Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 19 -

Cationic/Anionic/Living Polymerizations

Objectives

- To compare and contrast cationic and anionic mechanisms for polymerization, with reference to free radical polymerization as the most common route to high polymer.
- To emphasize the importance of stabilization of the charged reactive center on the growing chain.
- To develop expressions for the average degree of polymerization and molecular weight distribution for anionic polymerization.
- To introduce the concept of a “living” polymerization.
- To emphasize the utility of anionic and living polymerizations in the synthesis of block copolymers.

Effect of Substituents on Chain Mechanism

Monomer	Radical	Anionic	Cationic	Hetero.
Ethylene	+	-	+	+
Propylene	-	-	-	+
1-Butene	-	-	-	+
Isobutene	-	-	+	-
1,3-Butadiene	+	+	-	+
Isoprene	+	+	-	+
Styrene	+	+	+	+
Vinyl chloride	+	-	-	+
Acrylonitrile	+	+	-	+
Methacrylate esters	+	+	-	+

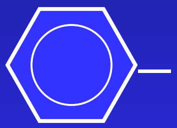
- Almost all substituents allow resonance delocalization.
- Electron-withdrawing substituents lead to anionic mechanism.
- Electron-donating substituents lead to cationic mechanism.

Overview of Ionic Polymerization: Selectivity

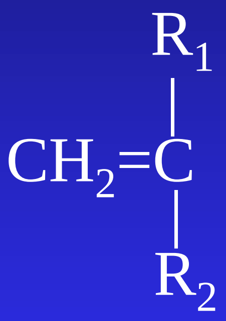
- Ionic polymerizations are more selective than radical processes due to strict requirements for stabilization of ionic propagating species.

Cationic: limited to monomers with electron-donating groups

RO-



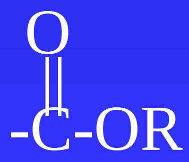
$CH_2=CH-$



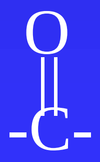
$CH_2=C(R_1)(R_2)$

Anionic: limited to monomers with electron-withdrawing groups

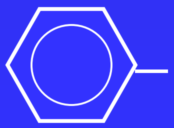
$-C\equiv N$



$-C(=O)-OR$



$-C(=O)-$



Overview of Ionic Chain Polymerization: Counterions

- A counterion is present in both anionic and cationic polymerizations, yielding ion pairs, not free ions.

Cationic: ~~~$C^+(X^-)$ Anionic: ~~~$C^-(M^+)$

- There will be similar effects of counterion and solvent on the rate, stereochemistry, and copolymerization for both cationic and anionic polymerization.

- Formation of relatively stable ions is necessary in order to have reasonable lifetimes for propagation. This is accomplished by using <u>low temperatures</u> (-100 to 50 °C) to suppress termination and transfer and <u>mildly polar solvents</u> (pentane, methyl chloride, ethylene dichloride).

Overview of Ionic Polymerization: Ion-pair Binding

There are four states of ion-pair binding:

I $\sim\sim\sim BA$ covalent bond	II $\sim\sim\sim B^+A^-$ tight or contact ion pair, intimate ion pair
III $\sim\sim\sim B^+\|\|A^-$ solvent-separated, loose ion pair	IV $\sim\sim\sim B^+ \quad + \quad A^-$ free ion, very reactive but low concentration

Most ionic polymerizations have equilibrium between ion pairs (II or III, depending upon solvent) and free ion (IV).

Overview of Ionic Chain Polymerization: Mechanistic Analysis

- Reactions are fast but are extremely sensitive to small amounts of impurities. Highly polar solvents (water, alcohols, ketones) will react with and destroy or inactivate the initiator. Moreover, heterogeneous initiators are used, making the nature of the reaction medium unclear and determination of the mechanism difficult.

- Termination by neutralization of the carbo-cation (carbonium ion, carbenium ion) occurs by several processes for cationic polymerization, but termination is absent for anionic polymerization.

Initiation of Cationic Chain Polymerization:

Protonic Acids HBr, HI

$$HA + (CH_3)_2C{=}CH_2 \rightarrow (CH_3)_3C^+(A^-)$$

Lewis Acids $AlCl_3$, BF_3, $SnCl_4$

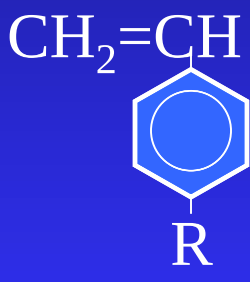
A co-initiator (water, protonic acids, alkyl halides) is needed to activate the Lewis acid.

$$BF_3 + H_2O \rightarrow BF_3\text{-}OH_2$$

$$BF_3\text{-}OH_2 + (CH_3)_2{=}CH_2 \rightarrow (CH_3)_2C^+(BF_3OH)^-$$

Cationic Chain Propagation: Monomer Structure

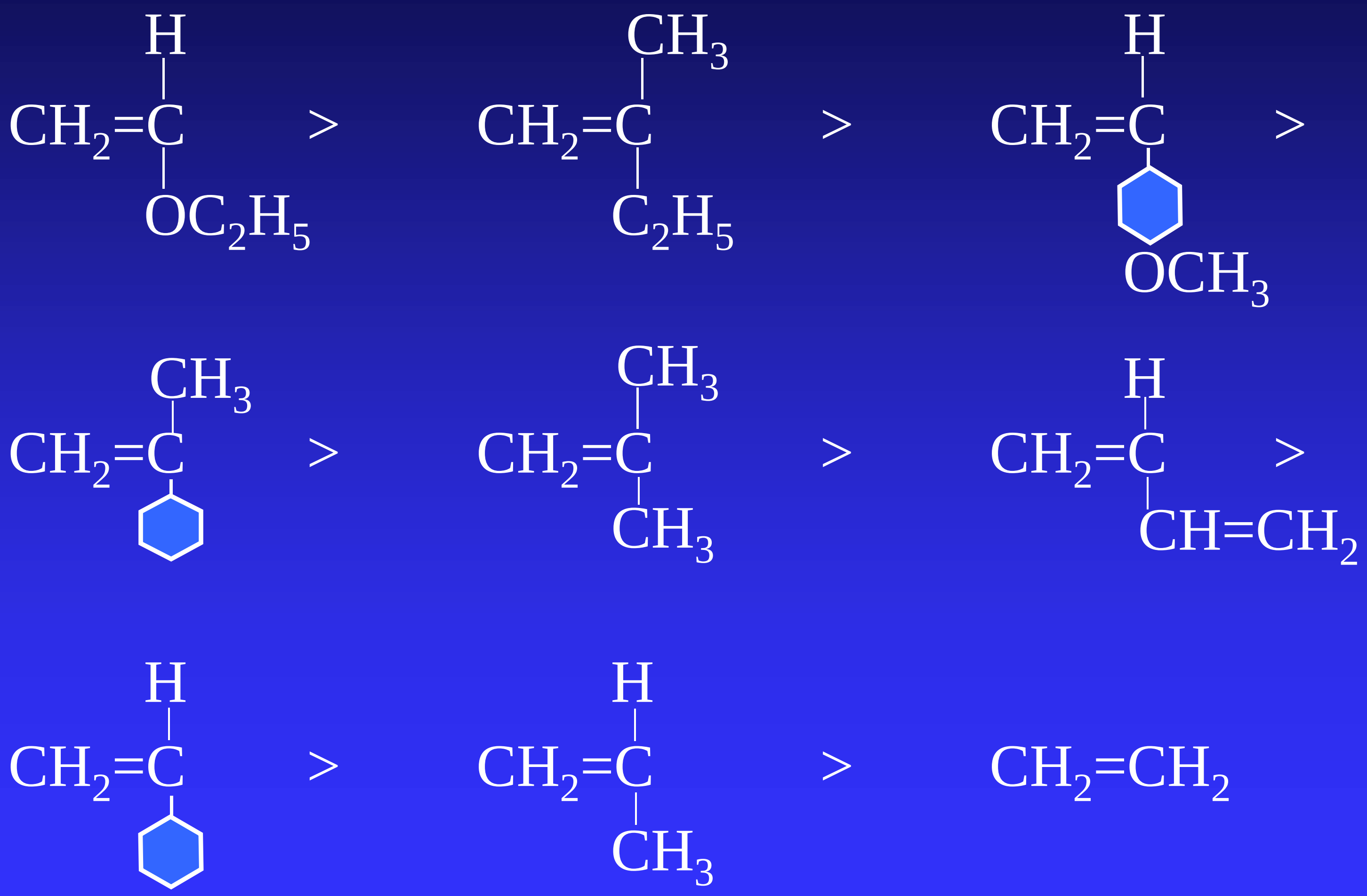
Substituents must be able to stabilize a formal positive charge. For olefins, tertiary > secondary > primary due to inductive effect. For styrenic monomers:



Monomer	k_p, liter/mole sec
R = Cl	0.0012
R = H	0.0037
R = CH_3	0.095
R = OCH_3	6

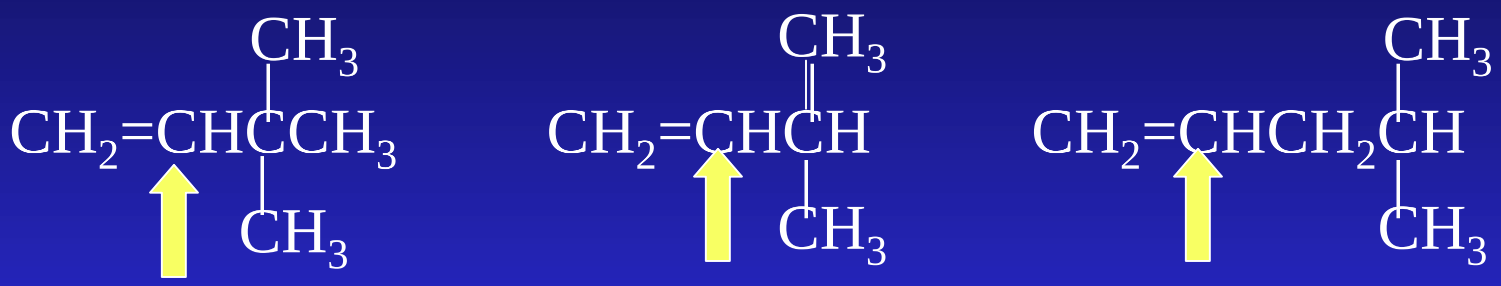
Steric effects dominate for ortho substitution in styrene, and all substituents reduce k_p irrespective of inductive effects.

Cationic Chain Propagation: Monomer Reactivity



Cationic Chain Propagation:
Intramolecular Rearrangement

Several olefins rearrange to a more stable cationic species:



$CH_2{=}CH\overset{CH_3}{\underset{CH_3}{C}}CH_3$ $CH_2{=}CH\overset{CH_3}{\underset{CH_3}{C}H}$ $CH_2{=}CHCH_2\overset{CH_3}{\underset{CH_3}{C}H}$

Rearrangement of a neopentyl cation to a t-amyl cation will always occur.

$$CH_3\overset{CH_3}{\underset{CH_3}{C}}C^+H_2 \rightarrow CH_2\underset{CH_3}{C^+}CH_2CH_3$$

Tertiary carbo-cations are 10 - 15 kcal/mole more stable than secondary carbo-cations.

Anionic Polymerization: Outline

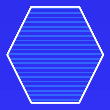
- Descriptive Chemistry
  - Initiation
    - Direct attack by base
    - Electron transfer
  - Termination
  - Effects of reaction medium
    - Solvent
    - Counterion
- Molecular Weight Distribution
  - Kinetic chain length
  - Anion concentrations
  - Number and weight average distributions

Anionic Initiation: Direct Attack by Base

$B: + CH_2{=}CHR \rightarrow BCH_2C{:}^{-}HR$ carbanion

- The strength of the base depends upon monomer reactivity.
- Monomers with strongly electron-withdrawing substituents require relatively weak bases (low pK_a).
- Ability of substituents to stabilize carbanions decreases as:

$-NO_2 > -C{=}O > -SO_2 > -CO_2 \sim -CN > -SO >$



$\sim -CH{=}CH_2 >>> -CH_3$

Types of Base Initiators:

- Base Initiators are often organometallic compounds or salt of a strong base, such as an alkali metal alkoxide.

Examples:

- Sodium metal in tetrahydrofuran.
- Potassium with liquid ammonia.
- Stable alkali metal complexes may be formed with aromatic compounds (e.g. Na/naphthalene) in ether.

Anionic Initiation:
Direct Electron Transfer from Alkali Metal

$$M\bullet + CH_2{=}CHR \rightarrow [CH_2{=}/\bullet CHR]^{-}M^{+}$$

monomer radical anion

$$2[CH_2{=}/\bullet CHR]^{-}M^{+} \rightarrow M^{+-}RHCCH_2CH_2CHR^{-+}M$$

dianion

Highly reactive radical anions usually dimerize.

The dianion allows propagation from both ends of the initiator.

Anionic Initiation: Transfer of an Electron to an Intermediate

$$M\bullet + A: \rightarrow A:\bullet^{-}M^{+}$$

$$A:\bullet^{-}M^{+} + CH_2{=}CHR \rightarrow [CH_2{=}/\bullet CHR]^{-}M^{+} + A:$$

monomer radical anion

- Stable alkali metal complexes may be formed with aromatic compounds (e.g. Na/naphthalene) in ether.
- Rapid dimerization often occurs due to high free radical concentration:

$$2[CH_2{=}/\bullet CHR]^{-}Na^{+} \rightarrow Na^{+-}RHCCH_2CH_2CHR^{-+}Na$$

Propagation from both ends!

dianion

Anionic Initiation:
Transfer of an Electron to an Intermediate

- For $R_i >> R_p$, all chains start at almost the same time. If there is no chain transfer and no termination, chains will have equal lifetime and grow to about the same size.

$$\overline{X}_n = \frac{[M]}{0.5[C]}$$

[M] = monomer concentration
[C] = aromatic complex concentration

- To obtain instantaneous initiation, the electron affinity of the monomer must be much greater than that of the aromatic compound.

Mechanism of Base Initiation: Relative Initiator Activity

Initiation could be instantaneous, of comparable rate, or much slower than propagation. If termination is absent,

$$\overline{X}_n = \frac{k_p}{k_i}$$

Termination

By impurities and transfer agents:

- Oxygen and carbon dioxide can react with propagating anions, and water will terminate the chain by proton transfer. Thus, the reactions must be carried out under high vacuum or in an inert atmosphere.

By nucleophilic attack of initiator on polar monomer:

- Polar monomers such as methyl methacrylate, methyl vinyl ketone, and acrylonitrile have substituents that will react with nucleophiles. These side reactions broaden the molecular weight distribution. To minimize the effect, use a less nucleophilic initiator, lower reaction temperatures, and more polar solvents.

Effect of Reaction Medium: Solvent

Solvent	Dielectric Constant	k_p (liter/mole sec)
Benzene	2.2	2
Dioxane	2.2	5
Tetrahydrofuran	7.6	550
1,2-Dimethoxyethane	5.5	3,800

Data from G. Odian, Principles of Polymerization, 3rd Ed., Table 5-9, p 383.

- As the dielectric constant increases, the solvating power of the reaction medium increases and there is an increased fraction of free ions (which are highly reactive).

Effect of Reaction Medium: Counterion

The separation between the counterion and the carbanion end group on the polymer is the major factor determining the rate, equilibrium, and stereochemistry.

Cation size ↓

Counterion	k_p, liter/mole sec	
	in tetrahydrofuran	in dioxane
Li+	160	0.94
Na+	80	3.4
K+	60-80	19.8
Rb+	50-80	21.5
Cs+	22	24.5
Free anion	65,000!	

Data from R.W. Lenz,Organic Chemistry of Synthetic High Polymers, 1967, p 425.

Tetrahydrofuran is a good solvating solvent ($\varepsilon = 7.4$)
Dioxane is a poor solvating solvent ($\varepsilon = 2.2$)

Outline

- Descriptive Chemistry
  - Initiation
    - Direct attack by base
    - Electron transfer
  - Termination
  - Effects of reaction medium
    - Solvent
    - Counterion
- Molecular Weight Distribution
  - Kinetic chain length
  - Anion concentrations
  - Number and weight average distributions

Kinetics of Anionic Polymerization: Reaction Set

Initiation:

$$GA \rightarrow G^+ + A^-$$

$$G^+ + A^- + M \rightarrow G^+ + AM^-$$

Note that the nature of the solvent will determine whether the propagating anion behaves as a free ion, AM^-, as a loose or tight ion pair, AM^-G^+, or both. We will assume free ions for this treatment.

Propagation:

$$AM^- + M \rightarrow AMM^-$$

$$AMM^- + M \rightarrow AM_2M^-$$

$$AM_{n-1}M^- + M \rightarrow AM_nM^-$$

Termination:

There is no termination step in the absence of impurities.

Rate of Polymerization

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

[A-] = total concentration of anions of all lengths

= $[\mathrm{GA}]_\mathrm{o}$ = concentration of initiator before dissociation

$$R_p = -\frac{d[M]}{dt} = k_p[GA]_o[M]$$

Integrate to obtain:

$$[M] = [M]_o \exp(-k_p[GA]_o t)$$

Kinetic Chain Length

$$\nu = \frac{\text{monomer consumed}}{\text{number of chain centers}}$$

$$\nu = \frac{[M]_o - [M]}{[GA]_o}$$

$$\nu = \frac{[M]_o}{[GA]_o}\left\{1 - \exp(-k_p[GA]_o t\right\}$$

At the completion of the reaction (long time),

$$\nu = \frac{[M]_o}{[GA]_o}$$

Average degree of polymerization:

$$\overline{X}_n = \frac{[M]_o - [M]}{[GA]_o} = \frac{[M]_o}{[GA]_o}\left\{1 - \exp(-k_p[GA]_o t\right\} = \nu$$

If the initiator is a dianion, then $\overline{X}_n = 2\nu$

Rate Equations for Anion Species

The kinetic treatment is somewhat analogous to that used for free-radical polymerization except that the steady-state approximation cannot be used.

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

$$\frac{d[AMM^-]}{dt} = k_p[M]\{[AM^-] - [AMM^-]\}$$

$$\frac{d[AMMM^-]}{dt} = k_p[M]\{[AMM^-] - [AMMM^-]\}$$

$$\frac{d[AM_nM^-]}{dt} = k_p[M]\{[AM_{n-1}M^-] - [AM_nM^-]\}$$

Relation of AM$^-$ Anion Concentration to ν

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

$$[M] = [M]_o \exp(-k_p[GA]_o t)$$

$$\int \frac{d[AM^-]}{[AM^-]} = -k_p[M]_o \int \exp\{-k_p[GA]_o t\} dt$$

Integrate with the condition that at t = 0, $[AM^-] = [GA]_o$

$$[AM^-] = [GA]_o \exp\left\{-\frac{[M]_o}{[GA]_o}\left(1 - \exp\{-k_p[GA]_o t\}\right)\right\}$$

Recall the kinetic chain length $\nu = \frac{[M]_o}{[GA]_o}\left\{1 - \exp(-k_p[GA]_o t\right\}$

$$[AM^-] = [GA]_o \exp(-\nu)$$

Relation of AMM$^-$ Anion Concentration to ν

$$\frac{d[AMM^-]}{dt} = k_p[M]\{[AM^-] - [AMM^-]\}$$

Eliminate time t from this rate equation through use of ν:

$$\nu = \frac{[M]_o}{[GA]_o}\left\{1 - \exp(-k_p[GA]_o t\right\}$$

$$\Downarrow$$

$$d\nu = k_p[M]_o \exp\{-k_p[GA]_o t\}dt \quad \Rightarrow \quad d\nu = k_p[M]dt$$

$$\Uparrow$$

$$[M] = [M]_o \exp(-k_p[GA]_o t) \qquad [AM^-] = [GA]_o \exp(-\nu)$$

$$\frac{d[AMM^-]}{d\nu} + [AMM^-] = [AM^-] = [GA]_o \exp(-\nu)$$

Relation of AMM$^-$ Anion Concentration to ν

$$\frac{d[AMM^-]}{d\nu} + [AMM^-] = [GA]_o \exp(-\nu)$$

This is a linear, first-order differential equation with solution:

$$\exp(\nu)[AMM^-] = \int \exp(\nu)[GA]_o \exp(-\nu) d\nu + C$$

where exp(ν) is an integrating factor and C is a constant of integration. Evaluate C from the condition that at ν = 0 (i.e. at t = 0) [AMM$^-$] = 0.

$$[AMM^-] = [GA]_o \nu \exp(-\nu)$$

Relation of AM_n^- Anion Concentration to ν

A similar treatment for [AMMM⁻] yields:

$$\frac{d[AMMM^-]}{d\nu} + [AMMM^-] = [GA]_o \nu \exp(-\nu)$$

The solution is obtained using the integrating factor exp(ν):

$$[AMMM^-] = \frac{1}{2}[GA]_o \nu^2 \exp(-\nu)$$

In general,

$$[AM_{n-1}M^-] = [GA]_o \frac{\nu^{n-1}\exp(-\nu)}{(n-1)!}$$

Number Average Distribution Function

$$[AM_{n-1}M^-] = [GA]_o \frac{\nu^{n-1}\exp(-\nu)}{(n-1)!}$$

At the completion of the polymerization,

$$\nu_\infty = \frac{[M]_o}{[GA]_o}$$

$$\mathrm{N_n} = \frac{\text{Number of anions containing n monomers}}{\text{Number of anions}}$$

$$N_n = \frac{[AM_{n-1}M^-]}{[GA]o}$$

This is a Poisson distribution.

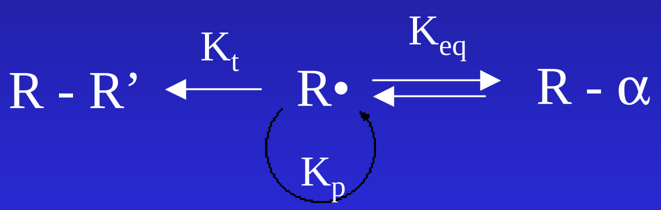
$$N_n = \frac{\nu_\infty{}^{n-1}\exp(-\nu_\infty)}{(n-1)!} = \frac{1}{(n-1)!}\left\{\frac{[M]_o}{[GA]_o}\right\}^{n-1}\exp\{-[M]_o/[GA]_o\}$$

Weight Average Distribution Function

$$W_n = \frac{n\exp(-\nu_\infty)\nu_\infty{}^{n-1}}{(\nu_\infty + 1)(n-1)!}$$

Living Free Radical Polymerization

- Definition: Polymerization in which radicals are not terminated
- Motivation: Superior molecular weight and polydispersity control, ease of block copolymerization, route to unique materials and architecture.
- Approach:
  - Reduce concentration of free radicals to prevent coupling termination.
  - Protect radicals reversibly with an endgroup α



$$R - R' \xleftarrow{K_t} \underset{\circlearrowleft K_p}{R\bullet} \overset{K_{eq}}{\rightleftharpoons} R - \alpha$$

  - Requirements:
    - $K_{eq} >> K_t$ ensures living conditions
    - $K_{eq} > K_p$ ensures low polydispersity and good molecular weight control
- Methods
  - Atom Transfer Radical Polymerization
  - Nitroxide-mediated LFRP