Polymer Chemistry
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Lecture - 19
Ionic Chain Polymerization (Contd.)
&
Chain Copolymerization

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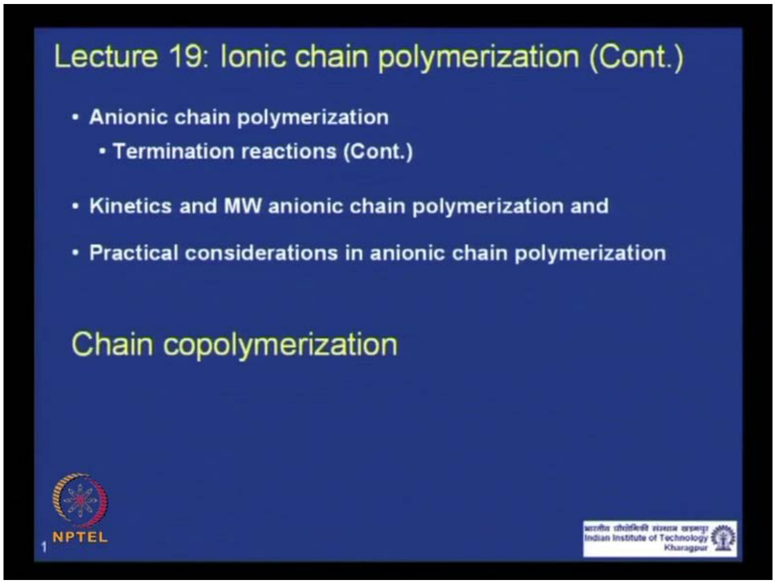

Lecture 19: Ionic chain polymerization (Cont.)

- Anionic chain polymerization
  - Termination reactions (Cont.)
- Kinetics and MW anionic chain polymerization and
- Practical considerations in anionic chain polymerization

Chain copolymerization

Welcome back to this portion of polymer chemistry and into this 19th lecture, I am going to cover rest of the discussion on anionic chain polymerization, and then I will start our discussion on chain copolymerization. In this lecture, we will try to cover anionic chain polymerization, which we started in the last lecture and will complete our discussion on termination reactions and then touch upon the kinetics of anionic chain polymerization and also the molecular weight in this type of polymerization. And then talk about briefly about the practical aspects of anionic chain polymerization and then we will start this chain copolymerization, which I will continue in the next lecture as well.

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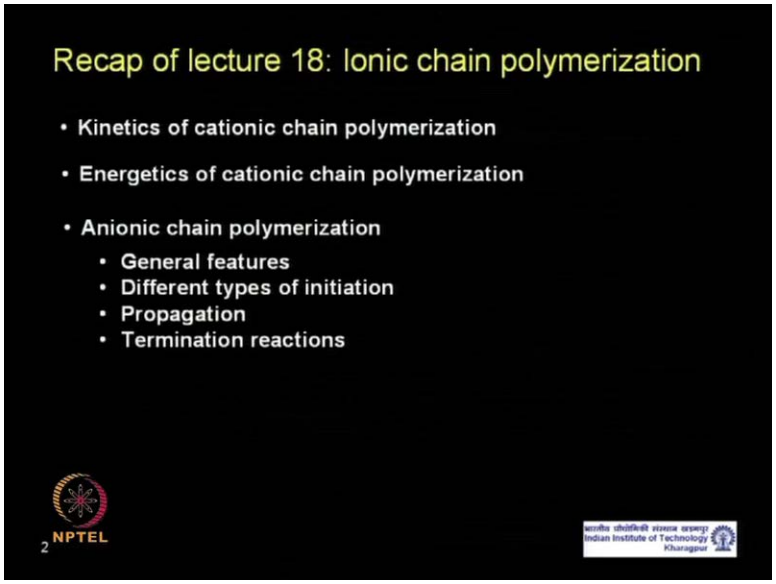

Recap of lecture 18: Ionic chain polymerization

- Kinetics of cationic chain polymerization
- Energetics of cationic chain polymerization
- Anionic chain polymerization
  - General features
  - Different types of initiation
  - Propagation
  - Termination reactions

Now, let us recap the lecture we had in the last time lecture 18, where we talked about the cationic chain polymerization of kinetic and energetics and we started our discussion on anionic chain polymerization and we talked about general features of ionic chain, anionic chain polymerization and different types of propagation, initiation, mechanisms, propagation and we just studied a few examples by which anionic chain polymerization can be terminated.

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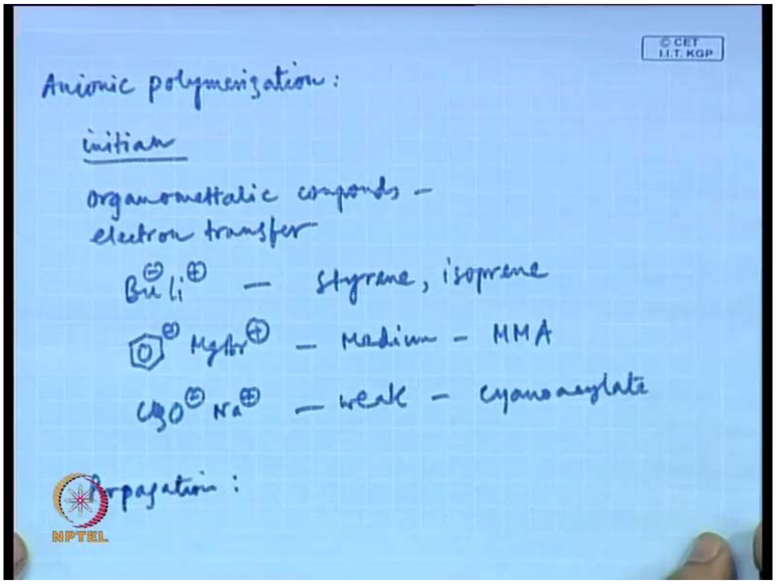

Anionic polymerization:

initiation

organometallic compounds -
electron transfer

$Bu^{\ominus}Li^{\oplus}$ — Styrene, isoprene

$C_6H_5^{\ominus}MgBr^{\oplus}$ — Medium - MMA

$CH_3O^{\ominus}Na^{\oplus}$ — weak - cyanoacrylate

Propagation :

Now, let us go back and just look at the initiation process once again. In anionic polymerization, we, we had discussed two types, mainly two types of initiator, one was organo-metallic compounds and another was electron transfer through electron transfer reaction.

Now, recollect from our discussion from last time, that we had. This had given example of butyl lithium, which is the very strong electrophile. So, the monomers, which does not propagate, which the monomers do not propagate with the very highly strongly stabilized anion, we required this, this strongly nucluophilic anion and this can be utilized to initiate anionic polymerization of styrene, isoprene. And initiator like this, which are medium nucleiophic, they can be utilized to initiate monomers like (( )).

And this type of initiators, which are weakly, very weak nucleophiles, they can be utilized to initiate a very strongly or highly stabilized propagating anions, like cyanoacylate, acylate, because cyanoacylate has two stabilizing groups. This has this, the propagating anion from cyanoacylate is highly stabilized, so you can actually anionically polymerize these cyanoacylate monomers with a weekly, very weak nucleophiles. So, you can also polymerize with strong nucleophiles as well, but this type of monomers can be polymerized anionically by weak, very weak nucleophiles.

Now, we talked about this electron transfer initiation by (( )), for example, gave this sodium and naphthalene and we talked about propagation step and how propagation step depends on the solvent polarity.

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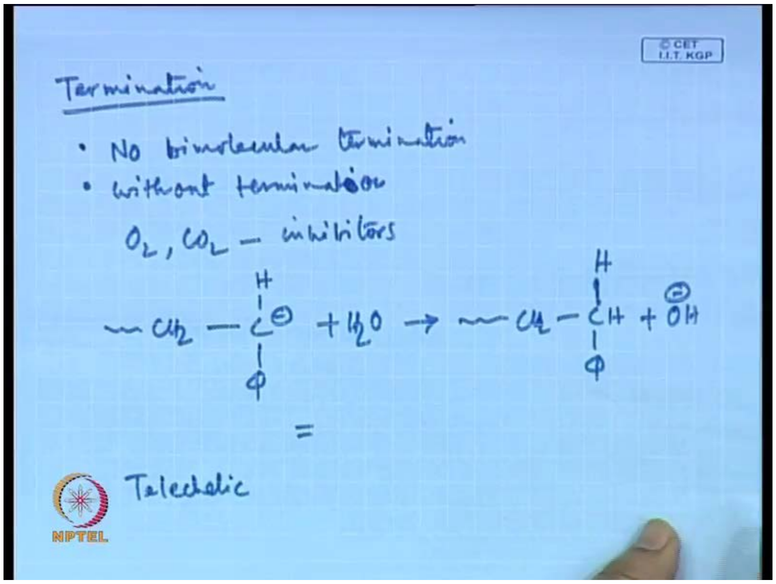

Termination

- No bimolecular termination
- without termination

O_2, CO_2 – inhibitors

$$\sim\sim CH_2 - \overset{H}{\underset{\phi}{C}}{}^{\ominus} + H_2O \rightarrow \sim\sim CH_2 - \overset{H}{\underset{\phi}{C}}H + \overset{\ominus}{O}H$$

=

Telechelic

And we started our discussion on termination reaction for anionic polymerization. Now, you can recollect from our discussion, that its anionic polymerization, you have no bimolecular termination and in fact, in absence of any side reaction, if you have taken care of the condition, reaction condition in such a way, that no impurities are present and you have taken care of all the other purity aspects, then most of this anionic polymerization, actually, actually propagate without termination. So, this anionic polymerization mainly happen without termination, as long as termination, as long you has have inert atmosphere and extremely clean glassware analyzing skills.

Things like O 2, CO 2, they actually inhibit the anionic chain polymerization by forming a peroxyl, peroxyl or carboxyl anion, which are very weak nucleophile, which cannot reinitiate a new anionic chain, so these are inhibitors. So, extreme care should be taken to remove this O 2, CO 2 type impurities.

Now, you can deliberately, in most cases laboratory, we do terminate a propagating anion by adding some external reagent. For example, if we add a polystyrene anion, we can add water and this chain gets terminated and you get OH minus, which is, this is a very weakly nucleophile, so it cannot further initiate anionic chain. So, reaction actually gets terminated in these steps. Now, utilizing this concept you can actually synthesize functionalized polymers, which are also called telechelic polymers, which we discussed in the last class.

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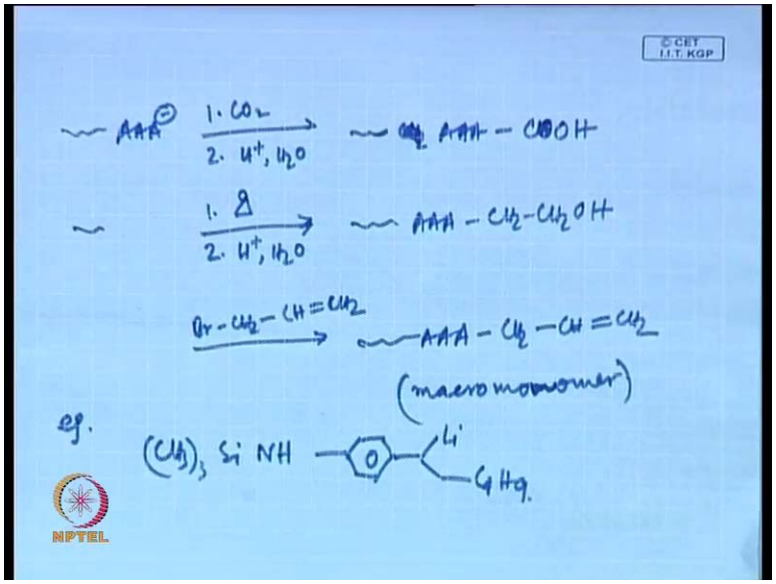

For example, if you terminate, say I write a general expression , expression for a vinyl polymer and we terminate by carbon dioxide and then acidify the reaction medium, you get carboxylic acid. You do the same thing, say, with ethylene oxide and then acidify, you get alcohol.

Now, you can even functionalize this by such reagent and here you can make a polymer with a functional group at the end, so it can be utilized. This polymer, which is also known as macromonomer because it can act as a monomer and start polymerization once more time physically with micromolecules behaving like monomers, so we often call this as a macromonomer. So, you can create in this way macromonomer, which you can utilize for further polymerization.

Now, you can synthesize telechelic polymers by taking an initiator, which is already functional group. For example, if I take a tri methyl silyl protected (( )). Now, you can initiate a polymer chain and at the end you can terminate the chain and then by acid hydrolysis you can make a interminated polymer. So, using this termination reaction, with a definite reagent you can actually create, you can terminate and as well, you can create the functional group at the end of the polymers, polymer chain, which is very useful and which can be utilized for several other applications.

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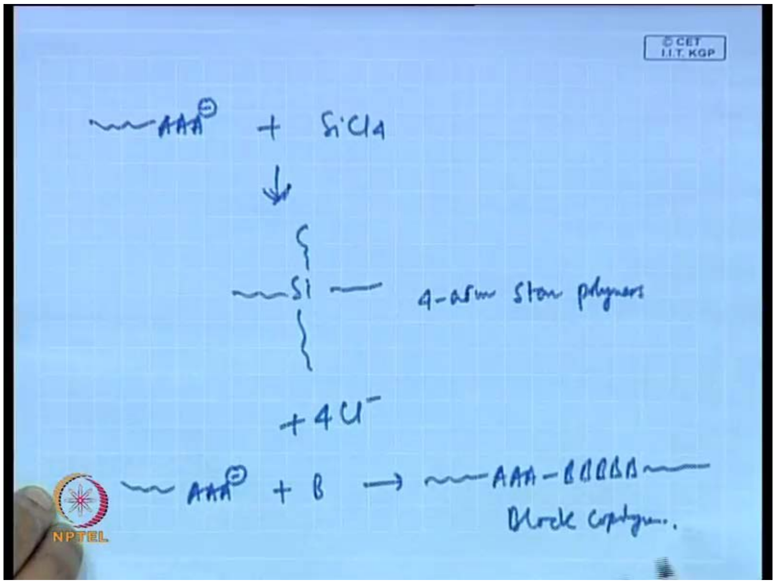

You can take help of couplic reaction and you can make four arm in case, say, four arm star polymer. So, these are the examples by which you know, these are examples how you can utilize the anionic polymers and can make, functionalize and the, and polymers of having different geometallic mineral. You make, as we have discussed several times in last lecture, that you can utilize this end and if you have, add a next second monomer, you actually make block copolymer as well. See, if you can, if you take this type of chain and you add second monomer B, then you can make a block copolymer.

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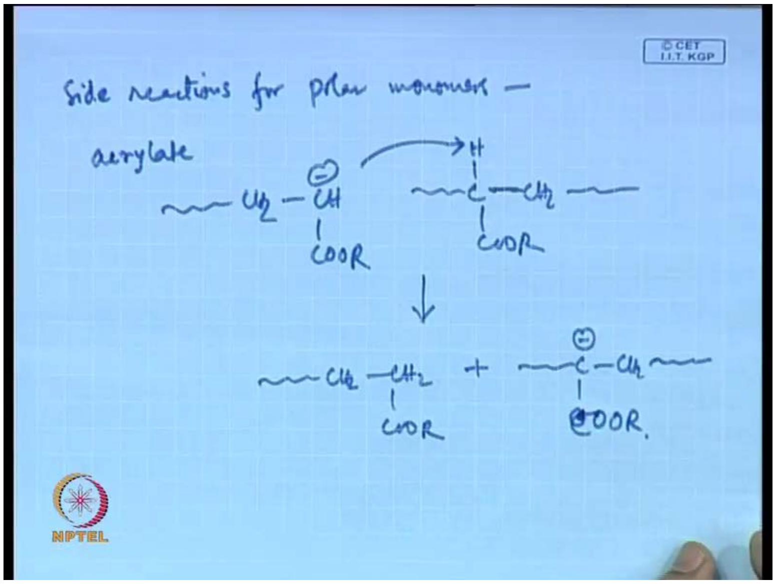

Side reactions for polar monomers –

acrylate

Now, in anionic polymerization, this, lot of side reactions can happen by which, by which the polymer chain can get terminated. And especially, if added for polar monomers, for example if I take an acrylate, and let us consider a propagating chain and it can actually abstract hydrogen. And can, this chain can get terminated and you can form, this can now reinitiate the polymers by which it can form branches. So, this one chain terminates, gets terminated by this side reaction and you can form branch in other growing chain.

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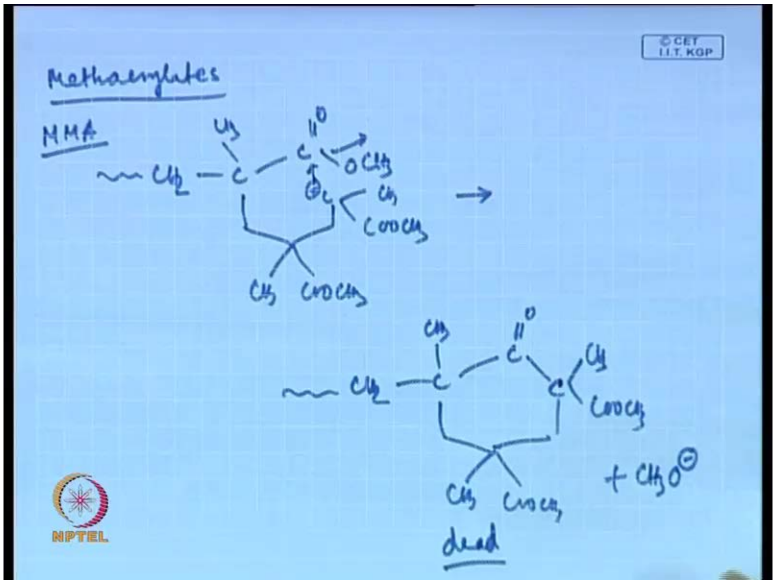

Methacrylates

MMA

Now, that is not applicable for monomers like methacrylates where this hydrogen is absent, but methacrylates actually can participate in several side reactions. For example, if I write this, say, place an example of methyl methacrylate, this is the chain end where you have a (( )). Now, it can actually form a cycle and it can knock out this methoxy and terminate this chain. So, I can write now, this is a dead chain, so the chain gets terminated and this is a weak nucleophile, as we discussed earlier. So, it actually often cannot reinitiate anionic polymerization and even it does, it actually slowed down the reaction a significant way.

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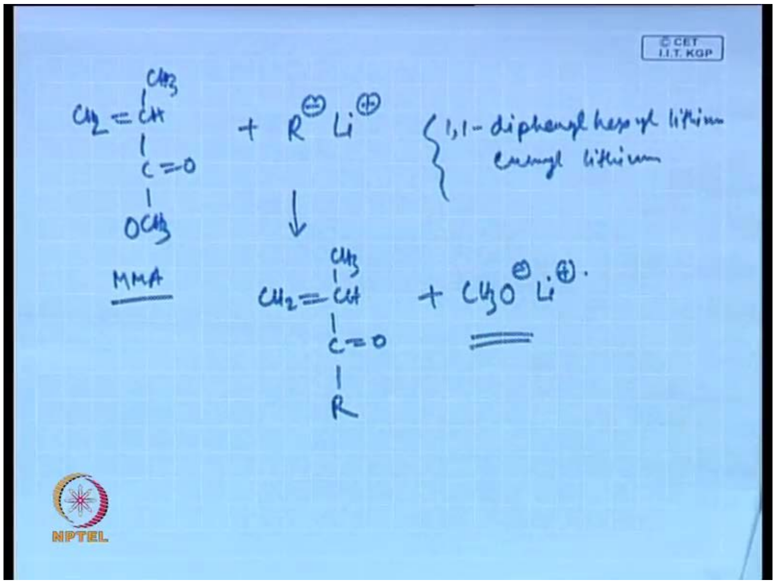

Now, another side reaction, which is very possible, very prominent in case of methyl methacrylate is as follows, is actually reaction on the monomer, not on the polymer. This is reaction monomer with the initiator molecule itself. Now, it can do a substitution reaction here, substitution nucleophilic reaction here and form again a methoxy group here.

Now, this, this is the different monomer all together compared to the original methyl methacrylate monomer. So, basically, now if the polymer start, it is actually the copolymer of methyl methacrylate and this, this monomer and also, not only it makes a copolymer, the reaction also gets significantly slowed down again because of the weak nucleophicity of this anion, generated anion.

Now, if the reaction is slow, slowed down, then the dispersity problems comes, you know the polymer has become much broader and the heaviness becomes difficult to maintain, so there strategies, which are utilized to minimize this side reactions is especially for the polar monomers. We discussed for examples, for example like for methacrylates.

Now, if to slow down this reaction one strategy is used very often is to make a bulk. You take a bulky anion initiator, so that spherically, this reaction, this substitution reaction becomes problematic. So, this, this reaction, this side reaction becomes difficult. For example, instead of taking butyl lithium, this is taking buthyl lithium, if you take a bulky lithium group like 1, diphenyl hexyl lithium or say, cumyl lithium. Now, in this case, because this groups, this R group in this case are very larger in size, this S, this side reaction of substitution nucleophilic reactions becomes slow down difficult, so you can actually suppress this side reaction.

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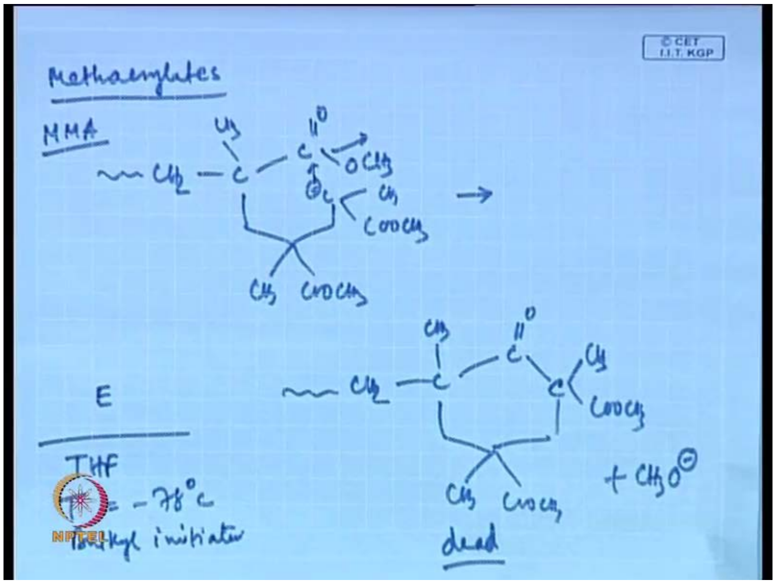

If you think about the side reaction, that intra-molecular cyclization reaction, which is discussed here and now fortunately, the activation energy for this reaction, activation for only for this reaction is higher compared to the normal propagation reaction. So, you can take advantage of that difference in activation energy and you can decrease the temperature.

Now, if you decrease the temperature both, the normal propagation and this inter-molecular circulation slow down, decreases. But because activation energy for this cyclic reaction is higher, so the drop in the rate of this cyclic reaction is much much higher compared to the normal propagation reaction. So, in that way you can actually minimize this side reaction. And another way to minimize this sort of size reaction is to use little polar molecular, polar solvent like THF. In that case you get solvent separated anions, initiator molecules.

So, you can actually combine these three strategies, like using polar molecular, polymer solvent like THF, THF and do reaction in much lower temperature, say like at minus 78 degree centigrade and use bulky initiator. So, by using these three strategies you can actually minimize this side reaction from methyl methacrylate and carry out addition anionic polymerization for methyl methacrylate and this similar sort of strategy can be applied for other polar monomers as well.

Now, as we have been talking, that this anionic polymerization proceeds without termination, but that does not mean, that this anionic chain ends, leave forever, not there are some intrinsic self-termination steps possible, which are actually very slow and extremely slow. So, in normal time frame you can call those reactions absent, but during a longer time frame those reaction could be significant and then by that process, that termination, the chain could be terminated.

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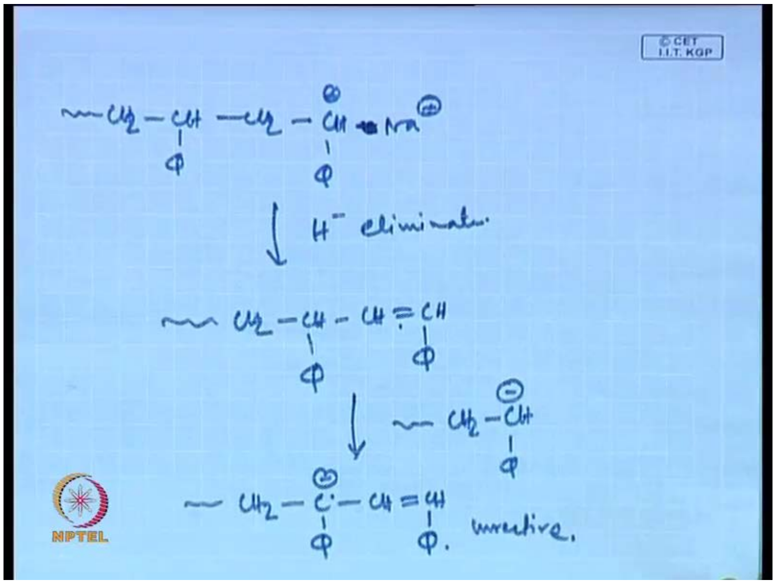

For example, if we take this electron transfer for initiation reaction of styrene. Now, you have seen, now it can undergo hydride elimination and form an ionic end. Now this actually can, this is a very acidic proton, so it can be easily abstracted by an anion, which could be another chain end, the styrile chain end. So, this proton can be abstracted by another propagating chain end and form... Now, this is unreactive molecule, so this is one example by which, that polystyrile anion is self-terminating and finally ending into unreactive or terminated polymer chain, but these reactions are very slow.

As you can see, hydride elimination is always slow and if you compare with a cationic polymerization we talked about, in that case it was actually proton elimination, which was much, comparably much easier things to happen. So, in comparison to cationic polymerization and anionic polymerization, anionic polymerization, anionic chain ends are much more stable compared to a cationic chain end. So, anionic, in anionic chain polymerization you actually consider, that this polymerization happen without any practical termination steps.

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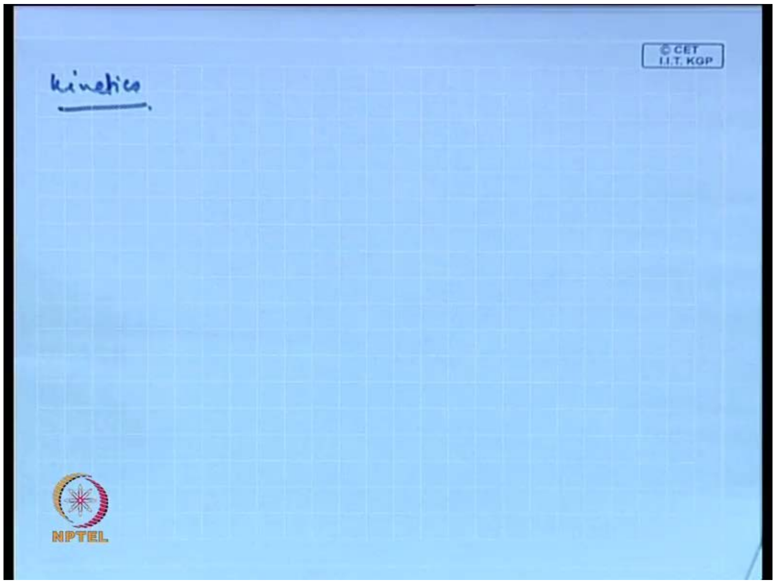

kinetics

Now, let us talk about this kinetics of anionic polymerization

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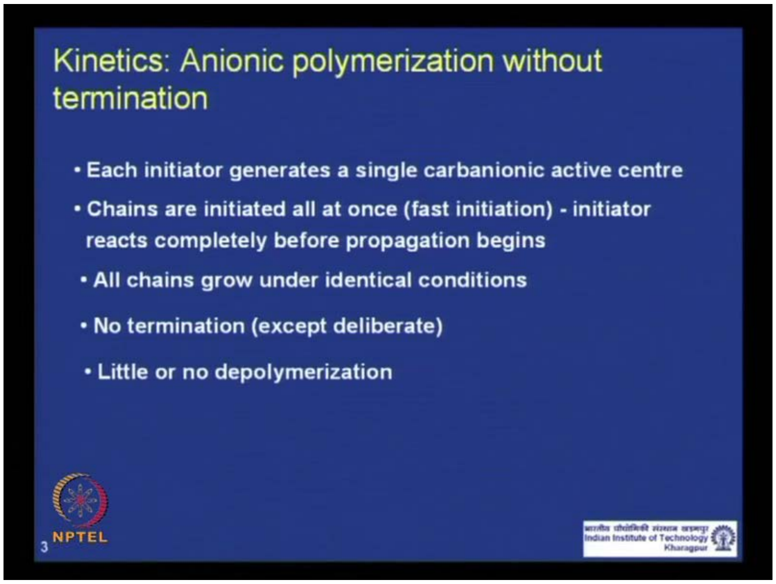

Kinetics: Anionic polymerization without termination

- Each initiator generates a single carbanionic active centre
- Chains are initiated all at once (fast initiation) - initiator reacts completely before propagation begins
- All chains grow under identical conditions
- No termination (except deliberate)
- Little or no depolymerization

Now, before we go in details, lets us recap what we learned in anionic polymerization, so that our kinetic understanding will become easier. Now, we know that in case of anionic polymerization the initiation is faster. Now, remember the discussion we had for radical, this polymerization, radical chain polymerization, where the initiation steps is much slower compared to propagation step, but in this case, this anionic polymerization, the initiation steps are much much faster compared to propagation steps. So, each initiator generates and also, each initiator, if you are talking about organic butane lithium or say, sodium and naphthalene electron transfer reaction, each initiator molecules actually generates single carbanionic center, active center.

So, basically number of moles of initiator is basically, will produce same number of moles of polymers at the end of the reaction. So, chains are initiated all at once because initiation steps are much faster. All the chains are initiated, all the chains are initiated at a go, so this all starts together and all the initiator actually gets consumed before propagation reaction actually starts. And as you can now visualize, that all the chains, now after initiation is complete all the chains will grow simultaneously under identical condition. And unless we have impurities, all we want to stop or terminate the reaction by adding some agent, they, there is no termination reaction. Actually, there is no or very little de-polymerization reaction depending on (( )) of sling temperature of the polymer as well.

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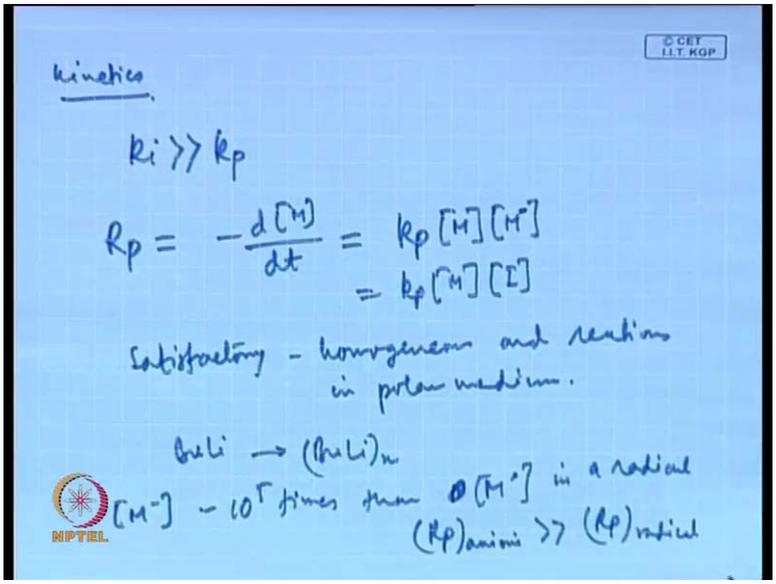

kinetics

$k_i >> k_p$

$$R_p = -\frac{d[M]}{dt} = k_p[M][M^-]$$
$$= k_p[M][I]$$

Satisfactory - homogeneous and reactions in polar medium.

$BuLi \rightarrow (BuLi)_n$

$[M^-]$ ~ 10^5 times than $[M^\cdot]$ in a radical

$(k_p)_{anionic} >> (k_p)_{radical}$

So, what, so we can write, that k i is much higher than k p, rate constant for the polymerization and rate of polymerization, which is again the standard way of writing k p. And again it is a, as we can remember the discussion for radical polymerization, we can write if there is bimolecular reaction between a monomer and a carbanionic chain end. So, we can write monomer concentration and the concentration of all the anionic, which is present in the reaction medium.

So, what is M minus? The concentration of all the anionic species, which is present in the reaction. It is same, it is same as the initiator concentration because as we discussed, that each initiator actually initiates one chain, so the concentration of the anions would be same as the concentration of the initiator molecules. Now, this expression is satisfactory for, for homogenous and reactions in polar medium. In non-polar medium what happens? There is a possibility that the initiator molecules can aggregate. For example, if you take a butyl lithium in non-polar medium, you can actually aggregate, and, and that depends on which butyl lithium group you are taking and number vary from 4 to 6 or something.

So, what, what is to do? Remember, that if, if you take a very non-polar medium or hydrocarbon medium, then this initiator molecules can actually aggregate effectively reducing the concentration of the available initiator, which means this you have to compensate or you have to take care of that correction in the concentration of initiator term to actually get the rate of polymerization. And as you can, you can visualize or you can explain that because there is no termination reaction and the generation of initiator or the initiation is much faster, the concentration of this anion, anionic species are much higher than a radical polymerization. For example, concentration of anionic species is almost like 10 to the power of 5 times higher than M dot in a radical chain polymerization, which makes R p for anionic is much higher than R p for radical and that is why this anionic reactions get over in very short time, even in few seconds. Sometimes the reaction is so faster, that in a fraction of seconds this polymerization is completed.

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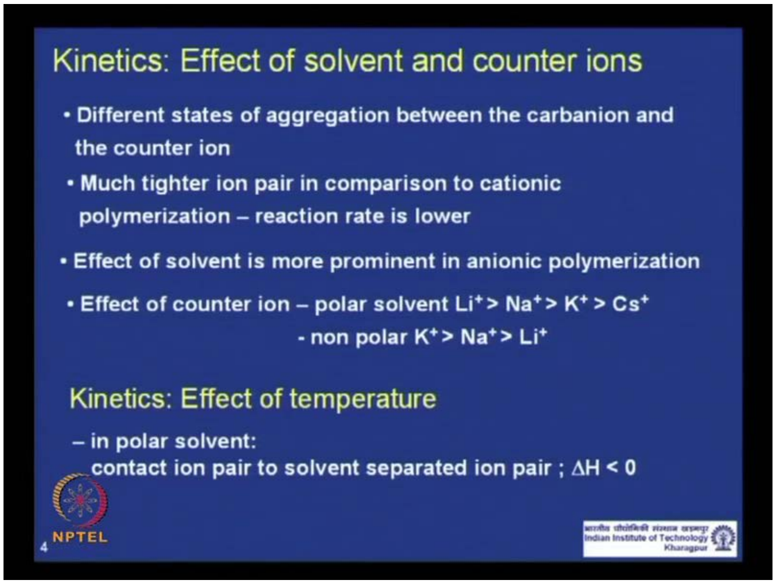

Kinetics: Effect of solvent and counter ions

- Different states of aggregation between the carbanion and the counter ion
- Much tighter ion pair in comparison to cationic polymerization – reaction rate is lower
- Effect of solvent is more prominent in anionic polymerization
- Effect of counter ion – polar solvent $Li^+ > Na^+ > K^+ > Cs^+$
  - non polar $K^+ > Na^+ > Li^+$

Kinetics: Effect of temperature

– in polar solvent:
contact ion pair to solvent separated ion pair ; $\Delta H < 0$

Now, what is the effect of solvent? We have discussed earlier, that the solvent plays a very important role in, in terms of rate of polymerization of this ionic polymerization, especially in case of anionic polymerization. Now, let us, we know, that at different state of aggregation we have discussed earlier, that this ion-pairs present in different state of aggregation forms a tight ion-pair to solvent separated ion-pair to completely free ion-pair. They could exist depending upon the polarity of the medium. They can exist in different state of aggregation and that state, that state of aggregation will be, will definitely determine the reactivity of the anionic groups at the same end. If this is, this is the ion-pairs are totally separated, they are free ion-pairs.

Obviously, the reactivity of the ions, end ions are higher, so the R p will be higher compared to if the ion-pairs are in contact, or will be tight in case of, if you have considered same solvent, same say, non-polar solvent. The cationic, in case of cationic polymerization, the ions are not as tight as in case of anionic polymerization because the size of the counter ions, like lithium, butyl lithium case or some, they are small, so the anions and the canions, cation in case of anionic polymerization are much more tight. So, for a given solvent, especially non, non-polar solvent, the rate of cationic polymerization is higher compared to anionic polymerization, is about 2 to 3 times higher and because in case of anions, anionic polymerization, they are in non-polar medium, they are tight.

So, effect of solvent polarity, if we increase the polarity, for polarity for both cases, cationic and anionic, the effect in case of anionic polymerization is much higher because to begin with, they are much tight and if you increase the polarity, they can be free. So, the reactivity goes up and if we talk about the effect of counter ion, so let us consider first the polar solvent. If you consider polar solvent, that means, the ions are either solvent separated or they are free anion and in that case, the salvation, the separation ion, separation is, is, is more feasible for a small ion like lithium, a small cation for lithium because lithium will be much more solvated in a polar solvent compared to a larger size ion, cation, like cesium cation or a potassium cation.

So, if you are talking about a polar solvent, then small counter ion, counter cation will help in separating those ion-pairs and hence the reaction will be to go up and in the case of non-polar solvent where the ions, the anion, carbanion and the counter ion are tight, then it is, if it is the size is higher, the, the ions are little loose, so the reactions is higher. So, in case of, in case of polar solvent for a given anion, lithium will, lithium cation will have a higher reactivity than sodium and potassium, cesium, and in a non-polar medium it would be, order would be reverse.

Now, what is the temperature of the reaction? In case of anionic polymers it is little complicated and it is not very generic way. You can actually explain the effect of temperature in case of anionic polymerization. It depends upon the ion-pair and the solvent, on the polarity of the solvent, but to say, at least, that in polar solvent you have. What happens if you increase the polar solvent, polarity of the solvent? The contact ion-pair gets separated and this process, by this process the ion individual ions gets solvated and as a result, its exothermic process.

Now, say, exothermic process, if you increase the temperature, the ions would be preferred to left hand side, which means, the ions will be moved towards tight ion-pairs sides, you know, comparatively.

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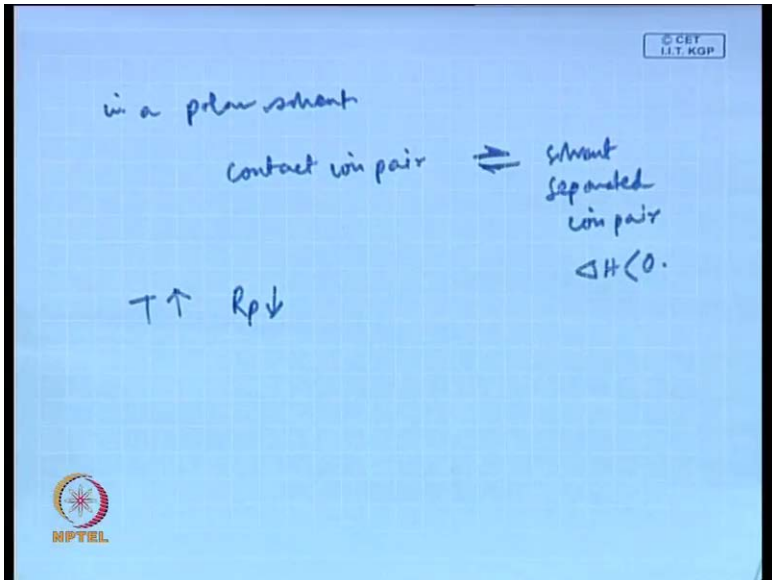

in a polar solvent

contact ion pair $\rightleftharpoons$ solvent separated ion pair

$\Delta H < 0.$

$T\uparrow \quad R_p\downarrow$

So, if you compare between the, within the, let me write down, write down these things, so in a polar solvent you have, say contact. As I said, all these are, these ion-pair aggregation are in equilibrium, they are always a very fast equilibrium, equilibrium exists between these two, say solvent separated ion-pair. As you know, these would have higher reactivity and higher reaction compared to these and this has exothermic reaction. So, if you increase the temperature what happens? This, this goes to left hand side, so in by and increase the proportion of contact ion-pair in this equilibrium and by that it decreases the rate of the reaction in non-polar solvent. Basically, there is no salvation, so del h is 0, so basically the temperature has minimal effect in terms of reaction rate.

Sometimes what happened in case of non-polar solvent, this aggregation of the initiator molecules, for example, like butane lithium, we just talked about the non-polar medium, butane lithium could be existing in an aggregated form. Now, that aggregation could be, could be affected by temperature and it is actually lower temperature. The aggregation is less, so as a result if you decrease the temperature the aggregation become less, so the reaction become faster, so the reaction rate goes up. So, in both cases, actually, decreasing the temperature actually might give you better, a higher reaction rate. So, we have now discussed, that kinetics, the rate of reaction in case of anionic polymerization.

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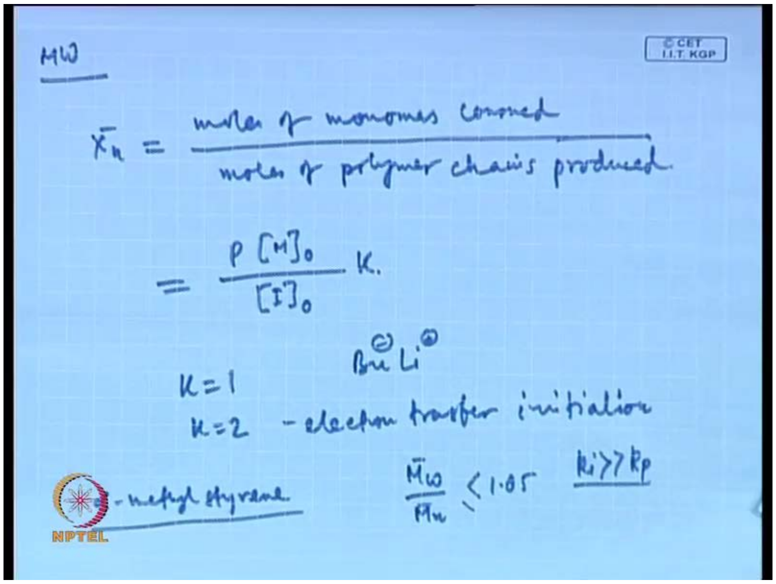

MW

$$\bar{X}_n = \frac{\text{moles of monomer consumed}}{\text{moles of polymer chains produced}}$$

$$= \frac{p\,[M]_0}{[I]_0}\,k.$$

$Bu^{\ominus}\,Li^{\oplus}$

$k = 1$

$k = 2$ - electron transfer initiation

-methyl styrene

$\frac{\bar{M}_w}{\bar{M}_n} \leq 1.05$

$k_i >> k_p$

And let us talk about the molecular weight of, molecular weight of the resulting polymers in, in an anionic polymerization. Now, we know, for a chain polymerization how you define the molecular rate, if we calculate, these are moles of monomers consumed divided by the moles of polymer chains produced. The moles of monomer, monomer chains, monomer consumes is given by the conversion multiplied by initiator in initial concentration of the monomer, whereas the moles of polymer chains is nothing but the moles of initiator molecules present at the beginning. Now, we will have to add a factor k, the k is 1 for case of initiation, where each initiator molecules forming one chain, like butyl lithium case, organ butyl lithium case, where each initiator molecules are actually forming one chain.

Now, in case of electro-transfer initiation, 2, remember, that the sodium - naphthalene case, actually 2 initiator molecules are forming 1 chain, so you have to multiply a factor 2 for that. So, electro, normal the most cases k is 1 and there are cases like the initiation by the electron transfer reaction where you have biradical, a chain goes from both the sides, so basically the number of chains actually become half effectively (( )). So, the molecular weight becomes twice, so k is 2 for initiation by electron transfer initiation.

If, if you have monomers, which, whose ceiling temperature, like alpha methyl styrene, alpha methyl styrene, which are very few where, whose ceiling temperature is very low, then you cannot just use this as such, then you have to consider the depolymerization reaction as well. But in most of the cases, this ceiling temperature is quite high compared to our reaction temperature. So, those depolymerization reaction do not contribute at all, so we do not have to worry about the backward reaction. So, we can use this expression to determine the number average degrees of polymerization in an ionic polymerization.

Now, what about the polydispersity? M w by M n, now this remains very narrow, say, less than 1.05, something like that. It remains very narrow as long as your initiation rate is much faster compared to propagations, so all the chains actually start. As long as we maintain this, this happens, then all the chains starts from same time and proceed or propagate for same time, so the polydispersity becomes very narrow and so, as long as you maintain or the reaction have initiation reaction is faster compared to propagation reaction. Now, also there is no termination reaction, if your, if your termination reaction, then number of chains would increase, then the expected one and as a result, your polidispersity would go up. So, as long as we maintain pure environment where you reduce or minimize or make no termination reaction and your initiation rate is much faster compared to propagation step, then you can actually get assured, that the polydispersity in anionic polymerization would be very narrow, so less than 1.05.

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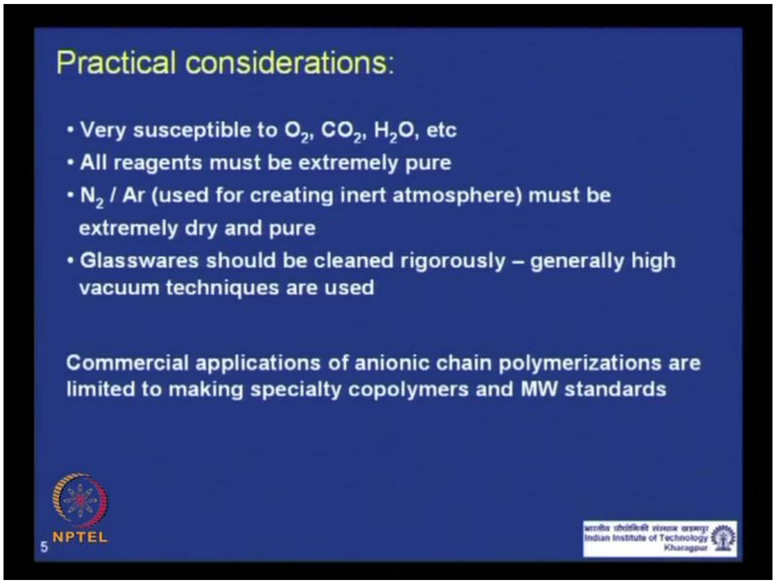

Practical considerations:

- Very susceptible to O_2, CO_2, H_2O, etc
- All reagents must be extremely pure
- N_2 / Ar (used for creating inert atmosphere) must be extremely dry and pure
- Glasswares should be cleaned rigorously – generally high vacuum techniques are used

Commercial applications of anionic chain polymerizations are limited to making specialty copolymers and MW standards

So, let us now compare few practical considerations. Now, we know, that we, we know, that we actually know all this things, but just to conclude this anionic polymerization part, but in practice what we need to do as we have seen, that the anionic polymerization is very susceptible to the impurities presents like oxygen, carbon dioxide, water, where if the moisture present, it immediately will kill the, kill the anion, carbanion. So, you have to be very careful, not having any presence of the, this impurities.

All the reagents, which are using monomers and initiator must be extremely pure, there should not be any other impurities because anionic, anionic, carboanions are very reactive, so they can, they can actually get react, they can actually react with the impurities and get terminated.

Now, to create an inert atmosphere, which typically use nitrogen and argon in the lab, so the nitrogen and argon you are using in the lab to create an inert atmosphere, that has to be extremely dry without moisture and extremely pure and that is a really challenging job for the scientist who actually practice this anionic polymerization. There are several columns by through which they send these gases before they actually can utilize this gases to pure the inert atmosphere in the reaction, in the reaction environment.

And your glasswares has to be cleaned in an, in practice they actually, the, the, the scientist who actually carry out anionic polymerization reaction, they actually film dry, which means, they actually heat the glasswares under flame and then apply vacuum continuously. So, anything, any oxygen, any moisture, which was absorbed or any impurities, which is, they are in the surface of the glassware, they get, they get cleaned up. So, as you can now recognize, that it is not a very simple reaction to carry out in a large scale, in industrial scales, where maintaining all these purity, all these reaction conditions are very difficult as also this reactions are typically down (( )). So, maintaining in a large scale industrial set up is quite difficult.

So, as you expect, that commercial applications of anionic chain polymerization are limited and they are not used for making any polymers, used for making many polymers and they are only utilized for making specifically copolymers and, and some molecular standards, where we require very narrow dispersion, which you can utilize for using standards, as molecular standards, which you can use for molecular weight determination.

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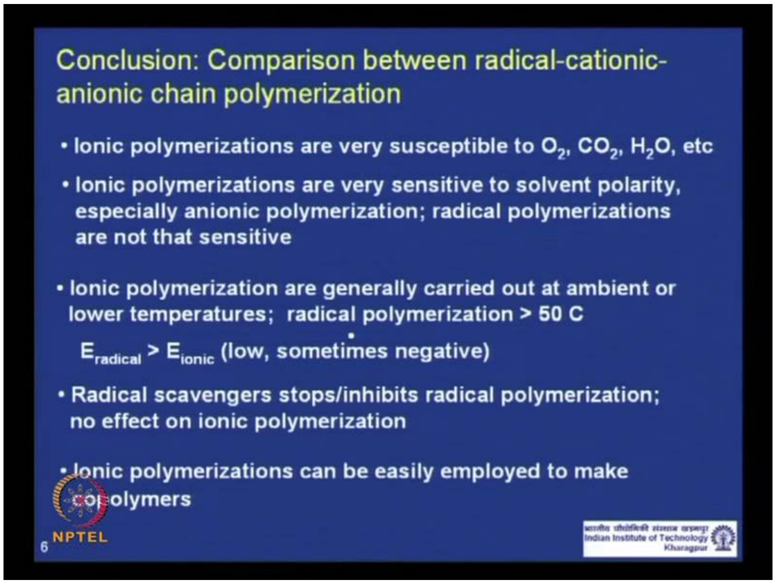

Conclusion: Comparison between radical-cationic-anionic chain polymerization

- Ionic polymerizations are very susceptible to O_2, CO_2, H_2O, etc
- Ionic polymerizations are very sensitive to solvent polarity, especially anionic polymerization; radical polymerizations are not that sensitive
- Ionic polymerization are generally carried out at ambient or lower temperatures; radical polymerization > 50 C

  $E_{radical} > E_{ionic}$ (low, sometimes negative)
- Radical scavengers stops/inhibits radical polymerization; no effect on ionic polymerization
- Ionic polymerizations can be easily employed to make copolymers

So, then end of this module of chain polymerization, let us conclude with just a few basic comparison between the radical and anionic chain polymerization we studied. And you know, that anionic polymerization is very susceptible to impurities, whereas radical chain polymerization are also sensitive are susceptible, but not to that extent of this ionic polymerization. You can actually afford to have some degree of this impurities in cases of radical chain polymerization and that is why this radical chain polymerization are utilized in industry, the large set up, much more frequently than ionic chain polymerization.

And ionic chain polymerization is very sensitive to solvent polarity, as we discussed from last week’s lectures and especially for anionic polymerization. Radical polymerizations are not sensitive in general, but there are some polar monomers, which can be sensitive to solvent polarity, but in general radical, as long as the monomers are soluble in the solvent you are using, your reaction should proceed well. Ionic reactions are generally carried out at ambient or lower temperature. As we have discussed, activation energy for radical reactions are much higher compared to the ionic group, ionic polymerization, which are very low and sometimes negative. So, as a result, radical polymerization is done at comparably higher temperature and typically higher than 50 degree centigrade in the lab and the industry.

And this is obvious, that radical scavengers stops, radical inhibits radical polymerization whereas it has no effect on ionic polymerization and this is, this is what, why you take trouble of all these reaction conditions for ionic polymerization. These ionic polymerizations can be easily employed to tailor-made copolymers, like block copolymers, anionic polymers, which have a very niche applications where you do not need any larger quantity, but in small. If you require small amount, then you can utilize this anionic polymerization or cationic polymerization, especially anionic polymerization, which are very useful to making block copolymer go with this. We come to the end of this module on chain polymerization.

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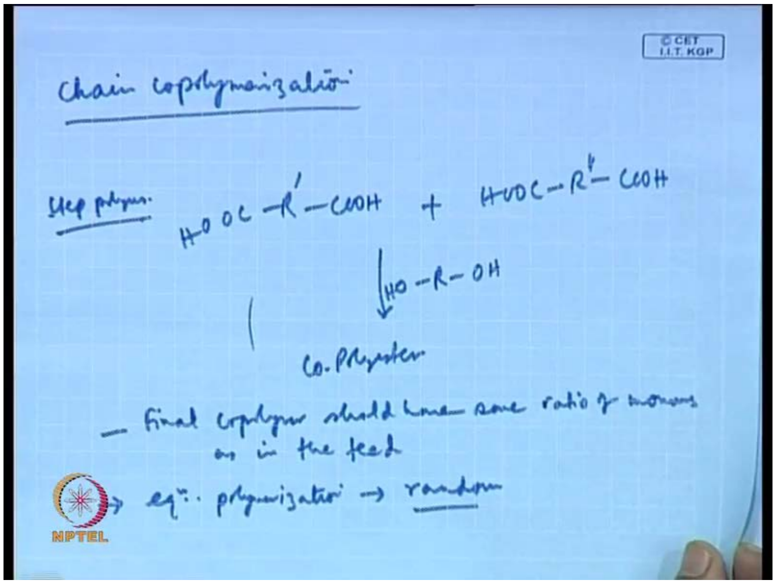

Chain copolymerization

Step polym.

$$HOOC-R'-COOH + HOOC-R''-COOH \xrightarrow{HO-R-OH} \text{Co-Polyester}$$

- final copolymer should have same ratio of monomers as in the feed

→ eqm. polymerization → random

What we now start is chain copolymerization, so let us start our discussion on chain copolymerization. Now, you remember, when we talk about step polymers, give example how you make a step copolymerization, if you have, say, two different acids, di-acids, you can react with diol and make a polyester and in that case it is a copolyester because it has got R dash and it actually consists of two monomers, two different di-acids. Now, as you anticipate or you realize, that in case of step copolymers the final co, copolymer should have same monomer, same ratio of the monomers as in the feed because as we know, that to make a high, high molecular polymer in case to step polymerization, the conversation has to be close to 100 percent and if its conversation is 100 percent, all the monomers actually are in polymer. So, what is the feed ratio of the different monomers has to be same as in the polymers as a copolymers as well.

And we also know, that chain step polymers actually is equilibrium polymerization, where the reaction is slow and different tapes are different sizes of polymer or polymers are in equilibrium. So, at the end, you will variably land up in a random copolymer, random arrangement of these two monomers, two functional, two monomers unless specific tapes where the reactions rates are very high. For example, reactions between acid chloride and alcohol and if you take out that, if you take out the resulting polymer from the solution, then there is a possibility, that you can get the arrangement of this two monomers other than random. For example, block in block nature, but in normal cases, in normal case, step polymer always gives you random copolymer.

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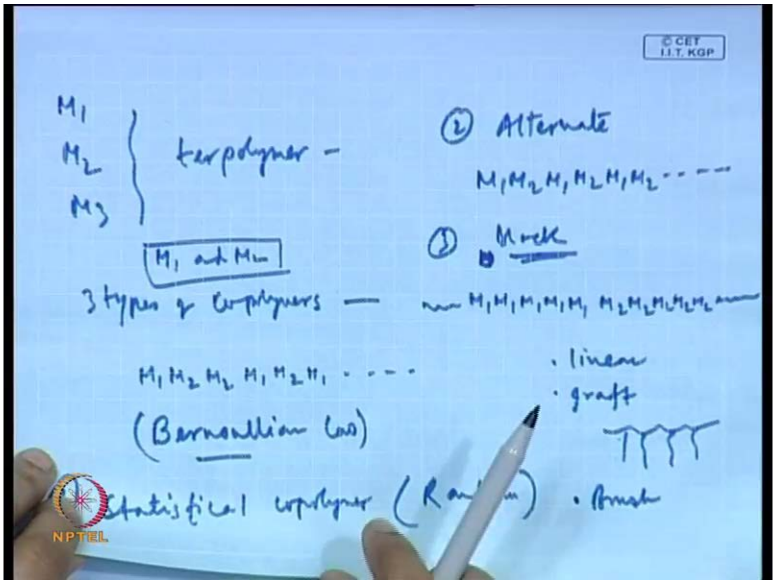

What happens in cases of chain copolymerization? Say, if you start with two monomers, M 1, M 2, you can have M 3, then typically we write, terpolymer, and that mostly three types of arrangement. So, if you consider M 1 and M 2, this three types of copolymers, you can have, which I think I have discussed in the first lecture, introduction one, these M 1 and M 2, the two monomers can get into the copolymer chain, statistically following a statistical law and one of the laws could be the Bernoullian statistics, which is basically nothing but the random arrangements of this molecules without any bias.

So, like there is no bias on the incorporation of the two monomers one after one, so there could be other statistical law, which the monomers can follow, but this small example, which actually gives a complete random arrangement of these two monomers. So, this is statistical copolymer and this particular case of, which is lot of time to make this two as equivalent, but they are not, in true sense they are not equivalent, random copolymers are not always statistical copolymers, but of course statistical copolymers are random copolymers. Only the statistical, statistical copolymers, which follow this law, they are called random copolymers, which are very common anywhere. Most of statistical copolymers are random copolymers, but not always.

The second type is alternate copolymer where you have alternate, exactly alternate arrangement of this two monomer and third is block, block copolymer where you have a significant longer chain of say, M 1and a significantly longer chain of M 3. It could be repetition of this, one polymer chain could have several blocks, but this length should be significantly higher so that we can call them block.

Now, block copolymers also could be different types, like linear, the type we just showed. It could be graft, graft block copolymer where basically one chain all form M 1 and with side chain of M 2 it could have brass arrangement where basically, where project into two-dimensional where you have surface of a, and the brasses are hanging of the other monomers. So, you can basically extend this graft polymer into another dimension to get brass copolymer. So, these are basically block copolymers, which have a long sequence of two different monomers.

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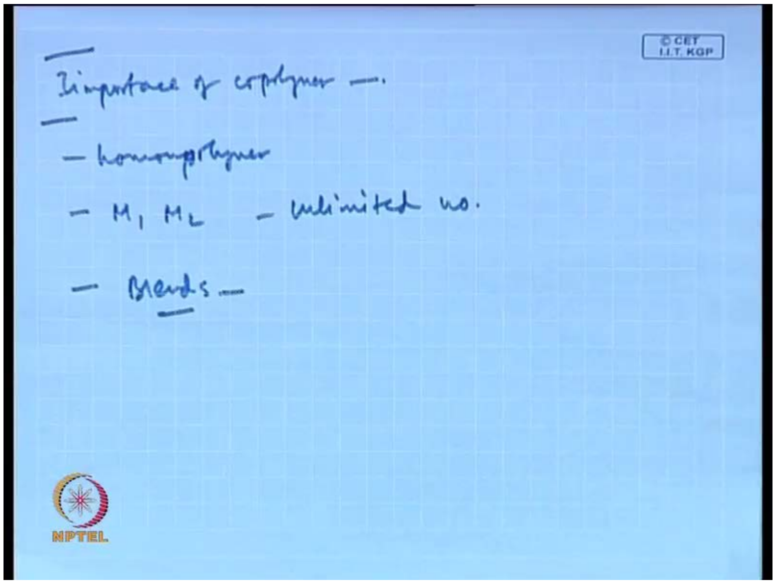

Importance of copolymer —.

- homopolymer
- M_1, M_2 — unlimited no.
- Blends —

Now, why do we need co polymer? What is the utility, importance? Now, with a homopolymer, with all the examples, we talked about polystyrene, poly methyl methaculate, polyvinyl acetenol and all these things, actually you can, the options are very, very few, in true sense you can have only a set a homopolymers, not much. You can actually name a lot of homopolymers, but they are, they are, that all the homopolymers, so your options are limited with homopolymers.

If you make copolymers, if you take M 1 and M 2, then you can choose from that monomer set and get several combination of M 2, M 1 and M 2 and not only that, for a given set of two monomers you can make different compositions, 0 100, 10 90 to 90 10 and different compositions of, not only you have choices of choosing two different monomers from a state of monomers, also you have choice of making different composition of this copolymer. So, basically there is a unlimited number of polymers, you can, copolymers you can make or polymers you can make by using copolymer.

Now, you can argue that you can mix this homopolymers or make a blend. You can always argue, that ok, I have all those homopolymers, now I can mix them in different proportions to get the composition of what I want, which will finally give the same composition, which you might get in the copolymers. But what happen if you start with two different homopolymers and mix them? Lot of time they do not mix, you know, we will talk about, maybe, later, later part of the this course, that polymers usually, hike, high molecular polymers, they do not exactly mix well.

So, what happens? You require a combination of homopolymer or combination of monomers. So, to get an average or to improve properties, so what we will do? We will start from this importance part in the next lecture and we will talk about the details of chain copolymerization in the next lecture.