need solvent with no protic groups (aprotic)
   => eliminate \(H_2O\) to get dry solvent
   \(O_2\)
   \(CO_2\)
   - Other reactive species like \(NH_2\), anything that can snatch \(H\) off
   “lifetime” of propagating anion can be very long
   (~ hours)

2. Need system with very rapid \(R_i \gg R_p\)
   fast initiation
   start polymerization at same time to get highly controlled MW + polydispersity
   All chains start at the same time and finish the monomer off
   ~ monodisperse MW distribution

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Lecture 20
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OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Kinetics of Living Polymerizations

1. initiation: \( R_i = k_i [I^- M] \)

2. propagation: \( R_p = k_p [M^- M] \)

Rapid initiation: \( [I_o] \approx [M^-] \)

\[ R_p = k_p [M] [I_o] \]
Living Polymerization

\[ R_p = -\frac{d[M]}{dt} = k_p[M^-][M] \]

\[ [M^-] = [I]_0 \] (assumes all initiator is active and available)

\[ \Rightarrow R_p = k_p[M][I]_0 \]

\[ \Rightarrow \ln \frac{[M]}{[M]_0} = k_p[M^-] = k_p[I] \]

constant

\[ \log \frac{[M]}{[M]_0} \]

slope = \( k_p[I] \)

time

\[ \bar{p}_n = \frac{[M]}{[I]} = \frac{\pi[M]}{[I]} \]

polymer grows at exactly the same rate (monomer initiated at exactly the same time)

\[ \Rightarrow \frac{[M]}{[I]} \]

\[ \bar{p}_n \] linear with time

\[ \Rightarrow \frac{[M]}{[I]} \]

time

\[ \therefore \text{ for complete conversion} \]

\[ \bar{p}_n = \frac{[M]}{[I]} \]

PDI: \[ \frac{M_w}{M_n} = 1 + \frac{\nu}{(\nu + 1)^2} \] (not real PDI, but for statistical purposes)
Where \( \nu = \text{kinetic chain length} \)

\[ \Rightarrow \text{as } \nu \uparrow, \quad \frac{M_w}{M_n} \rightarrow 1 \]

\[ \Rightarrow \text{predicts PDI } \sim 1.01 \rightarrow 1.001 \]

Poisson distribution instead of Gaussian distribution

**Solvent Characteristics**

Most common solvents
- pentane
- hexane
- cyclohexane
- benzene
- dioxane
- 1,2 dimethoxyethane
- \( \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3 \)
- tetrahydrofuran
- dimethyl formamide

\[ \text{H}_3\text{C} \text{– } \text{N} \text{– } \text{C} \text{– } \text{H} \]

- solvent must solvate monomer + polymer
  \[ \Rightarrow \text{function of polarity} \]

- important solvent effects in anionic polymerization
  - rate of polymerization highly dependent on accessibility
    - of \( \Theta \) (propagating anion)
  - association effects
  - degree of counterion/ion dissociation

**1. Association Effects:**

Low dielectric (nonpolar) solvents are poor environments for ions:
Possible to form micelle-like aggregates:

aggregation probabilities \( \uparrow \)
as polarity of solvent \( \downarrow \)
and as counterion size \( \downarrow \)
dependency on concentration:
as conc \( \uparrow \), agg \( \uparrow \)
\[
\{M^-\}_{n} \xleftarrow{K_e} nM^- \quad \text{let } n = \# \text{ of chains per aggregate}
\]

bracket denotes aggregate (assume all aggregates have same number of chains)

\[
K_e = \frac{[M^-]^n}{[M^-]_n^n} \quad \text{equilibrium constant}
\]

\[
[M^-] = K_e^{1/n} \left([M^-]_n\right)^{1/n}
\]

\[
R_p = \frac{d[M]}{dt} = k_p K_e^{1/n} \left[M\right]^{[M^-]_n^{1/n}}
\]

see 1/n dependency in rate of propagation with respect to \([M^-]\]

\[
[M^-]_n \propto [M^-] = [I]
\]

can assume \([I] \sim [M^-]_n\)

\[
\Rightarrow R_p \approx k_p K_e^{1/n} [M]^{[M^-]_n^{1/n}}
\]

If aggregation number is 2, \((n=2)\)

\[
R_p = k_p K_e^{1/2} \left[M\right]^{[M^-]_{2}^{1/2}}
\]

\[
\approx k_p K_e^{1/2} [M]^{[M^-]_{2}^{1/2}} \quad \text{aggregate form}
\]

2. Degrees of dissociation of counterion and chain

(happens much more frequently)

different degrees of dissociation:

Free ions:

\[
\text{Li} \quad \text{unimer}
\]

\[
\text{this species can propagate}
\]

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Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
ions are fully dissociated from negative charge

⇒ assume full availability of charge to react with monomer

Versus ... 2 types of ion pairs
a) unsolvated ion pairs (tight pairs)
   “contact ion pairs”

b) solvent separated ion pairs (loose ion-ion connections)
   solvent molecules separate ions
   thin layer of solvent that separates counterion from + charge

reaction rates of species are going to be different

\[ k_p \Rightarrow \text{rate constant for free ions} \]
\[ k_{pl} \Rightarrow \text{rate constant for all ion pairs} \]

and \[ k_{pl} = yk_{pll} + (1-y)k_p \]

parallel sign

\[ k_{pll} = \text{solvent separated pair} \]
\[ y = \text{fraction of solvent separated pair} \]

Equilibrium between free and dissociated ion pairs:

Dissociated rate constant

\[ K_D = \frac{[\text{contact ion pairs}][\text{Na}^+]^2}{[	ext{solvent separated pair}][\text{Na}^+]} \]

⇒ assume \[ [\text{Na}^+] = \frac{[\text{contact ion pairs}]}{[\text{solvent separated pair}]} \]

(no addition of NaCl that drives up [Na⁺])
\[ K_D = \frac{[\Theta]^2}{[\text{Na}^\Theta]} \]

Given that \([M^-]\) = concentration of all ionic sites (free and associated)

\[ \alpha = \frac{\# \text{ of dissociated (free) ions}}{\text{all ions}} \]

\[ K_D = \frac{\alpha^2 [M^-]}{(1 - \alpha [M^-])} = \frac{\alpha^2 [M^-]}{1 - \alpha} \]

solve for \(\alpha\):

\[ \alpha \approx \left( \frac{K_D}{[M^-]} \right)^{1/2} \]

assuming that \(\alpha\) = small

\[ \rightarrow \text{neglect } 1 - \alpha \text{ term in denominator} \]

\[ k_p = \alpha k_{p-} + (1 - \alpha) k_{pl} \]

\[ \Rightarrow R_p = -\frac{d[M]}{dt} = \left[ k_{pl} + \left( \frac{K_D}{[M^-]} \right)^{1/2} (k_{p-} - k_{pl}) \right] [M^-] \]

\[ \downarrow \]

\[ [1] \]
From last lecture

Association Effects

\[
\left[ M^- \right] = K_e^{1/n} \left[ M^- \right]_n^{1/n}
\]

\[
\left[ M^- \right]_n \times \left[ M^- \right] = [I]
\]

can assume conc. of initiator is equal to conc of propagating anion

\[
\approx \frac{1}{n} [I] \quad \text{e.g.}
\]

\[
\Rightarrow R_p = k_p K_e^{1/n} \left[ M \right] \left[ M^- \right]_n^{1/n}
\]

Dissociation

\[
\alpha = \frac{\text{# of dissociated (free) ions}}{\text{all ions}}
\]

\[
K_D = \frac{\alpha^2 \left[ M^- \right]}{1-\alpha}
\]

assuming \(1 - \alpha \rightarrow 1\) (small \(\alpha\))

\[
\Rightarrow \alpha \approx \left( \frac{K_D}{[M^-]} \right)^{1/2}
\]

\[
k_p = k_{p,\text{apparent}} = ak_p^- + (1 - \alpha)k_{p}\text{I}
\]

remember \(k_p^- = \text{propagation rate constant for free ion}\)

\(k_{p}\text{I} = \text{ion pair}\)

\(k_{p,\text{app}} = \text{apparent, or global, or pseudo rate constant}\)

\[
\Rightarrow R_p = k_{p,\text{app}} \left[ M \right] \left[ M^- \right]
\]

\[
\Rightarrow R_p = \left[ k_{p\text{I}} + \left( \frac{K_D}{[M^-]} \right) \left( k_p^- - k_{p}\text{I} \right) \right] \left[ M^- \right] \left[ M \right]
\]

\[
k_{p,\text{app}}
\]

Note: \(K_D \sim 10^{-7}\)

\[
\Rightarrow \alpha \approx 1\% \text{ free ions}
\]

If you know \(K_D\), you can find \(k_{p\text{I}}\), and \(k_p^- - k_{p}\text{I}\) by plotting

\[
k_p \text{ vs } \left( \frac{K_D}{[M^-]} \right)^{1/2}
\]

where \([M^-] = [I]\)

\[
\frac{k_p}{k_{p}\text{I}} = \left( k_p^- - k_{p}\text{I} \right)
\]

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
**Effects of Solvent Polarity on Polymerization**

Solvent effects in anionic polymerization.

To measure polarity, look at dielectric constant $\varepsilon$, which is a change in polarity.

Examples:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>dielectric const $\varepsilon$</th>
<th>$k_p$ (L/mol·s) with P.S.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.2</td>
<td>2</td>
</tr>
<tr>
<td>Dioxane</td>
<td>2.2</td>
<td>5</td>
</tr>
<tr>
<td>THF</td>
<td>7.6</td>
<td>550</td>
</tr>
<tr>
<td>1,2 dimethyl ether</td>
<td>5.5</td>
<td>3800</td>
</tr>
</tbody>
</table>

The ether group helps solvate system.

The ether group is very strong ligand for cations:

The best example for this is: crown ethers

- Crown ethers (Odian p. 435) increase the conc of free-ion propagating species, resulting in very large rate increases
- In addition, crown ethers & "glycines" (short PEO chains) are added to non-polar solvents to solvate cations (ex: Li$^+$ and Na$^+$)
Ion effects are also observed in ion dissociation/solvation

Ex: Ion Size: larger ions are more soluble in “neutral” solvents (no specific interaction)

\[ F = \frac{Q_+ \cdot Q_- \cdot e^2}{\epsilon \cdot r^2} \]

where \( r \) = distance between \( \oplus \) and \( \ominus \)

as ion size ↑
\( r ↑ \)
\( F ↓ \)
⇒ dissociation becomes easier

There are exceptions through: ether solvents are generally better at solvating smaller ions (Li\(^+\))

See Table 5-11: Anionic polymerization of styrene in THF

<table>
<thead>
<tr>
<th>counterions</th>
<th>( k_{pl} )</th>
<th>( k_{p \times 10^7} )</th>
<th>( k_p )</th>
<th>( k_{pl} ) for dioxene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>160</td>
<td>2.2</td>
<td></td>
<td>0.94</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>80</td>
<td>1.5</td>
<td></td>
<td>3.4</td>
</tr>
<tr>
<td>K(^+)</td>
<td>60-80</td>
<td>0.8</td>
<td>6.5\times10^4 (same ( k_p ) value)</td>
<td>19.8</td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>50-80</td>
<td>0.1</td>
<td></td>
<td>21.5</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>22</td>
<td>0.02</td>
<td></td>
<td>24.5</td>
</tr>
</tbody>
</table>

Stereospecificity

(affected by both solvent and ion)

Less polar solvents allow coordination effects - closer ion – counterion interactions (association pairs)

⇒ coordination effects w/ion become important
⇒ “” often favor isotactic placements
⇒ “” are greatest for small ions

Ex:

more dissociation for larger ion
Dienes

Butadiene  Isoprene

In polar solvents in anionic polymerization:

\[
\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \quad \longleftrightarrow \quad \text{CH}_2^\circ \text{CH}-\text{CH}=\text{CH}_2
\]

this structure is more stable

A good polar solvent has free ions and “1,2 addition” is preferred in dienes:

\[
\overset{\text{H}}{\text{C}} \quad \overset{\text{H}}{\text{C}}
\]

Polymer is similar to PVC

\[ T_g \sim 30-40^\circ C \]

Polymer is harder around room T

and this can be functionalized

In a non-polar solvent, coordination effects are strong
Delocalization decreases and thus, localized effects are strong

Li\(^+\) in particular directs addition to primary carbon:

\[
\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \quad \overset{\text{Li}}{\text{Li}}
\]

ion pair

1,4 addition is favored in this case.

\[
\overset{n}{\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2}
\]

1,4 polybutadiene:
- low \( T_g \)
- extremely flexible
- non-crystalline

Cis-Trans Considerations

What about –cis and trans?

\[
\quad \overset{\text{cis} \, 1,4}{} \quad \overset{\text{vs}}{} \quad \overset{\text{trans} \, 1,4}{}
\]

What is the percentage of cis and trans?
- trans form is slightly more favored (more accessible to monomer)
- can get trans over cis using a polar solvent
- can get cis over trans using a non-polar solvent, esp for Li\(^+\)
  (effect is weaker for larger ions)
- can get preference for cis with substituent on diene:

\[
\begin{array}{c}
\text{R} \\
\text{=}
\end{array}
\xrightarrow{	ext{reaction}}
\begin{array}{c}
\text{C} \\
\text{R}
\end{array}
\]

If we put all the effects together:

For butadiene:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Solvent</th>
<th>1,4 cis</th>
<th>1,4 trans</th>
<th>1,2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>pentane (non-polar)</td>
<td>35%</td>
<td>50%</td>
<td>15%</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>THF</td>
<td>0%</td>
<td>5%</td>
<td>95%</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>pentane</td>
<td>7%</td>
<td>25%</td>
<td>67%</td>
</tr>
<tr>
<td>K(^+)</td>
<td>pentane</td>
<td>12%</td>
<td>38%</td>
<td>50%</td>
</tr>
</tbody>
</table>

For isoprene

<table>
<thead>
<tr>
<th>Ion</th>
<th>Solvent</th>
<th>1,4 cis</th>
<th>1,2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>pentane</td>
<td>94%</td>
<td>6%</td>
</tr>
</tbody>
</table>

Li\(^+\) has extreme power in trans coordination: (sacrificing speed for structure)

**End Functionalization in Anionic Polymerization**

In living polymerization, \(\Theta\) “lives” until we intentionally “quench” the anion:

\[
\begin{array}{c}
\text{HO-R} \xrightarrow{\text{reaction}} \text{H} + \text{MeO}^-
\end{array}
\]

precipitate polymer
easily disposed

But

\[
\begin{array}{c}
\text{C} \xrightarrow{\text{reaction}} \text{C-H}
\end{array}
\]

is boring...

We can end functionalize with specific terminating agents:
React with anhydride:

Because the reaction goes to end, just add end capper in excess

Can have

- dionic initiator with 2 prop directions
  - have $\alpha$, $\Omega$ End functionalization
From Last Lecture

Diene polymerization:

<table>
<thead>
<tr>
<th>1,2 addition:</th>
<th>1,4 addition:</th>
</tr>
</thead>
</table>
| \[
\begin{array}{c}
\text{H}_2 \\
\text{C} \\
\text{C} \\
\text{H} \\
\text{H}_2
\end{array}
\]_n | \[
\begin{array}{c}
\text{H}_2 \\
\text{C} \\
\text{C} \equiv \text{C} \\
\text{H} \\
\text{H}_2
\end{array}
\]_n |

\(\text{cis:} \quad \text{trans: linkage}\)

<table>
<thead>
<tr>
<th>primarily cis:</th>
<th>primarily trans:</th>
</tr>
</thead>
<tbody>
<tr>
<td>crystallinity suppressed</td>
<td>semicrystalline mat</td>
</tr>
<tr>
<td>low crystallinity</td>
<td>w/T_m ↑ than 25°C</td>
</tr>
<tr>
<td>v. low T_g</td>
<td>⇒ used for synthetic rubbers</td>
</tr>
</tbody>
</table>

Living Polymerization

- allow intentional introduction of terminating group → \(\omega\) end-functionalization
  - \(\alpha - \omega\) functionalization with dianionic initiator
- introduce second monomer after first is consumed

\[
\begin{array}{c}
\text{\(\Theta\)} \\
\text{A} \\
\text{B} \\
\text{\(\Theta\)}
\end{array}
\] + \[
\text{\(\Theta\)} \\
\text{A} \\
\text{B} \\
\text{\(\Theta\)}
\] \(\rightarrow\) \[
\text{\(\Theta\)} \\
\text{A} \\
\text{B} \\
\text{\(\Theta\)} \\
\text{B} \\
\text{\(\Theta\)}
\] to yield a AnBm block copolymer
- can also have triblock copolymers: ABA triblocks
  - ABC triblocks
  - ABBB
  - ABA
  - ABC
  - ABB
  - BBA
  - BBB
  - ABBB
  - ABC
  - ABB
  - BBA
  - BBB
heptablocks (in literature)

But what limits it?
- we must consider the relative reactivities of the blocks:

\[
\begin{array}{c}
\text{\(\Theta\)} \\
\text{A} \\
\text{\(\Theta\)}
\end{array}
\] must be able to initiate monomer B

\[
\begin{array}{c}
\text{\(\Theta\)} \\
\text{A} \\
\text{\(\Theta\)}
\end{array}
\] must not undergo side reaction with B

\[
\begin{array}{c}
\text{\(\Theta\)} \\
\text{A} \\
\text{\(\Theta\)}
\end{array}
\] + B initiation must be rapid (want narrow polydispersity)
all groups get initiated at once → same prop. Rates
“Food Chain”

short list of monomers, in increasing electrophilicity

most aggressive:

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Ease of initiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethyl amino styrene, p-methoxy styrene, p-methyl styrene, α-methyl styrene</td>
<td>almost the same</td>
</tr>
<tr>
<td>styrene</td>
<td>A monomer in the list can initiate anything equal or below it</td>
</tr>
<tr>
<td>butadiene</td>
<td>Ex: ethylene oxide cannot initiate vinyl pyridine but can initiate vinylidene cyanides</td>
</tr>
<tr>
<td>isoprene</td>
<td>More reactive monomers → faster polymerization</td>
</tr>
<tr>
<td>vinyl naphthalene</td>
<td></td>
</tr>
<tr>
<td>p-chlorostyrene</td>
<td></td>
</tr>
<tr>
<td>vinyl pyridine</td>
<td></td>
</tr>
<tr>
<td>diphenyl ethylene (DPE)</td>
<td></td>
</tr>
<tr>
<td>alkyl methacrylates (MMA)</td>
<td></td>
</tr>
<tr>
<td>propiolactones</td>
<td></td>
</tr>
<tr>
<td>ethylene oxide</td>
<td></td>
</tr>
<tr>
<td>propylene sulfide</td>
<td></td>
</tr>
<tr>
<td>vinylidene cyanide</td>
<td></td>
</tr>
<tr>
<td>α-cyanoacrylates</td>
<td></td>
</tr>
</tbody>
</table>

**Example: Synthesis of a Diblock Copolymer**

want to make polystyrene–b–poly(methyl methacrylate)

PS–b–PMMA

A Must start with styrene

But this can react with the carboxylic Ester groups of MMA:

\[
\text{C} = \text{O} \quad \text{O} \quad \text{CH}_3
\]

B Add DPE

Because only one group of DPE, there is no effect on the properties of copolymer
Another Example: Synthesis of a Triblock Copolymer

Styrene–Butadiene–Styrene triblock
PS–b–PB–b–PS
SBS

Can make this polymer at least 3 different ways:
- consideration: styrene and butadiene are very close in reactivity
  So, butadiene can initiate styrene

1. Difunctional initiator: ex: Na naphthalene
   + butadiene

   \[ \text{PB} \]

   Consume B completely and then add styrene (S)

   \[ \text{Symmetric triblock b/c same prop. rate and time} \]

2. Add S+B+S in sequence (w/monomer fully consumed by each step)

3. First initiate PS
   a)
   \[ \text{PS} \]
   b) add butadiene + styrene together in big aliquot
      (in anionic polym, do not get alternating copolymers, get blocky behavior)

   - reactivity rates (anionic)
     \[ k_{ab} \gg k_{bs} \]
     \[ r_b = 14 \]
     \[ r_s = 0.03 \]
     growing B is preferred
• create block
  with PB (B preferred over S)
  ° then transition (both B and S)
  ° then completely PS (all that is left)

• this is done in industry
  - relatively simple
  - transitional regime enhances surface properties
    more diffuse interface
    → Better properties

4. Use a coupling agent
   (used for systems with no other options)
   i) grow diblock of PS–PB

   \[
   \text{S}^\ominus + \text{B} \text{S} \text{S} \text{B} \text{S} \text{B} \text{S} \text{B} \text{S} \text{B} \text{S} \text{B} \rightarrow \text{PS} \text{PB} \text{PS}
   \]

   ii) then add reactive coupling agents
       e.g. phosgene (extremely reactive)

   \[
   \text{PS} \text{PB} \rightarrow \text{PS} \text{Cl} \text{Cl} \text{PS}
   \]

   everytime you introduce a monomer or coupling agent, you risk the chance of impurities (can’t get ill-block copolymer or high MW copolymer)

other coupling agents: (Quantitative reactions)
Disadvantages of Coupling

- often get incomplete reaction (diblock + triblock)
- needs perfect stoichiometry (scale is very small)

Despite that, you can be creative:
Can use coupling to make “stars”

Or use short oligomer

Can make graft copolymers: (or comb copolymers)
From Last Time

comb/graft copolymers
e.g. $\text{PS}^\ominus$ onto PMMA backbone

![Diagram of comb/graft copolymer]

e.g. $\text{PEO}^\ominus$ onto chloromethylated PS backbone

![Diagram of comb/graft copolymer]

"Macromers": Many Mers $\rightarrow$ Polymer

e.g.

![Diagram of macromer synthesis]

free radical
$r_1$ and $r_2$ are similar
$r_1 r_2 \leq 1$
$\rightarrow$ alternating polymer

General fact: ionic propagation is more monomer selective than free rad: large diff between $r_1$ & $r_2$

dispersed on backbone

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
- hard to get random copolymer
  thus if you see a random copolymer, assume made by free radical
  NOT ionic polymerization
  consumes monomer very quickly, then the other monomer

Slide: structure and properties of polymers
- polymer and block copolymer morphology
- physical properties/deformation behavior
- diffusion & flow
- case studies: product design

→ mix 2 polymers (immiscible)
  → different arrangements w/different degrees of phase separation

Presentation: Examples of Block Copolymers

Materials: Advances in synthetic chemistry and statistical theory provide unparalleled
control over molecular-scale morphology in this class of macromolecules.” Physics
Today (February 1999): 33, 34, and 36.

\[
\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \\
\Delta S_{mix} \approx \frac{1}{N}
\]
as chain length ↑
solubility ↓

Degree of microphase separation controlled by \(\chi N\)
As \((\chi N) \uparrow\) get stronger separation

Hamley, I. W. Pages 1707 and 1705 in "Nanotechnology With Soft Materials." Angew.
Triblock Copolymers

\[ \begin{array}{c}
\text{A} \\
\text{B} \\
\text{C} \\
\text{B} \\
\text{A} \\
\text{B} \\
\text{A}
\end{array} \]


**Examples and Applications of Block Copolymers**
- nanostructures for magnetic storage
- membranes
- nanopatterns
- vehicles in solutions
- networks

Properties of copolymer
- random copolymer \( \rightarrow \) avg of properties: \( T_g \)
- time mixing
- block copolymer

\[ \begin{array}{c}
\text{PS} \\
\text{PB} \\
\text{PS}
\end{array} \]
\( T_g \sim -70^\circ C \)
\( T_g \sim 100^\circ C \)

\( \Rightarrow \) see both Tg phase transitions in thermogram
2 independent blocks

\[ \begin{array}{c}
\text{PS} \\
\text{PS} \\
\text{PS}
\end{array} \]
\( \rightarrow \) rubbery property
SBR
styrene butadiene rubber
**Anionic Polymerization**

\[
\text{CH}_3 \quad \text{H}_2\text{C} = \text{C} \quad \text{C} = \text{O} \quad \text{O} \quad \text{CH}_3
\]

methyl methacrylate

e\text{'}-drawing group

**Cationic Polymerization**

- need substituent that is e\text{'}-donating

e.g.

\[
\text{H}_2\text{C} = \text{CH} \quad \xrightarrow{\text{H}_2\text{C} = \text{C}^\oplus + \text{H}_2\text{C} = \text{CH}} \quad \text{H}_2\text{C} = \text{C}^\oplus \quad \text{H}_2\text{C} = \text{CH}
\]

propagating cation stabilized by e\text{'}-donating nature of :O:

Can also have propagating oxonium ions
e.g.

\[
\text{H}_2\text{C}^\oplus \quad \text{O} \quad \text{R}
\]

also ammonium ions
NOT limited to carbon chemistry

**Typical Cationic Monomers**

alkenes, isobutenes

\[
\text{H}_2\text{C} = \text{C} \quad \text{H}_2\text{C} = \text{C} \quad \text{R} \\
\text{H}_2\text{C} = \text{C} \quad \text{H}_2\text{C} = \text{C} \quad \text{CH}_3
\]
vinyl ethers

\[ R\overset{\text{H}_2\text{C}=\text{C}}{\text{O}}\text{R}' \]

vinyl acetates

\[ \text{H}_2\text{C}=\overset{\text{CH}_3}{\overset{\text{O}}{\text{C}}}\text{H}_3 \]

contrast with methyl methacrylate

\[ \text{H}_2\text{C}=\overset{\text{CH}_3}{\overset{\text{O}}{\text{C}}}\text{H}_3 \]

styrene*

* = also by anionic

\[ \text{H}_2\text{C}=:\overset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}\text{H}_2\text{C}=:\overset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}\text{H}_2\text{C}: \]

\[ \overset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}\text{H}_2\text{C}: \]

\[ \overset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}\text{H}_2\text{C}: \]

\[ \overset{\text{CH}_3}{\overset{\text{H}}{\text{C}}}\text{H}_2\text{C}: \]

some cyclics

epoxides*

tetrahydrofuran (THF)

lactanes

etc
Cationic Polymerization

Some differences between cationic and anionic polymerization
- Rates are faster for cationic
  (1 or more orders of magnitude faster than anionic or free radical)
- $\text{C}^\oplus$ is very reactive, difficult to control and stabilize
  $\rightarrow$ more transfer occurs
  $\rightarrow$ more side reactions
  $\rightarrow$ more difficult to form “living” systems
  $\rightarrow$ hard to make polymers with low PDI or block copolymers
- Living cationic only possible for a specific subset of monomers
- Most industrial cationic processes are not living
  - recent developments are improving this

Kinetic Steps for Cationic Polymerization

Initiation: Use Acids
- Protonic Acids (Bronsted): HA
  strong, but without nucleophilic counterion
  $\text{HClO}_4$, $\text{CF}_3\text{SO}_3\text{H}$, $\text{H}_2\text{SO}_4$, $\text{CFCOOH}$
  $\rightarrow \text{ClO}_4^-$
- Lewis Acids
  Often as initiator/coordination complexes
  helps stabilize counterions and prevent recombination
  $\text{BF}_3 + \text{H}_2\text{O} \leftrightarrow [\text{H}^+\text{BF}_3^-\text{OH}]$
  $\text{AlCl}_3 + \text{RCl} \leftrightarrow [\text{R}^+\text{AlCl}_4^-]$
  $\text{SbF}_5 + \text{HF} \leftrightarrow [\text{H}^+\text{SbF}_6^-]$

Equilibrium between anion-cation pair

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Carbenium salts with aromatic stabilization

\[
\begin{align*}
\text{C}-\text{C}-\text{Cl} & + \text{SbCl}_5 \rightarrow \text{C}^\oplus \text{SbCl}_6^\ominus \\
\end{align*}
\]

**Propagation**

\[
\begin{align*}
\text{CH}_2\text{C}^\oplus\text{A} & + \text{H}_2\text{C}\equiv\text{CHR} \rightarrow \text{CH}_2\text{C}^\oplus\text{A}\\
\text{initiation species} & \quad \text{vinyl monomer}\\
\end{align*}
\]

Note: rearrangements can occur, especially if a more stable carbocation can be formed (e.g. tertiary carbocation) (most common for 1-alkenes, \(\alpha\) olefins)

e.g. 2 methyl butene

\[
\begin{align*}
\text{H}_2\text{C}\equiv\text{CH} & \quad \text{H}_3\text{C}\equiv\text{CH}\text{CH}_3
\end{align*}
\]

This occurs via intramolecular hydride (H\(^-\)) shifts

Usually slow: If \(R_p \leq\) rearrangement rate, will get rearranged product

\[
\text{H}_2\text{C}\equiv\text{C}^\oplus\text{CH}_3
\]

If \(R_p >\) rearrangement rate, will get random copolymer

\[
\text{As } T\uparrow, m\uparrow \text{ (less rearrangement) } \quad \text{Rate of rearrangement does not increase as fast as rate of propagation.}
\]

Hydride shift NOT common for conjugated monomers like: styrene, vinyl ethers and isobutylene and other tertiary carbocations.

---

10.569, Synthesis of Polymers, Fall 2006  
Prof. Paula Hammond  
Lecture 25  
Page 2 of 7  

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
**Termination and Transfer (Several Possibilities)**

A) Termination with counterion: kills propagating cation, kinetic chain ($k_t$)

i) Combination

$$\begin{align*}
\sim \text{CH}_2\text{CH}_2\text{R}^+ &+ \text{CF}_3\text{COO}^- \\
&\xrightarrow{k_{t,\text{comb}}} \sim \text{CH}_2\text{C}^\ominus\text{O}^\ominus\text{C}^\ominus\text{CF}_3
\end{align*}$$

ii) Anion Splitting

$$\begin{align*}
\sim \text{CH}_2\text{CH}_2\text{R}^+ &+ \text{BF}_3\text{OH} \\
&\xrightarrow{k_{t,s}} \sim \text{CH}_2\text{C}^\ominus\text{OH} + \text{BF}_3
\end{align*}$$

B) Transfer or termination to impurity or solvent

To $\text{H}_2\text{O}$, $\text{ROR}$, $\text{NR}_3$, etc.

$$\begin{align*}
\text{HM}_n\text{M}_1(\text{IZ})^\ominus &+ \text{XA} \\
&\xrightarrow{k_{tr,s}} \text{HM}_n\text{MA} + \text{X}(\text{IZ})^\ominus
\end{align*}$$

e.g.

$$\begin{align*}
\sim \text{CH}_2\text{CH}_2\text{R}^+ &+ \text{ROR} \\
&\xrightarrow{} \sim \text{CH}_2\text{C}^\ominus\text{C}^\ominus\text{R}^+
\end{align*}$$

more stable than

$$\begin{align*}
\sim \text{CH}_2\text{CH}_2\text{R}^+ &+ \text{R}-\text{OH} \\
&\xrightarrow{} \sim \text{CH}_2\text{C}^\ominus\text{OR} + \text{H}^\ominus\text{A}^\ominus
\end{align*}$$

not as reactive, acts as retardant - will not propagate further

weak acid will not initiate

**All these processes kill chain length.**
Transfer (Kinetic Chain Maintained)

A) Proton transfer to monomer

\[ \begin{align*}
\text{H} & \text{H} \\
\text{C} & \text{C}^\circ \Theta_A \\
\text{H} & \text{R} + \text{H}_2\text{C} = \text{CH} \\
\rightarrow & \\
\text{C} & \text{C} \\
\text{H} & \text{H} \\
\text{R} & \\
\text{H}_3\text{C} & \text{C}^\circ \Theta_A \\
\end{align*} \]

B) Hydride ion transfer from monomer

\[ \begin{align*}
\text{CH}_2 & \text{C} \\
\text{H} & \text{R} + \text{H}_2\text{C} = \text{C} \\
\rightarrow & \\
\text{CH}_2 & \text{CH}_2 \\
\text{R} & \\
\text{H}_2\text{C} & \text{C}^\circ \Theta_A \\
\end{align*} \]

In general, chain transfer to monomer is favorable so \[ C_m \rightarrow \frac{k_{tr,M}}{k_p} \] can be sizeable.

C) Proton transfer to counterion

("spontaneous termination")

\[ \begin{align*}
\text{CH}_2 & \text{C} \\
\text{CH}_3 & \text{CH}_3 + \text{H}^\circ \Theta_A \\
\kappa_{tr,cl} & \\
\rightarrow & \\
\text{CH}_2 & \text{C} \\
\text{CH}_3 & \\
\text{CH}_2 & \\
\text{H}^\circ \Theta_A \\
\end{align*} \]

usually goes on to initiate again

protic acid initiators are possible
+Lewis acids are less likely

Usually propagates (does NOT kill chain)
**Kinetic Expressions**

**Initiation: Assume Lewis Acid Pair**

1. \[ \text{I} + \text{ZY} \underset{K}{\overset{Y(IZ)}{\rightleftharpoons}} \]

\[ Y(IZ) \] \[ + \text{M} \rightarrow YM(IZ) \]

2. \[ Y(IZ) \] \[ + \text{M} \rightarrow YM(IZ) \] often rate limiting

If step 2 is rate determining, then

\[ R_i = k_i [Y^+(IZ)][M] \]

\[ = k_i K [I\text{ZY}[M] \]

*R_i could be determined based on step 1. Then the expressions would be different.

**Propagation**

\[ YM(IZ) + \text{M} \rightarrow YM_j(IZ) \]

Assumption: chain length has little effect on reactivity

\[ R_p = k_p [YM_j(IZ)][M] = k_p [M^+][M] \]

Let \([M^+] = \text{total concentration of all-size propagating carbocations (ion pairs + free ions)}\]

**Termination**

Must determine primary means of termination (solvent, impurities, counterion combinations, or all?)

Example case: termination by counterion combination

\[ YM(IZ) \rightarrow YMI\text{Z} \Rightarrow R_t = k_{t,\text{comb}} [YM^+(IZ)^+] = k_{t,\text{comb}} [M^+] \]

If we assume steady state \([M^+] \]

\[ R_s = k_i [M^+] = k_i k [M][I\text{ZY}] = R_i \]

Steady state assumption is that \(R_t = R_i\)

\[ [M^+] = \frac{R_i}{k_i} \]

Going back to \(R_p\) with \([M^+] = \frac{R_i}{k_i}\)

\[ R_p = \frac{R_i k_p [M]}{k_i} = \frac{K k_i k_p [I\text{ZY}[M]^2}{k_i} \]

second order in \([M]\]

First order in \(R_i\)
(unlike free radical)

\( \bar{P}_N \) : No transfer (to monomer, solvent, counterion)

\[
\bar{P}_N = \frac{R_p}{R_t} = \frac{k_p[M]}{k_t}
\]

\( \bar{P}_N \) : If transfer occurs

- \( R_{tr,M} \): to monomer \( \rightarrow \) create new propagating chain
- \( R_{tr,S} \): to solvent \( \rightarrow \) create new cationic species
- \( R_{tr,Ci} \): to counterion \( \rightarrow \) recreate initiation

\[
\bar{P}_N = \frac{R_p}{R_t + R_{tr,M} + R_{tr,Ci} + R_{tr,S}}
\]

with

\[
R_{tr,M} = k_{tr,M} M^+ [M]
\]
\[
R_{tr,Ci} = k_{tr,Ci} M^+ [S]
\]

\[
\frac{1}{\bar{P}_N} = \frac{k_t}{k_p[M]} + \frac{k_{tr,Ci} [M]}{k_p[M]} + C_M + C_S + \frac{k_{tr,M}}{k_p} + \frac{k_{tr,S}}{k_p}
\]

Suppose transfer to solvent or impurity does not result in further propagation.

\( \text{e.g. } \text{NR}_3 \Rightarrow \text{HM}_N\text{M}^{(IZ)} {^\ominus} + \text{NR}_3 \rightarrow \text{HM}_N\text{M}^{(IZ)} \text{N}^- \text{R}^+ \text{R} \text{ Is stable}
\text{No further propagation}

This must be included in steady state \([M^+]\) expression

\[
R_p = \frac{k_k k_p [I][Z \gamma][M]}{k_t + \left( k_{tr,S} [S] \right)}
\]

\( \text{term from transfer like } \)

*does not effect \( P_N \) expression (do not include in \( P_N \) calc)

*Note: all of the above assumes the 2\textsuperscript{nd} initiation step is rate determining.

**Validity of Steady State Assumption**

Not really valid

- rxn rates very rapid (seconds – minutes)
- often \( R_t > R_t \)
- \([M^+]\) slowly increases with time
- \([M^+]\) reaches maximum late in polymerization
  then decreases with further conversion

Application of equations is merely an approximation of what really happens.
Cationic Polymerization

\[ R_p = \frac{K_k k_p [I][Z][Y][M]^2}{k_i} \]

Energetics of Cationic Polymerization

\[ R_p \propto \frac{k_i k_p}{k_i} \Rightarrow \frac{A_p A_t}{A_t} \exp \left( \frac{-E_p - E_t + E_t}{RT} \right) \]

\[-E_p - E_t + E_t = E_{RP} \sim 5-10 \text{kcal/mol} \]

- More directly impacted by T: transfer rates
- \(C_M\) ↓ by 100x for \(\Delta T\) from -30°C to 60°C
- Often use refrigeration for commercial processes
- \(E_{pa} = -E_p + E_t + \sum E_{tr}^{pn}\)
  - energy of transfer reactions

Example: Cationic Polymerization of Polyisobutylene (PIB)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{H}_2\text{C} & \quad \text{C} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

temp of polymerization: -100°C to -30°C

need a lot of refrigeration!

→ high rate of heat release

want \(R_p\) to be lower for control

(cationic is very rapid, faster than other polymerization methods)

- If used a good solvent for PIB → high viscosity early on (problem!)
- Thus, choose a decent solvent for monomer but poor solvent for polymer PIB
- Precipitation occurs as polymer is generated
Example: To Form Butyl Rubber

\[
\begin{align*}
n \text{H}_2\text{C} = \text{C} &+ m \text{H}_2\text{C} = \text{H} = \text{CH}_2 \\
\text{(isobutene)} & & \text{(isoprene)}
\end{align*}
\]

\[
\text{can form crosslinks with crosslinking agents}
\]

Solvent: CHCl₃
(also precipitant of polymer)

Butyl rubber: solvent resistant
Ex: gloves
- doesn’t break down in ozone (O₃)
  → chemically stable
- chem tank liners
- chem tubes

Cationic: very rapid, high MW
Difficult to control, PDI affected

Living Cationic Polymerization
- must have \( R_i \gg R_p \)
  (steady state is not a very good assumption)
- must eliminate cross-transfer processes (that limit chain growth)
  1. carbocation reactivity is lowered
  2. deter combination of counterion
  3. eliminate other impurities

Porous crystal particles
⇒ allow precipitation of monomer
⇒ continued chain growth
⇒ low η slurry
  low T's \( \eta, T \) control

Doesn’t crystallize even at low T
→ stiff and brittle
app: space shuttle

\[10.569, \text{Synthesis of Polymers, Fall 2006}\]
Prof. Paula Hammond

\[\text{Lecture 26}\]
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OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Examples

Vinyl ethers

\[
\begin{align*}
H_2C&=CH \\
+ OR' 
\end{align*}
\]

Initiator: HI + ZnI₂
Solvent: toluene
-40 to -25°C

Ethyl styrene

\[
\begin{align*}
H_2C&=CH \\
\text{(bicycle)} \\
+ CH_3
\end{align*}
\]

Initiator: CH₃COClO₄
Solvent: CH₂Cl₂/Toluene, -78°C

- Counterion choice is important
  e.g. Bulky counterion that cannot recombine or counterion attacks reversibly

\[
\text{C}^{+} + \text{X}^{-} \leftrightarrow \text{C}^{-} \text{X}
\]

- Styrenes, vinyl ethers, vinyl carbazoles, isobutylene
  can attach side groups

“Living” or “Quasi-living” b/c never completely get rid of transfer
PDI ~ 1.1 to 1.2 but good enough to get high yield polymers

**Ring-Opening of Cyclic Ethers**
(best example of ring-opening family)

\[
\begin{align*}
\text{(CH₂)_n} \\
\text{(n=2)} \Rightarrow \text{oxirane or epoxide}
\end{align*}
\]

Monomers:
- Ethylene oxide
- Propylene oxide
- or other epoxide rings

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OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
\[ n=3 \Rightarrow \text{oxetane, trimethylene oxide} \]
\[ n=4 \Rightarrow \text{oxolane, tetrahydrofuran} \]

where \( R \) does not affect polymerization

\[ n=6 \text{ keep increasing} \]

(for anionic polymerization: only epoxides can be polymerized)

\[ \text{b/c it has a huge angle strain, will open using anionic or cationic initiation} \]

anionic

\[ \text{can be done in controlled environment (living polymerization)} \]

\[ p_n \uparrow \text{slowly with conversion} \]

Rate, kinetics indicate living system

\[ R_p = k_p^{\text{app}} [M][M^-] \]

\[ \frac{p_n(t)}{[I]} = \frac{[M]_k - [M]_p}{[I]} \Rightarrow p_n = \frac{[M]_k}{[I]} \]

Can initiate with any oxyanion: CH3O- and its analogs

\[ \text{carboanion} \]

- all other cyclic ethers only go by cationic initiation

Examples: oxetanes

\[ \text{Initiators: strong acids: } \text{H}_2\text{SO}_4, \text{CF}_3\text{COOH} \]

or Lewis acid with counterions that don’t combine
Propagation Step

Termination Step

- Will happen if A" is nucleophilic → counterion combination
  (bad if irreversible)
  If H₂O is present (very good nucleophile)
  If :NH₂ is present

Use counterions that are stable
AsF₆⁻, PF₆⁻, SbCl₆⁻

Or very strong fluorosulfonic acids
CF₃SO₃H⁺
Only combine reversibly and rapidly

Initiate with mono- and bifunctional initiators

e.g.

F₃C—SO₃CH₃ + \[\text{cyclic monomer}\] → H₃C—O + \[\text{cyclic product}\]

or Triflic anhydride

\[\text{CF₃SO₂—O—SO₂CF₃} + n \text{cyclic monomer} \rightarrow \text{product}\]

large, bulky, only combines reversibly if at all

\[\text{CF₃SO₃}^-\] propagates in both directions

\[\text{CF₃SO₃}^-\]

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Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
want to avoid: \[ \{ \text{BF}_3/\text{H}_2\text{O}, \text{AlCl}_3/\text{HCl} \} \]

(temporarily)

→ causes shuffling ⇒ Flory distribution, hurts PDI

Best Living Systems

Pre-existing carbenium ions

\[ \text{C}_6\text{H}_5^-\text{C}^+=\text{O} \quad \text{SbF}_6^- \]

Carbenium ions

\[ \text{CH}_2\text{CH}_2^+=\text{O} \quad \text{PF}_6^- \]
\[ (\text{C}_6\text{H}_5)_2\text{C}^+=\text{H} \quad \text{BF}_4^- \]

Triflic systems

\[ \text{CF}_3\text{-SO}_2\text{-O-CH}_3, \text{etc} \]

Avoid: ROH

RNH$_3$

ROR

Other ethers (check relative reactivities)
Can intentionally terminate to get o-functionalities

\[ \sim(CH_2)_6 - \xrightarrow{H_2O} O(CH_2)_4-OH \]
\[ \sim(CH_2)_6 - \xrightarrow{NR_3} O(CH_2)_4-NR_3 \text{ tertiary amine group} \]
\[ \sim(CH_2)_6 - \xrightarrow{RNH_2} O(CH_2)_4-NHR \text{ primary amine} \]
\[ \sim(CH_2)_6 - \xrightarrow{Na^+} O(CH_2)_4-O^- \]
\[ \sim(CH_2)_6 - \xrightarrow{LiBr} O(CH_2)_4-Br \]

Ch. 7 Odian: Ring strain
Diff impacts of ring sizes
Issues of Equilibria (Ring-Opening Polymerization)
- particularly relevant with long lived polymerization processes
- "living" systems: step growth → revert to equilibrium

Ch 7 Odian

Effects of Ring Strain

\[(\text{CH}_2)_n\]

- 3-4 atoms → angle strain
- 5,7 atoms → torsional strain b/c of eclipsed conformations on neighboring atoms (not a planar condition, → chair conformation (6))
- 6 atoms → perfect situation (no angle, torsional strain, have chair conformation)
- 8-11 atoms → transangular strain (due to repulsive interactions w/in ring from H atoms) → much more pronounced when things are bigger then H-atoms
- 13 atoms → eliminate strains but difficult to make ends meet for polymerization

In general, 5 and 6 membered rings are more likely to undergo depropagation due to cyclic nature, or in non-ring opening polym, it’s a temperature effect

\[\text{THF} \rightarrow \text{PTMO}\]

\[\text{trioxane} \rightarrow \left\{\text{CH}_2\text{-O}\right\} \quad \text{depropagates into formaldehyde}\]

\[\text{highly volatile vaporizes at high T}\]

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Because of possible depropagation, for "Quasi-living" systems → living behavior to approach of [M]_n
But for more strained systems, have full conversion e.g. Ethylene oxide oxitanes

Siloxanes
• Accessible by anionic or cationic means

Step growth is also possible

Siloxanes form stable ring compounds → alleviate ring strains → also form

Anionic Ring Opening

D₃ and other trimers like it can be initiated by
- alkyl metal hydroxide
  \[
  \text{CH}_3\text{CH}_2\text{O}^- \ M^+
  \]
or \[ \text{HO}^- M^+ \] metal hydroxide
or \[ \text{CH}_3\text{Si-O}^- \ M^+ \] silanolate anion
(of course, can use butyl Li, strong initiators)

\[
\begin{align*}
A^+ + M^- & \rightarrow A-Si-O-Si-O^- M^+ \\
\text{propagate} & \\
- \ R \text{ group can be alkyl, cannot be H} & \\
\text{because Si-H is acidic} & \rightarrow \text{termination} & \\
- \ R \text{ group can be vinyl group} & \\
\text{or other non-reactive group} & \{ \text{with appropriate initiator} \}
\end{align*}
\]

**Cationic Propagation**

Can use D₃ or D₄ ← too stable to be made by anionic reaction only D₃ can be made by anionic reaction

\[
\text{protonate with acid initiator} \\
\text{(protonic acid like H₂SO₄ or use Lewis acid)}
\]

**Lactams**

form polyamids via “activated monomer” mechanism (cyclic amide)

\[
\begin{align*}
\text{(CH}_2\text{)}_m\text{NH} & \\
\text{most common: } m=5 & \\
& (\varepsilon\text{-caprolactone}) \text{ can go by anionic or cationic mechanisms}
\end{align*}
\]
**Anionic**

- Use metal or metal hydride as initiator

\[
\text{(M) + (MH)}
\]

Initiation

**Step 1**

\[
\text{(CH}_2\text{NH)} + \text{M} \rightleftharpoons \text{(CH}_2\text{N)}^- \quad + \quad \text{M}^+ + \frac{1}{2} \text{H}_2
\]

**Step 2**

slow step in initiation process

\[
\text{attacks carbonyl group}
\]

can be sped up by introducing a more reactive group (acyl lactam)

\[
\text{(CH}_2\text{NH)} + \text{(CH}_2\text{NH)}_2 \quad \rightarrow \quad \text{(CH}_2\text{N)}^- \quad + \quad \text{M}^+ \quad \text{very reactive}
\]

rapid H exchange

\[
\text{active monomer}
\]

**Can be used to create block copolymers**

Can have well-defined blocks with other vinyl monomers.
**Polyesters as Biodegradable Polymers**

**Poly**(α-hydroxy acids)

\[
\begin{align*}
\text{from} & \quad \text{OCHR} - \text{C} \quad \text{n} \\
\text{R}=\text{H} & \Rightarrow \text{polyglycolic acid (PGA)} \\
& \quad \text{(polyglycolide)} \\
\text{R}=\text{CH}_3 & \Rightarrow \text{polylactic acid} \\
& \quad \rightarrow \text{poly (L-lactide) (PLLA)} \\
& \quad \text{poly (D-L-lactide) (PDLLA)} \\
\text{copolymers: “PLGA” (vary composition to change } T_m \text{) and other mechanical properties}
\end{align*}
\]

- can proceed by anionic or cationic means
  - most common: anionic initiated by oxyanions

Details - can achieve living polymerization
  - commonly add catalyst that accelerates esterification e.g. stannous octanoate
  - can also change conditions to achieve step growth-like conditions (e.g. initiator, solvent conditions) condensation nature → control MW with alcohol endcappers

**Polylactones**

\[
\begin{align*}
\text{Anionic or cationic} \\
\text{Initiate with } \text{CH}_3\text{O}^- \\
m=3,4,5 (5 \text{ most common}) \\
\varepsilon\text{-caprolactone}
\end{align*}
\]
**Polymer Functionalization**

Can make a polymer with desired side group R via

- direct route

\[
\begin{align*}
H_2C=CH & \rightarrow \quad \text{H} \quad \text{H} \\
R & \quad \text{C} \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{R} & \quad \text{n}
\end{align*}
\]

- or perform reaction on existing polymer

  a) \[
  \begin{align*}
  H_2C=CH & \quad \text{X} \\
  \text{CH}_2 & \quad \text{C} \\
  \text{X} & \quad \text{n}
  \end{align*}
  \]

  b) \[
  \begin{align*}
  \text{CH}_2 & \quad \text{C} \\
  \text{R} & \quad \text{n}
  \end{align*}
  \]

Issues with reactions on polymers

Reactions on Polymers vs Reactions on Small Molecules

Small Molecule

\[
\begin{align*}
Y & \quad \text{X} \\
\quad & \quad \text{X} \\
\quad & \quad \text{X} \\
\quad & \quad \text{X}
\end{align*}
\]

react to form \[
\begin{align*}
\text{X} & \quad \text{Y}
\end{align*}
\]

Polymer Chain

\[
\begin{align*}
\text{X} & \quad \text{X} \\
\text{X} & \quad \text{X} \\
\text{X} & \quad \text{X} \\
\text{X} & \quad \text{X} \\
\text{X} & \quad \text{X} \\
\text{Y} & \quad \text{Y} \\
\text{Y} & \quad \text{nY}
\end{align*}
\]

1. Yield has different meaning

Small molecules: 80% yield

spin process

pre-product 80%

unreacted molecule + reagent 20%
Polymer chain: 80% yield $\rightarrow$ no separation to "pure" component form copolymer with 80% functionalized groups

2. Localized concentration effects

(e.g. high MW polymer in intermediate solvents)

polymer chains may "hide" access of reagent

very large solvent effects

3. Polymer morphology

(e.g. semicrystalline polymers)

→ can be relatively impermeable to solvent + reagent

Block copolymers in selective solvent

solvophobic block is less accessible to reaction can be advantageous for selective modification of blocks
Selective Hydrogenation

e.g.

\[ \text{PB} \xrightarrow{\text{H}_2/\text{Pt}} \text{PE} \]

rubber \quad \text{waxy crystalline solid}

\[ \left\{ \text{CH}_2-\text{CH} \right\} \xrightarrow{\text{polyV-cyclohexane}} \left\{ \text{CH}_2-\text{CH} \right\} \]

poly 1,4 cis polyisoprene (rubbery low T_g)

\[ \text{PI} \xrightarrow{\text{PEP}} \]

limit crystallinity

4. Sterics are amplified
Steric hindrance can reduce reactivity of neighboring units

\[ \left\{ \text{CH}_2-\text{C} \right\} + \text{R-I} \rightarrow \left\{ \text{CH}_2-\text{C} \right\} \]

reactive and can undergo substitutions

polyvinyl pyridine
PVP

\[ \begin{cases} 
\text{R} = \text{C}_4\text{H}_9 \text{ is 4x faster reaction rate than} \\
\text{R} = \text{C}_{18}\text{H}_{37} \\
\text{But rates are the same for} \end{cases} \]

\[ \left\{ \text{N} \right\} + \text{R-I} \]
Note: sterics can often be alleviated with alkyl or ethylene oxide

e.g.

\[
\begin{array}{c}
\text{easier, faster} \\
\text{rate}
\end{array}
\]

5. Electrostatics can play a role in reaction rate

- unfavorable to make a new \(N^+\) group here b/c of neighboring \(+^s\)
- by saturating with salt (e.g. \(\text{NaCl}\)) helps reduce distance between \(+\) and \(-\) charge

Debye length

\[\therefore \text{more able to react} \]

Consider Kinetics

\[
\begin{array}{c}
\text{AAA} \quad \text{AAABABAAA} \\
\downarrow k_0 \\
\text{AAABAAA} \quad \text{AAABAAA} \\
\downarrow k_1 \\
\text{vs.} \\
\text{if } k_0 = k_1 = k_2 \\
\text{Bernoullian distribution of} \\
\text{functionalization}
\end{array}
\]

different reactivity than previous with 2A partners
e.g. for highly reactive systems

\[ \text{CH}_2\text{C} - \text{C} - \text{C} - \text{O} \rightarrow \text{SOCl}_2 \rightarrow \text{CH}_2\text{C} - \text{C} - \text{C} - \text{Cl} \]

auto-acceleration (a.k.a. autocatalytic effects)

e.g. hydrolysis of PMMA

\[ \text{CH}_2 \text{H} - \text{C} - \text{CH}_3 \text{C} - \text{C} - \text{CH}_3 \text{C} - \text{C} - \text{CH}_3 \text{C} - \text{C} - \text{CH}_3 \] \[ \text{ HO}^\text{+} \rightarrow \text{CH}_3\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{CH}_3 \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{CH}_3 \]

(treat with strong base)

\[ k_2 \gg k_1 \Rightarrow \text{autocatalysis} \]

**Common Polymer Functionalization**

Make polymers that are otherwise inaccessible

1. Polyvinyl alcohol (PVA)

\[ \text{H}_2\text{C} - \text{O} - \text{C} - \text{O} - \text{C} - \text{O} - \text{CH}_3 \text{C} - \text{O} - \text{C} - \text{O} - \text{CH}_3 \]

\[ \text{CH}_2\text{CH} - \text{OH} \rightarrow \text{CH}_3\text{C} - \text{CH} - \text{OH} \]

not stable!!

stable form
Polyvinyl Acetate

\[
\begin{align*}
\text{CH}_2\text{CH} & \quad \text{free radical or cationic} \\
\text{O} & \quad \text{CH}_2\text{CH} \\
\text{C} & \quad \text{O} \\
\text{CH}_3 & \quad \text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{hydrolysis} & \quad \text{(acid or base)} \\
\text{CH}_2\text{CH} & \quad \text{OH} \\
\text{O} & \quad \text{C} \\
\text{CH}_3 & \quad \text{O} \\
+ & \quad \text{CH}_3\text{C} \\
\text{O} & \quad \text{OH}
\end{align*}
\]

Polyvinyl acetals are made from PVOH

\[
\begin{align*}
\text{CH}_2\text{CH} & \quad \text{OH} \\
\text{R-C} & \quad \text{OH} \\
\text{CH}_2\text{CH} & \quad \text{O} \\
\text{CH}_2\text{CH} & \quad \text{O} \\
\text{R} & \quad \text{H}
\end{align*}
\]

Also

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{H} & \quad \text{N} \\
\text{H} & \quad \text{N} \\
\text{H}_2\text{N}
\end{align*}
\]

Linear polyethylene imine

Aziridine

Instead use 2-ethyl-2-oxazoline (EOX)

2. Halogenation of vinyl polymers
   - improves water resistance
   - improves fire/flame stability (chlorination and some case 1 bromination)

Chlorination of natural rubber

Hydrochlorination

\[
\begin{align*}
\text{HCl} & \quad \text{CH}_2\text{CH} \quad \text{CH}_3 \\
& \quad \text{CH}_2\text{CH} \quad \text{CH}_3 \\
& \quad \text{CH}_2\text{CH} \quad \text{CH}_3
\end{align*}
\]

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Plain chlorination

Gives more Cl

\[
\text{Cl}_2 \rightarrow \left( -\text{CH}_2 - \text{C} - \text{C} - \text{CH}_2 \right)^+ \\
\text{Cl} \quad \text{H}
\]

Can add more Cl by free radical
→ aromatic substitutions next time
**Aromatic Substitutions**
e.g. chloromethylation

\[
\begin{align*}
\text{CH}_2\text{CH}_n & \xrightarrow{\text{SnCl}_4, \text{ClCH}_2\text{OCH}} \text{CH}_2\text{CH}_n \text{ CH}_2\text{Cl} \\
\{ & \text{good for nucleophilic substitution} \\
\end{align*}
\]

\[
\text{I} + \text{CH}_3\text{OH} + \text{N}_2\text{O} \xrightarrow{2 \text{NaOH}} \text{CH}_2\text{CH}_n
\]

**Other Useful Functionalizations**
- can use reactive amines
e.g.

\[
\begin{align*}
\text{CH}_2\text{CH}_n & \xrightarrow{\text{H}_2\text{N}} \text{NH}_3 + \text{R-CH}_2\text{Cl} \xrightarrow{} \text{NH-CH}_2\text{R} \\
\text{reactive site} & \xrightarrow{} \text{NH}_2 + \text{R-CH-CH}_2 \xrightarrow{\text{epoxide}} \text{NH-CH}_2\text{CH-R} \\
\end{align*}
\]

- methacrylate chemistry

\[
\begin{align*}
\text{H}_2\text{C} & \xrightarrow{\text{C}} \text{CH}_3 \\
\text{CO}_2\text{R'} & \xrightarrow{\text{CH}_3} \text{CH}_2\text{C} \xrightarrow{\text{hydrolyze}} \text{CH}_2\text{C} \\
\text{C} & \xrightarrow{\text{O}} \text{OH}
\end{align*}
\]
Used in Merrifield synthesis (step growth)

- hydrosilation

General reaction:

\[
R\text{Si}-H + \text{ vinyl group } \xrightarrow{\text{Pt}} R\text{SiCH}_2\text{CH}_2\text{R}
\]

On polymers:

\[
\text{Handout - 2-ethyl-2-oxazoline cationic ring-opening polymerization}
\]

Backbone can be converted to polyethylene amine.
Liquid Crystals (LC’s)

→ Board-shaped
  “calamitic” can orient preferentially

→ disc-shaped
  “discotic”

crystals orientation
domains of different orientation
guide light along domains

polydomains

Align LC → using EM field
  can allow light to pass through

Applications: displays – need mechanical stability
  storage – freeze in orientation and read later
  glassy polymer

→ How to attach LC to polymers

1. How to form polymer w/LC side group
2. Block copolymer: LC side chain block and glassy block
Design “Case Study” – LC Side Chain Polymers

- **Requirements**
  - **Backbone**: determines $T_g$
    - mechanical properties
    - chemical stability
    - can affect switching times/response times
- **Alkyl spacer group**
  - choose spacer group: alkyl and ethylene oxide (most common)
    - shorter leads to nematic phases
    - more flexible b/c CH$_2$O bond

- **Mesogen**
  - LC properties
    - optoelectronic response
    - alignment
time
dipole

Longer spacers form smectic phases
alkyl group will order

Unidirectional
Ordered
⇒ nematic

Stacked: 2D order
⇒ smectic
more ordered system
-Other factors
  - does PDI matter?
    For this application, it depends which phase you’re going for
    For LC polymers, can lose some less stable phases w/high PDI

Example:

\[
\begin{align*}
&\text{backbone} \\
&\text{(CH}_2\text{)}_5\text{C}=\text{O} \\
&\text{O} \\
&\text{O} \\
&\text{O} \\
&\text{O} \\
&\text{O} \\
&\text{C}_4\text{H}_4
\end{align*}
\]

<table>
<thead>
<tr>
<th>PDI</th>
<th>Increasing T →</th>
</tr>
</thead>
<tbody>
<tr>
<td>a 1.2</td>
<td>(S_F \rightarrow RN \rightarrow S_A \rightarrow N \rightarrow I)</td>
</tr>
<tr>
<td>b 2.9</td>
<td>(S_F \rightarrow N \rightarrow I)</td>
</tr>
</tbody>
</table>

- High MW/Low MW?
  - Oligometric → stable image
  - High MW → storage

- Selected polymer chem. (side group react w/backbone?)
  - need 100% substitution?

- \(S_F\) = smectic F
- I = isotropic clearing point
- N = nematic
Lecture 30: Surface Functionalization of Polymers, Graft Copolymerization, Approaches to Making Comb and Graft Architectures, Grafting onto Existing Polymer Surfaces, Surface Engineering Using Graft Copolymers

Papers by Zaschke et al, Adams + Gronski, Zentel, Finkelmann on Liquid Crystals

Potential Approaches to LC Polymers

A. Polymerization of an LC functionalized chain growth monomer

B. Step growth approach using a monomer w/functional group

C. Functionalization of existing backbone

Pros and Cons

A. Direct polymerization of functional chain growth monomer
   i) anionic
      pros: - controlled MW, MWD (monodispers)
             - can make block copolymers, $\alpha$-$\omega$ functionalized polymers
             - 100% substitution
      cons: - very reactive, could react with mesogen $M$
             (bulky side groups can impede propagation)
   ii) free radical
      pros: - works with broad range of monomers
             (more backbones accessible)
             - can make random copolymers with non-functional monomer
             (can go from 100% and approach 0% with Bernoullian distribution – depends on reactivity ratios)
      cons: - cannot have good control of MW
             - inability to make blocks

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
**B. Step growth**

\[ a \longrightarrow b \quad \text{or} \quad a \longrightarrow a + b \longrightarrow b , \text{etc...} \]

**Pros:**
- useful if we wish to combine with main chain group
- choose

**Cons:**
- low MW (except at high \( \pi \))
- slow reaction
- broad PDI

**C. Functionalization of existing polymer**
(polymer-analogueous rxns)

**Pros:**
- can approach polymerization of “base” monomer independent of side group reactivity, solubility, bulk
- can choose well-defined approaches
  \( \Rightarrow \) control MW
  \( \Rightarrow \) control PDI
- can change yield \( \Rightarrow \) change % substitution \( \Rightarrow \) random copolymers!

**Cons:**
- not easy to obtain 100% substitution (possible but depends on solvent, etc...)
- challenges in isolating polymer, depending on system (purification)
- sometimes functionalization (modification chemistry) can attack/affect backbone

Creating block copolymer with LC block/amorphous, etc

\[ \text{amorphous} \quad \text{amorphous} \]

Stabilize LC, C\(^*\): fast switching speed but fragile display
\( \rightarrow \) stabilize w/amorphous region

**Polymer Surface Functionalization**

**Motivation:**
- Improving adhesion
- Modify frictional properties
- Attach specific chemistries
- Modify barrier properties
Some Common Methods of Polymer (Plastic) Surfaces

- High energy surface treatments
  - Flame treatments
  - Corona treatments
  - Plasma treatments (CO₂, air, …)
  - γ-irradiation, e-beam

  - works on most plastic and resin surfaces (PE, PP)
    - e.g. w/ H₂SO₄/CrO₃
    - or basic solutions —OH , —C—OH
      (PP, LDPE, HDPE, polycarbonates, etc…)

- Modify specific groups on polymer chain
  - e.g. —C—OCH₃ of PMMA surfaces
  - or —— of PS surfaces
  - etc…


Modification of Solid Polymer Surface

e.g. the $\text{C} - \text{OCH}_3$ of PMMA slab

the $\text{C}_6\text{H}_5$ of PS surface

Surface reactivity

• must have access to functional groups
• interfacial energy may impact presentation of functional groups to surface
• surfaces are dynamic → small rearrangement can occur
• also have to consider surface impurities that might prevent or occlude access to functional groups
⇒ issues around solvent choice and surface properties

Solvent compatibility

Need to have reaction solvent that wets surface but does not dissolve the solid
⇒ By altering solvents, get differing degrees of penetration into surface (varying from hundreds of nm to Å’s)
⇒ Solvent impacts % yield and kinetics
⇒ availability of surface groups and solubility of reagent

Remember surfaces are heterogeneous
Have morphology (e.g. crystallinity)
Have potential for plasticization w/solvent

Functionalization of Surfaces with Polymers

“Grafting From” Approaches

1. Surface irradiation w/high energy + monomer

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
2. Covalent attachment of initiating species

\[
\begin{align*}
\text{OH} & \quad \text{OH} + \text{Cl-C-CH}_2-\text{CH}_2-\text{C-N=O-C-CH}_2-\text{CH}_2-\text{C-Cl} \\
\text{heat} & \quad \text{heat} + \text{monomer}
\end{align*}
\]

“Grafting To”

\[
\begin{align*}
\text{X} & \quad \text{Y} \quad \longrightarrow \quad \text{X-Y}
\end{align*}
\]

Anionic/Cationic

\[
\begin{align*}
\text{CH}_2-\text{CH} & \quad \text{EtO-C} \\
\text{EtO-C} & \quad \longrightarrow
\end{align*}
\]

Step Growth

\[
\begin{align*}
\text{OH} & \quad \text{Cl-C} \\
\text{e.g. polyester}
\end{align*}
\]

Issues for grafting to

Lower yields
Steric constraints to full coverage
Examples (Handout)

Free Radical
- Accounts for -50% of all mass production of polymers
  - Emulsion
  - Suspension
  - Bulk solution

Most robust method of chain growth
  - Insensitivity to solvent
  - Insensitivity to impurities (NH₃, H₂O)
  - Insensitivity to atmospheric conditions

Open to widest variety of chain growth monomers
  - vinyl halogens
    - \( \text{-----Cl} \)
    - \( \text{-----F} \)

  - vinyl esters
    - limited in ionic polymerization
    - easy in free radical polymerization
    - \( \text{-----O} \)
    - \( \text{-----C} \text{R} \)

  - acrylates
    - \( \text{-----H} \)
    - protic
    - \( \text{-----O} \)
    - \( \text{-----R} \)

  - NOT vinyl ethers
    - \( \text{-----OR} \)

First Attempts at Living Free Radical Polymerization

(Otsa et al, 1982)

Initiators:
- Initiator
- Transfer
- Termination
  - Plays all three roles

\[ \text{C}_2\text{H}_5 \]
\[ \text{N} \]
\[ \text{C} \]
\[ \text{S} \]
\[ \text{S} \]
\[ \text{C} \]
\[ \text{N} \]
\[ \text{C}_2\text{H}_5 \]
\[ \text{C}_2\text{H}_5 \]
Dissociation

\[ R \rightarrow 2I \cdot \]

\[ \text{IH} + nM \xrightarrow{\text{init.}} I-Mn \cdot \xrightarrow{I} \text{"termination"} \rightarrow I-Mn-I \]

\[ \begin{align*}
I-Mn \cdot &\quad \text{reversible} \\
\rightarrow &\quad + I. \\
&\quad M \\
IM_{n+1}^+ &\quad + IH \quad \rightarrow \quad IM_n^+ + IM^+ \\
&\quad \text{new chain} \\
IM_{n+1}^-I &\quad \text{transfer}
\end{align*} \]

Get increased molecular weight over time, but road PDI.

1985 = Solomon et al.

Introduced first nitroxide free radical systems.

→ act as “adducts” but not initiators

\[ \begin{align*}
\text{N} &\quad \text{O} \cdot \\
\left\{ \begin{array}{c}
\text{CH}_3 \\
\text{CN}
\end{array} \right\} \\
&\quad \text{+ AIBN} \\
\left\{ \begin{array}{c}
\text{CH}_3 \\
\text{CN}
\end{array} \right\} \\
&\quad \text{reversible bond}
\end{align*} \]
Original Free Radical Mechanism

Initiation
\[
\begin{align*}
I & \rightarrow R \\
M + R & \rightarrow RM
\end{align*}
\]

Propagation
\[
RM + rM \rightarrow R[M]_\text{rM}
\]

Termination
\[
\begin{align*}
2 R[M]_\text{rM} & \xrightarrow{\text{Combination}} \\
& \xleftrightarrow{\text{Disproportionation}}
\end{align*}
\]

Nitrooxide Stable Free Radical

"TEMPO"

Stable Free Radical Mechanism

Initiator Fragment

Few Termination Events

Small amount of free radical

For "living" system, need forward rate > \(R_p\)

Adduct breaks and then recombines
Free Radical Polymerization

Free radical is most versatile type of chain growth
→ Most monomers are available
→ Can be done in
  • emulsion
  • suspension
  • bulk
→ Most robust method: less sensitive to
  • solvent
  • impurity
  • atmospheric conditions
→ Limitations
  • broad
  • lack of control over PDI
  • difficult to make well defined block copolymers
→ Methods to improve upon traditional free radical
  • Stable Free Radical Polymerization (SFRP)
  • Atom Transfer Radical Polymerization (ATRP)

“Controlled Free Radical Polymerization”

Stable Free Radical Polymerization

TEMPO → stable nitroxy free radical

\[
\text{N}O
\]

Use with initiator that has a fast half life
Benzoyl peroxide (BPO) half life ≤ 3 minutes

Requirements for SFRP

• Stable free radical must NOT initiate polymerization
• \( R_{\text{SFRcomb}} > R_p \)
  rate of free radical combination
• Need \( R_i >> R_p \)
• \( R_t << R_p, R_{SFR} \)

This system first described by
Georges, Veregin, Kazmeier, Homer

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Results

- PDI’s as low as 1.1 – 1.5
- Can form diblocks and triblocks with acrylates and co-monomers (styrene) regardless of addition order!!
- Slow reaction times (30-70 hours)
  - rate can be increased with camphor sulfonic acid (~6 hours)
- High MWs achievable
- PDI’s narrower for higher ratios of TEMPO:BPO
- Initiation at high temps lowers PDI
  \( R_i \) (complete ~ 15 min)
- Higher temps \( \Rightarrow \)
  \( \frac{R_n}{R_i} = \frac{k_p[M][M^*]}{k_i[M^*]} \)
- Reaction has 2 stages
  1) TEMPO catalyzed decomposition of BPO
  2) Propagation through reversible TEMPO activation/deactivation

Disadvantages

- variability in PDI, MW
- different TEMPO/initiator/monomer combinations can yield different results

Kinetics for SFRP

\[ P_n \cdot + \cdot T \rightarrow K_{I} \rightarrow L_n \] (trapping)

\[ K_L = \frac{k_{L,t}}{k_{L,rev}} = \frac{[L_n]}{[P_n \cdot \cdot T]} \]

\[ [P_n \cdot] = \frac{[L_n]}{K_L [T]} \approx \text{constant} \]

much lower than in traditional free radical

generally \([T] \approx 5\%[P_n]\)

\[ R_{trap} = k_{L,t} [T][P_n \cdot] \gg R_p \]

termination rate is much lower as \( R_i \propto [P_n \cdot] \) and \( R_p \propto [P_n \cdot] \)
Probability of untrapped living chains meeting is very low (termination by combination is negligible).

**Atom Transfer Radical Polymerization (ATRP)**

Kinetics same as previously described.

**Requirements for Trapping Process to Work**

1. \( K_c = \frac{k_{L,f}}{k_{L,r}} \gg 1.0 \Rightarrow \text{forward rate is much faster} \)

2. Rate of free radical trapping >> propagation rate

3. \( R_p \gg R_i \) (if \([M]\) is low, usually true)

**ATRP Mechanism**

**Initiation**

1. \( R - X + LiM_i^{z+} \leq R \cdot + LiM_i^{(z+1)+}X \)
   
   alkyl    metal    halide    ligand    oxidized complex
   
   \( X = \text{Cl, Br} \quad M = \text{Cu, Ni, Pd, Ru, Fe} \)

2. \( R \cdot + \overset{k_{pR}}{\underbrace{R'}} \rightarrow \overset{k_{pR}}{\underbrace{P_1}} \cdot \)

**Propagation**

\( P_N - X + LiM_i^{z+} \rightarrow k_{iR} \rightarrow P_N \cdot + LiM_i^{(z+1)+}X \)

\( P_N \cdot + \overset{k_{pR}}{\underbrace{R'}} \rightarrow \overset{k_{pR}}{\underbrace{P_{N+1}}} \cdot \)

Can use a broad range of catalytic systems.

**Synthesis of Custom Polymers using Controlled Radical Polymerization**

⇒ Grow a linear polymer from a dendrimer.

⇒ Create a graft copolymer.
⇒ Transfer from ionic polymerization to controlled radical to create block copolymers otherwise inaccessible.

Pg 11112

Dendrimer Block Copolymer
Use of Aluminum Alkyls
⇒ low PDI's, promising approach
Table 1. Initiating and Terminating Species for Living Radical Polymerizations

<table>
<thead>
<tr>
<th>I.</th>
<th>X.</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>(C₂H₅)₂NCS</td>
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<tr>
<td>(C₆H₅)CO·</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>(CH₃)₂C-CN</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>(C₆H₅)CO·</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>C₆H₅</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>CH₃</td>
</tr>
<tr>
<td>6</td>
<td>11</td>
<td>CH₃</td>
</tr>
</tbody>
</table>

Nitroxide Stable Free Radicals

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Scheme 2. Living Polymerization of Acrylates and Methacrylates

\[
\begin{align*}
\text{Scheme 2. Living Polymerization of Acrylates and Methacrylates} \\
\text{AIBN} \\
\text{R=H or alkyl}
\end{align*}
\]
Here is an example involving an anionic polymerization that is then end capped with an initiator for ATRP,

![chemical diagram]

the additional step of hydrosilation of the vinyl groups on the siloxane is not needed for a simple PDMS and would look like:

![chemical diagram]

The details for the catalyst and ligand are in the review articles listed below.


SFRP - Useful for modifying surfaces  
- Generation of high adhesive surfaces

**Mechanism of Olefin Metathesis** (exchange double bonds)

**Transalkylation**

\[
\begin{align*}
R + \text{CH} &= \text{CHR}' \\
\text{RCH} &= \text{CHR} \\
\text{RCH} &= \text{CHR}' \\
\text{R} + \text{CH} &= \text{CHR} \\
\end{align*}
\]

**Transalkylidenation**

\[
\begin{align*}
\text{R'CH} &= \text{CHR}' \\
\text{RCH} &= \text{CHR} \\
\text{R'CH} &= \text{CHR}' \\
\text{R} + \text{CH} &= \text{CHR} \\
\end{align*}
\]

The double bonds exchange

**Cyclic Alkene**

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

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

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\begin{align*}
& \quad \text{-----} \\
\end{align*}
\]
Ring Opening Metathesis Polymerization (ROMP)

Catalytic Process $\Rightarrow$ Efficacy of process is dependent on catalyst
Polymer is also dependent on monomer structure

Potential monomers

1. C=C must be in a strained ring system

```
   O       ROMP  (no strain)
```

```
   O      ROMP  100% conversion
   cyclooctane  far from equilibrium
```

```
   [M]eqROMP

   O      ROMP  100% conversion
   cyclobutane

   O      ROMP  [M]eq
   cyclopentane (not as strained)
```

Mono, Bi and Tricyclic ROMP Monomers
Reactivity of Bi and Tricyclic >> Monocyclic

Examples of Norbornadienes

2. For typical monocyclic alkenes:
Substituents available are limited

\[ R \neq \text{NH}_2, \quad \text{COOH, } -\text{OR}' , \quad \text{OH} \]

Must use something less reactive.

3. Can’t polymerize cyclic alkene with R-substituent directly on C=C bond.

For bicyclics, (and tricyclics)
→ much faster rxn rates
→ always get 100% conversion due to high ring strain
→ less prone to secondary rearrangements of backbone (shuffling)
→ side reactions with catalyst are minimized
∴ can introduce some polar substituents

Schrock catalysts: W, Mo
(MIT)
Grubbs catalyst: Ru
(CalTech)

Norbornene will polymerize in its
functionalized forms → functionalized polymers

End-Capping Living ROMP – Wittig Reaction
Living ROMP

Very rapid with specific catalyst
~ tolerant catalysts for functional groups
→ very low PDI → 1.03 - 1.05
“perfect polymers” almost nature-like

Conducting Polymers

Conjugated polymers that allow e⁻ transfer along chain.
Polyacetylene
Chains should be oriented macroscopically.

π-orbitals overlapping

→ huge delocalization of e⁻

e⁻ can move back and forth on polymer chain ⇒ conjugation

⇒ conjugation

polyacetylene from HC≡CH (gas)

slightly explosive

1st record of polyacetylene → 2-N type polymer

(gas bubbled through solvent with solid phase catalyst)

⇒ powder ⇒ intractable (T_m too high insoluble)

James Feast

monomer

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{W/Sn} \\
\text{F}_3\text{C} & \quad \text{W/Al}
\end{align*}
\]

Durham Route

Synthesis of Diblocks
TriBlock Copolymers Containing Durham Polyacteylene
Shirakawa: coated walls of Schlang tube with catalyst, then admitted acetylene gas
⇒ form a thin film on glass walls
    silver, brittle, insoluble, intractable
⇒ confirmed e⁻ conductivity
    ~ 0.1 S/cm – 1 S/cm
Difficult to isolate acetylene
Conjugated Polymers (common) Heeger and MacDiarmid

Pyrrole

\[
\text{NH}_2 \rightarrow \text{polypyrrole}
\]

Aniline

\[
\text{NH}_2 \rightarrow \text{polyaniline}
\]

Thiophene

\[
\text{H} \rightarrow \text{polythiophene}
\]

favourable properties in terms of stability can be functionalized

Oxidation and Reduction Approaches to Polymerization

- Electrochemical
- Chemical (introduction of a reagent)

1. Reduction at cathode

\[
\text{R} \quad \quad \text{+ e}^- \quad \rightarrow \quad \text{R} \quad \quad \Theta \quad \quad \text{C} \quad \quad \text{H} \quad \quad \text{C} \quad \quad \text{H}
\]

radical anion

2. Oxidation at anode

\[
\text{R} \quad \quad \text{+ e}^+ \quad \rightarrow \quad \text{R} \quad \quad \Theta \quad \quad \text{C} \quad \quad \text{H} \quad \quad \text{C} \quad \quad \text{H}
\]

radical cation

Generate combination
Often radicals combine to generate dionic species.

**Electropolymerization of Pyrrole**

**Initiation**

\[
\text{N} \quad \text{N} \quad + e^{-}
\]

**Propagation**

\[
2\left[\text{N} \quad \text{N}\right]^{+} + \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad +2H^{+}
\]

**Termination**

\[
\text{N} \quad \text{N} \quad \text{H}_{2}O \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N}
\]
This lecture presented material covered in the following journal articles and reviews.

**Photorefractive Polymers**


**Polyphosphazenes**


**Polysilanes**


This lecture presented material covered in the following journal articles and reviews.

**Hydrogen Bonding in Polymeric Structures**

<table>
<thead>
<tr>
<th>Good Proton Donors</th>
<th>Good Proton Acceptors</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>CO</td>
<td>CO</td>
</tr>
<tr>
<td>NH₂</td>
<td>N⁺</td>
</tr>
<tr>
<td>R–N–C–N–R</td>
<td>SO₃⁻</td>
</tr>
<tr>
<td>PH₂</td>
<td>NO₂⁻</td>
</tr>
<tr>
<td>NH₂</td>
<td>N⁺R</td>
</tr>
<tr>
<td>R–OH</td>
<td>NH₂–R</td>
</tr>
</tbody>
</table>

Okay Proton Donors

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2-Dimensional Polymers


Electrochemical Polymerization


Self-Assembly of Viruses and Liquid Crystalline Polymers


Multilayer Assembly