Polymer Reaction Engineering
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Lecture - 41
Redox Initiation

Welcome to the Redox initiation mechanism under the edges of radical chain polymerization and if you recall that in the previous lecture, we initiated this thing with attributed to the Redox reaction and we discussed a couple of concepts attributed to this Redox initiation. Let us have a brief look about that what we discussed in the previous lectures.

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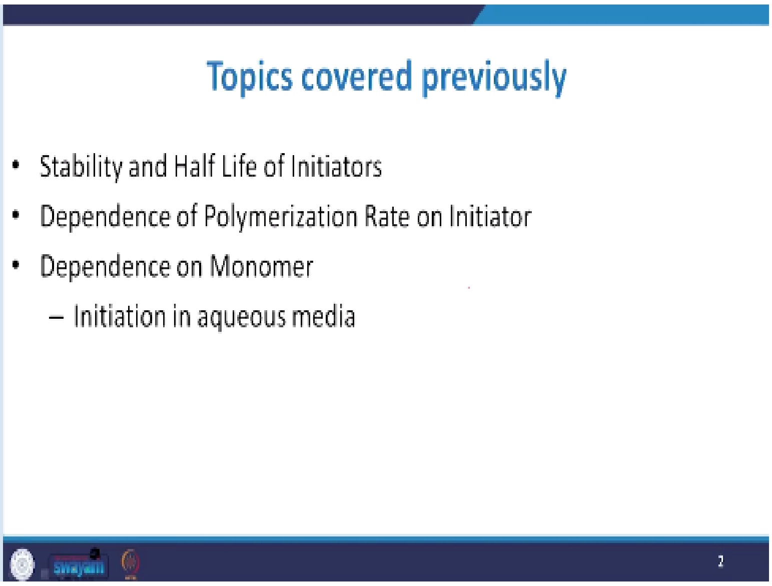

Topics covered previously

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

We discussed about the instability and half life of various initiator. We discussed about the dependence of polymerization rate on initiator. We had a discussion about the dependence on monomer with special attention to the initiation in aqueous media and if you recall that we discussed various mechanisms in the previous lecture related to this initiation aspect in aqueous media.

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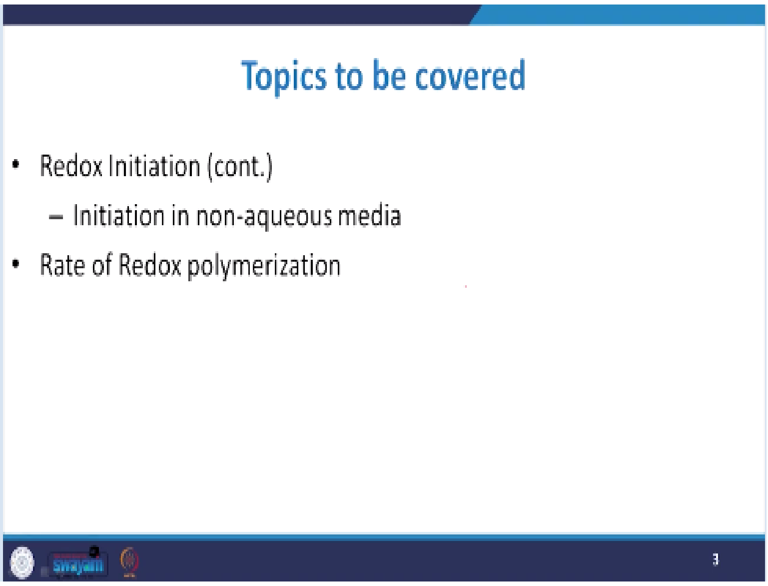

Topics to be covered

- Redox Initiation (cont.)
  - Initiation in non-aqueous media
- Rate of Redox polymerization

Now, in this particular lecture, we are going to discuss the Redox reaction, Redox initiation reaction, which we covered briefly in the previous lecture. And if you recall that in the previous lecture, we discussed the initiation in aqueous media. Now, the another concept is that what will happen in the non-aqueous media. So, we will have a look about that those concepts attributed to the Redox initiation in non-aqueous media.

Then we will try to cover the Redox polymerization rate. And again, it is a very, very good phenomena and a very interesting phenomena which need to be addressed under the head of polymerization reaction engineering. Now, let us discuss this thing under the edges of stability and half life of this initiator with the peroxomonosulfate.

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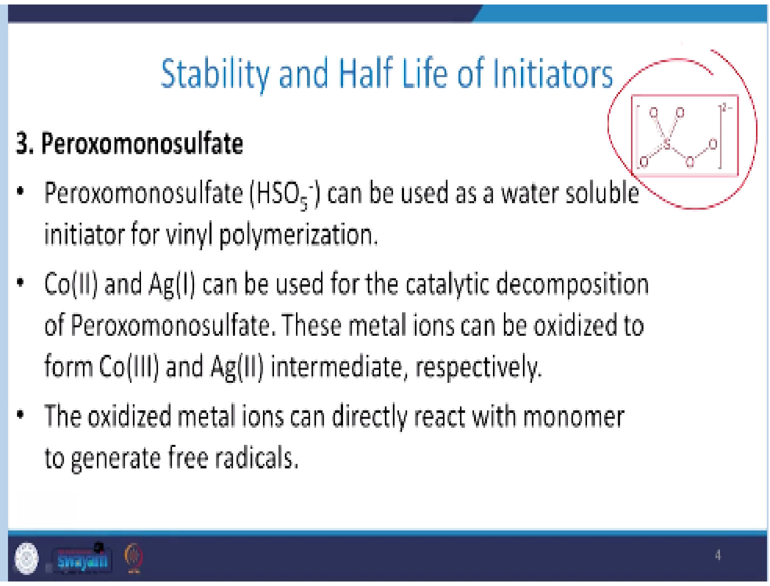

Stability and Half Life of Initiators

3. Peroxomonosulfate

- Peroxomonosulfate (HSO_5^-) can be used as a water soluble initiator for vinyl polymerization.
- Co(II) and Ag(I) can be used for the catalytic decomposition of Peroxomonosulfate. These metal ions can be oxidized to form Co(III) and Ag(II) intermediate, respectively.
- The oxidized metal ions can directly react with monomer to generate free radicals.

Now, you see that here we presented the small pictorial depiction of this peroxomonosulfate that is HSO_5^-. This can be used as a water soluble initiator for vinyl polymerization. Now, Co(II) and Ag(I) can be used for the catalytic decomposition of these peroxomonosulfate and these metal ions can be oxidised to form Co(III) and Ag(II) intermediate respectively.

So, these oxidised metal ion or oxidised metal ion can directly react with the monomer to generate the free radicals. Let us have a look about this particular thing.

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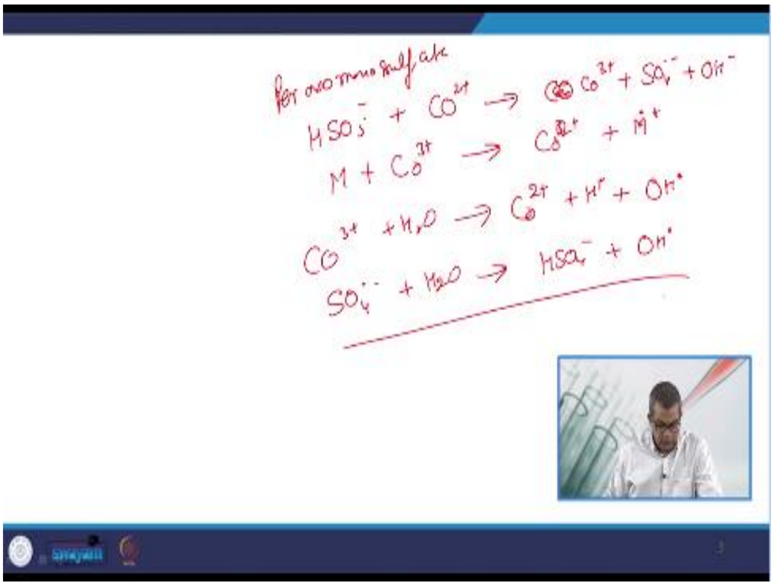

Per oxomono sulfate

$HSO_5^- + Co^{2+} \rightarrow Co^{3+} + SO_4^{\cdot -} + OH^-$

$M + Co^{3+} \rightarrow Co^{2+} + \dot{M}^+$

$Co^{3+} + H_2O \rightarrow Co^{2+} + H^+ + OH^\circ$

$SO_4^{\cdot -} + H_2O \rightarrow HSO_4^- + OH^\circ$

This peroxomonosulfate; now,

Per oxomono sulfate

$HSO_5^- + Co^{2+} \rightarrow Co^{3+} + SO_4^{\cdot -} + OH^-$

$M + Co^{3+} \rightarrow Co^{2+} + \dot{M}^+$

$Co^{3+} + H_2O \rightarrow Co^{2+} + H^+ + OH^\circ$

$SO_4^{\cdot -} + H_2O \rightarrow HSO_4^- + OH^\circ$

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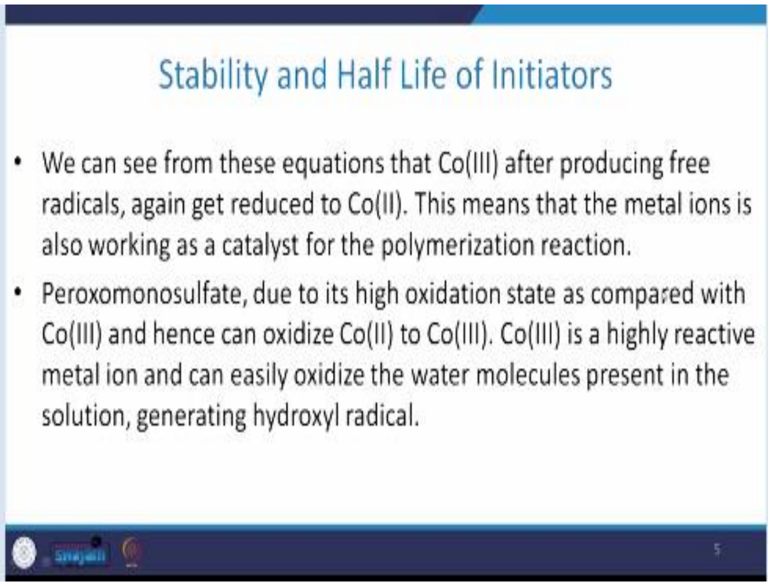
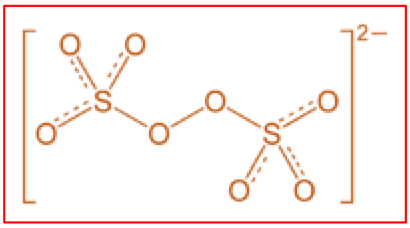


Stability and Half Life of Initiators

- We can see from these equations that Co(III) after producing free radicals, again get reduced to Co(II). This means that the metal ions is also working as a catalyst for the polymerization reaction.
- Peroxomonosulfate, due to its high oxidation state as compared with Co(III) and hence can oxidize Co(II) to Co(III). Co(III) is a highly reactive metal ion and can easily oxidize the water molecules present in the solution, generating hydroxyl radical.

Now, if you see that this can reduce to Co(II), now, this means that the metal ion is also working as a catalyst for the polymerization reaction. Now, peroxomonosulfate due to its high oxidation state as compared with the Co(III) and can oxidise Co(II) and Co(II), Co(III) and Co(III) is a highly reactive metal ion and it can easily oxidise the water molecules present in the solution and generating hydroxyl radical.

Let us have a look about this particular approach in this particular slide. Now, the rate of polymerization reaction, this shows the dependency of the order of say 1.5, 1, and 0.5 for acrylonitrile peroxomonosulfate and Co(II) respectively. And this was studied way ahead by Born and White and they describe this particular concept. Now, another thing is attributed to this concept is the peroxodiphosphate.



Now, sometimes, the metal ions like Ag(I), Co(II), V^{5+} and acids. They can form an efficient Redox spear with the peroxodiphosphate (PDP) in aqueous media for the polymerization of acrylonitrile.

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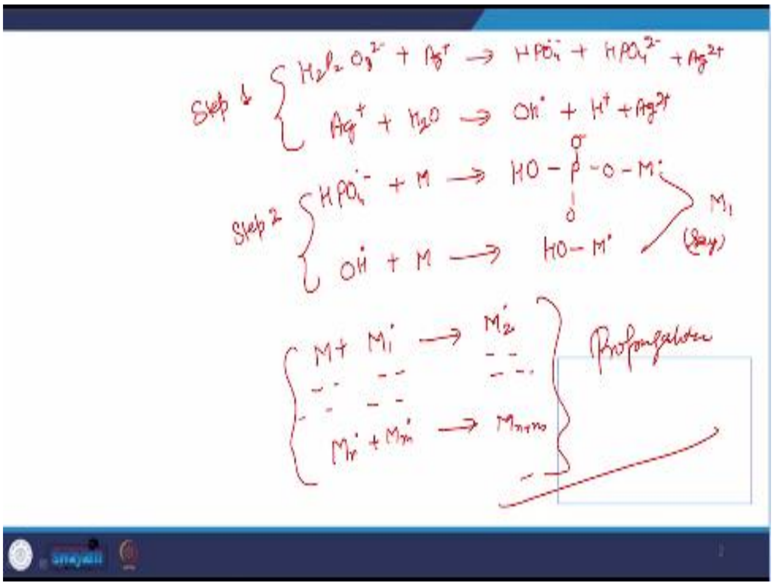
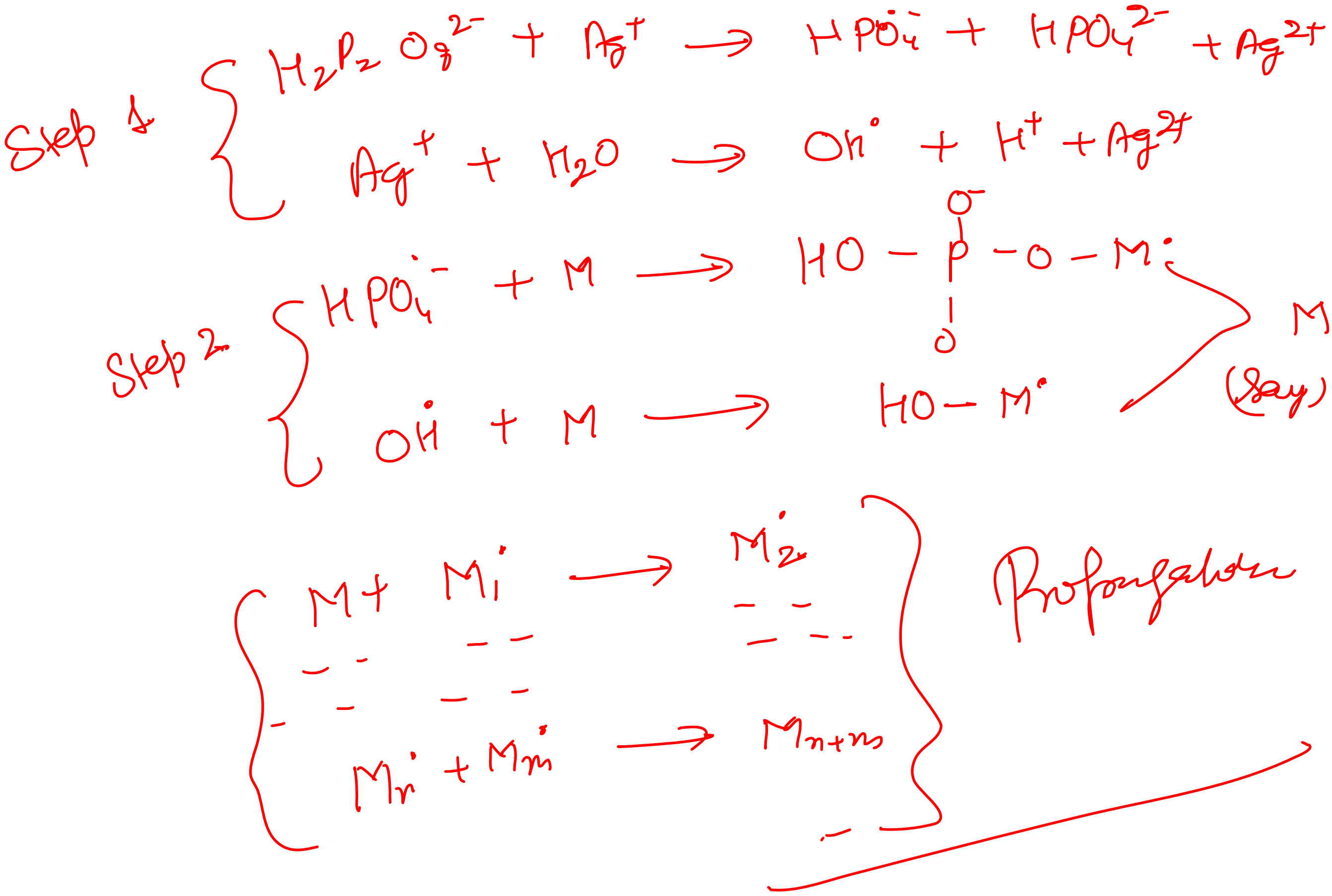


Step 1 $\begin{cases} H_2P_2O_8^{2-} + Ag^+ \rightarrow HPO_4^{\cdot -} + HPO_4^{2-} + Ag^{2+} \\ Ag^+ + H_2O \rightarrow OH^{\cdot} + H^+ + Ag^{2+} \end{cases}$

Step 2 $\begin{cases} HPO_4^{\cdot -} + M \rightarrow HO-\overset{O^-}{\underset{O}{P}}-O-M^{\cdot} \\ O\dot{H} + M \rightarrow HO-M^{\cdot} \end{cases}$ M_1 (say)

$\begin{cases} M + M_1^{\cdot} \rightarrow M_2^{\cdot} \\ \text{-- --} \\ M_n^{\cdot} + M_m^{\cdot} \rightarrow M_{n+m} \end{cases}$ Propagation

Now, the mechanism is almost similar to peroxodisulfate and it can be initiated as



Step 1 $\begin{cases} H_2P_2O_8^{2-} + Ag^+ \rightarrow HPO_4^{\cdot -} + HPO_4^{2-} + Ag^{2+} \\ Ag^+ + H_2O \rightarrow OH^{\cdot} + H^+ + Ag^{2+} \end{cases}$

Step 2 $\begin{cases} HPO_4^{\cdot -} + M \rightarrow HO-\overset{O^-}{\underset{O}{P}}-O-M^{\cdot} \\ O\dot{H} + M \rightarrow HO-M^{\cdot} \end{cases}$ M_1 (say)

$\begin{cases} M + M_1^{\cdot} \rightarrow M_2^{\cdot} \\ \text{-- --} \\ M_n^{\cdot} + M_m^{\cdot} \rightarrow M_{n+m} \end{cases}$ Propagation

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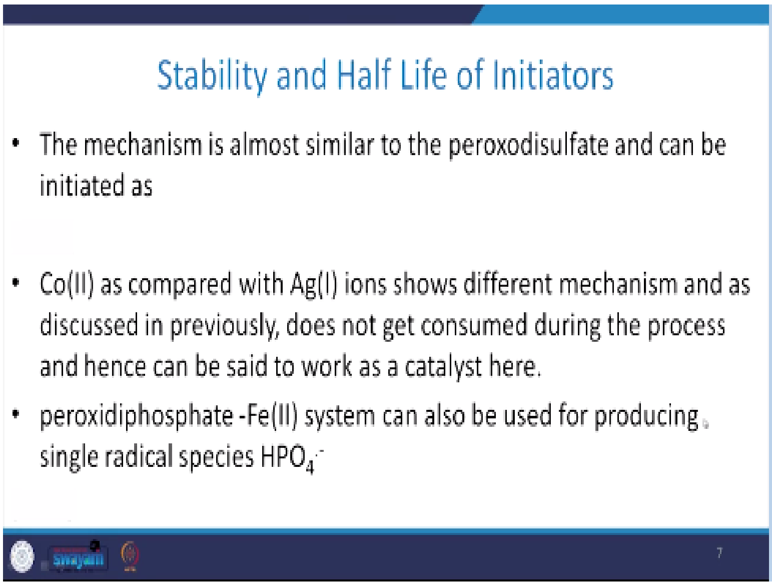

Stability and Half Life of Initiators

- The mechanism is almost similar to the peroxodisulfate and can be initiated as
- Co(II) as compared with Ag(I) ions shows different mechanism and as discussed in previously, does not get consumed during the process and hence can be said to work as a catalyst here.
- peroxidiphosphate -Fe(II) system can also be used for producing single radical species $HPO_4^{\cdot -}$

So, this is some of the things which are related to the polymerization part. Now, Co 2 as compared to the Ag 1 ions shows a different mechanism. And we have already discussed this thing; they does not consumed during the process and it can be set to work as catalyst over here. Now, peroxodiphosphate Fe(II) system can also be used for producing single radical, especially is of H PO$_4$•. So, let us give some more examples related to this particular concept.

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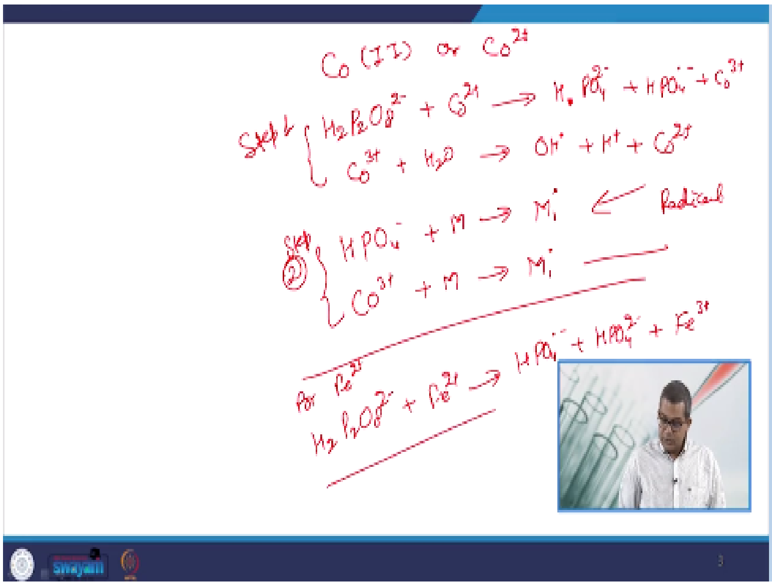

Co (II) or Co^{2+}

Step 1 $\left\{ \begin{array}{l} H_2P_2O_8^{2-} + Co^{2+} \rightarrow H_{\bullet}PO_4^{2-} + HPO_4^{\cdot -} + Co^{3+} \\ Co^{3+} + H_2O \rightarrow OH^{\cdot} + H^{+} + Co^{2+} \end{array} \right.$

Step ② $\left\{ \begin{array}{l} HPO_4^{\cdot} + M \rightarrow M_i^{\cdot} \leftarrow \text{Radical} \\ Co^{3+} + M \rightarrow M_i^{\cdot} \end{array} \right.$

For Fe^{2+}

$H_2P_2O_8^{2-} + Fe^{2+} \rightarrow HPO_4^{\cdot -} + HPO_4^{2-} + Fe^{3+}$

Now, we were talking about Co(II).

Co (II) or Co^{2+}

Step 1

$$H_2P_2O_8^{2-} + Co^{2+} \rightarrow H\,PO_4^{2-} + HPO_4^{\cdot -} + Co^{3+}$$

$$Co^{3+} + H_2O \rightarrow OH^{\circ} + H^{+} + Co^{2+}$$

Step ②

$$HPO_4^{\cdot -} + M \rightarrow M_1^{\cdot} \leftarrow \text{Radical}$$

$$Co^{3+} + M \rightarrow M_1^{\cdot}$$

For Fe^{2+}

$$H_2P_2O_8^{2-} + Fe^{2+} \rightarrow HPO_4^{\cdot -} + HPO_4^{2-} + Fe^{3+}$$

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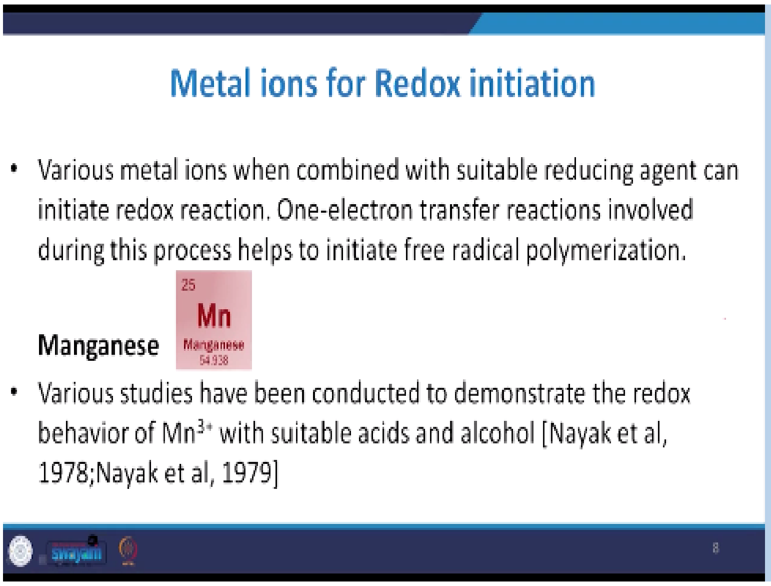

Metal ions for Redox initiation

- Various metal ions when combined with suitable reducing agent can initiate redox reaction. One-electron transfer reactions involved during this process helps to initiate free radical polymerization.

Manganese

- Various studies have been conducted to demonstrate the redox behavior of Mn^{3+} with suitable acids and alcohol [Nayak et al, 1978;Nayak et al, 1979]

So, this is the things which we are talking about in this particular lecture. Now, there are several metal ions been used for the Redox initiation. So, various metal ion so, when combined with the suitable reducing agent, they can initiate the Redox reaction. Now, one electron transfer reaction, they involved during this process, they helps to initiate free radical polymerization. One of this category is the manganese; you can see this representation Mn.

So, various studies being conducted by Nayak et al for the use of this manganese as a Redox behaviour with the suitable acrylic acid and alcohol. So, they studied and they carried out extensive work in this area and they demonstrated the Redox behaviour of these manganese ion. Now, for manganese 3 acrylic acid Redox system, the order of reactivity for acrylonitrile polymerization, they took the example of acrylonitrile polymerization.

So, they give the citric acid, then tartaric acid, ascorbic acid, oxalic acid, succinic acid, butyric acid, adipic acid etcetera. Now, for manganese ion alcohol reduction system, the order of reactivity is bit changed for MMA or methyl methacrylate polymerization. It becomes the 1-propanol, then glycerol, then ethylene glycol, isobutyl alcohol, 1-butanol, 1,2-propanediol, then cycloheptanediol, then cyclohexanediol, then cyclopentanediol.

So, this is the way, they can proceed for the different type of polymerization. So, these two examples implicates about the use of these manganese ion in the Redox initiation reaction. Now, since we discussed this thing, let us have a look about the mechanism which is involved in this particular type of manganese attributed to Redox initiation.

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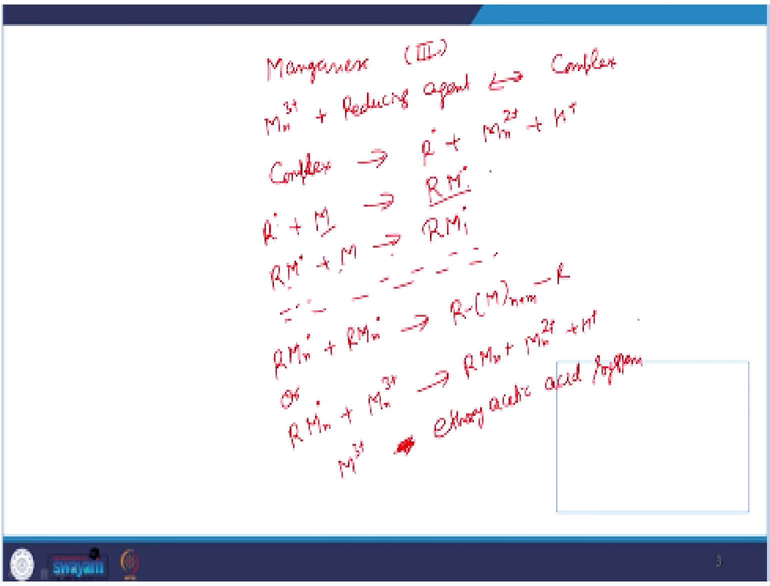

Manganese (III)

Mn^{3+} + Reducing agent $\rightleftarrows$ Complex

Complex $\rightarrow R^{\cdot} + Mn^{2+} + H^{+}$

$R^{\cdot} + M \rightarrow RM^{\cdot}$

$RM^{\cdot} + M \rightarrow RM_1^{\cdot}$

$RM_n^{\cdot} + RM_m^{\cdot} \rightarrow R-(M)_{n+m}-R$

or

$RM_n^{\cdot} + Mn^{3+} \rightarrow RM_n + Mn^{2+} + H^{+}$

Mn^{3+} ethoxy acetic acid [illegible]

Now, this here, you see that we are using manganese.

Manganese (III)

Mn^{3+} + Reducing agent $\longleftrightarrow$ Complex

Complex $\rightarrow$ $R^{\bullet} + Mn^{2+} + H^{+}$

$\underline{RM^{\bullet}}$.

$R^{\bullet} + \underline{M} \rightarrow RM_1$

$RM^{\bullet} + M \rightarrow$ — — — — — — — — —

— — — — — — $-R$

$RM_n^{\bullet} + RM_n^{\bullet} \rightarrow R-(M)_{n+m}-R$

Or

$RM_n^{\bullet} + Mn^{3+} \rightarrow RMn + Mn^{2+} + H^{+}$

M^{3+} ethoxy acetic acid system

Now, here Mn plus reducing agent; you may take any reducing agent; may become the complex and it is a very popular type of thing in the polymerization reaction and this complex whatever you formed in due course of time, it can give you this one. Now, this radical may get combination with the monomer to give you this radical monomer.

So, for example, in this Mn^{3+} ethoxy acetic acid system. Let us have a look about this one.

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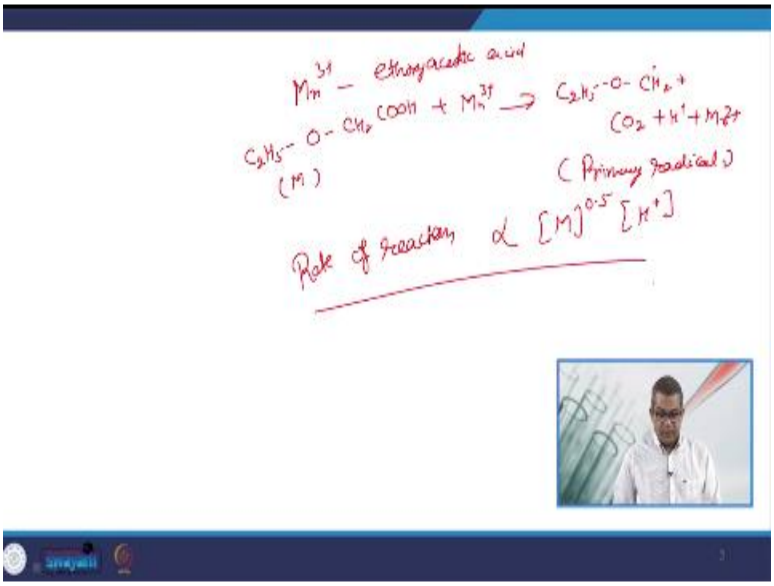

Mn^{3+} — ethoxyacetic acid

$$C_2H_5-O-CH_2COOH + Mn^{3+} \longrightarrow C_2H_5-O-\dot{C}H_2 + CO_2 + H^+ + Mn^{2+}$$

(M)

(Primary radical)

Rate of reaction $\propto [M]^{0.5}[H^+]$

This is my primary radical. You see that in this particular example, we are discussing this manganese concept. Now, here, the rate of reaction, sometimes, people ask about the rate of a reaction. So, the rate of reaction is directly proportional to this particular reaction or H plus. So, there is no dependency on this particular thing.

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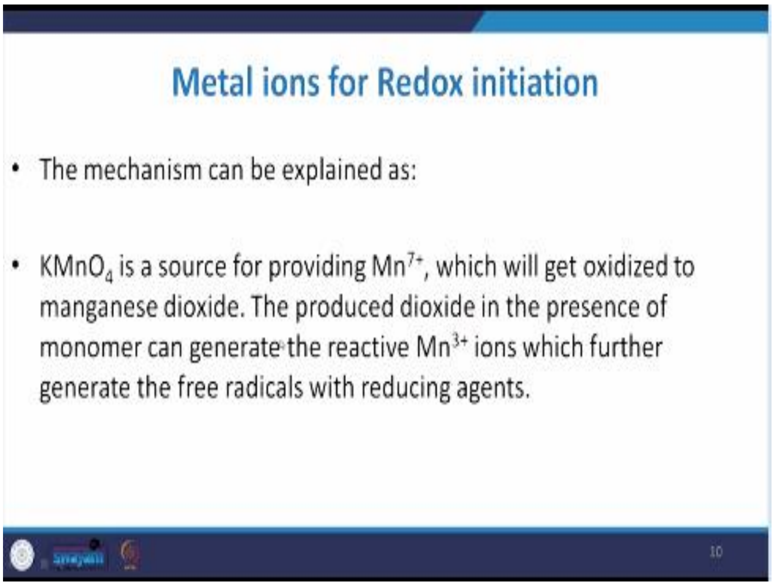

Metal ions for Redox initiation

- The mechanism can be explained as:
- $KMnO_4$ is a source for providing Mn^{7+}, which will get oxidized to manganese dioxide. The produced dioxide in the presence of monomer can generate the reactive Mn^{3+} ions which further generate the free radicals with reducing agents.

Now, if you see that this another example is attributed to the $KMnO_4$. Now, this $KMnO_4$ is a source of providing Mn^{7+} so, thing now, which in due course of time get oxidised to manganese dioxide. Now, this produce to dioxide in presence of monomer can generate the reactive Mn^{3+} ion, which further generate the free radicals with reducing agent. So, let us have a look about this mechanism in the separate slide.

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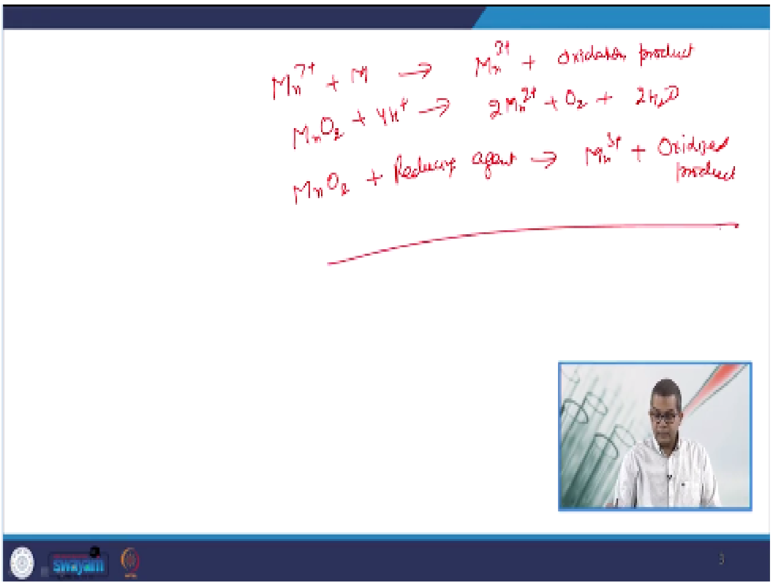

Now, here you see that

$Mn^{7+} + M \rightarrow Mn^{3+}$ + oxidation product

$MnO_2 + 4H^+ \rightarrow 2Mn^{2+} + O_2 + 2H_2O$

MnO_2 + Reducing agent $\rightarrow Mn^{3+}$ + Oxidized product

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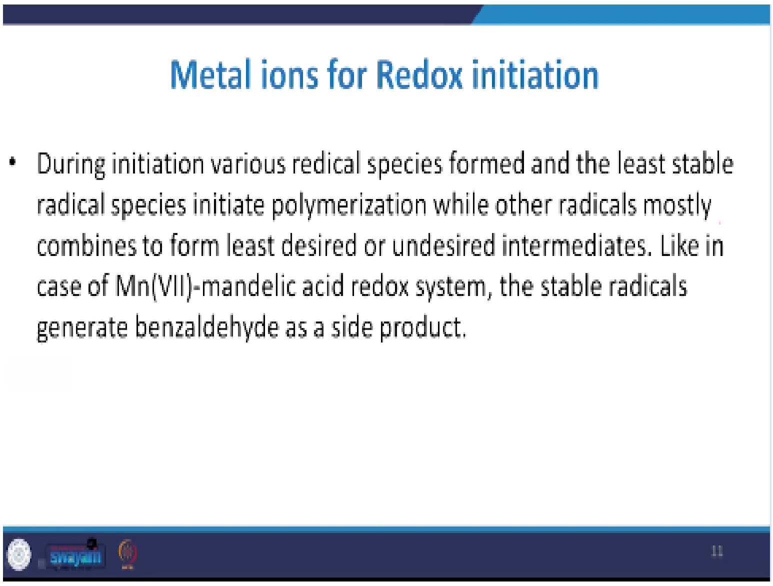

Metal ions for Redox initiation

- During initiation various redical species formed and the least stable radical species initiate polymerization while other radicals mostly combines to form least desired or undesired intermediates. Like in case of Mn(VII)-mandelic acid redox system, the stable radicals generate benzaldehyde as a side product.

Now, another example if we would like to have that is during the initiation step various radical species; they may formed and at least a stable ridiculous species initiate the polymerization while other radical mostly they combined to form least desired or sometimes undesired intermediate. So, sometimes, we are not very much interested in those intermediate.

So, let us say by an example in the case of Mn 7 mandelic acid Redox system that stable radical generate benzaldehyde as aside product. Let us have a look about this how this generation take place.

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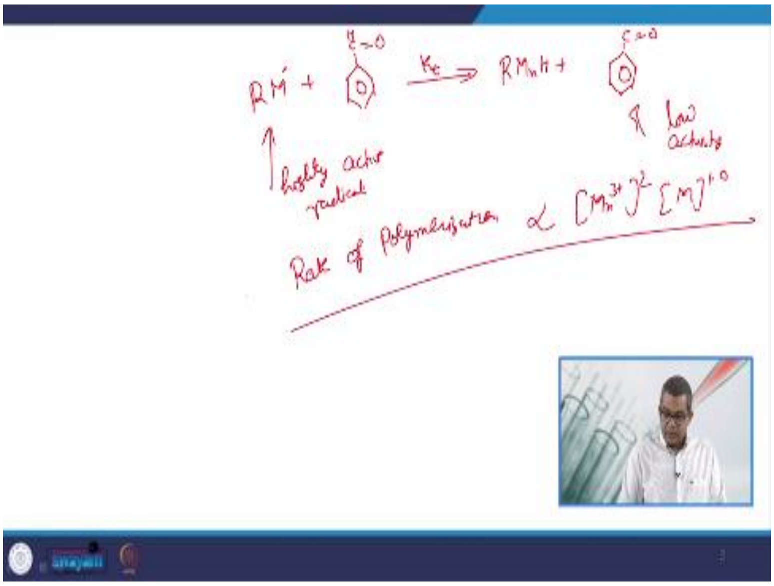
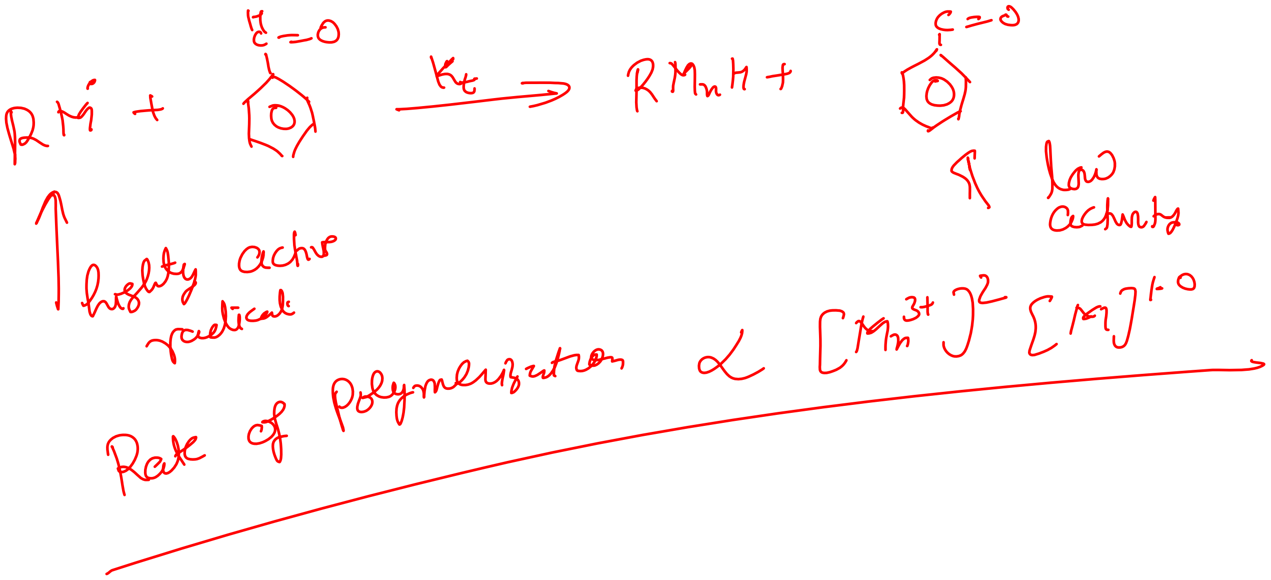


This is your radical which we generated previously, then it reacts and here, because we are much more interested in that termination, so, this is the rate of termination; then it gives you, now, here, this is highly active radical whereas, this is having a very much low activity. So, when we talk about the rate of polymerization, it is directly proportional to this. So, this is my rate of polymerization.



$$\text{Rate of Polymerization} \propto [Mn^{3+}]^{2}\,[M]^{1.0}$$

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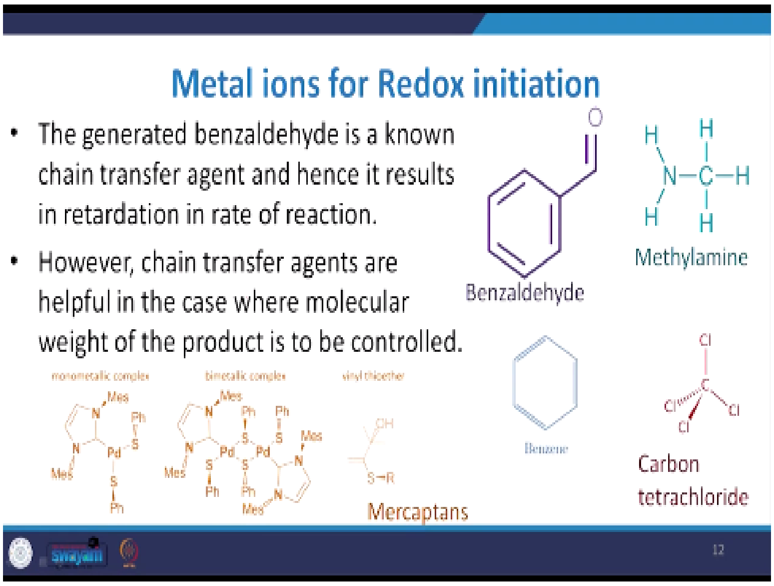

Metal ions for Redox initiation

- The generated benzaldehyde is a known chain transfer agent and hence it results in retardation in rate of reaction.
- However, chain transfer agents are helpful in the case where molecular weight of the product is to be controlled.

Now, then the generated benzaldehyde is usually known as a chain transfer agent and it results the retardation in the rate of reaction, because it is quite obvious; it carries the radical charge. Now, the chain transfer agents, they are helpful in case where molecular weight of the product is to be controlled. So, this is again how we can. We can see, there are various ways or various compounds through which you can control the rate of polymerization.

You can control the molecular weight of the product, because sometimes it is quite few required because you cannot allow the reaction to carry out for longer period because that case the molecular weight of that polymer may go on the higher side. Now, various examples of such chain transfer agents, they may include like aliphatic alcohols like ethanol, methanol, isopropyl alcohol, DMF etcetera.

There will be some methyl amine CCl_4, benzene, mercaptans. (sometimes, they influence metal and metal ion by activating them). Now, one point needs to be noted that the chain transfer agent if introduced intentionally, they can advance the radical formation by activating the higher state ions and other initiating species. So, this is intentionally and sometimes it is induced or introduced in the polymerization reaction.

Now, let us have example of these things like transition metals like V^{5+}, Co^{3+}, Cr^{6+}, Ce^{4+}, and Mn^{4+}, with thiourea, thioacetamide, thioglycolic acid and ethanethiol, they were used to for the polymerization of acrylonitrile and some people have studied their rate of polymerization and they found that the dependency in the order of 2 for monomer concentration.

Now, sometimes the use of advanced technology like electrode generation of metal ion like Mn^{3+}. This can increase the effectiveness of radical generation. So, this is again a very useful thing to carry out these radical chain polymerization. Another good example of this Redox reaction initiation is the cerium. Now, this cerium is having the molecular weight 58 and represented by Ce.

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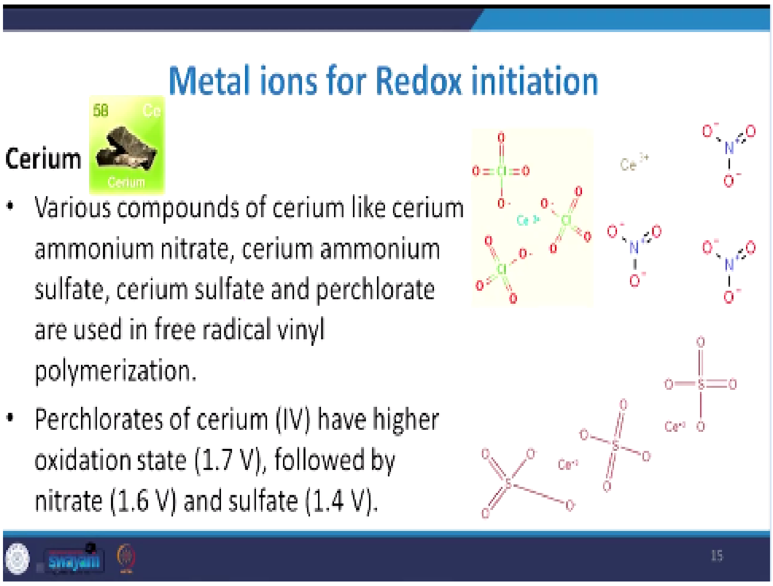

Metal ions for Redox initiation

Cerium

- Various compounds of cerium like cerium ammonium nitrate, cerium ammonium sulfate, cerium sulfate and perchlorate are used in free radical vinyl polymerization.
- Perchlorates of cerium (IV) have higher oxidation state (1.7 V), followed by nitrate (1.6 V) and sulfate (1.4 V).

Now, various compounds of cerium like cerium ammonium nitrate, cerium ammonium sulphate, cerium sulphate or perchlorate; they are used in free radical vinyl polymerization. So, the people find it more useful in different polymerization scheme. Now, perchlorates of cerium 4 have higher oxidation state. It is in the range of 1.7 volts followed by the nitrate and sulphate. So, you can see the different forms of cerium in this particular slide.

Now, usually when we talk about the mechanism, it is quite similar to the reaction involved using manganese metal ion, the cerium ion in the presence of a reducing agent like monomers etcetera, they form the complex compound and finally oxidised fusion rate the propagating free radicals. So, let us have a look about this mechanism apart related to the cerium.

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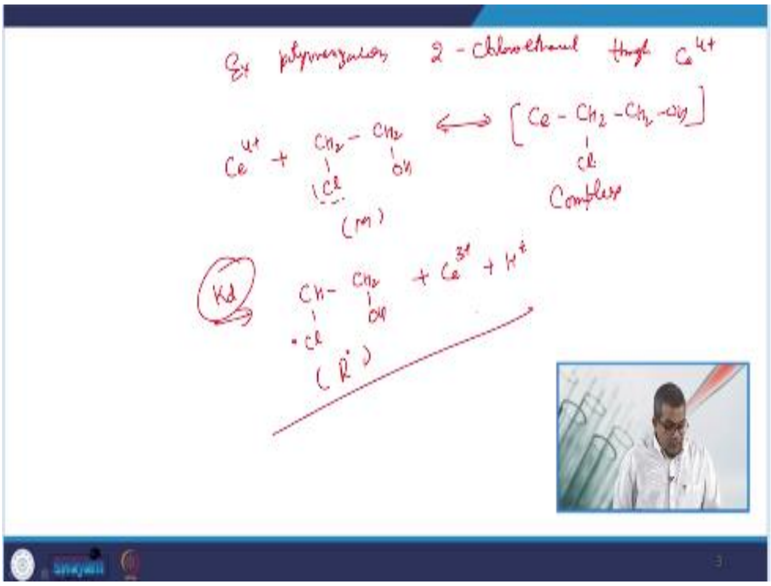
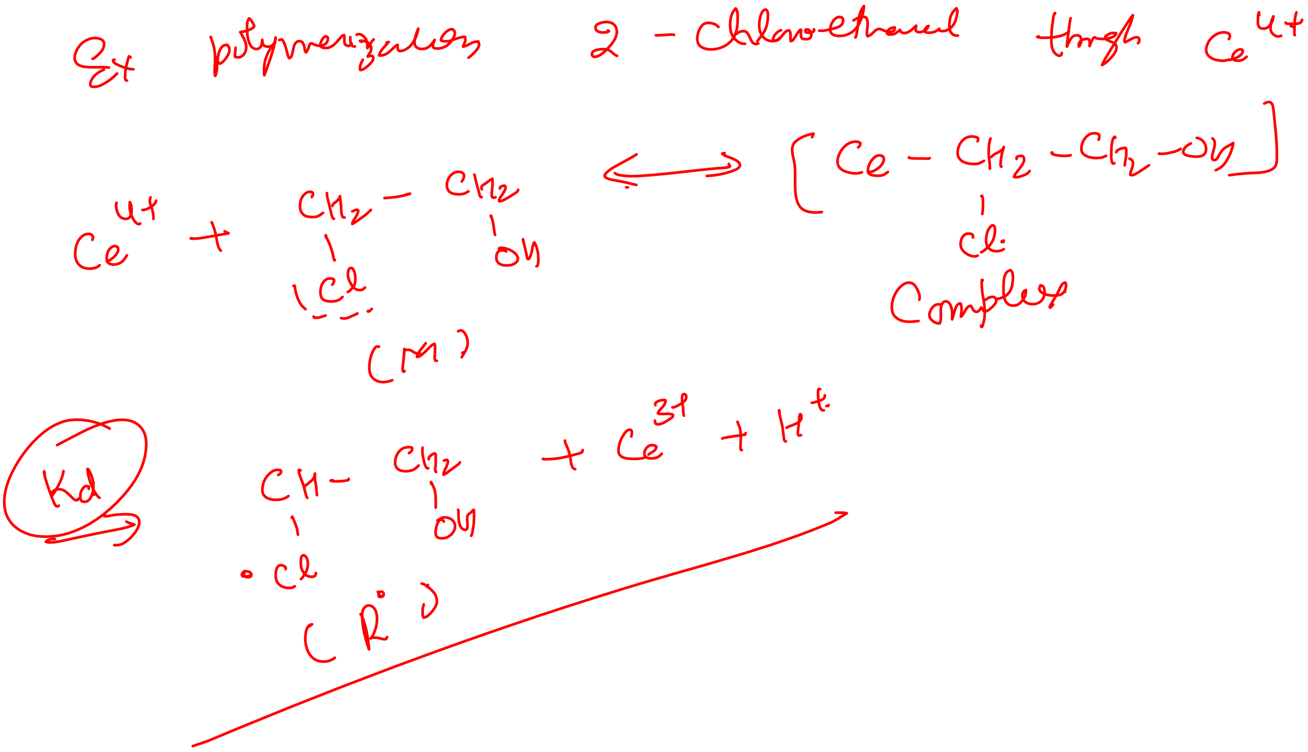


Now, let us take the example of polymerization of 2-chloroethanol through.



Now, if it forms with the complex, then it becomes Ce-CH$_2$Cl-CH2-OH. Now, this is my complex. Now, if we talk about the dissociation's step, so, definitely we have to look into the rate constant attributed to the dissociation, then it becomes this one. This at as a radical, we are having this Ce^{3+}.

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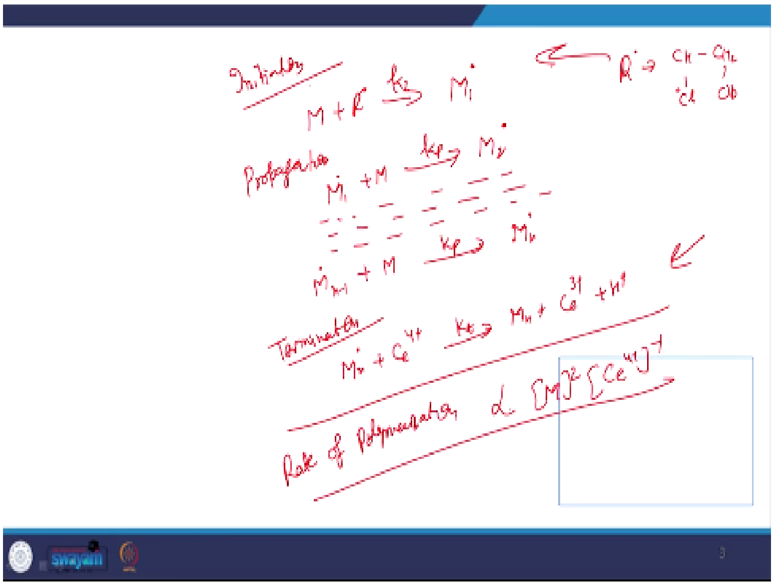

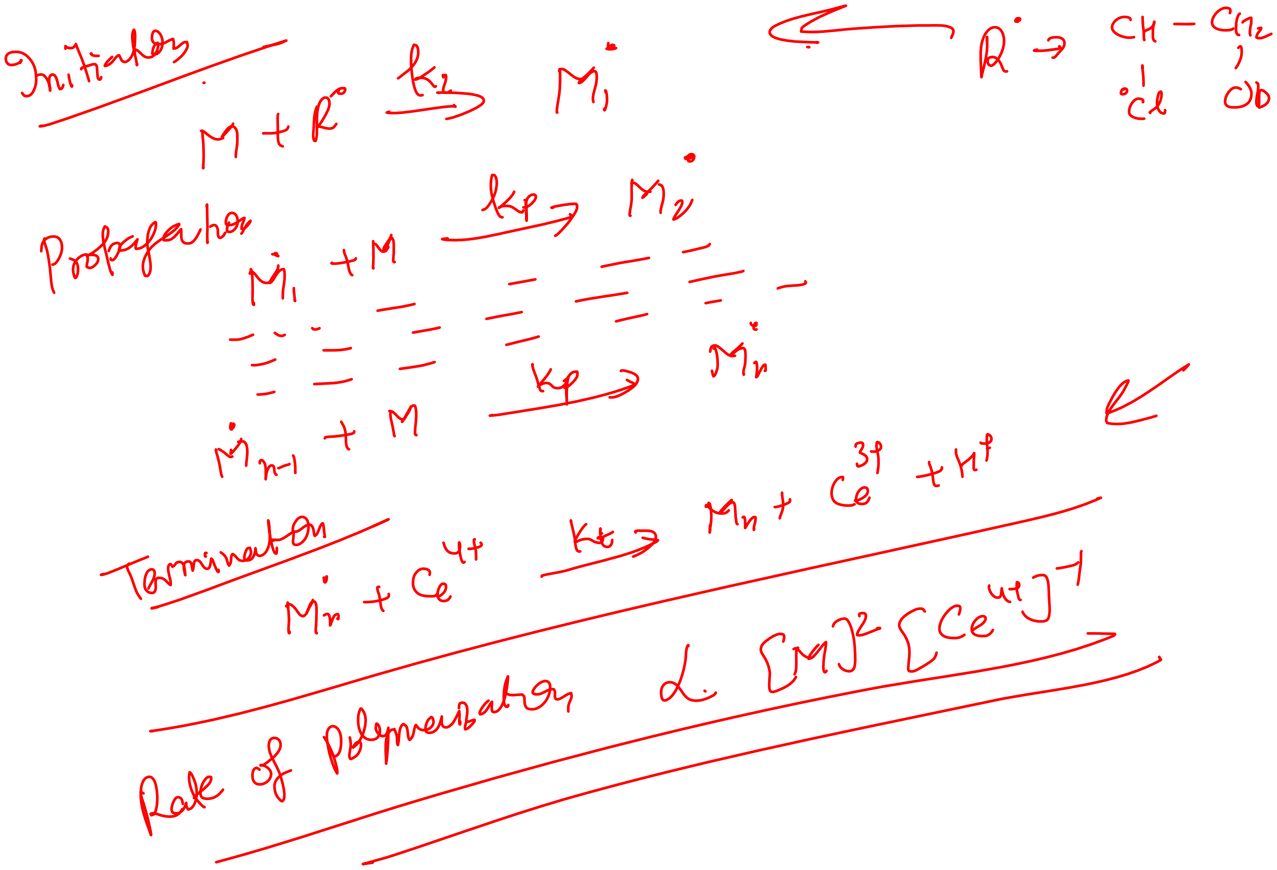

Initiation

$M + R^\bullet \xrightarrow{k_2} M_1^\bullet \leftarrow R^\bullet \to \underset{^\bullet Cl}{CH} - \underset{OH}{CH_2}$

Propagation

$M_1^\bullet + M \xrightarrow{k_p} M_2^\bullet$

$- - - - - - - - -$

$M_{n-1}^\bullet + M \xrightarrow{k_p} M_n^\bullet$

Termination

$M_n^\bullet + Ce^{4+} \xrightarrow{k_t} M_n + Ce^{3+} + H^+$

Rate of Polymerization $\propto [M]^2 [Ce^{4+}]^{-1}$

Now, foremost importance is attributed to that termination reaction, now, termination Ce^{4+}. So, this is my termination step. So, if you see that this is the complete; this completes the polymerization process. Now, we talk about the rate of polymerization that is directly proportional to Ce^{4+}. So, this is the rate of polymerization. Now, this Ce^{4+}, they can show effective radical polymerization in the presence of chelating agent, which usually not only work as a reducing agent, but also promote the initiation process.

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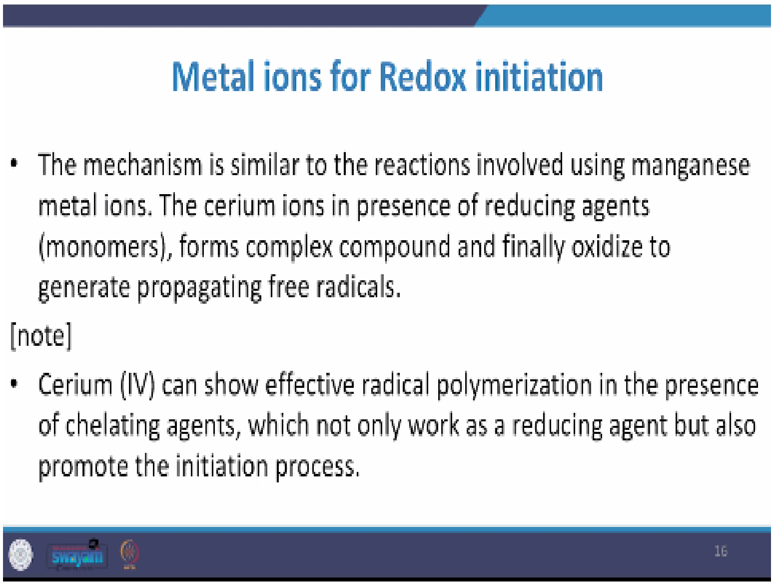

Metal ions for Redox initiation

- The mechanism is similar to the reactions involved using manganese metal ions. The cerium ions in presence of reducing agents (monomers), forms complex compound and finally oxidize to generate propagating free radicals.

[note]

- Cerium (IV) can show effective radical polymerization in the presence of chelating agents, which not only work as a reducing agent but also promote the initiation process.

So, cerium(IV), this can show the effective radical polymerization in the presence of chelating agent and sometimes do not work, it not only work as a reducing agent, but also promote the initiation process.

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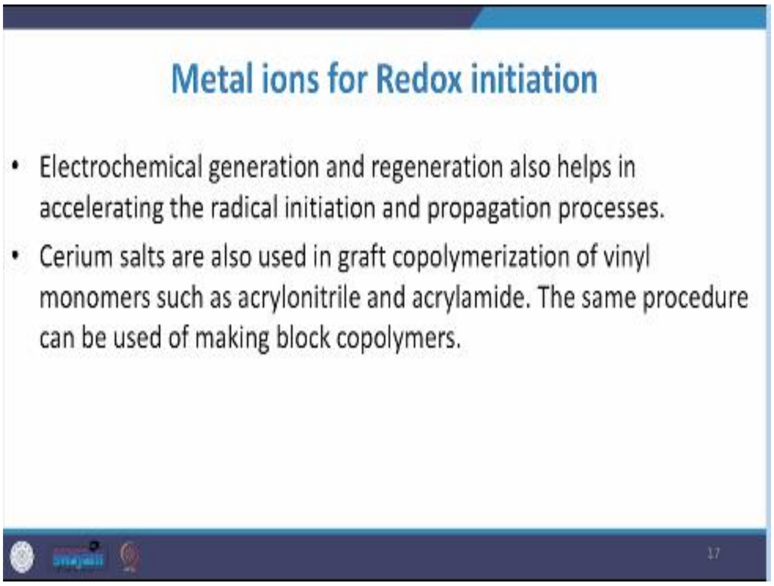

Metal ions for Redox initiation

- Electrochemical generation and regeneration also helps in accelerating the radical initiation and propagation processes.
- Cerium salts are also used in graft copolymerization of vinyl monomers such as acrylonitrile and acrylamide. The same procedure can be used of making block copolymers.

Now, you know that when we discuss about the metal ion for the Redox initiation, the electro chemical generation and regeneration, this also helps in accelerating the radical initiation and propagation process. So, the cerium salt which we discussed in the previous lecture, they are also used in the graft copolymerization of vinyl monomer such as acrylonitrile, acrylamide and same procedure can be used for making the block copolymers.

Now, let us have another metal related to the Redox initiation process that is cobalt. Now, it is a very strong oxidising agent and it is used to generate the OH radicals from hydroxyl ion and other organic compounds.

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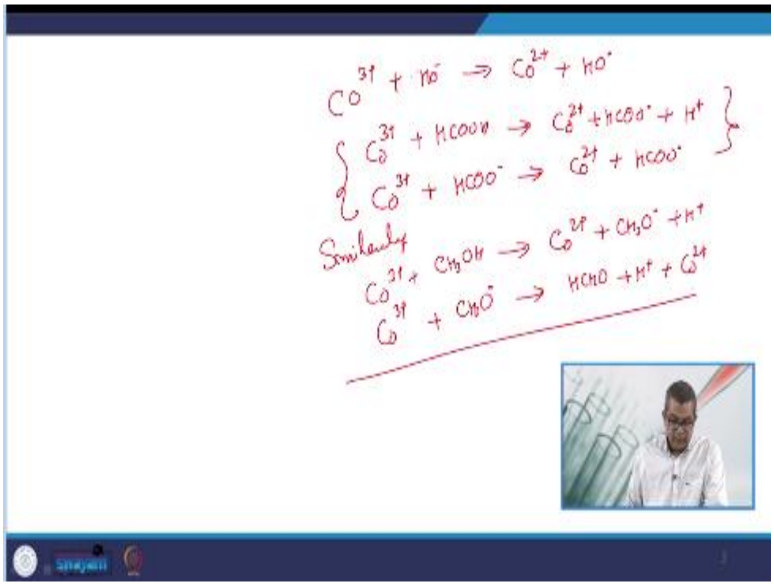


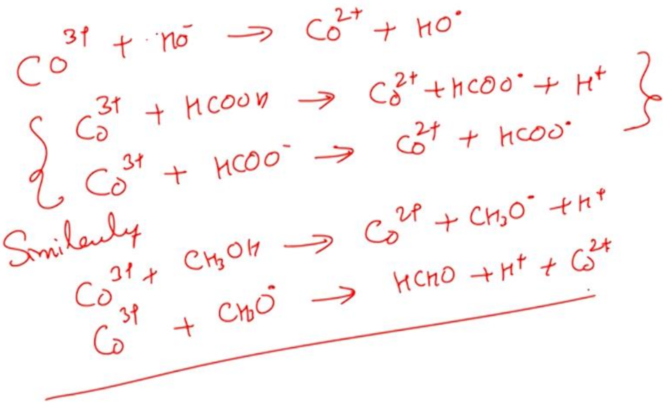
$$Co^{3+} + HO^- \rightarrow Co^{2+} + HO^\bullet$$

$$\left\{\begin{array}{l} Co^{3+} + HCOOH \rightarrow Co^{2+} + HCOO^\bullet + H^+ \\ Co^{3+} + HCOO^- \rightarrow Co^{2+} + HCOO^\bullet \end{array}\right\}$$

Similarly

$$Co^{3+} + CH_3OH \rightarrow Co^{2+} + CH_3O^\bullet + H^+$$

$$Co^{3+} + CH_3O^\bullet \rightarrow HCHO + H^+ + Co^{2+}$$



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Similarly

$$Co^{3+} + CH_3OH \rightarrow Co^{2+} + CH_3O^\bullet + H^+$$

$$Co^{3+} + CH_3O^\bullet \rightarrow HCHO + H^+ + Co^{2+}$$

So, this is the way through which we can proceed further.

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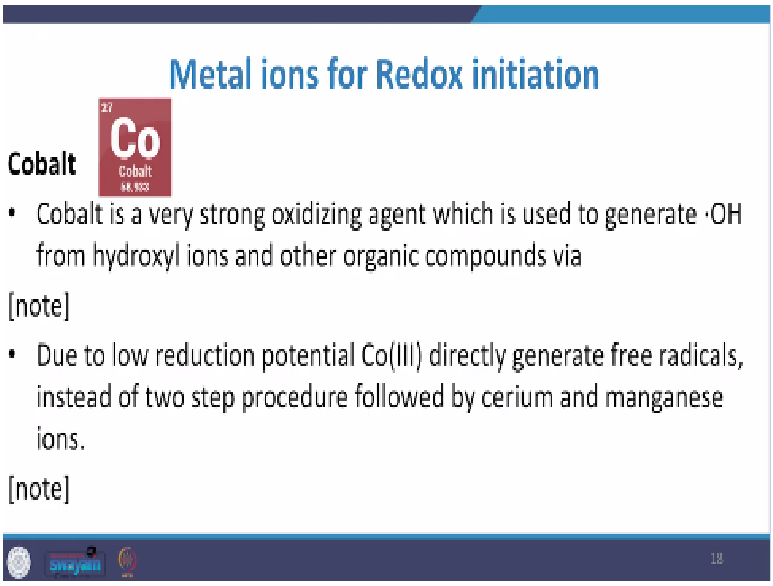

Metal ions for Redox initiation

Cobalt

- Cobalt is a very strong oxidizing agent which is used to generate ·OH from hydroxyl ions and other organic compounds via

[note]

- Due to low reduction potential Co(III) directly generate free radicals, instead of two step procedure followed by cerium and manganese ions.

[note]

Now, due to low reduction potential of this Co(III) ion, this directly generate the free radical in a sort of 2 step procedure which we discussed in case of a cerium and manganese ions in the previous lecture. Now, let us have a look about this particular thing.

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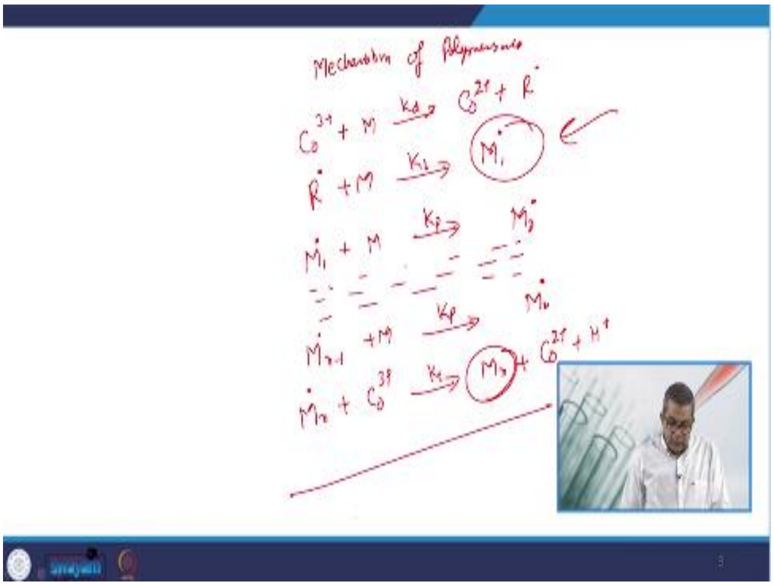


Mechanism of Polymerisation

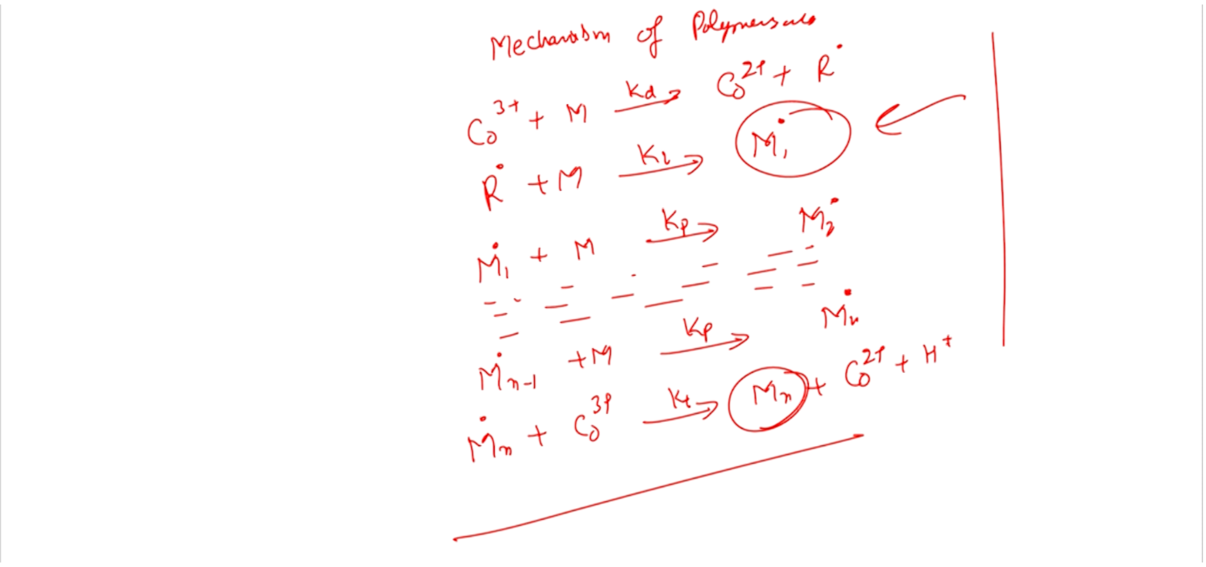
$$Co^{3+} + M \xrightarrow{k_d} Co^{2+} + \dot{R}$$

$$\dot{R} + M \xrightarrow{k_i} \boxed{\dot{M}_1}$$

$$\dot{M}_1 + M \xrightarrow{k_p} \dot{M}_2$$

$$\dot{M}_{n-1} + M \xrightarrow{k_p} \dot{M}_n$$

$$\dot{M}_n + Co^{3+} \xrightarrow{k_t} \boxed{M_n} + Co^{2+} + H^+$$



Mechanism of Polymerisation

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$\dot{M}_1 + M \xrightarrow{K_p} \dot{M}_2$

$\dot{M}_{n-1} + M \xrightarrow{K_p} \dot{M}_n$

$\dot{M}_n + Co^{3+} \xrightarrow{K_t} M_n + Co^{2+} + H^+$

This radical being generated. Now, this can initiate the polymerization process or a polymerization reaction for that and propagate the things as per our requirement. Now, here you see that we are using the K_p for the propagation.

Now, similarly, this becomes M, this one. So, after this when we try to see that what is the protocol for that termination of this particular polymerization reaction. Then again we need to help this cobalt and you see that Co^{3+}. It may get combined to give you Mn + Co^{2+} + H^+. So, this is my desired polymer. So, by this way you can see that we discussed about the mechanism of polymerization attributed to this cobalt Redox initiation.

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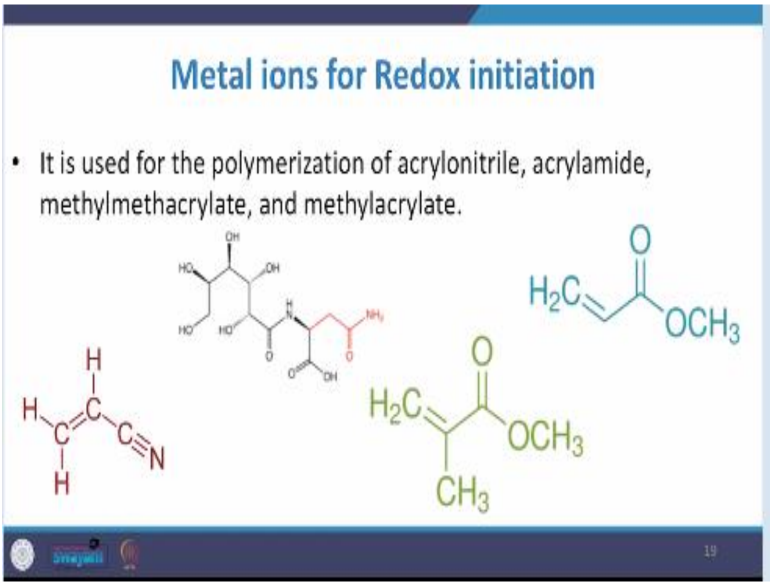

Metal ions for Redox initiation

- It is used for the polymerization of acrylonitrile, acrylamide, methylmethacrylate, and methylacrylate.

Now, it usually when we talk about the uses the polymerization of acrylonitrile, acrylamide, methyl methacrylate and methylacrylate. So, these are the various reaction schemes through which we can proceed for this polyacrylonitrile, polyacrylamide, polymethyl methacrylate and polymethylacrylate. So, these are the various things can be used and these are the various structure to be useful for this kind of Redox initiation.

Now, let us have a look about the initiation aspect in non-aqueous media which is our, you can say the foremost thing because previously we discussed about the initiation in aqueous media. So, organic peroxide usually in the presence of a strong reducing agent, like sometimes tertiary amine, formic acid, sulphonic acid, hydrogen hydrate, they can combine to generate free radicals and cationic species like you can see in this particular figure.

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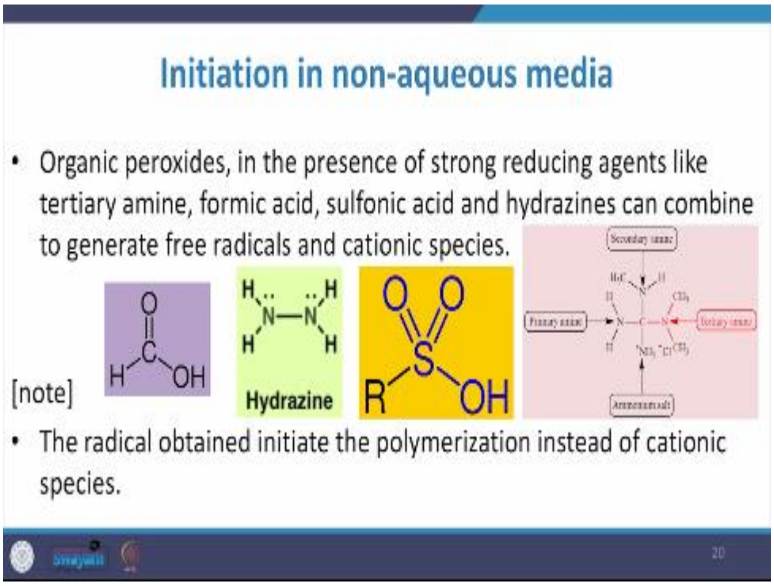

Initiation in non-aqueous media

- Organic peroxides, in the presence of strong reducing agents like tertiary amine, formic acid, sulfonic acid and hydrazines can combine to generate free radicals and cationic species.

[note]

- The radical obtained initiate the polymerization instead of cationic species.

Now, these radicals, they obtain initiate the polymerization in a state of a cationic species. So, let us have a look about the certain polymerization scheme attributed to this non-aqueous polymerization.

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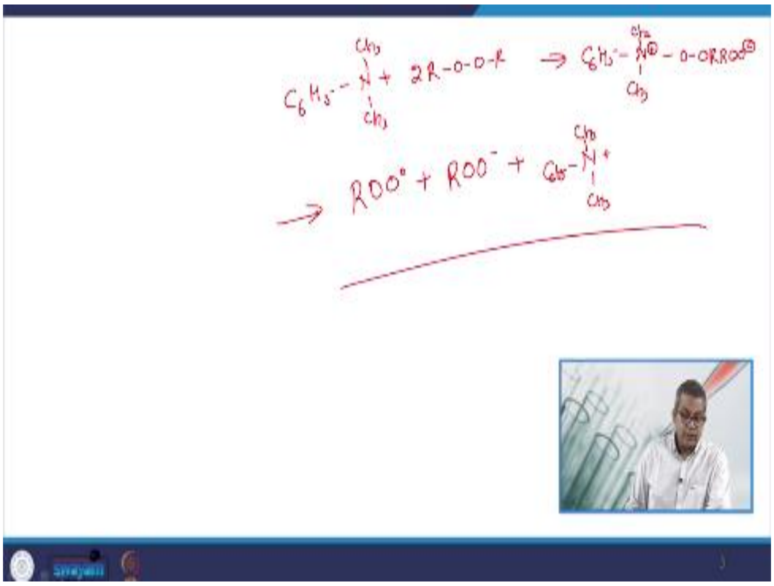
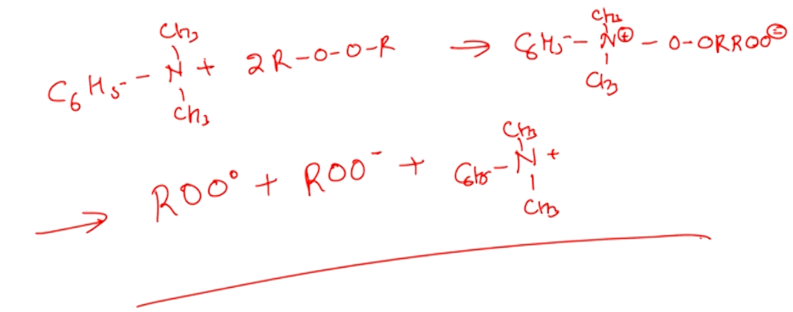


$$C_6H_5-\overset{CH_3}{\underset{CH_3}{N}} + 2R-O-O-R \rightarrow C_6H_5-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-O-ORROO^{\ominus}$$

$$\rightarrow ROO^{\circ} + ROO^{-} + C_6H_5-\overset{CH_3}{\underset{CH_3}{N}}{}^{+}$$

Now, here let us take this example



$$C_6H_5-\overset{CH_3}{\underset{CH_3}{N}} + 2R-O-O-R \rightarrow C_6H_5-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-O-ORROO^{\ominus}$$

$$\rightarrow ROO^{\circ} + ROO^{-} + C_6H_5-\overset{CH_3}{\underset{CH_3}{N}}{}^{+}$$

So, first step and then if you see that this is the Redox reaction under this non-aqueous media, this becomes; now, this is the polymerization process protocol for non-aqueous media. Now, this radicals which we discussed that they obtain they can initiate the polymerization process instead of cationic species.

Now, the propagating radicals those who are generally found to be terminated only through interaction with another propagating radical, but not with the initiating radicals. So, apart from peroxide, the transition metals, metal halide Redox system, they can also initiate the radical polymerization in non-aqueous media. These transition metal compounds, they need to be initiated by ligand transfer or a bonds season reaction to initiate the Redox reaction.

We will discuss this thing sometimes later. Now, the list of those organic and inorganic compound and metal ion used for the Redox polymerization is very vast and one cannot easily conclude that particular list, but from the discussion which we had carried out earlier, we can understand that the basic mechanism for Redox radical polymerization is more or less similar and can be understand through the rate of polymerization equation.

Now, let us have a look about the rate of Redox polymerization, because we had a discussion about the initiation part; we had a discussion about the aqueous and non-aqueous media, initiation steps in aqueous and non-aqueous media. Now, we discussed the mechanism the entire mechanism. Now, it is time to have a discussion about the rate of Redox polymerization.

So, the kinetics of polymerization usually triggered by Redox and typically fall into 2 groups depending on the termination mode. Now, in terms of propagation and termination step, many of these polymerization proceeds in the same way as other polymerization. So, the initiation and of course, the radical generation step is quite different. Now, if you compare with the thermal initiation one electron reaction occur in Redox initiation which leads to the production of a single radical at a time in a state of 2 radicals.

Therefore, the dependency of monomer concentration should be reduced to the factor of 1. Now, let us have a discussion or we say that the initiation propagation rates.

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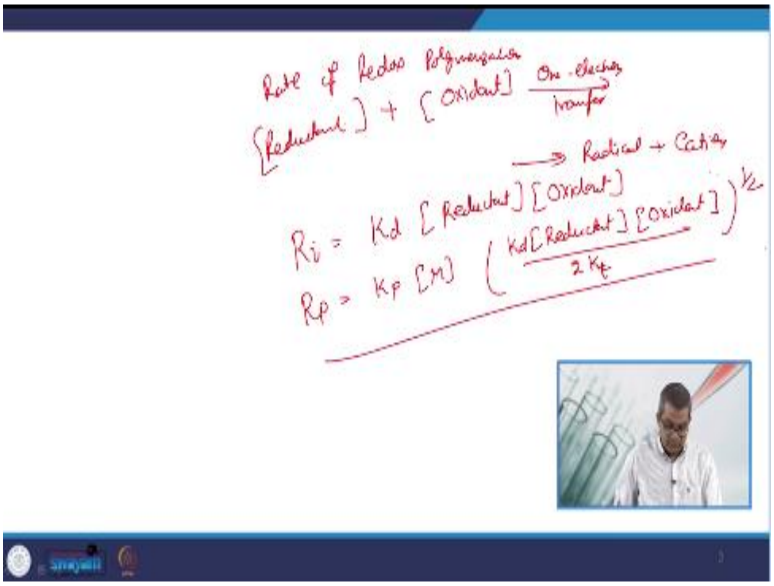


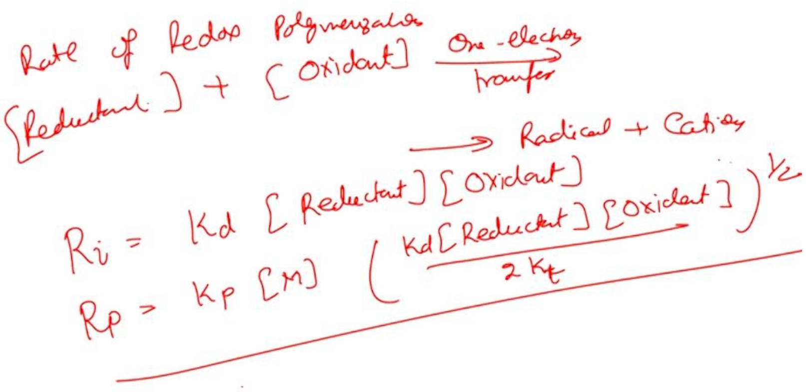
Rate of Redox Polymerization

$$[\text{Reductant}] + [\text{Oxidant}] \xrightarrow[\text{transfer}]{\text{One electron}} \text{Radical} + \text{Cation}$$

$$R_i = K_d\,[\text{Reductant}][\text{Oxidant}]$$

$$R_p = K_p\,[M]\left(\frac{K_d[\text{Reductant}][\text{Oxidant}]}{2K_t}\right)^{1/2}$$

We can write like this that is we are discussing that rate of Redox polymerization. Now, here is reductant and plus it combined with oxidants. So, here one electron transfer; it may become the radical plus cation.



Rate of Redox Polymerization

$$[\text{Reductant}] + [\text{Oxidant}] \xrightarrow[\text{transfer}]{\text{One-electron}} \text{Radical} + \text{Cation}$$

$$R_i = K_d\,[\text{Reductant}]\,[\text{Oxidant}]$$

$$R_p = K_p\,[M]\left(\frac{K_d\,[\text{Reductant}]\,[\text{Oxidant}]}{2K_t}\right)^{1/2}$$

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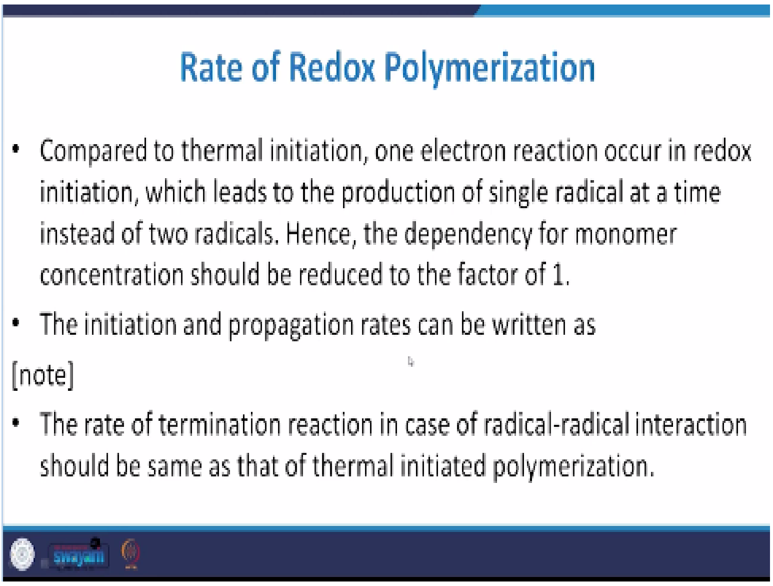

Rate of Redox Polymerization

- Compared to thermal initiation, one electron reaction occur in redox initiation, which leads to the production of single radical at a time instead of two radicals. Hence, the dependency for monomer concentration should be reduced to the factor of 1.
- The initiation and propagation rates can be written as

[note]

- The rate of termination reaction in case of radical-radical interaction should be same as that of thermal initiated polymerization.

Now, the rate of termination reaction in case of radical-radical interaction, it should be same as that of thermally initiated polymerization. Now, for the case of termination occurred due to the metal ion, the rate of termination can be written like this.

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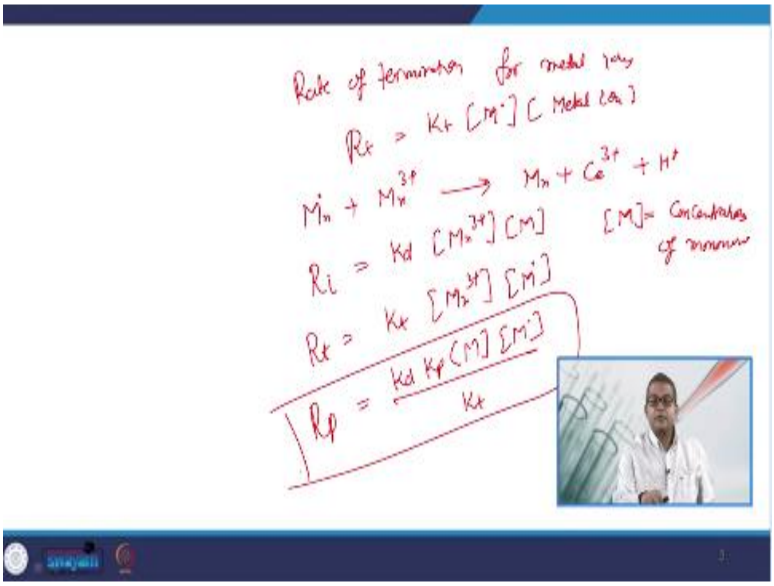


Rate of termination for metal ions

$R_t = K_t [M^{\cdot}][\text{Metal ion}]$

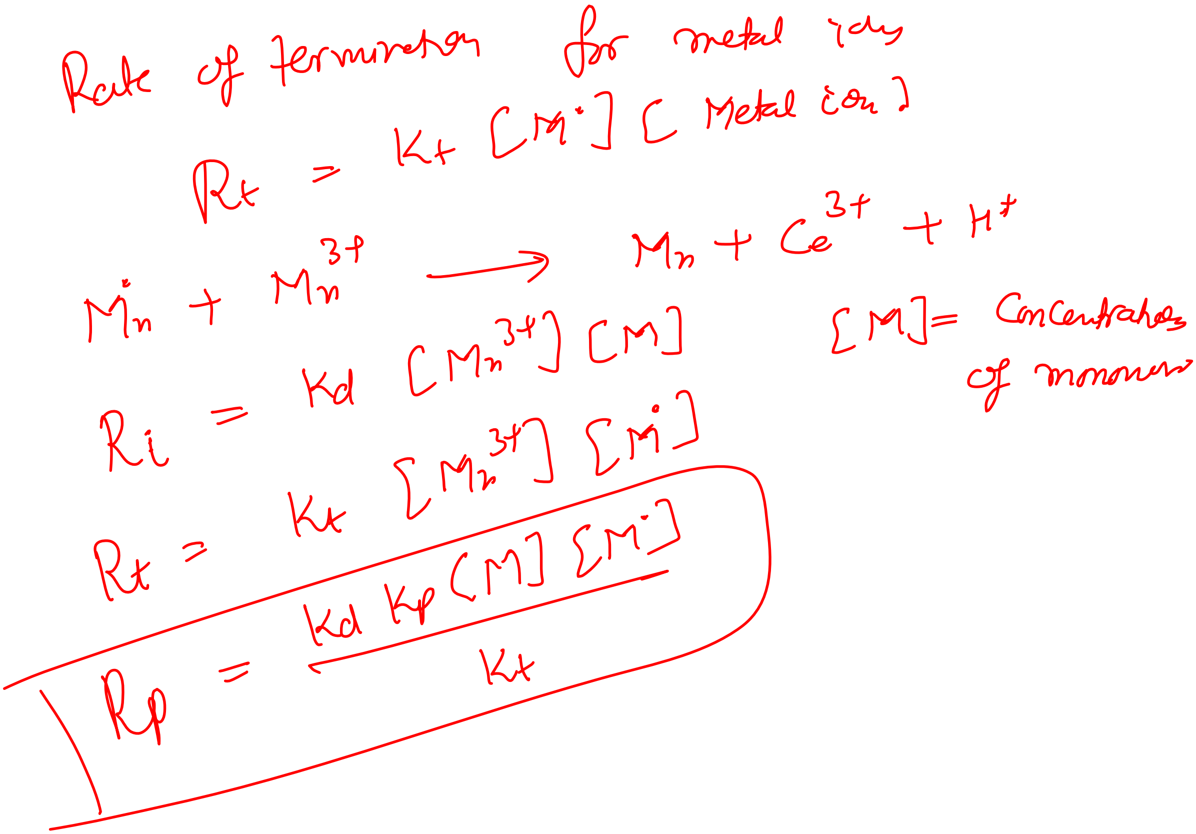
$\dot{M}_n + M_n^{3+} \longrightarrow M_n + Ce^{3+} + H^+$

$R_i = K_d [M_n^{3+}][M]$ [M]= Concentration of monomer

$R_t = K_t [M_n^{3+}][M^{\cdot}]$

$$\boxed{R_p = \frac{K_d K_p [M][M^{\cdot}]}{K_t}}$$

So, let us put that rate of termination for metal ions



Rate of termination for metal ions

$R_t = K_t [M^{\cdot}][\text{Metal ion}]$

$\dot{M}_n + M_n^{3+} \longrightarrow M_n + Ce^{3+} + H^+$

$R_i = K_d [M_n^{3+}][M]$ [M]= Concentration of monomer

$R_t = K_t [M_n^{3+}][M^{\cdot}]$

$$\boxed{R_p = \frac{K_d K_p [M][M^{\cdot}]}{K_t}}$$

So, this is my equation which is the desired one in this case.

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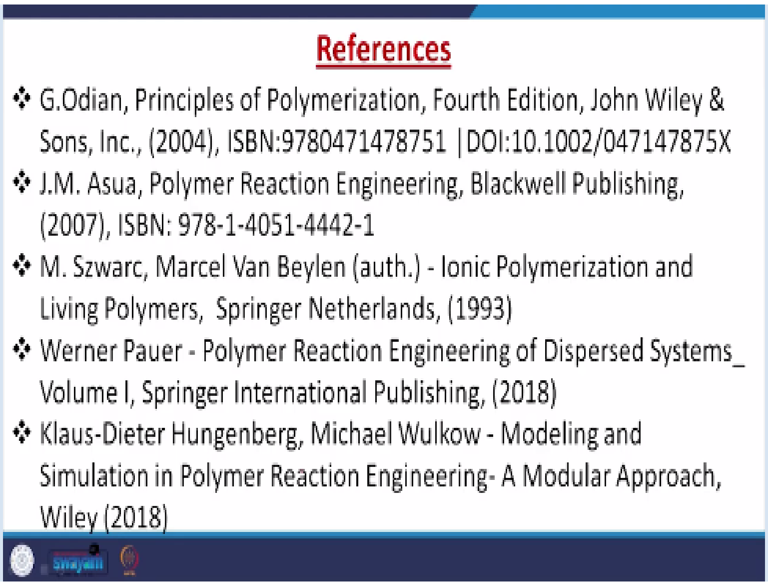

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So, in this particular lecture, we discussed about the importance of metal ions for Redox initiation. We discussed about different kind of a mechanism attributed to this initiation step especially giving emphasis to the non-aqueous media. We will carry on this particular discussion in the subsequent lecture. Thank you very much.