

General Approaches to Polymer Synthesis

- 1. **Addition** **Chain Growth**
 - Polymerization of Vinyl Monomers
 - Ring Opening Polymerization
 - Heterocyclics
 - Metathesis of Cyclic Olefins
- 2. **Condensation** **Step Growth**
 - Polymerization of A-B or AA/BB Monomers
- 3. **Modification of Preformed Polymers**
 - Polysaccharides
 - Peptides and Proteins
 - Synthetic Precursors

Current Strategies in Polymer Synthesis

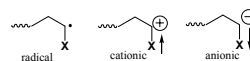
- Objectives: Precise Macromolecular Design
- 1. **Control of: Molecular Weight**
 - Molecular Weight Distribution
 - Composition
 - Sequence of repeat units
 - Stereochemistry
- 2. **Versatility**
 -

Anatomy of Addition Polymerizations

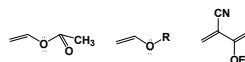
- **Initiation**
 - Generation of active initiator
 - Reaction with monomer to form growing chains
- **Propagation**
 - Chain extension by incremental monomer addition
- **Termination**
 - Conversion of active growing chains to inert polymer
- **Chain Transfer**
 - Transfer of active growing site by terminating one chain and reinitiating a new chain.

Polymerizability of Vinyl Monomers

Active Centers must be stable enough to persist through multiple monomer additions



- Typical vinyl monomers



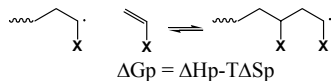
Polymerizability of Vinyl Monomers

Monomers	Radical	Cationic	Anionic	Complex Metal
Ethylene	+	-	+	+
Propylene	-	+/-	-	+
1,1-Dialkyl olefins	-	+	-	-
1,2-Dialkyl olefins	-	+	-	+
1,3-Dienes	+	+	+	+
Styrenes	+	+	+	+

Polymerizability of Vinyl Monomers

Monomers	Radical	Cationic	Anionic	Complex Metal
VCl	+	-	-	+/-
Vinyl esters	+	-	-	-
Acylates/methacrylates	+	-	+	-
Acrylonitriles / Acrylamides	+	-	+	-
Vinyl ethers	-	+	-	-
Substituted Styrenes	+	+/-	+/-	+/-

Thermodynamics of Polymerization



$\Delta H_p < 0$ π -bond \rightarrow σ -bond

$\Delta S_p < 0$ Loss of translational entropy

Polymerization favored below a ceiling temperature, T_c

$$T_c = \frac{\Delta H}{\Delta S}$$

Thermodynamics of Polymerization

Monomer	$-\Delta H_p$, kJ/mole	$-\Delta S_p$, J/K-mole	T_c , K (C) Observed
Ethylene	93	155	600 (327) 400
MMA	56	104	478(205) 220
α -Methyl styrene	35	110	318 (45) 61
Isobutylene	48	121	326 (123) 50

Free Radical Initiated Polymerization

- **Classical Free Radical Process**
- Applied to wide range of monomers
- Broad scope of experimental conditions
- Molecular weight can be controlled
- $M_w/M_n > 1.5 \rightarrow 2.0 \rightarrow$
- Statistical compositions and sequences
- Little stereochemical control

Free Radical Initiated Polymerization

- **Controlled Free Radical Polymerization**
- Broad range of monomers available
- Accurate control of molecular weight
- $M_w/M_n \cong 1.05$ --Almost monodisperse
- Blocks, telechelics, stars
- (Controlled molecular architecture)
- Statistical Compositions and Sequences

Types of Radical Initiators

- Application Temperatures, $T_{1/2} = 10$ hr.

150°C Hydroperoxides and Alkyl peresters

80°C Benzoyl Peroxide, AIBN, Persulfates

25°C AIBN + Light, Percarbonates,
Photoinitiators

0-5°C Redox Systems, $ROOH + Me^{++}$

Thermal Free Radical Initiators

- **Rate of Decomposition**

$R_d = k_d [I]$ where $k = A e^{-E_a/RT}$ and $A \approx 10^{15} \text{ sec}^{-1}$
To produce 10^{-7} to 10^{-6} radicals mole/l.sec,
 $E_a \approx 30-40$ kcal/mole (115-140 kJ/mole)

For 1st order reactions, half-life, $\tau = \ln 2/k$

- **Temperatures giving half lives of 10 hr considered optimum use temperatures**

Fate of Initiator Radicals

- Radical reactions

Recombination in solvent cage

Recombination in media

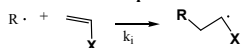
Reaction with polymer radicals (k_t)

Reaction with initiator (MIH)

Radical abstraction from polymer chains

Reaction with solvent or inhibitor

- Chain initiation, $R_i = 2 f k_d [I]$

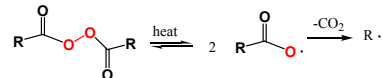


- Efficiency factor, $f = 0.1 - 0.9$

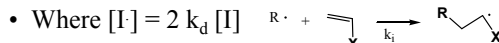
Kinetics of Polymerization

- Initiation steps

- $R_d = k_d [I]$



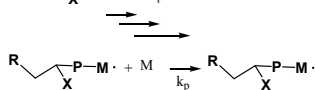
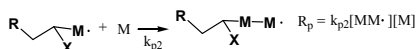
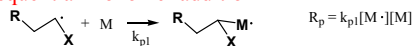
- $R_i = k_i [I] [M]$



- Add efficiency factor, $R_i = 2 f k_i [I] [M]$

Propagation Steps

- Sequential monomer addition

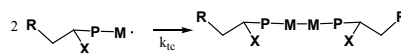


- Assume rate of addition is independent of radical size, $R_p = k_p [M][M]$

Termination Steps

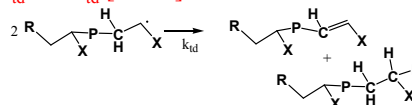
- Termination by coupling,

- $R_{tc} = 2 k_{tc} [RPM \cdot]^2$



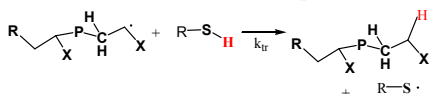
- Termination by disproportionation

- $R_{td} = 2 k_{td} [RPM \cdot]^2$

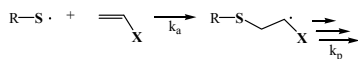


Chain Transfer

- Hydrogen transfer to growing polymer chain



- Reinitiation of growing chain using transferred radical



Rate Expressions for Radical Polymerization

- Overall growth of polymer

- $R_{poly} = R_i + R_p - R_t$

- $R_{poly} \sim R_p \quad R_p = k_p [M][M]$

– Assumptions: Contribution of R_i and R_t negligible for high degrees of polymerization

– Radical concentration based upon Steady State concentration of radicals, i.e. $R_i = R_t$

- $2 k_i f [I][M] = 2 (k_{tc} + k_{td}) [M \cdot]^2$

- $[M \cdot] = \{(k_i f) / (k_{tc} + k_{td})\}^{1/2} [I]^{1/2} [M]$

– Assume $[M]$ on initiation is negligible

- $[M \cdot] = \{(k_i f) / (k_{tc} + k_{td})\}^{1/2} [I]^{1/2}$

Rate Expressions for Radical Polymerization

- Overall rate of polymerization
- $R_p = k_p [M] \cdot [M]$
- $[M] = \{(k_i f) / (k_{tc} + k_{td})\}^{1/2} [I]^{1/2}$
- Then
- $R_{poly} = k_p \{(k_i f) / (k_{tc} + k_{td})\}^{1/2} [I]^{1/2} [M]$
- Rate of polymerization is proportional to:
 - square root of initiator concentration
 - First order in monomer concentration

Control of Molecular Weight

- Impact of initiator concentration

$DP \approx \nu = R_p / R_t$ where ν is the kinetic chain length

$$DP = \nu = \frac{R_p}{R_t} = \frac{R_p}{R_i}$$

$$DP = \frac{k_p [M] [M]}{k_t [M]^2}$$

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

For termination by coupling $DP = 2 \nu$

For termination by disproportionation, $DP = \nu$

Control by Chain Transfer

- Add chain transfer processes to termination processes

$$\frac{1}{DP} = \frac{k_t [M]^2 + k_{tr}[SH][M] + k_{tm}[M][M] + k_{td}[I][M]}{k_p [M] [M]}$$

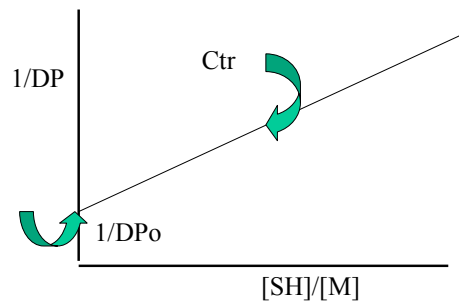
- Assume chain transfer to monomer and initiator are small

$$\frac{1}{DP} = \frac{k_t [M]^2 + k_{tr}[SH][M]}{k_p [M] [M]} = \frac{k_t [M]}{k_p [M]} + \frac{k_{tr}[SH]}{k_p [M]}$$

$$\frac{1}{DP} = \frac{1}{DP_0} + Ctr \frac{[SH]}{[M]}$$

- Where Ctr is the chain transfer constant

Calculation of Ctr



Types of Vinyl Polymerization

Method	Advantages	Disadvantages
Bulk (Neat)	Simple equipment Rapid reaction Pure polymer isolated	Heat buildup Gel effect Branched or crosslinked product
Solution	Good mixing Ready for application	Lower mol. Wt. Low R_{poly} Solvent Recovery
Suspension (Pearl)	Low viscosity Direct bead formation	Removal of additives
Emulsion	High R_{poly} Low Temperatures High Mol. Wt. High surface area latex	Removal of additives Coagulation needed Latex stability
Inverse Emulsion	Water in oil latex formed Inversion promotes dissolution in water	