Polymer Chemistry
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Lecture - 22
Chain Copolymerization (Contd.) And Ring Opening Polymerization

Welcome back to this course on polymer chemistry and in this lecture number 22, we are going to continue our first half our discussion on chain copolymerization.

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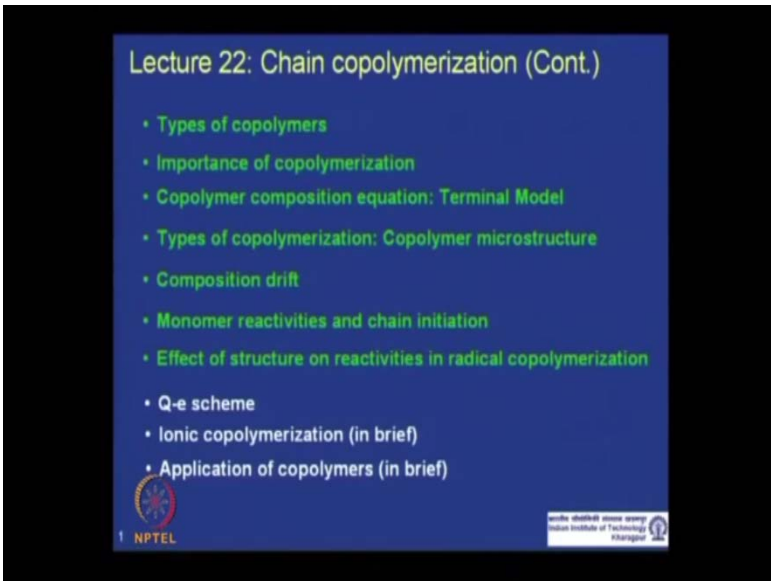

Lecture 22: Chain copolymerization (Cont.)

- Types of copolymers
- Importance of copolymerization
- Copolymer composition equation: Terminal Model
- Types of copolymerization: Copolymer microstructure
- Composition drift
- Monomer reactivities and chain initiation
- Effect of structure on reactivities in radical copolymerization
- Q-e scheme
- Ionic copolymerization (in brief)
- Application of copolymers (in brief)

We will cover the remaining parts of the chain copolymerization discussion we are having. And then take from there I will start a new topic or new synthetic procedure namely ring opening polymerization. Now, if you look at the slides we had during last 2 lectures the in our discussion on chain copolymerization, we basically covered these topics different types of copolymers, importance of copolymerization, and copolymer composition. Then microstructures, alternate random blocky structure, how the reactivity difference between the monomers actually give this type of copolymer microstructure.

And we have talked about copolymerization composition drift with time and then we talked about how the monomer reactivity’s and different types of chain initiation, you know types of chain initiation, actually determine these values of the reactivity ratios. In today's lecture we will just cover this treat of care we will talk about Q e scheme and then briefly about ionic copolymerization how that is different from radical copolymerization. And just a brief idea about the type of application this copolymers goes.

Now, in the last lecture we talked about different factors contributing to the reactivities of this the monomers and in turn the reactivity ratio the value of the reactivity ratio of these monomers. We talked about the resonance stabilization of the substituted group, we talked about the electron charge density, electronic charge density, we talked about the steric effect and so on. Now, all these factors actually contribute to the reactivity of the monomer in such a way that it is very difficult to distinguish, the contribution from each of these factors in the reactivity of the monomers.

Hence it is very difficult to get a quantitative idea or is very difficult to predict the reactivity ratios of the monomers from a given structure. Nonetheless one semi empirical method proposed by Price and Alphre is often used very commonly to sort of get the reactivity ratios of different monomers, and a ranking between different monomers in terms of their reactivities. And that is a semi empirical approach and this is the Q e's Q e scheme we are talking about.

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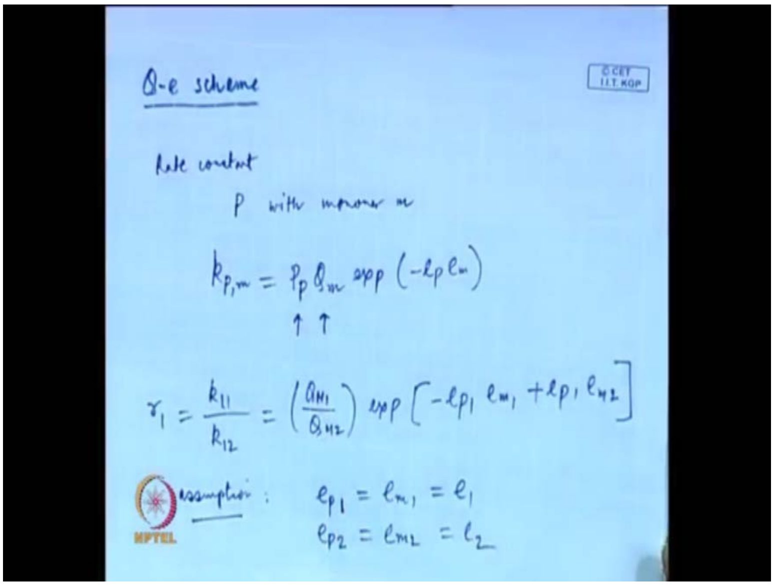

Q-e scheme

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Rate constant

P with monomer m

$$k_{P,m} = \underset{\uparrow}{P_P}\,\underset{\uparrow}{Q_m} \exp(-e_P e_m)$$

$$r_1 = \frac{k_{11}}{k_{12}} = \left(\frac{Q_{M1}}{Q_{M2}}\right) \exp\left[-e_{P1} e_{M1} + e_{P1} e_{M2}\right]$$

assumption : $e_{P1} = e_{M1} = e_1$

$e_{P2} = e_{M2} = e_2$

And this is we talking a continue our discussion on radical copolymerization so it is applicable for radical copolymerization. And this scheme is based on the assumption that the rate constant, rate constant of reaction between a propagating radical P this is a propagating radical P with a monomer, monomer m. Now this rate constant can write k P m this is rate constant for reaction between a propagating polymer radical P and a monomer m is given by these expression, where this 2 terms are the reactivity measure of the reactivity of the polymer like radical. And this is the measure of reactivity of the monomer and this two term e p and e m they are the measure of the electronic charges, electrostatic charges on the polymer radical and the monomer respectively.

So, if I write from this the expression for r 1 which is given by k 1e 1 by k 1 2 I should write. Now, this both cases the polymer radical is the same so this will get cancelled. So, I can write q for m 1 q for m 2 for 1, 1, 1 e m 2, you can get the expression from k 1 1 for k 1 1 k 2 and so the ratio you get these two, this because is the same radical 1 and 1. So, this cancel out so we get these were this is a the measure of reactivity of monomer 1 and this is the measure of reactivity of monomer 2. This is the charges electrostatic charges on the polymer radical and the monomer.

Now, another assumption is made in this approach is that e p 1 is same as e m 1 and we can and we write this as e 1. Assumption is that the electrostatic charge on the polymer radical, which has at the end in monomer 1 structure and the electrostatic charge on monomer is same. And which will I think as e 1 so similarly, we can write e p 2 e m 2 as e 2.

So, again the assumption is that the electrostatic charge on the polymer radical and the monomer are same, if the monomer residual end of the polymer radical is same as the monomer we are talking about. So, if I can write, similarly for r 2 Q now because Q is always talking about related to monomer. So, we can ignore or remove this term monomer m we can just write Q 1 and Q 2.

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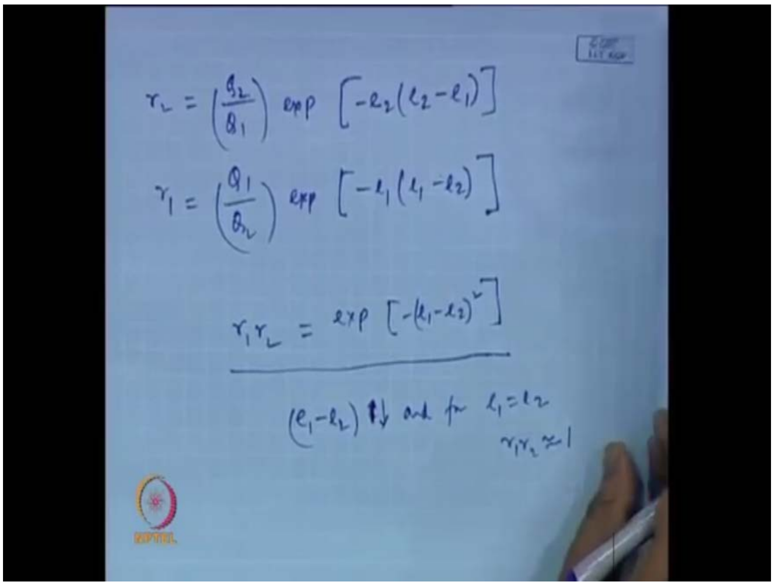

$$r_2 = \left(\frac{Q_2}{Q_1}\right) \exp\left[-e_2(e_2 - e_1)\right]$$

$$r_1 = \left(\frac{Q_1}{Q_2}\right) \exp\left[-e_1(e_1 - e_2)\right]$$

$$\underline{r_1 r_2 = \exp\left[-(e_1 - e_2)^2\right]}$$

$(e_1 - e_2) \uparrow\downarrow$ and for $e_1 = e_2$ $r_1 r_2 \approx 1$

So, now we can write Q 1 and Q 2 and we have seen r 1 Q 1 by Q 2 exponential minus e 1 minus e 2 essentially these 2 relates the reactivity ratios of the monomers to the electrostatic charge on the monomer. We do not have any charm which is related to the polymer radicals, these are all the terms are related to the monomer. So, basically this relates to the reactivity's of the two monomers and the electrostatic charge on the two monomers.

Now, if we multiply these two we get this value for r 1, r 2 which is basically the measure of we have seen earlier is a measure of alternating tendency. If it is close to 0 then they the will monomer will produce the alternating microstructure, if they are close to 1 then the 2 monomers will produce a random copolymer. And if they are equals both are equals to 1 then obviously r 1 r 2 will be equal to 1 then that will be exactly random copolymers.

So, r 1, r 2 will be given by if we can multiply these two given by exponential minus e 1 minus e 2 square. Now, this expression is in sink with our understanding till now. Now, if e 1 is a very close to e 2, that means the electronic charges of the double bond in the monomers are very close, then obviously this will become close to 1 and we get a random copolymers, random copolymers.

Now, if the double bond for the two monomer has different electrostatic charge, if they are then they are what will happen r 1 and r 2 would be close to 0. That means they are reactivity they will produce a more copolymer, which is more closer in alternate, alternate copolymer than a random copolymer. If e 1 minus e 2 goes up then it will be in an extreme because e 1 and e 2 will get a r 1, r 2 close to 1 which will give ideal copolymerization as we expect. And if they are think if this goes down so they are there equal and then we get these if they are different then r 1 r 2 will be closer to 0, producing a alternate copolymer which is in sink with our understanding, whatever we have discussed till now.

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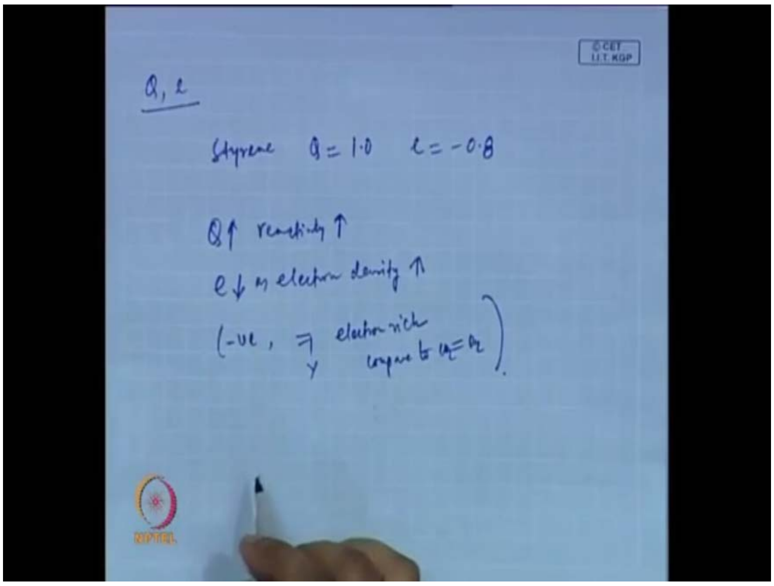

Q, e

Styrene $Q = 1.0$ $e = -0.8$

Q↑ reactivity ↑

e↓ ⇒ electron density ↑

(-ve, ⇒ electron rich compare to $CH_2=CH_2$).

Now, how do you get this values for Q and e now arbitrarily it has been assigned styrene. Styrene has been assigned so arbitrarily a value of Q is 1 and e is 1.0 and 0.8. And you and rest of the monomers are compared with the value of styrene, what you individual monomers or copolymerized with styrene and from the experimental values of r 1 and r 2, you can use these expressions where if you consider 1 as styrene. And then you know Q 1 you know u 1, hence you will from these to expression and you also know r 1 from experiment r 1 r 2 from experiment. So, from using these to expression you will be able to find out the values for Q 2 and e 2.

So, monomers are copolymerize with styrene and you get the experimental values of r 1 r 2 and from known values of styrene having Q is 1 and e is minus 0.8, you can get the unknown values for the second monomer. And once you get the individual values for different monomers, they are those values of Q and e are further defined by copolymerizing monomers other than styrene. Basically first copolymers as we styrene, get the experimental values of r 1 and r 2 get from the expression you get Q and e for the unknown monomers. And then if we find further this values of Q 1, Q and e for the other monomers by taking copolymers between them.

Now, obvious this is Q is measure of reactivity as we have seen and e is measure of electrostatic charge. So, if Q goes up the reactivity will go up and e goes down the value of e goes down because it is a measure of electron density, electrostatic charge. So, basically electron density on the double bond if there's a electron donating group then the electronic density or the electrostatic charge will go up, then Q value will be going up. And if this electron withdrawing group which basically reduces the electron density on the double bond. And hence the electrostatic charge it will be more of a lower number. So, electron density t goes down and electron density goes up and the value is negative e is negative, when the double bond in say this monomer the double bond it is electronic rich compared to a ethylene molecule it is a simple double bond.

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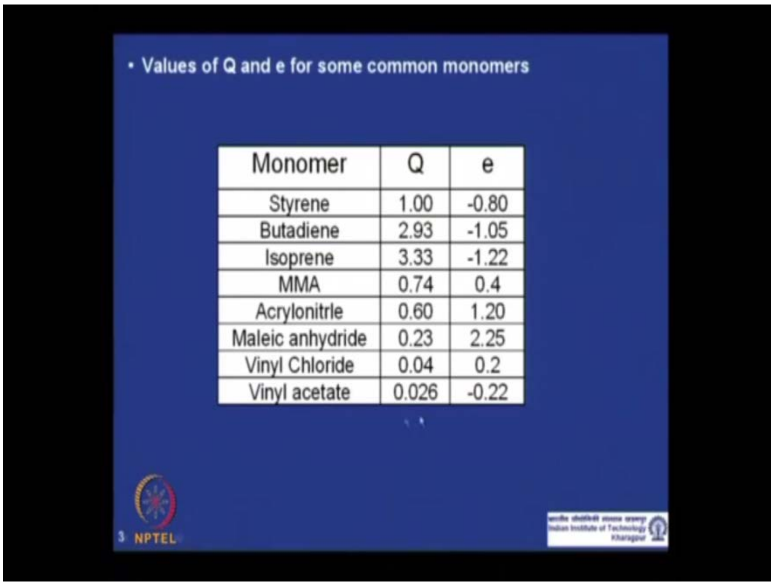

- Values of Q and e for some common monomers

Monomer	Q	e
Styrene	1.00	-0.80
Butadiene	2.93	-1.05
Isoprene	3.33	-1.22
MMA	0.74	0.4
Acrylonitrle	0.60	1.20
Maleic anhydride	0.23	2.25
Vinyl Chloride	0.04	0.2
Vinyl acetate	0.026	-0.22

So, if you so if you look at few data's of the numbers for Q and e the styrene is arbitrarily taken as 1 and minus 8 minus 0.8. And if you compare with other monomers so like other conjugate diene like isoprene and butadiene because there they can easily stabilize the radical by resonance, their reactivity is high so Q is high. And they also basically act as electron donating group so increase the electron density in the double bond. So, basically this value is negative and is negative means is equal to electron rich, negative is a charge for electron. So, negative means electronic rich.

Now, if you compare the monomers having electron withdrawing groups like M M A and acrylonitrle, the reactivity comes down compared to styrene because they cannot stabilize as much as styrene can do a propagating radical. Whereas, because they have electron with drawing group, the charge on the double bond actually lower, it is a more positive charge. So, you get a positive value and acrylonitrle is more strong electron withdrawing group. So, it has a positive value compared to M M A.

And compare this vinyl chloride and vinyl acetate, which is basically as we have known from our earlier discussions done in several times. The reactivity is very low because they cannot stabilize the radical the propagating radical so their reactivities are low so Q values are low. And they are dead basically they are weekly donating all the withdrawing groups so values are very low either positive or negative depending up on what is the electron with drawing effect or electron donating effect. Look at this monomer maleic anhydride we know the structure of maleic anhydride.

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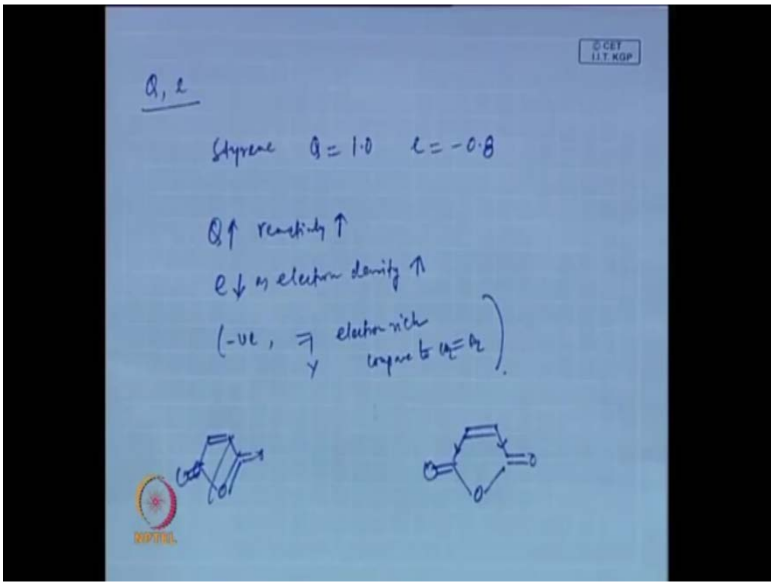

Q, e

Styrene Q = 1.0 e = -0.8

Q↑ reactivity ↑

e↓ ⇒ electron density ↑

(-ve, ⇒ electron rich compare to $CH_2=CH_2$).

Now, this is this is a very two very strong electron withdrawing group, so basically the electrostatic charge will be much more positive compared to a ethylene group. And that is why the value for e is quite high positive 2.25 and these values will vary it is not that these values are very fixed values, but these value might vary little bit depending up on the condition of the reaction among. So, but the trend will be mentioned so absolute values of this monomer Q and e value might change, but the trend will always remain same depending irrespective of the condition. And the because it cannot stabilize the radical much so we are reactivities also comes down. So, in general we can write that if monomer can stabilize the resonance, the propagating radical the resonance the reactivity is high.

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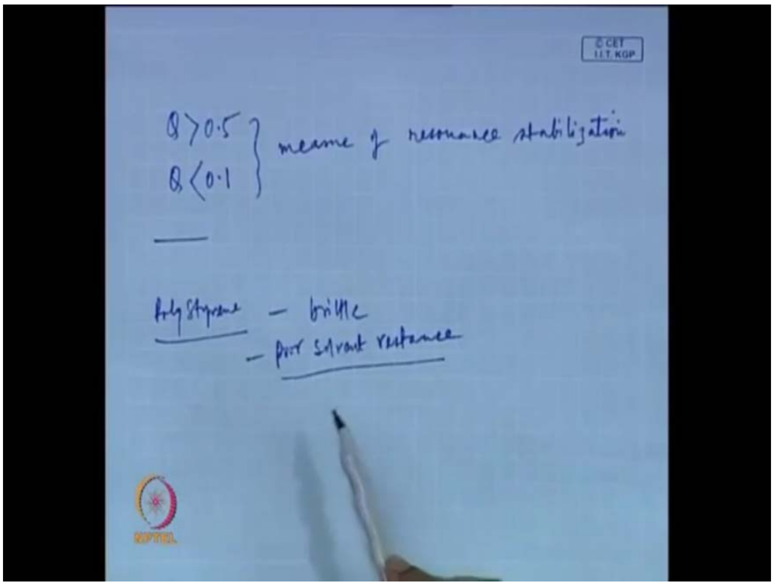

$Q > 0.5$ } measure of resonance stabilization
$Q < 0.1$ }

Polystyrene – brittle
– poor solvent resistance

Then Q would be greater than 5, if they cannot stabilize by resonance them Q would be lower so basically Q is a measure of resonance stabilization. Now, we can so if you know these values, when we know that if the two monomers which are having very electrostatic charge, having very positive charges like acrylonitrle and maleic anhydride. They will be difficult to copolymerize on the other hand if you take maleic anhydride the monomers are very much electrostatically positive. So, homo polymerization of maleic anhydride is very difficult, it does not happen.

Now, if you take maleic anhydride and copolymerize with something which has a negative value of e. That means they have a electron positive electron rich double bond. Then obviously there will be attraction between the two polar polarities and there will be possibilities for the copolymerization will be much easier. So, whereas, maleic anhydride does not homopolymerize it can easily copolymerize with butadiene or styrene because their charges are opposite. So, the monomers can attract each other and do the reaction.

So, basically now we know that with these how to both Q and e and how the basis of these values Q and e how to experimentally or semi empirically get these values of Q and e in comparison to arbitrarily they assigned values of styrene. And from the these values of Q and e we now can predict whether two monomers can will copolymerize or not and they are for their ranking in their activities also.

So, with these we will move to we will basically completed our discussion on radical copolymerization, we will move and discuss very briefly about ionic copolymerization. And ionic copolymerization and not very often done you know, typically as we have said earlier in our discussion earlier lectures that are an carrying out ionic polymerization is always difficult.

So, unless there is a specific requirement like you are making a specialty polymers like then there is no point of making these polymers by these ionic methods. That is why this copolymers are not usually synthesized by doing ionic copolymerization from a mixture of two or more monomers. But copolymerization is done by ionic polymerization to make block copolymers, where you first make a block of 1 monomer and then add the second block to get a block copolymers.

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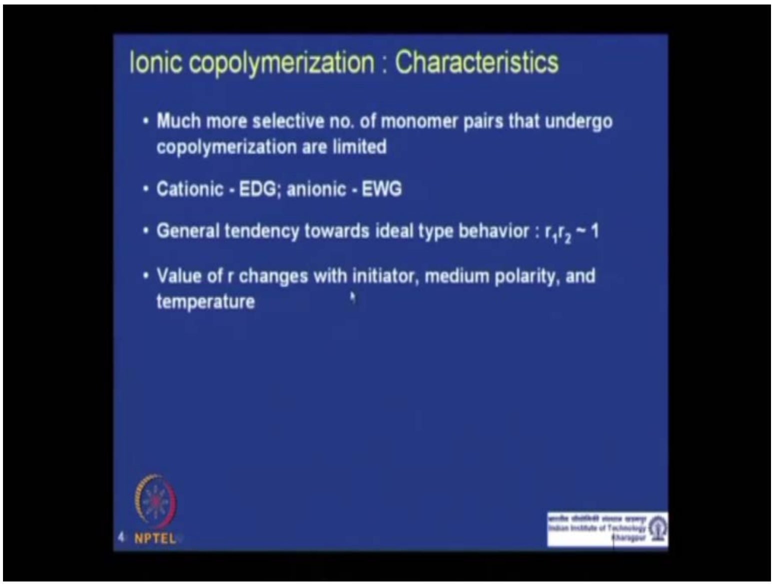

Ionic copolymerization : Characteristics

- Much more selective no. of monomer pairs that undergo copolymerization are limited
- Cationic - EDG; anionic - EWG
- General tendency towards ideal type behavior : $r_1r_2 \sim 1$
- Value of r changes with initiator, medium polarity, and temperature

Nonetheless if you compare ionic copolymerization and with radical copolymerization we can understand the differences and the in that way we can understand, say the characteristics of ionic copolymerization. Now, unlike radical copolymerization this ionic copolymerization is much more selective, you know. Not many monomer they undergo copolymerization, the number of co monomer here you can choose which you can use to make a copolymer by ionic method is limited. And we know that in case of radical copolymerization basically there are numerous options where you can choose two monomers and make a copolymer from there. And we know that cationic copolymer the monomers, which are having electron donating group as a substituent copolymer.

We will copolymerize by cationic method and the monomers having electron withdrawing group as a substituent under the copolymerization with ionic method. Typically or generally the tendency of this copolymerization are towards ideal behavior because when as I said that the number of monomers are limited. So, only those monomers, which are having reactivity towards the cation they undergo cationic polymerization and the monomers, which have reactivity towards and they go they undergo anionic copolymerization. So, we have the monomers which have undergo ionic copolymerization their reactivities are not too different. So, they typically or generally have a ideal type they make a typically ideal copolymers.

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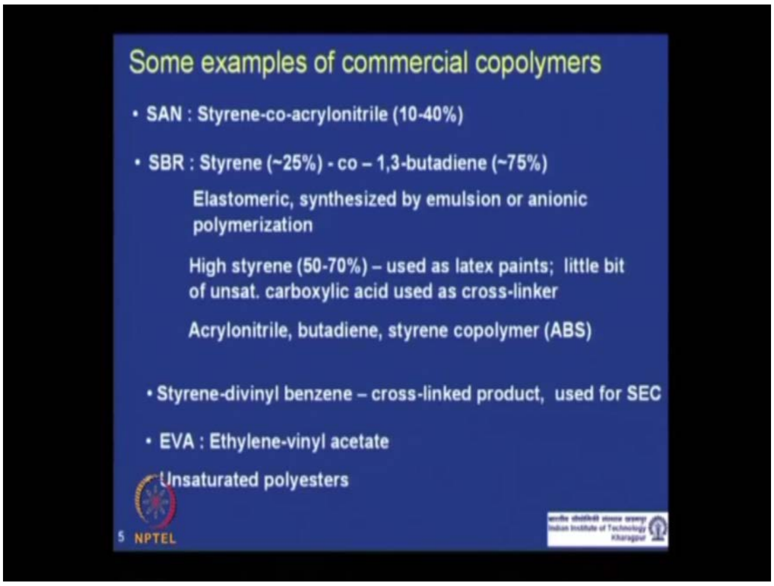

Some examples of commercial copolymers

- SAN : Styrene-co-acrylonitrile (10-40%)
- SBR : Styrene (~25%) - co – 1,3-butadiene (~75%)
  Elastomeric, synthesized by emulsion or anionic polymerization
  High styrene (50-70%) – used as latex paints; little bit of unsat. carboxylic acid used as cross-linker
  Acrylonitrile, butadiene, styrene copolymer (ABS)
- Styrene-divinyl benzene – cross-linked product, used for SEC
- EVA : Ethylene-vinyl acetate

Unsaturated polyesters

And of course, like a the homopolymerization we have discussed the reactivity of a ionic polymerization, which will depend up on the initiator you are choosing and the medium polarity solvent polarity and the temperature. So, if you talking about copolymerization the values r will change with the different types of initiators, medium polarity and temperature.

Some examples of the commercial copolymers as you said earlier the styrene is very styrene homo polymer or polystyrene, polystyrene is a very brittle polymer which breaks easily and also its having poor a very poor solvent resistance or chemical resistance. So, to improve what is done styrene is copolymerized with acrylonitrle, where the amount of acrylonitrle is limited to 10 to 40 percent by which you can or the solvent resistance property of styrene is improved.

So, this copolymer has improved solvent resistance property compared to polystyrene, but acrylonitrle is also brittle so poly acrylonitrle. So, brittle that if this copolymer does not have a significant improvement over, over the polystyrene molecule homo polymer in terms of brittleness. What is done a styrene butadiene rubber is used, where a rubber butadiene having a low T g it gives a rubbery domains in the copolymers and as a result this copolymer can becomes rubbery or elastomeric.

And these copolymers are typically synthesized by emulsion ionic polymerization, these copolymers with high styrene containing high amount of styrene can are used as a latex paint, where the styrene is cross-linked little bit with unsaturated di-carboxylic acid. And to combine or to improve both the solvent resistance and in and the impact properties of styrene one very common approach is taken is a making a for the star polymer where you have acrilonitrile which improves the solvent resistance, butadiene will improve the impact properties and styrene which gives you the heat resistance properties.

So, this is a very commonly used polymer as a homo polymer as a as such or as blend with some other homo polymers by polystyrene and polycarbonate and others. Styrene can be cross linked with small amount of divinyl benzeneum cross linker that will make cross linked spheres cross link product, which can be used as a packing material for the columns in size exclusion chromatography. And the other examples of copolymers which are available commercial like ethylene vinyl acetate copolymer unsaturated polysters and so on. The other examples, but I am not spending much time on discussing those applications here. What we will do now we will move to the next polymerization method, which is a ring opening polymerization or in short R O P.

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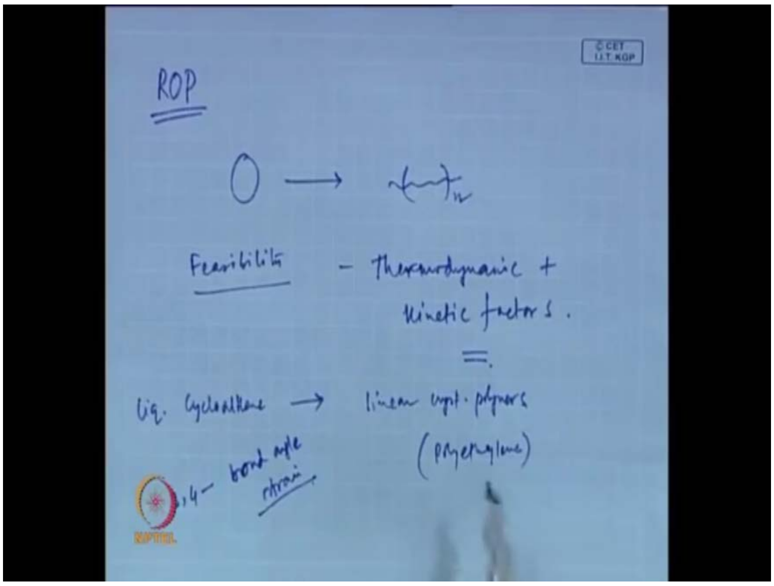

ROP

Feasibility – Thermodynamic + kinetic factors.

liq. Cycloalkane → linear cryst. polymers (polyethylene)

,4- bond angle strain

R O P by name as the name suggests it is a ring opening polymerization, so you have ring in monomer having ring structure and you polymerize it, and make a linear polymer. Now, the feasibility of this polymerization from a ring to linear product linear monomer to polycyclic monomer to a linear product, like all other reactions depends both on thermodynamic and thermo dynamic and last kinetic factor.

We have discussed this thermodynamic factor earlier also while discussing in ring formation, cyclic formation instead both polymerization if you can recollect from about over a fifth or sixth lecture where we talked about the tendency of cyclic ring formation in state growth polymerization the same logic apply here the thermodynamic factor. Now if you look the data compare so let us talk about the data.

And then we will can understand the thermodynamic factor in a more clearly. Now, this are the data of all the 3 del g Gibbs free energy change enthalpy change and entropy change. Now, I have made T del s to compare and put it in the same scale this is from cyclo alkane liquid cyclo alkane to linear crystalline polymers. Now, when you are talking about cyclohexene these are basically we are talking about polyethylene these are polymers whether you start from a three member four member five member these all leads to polyethylene.

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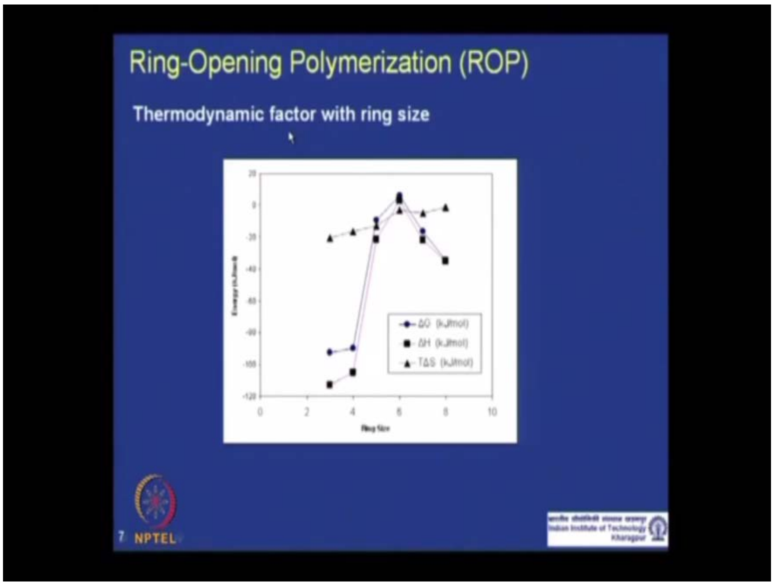

Ring-Opening Polymerization (ROP)

Thermodynamic factor with ring size

Now, these are these values here shown here these are all semi empirical values, they are not experimentally determined they are semi empirical values. Now, if you look at the data as the ring size increases from 3 to 4, 5, 6, 7, 8 now the ring the lower number ring 3 and 4 member ring, they are quite highly strained 3 4 member are strained because of 1 angle strain if they are having high energy because of 1 angle strain. Whereas, 5 member ring are strained due to eclipse confirmation and 7 8 member ring having also strained because of ((Refer Time: 33:05)) transformations.

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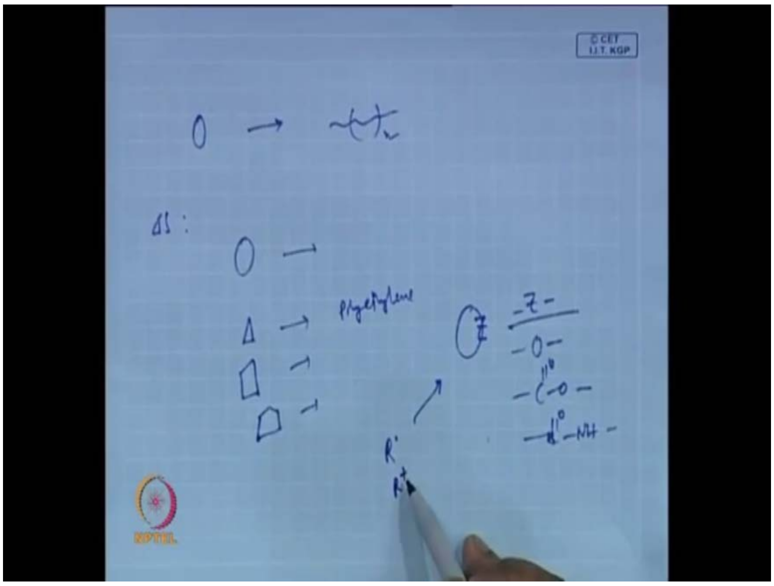

Now, if you if you look at this numbers, the enthalpy change on the polymerization from a 3 membered cyclic ring to a linear polymer it is highly negative. And if you just talk about linear polymers, what about first let us talk about del s now del s will be negative because the monomers are getting joined and making a linear, linear polymer.

Now, in if you talk about same molecular weight obviously if you have a larger ring, this number of monomers you require to make the same length of polymers. So your del s would be less negative, your if your ring size is larger. So, if you can and if you see that if your ring size increases your del s value is decreasing becoming less and less negative, but if you follow the del g value Gibbs free energy value and del h value they are almost having same trend.

So, basically the polymerization dictated mainly by the enthalpy change because 3 and 4 member ring are highly strained when they open up and polymerize and gives a lot of this energy, which was already which is getting released because of ring opening. Similar also true for high, high rings with size of 7, 8 carbon. 6 member ring is actually little higher than 0, if you compare slightly higher than 0. Basically 6 member ring is not thermodynamically feasible the opening ring the opening polymerization of 6 member ring is not thermodynamically feasible.

So, basically now from this thermodynamic data we know that it is easy ring open polymerize easy to carry out ring opening polymerization on 3, 4 member ring and say 7 ring. 5 member ring also will polymerize by ring opening method. Whereas 6 member ring is not that feasible to or basically it is not feasible to polymerize thermodynamically.

However, can you make take a say 3 member ring or a 4 member ring or say 5 member ring. Can you make polyethylene by this route this way, can you make polyethylene from either of this either of this by ring opening polymerization? The answer is no because it is not only determining by determined by thermodynamic feasibility, there has to be kinetic path way through which you can carry out the polymerization.

Basically this is saturated ring and there is no place where u can carry out a electrophilic or neutrophillic character by external and open the ring, and then carry out the polymerization. So, this is this molecules even if they are thermo dynamically feasible they do not undergo polymerization. So, what you need so you need a hetero atom in the ring in the cycling wave, which we have a ring like say ether molecule see this ether or a ester or say a amide they might can do there is if you use asilo base they can actually do nucleophilic or electrophilic attack on this ring and reopen. And then which can react with another ring cyclic molecules and let the chin propagate.

So, what we basically need what we basically no that simple cyclic rings like cyclo pentain or cyclo butane they do not undergo reopening polymerization. You require a ether atom, which will actually enabled electrophilic or a nucleophilic attack by external agents by which the rings will open. And then start the propagation reaction and which will finally, lead to a polymer molecule.

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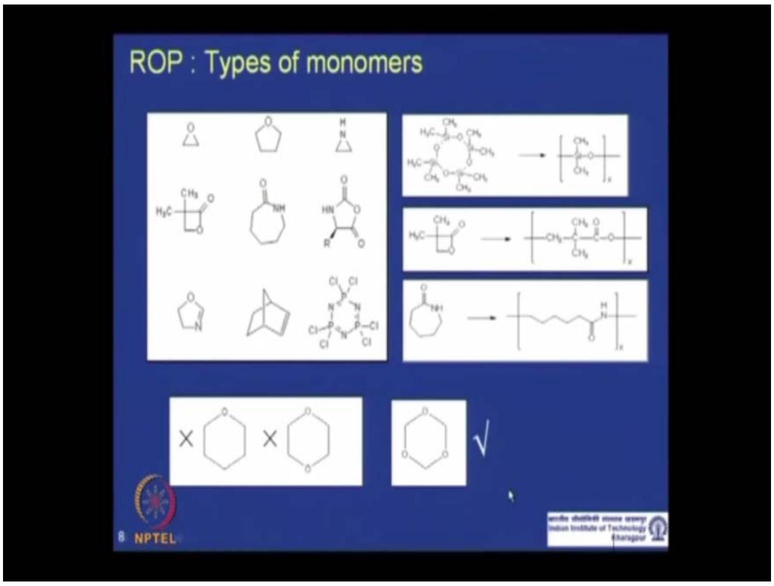

ROP : Types of monomers

So, the types of monomers we there is a there is a different structure where basically these are the types of monomer, you can do a re-opening polymerization. So, basically all have a hetero atom in the ring, whether it is a or ester or amides whatever is the case. Now, that actually enables a from external agents which will be open first and then propagate. This is this will form and get poly posphogen, if you have a cyclic cyloxin molecule it open up to give you linear poly cyle oxide. If You have a lactone give you poly ester if you have a lactum, it will cyclo lactum it will give you a linear poly amide molecules.

Now, the chart of the thermodynamic feasibility what we shown that was for ring cyclo alkenes not this type of monomers, where you have a hetero atom. So, the absolute value in this graph will change, if we consider now a cyclic ring hetero atom or the teams remains more or less same. So, again the strain of you know thermodynamic feasibility will decrease as you increase from c to c and then again go up if you increase the ring size. So, basically if you have cyclic ethers say tetra hydro ((Refer Time: 40:56))firen or a di oxine they do not undergo polymerization. Whereas this actually undergo ring opening polymerization. Now, let’s talk about few characteristics of a ring opening polymerization, and talk about the mechanism and kinetics of a ring opening polymerization.

Now, as we discussed if you have a cyclic ring here, then you need first to ring open the ring to open up and then start the propagation reaction. Now, see here radical initiator see radical initiator, now it is unlikely that this will inter act or react with this and ring opening, that is not very feasible. So, you either need a cation or a anion to sort of initiate a ring polymerization so initiation by…

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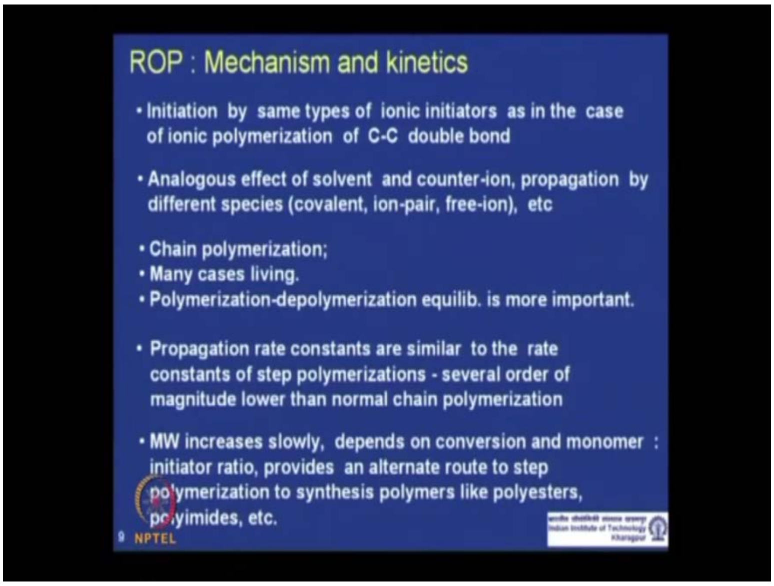

ROP : Mechanism and kinetics

- Initiation by same types of ionic initiators as in the case of ionic polymerization of C-C double bond
- Analogous effect of solvent and counter-ion, propagation by different species (covalent, ion-pair, free-ion), etc
- Chain polymerization;
- Many cases living.
- Polymerization-depolymerization equilib. is more important.
- Propagation rate constants are similar to the rate constants of step polymerizations - several order of magnitude lower than normal chain polymerization
- MW increases slowly, depends on conversion and monomer : initiator ratio, provides an alternate route to step polymerization to synthesis polymers like polyesters, polyimides, etc.

In case of ring opening polymerization the initiation is done by the same types of ionic initiators as in the case of ionic polymerization of carbon carbon double bonds. We have discussed in length about cation polymerization or an anionic polymerization of carbon carbon double bond. And those are the same types of initiators will be used to basically polymerize the cyclic rings and make a ring opening polymerization. So, radicals radical initiator is not a basically feasible in terms of in case of ring opening polymerization.

Now, because we are talking about initiation by ionic initiator so you have those different types of species, covalent specious between the ion and counter ion with it present as a covalence specious or ion pair or free ion goes different types of association between the reaction center and the possible. Hence there is tremendous effect of the solvent and the counters ion in case of ring opening polymerization as well, as was in the case of the linear ionic polymerization of the double bond.

Now, this is the chain polymerization that is interesting because the polymers you are making. See if you have a lactum your opening up and making a polyester or you have a lactum you are opening up and making a poly amide. Now, poly ester poly amides are typically synthesized we have discussed earlier they are synthesized by stiff polymerization, but in this case we are making the same types of polymers, which we knew till now that they are typically synthesized by step growth polymerization. They can be synthesized by ring opening polymerization from the cyclic monomers as well, and the mechanism here is chain polymerization.

So, basically a propagating chain a chain propagates and the monomers get added and the chain ends. So, the chain keep on propagating there is no reaction between two monomers or there is no reaction between two high molecular polymer chain as well. The same as the chain polymerization and in because you are talking about ionic polymerization in most cases they are leaving and we know that bi molecular term is not possible for ionic polymerization. If you take care of the reaction medium very well so that there is no impurities in these polymers that are leaving. So, you can make block of polymers of functional polymers at the end of the reaction, and in this case unlike a linear polymerization of the vinyl molecules, polymerization de polymerization equilibrium is very important.

Now, one different this ring opening polymerization with the normal chain polymerization, we know is that the rate constant for propagation is in its several order of maginitude lower than normal chain polymerization, it is actually of same order like in case of step growth polymerization. So, though this is a chain polymerization, but the reaction rate or the propagation rate constant is having much lower value compared to several order of magnitude growth in comparison to normal chain polymerization. And the values are similar to the step growth polymerization values.

So, the reaction is slower compared to your normal chain polymerization and as you know that we discussed this most cases this are leaving. So, the molecular weight of ring opening polymerization is dependent on the conversion. So, higher the conversion the higher the molecular weight. And also you can control the estimate or predict the molecular weight form the ration of monomer and the initiator as in the case of other leaving polymerization we know.

So, unlike step growth polymerization here you have control you can control the molecular weight by the ratio of monomer and initiator. And like the step growth polymerization the molecule will depend upon the conversion, but in case of step growth the high molecules are only get high conversion. But in case of ring opening you get slow increase in the molecular weight with the or the linear increase over the molecular weight with the conversion of monomer.

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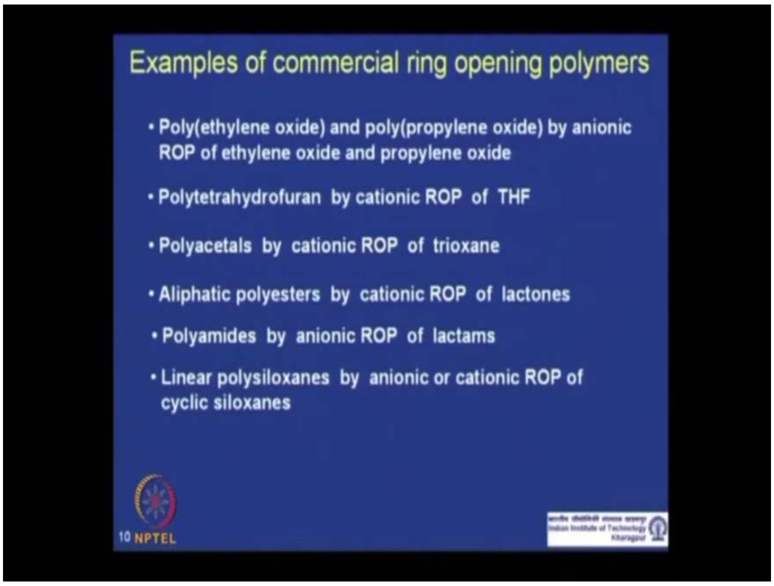

Examples of commercial ring opening polymers

- Poly(ethylene oxide) and poly(propylene oxide) by anionic ROP of ethylene oxide and propylene oxide
- Polytetrahydrofuran by cationic ROP of THF
- Polyacetals by cationic ROP of trioxane
- Aliphatic polyesters by cationic ROP of lactones
- Polyamides by anionic ROP of lactams
- Linear polysiloxanes by anionic or cationic ROP of cyclic siloxanes

Now, examples of before we come to examples let’s talk about the mechanism part of how, what are the ways this ring opening polymerization done if we know this is ionic polymerization…

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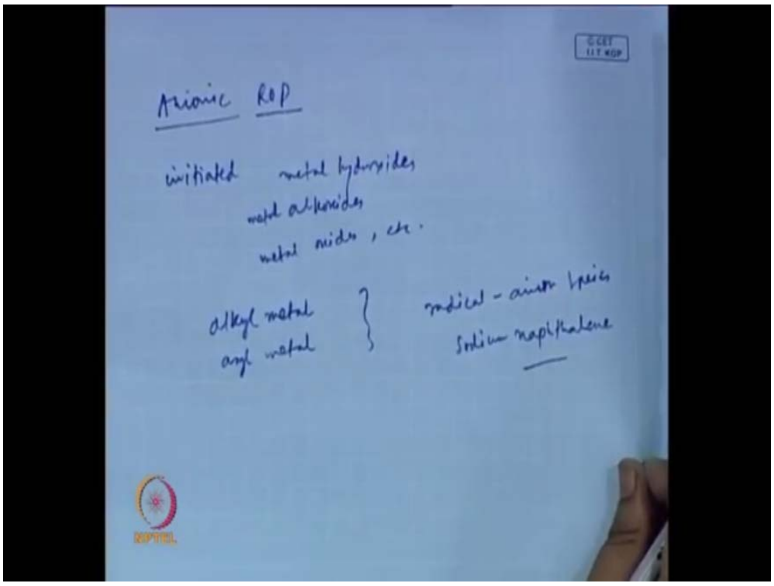

Anionic ROP

initiated metal hydroxides
metal alkoxides
metal oxides, etc.

alkyl metal
aryl metal } radical - anion species
Sodium naphthalene

So, let’s first talk about anionic R O P now the initiator is initiated by as I said same similar ionic initiators as in the case of linear chain anionic polymerization, like metal hydroxides alkoxides metal hydroxides or metal alkoxides or metal oxides etc. Or like we discussed alkyl metal alkyl lithium or aryl metal you can use to initiate the anionic chain polymerization or radical anion also anionic species like sodium, naphthalene they also they are same types of initiator, as we talked about the our discussion on anionic chain polymerization.

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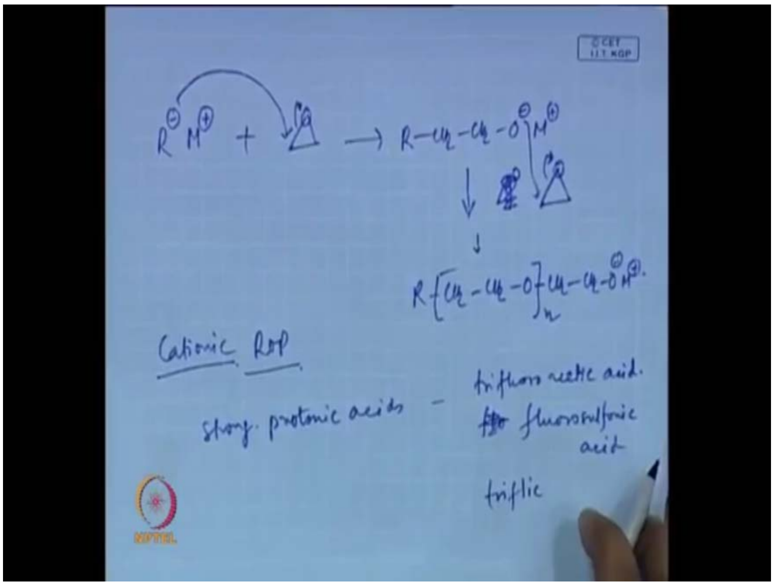

$R^{\ominus}M^{\oplus}$ + → $R-CH_2-CH_2-O^{\ominus}M^{\oplus}$

$R\left[CH_2-CH_2-O\right]_n CH_2-CH_2-O^{\ominus}M^{\oplus}$.

Cationic ROP

strong protonic acids - trifluoroacetic acid.
fluorosulfonic acid
triflic

Say you talk about say alkyl metal initiator you have a alkyl metal initiator, say I take a ethylene oxide. Now, there is a nucleophilic attack by this initiator and the ring will open up. So, you have this now this will again react with another monomer in similar way. So, you can write the general you can increase the number of state and you will get a your polymerization. Now, as I said that like other anionic polymerization this is a living polymerization. So, this at the end of the reaction if remains like this you can add a second monomer and you can block a polymer.

If you want to terminate the reaction you can exchange these with a say adding some water or alcohol, and then you can exchange like other we discussed earlier. Now, if we talk about a cationic ring opening polymerization. Now, here typically its strong protonic acids like say tri floro acetic acid or say fluoro sulfonic acid or say triflic acid which are the way this, this are our acids which are very strong acid are required to initiate a ring opening polymerization.

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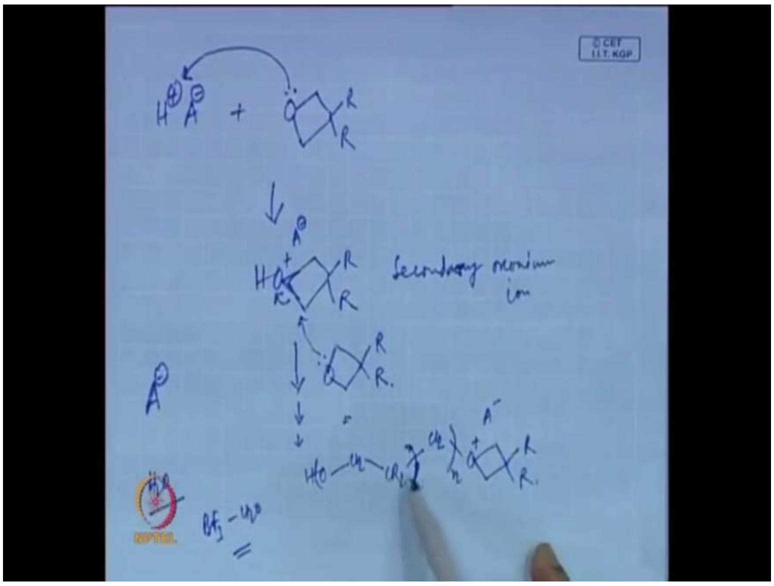

Now, let us say have so this will say talk about now a 4 member ether, now in this case there is a nucleophilic atom of the oxygen to the proton and you get, you actually form secondary oxonium ion, in all this cases you have a counter end associated with that you this will react with another monomer and propagate in the chain. So, can you make a polymer like this, this will form secondary oxomium ion this is, now we have been talking that we need a very a very strong acid because if you counter ion have sufficient acid is not that strong then this counter ion will have sufficient necleophillicity to either set up the oxonium ion or a proton and stop the reaction there itself.

So, for that you require very strong acids so that the necleophillicity of the counter ion will not be enough to compete with the addition of monomer or the reaction of monomer with the oxonium ion. Similarly, if we have little bit of moisture present in the medium or if you have water molecules, then this will easily compete with your monomer with oxinium ion and then terminate the or disrupt the reaction immediately.

So, like earlier when you talk about cationic polymerization here also you need to have a very stringent requirement of so that you do not have a moisture, any moisture present in the system. Now, other types of initiators we talked about the catalyst and co catalyst like B F 3 and H 2 O catalyst and other types can be also used in this cationic ring opening polymerization also.

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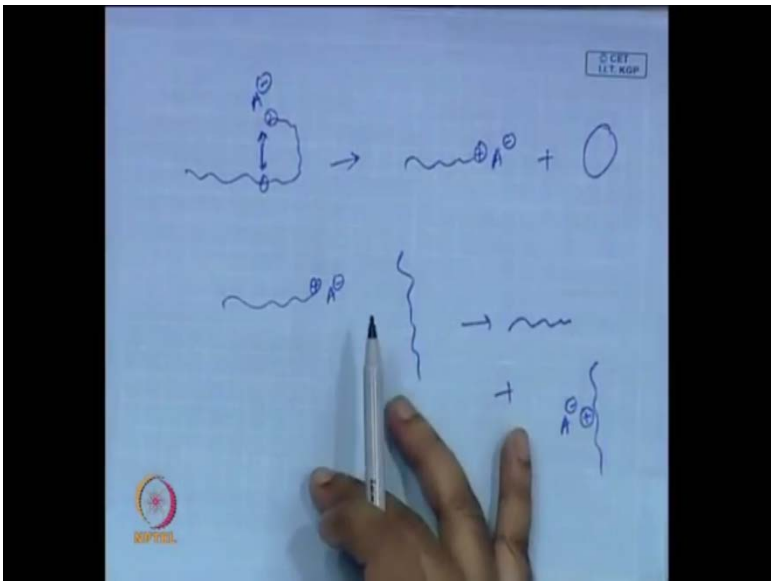

At the end as a this will remain leaving the only thing in case of cationic polymerization, as you can imagine that if your chain is having…is a linear chain at the end you have a cationic group and anionic counter end then you can oxygen here, then it can do intra molecular reaction and form a linear molecule as a ring molecule. Now, where it can also react with a another linear molecules and then stop this chain and form a sight in middle of another chain. So, form there a branching can happen so this are the side reactions where chain transfer takes place intra molecularly with in the chain form a ring structure and another linear molecule. Or if there are intra molecular chain transfer reaction happen then there will be possibility of in this case.

And this case also you want to stop the reaction, you can add agent through which by which it can external agents which will terminate the cationic chain. Now, with this I think we have discussed the ring opening polymerization, now let’s talk about few examples of commercial reopening polymerization, this are the typical this are the polymers which are available commercially which are made by ring opening polymerization. For example, poly ethylene oxide and poly proplyne oxide they are synthesized by anionic opening corresponding cyclic monomer of ethylene oxide, and propylene oxides.

Poly tera hydrofuran can be synthesized or the cationic ring opening polymerization of tetra hydro furan polyacetals are synthesized by cationic reopening polymerization of trioxane. And as I gave examples of aliphatic polyesters from lactones and polyamides from lactones and this is also very common where linear poly siloxanes or silicons are synthesized by anionic or cationic polymers of cyclic siloxanes so with these we end our discussion of ring opening polymerization. And in the next lecture we will start our discussion on stereo chemistry of polymerization and subsequently in other lecture, we will talk about coordination polymerization. So, we will start stereo chemistry of polymers and polymerization process in our next lecture.