Introduction to Polymer Science

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Lecture-13

Transfer Reactions, Effect of Temperature on Rate and MW, MW Description, Ceiling Temperature

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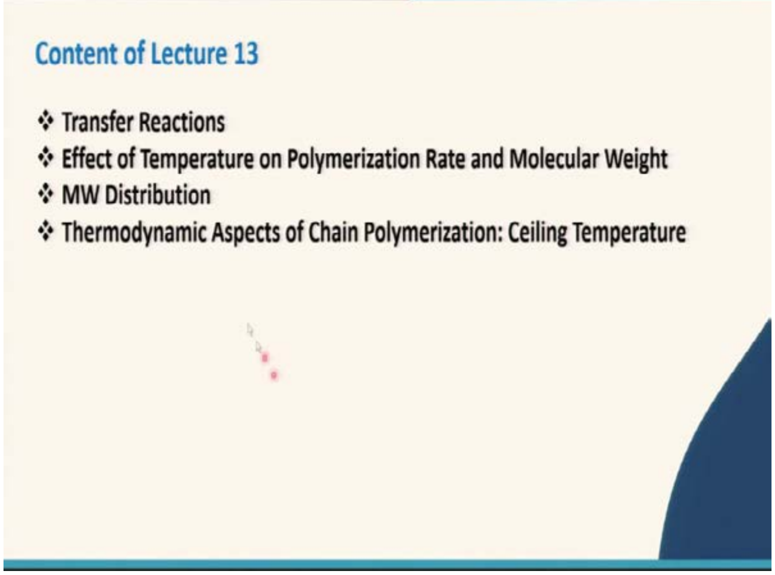

Content of Lecture 13

- Transfer Reactions
- Effect of Temperature on Polymerization Rate and Molecular Weight
- MW Distribution
- Thermodynamic Aspects of Chain Polymerization: Ceiling Temperature

Welcome back, in this lecture 13, we will talk about transfer reactions, the effect of temperature on polymerization rate and molecular weight, and briefly discuss molecular weight distribution, and also if possible discuss the thermodynamic aspect of chain polymerization and ceiling temperature.

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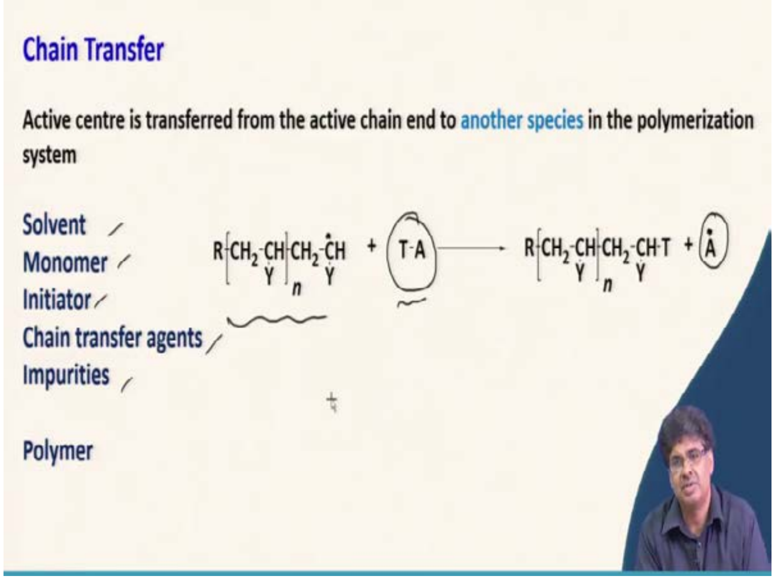

Chain Transfer

Active centre is transferred from the active chain end to another species in the polymerization system

Solvent

Monomer

Initiator

Chain transfer agents

Impurities

Polymer

$$R\left[CH_2-\underset{Y}{CH}\right]_n CH_2-\underset{Y}{\dot{C}H} + T{-}A \longrightarrow R\left[CH_2-\underset{Y}{CH}\right]_n CH_2-\underset{Y}{CH}-T + \dot{A}$$

We have been talking about three reactions. At first, when a radical is produced, it reacts with the monomer in the first initiation step, and then the radical reacts further with monomers to produce propagating chain, and at last, the propagating chains react with themselves to form a dead polymer chain, which is called termination reaction. Now, there is another possible reaction for a radical, especially the propagating radical in the reaction mixture. There is an active center and the radical center is transferred from one active chain end of propagating radical to another species in the polymerization system. So, once a propagating radical at the chain end reacts with another species it becomes a non-radical species and produces another new radical species. Hence, the radical gets transformed from one chain to another chain, and the possible species can be a solvent, monomer, or initiator. It could be deliberately added transfer agents which are generally called chain transfer agents. The general way to express or present this is if we have this propagating radical as shown and this reacts with a species expressed as T-A. The propagating radical abstracts this T and produces this new radical $A^{\cdot}$. Now, this new radical can react with the monomer and start a new chain. So, this is called a transfer reaction. As mentioned, this transfer agent could be a solvent, monomer, initiator, or we can add these transfer agents T-A from outside for controlling the molecular weight or functionalize the polymer chain. Thus, it could be a transfer agent, it could be impurities present or it could be the polymers that are produced during the polymerization reaction.

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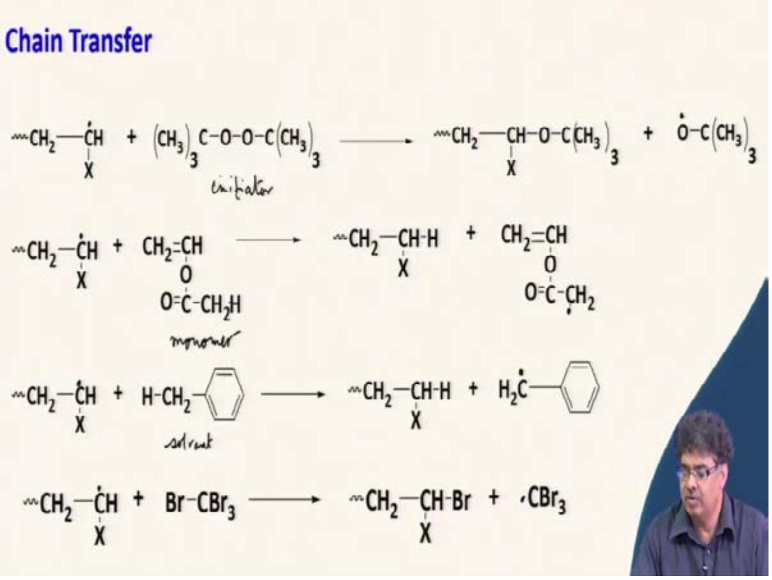

Chain Transfer

$$\sim CH_2-\underset{X}{\dot{C}H} + (CH_3)_3C-O-O-C(CH_3)_3 \longrightarrow \sim CH_2-\underset{X}{CH}-O-C(CH_3)_3 + \dot{O}-C(CH_3)_3$$

$$\sim CH_2-\underset{X}{\dot{C}H} + \begin{matrix} CH_2=CH \\ O \\ O=C-CH_2H \end{matrix} \longrightarrow \sim CH_2-\underset{X}{CH}-H + \begin{matrix} CH_2=CH \\ O \\ O=C-\dot{C}H_2 \end{matrix}$$

$$\sim CH_2-\underset{X}{\dot{C}H} + Br-CBr_3 \longrightarrow \sim CH_2-\underset{X}{CH}-Br + \cdot CBr_3$$

In case of tertiary butyl peroxide as initiator, the radical reacts with this initiator and produces a new radical, so the chain is stopped there, and a new radical is produced which can react further and initiate a chain. In case of vinyl acetate monomer as shown here, the propagating radical can react with this monomer and abstract a hydrogen atom from it, and produce a new radical and this radical can further initiate a chain. There may be toluene as solvent and the propagating radicals can abstract hydrogen from toluene and produce new radicals. We are talking about transfer to different agents like initiator, monomer, and solvent. In the last case, carbon tetrabromide (CBr_4) is added as a transfer agent, and a new radical species formed.

In all these examples what we have shown here, a propagating radical is reacting with another species and producing a new radical and the original propagating radical is becoming non-radical species. So, we can see that one original propagating radical is creating one dead polymer chain and another radical which is producing another polymer chain.

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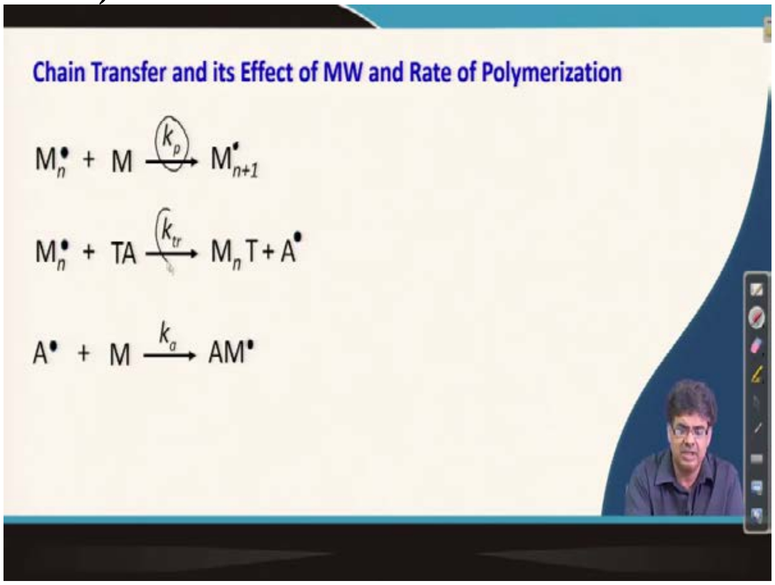

Chain Transfer and its Effect of MW and Rate of Polymerization

$$M_n^\bullet + M \xrightarrow{k_p} M_{n+1}^\bullet$$

$$M_n^\bullet + TA \xrightarrow{k_{tr}} M_nT + A^\bullet$$

$$A^\bullet + M \xrightarrow{k_a} AM^\bullet$$

Now, what is the effect of this chain transfer on the molecular weight of the polymer being produced and the rate of polymerization? Now, $M_n^{\cdot}$ is the original propagating radical which reacts with monomer M in a normal propagation step, which has a rate constant k_p. Now, if this undergoes a transfer reaction, then the original propagating radical gets killed and a new radical is produced. This new radical which is produced can react with monomer and further initiate a polymer chain. So, there are 3 corresponding rate constants, normal propagation rate constant k_p, transfer rate constant k_{tr}, another is re-initiation rate constant k_a. Now, depending upon the value or relative values of these rate constants, we can find out what is the effect of molecular weight and rate of polymerization. Now, as we have discussed that if chain transfer happens, no matter how fast or how slow, the molecular weight is going to decrease because originally one chain or one propagating radical was present. During transfer reaction, the previous radical becomes dead chain, and a new polymer chain is produced. If there was no transfer reaction, only one chain would be produced, but now we have 2 chains. So, basically, with the same number of monomers, more chains are produced. Thus, no matter what is the rate at which the chain transfer occurs, once the chain transfer happens, the molecular weight is going to decrease. To what extent it is going to decrease, it will depend on this relative value of these 3 rate constants k_p, k_{tr}, and rate of reinitiation.

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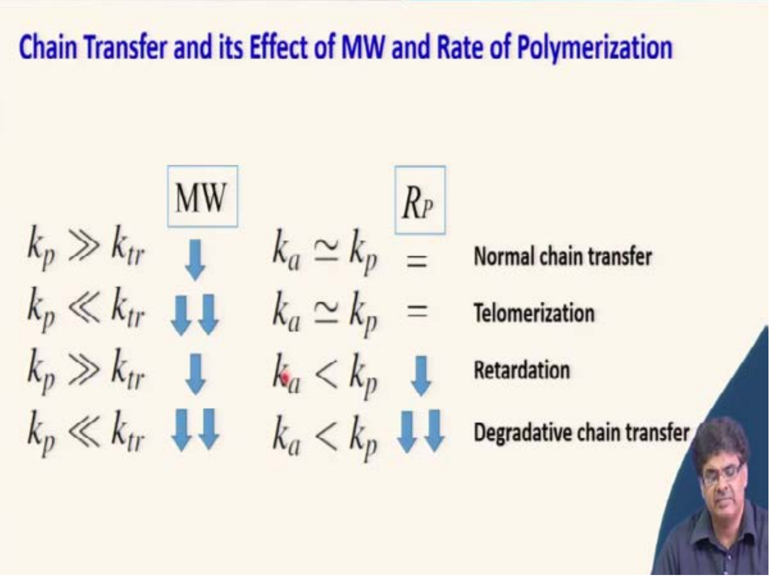

Chain Transfer and its Effect of MW and Rate of Polymerization

	MW		R_P	
$k_p \gg k_{tr}$	↓	$k_a \simeq k_p$	=	Normal chain transfer
$k_p \ll k_{tr}$	↓↓	$k_a \simeq k_p$	=	Telomerization
$k_p \gg k_{tr}$	↓	$k_a < k_p$	↓	Retardation
$k_p \ll k_{tr}$	↓↓	$k_a < k_p$	↓↓	Degradative chain transfer

So, if the original rate of propagation is much higher than the transfer reaction, the molecular weight will reduce, but to a lesser extent. If the original propagating rate was much lower compared to the transfer rate, then obviously there will be a drastic decrease in molecular weight. When the rate of reinitiation is the same as the original rate of propagation, then the rate of disappearance of monomer from the reaction mixture will remain the same because the new radical is consuming the monomers at the same rate as the original propagating radical was doing. So, there is no effect on the rate of polymerization. Now, if k_a, the rate of initiation is lower than the original k_p, then the rate of polymerization will be much lower than the original rate of polymerization. Now, combining those 2 cases, if k_p much greater than the k_{tr} and the k_a is similar to the k_p. Then we call it is normal chain transfer, If the k_p is much lower compared to k_{tr}, which means transfer is happening to a higher extent than the original propagation. In that case, the molecular weight will be drastically low, but the rate of polymerization would remain the same. The polymer is produced at the same rate, but the molecular weight of the polymer will be much lower, maybe oligomer type and those types of oligomers are known as telomeres. So, it is known as telomerization. Similarly, there will be retardation and degradative chain transfer reaction.

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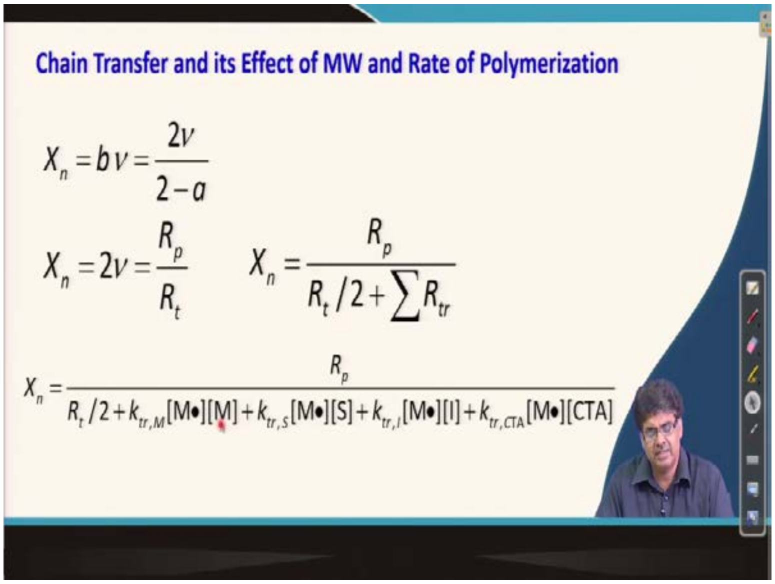

Chain Transfer and its Effect of MW and Rate of Polymerization

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

$$X_n = 2\nu = \frac{R_p}{R_t} \qquad X_n = \frac{R_p}{R_t/2 + \sum R_{tr}}$$

$$X_n = \frac{R_p}{R_t/2 + k_{tr,M}[M\bullet][M] + k_{tr,S}[M\bullet][S] + k_{tr,I}[M\bullet][I] + k_{tr,CTA}[M\bullet][CTA]}$$

Now, we know that degree of polymerization is related to the number of initiator fragments present per polymer chain, and this is the kinetic chain length which is expressed as

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

when *a* is the fraction of termination happening by coupling or combination way. For simplicity, we will consider that *a* is 1 which means almost all of the termination is happening by coupling routes.

So, we will write *a* = 1. So,

$$X_n = 2\nu = \frac{R_p}{R_t}$$

If there is a transfer reaction, then during the transfer reaction termination is also happening, some of the propagating radicals are also becoming dead and the polymer is getting produced. So, in this case, the degree of polymerization will be given by,

$$X_n = \frac{R_p}{\frac{R_t}{2} + \sum R_{tr}}$$

As more and more transfer happens, the degree of polymerization or the molecular weight of the resulting polymers becomes lower. So, what are the transfer reactions? We know that it could be with initiator or monomer or solvents, so, we just write those rate of reactions transfer reaction individually like,

$$X_n = \frac{R_p}{\frac{R_t}{2} + k_{tr,M}[\mathrm{M}^{\cdot}][\mathrm{M}] + k_{tr,S}[\mathrm{M}^{\cdot}][\mathrm{S}] + k_{tr,I}[\mathrm{M}^{\cdot}][\mathrm{I}] + k_{tr,CTA}[\mathrm{M}^{\cdot}][\mathrm{CTA}]}$$

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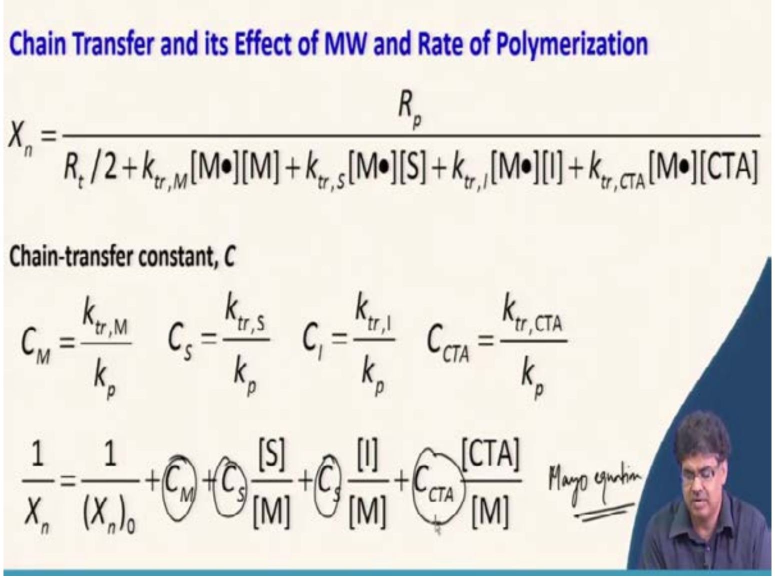

Chain Transfer and its Effect of MW and Rate of Polymerization

$$X_n = \frac{R_p}{R_t/2 + k_{tr,M}[\mathrm{M}\bullet][\mathrm{M}] + k_{tr,S}[\mathrm{M}\bullet][\mathrm{S}] + k_{tr,I}[\mathrm{M}\bullet][\mathrm{I}] + k_{tr,CTA}[\mathrm{M}\bullet][\mathrm{CTA}]}$$

Chain-transfer constant, *C*

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

$$\frac{1}{X_n} = \frac{1}{(X_n)_0} + C_M + C_S\frac{[\mathrm{S}]}{[\mathrm{M}]} + C_S\frac{[\mathrm{I}]}{[\mathrm{M}]} + C_{CTA}\frac{[\mathrm{CTA}]}{[\mathrm{M}]}$$

Mayo equation

For simplicity, we can reverse both sides and define different chain transfer coefficients. So, C_M is the chain transfer coefficient for monomers which is given by the rate constant for transfer to monomer divided by the original propagation rate constant $C_M = \frac{K_{tr,M}}{K_p}$.

Similarly, we can talk about solvent chain transfer coefficient, initiator chain transfer coefficient, and chain transfer coefficient for the chain transfer agent. When there is no transfer reaction happening, $(X_n)_0$ is the degree of polymerization without any chain transfer reaction as shown in the equation called a Mayo equation. So, the higher is the value of this chain transfer constant, the propensity to get chain transfer is higher.

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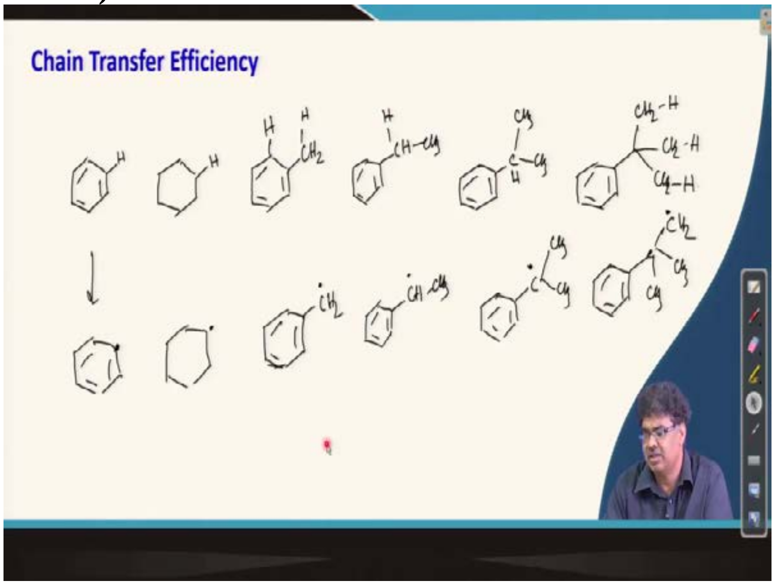

Chain Transfer Efficiency

So, if we want to compare between some solvents like benzene, cyclohexane, toluene, ethylbenzene, and so on. If a hydrogen abstraction happens there will be a radical generation as shown in the structures. Now, if we compare the stability of these radicals, we can compare which is the most feasible solvent and can participate in a chain transfer reaction. For example, toluene is not a very frequently used solvent in radical reactions because the solvent can take part in a chain transfer reaction, by doing that, it can decrease the molecular weight. By looking at the radical which will get produced we can compare the feasibility of transfer. Thus, if the new radicals which are produced are stable then the transfer reaction is very feasible. That is the reason there are some solvents like carbon tetrachloride, chloroform, toluene that are not usually used for the radical chain polymerization reaction.

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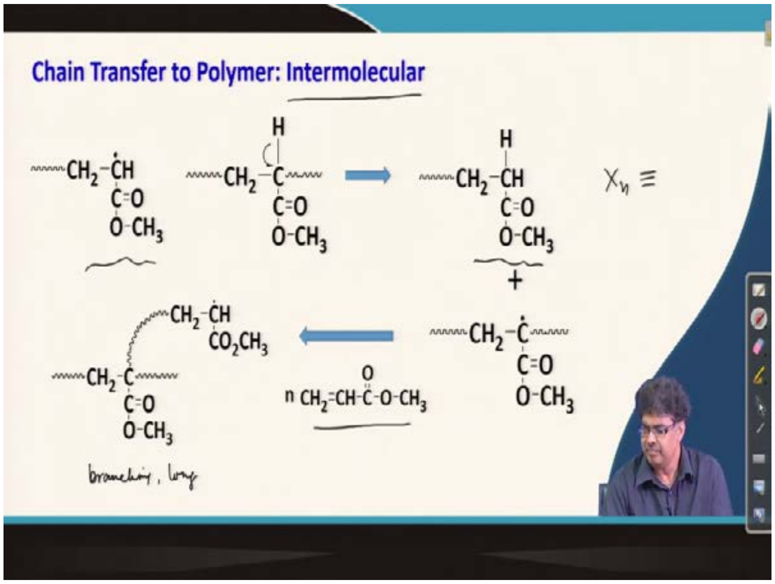

Chain Transfer to Polymer: Intermolecular

$X_n \equiv$

branching, long

Now, there could be chain transfer to the polymer and intermolecular chain transfer between the polymer molecules as well. In this case, a propagating radical can abstract a hydrogen atom from an existing polymer. The existing polymer produces a dead polymer chain and a new radical, which can react with monomer to produce a chain from the existing polymer. In intermolecular chain transfer, we get branching and the branches are long because polymerization is taking place. Now, in this case, there is no change in molecular weight or degree of polymerization. It remains the same because there is a transfer of polymer chains. So, there is no new chain, the chains were already existing.

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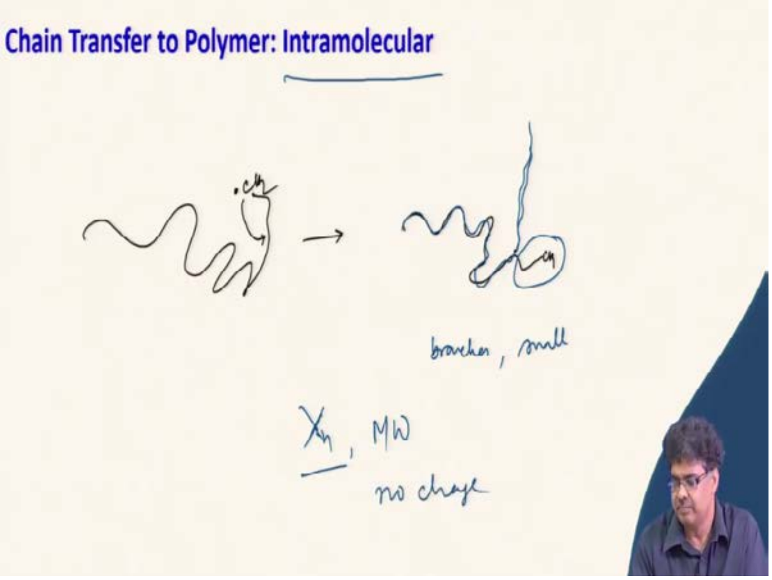

Chain Transfer to Polymer: Intramolecular

branches, small

X_n, MW

no change

For example, if we just take a simple case of, say a polyethylene chain with a propagating radical. Now it is doing backbiting and generating a radical. So, in this case, we are getting a new radical and the previous chain becomes non-radical. Now, the new radical can react with monomers and generate further chain. So, in this case, there is one main polymer and a small branch.
In case of intramolecular chain transfer, we will get branches, but the length of the branch should be small. But in the case of intermolecular, we will get long branches.

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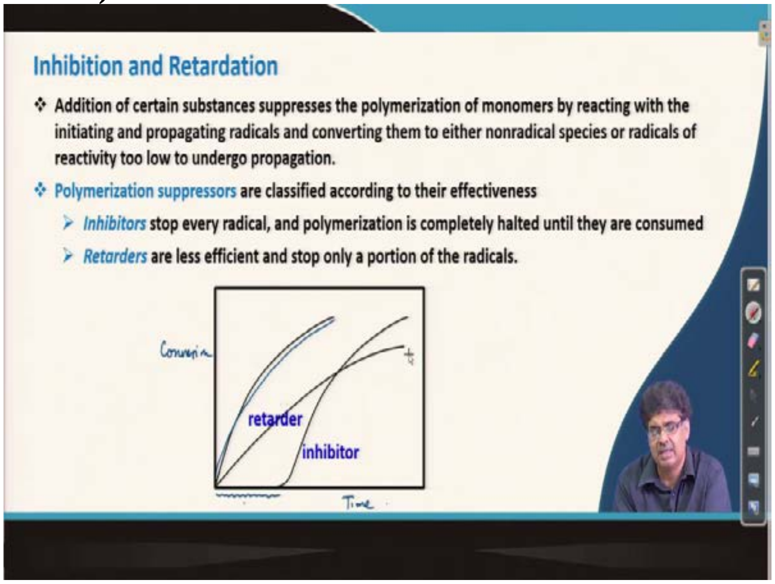

Inhibition and Retardation

- Addition of certain substances suppresses the polymerization of monomers by reacting with the initiating and propagating radicals and converting them to either nonradical species or radicals of reactivity too low to undergo propagation.
- Polymerization suppressors are classified according to their effectiveness
  - *Inhibitors* stop every radical, and polymerization is completely halted until they are consumed
  - *Retarders* are less efficient and stop only a portion of the radicals.

Now, there may be some compounds present in the medium which can be added deliberately or it can be present in the medium which obstructs or suppress the polymerization process. These substances suppress the polymerization of monomers by reacting with the initiating and propagating radical, and converting them into either non-radical species or radicals which have very low reactivity to undergo further propagation. These compounds are called polymerization suppressors and depending on their efficiency or effectiveness, we can classify them either as inhibitors or retarders. Inhibitors stop every radical initiation process as long as they are present in the reaction mixture and the polymerization can begin only after these inhibitors are consumed. In case of styrene monomer, the styrene bottle in the lab always comes with some stabilizer like benzoquinone because if the radicals get produced, then it kills the resulting radicals. As a result, it can stop the radical polymerization. So, there are some advantages to using inhibitors, retarders actually, they are less efficient and stop only a portion of the radicals present.

So, if we draw a scheme about conversion with time, then the original plot is shown where there is a normal reaction rate and if there is some inhibitor present, then till the inhibitor is consumed the rate is low. There is a time when all the inhibitors are getting consumed by the radicals, which are produced during the initial steps. So, after that the polymerization occurs at the same rate as if there is no inhibitor present. Retarders slow down the reaction rate from the beginning. So, we classify these polymerization suppressors as inhibitors and retarders depending upon their effectiveness. Oxygen is a very common inhibitor.

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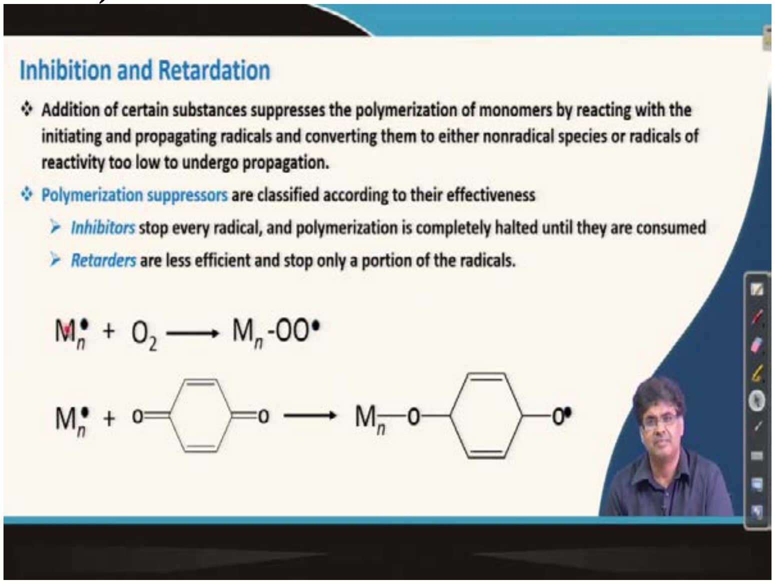

Inhibition and Retardation

- Addition of certain substances suppresses the polymerization of monomers by reacting with the initiating and propagating radicals and converting them to either nonradical species or radicals of reactivity too low to undergo propagation.
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  - *Inhibitors* stop every radical, and polymerization is completely halted until they are consumed
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$$M_n^{\bullet} + O_2 \longrightarrow M_n\text{-}OO^{\bullet}$$

Oxygen reacts with the propagating radical or initiating radical and form these peroxide radical which is very stable which can react with itself or react with another propagating radical and quench the radical. So, that is why in most cases radical polymerizations are carried out in absence of oxygen. So, the oxygen is removed by passing inert gases like nitrogen, argon. Sometimes if the oxygen has to be removed very effectively then we do a freeze-thaw mechanism by which we can remove the dissolved molecular oxygen in the reaction mixture. There are some other compounds like benzoquinone which can also react with the radicals and produce non-reactive species. They are not able to start a polymerization reaction, and these types of inhibitors are used as stabilizer for storing monomers. So, when somebody wants to use that monomer for polymerization, they need to distill out the monomer so that there is no inhibitor present in the monomers.

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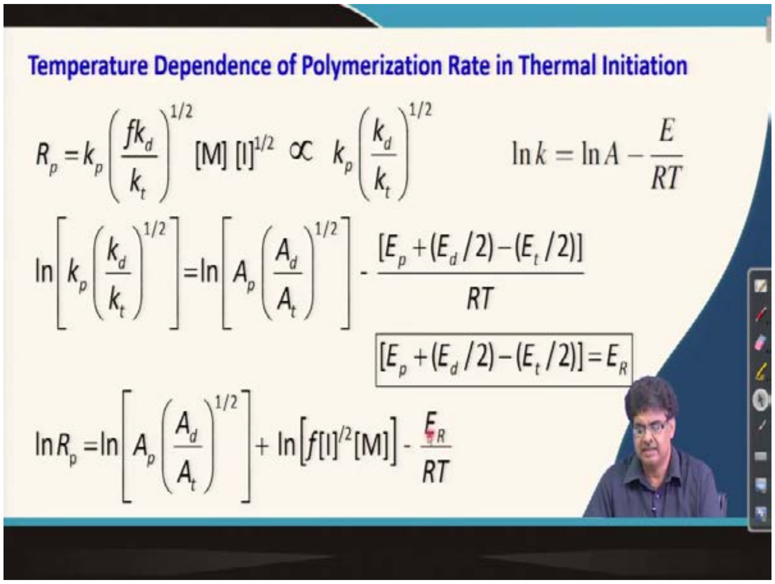

Temperature Dependence of Polymerization Rate in Thermal Initiation

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[\mathrm{M}]\,[\mathrm{I}]^{1/2} \propto k_p\left(\frac{k_d}{k_t}\right)^{1/2} \qquad \ln k = \ln A - \frac{E}{RT}$$

$$\ln\left[k_p\left(\frac{k_d}{k_t}\right)^{1/2}\right] = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] - \frac{[E_p+(E_d/2)-(E_t/2)]}{RT}$$

$$\boxed{[E_p+(E_d/2)-(E_t/2)]=E_R}$$

$$\ln R_p = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] + \ln\left[f[\mathrm{I}]^{1/2}[\mathrm{M}]\right] - \frac{E_R}{RT}$$

We will talk about temperature dependence on polymerization rate in thermal initiation and this is the rate expression we have talked about.

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

We can see this is proportional to these rate constants and we know from the Arrhenius equation how rate constants depend on temperature as given by this Arrhenius equation,

$$lnk = lnA - \frac{E}{RT}$$

E is the activation energy. Now, we have 3 rate constants in this particular case, rate of polymerization depends on 3 rate constants, k_p, k_d, and k_t. the activation energies of propagation, dissociation, and termination are E_p, E_d, and E_t respectively. The combination of all these activation energies will give us the activation energy for the polymerization reaction. So, taking the log of Arrhenius equation we can write,

$$ln\left[k_p\left(\frac{k_d}{k_t}\right)^{1/2}\right] = ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] - \frac{\left[E_p + \left(E_d/2\right) - \left(E_t/2\right)\right]}{RT}$$

Now, this complete activation energy is written as the activation energy for polymerization, and so we can simplify this and write this activation energy for polymerization.

$$lnR_p = ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] + ln\left[f[\mathrm{I}]^{1/2}[\mathrm{M}]\right] - \frac{E_R}{RT}$$

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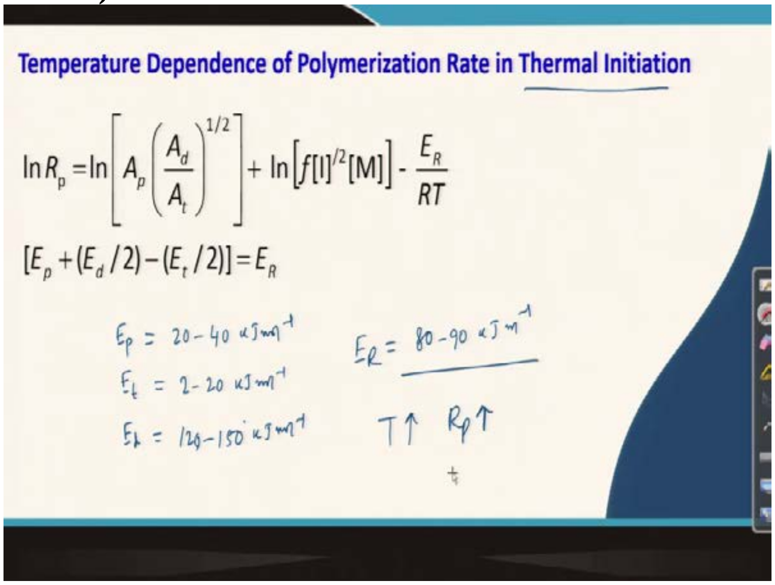

Temperature Dependence of Polymerization Rate in Thermal Initiation

$$\ln R_p = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] + \ln\left[f[\mathrm{I}]^{1/2}[\mathrm{M}]\right] - \frac{E_R}{RT}$$

$$[E_p + (E_d/2) - (E_t/2)] = E_R$$

E_p = 20-40 kJ mol^{-1}

E_t = 2-20 kJ mol^{-1}

E_d = 120-150 kJ mol^{-1}

E_R = 80-90 kJ m^{-1}

T↑ R_p↑

Where $\left[\mathrm{E_p} + \left(\mathrm{E_d}/2\right) - \left(\mathrm{E_t}/2\right)\right] = \mathrm{E_R}$

Now, the typical value for $\mathrm{E_p}$ is 20-40 kJ/mol and the activation energy of termination is about 2-20 kJ/mol. But the dissociation is a much slower reaction, so the activation energies are much higher, 120-150 kJ/mol. So if we put the values in this expression, we will get $\mathrm{E_R}$ around 80 to 90 kJ/mol. Now, because the activation energy is positive, as there is an increase in the temperature, the rate of polymerization will increase. Now, we will stop here and will talk about what is the effect of temperature on molecular weight in the next lecture.