Polymer Process Engineering

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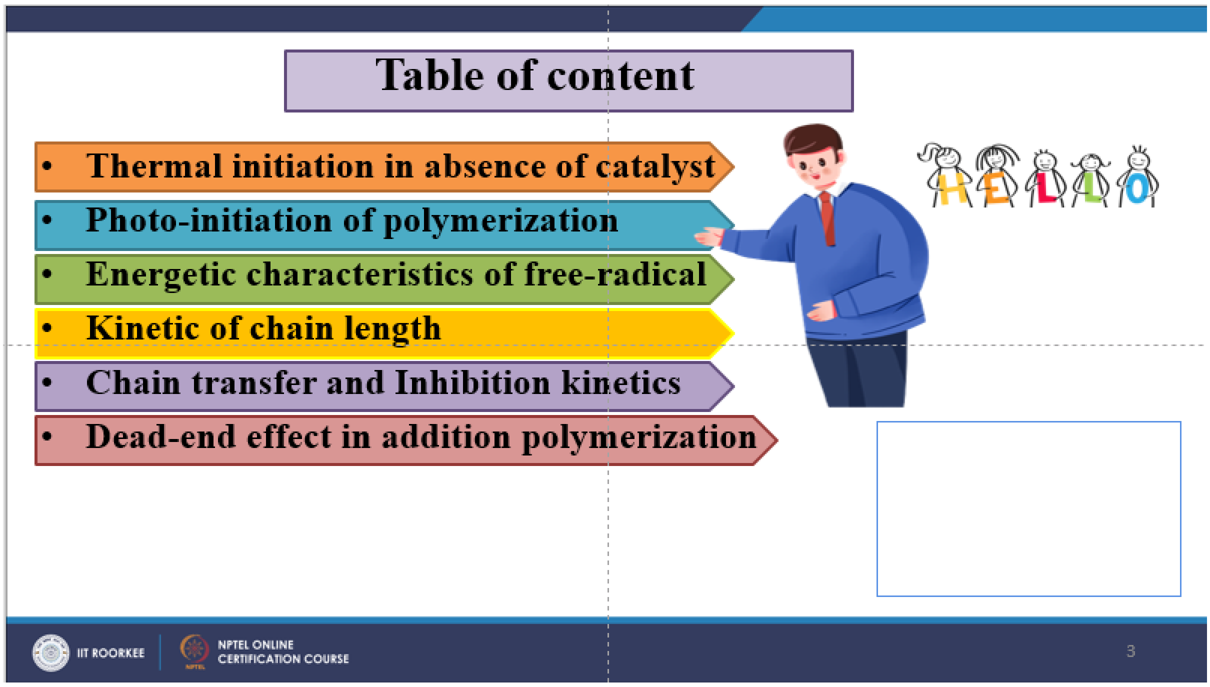
Lecture- 30

Chemical reaction engineering in polymers: Addition (Chain-Growth) Polymerization-III

Hello friends, welcome to the molecular weight distribution and addition and the channel chain reaction polymerization in the ages of chemical reaction engineering in polymers. Now before we proceed further, let us have an outlook that what we discussed in the previous lecture. We were discussing about the molecular weight distribution, then discussed about the addition polymerization, radical chain polymerization. Then we discussed about the overall rate of the polymerization and the gel effect in addition polymerization.



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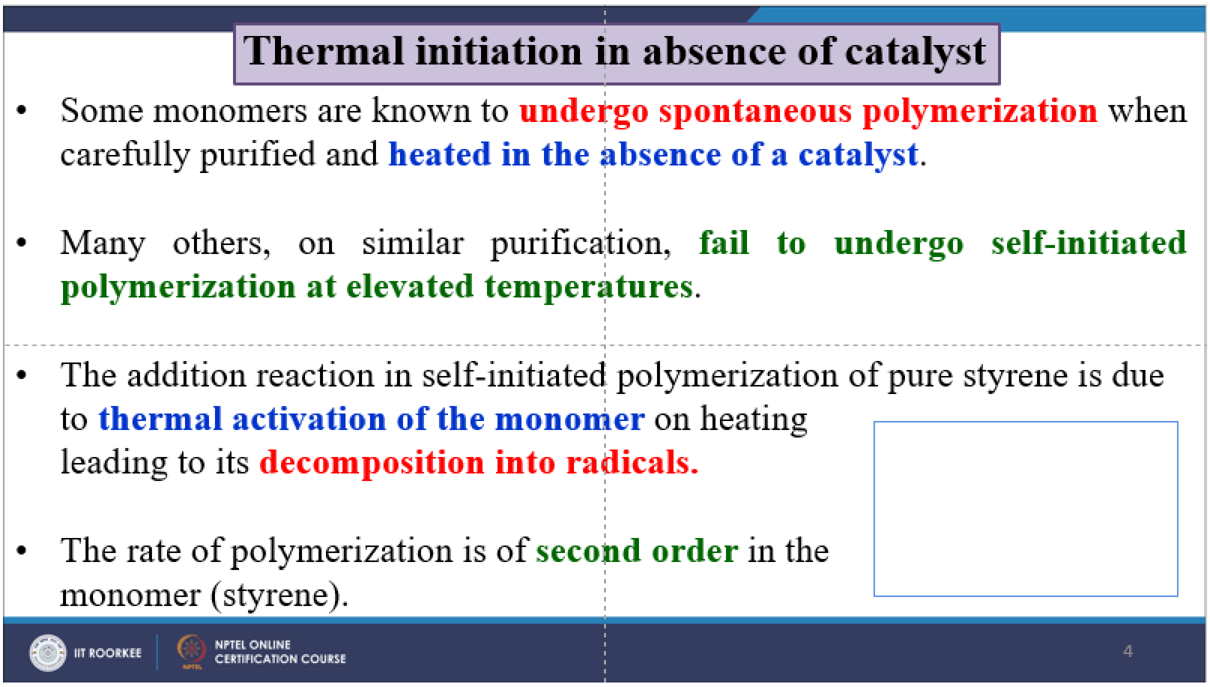
- Dead-end effect in addition polymerization

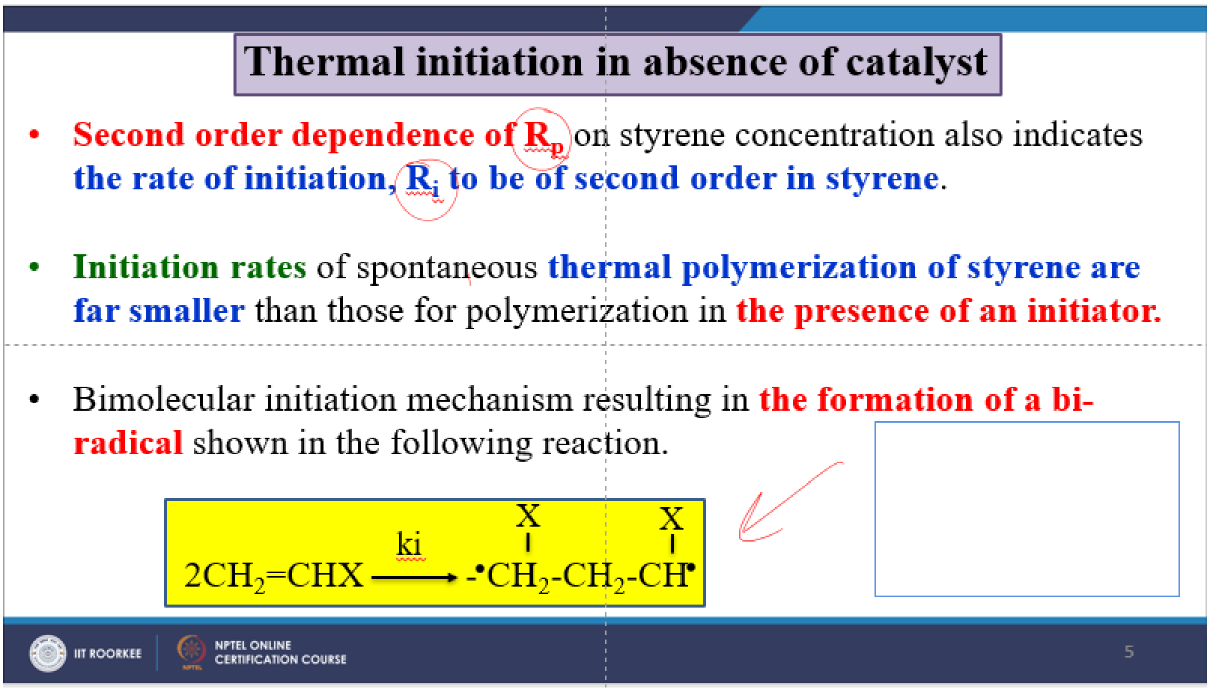
In this particular chapter, we are going to discuss the thermal initiation in absence of catalyst, photo initiation of polymerization, energetic characteristics of free radical. We will discuss about the kinetics of the chain length and then chain transfer and inhibition kinetics and dead-end effect in the addition polymerization.



Thermal initiation in absence of catalyst

- Some monomers are known to **undergo spontaneous polymerization** when carefully purified and **heated in the absence of a catalyst**.
- Many others, on similar purification, **fail to undergo self-initiated polymerization at elevated temperatures**.
- The addition reaction in self-initiated polymerization of pure styrene is due to **thermal activation of the monomer** on heating leading to its **decomposition into radicals.**
- The rate of polymerization is of **second order** in the monomer (styrene).

Now let us talk about the thermal initiation in absence of catalyst because sometimes all these reactions are perceived with the help of catalyst. So, it will be easy to see that what will be the effect of the thermal initiation in absence of catalyst. So, some monomers they are known to undergo the spontaneous polymerization when carefully purified and heated in the absence of catalyst. So many other on the similar purification fail to undergo self-initiated polymerization at elevated temperature.



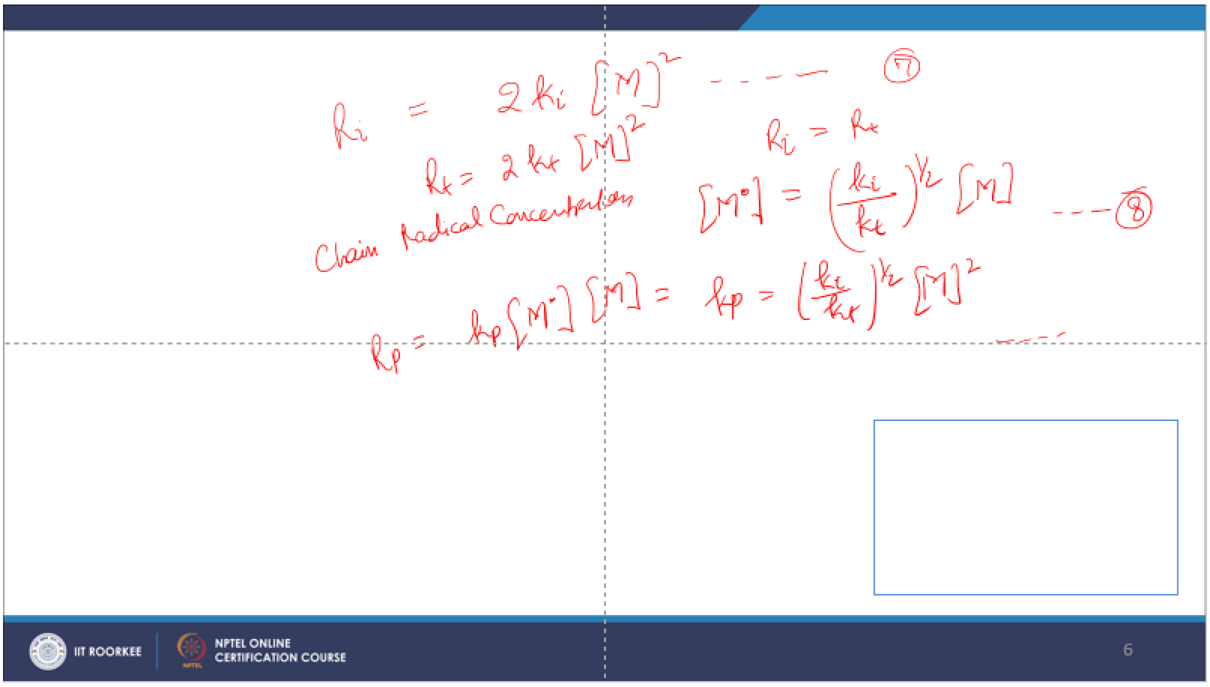
Thermal initiation in absence of catalyst

- **Second order dependence of R_p** on styrene concentration also indicates **the rate of initiation, R_i to be of second order in styrene**.
- **Initiation rates** of spontaneous **thermal polymerization of styrene are far smaller** than those for polymerization in **the presence of an initiator.**
- Bimolecular initiation mechanism resulting in **the formation of a bi-radical** shown in the following reaction.

$$2CH_2{=}CHX \xrightarrow{ki} \cdot\overset{X}{\overset{|}{C}}H_2\text{-}CH_2\text{-}\overset{X}{\overset{|}{C}}H\cdot$$

So, the addition reaction in self-initiated polymerization of pure styrene is due to the thermal activation of monomer on heating and leading to the decomposition into the radical. So, some sort of the monomers they are suo-moto once they initiated I mean when they heated to specified temperature they become the radical. So, there is no need for any third-party agent like catalyst. So, the rate of polymerization is of second order in that particular aspect. Now the second order dependence of RP on styrene concentration is also indicates the rate of initiation that is Ri to be the second order in styrene.

The initiation rates of spontaneous thermal polymerization of styrene are far smaller than those of polymerization in the presence of an initiator. So, this is the basic difference. Now the bimolecular initiation mechanism resulting in the formation of a biradical this can be shown in this particular reaction. Now see when we recall this particular reaction that is 2 CH2 CHX KI then radicals of CH CH2 initiation like this then the rate of initiation this Ri can be expressed as 2 KI into concentration of monomer to the power 2. This if you take the things into continuation with the previous lecture this can be represented as equation number 7.



$$R_i = 2k_i[M]^2 \quad \text{- - - -} \quad ⑦$$

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

$$R_i = R_t$$

Chain Radical Concentration

$$[M^\bullet] = \left(\frac{k_i}{k_t}\right)^{1/2}[M] \quad \text{- - -} \quad ⑧$$

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

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Now considering the bimolecular termination giving rate of termination so RT is equal to twice KT M to the power 2 and under steady state assumption if we give rise to Ri is equal to RT the chain radical concentration chain radical concentration can be expressed as radical M is equal to KI over KT to the power half into concentration of M this can be represented as equation 8. Now the rate of polymerization RP this can be given as RP is equal to KP into concentration of M radical into concentration of M and that is KP is equal to KI over KT to the power half M to the power 2 and that is equation number 9.

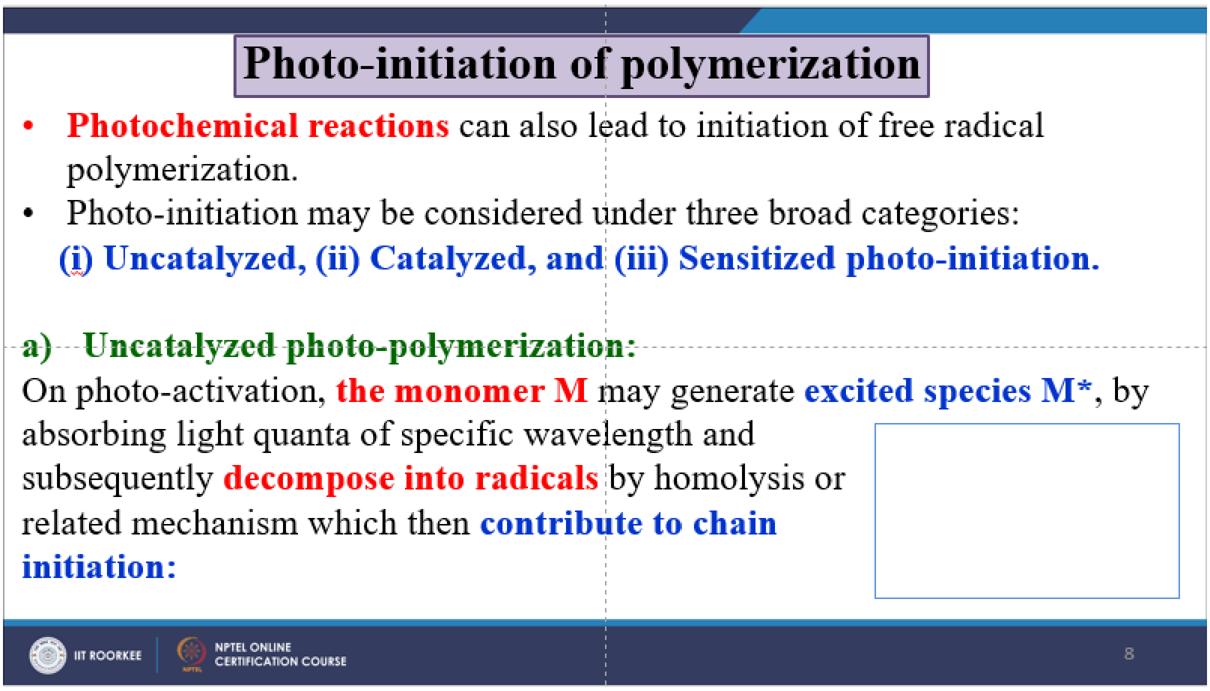

Photo-initiation of polymerization

- **Photochemical reactions** can also lead to initiation of free radical polymerization.
- Photo-initiation may be considered under three broad categories:
  (i) Uncatalyzed, (ii) Catalyzed, and (iii) Sensitized photo-initiation.

a) Uncatalyzed photo-polymerization:

On photo-activation, **the monomer M** may generate **excited species M***, by absorbing light quanta of specific wavelength and subsequently **decompose into radicals** by homolysis or related mechanism which then **contribute to chain initiation:**

Now let us talk about the photo initiation of polymerization the photochemical reaction can also lead to initiation of free radical polymerization and photo initiation may be considered under 3 broad categories one is the uncatalyzed then second is the catalyzed and third one is the sensitized photo initiation. Let us talk about the uncatalyzed photopolymerization. So, on photo activation the monomer M may generate excited species of M star by absorbing the quantum of the light of a specific wavelength and subsequently decompose into the radicals by homolysis or related mechanism which then contribute to chain initiation.

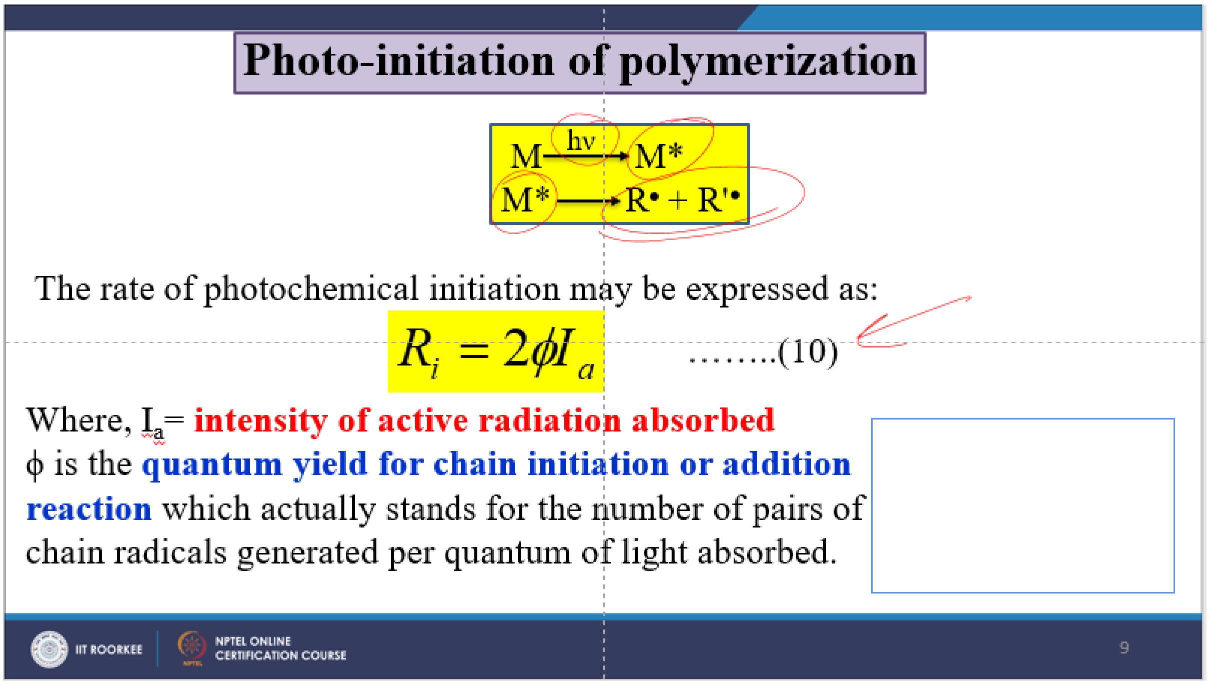

Photo-initiation of polymerization

$$M \xrightarrow{h\nu} M^*$$
$$M^* \longrightarrow R^\bullet + R'^\bullet$$

The rate of photochemical initiation may be expressed as:

$$R_i = 2\phi I_a \quad \text{........(10)}$$

Where, I_a= **intensity of active radiation absorbed**

ϕ is the **quantum yield for chain initiation or addition reaction** which actually stands for the number of pairs of chain radicals generated per quantum of light absorbed.

$R_i = 2\varphi I_a$

Like here you see that it absorbs the light and then gives the M radical and this M radical further form this R radicals. The rate of photochemical initiation this can be expressed by this particular equation Ri is equal to 2 phi Ia where Ia is the intensity of active radiation absorbed and phi is the quantum yield of chain initiation or addition reaction which actually stands for the number of pairs of chain radical generated per quantum of light absorbed. Now assuming that the incident light intensity does not miserably vary with the thickness of the reaction mass. Suppose this is the reaction and this is the light intensity so it is not it is independent of the reaction mass and Ia will be proportional to the product of the intensity of the incident light I naught epsilon is the molar absorption coefficient for the active radiation and the monomer concentration is so Ia is equal to epsilon I naught into concentration of M this is this can be represented as equation 11. So, if we combine this previous equation number 10 and 11 then we get this Rp value which can be represented as equation number 12.

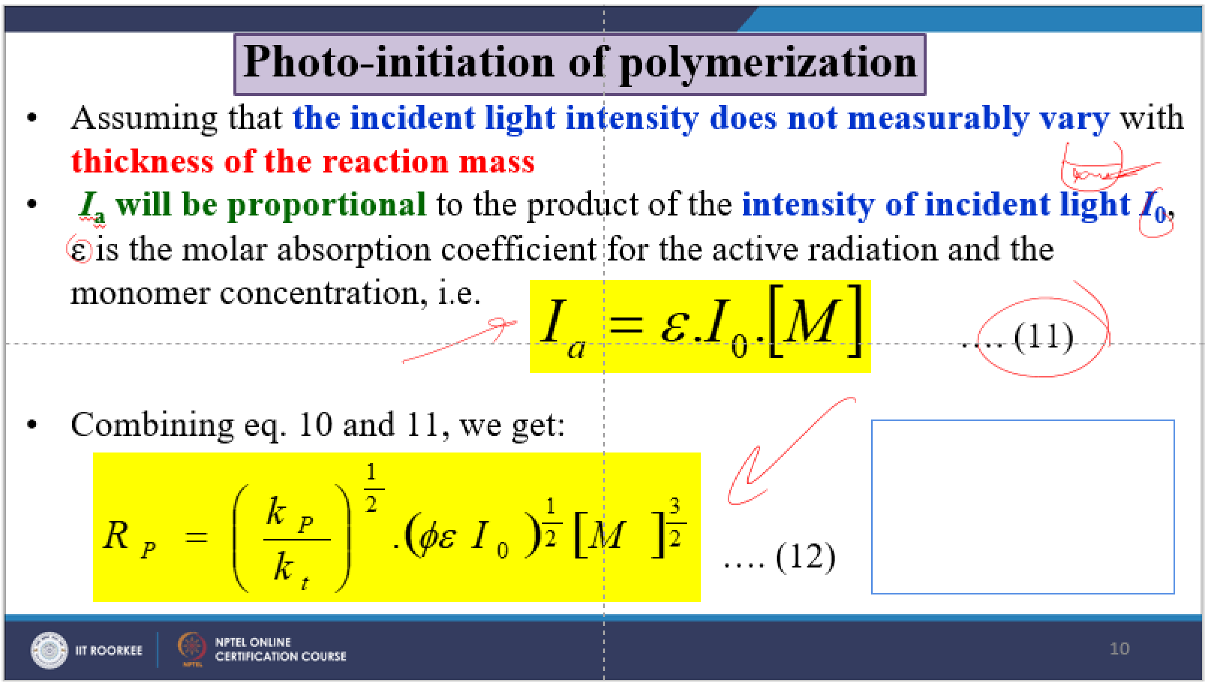

Photo-initiation of polymerization

- Assuming that **the incident light intensity does not measurably vary** with **thickness of the reaction mass**
- I_a **will be proportional** to the product of the **intensity of incident light** I_0, ε is the molar absorption coefficient for the active radiation and the monomer concentration, i.e. $I_a = \varepsilon . I_0 . [M]$ …. (11)
- Combining eq. 10 and 11, we get:

$$R_P = \left(\frac{k_P}{k_t}\right)^{\frac{1}{2}} .(\phi\varepsilon I_0)^{\frac{1}{2}} [M]^{\frac{3}{2}} \quad …. (12)$$

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Now let us talk about the second category that is a catalyzed photopolymerization. In the case of photopolymerize using the photo active additive as a catalyst or initiator in the monomer the photo initiator readily undergoes photolysis to generate the radicals which then initiate the chain polymerization. So, if you use a simple carbonyl compound such as ketone of a general formula R-C-O-O-R the radical generation reaction showing the photolysis of the ketone this can be represented as per this particular formula. Now many thermal initiators which produce specific radicals on thermal homolytic cleavage of a specific bond also undergo the photolytic decomposition to produce the same type of a radicals. Now the photo activation allows the use of wide range of chemicals as polymerization initiators in comparison with the thermal catalysts process.

$$I_a = \varepsilon . I_0 . [M]$$

$$R_P = \left(\frac{k_P}{k_t}\right)^{\frac{1}{2}} . (\varphi \varepsilon I_0)^{\frac{1}{2}} [M]^{\frac{3}{2}}$$

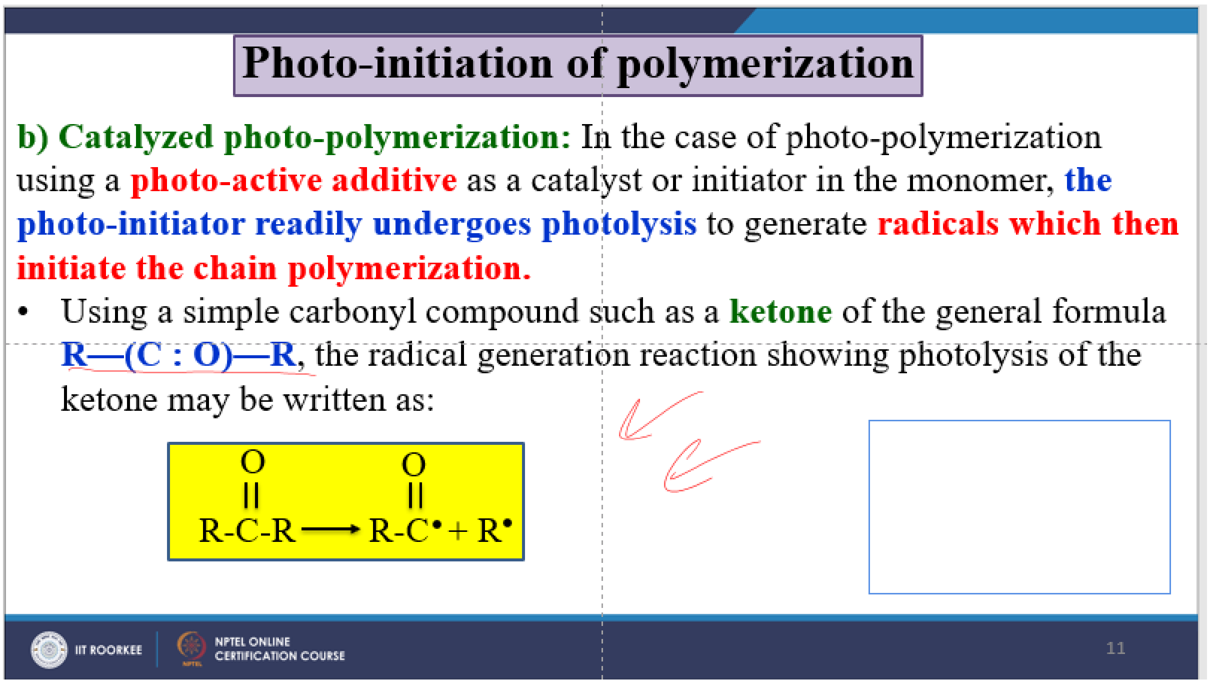


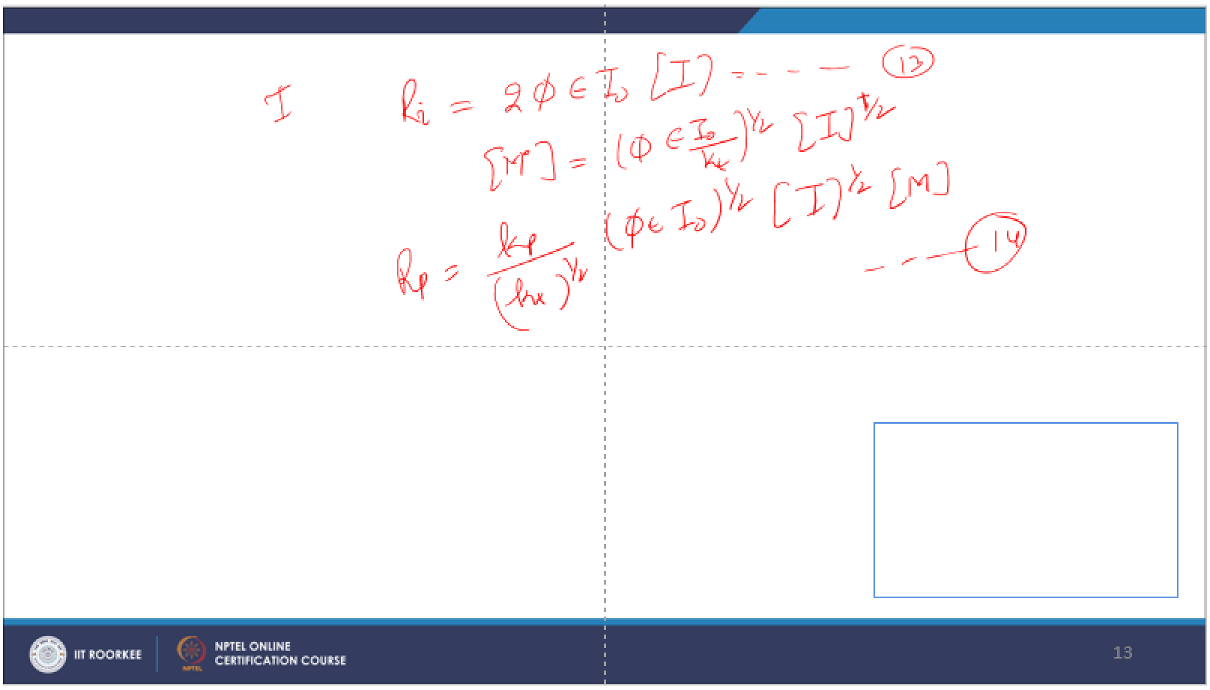
Photo-initiation of polymerization

b) Catalyzed photo-polymerization: In the case of photo-polymerization using a **photo-active additive** as a catalyst or initiator in the monomer, **the photo-initiator readily undergoes photolysis** to generate **radicals which then initiate the chain polymerization.**

- Using a simple carbonyl compound such as a **ketone** of the general formula **R—(C : O)—R**, the radical generation reaction showing photolysis of the ketone may be written as:

$$R\text{-}\overset{\overset{O}{||}}{C}\text{-}R \longrightarrow R\text{-}\overset{\overset{O}{||}}{C}^{\bullet} + R^{\bullet}$$

Now thermolysis occurs at a too high temperature and generally lead to the generation of a wide spectrum of radicals at various chemical bonds and they break up randomly. Now here if we see the rate of initiation using the photo initiator I this is given by R I is equal to 2 phi epsilon I naught into I that is equation number 13. Now hence the under steady state and assuming the bimolecular termination the concentration of M radical this can be represented which phi epsilon I naught over k t to the power half into I to the power half. The rate of related photo polymerization is given by R p is equal to k p over k t to the power half phi epsilon I naught to the power half into I to the power half this can be represented as equation number 14. Now the number average degree of polymerization is usually given by the average number of monomer molecule consumed per polymer molecule.



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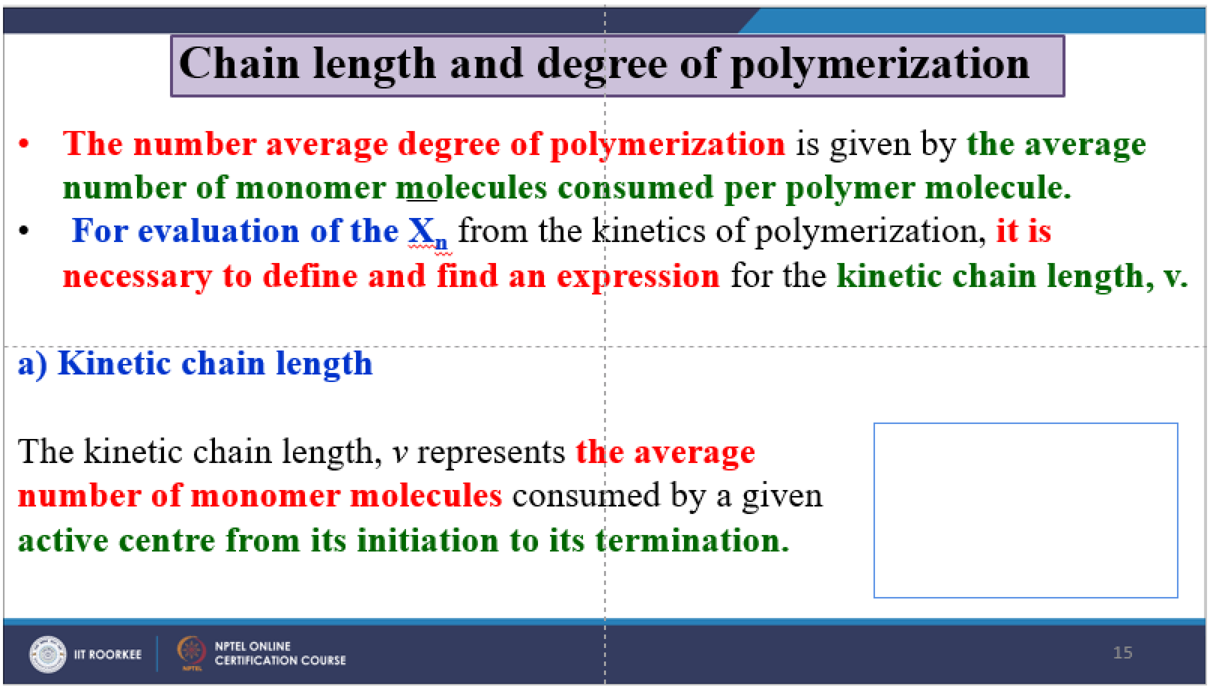
$$R_i = 2\phi\epsilon I_0 [I] \text{ ---- } ⑬$$

$$[M^{\bullet}] = \left(\frac{\phi\epsilon I_0}{k_t}\right)^{1/2} [I]^{1/2}$$

$$R_p = \frac{k_p}{(k_t)^{1/2}} (\phi\epsilon I_0)^{1/2} [I]^{1/2} [M] \text{ ---- } ⑭$$

So, the for evaluation of X n from the kinetic polymerization it is necessary to define and find an expression for the kinetic chain length and nu. Now the kinetic chain length the kinetic chain length nu represents the average number of monomer molecule consumed by the given active center from its initiation to its termination. Now here the kinetic chain length is viewed as a ratio of the rate of propagation R p to the rate of initiation or to the rate of termination R t. So, these three terms are very important rate of propagation, rate of initiation and rate of termination R t. Now since R i is equal to R t that is the rate of initiation is equal to rate of termination under the steady state condition.



Chain length and degree of polymerization

- **The number average degree of polymerization** is given by **the average number of monomer molecules consumed per polymer molecule.**
- **For evaluation of the X_n** from the kinetics of polymerization, **it is necessary to define and find an expression** for the **kinetic chain length, v.**

a) Kinetic chain length

The kinetic chain length, *v* represents **the average number of monomer molecules** consumed by a given **active centre from its initiation to its termination.**

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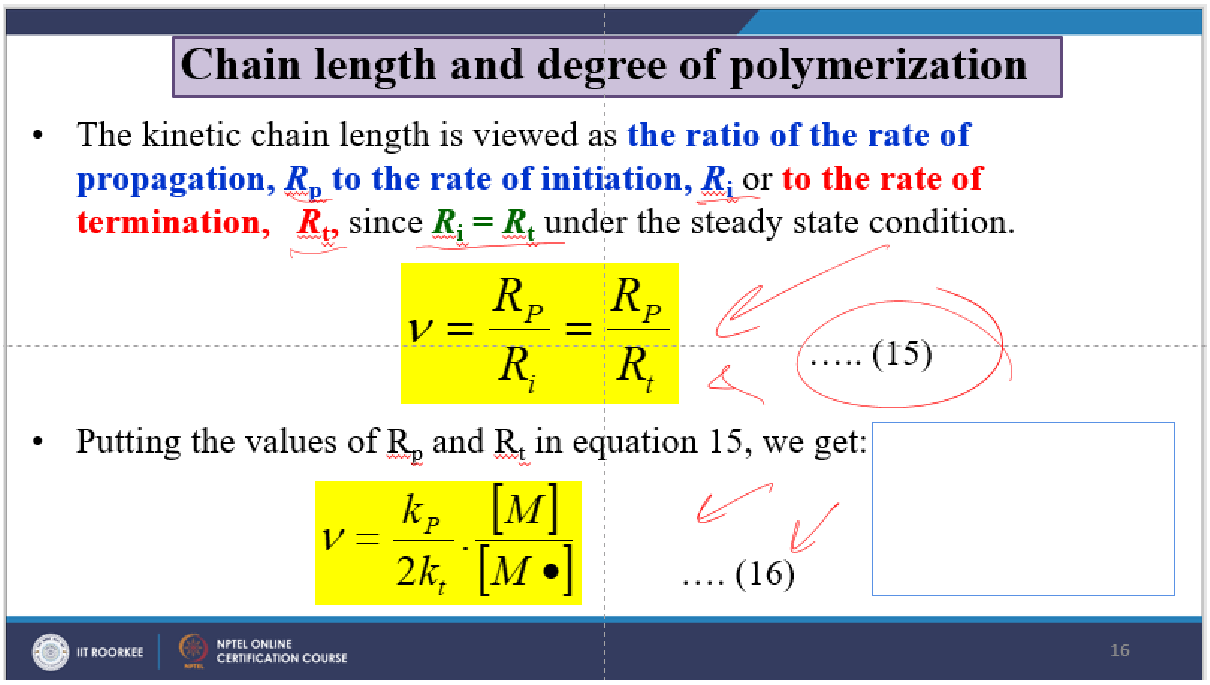
So, we can write that nu is equal to R p over R i is equal to R p over R t and that can be written as equation number 15. Now if we put the value of R p and R t in the equation 15 this in equation then we get nu is equal to K p over 2 K t into concentration of monomer and over concentration of monomer radical. So, this can be represented as equation number 16. So, if we eliminate the radical concentration term this m dot then the nu can be represented as nu is equal to K p to the power 2 over 2 K t into concentration of monomer to the power 2 over R p and that can be represented as equation 17. That the kinetic chain length is inversely proportional to the chain radical concentration.

$$\nu = \frac{R_P}{R_i} = \frac{R_P}{R_t}$$

$$\nu = \frac{k_P}{2k_t} \cdot \frac{[M]}{[M\bullet]}$$



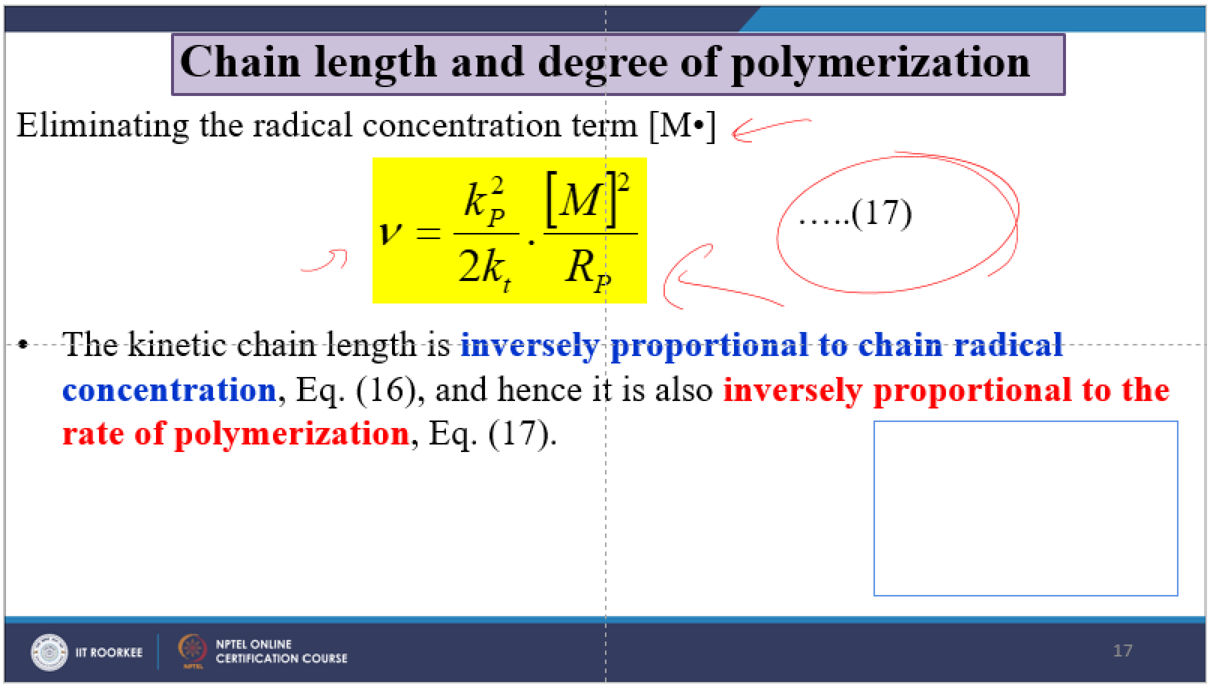
Chain length and degree of polymerization

- The kinetic chain length is viewed as **the ratio of the rate of propagation, R_p to the rate of initiation, R_i** or **to the rate of termination, R_t**, since $R_i = R_t$ under the steady state condition.

$$\nu = \frac{R_P}{R_i} = \frac{R_P}{R_t} \quad \text{….. (15)}$$

- Putting the values of R_p and R_t in equation 15, we get:

$$\nu = \frac{k_P}{2k_t} \cdot \frac{[M]}{[M\bullet]} \quad \text{…. (16)}$$



Chain length and degree of polymerization

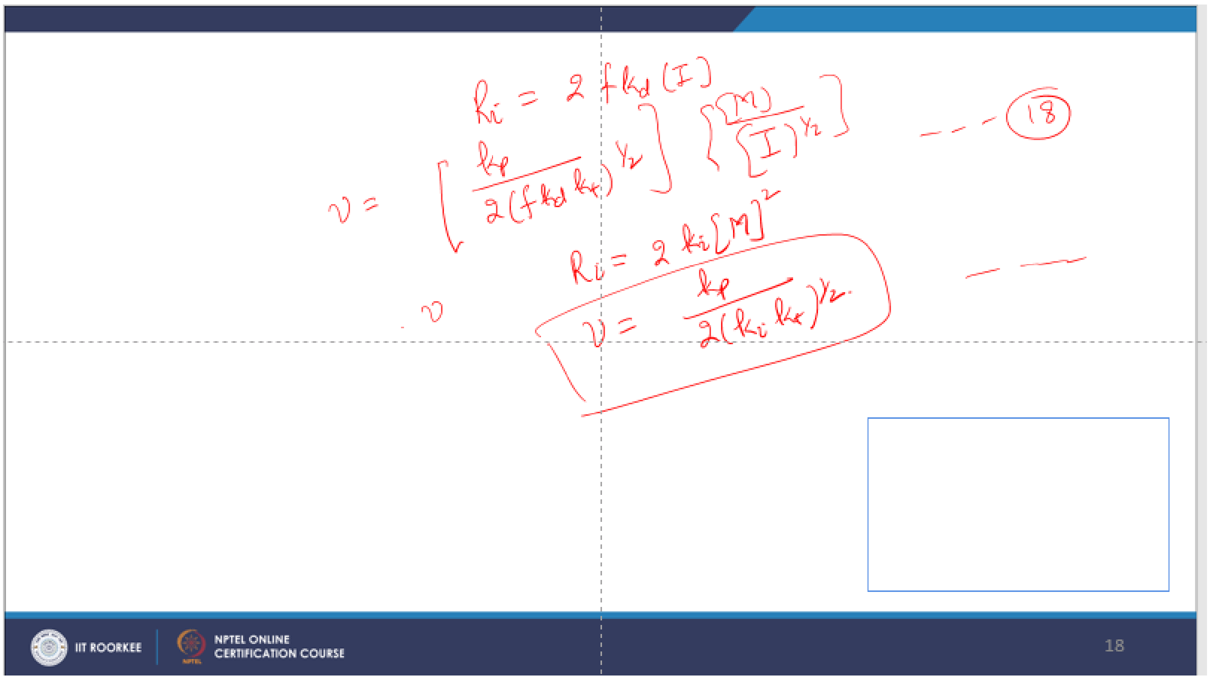
Eliminating the radical concentration term [M•]

$$\nu = \frac{k_P^2}{2k_t} \cdot \frac{[M]^2}{R_P} \quad \text{…..(17)}$$

- The kinetic chain length is **inversely proportional to chain radical concentration**, Eq. (16), and hence it is also **inversely proportional to the rate of polymerization**, Eq. (17).

So, equation 16 and hence it is also inversely proportional to the rate of polymerization this can be represented by the equation number 17. Now for polymerization initiated through the radical generated by the thermal decomposition of an initiator I the equation 6 which we represented earlier and R i that is equal to 2 F K d I this may be combined to give an alternate expression for nu. So, nu can be is K p over 2 F K d K t to the power half and then this can be concentration of m over initiator concentration to the power half this can be represented as equation 18.

$$\nu = \frac{k_P^2}{2k_t} \cdot \frac{[M]^2}{R_P}$$

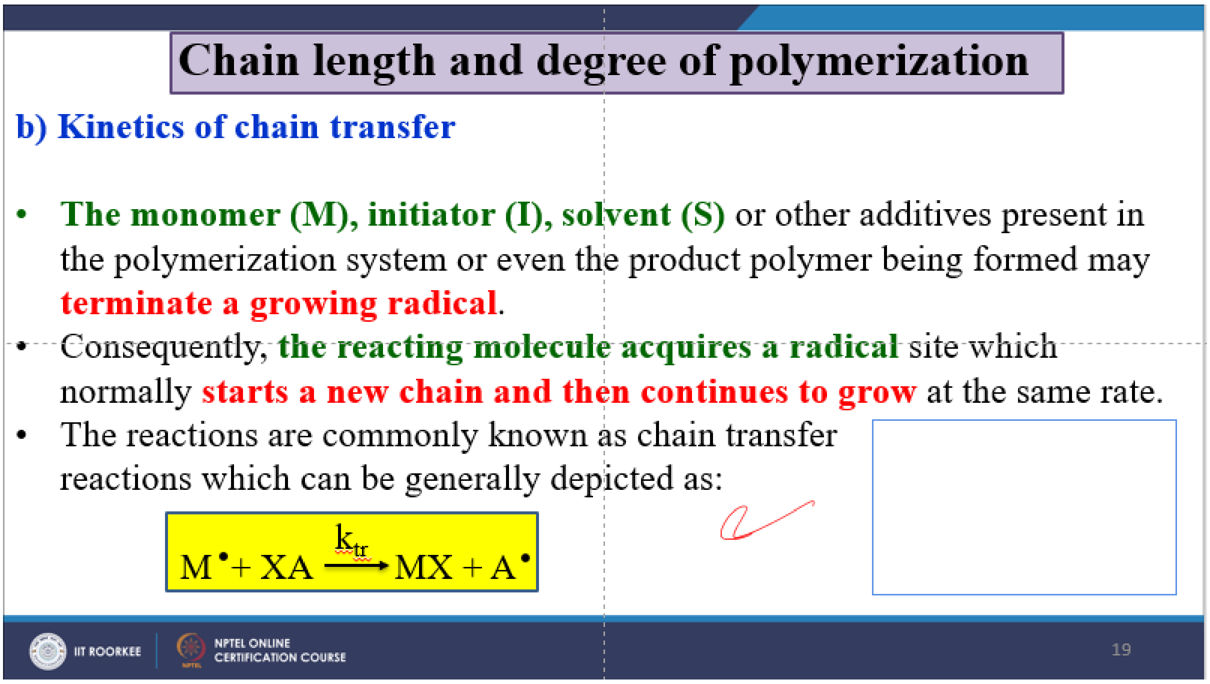


$$R_i = 2 f k_d (I)$$

$$\nu = \left[\frac{k_p}{2(f k_d k_t)^{1/2}} \right] \left\{ \frac{[M]}{[I]^{1/2}} \right\} \quad \text{---} \quad ⑱$$

$$R_i = 2 k_i [M]^2$$

$$\boxed{\nu = \frac{k_p}{2(k_i k_t)^{1/2}}}$$



Chain length and degree of polymerization

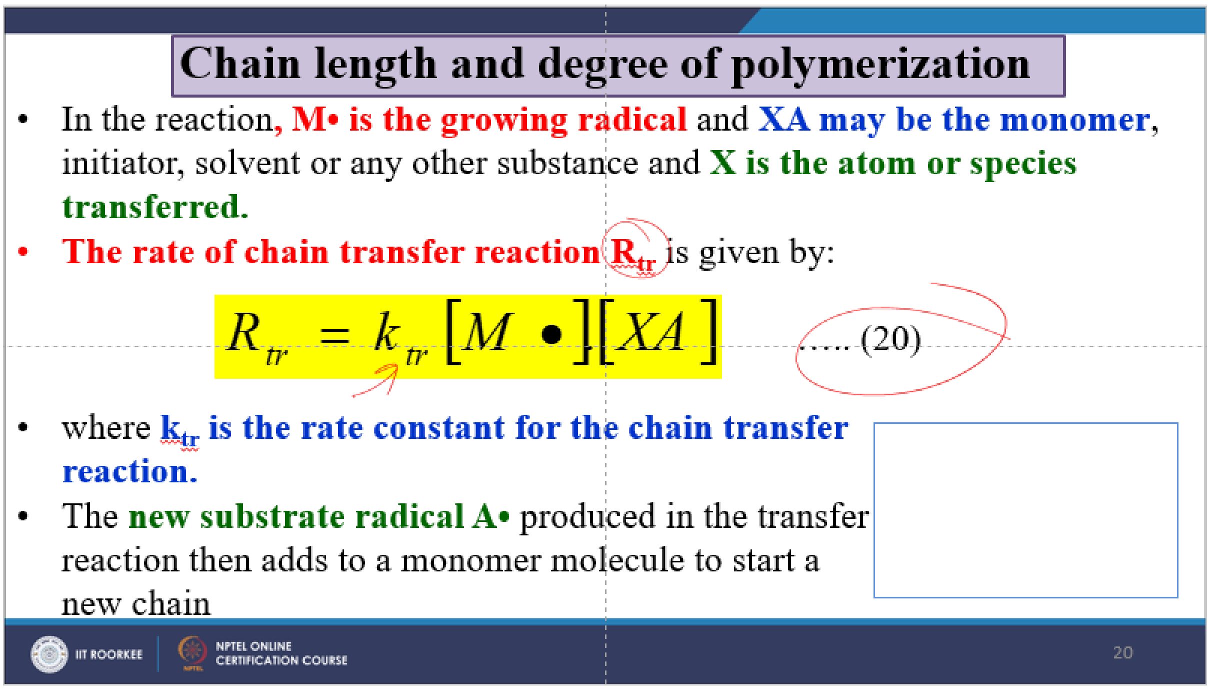
b) Kinetics of chain transfer

- **The monomer (M), initiator (I), solvent (S)** or other additives present in the polymerization system or even the product polymer being formed may **terminate a growing radical**.
- Consequently, **the reacting molecule acquires a radical** site which normally **starts a new chain and then continues to grow** at the same rate.
- The reactions are commonly known as chain transfer reactions which can be generally depicted as:

$$M^{\bullet} + XA \xrightarrow{k_{tr}} MX + A^{\bullet}$$

Now for purely thermal polymerization an alternative expression of nu may be obtained by if we combine the equation 9 which we discussed previously and R i is equal to 2 K i into concentration of m to the power 2. So, we get nu is equal to K p over 2 K i K t to the power half this can be represented as equation number 19.

Now let us talk about the kinetics of chain transfer. The monomer M initiator I and solvent S or other additive present in the polymerization system or even the product polymer being formed may terminate a growing radical because once the initiation occurs then propagation and then it is quite obvious to get the useful property of the polymer the chain must be terminated. Consequently, the reacting molecule acquires a radical site which normally starts a new chain and then continues to grow at the same rate. The reactions are commonly known as the chain transfer reaction which can be generally depicted as m dot plus X A is equal to K t r m X plus A dot. Now, this is where K t r represents the termination aspect.



Chain length and degree of polymerization

- In the reaction, **M• is the growing radical** and **XA may be the monomer**, initiator, solvent or any other substance and **X is the atom or species transferred.**
- **The rate of chain transfer reaction R_{tr}** is given by:

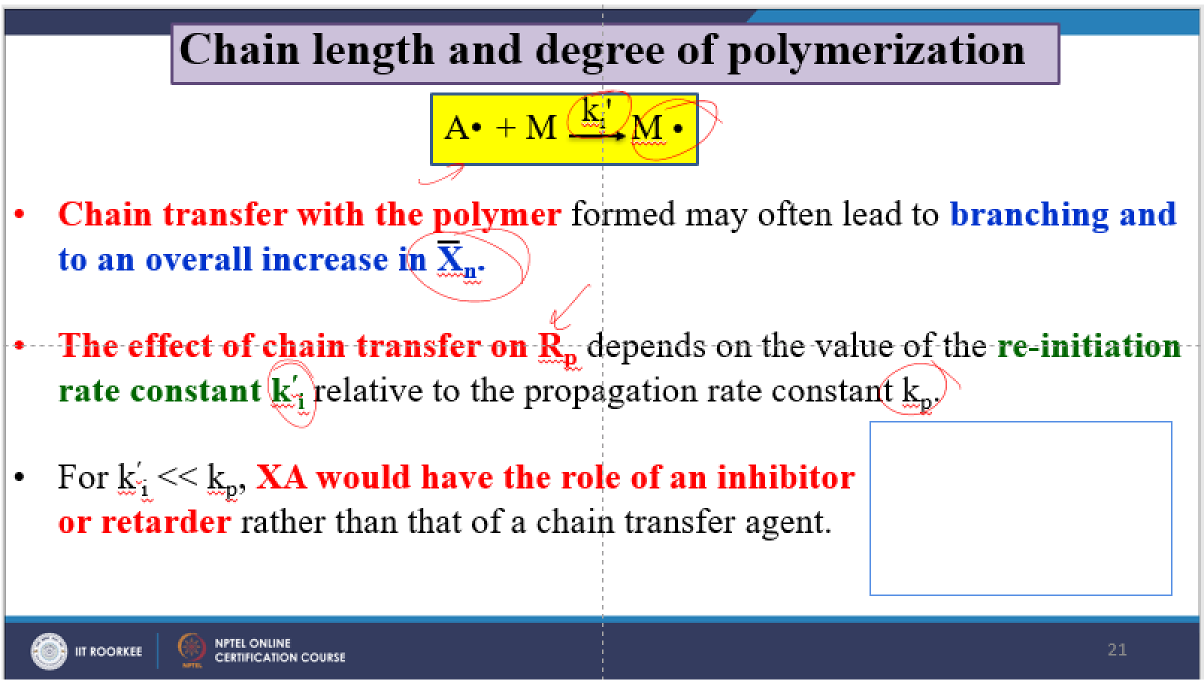
$$R_{tr} = k_{tr}[M\bullet][XA] \quad \text{.....(20)}$$

- where **k_{tr} is the rate constant for the chain transfer reaction.**
- The **new substrate radical A•** produced in the transfer reaction then adds to a monomer molecule to start a new chain

Rate of chain transfer reaction R_{tr}

$$R_{tr} = k_{tr}[M\bullet].[XA]$$

Now in the reaction m dot is the growing radical and X A may be the monomer initiator solvent or any other substance and X is the atom or a species that is transferred. So, the rate of chain transfer reaction R t r that is given by R t r is equal to K t r m dot X A and that is the equation number 20. So here this K t r is the rate constant for the chain transfer reaction. The new substrate radical A dot produced in the transfer reaction then adds to a monomer molecule to start a new chain. Now here this A dot plus m is equal to m dot and where the rate constant is K i dash.

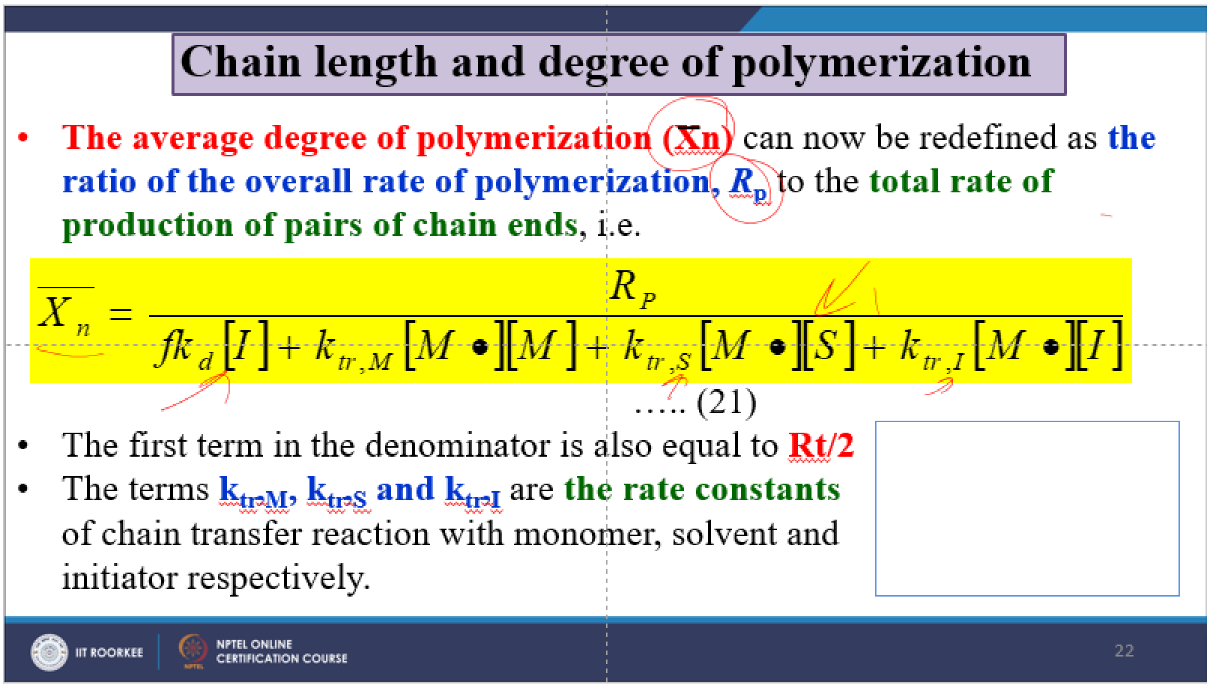


Chain length and degree of polymerization

$$A\bullet + M \xrightarrow{k_i'} M\bullet$$

- **Chain transfer with the polymer** formed may often lead to **branching and to an overall increase in $\bar{X}_n$.**
- **The effect of chain transfer on R_p** depends on the value of the **re-initiation rate constant k_i'** relative to the propagation rate constant k_p.
- For $k_i' \ll k_p$, **XA would have the role of an inhibitor or retarder** rather than that of a chain transfer agent.

Now the chain transfer with the polymer form may often lead to the branching and to an overall increase in number average molecule. Now the effect of chain transfer on R p that is the rate of propagation this depends on the value of the re initiation rate constant and that is K i dot this relative to the propagation rate constant K p. Now if you take a case that K i dash is less than less than the rate constant of propagation then X A would have the role of an initiator or retarder rather than that of a chain transfer agent. So the average degree of polymerization bar X n now bar X n now can be redefined as the ratio of the overall rate of polymerization R p to the total rate of production of pairs of chain end and thus this can be represented as the average degree of polymerization X n bar over R p over F K D concentration of i plus K t R m that is m dot m dot plus K t R is m dot then S plus K t R m dot i. The first term in this denominator is also equal to R t over t and the term K t R and K t R S and K t R S are the rate constant of the chain transfer reaction with monomer this represent the solvent and initiator respectively.



Chain length and degree of polymerization

- **The average degree of polymerization (Xn)** can now be redefined as **the ratio of the overall rate of polymerization, R_p** to the **total rate of production of pairs of chain ends**, i.e.

$$\overline{X}_n = \frac{R_P}{fk_d[I] + k_{tr,M}[M\bullet][M] + k_{tr,S}[M\bullet][S] + k_{tr,I}[M\bullet][I]}$$

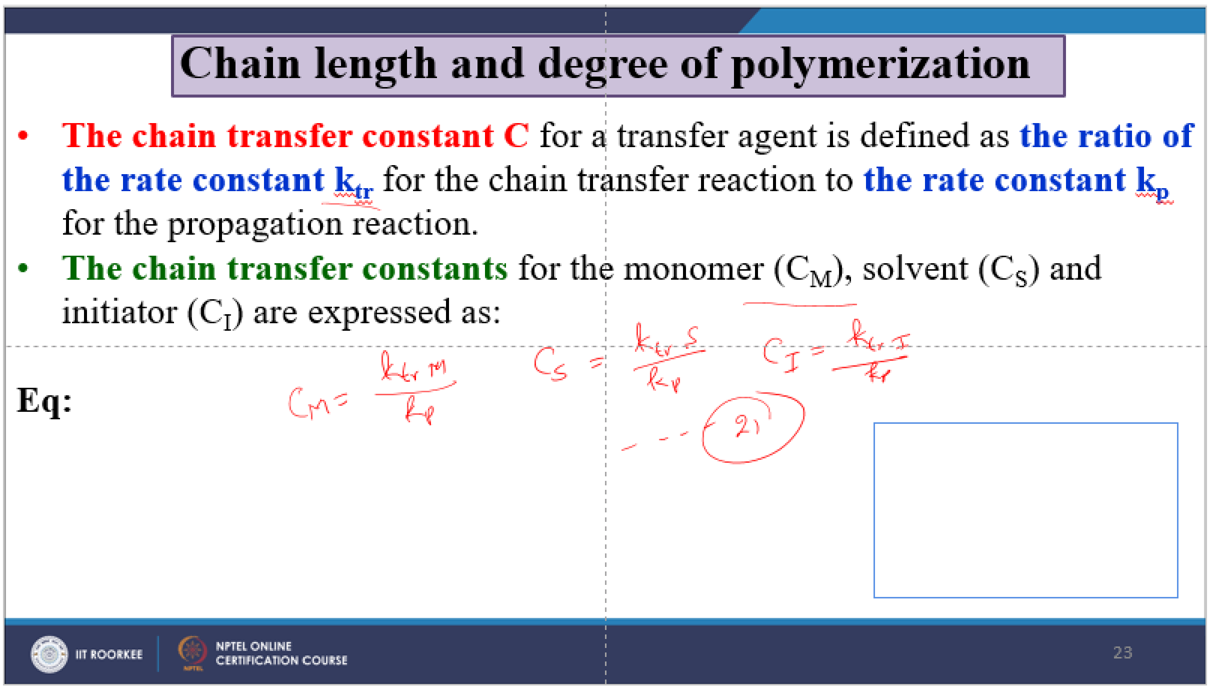
….. (21)

- The first term in the denominator is also equal to **Rt/2**
- The terms **$k_{tr,M}$, $k_{tr,S}$ and $k_{tr,I}$** are **the rate constants** of chain transfer reaction with monomer, solvent and initiator respectively.

So, the chain transfer constant C for the transfer agent is defined as the ratio of the rate constant K t R for the chain transfer reaction to the rate constant K p for the propagation reaction. Now the chain transfer constant for the monomer C m solvent C S and initiator C i this can be represented as C m is equal to K t R m over K p C S is equal to K t R S over K p and C i is equal to K t R i over K p this we can refer as equation number 21.

Total rate of production of pairs of chain ends

$$\overline{X_n} = \frac{R_P}{fk_d[I] + k_{tr,M}[M\bullet][M] + k_{tr,S}[M\bullet][S] + k_{tr,I}[M\bullet][I]}$$



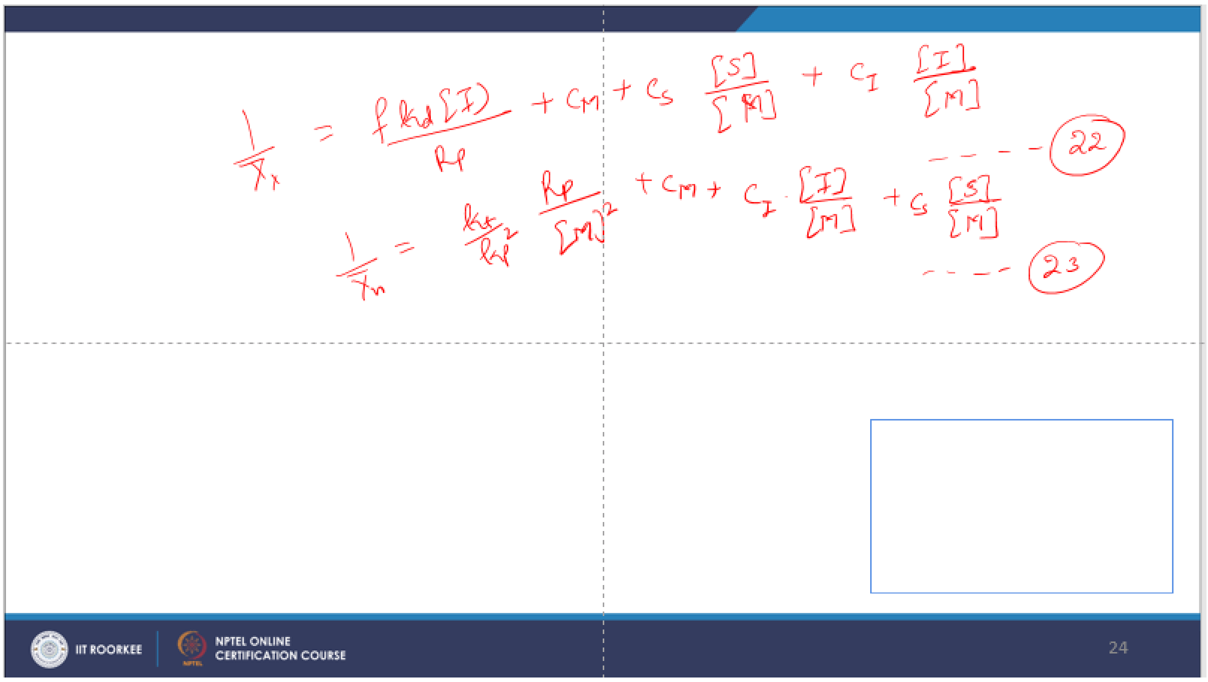
Chain length and degree of polymerization

- **The chain transfer constant C** for a transfer agent is defined as **the ratio of the rate constant k_{tr}** for the chain transfer reaction to **the rate constant k_p** for the propagation reaction.
- **The chain transfer constants** for the monomer (C_M), solvent (C_S) and initiator (C_I) are expressed as:

Eq:

$C_M = \frac{k_{tr\,M}}{k_p}$ $C_S = \frac{k_{tr\,S}}{k_p}$ $C_I = \frac{k_{tr\,I}}{k_p}$

- - - (21)

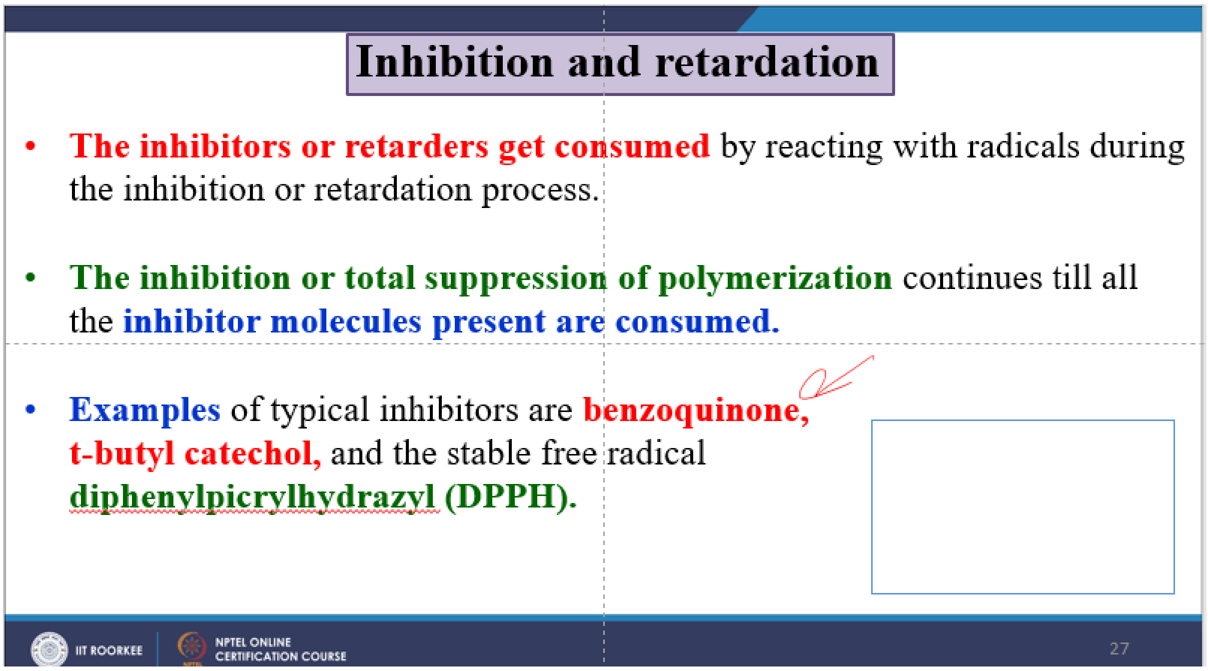


$$\frac{1}{\bar{X}_n} = \frac{f k_d [I]}{R_p} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]} \quad ----\ (22)$$

$$\frac{1}{\bar{X}_n} = \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + C_M + C_I \cdot \frac{[I]}{[M]} + C_S \frac{[S]}{[M]} \quad ----\ (23)$$

Now if we combine these equation 20 and 21 so we get 1 over bar X n is equal to F K D initiator concentration over R p plus C m plus C S S concentration of solvent then concentration of monomer plus C i concentration of initiator and concentration of monomer this can be represented as equation number 22. So which may also be expressed alternatively as 1 over X n bar X n is equal to K t over K p to the power 2 R p m to the power 2 plus C m plus C i bar C i into concentration of i over concentration m plus C S concentration of solvent over concentration of monomer this can be represented as equation number 23. Now there are certain substances which when present in the monomer or the polymerization system suppress the chain growth process to different degree there may be varying degree of suppression usually by reacting with the initiating radicals or with chain radicals.

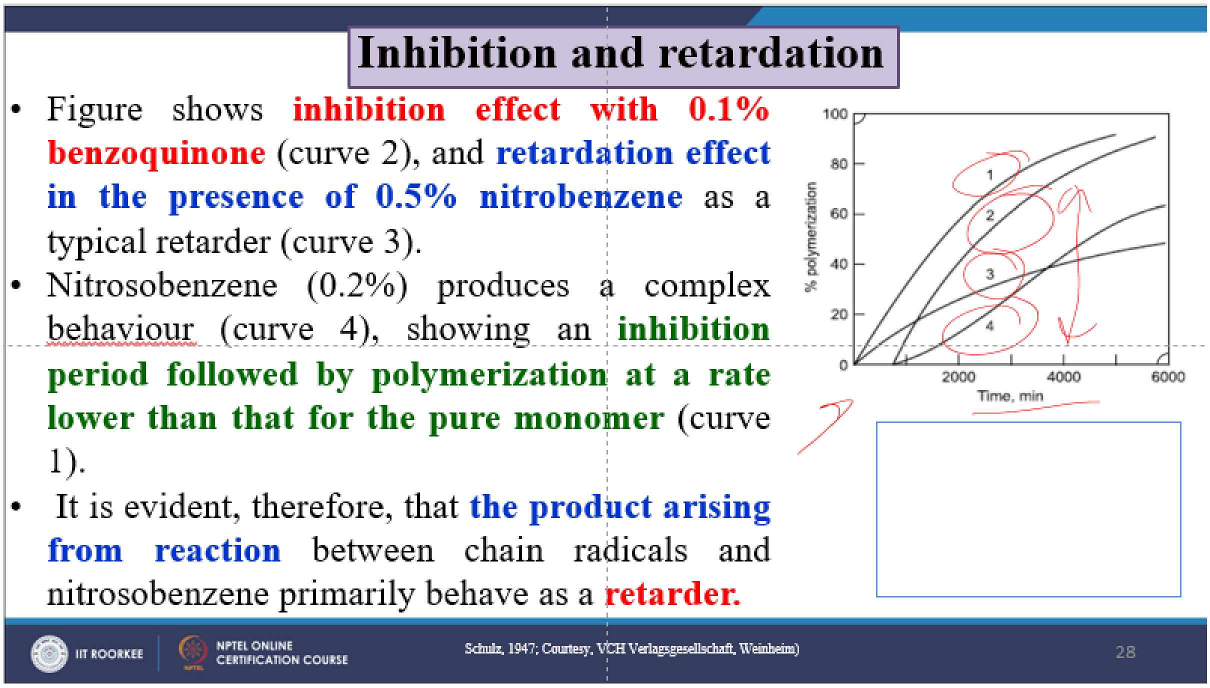
They convert the radicals to non radical species or inactive radicals or radicals too low in reactivity to undergo meaningful propagation and such substances or radicals scavengers are classified as inhibitors. Now let us talk about the inhibition and retardation. Now inhibitors effectively consume every radicals whatever being generated in due course of time in the system and completely suppress the polymerization and reduce the rate of polymerization substantially to 0. So the introduction of inhibitor should be at appropriate time. So on the other hand the substance not as effectively or much or less efficiently so that both the rate of polymerization and the degree of polymerization are reduced quite miserably without completely halting the propagation process and they are called as retarders.



Inhibition and retardation

- **The inhibitors or retarders get consumed** by reacting with radicals during the inhibition or retardation process.
- **The inhibition or total suppression of polymerization** continues till all the **inhibitor molecules present are consumed.**
- **Examples** of typical inhibitors are **benzoquinone, t-butyl catechol,** and the stable free radical **diphenylpicrylhydrazyl (DPPH).**

So, they reduce the rate of polymerization. Now the inhibitors or retarders they get consumed by reacting with the radicals during the inhibition or retardation process.

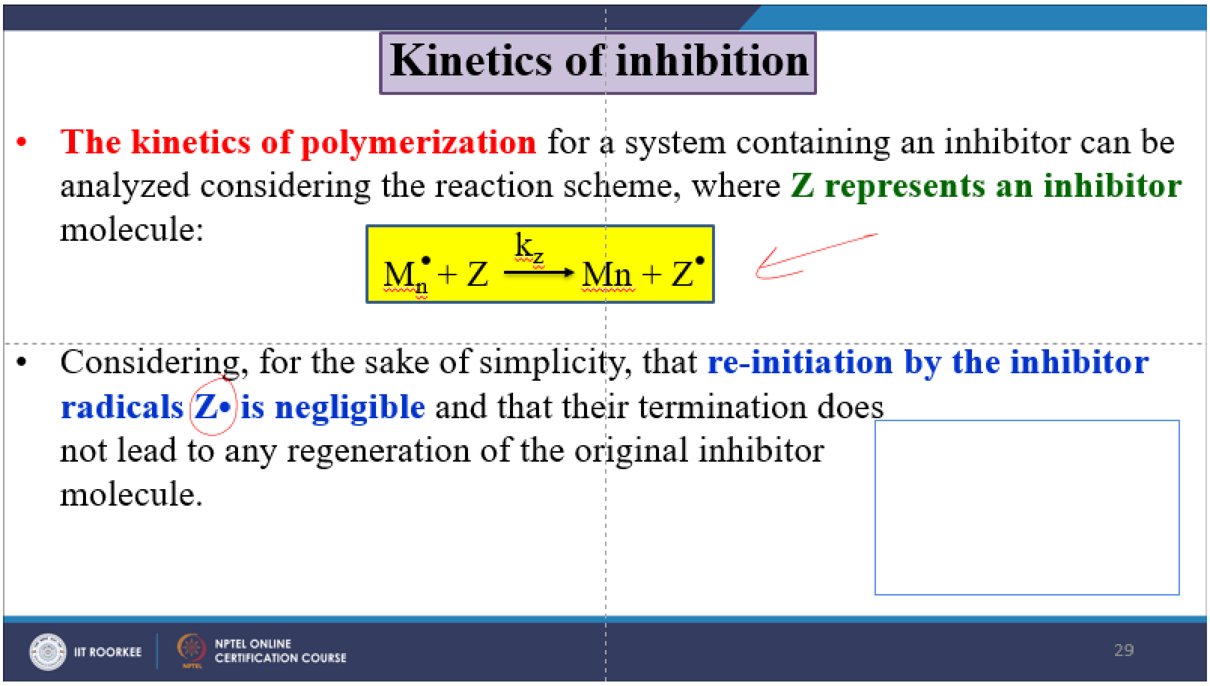


Inhibition and retardation

- Figure shows **inhibition effect with 0.1% benzoquinone** (curve 2), and **retardation effect in the presence of 0.5% nitrobenzene** as a typical retarder (curve 3).
- Nitrosobenzene (0.2%) produces a complex behaviour (curve 4), showing an **inhibition period followed by polymerization at a rate lower than that for the pure monomer** (curve 1).
- It is evident, therefore, that **the product arising from reaction** between chain radicals and nitrosobenzene primarily behave as a **retarder.**

Schulz, 1947; Courtesy, VCH Verlagsgesellschaft, Weinheim)

The inhibition or total suppression of the polymerization continues till all the inhibitors molecules they present reaction mass or a system they are get consumed. Now example of typical inhibitors are benzoquinone tertiary butyl catechol and the stable free radical some of the typical examples of inhibitors are enlisted over here. Now this particular figure shows the inhibition effect with 0.1 percent of benzoquinone this is represented as in the curve 2 and the retardation effect in the presence of 0.5 percent nitrobenzene as a typical retarder which you can see over here. The nitrobenzene 0.2 percent produces a complex behaviour showing the inhibition period followed by the polymerization at a rate lower than that of for the pure monomer which is represented as here. So, you see that the inhibition and retardation effect in this particular plot here which is plotted between the time and polymerization.



Kinetics of inhibition

- **The kinetics of polymerization** for a system containing an inhibitor can be analyzed considering the reaction scheme, where **Z represents an inhibitor** molecule:

$$M_n^\bullet + Z \xrightarrow{k_z} Mn + Z^\bullet$$

- Considering, for the sake of simplicity, that **re-initiation by the inhibitor radicals Z• is negligible** and that their termination does not lead to any regeneration of the original inhibitor molecule.

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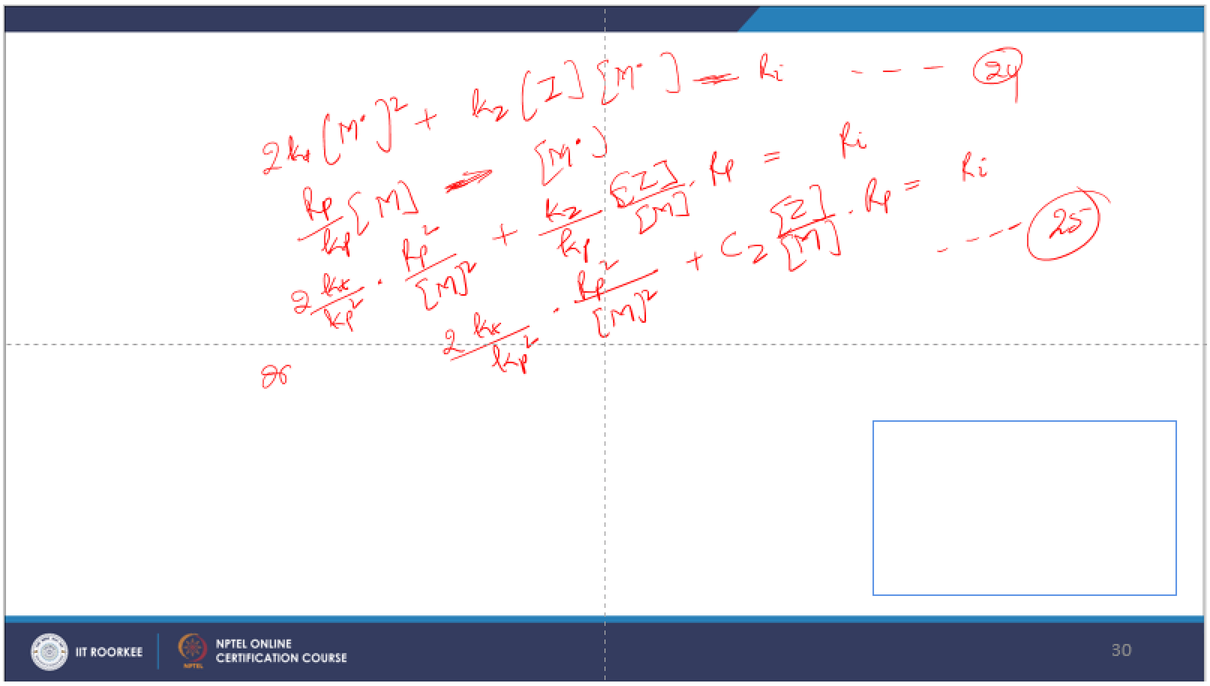
It is evident that the product arising from the reaction between the chain radical and nitrobenzene primarily behave as a retarder. Let us discuss about the kinetics of inhibition because it is quite important again it participates in the reaction mass that is why it is very important to have the discuss the kinetics of the inhibition. So, the kinetic of inhibition or the kinetic of polymerization for a system containing an inhibitor can be analyzed considering the reaction scheme. Now here let us take this particular reaction M radical M n radical plus Z k Z M n and Z dot where Z represents an inhibitor molecule. Now considering the sake of for the sake of simplicity the re-initiation by the inhibitor radicals Z dot is negligible and their termination does not lead to any regeneration of the original inhibitor molecule.



$$2k_t[M^\cdot]^2 + k_z[Z][M^\cdot] = R_i \quad \text{---} \; ⑳④$$

$$\frac{R_p}{k_p[M]} \rightarrow [M^\cdot]$$

$$2\frac{k_t}{k_p^2}\cdot\frac{R_p^2}{[M]^2} + \frac{k_z}{k_p}\frac{[Z]}{[M]}\cdot R_p = R_i$$

$$\frac{2k_t}{k_p^2}\cdot\frac{R_p^2}{[M]^2} + C_2\frac{[Z]}{[M]}\cdot R_p = R_i \quad \text{----} \; ㉕$$

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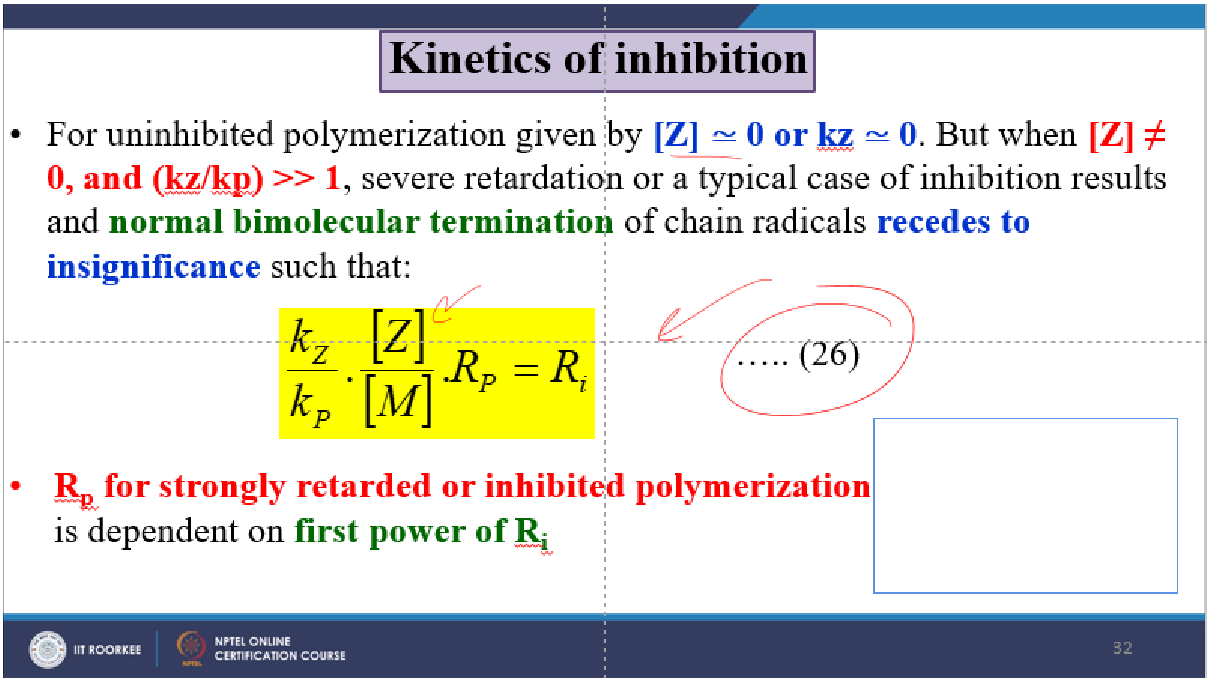
Now so the usual steady state assumption for the chain radical this gives 2 k T M dot to the power 2 plus k Z Z M dot is equal to r i. Let us say this equation number 24. Now if we substitute the term r p over k p concentration on M for the chain radical this gives 2 k T M dot we get twice k T over k p to the power 2 into r p concentration of M to the power 2 plus k Z which we have already represented k over k p into Z concentration of monomer to rate of propagation is equal to rate of initiation or twice k T over k p to the power 2 into r p to the power 2 into M to the power 2 C Z into Z into C Z. Over rate of propagation is equal to rate of initiation this can be represented as equation number 25 this is equation number 24. Now uninhibited polymerization is given by Z is equal to 0 or almost equal to 0 or k Z is equal to 0 but when Z is not equal to 0 or k Z over k p is greater than greater than 1 the severe retardation or a typical case of inhibition results and normal bimolecular termination of chain radical receded to the insignificant values such as k Z over k p into concentration of Z over concentration of M r p r i this is can be represented as equation number 26.



Kinetics of inhibition

- For uninhibited polymerization given by **[Z] $\simeq$ 0 or kz $\simeq$ 0**. But when **[Z] $\neq$ 0, and (kz/kp) >> 1**, severe retardation or a typical case of inhibition results and **normal bimolecular termination** of chain radicals **recedes to insignificance** such that:

$$\frac{k_Z}{k_P}\cdot\frac{[Z]}{[M]}.R_P = R_i \quad \text{..... (26)}$$

- **R_p for strongly retarded or inhibited polymerization** is dependent on **first power of R_i**

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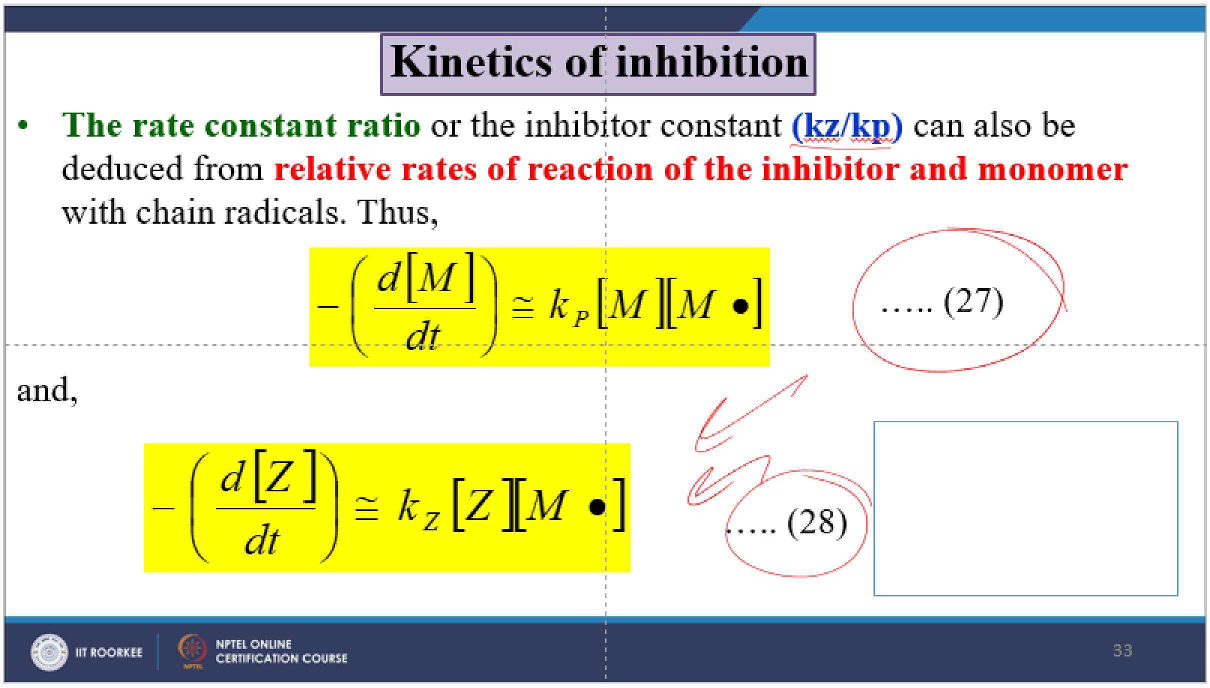
$$\frac{k_Z}{k_P}\cdot\frac{[Z]}{[M]}.R_P = R_i \text{ ....(26)}$$

Now rate of propagation for strongly retarded or inhibited polymerization is dependent on the first power of rate of initiation. So, the rate constant ratio or the inhibitor constant that is k Z over k p can also be deduced from the relative rates of reaction of the inhibitor and monomer with the chain radical. So, therefore minus d M over d T this can be equal to k p into M or M radical this can be represented as equation number 27 and minus d Z over d T is equal to k Z into Z into monomer radical this can be represented as equation number 28. So, equation 26 if you recall this equation, equation 26 readily follows and we can rearrange this gives to d Z over d M is equal to k Z over k p Z over M equal to C Z Z over M. Now for if we take a case that C Z is greater than greater than 1 for the polymerization or the monomer consumption rate will be negligible for a significant concentration of the inhibitor or strong retarder with progressive consumption of Z during the inhibition period the chain propagation assumes a competitive position only when concentration of Z reduces to a very low or insignificant values.



Kinetics of inhibition

- **The rate constant ratio** or the inhibitor constant **(kz/kp)** can also be deduced from **relative rates of reaction of the inhibitor and monomer** with chain radicals. Thus,

$$-\left(\frac{d[M]}{dt}\right) \cong k_P[M][M\bullet] \quad \text{..... (27)}$$

and,

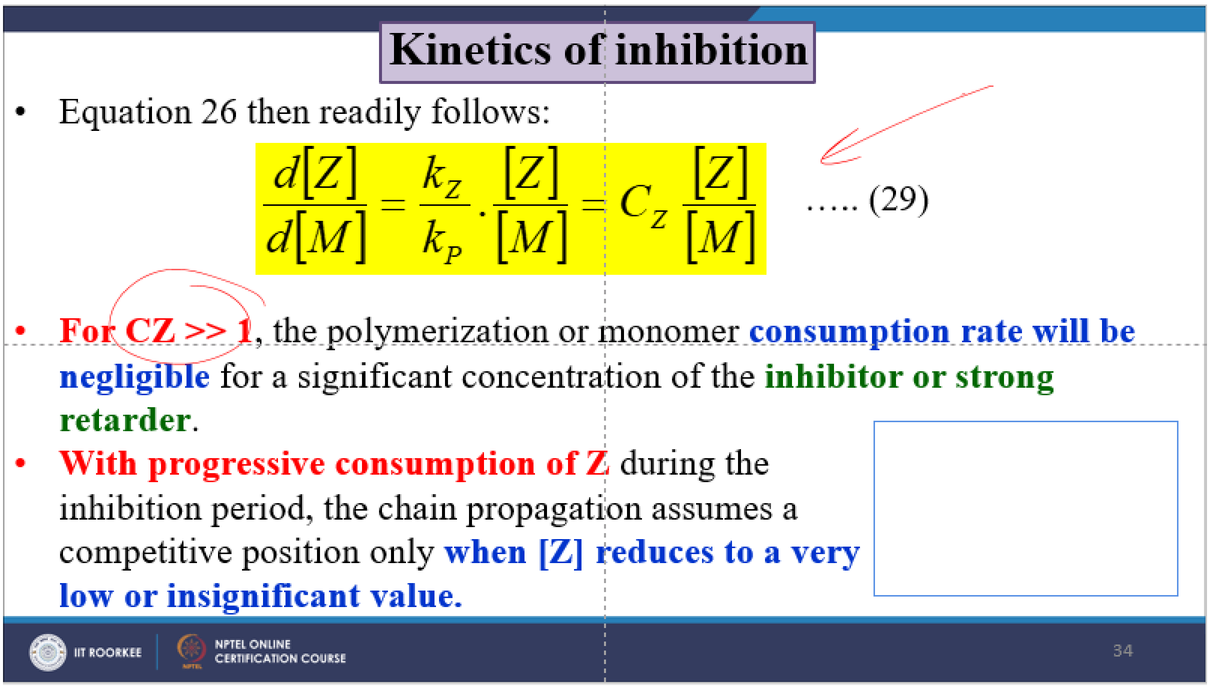
$$-\left(\frac{d[Z]}{dt}\right) \cong k_Z[Z][M\bullet] \quad \text{..... (28)}$$

So, equation 29 if we integrate this can give you this particular value log Z over Z naught is equal to C Z log M over M naught this can be represented as equation 30 where Z naught and M naught are the initial concentration of Z and M.

$$-\left(\frac{d[M]}{dt}\right) \cong k_P[M][M\bullet] \text{ ....(27)}$$

$$-\left(\frac{d[Z]}{dt}\right) \cong k_Z[Z][M\bullet] \text{ ....(28)}$$

$$\frac{d[Z]}{d[M]} = \frac{k_Z}{k_P}\cdot\frac{[Z]}{[M]} = C_Z\frac{[Z]}{[M]} \dots\dots\dots\dots\dots\dots.(29)$$

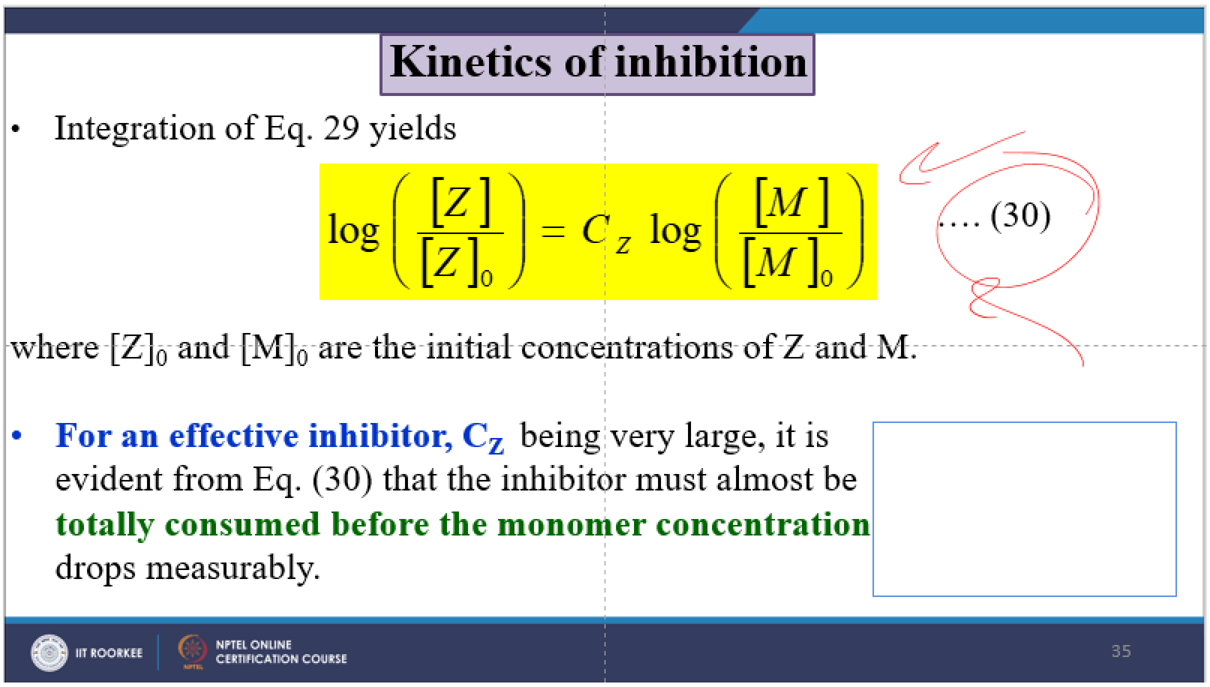


Kinetics of inhibition

- Equation 26 then readily follows:

$$\frac{d[Z]}{d[M]} = \frac{k_Z}{k_P} \cdot \frac{[Z]}{[M]} = C_Z \frac{[Z]}{[M]} \quad \ldots\ldots (29)$$

- **For CZ >> 1**, the polymerization or monomer **consumption rate will be negligible** for a significant concentration of the **inhibitor or strong retarder**.
- **With progressive consumption of Z** during the inhibition period, the chain propagation assumes a competitive position only **when [Z] reduces to a very low or insignificant value.**



Kinetics of inhibition

- Integration of Eq. 29 yields

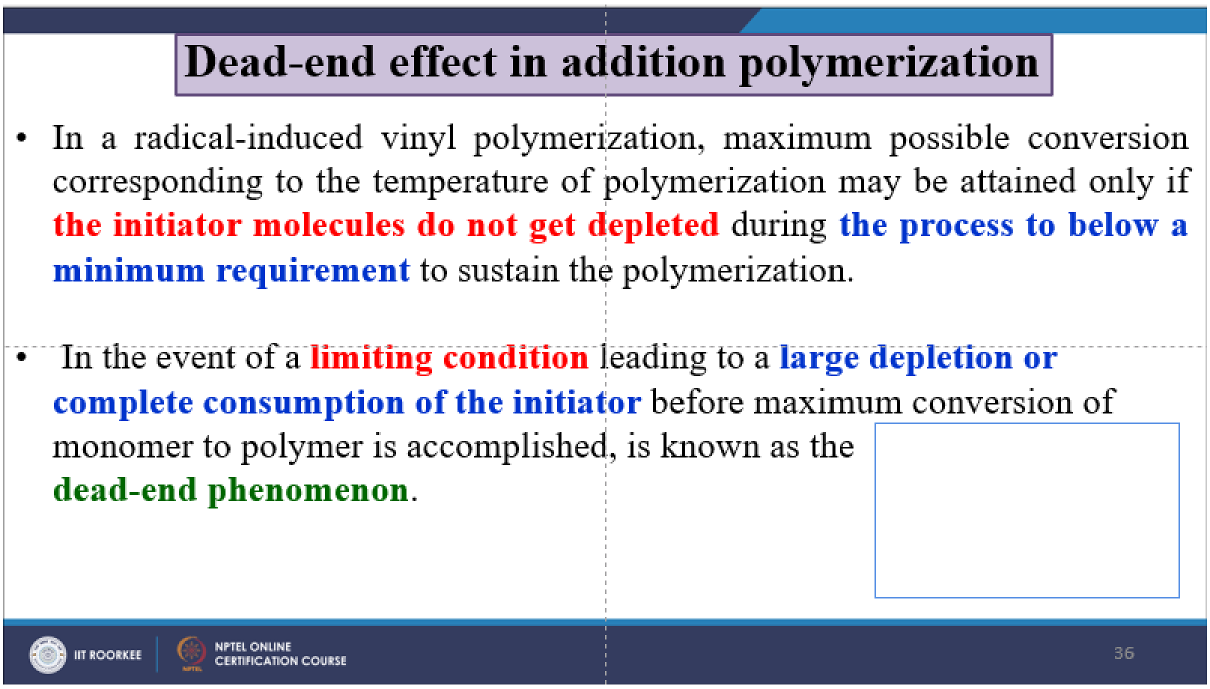
$$\log\left(\frac{[Z]}{[Z]_0}\right) = C_Z \log\left(\frac{[M]}{[M]_0}\right) \quad \ldots. (30)$$

where $[Z]_0$ and $[M]_0$ are the initial concentrations of Z and M.

- **For an effective inhibitor, C_Z** being very large, it is evident from Eq. (30) that the inhibitor must almost be **totally consumed before the monomer concentration** drops measurably.

$$\log\left(\frac{[Z]}{[Z]_0}\right) = C_Z \log\left(\frac{[M]}{[M]_0}\right)$$

Now for an effective inhibitor C Z being very large it is evident from this particular equation that the initiator must almost be totally consumed before the monomer concentration drops miserably. Let us talk about the dead-end effect in the addition polymerization in a radical induced vinyl polymerization maximum possible conversion corresponding to the temperature of polymerization may be attained only if the initiator molecule do not get depleted during the process to below a minimum requirement to sustain the polymerization this is quite obvious. Now in the event of limiting condition leading to large depletion or complete consumption of the initiator before maximum conversion of monomer to the polymer is accomplished. Now this is known as the dead-end phenomena.



Dead-end effect in addition polymerization

- In a radical-induced vinyl polymerization, maximum possible conversion corresponding to the temperature of polymerization may be attained only if **the initiator molecules do not get depleted** during **the process to below a minimum requirement** to sustain the polymerization.
- In the event of a **limiting condition** leading to a **large depletion or complete consumption of the initiator** before maximum conversion of monomer to polymer is accomplished, is known as the **dead-end phenomenon**.

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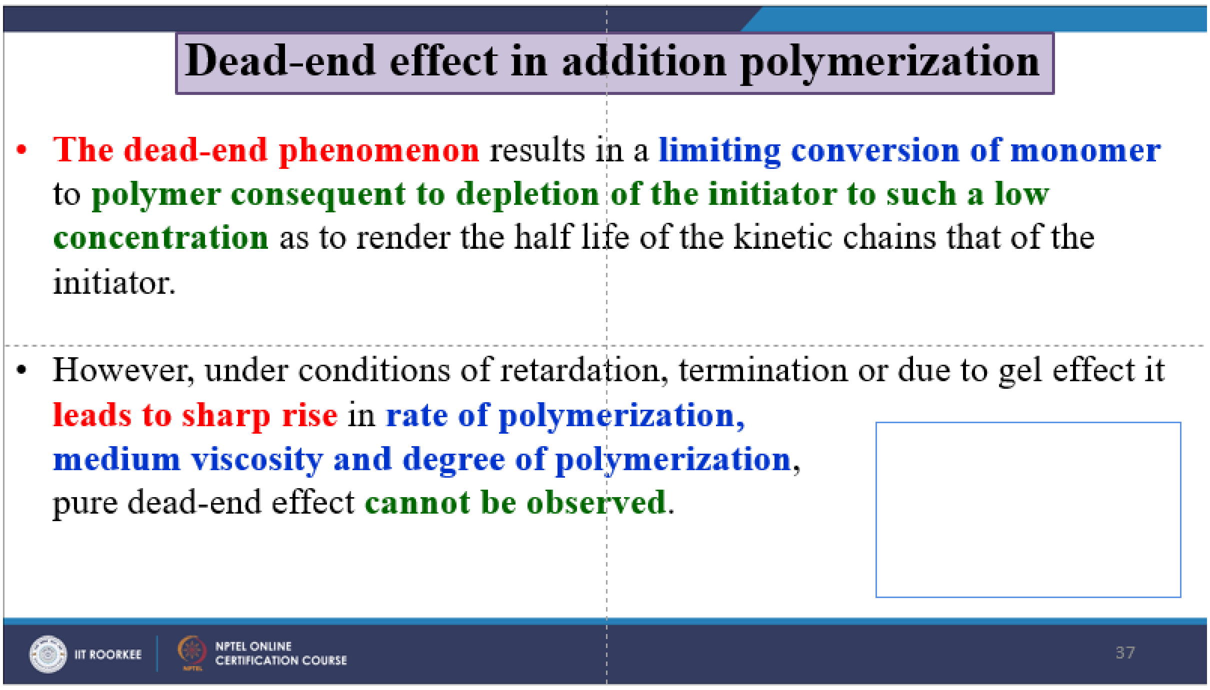
The dead-end phenomena usually results in the limiting conversion of monomer to polymer consequent to depletion of initiator to such a low concentration as to render the half-life of kinetic chain and that of the initiator.



Dead-end effect in addition polymerization

- **The dead-end phenomenon** results in a **limiting conversion of monomer** to **polymer consequent to depletion of the initiator to such a low concentration** as to render the half life of the kinetic chains that of the initiator.
- However, under conditions of retardation, termination or due to gel effect it **leads to sharp rise** in **rate of polymerization, medium viscosity and degree of polymerization**, pure dead-end effect **cannot be observed**.

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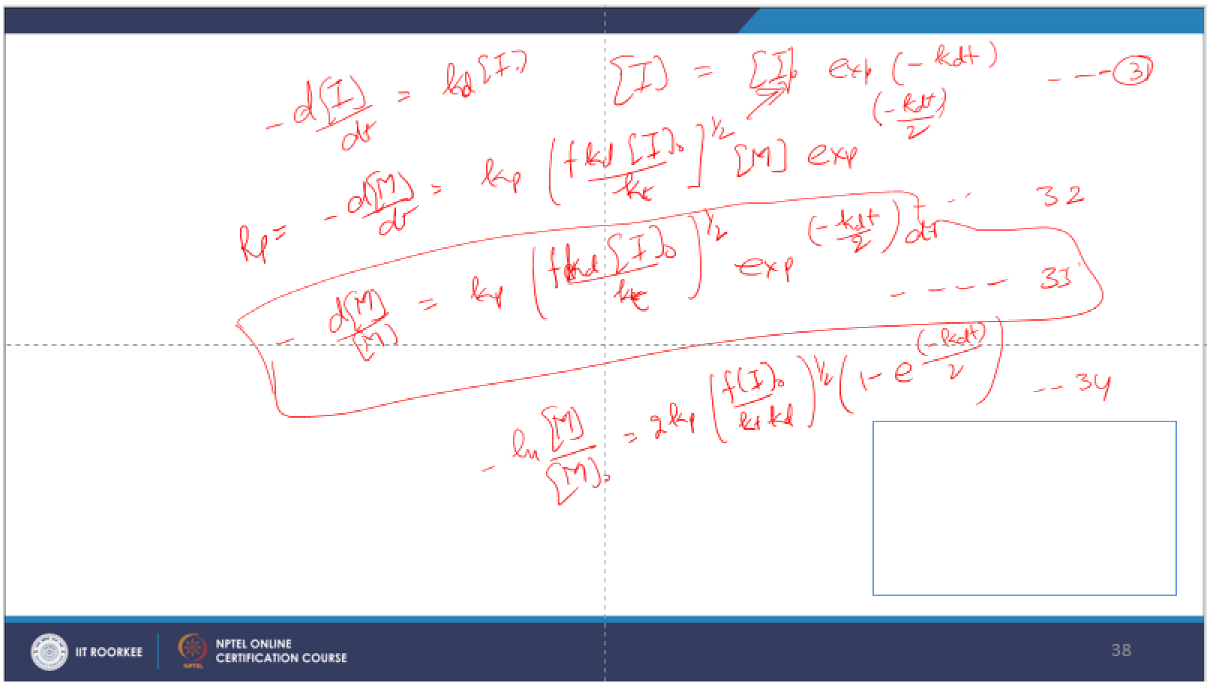
Now under the condition of say retardation termination or due to the gel effect it leads to sharp rise in the rate of polymerization medium viscosity and degree of polymerization the pure dead-end effect cannot be observed. Now in case of dead-end polymerization initiated by the thermal unimolecular decomposition of an initiator let us say I at the rate of initiator depletion is given by minus d I over dt that is equal to k d I.



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

$[I] = [I]_0 \exp(-k_d t)$ ---③

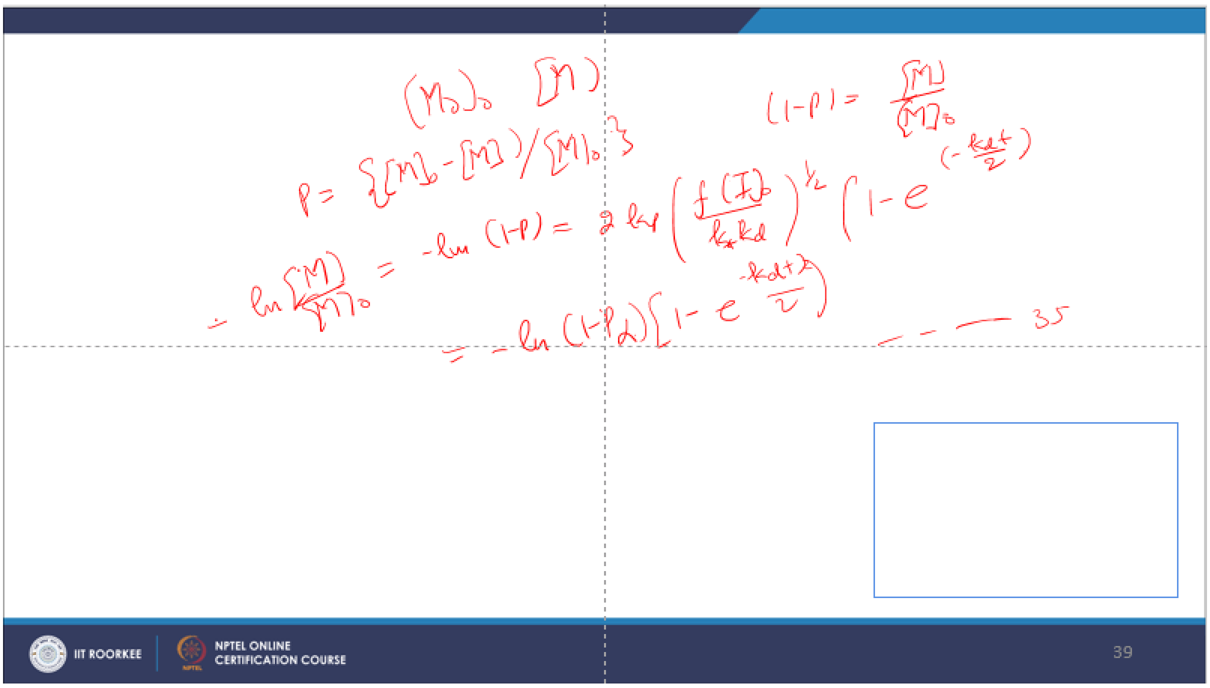
$\left(\frac{-k_d t}{2}\right)$

$R_p = -\frac{d[M]}{dt} = k_p\left(\frac{f k_d [I]_0}{k_t}\right)^{1/2}[M]\exp\left(\frac{-k_d t}{2}\right)$ --- 32

$$\boxed{-\frac{d[M]}{[M]} = k_p\left(\frac{f k_d [I]_0}{k_t}\right)^{1/2}\exp\left(\frac{-k_d t}{2}\right)dt}$$ ---- 33

$-\ln\frac{[M]}{[M]_0} = 2k_p\left(\frac{f[I]_0}{k_t k_d}\right)^{1/2}\left(1-e^{\left(\frac{-k_d t}{2}\right)}\right)$ -- 34

On if we integrate this one this can be given as I is equal to I naught exponential minus k dt this can be given as equation 31. Now where this I naught is the initial concentration of the initiator and the rate of polymerization r p can be given by this particular equation r p is equal to minus d m over dt that is equal to k p f k d I naught over k t to the power half m minus k dt over half this can be given as equation number 32.



$(M_0)_0 \quad [M)$

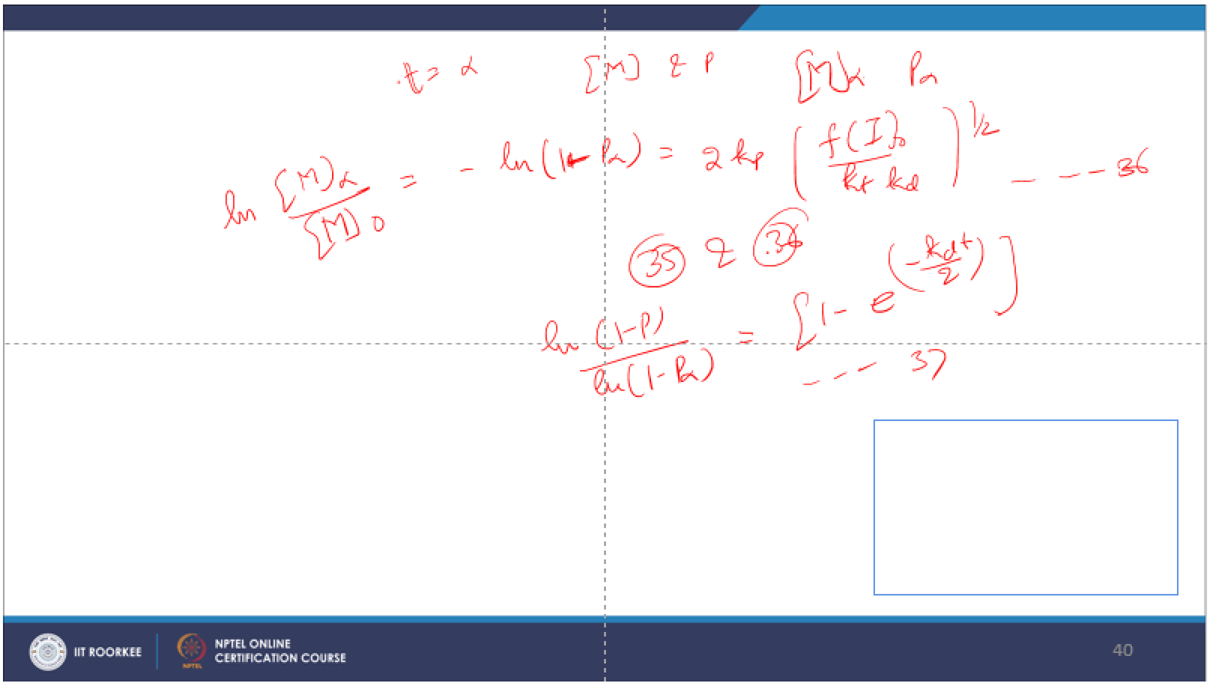
$(1-p) = \frac{[M]}{[M]_0}$

$p = \{[M]_0 - [M])/[M]_0\}$

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

$= -\ln(1-p_d)\{1-e^{\frac{-k_d t}{2}})$ ---- 35

So, if we arrange or rearrange one can obtain minus d m over m is equal to k p f k d into I naught over k t to the power half e to the power minus k dt over 2 dt this can be equation number 33 to more understandable this is equation. Now if we integrate this particular equation we will get minus ln m over m naught that is equal to 2 k p f I naught over k t k d to the power half into 1 minus e to the power minus k dt over half equation number 34. Now let m naught and m be the concentration of monomer at the start and after time t now so the extent of conversion p from a monomer to polymers can be represented as p is equal to m naught minus concentration of m over m naught and 1 minus p can be given as concentration of m over m naught. So the equation 34 which we derived previously this can be represented as minus ln concentration of m over m naught is equal to minus ln 1 minus p is equal to 2 k p f I naught k t k d to the power half 1 minus e to the power minus k dt over 2 and this is minus ln 1 minus p alpha into 1 minus e to the power minus k dt over 2 this can be represented as equation number 35. long times of reaction let us say t is equal to alpha the concentration of m and p attained the limiting value of m alpha and p alpha respectively.

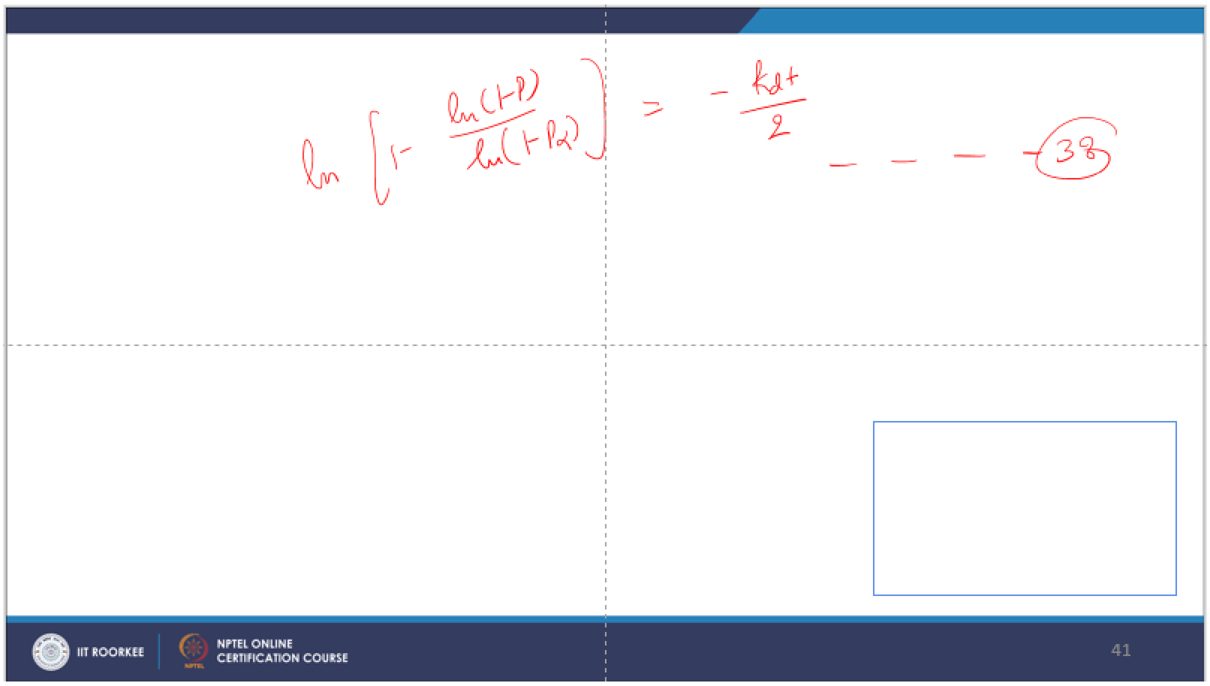


$t = \alpha$ $[M]$ & P $[M]_\alpha$ P_α

$$\ln \frac{[M]_\alpha}{[M]_0} = -\ln(1-P_\alpha) = 2k_p\left(\frac{f[I]_0}{k_t k_d}\right)^{1/2} \quad --- 36$$

③⑤ & ③⑥

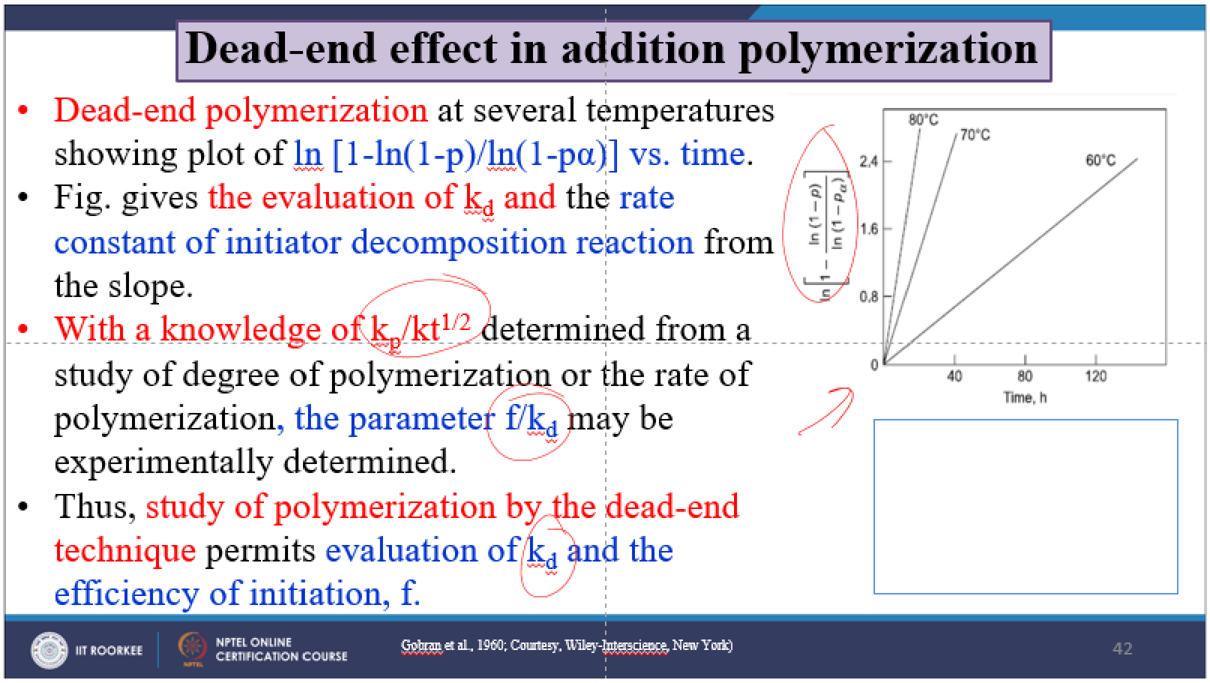
$$\frac{\ln(1-P)}{\ln(1-P_\alpha)} = \left[1-e^{\left(-\frac{k_d t}{2}\right)}\right] \quad --- 37$$



$$\ln\left[1-\frac{\ln(1-P)}{\ln(1-P_\alpha)}\right] = -\frac{k_d t}{2} \quad --- (38)$$

So that ln m alpha concentration of m naught is equal to minus ln 1 minus p alpha is equal to twice k p f I naught over k t k d to the power half this is equation number 36. So, if we combine the both the equation 35 and 36 so 35 and 36 then we will get ln 1 minus p over ln 1 minus p alpha this is equal to

1 minus e to the power minus k dt over 2 this is equation number 37. Now equation 37 this can be rearranged and expressed in a useful form if we take the logarithm that is ln 1 minus ln 1 minus p over ln 1 minus p alpha this is equal to minus k dt over 2 this is equation number 38. Now dead-end polymerization at several temperatures which can be represented like such kind of a plot like time versus the equation which we have previously derived the rate constant of initiator decomposition reaction from the slope. Now with the knowledge of k p over k t to the power half which determined from the study of the degree of polymerization or the rate of polymerization the parameter f over k d may be experimentally determined.



Dead-end effect in addition polymerization

- Dead-end polymerization at several temperatures showing plot of ln [1-ln(1-p)/ln(1-pα)] vs. time.
- Fig. gives the evaluation of k_d and the rate constant of initiator decomposition reaction from the slope.
- With a knowledge of $k_p/kt^{1/2}$ determined from a study of degree of polymerization or the rate of polymerization, the parameter f/k_d may be experimentally determined.
- Thus, study of polymerization by the dead-end technique permits evaluation of k_d and the efficiency of initiation, f.

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Gobran et al., 1960; Courtesy, Wiley-Interscience, New York)

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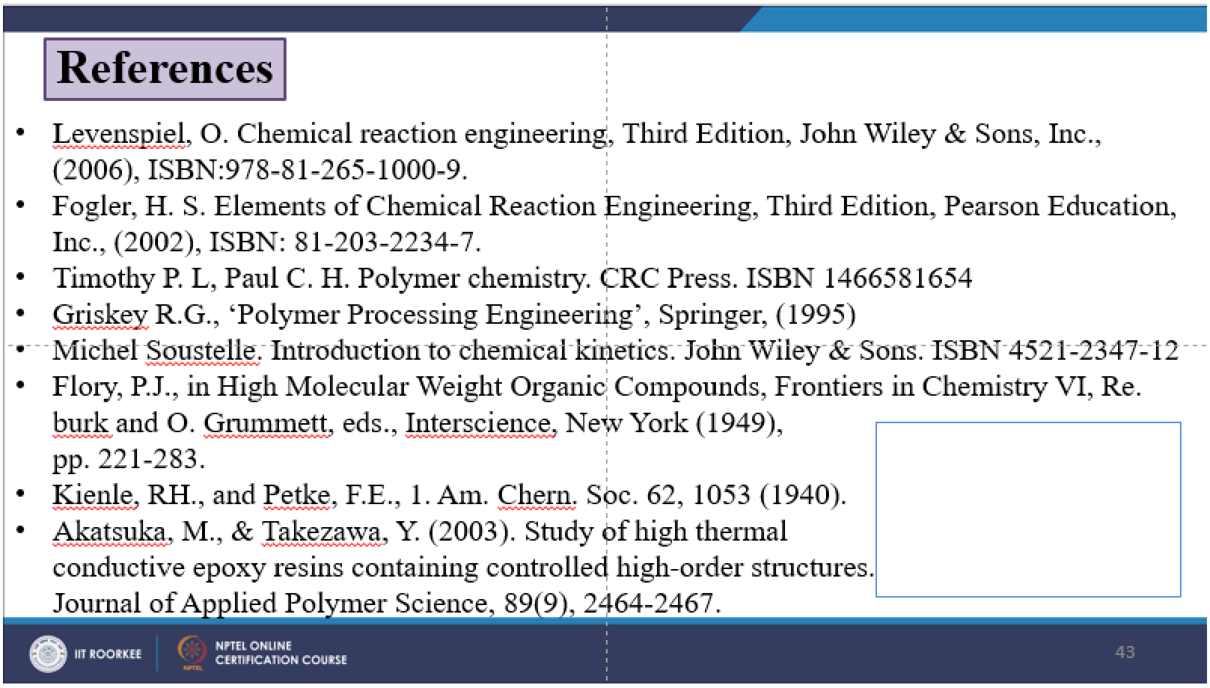
Therefore, the study of polymerization by the dead-end technique permits evaluation of k d and the efficiency of the initiator. So dear friends in this particular segment we discussed about the various kinetic aspect of addition polymerization and discuss the kinetic parameters and rate of reactions for different cases catalyzed, uncatalyzed all these things.



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For your convenience we have enlisted several references which you can use as per your need. Thank you very much.