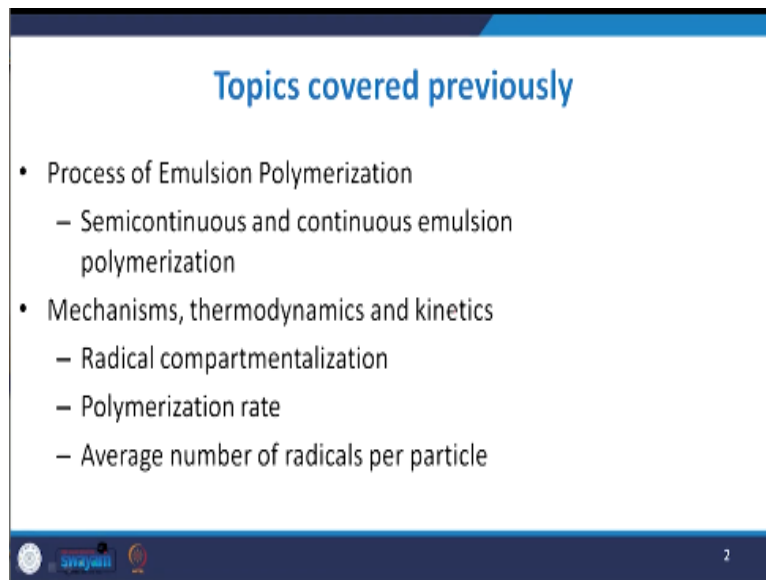**Polymer Reaction Engineering**
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Indian Institute of Technology – Roorkee

Lecture - 51
Nucleation, Morphology and Reactor Types - I

Welcome to the next part of emulsion polymerization. In this particular lecture, we are going to discuss with the concept of nucleation. Although, we have discussed part of this in the previous lecture. We will give the emphasis to the morphology and different type of reactors. So, just have a look about that what we discussed previously.

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Previously, we discussed about the process of emulsion polymerization under the edges of semi-continuous and continuous emulsion polymerization. Then, we discussed the mechanism and thermodynamic approaches and kinetic part under the head of radical compartmentalization, polymerization rate and average number of radicals per particle.

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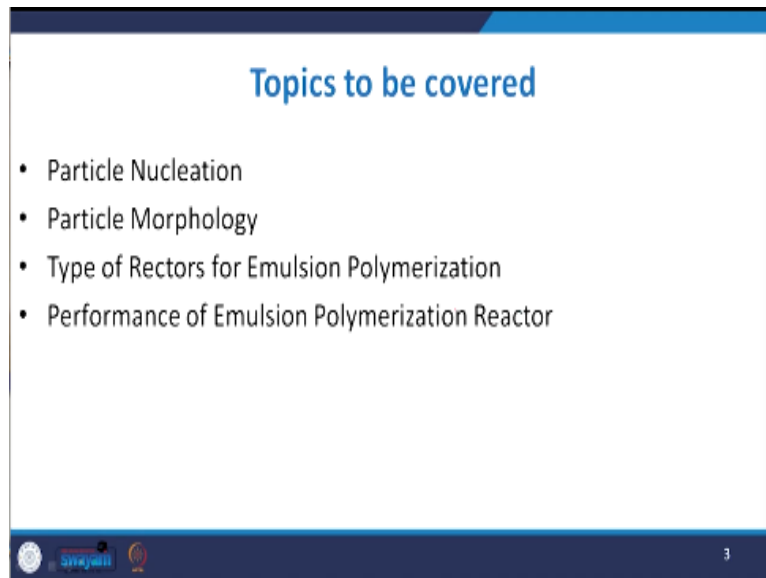
, in this particular lecture, we will start with the particle nucleation, then the particle morphology. We will have a discussion about the different type of reactors for emulsion polymerization. We will discuss about the performance approach of emulsion polymerization reactor, because this particular aspect is extremely important to for economics of any polymerization process.

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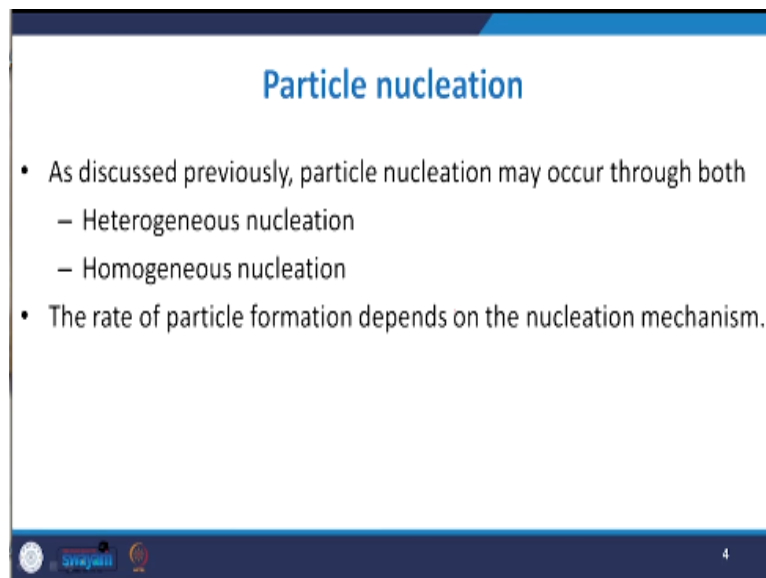
So, let us start with the particle nucleation. As we discussed previously, that the particle nucleation may occur through both either heterogeneous nucleation or homogeneous nucleation, we give the emphasis to these two nucleation approaches in the previous lecture. The rate of particle formation, it depends on the nucleation mechanism. , you can see that this when we talk about the heterogeneous nucleation.

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The rate of formation of polymer particles by heterogeneous nucleation is

$$R_{nuc} = \frac{k_{am}[P_{tot}]_w N_m}{V} \ (particles \ l^{-1} \ s^{-1}) \qquad \qquad .....(1)$$

where k_{am} is the rate coefficient for radical entry into the micelles

N_m is the number of micelles in the reactor

If you recall that in the previous lectures, we discussed about the formation of those micelles.

And we had a discussion about the role of those micelles in the polymerization process.

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, whenever we discussed or we represent this N m that is the number of micelles. Then obviously question may arise that how we can mathematically obtain the number of micelles in a particular reactor.

N_m is the number of micelles in the reactor given by:

$$N_m = \frac{(S_w - cmcV_w)N_A}{n_m} (micelles) \quad ....(2)$$

where "cmc" is the critical micelle concentration (mol l^{-1}) and

V_w the volume of the aqueous phase (in ltrs)

therefore, cmcV$_w$ is the amount of surfactant dissolved in the aqueous phase

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$n_m$is the aggregation number (average number of molecules of surfactant per micelle) and

S_w the amount of surfactant that is dissolved in the aqueous phase and forming micelles.

S_w can be calculated by means of the overall material balance for the surfactant:

$$S_w = S_T - \frac{A_p^*}{a_s} \quad ...(3)$$

This is the question number 3.

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Rate Expression: Heterogeneous Nucleation

Here, S_T is the total amount of emulsifier in the reactor (mol)

A^*_p, is the total surface area of the polymer particles (m^2)

$$A^*_p = 0.048 N_p^{0.33} \left(\frac{V_{pol}}{\phi^p_{pol}}\right)^{0.66} \ldots \ldots (4)$$

V_{pol} is the volume of polymer in the reactor and

ϕ^p_{pol} the volume fraction of polymer in the polymer particles

So, this represents the volume fraction of the polymer in the polymer that is why, it is represented as V.

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, when you talk about the rate expression in the homogeneous nucleation, because previously we discussed about the rate expression related to the heterogeneous equation. So, the oligo radicals, most are growing rate in the aqueous phase. So, when exceeds the maximum soluble

length, they provides the rate formation of particles. The critical length usually depends on the composition of the oligo radical.

The differentiation between the radicals developed from the initiator with the desorbed the radical help in to define the composition. , the oligomer is formed from the formal one needs a minimum length that is represented as ∂z to be sufficiently hydrophobic, because always we are looking for the micelle or critical micelle concentration. So, that is how it is to be sufficiently hydrophobic to enter into the polymer particles.

While oligomer developed through the desorbed radicals, they can penetrate into the particles directly. So, we can see that how they can go ahead with this approach.

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, when we talk about the rate expression, so, the rate of formation of particles, this can be defined through the rate of polymerization of oligo radicals of critical length. , there is a slight modification in the previous rate expression.

The rate of formation of particles can be defined through the rate of polymerization of oligoradicals of critical length:

$$R_{nuc} = \frac{k_p[M]_w\left(P_{Ijcrit} + P_{Micrit}\right)}{V} N_A \ (particles \ l^{-1} \ s^{-1})$$

$[M]_w$: concentration of monomer in the aqueous phase

P_{Ijcrit} : number of oligoradicals of critical length formed from the initiator

P_{micrit} : number of oligoradicals of critical length formed from the desorbed radicals

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Both of these can be calculated by balancing the radicals of both types in the aqueous phase, pseudo-steady-state conditions will apply

$$P_{Ijcrit} = \alpha_1^{jcrit-\delta z+1} \, \alpha_2^{\delta z-1} \, 2f \frac{k_I I}{k_p [M]_w} (mol)$$

$$P_{Micrit} = \frac{k_d \bar{n} N_p}{k_p [M]_w N_A} \alpha_1^{icrit} \, (mol)$$

here α_1 : probability of propagation of radicals capable to cross the threshold and enter into the polymer particles

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α_2 : probability of propagation of radicals generated from the initiator

Assumption: the radicals generated from the initiator with a length shorter than δ_z are too hydrophobic to enter into the organic phases

These probabilities are given by:

$$\alpha_1 = \frac{k_p[M]_w}{k_p[M]_w + k_{tw}[P_{tot}]_w + k_a\left(\frac{N_p}{N_A V_w}\right) + \delta_{(mic)}k_{am}\left(\frac{N_m}{N_A V_w}\right)}$$

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$$\alpha_2 = \frac{k_p[M]_w}{k_p[M]_w + k_{tw}[P_{tot}]_w}$$

$\delta_{(mic)} = 0$ if only homogeneous nucleation is applied

particle nucleation will happen by both heterogeneous and homogeneous mechanisms if;

  – The system contains water dissolvable monomers and

  – having concentration of surfactant sufficiently high enough so that micelles can be formed

So, this is the usual way through which you can represent this homogeneous nucleation.

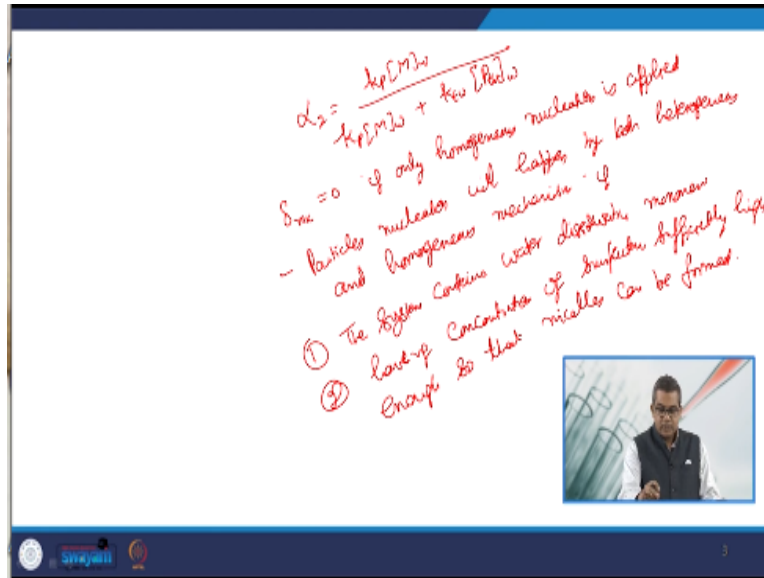Emulsifiers are generally used to stabilise the particle form through the homogeneous nucleation as we discussed in the previous lecture. , in micelles are not present that emulsifier will form through the existing polymer particles that may sometimes affect the rate of polymerization.

, it is to be noted that a particle is stability, they do not require the coverage of entire surface. It may be in the segmental way. , practically the partial coverage by emulsifier is found in most of the commercial polymers or latex. , this uncovered part because, if it is in the segmental set part, then some uncovered part may remain. , this uncovered part, this leads to the formation

of particle coagulation whether the nucleation occurred through homogeneous or heterogeneous or through combination of both of them.

So, this may lead to open another arena for the coagulation. , let us have a look about the particle nucleation. , first part in this category is the monomer partitioning. We have already discussed this monomer partitioning that during the interval 1 and 2 of a batch emulsion. The polymerization partitioning of the monomer occur between:

1. the monomer droplets;
2. the aqueous phase;
3. the polymer particles.

So, the monomer that diffuses through the aqueous phase continuously replaces the monomer that generates the polymer particles which was developed earlier. , if you recall the interval third. , in interval third, there are no droplets left and mostly all the monomer get located into the polymer particles, this indicates the end of nucleation. So, that means we are approaching towards the termination one.

So, however, when semi-batch processes used the continuous feeding of monomer into the polymerization reactor at high functional convergence happened with the polymer when sometimes, the monomer ratio near to 9:1 weight by weight. , the difference changes the scenario of such reactor from the batch reactor in such a way that the newly fed monomer droplet, they are occupies the reactor and interval third can be shifted to a higher extent.

, the polymerization proceeds in aqueous phase by a consumption of monomer arriving through diffusion. Therefore, both mass transfer and the rate of polymerization govern the concentration of monomer. Sometimes, in this particular approach, we need to look into the equilibrium equations.

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So,

- Equilibrium equations:

$$K_i^j = \frac{\phi_i^j}{\phi_i^w} \qquad \text{j = polymer particles, droplets}$$

- Material balances:

$$\phi_{pol}^p + \sum_i \phi_i^p = 1$$

$$\phi_{water}^w + \sum_i \phi_i^w = 1$$

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So, another approach that is the submission i phi i d that is this option is equal to 1.

$$\sum_i \phi_i^d = 1$$

$$V_p \phi_i^p + V_d \phi_i^d + V_w \phi_i^w = V_i$$

$$V_w \phi_{water}^w = V_{water}$$

$$V_p \phi_{pol}^p = V_{pol}$$

K_i^j : partition coefficient of monomer i between the phase j

ϕ_i^j :the volume fraction of monomer i in phase j,

the superscript w denotes the aqueous phase,

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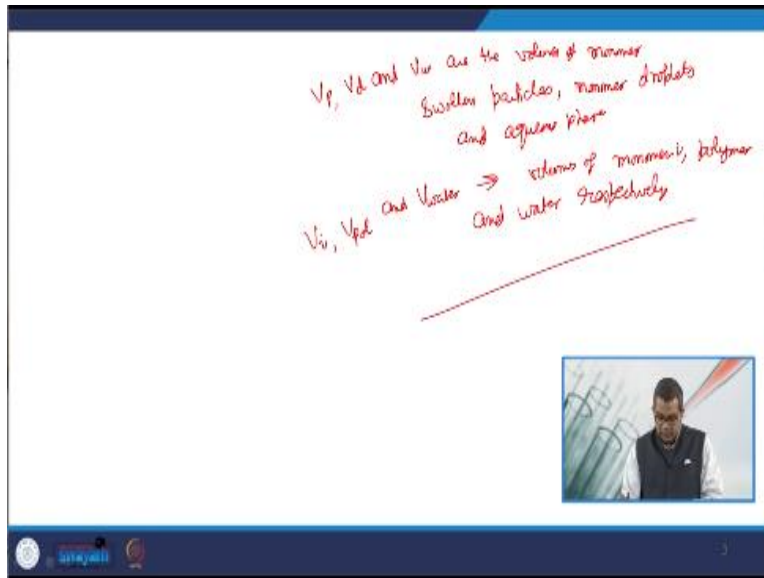
V_p, V_d and V_w are the volumes of monomer swollen particles, monomer droplets and aqueous phase, respectively, and

V_i , V_{pol} and V_{water} are the volumes of monomer i, polymer and water, respectively.

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So, this is the small notation related to this one. , let us under the head of this particle nucleation. Let us have a look about molecular weight that is a second parameter. , usually the average number of radicals attached per particle, they are set to be the controlling factor of molecular weights. , mathematical modelling is usually easy and precise to for calculating the molecular weight distribution of linear or non-linear polymers.

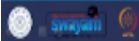, it works on the function of a rate of generation of different chains as we discussed. , therefore, it is important to include the rate of generation or parameter in the material balance characteristics of a particular reactor. Then, sometimes, linear polymers also play a very vital role. , if the monomer unit is mono-functional, that is it has only one functional group attached with the participating molecule. Then the polymerization does not include the chain transfer phenomena and then the linear polymers are formed.

So, therefore, this particular phenomena plays a vital role in deciding the fate of the polymers. , Smith-Ewart, they discussed a lot with the particle nucleation and they described the 2 cases, cases 1 and 2 and sometimes referred as 0, 1 system. , these cases or these case favours the linear polymerization as there is very less likelihood of occurrence of particles with more than 1 radical.

In fact, the system can be considered to be generated by the particles having no radical; with the particles having only one radical. So, due to the involvement of no radicals referred as 0 and 1 radical that is referred as 1. This is the case also termed as 0, 1 system and it plays a very

vital role or a prominent place in the study of emulsion polymerization. , the radical containing particle that tracks the particle having no radical or inactive by the chain transfer to monomer.

Then instantaneously that termination may occur upon the entry of 1 radical. So, this is sometimes, quite useful phenomenon and sometimes, it is undesired phenomena during the process of emulsion polymerization. Then the Smith-Ewart case number 3 that is the pseudo bulk system. In this case, as the particle contains more than 1 radicals, because this is quite common phenomenon may contains more than 1 radicals, the reaction kinetic favours bulk polymerization.

, the concentration of radicals present in the particles, they can be represented by this equation

$$\bar{n} = \left(\frac{k_a [R]_w}{2c} \right)^{0.5}$$

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Particle nucleation

Non-linear polymers

Non-linear polymers can be formed in radical polymerization by:-

- Intermolecular chain transfer i.e. by transferring the radical center from a polymeric radical to a different polymer chain.
- By various terminal bonds participating reactions such as disproportionation reaction, radical transfer to monomer, chain scission reaction, among others.
- Participation of multifunctional monomers

, sometimes, you may need to look into the non-linearity of the polymers or non-linear polymers. , these non-linear polymer, they can be formed in the radical polymerization by either by the intermolecular chain transfer that is by the transferring the radical centre from a polymeric radical to a different polymer chain. Sometimes, by various terminal bonds participating reactions, such as disproportionation reaction, radical transfer to monomer, chain scission reactions or others.

, sometimes, they can be formed by the participation of multifunctional monomers. Sometimes, it is quite common that multifunctional monomers, they are participating in any kind of a polymerization reaction. So, this may lead to the formation of non-linear polymers. Sometimes, intermolecular chain transfer reaction that can be referred as backbiting, they also promotes the non-linear polymerization.

However, sometimes this phenomena is not found to be effective in the molecular weights. So, all these processes except the backbiting, they tend to again activate the already dead polymer chains, sometimes, maybe because of the variety of reasons, the some dead polymer chains may be formed during the course of polymerization. , this increases the length of polymer through subsequent propagation step and finally, they terminate again.

So, it is just like that you are putting up, you are making those the dead polymer chain live with respect to various approaches. So, therefore, the polymerization proceeds with the several activation or deactivation cycles. Deactivation cycle means deactivation means, the polymer

chain may be come back and activation with the help of the several methodological can become the activated one.

, these repetitive activation and deactivation step results in increased the molecular weight and the formation of a suitable polymer network. So, mathematical modelling of such polymer is usually tutored by either the population balance or Monte Carlo methods. , you can go through some literature related to the mathematical modelling in depth for understanding these Monte Carlo and population balance.
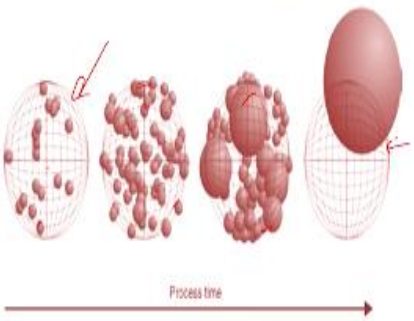
Although, we covered the population balance as this part is not intend to cover this particular approach. , let us have a look about the particle morphology. , the polymer formed through the composite material, they have various commercial advantages and they used in the different application. For example, the particles having an elastic core and a strong shell that can be used as an impact modifiers for polymer matrices.

On the other hand, a hardcore or soft shell based particles can found their application in speciality paints due to the lower minimum film formation temperature, as we discussed earlier that MFFT and non-stickiness of higher temperature. So, on one hand, you are having hardcore polymer and other one, you are having the soft fit type of things, so, that you can use in a variety of applications.
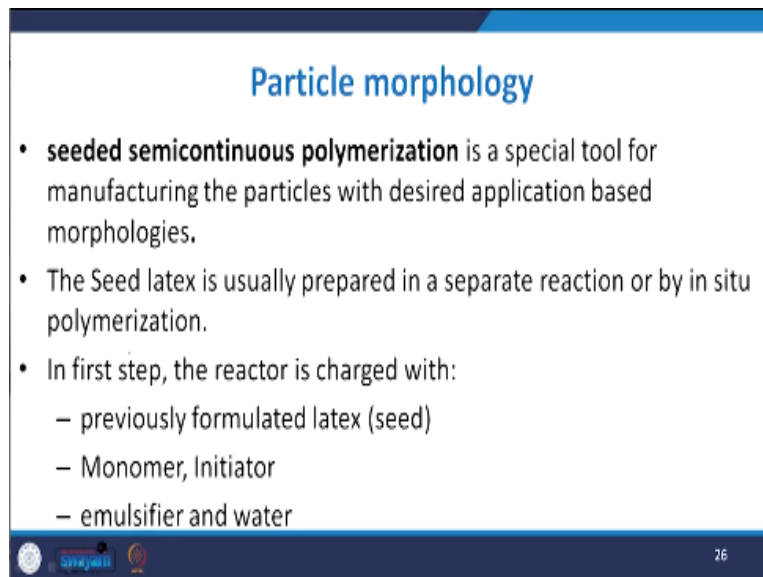
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, let us have a look about the evolution of particle morphology, because again it is play a very vital role. , sometimes, the hollow particles do their capability of encapsulating the large guest

molecule, they can work as an effective drug delivery system. So, this is the particle morphology plays a very vital role in the drug delivery system and that is becoming more and more common adays.

, it can also help in the process time evaluation of the particle morphology. , this is you can see that these are the hollow particles and the guest molecules are encapsulated like this and they form their own network within this system. And when this network become larger, larger than they just evacuated from the host particle. By this way, they can do their own work. And this is the proper methodology for effective drug delivery system or the formation of effective drug delivery system.
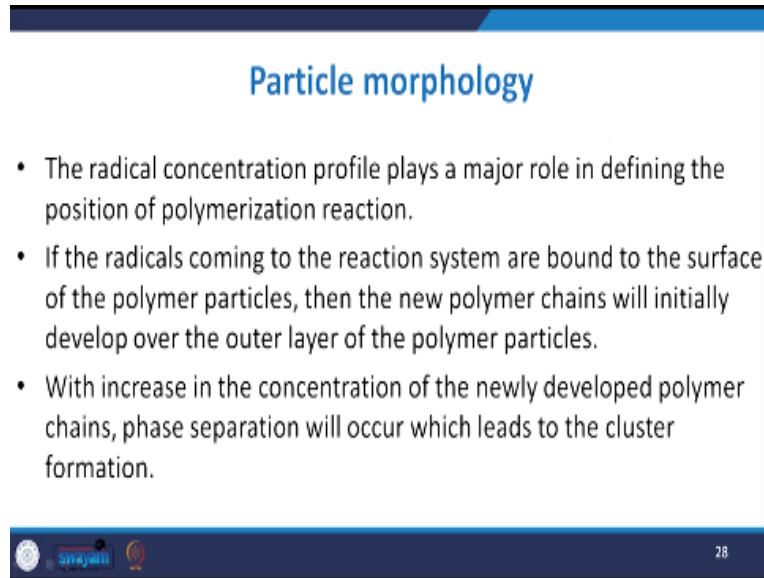
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, in detail if we try to develop the things that the seeded that semi-continuous polymerization is sometimes, a special tool for manufacturing the particles with desired application based morphologies. , in this category, the seed latex is usually prepared in a separate reaction or sometimes in situ polymerization or suo moto polymerization. In the first step, the reactor is charged with the previously formulated latexes that is sometimes referred as seed, you may have another phase like monomer, initiator, emulsifier and water.

, the polymerization of this initial charge usually take about 3 to 4 hours of a reaction time that depends on the seed that depends on the monomer being used. Then rest of the formulation is added. The reaction conditions are usually adjusted in such a way that the polymerization reaction can occur inside the existing a polymer particles. The radical concentration profile, this plays a very vital role in defining the position of polymerization reaction.

, if the radicals coming to the reaction system, they are bound to the surface of the polymer particle, then the new polymer chains will initially develop over the outer layer of the polymer particle, as we saw in this particular figure.
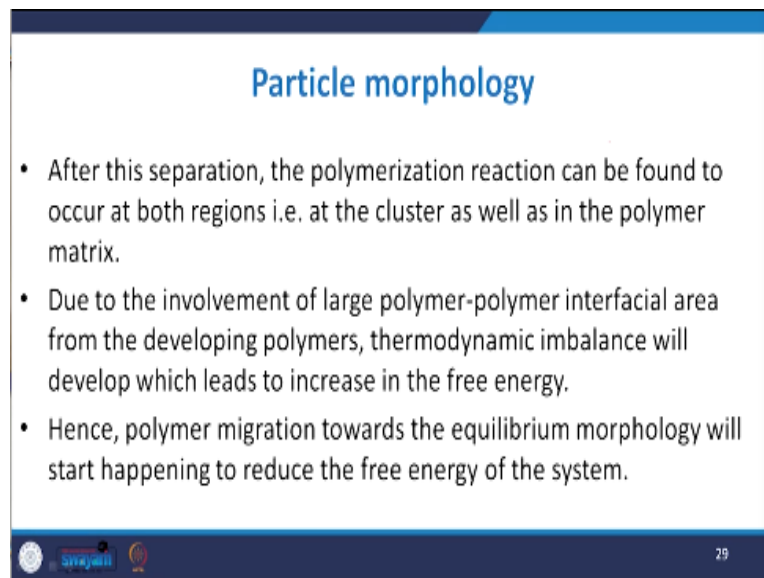
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, with increase in the concentration of newly developed polymer network or a chain, the phase separation may occur, which leads to the cluster formation.

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after this because when the cluster is formed, then there is a need to separate all those things. So, after this the separation the polymerization reaction, this can be found to occur at both regions like the cluster as well as in the polymer matrix. So, due to the involvement of large

polymer, polymer interfacial area from developing polymers, thermodynamic imbalance may develop, which may lead to the increase in the free energy.

Therefore, the polymer migration towards the equilibrium morphology will start happening to reduce the free energy of the system.

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, in this particular lecture, we discussed about the particle morphology. We had a discussion about the different mathematical approaches for determination of various polymer system especially emphasising to the emulsion polymerization. We will continue this particle morphological approach in the next lecture. Thank you very much.