Polymer Chemistry
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Lecture - 10
Radical Chain Polymerization (Contd.)

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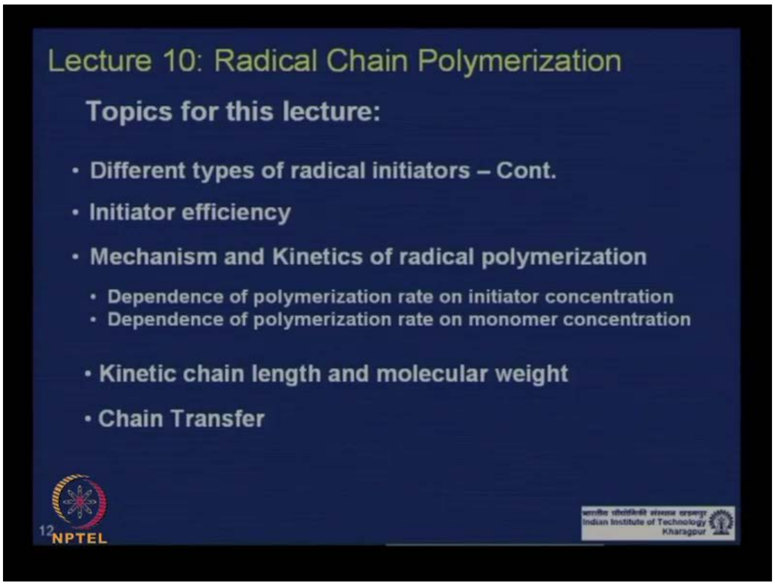

Lecture 10: Radical Chain Polymerization

Topics for this lecture:

- Different types of radical initiators – Cont.
- Initiator efficiency
- Mechanism and Kinetics of radical polymerization
  - Dependence of polymerization rate on initiator concentration
  - Dependence of polymerization rate on monomer concentration
- Kinetic chain length and molecular weight
- Chain Transfer

Welcome back, and we will start this tenth lecture, and we will continue our discussion on radical chain polymerization. And, in this lecture, this tenth lecture, I will try to complete the discussion on the different type of radical initiator, which we began in the last lecture, and briefly talk about the initiator efficiency. And then go into the mechanism and kinetics of radical polymerization, which will include the dependence of polymerization rate on initial, initiator concentration as well as monomer concentration. And we will talk about kinetic chain length and molecular weight of the polymer produced in chain polymerization, in this case radical chain polymerization, and we will try, if time permits, we can or we will start the chain transfer.

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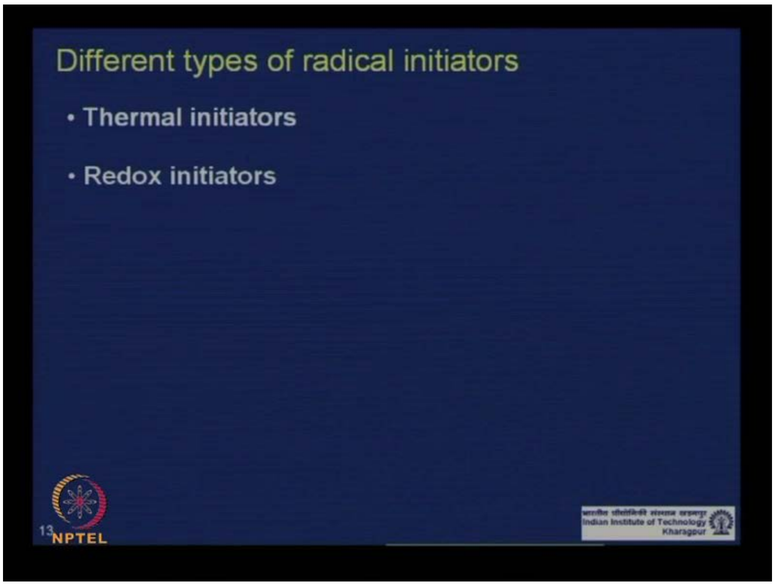

Different types of radical initiators

- Thermal initiators
- Redox initiators

And we talked about; we are actually talking about different types of initiators, which can be used, or which are typically used in radical chain polymerization. And, we talked about different types of initiator, which can be used or which can be utilized; for example, we talked about thermal initiator, where by applying heat we can dissociate homiletically a set of molecules or different types of molecules, for example, AIBN and benzyl peroxide, which we can use for radical chain polymerization as initiator.

We were talking about other methods of chain initiation radical generation, and we started a discussion on redox initiator. And, in the redox is basically reducing agent and the oxidizing agents, and I gave example of peroxides and a reducing agents like (( )) iron. And, we also talked about the peroxides and amine. And then, we start today with more options of redox initiator.

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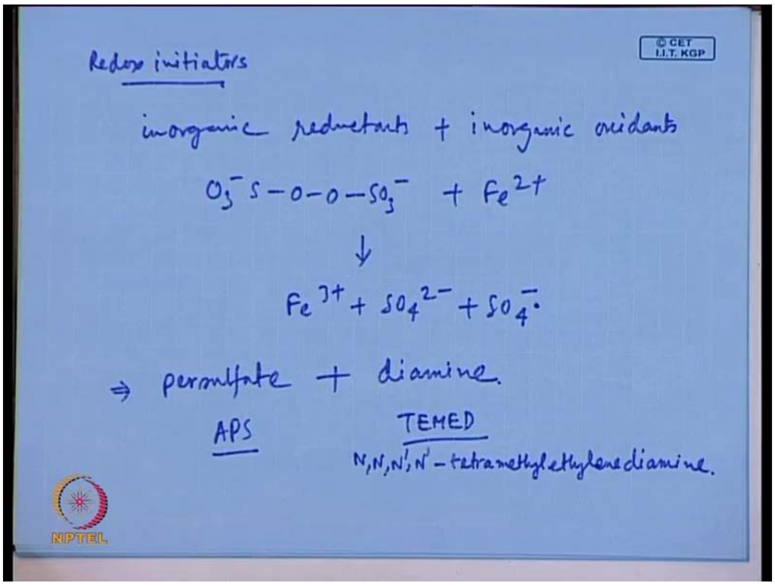

Redox initiators

inorganic reductants + inorganic oxidants

$$O_3^- S-O-O-SO_3^- + Fe^{2+}$$

$$\downarrow$$

$$Fe^{3+} + SO_4^{2-} + SO_4^{-\cdot}$$

⇒ persulfate + diamine

APS TEMED

N,N,N',N'-tetramethylethylenediamine.

So, let us continue this redox initiator discussion. We can take, we talked about this example of benzyl peroxide and diethyl amine in the last class. And, we also showed the values of k d and we found that, no, we seen that k d is much higher for this redox reactions; which means, redox reaction can be conducted redox; they have radical polymerization where radical is generated by a redox reaction can be done at lower temperature including (( )) temperature compared to the thermal initiator.

The third type initiator redox initiation could be inorganic reductants plus inorganic oxidants, which give rise to. The other examples could be per sulfate plus diamine, a very common or very popular use of this combination is typically used for making polyacrylamide gels, which is a combination of ammonium per sulfate APS and TEMED. You know, this reaction is very common and done in bio chemical laboratory for making polyacrylamide gel for polyacrylamide gel electrophoreses; TEMED is N, N, N dash, N dash, especially diamine tetra methyl ethylene diamine. So, the combination of per sulfate plus diamine gives the radical.

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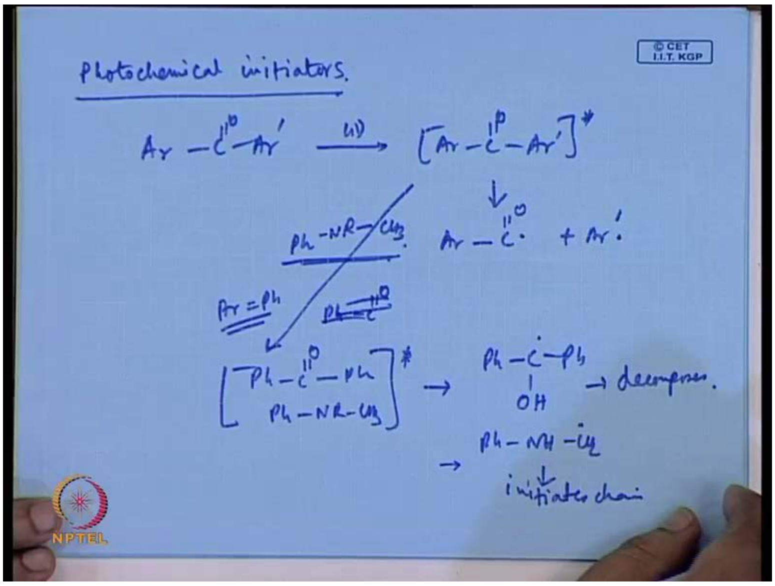

Now, we, we talked about thermal initiator. We now learned about the redox initiator. The other examples or other types, where you can utilize is, a photo chemical initiator, photo chemical initiator or photo initiator, in short. For example, here you can use aromatic Tetons. In this case, on photo, these molecules can absorb photon and go to a higher excited state, which can actually dissociated, dissociate to form a couple of radical.

Now, this can also react with, or photo sensitize another molecule; for example, if I have, from here, if I have another molecules, and if Ar is Ph. So, here, what we are showing here that, here at aromatic teton, which on photo radiation it absorb photons and go to a higher excited state which by itself it can break or dissociate homiletically forming radicals. Or, it can actually photo sensitize the another compound, and go to a, make a complex in excited state, which further can dissociate producing radicals; for example, if you have it react with a molecular this, form this is the composes, and this can initiate a chain polymerization.

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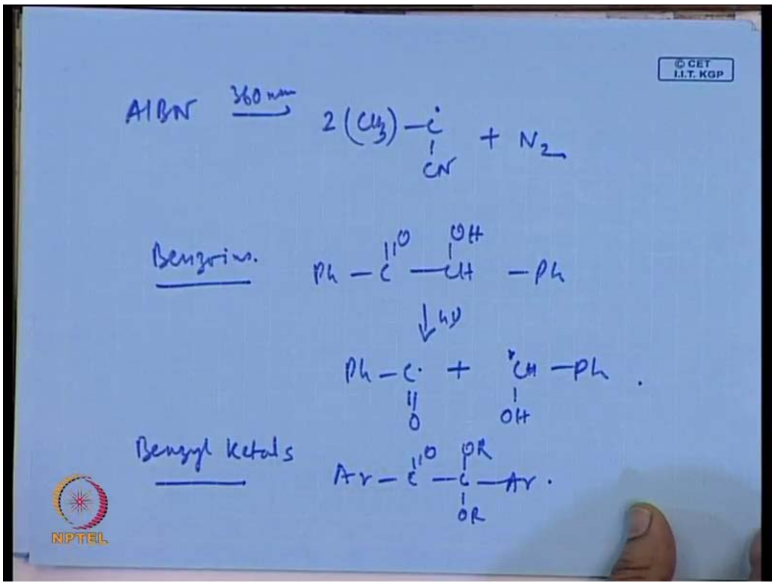

Simply this AIBN type molecule also can absorb photon and break into 2 radicals. Most commercially used radical initiators are like benzoins. For example, I have molecule like this, or you can have benzyl ketals, benzyl ketals where you have structure of that like this. These are the main type of photo initiator or photo chemical initiator used in commercial applications.

Now, the advantage of this photochemical reactions or photo chemical initiator is that you can do your polymerization reactions locally. If you have a, if you, if you have a reaction mixture, and if you can partition or you can cover some part with a opaque, opaque material, then the part which is exposed to the photons or light, that part will get polymerization.

So, it is, it is very, very useful to application, like film, where you can cover a part of the film, and you can keep part of the film uncovered; where if you sign light, that part will get polymerized, leaving the part where, which is covered as unpolymerized medium. So, if this photo polymerization method or the radical polymerization by photo initiators sometimes can be used, has a advantage; this can be used or it is used to apply or used to make polymers in a local or in a, whatever targeted part.

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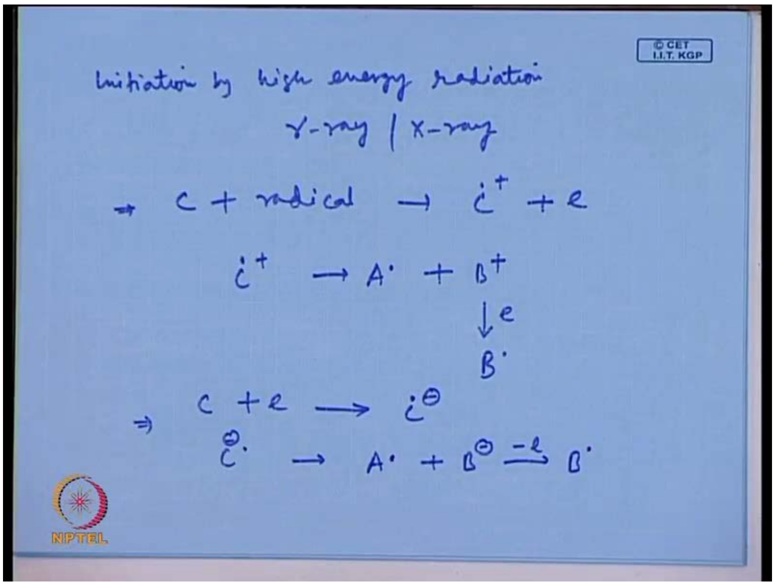

Initiation by high energy radiation

γ-ray | X-ray

$$\rightarrow C + \text{radical} \longrightarrow \dot{C}^{+} + e$$

$$\begin{tikzcd}\dot{C}^{+} \arrow[r] & A^{\cdot} + B^{+} \arrow[d, "e"] \\ & B^{\cdot}\end{tikzcd}$$

$$\Rightarrow C + e \longrightarrow \dot{C}^{\ominus}$$

$$\overset{\ominus}{\dot{C}} \longrightarrow A^{\cdot} + B^{\ominus} \xrightarrow{-e} B^{\cdot}$$

The other type of initiator is like a high by, initiation by high energy, energy radiation, like gamma ray or x ray. Now, these are very high energy. So, it, when it reacts with, say, some organic molecule, it can form radical cat ion and eject a electron; and this radical cat ion can dissociate into radical and a cat ion, which can capture this electron and form another radical.

There may be another possibility, where on this high energy radiation, is can capture a electron and form a radical anion; and these radical anion can dissociate into a radical anion, and which again gives away electron to form a radical. So, using very high energy radiation sources, we can apply or we can generate a radical, which can initiate the radical polymerization reaction.

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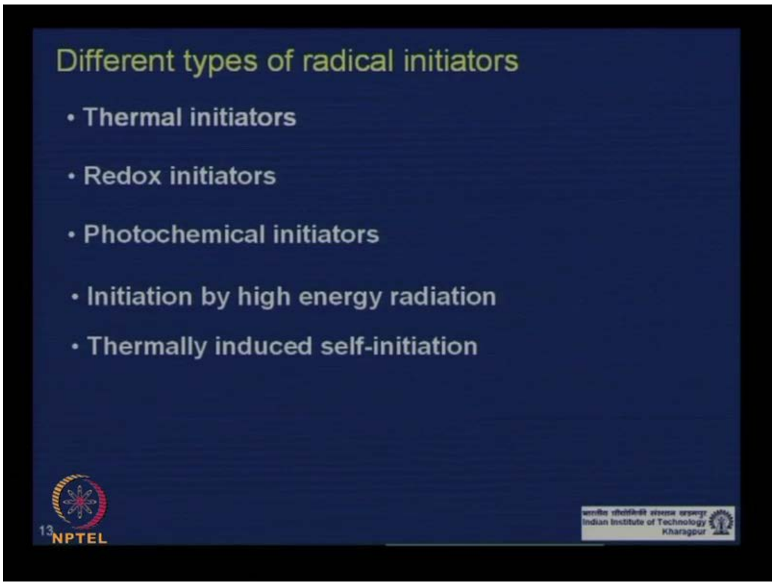

Different types of radical initiators

- Thermal initiators
- Redox initiators
- Photochemical initiators
- Initiation by high energy radiation
- Thermally induced self-initiation

The other type of possible initiation is the thermally induced self initiation; that means, the monomer itself, on thermal or on heating can gives rise to, or they can generate radical, but this not a very common way of generating radical; this is, has been proved only for, in the case of styrene.

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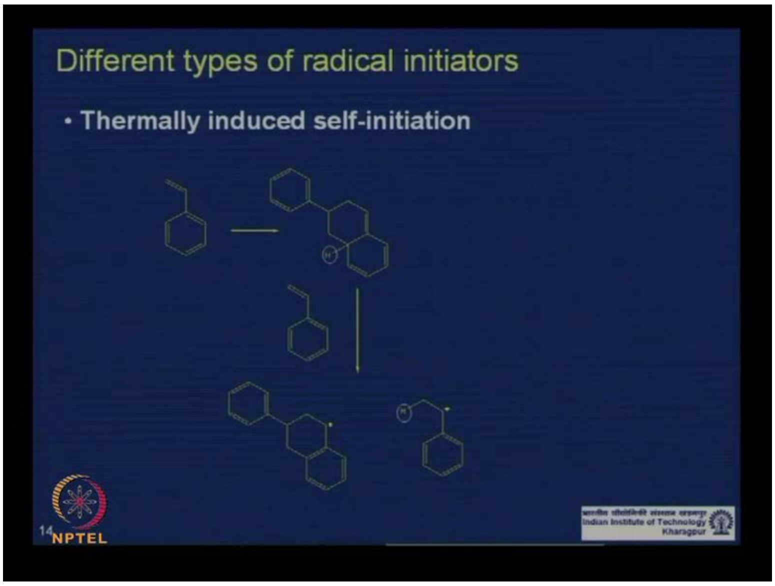

Different types of radical initiators

- Thermally induced self-initiation

And, this is the mechanism which is proposed for thermally induced self initiation of styrene, where styrene molecules, 2 styrene molecules by this capering first get dynamised; and then, this dynamised styrene molecule can react with a third styrene which extract a hydrogen atom forming two radicals, which can individually initiate the chain polymers. This is the proposed mechanism for styrene and it is initiated in troop.

But, this is, this thermal induced self initiation is not a very common and solution for styrene; so, this is very specific case for styrene. The other types of, there are few other special type, or very, a small applications of other types of radical generation, or other type initiator; for example, there are electro chemical initiator, if you have a salt of carboxylic acids, and present in electro chemical cell, then in (()) this carboxylic acids all can get ionized, oxidized to form a radical.

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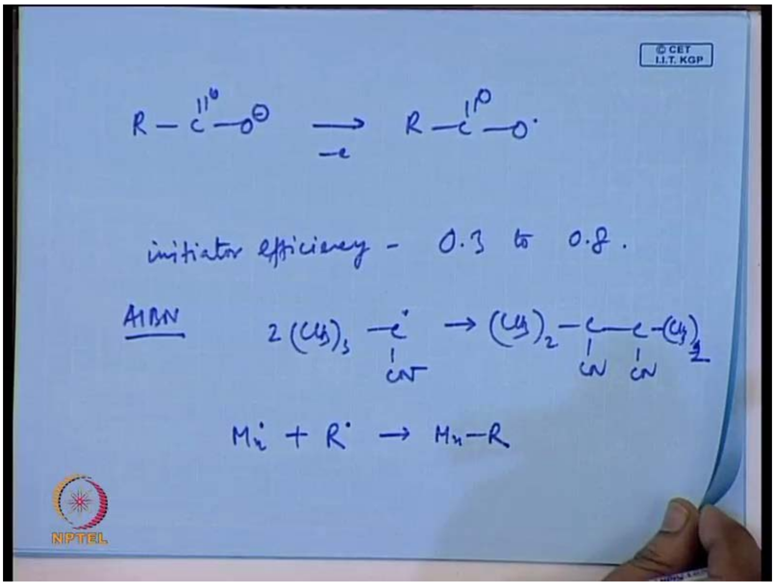

$$R-\overset{O}{\overset{\|}{C}}-O^{\ominus} \xrightarrow[-e]{} R-\overset{O}{\overset{|}{C}}-O^{\cdot}$$

initiator efficiency - 0.3 to 0.8.

AIBN

$$2\,(CH_3)_3-\underset{CN}{\underset{|}{\dot{C}}} \rightarrow (CH_3)_2-\underset{CN}{\underset{|}{C}}-\underset{CN}{\underset{|}{C}}-(CH_3)_2$$

$$M_n^{\cdot} + R^{\cdot} \rightarrow M_n-R$$

So, for example, if I write this; it can give up electron in a anion den can produce radical in a electorate. If you have a, if you want to do electro chemical polymerization or electro chemical radical polymerization, you can, you use this technique to start the polymerization. So, by this time, we now know the different types of, different types of initiation possibilities; that means, different types of molecules which can be used as initiator to generate radical in the reaction medium and not only the molecule, but the ways they can produce radical; for example, by thermal, by photo, or by electro chemical, we just talked about, or the radical can be generated by a very high energy radiations like gamma ray or x ray.

Now, if you talk about, if the, all the radicals which are produced, do they, do they all react, or do they initiate a polymerization? Not always. And, or the fraction of the radicals which are produced by homiletic cleavage or the redox reaction of the initiator molecules; they are not 100 percent of those starts a chain polymerization, or the initiate chain polymerization, in part of which are get lost. And, the fraction of which, of the radicals generated during this initiation processes which start the initiation reaction is termed as initiator efficiency. And, is typically the initiator efficiencies, initiator efficiencies lie around say 0.3 to 0.8, which means that the, among all the radical species which are generated around 30 percent to 80 percent of the radicals, actually generate or initiate a chain polymers.

What about, what happens is, rest of the radicals which do not generate or initiate chain polymers? They get destroyed to form dead molecules. For example, if you take AIBN, you have seen that AIBN on dissociating to this, this species; now, they can again recombine by reacting with themselves and form these molecule. In this case, part of the radicals which were generated by homiletic cleavage of AIBN, they are getting destroyed; in the sense, they are becoming inefficient, inefficient or dead, non radical species by reacting with themselves. So, part of which are lost. In propagating chain, which are expressed as, M n dot, can also react with these, a radical primary radical, and form a dead molecule.

So, by these are, these are the few ways, where the radicals which got generated by the initiator molecules, they get destroyed and form non reactive molecules.

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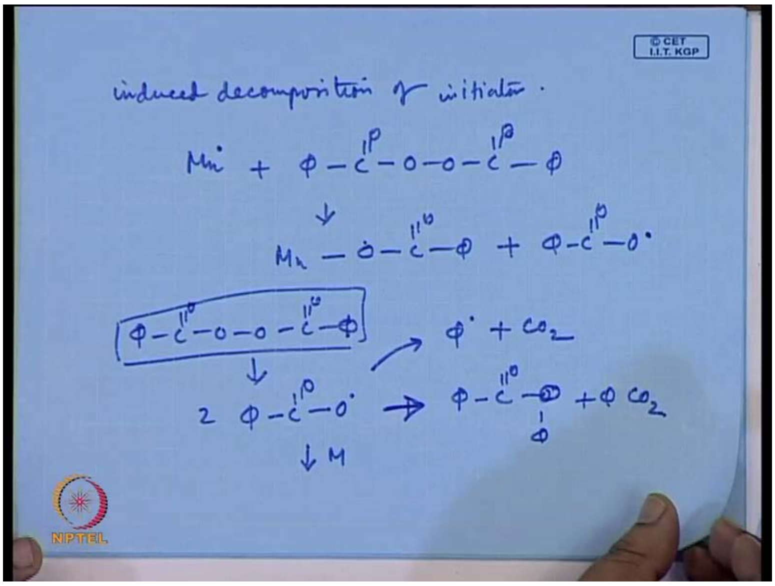

Other examples, like we will take a benzyl peroxide example. And, we will talk about induced decomposition of initiator; or, if I have a propagating radical; now, if give example of benzyl peroxide, it can, the propagating radical can react with initiator molecules and form a another radical.

Now, these molecules, in normal case, where supposed to generate 2 radicals, but in this case on reacting with a chain, propagating chain, it is only producing 1 radicals. So, the efficiency of the radical initiator is decreased. And, not only that, they can undergo, these radicals which are produced initially they can undergo (()) reaction and get destroyed, or get formed into non radical species. For example, again take the example, we can take the example of benzyl peroxide; it get dissociated to case; now, 2 of these can react and form C O 2; this can react with monomer, and there are several side reaction possible with these; and, by this sort of side reaction; these all can undergo phi dot plus C O 2. Now, this can further undergo several side reactions.

So, if there were no side reaction, the amount of radicals it was generating; now, it has reduced because this so many side reaction. Or, in other words, all the radicals which are getting generated by homiletic cleavage of this benzyl peroxide, they are not participating, or they are not initiating a chain; which means, that is the, they are getting lost in doing non polymerization reaction. So, that is the reason that not 100 percent initiator is efficient; and part of it, which, like 30 to 80 percent of radicals generated initially; they actually initiate a polymerization reaction.

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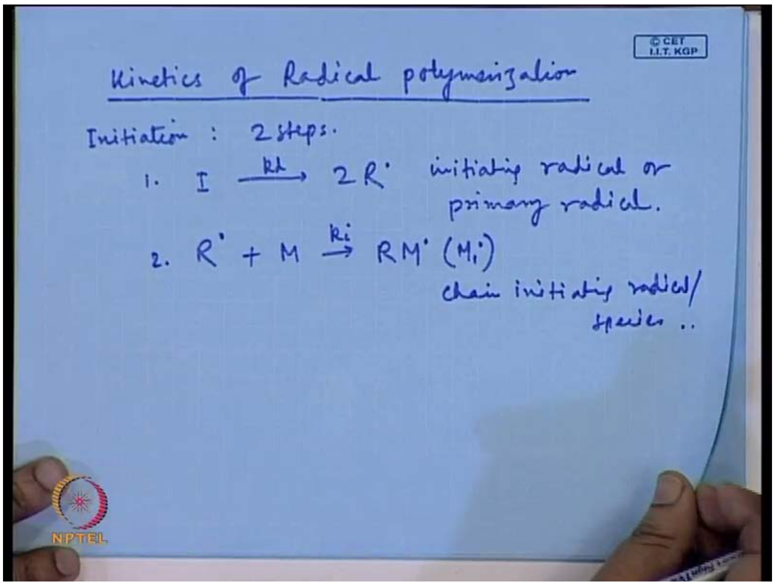

Kinetics of Radical polymerization

Initiation : 2 steps.

1. $I \xrightarrow{k_d} 2R^{\cdot}$ initiating radical or primary radical.

2. $R^{\cdot} + M \xrightarrow{k_i} RM^{\cdot}\ (M_1^{\cdot})$ chain initiating radical/species ..

So, we have talked about different initiator, and different way of, different types of initiator, and the how the efficiency of initiator? Now, let us talk about kinetics of radical polymerization. As we know, the first step is initiation. An initiation consist of 2 steps: 1- initiator molecules produce 2 radical species, which is the initiating radical or is called the primary radical. This primary radical react with a monomer R M dot. We are just, for short, we are writing M 1 dot here. This is chain initiating radical or species. So, these are, the initiation step is actually consist of 2 short steps- 1 and 2.

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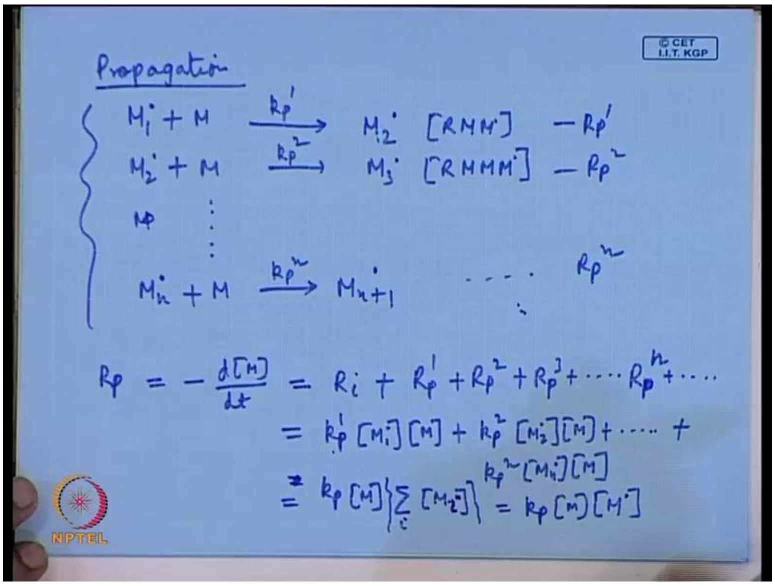

Propagation

$M_1^{\cdot} + M \xrightarrow{k_p^1} M_2^{\cdot}\ [RMM^{\cdot}]$ — R_p^1

$M_2^{\cdot} + M \xrightarrow{k_p^2} M_3^{\cdot}\ [RMMM^{\cdot}]$ — R_p^2

$\vdots$

$M_n^{\cdot} + M \xrightarrow{k_p^n} M_{n+1}^{\cdot}$ . . . . R_p^n

$$R_p = -\frac{d[M]}{dt} = R_i + R_p^1 + R_p^2 + R_p^3 + \cdots R_p^n + \cdots$$

$$= k_p^1[M_1^{\cdot}][M] + k_p^2[M_2^{\cdot}][M] + \cdots + k_p^n[M_n^{\cdot}][M]$$

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

And, then, these chain initiating radical react with another monomer, M 1 dot plus M, M 2 dot; this again react with forming M 3 dot. M 2 dot is R M M dot, this is R M M M dot, and so on. This you can write many steps, and in general, I can write dot. Now, these steps are part of propagation. So, we had initiation in earlier page. Now, we know propagation, and this can undergo termination; third step, we will talk to that in a minute.

Now, rate of polymerization, R p, is given by rate of consumption of monomers. Now, it is assuming that the monomers which are getting consumed, they are reacting and forming polymerization, they are becoming part of polymerization. Now, what are the step, what are the stages or what are the reactions the monomer is getting consumed? We talked about, in the initiation reaction; here, the monomer is getting consumed. So, I write, initiator rate there, and plus, all these steps.

So, if I write these steps R p 1, R p 2, R p n, and so on. So, R p 1 plus, R p 2 plus, R p 3 plus, R p n plus, so on. Now, because this is very small, very small amount of monomer get consumed in the initiation reaction, we can ignore this; and we can write R p as a sum of all these propagating steps. Now, if I write rate constant for these individual step as k p 1, k p 2, k p n, then what is the individual step? R p 1 is given by k p 1, M 1 dot, M plus, R 2 is given by k p 2, M 2 dot, M plus, so on; and, this R p n is given by k p n, M n dot, M.

Now, it is very difficult. If you want to find out these, you have to know all these rate constant- k p 1, k p 2, k p n, k p 3, k p 4, and all this things; that is practically impossible. So, what is assumed? That, all these rate constant for all these propagating reactions, they are same. It is similar to the assumption we made for step growth polymerization, the assumption of equal reactivity of the functional group. So, remember, we talked about in step polymerization that the reactivity of the functional group present at the end of the oligomeric chain or a polymeric chain, does not depends on what is present in the other side, whether the other group is reacted, or what is the length the oligomer.

Similarly, in this case, the reactivity of this radical does not depend; we are assuming that it does not depend on the size of the molecules. So, there is a M 1, M 2, or, because the system is large, and we know that it has been experimentary proof also that, the rates, rate constants become very, or becomes same as long as, as soon as they become this chain contain 2 to 3 monomers; as long as these chains are 2 to 3 monomers, the rates, all the rates become, all the rate constants become equal.

So, that is the assumption we are making that, all these rate constants are equal; and, so, we can write all the rate constant as k p, and M is there, and everywhere. So, I can name M; and also, we are drawing, write the summation of M i dot. So, these all are same; k p 1, k p 2, k p n, these are all same. So, I can take it out. And, then, M is present in everywhere. So, M is also taken out. And, a summation of all the other terms, M 1 dot, M 2 dot, M 3 dot, M n dot. So, this is i, i dot. So, these term, I can simply write k p M and M dot; I am just writing the M dot. So, M dot is; this is the summation of the concentration of all the radicals present; all the propagating radicals present in the reaction medium.

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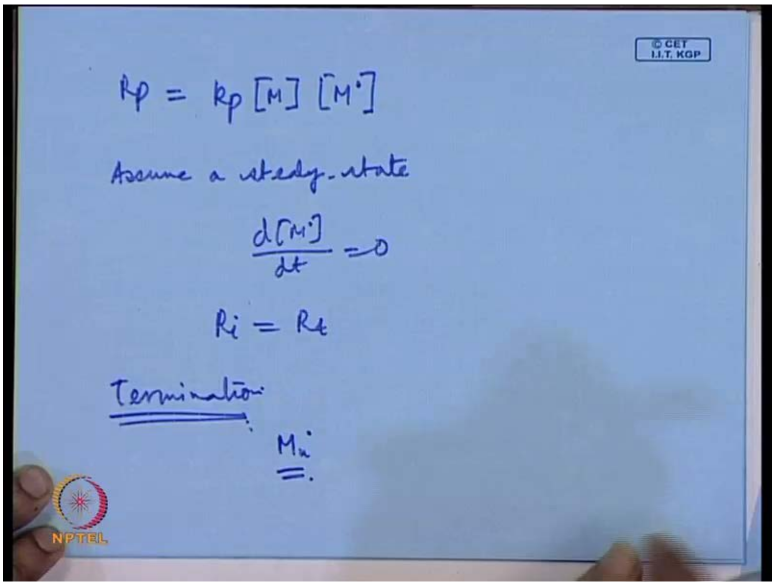

$R_p = k_p [M] [M^\cdot]$

Assume a steady-state

$$\frac{d[M^\cdot]}{dt} = 0$$

$R_i = R_t$

Termination

$M_n^\cdot$

So, these; so, R p now given up, given by k p rate constant for all those individual steps, monomer concentration, and this is the summation of the concentration of all the propagating radicals of the, all the chain radicals; this is the sum of all those things.

Now, experimentally, or; this is the unknown quantity. We cannot, this is very difficult to measure this, this quantity experimentally. So, how do you get this rate of polymerization? We assume a steady state, where; now, immediately after the reaction starts, the change in radical, total radical concentration becomes 0 with time; which means that, the radicals are consumed at the same rate, as they are getting produced. Now, radical get produced in the initiation reaction and they get destroyed in the termination reaction, which we just going to talk in a minute.

So, as soon as the reaction start, within a very short period of time, the rate of initiation becomes same as rate of termination; as a result, the concentration of these total radical species, rate radical propagating radical become constant at during the entire polymerization reaction; and that is not very unusual, because we, when we do the kinetics of the first reactions with having intermediates, then we always assume steady state, and we do the kinetics in that way. So, in a steady state, the rate of initiation is equals to rate of termination.

Now, what is the rate of termination? We talk about termination step now. How this radical, M n dot, they can get terminated?

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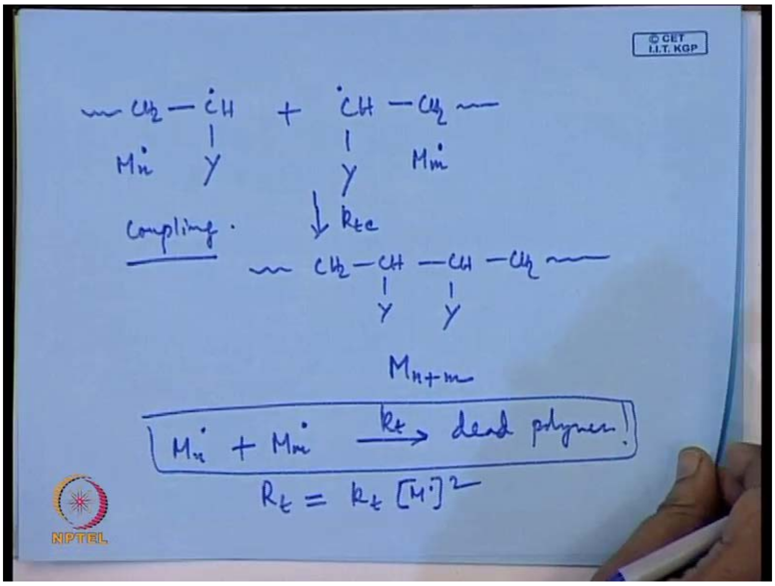

$$\boxed{M_n^{\cdot} + M_m^{\cdot} \xrightarrow{k_t} \text{dead polymer!}}$$

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

If I talk about the, that same structure, take out that same simple monomer; now, how this can get terminated? They can get terminated reacting with the same molecule, and by coupling reaction they can. So, that is k termination by coupling; this is a coupling process. So, if I write this as M n dot, this is a M m dot, then this will be M n plus m. Now, they can get terminated by other type of reaction, disproportionate reaction as well.

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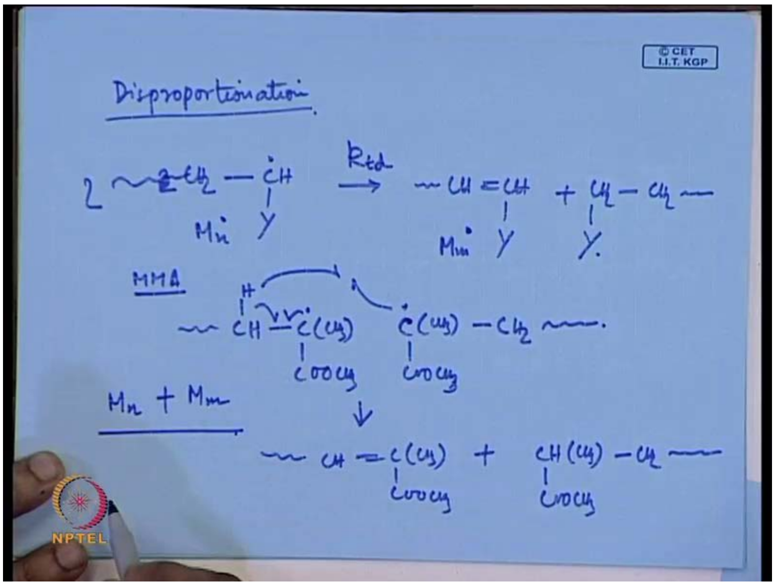

Disproportionation

$$2 \sim \underset{M_n^\cdot}{CH_2}-\underset{Y}{\underset{|}{\dot{C}H}} \xrightarrow{k_{td}} \sim \underset{M_m^\cdot}{CH}=\underset{Y}{\underset{|}{CH}} + \underset{Y}{\underset{|}{CH_2}}-CH_2\sim$$

MMA

$$\sim \overset{H}{\overset{|}{CH}}-\underset{COOCH_3}{\underset{|}{\dot{C}(CH_3)}} \quad \underset{COOCH_3}{\underset{|}{\dot{C}(CH_3)}}-CH_2\sim$$

$$\downarrow$$

$$\sim CH=\underset{COOCH_3}{\underset{|}{C(CH_3)}} + \underset{COOCH_3}{\underset{|}{CH(CH_3)}}-CH_2\sim$$

$M_n + M_m$

Disproportionation, 2 of these. For example, if I talk about methyl methacrylate, like this is the form to difference this. So, if I write M n dot here, and this is M m dot, and this reaction is k termination by disproportionation, then it gives again M n plus M m.

So, here, the molecular weight, on termination the molecular weight does not change, ignoring the difference of 2 hydrogen here, between this two. So, in this case, the molecular weight remain unchanged; it becomes the dead polymers, as same as the size of the reacting polymer.

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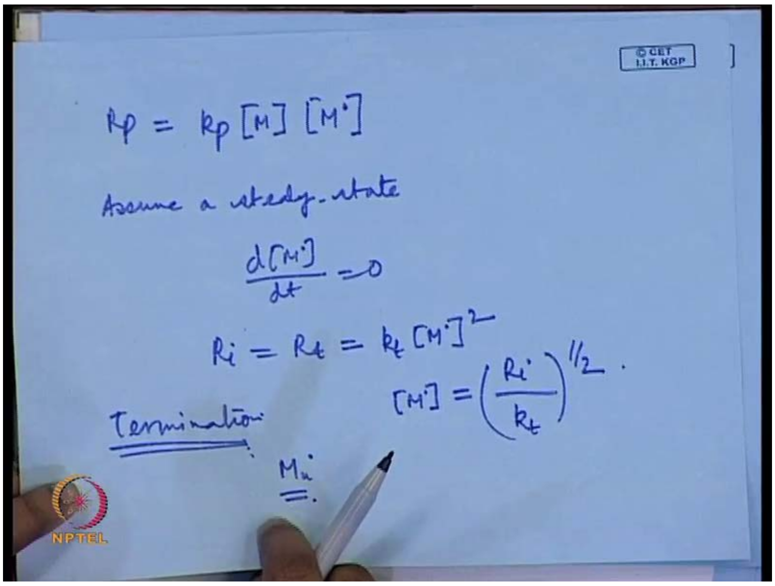

$R_p = k_p[M][M^\cdot]$

Assume a steady-state

$$\frac{d[M^\cdot]}{dt} = 0$$

$$R_i = R_t = k_t[M^\cdot]^2$$

$$[M^\cdot] = \left(\frac{R_i}{k_t}\right)^{1/2}$$

Termination

$M_n^\cdot$

Where, in the earlier case, it is, the length of the final terminated chain is the summation of the size of the 2 reacting species. Now, in general, we can write M n dot plus M m dot gives write k t is the dead polymer.

So, if I write this, then it, in general, it takes care of both the coupling reaction and the initiation. In both cases, these 2 radical, propagating radical reacting and forming dead polymer. So, what is the rate of this termination step? Is given by k t M dot square, because it is a bi molecular reaction. So, now, this is again, the M dot is the summation of concentration of the, all the propagating radical.

So, now, I write this rate of termination is now got there it is a bi molecular reaction. So, k t multiplied by M dot square. So, from that we can find the M dot as R i by k t, to the power half.

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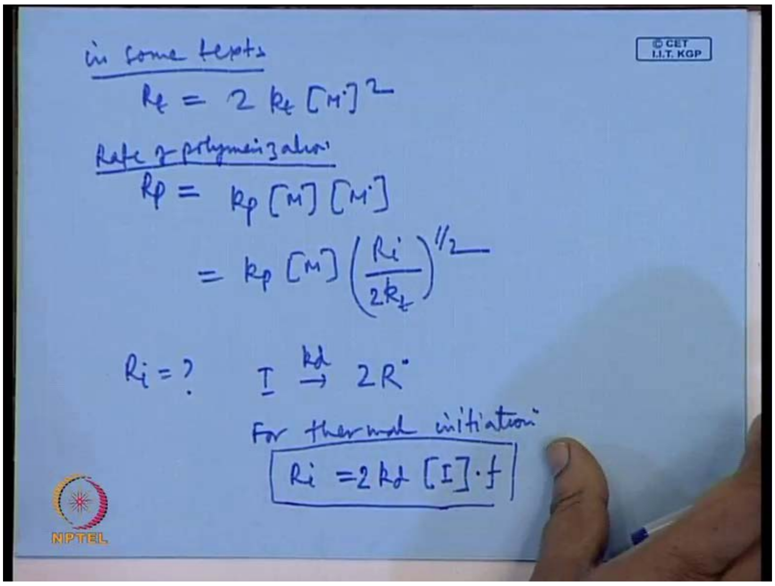

in some texts

$$R_t = 2 k_t [M^\cdot]^2$$

Rate of polymerization

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

$$= k_p [M] \left(\frac{R_i}{2k_t}\right)^{1/2}$$

$R_i = ?$ $\quad I \xrightarrow{k_d} 2R^\cdot$

For thermal initiation

$$\boxed{R_i = 2 k_d [I] \cdot f}$$

Now, in some cases, in some text, they follow that R t is, rate of termination is twice k t M dot square. Now, this term twice is introduced; in some text, this twice is introduced, because that the 1 termination reaction is effective in bringing the termination of 2 radical. So, this 2 terms we introduced. Now, if is, it is up to you, whether you want to write 2, or if you do not want to write 2; but, if you write 2 here, then similarly when in initiation reaction a homiletic cleavage gives up 2 radicals, you have to write 2 as well. So, that gives, 2 cancels out.

And, if you choose not to write 2, then during the initiation reaction also you have to choose not to write 2 in the; it will come back that initiation reaction, rate of initiation, again when you write the expression for R i, rate of initiation. So, R p, rate of polymerization, polymerization, we have deduced earlier, M n dot, which will now become M R I by k t; now, let us write 2 here; let us follow this convention. So, I write 2, and this is what the rate of polymerization is. So, we have to know R i.

Now, R i is, this is for thermal initiation. So, how do I write the R i? We write, this is k d I. Now, again, because this is produced and we are following that, we should write 2 here, during the termination rate. So, here also we write 2. And, also, with our knowledge, that all the radicals which are generated by the homiletic cleavage of the initiator molecule, they do not react or they do not initiate the chain polymerization; the fraction of the radicals which generated here, some of them actually initiate the radical polymerization; and so, we multiplied term f, which is here the efficiency.

So, this would give the total expression for the rate of initiation; rate constant of the dissociation, initiate the concentration, this is the efficiency of initiator, and 2 we are writing because we are following the same conventions 2 here, and the logic is that because 1 initiator molecule is giving up 2 radicals which are initiating 2 chains, we are writing 2 here.

Now, if we go back and look at this or compare this initiation reaction which we wrote earlier, and you can argue that we are not, we are not talking about, or we are taking, not taking this reaction in the consideration, when we are determining R i. Now, they are fact that this is the very first reaction. These, as well as the all the propagating reactions, they are very fast compared to the initial dissociation reaction of the initiator molecule into 2 react, 2 radicals. So, the initiation reaction actually depend on the first step, not atall on the second step.

So, when we are considering rate of initiation, we are only taking or only considering, considering this k d, not the k i. So, that, this is clear that, inspite of they having 2 step in the initiation process, we are taking the slower step which is basically the rate determining step for the initiation process.

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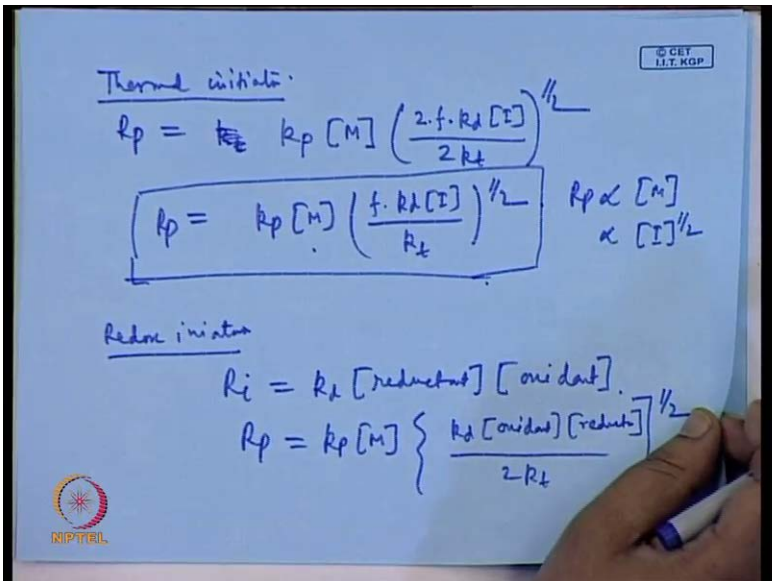

Thermal initiator:

$$R_p = \cancel{k_t}\ k_p [M] \left(\frac{2 \cdot f \cdot k_d [I]}{2 k_t}\right)^{1/2}$$

$$\boxed{R_p = k_p [M] \left(\frac{f \cdot k_d [I]}{k_t}\right)^{1/2}}$$

$R_p \propto [M]$

$\propto [I]^{1/2}$

Redox iniator

$$R_i = k_d [\text{reductant}][\text{oxidant}].$$

$$R_p = k_p [M] \left\{ \frac{k_d [\text{oxidant}][\text{reductant}]}{2 k_t} \right]^{1/2}$$

So, finally, let us talk about the final expression for rate of polymerization. This rate of polymerization R p. Now, this is for thermal initiator; it is given by, R p is given by k t, k p, M, R i; R i is twice f k d I, twice k t to the power half. This 2 cancels out. So, k p, M, f k d, I, k t, to the power half. Now, this is for thermal initiator. What is, it would look like, for a redox initiator? A redox initiator is, rate of initiator is, k d, concentration of reductant oxidant. So, R p would be k p, M, k d, oxidant by reductant concentration by, twice k t to the power half.

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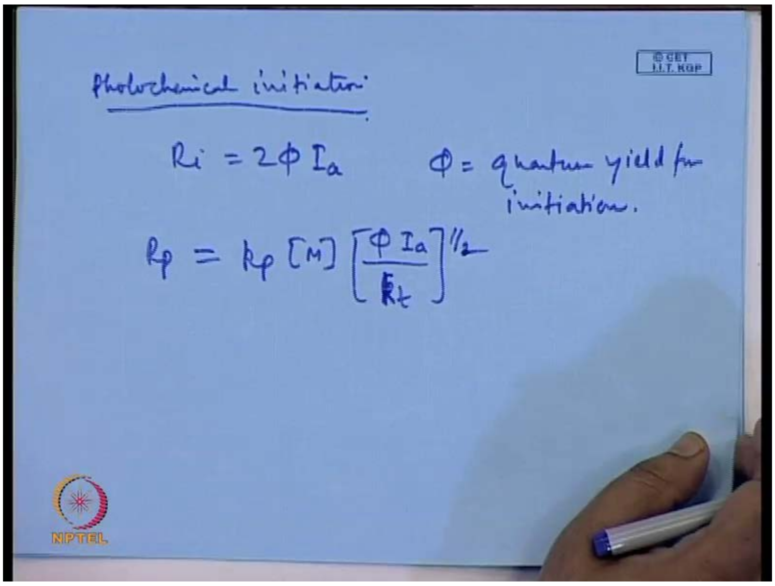

Photochemical initiation:

$R_i = 2 \phi I_a$

ϕ = quantum yield for initiation.

$$R_p = k_p [M] \left[\frac{\phi I_a}{k_t}\right]^{1/2}$$

For a photo chemical initiation or photo initiation, R i is twice fie I a; I a is the intensity of the radiation, and fie is the quantum yield for initiation is similar to efficiency f for thermal initiation, this fie is the quantum yield for initiation. So, for this type of initiation, we can write R p is M, fie I a by k t, to the power half.

So, we talked about a different, the most common rate expression for rate of polymerization; whether it is, it has initiated by thermal initiator or redox initiator or by photo chemical initiation, these are the most common root of initiating a radical polymerization. So, we know the rate expressions for the rate of polymerization.

Now, let us go back and look at this thermal initiator, which is the most common; R p is given by this, which means rate of polymerization is directly proportional to the concentration of monomer; and, it is actually directly proportional to the square root of the concentration of initiator. So, R p is proportional to the concentration of the monomer, and it is proportional initiator concentration.

So, if you increase the concentration during a radical polymerization, then you know the rate will increase, but of course at the proportional to the square root of the initiator concentration; and, if you increase the monomer concentration, then rate will be a increasing, rate of polymerization would be increasing in, as a direct, directly proportion.

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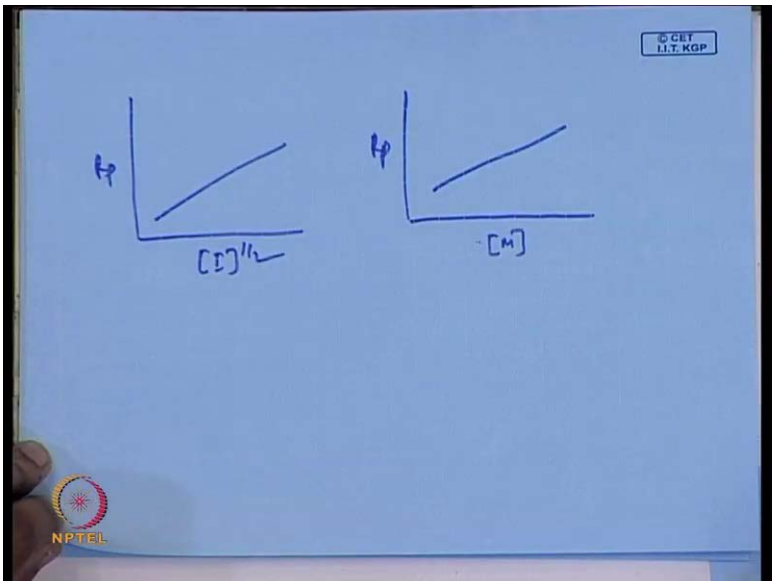

So, if you plot; and, this has been shown experimentally; if I have this plot R p, rate of polymerization with I to the power half square root of I, it gives a straight line, so as this.

Now, sometimes, experimentally it is found, then it is not a directly proportional to the power for initiator; it could be more than 1. So, like 3 by 2, some cases, experimentally it might, you might find out or some cases it might be even lower. Now, that indicates that, now that indicates that; see if we, if the rate of polymerization dependent not directly, not to the power 1, but more than 1 select 3 by 1.5; which means, that this monomer also taking part in generating radicals. So, that might have in few cases, where the monomer can take part in homiletic cleavage and generate radical, or it can react with some other molecule, initiator molecules and produce the radical.

So, it the monomer itself take part in the initiation reaction, then there is another terms comes. So, you get a half here, a additional half. So, this becomes 1.5. Similarly, if you see that this is not following, this actually following even less than that; which means, that some of the initiator react initiator which are produced, they are actually; even you know they form the radicals which are produced by, and form the initiator molecules, they are not taking part. So, the efficiency actually comes down, came down during the reaction.

So, which also means that as the reaction progress, both the concentration of monomer and the initiator comes down; which means, as the reaction progress with time, the rate of polymerization also comes down. But there is, there is the special case at the end of the reaction, if the monomer concentrating I, which we will talk about in the later lecture.

So, again to form, again write the; now if you go back to this expression, besides this term, this is called as concentration term monomers; and, the concentration of monomer and concentration of initiator, these are also determine your rate of polymerization. So, and which will depend upon the temperature. If we increase the temperature, then depending how it is effecting the values of k d I, k t and R p, the rate will vary. Now, we will come in the later lecture, what is the effect of temperature on a rate of polymerization?

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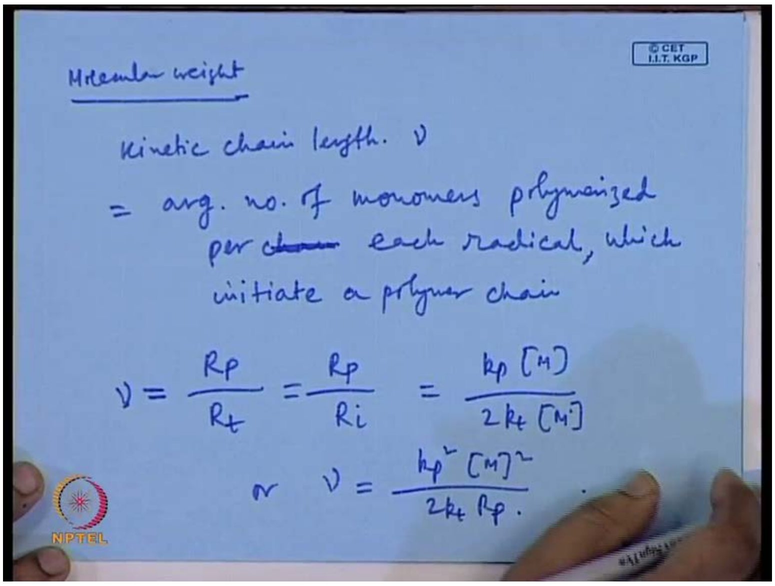

Molecular weight

Kinetic chain length. ν

= avg. no. of monomers polymerized per each radical, which initiate a polymer chain

$$\nu = \frac{R_p}{R_t} = \frac{R_p}{R_i} = \frac{k_p[M]}{2k_t[M^{\cdot}]}$$

$$\text{or} \quad \nu = \frac{k_p^2[M]^2}{2k_t R_p}.$$

Now, let us talk about a molecular weight in radical chain polymerization. Now, before we molecule, we come to the discussion of molecular weight, we will define a term kinetic chain length, nu, which is average number of monomers polymerized per each radical, which initiate a polymer chain. So, it is a average number of monomers which polymerize per radical; per radical, which actually polymerize, which actually initiate the polymerization; not the, as we said that some of the radicals get, you know, consumed by side reactions, or some other reactions, we do not initiate polymer chain. And, this is the average number of monomers polymerized per radicals which initiate a polymer chain.

So, it is, how can you write in simple term? It is rate of polymerization, divided by rate of termination, or as steady state assumption, it is same as the radius of a rate of initiation. So, we can write nu as k p M; from your the last expressions, which we decided in the last few pages, we can write these as same.

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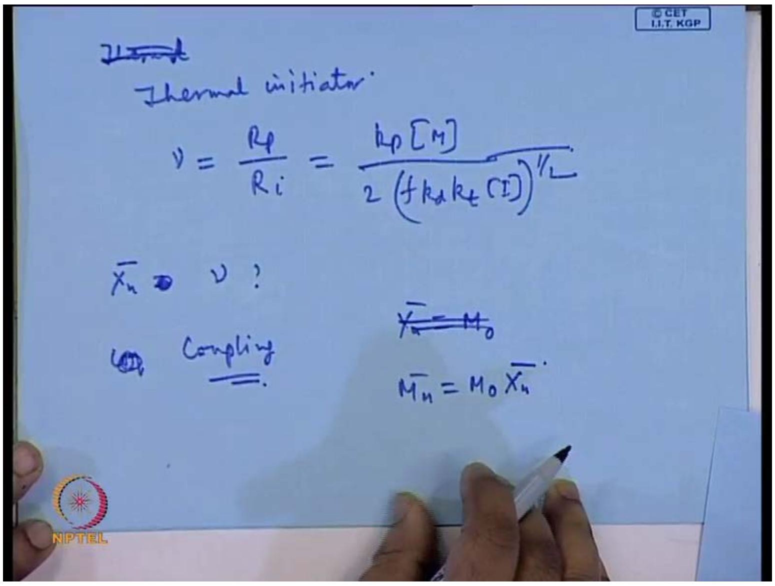

Thermal initiator.

$$\nu = \frac{R_p}{R_i} = \frac{k_p[M]}{2(f k_d k_t [I])^{1/2}}$$

$\bar{X}_n$ ν ?

Coupling

$\bar{M}_n = M_0 \bar{X}_n$

And, if we consider only the case of thermal initiator, then nu is equal to R p by R I, k p M. So, nu is the average number of monomers which is getting polymerized per radicals. You should consider the radicals which are only, the only those radicals which are initiating a polymer chain. So, what would be the average molecular? What will be the relation between the degrees or average degrees of polymerization with nu? And, how these are related? Average degrees of polymerization and this nu, if the polymerization is done by coupling, coupling, then M n would be, X n bar would be, the average degrees of polymerization would be twice nu; nu is the average number of monomers consumed in this chain. So, the degrees of polymerization will be summation of this, plus this.

And, we are talking about average. So, it is 2 nu. If it is gets terminated by the disproportionation reactions, we seen earlier; then average degrees of polymerization is nu, because the number of monomers, average numbers of monomers per radical is the size of this chain. And, we know that X n is M w, M n bar is M 0 X n bar. So, which means, if the kinetic chain length; there are kinetic chain length which basically, a number of radicals, number of monomers which consumed per radicals. So, you have a radical propagating chain and another propagating chain. If they are in, terminated by a coupling reaction, then you have twice nu is the molecular weight, average molecular, average degrees of polymerization; whereas, if they are terminated by disproportion reactions, then the average degrees of polymerization would be equals to the kinetic chain length nu.

And, how do you determine, what are the number of molecules? If they are terminated by coupling reaction, then every dead chain would have two species from the initiator molecule, the fragments, residual fragment form initiator molecule. And if they are terminated by disproportionation, then they will have 1 residue from the initiator molecules. Now, what we will do in the next lecture? We will continue from these, and talk about termination reactions or transfer reactions.