Polymer Reaction Engineering
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Lecture – 39
Radical Chain Polymerization Half Life, Propagation and Termination – I

Welcome to the next lecture of half life, propagation and termination step of radical chain polymerization. So, if you recall that previously we studied about the concept of precipitation of polymer.

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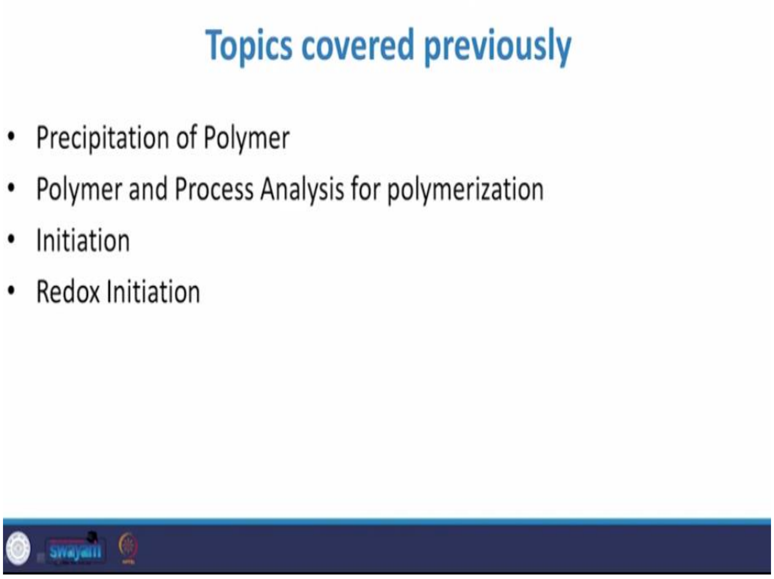

Topics covered previously

- Precipitation of Polymer
- Polymer and Process Analysis for polymerization
- Initiation
- Redox Initiation

Then, we discussed about the polymer and different type of approaches attributed to the process analysis of polymerization process. And then we discussed about the initiation part. Then we discussed briefly about the redox initiation especially we gave major emphasis to the redox initiation.

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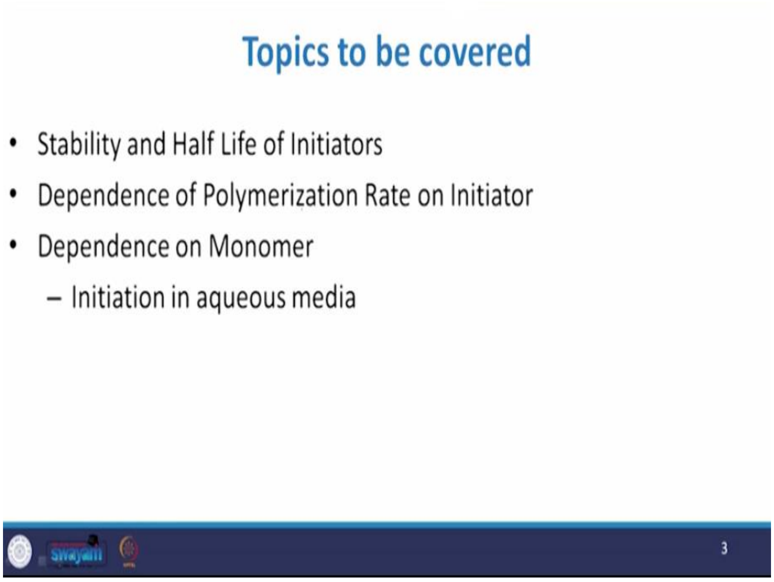

Topics to be covered

- Stability and Half Life of Initiators
- Dependence of Polymerization Rate on Initiator
- Dependence on Monomer
  - Initiation in aqueous media

Now, in this particular chapter, we are going to discuss about the stability and half life of initiator. Now, this is a very important concept of initiator, because we cannot overlook the importance of initiator in any kind of polymerization reaction. So, the stability and half life time of the initiator is very important. We will discuss about the dependency of polymerization rate on initiator. Again, this is the mathematical approach.

Then we will discuss about the dependency of those initiator on monomer. That is initiation, either aqueous media.

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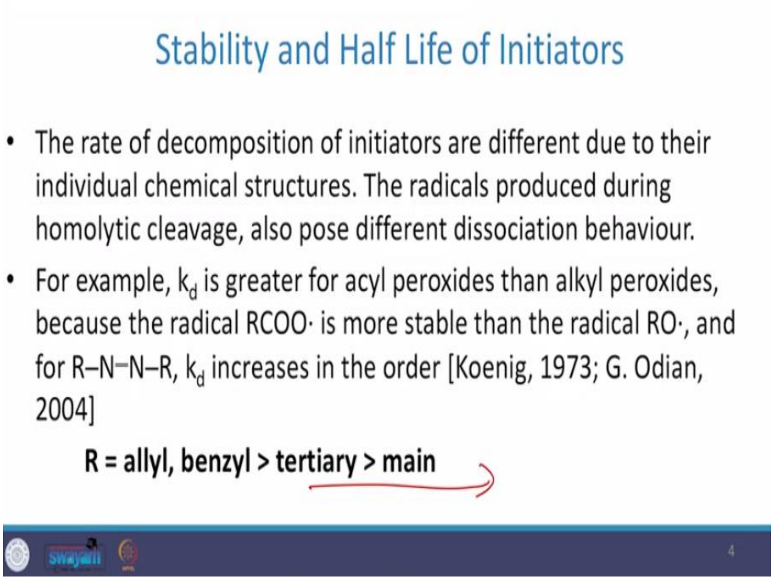

Stability and Half Life of Initiators

- The rate of decomposition of initiators are different due to their individual chemical structures. The radicals produced during homolytic cleavage, also pose different dissociation behaviour.
- For example, k_d is greater for acyl peroxides than alkyl peroxides, because the radical RCOO· is more stable than the radical RO·, and for R–N=N–R, k_d increases in the order [Koenig, 1973; G. Odian, 2004]

  R = allyl, benzyl > tertiary > main

So, let us start with the stability and half life of initiator. Since, we discussed about the decomposition concept of initiator and this particular decomposition concept is very much important in while discussing this stability in half life period of initiator. Now, the rate of decomposition of initiator usually they are different due to their individual chemical structure. If you recall in the previous lecture, we discussed about various initiators.

And In-situ A gave you information about the structure of those initiator. So, the radicle produced during the homolytic cleavage also posed a different dissociation behaviour. And if you recall that we discussed about the rate of dissociation of those initiator also. So, when we talk about the rate of dissociation or dissociation rate constant k d, this k d is greater for acyl peroxide than alkyl peroxide.

Now, because the radical RCOO is more stable than the radical RO and for R N NR this k d is increases in the order. And this was very much particular analysis is very much being carried out by Odian and Koenig. Now, here R stands for alkyl, benzoyl and tertiary. So, if you see the increasing order, you can find it out this place.

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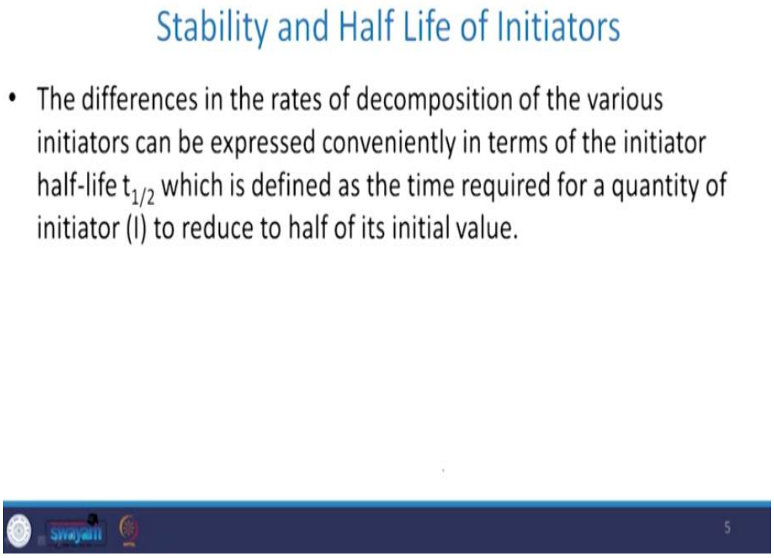

Stability and Half Life of Initiators

- The differences in the rates of decomposition of the various initiators can be expressed conveniently in terms of the initiator half-life $t_{1/2}$ which is defined as the time required for a quantity of initiator (I) to reduce to half of its initial value.

Now, the differences in the rate of decomposition of various initiators this can be expressed conveniently in terms of initiator half life. And sometimes referred as t half, which is in a broad spectrum defined as the time required for a quantity of initiator I to reduce to half of its initial value. So, this is the half life time it attributed to the time factor.

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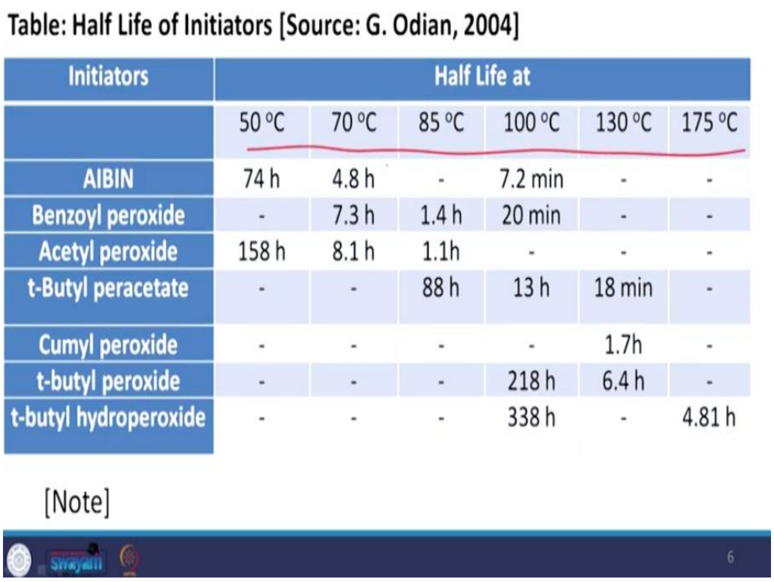

Table: Half Life of Initiators [Source: G. Odian, 2004]

Initiators	Half Life at					
	50 °C	70 °C	85 °C	100 °C	130 °C	175 °C
AIBIN	74 h	4.8 h	-	7.2 min	-	-
Benzoyl peroxide	-	7.3 h	1.4 h	20 min	-	-
Acetyl peroxide	158 h	8.1 h	1.1h	-	-	-
t-Butyl peracetate	-	-	88 h	13 h	18 min	-
Cumyl peroxide	-	-	-	-	1.7h	-
t-butyl peroxide	-	-	-	218 h	6.4 h	-
t-butyl hydroperoxide	-	-	-	338 h	-	4.81 h

[Note]

Now, if in this particular table, you see that people already studied about the dependency of half life or half life approach of different initiator with respect to the temperature profile. So, this is very useful information carried out by the George Odian. Now, in this particular approach, if you see that we have enlisted different initiators like AIBN, benzoyl peroxide, acetyl peroxide, tertiary butyl peracetate, cumyl peroxide, tertiary butyl peroxide etcetera.

Then if you see that here, we have listed the different temperature profiles. You can find out the ways based on your requirement that how much the high half life that particular initiator possesses. So, this is a very useful information attributed to this particular concept. Now, before we discuss further.

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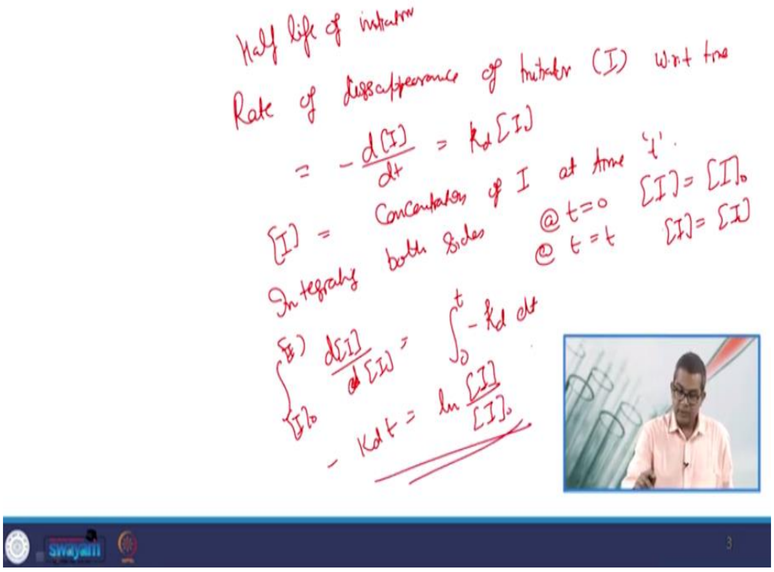

Half life of initiator

Rate of disappearance of initiator (I) w.r.t time

$= -\frac{d[I]}{dt} = k_d[I]$

$[I]$ = Concentration of I at time 't'.

Integrating both sides $@ t=0 \quad [I]=[I]_0$

$@ t=t \quad [I]=[I]$

$$\int_{[I]_0}^{[I]} \frac{d[I]}{[I]} = \int_0^t -k_d\, dt$$

$$-k_d t = \ln\frac{[I]}{[I]_0}$$

Then we have we can have a look about the mathematical approach of these half life of initiators. So, initiators that is rate of disappearance of initiator I this with respect to time. This can be given as

Half life of initiator

Rate of dissappearance of initiator (I) w.r.t time

$$= -\frac{d[I]}{dt} = k_d[I]$$

$[I]$ = Concentration of I at time 't'.

Integrating both sides

@ $t=0$ $[I] = [I]_0$

@ $t = t$ $[I] = [I]$

$$\int_{[I]_0}^{[I]} \frac{d[I]}{\cancel{d}[I]} = \int_0^t -k_d\,dt$$

$$-k_d t = \ln\frac{[I]}{[I]_0}$$

Now, at t is equal to 0 the initial initiator concentration may be put as I naught at t is equal to t that the concentration I may be represented as I. So, if we perform the integration then this I naught this can be represented as 0 to t minus k d dt or minus k d t is equal to ln I upon I naught. So, this is the thing.

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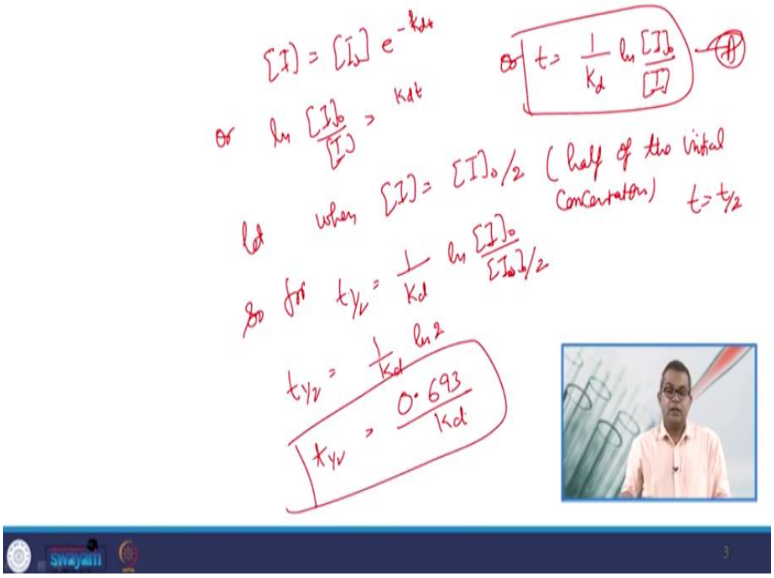

$$[I] = [I_0]\, e^{-k_d t}$$

or $\ln \frac{[I]_0}{[I]} = k_d t$

or $\boxed{t = \frac{1}{k_d} \ln \frac{[I]_0}{[I]}}$ — Ⓐ

let when $[I] = [I]_0/2$ (half of the initial Concentration) $t = t_{1/2}$

So for $t_{1/2} = \frac{1}{K_d} \ln \frac{[I]_0}{[I]_0/2}$

$t_{1/2} = \frac{1}{K_d} \ln 2$

$\boxed{t_{1/2} = \frac{0.693}{K_d}}$

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Then we can go with I is equal to I naught to the power e to the power minus k dt or ln I naught upon I is equal to k dt or t is equal to 1 upon k d ln I upon I naught upon concentration of I at time t. Now, let this is one equation. Now, let us say that when I is equal to I naught on 2. That is the half of the initial concentration. Then t is equal to say t by 2. So, for t half is equal to 1 upon k d ln I naught upon I naught by 2.

So, t half is equal to 1 upon k d ln 2 or t half is equal to 0.693 upon k d. So, this is the half life equation, which is again very useful equation for pertaining this type of information.

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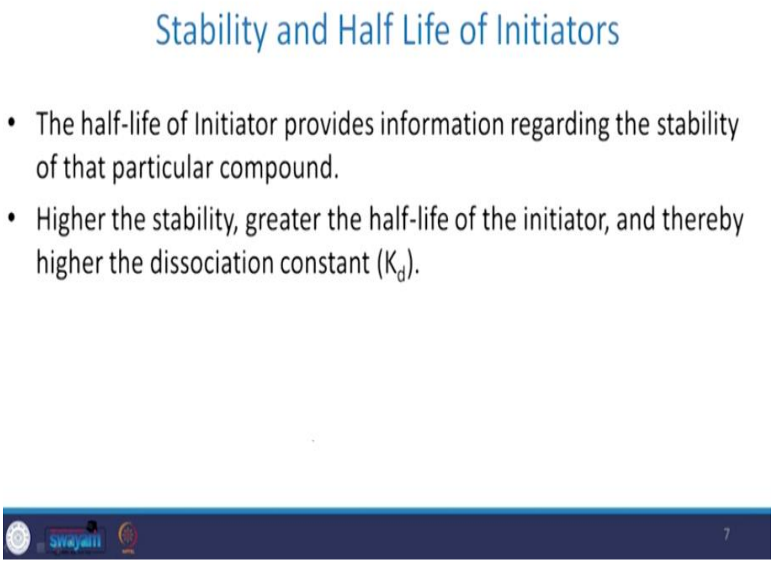

Stability and Half Life of Initiators

- The half-life of Initiator provides information regarding the stability of that particular compound.
- Higher the stability, greater the half-life of the initiator, and thereby higher the dissociation constant (K_d).

Now, the half life of initiator provides information regarding the stability of that particular compound. Now, higher the stability, greater the half life of the initiator, and thereby the higher the dissociation constant. So, it gives you an opportunity or it gives you an information related to the usefulness of that particular initiator in a particular polymerization reaction. Now, let us have a look about the dependence of a polymerization rate on initiator.

Now, we have previously derived the rate of propagation in the previous lectures which can be represented as R p is equal to K p fK d K p square upon K t to the power half concentration of a monomer concentration of initiator to the power half.

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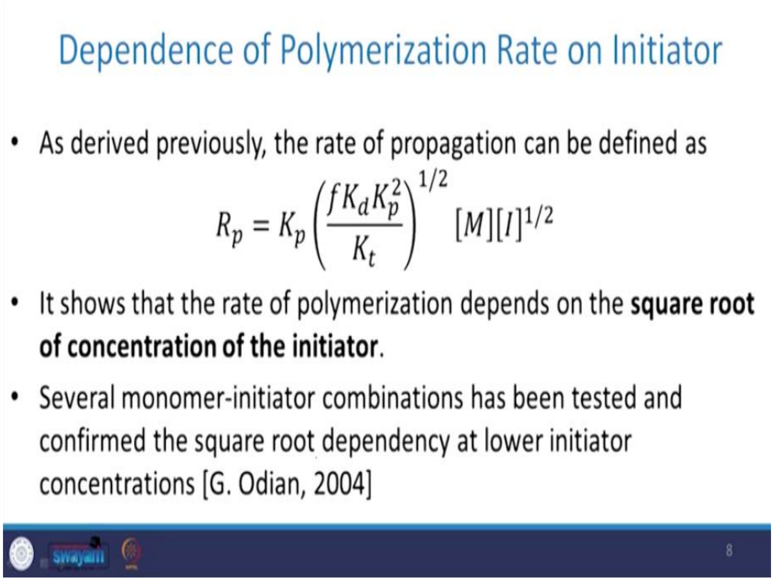

Dependence of Polymerization Rate on Initiator

- As derived previously, the rate of propagation can be defined as

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

- It shows that the rate of polymerization depends on the **square root of concentration of the initiator**.
- Several monomer-initiator combinations has been tested and confirmed the square root dependency at lower initiator concentrations [G. Odian, 2004]

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

Now, it shows that the rate of polymerization depends on square root of concentration of initiator. Now several monomer initiator concern concentration or a combination people have tested and confirmed that the square root dependency at lower initiator concentration are valid and the foremost work being carried out by George Odian. Now, here you can see or you can have a look about the square root dependency of initiator with the help of this particular plot.

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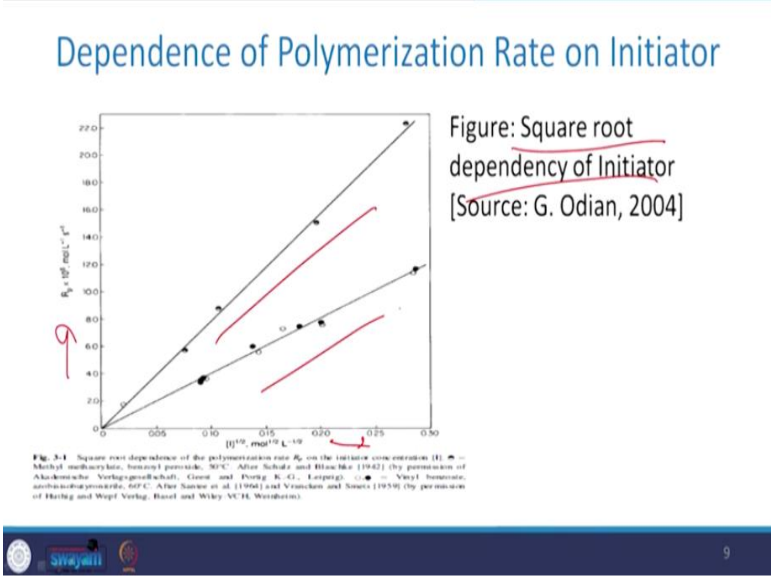
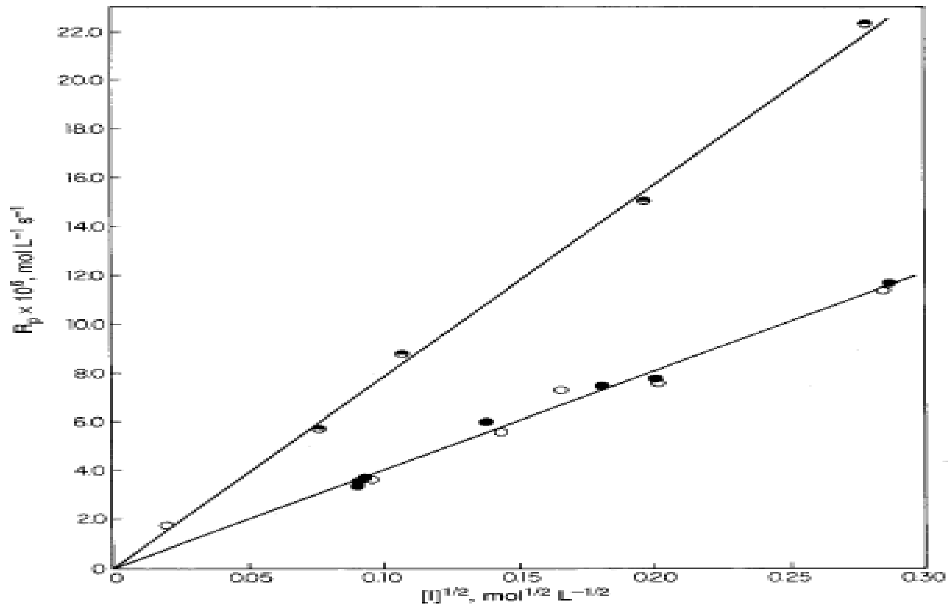


Dependence of Polymerization Rate on Initiator

Fig. 3-1 Square root dependence of the polymerization rate R_p on the initiator concentration [I]. ● = Methyl methacrylate, benzoyl peroxide, 50°C. After Schulz and Blaschke [1942] (by permission of Akademische Verlagsgesellschaft, Geest and Portig K.-G., Leipzig). ○,● = Vinyl benzoate, azobisisobutyronitrile, 60°C. After Santee et al. [1964] and Vrancken and Smets [1959] (by permission of Hüthig and Wepf Verlag, Basel and Wiley-VCH, Weinheim).

Figure: Square root dependency of Initiator [Source: G. Odian, 2004]



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Where you can see the dependency of the polymerization rate with respect to the concentration initiator concentration, you see that the straight line is coming out. So, this type of approach or this type of a plot helps you to find out the proper efficacy of initiator. Now, in some other circumstances, variation from this behaviour is usually observed at very high concentration of initiator, the order of R p or rate constant for propagation.

That dependency on concentration initiator concentration can be found to be less than half. Now, sometimes people ask about the reason for this particular thing. The reason behind such divergence this can be attributed to the decrease in the cage efficiency of f. So, if you recall that we discussed the concept of cage efficiency in the previous lectures. Sometimes, this may be the due to the fact that the concentration of initiator radical it increases.

And thereby the probability of facing of a propagation of radical with initiator radical also increases. Therefore, the chance of termination increases. So, all these things if you see that, they are interlinked. And this phenomena can be decreased in the case in the concept of a case efficiency. So, people have discussed that what at what point of time it decreases? So, Berger et al. they find out that it decreases with the cage efficiency f.

So, this relates the dependency of polymerization rate on initiation. Another reason for this divergence, this can be attributed with the fact that, with increase in polymerization reaction, the monomer concentration usually decreases. And that is quite obvious. So, when the monomer concentration becomes too low, that the initiator radical starts neutralizing the propagating radicals, because they are present in the sufficient quantity in that reaction mass.

And they are not finding the monomer concentration at par with the requirement. Therefore, they start neutralizing the propagating radicals. And sometimes this phenomena is again very useful to truncate the polymerization step at any point of time. So, this can also be happened if a bimolecularly decomposing initiator generate one radical having very less or sometimes even without having any tendency for chain initiation reaction.

But sometimes they may have the potential to terminate the propagating radical. So, this is again a very important phenomena which we need to address. Now, as the initiation reaction proceeds the concentration of unreacted radical increases with the time. And finally, when entropy decreases, this is if you see that this is the one of the most important phenomena to carry out the efficacy of any reaction.

So, when the entropy decreases, it starts reacting with the propagating radicals. So, this can be this can happen if one of the initiator radicle they have the bond dissociation energy sometimes lesser than the energy required to break the bond of monomer. Now, when the propagating radical forms the energy of such radical is enough to form a bond with the propagating radical.

So, sometimes this can reduce the dependency with the concentration of initiator to one third of the concentration. This people have already reported in the literature. Now, these 3 type of termination behaviours which we discussed in the previous slides. This can be termed as a primary termination because the termination occur due to the primary initiator radicles. Now, if the radicle passes on its character to other reaction mass, then it may become the secondary one.

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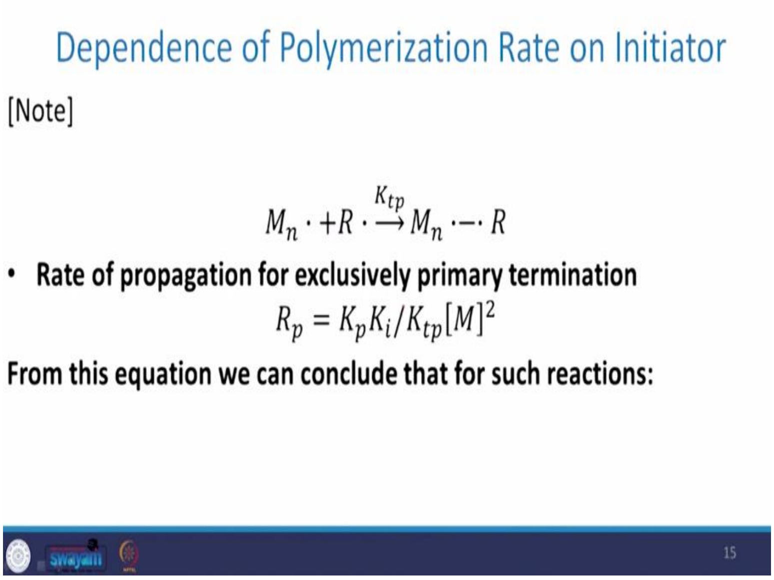

Dependence of Polymerization Rate on Initiator

[Note]

$$M_n \cdot + R \cdot \xrightarrow{K_{tp}} M_n \cdot - \cdot R$$

- Rate of propagation for exclusively primary termination

$$R_p = K_p K_i / K_{tp} [M]^2$$

From this equation we can conclude that for such reactions:

Now, let us have a look about the primary termination aspect.

$$\boldsymbol{M_n \cdot + R \cdot \xrightarrow{K_{tp}} M_n \cdot - \cdot R}$$

- **Rate of propagation for exclusively primary termination**

$$\boldsymbol{R_p = K_p K_i / K_{tp} [M]^2}$$

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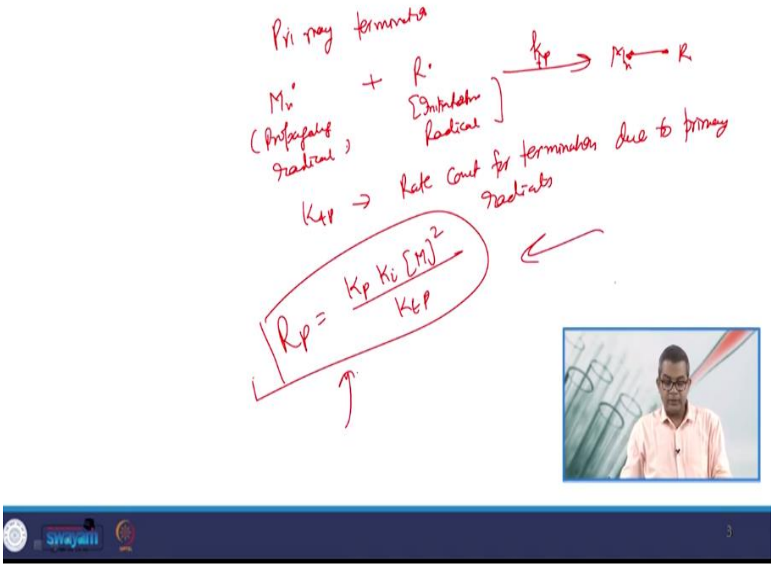

Pri mary terminatio

$M_n^{\cdot}$ (Propagating radical) + $R^{\cdot}$ [Initiator Radical] $\xrightarrow{K_{tp}}$ $M_n \cdot - \cdot R$

K_{tp} → Rate Const for termination due to primary radicals

$$\boxed{R_p = \frac{K_p K_i [M]^2}{K_{tp}}}$$

Now, here we will discuss this particular important approach termination. Now, here this M n is the propagating radical. This reacts with the initiator radical. This is the initiator radical. This is my rate constant. It forms this one. Now, here this one is represented as K tp. Now, this K tp is the rate constant for termination due to primary radicles. Therefore, when primary termination absolutely proceeds the whole termination step.

Primary termination

$M_n^\bullet$ (Propagating radical) + $R^\bullet$ [Initiation Radical] $\xrightarrow{K_{tp}}$ $M_n—R$

K_{tp} → Rate Const for termination due to primary radicals

$$R_p = \frac{K_p K_i [M]^2}{K_{tp}}$$

Then the rate of propagation can be determined as R p is equal to K p K i concentration of monomer. So, this is the thing which gives you the rate constant or rate of propagating reaction. The rate of a reaction is directly proportional to the square root of a monomer concentration as it is evident from this particular equation which we developed previously.

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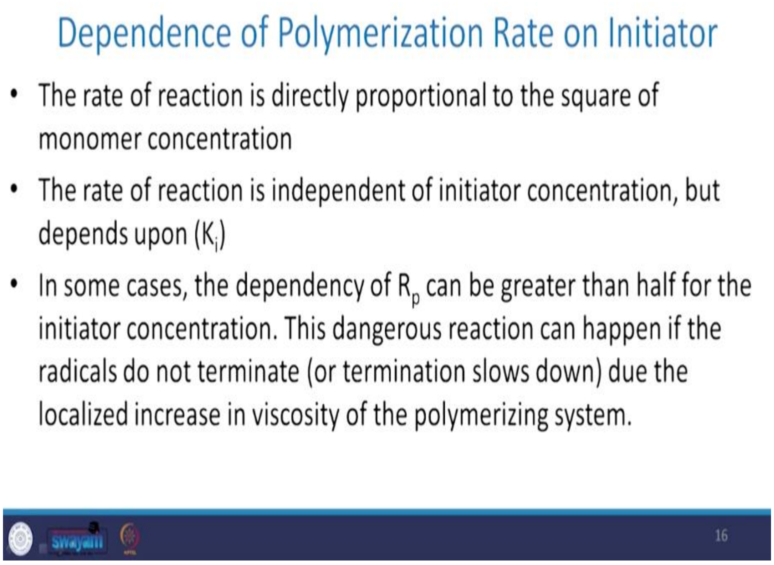

Dependence of Polymerization Rate on Initiator

- The rate of reaction is directly proportional to the square of monomer concentration
- The rate of reaction is independent of initiator concentration, but depends upon (K_i)
- In some cases, the dependency of R_p can be greater than half for the initiator concentration. This dangerous reaction can happen if the radicals do not terminate (or termination slows down) due the localized increase in viscosity of the polymerizing system.

And the rate of reaction is independent of initiator concentration, but usually depends on K_i. So, in some cases the dependency of R_p that is the rate of propagation can be greater than half for the initiator concentration. So, this dangerous reaction I mean this is a very undesired situation. So, this dangerous reaction can happen if the radical do not terminate or sometimes it may happen that the termination slows down.

So, if they do not terminate due to localized increase in the viscosity of the polymerizing system. So, this is highly undesirable situation. Sometimes, usually the rate of a polymerization shows first order dependency on monomer concentration. Let us give an example of methyl methacrylate polymerization. This shows the first order relationship. Hence, the polymerization rate can show higher than first order dependency.

The best example of this type of polymerization of styrene in chlorobenzene solution at 120 degrees Celsius, this shows the 1.5 order of dependency and the monomer was initiated tertiary butyl peresters. Now, if styrene is polymerized in toluene solution at 80 degrees Celsius using benzoyl peroxide initiator, then the order of dependency increases with increase in the monomer concentration.

And people have reported that it is 1.18 at when the monomer concentration equals to 1.8 and 1.36 at when the monomer concentration equals 2.4. So, Horikx and Hermans have carried out this particular study way back in 1953. So, people debated about this particular corrector. So, one explanation for such change this can be attributed to the fact that the rate of initiation unlike the assumption as whatever we have taken they depends on the concentration of monomer.

Now, if initiator efficiency is directly proportional to the first order of monomer concentration, then R_i depends on the first order of monomer concentration. And rate of propagation dependency will increase from half to say 1.5. So, the moles the mode of initiation such as thermal sometimes photolytic, sometimes redox or sometimes ionization reaction, they also affect the monomer behaviour.

And once the behaviour of monomer changes, then the this polymerization rate subsequently being changed. Some of the compounds are a functional group when present or sometimes attached with other compound in an initiation process. They can also improvise the dependency of initiation reaction with respect to the monomer. So, people have carried out extensive work in this particular approach.

One example is the tertiary butyl hydroperoxide styrene system. So, when used as an initiator, the presence of styrene increases as the initiator efficiency for the monomer concentration in a from a the order of 1 to 1.5 because in situ presence of styrene within the system. So, when tertiary butyl hydroperoxide or styrene when used alone, they show the dependency of the order of 1.

$$M + I \rightarrow M\cdot + R\cdot$$

Now, this increased decomposition rate is sometimes said to be favoured by the molecule induced homolysis reaction, and it is represented as monomer initiator and like this.

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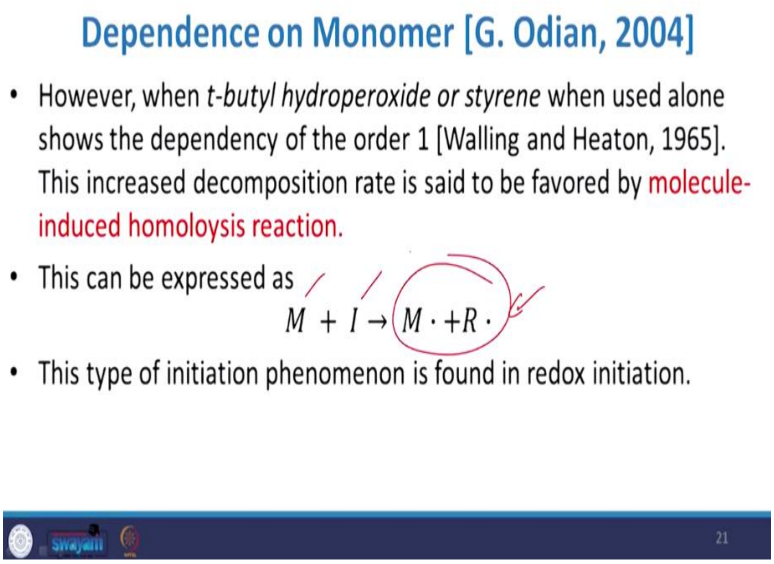

Dependence on Monomer [G. Odian, 2004]

- However, when *t-butyl hydroperoxide or styrene* when used alone shows the dependency of the order 1 [Walling and Heaton, 1965]. This increased decomposition rate is said to be favored by molecule-induced homoloysis reaction.
- This can be expressed as
$$M + I \rightarrow M\cdot + R\cdot$$
- This type of initiation phenomenon is found in redox initiation.

Now, this type of initiation phenomena is somewhere found in the redox initiation. Now, let us move to the redox initiation. Previously in the previous lecture, we studied brief about this redox initiation. Now, we can say that virtually all radical chain polymerization reactions, they require a unique and independent initiation step in which free radicals are sometimes being generated in reaction mass.

Now, the initiation step usually it is very critical and activation energy, it is a very common phenomena. So, the activation energy barrier, this plays a very vital role during the selection of initiator compound as well as what kind of initiation process being used for a specific polymerization reaction. So, we have discussed a priori that the bond dissociation limit for covalent bond breakage is somewhere around 100 to 170 kilojoules per mole through thermal initiation rate reaction.

They are very narrow. Hence, it limits the use of compound those who are having activation energy either above or below this limit. Now, second important thing which we need to address that the concentration of free radicals present in the process, which is increased to a substantial amount that can lead to an unwanted reactions or reaction such as primary termination or sometimes self-combination.

So, this type of termination sometimes may lead to the improper product concentration improper product parameters or and you may face the difficulty during the course of further processing. Redox reaction sometimes people say that this is another kind of initiation phenomena where electron transfer sometimes carried out between the 2 molecules through either oxidation reduction reaction or some other way.

Now, then, the bond dissociation occurs at the acceptor molecule to generate a free radical. Now, this particular thing is again important because people may ask that what should be the priority order to generate the free radicals. So, this solves this particular query. Now redox initiation or redox activation, they found several application in the polymerization industry. So, it is always favoured for conducting low temperature emulsion polymerization.

So, this very important thing which one should have in their mind while designing the polymerization process for various industries for a very specific use. Now, redox initiator they have advantage of lower activation energy for initiation reaction and they can produce the radicle to a substantial amount over a wide range of temperature. Now, because of this lower activation energy this is somewhere in the range of say 40 to 80 kilojoules per mole.

This demands redox initiation which can be conducted various chemical reaction at a very moderate temperature range, sometimes below 50 degrees Celsius or sometimes even lower than 0 degree Celsius. So, this is again a very important aspect to look into. The lower activation energy greatly reduces the possibility of side chain reaction and increases the yield. So, this is the plus point of these redox reaction.

And these reactions have a very short induction period. Therefore, the reaction proceeds quickly. So, the economics of the polymerization process can be improvised. However, they these reactions also have some limitations such as a lower efficiency than the thermal initiation.

And you need to put forward a complex control of those initiator. So, these are some of the limitation of these redox initiation.

Now, secondly, the addition of charged metal ions and sometimes the counter ion, they can affect the electrostatic stability of the system. So, these reactions are also referred as the pH sensitive reaction. Therefore, the usually the weak acids they are used to perform certain chemical reaction. So, these are the either you can say the plus point or the negative points etcetera.

Now, in this particular chapter, we discussed about the concept of redox reaction, we discussed the concept of a half life and we had a discussion that how this half life played a vital role in deciding the fate of the polymerization reaction. We developed the mathematical equation which pertains to this half life concept. And we had a discussion about the various half life attributed to the different type of initiators.

And what is the dependency over the period of time? We had a brief discussion about the bond dissociation and its energy and In-situ effect to the initiator.

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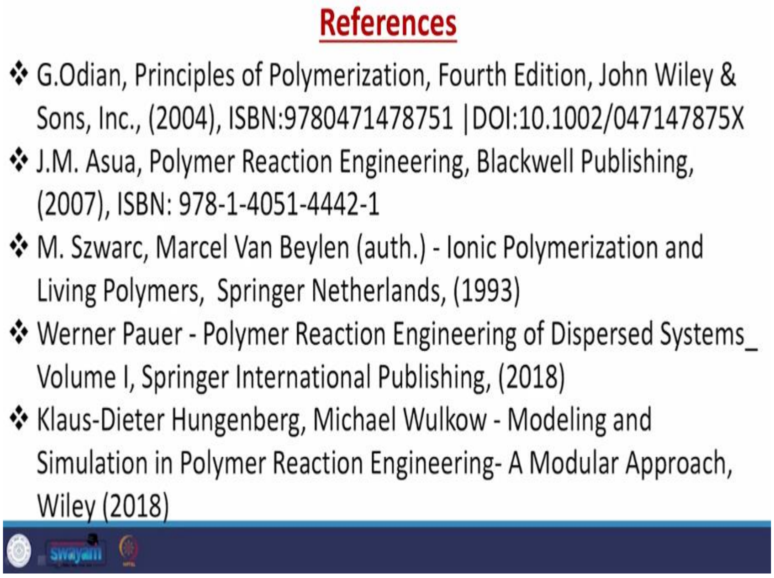

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So, we will carry out this particular discussion especially related to the initiation in the aqueous media in the next lecture, thank you very much.