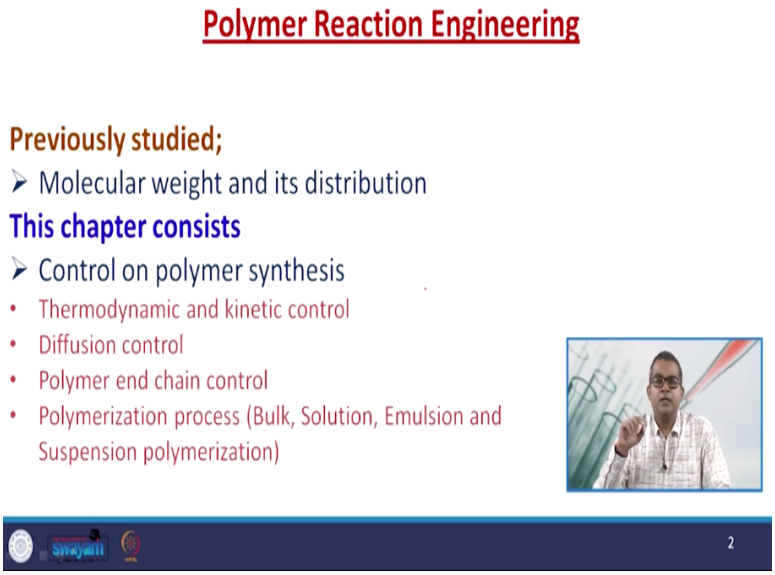
Polymer Reaction Engineering
Prof. Shishir Sinha
Department of Chemical Engineering
Indian Institute of Technology Roorkee

Lecture - 08
Control on Polymer Synthesis-I

Welcome to the control on polymer synthesis chapter under the head of polymer reaction engineering. Earlier we had a brief discussion about the molecular weight and its distribution.

(Refer Slide Time: 00:38)



We learn about the efficacy of the molecular weight. We learn about the different kind of molecular weight and what is their importance. We discussed about the number average, weight average, molecular weights. So, we discuss about their importance for the deciding the properties of the polymer structure.

Now, whenever we talk about these molecular weight or distribution or a polymerization reaction, then we need to look into the various kind of a control methodology in the polymeric system or the polymer synthesis. The reason is that because if you recall the previous lecture, we studied about the chain distribution network and chain carries the different number of monomers.

And that is why we do have a range of polymer molecular weights not the specific molecular weight. Like suppose, you talk about the polyethylene, it carries a range of molecular weight it is not the specific molecular weight like x, y, z etcetera. So, whenever we talk about this

sequential thing then the control methodology of these polymers synthesis came into existence.

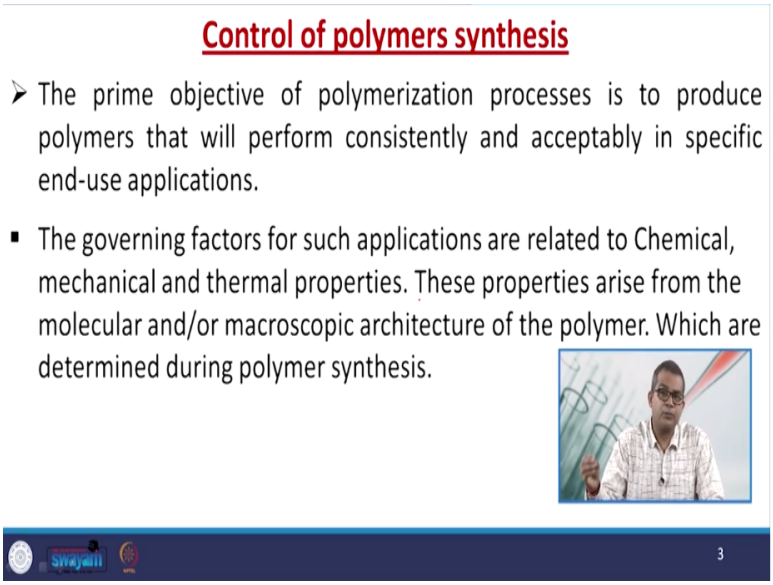
Now, when we talk about these control methodologies, there are various parameters associated with this particular type of approach. Because see, there are different type of chemical reactions we studied that the graph polymer, copolymers various kinds of the polymerization tools. Then based on this particular approach, you need to control the molecular weight.

You need to control the chain propagation and you need to see that at what point of time you need to truncate the polymerization reaction so that you can have the polymer with the desired properties. Because if you go on increasing the rate the polymerization process then sometimes the mass will become so viscous that it will not have any kind of a practical approach.

So, whenever we talk about the control methodology on various kinds of polymer synthesis, there are couples of segments which we need to take into account like thermodynamic approach, various type of kinetic controls etcetera, then diffusion control diffusion is a very important phenomena in the polymeric system. Then, polymer end chain control which is a very important thing which we need to look into.

And what is their impact of this different type of parameter into the polymerization process like bulk polymerization solution, emulsion suspension polymerization. So, we will discuss all these things in this particular head.

(Refer Slide Time: 03:20)

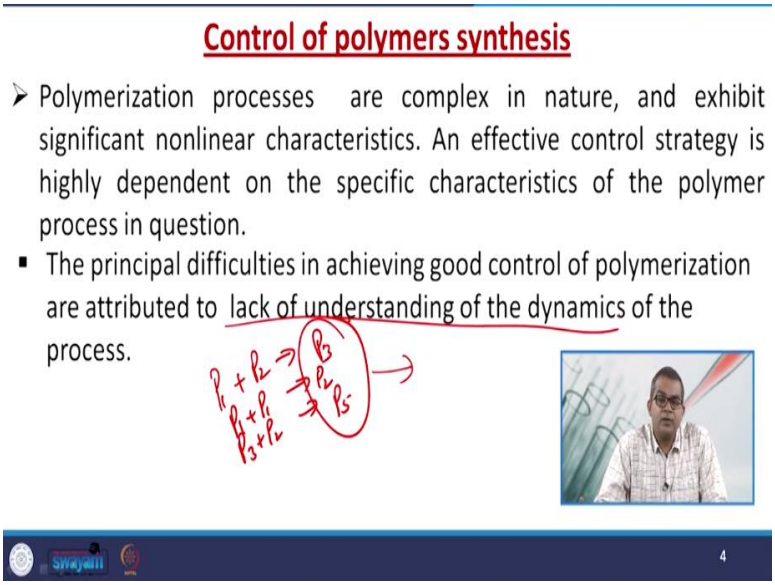


Now, if we discuss about the control of polymer synthesis, the prime objective of polymerization process is to produce the polymer that will perform consistently and acceptability in the specific end use application. Sometimes, as you discussed that you need the flexible polymer, sometimes you may require some stiff polymer.

So, based on their requirement, based on the end use, based on the specific application required and to minimize the efforts, minimize the efforts with respect to the engineering applications like environment, energy etcetera. Then, we need to look into the control methodology. The governing factor for such kind of polymerization applications, they are broad spectrum related to the chemical, mechanical and thermal properties.

Now, these properties arise from the molecular or macroscopic architecture of a polymer. If you recall that we discuss about the graph polymer we will discuss about other polymerization approaches. So, these properties are attributed to those kinds of architecture.

(Refer Slide Time: 04:45)

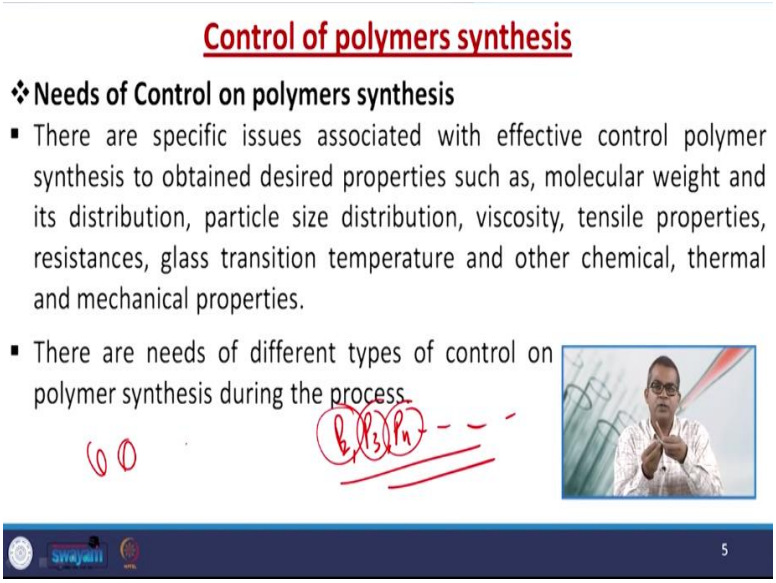


Now, usually this architecture is defined during the process of polymer synthesis. Now, if you see that the polymerization processes, they are very complex in nature. They are very complex and exhibit the significant nonlinear characteristics. Now, an effective control strategy is usually required for the specific characterization of any kind of polymer which is in process.

Now, when we try to go for this polymerization process, the main difficulty in achieving the good control of polymerization, they are attributed to the lack of understanding of the dynamics of the process. If you recall that we discussed about the different type of chains, like P_1 plus P_2, this gives the P_3. P_1 plus P_1, P_2 and so on. So, contributory effect of these polymeric chains, it is having the vast impact in the final property of the polymer.

And moreover, because it is you can say that the regular process or carrying out process, so, therefore, the difficulty people may face the difficulty in the understanding of the various dynamics attributed to this particular process. So, therefore, this particular difficulty creating lot of problem while having while designing the control methodology of any kind of polymer synthesis.

(Refer Slide Time: 06:19)



So, based on this particular requirement, let us have a look about the need of control on the polymer synthesis. Now, as a couple of issues discussed in the previous slides, there are specific issues, they are associated with the effective control methodology of the polymer synthesis. They may require to have a desired product such as the molecular weight distribution.

Because if you see the previous slide, we have discussed about the P_2, P_3, P_4, etcetera. Then you may see that there is a wide spectrum of molecular weight distribution. So, when we discuss about the molecular weight distribution, when we discuss about different type of chains like P_1, P_2, P_3, etcetera. Then we cannot overlook the importance of a particle size distribution.

So, because the particle size distribution the drive is may be different for all type of polymers. Now, if we go on in the increasing number of chains and increasing number of in situ monomers, then we cannot overlook the importance of the viscosity, because if you carry on all kind of a polymerization for a longer time, then it may create a problem of viscosity.

And sometimes may have a larger viscosity, then you may have a problem in processing further processing. Suppose, you wish to put all kind of this polymer into a different mold, then sometimes you may not be able to achieve this kind of result. And sometimes if you to reduce the viscosity, you need to put some solvent or you may need to require to give some kind of heat treatment, etcetera.

Again, you need to put more and more effort with respect to the economics of that particular process. So, viscosity is again very important thing. Now, the tensile properties, although if you go for the larger chain, then definitely you may have good tensile properties by simultaneously other aspects, they came into existence for this particular thing, then, different type of resistance one resistance is attributed to the viscosity. And the other resistance may be attributed to the chain length, etcetera.

Now, we always talk about the chain length of this polymeric system. Now, these chains when you see that, they formed, they are sometimes entangled with each other. Now, entanglement means that suppose these are the different chains, my fingers and when they are in the you can say in the idle state, they are entangled to each other. Now, if you supply a little quantity of heat to this one, then these chains try to unentangled.

And that is why you observe these phenomena of the flowing of that particular polymer just I am giving you an example related to the polyethylene or suppose, I am having this pen with me. And if you observe that when I supply to it little amount of heat to this particular polyethylene pen, then you may see that there is some flexibility and thereafter if you supply if I carry on this particular heating treatment, then one stage will come when this particular polymer will try to flow.

So, this is the phenomena is attributed to the chain. Now, when I supply the heat to this entangle chain then these chains are trying to align themselves. And that is the critical point. And the critical point is related to the flowing characteristics of this this polymer. Now, when they start the flowing or they acquired some flexibility or they acquire some rubbery type of thing, that particular temperature is called the glass transition temperature.

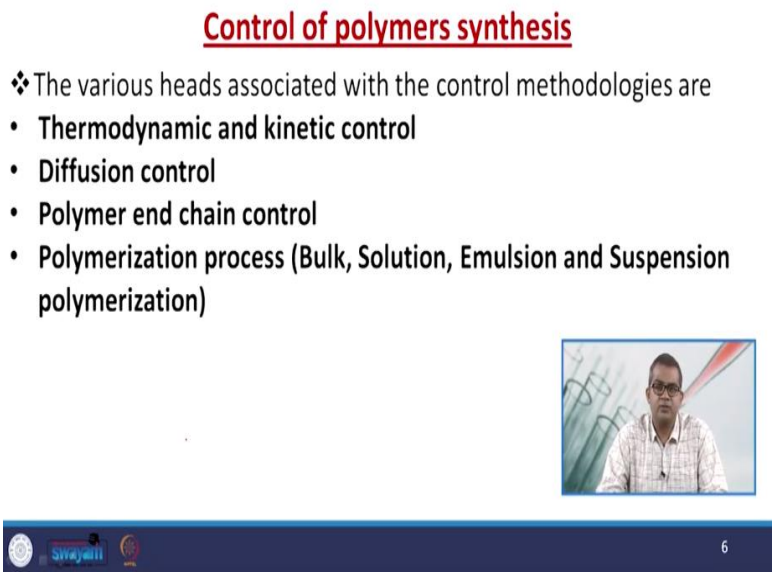
Now, remember when we try to correlate the things with the help of molecular weight, because the if you are having the larger molecular weight then there may be two possibilities one is that you are having the larger sized chains and second is that you may have a some medium or a small sized number of chains on the larger segment. So, in that case in both the cases, this glass transition temperature plays a very vital role.

So, this glass transition temperature attributes to the property of the molecule, property of that particular polymer. So, larger the molecular weight it is having the greater impact to the glass

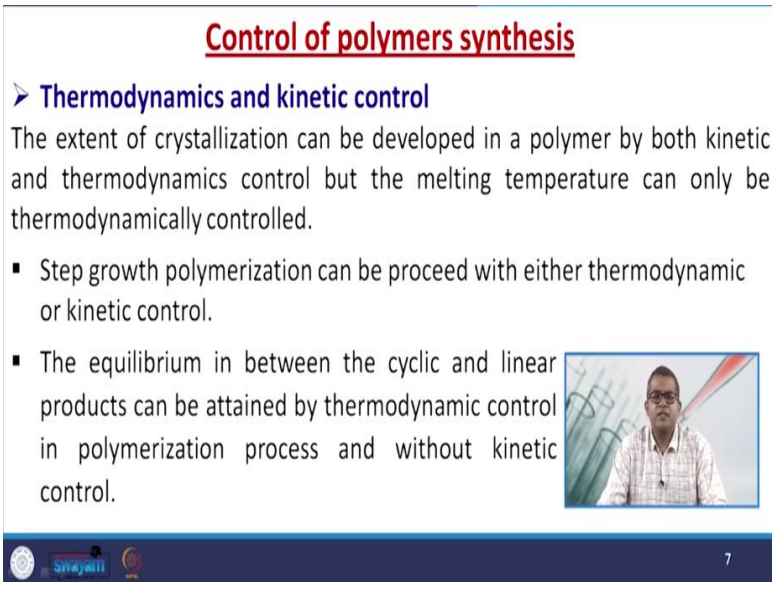
transition temperature. Apart from this, there are other chemical, thermal and mechanical properties, which also play a very vital role by deciding the properties of the polymer. So, therefore, there is an utmost need to control the polymer synthesis.

During the process of this control, we already discussed that there are couple of factors which we need to encounter and there are need of a different type of control methodology during the process. Now, let us have a look about those kinds of methodologies like thermodynamic kinetic control, diffusion control, etcetera.

(Refer Slide Time: 11:50)



(Refer Slide Time: 11:52)



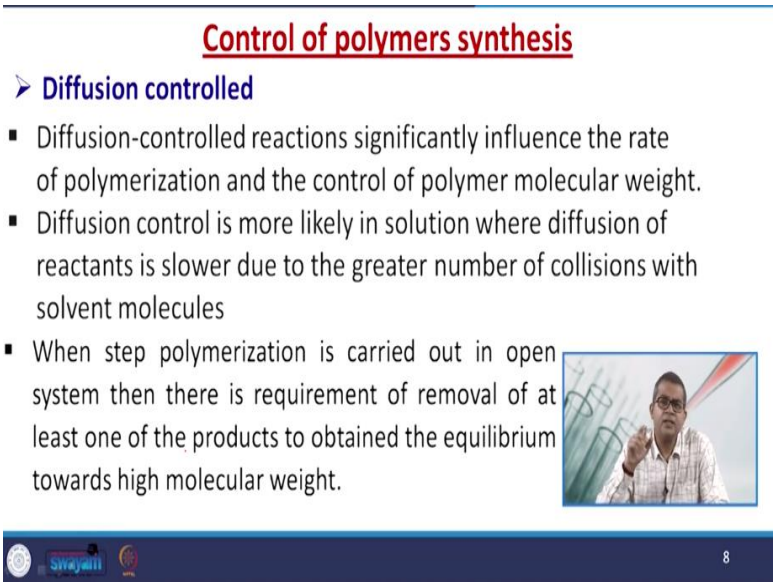
So, let us have a first thing into consideration that is the thermodynamic and kinetic control. Now, the extent of crystallization because polymers they may have a crystal or amorphous

structure, we will discuss this particular approach sometimes later. So, the extent of crystallization this can be developed in polymer by both kinetic and thermodynamic control.

But the melting temperature can only be thermodynamically controlled. So, we discussed this melting temperature issue couple of slides back. So, when we talk about the step growth polymerization that can be processed associated with either thermodynamic or kinetic control. Now, equilibrium in between the cyclic or a linear product can be attained by the thermodynamic controlling polymerization process and without kinetic control.

So, there is a slight difference between the thermodynamic and kinetic control. Now, if you recall in the last lecture, we discussed about the formation of cyclic and sometimes the ring opening of these monomers to form some branched chains, some linear polymer etcetera. So, this type of approach the thermodynamic control approach is extremely important in this consideration.

(Refer Slide Time: 13:17)



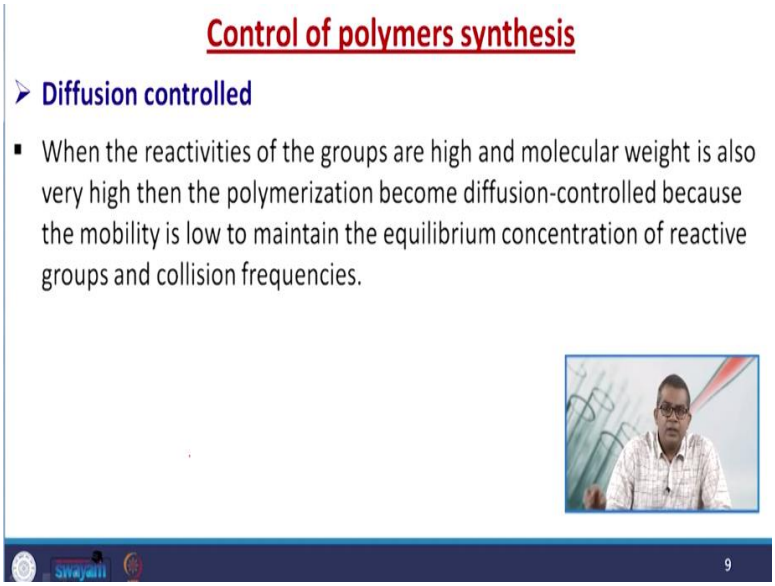
And other is the diffusion control. Now, diffusion-controlled reactions they significantly influence the rate of polymerization and the control of molecular weight. So, when we talk about the molecular weight control, then you cannot overlook the importance of this diffusion control. Now, diffusion control is more likely in the solution where the diffusion of reactant is slower due to the greater number of collisions with the solvent molecules.

Sometimes you may need to incorporate several solvent molecules for the processing or the for the polymer synthesis. So, this phenomenon is extremely useful while taking such kind of

situation into cognizance. So, whenever you carry out the step growth polymerization in an open system, then there is a requirement of a removal of at least one of the products to obtain the equilibrium towards high molecular weight.

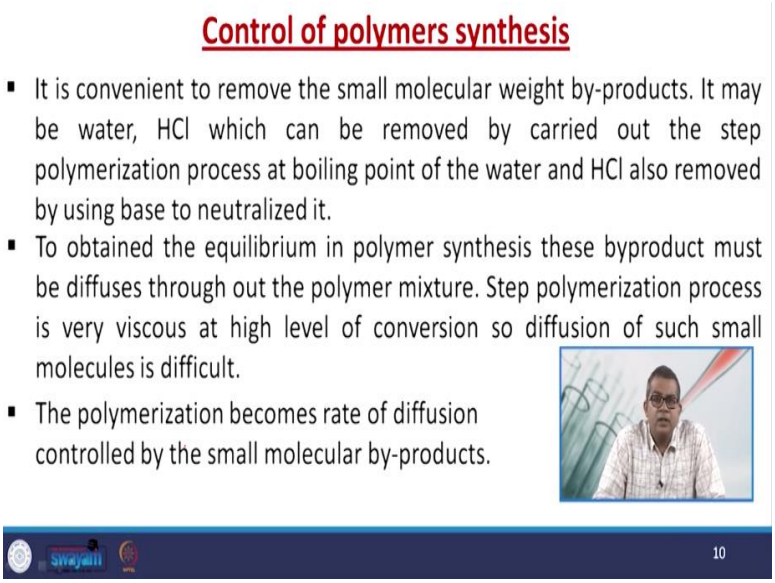
We discussed this thing in the formation of nylons. So, you need to remove one of the products to carry out the proper efficiency of that particular step growth polymerization reaction. So, this particular approach is extremely important in that kind of polymer synthesis.

(Refer Slide Time: 14:35)



Now, when the reactivity is of the group, they are high and molecular weights are also very high, then the polymerization process becomes diffusion control. Now, because the mobility is low due to the maintenance of equilibrium concentration of various kinds of reactive groups and collision frequency. So, these two phenomena are again you can see the governing factor while we discuss about the diffusion control.

(Refer Slide Time: 15:11)



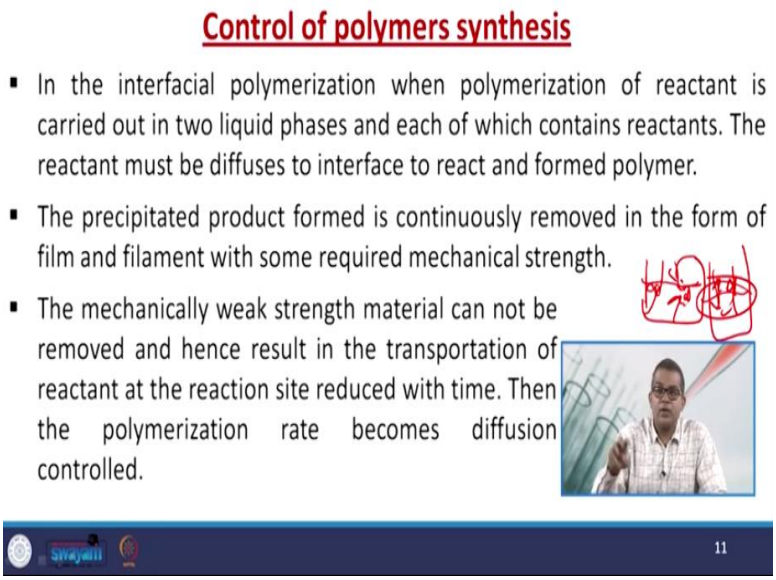
Now, it is convenient to remove the small molecular weight by product because sometimes because of the operational difficulty, the heavier product, sometimes it will be very difficult to remove from the reaction mass. So, if you recall the nylon synthesis just take the example of this nylon synthesis maybe water HCL which can be removed by carrying out the step polymerization process at boiling point of water.

Similarly, HCL also be removed by using base to neutralize it so that depends on the byproduct which you require to remove from that particular reaction mass. So, it is very convenient thing to make equilibrium in your favorable situation. Now, to obtain the equilibrium in various kind of a polymer synthesis these byproducts must be diffused throughout the polymer mixture.

Now, instead if you take the example of a ester growth polymerization process, this is usually very viscous at high level of conversion. So, you can say the diffusion of such a small molecule is sometimes very difficult. So, you need to adopt some more methodology to carry out this particular type of diffusion approach.

Now, the polymerization becomes rate of diffusion control by small molecule byproduct is a usual phenomenon in chemical reaction engineering. And that is why sometimes it is called the rate governing step. So, how much water or how much HCL you are removing from that particular system that becomes the rate of diffusion control.

(Refer Slide Time: 17:08)



Now, sometimes in the interfacial polymerization, when polymerization of reactant is carried out in two liquid phases, and each of which contains the reactant, the reactant must diffuse to interface to react and form the polymer. Just a small you can say, I am giving you a small diagram. Now, here there are two types of things in the liquid phase. So, any of these cases must diffuse to this interfacial thing so that they can react to each other and they carry out the desired polymerization process.

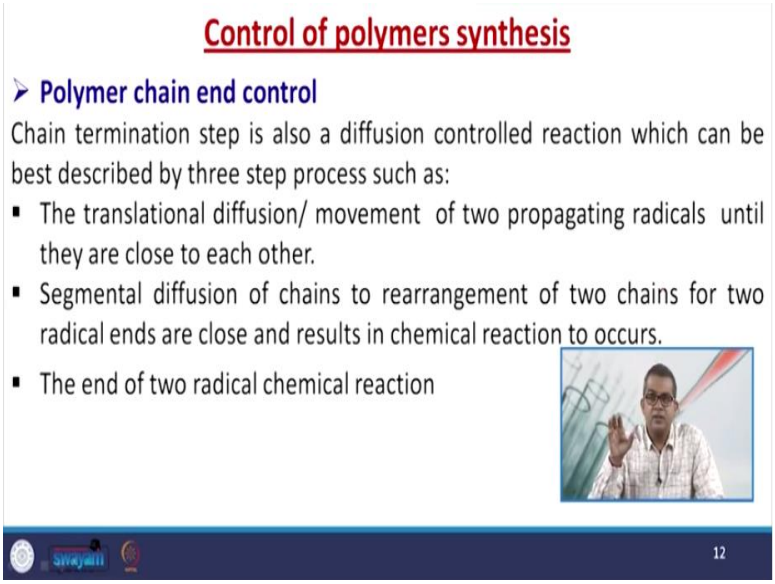
Whenever, because when they are carrying out the polymerization process, so, you may get the precipitated product. So, the precipitated product formed usually is continuously removed in the form of maybe in the form of film or maybe in the form of some other gel type of structure. And the filament of some other things may require certain mechanical approach.

And this may carry certain type of mechanical strength whenever they form in this particular type of interfacial polymerization. Sometimes, you may experience the mechanically weak strength material. So, the mechanically weak strength material cannot be removed easily. Hence, the result in the transportation of a reactant at the reaction site reduced with the time.

See, again just I am giving another thing like here you are performing the polymerization reaction and you are not able to remove the product. In that case, this product may create the hindrance of reactant and sometimes it may create a problem. So, the reaction side they are sometimes reduced with the time and thereby, there may be some difficulty in the polymerization reaction. And that particular type of polymerization rate becomes diffusion control.

Now, another approach is the polymer chain and control. Now, we always know that the termination is an integral part of our polymerization process. As you recall that there are all polymerization processes are three step process, initiation, propagation and termination. So, whenever you achieve the desired result, it is the utmost responsibility of any engineer is to truncate the reaction at this at that particular juncture so that it cannot proceed further so that you can have the desired property in your system.

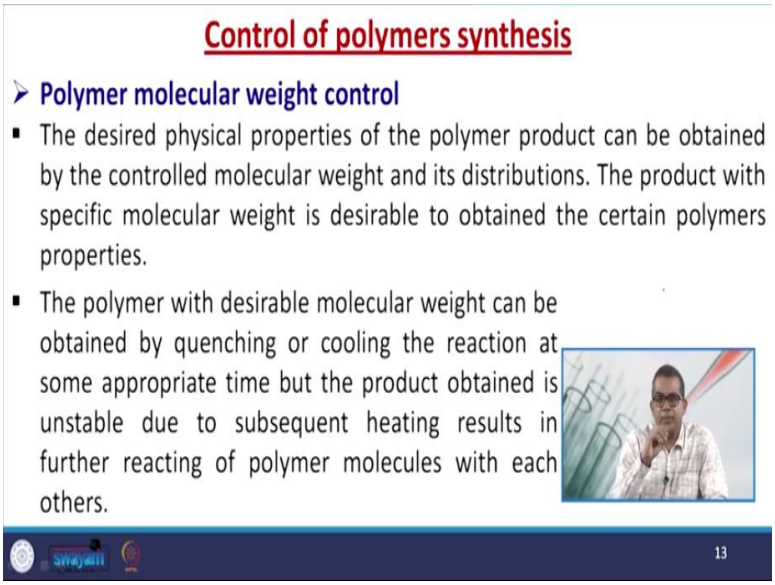
(Refer Slide Time: 20:07)



So, the chain termination step is usually termed as the diffusion control reaction, which can be best described by the three processes. Let us have a look of these three processes step processes. One is that the translational diffusion movement of two propagating radicals until they are close to each other. Second one is the segmental diffusion of chain to rearrangement of two chains for two radical ends and closed and result in the chemical reaction to occur.

The third one is that end of two radical chemical reactions so that you can truncate the things as per the reaction proceeds. Another good approach is to have the polymer molecular weight control.

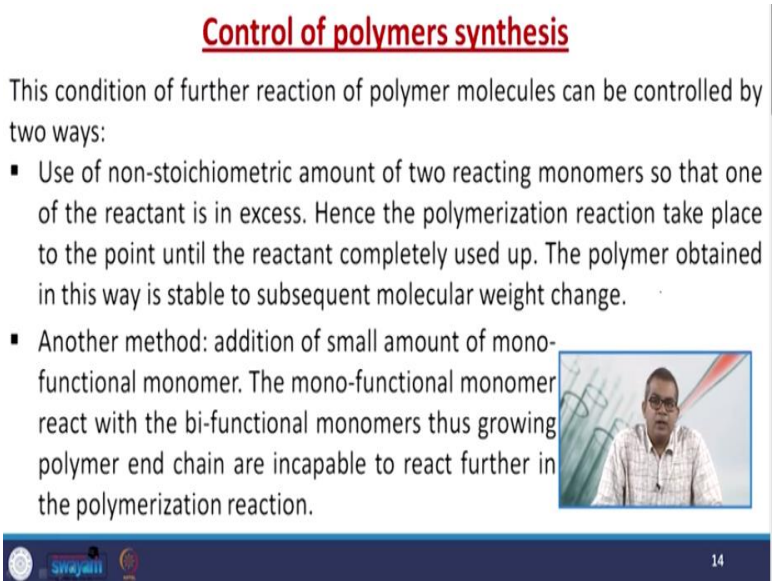
(Refer Slide Time: 20:58)



Now, this is again very important, because continuously we are discussing the importance of the molecular weight and in situ different type of properties are attributed to this molecular weight. Now, the desired physical properties of polymer product usually can be obtained by the controlled molecular weight and its distribution. So, this is having a very important step in the polymer synthesis.

The product with the specific molecular weight is desirable to obtain the certain polymer properties. Sometimes the polymer with the desirable molecular weight, it can be obtained by the quenching or cooling the reaction at some appropriate time. But the product obtained is usually unstable due to the subsequent heating result and in further reacting of the polymer molecules with each other. So, this is one of the best methodology to control the polymeric molecular weight.

(Refer Slide Time: 22:02)



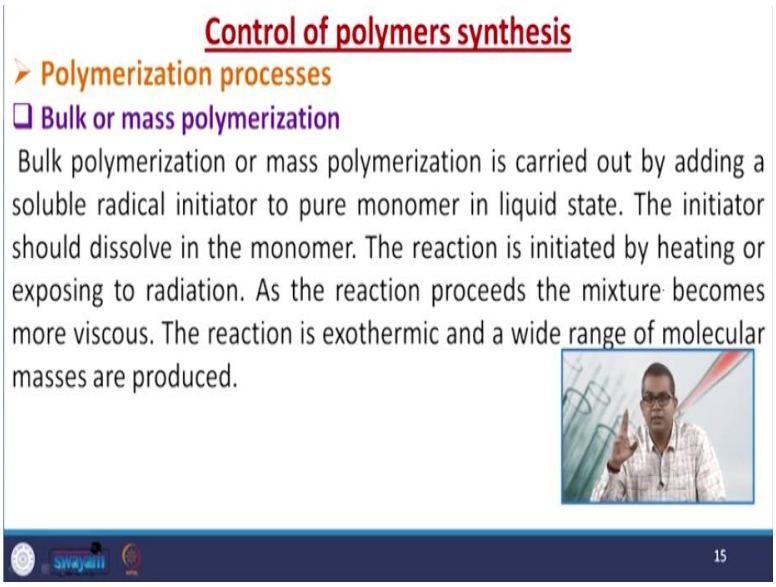
Now, this condition usually is further reaction of polymer molecule. This can be controlled by two ways. One is either you use the non-stoichiometric amount of two reacting monomer so that one of the reactant may be in excess. It is a very common phenomena in reaction engineering. Now, the polymerization reaction takes place to the point until the reactant completely used. So, that is you can say this is a very common phenomena and let it go policy.

The polymer obtained in this way is stable and subsequent molecular weight stable to subsequent molecular weight chain. The reason is that all the reactive molecules, all the reactive sites are exhausted. So, they cannot proceed further for any kind of polymerization reaction and that is why the molecular weight usually does not change. And other protocol is that additional addition of a small amount of mono functional monomer.

Now, this mono functional monomer reacts with those kind of a bi functional monomer thus growing polymer end chain. They are incapable to react further in the polymerization reaction. So, you can say these two methodologies are very much useful for the termination step of polymerization process so that you can control the molecular weight. You can control the chain size so that they this particular protocol does not affect any kind of adverse properties of the polymeric system.

Now, in this segment, last control methodology is obviously, the polymerization process. Now, you can say these are having the certain segments; one is the bulk or mass polymerization.

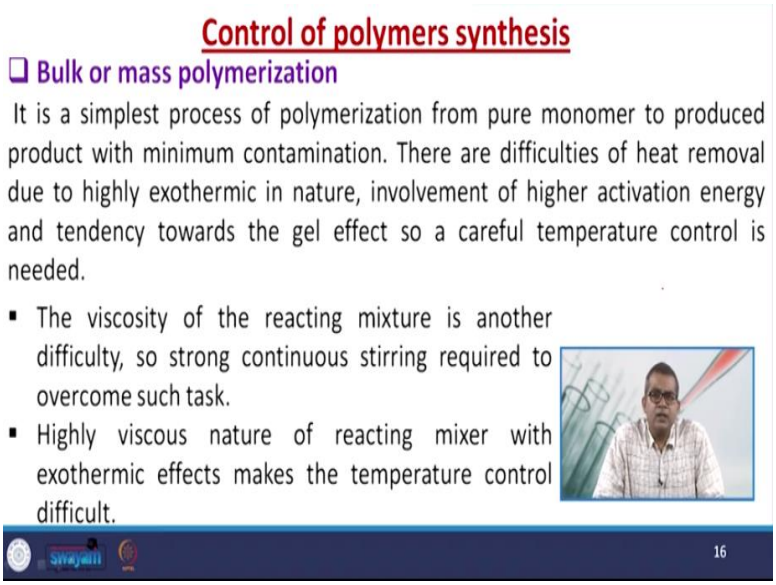
(Refer Slide Time: 24:01)



The bulk polymerization or mass polymerization is usually carried out by adding a soluble radical initiator, recall initiation, propagation and termination. So, addition of soluble radical initiator to the pure monomer in liquid phase, now, the initiator should dissolve in the monomer usually the reaction is initiated by heating or exposing to radiation etcetera. Now, as the reaction proceeds, the mixtures become more and more viscous.

So, this reaction is obviously, this reaction is in exothermic approach and a wide range of molecular masses are produced. So, you will have again a broad spectrum of molecular weight distribution. Sometimes this is a very useful thing.

(Refer Slide Time: 24:54)



Now, this bulk polymerization process is simplest process of polymerization from pure monomer to produced product with a minimum contamination. Now, there are various difficulties of heat removal due to the highly exothermicity in the nature and you will have to be very precise may be attributed to the cooling channels cooling coils etcetera. Now, since this is having a very high exothermicity in the nature, there may be an involvement of higher activation energy and tendency towards the gelation or gel effect.

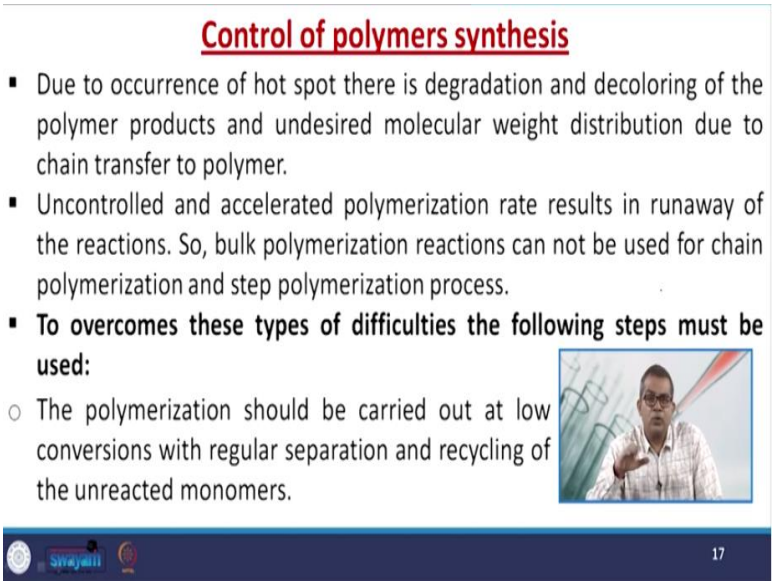
So, the careful temperature control is always desirable for this particular type of polymerization process. The viscosity of the reacting mixture is another difficulty. Therefore, the strong continuous stirring is required to overcome such task and that is why if you carry on this particular polymerization process, sometimes it may require more and more electrical energy or more and more energy input for to carry out this stirring process.

And now, highly viscous nature of reacting mixture with the exothermic effect makes the temperature control extremely difficult. Now, whenever you perform such kind of a polymerization thing, then you have to be very precise because you are dealing with the two major approaches one is viscosity and second one is the exothermicity of the reactant mass.

Now, the viscosity because viscosity is continuously increasing, that is why the proper distribution of the temperature within the reaction mass is extremely difficult and that is why you need to put more and more stirring effort in the reaction mass. Now, there may be a chance of development of hot spots within the reaction mass so that due to this occurrence of hot spot, there may be a degradation or declaration of the polymer product and undesired molecular weight distribution may be attributed due to the chain transfer to polymer.

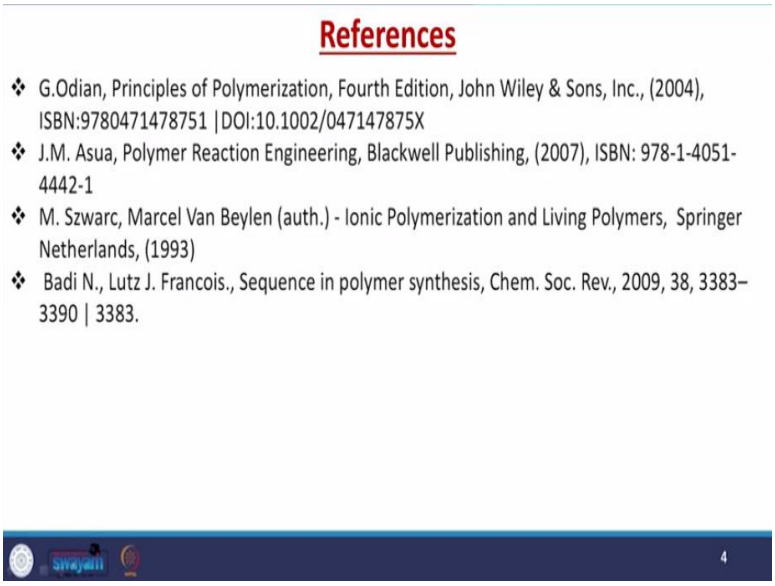
Now, uncontrolled and accelerated polymerization rate sometimes results in a runaway type of thing. Because, see this type of reaction are temperature sensitive as well as the viscosity.

(Refer Slide Time: 27:29)



So, bulk polymerization reaction because of this particular shortcoming the bulk polymerization reaction cannot be used for the chain polymerization and step polymerization process. Now, to overcome these types of difficulties, there are various steps need to be used. One is that polymerization should be carried out at low conversions with our regular separation and recycling of unreacted monomers. Therefore, the precise control is essential.

(Refer Slide Time: 27:58)



So, in this particular lecture, we discussed about the brief discussion about the control methodology. And we discussed about what is the importance of these controlled methodologies in the polymer system. And we took one example of bulk polymerization to explain the things in this direction. In the next lecture, we will try to explain this control methodology with the help of solution polymerization. Thank you very much.