Chapter 7. Ionic polymerization

7.1 Introduction

7.2 Cationic polymerization

7.3 Anionic polymerization

7.4 Group transfer polymerization

7.1 Introduction

- **Presence of counterions (= gegenions)**

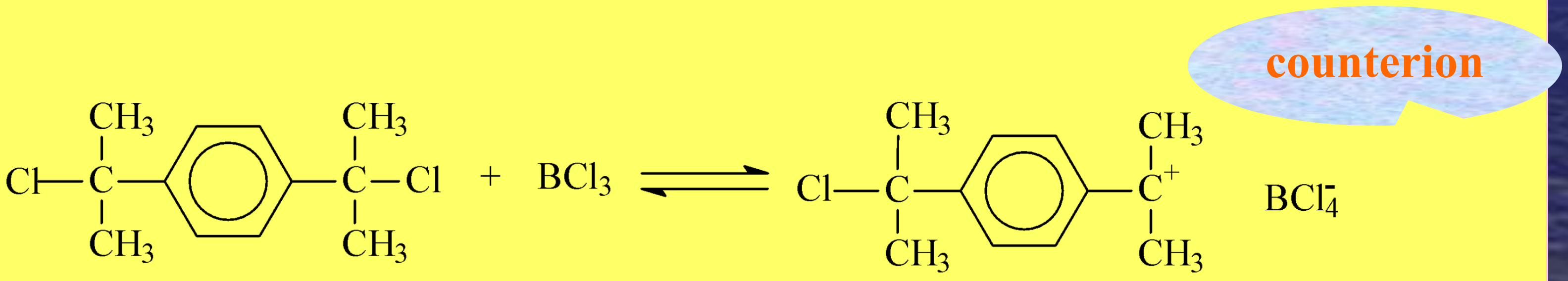
⇨ **Influence of counterions**

- **Solvation effect**

⇨ **more complex than free radical polymerizations**

but more versatile

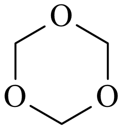
ex)



7.1 Introduction

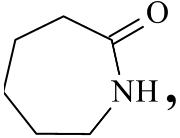
- **Application :**

  in ring-opening polymerizations of cyclic ethers



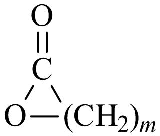
,

lactams



,

lactones



and in the polymerization of aldehydes

$RC(=O)H$,

ketones

$RC(=O)R'$

- **Commercial processes (Table 7.1)**

  far fewer in number

  reflect a much narrower choice of monomers

  - monomers must contain substituent groups capable of stabilizing carbocations or carbanions
  - the necessity for solution polymerzation

TABLE 7.1. Commercially Important Polymers Prepared by Ionic Polymerization

Polymer or Copolymer	*Major Uses*
Cationic[a]	
Polyisobutylene and polybutene[b] (low and high molecular weight)	Adhesives, sealants, insulating oils, lubricating oil and grease additives, moisture barriers
Isobutylene-isoprene copolymer[c] (“butyl rubber”)	Inner tubes, engine mounts and springs, chemical tank linings, protective clothing, hoses, gaskets, electrical insulation
Isobutylene-cyclopentadiene copolymer	Ozone-resistant rubber
Hydrocarbon[d] and polyterpene resins	Inks, varnishes, paints, adhesives, sealants
Coumarone-indene resins[e]	Flooring, coatings, adhesives
Poly(vinyl ether)s	Polymer modifiers, tackifiers, adhesives
Anionic[f]	
cis-1,4-Polybutadiene	Tires
cis-1,4-Polisoprene	Tires, footware, adhesives, coated fabrics
Styrene-butadiene rubber (SBR)[g]	Tire treads, belting, hose, shoe soles, flooring, coated fabrics
Styrene-butadiene block and star copolymers	Flooring, shoe soles, artificial leather, wire and cable insulation
ABA block copolymers (A= styrene, B=butadiene or isoprene)	Thermoplastic elastomers
polycyanoacrylate[h]	Adhesives

---

[a] $AlCl_3$ and BF_3 most frequently used coinitiators.
[b] ”Polybutenes” are copolymers based on C_4 alkenes and lesser amounts of propylene and C_5 and higher alkenes from refinery streams.
[c] Terpolymers of isobutylene, isoprene, and divinylbenzene are also used in sealant and adhesive formulations.
[d] Aliphatic and aromatic refinery products.
[e] Coumarone (benzofuran) and indene (benzocyclopentadiene) are products of coal tar.
[f] n-Butyllithium most common initiator.
[g] Contains higher cis content than SBR prepared by free radical polymerization.
[h] Monomer polymerized by adventitious water.

7.2 Cationic polymerization

7.2.1 Cationic initiators

7.2.2 Mechanism, kinetics, and reactivity in cationic polymerization

7.2.3 Stereochemistry of cationic polymerization

7.2.4.Cationic copolymerization

7.2.5 Isomerization in cationic polymerization

7.2.1 Cationic Initiators

- The propagating species : **carbocation**

Initiation

$$E^{+} + CH_2{=}CR_2 \longrightarrow ECH_2\overset{+}{C}R_2 \tag{7.1}$$

Initiator → mineral acid : H_2SO_4, H_3PO_4

lewis acid : $AlCl_3$, BF_3, $TiCl_4$, $SnCl_4$

Coinitiator →

$$BF_3 + H_2O \rightleftharpoons HOBF_3^{-}H^{+}$$

$$AlCl_3 + RCl \rightleftharpoons AlCl_4^{-}R^{+}$$

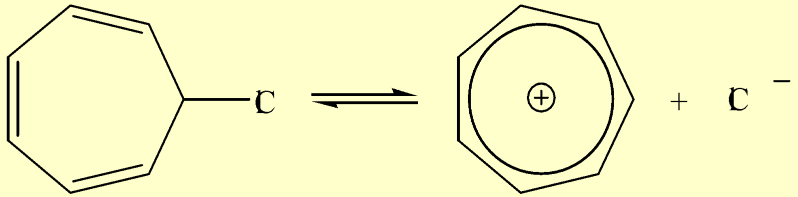
7.2.1 Cationic Initiators

- Very active Lewis acid → autoionization

$$2AlBr_3 \rightleftharpoons AlBr_4^- AlBr_2$$

- Other initiators

$$(C_6H_5)_3C \rightleftharpoons (C_6H_5)_3C^+ + C^- \quad \textbf{(7.5)}$$



(7.6)

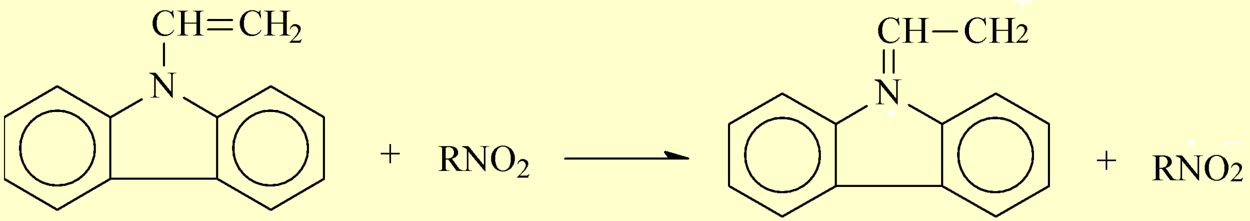
$$I_2 + CH_2{=}CR_2 \rightleftharpoons ICH_2CIR_2 \rightleftharpoons ICH{=}CR_2 + HI \quad \textbf{(7.7)}$$

$$ICH_2CIR_2 \rightleftharpoons ICH_2\overset{+}{C}R_2I^- \quad \textbf{(7.8)}$$

7.2.1 Cationic Initiators

- Other initiators

$$M + A \longrightarrow M^{\bullet +} + A^{\bullet -} \qquad (7.9)$$



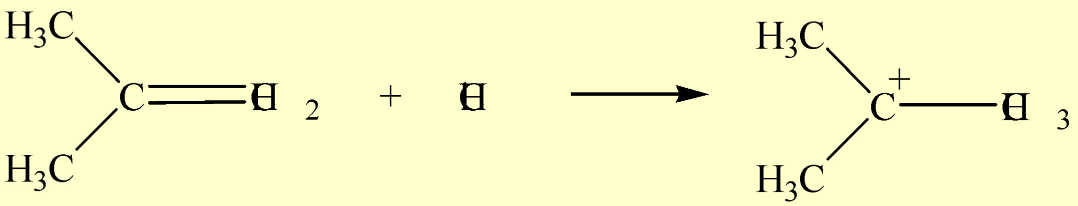
(7.10)

7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

A. Carbocationic Initiation.

B. addition of the electrophilic species – the more stable carbocation intermediate is formed.

(Markovnikov's rule)



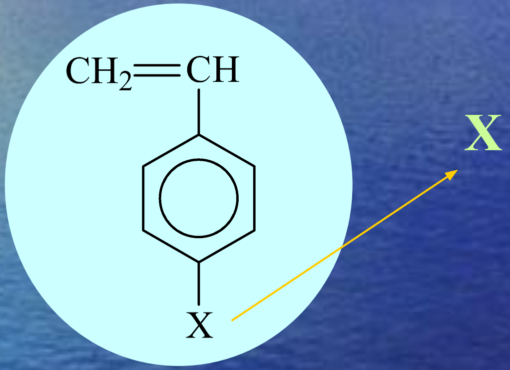
Stability of carbocation

$(CH_3)_2C{=}CH_2 > CH_3CH{=}CH_2 > CH_2{=}CH_2$

7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

A. Carbocationic Initiation.

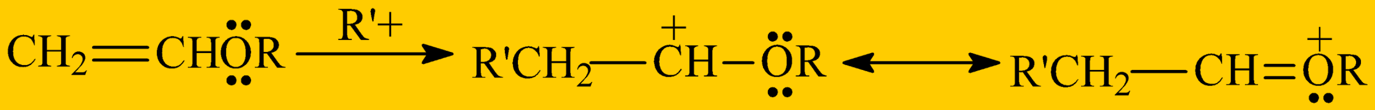
- For a series of para-substituted styrenes, the reactivity for substituent group



$OCH_3 > CH_3 > H > Cl$

(Because of steric hindrance)

- Vinyl ethers



$$CH_2{=}CH\ddot{O}R \xrightarrow{R'+} R'CH_2{-}\overset{+}{C}H{-}\ddot{O}R \longleftrightarrow R'CH_2{-}CH{=}\overset{+}{O}R \quad (7.11)$$

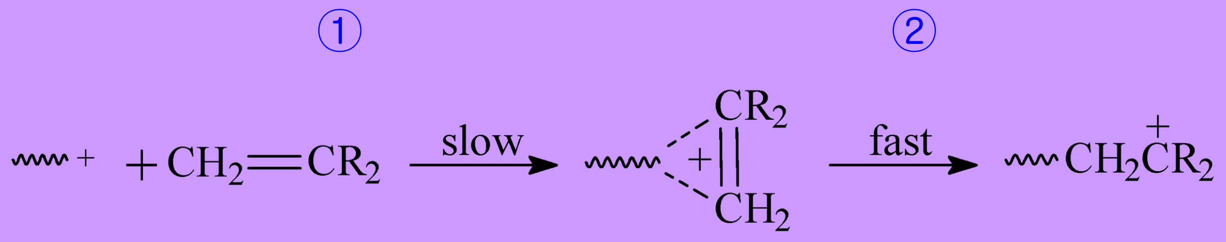
7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

B. Propagation Step

- Two Step

① *π*-complex of chain end and approaching monomer

② formation of covalent bond



$$\sim\!\sim\!\sim^{+} + CH_2{=}CR_2 \overset{①}{\xrightarrow{\text{slow}}} \sim\!\sim\!\sim\begin{matrix} CR_2 \\ + \| \\ CH_2 \end{matrix} \overset{②}{\xrightarrow{\text{fast}}} \sim\!\sim\!\sim CH_2\overset{+}{C}R_2 \qquad (7.12)$$

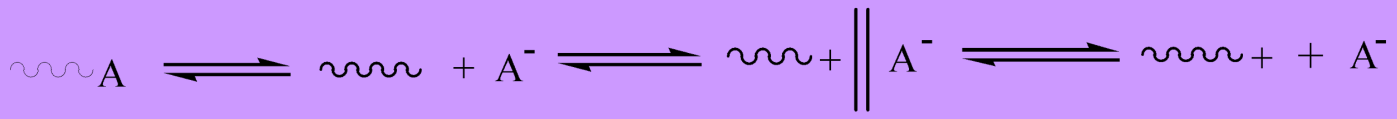
7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

C. Influences polymerization rate

① Solvent polarity

(polarity 🚩 → favors the initiation step)

② Degree of association between the cationic chain end and counterion (A^-)



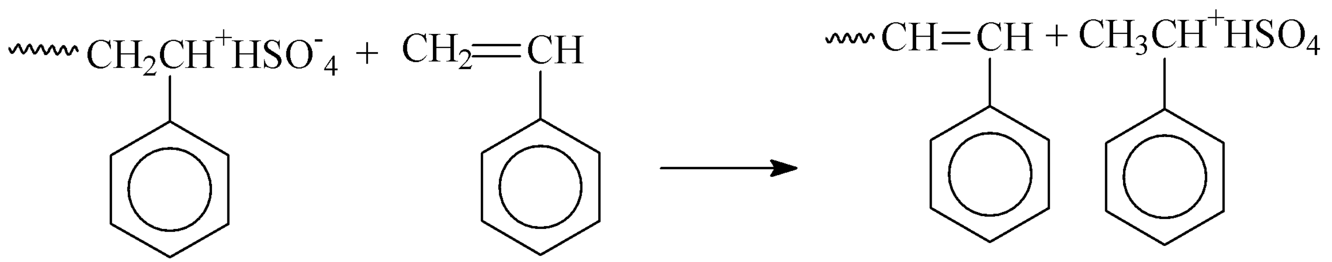
Covalent **Intimate ion pair** **Solvent-separated ion pair** **Solvated ions**

(7.13)

7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

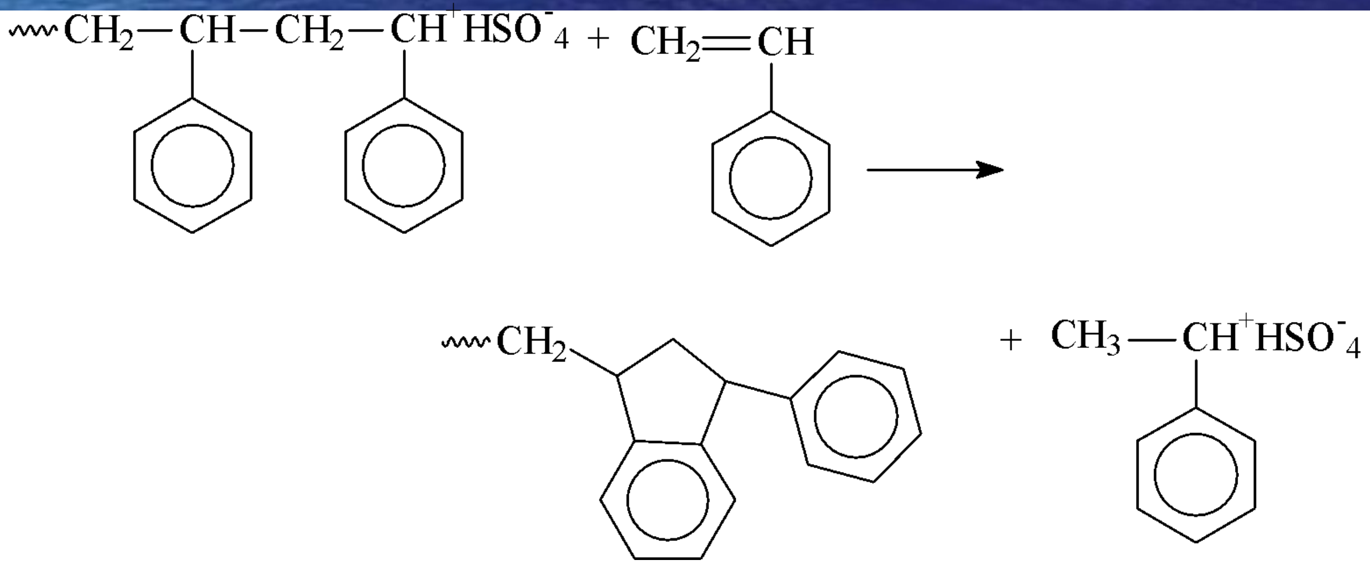
D. Chain transfer reaction

1. With monomer :



(7.14)

2. By ring alkylation

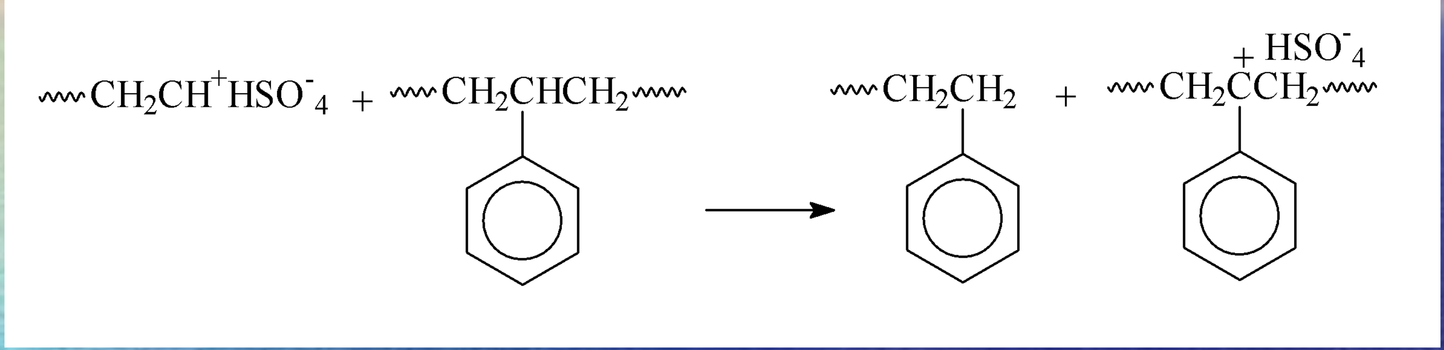


(7.15)

7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

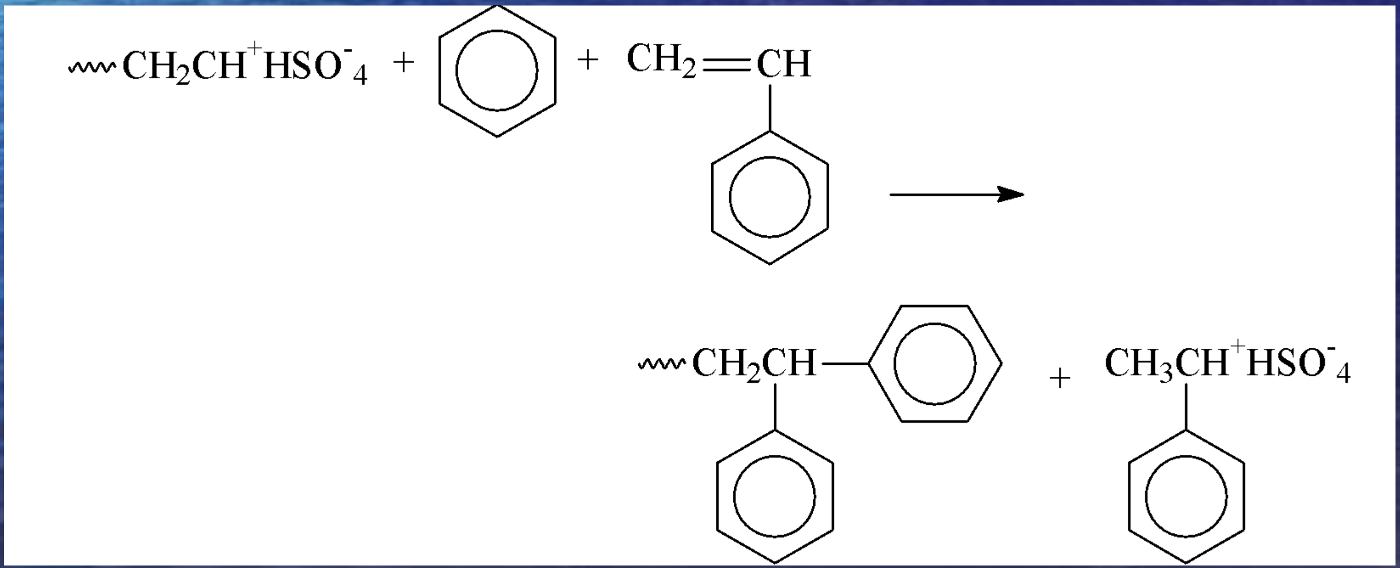
D. Chain transfer reaction

3. By hydride abstraction from the chain to form a more stable ion :



(7.16)

4. With solvent-for example, benzene-by electrophilic substitution :



(7.17)

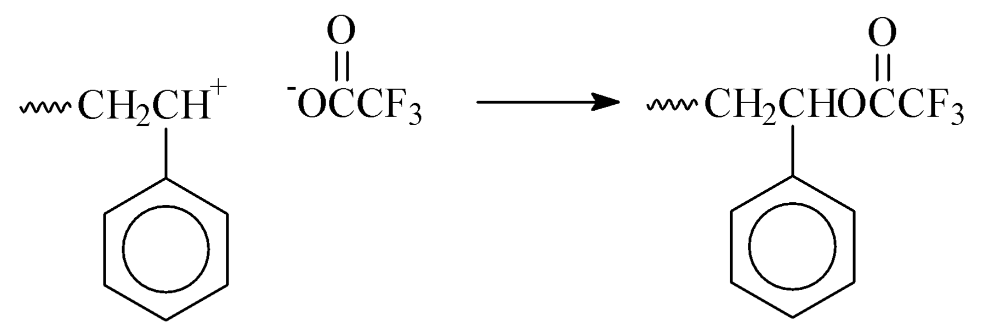
7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

E. Termination reaction

Termination are the combination of chain end with counterion.

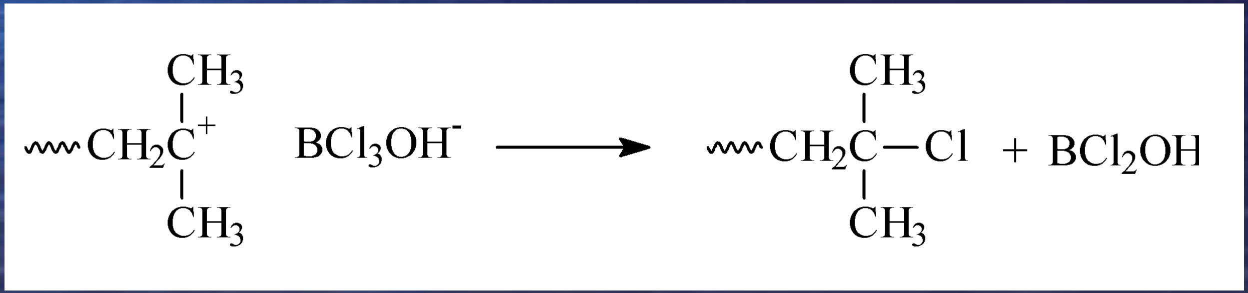
① styrene + CF_3COOH

initiator



(7.18)

② Isobutylene + BCl_3/H_2o



$$\sim\!\sim CH_2\overset{CH_3}{\underset{CH_3}{C^+}}\quad BCl_3OH^- \longrightarrow \sim\!\sim CH_2\overset{CH_3}{\underset{CH_3}{C}}-Cl + BCl_2OH$$

(7.19)

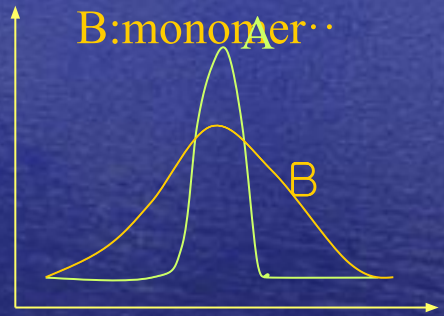
7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

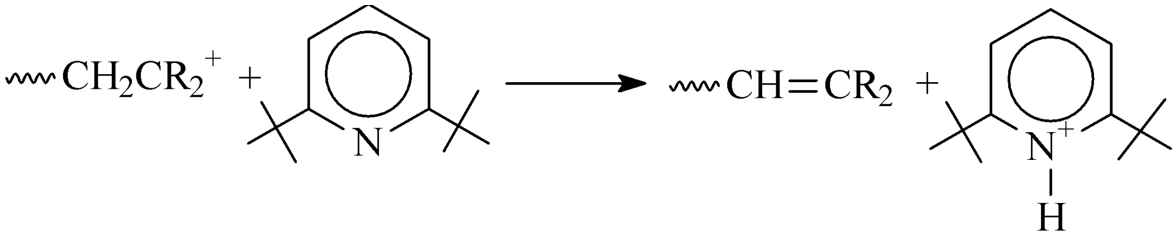
F. Proton trap

- It intercepts the proton before it transfers to monomer.
- The result

lower overall yield
higher molecular weight
lower polydispersity index.

A:proton trap··
B:monomer··





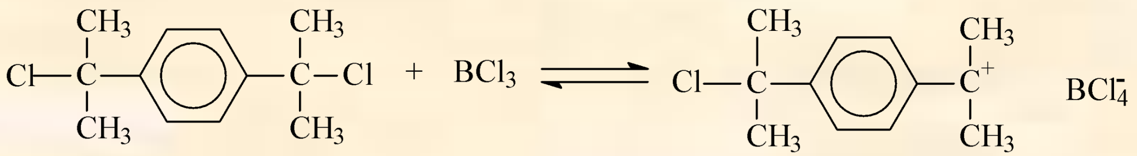
(7.20)

7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

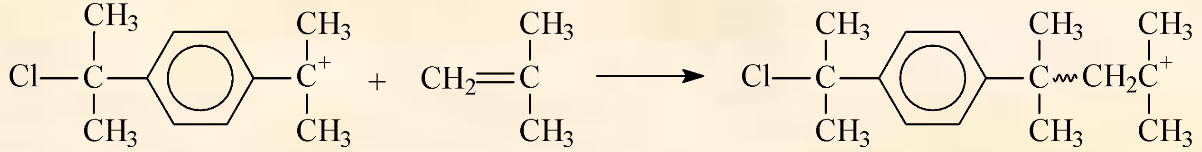
G. Telechelic Polymer

inifer

(bifunctional compound)



(7.21)



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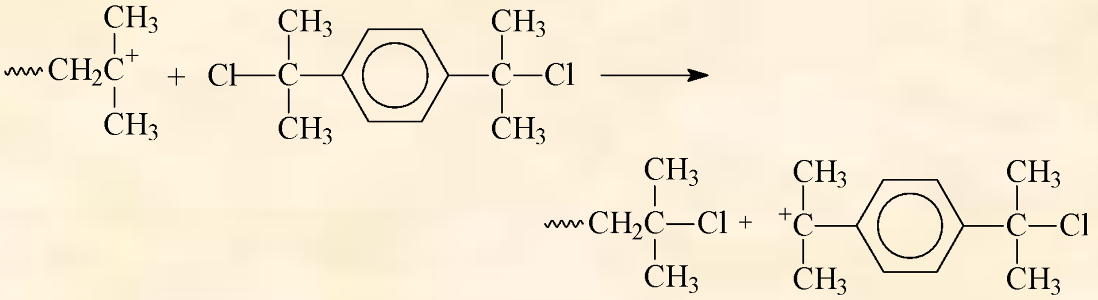
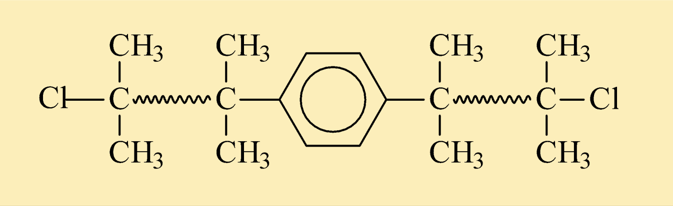
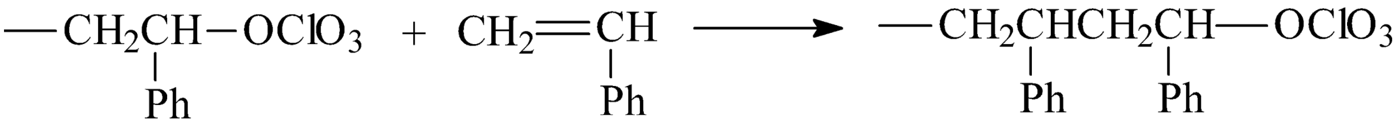


(7.23)



7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

H. Pseudocationic Polymerization



$$-CH_2\underset{\substack{|\\ Ph}}{CH}-OClO_3 + CH_2{=}\underset{\substack{|\\ Ph}}{CH} \longrightarrow -CH_2\underset{\substack{|\\ Ph}}{CH}CH_2\underset{\substack{|\\ Ph}}{CH}-OClO_3 \qquad (7.24)$$

- The propagating chain end is a covalently bonded perchlorate ester
- The reaction proceeds at a much slower compared with most cationic processes.

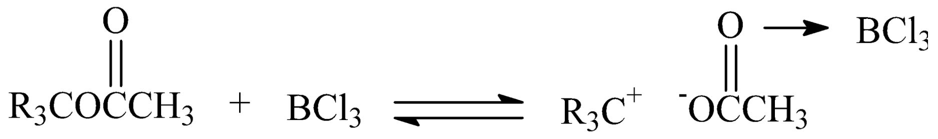
7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

I. To prepare living polymers under cationic conditions.

(Termination or chain transfer reaction 없이 중합반응이 종결되는 예)

ex1) **Tertiary ester + BCl_3 / Isobutylene polymerization**

① **formation of tertiary carbocation-initiating species.**

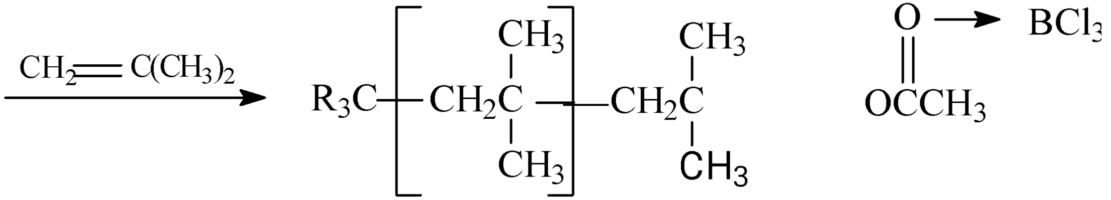


$$R_3CO\overset{O}{\overset{\|}{C}}CH_3 + BCl_3 \rightleftharpoons R_3C^{+}\ {}^{-}O\overset{O \rightarrow BCl_3}{\overset{\|}{C}}CH_3$$

(7.27)

② **Polymerization to yield polyisobutylene terminated**

: appearance of a very tightly bound – but still active – ion pair



$$\xrightarrow{CH_2{=}C(CH_3)_2} R_3C\left[CH_2\overset{CH_3}{\underset{CH_3}{C}}\right]CH_2\overset{CH_3}{\underset{CH_3}{C}}\quad O\overset{O \rightarrow BCl_3}{\overset{\|}{C}}CH_3$$

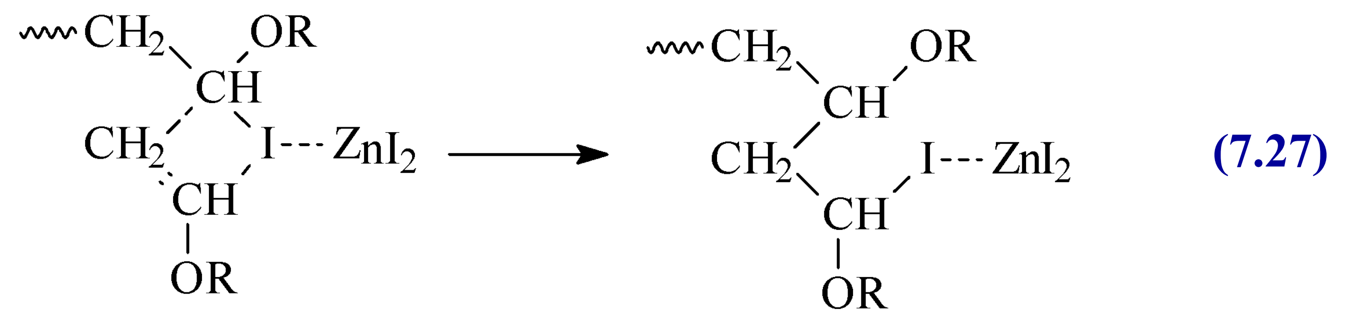
(7.26)

7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

I. To prepare living polymers under cationic conditions.

(Termination or chain transfer reaction 없이 중합반응이 종결되는 예)

ex2) I_2 / HI or I_2 / ZnI_2 : vinyl ether propagation



(7.27)

- **Living Polymer**
  - Termination이 전체적으로 멈춘 곳에서 chain end가 여전히 active 한 성질을 가지고 있는 polymer
  - Monomer 첨가 시 분자량이 증가하며 starting monomer와 다를 경우 block copolymer형성
  - 매우 길고 anionic polymerization에 많이 이용
  - 대부분의 living polymer는 낮은 온도에서 합성
  - Living polymer란 용어는 정지 반응이 일어나지 않는 이온 중합에 이용

7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

J. Kinetics

Expression of general initiation, propagation, termination, and transfer rates

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

$$R_p = k_p[M][M^+]$$

$$R_t = k_t[M^+]$$

$$R_{tr} = k_{tr}[M][M^+]$$

$[I]$: molar concentration of initiation

$[M]$: molar concentration of monomer

$[M^+]$: molar concentration of cationic chain end

As with free radical polymerization approximation to a steady state for the growing chain end.

thus $\boxed{R_i = R_t}$

$$k_i[I][M] = k_t[M^+] \quad \text{or} \quad [M^+] = \frac{k_i[I][M]}{k_t}$$

7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

TABLE 7.2. Representative Cationic propagation Rate Constants, R_P[a]

Monomer	*Solvent*	*Temperature (^{o}C)*	*Initiator*	*k_p (L/mol s)*
Styrene	**None**	**15**	**Radiation**	**3.5×10^6**
α-Methylstyrene	**None**	**0**	**Radiation**	**4×10^6**
i-Butyl vinyl ether	**None**	**30**	**Radiation**	**3×10^5**
i-Butyl vinyl ether	**CH_2Cl_2**	**0**	**$C_7H_7^+SbCl_6^-$**	**5×10^3**
i-Butyl vinyl ether	**CH_2Cl_2**	**0**	**$C_7H_7^+SbCl_6^-$**	**3.5×10^3**
Methyl vinyl ether	**CH_2Cl_2**	**0**	**$C_7H_7^+SbCl_6^-$**	**1.4×10^2**
2-Chloroethyl vinyl ether	**CH_2Cl_2**	**0**	**$C_7H_7^+SbCl_6^-$**	**2×10^2**

[a] Data from Ledwith and Sherrington.[19]

7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

Substituting for $[M^+]$ in R_p, one obtains

$$R_p = \frac{k_p k_i [I][M]^2}{k_t}$$

In the absence of any chain transfer,
(the kinetic chain length = $\bar{\nu}$)

$$\bar{\nu} = \overline{DP}$$

$$\bar{\nu} = \overline{DP} = \frac{R_p}{R_t} = \frac{k_p[M][M^+]}{k_t[M^+]} = \frac{k_p[M]}{k_t}$$

If transfer is the predominant mechanism controlling chain growth,

$$\bar{\nu} = \overline{DP} = \frac{R_p}{R_{tr}} = \frac{k_p[M][M^+]}{k_{tr}[M][M^+]} = \frac{k_p}{k_{tr}}$$

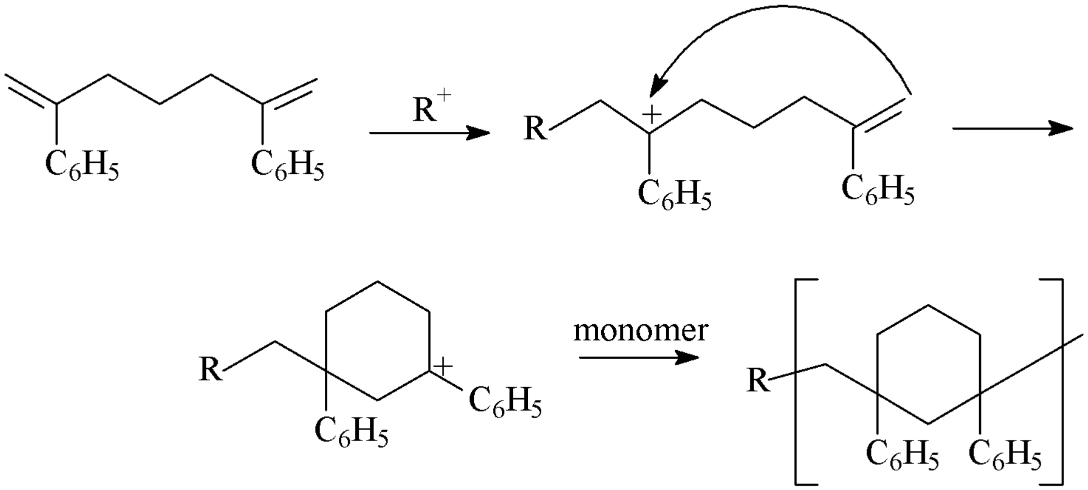
7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

K. Difference between free radical and cationic processes.

	free radical process	*cationic process*
propagation rate (R_p)	proportional to the square root of initiator concentration $$R_p = k_p[M]\sqrt{\frac{fk_d[I]}{k_t}}$$	first-order dependence $$R_p = \frac{k_p k_i [I][M]^2}{k_t}$$
$\overline{DP}$ ($\bar{\nu}$)	dependent of initiator concentration $$\overline{DP} = \frac{k_p[M]}{2\sqrt{(fk_t k_d[I])}}$$	independent of initiator concentration $$\overline{DP} = \frac{k_p[M]}{k_t}$$

7.2.2 Mechanism, Kinetics, and Reactivity in Cationic Polymerization

L. Nonconjugation diene – Cationic cyclopolymerization



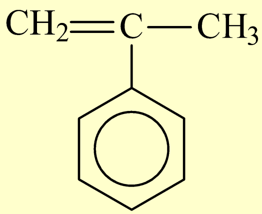
(7.28)

7.2.3 Stereochemistry of Cationic Polymerization

- Cationic Polymerization → lead to stereoregular structures.

ex) vinyl ether $R-O-CH=CH_2$

α - methylstyrene



- Vinyl ether observation resulting

(1) greater stereoregularity is achieved at lower temperatures

(2) the degree of stereoregularity can vary with initiator

(3) the degree and type of stereoregularity (isotactic or syndiotactic) vary with solvent polarity.

7.2.3 Stereochemistry of Cationic Polymerization

- **Solvent effect**

EX) t-butyl vinyl ether

[forms isotactic polymer in nonpolar solvents.

forms mainly syndiotactic polymer in polar solvents.

(cationic chain end and the counterion are associated)

7.2.3 Stereochemistry of Cationic Polymerization

- **Solvent effect**

- **In polar solvents both ions**

  1) be strongly solvated

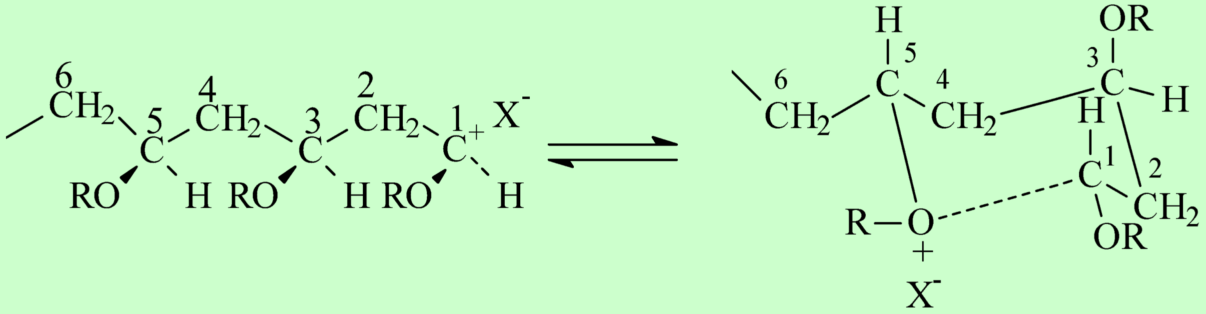
  2) the chain end – exist as a free carbocation surrounded by solvent molecules

- **In nonpolar solvents**

  1) association between carbocation chain end and counterion would be strong

  2) counterion could influence the course of steric control.

• Models proposed for vinyl ether polymerization



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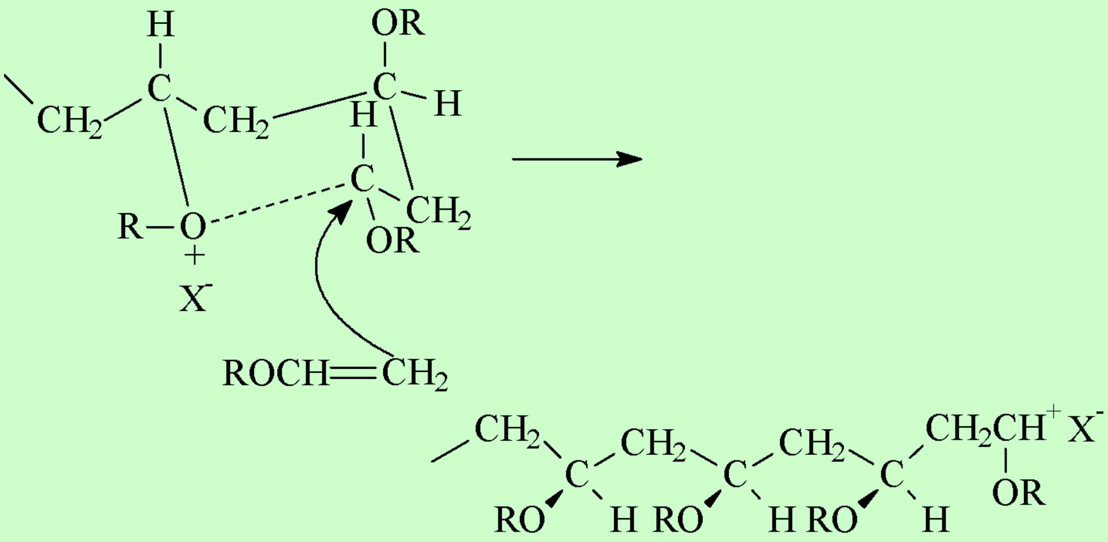

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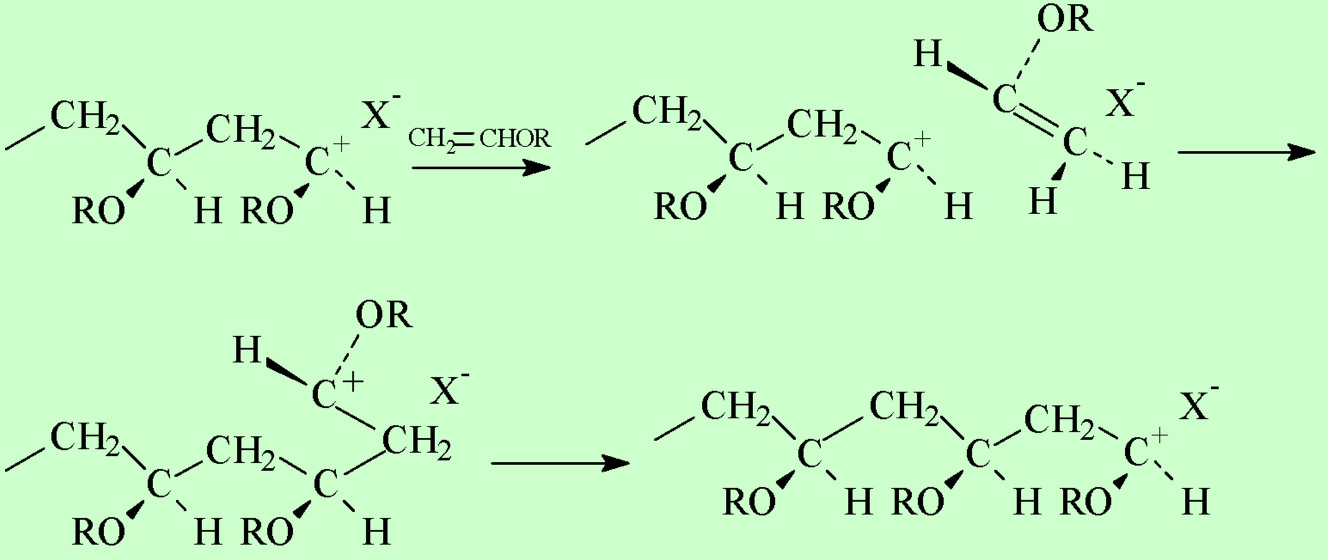
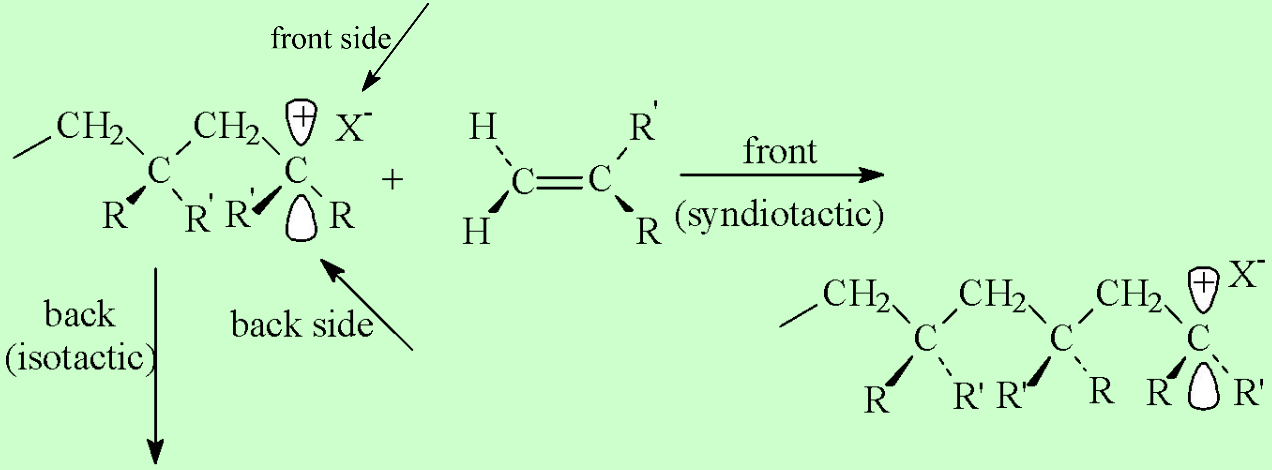
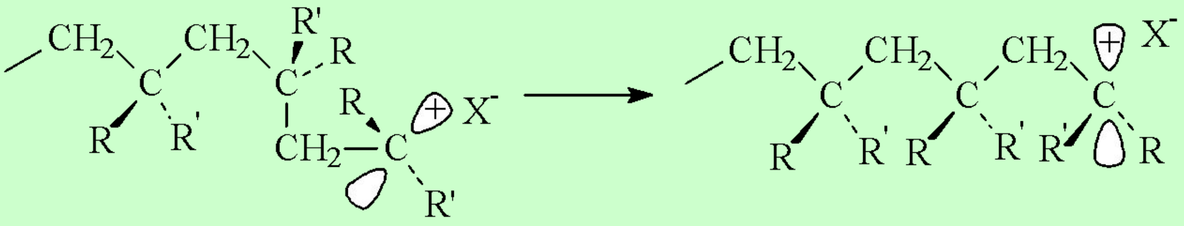

CH₂=CHOR

(7.31)


front side
back side
front
(syndiotactic)
back
(isotactic)

(7.32)



(7.33)

7.2.4 Cationic Copolymerization

A. Copolymerization equation

- the situation is complication by counterion effects.

B. Reactivity ratios vary with initiator type and solvent polarity.

C. Temperature – unpredictable effect

D. Steric effects (Table 7.3)

E. commercial cationic copolymers – butyl rubber
(prepared from isobutylene and isoprene.)

protective clothing

tire inner tubes

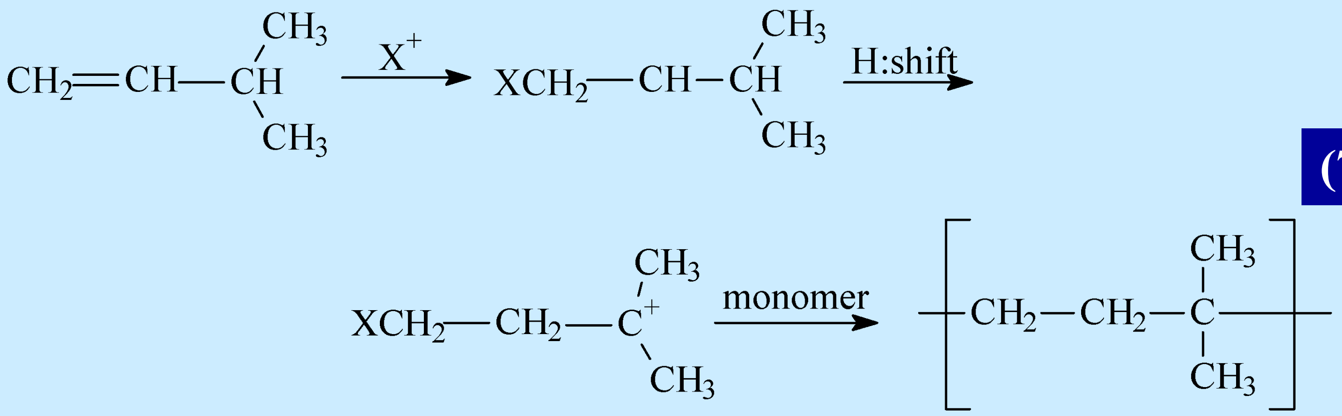
TABLE 7.3. Representative Cationic Reactivity Rations (r)[a]

Monomer 1	*Monomer 2*	*Coinitiator*[b]	*Solvent*[b]	Temperature (°C)	*r1*	*r2*
Isobutylene	1,3-Butadiene	$AlEtCl_2$	CH_3Cl	-100	43	0
	1,3-Butadiene	$AlCl_3$	CH_3Cl	-103	115	0
	Isoprene	$AlCl_3$	CH_3Cl	-103	2.5	0.4
	Cyclopentadiene	$BF_3 \cdot OEt$	$PhCH_3$	-78	0.60	4.5
	Styrene	2	EtCl	0	1.60	1.17
	Styrene	$SnCl_4$	CH_3Cl	-92	9.02	1.99
Styrene	α-Methylstyrene	$AlCl_3$	$PhCH_3$	-78	1.2	5.5
	α-Methylstyrene	$TiCl_4$	EtCl	0	0.05	2.90
	p-Methylstyrene	$SnCl_4$	CCl_4	-78	0.33	1.74
	trans-β-Methyl-styrene	$SnCl_4$ $SnCl_4$	CH_2Cl_2	0	1.80	1.10
p-Chlorostyrene	cis-β-Methyl-styrene	$SnCl_4$	$CCl_4/PhNO_2$(1:1)	0	1.0	0.32
	trans-β-Methyl-styrene	$SnCl_4$	CCl4/PhNO2(1:1)	0	0.74	0.32
Ethyl vinyl ether	i-Butyl vinyl ether	BF_3	CH_2Cl_2	-78	1.30	0.92
2-Chloroethyl vinyl ether	α-Methylstyrene	BF_3	CH_2Cl_2	-23	6.02	0.42

[a] Data from Kennedy and Marechal.[5]

[b] Et = C_2H_5, Ph = phenyl.

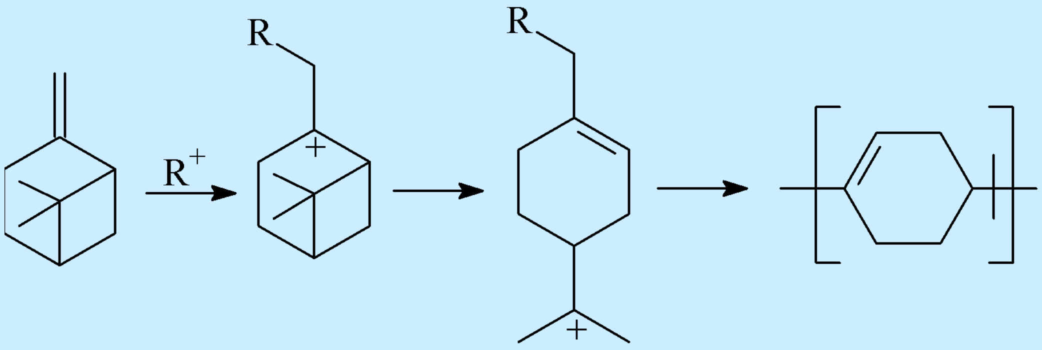
7.2.5 Isomerization in Cationic Polymerization



$$CH_2{=}CH{-}\underset{CH_3}{\overset{CH_3}{CH}} \xrightarrow{X^+} XCH_2{-}CH{-}\underset{CH_3}{\overset{CH_3}{CH}} \xrightarrow{\text{H:shift}}$$

$$XCH_2{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C^+}} \xrightarrow{\text{monomer}} \left[CH_2{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}} \right]$$

(7.34)



(7.35)

7.3 Anionic Polymerization

7.3.1 Anionic initiators

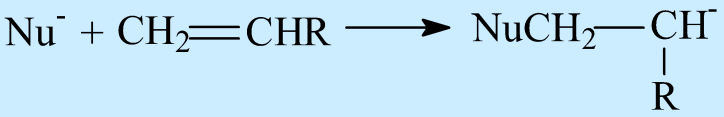
7.3.2 Mechanism, kinetics, and reactivity in anionic polymerization

7.3.3 Stereochemistry of anionic polymerization

7.3.4 Anionic copolymerization

7.3.1 Anionic Initiators

- **Propagating chain - carbanion**



$$Nu^- + CH_2{=}CHR \longrightarrow NuCH_2{-}\underset{\displaystyle R}{\underset{|}{CH^-}}$$

(7.36)

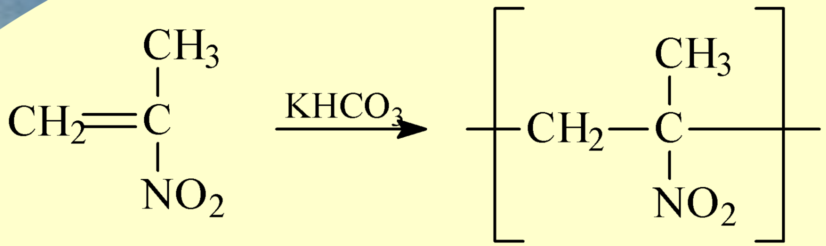
Monomers having substituent group – stabilizing a carbanion

resonance or induction

- Examples – nitro, cyano, carboxyl, vinyl, and phenyl.

7.3.1 Anionic Initiators

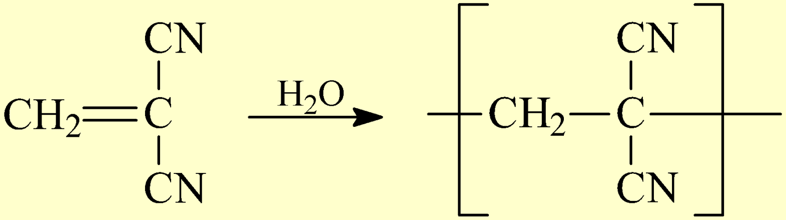
- The strength of the base necessary to initiate polymerization depends in large measure on monomer structure



$$\mathrm{CH_2{=}\underset{NO_2}{\overset{CH_3}{C}}} \xrightarrow{\mathrm{KHCO_3}} \left[\mathrm{CH_2-\underset{NO_2}{\overset{CH_3}{C}}} \right]$$

(7.37)

high reactivity



$$\mathrm{CH_2{=}\underset{CN}{\overset{CN}{C}}} \xrightarrow{\mathrm{H_2O}} \left[\mathrm{CH_2-\underset{CN}{\overset{CN}{C}}} \right]$$

(7.38)

➡ **cyanoacrylate adhesives**

7.3.1 Anionic Initiators

- **Two basic types**

  - that react by addition of a negative ion

  - that undergo electron transfer.

① The most common initiators that react by addition of a negative ion

- simple organometallic compounds of the alkali metals

- For example : butyllithium

- Character of organolithium compounds
  - low melting
  - soluble in inert organic solvents.

- Organometallic compounds of the higher alkali metals
  - more ionic character
  - generally insoluble

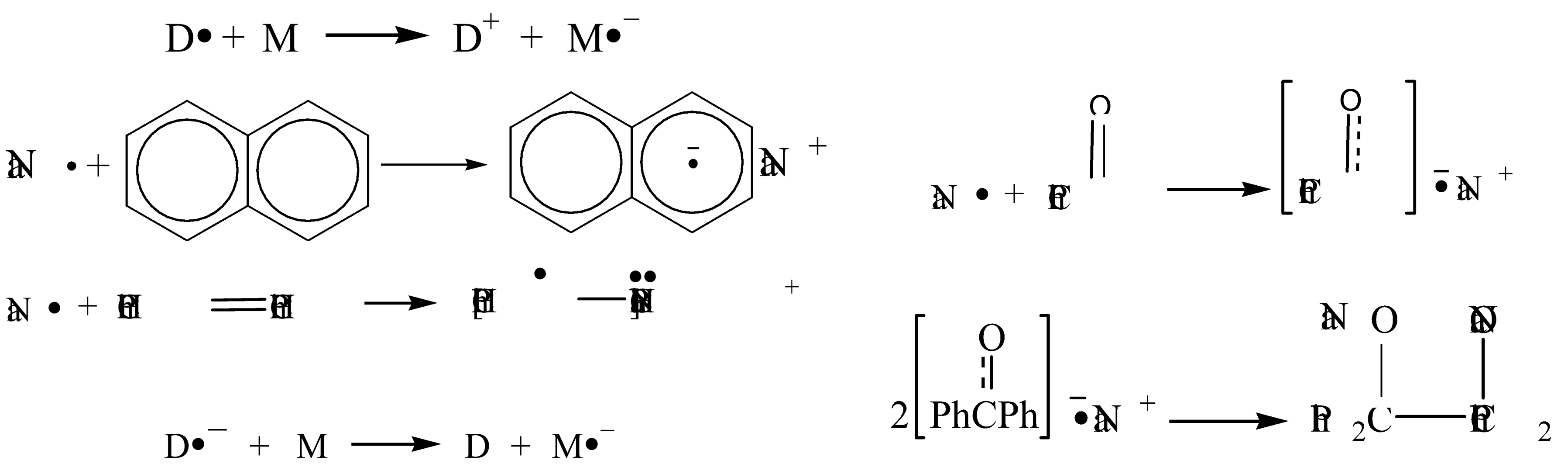
7.3.1 Anionic Initiators

② Electron transfer (charge transfer)

- by free alkali metal : solutions in liquid ammonia or ether solvents
  suspensions in inert solvents

- by addition complex of alkali metal and unsaturated or aromatic compounds.

  - **Electron transfer processes (involving metal donor D· , monomer M)**



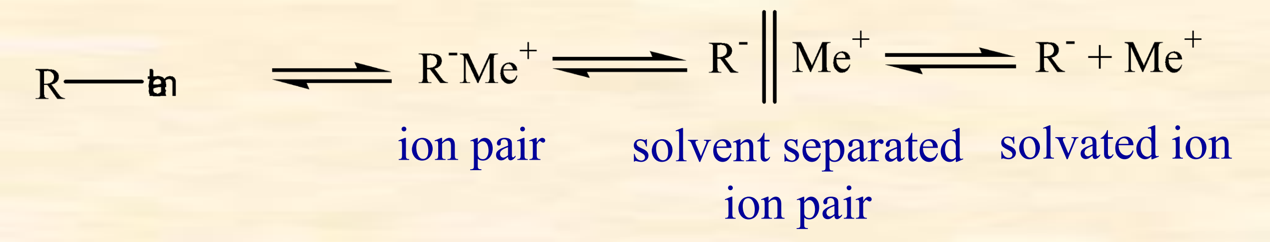
$D\bullet + M \longrightarrow D^{+} + M\bullet^{-}$

$D\bullet^{-} + M \longrightarrow D + M\bullet^{-}$

7.3.2 Mechanism, kinetics, and reactivity in anionic polymerization

A. Mechanism을 변화시킬 수 있는 요인

a. solvent polarity



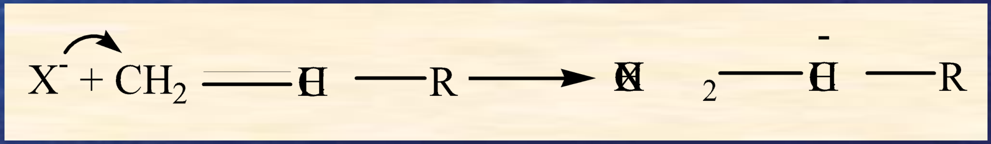
ion pair

solvent separated ion pair

solvated ion

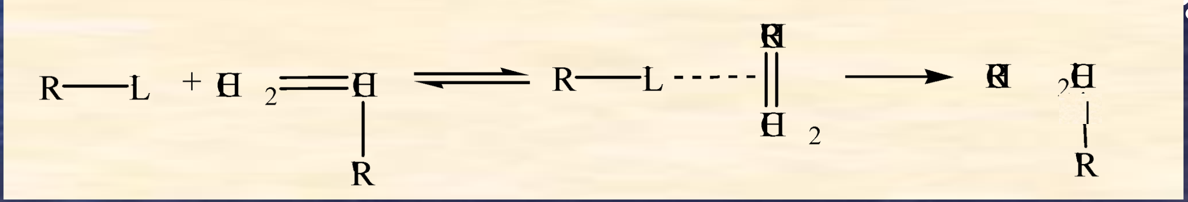
Degree of association of ion counterion의 역할

- **polar solvent : solvated ion 우세**



- **non polar solvent : 이온들간의 association우세 → π –**

성



7.3.2 Mechanism, kinetics, and reactivity in anionic polymerization

b. Type of cation (counterion)

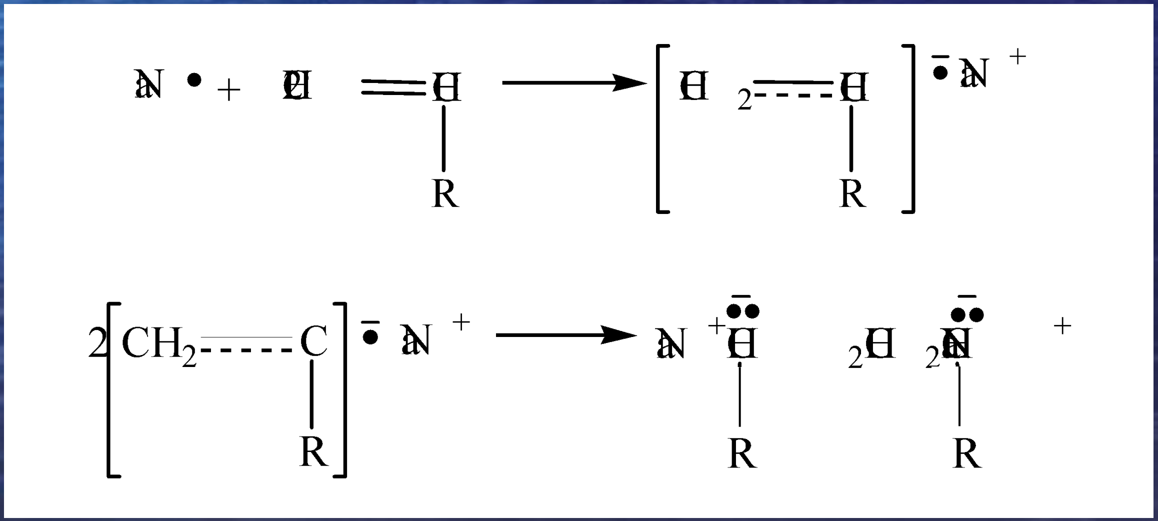
c. Temperature

B. The rate of initiation

- initiator 와 monomer의 structure에 의존

C. Initiation by electron transfer

dianion 생성



(7.46)

(7.47)

7.3.2 Mechanism, kinetics, and reactivity in anionic polymerization

D. Kinetic

$$KNH_2 \rightleftharpoons K^+ + NH_2^-$$

$$NH_2^- + M \longrightarrow H_2N{-}M^-$$

$$\bar{\nu} = \overline{DP}$$

Because the second step is slow relative to the first,

$$R_i = k_i[NH_2^-][M]$$

Chain termination is known to result primarily by transfer to solvent:

$$H_2N(M)_n^- + NH_3 \longrightarrow H_2N(M)_nMH + NH_2^-$$

Rate expressions for propagation and transfer may be written in the conventional way:

$$R_p = k_p[M][M^-]$$

$$R_{tr} = k_{tr}[M^-][NH_3]$$

7.3.2 Mechanism, kinetics, and reactivity in anionic polymerization

D. Kinetic

Assuming a steady state whereby $R_i = R_{tr}$

$$k_i[NH_2^-][M] = k_{tr}[M^-][NH_3]$$

and

$$[M^-] = \frac{k_i[NH_2^-][M]}{k_{tr}[NH_3]}$$

Substituting in R_p we obtain

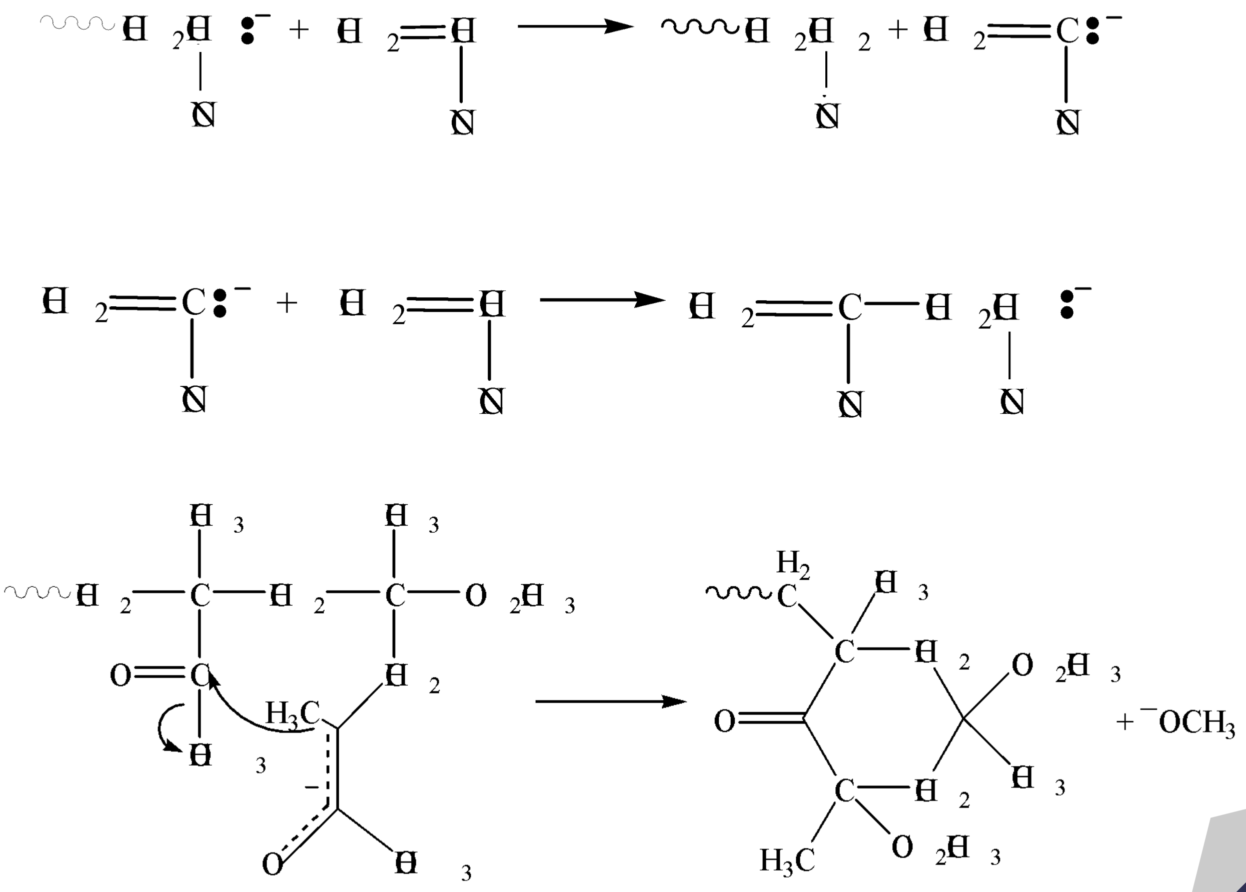
$$R_p = \frac{k_p k_i[NH_2^-][M]^2}{k_{tr}[NH_3]}$$

The average kinetic chain length, $\bar{\nu}$ is expressed as

$$\bar{\nu} = \frac{R_p}{R_{tr}} = \frac{k_p[M][M^-]}{k_{tr}[M^-][NH_3]} = \frac{k_p[M]}{k_{tr}[NH_3]}$$

7.3.2 Mechanism, kinetics, and reactivity in anionic polymerization

E. Other types of transfer reactions



7.3.2 Mechanism, kinetics, and reactivity in anionic polymerization

F. In $R_i \rangle R_p$ — Living Polymerization

When impurities are rigorously excluded

When the polymerization temperature is kept low

living anionic polymers can be made

$$\frac{d[M]}{dt} = k_p[I]_o[M]$$

all chains begin to grow simultaneously.

$$[M] = [M]_o e^{k[I]t}$$

No termination, no chain transfer reaction.

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

as monomer is completely consumed.

$$\bar{\nu} = \frac{[M]_o}{[I]_o} = \overline{DP}$$

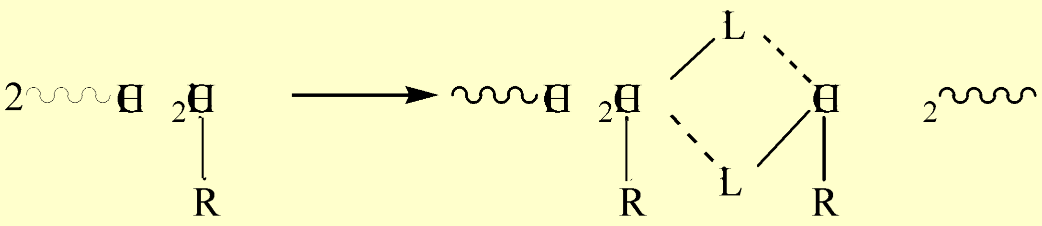
electron transfer initiators

$$\overline{DP} = 2\bar{\nu}$$

7.3.2 Mechanism, kinetics, and reactivity in anionic polymerization

G. Important factor in propagation rate.

a. Association between counterion and terminal carbanion



(7.54)

TABLE 7.4. Representative Anionic Propagation Rate Constants, k_p, for Polystyrene[a]

Counterion	*Solvent*	*k_p (L/mol s)[b]*
Na^+	Tetrahydrofuran	80
Na^+	1,2-Dimethoxyethane	3600
Li^+	Tetrahydrofuran	160
Li^+	Benzene	10^{-3}-10^{-1}[c]
Li^+	Cyclohexane	$(5\text{-}100)\times10^{-5}$[c]

[a] Data from Morton.[30]

[B] at 25°C unless otherwise noted.

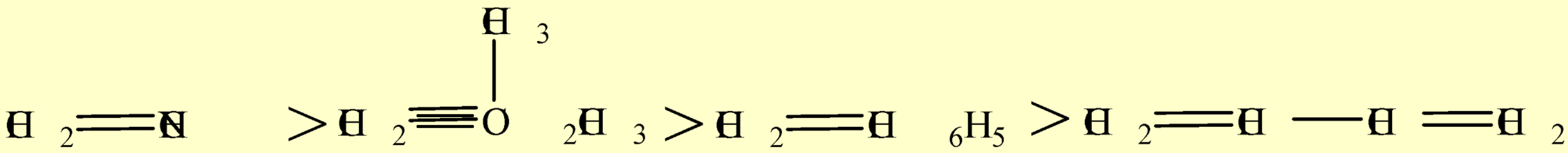
[c] Variable temperature.

7.3.2 Mechanism, kinetics, and reactivity in anionic polymerization

G. Important factor in propagation rate.

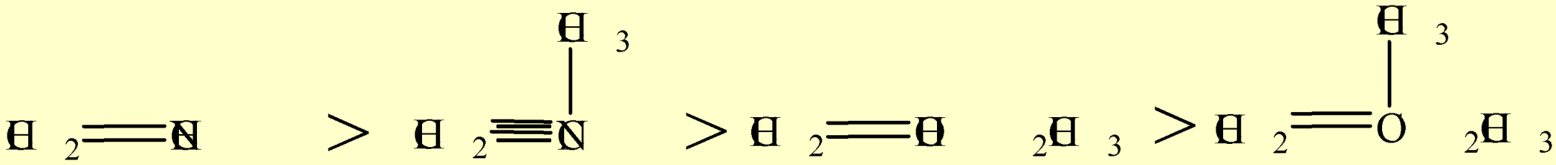
b. Monomer structure

inductive destabilization of the carbanion



$CH_2{=}CHCN > CH_2{=}C(CH_3)COOCH_3 > CH_2{=}CHC_6H_5 > CH_2{=}CH{-}CH{=}CH_2$

steric effect



$CH_2{=}CHCN > CH_2{=}C(CH_3)CN > CH_2{=}CHCOOCH_3 > CH_2{=}C(CH_3)COOCH_3$

7.3.3 Stereochemistry of anionic polymerization

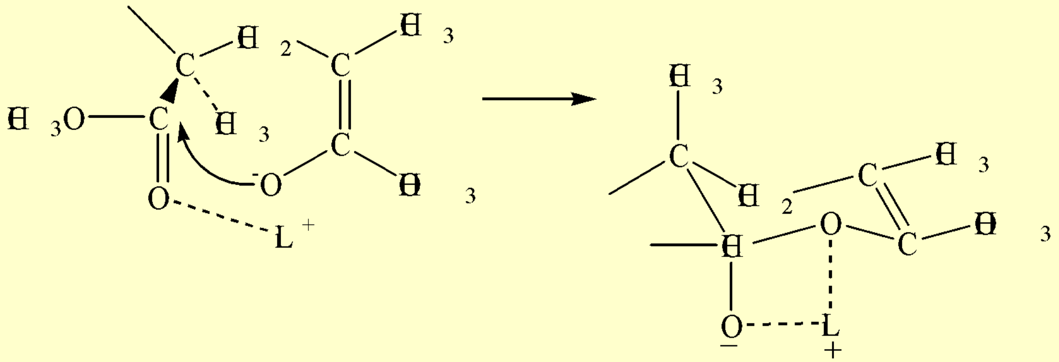
A. Stereochemical of nondiene vinyl monomer

With soluble anionic initiators (homogeneous conditions) at low temperatures,

polar solvents favor syndiotactic placement

nonpolar solvents favor isotactic placement.

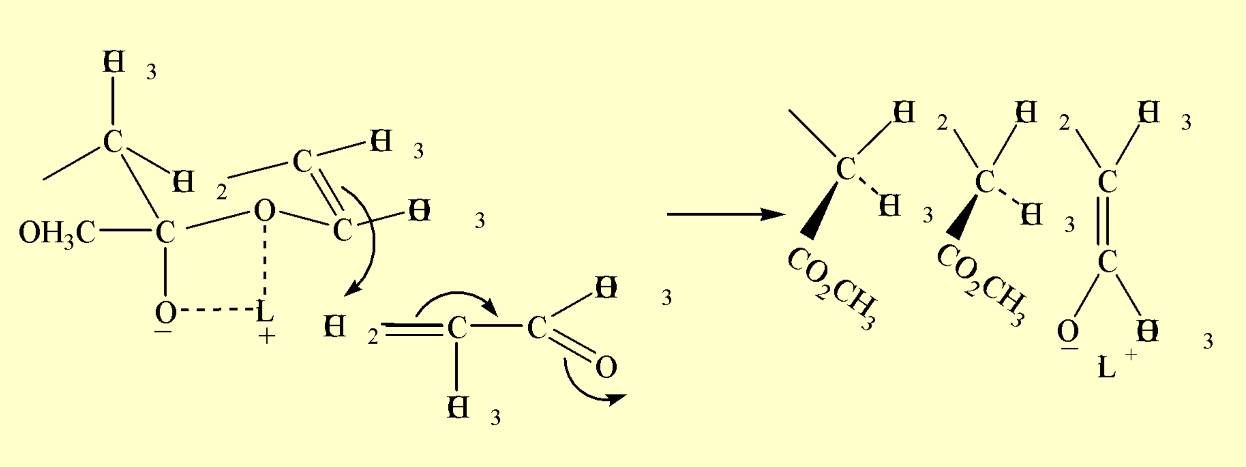
(stereochemistry depends in large measure on the degree of association with counterion, as it does in cationic polymerization)



(7.55)

7.3.3 Stereochemistry of anionic polymerization

A. Stereochemical of nondiene vinyl monomer



(7.56)

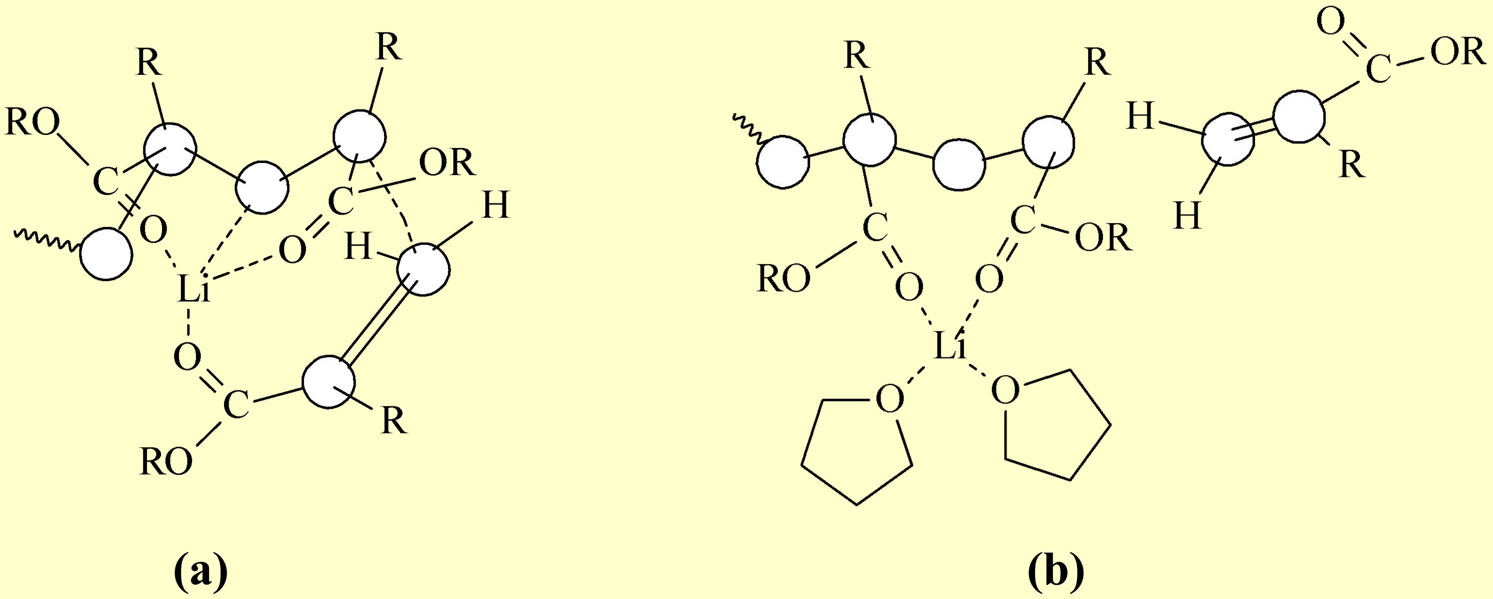
level of isotactic placement decreases –

as the solvent polarity is increased
or as lithium is replaced with the less strongly coordinating higher alkali metal ions.

7.3.3 Stereochemistry of anionic polymerization

A. Stereochemical of nondiene vinyl monomer

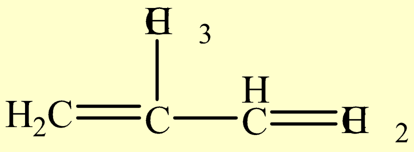
- Effect of solvent



SCHEME 7.1. (a) Isotactic approach of methyl methacrylate in a nonpolar solvent(b) Syndiotactic approach of methyl methacrylate in tetrahydrofuran.(Circles represent backbone or incipient backbone carbons: R=methyl. Backbone hydrogens omitted.)

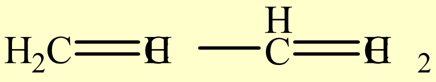
7.3.3 Stereochemistry of anionic polymerization

B. Stereochemical of Dienes



$H_2C{=}C(CH_3){-}CH{=}CH_2$

isoprene



$H_2C{=}CH{-}CH{=}CH_2$

1,3-butadiene

- **catalyst, solvent의 영향**

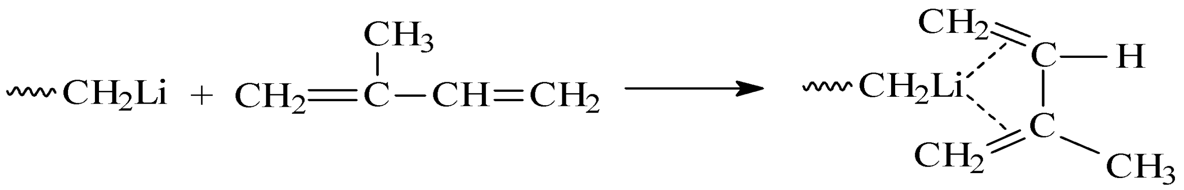
Li-based initiator/nonpolar solvents
cis-1,4 polymer의 생성이 증가

ex) Isoprene/BuLi/pentane or hexane
→ cis-1,4 polyisoprene

7.3.3 Stereochemistry of anionic polymerization

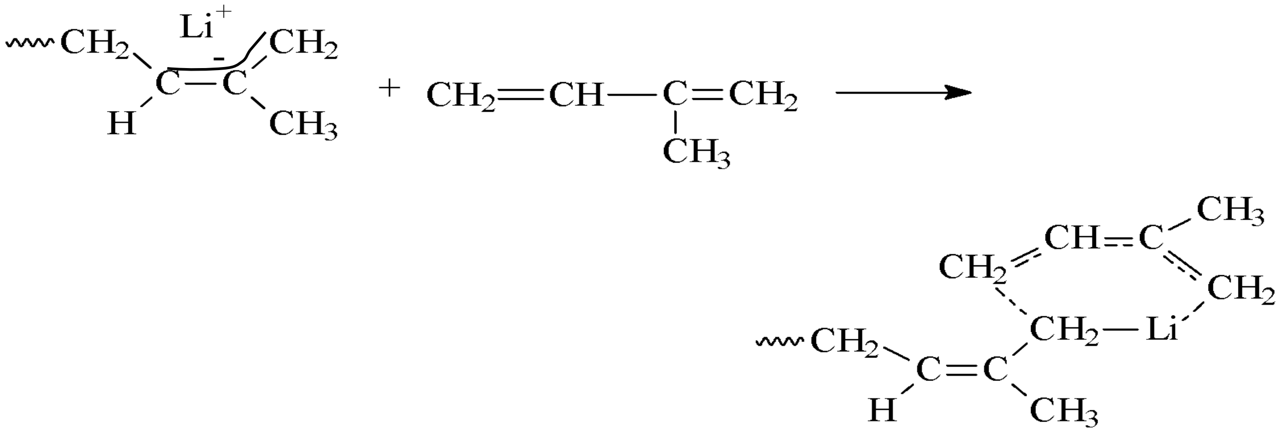
- **formation of *cis*-polyisoprene – lithium's ability**

s-cis comformation by pi complexation – hold isoprene



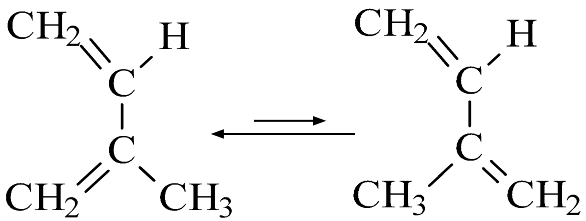
(7.57)

forming a six-membered ring transition state
– "lock" the isoprene into a *cis*-configuration



(7.58)

steric effect



(7.59)

7.3.4 Anionic Copolymerization

- **Complicating factors of counterion.**

① solvating polar of the solvent

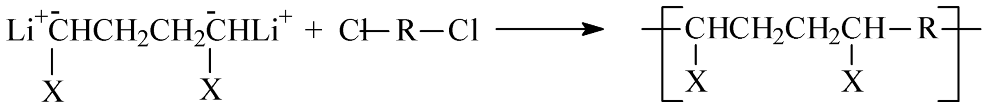
② temperature effect

Table 7.5

③ electron transfer initiator 사용

free radical polymerization
Anionic polymerization

competition



$$\mathrm{Li^{+}\underset{X}{\overset{-}{C}}HCH_2CH_2\underset{X}{\overset{-}{C}}HLi^{+} + Cl\!-\!R\!-\!Cl \longrightarrow \left[\underset{X}{C}HCH_2CH_2\underset{X}{C}H\!-\!R\right]}$$

(7.60)

④ contrasts between homogeneous and heterogeneous polymerization systems.

→ **relatively few reactivity ratios**

TABLE 7.5. Representative Anionic Reactivity Ratios (r)[a]

Monomer 1	Monomer 2	Initiator[b]	Solvent[c]	Temperature[d] (°C)	r_1	r_2
Styrene	Methyl methacrylate	Na	NH_3		0.12	6.4
		n-BuLi	None		[e]	[e]
	Butadiene	*n*-BuLi	None	25	0.04	11.2
		n-BuLi	Hexane	25	0.03	12.5
		n-BuLi	Hexane	50	0.04	11.8
		n-BuLi	THF	25	4.0	0.3
		n-BuLi	THF	-78	11.0	0.4
		EtNa	Benzene		0.96	1.6
	Isoprene	*n*-BuLi	Cyclohexane	40	0.046	16.6
	Acrylonitrile	RLi	None		0.12	12.5
	Vinyl acetate	Na	NH_3		0.01	0.01
Butadiene	Isoprene	*n*-BuLi	Hexane	50	3.38	0.47
Methyl methacrylate	Acrylonitrile	$NaNH_2$	NH_3		0.25	7.9
		RLi	None		0.34	6.7
	Vinyl acetate	$NaNH_2$	NH_3		3.2	0.4

[a] Data from Morton.[30]

[b] Bu=butyl, Et=ethyl, R=alkyl.

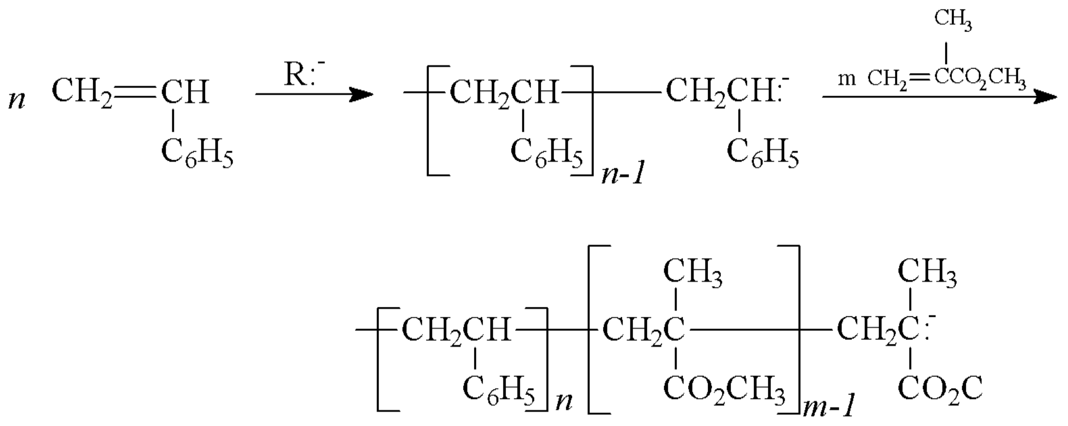
[c] THF=tetrahydrofuran.

[d] Temperature cot specified in some instances.

[e] No detectable styrene in polymer.

7.3.4 Anionic Copolymerization

- formation of block copolymers by the living polymer method.



$$n\,CH_2{=}\underset{C_6H_5}{CH} \xrightarrow{R:^-} \left[CH_2\underset{C_6H_5}{CH}\right]_{n-1} CH_2\underset{C_6H_5}{CH}:^- \xrightarrow{m\,CH_2{=}\overset{CH_3}{C}CO_2CH_3} \left[CH_2\underset{C_6H_5}{CH}\right]_{n} \left[CH_2\overset{CH_3}{\underset{CO_2CH_3}{C}}\right]_{m-1} CH_2\overset{CH_3}{\underset{CO_2C}{C}}:^-$$

(7.61)

7.3.4 Anionic Copolymerization

• Commercial block copolymers

- ABA triblock polymers – Greatest commercial success

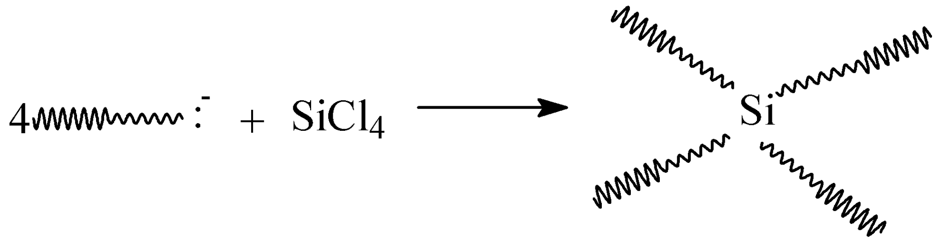
  ex) styrene-butadiene-styrene

$$\mathrm{B} \xrightarrow{\text{initiator}} \mathrm{B}:^{-} \xrightarrow{\text{combination}} {}^{-}:\mathrm{BB}:^{-} \xrightarrow{\mathrm{B}} {}^{-}:\mathrm{BBBBBBBBBB}:^{-} \xrightarrow{\mathrm{S}} {}^{-}:\mathrm{SSSSSBBBBBBBBBBSSSSS} \qquad (7.62)$$

- star-block (radial)

– much lower melt viscosities, even at very high molecular weights

ex) silicon tetrachloride



(7.63)

7.4 Group Transfer Polymerization (GTP)

(In the 1980s a new method for polymerizing acrylic-type monomers)

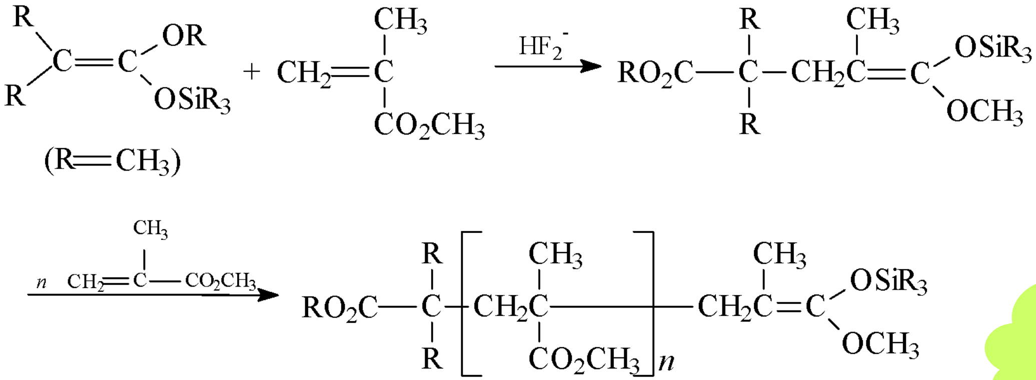
• GTP의 특성

① Anionic polymerization에서 흔히 사용되는 monomer를 사용 →

Living polymer로 전환

② Propagating chain → Covalent character

③ Organosilicon의 개시제로 사용



$$R_2C{=}C(OR)(OSiR_3) + CH_2{=}C(CH_3)CO_2CH_3 \xrightarrow{HF_2^-} RO_2C{-}CR_2{-}CH_2C(CH_3){=}C(OSiR_3)(OCH_3)$$

$(R{=}CH_3)$

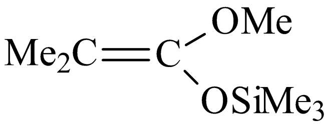
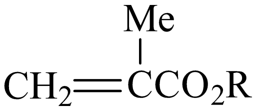
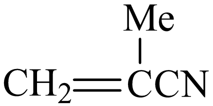
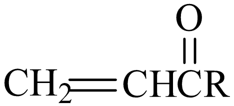
(7.64)

$$n\,CH_2{=}C(CH_3){-}CO_2CH_3 \longrightarrow RO_2C{-}CR_2{-}[CH_2C(CH_3)(CO_2CH_3)]_n{-}CH_2C(CH_3){=}C(OSiR_3)(OCH_3)$$

living polymer

Organosilicon에서 SiR_3가 transfer되어 중합을 형성(GTP)

TABLE 7.6. Representative Compounds Used in Group Transfer Polymerization

Monomers[a]	***Initiators***[a]	***Catalysts***[a]	***Solvents***
$CH_2{=}CHCO_2R$		Anionic[b]	Acetonitrile
 $CH_2{=}C(Me)CO_2R$	$Me_3SiCH_2CO_2Me$	HF_2^-	1,2-Dichloroethane[d]
$CH_2{=}CHCONR_2$	Me_3SiCN	CN^-	Dichloromethane[d]
$CH_2{=}CHCN$	$RSSiMe_3$	N_3^-	N,N-Dimethylacetamide
 $CH_2{=}C(Me)CN$	$ArSSiMe_3$	Me_3SiF_2	N,N-Dimethylformamide
 $CH_2{=}CHC(=O)R$		Lewis acid[c]	Ethyl acetate
		ZnX_2	Propylene carbonate
		R_2AlCl	Tetrahydrofuran
		$(R_2Al)_2O$	Toluene[d]

---

[a] R=alkyl, Ar=aryl, Me=methyl, X=halogen.

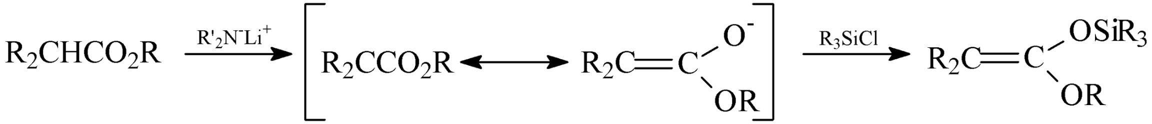
[b] 0.1 mol% relative to initiator.

[c] 10-20 mol% relative to monomer.

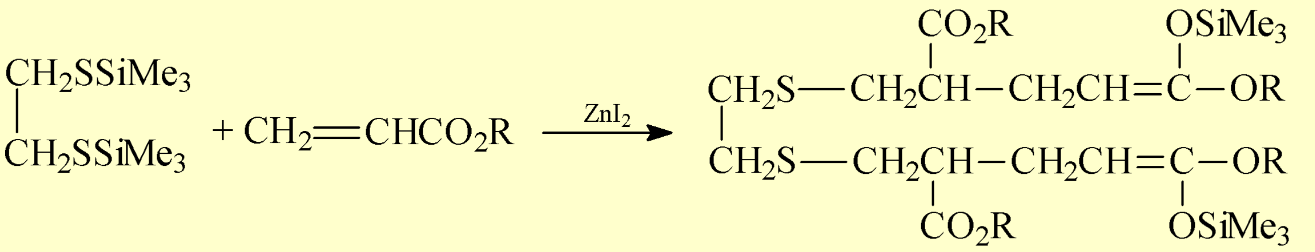
[d] Preferred with Lewis acid catalysts.

7.4 Group Transfer Polymerization (GTP)

*** Synthesis of initiator**



두 개의 작용기를 갖는 개시제 사용 ➡ 사슬의 양끝에서 성장



$$\begin{array}{l} CH_2SSiMe_3 \\ | \\ CH_2SSiMe_3 \end{array} + CH_2{=}CHCO_2R \xrightarrow{ZnI_2} \begin{array}{l} CH_2S{-}CH_2\overset{CO_2R}{\overset{|}{C}H}{-}CH_2CH{=}\overset{OSiMe_3}{\overset{|}{C}}{-}OR \\ | \\ CH_2S{-}CH_2\underset{CO_2R}{\underset{|}{C}H}{-}CH_2CH{=}\underset{OSiMe_3}{\underset{|}{C}}{-}OR \end{array} \qquad (7.65)$$

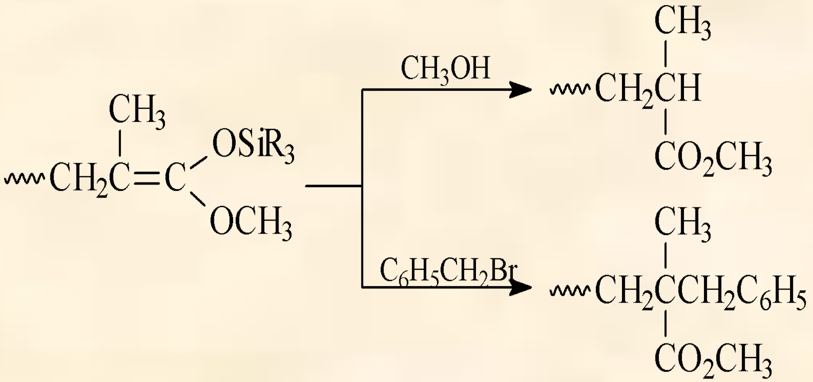
7.4 Group Transfer Polymerization (GTP)

- Speciality

① Once the monomer is consumed, a different monomer may be added

② chain can be terminated by removal of catalyst.

③ chain can be terminated by removal by protonation or alkylation.

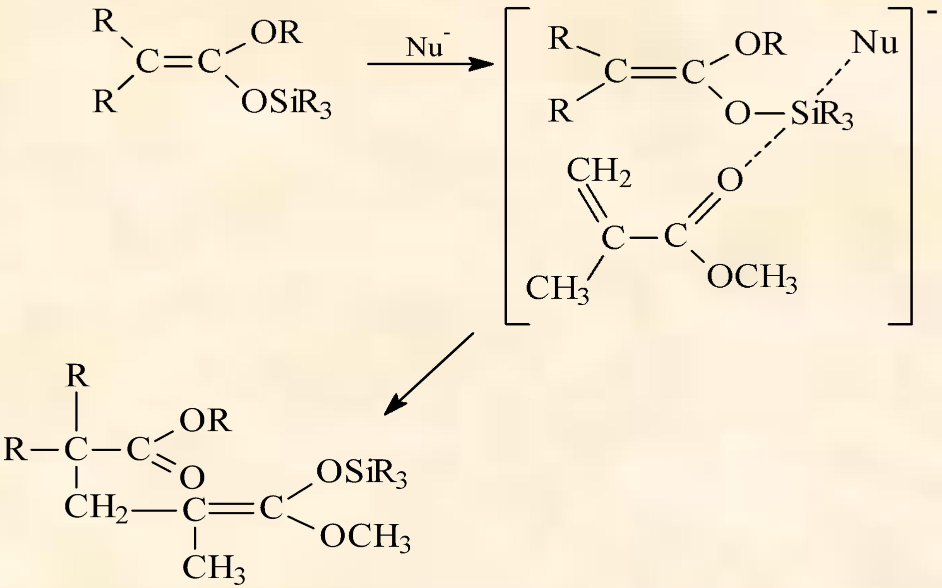


$$\sim CH_2C(CH_3){=}C(OSiR_3)(OCH_3) \xrightarrow{CH_3OH} \sim CH_2CH(CH_3)CO_2CH_3 \qquad (7.66)$$

$$\sim CH_2C(CH_3){=}C(OSiR_3)(OCH_3) \xrightarrow{C_6H_5CH_2Br} \sim CH_2C(CH_3)(CO_2CH_3)CH_2C_6H_5 \qquad (7.67)$$

7.4 Group Transfer Polymerization (GTP)

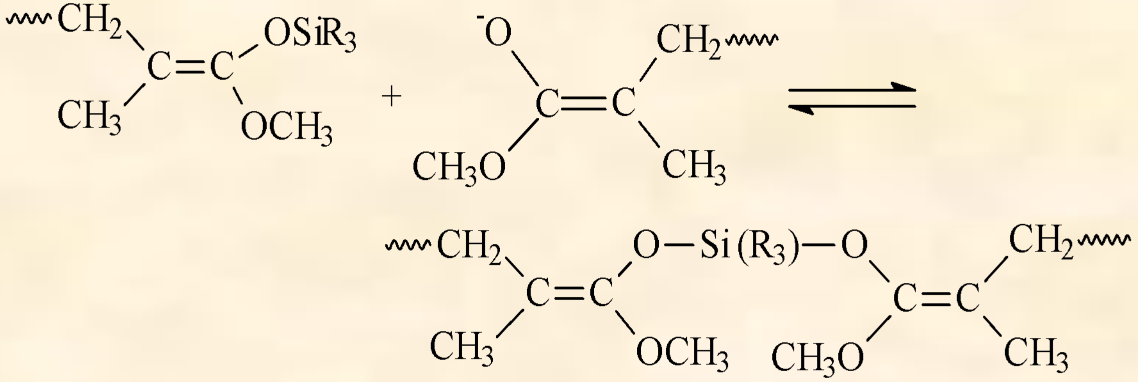
- **GPT mecahanism**



(7.68)

7.4 Group Transfer Polymerization (GTP)

- **Chain transfer of GPT**



(7.69)