Introduction to Polymer Science
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Lecture – 15
Thermodynamics of Chain Polymerization, MW distribution, Common Polymers

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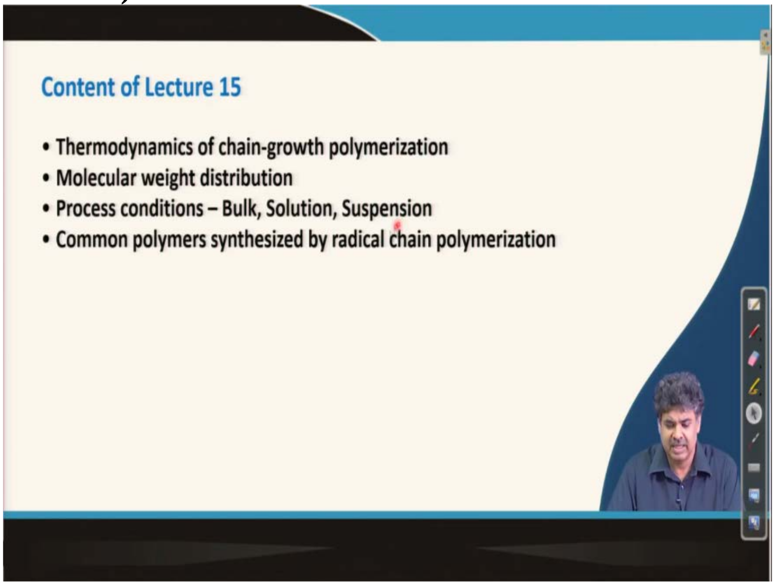

Content of Lecture 15

- Thermodynamics of chain-growth polymerization
- Molecular weight distribution
- Process conditions – Bulk, Solution, Suspension
- Common polymers synthesized by radical chain polymerization

Welcome back to lecture 15, we will talk about the remaining part of the energetics portion briefly and then talk about the thermodynamics of chain-growth polymerization, molecular weight distribution, and quickly go through the different processes of making radical chain polymers and some common polymers synthesized by radical chain polymerization.

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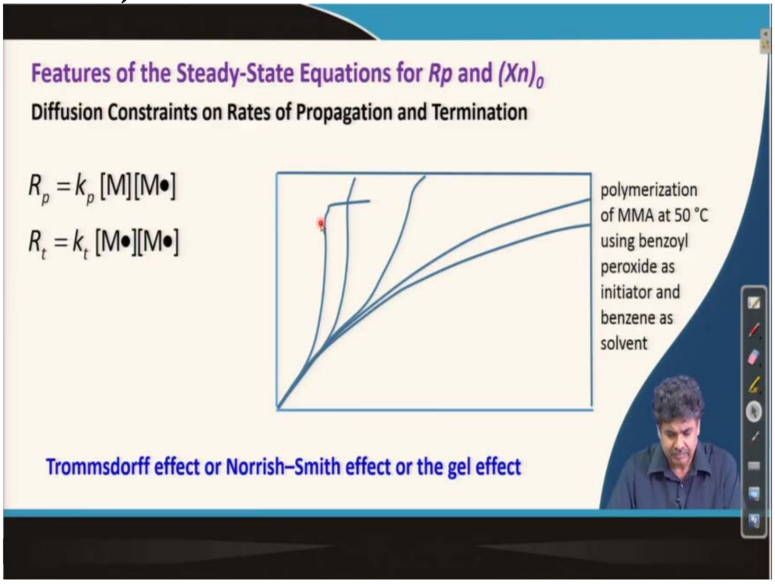

Features of the Steady-State Equations for R_p and $(X_n)_0$

Diffusion Constraints on Rates of Propagation and Termination

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

$$R_t = k_t[M\bullet][M\bullet]$$

polymerization of MMA at 50 °C using benzoyl peroxide as initiator and benzene as solvent

Trommsdorff effect or Norrish–Smith effect or the gel effect

This is what we learned in the last lecture that, when the conversion of radical chain polymerization is high, the termination reaction becomes slower and slower because, the termination reaction becomes diffusion-controlled as the size of the propagating radical is large and the viscosity of the reaction medium is high. As a result, the gel effect happens which is a sudden increase in the reaction rate and increase in the molecular weight of the polymers produced. We also discussed that the gel effect happens at lower conversion when the monomer concentration is higher in the reaction medium.

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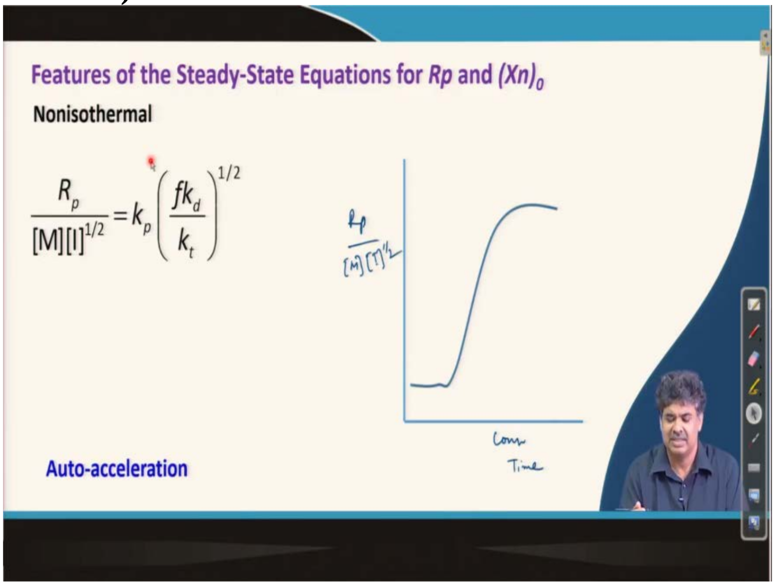

Features of the Steady-State Equations for *Rp* and *(Xn)*$_0$

Nonisothermal

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

Auto-acceleration

Now, we assumed that we were able to remove the heat from the reaction medium which is getting generated in the polymerization reaction. Unless the produced heat is removed very effectively, there is a possibility that local heat gets accumulated and the temperature can go up in the reaction medium. So, we then call that is a nonisothermal reaction. We know that the rate of polymerization is given by this expression -

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

if this, k_p, k_d, and k_t are fixed if there is no change in temperature. So, these rate constants should remain fixed when we can remove the heat from the reaction medium very effectively and the temperature remains fixed. But, if we cannot remove the heat, then the temperature goes up, as a result, this composite reaction rate constant also goes up. This is kind of an auto acceleration that happened because, we are not able to remove the heat from the medium, and the reaction rate increases as the temperature increases. As a result, more and more heat is generated. This is called auto acceleration, and this might lead to a gel effect. Of course, in this case, because the reaction rate is much higher, the molecular weight which got produced might be also lower. In some cases, the gel effect may happen and some cases may not happen. Auto acceleration and gel effects are two independent phenomena. Of course, some texts might mention that auto acceleration and gel effects are the same, but although, these two actually may land up in the same situation, their origin are different. Gel effects are because of the viscosity of the medium becomes high and the termination reaction becomes diffusion-controlled, whereas auto acceleration happens because of nonisothermal condition, as we cannot remove the heat from the system properly. The temperature of the reaction medium goes up, the reaction rate also goes up.

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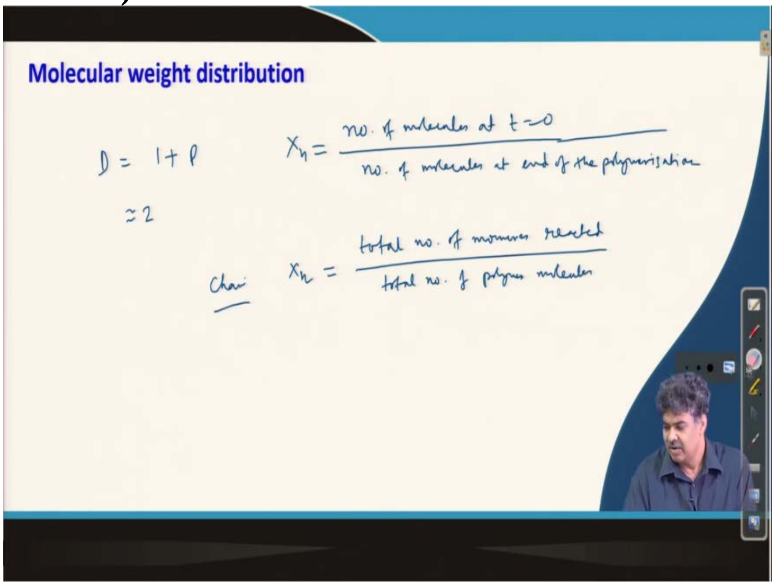

Molecular weight distribution

$Đ = 1 + p$

$\simeq 2$

$$X_n = \frac{\text{no. of molecules at } t = 0}{\text{no. of molecules at end of the polymerisation}}$$

Chain

$$X_n = \frac{\text{total no. of monomers reacted}}{\text{total no. of polymer molecules}}$$

Let us move to the next topic of molecular weight distribution. For step-growth polymerization we have seen that the dispersity, Đ = $(1 + p)$ where 'p' is the functional group conversion. Now, there is a little difference in the case of the degree of polymerization value in step-growth polymerization. In the case of step-growth, we know the degree of polymerization X_n is given by,

$$X_n = \frac{the\ number\ of\ molecules\ at\ time\ t\ =\ 0}{number\ of\ molecules\ at\ the\ end\ of\ the\ polymerization}$$

This is because in the case of step-growth polymerization, we have discussed many times that the entire mass, the entire reaction medium is the product, and we do not isolate the monomer, oligomer, or anything.

Now, in the case of chain polymerization, we know that the polymer product is not the entire reaction product. It is the isolated polymers from the reaction medium. So, in this case, we know the equation is -

$$X_n = \frac{total\ number\ of\ monomers\ reacted}{total\ number\ of\ polymer\ molecules}$$

The product of step-growth polymerization is the entire reaction mixture, whereas, in the case of chain-growth polymerization, this is the isolated polymers. For getting high molecular weight, p is required to be close to 1 for a step-growth polymerization. So, Đ is always close to 2 for a high molecular weight polymer sample generated from step-growth polymerization.

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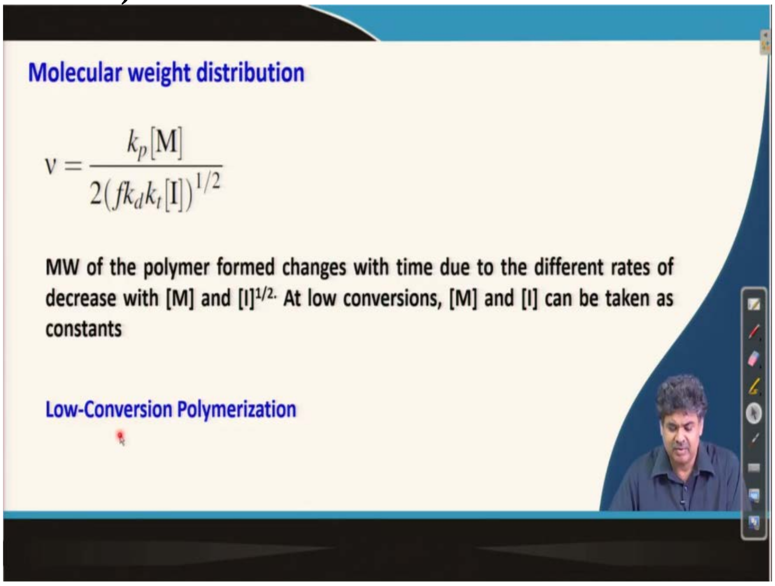

Molecular weight distribution

$$\nu = \frac{k_p[\mathrm{M}]}{2(fk_dk_t[\mathrm{I}])^{1/2}}$$

MW of the polymer formed changes with time due to the different rates of decrease with [M] and $[\mathrm{I}]^{1/2}$. At low conversions, [M] and [I] can be taken as constants

Low-Conversion Polymerization

We know the expression for kinetic chain length is related to molecular weight and degree of polymerization. The expression looks like,

$$v = \frac{k_p[\mathrm{M}]}{2(fk_dk_t[\mathrm{I}])^{1/2}}$$

Now, the molecular weight or degree of polymerization depends on the ratio of the concentration of monomer to $[\mathrm{I}]^{1/2}$. As the reaction proceeds, the ratio changes. As a result of the change of the value of this ratio, the size of the molecules which are getting produced at the different times of polymerization might be different. Hence, we might get a bit high or large polydispersity value.

In low conversion region, we can assume that the concentration of monomer and concentration of initiator remains same. So, at low conversion, we assume that the concentration of monomer and initiator are constant. So, in case of low conversions,

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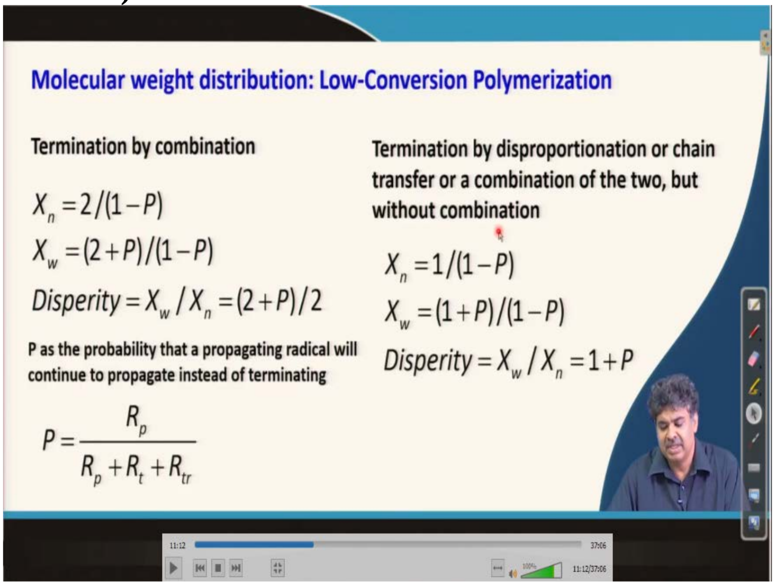

Molecular weight distribution: Low-Conversion Polymerization

Termination by combination

$$X_n = 2/(1-P)$$

$$X_w = (2+P)/(1-P)$$

$$Disperity = X_w / X_n = (2+P)/2$$

P as the probability that a propagating radical will continue to propagate instead of terminating

$$P = \frac{R_p}{R_p + R_t + R_{tr}}$$

Termination by disproportionation or chain transfer or a combination of the two, but without combination

$$X_n = 1/(1-P)$$

$$X_w = (1+P)/(1-P)$$

$$Disperity = X_w / X_n = 1+P$$

we have two situations, one we consider the termination by combination reaction, then the degree of polymerization will be expressed as

$$X_n = \frac{2}{(1-P)}$$

and,

$$X_w = \frac{(2+P)}{(1-P)}$$

P is little different in this case, P is the probability that a propagating radical will continue to propagate instead of terminating. So, it is the chance factor.

Now, a propagating radical can participate in three types of reactions - propagation, termination and transfer reaction. So, the probability is given by,

$$P = \frac{R_p}{R_p + R_t + R_{tr}}$$

If the termination is given by disproportionation or chain transfer or a combination of the above two, but without combination or coupling the expressions are,

$$X_n = \frac{1}{(1-P)}$$

$$X_w = \frac{(1+P)}{(1-P)}$$

$$Dispersity = \frac{X_w}{X_n} = 1 + P$$

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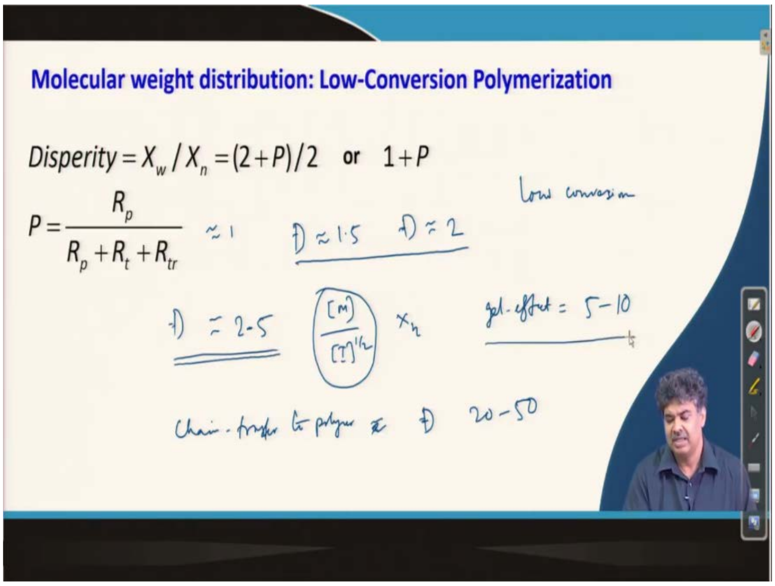

Molecular weight distribution: Low-Conversion Polymerization

$Disperity = X_w / X_n = (2+P)/2$ or $1+P$

$P = \frac{R_p}{R_p + R_t + R_{tr}} \approx 1$

Low conversion

Đ ≈ 1.5 Đ ≈ 2

Đ $\approx 2\text{-}5$

$\boxed{\frac{[M]}{[I]^{1/2}}} \; x_n$

gel-effect = 5-10

Chain-transfer to polymer $\approx$ Đ 20-50

For a high molecular weight polymer, the rate of propagation is much higher compared to the rate of termination or rate of transfer, the value of P is nearly equal to 1. For the low conversion region, the disparity value will be somewhere between 1.5 to 2. The highest value or the limiting value can be 2. But after synthesizing a polymer by radical chain polymerization, we genrally see the value of dispersity is much higher, it is generally between 2 to 5. That is because, we know, this factor which determines the X_n value keeps on changing as polymerization proceed. The chain sizes or the molecular sizes keep on changing, as a result, we get a large distribution for the total polymer sample, which is around 2 to 5. If the gel effect happens then it goes even higher because in that case uncontrolled molecular weight or large molecular weight formation take place. It can go from 5 to 10 or even we can get a polydispersity index or dispersity as high as 20 to 50. In a normal case, at low conversion we should get a dispersity value is between 1.5 to 2, but in the real case when you synthesize a polymer sample you may get a dispersity value between 2 to 5, but if gel effects happen then polydispersity may become even higher.

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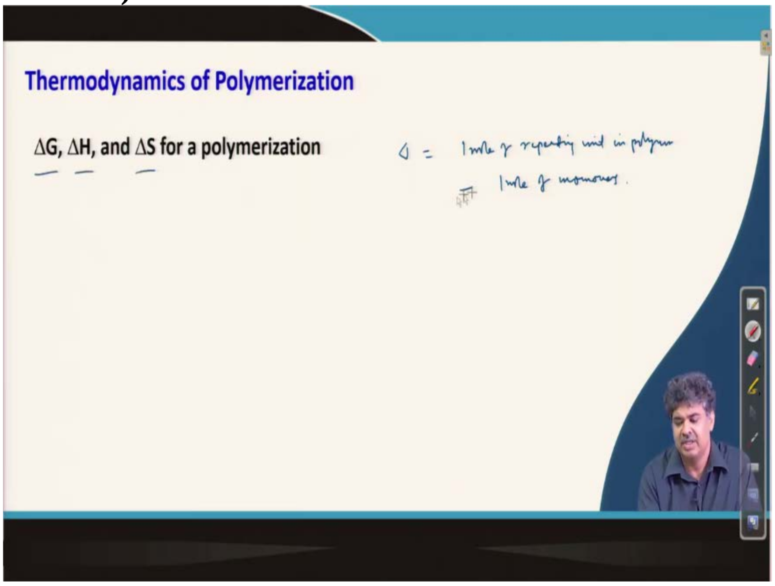

Thermodynamics of Polymerization

ΔG, ΔH, and ΔS for a polymerization

Δ = 1 mole of repeating unit in polymer

− 1 mole of monomers.

Let us move to the next topic, the thermodynamics of polymerization. We consider the ΔG, ΔH, ΔS for the polymerization reaction, in this case, Δ is the difference corresponds to –

$$\Delta = 1\, mole\ of\ repeating\ unit\ in\ polymer - 1\, mole\ of\ monomers$$

For example, for synthesis of polystyrene molecules, Δ corresponds to (1 mole of styrene in polymer - 1 mole of styrene as a monomer). If we think about poly(ethylene terephthalate), 1 mole of terephthalate repeat unit contains both terephthalic acid and ethylene glycol. So, in this case, Δ corresponds to (1 mole of repeat unit - 1 mole of terephthalic acid and 1 mole of ethylene unit).

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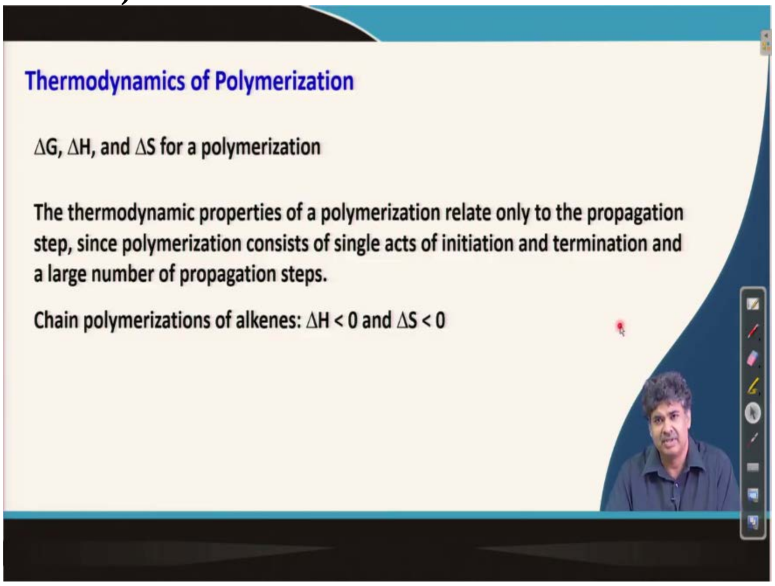

Thermodynamics of Polymerization

ΔG, ΔH, and ΔS for a polymerization

The thermodynamic properties of a polymerization relate only to the propagation step, since polymerization consists of single acts of initiation and termination and a large number of propagation steps.

Chain polymerizations of alkenes: ΔH < 0 and ΔS < 0

Now, the thermodynamic properties of polymerization relate only to the propagation step, since polymerization consists of single acts of initiation and termination and a large number of propagation steps. Mainly the propagation steps are involved in polymerization. Most cases, chain polymerization occur for alkenes. π bonds of the monomers get converted to single bond as a result ΔH value is negative i.e. the reaction is exothermic. As the monomers get tied up to form large polymer molecule, the entropy is lowered because of restrictions in degrees of freedom. So, eventually, if we combine these two, you will see that in most cases, for chain polymerization of alkenes, ΔG is negative.

Hence, thermodynamically, the chain polymerization is a favorable process, but whether a monomer will polymerize or not, that will depend on the kinetic factors. The electronic factor and the steric factor are important to initiate the chain. So, all these factors will come in combinations to see whether that chain polymerization takes place or not. But thermodynamically a chain polymerization is a feasible process mainly because of the large exothermic heat involved in this polymerization process.

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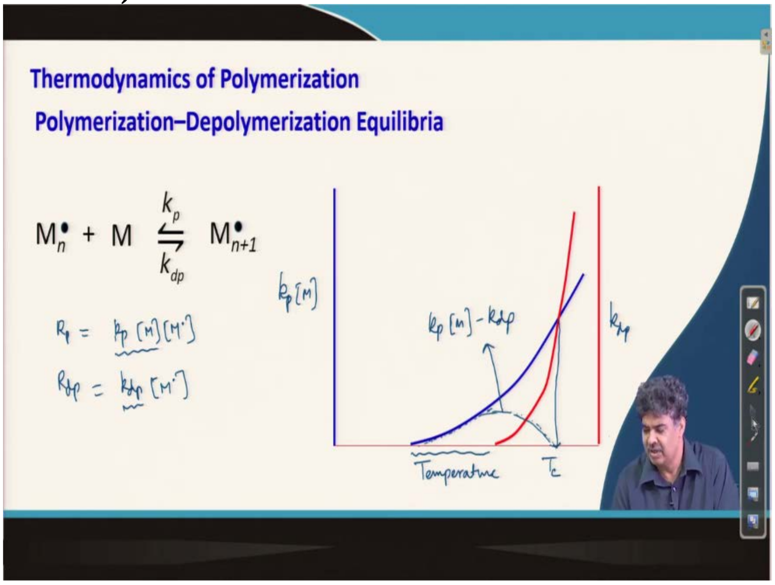

Thermodynamics of Polymerization

Polymerization–Depolymerization Equilibria

$$M_n^\bullet + M \underset{k_{dp}}{\overset{k_p}{\leftrightharpoons}} M_{n+1}^\bullet$$

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

$$R_{dp} = \underset{\sim}{k_{dp}}[M^\cdot]$$

Till now, we have been talking about mainly forward reactions, monomers react with a radicals and become a radical of higher size. But, there is a possibility that the reverse reaction may also happen, we need to consider the depolymerization reaction also. In equilibrium, from the thermodynamic point of view, rate of polymerization is same as the rate of depolymerization reaction.

We can write the polymerization reaction like this,

$$M_n^\cdot + M \leftrightharpoons M_{n+1}^\cdot$$

the forward reaction is a polymerization reaction and the backward reaction is called the depolymerization reaction. k_p, a rate constant that corresponds to forward reaction, and $k_{dp,}$ a rate constant for the backward reaction. The rate of forward reaction of polymerization is given by $k_p[M][M]^{\cdot}$, and the backward reaction by $k_{dp}[M]^{\cdot}$.

The concentration of radical species is the same in both cases. The comparison needs to be done between the terms $k_p[M]$ and k_{dp}, because $[M]^{\cdot}$ is present on both the sides. So, if we plot $k_p[M]$ with temperature, as the thermal initiation increases with the forward reaction also increases with temperature. Now, the reverse reaction also increases with temperature. So, if we plot the reverse reaction on another axis, then we can see that this also increases with temperature. However, there is a temperature range where the reverse reaction is almost negligible. If we do reaction in this range of temperature, then we have a negligible amount of reverse reaction or depolymerization reaction.

In principle, we can have a temperature which is called say T_c, for time being, where the degree of the forward reaction is same as the rate of backward reaction and the net polymerization is zero. So, in this case, we have the equilibrium where the rate of the polymerization reaction and the rate of depolymerization reaction are same.

The difference between the forward reaction and backward reaction is given by $k_p[M] – k_{dp}$. So, up to the temperature shown in the graph, mainly the polymerization reaction occurs, after this, both reactions take place, and at a certain temperature both become equal. So, no net polymerization reaction takes place and we call this temperature ceiling temperature.

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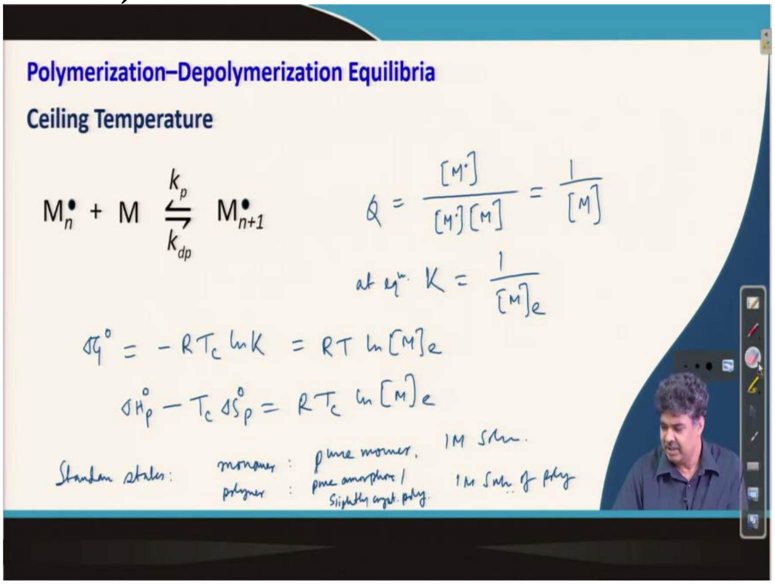

Polymerization–Depolymerization Equilibria

Ceiling Temperature

$$M_n^{\bullet} + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^{\bullet}$$

$$Q = \frac{[M^{\cdot}]}{[M^{\cdot}][M]} = \frac{1}{[M]}$$

$$\text{at eq}^{\text{m}}.\ K = \frac{1}{[M]_e}$$

$$\Delta G^{\circ} = -RT_c \ln K = RT \ln [M]_e$$

$$\Delta H_p^{\circ} - T_c \Delta S_p^{\circ} = RT_c \ln [M]_e$$

Standard states:
monomer : pure monomer, 1M Soln.
polymer : pure amorphous / Slightly cryst. poly. 1M Soln. of poly

Let us discuss more ceiling temperature now. So for this reaction, if we talk about the equilibrium constant and we require the concentrations of total monomer and the total radical species in the medium. The equilibrium constant is given by K = 1/[M]$_e$, and for any non-equilibrium situation, we should we should write Q, reaction quotient, instead of K.

We can write,

$$\Delta G^0 = -RT_c \ln K$$

ΔG^0 is standard Gibbs free energy of polymerizatio, T_c is the temperature where this reaction equilibrium takes place, Celing temperature. So it can be written as,

$$\Delta G^0 = -RT_c \ln K = RT_c[M]_e$$

$$\Delta H_p^0 - T_c \Delta S_p^0 = RT_c[M]_e$$

In the standard state, the monomer is either a pure monomer or a one molar solution, and for polymer it is either one molar solution of polymer, or a pure amorphous or slightly crystalline polymer. So, this is the standard state we should keep in our mind.

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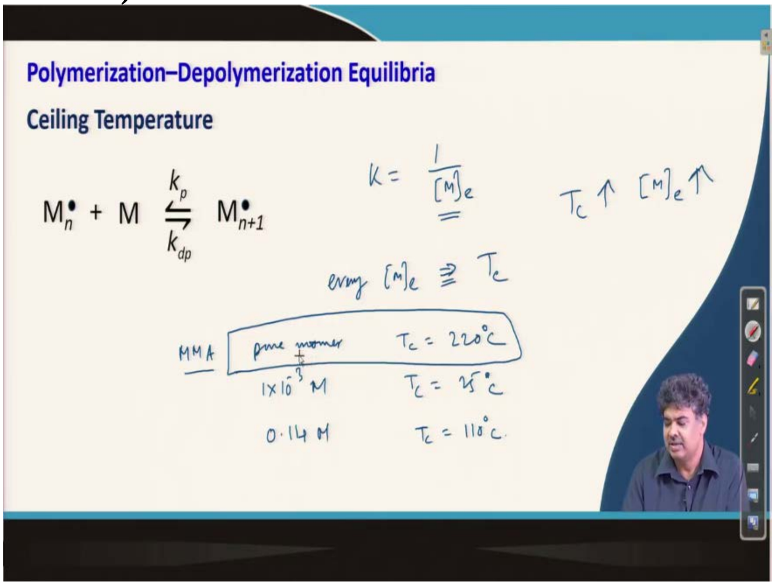

Polymerization–Depolymerization Equilibria

Ceiling Temperature

$$M_n^{\bullet} + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^{\bullet}$$

$$K = \underline{\underline{\frac{1}{[M]_e}}}$$

$T_c \uparrow \quad [M]_e \uparrow$

every $[M]_e \Rrightarrow T_c$

$\underline{\text{MMA}}$

$\boxed{\text{pure monomer} \quad T_c = 220^\circ C}$

1×10^{-3} M $\quad T_c = 25^\circ c$

0.14 M $\quad T_c = 110^\circ c.$

We have seen that K is given by 1/[M]$_e$, the equilibrium constant depends on the monomer concentration in equilibrium. For every equilibrium monomer concentration, [M]$_e$ we should have a corresponding T_c. For example, if we consider methyl methacrylate (MMA), for pure monomer the T_c value is 220 °C. This means if we consider polymerizing pure monomer, it will not be possible to get any polymer for reactions done at 220 °C or higher. If we consider the T_c as 25 °C, then the corresponding concentration for monomer is 1×10^{-3} moles/L. This means if we do the reaction at 25 °C, the reaction is continued till the monomer concentration becomes this low. For 110 °C, this concentration is 1.4 M. This means, for every temperature we have a corresponding equilibrium monomer concentration and when the temperature goes up the concentration of free monomer present in the equilibrium also goes up. So, as T_c goes up, free monomer concentration in the reaction mixture goes up. We can have T_c for any temperature and a corresponding monomer concentration. So, each temperature can be at T_c or Ceiling temperature with a corresponding equilibrium monomer concentration. But there are some texts which consider T_c as the temperature where the equilibrium monomer concentration is the pure monomer which is not correct. Now, if T_c goes up, the equilibrium monomer concentration also goes up. So, at 220 °C if we want to polymerize MMA, we cannot do it because, pure monomer is the equilibrium condition.

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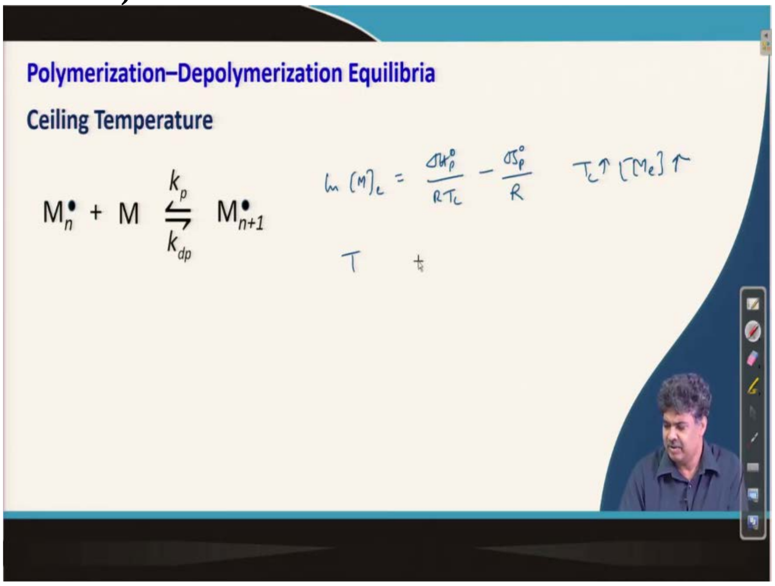

Polymerization–Depolymerization Equilibria

Ceiling Temperature

$$M_n^\bullet + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^\bullet$$

$$\ln [M]_e = \frac{\Delta H_p^0}{RT_c} - \frac{\Delta S_p^0}{R} \qquad T_c \uparrow [M_e] \uparrow$$

T

We can write this expression,

$$\ln\,[\mathrm{M}]_e = \frac{\Delta H_p^0}{RT_c} - \frac{\Delta S_p^0}{R}$$

T_c goes up as equilibrium monomer concentration as ΔH is negative (exothermic reaction).

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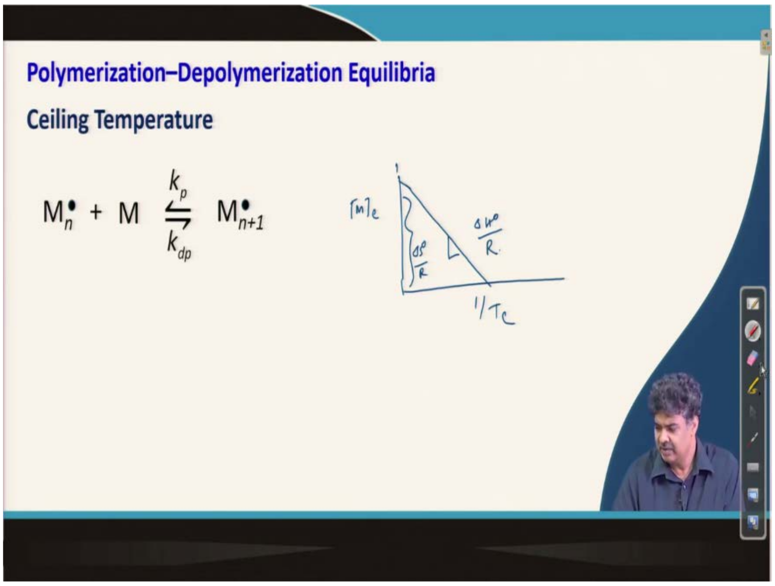

Polymerization–Depolymerization Equilibria

Ceiling Temperature

$$M_n^\bullet + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^\bullet$$

If we want to find out ΔH^0 experimentally then we can plot $[M]_e$ vs $1 / T_c$ as shown, the intercept would be $\Delta S^0 / R$ and the slope would be $\Delta H^0 / R$.

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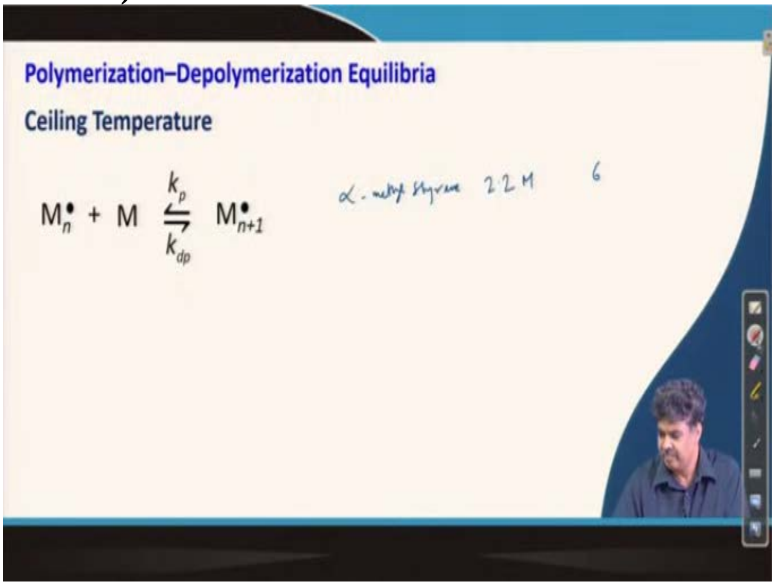

Polymerization–Depolymerization Equilibria

Ceiling Temperature

$$M_n^\bullet + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^\bullet$$

α-methyl styrene 2.2 M 6

There are some monomers for which T_c is very low for example if I take out talk about α-methyl styrene.

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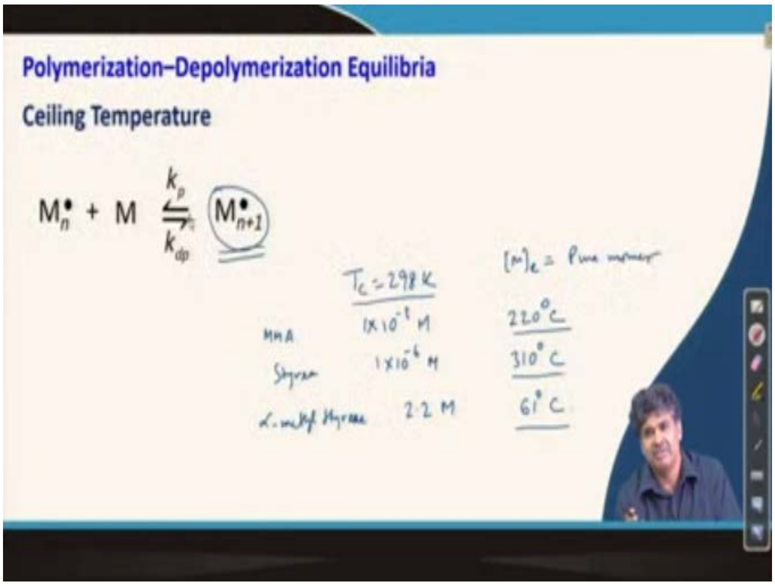

Polymerization–Depolymerization Equilibria

Ceiling Temperature

$$M_n^\bullet + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} \underline{\underline{\boxed{M_{n+1}^\bullet}}}$$

	$T_c = 298$ K	$[M]_c$ = Pure monomer
MMA	1×10^{-3} M	220 °C
Styrene	1×10^{-6} M	310 °C
α-methyl styrene	2.2 M	61 °C

T_c for pure MMA is 220 °C, for pure styrene is 310 °C and for pure α methyl styrene is 61 °C. So, if we want to carry out a polymerization reaction for MMA at 298 K, the monomer concentration has to be above this concentration written here, then only the forward reaction or polymerization reaction takes place. If the monomer concentration is lower than this, then we cannot carry out the polymerization reaction. So, if we want to do a bulk polymerization that means, want to polymerize the pure monomer, we have to do a reaction at lower than T_c, only then the polymerization can be started.

Now there is also a false impression that if we take a poly(MMA) or poly(methyl methacrylate) above 220 °C, it will depolymerize to become a monomer. But that is not correct; because this depolymerization reaction happens only when a radical is present. Now, if the polymerization is complete, there is no radical present in the medium, the depolymerization reaction does not happen. For depolymerisation to happen, we have to initiate, like heating up some initiating species in the system. In this case, if we keep the poly(MMA) or polystyrene above this temperature, the reverse reaction might happen and the polymer might depolymerize, we call it as unzipping of the polymer. So that we need to keep in mind that if we are taking the polymer to a higher temperature, which we do take during processing of polymers, we should devoid of generating radical species which might induce that depolymerization reaction.

We will stop now for this lecture. In the next lecture, we will talk about different processes of synthesizing polymers by radical polymerization.