Introduction to Polymer Science
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Lecture - 16
Process Conditions, Emulsion Polymerization

Welcome back to this lecture 16. We will discuss different process conditions for synthesizing polymers and also talk about emulsion polymerization in little detail.

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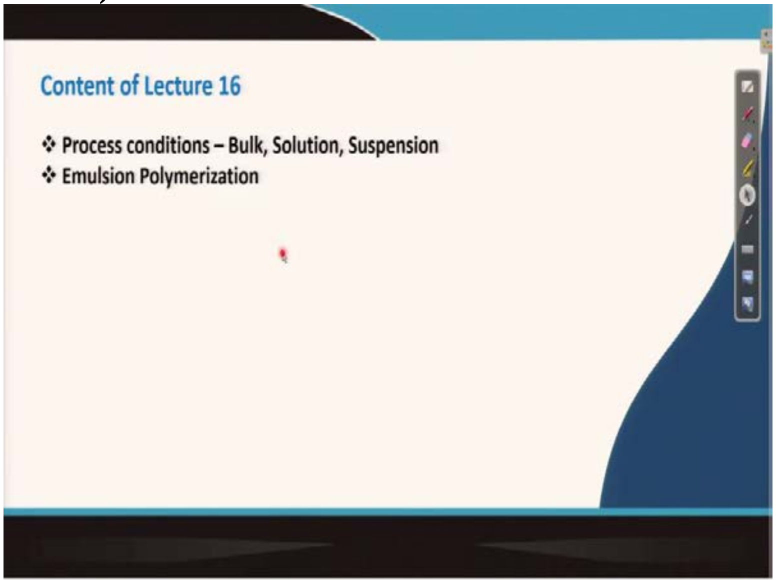

Content of Lecture 16

- ❖ Process conditions – Bulk, Solution, Suspension
- ❖ Emulsion Polymerization

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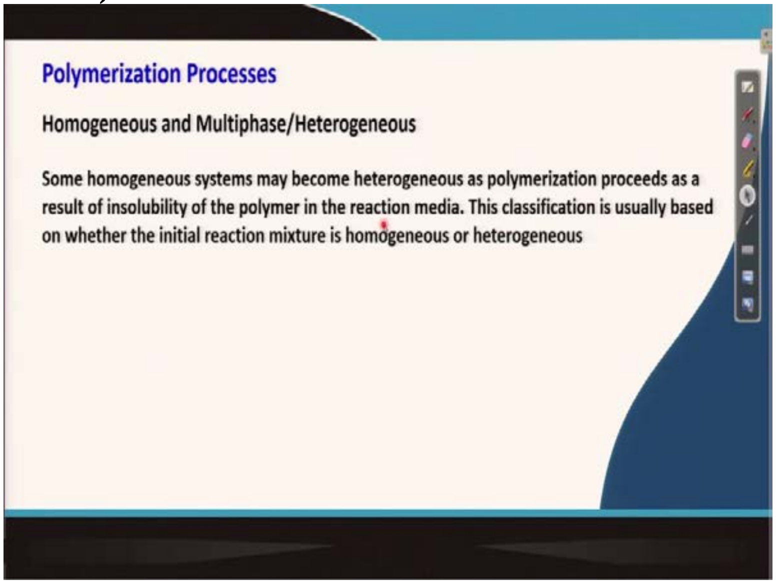

Polymerization Processes

Homogeneous and Multiphase/Heterogeneous

Some homogeneous systems may become heterogeneous as polymerization proceeds as a result of insolubility of the polymer in the reaction media. This classification is usually based on whether the initial reaction mixture is homogeneous or heterogeneous

We have learned how to synthesize polymers by radical chain polymerization. Now, in this lecture, we will learn about different polymerization processes. That is not restricted only to radical chain polymerization; rather any polymerization process can be carried out by the processes which we are going to discuss in this lecture. There could be 2 possibilities one is homogeneous, the second one is either heterogeneous or multi-phase.

Now, some homogeneous systems can become heterogeneous as the polymerization proceeds, because the resulting polymer may be not soluble in the reaction medium. As a result the polymer might get precipitated and the solution might become heterogeneous from homogeneous. Usually, we classify the polymerization process looking after the initial behavior or initial phase of the reaction mixture.

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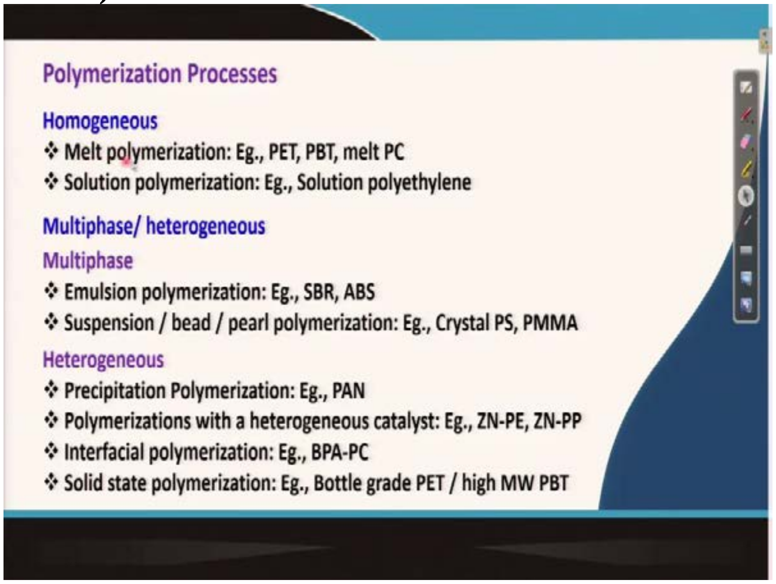

Polymerization Processes

Homogeneous

- Melt polymerization: Eg., PET, PBT, melt PC
- Solution polymerization: Eg., Solution polyethylene

Multiphase/ heterogeneous

Multiphase

- Emulsion polymerization: Eg., SBR, ABS
- Suspension / bead / pearl polymerization: Eg., Crystal PS, PMMA

Heterogeneous

- Precipitation Polymerization: Eg., PAN
- Polymerizations with a heterogeneous catalyst: Eg., ZN-PE, ZN-PP
- Interfacial polymerization: Eg., BPA-PC
- Solid state polymerization: Eg., Bottle grade PET / high MW PBT

Now, in homogeneous we can have melt polymerization or solution polymerization, in multiphase we can have emulsion polymerization, suspension, bead, or pearl polymerization. In heterogeneous, we can have this precipitation polymerization, polymerization with heterogeneous catalyst, interfacial polymerization, and solid-state polymerization.

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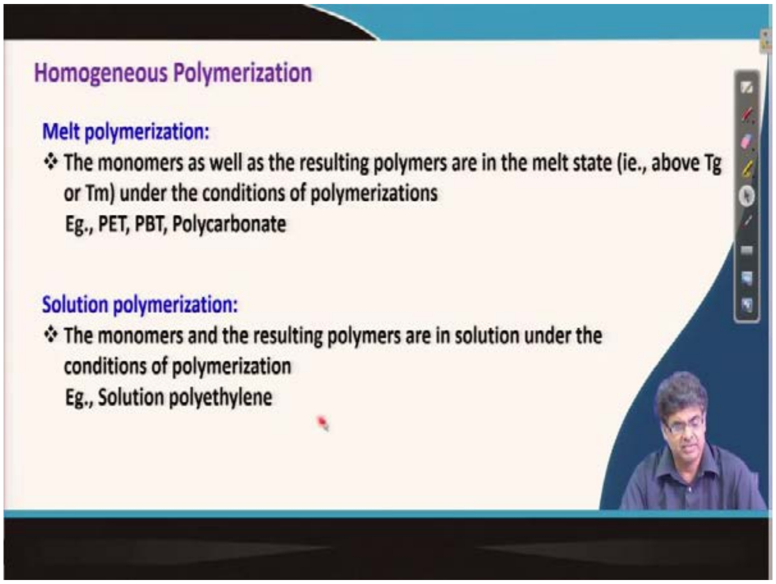

Homogeneous Polymerization

Melt polymerization:

- The monomers as well as the resulting polymers are in the melt state (ie., above Tg or Tm) under the conditions of polymerizations
  Eg., PET, PBT, Polycarbonate

Solution polymerization:

- The monomers and the resulting polymers are in solution under the conditions of polymerization
  Eg., Solution polyethylene

In melt polymerization, as the name suggests that the reaction is carried out in the molten state where monomers, as well as the resulting polymers, are in melt state that is, the resulting polymers are above their T_g (glass transition temperature) or melting point so that the polymer chains behave like a melt. For example, poly(ethylene terephthalate), poly(butylene terephthalate), polycarbonate are some examples. In solution polymerization, the monomer and the resulting polymers are soluble in the solvent and an example is solution polyethylene.

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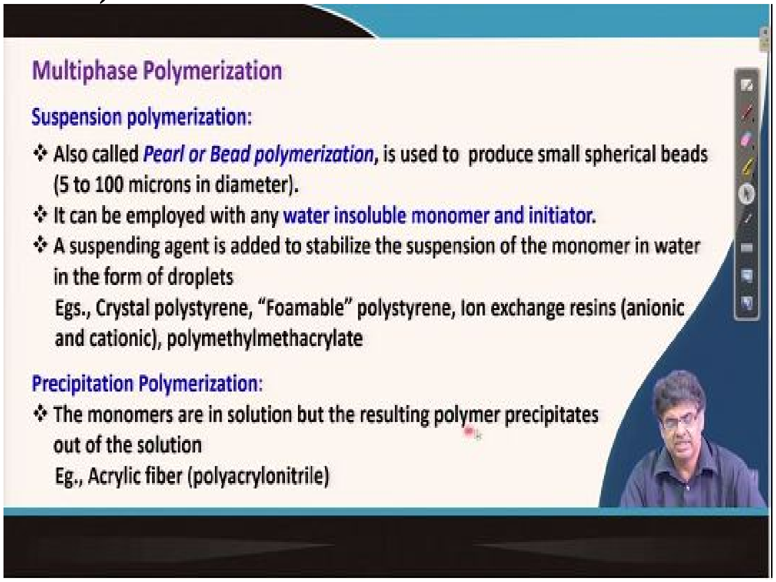

Multiphase Polymerization

Suspension polymerization:

- Also called *Pearl or Bead polymerization*, is used to produce small spherical beads (5 to 100 microns in diameter).
- It can be employed with any water insoluble monomer and initiator.
- A suspending agent is added to stabilize the suspension of the monomer in water in the form of droplets
  Egs., Crystal polystyrene, "Foamable" polystyrene, Ion exchange resins (anionic and cationic), polymethylmethacrylate

Precipitation Polymerization:

- The monomers are in solution but the resulting polymer precipitates out of the solution
  Eg., Acrylic fiber (polyacrylonitrile)

Similarly, for multiphase polymerization, we can have suspension polymerization, which is also called pearl or bead polymerization because the resulting polymer products become spherical beads that look like pearls. That is why sometimes these terms pearl or bead polymerization are used for this suspension polymerization. Now, it can be employed with any water-insoluble monomer and initiator. Both the monomer and the initiator are not soluble in the water, but the initiator is soluble in the monomer. The monomer and the initiator are suspended in the water phase by using suspending agents and also by vigorous stirring. These suspending agents could be surfactants or some water soluble polymers and the polymerization happens within the monomer droplets. Some of the examples, like crystal polystyrene, foamable polystyrene, ion-exchange resins which contain spherical cross-linked beads, and so on. Precipitation polymerization is where the monomers are in solution, but the resulting polymers precipitate out of the solution like acrylic fiber, like polyacrylonitrile.

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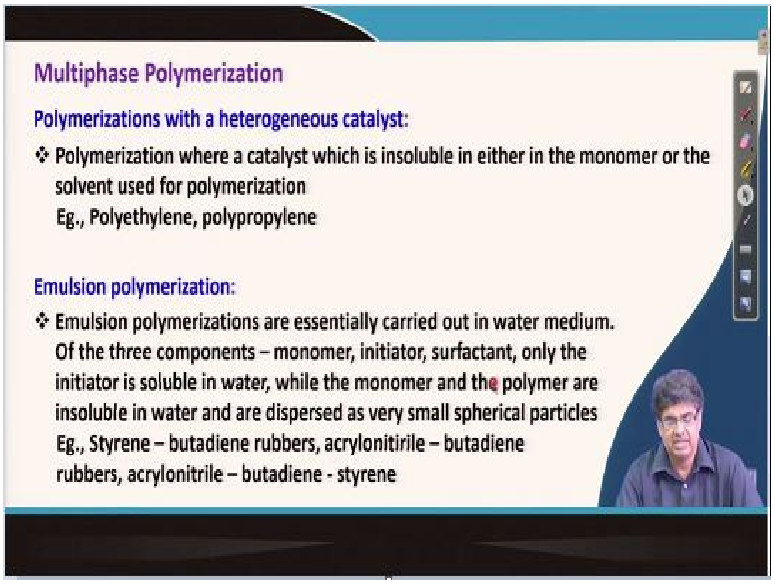

Multiphase Polymerization

Polymerizations with a heterogeneous catalyst:

- Polymerization where a catalyst which is insoluble in either in the monomer or the solvent used for polymerization
  Eg., Polyethylene, polypropylene

Emulsion polymerization:

- Emulsion polymerizations are essentially carried out in water medium. Of the three components – monomer, initiator, surfactant, only the initiator is soluble in water, while the monomer and the polymer are insoluble in water and are dispersed as very small spherical particles
  Eg., Styrene – butadiene rubbers, acrylonitirile – butadiene rubbers, acrylonitrile – butadiene - styrene

Now, in multiphase polymerization, polymerization occurs in presence of a heterogeneous catalyst and the catalyst is insoluble either in the monomer or in the solvent used in the polymerization. The catalyst remains as a separate phase altogether. So, that is why we call this heterogeneous polymerization or multiphase polymerization. We will discuss this in the next 2-3 lectures. We will talk about this synthesis of polyethylene or polypropylene by a multiphase polymerization reaction. We will talk in more detail about emulsion polymerization after some time. Emulsion polymerization is essentially carried out in a water medium and between the three components, monomer initiator, surfactant, only the initiator is soluble in water. We will discuss these in detail in a few minutes.

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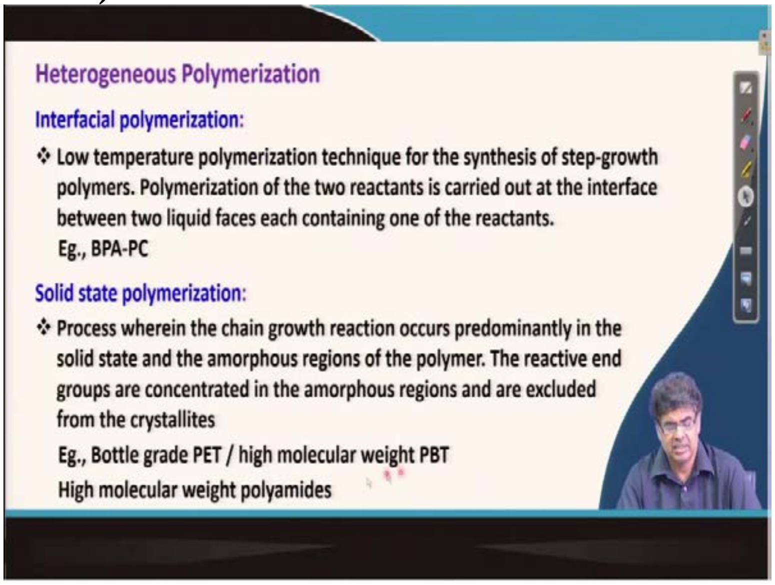

Heterogeneous Polymerization

Interfacial polymerization:

- ❖ Low temperature polymerization technique for the synthesis of step-growth polymers. Polymerization of the two reactants is carried out at the interface between two liquid faces each containing one of the reactants.
  Eg., BPA-PC

Solid state polymerization:

- ❖ Process wherein the chain growth reaction occurs predominantly in the solid state and the amorphous regions of the polymer. The reactive end groups are concentrated in the amorphous regions and are excluded from the crystallites
  Eg., Bottle grade PET / high molecular weight PBT
  High molecular weight polyamides

Interfacial polymerization is utilized for synthesizing step-growth polymers at a lower temperature. Usually, step-growth polymers are synthesized at higher temperatures because the rate of reactions is generally very high and we need very high conversion to achieve a meaningful molecular weight for step-growth polymers. However, we usually try to avoid high temperature during polymerization. It can be done using interfacial polymerization where polymerization of the 2 reactants is carried out at the interface between 2 liquid phases. For example, polycarbonate and methylene chloride are in the aqueous phase and organic phase. In the interface, the reaction happens and because we stir the reaction at a very high speed, there is a continuous generation of large interfacial area. That is the reason the reaction become much faster. For example, Bisphenol A polycarbonate.

Solid-state polymerization is a process in which the chain-growth reaction occurs predominantly in the solid state and the amorphous region of the polymer. The reactive end groups are concentrated in the amorphous region and are excluded from the crystallites. So, there is a chain growth happening, and the other side of the chain where the active chain is not present that becomes the crystallites and the chain ends becomes part of the amorphous region. Hence the reaction happens in the amorphous region and this is how solid state polymerization happens. Some examples are bottle grade polyethylene terephthalate, high molecular weight polybutylene terephthalate, high molecular weight polyamides, and so on.

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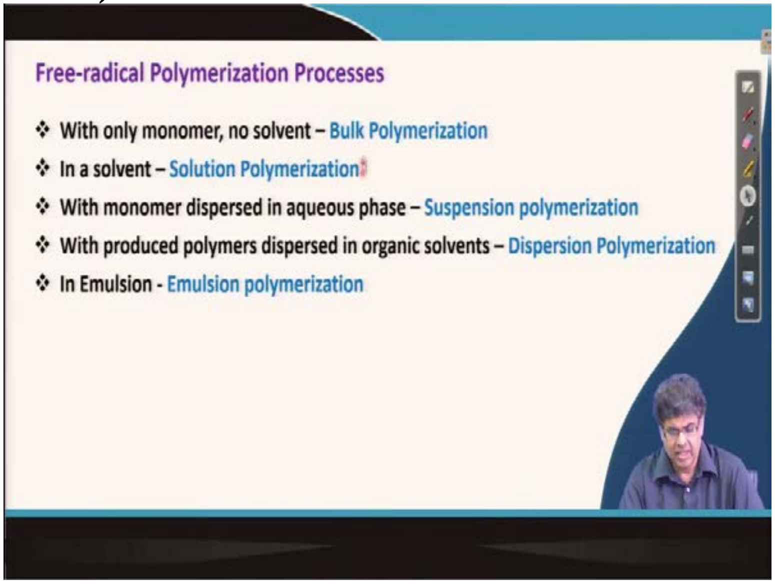

Free-radical Polymerization Processes

- With only monomer, no solvent – Bulk Polymerization
- In a solvent – Solution Polymerization
- With monomer dispersed in aqueous phase – Suspension polymerization
- With produced polymers dispersed in organic solvents – Dispersion Polymerization
- In Emulsion - Emulsion polymerization

Now, we will talk about the common processes which are used for free radical polymerization. When only monomer is present without any solvent then it is called bulk polymerization. So, in bulk polymerization, the initiator also gets soluble in the monomer. In a solvent, we get solution polymerization. When the monomers are dispersed in the aqueous phase we have suspension polymerization and if the produce polymers are dispersed in an organic solvent, then it is called dispersion polymerization while in emulsion, there is emulsion polymerization. We will discuss each of the benefits and the advantages and disadvantages of these 4 processes briefly and then go into slight detail about emulsion polymerization because this is one of the most important industrial processes of making polymers via free radical polymerization.

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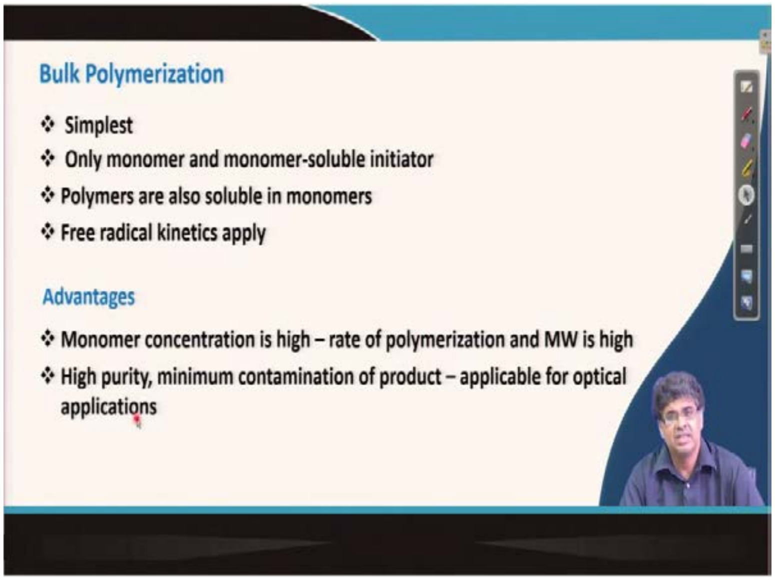

Bulk Polymerization

- Simplest
- Only monomer and monomer-soluble initiator
- Polymers are also soluble in monomers
- Free radical kinetics apply

Advantages

- Monomer concentration is high – rate of polymerization and MW is high
- High purity, minimum contamination of product – applicable for optical applications

In the case of bulk polymerization, as the name suggests, there is no other thing present other than the monomer and the initiator. So, this is the simplest method where only monomer and monomer soluble initiators are present. We have the reaction mixture where only the monomer and monomer soluble initiator are present and the produced polymers are also soluble in the monomer. The advantages are that the monomer concentration is very high and we have learned from our kinetic equations that as the monomer concentration increases, the reaction rate also increases as well as high molecular weight polymers are produced. As there is no other, ingredient other than monomer and initiator, the produced polymers are highly pure. So, these can be used as an optical grade where the applications deal with light, where the presence of even a very small amount of impurities is also very detrimental.

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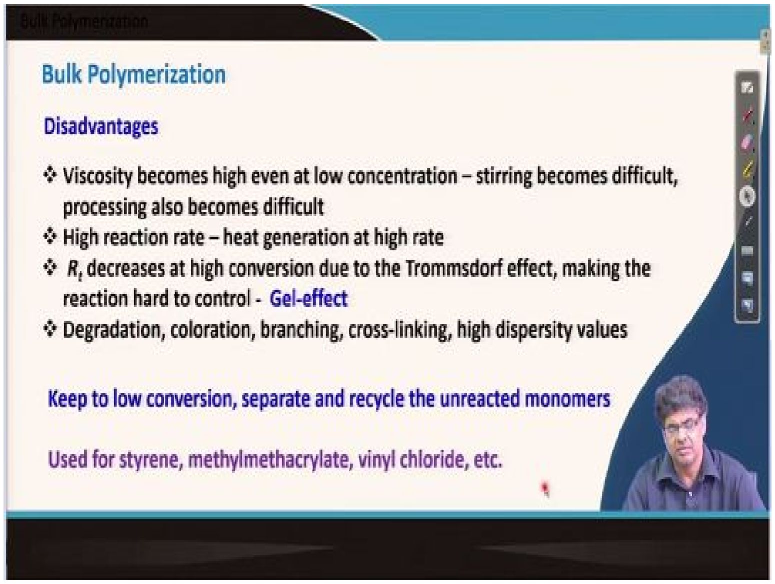

Bulk Polymerization

Disadvantages

- Viscosity becomes high even at low concentration – stirring becomes difficult, processing also becomes difficult
- High reaction rate – heat generation at high rate
- R_t decreases at high conversion due to the Trommsdorf effect, making the reaction hard to control - Gel-effect
- Degradation, coloration, branching, cross-linking, high dispersity values

Keep to low conversion, separate and recycle the unreacted monomers

Used for styrene, methylmethacrylate, vinyl chloride, etc.

Now, as the monomer concentration is very high there will be obviously some disadvantages associated with this process, e.g. viscosity becomes high even at low concentrations because there no solvent is present, and stirring becomes increasingly difficult. In this case, the reaction rate is high, and as we know that the polymerization reaction is an exothermic process, the heat generation also happens at a higher rate unless there is a very effective way of removing the generated heat from the reaction mixture. As a result, the generated heat will accumulate and it will produce high temperature locally and we get those complications like Gel-effect or Thomson effect. As the viscosity goes up, the polymerization becomes diffusion controlled. As we discussed in the last class that the long chain propagating radicals cannot diffuse at a high rate to come close to each other and terminate the chain. As a result, the termination becomes lower and we get gel-effect. As the temperature increases locally, degradation may happen that results in discoloration. Besides, branching and crosslinking may also happen and so the dispersity value also go up.

Now, what is practically done in an industrial process? The conversion is kept at a low value and the polymer products are taken out of the reaction mixture and then the polymerization process is restarted. So, we take out the produced polymer in batches from the reactor so that we do not go to that conversion level where the dispersity becomes high. This process is used for styrene methyl methacrylate, vinyl chloride, etc.

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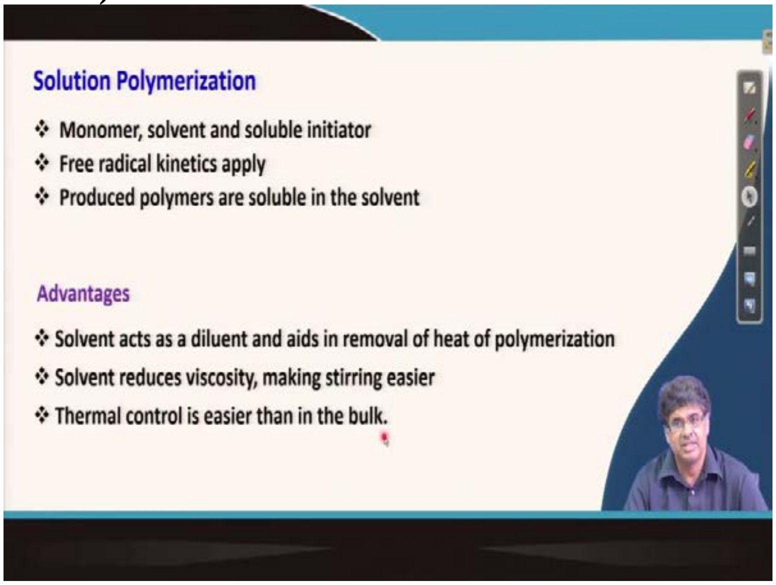

Solution Polymerization

- Monomer, solvent and soluble initiator
- Free radical kinetics apply
- Produced polymers are soluble in the solvent

Advantages

- Solvent acts as a diluent and aids in removal of heat of polymerization
- Solvent reduces viscosity, making stirring easier
- Thermal control is easier than in the bulk.

In the case of solution polymerization, the monomer, solvent, and solvent soluble initiator are present. So, we dissolve the monomer and the initiator in the solvent, and carry out free radical polymerization. The produced polymers are also soluble in the solvent. As the reaction is performed in the solvent, there are advantages e.g. the viscosity buildup we talked about for bulk polymerization does not happen here. So, solvent reduces the viscosity and making the stirring easier, and thermal control is easier than bulk. The solvent can act as a diluent and also helps in the removal of the heat of polymerization.

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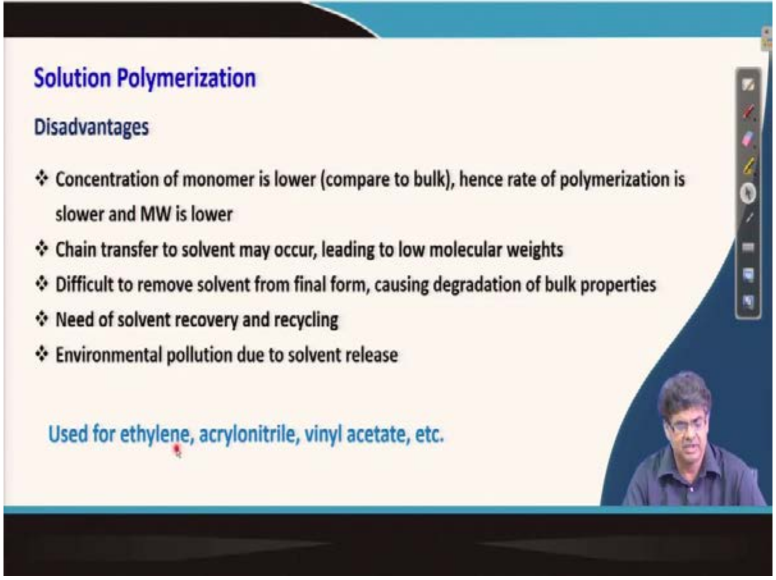

Solution Polymerization

Disadvantages

- Concentration of monomer is lower (compare to bulk), hence rate of polymerization is slower and MW is lower
- Chain transfer to solvent may occur, leading to low molecular weights
- Difficult to remove solvent from final form, causing degradation of bulk properties
- Need of solvent recovery and recycling
- Environmental pollution due to solvent release

Used for ethylene, acrylonitrile, vinyl acetate, etc.

The disadvantages because we are using solvent comes with itself. Several disadvantages like in most cases if it is an organic solvent, then there is a problem, environmental problem. You have to recycle the solvent and reuse the solvent preferably, but that may involve cost. Also, because the concentration of monomer is low as compared to bulk, the rate of polymerization and molecular weight is lower as we know from our kinetics of radical chain polymerization. One important thing is that chain transfer to the solvent may happen and as a result the molecular weight may come down. Sometimes it is difficult to remove the solvent from the final polymer product which causes the degradation of the bulk properties. Since you do not have pure polymer, you have solvent trapped, then it gives degradation of the bulk property of the resulting material and of course, as I discussed we need to recycle the solvent and recover the solvent as much as possible. Since we are using solvent, especially if you are using organic solvent, the environmental pollution due to the solvent release happens and these are used for some low molecular ethylene, acrylonitrile, vinyl acetate etc.

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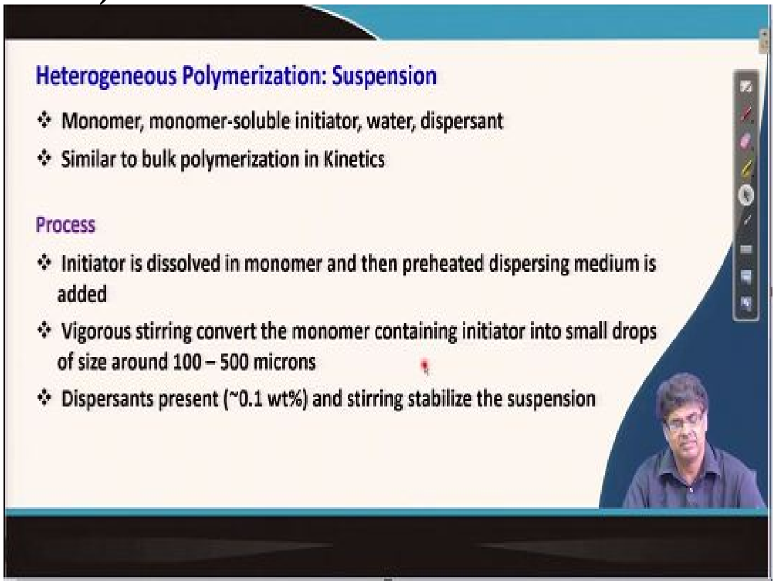

Heterogeneous Polymerization: Suspension

- Monomer, monomer-soluble initiator, water, dispersant
- Similar to bulk polymerization in Kinetics

Process

- Initiator is dissolved in monomer and then preheated dispersing medium is added
- Vigorous stirring convert the monomer containing initiator into small drops of size around 100 – 500 microns
- Dispersants present (~0.1 wt%) and stirring stabilize the suspension

Let us come to heterogeneous polymerization. Suspension polymerization: in this case we require monomer and monomer soluble initiator, water and dispersant. Basically this is like a bulk polymer, but instead of having the entire reaction container as a bulk, we are going to do the reaction in small droplets, that resembles numerous bulk reactors which are dispersed in aqueous medium. So, the kinetics will be similar as bulk polymer and initially, the initiator is dissolved in the monomer and then they are added to a preheated dispersing medium which is water, and vigorous stirring actually converts this monomer containing initiator into small droplets size around 100 to 500 microns and there are dispersed like surfactant or water soluble polymers or some othe component which basically stabilize this suspension, and this is aided by vigorous stirring. Once we heat the reaction in presence of, say, a thermal initiator, then the polymerization starts inside those droplets and as a result this is similar to bulk polymerization. In this case the monomer concentration is high but because we are doing in aqueous medium the heat generation can be removed quite effectively.

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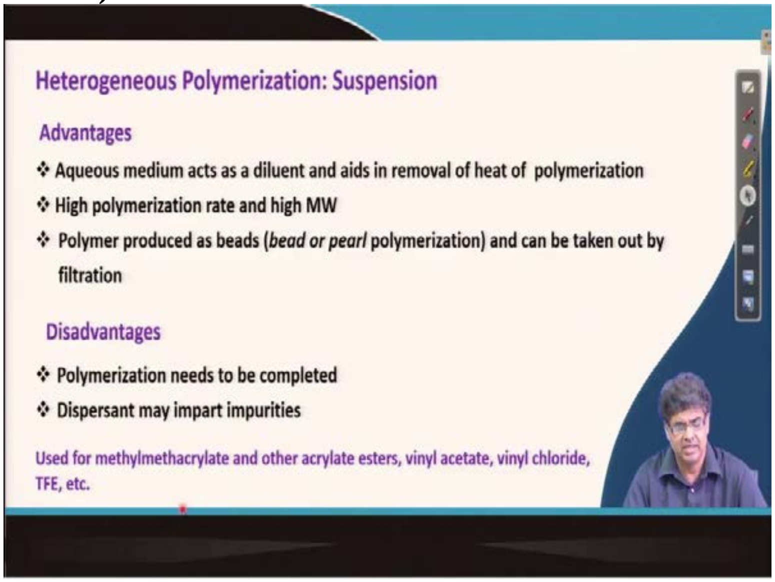

Heterogeneous Polymerization: Suspension

Advantages

- Aqueous medium acts as a diluent and aids in removal of heat of polymerization
- High polymerization rate and high MW
- Polymer produced as beads (*bead or pearl* polymerization) and can be taken out by filtration

Disadvantages

- Polymerization needs to be completed
- Dispersant may impart impurities

Used for methylmethacrylate and other acrylate esters, vinyl acetate, vinyl chloride, TFE, etc.

These are the advantages. We said that aqueous medium acts as a diluent and aids in removal of heat of polymerization, high polymerization rate and high molecular weight and the polymer produced is in the form of beads and so they can be taken out by filtration easily. Disadvantage is that the polymerization need to be completed, otherwise the beads which may have residual monomer may not be useful. So, the reaction needs to be completed. The additional dispersant we are using for suspending this particle in aqueous medium, if cannot remove effectively, then that will impart impurities in the product. These are used for methylmethacrylate and other acrylate esters, vinyl acetate, vinyl chloride, Tetrafluoroethylene etc.

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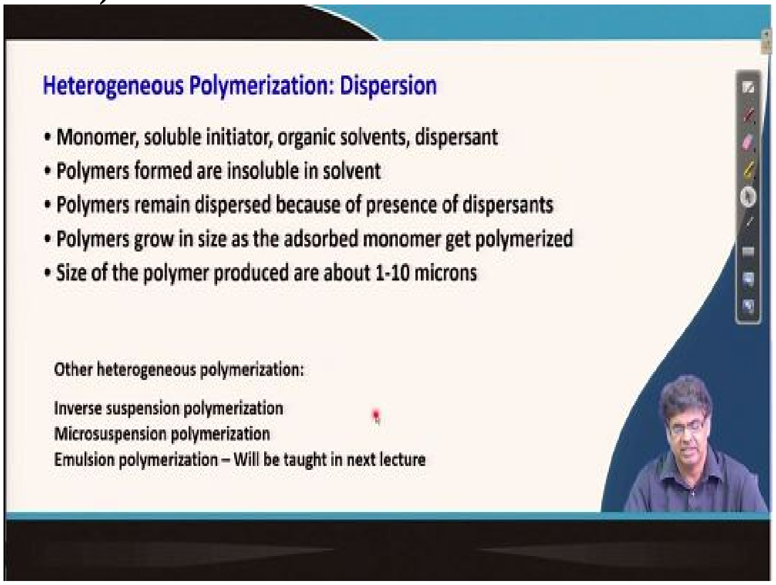

Heterogeneous Polymerization: Dispersion

- Monomer, soluble initiator, organic solvents, dispersant
- Polymers formed are insoluble in solvent
- Polymers remain dispersed because of presence of dispersants
- Polymers grow in size as the adsorbed monomer get polymerized
- Size of the polymer produced are about 1-10 microns

Other heterogeneous polymerization:

Inverse suspension polymerization
Microsuspension polymerization
Emulsion polymerization – Will be taught in next lecture

This is another heterogeneous polymerization possible where basically the resulting polymers are not soluble in the aqueous medium. So, basically they get precipitated and they actually act as nucleation sites for further monomers. Thus polymerization happens in the droplets in case of suspension polymerization, whereas here, the polymerization will happen on the particles produced by the precipitated polymers. So, monomer and soluble initiator are used in organic solvent in this case. Unlike aqueous solvents in case of suspension polymerization, generally we use organic solvents and we have dispersant present which disperse the produced polymer particles. Polymers are formed in solvent and polymers remain dispersed because of presence of dispersant. Polymers grow in size by absorption of monomers on the polymer particles which gets polymerized further, and we get large polymer size in this case. There are other heterogeneous polymerization processes are possible like inverse suspension polymerization, micro suspension polymerization and emulsion polymerization which we will discuss in this lecture.

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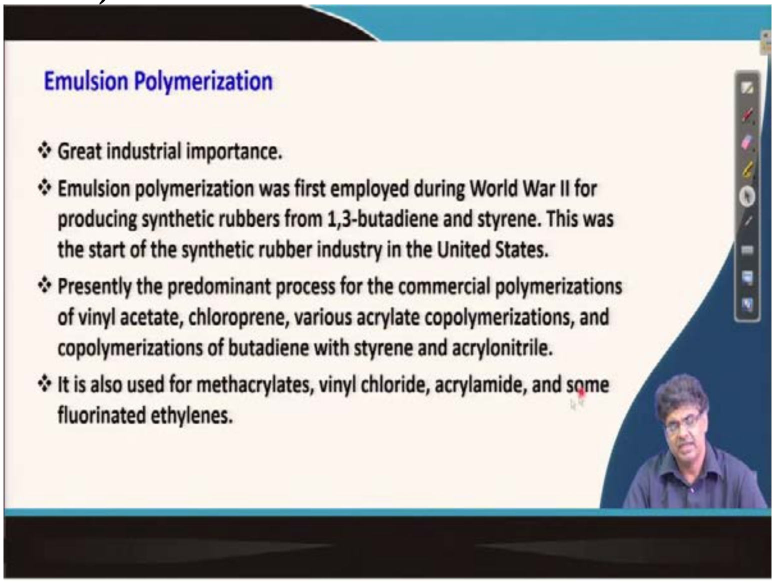

Emulsion Polymerization

- Great industrial importance.
- Emulsion polymerization was first employed during World War II for producing synthetic rubbers from 1,3-butadiene and styrene. This was the start of the synthetic rubber industry in the United States.
- Presently the predominant process for the commercial polymerizations of vinyl acetate, chloroprene, various acrylate copolymerizations, and copolymerizations of butadiene with styrene and acrylonitrile.
- It is also used for methacrylates, vinyl chloride, acrylamide, and some fluorinated ethylenes.

Let us talk about emulsion polymerization. This is important because it has a great industrial importance. In fact, emulsion polymerization was first employed during World War 2 for producing synthetic rubbers from 1-3 butadiene and styrene. And this was the start of synthetic rubber industry in the United States in those days. Presently, it is a predominant process for commercial productions of vinyl acetate, chloroprene, various acrylate copolymers and copolymers of butadiene, styrene and acrylonitrile and is also used for methacrylates, vinyl chloride, acrylamide and some fluorinated ethylenes.

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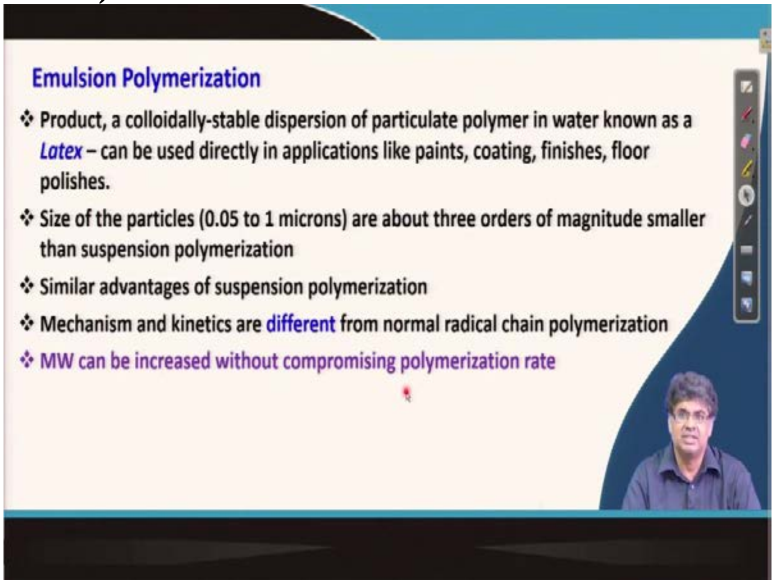

Emulsion Polymerization

- Product, a colloidally-stable dispersion of particulate polymer in water known as a *Latex* – can be used directly in applications like paints, coating, finishes, floor polishes.
- Size of the particles (0.05 to 1 microns) are about three orders of magnitude smaller than suspension polymerization
- Similar advantages of suspension polymerization
- Mechanism and kinetics are different from normal radical chain polymerization
- MW can be increased without compromising polymerization rate

Now, most important is that the polymer product which we get from emulsion polymerization are actually colloidally-stable dispersion particulate polymer in water known as Latex. So, basically in this case, the product comes as a coloidally-stable, means that we get particular polymers which are stable by absorption of surfactant or emulsifier molecules. The product is the reaction mixture itself when we call this as Latex and it can be used directly for applications like paints, coatings, finishes floor polishes. Of course, we need to add other ingredients like pigments and stabilizers and so, on. The size of the particles in this case are much lower than the suspension polymerization or dispersion polymerization. Here we are talking about maximum 1 micron which is, even it could go even much lower, as low as 0.05 micron, is about 3 orders of magnitude smaller than this polymer beads which we get from suspension polymerization.

Since we are doing the reaction in a suspended medium, the heat release and removal are taken care. As the reaction is carried out in aqueous medium, mechanism and kinetics are different in this case than the normal radical chain polymerization kinetics which we discussed couple of lectures back. We will discuss the mechanism and the kinetics briefly in coming slides.

One of the most important aspects in terms of kinetics is that the molecular weight of the polymers produced can be increased without compromising the polymerization rate. Remember that in normal radical chain polymerization, if we increase the temperature or if we increase the initiator quantity, we get a higher reaction rate, but as a compromise, we actually achieve decreased molecular weight. This disadvantage can be overcome by using emulsion processes were molecule weight and the reaction rate, both can be increased simultaneously.

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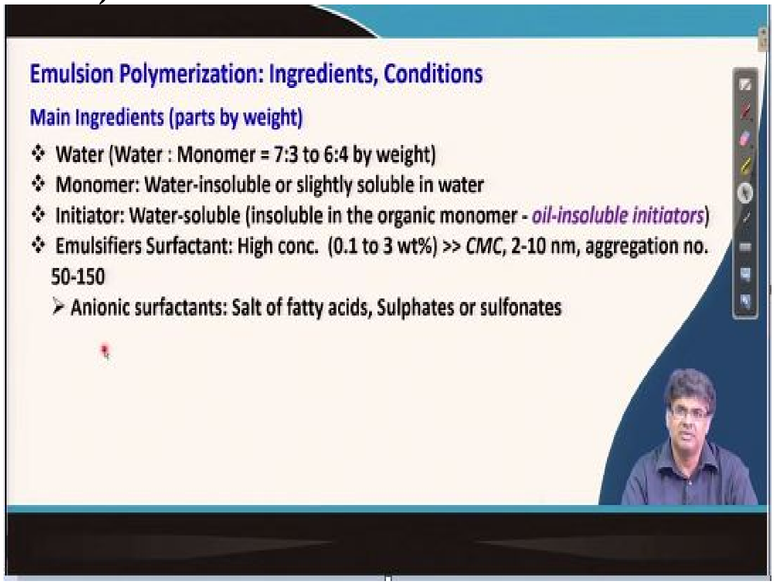

Emulsion Polymerization: Ingredients, Conditions

Main Ingredients (parts by weight)

- Water (Water : Monomer = 7:3 to 6:4 by weight)
- Monomer: Water-insoluble or slightly soluble in water
- Initiator: Water-soluble (insoluble in the organic monomer - *oil-insoluble initiators*)
- Emulsifiers Surfactant: High conc. (0.1 to 3 wt%) >> *CMC*, 2-10 nm, aggregation no. 50-150
  - Anionic surfactants: Salt of fatty acids, Sulphates or sulfonates

In a typical reaction mixture of emulsion polymerization, we have these ingredients. Of course we have a dispersing medium which is water and we have water insoluble monomer, or may be slightly soluble in water and typically the ratio of water and monomer is about 7 : 3 to 6 : 4 by weight. So, water is present as a major part in an emulsion polymerization. In case of bulk polymerization or suspension polymerization, we talked about the initiator being oil-soluble, or soluble in the monomer phase, but in this case we are talking about the initiator being water soluble and insoluble in the organic monomer. So, basically we are talking about oil insoluble initiator in this case. The monomer is water insoluble and the initiator is water soluble or oil insoluble. Also, we need emulsifiers which are nothing but surfactants that help in dispersing the monomer droplets and the polymer particles which gets produced during this emulsion polymerization and are used in high concentration, about 0.1 to 3 weight percent which is much higher than the critical micellar aggregation concentration and the size of the micelles which could get produced from the surfactants it is about 2 to 10 nm. In each micelle, we have about 50 to 150 number of surfactants which we call aggregation number.

The typical anionic surfactants that are used are like salt of fatty acids, sulphates or sulfonates. There are other ingredients also that are added occasionally like chain transfer agents, some inorganic salts and some other ingredients which help in improving a property of the polymer that is produced. Chain transfer agents basically helps us to control the molecular weight of the produced polymer.

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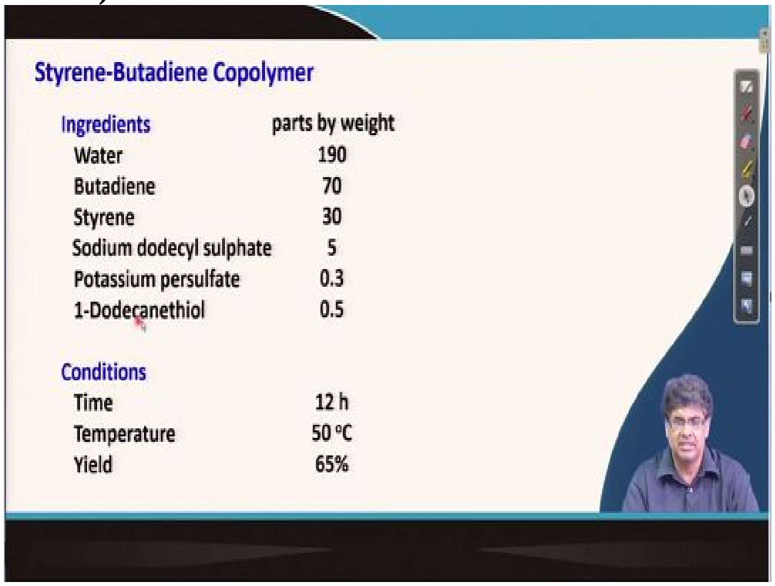

Styrene-Butadiene Copolymer

Ingredients	parts by weight
Water	190
Butadiene	70
Styrene	30
Sodium dodecyl sulphate	5
Potassium persulfate	0.3
1-Dodecanethiol	0.5

Conditions	
Time	12 h
Temperature	50 °C
Yield	65%

So, these are examples of some recipe of emulsion polymerization like styrene-butadiene copolymer. The emulsifier surfactant is sodium dodecyl sulphate and the initiator is potassium persulfate which is water soluble and dodecanethiol is a chain transfer agent in this case.

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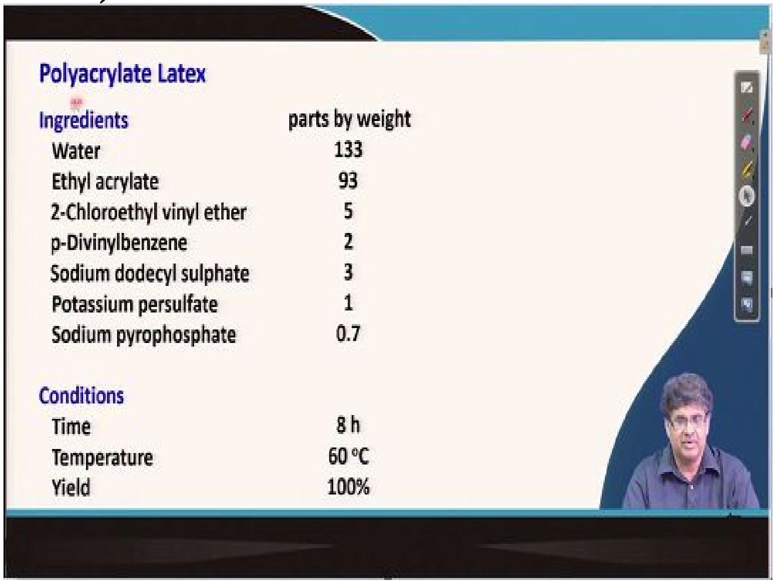

Polyacrylate Latex

Ingredients	parts by weight
Water	133
Ethyl acrylate	93
2-Chloroethyl vinyl ether	5
p-Divinylbenzene	2
Sodium dodecyl sulphate	3
Potassium persulfate	1
Sodium pyrophosphate	0.7

Conditions	
Time	8 h
Temperature	60 °C
Yield	100%

An example is polyacrylate latex where we have a divinylbenzene which is a crosslinker. So, the polymer particles will be cross linked and we have a dispersant or surfactant and a water soluble initiator.

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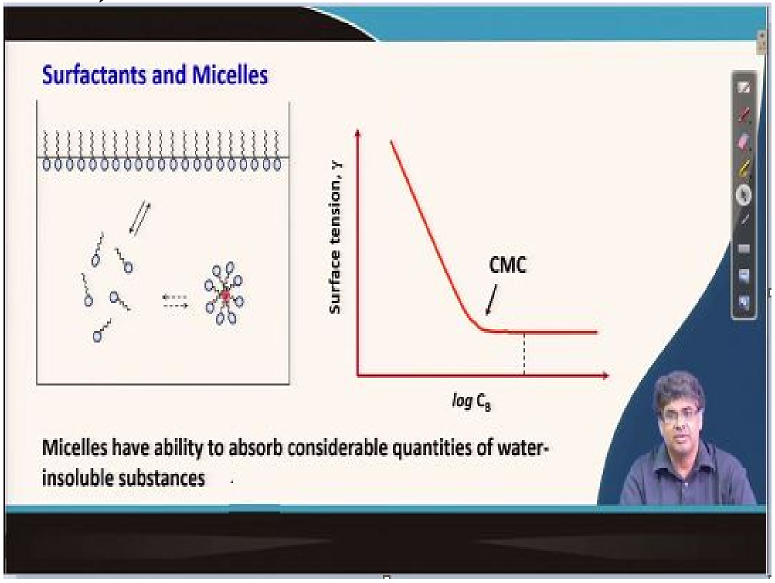

Surfactants and Micelles

Micelles have ability to absorb considerable quantities of water-insoluble substances

Now, before we go to the mechanism of emulsion polymerization, just remind you what is surfactant micelle. Surfactants are surface active agents which consist of both hydrophilic and hydrophobic part. In the cartoon shown, this sphere is the head group that represents the hydrophilic group and this tail is long chain hydrophobic group. When we add these surfactants they get soluble in water medium to some extent and due to their surface activity they move into surface and they actually arrange such way that hydrophobic tail part it is in the oil phase and the hydrophilic head is touching the surface of aqueous phase. Now, as we increase the concentration of surfactant in aqueous medium more and more surfactant goes to the surface. As a result the surfactants comes down, because more and more water molecules are replaced by surfactant molecule and after some time when there is no space in the interface or the surface they actually arrange in such a way that the hydrophobic tails are inside, away from water molecules and the hydrophilic heads are outside these spherical droplets in contact with water molecules. These head groups could be charged as we have seen for dodecyl sulfate molecules, sodium group, and if they are charged, there could be counter ions associated with these as well. As you can see that after some time, these surfactants will form spherical micelles, as we add more and more surfactant molecules. The concentration at which this happens is called critical micelle concentration. So, if we increase the surfactant concentration, more and more micelles are generated without changing the surface tension value and the good part is that these micelles can actually absorb or dissolve considerable quantities of waters insoluble substances because the inside is hydrophobic in nature where the micelles can dissolve the hydrophobic molecules.

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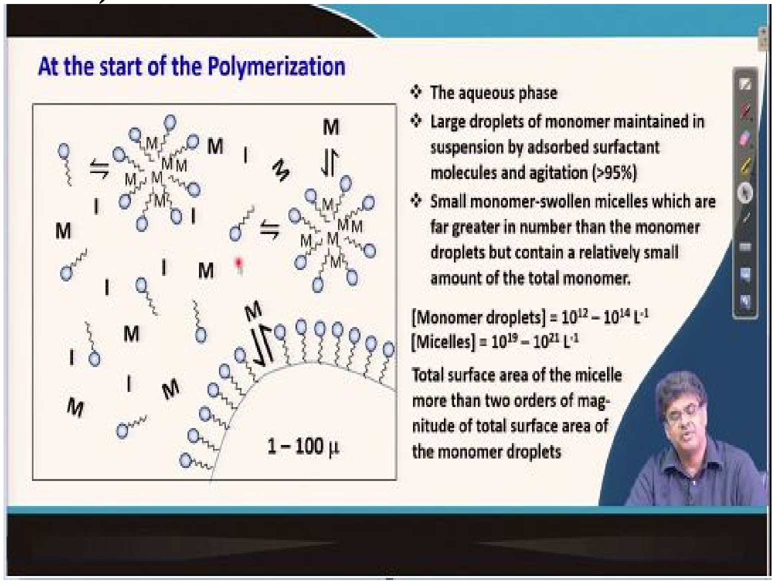

At the start of the Polymerization

- The aqueous phase
- Large droplets of monomer maintained in suspension by adsorbed surfactant molecules and agitation (>95%)
- Small monomer-swollen micelles which are far greater in number than the monomer droplets but contain a relatively small amount of the total monomer.

[Monomer droplets] = $10^{12} - 10^{14}$ L^{-1}
[Micelles] = $10^{19} - 10^{21}$ L^{-1}

Total surface area of the micelle more than two orders of magnitude of total surface area of the monomer droplets

So, at start of the emulsion polymerization, the situation looks like this. We have surfactants added. Now some surfactant molecules are present as monomeric molecules, some would be of course in the surface which we have not shown here, and some will be present as micelles. Now, we have these water insoluble monomers, there will be of course, slight solubility. So, we have shown these soluble monomers in this aqueous phase by this letter M, but some of the monomers will get dissolved in the hydrophobic core of the micelles. As a result the micelle will basically swell little bit as in absence of these dissolved monomers they probably would have a smaller size, but because these monomers are dissolved, they are now actually of little higher size. The micelles are little swollen. There are initiator molecules which are, which are basically soluble in water. A large amount of monomer molecules is presence as large droplet of size 1 to 100 microns, which are stabilized by this absorption of by these surfactant molecules. So, at the beginning of the emulsion polymerization we have large monomer droplets which are stabilized by surfactant adsorption of surfactant molecules, of sizes typical 1 to 100 micron. We have micelles, which are swollen by dissolving the monomers in the core hydrophobic core, and we have some surfactant molecules, some monomer dissolved in aqueous medium as well as the initiator molecules soluble in water.

Also, you must note that, the miclles are not static structure they are in equilibrium with the monomeric surfactant. Even the monomers which are dissolved in this micelle, they are in equilibrium with the monomers present in the solution. So as the monomer droplets are in equilibrium with the monomer present in the aqueous medium so, whenever there is a shortfall of any of these like if there is a shortfall of monomers in this micelle core, then this monomer from droplet can go in to replace that monomer. Or if there is a shortfall of monomer in aqueous solution, then these droplets can supply monomer to the aqueous medium. In the aqueous phase, large droplet of monomers are maintained in suspension by absorbed surfactant molecules and agitation. These large monomer droplets are more than 95% by weight and the small monomer swollen micelles are far greater in number than the monomer droplets, but contains relatively small amount of total monomer.

It is important to note that monomer droplets number or concentration is like these 10^{12} to 10^{14} L^{-1}. So, per liter we have these many monomer droplets. But look at the number of micelles or monomer swollen micelles. They are much higher, about 7 orders of magnitude more than the number of monomer droplets. So, effectively, because the number of micelles are much higher compared to monomer droplets, the total surface area of micelles is much more than the magnitude of the total surface area of these monomer droplets which is actually about 2 orders of magnitude higher. The surface area of these micellar large particles are much more, about two orders of magnitude more than the surface area of these particles. So, basically if we produce something here, there is a chance of colliding with this is much more than colliding with these large droplets. So, with this I will stop here for this lecture and then I will talk about what happens after the reaction starts in this emulsion polymerization.