Copolymerization

<u>At the end of this lecture, you should be able to:</u>

- Understand what the copolymer and copolymerization is.
- List the types of copolymers.
- Understand the importance of copolymerization.
- Understand the mechanism of copolymerization.
- Make some calculations regarding copolymerization reactions.

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1. Copolymerization and Copolymer

chain polymerizations can be carried out with mixtures of two monomers to form polymeric products with two different structures in the polymer chain (not as condensation polymerization). This type of chain polymerization process in which two monomers are simultaneously polymerized is termed a copolymerization, and the product is a copolymer. It is important to stress that the copolymer is not an alloy of two homopolymers but contains units of both monomers incorporated into each copolymer molecule. The process can be depicted as

$$M_1 + M_2 \longrightarrow \sim M_1M_2M_2M_1M_2M_2M_2M_1M_1M_2M_2M_1M_1M_2M_1M_1M_1M_2M_2M_1M_1 \sim$$

The two monomers enter into the copolymer in overall amounts determined by their relative concentrations and reactivities. The simultaneous chain polymerization of different monomers can also be carried out with mixtures of three or more monomers. Such polymerizations are generally referred to as multicomponent copolymerizations; the term terpolymerization is specifically used for systems of three monomers.

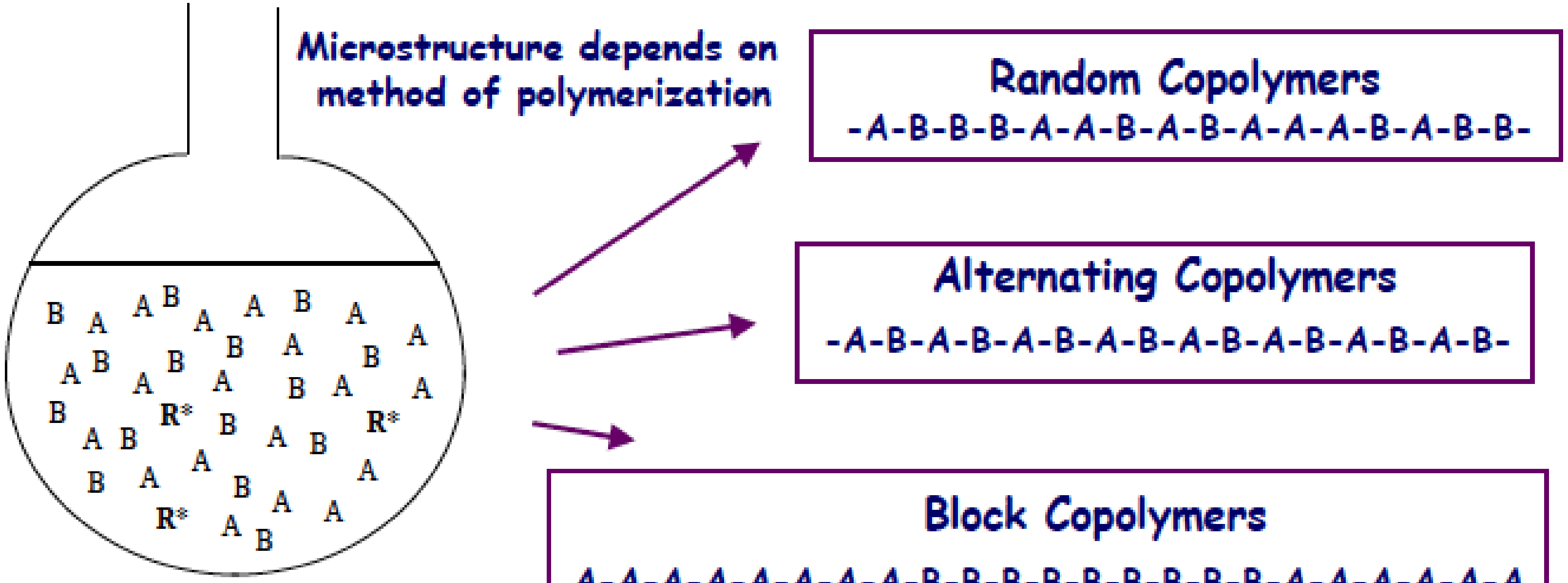
2. Importance of Copolymerization

Only about one-third of the total is styrene homopolymer. Polystyrene is a brittle plastic with low impact strength and low solvent resistance. Copolymerization as well as blending greatly increase the usefulness of polystyrene. Styrene copolymers and blends of copolymers are useful not only as plastics but also as elastomers. Thus copolymerization of styrene with acrylonitrile leads to increased impact and solvent resistance, while copolymerization with 1,3-butadiene leads to elastomeric properties. Combinations of styrene, acrylonitrile, and 1,3-butadiene improve all three properties simultaneously. This and other technological applications of copolymerization.

3. Types Of Copolymers

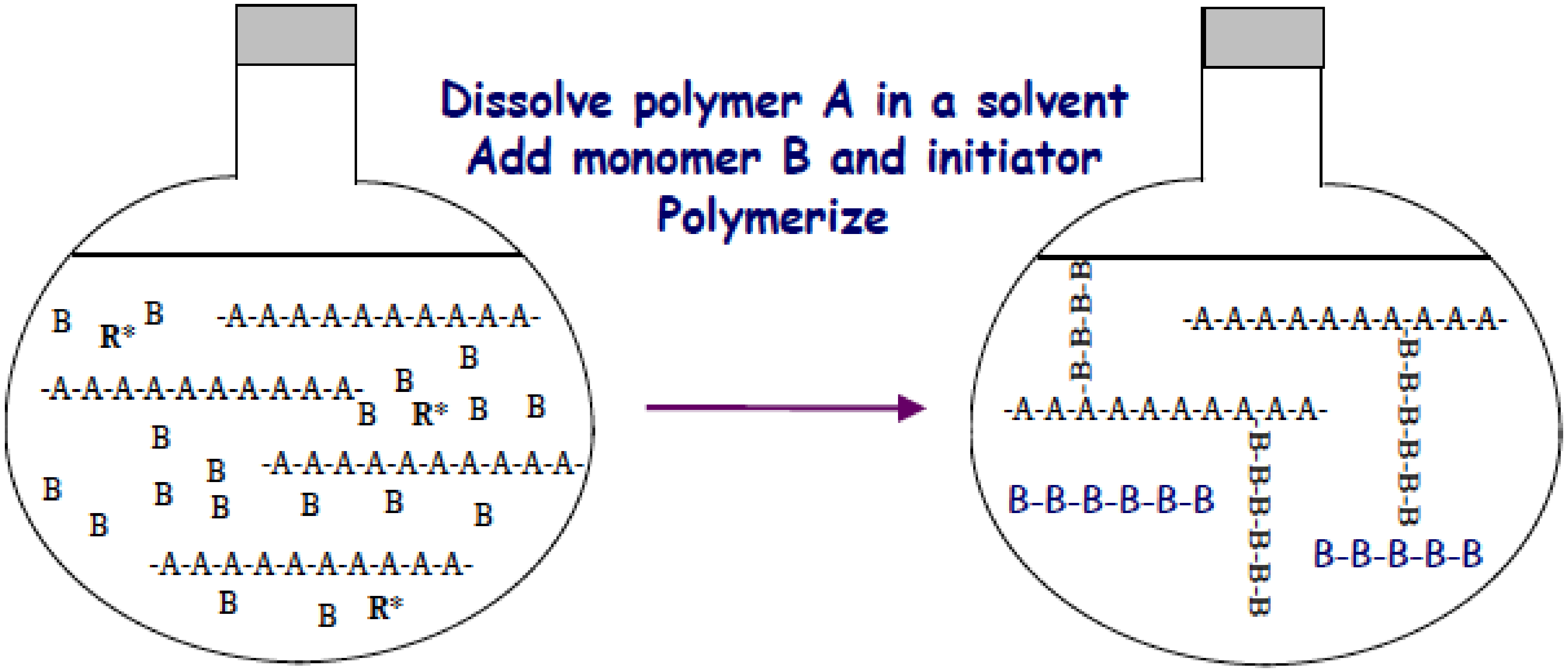
If monomer (A) Reacted with Monomer (B) by chain growth polymerization , the structure of polymer formed are:

1. Random Copolymers.
2. Alternating Copolymers.
3. Block Copolymers.
4. Crafted Copolymers.



The post polymerization make a “ crafted Copolymer” :

Examples:
High Impact Polystyrene (HIPS)
Acrylonitrile / Butadiene / Styrene (ABS)



4. Kinetic Of Radical Copolymerization
(Terminal Model; Monomer Reactivity Ratios)

If it is assumed that the reactivity of the propagating species is dependent only on the monomer unit at the end of the chain (referred to as the end or ultimate unit), four propagation reactions are then possible. Monomers M1 and M2 can each add either to a propagating chain ending in M1 or to one ending in M2, that is:

Reaction	Rate equation
$M_1\cdot + M_1 \rightarrow M_1\cdot$	$k_{11}[M_1\cdot][M_1]$
$M_1\cdot + M_2 \rightarrow M_2\cdot$	$k_{12}[M_1\cdot][M_2]$
$M_2\cdot + M_1 \rightarrow M_1\cdot$	$k_{21}[M_2\cdot][M_1]$
$M_2\cdot + M_2 \rightarrow M_2\cdot$	$k_{22}[M_2\cdot][M_2]$

where **k**11 is the rate constant for a propagating chain ending in M1 adding to monomer M1, **k**12 that for a propagating chain ending in M1 adding to monomer M2, and so on.

The rates of disappearance of monomers M1 and M2 are given by

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

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

Dividing Eq.(1) & Eq.(2):

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

At steady State:

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

Dividing the top and bottom of the right side of Eq.3 by $k_{21}[M_2][M_1]$ and combining the result with the parameters r_1 and r_2, which are defined by:

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

Finally , one can obtain a equation in terms of r_1 and r_2 as follows:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \qquad (4)$$

5. COPOLYMER COMPOSITION

The copolymerization equation can also be expressed in terms of mole fractions instead of concentrations. If f_1 and f_2 are the mole fractions of monomers M1 and M2 in the feed, and F_1 and F_2 are the mole fractions of M1 and M2 in the copolymer, then

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \quad \& \quad F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$

From the above two equations :

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

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

Reactivity Ratios of Some Monomers

Monomer 1	Monomer 2	r_1	r_2	T (°C)
Acrylonitrile	1,3-Butadiene	0.02	0.30	40
	Methyl methacrylate	0.15	1.22	80
	Styrene	0.04	0.40	60
	Vinyl acetate	4.2	0.05	50
	Vinyl chloride	2.7	0.04	60
1,3-Butadiene	Methyl methacrylate	0.75	0.25	90
	Styrene	1.35	0.58	50
	Vinyl chloride	8.8	0.035	50
Methyl methacrylate	Styrene	0.46	0.52	60
	Vinyl acetate	20	0.015	60
	Vinyl chloride	10	0.1	68
Styrene	Vinyl acetate	55	0.01	60
	Vinyl chloride	17	0.02	60
Vinyl acetate	Vinyl chloride	0.23	1.68	60

THANK YOU
FOR YOUR LISTENING