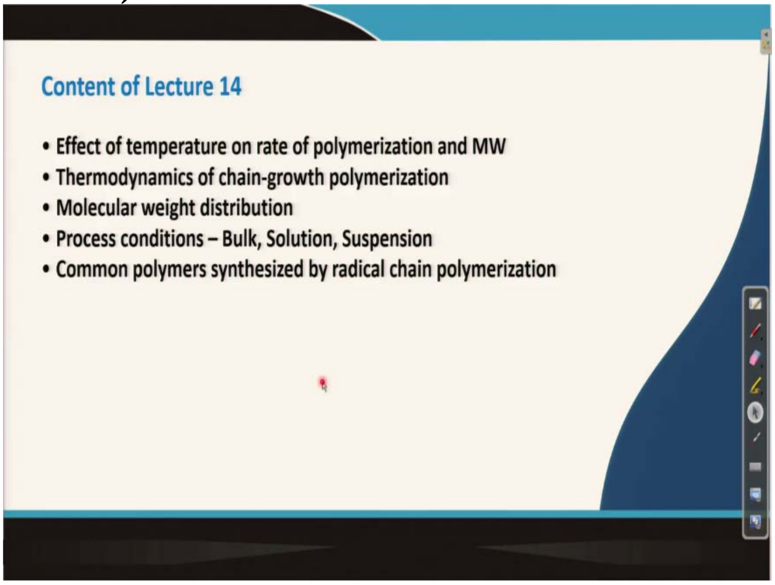
Introduction to Polymer Science
Prof. Dibakar Dhara
Department of Chemistry
Indian Institute of Technology – Kharagpur

Lecture – 14
Energetics and Thermodynamics of Chain Polymerization, MW distribution, Common Polymers

(Refer Slide Time: 00:34)

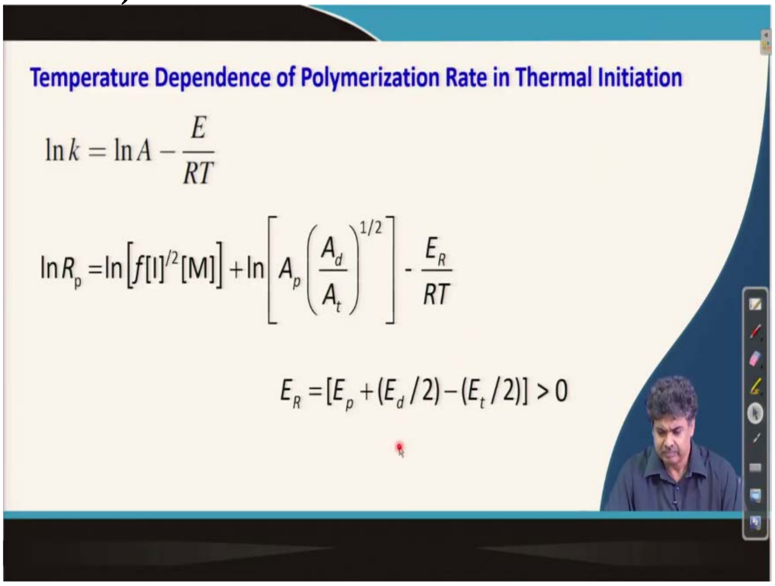


Content of Lecture 14

- Effect of temperature on rate of polymerization and MW
- Thermodynamics of chain-growth polymerization
- Molecular weight distribution
- Process conditions – Bulk, Solution, Suspension
- Common polymers synthesized by radical chain polymerization

Welcome back. In this lecture, we will continue our discussion on the energetics of radical chain polymerization. We will also discuss the thermodynamics of chain polymerization, molecular weight distribution, and give the examples of some common polymers, which are synthesized by radical chain polymerization. These are the topics we will try to cover in this lecture, maybe we will spill over a few of these topics to the next lecture.

(Refer Slide Time: 00:53)



Temperature Dependence of Polymerization Rate in Thermal Initiation

$$\ln k = \ln A - \frac{E}{RT}$$

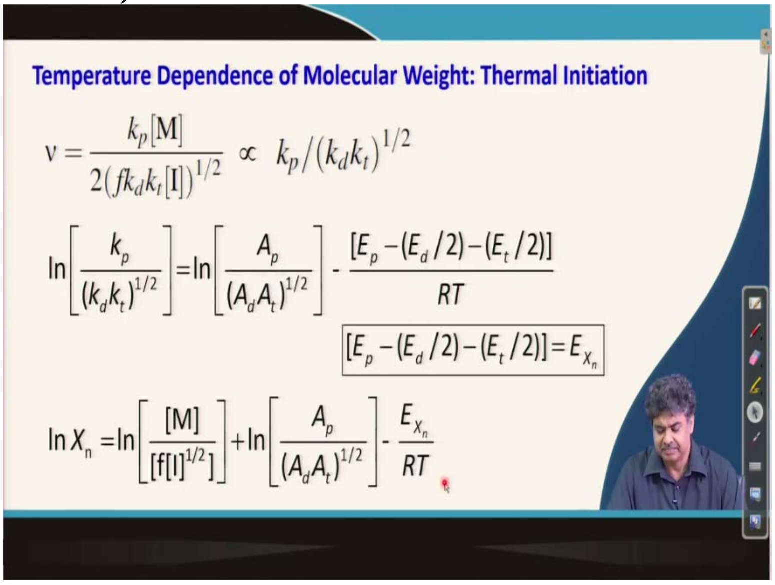
$$\ln R_p = \ln\left[f[\mathrm{I}]^{1/2}[\mathrm{M}]\right] + \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] - \frac{E_R}{RT}$$

$$E_R = [E_p + (E_d/2) - (E_t/2)] > 0$$

We have started discussing temperature dependence of polymerization rate for thermal initiation in the last lecture. The Arrhenius equation is $lnk = lnA - \frac{E}{RT}$ where A is the pre-exponential factor, E is the activation energy, k is the rate constant. In the case of radical chain polymerization, we have three rates which are involved in polymerization process - initiation, propagation and termination.

The effect of temperature on polymerization rate would depend on how the temperature affects all these three rates. We have shown in the last lecture that the rate of polymerization can be expressed by using the Arrhenius equation and E_R is the composite or combination of the activation energies of propagation, decomposition and termination. We showed that this is a positive quantity, which means that with increase in temperature, the reaction rate for thermal initiation goes up.

(Refer Slide Time: 02:13)



Temperature Dependence of Molecular Weight: Thermal Initiation

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

$$\ln\left[\frac{k_p}{(k_dk_t)^{1/2}}\right] = \ln\left[\frac{A_p}{(A_dA_t)^{1/2}}\right] - \frac{[E_p-(E_d/2)-(E_t/2)]}{RT}$$

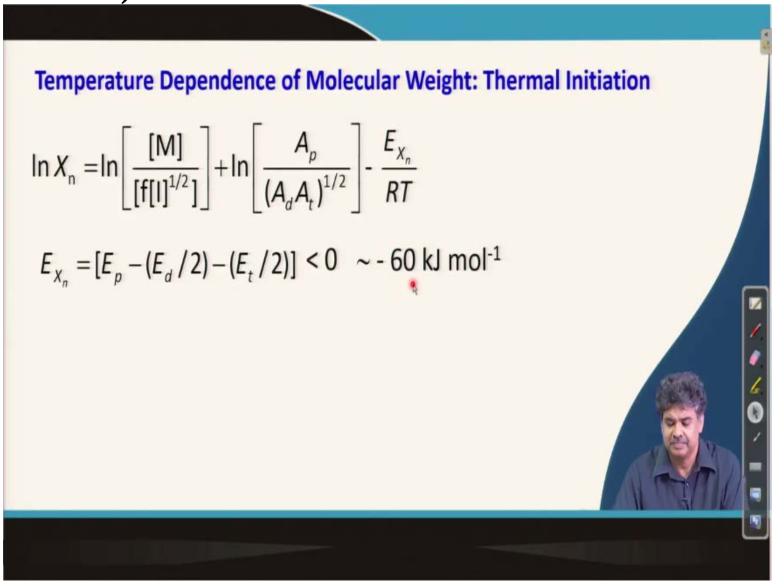
$$\boxed{[E_p-(E_d/2)-(E_t/2)]=E_{X_n}}$$

$$\ln X_n = \ln\left[\frac{[\mathrm{M}]}{[f[\mathrm{I}]^{1/2}]}\right] + \ln\left[\frac{A_p}{(A_dA_t)^{1/2}}\right] - \frac{E_{X_n}}{RT}$$

Now, let us talk about how molecular weight depends on temperature or how temperature affects molecular weight in radical chain polymerization. We will first talk about thermal initiation. This is the expression we derived in the last few lectures. The kinetic chain length is also affected by molecular weight or degree of polymerization. Now, it is proportional to these rate constants. So, we take the logarithm of this expression and we get, in this case, the activation energy. Molecular weight formation or degree of polymerization is given by this composite expression, and for thermal initiation, E_d is the highest compared to E_p and E_t. We can write X_n from this expression like this,

$$lnX_n = ln\left[\frac{[\mathrm{M}]}{f[\mathrm{I}]^{1/2}}\right] + ln\left[\frac{A_p}{(A_dA_t)^{1/2}}\right] - \frac{E_{x_n}}{RT}$$

(Refer Slide Time: 03:51)



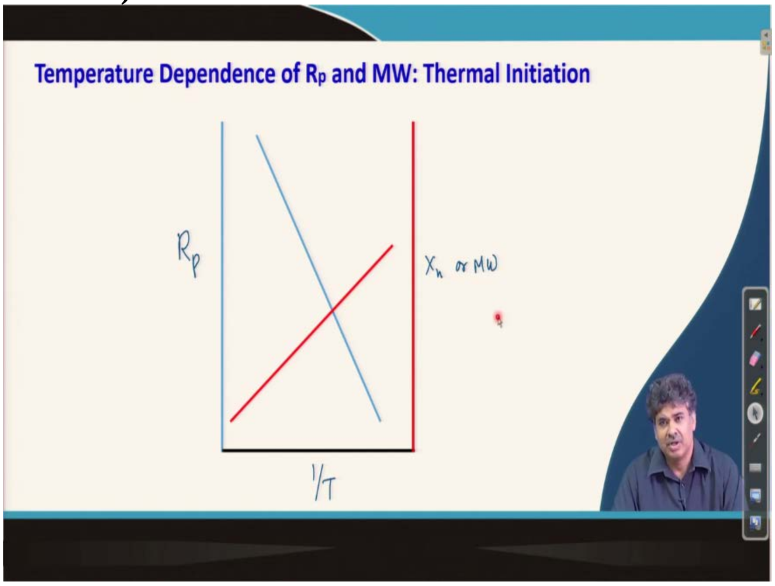
Temperature Dependence of Molecular Weight: Thermal Initiation

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

$$E_{X_n} = [E_p - (E_d/2) - (E_t/2)] < 0 \quad \sim -60 \text{ kJ mol}^{-1}$$

The activation is a combination of composite activation energy of degree of polymerization or activation energy of molecular weight buildup. The difference, in this case, there is a negative sign compared to a positive sign in the case of the rate of polymerization. So, this would be a negative quantity and the value is approximately -60 kJ / mole, which means that with increasing temperature, the molecular weight or degree of polymerization gets reduced.

(Refer Slide Time: 04:50)

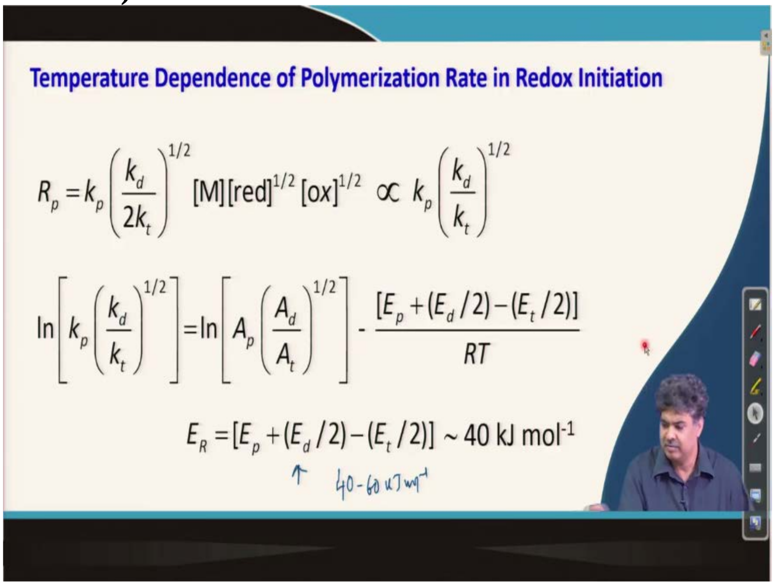


Temperature Dependence of R_p and MW: Thermal Initiation

If we plot the temperature effect on the rate of polymerization and molecular weight in thermally initiated radical chain polymerization. From the plot R_p, with 1 / T, we see that, the rate increases with temperature. If we plot the degree of polymerization or molecular weight X_n vs 1 / T, then it is seen that X_n or molecular weight, decreases with temperature.

So, if we want to increase the reaction rate, we can increase the temperature. But the downside is that if we increase the temperature in thermal initiated polymerization, the number average molecular weight value will decrease. This is because with increasing the temperature, more and more radical gets produced. So, more and more termination reaction occurs and the molecular weight number or values come down.

(Refer Slide Time: 06:33)



Temperature Dependence of Polymerization Rate in Redox Initiation

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

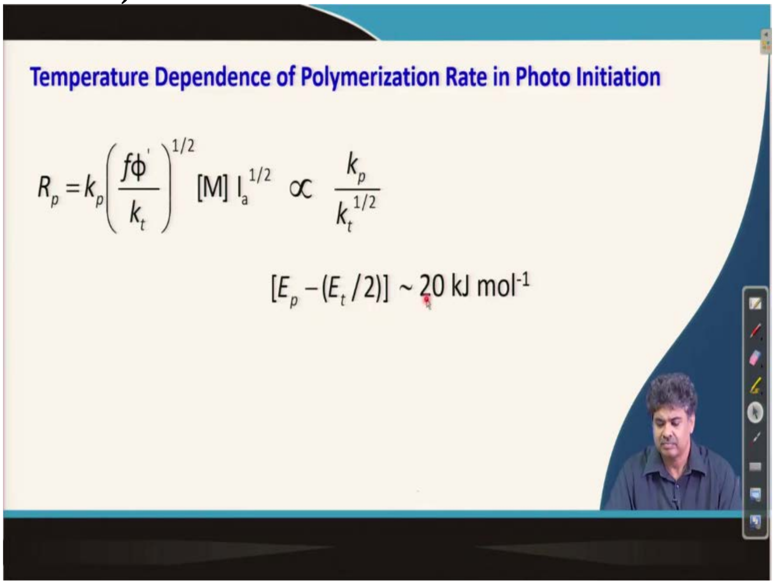
$$\ln\left[k_p \left(\frac{k_d}{k_t}\right)^{1/2}\right] = \ln\left[A_p \left(\frac{A_d}{A_t}\right)^{1/2}\right] - \frac{[E_p + (E_d/2) - (E_t/2)]}{RT}$$

$$E_R = [E_p + (E_d/2) - (E_t/2)] \sim 40 \text{ kJ mol}^{-1}$$

↑ 40-60 kJ mol^{-1}

Now, let us talk about the temperature dependence of polymerization rate for redox polymerization. In the redox polymerization, we have seen this expression earlier, which means that the redox polymerization rate also depends on these three rate constants, and we have similar expressions like thermal initiation. The only difference between thermal initiation and redox initiation is related to the value of this dissociation activation energy. The dissociation activation energy of propagation and activation energy for termination remain same because they are the same reaction. Only the initiation mechanism is different in the case of radical initiator and thermal initiator. In redox initiation, we will talk about photoinitiation. The value of the dissociation activation energy differs for different initiation mechanisms and for a redox initiation this value is typically around 40 to 60 kJ/mole.

(Refer Slide Time: 08:14)



Temperature Dependence of Polymerization Rate in Photo Initiation

$$R_p = k_p \left(\frac{f\phi'}{k_t}\right)^{1/2} [M]\, I_a^{1/2} \propto \frac{k_p}{k_t^{1/2}}$$

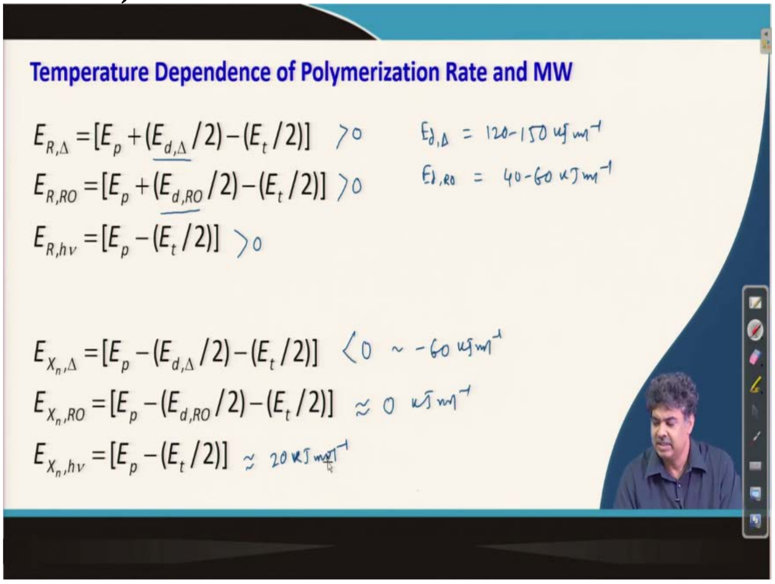
$$[E_p - (E_t/2)] \sim 20 \text{ kJ mol}^{-1}$$

What about the reaction rate in photopolymerization? The expression for the reaction rate is-

$$R_p = k_p \left(\frac{f\Phi'}{k_t}\right)^{1/2} [\mathrm{M}] I_a^{1/2} \propto \frac{k_p}{k_t^{1/2}}$$

in this case, the reaction rate is dependent only on k_p and k_t because the dissociation mechanism does not depend on temperature, it only depends on the intensity of the light which is initiating the photodissociation. So, the reaction rate is proportional to $k_p / k_t^{1/2}$. We can get the composite activation energy like [E_p - (E_t / 2)]. This value is again positive, but the magnitude of this value is quite less like 20 kJ/mol. So, in this case, the effect of temperature on polymerization rate is mild.

(Refer Slide Time: 09:26)



Temperature Dependence of Polymerization Rate and MW

$E_{R,\Delta} = [E_p + (\underline{E_{d,\Delta}}/2) - (E_t/2)] > 0$ $E_{d,\Delta} = 120\text{-}150$ kJ mol^{-1}

$E_{R,RO} = [E_p + (\underline{E_{d,RO}}/2) - (E_t/2)] > 0$ $E_{d,RO} = 40\text{-}60$ kJ mol^{-1}

$E_{R,h\nu} = [E_p - (E_t/2)] > 0$

$E_{X_n,\Delta} = [E_p - (E_{d,\Delta}/2) - (E_t/2)] < 0 \sim -60$ kJ mol^{-1}

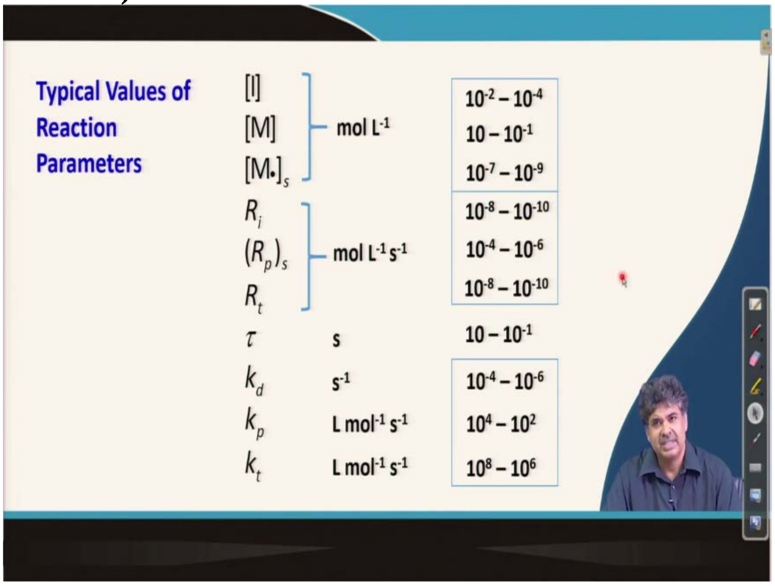
$E_{X_n,RO} = [E_p - (E_{d,RO}/2) - (E_t/2)] \approx 0$ kJ mol^{-1}

$E_{X_n,h\nu} = [E_p - (E_t/2)] \approx 20$ kJ mol^{-1}

Now we are talking about the temperature dependence on polymerization rate and molecular weight. First we talked about the polymerization rate. The E_d for thermal initiation is higher, which is approximately 120 to 150 kJ/mol. Whereas E_d in the case of redox initiation is about 40 to 60 kJ/mol. So, the effect of temperature in the case of thermal initiated polymerization will be much higher than the effect of temperature on redox initiated polymerization. The effect of temperature on the photopolymerization rate is small.

Now, if we talk about molecular weight, then again this is a negative quantity because this value of E_d is high. So it is a negative quantity and for thermal initiation, it comes around - 60 kJ/mol. Whereas, for redox initiation, it comes close to 0, and for photopolymerization, it is almost 20 kJ/mol. So, in the case of a thermally induced initiation, the molecular weight comes down with increasing temperature, but, in the case of redox initiation, the molecular weight is almost independent of temperature. In the case of photopolymerization, the molecular weight is mildly dependent on temperature. In the case of photopolymerization, both the rates of reaction and the molecular weight increases slightly with temperature, that is the only exception compared to the other two.

(Refer Slide Time: 12:45)



Typical Values of Reaction Parameters

$[I]$	mol L^{-1}	$10^{-2} - 10^{-4}$
$[M]$		$10 - 10^{-1}$
$[M\bullet]_s$		$10^{-7} - 10^{-9}$
R_i	mol L^{-1} s^{-1}	$10^{-8} - 10^{-10}$
$(R_p)_s$		$10^{-4} - 10^{-6}$
R_t		$10^{-8} - 10^{-10}$
τ	s	$10 - 10^{-1}$
k_d	s^{-1}	$10^{-4} - 10^{-6}$
k_p	L mol^{-1} s^{-1}	$10^{4} - 10^{2}$
k_t	L mol^{-1} s^{-1}	$10^{8} - 10^{6}$

Now let us revise the typical value of the reaction parameters. There are three concentration terms, the concentration of initiator [I], the concentration of monomer [M], and the concentration of radical species at steady state $[M.]_s$, ‘s’ as subscript mean we are talking about steady-state value. So the unit will be in concentration moles/liter.

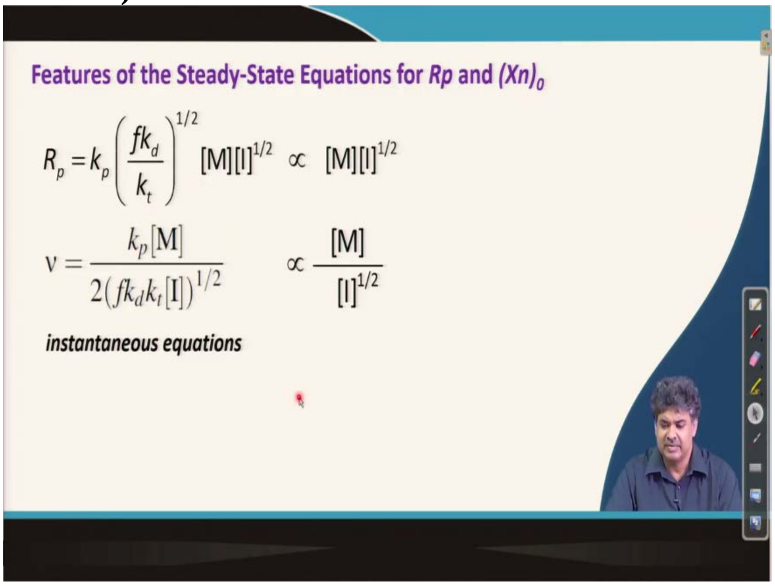
In a typical radical chain polymerization, the initiator concentration is much lower compared to monomer concentration, and the concentration of radical species at a steady state is very low. It is very difficult to experimentally determine the amount or the concentration of radical species at the steady state.

These three are the rate of initiation R_i, rate of propagation at steady state $(R_p)_s$, and rate of termination R_t. The unit of these rates would be concentration by time. The initiation rate is very slow whereas the rate of propagation is much higher.

The average lifetime of a radical before it gets terminated comes around 0.1 seconds to 10 seconds. Which means that the average lifetime of a radical is very low, k_d is the dissociation rate constant, which is a first-order reaction with a unit of second^{-1}. For the second-order reactions, the unit is L mol^{-1} s^{-1} and the corresponding value of k_d , k_p and k_t are given. R_t is quite small because the concentration of radicals is very small. If the rate of termination was very high then obviously, there would not have been any polymerization, because, inherently the reaction rate constant for termination is very high. Whereas in the case of propagation, the reactions are between a monomer and a radical, monomer concentration is much higher compared to the radical species. That is why even if the rate constant is lower in this case, the reaction rate is higher compared to the termination reaction. k_t corresponds to the reaction between two radicals whereas k_p corresponds to the reaction between one monomer and one radical species. That is why the rate constant for termination reaction is much higher than propagation. On the other hand, the dissociation reaction is not a radical reaction, this is inherently much slower. The rate constant is much lower compared to the other two radical reactions.

To summarize that both the initiation rate and the dissociation rate constants are low, but the inherent reaction rate constant for termination reaction is very high, even higher than the rate constant for propagation. But because the concentration of radical species is very low in the reaction medium, the rate of termination is lower compared to the rate of propagation. As a result, we have polymer production before a radical species get terminated.

(Refer Slide Time: 19:12)



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

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

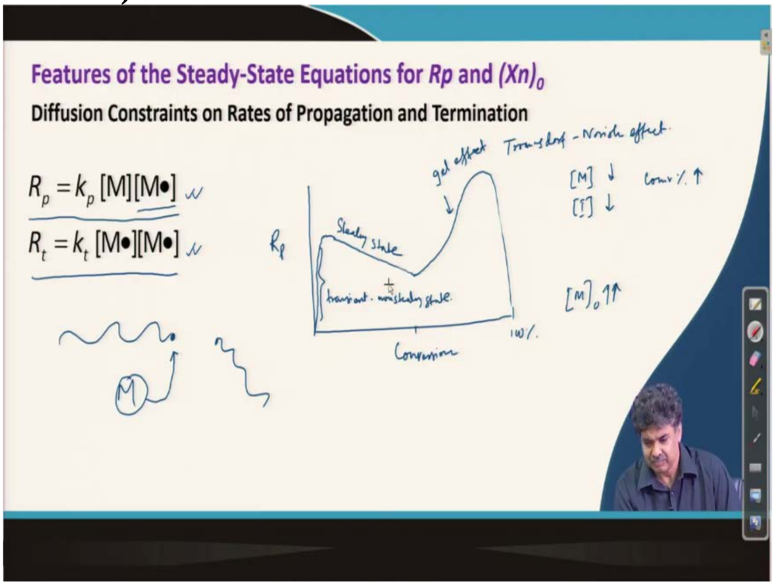
$$\nu = \frac{k_p[\mathrm{M}]}{2(fk_dk_t[\mathrm{I}])^{1/2}} \propto \frac{[\mathrm{M}]}{[\mathrm{I}]^{1/2}}$$

instantaneous equations

Now, there are some features of the steady-state equation for the rate of polymerization and degree of polymerization. Here, naught means the degree of polymerization in absence of any transfer reactions. The expressions for the rate of polymerization and the kinetic chain length are related to molecular weight and degree of polymerization.

Let us focus on the concentration of monomer and concentration of initiator. The rate of polymerization is dependent on the monomer and initiator concentrations, whereas, the molecular weight and degree of polymerization are dependent on these factors. As the polymerization reaction progresses, both the monomer concentration and the initiator concentration come down. As a result, the reaction rate should become lower and lower. Ultimately, when all the monomers will be consumed, the reaction rate should become zero. The molecular weight depends on how the ratio $[\mathrm{M}]/[I]^{1/2}$ changes, and that is a very complicated scenario. As a result, the molecular weight could be different at the beginning, middle, or at the later stage of polymerization, because this ratio may not remain the same at different time of polymerization. Sometimes what happened in commercial production they charge the monomer and initiator intermittently to keep this ratio almost the same so that the molecular weight of the resulting polymers remain more or less the same. So that we do not have a large distribution of molecular weight. It should also be remembered, that, as this concentration of monomer and initiator keep on changing, so, these rate equations are instantaneous equations.

(Refer Slide Time: 22:06)



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

Diffusion Constraints on Rates of Propagation and Termination

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

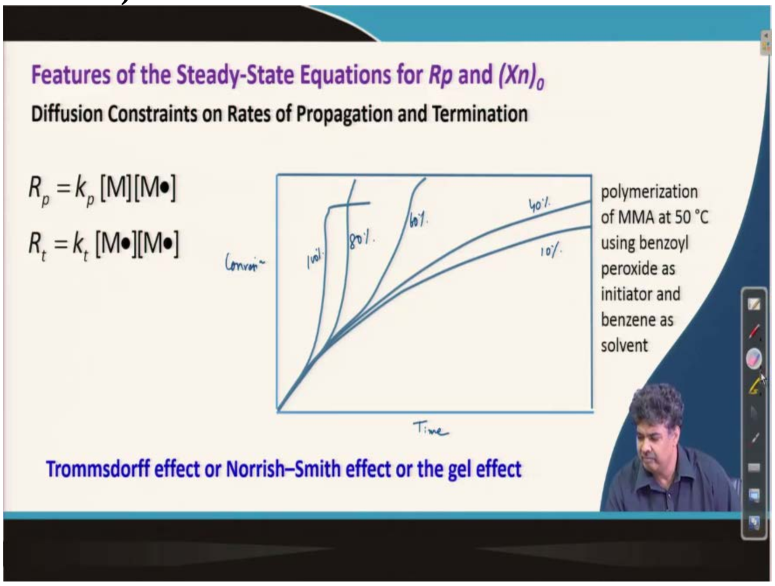
$R_t = k_t [M\bullet][M\bullet]$

It may happen that diffusion of the radical species can also affect the rate of propagation and termination. For example, we know, in the rate of propagation or rate of polymerization one radical species and one monomer are involved, whereas, in case of termination, two radical species are involved. Now, ideally, as we have seen in the last slide, that if we plot rate versus conversion then after some time we get a steady-state. As conversion increases, both monomer concentration and initiator concentration come down. So, in a steady-state, the reaction rate should slowly or steadily come down. However, at the latter stage of polymerization, the conversion is very high and the reaction mixture contains lots of polymers and the viscosity of the medium is very high. Now, as a result of this, the diffusion of the radical species becomes slower. It should be noten again that the termination reaction takes place between two radicals, all the radicals move around randomly and when they collide the termination reactions take place.

Now, if the viscosity of the reaction is very high such that the translational diffusion of the radicals are low, hence, they cannot come close to each other. So, the reaction cannot happen. In the case of polymerization reaction or propagation reaction, one radical species is involved. As the propagating radical has a longer size, it's diffusion coefficient is going to be much slower than a monomer species. Because of the smaller size, monomers can diffuse much faster compared to a propagating radicals which have larger size. As a result, the propagation reaction can continue because the monomers can diffuse and collide with the radical species. But, the termination reaction becomes diffusion-controlled because it requires two radical species to collide and interact with each other. A situation arise when propagation reactions continue at a nearly unchanged rate, but termination becomes slower, as a result effective rate of polymerization goes up. If radical propagation continues without any termination, the molecular weight effectively becomes very large and so large that the polymer cannot move. The preactions mixture bocomes like a gel, although we can not term this as a proper gel as per the definition, because it is not cross-linked. As the sample cannot be moved, it becomes like a gel and we call this as gel effect. This is also called Trommsdorff–Norrish effects because they are the scientists who discovered this. Once, the gel effect sets in, polymerization rate comes down and becomes negligible. In summary, in radical chain polymerization, we may have different regions like transient non-steady state, steady-state, and gel effect.

We understood that in a normal radical chain polymerization, immediately after a very short period, the reaction reaches a steady-state. The polymerization reaction rate becomes slower and slower as the concentration of monomer and initiator keeps on coming down. But at the later state when the conversion is high and the viscosity of the polymer mixture is very high, the diffusion of the propagating radical becomes slower and the reaction becomes diffusion control. So, the propagation reaction continues to happen, but the radical termination reaction becomes much lower. As a result, the reaction rate goes up and the molecular weight also goes up because there is no termination reaction and we get a gel-like material. If the monomer conversion percentage is higher, then more and more polymers will generate and viscosity will be much higher compared to a situation where we have fewer monomers, more solvent in the mixture.

(Refer Slide Time: 30:20)



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

Diffusion Constraints on Rates of Propagation and Termination

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

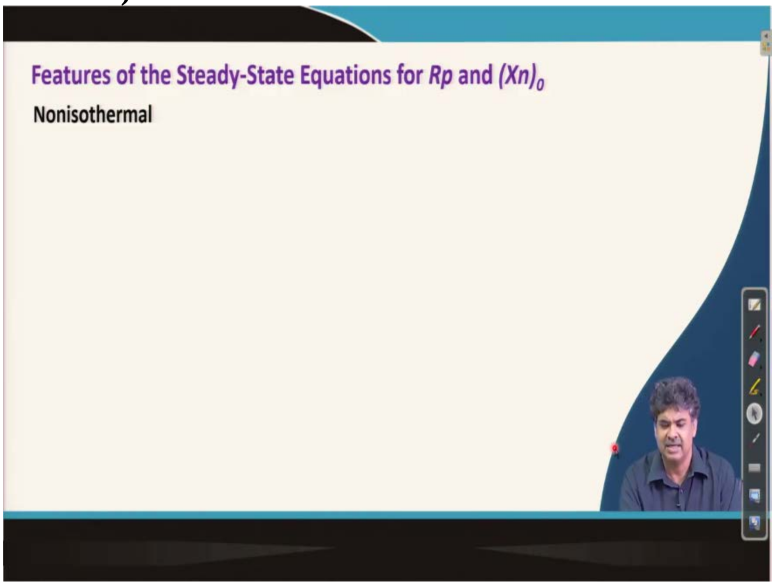
$R_t = k_t [M\bullet][M\bullet]$

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

If we do the same reaction with different initial concentrations, we will have this kind of figures. In this case, we can plot conversion versus time. In this figure, the initial percentage of monomer is 10%, 40%, 60%, 80%, and 100% for five different cases. We can see that when the concentration of the monomer in the reaction mixture is low, then the reaction can go for a longer time. But when the concentration becomes much higher, then this gel effect occurs at a much lower time and at lower conversion value, because the viscosity of the polymers or the viscosity of the medium becomes much higher even at low conversion. And if the T_g, is higher than the reaction temperature then the polymers become very hard glassy. If the polymers become glassy material, then no further reaction is possible. So, even if we start the reaction with pure monomer, we cannot complete the reaction to 100% level.

(Refer Slide Time: 32:58)



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

Nonisothermal

We will start with the nonisothermal situation in the next lecture.