Copolymerization

At the end of this lecture, you should be able to:

- 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.
- Predict the copolymer types from the calculation.

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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

Example (1)

The reactivity ratios for the copolymerization of methyl methacrylate (1) and vinyl chloride (2) at 68° C are r_1 = 10 and r_2= 0.1. To ensure that the copolymer contains an appreciable quantity (>40% in this case) of the vinyl chloride, a material engineer decided to carry out the copolymerization reaction with a feed composed of 80% vinyl chloride. Will the engineer achieve his objective?

Solution

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} = \frac{10(0.2)^2 + (0.2)(0.8)}{10(0.2)^2 + 2(0.2)(0.8) + 0.1(0.8)^2}$$

$$= 0.714$$

$$F_2 = 1 - F_1 = 0.286.*$$

If the difference in the reactivities of the two monomers is large, it is impossible to increase the proportion of the less-reactive monomer in the copolymer simply by increasing its composition in the feed.

Example (2)

What is the composition of the copolymer formed by the polymerization of an equimolar mixture of butadiene (1) and styrene (2) at 50 °C? Which monener do you except having a faster reaction rate ?

Solution

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

$$= \frac{1.35(0.5)^2 + (0.5)^2}{1.35(0.5)^2 + 2(0.5)^2 + 0.58(0.5)^2}$$

$$= 0.60$$

$$k_{11} = 1.35\ k_{12}\ ,\ \ k_{22} = 0.58\ k_{21}$$

Example (3)

Plot graphs showing the variation of the instantaneous copolymer composition F1 with monomer composition for the following systems:

I. Vinyl acetate (1), maleic anhydride (2), 75° C, r_1 = 0.055, r_2 = 0.003.

II. Styrene (1), vinyl acetate (2), 60° C, r_1 = 55, r_2 = 0.01.

III. Vinyl chloride (1), methyl methacrylate (2) 68° C, r_1 = 0.1, r_2 = 10

Solution

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

Assume f_1 values between 0 to 1 (because fraction)

f_1 = 0.1 >>>>> f_2 = 0.9 (from Eq.* find F_1)

f_1 = 0.3 >>>>> f_2 = 0.7 (from Eq.* find F_1)

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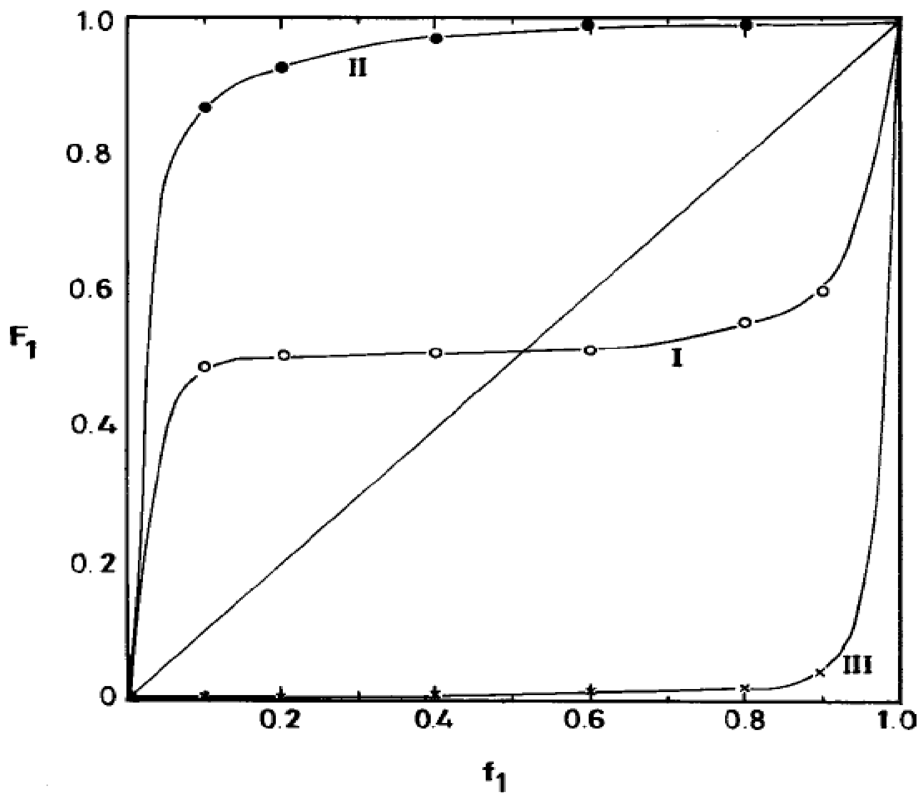
f_1 = 0.9 >>>>> f_2 = 0.1 (from Eq.* find F_1)



Types of Copolymerization Behavior

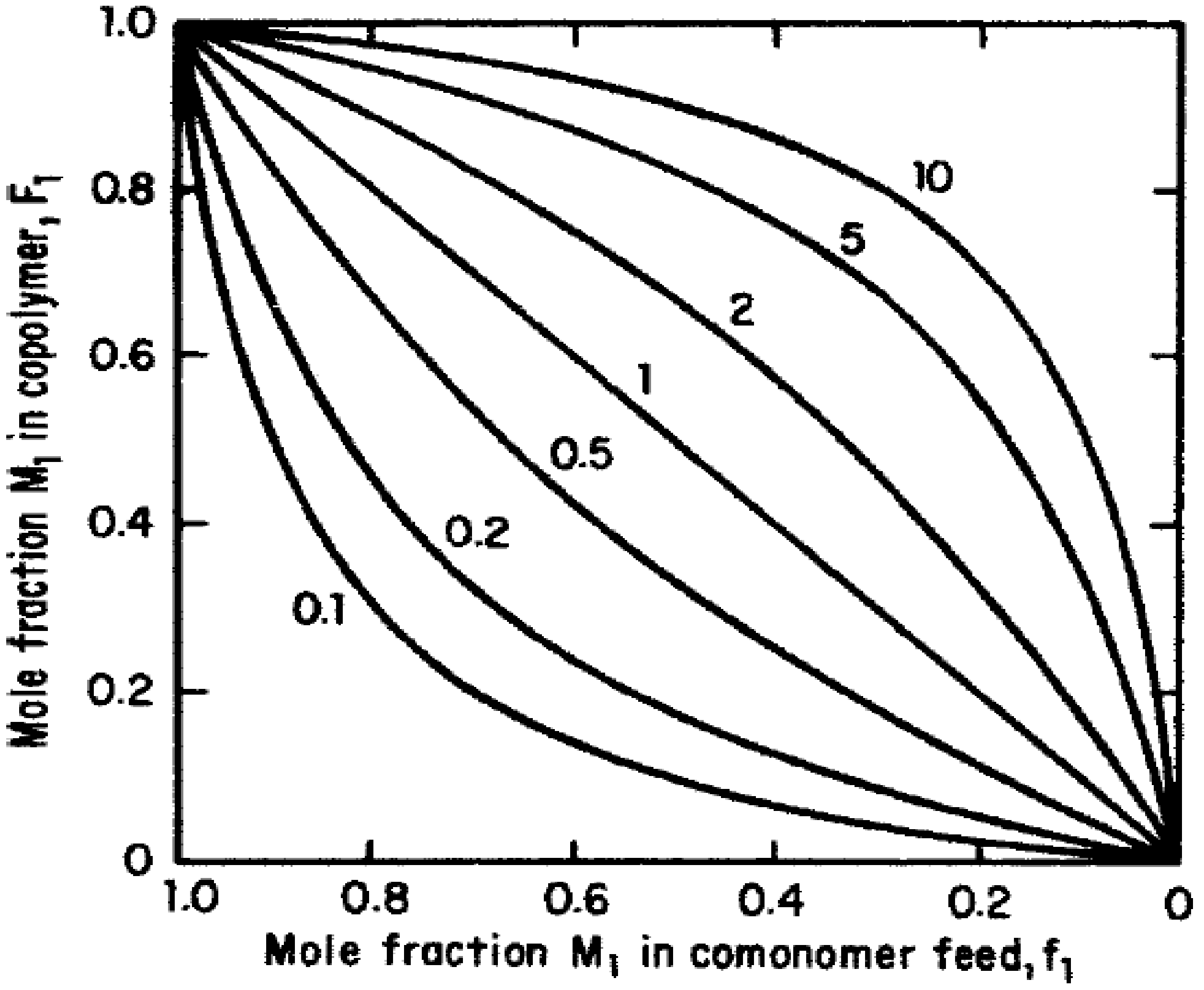
(1) Random Copolymerization: $r_1.r_2=1$

Case (1): When $r_1.r_2 = 1$ (ideal case), the two monomers show equal reactivities toward both propagating species. The copolymer composition is the same as the feed composition with a random placement of the two monomers along the copolymer chain. Such behavior is referred to as **random** or **Bernoullian**.

Case (2): For the case where the two monomer reactivity ratios are different, that is, $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$, one of the monomers is more reactive than the other toward both propagating species. The copolymer will contain a larger proportion of the more reactive monomer in random placement.

$$r_1 r_2 = 1, \quad \text{then}$$

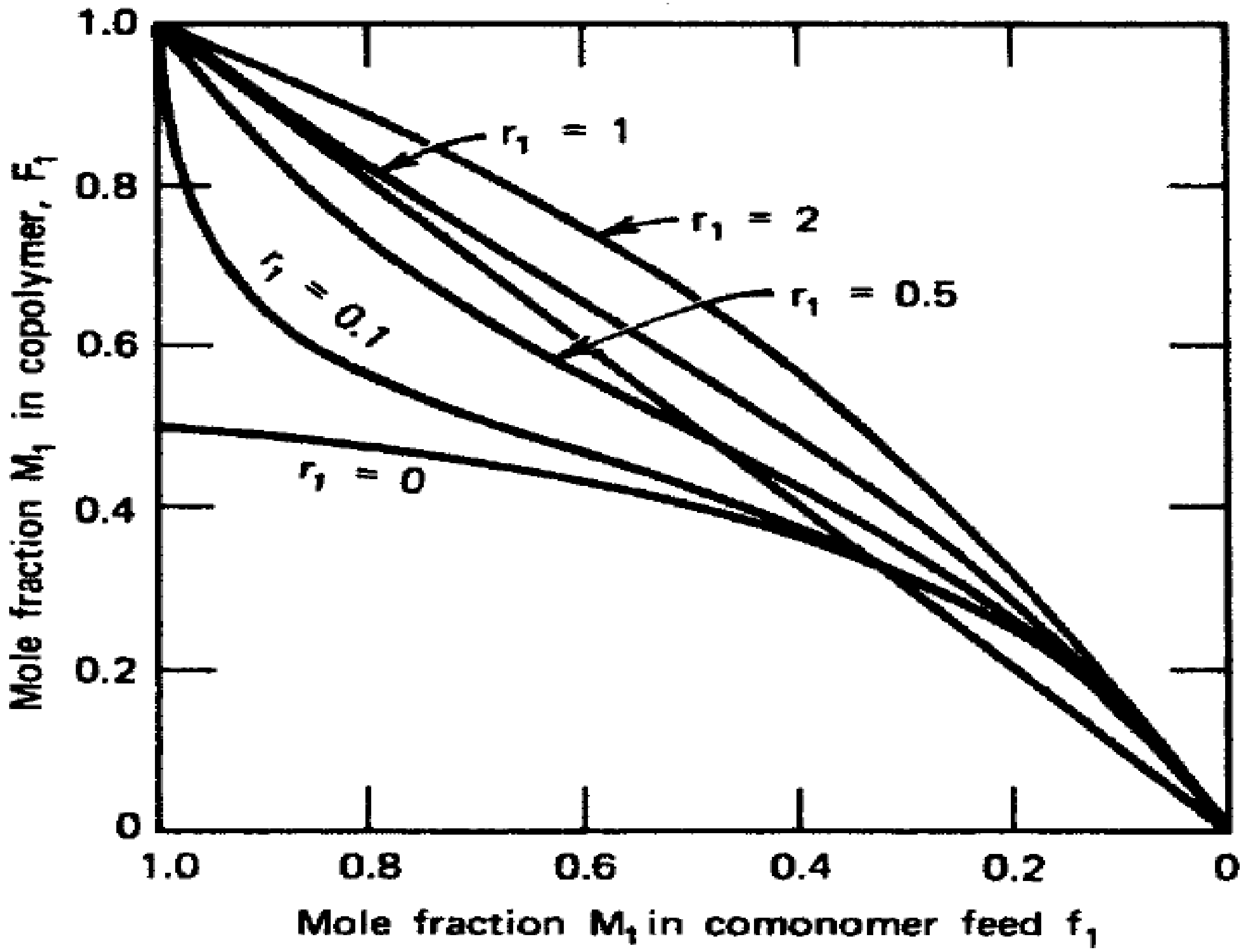
$$r_1 = 1/r_2 \quad \text{or} \quad k_{11}/k_{12} = k_{21}/k_{22}$$



1.0
0.8
0.6
0.4
0.2
0
Mole fraction M1 in copolymer, F1
1.0
0.8
0.6
0.4
0.2
0
Mole fraction M1 in comonomer feed, f1
10
5
2
1
0.5
0.2
0.1

(2) Alternating Copolymerization: $r_1.r_2$=zero

The behavior of most copolymer systems lies between the two extremes of ideal and alternating copolymerization. As the $r_1.r_2$ product decreases from one toward zero, there is an increasing tendency toward alternation. Perfect alternation occurs when r_1 and $r_2$are both zero. The tendency toward alternation and the tendency away from ideal behavior increases as $r_1$and r_2 become progressively less than unity. The range of behaviors can be seen by considering the situation where r_2 remains constant at 0.5 and r_1 varies between 2 and 0. Figure below shows the copolymer composition as a function of the feed composition in these cases. The curve for $r_1 = 2$ shows the ideal type of behavior described previously. As r_1 decreases below 2, there is an increasing tendency toward the alternating behavior with each type of propagating species preferring to add the other monomer.



1.0
0.8
0.6
0.4
0.2
0
1.0
0.8
0.6
0.4
0.2
0
Mole fraction M_1 in copolymer, F_1
Mole fraction M_1 in comonomer feed f_1
$r_1 = 1$
$r_1 = 2$
$r_1 = 0.5$
$r_1 = 0.1$
$r_1 = 0$

(3) Block Copolymerization: $r_1 > 1$; $r_2 > 1$

If both r_1 and r_2 are greater than unity (and therefore, also $r_1 r_2 > 1$) there is a tendency to form a block copolymer in which there are blocks of both monomers in the chain. This type of behavior is rarely encountered.

THANK YOU
FOR YOUR LISTENING