CHAIN COPOLYMERIZATION

Chapter 06

Lecture 07

Definition : Homopolymer and Copolymer

- Homopolymer
- Copolymer

$M_1 + M_2 \rightarrow$

$\sim M_1M_2M_2M_1M_2M_2M_2M_1M_1M_2M_1M_1M_2M_2M_1M_1M_1\sim$

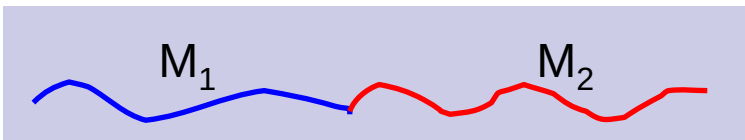
- Molar Ratio
- Reactivity

Importance of Chain Copolymerization

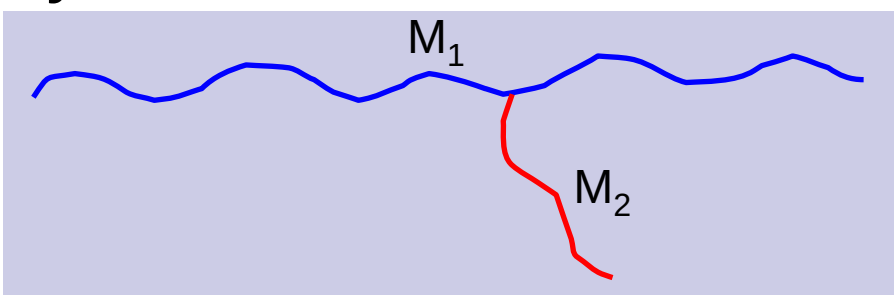
- Studying the effect of chemical structure on reactivity
- Tailor-making a polymer product with desired properties
- Examples:
  - Polystyrene — brittle, low impact strength, low solvent resistance
  - Poly(styrene-acrylonitrile) — ↑ impact & solvent resistance
  - Poly(styrene-butadiene) — elastomer
  - Terpolymer — improve all properties mentioned

Types of Copolymers

- Random copolymer: *-ran-* ex: poly(styrene-ran-acrylonitrile)
- Alternating copolymer: *-alt-* ex: poly(styrene-alt-acrylonitrile)
- Block copolymer:



- Graft copolymer:

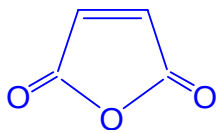


※ If the type of copolymer is not specified → using *-co-*

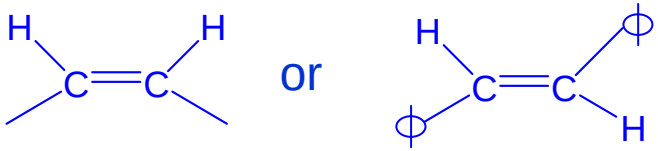
Copolymer Composition

- Copolymerization Equation ; Monomer Reactivity Ratio
  - ⇨ Polymer composition (product) $\overset{\text{usually}}{\neq}$ polymer composition (feeding)
  - ⇨ Reactivity in homopolymerization
  - ⇨ Reactivity in copolymerization

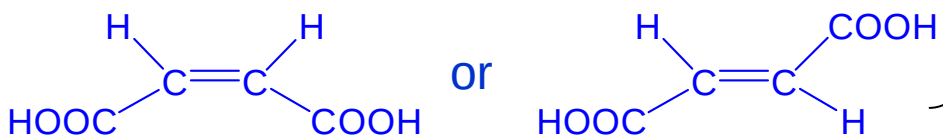
※ Maleic anhydride



Stilbene



Fumaric ester



Copolymerization
>> Homopolymerization

First-Order Markov (Terminal Model) of Copolymerization

Assume: The chemical reactivity of the propagating chain (free-radical, carbocation, or carbanion) in a copolymerization

1. Dependent only on the identity of the monomer unit at the growing end
2. Independent on the chain composition, chain length…….

$$M_1^* + M_1 \xrightarrow{K_{11}} M_1^*$$ (homopropagation ; self-propagation)

$$M_1^* + M_2 \xrightarrow{K_{12}} M_2^*$$ (cross-propagation ; crossover reaction)

$$M_2^* + M_1 \xrightarrow{K_{21}} M_1^*$$

$$M_2^* + M_2 \xrightarrow{K_{22}} M_2^*$$

First-Order Markov (Terminal Model) of Copolymerization

Assume: All propagation reaction are irreversible

The rates of disappearance:

$$\frac{-d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \qquad \text{Eq(1)}$$

$$\frac{-d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] \qquad \text{Eq(2)}$$

Dividing Eq(1) by Eq(2):

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]} \qquad \text{Eq(3)}$$

Assume: All reaction species (M1* and M2*) reach a steady-state concentraction. (for removing the terms of [M1*] & [M2*] in eq.)

i.e. Both [M1*] and [M2*] remain constant the rates of interconversion are equal.

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2] \qquad \text{Eq(4)}$$

First-Order Markov (Terminal Model) of Copolymerization

Combine Eq(3) , Eq(4) and make a rearrangement:

$$\frac{d[M_1]}{d[M_2]} = \frac{\frac{k_{11}k_{21}[M_2^*][M_1]^2}{K_{12}[M_2]} + k_{21}[M_2^*][M_1]}{k_{22}[M_2^*][M_2] + k_{21}[M_2^*][M_1]}$$

Define: $r_1 = \frac{k_{11}}{k_{12}}$; $r_2 = \frac{k_{22}}{k_{21}}$ (monomer reactivity)

When r > 1 homopolymerization > cross-reaction

r < 1 homopolymerization < cross-reaction

r = 0 unable to undergo homopolymerization

Then,

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

Copolymerization equation ;
Copolymer composition equation

First-Order Markov (Terminal Model) of Copolymerization

Define: The mole fraction of monomer M_1 in the feed

$$f_1 = 1-f_2 = \frac{[M_1]}{[M_1] + [M_2]}$$

The mole fraction of monomer M1 in the copolymer

$$F_1 = 1-F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$

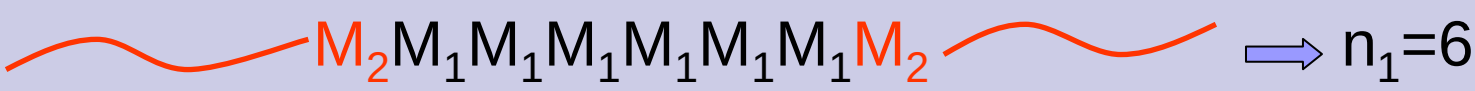
Then, the copolymer composition equation can be written as :

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

Statistical Derivation of Copolymerization Equation

$\overline{n}_1$: the average of M_1 monomer units that follow each other consecutively in a sequence uninterrupted by M_2 units but bounded on each end of the sequence by M_2 units

ex:



P_{11}: the transition (conditional) probability for forming M_1M_1 dyad in the copolymer chain

P_{12}: the transition (conditional) probability for forming M_1M_2 dyad in the copolymer chain

P_{21}: the transition (conditional) probability for forming M_2M_1 dyad in the copolymer chain

P_{22}: the transition (conditional) probability for forming M_2M_2 dyad in the copolymer chain

Statistical Derivation of Copolymerization Equation

Therefore,

$$P_{11} = \frac{\left(\text{the rate for } M_1^* \text{ adding } M_1\right)}{\left(\text{The sum of the rates for } M_1^* \text{ adding } M_1 \text{ and } M_2\right)}$$

$$= \frac{k_{11}[M_1^*][M_1]}{k_{11}[M_1^*][M_1] + k_{12}[M_1^*][M_2]} = \frac{r_1[M_1^*][M_1]}{r_1[M_1^*][M_1] + [M_1^*][M_2]}$$

$$= \frac{r_1}{r_1 + ([M_2]/[M_1])}$$

$$P_{12} = \frac{k_{12}[M_1^*][M_2]}{k_{11}[M_1^*][M_1] + k_{12}[M_1^*][M_2]} = \frac{[M_2]}{r_1[M_1] + [M_2]}$$

Statistical Derivation of Copolymerization Equation

The number average sequence length n_1 of monomer M_1:

$$\bar{n}_1 = \sum_{X=1}^{\infty} X(N_1)_X = (N_1)_1 + 2(N_1)_2 + 3(N_1)_3 + 4(N_1)_4 + \cdots\cdots$$

$(N_1)_x$: the probability of forming a sequence of M_1 units with length X

$\because$ $\underbrace{M_1M_1}_{P_{11}}M_1M_1M_1M_2$

$P_{11}\underbrace{P_{11}}$

$P_{11}P_{11}\underbrace{P_{11}}$

$P_{11}P_{11}P_{11}\underbrace{P_{11}}$

$P_{11}P_{11}P_{11}P_{11}P_{12}$ $\quad\therefore (N_1)_5 = P_{11}^4P_{12}$

Therefore:

$$(N_1)_X = (P_{11})^{(X-1)}P_{12} \qquad \because P_{11} < 1, \text{ series expansion}$$

$$n_1 = P_{12}\left(1 + 2P_{11} + 3P_{11}^{\ 2} + 4P_{11}^{\ 3} + \cdots\right)$$

$$= \frac{P_{12}}{(1-P_{11})^2} = \frac{1}{P_{12}} = \frac{r_1[M_1]+[M_2]}{[M_2]}$$

Statistical Derivation of Copolymerization Equation

$$\overline{n}_2 = \frac{P_{21}}{(1-P_{22})^2} = \frac{1}{P_{21}} = \frac{r_2[M_2] + [M_1]}{[M_1]}$$

$$\frac{\overline{n}_1}{\overline{n}_2} = \frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1]+[M_2])}{[M_2]([M_1]+r_2[M_2])}$$

- ➔ Holds for both steady-state and nonsteady-state.
- ➔ The reactivity of a propagating species is dependent only on the ultimate unit.
- ➔ No depropagation occur.
- ➔ The formation of a high *MW* polymer.

Range of Applicability of Copolymerization Equation

- Applicable to radical, cationic, and anionic chain copolymerization.
- Independent on the differences in the rates of initiation and termination.
- Independent on the absence or presence of inhibitors or chain transfer agents.
- The copolymer must be a high polymer.

Range of Applicability of Copolymerization Equation

The values of monomer reactivity ratio, r, for any particular comonomer pair can be very different depending on the mode of initiation

Ex:	styrene	methyl methacrylate
radical	0.52	0.46
cationic	10	0.1
anionic	0.1	6

Fig. 6-1

Dependence of the instantaneous copolymer composition F1 and the initial comonomer feed composition f1 for Styrene-MMA

Types of Copolymerization Behavior

1) Ideal copolymerization : $r_1 r_2 = 1$
2) Alternating copolymerization : $r_1 = r_2 = 0$
3) Block copolymerization : $r_1 > 1$, $r_2 > 1$

Ideal copolymerization (r_1r_2=1)

Two types of propagating species M1* and M2* show the same preference for adding one or the other of the two monomers.

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

So, the relative rates of incorporation of the two monomers into the copolymer are independent of the identity of the unit at the end of the propagating species.

The copolymerization equation becomes

$$\frac{d[M_1]}{d[M_2]} = \frac{r_1[M_1]}{[M_2]} \quad \text{or} \quad F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

Ideal copolymerization ($r_1 r_2 = 1$)

∗ Most ionic copolymerizations are characterized by the ideal type of behavior

when $r_1 = r_2 = 1$ → Random (Bernoullian) copolymer

$r_1 > 1$, $r_2 < 1$

or $r_1 < 1$, $r_2 > 1$

} → The copolymer will contain a larger proportion of the more reactive monomer in random placement

↓

Fig. 6-2

Dependence of the instantaneous copolymer composition F_1 and the initial comonomer feed composition f_1 for the indicated values of r_1

$r_1 r_2 = 1$

Alternating copolymerization $r_1=r_2=0$

The propagating chain preferentially react with the different type of monomer as the chain-end ⇒ alternating copolymer

The copolymerization equation is written as:

$$\frac{d[M_1]}{d[M_2]} = 1 \quad \text{or} \quad F_1=0.5$$

Dependence of the instantaneous copolymer composition F_1 on the initial comonomer feed composition f_1

r_2=0.5

Block copolymerization (r_1>1, r_2>1)

This type of behavior has been encountered only in a few copolymerization initiated by coordination catalysts.

∗ If $r_1 >> r_2$ ⟹ block copolymer

Ex: styrene - vinyl acetate

55 0.01 monomer reactivity ratio (by radical polymerization)

Variation of Copolymer Composition with Conversion

- Instantaneous copolymer composition : at very low degrees of conversion (<5%).

Consider:

1) A system initially containing a total of M moles of the two monomers.
2) $F_1 > f_1$ (i.e. M_1 is richer in copolymer than in feed)
3) dM moles of monomers have been copolymerization.

Then

1) Number of moles of M_1 in copolymer = $F_1 dM$
2) Number of moles of M_1 in feed = $(M-dM)(f_1-df_1)$

$$F_1 dM = \underbrace{Mf_1}_{\text{\# of moles of } M_1 \text{ before reaction}} - \underbrace{\left[(M-dM)(f_1-df_1)\right]}_{\text{\# of moles of } M_1 \text{ after reaction}}$$

$$= Mdf_1 + f_1 dM - dMdf_1$$

($dMdf_1$ → 0)

Variation of Copolymer Composition with Conversion

$$\frac{dM}{M} = \frac{1}{F_1 - f_1} df_1$$

Sub 0 : initial value

$$\int_{M_0}^{M} \frac{dM}{M} = \ln \frac{M}{M_0} = \int_{(f_1)_0}^{f_1} \frac{df_1}{(F_1 - f_1)}$$

Recalling , for a given set of r_1 and r_2 ,

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

therefore,

$$1 - \underbrace{\frac{M}{M_0}}_{\text{Degree of conversion}} = 1 - \left[\frac{f_1}{(f_1)_0}\right]^{\alpha} \left[\frac{f_2}{(f_2)_0}\right]^{\beta} \left[\frac{(f_1)_0 - \delta}{f_1 - \delta}\right]^{\gamma}$$

and $\alpha = \frac{r_2}{1 - r_2}$ $\beta = \frac{r_1}{1 - r_1}$ $\gamma = \frac{1 - r_1 r_2}{(1 - r_1)(1 - r_2)}$ $\delta = \frac{1 - r_2}{2 - r_1 - r_2}$

Fig. 6-4 , Fig. 6-5 , Fig. 6-6

Variations in feed and copolymer compositions with conversion for styrene (M_1) - methyl methacrylate (M_2)

$(f_1)_0 = 0.80$, $(f_2)_0 = 0.20$

$r_1=0.53$, $r_2=0.56$

Dependence of the instantaneous copolymer composition F_1 on the initial comonomer feed composition f_1 and the percent conversion of styrene (M_1)-2-vinylthiophene (M_2)

r_1=0.53

r_2=3.10

Distribution of copolymer composition at 100% conversion for styrene-2-vinylthiophene at the indicated values of mole fraction styrene in the initial comonomer feed

Microstructure of Copolymer

- Sequence-length distribution

the distributions of the various lengths of the M_1 and M_2 sequence.

- The probability of forming M_1 sequence of length X : $(N_1)_x = (P_{11})^{(x-1)}P_{12}$
- The probability of forming M_2 sequence of length X :

Recalling: $P_{11} = \dfrac{r_1}{r_1 + \left(\dfrac{[M_2]}{[M_1]}\right)}$ $P_{12} = \dfrac{[M_2]}{r_1[M_1]+[M_2]}$

$P_{22} = \dfrac{r_2[M_2]}{r_2[M_2]+[M_1]}$ $P_{21} = \dfrac{[M_1]}{r_2[M_2]+[M_1]}$

Fig. 6-9 , Fig. 6-10

∗ High-resolution NMR is a powerful tool for analysis of copolymer microstructure.

➔ An alternate method for evaluating the monomer reactivity ratios.

Sequence-length distribution for an ideal copolymerization with $r_1 = r_2 = 1$ and $f_1 = f_2$

$P_{11}=P_{22}=P_{12}=P_{21}$

2ad =25%
3ad = 12.5%
4ad = 6.25%
5ad = 3.13%

Sequence-length distribution for an ideal polymerization with $r_1 = 5$, $r_2 = 0.2$ and $f_1 = f_2$

$P_{11} = P_{21} = 0.8333$
$P_{12} = P_{21} = 0.1667$

Sequence-length Distribution for an Alternating Copolymerization $r_1 = r_2 = 0.1$ and $f_1 = f_2$

$P_{11} = P_{22} = 0.0910$
$P_{12} = P_{21} = 0.9090$

Multicomponent copolymerization

Terpolymerization : M_1, M_2, M_3

$M_1^* + M_1 \rightarrow M_1^*$	$R_{11}=K_{11}[M_1^*][M_1]$
$M_1^* + M_2 \rightarrow M_2^*$	$R_{12}=K_{12}[M_1^*][M_2]$
$M_1^* + M_3 \rightarrow M_3^*$	$R_{13}=K_{13}[M_1^*][M_3]$
$M_2^* + M_1 \rightarrow M_1^*$	$R_{21}=K_{21}[M_2^*][M_1]$
$M_2^* + M_2 \rightarrow M_2^*$	$R_{22}=K_{22}[M_2^*][M_2]$
$M_2^* + M_3 \rightarrow M_3^*$	$R_{23}=K_{23}[M_2^*][M_3]$
$M_3^* + M_1 \rightarrow M_1^*$	$R_{31}=K_{31}[M_3^*][M_1]$
$M_3^* + M_2 \rightarrow M_2^*$	$R_{32}=K_{32}[M_3^*][M_2]$
$M_3^* + M_3 \rightarrow M_3^*$	$R_{33}=K_{33}[M_3^*][M_3]$

➔ 9 possible reaction routes

Six monomer reactivity ratios

$R_{12}=K_{11} / K_{12}$

$R_{13}=K_{11} / K_{13}$

$R_{21}=K_{22} / K_{21}$

$R_{23}=K_{22} / K_{23}$

$R_{31}=K_{33} / K_{31}$

$R_{32}=K_{33} / K_{32}$

Multicomponent copolymerization

The rates of disappearance of monomers:

$$-\frac{d[M_1]}{dt} = R_{11} + R_{21} + R_{31}$$

$$-\frac{d[M_2]}{dt} = R_{12} + R_{22} + R_{32}$$

$$-\frac{d[M_3]}{dt} = R_{13} + R_{23} + R_{33}$$

Assume: All reactive radicals reach the steady-state concentrations.

$$R_{12} + R_{13} = R_{21} + R_{31}$$ (Disappearance rate=generation rate)

$$R_{21} + R_{23} = R_{12} + R_{32}$$

$$R_{31} + R_{32} = R_{13} + R_{23}$$

Multicomponent copolymerization

Therefore, the terpolymer composition equation can be expressed as：

$d[M_1] : d[M_2] : d[M_3] =$

$$[M_1]\left\{\frac{[M_1]}{r_{31}r_{21}}+\frac{[M_2]}{r_{21}r_{32}}+\frac{[M_3]}{r_{31}r_{23}}\right\}\left\{[M_1]+\frac{[M_2]}{r_{12}}+\frac{[M_3]}{r_{13}}\right\}$$

$$:\ [M_2]\left\{\frac{[M_1]}{r_{12}r_{31}}+\frac{[M_2]}{r_{12}r_{32}}+\frac{[M_3]}{r_{32}r_{13}}\right\}\left\{[M_2]+\frac{[M_1]}{r_{21}}+\frac{[M_3]}{r_{23}}\right\}$$

$$:\ [M_3]\left\{\frac{[M_1]}{r_{13}r_{21}}+\frac{[M_2]}{r_{23}r_{12}}+\frac{[M_3]}{r_{13}r_{23}}\right\}\left\{[M_3]+\frac{[M_1]}{r_{31}}+\frac{[M_2]}{r_{32}}\right\}$$

Multicomponent copolymerization

Assume:

$$R_{12}=R_{21}\ ;\ R_{23}=R_{32}\ ;\ R_{31}=R_{13}$$

The equation can be simplified to be:

$$d[M_1] : d[M_2] : d[M_3] =$$

$$[M_1]\left\{[M_1]+\frac{[M_2]}{r_{12}}+\frac{[M_3]}{r_{13}}\right\}$$

$$: \quad [M_2]\frac{r_{21}}{r_{12}}\left\{\frac{[M_1]}{r_{21}}+[M_2]+\frac{[M_3]}{r_{23}}\right\}$$

$$: \quad [M_3]\frac{r_{31}}{r_{13}}\left\{\frac{[M_1]}{r_{31}}+\frac{[M_2]}{r_{32}}+[M_3]\right\}$$

Table 6-1

Predicted and Experimental Compositions in Radical Terpolymerization

Radical Copolymerization

- Effect of reaction conditions
  - Reaction medium
    - feed composition
      - Homogeneous : bulk , solution
      - Heterogeneous
    - monomer reactivity ratios
  - Temperature effect
  - Pressure effect
- Reactivity
  - Resonance effects
  - Steric effects
  - Alternation: Polar effects and complex participation
- Rate of Copolymerization
  - Chemical-controlled termination
  - Diffusion-controlled termination

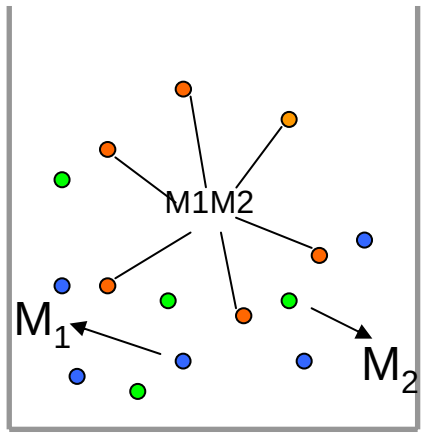
Reaction medium - feed composition

∗ Emulsion polymerization :

⇨ monomer droplets , dispersion medium.

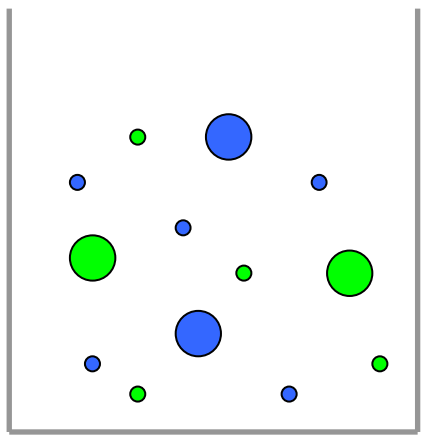
Micelles
Solubility in micelles
Diffusion into micelles

⇨ $f_{1,\ feed} \neq f_{1,\ micelles}$



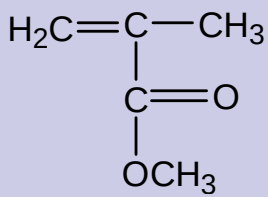
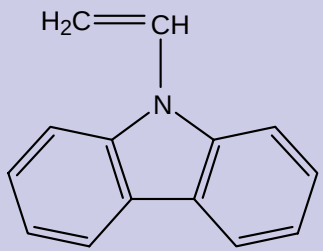
∗ Suspension polymerization:

⇨ Solubility in dispersing medium



Reaction medium- monomer reactivity ratio

∗ Poor solubility of the copolymer product in the reaction medium

	Methyl methacrylate (MMA)	N-vinylcarbazole (NVC)
		
r (benzene)	1.80	0.06
r (MeOH)	0.57	0.75

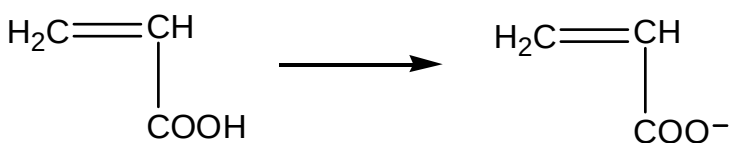
➔ The propagating copolymer chains are completely soluble in benzene form microheterogeneous in MeOH

➔ Adsorption on copolymer chains : NVC > MMA

Reaction medium- monomer reactivity ratio

* Viscosity → mobility of monomer

* pH value (especially for acidic or basic monomer)

At pH=9, 

electrostatic repulsion

Reaction medium- monomer reactivity ratio

* Polarity of the reaction medium
  - Complexation (eg. polar solvent-polar monomer)
  - Ionization

➔ The reactivity of polar monomer usually decreases in polar solvent.

Temperature Effect

$$K = A\exp\left(\frac{-E}{RT}\right)$$ Activation energy $$r_1 = \frac{K_{11}}{K_{12}} = \frac{A_{11}}{A_{12}}\exp\left[\frac{(E_{12} - E_{11})}{RT}\right]$$

- The activation energies for radical propagation are usually relatively small.
- For most pairs of monomers : E_{12}-E_{11} < 10 KJ/mole

The monomer reactivity ratio is usually insensitive to Temperature

ex1 :	styrene	1,3-butadiene	ex2 :	styrene	MMA
r(5℃)	0.64	1.4	r(60℃)	0.52	0.46
r(45℃)	0.60	1.8	r(131℃)	0.59	0.54

However, if E_{12}-$E_{11} \neq 0$

Temp ↗ ⇒ selectivity of monomer ↘

Pressure Effect

The monomer reactivity ratio varies with pressure according to

$$\frac{d \ln r_1}{dP} = \frac{-\left(\Delta V_{11} - \Delta V_{12}\right)}{RT}$$

ΔV_{11}^*: The propagation activation volume for radical M_1^* adding monomer M_1

ΔV_{12}^*: The propagation activation volume for radical M_1^* adding monomer M_2

- P↗ ⇒ propagation rate ↗
- ∵ $(\Delta V_{11}^* - \Delta V_{12}^*) < \Delta V_{11}^*, \Delta V_{12}^*$

  ⇒ r is insensitive to ΔP
- P↗ ⇒ monomer selectivity ↘

  (approach to ideal copolymerization)

Pressure Effect

Ex:

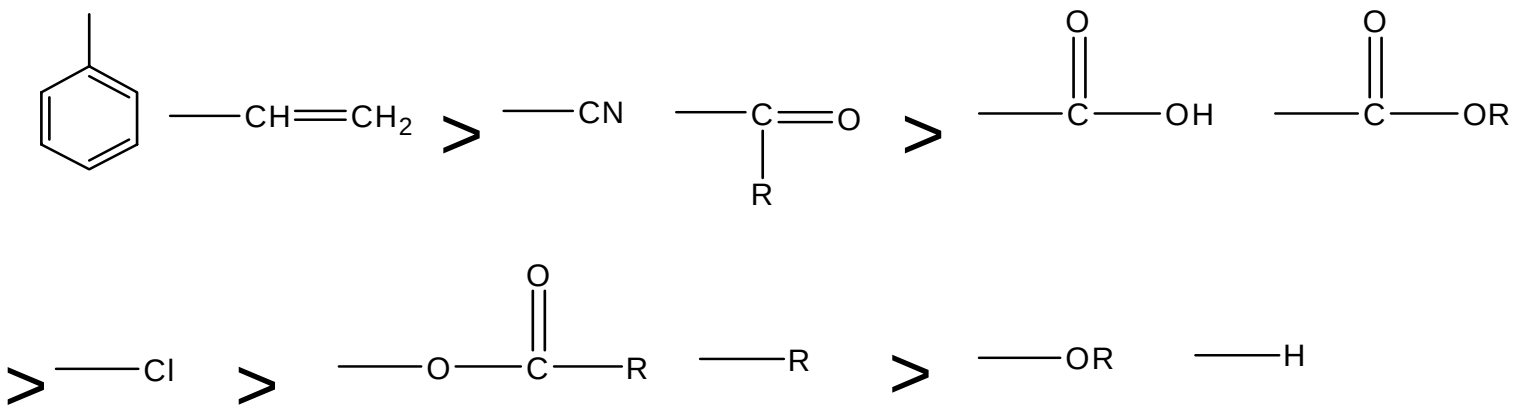
	styrene – acrylonitrile
r_1r_2 (1atm)	0.026
r_1r_2 (1000atm)	0.077

Ex:

	MMA – acrylonitrile
r_1r_2 (1atm)	0.16
r_1r_2 (1atm)	0.91

Reactivity - Resonance effect

- Resonance Effects:
  - Resonance stabilization ↗ ⇨ monomer reactivity ↗
  - Substituents increase the reactivity of a monomer toward radical attack in the general order :



Reactivity - Resonance effect

➔ Unsaturated linkages are most effective in stabilizing the radicals

∵ the loosely bonded π – e^- are available for resonance stabilization

➔ Only the nonbonding e^- on halogen or oxygen are available for interaction with a radical

⇒ Cl > acetoxy > ether

Radical Reactivity

- The order of substituents in enhancing radical reactivity is the opposite of their order in enhancing monomer reactivity.

- The effect of a substituent on radical reactivity is considerably larger than its effect on monomer reactivity.

  Vinyl acetate radical is about 100~1000 times more reactive than styrene radical toward a given monomer. But, styrene monomer is only 50~100 times more reactive than vinyl acetate monomer toward a given radical.

Radical Reactivity

- Consider a system:

$$R^* + M \rightarrow R^*$$

$$R^* + M_s \rightarrow R_s^* \quad \leftarrow \text{Stabilized radical}$$

$$R_s^* + M \rightarrow R^*$$

$$R_s^* + M_s \rightarrow R_s^*$$

M_s : stabilized monomer

The order of the reaction rate :

$$R^* + M_s > R^* + M > R_s^* + M_s > R_s^* + M$$

Reaction coordination diagram for the reaction of a polymer radical with a monomer

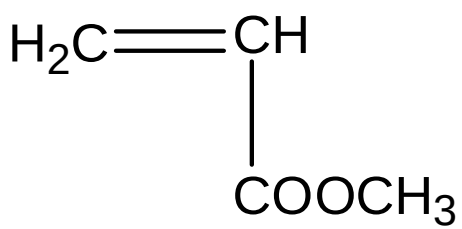
Radical Reactivity

Therefore,

- Monomers without stabilizing substituents (eg. vinyl chloride, vinyl acetate….) will self-propagate faster than those with stabilizing substituents (eg. styrene).

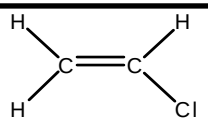
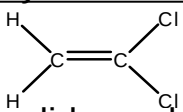
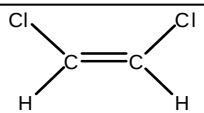
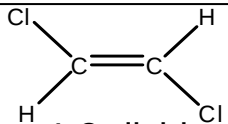
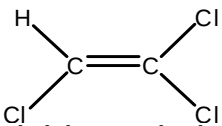
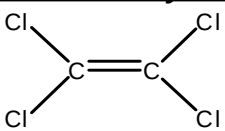
- Copolymerization will occur primarily between two monomers with stabilizing substituents or between two monomers w/o stabilizing substituents.

  ⇨ The copolymerization of styrene-vinyl acetate is not efficient.



Reactivity - Steric effect

Rate constant (K_{12}) for radical-monomer reactions

monomer	Polymer: Vinyl acetate	Polymer: styrene	Radical: acrylonitrile
 Vinyl chloride	10,000	9.7	725
 Vinylidene chloride	23,000	89	2,150
 Cis-1.2-dichloroethylene	365	0.79	—
 Trans-1.2-dichloroethylene	2,320	4.5	—
 trichloroethylene	3,480	10.3	29
 tetrachloroethylene	338	0.83	4.2

x 6

Reactivity –

Polarity Effect and Complex Participation - Alternation

- Polarity difference between two monomers ↗
  ⇨ Tendency toward alternation copolymerization ↗

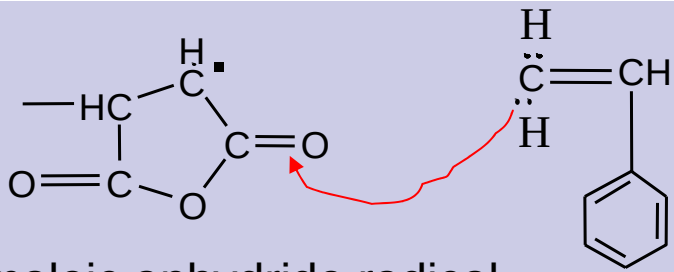
Values of $r_1 r_2$ in Radical Copolymerization

Reactivity –

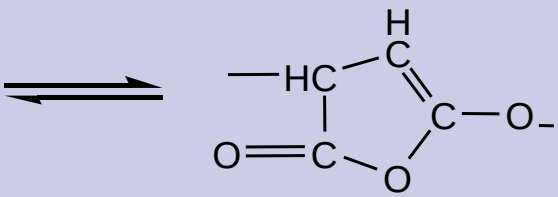
Polarity Effect and Complex Participation - Alternation

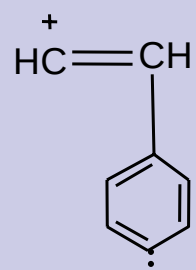
Two possible mechanisms :

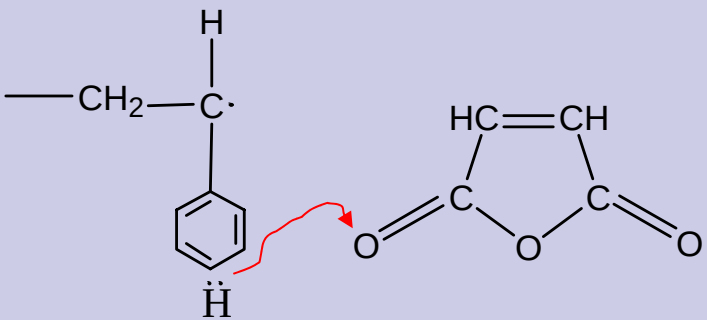
1) The partial e-transfer between the e-donor and e-acceptor species stabilizes the transition state.

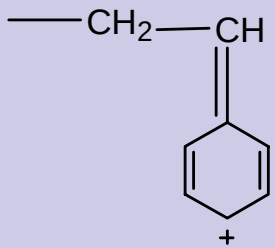


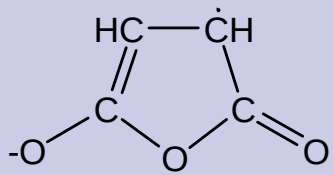
maleic anhydride radical











Reactivity –

Polarity Effect and Complex Participation - Alternation

2) Formation of a 1:1 complex between donor and acceptor monomers ⇒ polymerization of these complexes.

$$M_1 + M_2 \rightleftharpoons M_1M_2$$

complex

$$\sim MM_2^{\bullet} + M_1M_2 \longrightarrow \sim M_1M_2M_1M_2^{\bullet}$$

Reactivity –

Polarity Effect and Complex Participation - Alternation

a) Spectroscopic (UV and NMR) evidence for the formation of charge transfer complexes.

b) Alternation copolymerization occurs over a wide range of feed compositions and a high reaction rate was observed at or near the equimolar feed composition , which corresponds to the max. conc. of complex.

c) Small effect on molar weight for adding chain-transfer agents.

d) Some alternating copolymerization proceed spontaneously w/o adding free-radical initiator.

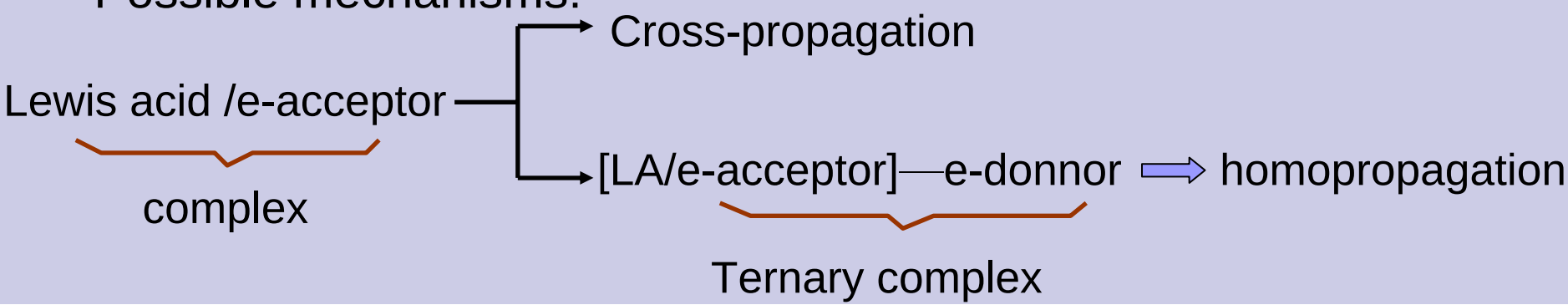
∵ e-transfer between monomers leads to radical formation

Reactivity –

Polarity Effect and Complex Participation - Alternation

➔ To some comonomer pairs , the addition of a Lewis acid ($ZnCl_2$, dialkyl aluminum chloride , alkylaluminum sesquichloride [$AlR_{1-5}Cl_{1-5}$]) increases the tendency to form alternating copolymer.

Possible mechanisms:



➔ Temperature ↗ ⇒ Alternation tendency ↘

➔ Total monomer conc. ↘ ⇒ Alternation tendency ↘

Rate of copolymerization

Two approaches:

A. chemical-controlled termination

Assume:

the termination reaction to proceed by chemical control

For propagation reactions:

$$M_1^* + M_1 \rightarrow M_1^*$$
$$M_1^* + M_2 \rightarrow M_2^*$$
$$M_2^* + M_1 \rightarrow M_1^*$$
$$M_2^* + M_2 \rightarrow M_2^*$$

Rate of copolymerization

Three termination reactions:

$$M_1^* + M_1^* \rightarrow$$

$$M_2^* + M_2^* \rightarrow$$

$$M_1^* + M_2^* \rightarrow$$

The overall rate of copolymerization = the sum of the 4 propagation rates

Rate of copolymerization

Assume:

each type of radical reaches its own steady-state concentration (i.e. inter conversion rates are equal)

Assume :

the total concentration of radicals is also on steady-state.

Therefore,

Rate of copolymerization

Where,

$$\delta_1 = \left(\frac{2K_{t11}}{K_{11}^2} \right)^{1/2} \qquad \delta_2 = \left(\frac{2K_{t22}}{K_{22}^2} \right)^{1/2}$$

$$\Phi = \left(\frac{K_{t12}}{2(K_{t11}K_{t22})^{1/2}} \right)$$

K_{t12}: Cross-termination rate constant

$(K_{t11}K_{t22})^{1/2}$: Geometric mean of the rate constants for self-termination of like radicals

The cross-termination is statistically favored over like-radical-termination by a factor of 2

- $\Phi > 1 \Rightarrow$ cross-termination is favored
  $\Phi < 1 \Rightarrow$ self-termination is favored
- $r_1 r_2 \rightarrow 0$ (i.e. toward alternation), $\Phi \uparrow$ (i.e. cross-termination)
  $\Rightarrow$ polar effect leads to the tendency toward cross-termination

Rate of copolymerization

B. diffusion-controlled termination

- It is well established that termination in radical polymerization is generally diffusion-controlled.

Consider the termination as the reactions:

$$\left.\begin{array}{l} M_1^* + M_1^* \\ M_1^* + M_2^* \\ M_2^* + M_2^* \end{array}\right\} \xrightarrow{K_{t(12)}} \text{Dead polymer}$$

∗ The termination rate constant $K_{t(12)}$ is a function of the copolymer composition.

Rate of copolymerization

Assume:

the total concentration of radicals is on the steady-state.

$$R_t = 2K_{t(12)}([M_1^*]+[M_2^*])^2$$

Assume :

each type of radical reaches a steady-state concentration.

$$K_{21}[M_2^*][M_1] = K_{12}[M_1^*][M_2]$$

Combining these equations with the propagation rate equation,

$$R_p = \frac{(r_1[M_1]^2+2[M_1][M_2]+r_2[M]^2)R_t^{1/2}}{K_{t(12)}^{1/2}\left\{\left(\frac{r_1[M_1]}{K_{11}} + \frac{r_2[M_2]}{K_{22}}\right)\right\}}$$

Ionic Copolymerization

- Ionic Copolymerization v.s. Radical Copolymerization:

  ➔ Ionic copolymerization are much more selective.

  ➔ Cationic copolymerization is limited to monomers with e-donating substituents.

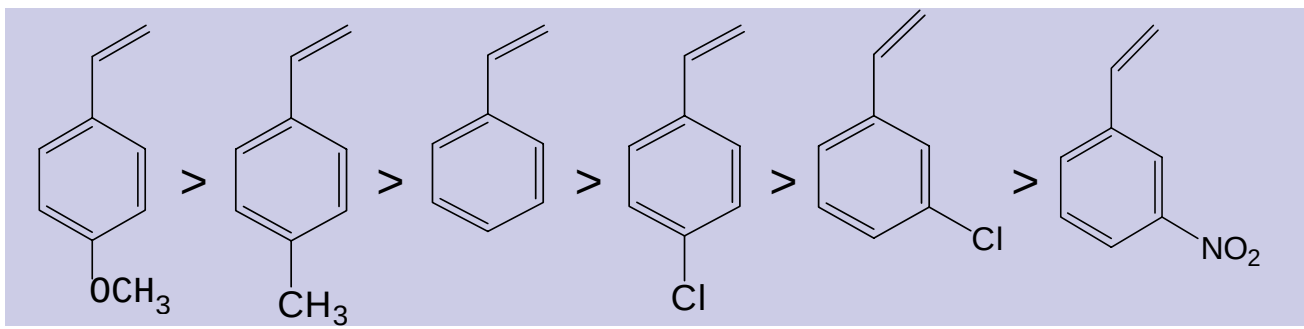
  ➔ Anionic copolymerization is limited to monomers with e-withdrawing substituents.

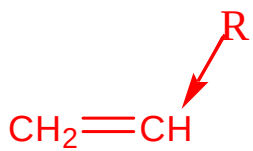
  ➔ The monomer reactivity ratio for ionic copolymerization is sensitive to the changes in the initiator, reaction medium, or temperature.

Cationic Copolymerization

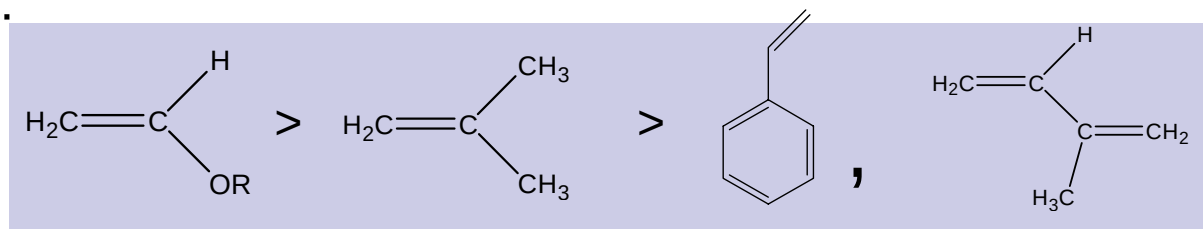
- Reactivity is often influenced to a larger degree by the reaction conditions (solvent, counterion, temperature) than by the structure of the monomer.
  - ⇨ Not as well defined as radical copolymerization
- The effect of a substituent on the reactivity of a monomer:
  - the extent to increase the electron density on the double bond.
  - the ability to resonance stabilize the carbocation

ex1:



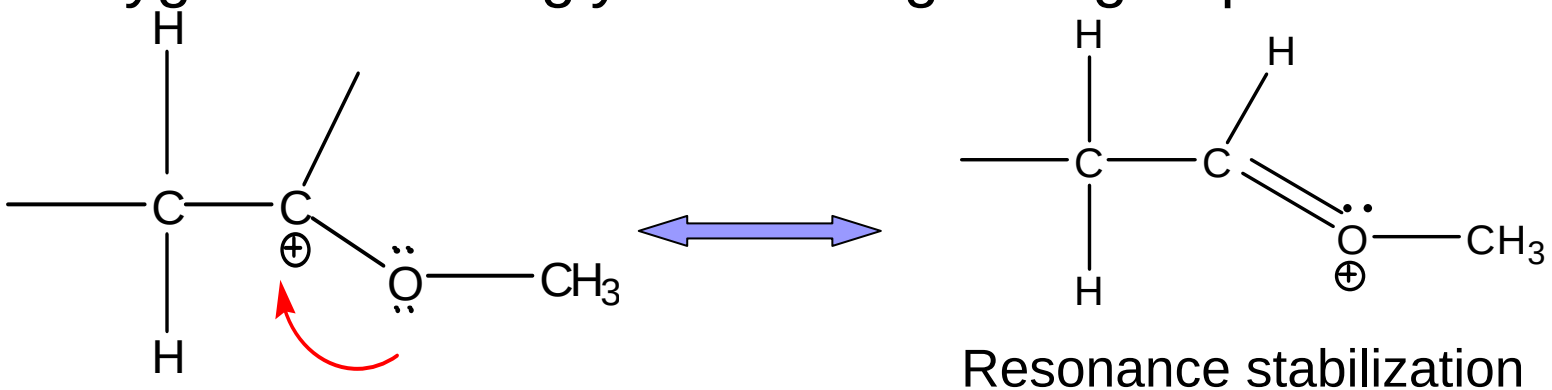


ex2:



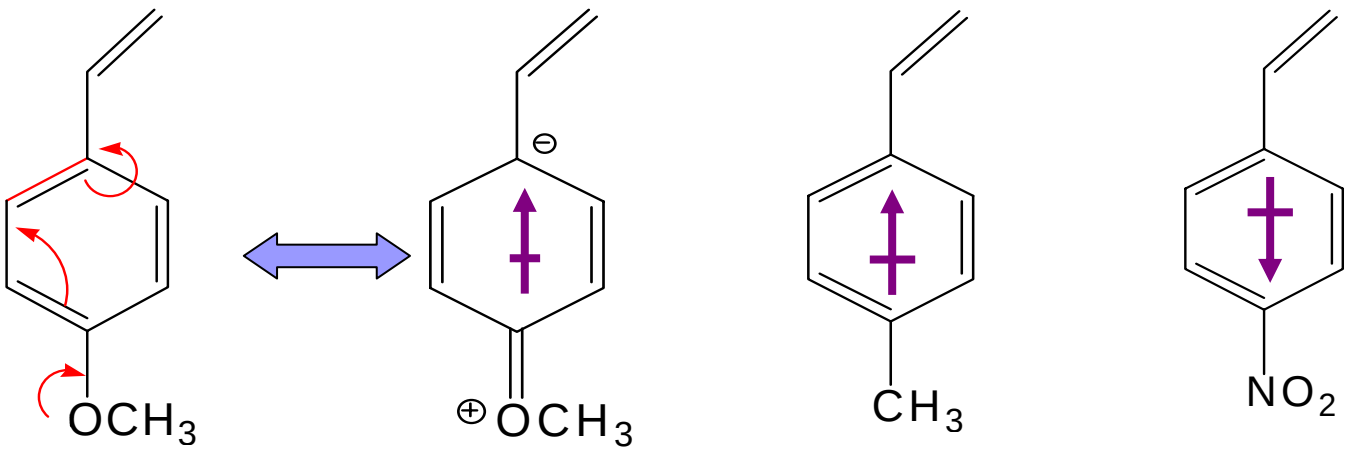
Cationic Copolymerization

∗ Oxygen is a strongly electronegative group.



Resonance stabilization

Resonance-donating

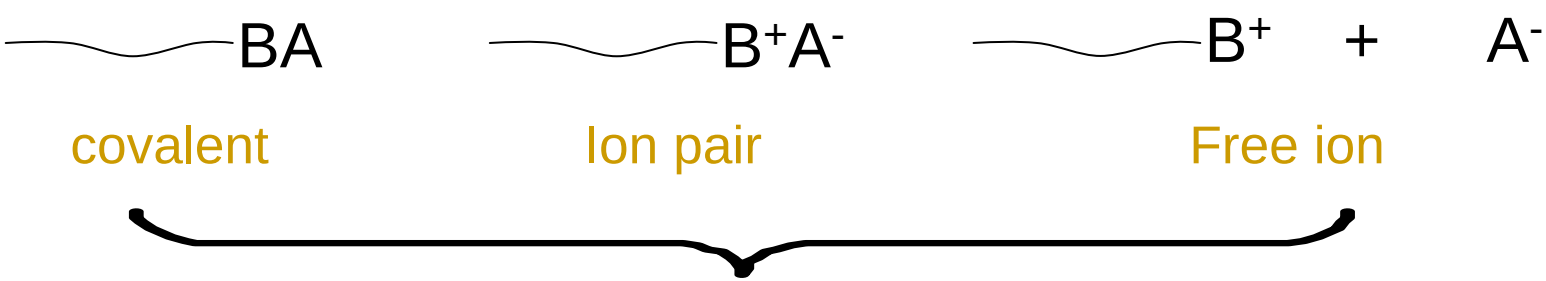


Distance ↘ ➔ field effect ↗

Field effect

Effect of solvent and counterion

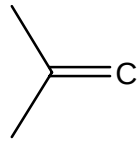
- Solvent and counterion changes ⇨ alterations in the relative amounts of the different types of propagating center.



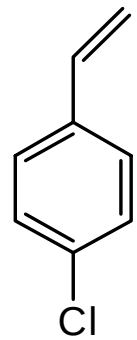
⇨ Complex and difficult to predict

Effect of solvent on r values

r			
isobutylene	P-chlorostyrene	solvent	initiator
1.01	1.02	n-hexane	$AlBr_3$
14.7	0.15	nitrobenzene	$AlBr_3$



isobutylene



P-chlorostyrene

- The propagating centers in the nonpolar medium (*n*-hexane) are preferentially solvated by the more polar monomer (*p*-chlorostyrene).

  ⇒ ↗ the cone. of *p*-chlorostyrene at the reaction site.

- In the polar nitrobenzene, the propagating centers are completely solvated by the solvent.

  ⇒ more reactive isobutylene exhibits its greater reactivity

Effects of solvent and counterion on copolymer composition in styrene-p-methylstyrene copolymerization (Feed= 1:1)

		% styrene in copolymer		
	initiator	toluene	1,2-dichloroethane	nitrobenzene
initiation effectiveness ↑	$SbCl_5$	46	25	28
	AlX_3	34	34	28
	$TiCl_4$, $SnCl_4$	28	27	27
	Cl_3CCOOH	—	27	30
	I_2	—	17	—

- Initiator : $SbCl_5$ (strongest) ; I_2 (weakest)
  - ➔ polymerization by I_2 and trichloroacetic acid proceed predominantly through colvalent species.
- For high polarity solvents (1,2-dichloroethane , nitrobenzene) , the copolymer composition is insensitive to the initiator.
- The copolymer composition is insensitive to the solvent polarity for any initiator except $SbCl_5$(strongest).

Effect of solvent and counterion

- $SbCl_5$ system :

  solvent polarity ↗ ⇒ styrene content in copolymer ↘

- Low polarity solvent (toluene) system :

  initiator strength ↘ ⇒ styrene content ↘

  Polarity , reactivity : *p*-methylstyrene > styrene

  - In poor solvent (toluene) :
    - preference on the solvation of the propagating ion pairs : *p*-methylstyrene > styrene
    - Initiation ability ↘ ⇒ selectivity ↗ ⇒ styrene content ↘
  - In good solvent :
    - ability to complex with propagating centers : solvent > monomer

    ⇒ the influence of the counterions in the reaction ↘

    ⇒ copolymer composition is determined primarily by the chemical reactivity of the monomers.

Effect of temperature

- Ionic copolymerization have a greater spread of propagating activation energies than radical copolymerization

$\triangle T$ has a greater influence on monomer reactivity ratios

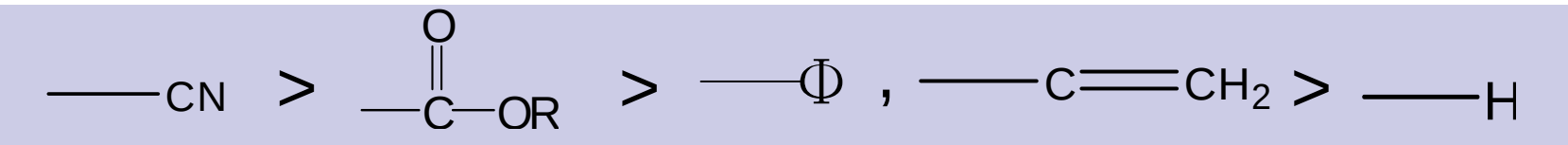
- $T \nearrow \Rightarrow$ $r \rightarrow 1$
  r deviates from 1

} No general trend

Anionic Copolymerization

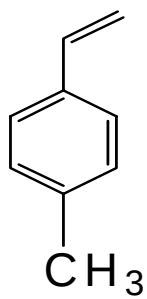
Monomer reactivity:

- Anionic copolymerization $\overset{\text{opposite}}{\longleftrightarrow}$ cationic copolymerization
- Enhanced by e-withdrawing substituents and resonance stabilization
- General order :



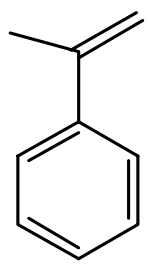
- Tend to be ideal behavior
- Steric effects ⟹ alternative copolymerization

styrene-*p*-methylstyrene



r_1=5.3, r_2=0.18,
r_1r_2=0.95 (ideal)

styrene-α-methylstyrene



r_1=35, r_2=0.003,
r_1r_2=0.11 (→alternation)

Effect of Solvent and Counterion

Effect of Solvent and Counterion on Copolymer Composition in Styrene-Isoprene Copolymerization

Solvent	% Styrene in Copolymer for Counterion	
	Na^+	Li^+
None	66	15
Benzene	66	15
Triethylamine	77	59
Ethyl ether	75	68
Tetrahydrofuran	80	80

- 25℃, Initiator: n-BuLi Relative rate of homopolymerzation: styrene＞isoprene
- In poor solvent: Isoprene is preferentially complexed by Li^+ → rich in copolymer
- In good solvent: The influence of monomer solvation is much less important
- The quantitative effect of solvent on copolymer composition is less for more loosely bound Na**+** counterion.

Deviations from Terminal Copolymerization Model

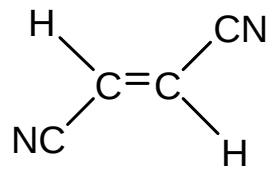
Two important assumptions for Terminal Copolymerization Model :

- Kinetic nature:
  The reactivity of the propagating species depend only on the type of monomer at the terminal of the propagating chain.
- Thermodynamic nature:
  All propagation reactions are irreversible.

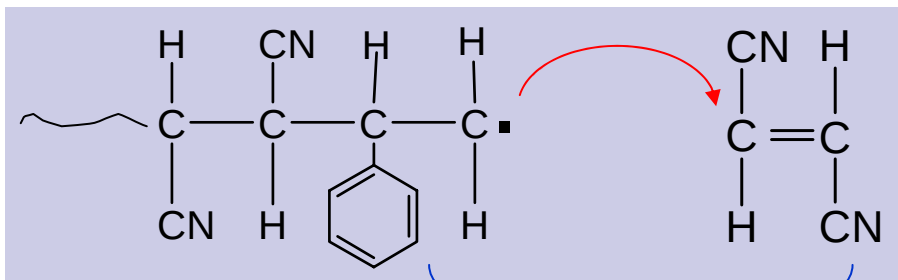
→ **Not always true for some systems!**

Kinetic Penultimate Behavior (Second-Order Markov Behavior)

- The reactivity of the propagating species is affected by the next-to-last (penultimate) monomer unit.
- Observed in many radical copolymerization with monomers containing highly bulky or polar substituents.

Example: styrene + fumaronitrile ()

(M_1) (M_2)



low reactivity

∵ Steric and polar repulsions between the penultimate fumaronitrile unit in the propagating chain and the incoming fumaronitrile monomer.

Mathematical Treatment of Penultimate Effect

Eight propagating reactions:

$$\sim M_1M_1^* + M_1 \xrightarrow{K_{111}} \sim M_1M_1M_1^*$$

$$\sim M_1M_1^* + M_2 \xrightarrow{K_{112}} \sim M_1M_1M_2^*$$

$$\sim M_2M_1^* + M_1 \xrightarrow{K_{211}} \sim M_2M_1M_1^*$$

$$\sim M_2M_1^* + M_2 \xrightarrow{K_{212}} \sim M_2M_1M_2^*$$

$$\sim M_1M_2^* + M_1 \xrightarrow{K_{121}} \sim M_1M_2M_1^*$$

$$\sim M_1M_2^* + M_2 \xrightarrow{K_{122}} \sim M_1M_2M_2^*$$

$$\sim M_2M_2^* + M_1 \xrightarrow{K_{221}} \sim M_2M_2M_1^*$$

$$\sim M_2M_2^* + M_2 \xrightarrow{K_{222}} \sim M_2M_2M_2^*$$

Four reactivity ratios:

$$r_1 = \frac{K_{111}}{K_{112}} \qquad r_1' = \frac{K_{211}}{K_{212}} \qquad r_2 = \frac{K_{222}}{K_{221}} \qquad r_2' = \frac{K_{122}}{K_{121}}$$

Mathematical Treatment of Penultimate Effect

$$\frac{-d[M_1]}{dt} = K_{111}[M_1M_1^*][M_1] + K_{211}[M_2M_1^*][M_1] + K_{121}[M_1M_2^*][M_1] + K_{221}[M_2M_2^*][M_1]$$

$$\frac{-d[M_2]}{dt} = K_{112}[M_1M_1^*][M_2] + K_{212}[M_2M_1^*][M_2] + K_{122}[M_1M_2^*][M_2] + K_{222}[M_2M_2^*][M_2]$$

$$\frac{d[M_1]}{d[M_2]} = \frac{K_{111}[M_1M_1^*][M_1] + K_{211}[M_2M_1^*][M_1] + K_{121}[M_1M_2^*][M_1] + K_{221}[M_2M_2^*][M_1]}{K_{112}[M_1M_1^*][M_2] + K_{212}[M_2M_1^*][M_2] + K_{122}[M_1M_2^*][M_2] + K_{222}[M_2M_2^*][M_2]}$$

Assume: Steady-state concentration for all reactive species (elimination = generation)

$$K_{121}[M_1M_2^*][M_1] + K_{221}[M_2M_2^*][M_1] = K_{112}[M_1M_1^*][M_2] + K_{212}[M_2M_1^*][M_2]$$

Mathematical Treatment of Penultimate Effect

Define:

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

Copolymer composition equation with kinetic penultimate effect

$$\frac{d[M_1]}{d[M_2]} = \frac{1 + \frac{r_1' x(r_1 x + 1)}{(r_1' x + 1)}}{1 + \frac{r_2'(r_2 + x)}{x(r_2' + x)}}$$

➔ If $r_2 = r_2' = 0$ (in capable of self-propagation)

The copolymer composition equation can be simplified to

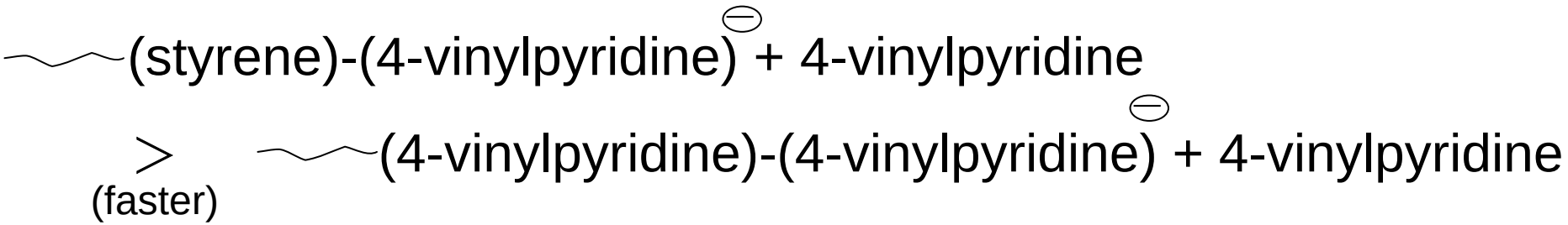
$$\frac{d[M_1]}{d[M_2]} - 1 = \frac{r_1' x(r_1 x + 1)}{r_1' x + 1}$$

Kinetic Penultimate Effect in the radical copolymer of Styrene (M_1) — Fumaronitrile (M_2)

- Copolymer composition $\frac{d[M_1]}{d[M_2]}-1$ vs. comonomer feed composition X
- Solid line: theoretical plot calculated from $\frac{d[M_1]}{d[M_2]}-1=\frac{r_1' x(r_1 x+1)}{r_1' x+1}$ with r_1=0.072, r_1'=1.0
- dashed line: calculated from the copolymer composition equation based on 1st-order Markov model
- Open circle: experimental data

Penultimate Effect

Ex: Anionic copolymerization of styrene and 4-vinylpyridine



∴ The 4-vinylpyridine penultimate unit acts as e- sink and hinders bond formation with the approaching monomer.

➔ Detections on the penultimate effects:

- Experimentally determine copolymer compositions precisely and accurately.
- Easily detected in experiments carried out at very low or very high f1 values.

Depropagation during Copolymerization (Thermodynamic approach)

The alternation of copolymer compositions in copolymerization processes is accounted for the tendency of one of the monomers to depropagate in certain conditions.

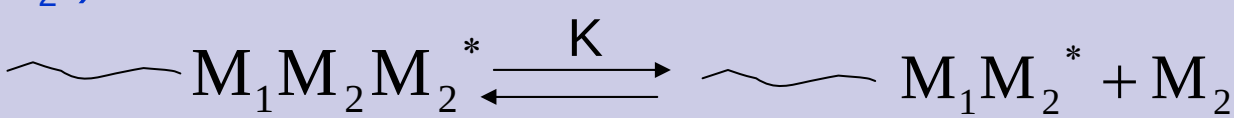
- Monomer concentration dependence.
- Temperature dependence.

Consider a monomer pair (M_1-M_2) system:

- Case Ⅰ

  Assume:

  1. M_1 has absolutely no tendency to depropagate irrespective of the proceeding units in the chain.
  2. M_2 has no tendency to depropagate if it is attached to an M1 units. (~ M_1M_2*)
  3. M_2 tends to depropagate if it is attached to another M_2 unit. (~ M_2M_2*)



Depropagation during Copolymerization (Thermodynamic approach)

The copolymer composition equation in this case is:

$$\frac{d[M_1]}{d[M_2]} = \frac{(r_1[M_1]+[M_2])(1-\alpha)}{[M_2]}$$

Where,

$$\alpha = \frac{1}{2}\left(\left\{1+K[M_2]+\left(\frac{K[M_1]}{r_2}\right)\right\} - \left[\left\{1+K[M_2]+\left(\frac{K[M_1]}{r_2}\right)\right\}^2 - 4K[M_2]\right]^{\frac{1}{2}}\right)$$

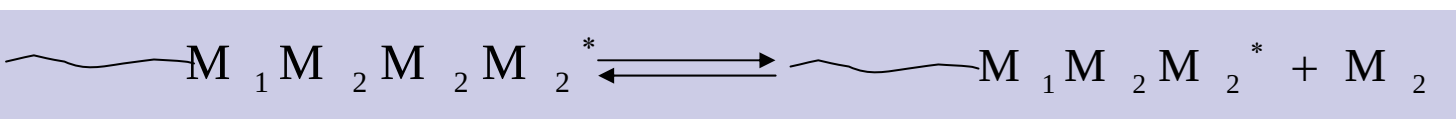
K : equilibrium constant

- Case Ⅱ

  Assume:

  (1) and (2) are the same as case Ⅰ.

  (3) M_2 tends to depropagate only when it is attached to a sequence of two or more M_2 units ($M_2M_2M_2$*)



Depropagation during Copolymerization (Thermodynamic approach)

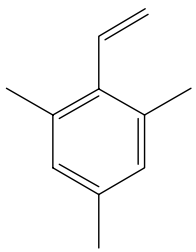
The copolymer composition equation in this case is:

$$\frac{d[M_1]}{d[M_2]} = \frac{\left\{\left(\frac{r_1[M_1]}{[M_2]}\right)+1\right\}\left\{\alpha r + \left[\frac{\alpha}{1-\alpha}\right]\right\}}{\alpha r - 1 + \left\{\frac{1}{1-\alpha}\right\}^2}$$

Where, $r = \dfrac{\left\{K[M_2] + \dfrac{K[M_1]}{r_2} - \alpha\right\}}{K[M_2]}$

K : equilibrium constant

Example: Anionic copolymerization of vinylmesitylene- α -methylstyrene



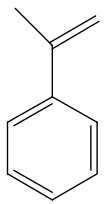
(M_1)

vinyl mesitylene

- T= -78 ℃ → depropagation is negligible
- T= 0 ℃

$[M_1] > [M_1]_C$ (0.75 moles/l) → depropagation is not important.

$[M_1] < [M_1]_C$ at constant $\dfrac{[M_1]}{[M_2]}$



(M_2)

α -methystyrene

→ depropagation is significant and the content of M_2 in copolymer ⬇

Effect of depropagation on copolymer composition in the anionic copolymerization of vinylmesitylene(M_1) — α-methystyrene(M_2)

T=0℃

f_2=0.91

- Solid-line and open-circle: experimental data
- Broken-lines: predictions from models (r_1=0.20, r_2=0.72)
- K is obtained from the polymerization-depolymerization equilibrium data for the homopolymerization of M_2
- Case Ⅱ is better than Case Ⅰ in the experiment.

Copolymerization with Complex Participation

The comonomer complexes (e.g.$\overline{M_1M_2}$) participate in the propagation reaction and compete with each of the individual monomers.

Eight propagation steps:

$$M_1^* + M_1 \xrightarrow{K_{11}} M_1^*$$

$$M_1^* + M_2 \xrightarrow{K_{12}} M_2^*$$

$$M_2^* + M_1 \xrightarrow{K_{21}} M_1^*$$

$$M_2^* + M_2 \xrightarrow{K_{22}} M_2^*$$

$$M_1^* + \overline{M_1M_2} \xrightarrow{K_{\overline{112}}} M_2^*$$

$$M_1^* + \overline{M_2M_1} \xrightarrow{K_{\overline{121}}} M_1^*$$

$$M_2^* + \overline{M_1M_2} \xrightarrow{K_{\overline{212}}} M_2^*$$

$$M_2^* + \overline{M_2M_1} \xrightarrow{K_{\overline{221}}} M_1^*$$

Six reactivity ratios:

$$r_1 = \frac{K_{11}}{K_{12}} \qquad r_2 = \frac{K_{22}}{K_{21}}$$

$$r_1' = \frac{K_{\overline{112}}}{K_{\overline{121}}} \qquad r_1' = \frac{K_{\overline{221}}}{K_{\overline{212}}}$$

$$r_1'' = \frac{K_{\overline{121}}}{K_{12}} \qquad r_1'' = \frac{K_{\overline{212}}}{K_{21}}$$

Copolymerization with Complex Participation

The copolymer composition obtained by the statistical approach is:

$$\frac{d[M_1]}{d[M_2]} = \frac{(1-P_{12})(P_{21}+P_{\overline{221}})+(1-P_{22})(P_{12}+P_{\overline{112}})}{(1-P_{11})(P_{21}+P_{\overline{221}})+(1-P_{21})(P_{12}+P_{\overline{112}})}$$

Define: the transition probabilities-

$$P_{11} = \frac{r_1[M_1]}{\sum R_1} \qquad P_{12} = \frac{[M_2]}{\sum R_1}$$

$$P_{\overline{121}} = \frac{r_1''[\overline{M_1M_2}]}{\sum R_1} \qquad P_{\overline{121}} = \frac{r_1'r_1''[M_1M_2]}{\sum R_1}$$

$$P_{21} = \frac{[M_1]}{\sum R_2} \qquad P_{22} = \frac{r_2[M_2]}{\sum R_2}$$

$$P_{\overline{221}} = \frac{r_2'r_2''[\overline{M_1M_2}]}{\sum R_2} \qquad P_{\overline{212}} = \frac{r_2''[\overline{M_1M_2}]}{\sum R_2}$$

$$\sum R_1 (\text{the sum of the rxn rates of } M_1^*) = r_1[M_1]+[M_2]+r_1''[\overline{M_1M_2}](1+r_1')$$

$$\sum R_2 = [M_1]+r_2[M_2]+r_2''[\overline{M_1M_2}](1+r_2')$$

Copolymerization with Complex Participation

- The complex participation model predicts a variation of the copolymer composition with
  - temperature
  - monomer concentration

- T ↗ ⇨ 〔monomer complex〕 ↘
- 〔monomer〕 ↗ at fixed f_1 ⇨ 〔monomer complex〕 ↗

Copolymerizations Involving Dienes - Crosslinking

- Diene: a monomer contains two double bonds.
  ⇒ often used to obtain a crosslinked structure.

- Reaction time (early or late): the relative reactivities of the two double bonds of the diene.
- Extent of crosslinking: the amount diene relative to the other monomer.

Crosslinking

Case Ⅰ - Copolymerization of monomer A with diene BB

Assume:

All double bonds have the same reactivity (i.e. the A double bonds and both B double bonds)

- $r_1=r_2$, $F_1= f_1$
- P: the fraction of all (A and B) double bonds reacted.

  P〔A〕: the number of type-A double bond reacted.

  P〔B〕: the number of type-B double bond reacted.

  P^2〔B〕: the number of BB monomer having both double bonds reacted.

  〔A〕: the conc. of type-A double bond.

  〔B〕: the conc. of type-B double bond.

  〔BB〕: the conc. of BB

  } 〔B〕=2〔BB〕

Crosslinking

- The number of crosslinks
  - = the number of BB monomer molecules in which both B double bonds are reacted
  - = P^2〔BB〕
- The number of polymer chains
  - = (the total number of A and B double bonds reacted)
  - ÷ (the degree of polymerization)
  - = $\dfrac{([A]+[B])P}{\overline{X}_w}$ → degree of polymerization
- The critical extent of reaction at the gel point P_c:

The number of crosslinks per polymer chain=1/2

$$\therefore \frac{P^2[BB]}{\{([A]+[B])P\}/\overline{X}_w} = \frac{1}{2} \Rightarrow P_c = \frac{[A]+[B]}{2[BB]\overline{X}_w} = \frac{[A]+[B]}{[B]\overline{X}_w}$$

Crosslinking in the copolymerization of Styrene-Divinylbenzene

Mole Fraction of DVB	Gel Point (P_c)	
	Calculation	Observation
0.004	0.21	0.16
0.008	0.10	0.14
0.02	0.042	0.076
0.032	0.026	0.074
0.082	0.010	0.052
0.30	0.0042	0.045

- Mole fraction of DVB ↗ ➔ P_c ↘
- The calculation from model: good in low conc. regime
- If 〔DVB〕is too high ➔ intramolecular cyclization
  ➔ Calculated P_c ＜Observed P_c

Crosslinking in the copolymerization of Styrene-Divinylbenzene

An alternate expression for P_c:

$$P_c = \frac{1-q}{\left[af(f-2)(q+\frac{\xi}{2})\right]}$$

q : (the propagation rate)/ (propagation rate + termination rate + transfer rate)

ξ : (the termination rate)/(termination rate + transfer rate)

f : functionality of diene (=4 ;∵each double bond is bifunctional)

a : the fraction of all functional groups in the reaction mixture belonging to the diene.

Crosslinking

Case Ⅱ : A+BB

The reactivities of the two groups are not equal.

The critical extent of reaction at gelation is:

$$P_c = \frac{(r_1[A]^2 + 2[A][B] + r_2[B]^2)^2}{X_w[B]([A]+[B])(r_2[B]+[A]^2}$$

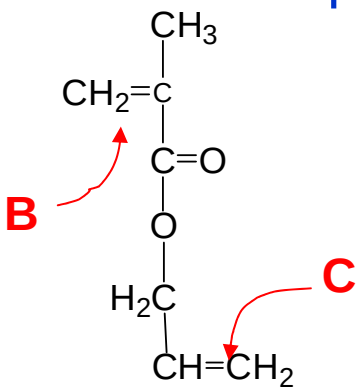
If [A] >> [B] (general case), then $P_c = \frac{[A]r_1^{\ 2}}{[B]\overline{x}_w}$

- When $r_2 > r_1$ (the double bonds of the diene are more reactive than that of the other monomer)
  ➔ crosslinking occurs in the early stages.
- When $r_1 > r_2$
  ➔ crosslinking occurs in late stages.

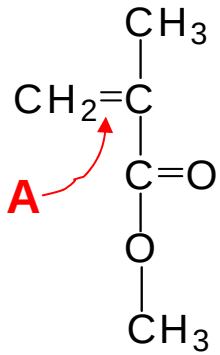
Crosslinking

Case Ⅲ: Monomer A+ Diene BC

Groups A and B have equal reactivity, but group C has a much lower reactivity.



alkyl methacrylate



methyl methacrylate

Crosslinking does not occur until relatively late in the reaction

The reactivity ratio:

$$r = \frac{K_{AC}}{K_{AA}} = \frac{K_{AC}}{K_{AB}} = \frac{K_{BC}}{K_{BA}} = \frac{K_{BC}}{K_{BB}}$$

Then, the critical extent of reaction at gelation is given by

$$P_c = 1 - \exp\left[\frac{-1}{2q\overline{X}_w r}\right]$$

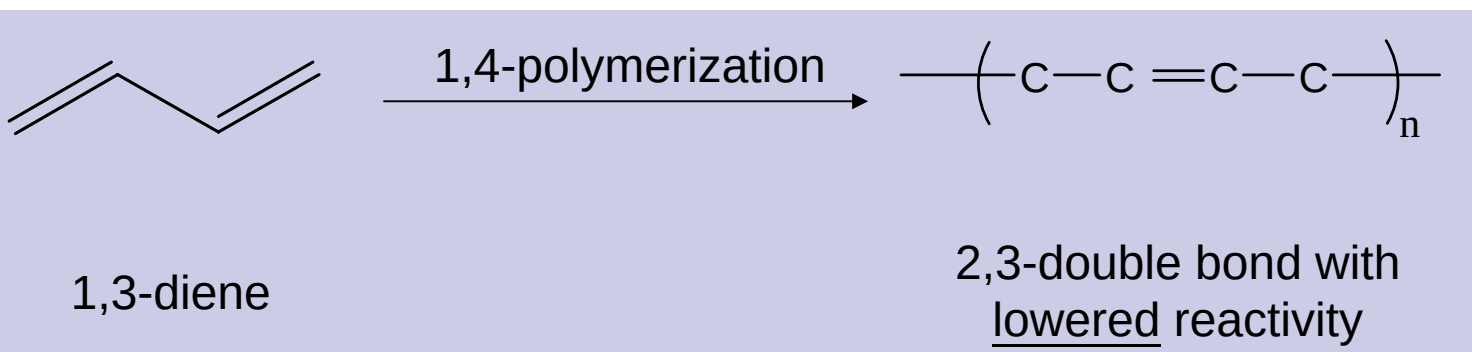
q: the mole fraction of the diene in the initial comonomer feed.

Crosslinking

- In general, the gelation point can be delayed by
  - ➔ reducing the amount of the diene
  - ➔ adding chain-transfer agent
  - ➔ choosing a diene monomer in which one of the double is much less reactive to the others.

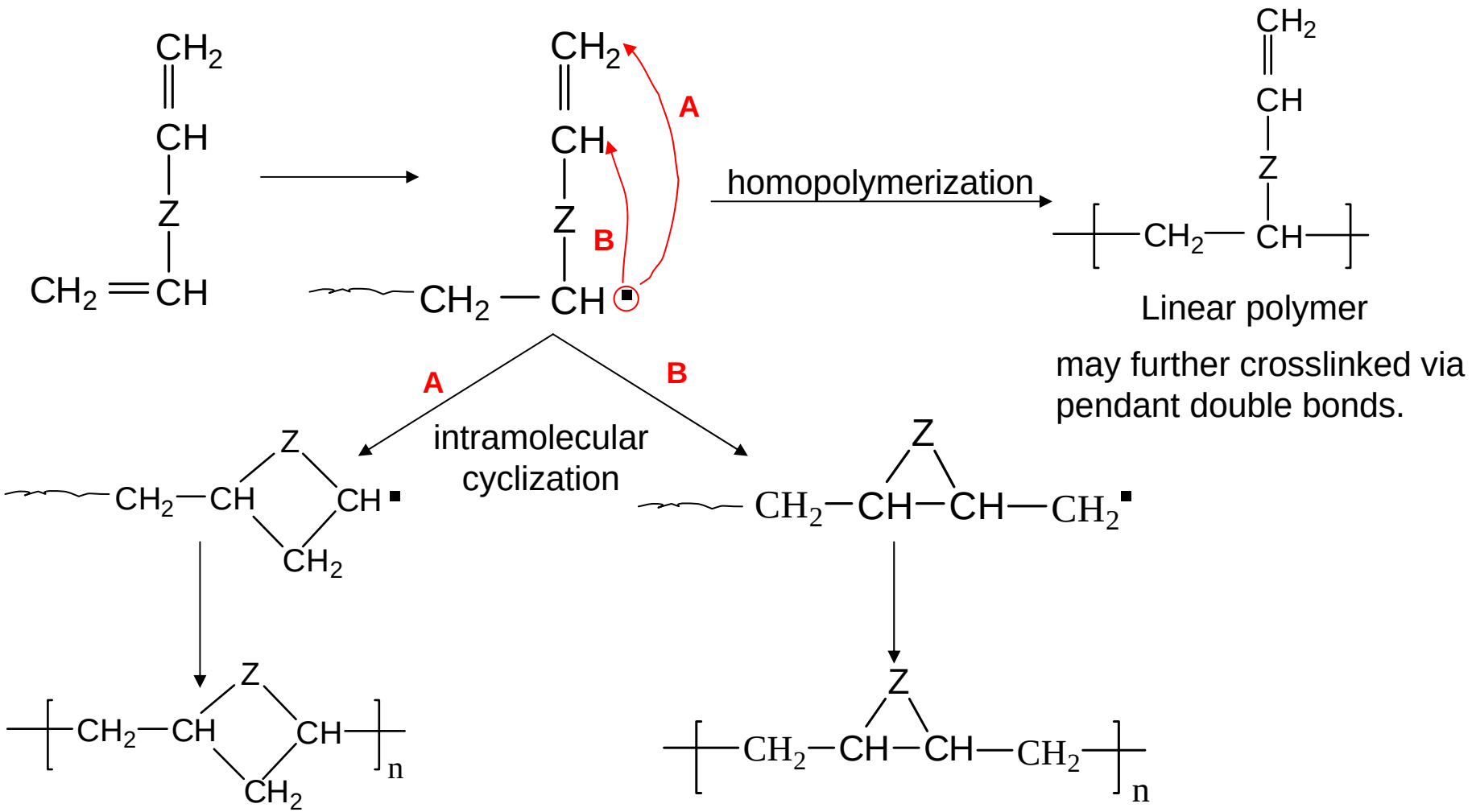
- Sometimes, the reaction of one of the double bonds of the diene results in a decrease in the reactivity of the remaining double bond
  - ➔ Similar to the assumption of Case Ⅲ

Ex:



Cyclopolymerization:

Alternating Intra-Inter molecular polymerization

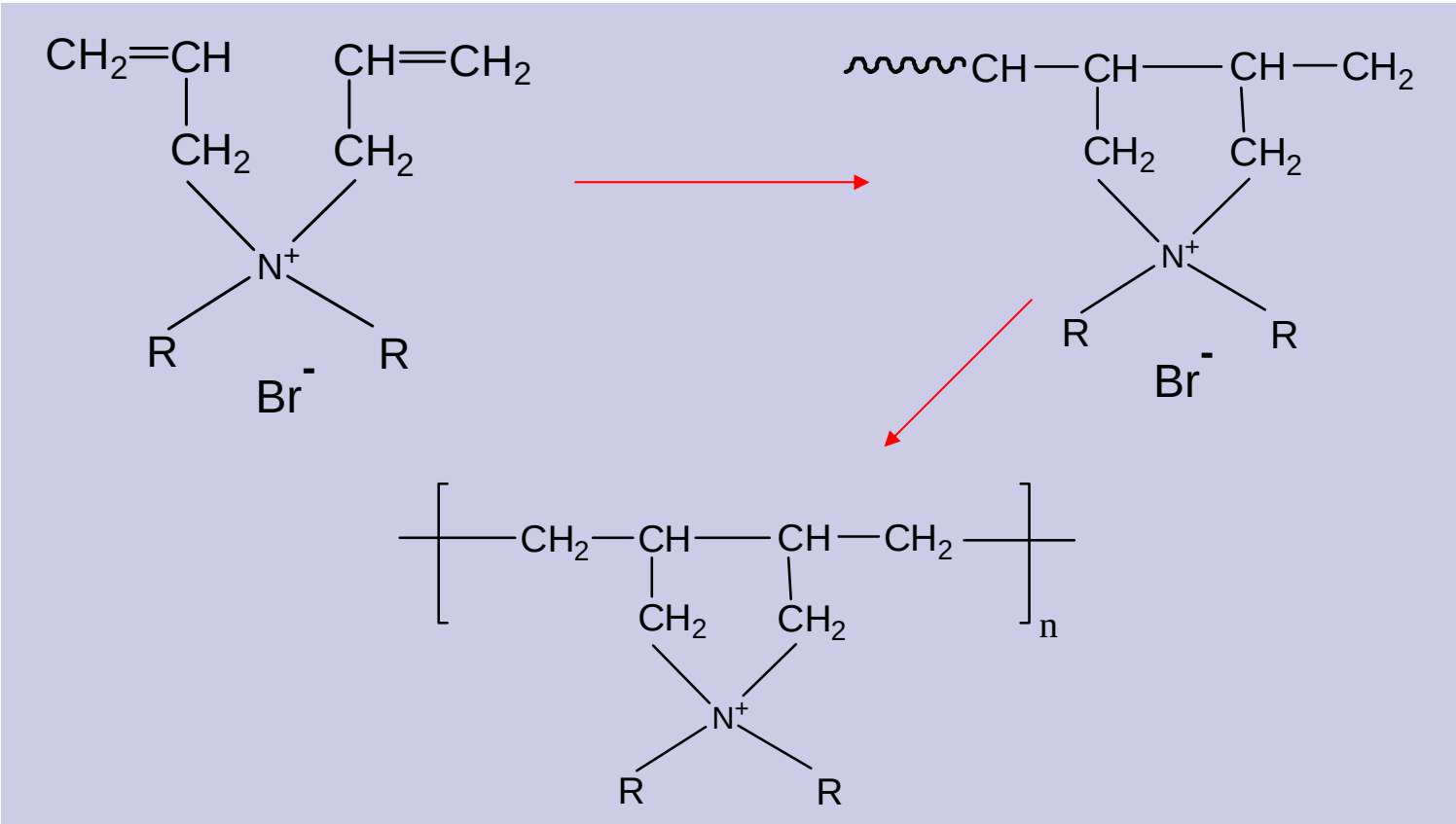


Cyclopolymerization:
Alternating Intra-Inter molecular polymerization

Example:

Radical polymerization of diallyl quaternary ammonium salt

➔ Soluble, uncrosslinked polymers with little or no residual unsaturation

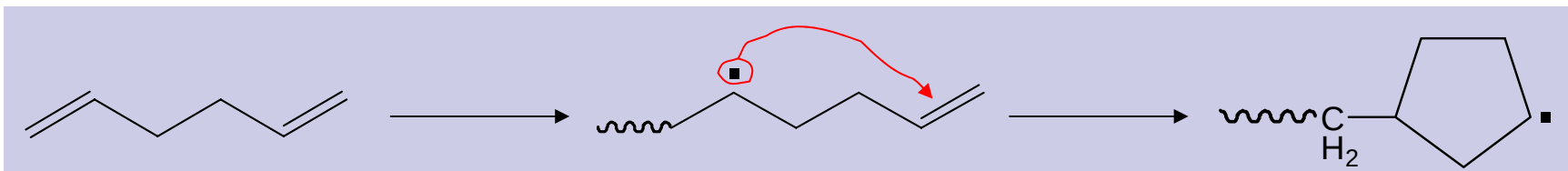


Cyclopolymerization:
Alternating Intra-Inter molecular polymerization

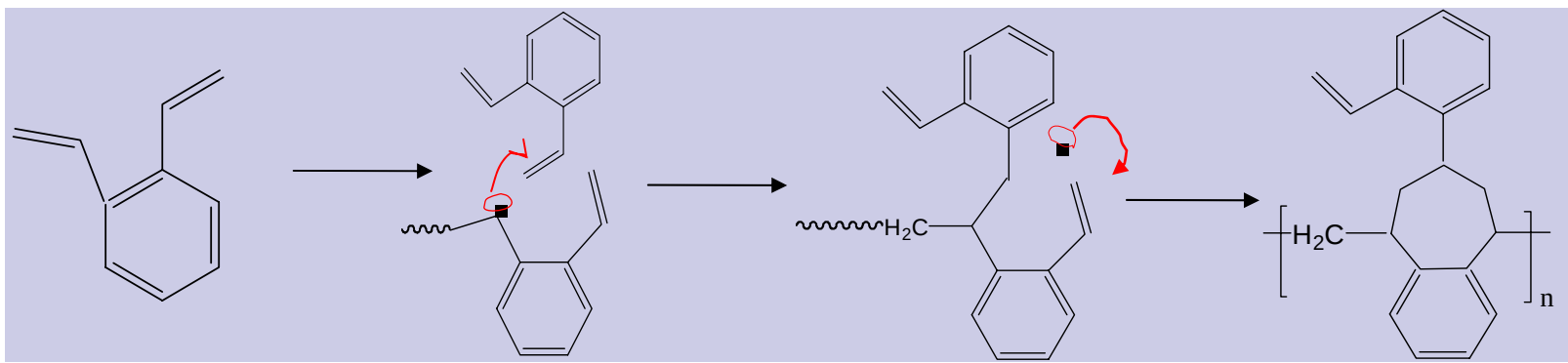
- The extent of cyclization generally increases in the following order:

  5 and 6-membered rings > 7 or longer-membered rings

- Usually, 1.5-dienes → 5-membered ring
  Ex: 1.5-hexadiene



However, polymerization of *o*-divinynyl benzene → 7- membered ring



Cyclopolymerization:
Alternating Intra-Inter molecular polymerization

- Intermolecular propagation R_p
  Intramolecular cyclization R_c } competition

The fraction of cyclized units: $$f_c = \frac{R_c}{R_c + R_p}$$

where, $$R_p = 2K_p[M^*][M]$$
$$R_c = K_c[M^*]$$

∵〔M〕=conc. of diene monomer
(Not double bonds)

therefore, $$f_c = \frac{K_c[M^*]}{K_c[M^*] + 2Kp[M^*][M]} = \frac{K_c}{K_c + 2Kp[M]}$$ or $$\frac{1}{f_c} = 1 + \frac{2K_p[M]}{K_c}$$

* 〔M〕↘ ➔ the extent of cyclization ↗
〔M〕↗ ➔ the extent of cyclization ↗

Cyclopolymerization:
Alternating Intra-Inter molecular polymerization

$$\frac{1}{f_c} = 1 + \frac{2K_p[M]}{K_c}$$

- f_c vs. 〔M〕:
  the cyclization ratio (K_c/K_p): obtained from the slope of the plot
- For most symmetrical 1,6-dienes,

$$\frac{K_c}{K_p} : \text{2~20 moles/l}$$

- Activation energy: cyclization > intermolecular propagation
  T ↗ ➔ Tendency to cyclization ↗
- Solvent polarity ↗ ➔ Cyclization ↗ (Not understood yet!)

Cyclopolymerization:
Alternating Intra-Inter molecular polymerization

- Ring sizes = 7 or larger ➔ cyclization ↘ (sharply)

  Some exceptions:

  diallyl ester ⟶ 15~20% of cyclization ring structure containing up to 17 atoms.

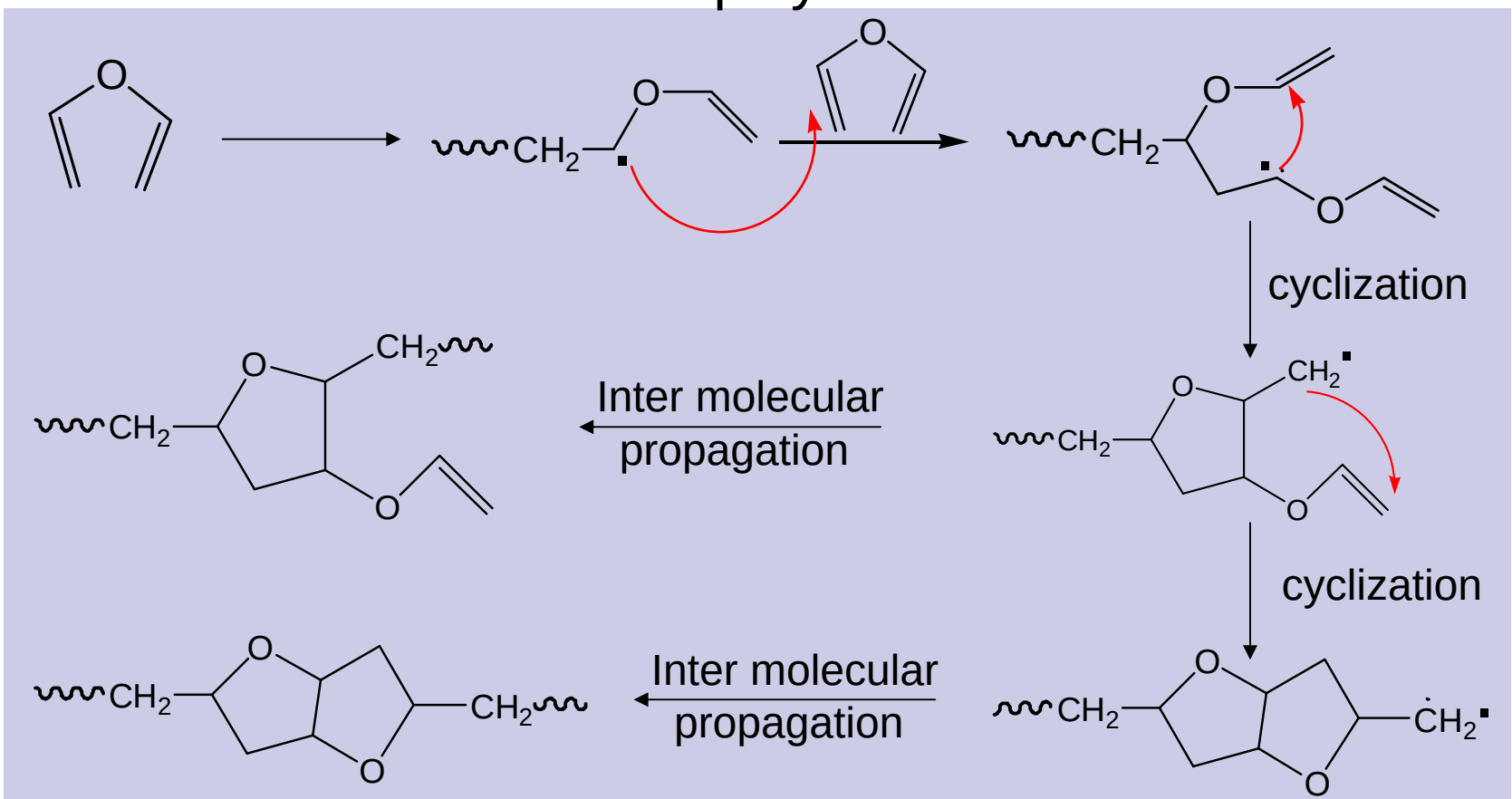
  o-dially phthalate ⟶ 40% cyclization

Cyclopolymerization:
Alternating Intra-Inter molecular polymerization

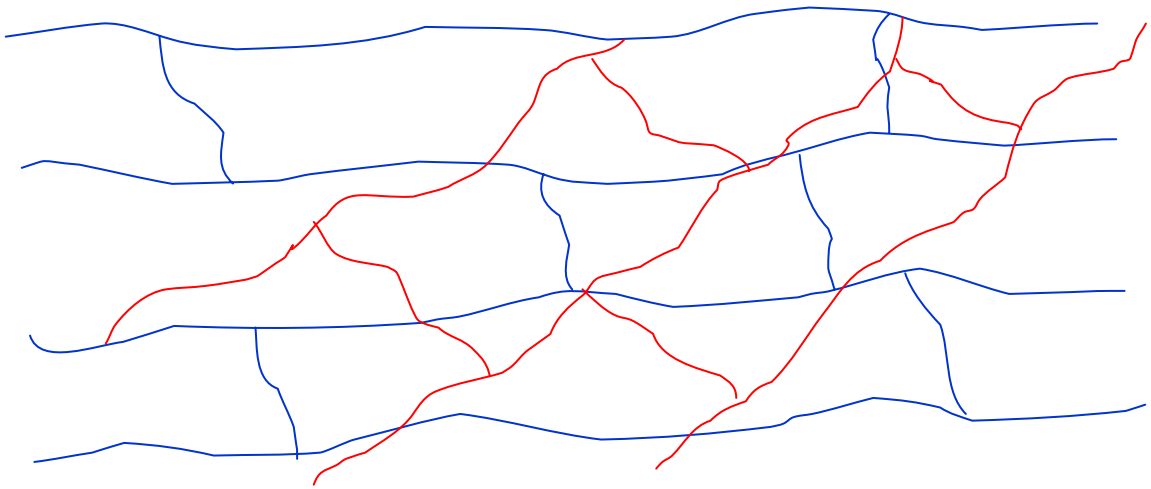
Some copolymerizations ➡ very complex ring structures

Example: polymerization of divinyl ether

→ uncrosslinked polymers with little unsaturation.

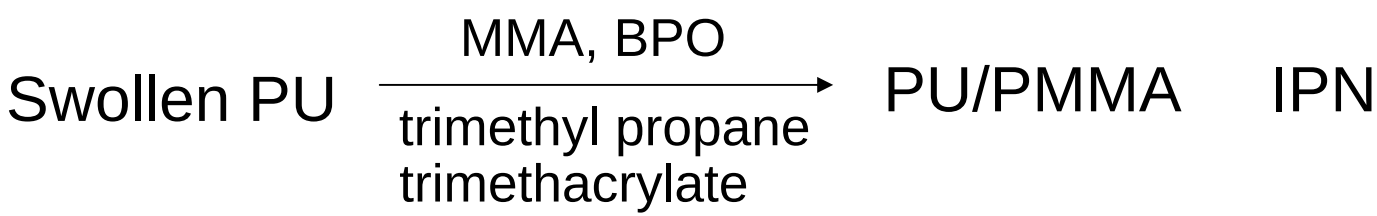


Interpenetrating Polymer Networks (IPN)

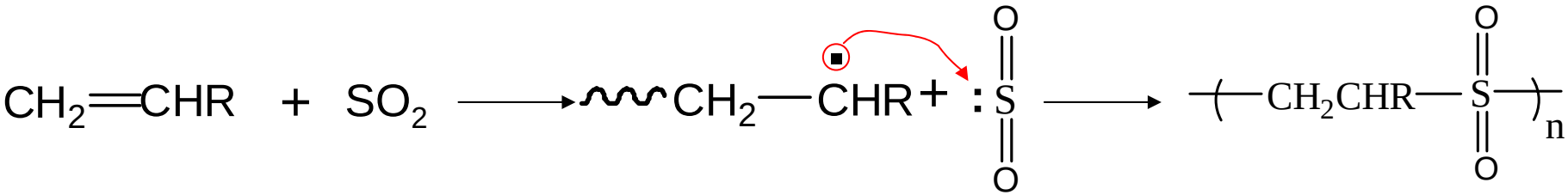


Combination of the properties of two different crosslinked polymers

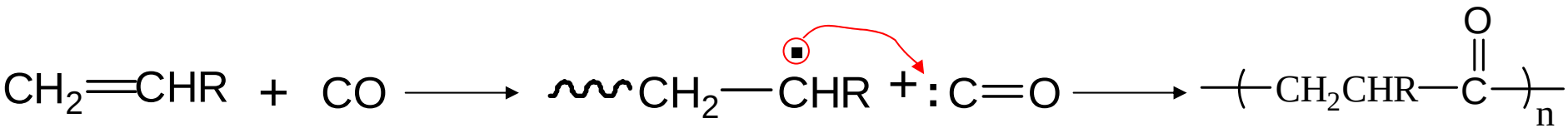
Example:



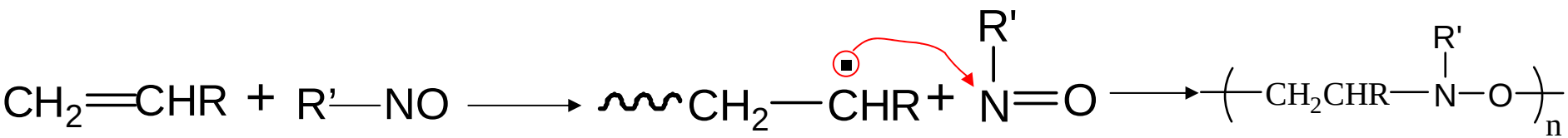
OTHER COPOLYMERIZATIONS : Radical Copolymerization of Alkenes

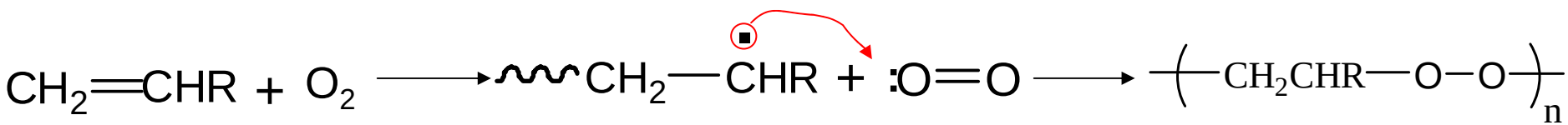


polymeric sulfones



ketones





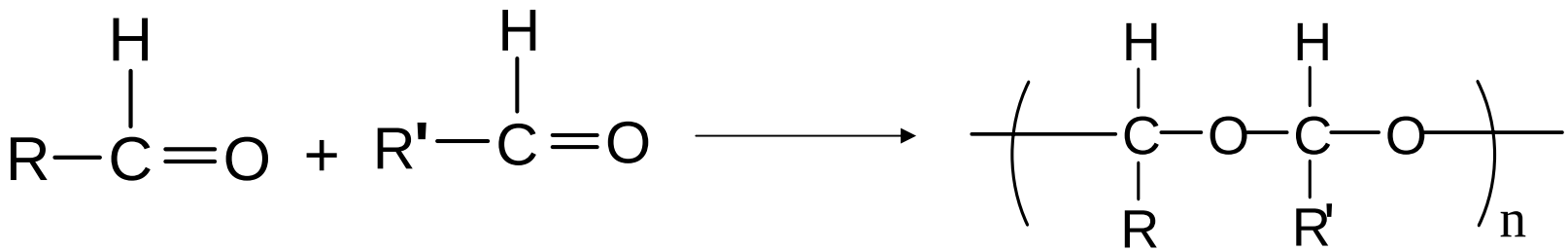
peroxide

Radical Copolymerization of Alkenes

- **Reactions with sulfur dioxide:**
  - Only for alkenes w/o strong e- withdrawing substituents (form reactive radicals).
    such as : α-olefins, vinyl chloride, vinyl acetate

    → Yielding 1:1 alternating copolymers (∵polar effect between the electropositive SO_2 and electronegative alkene)
  - Stable radical → less SO_2 content in copolymer
  - Monomers with strong e- withdrawing groups (e.g.-CN)
    ⟶✕ copolymers
    ∵Polar repulsions of electrophilic sulfur dioxide
  - Substituents: bulky or electropositive ↗ → depropagation ↗
- **Reactions with oxygen and quinones:**
  - ➔ Very slow copolymerization rates
    → Usually classified as retardation or inhibition reactions

Copolymerization of Carbonyl Monomers



- Not common
- The general tendency of the copolymerization is ideal behavior. But, bulky substituent ⟶ tend to form alternation

Applications of Copolymerization : Styrene

- SBR rubber: styrene-1,3-butadiene
  - ➔ Styrene(25%) + 1,3-butadiene(75%)
    - — produced by emulsion polymerization (some by anionic polymerization)
    - — tensile strength: similar to natural rubber
    - — uses: tire, belting, hose..
  - ➔ Styrene(50-70%)-1,3-butadiene(30-50%)
    - — latex paint
  - ➔ Carboxylated SBR
    - — Copolymerized with small amount of carboxyl groups
    - — Backing material for carpets

can be used for further crosslinking

- Styrene-divinyl benzene

  Packing materials of GPC and ion-exchange