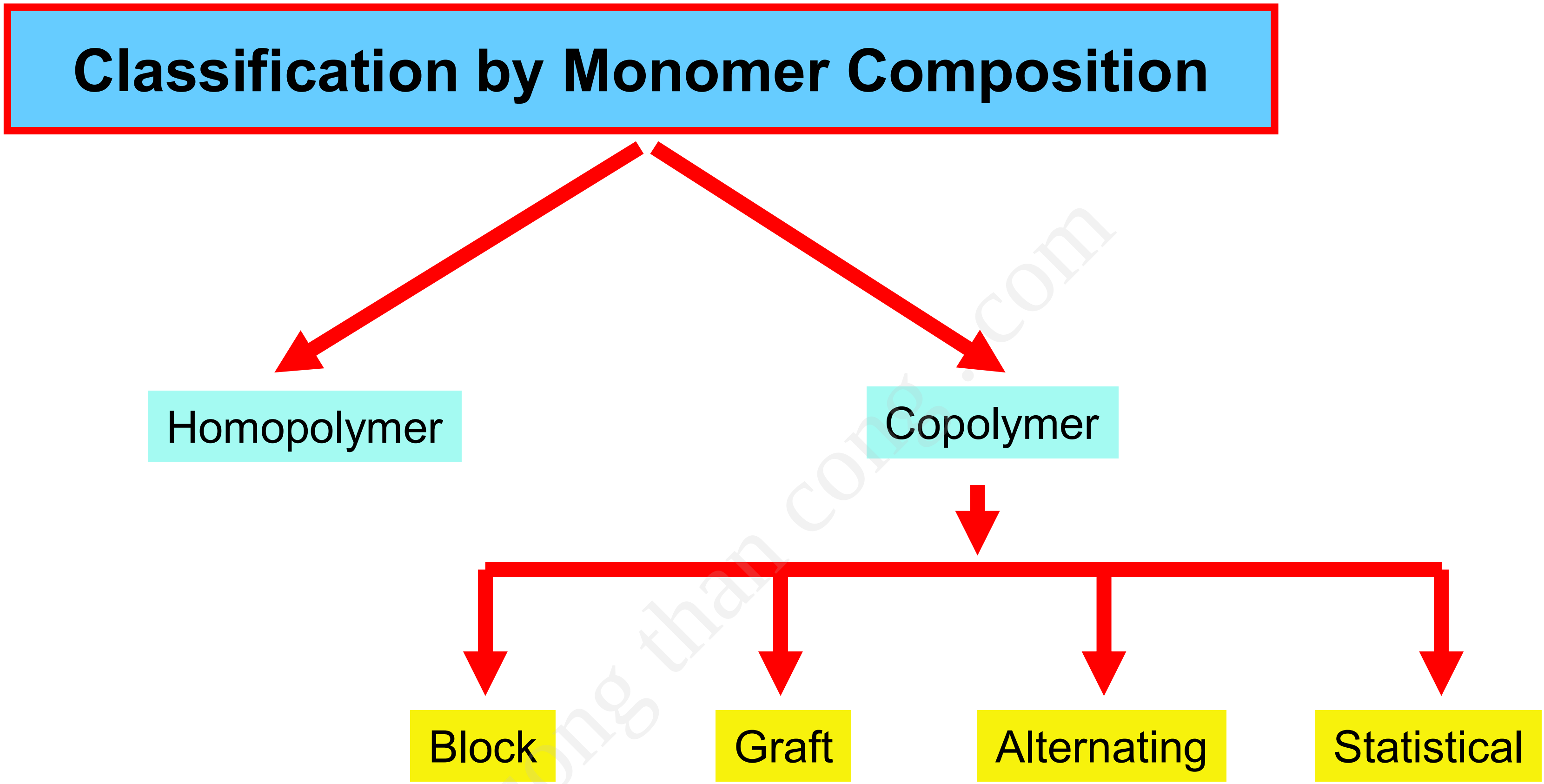
Copolymer

Classification by Monomer Composition


Homopolymer

Copolymer

Block

Graft

Alternating

Statistical

Homopolymer

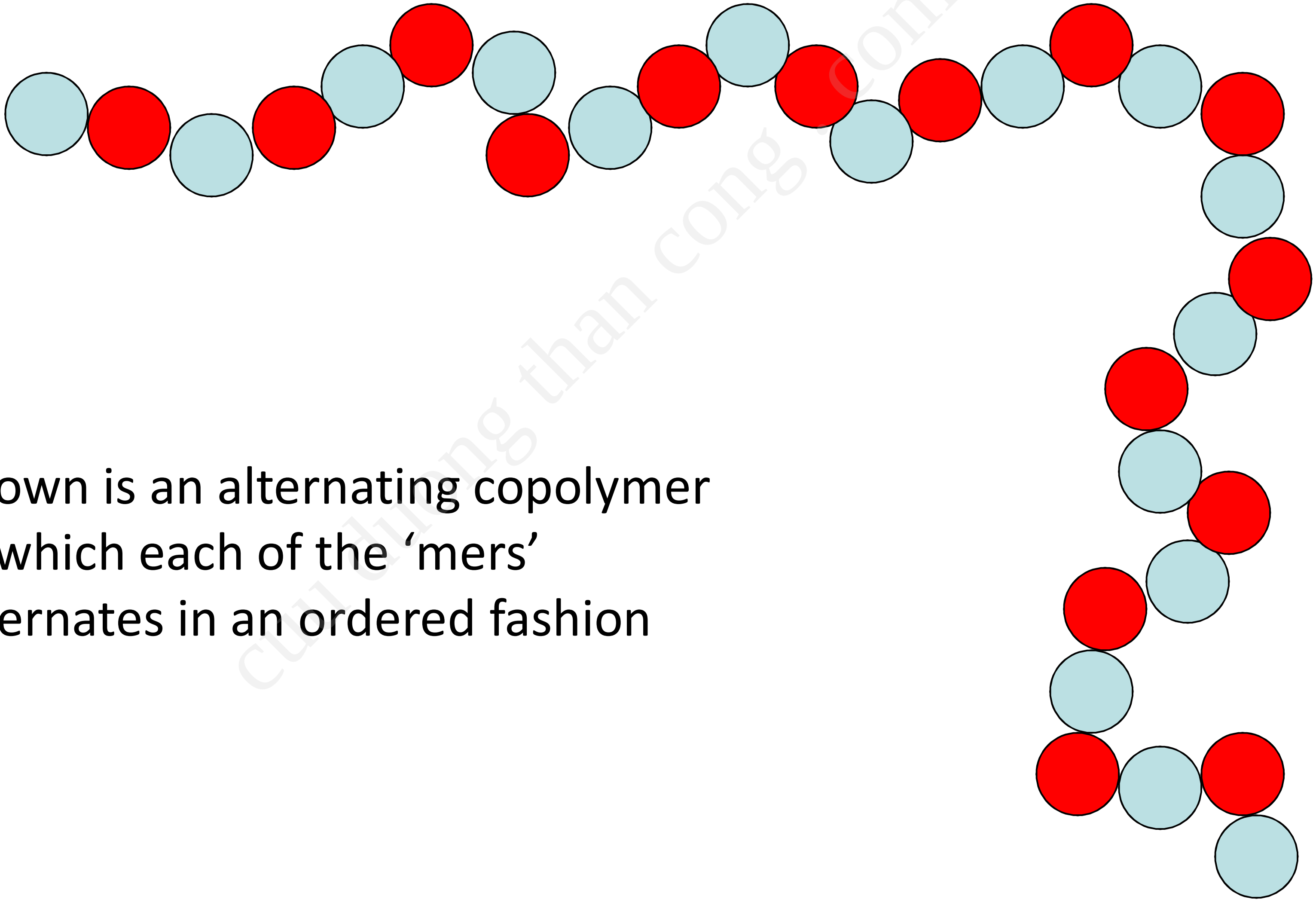
Consist of only one type of constitutional repeating unit (A)

AAAAAAAAAAAAAAA

copolymer

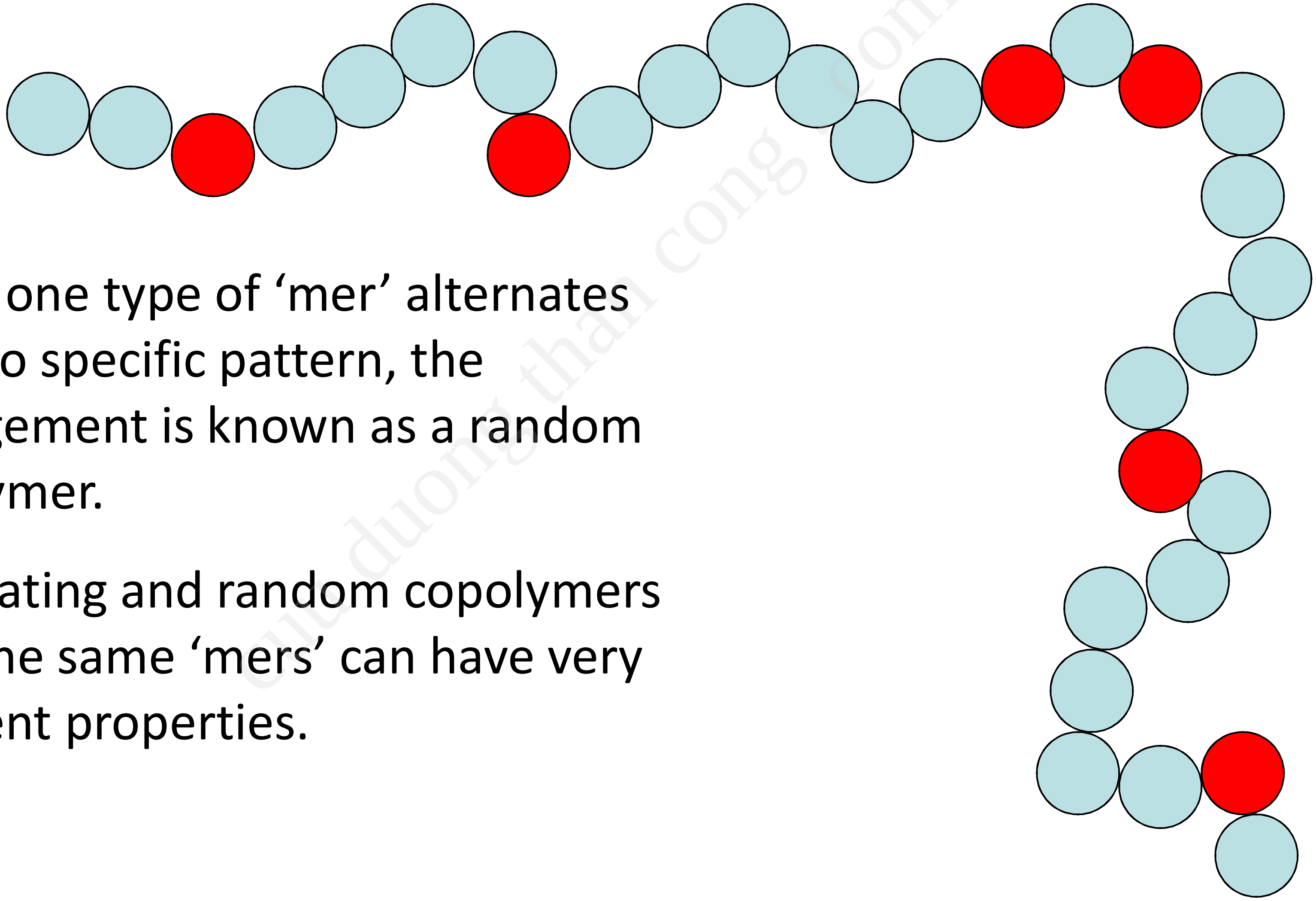
Consists of two or more constitutional repeating units (A.B)

Alternating copolymer



Shown is an alternating copolymer in which each of the 'mers' alternates in an ordered fashion

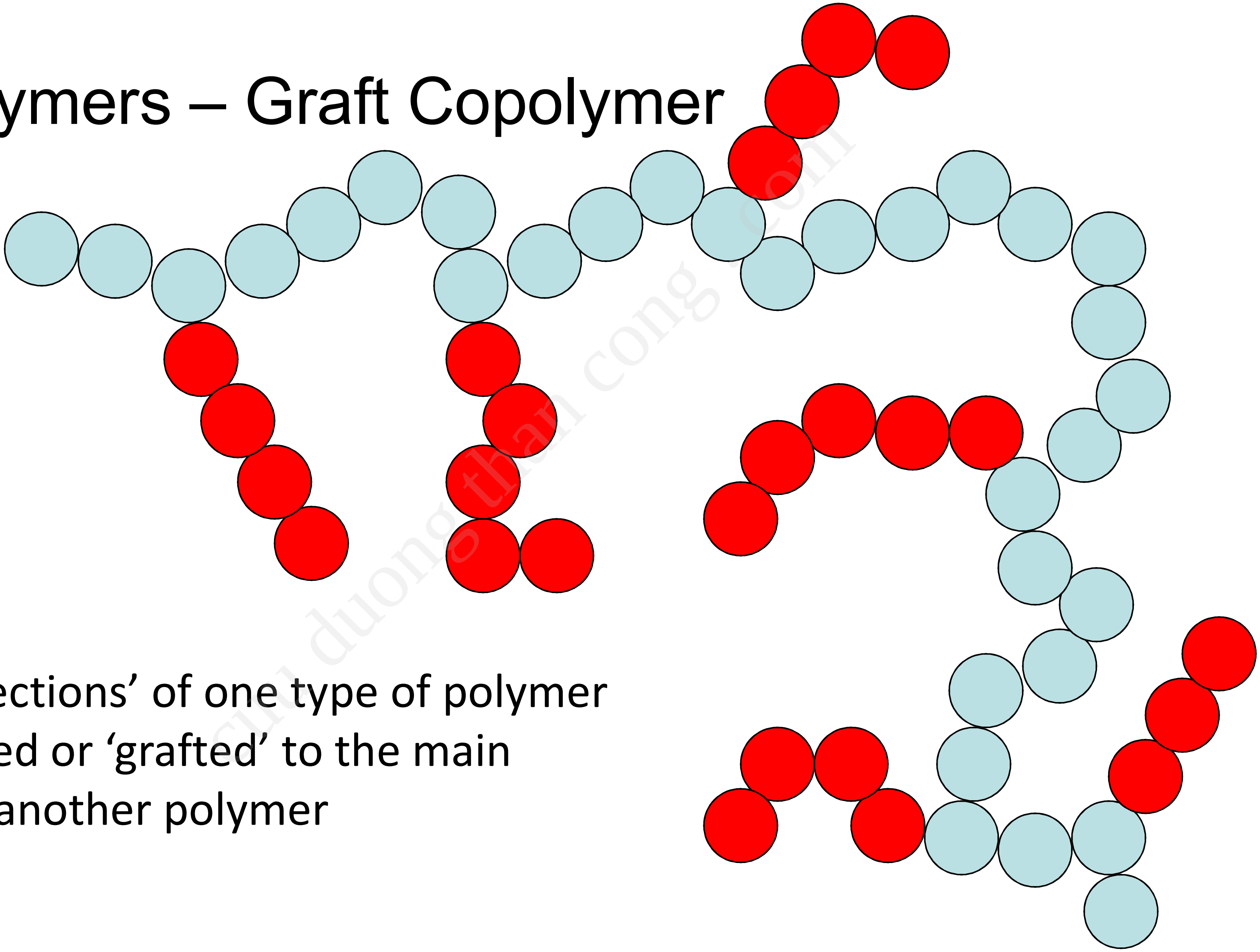
Statistical copolymer (Random)



When one type of ‘mer’ alternates with no specific pattern, the arrangement is known as a random copolymer.

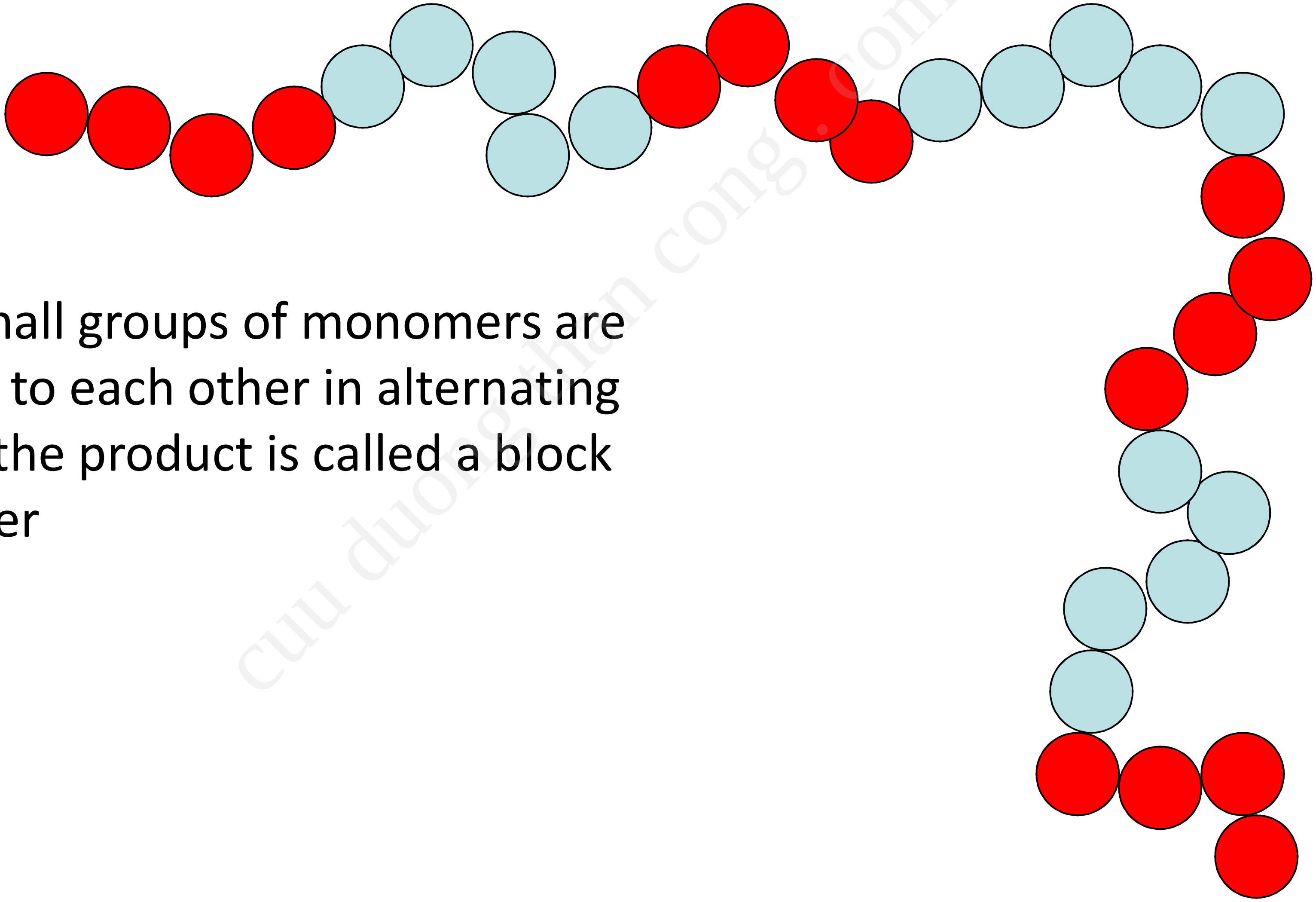
Alternating and random copolymers with the same ‘mers’ can have very different properties.

Copolymers – Graft Copolymer



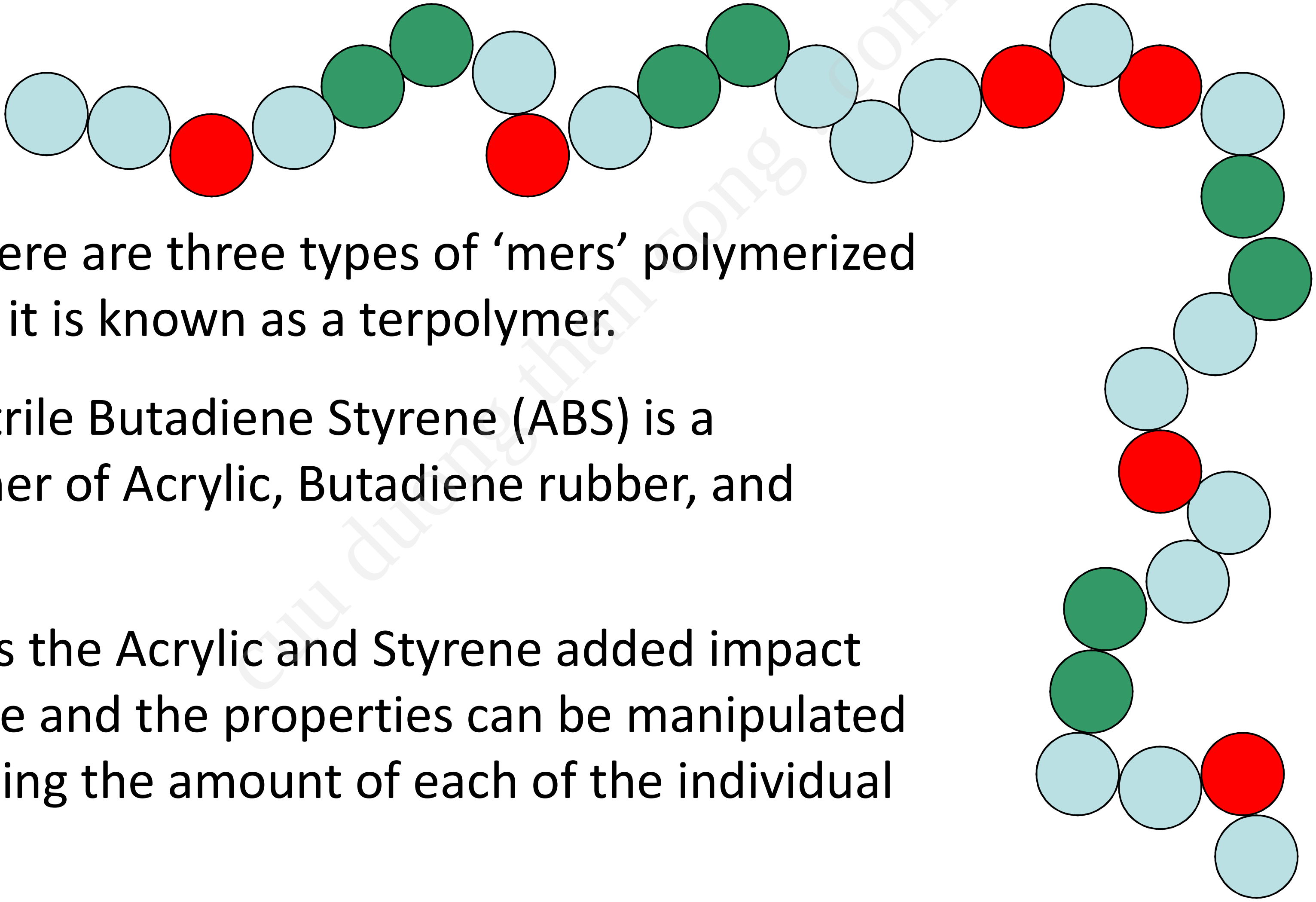
When ‘sections’ of one type of polymer is attached or ‘grafted’ to the main chain of another polymer

Copolymers – Block Copolymer



When small groups of monomers are attached to each other in alternating fashion, the product is called a block copolymer

Terpolymer



When there are three types of ‘mers’ polymerized together it is known as a terpolymer.

Acrylonitrile Butadiene Styrene (ABS) is a terpolymer of Acrylic, Butadiene rubber, and Styrene.

This gives the Acrylic and Styrene added impact resistance and the properties can be manipulated by changing the amount of each of the individual ‘mers’

Các phương pháp tổng hợp copolyme?

Bản chất monome

Tâm cuối mạch

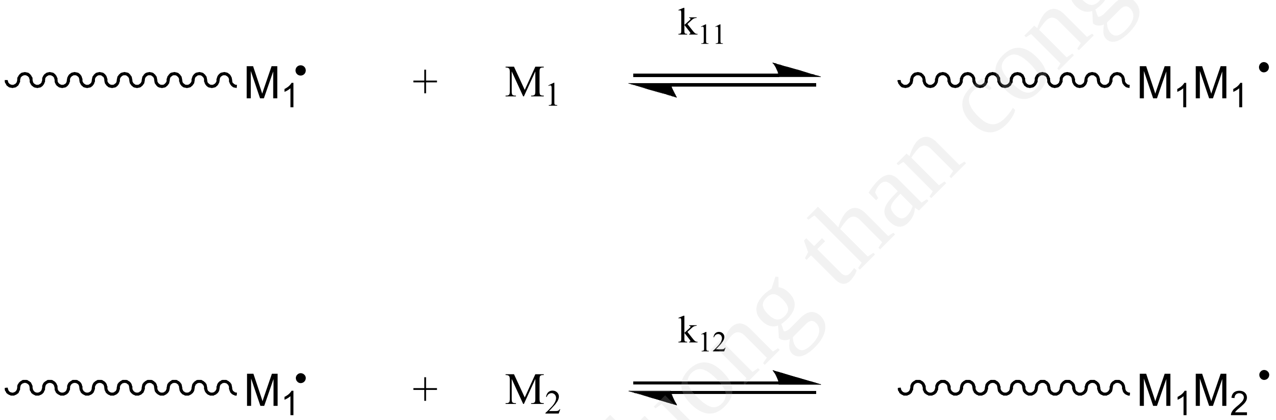
Chất khơi mào

Đồng trùng hợp gốc tự do

Xúc tác

Điều kiện phản ứng

Copolymerization Kinetics

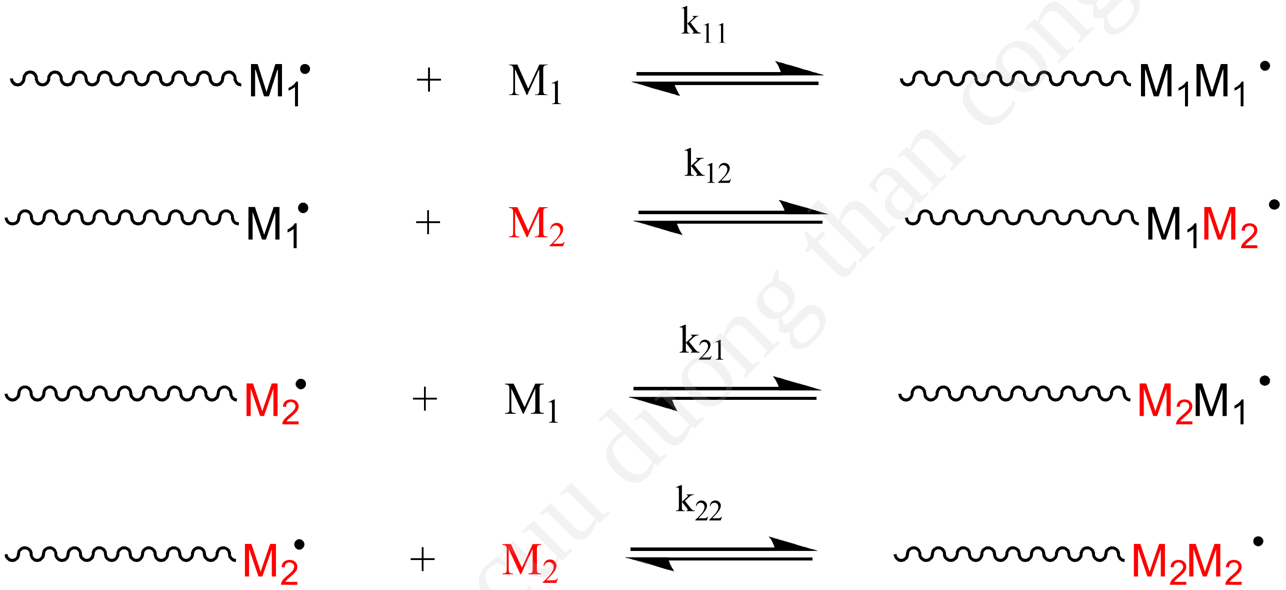


Homo-propagation

Cross-propagation

Terminal Model

Copolymerization Kinetics



$$\sim\!\sim\!\sim M_1^\bullet + M_1 \xrightleftharpoons{k_{11}} \sim\!\sim\!\sim M_1M_1^\bullet$$ **Homo-propagation**

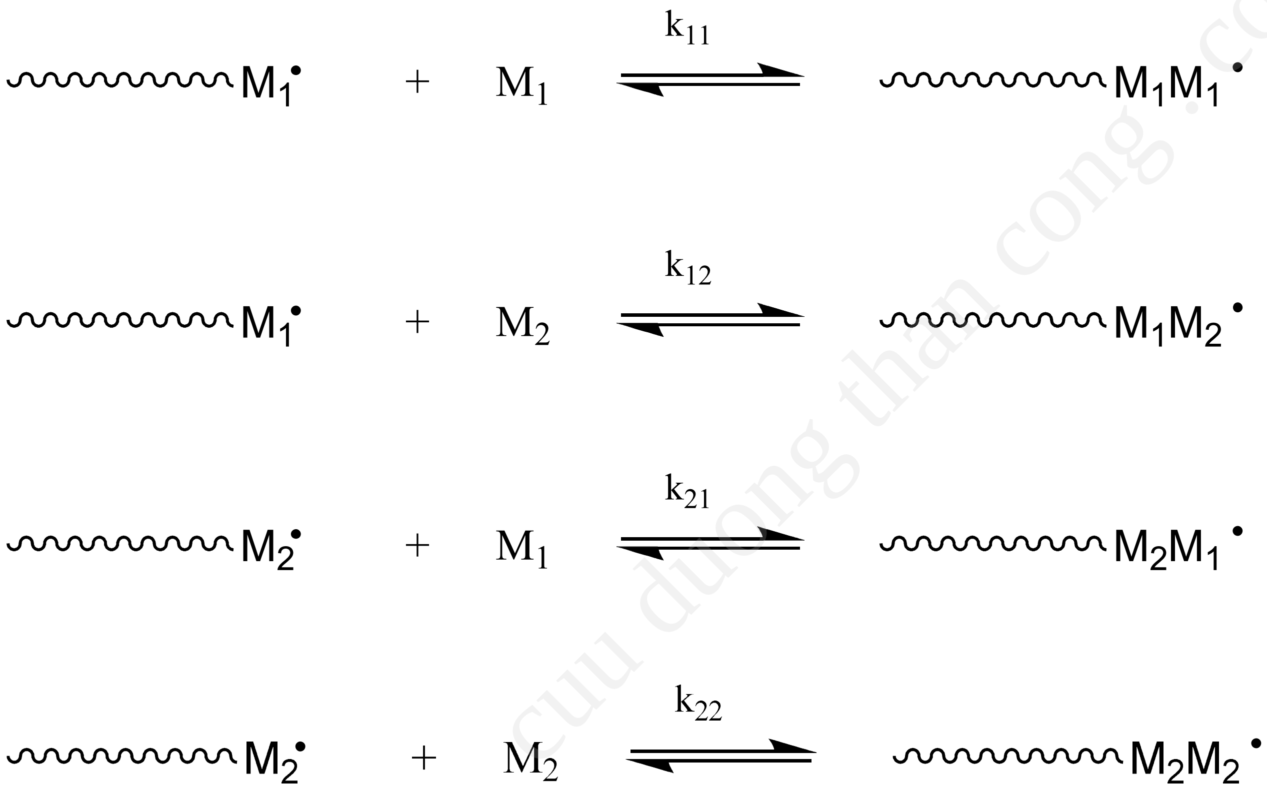
$$\sim\!\sim\!\sim M_1^\bullet + M_2 \xrightleftharpoons{k_{12}} \sim\!\sim\!\sim M_1M_2^\bullet$$ **Cross-propagation**

$$\sim\!\sim\!\sim M_2^\bullet + M_1 \xrightleftharpoons{k_{21}} \sim\!\sim\!\sim M_2M_1^\bullet$$ **Cross-propagation**

$$\sim\!\sim\!\sim M_2^\bullet + M_2 \xrightleftharpoons{k_{22}} \sim\!\sim\!\sim M_2M_2^\bullet$$ **Homo-propagation**

Terminal Model

Copolymerization Kinetics



$$\sim\sim\sim M_1^{\bullet} + M_1 \overset{k_{11}}{\rightleftharpoons} \sim\sim\sim M_1M_1^{\bullet} \qquad R_{p11} = k_{11}[M_1\bullet][M_1]$$

$$\sim\sim\sim M_1^{\bullet} + M_2 \overset{k_{12}}{\rightleftharpoons} \sim\sim\sim M_1M_2^{\bullet} \qquad R_{p12} = k_{12}[M_1\bullet][M_2]$$

$$\sim\sim\sim M_2^{\bullet} + M_1 \overset{k_{21}}{\rightleftharpoons} \sim\sim\sim M_2M_1^{\bullet} \qquad R_{p21} = k_{21}[M_2\bullet][M_1]$$

$$\sim\sim\sim M_2^{\bullet} + M_2 \overset{k_{22}}{\rightleftharpoons} \sim\sim\sim M_2M_2^{\bullet} \qquad R_{p22} = k_{22}[M_2\bullet][M_2]$$

Terminal Model

Copolymerization Kinetics

The rate of disappearance of M_1 and M_2 can be expressed as:

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

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

Copolymerization Kinetics

The ratio of the two rates is then:

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{k_{11}\,[M_1\bullet]\,[M_1] + k_{21}\,[M_2\bullet]\,[M_1]}{k_{12}\,[M_1\bullet]\,[M_2] + k_{22}\,[M_2\bullet]\,[M_2]}$$

Simplify:

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

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{k_{11}\,[M_1\bullet]/[M2\bullet] + k_{21}}{k_{22} + k_{12}\,[M_1\bullet]/[M2\bullet]}\right) \quad \text{......①}$$

Copolymerization Kinetics

Assume the Steady State Approximation:

The concentrations of $M_1\bullet$ and $M_2\bullet$ are constant

Therefore:

The rate of addition of $M_1\bullet$ to M_2 will equal
The rate of addition of $M_2\bullet$ to M_1

$$-\frac{d\,[M_1]}{dt} = k_{11}\,[M_1\bullet]\,[M_1] + k_{21}\,[M_2\bullet]\,[M_1] = 0$$

$$-\frac{d\,[M_2]}{dt} = k_{12}\,[M_1\bullet]\,[M_2] + k_{22}\,[M_2\bullet]\,[M_2] = 0$$

$$k_{12}\,[M_1\bullet]\,[M_2] = k_{21}\,[M_2\bullet]\,[M_1] \Rightarrow \frac{[M1\bullet]}{[M2\bullet]} = \frac{k_{21}[M_1]}{k_{12}[M_2]} \quad \text{……②}$$

Copolymer Equation

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_1]}{[M_2]}\left(\frac{k_{11}\,[M_1\bullet]/[M2\bullet] + k_{21}}{k_{22} + k_{12}\,[M_1\bullet]/[M2\bullet]}\right) \quad ......①$$

$$\frac{[M1\bullet]}{[M2\bullet]} = \frac{k_{21}[M_1]}{k_{12}[M_2]} \quad ......②$$

From ① and ② ⟹ **Copolymer Eq:**

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

where

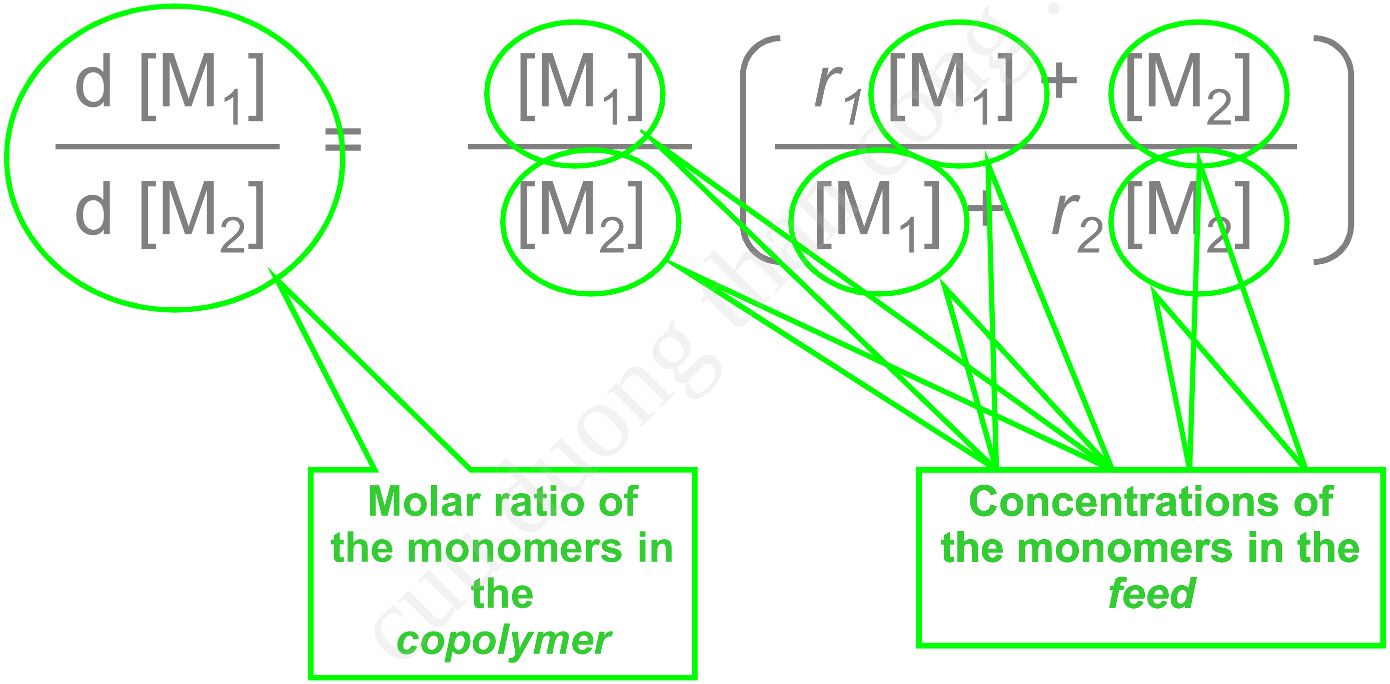
$$r_2 = \frac{k_{22}}{k_{21}}$$

$$r_1 = \frac{k_{11}}{k_{12}}$$

← **monomer reactivity ratio**

Copolymerization Kinetics

Copolymer Composition Equation:



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

Molar ratio of the monomers in the *copolymer*

Concentrations of the monomers in the *feed*

Meaning of r & Definition of f_1, F_1

Meaning of r

r_1 **characterizes the reactivity of the 1 radical with respect to the two monomers, 1 and 2**

$r_1 > 1$ **then homopolymerization growth is preferred**

$r_1 = 0$ **then only reaction with 2 will occur**

Define f_1, F_1

f_1, f_2 : mole fractions of monomers in feed
F_1, F_2 : mole fractions of monomers in polymer

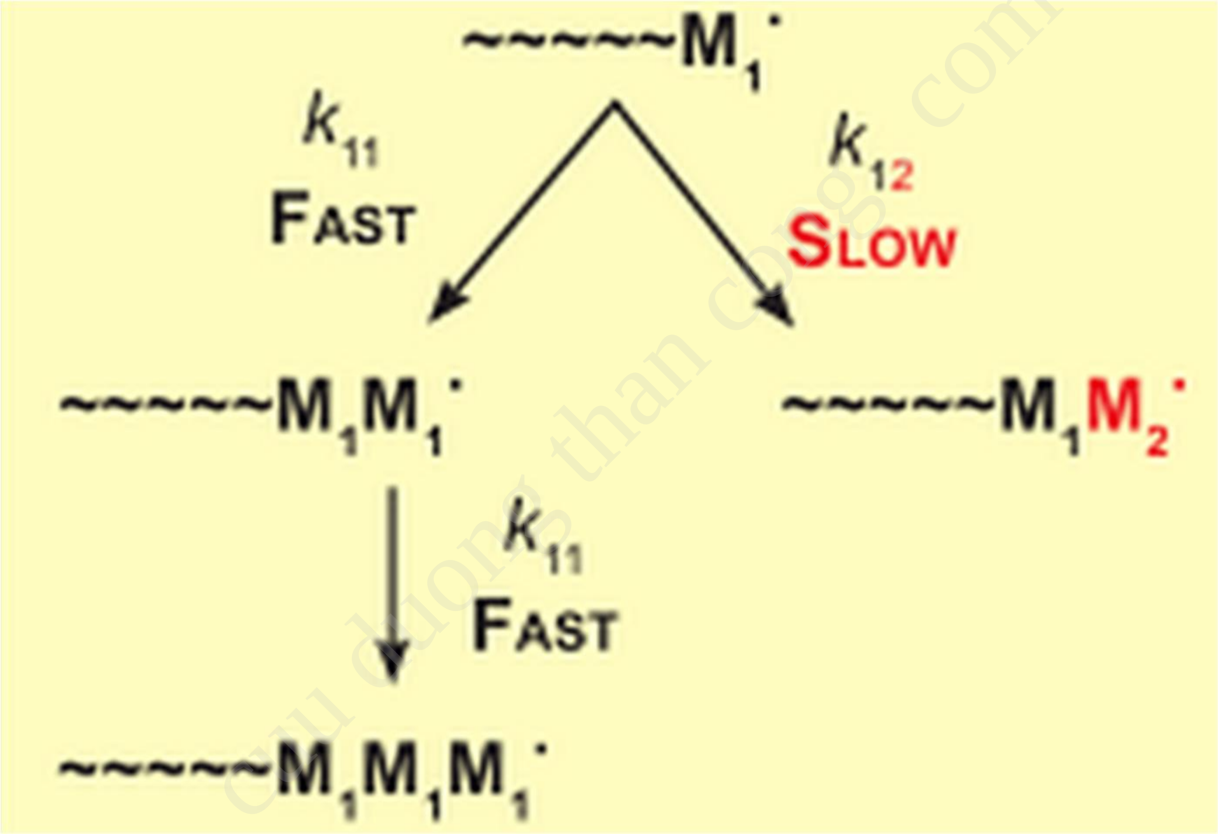
$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1 + M_2]} \quad \text{......③}$$

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad \text{......④}$$

From ③, ④

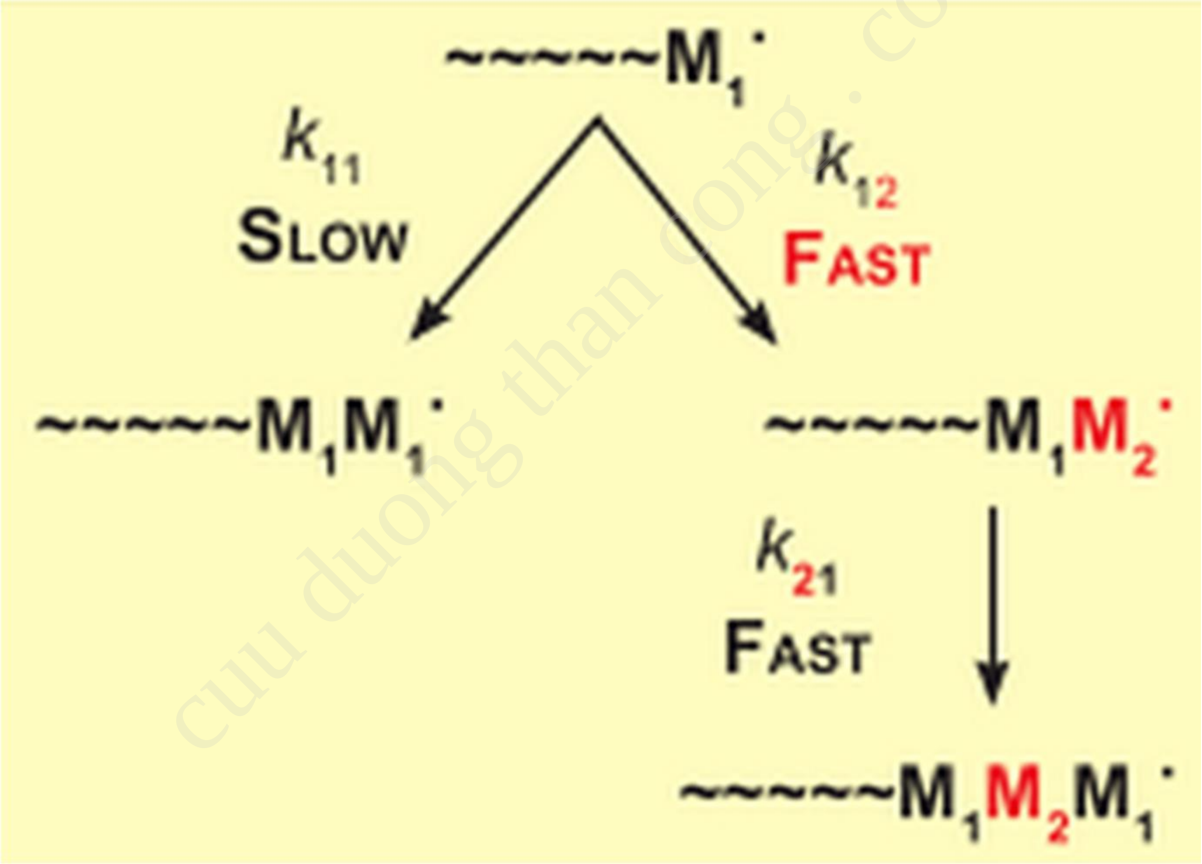
$$F_1 = \frac{r_1 f_1^{\,2} + f_1 f_2}{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}} \quad \text{......⑤}$$

- Nếu $k_{11} >> k_{12}$ và $k_{22} >> k_{21}$



$r_1 > 1$: ~~M_1* ưu tiên phản ứng với monome M_1 (homopolyme hóa)

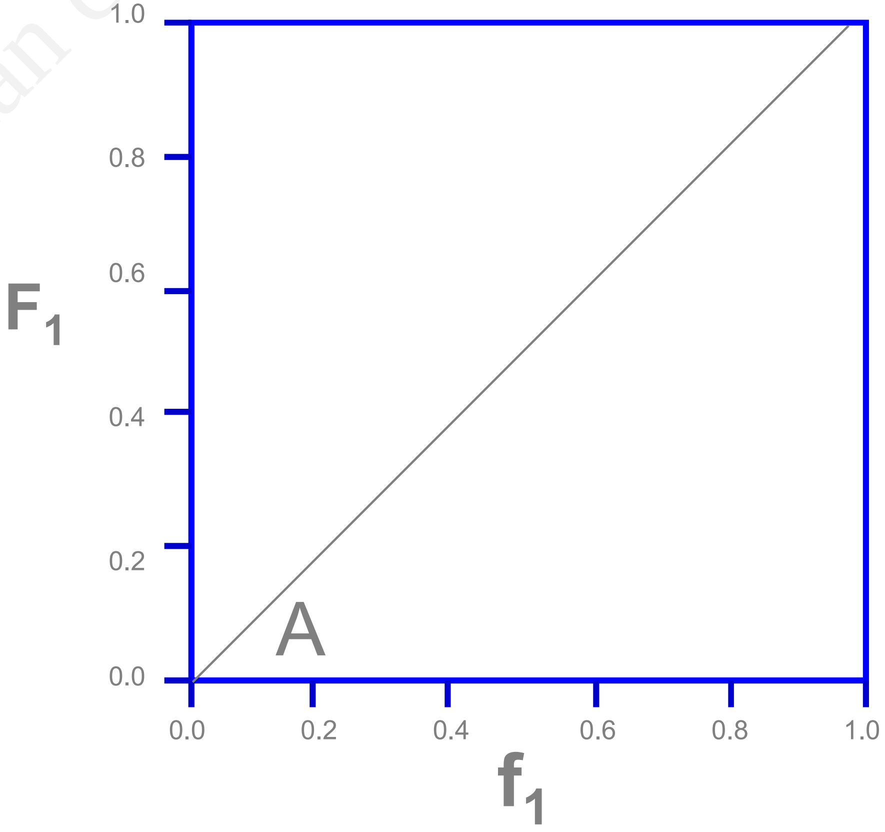
- Nếu $k_{12} >> k_{11}$ và $k_{21} >> k_{22}$



•$r_1 < 1$: ~~M_1* ưu tiên phản ứng monome M_2 (copolyme hóa)

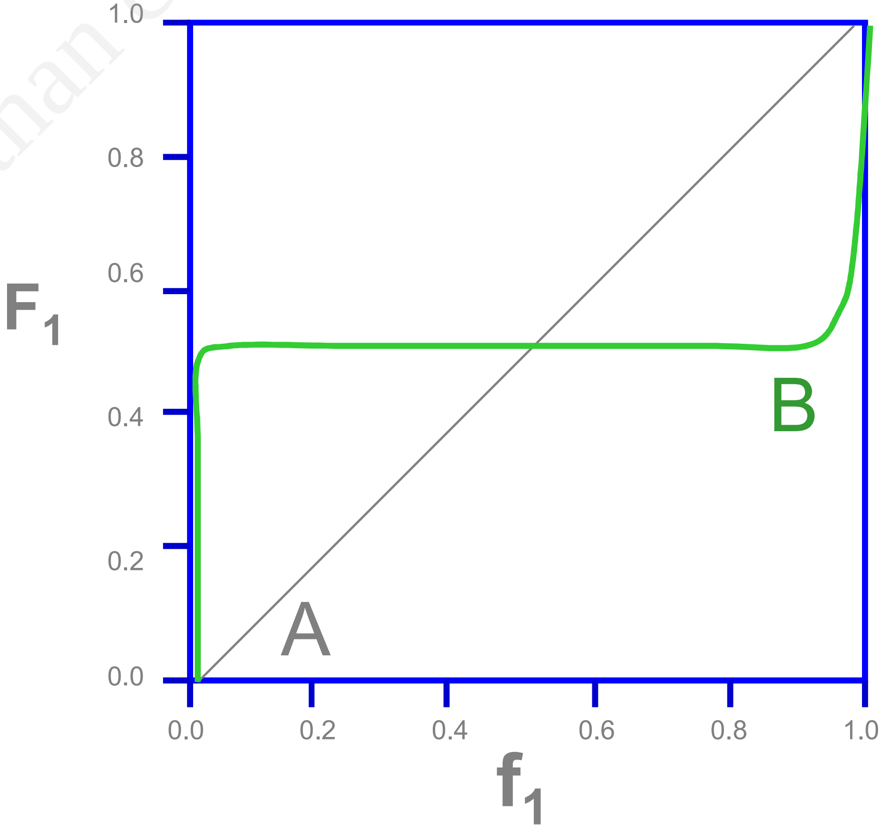
Copolymerization Examples

- $r_1 = r_2 = 1.0$
  - Monomers exhibit no preference for homo-propagation vs cross-propagation
  - Truly random copolymer results
  - $F_1 = f_1$
  - Ethylene / vinyl acetate
  - Styrene/4-chlorostyrene



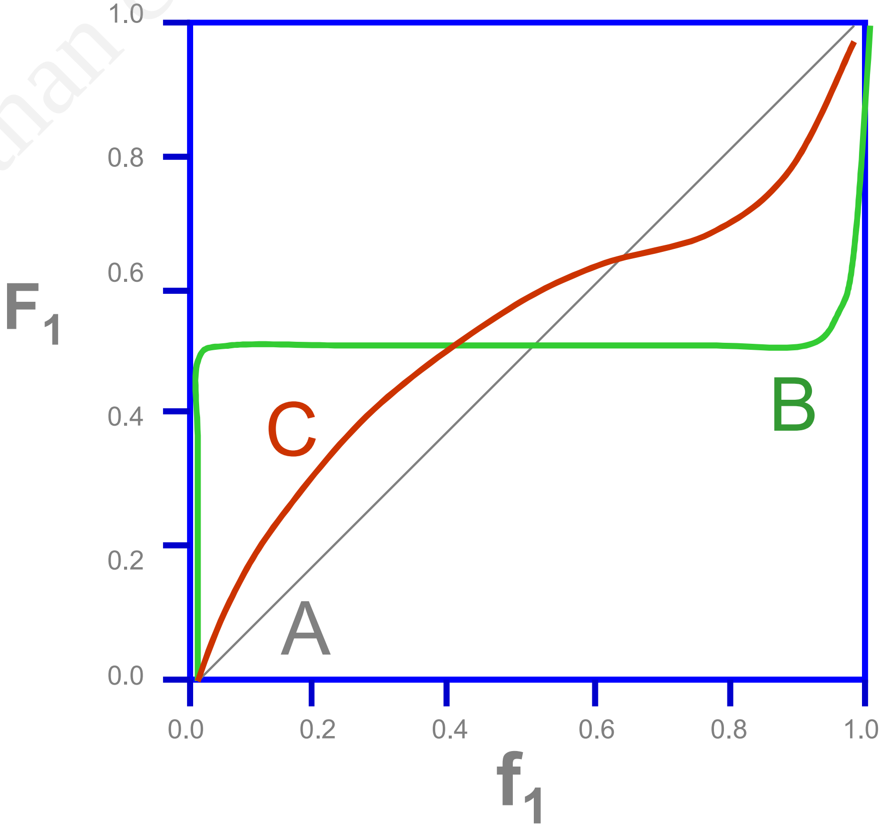
Copolymerization Examples

- $r_1 = r_2 = 1.0$
- $r_1 = r_2 = 0.0$
  - Monomers exhibit tendency to cross-propagate
  - Alternating copolymer results
  - $F_1 = 0.5$
  - Styrene / maleic anhydride
  - TFE / ethylene



Copolymerization Examples

- $r_1 = r_2 = 1.0$
- $r_1 = r_2 = 0.0$
- r_1 and r_2 between 0 and 1.0
  - – Common
  - – Cross-over point
    - Azeotropic polymerization



Alternating Copolymerization

Mean of Cross-over Point

$$F_1 = f_1$$

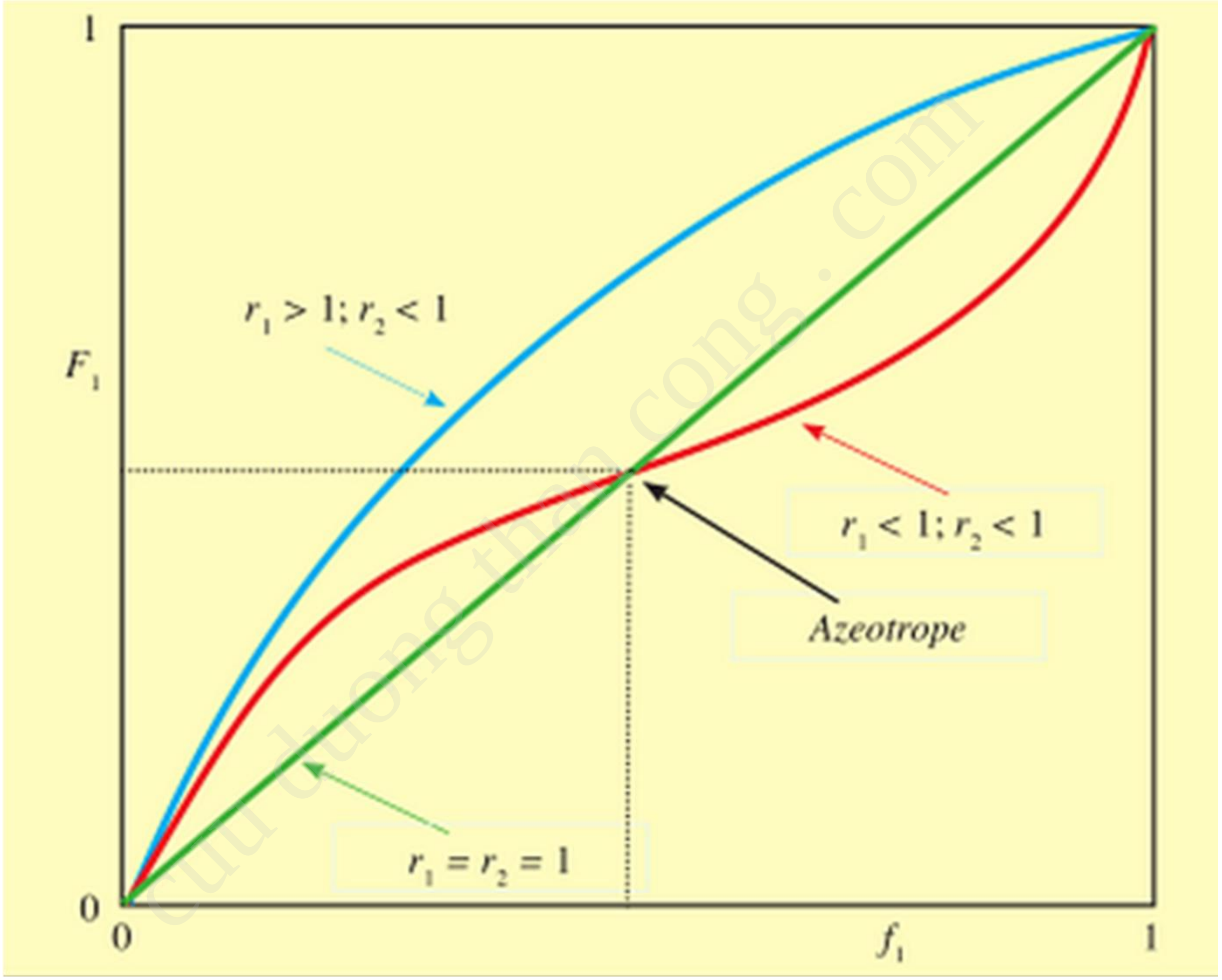
At these crossover points the copolymer and feed compositions are the same and copolymerization occurs without a change in the feed composition

Such copolymerizaions are termed Azeotropic copolymeriztions.

Condition of Azeotropic copolymeriztion

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \quad \textbf{and} \quad \frac{[M_1]}{[M_2]} = \frac{(r_2 - 1)}{(r_1 - 1)}$$

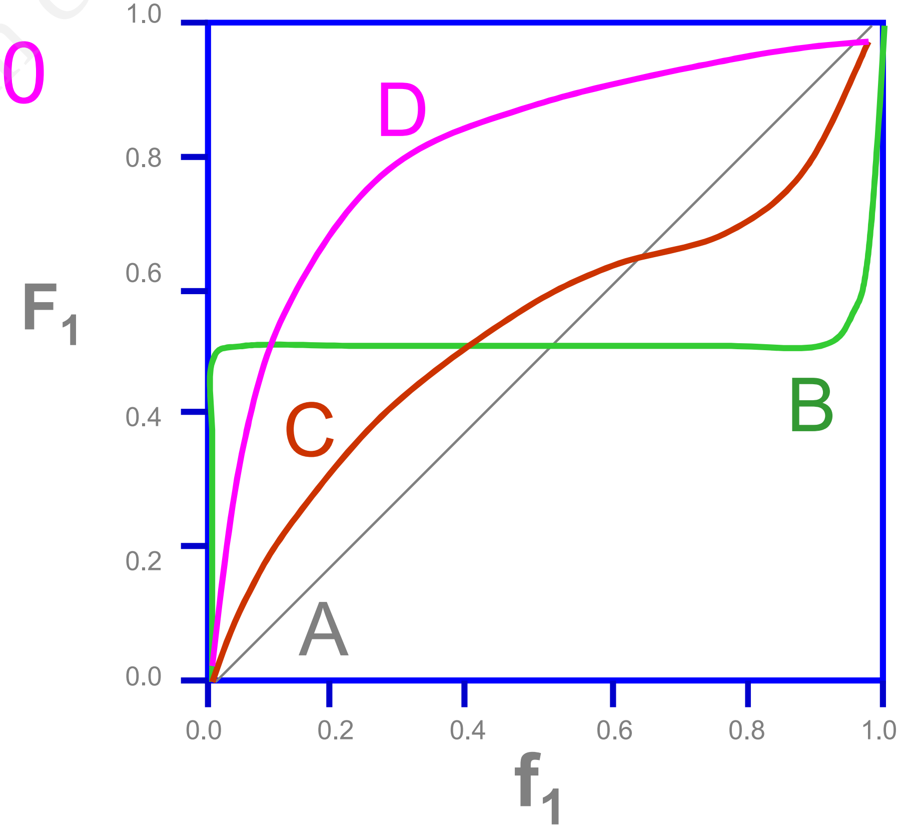
$$\because \quad F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} = \frac{[M_1]}{[M_1] + [M_2]} = f_1$$


1
0
0
1
F_1
f_1
$r_1 > 1; r_2 < 1$
$r_1 < 1; r_2 < 1$
Azeotrope
$r_1 = r_2 = 1$

Copolymerization Examples

- $r_1 = r_2 = 1.0$
- $r_1 = r_2 = 0.0$
- r_1 and r_2 between 0 and 1.0
- $r_1 >> 1.0$ and $r_2 << 1.0$
  - – $r_1 > 1.0$ and $r_2 < 1.0$
  - – $r_1 >> 1.0 >> r_2$

  Significant drift in feed ratio



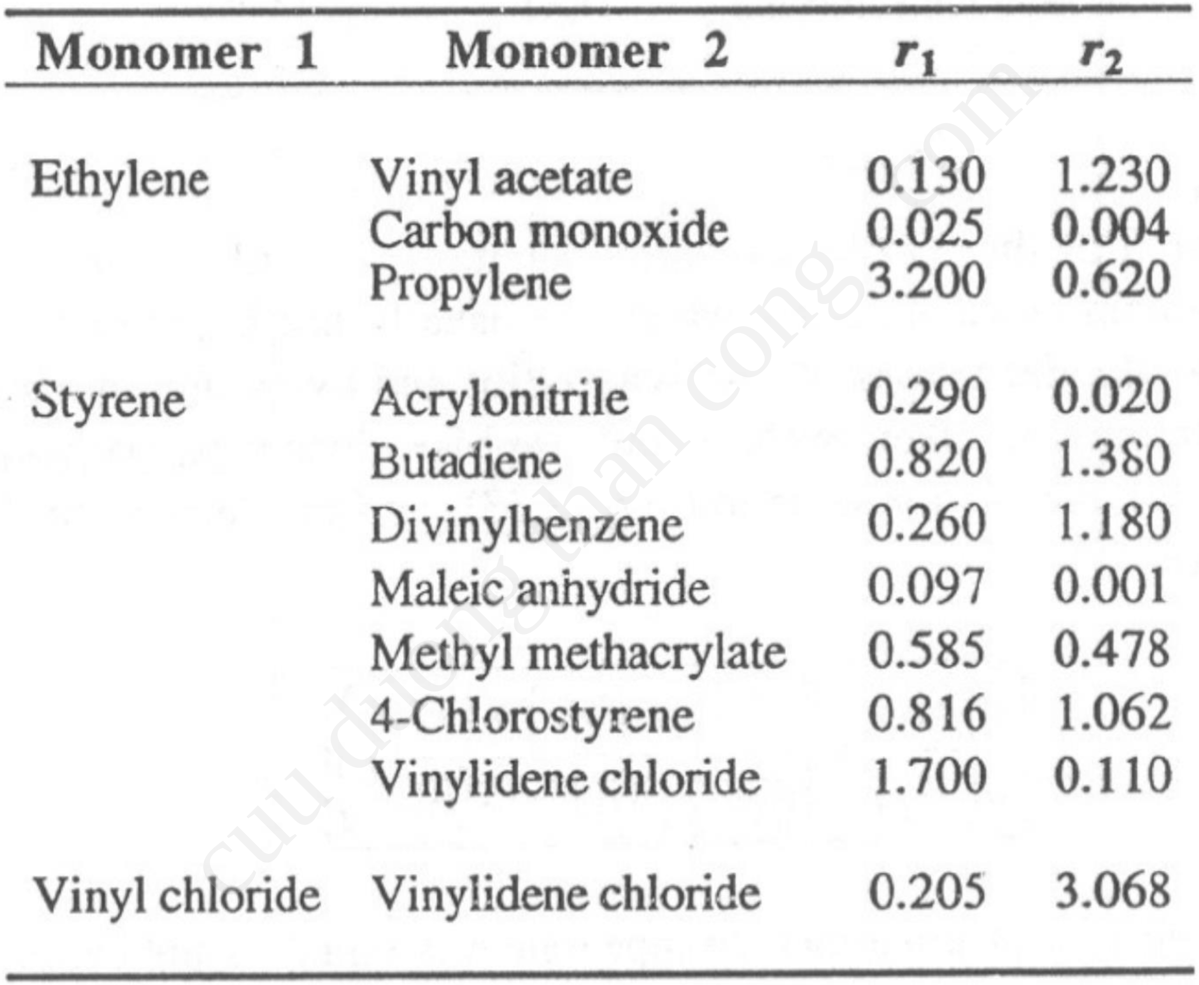
$r_1 = r_2 >> 1$

- $r_1 = \infty$ thì $k_{12} = 0$
- $r_2 = \infty$ thì $k_{21} = 0$
- Chuỗi copolyme kết thúc bằng tâm hoạt động M1 chỉ cộng M1.
- Chuỗi copolyme kết thúc bằng tâm hoạt động M2 chỉ cộng M2.
- Tạo homopolyme, sản phẩm là hỗn hợp 2 polyme.

Composition drift

- Các thành phần của hỗn hợp monome thay đổi với độ chuyển hóa ngày càng tăng, cũng như các thành phần của các chuỗi polymer.
- Khi xác định r, tại độ chuyển hóa thấp, vào cuối thí nghiệm, tỷ lệ nồng độ monomer là cơ bản giống như lúc đầu.
- Tuy nhiên, nếu muốn độ chuyển hóa cao, thành phần mong muốn của copolyme có thể đạt được bằng cách thêm monomer phản ứng mạnh hơn một cách tính toán.

r_1 & r_2 ?



Monomer 1	Monomer 2	r_1	r_2
Ethylene	Vinyl acetate	0.130	1.230
	Carbon monoxide	0.025	0.004
	Propylene	3.200	0.620
Styrene	Acrylonitrile	0.290	0.020
	Butadiene	0.820	1.380
	Divinylbenzene	0.260	1.180
	Maleic anhydride	0.097	0.001
	Methyl methacrylate	0.585	0.478
	4-Chlorostyrene	0.816	1.062
	Vinylidene chloride	1.700	0.110
Vinyl chloride	Vinylidene chloride	0.205	3.068

M1	M2	r1	r2	r1r2
Acrylamide	Acrylic acid	1.38	0.36	0.5
	Methyl acrylate	1.30	0.05	0.07
	Vinylidene chloride	4.9	0.15	0.74
Acrylic acid	Acrylonitrile (50°C)	1.15	0.35	0.40
	Styrene	0.25	0.15	0.04
	Vinyl acetate (70°C)	2	0.1	0.2
Acrylonitrile	Butadiene	0.25	0.33	0.08
	Ethyl acrylate (50°C)	1.17	0.67	0.78
	Maleic anhydride	6	0	0
	Methyl methacrylate	0.13	1.16	0.15
	Styrene	0.04	0.41	0.16
	Vinyl acetate	4.05	0.06	0.24
	Viny chloride	3.28	0.02	0.07
Butadiene	Methyl methacrylate	0.70	0.32	0.22
	Styrene	1.39	0.78	1.08
Chlorotrifluoroethylene	Tetrafluoroethylene	1.0	1.0	1.0
Isoprene	Styrene	1.98	0.44	0.87
Maleic anhydride	Methyl acrylate	0	2.5	0
	Methyl methacrylate	0.03	3.5	0.11
	Styrene	0	0.02	0
	Vinyl acetate (70 °C)	0.003	0.055	0.0002

Methyl acrylate	Acrylonitrile	0.67	1.26	0.84
	Styrene	0.18	0.75	0.14
	Vinyl acetate	9.0	0.1	0.90
	Vinyl chloride	5	0	0
Methyl isopropenyl ketone	Styrene (80°C)	0.66	0.32	0.21
Methyl methacrylate	Styrene	0.50	0.50	0.25
	Vinyl acetate	20	0.015	0.30
	Vinyl chloride	12.5	0	0
α–Methylstyrene	Maleic anhydride	0.038	0.08	0.003
	Styrene	0.38	2.3	0.87
Styrene	p-Chlorostyrene	0.74	1.025	0.76
	Fumaronitrile	0.23	0.01	0.002
	p-Methoxystyrene	1.16	0.82	0.95
	Vinyl acetate	55	0.01	0.55
	Vinyl chloride	17	0.02	0.34
	2-Vinylpyridine	0.56	0.9	0.50
Vinyl acetate	Vinyl chloride	0.23	1.68	0.39
	Vinyl laurate	1.4	0.7	0.98
Vinyl chloride	Diethyl maleate	0.77	0.009	0.007
	Vinylidene chloride	0.3	3.2	0.96
N-Vinylpyrrolidone	Styrene(50°C)	0.045	15.7	0.71

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[a] Data from Polymer Handbook, Temperatures other than 60 C shown in parentheses.

Experimental Determination of r1 & r2

1. **Mayo and Lewis**

rearrange copolymer eq. and can get

$$r_2 = \frac{[M_1]}{[M_2]} \cdot \left\{ \frac{d[M_2]}{d[M_1]} \left[1 + \frac{r_1[M_1]}{[M_2]} \right] - 1 \right\}$$

monomer comp

$$[M_1]/[M_2]$$

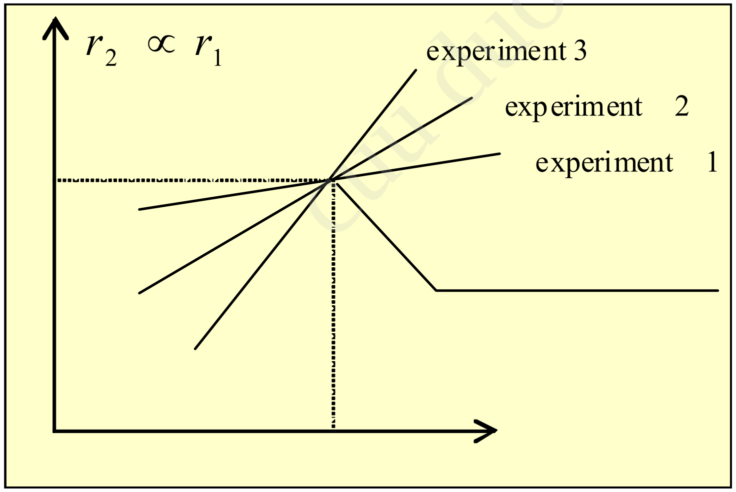
⋮

copolymer comp.

$$d[M_1]/d[M_2]$$

⋮

then vary r_1 value (put) and do again



Experimental Determination of r_1 & r_2

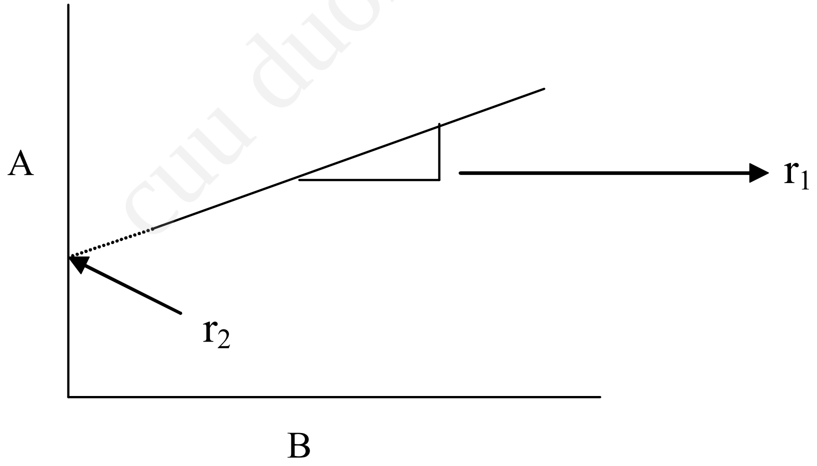
2. Finemann and Ross

Recall

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

$$\underbrace{\frac{f_1(1-2F_1)}{F_1(1-f_1)}}_{\substack{\textbf{A}\\ \textbf{const.}}} = r_2 + \underbrace{\frac{f_1^{\,2}(F_1-1)}{F_1(1-f_1)^2}}_{\substack{\textbf{B}\\ \textbf{const.}}} \cdot r_1$$

at low conversion



Slope : r_1
Intersection : r_2

Structure and Reactivity

@ Q-e scheme of Alfred Price

As know r, prediction is possible to polar, resonance effect
Guidance to chemists

$$k_{ij} = P_i Q_j \exp(-e_i e_j)$$

where P : hoạt tính của tâm hoạt động (active center reactivity)
Q : hoạt tính của monome (monomer reactivity)
e_1 and e_2 are the polarity of the radical M_1• and M_2 • respectively.

$$r_i = \frac{k_{ii}}{k_{ij}} = \frac{P_i Q_i \exp(-e_i e_i)}{P_i Q_j \exp(-e_i e_j)}$$

$$\boxed{r_i = \frac{Q_i}{Q_j} \exp[-e_i(e_i - e_j)]}$$

Q – e scheme

$$e_1 = e_2 \pm \sqrt{-ln(r_1 \cdot r_2)}$$

$$Q_1 = \frac{Q_2}{r_2} \cdot e^{\pm e_2 \sqrt{-ln(r_1 \cdot r_2)}}$$

	P	e	Q
St	1	-0.8	1
AN	58.23	1.233	0.4
MA	21.03	0.577	0.42
MMA	2.413	0.397	0.24
VAc	751.3	-0.027	0.024

Monomer	Q	e
Acrylamide	0.23	0.54
Acrylonitrile	0.48	1.23
Butadiene	1.70	-0.50
Ethylene	0.016	0.05
Isobutylene	0.023	-1.20
Isoprene	1.99	-0.55
Maleic anhydride	0.86	3.69
Methacrylic acid	0.98	0.62
Methyl methacrylate	0.78	0.40
N-Vinyl pyrrolidone	0.088	-1.62
Styrene	1.00	-0.80
Vinyl acetate	0.026	-0.88
Vinyl chloride	0.056	0.16
Vinylidene chloride	0.31	0.34

Effect of Reaction Condition

Reaction medium

Depend on Solubility, PH, Viscosity, and Polarity

Temperature

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{A_{11}}{A_{12}} \exp\left[\frac{(E_{12} - E_{11})}{RT}\right]$$

But the effect of temperature on r is not large

Pressure

$$\frac{d \ln r_1}{dP} = \frac{-(df_1 \Delta V_{11} - \Delta V_{12})}{RT}$$

But the effect of pressure on r is not large

Reactivity

@ Substituent Effects

Φ, CH2=CH- > -C≡N, -COR > -COOH, -COOR > -Cl > -O-COR, -R > -OR, -H

monomers increase relative reactivity by resonance stabilization.
The resonance stability of the monomer increases the reactivity of the monomer.

The resonance stability of the radical is weakened reactivity of the radical.

Effect of Reaction Condition

Structure and Reactivity

- I. Resonance Stabilization
- II. Polar Effects
- III. Steric Effects

I.Resonance Stabilization

Substituent on Double Bond	Relative Reactivity of Monomer
-H, $-OCH_3$	1
-OAc, $-CH_3$	1.5-5
-Cl	3-20
-COO, -COOH	20-60
-CN, -COR	30-60
$-C_2H_3$, $-C_6H_5$	50-100

Table 6-4 Rate Constant(k_{12}) for Radical-Monomer Reactions

	Polymer Radical								
Monomer(M_1)	Butadiene	Styrene	Methyl Metacrylate	Acrylonirile	Methyl Acrylate	Vinyl Acetate	Vinyl Chloride	Q_1	e_1
Butadiene Styrene Methyl methacrylate Acrylonitrile Methyl acrylate Vinyl chloride Vinyl acetate	100 70 130 330 130 11	280 165 314 413 215 9.7 3.4	2,060 1,130 515 422 268 52 26	98,00 0 49,00 0 13,10 0 1,960 1,310 720 230	41,800 10,045 4,180 2,510 2,090 520 530	230,00 0 154,00 0 46,000 23,000 0,100 2,300	319,00 0 550,00 0 110,000 225,00 0 187,00 0 11,000 6,490	2.39 1.00 0.74 0.60 0.42 0.04 4 0.02 6	- 1.05 - 0.80 0.40 1.20 0.60 0.20 - 0.22