Polymer Reaction Engineering
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Lecture – 35
Rate of Polymerization

Welcome to the rate of polymerization lecture under the head of radical chain polymerization. If you recall previously we discussed about the different modes of propagation of monomer units, in which we discussed about the head to head and head to tail type of propagation steps in of different monomer units.

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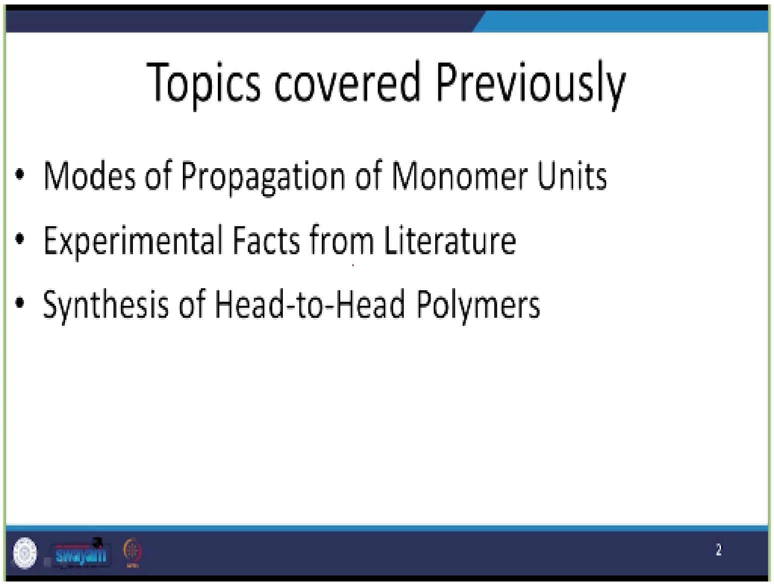

Topics covered Previously

- Modes of Propagation of Monomer Units
- Experimental Facts from Literature
- Synthesis of Head-to-Head Polymers

Then we discussed about the experimental facts related to these head to head and head to tail type of propagation is streams. then, we pay a little attention to the synthesis of various head to head polymerization processes. And we discussed with the help of a several cases and several examples. Now, in this particular lecture, we are going to discuss this initiation, propagation and termination.

So, continuously if you recall that we are emphasising the fact that this polymerization reaction usually carried out with the 3 steps. One is initiation through which you can initiate the polymerization process and then propagation in which all these monomer units and different chains of whatever polymer polymer chains are being developed in due course of time they propagate themselves to form a bigger chain, etcetera.

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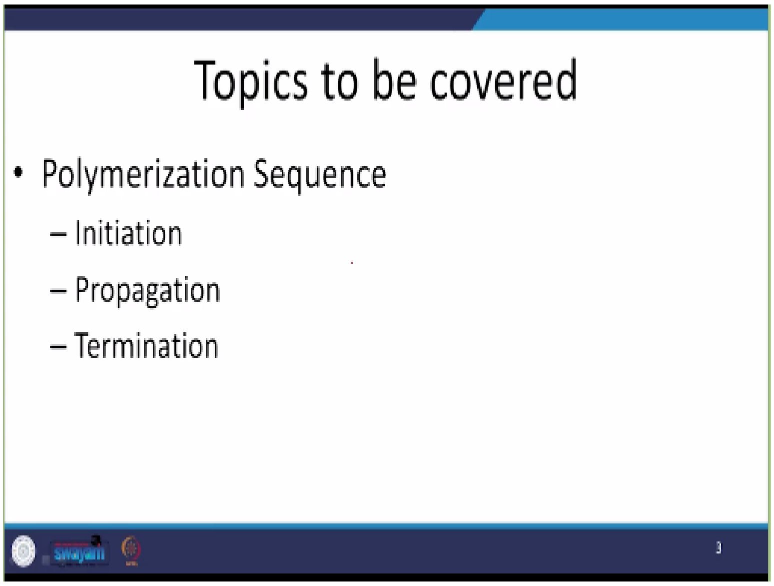

Topics to be covered

- Polymerization Sequence
  - Initiation
  - Propagation
  - Termination

And the termination step because it is of equally important with respect to the initiation and propagation. Because at appropriate time, all these polymerization process needs to be truncated so that we can have the appropriate property, appropriate viscosity, appropriate molecular weight so that whatever polymer being generated in due course of time can be processed adequately.

So, we are going to discuss this particular sequence in this lecture. So, let us have a start with this polymerization sequence.

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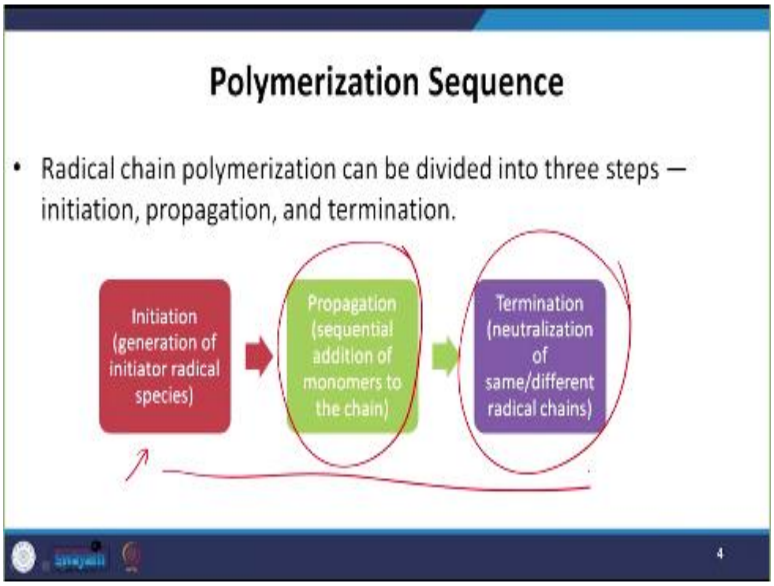

Polymerization Sequence

- Radical chain polymerization can be divided into three steps — initiation, propagation, and termination.

Initiation (generation of initiator radical species)

Propagation (sequential addition of monomers to the chain)

Termination (neutralization of same/different radical chains)

Now, the radical chain polymerization can be divided into 3 steps, as we are talking about that initiation that the generation of initiated radical spaces maybe, with the help of a functional group maybe, with the help of some other external approaches etcetera. Then propagation that is the sequential addition of a monomer to the chain that depends on the protocol you are following so that you can get a different type of properties of polymer which is required for your actual product.

Then the termination if you recall that we discussed various approaches of termination and which one was the the neutralisation and another one was the killing of those radical chains etcetera. So, these 3 steps are integral part of radical chain polymerization.

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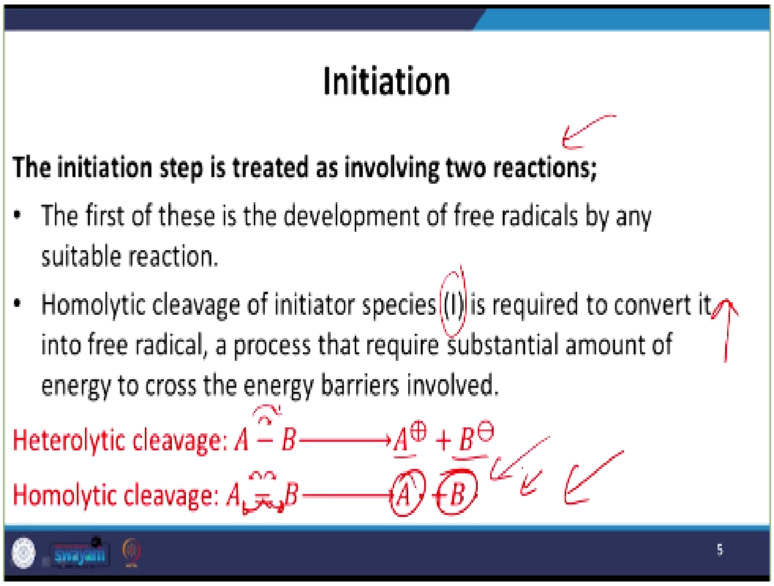

Initiation

The initiation step is treated as involving two reactions;

- The first of these is the development of free radicals by any suitable reaction.
- Homolytic cleavage of initiator species (I) is required to convert it into free radical, a process that require substantial amount of energy to cross the energy barriers involved.

Heterolytic cleavage: $A \overset{\frown}{-} B \longrightarrow A^{\oplus} + B^{\ominus}$

Homolytic cleavage: $A \overset{\frown\frown}{-} B \longrightarrow A + B$

Now, let us have a look or about the initiation steps. So, usually when we carry out the initiation process, this is treated as with the 2 reaction in in series, The first of these is the development of free radical by any suitable reaction. Then, the homolytic cleavage of initiator species I which is designated as I is required to convert it into the free radical a process that require the substantial amount of energy to cross the energy barrier required involved.

So that it can facilitate the propagation step or it can induce some sort of a energy to the reaction mass, so that they can perform the polymerization reaction or they can start the polymerization reaction adequately. Now, again, if we see that, based on this particular aspect, there are 2 type of cleavages, one is heterolytic you see that here 2 things are A and B. Now, there is a transfer of charges, then you see that these are the developed ions, A + and B minus.

Heterolytic cleavage: $A\overset{\frown}{-}B \longrightarrow A^{\oplus} + B^{\ominus}$

Homolytic cleavage: $A\overset{\frown\frown}{-}B \longrightarrow A\cdot + B\cdot$

And the homolytics is that is the formation of the radical that means this in a rough word you can say that this particular bond is break, then these 2 radicals are being generated. So, they can cross the substantial amount of they they may have substantial amount of energy to cross energy barrier, which we discussed a couple of minutes ago.

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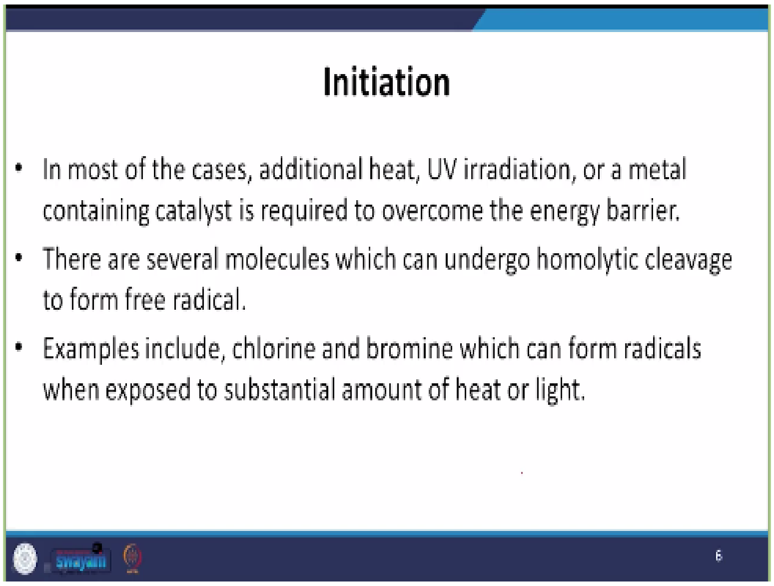

Initiation

- In most of the cases, additional heat, UV irradiation, or a metal containing catalyst is required to overcome the energy barrier.
- There are several molecules which can undergo homolytic cleavage to form free radical.
- Examples include, chlorine and bromine which can form radicals when exposed to substantial amount of heat or light.

Now, in most of the cases, additional heat or sometimes ultraviolet irradiation or sometimes metal containing catalyst, they play a very vital role to overcome the such type of energy barrier or in situ energy barrier. Now, there are several molecules which can undergo the homolytic cleavage this one, to form the free radical. Now, you see that these are the, again I am repeating that these are termed as the free radical.

Now, these example includes the chlorine and bromine which can form the radical when exposed to the substantial amount of heat or light. Now, let us have an example of these particular thing.

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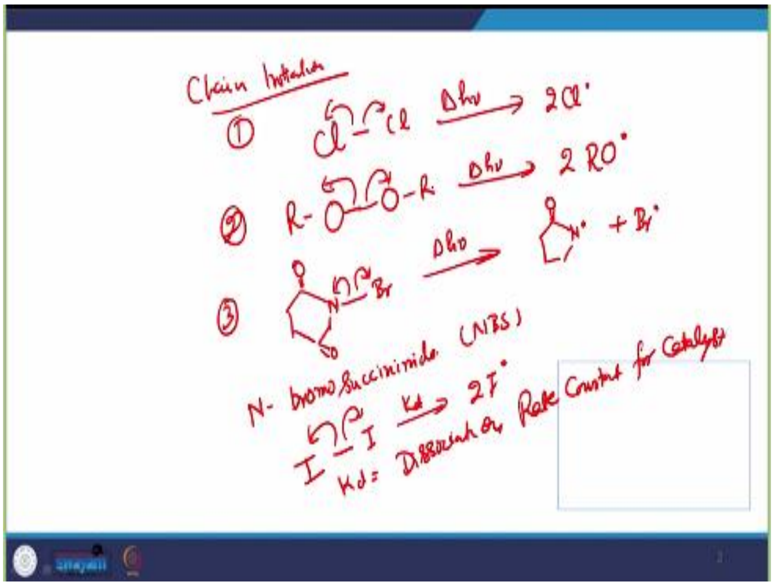

Chain Initiation

① $Cl-Cl \xrightarrow{\Delta h\nu} 2Cl^\bullet$

② $R-O-O-R \xrightarrow{\Delta h\nu} 2RO^\bullet$

③ $\xrightarrow{\Delta h\nu}$ $+ Br^\bullet$

N- bromo Succinimide (NBS)

$I-I \xrightarrow{K_d} 2I^\bullet$

K_d = Dissociation or Rate Constant for Catalyst

Now, here the chain initiation. Now, first example is chlorine. Now, if you see, we are forming this chlorine radical with the help of so, it gives you 2 chlorine radicals. Similarly, if you see with the help of a certain quantity of energy. Now, let us take some more example of phenyl ring. Now, this is, + Br•. So, this is and bromosuccinimide. Let us take the example of iodine. This is the formation of iodine radical (I•).

Now, here this K_d is equal to dissociation constant for catalyst. So, this is the these are the brief examples of initiation step. Now, other such examples include the chlorofluorocarbon, peroxide, halogenated amides, etcetera. Now, the second step of initiation, it involves the attachment of these initiator radicals to the first monomer molecule to generate the chain initiating radicals. Now, let us have an example of these type of approaches.

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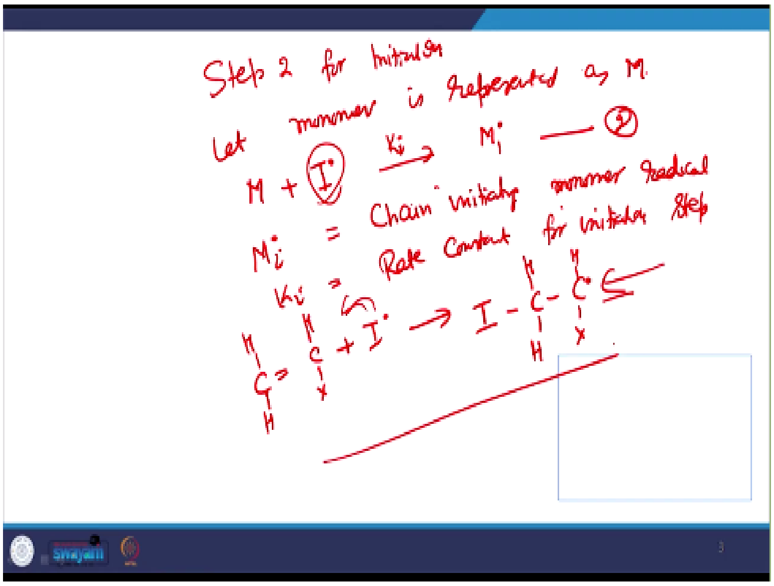

Step 2 for Initiation

Let monomer is represented as M.

$M + I^\bullet \xrightarrow{K_i} M_i^\bullet$ —— ②

$M_i^\bullet$ = Chain initiating monomer radical

K_i = Rate Constant for initiation Step

$CH_2=CHX + I^\bullet \rightarrow I-CH_2-CH^\bullet X$

This is you can refer to as step 2 for the initiation. Now, let the monomer is represented as M. Now, here M + I, which we described earlier that is the this is the radical then K_i is equal to M_1. Let us represent it as, if we represent this like 1, then let us represent it as 2. Now here, this M_i• is the chain initiating monomer radical and the K_i is the rate constant for initiation step.

Now, let us have an example of this one. This is + this is the iodine radical (I•). It is. Now, you see here this one, this radical is transferred from here to this one. So, it can again start the polymerization reaction effectively. Now, the step consists of this M_1, which we discussed in the previous slide by the successive addition of large number of monomer molecules. Now, when we talk about the addition of a new monomer generated.

Now, it generates a new radical with the same uniqueness as the previous one, except that it will have a longer chain due to the addition of monomer units.

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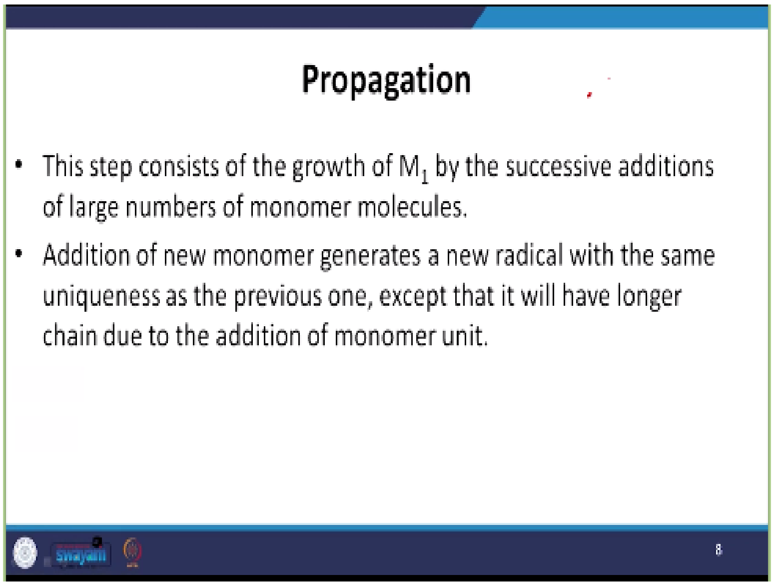

Propagation

- This step consists of the growth of M_1 by the successive additions of large numbers of monomer molecules.
- Addition of new monomer generates a new radical with the same uniqueness as the previous one, except that it will have longer chain due to the addition of monomer unit.

See, because it acts as a seed unit for the further propagation. So, that is why it has a longer chain unit because of subsequent or a sequential addition of these monomer chains. Now, let us have an exam another example of this one that is the chain propagation.

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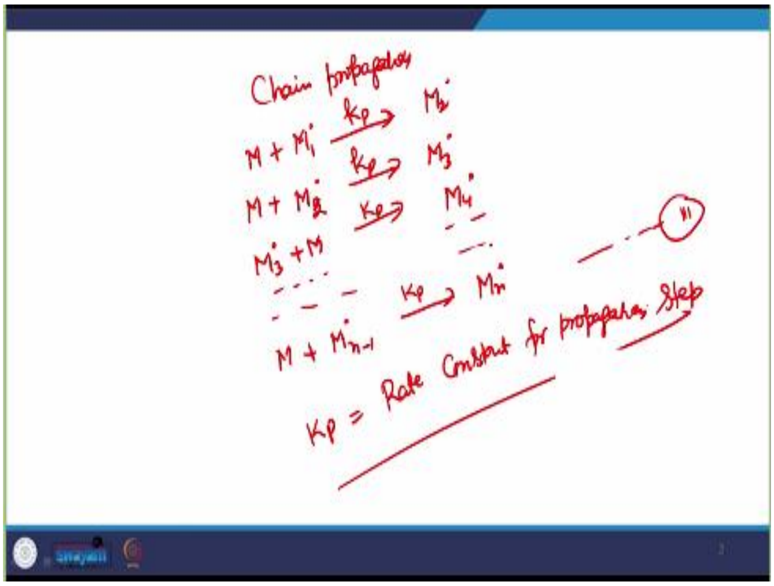

Chain propagation

$$M + M_1^{\bullet} \xrightarrow{K_p} M_2^{\bullet}$$
$$M + M_2^{\bullet} \xrightarrow{K_p} M_3^{\bullet}$$
$$M_3^{\bullet} + M \xrightarrow{K_p} M_4^{\bullet}$$
$$\cdots \qquad \cdots$$
$$M + M_{n-1}^{\bullet} \xrightarrow{K_p} M_n^{\bullet} \quad \text{---} \quad \text{(iii)}$$

K_p = Rate Constant for propagation Step

Now, this one is your monomer and this one is the monomer radical. Now, you see that this becomes this one, then again M + M_2 radical, this may become M_3 and this M_3 + M this may become M_4 and so on. So, similarly, M + M_{n-1}• this becomes this one. Now, let us say this is my equation number 3. Now, here the K p is the rate constant for propagation step.

So, this is again a very you can say a very useful thing, especially when we talk about the propagation step. The value of this K_p for most monomer in radical polymerization is larger than those usually encountered in a step polymerization. Let us have a foremost important thing in this polymerization process that is called the termination. Because it is very impractical thing that if you keep on getting on this polymerization step up to a very infinite time, and where you can, you cannot control the things.

And all the reaction mass will become useless if you are not able to control all those things. So, termination plays a very vital role. Now, this chain termination happens when 2 free radicals react with each other to form a stable or a neutral molecule. Therefore, It is a biomolecular type of thing like this.

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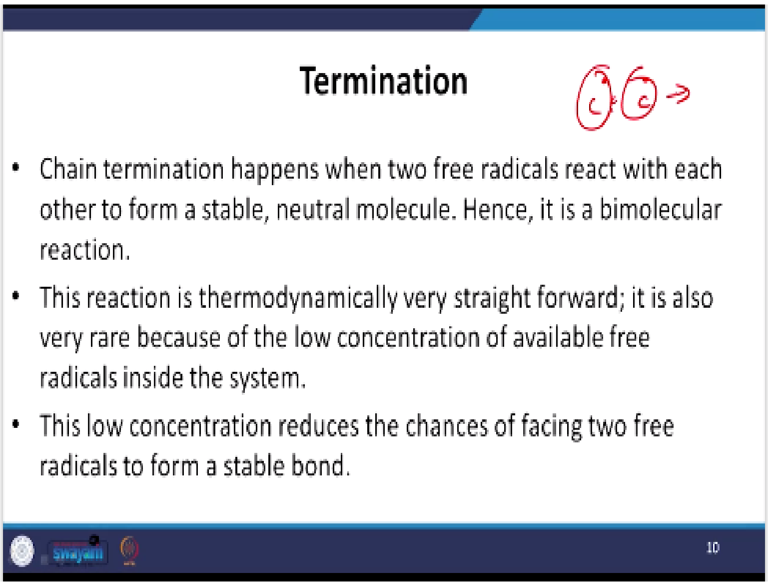

Termination

- Chain termination happens when two free radicals react with each other to form a stable, neutral molecule. Hence, it is a bimolecular reaction.
- This reaction is thermodynamically very straight forward; it is also very rare because of the low concentration of available free radicals inside the system.
- This low concentration reduces the chances of facing two free radicals to form a stable bond.

Here you are having say 2 radicals and they if they are combined together then they the entire thing will become neutralised. Now, this reaction is thermodynamically very straightforward, and it is very rare, because of the low concentration of available free radicals inside the system. Now, this low concentration sometimes reduces the chances of facing 2 free radicals to form a stable bond. So, this is a very, very unique type of thing in this particular phenomena.

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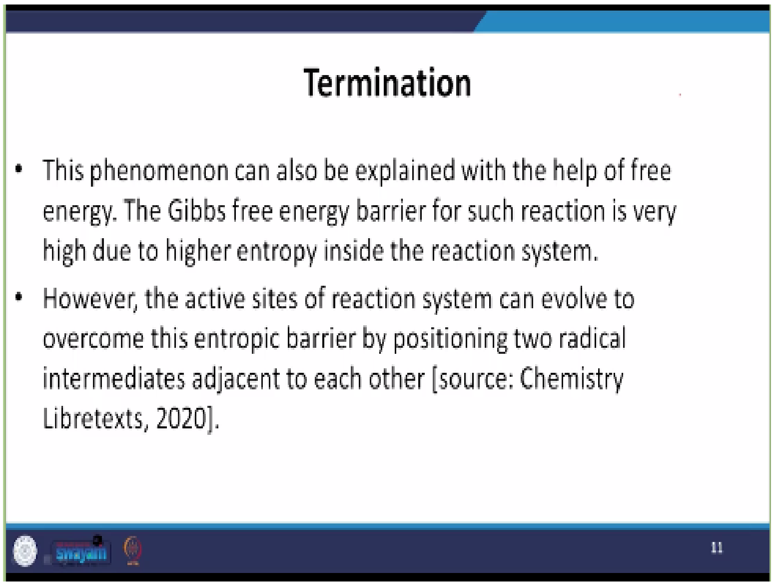

Termination

- This phenomenon can also be explained with the help of free energy. The Gibbs free energy barrier for such reaction is very high due to higher entropy inside the reaction system.
- However, the active sites of reaction system can evolve to overcome this entropic barrier by positioning two radical intermediates adjacent to each other [source: Chemistry Libretexts, 2020].

So, this phenomenon can also be explained with the help of a free energy because you see that the Gibbs free energy is very vital, plays a very vital role in deciding the fate of any kind of a chemical reaction whether it is a polymerization reaction or normal reaction. Now this Gibbs free energy barrier for such reaction is very high, due to higher entropy inside the reaction system.

However, the active sites of reaction system can evolve to overcome this type of entropic barrier by positioning 2 radical intermediates adjacent to each other. the termination step of a free radical occur usually occurs in 2 ways, either by a coupling reaction or a combination reaction. this bi-molecular interaction of 2 radicals to form one saturated polymer, let us have a look about this particular example.

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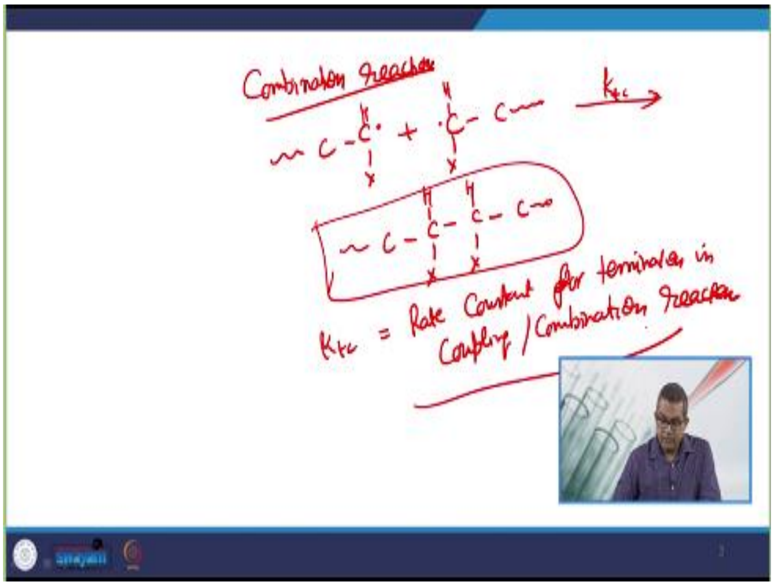

Combination reaction

K_{tc} = Rate Constant for termination in Coupling / Combination reaction

Here this is we are talking about the the combination reaction. Now, this is the 2 free radicals. Now, here this is K tc This is the rate constant of termination in coupling reaction. Now, you see the neutralised molecule will become like this. So, this is the neutralised one. You see that there is no free radical present in in this particular molecule. So, K tc is equal to the rate constant for termination and coupling or combination reaction.

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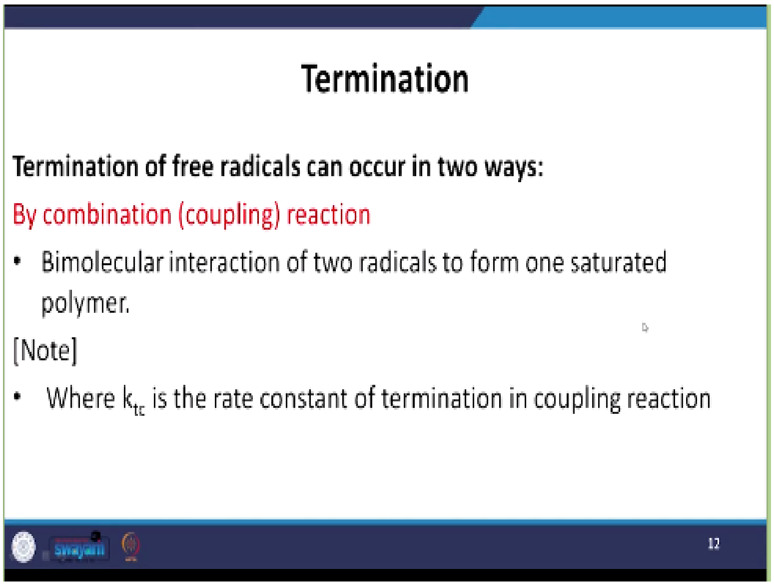

Termination

Termination of free radicals can occur in two ways:

By combination (coupling) reaction

- Bimolecular interaction of two radicals to form one saturated polymer.

[Note]

- Where k_{tc} is the rate constant of termination in coupling reaction

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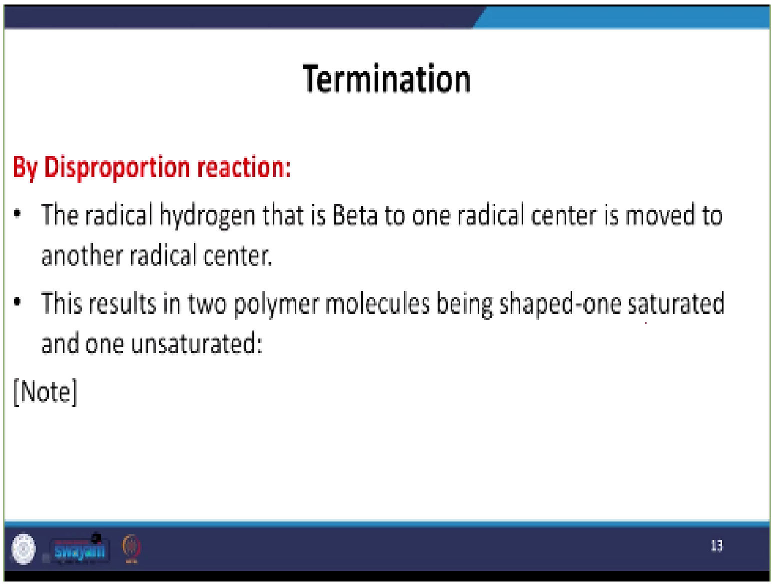

Termination

By Disproportion reaction:

- The radical hydrogen that is Beta to one radical center is moved to another radical center.
- This results in two polymer molecules being shaped-one saturated and one unsaturated:

[Note]

Now, another termination protocol is this is by the disproportion reaction. Now, the radical hydrogen that is the beta to one radical centre is moved to the another radical centre. So, by this way it can occur in the polymerization radical chain polymerization step. Now, this results in 2 polymer molecules being shaped. One saturated one and other one is unsaturated one. Let us have a representation of these disproportionate reaction.

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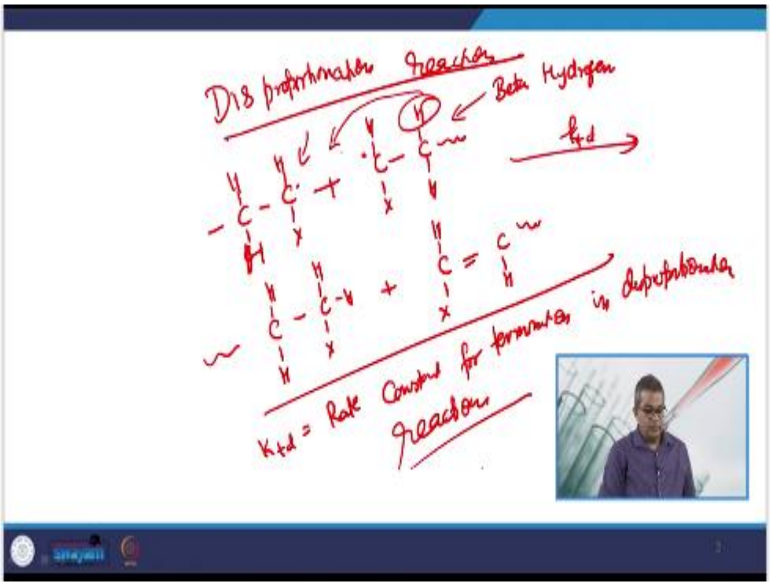

Nation reaction. Now here. Now, you see here this is the radical one. Now, here this is the beta hydrogen. Let us have this K_{td}. This is the rate constant for termination in disproportionation reaction. Now, this H is moving like this. So, you have you are having two molecules. So, these are the two molecules which we were talking about. So, this is K_{td}, the rate constant for termination in reaction.

You see in the previous slide that we produced 2 molecules one saturated one another one unsaturated. Now, the termination can also take place through a combination of coupling disproportionation. Now, the 2 distinct termination modes can be commonly described as this particular protocol.

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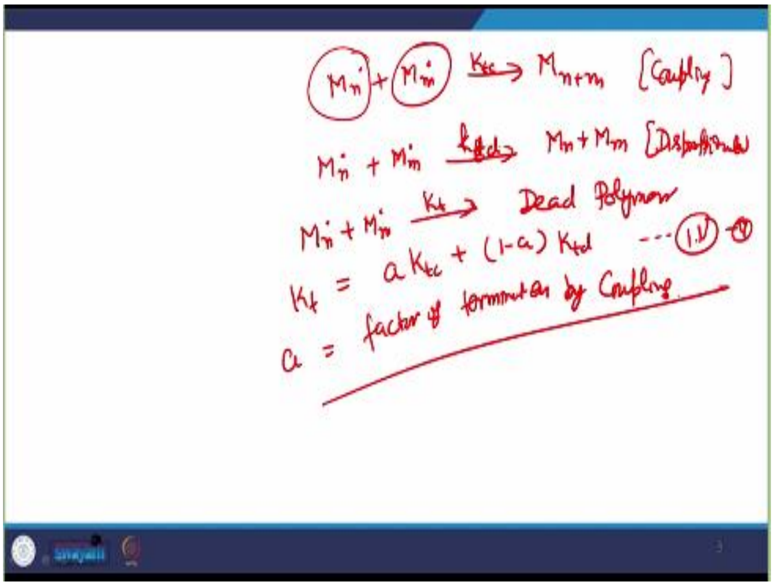

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{K_{tc}} M_{n+m} \quad [\text{Coupling}]$$

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{K_{td}} M_n + M_m \quad [\text{Disproportionation}$$

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{K_t} \text{Dead Polymer}$$

$$K_t = a K_{tc} + (1-a) K_{td} \quad \text{---} \; (1.V) - ④$$

a = factor of termination by Coupling

That is, you see we discussed this thing a bit earlier. Here are two things, two radicals are there. M_n• and radical M_m•. And this K_{tc} is having its usual meaning. Now this is called the coupling one. Now, another form is K_{td}. This is M_n + M_m. That is called the disproportionation. Now, if we combined both the things we may have M_n^+, that is it will give you a dead Polymer. Now, here that K_{tc}, K_t will become K_{tc} + (1-a) K_{td}. This is you can say represented as fourth equation, R.

Now, a is that factor of termination by coupling. So, this is the way through which you can see that we have described these termination possibilities. Now, the propagation step or propagation reaction will proceed indefinitely until all the monomers in the reaction system either depleted or they may get calm combined with some other molecules etc. So, this reaction or this propagation reaction process will proceed till unless it is due to the strong inclination towards the termination.

As I described earlier that this termination step is extremely important and one should not overlook the importance of this particular reaction because of the controlling of the molecular weight. Now, George Odian, he described the typical rate constant constants in termination steps and he found that it is in the range of 10^6 to 10^8 litre per mole per second or magnitude order greater than the constants in the propagation cycle.

Now, in this particular chapter we discussed the initiation, propagation and termination step of radical chain polymerization, special emphasising that how these steps are either classified or subdivided into the different categories.

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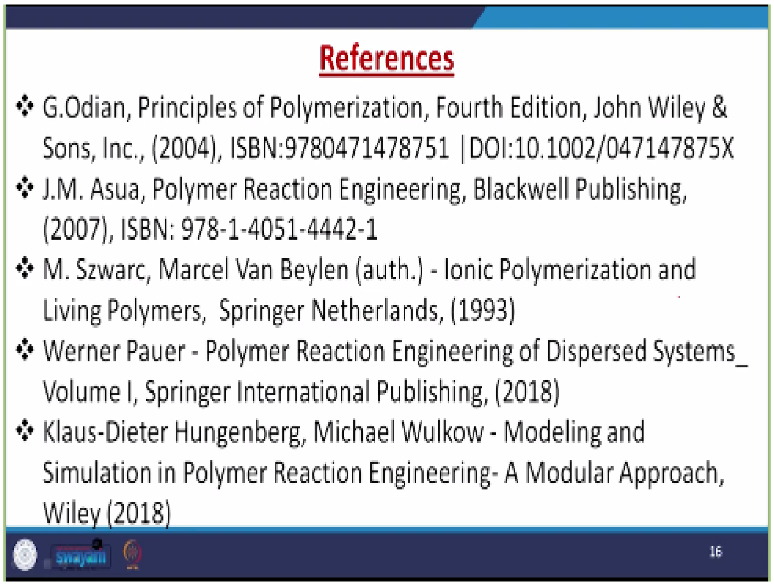

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Now, if you wish to have further reading, we have enlisted several references and you can go through all these references whenever you feel trouble in this particular chapter. Thank you very much.