Introduction to Polymer Science
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Lecture - 17
Emulsion Polymerization (Contd.), Common Polymers by Radical Chain Polymerization, RDRP

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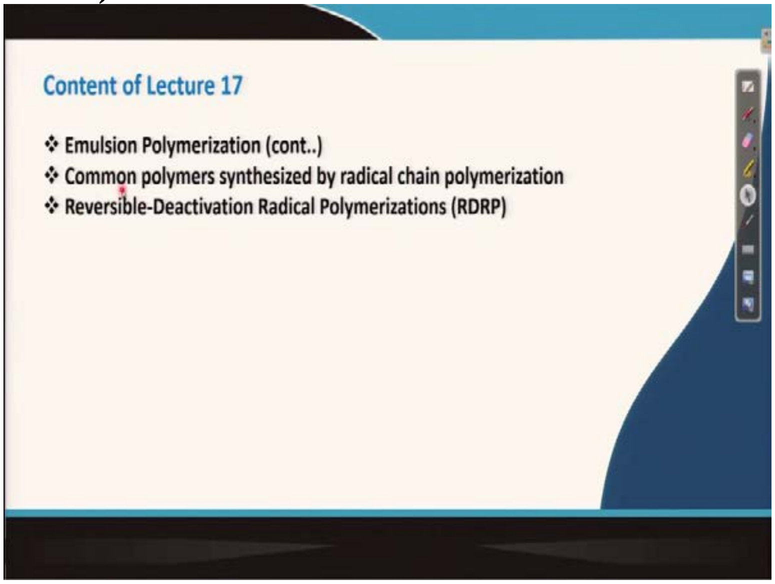

Content of Lecture 17

- ❖ Emulsion Polymerization (cont..)
- ❖ Common polymers synthesized by radical chain polymerization
- ❖ Reversible-Deactivation Radical Polymerizations (RDRP)

Welcome back, in this lecture 17, I will continue my discussion on emulsion polymerization and also give you some examples about common polymers that are synthesized by radical chain polymerization. And if time permits, I will talk about this RDRP polymerization.

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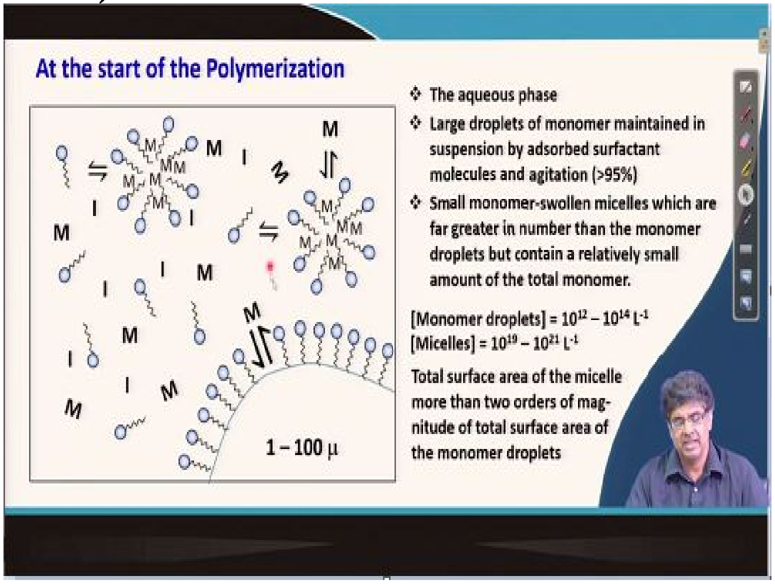

At the start of the Polymerization

- ❖ 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

Now, let us revisit the last slide of the last lecture. This slide shows the situation at the beginning of the emulsion polymerization, where the medium contains large droplets that are stabilized by surfactant molecules and monomer-swollen micelles. Some dissolved monomer molecules are also present; initiator molecules, which are soluble in the aqueous medium, are also present. It should be noted that the number of these monomer droplets are much lower compared to the number of the monomer swollen surfactant micelles. As a result, the total surface area of the monomer swollen surfactant micelles are about two orders of magnitude higher than the surface area of the monomer droplets. So, any species which is present in the aqueous medium, it is highly likely that it will collide more often with this monomer swollen micelles than the monomer droplets.

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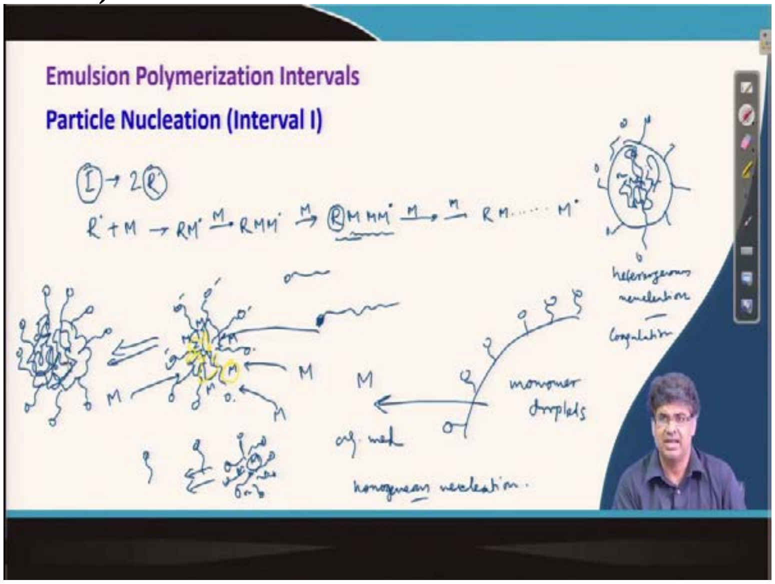

Emulsion Polymerization Intervals

Particle Nucleation (Interval I)

$$I \rightarrow 2R^{\cdot}$$

$$R^{\cdot} + M \rightarrow RM^{\cdot} \xrightarrow{M} RMM^{\cdot} \xrightarrow{M} RMMM^{\cdot} \xrightarrow{M} \xrightarrow{M} RM \cdots\cdots M^{\cdot}$$

Once we start the reaction by generating initiator radicals, e.g. by heating, the monomer molecules that are present in that aqueous phase, though in small concentration, will react with the radicals and start the chains. Potassium per sulfate is often used as initiator as we have shown in the case of synthesis of styrene-butadiene rubber and acrylate polymers.

Now, this addition of monomers will continue for a few monomers. You can imagine that, as the monomers are not soluble in aqueous medium, then, these oligomeric chains which contain few monomer molecules, are definitely expected to be even lower soluble than the monomers in aqueous medium. These oligomeric propagating radicals contain a hydrophobic part formed by the addition of monomers and a hydrophilic part coming from the hydrophilic initiator molecule. Hence, these oligomeric radicals should behave like surface-active agents in the aqueous medium. Now, there are three possibilities for these oligomeric propagating radicals to progress. First, they can undergo normal termination reaction and get precipitated from the aqueous medium. Second, they can continue to capture few more monomers and get longer in size, and third, they can partition in some nonpolar region like the micelle core, which are hydrophobic in nature, or in the monomer droplets as inside of the monomer droplets is nonpolar, hydrophobic. Nevertheless, the third option is the most likely possibility because of surface-active nature of the oligomeric radicals. Now, as I discussed few times in last lecture as well as at the beginning of this lecture, because the surface area of the monomer swollen micelles are much higher than the monomer droplets, it is most likely that the oligomeric chains will partition inside the micelles containing the monomer molecules.

Micelles are charged in this case, as we are using anionic surfactant and some of the micelles contain monomers dissolve in them and we term them as monomer-swollen micelles. So, when the oligomeric propagating radicals partition inside these monomer-swollen micelles, they will start reacting with the monomers present inside the micelles. Now, the radicals have no problem about solubility, as they are soluble in the hydrophobic core of the micelles.

Once the monomer present in the inside of micelles, the oligomeric chains will grow inside the micelles. The propagating chains will continue to react with the monomers and the monomer molecules will be consumed inside the micelle. To maintain the equilibrium concentration of monomers in different phases, some monomer molecules that are present in the aqueous medium, will now partition inside the micelle. The propagating radicals present in the micelles will capture these monomer molecules and the chain will grow further before they are terminated. Once the second radical gets in one micelle, the two radicals react immediately and the chains are terminated, because the size of the micelles is very small. Subsequently, when another radical comes in, it will restart a new polymer chain by reacting with the monomers present. Consequently, concentration of the monomers that are present in the aqueous medium will deplete, and to maintain the equilibrium, the monomer droplets that are stabilized by surfactant molecules will supply monomers to the aqueous medium.

So, with time the large monomer droplets will keep on supplying the monomers to the growing polymer particles in micelles through aqueous medium. The monomers will come from the monomer droplets and then move to the micellar particles. Soon, the micelles will become larger, then they will not remain as a micelles, they will become like polymer particles, which stabilized by surfactants. Such a particle begins as a micellar-swollen particle, then as more and more monomers diffuse in from the aqueous medium to this hydrophobic inside core, this will become larger. After sometime, it will not be considered as a micelle but as a polymer particle that is stabilized by the surfactant molecules. This requires more and more surfactant molecules to be available for stabilizing the polymer particles. Some surfactant molecules were present initially as monomaniac units in the aqueous medium, which will stabilize the growing polymer particles at the beginning. Hence, the concentration of the surfactant molecules will be depleted soon in the aqueous medium. To maintain the equilibrium, the other inactive micelles that are present will now disintegrate and supply surfactant monomers to the medium.

Once again, let me brief this situation, at start the polymerization, some initiator molecules that are soluble in aqueous medium will dissociate to produce $R^{\cdot}$, which will react with monomers present in the aqueous phase and start initiate the polymer chain, which will further react with the monomers that are present in the solution and grow into oligomeric chain. Now, this oligomeric chain has three possibilities. First, it can be terminated by reacting with some other radical present and are precipitated. There is another possibility where it can actually grow in size and then precipitate as active radical, which can adsorb or absorb monomers from the medium and start polymerizing on to itself. In this case, it is not a micellar particular; it is a polymer particle itself. In this case, oligomer is precipitated and absorbs more and more monomers from the medium on it and polymerization may occur on this. So, in this case, a polymer particle is being produced which is now stabilized by the surfactant molecules. This second possibility is termed as heterogeneous nucleation. Now, these polymer particles could coagulate with themselves and form a larger particle that can further adsorb monomers, and polymerization may continue. Therefore, sometimes, this is also termed as coagulation nucleation. However, as I said that these two possibilities are less likely.

The third and most likely possibility is what was described in detail in the previous page, which is termed as homogeneous nucleation. The oligomeric radicals being surface active in nature owing to presence of a hydrophilic head group and long hydrophobic tail, diffuse inside the monomer-swollen micelles because their surface area are much higher than the monomer droplets. Polymerization continues inside the micelles and once the chains grow enough in size, more and more monomers are supplied into this growing polymer chain from the aqueous medium, which in turn are compensated from the monomer droplets. As the micelles grow in size, we get polymer particles stabilized by surfactants and these surfactants are supplied by the dissociation of the inactive micelles. Please note that, the monomer-swollen micelles or the polymer particles can always have one active radical, once the second radical gets in, because the very small size of these particles, the two radicals will immediately react with each other and terminate the chain. Polymerization cannot start until a new propagating radical comes in and re-start a new chain. Therefore, the monomer-swollen particles or polymer particles can have either one or zero active radical. Therefore, they stay either as dormant particles or as active particles containing one propagating radical.

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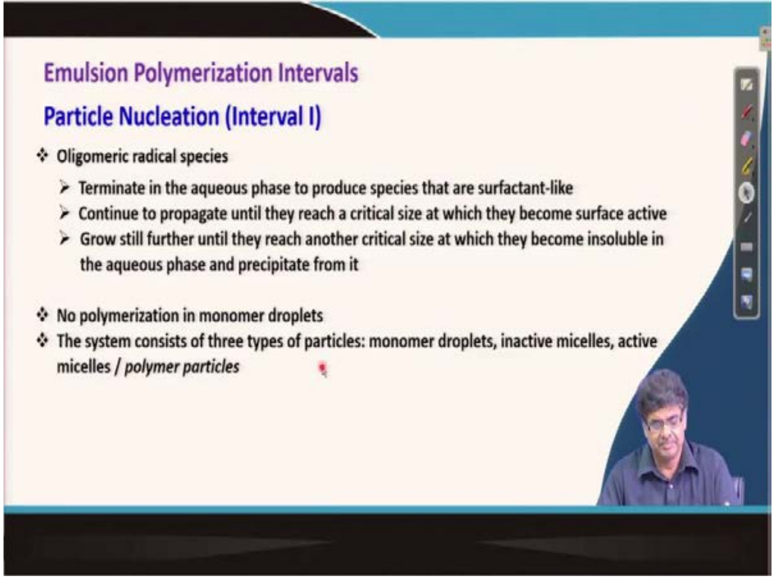

Emulsion Polymerization Intervals

Particle Nucleation (Interval I)

- Oligomeric radical species
  - Terminate in the aqueous phase to produce species that are surfactant-like
  - Continue to propagate until they reach a critical size at which they become surface active
  - Grow still further until they reach another critical size at which they become insoluble in the aqueous phase and precipitate from it
- No polymerization in monomer droplets
- The system consists of three types of particles: monomer droplets, inactive micelles, active micelles / *polymer particles*

The oligomer radical species can get terminated in aqueous phase to produce dead oligomer species or can continue to propagate until they reach a critical size when they becomes surface active and as a resut, get partitioned inside the micellar core. As a third possibility, they continue to grow in size until they reach another critical size when they become insoluble in the aqueous phase and are precipitated. Because the radicals are still active, they can continue the polymerization reaction in the precipitated phase. This is heterogeneous nucleation.

No polymerization happens inside the monomer droplets as the surface area of monomer droplets are much lower compared to the micellar surface area. In this situation, which we call as *Interval I*, we have three types of particles - monomer droplets that do nothing but supply monomers with time to the active polymer particles, inactive micelles that supply surfactant molecules and monomers with time to the active particles, and active micelles or polymer particles. Now, this situation continues until more and more active particles get generated, at around 10 to 15% conversion, all the inactive micelles disappear from the system. This means there is no new micellar particle or polymer particles are being generated, we reach the end of *Interval I*. So, at the end of the *Interval I*, the number of active particles or polymer particles remain same. Now, as reaction progress further, monomers come in from the monomer pool of monomer droplets and polymerization can happen within the active micellar or polymer particles.

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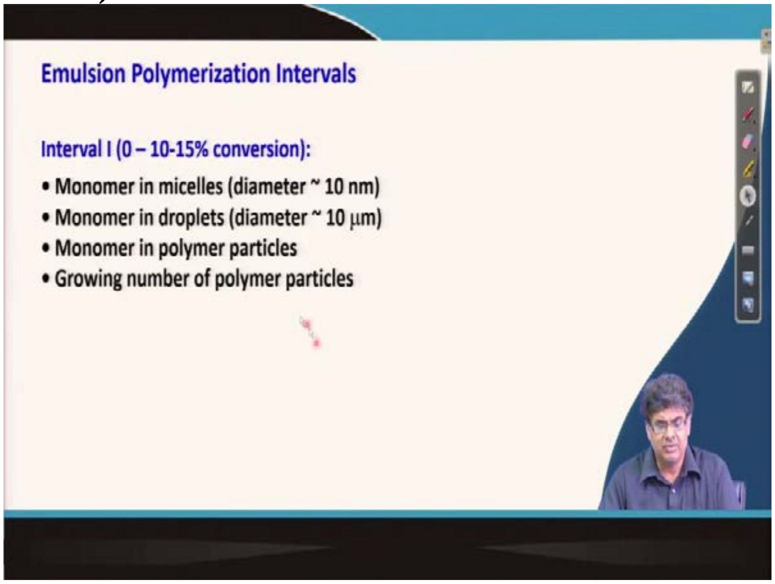

Emulsion Polymerization Intervals

Interval I (0 – 10-15% conversion):

- Monomer in micelles (diameter ~ 10 nm)
- Monomer in droplets (diameter ~ 10 μm)
- Monomer in polymer particles
- Growing number of polymer particles

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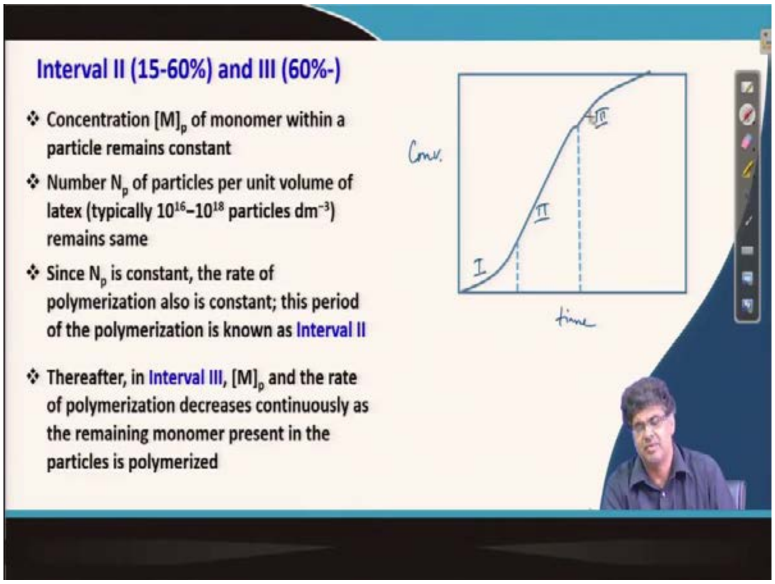

Interval II (15-60%) and III (60%-)

- Concentration $[M]_p$ of monomer within a particle remains constant
- Number N_p of particles per unit volume of latex (typically 10^{16}–10^{18} particles dm^{-3}) remains same
- Since N_p is constant, the rate of polymerization also is constant; this period of the polymerization is known as Interval II
- Thereafter, in Interval III, $[M]_p$ and the rate of polymerization decreases continuously as the remaining monomer present in the particles is polymerized

This is when the *Interval II* starts, as the concentration of monomers within the particles remains constant. Once the monomers in the particles are consumed, they get compensated form the monomer droplets through aqueous medium. The number of the active particles, which are either micellar particles or polymer particles, per unit volume of the reaction mixture is static, typically 10^{16} to 10^{18} and it remains same. Moreover, since the number of particles remains same, the rate of polymerization is constant, because most of the polymerization reactions happen only within these particles. In the *Interval II* where the number of particles remains same, of which some particles are active and some are dormant. On further polymerization, these particles slowly grow in size until the monomer pools stop supply of monomers. After the monomer droplets are consumed, which is the end of *Interval II* , there is no monomer present in aqueous medium or as a pool, then whatever monomers which has already are in these particles will continue to react with the propagating radicals and generate polymers. The monomer concentration within these active particles slowly comes down; as a result, the rate of reaction also comes down. The plots of conversion versus time for the three intervals are shown in the Figure. At the beginning, in *Interval I*, the number of active particles increases because more and more propagating radicals are partitioned in monomer-swollen micelle. The reaction rate is increases with more number of micelles are activated. When the surfactants are consumed from the aqueous medium, no new particles can generate, as the result, the number of active radicals in the reaction becomes fixed. This is when *Interval II* starts and the rate of reaction remains same. In this interval, monomers are supplied from the monomer pools to the active particles via aqueous medium. Once that supply get over, because the monomer droplets are consumed, *Interval III* starts, then only thing happen, only the monomers which are already present in the active particles get reacted. Therefore, the concentration of monomers inside the particles comes down and reaction rate becomes lower.

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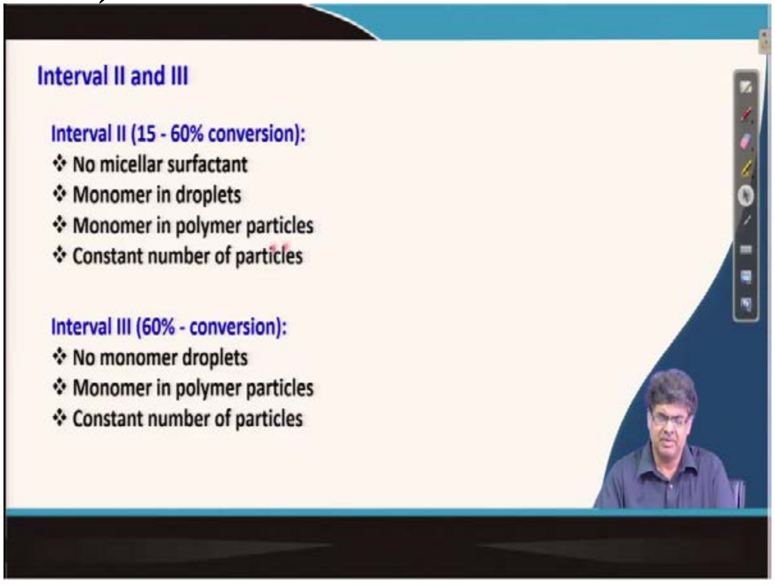

Interval II and III

Interval II (15 - 60% conversion):

- No micellar surfactant
- Monomer in droplets
- Monomer in polymer particles
- Constant number of particles

Interval III (60% - conversion):

- No monomer droplets
- Monomer in polymer particles
- Constant number of particles

So, in *Interval II*, no inactive micelles exits, monomers are present in droplet and in constant number of polymer particles. In *Interval III*, no monomer droplets exists, monomers are only in constant number of polymer particles in which they are reacted.

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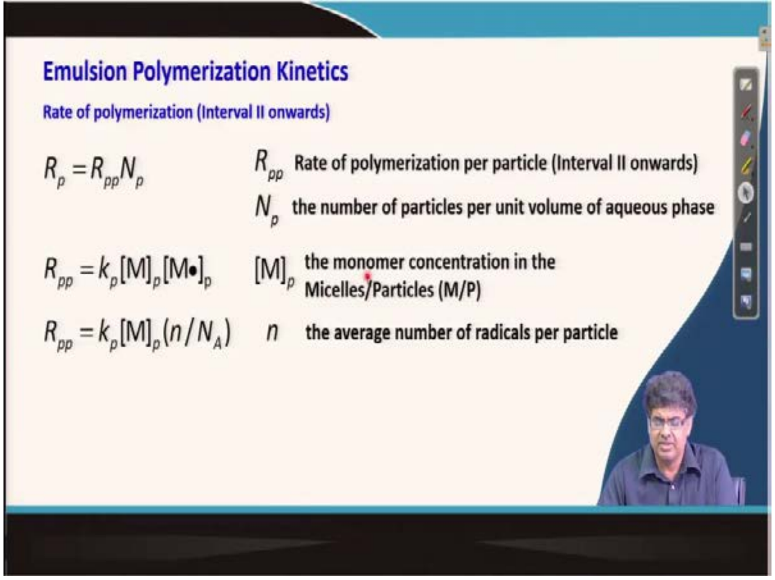

Emulsion Polymerization Kinetics

Rate of polymerization (Interval II onwards)

$$R_p = R_{pp} N_p$$

R_{pp} Rate of polymerization per particle (Interval II onwards)

N_p the number of particles per unit volume of aqueous phase

$$R_{pp} = k_p [\mathrm{M}]_p [\mathrm{M}\bullet]_p$$

$[\mathrm{M}]_p$ the monomer concentration in the Micelles/Particles (M/P)

$$R_{pp} = k_p [\mathrm{M}]_p (n / N_A)$$

n the average number of radicals per particle

Let us talk about the kinetics now. It is little different from the normal radical chain polymerization. We will discuss the rate of polymerization solely during *Interval II* onwards, the *Interval II* and *Interval III*. At the beginning during *Interval I*, the number of active micelles or number of particles are not fixed. So, in this interval, the rate actually depends on both the rate at which new particles are getting generated as well as the inherent reaction rate within these particles. Additionally, the reaction spends most time in the active form during *Interval II* onwards. The rate of polymerization in the *Interval II* is given by the rate of polymerization in one particle multiplied by the number of such particles per unit volume or concentration of such particles. The rate of polymerization is given by,

$$R_p = R_{pp} N_p$$

where, R_{pp} is the rate of polymerization per particle and N_p is the number of such particles per unit volume in aqueous phase. Within a particle, the rate is given by the normal radical chain polymerization,

$$R_{pp} = k_p[M]_p[M^{\cdot}]_p$$

where k_p is the inherent rate constant, $[M]_p$ and $[M^{\cdot}]_p$ are the concentration of monomers and concentration of propagating radical species within one active particle, respectively. Now, if the average number of propagating radical species within one particle is '*n*', then we divide *n* by Avogadro number to get the concentration of the radicals within one particle. So, we get the rate,

$$R_{pp} = k_p[M]_p(n/N_A)$$

where, (n/N_A) is the average concentration of radicals per particle.

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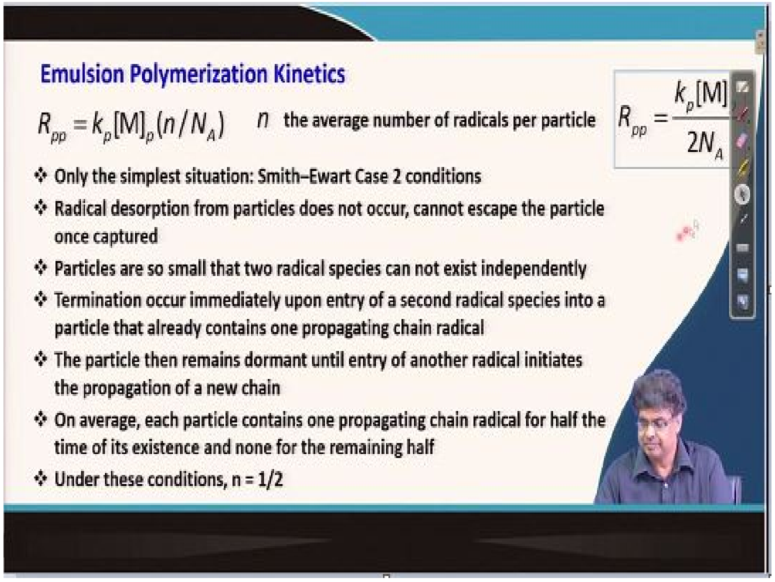

Emulsion Polymerization Kinetics

$R_{pp} = k_p[M]_p(n/N_A)$ n the average number of radicals per particle

$$\boxed{R_{pp} = \frac{k_p[M]}{2N_A}}$$

- Only the simplest situation: Smith–Ewart Case 2 conditions
- Radical desorption from particles does not occur, cannot escape the particle once captured
- Particles are so small that two radical species can not exist independently
- Termination occur immediately upon entry of a second radical species into a particle that already contains one propagating chain radical
- The particle then remains dormant until entry of another radical initiates the propagation of a new chain
- On average, each particle contains one propagating chain radical for half the time of its existence and none for the remaining half
- Under these conditions, n = 1/2

Now, what is the average number of radicals per particle? We will restrict our discussion in the simplest situation which we is termed as Smith-Ewart Case 2 condition, and in this case, we are considering that a radical once get absorbed or come inside a monomer-swollen micelle, it cannot desorb. This means that, a radical cannot escape once captured and, as a particle is so small, as discussed earlier also, that two active radical species cannot exist independently. As soon as a second radical gets in the particle, the two radicals react with each other to terminate the chains by bimolecular reaction. The particle then remains dormant until entry of another radical that re-initiate the propagation and a new chain formation starts. Hence, on average each particle contains either one active propagating radical or zero active propagating radical. Therefore, on average, half the time a particular particle stays as active particle and half the time it the stays as a dormant particle. So, on average it *n* =1/2.

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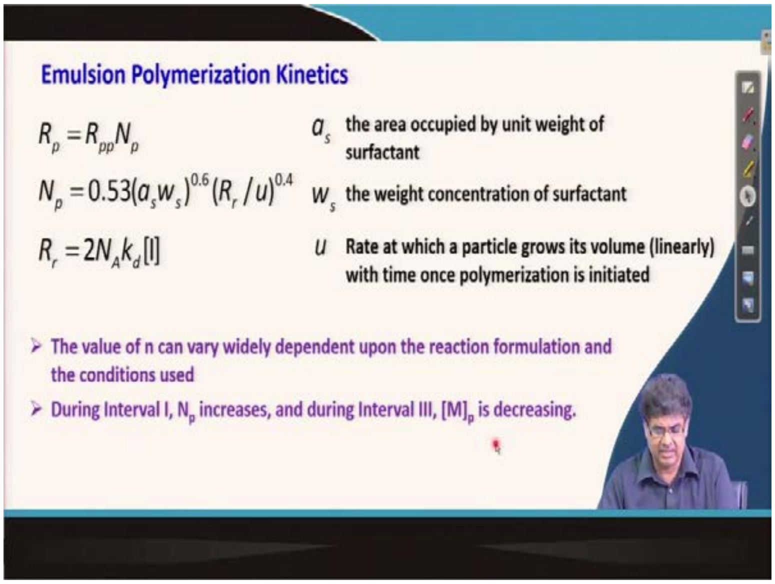

Emulsion Polymerization Kinetics

$R_p = R_{pp}N_p$

$N_p = 0.53(a_s w_s)^{0.6}(R_r/u)^{0.4}$

$R_r = 2N_A k_d[I]$

a_s the area occupied by unit weight of surfactant

w_s the weight concentration of surfactant

u Rate at which a particle grows its volume (linearly) with time once polymerization is initiated

- The value of n can vary widely dependent upon the reaction formulation and the conditions used
- During Interval I, N_p increases, and during Interval III, $[M]_p$ is decreasing.

After discussing the value of n, let us know the number of particles present during *Interval II* and beyond. Not going in the discussion in detail, the number of particles is given by this expression,

$$R_p = R_{pp}\, N_p$$

$$N_p = 0.53\ (a_s w_s)^{0.6}\ (R_r/u)^{0.4}$$

$$\text{where } R_r = 2N_A\, k_d\ [I]$$

where, R_r is the rate of initiation of radical species and a_s is the area occupied by the unit weight of surfactant, w_s is the of weight concentration of surfactant, and u is the rate at which a particle grows its volume which is varies linearly with time once the polymer is initiated. The value of N_p can vary widely depending on the reaction formula and conditions used. During *Interval II*, the number of particles increases, during *Interval III*, the concentration of monomer decreases within each particle.

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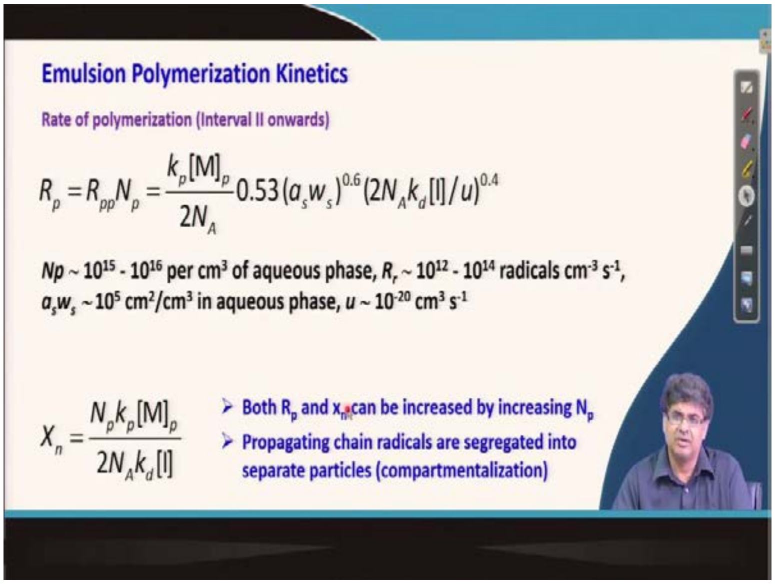

Emulsion Polymerization Kinetics

Rate of polymerization (Interval II onwards)

$$R_p = R_{pp}N_p = \frac{k_p[M]_p}{2N_A}0.53(a_s w_s)^{0.6}(2N_A k_d[I]/u)^{0.4}$$

$Np \sim 10^{15}$ - 10^{16} per cm^3 of aqueous phase, $R_r \sim 10^{12}$ - 10^{14} radicals $cm^{-3}\ s^{-1}$,
$a_s w_s \sim 10^5\ cm^2/cm^3$ in aqueous phase, $u \sim 10^{-20}\ cm^3\ s^{-1}$

$$X_n = \frac{N_p k_p[M]_p}{2N_A k_d[I]}$$

- Both R_p and x_n can be increased by increasing N_p
- Propagating chain radicals are segregated into separate particles (compartmentalization)

So, if we combine the two expressions, rate of polymerization per particle and number of such particles or concentration of particles, we get this expression for rate of reaction,

$$R_p = R_{pp}N_p = \frac{k_p[M]_p}{2N_A}0.53(a_s w_s)^{0.6}\left(2N_A k_d\ {}^{[I]}\!/_{u}\right)^{0.4}$$

The typical values of the parameters are provided in the slide. Without going into the derivation, we can also write the expression for number-average degrees of polymerization as

$$X_n = \frac{N_p k_p[M]_p}{2N_A k_d[I]}$$

If you look at the above expressions, rate of polymerization and degree of polymerization, we can now increase R_p and degree of polymerization X_n by increasing the number of particles. So, if we increase the surfactant concentration in the medium, we can increase the number of such particles, and by doing so, we can increase the rate of polymerization as well as the size or molecular weight of the resulting polymers.

This is possible because the propagating radicals are segregated into different compartments, different active particles, but in normal radical chain polymerization, they are not, they all are present in same medium. Because of this, in normal radical chain polymerization, as the concentration of propagating radicals goes up, they undergo bimolecular termination reaction immediately, which results in decrease of the molecular weight. However, in case of emulsion polymerization, as we can separate these propagating radicals in the different compartments, we can generate a higher rate of polymerization without compromising the molecular weight.

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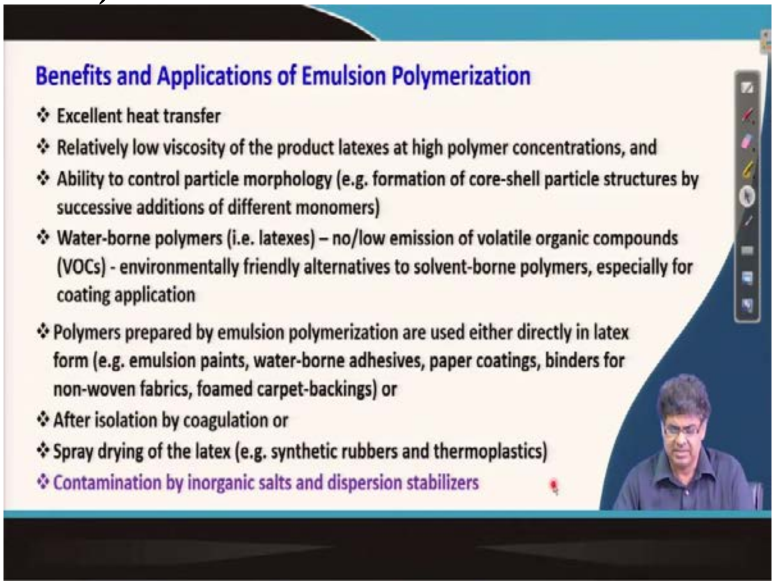

Benefits and Applications of Emulsion Polymerization

- Excellent heat transfer
- Relatively low viscosity of the product latexes at high polymer concentrations, and
- Ability to control particle morphology (e.g. formation of core-shell particle structures by successive additions of different monomers)
- Water-borne polymers (i.e. latexes) – no/low emission of volatile organic compounds (VOCs) - environmentally friendly alternatives to solvent-borne polymers, especially for coating application
- Polymers prepared by emulsion polymerization are used either directly in latex form (e.g. emulsion paints, water-borne adhesives, paper coatings, binders for non-woven fabrics, foamed carpet-backings) or
- After isolation by coagulation or
- Spray drying of the latex (e.g. synthetic rubbers and thermoplastics)
- Contamination by inorganic salts and dispersion stabilizers

Let us discuss the benefits and applications of emulsion polymerization. As we are carrying out the polymerization like a suspension polymerization, excellent heat transfer is possible; relatively low viscosity of the product latexes even at high polymer concentration; it has the ability to control the particle morphology by controlling the surfactant concentration, monomer concentration, and so on to form a core-shell particle; and we can actually add a second monomer to make a graft polymerization from the core of these particles.

And the major advantage is that the product of the polymerization reaction, *Latex*, is waterborne polymer. There is no or low emission of volatile organic compounds or VOCs. So, it is environmentally friendly alternative to solvent borne polymers especially for coating applications. If you have an organic solvent borne polymer, during coating application, a lot of vaporization happen which is a toxic and environmentally unfriendly. Polymers prepared by the emulsion polymerization are mainly used directly in *Latex* form. For example, emulsion, paints, waterborne adhesive, paper coatings, binders and so on. It can also be isolated if required by coagulation, we can add salts to the medium to remove the stabilizer surfactant molecules to coagulate. We can use the product after spray drying of the *Latex* for example, synthetic rubbers and thermoplastics.

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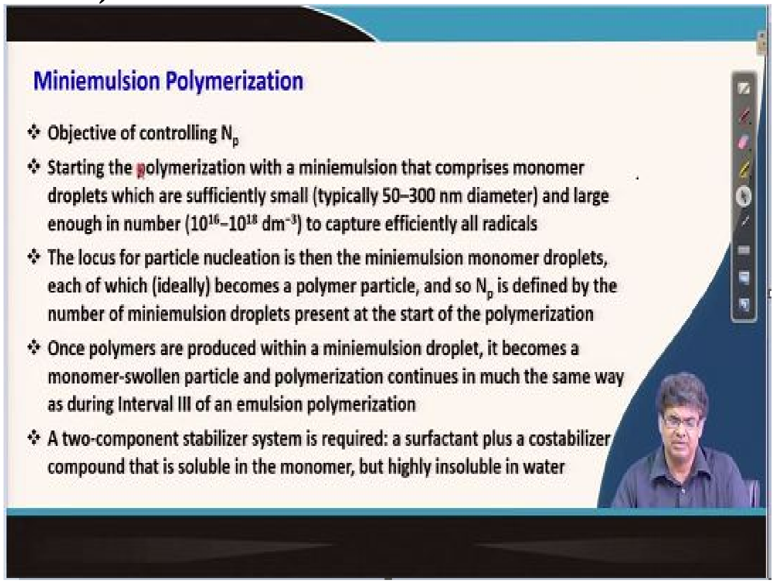

Miniemulsion Polymerization

- Objective of controlling N_p
- Starting the polymerization with a miniemulsion that comprises monomer droplets which are sufficiently small (typically 50–300 nm diameter) and large enough in number (10^{16}–10^{18} dm^{-3}) to capture efficiently all radicals
- The locus for particle nucleation is then the miniemulsion monomer droplets, each of which (ideally) becomes a polymer particle, and so N_p is defined by the number of miniemulsion droplets present at the start of the polymerization
- Once polymers are produced within a miniemulsion droplet, it becomes a monomer-swollen particle and polymerization continues in much the same way as during Interval III of an emulsion polymerization
- A two-component stabilizer system is required: a surfactant plus a costabilizer compound that is soluble in the monomer, but highly insoluble in water

I just quickly go through one more emulsion type polymerization but miniemulsion, as the name suggests that miniemulsion means the size of the emulsion particles are even smaller. In this case, we generate smaller micellar particles in large number so that we do not require generating more and more active particles with time. At the beginning, we have large number of miniemulsion particles so that all the radicals can be accommodated in these small emulsion particles or miniemulsion particles. As a result, finally at the end of polymerization, we get small emulsion particles, and we call that product as a miniemulsions. The objective is to control the number of particles by starting the polymerization with a miniemulsion that comprises monomers droplets, which is sufficiently small, typical value of diameter is given in the slide and large enough number so that it can efficiently capture all the radicals.

In this case, nucleation happened within the miniemulsion monomer droplets, which become polymer particles, and in this case, the number of particles given by the number of miniemulsion droplets present in the start of the polymers. Once the polymers produced are produced within the miniemulsion droplets, they become solid droplets and polymers continuous in much, the same way as *Interval III* of emulsion polymerization. So, we do not need to supply any more monomers from outside. So, when the monomers within these miniemulsion droplets get consumed, the reaction is complete. We can use the similar technique where we can use a cross-linker, then we can actually prepare cross-linked microgels.

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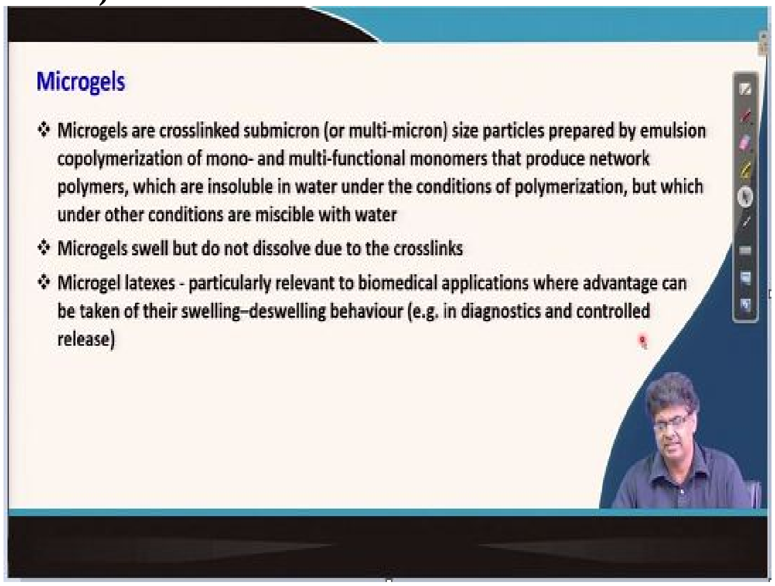

Microgels

- Microgels are crosslinked submicron (or multi-micron) size particles prepared by emulsion copolymerization of mono- and multi-functional monomers that produce network polymers, which are insoluble in water under the conditions of polymerization, but which under other conditions are miscible with water
- Microgels swell but do not dissolve due to the crosslinks
- Microgel latexes - particularly relevant to biomedical applications where advantage can be taken of their swelling–deswelling behaviour (e.g. in diagnostics and controlled release)

Microgels are cross-linked submicron sized particles prepared by emulsion copolymerization with mono- and multi- functional monomers. Microgels are network polymers that are insoluble in water under some condition, but, under some other condition, the polymer particles are actually miscible with water, but as they are cross-linked, they cannot be solubilized in the water. They can be swelled in water. Microgels are nowadays getting useful in several applications, most of which are in biomedical applications that take advantage of their swelling ability in some conditions and deswelling in some other conditions. For example, if we use some temperature sensitive polymers like poly(N-isopropyl acrylamide), then by just varying the temperature of the aqueous solution we can have the microgels swell or deswell and by doing that they can release the drug or some other molecules which are inside the microgels. Therefore, they are very useful in diagnostics and control release.

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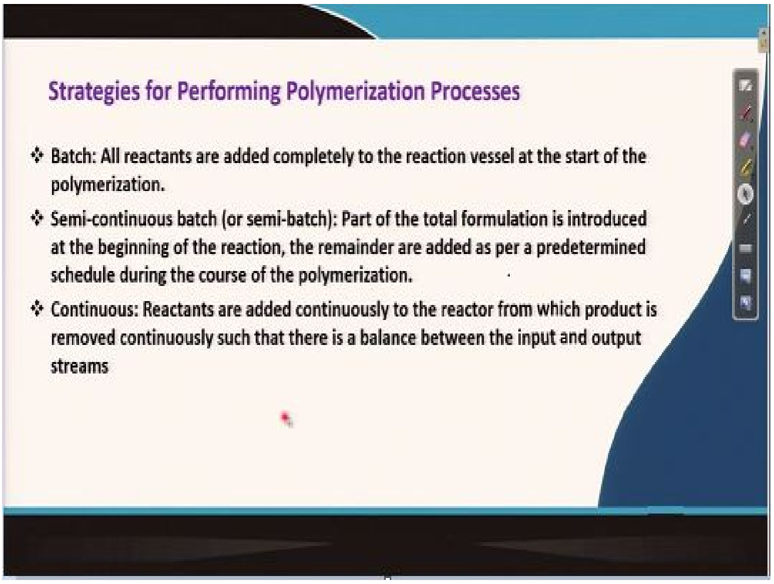

Strategies for Performing Polymerization Processes

- Batch: All reactants are added completely to the reaction vessel at the start of the polymerization.
- Semi-continuous batch (or semi-batch): Part of the total formulation is introduced at the beginning of the reaction, the remainder are added as per a predetermined schedule during the course of the polymerization.
- Continuous: Reactants are added continuously to the reactor from which product is removed continuously such that there is a balance between the input and output streams

Let me discuss this slide and then it will stop. This is known to you that like any other chemical processes, polymerization can be also done by batch processes, semi-continuous process or semi batch processes, or in continuous processes. You probably know these processes; in batch process all the reactants are present from beginning in the reaction vessels, and in semi-continuous or semi-batch processes some ingredients are added in between. In the continuous processes, the reactants are added continuously and the polymers are taken out continuously to keep a balance of input and output. With this, I will stop this lecture and in the next lecture, I will describe few common polymers that are made by radical chain polymerization, and talk about living radical polymerization techniques.