Polymer Process Engineering
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Lecture 29
Chemical reaction engineering in polymers: Addition (Chain-Growth) Polymerization-II

Hello friends, welcome to the molecular weight distribution and addition polymerization. That is a chain reaction polymerization under the edges of chemical reaction engineering in polymeric systems. So, previously we have discussed about the self-catalysed step growth, step growth in the and gel point, the molecular weight distribution, molecular weight control. We discussed about the quantitative aspect of molecular weight and molecular weight distribution. In this particular lecture, we are going to cover the molecular weight distribution which we left in the previous lecture. Then, we will discuss about the addition polymerization.

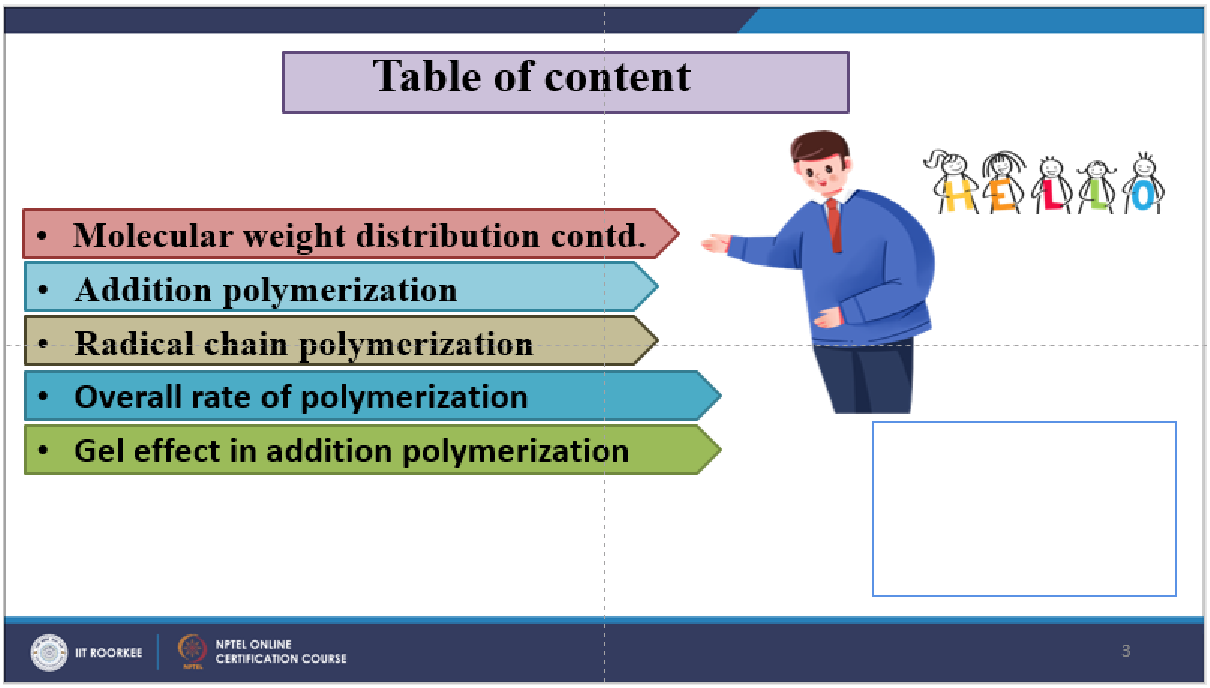
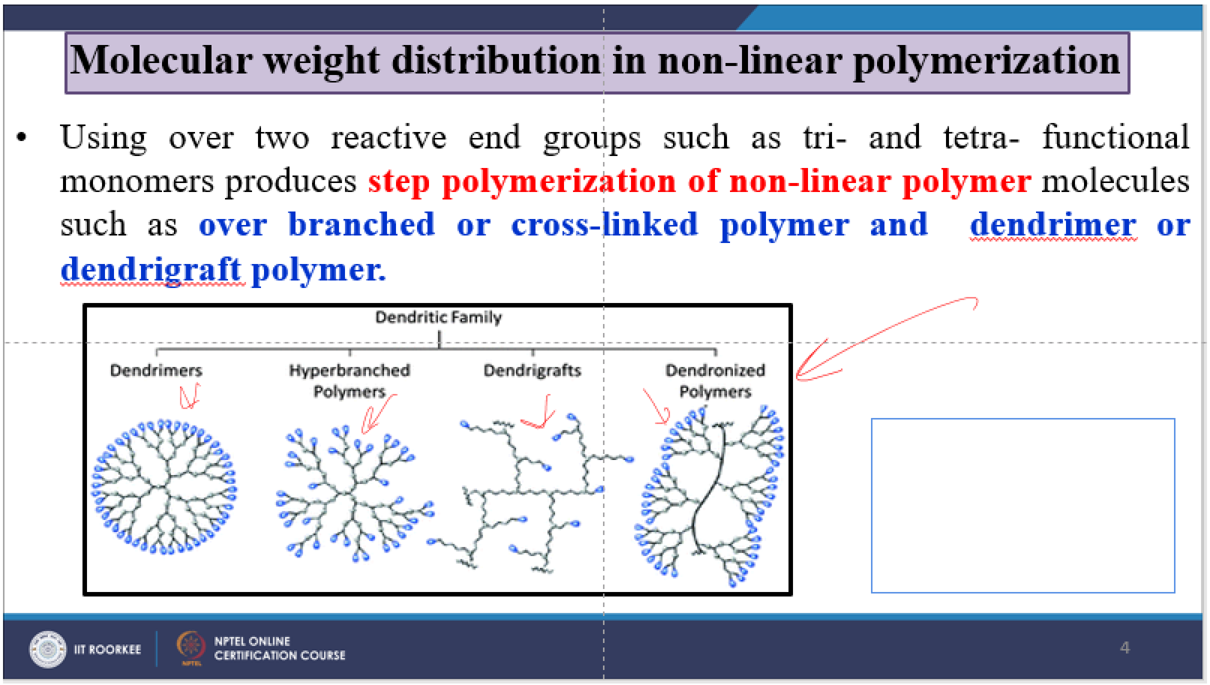


Table of content

- Molecular weight distribution contd.
- Addition polymerization
- Radical chain polymerization
- Overall rate of polymerization
- Gel effect in addition polymerization

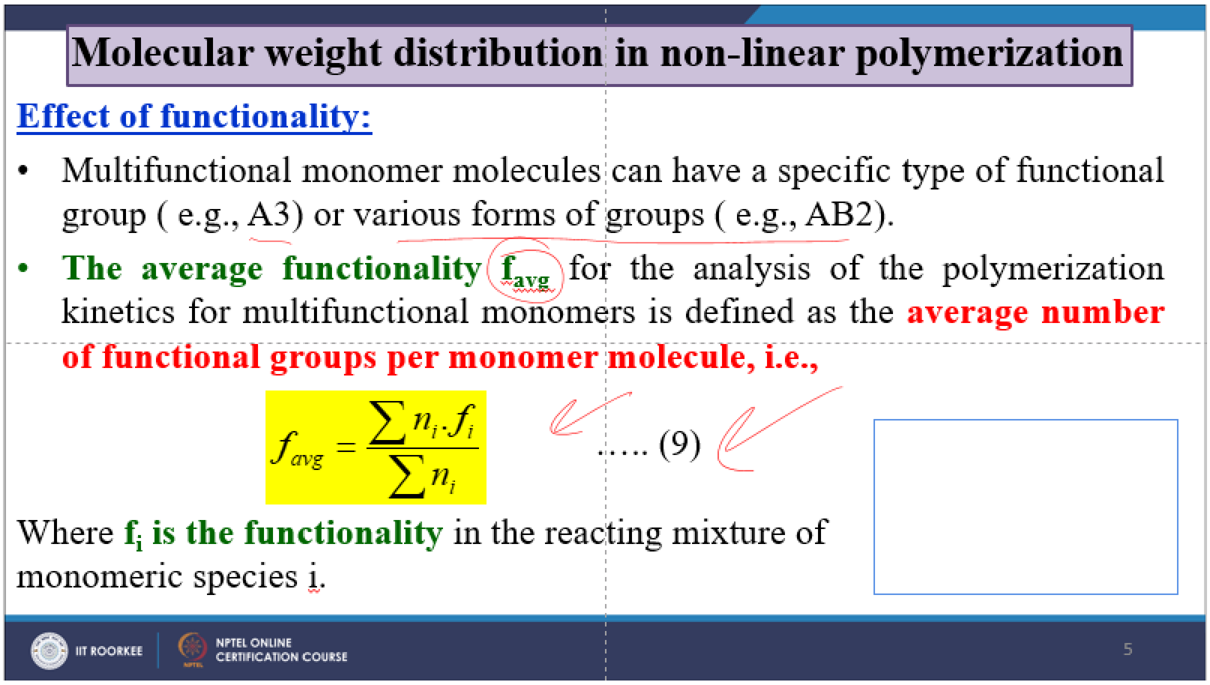
Apart from this, we will discuss about radical chain polymerization, and we will discuss about the overall rate of polymerization and gel effect in addition to polymerization. So, let us talk about the molecular weight distribution in non-linear polymerization using over two reactives and groups such as tri and etcetera functional monomer. This produces the step polymerization of non-linear polymer molecules such as over branched or cross-linked polymer and dendrimers or dendri graph polymers, which you can see like here you are having the dendri graph polymers, then dendronized polymers, then hyperchanged, hyperbranched polymers and these are the dendrimers. Now, the functionality plays a vital role.



Molecular weight distribution in non-linear polymerization

- Using over two reactive end groups such as tri- and tetra- functional monomers produces **step polymerization of non-linear polymer** molecules such as **over branched or cross-linked polymer and dendrimer or dendrigraft polymer.**

So, let us talk about the effect of functionality. So, the multifunctional monomer molecule they can have a specific type of functional groups like A3 or various forms of groups like AB2. So, the average functionality that is f average of the for the analysis of polymerization kinetics for multifunctional monomer is defined as the average number of functional groups per monomer molecule, and that is f AB f average that is equal to summation of n i f i over summation of n i where f i is the functionality in the reacting mixture of monomeric species and this is represented as equation number 9. Now, the polymerization of a vinyl or related monomer M is induced in presence of a free radical initiator. So, the I this is I, which I is the initiator, this may be expressed as like initiator decomposition.



Molecular weight distribution in non-linear polymerization

Effect of functionality:

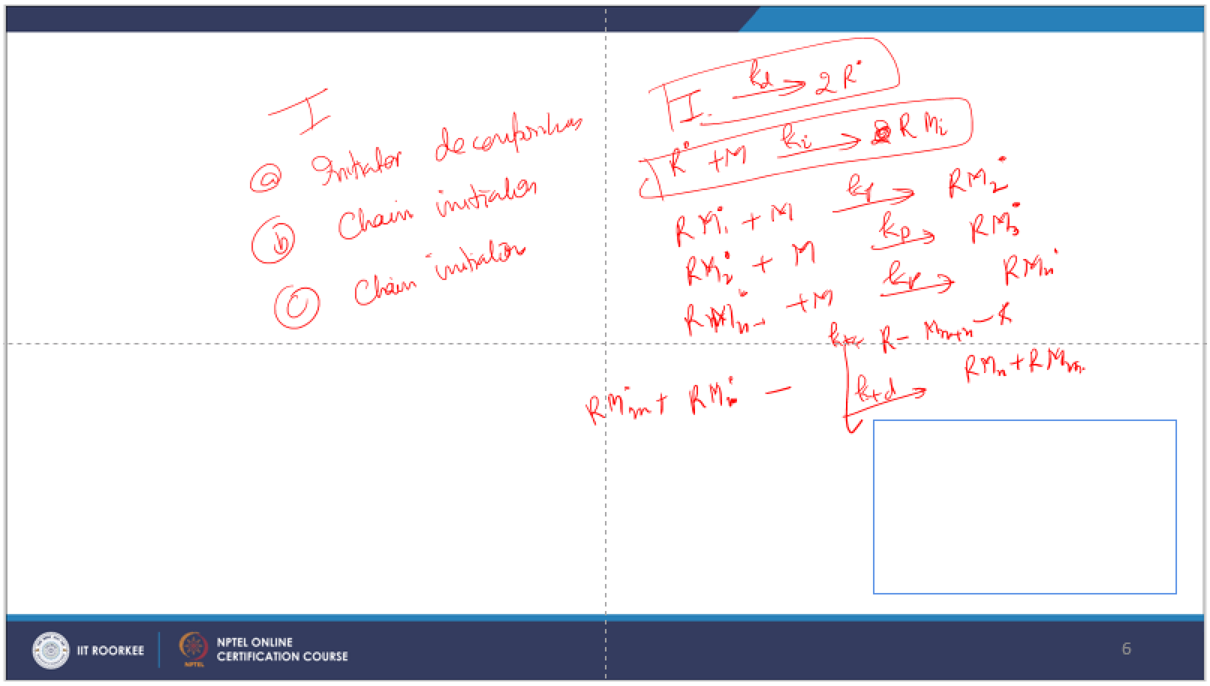
- Multifunctional monomer molecules can have a specific type of functional group (e.g., A3) or various forms of groups (e.g., AB2).
- **The average functionality** (f_{avg}) for the analysis of the polymerization kinetics for multifunctional monomers is defined as the **average number of functional groups per monomer molecule, i.e.,**

$$f_{avg} = \frac{\sum n_i . f_i}{\sum n_i} \quad \ldots\ldots (9)$$

Where f_i **is the functionality** in the reacting mixture of monomeric species i.

the **average number of functional groups per monomer molecule, i.e.,**

$$f_{avg} = \frac{\sum n_i . f_i}{\sum n_i}$$


I

ⓐ Initiator decomposition

ⓑ Chain initiation

ⓒ Chain initiation

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

$R^\cdot + M \xrightarrow{k_i} RM_i^\cdot$

$RM_1^\cdot + M \xrightarrow{k_p} RM_2^\cdot$

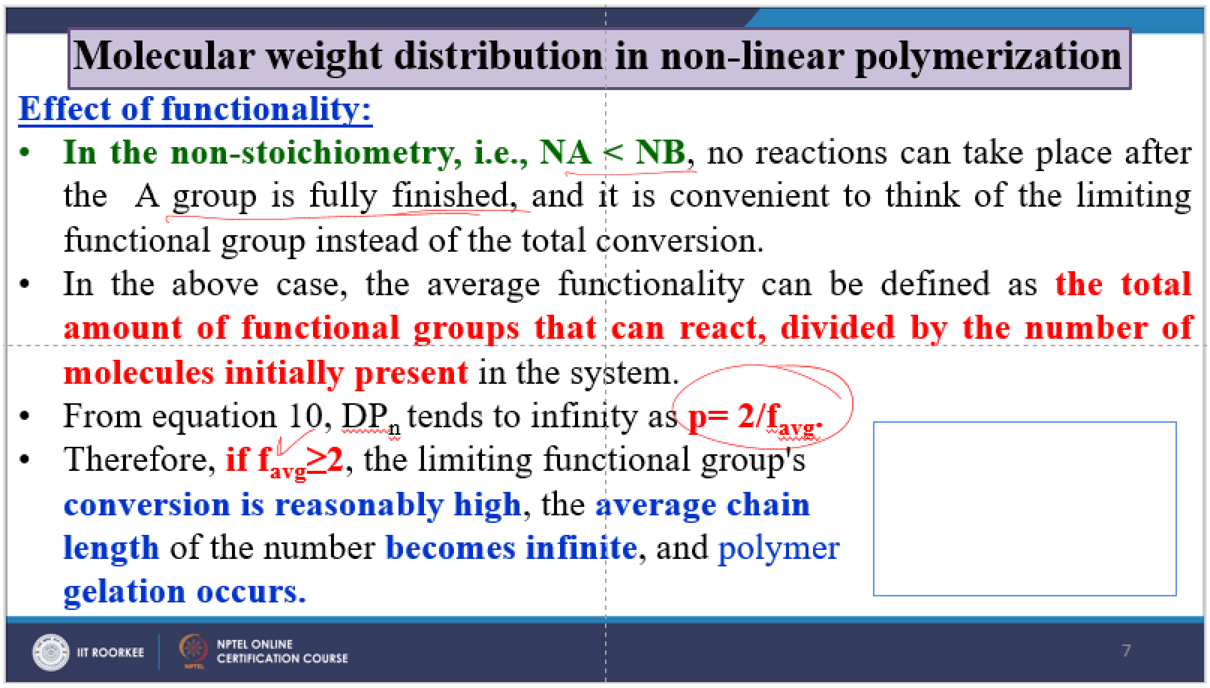
$RM_2^\cdot + M \xrightarrow{k_p} RM_3^\cdot$

$RM_{n-1}^\cdot + M \xrightarrow{k_p} RM_n^\cdot$

$RM_m^\cdot + RM_n^\cdot \xrightarrow{k_{tc}} R-M_{m+n}-R$

$\xrightarrow{k_{td}} RM_n + RM_m$

So, I that is k d first this is the initiator decomposition, then we start the chain initiation, this is k i R m i, then again the chain initiation for other components, this is R m 1, then R m k p sometimes referred as propagation because the formation of different chains, then R m 2 k p R m 3, then R m R m in a generic term plus m, this is the chain initiation and then we may have this R m in a generic term, this the formation of the polymeric chain, this can be k t c, and another one can be R m and R n and this can be k t d. Now, the non-stoichiometric that is n a is less than n b no reaction can take place after the group this is fully finished and it is convenient to think that limiting the functional group instead of the total conversion. So, in that case the average functionality can be defined as the total amount of functional groups that can react and that is divided by the number of molecules initially present in the system. Now, from this equation, the d p n which we have already discussed in the previous lecture tends to infinity as p is equal to 2 over f average. Therefore, if this f average is greater than equal to 2 the limiting functional groups the conversion is reasonably high and the average chain length of the number becomes infinite and the polymer gelation occurs.

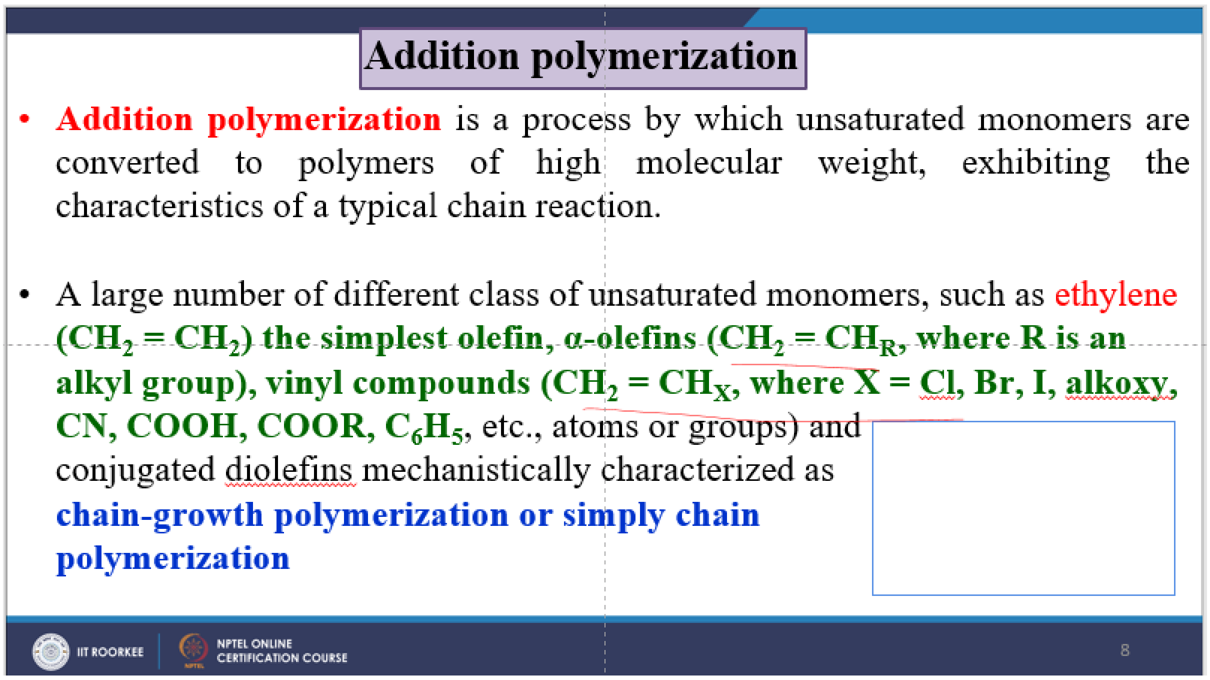


Molecular weight distribution in non-linear polymerization

Effect of functionality:

- **In the non-stoichiometry, i.e., NA < NB,** no reactions can take place after the A group is fully finished, and it is convenient to think of the limiting functional group instead of the total conversion.
- In the above case, the average functionality can be defined as **the total amount of functional groups that can react, divided by the number of molecules initially present** in the system.
- From equation 10, DP_n tends to infinity as **$p = 2/f_{avg}$.**
- Therefore, **if $f_{avg} \geq 2$**, the limiting functional group's **conversion is reasonably high**, the **average chain length** of the number **becomes infinite**, and polymer **gelation occurs.**

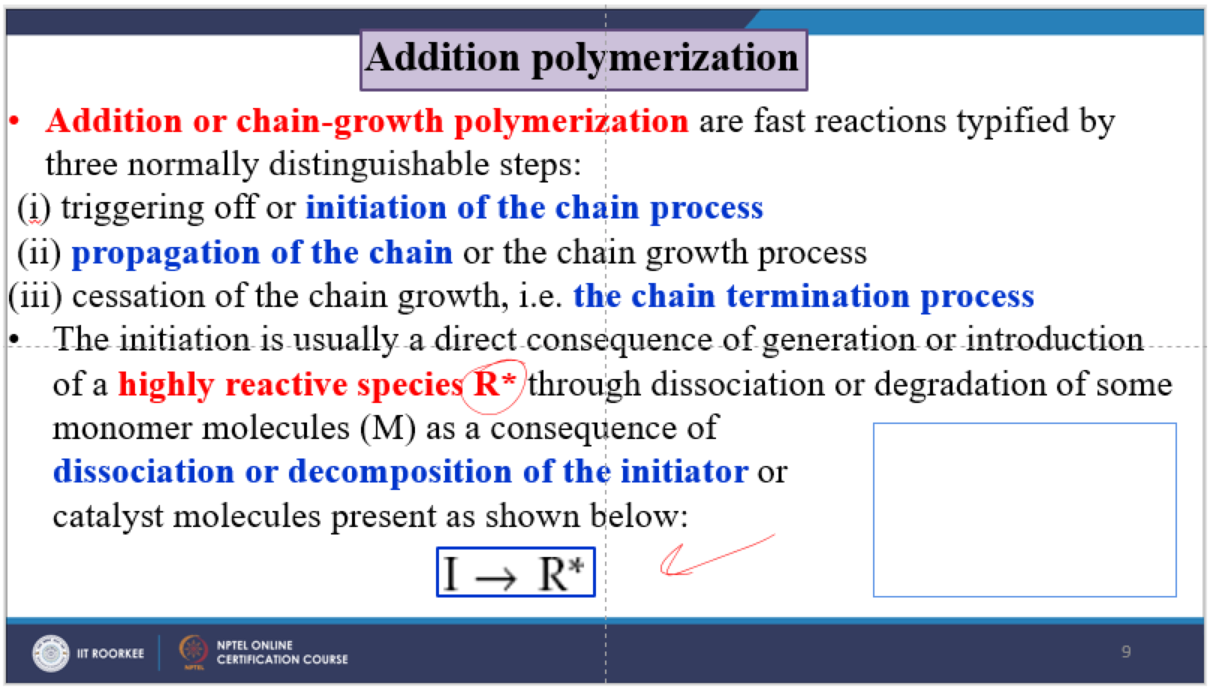
Let us talk about the addition polymerization. Addition polymerization is a process by which unsaturated monomers are converted to polymers of high molecular weight exhibiting the characteristics of a typical chain reaction. So, a large number of different classes of unsaturated monomers such as ethylene like CH 2 double bond CH 2 is a simplest olefin alpha olefins CH 2, CHR where R is an alkyl group, vinyl compound like CH 2 CH X where X is either chlorine, bromine, iodine, alkoxy these are the conjugated olefins mechanically characterized as a chain growth polymerization or simple chain polymerization. Now, they are the addition or chain growth polymerization is the fast reaction typified by 3 different distinguishable steps. One is the triggering of that is the initiation, the second is the propagation and the third is the termination step.



Addition polymerization

- **Addition polymerization** is a process by which unsaturated monomers are converted to polymers of high molecular weight, exhibiting the characteristics of a typical chain reaction.
- A large number of different class of unsaturated monomers, such as ethylene **($CH_2 = CH_2$) the simplest olefin, α-olefins ($CH_2 = CH_R$, where R is an alkyl group), vinyl compounds ($CH_2 = CH_X$, where X = Cl, Br, I, alkoxy, CN, COOH, COOR, C_6H_5,** etc., atoms or groups) and conjugated diolefins mechanistically characterized as **chain-growth polymerization or simply chain polymerization**

The initiation is usually a direct consequence of the generation or introduction of highly reactive species that is referred as R naught through the dissociation or degradation of some monomer molecules as a consequence of a dissociation or decomposition, which we can be represented as I can be dissociated or can be composed to R ionic. Now, the reactive species, which may be a free radical cation, anion whatever which readily attacks the unsaturated monomer molecule if the conditions are favourable and adds itself to the monomer molecules by opening the reactive species may be free radical cation or anion which readily attacks to the unsaturated monomer molecule if conditions are favourable adds itself to the monomer molecule by opening a pi bond to form a fresh reactive centre that is a radical cation or anion depending on the nature of the radical and prevailing the chemical environment. The new reactive centres they add to another monomer molecule M and the process is repeated in quick succession, leading many more monomer molecules to add to the same growing species at its reactive or growth centric to carry out on the propagation of the chain process. Now here, let us discuss about the termination because we have discussed the initiation, and decomposition initiation in the previous slides. Now, let us talk about the termination.



Addition polymerization

- **Addition or chain-growth polymerization** are fast reactions typified by three normally distinguishable steps:

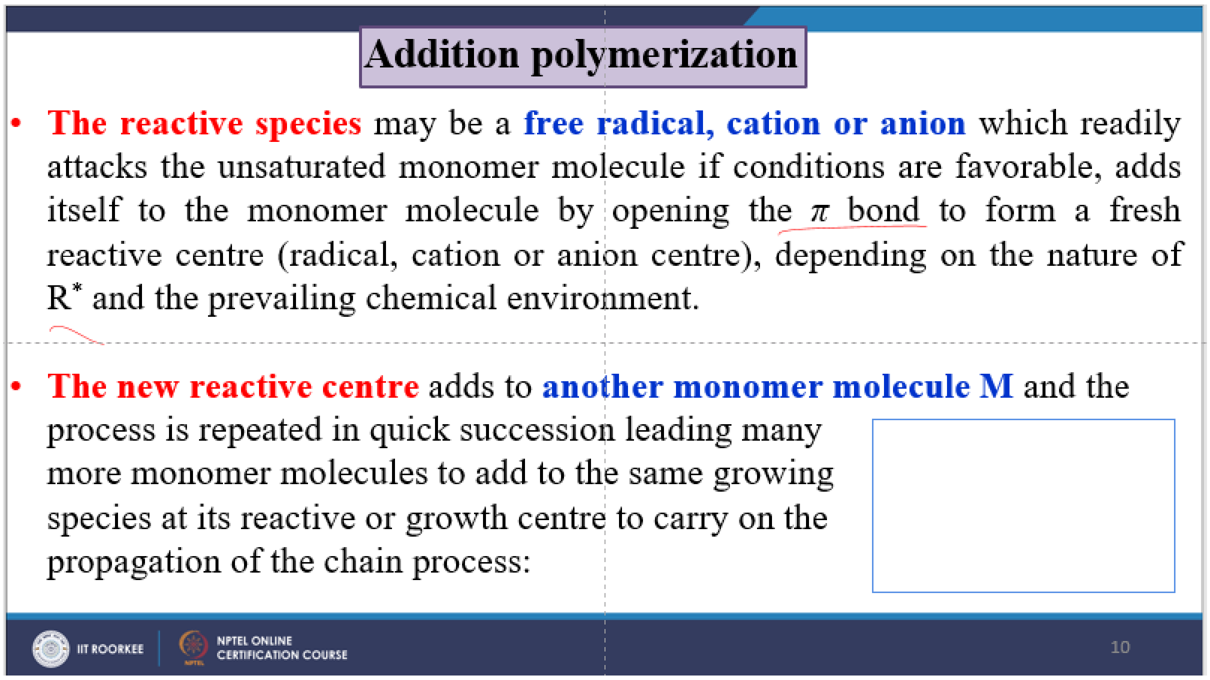
(i) triggering off or **initiation of the chain process**

(ii) **propagation of the chain** or the chain growth process

(iii) cessation of the chain growth, i.e. **the chain termination process**

- The initiation is usually a direct consequence of generation or introduction of a **highly reactive species R*** through dissociation or degradation of some monomer molecules (M) as a consequence of **dissociation or decomposition of the initiator** or catalyst molecules present as shown below:

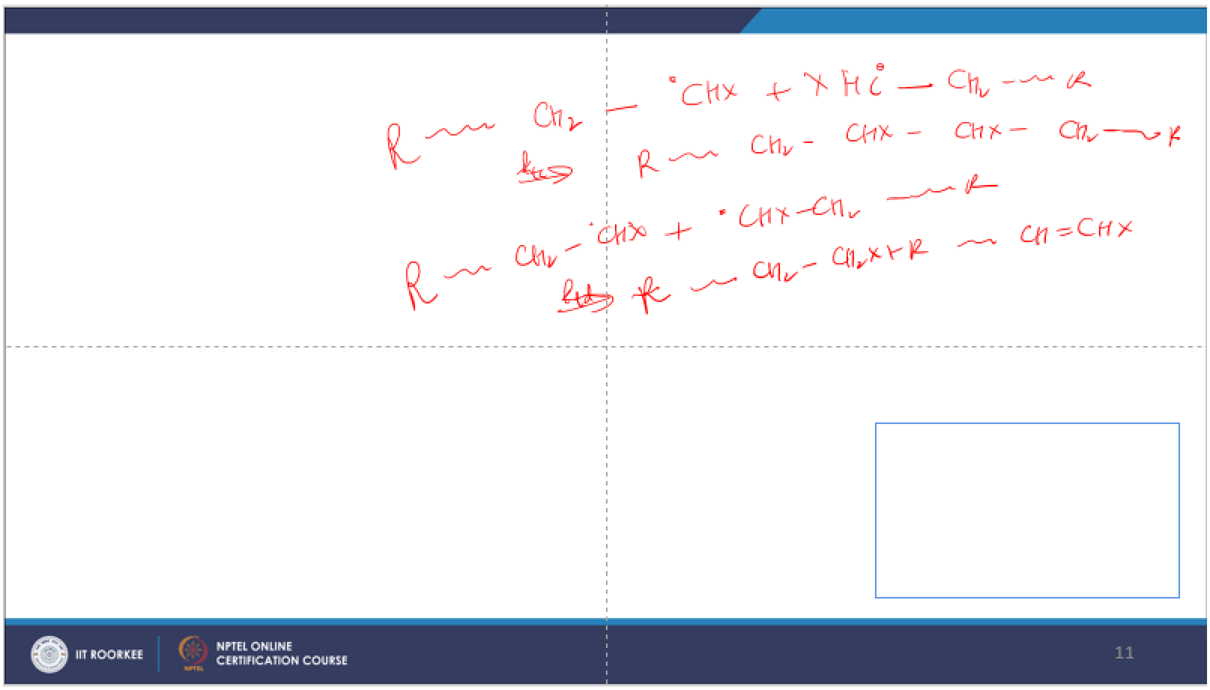
$$\boxed{I \rightarrow R^*}$$



Addition polymerization

- **The reactive species** may be a **free radical, cation or anion** which readily attacks the unsaturated monomer molecule if conditions are favorable, adds itself to the monomer molecule by opening the π bond to form a fresh reactive centre (radical, cation or anion centre), depending on the nature of R^* and the prevailing chemical environment.
- **The new reactive centre** adds to **another monomer molecule M** and the process is repeated in quick succession leading many more monomer molecules to add to the same growing species at its reactive or growth centre to carry on the propagation of the chain process:

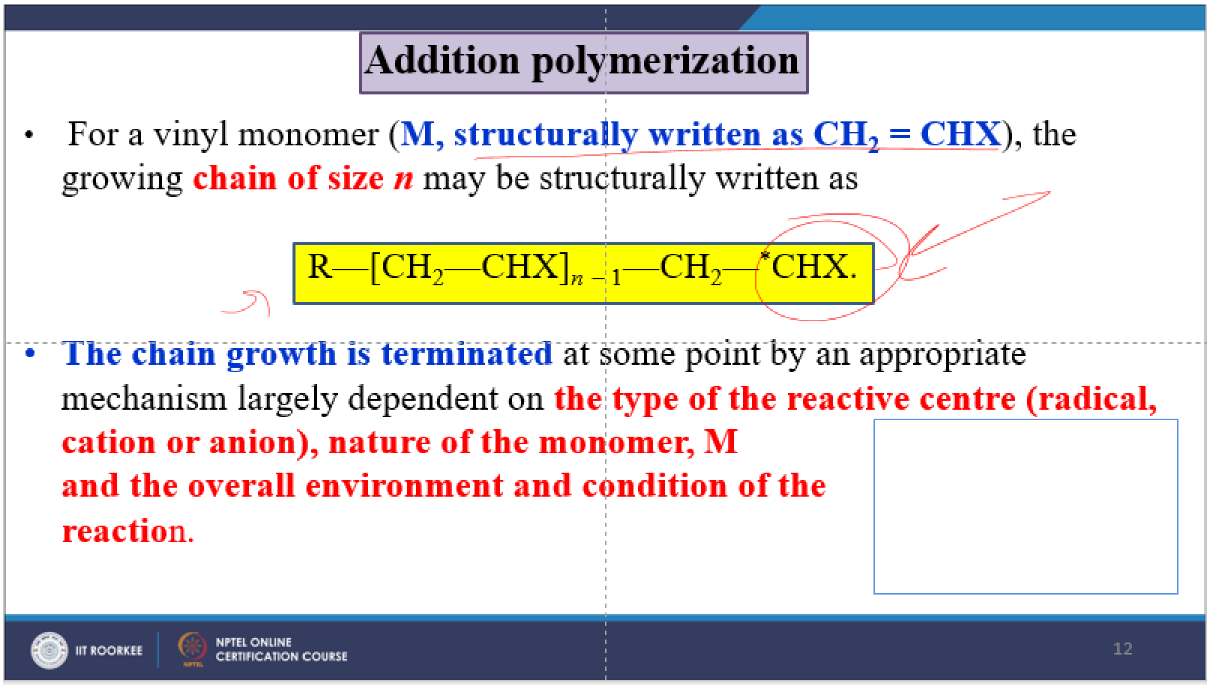
This is these are the radicals and CH2CHXCHXCH2R. Now, termination by disproportionation reaction which we discussed earlier that is R CH2CHX radical plus radical CHXCH2R KTD CH2CH2X plus R CHCHX. For vinyl monomer M let us take the structurally written as CH2 double bond CHX the growing chain of size N may be structurally written as like this. So, the chain growth is terminated at some point by an appropriate mechanism largely depend on the type of the reactive centre that is radical, maybe cation, anion and the nature of the monomer M and the overall environment condition of the reaction. So, on the basis of steady-state assumption this radical M this may be expressed as F Kd over Kt to the power half.



$$R\sim CH_2-\dot{C}HX + X H\dot{C}-CH_2\sim R \xrightarrow{k_{tc}} R\sim CH_2-CHX-CHX-CH_2\sim R$$

$$R\sim CH_2-\dot{C}HX + \dot{C}HX-CH_2\sim R \xrightarrow{k_{td}} R\sim CH_2-CH_2X + R\sim CH=CHX$$

The expression of the rate propagation R p because initiation propagation termination these 3 are the steps this can be represented as K p over K t to the power half F Kd to the power half i. Let us say this is equation 3. Now, where R is this R is the free radical generated from the initiation or initiator R m 1 R m 1 radical or R m 2 radical or R m 3 etcetera. They are the growing polymer chain and each bearing a free valency of the radical centre at the chain end and R m R m n R m n all these things are the dead polymer molecule which are obtained that means they cannot further grow. So, the common feature of the vinyl polymerization is that the active centre of the kinetic chain is retained by a single molecular species throughout the chain growth or chain propagation process.



Addition polymerization

- For a vinyl monomer (**M, structurally written as $CH_2 = CHX$**), the growing **chain of size *n*** may be structurally written as

$$R—[CH_2—CHX]_{n-1}—CH_2—{}^{*}CHX.$$

- **The chain growth is terminated** at some point by an appropriate mechanism largely dependent on **the type of the reactive centre (radical, cation or anion), nature of the monomer, M and the overall environment and condition of the reaction.**

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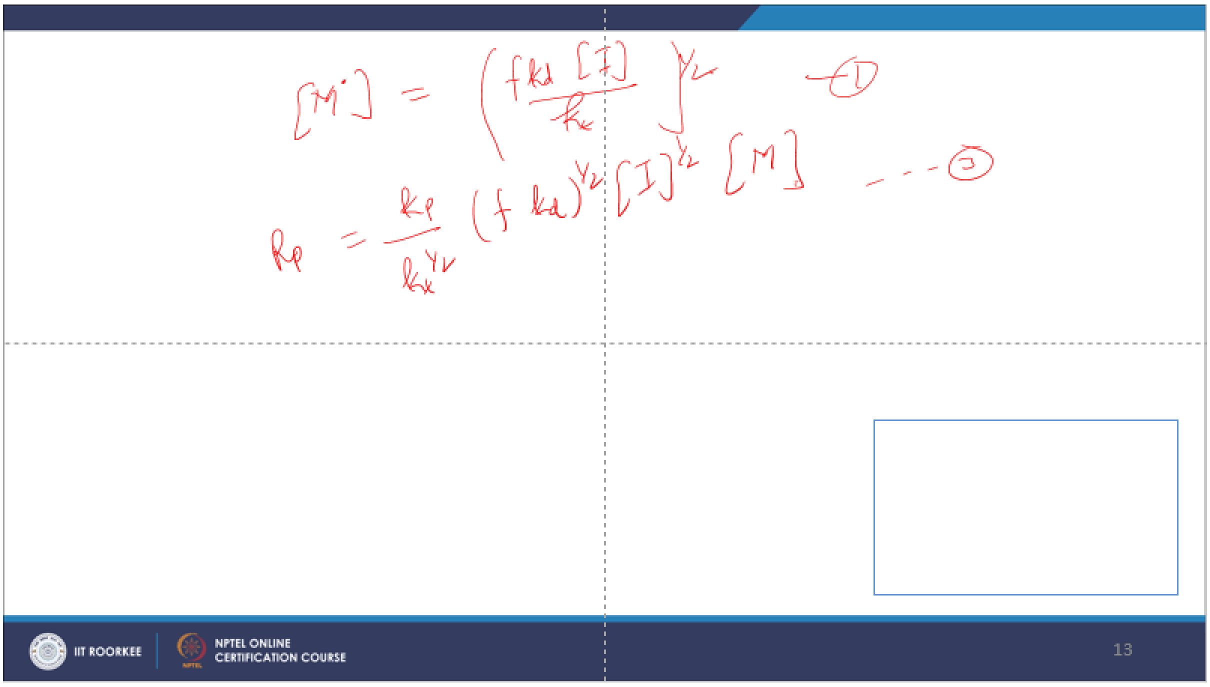

$$[M^{\cdot}] = \left(\frac{f k_d [I]}{k_t}\right)^{1/2} \quad —①$$

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

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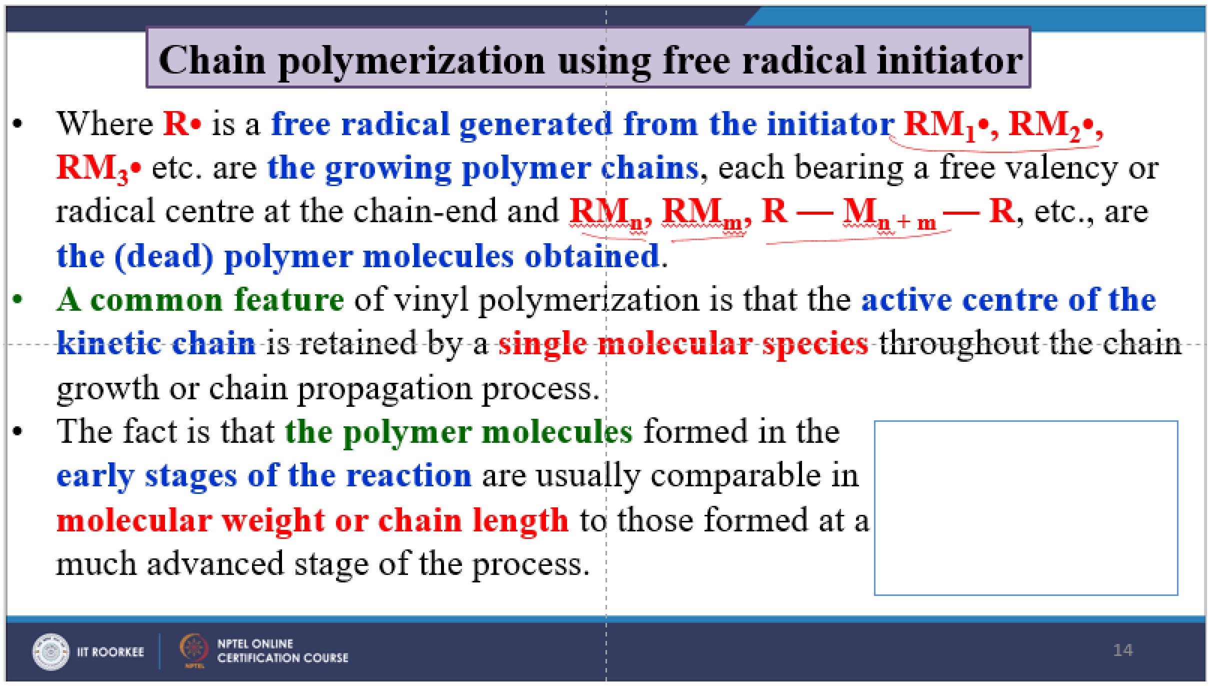
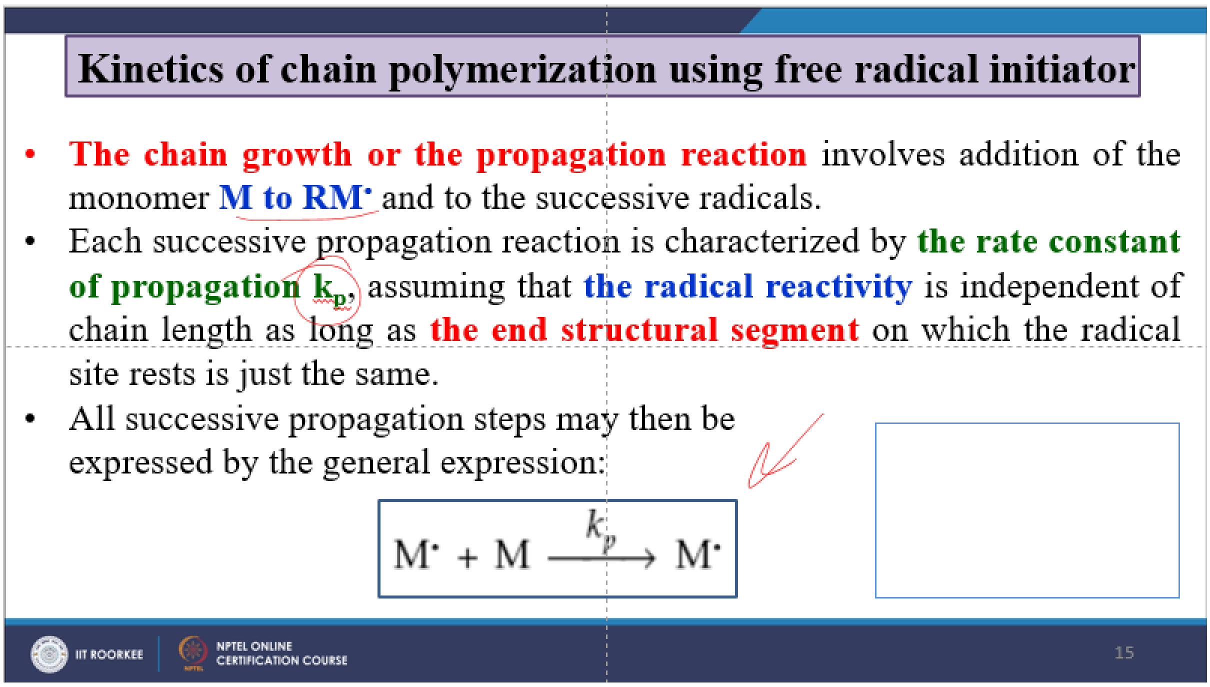
So, the fact is that the polymer molecules formed in the early stage of reaction are usually comparable in the molecular weight or chain length to those formed at a much-advanced stage of the process. Now, when we talk about the kinetics of chain polymerization using free radical initiation, the chain growth or propagation reaction involves the addition of a monomer that is M or the 2 radical R m and to the successive radicals. So, each successive propagation reaction is characterized by the rate constant of propagation that is called k p assuming that the radical reactivity is independent of the chain length as long as the end structural segment on which the radical site rests is just the same. So, the all successive propagation step may then be expressed by the general expression that is M radical plus M k p M radical. Let us talk about the termination aspect.



Chain polymerization using free radical initiator

- Where **$R\bullet$** is a **free radical generated from the initiator** **$RM_1\bullet$, $RM_2\bullet$, $RM_3\bullet$** etc. are **the growing polymer chains**, each bearing a free valency or radical centre at the chain-end and **RM_n, RM_m, $R — M_{n+m} — R$**, etc., are **the (dead) polymer molecules obtained**.
- **A common feature** of vinyl polymerization is that the **active centre of the kinetic chain** is retained by a **single molecular species** throughout the chain growth or chain propagation process.
- The fact is that **the polymer molecules** formed in the **early stages of the reaction** are usually comparable in **molecular weight or chain length** to those formed at a much advanced stage of the process.

The termination of polymerization is a bimolecular in nature and it involves the reaction between a pair of a chain radical leading to a complete destruction of 2 chain radicals in each incident of the termination reaction and the production of what is known as the dead polymer. The termination reaction by 2 different modes they represent the coupling or mutual combination of 2 chain radicals characterized by the rate constant k t c and disproportionation of chain radicals characterized by the rate constant k d t. Now, here you see that the rate of initiation, rate of initiation this can be expressed as r i 2 k i M 2. Now considering the bimolecular termination giving rise or giving the rate of termination that is r t is equal to 2 k t M to the power 2 and under steady state assumption giving rise to say r i is equal to r t the chain radical concentration may be expressed as k 1 k k i over k t to the power half M. Now the rate of polymerization r p is expressed as r p is equal to k p M radical into M which is equal to k p k i over k t to the power half M to the power 2.

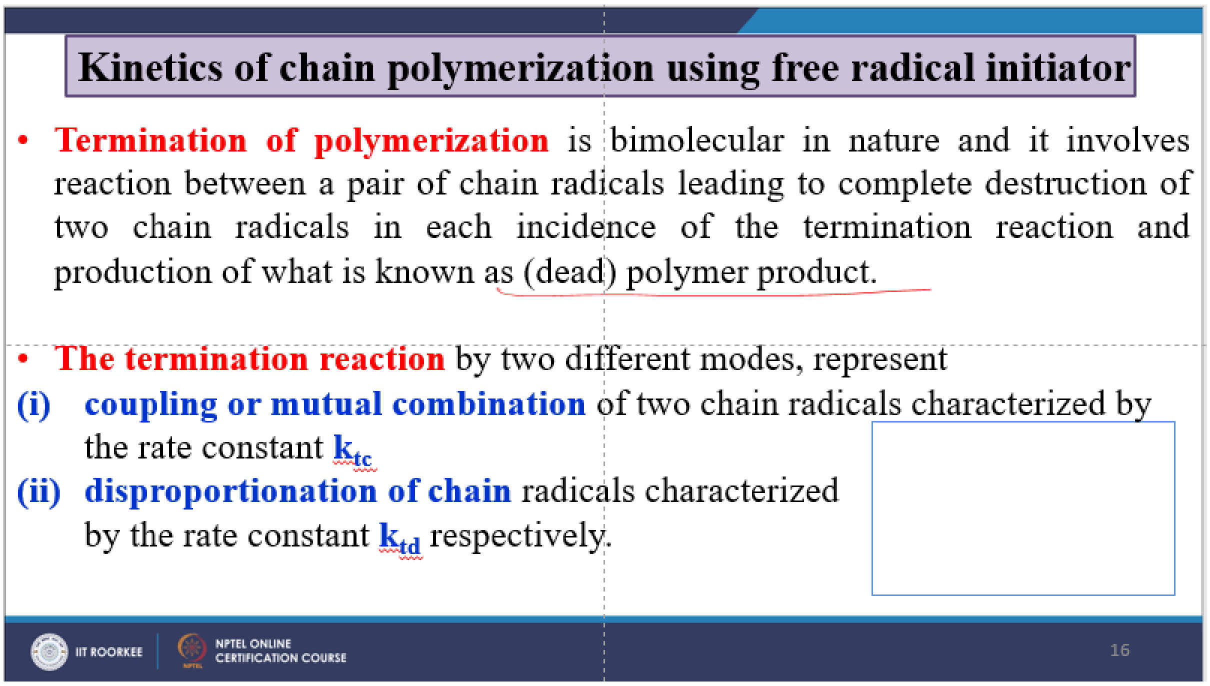


Kinetics of chain polymerization using free radical initiator

- **The chain growth or the propagation reaction** involves addition of the monomer **M to RM$^\cdot$** and to the successive radicals.
- Each successive propagation reaction is characterized by **the rate constant of propagation k_p**, assuming that **the radical reactivity** is independent of chain length as long as **the end structural segment** on which the radical site rests is just the same.
- All successive propagation steps may then be expressed by the general expression:

$$\boxed{M^\cdot + M \xrightarrow{k_p} M^\cdot}$$

So, for the kinetics purpose the bimolecular mechanism of termination alone is important and the exact mode that is the combination or disproportionation does not make any difference. So that the termination step may be simply expressed as M radical and M radical that is k t that you will get the dead polymer product that is 2 radicals they can combine together to neutralize the radical charge and they give the dead polymer. Now here this k t is the overall rate constant of a bimolecular termination and which is referred as k t is equal to k t c plus k t d. Now let us talk about the rate of chain initiation now decomposition of lone initiator it involves the bile it involves the homolytic cleavage of a weak bond in the molecule such that the chain initiating radicals are generated in pairs.

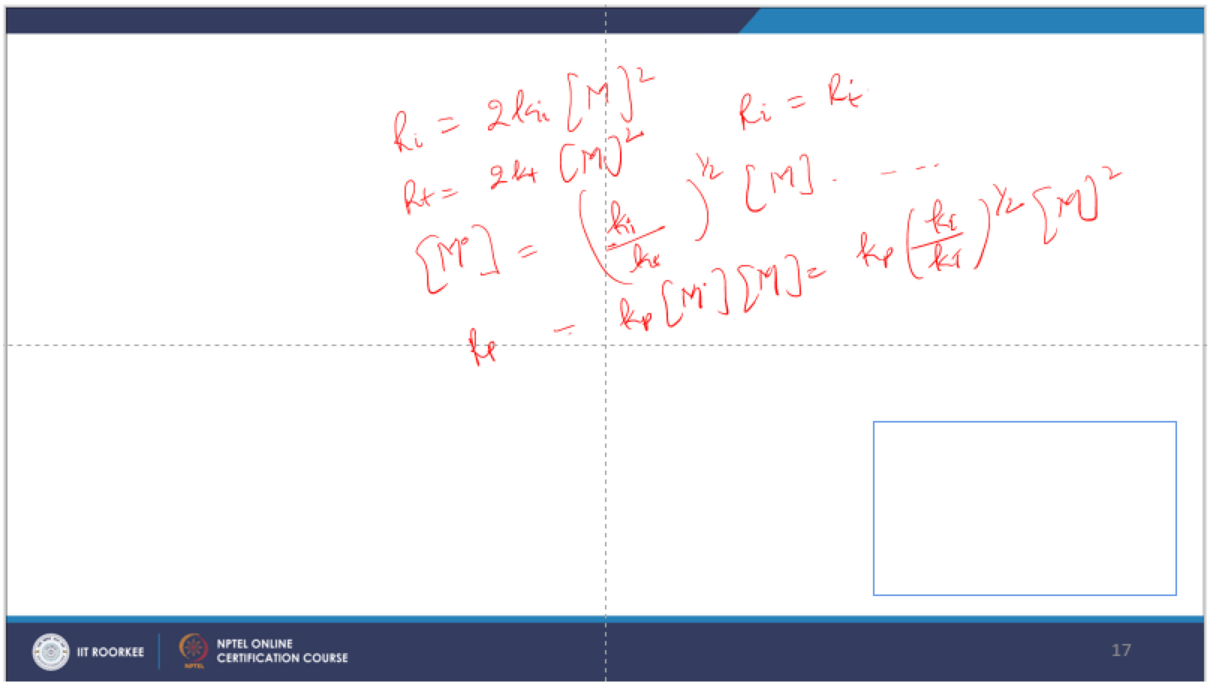


Kinetics of chain polymerization using free radical initiator

- **Termination of polymerization** is bimolecular in nature and it involves reaction between a pair of chain radicals leading to complete destruction of two chain radicals in each incidence of the termination reaction and production of what is known as (dead) polymer product.
- **The termination reaction** by two different modes, represent

(i) **coupling or mutual combination** of two chain radicals characterized by the rate constant k_{tc}

(ii) **disproportionation of chain** radicals characterized by the rate constant k_{td} respectively.



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

$R_t = 2k_t[M]^2$

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

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

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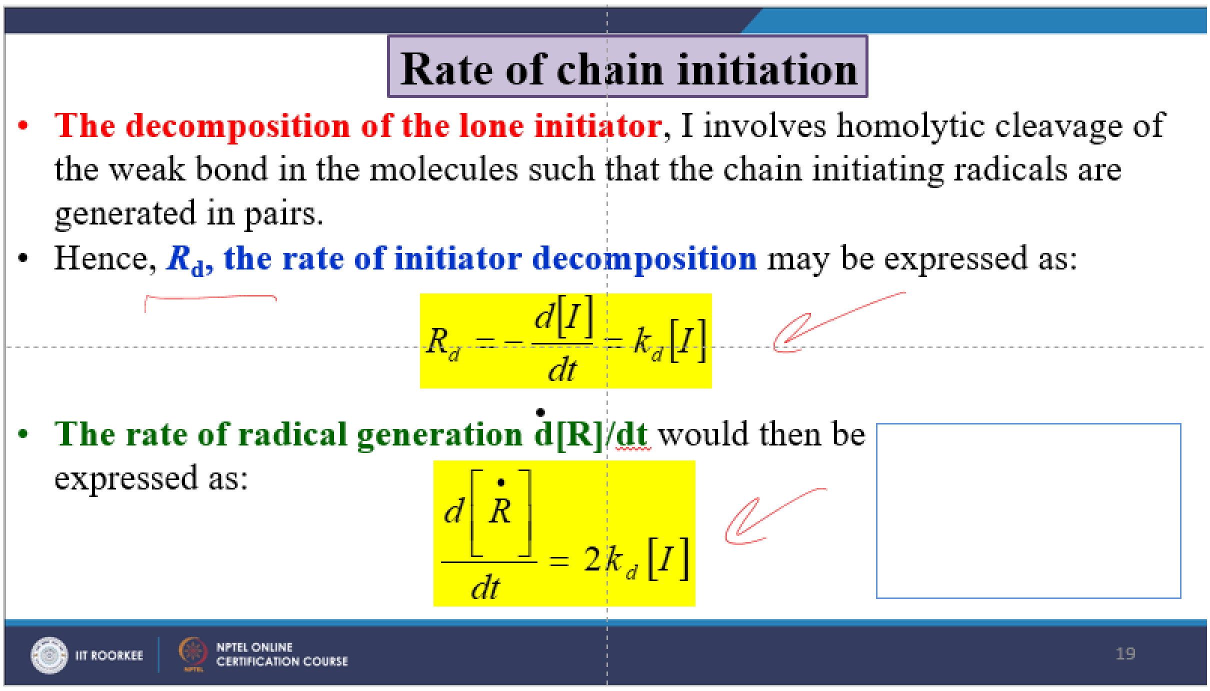
Now here r d is the rate of initiator decomposition this may be expressed as r d is equal to minus d i over d t is equal to k d i concentration of i the rate of radical generation d concentration of r over d t this would be the radical r d over d t equal to 2 k t concentration of i.



Rate of chain initiation

- **The decomposition of the lone initiator**, I involves homolytic cleavage of the weak bond in the molecules such that the chain initiating radicals are generated in pairs.
- Hence, ***R*$_d$, the rate of initiator decomposition** may be expressed as:

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

- **The rate of radical generation $d[\dot{R}]/dt$** would then be expressed as:

$$\frac{d[\dot{R}]}{dt} = 2k_d[I]$$

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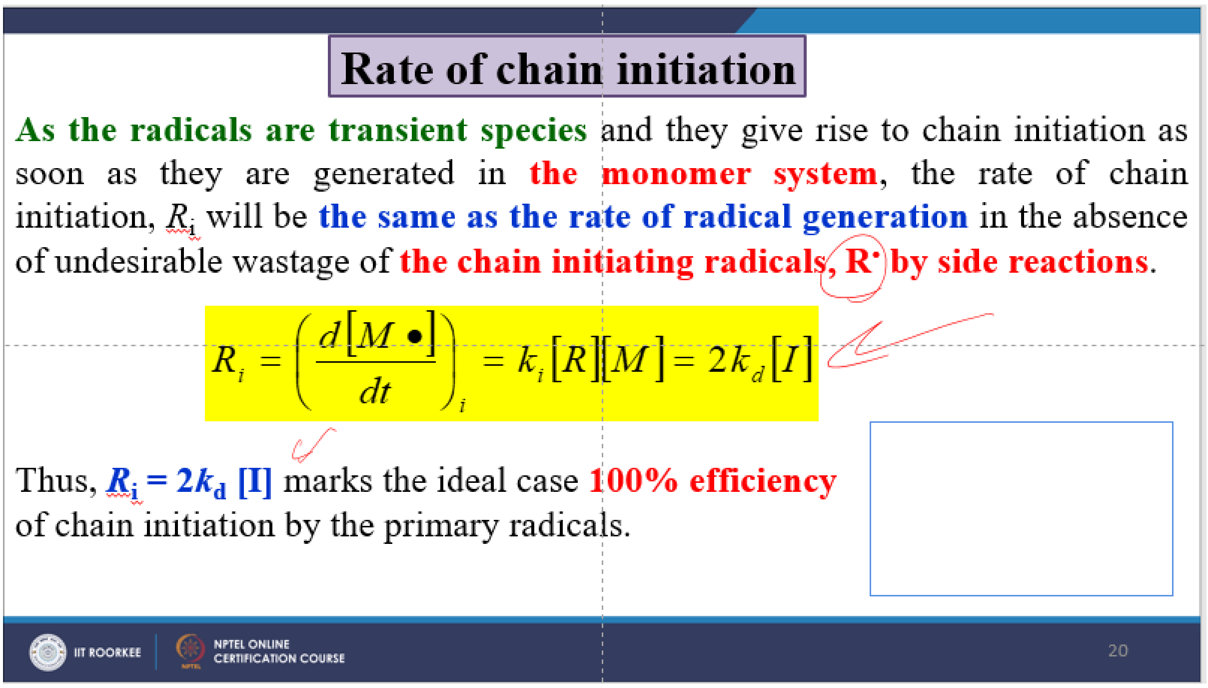
R_d, the rate of initiator decomposition may be expressed as

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

- **The rate of radical generation d[R]/dt** would then be expressed as:
- $\frac{d[\dot{R}]}{dt} = 2k_d[I]$

- The chain initiating radicals R by side reaction
- $R_i = \left(\frac{d[M\bullet]}{dt}\right)_i = k_i[R][M] = 2k_d[I]$
- **R_i = 2k_d [I] marks the ideal case 100% efficiency of chain initiation by the primary radicals.**



Rate of chain initiation

As the radicals are transient species and they give rise to chain initiation as soon as they are generated in the monomer system, the rate of chain initiation, R_i will be the same as the rate of radical generation in the absence of undesirable wastage of the chain initiating radicals, R$^\bullet$ by side reactions.

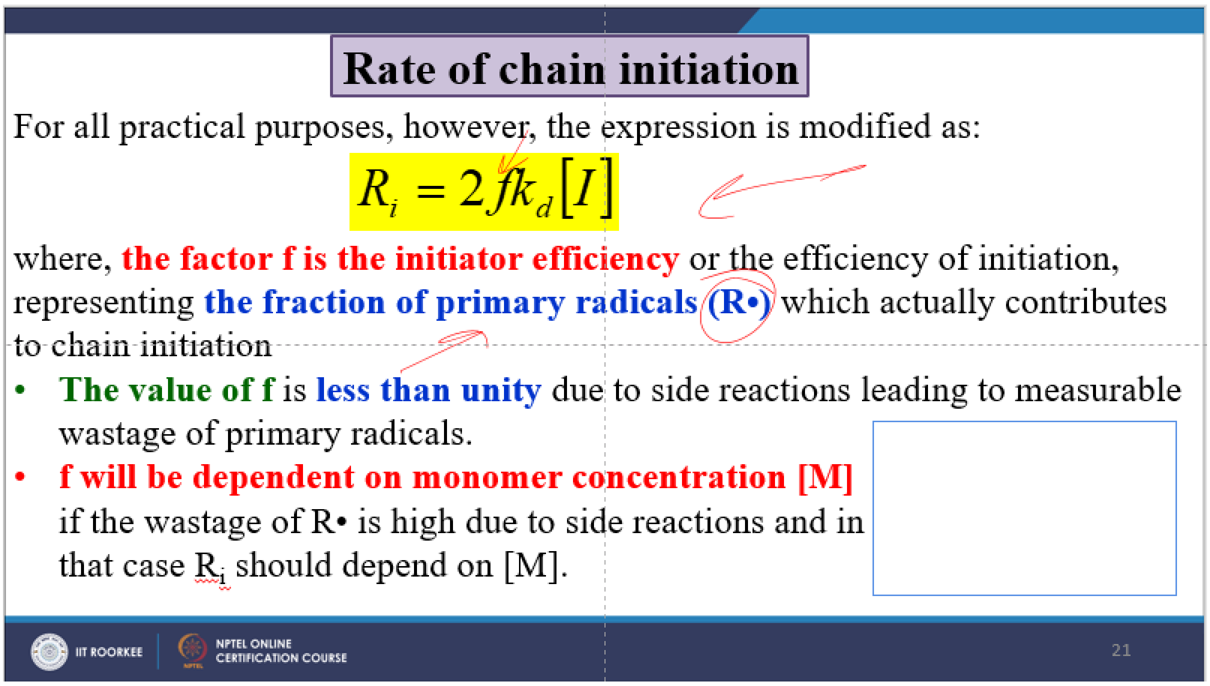
$$R_i = \left(\frac{d[M\bullet]}{dt}\right)_i = k_i[R][M] = 2k_d[I]$$

Thus, $R_i = 2k_d$ [I] marks the ideal case 100% efficiency of chain initiation by the primary radicals.

Now as the radicals are transient species and they give rise to the chain initiation as soon as they are generated in the monomer system the rate of chain initiation r i will be the same as the rate of radical generation in the absence of undesirable wastage of the chain initiating radicals are by side reaction. So, this can be represented as r i is equal to d radical of m over d t is equal to k i concentration of r concentration of m is equal to 2 k d concentration of i for r i this is the 2 k d i this makes the ideal case that is a 100 percent efficiency of the chain initiation by the primary radicals.

For all practical purposes, however, the expression is modified as:

$$R_i = 2fk_d[I]$$



Rate of chain initiation

For all practical purposes, however, the expression is modified as:

$$R_i = 2fk_d[I]$$

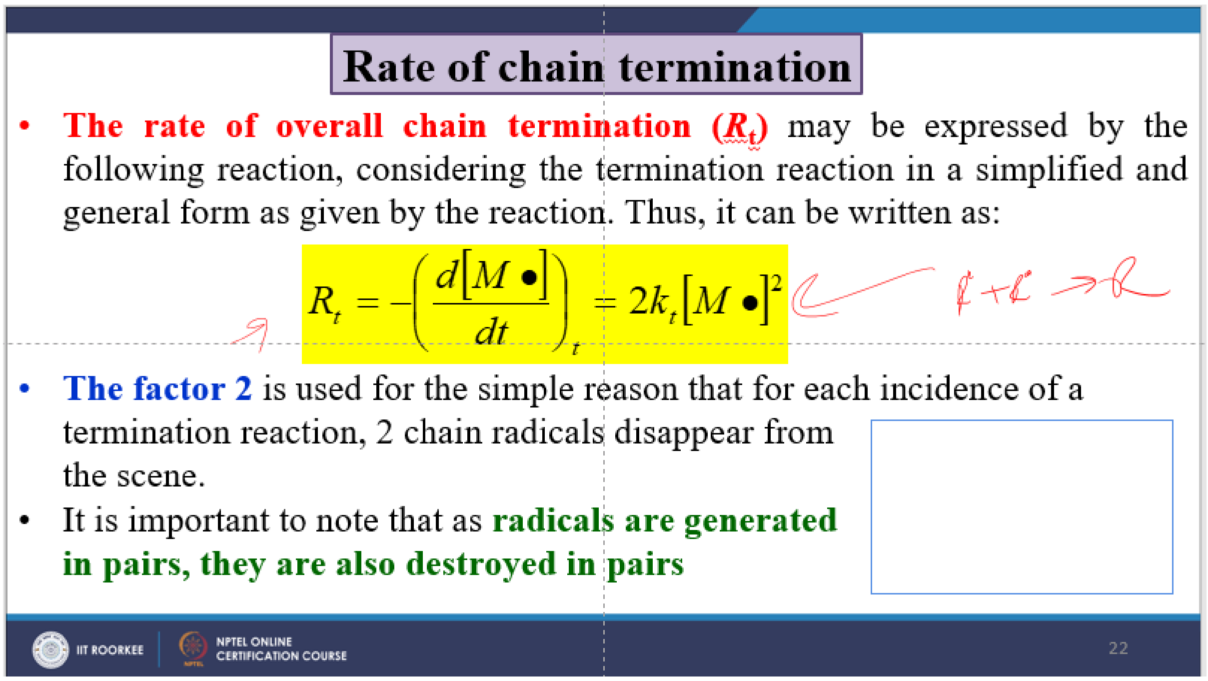
where, **the factor f is the initiator efficiency** or the efficiency of initiation, representing **the fraction of primary radicals (R•)** which actually contributes to chain initiation

- **The value of f** is **less than unity** due to side reactions leading to measurable wastage of primary radicals.
- **f will be dependent on monomer concentration [M]** if the wastage of R• is high due to side reactions and in that case R_i should depend on [M].

Now for all practical purposes however the expression is modified as r i is equal to 2 f k d i for where the factor f this factor is the initiator efficiency or the efficiency of the initiation this is represented by the fraction of primary radicals which actually contributes to the chain initiation. So, the value of f is less than unity due to the side reactions leading to the measurable wastage of primary radicals. Now f will be dependent on the monomer concentration m if the wastage r is high due to side reaction and in that case r i should be dependent on concentration of monomer.

The rate of overall chain termination (Rt)

$$R_t = -\left(\frac{d[M\bullet]}{dt}\right)_t = 2k_t[M\bullet]^2$$



Rate of chain termination

- **The rate of overall chain termination (R_t)** may be expressed by the following reaction, considering the termination reaction in a simplified and general form as given by the reaction. Thus, it can be written as:

$$R_t = -\left(\frac{d[M\bullet]}{dt}\right)_t = 2k_t[M\bullet]^2$$

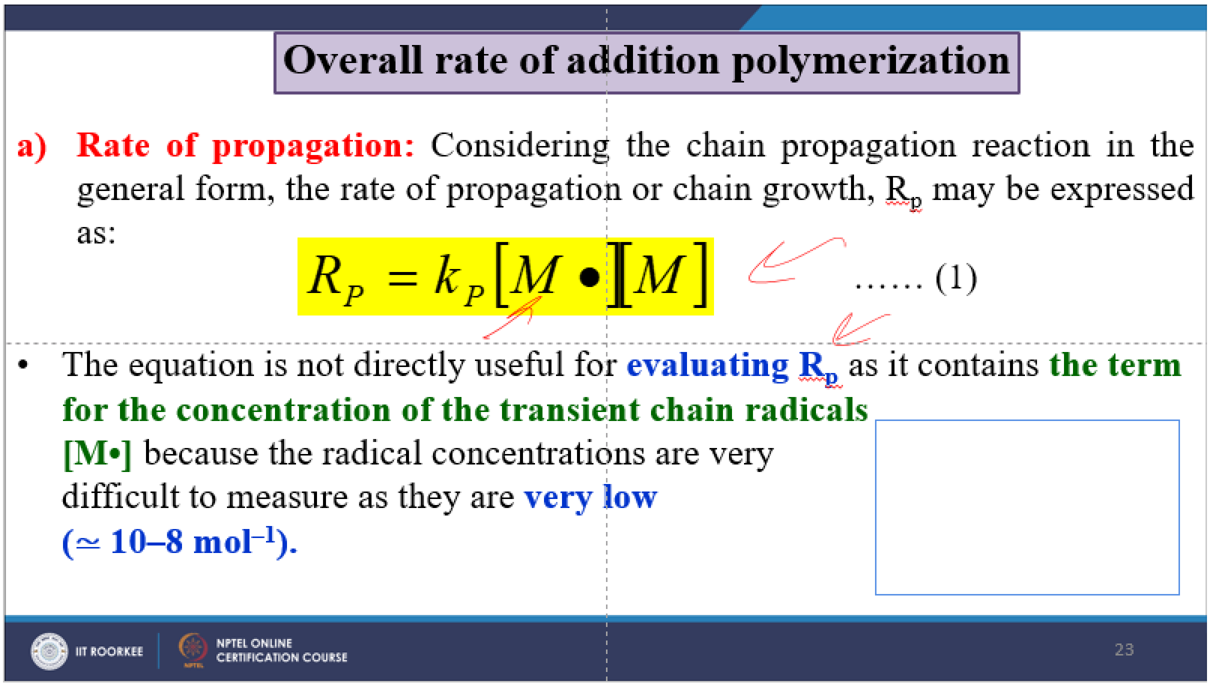
$R^{\bullet} + R^{\bullet} \rightarrow R$

- **The factor 2** is used for the simple reason that for each incidence of a termination reaction, 2 chain radicals disappear from the scene.
- It is important to note that as **radicals are generated in pairs, they are also destroyed in pairs**

The rate of overall termination r t this may be expressed by this particular reaction considering the termination reaction in a simplified and a general form as per the reaction mechanism and thus mathematically we can represent as r t is equal to minus d concentration of m monomer over dt is equal to 2 k concentration of m radical to the power 2. The factor 2 is used for the simple reason that each incidence of a termination reaction 2 chain radicals disappears like this one. So, it is important to note that the radicals are generated in pairs they are also destroyed in pairs otherwise one active radical will be there. Now rate of propagation now considering the chain propagation reaction in the general form the rate of propagation or the chain growth r p this may be expressed as r p is equal to k p m radical and concentration of m. This equation is not directly useful for the evaluating the rate of propagation as it contains the term for the concentration of transient chain radicals because the radical concentration is very difficult to measure as they are very low and that is maybe 10 to the power minus 8 mole inverse.

Rate of propagation

$$R_P = k_P[M\bullet][M]$$



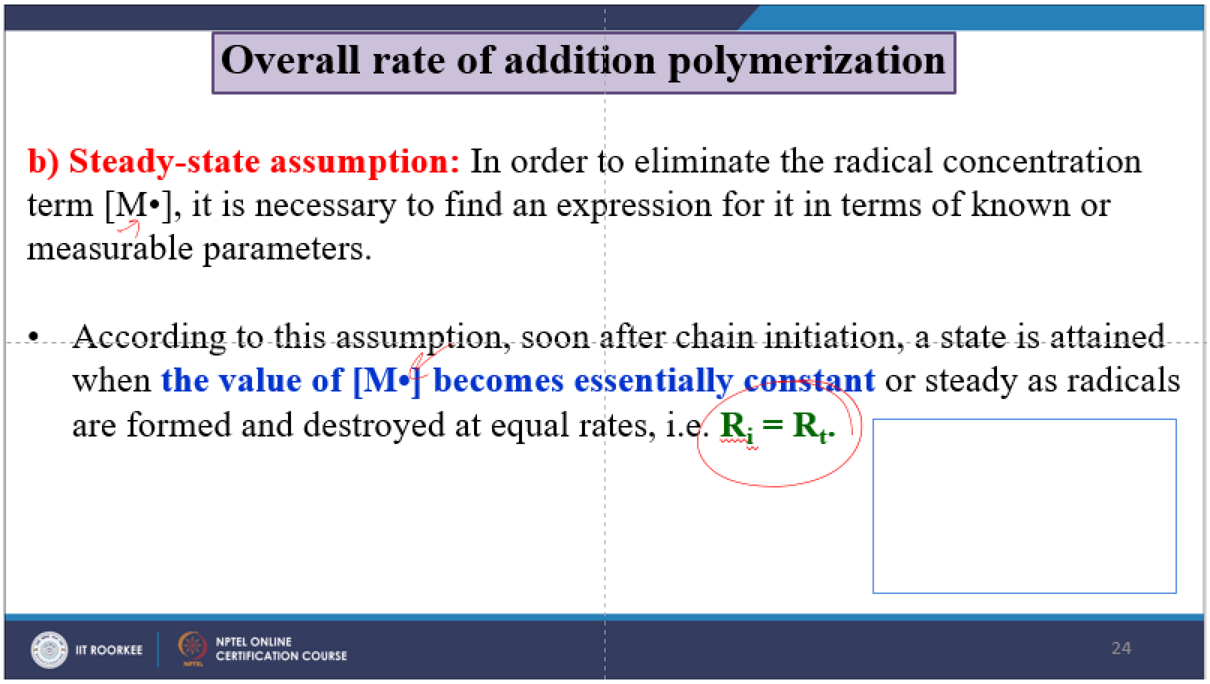
Overall rate of addition polymerization

a) Rate of propagation: Considering the chain propagation reaction in the general form, the rate of propagation or chain growth, R_p may be expressed as:

$$R_P = k_P[M\bullet][M] \quad \ldots\ldots (1)$$

- The equation is not directly useful for **evaluating R_p** as it contains **the term for the concentration of the transient chain radicals [M•]** because the radical concentrations are very difficult to measure as they are **very low (≃ 10–8 mol^{-1}).**

So, if we talk about the overall adhesion of overall rate of adhesion polymerization now steady state assumption is that in order to eliminate the radical concentration term m it is necessary to find an expression for it in terms of known or measurable parameters.



Overall rate of addition polymerization

b) Steady-state assumption: In order to eliminate the radical concentration term [M•], it is necessary to find an expression for it in terms of known or measurable parameters.

- According to this assumption, soon after chain initiation, a state is attained when **the value of [M•] becomes essentially constant** or steady as radicals are formed and destroyed at equal rates, i.e. $R_i = R_t$.

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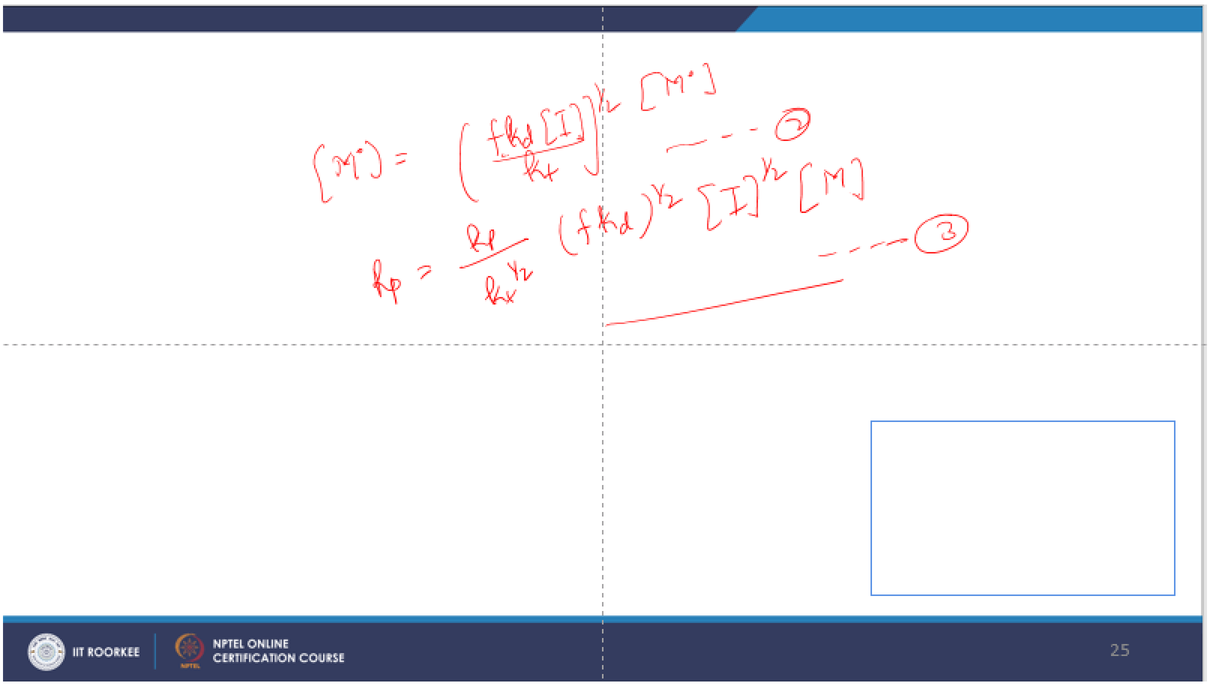
So as per this assumption soon after the chain initiation a state is attained where the value of this m radical become essentially constant or steady as radicals are formed and destroyed at equal rates that is r i is equal to r t. So on the basis of the steady state assumption the concentration of m radical this can be expressed as f k d concentration of initiator over k t to the power half this can be represented as equation 2. Now the expression for rate of propagation r p this reduces to r p that is equal to k p over k t to the power half f k d to the power half into initiator concentration to the power half into m. So, this can be represented as equation number 3.



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

$$R_p = \frac{k_p}{k_t^{1/2}} (f k_d)^{1/2} [I]^{1/2} [M] \quad --- ③$$

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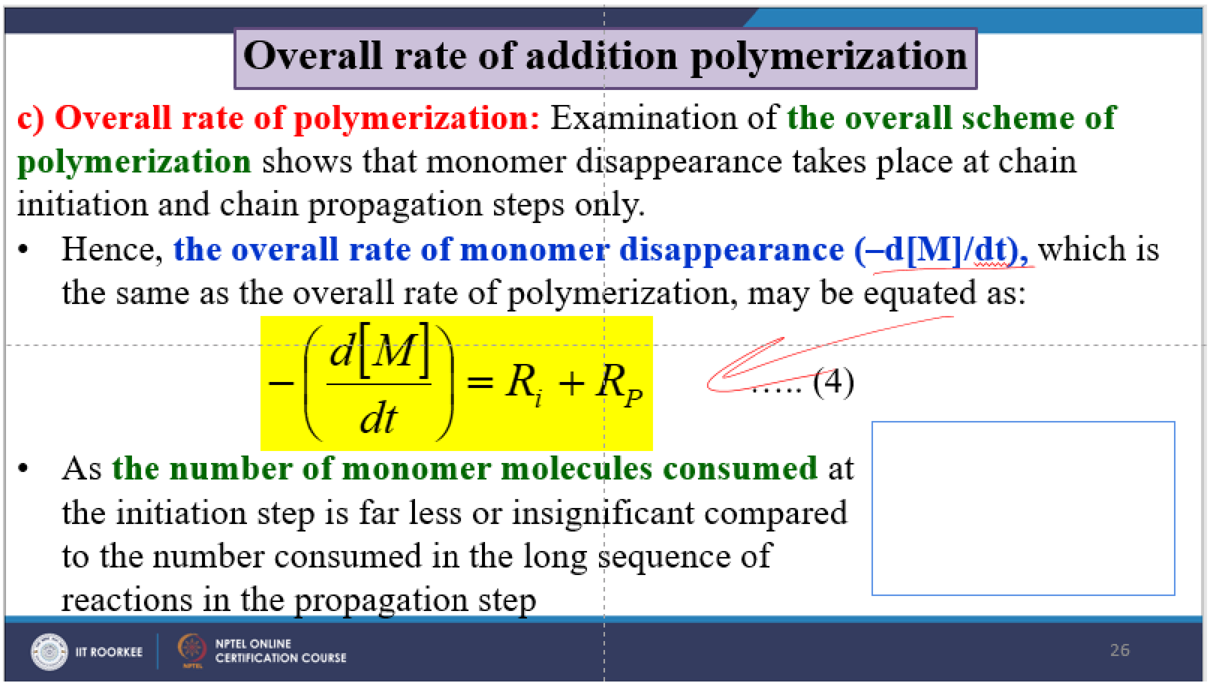
So, by this way we can represent this both concentration of m radical and r p. Now if we talk about the overall polymerization now examining the overall scheme of polymerization this shows that the monomer disappearance takes place at a chain initiation and chain propagation steps only. Hence the overall rate of a monomer disappearance that is d minus d m over d t which is the same as the overall rate of polymerization this can be expressed as minus d m over d t is equal to r i plus r p. So as a number of monomer molecules consumed at the initiation step is far less or insignificant compared to the number of consumed and the long sequence of reaction in the propagation step. So, the overall rate of polymerization is for all practical purposes simply equated to the rate of propagation that is r p.

- the overall rate of polymerization, may be equated as:
- $-\left(\frac{d[M]}{dt}\right) = R_i + R_P$
- The overall rate of polymerization is, for all practical purposes, simply equated to the rate of propagation, R_P. Therefore, overall rate of polymerization
- $-\left(\frac{d[M]}{dt}\right) = R_P = \frac{k_P}{k_t^{\frac{1}{2}}}.(fk_d)^{\frac{1}{2}}.[I]^{\frac{1}{2}}.[M]$

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



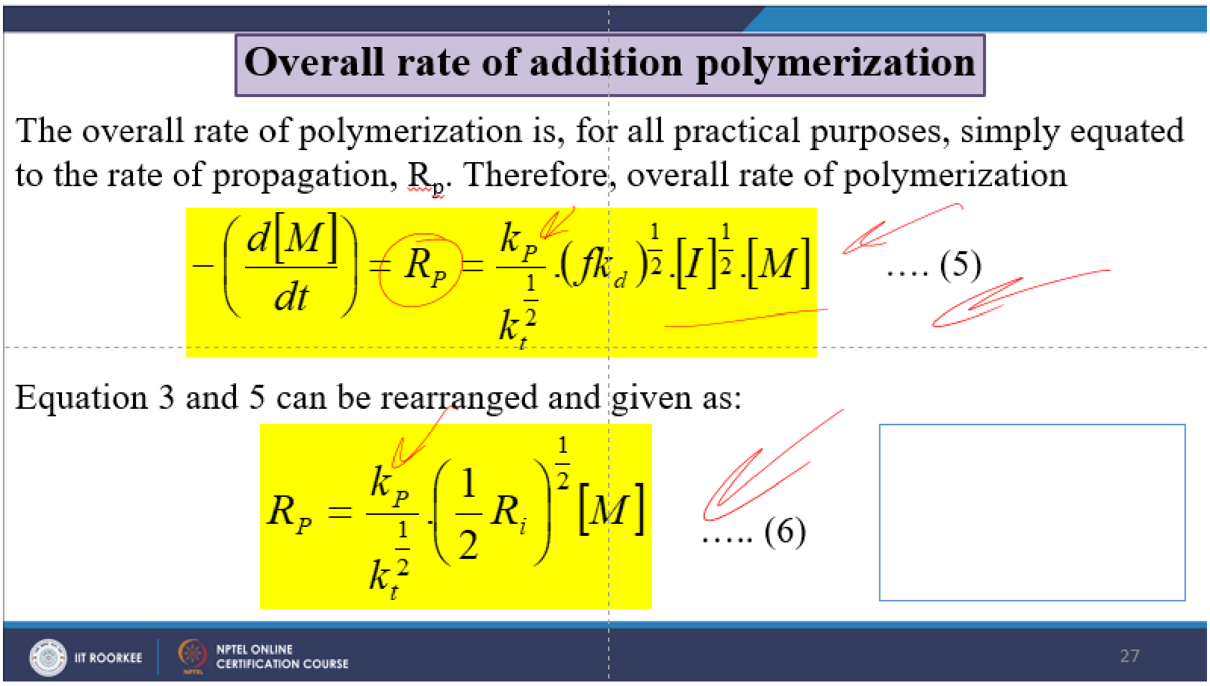
Overall rate of addition polymerization

c) Overall rate of polymerization: Examination of **the overall scheme of polymerization** shows that monomer disappearance takes place at chain initiation and chain propagation steps only.

- Hence, **the overall rate of monomer disappearance (–d[M]/dt),** which is the same as the overall rate of polymerization, may be equated as:

$$-\left(\frac{d[M]}{dt}\right) = R_i + R_P \qquad \text{….. (4)}$$

- As **the number of monomer molecules consumed** at the initiation step is far less or insignificant compared to the number consumed in the long sequence of reactions in the propagation step



Overall rate of addition polymerization

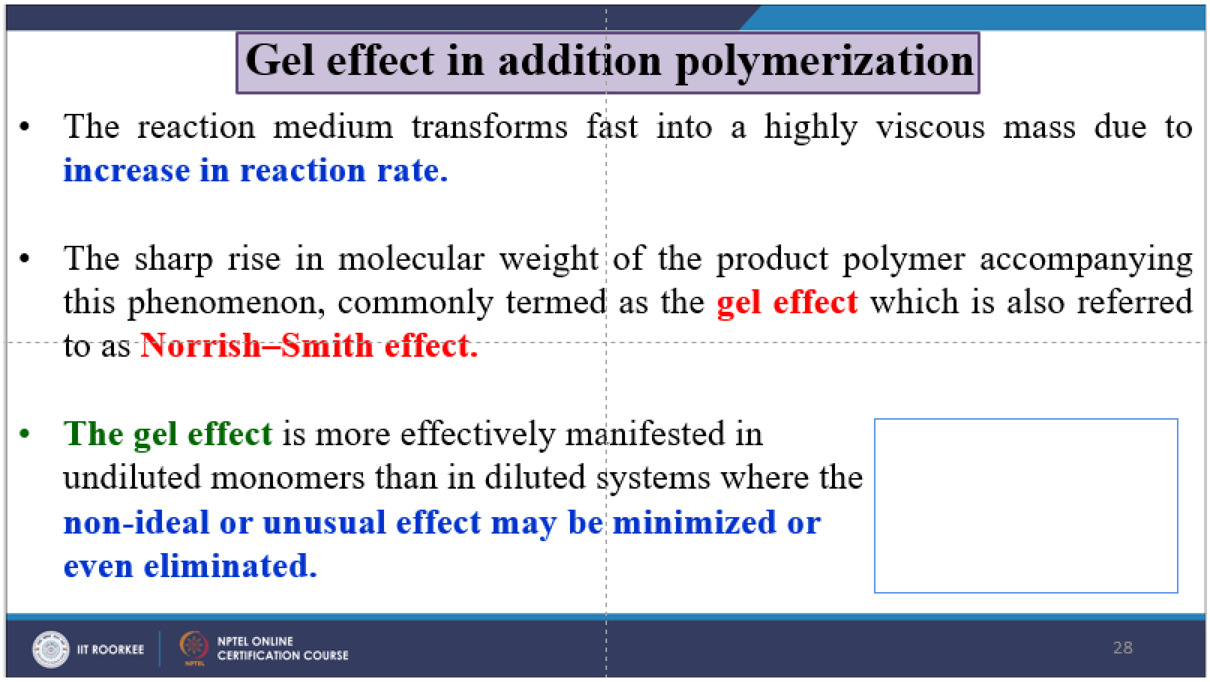
The overall rate of polymerization is, for all practical purposes, simply equated to the rate of propagation, R_p. Therefore, overall rate of polymerization

$$-\left(\frac{d[M]}{dt}\right) = R_P = \frac{k_P}{k_t^{\frac{1}{2}}}.(fk_d)^{\frac{1}{2}}.[I]^{\frac{1}{2}}.[M] \quad \ldots. (5)$$

Equation 3 and 5 can be rearranged and given as:

$$R_P = \frac{k_P}{k_t^{\frac{1}{2}}}.\left(\frac{1}{2}R_i\right)^{\frac{1}{2}}[M] \quad \ldots.. (6)$$

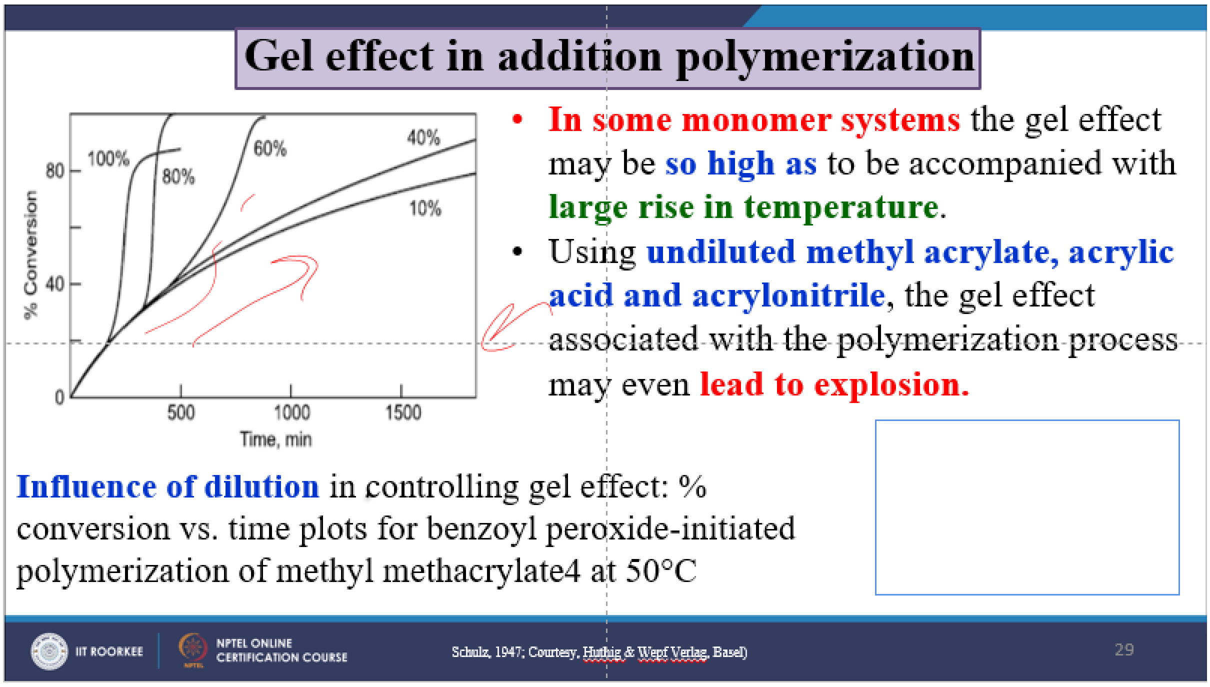
Therefore, overall rate of polymerization can be given as minus d m over d t that is equal to r p k p over k t to the power half f k d to the power half i to the power half and concentration of monomer. So, if we club equation 3 and this equation this can be represented as r p is equal to k p over k t to the k to the power half into 1 by 2 r i to the power half into concentration of m. Let us talk about the gel effect in the addition polymerization. The reaction medium transforms fast into the highly viscous mass due to increase in the reaction rate. The sharp rise in molecular weight of the product polymer accompanying this particular phenomenon commonly termed as a gel effect which is also referred as Norrish Smith effect.



Gel effect in addition polymerization

- The reaction medium transforms fast into a highly viscous mass due to **increase in reaction rate.**
- The sharp rise in molecular weight of the product polymer accompanying this phenomenon, commonly termed as the **gel effect** which is also referred to as **Norrish–Smith effect.**
- **The gel effect** is more effectively manifested in undiluted monomers than in diluted systems where the **non-ideal or unusual effect may be minimized or even eliminated.**

Now this gel effect is more effectively manifested in undiluted monomer than in diluted system where non-ideal or unusual effect may be minimized or even eliminated. Now here in some of the monomer system the gel effect may be so high as to company by the large rise in temperature. So, using undiluted methyl acrylate or acrylic acid or acrylonitrile the gel effect associated with the polymerization process may even lead to the explosion and various accidents they do occur in past just because of this situation. Now influence of dilution in controlling gel effect percent conversion versus time plot is given here. This is for the benzoyl peroxide-initiated polymerization of methyl methacrylate at 50 degree Celsius.



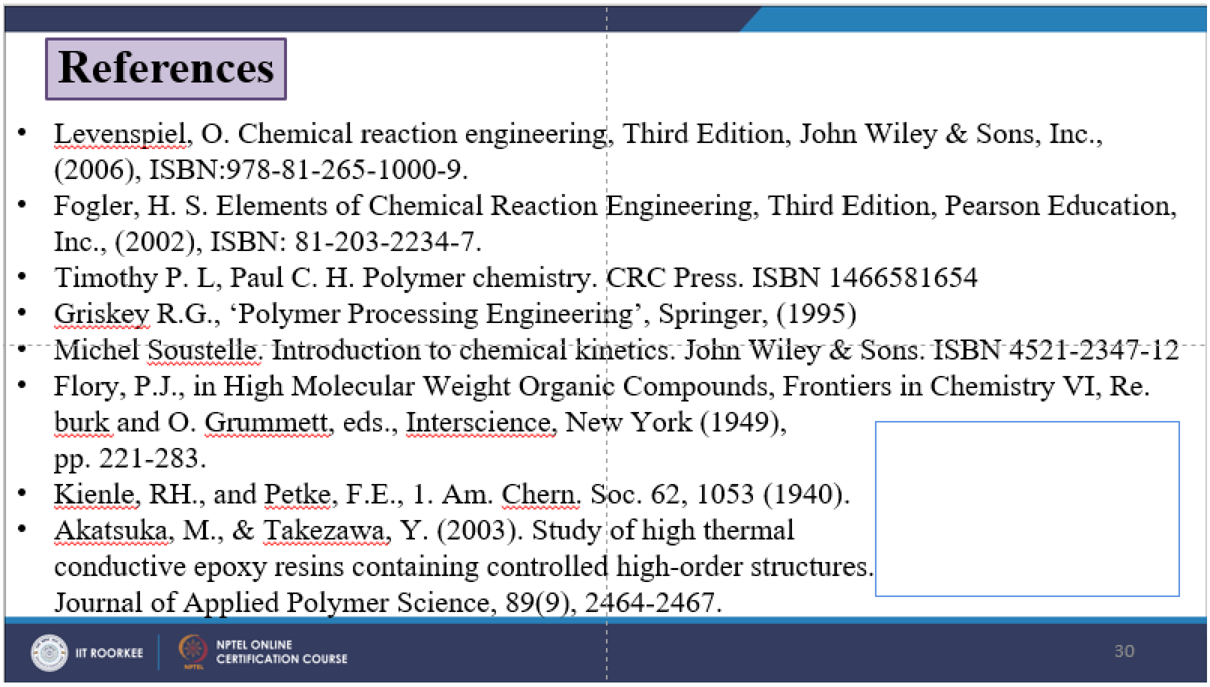
Gel effect in addition polymerization

- **In some monomer systems** the gel effect may be **so high as** to be accompanied with **large rise in temperature**.
- Using **undiluted methyl acrylate, acrylic acid and acrylonitrile**, the gel effect associated with the polymerization process may even **lead to explosion.**

Influence of dilution in controlling gel effect: % conversion vs. time plots for benzoyl peroxide-initiated polymerization of methyl methacrylate4 at 50°C

Schulz, 1947; Courtesy, Huthig & Wepf Verlag, Basel)

You can see the effect in the different domain of the different concentration. So dear friends in this particular aspect we discussed the various aspects of addition polymerization, different effects and for your convenience we have enlisted a large number of references.



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You can go ahead with the further studies as per your convenience and as per your choice. Thank you very much.