Introduction to polymer science
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Lecture – 22
Copolymerization (contd.,)

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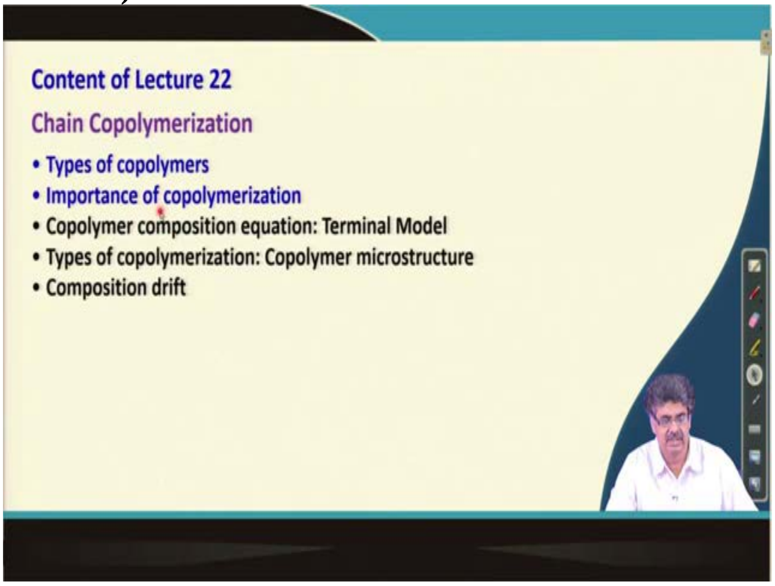

Content of Lecture 22

Chain Copolymerization

- Types of copolymers
- Importance of copolymerization
- Copolymer composition equation: Terminal Model
- Types of copolymerization: Copolymer microstructure
- Composition drift

Welcome back, in this lecture 22, which will be the last lecture for polymer synthesis module, I will talk about copolymerization is a continuation from the last lecture 21. In this lecture, these are the topics I plan to cover, the first two topics were already covered in last lecture and I will cover from the third topic in this lecture.

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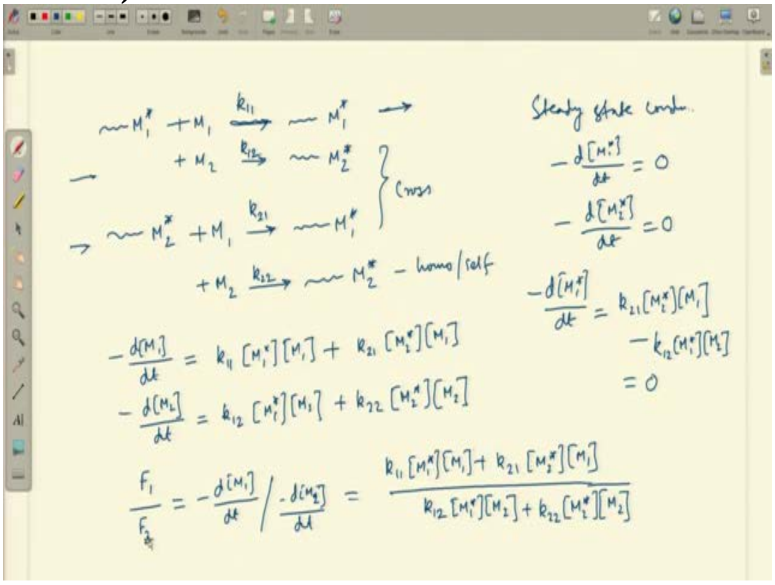

$$\sim M_1^* + M_1 \xrightarrow{k_{11}} \sim M_1^*$$
$$+ M_2 \xrightarrow{k_{12}} \sim M_2^*$$
$$\sim M_2^* + M_1 \xrightarrow{k_{21}} \sim M_1^*$$

Cross

$$+ M_2 \xrightarrow{k_{22}} \sim M_2^*$$

– homo/self

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]$$
$$-\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]$$
$$\frac{F_1}{F_2} = -\frac{d[M_1]}{dt} \Big/ -\frac{d[M_2]}{dt} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]}$$

Steady state condn.

$$-\frac{d[M_1^*]}{dt} = 0$$
$$-\frac{d[M_2^*]}{dt} = 0$$
$$-\frac{d[M_1^*]}{dt} = k_{21}[M_2^*][M_1] - k_{12}[M_1^*][M_2] = 0$$

Now, I discussed that in normal chain polymerization, the rate of polymerization depends on rate of propagation, because most of the monomers are consumed during propagation step. We write the general propagation steps, when M_1* reacts with M_1 giving back M_1*, we can write this as rate constant as k_{11}. The first '1' in the rate constant stands for this active species and the second number stands for the monomer. Now, M_1* can again react with M_2 giving you M_2*, we write the rate constant as k_{12}. So, k_{11} is the rate constant for self-polymerization where active chain end is reacting with similar type of monomer producing similar chain ends.

We can also write two other constants for M_2* - this can react with M_1 producing M_1* or it can react with M_2 producing M_2*. So, for the first case we write k_{21} and for the second k_{22}, respectively. k_{12} and k_{21} are the two cross reactions whereas and these, k_{11} and k_{22} are for the homo or self-reactions.

AS written in the slide, in the first and the third reaction, M_1 is consumed. So, if we want to write rate of polymerization or rate of disappearance of M_1, we can write -

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

Similarly, M_2 is being consumed in the second and fourth reaction, we can write -

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

$\frac{d[M_1]}{dt}$ is the rate of disappearance of M_1 and $\frac{d[M_2]}{dt}$ is the rate of disappearance of M_2. Now, disappearance of monomer means, the monomers are being incorporated in the polymer chain. So, if we write the F_1 and F_2 are the mole fractions of M_1 in the polymer and mole fraction of M_2 in the polymer, respectively then F_1/F_2 will be given by the rate of disappearance of M_1 divided by the rate of disappearance of M_2.

Hence, we can write,

$$\frac{F_1}{F_2} = -\frac{d[M_1]}{dt} \Big/ -\frac{d[M_2]}{dt} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]}$$

Now, at the steady state, the rates of disappearance of the active radical active species are zero. Hence, d[M_1*]/dt and d[M_2*]/dt are 0. Now, if you can see the reactions in the slide, when M_1* reacts with M_1 producing M_1*, results no change in concentration of M_1* as in the first reaction.

Similarly, there is no change in concentration of M_2* in the fourth reaction. M_1* is only disappearing in the second reaction, and M_1* is getting producing in the third reaction. So, if we want to write d[M_1*]/dt then we can write k_{21}[M_2*][M_1] - k_{12}[M_1*][M_2]. So, applying the steady state application, we can put this as 0. We can use this relation in deriving the expression for F_1/F_2 as shown in the next slide.

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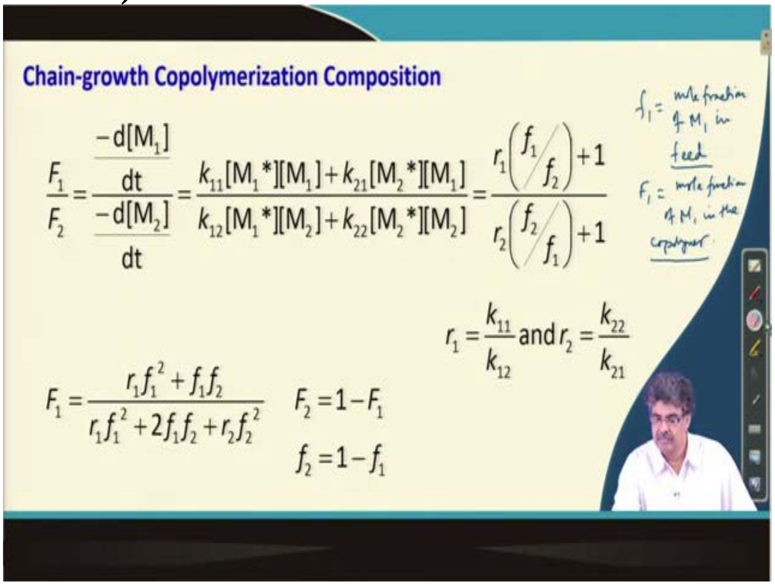

Chain-growth Copolymerization Composition

$$\frac{F_1}{F_2} = \frac{\frac{-d[M_1]}{dt}}{\frac{-d[M_2]}{dt}} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]} = \frac{r_1\left(\frac{f_1}{f_2}\right)+1}{r_2\left(\frac{f_2}{f_1}\right)+1}$$

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

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad F_2 = 1 - F_1$$

$$f_2 = 1 - f_1$$

f_1 = mole fraction of M_1 in feed

F_1 = mole fraction of M_1 in the copolymer.

The expression for F_1/F_2 is given by the ratio of disappearance of M_1 divided by rate of disappearance of M_2. We have discussed the two rates in the last slide, and this can be simplified using the steady state approximation and this will yield the following formula, where f_1 is the mole fraction of the M_1.

$$\frac{F_1}{F_2} = -\frac{d[M_1]}{dt} \Big/ -\frac{d[M_2]}{dt} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]} = \frac{r_1\left({f_1}/{f_2}\right)+1}{r_2\left({f_2}/{f_1}\right)+1}$$

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

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

Similarly, f_2 is the mole fraction M_2 in the feed and F_1 is the mole fraction of M_1 in the copolymer. When we mention capital (upper case) F, we are talking about the mole fraction in the copolymer, and when we mention small *f*, or lower case *f*, we are talking about in mole fraction in the feed. Here, r_1 is k_{11}/k_{12}, r_2 is k_{22}/k_{21}, k_{11} and k_{22} are the rate constant for homo-polymerization or homo reactions, and k_{12} and k_{21} are for the cross reactions. Therefore, if we simplify this, we can get this expression for F_1. Similarly, we can get for F_2 or we can just get F_2 by $(1 – F_1)$. Similarly, the feed monomer fraction also, $f_2 = (1 - f_1)$.

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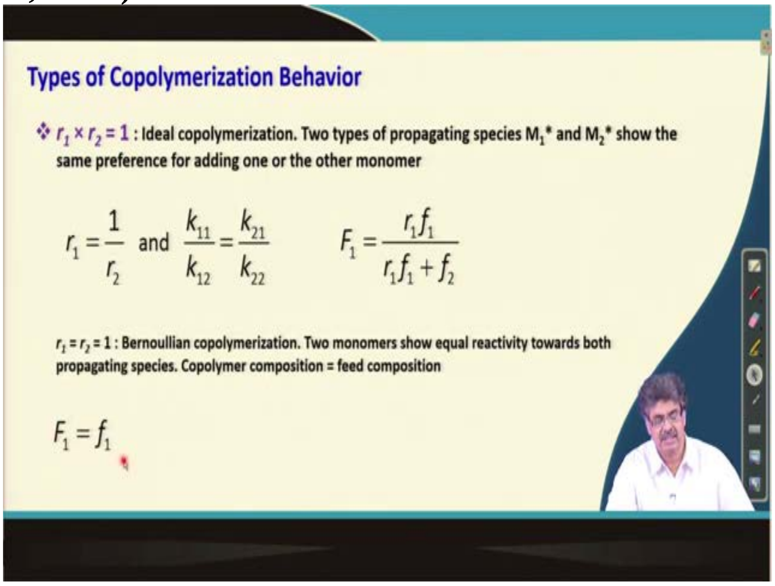

Types of Copolymerization Behavior

- $r_1 \times r_2 = 1$: Ideal copolymerization. Two types of propagating species M_1^* and M_2^* show the same preference for adding one or the other monomer

$$r_1 = \frac{1}{r_2} \quad \text{and} \quad \frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}} \qquad F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2}$$

$r_1 = r_2 = 1$: Bernoullian copolymerization. Two monomers show equal reactivity towards both propagating species. Copolymer composition = feed composition

$$F_1 = f_1$$

Now, these typical copolymerization behaviours are possible. We have defined r_1 and r_2. r_1 once again, is the rate of homo-polymerization divided by rate of cross polymerization. If we consider M_1^*, it can react with M_1 (k_{11}) or it can react with M_2 (k_{12}). So, r_1 gives the relative tendency of M_1^* active chain ends to react with M_1 or M_2. If r_1 is greater than 1, then of course, the tendency of homopolymerization or M_1^* reacting with a M_1 is higher compared to a cross-polymerization or a M_1^* is reacting to M_2. Similarly, if r_1 is 0, then obviously, there is no tendency of M_1^* to react with M_1, but it can react with M_2. If I have r_1 less than 1 that means, the tendency of M_1^* to react with M_2 is higher than the tendency to react with M_1. So, tendency of alternative arrangement is more than tendency of consecutive arrangement of monomers.

We will talk about the first case where $r_1 \times r_2$, r_1 multiplied by r_2 is 1, which we call *Ideal Copolymerization*. In this case, as we can see r_1 is $1/r_2$. Therefore, k_{11} divided by $k_{12} = k_{21}/k_{22}$. So, $M_1^*$and M_2^* show the same preference for adding one or the other monomer, this actually tends toproduce a random arrangement of M_1 and M_2 in the copolymer. But if r_1 is greater than 1, obviously, M_1 will get into the copolymer chain in greater extent, as long as there is no shortage of M_1 in the monomer mixture. Moreover, for this condition, if r_1 multiply by r_2 is 1, we can get a simplified expression of F_1 as, $F_1 = \frac{r_1 f_1}{r_1 f_1 + f_2}$

Another special case for this one is where r_1 and r_2 both are equal to 1 we call this special case as Bernoullian copolymerization. In this case, the two monomers show equal reactivity towards both propagating species. M_1^* has same reactivity towards M_1 or M_2. Similarly, for M_2^* has same reactivity towards M_1 or M_2. Hence, the copolymer composition always equals to the feed composition. Therefore, F_1 is equals to f_1.

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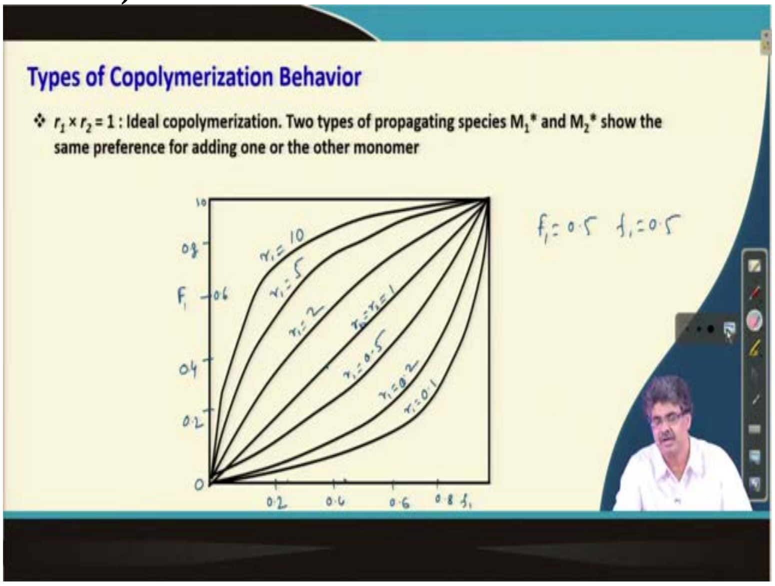

Types of Copolymerization Behavior

- $r_1 \times r_2 = 1$: Ideal copolymerization. Two types of propagating species M_1^* and M_2^* show the same preference for adding one or the other monomer

In case of *Ideal Copolymerization*, let us plot F_1 versus f_1, considering $f_1 = 0.5$, for different values of r_1, In case of $r_1 = r_2 = 1$, F_1 and F_2 should be same as f_1 and f_2. So, $F_1 = 0.5$ corresponds to $f_1 = 0.5$, mole ratio of monomers in the copolymer will be same as the monomer feed mole ratio. Now, if we have other values, then r_1 is not equal to r_2, for example, for r_1 of 10, 5, 2, 0.5, 0.2, 0.1, r_2 would be reciprocal of r_1. The F_1 versus f_1 plots for these values of r_1 are shown in the slide. For $r_1 > 1$, M_1 will get into the copolymer in higher extent compared to M_2. So, for $r_1 = 10$, if we consider 20 mol% M_1 in the feed ($f_1 = 0.2$), then $F_1 \sim 0.7$, 70 mol% M_1 in the copolymer. But for the cases where r_1 is less than 1, then the fraction of M_1 present is the copolymer is less compared to the feed concentration, $F_1 < f_1$.

If the M_1 is more reactive than the M_2, then r_1 value will be more than 1, as a result, M_1 will get into the copolymer in a greater extent. So, for first set of chains or when the conversion is low, the chains will have more of M_1, and as a result, the composition of the monomer mixture will change because M_1 will be used up at more extent compared to M_2. Eventually, the ratio of monomers in the mixture will be high with M_2. As a result, later on, the polymer chains will have more M_2 in the copolymer chain. Therefore, there will be differences in the composition of the copolymers, which are produced at the beginning of the polymerization, in the middle of the polymerization, and in the end of the polymerization. So, we will have a composition drift.

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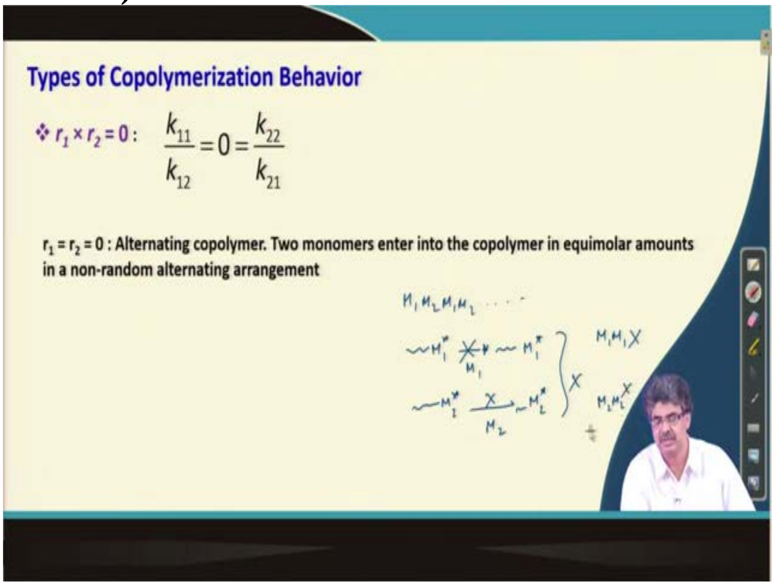

Types of Copolymerization Behavior

❖ $r_1 \times r_2 = 0$: $\frac{k_{11}}{k_{12}} = 0 = \frac{k_{22}}{k_{21}}$

$r_1 = r_2 = 0$: Alternating copolymer. Two monomers enter into the copolymer in equimolar amounts in a non-random alternating arrangement

$M_1M_2M_1M_2 \cdots$

$\sim M_1^* \xrightarrow[M_1]{\times} \sim M_1^*$ M_1M_1 X

$\sim M_1^* \xrightarrow[M_2]{X} \sim M_2^*$ M_2M_2 X

The second case, if we have r_1 multiplied by r_2 is 0. Obviously, this can happen if either (or both) of them is 0. So, r_1 is 0, r_2 not equal to 0; or r_2 is 0, r_1 not equal to 0; or $r_1 = r_2 = 0$. So, in this case, M_1 has no tendency to react with M_1^* of the propagating chain, which means there will be tendency to generate alternate copolymer because the tendency of homopolymer or two monomers sitting next to each other in the copolymer chain is lower. As a result, there is always a tendency of alternative copolymer formation in this situation. Now, in a special case where r_1 and r_2 both are zero, then obviously, neither M_1 or M_2 has any tendency to make self-copolymerization, hence, we will get a perfectly alternating copolymer. Therefore, the resulting copolymer will have $M_1M_2M_1M_2$ type rearrangement, because M_1 will not react with M_1 producing M_1^* and M_2^* will not react with M_2 to produce M_2^*, the possibility of two M_1 sitting next to each other is equal to zero. Similarly, in this case, possibility of two M_2 sitting next to each other is also zero. So, we will get perfectly alternating copolymer, and in case of perfectly alternating copolymer, both F_1 and F_2 have value equal to 0.5, that means, the mole percentage of M_1 and M_2 in the copolymer will be 0.5 because the perfectly alternating arrangement of the monomers in the copolymer.

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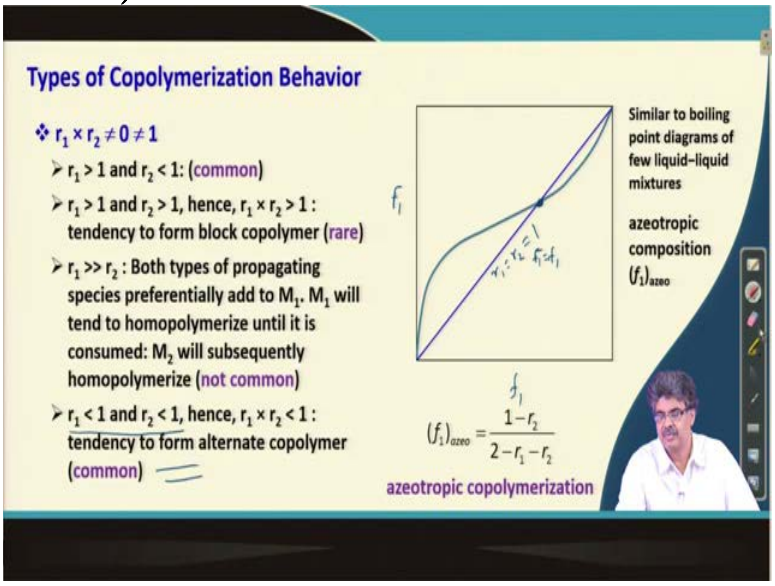

Types of Copolymerization Behavior

- $r_1 \times r_2 \neq 0 \neq 1$
  - $r_1 > 1$ and $r_2 < 1$: (common)
  - $r_1 > 1$ and $r_2 > 1$, hence, $r_1 \times r_2 > 1$: tendency to form block copolymer (rare)
  - $r_1 >> r_2$: Both types of propagating species preferentially add to M_1. M_1 will tend to homopolymerize until it is consumed: M_2 will subsequently homopolymerize (not common)
  - $r_1 < 1$ and $r_2 < 1$, hence, $r_1 \times r_2 < 1$: tendency to form alternate copolymer (common)

Similar to boiling point diagrams of few liquid-liquid mixtures

azeotropic composition $(f_1)_{azeo}$

$$(f_1)_{azeo} = \frac{1-r_2}{2-r_1-r_2}$$

azeotropic copolymerization

We will move to the third possibility where the r_1 multiplied by r_2 is neither 0 or 1 and there could be many possibilities in this particular option.

First one is that r_1 is greater than 1, r_2 is less than 1 or vice versa, where r_1 less than 1 and r_2 greater than 1, but the discussion is same. This is quite common in case of copolymerization. In this case, there is more tendency of random arrangement of monomers in the copolymer similar to the ideal copolymerization. Because r_1 is greater than 1 and r_2 is less than 1, at the beginning, M_1 will be more in the copolymer chain and later on when M_1's are consumed, at the later stage, when the mixture contains more of M_2, we will get copolymer chains with more M_2.

The second option would be both are greater than 1, which is rare, does not happen very frequently. In this case, tendency of self-polymerization is more, there will be tendency of block copolymer formation, the segments of block in the copolymer will be more if we have both r_1 and r_2 greater than 1. Then, the third option is where $r_1 >> r_2$ or vice versa. In this case, both the propagating species preferentially add to M_1. So, in this case both the propagating species M_1^* as well as M_2^*, preferentially add to M_1. As a result, M_1 is consumed first, because M_1 is more reactive towards M_1^* as well as M_2^*. Therefore, first homopolymer of M_1 is formed and then when M_1 monomers are consumed from the system, we will have M_2 homopolymer. In this case, possibility of copolymerization is less. The result is that we first have M_1

homopolymer followed by M_2 homopolymer, but this is not a common scenario. Another common scenario is where both are less than 1, which means of course, their multiplication will also produce less than 1, and in this case, M_1 has more tendency to react with M_2*and M_2 has more tendency to react with M_1* which means, the tendency of alternate copolymer are more.

For the cases where r_1 is less than 1 and r_2 is less than 1, or both r_1 and r_2 is greater than 1, which is not very common, we actually get this type of curve. For example, let us consider both r_1 and r_2 are less than 1. In this case, first, the monomer M_1 get consumed more and as the composition changes, we land up in this point, where F_1 is same as f_1 which means, at this point the monomer ratio of $M_1 : M_2$ in the feed or in the mixture is same as $M_1 : M_2$ in the copolymer. There will be no further change in composition because the two monomers are consumed in the same extent as their current or at the instantaneous molar ratio in the mixture. This is similar to a boiling point diagram for few liquid-liquid mixtures and this point is called azeotropic mixture or azeotrope. Therefore, in this case, we have a azeotropic composition and this azeotropic combination can be obtained as this using the formula $(f_1)_{azeo} = \frac{1 - r_2}{2 - r_1 - r_2}$

This type of copolymerization is called azeotropic copolymerization and that mostly happen in this case, where both r_1 and r_2 are less than 1. This is also possible for this case, where both r_1 and r_2 is greater than 1, but this is rare as we mentioned.

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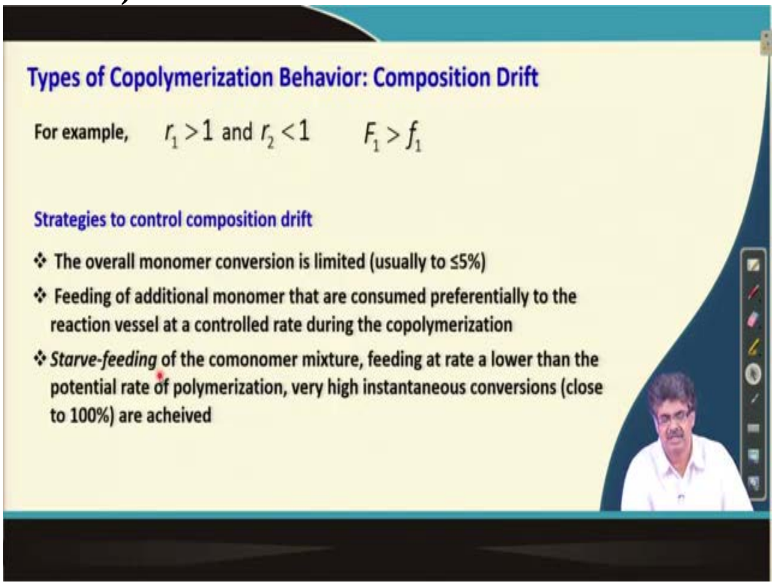

Types of Copolymerization Behavior: Composition Drift

For example, $r_1 > 1$ and $r_2 < 1$ $F_1 > f_1$

Strategies to control composition drift

- The overall monomer conversion is limited (usually to ≤5%)
- Feeding of additional monomer that are consumed preferentially to the reaction vessel at a controlled rate during the copolymerization
- *Starve-feeding* of the comonomer mixture, feeding at rate a lower than the potential rate of polymerization, very high instantaneous conversions (close to 100%) are acheived

We talked about the composition drift earlier as well. For example, if r_1 is greater than 1 and r_2 less than 1, then at the beginning, M_1 will be consumed more so, the copolymer chains will have more M_1, later on when M_1 is consumed from the reaction mixtures, the reaction mixture will have more M_2 and the copolymers which are getting produced will have more M_2.

Production of different composition of the polymers at the beginning, middle and end is problematic because the final copolymers will have different types of composition, which might give a very broad property of the polymer chains. Generally, in an industrial setup, nobody wants such a broad distribution of composition. So, 2-3 tricks are adopted to maintain the similar composition throughout the polymerization. The first is to limit the reaction to a very low conversion but this is not a practical way of controlling the composition. Another thing is possible that we can actually supply the monomer that is being consumed at a faster rate at a predetermined rate. So that $M_1 : M_2$ or the ratio of M_1 and M_2 in the copolymer remains same throughout the reaction. As a result, the resulting copolymers will have same composition throughout the polymerization, for this we need to supply or add the more reactive monomer in a controlled rate and during the entire copolymerization. The third possibility is starve-feeding that means, we can supply or add in the reaction mixture in lower amount of total monomer compared to the potential rate of polymerization. Therefore, effectively once the polymerization starts it can immediately consume all monomers. The conversion reaches 100 % very quickly and as a result, the copolymer chains will have almost similar composition.

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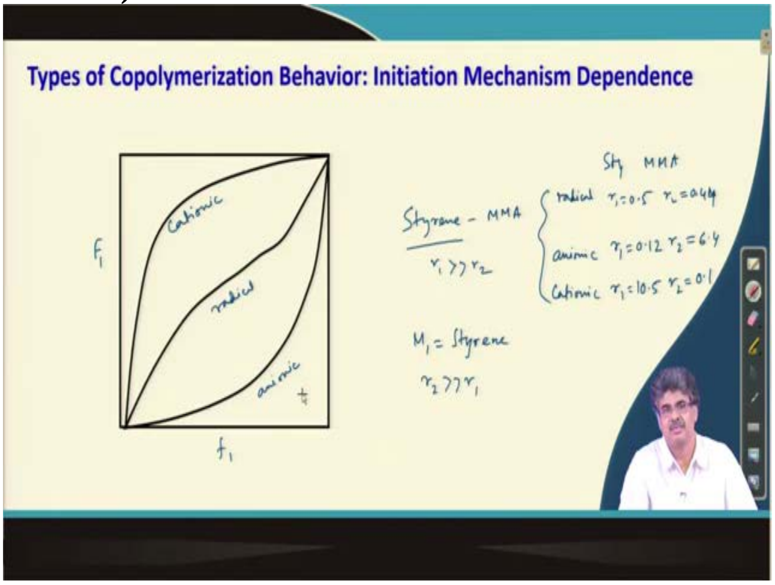

Types of Copolymerization Behavior: Initiation Mechanism Dependence

Sty MMA

Styrene - MMA

$r_1 >> r_2$

radical $r_1 = 0.5$ $r_2 = 0.44$

anionic $r_1 = 0.12$ $r_2 = 6.4$

Cationic $r_1 = 10.5$ $r_2 = 0.1$

M_1 = Styrene

$r_2 >> r_1$

The r_1, r_2 values will also depend on the type of initiation, for example, if we consider copolymerization of styrene and methyl methacrylate, we will the plots as shown in the slide. F_1 and f_1 correspond to styrene (M_1). Three plots are shown for cationic, radical and anionic polymerization. In case of cationic polymerization, styrene is more reactive, as we discussed earlier. Hence, this will have r_1 much higher compared to r_2. Similarly, r_2 will have much higher value than r_1 in case of anionic polymerization because methyl methacrylate is more reactive then styrene, as we discussed earlier. In case of radical r_1 is 0.5 and r_2 is 0.44. They are almost similar as their relativities in radical polymerization. For anionic, styrene has much lower reactivity compared to MMA, and for cationic r_1 is 10.5 and r_2 is 0.1. Therefore, it is not only the monomer pair, but also the type of initiation that we use will also determine the nature of copolymerization and the composition of the copolymers produced in this polymerization.

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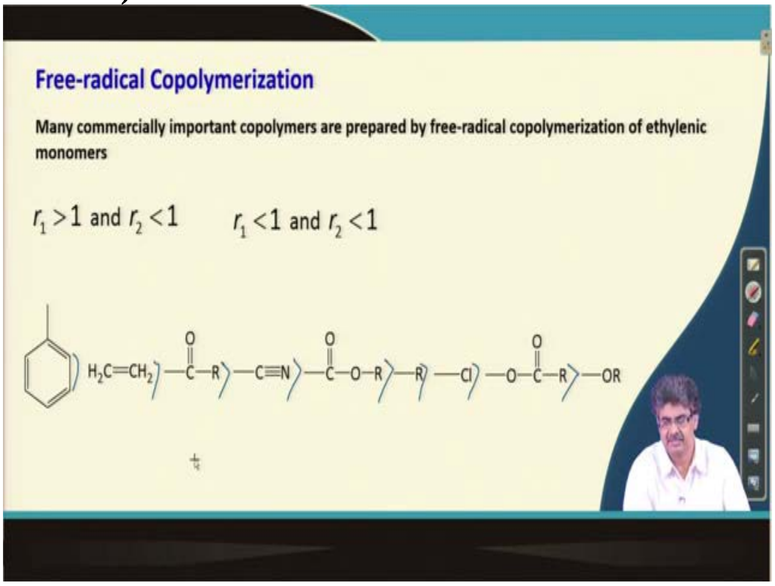
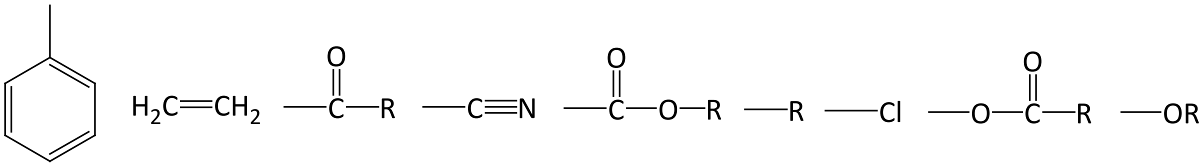


Free-radical Copolymerization

Many commercially important copolymers are prepared by free-radical copolymerization of ethylenic monomers

$r_1 > 1$ and $r_2 < 1$ $r_1 < 1$ and $r_2 < 1$

Many commercially important copolymers are prepared using free-radical copolymerization of ethylenic monomers; I have talked about some of the examples in the last class. There are two common scenarios - r_1 is greater than 1 while r_2 is less than 1, and both are less than 1. These values depend on the reactivity of the monomers and typically, for free-radical copolymerization the reactivity order is given by (reactivity decreases as we move right)



The reason of this reactivity differences are steric, resonance stabilization of the resulting propagating radical, which we discussed earlier.

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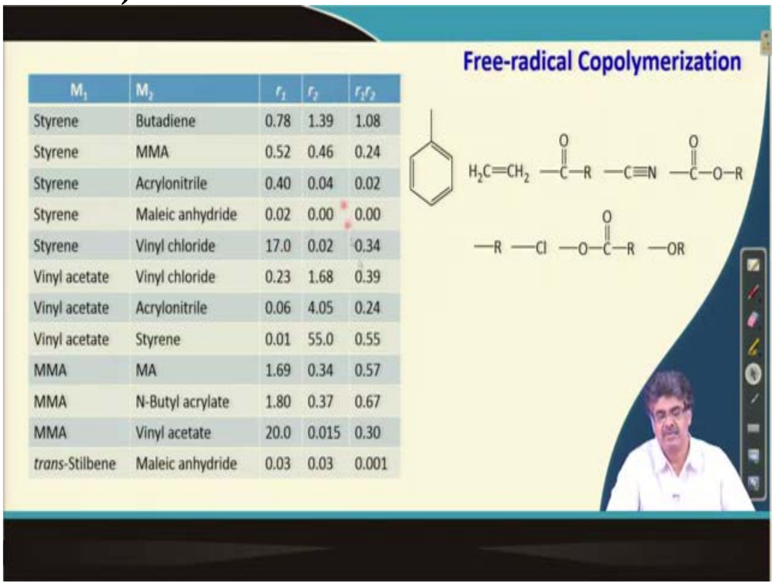

Free-radical Copolymerization

M_1	M_2	r_1	r_2	r_1r_2
Styrene	Butadiene	0.78	1.39	1.08
Styrene	MMA	0.52	0.46	0.24
Styrene	Acrylonitrile	0.40	0.04	0.02
Styrene	Maleic anhydride	0.02	0.00	0.00
Styrene	Vinyl chloride	17.0	0.02	0.34
Vinyl acetate	Vinyl chloride	0.23	1.68	0.39
Vinyl acetate	Acrylonitrile	0.06	4.05	0.24
Vinyl acetate	Styrene	0.01	55.0	0.55
MMA	MA	1.69	0.34	0.57
MMA	N-Butyl acrylate	1.80	0.37	0.67
MMA	Vinyl acetate	20.0	0.015	0.30
trans-Stilbene	Maleic anhydride	0.03	0.03	0.001

Some of the values for several monomer pairs are given in the table for radical copolymerization.

M_1	M_2	r_1	r_2	r_1r_2
Styrene	Butadiene	0.78	1.39	1.08
Styrene	MMA	0.52	0.46	0.24
Styrene	Acrylonitrile	0.40	0.04	0.02
Styrene	Maleic anhydride	0.02	0.00	0.00
Styrene	Vinyl chloride	17.0	0.02	0.34
Vinyl acetate	Vinyl chloride	0.23	1.68	0.39
Vinyl acetate	Acrylonitrile	0.06	4.05	0.24
Vinyl acetate	Styrene	0.01	55.0	0.55
MMA	MA	1.69	0.34	0.57
MMA	N-Butyl acrylate	1.80	0.37	0.67
MMA	Vinyl acetate	20.0	0.015	0.30
trans-Stilbene	Maleic anhydride	0.03	0.03	0.001

We can see that for the monomer pair of styrene and maleic anhydride, both are nearly zero, which means that styrene and maleic anhydride only form alternating copolymer, and maleic anhydride actually cannot make homopolymer by itself. Similarly, for styrene and acrylonitrile, the value of styrene is much higher compared to acrylonitrile. So, tendency of copolymer drift will be higher in the beginning and more styrene will be consumed. For styrene-vinyl chloride,

r_1 is 17 and r_2 is 0.2, this is because styrene is much more reactive in case of radical than vinyl chloride, which is very less reactive in radical polymerization. Similarly, stilbene and maleic anhydride, do not form homopolymers, they actually make alternative copolymer. In mixture of MMA and vinyl acetate, MMA is quite reactive in radical polymerization because of the stabilization of the propagating radical by the substituting group, but vinyl acetate not reactive in radical polymerization. The reactivity value will depend on this reactivity of the monomers that in turn depends on the type of initiation.

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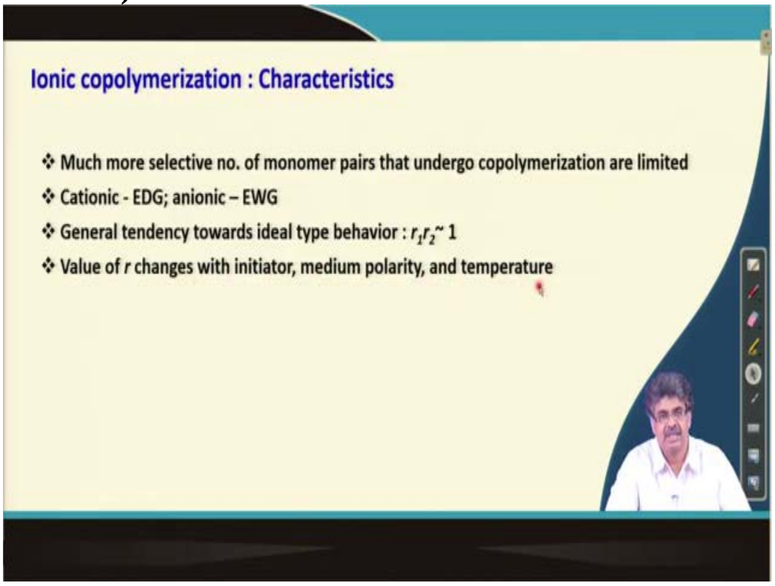

Ionic copolymerization : Characteristics

- Much more selective no. of monomer pairs that undergo copolymerization are limited
- Cationic - EDG; anionic – EWG
- General tendency towards ideal type behavior : $r_1r_2 \sim 1$
- Value of *r* changes with initiator, medium polarity, and temperature

Ionic copolymerizations are much more selective, and not very frequently used commercially Very less number of monomer pairs can be copolymerized by ionic method. For cationic polymerization, monomers containing electron-donating group will be more active whereas for anionic polymerization monomers containing electron-withdrawing group will be preferred. The value of *r* also changes with initiator, medium polarity, and temperature.

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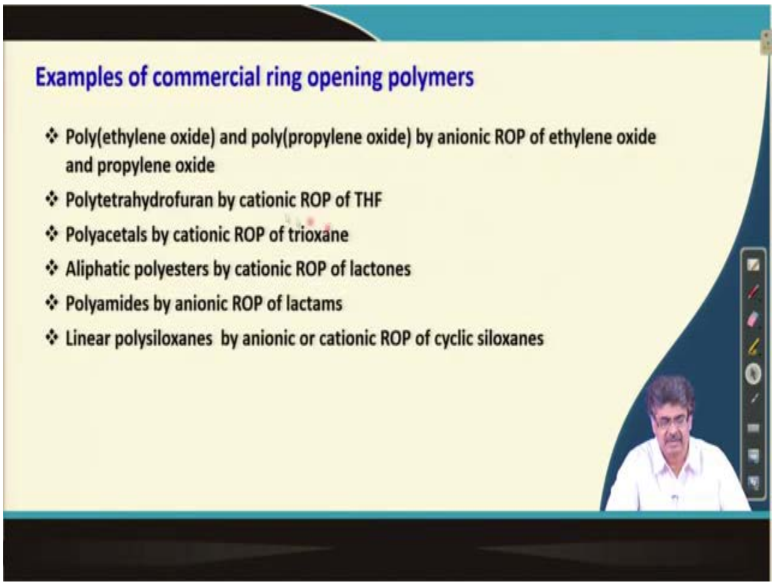

Examples of commercial ring opening polymers

- Poly(ethylene oxide) and poly(propylene oxide) by anionic ROP of ethylene oxide and propylene oxide
- Polytetrahydrofuran by cationic ROP of THF
- Polyacetals by cationic ROP of trioxane
- Aliphatic polyesters by cationic ROP of lactones
- Polyamides by anionic ROP of lactams
- Linear polysiloxanes by anionic or cationic ROP of cyclic siloxanes

Some of the commercial copolymers that are prepared by the ring-opening polymerization are shown in the slide. For example, copolymers of polyethylene oxide and polypropylene oxide are prepared by anionic ring-opening copolymerization of ethylene oxide and propylene oxide. and some of the examples also given below. To reiterate, this examples are just for your information, not to be remembered.

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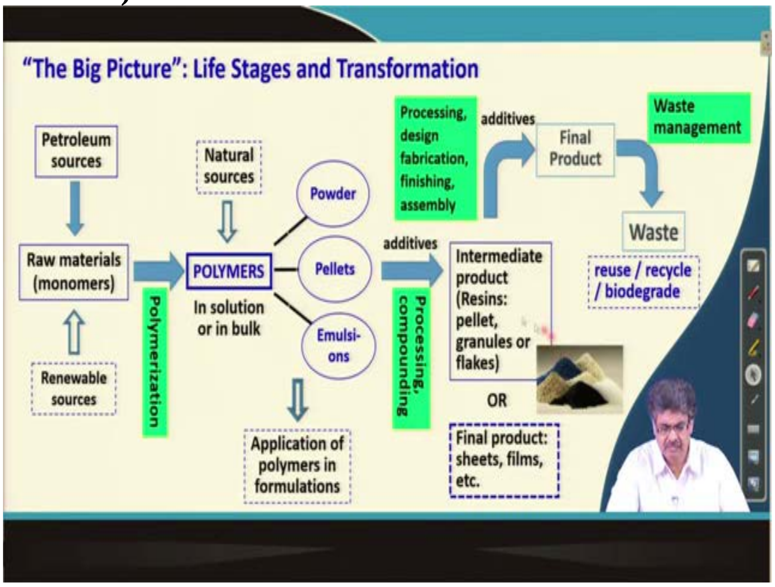

"The Big Picture": Life Stages and Transformation

Petroleum sources

Raw materials (monomers)

Renewable sources

Polymerization

Natural sources

POLYMERS

In solution or in bulk

Powder

Pellets

Emulsions

Application of polymers in formulations

additives

Processing, compounding

Intermediate product (Resins: pellet, granules or flakes)

OR

Final product: sheets, films, etc.

Processing, design fabrication, finishing, assembly

additives

Final Product

Waste management

Waste

reuse / recycle / biodegrade

We have shown this slide in the introductory lecture. We now have completed the discussion on this synthesis part. We have now discussed how to make polymers from monomers in some detail. I could not go into very high depth because of time crunch, but, for an introductory level course, this should be sufficient for you to have a knowledge of different polymerization mechanisms and the principle behind those mechanisms.

The typical commercial polymers that are synthesized using various types of polymerization are also mentioned. We now know how to prepared polymers. Now, we need to find out the actual composition of the polymer, the molecular weight, the size, the end group, the microstructure etc. We will start our discussion in this direction from the next lecture onwards; I will start discussing polymer characterization.