Polymer Chemistry
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Lecture - 18
Ionic chain Polymerization (Contd.)

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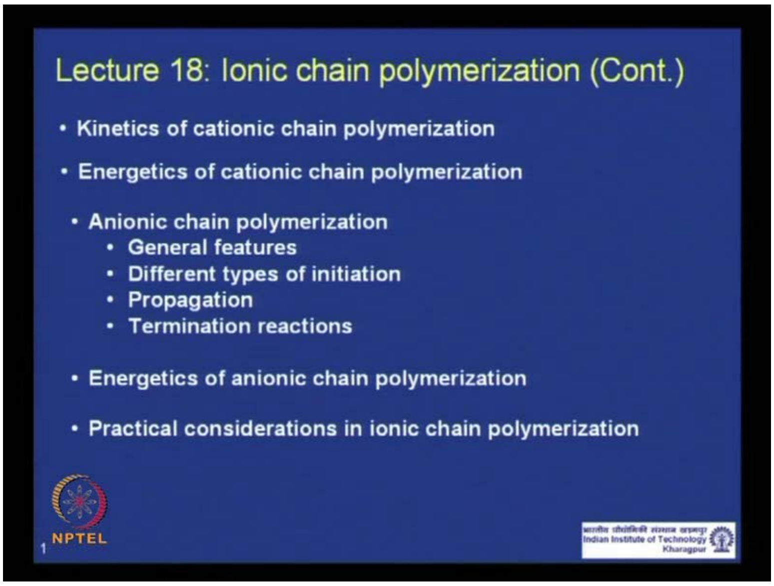

Lecture 18: Ionic chain polymerization (Cont.)

- Kinetics of cationic chain polymerization
- Energetics of cationic chain polymerization
- Anionic chain polymerization
  - General features
  - Different types of initiation
  - Propagation
  - Termination reactions
- Energetics of anionic chain polymerization
- Practical considerations in ionic chain polymerization

Welcome back to this course on polymer chemistry and this eighteenth lecture, we will continue our discussion on ionic chain polymerization. And in this project we will discuss the leftover discussion on the termination reaction in cationic chain polymerization. We will also discuss the kinetics and energetics of cationic chain polymerization and then move to anionic chain polymerization talk about the features of anionic polymerization, and then like the cationic chain polymerization talk about different ways of initiation and propagation and termination reactions. And briefly we will touch upon the energetics of this anionic chain polymerization, and then in the end we will talk about this, a few practical considerations for anionic chain polymerization, both cationic and anionic.

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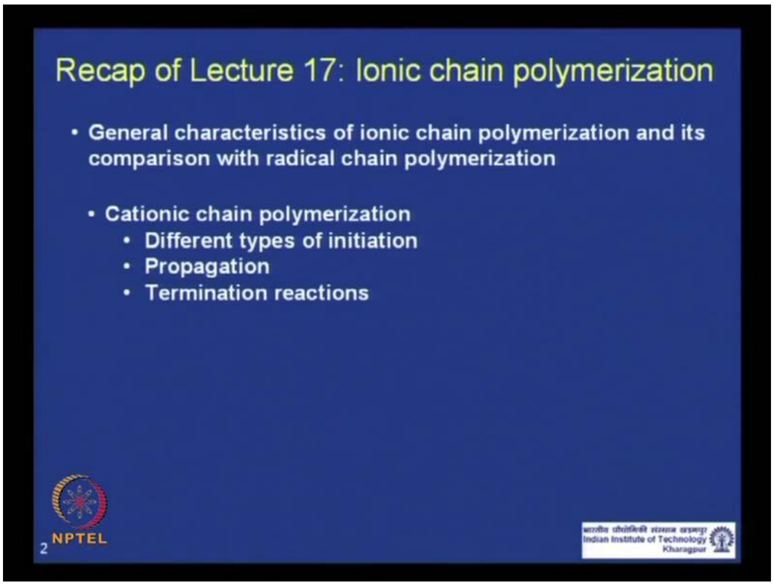

Recap of Lecture 17: Ionic chain polymerization

- General characteristics of ionic chain polymerization and its comparison with radical chain polymerization
  - Cationic chain polymerization
    - Different types of initiation
    - Propagation
    - Termination reactions

Now, let us just quickly recap what we covered in last lecture on ionic chain polymerization. We talked about general features of all the characteristics of ionic chain polymerization and its comparison with radical polymerization. We talked about selectivity of the monomers with about the importance of solvent polarity in case of ionic polymerization. We talked about the nature reaction is very fast reaction and we also talked about the inherent difference in the termination reaction between radical chain polymerization and ionic chain polymerization. We talked about cationic chain polymerization in particular detail where we talked about different types of initiation reactions and then propagation.

And we just initiated discussion on termination and as we discussed, that in case of both cationic and anionic, polymerization is bimolecular, bimolecular reactions between these propagating species is (( )), so termination is not that, done that way. Typically, the terminations happen or typical termination happens in by the chain transfer and there are several possibilities of chain transfer reaction in case of cationic chain polymerization. And we just started giving examples, which chain transfer with monomeric species and what we will do. We will just begin our discussion in this lecture from that page.

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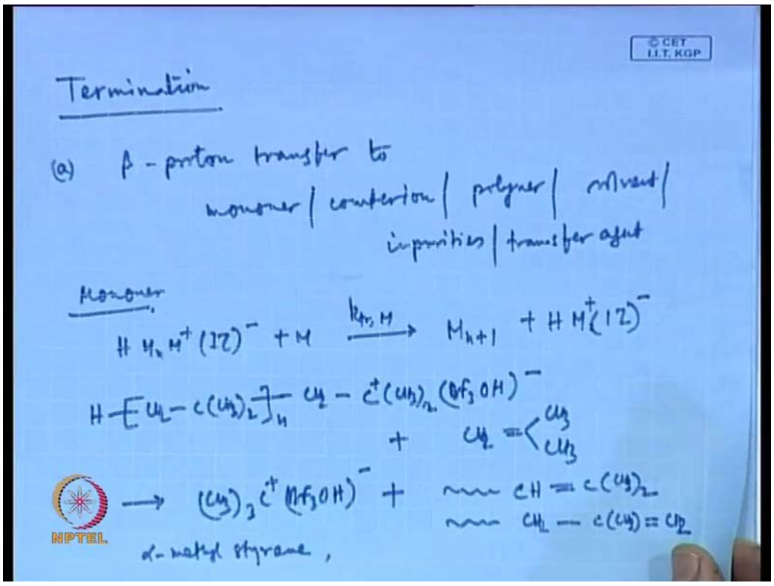

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Termination

(a) β - proton transfer to monomer | counterion | polymer | solvent | impurities | transfer agent

Monomer

$$H M_n M^+ (IZ)^- + M \xrightarrow{k_{tr,M}} M_{n+1} + H M^+ (IZ)^-$$

$$H-[CH_2-C(CH_3)_2]_n-CH_2-\overset{+}{C}(CH_3)_2 (BF_3OH)^- + CH_2=C\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

$$\longrightarrow (CH_3)_3\overset{+}{C}(BF_3OH)^- + \begin{matrix} \sim\sim CH=C(CH_3)_2 \\ \sim\sim CH_2-C(CH_3)=CH_2 \end{matrix}$$

α-methyl styrene,

NPTEL

We were discussing in this last lecture the termination by beta proton transfer to different species and we gave examples of the transfer reaction with monomer. And just note the rate constant we are giving and with the same rate constant, the same notation, what we used for radical chain polymerization, k tr M I. just said, that there could be two possible double bond in case of this monomers, like isobutylene, alpha methyl styrene. But for the examples, monomers like styrene, it will be only one double bond possible because in case of styrene you have only one possibilities of beta transfer.

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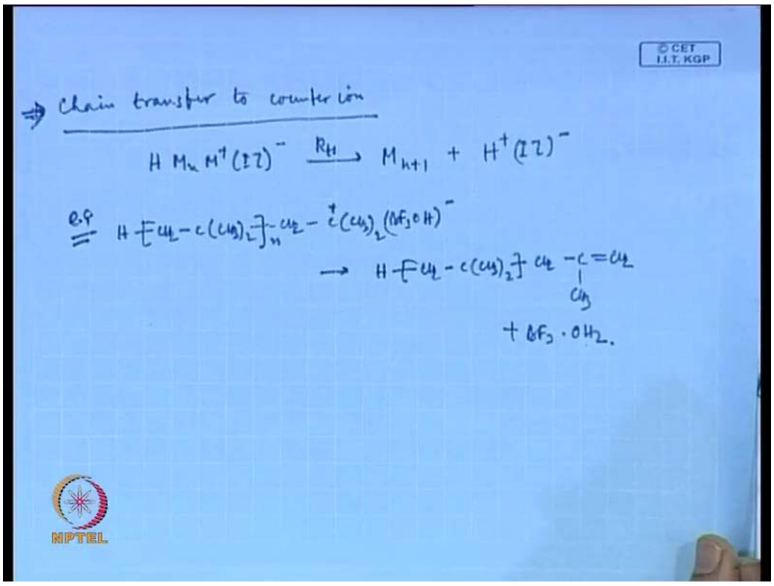

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⇒ Chain transfer to counterion

$$H M_n M^+ (IZ)^- \xrightarrow{k_H} M_{n+1} + H^+ (IZ)^-$$

e.g. $H-[CH_2-C(CH_3)_2]_n-CH_2-\overset{+}{C}(CH_3)_2(BF_3OH)^-$

$$\longrightarrow H-[CH_2-C(CH_3)_2]_n CH_2-\underset{CH_3}{C}=CH_2 + BF_3\cdot OH_2.$$

NPTEL

Now, let us talk about other possibilities. In this case we talked about chain transfer to counter ion. And these, these are basically similar as in the case of transfer to monomers, so I am just going through quickly these different types of chain transfer. Here, the proton is transferred to the counter ion itself. So, you get a dead polymer class species as in the case of the transfer to the monomer. And in, like in monomer case, the resulting species out of or as a result of chain transfer reaction is same as the initiating species. You remember, if you recall this initiating species for this reaction of polymerization of isobutylene by BF 3 plus water, this was the initiating species.

So, what happened is, in spite of this chain transfer reaction, the rate of polymerization does not slow down because this has the same reactivity with the existing kinetic chain, only thing happens because of this chain termination, chain transfer, the molecular weight actually gets reduced. Similarly, in this case, this can again reinitiate a cationic polymerization. So, rate does not get influenced much, whereas the molecular weight get drops. And this is again using the same examples, (( )) the chain transfer to counter ion.

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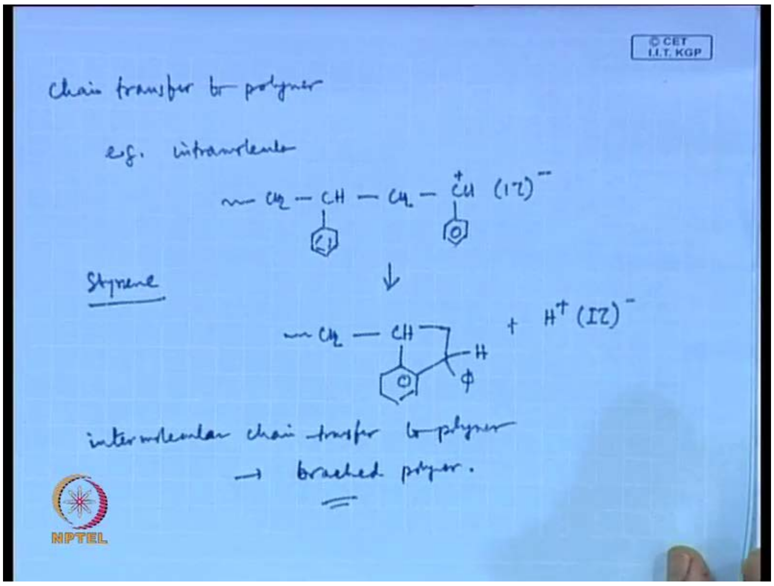

Chain transfer to polymer is possible and for example, this is the styrene polymerization, cationic polymerization. In this case, intra-molecular photon transfer is possible, which actually gives you a dead polymer chain and again initiated to coinitiator complex and if inter-molecular chain transfer happen, chain transfer to polymer happens, then you get a branched, branched chain or you get branched, branched polymer.

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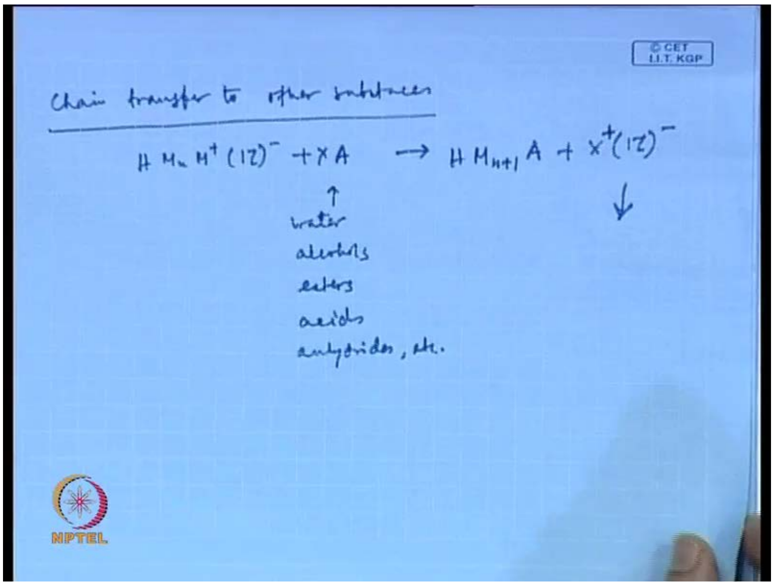

Chain transfer to other substances

$$HM_nM^+(IZ)^- + XA \longrightarrow HM_{n+1}A + X^+(IZ)^-$$

↑ (under XA)
water
alcohols
esters
acids
anhydrides, etc.

↓ (under $X^+(IZ)^-$)

So, this is very similar to reactions we have discussed in case of chain radical chain polymerization. Chain transfer also can be possible to the other substance, whether it is present as in impurities or you have added deliberately as a chain transfer agent to control the molecular weight. For example, this is generic structure of the chain transfer agent, which could be water, alcohols, esters, acids or anhydride, etcetera. And it can participate in the chain transfer reaction and giving away new catalyst, cocatalyst complex, which again can reinitiate a cationic chain polymerization. So, again this reduces the molecular weight of the cationic chain polymerization.

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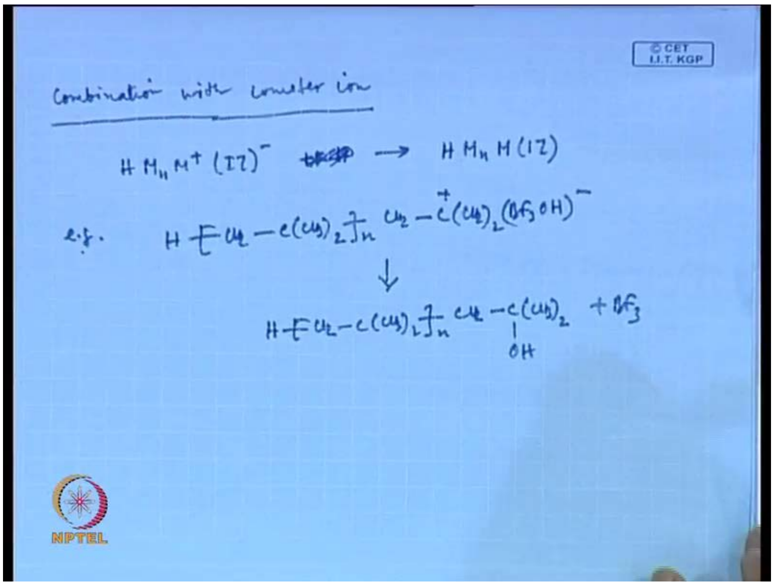

Combination with counter ion

$$HM_nM^+(IZ)^- \longrightarrow HM_nM(IZ)$$

e.g.

$$H\left[CH_2-C(CH_3)_2\right]_n CH_2-\overset{+}{C}(CH_3)_2(BF_3OH)^-$$

$$\downarrow$$

$$H\left[CH_2-C(CH_3)_2\right]_n CH_2-\underset{OH}{\underset{|}{C}}(CH_3)_2 + BF_3$$

Now, there is one more termination is possible, which is not a transfer reaction, which is basically in true sense, which is a termination reaction where this counter ion and this ionic species, the cationic properties can species combine into to form a covalent ball. For example, for generic expression we are using, it can be, it can be shown here and the examples of isopropylene polymerization will be (( )) in water, you can write a termination reaction like this. Now, in this case it is a true termination reaction because here you are not forming anything else, we can restart the, or reinitiate the polymerization.

As you know, in absence of water this cannot initiate the chain by itself. So, this is in that sense not a transfer reaction and it is a true sense a termination reaction, and you can just note down the example of this termination reaction. Now, there could be some agents, reagents present, like in case of radical chain polymerizations where this reagent actually can slow down the cationic chain polymerization considerably.

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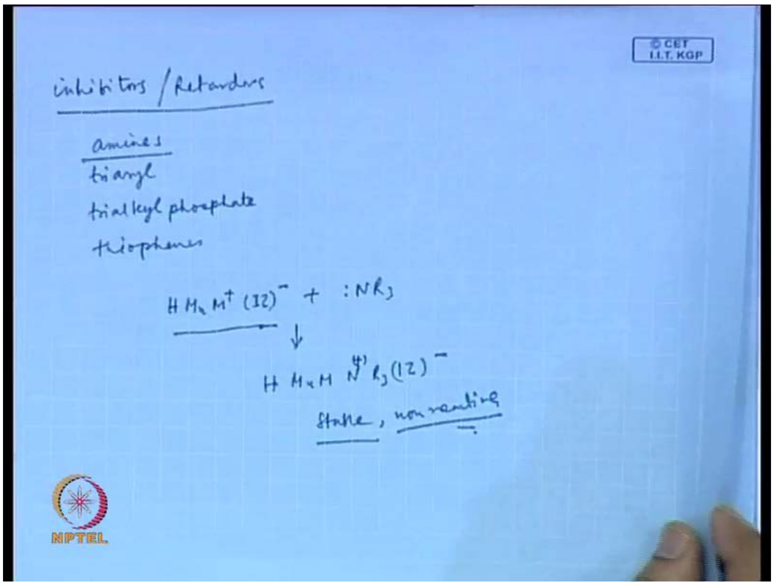

inhibitors / Retarders

amines
triaryl
trialkyl phosphate
thiophenes

$$HM_nM^+(IZ)^- + :NR_3$$
$$\downarrow$$
$$HM_nM\overset{(+)}{N}R_3(IZ)^-$$

stable, non reactive

So, they can act as inhibitor or retarder in case of cationic chain polymerization, like we talked about different retarder or inhibitor, like (( )) in case of radical chain polymerization. In this case also there could be other reagents possible, which you, if you add or present are as impurities, it can retard or inhibit the chain polymerization, cationic chain polymerization. For examples, amines, triaryls, trialkyl phosphates, triophenes, they can actually act as inhibitor. For example, you take specific example of amines, they can react with this propagating species and form a complex, such in this case this cationic species is very stable and they are nonreactive towards the monomer.

So, once this is formed, this cannot reinitiate or this cannot actually take part in further propagation reactions, which means, this chain actually gets inhibited by this type of reaction. So, like radical chain polymerization there are molecules or reagents, which you can or may be undesirably they are present in they can be present in cationic chain polymerization. So, we just talked about different possible possibilities of initiation reaction, propagation reactions and types of termination reactions possible in case of cationic chain polymerization.

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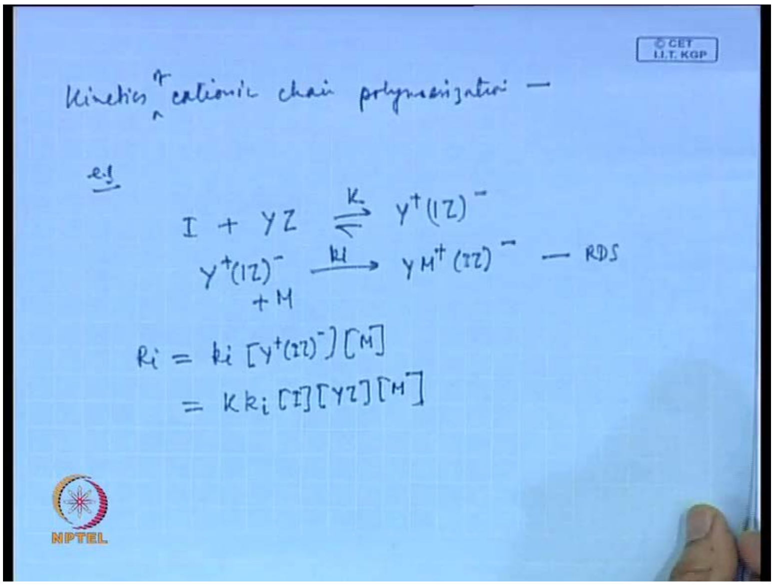

Kinetics of cationic chain polymerization –

e.g.

$$I + YZ \underset{}{\overset{K}{\rightleftharpoons}} Y^+(IZ)^-$$

$$Y^+(IZ)^- + M \xrightarrow{ki} YM^+(IZ)^- \text{ — RDS}$$

$$Ri = ki\,[Y^+(IZ)^-][M]$$

$$= K k_i [I][YZ][M]$$

Now, let us talk about the kinetics of or get some, introduce kinetic expression in case of cationic chain polymerization. Again, we will consider, like I said, we consider, consider the most important example of the initiation reaction and we consider the generic expression… minus, and so these are the two steps consist, you know, make the initiation reactions. As I mentioned earlier, that this is your rate determining step, so the rate constant for this reaction is considered.

See, if I write expression for rate of initiation, it would be ki, concentration of this species, Y plus IZ minus and concentration of monomer. As I mentioned earlier, that here in the rate expression for initiation reactions this monomer is appearing where in case of radical chain polymerization, monomers was not present in terms of, in the rate expression of the initiation reaction. Now, if you get the value for this form this equilibrium, we can write ki I YZ M.

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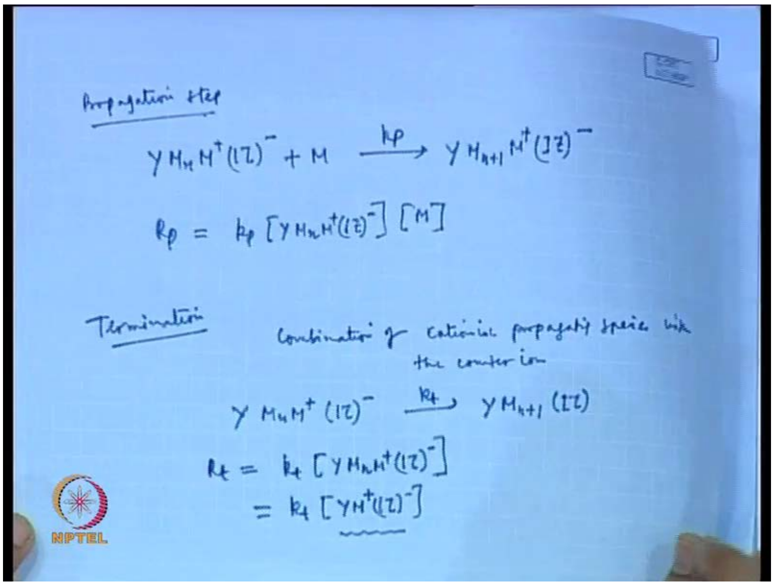

Propagation step

$$YM_nM^+(IZ)^- + M \xrightarrow{k_p} YM_{n+1}M^+(IZ)^-$$

$$R_p = k_p[YM_nM^+(IZ)^-][M]$$

Termination

Combination of cationic propagating species with the counter ion

$$YM_nM^+(IZ)^- \xrightarrow{k_t} YM_{n+1}(IZ)$$

$$R_t = k_t[YM_nM^+(IZ)^-]$$

$$= k_t[\underbrace{YM^+(IZ)^-}]$$

Let us write the propagation step, write this generic expression. So, rate of polymerization, R p, is given by k p, concentration of… And the monomer. Termination reactions, now let us consider the true termination reaction, which is the combination of the cationic propagating species with the counter ion. We are not considering for this kinetic expression, the other time transfer reaction, so we can write k t (( )) IZ.

So, R t, rate of termination is given by the concentration of… Now, for simplicity just write, like the earlier case where in case of radical polymerization let us write this only, M plus… So, this is the summation of concentration of all the cationic species present in the reaction medium, M 1, M 2, M 3 and so on. So, for simplicity we are just writing, omitting this subscript and writing this M plus. Again, this is the summation of the concentration of all the cationic species, propagating species present in the medium.

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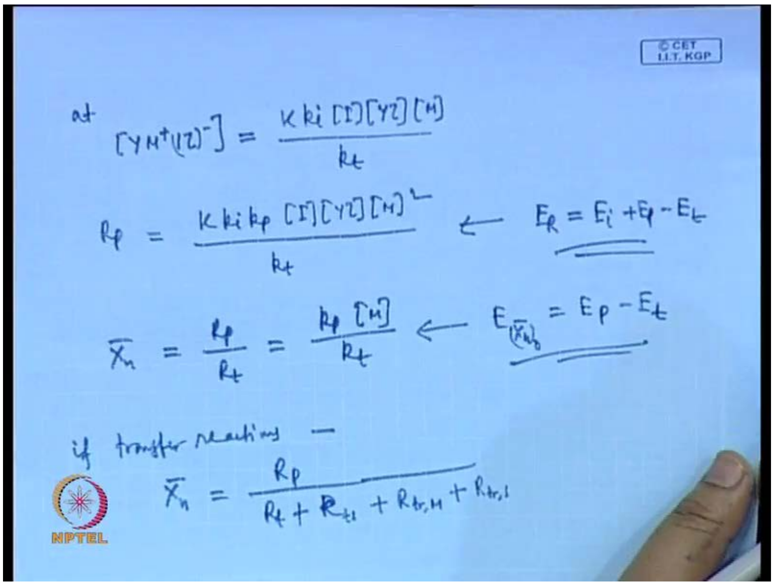

at

$$[YM^+(IZ)^-] = \frac{K k_i [I][YZ][M]}{k_t}$$

$$R_p = \frac{K k_i k_p [I][YZ][M]^2}{k_t} \leftarrow \underline{\underline{E_R = E_i + E_p - E_t}}$$

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{k_p [M]}{k_t} \leftarrow \underline{\underline{E_{(\bar{X}_n)} = E_p - E_t}}$$

if transfer reactions –

$$\bar{X}_n = \frac{R_p}{R_t + R_{ts} + R_{tr,M} + R_{tr,S}}$$

Now, at steady state you can equate R i n R t to get the concentrate, concentration of… like, in case of, we have a similar approach in case of radical chain polymerization, so we get this. So, R p similarly can be obtained in k p I YZ. Here, the rate of polymerization depend on the square of this monomer concentration where in case of radical polymerization, if you remember, is the, it was related to the concentration of monomer.

That is because this monomer is appearing in the rate expression of the initiation reaction, as well in ionic polymerization, whether in the case of radical polymerization this monomer was absent in the initiation reaction. So, I can write the degree of polymerization, like R p by R t, which gives k p M by k t. Now, similarly, transfer reactions happen, I can write X n R p plus summation of all the chain terminating reactions. So, R ts plus R transfer monomer plus R transfer solvent and so on.

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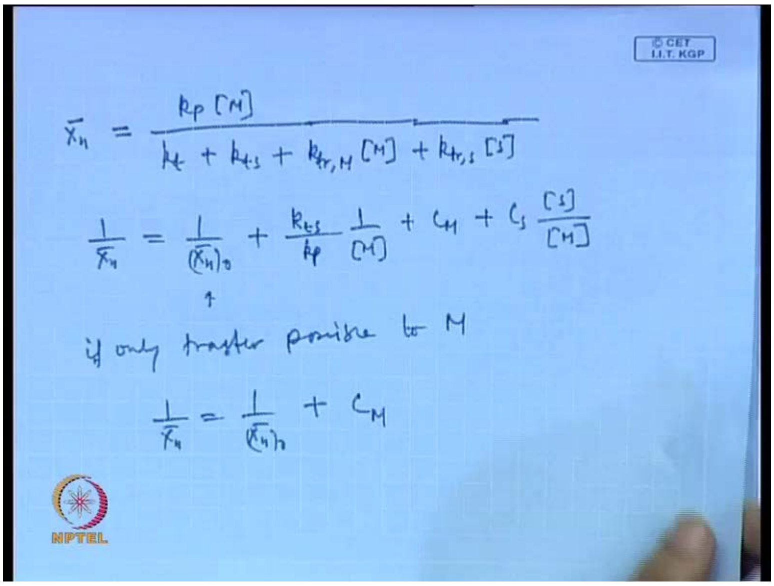

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$$\bar{X}_n = \frac{k_p[M]}{k_t + k_{ts} + k_{tr,M}[M] + k_{tr,s}[S]}$$

$$\frac{1}{\bar{X}_n} = \frac{1}{(\bar{X}_n)_0} + \frac{k_{ts}}{k_p}\frac{1}{[M]} + C_M + C_s\frac{[S]}{[M]}$$

↑

if only transfer possible to M

$$\frac{1}{\bar{X}_n} = \frac{1}{(\bar{X}_n)_0} + C_M$$

So, we can just simply write X n as k p M k t k ts chain transfer to the counter ion, chain transfer to the monomer and chain transfer to the solvent or any other substance or you can add, if they are other chain transfer reactions present. So, similarly, like in case of chain polymerization we can write this (( )) expression. This is X n bar 0 is the degree, number of degrees of polymerization, absence of any chain transfer reaction.

So, if if only transfer possible to monomer, then you can write X n bar is plus C M. So, the more the transfer reaction, obviously, the average degrees of polymerization comes down so as same, same discussion you can have what we had for the (( )) reaction, chain radical polymerization. So, increasing the solvent concentration, which is taking part in the chain transfer reaction or increasing the monomer concentration or similar, similar thing, we can describe exactly like the chain transfer reactions for radical polymerization.

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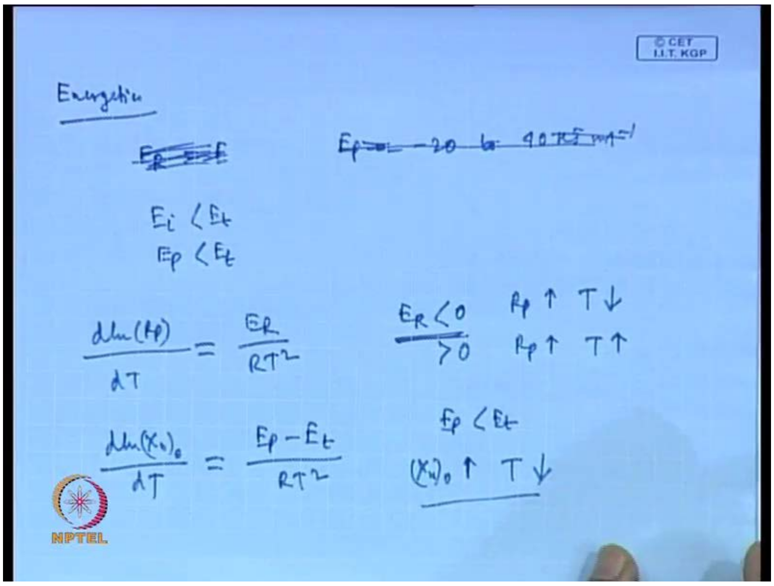

Energetics

~~E_p = −20 to 40 KJ mol^{-1}~~

$E_i < E_t$

$E_p < E_t$

$$\frac{d\ln(R_p)}{dT} = \frac{E_R}{RT^2}$$

$E_R < 0$ $R_p \uparrow$ $T \downarrow$

> 0 $R_p \uparrow$ $T \uparrow$

$$\frac{d\ln(\bar{X}_n)_0}{dT} = \frac{E_p - E_t}{RT^2}$$

$E_p < E_t$

$(\bar{X}_n)_0 \uparrow$ $T \downarrow$

So, let us talk about the energetic, which means, that the effect of the temperature on the reaction rate and molecular weight, like in case of radical polymerization if you just recollect this, this is the expression for your R p, rate of polymerization, and this is the expression for your average degrees of polymerization. So, we can write, similarly activation energy for reaction E i, initiation, plus E propagation minus termination and E X n bar 0 in absence of any chain transfer rate reagent we can write this.

Now, typically in case of cationic polymerization both E i and E p are lower than the termination activation energy as can be justified because that bimolecular termination is not possible and E p values are typically for minus 20 to 40 kilojoule per mole, which also depends on the monomer structure for same monomers. It, the activation general propagation will of course, depends on the initiator or coinitiator and the solvent. For example, thus, lets, this E p values is around no E p around, comes around, say 22. Let us go back and this E r value, it can be positive or negative and values is typically from minus 20 to 40 kilo joule per mole.

So, if I want to find out the defect of rate of cationic chain polymerization with temperature we get this E R like R t case and depending upon the value or sign of E R you can tell whether the reaction rate will increase with temperature or not. If this E R is negative, then R p goes up with temperature goes down; if it is positive, then R p goes up with increasing temperature.

Now, do not confuse, that activation energy for reaction is negative. No single reaction cannot, no single reaction can have negative activation energy. The activation energy for reaction in cationic chain polymerization could be negative, that is because it is a combination of activation energy for initiation, propagation and termination reaction. If that activation energy for the termination is higher than the combination of activation energy of initiation plus propagation, then it will become negative, so the rate increases with the temperature. If this is negative, if it is positive, then the rate of reaction increases with the temperature.

Similarly, you can write the expression for the molecular weight X n 0 in absence of chain termination reaction. Now, as we just said, that E P is less than E t, most cases, most general cases, so this is negative, which means, that X n 0 goes up with decrease in temperature. So, the molecular weight always decreases, sorry, molecular weight always goes up. If you decrease the temperature of the reaction, that is why cationic polymerization. But any chain polymerization in most cases performed in a (( )) environment or sub-zero temperature.

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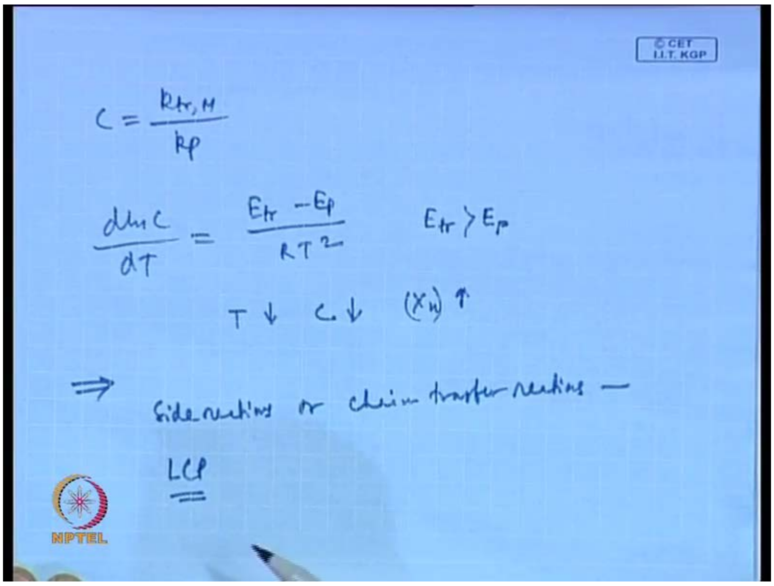

$$C = \frac{k_{tr,M}}{k_p}$$

$$\frac{d\ln C}{dT} = \frac{E_{tr} - E_p}{RT^2} \qquad E_{tr} > E_p$$

$$T \downarrow \quad C \downarrow \quad (X_n) \uparrow$$

$\Rightarrow$ Side reactions or chain transfer reactions —

$\underline{\underline{LCP}}$

Now, if you consider this chain transfer reaction or chain transfer constant, C is, say for chain transfer to the monomer is given by k tr is this d ln C by dT is given by E tr minus E p is divided by R T square. Now, typically E transfer is higher than E p, so which means, that with T, with increase in, decrease in temperature C also goes down, which means, X n goes up.

So, we found, that even for the reactions where transfer reaction is absent, if we decrease temperature the molecular weight goes up. The cases where transfer reaction present, the transfer constant goes down with decrease in temperature, as a result, that molecular weight goes up.

So, for cationic chain polymerization, no matter whether chain transfer reaction is present or not, you always end up having higher molecular weight. If you decrease the temperature, now whether that also simultaneously increases the rate of the polymerization that depends on the value of the activation energy for reactions. If it is negative, then with decreasing temperature you get increase in polymerization rate, but if it positive, then with decrease in temperature you get reduction in the polymerization rate.

Now, if we can, if you can do reactions where you do not have these side reactions or this chain transfer reaction, then you can keep this propagating cations, cationic propagating chains alive and you can get living cationic polymerization. Now, we are not going to details about the living cationic polymerization in this course, but there are, though it is very difficult in case of cationic polymerization, in, in a very careful manner if you can do reactions where you reduce or minimize the chain transfer reaction and the side reactions, then there is a possibility, that you can get a living chain polymerization.

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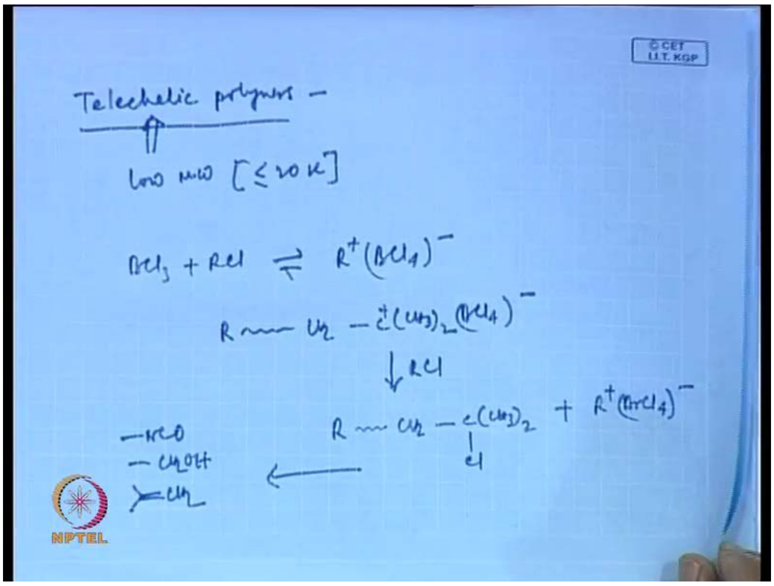

Now, this cationic chain polymerization can be utilized to synthesize telechelic polymers as well, where telechelic term means, low molecular weight, typically less than 20K molecular weight with a functional group at end, which can be utilized for further reaction. For example, we take this reaction, general reaction. So, you can consider these, reactions of this with isobutylene and you get propagating chain like this, which can again react with alkyl halide. You know now, this chloride can be utilized, reacted to form several types of (( )) groups, say like NCO or CH 2 H or (( )) group or something like that.

So, by this way you can, you can terminate a cationic chain polymers with a desired molecule, in this case alkly halide, and you can make functional groups at the end, which you can utilize to form different functional groups and then for the reactions impossible in that functional groups. Sometimes in cationic polymerization you also, if you do a characterization of the polymers you gained at the end of cationic chain polymerization you might get or you might see there is a bimodel distribution on the molecular weight.

Now, in that case what might had happened, that there could be possibility of simultaneously present of two different types of this ionic associated counterions. And as we know, that the reactivities of the free counterions or the solvent separated counterions are much different than tight iron-pairs. If they are present in significant amount, then they will propagate in a different way that might lead to different, differentiate of molecular weights, which might results in a bimodal type distribution of these resulting polymers.

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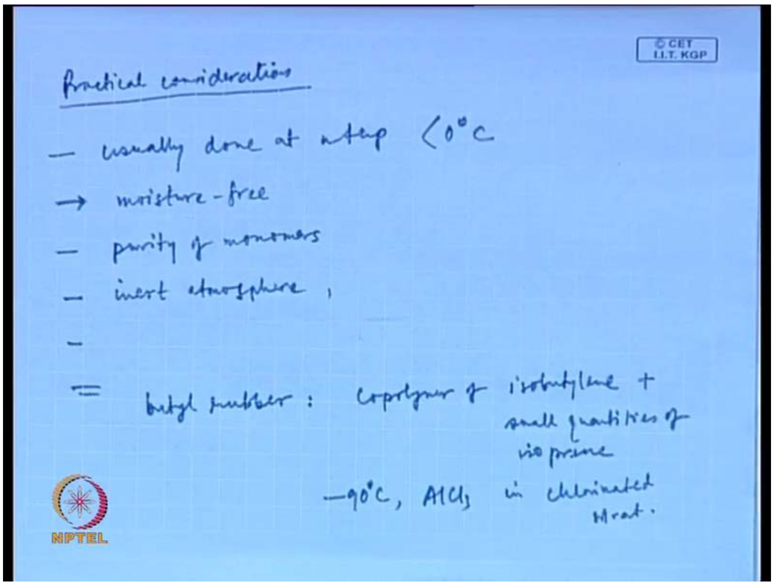

Practical considerations

- usually done at a temp < 0°C
→ moisture-free
- purity of monomers
- inert atmosphere ,
-
= butyl rubber : copolymer of isobutylene + small quantities of isoprene

−90°C, $AlCl_3$ in chlorinated Mrat.

Now, what are the practical considerations in case of, say, cationic chain polymerization? For a successful cationic chain polymerization, as we just discussed, usually done, usually done at a temperature lessen than 0 degree centigrade because as we have seen, that with reducing temperature you can get a higher molecular weight or molecular weight increases with a decreasing temperature.

Now, you have to maintain moisture free environment and if you, and if you are actually using H 2 as a cocatalyst, then we should add H 2 O in the (( )) symmetric amount with respect to the catalyst because moisture or H 2 is present in excess than what you desired as a cocatalyst. Then the cationic propagating species will react immediately with the water molecule and terminate the polymerization or propagating chain. And for the same reason, the purity of, purity of monomers are very important.

If there are impurities, which can undergo side reaction, do chain transfer reactions, then there molecular build up is a problem and these reactions, because oxygen is also a (( )). For this cationic polymerization an inert atmosphere is needed and for that the nitrogen or the argon gas, which are used for creating the inert atmosphere. They must be purified very (( )) and because these reaction are very fast reaction, sometimes it happens in seconds and the cationic chains reactions, actually you can make arrangements to, to perform the reaction, you might have to arrange or purify the monomer and the gas nitrogen, argon and you have to make this your container or the reactor moisture free. For that you might spend lot of time, but reaction happens very quickly within second and because it happens so quickly, generate lots of heat and sometimes there is a heat management is also a problem.

Now, for all these reasons, as I said in the very beginning, that doing or carrying out this cationic chain polymerization in large scale industrial scenario is very difficult, that is why, this cationic chain polymerization are not practiced commercially for many monomers. The only monomers, which are synthesized in commercial scales is butyl rubber. Butyl rubber, which is basically copolymer of isobutylene, the example of which we get many times in this lecture and small quantities of isoprene, this is done at very low temperature, 90 degree centigrade with aluminum chloride catalyst and in chlorinated solvent. Now, this butyl rubber has remained flexible at low temperature, like minus 50 degree. So, they are used in the inert use of the tyres engineer, autobody mounts and electrical cable insulator, protective gloves, etcetera and some form of (( )) stoppers. So, this is the only polymers or copolymers used, which utilized this cationic chain polymerization commercially.

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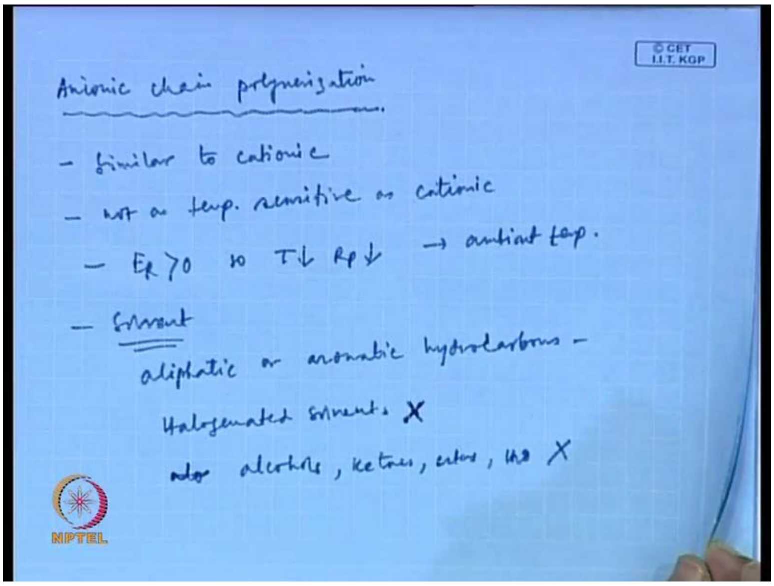

Anionic chain polymerization

- similar to cationic
- not as temp. sensitive as cationic
  - $E_R > 0$ so T↓ R_p↓ → ambient temp.
- Solvent
  aliphatic or aromatic hydrocarbons –
  Halogenated solvents X
  also alcohols, ketones, esters, etc X

Now, let us move to the next topic of anionic chain polymerization. Now, it is similar to cationic, but there are some significant differences as well. One difference is that the difference in the activity of these different ion-pairs is much, much strong in case of anionic polymers, anionic chain reactions, which means, that reactivity of free ion, the difference in reactivity of free ion-pair, which is a tight ion-pair, is much more important in case of ionic chain polymer, anionic chain polymerization than in case of cationic chain polymerization. There could be the other differences as well and this is not, at not, as temperature sensitive, as cationic polymerization.

And generally, E R, the activation of (( )) is positive, small positive. So, if you decrease temperature, rate of reaction goes down. So, generally reactions are down at ambient temperature or may be slightly higher than ambient temperature solvent is very important, even more in case of anionic polymerization you can, the solvents are mainly used is aliphatic or aromatic hydrocarbons. You cannot use halogenated solvents, which were suitable for cationic polymerization because they are fissile (( )) reactions with the carbon ions and other polar solvents like alcohols or ketones, esters also cannot be used, as well as, H 2 O cannot be used because the same reason of cationic, because they can very quickly react with the carboionic propagating species and terminate the chain reaction.

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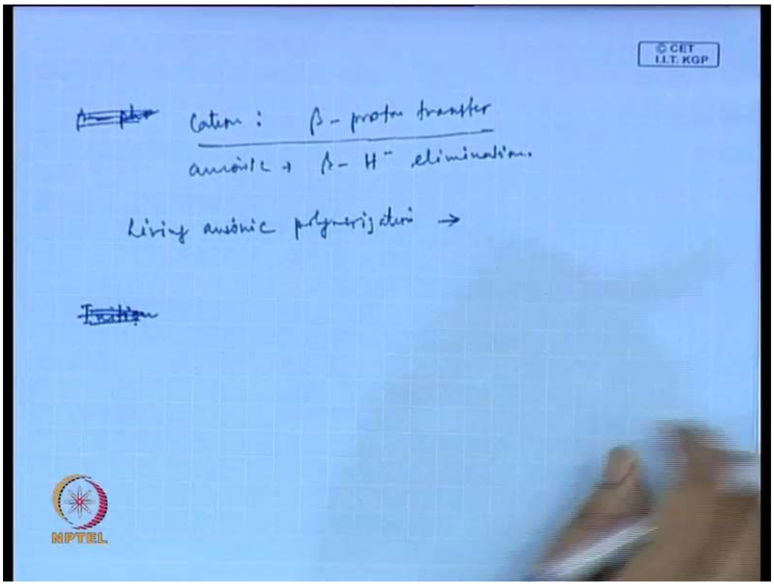

Cation : β - proton transfer

anionic → β - H^- elimination.

Living anionic polymerization →

Now, other difference of anionic polymerization with cationic polymerization is this possibility of the transfer reaction. Now, in case of cationic we have seen, that in case of cationic we have seen very fissile beta proton transfer or elimination reaction happening for this transfer reaction, where in case of anionic polymerization you require beta hydride elimination for those transfer reactions with monomer solvent and counterion, all these things to happen.

Now, hydride elimination is not very easy thing. So, this extent of transfer reaction for anionic polymerization is much less compared to cationic polymerization, which means, that the side reactions and the, cation, the chain transfer reactions are very less if you have a very pure monomer and moisture free environment. That is why, leaving anionic polymer polymerization, leaving anionic polymerization is comparatively easier than cationic polymerization because you, in case of cationic polymerization, these transfer reactions are very common and fissile, where in case of anionic this transfer reaction is required beta hydride elimination, which is, which is not easy thing. So, leaving anionic polymerization is quite often easily achieved compared to a living cationic polymerization.

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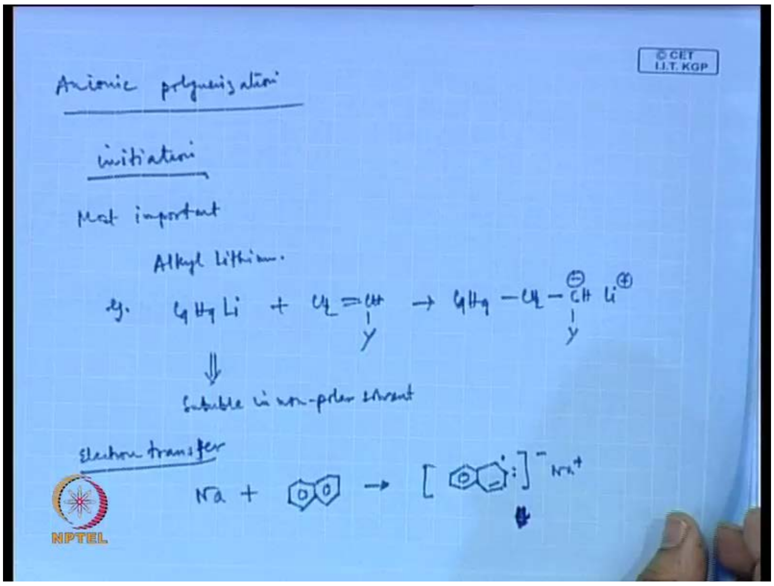

Anionic polymerization

initiation

Most important

Alkyl lithium.

eg. $C_4H_9Li + CH_2=CH(Y) \rightarrow C_4H_9-CH_2-\overset{\ominus}{C}H(Y)\ Li^{\oplus}$

⇓

Soluble in non-polar solvent

Electron transfer

$Na + \rightarrow [\quad]^{-} Na^{+}$

Now let us talk about the three steps, initiation, in case of anionic polymerization are initiation. Most important is using alkyl lithium. For example, I have this butyl lithium, which can react with monomers CH 2… This alkyl lithiums are equal to, make this, this curve initiator soluble in organic solvent or soluble in non-polar solvent, as we have seen earlier, how we have discussed earlier, that anionic polymers are typically down at aliphatic hydrocarbons, aromatic hydrocarbons.

Other initiations possible by electron transfer, electron transfer, for example, reaction between sodium and naphthalene. Now, this can react with 1 mole of same molecules, let us, this is another possibility where sodium can react with naphthalene by electron transfer, you can generate anionic species, which can initiate it, can react with the monomer to initiate the chains.

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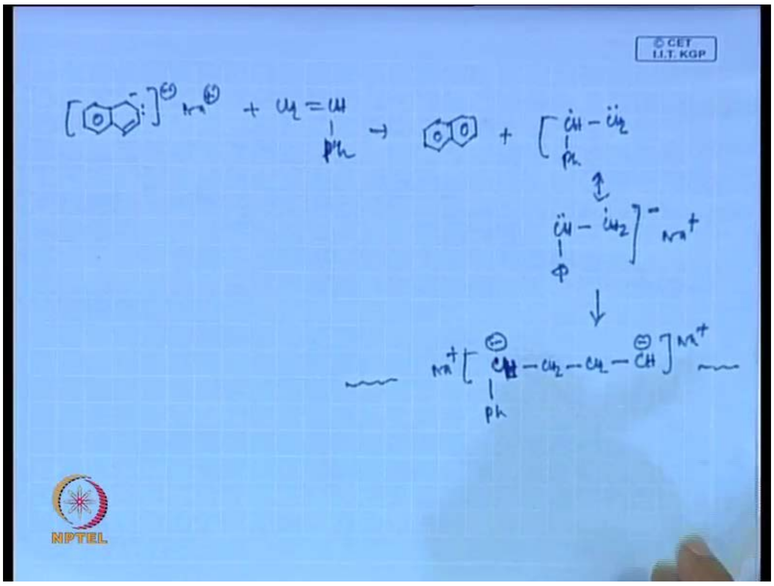

If I write the chain initial reaction for that electron transfer reaction, it can react with the monomer to initiate the chain say Y s, styrene, we are talking about styrene polymerization here. This, it is, in it now this can primarize. This is the example of how initiation is done with electron transfer. In this case we took example of sodium and naphthalene and in this case you can see this final or initiate thing chain (( )) species form is this, which actually can extend or propagate from both the sides. So, you can have reactions happening in both the, propagation happening in both the sides.

If we talk about the, this propagation of this butyl lithium reaction, which is, this is butyl lithium, which is common and more important.

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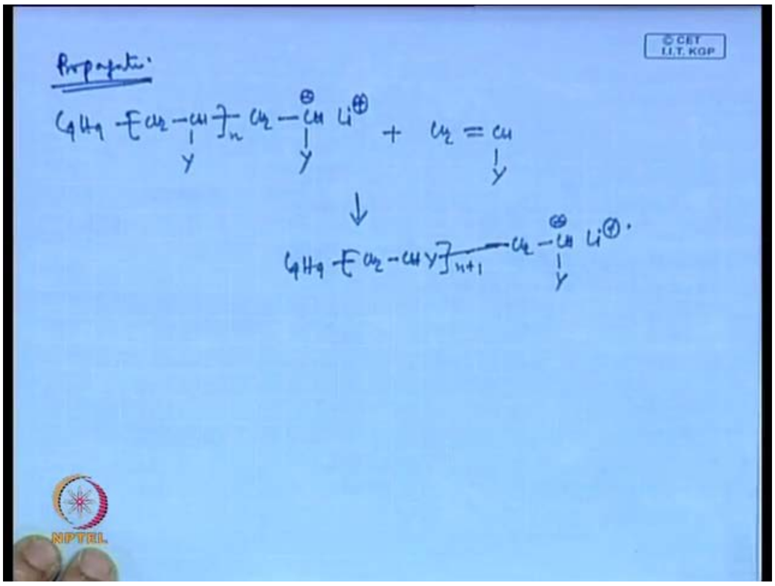

Let me write the propagation reaction for that, generic propagation reaction, and if you talk about the propagation reaction of this, this species, then you can write propagation reaction.

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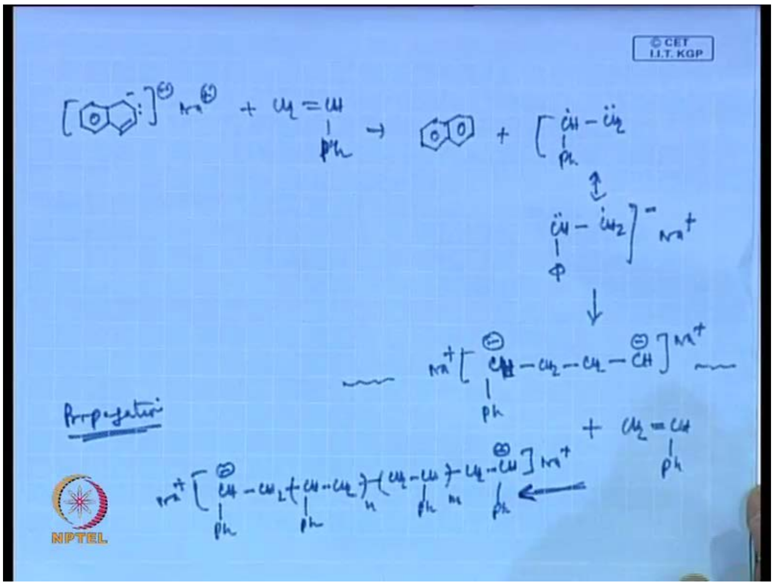

This plus…

Basically, this, as I said, it can propagate from both the sides. This is what the propagation reaction will generically look like. Now, this, these are the examples where you do not have an inherent termination reaction.

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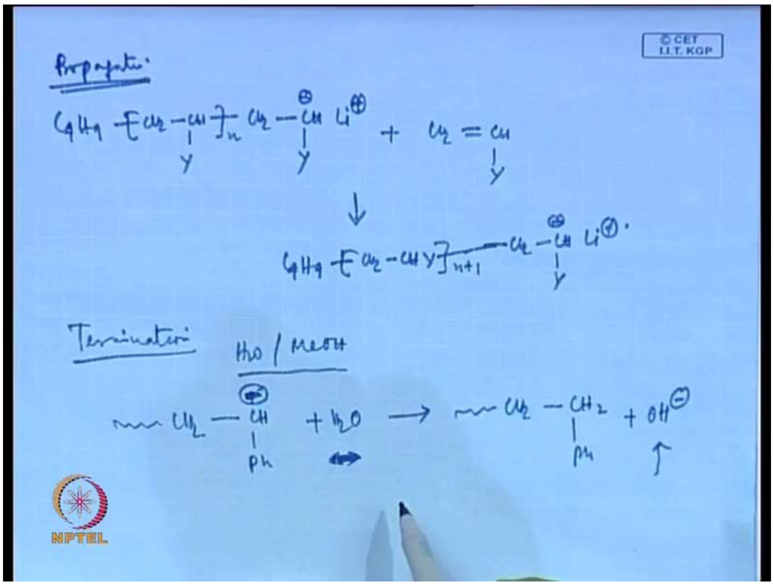

In both this case, this initiation by alkyl lithium and also by this electron transfer, you do not have any inherent termination reaction. So, the reaction can proceed without a termination reaction or and the reaction of the propagating chain can remain leaving. But if you, if you want to stop the reaction for whatever reason, then you can add an agent, which could be alcohol or water, which can actually react with, immediately with these active anionic carboionic chain end and stop the reaction.

So, termination reaction, if you can add H 2 O or say methanol or any other alcohol and which can terminate this reaction very quickly. Now, this is not sufficiently neucleofilic to reinitiate a chain polymerization, which also means, that if you have H 2 O present, undesired H 2 O present giving the polymerization medium, in a, in the polymerization medium, then it has very detrimental effect in terms of molecular rate build up because if there are trace amount of history also, this will immediately react with the propagating carbon ion anionic end and stop the reaction immediately, which will have very detrimental effect in terms of building molecular weight.

Now, they are (( )), there are, there are not (( )) termination reactions for these type of initiation or propagation reaction, but some polar monomers can have side reactions present, which actually can, which actually can determine or be detrimental for your molecular weight build up. And there are other possible initiation reactions, which we will discuss in the next lecture where inherently, there could be termination reactions possible.

So, what we have done in this lecture? We have talked about general features of anionic polymerization. Anionic polymerizations, as I said that it is much more solvent dependent compared to cationic, cationic chain polymerization. And the inherent termination reactions, as in the case of cationic polymerization by beta proton elimination, in that cationic polymerization case are not present here because beta hydride elimination is difficult. So, it is always comparatively easy to carry out leaving anionic polymerization than leaving cationic polymerization.

And we talk to define initiations possibilities of this anionic polymerization and most important of this is using alkyl lithium. And there are other possibilities using these where electron transfer reactions, examples given sodium and naphthalene, and as this, as if seen this propagation state, that termination is not present. So, if one requires to terminate the chain, you can add externally this H 2 O or alcohol to terminate the chain. But there are some polar monomers, like methyl methaculate or methyl vinyl ketone, which can undergo side reaction, which actually restrict the molecular build up.

In next lecture what we will talk? We will start giving that example of the side reactions in case of the polar monomers like methyl methaculate or (( )) or methyl vinyl or methyl ketones where the side reactions, the molecular build up is difficult. And also, we gave example of other type of initiation reactions where there could be inherent termination reaction. And in the in next, next lecture you also consider the little bit of energetic, how the temperature affects the anionic polymerization and how the molecular weight distribution is in case of anionic chain polymerization and how to get the molecular weight from the initial monomer and initiator ratio. So, with this we, I stop this lecture and in the next lecture I will continue with this anionic chain polymerization. And and we will start the other type of polymerization in the second half or the latter half of the next lecture.