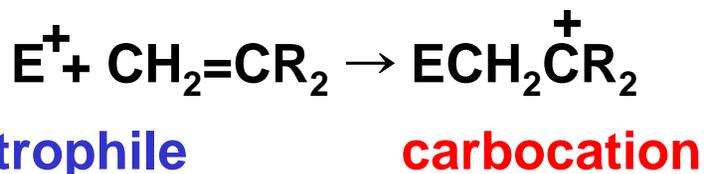


# Chapter 7. Ionic Polymerization

## 7.2. Cationic Polymerization



### 7.2.1. Cationic Initiators

1) **Protonic acids:**  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$

2) { **Lewis acids:**  $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$   
(Coinitiator)  
+  
**Proton donor or cation source:**  $\text{H}_2\text{O}$ , **alkyl chloride**  
(Initiator)

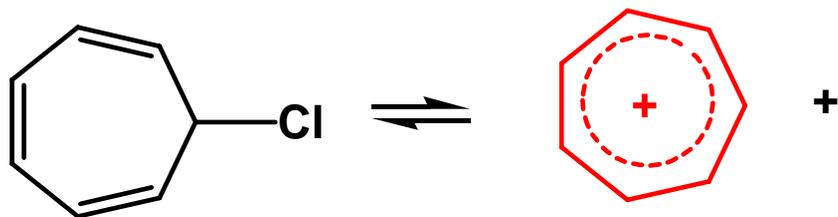


### 3) Autoinitiation



Lewis acid and  
cation source  
are the same

### 4) Ionizable compounds

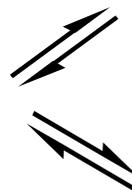
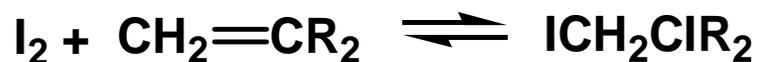


Stable carbocation

∴ Only useful with  
very reactive monomers  
such as vinyl ethers

Tropylium chloride

### 5) I<sub>2</sub>

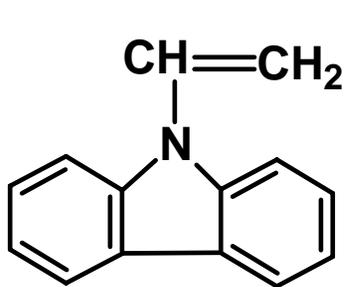


In situ generation of HI



Ion-pair formation

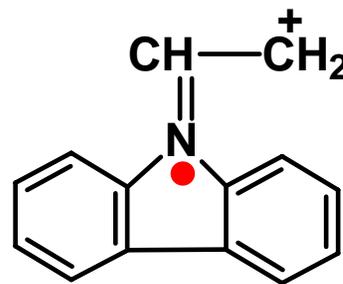
6)  $M + A \rightarrow M^{\bullet+} + A^{\bullet-}$  **Electron transfer process**



**Electron donor**



**Electron acceptor**



**Radical cation**



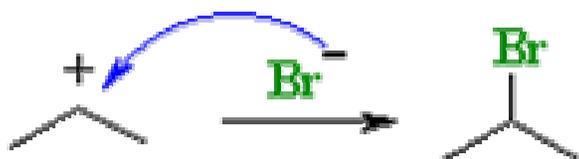
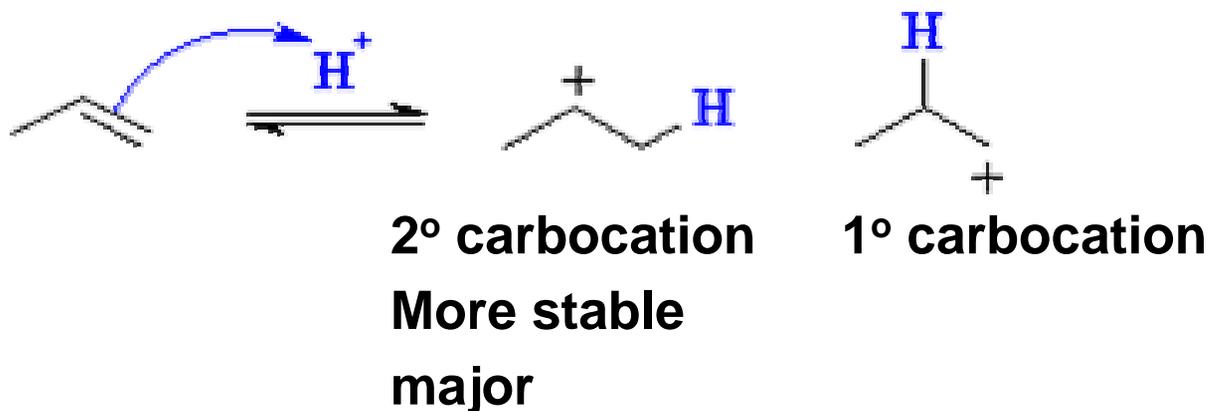
## 7.2.2. Mechanism, Kinetics, and Reactivity in Cationic Polymerization

### o Markovnikov's rule

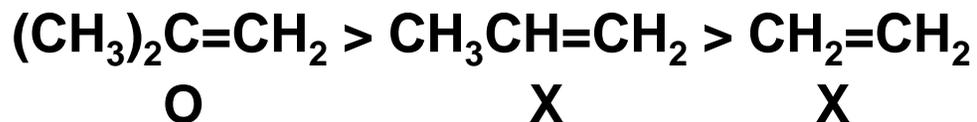
Addition of electrophile to monomer

→ The more stable carbocation intermediate is formed.

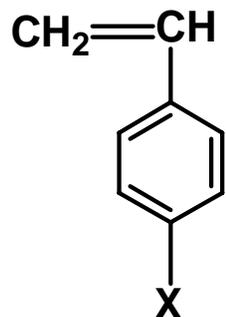
When an **unsymmetrical alkene** undergoes **addition** with **E-Nu**, then the **electrophile, E**, adds to the **carbon** of the alkene that has the **greater number of hydrogen substituents**, and the nucleophile, **Nu**, to the carbon of the alkene with the **fewer number of hydrogen substituents**"



o **Rate of addition** to aliphatic monomers



Only isobutylene provides the requisite **carbocation stability** for cationic polymerization



Reactivity (**para**-substituted)



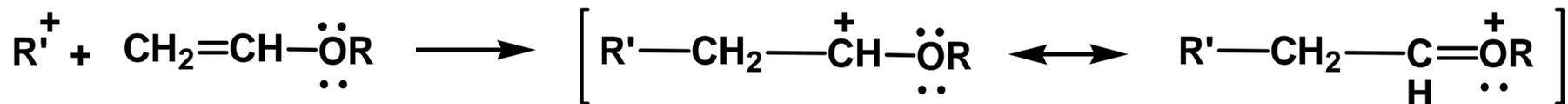
**Electron-donating**

**Electron-withdrawing**

**Ortho** substituents retard the addition

∴ Steric hindrance

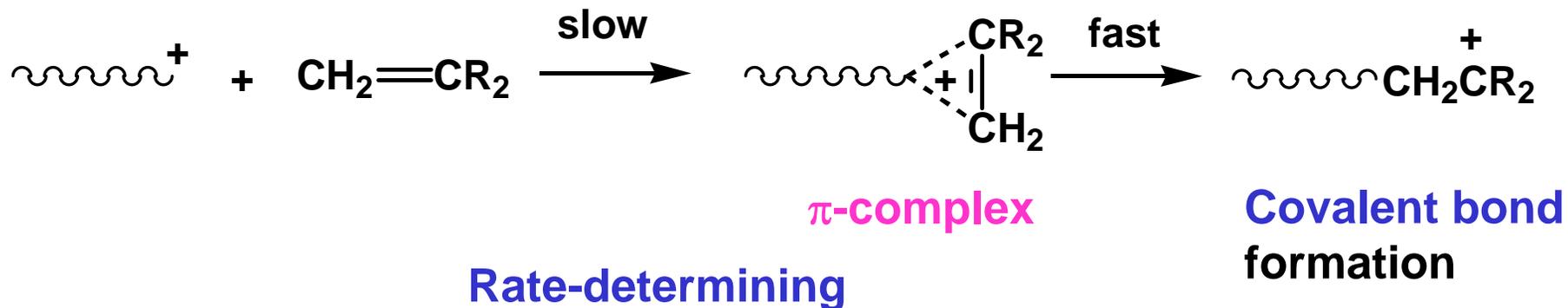
**Vinyl ether**: particularly reactive



**Delocalized carbocation**

## o Propagation

### Two steps



## o Solvent effect

As solvent **polarity**  $\uparrow$ ,  $R_i$   $\uparrow$

$\therefore R_i$  : **charged species** is generated

Polar solvent **stabilizes** the **charged species**

## Degree of association between **cationic chain end** and **anion (A<sup>-</sup>)**



**covalent**

**intimate ion pair**

**solvent-separated**

**solvated ions**

= contact ion pair

ion pair

= free ions

Small  $R_p$

Large  $R_p$

The **more intimate** the association, the **lower the  $R_p$** .

In **poorly solvating solvents**

As **solvent polarity**  $\uparrow$ ,  $R_p$   $\uparrow$

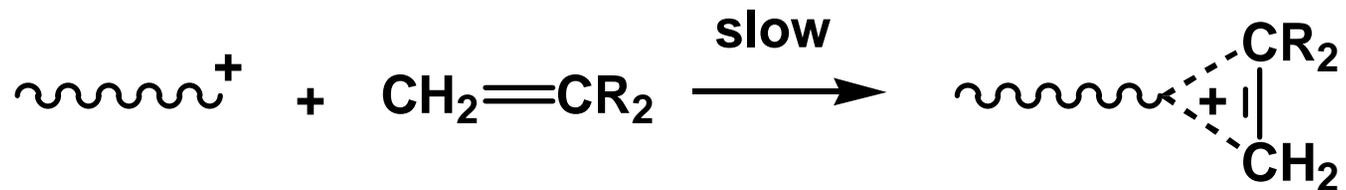
$\therefore$  more separation

In **solvating solvents (ether solvent)**

As **solvent polarity**  $\uparrow$ ,  $R_p$   $\downarrow$

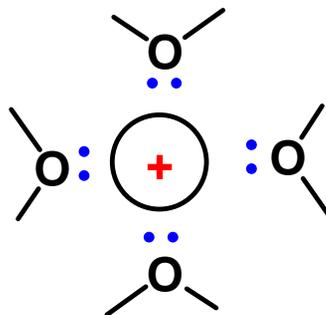
$\therefore$  **less  $\pi$ -complex** formation

**Polar solvent stabilizes the initial state** (monomer + ion pair) at the expense of the **transition complex** (charge is **dispersed over a larger volume**).



**Polar solvent stabilizes  
the initial state**

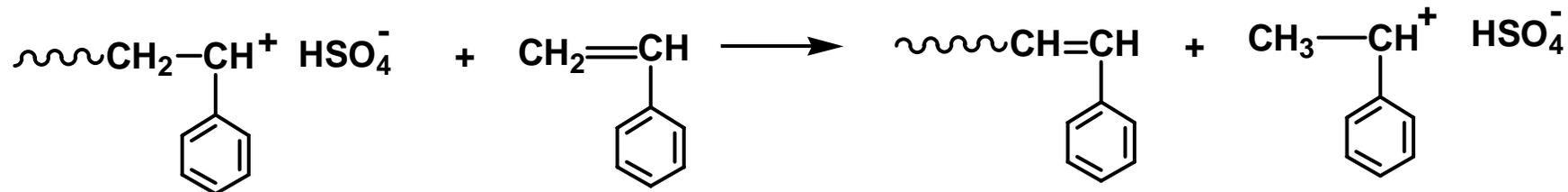
**Charge is dispersed  
over a larger volume**



o Chain transfer reactions

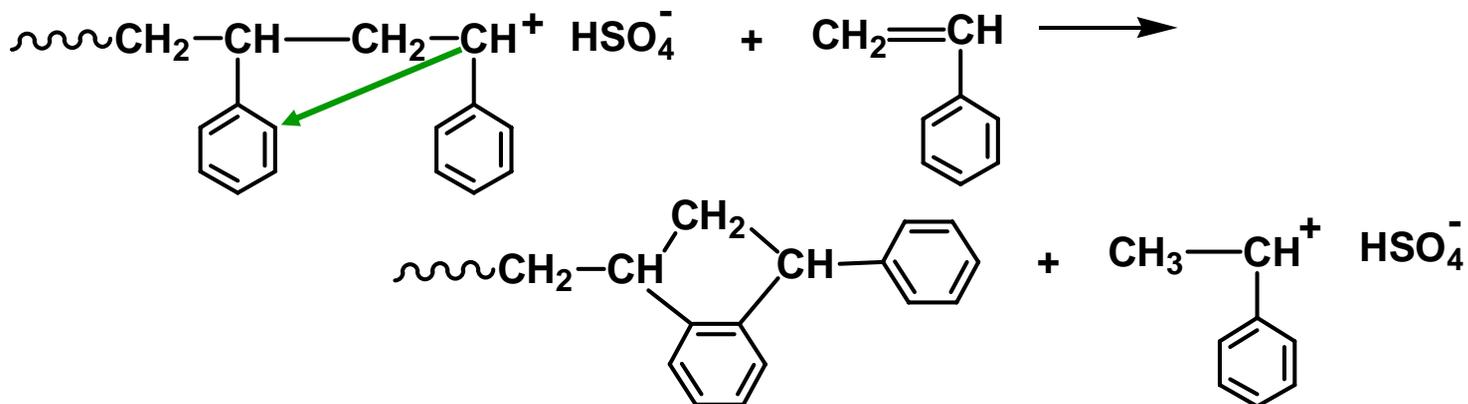
M = styrene, I = H<sub>2</sub>SO<sub>4</sub>

1) With monomer

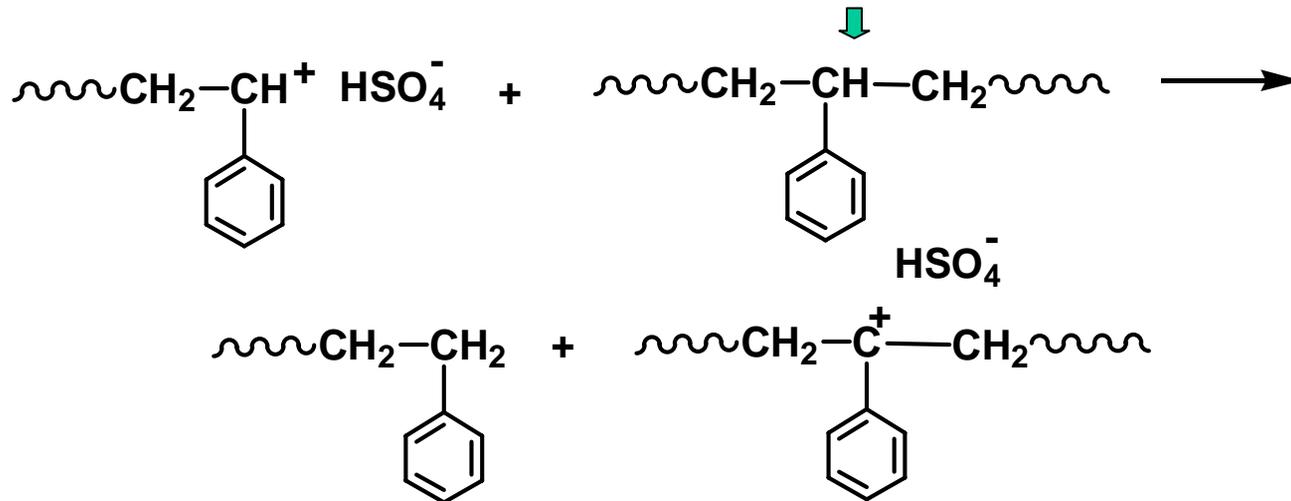


2) By ring alkylation

Electrophilic substitution

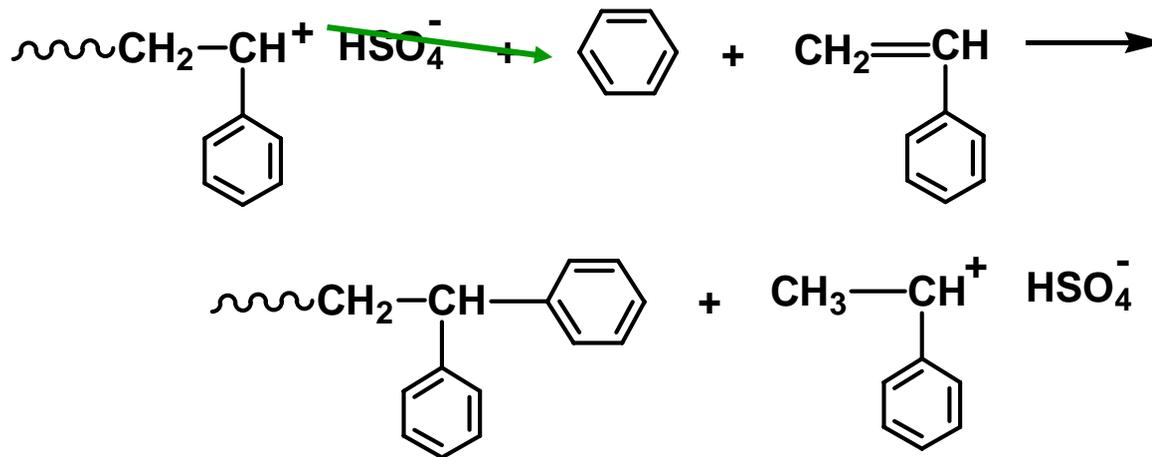


3) By **hydride abstraction** from the **chain** to form a **more stable ion**



**Chain branching**

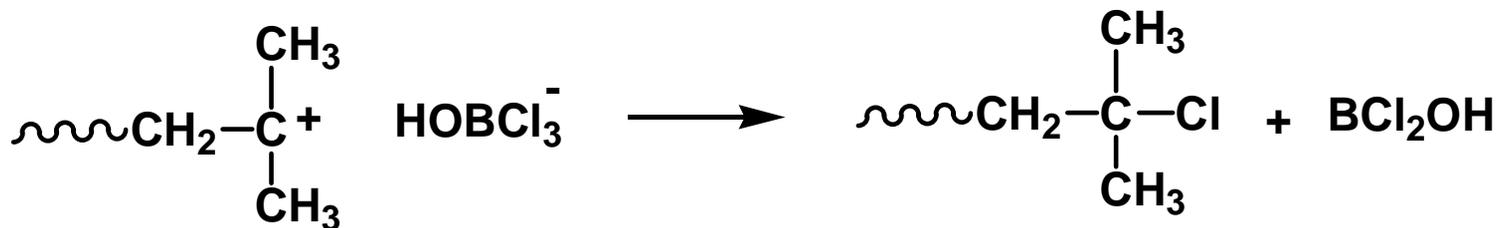
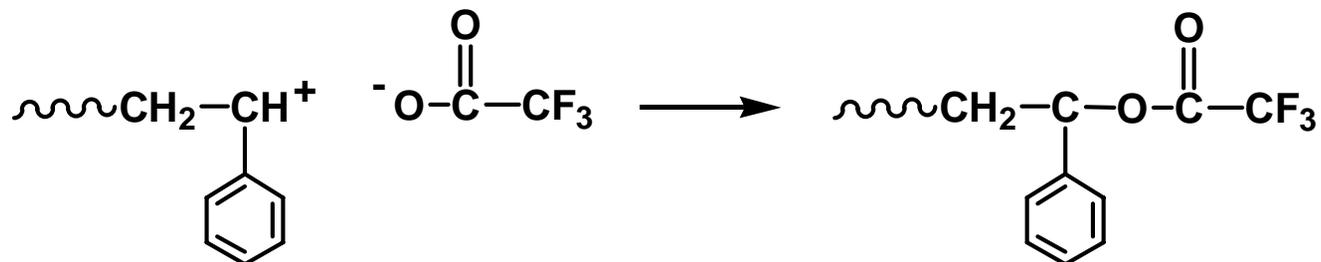
4) With **solvent** by **electrophilic substitution**



o **Termination** reactions

**Combination** of **chain end** with **counterion**

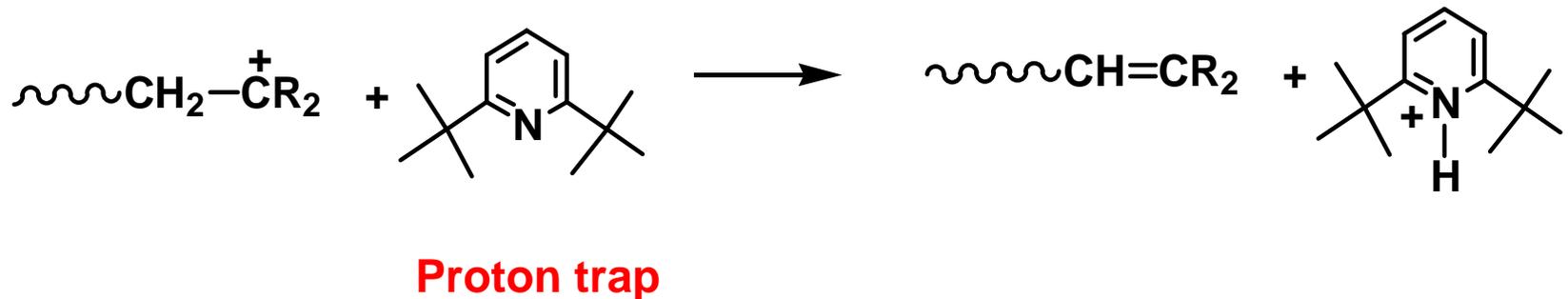
(i.e., change from **ionic** to **covalent** bonding)



o Chain transfer to monomer is so common

**Proton trap** intercepts **proton** before it transfers to monomer.

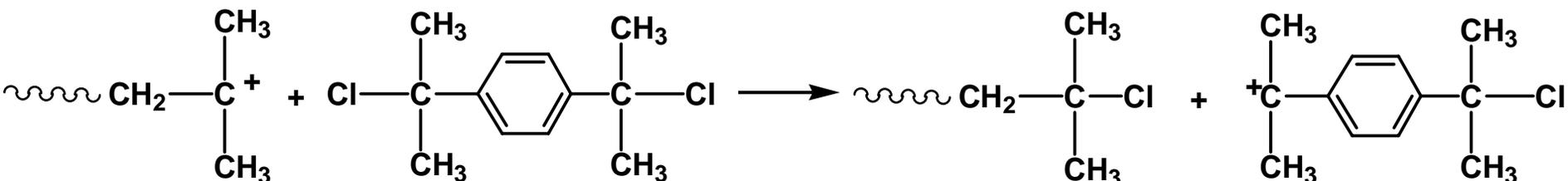
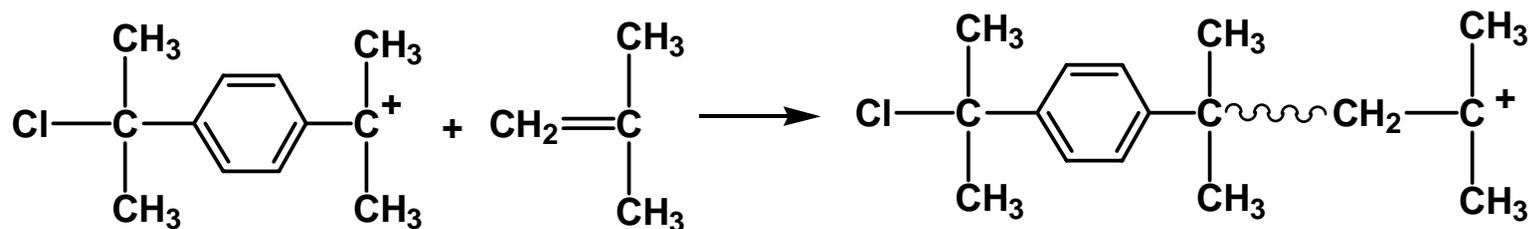
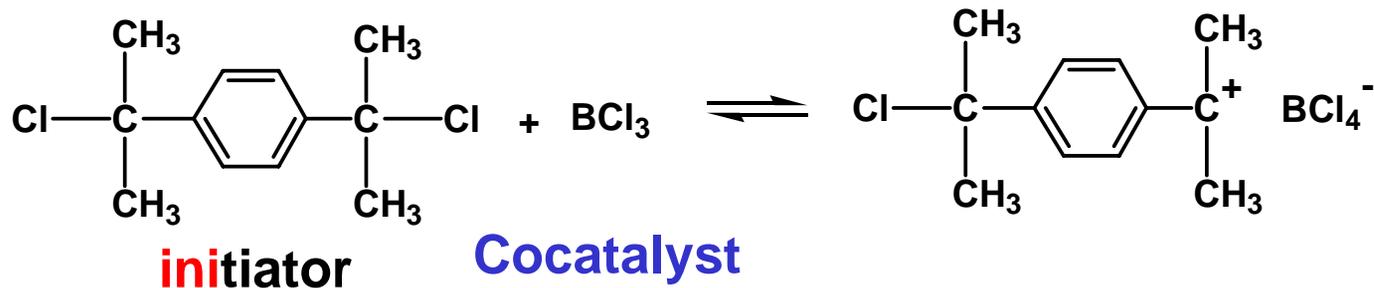
→ Lower overall yield, higher mol. wt., lower polydispersity index



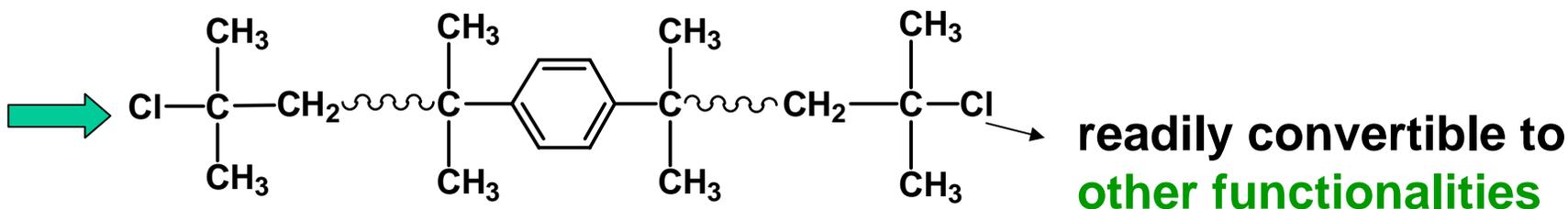
The bulky **t-butyl** groups prevent reaction with electrophiles larger than the **proton**.

## o Telechelic polymers

**Inifer:** initiator + chain transfer agent



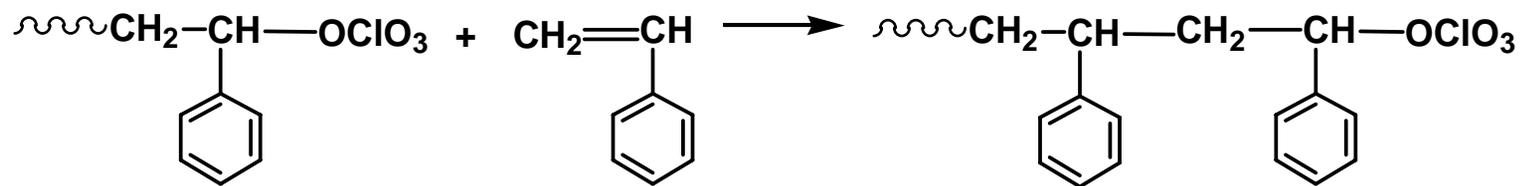
**chain transfer agent**



o **Pseudocationic** polymerization

**I** =  $\text{HClO}_4$ , **M** = styrene, **S** = **hydrocarbon** solvent

$R_p$  **much slower** compared with most cationic processes.

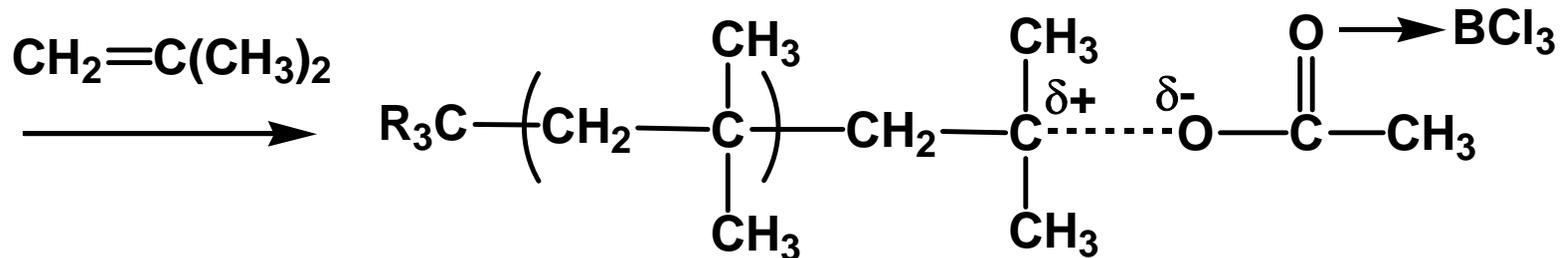
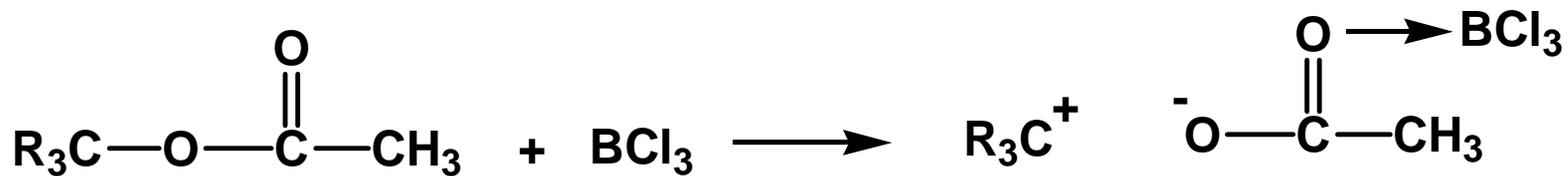


**Covalently bonded**  
perchlorate ester

**Monomer is inserted**  
between C-O bonds

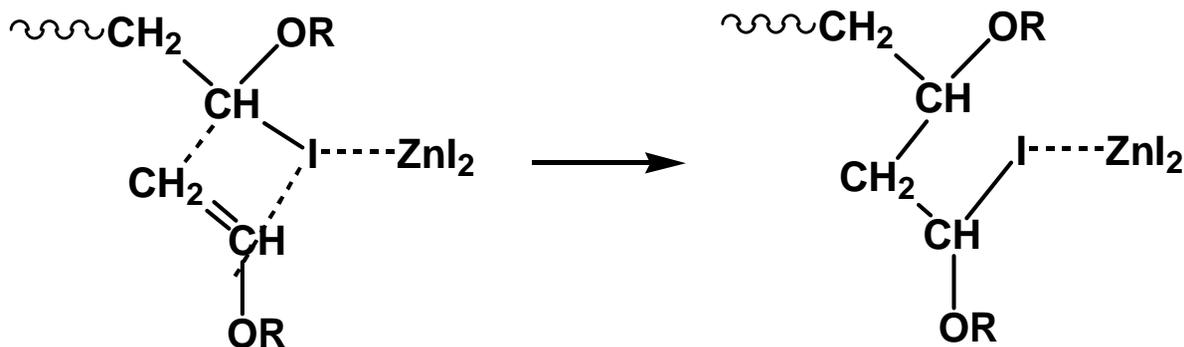
o **Living cationic** polymerization

M = isobutylene, I = **tertiary ester** + **BCl<sub>3</sub>**



**Very tightly bound**  
But **still active ion pair**

**M = vinyl ether**, **I = I<sub>2</sub>/HI** or **I<sub>2</sub>/ZnI<sub>2</sub>**



**Insertion** of monomer into an **activated C-I** bond

**Low polydispersity**,

**Block copolymers** are formed upon addition of a **second monomer**

## Kinetics

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

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

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

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

## Steady-state assumption

$$R_i = R_t$$

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

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

Table 7.2 Cationic Propagation Rate Constants,  $k_p$

Monomer	Solvent	Temperature(°C)	Initiator	$k_p$ (L/mol s)
Styrene	None	15	Radiation	$3.5 \times 10^6$
$\alpha$ -Methylstyrene	None	0	Radiation	$4 \times 10^6$
<i>i</i> -Butyl vinyl ether	None	30	Radiation	$3 \times 10^5$
<i>i</i> -Butyl vinyl ether	CH <sub>2</sub> Cl <sub>2</sub>	0	C <sub>7</sub> H <sub>7</sub> <sup>+</sup> SbCl <sub>6</sub> <sup>-</sup>	$5 \times 10^3$
<i>t</i> -Butyl vinyl ether	CH <sub>2</sub> Cl <sub>2</sub>	0	C <sub>7</sub> H <sub>7</sub> <sup>+</sup> SbCl <sub>6</sub> <sup>-</sup>	$3.5 \times 10^3$
Methyl vinyl ether	CH <sub>2</sub> Cl <sub>2</sub>	0	C <sub>7</sub> H <sub>7</sub> <sup>+</sup> SbCl <sub>6</sub> <sup>-</sup>	$1.4 \times 10^2$
2-Chloroethyl vinyl ether	CH <sub>2</sub> Cl <sub>2</sub>	0	C <sub>7</sub> H <sub>7</sub> <sup>+</sup> SbCl <sub>6</sub> <sup>-</sup>	$2 \times 10^2$

In the **absence** of any **chain transfer**

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

If **transfer** is the predominant mechanism controlling chain growth

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

**Cationic**

$$R_p \propto [I], [M]^2$$

$$\bar{v} \propto [M], \text{ independent of } [I]$$

**Free radical**

$$R_p \propto [I]^{1/2}, [M]$$

$$\bar{v} \propto [I]^{-1/2}, [M]$$

The difference arises from **radical disproportionation** and **combination reactions** characteristic of free radical termination.

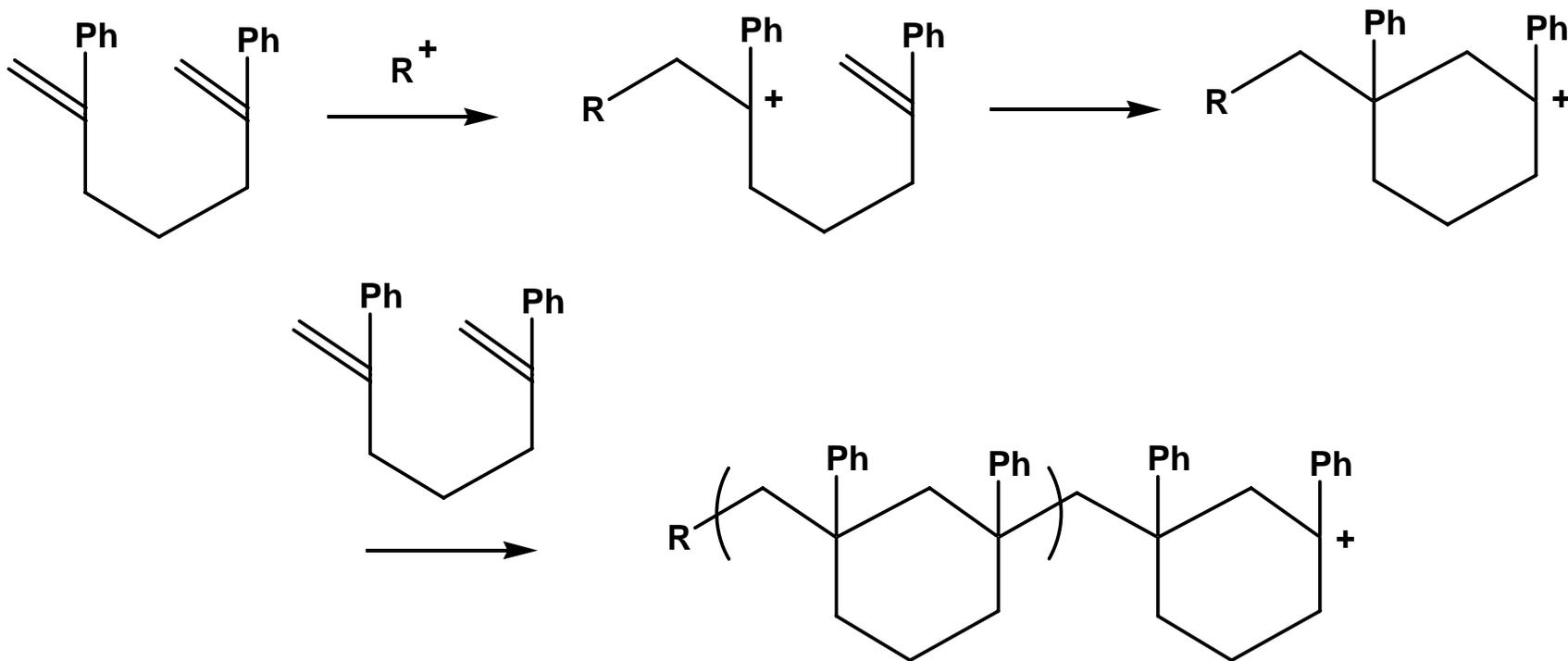
Increasing **[I]** increases the **probability of radical termination**, which is **not** the case in **cationic polymerization**.

o Diene monomers

**Cationic** polymerization only for **copolymer** synthesis

o **Nonconjugated dienes**

Cationic **cyclopolymerization**



## 7.2.3 Stereochemistry of Cationic Polymerization

- (1) Greater stereoregularity at lower temperature
- (2) Degree of stereoregularity varies with initiator  $\leftrightarrow$  counterion
- (3) Degree and type of stereoregularity (isotactic or syndiotactic) vary with solvent polarity



In polar solvents : both carbocation chain end and counterion are strongly solvated  $\therefore$  free carbocation

$\rightarrow$  Syndiotactic placement

In nonpolar solvents : strong association between carbocation chain end and counterion

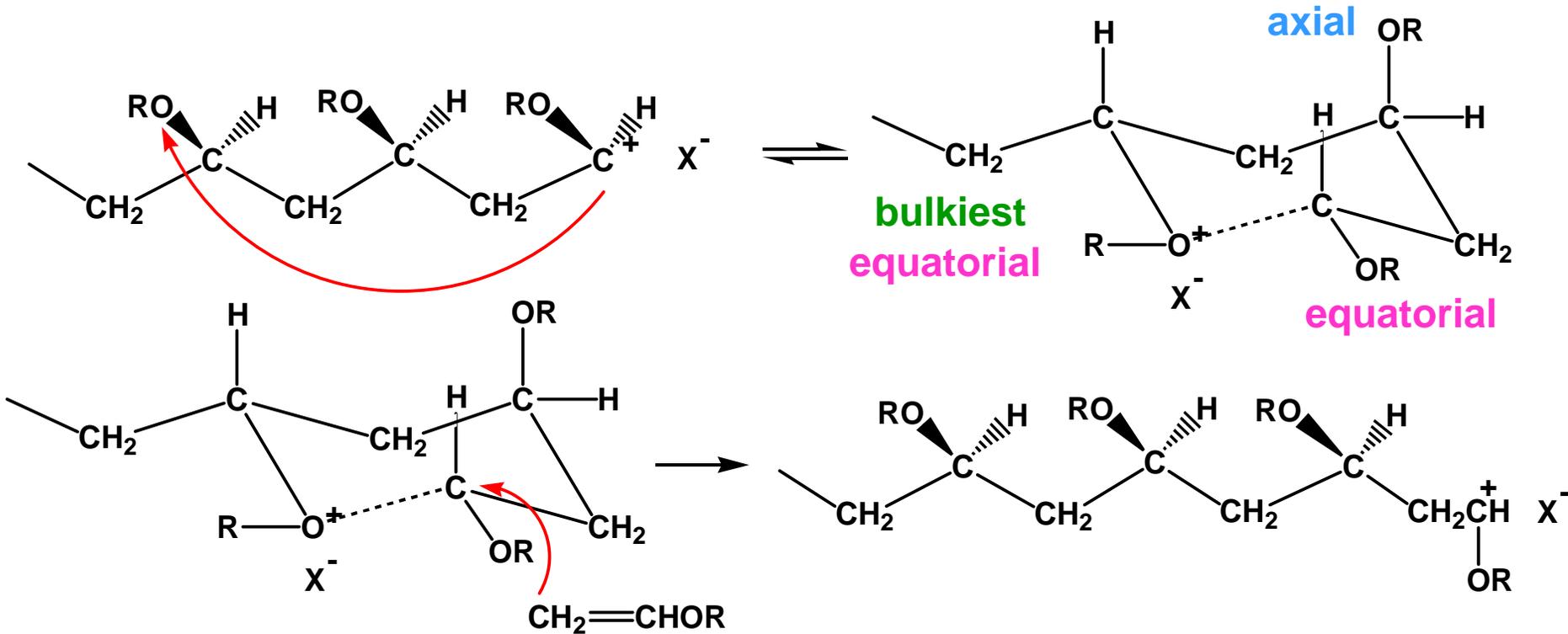
$\rightarrow$  Isotactic placement

# Isotactic poly(vinyl ether)

Several models have been proposed

## 1) Six-membered cyclic chain end

Formed by coordination of the **carbocation** of the terminal carbon with the **oxygen** of the alkoxy group attached to the **fifth carbon atom**

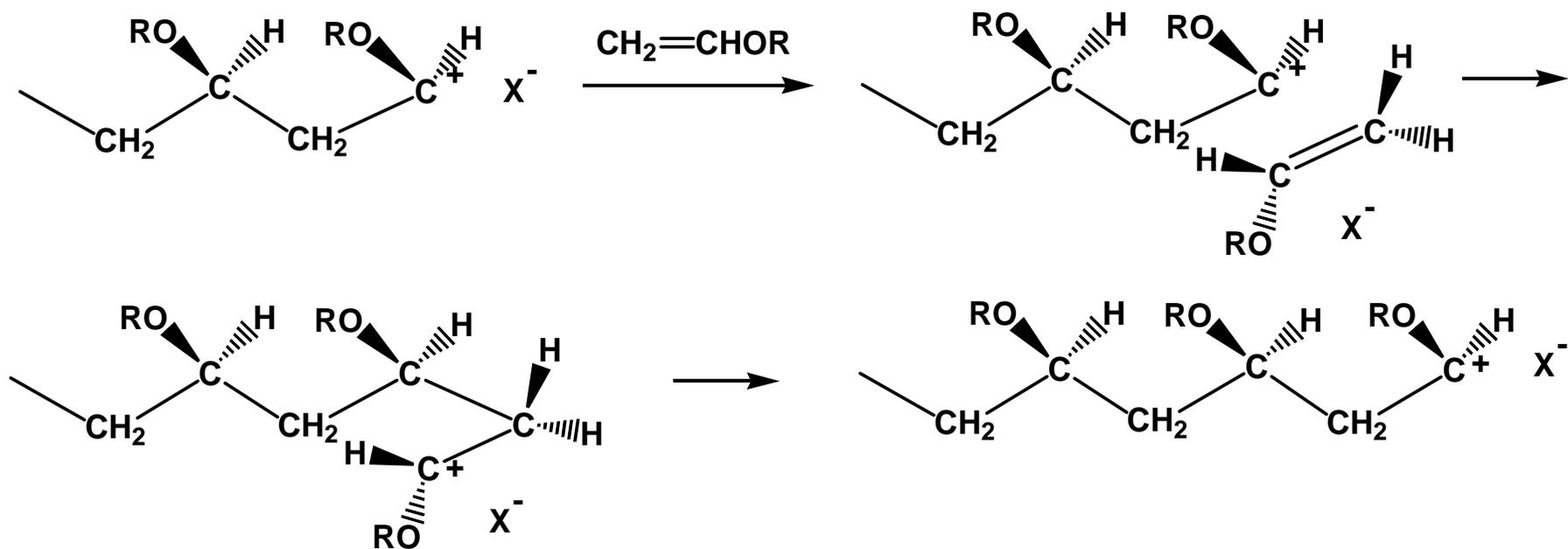


**Attack** of monomer at  $\text{C}_1$  **from the backside** causing **inversion**.

$\therefore$  Alkoxy group at  $\text{C}_1$  have the same configuration as that at original  $\text{C}_3$

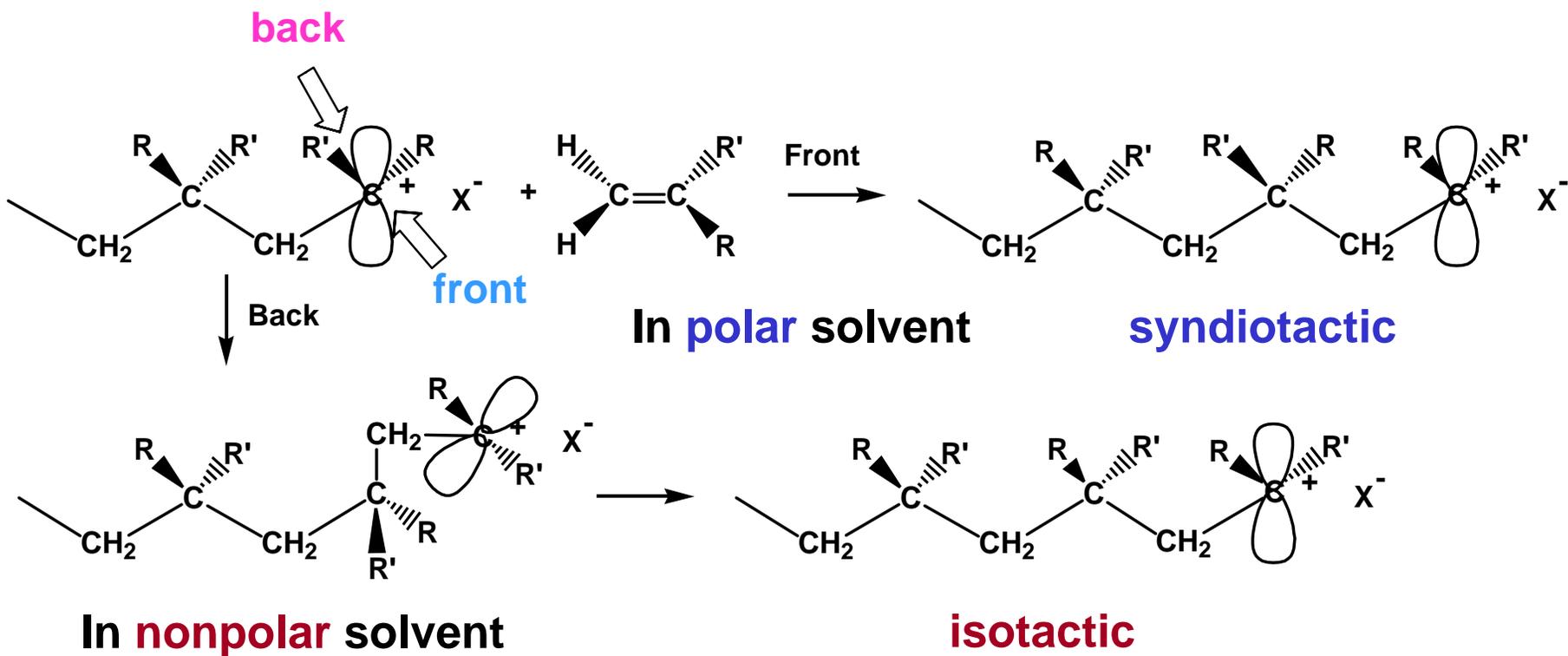
## 2) Strong **carbocation chain end** - **counterion association**

**Insert** monomer: alkoxy groups are **anti** to one another



As long as **propagation** proceeds **faster than rotation** about carbon-carbon bonds in the chain, a regular repeating **isotactic** polymer results.

### 3) $sp^2$ hybridization of the terminal chain carbon atom



## Poly( $\alpha$ -methylstyrene)

Due to **two bulky groups** on the 3rd carbon, **back-side attack is hindered**.

$\therefore$  **Syndiotactic placement** is favored in **both polar** and **nonpolar solvents**.

Although **isotacticity**  $\uparrow$  as **solvent polarity**  $\downarrow$

## Poly(vinyl ether)

Being **less hindered**, exhibit a more pronounced preference for **isotactic placement** in **nonpolar solvents**

As **T**  $\uparrow$ , **electroregularity**  $\downarrow$

Can be interpreted in terms of **small difference in activation energy** for **front- and back-side attack** as well as of the effect on **conformational mobility** of the growing chain.

**Counterion-monomer interactions** are assumed to be **negligible**, since both may be considered “**electron rich**”

The **last model** satisfactorily explains most of the experimental observations.

## 7.2.4 Cationic Copolymerization

### Table 7.3 Reactivity ratios

Counterion effect

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

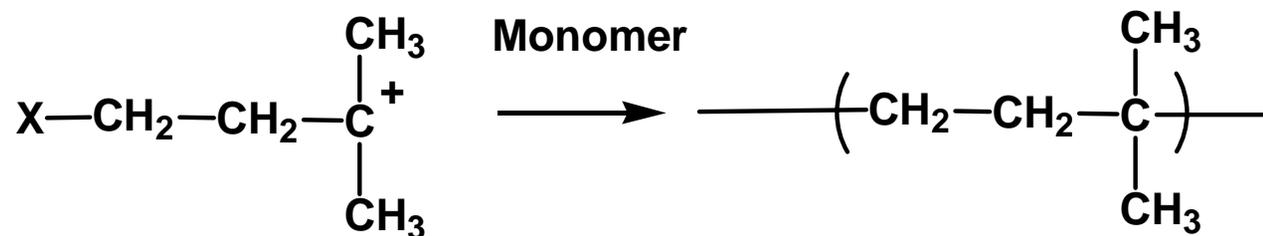
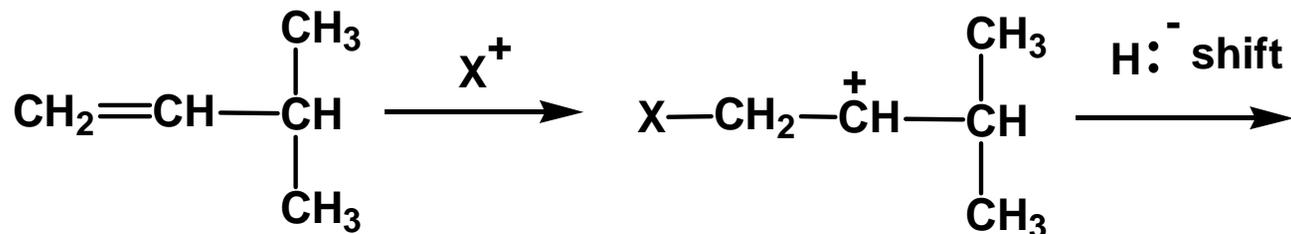
**No** apparent **tendency for alternating** copolymers to form.

**Block copolymers** or **homopolymer blends** are more **likely**.

## Table 7.3 Cationic Reactivity ratios

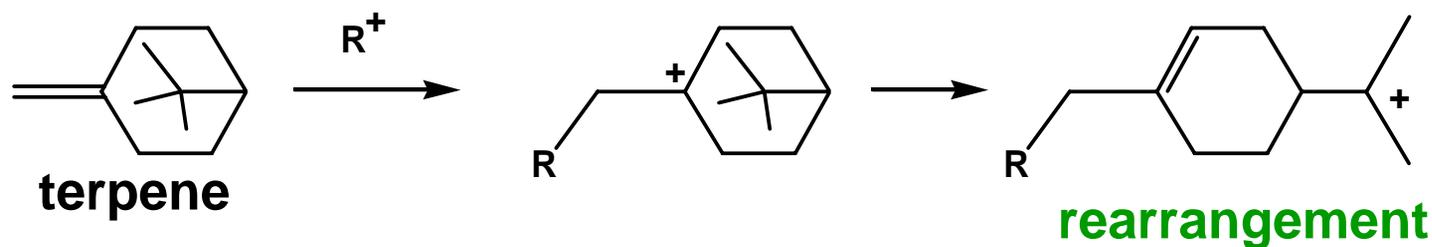
Monomer 1	Monomer 2	Coinitiator	solvent	Temperature (°C)	r <sub>1</sub>	r <sub>2</sub>
Isobutylene	1,3 Butadiene	AlEtCl <sub>2</sub>	CH <sub>3</sub> Cl	-100	43	0
	1,3-Butadiene	AlCl <sub>3</sub>	CH <sub>3</sub> Cl	-103	115	0
	Isoprene	AlCl <sub>3</sub>	CH <sub>3</sub> Cl	-103	2.5	0.4
	Cyclopentadiene	BF <sub>3</sub> ·OEt <sub>2</sub>	PhCH <sub>3</sub>	-78	0.60	4.5
	Styrene	SnCl <sub>4</sub>	EtCl	0	1.60	0.17
	Styrene	AlCl <sub>3</sub>	CH <sub>3</sub> Cl	-92	9.02	1.99
Styrene	$\alpha$ -Methylstyrene	TiCl <sub>4</sub>	PhCH <sub>3</sub>	-78	1.2	5.5
	$\alpha$ -Methylstyrene	SnCl <sub>4</sub>	EtCl	0	0.05	2.90
	<i>p</i> -Methylstyrene	SnCl <sub>4</sub>	CCl <sub>4</sub>	-78	0.33	1.74
	<i>trans</i> - $\beta$ -Methyl- styrene	SnCl <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	0	1.80	0.10
P-Chlorostyrene	<i>cis</i> - $\beta$ -Methyl- styrene	SnCl <sub>4</sub>	CCl <sub>4</sub> /PhNO <sub>2</sub> (1:1)	0	1.0	0.32
	<i>trans</i> - $\beta$ -Methyl- styrene	SnCl <sub>4</sub>	CCl <sub>4</sub> /PhNO <sub>2</sub> (1:1)	0	0.74	0.32
Ethyl vinyl ether	<i>i</i> -Butyl vinyl ether	BF <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-78	1.30	0.92
2-Chloroethyl vinyl ether	$\alpha$ -Methylstyrene	BF <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-23	6.02	0.42

## 7.2.5 Isomerization



More **stable tert-carbocation**

**1,3-addition polymer**

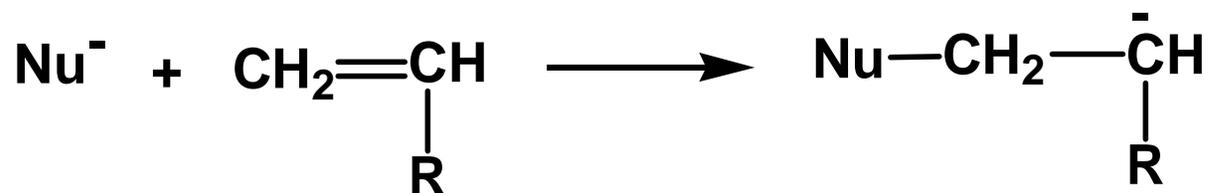


**Ozone-resistant elastomer** upon **copolymerization** with **isobutylene**

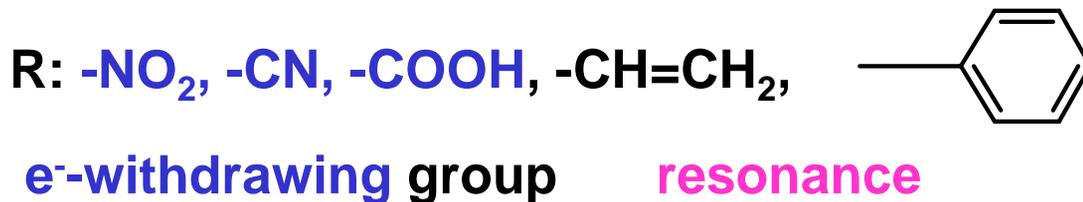
## 7.3 Anionic Polymerization

### 7.3.1 Anionic Initiators

Initiation: nucleophilic addition to monomer



where



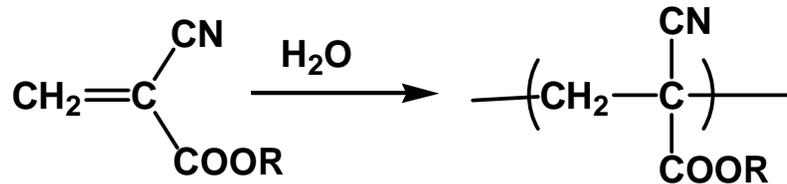
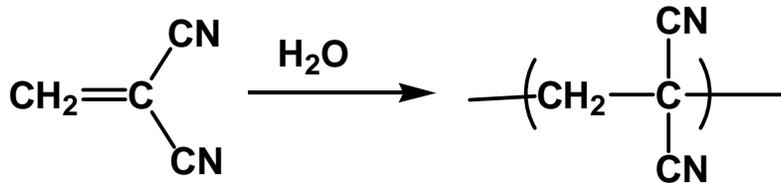
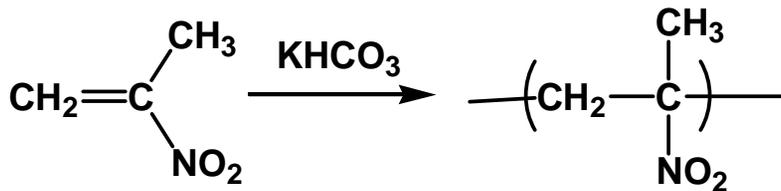
## o Initiators

### Weak base initiator

For **monomer** with **strong e<sup>-</sup> withdrawing group**

### Strong base initiator

For **monomer** with **phenyl** or **weak e<sup>-</sup> withdrawing group**



**Super glue**

**Cyanoacrylate adhesive**

## 1. Initiators that react by **addition** of a **negative ion**



**Organometallic compounds** of the **alkali metals** : e.g. **butyllithium**

**Organolithium** compounds: **low melting** and **soluble** in inert organic solvents

## 2. Initiation by **electron transfer**

### 1) Free **alkali metals**

In liquid ammonia, ether solvents

2) **Complexes** of **alkali metals** and **unsaturated** or **aromatic compounds**

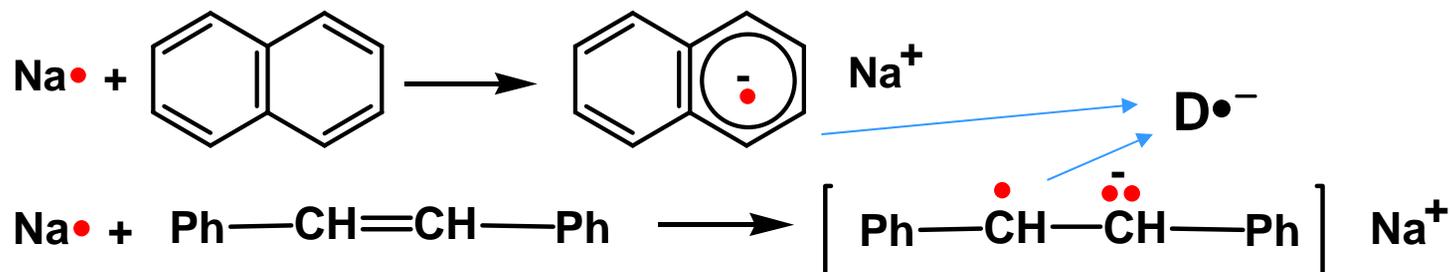
## Electron transfer



Metal  
Electron  
donor

Monomer

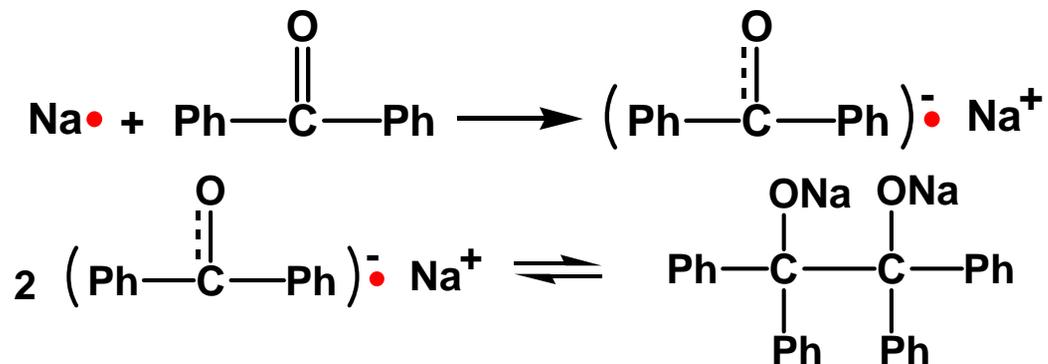
Addition complexes of **alkali metals** and **naphthalene** or **stilbene**



Reaction with **monomer**



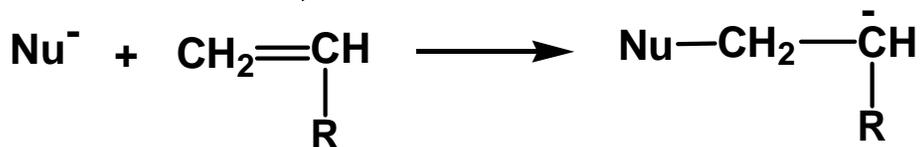
Addition complexes (called **ketyls**) of **alkali metals** and nonenolizable ketones, such as **benzophenone**



## 7.3.2 Mechanism, Kinetics, and Reactivity

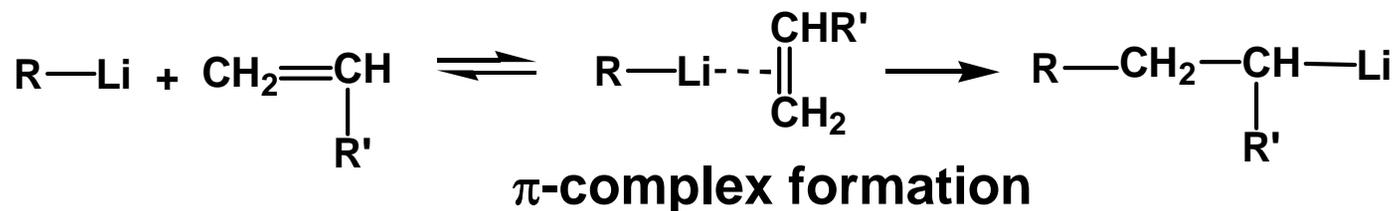
{ **Li compounds**  $\rightarrow$  **Covalent** carbon-metal bonds  
**Higher alkali metals**  $\rightarrow$  **More ionic** bonds

In **polar solvents**, **free solvated ions**  $\rightarrow$  **addition** of **anion** to **monomer**

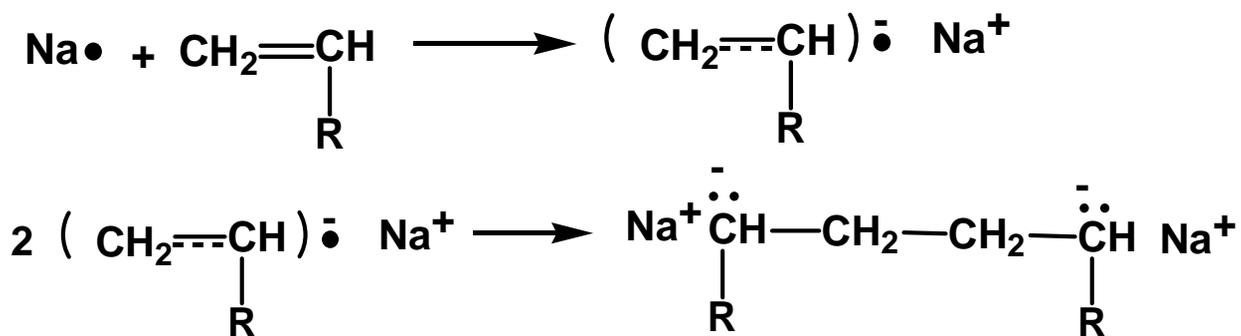


In **nonpolar solvents**, close **association** between ions

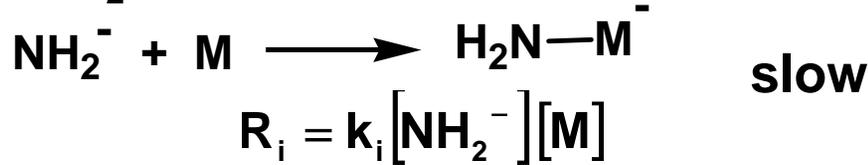
**$\pi$ -complex** formation



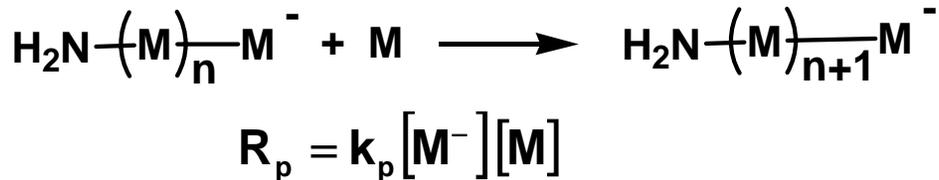
Initiation by **e<sup>-</sup> transfer**



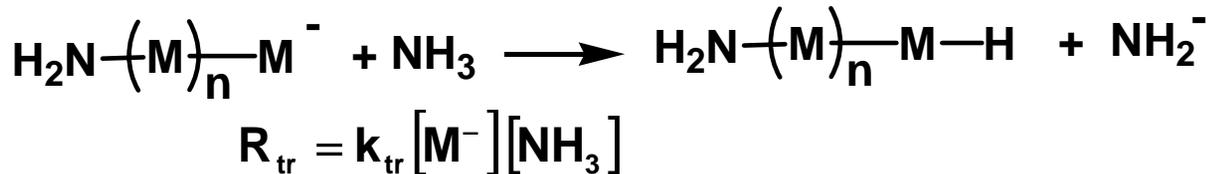
# Potassium amide-initiated polymerization in liquid ammonia



## Propagation



## Chain termination: transfer to solvent



## Steady-state assumption

$$R_i = R_{tr}$$

$$k_i [\text{NH}_2^-] [\text{M}] = k_{tr} [\text{M}^-] [\text{NH}_3]$$

$$R_p = \frac{k_p k_i [\text{NH}_2^-] [\text{M}]^2}{k_{tr} [\text{NH}_3]}$$

$$\Rightarrow [\text{M}^-] = \frac{k_i [\text{NH}_2^-] [\text{M}]}{k_{tr} [\text{NH}_3]}$$

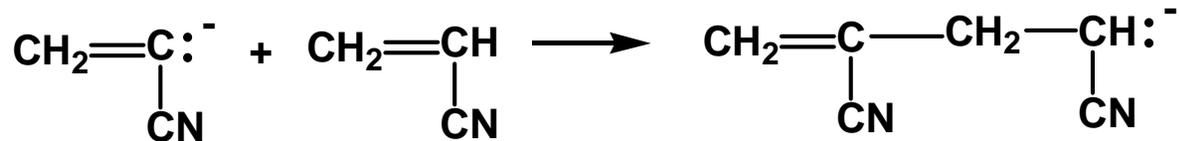
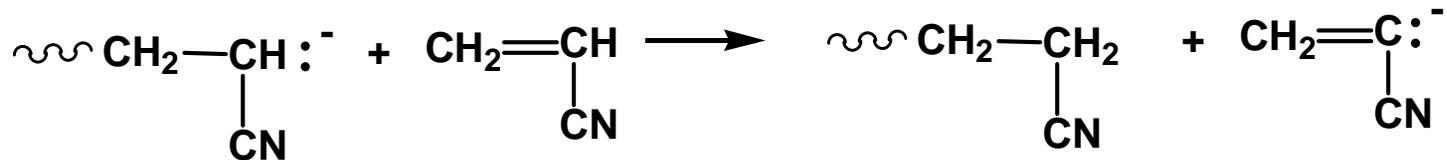
$$\bar{v} = \frac{R_p}{R_{tr}} = \frac{k_p [\text{M}^-] [\text{M}]}{k_{tr} [\text{M}^-] [\text{NH}_3]} = \frac{k_p [\text{M}]}{k_{tr} [\text{NH}_3]}$$

$$\bar{v} = \overline{\text{DP}}$$

## o Chain transfer to monomer

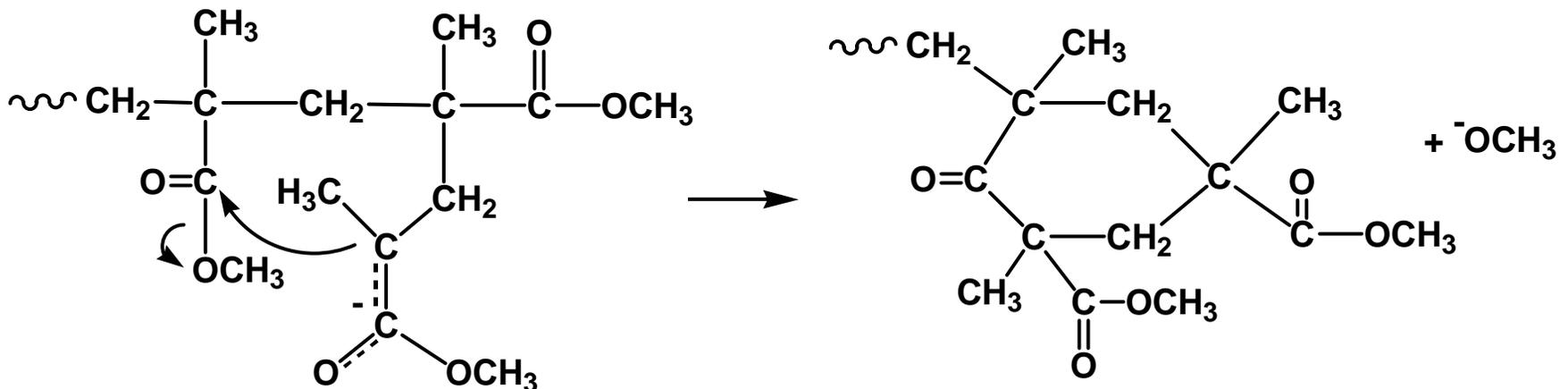
➡ Initiation by the resultant vinyl anion

➡ Unsaturated end groups



## o Termination mechanism in MMA polymerization

**Backbiting nucleophilic displacement** of methoxide by the **enolate anion chain end** to form a cyclohexanone ring.



## o Living anionic polymerization

e.g., M = styrene, I = naphthalenesodium, T = -78°C

$$R_i \gg R_p \quad -\frac{d[M]}{dt} = k_p [I]_0 [M]$$

where  $[I]_0$  = initial concentration of initiator

$$\frac{d[M]}{[M]} = -k_p [I]_0 dt \quad \ln \frac{[M]}{[M]_0} = -k_p [I]_0 dt \quad [M] = [M]_0 e^{-k_p [I]_0 dt}$$

**No termination or chain transfer reactions**

$$\bar{v} = \frac{[M]_0 - [M]}{[I]_0} \quad \bar{v} = \frac{[M]_0}{[I]_0} \quad \text{M completely consumed}$$

For **simple anionic initiator** (e.g., BuLi)

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

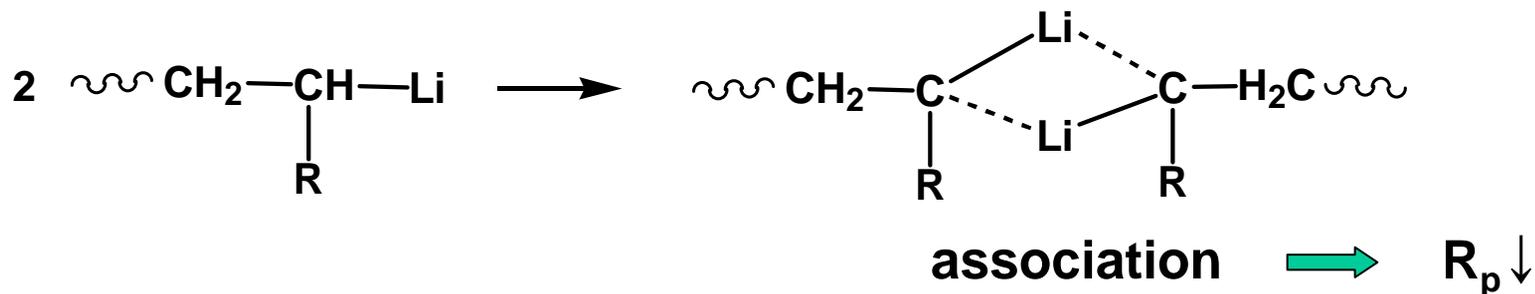
For **electron-transfer initiators**

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

**Narrow molecular weight distribution**

## Table 7.4 $k_p$ for polystyrene

In **poorly solvating** hydrocarbon solvents



**Larger alkali metal cations**  $\longrightarrow$  **Weaker coordination** than  $\text{Li}^+$   
 $\longrightarrow R_p \uparrow$

In a **more polar solvating medium** (e.g., ether)

$\text{Li}^+$  the **most strongly solvated** of the alkali metal cations

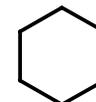
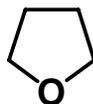
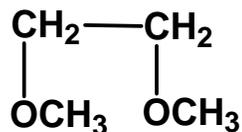
Li-based initiators the **fastest**  $R_p$

Table 7.4  $k_p$  for polystyrene

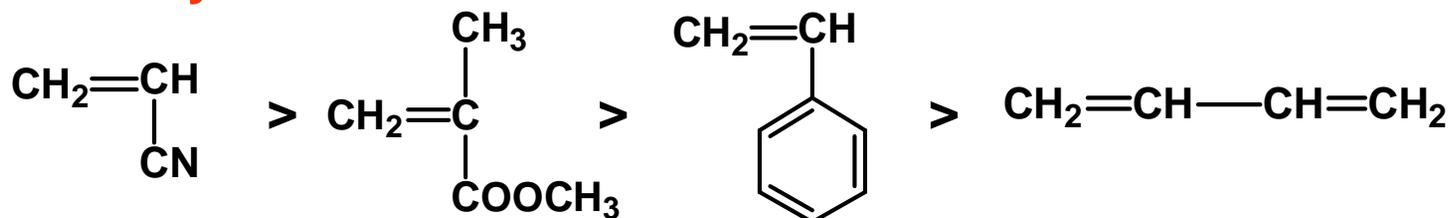
Counterion	Solvent	$k_p$ (L/mol s)
Na <sup>+</sup>	Tetrahydrofuran	80
Na <sup>+</sup>	1,2-Dimethoxyethane	3600
Li <sup>+</sup>	Tetrahydrofuran	160
Li <sup>+</sup>	Benzene	$10^{-3}$ - $10^{-1}$
Li <sup>+</sup>	Cyclohexane	$(5-100) \times 10^{-5}$

## Solvating power

1,2-dimethoxyethane > tetrahydrofuran > benzene > cyclohexane



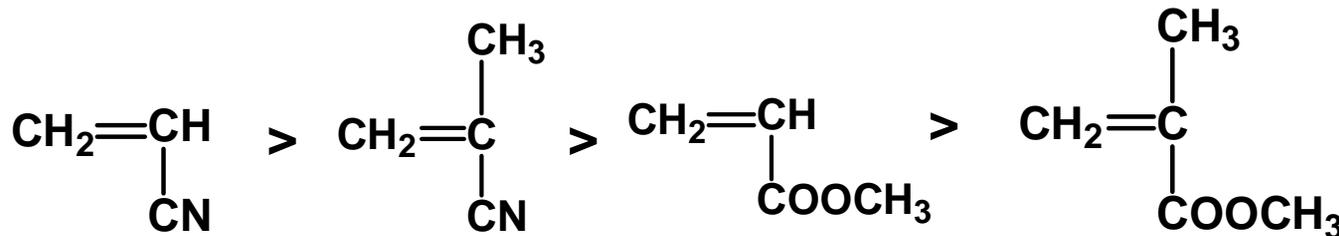
## Reactivity of monomer



e<sup>-</sup>-withdrawing

resonance

Methyl substitution on the α-carbon →  $R_p \downarrow$



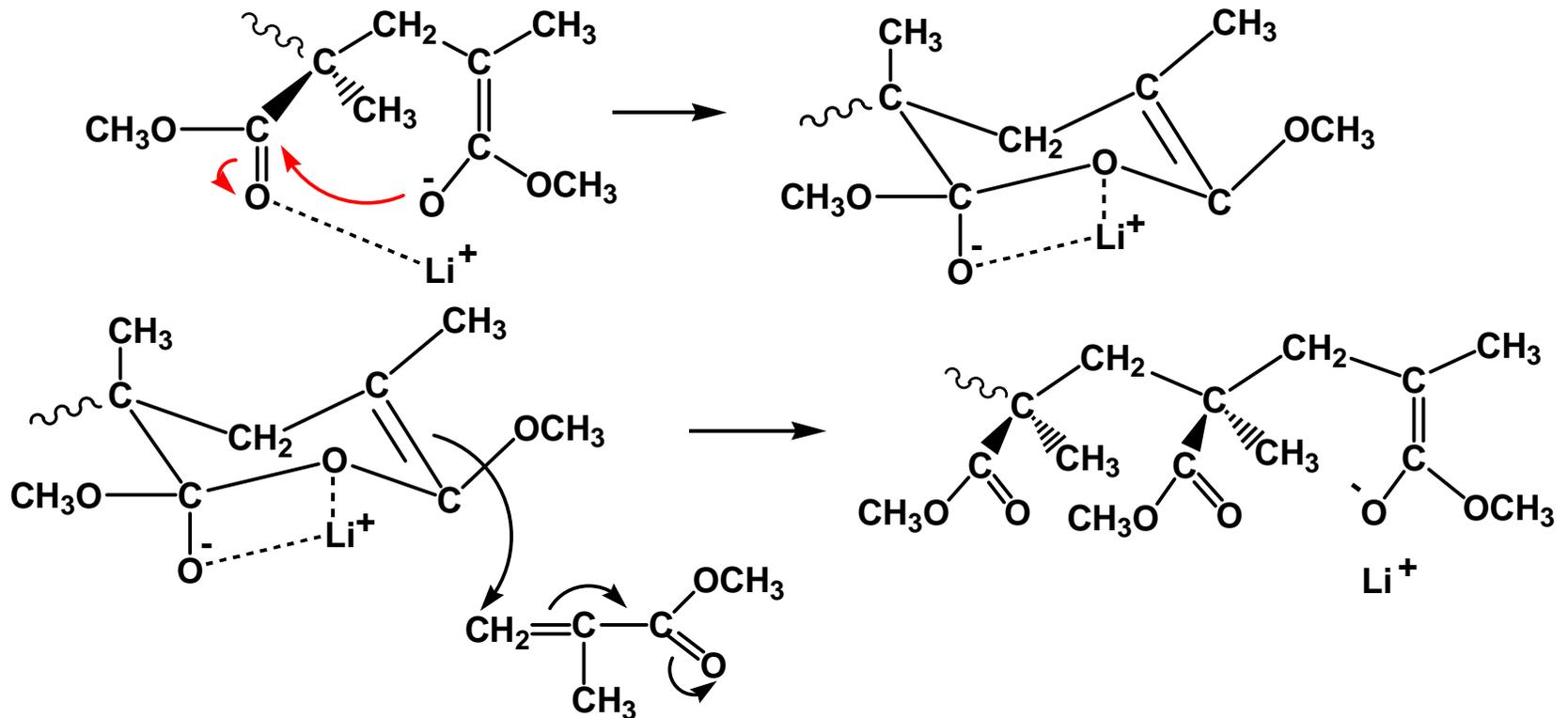
∴ **induction destabilization** of the carbanion and **steric interference** with both chain-end solvation and approach of monomer

### 7.3.3 Stereochemistry of Anionic Polymerization

**Polar solvents:** favor **syndiotactic** placement

**Nonpolar solvents:** favor **isotactic** placement

#### o Six-membered cyclic chain end

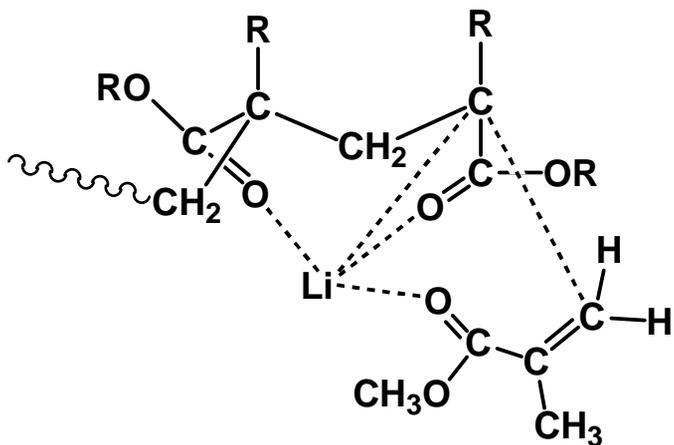


**Isotactic** placement ↓ as { Solvent **polarity** ↑  
Lithium → **Less strongly coordinating**  
**higher alkali metal ions**

o Ion pairing

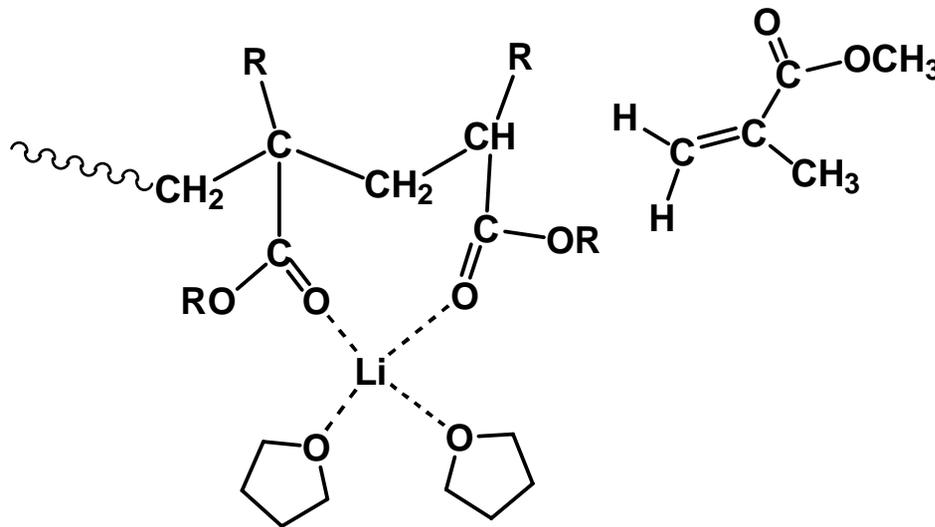
Counterion-monomer  
coordination  $\Rightarrow$  isotactic

In nonpolar solvents



Counterion-solvent  
coordination  $\Rightarrow$  syndiotactic

In polar solvents



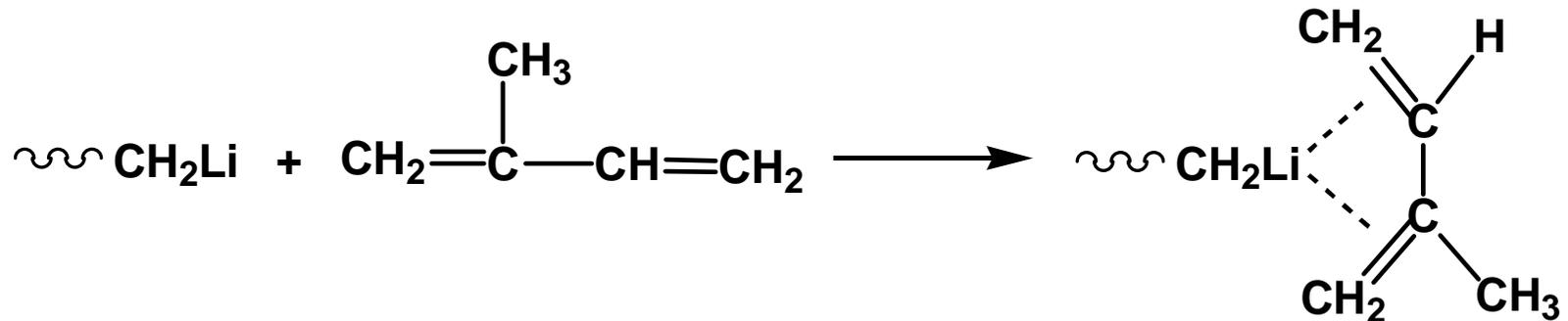
o **Diene** Polymerization: isoprene, 1,3-butadiene

**cis-1,4 polymerization** ↑ By **Li-based** initiators  
In **nonpolar** solvents

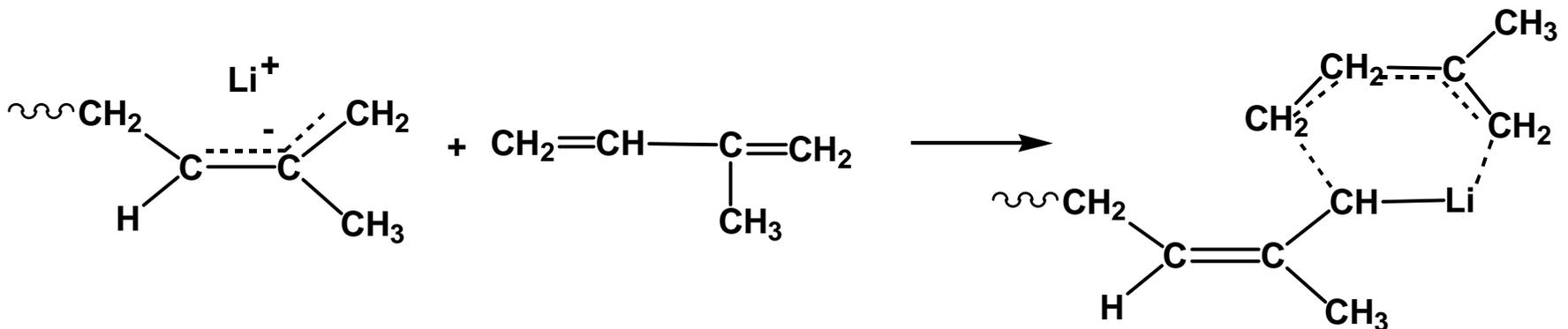
e.g., Almost entirely **cis-1,4 isoprene** = “**synthetic natural rubber**”

**BuLi** initiator in **pentane or hexane**

1) **s-cis conformation** by  **$\pi$ -complexation**



2) Cis configuration by forming a **six-membered ring** transition state

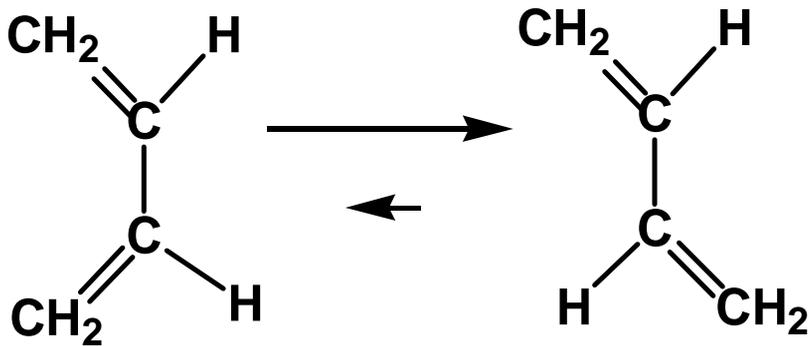


# Cis-1,4-poly(1,3-butadiene) configuration

Somewhat lower stereospecificity

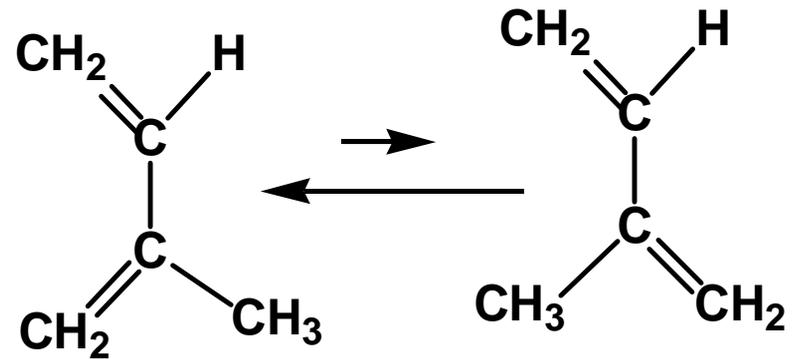
∴ **BD**

Favors **s-trans** conformation



**isoprene**

Favors **s-cis** conformation



## 7.3.4 Anionic copolymerization

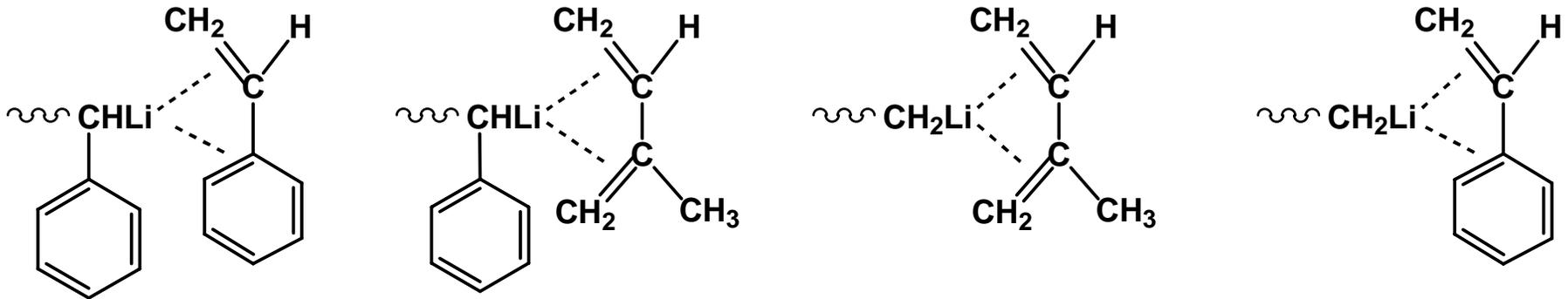
Table 7.5 Anionic Reactivity Ratios

### ● Solvent effect

	$r_1$	$r_2$
$M_1 = \text{St}$ $M_2 = \text{BD}$ $I = n\text{-BuLi}$ $S = \text{hexane}$ $T = 25^\circ\text{C}$	0.03	12.5
$M_1 = \text{St}$ $M_2 = \text{BD}$ $I = n\text{-BuLi}$ $S = \text{THF}$ $T = 25^\circ\text{C}$	4.0	0.3

In homopolymerization, **St** is **more reactive** than **BD**

**Polystyryl anion** exhibits **preference** towards **BD** in **hexane**



The role of **counterion** is effectively **nullified** in **THF**

# Table 7.5 Anionic Reactivity Ratios

Monomer 1	Monomer 2	Initiator	Solvent	Temperature (°C)	r <sub>1</sub>	r <sub>2</sub>	
Styrene	MMA	Na	NH <sub>3</sub>		0.12	6.4	
		n-BuLi	None				
	Butadiene	n-BuLi	None	None	25	0.04	11.2
			Hexane	Hexane	25	0.03	12.5
			Hexane	Hexane	50	0.04	11.8
			THF	THF	25	4.0	0.3
			THF	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 <sub>3</sub>		0.01	0.01		
Butadiene	Isoprene	n-BuLi	Hexane	50	3.38	0.47	
MMA	Acrylonitrile	NaNH <sub>2</sub>	NH <sub>3</sub>		0.25	7.9	
		RLi	None		0.34	6.7	
	Vinyl acetate	NaNH <sub>2</sub>	NH <sub>3</sub>		3.2	0.4	

● T effect

			$r_1$	$r_2$
$M_1 = \text{St}$	$M_2 = \text{BD}$	$I = n\text{-BuLi}$		
$S = \text{hexane}$	$T = 25^\circ\text{C}$		0.03	12.5
	$T = 50^\circ\text{C}$		0.04	11.8
	$S = \text{THF}$	$T = 25^\circ\text{C}$	4.0	0.3
		$T = -78^\circ\text{C}$	11.0	0.4

Not to any appreciable extent in hexane

Solvation is felt more strongly at lower T in THF

● **Homogeneous** and **heterogeneous** processes

$M_1 = \text{St}$   $M_2 = \text{MMA}$   $I = \text{Na}$        $S = \text{NH}_3$        $r_1 = 0.12$        $r_2 = 6.4$

$M_1 = \text{St}$   $M_2 = \text{MMA}$   $I = \text{n-BuLi}$   $S = \text{none}$        $r_1 = 0$        $r_2 = \infty$

No detectable styrene in polymer

**Homogeneous**

Soluble n-BuLi  $\Rightarrow$  only **PMMA** is formed

$\therefore$  **MMA** is **more reactive** than St

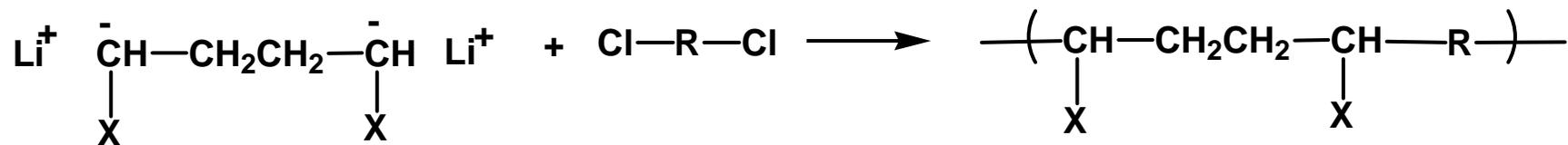
**Heterogeneous**

**Insoluble** metallic lithium or MeLi  $\Rightarrow$  **Block copolymer**

$\therefore$  Initial **St polymerization** on the **initiator surface**  $\Rightarrow$

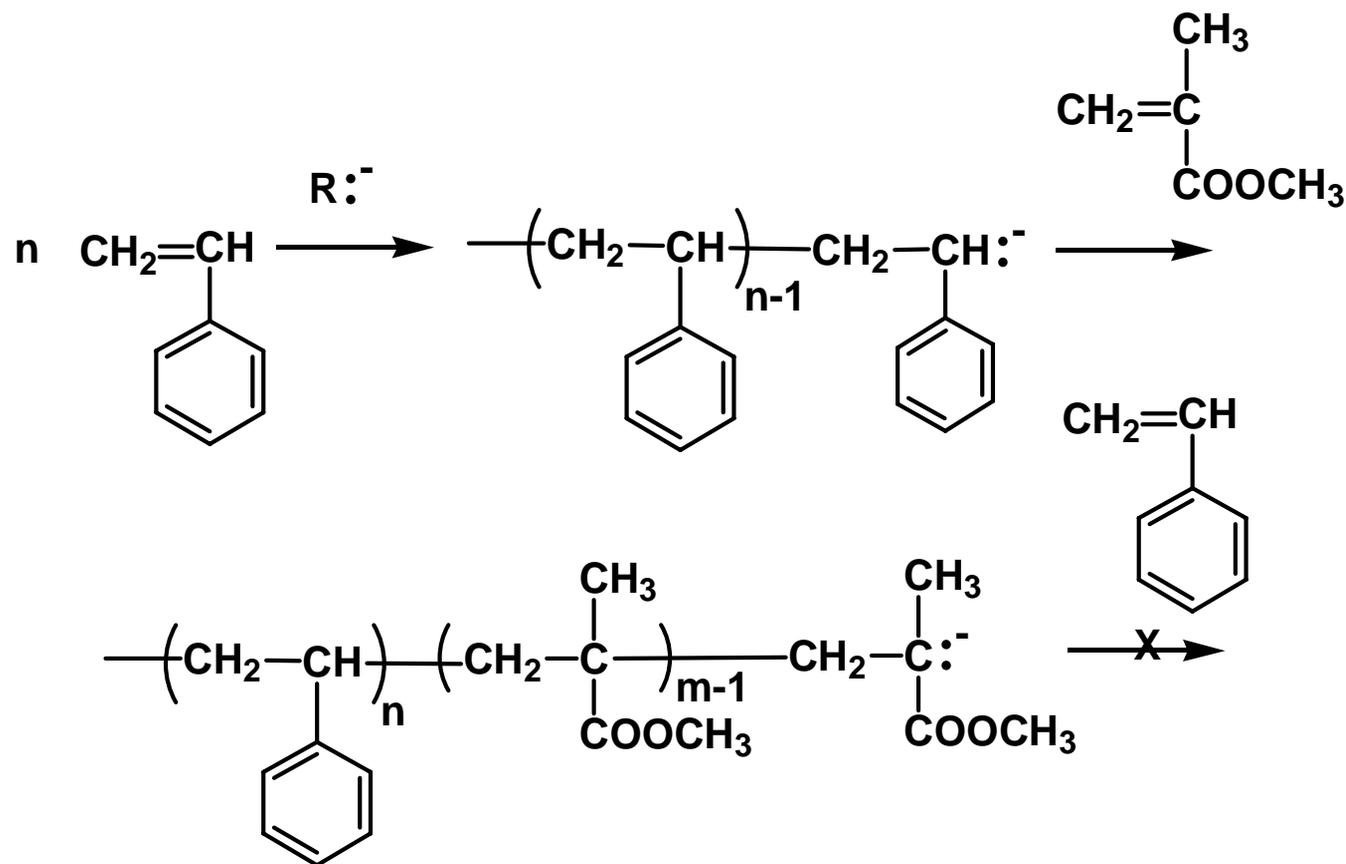
Detachment  $\Rightarrow$  Initiation of **MMA** by detached polystyryl anion

● **Nucleophilic displacement** of **aliphatic dihalides** by the **dianion**  
Formed by **electron transfer initiation**



● **Block copolymers** by **living polymerization** method

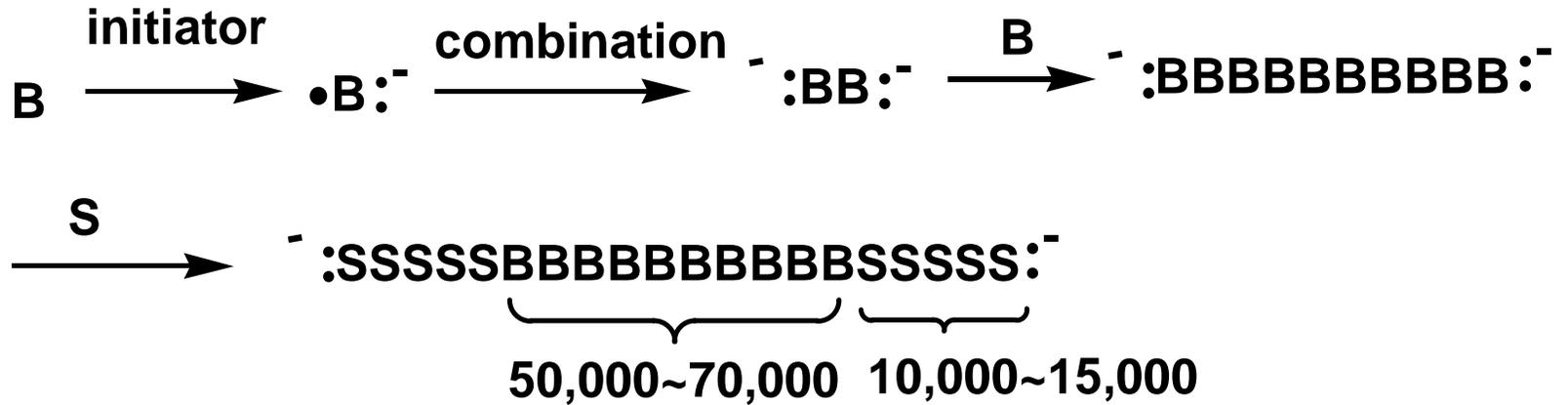
**Polystyrene-block-poly(methyl methacrylate)**



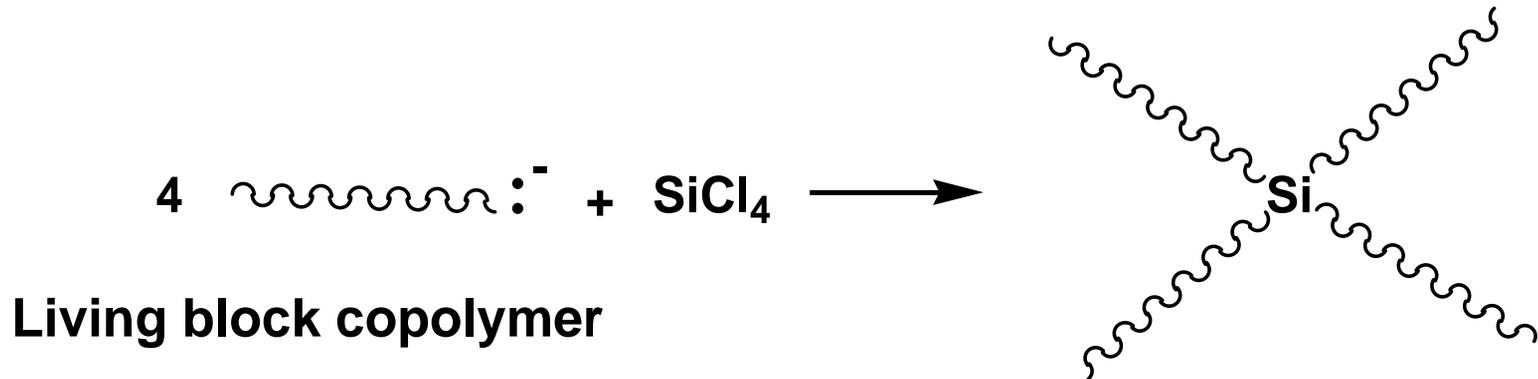
If **MMA** was polymerized first, the **copolymer** would **not form**.

$\therefore$  Living **PMMA** is **not basic enough** to add to **styrene**

● **St-BD-St (SBS) triblock polymer**



● **Star-block (radial) copolymer**

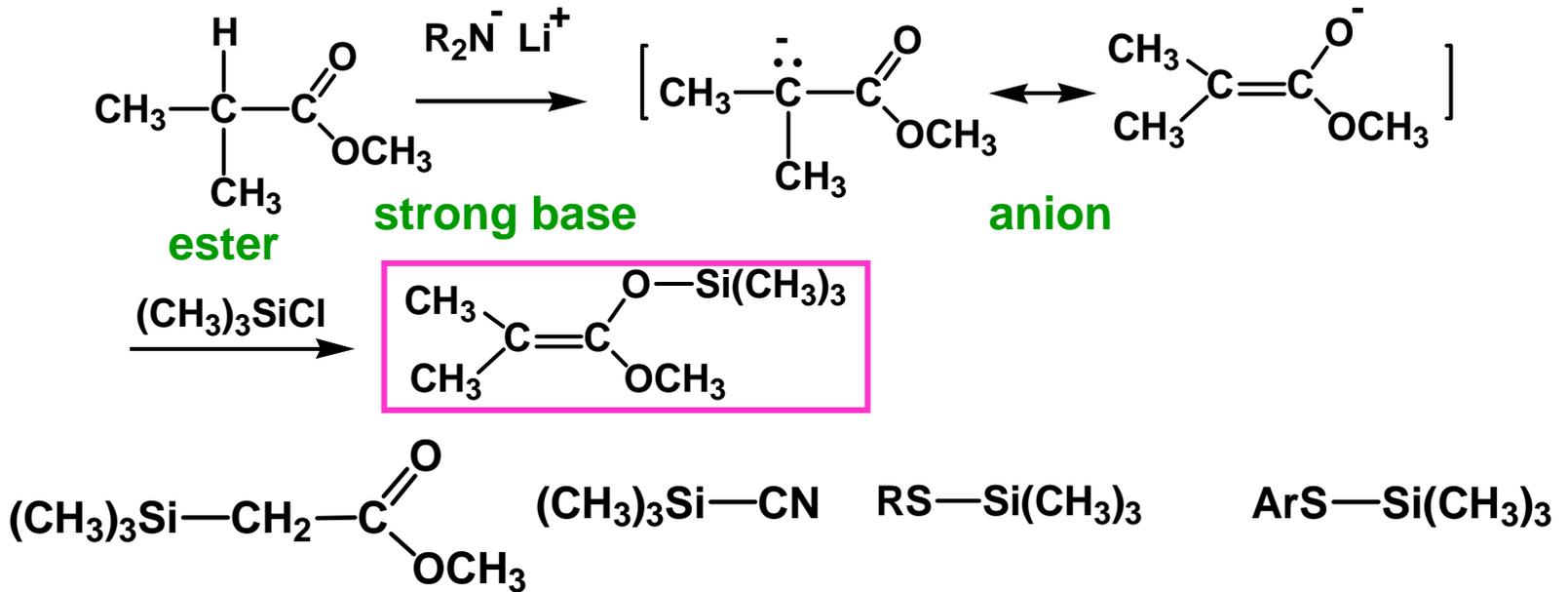


Major **advantage**: **much lower viscosities** than their linear counterparts

# 7.4 Group Transfer Polymerization (GTP)

→ Living polymers at room temp or above

● **Initiators** : **-SiMe<sub>3</sub>** compound      Transfer to **carbonyl oxygen**



● **Catalysts** : **Anion** or **Lewis acid**



Donate electron to **silyl** group



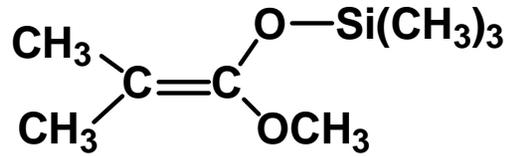
withdraw electron from **monomer**

# TABLE 7.6 Compounds used in Group Transfer Polymerization

monomers	initiators	catalysts	solvent
$\text{CH}_2=\text{CHCO}_2\text{R}$	$\text{Me}_2\text{C}=\text{C} \begin{array}{l} \diagup \text{OMe} \\ \diagdown \text{OSiMe}_3 \end{array}$	<b>Anionic</b> $\text{HF}_2^-$ $\text{CN}^-$ $\text{N}_3^-$ $\text{Me}_3\text{SiF}_2$	Acetonitrile 1,2-Dichloroethane Dichloromethane N,N-Dimethylacetamide N,N-Dimethylacetamide
$\begin{array}{c} \text{Me} \\   \\ \text{CH}_2=\text{C} \\   \\ \text{CO}_2\text{R} \end{array}$	$\text{Me}_3\text{SiCH}_2\text{CO}_2\text{Me}$	<b>Lewis acid</b> $\text{ZnX}_2$	Ethyl acetate Propylene carbonate
$\text{CH}_2=\text{CHCONR}_2$	$\text{Me}_3\text{SiCN}$	$\text{R}_2\text{AlCl}$ $(\text{R}_2\text{Al})_2\text{O}$	Tetrahydrofuran Toluene
$\text{CH}_2=\text{CHCN}$	$\text{RSiMe}_3$		
$\begin{array}{c} \text{Me} \\   \\ \text{CH}_2=\text{C} \\   \\ \text{CN} \end{array}$	$\text{ArSiMe}_3$		
$\begin{array}{c} \text{O} \\    \\ \text{CH}_2=\text{CHC} \\   \\ \text{R} \end{array}$			

● **GTP**

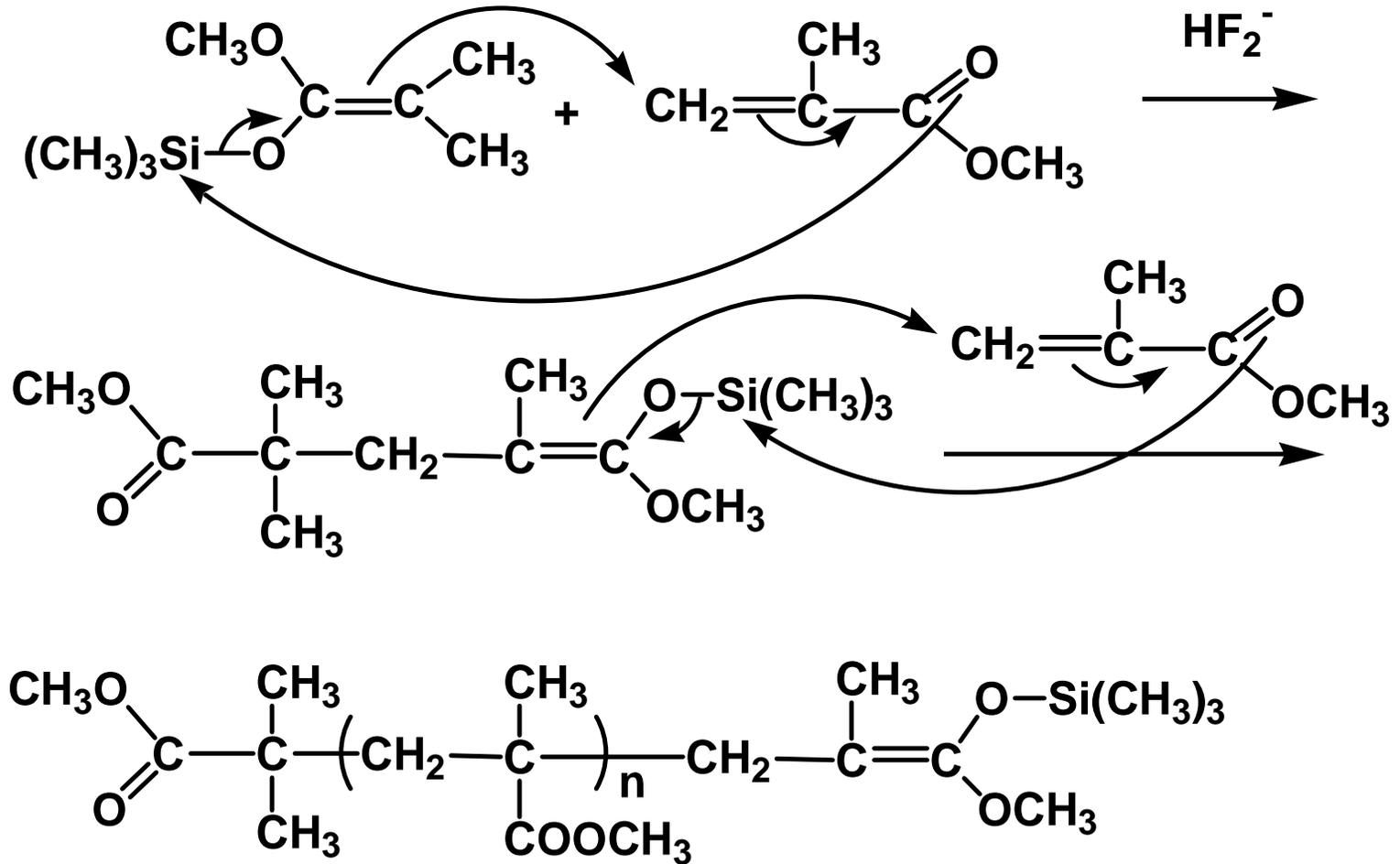
**MMA**



**initiator**

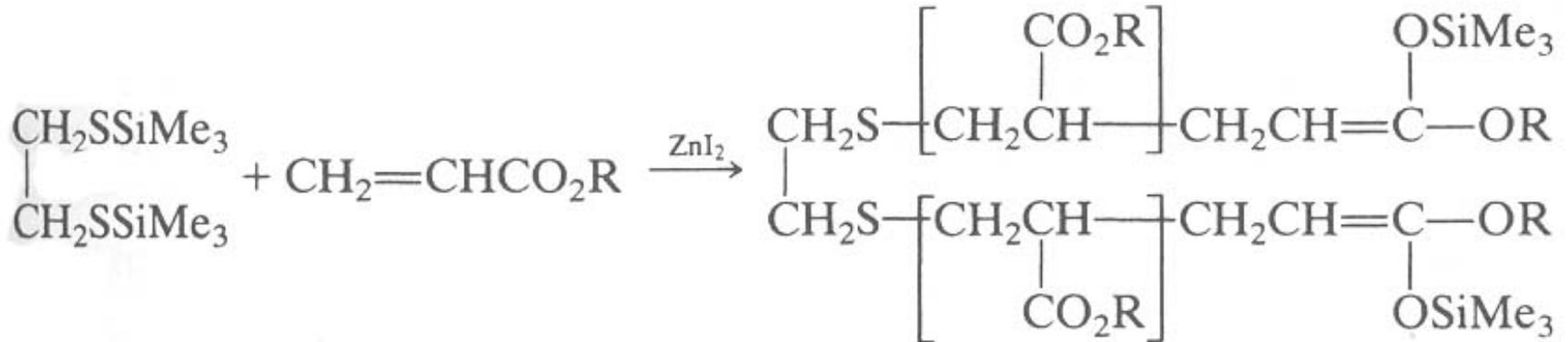


**catalyst**



- **Difunctional initiator**

Chain propagates from **each end**

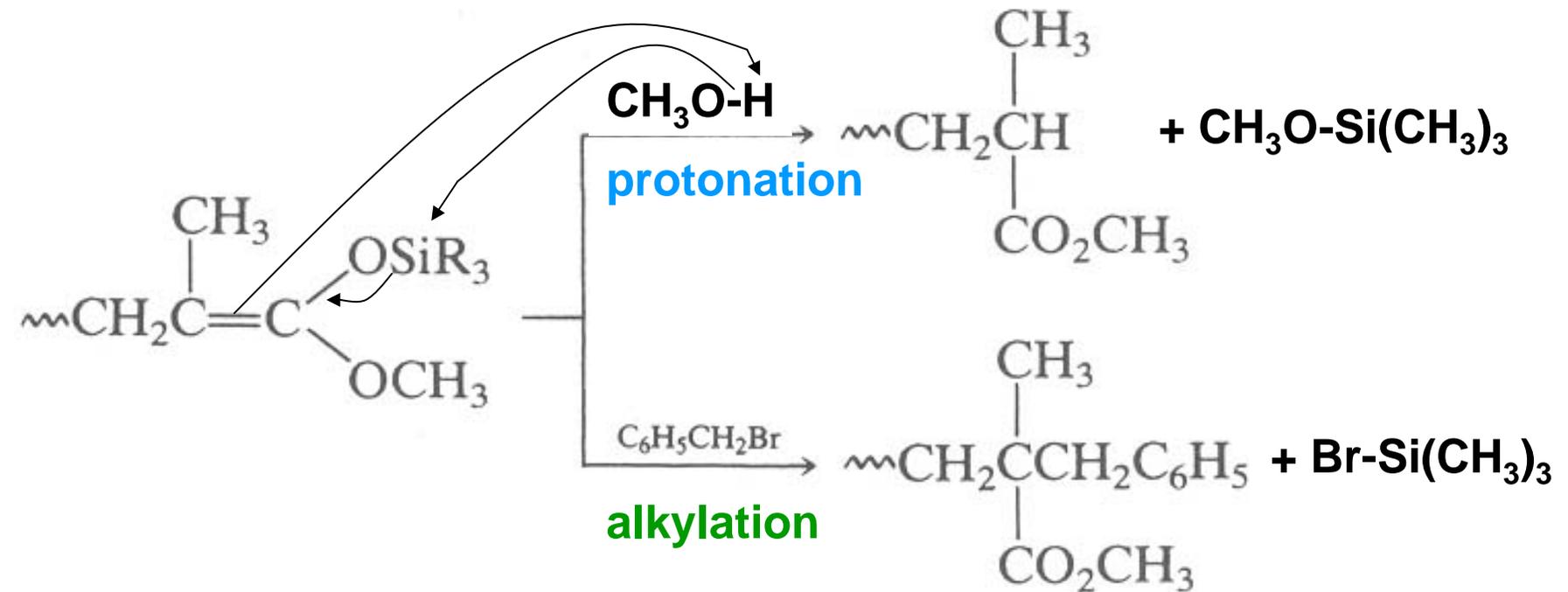


- **Block copolymer**

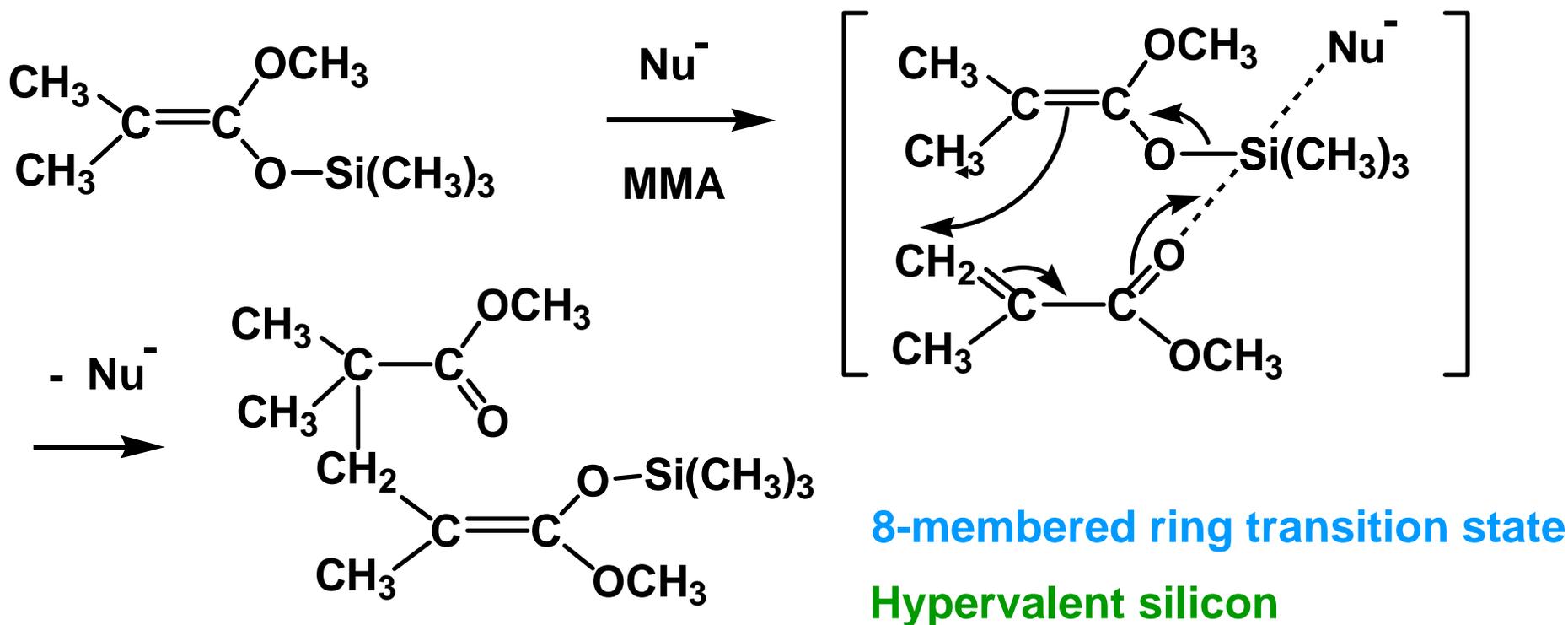
Once the monomer is consumed, a **different monomer** may be added.

## ● Termination

Removal of **catalyst**, **protonation**, **alkylation**



## ● Mechanism 1

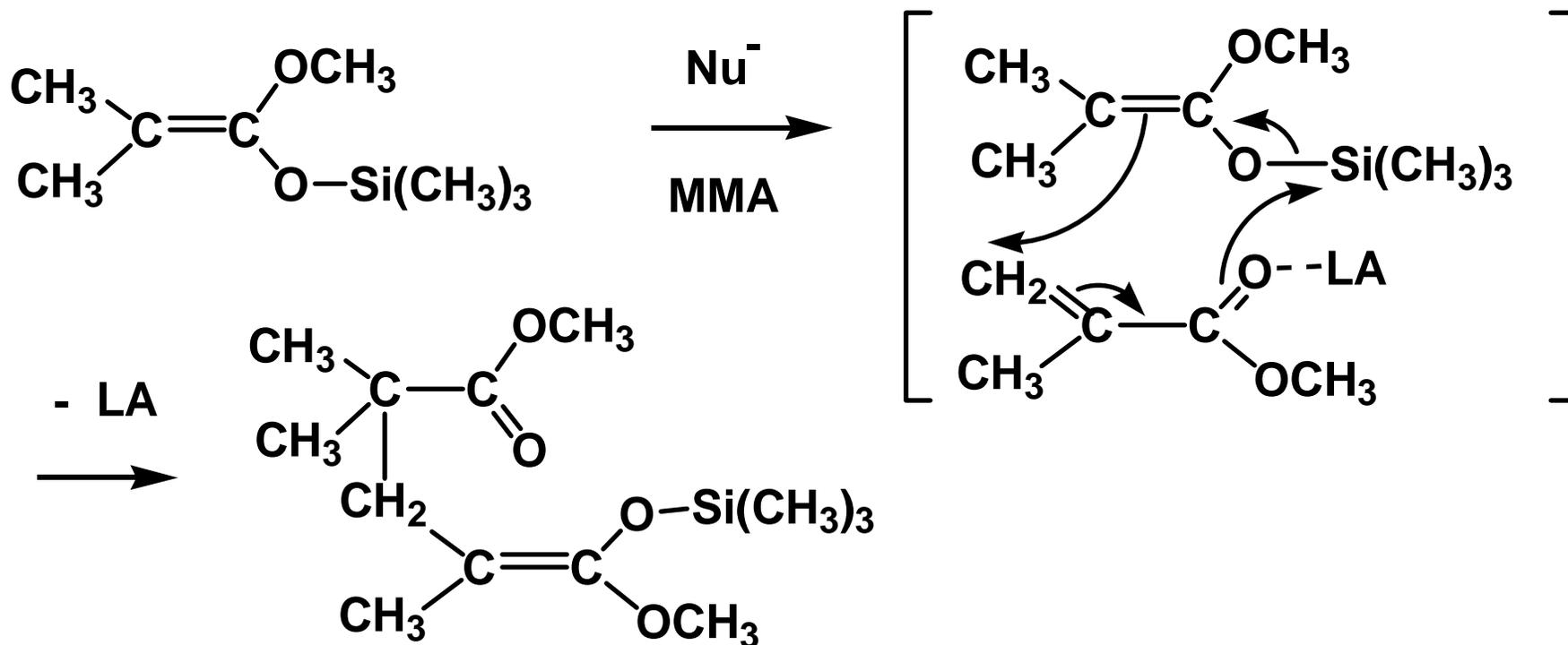


Propagating chain is **completely covalent**

Hypervalent silicon intermediate is formed by **activation with the nucleophilic catalyst** ( $\text{Nu}^-$ )

**Silyl group** is **transferred to carbonyl group** of the incoming monomer molecule via 8-membered ring transition state

## Where Lewis acid catalysts are used



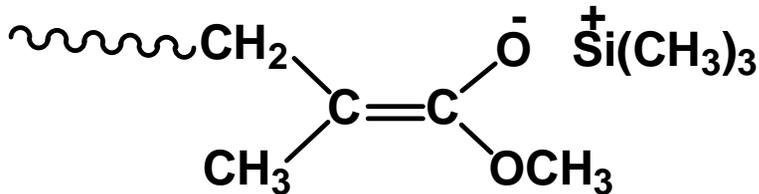
Catalyst **coordinates** the **carbonyl oxygen** of **monomer**

→ rendering the monomer **more susceptible to nucleophilic attack** by the initiator

## ● Mechanism 2

Propagating species: **enolate anions**

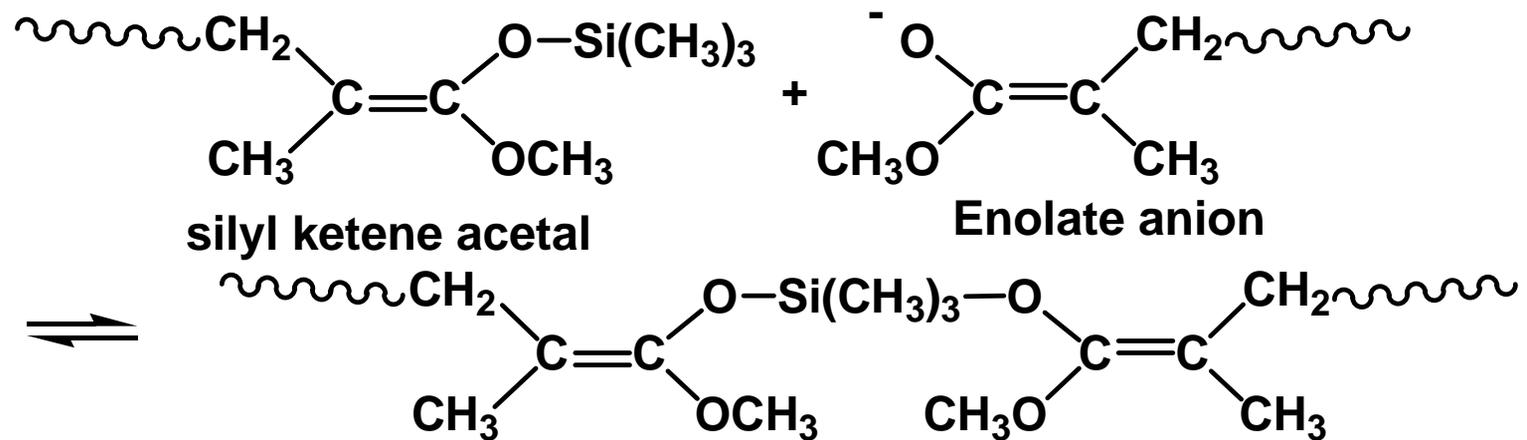
As in conventional **anionic polymerization** of acrylate monomers



**GTP** and conventional **anionic polymerizations** are remarkably **similar** in terms of polymer **tacticity** and **reactivity ratios** in copolymerization.

GTP of **MMA** exhibits the same **backbiting chain terminating** reaction.

Silyl group undergoes **intermolecular exchange**, which is **inconsistent** with the proposed GTP mechanism



Enolate anion and silyl ketene acetal chain ends are in rapid equilibrium with a hypervalent silicon complex

The silicon complex provides

Low eqm conc of enolate anions for propagation and mechanism for maintaining living chain ends

Cf.

o Termination mechanism in MMA polymerization

**Backbiting nucleophilic displacement** of methoxide by the **enolate anion chain end** to form a cyclohexanone ring.

