Polymer Reaction Engineering
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Lecture – 59
Ionic Polymerization - IV

Welcome to the next module of this ionic polymerization. Now, if you recall that previously we discussed about the cationic polymerization of carbon-carbon double bond.

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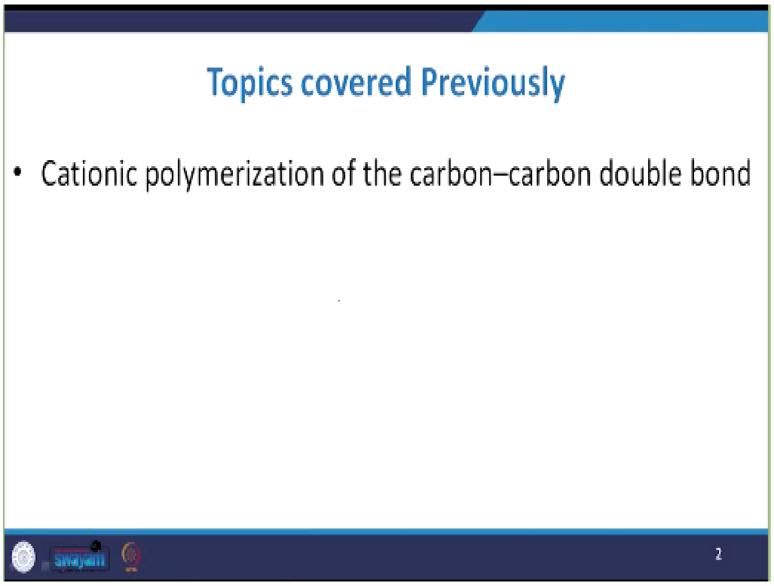

Topics covered Previously

- Cationic polymerization of the carbon–carbon double bond

In this head, we discussed about the various Initiation Protocol for this cationic polymerization. We discussed about the photo initiation effect we discussed about the radiation induced initiation steps etcetera. Now, in this particular chapter, we will discuss about the propagation, chain transfer and termination and the kinetics of cationic polymerization.

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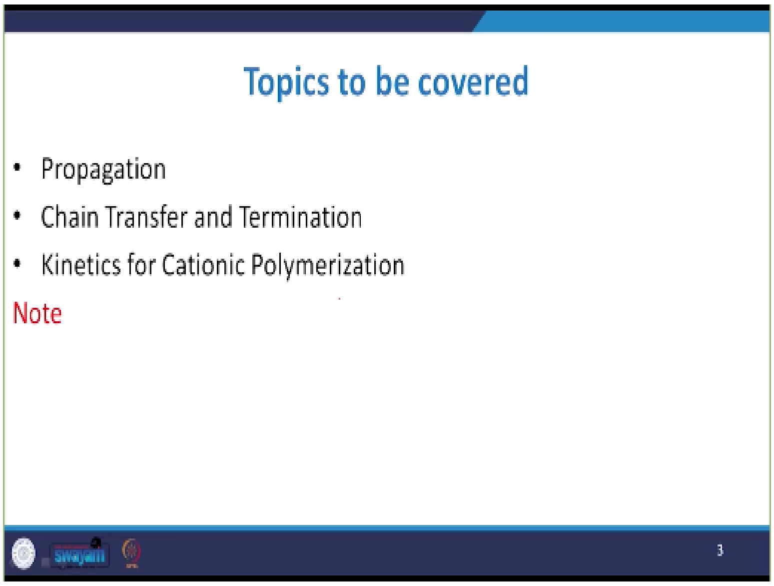

Topics to be covered

- Propagation
- Chain Transfer and Termination
- Kinetics for Cationic Polymerization

Note

So, because this particular lecture deliberated more towards the basic mechanism of the this cationic polymerization. So, let us have a look about this propagation step.

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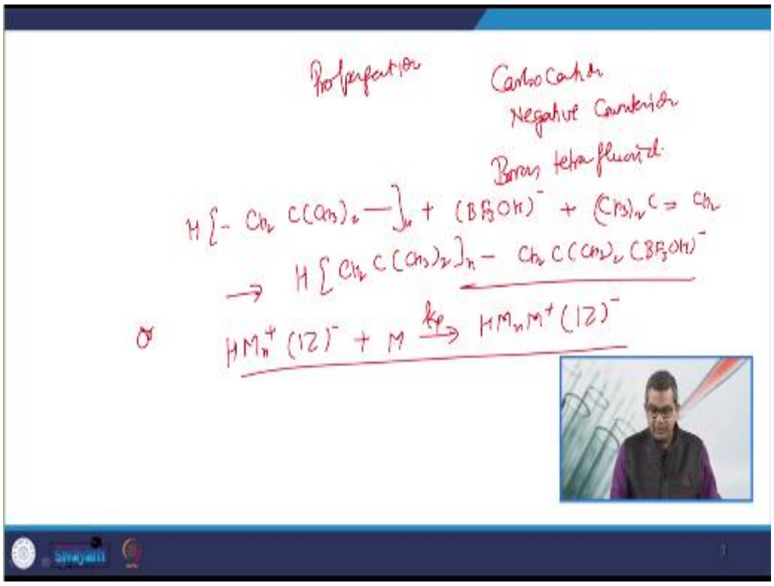

Propagation

Carbocation

Negative Counterion

Boron tetrafluoride

$$H\{-CH_2C(CH_3)_2-\}_n + (BF_3OH)^- + (CH_3)_2C=CH_2$$

$$\rightarrow H[CH_2C(CH_3)_2]_n - CH_2C(CH_3)_2(BF_3OH)^-$$

or

$$HM_n^+(IZ)^- + M \xrightarrow{k_p} HM_nM^+(IZ)^-$$

Propagation

The initiator ion pair (consisting of the carbocation and its negative counterion) produced in the initiation step (taking the example of boron tetrafluoride in continuation) proceeds to propagate by successive additions of monomer molecules

$$H[-CH_2C(CH_3)_2 -]_n^+ (BF_3OH)^- + (CH_3)_2C = CH_2 \rightarrow H[CH_2C(CH_3)_2]_n - CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^-$$

Now, in the propagation step the initiator ion pair usually consisting of carbocations and its negative counterions. So, these 2 things counter ions they produced usually in the initiation step with the example of say, if you recall in the previous lecture, we discussed about the Boron tetrafluoride. And in continuation process, if you recall that we discussed a lot of various techniques for this initiation step.

or

$$HM_n^+(IZ)^- + M \xrightarrow{K_p} HM_nM^+(IZ)^-$$

Now, this is the more appropriate form to represent in the reaction engineering concepts. So, when you try to develop the reaction mechanism, then it facilitates the things.

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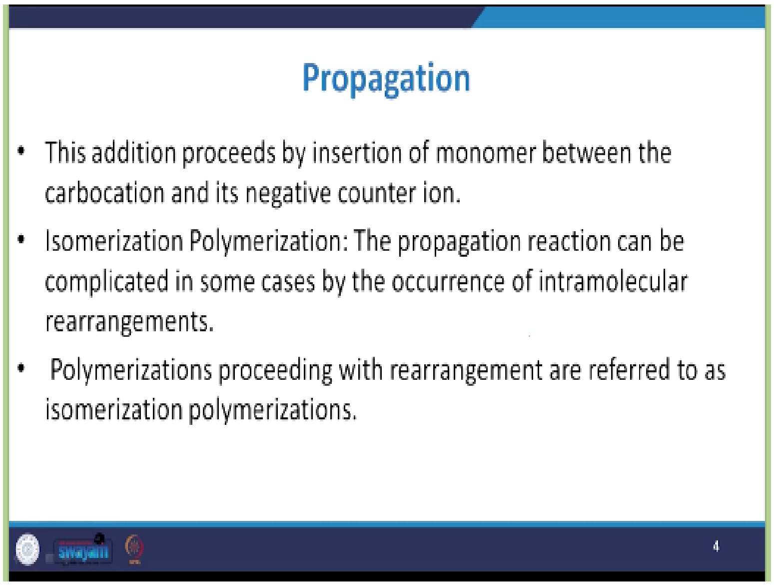

Propagation

- This addition proceeds by insertion of monomer between the carbocation and its negative counter ion.
- Isomerization Polymerization: The propagation reaction can be complicated in some cases by the occurrence of intramolecular rearrangements.
- Polymerizations proceeding with rearrangement are referred to as isomerization polymerizations.

If we talk about this particular in addition process, usually it is by the insertion of monomer between the carbocation and its negative counterion as discussed in the previous reaction. Now, sometimes isomerization polymerization need to be addressed. Now, the propagation reaction this can be complicated in some cases by the occurrence of intramolecular rearrangement, because it is the suo moto habit of all these polymer chains for this intramolecular rearrangement.

So, the polymerization proceeding with rearrangements they are referred to as the isomerization and polymerization and when we need to address this issue, one must be very selective in this approach. Extensive rearrangement during propagation occurs for a variety of 1-alkenes (α-olefins).
e.g. Propene, 1-butene, and higher 1-alkenes yield oligomers with highly irregular structures due to various combinations of 1,2-hydride and 1,2-methide shifts.
The propagating secondary carbocations are insufficiently stable to propagate without extensive rearrangement.
Simultaneously, only oligomers are formed since none of the rearrangement pathways are favorable for rapid propagation.
The extent of rearrangement during cationic propagation will depend on the:
relative stabilities of the propagating and rearranged carbocations and the relative rates of propagation and rearrangement.
Both factors favor propagation without rearrangement for monomers such as styrene, indene, acenaphthylene, coumarone, vinyl ethers, and isobutylene.

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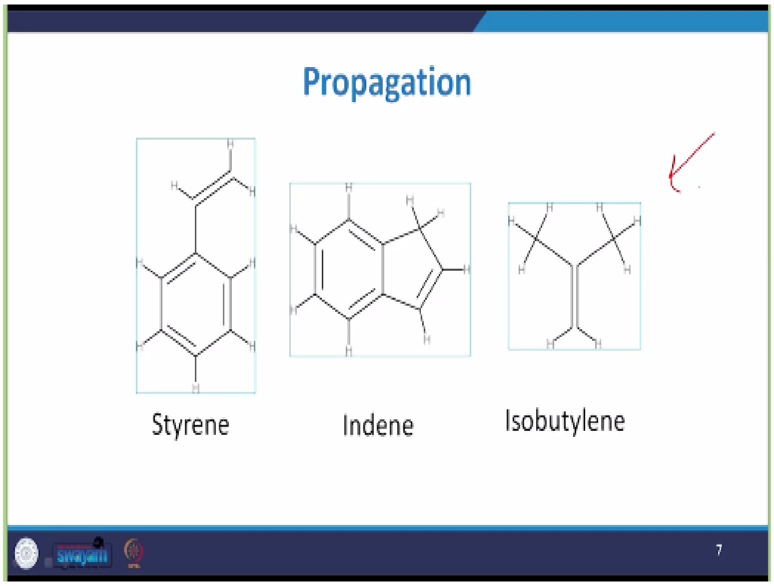

Propagation

Styrene

Indene

Isobutylene

Now, these are the structures, which are equally important when we try to develop the rearrangement patterns under the aegis of isomerization of those polymetric species or the under polymerization process. Now, not only these monomers propagate via reasonably stable carbocations, such as tertiary benzyl oxy carbocations. The Carbocations have no roots available for a rearrangement to more stable Carbocations.

So, it is a very, you can say the tedious type of a situation. Now isomerization polymerization yield high molecular weight products. So, when reaction proceeds further through a relatively simple rearrangements route involving stable carbocations. Now, when we talk about the chain transfer and termination, various reactions sometimes led to the termination of chain growth in cationic polymerization reaction.

Now, see, these two things the chain transfer and termination both are equally important compared to the propagation. The reason is that whenever you require the polymer to have a desired property, then you need to truncate the polymerization at appropriate time and appropriate juncture. So, that is why this chain transfer sometimes you may transfer the charge sometimes you may chant transfer the radicals and by any means, you need to tell me the things too that is why this particular concept is extremely important to address.

Now, many of the reactions those who terminate the growth of a propagating chain sometimes they do not sometimes they do. So, the termination kinetics chain or termination kinetics need to be addressed properly. Now terminate the kinetic chain sometimes they may be formation of a new propagating species is generated in the in the process and sometimes it is quite advantageous sometimes it is disadvantageous.

Now, the disadvantageous may sometimes it may promote to the formation of other polymeric chains those polymeric Chain sometimes may not be desired one.

β-proton Transfer

Transfer of a β-proton from the propagating carbocation is the most important chain-breaking reaction.

It occurs readily because much of the positive charge of the cationic propagating center resides not on carbon, but on the β-hydrogens because of hyper-conjugation.

Monomer, counter ion or any other basic species in the reaction mixture can abstract a b-proton.

Chain transfer to monomer involves transfer of a b-proton to monomer with the formation of terminal unsaturation in the polymer.

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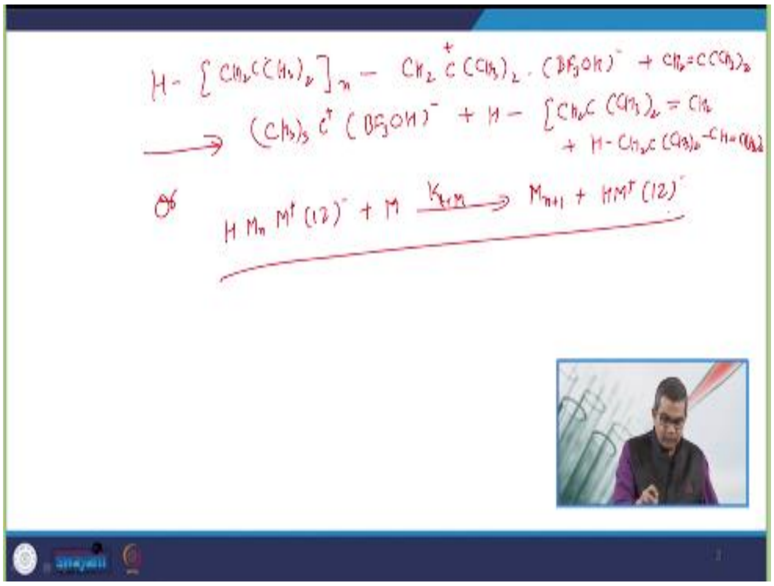

$$H-[CH_2C(CH_3)_2]_n - CH_2\overset{+}{C}(CH_3)_2.(BF_3OH)^- + CH_2=C(CH_3)_2$$

$$\longrightarrow (CH_3)_3C^+(BF_3OH)^- + H-[CH_2C(CH_3)_2=CH_2 + H-CH_2C(CH_3)_2-CH=C(CH_3)_2$$

or

$$HM_nM^+(IZ)^- + M \xrightarrow{K_{tr,M}} M_{n+1} + HM^+(IZ)^-$$

$H{-}[CH_2C(CH_3)_2]_n - CH_2\overset{+}{C}(CH_3)_2.(BF_3OH)^- + CH_2 = C(CH_3)_2 \longrightarrow (CH_3)_3C^+(BF_3OH)^- + H - [CH_2C(CH_3)_2 = CH_2 + H - CH_2C(CH_3)_2 - CH = C(CH_3)_2$

Or

$$HM_nM^+(IZ)^- + M \xrightarrow{K_{tr,M}} M_{n+1} + HM^+(IZ)^-$$

There are two different types of β-protons, and two different unsaturated end groups are possible for isobutylene as well as some other monomers such as indene and α-methyl styrene. The relative amounts of the two end groups depend on the counter ion, identity of the propagating center, and other reaction conditions.

Only one type of unsaturated end group (i.e. internal group) is possible for other monomers such as styrene, ethyl vinyl ether, and coumarone.

It should be noted that the kinetic chain is not terminated by this reaction since a new propagating species is regenerated.

Chain transfer to monomer is on much more favorable terms with propagation in many cationic polymerizations compared to radical polymerization.

So, only one type of unsaturated end group that is referred as an internal group is possible for other monomers such as styrene, ethyl vinyl ether etcetera. Now, it should be pointed out at this juncture that the kinetic chain is not terminated by this reaction, since the new propagating species is already generated, and it is equally active in the reaction mass. So, therefore, it is not been terminated you can't say that this is terminated.

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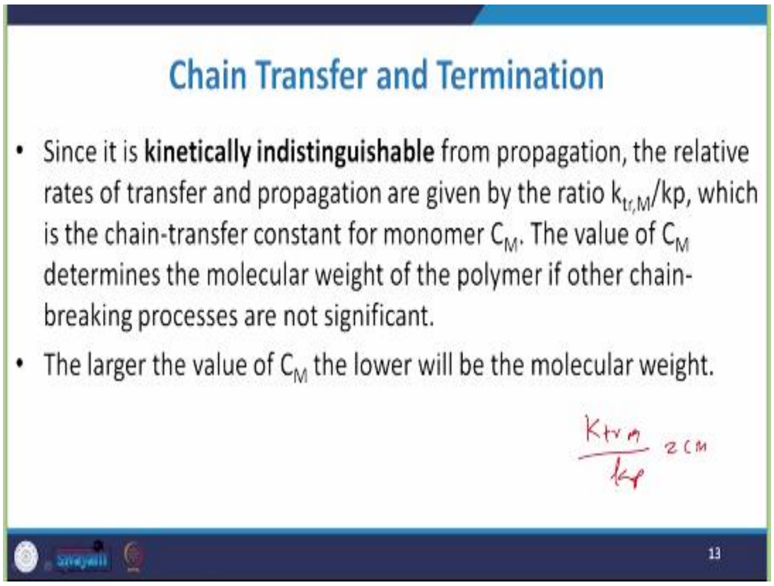

Chain Transfer and Termination

- Since it is **kinetically indistinguishable** from propagation, the relative rates of transfer and propagation are given by the ratio $k_{tr,M}/kp$, which is the chain-transfer constant for monomer C_M. The value of C_M determines the molecular weight of the polymer if other chain-breaking processes are not significant.
- The larger the value of C_M the lower will be the molecular weight.

$$\frac{K_{trm}}{kp} = CM$$

Since it is **kinetically indistinguishable** from propagation, the relative rates of transfer and propagation are given by the ratio $k_{tr,M}$/kp, which is the chain-transfer constant for monomer C_M. The value of C_M determines the molecular weight of the polymer if other chain-breaking processes are not significant.
The larger the value of C_M the lower will be the molecular weight.

The value of C M determines the molecular weight of the polymer if other chain breaking processes are not significant. So, in your molecular weight distribution plays a vital role. Now, the larger the value of C M the lower will be the molecular weight, it is quite obvious to this particular mathematical equation.

Now, chain transfer to monomer is the principal reaction that limits polymer molecular weight for most monomers, specially at reaction temperature higher than say about 20 ^{o}C. Now, since, the chain transfer to monomer generally has a higher activation energy than propagation, it is usually suppressed by working at a low reaction temperature.

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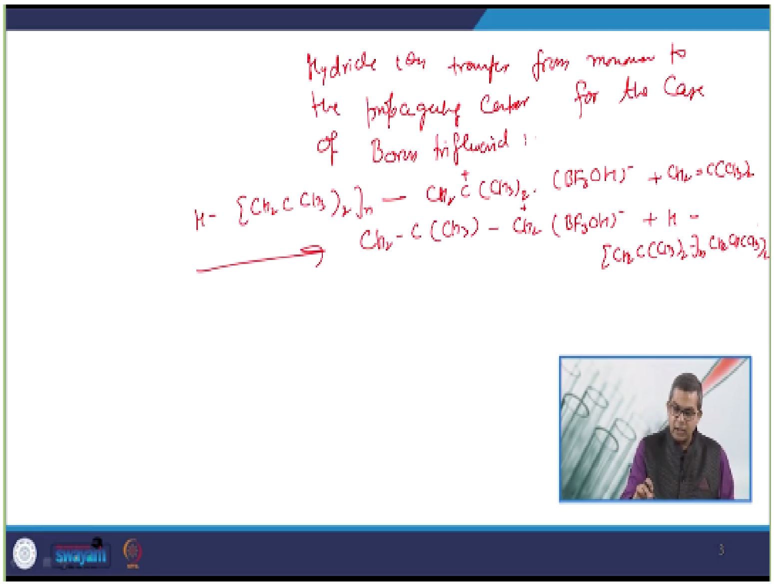

Hydride ion transfer from monomer to
the propagating center for the Case
of Boron trifluoride :

$H-[CH_2C(CH_3)_2]_n - CH_2\overset{+}{C}(CH_3)_2 . (BF_3OH)^- + CH_2=C(CH_3)_2 \longrightarrow CH_2-C(CH_3)-\overset{+}{C}H_2(BF_3OH)^- + H-[CH_2C(CH_3)_2]_n CH_2CH(CH_3)_2$

chain transfer to monomer reaction involving hydride ion transfer from monomer to the propagating center for the case of boron trifluoride is:

$$H{-}[CH_2C(CH_3)_2]_n - CH_2\overset{+}{C}(CH_3)_2.(BF_3OH)^- + CH_2 = C(CH_3)_2 \longrightarrow CH_2 - C(CH_3) - \overset{+}{C}H_2(BF_3OH)^- + H - [CH_2C(CH_3)_2 -]_n CH_2CH(CH_3)_2$$

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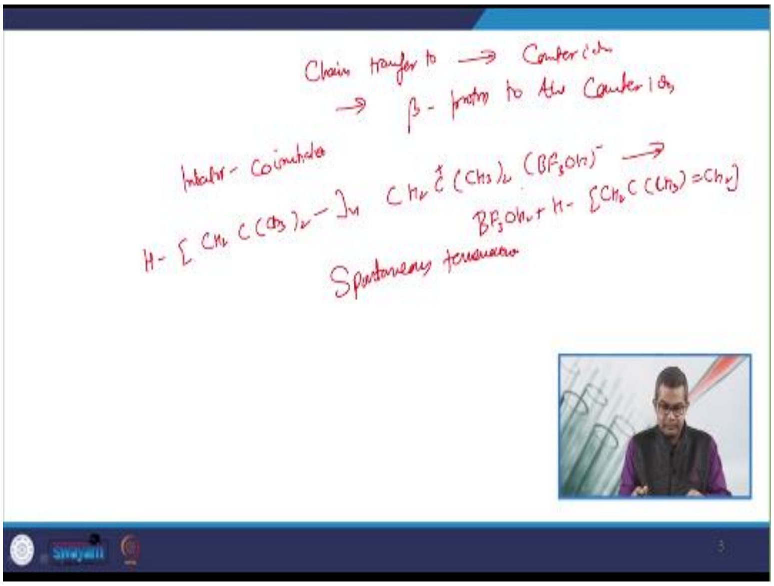

Chain transfer to → Counter ion
→ β- proton to the Counter ion

Initiator - Coinitiator

$H-[CH_2C(CH_3)_2-]_n CH_2\overset{+}{C}(CH_3)_2 (BF_3OH)^- \longrightarrow BF_3OH_2 + H-[CH_2C(CH_3)=CH_2]$

Spontaneous termination

Chain transfer to counter ion involves transfer of a β-proton to the counter ion.

The initiator–coinitiator is regenerated by its expulsion from the propagating species and, as in chain transfer to monomer, the polymer molecule has a terminal double bond

$$H - [\, CH_2C(CH_3)_2 -]_n CH_2\overset{+}{C}(CH_3)_2(BF_3OH)^- \longrightarrow BF_3.OH_2 + H - [CH_2C(CH_3) = CH_2$$

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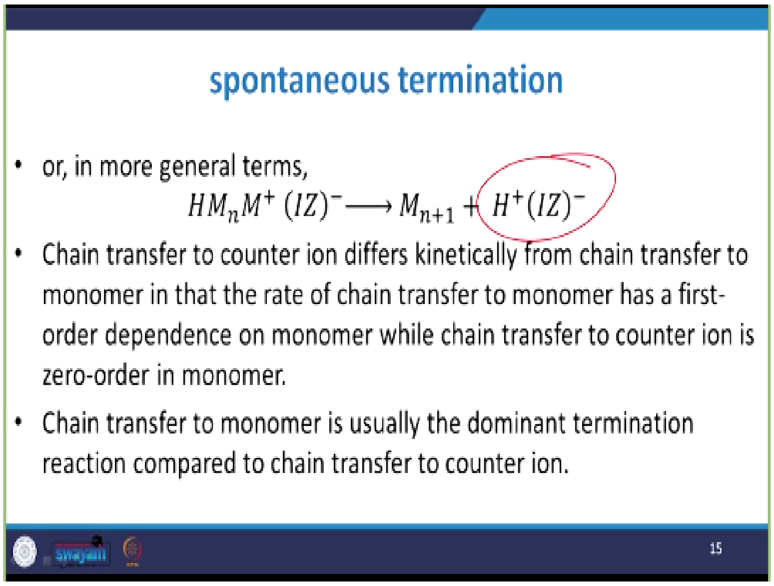

spontaneous termination

- or, in more general terms,

$$HM_nM^+ (IZ)^- \longrightarrow M_{n+1} + H^+(IZ)^-$$

- Chain transfer to counter ion differs kinetically from chain transfer to monomer in that the rate of chain transfer to monomer has a first-order dependence on monomer while chain transfer to counter ion is zero-order in monomer.
- Chain transfer to monomer is usually the dominant termination reaction compared to chain transfer to counter ion.

When we talk about the spontaneous termination sometimes we may say that if it is in the more generic term like you can represent as

$$HM_nM^+ (IZ)^- \longrightarrow M_{n+1} + H^+(IZ)^-$$

Now, the chain transfer to counter ion use well it differs kinetically in that the rate of chain transfer to monomer has a first order dependency on monomer while chain transfer to counter ion is zero-order in monomer.

Now, when we talk about the chain transfer to monomer this is usually the dominant termination reaction compared to the chain transfer to counter ions. Now, when we talk about the chain transfer to beta proton or to other basic substances in the reaction mixture, it is quite evident that it also possible the various beta proton transfer reaction, they limit the polymer molecule weight molecular weight, but do not terminate the kinetic chain. Let us have a look about the combination with the counter ion because we discussed about the importance of this counter ion. Termination by combination of the propagating center with the counterion occurs,

$$HM_nM^+ (IZ)^- \overset{k_t}{\rightarrow} HM_nMIZ$$

we can write this one and the rate constant for the termination is given by K t hmm m IZ. Now, alternatively, the propagating ion may combine with anionic fragments from the counter ion.

Now, the termination by the combination sometimes this differ from the other modes of termination in that particular kinetics which we discussed. Now, this chain is usually terminated since the counter ion of the initiator coinitiator complex, it decreases. At last when we discuss about the chain transfer to Polymer now, there are several chain transfer to polymer reactions are possible in cationic polymerization.

The transfer of cationic propagating centre, this can occur either by electrophilic aromatic substitution or hydride transfer. Now, intramolecular when we talk about the intramolecular electrophilic aromatic substance or some times, if you recall that we refer to it as backbiting, when it occurs in the polymerization of styrene. So, it may effect the other aromatic monomer with the forming a formation of terminal internal structure and the regeneration of sometimes a regeneration of initiator coinitiator complex.

So, we have discussed the various modes of termination now, let us have a look about the other modes of termination.

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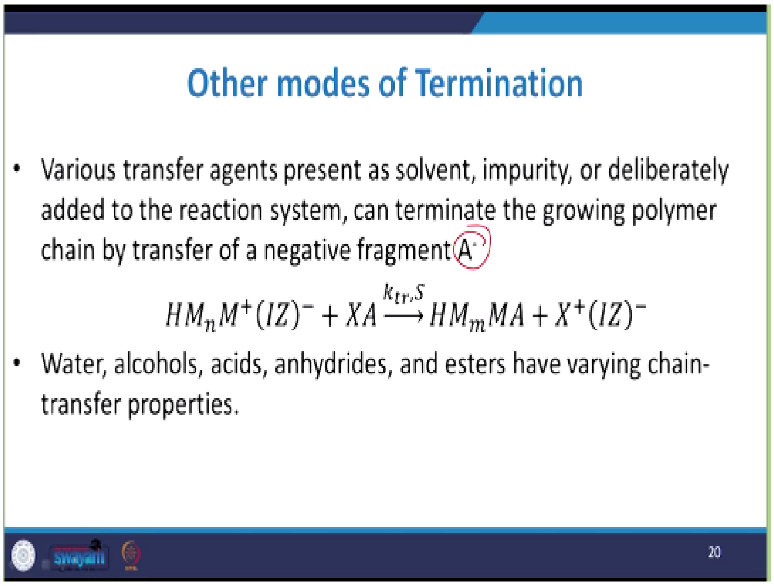

Other modes of Termination

- Various transfer agents present as solvent, impurity, or deliberately added to the reaction system, can terminate the growing polymer chain by transfer of a negative fragment A^-

$$HM_nM^+(IZ)^- + XA \xrightarrow{k_{tr,S}} HM_mMA + X^+(IZ)^-$$

- Water, alcohols, acids, anhydrides, and esters have varying chain-transfer properties.

Various transfer agents present as solvent, impurity, or deliberately added to the reaction system, can terminate the growing polymer chain by transfer of a negative fragment A^-

$$HM_nM^+(IZ)^- + XA \xrightarrow{k_{tr,S}} HM_mMA + X^+(IZ)^-$$

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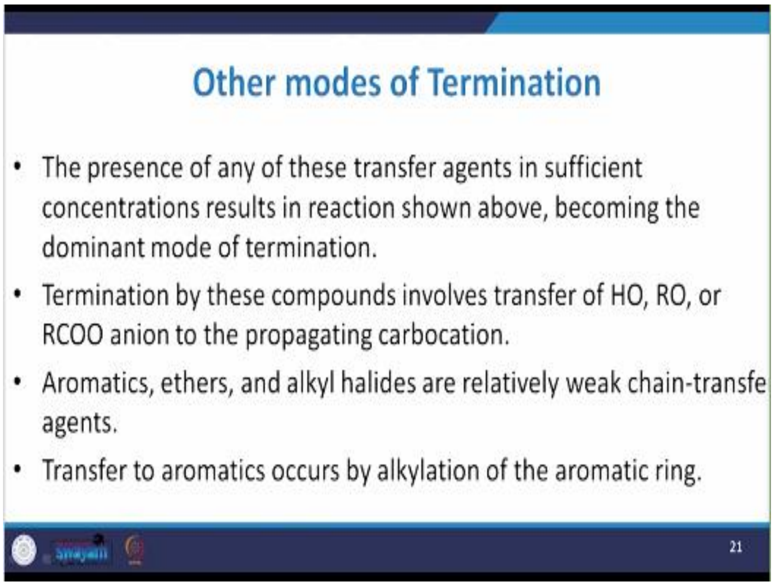

Other modes of Termination

- The presence of any of these transfer agents in sufficient concentrations results in reaction shown above, becoming the dominant mode of termination.
- Termination by these compounds involves transfer of HO, RO, or RCOO anion to the propagating carbocation.
- Aromatics, ethers, and alkyl halides are relatively weak chain-transfe agents.
- Transfer to aromatics occurs by alkylation of the aromatic ring.

The presence of any other or any of these transfer agent in the sufficient concentration sometimes results in reaction which we showed in this particular slide becoming the dominant mode of termination. Now, termination by these compounds sometimes involve the transfer of HO or RO or RCOO anion to the propagating carbocation. Aromatic ether and alkyl halides are relatively weak chain-transfer agents.

Now, transfer to the aromatics occur by alkylation of the aromatic ring. Although chain transfer agent usually decreases the degree of polymerization in proportion to its concentration, it is not expected to affect the polymerization rate, since initiator coinitiator complex should be regenerated on transfer. Sometimes, one finds that the more active transfer agents like water, alcohol and acid they do decrease the polymerization rate that is they function as inhibitors or retarders etcetera.

So, the decrease in the polymerization rate is usually caused by inactivation of a coinitiator by reaction with the chain transfer agent. Now, sometimes we will talk about the example so, other example of chain inhibitors retarders are like amines, tri aryl or tri alkyl phosphines, thiophenes these are benzoquinone etcetera. These are the other inhibitors are retarders. Now, let us discuss about the kinetics of cationic polymerization.

Now, overall kinetics vary considerably depend largely on the mode of termination in a particular system. Now, we may consider the case of termination exclusively, sometimes by the combination of the propagating centres with the counterion.

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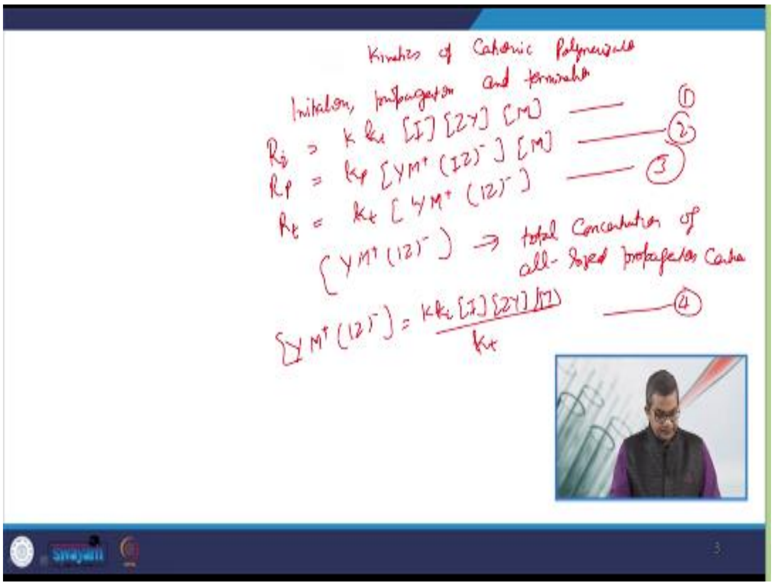

Kinetics of Cationic Polymerization

Initiation, propagation and termination

$R_i = K k_i [I][ZY][M]$ —— ①

$R_p = k_p [YM^+(IZ)^-][M]$ —— ②

$R_t = k_t [YM^+(IZ)^-]$ —— ③

$[YM^+(IZ)^-] \rightarrow$ total Concentration of all-sized propagation Centers

$[YM^+(IZ)^-] = \frac{K k_i [I][ZY][M]}{k_t}$ —— ④

Kinetics of cationic polymerization cationic polymerization

The kinetic scheme of initiation, propagation, and termination consists of :

$R_i = K k_t [I][ZY][M]$ (1)

$R_p = k_p [YM^+(IZ)^-][M]$ (2)

$R_t = k_t [YM^+(IZ)^-]$ (3)

Where $[YM^+(IZ)^-]$ is the total concentration of all-sized propagation centers:

$[YM^+(IZ)^-] = \frac{K k_i [I][ZY][M]}{k_t}$ (4)

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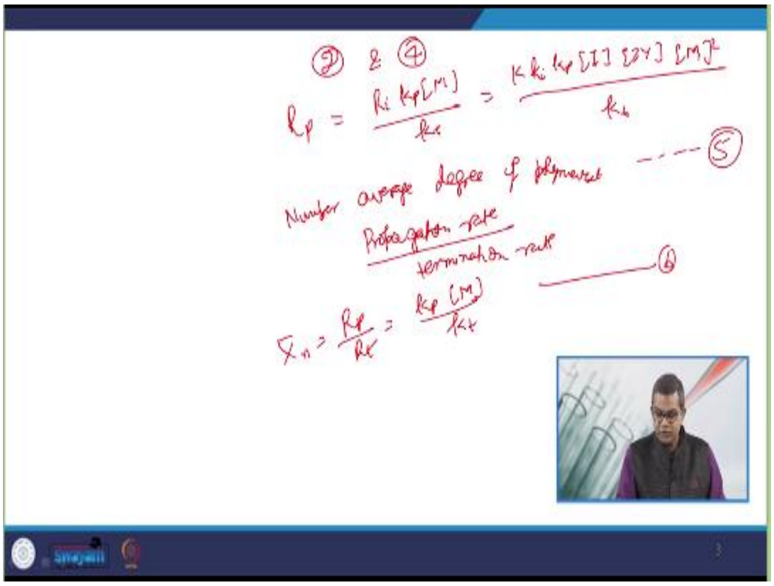

② & ④

$R_p = \frac{R_i k_p [M]}{k_t} = \frac{K k_i k_p [I][ZY][M]^2}{k_t}$ ---- ⑤

Number average degree of polymerization

$\frac{\text{Propagation rate}}{\text{termination rate}}$ —— ⑥

$\bar{X}_n = \frac{R_p}{R_t} = \frac{k_p [M]}{k_t}$

Combining equations (2) and (4) yields the rate of polymerization as

$$R_p = \frac{R_i k_p[M]}{k_t} = \frac{K k_i k_p[I][ZY][M]^2}{k_t} \qquad (5)$$

The number average degree of polymerization is obtained as the propagation rate is divided by the termination rate:

$$\overline{X_n} = \frac{R_p}{R_t} = \frac{k_p[M]}{k_t} \qquad (6)$$

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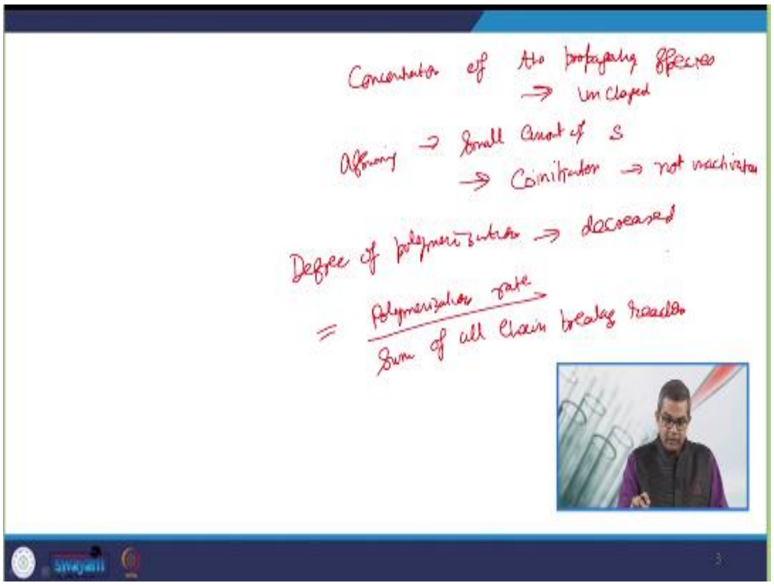

Concentration of the propagating species → unchanged

Assuming → small amount of S
→ Coinitiator → not inactivated

Degree of polymerization → decreased

$= \frac{\text{Polymerization rate}}{\text{Sum of all chain breaking reactions}}$

When chain breaking involves chain transfer to monomer, spontaneous termination, and chain transfer to chain-transfer agent S (water, impurities etc), in addition to combination with the counterion, the concentration of the propagating species remains unchanged (assuming relatively small amounts of S such that the coinitiator is not inactivated), and the polymerization rate is again given by Eq. (5).

However, the degree of polymerization is decreased by these other chain-breaking reactions and is given by the polymerization rate divided by the sum of all chain-breaking reactions:

$$\overline{X_n} = \frac{R_p}{R_t + R_{ts} + R_{tr,S} + R_{tr,M}} \qquad (7)$$

Where,

$$R_{ts} = k_{ts}[YM^+(IZ)^-] \qquad (8)$$

$$R_{tr,M} = k_{tr,M}[YM^+(IZ)^-][M] \qquad (9)$$

$$R_{tr,S} = k_{tr,S}[YM^+(IZ)^-][S] \qquad (10)$$

if we talk about the degree of polymerization usually it is decreased.

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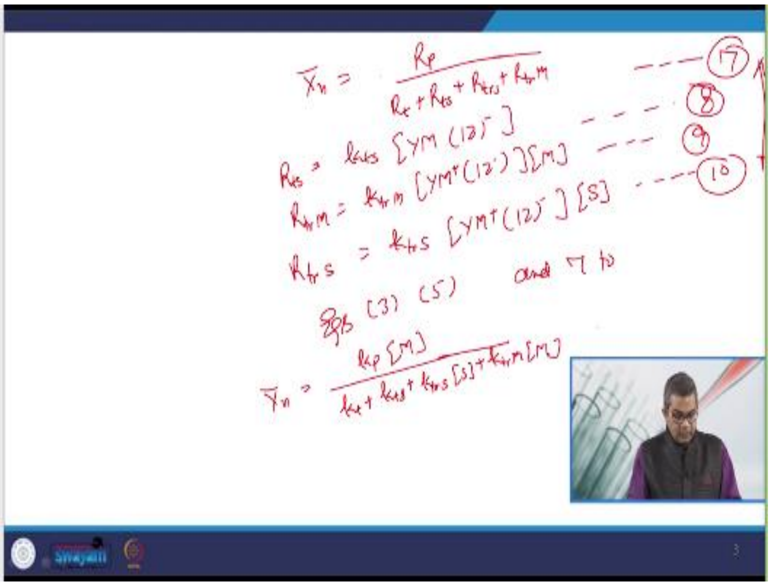

$\overline{X}_n = \frac{R_p}{R_t + R_{ts} + R_{trs} + R_{trM}}$ ---- ⑦

$R_{ts} = k_{ts}[YM(12)^-]$ ---- ⑧

$R_{trM} = k_{trM}[YM^+(12^-)][M]$ ---- ⑨

$R_{trS} = k_{trS}[YM^+(12)^-][S]$ ---- ⑩

Eqs (3) (5) and 7 to

$\overline{X}_n = \frac{k_p[M]}{k_t + k_{ts} + k_{trs}[S] + k_{trM}[M]}$

Therefore, combining equations 3,5, and 7 to 10, we get;

$$\overline{X_n} = \frac{k_p[M]}{k_t + k_{ts} + k_{tr,S}[S] + k_{tr,M}[M]} \qquad (11)$$

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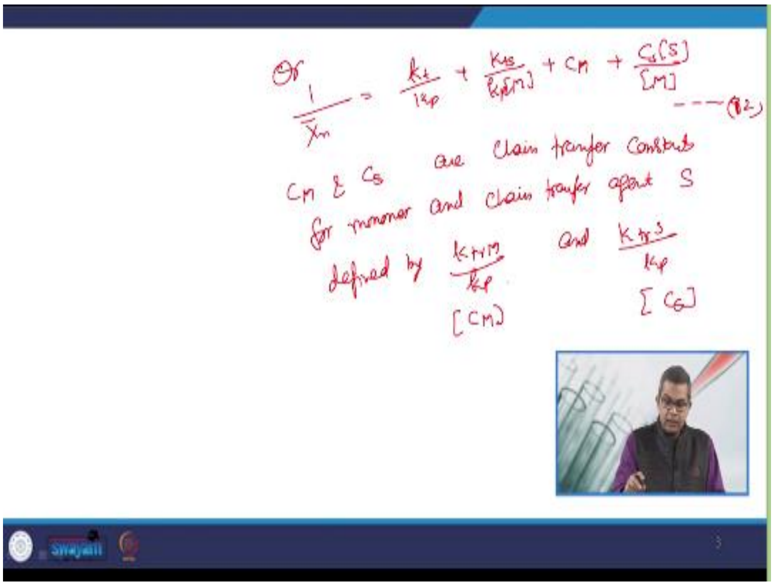

Or $\frac{1}{\overline{X}_n} = \frac{k_t}{k_p} + \frac{k_{ts}}{k_p[M]} + C_M + \frac{C_S[S]}{[M]}$ ---- (12)

C_M & C_S are chain transfer constants for monomer and chain transfer agent S defined by $\frac{k_{trM}}{k_p}$ and $\frac{k_{trS}}{k_p}$

$[C_M]$ $[C_S]$

Or

$$\frac{1}{\overline{X_n}} = \frac{k_t}{k_p} + \frac{k_{ts}}{k_p[M]} + C_M + \frac{C_S[S]}{[M]} \qquad (12)$$

Where, C_M and C_S are the chain-transfer constants for monomer and chain-transfer agent S defined by $k_{tr,M}/k_p$ and $k_{tr,S}/k_p$, respectively.

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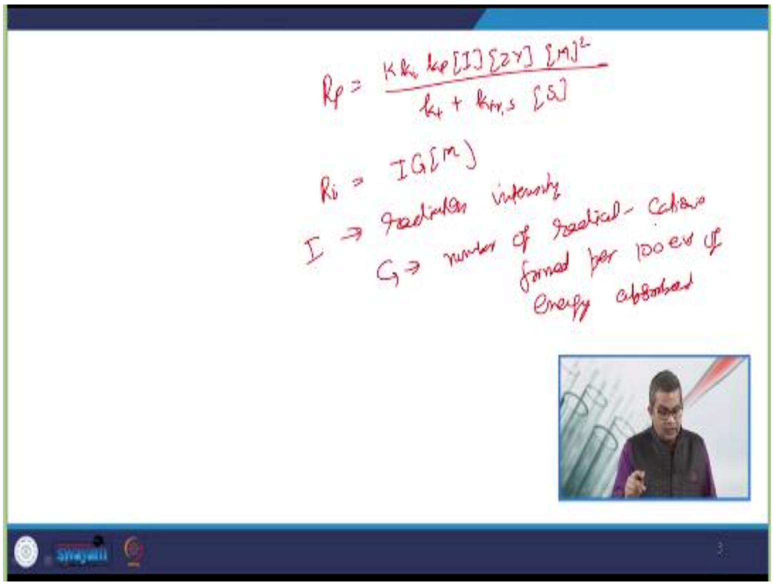

$$R_p = \frac{K k_i k_p [I][ZY][M]^2}{k_t + k_{tr,S}[S]}$$

$$R_i = IG[M]$$

$I \rightarrow$ radiation intensity

$G \rightarrow$ number of radical-cations formed per 100 eV of energy absorbed

For the case where chain transfer to S terminates the kinetic chain, the polymerization rate is decreased and is given by

$$R_p = \frac{K k_i k_p [I][ZY][M]^2}{k_t + k_{tr,S}[S]} \qquad (13)$$

In the usual situation the radiolytic reaction determines the rate of initiation and R_i is given by

$$R_i = IG[M] \qquad (14)$$

where I is the radiation intensity and G is the number of radical–cations formed per 100 eV of energy absorbed.

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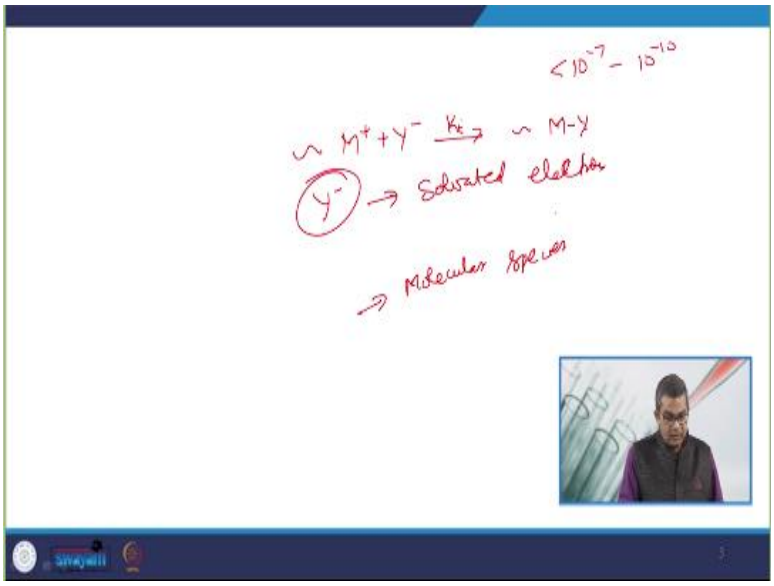

$< 10^{-7} - 10^{-10}$

$$\sim M^+ + Y^- \xrightarrow{k_t} \sim M\text{-}Y$$

$\boxed{Y^-} \rightarrow$ Solvated electron

$\rightarrow$ Molecular species

In sufficiently pure systems (concentrations of water and other terminating agents $<10^{-7} - 10^{-10}$ M), termination of the propagating carbocation centers occurs by combination with a negative fragment Y^-

$$\sim M^{+} + Y^{-} \xrightarrow{k_{t\prime}} \sim M{-}Y \qquad (15)$$

Y^- is either a solvated electron (displaced electron formed during the radiolytic reaction) or the product of the electron having reacted with some compound in the reaction system.

If Y^- is an electron, the propagating carbocation centers are converted to radical centers that subsequently undergo reaction with some species in the reaction system to form molecular species.

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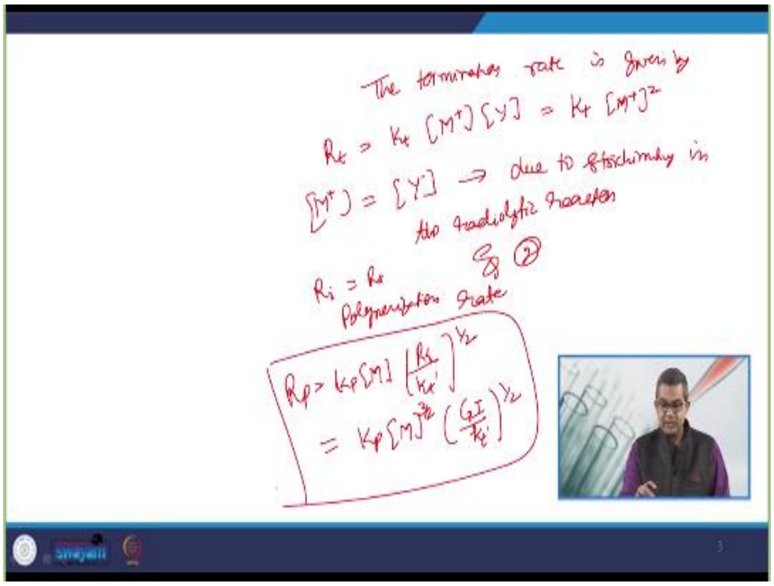

The termination rate is given by

$R_t = K_t [M^+][Y] = K_t [M^+]^2$

$[M^+] = [Y] \rightarrow$ due to stoichiometry in the radiolytic reaction

$R_i = R_t$ Eq ②

Polymerization rate

$$\boxed{R_p = k_p[M]\left[\frac{R_i}{k_t'}\right]^{1/2} = K_p[M]^{3/2}\left(\frac{GI}{k_t'}\right)^{1/2}}$$

The termination rate is given by

$$R_{t\prime} = k_{t\prime}[M^+][Y] = k_{t\prime}[M^+]^2 \qquad (16)$$

Where $[M^+] = [Y^-]$ due to the stoichiometry in the radiolytic reaction.

Setting $R_i = R_{t'}$ and combining the result with Eq. (2) yields the polymerization rate as

$$R_p = k_p[M]\left(\frac{R_i}{k_{t'}}\right)^{\frac{1}{2}} = k_p[M]^{\frac{3}{2}}\left(\frac{GI}{k_{t'}}\right)^{\frac{1}{2}} \qquad (17)$$

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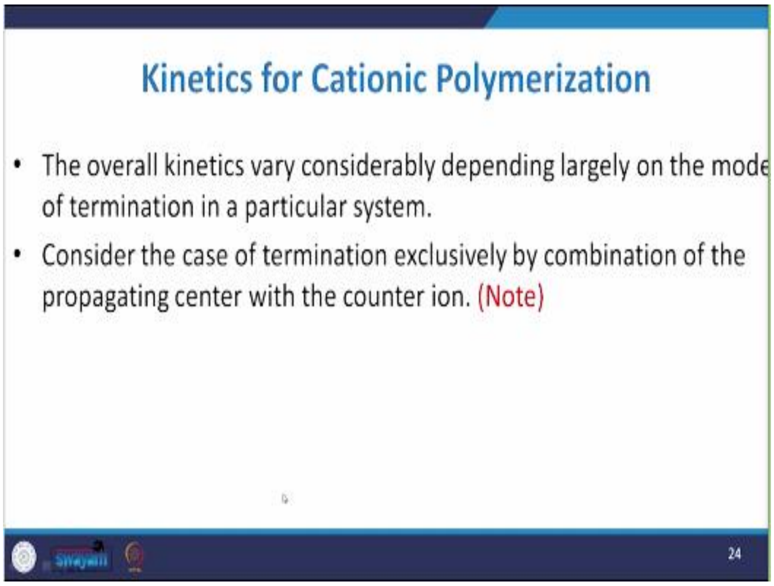

Kinetics for Cationic Polymerization

- The overall kinetics vary considerably depending largely on the mode of termination in a particular system.
- Consider the case of termination exclusively by combination of the propagating center with the counter ion. (Note)

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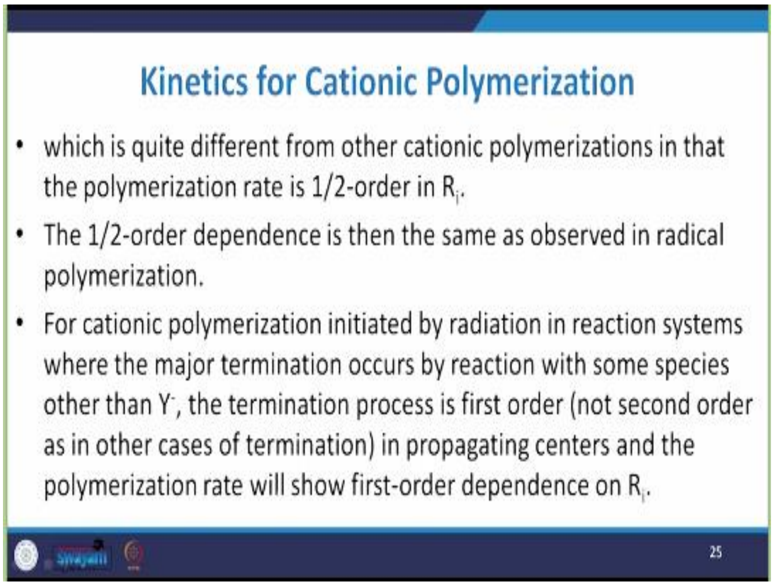

Kinetics for Cationic Polymerization

- which is quite different from other cationic polymerizations in that the polymerization rate is 1/2-order in R_i.
- The 1/2-order dependence is then the same as observed in radical polymerization.
- For cationic polymerization initiated by radiation in reaction systems where the major termination occurs by reaction with some species other than Y^-, the termination process is first order (not second order as in other cases of termination) in propagating centers and the polymerization rate will show first-order dependence on R_i.

Now, this particular thing is quite different from other cationic polymerization in that the polymerization rate is half order in R_i. Now, this half order dependence is same as observed in the radical polymerization. So, for cationic polymerization initiated by radiation in reaction systems, where the major termination occurs by the reaction with some species other than Y^- the termination process is first order not the second order.

As in the case of termination, which you previously discussed and the termination process in the propagating centre and the polymerization rate will show the first order dependency on R_i. So, by this way, we discussed the kinetic of cationic polymerization. And in this chapter we gave the emphasis of initiation, propagation and termination and we developed the the polymerization rate equation with the help of several concepts which we discussed in in the previous lecture as well as in this lecture.

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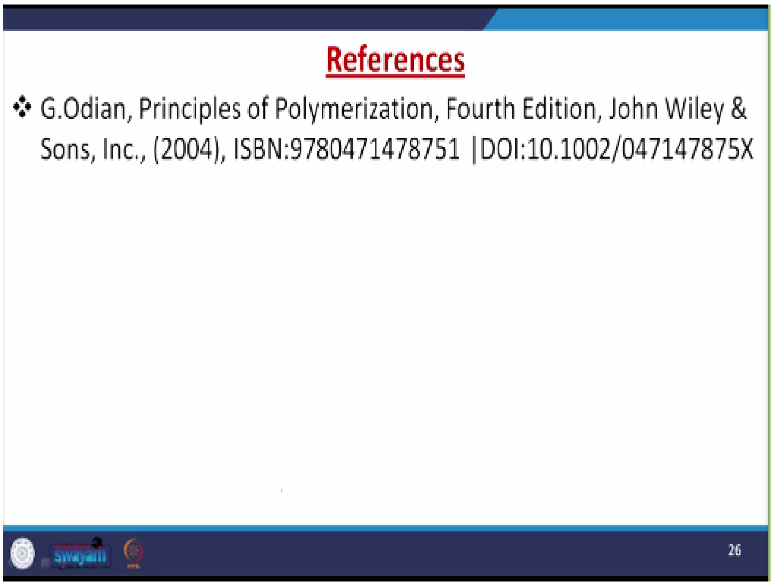

References

- G.Odian, Principles of Polymerization, Fourth Edition, John Wiley & Sons, Inc., (2004), ISBN:9780471478751 |DOI:10.1002/047147875X

And again, if you wish to have further studies we have listed these references for your convenience. Thank you very much.