Polymer Reaction Engineering
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Lecture – 38
Radical Chain Polymerization Process Analysis – II

Welcome to the second segment of process analysis under the head of radicle chain polymerization. Let us again have a brief look at what we are going to cover in this second segment. If you recall that we have carried out the detailed discussion of the characterization tool on various rate.

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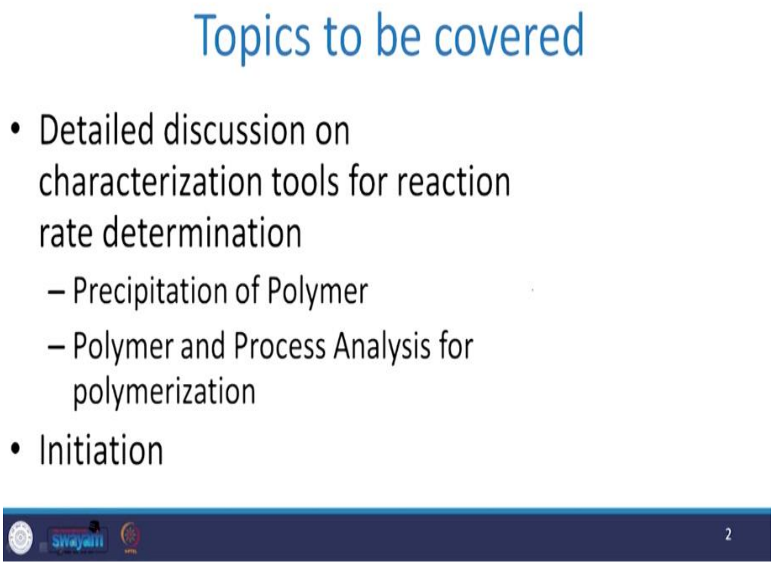

Topics to be covered

- Detailed discussion on characterization tools for reaction rate determination
  - Precipitation of Polymer
  - Polymer and Process Analysis for polymerization
- Initiation

Determining steps under the aegis of precipitation of polymer, polymer and process analysis for polymerization step. So, in the previous lecture, we discussed about the precipitation concept of polymers. And we started the discussion about the process analysis for various steps of polymerization. So, in this particular chapter, we will continue about the process analysis concept for the polymerization.

And we will discuss about the initiation process of these radical chain polymerization under the aegis of process analysis. Now, if you recall that we truncated that the point of nuclear magnetic resonance. Now, again we go to the detail about the mass spectrometry. Now, this mass spectrometry, MS or sometimes referred as MS. This can also be used especially when it is in the coupled form due to the limitation of analysis software very small fragments in mass spectrometry.

Now, this can be utilized to find out more accurate and highly quantitative analysis of various polymer samples. And in situ, it is helpful to determine the composition of those polymer samples. Now, another good instrument or instrumental analysis tool is dilatometry. This is very good technique to use for analysis of chain polymerization reaction. Now, it easily measures the change in volume during the process of polymerization.

Now, see, why we are talking about the concept of change in volume? Sometimes because of various or variety of reason, and because of the availability of reactive sites, maybe the free radical, may be some reactive groups, maybe double bond, triple bond. Some sort of volume change may experience during the course of polymerization. So, dilatometry is used to find out those changes and to analyze the effect of these volume change.

And in situ, it gives you the information related to the chemical structure of those polymers. So, these this technique is extremely useful and a very popular technique. Now, the polymerization usually is performed in a kalimetric volumetric vessel. As the monomer decreases, it decreases the volume of solution, which is then measured with respect to time. So, this is the concept of dilatometry.

Now, for instance, the polymethyl methacrylate, PMMA, the density is 20.6% lower than its monomer density. So, it is very useful information. And you can see that it is a significant change with respect to the volume or a density. Now, this density difference can be accurately measured. And this provides the information regarding the rate of polymerization. So, it is a very useful tool for this particular approach.

Now, by this way, we gave you a brief information about the various instrumental technique used for the characterization of polymerization process or polymer samples. Now, Let us have a look about the initiation steps. Now, initiators these are the chemicals they are being used to produce radicals for performing radical chain polymerization. As if you recall that in the very first lecture, we discussed about this particular concept which was related to the start of the radical chain polymerization.

Now, the rate of initiation simply depends upon the reaction involved during the radical production. So, it cannot be generalized or you cannot generalize all these things pertaining to this particular initiation aspect. You should not be get confused that initiator with the catalyst. As the initiator got consumed during the initiation step while catalyst they do not consume during the process, and they can be regenerated over the period of time.

So, this is the broad difference between the initiator and catalyst. And sometimes during the polymerization process, you may require the catalyst apart from the initiator. So, you should not be get confused with the catalyst. Now, the initiator should be a stable compound under the normal storage condition or sometimes under the refrigerated condition. And it should be able to decompose and produce free radical at high temperature, usually below 150 degrees Celsius.

These are the certain limiting temperature, but, we should not follow rigorously of these temperature domains. There are several ways to produce radicals from initiator, which will be discussed during the different sections of this particular chapter. Now, let us before we go into the detail of this initiation step. Let us have a discussion about the initiator and its different types.

Now, during the thermal decomposition, so, homolytic fission of molecule occurs, where each fragments retain one of the originally bonded electrons.

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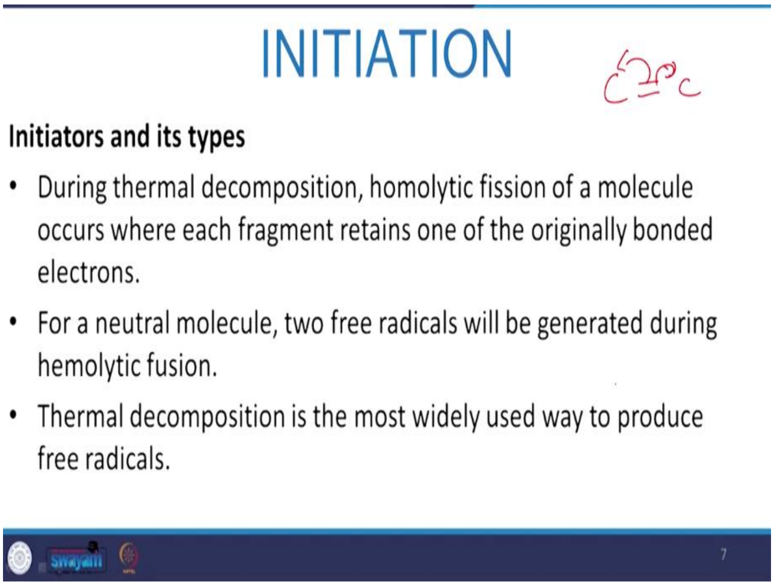

INITIATION

$\leq 150^{\circ}C$

Initiators and its types

- During thermal decomposition, homolytic fission of a molecule occurs where each fragment retains one of the originally bonded electrons.
- For a neutral molecule, two free radicals will be generated during hemolytic fusion.
- Thermal decomposition is the most widely used way to produce free radicals.

So, if you recall in the previous lectures, we discussed that suppose, you are having this two this double bond. So, one of the originally bonded electrons they may past they may fragmented to provide the radicals to each other. For neutral molecule, 2 free radicals will be generated during the hemolytic fusion. And some thermal decomposition is carried out for the initiation step. So, thermal decomposition is most widely used way to produce the free radicals.

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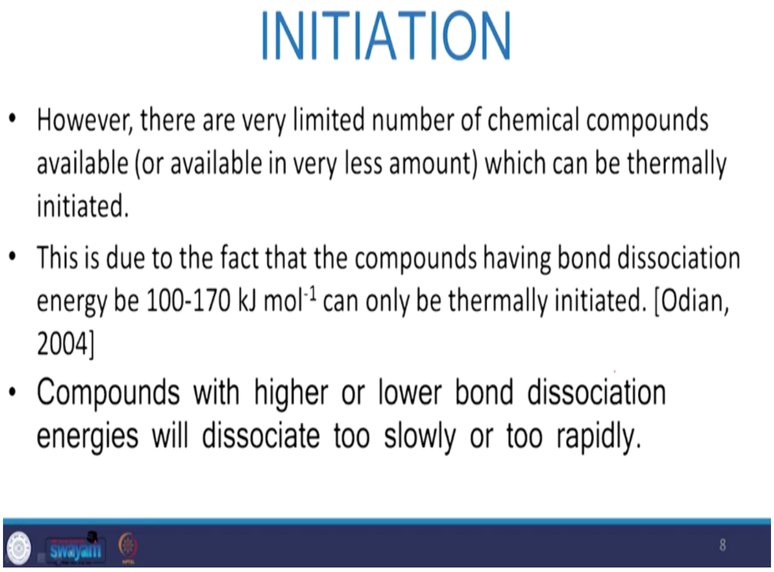

INITIATION

- However, there are very limited number of chemical compounds available (or available in very less amount) which can be thermally initiated.
- This is due to the fact that the compounds having bond dissociation energy be 100-170 kJ mol^{-1} can only be thermally initiated. [Odian, 2004]
- Compounds with higher or lower bond dissociation energies will dissociate too slowly or too rapidly.

Now, there are very limited number of chemical compounds available or you can say very less amount which can be thermally initiated. Now, this is this may be the due to the fact that compounds having the bond dissociation energy that may be 100 to 170 kilojoules per mole. It can only be thermally initiated. Now, compound with higher or a lower bond dissociation energy will dissolve too slowly or too rapidly. So, these are the several things you need to look into while you go for initiation study.

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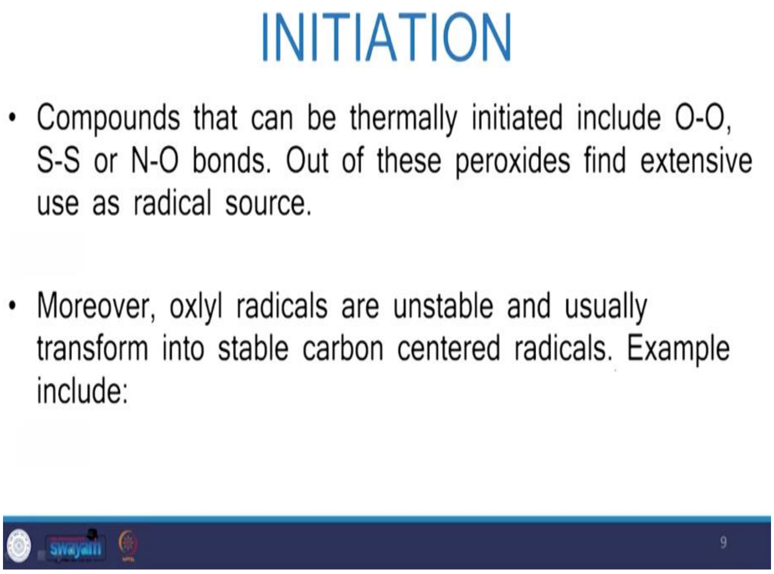

INITIATION

- Compounds that can be thermally initiated include O-O, S-S or N-O bonds. Out of these peroxides find extensive use as radical source.
- Moreover, oxlyl radicals are unstable and usually transform into stable carbon centered radicals. Example include:

Now, compound that can be thermally initiated, this may include the O-O, S-S or N-O bonds. Out of these, the peroxides find extensive use as radical source. So, let us have a brief look about these peroxide bond.

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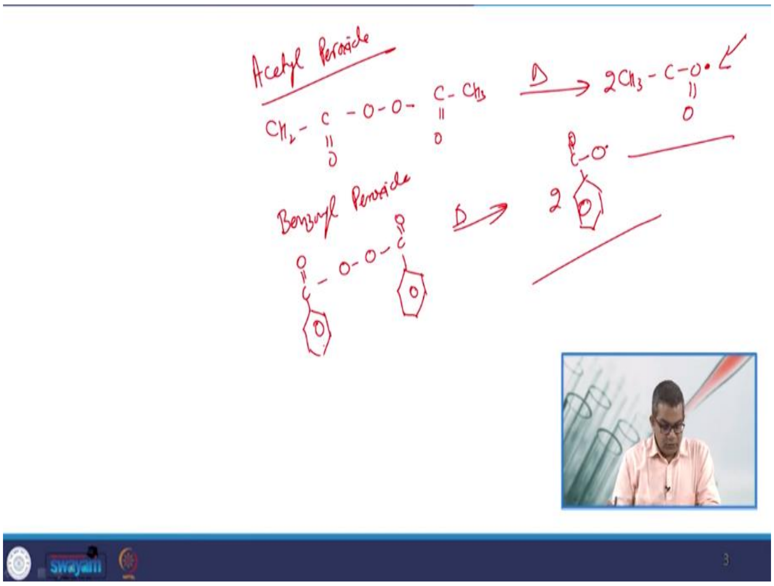
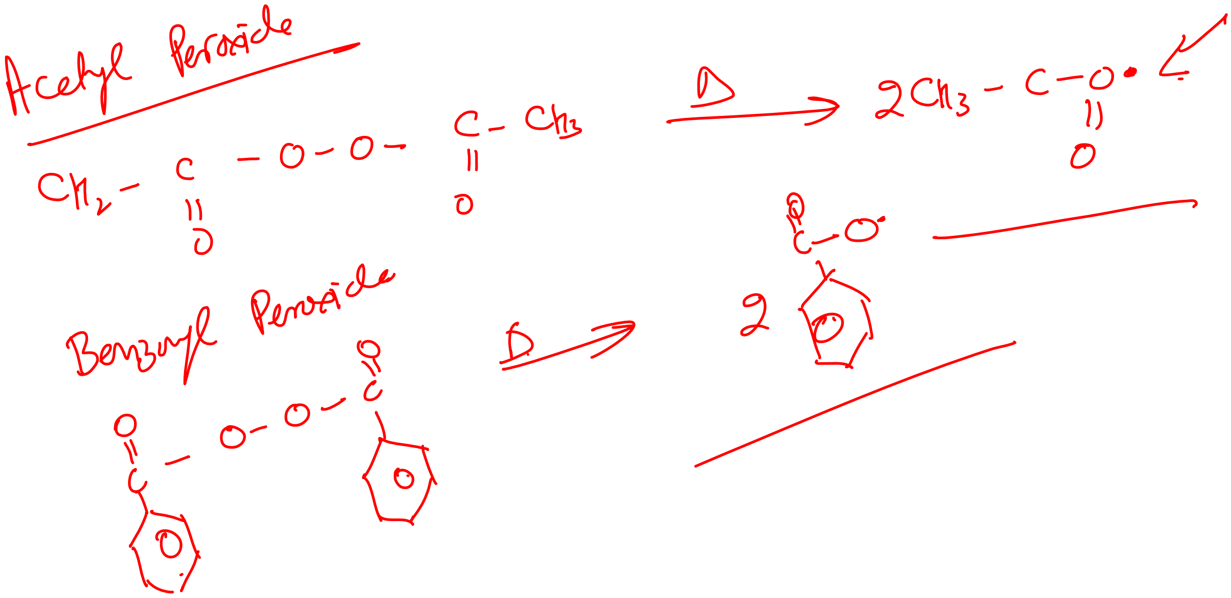


So, let us take the example of acetyl peroxide. Now, here you see



the CH 3 C double bond O O. Now, you are performing some dissociation step. Then it gives you CH 3 C. Now, here you see that this is the example or this is the formation of a radical. Now, similarly, if you take the example of benzoyl peroxide, now, here this is the phenyl ring. Now, if you go for dissociation then you may get the 2 radicals. So, these 2 are.

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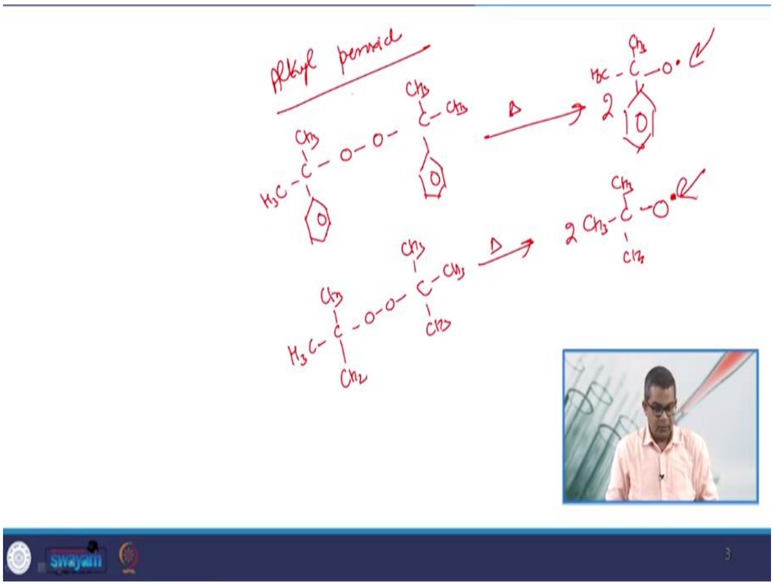
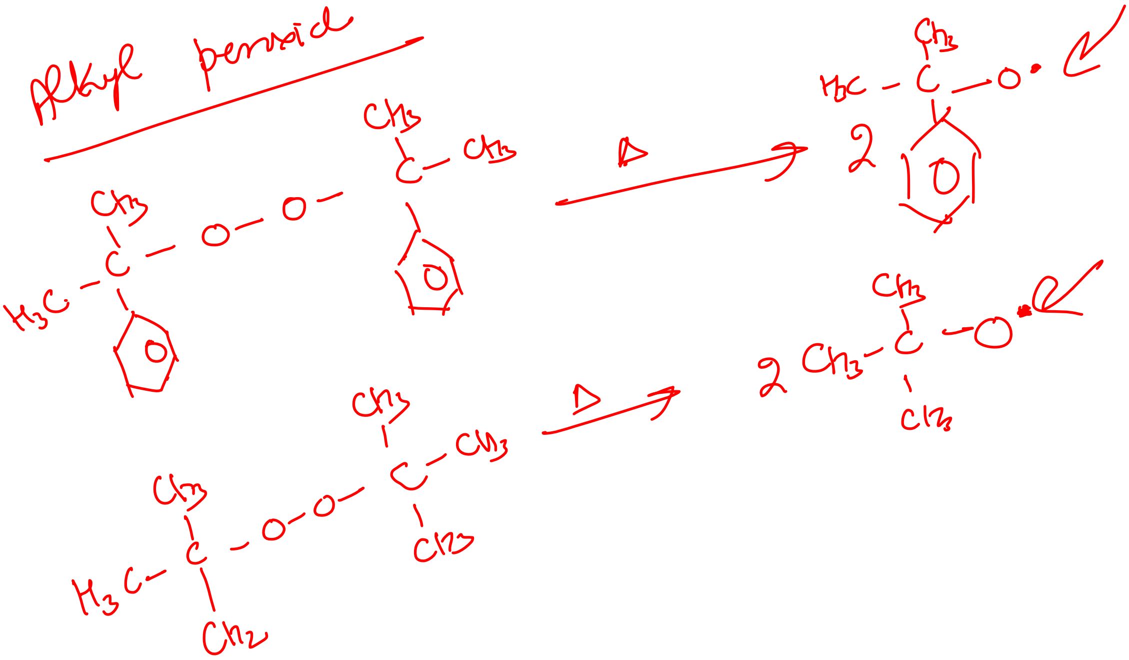


Similarly, if you see the example of alkyl peroxide, so, again you may see



So, here you see that these are the some of the radicals being formed in due course of time. Now, sometimes, if you see that the oxyl radicals are they are unstable and usually transform into this stable carbon centers radicals.

So, again, we would like to give you couple of examples related to the this particular approach.

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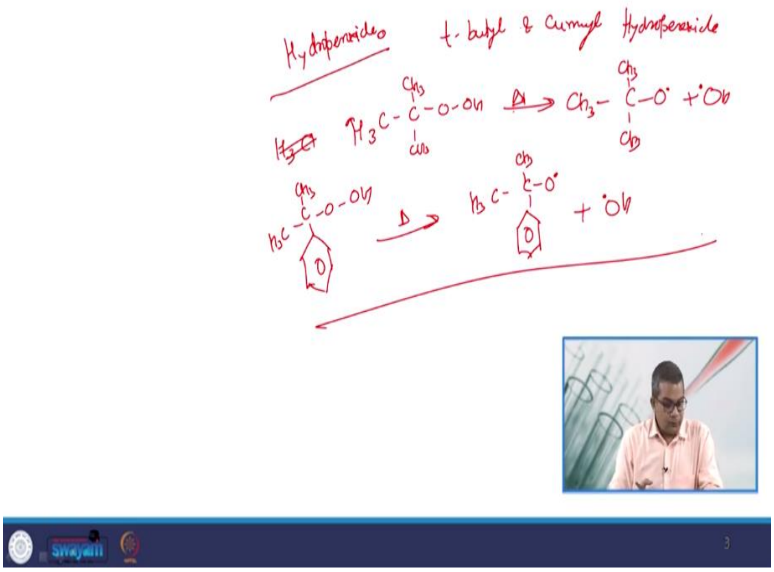
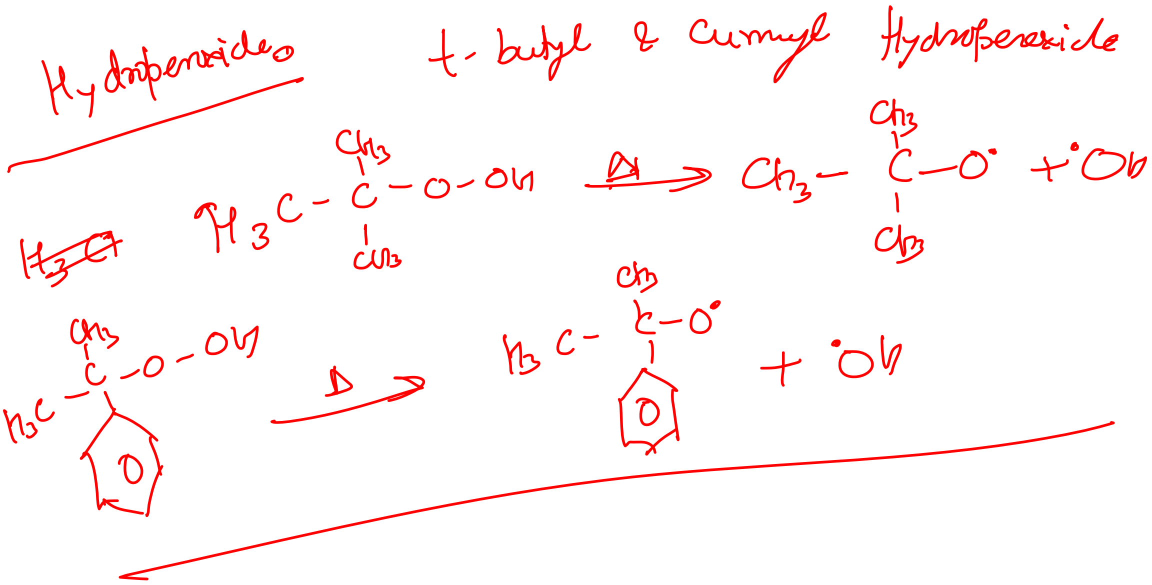


But, before we go into the detail, let us have a couple of more examples related to the hydroperoxides so that the things would be more clear in the approach like hydroperoxide such as tertiary butyl cumyl hydroperoxide, tertiary butyl hydroperoxide. So, here this you can see



Now, here you see that there is a formation of a radical and some more example pertaining to this particular approach.

Here you are having the phenyl rings. So, these are the couple of examples related to the this hydroperoxide etcetera.

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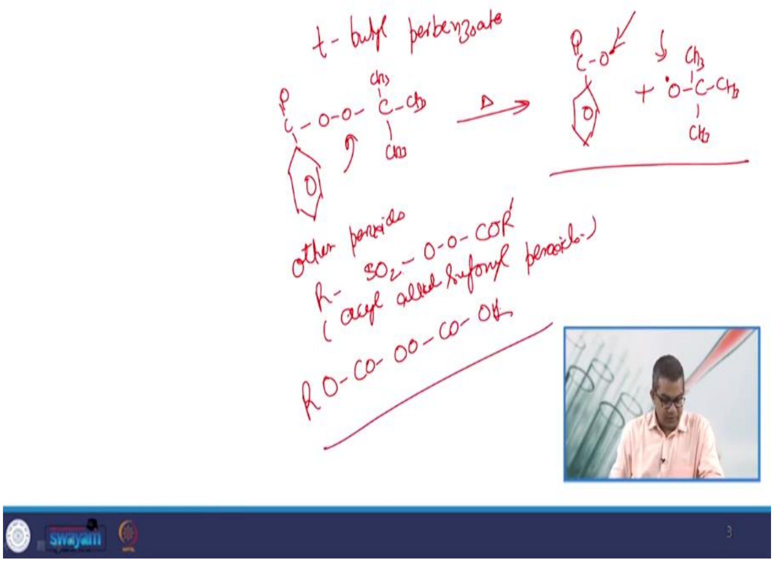
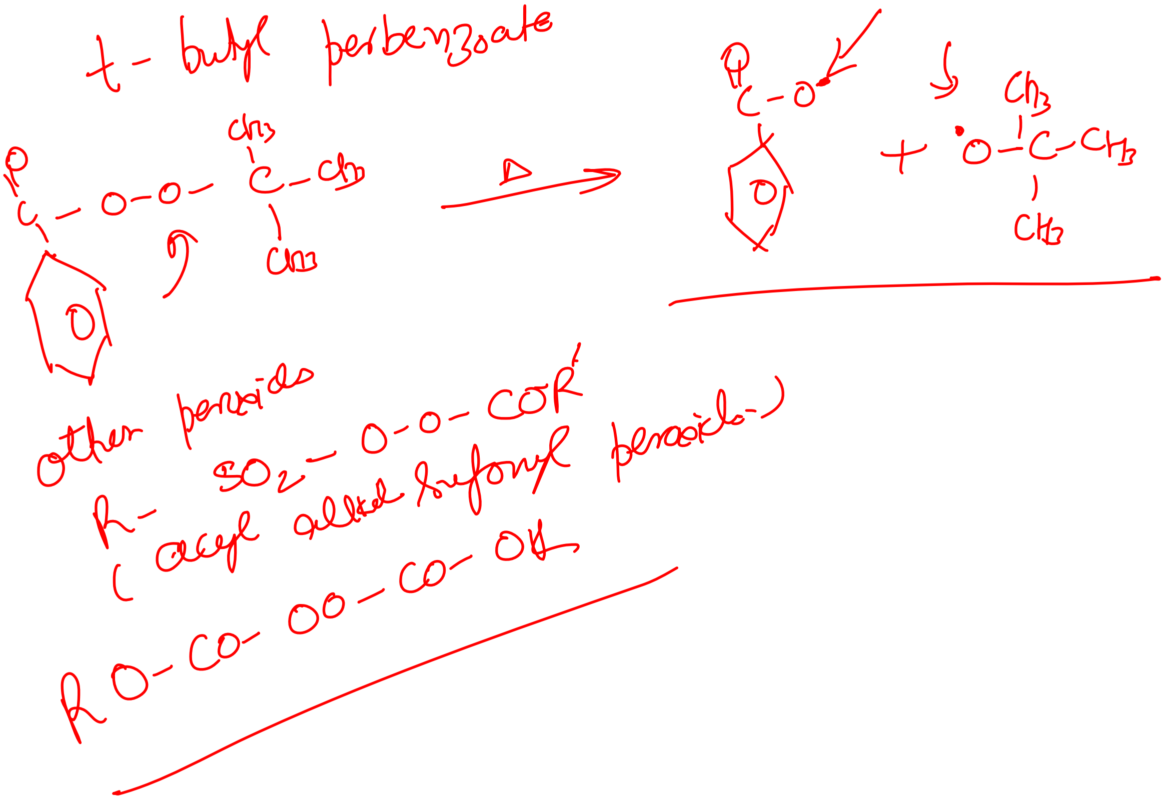


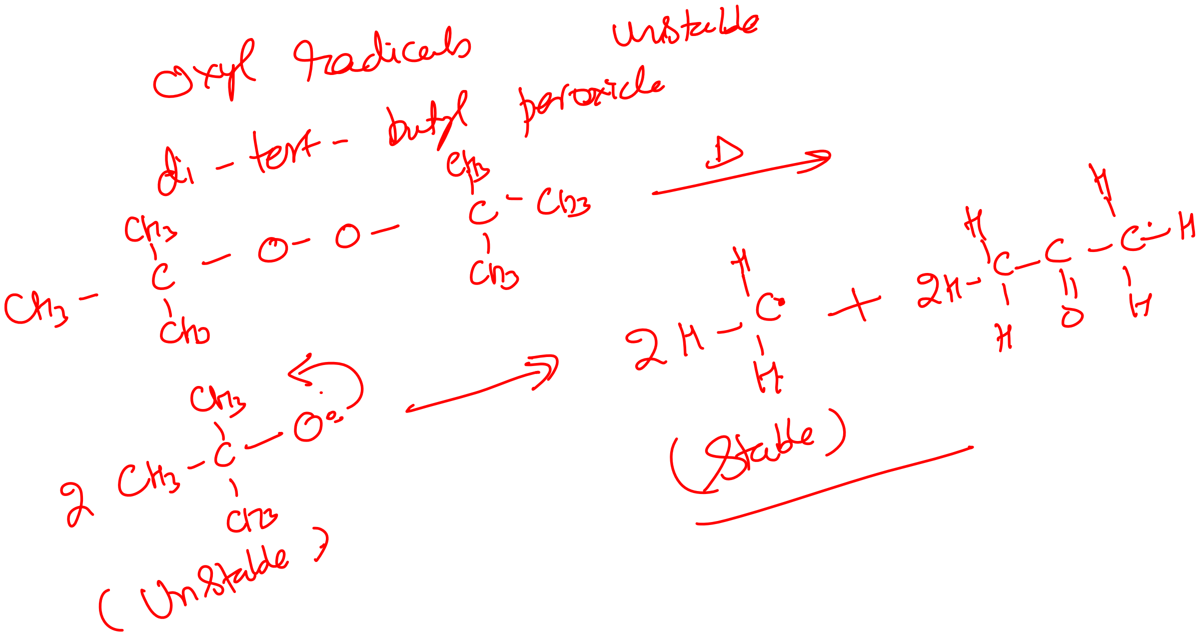
Now, if we take the example related to the peresters like tertiary butyl perbenzoate. One of the example is that tertiary butyl perbenzoate.



Now here it get dissociated to form the 2 different radicals. Here you see that one is having the phenyl ring this one. Now, here this is the radical. Another one is, so by this way, you see that this bond get dissociated, and it forms the 2 distinct radicals.

There are some other peroxide if you talk about like R SO 2, this is alkyl sulfonyl peroxide. Similarly another example of such kind of approach is dialkyl peroxydicarbonate. So, these are the couple of examples pertaining to this particular approach. And these are certain the the radicals which we discussed, they are certainly they are unstable and usually transform into some of the stable centered radicals, etcetera.

Now, let us have a look about certain other oxyl radicals, which we just skipped this because of the certain other limitations. I would like to give you some stable and unstable concept prior to this azo compounds.



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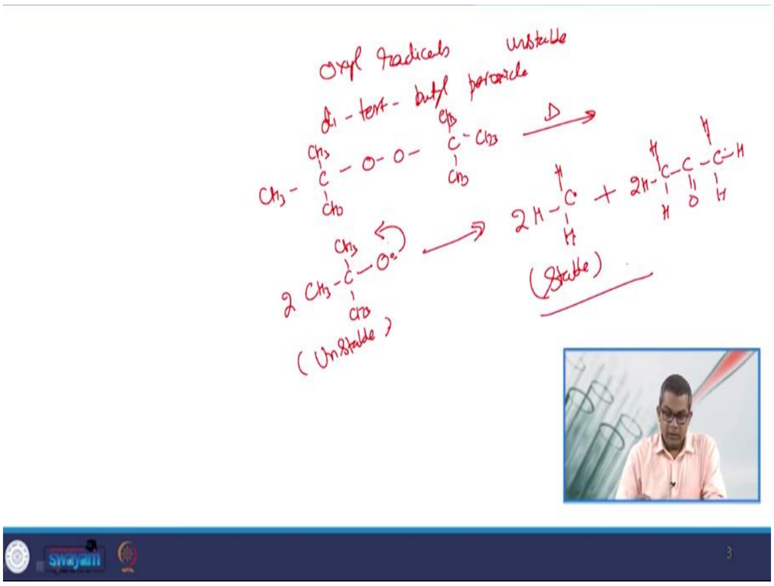

So, if you take this oxyl radicals into consideration. So, usually they are unstable. Like one example is di tertiary butyl peroxide. Now, here this CH 3 C CH 3 O O then C CH 3 CH 3. If you see there are unstable and stable one. Just I am giving with unstable. Here twice CH 3 C.

Now, this is an unstable one. Now, it may go to stable one because now here you see that this transform into here and another one is 2H C C double bond O C H H. Now, this is the stable one you see.

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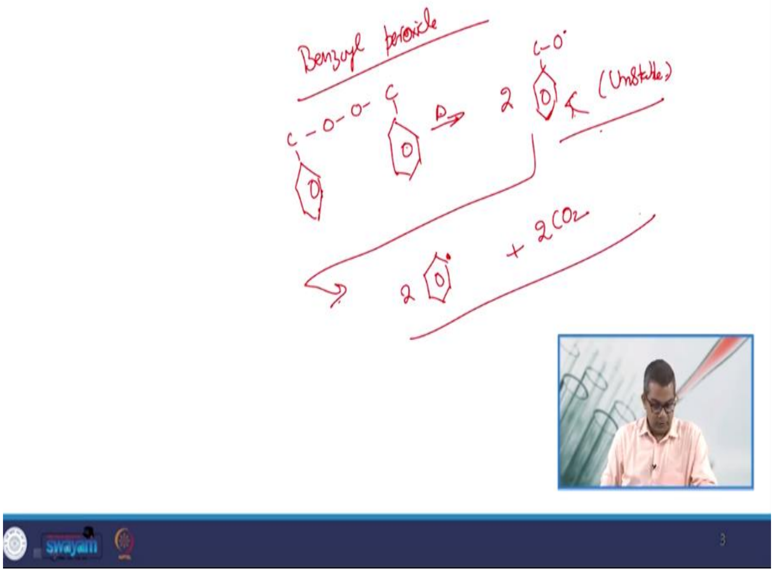
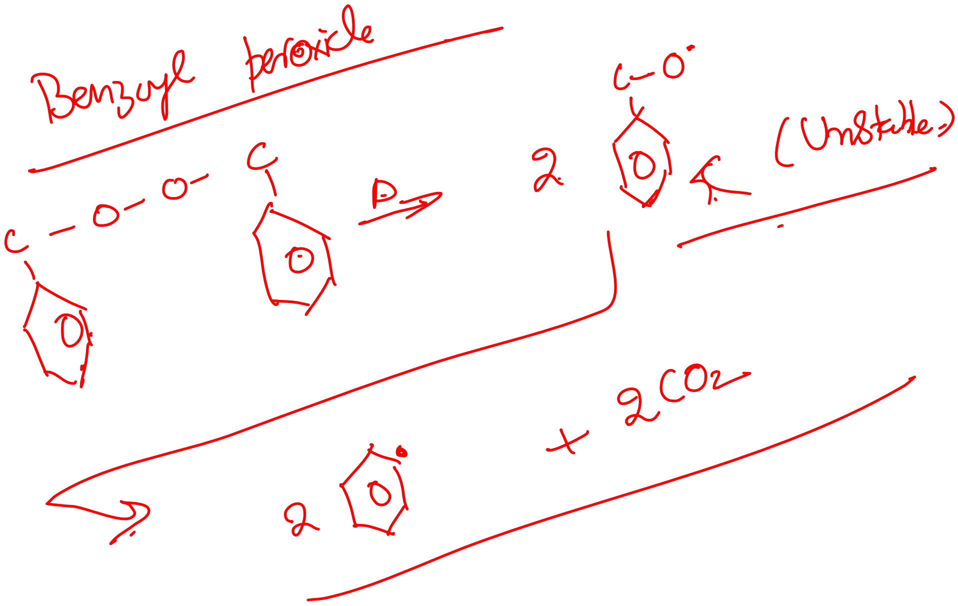
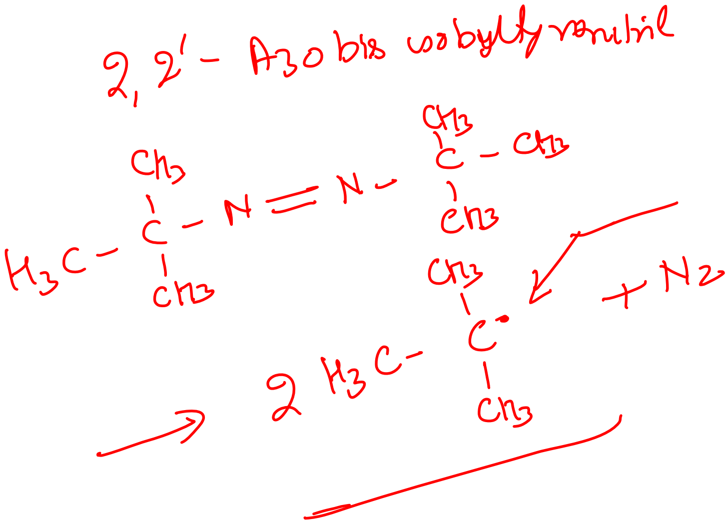


Similarly, if you see the benzoyl peroxide let us another give you with the example of benzoyl peroxide. Now, this is your benzoyl peroxide. Now, here you will see that these unstable one radical which is there then converted into the stable one. Now, you see plus twice CO 2. So, this one is unstable. You see over here. And this is then get converted into the stable one.



So, this is this gives you a brief outline about that these are unstable and transform into stable one in the carbon centered radical. So, this is you can say is a good concept and this always you need to look into while you decide the any kind of rate expression pertaining to the initiation step. Sometimes azo compounds they also find several uses as initiator. The best example is azoisobisbutyronitrile.

So, this is one of the most popular initiator being used in polystyrene divinylbenzene synthesis. And this P PS divinylbenzene is a very good support for various kind of ion exchangers, various kind of a catalyst etcetera. So, it is a very good initiator in the in such kind of suspension polymerization scheme. So, when we talk about its usefulness, then we need to look into the various aspects associated with these azo compounds which are being used as an initiator.



Sometimes other components like 2,2’-azobis(2,4-dimethylpentanenitrile), 4,4’-azobis(4-cyanovaleric acid), and 1,1’-azobis(cyclohexanecarbonitrile) being used. So, people have studied a lot related to the use of these azo compounds or the as being used as the initiator. Now, let us have a look about some basic chemistry of aspect of these azo compounds.

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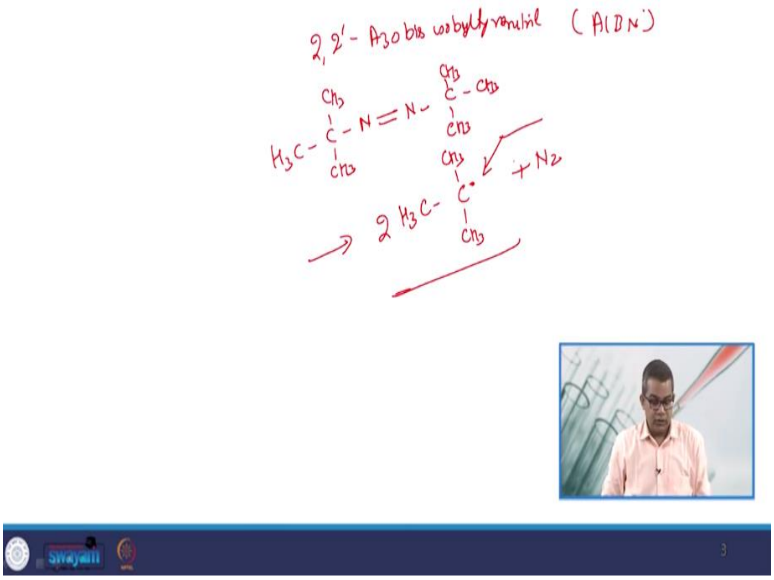

Let us give the example of azoisobisbutyronitrile or is referred as AIBN. Now, azobisisobutyronitrile, AIBN. Now, here CH 3; now, this particular double bond plays a very vital role. Now, how it can start the initiation step? Let us have a good look. Now see here, this radicle or this functionality attracts the basic concept of initiation. And that is why this particular functionality make it a good candidate for the initiation in a reaction or initiation step.

Now, the CN or carbon nitrogen bond azo compound, so, unlike peroxide bond, they have a high bond dissociation energy. Sometimes it is in the range of 290 kilojoules per mole. Trust me, it is a very high bond energy, but the reaction proceeds due to the possibility of formation of nitrogen molecule as it is evident in the previous example. Sometimes people looked into the other initiators and tried a lot to find out the other initiators being used in the initiation step.

So, they found that some dye sulfides or tetrazines they are the other initiators being used for this the process of speciality polymerization. Now, when we are having the large galaxy or large spectrum of initiators available maybe azo initiator, maybe dye sulfide, maybe tetrazines etcetera, so, we are having the largest spectrum of initiator available for the radicle chain polymerization.

Then question arises that what should be the selection criteria for all those initiators? So, the selection of an initiator usually depends on various operating conditions. Sometimes, it relates to the reaction temperature and that is a very case sensitive in case of the polystyrene divinylbenzene suspension polymerization and sometimes the rate of homolytic cleavage. So, George Odian, he studied a lot.

And he devised the protocol through which one can assess that which kind of initiator is, should be used for the polymerization reaction of interest. So, this particular concept, whenever you use initiator, then this particular concept pertaining to the operating condition should be looked into. Let me give you some examples related to the this operating protocol. For example, that the operating condition for AIBN that is azobisisobutyronitrile is in the range of 50 to 70 degrees Celsius.

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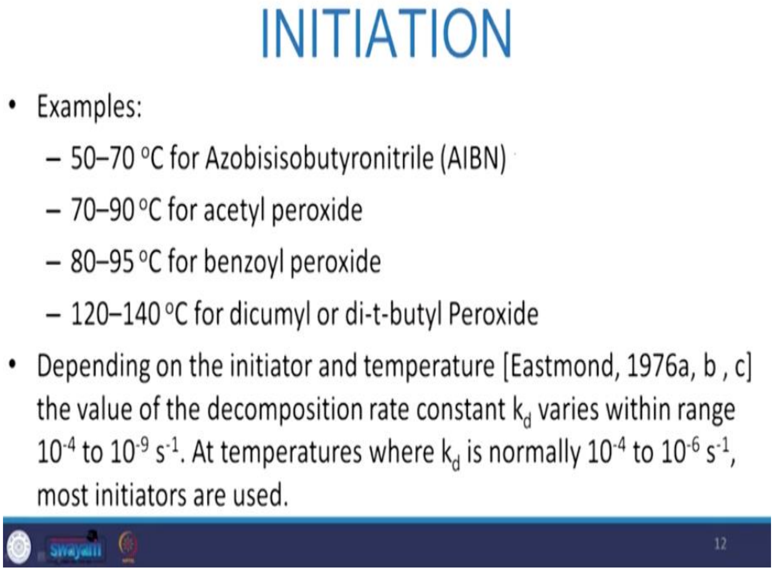

INITIATION

- Examples:
  - 50–70 °C for Azobisisobutyronitrile (AIBN)
  - 70–90 °C for acetyl peroxide
  - 80–95 °C for benzoyl peroxide
  - 120–140 °C for dicumyl or di-t-butyl Peroxide
- Depending on the initiator and temperature [Eastmond, 1976a, b , c] the value of the decomposition rate constant k_d varies within range 10^{-4} to 10^{-9} s^{-1}. At temperatures where k_d is normally 10^{-4} to 10^{-6} s^{-1}, most initiators are used.

If you talk about the acetyl peroxide, the example we have already discussed, it is in the range of 70 to 90 degrees Celsius. Now, if we talk about the benzoyl peroxide, it is somewhere in the range of 80 to 90 degrees Celsius. And if you talk about the dicumyl di tertiary butyl peroxide, then it is in the range of say 120 to 140 degree Celsius. So, depending upon the initiator depending upon the polymerization conditions some people have discussed.

And some people have find out the proper operating parameters based on the various rate constants associated with those polymerization reaction. So, Eastmond, the he discussed about this particular thing and he find out the decomposition rate constant or he find out the values of various decomposition rate constant k d which we discussed earlier in the previous lectures.

He find that this K_d varies within the range of 10 to the power minus 4 to 10 to the power minus 9 second inverse. Now, at temperature where K_d is normally 10 to the power minus 4 to 10 to the power minus 6 per second, this is one of the most popular the dissociation rate constant where most of the initiators are being used. So, this is you can say he analyzed various approaches related to this decomposition rate constant.

And he suggested that most initiators what we are using in the radical chain polymerization, they are having the dissociation rate constant K_d within the range of 10^{-4} to 10^{-6} per second. The bond dissociation energy of peroxide and azo compounds usually falls under this operating temperature ranges so which we have discussed in this particular approach.

Also, the stability and abundance of these compounds, they are much promising as compared to other initiators. And this is the reason why these compounds they find their great utility as an initiator. So, this solves the query in your mind that why we are very much choosy about those initiator? So, just because of this concept, stability and abundance of these compound. This these two things or two approaches offers the best candidate for those compound to be used as an initiator.

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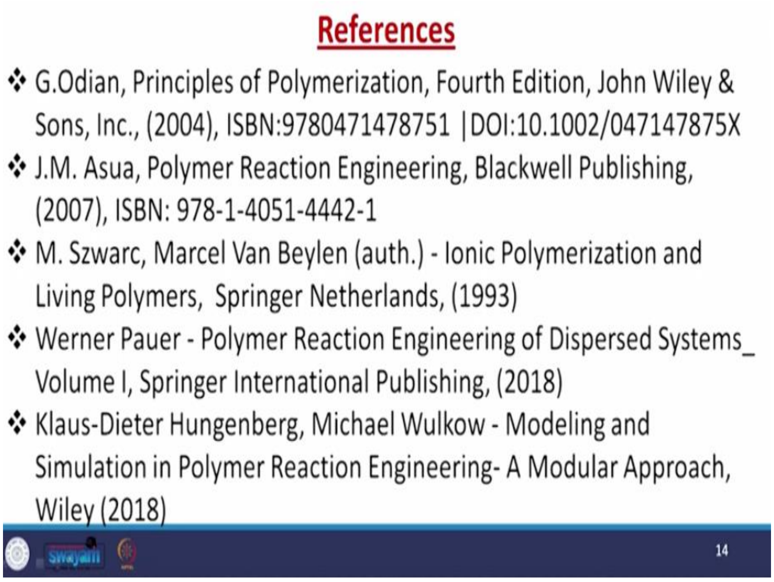

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Now, by this way, we are concluding this particular approach and then the process analysis concept in 2 segments.

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We discussed about the various instrumental techniques being used to carry out the characterization of the polymers being developed in due course of time. We discussed about the concept of initiation. We discussed about the efficacy of dissociation rate constant. And we gave you a brief outlook about the literature being available or the work being carried out by the various researchers so that we can have most optimum dissociation rate constant in picture.

Now, based on this particular approach, if you have any query pertaining to this particular thing, we have enlisted several references for your convenience. You can have more look about those queries in the references. So, by this way, we are concluding this particular process analysis under the aegis of radical chain polymerization, thank you very much.