Polymer Chemistry
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Lecture - 7
Step-growth Polymerization (Contd.)

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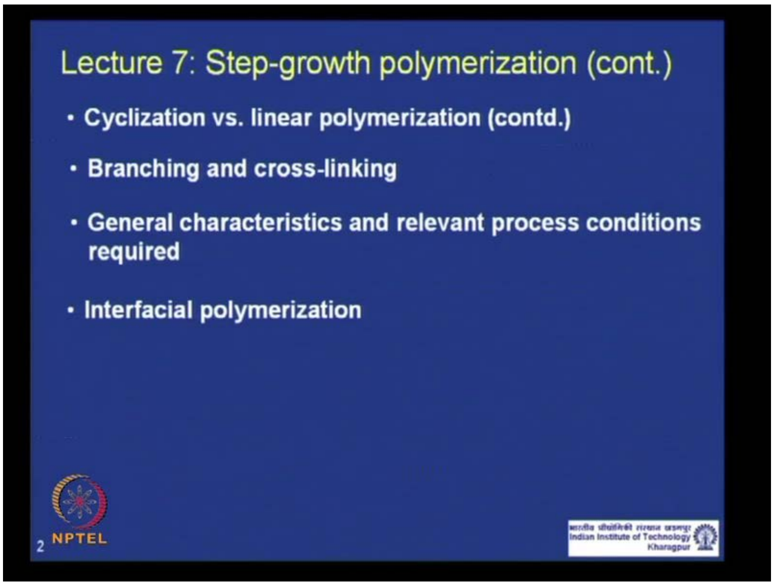

Lecture 7: Step-growth polymerization (cont.)

- Cyclization vs. linear polymerization (contd.)
- Branching and cross-linking
- General characteristics and relevant process conditions required
- Interfacial polymerization

Welcome to this seventh lecture of this course on polymer chemistry. Today, we will continue the discussion we had on step growth polymerization.

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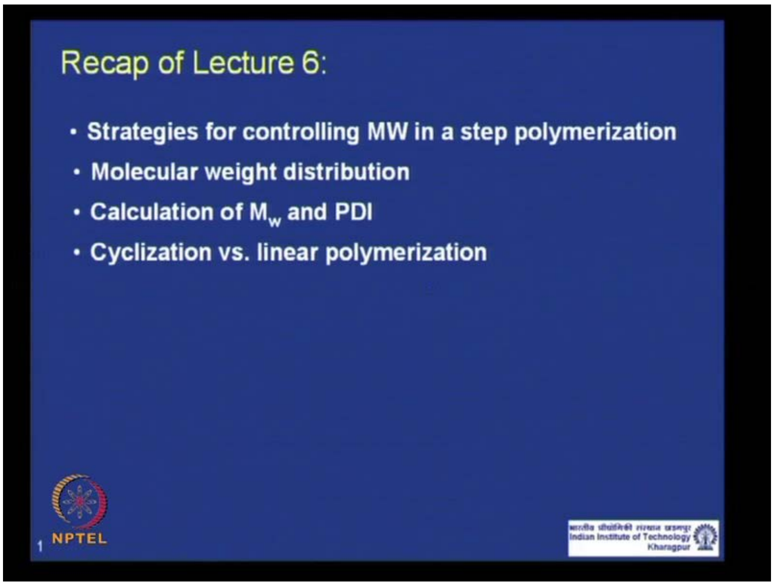

Recap of Lecture 6:

- Strategies for controlling MW in a step polymerization
- Molecular weight distribution
- Calculation of M_w and PDI
- Cyclization vs. linear polymerization

Before we start the topics of the 7 th lecture, let us recap what we have studied in the last lecture. In the last lecture we had studied the mechanism, the strategies by which we can control the molecular weight of a step polymer. They are sometime, as I mentioned in last lecture, that you might require to control, restrict the molecular weight of the polymer you are making.

And we discussed the two methods, one being that you use a slightly (( )) stoichiometry, one of the monomer in little excess. And the second was that you can add a mono-functional monomer in slight amount by, then by doing this you can control the molecular weight.

You also studied the molecular weight distribution and we found that, we found that in, in case of number fraction of the different molecular weight chains, the lower molecular weight chains, the the chains, which are having lower molecular weights, they represent in maximum number. Now, if you talk about weight fraction, then the weight fraction of different chain length molecular weight was maximum for a given molecular weight.

We did a calculation to find out, that M W and corresponding PDI, poly dispersity index, which is M w by M n and which we found, that it is PDI equals to 1 plus p. That means, for most of the polymerization, step polymerization, when you are making high enough molecular weight as we know by this time, that p should be very close to 1, that means, for any given high molecular weight step polymer the polydispersity is expected to be very close to 2.

But I said, that in practice, in industry, when one makes a step polymer, seldom the distribution, the PDI value comes to around 2, always it is found to be slightly above 2, say between 2 to 2.5 and so on. I said the reason as well, that because there are possibilities of size reaction and one such size reaction being cyclization, there is invariably formation of some small molecular weight cyclic molecules and as a result, when you have the small molecular weight cyclic formation, both the M w and M n comes down. But as we know, that small molecular weight effects M n more, that means, the percentage of drop in M n is more than percentage domain M n and M w. As a result, M w by M n goes up. So, the PDI goes beyond 2.

We also discussed at the end different ways of a molecule, whether it is a monomer or a oligomer, can undergo cyclization and we will continue that discussion today. And I talked about two options in a monomer, they can intramolecularly cyclize or in oligomer, they can, if their reactive functional group, they can cyclize as well.

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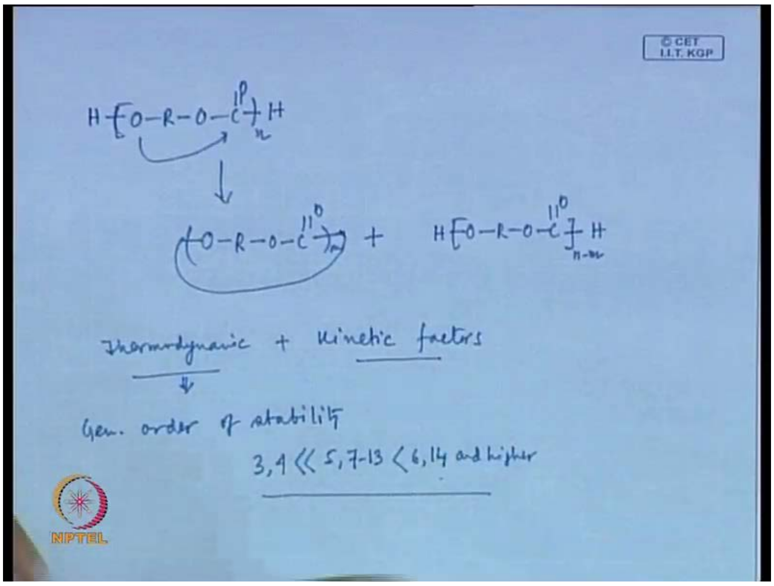

$$H\text{-}[O-R-O-\overset{O}{\overset{\|}{C}}]_n\text{-}H \longrightarrow [O-R-O-\overset{O}{\overset{\|}{C}}]_m + H[O-R-O-\overset{O}{\overset{\|}{C}}]_{n-m}H$$

Thermodynamic + kinetic factors

↓

Gen. order of stability

3, 4 << 5, 7-13 < 6, 14 and higher

Now, there is a third, third option where a growing chain can polycyclize, let us look at that option as well. Say, you have an oligomer or a polymer chain of hydroxy-carboxylic acid, which is polyester. Now, this can undergo intermolecular nucleophilic substitution reaction, which we called back biting, is basically the one end of the polymer chain is biting back in the main chain of the polymer forming a cyclic molecule and another molecule. So, this is another way we can cyclic and form and this is the process is called backbiting, from the end of the polymer chain to the back bone of the existing polymer chain. So, that is backbiting by substitution nucleophilic reaction.

Now, as I said that the extent of cyclization in comparison to linear polymerization depends upon both, thermodynamic factor and as well as kinetic factor. So, it depends upon both. Now, we started discussing about the thermodynamic factor. Thermodynamic factor is nothing but the stability of the forming cyclic rings.

For example, we know from our organic chemistry knowledge, that general order, general order of stability of different, of different ring structure follows in the following order, that a ring containing three or four atom in a ring is least stable or lowest, lowest compared to a 5-membered or 7 to 13-membered ring, which is even lower stable than 6-membered or a 14-membered ring and higher and that we know from our organic chemistry knowledge. That is because we have, in a small ring we have more ring strain and torsional (( )) in a big chain you have a torsional strain as well. So, obviously, formation of 6-membered or 4-membered or higher membered ring will be always preferred thermodynamically compared to a ring size having 3-membered or 4-membered in it. So, which means, that in thermodynamics, factors will favor formation of a 6-membered or 4-membered or higher membered ring in case of cyclic formation.

Now, does it mean, that always you have formation of cyclic, for example, 14 and higher members? Now, as you can imagine, that if you have a polymer chain or oligomer chain having 14 or higher carbon atom or other atoms in, in the, in the backbone, now this is, this trend is valid for, not only for rings having only carbon atom in the ring, but it also valid for the rings where you have heteroatom, like say for example, ethers or esters or amides as well. This is true for almost every possible ring.

Now, I was talking about, that if you have a larger ring, larger linear molecules, say having 14 or higher number of atoms in the, in the ring, in the linear molecules, then they have so many conformation, this, as the more or the higher is the number of atoms or longer is the chain, you have more number of conformation of that molecule possible. And so the probability, that any conformation will have this two reactive function groups coming close to each other, so that they can react and form ring is always very low. So, if you, you can imagine as well, that as you grow longer and longer the number of conformations, which will enable the two functional groups at the present at the end to come closer and react and form ring will be lower and lower. So, in terms of kinetic factor the higher the chain length, the lower is the possibility of formation of ring.

Now, if you talk about the rate of polymerization, which will help us in designing reaction conditions, which will minimize the cyclic formation, let us look at the rate of ring formation or cyclization and, and the linear polymerization. Now, as we can imagine or understand by now, that ring formation is a mono, unimolecular process, whether linear polymerization is a bimolecular process?

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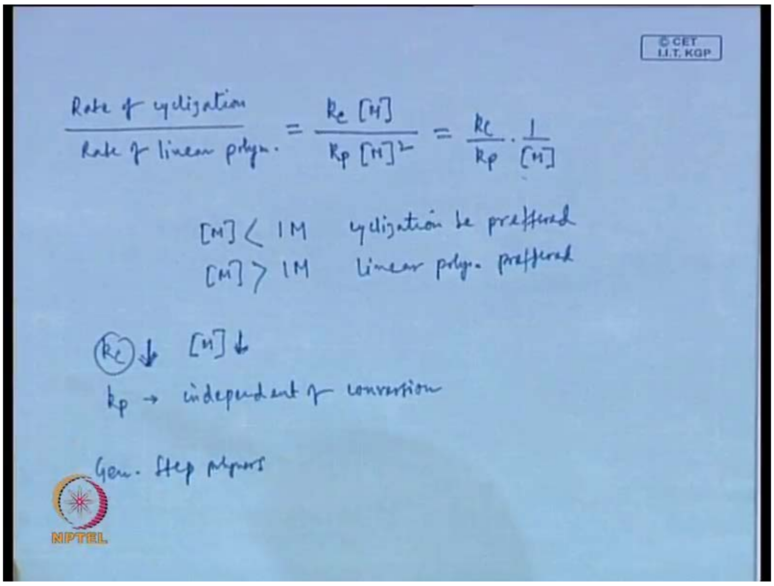

$$\frac{\text{Rate of cyclization}}{\text{Rate of linear polym.}} = \frac{k_c [M]}{k_p [M]^2} = \frac{k_c}{k_p} \cdot \frac{1}{[M]}$$

$[M] < 1M$ cyclization be preffered
$[M] > 1M$ linear polym. preffered

$k_c \downarrow$ $[M] \downarrow$
$k_p \rightarrow$ independent of conversion

Gen. step polymers

So, I can write the rate of cyclization versus rate of linear polymerization is k c rate constant for cyclization and because it is a unimolecular intramolecular reaction, so we have this. And rate of k, polymer, polymerization and because it is a bimolecular reaction, so we have M square, which gives us k c by k p 1 by M.

Now, as long, as long as M is less than 1, molar cyclization will be preferred. If M is higher than 1 molar, then linear polymerization will be preferred that you can see from this expression. Let us, only from the concentration of the monomer you can find out, that if it is below 1, then rate of this, rate of cyclization will be higher and if it is above 1, this will be a fraction. So, the linear formation will be rate of polymerization will be higher.

So, it is always advisable, it is always advisable, that to minimize the cyclization, we always use the maximum possible concentration of the monomers and the base can, we can do if you do a bulk polymerization, that means, which we are doing the reaction with the monomers and, and the catalyst, if required. So, so that is the maximum possible concentration you can have in, in to minimize the cyclization.

Now, what happen to k c and k p? As, as a reaction progresses or the conversion goes up, now as we know, that k p is independent of, independent of conversion or the reaction, time of reaction and which comes from the fact of the assumption of equal reactivity of the functional group and we have seen in earlier lectures, that experimentally, that is also true, that rate is independent, rate independent on the conversion. So, k p is constant throughout this process.

So, now what happens, what happen to k c, rate constant for cyclization? Now, as we have seen just now from the last page, that if you grow the chain, as the reaction progresses, that more and more conversion happens, the chain grows. Now, as the chain grows, the possibility, the kinetic feasibility of the two functional groups present at the end coming and reacting to form ring, ring, comes down, which means, that k c comes down as a reaction progresses because the kinetic feasibility, that the longer the chain, that chances, that two end will come and react each other forming intra-molecular reaction, forming a ring, is always lower. So, as the reaction progresses, as p progresses, k c comes down.

Now, you can also argue, that as the reaction progresses, the monomer, the monomer concentration, in this case monomer means the species, which is forming the cyclic, that also comes down because you know, the time goes, the monomer molecule react. So, the concentration of the species, which is forming intra-molecular reaction, which is carrying out, which is undergoing intra-molecular reactions to form cyclic also come down. So, then the rate of cyclization also should increase in that process. So, if the k c come down with concentration, with conversion, the cyclization should come down, whereas this is acting in opposite direction. As the concentration of monomers comes down, the rate of cyclization will go up.

Now, it, it has been generally found fortunately, that this effect is less compared to this, which means, for general step polymers when you go for higher and higher conversion, the rate of cyclization comes down because the k c, the value of k c comes down because of kinetic feasibility. So, that is, that is good. So, as we, in most cases the cyclization tendency comes down as we make higher and higher molecular weight.

Now, what is the, what is the problem if I have some, few cyclic molecules in, in the polymer at the end of the polymerization? First of all, we have seen, that presence of this small molecular cyclics will increase the polydispersity index, which means, the distribution of the polymers chains and which effect property in, in several cases, not coming to specific examples, but it, it, it does effect the polymer property in, in several cases.

And also, if this cyclics are present in the polymer mixture, they are sometimes very detrimental in the polymer property. Because during the polymer processing, when you take this polymer and process mix with something compound and then take that compound at granules to make some final product by say, molding process, being low molecular weight this cyclic molecules tend to come up to the surface. They, they preferred, they are, they prefer to be in surface. So, during the molding process, they actually migrate to the surface and they prefer to be in the surface, which actually is very detrimental from the products properly point of view.

So, in most cases it is preferred, it is done, that at the end of the reaction some additional steps are done to strip off the cyclic molecules, small cyclic molecules from the final product, so that when you take that polymer, which is in the, at the end of the reaction, which you are taking forward for molding process, which will be, have least amount of cyclic, cyclic molecule present.

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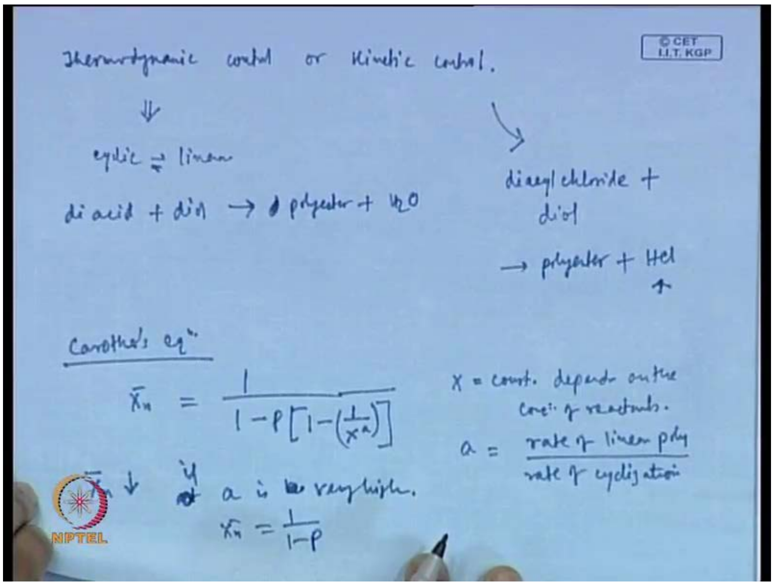

Thermodynamic control or Kinetic control.

$\Downarrow$

cyclic $\rightleftharpoons$ linear

di acid + diol $\rightarrow$ polyester + H_2O

diacyl chloride + diol

$\rightarrow$ polyester + $HCl \uparrow$

Carother's eqn

$$\bar{X}_n = \frac{1}{1-p\left[1-\left(\frac{1}{x^a}\right)\right]}$$

x = const. depends on the conc. of reactants.

$$a = \frac{\text{rate of linear poly}}{\text{rate of cyclization}}$$

$\bar{X}_n \downarrow$ if a is very high.

$$\bar{X}_n = \frac{1}{1-p}$$

So, now we, this reaction step, reaction can process, you know, undergo in thermodynamic control way or a kinetic control way. What is thermodynamic control? Now, in this case, the linear and cyclic molecules, they are, during the entire reaction they are in equilibrium, whereas in kinetic control process they are not in equilibrium. The reaction proceeds without establishing a equilibrium between the cyclic and linear species here. Whereas, in terminal control polymerization, there is equilibrium, between cyclic molecules and linear molecules there is a equilibrium. So, entire, during the entire process, polymerization process, this equilibrium exist.

Now, this one example we can give, the normal, excuse me, normal hydroxyl acid, you know, normal ester formation, polyester formation from diacid plus diol to give polyester plus H 2 O. Now, as you can see, the H 2 O can take part as long as H 2 O present in medium, they can take part and hydrolyze the cyclic molecules and so that they can, cyclic molecules open up and undergo further linear polymerization or take part in further linear polymerization, and new cyclic small molecular formation take place and so on. So, in this case the reaction proceeds maintaining equilibrium between cyclic and linear polymerization.

In case of kinetic control, as I said, that it does not maintain the equilibrium. For example, if you have a diacyl chloride plus diol, which forms polyester plus HCl. Now, HCl does not take part in reaction with the polyester, whether it is cyclic or linear polyester, which means, that in this case there is no equilibrium present between the cyclic and the linear polymer molecule.

So, what is the effect of formation of cyclics in the molecular weight or the degree of polymerization of the final polymers, which can be arrived from Carother's equation and without going into derivation we can write, that X n is 1 by 1 minus P, where x is a constant, depends on concentration of the reactants and a is rate of linear polymerization by rate of cyclization.

Now, this two term, this, this expression is not very useful because the values for x and a are not available for most cases. So, so this is, this is good to know the expression, but this is not very useful because we are, we do not know the values of x and a all the time and as a goes lower, that if more cyclization happen, X n comes down compared to if there were no cyclization, which in this case X n was 1 by 1 minus P.

In case of absence of any cyclization, just pure linear, linear chain formation we have seen the Carother's, Carother's equation from earlier lectures, that X n is 1, 1 over 1 minus P. So, because of cyclization x n comes down. So, more and more cyclization happen, the degrees of polymerization also come down. As we realized in the beginning of this lecture as well, that as the more cyclic molecules, small molecules form, it affects both, the degrees of polymerization number, average degrees of polymerization and the weight average degrees of polymerization, but it affects more the number average degrees polymers compared to weight average degrees of polymerization. So, you get the PDI higher than 2.

Now, at a is very high, is very high, if, if a is very high, that means, almost absence of cyclization, then X n would be 1 minus 1 minus p, which is basically giving us back the the original Carothers equation for linear polymerization, linear step polymerization.

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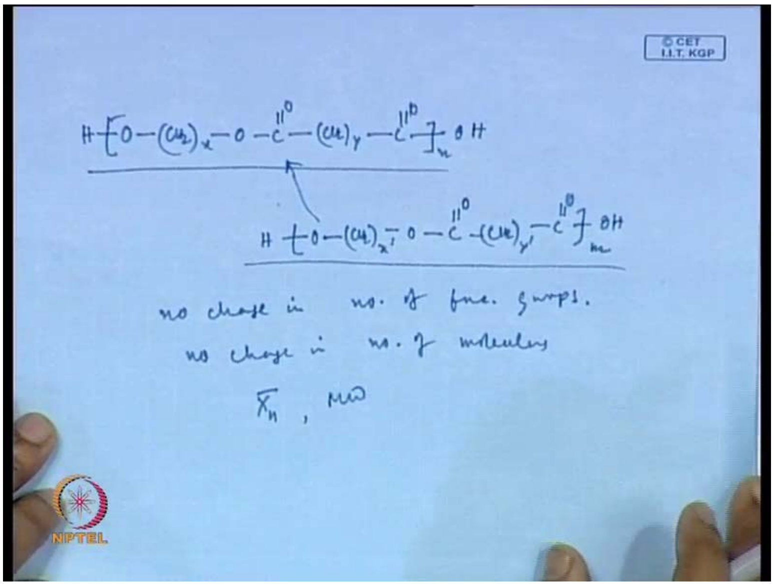

$H{-}\left[O-(CH_2)_x-O-\overset{\overset{O}{\|}}{C}-(CH_2)_y-\overset{\overset{O}{\|}}{C}-\right]_n OH$

$H{-}\left[O-(CH_2)_{x'}-O-\overset{\overset{O}{\|}}{C}-(CH_2)_{y'}-\overset{\overset{O}{\|}}{C}\right]_m OH$

no change in no. of func. groups.

no change in no. of molecules

$\bar{X}_n$, MW

Now, one thing also we should remember in case of step polymerization, that the chains, when the chains are forming during the reactions, the chains can, there is a possibility, that chains can also undergo exchange reaction between them and making the chains reacting with each other. For example, if I take a…

This again coming back to the example of polyester.

Now, this molecule can again and do a nucleophilic substitution reaction and they can exchange the parts in two different chains, but in this case there is no change in number of functional group, functional groups. So, so no change in number of molecules, either as a result no change in X n bar, no change in molecular weight as well. So, this statistically does not have any significance in terms of final polymer product, in terms of their molecular weight or molecular distribution.

But this is, you should have, you know, you should have knowledge, that during the chain, during the polymerization the chains can undergo exchange reaction between them and they can be subtle, like if you have two different, if you are starting with, say for example, if you are not starting with two monomers A and (( )) type, your type, you are starting with different oligomers and carrying out the reaction from there. If you are starting with two different oligomers and you are starting the reaction from there, at the end of the polymerization you will find that this chains are reshuffled and they have a uniform composition across. But when you are starting with the monomers, it does not matter, you will finally going to get the same polymers, whether there is or there is not any reshuffling exchange reaction between the two growing chain. This is just for your knowledge.

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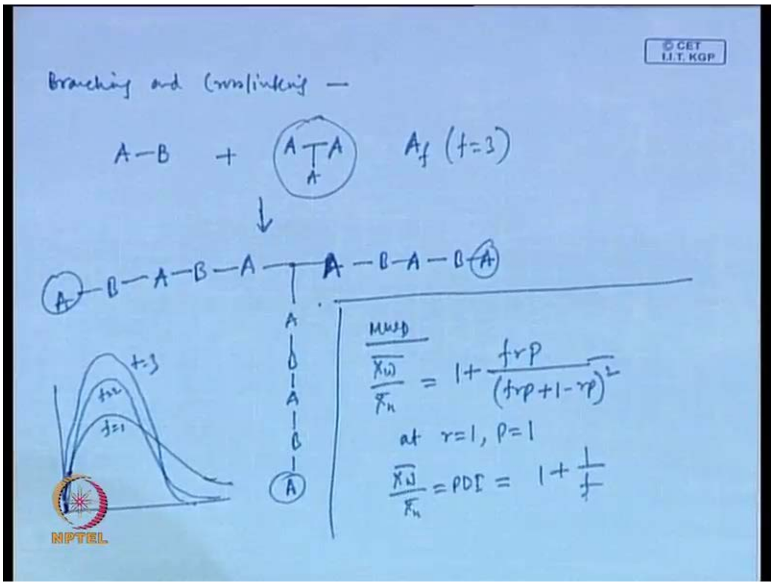

Branching and Crosslinking –

$A-B + A_f \ (f=3)$

MWD

$$\frac{\bar{X}_w}{\bar{X}_n} = 1 + \frac{frp}{(frp+1-rp)^2}$$

at $r=1$, $P=1$

$$\frac{\bar{X}_w}{\bar{X}_n} = PDI = 1 + \frac{1}{f}$$

Now, let us go to next topic which is branching and cross-linking. Let us say, I have a molecule A and B functional group and I have a molecule like this, which have three A functional group and how they will react. Obviously, A can only react with B. So, it will react with B, other side will be A, again this will react with B, so other side will be A. similarly, this side, it will react with B, other side will be A. And similarly so here also it will react with B A B A, something like that. Now, you can see this, in this case you always have A group at the end.

Now, this is the branch, this is the main linear, linear chain and this is the branch and number of branch, obviously, will be depend upon the, the moles of this, this group. Now, we are writing this is A f, where f is 3 here. So, f is the number of functional group present in this molecule. So, f is 3 here. So, you can understand that in this case, always the ends will have a functional group of A, which cannot react with each other. You know, growing chain, cannot react with this only react with the monomer.

So, if I, will this branch react with any other chain growing chain? No, if I have to, if this branch has to react with any other chain, any other polymer chain, then it has to find B group, which it can react, but there is not any polymer chain having free B group at the end, which means, that it cannot undergo reaction with another chain, which means, in this case there would not be any cross-linking between two polymer chain. Cross-linking is when you have a branch or you have a connection between two chains. If I had a chain here, then this is the cross-linking, it would have been cross-linking.

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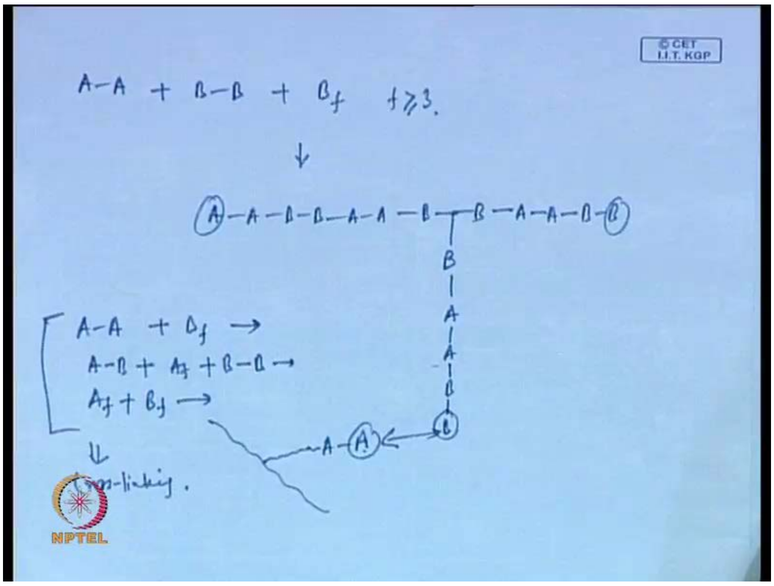

So, let us take another example. How it will react? This one, A A plus B B B f and where f is 3 or higher. Obviously, this reaction will be A A B B B A. Suppose, this B comes here and you have B B. Suppose we are talking about f is 3, this will react with A A. Again, B B, this will react with A A and B B and so on. Now, in this case you have A B or if you have here A that means, in the polymers you can have the two functional groups at the end. So, if I have some polymer chain, which branch having A A at the end, now what will happen? This two can react and form a connection between two linear chains.

Now, this is what cross linking is all about. In earlier case, there was no cross-linking possible between two linear chains, but in this case, because they are functional group, free functional group present, both types, it can undergo a cross-linking reaction. What are the other types it can undergo? If I have, say like, A A plus B f type, it can undergo cross-linking, you can visualize, yourself plus A f plus few B B molecule, then also it can cross link, from cross link, or you can have, if you have A f plus B f molecule, this, all this can form cross-links, cross linking. So, you understand, if I have a poly-functional group, which have functionality more than 2, 3 or more, then there is a depending upon which reaction system, which are, we are talking about, if there is possibility that it form, it may form cross link.

Now, what is a molecular weight distribution? In this case, I go back this and write the molecular weight distribution again without going into the derivation where X w y X n is given by 1 plus f r p. You know all the term here, f r p plus 1 minus r p square and at r is equal to 1, p is 1. This X w X n, which is the polydispersity index will land up 1 plus 1 f. So, that is your molecular weight distribution. If f is 1, molecular weight distribution would be, say, if I take this molecule, just one, one of functional group and obviously, it will be, we discussed that earlier, it will be like a linear polymerization with presence of small amount of monofunctional group. If A, A f is 2, physical A and A, it will be, it will be much narrow distribution. If f is 1, then it will be, if the distribution is like this, if the distribution is like this, for f is 1, if I increase f, it will be narrower. If f is 3, it will become even narrower. So, this f is 1, f is 2, f is 3.

So, when you have more and more branching in this case, the chains are the dispersion the, the polymer chains are having lower and lower poly dispersity. So, basically in this case, low molecular weight chain are not present in that amount and that number if there was no this multifunctional poly-functional group.

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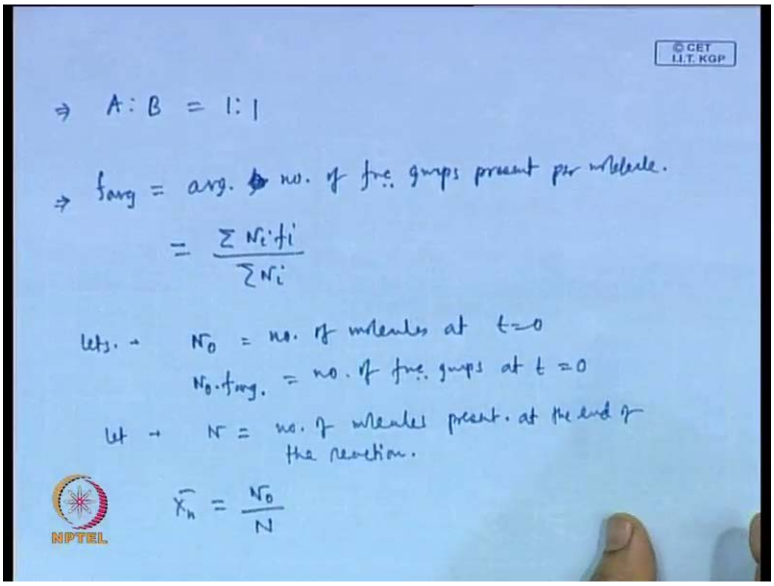

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$\Rightarrow$ $A : B = 1 : 1$

$\Rightarrow$ f_{avg} = avg. no. of func. grups present per molecule.

$$= \frac{\sum N_i f_i}{\sum N_i}$$

lets. → N_0 = no. of molecules at $t = 0$

$N_0 \cdot f_{avg.}$ = no. of func. grups at $t = 0$

let → N = no. of molecules present. at the end of the reaction.

$$\bar{X}_n = \frac{N_0}{N}$$

Now, what will be the poly number of, average number of molecular weight in the second case, this one? Let us go and try to derive that. Now, for simplicity, let us start with, I have a system where A is to be, to functional group, that is the simplest thing we have been discussing, they are in equal number, so 1 is to 1. So, and also we define a term f average, which is the average number of functional groups present per molecule, per molecule, which will be given by N i f i total n i, if n i is the, n i is number of molecules having f i functional, fi functional groups. So, that is, that we are defining this term and we are assuming for simplicity, that, this is the condition we are having.

Now, let us consider that N 0 is the number of molecules at t is equal to 0. At the beginning, N 0 is number of molecules. So, what is the number of functional group? N 0 multiplied by f average because f average is number of functional groups present per molecule on average. So, that is the number of functional group present at t is equal to 0. Also, let N is the number of molecule present, molecules present, at the end of the reaction what will be X n? As you know earlier, that is N 0 by N. Now, we know that N is the number of molecules present.

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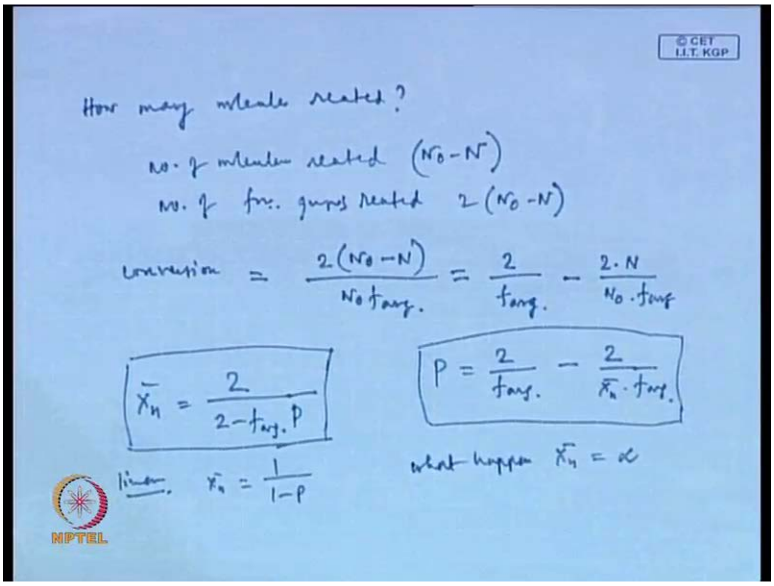

How many molecule reacted?

no. of molecules reacted $(N_0 - N)$

no. of fn. groups reacted $2(N_0 - N)$

$$\text{conversion} = \frac{2(N_0 - N)}{N_0 f_{avg.}} = \frac{2}{f_{avg.}} - \frac{2 \cdot N}{N_0 \cdot f_{avg}}$$

$$\boxed{\bar{X}_n = \frac{2}{2 - f_{avg.} P}} \qquad \boxed{P = \frac{2}{f_{avg.}} - \frac{2}{\bar{X}_n \cdot f_{avg.}}}$$

linear. $\bar{X}_n = \frac{1}{1-P}$

what happen $\bar{X}_n = \alpha$

Now, after end of reaction and N 0 was the number of molecules present at the beginning, so how many number of molecules reacted? How many molecules reacted? N 0 was number of molecules in the beginning and N is the number of molecules now. So, number of molecules reacted, so number of molecules reacted is N 0 minus N.

So, number of functional group reacted, now when one molecule disappears how many number of function group is reacting? Two functional groups, so number of functional group reacted, groups reacted is twice N 0 by N. So, what is a conversion? So, conversion is number of molecules reacted, number of function group reacted and the number of functional group originally present, so that is a fraction, that is a conversion, which gives you 2 by f average minus twice N by N 0 f average or twice f average minus twice X n f average because N 0 by N is your X n. As we talked about, we can rearrange this also to get X n is 2 by 2 minus f average into P.

So, in this case, this is X n, this is your P, this is conversion. From this expression we can know, that if f average is higher, more than 2, then for given P value, given conversion we will get a higher molecular weight, higher degrees of polymerization in comparison to linear polymer. For linear polymer what was there for linear X n was, 1 by 1 minus P. If you will recollect, see, for a given P, f average is more than 2, then this number will be higher compared to the X n obtained in linear polymer. So, we will, even without pushing the reaction to very high conversion we can make high molecular weight in this case.

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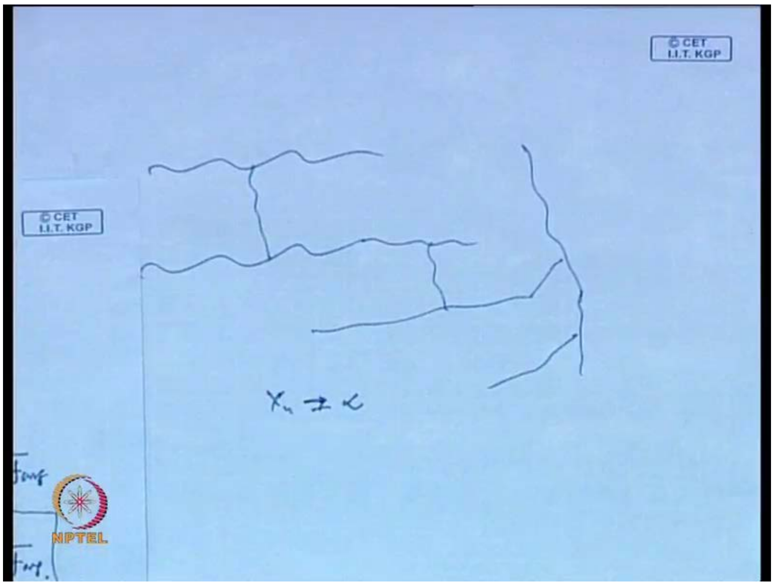

If you talk about P, what happens, that what happen when X n is infinity, when X n can become infinity? If the reaction, if the molecules in all the chains, now tied up in all the chains, if i have say something like this, polymer chains are growing. Now, I have cross link here, here and there somewhere, somewhere like this, something like this, what is a molecular weight of this polymer? These are all, all chains are connected, there is no individual molecular weight if the, all at the point when are complete network formation, that is, when the molecular weight becoming 20, and that is a point you can visibly see the gel formation. Gel formation means, which is not soluble in the medium, which is insoluble in any solvent, all in bulk as well.

So, that when the molecular weight becomes infinity, X n becomes infinity, that means, basically, you have the entire molecular polymers unfrosting to each other. Then the first sign of gel formation happen and we call that as a gel polymer. So, when molecular weight becomes infinity for the first time at what conversion, that conversion is turned as the gel point.

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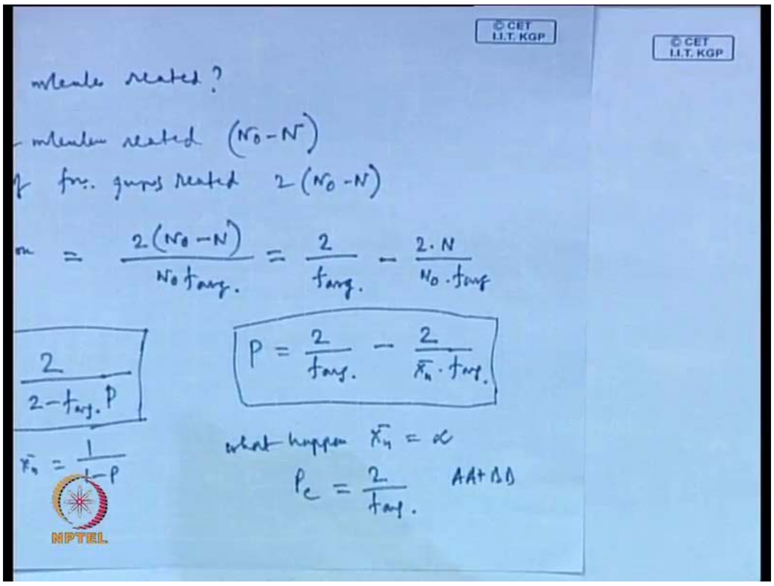

molecule reacted ?

molecules reacted $(N_0 - N)$

f fn. groups reacted $2(N_0 - N)$

$$= \frac{2(N_0 - N)}{N_0 f_{avg.}} = \frac{2}{f_{avg.}} - \frac{2 \cdot N}{N_0 \cdot f_{avg}}$$

$$\boxed{\frac{2}{2 - f_{avg.} P}}$$

$$\boxed{P = \frac{2}{f_{avg.}} - \frac{2}{\bar{X}_n \cdot f_{avg.}}}$$

$$\bar{X}_n = \frac{1}{1-P}$$

what happen $\bar{X}_n = \propto$

$$P_c = \frac{2}{f_{avg.}}$$

AA+BB

So, what is a gel point? When X n is infinity, so P c, P critical, which, that, which conversion the, the conversion at which there is a first time of gel formation or the network formation, we call that as gel point and which gives you by, 2 by f average. If there is only AA plus BB tied molecule and obviously, f average 2, when that can only happen when P is 1.

We know, that for linear polymerization the infinite molecular happen only when everything is reactive, the, all the monomers are reactive forming a single chain. It is basically give you an infinitly molecular… So, that (( )) happens when P is 1, but if f average is more than 2, then at a lower value you can make a gel point and a gel. Now, from a practical point of you, maybe, I will come in the next lecture, that what is the utility of these branches, branch formation or a cross link formation.

Now, what is, what is the problem in if we have cross link formation or if there could be, in some cases there could be some advantage, some property advantage if we have lightly cross link network present in your polymer system, that I will discuss in the next lecture and with giving you some examples of where this deliberately, this uncross-linking is done to utilize that polymer for a special property.

Now, we almost completed our discussion on the mechanism aspect of the theoretical basis of step polymerization. Now, onwards what we, I am going to discuss is, what is the procession, what are the process condition to make the high molecular rate successful step polymerization. And in next lecture what I am planning is to give the process of synthesizing different step polymers, like polyesters, polycarbonate, (( )) and it give you the chemistry of what is the reaction is carried out in real sense, in practical sense, to make this (( )) step polymer. So, next lecture I will complete that discussion on step polymerization.

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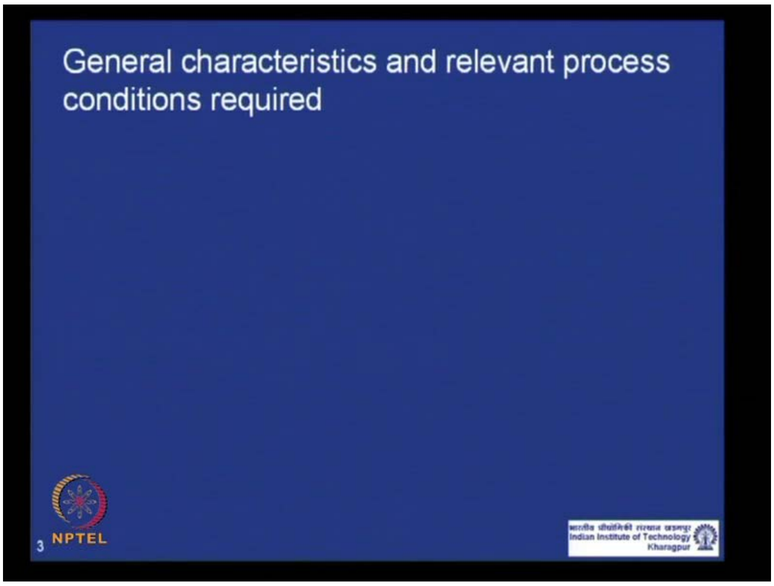

General characteristics and relevant process conditions required

Now, let us begin with, let us see what is a process? What are the process conditions required for a successful step polymerization?

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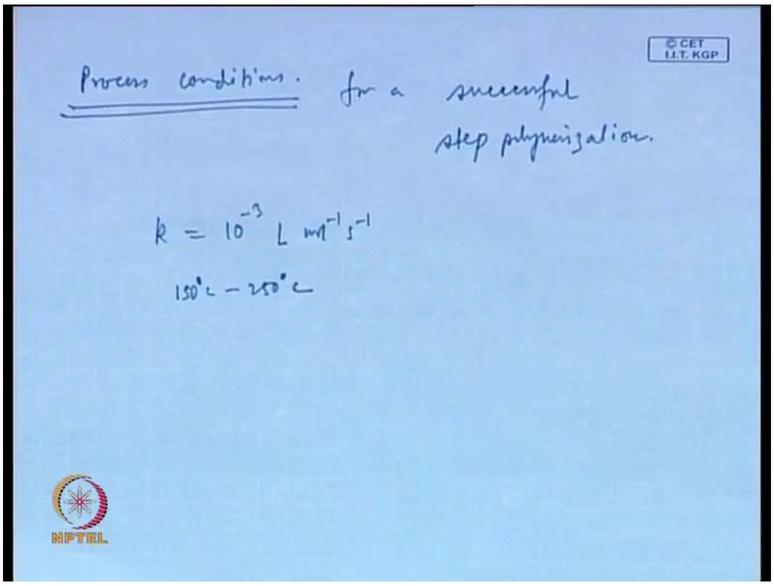

Process conditions. for a successful step polymerization.

$k = 10^{-3}\ L\ mol^{-1}\ s^{-1}$

$150^{\circ}C - 250^{\circ}C$

We have seen, that during are discussions we have covered everything now. We have mentioned everything, now I am just summarizing one after one point, so that I will give you complete picture, what are the parameters, what are the conditions you must have in place, so that we make a successful higher molecular weight step polymer.

Let us go and see point by point and the slide first, that reaction rates, you know, reaction rates are generally slow for this poly, step polymers in typically rate constant are of the order of 10 to the power 3 liter mole inverse second inverse, which is very low. So, it cannot be done at room temperature. So, high temperature is required at typically 150 degree to say, 250 degree centigrade is the temperature, is typically applied or this temperature where the polymerization is carried out. So, high temperature is required to, to facilitate, to make the reaction faster.

And you also know from our kinetics, we (( )) the kinetics. Remember, that the molecular weight was proportional to (( )), related to the initial monomer concentration N 0. We can recollect there, which means, that this always preferred to a step polymerization with high monomer concentration, which means, that if you are doing it in a solution, then you do it in a higher concentration and if it is possible to do in a bulk where we have only the monomers and the catalyst, that is the preferred situation.

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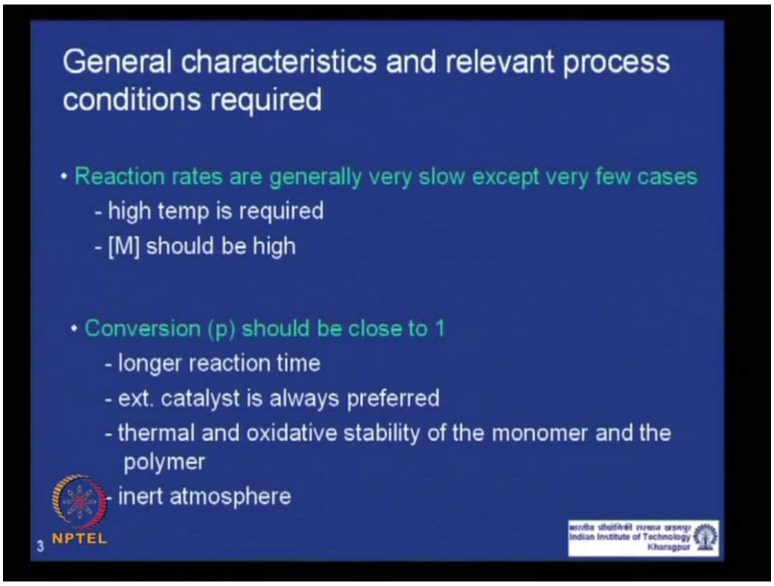

General characteristics and relevant process conditions required

- Reaction rates are generally very slow except very few cases
  - high temp is required
  - [M] should be high
- Conversion (p) should be close to 1
  - longer reaction time
  - ext. catalyst is always preferred
  - thermal and oxidative stability of the monomer and the polymer
  - inert atmosphere

Next, we know, that to make a high molecular weight, P should be close to 1, the conversion, the conversion and from kinetics discussion we have seen, that to have P close to 1, very high number, we have to continue the reaction for a longer time. There is no other, there is no, no other alternate rules by which we can achieve P very high, close to 1 without, you know, keeping the reaction for a longer time; there is no other rules. We have to keep the reaction, or continue the reaction for a longer time to have the P value close to 1, which means, that if you have some monomer or the resulting polymer or oligomer are not thermally stable.

Then, it is a problem, that those might degrade and generate some impurities in the polymer, which can generate color or which can degrade the polymer in later stage and, and it will not give you (( )), not give you the properties, which you are looking for from that polymers. So, it is, it is always preferred, that thermally stable polymers, the thermally stable polymers should be utilized in the polymerization. And if you know also, that if it is in high temperature and if there is a presence of oxygen, then thermo (( )) duration is a, is a very feasible way of degrading any organic molecules.

So, it is always preferred, that reaction if possible, should be done in an inert atmosphere, like nitrogen atmosphere, argon atmosphere, so that you are taking away the possibility or minimize, or minimizing the possibility of oxidative, thermo-oxidative degradation of the monomer or the resulting oligomer or polymer molecules. And as is, as we discussed, that external catalyst is always preferred than an internal catalyst, that basically with internal catalyst, outside catalyst, it is very difficult, even more difficult to (( )) high molecular, so external catalyst is always preferred.

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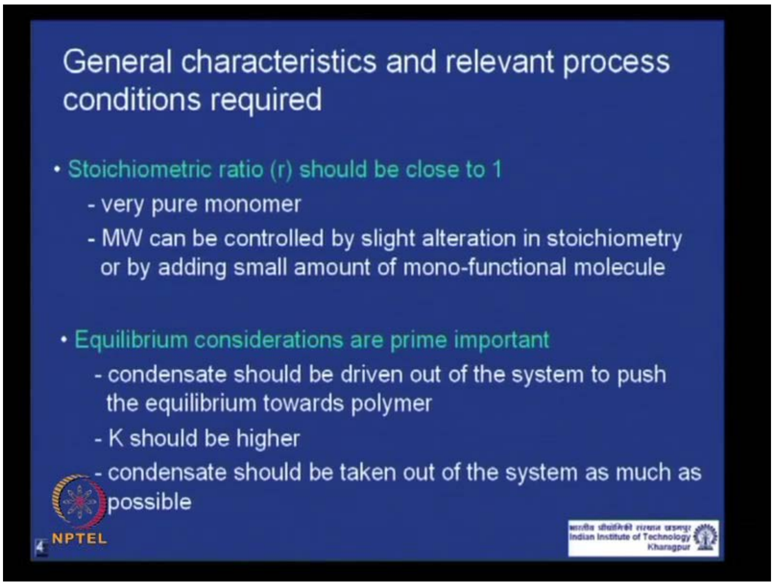

General characteristics and relevant process conditions required

- Stoichiometric ratio (r) should be close to 1
  - very pure monomer
  - MW can be controlled by slight alteration in stoichiometry or by adding small amount of mono-functional molecule
- Equilibrium considerations are prime important
  - condensate should be driven out of the system to push the equilibrium towards polymer
  - K should be higher
  - condensate should be taken out of the system as much as possible

Next point is, you know, stoichiometric ratio r should be close to 1. We have seen that when r is not close to 1, the molecular rate becomes slower. Now, to have r is close to 1, you first have to know the purity of the monomer and if there is an impurity, you do not know what you are putting in the reaction. So, it is always advisable, it is always preferred and always industrial, it is always done to have monomer, which are extremely pure, very pure, so that you know what you are putting if you are adding two monomers.

Assuming, that they are close to 1is to one or whatever target molecular rate you are looking for, that has to be the same what you are giving. That means, the monomers has to be very pure and you know, if required, you can change the ratio r slightly. Put one of them in excess, so that the molecular weight is controlled if you have some molecular weight in your target and that can also be done by adding small molecules, small amount of monofunctional molecules.

You have also seen, that equilibrium are very, equilibrium is, equilibrium consideration are also very important, prime important. We, we have seen, that in the most cases, this poly (( )) are step polymers, are equilibrium reaction. So, to have the product formation you have to take out the small molecular rate, condense it out of the system. You have to write that out by applying a low pressure, that will affect in vacuum and high temperature and so that your reaction proceed towards the product side, towards the polymers side.

You have also seen, that it is always preferred, that you have a higher k value, higher equilibrium constant. Now, what happens if you have higher k? Then for, for given polymer, for targeting same polymer molecular weight it can actually live with the small amount of, mono, more amount of condensate in the system if you have comparing into reaction having one, having higher equilibrium constant. Then in that case, you can live, build that high molecular weight leaving little excess amount of the condensate. So, it is always preferred, that you take out as much as condensate as possible by your system, by your technique and also, you also design the monomers, so that reactivity is higher and so the equilibrium constant is higher.

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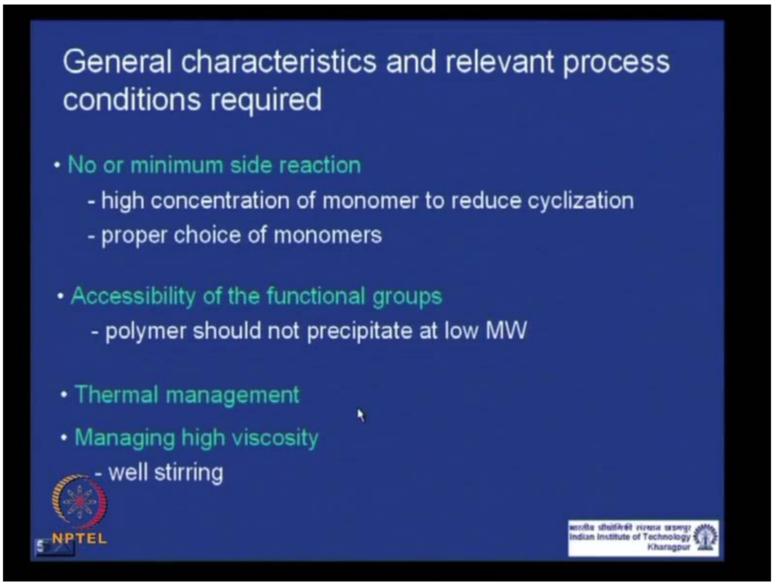

General characteristics and relevant process conditions required

- No or minimum side reaction
  - high concentration of monomer to reduce cyclization
  - proper choice of monomers
- Accessibility of the functional groups
  - polymer should not precipitate at low MW
- Thermal management
- Managing high viscosity
  - well stirring

Next point is, no or minimum side reaction. We know, that this side reactions cyclic formation, if cyclic formation takes place too much time, they will come out of the reaction and your (( )) goes up. If your side reaction is forming some molecules, which act as a chain stopper, which is like act as end of mono-functional group, if your side reactions are producing some molecules, which are mono-functional, which act as chains stopper, then it will harm your building up the molecular. It will stop the molecule there itself.

And if your monomers, if your side reactions, which hinder the reactivity of a functional group, if you have some species, which is generating, which is affecting the reacting functional group, that also will hinder your, you know, reactivity of the functional group, hence the polymer formation. So, proper choice of monomer is also very important.

And as we have seen, that to reduce the cyclic formation, cyclic molecules formation, it is preferred, that we do the reaction in high concentration of monomer. We have seen just now, that in earlier today, that it is always preferred to have a monomer present in high concentration, so that we can reduce the cyclic formation. We have also seen that is important, that we have the functional groups present in the (( )). During the reaction if some molecules oligomer are forming, which are say, precipitate out of the solution, if you are doing the reaction in a solution, if the oligomer precipitate out, then the functional groups are not available to reaction. So, it is always your solvent or the mediums should be such that your function groups are always accessible, should be always accessible to react.

Now, the two other things are thermal management because polymerization reactions are exothermic. So, as more and more reaction is happening, more and more get, heat get generated, but fortunately the exothermicity or the amount of heat generated for in a step growth polymerization is not high. So, managing the heat, generate, generation or the heat generation during the polymerization is quiet not difficult.

And next point is managing the high viscosity. As we progress, the molecular rate goes up and again, fortunately, the molecular rate goes up to high, very high level at the end of the polymerization and on the P is very high. So, except the, when except the situation is, P is very high, the viscosity of medium remains manageable and at the high viscosity in, at the high conversion in a time frame the polymer goes up and viscosity also goes up. So, we need to have very good (( )) mechanism, so that the, the (( )) can be exposed to the vacuum you are applying, so that you can push the reaction towards the product side.

Now, if you have this of most of covers, all the conditions, all the criteria if you have need to follow a successful completion of a step polymer. Now, let us, you, you follow all the, let us, you follow all the, all this, everything, all this points, which we covered in, in last 5, 10 minutes, you, you follow exactly all the things according to my direction or according to direction given in a book and end of the reaction, you find, that there is no molecular builder, it just forms oligomer. So, you, you think, that whatever I am just talking is, is not correct or whatever is written in the book is not correct, you might think that way, but it is not you have to think little higher. Then where this, your experience comes, your experience of polymers synthesis terms, what we will do? We will start from that point that even if you follow the requirement of successful step polymerization, here could be some other reasons, which you need to, you know, be careful, so that you have a successful buildup of high molecular weight in a step polymers polymerization process. So, we will visit, we just this we will just begin with that in the next lecture and complete at the module on step growth polymerization by looking at the synthetic procedure of the several step polymers.