Polymer Chemistry
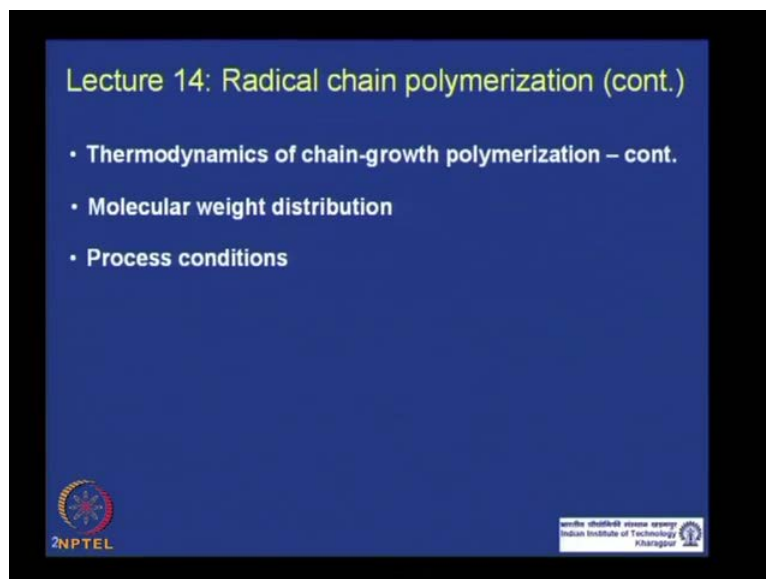**Prof. Dibakar Dhara**
Department of Chemistry
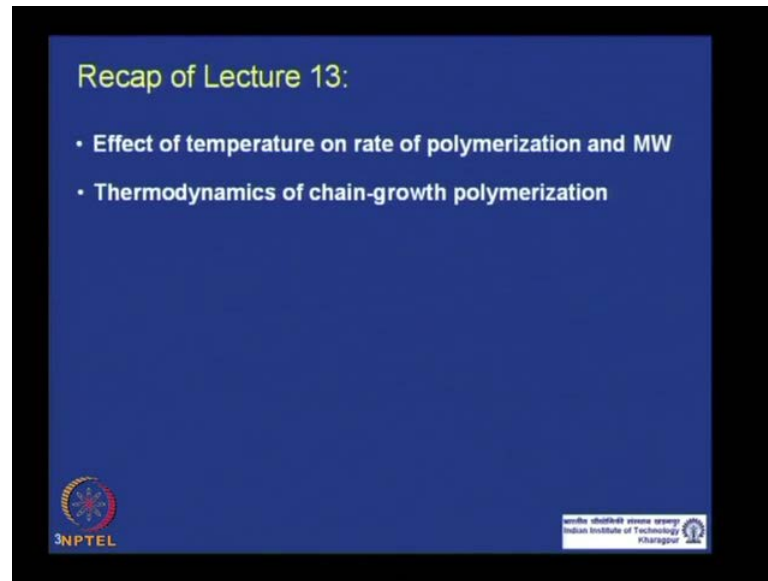**Indian Institute of Technology, Kharagpur**

Lecture - 14
Radical Chain Polymerization (Contd.)

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Welcome to this lecture fourteen of the course on polymer chemistry. In this fourteenth lecture I plan to you know continue the discussion we had on the thermodynamics of radical polymerization, which is valid for other chain growth polymerizations as well. We talk about the molecular weight distribution and we will talk about different processes, different polymerization processes for radical polymerization.
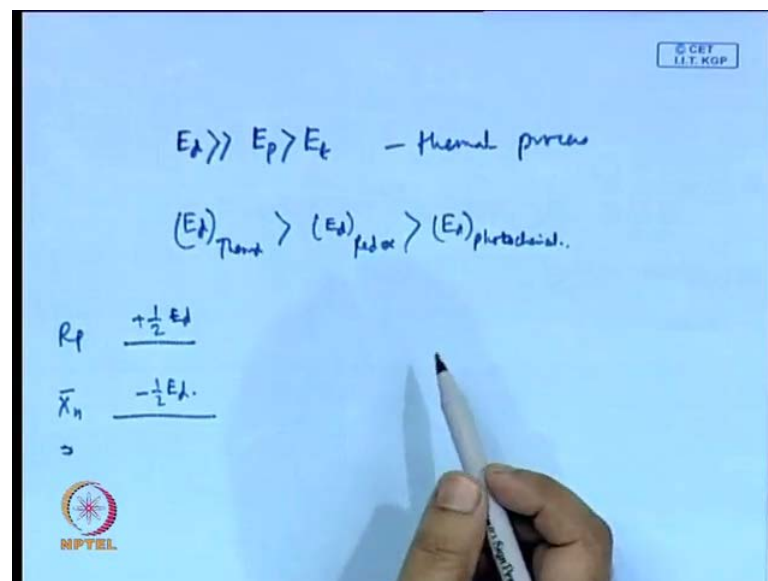
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Let us just recap couple of minutes on the topics we covered in last lecture. We talked about the dependence on temperature, dependence of rate of polymerization and molecular weight on the temperature for radical polymerization initiated by different mechanism, thermal initiator, photochemical initiator and redox initiator. We in summary we knew that the initiation process is more slower and had the highest activation energy for thermal process. And also E d for thermal was higher than E d for redox than E d or a photochemical process.

Now, you also remember in R p term there was plus half E d term on the numerator and in case of X n there was minus half E d term in the activation energy. So, between this three processes thermal process redox process and photochemical processes. Thermo, thermal process because E d is highest it was getting effected by the temperature rise. The increase in the rate of polymerization was much higher in case of polymerization initiated by a thermal initiator, then redox initiator and then photo chemical initiator.

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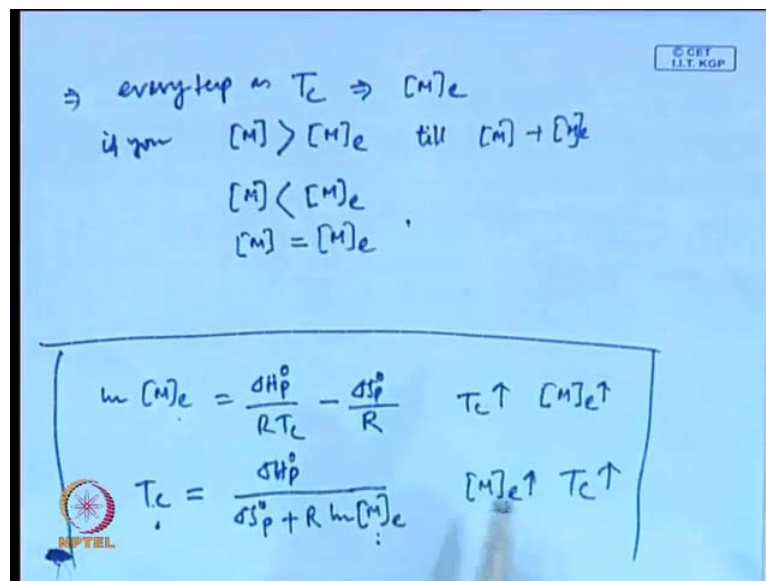
In case of molecular weight, again similar order, the molecular was getting dropped or reduced with increasing temperature mostly for thermal initiated reaction then for redox reaction and for photo chemical reaction because E d is actually 0. It was actually going up mildly. (( )) In case of photochemical reaction it actually gets slight increase in molecular weight with increase in temperature. And we were talking about the T c ceiling temperature and the equilibrium concentration of free monomer and we got this two expression. And we from this expression we know that every temperature; typically what we do in a in lab you actually start a reaction say in a beaker or in a round bottom flask and keep in a oil bath maintained or in some other (( )) maintained in a constant temperature.

Typically we do reaction polymerization reaction as well in a isothermal condition you know. Now, each temperature you can consider, your reaction temperature you can consider as a ceiling temperature. The equilibrium value of the free monomer

concentration at that temperature determined by this value, del H p and del S p. So, that reaction at the temperature will continue till the free monomer concentration reach to the equilibrium value of the free monomer concentration related to that temperature.

And typically, for the monomers which we know undergo polymerization process, this equilibrium value of the free monomer concentration is very low. So, we consider we assume that the polymerization is easy and polymerization undergo the monomers undergo almost quantity polymerization or convert almost nearly hundred percent. If we increase the temperature of your reaction then what happens, M e goes up. If you do a higher reaction at higher temperature then equilibrium concentration comes goes up that means your polymerization reaction stop at a higher free monomer concentration. So, if you choose to do in a higher temperature then you will always land up in a higher amount of unreacted monomer even if your reaction is complete or reached equilibrium.

And if you keep on increasing the temperature, one temperature will come where that equilibrium concentration is equals to the free monomer concentration your know pure pure monomer concentration. That means you can never polymerize at that temperature or beyond that temperature, which is 61 degree for methyl alpha methyl styrene we just talked about. 69 degree the free equilibrium concentration of the equilibrium concentration the free monomer alpha methyl styrene was equal to the pure monomer concentration. So, at 61 degree or beyond 61 degree you cannot at all polymerize alpha methyl styrene.

As we can see that the T c value depends or the relation between T c and M e depends on the values of del H and del S p. As I discussed at the last part of my lecture last lecture that delta is between polymer and monomer is basically change in entropy due to the translation motion vibration or rotational entropies and the rotational and vibration entropies of the monomer lost due to polymerization is actually gained in polymer. So, they do not take part or contribute too much in the delays value of polymerization, is basically that translational entropy drop for the monomers and which practically does not depend on the monomer structure.

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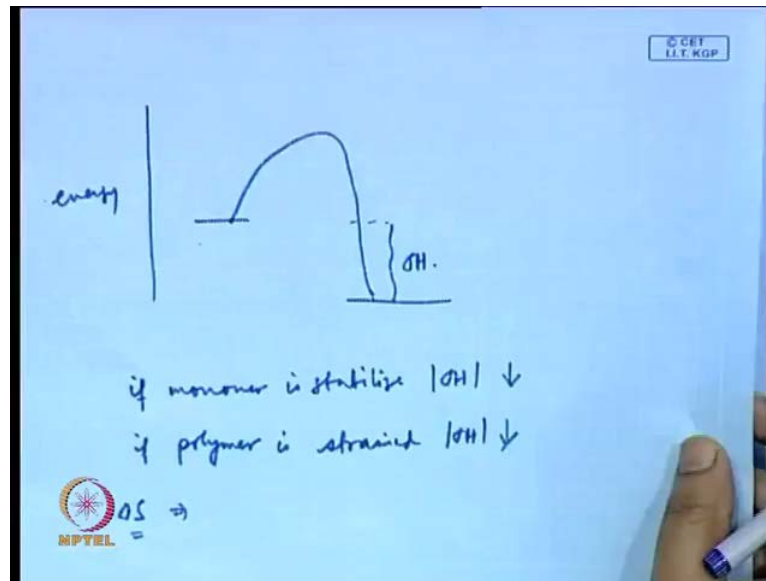
So, you will see that del S value is more or less more or less same for most of the monomers. But del H value will change as we were discussing in last lecture and that will depend upon the amount of stabilization which could be due to resonance or inductive effective or by hyper conservation or by the inter monomer complexes. If more stabilization means lower value of del H which means lower value of T c and the higher the strain, that means higher is the energy of the polymer again the lower is the magnitude of the del H value.

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Now, let us consider or let us compare few monomers and their del S. Now, del S and del G 0. So, let us compare between this two values. Now, del S del H in this case is for pure monomer. Pure monomer is getting converted to a pure polymer which is completely amorphous or slightly crystalline. Where in case of del S a one molar solution, it could be either of this two, you have to pure monomer is converted into pure polymer which is either completely crystalline or slightly amorphous, del S you can also consider from pure to pure or a one molar solution of the monomer to a one molar solution of the polymer repeat unit.

Now, this context you can appreciate that del H value does not depend on the concentration of the monomer whereas, del S value does depend. del S value is dependent on the concentration of the monomer. Now, let us compare the values between few monomers and see whether how the monomer structure contribute to the values of, now the simplest monomer is ethylene and in case of ethylene this is from a pure gas to a polymer solid polymer. This is 93 kilo g per mole and this is 155, compare this with this vinyl acetate. Now, this value is quite high. This will be higher from any other because he was talking about this is a gas phase reaction.

The gas gaseous monomer is getting transferred to a polymer. So, obviously drop in entropy will be much higher, these are negative numbers. Sorry, so this will be much higher. When you talk about the solution phase then this values will be similar. This is minus 88 minus 110, acrylonitrile minus 76 minus 109, methyl acrylate 78, M M A minus 56, propane minus 84, one butyne minus 84, isobutylene minus 48, two more styrene minus 73 and alpha methyl styrene minus 35. This is minus 100, minus 104, 121. Now, you can see that this del H more or less same. Now, as I said that this will be definitely higher because you are talking about a gas phase reaction or gaseous molecules is converted to a solid whereas, this case it is all liquid monomer you are talking about.
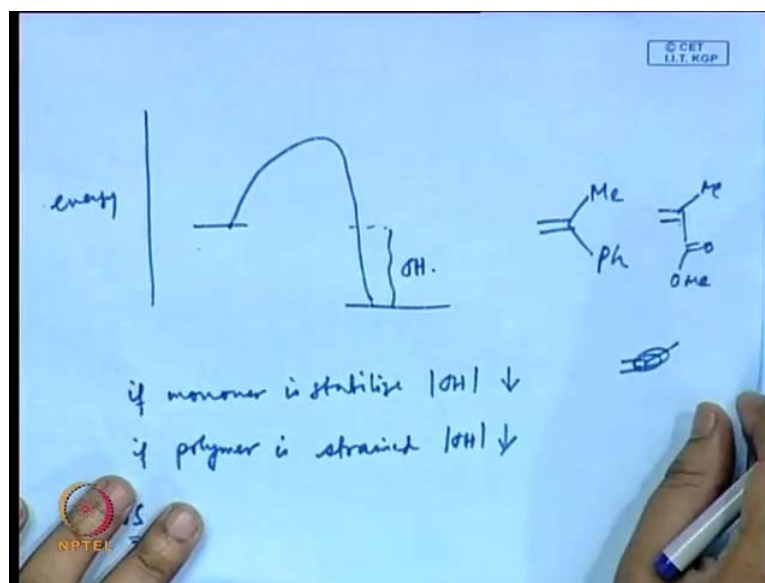
Now, let us compare between first styrene and alpha methyl styrene. Obviously this alpha methyl styrene have a much lower del H value. Now, that is because this polymer made from this one one substituted alkynes are going to generate when this five one this s p 2 is converted to s p 3 they are going to give lot of strain. If this alpha methyl styrene is converted to a polymer obviously because of this presence of this groups the polymer will be much more strained compared to the monomer which is a planer molecules. There is no strain of these groups.

So, this happens for most of the one one substituted alkynes. Resulting polymers is have much higher strain compared to if there was no such bulky groups. So, as a result alpha methyl styrene has much lower del H value compared to the styrene. The monomer stabilization is more or same between styrene and alpha methyl styrene. Similar case for M M A, M M A also a one one substituted and same logic can apply here because these are resulting a strain polymer the del H actually. The magnitude of del H comes down. You can compare between the values between M A and M M A.

If we compare between M A and M M A they are very close. They are close, but M M A is having much lower because in case of one one substituted the strain is much more compared to if have a only one substituted monomer. So, a polymer resulting from M M A will be much more strained compared to a polymer from just methyl acrylate. If you compare between say propyne and acrylonitrile propyne and acrylonitrile, so if you C H
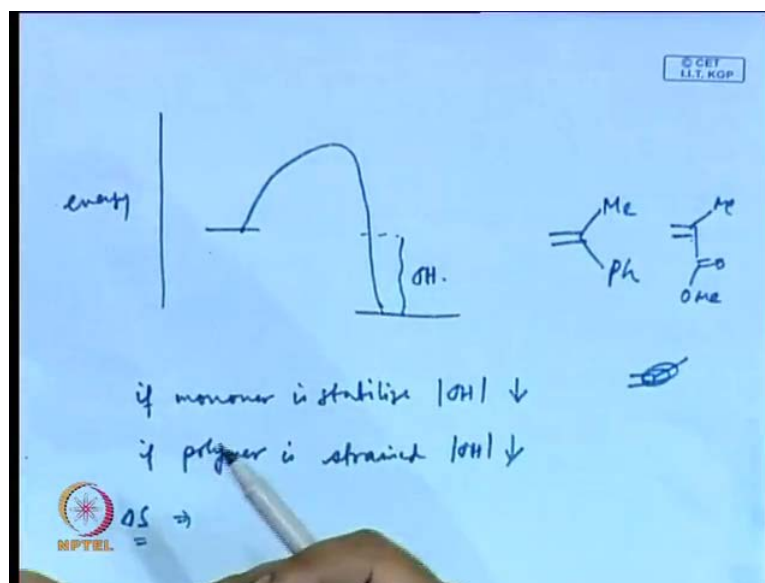
3 and C N. Obviously resulting polymers which have similar strain. So, it determine the del H value determined by the stabilization of the this double bond. And this case presence of electron withdrawing C N group this will be more stabilized. So, that value of acrylonitrile polymerization will be lower, so that 76 compared to 84.

So, anything you do to stabilize the double bond it will lower the magnitude of the del H p. If you do anything which will increase the strain in the resulting polymer that will also reduce the decrease in the value of del H. And as decrease in the value of del H which means thermodynamic feasibility will also comes down. We can compare between say one butyne and one tribu butyne. Obviously one tribu butyne has much more stabilization. So, it will have much lower del H value. If you if you compare between the acrylic acid and say acrylonitrile and acrylic acid.

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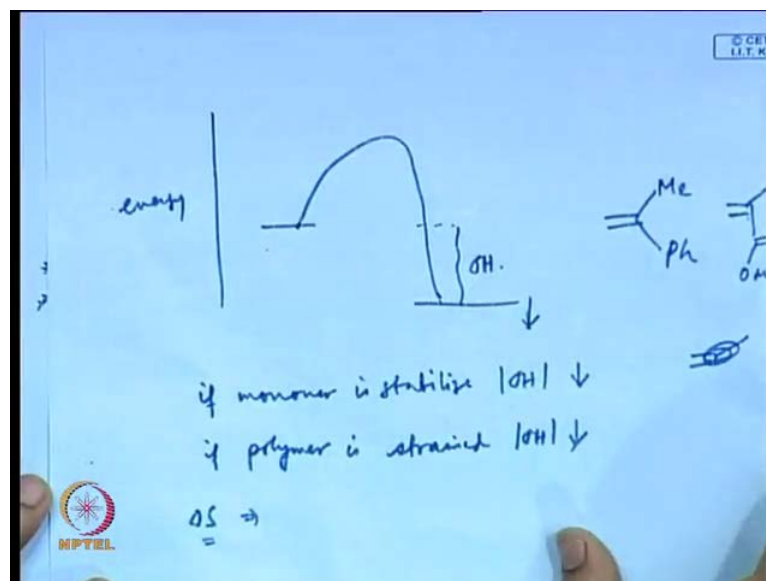
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Actually can form hydrogen bonding between the molecules which actually stabilizes the molecules lower compared to be when it get converted to polymer. If its compared polymers this groups cannot line up to form hydrogen bonding. So, the hydrogen bonding in acrylic acid polymer is much lower compared to acrylic acid monomer, which means del H value will be lower for acrylic acid compared to say acrylonitrile. So, we talked about the stabilization of the monomer due to resonance, inductive effect or by hydrogen bonding or dipro interaction between the monomers and increase in the strain behavior of the resulting polymer, which all this factors are against thermodynamic feasibility because the del H value comes down.

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Now, the values for tetrafluoroethylene is very high extremely high del H value which is is very difficult to is actually 163, trifluoroethylene is 163. Now, that is very high, it is very difficult to explain. It could be due to that resulting polymers have because because have a strong association. So, this actually goes down because chlorines are induced lot dipole movement. So, there could be a attractive interaction between the polymer molecule. And in this case that might go down with could results in the increase in the magnetitude of the del H that is one way to explain the high value of del H of high value of magnetitude of del H in case of trifluoroethylene to poly tetrafluoroethylene tetrafluoroethylene to poly tetrafluoroethylene.

Now, this value of del H is also important because that dictate you the exothermicity of the reactions. And if you have some knowledge about the exothermicity then you can actually control your, you can take out the the heat generated. If the heat is, you cannot effectively remove the heat which is getting generated by this exothermic polymer reaction then it will accumulate and it will increase the temperature local temperature. It will increase the reaction rate and decrease the molecular weight in a uncontrolled way. So, having a knowledge of del H is very important for a chemical engineer. So, that it he can design a process whereby he can effectively remove the heat generated due to the polymer reaction so that reaction remain isothermal during the polymerization process.
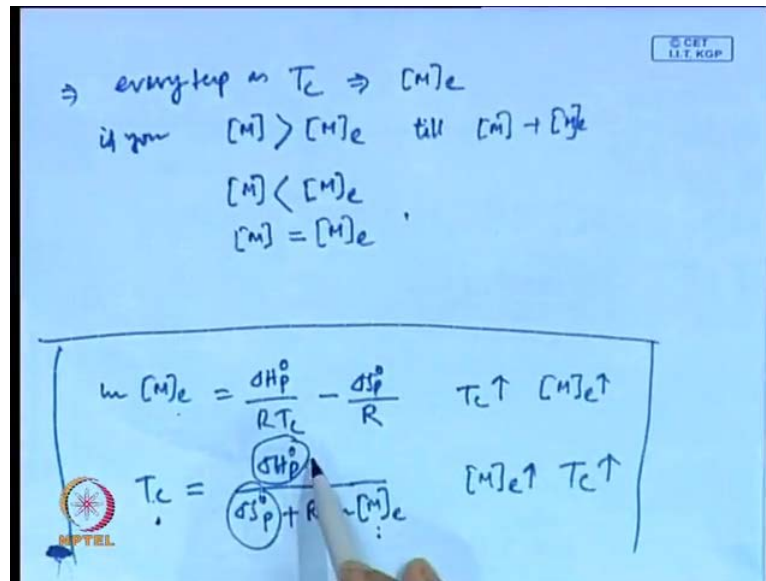
So, this alpha methyl styrene has a minimum of del H value. Of course, if you go back and see this one if this is low for a given M e, this will be lower because this more or less same. So, if it this goes down T c also goes down. If you consider this as a pure monomer, if you fix this concentration pure monomer as this goes down T c goes down. So, which means that for a pure monomer T c is much lower for alpha methyl styrene compared to a styrene which means that alpha methyl styrene cannot be polymerized. Whereas, molecule like styrene can be easily polymerized to a very low equilibrium value of free monomer in the mixture.
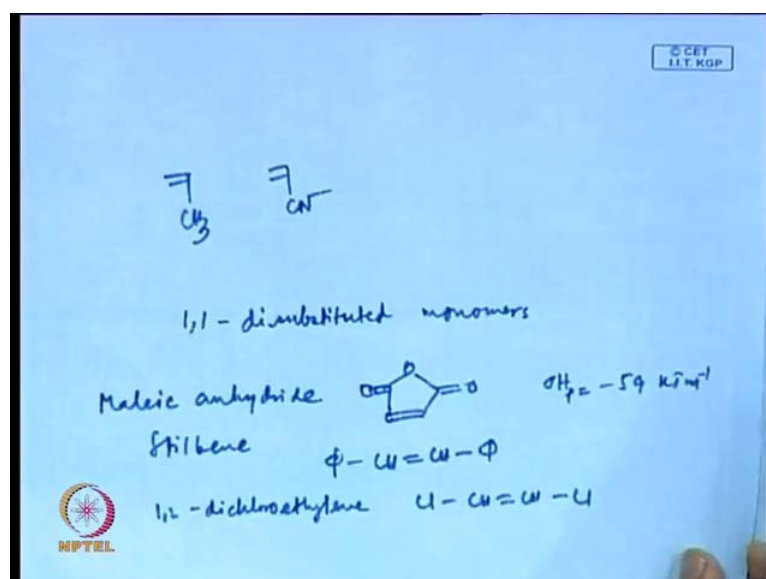
Now, we have talked about that one one substituted disubstituted monomers also difficult to polymerize. We talked about in the initial lectures when we introduced the radical polymerization about five six lectures back. For example, if you consider say maleic anhydride, stilbene or say one two simply one two dichloroethylene. Now, this this monomers have quite significant value of del H, for say for maleic anhydride this is about minus 59 kilojoule per mole, which means it is not the the fact maleic anhydride is very difficult to polymerize. It is not due to its magnitude its value of del H polymerization. Now, what is the reason that this monomers are difficult to polymerize?

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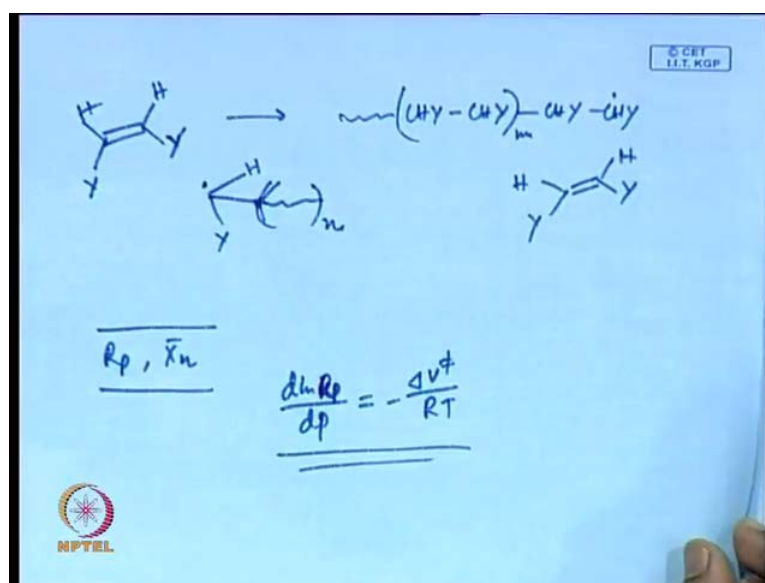
That is because of you if you have say polymer, a monomer like this where you have substituted one two substituted and you have a radical, if radical approaching this double bond which gets very restricted because of this substitutions. What is the radical? It is generates when it propagate at the end is basically C H to Y C H to C H Y and so on. This is the radical is get generated this is the propagating radical. Now, when this has to further take part in polymerization it has to approach this monomer. Now, that approach becomes very sterically hindered because of presence of all this one one substitution. And that is the reason this is very difficult and and that is why this reactions are very difficult to carry out.

Now, that so we talked about the T c and the values of del H and del S. The R p and X n the molecular weight can be also dependent on the pressure as well, though it is not that

significant as temperature. If the change in d R p says del V star by R T, we can write similarly, activation energy in case of temperature. You can write activation volume in case of pressure depending up on the value of this activation. Activation volume is the change in volume from either monomer goes from monomer state to transition state. If the volume is lower in transition state then del V will be negative. If the volume of the transition state is higher than the monomer volume then del V activation volume will be positive.

If this is positive then rate of polymerization will go up with temperature and if its negative if it is negative then it will go down. You can get it from this expression and it is not very significant. We, the effect of pressure is not that significant for addition polymerization. And it seldom practice the in the increase in rate of polymerization can be achieved much easily then by increasing the temperature than increasing the pressure. When you increased your temperature as much as possible even if you do not get a appreciable polymerization rate then people actually increase the polymerization increase the pressure to get a higher polymerization rate.

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Now, let us talk about, we will not spend too much time on the effect of the pressure on the rate of polymerization and molecular weight because it is not very significant as I said. That effect of temperature is much more significant. So, you can if you want to increase the polymerization rate you can do it much easier way by increasing the

temperature. If you run out of the option of increasing temperature then people try to increase the pressure to increase the rate of polymerization. Now, let us talk about the molecular weight distribution in case of radical polymerization. Now, again in case of radical polymerization, it is little complicated because the molecular weight forms during defined times of polymers are different. If you recollect the value for say your X n say this is your average degrees of polymerization for a thermal initiated polymerization.

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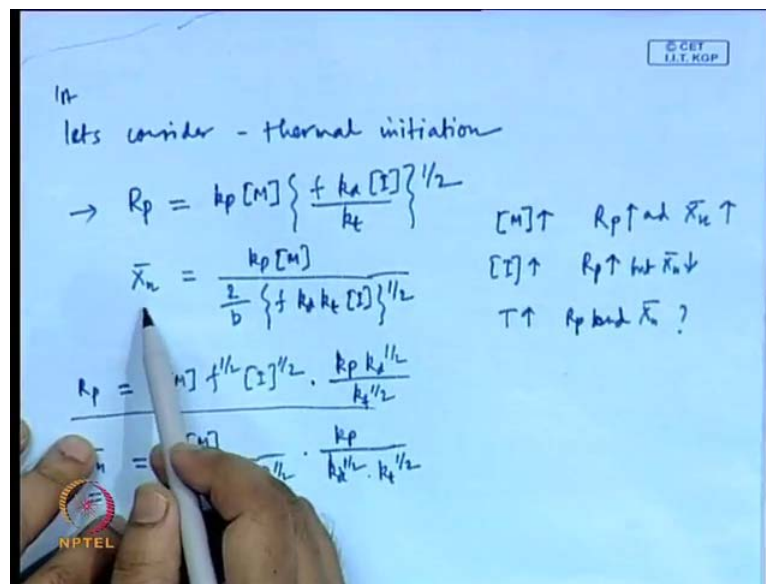
Now, with time the value of M and I changes. And changes means decrease, the mono monomer is converted to polymers. The monomer consistent drops as well as the initiator concentration drop. But the drop in initiator concentration is much more compared to drop in monomer concentration. That means the molecular weight is more compared to the molecular weights which were getting generated before. So, at if you consider these expressions with time goes molecular concentration the monomer drops so as the concentration of the initiator. Now, the drop in I is much sharper compared to drop in M concentration of M, which means that X n the average degrees of polymerization or the molecular weight increases with time.

So, which means that the molecular distribution if you consider the entire reaction is very complicated because at any instantaneous time the the molecular weight is different. If you talk about the molecular at the beginning of the reaction, that is quite different than the molecular weight of the polymers which are at the end of the reaction. One more

fundamental difference in case of radical polymerization with the step growth polymerization, I spent some time in lecture probably couple of lecture back. That in case, of step growth polymerization step growth polymerization the polymer is considered the entire mass.

You start with a monomer you complete the polymerization reaction. You consider the entire reaction mixture is the polymer, which includes monomers dimmer oligomers and high polymers high molecular weight polymers. So, that entire mixture is your polymer sample. So, the P D I you got one plus P which is for the entire polymer which includes small molecules as well as the high molecular weights. So, how did we get that X n bar remember X n bar was the number of molecules at t is equal to 0 and number of by divided by molecules at end of the polymerization. We considered all the numbers all the molecules present in at the end of the polymerization which includes monomer dimmer oligomer and everything.

So, which which are considering the small molecules also as a part of polymers and we are getting the polydispersity of 1 plus 3. We discusses that during the polymers there could be cyclic reaction formation or the side reaction for which small molecular weight generate which which result in higher P D Ivalue of higher than 2. But in case if you getting a P D I value is one point less than 2 for a polymers which you have taken out from the solution which means that the low molecular samples which might have left in the solution. So, you are getting the polymer precipitate from your reaction mixture devoid of the small molecules. So, basically you were narrowing your distribution. So, you are getting less than 2 value if you have if you have a less than 2 value.

Now, in case of radical polymerization how do we define radical polymerization how do you define the X n is the total total number of monomers reacted, I hope it is all visible this is not very sharpen, by total number of polymer molecules. Now, these are high molecular weight polymers these are high molecular weight polymers which you isolate after the reactions. So, this does not contain the unreacted monomer. So, that is the fundamental difference between X n in case of radical polymerization and in X n in case of step growth polymerization. Now, in in case of step growth polymers X n is considered at the end of the reaction. Where in case of radical polymerization X n varies each time the dead polymer chains are forming. So, X n will vary with the time.

What is the value of X n for radical chain polymerization? We will not go into very details into derivation. Say, at low conversion that means at the beginning of the reaction low conversion X n bar is given by 1 by 1 minus P X w n given by 1 plus P 1 minus P and X w bar X n bar P D I given by 1 plus p. Now, these are for for case if one polymer is formed from one kinetic chain which means termination by disproportionation or by transfer this is apply to this. Now, this case P is probability that the propagating radical will continue to propagate and build polymer. P is not the conversion unlike step growth P is not a conversion here.

P is a probability that a propagating radical will continue to propagate that means continue to react with monomer. It should be given by the ratio of rate of propagation with rate of propagation plus rate of termination plus rate of transfer. So, a radical a kinetic chain or a propagating radical can undergo three reaction it can again reactive with the monomer and propagate, it can terminate, it can transfer. What is the probability, is the probability given by the rates rate of propagation divided by total rates which is summation of propagation plus termination plus transfer.

Now, in case for high polymers for high molecular weight polymers high molecular weight polymers again the probability is always the probability of propagation is higher because that is why it is propagating P also tends to 1. Because, it is making high polymer high molecular weight polymer that means it is undergoing more times of

propagating reaction than a terminating reaction or a transfer reaction which means probability is close to 1.

For polymers getting terminated by Combination

$$\bar{X}_n = \frac{2}{1-P}$$

$$\bar{X}_\omega = \frac{2+P}{1-P}$$

$$PDI = \frac{2+P}{2}$$

$$PDI \Rightarrow 1.5 \rightarrow 2$$

Radical chain polymerization —

(at conv)

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

$$\bar{X}_\omega = \frac{1+P}{1-P}$$

$$PDI = \frac{\bar{X}_\omega}{\bar{X}_n} = 1+P$$

if one polymer is formed from one kinetic chain. → termination by disproportionation or by transfer.

P = prob. that the propagating radical will continue to propagate and build polymer $= \dfrac{R_p}{R_p + R_t + R_{tr}}$

high conv $P \rightarrow 1$

Now, if for for a polymer getting for polymers getting terminated by combination that means one polymer is getting formed from two kinetic chain. Obviously, the distribution will be the narrower and the molecular weight will be higher. So, X n is 2 by instead of 1 by 1 P is 2 by 1 p and X w is 2 plus P 1 minus P. So, P D I is 2 plus P by 2. So, this these are remember this at low conversion we are talking about reaction has just started.

Reaction has not progressed too much so the concentration of monomer and concentration of initiator has not changed much. So, ration of monomer by I to the power half is this ration has not changed much, at low conversion it will not change much.

So, the molecular weight, the average number of degrees of polymerization the weight average degrees of polymerization and the P D I is given by this expressions. I am not going in detail in derivation of this process is complicated process. Whereas, P is given the probability of the propagation radical will continue to propagate and build polymer which is R p divided R p plus R t and are transfer, where if the polymer is terminated by combination reaction than this gives by this. And as I said for high molecular weight polymer P is 1. So, the P D I value will be between this is 1.5 to the case where we have termination by this propagation of transfer this 2. So, this is expected that at low conversion the polydispersity will between 1.5 to 2.

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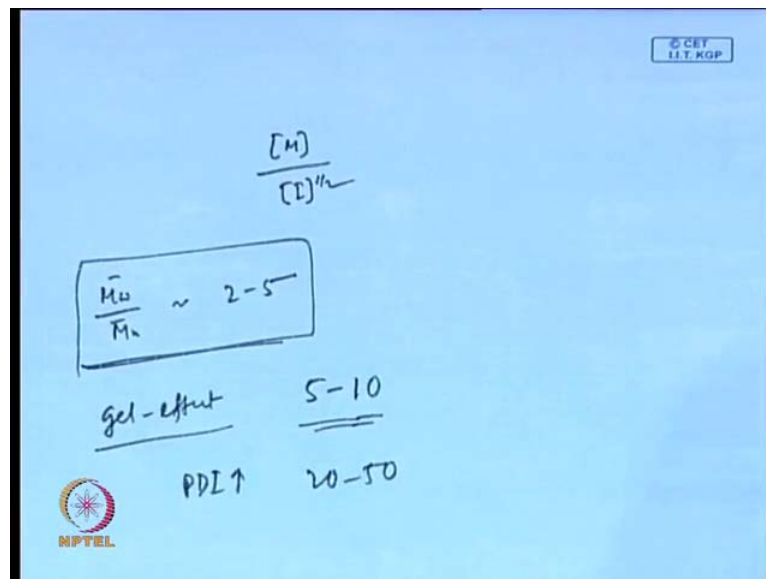
Now if the reaction continues the, this value changes and is actually it is become higher because the drop in as I said drop in initiator concentration is much faster compared to drop in monomer concentration. So, the chain length the degrees of polymerization goes up. So, if you consider the total polymerization so obliviously, the broadness will be much higher. The reaction, the polymers made at the begin will be lower molecular weight comparatively lower molecular weight. And have if you increase the temperature.

if you increase the time the polymer molecular weight will be higher and higher. So, you have a much more broader polymer distribution.

So, if you at the end of the polymerization if you consider the M w by M n value will be quite high and its typically between 2 to 5. You understand that a low conversion it is, it was between 1.52 to 2, but at the temperature as the time goes up the polymer molecular weights increases increases. So, that distribution actually goes up. Starting from low molecular weight at the beginning to high molecular weights at the at the end thE distribution goes up. So, you typically the value of P D I comes around 2 to 5. And if there are gel effect effect like gel effect and all this things were molecular weight shoots up at the end because the reason we talked about in the last class it could end up a P D I value of 5 to 10.

If there are gel effect then what happen you know that branching might happened and if branching happen between or the which results from chain transfer two polymer. If intermolecular chain transfer happen then the P D I goes up further. For inter intra polymer chain transfer there is no change in molecular weight or molecular weight distribution either. So, if the there are branching happening because of inter molecular chain transfer as gel effect then P D I goes up and it could be as high as 20 to 50. Basically, these are not the polymers you want you want polymers which are as narrower as possible. So, that is why you would like to avoid this gel effect and and branching and and so on. So, that you can get narrower and this is the most typical values of P D I you get from a normal polymerization radical polymerization reaction.

Now, what, I will talk about that we talked about the effect of temperature, thermodynamics of polymer, different molecular weight distribution. Now, talked about how the polymers are done you know. We talked about all the theory and principle behind molecular weights rates and all this. Now, the practical part how the monomers are usually polymerized in a in a industry scenario or in the lab. There could be several processes. You can do the polymerization only with a monomer and we call it a bulk polymerization. You can dissolve the monomer in a solvent and do the polymerization then it is named as solution polymerization. You can disperse the monomers in aqueous phase and do the polymerization, you call this suspension polymerization.
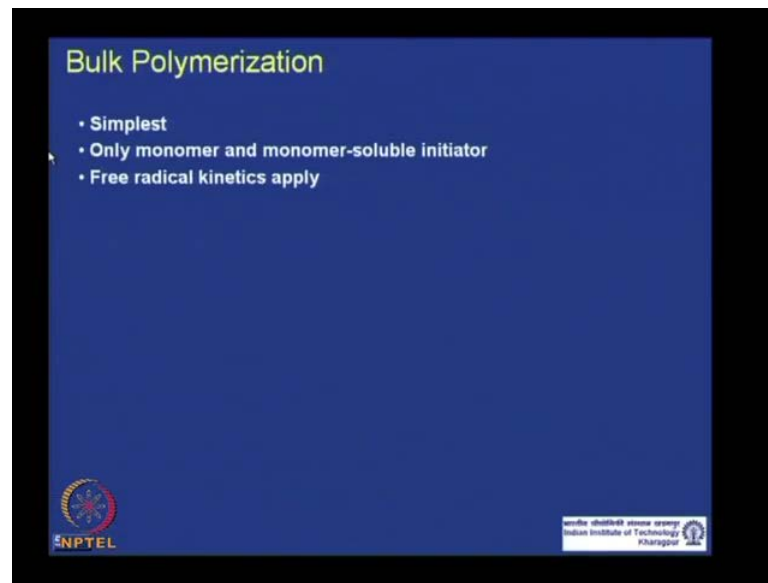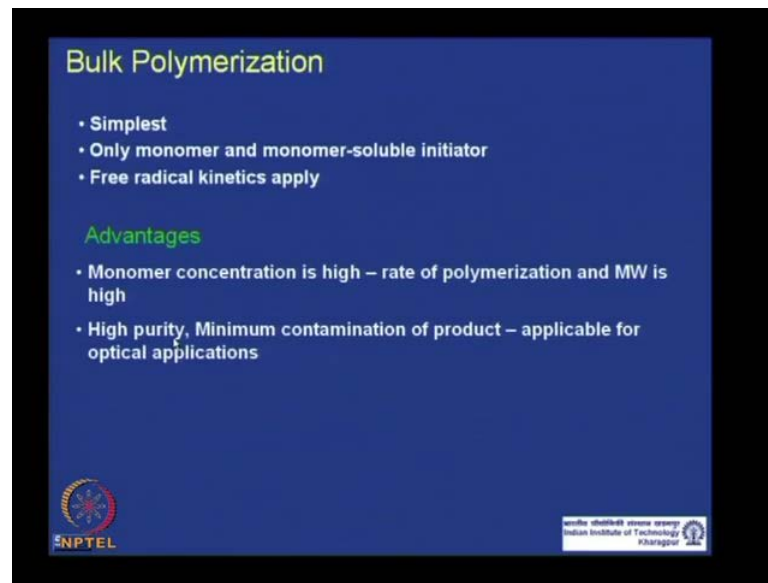
You can do it in a disperse dispersed resulting polymer the produced polymer could be dispersed in organic solvent and you can continue the polymerization as the polymers remain in disperse. We call that as a dispersion polymerization. And you can do the polymerization in emulsion as well. We talk about of each of this brief. We will spend most time on emulsion polymerization and so let us start about the bulk polymerization. As I said is the most simple or the simplest polymerization. You have to take the monomer and a initiator which is soluble in the monomer. So, you take the monomer you dissolve the initiator and heat the monomer to start the or to initiate the reaction.

And obviously, what is advantage here? Advantage is that we have seen that the reaction polymer polymer reaction rate as well as the molecular weight goes up with increase in monomer concentration, which is not true for increasing initiator concentration for initiator increase in initiator concentration rate goes up, but the molecular weight comes down. If you remember that discussion we had just few few minutes. But monomer actually, if you increase the monomer both the reaction rate and the molecular weight goes up and this is the maximum concentration you can do. You can get maximum concentration monomer if you do in a pure state, so monomer concentration is high.

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So, rate of polymerization molecule is high and because you are not using any other chemical solvents or other things this gives you high purity polymers and gives you minimum contamination of the product. And that can be applied in optical applications like C D E and you know other things where you require very clean polymers. Obviously, this has lot of disadvantages. For example, because your concentration is very high even at low concentration even at low conversion the viscosity goes up because the medium viscous if the polymer is viscosity goes up. And as the viscosity goes up you cannot start the reaction medium very effectively and if you cannot start you cannot dissipate the heat generated due to exothermic polymerization.

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And as a result what happened, you there is a local heat generation which actually can degrade your polymers which actually can degrade the polymer molecules and can generate coloration in your polymers. So, viscosity becomes high and stirring become difficult. And at the end of the polymer also polymerization also, if the viscosity of the resulting you are your final polymer is very high then processing also becomes very difficult. As I know as we know that high monomer gives high reaction rate. So, heat generation is high rate and as a result local heat formation takes place coloration and degradation takes place.

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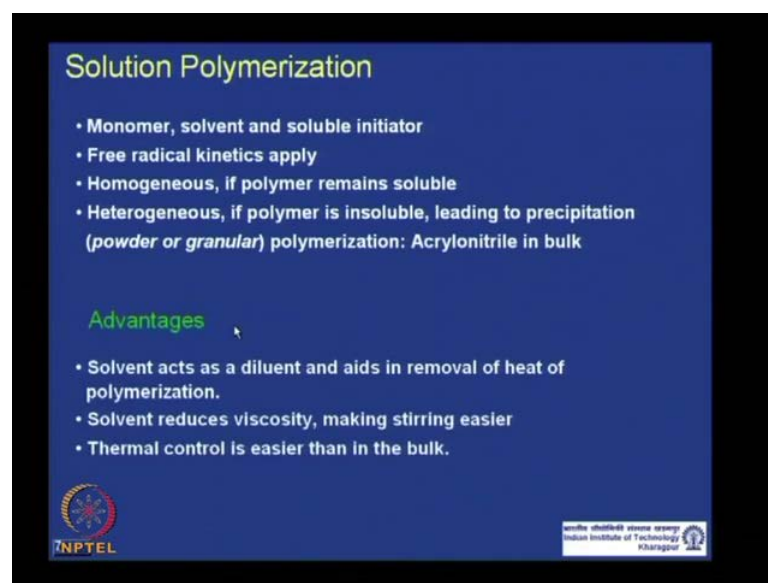
So, what is done it is still done? It is still utilized for say making styrene, poly styrene, poly methyl acrylate, poly vinyl chloride. Typically, what is done you start the reaction and keep it at low conversion so that build up is not too high not unmanageable. Then stop the reaction take out the polymer and restart the reaction again. So, that you can get high molecular weight, high rate of polymerization without building very high viscosity. So, you have to do actually stop starts stop start stop reaction where you start the reactions stop at low conversion and then you stop and take the polymer out. Another strategy is taken for making sheets and all this things that you make a pre-polymer which is not very high molecular weight.

You make a p polymer so the viscosity is not high and then that pre-polymer is poured into a mold in this case sheet. And then you you want to get the polymer in a final form of a sheet. So, you pour that pre-polymer into the sheet and then without starting you do the reaction. So, the reaction rate will be faster and high molecular weight produced and it will you do not need to process it. It will, it will become like a sheet. So, you do not you are not aiming for processing this thing or you are not aiming for for heat management all this things. You are not targeting that. You are taking this pre-polymer putting in a sheet type mold and then finishing the polymerization. You actually, gel effect is a beneficial for this thing.

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So, that you can make a high molecular weight and reaction get faster and you get the final formed final polymer in terms of a sheet. So, these are the things these are strategies are applied for in industry for using bulk polymerization. We move to solution polymerization where you have require monomer solvent and a soluble solvent soluble initiator. In this case, you require initiator to be in the solvent and free radical kinetic normal can be applied. It could be homogeneous, if the polymer formed remain in in the solution it will be heterogeneous. If the polymer is insoluble and precipitate out once it forms and once it precipitate outs it can form powder or granular.

So, sometimes this this polymerization is called powder or granular polymerization. For example, acrylonitrile in bulk or acrylonitrile in water in this case, it should be water. If you start polymerization acrylonitrile in water, poly acrylonitrile is not solvable in water, so its precipitated out you get acrylonitrile powder or granular. Obviously, advantage the advantage disadvantage which we had for your bulk polymerization. In this case, you do not have those problems because you are doing in a solution then heat heat transfer can takes place efficiently because it is solution viscosity does not build up. So, there is no question of local heat formation, local spot formation, hot spot formation and degradation of molecules and thermal control becomes easier.

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 Now, what is disadvantage obviously you are doing a solutions of monomer concentration goes down which means rate of polymerization becomes lower and

molecular weight becomes lower. And unless if you do not choose the solvent very carefully the solvent can participate in chain transfer reaction, reduce your molecular weight further, so you have to be very careful. Now of course, sometimes is very difficult to remove the solvent quantitatively from the polymer no matter how much vacuum you applied it is very difficult some times because solvents stick to the polymer. So, it is sometimes very difficult to take out all the solvents from the polymer quantitively.

And that is very detrimental for the properties of the you know final polymers, you do not want solvent to be contaminating your polymers. Now of course, you cannot throughout all the solvents unit solvent recovery and recyclic which is a very hazardous for this. We are talking about organic solvent, so it is not very environmental friendly and the person scientist finally either. You know we not want somebody working in the lab with the huge amount of organic solvent that is health hazardous well as the environmental hazardous. These are the disadvantage for a solution polymerization, but still use for making polyethylene poly acrylonitrile or polyethylene acetate.

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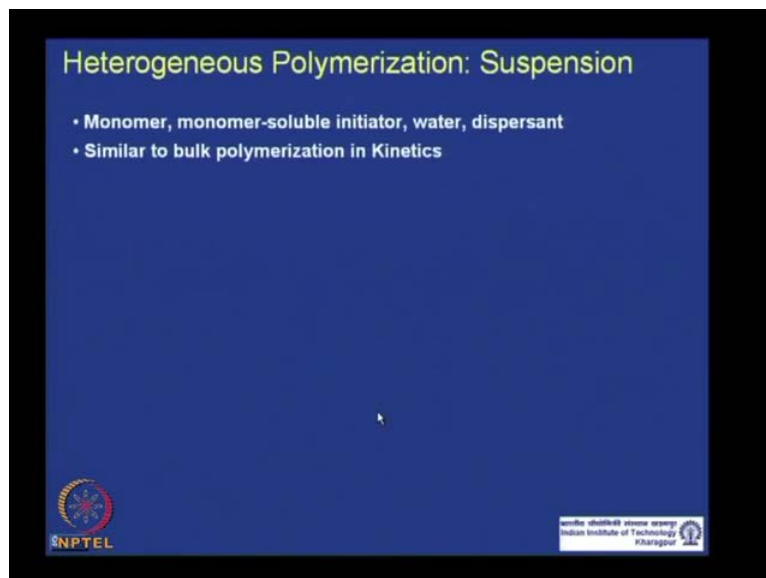
There is a third type of polymerization we talking about where is a heterogeneous polymerization it could be suspension or dispersion. In case of, suspension monomer and monomer soluble water suspension polymers are nothing but bulk polymerization done in in small volumes. You make this small volumes of bulk polymers distributed in a or

dispersed in a aqueous solution. So, all the disadvantage of the bulk polymers should not be present here because you are doing in a small small volumes and small droplets and because its present in a in a surrounded by aqueous medium. So, heat dispersion heat dissipation is easy, viscosity is does not build up its not a problem.

What you do, you dissolve take your monomer dissolve the initiator in the monomer and then on that you add your dispersing medium which is already heated in the temperature you want to do your reaction. So, you take the monomer along with your initiator you add the preheated dispersing medium and then reversely start. Once, you start this monomers containing the initiator will form droplets. And it will remain dispersed because you have added in that reaction medium and dispersions which are typically water soluble polymers like polyethylene glycol or some inorganic particles which actually get absorbed on this particles and prevent them to coulis.

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So, that they remain in the as a dispersion form because you have this soluble water soluble polymers or the ionic particles which actually act as a stabilizer for this droplets. So, what you do initially, you initiate is dissolved in the monomer and then preheated dispersing minimum added. And vigorous starting converts the monomer containing initiator into strong small droplets of 100 to 500 microns, and because dispersant presence which are very small amount 0.1 weight percent. And because you are continually stirring this actually stabilized the suspension, so the poly.

Now, you have the monomer droplets along with the initiator molecules has a small droplets which are dispersed in the aqueous solution. Now, you are doing the bulk polymerization in the small droplets. So, all the advantages of bulk polymerization is remain still intact high polymerization rate, high molecular weight, very pure monomers. And once the polymerization is complete you can just filter out and get the final polymers in a beads form. That is why some times it call as a bead or a pearl polymerization.

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So, you can remain maintain all the advantages of the high polymer bulk polymerization and you can get the polymers by filtration as a beads. Now, these beads should not stick which other. It should be rigid if you want to isolate these polymers as a bead then it should be rigid and it should not stick to each other. Now, that happens if your polymer glass transition is is way above your room temperature. The temperature you are taking out if your glass transition temperature your polymer is close to that room temperature or little higher than the polymer will be soft. And if the polymers are soft then they will stick to each other.

So, this methods is typically applied for the polymers which have the high glass transition temperature like methyl methacrylate and all this things. So, we will start from this point and talk about the dispersion polymerization and emulsion polymerization in the next lecture.