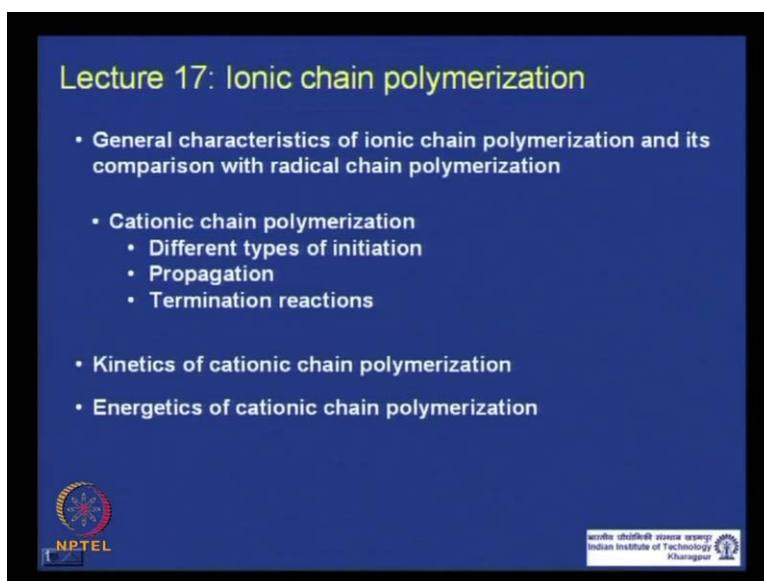


Polymer Chemistry
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Lecture - 17
Ionic chain Polymerization

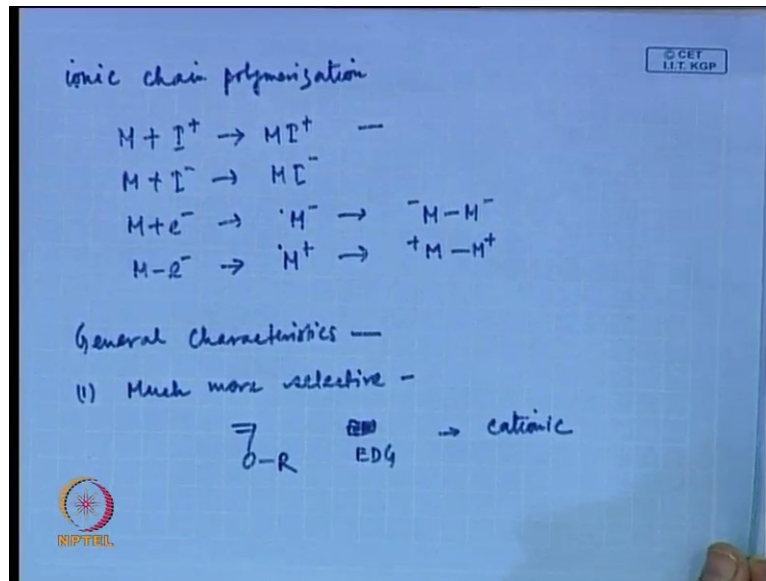
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Welcome back to this course on polymer chemistry and in today's lecture, which is lecture number seventeen, I am going to cover or begin our discussion on ionic chain polymerization.

Now, in this lecture I plan to cover discuss the general characteristics of ionic chain polymerization, and while discussing I will compare how this ionic chain polymerization compares with radical chain polymerization. And then we will go to cationic chain polymerization and talk about different types of initiation for cationic chain polymerization, and then go to propagation and termination reactions in cationic chain polymerization. And then I will talk about kinetics of cationic chain polymerization and then energetics of cationic chain polymerization. And in next lecture, I plan to talk about the other type of ionic polymerization, which is anionic chain polymerization.

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Now, let us begin our discussion on ionic chain polymerization. Now, as the name suggest, in this case the initiation is from an anionic species, whether it is a cation or anion. Say, if I consider M as a monomer and I is a, initiation, initiator, then it could be a cation or an anion, which will, according to which we name cationic polymerization or anionic polymerization. It could be acceptance of electron giving rise to a radical anion or removal of an electron, which gives to radical cation, which two of which might combine to give you a dianion or a dication which can further initiate the chain reactions from both the sides. So, this is example, this is a case of cationic polymerization. This is a case of cationic polymerization and this two are the case of anionic polymerization.

Now, in this case, the ionic species are the initiator or rather the initiators are ionic species, so as the propagating species also ionic. Now, the some polymerization, for example, initiation by coordination or semi clock side, which also progress through an ionic species, propagating, propagates through ionic species route, but those we are not going to cover as an ionic chain polymerization. So, ionic chain polymerization we will consider only when both the initiation and the propagation reaction is by ionic species.

Now, like radical chain polymerization, these ionic chain polymers, polymerization reactions are not very popular commercially. There are main, too main reasons why

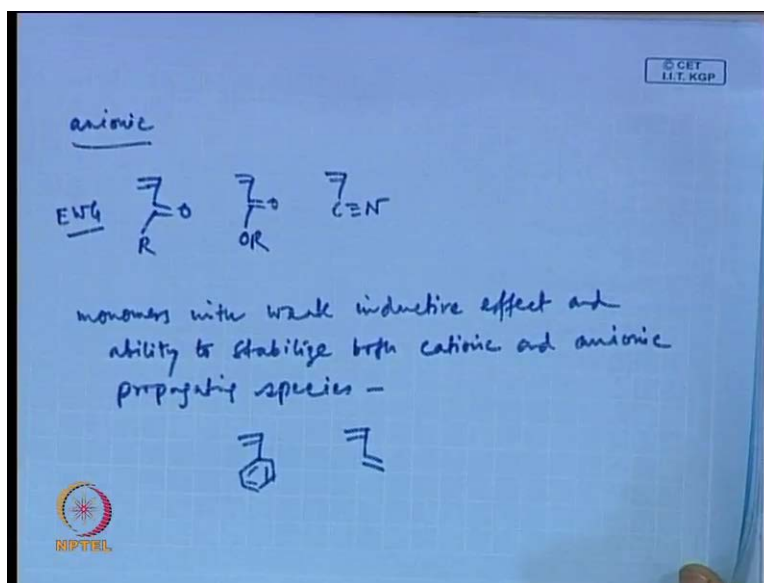
they are not so utilized commercially. One is that stringent requirement of polymerization in case of this ionic polymerization. We require very, stringent, stringent conditions, which are difficult to achieve in a large industrial scale and also, this ionic polymerization are very selective, which means, that not every monomer can be polymerized by ionic polymerization, unlike, unlike radical case where most of the, poly, monomers, double bond (()) monomers can be polymerized by radical chain polymerization we can assume. So, these are the main two reasons why this ionic chain polymerization, are not practiced that commercially in that scale.

And so in that sense, it is not that important like radical chain polymerization. However, this polymerization is ionic chain polymerization, gives us opportunity to synthesize specialized polymers, like block copolymers or tellically polymers, which are basically (()) type polymers, (()) having functional groups at the end of the chain, which we can, we utilized for the, for another reactions.

So, let us start the discussion on ionic polymerization and let us talk about first the general characteristics. And while talking these general characteristics of ionic polymerization we will compare its differences or its likeliness with the chain, radical chain polymerization. First is that as I just said, that it is, it is much more selective, much more selective.

Now, why do we started our discussion on chain polymerization? We talked about, that this monomers like this ether, which have electron donating group like there oxygen, which can be lone pair, can be donated if it is a cationic centre here. Now, this type of monomers can be polymerized by cationic chain polymer, polymerization reaction because the resulting cationic propagating (()) can be stabilized by the electron donating, mechanizing donation by the oxygen from here.

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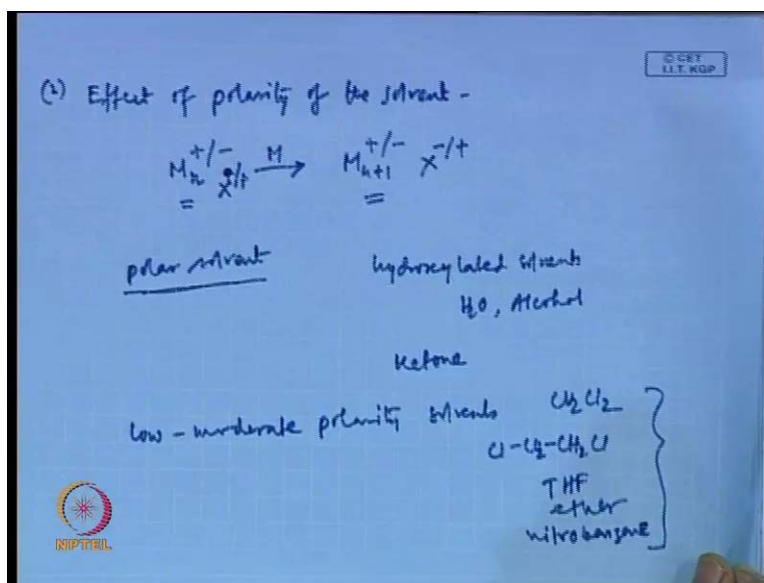
Now, for anionics, for anionic chain polymerization we need to have monomers, which have electron withdrawing group, electron withdrawing group, which could be, as we discussed earlier, something like this, (()), acrylates or methacrylates, and, and so on, with this can be polymerized anionically because the resulting anion can be stabilized by this resonance with the carbonyl bond.

So, in that sense, this anionic and cationic polymerization at very (()) and only if the monomer has, monomer with, monomers with, with inductive effect and ability to stabilize the propagating species by resonance in the, both for cationic and anionic, then this monomers can be polymerized by both cationic and anionic. So, if I write on the, complete this sentence, in that you can able to do, stabilize both cationic and anionic propagating species. For example, you have styrene where both cationic and anionic can be stabilized by resonance with this aromatic group or say, (()) cation, resulting cation or anionic can be stabilized by resonance from this double bond.

As we see, we have seen now from this discussion, that not every monomer can be polymerized by anionically and there is a set of polymer, a set of monomers, which can be polymerized anionically. And you know, less number of monomers can be polymerized cationically, and there are even lesser number polymers, which can be polymerized by both anionic and cationic polymerization. While in case of radical we have seen, that all this, this monomers or this monomers or this can be all

polymerized by radical chain polymerization. So, in that case, in that composition radical is a, radical chain polymerization is much less sensitive compared to the ionic polymerization.

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Now, second characteristics, if you want to talk about, is the effect of polarity, effect of polarity of the solvent. It is not only polarity, but the capability of the solvent molecules to solvate the ionic species giving the chain propagation.

Now, as you have seen earlier, that a propagation reaction can be (()) this. It is either cationic species or anionic species. Now, this anionic species or cationic species, they are not present alone in the medium, they are always associated with or accompanied by a counter ion. For the positive it is an anion, for negative it is a cation. So, this propagating chain are always of this ionic group, are always accompanied by a counter ion of oppositely charged, that is always happens.

Now, depending on the association behavior of these two species, the active center and the counter ion, the reactivity of the propagating species varies. What I mean, that if they are very tightly bound, they are very tight (()), then obviously, the accessibility of, or the reactivity of this ionic center are less. So, the propagating species is less reactive. While if you compare with the situation where they are well separated, they are like free, free hands. Now, if they are free, then obviously, they are more accessible and the reactivity of this propagating species, ionic propagating

species are much more reactive or much more reactive compared to situation when they are tight ion-pair.

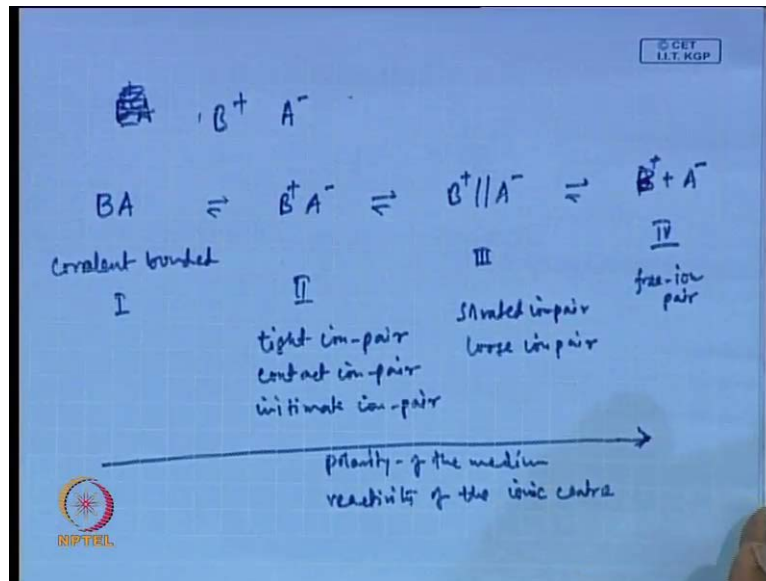
So, it is always preferred, that you have a polar solvent, it is, this is always preferred. We do ionic reaction in a polar solvent because if you have polar solvent, then this oppositely charge ions, ions will be well separated in the medium and if they are well separated, obviously, the reactivity of the active center in the propagating chain will be higher. So, you have a higher rate of reaction or an eventually higher molecular build up.

Now, often if you use polar solvent, for example if you use hydroxylated solvents, hydroxylated solvents like say, H₂O or alcohol, what happens? This, this reacts, this hydroxylated solvents react very, very fast, you know, very effectively they react with this ionic species and then stop the chain. So, these ionic centers are destroyed with reaction of this hydroxyl, hydroxy molecules, H₂O or alcohol. If you have other polar solvents, like say ketone, what happens? This ketone loop complex form complex with this ionic species and then once they form complex, the reactivity of this ionic species are lost. So, you do not have an effective polymerization happening.

So, you require a polar solvent to have these charges separated and ions as free as possible. Similarly, if you use very high polar solvents, like hydroxylated solvents or ketone, then the reaction actually gets stopped by reaction of these solvent molecules with the reactive species. So, eventually or practically, a low to moderate polarity solvents like, say methylene chloride or say, methylene dichloride or THF, (()) or ether or nitrobenzene.

So, these are the examples of some of the solvents, which have, medium, low to medium polarity and does not high react with those ionic species. They, they actually can be used for ionic species polymerization, but this is, these are not very generic in the sense, that the solvents, this solvents also can react with anionic species as well. So, we have, we will discuss specifically for the requirement of solvent. We will talk about cationic and anionic polymerization individually.

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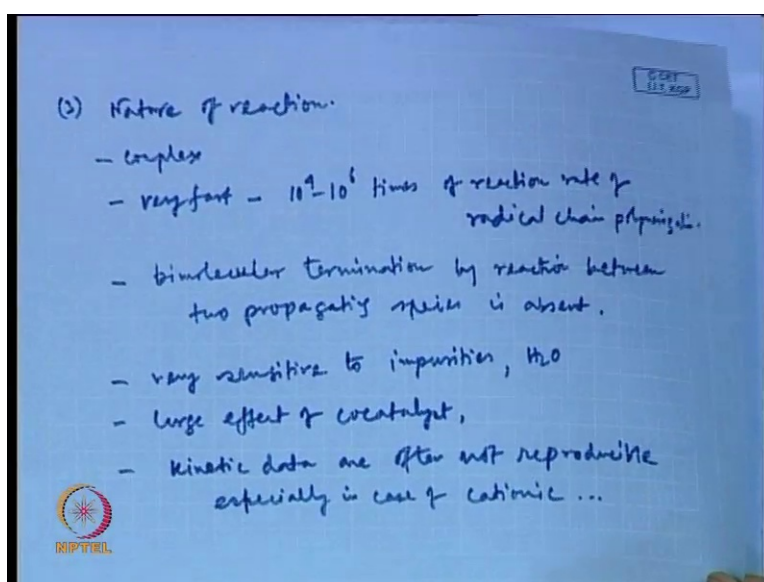
Now, how this, if you want to write a, a generic structure of, say, to write, write a cationic propagating species, which have, which (()) a cationic reactive centre and a counter ion, which is represented by A minus, so what are the possible states they can represent? One, they can be completely covalent bonding, covalent bonded, covalent bonded, one. Two, they can be tight ion-pair; these are very tight, no solvent molecule in between. So, tight ion-pair or sometimes it is called contact ion-pair or see, some people say intimate ion-pair. Same thing is called with different names. It can be present as solvated. So, solvated has three solvated ion-pair or loose ion-pair or they can be totally free, free ion-pair. So, these are the possible, depending upon the polarity of the medium this could be the four possible association states between these two ionic species.

Now, it, we have given examples of cation and anion here where the propagating species is B plus, is said the both cationic polymerization, the propagating species in cationic polymerization. But it can be true; this post can be true for the other anionic polymerization as well. Now, obviously, with the increase in the polarity of the medium, if you increase the polarity of the medium, this, this, the more polar means, the ions get solvated and then finally, get as free ion, ion-pair. So, as the reactivity of the ionic centre, obviously, the free is the ionic center it gets, it becomes more reactive. So, which means and in some cases these, these are not present isolately,

they actually remain in equilibrium and equilibrium shifts depending upon the polarity of the medium.

So, in this way you can understand, that solvents play, solvent means, I mean polarity of the solvent plays a very important role in terms of reactivity of these ionic reactions. And if you compare with radical chain polymerization, solvent polarity actually has no such role to play in case of radical chain polymerization. You have to only check whether the solvent can solubilize the monomer or the reagent and it, solvent should not participate in the undesired chain transfer reactions. So, this type of solvent dependent reactivity was absent in case of radical chain polymerization.

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So, third characteristic we can talk about and compare the nature of reaction. Now, this, these are complex reactions as we will find out from further discussion, that these are complex reaction and they are very fast. They are fast; they are about, say, 10 to the power 4 to 10 to the power of 6 times of the reaction rate of radical chain polymerization. So, they are very fast and this fast nature of this reaction is due to the fact, that the accumulation of this active centers.

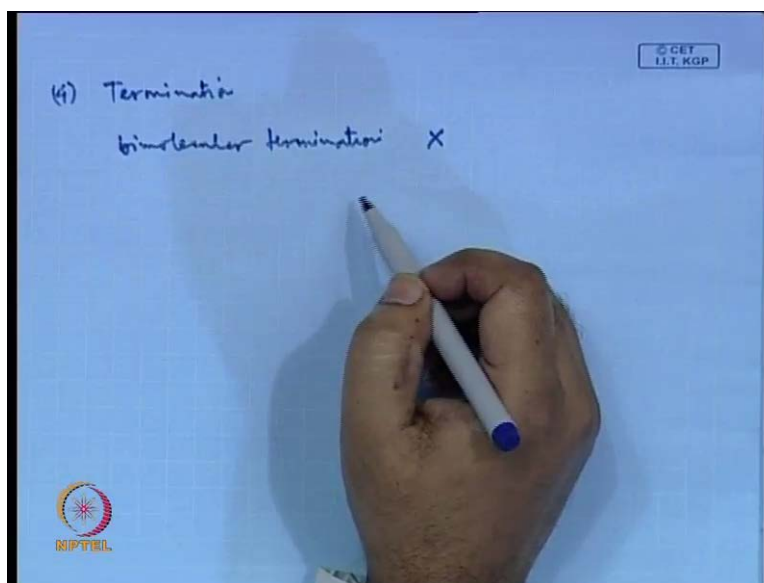
And as we will immediately discuss, that in case of ionic reaction, this bimolecular, molecular, termination bimolecular termination by reaction between two propagating species is absent or absent because they are anionic charge. One cation cannot react with another cation, cationic propagating species and terminate the reactions in case

of radical. What you have seen, that radical, two radical propagating species can react with each other and can terminate either by combination or by (()) in case of cationic, anionic polymerization or cation polymerization. Because they have seen this propagation species are similarly charged, they cannot react with each other and terminate the chains. As a result, there is a huge increase in the concentration of these active centers in the medium and as a result, the reaction is very fast.

But in case of radicals we have seen, that the steady state concentration of the active radicals is very low and as a result, the propagation was comparatively low in a slower, in comparison to these ionic polymerization. And as these ionic centers are very reactive, they are very sensitive to, very sensitive to impurities, which includes moisture because they are very active, reactive. These ionic centers are very reactive, they are very sensitive to this impurities where you know, that radical, though radical chain polymerization are sensitive to impurities, but they are not as radical chain polymerization, is not as sensitive as in case of ionic chain polymerization and sometimes large effect of, large effect of cocatalyst. Cocatalyst are nothing but small inorganic compounds, like say H_2O , can be observed in case of ionic polymerization have, which was not the case of radical polymerization.

And as the reaction is very fast and complex, this kinetic data, kinetic data are often, often not reproducible because this kinetic data is not always reproducible, especially in this case of kinetics, especially in case of cationic polymerization, cationic, the mechanism and the mechanism on kinetics of this ionic polymerization, especially cationic chain polymerization is still not completely understood (()), to understand the mechanism in kinetics of this ionic polymerization, especially the cationic one, because as I said, these reactions are very fast and not reproducible.

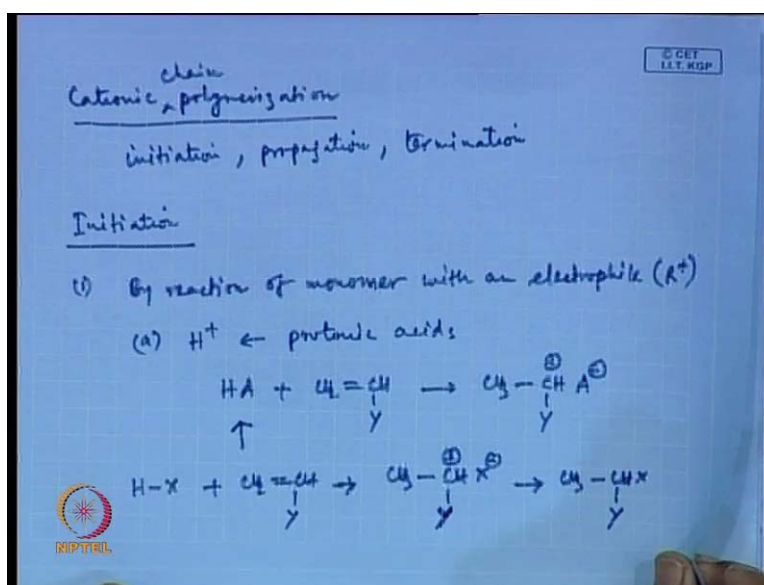
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And as I said earlier, this four is your, the termination reactions. As I said, that bimolecular termination is not possible, bimolecular termination by the action of two propagating species is not possible and so if you can suppress the other, other reactions, which are chain transfer reaction, if you can suppress those, you can actually keep this chains, this ionic chains as living because you can, because the inherent or intrinsic termination reaction between the propagating species are not there, they are absent.

So, if you can stop the side reactions, which includes the chain transfer reaction, then you can actually make this chain alive or this polymerization could be living polymerization and that is especially true for anionic polymerization. You will find out in later discussion, that in case of cationic there are other ways, which are likely like chain transfer reactions, but in case of anionic it is comfortably easy to make polymerization, leaving chain polymerization. Whereas, in case of radical, we know, that this termination can be possible by bimolecular reaction of the two propagating new species.

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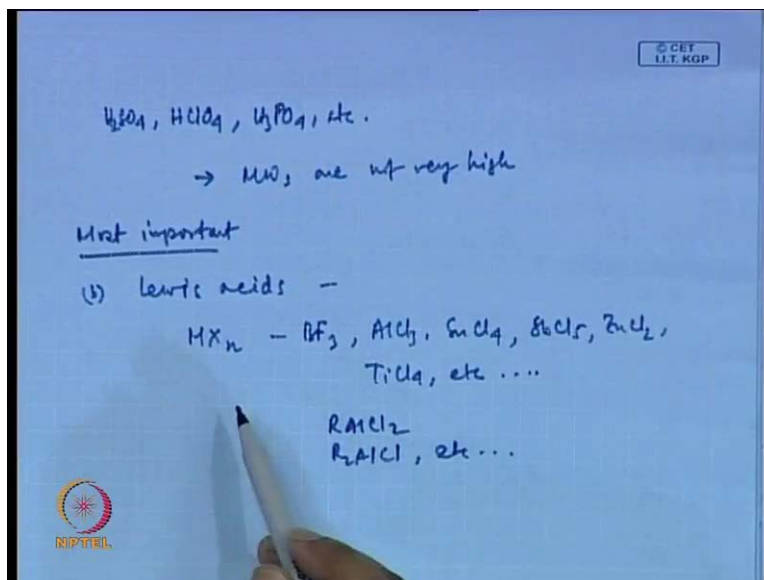
So, let us now talk in detail about the cationic polymerization. So, let us talk about and again, like radical polymerization if any chain polymerization, this cationic chain polymerization we were discussing. So, I should write cationic chain polymerization. So, it consists of three steps: initiation, propagation and termination.

First, let us talk about different types of initiation reactions, different types of initiation reaction and first one is, which is more common is, by reaction of monomer with an electrophile, say R^+ and this electrophile could be H^+ , which you get it from protonic acids. Now, if I write generic way, H^+ plus A^- , generic structure of a monomer, it gives you $CH_2=CH-Y$, cationic species, and A^- . This is counter A^- , is the counter ion.

Now, HX would be strong enough if these acids should be stronger enough to produce significant concentration of the protonal species, so that it can initiate, react with the monomer. And A^- , the counter ion, should not be heavy, strong nucleophile because if it is a very strong nucleophile, then it can react with the cationic group and make a covalent bond and stop the reaction there itself. For example, if I consider a case of halogen acids like HX and take the generic structure of the monomer with the reaction, we put on electrophilic reaction, it will form the same initiating species, but because this halogen anion is (X^-), is so strong

nucleophile, it will actually combine again and form a covalent bond. So, your reaction stops there. You cannot have the reaction progressing further.

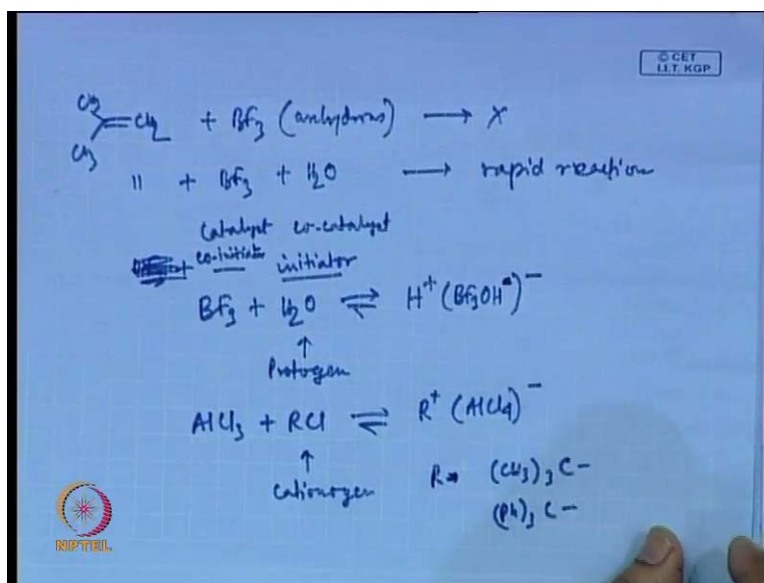
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So, so other protonic acids like H_2SO_4 or say, $HClO_4$ or phosphoric acid. They are used, they can be used because these counter ions are not so strong nucleophile like halide ions, but still this, this, because they are, they are also significantly nucleophilic, this cannot build very high molecular weight polymers by cationic chain polymerization. So, these are limited and the molecular weight, molecular weights are not very high for this proton by this reaction, cationic reaction by this protonation.

So, most, most popular, most important, this electrophilic reaction is reaction of Lewis acids. So, that is B, with the Lewis acid I can write generic structures like MX_n for Lewis acids. Example could be BF_3 , $AlCl_3$, $SnCl_4$, $SbCl_5$, $ZnCl_2$, $TiCl_4$, and so on, or they are (()) derivatives, like $RAlCl_2$, R_2AlCl and so on. So, these are Lewis, Lewis acid can be used for supplying an electrophile for reaction with the monomer, but it is this Lewis acids are seldom used alone.

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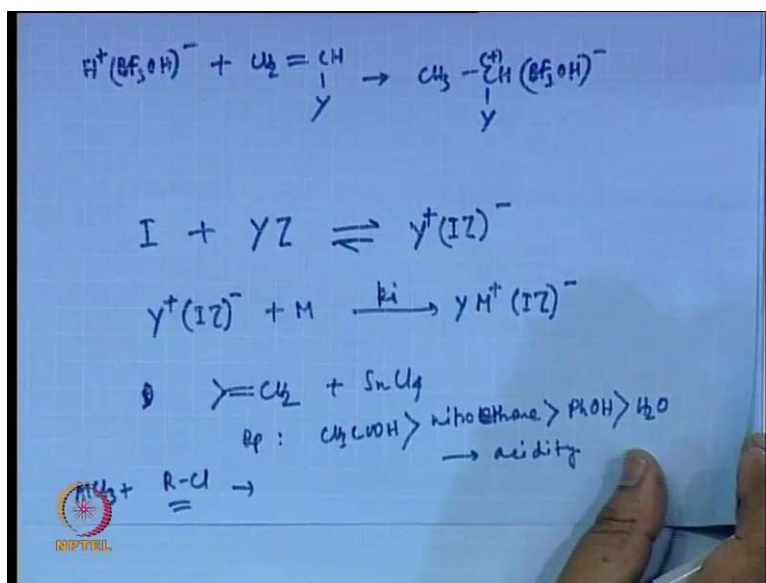


For example, if you take a reaction of isobutylene plus anhydrous BF₃, anhydrous BF₃, then there is no reaction. But at the moment you add little bit of water along with this mix, so you have the same reaction with BF₃ plus H₂O, then there is a rapid reaction. So, these examples showing as these Lewis acids, which we just showed in the last page, they are often used along with a second catalyst or cocatalyst, which can be water molecules or some other molecules. We will just give examples in few minutes.

So, if you consider this case the reaction happens like this. BF₃ plus H₂O makes a complex or we can use other Lewis acids and we can use this alkyl halides as a cocatalyst and this case, the complex found is like this. So, this case, this is a protogen, which is basically proton donor protogen and this is cationogen, which is a cationic species donor or carbocationic, carbocation donor. Now, this is called nowadays initiator because this is the species, which is supplying the H plus or R plus (()). This is coinitiator, coinitiator, BF₃ or AlCl₃ are, sometimes they are called this BF₃ or AlCl₃, called catalyst and this initiator called cocatalyst.

So, you should be careful about this nomenclature, other you called this as initiator and coinitiator or you called this as catalyst and this is the cocatalyst. Now, I can write generic reaction for this type of reaction. Now, once you form this, again react with the monomer and form the initiating species, which let us write in next page.

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Similarly, you can write this similar reaction for this aluminum chloride and alkyl halide reaction. This alkyl halide could be, say for example, R could be tertiary carbon or could be a triphenyl carbon group. So, this is example of alkyl halide, which is used for this cocatalyst or initiator in this reaction. So, I, I can write a generic equation or expression, say I, I for the initiator and YZ, this is for your coinitia, I for the coinitiator, this is for the initiator or this for catalyst and this is for the cocatalyst, giving rise to a cationic species and a counter ion. This is I and which then react with a monomer forming the chain initiating spices. Now, we are writing k_i for this reaction because it has been found out, that of these two reactions, this is the two reactions, consists of chain reaction, chain initiation reaction.

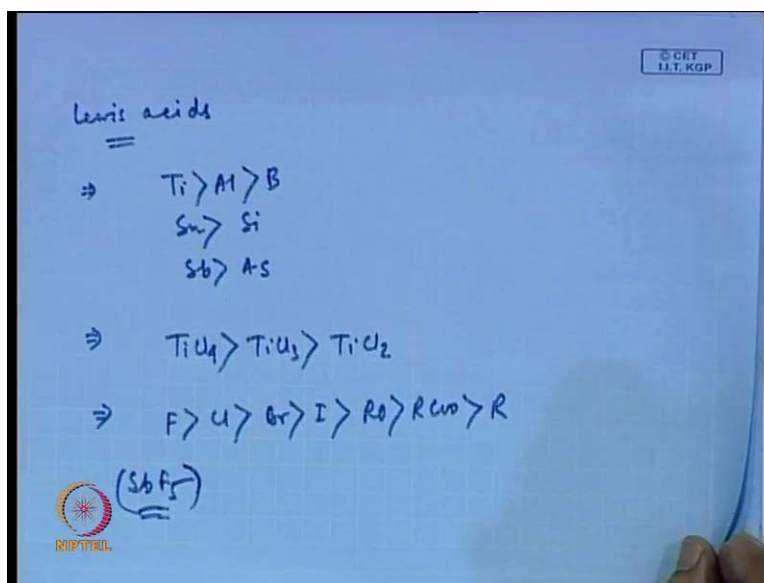
This, this is the step, which is rate determining step. So, we will consider this reaction while calculating or while determining the, or looking at the kinetics of this chain polymerization. Remember, if you compare with the radical chain polymerization, this was the first reaction compared to the step, the first step, where radical was getting generated from the initiator molecule and we considered that as a rate determining step for radical chain polymerization. But in this ionic chain polymerization we, this is the faster reaction step where this is the slower and rate determining step. So, for ionic reaction monomer also participate in the chain initiation reaction where in case of radical monomer was not actually part of the chain initiating expression

Now, the reaction rate also depend, depends on this YZ, which is basically a cocatalyst. It will also influence the polymerization rate because the activity of the initiation complex depends how readily it can transfer a proton to the monomer and that in turn depends on the acidity of this cocatalyst. For example, if I consider ionic, cationic polymerization of isobutylene by tin chloride catalyst, then the reactivity of this reaction or the rate of reaction follows R_p , follows in the order like this, nitroethane, nitroethane, phenol, water, which is basically the ranking of the acidity of this cocatalyst.

So, basically the type of cocatalyst also influence the polymerization because the acidity of this, this complex, the activity of this complex depends on how readily it can supply this cationic species, where I say proton or in this case it is a proton or a carbocation to the monomer, and for a proton or protogen or a proton supplier, it depends on the acidity of the cocatalyst. So, it follows this trend and for the carbon cationic generator like RCl, like $AlCl_3$ plus, this reaction. Now, this reaction (()) complex, the, the activity, the total polymerization rate dependence on this RCl is little complex and we will keep the discussion for this course.

So, you should just remember that the, the structure of the cocatalyst also determines the rate of polymerization and also affect the rate of polymerization, and we will now see that. Obviously, I, the catalyst or the coinitiator also affects the rate of polymerization.

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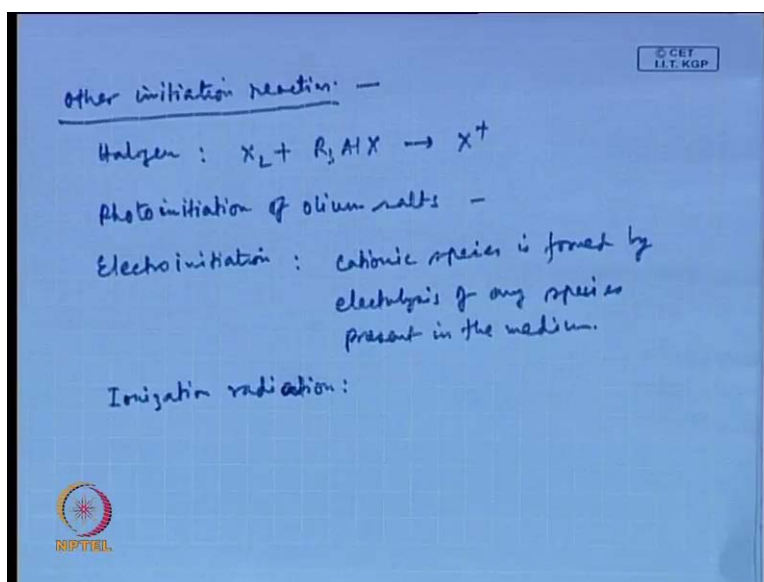
Now, now Lewis, Lewis acid, we are talking about this reaction are the initiation, is by Lewis acids. So, Lewis acidity of these defined metals increases with atomic number. We know that Lewis acidity follow this order. This Lewis acidity of this defined metals increases with the atomic numbers. So, for a single metal, say, if we consider titanium, then again the Lewis acidity increases with the oxidation number. So, $TiCl_4$ have more Lewis acidity compared to, $TiCl_3$ than this. So, for, if you compare with defined, different metal is basically atomic number. It will determine the Lewis acidity and for same, same metal is the oxidation state increases, the Lewis acidity increases and also the Lewis acidity.

For a single metal follow this trend of the ligand. If this ligand, they follow this, so obviously, if the ligands are fluorine or chloride, they have much more Lewis acidity compared to the ligands are, this is, this is from your basic knowledge from inorganic chemistry, basic knowledge and this is, from this expression, you know, this is strongest Lewis acid and this is, not always we use this though it is a very strong Lewis acid, for all the cationic reaction.

We will not use this as a catalyst or a cointiator because rather than other complication if the reaction, it is too fast, then the side reactions also come in the picture, the side reaction also increases. If the side reaction rate also increases, then again the problem of molecular build up come. So, though this trend is there, now

while choosing the catalyst or the coinitiator, it is, it is not this general trend is always followed, you have to keep the other factors in mind as well. So, we talked about the initiator reaction with by this reaction of the monomers with the electrophile.

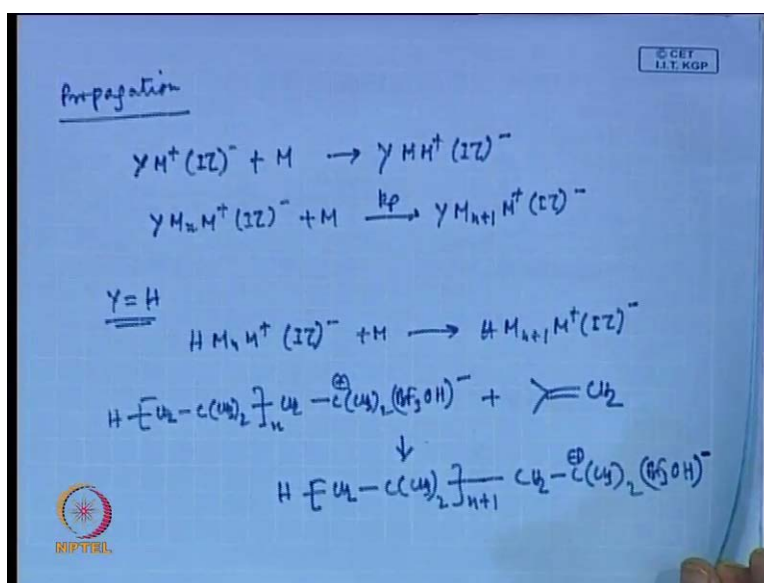
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Now, there are other initiation reactions, other initiation reactions, for example, halogen, halogen can be reacting with more acidic Lewis acid and gives out cation, halogen cation. This can be initiation; can be done by photo initiation of oxonium salts. It can be done by electro initiation where cationic species is formed by electrolysis of any species present in the medium or it can be done by ionic, ionization radiation, like in the case of radical the initiation can be done by ionization (()). So, these are the other possible ways of initiating a cationic polymerization. But as I mentioned in earlier, these are the generic examples, which we get in this page. These are the most common example of or the most important initiation reaction.

So, we will talk about kinetic. So, energetic, we will consider this generic initiation step and also consider this initiation step, of, for the discussion because this is the most important of the initiation step we just discussed.

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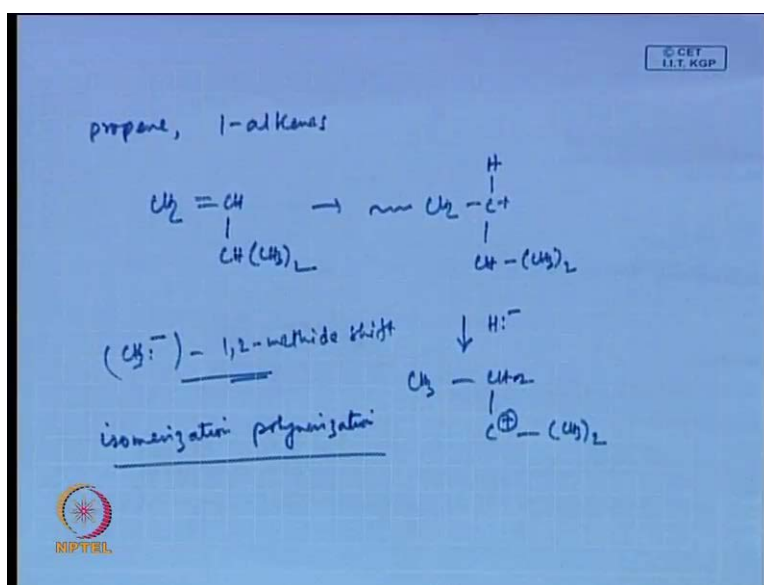
So, let us now discuss the propagation step. Propagation, we have already seen the different types of initiation possibility and as I said, we will consider the generic case, we, as I showed there.

So, this, this was the initiation reactions. So, you have this initiator, coinitiator complex, which starts the chain initiation. I write this in the next page, it can react with the name and start the chain propagation reaction and I can write a generic expression of this in this way plus M kp n plus 1 M plus IZ minus. If Y is H, the photogens we can write H M n M plus IZ minus. For examples, that Ba 3 water case, I can write this is a proton donor. So, I can write...

This is the reaction of isobutylene catalysed by this reaction. I just recall from your earlier decision, I am writing the propagating reactions here. This, on reacting on with isobutylene, will produce the...

So, these are the examples of the propagating steps and sometimes this propagation reaction could be complicated and because of this one two hydride shift, but that is not very common.

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I will just give you an example when this propagating steps could be little complicated and by hydride shift or (()) shift and that is applicable for say, propene or one alkene, one alkenes, take example.

Now, this can undergo a hydride shift and from this carbo cation. So, as a result more complicated products actually form when there is type of hydride shift or some cases methide shift, some cases shift one two methide shift. If this happens, the reactions become very complicated and we call that sometimes isomerization polymerization as well. But this is not common; this is especially applicable to some monomers.

The example we gave, most common propagation steps are in this page, what we just discussed now and as you can realize, that the rate of propagation will depend on the solvents. We discussed in length the effect of solvent polarity and if the polarity of the solvents is high, then this ion-pair will be more towards a solvated or free ion-pairs, then in the reactivity of this cationic species will be higher. So, the rate of polymerization will be higher.

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8. polymerization of styrene by HClO₄

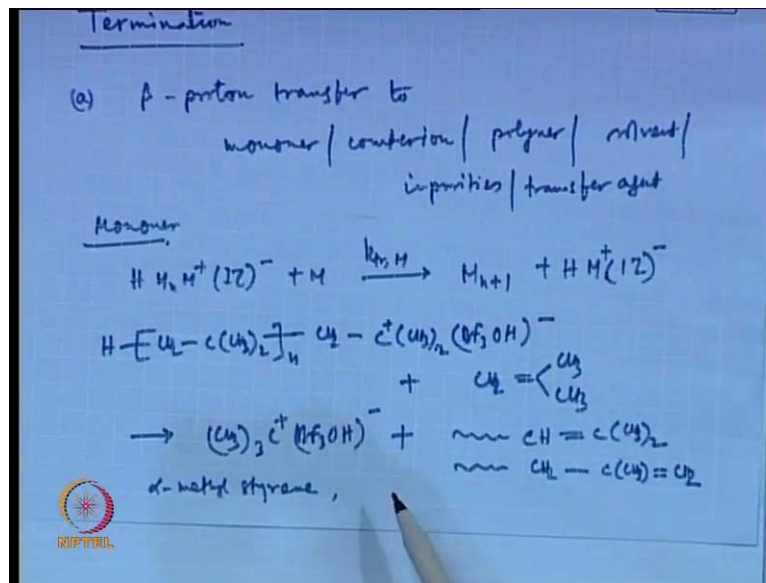
Solvent [CCl ₄ : (C ₂ H ₅ Cl) ₂]	ε	k _p	L mol ⁻¹ s ⁻¹
100 : 0	2.3		0.0012
40 : 60	5.16		0.4
20 : 80	7.0		3.2
0 : 100	9.72		17.0

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Now, let us have, let us see some data related to convince that understanding. Say, let us take example of styrene, polymerization of styrene by or chloric acid HClO₄ solvent is a mixture of CCl₄ and ethylene dichloride. This is a dielectric, resulting dilating constant and this is your k_p liter mole inverse second inverse. If you have pure CCl₄, obviously, this is more non-polar, dielectric constant is 2.3 and the rate is low. When you increase the polarity by adding ethylene dichloride, dichloethane, EU, say in 40-60 mixture, your dielectric constant goes up, your reaction goes up. If you consider further, 20, 80, 7 and this is 3.2, 3.2, 0, 100, 9.72 and this is 7.

So, if this is the data to convince you, that if you increase the polarity, which is given by dielectric constant, the rate constant or the rate of the polymerization reaction increases.

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So, we just discussed the propagation steps, now let us talk about different possible termination steps in cationic chain polymerization and as one more time, that it cannot, termination does not happen by bimolecular reaction of the propagating species and generally, the termination happens by transfer reactions. For example, one beta proton transfer to either monomer or counter ion or say polymer itself, solvent or some impurities, which is present or a transfer agent, like the case of chain radical polymerization, we talk about the chain transfer is possible.

And for example, if we consider the beta proton transfer to monomer, I can write k transfer monomer just like the radical polymerization. If we consider the same examples of isobutylene polymerization by BF₃ and H₂O, this can transfer beta proton to the monomer and can form this and plus the 2 2 beta proton, one is here and one is this hydrogen. So, one, depending on which proton is leaving you can get actually two structures with double bond. If this comes out, then you get a chain end with CH₂. If this proton goes out and if something, one of the protons goes out from there, then you get CCH and that is possible, these are possible for other monomers where this is, these two types of double bond is a possibility.

For example, like you have alpha methane styrene in case of, say, example, the monomers like styrene, where you always get only one possible double bond because there is only one possible beta hydrogen to be eliminated. So, this is very common,

this is very important termination process and it could be, this termination could happen to one of the, or any of the other agent as well.

We just gave an example with the monomer and what we will do in the next lecture, we will talk about the other termination possibilities and will discuss the kinetics and the energetics of the cationic polymerization, cationic chain polymerization and then also discuss the characteristics and other features of anionic chain polymerization.