Introduction to Polymer Science

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Lecture-10

Types of Chain Polymerization, Mechanism, and Kinetics of Radical Chain Polymerization

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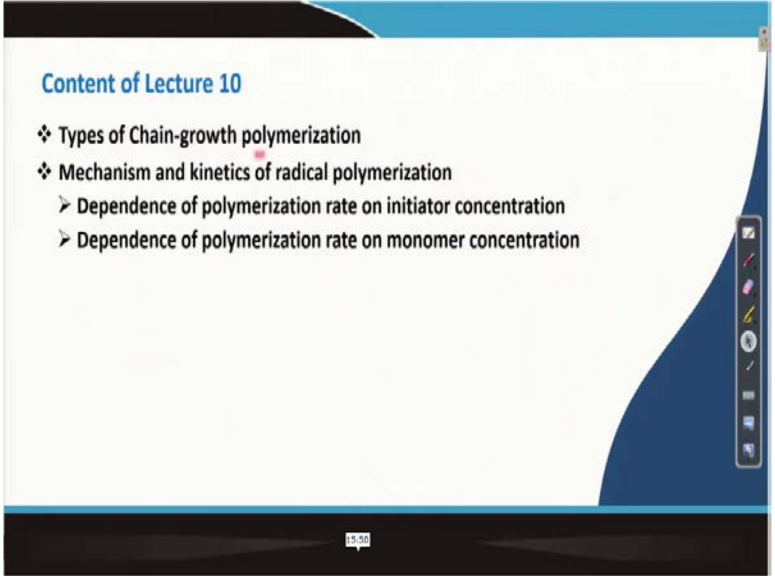

Content of Lecture 10

- Types of Chain-growth polymerization
- Mechanism and kinetics of radical polymerization
  - Dependence of polymerization rate on initiator concentration
  - Dependence of polymerization rate on monomer concentration

Welcome back to this lecture, we will start module 3, which is radical chain polymerization. The content of this lecture is as follows and talks about types of chain growth polymerization, their mechanism and kinetics of radical polymerization

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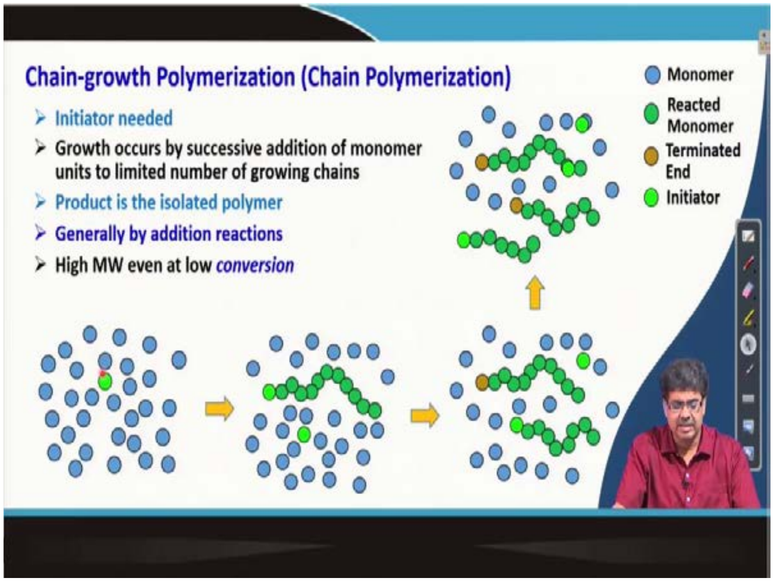

Chain-growth Polymerization (Chain Polymerization)

- Initiator needed
- Growth occurs by successive addition of monomer units to limited number of growing chains
- Product is the isolated polymer
- Generally by addition reactions
- High MW even at low *conversion*

We have already discussed chain-growth polymerization or simply chain polymerization. We have observed that an initiator which initiates the chain, forms a polymer by adding the monomers one after one at the end. These propagating chains get terminated and we get polymer samples. So, in this case, the initiator is required to initiate the chain, and the growth occurred by successive addition of the monomer units to the limited number of growing chains. Another important thing is that we need to isolate the polymer chains at the end of the polymerization. Thus, our actual product is the isolated polymer chains, not the mixture. Generally, in the case of the addition polymerization, large polymer chain starts getting produced as soon as the initiation happens.

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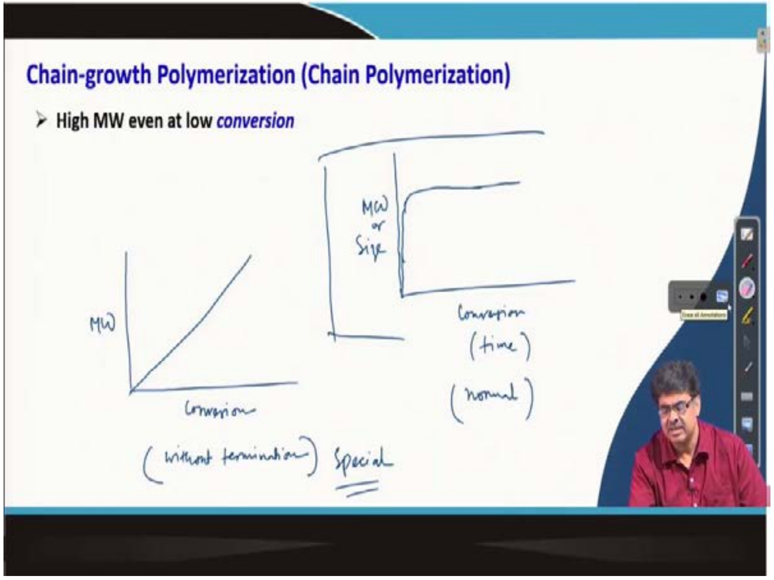

Chain-growth Polymerization (Chain Polymerization)

- High MW even at low *conversion*

So, in the plot of the conversion or time with molecular weight or size, the high molecular weight polymers will be generated after the starting of the reaction immediately. Initially at the low conversion, a large number of monomer units present in its chain. So, the molecular weight of the polymer is high even at very low conversion.

In the case of normal chain polymerization, if the termination reaction stops by any means and the chains keep on increasing in molecular weight, we get a linear increase in molecular weight with conversion. So, here we have seen a chain polymerization without termination of the propagating chains and we require a special technique for this special case that will be discussed later. However, we get a statistical termination in the case of the standard normal chain polymerization process. This is the case where even at the beginning at low conversion, we get high molecular weight polymer formation and as more monomer gets polymerize with time, the amount of polymer increases, not the molecular weight. So, the molecular weight almost remains the same with time, except the very last time at the end of the polymerization. So, the molecular weight remains almost the same during the entire duration, but the amount of polymer increases with time.

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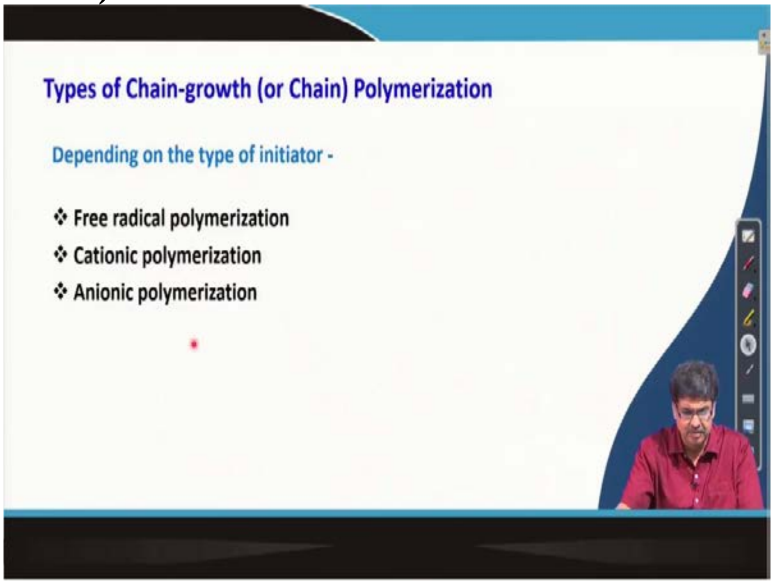

Types of Chain-growth (or Chain) Polymerization

Depending on the type of initiator -

- Free radical polymerization
- Cationic polymerization
- Anionic polymerization

Now, the type of chain-growth polymerization depends on the initiator which we discussed earlier. Depending on the initiator, we can have free-radical polymerization, cationic polymerization, or anionic polymerization. If the initiator is a cation then we call it a cationic polymerization and so on.

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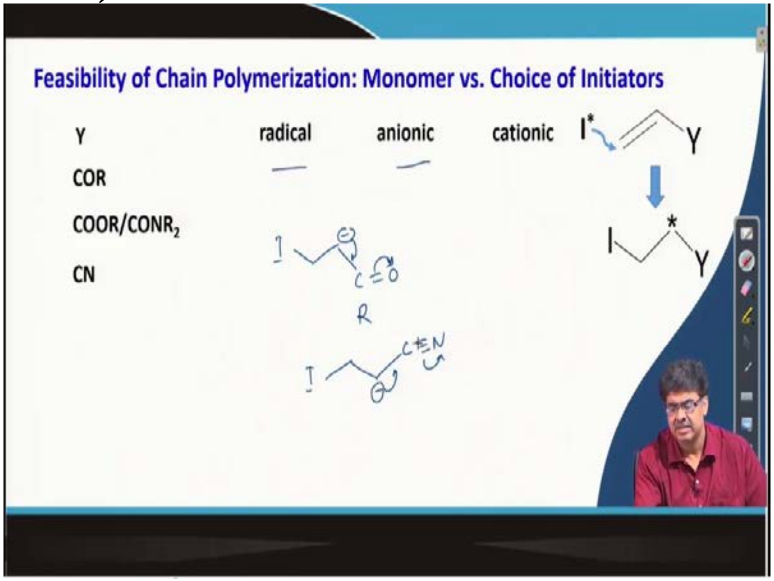

Feasibility of Chain Polymerization: Monomer vs. Choice of Initiators

Y	radical	anionic	cationic
COR	—	—	
COOR/CONR$_2$			
CN			

Now, which of these initiation mechanisms we should try? We should be looking at the monomer structure. We should design the type of chain polymerization to employ. If a structure I* which could be either a radical, cation, or anion, attack a monomer during the first initiation step, then depending on this substituent Y, whether it can stabilize these radicals or cations or anions, the reaction may proceed or may not. If this species is very unstable then we will not get sufficient molecular weight or the reaction will not proceed and if it is too stable then it will not react at all. In a normal scenario, if we can stabilize the intermediate radical, cation, or anion then the polymerization would be comparably feasible. Now, if we have a cation or an anion, to begin with, then in presence of an electron-withdrawing group either by inductive effect or by resonance, this species would get stabilized and result in a fruitful polymerization. So, we will have a table to show, depending upon Y, what type of chain polymerization is feasible. So, in the case of COR and CN, the anion provides a feasible reaction. Similarly, if the intermediate is radical, then it can also be stabilized for this type of substituent. Thus, radical polymerization and anion polymerization are feasible.

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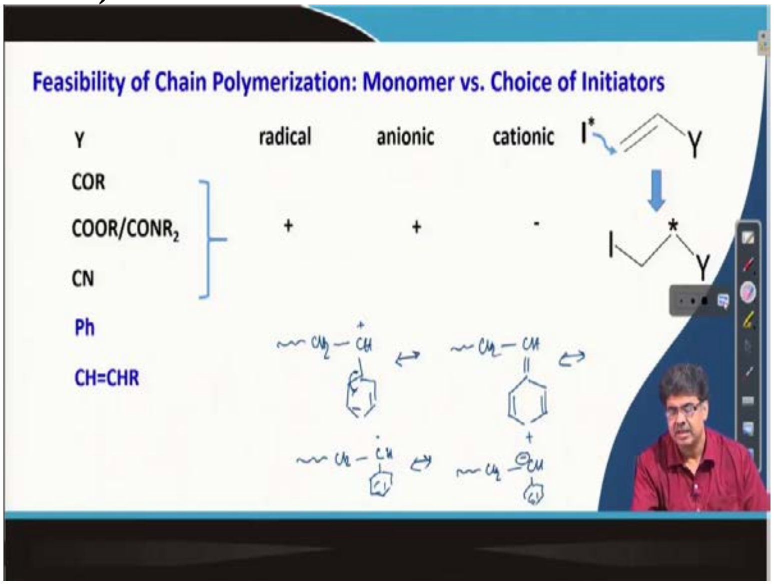

Feasibility of Chain Polymerization: Monomer vs. Choice of Initiators

Y	radical	anionic	cationic
COR	+	+	-
COOR/CONR$_2$			
CN			
Ph			
CH=CHR			

If we have a cationic chain having a benzene ring, they will have resonance stabilized structures. Now, this stabilization can happen if the intermediate is radical. A similar resonance structure is possible for an anion also. Now, if we have a substituent like a phenyl group, then we will have all three possibilities, e.g. for styrene molecule, a cationic polymerization or anionic polymerization, or radical polymerization. That is also true for these structures because these can also participate in resonance stabilization. So, in this case, we can think that the substitution will lead to all 3 types of polymerization.

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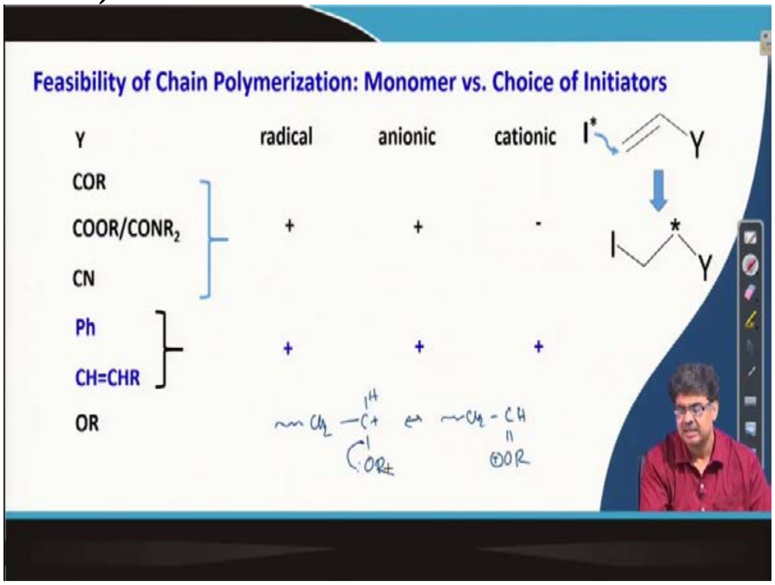

Feasibility of Chain Polymerization: Monomer vs. Choice of Initiators

Y	radical	anionic	cationic
COR	+	+	-
COOR/CONR$_2$			
CN			
Ph	+	+	+
CH=CHR			
OR			

$\sim CH_2-\overset{H}{\underset{\ddot{O}R}{C^+}} \leftrightarrow \sim CH_2-\underset{\oplus OR}{\underset{\|}{CH}}$

If we talk about the OR group then some sort of stabilization is possible by donation of this lone pair on the oxygen. So, in this case, it is possible to have polymerization by cationic mechanism but if it is an anionic then the stabilization would be very difficult.

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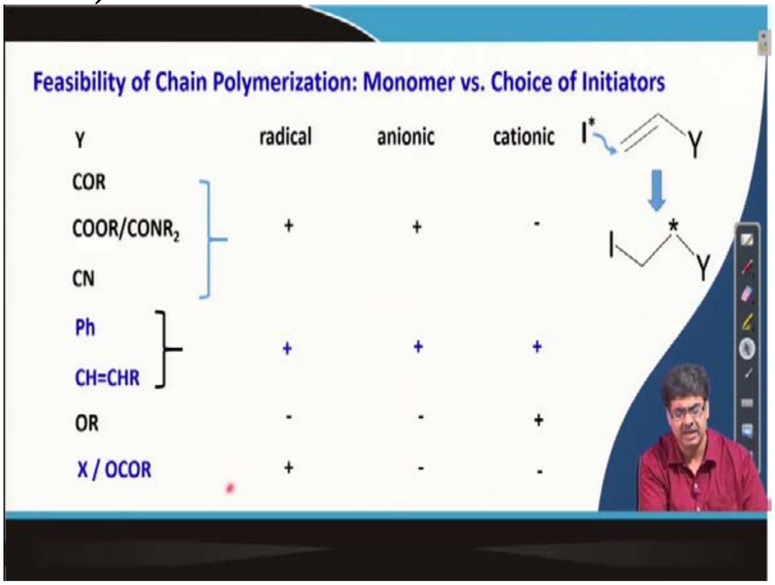

Feasibility of Chain Polymerization: Monomer vs. Choice of Initiators

Y	radical	anionic	cationic
COR	+	+	-
COOR/CONR$_2$			
CN			
Ph	+	+	+
CH=CHR			
OR	-	-	+
X / OCOR	+	-	-

If we have X (halogen) or OCOR as substituent, they cannot stabilize anion/cation due to the presence of lone pairs on heteroatom and also because of their electron-withdrawing effect. So, this type of substitution leads to difficulty in polymerization by chain polymerization. However, it might happen by radical polymerization.

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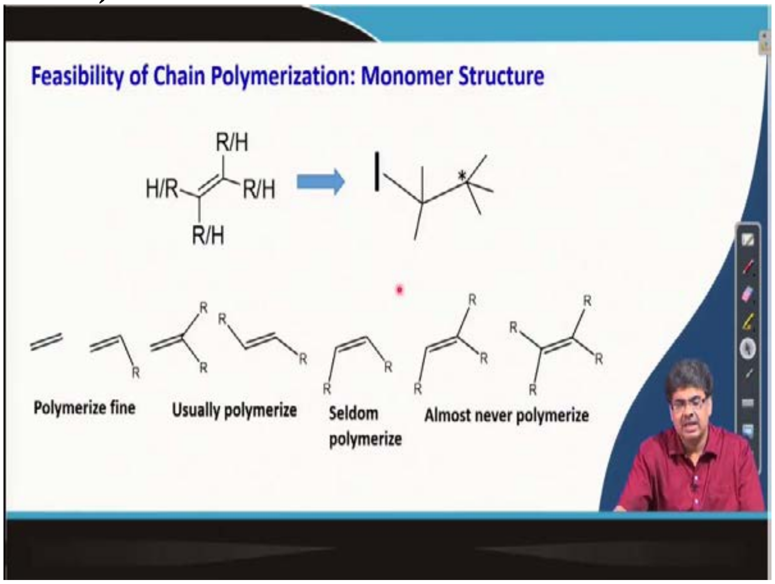

Feasibility of Chain Polymerization: Monomer Structure

Polymerize fine

Usually polymerize

Seldom polymerize

Almost never polymerize

Now, we will talk about electronic stabilization. For example, if there are more substitutions around the double bond, then is very difficult for this type of monomers to polymerize. It rarely polymerizes and if there is no substitution or a single substitution, it is polymerized very easily. Now, there is no substitution in this particular case of ethylene. So, here it can be polymerized radically but because of the non-existence of any stabilization mechanism, we cannot make large molecular weight or sufficiently high molecular weight polyethylene by radical polymerization. This type of substitution easily leads to polymerization, but this type of substitution does not relate to the feasibility of polymerization. So, in this slide, we learn that the number of substitutions is also important to have a feasible chain polymerization.

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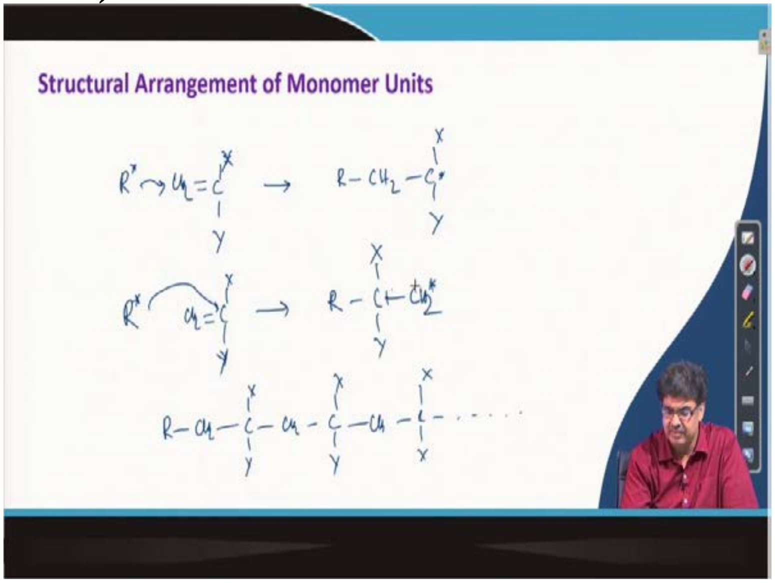

Structural Arrangement of Monomer Units

Now, we talk about the structural arrangements of the monomer units during polymerization. For example, a radical or cation or anion can attack the first carbon and get this structure. Similarly, if it attacks the other carbon, we get this structure shown in the second case. Now, if this happens continuously then we get a structure like this and so on. But if it attacks alternately, then we can land up in a different structure, which we can show. In the last case, a similar arrangement has been removed but there is another possible arrangement.

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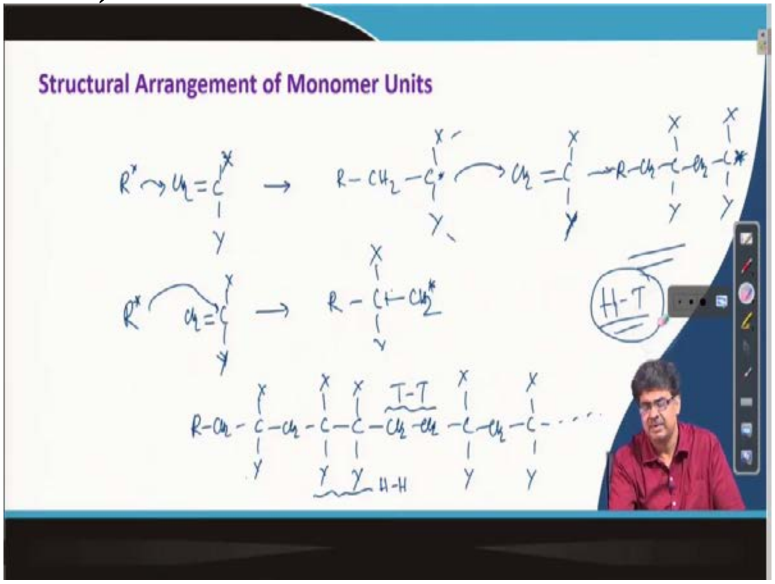

Structural Arrangement of Monomer Units

In this case, there is a reversal in the site of the attack and so we call, head to head arrangement i.e. h-h or tail to tail t-t arrangement. We can do otherwise also. But this is highly unlikely because if we look at the two structures, this is always feasible because of the stabilization by all of this x and y group. So, when it further attacks a second monomer, it will always prefer to attack in head to tail arrangement. Head to tail arrangement is always preferred to either a h-h or t-t arrangement. So, this head-to-tail arrangement is almost exclusively formed during chain-growth polymerization. Now, we will look for the mechanism of radical polymerization. We will come back to cation or anionic polymerization briefly in a later lecture.

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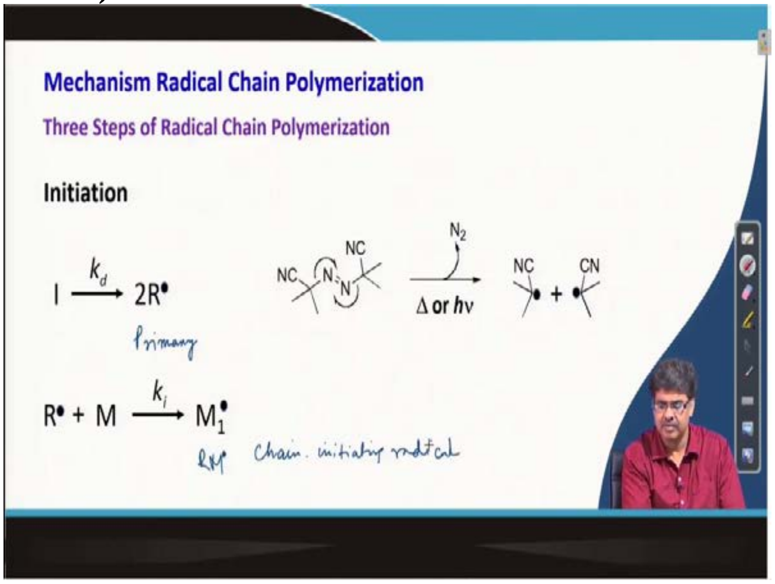

Mechanism Radical Chain Polymerization

Three Steps of Radical Chain Polymerization

Initiation

$$I \xrightarrow{k_d} 2R^\bullet$$

Primary

$$R^\bullet + M \xrightarrow{k_i} M_1^\bullet$$

RM• Chain. initiating radical

So, there are three steps of radical chain polymerization, first step is initiation. So, in this case, an initiator molecule gets dissociated to form two radicals and we have a rate constant associated with this step. For example, we have an AIBN molecule that gets dissociated and forms two radicals. Once this radical forms, it immediately attacks a monomer molecule and forms this $M_1^\cdot$. So, we call this $M_1^\cdot$ as a primary polymer radical because this will further attack another M monomer and start the chain. We call this a chain initiating radical.

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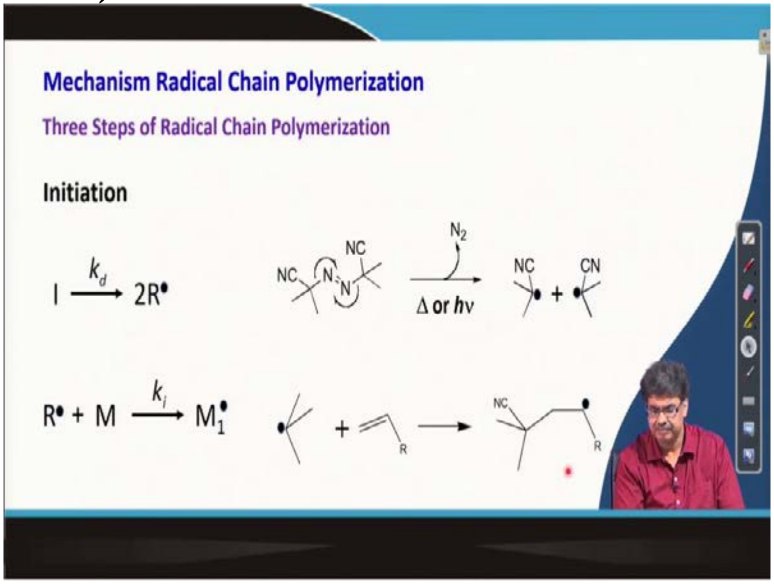

Mechanism Radical Chain Polymerization

Three Steps of Radical Chain Polymerization

Initiation

$$I \xrightarrow{k_d} 2R^\bullet$$

$$R^\bullet + M \xrightarrow{k_i} M_1^\bullet$$

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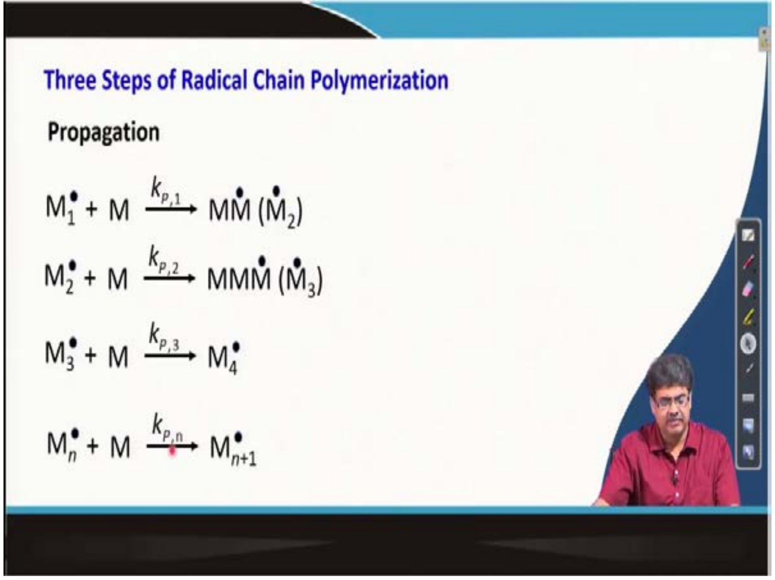

Three Steps of Radical Chain Polymerization

Propagation

$$M_1^\bullet + M \xrightarrow{k_{p,1}} M\overset{\bullet}{M}\ (\overset{\bullet}{M}_2)$$

$$M_2^\bullet + M \xrightarrow{k_{p,2}} MM\overset{\bullet}{M}\ (\overset{\bullet}{M}_3)$$

$$M_3^\bullet + M \xrightarrow{k_{p,3}} M_4^\bullet$$

$$M_n^\bullet + M \xrightarrow{k_{p,n}} M_{n+1}^\bullet$$

The second step is propagation, the first chain initiator radical reacts with another monomer to form a $MM^{\cdot}$ radical. So, there should be the initiating species R in all these cases and we are writing, $M_2^{\cdot}$ instead of $MM^{\cdot}$ for simplicity. So, in the first step once initiation happens, this radical first attacks the monomer to form this first chain initiating radical. Similarly, this $M_2^{\cdot}$ attacks another monomer to produce $M_3^{\cdot}$and we get the second rate constant. In the same way, we get $M_4^{\cdot}$. Thus, we can write a M_n + M give us $M_{n+1}^{\cdot}$ in a general form. So, n + 1 number of monomers are present in this propagating radical and we can write a rate constant for this.

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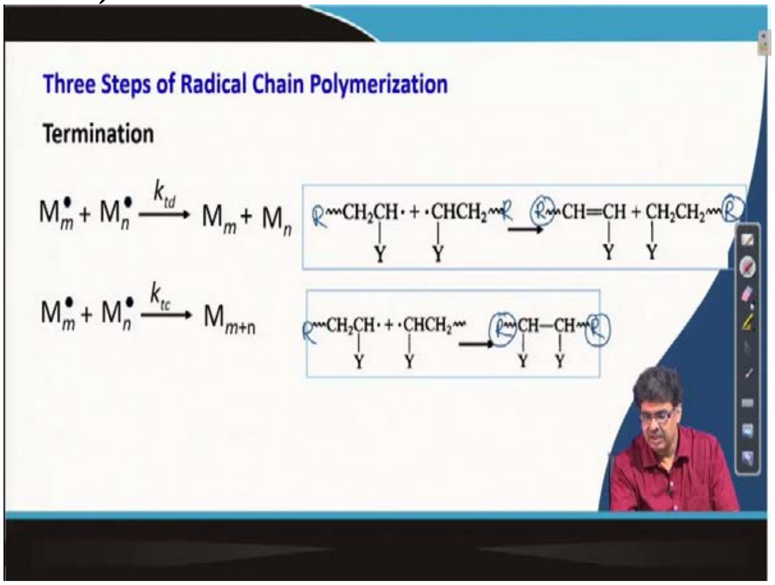

Three Steps of Radical Chain Polymerization

Termination

$$M_m^\bullet + M_n^\bullet \xrightarrow{k_{td}} M_m + M_n$$

$$R\text{~~}CH_2\underset{Y}{CH}\cdot + \cdot\underset{Y}{CH}CH_2\text{~~}R \rightarrow R\text{~~}CH{=}\underset{Y}{CH} + \underset{Y}{CH_2}CH_2\text{~~}R$$

$$M_m^\bullet + M_n^\bullet \xrightarrow{k_{tc}} M_{m+n}$$

$$R\text{~~}CH_2\underset{Y}{CH}\cdot + \cdot\underset{Y}{CH}CH_2\text{~~} \rightarrow R\text{~~}\underset{Y}{CH}-\underset{Y}{CH}\text{~~}R$$

So, those propagating radicals can interact with each other due to the reactivity of the radicals. They can molecularly react with each other and terminate the chain. This can happen in two ways, one is disproportionation; we write the corresponding rate constant as k_{td} i.e. termination by disproportionation. So, in that case, we get two polymer chains, the structure is shown here. There is another possible way to do termination, by coupling. The k_{tc} means termination by coupling. In that case, these two are joined to each other and we get a single polymer chain from two radicals. So, we should remember that all this chain has started with a chain initiating radical species, at the beginning. So, in this case when the termination occurs by disproportionation then each polymer will have one chain initiating species.

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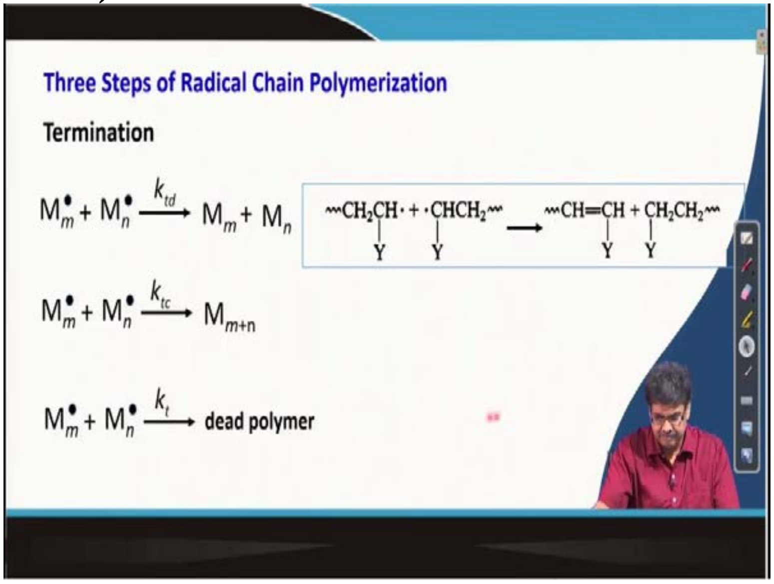

Three Steps of Radical Chain Polymerization

Termination

$$M_m^\bullet + M_n^\bullet \xrightarrow{k_{td}} M_m + M_n$$

$$\sim CH_2\underset{Y}{CH}\cdot + \cdot\underset{Y}{CH}CH_2\sim \longrightarrow \sim\underset{Y}{CH}{=}CH + \underset{Y}{CH_2}CH_2\sim$$

$$M_m^\bullet + M_n^\bullet \xrightarrow{k_{tc}} M_{m+n}$$

$$M_m^\bullet + M_n^\bullet \xrightarrow{k_t} \text{dead polymer}$$

The termination which is done by the coupling process results in the polymer chain having two chain initiating species. So, in general, we can write the termination as $M_m^\cdot + M_n^\cdot$ dead polymer inthe k_t termination step.

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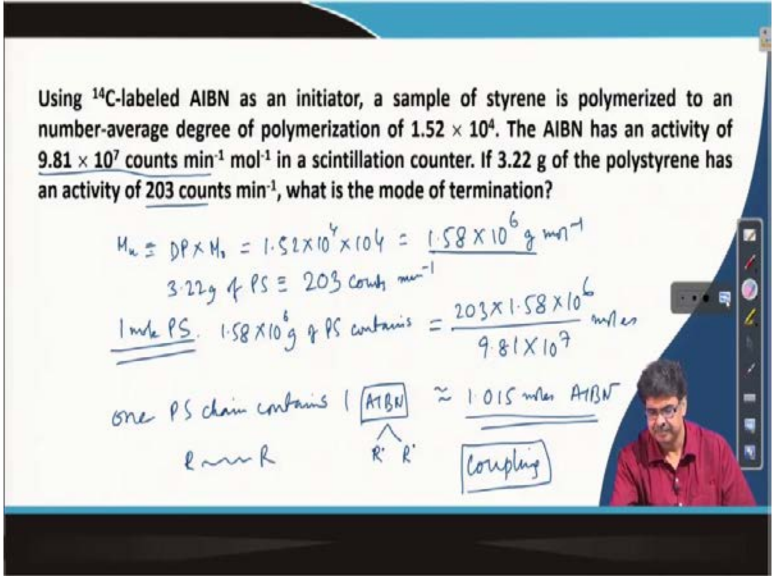

Using ^{14}C-labeled AIBN as an initiator, a sample of styrene is polymerized to an number-average degree of polymerization of 1.52×10^4. The AIBN has an activity of 9.81×10^7 counts min^{-1} mol^{-1} in a scintillation counter. If 3.22 g of the polystyrene has an activity of 203 counts min^{-1}, what is the mode of termination?

$M_n = DP \times M_0 = 1.52 \times 10^4 \times 104 = \underline{1.58 \times 10^6} \text{ g mol}^{-1}$

$3.22\text{g of PS} \equiv 203 \text{ counts min}^{-1}$

$\underline{\underline{\text{1 mole PS}}}$. $1.58 \times 10^6\text{g of PS contains} = \dfrac{203 \times 1.58 \times 10^6}{9.81 \times 10^7}$ moles

one PS chain contains 1 $\boxed{\text{AIBN}}$ $\approx \underline{\underline{1.015 \text{ moles AIBN}}}$

R~~~R R˙ R˙ $\boxed{\text{Coupling}}$

We discussed that each polymer chain will have one initiator molecule if the termination occurs by the disproportionation and each polymer chain will have two initiators species at the two ends if the termination takes place by the coupling. So, if we can quantify the amount or the number of initiator molecules or initiating species per polymer chain, then we can find out what is the mode of termination. For example, in this case, AIBN is an initiator which was carbon radio labeled basically.

It is given that one mole of ABIN has 9.81×10^7 counts and 3.22 grams of this resulting polystyrene has an activity of 203 counts, then what is the mode of termination? So, M_n is given by the degree of polymerization multiplied by the molecular weight of the repeat structural unit, which in this case polystyrene is 104, which gives us 1.58×10^6 grams per mole. So, 3.22 grams of polystyrene is equivalent to this given 203 counts per minute. So, 1 mole polystyrene which has 1.58×10^6 grams of polystyrene contains how many AIBN? We can just do this simple rearrangement we get 1.015 moles of AIBN present.

So as we can see that, 1 mole of polystyrene gives approximately 1 mole of AIBN which means one polystyrene chain contains one AIBN. Now each AIBN produces two radical species that means, one polystyrene chain contains two initiating species at both the side, which means the termination is exclusively by the coupling in this case. So, this is an example to find out the mode of termination.

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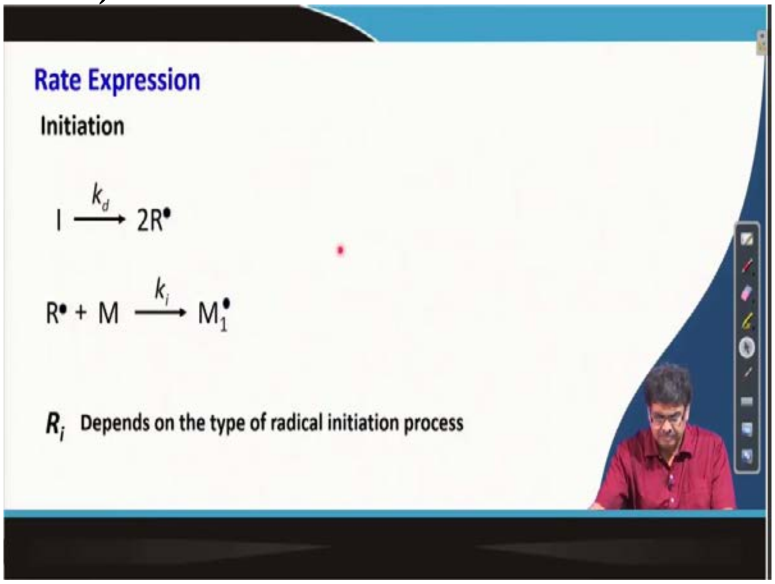

Rate Expression

Initiation

$$I \xrightarrow{k_d} 2R^\bullet$$

$$R^\bullet + M \xrightarrow{k_i} M_1^\bullet$$

R_i Depends on the type of radical initiation process

Now we will go to the rate expression. So, the initiation happens in two steps as we discussed earlier. This is the first step dissociation occurs where we get these two radicals and then immediately it initiates the first monomer. These two steps are together known as the initiation step. We write R_i is the rate of initiation and depends on the radical initiation process, that is the process by which we are generating this radical. It could be either by heat or photochemically by shining light or by redox processes. So, this rate of initiation depends on the type of initiation process and we will come back and discuss, how to find out R_i depending upon the type of initiation a little later.

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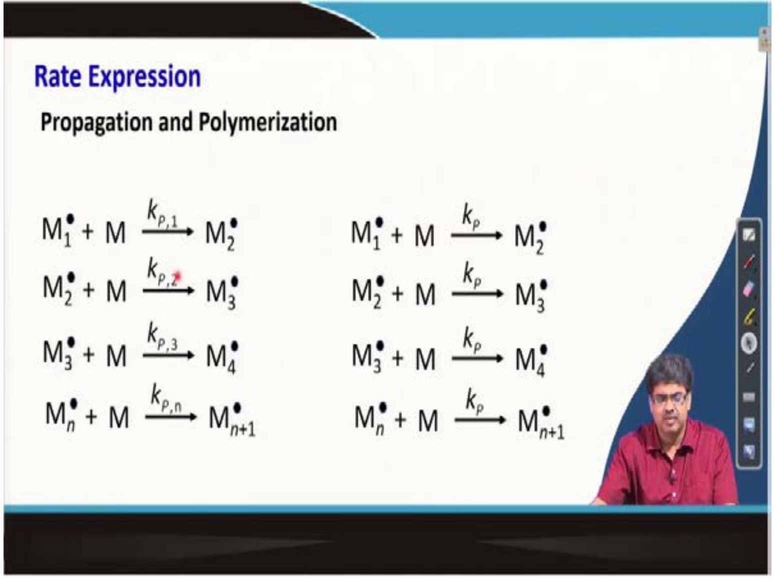

Rate Expression

Propagation and Polymerization

$$M_1^\bullet + M \xrightarrow{k_{p,1}} M_2^\bullet \qquad M_1^\bullet + M \xrightarrow{k_p} M_2^\bullet$$

$$M_2^\bullet + M \xrightarrow{k_{p,2}} M_3^\bullet \qquad M_2^\bullet + M \xrightarrow{k_p} M_3^\bullet$$

$$M_3^\bullet + M \xrightarrow{k_{p,3}} M_4^\bullet \qquad M_3^\bullet + M \xrightarrow{k_p} M_4^\bullet$$

$$M_n^\bullet + M \xrightarrow{k_{p,n}} M_{n+1}^\bullet \qquad M_n^\bullet + M \xrightarrow{k_p} M_{n+1}^\bullet$$

Now, in the case of propagation, we have written different rate constants for different steps. Here, the reaction is the same i.e. the reaction between the monomer and a radical which is also of similar structure. Thus, it is very safe and very justifiable to assume that all these reactions proceed with the same rate constant. In this case, we will remove these 1, 2, 3… n numbers.

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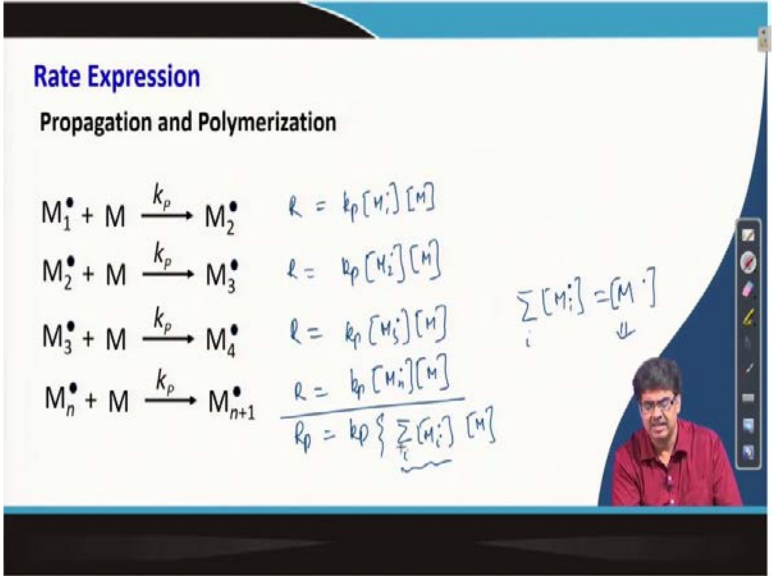

Rate Expression

Propagation and Polymerization

$$M_1^\bullet + M \xrightarrow{k_p} M_2^\bullet \qquad R = k_p[M_1^\cdot][M]$$

$$M_2^\bullet + M \xrightarrow{k_p} M_3^\bullet \qquad R = k_p[M_2^\cdot][M]$$

$$M_3^\bullet + M \xrightarrow{k_p} M_4^\bullet \qquad R = k_p[M_3^\cdot][M]$$

$$M_n^\bullet + M \xrightarrow{k_p} M_{n+1}^\bullet \qquad R = k_p[M_n^\cdot][M]$$

$$R_p = k_p \left\{ \underbrace{\sum_i [M_i^\cdot]} [M] \right.$$

$$\sum_i [M_i^\cdot] = [M^\cdot]$$

$$\Downarrow$$

So, all these steps go at the same rate. Consequently, we will have the same rate constant for all these steps. Now we can write individual rates. So, the rate for the first step is to be k_p $[M_1^\cdot]$ [M]. Similarly for the next two steps, we can write k_p $[M_2^\cdot]$ [M] and k_p $[M_3^\cdot]$ [M] respectively. So, we can write $k_p\sum[M_i^\cdot][M]$ to get the total rate of propagation where k_p is common for all these cases. So, this is the term which is the summation of all the radicals present in the reaction mixture and we write this term equals to simply $[M^\cdot]$ i.e. $\sum[M_i^\cdot]=[M^\cdot]$, which is the concentration of all the propagating radical species present in the reaction mixture. So, we can simply write this now

$$R_p = k_p \sum[M^\cdot][M]$$

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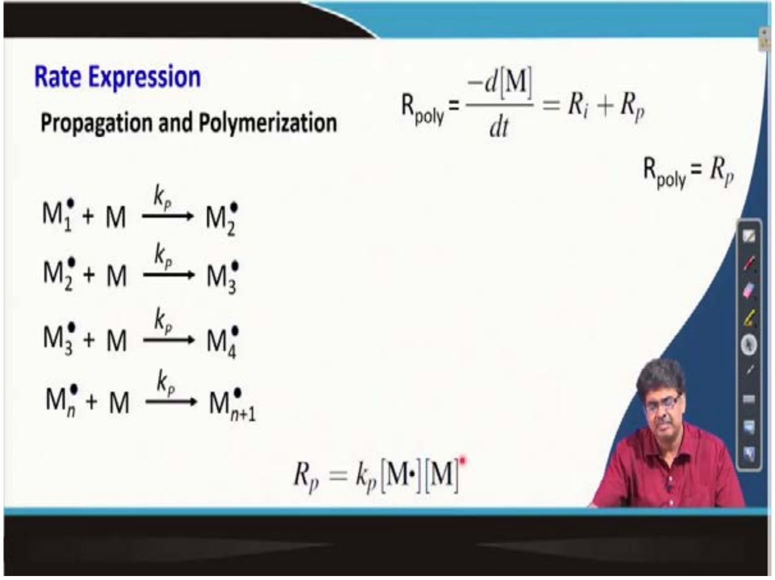

Rate Expression

Propagation and Polymerization

$$R_{poly} = \frac{-d[\mathrm{M}]}{dt} = R_i + R_p$$

$$R_{poly} = R_p$$

$$M_1^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet}$$

$$M_2^{\bullet} + M \xrightarrow{k_p} M_3^{\bullet}$$

$$M_3^{\bullet} + M \xrightarrow{k_p} M_4^{\bullet}$$

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet}$$

$$R_p = k_p[\mathrm{M}\bullet][\mathrm{M}]$$

So, the rate of polymerization is given by the rate of disappearance of monomers. Now monomer disappears in the initiation step and during all these propagation steps. So, we can write the rate of polymerization is given by the rate of initiation plus the rate of propagation.

$$R_{poly} = \frac{-d[\mathrm{M}]}{dt} = R_i + R_p$$

Now, we can see that one monomer disappears in the initiation stage only. There are many propagation steps we can consider this equivalent to R_p. The rate of polymerization is given by the rate of propagation and we have already found that the rate of propagation is given by,

$$R_p = k_p[M^{\cdot}][M]$$

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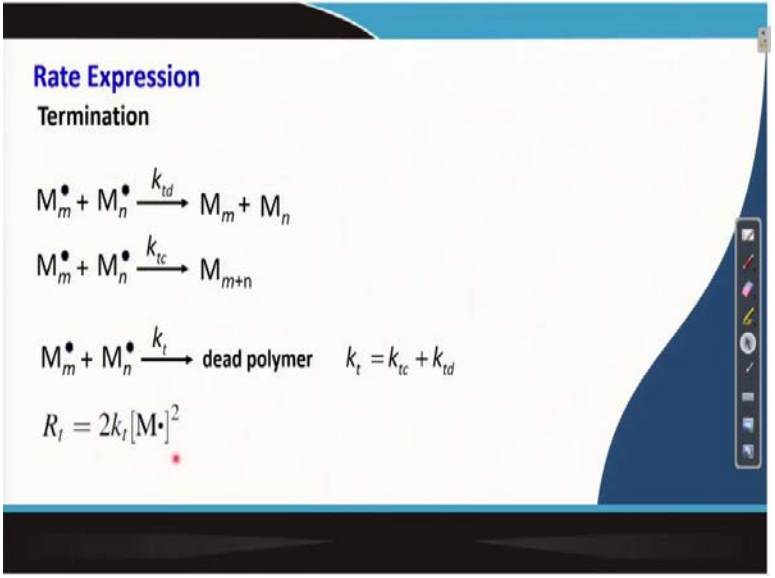

Rate Expression

Termination

$$M_m^\bullet + M_n^\bullet \xrightarrow{k_{td}} M_m + M_n$$

$$M_m^\bullet + M_n^\bullet \xrightarrow{k_{tc}} M_{m+n}$$

$$M_m^\bullet + M_n^\bullet \xrightarrow{k_t} \text{dead polymer} \qquad k_t = k_{tc} + k_{td}$$

$$R_t = 2k_t[\mathrm{M}\cdot]^2$$

Now in the termination step, we have possible two ways of termination - one by disproportionation, another by coupling. So, we can write that k_t is the summation of these two steps and in this case, the rate is given by $R_t = 2k_t[M^\cdot]^2$. Now, this term 2 is coming because each reaction stops two propagating radicals. So, this is a convention to use two but some texts may not use this 2. However, we should remember this during the discussion on the rate of initiation. So, we will stop here, we have discussed the rate of initiation, the rate of propagation, and the rate of termination. We will discuss how to find out this concentration of this term in the next lecture.