fPolymer Reaction Engineering
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Lecture - 50
Emulsion Polymerization Semi-Continuous Polymerization

Welcome to the next segment of emulsion polymerization. In this segment, we will discuss about the semi-continuous polymerization. So, let us have a brief look about that what we covered previously. We discussed about the emulsion polymerization. We had a discussion about the micro-structural features of the emulsion polymerization which we discussed various parameters associated with the emulsion polymerization.

Then we had discussed about the various factors affecting the emulsion polymerization. And we start the process of emulsion polymerization under the edges of batch polymerization.

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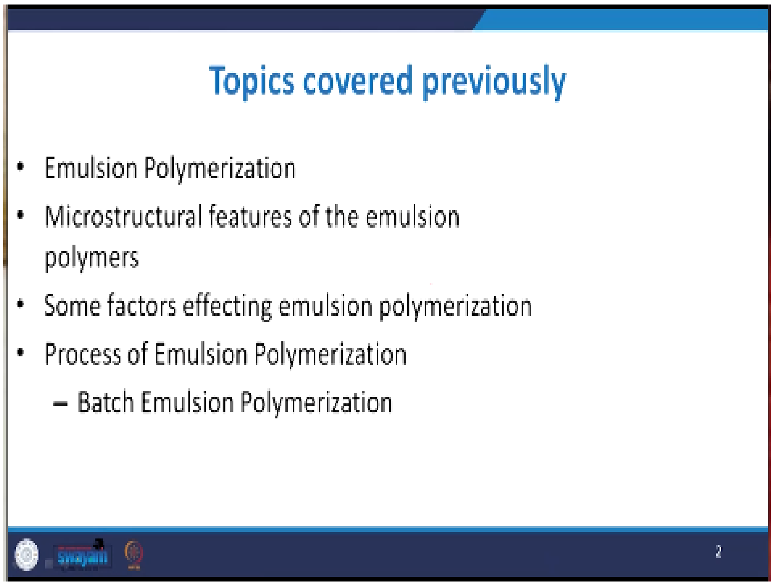

Topics covered previously

- Emulsion Polymerization
- Microstructural features of the emulsion polymers
- Some factors effecting emulsion polymerization
- Process of Emulsion Polymerization
  - Batch Emulsion Polymerization

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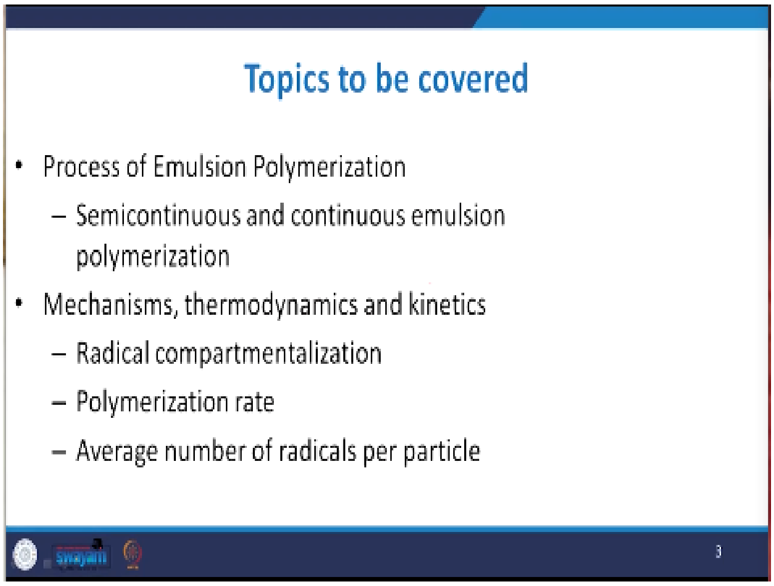

Topics to be covered

- Process of Emulsion Polymerization
  - Semicontinuous and continuous emulsion polymerization
- Mechanisms, thermodynamics and kinetics
  - Radical compartmentalization
  - Polymerization rate
  - Average number of radicals per particle

In this particular chapter, we are going to discuss with the semi-continuous and continuous emulsion polymerization. we will have a discussion about the mechanism, thermodynamics and kinetic approaches of radical compartmentalization, then polymerization rate. We will discuss about the average number of radicals per particle.

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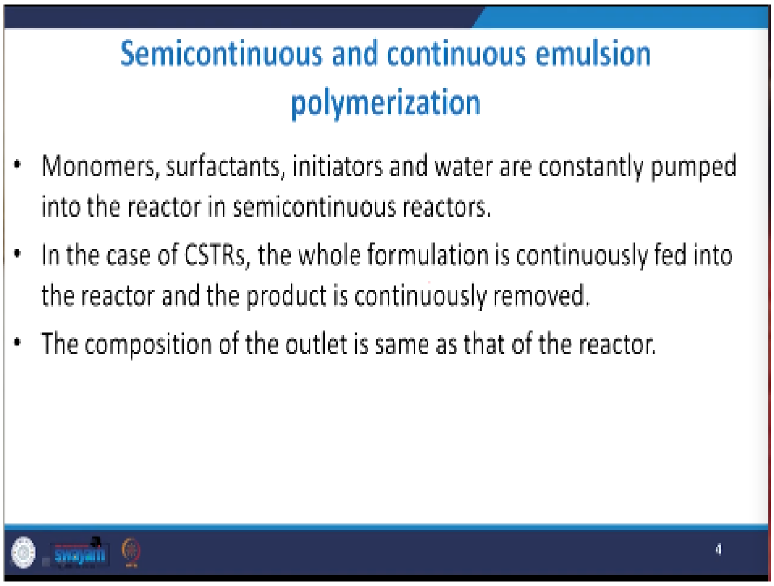

Semicontinuous and continuous emulsion polymerization

- Monomers, surfactants, initiators and water are constantly pumped into the reactor in semicontinuous reactors.
- In the case of CSTRs, the whole formulation is continuously fed into the reactor and the product is continuously removed.
- The composition of the outlet is same as that of the reactor.

Now, let us have the start with the semi-continuous and continuous emulsion polymerization. Now, as we recall that the integral part of emulsion polymerization or monomers, surfactant, initiators and water, so, all these are constantly pumped into the reactor in the semi-continuous reactor. Now, everyone is ingredient or in the recipe form, they are having a very vital role in the emulsion polymerization like surfactant, they change the surface energy; then initiated, they can trigger the polymerization reaction; water is dispersion media.

So, everything is having its shown importance. Now, in case of continuous stirred tank reactor, the entire formulation is continuously fed into the reactor and the product is continuously removed. So, the composition of outlet is same as that of the reactor. So, that is the beauty of this CSTR. Now, if you recall that we discussed about the homogeneous nucleation and heterogeneous nucleation in the previous lectures.

So, for homogeneous nucleation to occur, there should be sufficient free emulsifier available to stabilise the oligo radicals that precipitate in the aqueous phase. Now, for heterogeneous nucleation to occur, there should be sufficient free emulsifier available to saturate the surface of the existing interfaces with respect to the particle monomer droplets and thereby the formation of micelles.

Now, the nucleation of a new particle drop can be done by adding either additional amount of surfactant at different interface during the semi-continuous process. The monomer droplets will be found inside the reactor until the rate of monomer addition exceeds the polymerization rate. Sometimes, the presence of monomer available inside the system that reduces the proficiency of regulating the polymer characteristics, which is usually undesirable for the emulsion polymerization process.

Moreover, the availability of free monomer in excess can endanger the operational safety. So, sometimes, these are the very crucial points and with the help of various factors involved in the polymerization process and optimization is always desirable before we proceed for the polymerization reaction. Now, let us have a discussion about the mechanism thermodynamics and kinetics of this emulsion polymerization. Now, in emulsion polymerization, most of the polymerization occur in the polymer particles.

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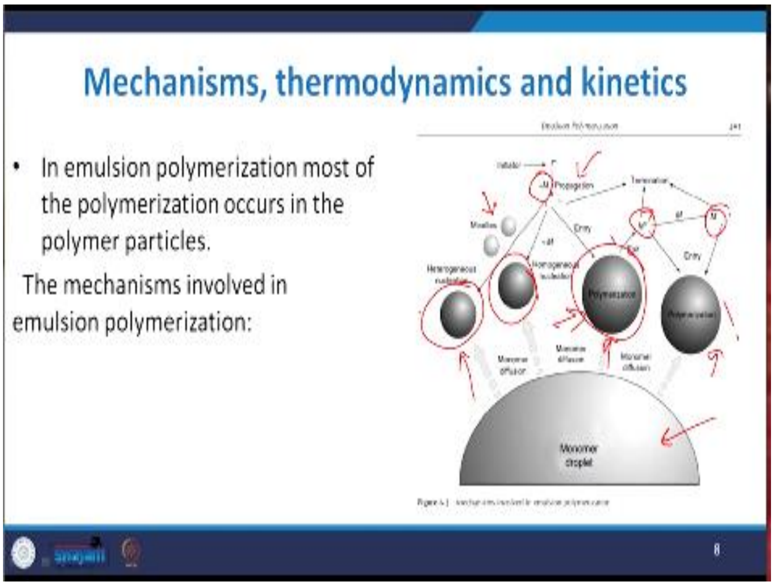

Mechanisms, thermodynamics and kinetics

- In emulsion polymerization most of the polymerization occurs in the polymer particles.

The mechanisms involved in emulsion polymerization:

So, this, the mechanism involved in the emulsion polymerization is as such like here, you see that this is the monomer droplets. And here, there are 2 nucleation steps homogeneous and heterogeneous one. So, there is a continuous monomer diffusion because usually if we go to the process, the initiator triggers this propagation reaction with the help of monomer. And in this particular approach, there is a formation of homogeneous nucleation or heterogeneous nucleation with the help of these micelles.

So, these monomer droplets tends to diffuse to these heterogeneous and homogeneous nucleating particles and thereby, they start the polymerization process in situ. Now, when we talk about that termination step, then the termination is step, this is the propagation step. So, when we talk about the termination step, the termination step always requires certain approaches.

One is maybe the combination of free radicals, maybe another aspect, maybe related to the formation of the combination of these monomer particles with the inhibitors etcetera. So, based on the things which we discussed a priori, they can go for either this process or this process to give you the polymers. So, this is a very small mechanism involved in this emulsion polymerization.

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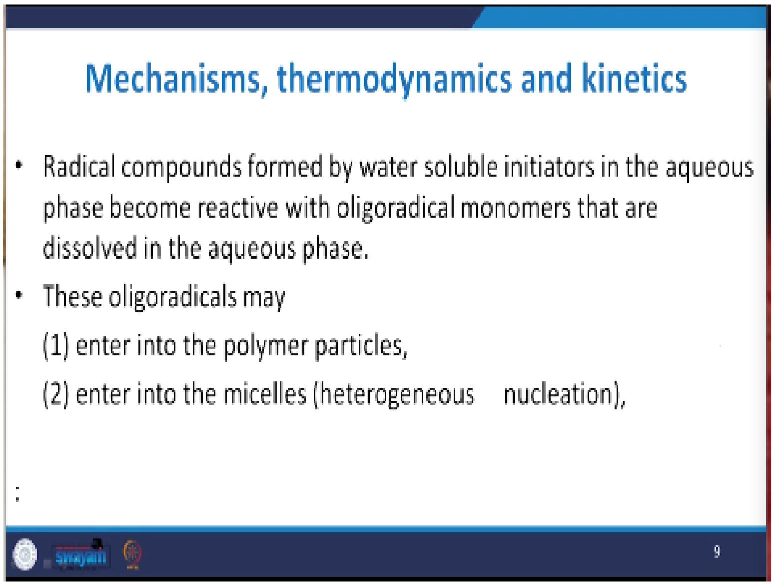

Mechanisms, thermodynamics and kinetics

- Radical compounds formed by water soluble initiators in the aqueous phase become reactive with oligoradical monomers that are dissolved in the aqueous phase.
- These oligoradicals may

  (1) enter into the polymer particles,

  (2) enter into the micelles (heterogeneous nucleation),

:

So, let us categorise the things in this particular approach the radical compounds, they are usually formed by water soluble initiator in the aqueous phase, they become reactive with the oligo radicals monomer and that are dissolved in the aqueous phase. So, these oligo radicals may enter into the polymer particles or enter into the micelles as we see in this particular figure. So, it may enter into the heterogeneous nucleation like here, they can they can enter into the heterogeneous nucleation.

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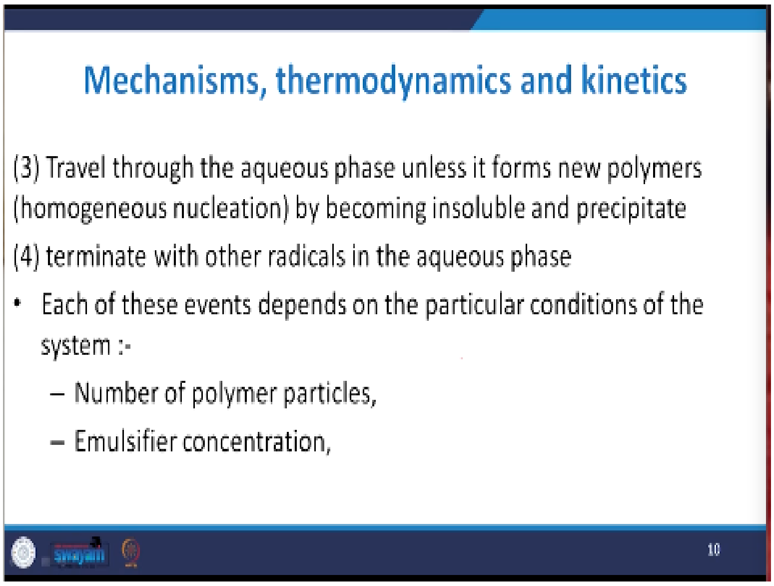

Mechanisms, thermodynamics and kinetics

(3) Travel through the aqueous phase unless it forms new polymers (homogeneous nucleation) by becoming insoluble and precipitate

(4) terminate with other radicals in the aqueous phase

- Each of these events depends on the particular conditions of the system :-
  - Number of polymer particles,
  - Emulsifier concentration,

Now, they travelled through the aqueous phase, unless it forms a new polymer, maybe the homogeneous nucleation by becoming insoluble and precipitate. Then they terminate with other radicals in the aqueous phase. Now, if you see that they terminate in the aqueous phase to give a room for other radicals. Now, each of these even this depends on the particular condition of the system.

Now, these conditions maybe the number of polymer particles or the emulsifier concentration or initiator concentration, sometimes, type of monomer play a very vital role and its concentration. So, these mechanisms involve the transformation of chain into small molecules, which finally forms small radicals. Now, these small radicals sometimes, may exit the polymer particles diffusing into the aqueous phase.

Now, let us have a look about the radical compartmentalization. Now, during the polymerization, the radicals are spread among the polymer particles within the system. And that is quite obvious that these radicals are spread during the polymer particles to facilitate the further polymerization process. Now, the particles, they are so small in size that there are only few radicals per particles or on average less than 1 radical part particles.

So, that compartmentalization of radicals between particles has important effects on polymerization reaction rate as well as on the polymer micro-structure. Now, radical in different particles cannot terminate by bio-molecular termination, sometimes or consequently, the overall radical concentration in emulsion polymerization is usually higher than in bulk polymerization.

So, this means that the polymerization rate in emulsion polymerization is significantly higher than the bulk polymerization. So, let us talk the overall concentration of radical increases as a number of particle increases and that is quite obvious, that is by decreasing the particle size of given solid contain. So, this thing is quite obvious in line with this concept. Now, this particular approach gives a further way of increasing polymerization rate in addition to increasing the temperature due to the initiator concentration.

So, that means the exothermocity is on the way. Now, the radical compartmentalization also result in the longer lifetime of the radical, sometime, leading to the higher molecular weight. So far the systems, the polymer chain expense until the second radical joints the polymer particle and comes to and with the rising one. So, therefore, the chain length is inversely proportional to the entry frequency.

So, whenever we talk about this for a given concentration of initiator, the frequency of radical entry, it decreases with the number of particles, therefore, the molecular weight increases. Now, as a consequence in emulsion polymerization, the polymerization rate and the molecular weight, it can be increased simultaneously by nearly increasing the number of particles. So, usually this phenomena is not possible in bulk solution and the suspension free radical polymerization technique.

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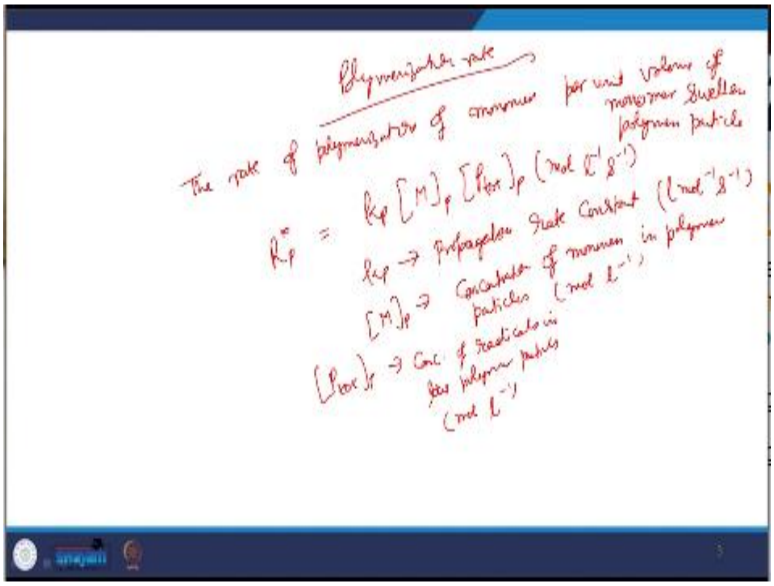

Polymerization rate

The rate of polymerization of monomer per unit volume of monomer swollen polymer particle

$R_p^* = k_p [M]_p [P_{tot}]_p$ (mol $l^{-1} s^{-1}$)

$k_p \rightarrow$ Propagation rate constant (l mol^{-1} s^{-1})

$[M]_p \rightarrow$ Concentration of monomer in polymer particles (mol l^{-1})

$[P_{tot}]_p \rightarrow$ Conc. of radicals in the polymer particles (mol l^{-1}

Now, let us have a look about the polymerization rate because polymerization rate also play a very vital role in deciding the fate of these radicals.

The rate of polymerization of monomer per unit volume of monomer swollen polymer particle, R^*_p, is

$$R_p^* = k_p[M]_p[P_{tot}]_p \ (mol\, l^{-1}s^{-1})$$

$k_p$is the propagation rate constant (l mol^{-1}s^{-1})

$[M]_p$ the concentration of monomer in the polymer particles (mol l^{-1}) and

$[P_{tot}]_p$ the concentration of radicals in the polymer particles (mol l^{-1}).

So, this is the rate polymerization rate deciding step. Now, this P tot p, this can be expressed in terms of average number of radicals per particle.

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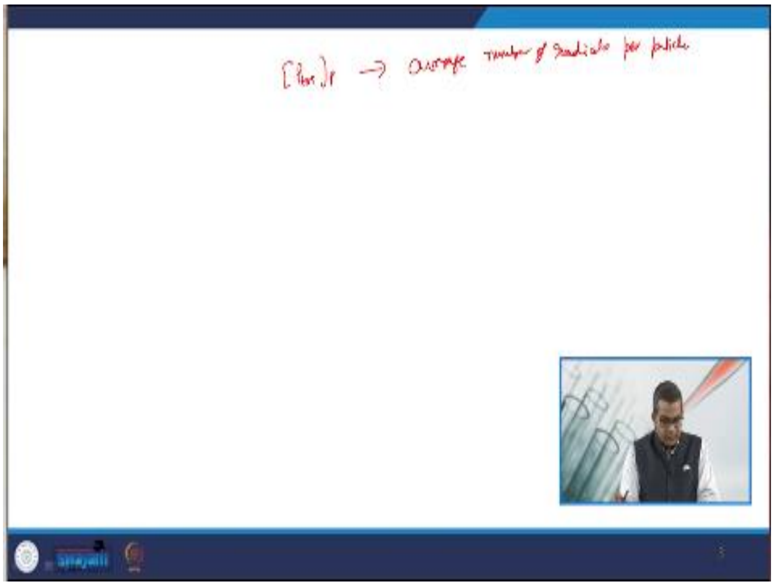

$[R_{tot}]_p$ → average number of radicals per particle

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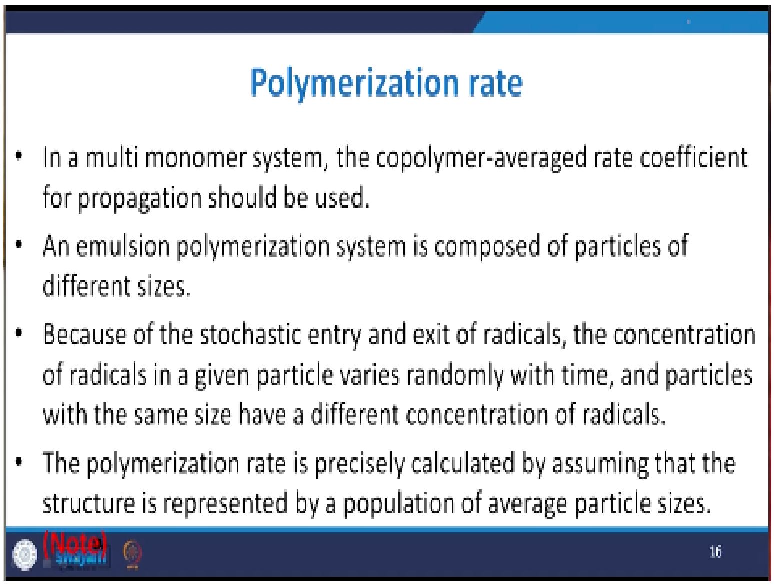

Polymerization rate

- In a multi monomer system, the copolymer-averaged rate coefficient for propagation should be used.
- An emulsion polymerization system is composed of particles of different sizes.
- Because of the stochastic entry and exit of radicals, the concentration of radicals in a given particle varies randomly with time, and particles with the same size have a different concentration of radicals.
- The polymerization rate is precisely calculated by assuming that the structure is represented by a population of average particle sizes.

(Note)

Now, in multi-monomer system, the copolymer average rate coefficient for propagation should be used. So, an emulsion polymerization system is composed of particles of different size. Because of the stochastic entry and exit of radicals, the concentration of radical given particle varies randomly with time and the particles with the same size have a different concentration of radicals.

Now, the polymerization rate is precisely calculated by assuming the structure usually represented by a population of average particle size. So, let us have a look about this thing.

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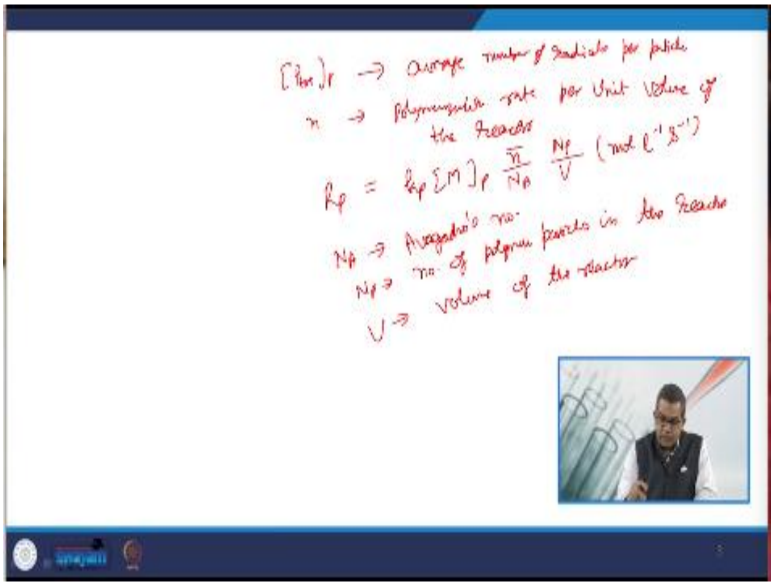

$[P_{tot}]_p$ → average number of radicals per particle

n → polymerization rate per unit volume of the reactor

$R_p = k_p [M]_p \frac{\bar{n}}{N_A} \frac{N_p}{V}$ (mol $l^{-1} s^{-1}$)

N_A → Avogadro's no.

N_p → no. of polymer particles in the reactor

V → volume of the reactor

$[P_{tot}]_p$ can be expressed in terms of the average number of radicals per particle, n, in such a way that the polymerization rate per unit volume of the reactor, R_p, is given by:

$$R_p = k_p[M]_p \frac{\bar{n}}{N_A}\frac{N_p}{V}(mol\, l^{-1} s^{-1})$$

N_A is Avogadro's number

N_p the number of polymer particles in the reactor

V the volume of the reactor

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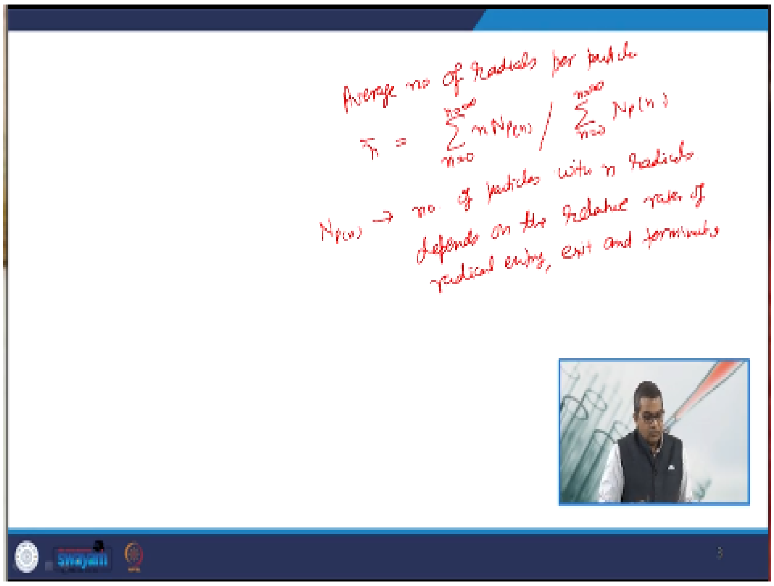

Average no of radicals per particle

$\bar{n} = \sum_{n=0}^{n=\infty} n N_{p(n)} / \sum_{n=0}^{n=\infty} N_{p(n)}$

$N_{p(n)}$ → no of particles with n radicals

depends on the relative rates of radical entry, exit and termination

The average number of radicals per particle is defined as follows:

$$\bar{n} = \sum_{n=0}^{n=\infty} nN_{p(n)} \Big/ \sum\nolimits_{n=0}^{n=\infty} N_{p(n)}$$

where $N_{p(n)}$ is the number of particles with n radicals, which depends on the relative rates of radical entry, exit and termination.

Now, when we talk about the rate of radical entry, then the question arises that how we can express this thing.

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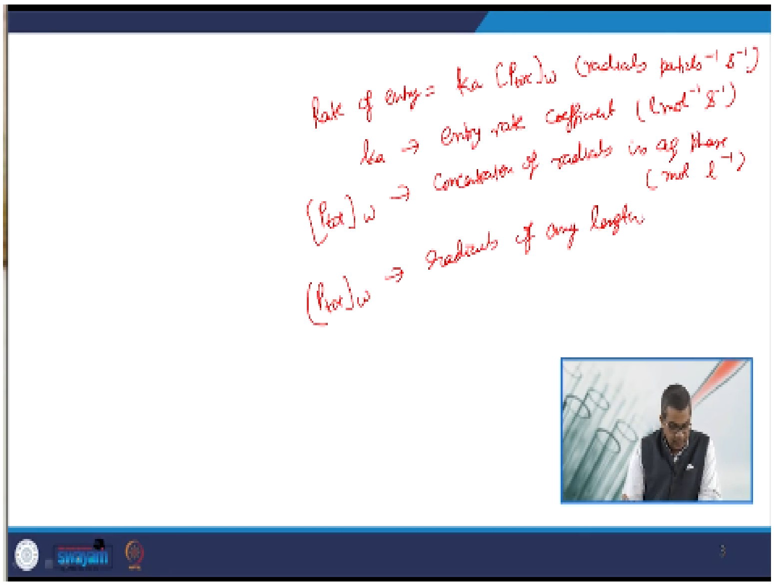

Rate of entry = $k_a [P_{tot}]_w$ (radicals particle^{-1} s^{-1})

k_a → Entry rate coefficient (l mol^{-1} s^{-1})

$[P_{tot}]_w$ → Concentration of radicals in aq phase (mol l^{-1})

$[P_{tot}]_w$ → radicals of any length

The rate for radical entry can be expressed as follows

$$Rate\ of\ entry = ka[P_{tot}]_w\ (radicals\ particle^{-1}s^{-1})$$

where k_a is the entry rate coefficient (l mol^{-1}s^{-1})

$[P_{tot}]_w$ the concentration of radicals in the aqueous phase (mol l $^{-1}$)

It is to be noted that $[P_{tot}]_w$ includes radicals of any length

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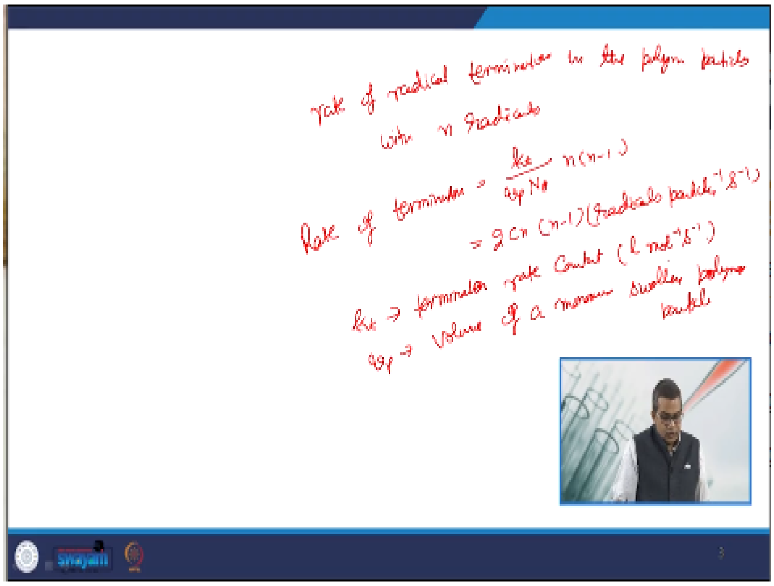

rate of radical termination in the polym. particle with n radicals

Rate of termination = $\frac{k_t}{v_p N_A} n(n-1)$

= 2cn (n-1) (radicals particle^{-1} s^{-1})

k_t → termination rate Const (l mol^{-1} s^{-1})

v_p → Volume of a monomer swollen polymer particle

- So, another approach is another thing is that we should talk about the rate of radical termination. The rate of radical termination in the polymer particles with n radicals is:

$$Rate\ of\ termination\ = \frac{k_t}{v_p N_A} n(n\ -\ 1) = 2cn(n\ -\ 1)\ (radicals\ particle^{-1} s^{-1})$$

k_t is the termination rate constant (l mol^{-1} s^{-1}),

v_p is the volume of a monomer swollen polymer particle.

So, when we talk about this particular approach, then we can assume that the pseudo first order rate coefficient.

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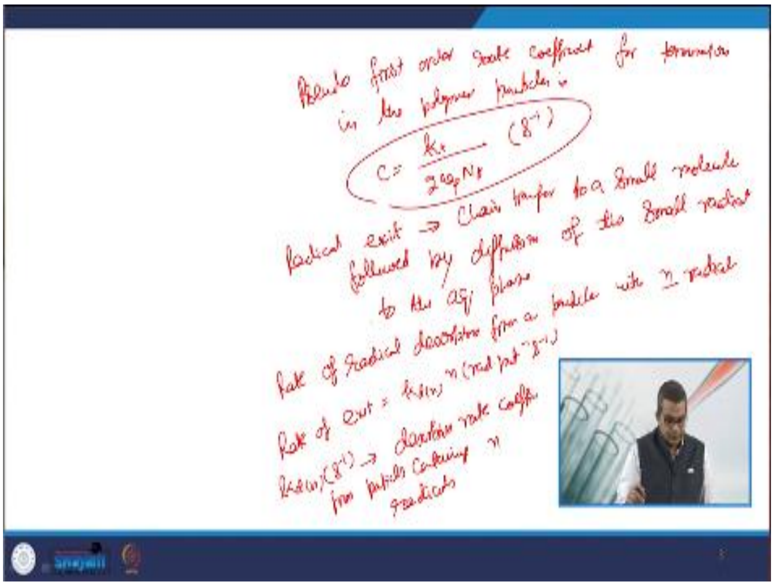

Pseudo first order rate coefficient for termination in the polymer particles is

$$C = \frac{k_t}{2 v_p N_A} \ (s^{-1})$$

Radical exit → Chain transfer to a small molecule followed by diffusion of the small radical to the aq. phase

Rate of radical desorption from a particle with n radical

Rate of exit = $k_{d(n)} n$ (rad part^{-1} s^{-1})

$k_{d(n)}$ (s^{-1}) → desorption rate coeffi. from particle containing n radicals

the pseudo-first order rate coefficient for termination in the polymer particles is:-

$$c\ = \frac{k_t}{2 v_p N_A} (s^{-1})$$

Radical exit occurs by chain transfer to a small molecule followed by diffusion of the small radical to the aqueous phase.

The rate of radical desorption from a particle with n radicals is :-

$$Rate\ of\ exit\ =\ k_{d(n)} n\ (radicals\ particle^{-1}\ s^{-1})$$

$k_{d(n)}$ (s^{-1}) is the desorption rate coefficient from particles containing n radicals.

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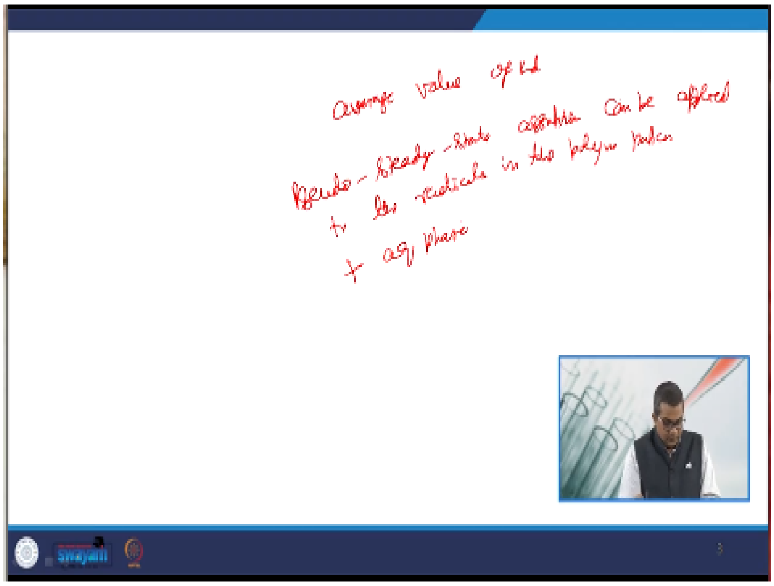

average value of kd

Pseudo-steady-state assumption can be applied to the radicals in the polymer particles

+ aq phase

The rate of radical desorption from a particle with n radicals is :-

$$Rate\ of\ exit\ =\ k_{d(n)}n\ (radicals\ particle^{-1}\ s^{-1})$$

$k_{d(n)}$ (s^{-1}) is the desorption rate coefficient from particles containing n radicals.

The desorption rate coefficient depends on the number of radicals per particle. However, the mathematical treatment simplifies substantially if an average value, k_d, is used.

Practically, the pseudo-steady-state assumption can be applied to the radicals in the polymer particles and in the aqueous phase.

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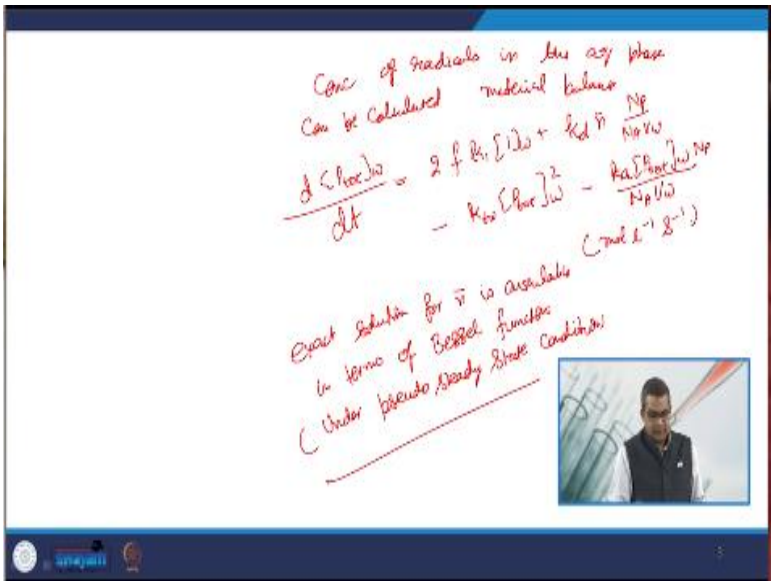

Conc of radicals in the aq phase

can be calculated material balance

$$\frac{d[P_{tot}]_w}{dt} = 2 f k_I [I]_w + k_d \bar{n} \frac{N_p}{N_A V_w} - k_{tw} [P_{tot}]_w^2 - \frac{k_a [P_{tot}]_w N_p}{N_A V_w}$$

(mol l^{-1} s^{-1})

Exact solution for $\bar{n}$ is available in terms of Bessel function

(Under pseudo steady state condition

The concentration of radicals in the aqueous phase can be calculated by means of the following material balance:

$$\frac{d[P_{tot}]_w}{dt} = 2fk_I[I\,]_w + k_d\bar{n}\,\frac{N_p}{N_AV_w} - \ k_{tw}[P_{tot}]_w^2 - \frac{k_a[P_{tot}]_wN_p}{N_AV_w}\ (mol\ l^{-1}\ s^{-1})$$

Under pseudo steady-state conditions the exact solution for $\bar{n}$ is available in terms of Bessel functions, but it is not easy to use.

So, this is the under pseudo steady state condition. So, again this is not an easy task to perform such type of a calculation.

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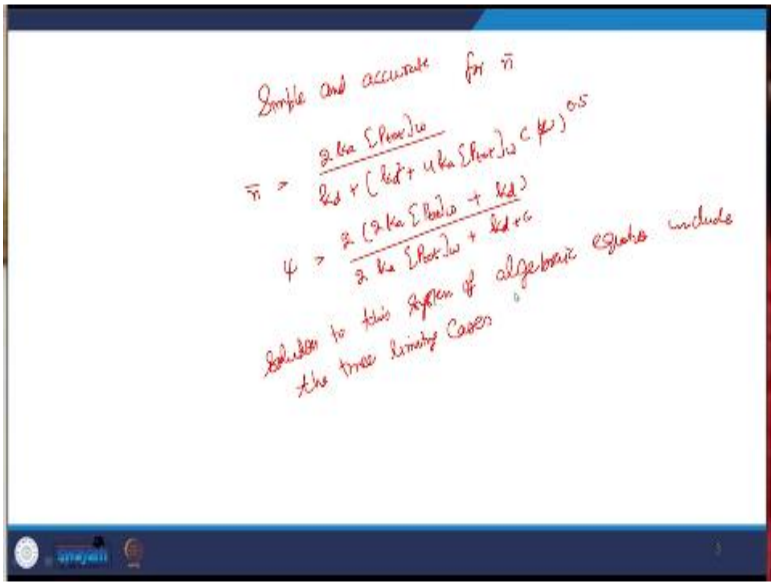

Simple and accurate for $\bar{n}$

$$\bar{n} = \frac{2k_a[P_{tot}]_w}{k_d + (k_d^2 + 4k_a[P_{tot}]_w c\psi)^{0.5}}$$

$$\psi = \frac{2(2k_a[P_{tot}]_w + k_d)}{2k_a[P_{tot}]_w + k_d + c}$$

Solution to this system of algebraic eqns include the three limiting cases

A simpler and accurate equation for $\bar{n}$ is as follows:

$$\bar{n} = \frac{2k_a[P_{tot}]_w}{k_d + (k_d^2 + 4k_a[P_{tot}]_w c\psi)^{0.5}}$$

$$\psi = \frac{2(2k_a[P_{tot}]_w + k_d)}{2k_a[P_{tot}]_w + k_d + c}$$

The solution of this system of algebraic equations includes the three limiting cases of the pioneering work of Smith and Ewart .

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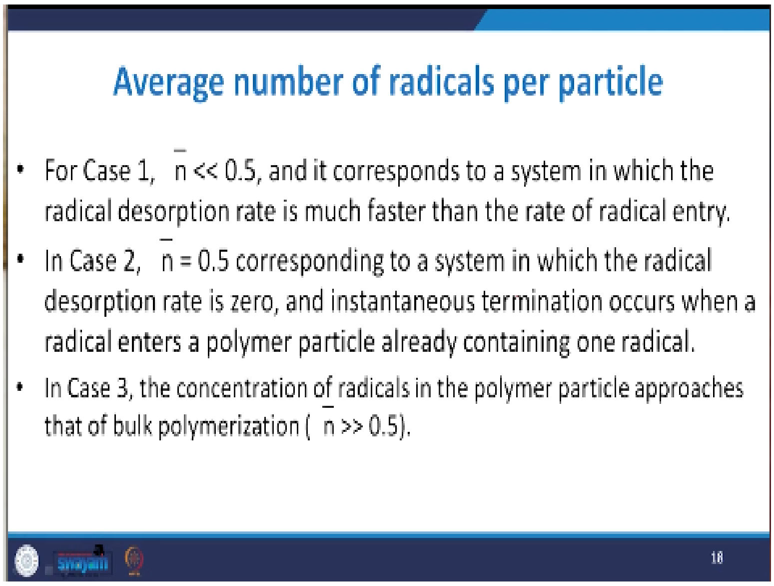

Average number of radicals per particle

- For Case 1, $\bar{n} << 0.5$, and it corresponds to a system in which the radical desorption rate is much faster than the rate of radical entry.
- In Case 2, $\bar{n} = 0.5$ corresponding to a system in which the radical desorption rate is zero, and instantaneous termination occurs when a radical enters a polymer particle already containing one radical.
- In Case 3, the concentration of radicals in the polymer particle approaches that of bulk polymerization ($\bar{n} >> 0.5$).

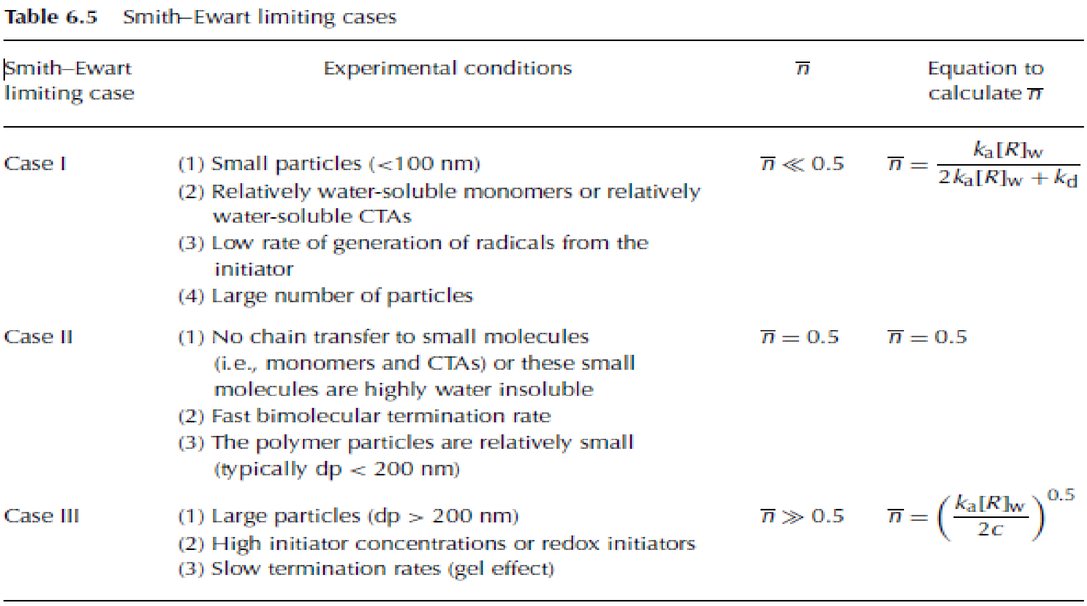

Table 6.5 Smith–Ewart limiting cases

Smith–Ewart limiting case	Experimental conditions	$\bar{n}$	Equation to calculate $\bar{n}$
Case I	(1) Small particles (<100 nm) (2) Relatively water-soluble monomers or relatively water-soluble CTAs (3) Low rate of generation of radicals from the initiator (4) Large number of particles	$\bar{n} \ll 0.5$	$\bar{n} = \frac{k_a[R]_w}{2k_a[R]_w + k_d}$
Case II	(1) No chain transfer to small molecules (i.e., monomers and CTAs) or these small molecules are highly water insoluble (2) Fast bimolecular termination rate (3) The polymer particles are relatively small (typically dp < 200 nm)	$\bar{n} = 0.5$	$\bar{n} = 0.5$
Case III	(1) Large particles (dp > 200 nm) (2) High initiator concentrations or redox initiators (3) Slow termination rates (gel effect)	$\bar{n} \gg 0.5$	$\bar{n} = \left(\frac{k_a[R]_w}{2c}\right)^{0.5}$

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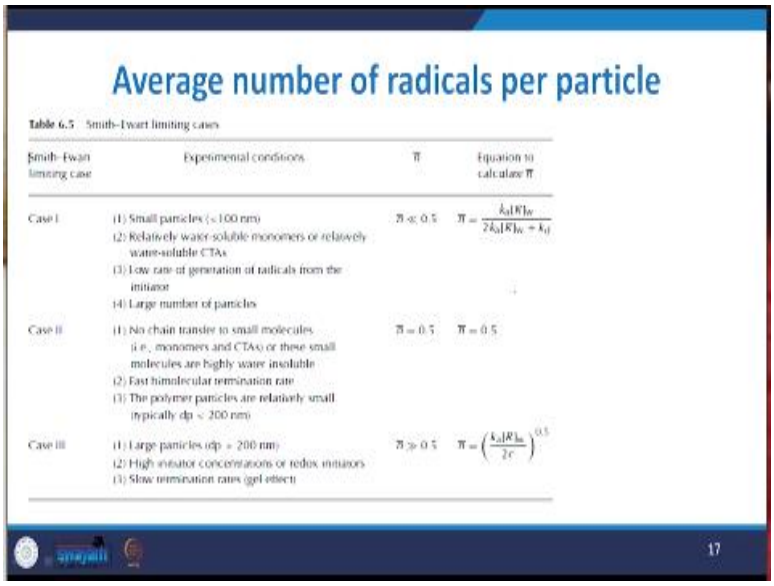

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For ease of study, we have enlisted several average number radicals per particles based on the discussion which we applied in all 3 cases.

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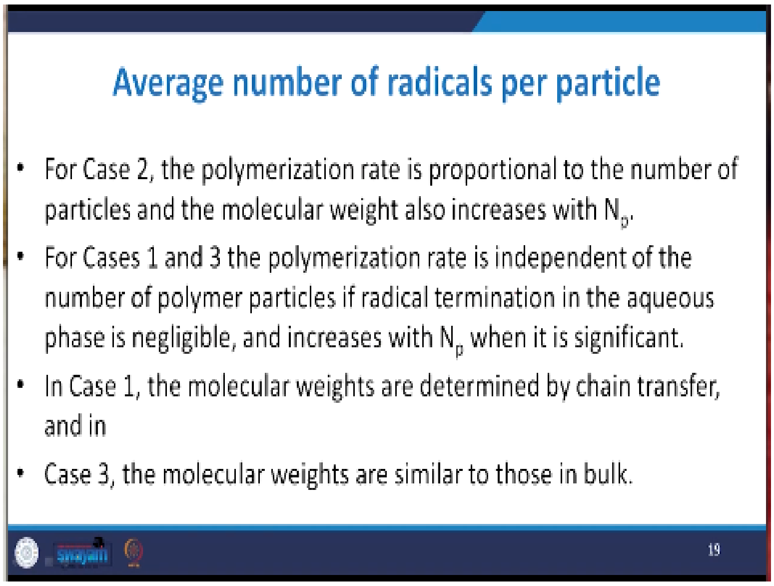

Average number of radicals per particle

- For Case 2, the polymerization rate is proportional to the number of particles and the molecular weight also increases with N_p.
- For Cases 1 and 3 the polymerization rate is independent of the number of polymer particles if radical termination in the aqueous phase is negligible, and increases with N_p when it is significant.
- In Case 1, the molecular weights are determined by chain transfer, and in
- Case 3, the molecular weights are similar to those in bulk.

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- In Case 1, the molecular weights are determined by chain transfer, and in
- Case 3, the molecular weights are similar to those in bulk.

So, that is the difference between case 1 and case 3. Now, when we talk about the radical concentration profile, the oligo radical derived from many water soluble initiators contain in organic moiety. So, when the oligo radical enter into the polymer particle, the inorganic fragment tends to stay in the aqueous phase entering of radicals to the surface of the particle.

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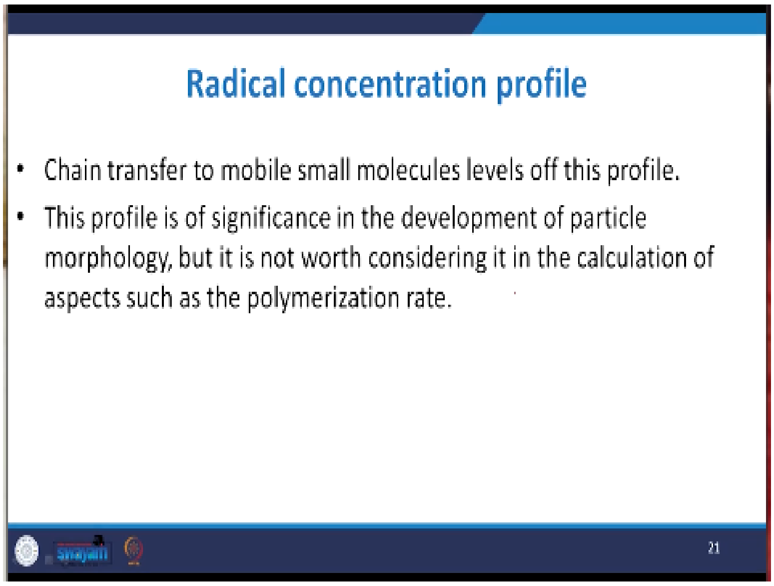

Radical concentration profile

- Chain transfer to mobile small molecules levels off this profile.
- This profile is of significance in the development of particle morphology, but it is not worth considering it in the calculation of aspects such as the polymerization rate.

So, this may lead to the decreasing towards the centre radical concentration profile in the particle. So, the chain transfer to the mobile small molecules level of this particular profile and this profile is of the significance in the development of particle morphology, but it is not worth considering in the calculation aspect such as polymerization rate etcetera.

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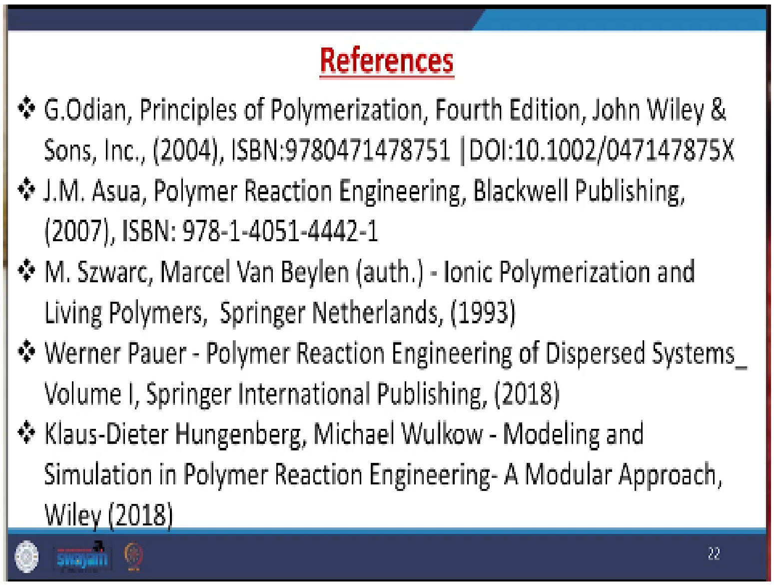

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So, in this particular chapter, we discussed the various aspect especially the mathematical relationship for describing different aspects of emulsion polymerization, the special emphasis was given to the CSTR and semi-batch reactors. Again, if you wish to have further study, we have listed several good references for your convenience. You can have a look of all those references for your future studies. Thank you very much.