Introduction to Polymer Science
Prof. Dibakar Dhara
Department of Chemistry
Indian Institute of Technology - Kharagpur

Lecture-11
Kinetics of Radical Chain Polymerization (Contd.), Various Types of Initiators

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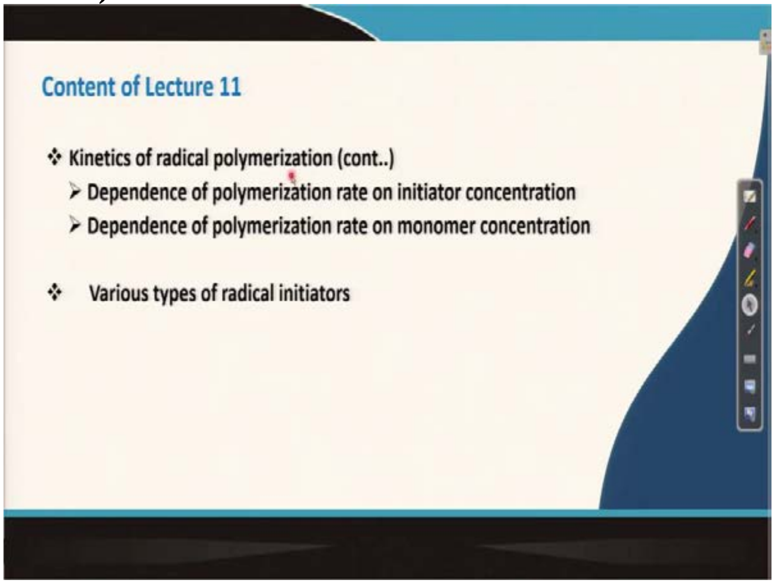

Content of Lecture 11

- ❖ Kinetics of radical polymerization (cont..)
  - ➢ Dependence of polymerization rate on initiator concentration
  - ➢ Dependence of polymerization rate on monomer concentration
- ❖ Various types of radical initiators

Welcome back. In this module, we are talking about radical chain polymerization and we have discussed kinetics of radical chain polymerization in the last class. We will continue with that and also talk about various types of initiators in this lecture.

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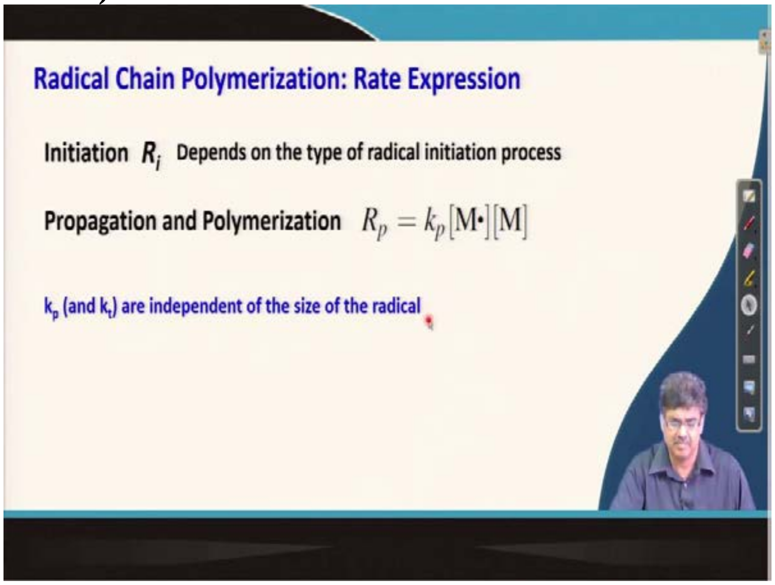

Radical Chain Polymerization: Rate Expression

Initiation R_i Depends on the type of radical initiation process

Propagation and Polymerization $R_p = k_p[\text{M}\bullet][\text{M}]$

k_p (and k_t) are independent of the size of the radical

Now, in the last lecture, we have discussed the rate of radical chain polymerization and we described that the initiation process depends on the type of initiator used and so, the rate of initiation R_i also depends on the radical initiation process which I will discuss after some time. I also discussed that the rate of propagation and polymerization both are similar because the rate of polymerization is given by the rate of disappearance of monomers from the medium, which is almost governed by the rate of propagation given by the expression.

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

where $[\text{M}^{\cdot}]$ is given by the total concentration of radicals present in the reaction mixture. We had considered that the rate of all radical reactions are equal, which means it is independent of the size of the radical. So, even if the propagating radicals are small or large, their reactivities are equal. This is a similar assumption as we have taken for step-growth polymerization, where we discussed the equal reactivity of functional groups. This is a fair assumption as we described and it is also experimentally proven.

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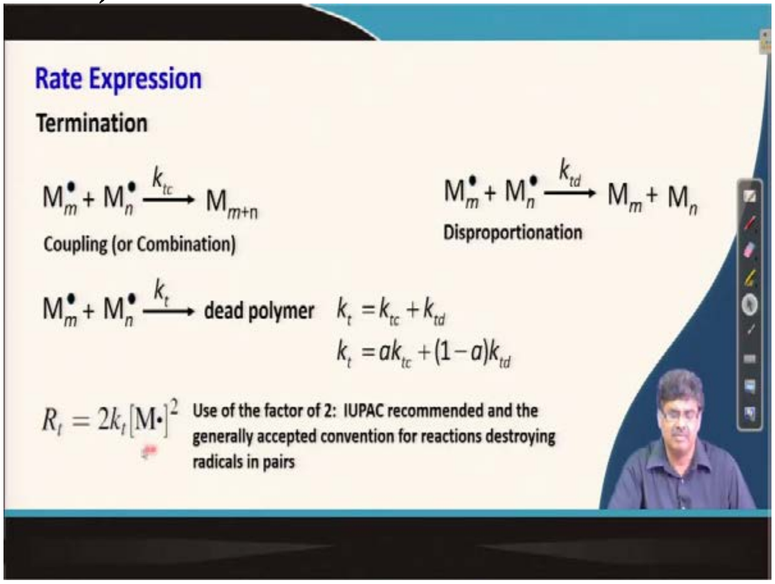

Rate Expression

Termination

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

Coupling (or Combination)

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

Disproportionation

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

$$k_t = ak_{tc} + (1-a)k_{td}$$

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

Use of the factor of 2: IUPAC recommended and the generally accepted convention for reactions destroying radicals in pairs

Now, we will move to the termination step. Termination is done by biomolecular interaction between the two propagating radicals and that can be done in two ways - either by coupling or combination and the second is by disproportionation reaction. In the case of coupling, we get a single polymer chain from two propagating radicals, whereas in the case of disproportionation we get two polymer chains from two propagating radicals.

$$\mathrm{M}_m^{\cdot} + \mathrm{M}_n^{\cdot} \overset{k_{tc}}{\rightarrow} \mathrm{M}_{m+n} \text{ [Coupling or combination]}$$

$$\mathrm{M}_m^{\cdot} + \mathrm{M}_n^{\cdot} \overset{k_{td}}{\rightarrow} \mathrm{M}_m + \mathrm{M}_n \text{ [Disproportionation]}$$

So, in general, we can write, this is the termination step, where k_t includes both these: k_{tc} for coupling or combination, k_{td} for disproportionation, and if these two are equal, then we can just write k_t as the summation of k_{tc} and k_{td}. They are not in equal proportion and in most cases, the termination happens by coupling or combination process than disproportionation reaction.

$$\mathrm{M}_m^{\cdot} + \mathrm{M}_n^{\cdot} \overset{k_t}{\rightarrow} dead\ polymer \quad k_t = k_{tc} + k_{td}$$

$$k_t = ak_{tc} + (1-a)k_{td}$$

If we assume that a is the fraction of propagating radical which is getting terminated by a combination process, then $(1 - a)$ would be the fraction of propagating radicals which are getting terminated by disproportionation reaction then k_t would be $[ak_{tc} + (1 - a)k_{td}]$. So, the rate of termination is given by the rate of this reaction $k_t[\mathrm{M}^{\cdot}]^2$. Now, this term 2 is a factor that is used for a generally accepted convention, and it is also recommended by IUPAC for the reactions which are destroying radicals in pairs. In each of these termination reactions two propagating radicals are getting destroyed, and that is why factor 2 is appearing here. Now, it can also be noticed that in the case of initiation reactions where one initiation reaction is producing 2 radicals, then also you will use this term 2. Also, there are some text or some books which do not use 2, they just write $R_t = k_t[M^\cdot]^2$ but it does not matter. The outcome one will get using this expression will remain the same whether we use 2 or not.

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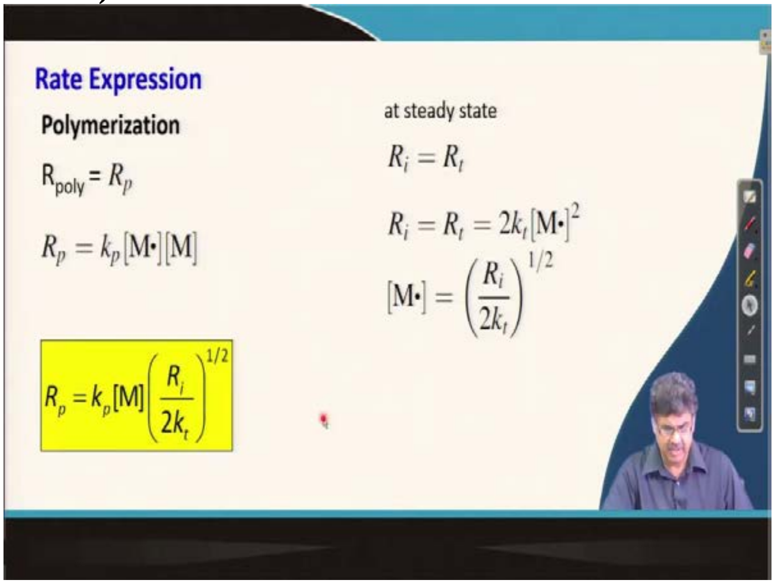

Rate Expression

Polymerization

$R_{poly} = R_p$

$R_p = k_p[M\bullet][M]$

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

at steady state

$R_i = R_t$

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

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

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

As we discussed, the rate of polymerization is given by the rate of propagation, $[M^\cdot]$ is the total concentration of radicals present in the reaction mixture. Now, determining this experimentally is difficult, because for two reasons. One is that the concentration of this is very low, about 10^{-8} molar, and also these are very reactive transient radicals. Hence, we take a steady-state assumption, which means we consider that the change of this $M^\cdot$ radical concentration with time is zero. That means the number or concentration of radicals remains the same with time, which also means that the rate at which the radicals are getting generated, which is given by the rate of initiation, is the same as the rate at which the radicals are getting destroyed. So, the rate of initiation is equal to the rate of termination.

At a steady-state,

$$R_i = R_t$$

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

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

Now, this is not unique for a polymerization reaction or radical polymerization chain reaction, the assumption of steady-state is very common for any reaction where the intermediate is having very low concentration and a very low lifetime and hence, we will go forward with this assumption which is a very fair assumption and indeed, this steady-state happens very quickly, within minutes in a normal radical chain polymerization.

So, we considered that $R_i = R_t$ and which equals to $2k_t[\mathrm{M}^{\cdot}]^2$. So, from this expression, we can get the expression for the total radical concentration, which is given by $[\mathrm{M}^{\cdot}]$ and we can use this to get the rate of polymerization or rate of propagation. This is a very useful expression for further discussion.

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

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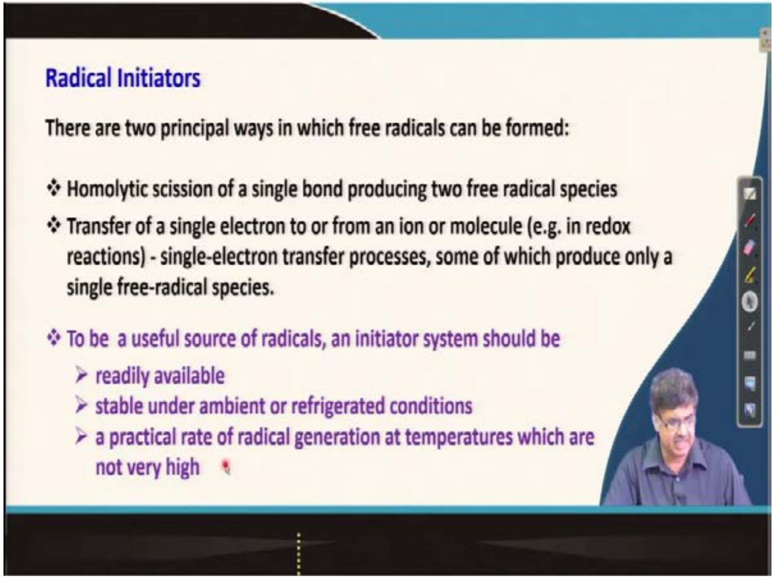

Radical Initiators

There are two principal ways in which free radicals can be formed:

- Homolytic scission of a single bond producing two free radical species
- Transfer of a single electron to or from an ion or molecule (e.g. in redox reactions) - single-electron transfer processes, some of which produce only a single free-radical species.
- To be a useful source of radicals, an initiator system should be
  - readily available
  - stable under ambient or refrigerated conditions
  - a practical rate of radical generation at temperatures which are not very high

Now, if we go back, this rate of propagation or rate of polymerization depends on the type of radical initiation which is given by this R_i which is the rate of initiation. So, we will discuss different types of radical initiators and there are mainly two principal ways in which we can generate free radicals, one by homolytic scission of a single bond which produces two free radical species and second by transfer of a single electron to or from an ion or molecules like what happens in a redox reaction. Sometimes, a single electron transfer process produces a single free radical species. The first case generally produces two radical species, and in the second situation, in most cases we get single free radical species. Now, to be a successful initiator, the compound must have few attributes, like it should be commercially readily available, must be stable under an ambient or refrigerated condition so that we can do the reaction or store it in the laboratory or plant. Also, it should generate radicals at a practical rate within a practical temperature range and not at a very high temperature. Then in that case the compound will not be useful for practical applications.

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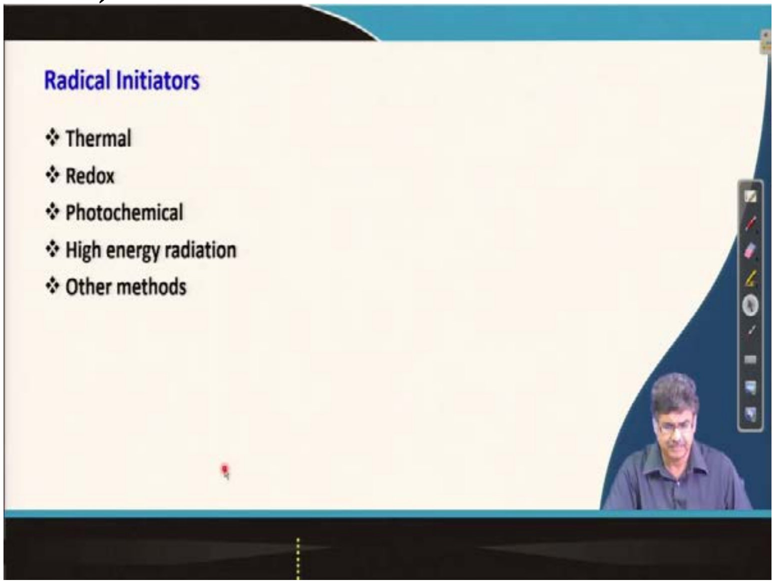

Radical Initiators

- Thermal
- Redox
- Photochemical
- High energy radiation
- Other methods

These are the typical ways we can generate radicals by thermal, redox, photochemical, high energy radiation, and other methods. The thermal method of initiating is the most used in both industry and academic institutions, so we will mainly focus our lecture or discussion on thermal initiation, but we will give examples about the other cases and discuss it briefly.

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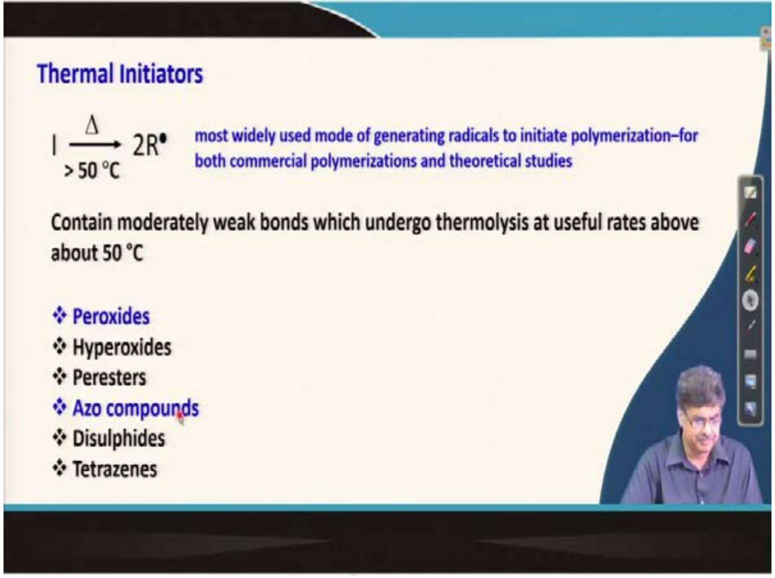

Thermal Initiators

$I \xrightarrow[> 50\,^{\circ}C]{\Delta} 2R^{\bullet}$ most widely used mode of generating radicals to initiate polymerization–for both commercial polymerizations and theoretical studies

Contain moderately weak bonds which undergo thermolysis at useful rates above about 50 °C

- Peroxides
- Hyperoxides
- Peresters
- Azo compounds
- Disulphides
- Tetrazenes

No we will talk about thermal initiators. In this case, the initiator molecule gets homolytically cleaved on heating and produces 2 radicals, and as mentioned that this is the most widely used mode of generating radicals to initiate polymerization for both commercial polymerizations and theoretical studies. Now, this initiation process has to take place at a practical rate at a moderate temperature like normally if we do the reaction in a solvent having a particular boiling point. So, we must use a radical initiator which we can use in that particular solvent. Thus it should have moderately weak bonds which undergo thermally induced homolysis at a useful rate above 50 ºC and below 100 - 120 ºC, which is the most useful temperature range. If it has a very weak bond, then it might get homolytically cleaved below 50 ºC, which is not useful because our laboratory temperature (ambient temperatures) sometimes goes very high even close to 40 – 45 ºC. Then these compounds might get dissociated even before we are adding to a polymerization reactor. So, it should not have a very weak bond, to avoid homolytic cleavage at a lower temperature (room temperature), and it also should not be very highly stable so that we need a very high temperature to get radicals from it. So, typical bond energy associated with the thermal initiator is about 100 to 170 kJ/mole and the typical bond which can give you these type of bond energies are peroxides, S-S bond, N-O bond, these type of bonds. So, we generally take the type of compounds with the type of bonds we mentioned, like, peroxides, hyperoxides, peresters, azo compounds, disulfides, tetrazenes, and so on. Now, out of all these possible thermal initiators, in most cases, peroxides and the azo compounds are used in a radical chain polymerization. So, we will only discuss the use of examples of peroxides and azo compounds for this lecture.

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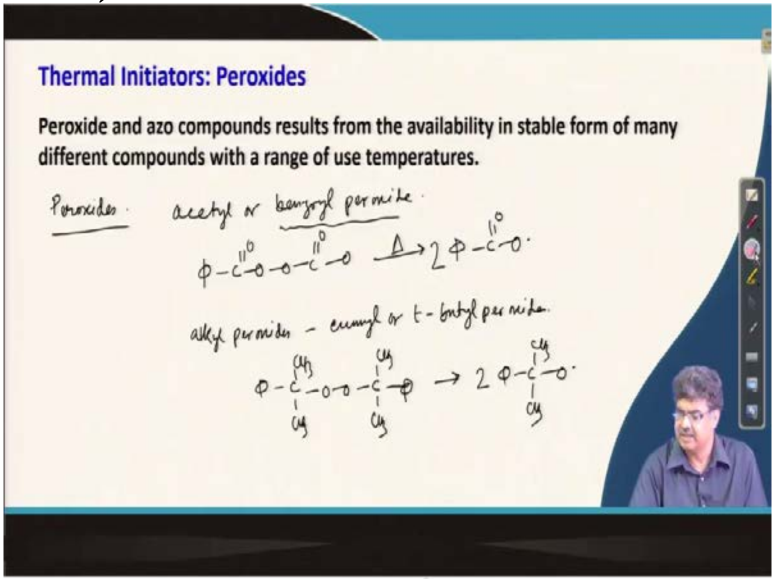

Thermal Initiators: Peroxides

Peroxide and azo compounds results from the availability in stable form of many different compounds with a range of use temperatures.

Peroxides. acetyl or benzoyl peroxide.

$\phi-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-O \xrightarrow{\Delta} 2\,\phi-\overset{O}{\overset{\|}{C}}-O^{\cdot}$

alkyl peroxides - cumyl or t-butyl peroxide.

$\phi-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-\phi \rightarrow 2\,\phi-\underset{CH_3}{\overset{CH_3}{C}}-O^{\cdot}$

We can have different peroxides and azo compounds available which are useful within a practical range of temperatures. Example for peroxides are like acetyl or benzoyl peroxide which are very useful.. One very common example of this radical initiator is benzoyl peroxide, which is very commonly used for radical reactions both in an industrial setup and in a laboratory setup. Benzoyl peroxide, on heating it gives two φ-COO$^{\cdot}$ radicals. We can also have alkyl peroxides like cumyl or tertiary butyl peroxides, it gives two $\varphi\text{-}C(CH_3)_2O^{\cdot}$ Now, this radical which is getting generated in either case has to get stabilized, otherwise, it will get destroyed very quickly and it will not be able to participate in further chain initiation reactions. This is the reason why we have this acetyl or benzoyl group or substituted alkyl peroxides. If you have a simple alkyl peroxide then it will not be the useful initiator.

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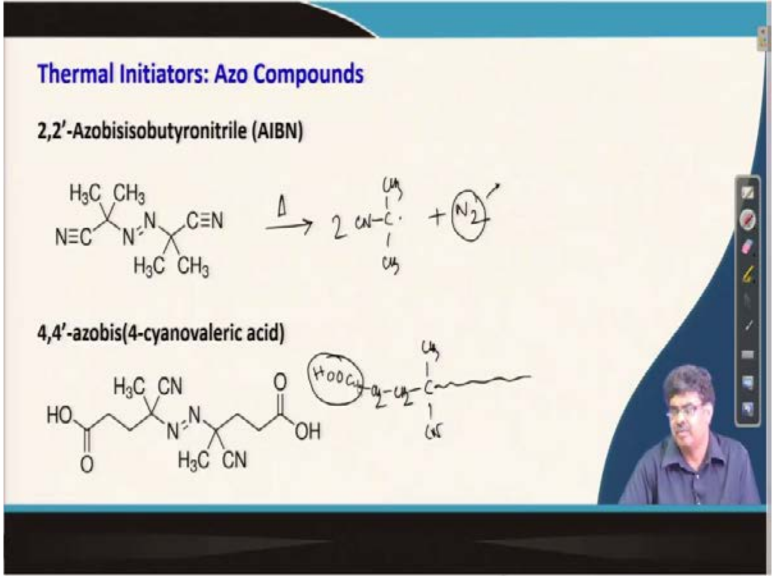

Thermal Initiators: Azo Compounds

2,2’-Azobisisobutyronitrile (AIBN)

4,4’-azobis(4-cyanovaleric acid)

So, next, we can move on to the other example of azo initiators. For example, a very commonly used initiator is 2, 2’-azobisisobutyronitrile (commonly mentioned as AIBN), which is a very commonly used initiator. In this case, the easy dissociation is not because of a weak bond or a moderately weak bond, but when it dissociates it gives very stable nitrogen gas, that is why we can easily get this reaction. This homolytic cleavage is a very feasible reaction in this particular case, and that is why it is very commonly used in practical applications like polymerization reactions. This is not water soluble, so to do a reaction in an aqueous medium one should look for azo components that are water soluble. One such example is 4, 4’-azobis(4-cyanovaleric acid) where we have two acidic groups on both sides. Also, this is water soluble so we can use this as an initiator. Now one interesting thing for this initiator that we must know is that the radicals generated in this place will have a COOH group and $C^{\cdot}$ at the ends of the chain. So the polymer chain will have these COOH groups at the end and one can utilize this group for doing further reactions on this polymer. So, this initiator gives you the advantage of using the end groups for further polymerization reaction on the polymer.

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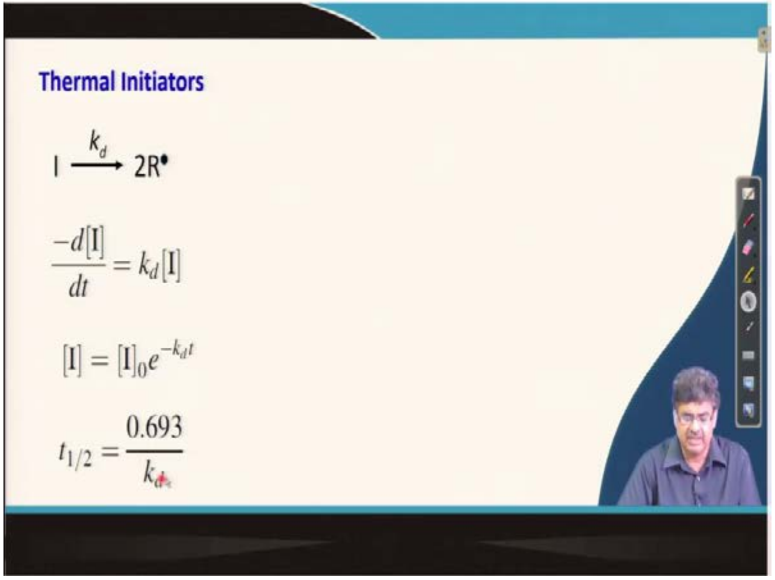

Thermal Initiators

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

$$\frac{-d[I]}{dt} = k_d[I]$$

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

$$t_{1/2} = \frac{0.693}{k_d}$$

Now, we have discussed few examples of thermal initiators and the rate of decomposition of this thermal initiator is given by the rate of this reaction, and for dissociation reaction, we can consider the rate as negative of the disappearance of the initiator molecule with time. The rate of disappearance of the initiator molecules with time is given by $k_d[I]$.

$$I \overset{k_d}{\rightarrow} 2R^{\cdot}$$

$$\frac{-d[I]}{dt} = k_d[I]$$

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

$$t_{1/2} = \frac{0.693}{k_d}$$

We can express [I] this way, where $[I]_0$ is the initial initiator concentration in this case, and this is the first-order decomposition. So, you can get $t_{1/2}$ value, which is the time at which half of the initiators have decomposed as given above. This is a very well known expression for first-order reactions, where k_d is the dissociation constant.

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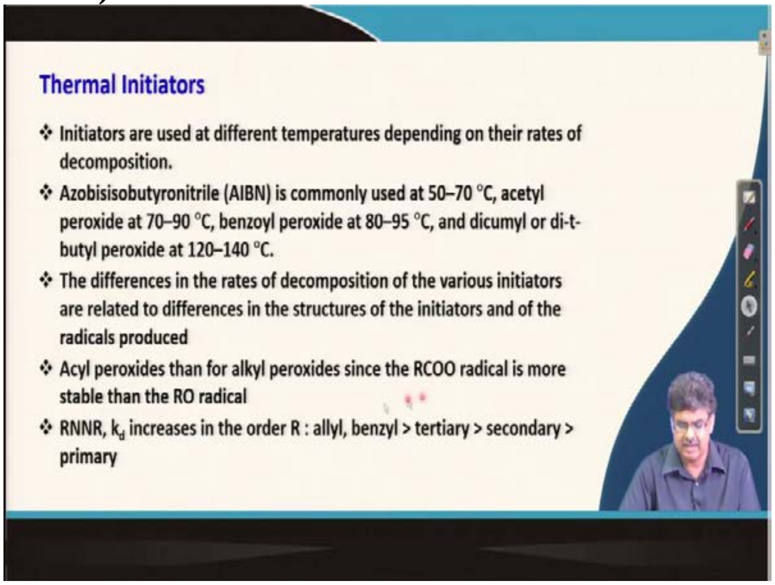

Thermal Initiators

- Initiators are used at different temperatures depending on their rates of decomposition.
- Azobisisobutyronitrile (AIBN) is commonly used at 50–70 °C, acetyl peroxide at 70–90 °C, benzoyl peroxide at 80–95 °C, and dicumyl or di-t-butyl peroxide at 120–140 °C.
- The differences in the rates of decomposition of the various initiators are related to differences in the structures of the initiators and of the radicals produced
- Acyl peroxides than for alkyl peroxides since the RCOO radical is more stable than the RO radical
- RNNR, k_d increases in the order R : allyl, benzyl > tertiary > secondary > primary

Now, the use of initiators depends on the temperature at which we want to do the reaction. So, one can use a different temperature depending on the rate of initiator decomposition. If the rate of decomposition is very high, then we can use a comparatively lower temperature and if the rate of decomposition is low, then we need to use a higher temperature and that idea we can get from the $t_{1/2}$ value of different thermal initiators at different temperatures. In general, AIBN is commonly used at 50 – 70 ºC, and acetyl peroxide is used at 70 – 90 ºC, benzoyl peroxide used at 80 – 95 ºC temperature. So, depending on the reaction temperature, we can choose which initiator molecule we should use. This difference in dissociation rate or decomposition rate is due to the substituents present on each molecule, for example, we discussed acyl peroxide and alkyl peroxide. And because in acyl peroxide, we will have $RCOO^{\cdot}$ wherein alkyl peroxide we will have $RO^{\cdot}$. So obviously radicals generated from acyl peroxides will be more stable than $RO^{\cdot}$. So the rate of decomposition for acetyl peroxide will be higher than alkyl peroxide. Similarly, for azo compounds, if the resulting radical is stabilized either by resonance or by electron donating groups, we can have a higher rate of decomposition.

So, as an example, acyl peroxides have a higher conversion rate than alkyl peroxides and because it gives a stable $RCOO^{\cdot}$ radical. For azo compounds, the rate of decomposition increases in the order of these R groups like allyl, benzyl > tertiary > secondary > primary, because of their ability to stabilize the resulting radical.

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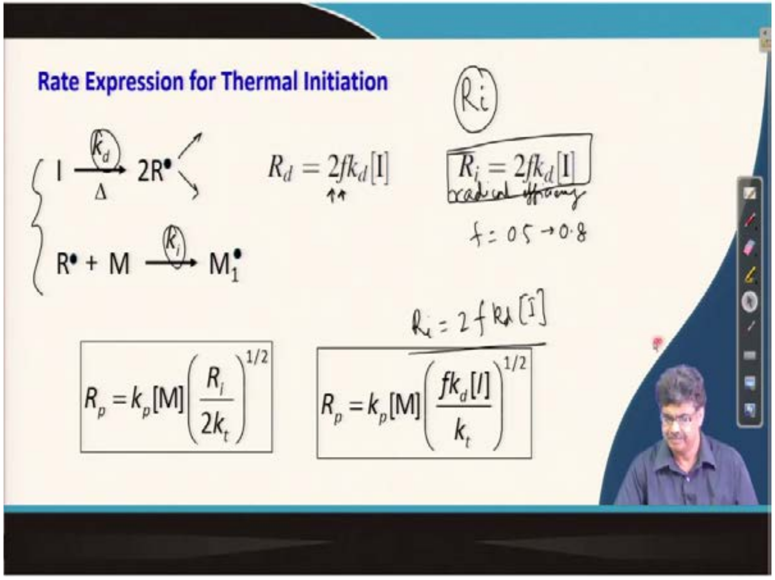

Rate Expression for Thermal Initiation

$$\mathrm{I} \xrightarrow[\Delta]{k_d} 2\mathrm{R}^{\bullet}$$

$$\mathrm{R}^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{M}_1^{\bullet}$$

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

$$R_i$$

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

radical efficiency

$f = 0.5 \to 0.8$

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

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

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

In order to discuss the initiation reaction, we need to find out what is the rate of initiation given by R_i for different initiation processes. Let us begin with thermal initiation, which we just discussed now. This is the first step of initiation reaction that we discussed earlier, a decomposition step with the rate of decomposition k_d. Once the radical forms, it immediately reacts with the first monomer, which will start the initiation reaction and the rate constant associated with this step is k_i.

$$\mathrm{I} \xrightarrow{k_d,\ \Delta} 2\mathrm{R}^{\cdot}$$

$$\mathrm{R}^{\cdot} + \mathrm{M} \overset{k_i}{\rightarrow} \mathrm{M}^{\cdot}{}_1$$

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

So the rate of dissociation (R_d) is given by the above equation, where k_d is the rate constant of dissociation and the factor 2 used in this case is because each dissociation is producing 2 radicals, which generates two polymers. Similarly, in the case of termination, for each termination reaction two radicals get deactivated. In each initiation reaction two radicals are getting produced, so, we can use f as the efficiency of the radical initiator. That means, out of the radicals which got produced during this decomposition reaction, f gives what fraction of the radicals could initiate polymerization reaction, and its value is generally between 0.5 to 0.8. That is because some of the radicals which get generated due to this decomposition reaction might get destroyed either by coupling with each other or due to reaction with others. We may discuss a little bit more about this radical efficiency later. This reaction take place by the above mentioned steps, but initiation is a much slower step than the second one. This is a radical reaction, so, the second step is a much faster reaction compared to the initiator dissociation reaction. Hence, this rate of initiation is given by the rate of dissociation. So, R_i is the rate of dissociation, which is the same as the rate of initiator dissociation (R_d) as the initiator step is much slower and rate determining step.

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

Now, we place this R_i in the equation of R_p that we have discussed previously.

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

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

Therefore, we get the expression for the rate of polymerization for a thermally initiated polymerization reaction as given above. The rate is directly proportional to the concentration of monomer and to the square root of initiator concentration.

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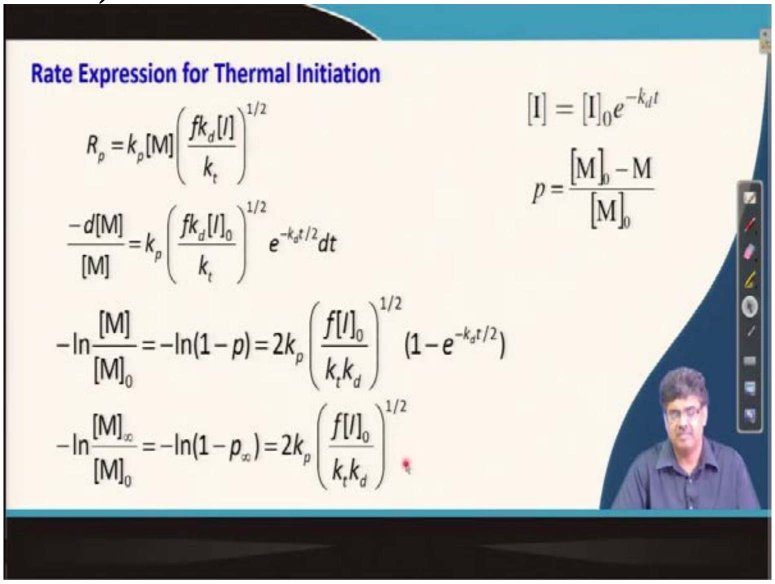

Rate Expression for Thermal Initiation

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

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

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

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

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

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

Now that we have deduced the equation for the rate of polymerization (R_p), we can further extend the expression using the initial initiator concentration (I_0). Another term p can be introduced, which means that the fraction of monomer getting consumed during polymerization.

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

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

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

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

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

So, we can write the rate of polymerization as the disappearance of monomer expressed as -d[M]/[M]. After replacing, we can rearrange and integrate to get the above expression. Here, we can calculate the conversion which means the percentage of monomer molecules that got consumed with time, if we know the initiator concentration and the other rate constants. Now, at the end time of the polymerization which is infinity, we can replace the time t with infinity, then we can get what is the maximum possible conversion we can achieve during a radical chain polymerization. Then we can calculate the p_∞ value, which is the maximum possible fraction of monomers that can be polymerized in a radical chain polymerization. We can use this expression to solve numerical problems later and we will also talk about the molecular weight in radical chain polymerization in the next lecture.