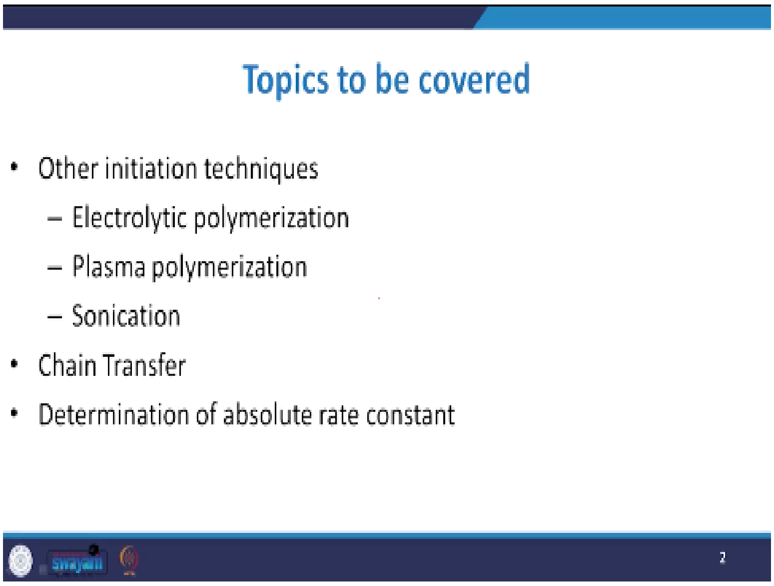
Polymer Reaction Engineering
Prof. Shishir Sinha
Department of Chemical Engineering
Indian Institute of Technology – Roorkee

Lecture – 44
Other Initiation Techniques - II

Welcome to this second lecture of other techniques attributed to the initiation polymerization under the head of radical chain polymerization. If you recall that in the previous lecture, we discussed about the electrolytic polymerization.

(Refer Slide Time: 00:43)



Topics to be covered

- Other initiation techniques
  - Electrolytic polymerization
  - Plasma polymerization
  - Sonication
- Chain Transfer
- Determination of absolute rate constant

We had a discussion about the plasma polymerization. We discussed about the mechanism of sonication for this initiation protocol. We had a discussion about the chain transfer protocol for this initiation technique. And we discussed the various mathematical equations along with the advantages and few disadvantages. Now, in this particular chapter, we are going to discuss with the determination of absolute rate constant.

Now, this absolute rate constant plays a very vital role in radical chain polymerization. You can have a look and we will discuss the mathematical approach and development of mathematical equations which are useful for this particular absolute rate constant concept. Now, see, we have discussed all the things attributed to the initiation other techniques. So, we can conclude that in radical chain polymerization, there are 5 different type of rate constants.

If you recall that in the various lecture, we discussed about all these rate constants. Now, there are 5 different type of rate constants which determine the overall rate of reaction.

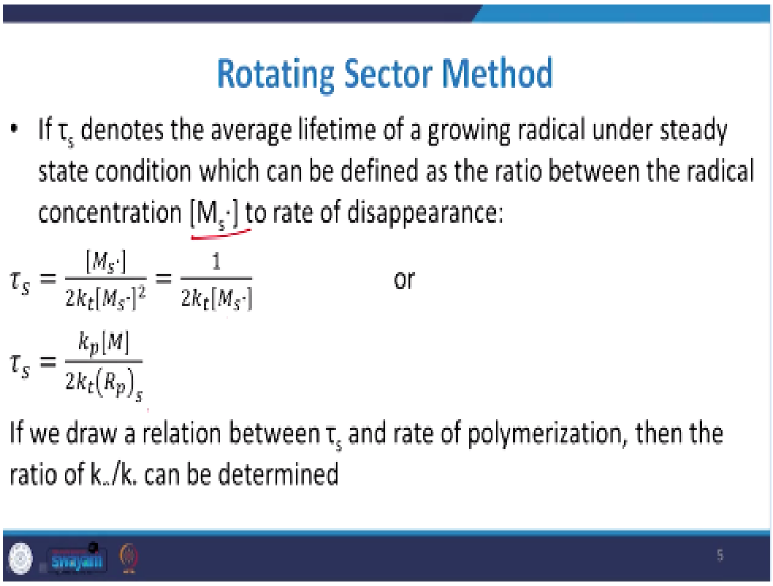
- Rate constant for Initiation (k_i)
- Rate constant for Propagation (k_p)
- Rate constant for Termination (k_t)
- Rate constant for Chain transfer (k_{tr})
- Rate constant for Inhibition (k_{in})

Now, these we have enlisted that is the rate constant for initiation will describe the rate constant for propagation of various protocols; the rate constant for the termination and if you see that during the concept of chain transfer, we introduced another rate constant for chain transfer that is k_{tr}. And then in due course of time, we discussed the rate constant for inhibition that is referred to as k_{in}. Rate constant for Initiation can be evaluated using the polymerization data obtained under steady state condition.

Rate constant for Propagation can be determined through **rotating sector method** (old method) **and pulsed laser polymerization–size exclusion chromatography (PLP-SEC)** (new method)

This is a newer concept for the determination of rate constant for the propagation step. Now, let us have a brief outlook for this rotating sector method.

(Refer Slide Time: 03:25)



Rotating Sector Method

- If τ_s denotes the average lifetime of a growing radical under steady state condition which can be defined as the ratio between the radical concentration $[M_s\cdot]$ to rate of disappearance:

$$\tau_S = \frac{[M_S\cdot]}{2k_t[M_S\cdot]^2} = \frac{1}{2k_t[M_S\cdot]} \qquad \text{or}$$

$$\tau_S = \frac{k_p[M]}{2k_t\left(R_p\right)_s}$$

If we draw a relation between τ_s and rate of polymerization, then the ratio of k../k. can be determined

- If τ_s denotes the average lifetime of a growing radical under steady state condition which can be defined as the ratio between the radical concentration $[M_s\cdot]$ to rate of disappearance:

$\tau_s = \frac{[M_s\cdot]}{2k_t[M_s\cdot]^2} = \frac{1}{2k_t[M_s\cdot]}$ or

$$\tau_s = \frac{k_p[M]}{2k_t\left(R_p\right)_s}$$

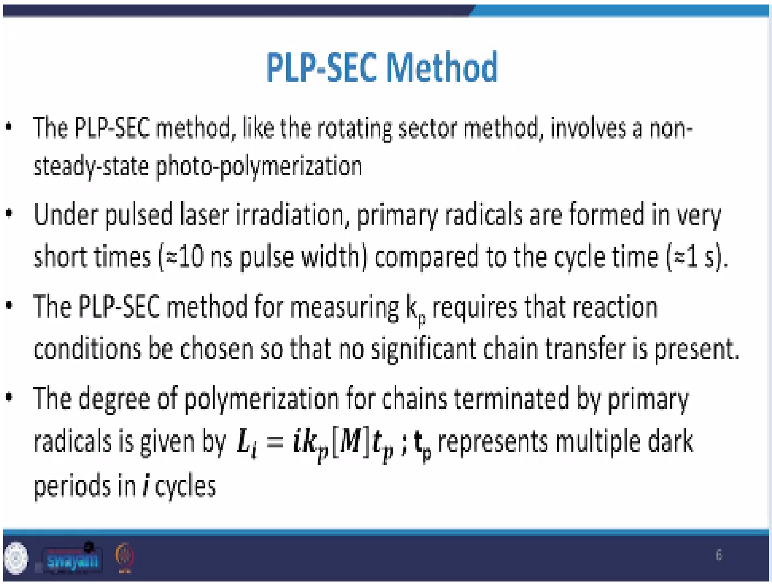
If we draw a relation between τ_s and rate of polymerization, then the ratio of k_p/k_t can be determined

Let us have a look about the PLP-SEC method.

This is like the rotating sector method; this involves a non-steady state photo-polymerization. Under pulsed laser irradiation, primary radicals are formed in very short times (≈10 ns pulse width) compared to the cycle time (≈1 s).

So, this pulse laser protocol photo-polymerization SEC method for the measuring of the rate constant for propagation, this requires the reaction conditions be chosen so that no significant chain transfer is usually present.

(Refer Slide Time: 05:14)



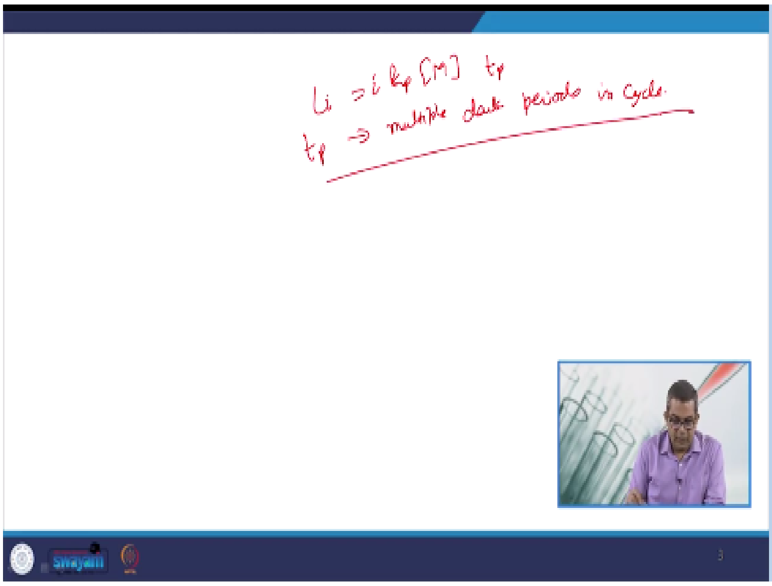
PLP-SEC Method

- The PLP-SEC method, like the rotating sector method, involves a non-steady-state photo-polymerization
- Under pulsed laser irradiation, primary radicals are formed in very short times (≈10 ns pulse width) compared to the cycle time (≈1 s).
- The PLP-SEC method for measuring k_p requires that reaction conditions be chosen so that no significant chain transfer is present.
- The degree of polymerization for chains terminated by primary radicals is given by $\boldsymbol{L_i = ik_p[M]t_p}$; t_p represents multiple dark periods in ***i*** cycles

Now, this PLP-SEC method for measuring the rate constant for propagation, it requires that reaction condition which needs to be chosen, so, that there will be no significant chain transfer is present. The degree of polymerization for chains terminated by primary radicals is given by

$\boldsymbol{L_i = ik_p[M]t_p}$ **;** $\boldsymbol{t_p}$ represents multiple dark periods in ***i*** cycles

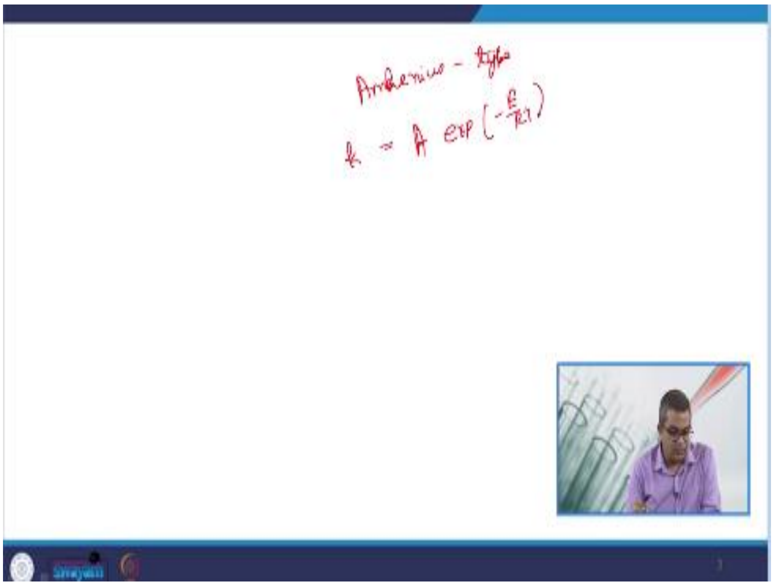
(Refer Slide Time: 05:37)



$L_i = i k_p [M]\ t_p$

$t_p \Rightarrow$ multiple dark periods in cycle.

(Refer Slide Time: 06:04)



Arrhenius - type

$k = A \exp\left(-\frac{E}{RT}\right)$

- Each of the rate constants for initiation, propagation, and termination can be expressed by an Arrhenius-type relationship:

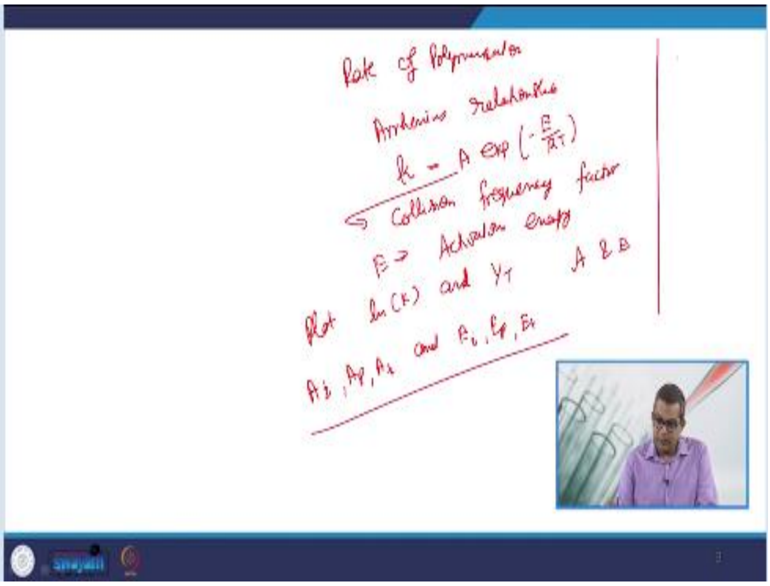
$$k = A \exp\left(-\frac{E}{RT}\right)$$

Where, A is the collision frequency factor, E is the activation energy

The plot between ln(k) and 1/T allows the determination of A and E

The related terms of A and E for initiation, propagation and termination is represented as; A_i, A_p, A_t, and E_i, E_p, E_t, respectively.

(Refer Slide Time: 06:31)



Rate of Polymerization

Arrhenius relationship

$k = A \exp\left(-\frac{E}{RT}\right)$

A → Collision frequency factor

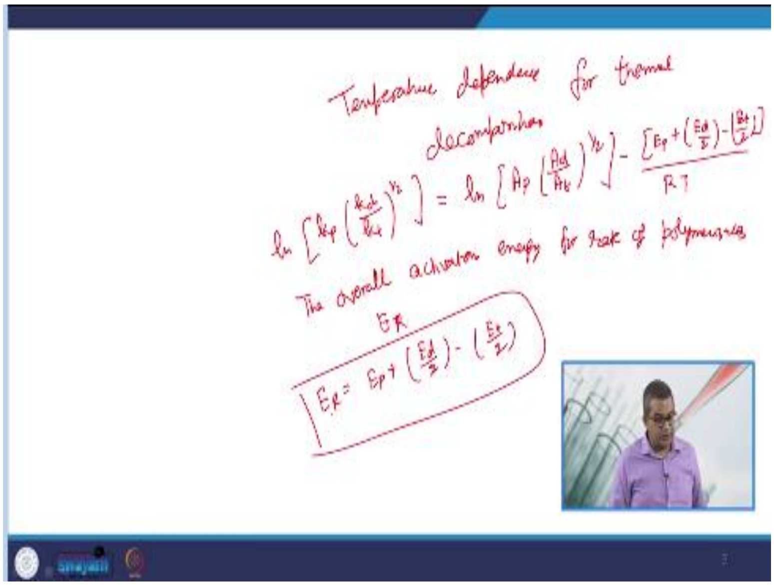
E → Activation energy

Plot ln(k) and 1/T A & E

A_d, A_p, A_t and E_d, E_p, E_t

So, if you recall that we discussed that initiation, propagation and termination.

(Refer Slide Time: 08:12)



Temperature dependence for thermal decomposition

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

The overall activation energy for rate of polymerization E_R

$\boxed{E_R = E_p + \left(\frac{E_d}{2}\right) - \left(\frac{E_t}{2}\right)}$

Now, the temperature dependence of thermal decomposition can be given by; this is the temperature difference dependence for thermal decomposition, this can be given by

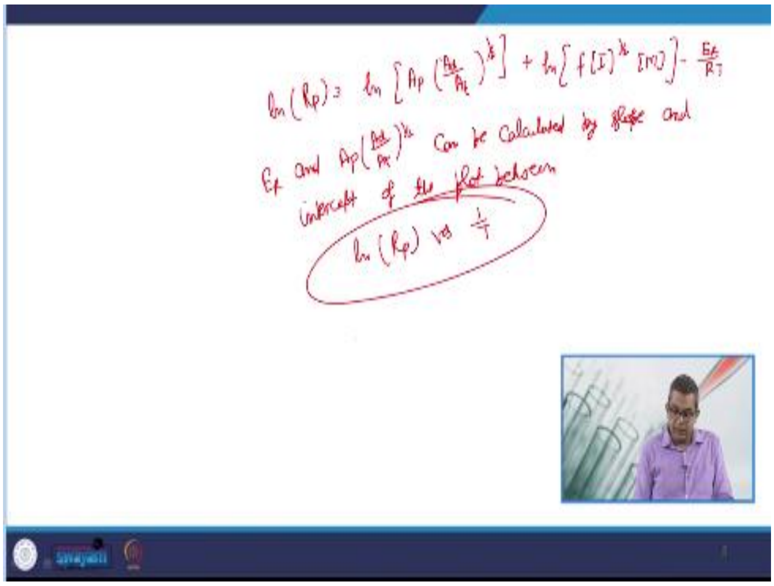
- The temperature dependence for thermal decomposition can be given as

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

The overall activation energy for rate of polymerization E_R is;

$$E_R = E_p + \left(\frac{E_d}{2}\right) - \left(\frac{E_t}{2}\right)$$

(Refer Slide Time: 10:29)



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

E_R and $A_p\left(\frac{A_d}{A_t}\right)^{1/2}$ can be calculated by slope and intercept of the plot between

$\ln(R_p)$ vs $\frac{1}{T}$

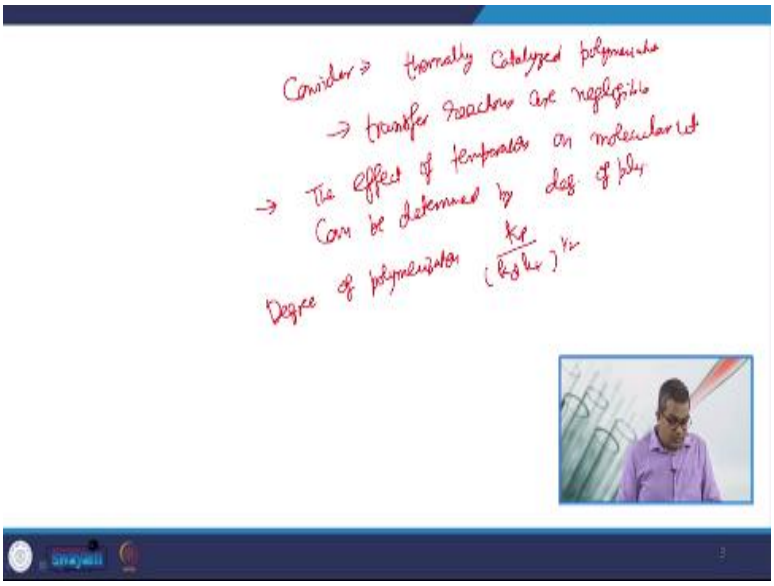
- Therefore;

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

E_R and $A_p\left(\frac{A_d}{A_t}\right)^{\frac{1}{2}}$ can be calculated by slope and intercept of the plot between $\ln(R_P)$ vs 1/T

So, this is again, this is very important factor through which you can calculate the slope and intercept of the plot. So, you need to plot these things and by this way, you can calculate the same.

(Refer Slide Time: 12:01)



Consider ⇒ thermally catalyzed polymerization

→ transfer reactions are negligible

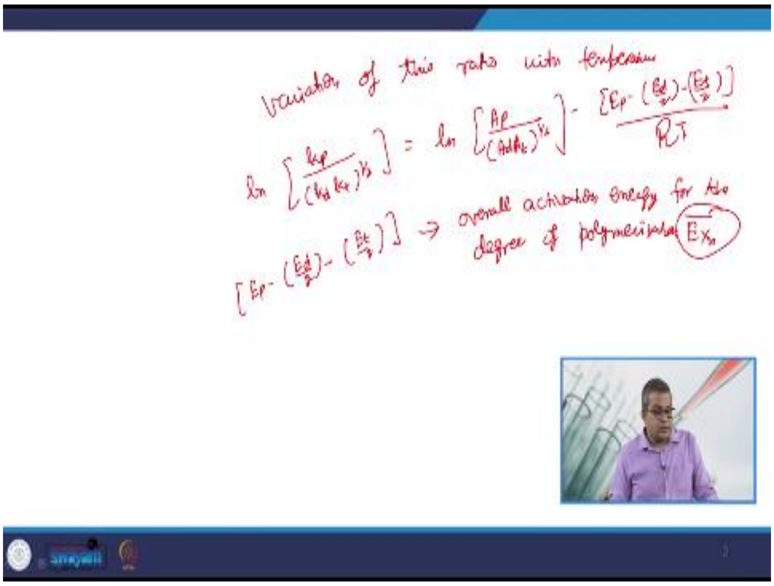
→ The effect of temperature on molecular wt can be determined by deg. of poly.

Degree of polymerization $\frac{k_p}{(k_d k_t)^{1/2}}$

- considering a thermally catalyzed polymerization where transfer reactions are negligible
- The effect of temperature on the molecular weight can be determined by using the degree of polymerization factor $\frac{k_p}{(k_d k_t)^{\frac{1}{2}}}$
- The variation of this ratio with temperature is given by:

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

(Refer Slide Time: 13:34)



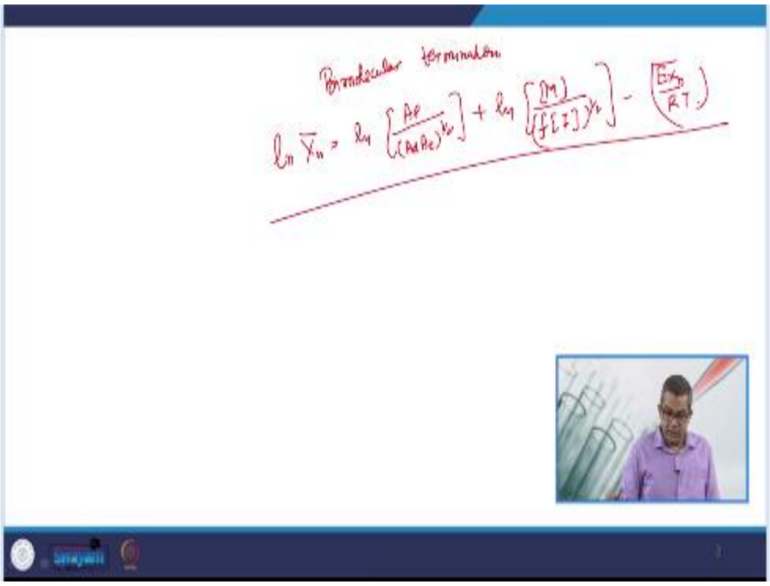
Variation of this ratio with temperature

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

$\left[E_p - \left(\frac{E_d}{2}\right) - \left(\frac{E_t}{2}\right)\right] \rightarrow$ overall activation energy for the degree of polymerization $\boxed{E_{\overline{X}_n}}$

- $\left[E_p - \left(\frac{E_d}{2}\right) - \left(\frac{E_t}{2}\right)\right]$ is the overall activation energy for the degree of polymerization $E_{\overline{X_n}}$

(Refer Slide Time: 15:35)



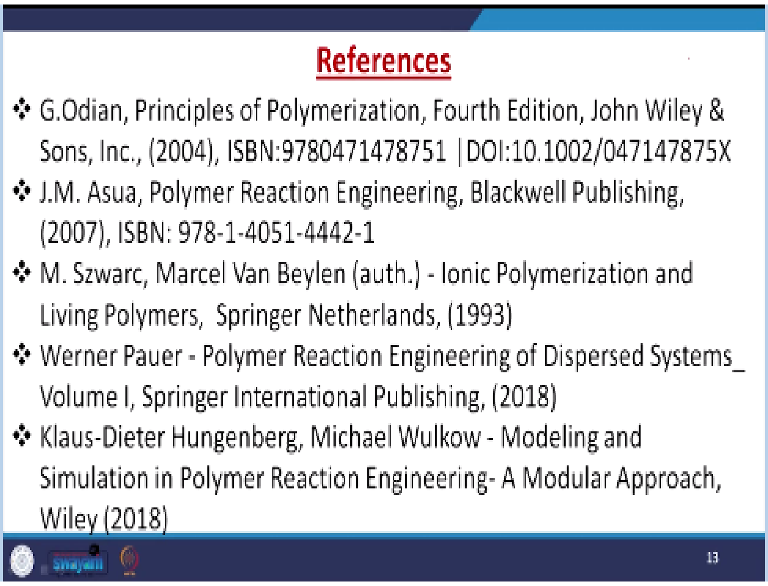
Bimolecular termination

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

- For bimolecular termination;

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

(Refer Slide Time: 16:35)



References

- G.Odian, Principles of Polymerization, Fourth Edition, John Wiley & Sons, Inc., (2004), ISBN:9780471478751 |DOI:10.1002/047147875X
- J.M. Asua, Polymer Reaction Engineering, Blackwell Publishing, (2007), ISBN: 978-1-4051-4442-1
- M. Szwarc, Marcel Van Beylen (auth.) - Ionic Polymerization and Living Polymers, Springer Netherlands, (1993)
- Werner Pauer - Polymer Reaction Engineering of Dispersed Systems_ Volume I, Springer International Publishing, (2018)
- Klaus-Dieter Hungenberg, Michael Wulkow - Modeling and Simulation in Polymer Reaction Engineering- A Modular Approach, Wiley (2018)

So, by this way, we discussed the different rate equations and we discussed the 5 different type of rate constant attributed to the all aspect of this radical chain polymerization. And in this lecture, we discussed the generation of the different other rate constants with the help of Arrhenius equation. So, in case if you have any query and other things, you may refer the different references which you have listed in this particular slide. Thank you very much.