Polymer Reaction Engineering
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Lecture – 36
Rate Expression

Welcome to the rate expression lecture under the head of radical chain polymerization. Now, this is in continuation with the previous discussion. Now, if you recall that in the previous lecture, we were discussing about the different polymerization sequences, initiation, propagation and termination. And we gave a lot of deliberations related to the importance of these initiation, propagation and termination steps.

And, we developed a couple of equations which we will utilised in this particular lecture, especially related to the the propagation and termination. And we especially, in combination or disproportionation equations will be more useful for the discussion in this particular lecture. Now, let us have a brief look that what are the topics which we are going to cover in this particular lecture.

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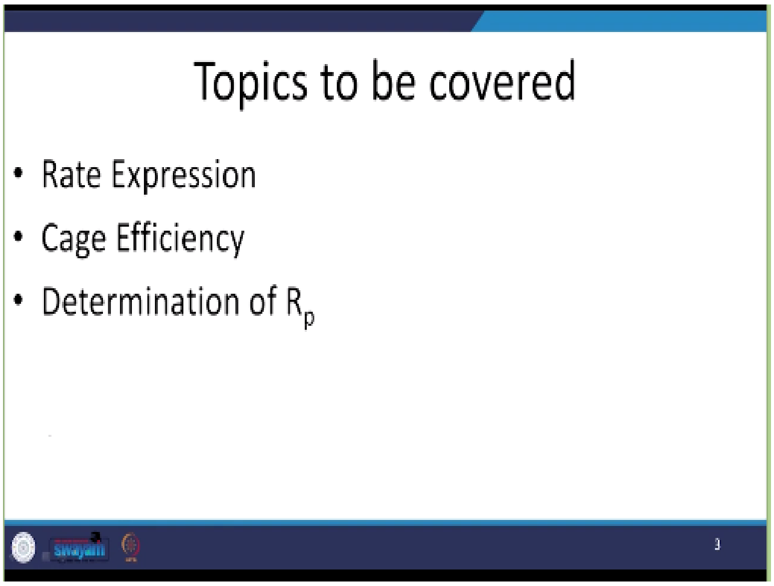

Topics to be covered

- Rate Expression
- Cage Efficiency
- Determination of R_p

we will discuss about the rate expression concepts. you know that I discussed about the rate constants in the previous lecture. then, we will discuss that how we can represent these rate expressions, then, we will discuss about the cage efficiency and we will determination of R p. Now, let us have a look about the rate expression.

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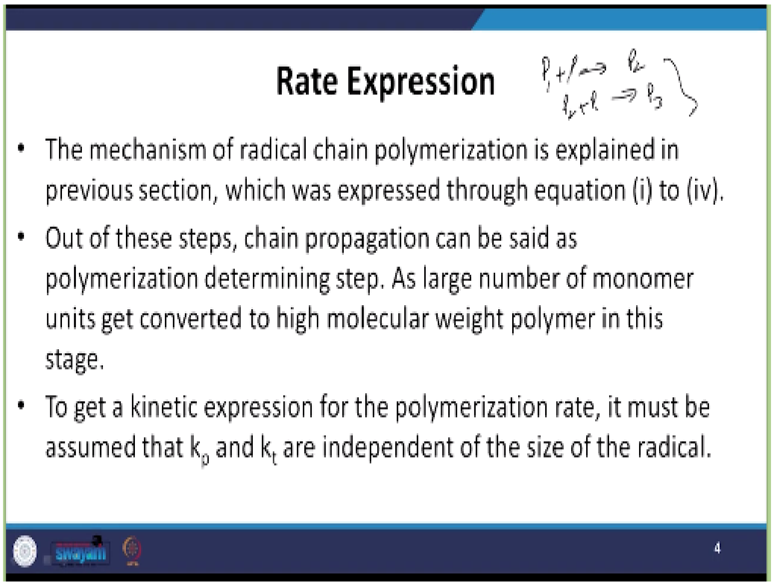

Rate Expression

$P_1 + P \to P_2$

$P_2 + P \to P_3$

- The mechanism of radical chain polymerization is explained in previous section, which was expressed through equation (i) to (iv).
- Out of these steps, chain propagation can be said as polymerization determining step. As large number of monomer units get converted to high molecular weight polymer in this stage.
- To get a kinetic expression for the polymerization rate, it must be assumed that k_p and k_t are independent of the size of the radical.

the mechanism of radical chain polymerization is usually explained in various sections, which we discussed previously. And we have expressed several equations like if you recall equation number 1 to 4 during that termination and propagation step. So, out of these steps, the chain propagation can be said as the polymerization determining step. that is a step number 2.

Now, as larger number of monomers or monomer unit they get converted into the high molecular weight polymer in this particular state. If you recall that we discussed this thing like P_1 + P when they combine to form the P_2 and then P_2 + P when they get to get P_3 and so, and so on, like this so that the molecular weight weight may have the sequential approaches.

Now, to get a kinetic expression of for the polymerization rate, it must be assumed that the k_p and k_t they are independent of the size of radical. This thing must be treated as purely an assumption.

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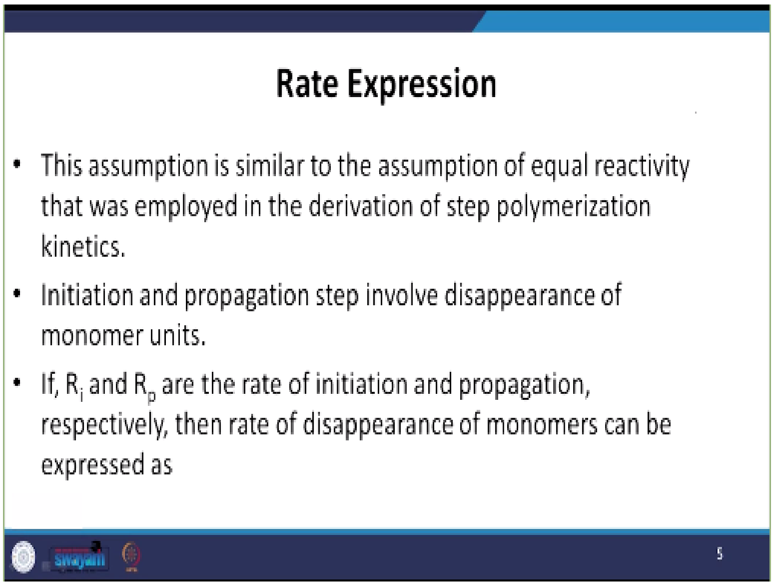

Rate Expression

- This assumption is similar to the assumption of equal reactivity that was employed in the derivation of step polymerization kinetics.
- Initiation and propagation step involve disappearance of monomer units.
- If, R_i and R_p are the rate of initiation and propagation, respectively, then rate of disappearance of monomers can be expressed as

Now, this assumption is usually similar to the assumptions of equal reactivity that was employed in the derivation of a step polymerization and kinetics which we discussed previously. Now, initiation and propagation step they involve the disappearance of monomer units, which we already discussed and in the next slide we are going to discuss. Now, if R_i and R_p they are the rate of initiation and propagation respectively, this one R_i and R_p then the rate of disappearance of a monomial we can express like this particular equation.

Rate of disappearance of monomer

$$-\frac{d(M)}{dt} = R_i + R_p \longrightarrow \textcircled{V}$$

$$R_i << R_p$$

$$-\frac{d(M)}{dt} \cong R_p \longrightarrow \textcircled{VI}$$

The rate of propagation can be expressed as

$$M + M^{\cdot} \xrightarrow{k_p} M_i^{\cdot}$$

$$R_p = K_p [M] [M^{\cdot}] \longrightarrow \textcircled{VII}$$

M = monomer concentration

$M^{\cdot}$ = total concentration of all chain radicals

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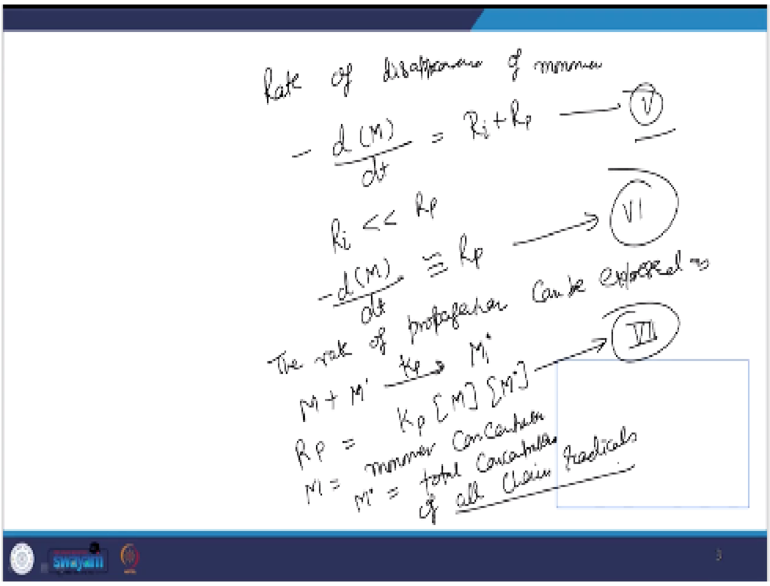

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The rate of disappearance of monomer you can represent like Ri + R p. Now, in continuation with the previous discussion, we may represent like equation number 5. Now, during the polymerization the number of monomers used in initiation is very less and when compared with the chain propagation. So, in that case we can neglect R_i. So, by this way we can put forward the things like like R_i is less than less than R_p.

And then we can write this equation like R_p let us represent like equation number 6. Now the rate of propagation the rate of propagation we can express, this one if you recall that our rate of propagation was there, this is the propagation rate constant and this one like this. So, R_p there that is the rate of propagation, it is equal to this is. This becomes the equation number 7. Now, here M is the monomer concentration and M• is the total concentration of all chain radicals.

So, this is the way through which you can tentatively represent the rate constant. Now, in this case now, this equation cannot be used directly because measurement of free radical concentration is extremely difficult or as it is available in a very less quantity. Therefore, M radical or M• needs to be replaced in this equation number 7. Now to achieve this another assumption is to be taken that initially the radical concentration increases and almost instantly instantantly it gains a constant value.

So, it can be said said that polymerization occurs at a steady state. The radical concentration from initiation to termination stage can be considered as constant. Now, let us have a look about this particular approach.

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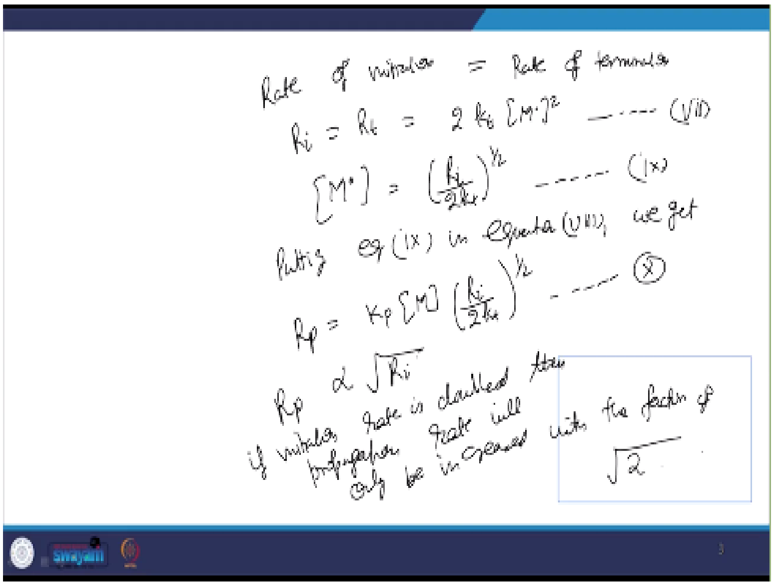

Rate of initiation = Rate of termination

$R_i = R_t = 2k_t[M\cdot]^2$ ------ (VIII)

$[M^\circ] = \left(\frac{R_i}{2k_t}\right)^{1/2}$ ------ (IX)

Putting eq (IX) in equation (VIII), we get

$R_p = K_p[M]\left(\frac{R_i}{2k_t}\right)^{1/2}$ ------ (X)

$R_p \propto \sqrt{R_i}$

if initiation rate is doubled then propagation rate will only be increased with the factor of $\sqrt{2}$.

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So, the rate of initiation let us assume that it is equal to the rate of termination. So, R_i is equal to R_t or $2k_t$. This may be represented as equation number 8. Or $M\bullet$ is equal to, now, putting the equation we may put equation 9 in equation number 8. So, we get R_p is equal to k_p, this is equation number 10. Now, from this equation, we can conclude that our rate of propagation reaction is proportional to rate of initiation.

So, if initiation rate is doubled then propagation rate will only be increased with the factor of. So, this is again a very good phenomenon.

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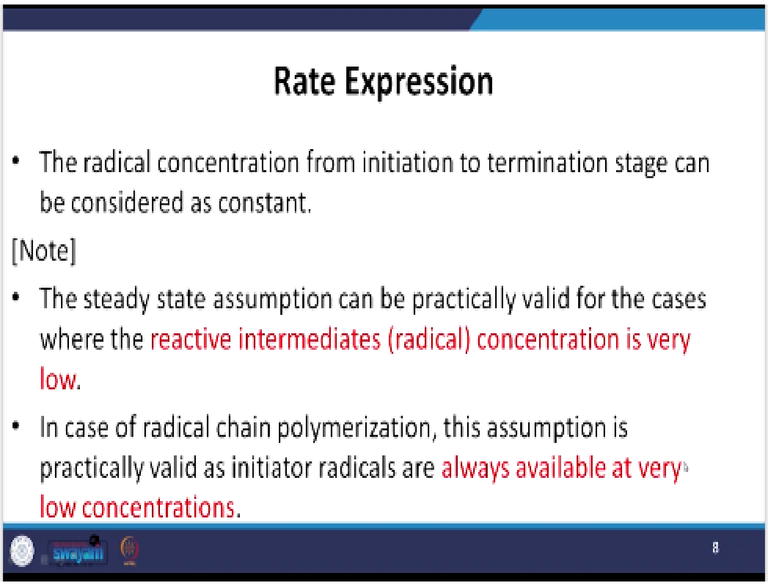

Rate Expression

- The radical concentration from initiation to termination stage can be considered as constant.

[Note]

- The steady state assumption can be practically valid for the cases where the reactive intermediates (radical) concentration is very low.
- In case of radical chain polymerization, this assumption is practically valid as initiator radicals are always available at very low concentrations.

Now, the steady state assumptions which we are using is can be practically valid for the cases where the reactive intermediates or radical concentration is very low. Now, in case of radical chain polymerization, this particular assumption is practically valid as initiator radicals are always available at a very low concentration. Now, the steady state assumption for several polymerization reaction has also been experimentally validated the various researchers.

So, after a period of time, standard polymerization reaches at steady state which can be at most one minute or sometimes it is less than one minute. Now, there is no definition as to whether termination is by coupling or disproportionation reaction as both obey the same type of kinetics and the particular reaction form. Now, sometimes the use of factor 2 in the termination rate equation, this follows that the convention widely accepted for the reaction, which usually kill the radicals in pair, it is due to the fact that radical being produced in pairs.

this convention is also preferred by IUPAC System while using the polymer literature. It should be noted that equation of 2 was always or sometimes not always been adopted. Now, dependence of polymerization rate on a square root which we discussed in the previous slide, square root of the initiation rate has an important conclusion. Now, the reason behind for such a slower increase in propagation reaction, it can usually be explained in various ways.

When initiated radicals, they are produced in a higher amount, it may give rise to the concentration of free radicals inside the reaction system. As entropy of the system decreases, which results in decrease in free energy barrier and that attributed to the Gibbs free energy. Now, this decrements lead to the rise of biomolecular reaction between the free radicals. Hence, most of the free radical get terminated within a short span of time.

Now, let us have a look about the cage efficiency. Now, the first assumption while deriving the rate of propagation, that that is which we developed in this equation, which if you see that this equation number 10, which can be rearranged into the different form.

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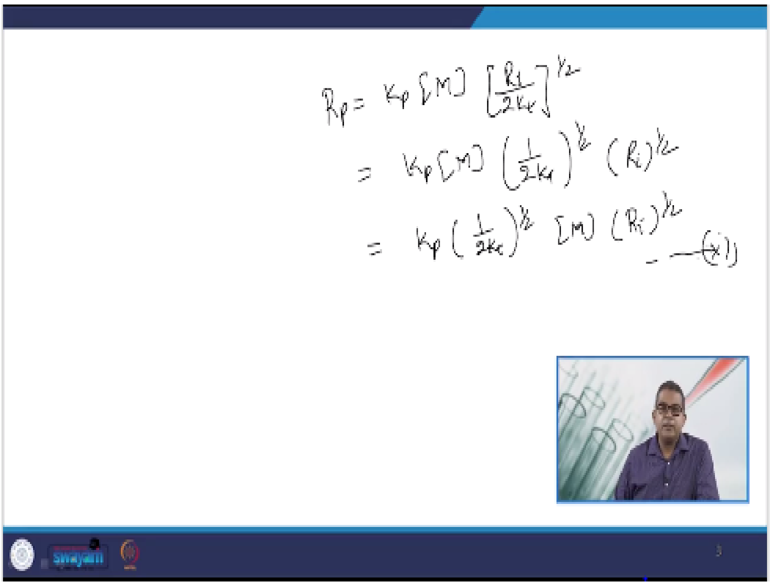

That is R p R i upon. Or this is the 1 up on 2k t, the rate of initiation. Or this is 1 upon 2k t half. This is the question number 11.

$$R_p = K_p[M]\left[\frac{R_i}{2K_t}\right]^{1/2}$$

$$= K_p[M]\left(\frac{1}{2K_t}\right)^{1/2}(R_i)^{1/2}$$

$$= K_p\left(\frac{1}{2K_t}\right)^{1/2}[M](R_i)^{1/2} \quad \text{---} (11)$$

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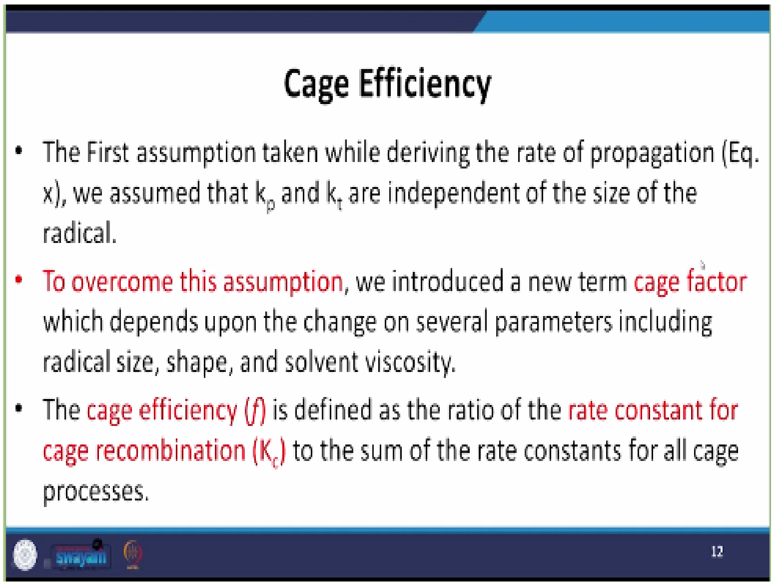

Cage Efficiency

- The First assumption taken while deriving the rate of propagation (Eq. x), we assumed that k_p and k_t are independent of the size of the radical.
- To overcome this assumption, we introduced a new term cage factor which depends upon the change on several parameters including radical size, shape, and solvent viscosity.
- The cage efficiency (*f*) is defined as the ratio of the rate constant for cage recombination (K_c) to the sum of the rate constants for all cage processes.

Now, if you see the equation number 10 we assume that the rate constant of propagation and rate constant of termination are independent of the size of the radical. Now, because we have taken the assumption and to be things to make the things more realistic in nature, we need to overcome these assumptions. So, to overcome these assumptions, we introduced a new term that is called the cage factor.

Now, this cage factor depends upon the change on several parameters including the radical size, shape, sometimes solvent viscosity, etcetera. And the cage efficiency sometimes referred as "*f*" is defined as the ratio of rate constant for cage combination, that is referred as K_c to the sum of rate constant of all cage processes. So, this K_c is usually the sum of rate constants for all cage processes.

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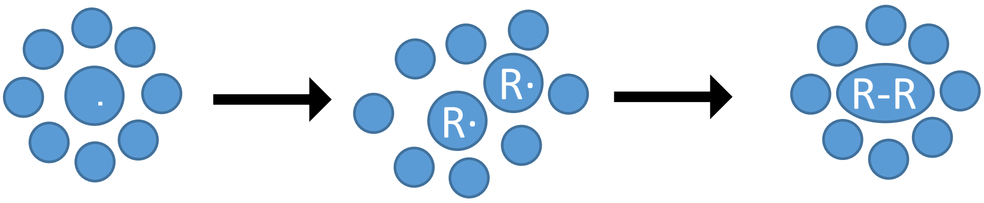
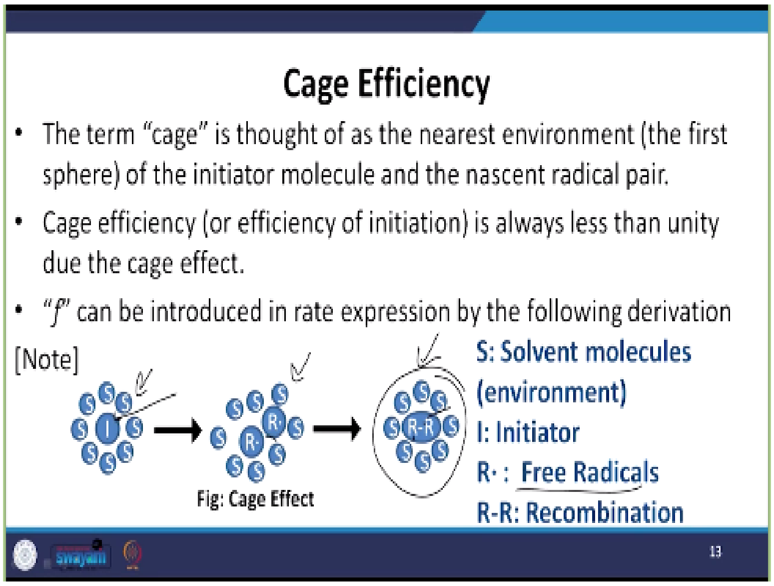


Fig: Cage Effect

S: Solvent molecules (environment)
I: Initiator
R· : Free Radicals



Cage Efficiency

- The term "cage" is thought of as the nearest environment (the first sphere) of the initiator molecule and the nascent radical pair.
- Cage efficiency (or efficiency of initiation) is always less than unity due the cage effect.
- "*f*" can be introduced in rate expression by the following derivation

[Note]

Fig: Cage Effect

S: Solvent molecules (environment)
I: Initiator
R· : Free Radicals
R-R: Recombination

Now, the term cage is thought of as the nearest environment the first sphere of the initiator molecule and the nascent radical pair. See, whenever we talk about the initiator molecule, it may be surrounded by various things like nascent radical pair, sometimes it may be surrounded by the polymer chain if it is survived in due course of time. So, the cage efficiency or efficiency of initiation sometimes it is referred as the efficiency of initiation is always less than unity due to the cage effect.

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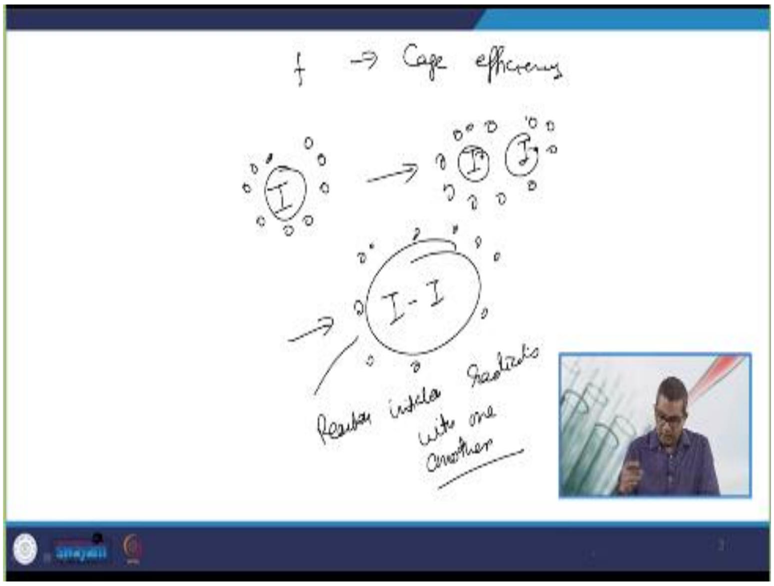

Now, *f* this can be introduced in the rate expression, we can look at things like this. Now, if we denote *f* as the cage efficiency and recall that it is defined as the ratio of the rate constant for cage recombination k_c and the sum of the rate constant for all case proportions. So, we are having, this is the initiator molecule. Now, you see here. Now, this is a reaction of initiation radicals with one another.

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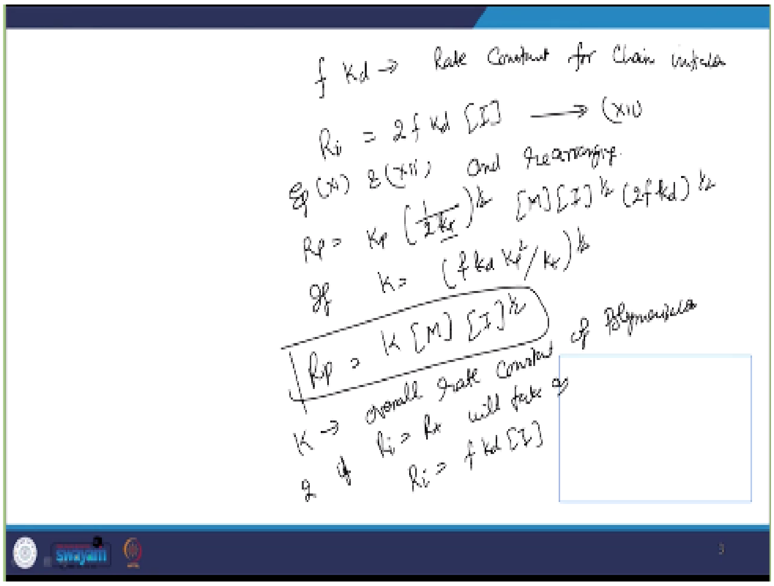


f Kd → Rate Constant for Chain initiator

$R_i = 2 f K_d [I] \longrightarrow$ (XII)

Eq (XI) & (XII) and rearranging.

$R_p = K_p \left(\frac{1}{2K_t}\right)^{1/2} [M][I]^{1/2} (2 f K_d)^{1/2}$

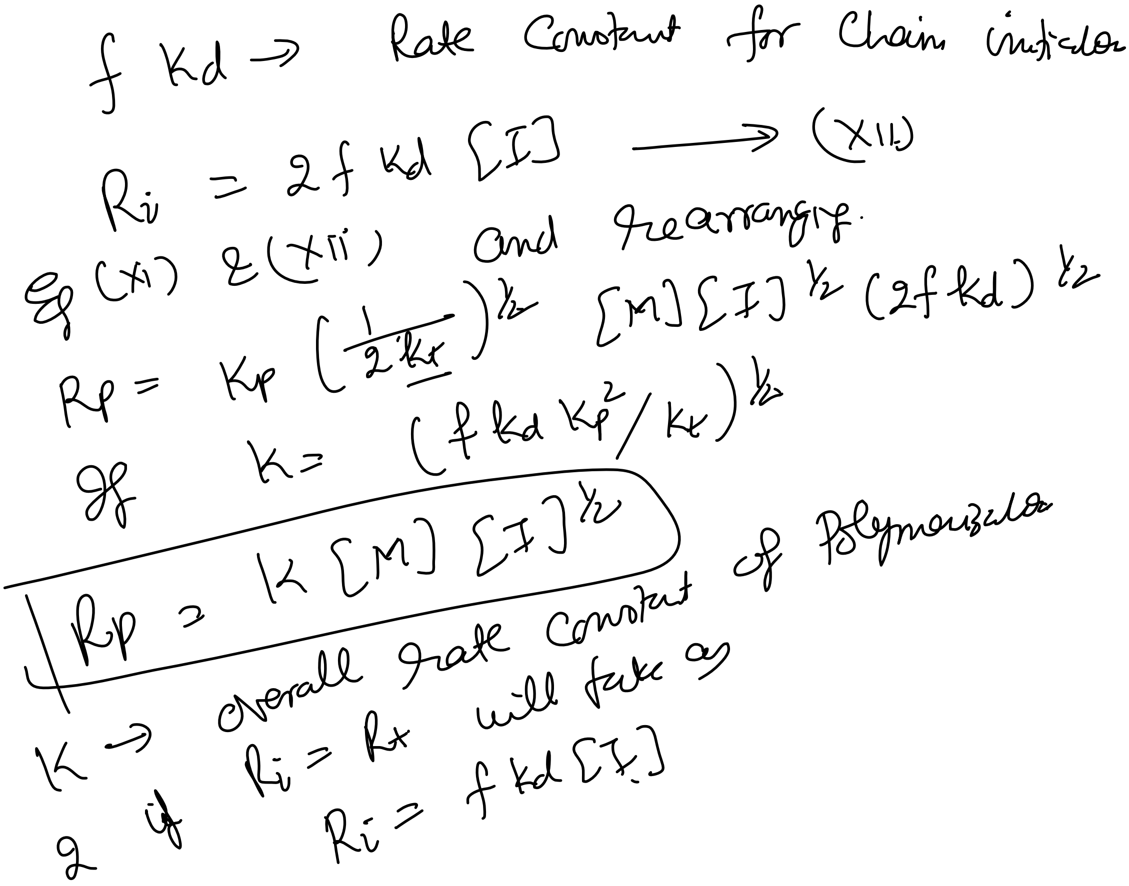
If $K = (f K_d K_p^2 / K_t)^{1/2}$

$\boxed{R_p = K [M][I]^{1/2}}$

K → overall rate constant of polymerization

if $R_i = R_t$ will take as

2 if $R_i = f K_d [I]$



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2 if $R_i = f K_d [I]$

So, the rate constant for the chain initiation can be written as fk d, this is the rate constant for chain initiation. So, $R_i = 2f K_d$ like this, this is equation number 12. Now, if we combine that equation 11 and equation 12 and re arranging then we may have $R_p = K_p$ that is the rate constant under the propagation head upon $2k_t^{1/2}$. This is the rate constant of termination.

Now, if k is equal $(2fk_dk_p^2)^{1/2}/K_t$, then R_p is equal to K M $I^{1/2}$. Now K is called the overall rate constant of polymerization. Now, the value of K is taken differently from different literature It can also be multiplied with the 2 with if R_i is equal to R_t. will take as R_i is equal to fk_dI.

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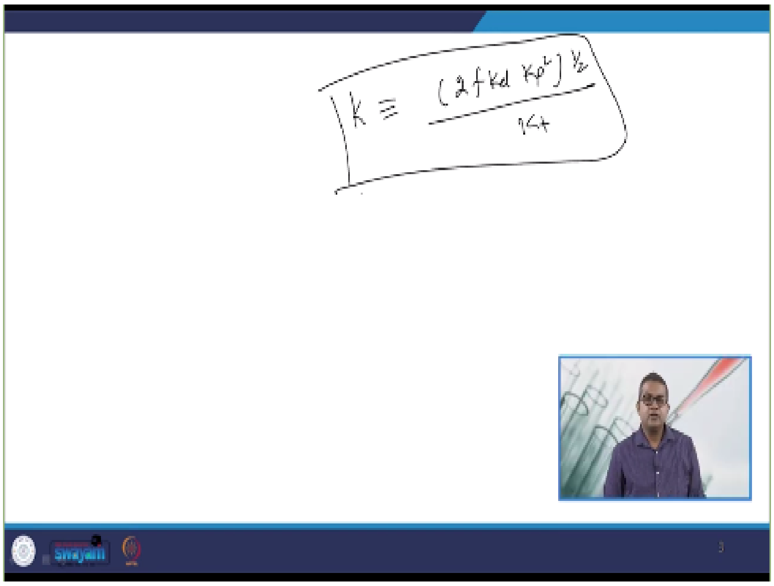

$$k = \frac{(2 f k_d k_p^2)^{1/2}}{k_t}$$

Then K is equal to $2fk_d/k_t$. So, this is the generalised equation which you can see that is represents the rate constant. Now, this is the pictorial diagram, which we are discussing about. Now, here this is the initiator and you see that the solvent molecules they are surrounded and you see that, this gauge efficiency is represented by this one. Now, R represents the free radicals and R-R is the recombination and I is the initiator. So, this is the pictorial diagram to represent the things.

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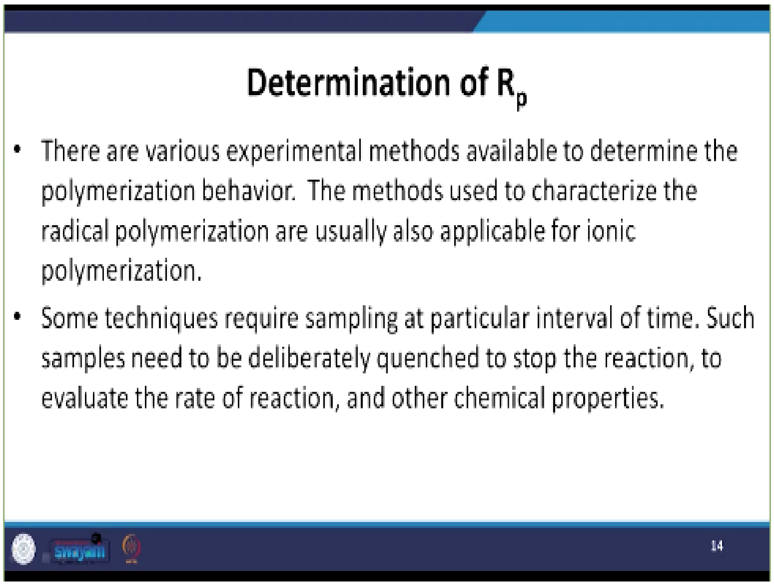

Determination of R_p

- There are various experimental methods available to determine the polymerization behavior. The methods used to characterize the radical polymerization are usually also applicable for ionic polymerization.
- Some techniques require sampling at particular interval of time. Such samples need to be deliberately quenched to stop the reaction, to evaluate the rate of reaction, and other chemical properties.

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We have already discussed this the rate constant for the propagation steps and there are various experimental methods available as on date to determine the polymerization behaviour. the methods used to characterise the radical polymerization are also applicable for ionic polymerization. Some techniques they require sampling at a particular interval of time. Such samples need to be deliberately quenched to stop the reaction to evaluate the rate of reaction and other chemical properties.

And sometimes to evaluate the by-products whatever developed in due course of time. However, there are some new and advanced tools available for which helps them continuously monitoring the experiment and obtaining the better results. Most of these characterization techniques, they are usually same for analysing the step growth polymerization.

We for the ease of the listener and ease of use some of these methods which we are going to apply in the determination of this rate constant for propagation step we are going to discuss here. One thing is that the physical separation and isolation, they usually in this category, because it is very important to know that efficacy of the polymerization process. So, in this case, the samples usually taken out from the polymerization reaction system for a particular interval of time.

And then the samples are usually isolated, followed by drying, weighing etc, this is the usual protocol. And the isolation is usually performed through the precipitation technique, which requires addition of some non-solvents. Now, this particular technique is very useful for chain polymerization reaction containing monomer and high molecular weight polymers. now, however, delicates of step polymerization sample, it contains various low molecule products like as an intermediate or a co product or by-product etcetera, whose solubility differences nearly similar has this technique.

These techniques cannot be applied for such type of a system. Moreover, this process is time consuming and require a great care, but is found to be the cost effective and then other methods applicable as on date or available as on date. Another thing is attributed to the chemical and spectroscopic analysis. For example, vinyl monomer, the titration of the unreacted double bond molecule using the bromine. This can be useful to determine the rate of propagation in a particular interval of time.

Spectroscopically an increase in absorption signals suggest that the formation of polymer. So, various devices like infrared, ultraviolet, NMR among other, they are widely used for this purpose. Now, due to advantages of including the continuous monitoring and better efficiency, these devices or these tools are widely applicable in such type of polymerization characterization.

Now, certain substance they play a very vital role in inhibition and retardation of a polymerization process. So, these substances if they are present in the reaction system suppresses the polymerization reaction by neutralising the radical species or by decreasing the reactivity of the propagating radicals to load to undergo propagation. So, as per the effectiveness of substance, it can be divided into 2 parts, one is inhibitors, another one is the retarders.

So, let us have a brief look about these 2 subsets. Inhibitors, they stop each radical and halt the propagation step until the radicals are being consumed in due course of time. One best example of this particular approach is benzoquinone. There are certain retarders, they are less reactive compounds and which partially stops the reaction. The best example they are the nitrobenzene.

So, impurities sometimes the impurities various impurities may present in the monomer or sometimes solvent they can act as suppressor. So, these compounds are having some commercial uses, therefore, they are having more and more importance. So, reaction inhibitors are added to monomer to avert the premature thermal polymerization during the transportation, sometimes storage sometimes in the delivery concepts etc.

So, either these inhibitors, they are removed before the polymerization or additional initiator is usually provided to compensate this effect so that they can compensate they can even suppress the involvement of these inhibitors in the reaction mass. Now, the inhibition reaction with the inhibitors or retarders they can be written like this.

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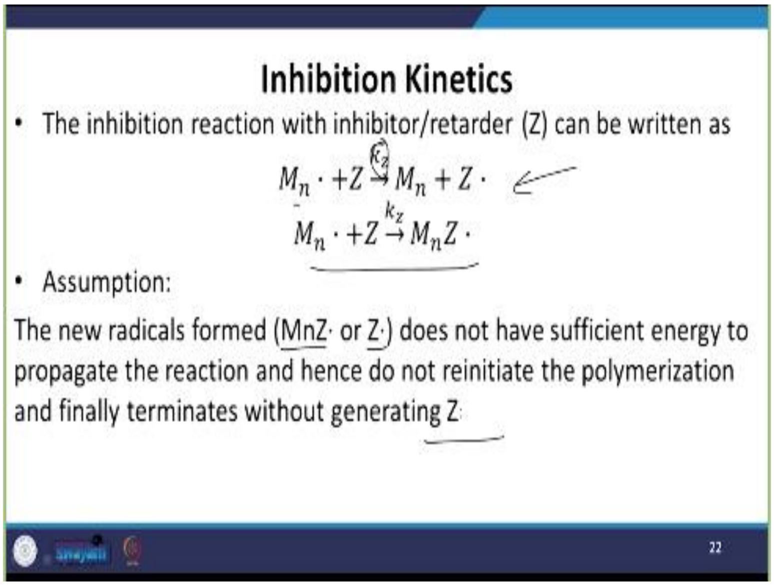

Inhibition Kinetics

- The inhibition reaction with inhibitor/retarder (Z) can be written as

$$M_n \cdot + Z \xrightarrow{k_z} M_n + Z \cdot$$

$$M_n \cdot + Z \xrightarrow{k_z} M_n Z \cdot$$

- Assumption:

The new radicals formed (MnZ· or Z·) does not have sufficient energy to propagate the reaction and hence do not reinitiate the polymerization and finally terminates without generating Z·

$$M_n \cdot + Z \xrightarrow{k_z} M_n + Z \cdot$$

$$M_n \cdot + Z \xrightarrow{k_z} M_n Z \cdot$$

M n + Z that is this inhibition rate constant M n + Z • that is the Z radical and then it gives the things. Now the new radical you see that the new radicals they are formed M n Z radical or Z radical, they does not have sufficient energy to propagate the reaction. Hence, they do not re initiate the polymerization and finally terminates without generating substantial Z in due course of time.

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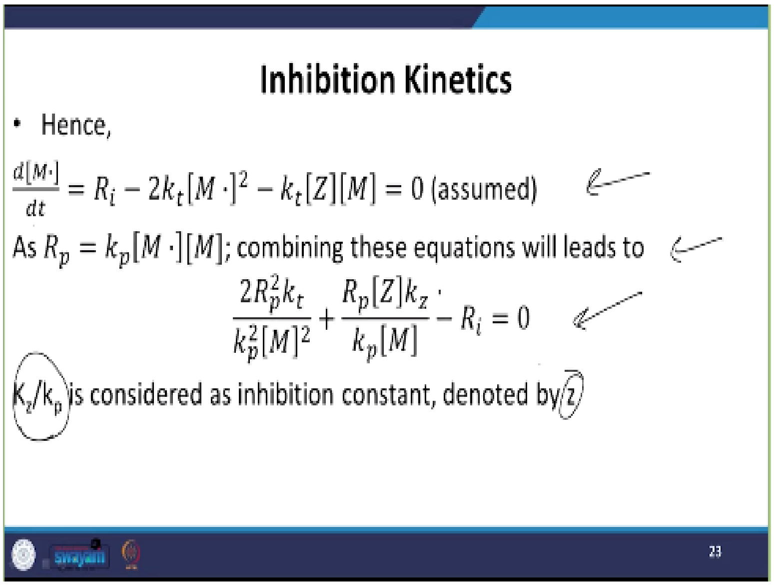

Inhibition Kinetics

- Hence,

$$\frac{d[M\cdot]}{dt} = R_i - 2k_t[M\cdot]^2 - k_t[Z][M] = 0 \text{ (assumed)}$$

As $R_p = k_p[M\cdot][M]$; combining these equations will leads to

$$\frac{2R_p^2 k_t}{k_p^2[M]^2} + \frac{R_p[Z]k_z}{k_p[M]} - R_i = 0$$

K_z/k_p is considered as inhibition constant, denoted by z

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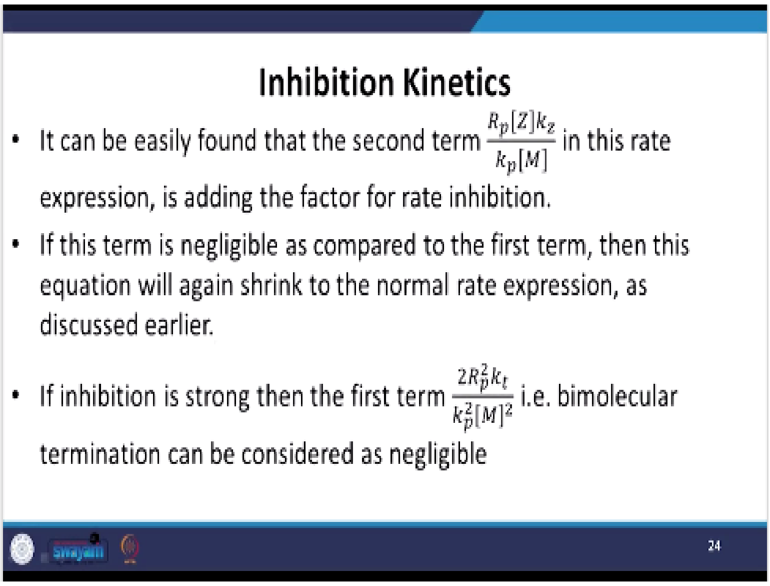

Inhibition Kinetics

- It can be easily found that the second term $\frac{R_p[Z]k_z}{k_p[M]}$ in this rate expression, is adding the factor for rate inhibition.
- If this term is negligible as compared to the first term, then this equation will again shrink to the normal rate expression, as discussed earlier.
- If inhibition is strong then the first term $\frac{2R_p^2k_t}{k_p^2[M]^2}$ i.e. bimolecular termination can be considered as negligible

Now, you can easily found that the second term this one second term ($\frac{R_p[Z]k_z}{k_p[M]}$) in this rate expression is adding the factor of rate of inhibition. Now, if this term is negligible as compared to the first one, this one then this equation will again shrink to normal rate expression as we discussed priorly. Now, for inhibition, if this inhibition is stronger than this first term ($\frac{2R_p^2k_t}{k_p^2[M]^2}$) that is a biomolecular termination can be considered as negligible. So, this is foremost thing that you need to consider while designing such kind of kinetics.

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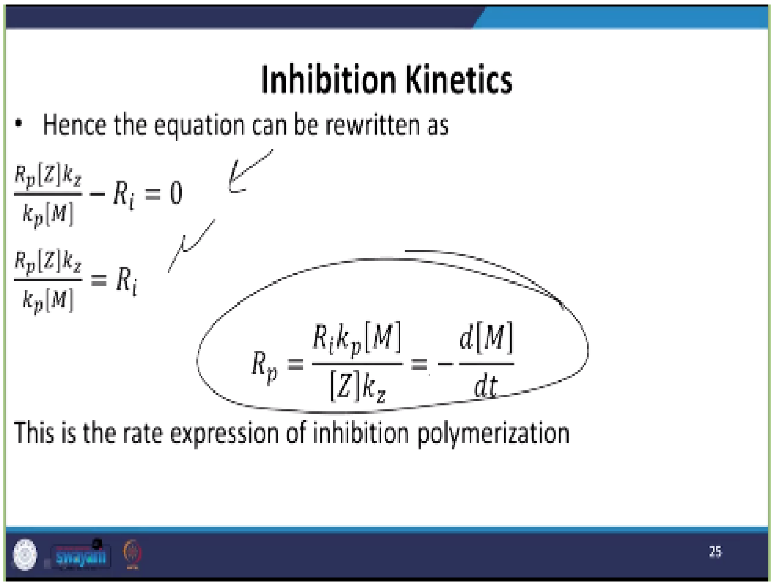

Inhibition Kinetics

- Hence the equation can be rewritten as

$$\frac{R_p[Z]k_z}{k_p[M]} - R_i = 0$$

$$\frac{R_p[Z]k_z}{k_p[M]} = R_i$$

$$R_p = \frac{R_i k_p[M]}{[Z]k_z} = -\frac{d[M]}{dt}$$

This is the rate expression of inhibition polymerization

So, we can write the equation like this.

$$\frac{R_p[Z]k_z}{k_p[M]} - R_i = 0$$

$$\frac{R_p[Z]k_z}{k_p[M]} = R_i$$

So, R_p is the rate expression for the inhibition polymerization can be represented as

$$R_p = \frac{R_i k_p[M]}{[Z]k_z} = -\frac{d[M]}{dt}$$

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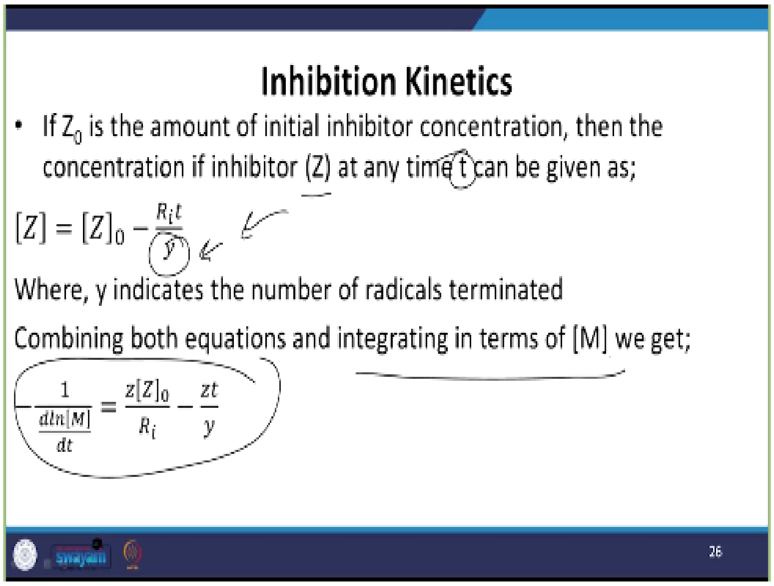

Inhibition Kinetics

- If Z_0 is the amount of initial inhibitor concentration, then the concentration if inhibitor (Z) at any time t can be given as;

$$[Z] = [Z]_0 - \frac{R_i t}{y}$$

Where, y indicates the number of radicals terminated

Combining both equations and integrating in terms of [M] we get;

$$-\frac{1}{\frac{d\ln[M]}{dt}} = \frac{z[Z]_0}{R_i} - \frac{zt}{y}$$

Now, if Z_0 is the amount of initial inhibitor concentration, then the concentration of inhibitors Z at any time t can be given as

$$[Z] = [Z]_0 - \frac{R_i t}{y}$$

Now, this indicates the number of radicals terminated and combining both the equation if we combine both the equation then we may have this equation into the picture after integrating in terms of concentration of M.

$$-\frac{1}{\frac{dln[M]}{dt}} = \frac{z[Z]_0}{R_i} - \frac{zt}{y}$$

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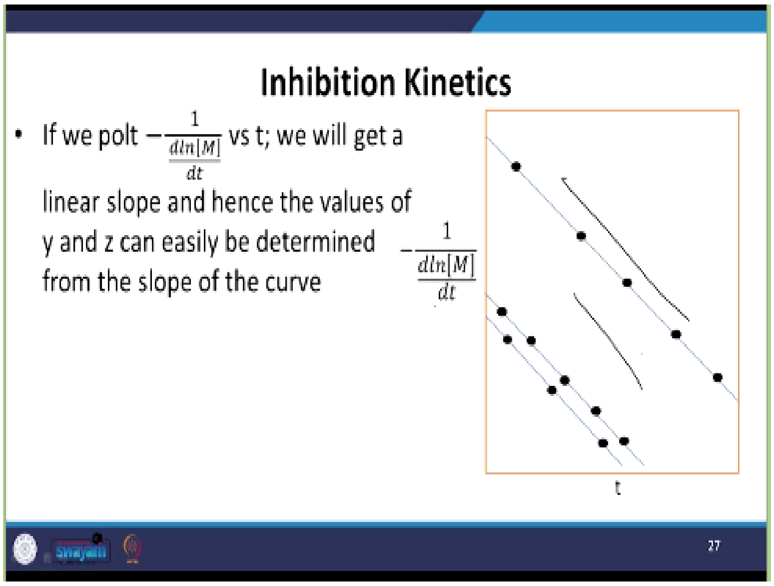
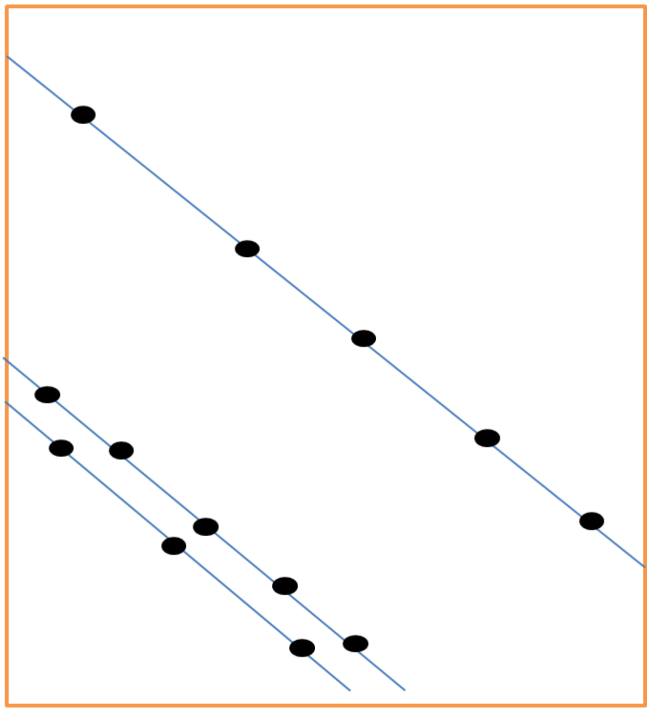


Inhibition Kinetics

- If we polt $-\frac{1}{\frac{dln[M]}{dt}}$ vs t; we will get a linear slope and hence the values of y and z can easily be determined from the slope of the curve

Now, sometimes if we plot this $-\frac{1}{\frac{dln[M]}{dt}}$ vs t, so, we get a linear slope. You see, linear slope has the value of y and Z, you can easily determine from the slope of the curve.

$$-\frac{1}{\frac{dln[M]}{dt}}$$



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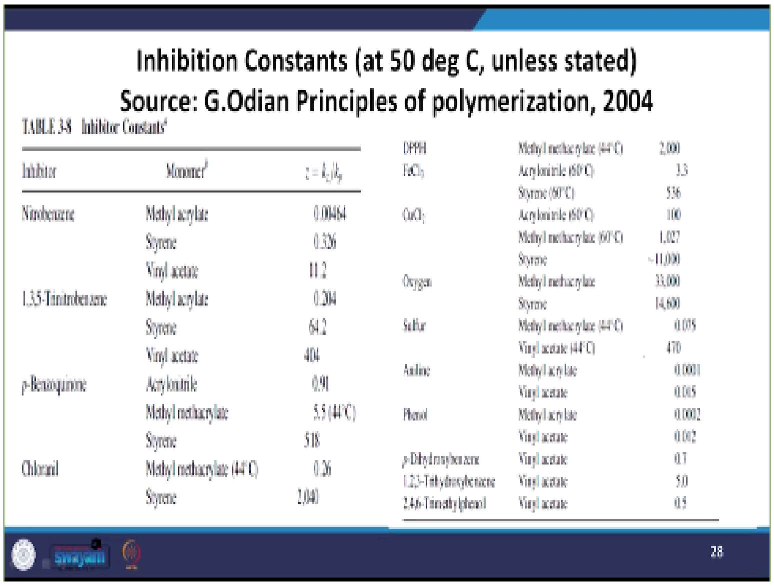

Inhibition Constants (at 50 deg C, unless stated)

Source: G.Odian Principles of polymerization, 2004

TABLE 3-8 Inhibitor Constants[a]

Inhibitor	Monomer[b]	$z = k_z/k_p$
Nitrobenzene	Methyl acrylate	0.00464
	Styrene	0.326
	Vinyl acetate	11.2
1,3,5-Trinitrobenzene	Methyl acrylate	0.204
	Styrene	64.2
	Vinyl acetate	404
p-Benzoquinone	Acrylonitrile	0.91
	Methyl methacrylate	5.5 (44°C)
	Styrene	518
Chloranil	Methyl methacrylate (44°C)	0.26
	Styrene	2,040
DPPH	Methyl methacrylate (44°C)	2,000
$FeCl_3$	Acrylonitrile (60°C)	3.3
	Styrene (60°C)	536
$CuCl_2$	Acrylonitrile (60°C)	100
	Methyl methacrylate (60°C)	1,027
	Styrene	~11,000
Oxygen	Methyl methacrylate	33,000
	Styrene	14,600
Sulfur	Methyl methacrylate (44°C)	0.075
	Vinyl acetate (44°C)	470
Aniline	Methyl acrylate	0.0001
	Vinyl acetate	0.015
Phenol	Methyl acrylate	0.0002
	Vinyl acetate	0.012
p-Dihydroxybenzene	Vinyl acetate	0.7
1,2,3-Trihydroxybenzene	Vinyl acetate	5.0
2,4,6-Trimethylphenol	Vinyl acetate	0.5

Now, George Odian has calculated several inhibition constants at 50 degree Celsius or sometimes he stated the things. If you see this particular table represents his findings and the detail is steady.

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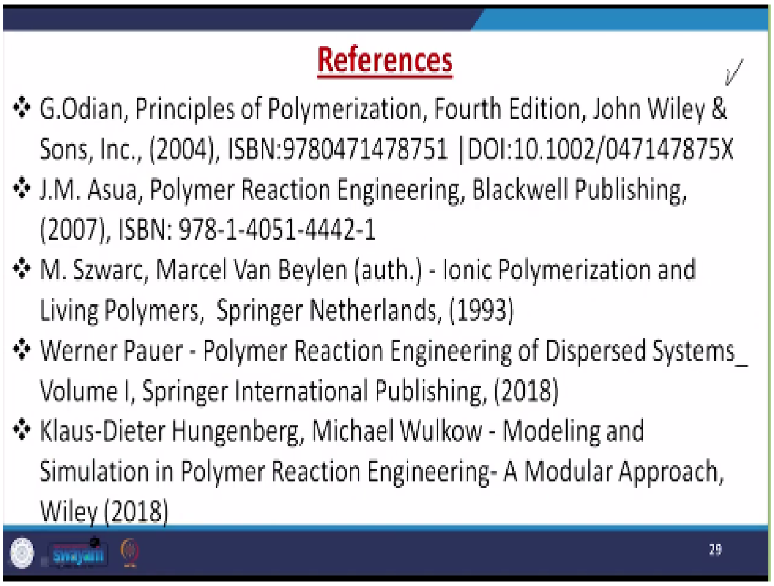

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- J.M. Asua, Polymer Reaction Engineering, Blackwell Publishing, (2007), ISBN: 978-1-4051-4442-1
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You can have in the literature which we have enlisted especially this particular book is extremely important. So, in this particular chapter, we have discussed about the rate kinetics and rate of a reaction for different steps whether it is initiation, propagation and termination and if you wish to have further study in this particular thing, we have already enlisted 4, 5 different references for the future reading. By this way, we are summing up this particular lecture. Thank you very much.