Polymer Reaction Engineering
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Lecture – 40
Radical Chain Polymerization Half Life, Propagation & Termination - II

Welcome to the chapter of half life, propagation and termination, Part 2 under the head of radical chain polymerization. So, if you recall that in the previous lecture we have studied about the stability and half life of different initiator.

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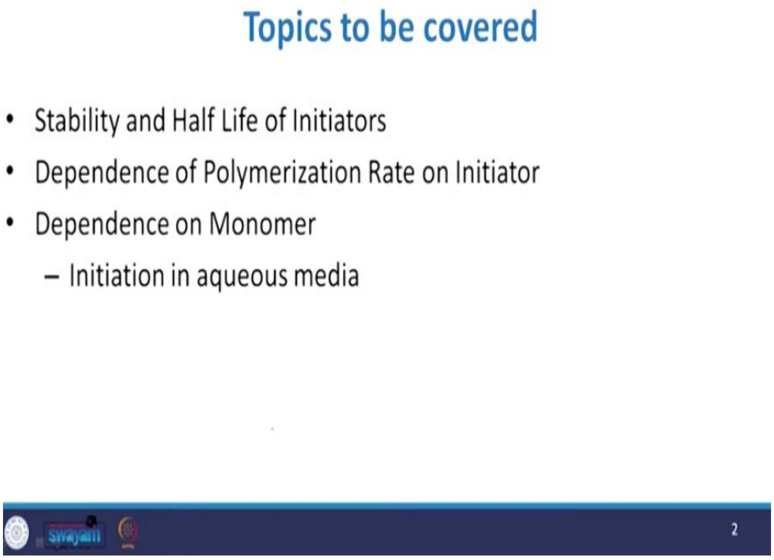

Topics to be covered

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

We discussed about the mathematical equations which are attributed to the half life of different initiator. We had a discussion about the dependency of polymerization rate on initiator how these initiator play a vital role in the determining steps of polymerization process. We are discussing about the dependency on monomer with respect to the initiation in the aqueous media.

So, and in that particular aegis, we were discussing about the redox reaction which are very important in the polymeric system. Let us continue with this particular topic which is attributed to the redox initiation. So, we can say that virtually all radical chain polymerization reaction they require a unique and independent initiation step in which free radicals are generated in the reaction system.

If you recall the previous lecture, we discussed about the generation concept of those free radicals as well as what are the importance of those free radicals especially in the propagation especially in the with respect to the termination step. So, that is why they require a unique and independent initiation step. Now, this initiation step is very critical and the activation energy barriers they play a very important role during the selection of initiator compound.

Because sometimes the question may be triggered in our mind that what are the selection criteria for the different kind of initiation? Though we have discussed several issues related to this in the previous lecture. But sometimes if you say that activation energy barriers they play a very vital role, so, the type of initiation process to be used for a specific polymerization process usually being determined by the activation energy barrier concept.

+, what kind of a different initiator you are using for your polymerization system? Now, we had a discussion about the bond dissociation energy attributed to the initiator so that the free radicals may get generated in due course of time. So, the bond dissociation energy limit for various covalent breakage may be in the range of say 100 to 170 kilojoules per mole through the thermal initiation reaction.

Now, this energy limit is very low or very narrow. Therefore, it limits the use of various compounds having activation energy above or below this limit. So, this is one of the limiting factor which you can say for the choice of initiator. Now, second important parameter which we would like to discuss is that the concentration of a free radical present in the process which if increased to a substantial amount can lead to unwanted reaction such as primary termination or self-combination.

Now, these 2 things as you recall that they are very important especially in case of polymerization process. Now, because sometimes they may not perform the duty of initiation for which they are designed to because of the primary termination. And sometimes they may go for self-combination so that practically they are dead in nature. So, that is why this concentration role play a very vital role.

And if you recall in the previous lecture, we discussed the k i which is the rate constant for the initiator the concentration of free radical. So, you have to be very particular about this aspect that is attributed to the concentration of free radical. Now, let us have look about the redox initiation. Now, redox initiation is another kind of initiation phenomena where electron transfer carried out between the 2 molecules through oxidation, reduction, reaction.

And then the bond dissociation may occur at the acceptor molecule to generate the free radical. This again pose one more opportunity for the initiation of polymerization reaction. Now, redox initiation or sometimes it is termed as redox activation. It is found in several applications in the polymerization process or in the commercial scale. So, it is always favoured for conducting a low temperature emulsion polymerization.

So, more and more application it is attributed to the low temperature emulsion polymerization. Now, these redox initiators have advantage of lower activation energy. If you recall that previously we discussed about the higher activation energy concept. So, they are having the advantage of lower activation energy for initiation reaction. And they can produce radical to a substantial amount over a wide range of temperature range.

So, they are having very wide spectrum related to the polymerization reaction. Now, because of the low activation energy that is in the range of say 40 to 80 kilojoules per mole. The redox reaction or redox initiation can conduct the chemical reaction at moderate temperature range may be below 50 degree Celsius or even lower than 0 degree Celsius. So, this is one of the + point which the redox initiation process they offer.

So, this requirement of a lower activation energy usually reduces the possibility of any kind of a side chain reaction and increase the yield. So, it helps in twofold; One is that in case of a formation of any side product or any byproduct then you may encounter the problem of a separation and your yield may go down. But because of this low activation energy the possibility of formation of those side products or byproducts are minimal.

So, in that case you may it may help to increase the yield. Additionally, you may say that these reactions have a very short induction period. Hence the reaction proceeds quickly. And that is why this particular approach is very much popular in some of the industries because the short induction period offers low economic burden to the industry. Now, they are having certain limitations too. Like lower efficiency than the thermal initiation.

And that is again a very challenging approach and complex control of initiator because we discussed that initiator play a very vital role. And especially sometimes they may induced for the self-combination. They may induce the dead of to promote the deadly character of monomer radical. So, the control of those initiator is extremely important in that particular approach. These redox reactions have certain limitations.
Sometimes the addition of charged metal ion and counter ion can affect the electrostatic stability of the system. So, these reactions are also the pH sensitive. So, therefore usually weak acids are used for performing any chemical reaction. Now, the pH sensitivity is again posing some limitation to these type of reaction. Because sometimes you are using certain acidic media certain base media for to carry out the polymerization reaction.

So, you have to be very particular. You have to be very case sensitive. You have to be very cautious while carrying out this type of initiation reaction under the aegis of radical chain polymerization. So, these type of things are extremely important to be look into. Now, let us move to the initiation process in the aqueous media. So, we will discuss several aspects related to the this aqueous media because aqueous media plays a very vital role in the radical chain polymerization.

So, first step in this category is lead to the peroxide concept. Now, hydrogen peroxide H_2O_2 is a well-known and very commonly used chemical for the production of hydroxyl free radical. See in the previous lecture we had a discussion about this concept of hydroxyl free radicals. And, how they facilitate the radical chain polymerization? So, this hydrogen peroxide they are it is a very common chemical used for the production of such kind of a free radical.

These hydroxyl radicals they have a very high oxidation potential around 2.8 volt. Hence we can use as a chemical in wastewater treatment for mineralizing various persistent pollutants etcetera. So, it is a very common thing for as a bleaching agent in the chemical operation or a chemical processes. Fenton reagent again which is combination of a ferrous salt and hydrogen peroxide. It was discovered in J H Fenton in 1894.

Now, he reported that the hydrogen peroxide can be activated by a ferrous salt to oxidize tartaric acid. So, this was a very good study and it attributed for the major problem in the wastewater paraphernalia. Now, it involves the reaction of peroxides with iron ions to form the active oxygen species. Now, let us discuss some of the reactions which can better show the mechanism what kind of mechanism involved.

And these mechanisms are equally important in the polymer reaction engineering especially with respect to the radical chain polymerization.

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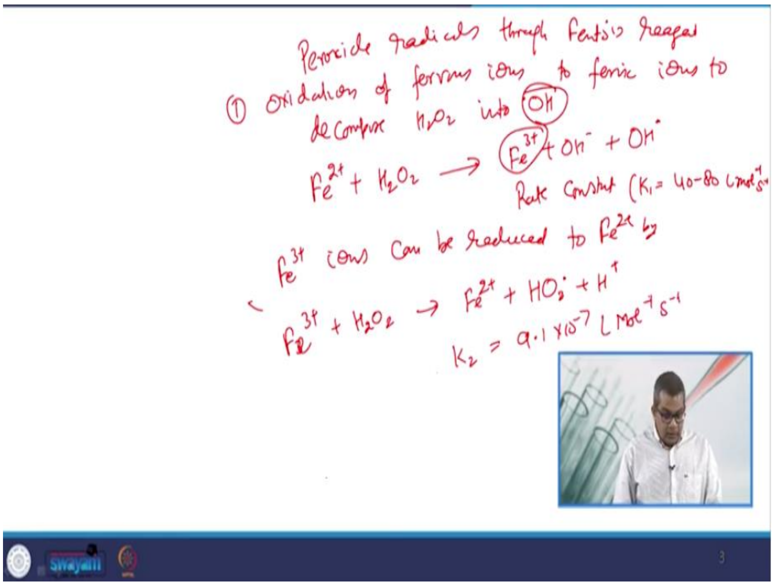

Peroxide radicals through Fenton's reagent

① oxidation of ferrous ions to ferric ions to decompose H_2O_2 into $\boxed{OH}$

$Fe^{2+} + H_2O_2 \rightarrow \boxed{Fe^{3+}} + OH^- + OH^\bullet$

Rate Constant (K_1 = 40-80 L mol^{-1} s^{-1}

Fe^{3+} ions can be reduced to Fe^{2+} by

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+$

$K_2 = 9.1 \times 10^{-7}$ L mol^{-1} s^{-1}

Now, this is the peroxide radicals through Fenton's reagent. Now, let us take first example. That is the oxidation of ferrous ions to ferric ions to decompose H_2O_2. So, if you recall that our main intention is to produce this hydroxyl radicle. Now, here this Fe^{2+} + H_2O_2 this gives you Fe^{2+} + OH^- + $OH\bullet$. Now, here the rate constant that is K_1 is somewhere around 40 to 80 mole inverse second inverse.

Now, this generated Fe^{3+} ions can be reduced to Fe^{2+} by

Fe^{3+} + H_2O_2 gives Fe^{2+} + $HO_2\bullet$ + H^+

Now, here the rate constant K_2 is around 9.1 into 10^{-7}.

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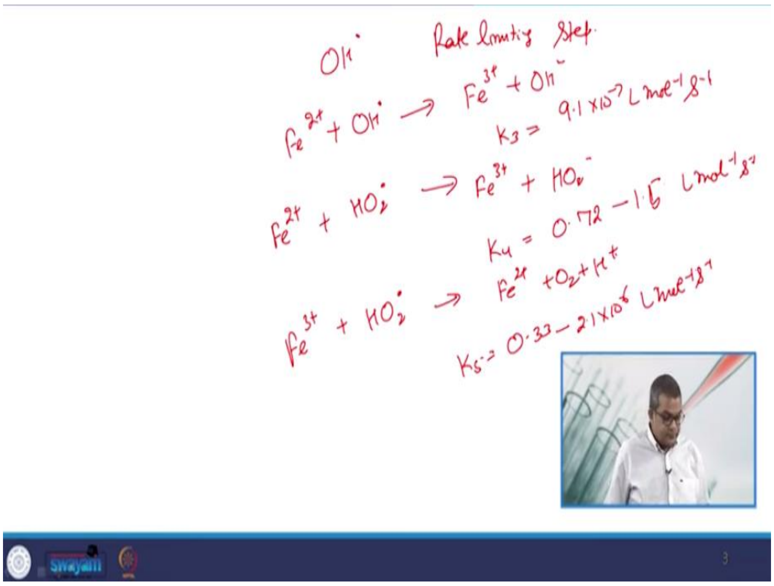

$OH^\bullet$ Rate limiting step.

$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^-$

$K_3 = 9.1 \times 10^{-7}\ L\ mol^{-1}\ s^{-1}$

$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^-$

$K_4 = 0.72 - 1.5\ L\ mol^{-1}\ s^{-1}$

$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+$

$K_5 = 0.33 - 2.1 \times 10^{6}\ L\ mol^{-1}\ s^{-1}$

Now, the rate limiting step where this OH• radical can be consumed this can be written as whenever we talk about the rate limiting step then it can be

$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^-$

Now, here the rate constant is $K_3 = 9.1 \times 10^{-7}$ Lmol^{-1}s^{-1}.

Now, this another $Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^-$

Now, here the rate constant can be written as 0.72 -1.5 Lmole^{-1} s^{-1}.

Now, $Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+$

So, another rate constant which is in the range of 0.33 - 2.1 X 10^{-6} l mol^{-1} S^{-1}.

So, this is now if you see that the generated radicals.

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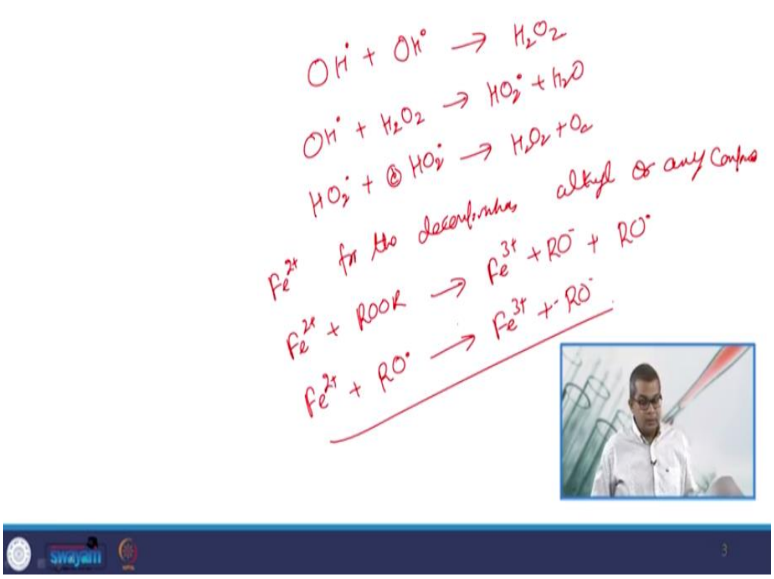

$OH^\bullet + OH^\bullet \rightarrow H_2O_2$

$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O$

$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$

Fe^{2+} for the decomposition alkyl or any Compo

$Fe^{2+} + ROOR \rightarrow Fe^{3+} + RO^- + RO^\bullet$

$Fe^{2+} + RO^\bullet \rightarrow Fe^{3+} + RO^-$

$OH^{\circ} + OH^{\circ} \rightarrow H_2O_2$

$OH^{\circ} + H_2O_2 \rightarrow HO_2^{\circ} + H_2O$

$HO_2^{\circ} + HO_2^{\circ} \rightarrow H_2O_2 + O_2$

Fe^{2+} for the decomposition alkyl or any compound

$Fe^{2+} + ROOR \rightarrow Fe^{3+} + RO^{-} + RO^{\circ}$

$Fe^{2+} + RO^{\circ} \rightarrow Fe^{3+} + RO^{-}$

That is and can also react among themself or with H_2O_2 to produce less oxidation potential compounds. So, whatever we have generated in the previous equations they can also react on their own to form either H_2O_2 or other less oxidation potential compound. Like this that OH radical may combine with this radical to give you H_2O_2. Similarly, OH• radical may combine this hydrogen peroxide which generated over here to give you this radical.

And similarly another option is $H_2O_2 + O_2$. So, these radicals although they produced during the course of this combination, but they are very less effective, compared to the previous one. So, similarly, if as discussed for H_2O_2 this Fe^{2+} ion can also be used for the decomposition of alkyl or any -ayl compounds.

So, this is the basic concept or basic mechanism of a Fenton mechanism which we discussed here.

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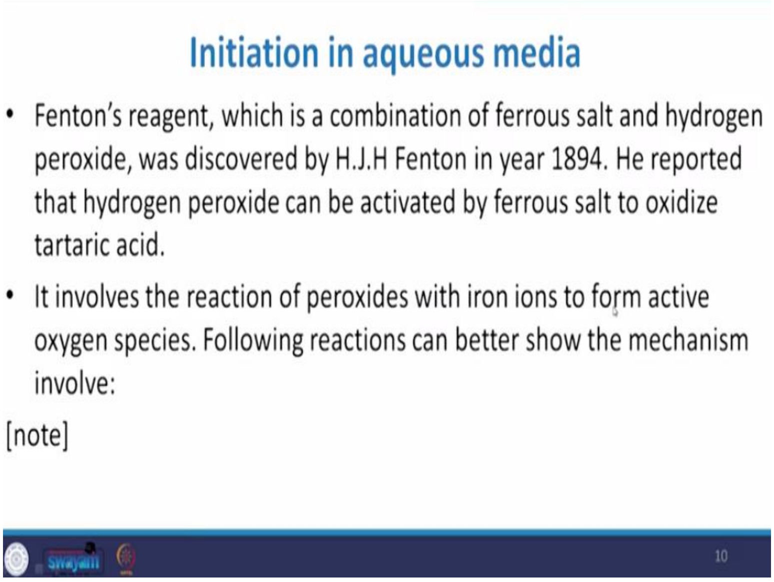

Initiation in aqueous media

- Fenton's reagent, which is a combination of ferrous salt and hydrogen peroxide, was discovered by H.J.H Fenton in year 1894. He reported that hydrogen peroxide can be activated by ferrous salt to oxidize tartaric acid.
- It involves the reaction of peroxides with iron ions to form active oxygen species. Following reactions can better show the mechanism involve:

[note]

And if you see that this particular concept is extremely useful in radical chain polymerization. Now, apart from this another important concept is attributed to the persulfate. Now, which the similar type of reaction which we discussed previously they can occur for various disulfides persulfates and elemental hydrogen compounds. Now, let us have a look about this particular approach like for the persulfate.

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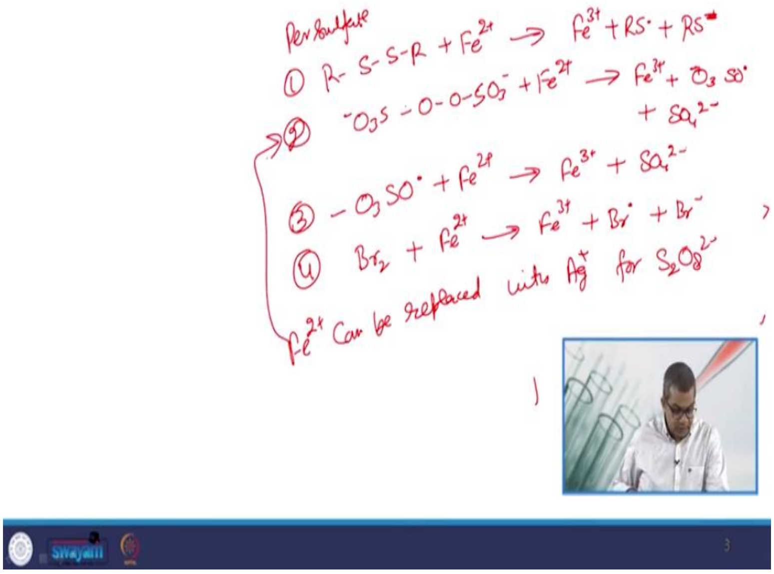

Persulfate

① $R-S-S-R + Fe^{2+} \rightarrow Fe^{3+} + RS^{\cdot} + RS^{-}$

② $^{-}O_3S-O-O-SO_3^{-} + Fe^{2+} \rightarrow Fe^{3+} + {}^{-}O_3SO^{\cdot} + SO_4^{2-}$

③ $-O_3SO^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}$

④ $Br_2 + Fe^{2+} \rightarrow Fe^{3+} + Br^{\cdot} + Br^{-}$

Fe^{2+} Can be replaced with Ag^{+} for $S_2O_8^{2-}$

Persulfate

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④ $Br_2 + Fe^{2+} \rightarrow Fe^{3+} + Br^{\cdot} + Br^{-}$

Fe^{2+} can be replaced with Ag^{+} for $S_2O_8^{2-}$

So, sometimes this Fe^{2+} which you can be replaced with silver ion for $S_2O_8^{2-}$ in this equation.

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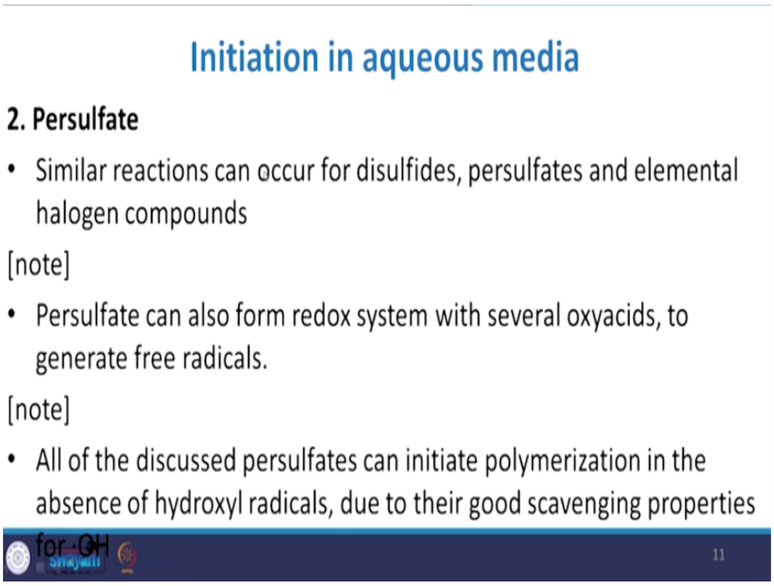

Initiation in aqueous media

2. Persulfate

- Similar reactions can occur for disulfides, persulfates and elemental halogen compounds

[note]

- Persulfate can also form redox system with several oxyacids, to generate free radicals.

[note]

- All of the discussed persulfates can initiate polymerization in the absence of hydroxyl radicals, due to their good scavenging properties for ·OH

This is again a very important thing. So, these persulfates they can also form the redox system with the several oxy acids to generate the free radicals and which we discussed that persulfate can initiate the polymerization reaction in the absence of hydroxyl radicals due to their good scavenging properties. Let us give an example related to this particular concept and in continuation with the previous handout.

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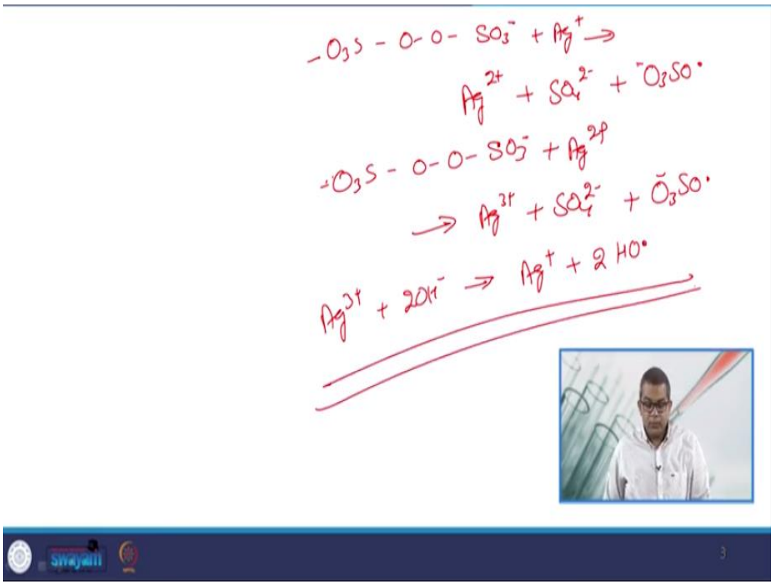

$$^{-}O_3S-O-O-SO_3^{-} + Ag^{+} \rightarrow Ag^{2+} + SO_4^{2-} + {}^{-}O_3SO^{\bullet}$$

$$^{-}O_3S-O-O-SO_3^{-} + Ag^{2+} \rightarrow Ag^{3+} + SO_4^{2-} + {}^{-}O_3SO^{\bullet}$$

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

$$^{-}O_3S-O-O-SO_3^{-} + Ag^{+} \rightarrow Ag^{2+} + SO_4^{2-} + {}^{-}O_3SO^{\bullet}$$

$$^{-}O_3S-O-O-SO_3^{-} + Ag^{2+} \rightarrow Ag^{3+} + SO_4^{2-} + {}^{-}O_3SO^{\bullet}$$

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

Now, this is again produced the radical which is again very important thing need to be addressed. Now, we were discussing about the persulfate with oxy acids. So, let us have another example related to this.

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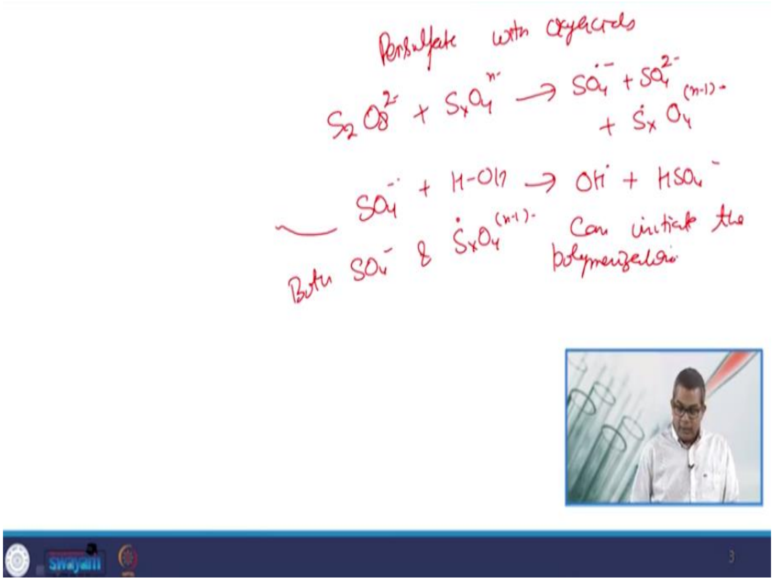

Persulfate with oxyacids

$S_2O_8^{2-} + S_xO_4^{n-} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + \dot{S}_xO_4^{(n-1)-}$

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

Both $SO_4^{\cdot -}$ & $\dot{S}_xO_4^{(n-1)-}$ can initiate the polymerization

Persulfate with oxyacids

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

Both $SO_4^{\cdot -}$ & $\dot{S}_xO_4^{(n-1)-}$ can initiate the polymerization

That is persulfate with oxy acids. So, this is the way through which you can represent.

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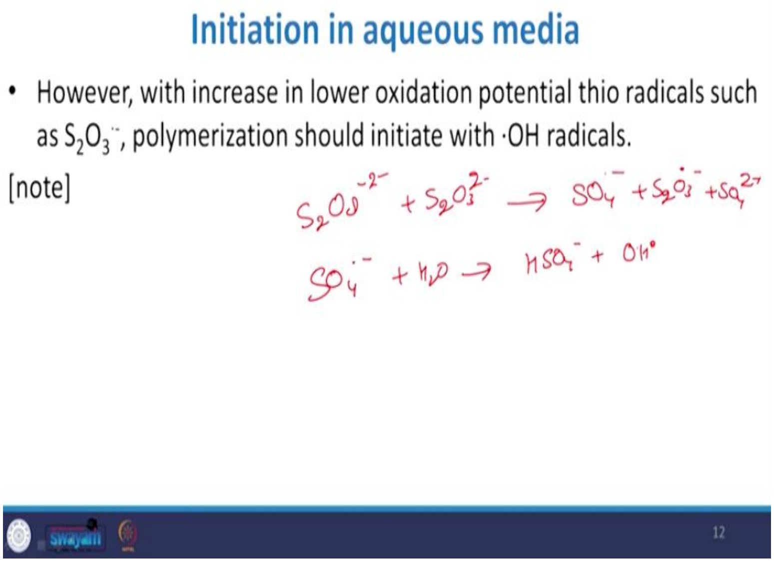

Initiation in aqueous media

- However, with increase in lower oxidation potential thio radicals such as $S_2O_3^{\cdot -}$, polymerization should initiate with ·OH radicals.

[note]

$$S_2O_8^{2-} + S_2O_3^{2-} \rightarrow SO_4^{\cdot -} + S_2O_3^{\cdot -} + SO_4^{2-}$$

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

Now, this however will with increase in the lower oxidation potential the thio radicals such as S 2 O 3 negatively charged, the polymerization should initiate with OH radical.

$$S_2O_8^{2-} + S_2O_3^{2-} \longrightarrow SO_4^{\cdot -} + S_2O_3^{\cdot -} + SO_4^{2-}$$

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

So, this is again this reflects the initiation process in aqueous media.

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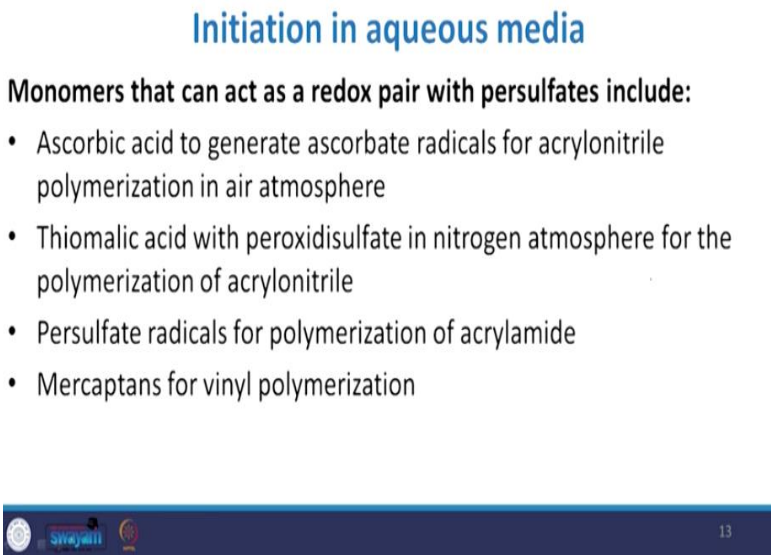

Initiation in aqueous media

Monomers that can act as a redox pair with persulfates include:

- Ascorbic acid to generate ascorbate radicals for acrylonitrile polymerization in air atmosphere
- Thiomalic acid with peroxidisulfate in nitrogen atmosphere for the polymerization of acrylonitrile
- Persulfate radicals for polymerization of acrylamide
- Mercaptans for vinyl polymerization

Now, at last we can discuss about that monomer that can act as a redox pair with persulfates include now ascorbic acid to generate ascorbate radicals for acrylonitrile polymerization in air atmosphere. It is a very useful thing and it is very important concept. Thiomalic acid with peroxidisulfate in nitrogen atmosphere for the polymerization of acrylonitrile. Then it can be used in the persulfate radicals can be used for the polymerization of acrylamide.

And mercaptans can be used for the vinyl polymerization. So, these are several examples attributed to the in which the monomer can act as a redox pair. Now, the rate of polymerization reaction usually depends upon the selection of initiator species. And we discuss this thing that what is the importance of this selection protocol during the polymerization of radical chain?

Now, let us have an example for this particular approach that if ascorbic acid peroxidisulfate redox pair is used for the polymerization of say acrylonitrile, the rate of reaction usually shows the dependency on the square of monomer concentration which we already discussed in the previous lecture that how the rate constant or rate of the reaction depends or rate of dissociation of initiator depends on?

So, the square of monomer concentration the first order of ascorbic acid and the half order of peroxidisulfate concentration so or if they have discussed this particular concept in 1985. Now, while if thiomalic acid peroxidisulfate redox pair is used for the polymerization of acrylonitrile, the rate of a reaction usually depends on the first order of monomer concentration and 0.4 on thiomalic acid and 0.6 to say 0.75 on peroxidisulfate concentration.

So, this was again discussed with the Tajuddin in 86 and they find out these values through the extensive research being carried out by them.

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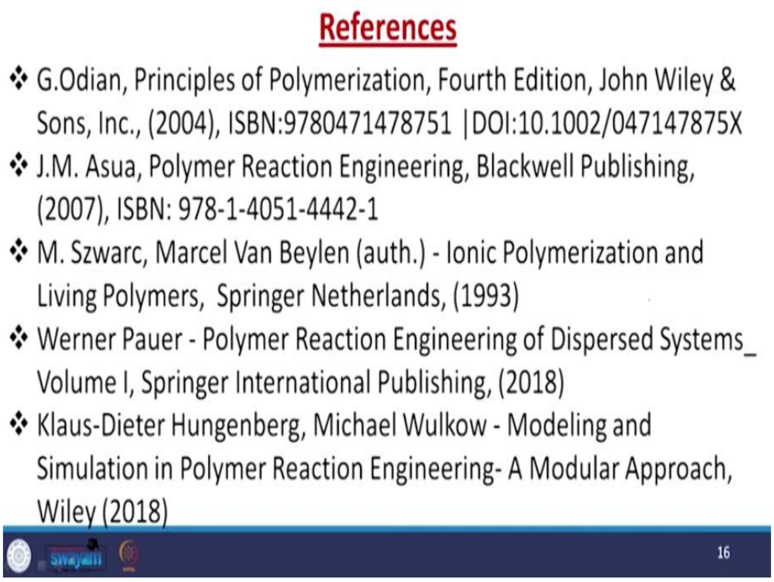

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So, in this particular lecture we discussed about the initiation under the aegis of aqueous media. We discussed the various mechanism. We discussed the various research findings being carried out by the noted workers in the said field. And if I wish to have further reading or further knowledge or wish to go into deep you can refer to these references which are enlisted in this particular slide, thank you very much.