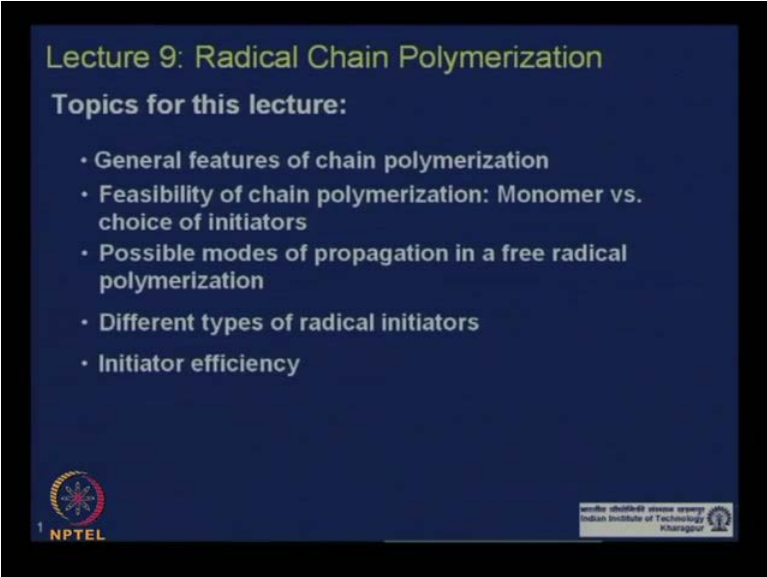


Polymer Chemistry
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Lecture - 09
Radical Chain Polymerization

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Lecture 9: Radical Chain Polymerization

Topics for this lecture:

- General features of chain polymerization
- Feasibility of chain polymerization: Monomer vs. choice of initiators
- Possible modes of propagation in a free radical polymerization
- Different types of radical initiators
- Initiator efficiency

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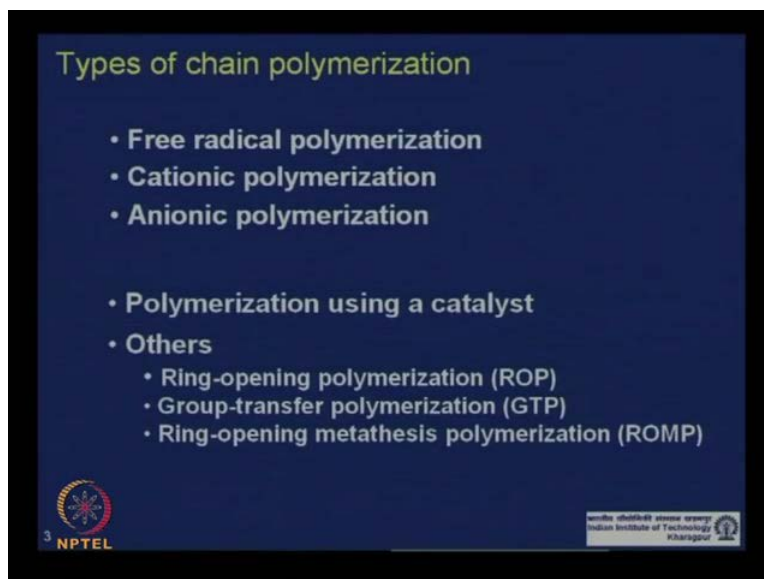
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Welcome back to this course on polymer chemistry, and today we are going to move from of discussion, on step growth polymers to chain growth polymerization. And we will begin with radical chain polymerization, for about four to five lectures, followed by ionic polymerization, and other types of chain polymerization, later lectures. In this lecture we are going to cover, general features of chain polymerization, which we will basically revisit from our introduction lecture. And then we will talk about feasibility of chain polymerization, how the structure of monomers determines, which type of initiator would choose, and different modes of propagation of a free, in a free radical polymerization, different types of initiator and initiator efficiency.

Now let us revisit, the discussion we had on chain polymerization in first two, lectures during introduction. What are the general features of a, chain polymerization process. In the step polymerization we have seen that we need, at least two functional groups, so that the reaction

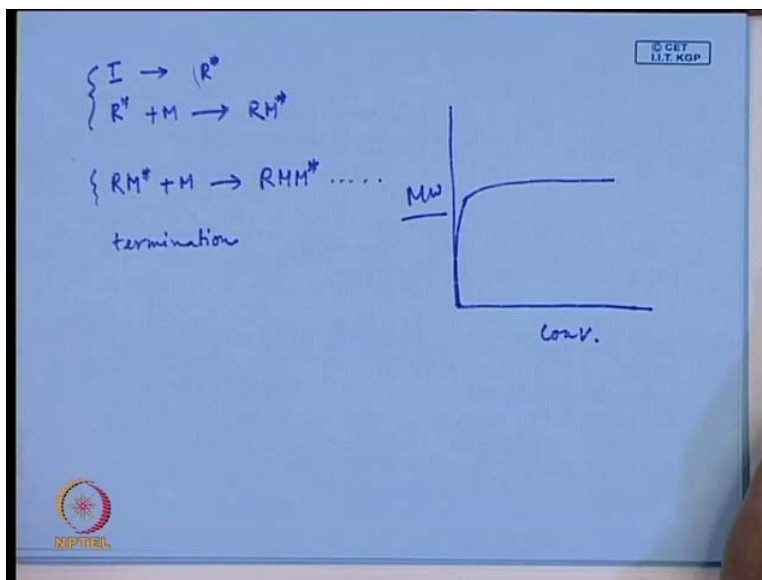
can happen between the functional groups, but in case of chain polymerization, we need one functional group, mono functional group, in most cases it is a double bond. We can do polymerization, chain polymerization with more than one functional group as well, but then in that case like the previous case of step polymerization, it will give cross linking in the polymerization, not the complete linear polymerization. So if you have only one functional group in this case double bond, it is sufficient to give you linear polymers.

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Now, polymerization, chain polymerization are in general consist of three steps; three main step, initiation, propagation, and termination.

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In initiation step, initiator reactive species R is formed, from initiator molecule I, this reactive species then react with a monomer, gives you a chain initiating species. This will initiate chain, by reaction reacting with further monomers, forming extended chain, and this will progressed to make a complete polymers. So this is part of initiation steps, this is propagation steps, and also we have termination step. You also have another step; you know another possible step like, transfer, reactions which we will discuss when it is necessary. So in this case, you require a reactive species, to initiate the polymer chain, unlike in step polymerization, where you did not require a, in the reactive species.

And depending upon this nature of this reacting species R splash, you can classify these chain polymerization reactions in different types; for example if the R star is, reactive species in this case, is a free radical, then we name this reaction or polymerization as a free radical polymerization. If this is a cation, then it is a cationic polymerization, if this is a anion, then it is a anionic polymerization. chain polymerization could be other types as well, for example polymers using, type of, other type of catalyst like (()) catalyst, and also it could be, different other types which are not the majority, or a major class of chain polymerization, but they also are part of the group of chain polymerization; for example ring-opening polymerization, group-transfer polymerization and so on. We will talk about these polymerizations, when in a later lectures briefly.

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General features of chain polymerization

- Usually monofunctional monomer
- Polymerization consists of three main steps
 - Initiation, propagation, and termination
- Usually no loss of molecular fragments
- High conversion is not a requisite for high MW
- Monomer is present throughout, but its concentration decreases steadily
- Growth occurs *only* by addition of monomer to active chain end
- Only monomer and polymer are present during reaction.

High reaction exotherms and low activation energies

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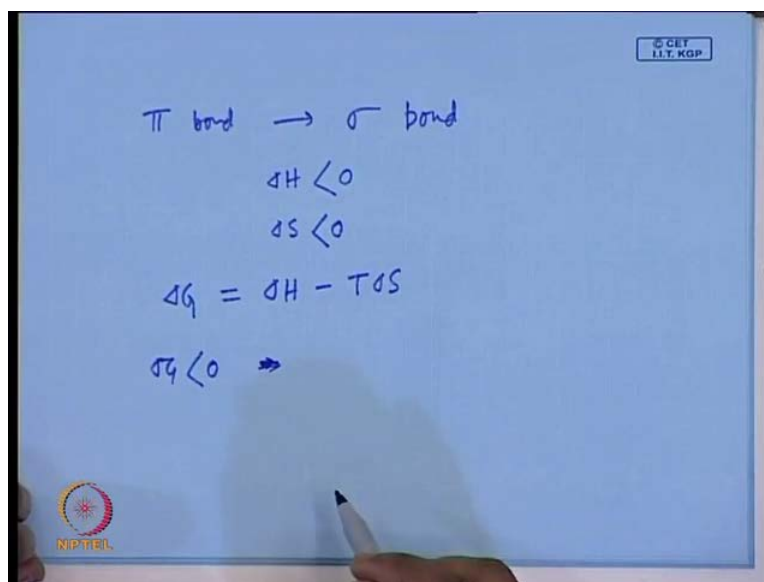
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We will come back to the general features of chain polymerization, we by this time you know that, we can build linear polymers in chain polymers from a mono functional group. Then chain polymerization is usually consist of three main step; initiation, propagation, and termination. And usually there is no loss of molecular fragments, like, in case step polymers, we had stormed, small molecular condensates, where coming out, during polymerization process, but in this case there is no loss of fragments. And we also know from our original discussion that, we don't require high conversion. Unlike a step growth polymerization, where we require a high conversion to a high molecular rate, in this case, we do not require a high conversions to build a high molecular rate.

If you recollect from the discussion we had, in the first two lectures that, in case of chain polymerization, the molecular rates builds very soon, and then it says, at very low conversion itself, it builds very high molecular weight, and the molecular weight remains has high, you know and very high during the conversion. There are some other things might results, in change in this nature of the, this line, at very high conversion, which will come back in the proper time. So in this case we have seen, from earlier case as well, and earlier discussion as well, that at very low conversion itself, molecular weight obtained is high, and there is the time progress, more and more number polymer chains form, and, but the molecular weight remains more or less similar, which is very high.

Now in this polymerization, chain polymerization monomers are, monomer is present throughout, but its concentration decreases gradually or steadily, and we also know that in, during this chain polymerization we have only monomer, or high molecular weight polymers. We do not have these intermediate molecular weight oligomers, like in step growth polymerization. We have either monomer, or high molecular weight polymers, and also have you know, this initiator molecules, and solvent if we required this chain. In case of chain growth polymerization, our chain grows only by addition of reactive species, or the monomer at the end. At one end of the growing chain, if the polymer progresses, then a monomer is always added at the end of the polymers, to grow the chain further. And these chain reactions are typically have very high exotherms, and low activation energy, and if you just think little more about the, mechanism of this chain polymerization.

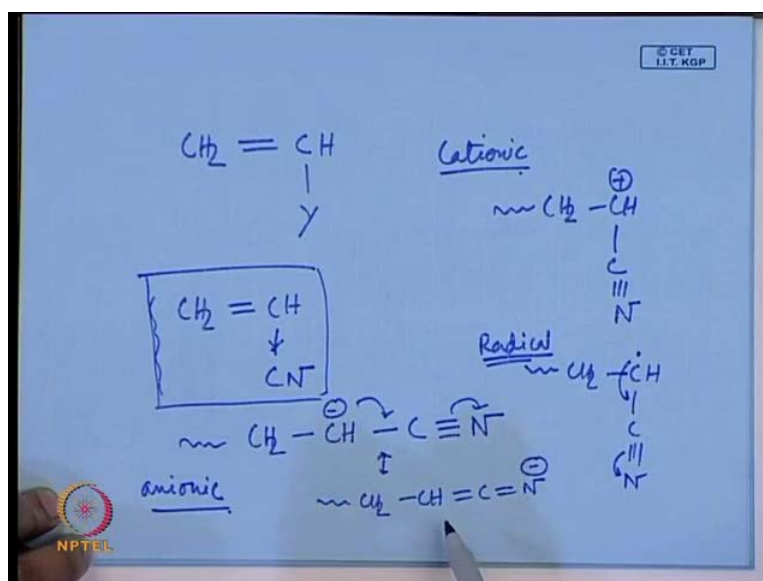
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Typically, you have a pi bond, is converting to a sigma bond during this chain polymerization, or which is starting from a double bond. Now this is having a, differently having an exothermic nature, this reaction. And we also know that, we also can imagine that, when the monomers add on to form a high molecular weight polymer, the translational and rotational degrees of freedom decreases. so in this case the entropy change is also lower, so if you think about the thermodynamics of this chain polymerization, briefly, at this movement, because this is exothermic negative, and this is also negative, so there is a completion between these two terms.

And in normal temperature, typically the reaction temperature, it is the temperature, where we do reactions, this dominates so the reaction these chain polymerization are; thermo dynamically feasible, in most cases are not. This ΔG is less than zero, for the typical temperature, where we do reactions in the lab, which means that, most of these double bond containing monomers should polymerize given is thermo dynamic feasibility, but if you think there is the kinetic, about the kinetic factor, not every monomer not every monomer containing double bond, can be polymerized with, every type of initiator, that depends upon the structure. The initiator which is best, or which can polymerize a monomer, containing a double bond, will depend upon the monomer structure.

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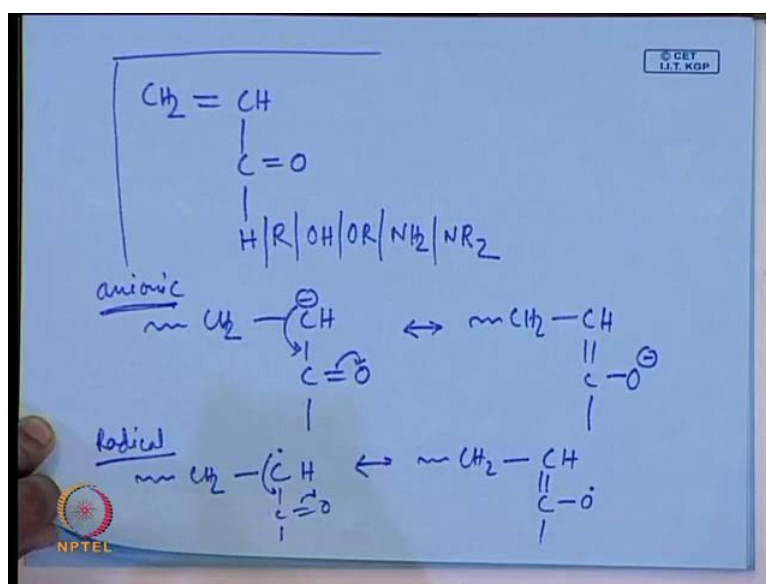
For example, if we take a simple monomer; say we take a very simple monomer like this, where y is a substituent. now the feasibility of this monomers, to undergo polymerization, chain polymerization, by a radical or cation or a anion, would depend upon the reactivity of this double bond, and also the stability of the species which formed, due to reaction of this monomer, and the reactive species, R^* which we talked about in the last page, which in turns depends upon, the inductive effect and the resonance resonating effect of this substituent group y . for example if I have; say y as a electron withdrawing group as nitron, so if consider a molecule like this, C N . Now it is a electron withdrawing group, which means that, because this is present the reactivity of this double bond towards a electro file, increases, and also if

there is an anionic charge here, which can be easily stabilized by the resonating effect of the nitrate group. So if I have an anionic species, reacting with this monomer, it will form for example; say CH₂.

Now it can stabilize, and from like this. so this is, this monomer acyl nitrate, will be very much feasible, reaction of this monomer will be feasible by an anionic initiators, so it can undergo chain polymerization by an anionic initiator, because you have an electron withdrawing group, which can, which actually increases the reactivity of this double bond towards electrophile, and also it stabilizes the reacting species which formed, because of the reaction of this monomer, with the reactive species. But if you have a cationic initiator for this case, and if you have an anionic initiator, if you have a cationic initiator for this case, then if it has to react, and form something like this.

Now this will not be stabilized by this substituent's. So, these monomers, will not undergo a cationic polymerization, it will undergo anionic polymerization, now if you have a radical for example, if your radical initiator, then it will form. Now this can also get stabilized by the process of resonance, which means that this acyl nitride monomer, can be polymerized by an anionic initiator, and a radical initiator, but not by a cationic initiator. We will take some other example.

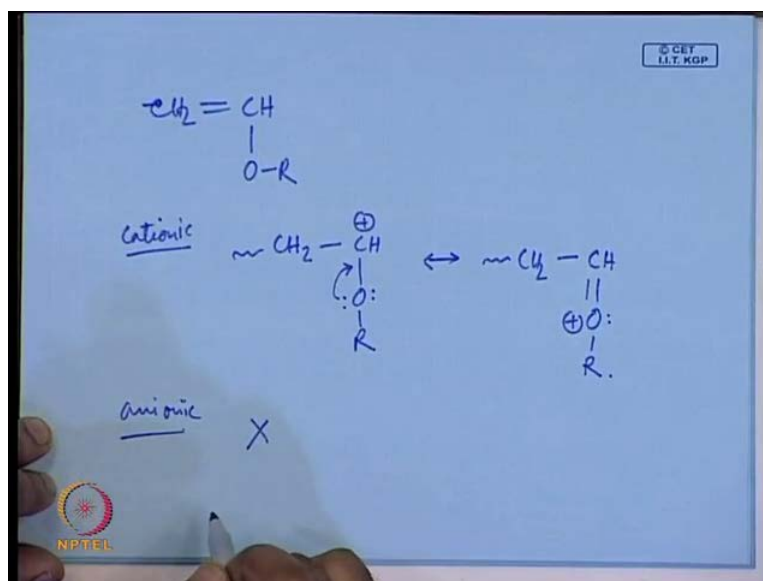
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For example we have, a monomer like this, it could be a aldehyde group. The substitution could be aldehyde group, or a say ketone, or a acid, or ester, or amine, amide, like this, so it could be any of this groups. Now when this monomers undergo anionic polymerization, it will form a species like this. It could be any of this species, which we wrote here. Now in this case also, this can get stabilized by resonance, and this will form this. So this is also another set of monomers, which can be easily polymerized, by a anionic initiator.

Similarly this can be also polymerized, for a radical polymerization, because again this, like the earlier case, this can undergo resonance and form this. So this type of monomer, which contain this side of, there is a carbonic carbonyl group here, they can easily undergo anionic polymerization, they can undergo radical polymerization. But like the earlier case they cannot, this side of monomers cannot undergo, a chain polymerization initiated by a cationic species, because then if you are a cationic group here, it will not be stabilized by resonance.

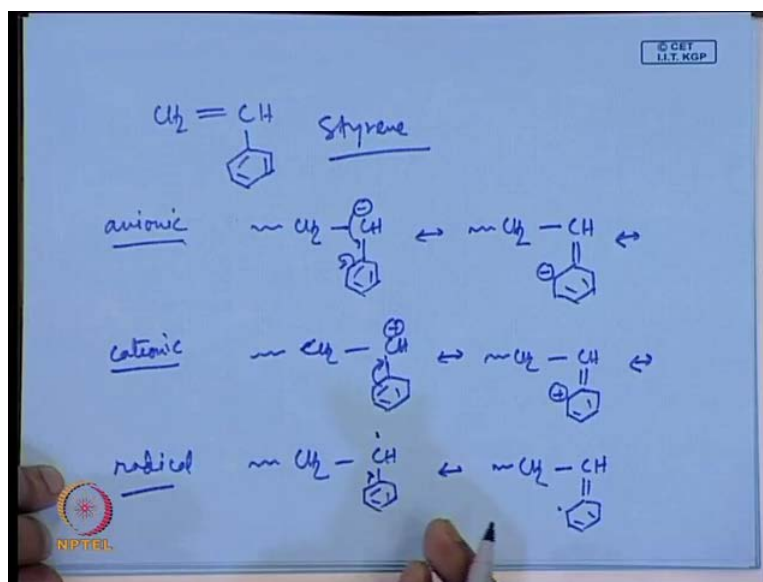
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Now, if you talk about this monomer. Now this monomer, if I polymerize with a cationic initiator, then it will be a cationic species now. Now again this can be stabilized, by resonance, by this. So if you have a monomer like this, then it can be polymerized, by a cationic species, anionic; no it cannot be polymerized by, cannot be anionic species, because if you have a strong electron withdrawing group here, so anionic cannot be. If you have a resonating group

here, which is electron donating neutron pushing, so it cannot stabilize a anionic group here, even if there is a weak electron withdrawing, group of by electron effect of this, word group by in the inducting effect.

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Now if you have monomer like this, styrene. If you have monomer like styrene, then what happened if you have a anionic case, I have other resonating structures if you have a cationic, and so as radical. If you have a radical group, then it can also be stabilized by by this substituent group. Now if I have a react, if I have a monomer like styrene, you can see that in each of these cases anionic, cationic, and radical, the reactive species which is forming, because of the reaction of the monomer, with the previous reactive species, can be easily stabilized by a resonation structure in all the three cases.

So styrene is example, where styrene can be polymerized other way anionic cationic, or a radical group has well as as well as radical group. So these are the examples how the structure of monomer will determine, whether it can undergo chain polymerization by anionic species, anionic initiator, or a cationic initiator, or radical initiator, and we have seen the examples of several monomers, and let us see the table and we summarize, whatever we are just learned in first last five ten minutes.

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Feasibility of chain polymerization: Monomer vs. choice of initiators

$\text{H}_2\text{C}=\text{CH}-\text{Y}$

Y	radical	anionic	cationic
COR	+	+	-
COOR/CONR ₂	+	+	-
CN	+	+	-
Ph	+	+	+
CH=CHR	+	+	+
OR	-	-	+
X / OCOR	+	-	-

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So if I have a simple monomer like this, if I can have y as c o r, then we know its can be polymerized by, both radical and anionic, it cannot be polymerized by cationic. If you have a acid or ester or amide, it can also be polymerized by radical under less anionic, if you have a nitride, again it can be polymerized by radical and anionic, not by cation. for example if you have a, it is the substitution of phenyl group, styrene, in case of styrene then it can be polymerized by all three, and if you have a another double bond hanging from the, the original double bond then also it can be stabilized, by any of these three mechanisms anionic, cationic, and radicals, which can be polymerized by all three mechanism.

We just seen that it is a ether, then it can be polymerized by cationic, it can be difficultly polymerized by radical also, but most preferred choice of polymerizing a ether group, hanging from a double bond is to use cationic polymerization. if it is a halogen, then its halogen is having weak inducting effect electron withdrawing inactive effect, and a weak electron donating or a electron pushing resonating effect, so because both this electron donating and withdrawing, f strains are weak, so it actually does not get polymerize either by anionic or cationic, it only gets polymerized by the radical mechanism, like vinyl chloride, and for example. So there are other possible substitutes, which you can imagine, and depending upon the chemistry, behind it you can find out, or you can decide, whether which one to try out fast,

which is the most easiest way, it can get polymerized, and if it is polymer, can be polymerized by radical that is a most easiest way of polymerizing, you know polymer process of this three.

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Radical Chain Polymerization: Monomers

- Monomer containing double bond between C atoms
 - Ethylene, styrene, butadiene, isoprene etc
- Monomer containing EWG polymerize effectively
 - methylmethacrylate, acrylamide, vinyl chloride, acrylonitrile, vinyl acetate, etc.

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So we come at now, only to radical polymerization. Radical polymerization, we are talking about the chain polymerization, and different structure and different initiator now we, start solely on radical chain polymerization. So what are the types, we can what are the types of monomers, can be used for radical polymerizations, monomer containing double bond between carbon atom. the examples we have just seen ethylene styrene butadiene isoprene etcetera, and if the monomer containing electron donate withdrawing group, then it the polymer visibility of the double bond actually goes up, because the reasons we just talked about in last time fifteen minutes. For examples like methylmethacrylate acrylamide, vinyl chloride, acrylonitrile vinyl acetate, etcetera can be very easily polymerizable, by a radical initiator.

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Radical Chain Polymerization: Monomers that can not be polymerized / difficult to polymerize

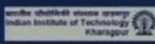

- Monomer containing more substituents around double bond do not polymerize effectively
 - Compare between 1-butene and 2-butene
- Unsymmetrically disubstituted unsaturation -
 - 2,3-dimethylbutene, etc
- Monomer containing bulky substituents -
 - 1,1-diphenyl ethylene

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Now, what are the monomers it is difficult to polymerize, or cannot be polymerized at all. If there are more substituent's, both the carbonate terms in the example, we said just showed in the last pages, where you have $\text{CH}_2\text{C}(\text{H})\text{Y}$, instead of one substitute, if you have substitution in the both the carbon, then it becomes more difficult. For example, if you compare one butane and two butane, it is easier to polymerize one butane than two butane. and if it is substitution is bulky, so like if you have a biphenyl ethylene, one ethyl ethylene, then it is very difficult to polymerize, and if you have tri substitute or tetra substitute, then also its very difficult to polymerize.

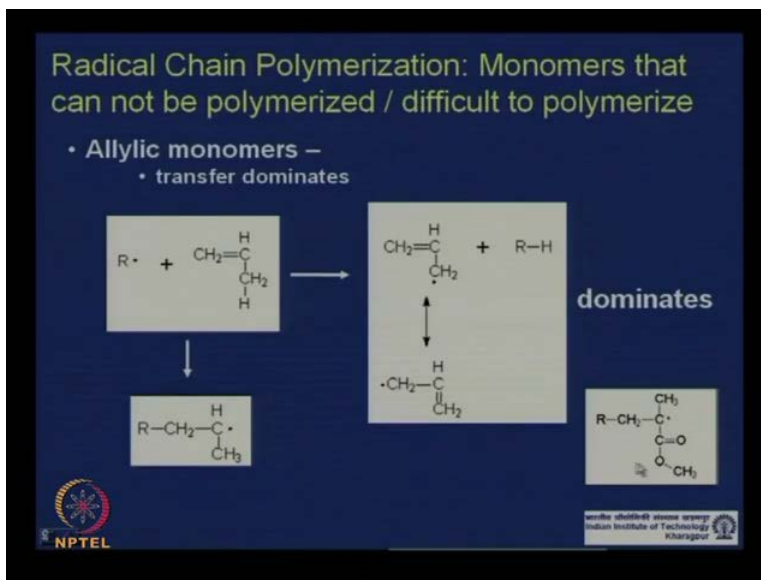
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$\text{H}_2\text{C}=\text{CH}_2$	Unsubstituted (ethylene) Works fine.
$\text{H}_2\text{C}=\text{CH}-\text{R}$	Monosubstituted Works fine.
$\text{H}_2\text{C}=\text{C}\begin{matrix} \text{R} \\ \text{R} \end{matrix}$	1,1-Disubstituted Usually works.
$\text{R}-\text{HC}=\text{CH}-\text{R}$	1,2-Disubstituted Seldom works.
$\text{R}-\text{HC}=\text{C}\begin{matrix} \text{R} \\ \text{R} \end{matrix}$	Trisubstituted Almost never works.
$\text{R}-\text{C}(\text{R})=\text{C}(\text{R})-\text{R}$	Tetrasubstituted Almost never works.



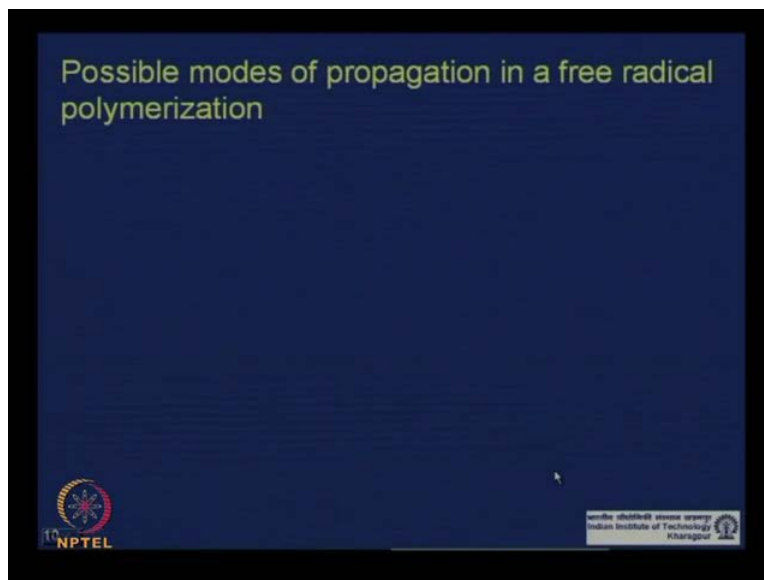
So if I want to summarize, just plane structure in short of substitutions. If you have no substitution, its work fine in radical, if you have monosubstituted, it works fine, except the case where it is C H 3 propylene, will come back of why it is so. And if you have disubstitution in single carbon, and unless they are not bulky, it usually works if they are very bulky, then because of the esoteric reasons they did not work and the... Now, from here if you go, move from more and more substitution, the reaction will become more and more difficult, like this is very difficult, and this two trisubstituted and tetra substituted almost never works in a radical polymerization.

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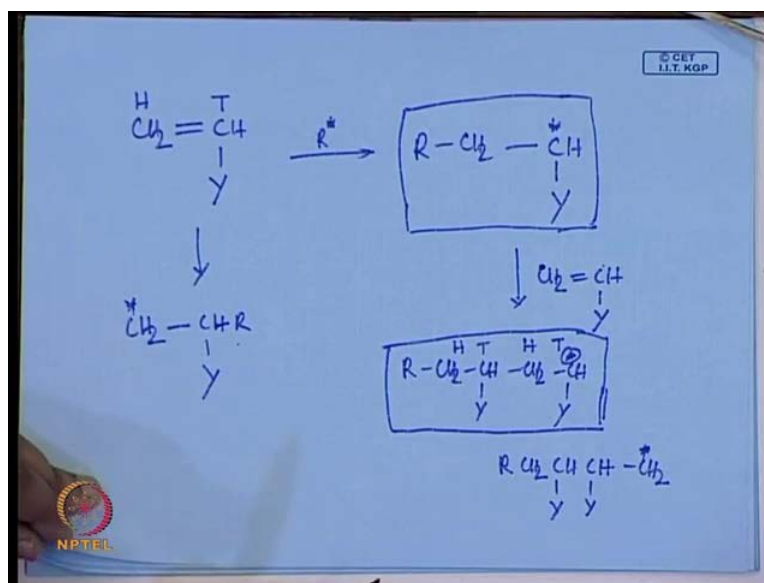
So, what I mean the case of this allylic monomer. For example the propylene, we just mentioned in the last slide. If you have radical, then it can react with a poly propylene to form, a initiating chain initiating species, which can react with other propylene monomer, and progress the chain or propagate the polymer chain, and this can be stabilized inductively by this. So there should not be any problem, in that sense. But, if you compare the other alternative, which is shown here. If this R dot abstract a hydrogen from here, from neutral species R H, then you have this radical species generated. Now, which is even much stable stabler than the previous case, because here in this case it is stabilized by resonance. So in most cases, this reaction, this reaction dominates than these reactions, so it's this is one of the cases of transfer. So this is for these reasons this pro propylene is difficult to polymerize by radical, and this does not happen if you have to say, monomer like methylmethacrylate, where there is no possibilities, this possibility does not arise.

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Now, how a, if you have a monomer like this, C H 2, again come back to that very simple monomer. Now this can react with r star, r star can react on this carbon or this carbon, if it reacts with this carbon when it forms y, and if this reacts with this carbon, then form something like this.

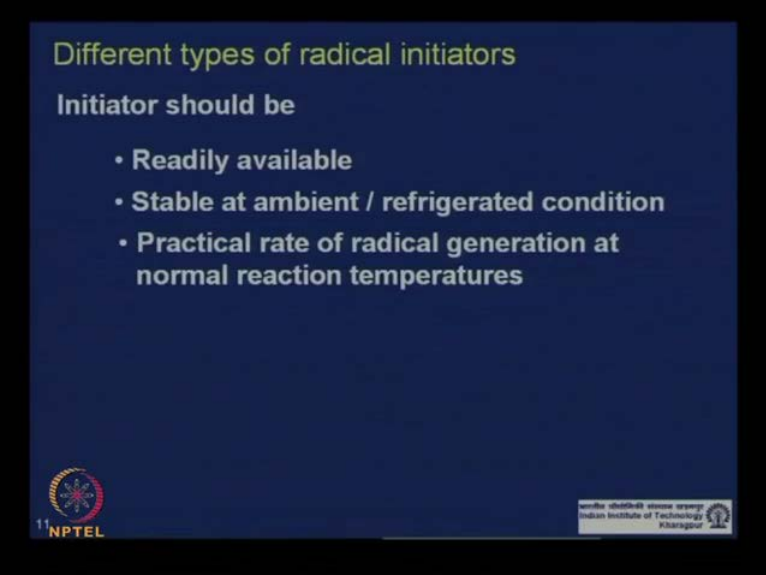
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Now, how does it propagate, this can react with either of these two carbon, in terms of possibilities, so if its react with this, then it forms. If this reacts with other side, then it forms, as species like this. Now given this two structure, now the fact that, this monomer which is reacting with this reactant species, which means that, whether this is radical or cat ion or anion, will get stabilized, by the substitution y present. So it is always given these and this choice, because the presence of this stabilizing group y as a substituent. This reaction, this side is always preferred, unlike not this. So approach of R to this carbon is always preferred over this carbon. Now if you have. So this is dominating or this almost exclusively formed, compared to this, because of the electronic stabilization of the y group. Now this can, for the same reason, this is preferred, compared to this. And here it is, it is the additional factor that, you have a group.

The approach of these, if it is the approach from this side, it will be even satirically hinders. So it is approach from this carbon is, preferred, both electronically and satirically. So if I write this side as head, and this is tail. Then finally, we get a polymer which has in head tail head tail arrangement. So in chain polymerization, you have, finally when the polymer formed, you get a head tail head tail arrangement, not any of these, if, whether it is a head or tail does not matter, you can have a tail head tail head tail head arrangement as well, does not matter, but it is basically alternate, head tail head tail head tail type arrangement in the polymer structure of the monomers. This is because of both satirical electronic, and steri creations.

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Different types of radical initiators

Initiator should be

- **Readily available**
- **Stable at ambient / refrigerated condition**
- **Practical rate of radical generation at normal reaction temperatures**

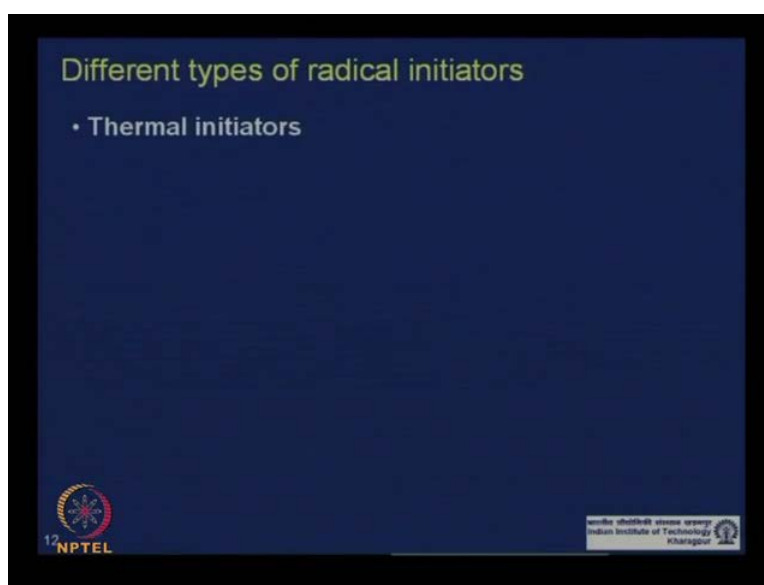
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Now, we are talking about radical polymerization, and what are the different types of initiator we can use. Now what is the source for initiator, we require a radical species to initiate the polymer chain, and we now we will look at what are the molecules which, or what are the possible ways we can generate radical, in the reaction medium. Now to have a radical species, to generate a radical species in the reaction medium, you should always prefer or it is very logical that, the radical should not generate at in ambient conditions, like room temperature, where you store this, your monomer or the initiator itself. While storing it should not generate radicals, or it is the initiator molecules should not be such that, it is very difficult.

You require very high temperature to, generate a radical form that initiator molecules, and also this, radical the initiator molecules would generate radical, in a moderate rate, so that they can be utilized in the reaction, it should not be very fast. If it is very fast radical generation, then the reaction will be extremely fast, and because this chain polymerization is exothermic, reaction is very fast, and you can imagine the amount of heat generated, during the reaction, which could be a hazard, it can actually explode, if it the reaction which is too high, and if is too slow then your reaction will take much longer, your radical generation is too low, then your reaction will take much longer time.

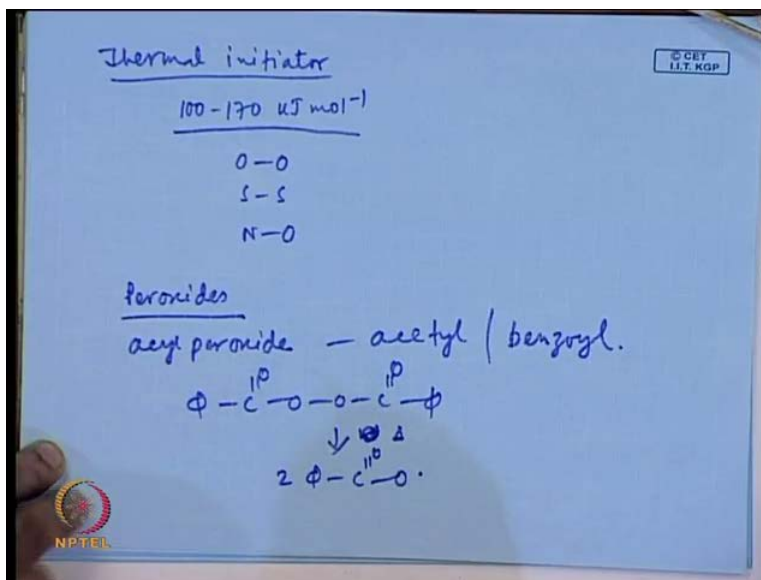
So there are three criteria say initiators should fulfill; one is that it should be readily available off course, specially for commercial application, it should be readily available, and it should be stable, at amnion condition if you are storing it in amnion condition at room temperature, even if you are storing in a refrigerator, it should be stable in that condition, it should not generate radical, under the condition of storage. And off course the third one we just talked about, that it should generate radical in a practical rate, at normal reaction temperature, it should not be too slow, for the reactions to take much longer time, or it should not be too high, then there are there are possibilities of hazard, because of a exothermic reaction happening in much faster rate. So, what are the initiators, we are initiated procedure, we typically use in a radical chain polymerization.

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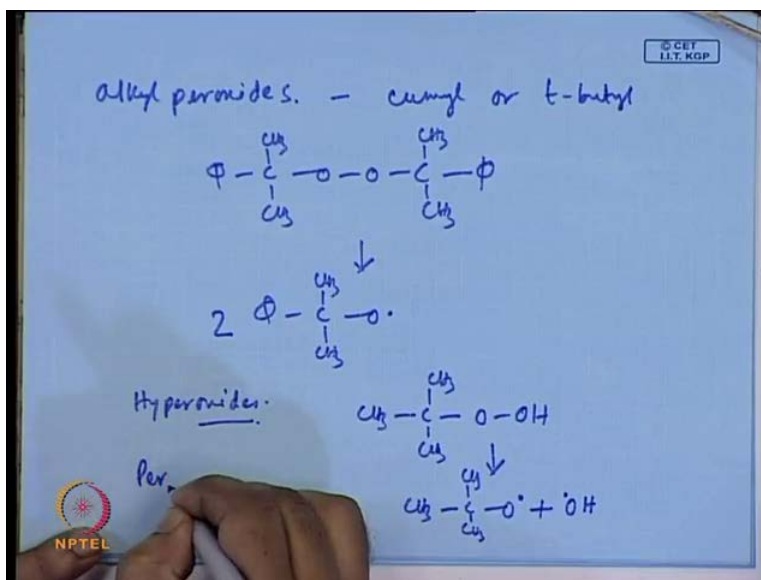
First one is, thermal initiator, and thermal initiator is, a initiation by homolicious of a molecule, by thermal energy, leading to formation of two radicals, and the typically. Here we are talking about homoliticalic leaving one bond, and making two radical. Now the bond energy should be such that, the bond should not leave at low temperature at room temperature, or it should not be very high. The bond innovation will not be very hicks, so that you require a, much higher temperature, to break that homiletically. So the typical range of bond energy, which are used for a initiator, to be applicable has a thermal initiator is, around 100 to 170 kilo joule per mol.

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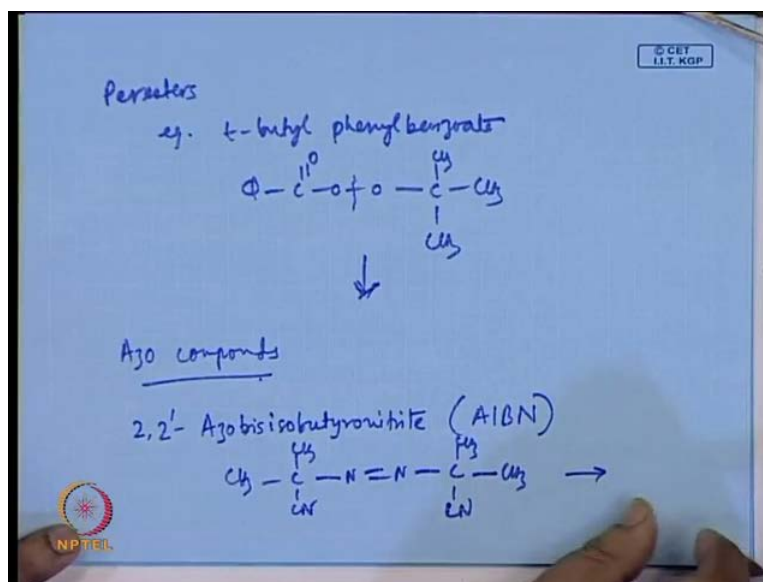
And typically if you have, this peroxides, or this s s bonds or if you have n o bonds in your molecules; these bonds typically having bond dissociates energy of this range, so they form on hitting, and a normal, the reaction temperature they form radical, each molecule form two radicals. For example if you consider this peroxides, could be acyl peroxide acetyl or benzyl; for example, if I write the structure of benzoylperoxide, it can break homiletically on thermal energy, on hitting to c o dot.

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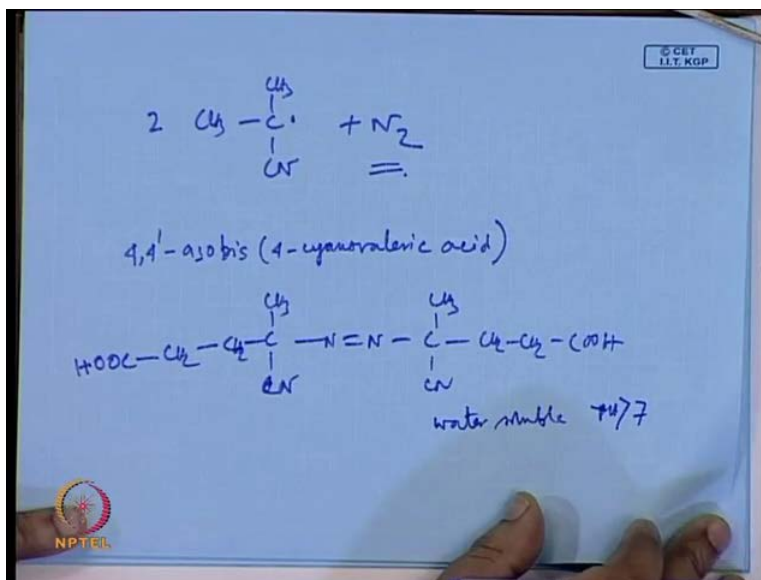
Now we can have alkyl peroxides as well; for example cumyl or t-butyl peroxides. Let us take example of cumyl peroxide, it can dissociate into two such radicals. Also this hydro peroxides; for example t-butyl hydro peroxide, it can also undergo homolytic cleavage forming two radicals. Other examples also like peresters, let us talk about in next page.

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For example t-butyl phenyl benzoate, it can break from here, and form two different radicals. Now, the other main types of initiator, thermal initiator are azo compounds. For example 2,2-diazo bis isobutyronitrile, which is most commonly named as, or called as AIBN, which is having this following structure. Now this can break into two species, let us write in the next page.

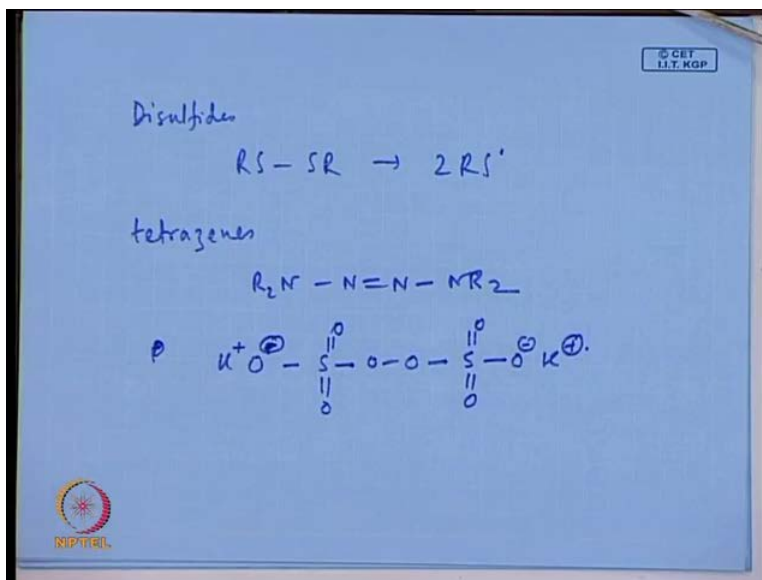
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Plus N 2. Now in this case, this, the bond C N bond is not, this bond is not of the, having that bond dissociation energy, between 100 to 170 kilo joule per mol; that's the bond energy, optimal bond energy talked about. This is actually having higher 290 kilo joule per mol, but because of this nitrogen generation, this molecule, this dissociation also becomes feasible, or very much feasible at normal reaction temperature. Other examples of azo compounds are, for example 4 4 dash azo bis cyanovaleric acid.

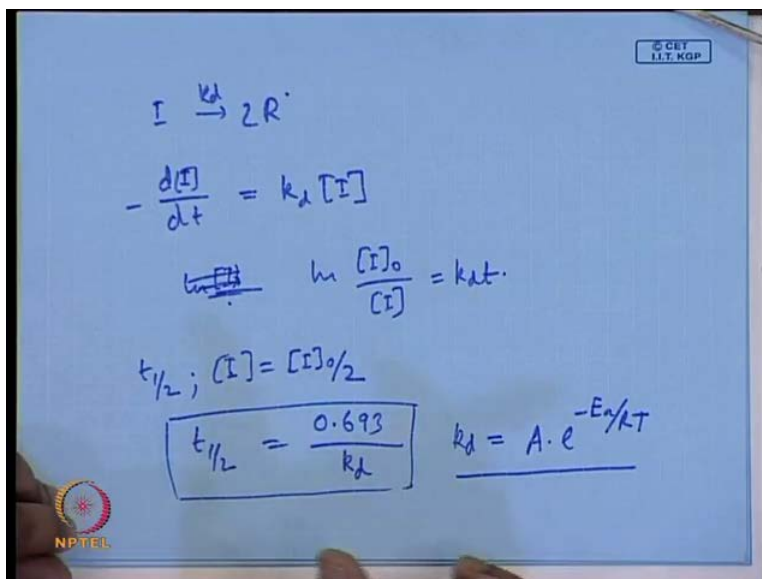
So, these are the examples, typical example of this azo compounds of this. This compounds specifically is that it is water soluble, water soluble at p h greater than 7, so you can use this azo compounds at acquits medium as well. So that it can be used for generating, or radical polymerization is acquits medium as well, whereas A I B N can be used in the radical polymerization in organic solvents, so organic medium. The other types of this radical initiator are, like for example disulfide.

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I have R S and S R, giving 2 R S dot, or I have tetrazenes, which breaking and giving 2 R N to R 2 N dot plus nitrogen, or it could be other peroxides; for example you have potassium, it can have these peroxides as well. So these are the typical examples of the radical initiators. These are the generally used radical initiator, and most common is A I B N and benzyl peroxides which are used in the lab.

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Now, this radical is generated from an initiator species, now if I want to find out how fast this radical generation happens, we can write this rate equation, which is basically dissociation constant, multiplied by the initiator concentration, this follows first order kinetics, so it's multiplied by initiator concentration, which will give you, this on interrogation, where I_0 is the concentration of initiator at $t = 0$, and this is some other t . Now if you define $t_{1/2}$, where a time, where I is I_0 by 2, if you define $t_{1/2}$ as the time, where the concentration of initiator has halved, then you can write $t_{1/2}$ is, can put I is I_0 by 2, you can get this.

So from the dissociation constant you can get the $t_{1/2}$ value, and these dissociation constant also, or the rate constant for dissociation reaction, also depend upon the temperature, where you are doing your reaction. Now, if you want to do a reaction, and you should have prior knowledge about the initiator molecule, prior knowledge about their $t_{1/2}$ value, or the time it takes to become half. Then you can choose your reaction temperature, or if you want to do your reactions some particular temperature, or a range of temperature, then you can choose the proper initiator for your reaction. For example if I look at the $t_{1/2}$ values for some commonly used initiators.

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	50°C	70°C	85°C	100°C
AIBN	7.9 h	4.8 h	-	7.2 min.
BPO	-	7.3 h	1.4 h	20 min.

AIBN : 60°C - 80°C
 BPO : 80°C - 95°C

typical values of $k_d = 10^{-4} - 10^{-9} \text{ s}^{-1}$
 average range $k_t = 10^{-4} - 10^{-6} \text{ s}^{-1}$

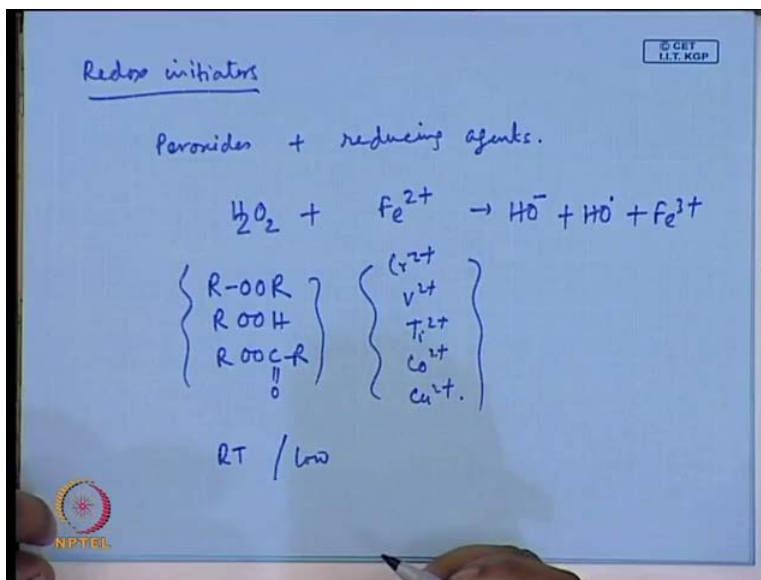
For example, if I take very commonly used example, like AIBN and benzyl peroxides, said BPO, benzyl peroxide, and if I write the values of $t_{1/2}$, $t_{1/2}$ then let us have these numbers.

So if these are the $t_{1/2}$ numbers, for commonly used initiator AIBN and BPO. So, AIBN have $t_{1/2}$ value of at 50 degree centigrade about 74 hours, whereas 100 degree centigrade, which has a $t_{1/2}$ of 7.2 minutes; that means if you use AIBN as the initiator, for reaction which you are carrying out at 100 degree centigrade, then your reaction is very fast, it will complete, and all the AIBN, at least half of the AIBN will consumed in 7 minutes, so you can imagine your reaction is very fast. Whereas if you do at 50 degree centigrade, then even its 74 hours, so almost like three days you have, half of the initiator is dissociated to form radical, so that means it is too slower reaction, if you do it at 50 degree centigrade.

So for that is the example AIBN is typically used as around 60 to 80 degree centigrade, and benzyl peroxide typical reaction temperature is between 80 to 95 degree centigrade. And $t_{1/2}$ value for, at 10 hours the temperature at which, $t_{1/2}$ value becomes 10 hours, its typically the most, what I say, most used temperature, where $t_{1/2}$ is 10 hours, and for that AIBN is about 60 degree centigrade and BPO is about 65 degree centigrade, but it is all depends upon how fast you want to carry out reaction, you have to choose your temperature accordingly; for example AIBN, and if you want to use a 100 degrees, it is too faster reaction. So it is always recommended that you should use AIBN at this range, and BPO in this range, to have a moderate reaction rate.

Now we have, and typical this values of k_d 's are. Typical values of k_d for thermal initiator is, 10^{-4} to 10^{-9} second inverse, and the usage range, where your k_d is formed 10^{-2} to 10^{-6} centimeter. The temperature where your k_d is lies between these; that is the temperature, where the reaction is typically done. So we have now know, that what are the molecules are typically used for thermal initiation, and what are the criteria in that initiator molecule should be, and looking at the $t_{1/2}$ values at different temperature, we should choose a temperature, and a initiator combination, for a particular reaction if you want to do a reaction for a particular temperature, then if you choose a initiator molecule accordingly.

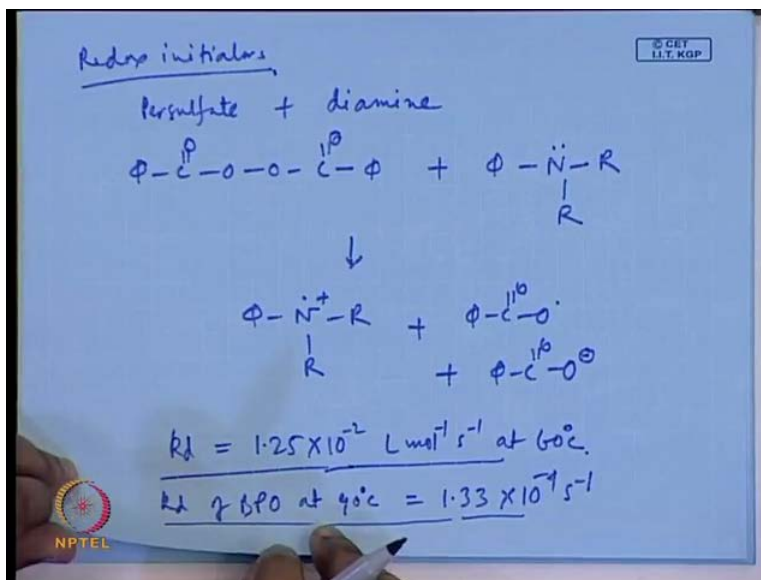
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So, now let us move to other type of initiator, and next let us look for redox initiator. So let us look for redox initiators, and the name suggest if you have a reluctant and have a oxidants, so for example if you have a peroxide, plus a, this is oxidizing agent plus a, reducing agent. For example, if you have a hydrogen peroxide plus farers, so it is giving to H O minus plus H O dot plus F e 3 plus. Instead of hydrogen peroxide, you can use the other peroxides, so hydro peroxides as well, and this case you can use other ions as well.

These are the types you can use here, and you can type here, but the general reaction is same, and the reaction is much faster, and it can be done at room temperature, or even at lower temperature 0 to 5 degree centigrade, or something. If you want to do a reaction at low temperature for whatever reason, then this is the initiator system, you can apply and as these things are soluble in acquits medium, you can carry out the acquits radical polymerization using, redox initiator like this, or even if you want to do a, your radical polymerization in emulsions, then also this type of reactions can be initiator can be used.

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The other type of redox initiator, are the example of redox initiator is, per sulfate and di amine plus di amine, again a combination of redox reducing and oxidizing agents. So benzyl peroxide and, say n diethyl, I mean if R is ethyl group, then it reacts and give this. Now k d of this reaction is, at 60 degree centigrade. Whereas, k d for B P O at 90 degree centigrade was 1.33 into 10 to the power minus 4 second inverse. Which means that, this is much faster, this redox reaction is much faster, so generation of radical by redox initiator can be done at much lower temperature, room temperature, or even lower temperature.

Whereas in B P O, the case of thermal initiator, the reaction rate is much lower. So, you need a higher temperature, for doing the polymerization reaction. So what we will do in the next lecture, we will continue this, the other types of initiator, and including the remaining example of, the redox, the possibilities of redox initiator. So we will come back and start in the next lecture from this redox, the other example of redox initiators.