Introduction to Polymer Science
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Lecture-12
Thermal Initiation (Contd.), Molecular Weight and Kinetic Chain Length, Other Types of Radical Initiators, Transfer Reactions

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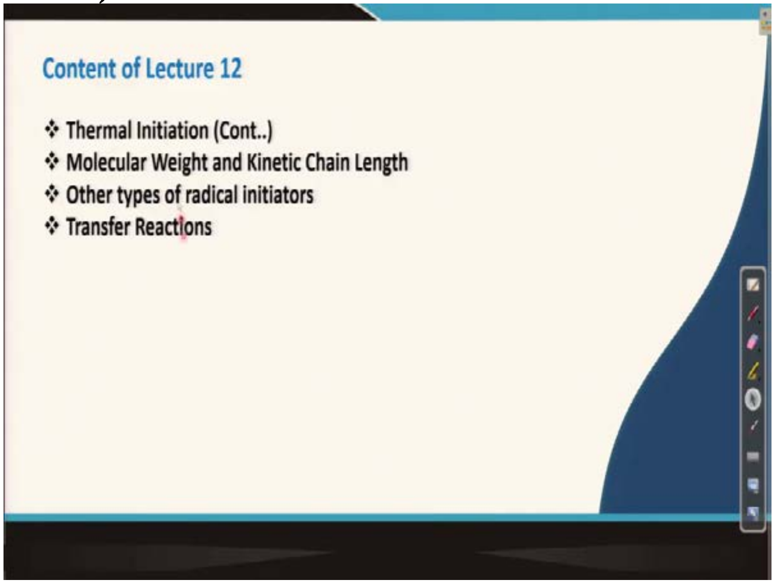

Content of Lecture 12

- ❖ Thermal Initiation (Cont..)
- ❖ Molecular Weight and Kinetic Chain Length
- ❖ Other types of radical initiators
- ❖ Transfer Reactions

Welcome back to this lecture 12. Let us continue our discussion on thermal initiation, which started in the last lecture. We will also talk about molecular weight and kinetic chain length and also discuss a few other types of radical initiators and will start the discussion on transfer reactions in radical chain polymerization.

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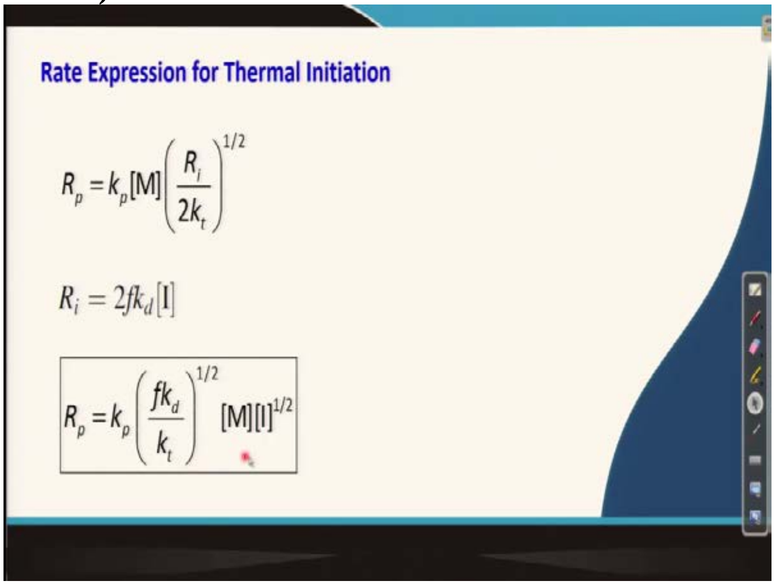

Rate Expression for Thermal Initiation

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

$$R_i = 2fk_d[I]$$

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

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

$$R_i = 2fk_d[I]$$

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

In this expression for the rate of polymerization which we derived before, in case of thermally initiated polymerization, R_i can be replaced to give the above expression, which we discussed in the last lecture as well.

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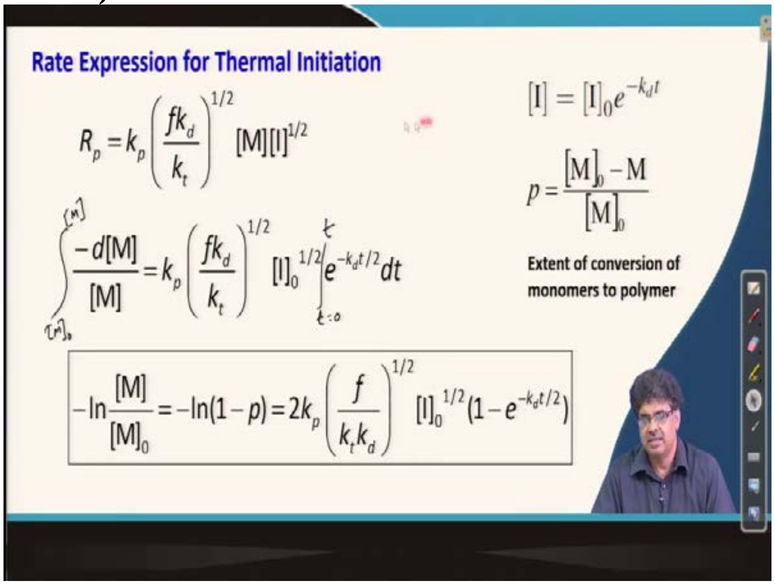

Rate Expression for Thermal Initiation

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[\mathrm{M}][\mathrm{I}]^{1/2}$$

$$\int_{[M]_0}^{[M]}\frac{-d[\mathrm{M}]}{[\mathrm{M}]} = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[\mathrm{I}]_0^{1/2}\int_{t=0}^{t} e^{-k_d t/2}dt$$

$$\boxed{-\ln\frac{[\mathrm{M}]}{[\mathrm{M}]_0} = -\ln(1-p) = 2k_p\left(\frac{f}{k_t k_d}\right)^{1/2}[\mathrm{I}]_0^{1/2}\left(1-e^{-k_d t/2}\right)}$$

$$[\mathrm{I}] = [\mathrm{I}]_0 e^{-k_d t}$$

$$p = \frac{[\mathrm{M}]_0 - \mathrm{M}}{[\mathrm{M}]_0}$$

Extent of conversion of monomers to polymer

$$[\mathrm{I}] = [\mathrm{I}]_0 e^{-k_d t}$$

$$p = \frac{[\mathrm{M}]_0 - [\mathrm{M}]}{[\mathrm{M}]_0}$$

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[\mathrm{M}][\mathrm{I}]^{1/2}$$

$$\int_{[\mathrm{M}]_0}^{[\mathrm{M}]}\frac{-d[\mathrm{M}]}{[\mathrm{M}]} = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[\mathrm{I}]_0^{1/2}\int_{t=0}^{t} e^{-k_d t}dt$$

$$-\ln\frac{[\mathrm{M}]}{[\mathrm{M}]_0} = -\ln(1-p) = 2k_p\left(\frac{f}{k_t k_d}\right)^{1/2}[\mathrm{I}]_0^{1/2}\left(1-e^{-k_d t/2}\right)$$

Now, we can replace the rate of polymerization in differentiation form with the rate of disappearance of monomers from the reaction mixture and we can integrate this expression from monomer at 0 time to some time at t, where $[\mathrm{M}]_0$ is the initial monomer concentration, M is monomer concentration at time t and p is called the extent of conversion of monomer to the polymers. Similar to our discussion on the extent of polymerization being the percentage or fraction of functional groups converted in step-growth polymerization, we can also express [I] in this way as this is a first-order decomposition reaction.

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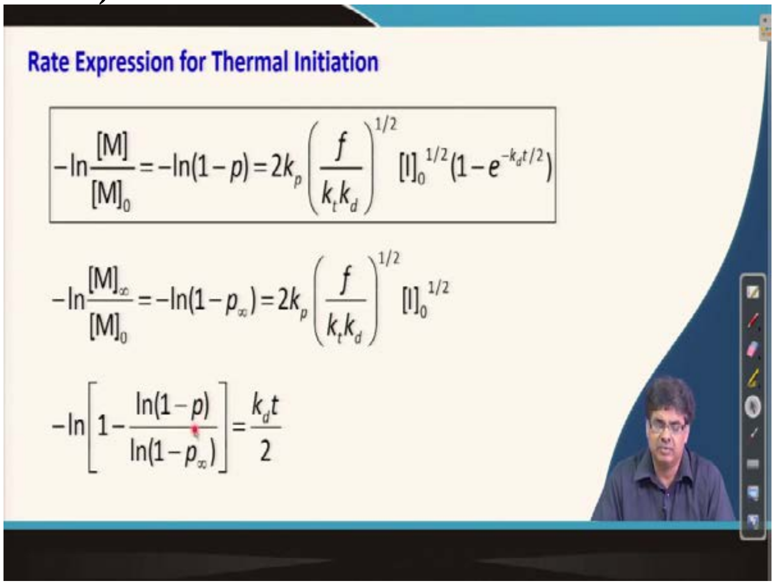

Rate Expression for Thermal Initiation

$$\boxed{-\ln\frac{[\mathrm{M}]}{[\mathrm{M}]_0} = -\ln(1-p) = 2k_p\left(\frac{f}{k_t k_d}\right)^{1/2}[\mathrm{I}]_0^{1/2}(1-e^{-k_d t/2})}$$

$$-\ln\frac{[\mathrm{M}]_\infty}{[\mathrm{M}]_0} = -\ln(1-p_\infty) = 2k_p\left(\frac{f}{k_t k_d}\right)^{1/2}[\mathrm{I}]_0^{1/2}$$

$$-\ln\left[1-\frac{\ln(1-p)}{\ln(1-p_\infty)}\right] = \frac{k_d t}{2}$$

$$-\ln\frac{[\mathrm{M}]_\infty}{[\mathrm{M}]_0} = -\ln(1-p_\infty) = 2k_p\left(\frac{f}{k_t k_d}\right)^{1/2}[\mathrm{I}]_0^{1/2}$$

$$-\ln\left[1-\frac{\ln(1-p)}{\ln(1-p_\infty)}\right] = \frac{k_d t}{2}$$

Now, from this expression, we can calculate k_d by finding out or determining the amount of monomer present in the medium after sometime and if we do it 2-3 different times, from those results we can find out what is the value of k_d. For example, if we leave the reaction for a long enough time, almost like infinite time when there is no further reaction, then we will replace p with p_∞. So, $[\mathrm{M}]_\infty$ is the concentration of monomers present when the reaction is completed or when enough time has been given for reaction to happen and p_∞ is the conversion at long enough time. So, if we know the value of p and p_∞ then we can get the value of k_d.

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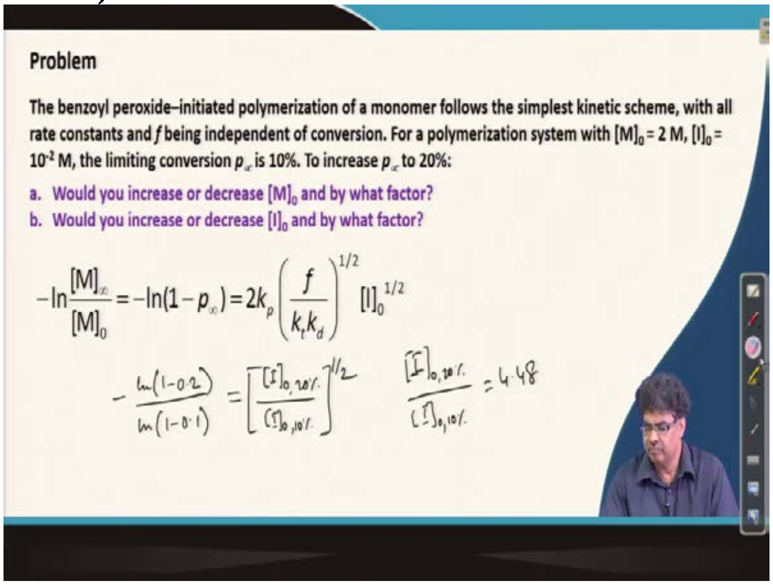

Problem

The benzoyl peroxide–initiated polymerization of a monomer follows the simplest kinetic scheme, with all rate constants and *f* being independent of conversion. For a polymerization system with $[M]_0 = 2$ M, $[I]_0 = 10^{-2}$ M, the limiting conversion p_∞ is 10%. To increase p_∞ to 20%:

a. Would you increase or decrease $[M]_0$ and by what factor?
b. Would you increase or decrease $[I]_0$ and by what factor?

$$-\ln\frac{[M]_\infty}{[M]_0} = -\ln(1-p_\infty) = 2k_p\left(\frac{f}{k_t k_d}\right)^{1/2}[I]_0^{1/2}$$

$$-\frac{\ln(1-0.2)}{\ln(1-0.1)} = \left[\frac{[I]_{0,20\%}}{[I]_{0,10\%}}\right]^{1/2} \qquad \frac{[I]_{0,20\%}}{[I]_{0,10\%}} = 4.48$$

Let us solve a numerical problem. We are talking about the benzoyl peroxide associated polymerization of a monomer that follows the simple kinetics scheme which we just discussed, where rate constant and f being independent of conversion for a polymerization system. M_0 is given 2.0 M, I_0 is also given 10^{-2} M and the limiting conversion p_∞ is given as 10% which means 0.1. So, to increase p_∞ from 10% to 20%, what we need to do? Should we increase or decrease the factors $[M]_0$ and/or $[I]_0$? The expression involving p_∞ does not include $[M]_0$ here. We cannot change $[M]_0$ and increase the p_∞ value from 10% to 20%. We can change the initial initiator concentration $[I]_0$ to change the p_∞ value. So, we can write 0.2 for our target p_∞ value required. So, this gives the ratio of ($[I]_0$ at 20%) / ($[I]_0$ at 10%) as 4.48. So, we have to increase the initial initiator concentration almost 4.5 times to increase the limiting monomer conversion from 10% to 20%.

$$-\frac{\ln(1-0.2)}{\ln(1-0.1)} = \left[\frac{[I]_{0,20\%}}{[I]_{0,10\%}}\right]^{1/2};\ \frac{[I]_{0,20\%}}{[I]_{0,10\%}} = 4.48$$

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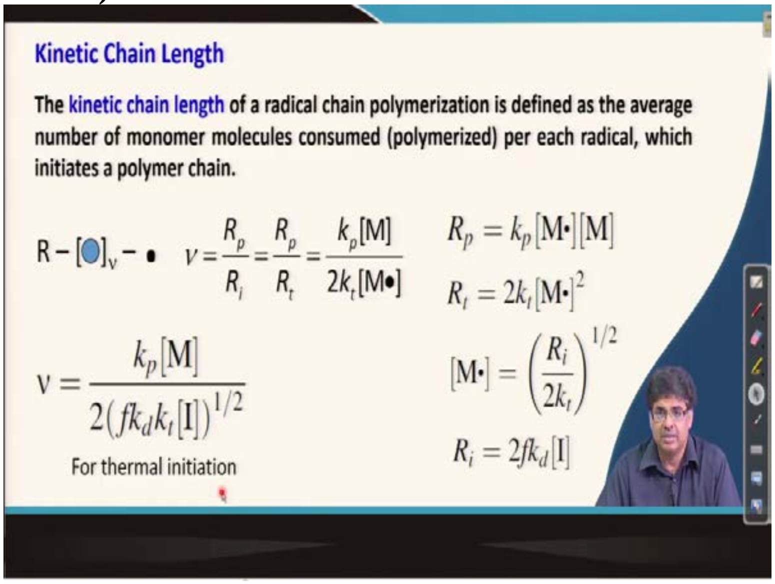

Kinetic Chain Length

The **kinetic chain length** of a radical chain polymerization is defined as the average number of monomer molecules consumed (polymerized) per each radical, which initiates a polymer chain.

$\mathrm{R}-[\bullet]_{\nu}-\bullet$ $\quad \nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[\mathrm{M}]}{2k_t[\mathrm{M}\bullet]}$

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

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

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

$$\nu = \frac{k_p[\mathrm{M}]}{2(fk_dk_t[\mathrm{I}])^{1/2}}$$

For thermal initiation

$$R_i = 2fk_d[\mathrm{I}]$$

Next, let us discuss kinetic chain length. Kinetic chain length is related to the molecular weight of the polymer produced in this reaction. We will discuss molecular weight later. First, let define what is kinetic chain length. The kinetic chain length of radical chain polymerization is defined as the average number of monomer molecules consumed or polymerized per each radical, which initiates a polymer chain.

Let's elaborate in this way. Say a radical $R^{\cdot}$ initiates a polymerization reaction and we get a propagating radical. So, each propagating radical is a kinetic chain and the number of monomer molecules consumed per or polymerized per $R^{\cdot}$ in this particular case is called the kinetic chain length. So ν is the kinetic chain length for this particular propagating radical or kinetic chain.

For example, if we think that for a unit time, let us say in 1 minute, 500 monomers are polymerized or consumed. Now at the same time, 5 radicals initiated polymer chains in 1 minute. So, in 1 minute 500 monomers have been consumed, which is nothing but the rate of polymerization R_p because R_p is described as the rate of disappearance of monomer or consumption of monomer.

Again, 5 is the number of radicals that initiate the polymer chain. So, this is nothing but the rate of initiation, R_i. Now, in this case, 500 monomers are consumed and 5 radicals initiated polymer chains. So, for each polymer chain or propagating polymer chain in this case we will have on an average 500 / 5 monomers which means the kinetic chain length for this case on average is 100 and which is given by R_p/R_i. So, for a given time, if we divide the rate of polymerization or rate of consumption of monomer from the reaction mixture by the rate of initiation of the polymer chain, we should get the kinetic chain length (ν), which is the number of monomer units consumed per each radical. Now, we can also write this is equivalent to R_t because, from this steady-state assumption, we know $R_i = R_t$.

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

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

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

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

$$R_i = 2fk_d[\mathrm{I}]$$

$$\nu = \frac{k_p[\mathrm{M}]}{2(fk_dk_t[\mathrm{I}])^{1/2}}$$

So we get the kinetic chain-link expression for thermally initiated radical polymerization. So, once again kinetic chain length is the number of monomer units consumed per each radical produced which initiated the polymer chain.

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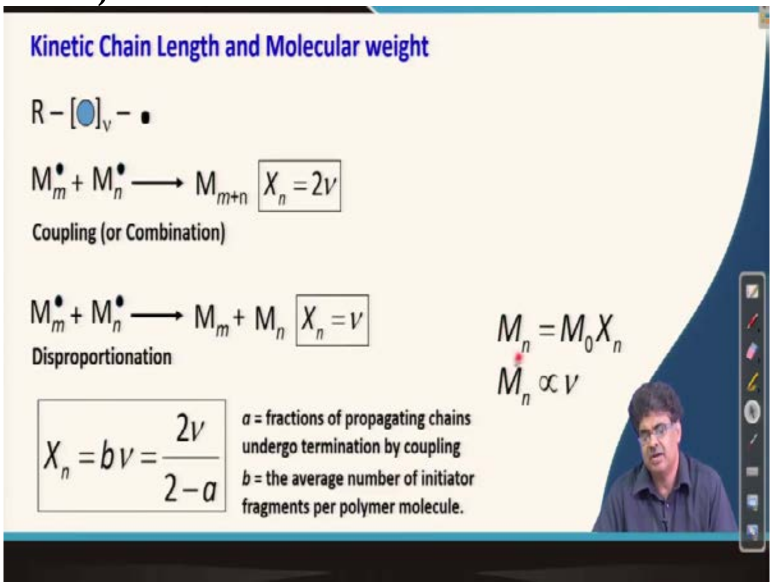

Kinetic Chain Length and Molecular weight

$R-[\,\bullet\,]_{\nu}-\bullet$

$M^\bullet_m + M^\bullet_n \longrightarrow M_{m+n}$ $\boxed{X_n = 2\nu}$

Coupling (or Combination)

$M^\bullet_m + M^\bullet_n \longrightarrow M_m + M_n$ $\boxed{X_n = \nu}$

Disproportionation

$\boxed{X_n = b\nu = \frac{2\nu}{2-a}}$

a = fractions of propagating chains undergo termination by coupling

b = the average number of initiator fragments per polymer molecule.

$M_n = M_0 X_n$

$M_n \propto \nu$

Now, what is the relation between kinetic chain length and molecular weight? We know that the propagating radical get terminated mainly by 2 methods, one by combinational, coupling method which is the most abundant or most feasible way of getting terminated, and the other is by disproportionation.

In the case of coupling, we have one radical and another radical which combine or couple to give us a single polymer chain. Now, what is the number of initiator residues present in this chain? So, if two propagating radicals react we get a single polymer chain, and in this case, on two ends we have two initiator residues. So, if the termination happens by combination or coupling, then the degree of polymerization is given by twice the kinetic chain length and the number of initiator residues present in a single polymer chain is given by 2 because at both sides we have one initiator residue.

Now, if the termination happens by disproportionation then we have two polymer chains, which give 2 kinetic chains or 2 propagating radicals giving 2 chains. So, on average, the value of the degree of polymerization would be equal to kinetic chain length. In this case, there would be 1 initiator residue for the polymer chain.

$$For\ coupling, \qquad \mathrm{M}_m^{\cdot} + \mathrm{M}_n^{\cdot} \rightarrow \mathrm{M}_{m+n}\,;\ X_n = 2\nu$$

$$For\ disproportionation, \qquad \mathrm{M}_m^{\cdot} + \mathrm{M}_n^{\cdot} \rightarrow \mathrm{M}_m + \mathrm{M}_n\,;\ X_n = \nu$$

$$X_n = b\nu = \frac{2\nu}{2-a}$$

So, in general, we can write the degree of polymerization by ‘bν’, b is the average number of initiator fragments or initiator residues per polymer chain and we can just rearrange this to get this expression where a is the fraction of propagating chains undergoing termination by coupling reaction. Now, we know M_n is given by M_0, which is the monomer molecular weight or structural unit molecular weight, multiplied by the degree of polymerization. In this case, we are talking about the number average degree of polymerization. If we are using X_w, then we also can get M_w in this case. So, this is how M_n or number average molecular weight or molecular weight is related to kinetic chain length through the degree of polymerization. So, we know from these expressions that M_n or molecular weight is proportional to the kinetic chain length and we have found out the kinetic chain length, the expression for a kinetic chain in the last slide.

$$\mathrm{M}_n = \mathrm{M}_0 X_n$$

$$\mathrm{M}_n \propto \nu$$

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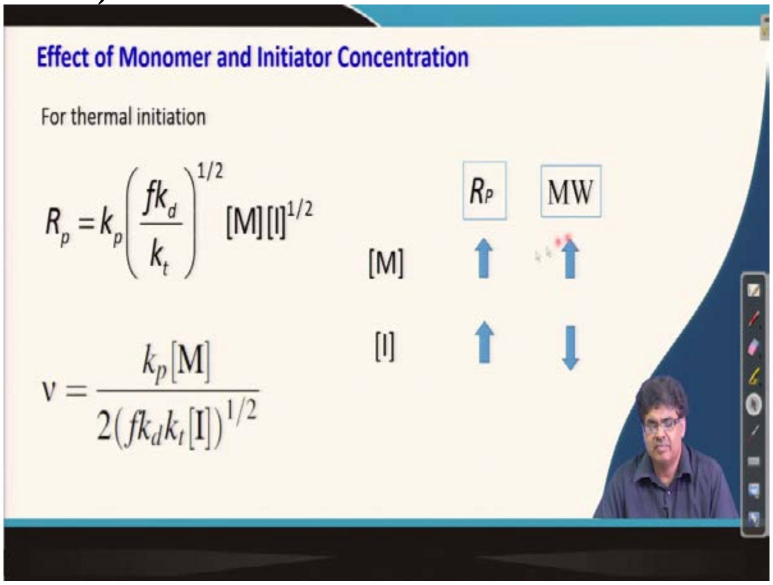

Effect of Monomer and Initiator Concentration

For thermal initiation

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[\mathrm{M}][\mathrm{I}]^{1/2}$$

$$\nu = \frac{k_p[\mathrm{M}]}{2(fk_dk_t[\mathrm{I}])^{1/2}}$$

	R_p	MW
[M]	↑	↑
[I]	↑	↓

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[\mathrm{M}][\mathrm{I}]^{1/2}$$

$$\nu = \frac{k_p[\mathrm{M}]}{2(fk_dk_t[\mathrm{I}])^{1/2}}$$

The expressions are for the rate of polymerization and second one for kinetic chain length, which is also proportional to molecular weight. This is of course, for thermal initiation polymerization. If we can look at this expression, if we increase molecular weight, then both the rate of polymerization and molecular weight or kinetic chain length increases. If we increase the initiator concentration, then the rate of polymerization will increase, but the molecular weight or the kinetic chain length decreases. So, it is always preferable to do a radical chain polymerization at a higher monomer concentration to get a high rate of polymerization as well as high molecular weight but there are some problems of using high monomer concentration, which we will discuss in coming lectures.

Hence we should know that if we want to increase the rate of polymerization and molecular weight, we can increase the monomer concentration, but if we increase the initiator concentration, then it increases the rate of polymerization but it does not increase or decrease the molecular weight.

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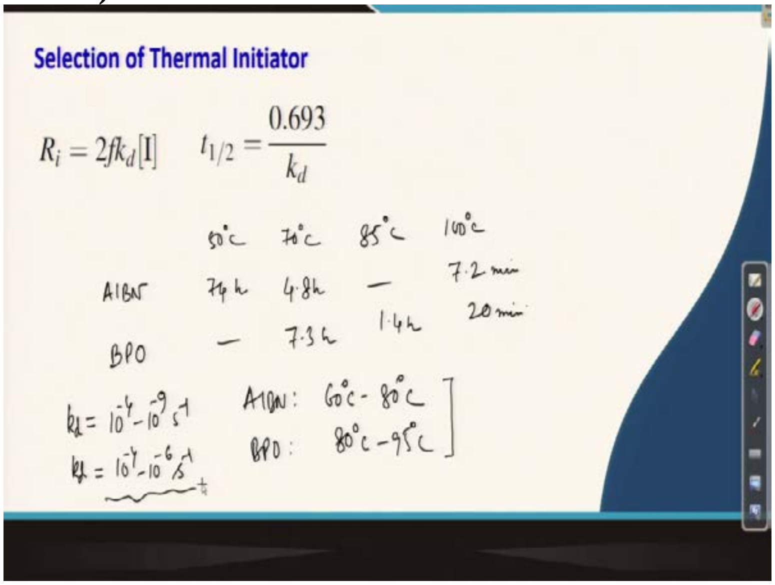

Selection of Thermal Initiator

$R_i = 2fk_d[\mathrm{I}]$ $\quad t_{1/2} = \frac{0.693}{k_d}$

	50°C	70°C	85°C	100°C
AIBN	74 h	4.8h	—	7.2 min
BPO	—	7.3 h	1.4 h	20 min

$k_d = 10^{-4} - 10^{-9}\ s^{-1}$

$\underbrace{k_d = 10^{-4} - 10^{-6}\ s^{-1}}$

AIBN: 60°C - 80°C

BPO: 80°C - 95°C

Now, how to select the thermal initiator for the polymerization, and that can be decided by the $t_{1/2}$ value and what is the time of experiment required. For example, if we can use the value for some of the $t_{1/2}$ values for common initiators like AIBN, the values are, for 50 ºC it is 74 hours, at 70 ºC it is 4.8 hours, at 85 ºC it is not reported, at 100 ºC it is 7.2 minute. The same for benzoyl peroxide is not reported, 7.3 hours, 1.4 hours, 20 minutes, respectively.

	50 ºC	70 ºC	85 ºC	100 ºC
AIBN	74 h	4.8 h	-	7.2 min
Benzoyl peroxide	-	7.3 h	1.4 h	20 min

So, if we look at this data, generally we look for an initiator which has half an hour between in this range. If we do the reaction say with AIBN at a very high temperature of 100 ºC, the most of the initiators will decompose very fast, half of the initiators will decompose in 7.2 minutes. So, the reaction rate will be very fast, but as a result what will happen? The molecular weight will be drastically low as well as if the rate of polymerization is very high, there are some problems which we will discuss in coming slides.

So, generally, AIBN is used in the range of 60 ºC to 80 ºC and benzoyl peroxide is used in 80 ºC to 95ºC. The reaction temperature required is given by the solvent which we are using. Depending on that we choose the radical initiator which we want to use for our polymerization reaction. A typical value for the dissociation or the rate constant for dissociation is around 10^{-4} to 10^{-9} s^{-1}, and the practical value for k_d is 10^{-2} to 10^{-6} s^{-1}. So, this is the required k_d value generally we use for the standard polymerization, radical polymerization reaction.

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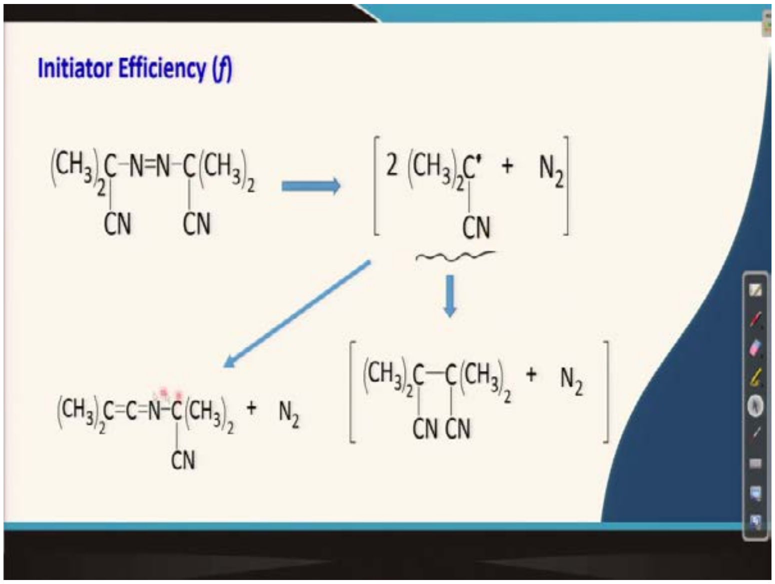

Initiator Efficiency (*f*)

$$(CH_3)_2\underset{\substack{|\\ CN}}{C}-N=N-\underset{\substack{|\\ CN}}{C}(CH_3)_2 \rightarrow \left[2\,(CH_3)_2\underset{\substack{|\\ CN}}{C^{\bullet}} + N_2\right]$$

$$\left[(CH_3)_2\underset{\substack{|\\ CN}}{C}-\underset{\substack{|\\ CN}}{C}(CH_3)_2 + N_2\right]$$

$$(CH_3)_2C=C=N-\underset{\substack{|\\ CN}}{C}(CH_3)_2 + N_2$$

Now, we also know there is a term in the rate of initiation and rate of polymerization and also in kinetic chain length, which is *f*, initiator efficiency. Initiator efficiency is nothing but the fraction of radicals that got produced in the first step which actually could start a polymerization process. For example, if the initiator generates 100 radicals in the first dissociation step and out of which 80 starts a polymerization chain and 20 get lost by some other mechanism, then, the efficiency would be 0.8 or 80%. For example, in the case of AIBN two radicals are formed as shown in the slide and then these can self-react with each other or these radicals can react with each other and form normal radical species, which will be unable to start the polymerization reaction. Similarly, it can also react with itself to form this molecule.

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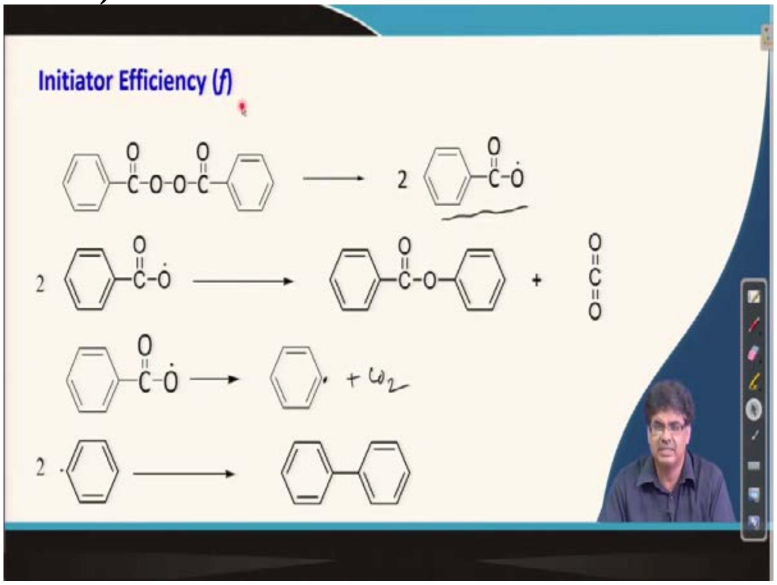

Initiator Efficiency (*f*)

Another example could be benzoyl peroxide. Benzoyl peroxide can produce C_6H_5-$COO^{\cdot}$ radical and this is the radical first produced from benzoyl peroxide and these can react with itself and produce a non-radical species. So, some of the radicals are lost in this way and this can also dissociate to form a radical like $C_6H_5^{\cdot}$ and carbon dioxide, which can also react with each other among themselves to form non-radicals species. So, these are some of the examples of how these radicals which are produced in the first step of dissociation can get destroyed and not used for starting a polymerization chain, and the fraction of the radicals which got generated in the first dissociation step used for polymerization chain initiation is called initiator efficiency.

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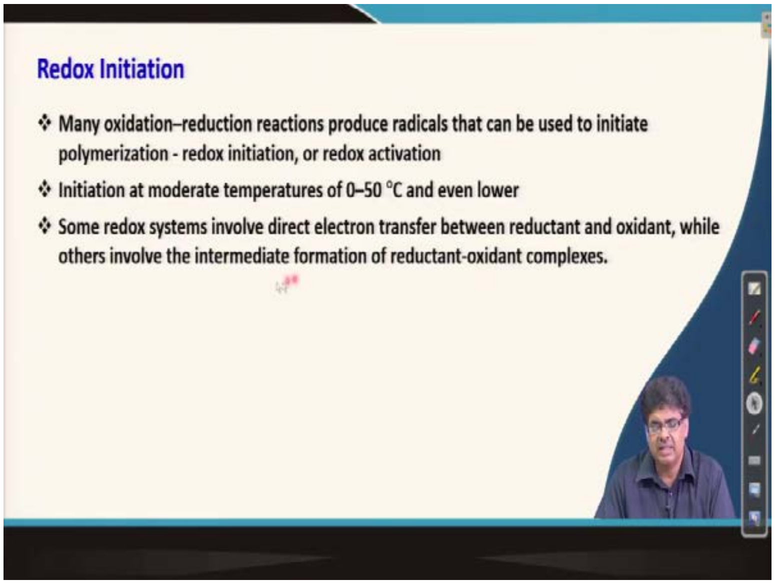

Redox Initiation

- Many oxidation–reduction reactions produce radicals that can be used to initiate polymerization - redox initiation, or redox activation
- Initiation at moderate temperatures of 0–50 °C and even lower
- Some redox systems involve direct electron transfer between reductant and oxidant, while others involve the intermediate formation of reductant-oxidant complexes.

Now, after going through the initiation via a thermal mechanism, there are other mechanisms for initiation, for example, redox initiation, and we will not discuss them in detail because the thermal initiation method is the most used in both industry and academia. Many oxidation-reduction reactions produce radicals that can be used for initiating polymerization reactions and we call that process redox initiation or redox activation. The advantage is that this initiation can take place at a moderate temperature as well as lower temperature. Some of these redox systems involve direct electron transfer between reductant and oxidant while others involve the intermediate formation of reductant oxygen complex.

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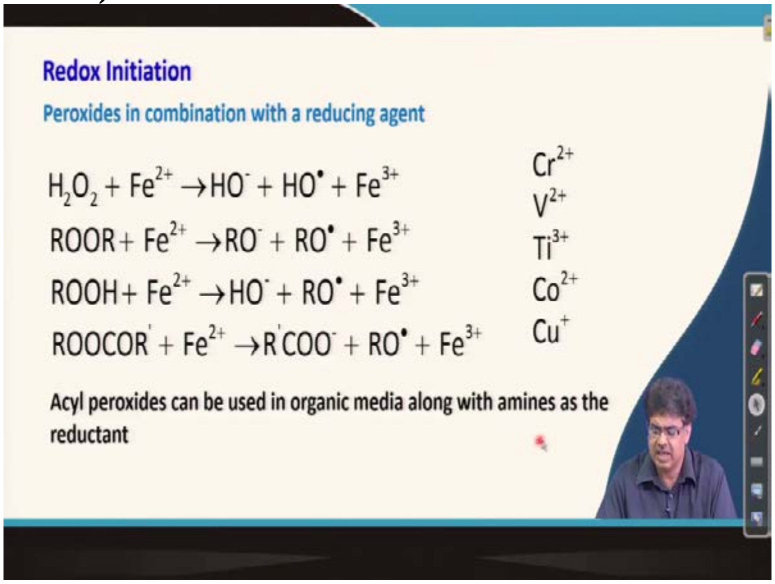

Redox Initiation

Peroxides in combination with a reducing agent

$$H_2O_2 + Fe^{2+} \rightarrow HO^- + HO^\bullet + Fe^{3+}$$

$$ROOR + Fe^{2+} \rightarrow RO^- + RO^\bullet + Fe^{3+}$$

$$ROOH + Fe^{2+} \rightarrow HO^- + RO^\bullet + Fe^{3+}$$

$$ROOCOR' + Fe^{2+} \rightarrow R'COO^- + RO^\bullet + Fe^{3+}$$

Cr^{2+}
V^{2+}
Ti^{3+}
Co^{2+}
Cu^{+}

Acyl peroxides can be used in organic media along with amines as the reductant

Some of the examples of redox initiations are peroxide in a combination of reducing agents like hydrogen peroxide with ferrous iron giving hydroxyl radical and ferric iron. Other peroxides can be used, some of them with generic structures as shown here. These can undergo oxidation-reduction reactions to produce these radicals, and not only we can use ferrous ions, but we can use other ions also which can then get oxidized and reduce the peroxides to form radicals. There are also other ways to generate, for example, acyl peroxides can be used in organic media along with amines as reductants, and one example is benzoyl peroxide.

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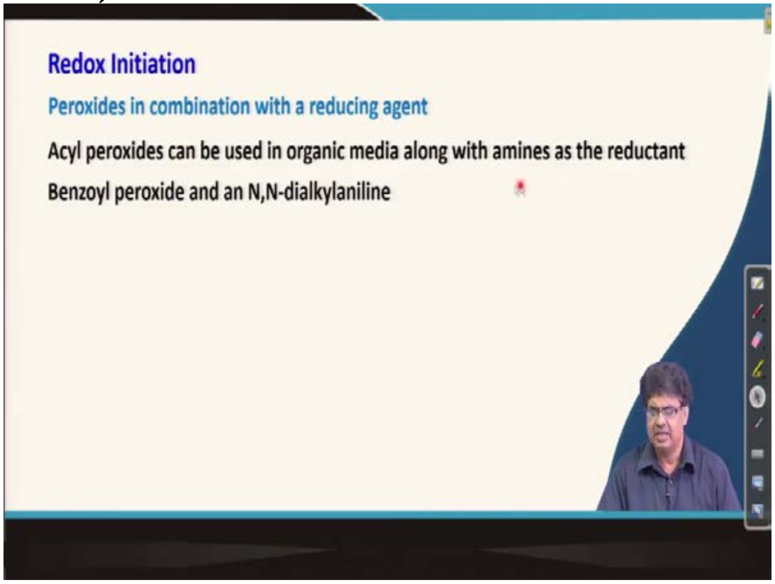

Redox Initiation

Peroxides in combination with a reducing agent

Acyl peroxides can be used in organic media along with amines as the reductant

Benzoyl peroxide and an N,N-dialkylaniline

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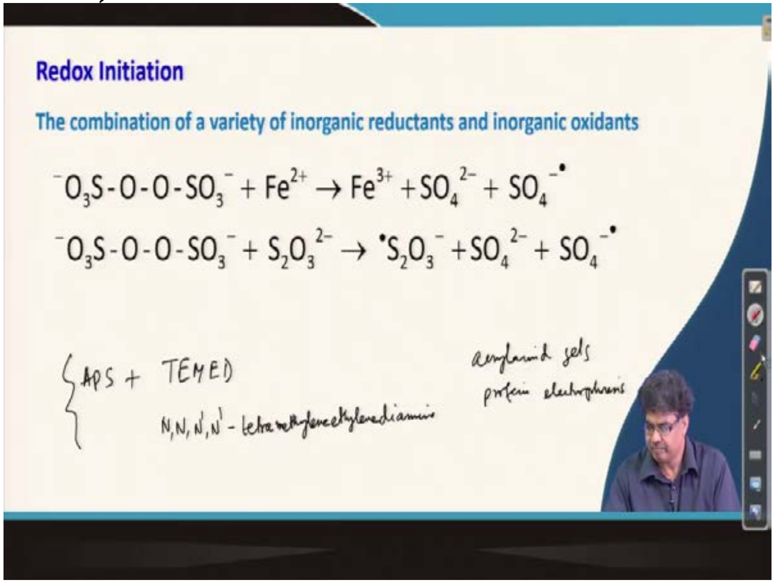

Redox Initiation

The combination of a variety of inorganic reductants and inorganic oxidants

$$^{-}O_3S-O-O-SO_3^{-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-\bullet}$$

$$^{-}O_3S-O-O-SO_3^{-} + S_2O_3^{2-} \rightarrow {}^{\bullet}S_2O_3^{-} + SO_4^{2-} + SO_4^{-\bullet}$$

APS + TEMED

N,N,N',N'-tetramethylethylenediamine

acrylamide gels

protein electrophoresis

In the case of benzoyl peroxide, the advantage is that we can use this in an organic medium. The other example for redox initiation is a combination of a variety of inorganic reductants and inorganic oxidants, for example, persulfates and ferrous ion-producing this anion radical and we can use this system as well. There is a very common example, which is used in biology labs for making acrylamide gels for electrophoresis. In that case, the radical initiator used is ammonium persulfate APS plus a diamine generally called TEMED, N, N, N', N'-tetramethylethylenediamine. This is a very standard initiator often used for making acrylamide gels which is a very standard technique in biology labs for doing protein electrophoresis.

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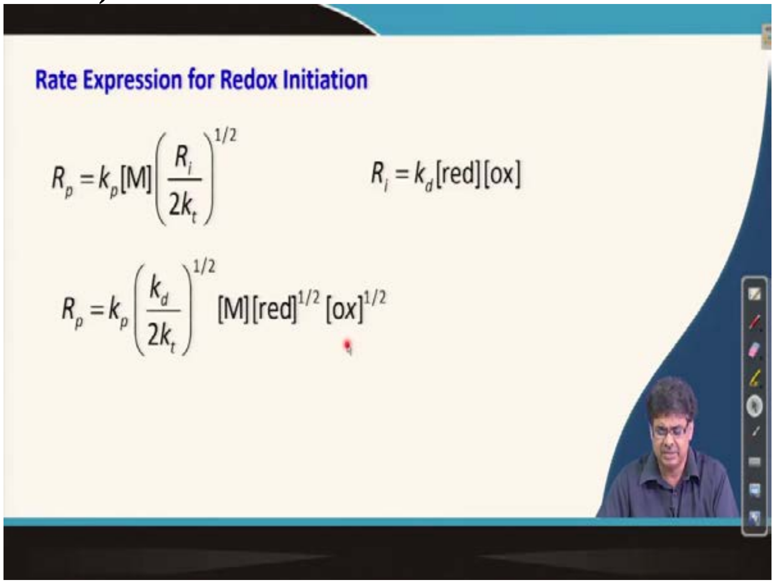

Rate Expression for Redox Initiation

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

$$R_p = k_p\left(\frac{k_d}{2k_t}\right)^{1/2}[M][red]^{1/2}[ox]^{1/2}$$

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

$$R_i = k_d[red][ox]$$

$$R_p = k_p\left(\frac{k_d}{2k_t}\right)^{1/2}[\mathrm{M}][red]^{1/2}[ox]^{1/2}$$

So if we now know the examples of redox initiation and the rate expression. We again use the same rate of polymerization and in this case, we will use the rate of initiation for redox initiation, which is given by k_d multiplied by the concentration of reductant and concentration of oxidant. So, we replace this R_i with this expression to get this expression for R_p

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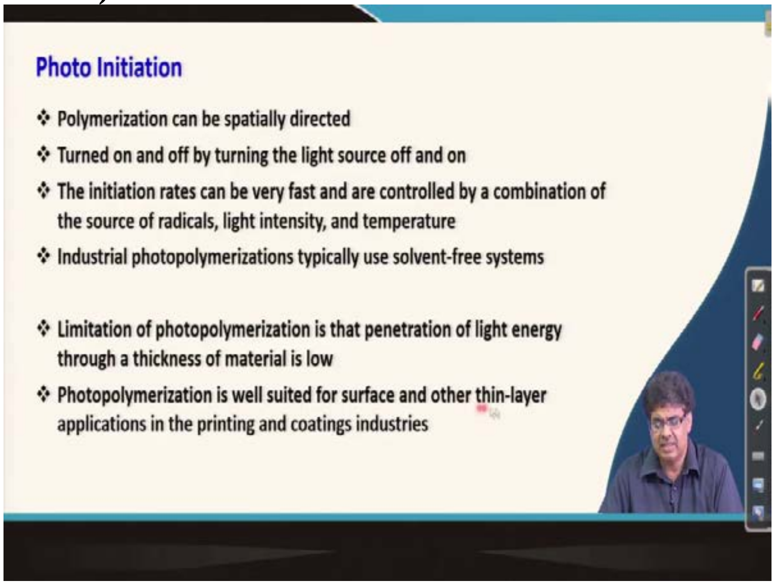

Photo Initiation

- Polymerization can be spatially directed
- Turned on and off by turning the light source off and on
- The initiation rates can be very fast and are controlled by a combination of the source of radicals, light intensity, and temperature
- Industrial photopolymerizations typically use solvent-free systems
- Limitation of photopolymerization is that penetration of light energy through a thickness of material is low
- Photopolymerization is well suited for surface and other thin-layer applications in the printing and coatings industries

There is another common way to use the initiation process that is photoinitiation, and the advantage of photoinitiation is that polymerization can be done if we can direct the light in a part of the reaction mixture to polymerize it. Also we can switch off or switch on the polymerization by switching off and on the light. The initiation rate also can be very fast and can be controlled by a combination of factors like a source of radicals, light intensity, and temperature. The advantage is that industrial photopolymerization is typically used for solvent-free systems, which is very environmentally friendly, but the disadvantage is that the light cannot enter deep in a reaction mixture. If the reaction mixture thickness is low, like if you want to do polymerization in a film or coatings, then a photopolymerization is probably preferable because in that case, light does not need to penetrate a higher thickness. So, in this case, photopolymerization is well suited for surfaces and other thin layer applications like printing and coating industries.

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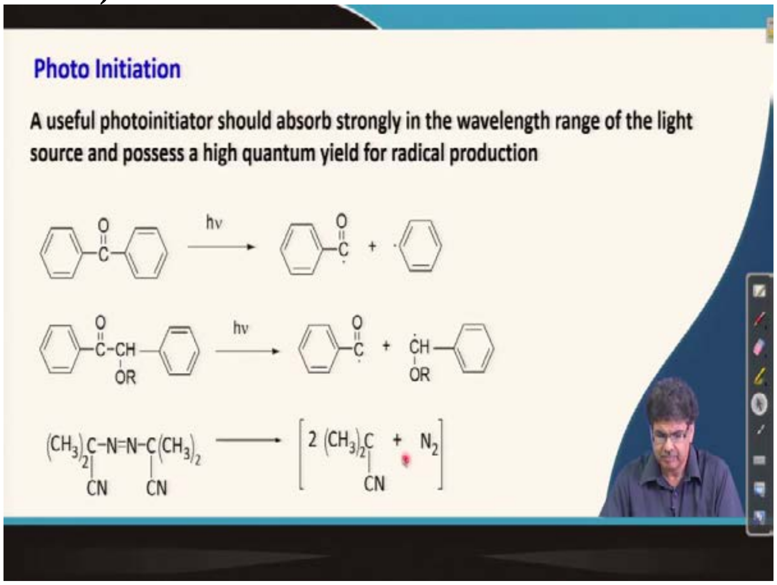

Photo Initiation

A useful photoinitiator should absorb strongly in the wavelength range of the light source and possess a high quantum yield for radical production

Some of the examples of photoinitiators are benzoketones, benzions and even AIBN also can produce radicals on shining light and these are some of the examples which are generally used for photopolymerization.

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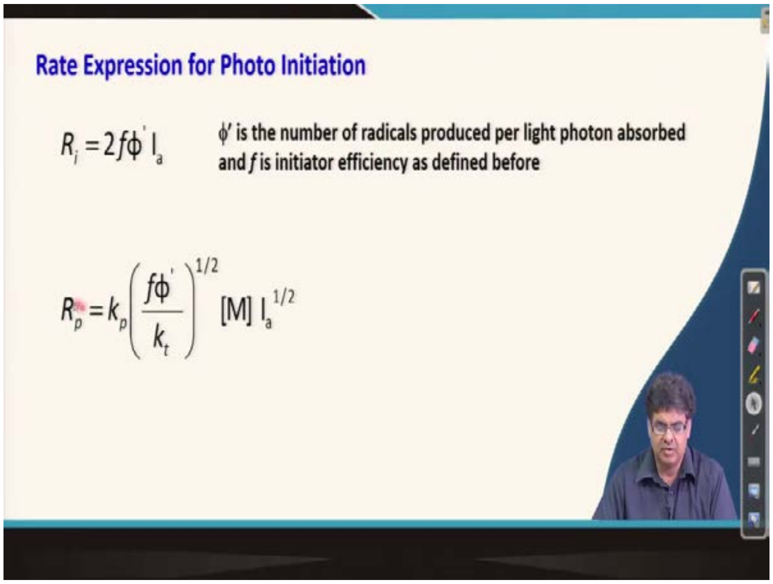

Rate Expression for Photo Initiation

$R_i = 2f\phi' I_a$

ϕ' is the number of radicals produced per light photon absorbed and f is initiator efficiency as defined before

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

$$R_i = 2f\phi' I_a$$

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

The rate expression is given by this, the rate of initiation is given by, R_i, in this case, is twice of $f\Phi' I_a$, where I_a is the intensity of light and Φ' is the number of radicals produced per light photon absorbed and f is the initiator efficiency as we described before. So, the rate of polymerization will be just replacing the R_i, we get the expression.

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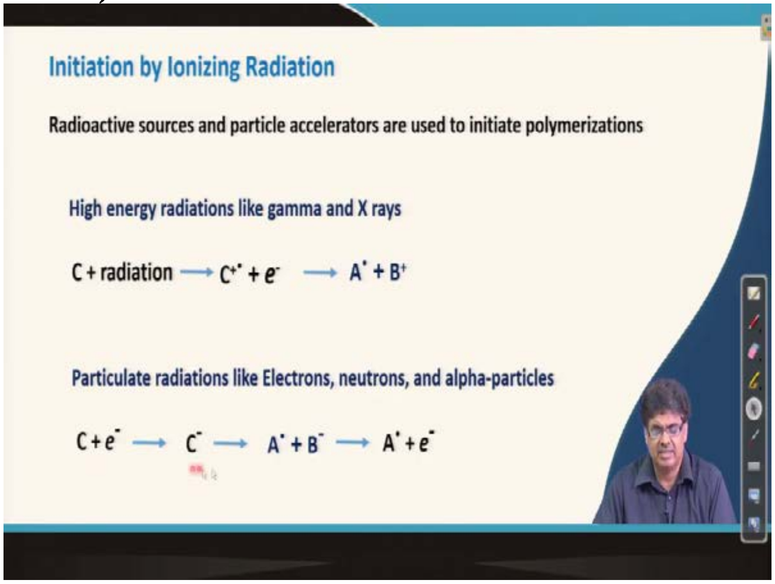

Initiation by Ionizing Radiation

Radioactive sources and particle accelerators are used to initiate polymerizations

High energy radiations like gamma and X rays

$$C + \text{radiation} \longrightarrow C^{+\bullet} + e^- \longrightarrow A^\bullet + B^+$$

Particulate radiations like Electrons, neutrons, and alpha-particles

$$C + e^- \longrightarrow C^- \longrightarrow A^\bullet + B^- \longrightarrow A^\bullet + e^-$$

There are other methods, which are sometimes used for radical initiation. One example is ionizing radiation which is by either using a radioactive source and particle accelerator or using very high energy radiation, for example, gamma rays and X rays. The mechanism is very complex, but some of the simpler ways to show the mechanism of formation of radicals by high energy radiation is shown here in the slide. Examples like particulate radiation, like electrons beam, neutron beam, alpha particle and in that case this is the simpler way of showing, how the radical is produced in that radiation but the process is complex.

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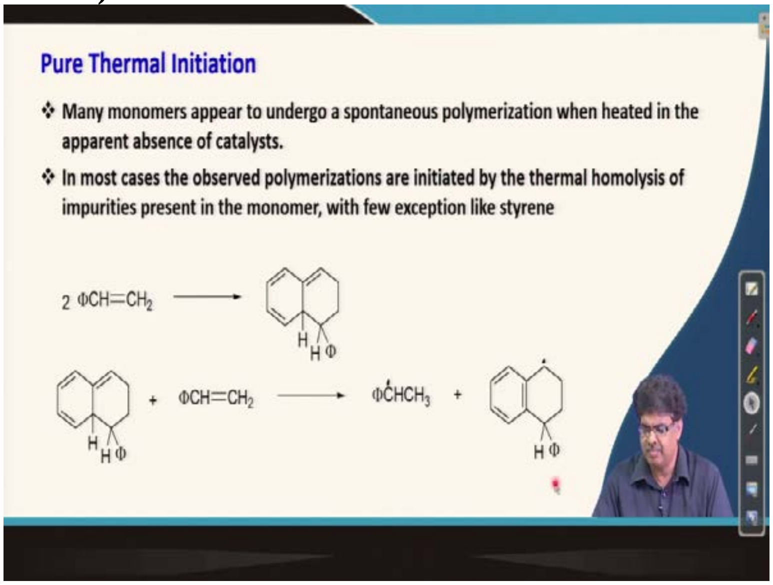

Pure Thermal Initiation

- Many monomers appear to undergo a spontaneous polymerization when heated in the apparent absence of catalysts.
- In most cases the observed polymerizations are initiated by the thermal homolysis of impurities present in the monomer, with few exception like styrene

There is also a possibility that sometimes we store monomer samples in the lab or plant, it sometimes actually gets polymerized by itself especially if we keep it outside room. This happens during summer time especially if we keep a bottle of styrene outside and it is always found out that after few months or so, the content of the bottle becomes a glassy material, and the styrene inside the bottle is polymerized. Tthat happened because the monomer itself produces radicals and initiates the chain reaction but that does not happen for everything. It happens, if we look carefully then we can find out that the impurities present like peroxide or some other impurities, which are present, dissociate themselves to produce radicals in the ambient condition in presence of light and they start the radical polymerization process. There are a few exceptions like styrene. In the case of styrene, 2 styrenes dimerize by Diels-Alder way, in which one hydrogen atom transfer happens between the dimer and a styrene monomer to produce these 2 radicals shown in the slide, which start polymerization and form polystyrene. So, styrene is very difficult to store unless we keep it at low temperature and in dark. So most of the styrene bottles come with a little bit of stabilizer. We will talk about stabilizers in the next lecture. We completed the examples and the rate expression for the different types of the initiation process.