Introduction to polymer science
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Lecture – 21
Ring-opening polymerization, Copolymers

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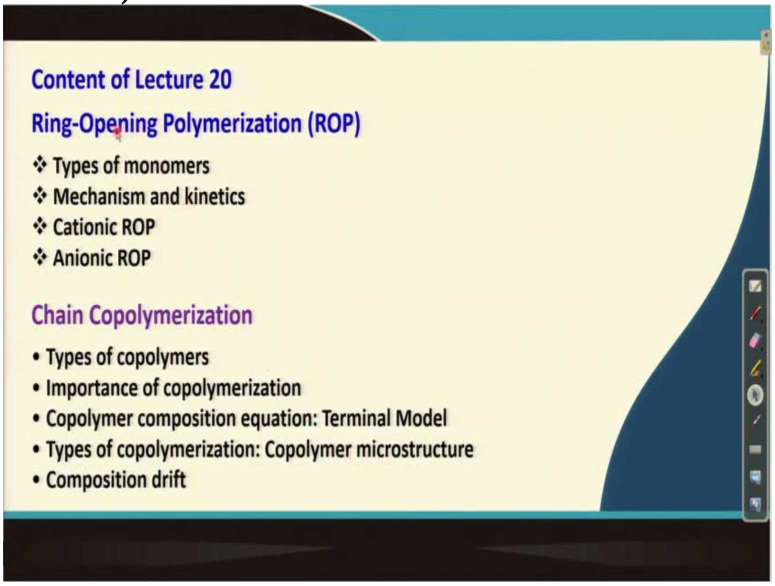

Content of Lecture 20

Ring-Opening Polymerization (ROP)

- ❖ Types of monomers
- ❖ Mechanism and kinetics
- ❖ Cationic ROP
- ❖ Anionic ROP

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 21, I will discuss about ring-opening polymerization and also discuss few aspects of copolymerization or copolymers. Now, there are two main topics I am trying to cover, one is ring-opening polymerization and chain copolymerization and these are the sub topics which I plan to cover.

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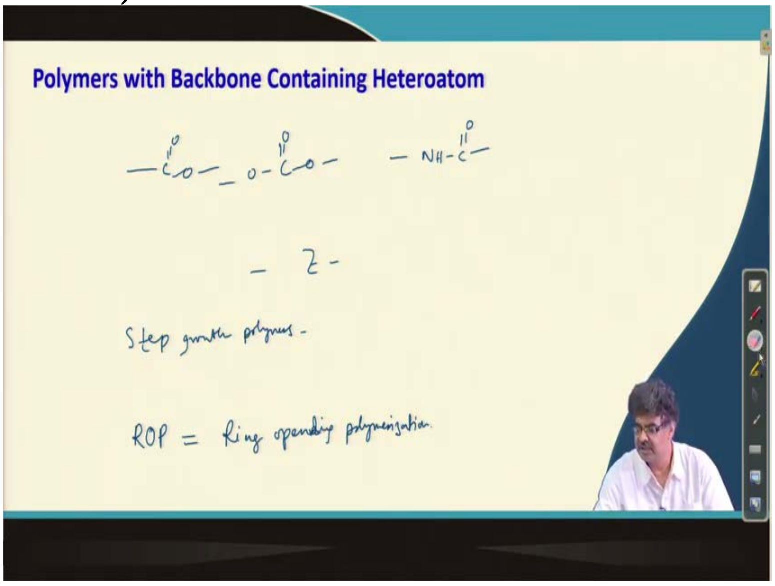

Polymers with Backbone Containing Heteroatom

$-\overset{O}{\overset{\|}{C}}-O- \quad -O-\overset{O}{\overset{\|}{C}}-O- \quad -NH-\overset{O}{\overset{\|}{C}}-$

$-Z-$

Step growth polymers -

ROP = Ring opening polymerization

Generally, we have seen that polymers with heteroatom backbone, like polyester, polycarbonate or some other polymers having Z in the backbone where Z is heteroatom, are generally synthesized by step growth polymerization that we have discussed in details. These polymers can also be synthesized by another method that we call as ROP or Ring-Opening Polymerization.

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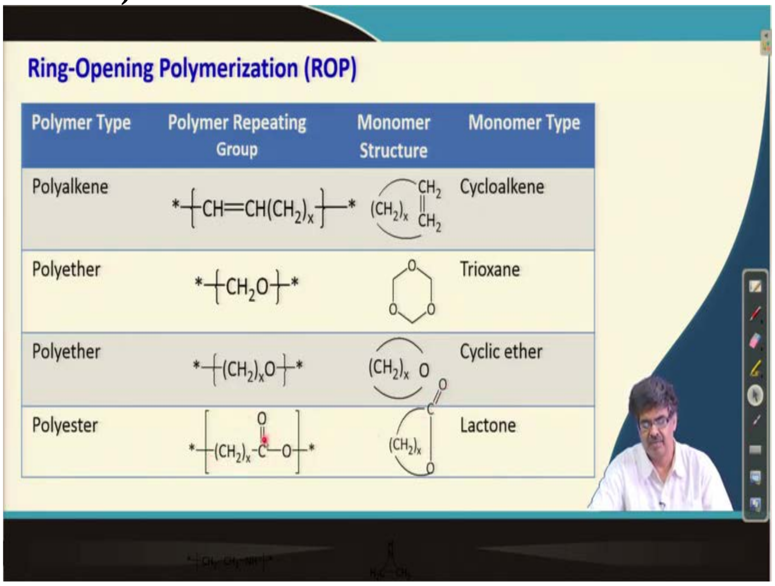

Ring-Opening Polymerization (ROP)

Polymer Type	Polymer Repeating Group	Monomer Structure	Monomer Type
Polyalkene	$*\!-\!\left[CH{=}CH(CH_2)_x\right]\!-\!*$	$(CH_2)_x$ CH_2 $\|$ CH_2	Cycloalkene
Polyether	$*\!-\!\left[CH_2O\right]\!-\!*$	O O O	Trioxane
Polyether	$*\!-\!\left[(CH_2)_xO\right]\!-\!*$	$(CH_2)_x$ O	Cyclic ether
Polyester	$*\!-\!\left[(CH_2)_x-\overset{O}{\overset{\|}{C}}-O\right]\!-\!*$	$(CH_2)_x$ C O O	Lactone

In ring-opening polymerization, one cyclic monomer is ring-opened to make polymer and some of the examples are shown in the slide. For example, this is the monomer structure, the cycloalkene is ring opened to make a polyalkene polymer, cyclic ethers can be ring-opened to form polyether type polymers. We can have another type of cyclic ether which can be ring opened and to form polyether as shown in the slide. Cyclic lactone can be ring opened to form polyester. There are other examples like cyclic lactum to polyamides, cyclic siloxanes to polysiloxanes. Phosphazenes and substituted phosphazenes can be formed form cyclic monomers and for aziridine type monomers on ring-opening can give polyamine type polymers.

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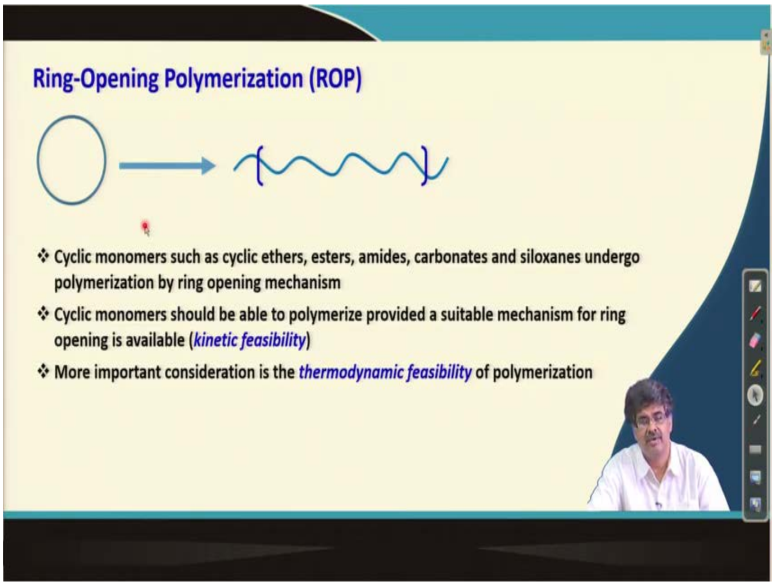

Ring-Opening Polymerization (ROP)

- Cyclic monomers such as cyclic ethers, esters, amides, carbonates and siloxanes undergo polymerization by ring opening mechanism
- Cyclic monomers should be able to polymerize provided a suitable mechanism for ring opening is available (*kinetic feasibility*)
- More important consideration is the *thermodynamic feasibility* of polymerization

The general way to represent the ROP is shown in the slide, a cyclic monomer on ring-opening gives a linear polymer, and cyclic monomers such cyclic ethers, ester, amides, carbonate siloxanes undergo ring-opening polymerization. Now, cyclic monomers will be able to polymerize provided there is a suitable mechanism by which we can actually initiate and make the polymerization kinetically feasible. Therefore, we should have some monomers which we can actually ring-open by either ionic or radical way. More importantly, this opening of ring and subsequent polymerization has to be thermodynamically feasible. We know that the ring structure is strained, especially if the ring size is very low and very large. So, obviously, if we ring-open a small size ring or a large size ring, then there is a possibility that this ring strain is released, and the polymerization becomes thermodynamically feasible.

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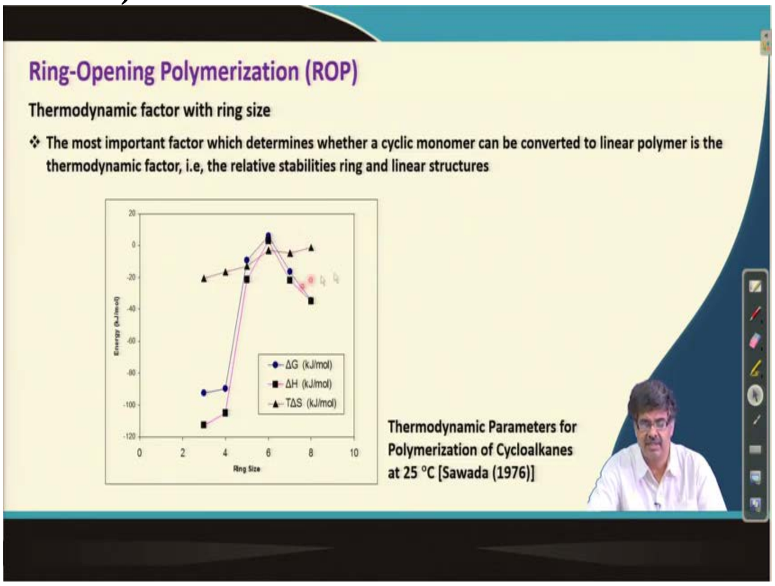

Ring-Opening Polymerization (ROP)

Thermodynamic factor with ring size

- The most important factor which determines whether a cyclic monomer can be converted to linear polymer is the thermodynamic factor, i.e, the relative stabilities ring and linear structures

Thermodynamic Parameters for Polymerization of Cycloalkanes at 25 °C [Sawada (1976)]

For example, if we talk about polymerization of cycloalkanes, when we have a ring size of 3 or 4, then the ring strain is quite high. As a result, the ring-opening polymerization energy per mole is very high, the reaction is exothermic as the ring strain is released, which is thermodynamically favourable. When we have little larger size molecule like 7 membered ring or 8 membered ring, then also there is ring strain associated with the rings and as a result, it is also thermodynamically feasible. However, when the ring size is 5, 6, 7, then the tendency of ring opening actually becomes lesser and lesser especially for 6 membered rings, hence it is normally difficult to polymerize these rings by ring-opening polymerization. Therefore, the most important factor, which determines whether a cyclic monomer can be converted to a linear polymer, is a thermodynamic factor that is the relative stabilities of the ring and linear structure as we just described.

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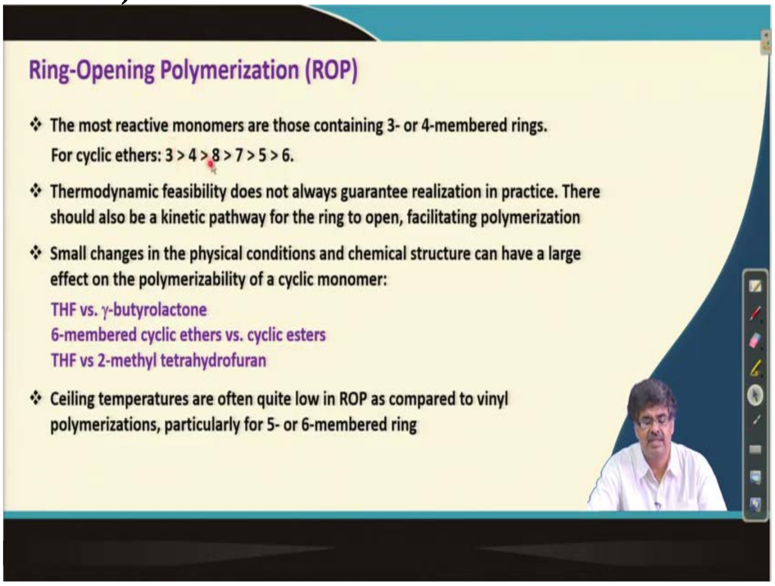

Ring-Opening Polymerization (ROP)

- The most reactive monomers are those containing 3- or 4-membered rings.
  For cyclic ethers: 3 > 4 > 8 > 7 > 5 > 6.
- Thermodynamic feasibility does not always guarantee realization in practice. There should also be a kinetic pathway for the ring to open, facilitating polymerization
- Small changes in the physical conditions and chemical structure can have a large effect on the polymerizability of a cyclic monomer:
  THF vs. γ-butyrolactone
  6-membered cyclic ethers vs. cyclic esters
  THF vs 2-methyl tetrahydrofuran
- Ceiling temperatures are often quite low in ROP as compared to vinyl polymerizations, particularly for 5- or 6-membered ring

So, most reactive monomers are those containing 3 and 4-membered ring, because the ring strains are much higher in those cases. For cyclic ethers, the tendency of polymerization according the ring sizes follows the order - 3, 4, then 8, 7, 5, 6. Six-membered ring has the least tendency to polymerize by ring-opening because the ring stain is minimum for 6 membered ring. Of course, thermodynamic feasibility does not always guarantee polymerization in practice, because there has to be a kinetic pathway for the ring to open, which facilitates the polymerization.

Small changes in physical condition and chemical structures actually can have a large effect in polymerizability of cyclic monomers. For example, THF and gamma-butyrolactone are 5 membered rings, but THF can be polymerized catatonically which cannot be applied for the other monomer. Similarly, there are differences in the ring-open ability for 6-membered cyclic ethers versus cyclic esters or THF versus 2-methyl tetrahydrofuran. Substituent actually makes a lot of difference in their ability to form linear polymer by ring-opening as ceiling temperature often quite low. Ceiling temperature takes care of the reversible nature of the polymerization, it is the temperature at which the rate of forward reaction or the rate of polymerization is same as rate of depolymerization. In case of ring-opening polymerization, the ceiling temperature is quite low compared to vinyl polymerizations particularly for 5-membered and 6-membered rings and that is another reason the feasibility of 5, 6-membered rings for undergoing ring opening polymerization are quite low.

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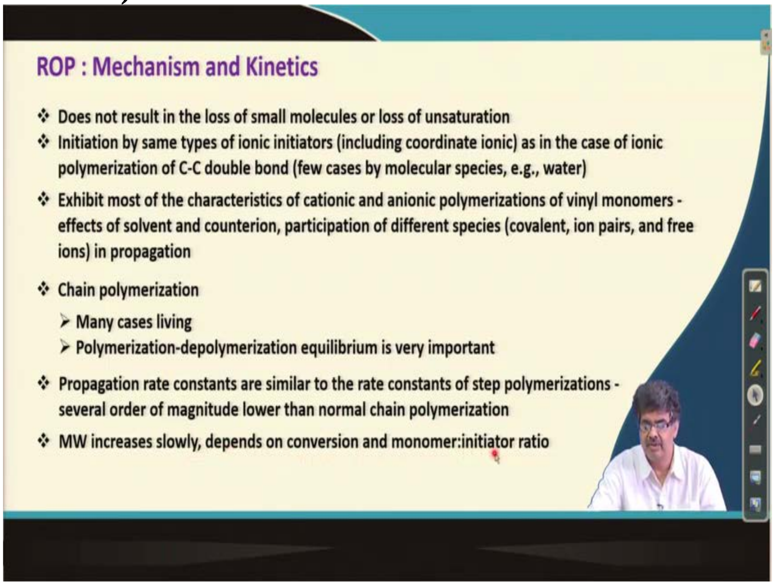

ROP : Mechanism and Kinetics

- Does not result in the loss of small molecules or loss of unsaturation
- Initiation by same types of ionic initiators (including coordinate ionic) as in the case of ionic polymerization of C-C double bond (few cases by molecular species, e.g., water)
- Exhibit most of the characteristics of cationic and anionic polymerizations of vinyl monomers - effects of solvent and counterion, participation of different species (covalent, ion pairs, and free ions) in propagation
- Chain polymerization
  - Many cases living
  - Polymerization-depolymerization equilibrium is very important
- Propagation rate constants are similar to the rate constants of step polymerizations - several order of magnitude lower than normal chain polymerization
- MW increases slowly, depends on conversion and monomer:initiator ratio

Now, for ring-opening polymerization, the initiation does not result in the loss of small molecule or loss of unsaturation Ring-opening polymerization is initiated by same type of ionic initiators including coordinate ionic, the example that was given for in 1,3-butadiene case, as in the case of ionic polymerization of carbon carbon double bond. So, similar types of initiators that we have explained during ionic chain polymerization like cationic initiators, anionic initiators can be used for ring-opening polymerization as well.

Some cases molecular species like water can also be used as the initiator for ring-opening polymerization. Because the initiation is done mainly by ionic species, the polymerization actually exhibits most of the characteristics of cationic and anionic polymerization of vinyl monomers including the effect of solvent and counterion. As you can guess, or you can understand that this is ring-open as shown in the slide.

Once ring-opened, next monomer actually comes in attack the active centre and the polymerization goes on by adding addition of one monomer at a time. Therefore, it is a chain polymerization, not step polymerization. Moreover, in many cases because we are talking about ionic initiation, these are living polymers. In addition, as I said earlier, the polymerization-depolymerization equilibrium is very important in ring-opening polymerization.

This is important that, although it is a chain polymerization, all the polymerization rates are actually similar to rate constants of step polymerizations, not same as chain polymerizations. Therefore, they are actually several orders of magnitude lower than normal chain polymerization. As a result, molecular weight increases slowly, which depends on the conversion and monomer to initiator ratio.

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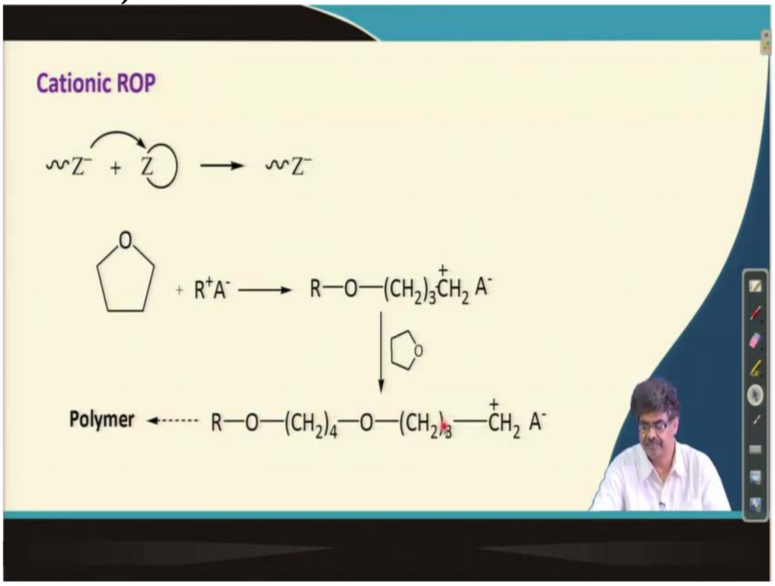

Cationic ROP

Now, an example of cationic ring-opening polymerization is shown in the slide. In case of cationic polymerization, initiator can be strong protonic acids like trifluoro acetic acid, fluoro sulfonic acid, triflic acid. These are strong acids, which can be used as initiator for cationic ring-opening polymerization. There are actually two mechanisms possible, one case the counter ion actually remains with the cationic where the cation is a part of ring. The second monomer attacks to the active center and the polymerization progress like as shown, where the active center is the cyclic monomer as such with the counter ion and active species. The is second mechanism is similar but in second type of mechanism, instead of the first ring being remained as ring structure, it actually opens up and the second monomer attacks as shown in the active center and linear chain polymerization actually gets synthesized.

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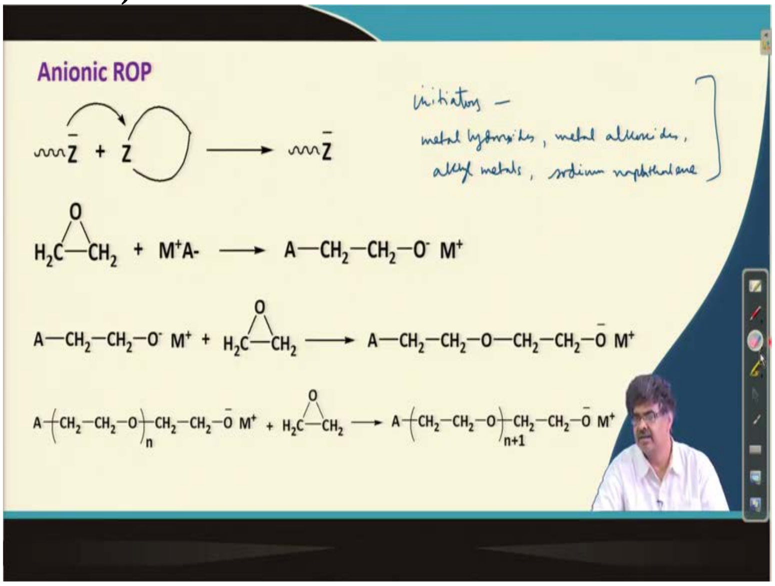

Anionic ROP

initiators –
metal hydroxides, metal alkoxides,
alkyl metals, sodium naphthalene

Similarly, in case of an anionic initiation, the second type of mechanism is most likely to happen. In this case, the initiators are generally used as we discussed during the anionic polymerization, like metal hydroxides or metal alkoxides and alkyl metals or like sodium naphthalene. The mechanism is similar as we discussed for the cationic polymerization. The initiator actually ring-open and form an active center at the end of this chain, which attacks another monomer that become part of the growing chain. In this way the polymerization takes place and at the end of this polymerization, we have the anion present at the end similar to presence of cationic ends in cationic ROP. This is why there is a possibility of these chains being living, unless we deliberately quench or terminate the chain using a quencher. As a result, because of living nature, generally the size of the ring-opening polymers actually get determined by the initiator to monomer ratio or monomer to initiator ratio. The lower is the ratio of monomer to initiator, the higher is the molecular weight produced by this ring-opening polymerization.

There are not many commercial polymers are produced by ring opening polymers. Therefore, we will keep our discussion on this polymerization in brief, and we will move to our next topic of Chain copolymerization.

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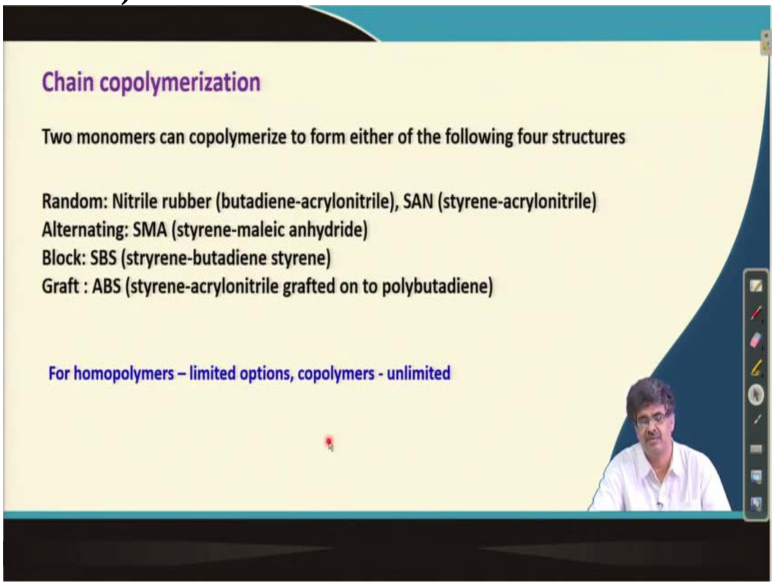

Chain copolymerization

Two monomers can copolymerize to form either of the following four structures

Random: Nitrile rubber (butadiene-acrylonitrile), SAN (styrene-acrylonitrile)
Alternating: SMA (styrene-maleic anhydride)
Block: SBS (strryene-butadiene styrene)
Graft : ABS (styrene-acrylonitrile grafted on to polybutadiene)

For homopolymers – limited options, copolymers - unlimited

As we discussed during our introductory lectures, that when we polymerize two monomers simultaneously, they form copolymers, which can have different arrangements. They can have a random arrangement, an alternate arrangement, they can have blocky arrangement or we can have graft type copolymers. Some of the commercial copolymers with random structure and alternative structure and other structures are shown in the slide.

For homopolymers, we have limited options, but for copolymers we have unlimited options. The numbers of homopolymers are given by number of monomers that we can polymerize, but in case of copolymer, we can actually change the ratio of the monomers, we can have different microstructures. Therefore, the possibilities of synthesizing copolymers are endless, unlimited, and that is in our hand. According to our wish, we can actually change the composition or microstructure to generate unlimited copolymers.

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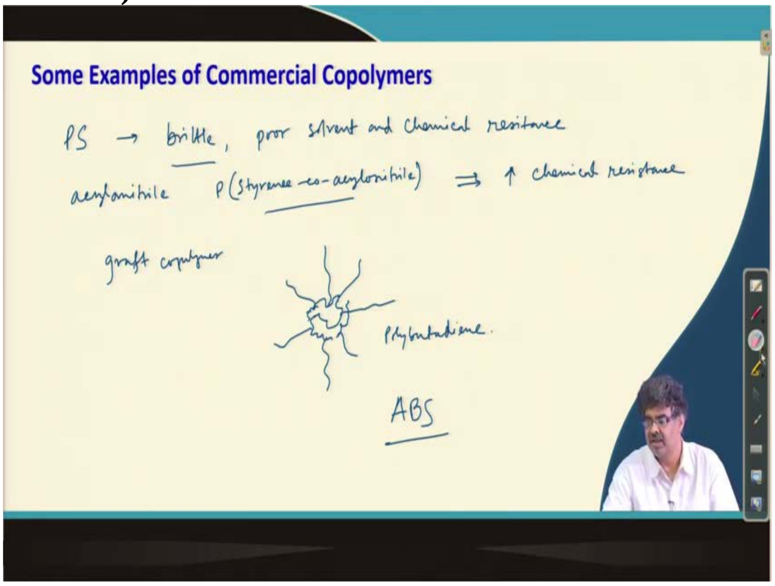

Some Examples of Commercial Copolymers

PS → brittle, poor solvent and Chemical resitance

acrylonitrile P(styrene-co-acrylonitrile) ⇒ ↑ chemical resistance

graft copolymer

Polybutadiene.

ABS

We will give a specific example of an important commercial copolymer. Let us talk about polystyrene, PS. PS is brittle in nature, has poor solvent and chemical resistant. Therefore, if we add acrylonitrile and make a copolymer, polystyrene-co-acrylonitrile, then we can increase the chemical resistant because of presence of the acrylonitrile segment in the copolymers. However, this will not solve the brittleness of polystyrene. So, for that a graft copolymer is synthesized, graft copolymer where a polybutadiene core is first synthesized, which have the double bonds of butadiene units and on top of these double bonds, we can generate this polystyrene-polyacrylonitrile copolymer. Therefore, we have a polybutadiene core, and we have the polystyrene-acrylonitrile copolymers are grafted on the core. We have acrylonitrile butadiene styrene copolymer, which is known as ABS. Now, because of the presence of this polybutadiene core, which is rubbery material, brittleness of this original polystyrene is quite significantly improved. This is an example of quite useful copolymer.

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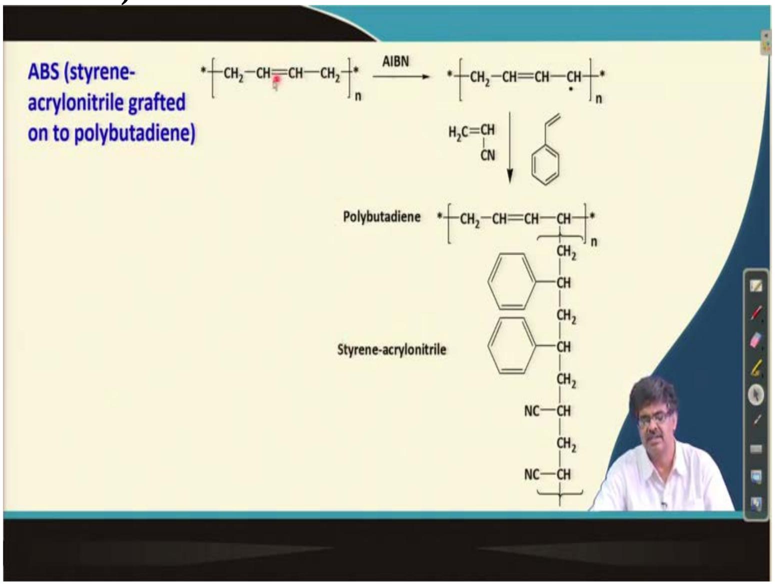

ABS (styrene-acrylonitrile grafted on to polybutadiene)

This slide gives you the example with chemical structures. As I have said that, we first polymerize butadiene to make polybutadiene core and on which we build a copolymer of styrene and acrylonitrile to make polystyrene-polyacrylonitrile graft.

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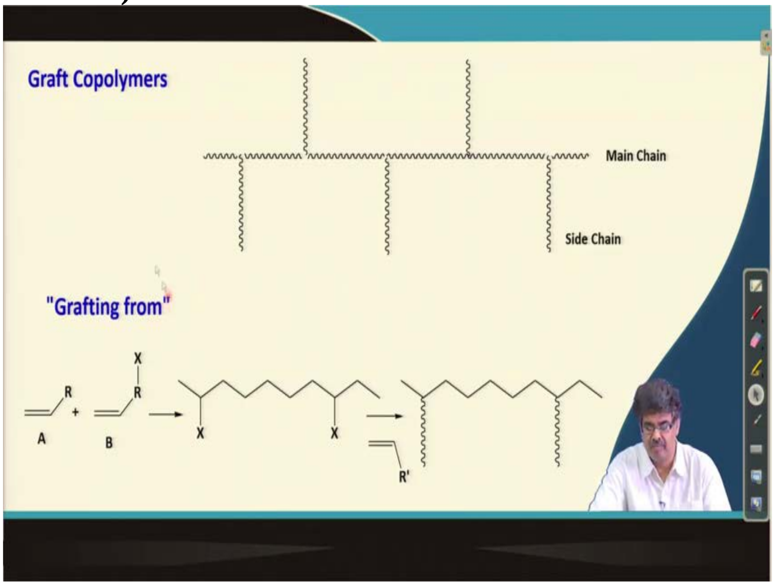

Graft Copolymers

"Grafting from"

So, this is example of graft copolymerization. Graft copolymers have linear main chain polymers with these side chains that are grafted on to the main polymer chain. This type of graft copolymers, e.g., ABS, could be synthesized in two ways. First, is grafting through, in this case, we have two monomers, one of the monomers contains long chain polymeric segment. So, on polymerization, we can have the backbone resulting from the carbon-carbon double bonds with these hanging polymer chains. Therefore, here we are talking about grafting through. There is another possibility where we can first polymerize one monomer containing function groups, which can be used for further polymerization to make polymers, or we can have a polymer with the functional groups with these functional groups to synthesized graft copolymer. So, there are two techniques - one is ‘grafting from’ and the other is ‘grafting through’ or ‘grafting to’ for making graft copolymers.

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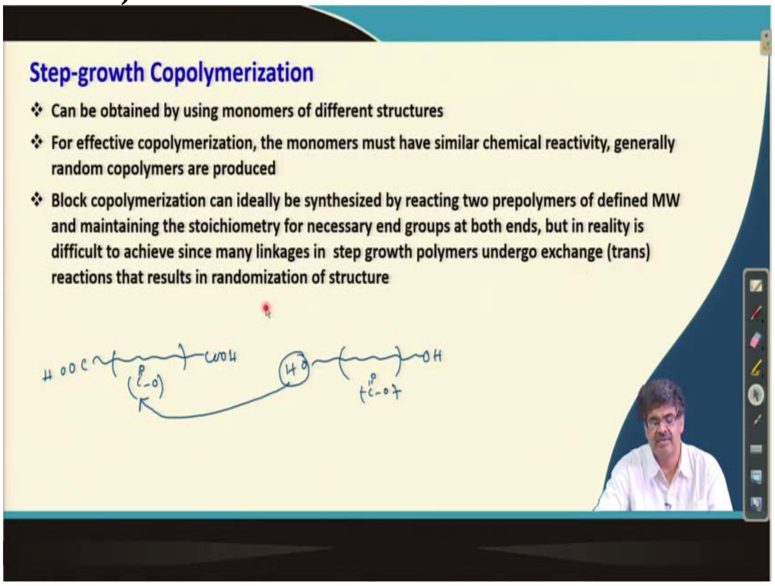

Step-growth Copolymerization

- Can be obtained by using monomers of different structures
- For effective copolymerization, the monomers must have similar chemical reactivity, generally random copolymers are produced
- Block copolymerization can ideally be synthesized by reacting two prepolymers of defined MW and maintaining the stoichiometry for necessary end groups at both ends, but in reality is difficult to achieve since many linkages in step growth polymers undergo exchange (trans) reactions that results in randomization of structure

Step-growth copolymers are not very important in the commercial aspect, because not many step-growth copolymers are used. There are some examples, but it is not as popular as chain growth copolymers, and the step-growth copolymerization can be obtained by using monomers with different structures and for effective copolymerization, the reactivity of the monomers must be similar to generate copolymers and generally step-growth copolymerization produce random copolymers.

If we have, for example, one polymer with COOH end and another with OH end, then in principle, we can couple these two to make block copolymer - one block is from one polymer, another block from the other. However, in reality, the polymers also have functional groups in the backbone like, for example COO groups for polyesters. Now, the end groups can react with the backbone functional groups and undergo exchange reactions. As a result, even though the initial few polymers are synthesized as block copolymer, with time because of the exchange reactions, the ultimate polymers tend to become more of a random copolymer. Therefore, making block copolymer using step copolymers are actually difficult and even if we can make at the beginning, but later on, during polymerization and processing steps, these might undergo these exchange reactions or trans reactions and actually generate random structure. So, block copolymers can ideally be synthesized by reacting to prepolymers with defined molecular weight like the examples we have shown in the slide. We can actually have the required stoichiometry by using one of the prepolymer in excess, the one that we would like to have in the end group, but in reality as I explained that, it is difficult to achieve this block copolymer because many linkages in step-growth polymers undergo exchange reactions or trans reactions, which results in randomization of structures.

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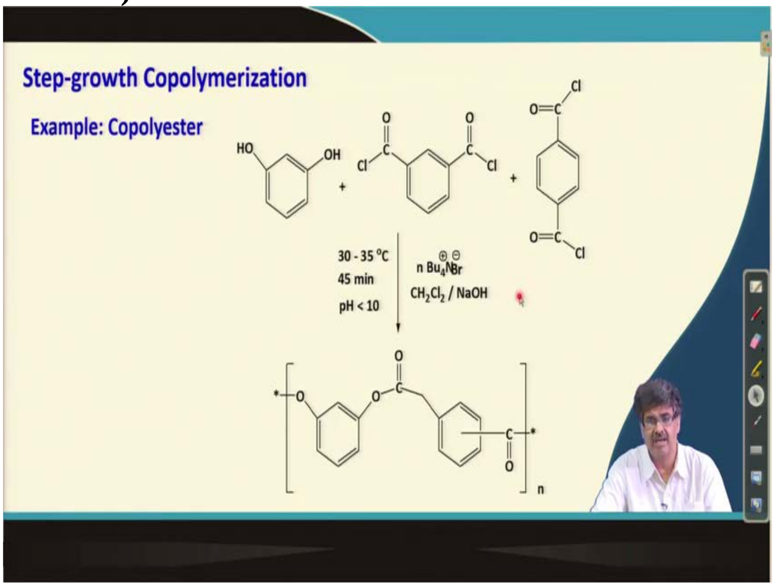

Step-growth Copolymerization

Example: Copolyester

30 - 35 °C
45 min
pH < 10

n $Bu_4\overset{\oplus}{N}\overset{\ominus}{Br}$
CH_2Cl_2 / NaOH

Next, we will move to more important chain copolymerization, before that, let me give examples of commercial step-growth polymers. This is an example of a commercially available copolyester. This is the alcohol group, and this is the two acid chlorides, which are used to make this copolymer. There are only few examples of commercial step-growth polymers.

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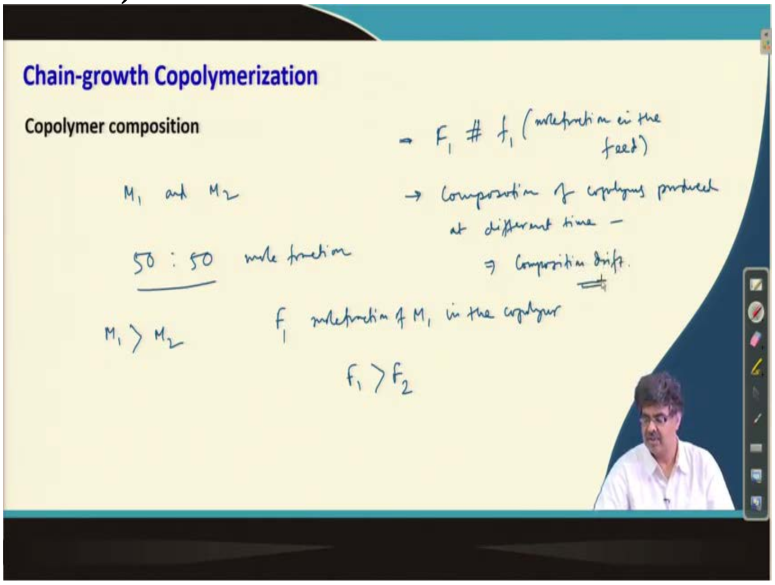

Chain-growth Copolymerization

Copolymer composition

M_1 and M_2

$\underline{50 : 50}$ mole fraction

$M_1 > M_2$

F_1 molefraction of M_1 in the copolymer

$F_1 > F_2$

→ $F_1 \# f_1$ (molefraction in the feed)

→ Composition of copolymers produced at different time –

⇒ Composition drift.

Now, we will move to copolymers that are more important from commercial aspect, to the chain-growth copolymerization. Let us start the discussion for chain-growth copolymerization with two monomers, M_1 and M_2, and at the beginning, we also consider a 50-50 mixture in terms of number or moles or 0.5, 0.5 mole fraction in the beginning. Now, if the reactivity of M_1 is greater than M_2, the initial copolymers will have more M_1 in the copolymer backbone, which means if we write F_1 as the mole fraction of M_1 in the copolymer, in this case, F_1 will be greater than F_2, the mole fraction of M_2 in the copolymer. As the reactivity of M_1 is greater than M_2, as a result, the copolymers formed at the beginning may have higher mole fraction of M_1 than the copolymers formed later, hence, the composition during the polymerization may be different in different time. So, in the beginning when the two monomers were in equal mole fraction 50:50, the resulting polymers will have more of M_1, but later on as more M_1 get consumed, the reaction mixture eventually will have more M_2. Therefore, the later polymers will have more M_2 in the polymer structure. We can have differences in the monomer concentration in the copolymers compared to feed. Therefore, F_1 may not be equals to f_1, f_1 being the mole fraction in the feed composition. If we talk about 50-50 mixture by mole in the feed, f1 will be 0.5. Composition of the copolymers produced at different time during the copolymerization maybe different. We term this as composition drift.

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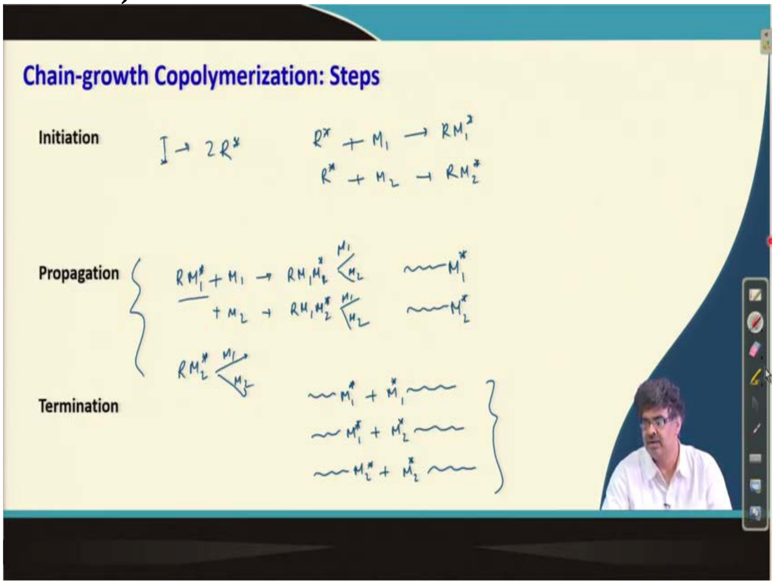

Chain-growth Copolymerization: Steps

Initiation

$I \rightarrow 2R^*$

$R^* + M_1 \rightarrow RM_1^*$

$R^* + M_2 \rightarrow RM_2^*$

Propagation

$RM_1^* + M_1 \rightarrow RM_1M_1^* \begin{smallmatrix} M_1 \\ M_2 \end{smallmatrix}$

$+ M_2 \rightarrow RM_1M_2^* \begin{smallmatrix} M_1 \\ M_2 \end{smallmatrix}$

$RM_2^* \begin{smallmatrix} \xrightarrow{M_1} \\ \xrightarrow{M_2} \end{smallmatrix}$

$\sim\sim M_1^*$

$\sim\sim M_2^*$

Termination

$\sim\sim M_1^* + M_1^* \sim\sim$

$\sim\sim M_1^* + M_2^* \sim\sim$

$\sim\sim M_2^* + M_2^* \sim\sim$

In chain copolymerization, we will still have the normal three steps, initiation, propagation, and termination. In this case, if we write, as shown in the slide, that we have two R*, R* can react with the M_1 producing RM_1^* and/or it can react with M_2 to produce RM_2^*. Now, RM_1^* can react with another M_1 producing $RM_1M_1^*$ or it can react with M_2 to produce $RM_1M_2^*$. Now, $RM_1M_1^*$ can again further react with either M_1 or M_2 or $RM_1M_2^*$ can also further react with M_1 or M_2. Similarly, RM_2^* can react with M_1 or M_2 and so on. We will represent the propagating chains as a chain having either M_1^* or M_2^* at the end as the end of a propagating chain decides its reactivity. Therefore, we represent the chain like as shown in the slide.

The only difference than normal chain homo-polymerization is that, each active centre has chances to react with two different monomers instead of single monomer in case of homo-polymerization. As a result, there is possibility of producing different microstructure within the copolymers that are produced which will be discussed. Termination can be done by either M_1^* reacting with M_1^* either by disproportionation or by coupling, M_1^* reacting with M_2^* or M_2^* reacting with M_2^*, these are the usual possibilities. In case of homopolymer, we have only one possibility between two propagating chains having same active center and they can get dominated either by disproportionation or coupling, but in this case, there are three possibilities, three combinations are possible. So, this is as I explained, that the main difference is in the propagation step where each propagating chain with the active centre at the end. In case of copolymerization the active end has possibly to react with two monomers rather than one single monomer in case of homo polymerization.

Now we will move to the kinetics part of chain copolymerization. As we know that the rate of chain polymerization depends mainly on rate of propagation because almost all the monomers are consumed during propagation step. Hence, rate of propagation will be equivalent to rate of polymerization. With this, I will stop here, and in next lecture, I will talk briefly about this chain copolymerization.