

# Chapter 6. Free Radical Polymerization

## 6.1. Introduction

Table 6. 1 Commercially Important Vinyl Polymers

## 6. 2 Free Radical Initiators

Four types

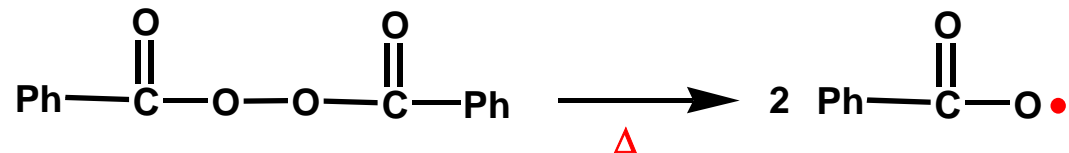
- Peroxides and hydroperoxides
- Azo compounds
- Redox initiators
- Photoinitiators

## 6.2.1. Peroxides and Hydroperoxides

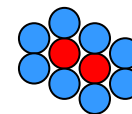
( ROOR )

( ROOH )

### Thermal homolysis



### Decomposition



### Radical combination



### Wastage reaction

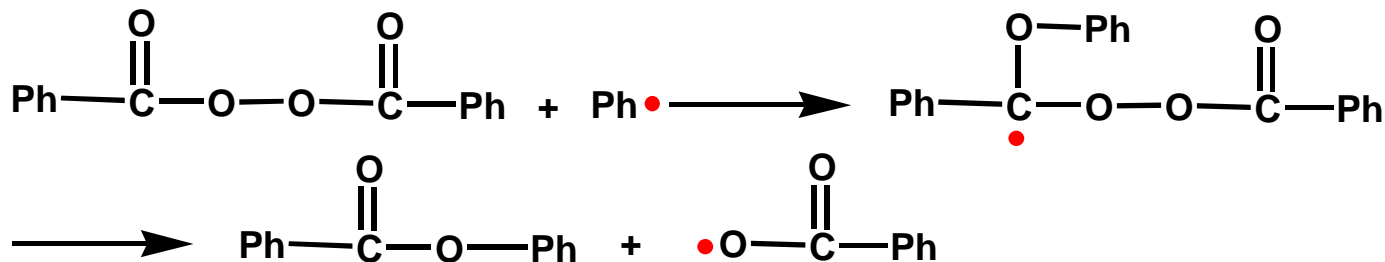


∴ Cage effect

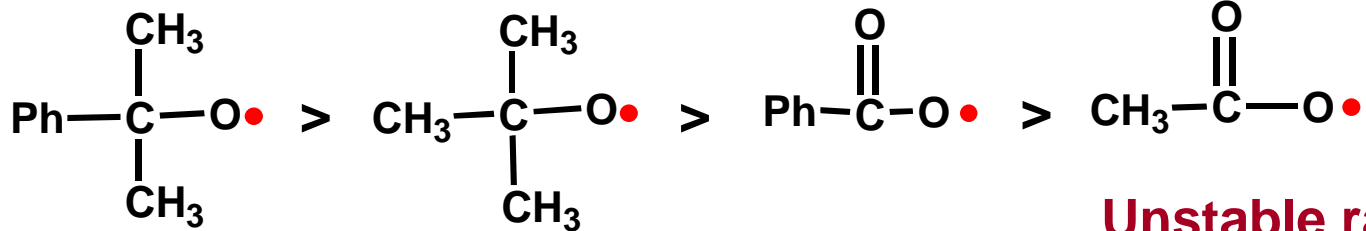
(confining effect of solvent molecules)

### Induced decomposition

### Wastage reaction



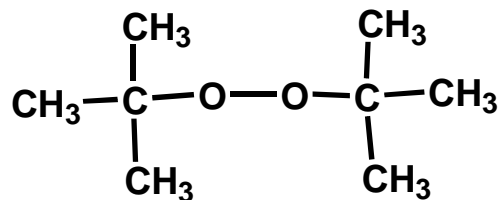
## Radical stability



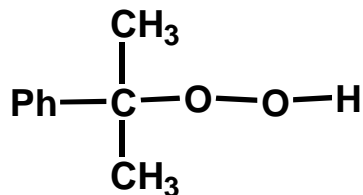
**Stable radical**  
**Less wastage reaction**

**Unstable radical**  
**More wastage reaction**

## Half-lives

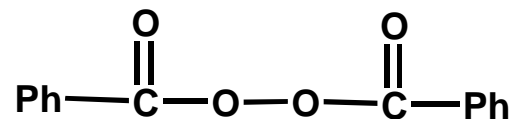


**1.38 h at 145°C**

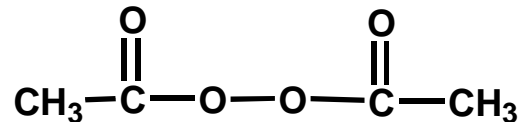


**1.7 h at 130°C**

## BPO (Benzoyl peroxide)

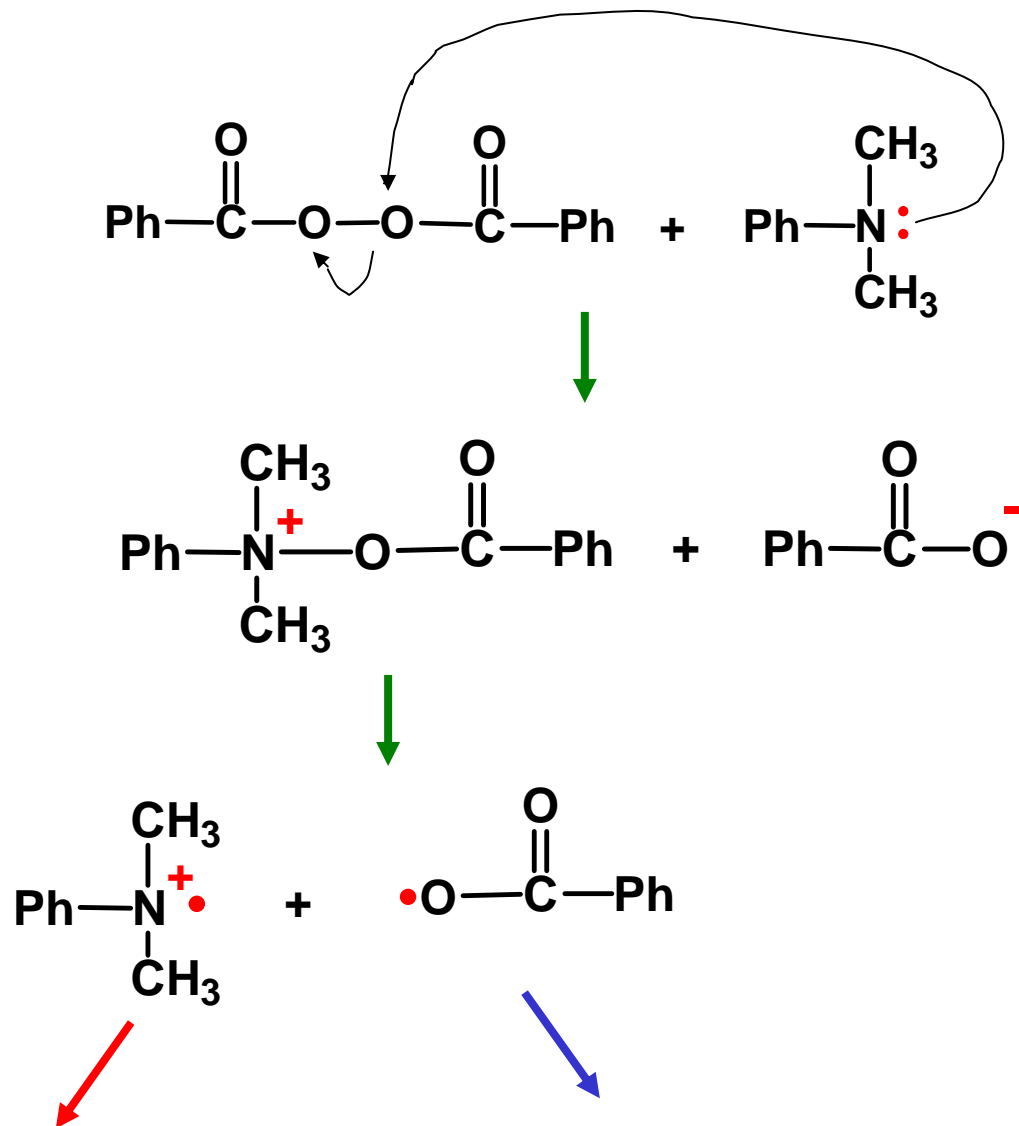


**1.4 h at 85°C**



**1.1 h at 85°C**

## Promoters



**No initiation of polymerization**

**∴ No N in polymers**

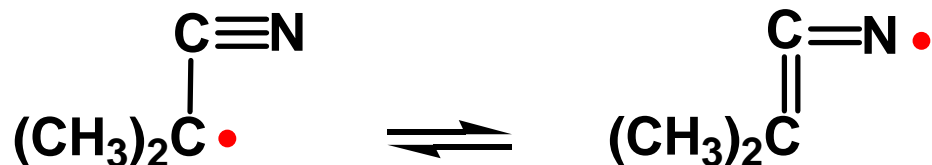
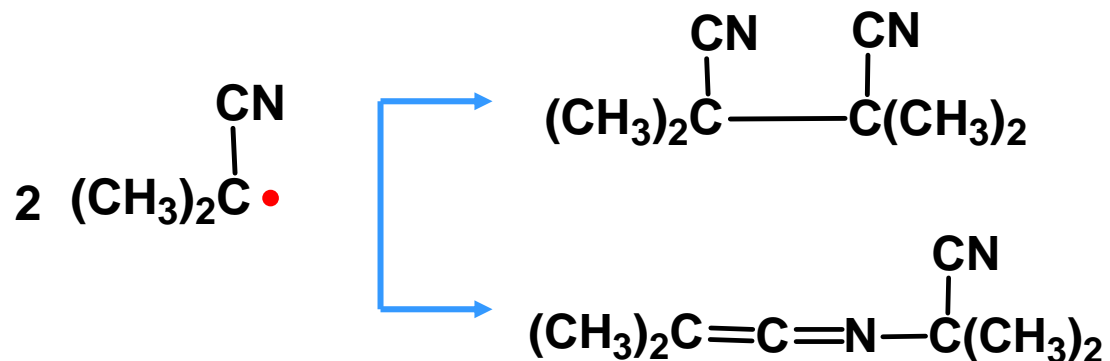
**Initiation of polymerization**

## 6.2.2. Azo Compounds



AIBN (Azobisiso(butyronitrile))

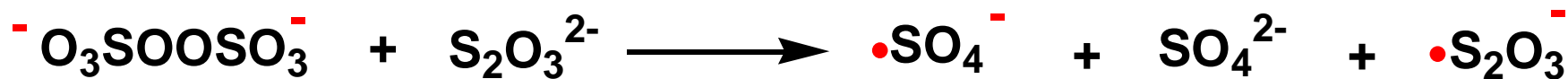
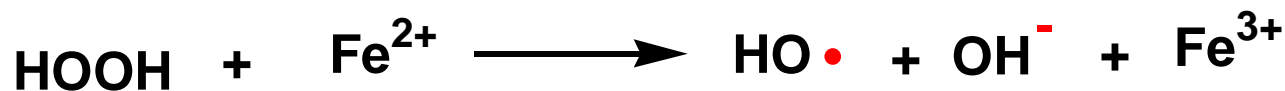
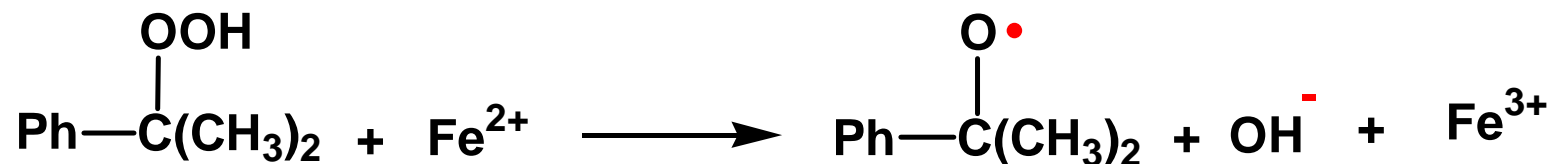
Radical combination



### 6.2.3. Redox Initiators

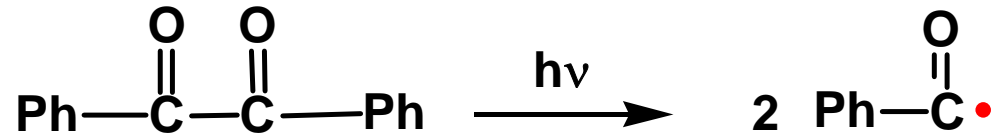
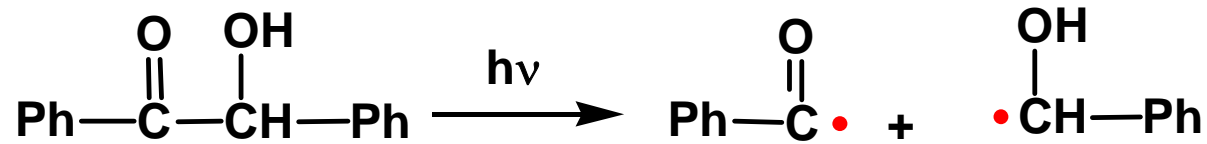
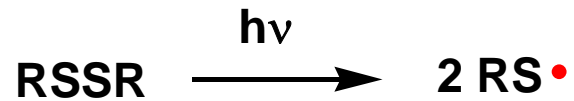
Production of free radicals by **one-electron transfer** reactions.

Useful in **low-temp polymerization** and **emulsion polymerization**



Radicals in aqueous phase

## 6.2.4. Photoinitiators

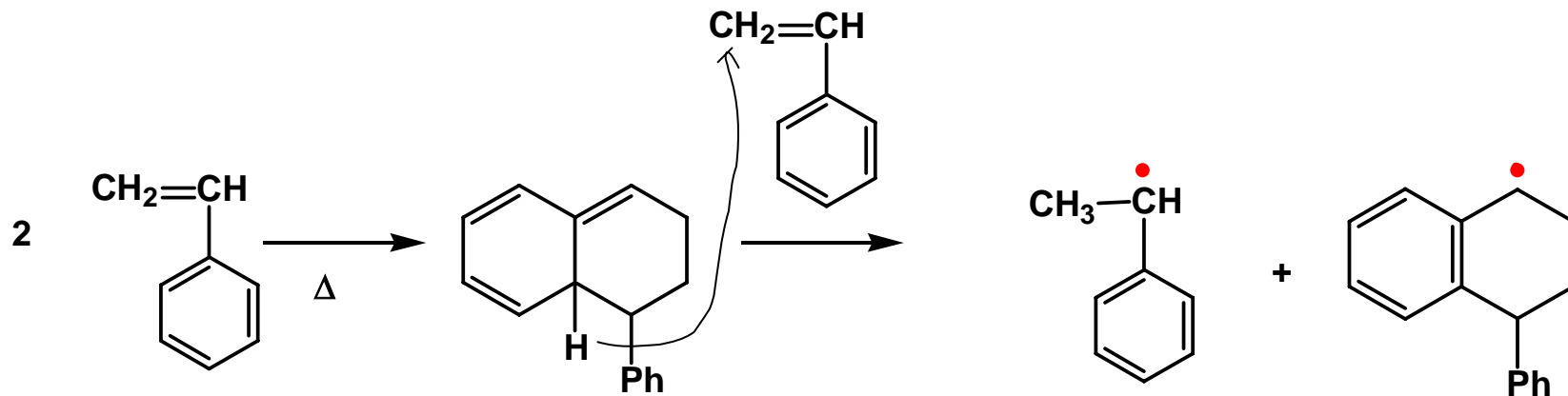


The **major advantages** of photoinitiation:

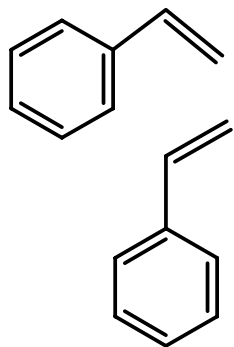
- The reaction is essentially **independent of temp**
- Polymerization may be conducted even at very **low temperatures**
- Better control** of the polymerization reaction

The reaction **can be stopped** simply by removing the **light source**

## 6.2.5. Thermal Polymerization



**Diels-Alder dimer**



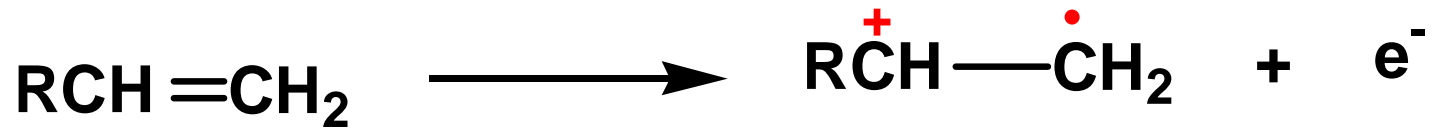
Transfer of **H atom** to monomer

**Molecule-induced homolysis**

**Rapid formation of radicals by reaction of nonradical species**



## 6.2.6. Electrochemical Polymerization



**Radical ions** : initiate **free radical** or **ionic polymerization** or both

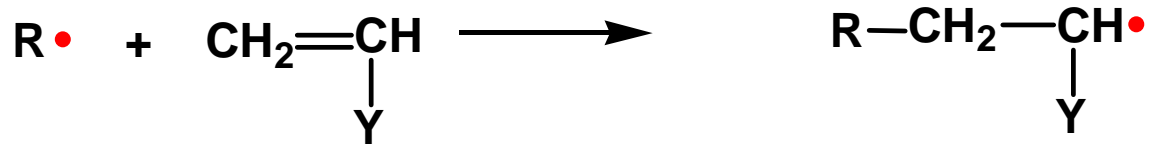
Particularly useful for **coating metal surfaces** with polymer films

## 6.3 Techniques of Free Radical Polymerization Techniques

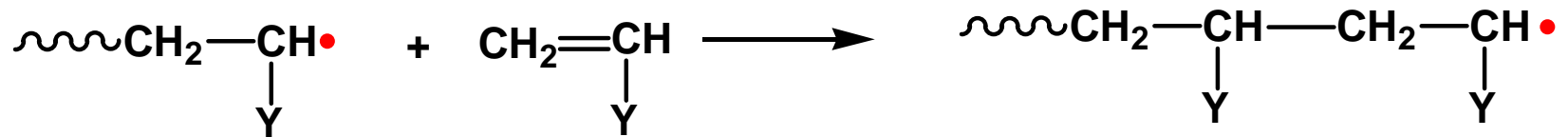
Method	Advantages	Disadvantages
<b>Bulk</b>	Simple No contaminants added	Rxn <b>exotherm difficult to control</b> <b>High viscosity</b>
<b>Suspension</b>	Heat readily dispersed Low viscosity Obtained in granular form	Washing and drying required <b>Agglomeration</b> may occur Contamination by stabilizer
<b>Solution</b>	Heat readily dispersed Low viscosity Used directly as solution	Added <b>cost of solvent</b> <b>Solvent difficult to remove</b> Possible <b>chain transfer</b> with solvent Possible environmental <b>pollution</b>
<b>Emulsion</b>	Heat readily dispersed Low viscosity <b>High MW</b> obtainable Used directly as emulsion. Works on tacky polymers	<b>Contamination</b> by emulsifier <b>Chain transfer agents</b> often needed Washing and drying necessary

## 6.4 Kinetics and Mechanism of Polymerization

Initiation { Formation of the **initiator radical**  
          { **Addition** of the initiator radical to monomer

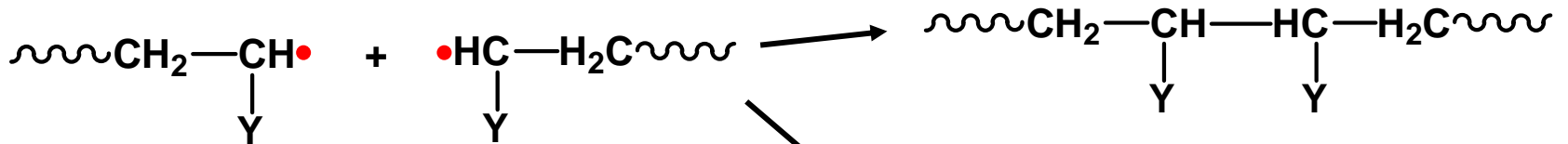


Propagation



Termination

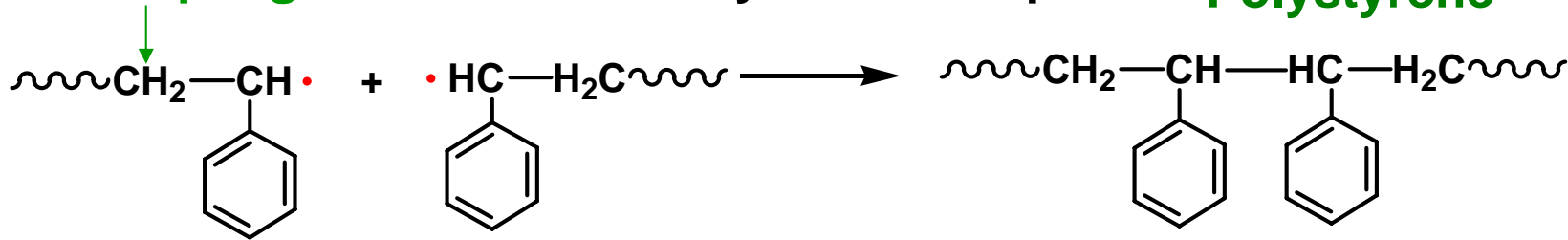
Coupling or combination



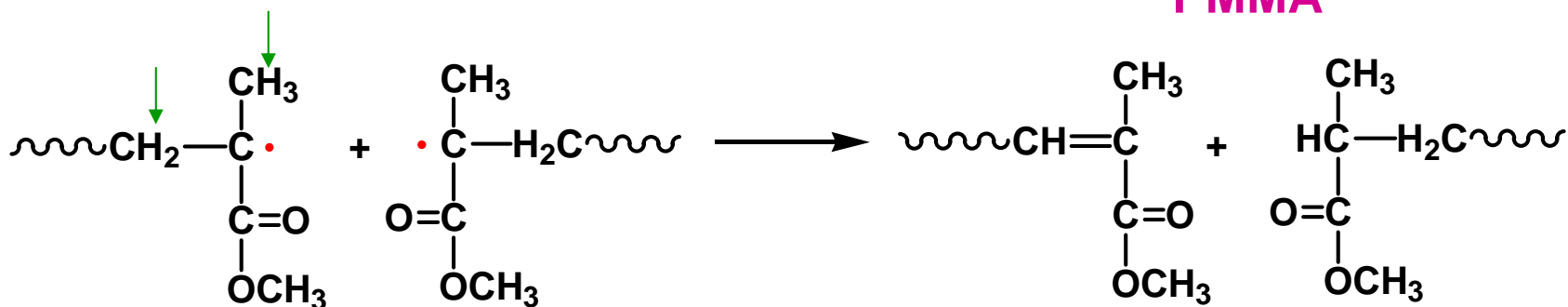
Disproportionation



**Coupling** almost exclusively at low temp

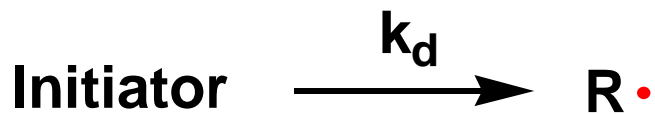


**Disproportionation**



∴ { **Steric repulsion**  
**Electrostatic repulsion**  
Availability of  $\alpha$  H for H transfer      PMMA 5; PSt 2

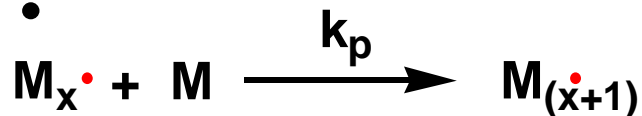
## Initiation



## Propagation



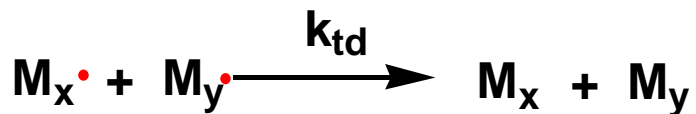
•  
•  
•



## Termination



Coupling



Disproportionation

## Initiation rate ( $R_i$ )

$$R_i = \frac{d[M\bullet]}{dt} = 2fk_d[I]$$

where

$$\begin{cases} [M\bullet] = \text{total conc of chain radicals} \\ [I] = \text{molar conc of initiator} \\ f = \text{initiator efficiency} = 0.3 \sim 0.8 \end{cases}$$

## Termination rate ( $R_t$ )

$$R_t = -\frac{d[M\bullet]}{dt} = 2k_t[M\bullet]^2$$

## Steady-state assumption

$$R_i = R_t$$

$$2fk_d[I] = 2k_t[M\bullet]^2 \quad [M\bullet] = \sqrt{\frac{fk_d[I]}{k_t}}$$

## Propagation rate ( $R_p$ )

$$R_p = -\frac{d[M]}{dt} = k_p[M\bullet][M] = k_p[M] \sqrt{\frac{fk_d[I]}{k_t}}$$

$$R_p \propto \sqrt{[I]}, [M]$$

Average **kinetic chain length** ( $\bar{v}$ )

= Average **# of monomer units** polymerized **per chain** initiated

$$\bar{v} = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p [M\bullet][M]}{2k_t [M\bullet]^2} = \frac{k_p [M]}{2k_t [M\bullet]} = \frac{k_p [M]}{2(fk_t k_d [I])^{1/2}}$$

$$\overline{DP} = \begin{cases} \bar{v} & \text{Disproportionation} \\ 2\bar{v} & \text{Coupling} \end{cases}$$

- **Gel effect**, Trommsdorff effect, Norris-Smith effect

Occurs in **bulk** or **concentrated solution** polymerizations

$\eta \uparrow \Rightarrow$  Chain mobility  $\downarrow \Rightarrow R_t \downarrow \Rightarrow [M\cdot] \uparrow \Rightarrow$

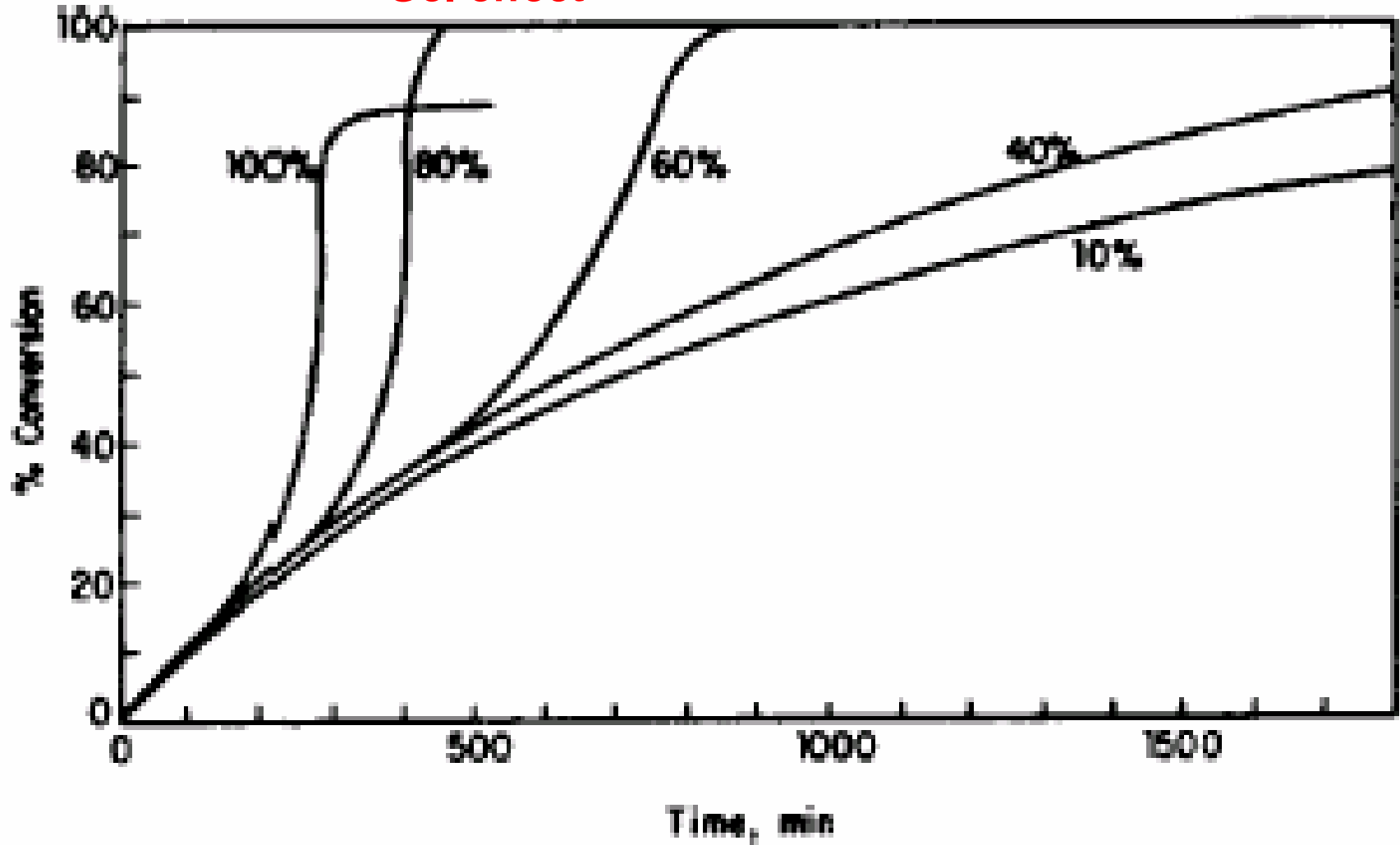
$R_p \uparrow \Rightarrow$  **Release of more heat  $\Rightarrow R_i \uparrow \Rightarrow R_p \uparrow$**

**Autoacceleration  $\Rightarrow$  Explosion**



# Polymerization of MMA in benzene 50°C benzoylperoxide

**Gel effect**



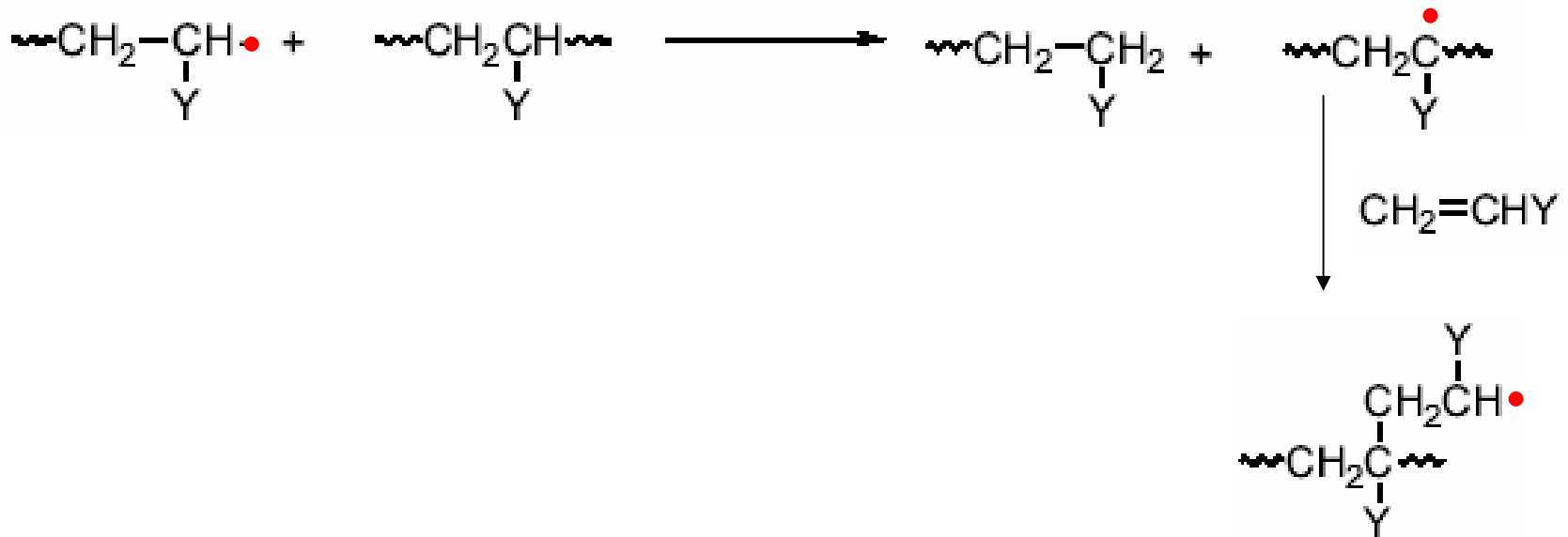
- **Chain transfer** reactions

Transfer of reactivity from the growing polymer chain to another species

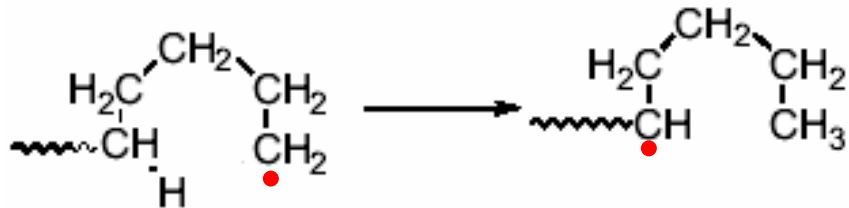
1) C.T. to Polymer

Chain-end radical abstract a H atom from a chain

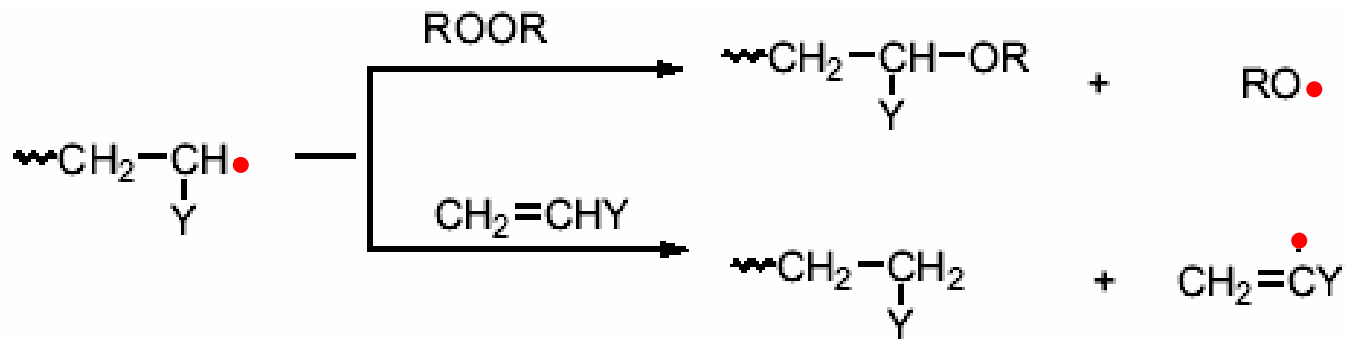
→ **Chain branching**



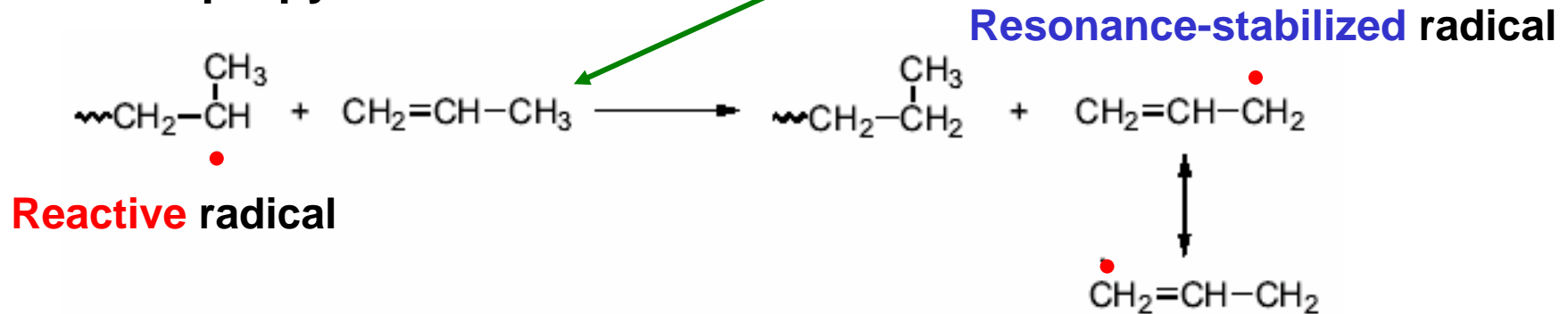
## 2) Backbiting : intramolecular chain transfer



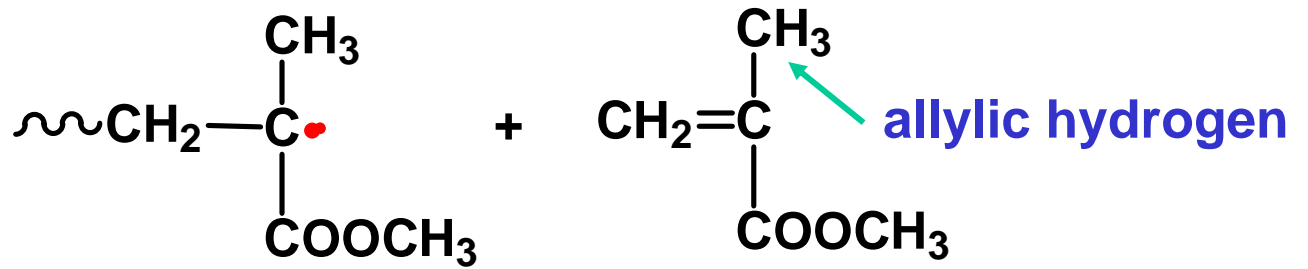
## 3) C.T. to Initiator or Monomer



Important with monomers containing **allylic hydrogen**,  
such as propylene

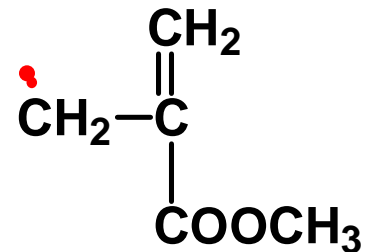
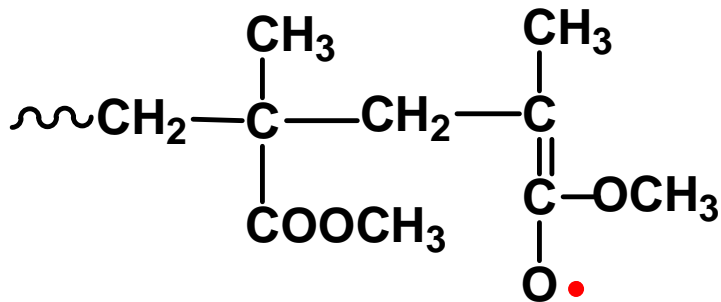
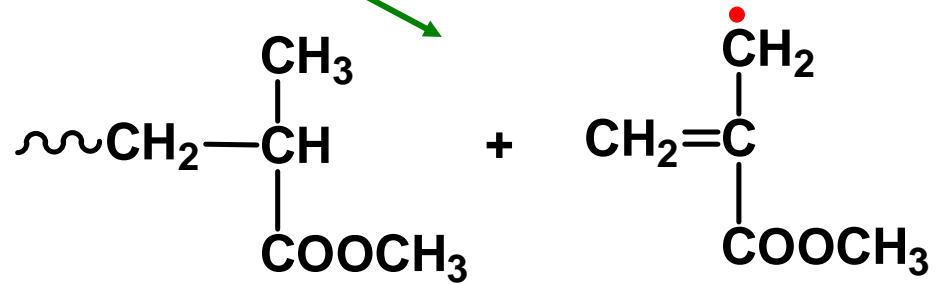
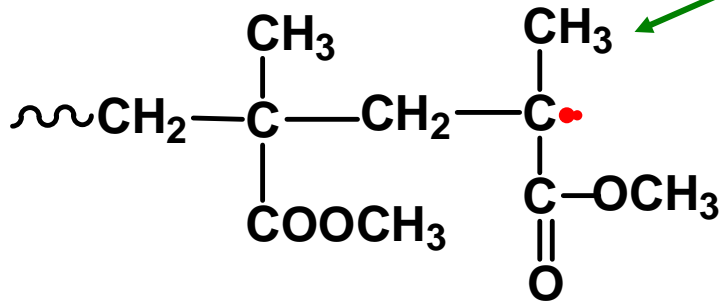


∴ **High-mol-wt polypropylene cannot be prepared**  
by free radical polymerization



Propagation

C.T. to monomer



Resonance-stabilized radical

Resonance-stabilized radical

∴ High-mol-wt **PMMA** can be prepared by free radical polymerization

#### 4) C.T. to Solvent or Chain transfer agents

$\text{CCl}_4$



Thiol (RSH)



## Transfer reaction rate

$$R_{tr} = k_{tr} [M \bullet][T]$$

where T = transfer agent

## Kinetic chain length

$$\bar{v} = \frac{k_p [M]}{2k_t [M \bullet]} \quad \text{w/o transfer agent}$$

$$\bar{v}_{tr} = \frac{R_p}{R_t + R_{tr}} = \frac{k_p [M \bullet][M]}{2k_t [M \bullet]^2 + \sum k_{tr} [M \bullet][T]} = \frac{k_p [M]}{2k_t [M \bullet] + \sum k_{tr} [T]}$$

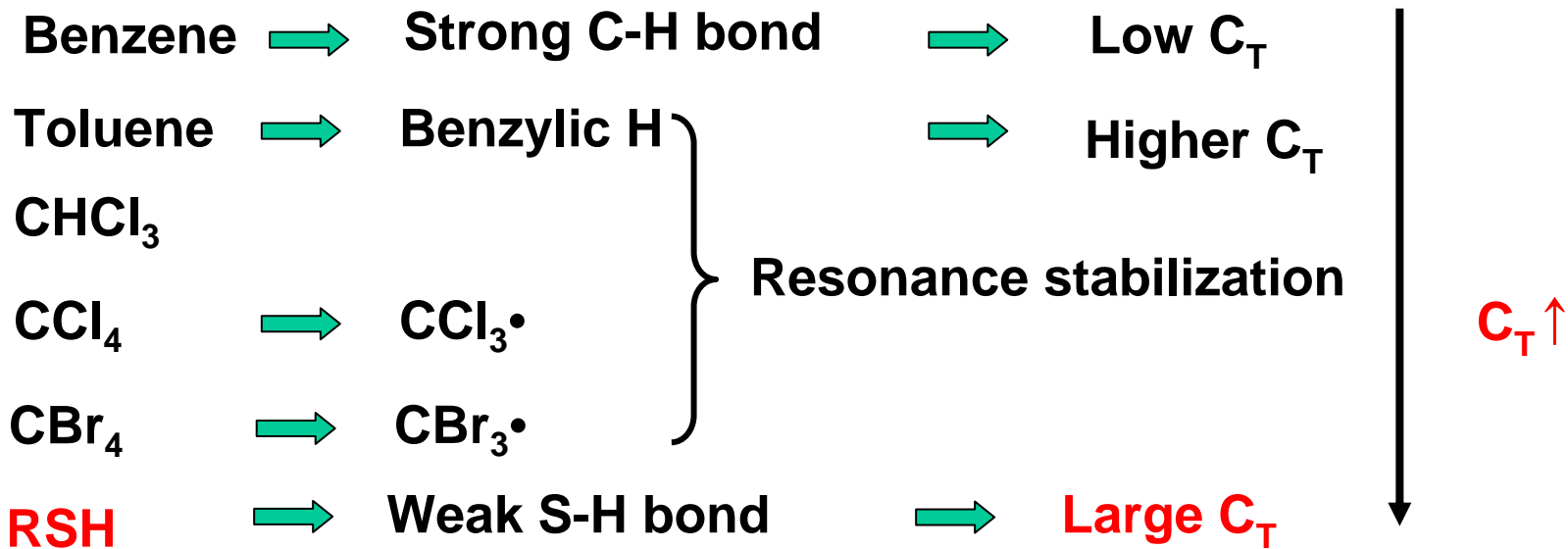
with transfer agent

$$\frac{1}{\bar{v}_{tr}} = \frac{2k_t [M \bullet] + \sum k_{tr} [T]}{k_p [M]} = \frac{1}{\bar{v}} + \frac{\sum k_{tr} [T]}{k_p [M]} = \frac{1}{\bar{v}} + \frac{\sum C_T [T]}{[M]}$$

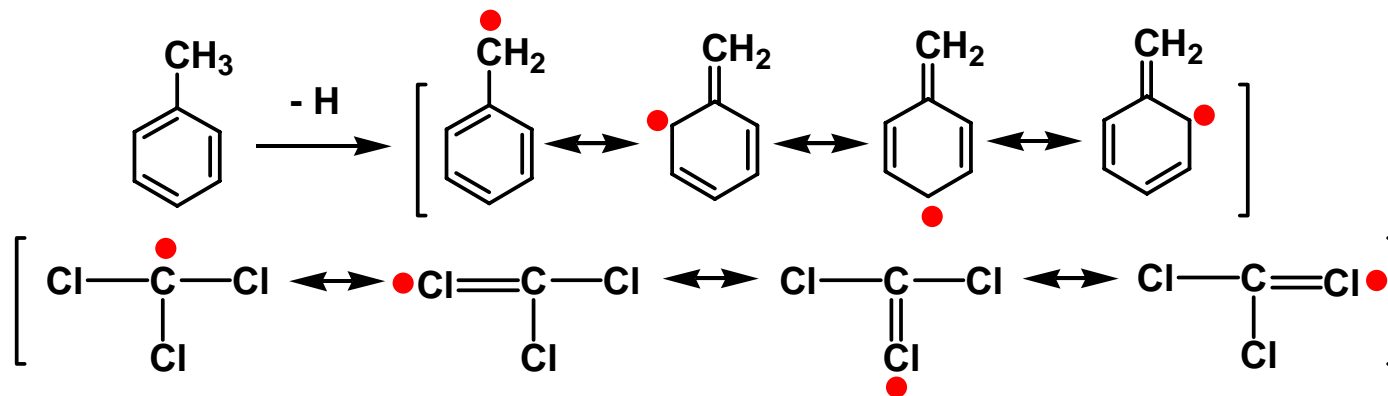
$$\frac{k_{tr}}{k_p} = C_T \quad \text{Chain transfer constant}$$

$$\frac{1}{\bar{v}_{tr}} = \frac{1}{\bar{v}} + \frac{\sum C_T [T]}{[M]}$$

Table 6.5  $C_T$  for St and MMA



When **[T] is high**,  $k_{tr} \gg k_p \Rightarrow$  **Very-low-mol-wt polymer**  
**Telomerization** **Telomer**

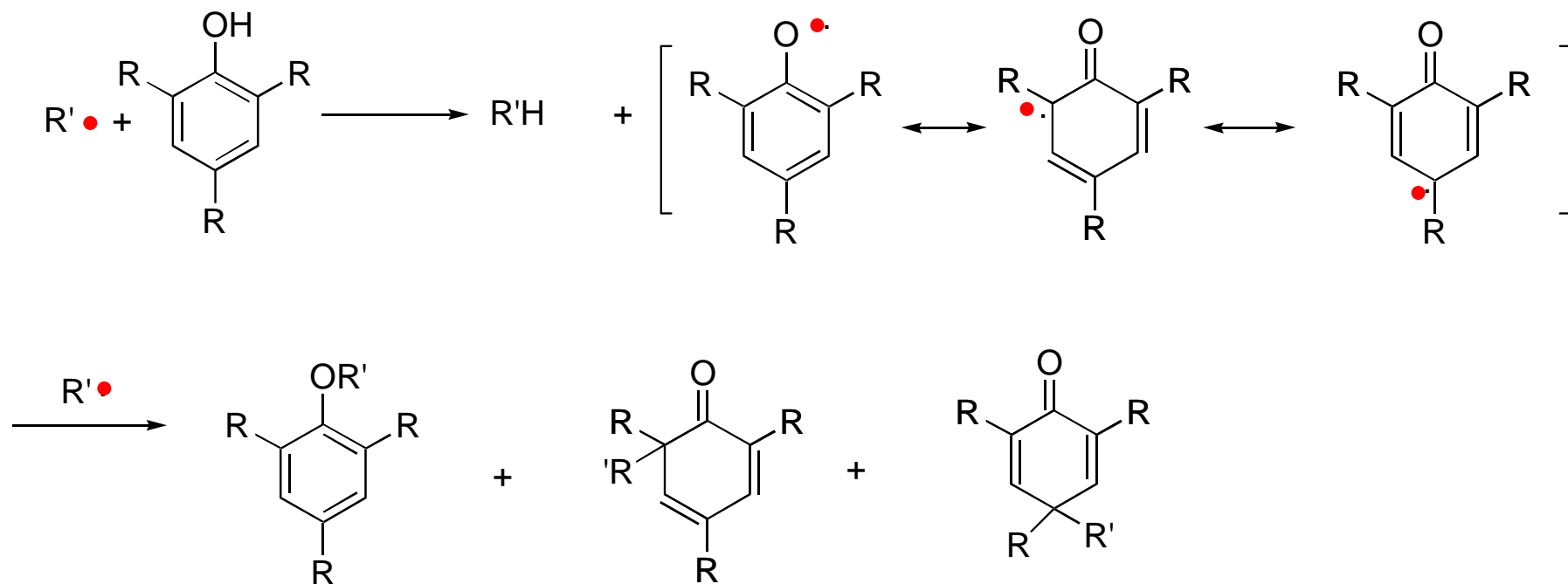


## o Inhibitors

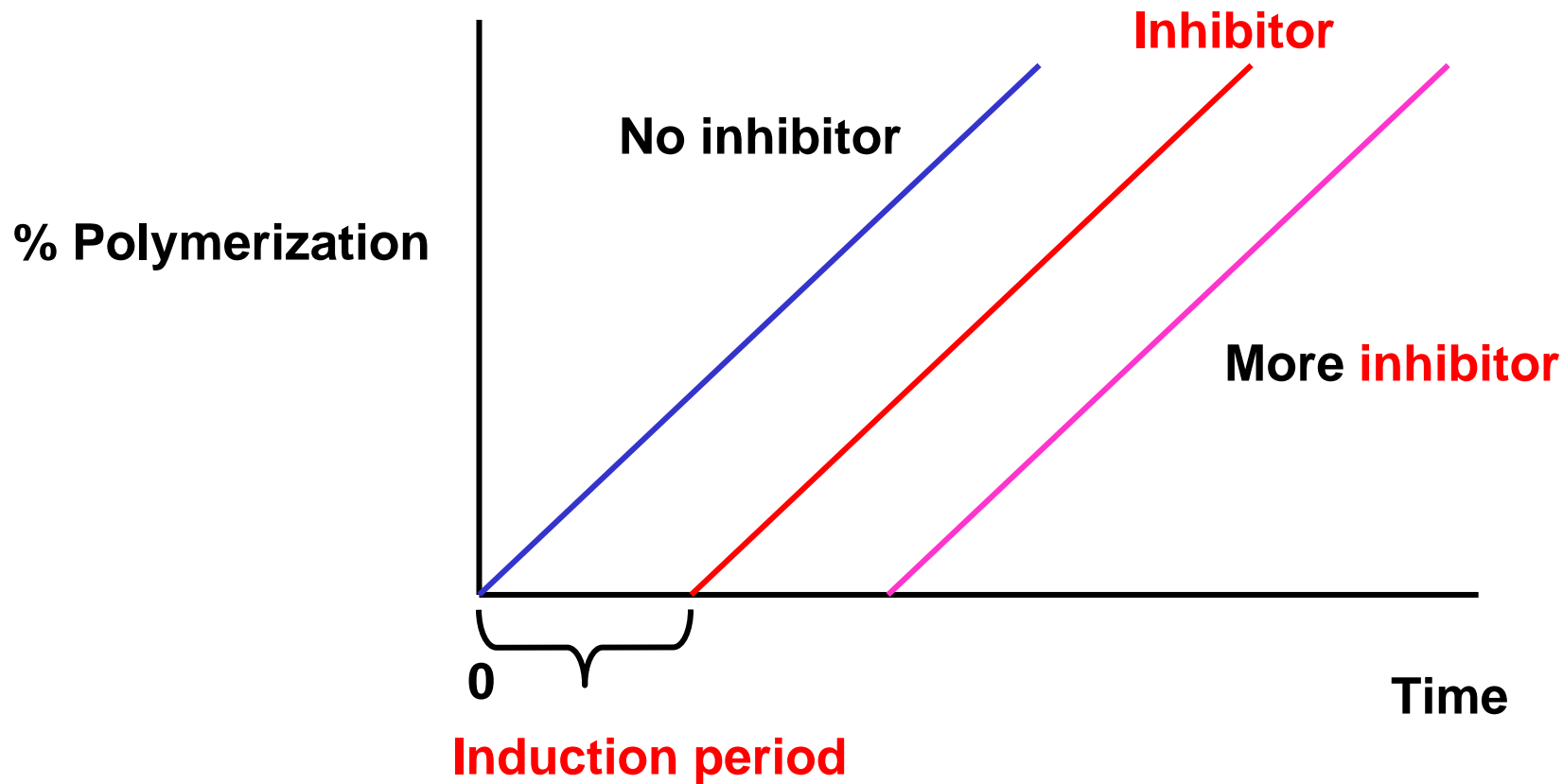
Added to monomers to **prevent polymerization** during shipment or storage

**Must be removed** by distillation of monomer or extraction

### Alkylated Phenol







**Induction periods** are **common** even with **purified monomer** because of the presence of **oxygen**, which is, itself, an **inhibitor**.

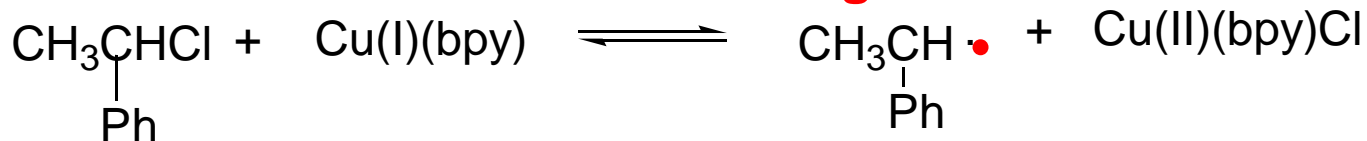
o Living free radical Polymerization

**No** chain **termination** or **chain transfer**

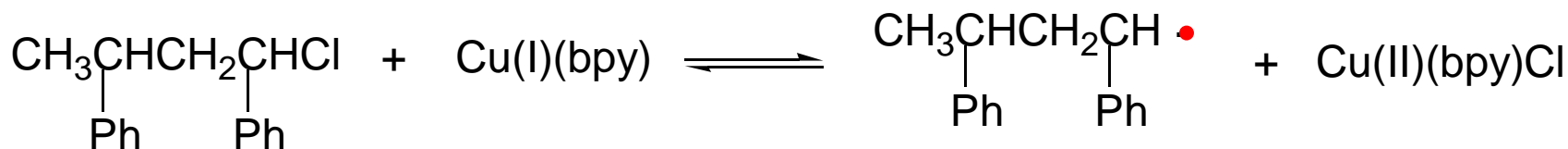
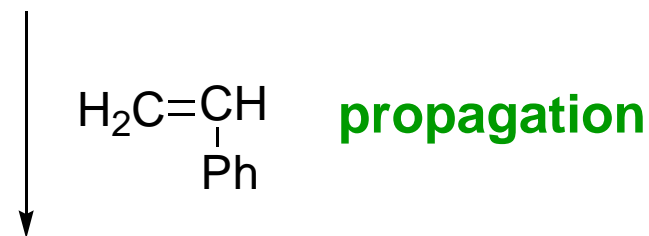
o **Atom Transfer Radical Polymerization (ATRP)**

Polymerization of **styrene**

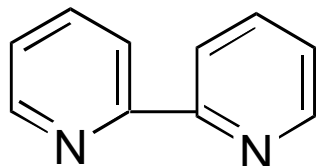
Transfer of **Halogen** atom



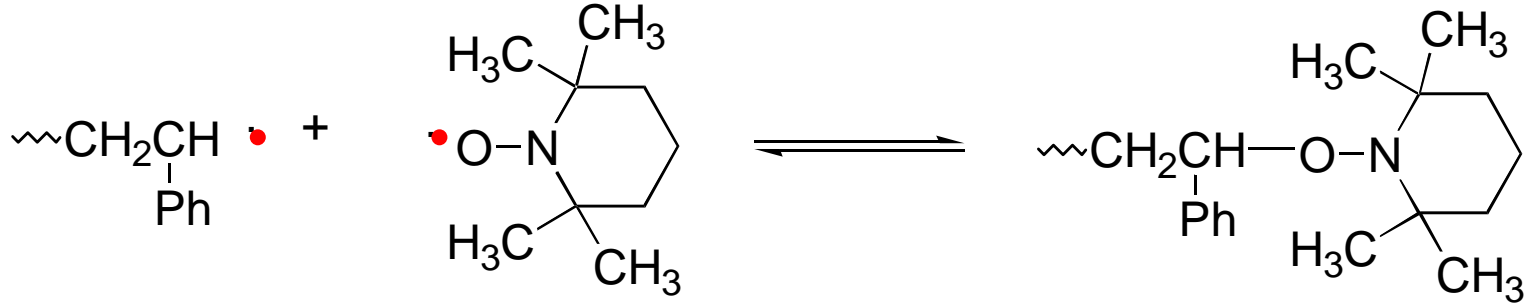
**Preventing** radical **termination** reactions from occurring



bpy = bipyridyl =



## o Addition of a **Stable Free Radical**



**TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl)**

**Too stale** to initiate polymerization

**Promotes decomposition of BPO** to benzoyloxy radicals

**Propagation**

**Prevent termination**

$$\overline{DP} = \frac{[M]_0}{[I]_0}$$

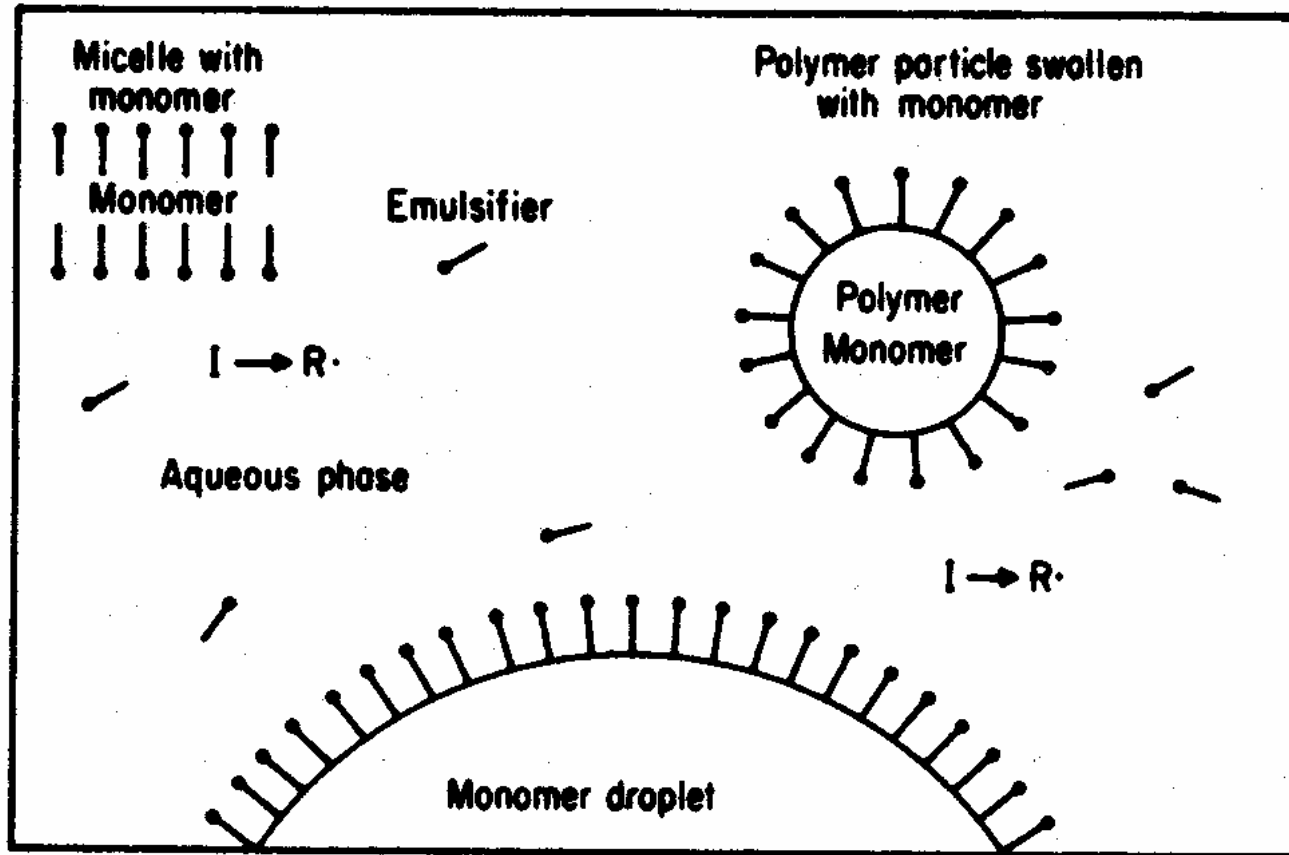
All the chains are **initiated at about the same time.**

**No chain termination or transfer reactions.**

The **chains all grow** to approximately **the same length.**

**Polydispersity is low.**

## o Emulsion Polymerization



Smith-Ewart kinetics

$$R_p = k_p [M] \left( \frac{N}{2} \right)$$

where  $[M]$  = concentration of monomer in the polymer particle  
 $N$  = # of polymer particles

## Rate of radical entry into the particle

$$\rho = \frac{R_i}{N}$$

## Average kinetic chain length

$$\bar{v} = \frac{k_p [M]}{\rho} = \frac{k_p [M]}{\frac{R_i}{N}} = \frac{k_p [M] N}{2fk_d [I]}$$

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

$$N = k \left( \frac{R_i}{\mu} \right)^{0.4} (a_s [E])^{0.6}$$

where

- $k = \text{constant (0.37~0.53)}$
- $\mu = \text{rate of increase in the volume of a polymer particle}$
- $[E] = \text{concentration of micellar emulsifier}$
- $a_s = \text{interfacial area occupied by an emulsifier molecule in the micelles}$

$$N \propto [I]^{0.4}, [E]^{0.6}$$

$$R_p \propto [I]^{0.4}, [E]^{0.6}$$

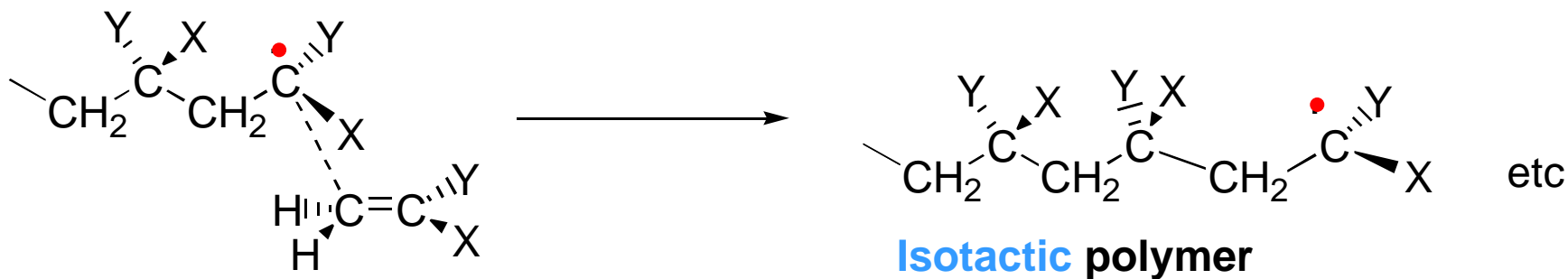
$$\overline{DP} = \bar{v} \propto [I]^{-0.6}, [E]^{0.6}$$

## 6.5. Stereochemistry of Polymerization

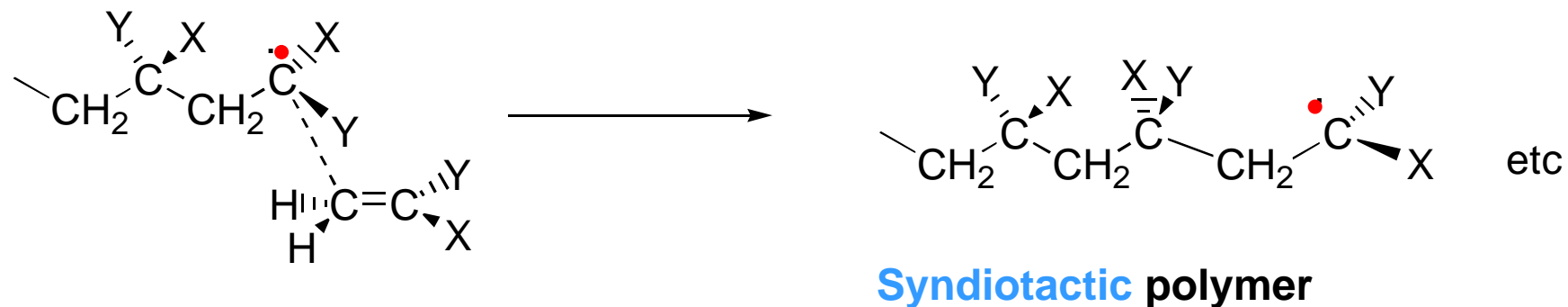
**Steric** and **electrostatic interactions** are responsible for stereochemistry of free radical polymerization

### 1) Interaction between **Terminal** unit & **Monomer**

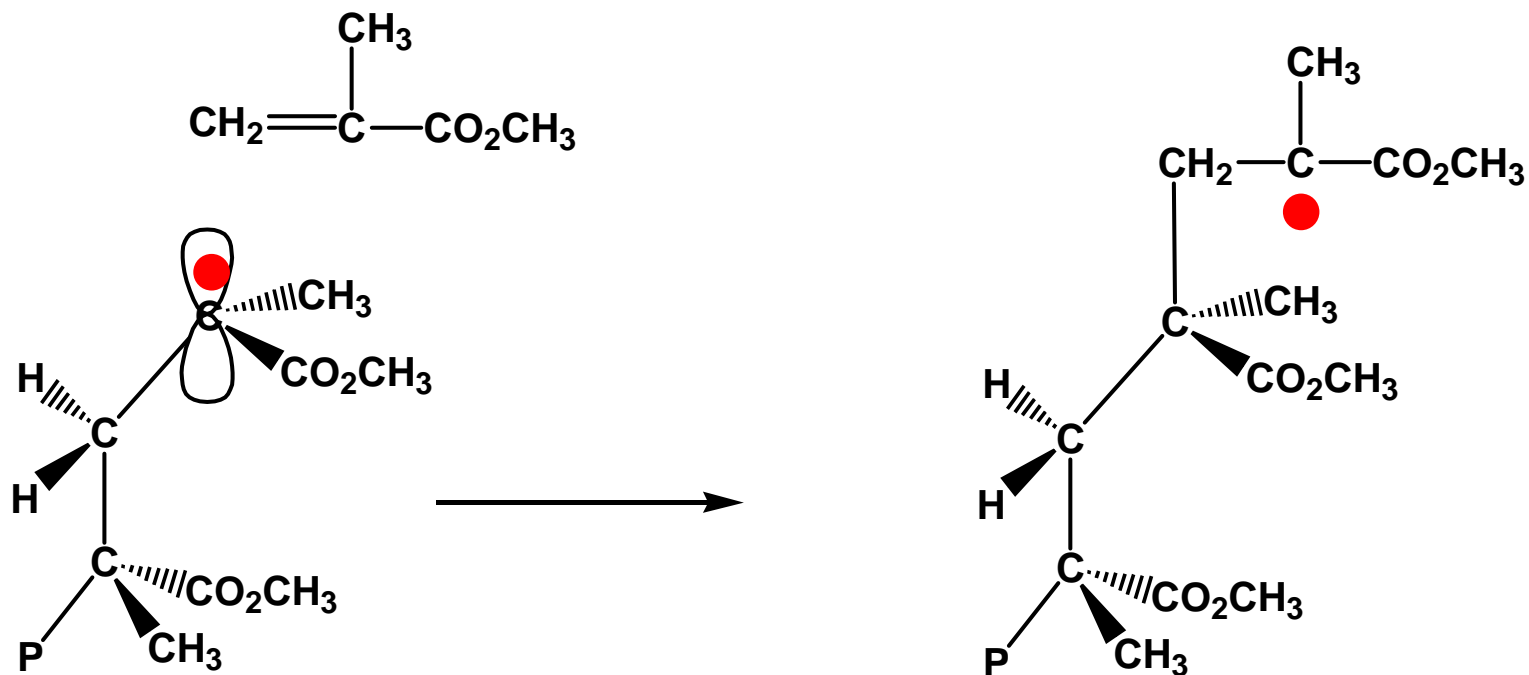
#### Mirror approach



#### Nonmirror approach



## 2) Interaction between Terminal unit & Penultimate unit



**Syndiotactic**

If **terminal carbon** has **sp<sup>2</sup> planar** structure,

Interaction between **terminal unit** & **monomer** is dominant factor

If **terminal carbon** has **sp<sup>3</sup>** hybridization,

Interaction between **penultimate** unit & **terminal** unit is dominant factor

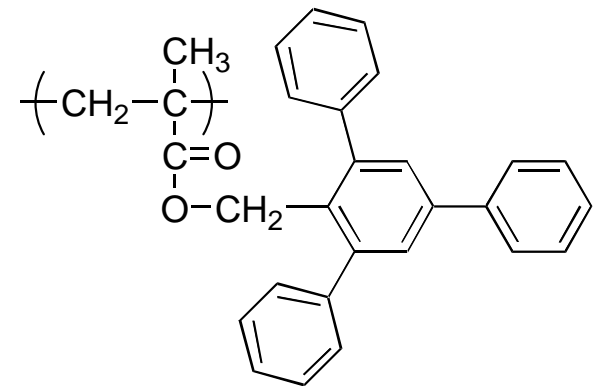
Stereoregularity  $\uparrow$  as  $T \downarrow$

Free radical polymerization of MMA at  $T < 0\text{ }^{\circ}\text{C}$

$\rightarrow$  **Crystalline** polymer

**Syndiotactic**

(Expect) As **size** of substituent groups  $\uparrow$ , **stereoregularity**  $\uparrow$



(Experiment) **bulkier** substituent

**Less syndiotactic** than PMMA under the same conditions



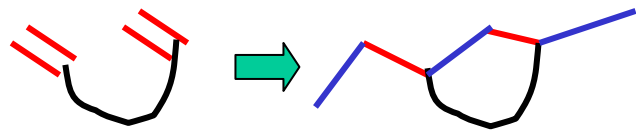
## 6.6 Polymerization of Dienes

### 6.6.1. Isolated Dienes

**Cooperative addition** of one double bond to the other of the monomer



**Cyclic polymer**



5- or 6-membered ring

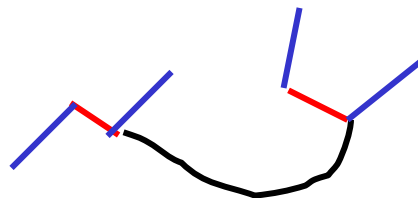
**Cyclopolymerization:**

Formation of a cyclic structural unit in a propagation step

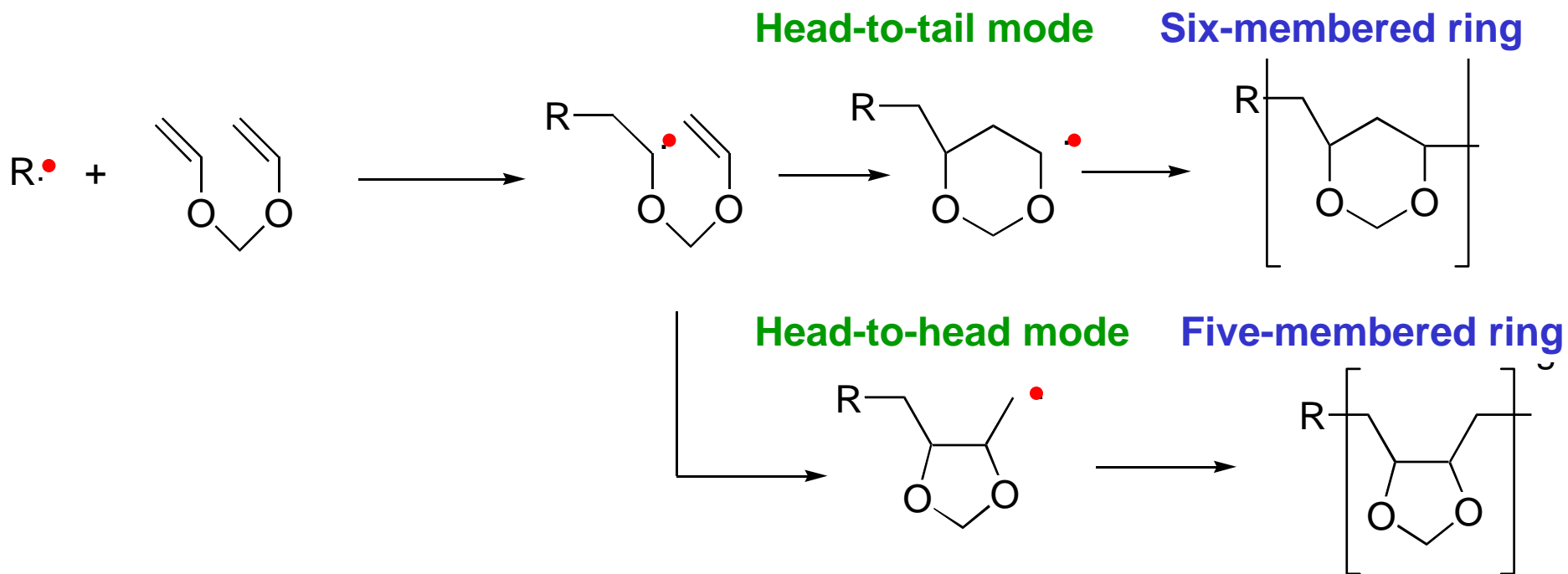
**Independent reaction**



**Crosslinked polymer**



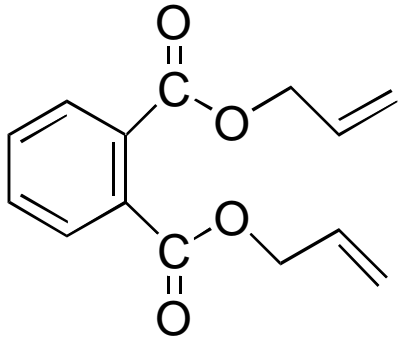
# Cyclopolymerization of divinylformal



Diallyl monomer

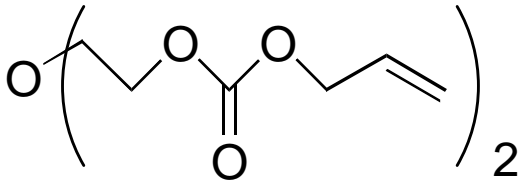


Highly crosslinked polymers



Diallyl phthalate

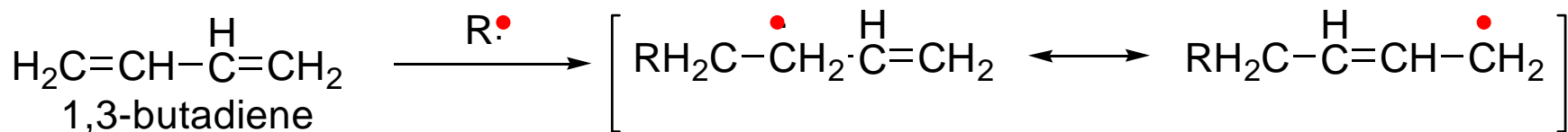
Used for manufacturing electrical or electronics items (circuit boards, insulators, television components, etc) preimpregnating glass cloth or fiber for fiber-reinforced plastics



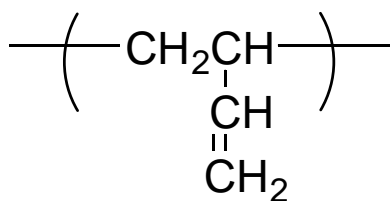
Used for applications requiring good optical clarity (eyewear lenses, camera filters, panel covers, and the like)

Diethylene glycol bis(allyl carbonate)

## 6.6.2. Conjugated Dienes



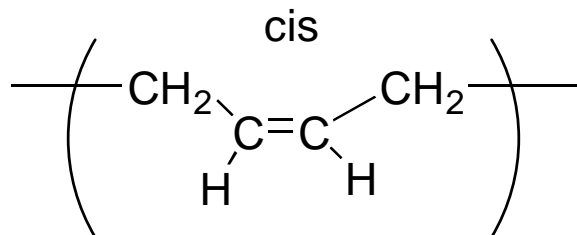
1,2-addition



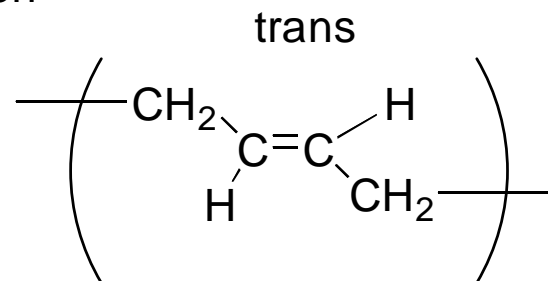
Pendant vinyl groups

**20%**

1,4-addition

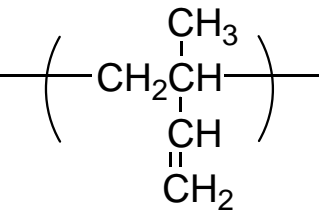
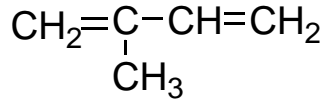


unsaturation in the chain

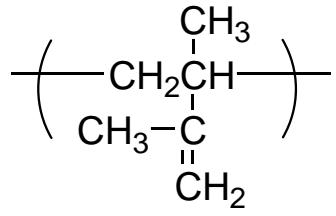


**80%**

Isoprene (2-methyl-1,3-butadiene)



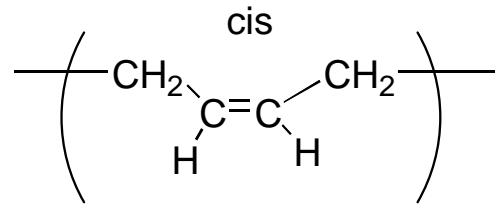
1,2-addition



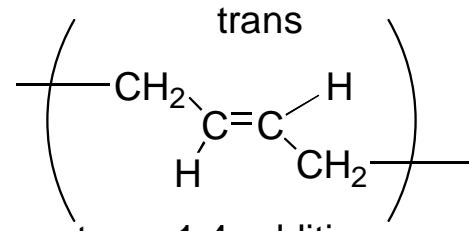
3,4-addition



10%



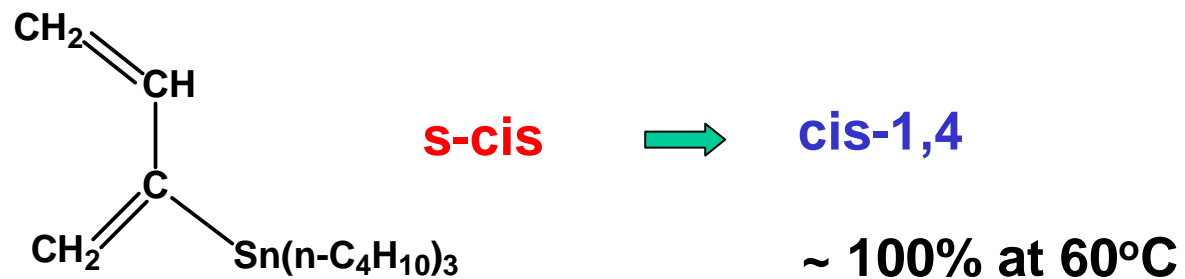
cis-1,4-addition  
Natural rubber  
(Hevea)



trans-1,4-addition

**Predominant**

As **T** ↑ , **cis-1,4** ↑



**Table 6.6 Structures of Free Radical-Initiated Diene Polymers**

<i>Monomer</i>	<i>Polymerization Temperature( °C)</i>	<i>percent</i>			
		<b>cis-1,4</b>	<b>trans-1,4</b>	<b>1,2</b>	<b>3,4</b>
<b>Butadiene</b>	-20	6	77	17	-
	20	22	58	20	-
	100	28	51	21	-
	233	43	39	18	-
<b>Isoprene</b>	-20	1	90	5	4
	-5	7	82	5	5
	50	18	72	5	5
	100	23	66	5	6
	257	12	77	2	9
<b>Chloroprene</b>	-46	5	94	1	0.3
	46	10	81-86	2	1
	100	13	71	2.4	2.4

## 6.7 Monomer Reactivity



o Three factors in monomer reactivity

1) Resonance stabilization of free radicals:  $k_p \downarrow$



Reactive monomer

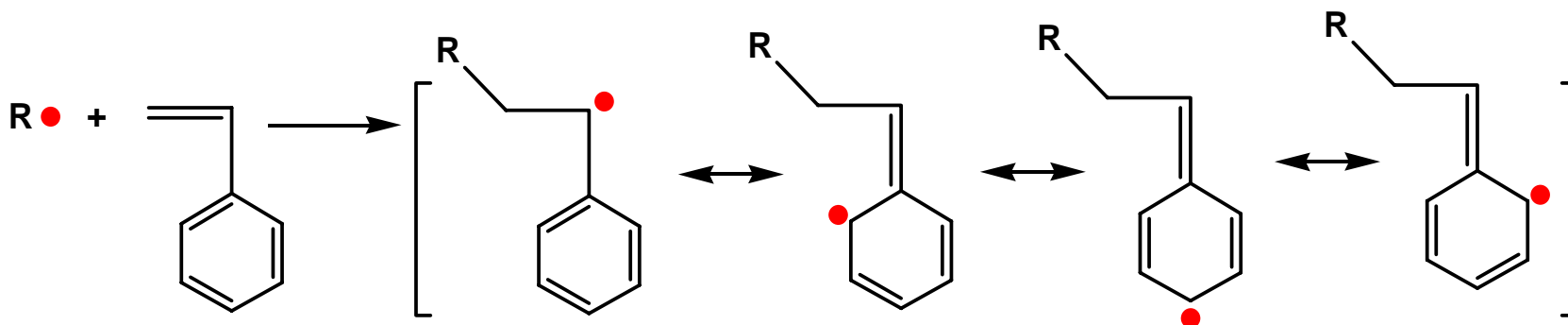
Stable monomer

Stable radical

Reactive radical

Inverse relationship between monomer reactivity and  $k_p$

Radical reactivity is the major factor.



Reactive monomer

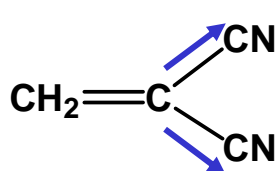
Stable radical



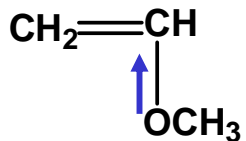
## 2) Polarization of double bond by substituents: $k_p \downarrow$

Extreme polarization prevents free radical polymerization

e.g.

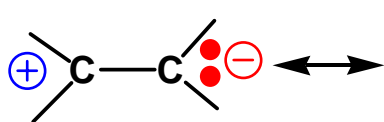


Anionic

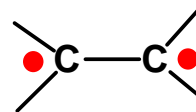
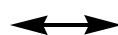
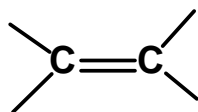


Cationic polymerization

No radical polymerization

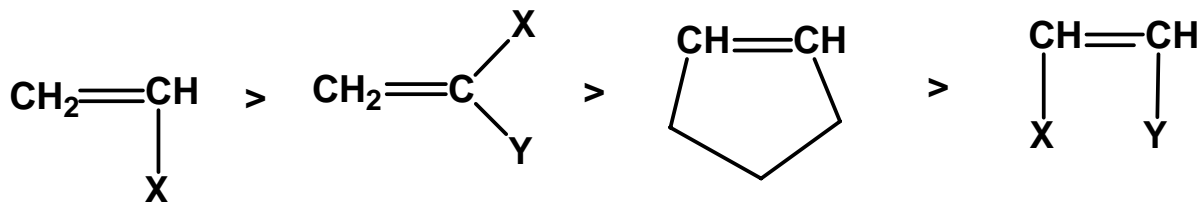


Heterolytic fission

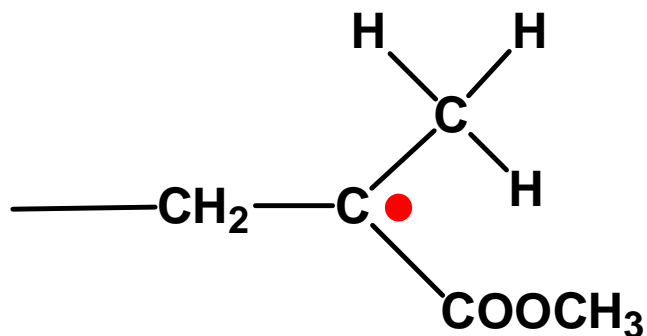


Homolytic fission

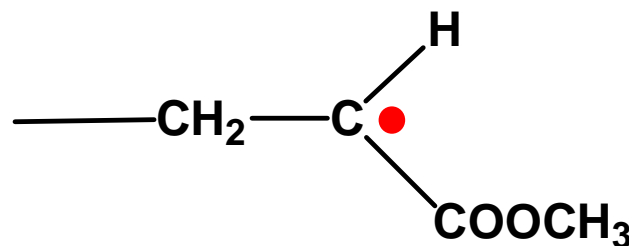
## 3) Steric hindrance: $k_p \downarrow$



$k_p$ : **MMA < MA**



**MMA**



**MA**

∴ **Resonance stabilization of the radical** by **hyperconjugation** and **steric hindrance**



**Overlap of p-orbital with  $\sigma$  bonds**

o **Free energy of polymerization**

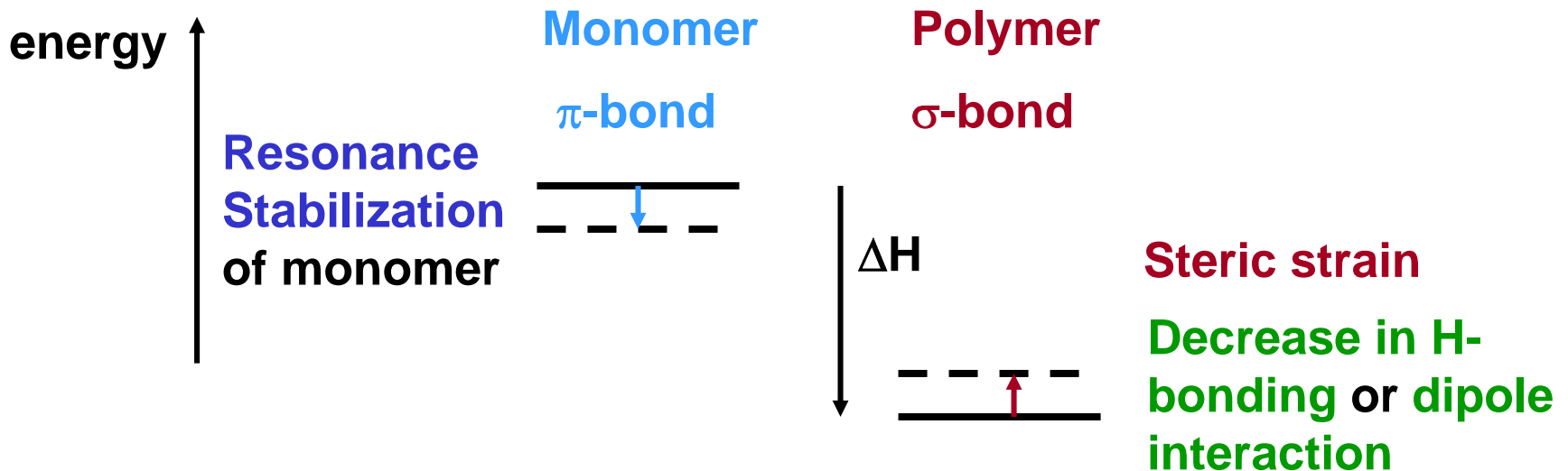
$$\Delta G_p = \Delta H_p - T\Delta S_p$$

- $\Delta H < 0$  : **exothermic**,  $\pi$ -bond in monomer  $\rightarrow$   $\sigma$ -bond in polymer  
 favorable
- $\Delta S < 0$  : **monomer**  $\rightarrow$  **covalently bonded** chain structure  
 unfavorable  $\therefore$  Degree of **freedom** (randomness)  $\downarrow$

(1) The higher the **resonance stabilization of monomer**,  $|\Delta H| \downarrow$

(2) **Steric strain in polymer**,  $|\Delta H| \downarrow$

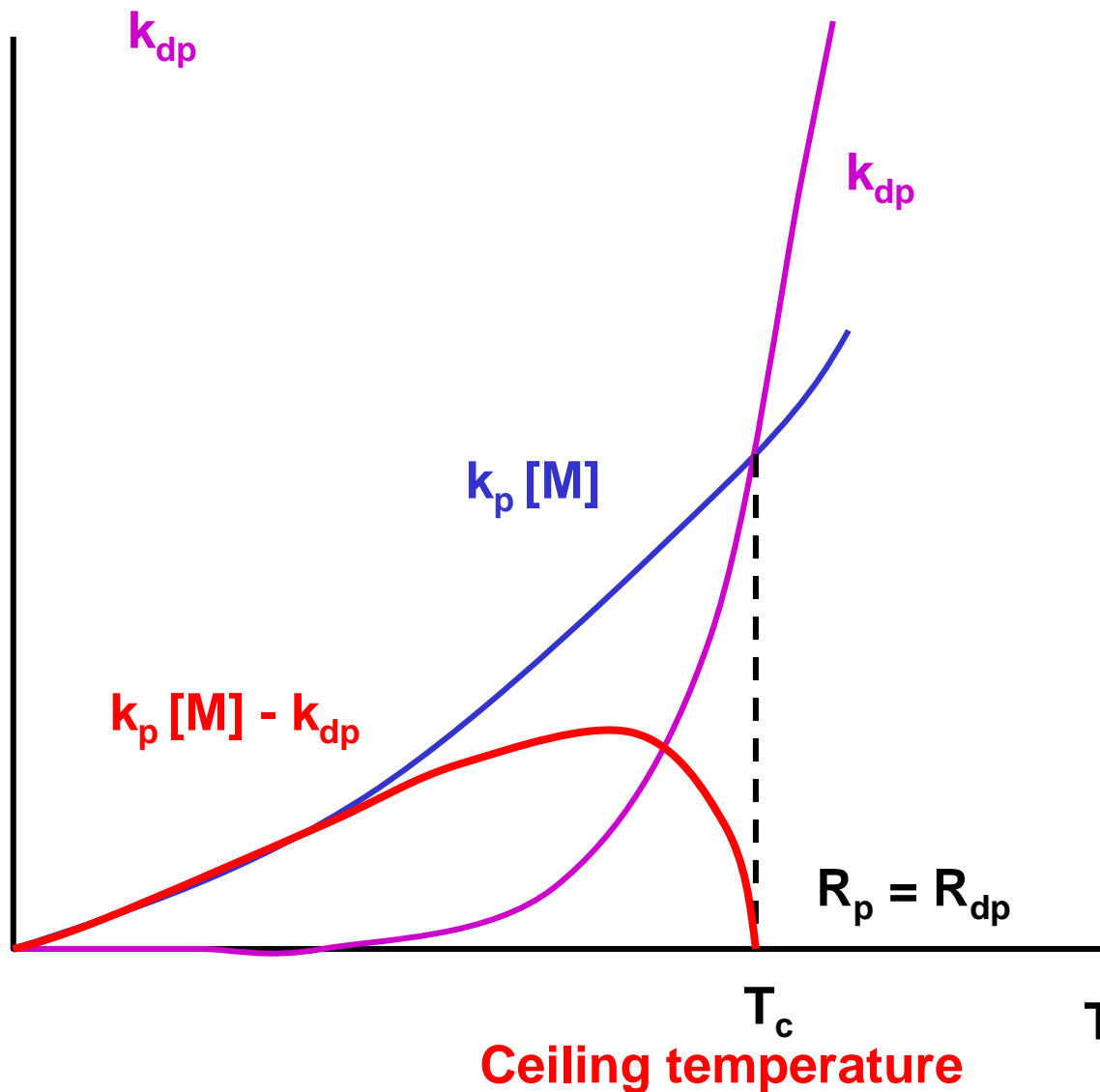
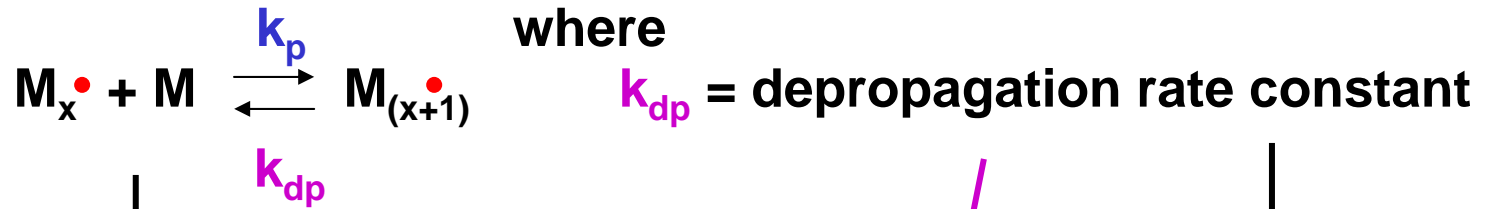
(3) **Decrease in H-bonding** or dipole interaction on **polymerization**,  $|\Delta H| \downarrow$



**Table 6.7  $\Delta H$  and  $\Delta S$  of Polymerization**

<i>Monomer</i>	$-\Delta H$ (kJ/mol)	$-\Delta S$ (J/mol)
Acrylonitrile	77	109
1,3-Butadiene	78	89
<b>Ethylene</b>	<b>109</b>	155
Isoprene	75	101
<b>Methyl methacrylate</b>	<b>65</b>	117
Propylene	84	116
<b>Styrene</b>	<b>70</b>	104
Tetrafluoroethylene	163	-
<b>Vinyl acetate</b>	<b>90</b>	-
Vinyl chloride	71	-

## o Polymerization-depolymerization Equilibrium



At  $T_c$

$$k_p [M \bullet][M] = k_{dp} [M \bullet]$$

Equilibrium constant

$$K = \frac{[M \bullet]}{[M \bullet][M]_e} = \frac{1}{[M]_e} = \frac{k_p}{k_{dp}}$$

where  $[M]_e$  = equilibrium **monomer concentration**

$$\Delta G = \Delta G^\circ + RT \ln K$$

where  $\Delta G^\circ = \Delta G$  in **standard state**  
(**pure monomer** or **1-M solution monomer**,  
pure polymer or 1-M repeating units of polymer)

At equilibrium

$$\Delta G = 0$$

$$\Delta G^\circ = \Delta H^\circ - T_c \Delta S^\circ = -RT_c \ln K = RT_c \ln [M]_e$$



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

or

$$\ln [M]_e = \frac{\Delta H^\circ}{RT_c} - \frac{\Delta S^\circ}{R}$$

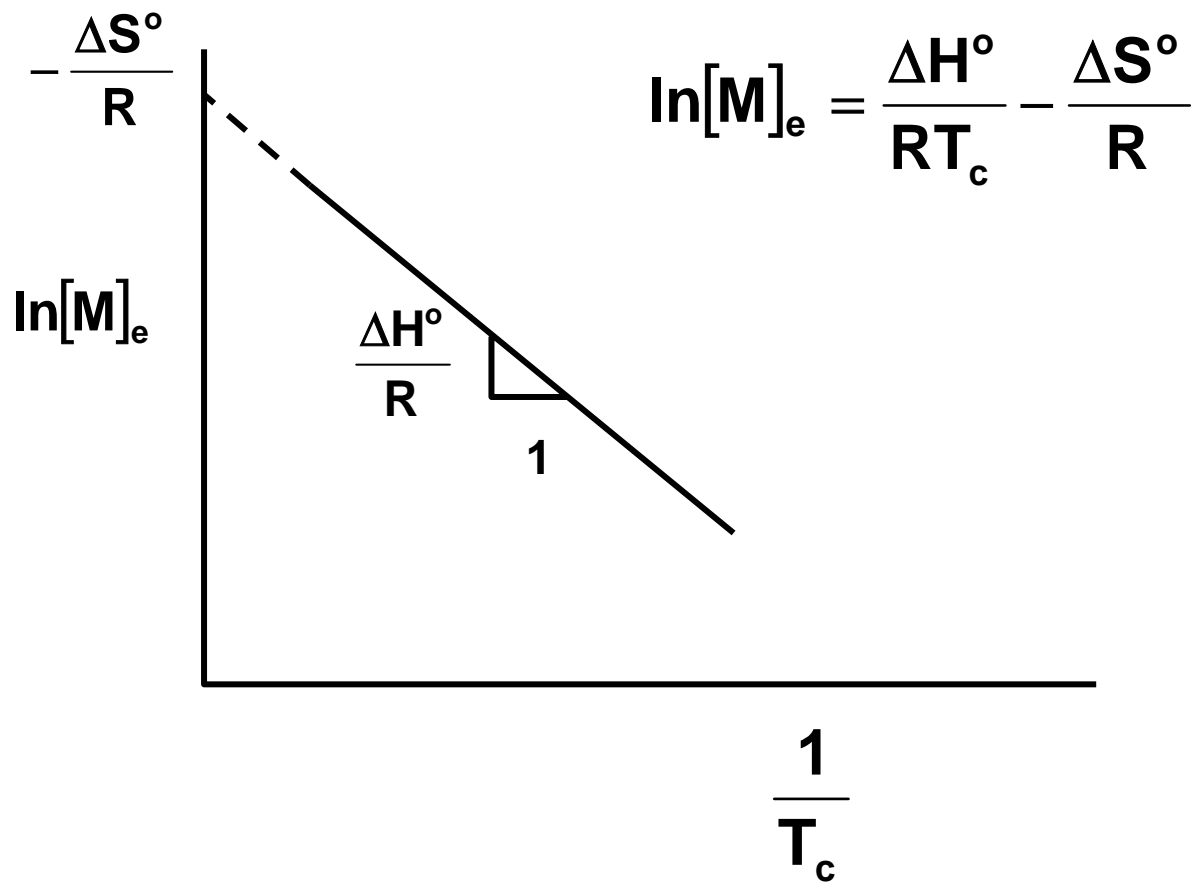
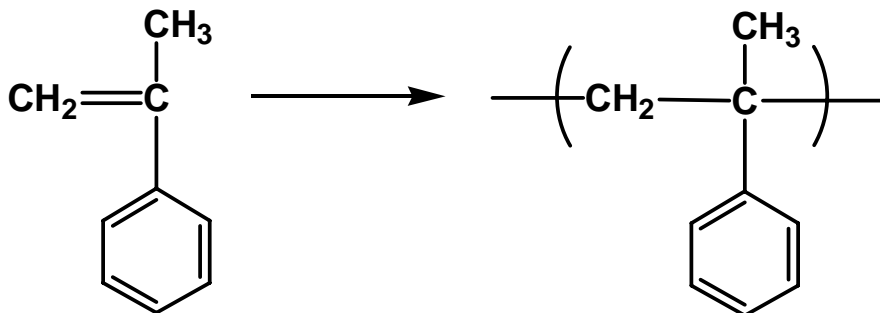


Table 6.8  $T_c$  of Pure Liquid Monomers

<i>Monomer</i>	$T_c$ (°C)
1,3-Butadiene	585
Ethylene	610
Isobutylene	175
Isoprene	466
<b>Methyl methacrylate</b>	<b>198</b>
<b><math>\alpha</math>-Methylstyrene</b>	<b>66</b>
Styrene	395
Tetrafluoroethylene	1100

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



→  $-\Delta H = 35 \text{ kJ/mol}$

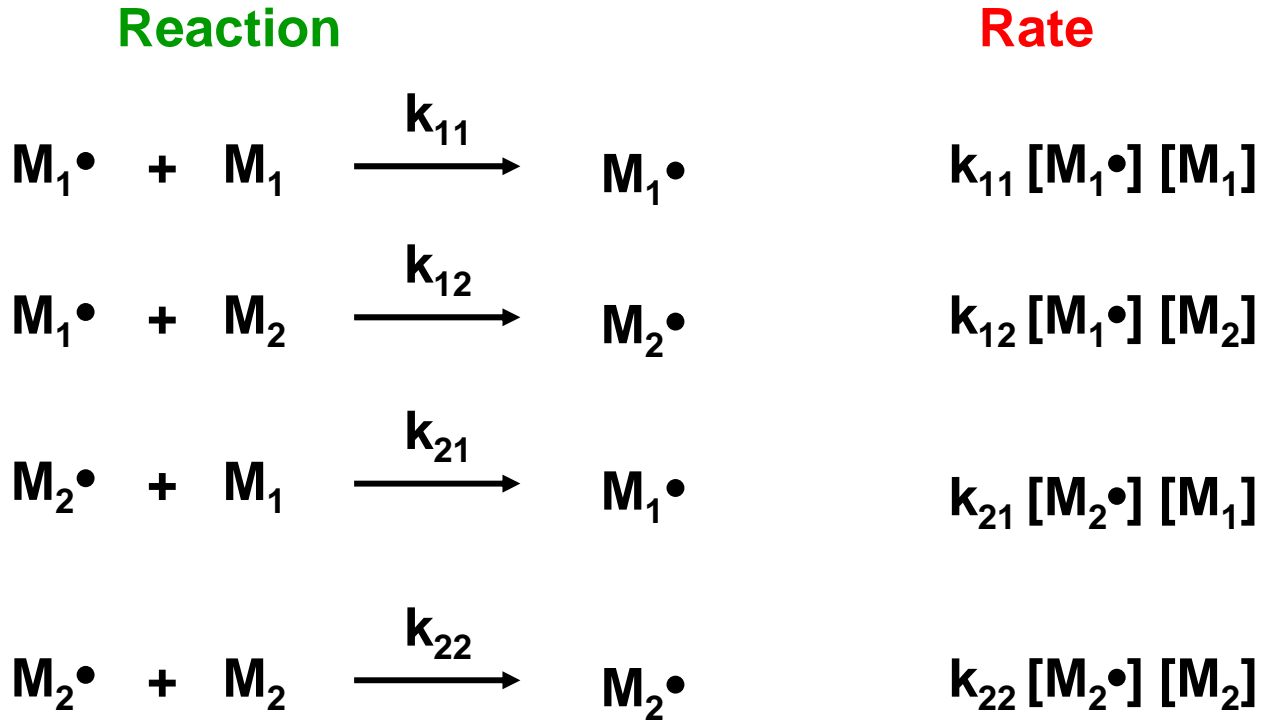
$T_c = 66 \text{ }^\circ\text{C}$

**Resonance** stabilization

**Steric strain** in polymer



## 6.8 Copolymerization



where  $k_{11}$  and  $k_{22}$  : **self-propagation** rate constant

$k_{12}$  and  $k_{21}$  : **cross-propagation** rate constant

- o **Steady-state** assumption for  $[M_1\bullet]$  and  $[M_2\bullet]$

$$k_{12} [M_1\bullet] [M_2] = k_{21} [M_2\bullet] [M_1]$$

- o Rate of **consumption** of  $M_1$  and  $M_2$

$$-\frac{d[M_1]}{dt} = k_{11} [M_1\bullet] [M_1] + k_{21} [M_2\bullet] [M_1]$$

$$-\frac{d[M_2]}{dt} = k_{12} [M_1\bullet] [M_2] + k_{22} [M_2\bullet] [M_2]$$

$$[M_1\bullet] = \frac{k_{21} [M_1] [M_2\bullet]}{k_{12} [M_2]}$$

- o **Instant composition** of copolymer

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{k_{11} [M_1\bullet] + k_{21} [M_2\bullet]}{k_{12} [M_1\bullet] + k_{22} [M_2\bullet]} \right)$$

- o **Monomer reactivity ratio**

$$\frac{k_{11}}{k_{12}} = r_1 \quad \frac{k_{22}}{k_{21}} = r_2$$

- o **Copolymer (composition) equation**

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{r_1 [M_1] + [M_2]}{[M_1] + r_2 [M_2]} \right)$$

o **Instantaneous composition** of feed and polymer

$$\left\{ \begin{array}{l} f_1 = \text{mole fraction of } M_1 \text{ in the feed} \\ f_2 = \text{mole fraction of } M_2 \text{ in the feed} \\ F_1 = \text{mole fraction of } M_1 \text{ in the copolymer} \\ F_2 = \text{mole fraction of } M_2 \text{ in the copolymer} \end{array} \right. \quad \begin{array}{l} f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \\ F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \end{array}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right) \quad \frac{d[M_1]}{d[M_2]} = \frac{F_1}{1 - F_1} \quad \frac{[M_1]}{[M_2]} = \frac{f_1}{f_2}$$

$$\frac{F_1}{1 - F_1} = \frac{f_1}{f_2} \left( \frac{r_1 f_1 + f_2}{f_1 + r_2 f_2} \right) \quad \frac{1 - F_1}{F_1} = \frac{1}{F_1} - 1 = \frac{f_2}{f_1} \left( \frac{f_1 + r_2 f_2}{r_1 f_1 + f_2} \right)$$

$$\frac{1}{F_1} = \frac{f_2}{f_1} \left( \frac{f_1 + r_2 f_2}{r_1 f_1 + f_2} \right) + 1 = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{r_1 f_1^2 + f_1 f_2}$$

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

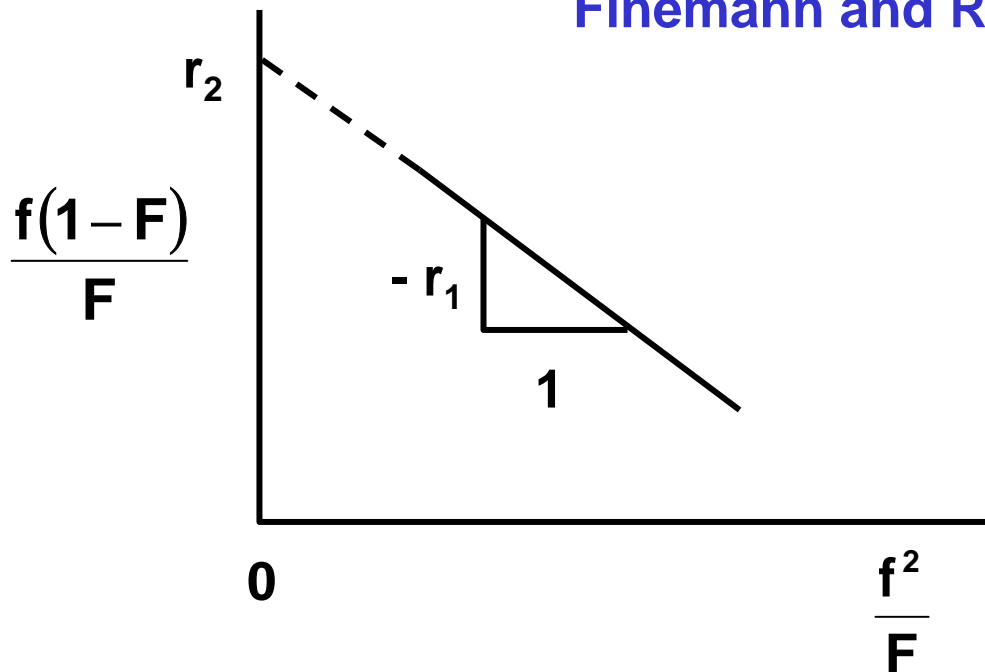
$$F = \frac{F_1}{F_2} = \frac{d[M_1]}{d[M_2]} \quad f = \frac{f_1}{f_2} = \frac{[M_1]}{[M_2]}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right) \quad F = f \left( \frac{r_1 f + 1}{f + r_2} \right) = \frac{r_1 f^2 + f}{f + r_2}$$

$$fF + r_2 F = r_1 f^2 + f$$

$$\frac{f(1-F)}{F} = r_2 - \left( \frac{f^2}{F} \right) r_1$$

Finemann and Rose Equation



$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

1)  $r_1 = r_2 = 1$

No preference for homopolymerization or copolymerization

→ Random copolymer

$$F_1 = f_1$$

e.g.  $M_1 = \text{ethylene}$        $M_2 = \text{vinyl acetate}$   
 $r_1 = 0.97$                        $r_2 = 1.02$

2)  $r_1 = r_2 = 0$

Alternating copolymer

$$F_1 = 0.5$$

e.g.  $M_1 = \text{styrene}$                $M_2 = \text{maleic anhydride}$   
 $r_1 = 0.041$                        $r_2 = 0.01$

3)  $0 < r_1, r_2 < 1$

More common

e.g.  $M_1 = \text{styrene}$        $M_2 = \text{methyl methacrylate}$   
 $r_1 = 0.52$                        $r_2 = 0.46$

Azeotropic copolymerization

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}$$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right)$$

$$\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} = 1$$

$$\frac{[M_1]}{[M_2]} = \frac{1 - r_2}{1 - r_1}$$

$$f_1 = \frac{1 - r_2}{2 - r_1 - r_2}$$

4)  $1 \ll r_1$  and  $r_2 \ll 1$

Essentially **homopolymer**

e.g.  $M_1 = \text{styrene}$        $M_2 = \text{vinyl acetate}$

$r_1 = 55$                        $r_2 = 0.01$

$M_1 = \text{styrene}$        $M_2 = \text{vinyl chloride}$

$r_1 = 17$                        $r_2 = 0.02$

5)  $r_1 \cdot r_2 = 1$       **Ideal copolymerization**

cf.  $r_1 = r_2 = 1$       Real random copolymerization

$$\frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}$$

The more  $r_1$  and  $r_2$  **diverge**, the **less random**

e.g.  $M_1 = \text{MMA}$        $M_2 = \text{vinyl chloride}$

$r_1 = 10$                        $r_2 = 0.1$

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + \frac{f_2^2}{r_1}} = \frac{r_1^2 f_1^2 + r_1 f_1 f_2}{r_1^2 f_1^2 + 2r_1 f_1 f_2 + f_2^2} = \frac{r_1 f_1 (r_1 f_1 + f_2)}{(r_1 f_1 + f_2)^2} = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

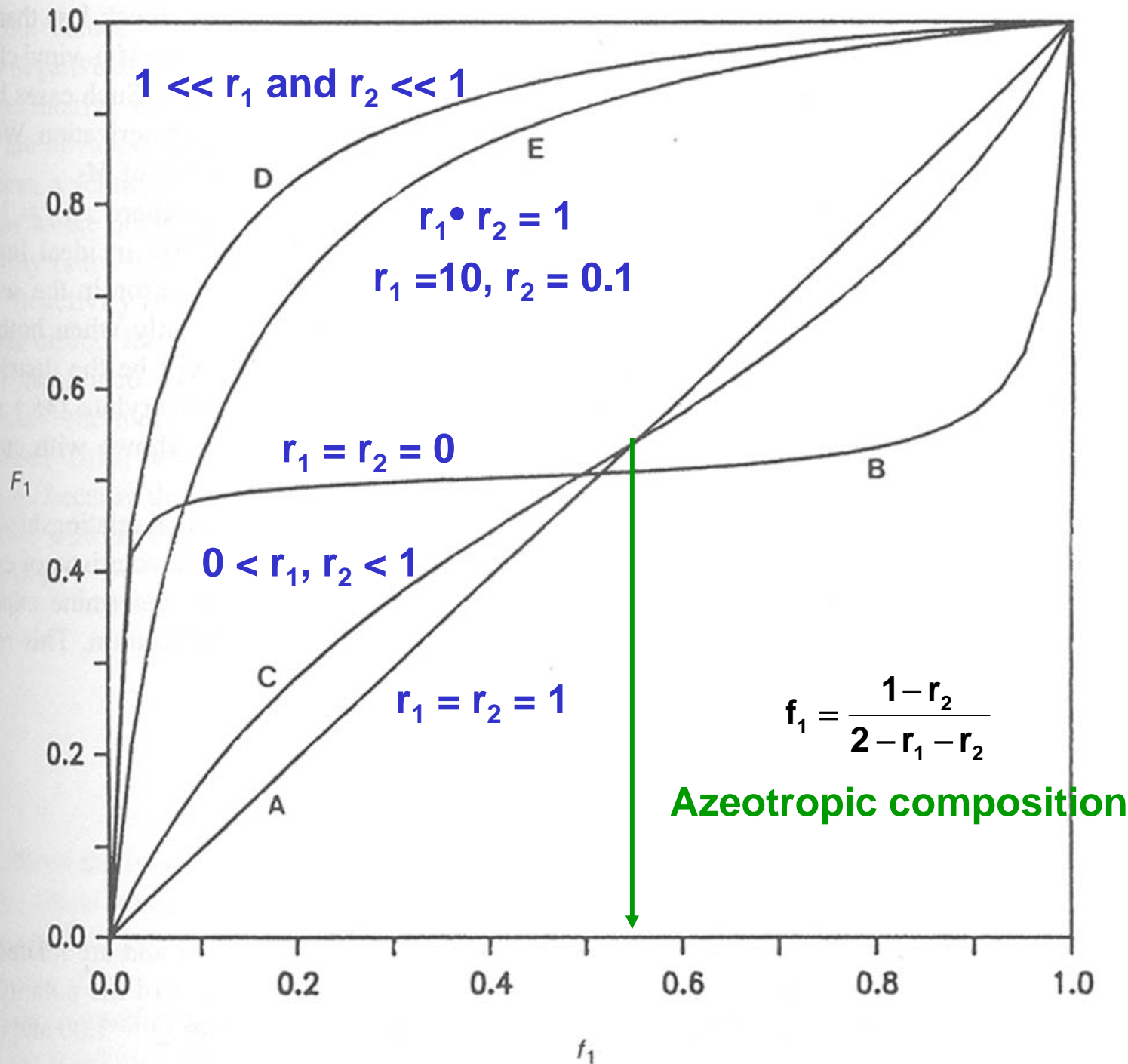
cf. **Ideal solution**

$$\frac{P_1}{P_1 + P_2} = \frac{X_1 P_1^\circ}{X_1 P_1^\circ + X_2 P_2^\circ} = \frac{X_1 \frac{P_1^\circ}{P_2^\circ}}{X_1 \frac{P_1^\circ}{P_2^\circ} + X_2}$$

**Table 6.9 Reactivity Ratios**

$M_1$	$M_2$	$r_1$	$r_2$	Temperature( $^{\circ}C$ )
<b>Styrene</b>	<b>Methyl methacrylate</b>	<b>0.52</b>	<b>0.46</b>	<b>60</b>
<b>Styrene</b>	<b>Acrylonitrile</b>	<b>0.40</b>	<b>0.04</b>	<b>60</b>
<b>Styrene</b>	<b>Vinyl acetate</b>	<b>55</b>	<b>0.01</b>	<b>60</b>
<b>Styrene</b>	<b>Maleic anhydride</b>	<b>0.041</b>	<b>0.01</b>	<b>60</b>
<b>Styrene</b>	<b>Vinyl chloride</b>	<b>17</b>	<b>0.02</b>	<b>60</b>
<b>Styrene</b>	<b>1,3-Butadiene</b>	<b>0.58</b>	<b>1.35</b>	<b>50</b>
<b>Styrene</b>	<b>Isoprene</b>	<b>0.54</b>	<b>1.92</b>	<b>80</b>
<b>Methyl methacrylate</b>	<b>Vinyl chloride</b>	<b>10</b>	<b>0.1</b>	<b>68</b>
<b>Methyl methacrylate</b>	<b>Vinyl acetate</b>	<b>20</b>	<b>0.015</b>	<b>60</b>
<b>Methyl methacrylate</b>	<b>Acrylonitrile</b>	<b>1.20</b>	<b>0.15</b>	<b>60</b>
<b>Methyl methacrylate</b>	<b>1,3-Butadiene</b>	<b>0.25</b>	<b>0.75</b>	<b>90</b>
<b>Ethylene</b>	<b>Tetrafluoroethylene</b>	<b>0.38</b>	<b>0.1</b>	<b>25</b>
<b>Ethylene</b>	<b>Acrylonitrile</b>	<b>0</b>	<b>7</b>	<b>20</b>
<b>Ethylene</b>	<b>Vinyl acetate</b>	<b>0.97</b>	<b>1.02</b>	<b>130</b>





## Q-e Scheme (Alfrey-Price Treatment)

$$k_{12} = P_1 Q_2 \exp(-e_1 e_2)$$

where

$$\begin{cases} P_1 = \text{reactivity of radical } M_1^\bullet \\ Q_2 = \text{reactivity of monomer } M_2 \\ e_1 = \text{polarity of monomer } M_1 \\ e_2 = \text{polarity of monomer } M_2 \end{cases}$$

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{P_1 Q_1 \exp(-e_1 e_1)}{P_1 Q_2 \exp(-e_1 e_2)} = \left( \frac{Q_1}{Q_2} \right) \exp[-e_1(e_1 - e_2)]$$

$$r_2 = \left( \frac{Q_2}{Q_1} \right) \exp[-e_2(e_2 - e_1)]$$

Styrene: **standard**

$$Q = 1.00$$

**Resonance factor**  
(+ **steric factor**)

$$e = -0.80$$

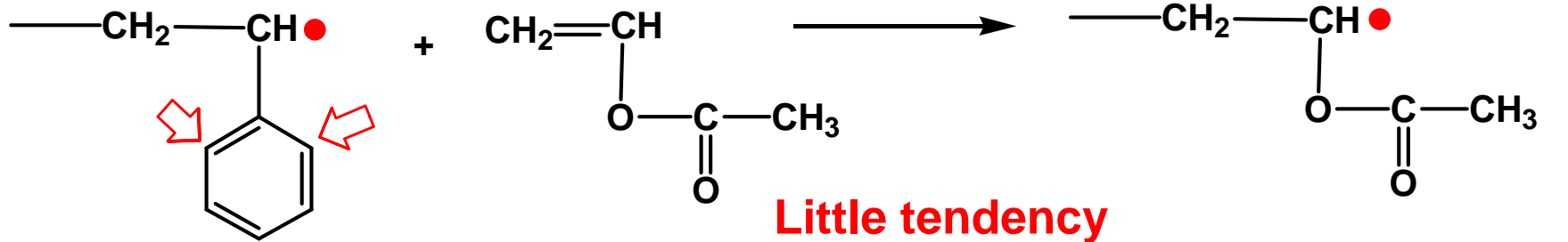
**Polarity factor**

**+** : **electron-withdrawing** group

**-** : **electron-donating** group

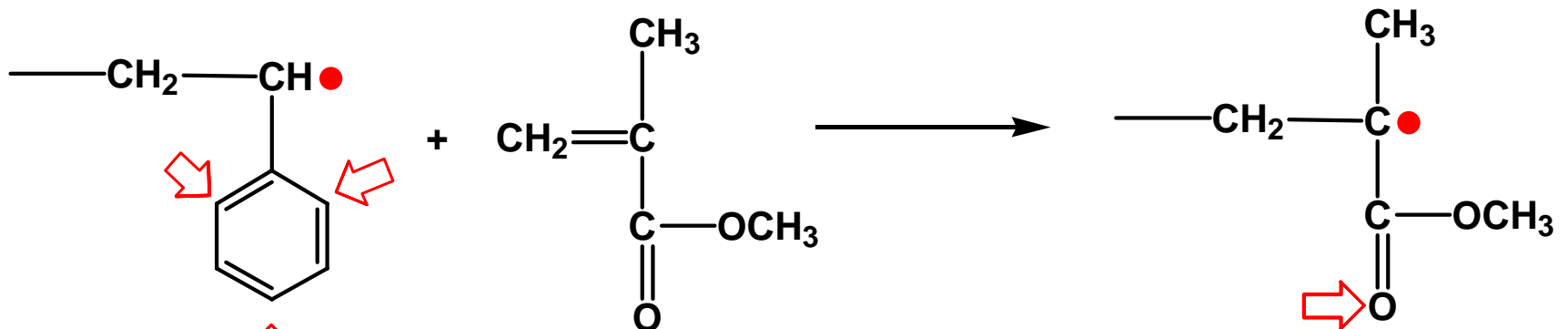
**Table 6.10 Reactivity (Q) and Polarity (e) of Monomer**

<i>Monomer</i>	Q	e
1-vinylnaphthalene	1.94	-1.12
p-Nitrostyrene	1.63	0.39
p-Methoxystyrene	1.36	-1.11
Styrene	1.00	-0.80
Methyl methacrylate	0.74	0.40
Acrylonitrile	0.60	1.20
Methyl acrylate	0.42	0.60
Vinyl chloride	0.044	0.20
Vinyl acetate	0.026	-0.22



**Resonance-stabilization**

**No resonance-stabilization**



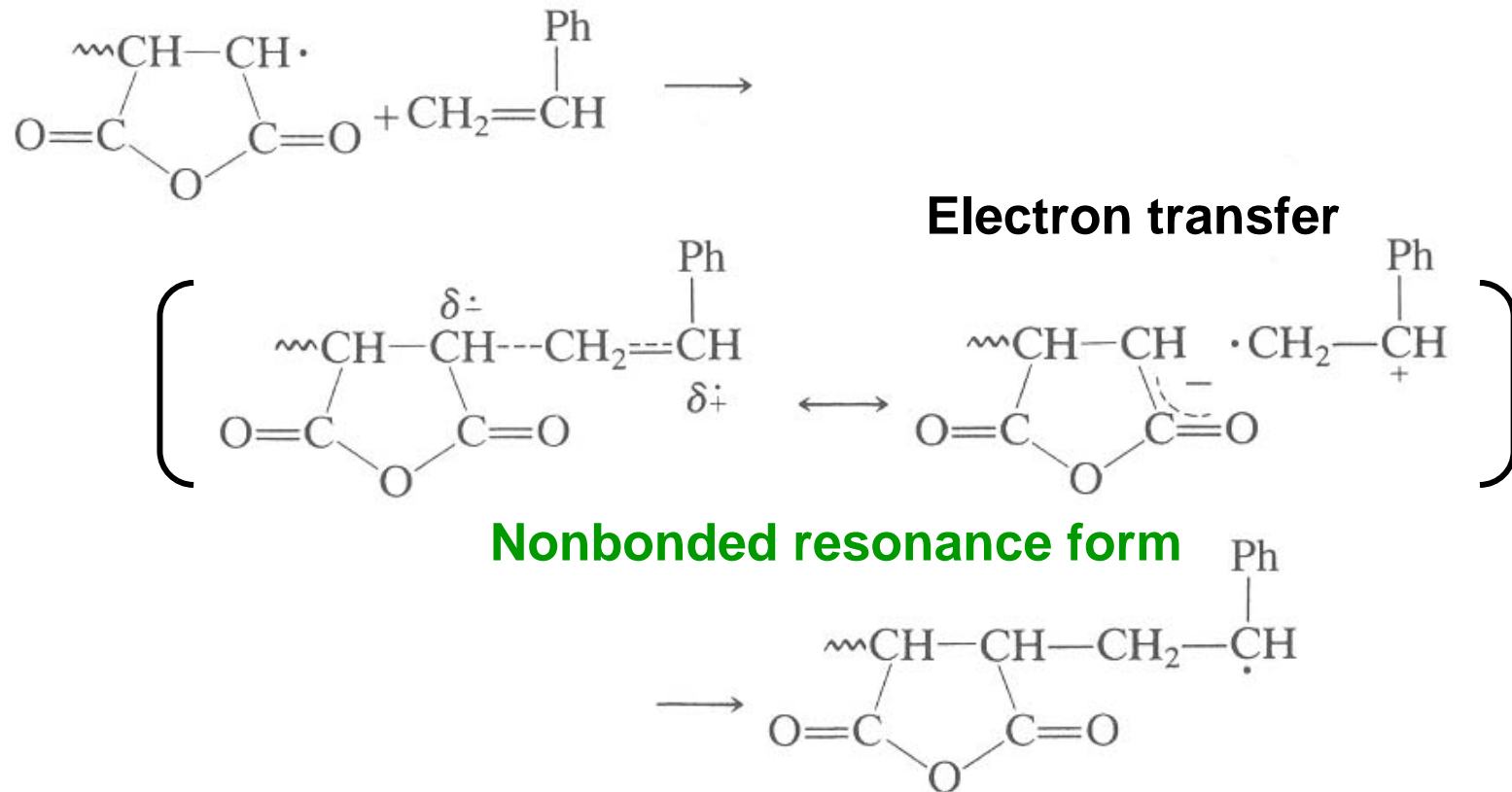
Each radical has about **twice** as much tendency to react with its opposite monomer

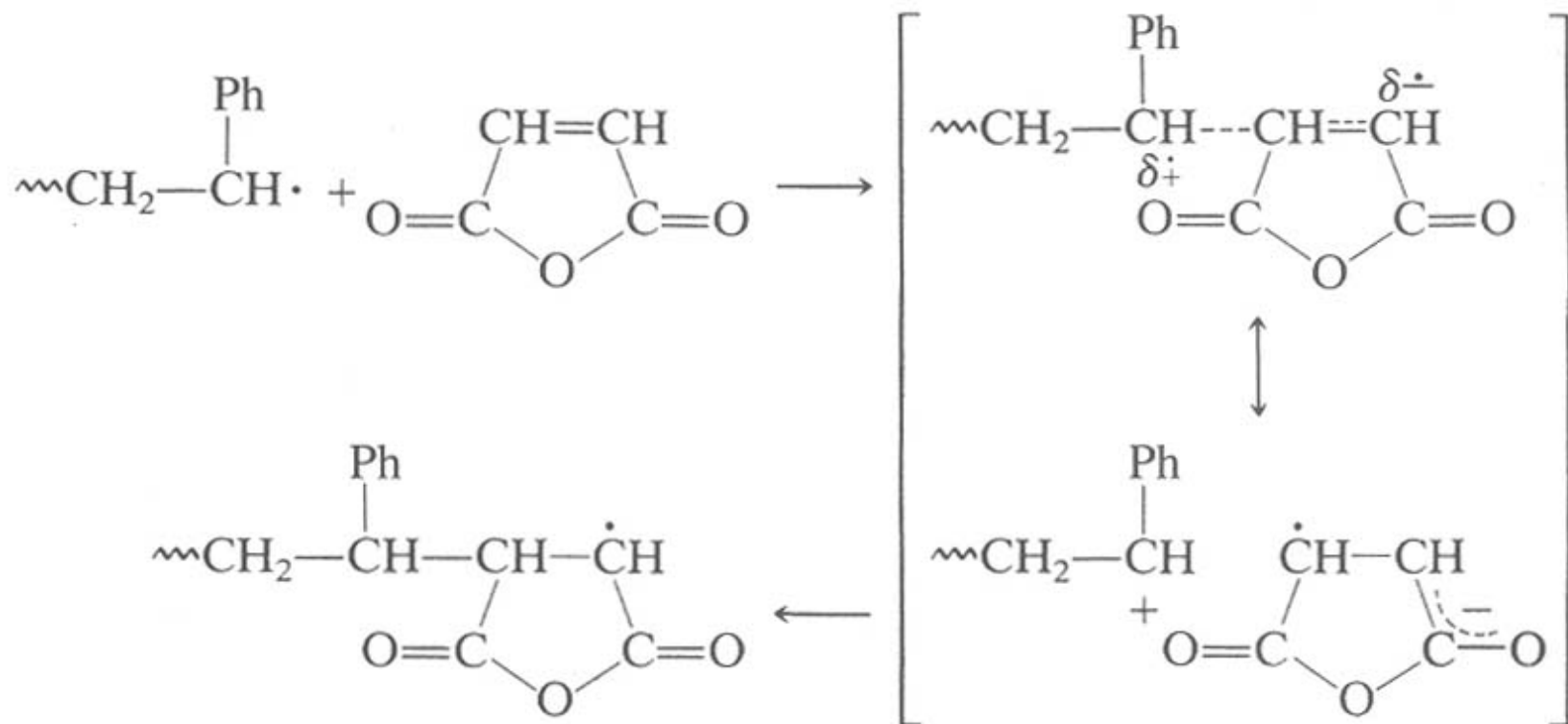
$\therefore$  **Polar effect**

# Copolymerization of **styrene** and **maleic anhydride**

Strong tendency toward **alternation** ( $r_1$  and  $r_2 = \sim 0$ )

## 1) **Polar effects** in the **transition state**



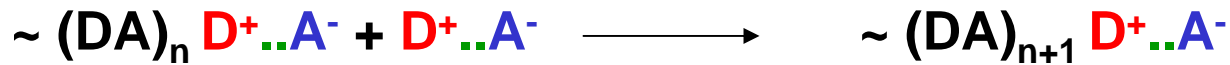


**Electron transfer**

**Nonbonded resonance form**

## 2) Formation of **Charge-transfer complexes** between comonomers

Homopolymerization of charge-transfer complex



charge-transfer complex

<Evidence>

(1)  $R_p$  maximum when **monomer composition ratio = 1:1**

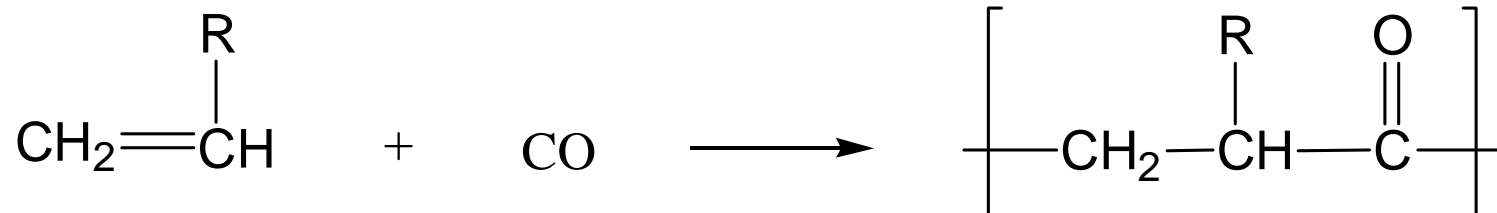
→ maximum conc. of **donor-acceptor complex**

(2) **Alternation** is independent of monomer feed ratios, and **other reactive monomers** included with the feed **fail to react** while alternating copolymer is forming

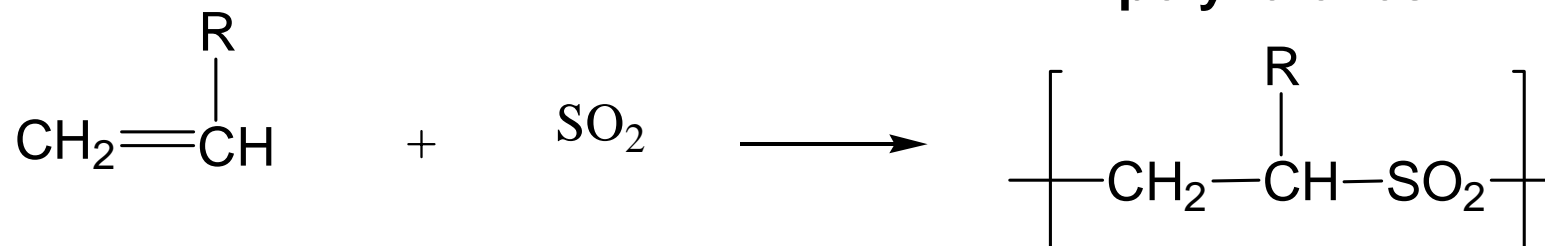
(3)  $R_p$  is enhanced by addition of **Lewis acids**, which increase the **acceptor properties** of one of the monomers

(4) **Chain transfer agents** have little effect on the mol. wt. of the copolymer

Other compounds that undergo free radical-initiated copolymerization with vinyl monomers are **CO** and **SO<sub>2</sub>**



**polyketones**



**polysulfones**

**alternation**