Polymers: Concepts, Properties, Uses and Sustainability

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Week 9
Polymer Processing and Recycling Techniques

Lecture-67
Polymerization reactors

Hello everyone, we continue with our ninth week of lectures. We are looking at polymer processing and recycling techniques. In this course on polymers which is covering different facets related to polymeric materials. As we discussed several aspects of processing of polymers and recycling, polymerization is an important aspect. And so let us look at the manufacturing of polymers itself especially from the point of view of mode of polymerization or process of polymerization.

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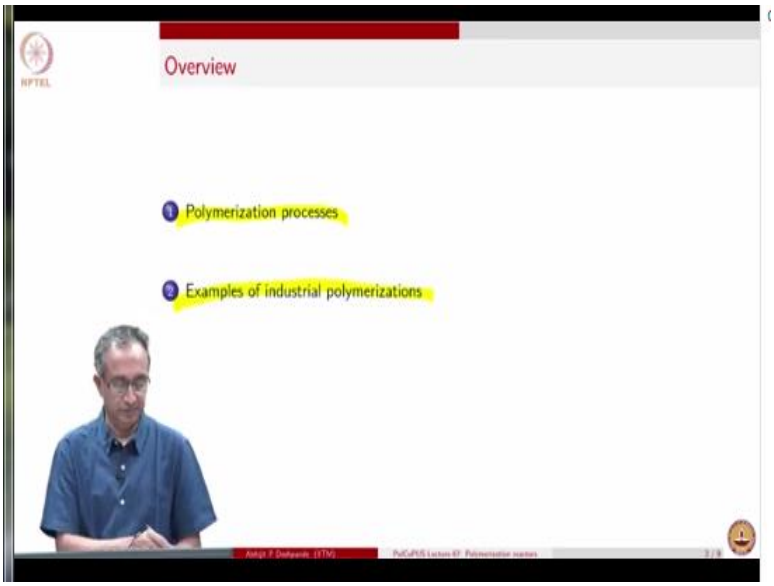

And so the focus will remain on what are the commercial set of processes which are used in case of many important polymers. So, we look at what are these different polymerization processes and look at some of the examples of industrial polymerizations.

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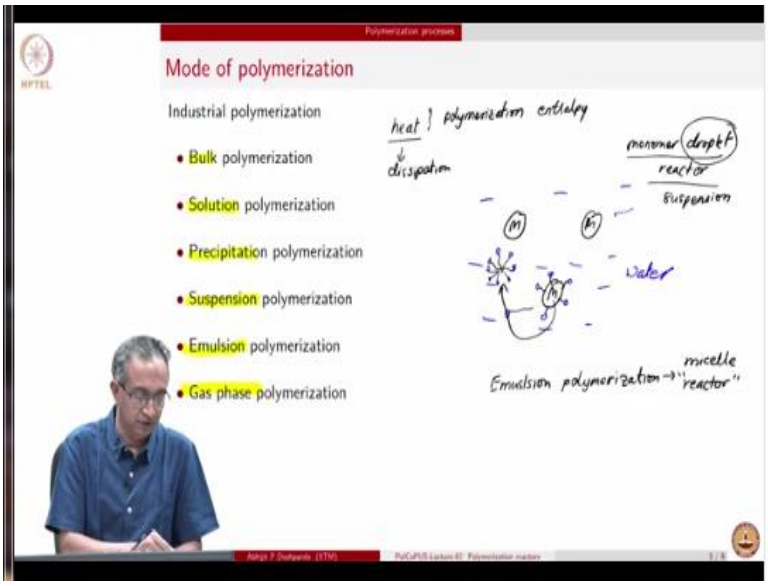

So, largely when we look at the set of polymerization processes which are used in industry they are bulk polymerization or it is also referred to as the mass polymerization. Basically monomer is taken along with initiator; let us say if it is a free radical polymerization. And then reaction is carried on and there is no solvent, there is no other medium, so that is why it is called bulk polymerization.

This is a solution polymerization where solvent is added. So, in some sense bulk polymerization also there is a solution, the solution of polymer in monomer because it starts with monomer and initiator and or monomers which are reacting. And then slowly molecular weight builds up but this is still a single phase mixture in case of bulk polymerization. In second case also but we have a third component which is called the solvent. So, we have monomer, initiators or other catalysts or whatever the case maybe and also the polymer which is being forming due to the reactions but then the third component is solvent. In case the polymer is not soluble beyond a certain molecular weight quite often this is the case when we have let us say a semi crystalline polymer. So, then there will be crystallization, polymer would crystallize out.

Or polymer solubility depends on the molar mass and so beyond a certain molar mass the polymer may precipitate out. So, in that case polymerization occurs till a certain molar mass is reached and then precipitation happens. So, we can get basically particles in this precipitation polymerization. Very similar is the case in case of suspension and emulsions also. In both cases we prepare monomer and solvent which is let us say water, so monomer and water mixture is prepared. Since monomer is not soluble in water what we get is a in emulsion, so monomer

droplets are distributed. So, what we have is monomer droplets which are distributed. And then surrounding is a medium, solvent medium but it is not really solubilizing the monomer itself. And now the droplets act as reactors, so each and every droplet reaction can happen. So, if monomer droplet acts as a reactor then we call it suspension polymerization.

We can also prepare this emulsion as it is called because when one phase is distributed in another we refer to it as emulsion using a surfactant molecule. And so, if we use a surfactant molecule which has let us say head group which is water loving and then a tail group which is monomer loving, then what happens is many of these quantities will basically go and adsorb on the monomer droplets. But we can add this surfactant molecule in larger quantities, so that we also get what are called micelles. And in emulsion polymerization it is the micelle which is the reactor or reaction happens in the micelle. So, what needs to happen is monomer has to go through the sparingly soluble monomer that will be in water, it will go from the droplet phase to the micelle. Now can you think, why would this be advantageous compared to the monomer as a droplet reactor?

So, the answer to this lies in the fact is how effectively when we create an emulsion of monomer in water, how effectively can we control the size of that droplet? Because remember once the reaction happens in the droplet itself, the size of the droplet will determine the final polymer particle size that we get. And if let us say our droplet distribution is not very effective, we have wide ranging sizes then eventual polymer particles will also have wide ranging sizes. However in case of emulsion the micelle is where the reaction happens and the total amount of surfactant can give you basically the size which is related to the micelle and number of micelles are determined based on the overall amount of surfactant added. So, therefore we have a much better control on the sizes of the final particles that we get. So, many of the polymers multiple operations are possible and then depending on the history of that particular industry or depending on the R&D history one or the other method is used.

Whenever there is a catalyst involved and there is a heterogeneous reaction, where the monomers adsorb on a catalyst surface and then polymer grows, we have the gas phase polymerization. In all of this an important component is related to heat and dissipation of this heat and I am sure all of you can immediately recognize that this comes because of polymerization enthalpy or enthalpy of polymerization or heat release due to polymerization.

And this will lead to a temperature increase and so an effective polymerization process or an effective mode of polymerization will ensure that this heat gets dissipated. In bulk polymerization there is a significant problem because as monomer starts becoming polymer the viscosity increases quite a bit, then our mixing capability reduces. And if mixing is not proper then what happens is polymerization proceeds even more rapidly, temperature rise happens even more quickly and then therefore there is a possibility of hotspots. And if such heterogeneities are there in a overall polymerization reactor, what we get is a very broad molecular size distribution. So, molar mass and it is control is not as effective in bulk polymerization as opposed to the other polymerizations. So, that is why each of these techniques is used depending on the processes involved.

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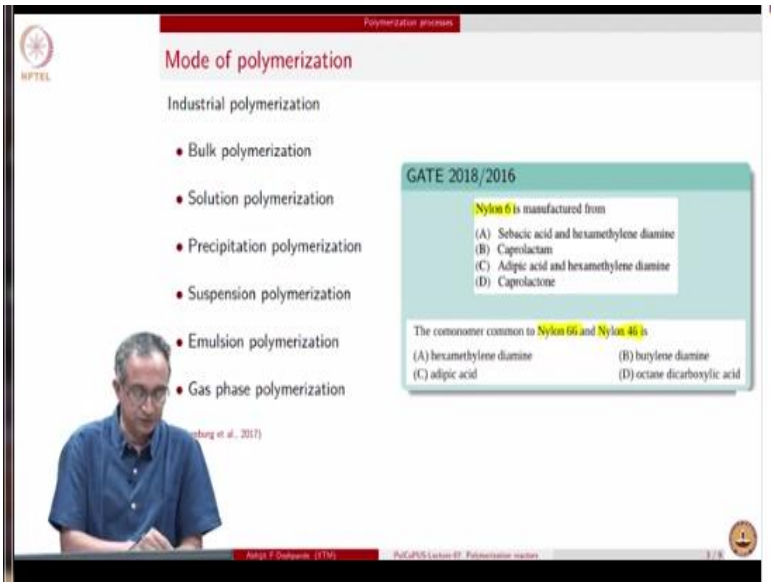

One of the aspects which we all should be familiar with is in terms of you know which monomers are used for which type of polymer. And this question tries to ask that for 2 different monomers in one case, nylon 66 and nylon 46 and then nylon 6 in another case. And it is related to what are the set of monomers that are used to produce these polymers on a bulk scale in industries. So, I am sure you can read through resources to try to figure out the answers to these questions.

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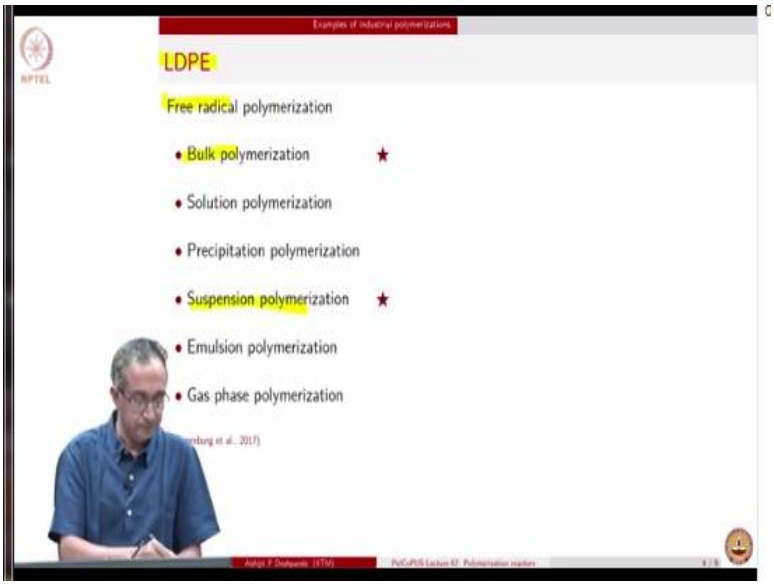

So, let us now survey quickly what are the modes of polymerization which are dominantly used when industrial scale polymers are manufactured. The first example that we will take is the low density polyethylene which is produced in very large quantities. And it is a free radical polymerization mechanism which is used and largely we use bulk polymerization and suspension polymerization for production of this.

So, the overall history of LDPE it is discovery and it is initial production all happened with the bulk polymerization, so therefore it is a still continued to this day. Suspension polymerization is better in the sense that heat dissipation is easy because of the presence of the surrounding medium in which the monomer droplets are distributed.

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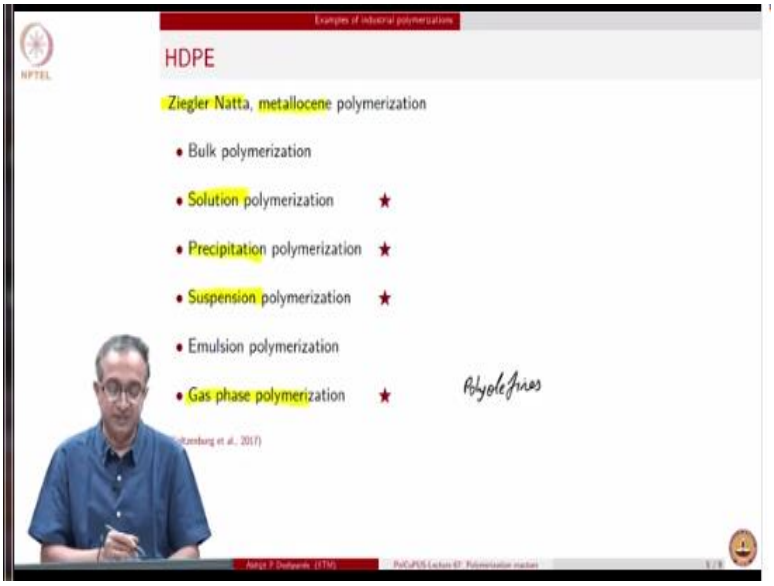

If you look at HDPE which is a polymer, which is possible because of the catalysts and the Ziegler Natta the historical catalyst as well as metallocene catalyst which have been around for the two decades. And the here you can see that the processes which are used are either solution or precipitation polymerization which has essentially the same set of processes. It is just that in precipitation polymerization, the polymer molar mass is significantly higher, so that precipitation happens. Also suspension polymerization can be used as to avoid the issues related to heat dissipation. However, the most common method these days for production of large quantities of HDPE and also polypropylene for example. So, large quantity of polyolefins these days are made using the catalytic route 2 polymerization. And we also have the fluidization technology which is very effective. In which case solid particles mixed with gas can be fluidized and the overall mixture behaves like a fluid.

And so you can mix and do a very effective control on concentrations and everything else in this fluidized gas phase polymerization process. And the amount of catalyst used is very small, so in fact for these very fine particles of catalyst can be used in very large amount of polymers can be produce this way. And given that it is a catalytic process, the control on branching or molar mass and all of that is very effective. So, that is why gas phase polymerization is the preferred route for polyolefins these days.

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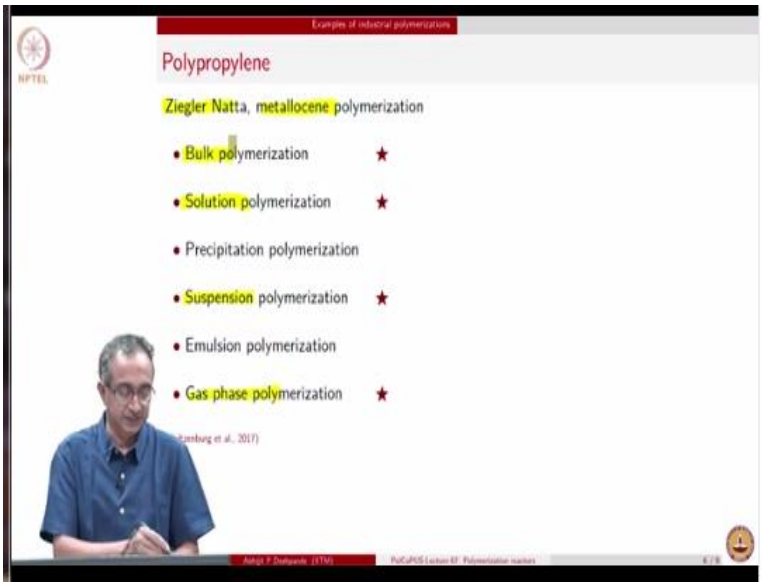

So, even for polypropylene therefore the gas phase polymerization is quite commonly used. So, if you just look at any survey and if you just let us say search for gas phase polymerization,

polypropylene, you will say that each major industrial house, each major company will say that they have processes which are related to gas phase polymerization of polypropylene. It can also like polyethylene be done using suspension or solution polymerization.Basically, these catalysts can be dispersed in a solvent and then solution or suspension polymerization can be done. And of course historically again like LDPE some of polypropylene can be made especially if the polypropylene is atactic it can be made using bulk polymerization techniques.

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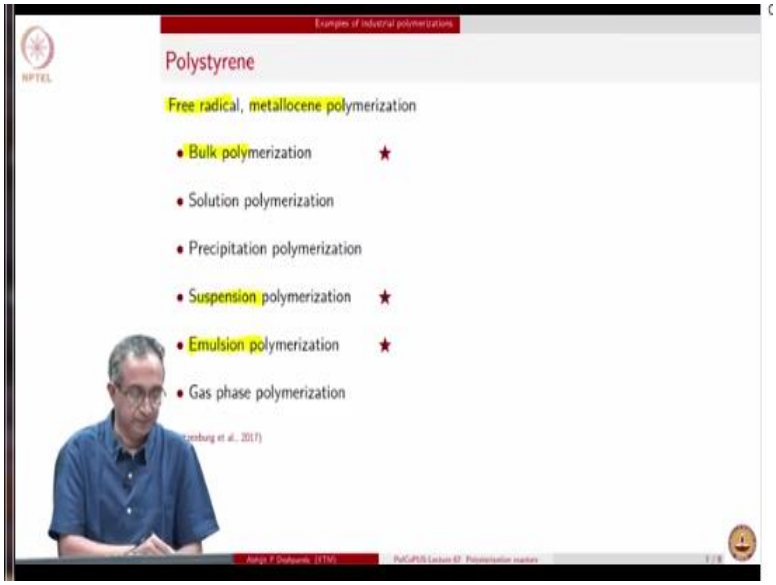

Polystyrene which is also one of the largely produced polymer, it is reaction can be free radical or also metallocene. In fact using metallocene we can also get tactic polymers, in the sense we can control the tacticity we can get syndiotactic or isotactic polystyrene. This was not possible prior to the discovery of metallocene catalyst, so generally therefore polystyrene is used as a commodity polymer.

But if you can make isotactic or syndiotactic the properties improve significantly. And again since currently amorphous polystyrene is the dominant product we use bulk polymerization and suspension polymerization. But lately more and more emulsion polymerization, so that we get an effective control on the particle size distribution of polymer particles that we get. Because in subsequent processing becomes quite easy even we have a very well defined particle size distribution for the polymer particles.

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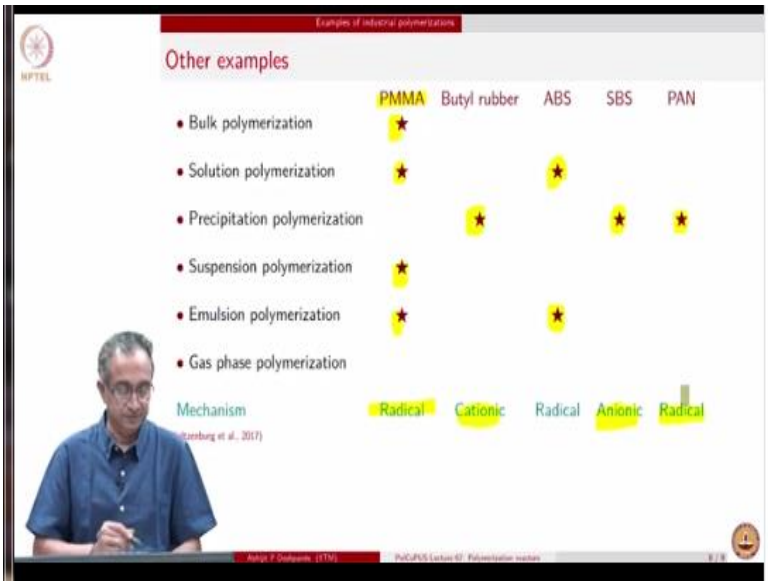

There are a few other examples polymers such as PMMA which is again free radical polymerization of methyl methacrylate and so poly methyl methacrylate again can be made using bulk solution, suspension and emulsion. So, you can see certain commonalities many of these free radical based polymers bulk polymerization solution and suspension polymerization are preferred routes. On the other hand butyl rubber which has a cationic polymerization mechanism, it is a largely produced using precipitation polymerization. acrylonitrile butadiene styrene which is again a terpolymer of these 3 different components, can be made either using solution or emulsion phase. But SBS which is anionic polymerization again is used precipitation polymerization for production of it.

Polyacrylonitrile which is again a CH_2-CH-CN it is a vinyl family of monomers and that can also be made using precipitation polymerization. So, why one is used over the other, sometimes the reason or historical sometimes for better control gas phase and emulsion polymerizations have been preferred over the traditional routes such as bulk and solution polymerizations.

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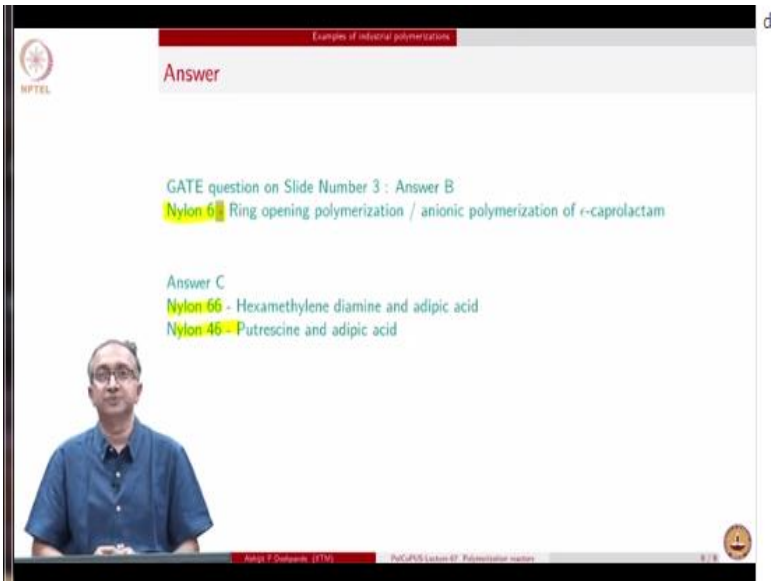

So, with this we come to close of this lecture which reviewed the polymerization processes that are available. And the question related to the exam which was based on you know what are the different monomers that are used for different set of nylons. I am sure you can get the information based on your knowledge or looking at the literature. So, with this we will close the lecture, thank you.