Polymer Reaction Engineering
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Lecture - 53
PSD and Implementation of the Process – I

Welcome to the next head of emulsion polymerization. In this segment we will discuss about the particle size distribution theory under the areas of emulsion polymerization, then we will discuss about the implementation of the process in emulsion polymerization process. before we start let us have a look about that what w0e discussed previously.

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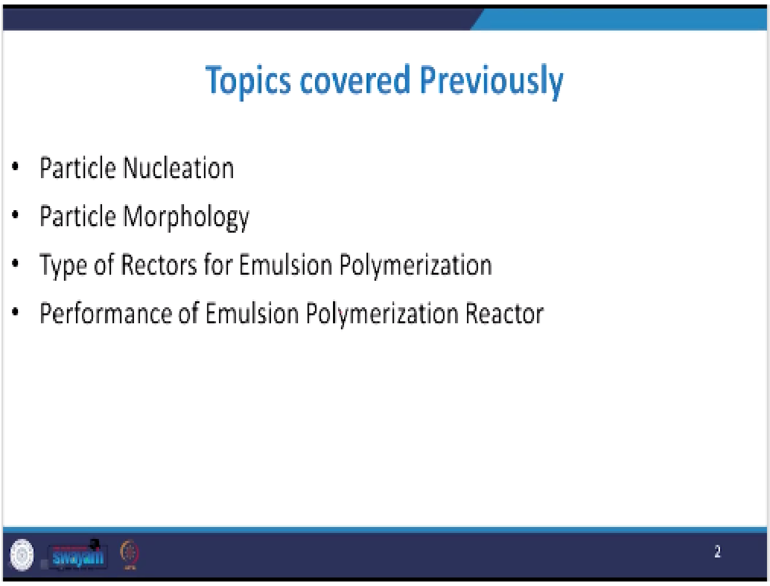

Topics covered Previously

- Particle Nucleation
- Particle Morphology
- Type of Rectors for Emulsion Polymerization
- Performance of Emulsion Polymerization Reactor

We discussed the particle nucleation concept in which we discussed about the growth of polymer particles in under the aegis of emulsion polymerization. We discussed the West various factors involved in the particle morphology under the aegis of emulsion polymerization. During the course of study, we discussed about the various reactors being involved in the emulsion polymerization process and their performance of various reactors under the head of emulsion polymerization.

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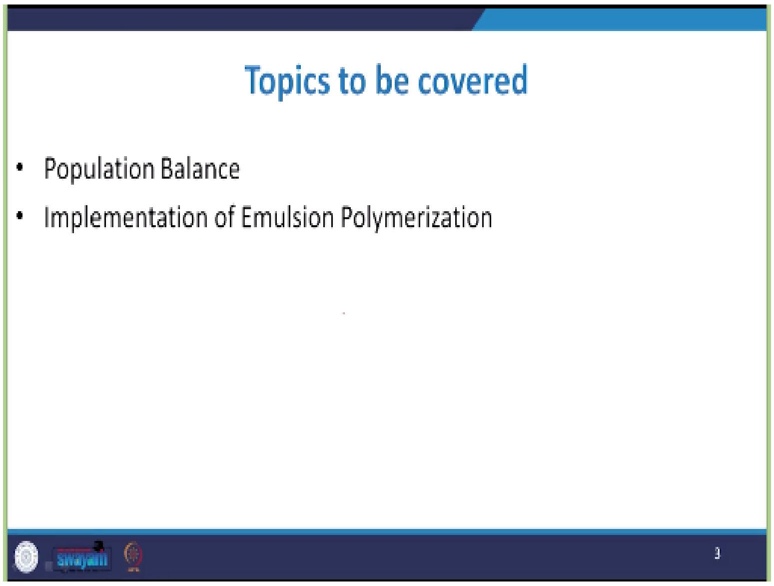

Topics to be covered

- Population Balance
- Implementation of Emulsion Polymerization

in this particular lecture, we will discuss about the concept of population balance to be implemented in emulsion polymerization process and implementation of all those things into the emulsion polymerization process.

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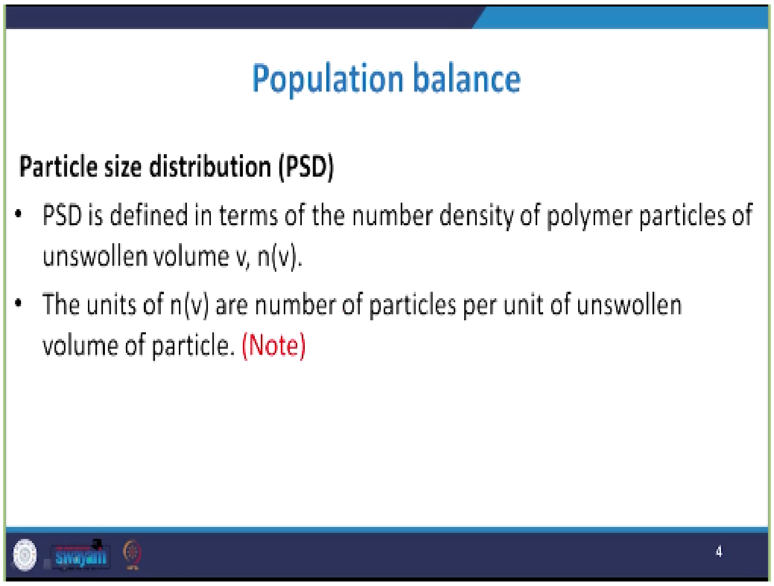

Population balance

Particle size distribution (PSD)

- PSD is defined in terms of the number density of polymer particles of unswollen volume v, n(v).
- The units of n(v) are number of particles per unit of unswollen volume of particle. (Note)

if you see that the particle size distribution this particular aspect we have covered previously, this particle size distribution is defined in terms of number density of polymer particles of unswollen volume v, which is represented as n (v). as you recall that we discussed about the efficacy of the particle size distribution.

Because, usually the polymerization process is tutored by various kind of polymer chain and the size and numbers of those monomers, they also depend on the various factors and whenever the size of those polymer chain increases or decreases, then it affects the the molecular weight distribution. And we all know that molecular weight distribution plays a very vital role in deciding the properties of Polymer.

So, that is why the particle size distribution is very much important in calculating the different properties of the various polymers being generated or produced in course of emulsion polymerization. So, the units of n (v) are number of particles per unit of unswollen volume of particles. So, let us have a look about the mathematical approach of this population balance.

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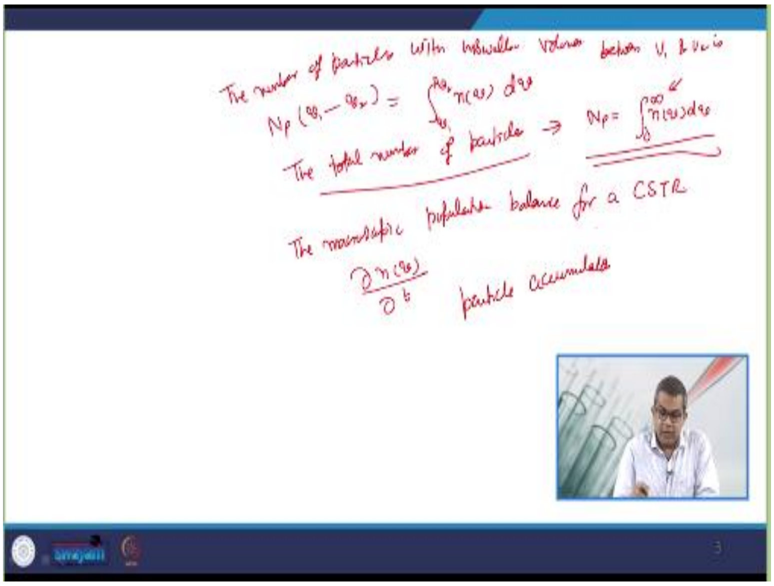

The number of particles with unswollen volume between v, & v₂ is

$N_p(v_1 - v_2) = \int_{v_1}^{v_2} n(v)\, dv$

The total number of particle → $N_p = \int_0^{\infty} n(v)\, dv$

The macroscopic population balance for a CSTR

$\frac{\partial n(v)}{\partial t}$ particle accumulation

The number of particles with unswollen volumes between v_1 and v_2 is

$$N_p(v1 \rightarrow v2) = \int_{v_1}^{v_2} n(v) dv$$

The total number of particles is:

$$N_p = \int_0^{\infty} n(v) dv$$

And because we have given the enough room for the development of those number of particles and you know that during the particle size distribution, this particular approach is extremely important. So, if we looked at the macroscopic population balance balance for any CSTR then it can be represented as like this. So, this is called the particle accumulation.

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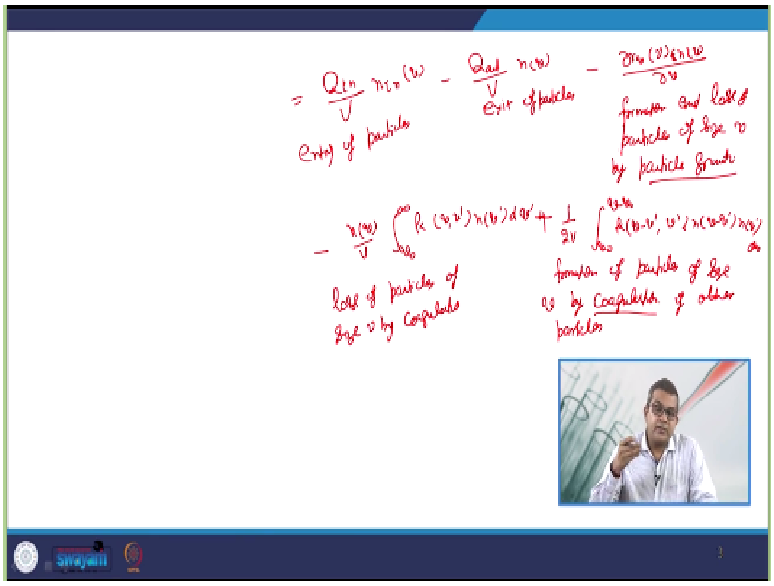

$$= \frac{Q_{in}}{V} n_{in}(v) - \frac{Q_{out}}{V} n(v) - \frac{\partial r_v(v) n(v)}{\partial v}$$

entry of particle

exit of particle

formation and loss of particle of size v by particle growth

$$- \frac{n(v)}{V} \int_{v_0}^{\infty} k(v, v') n(v') dv' + \frac{1}{2V} \int_{v_0}^{v-v_0} k(v-v', v') n(v-v') n(v') dv'$$

loss of particle of size v by coagulation

formation of particle of size v by coagulation of other particles

The macroscopic population balance for a CSTR is

$$\underbrace{\frac{\partial n(v)}{\partial t}}_{particle\ accumulation}$$

$$= \underbrace{\frac{Q_{in}}{V} n_{in}(v)}_{entry\ of\ particles} - \underbrace{\frac{Q_{out}}{V} n(v)}_{exit\ of\ particles} - \underbrace{\frac{\partial r_v(v) n(v)}{\partial v}}_{\substack{formation\ and\ loss\ of \\ particles\ of\ size\ v \\ by\ particle\ growth}}$$

$$- \underbrace{\frac{n(v)}{V} \int_{v_0}^{\infty} k(v, v') n(v') dv'}_{\substack{loss\ of\ particles\ of \\ size\ v\ by\ coagulation}} + \underbrace{\frac{1}{2V} \int_{v_0}^{v-v_0} k(v-v', v') n(v-v') n(v') dv'}_{\substack{formation\ of\ particle \\ of\ size\ v\ by\ coagulation \\ of\ other\ particles}}$$

One is related to the particle growth, another one is related to coagulation aspect. see coagulation of other particles.

see, if you recall that when we discussed this particle size distribution, in that category, we discussed both the concept that some particles may grow in situ and sometimes they may go in that coagulation with other particles maybe p 1 may be attached with p 2, p 3, p 4 and so on. Sometimes other particles like catalytic approach, initiators etcetera, they may participate in this type of approach. So, we have to look these aspect while developing any kind of mathematical equation.

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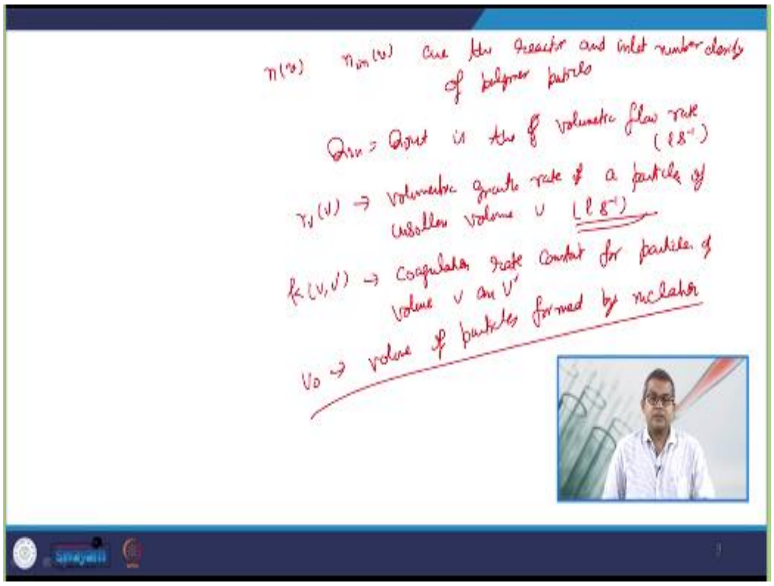

$n(v)$ $n_{in}(v)$ are the reactor and inlet number density of polymer particles

$Q_{in} = Q_{out}$ is the of volumetric flow rate $(l\,s^{-1})$

$r_v(v) \rightarrow$ volumetric growth rate of a particle of unswollen volume v $(l\,s^{-1})$

$k(v,v') \rightarrow$ coagulation rate constant for particles of volume v and v'

$v_0 \rightarrow$ volume of particles formed by nucleation

where n(v) and $n_{in}(v)$ are the reactor and inlet number density of polymer particles,

$Q_{in} = Q_{out}$ is the volumetric flow rate (l s−1),

$r_v(v)$ the volumetric growth rate of a particle of unswollen volume v (l s−1) ,

k(v, v’) the coagulation rate constant for particles of volumes v and v’, and

v_0 is the volume of particles formed by nucleation.

Most emulsion polymerizations are generated in the semi continuous stirred tank reactor and that is why we adopt this particular approach of implementation in the emulsion polymerization.

And sometimes, we are always looking for efficient production. whenever we look for this efficient production to achieve these higher production rate, the scale of semi continuous stirred tank reactor is to be increased from 50 to 60 metre cube for various new units. The production is usually limited by heat removal capacity of the reactor as these react reactions are exothermic in nature.

So, in terms of chemical kinetics, the polymerization allows to proceed in better pace then that can be achieved commercially in in the industrial practice. So, the use of heat optimization technique sometimes referred as reflux cooling, these can be implemented and high pressure monomers like vinyl acetate, they allow the use of such kind of techniques. So, for the example, these high vapour pressure vinyl acetates, they are having the high vapour pressure.

And that is why they can be used these kinds of techniques or reflux cooling etcetera. This can be used for the production of polymers from vinyl acetate. However in case of monomer exerting low vapour pressures like methyl methacrylate or butyl acrylate reflects the cooling cannot be used as the sufficient pressure cannot be achieved inside the reactor. So, that is why you cannot perform the proper energy efficient system and if you are adopting this reflux cooling concept.

So, to overcome this particular limitation, and to improvise the efficiency of heat removal, the reaction medium is usually recirculated through external heat transfer unit, maybe the heat exchanger or maybe some type of heating fluids etcetera. So, whatever heat you recovered from these heat exchanger can be used to increase the temperature of feed inside the reactor for the heat optimization.

Ah now to increase the temperature of inlet water if required for heating, then, another approach is that this polymerization reaction can also begin at a lower temperature and the heat evolved can be finally used to raise the temperature inside the reaction chamber. So, these are the several things which we need to look into during the implementation aspect of these emulsion polymerization.

safety is very important consideration in all kind of polymerization reaction and in the practical approach of polymer reaction engineering. the reason is quite obvious that because of the exothermic nature of polymerization reaction, the reactors are prone to undergo thermal runaway and whenever there is a thermal runaway, there is a chance of material loss there may be chance of high viscous solution, sometimes it may create a a blast to the reactor.

So, in case of emulsion polymerization, the low viscosity of polymeric products sometimes referred as latex and involvement of water in the reaction system yet to reduce the chances of thermal runaway. So, sometimes you are having very good liberty to to change the temperature profile of the reactor because of the involvement of water. So, sometimes you may add cooling water sometimes you may add with chilled water etcetera so that you can avoid the thermal runaway reactions.

there are several other factors that can trigger such conditions like sometimes the failure of cooling system which can be occur due to the instrument instrument failure or interruption in power supply. This can cause several bad effect to the reaction and product like deterioration on the product quality, serious pressure buildup inside the reactor and sometimes if you are using the catalytic approach, then these catalysts may trigger the reaction just like anything.

So, that is why this type of minute thing need to be addressed adequately. Industrially very high pressure changes up to this the range of 600 kilo Pascals this has been observed due to the thermal runaway in the emulsion polymerization reaction. there are several pressure handling devices available commercially like rupture disc ventilation line to safeguard the reactor from the reaction over pressure.

And practical measures such as limiting the amount of free monomer inside the reactor that can also help to reduce the chance of thermal runaway reaction. So, the key point in this type of safety approaches is that you sensitise or you must be in a position to look the near misses or near difficulties being carry on within the polymerization reactor only then you can adopt all kinds of such practical measures to overcome the problem of thermal runaway.

another approach which one should look into that is the quality of polymer. The quality of polymer is a dominant factor which governs the type of reactor and the reaction condition of the polymerization process. The reason is that, this is the ultimate thing which which you are looking for and if its the quality deteriorates, then definitely your economics or process economics etcetera will go on fall.

So, that is why this particular approach is invites very serious attention. the polymers are might micro structurally correct tries to obtain the information regarding the quality of the product. for the most important and popular microstructure parameter are listed like the copolymer composition. this is one of the most important microstructure parameter that is to obtain the desired properties inside the polymerization product, a several monomer of the different activity and water solubility are combined together to form a hybrid mixture.

So, this is again a triggering approach to get more and more quality polymer product from emulsion polymerization. operating under the limited monomer supply condition, this helps to control the copolymer composition, so that you can improvise the quality of the polymer. The method to achieve such process conditions is usually by feeding the monomer mixture to a lower rate than the rate of polymerization.

So, the protocol which you are following in this particular segment is quite critical. owing to the fact that the different monomer partitioning the composition of polymer formed in the aqueous phase is separate from that of the polymer formed in the polymer particle. The fraction of polymer produced in the aqueous phase is small, but can have a strong effect on its properties.

For example, the formation of acrylic acid rich polymer chain that affects the stability of latex, the sheer strength of adhesive endopic strength of coated paper. So, this is very best example to address this particular issue. The blends of copolymer of a different composition may be obtained by varying the monomer ratio in the feed. as the polymer chains are formed in a very short period of time.

The composition of each chain is constant along the chain so, except for a case of the system in which the intramolecular chain transfer of the polymer occur. So, for such condition because these conditions are always important. So, for such condition each branch has a composition of monomer fed in the moment in which it was formed. So, the maybe it may be from the nucleation stage it may be from the the the change in the morphological approach frame. So, it all depends on the circumstances.

additional advantage related to the monomers starved process is that the chance of reaction inhibition reaction, this minimises as the concentration of monomer inside the reactor is very low. A disadvantage is that sometimes the process is not conducted at the maximum production rate that means, some things you need to get optimised over the period of time.

So, the maximum output and good polymer composition can be achieved simultaneously when appropriate online monitoring systems are available. let us have a look about the to achieve this particular goal.

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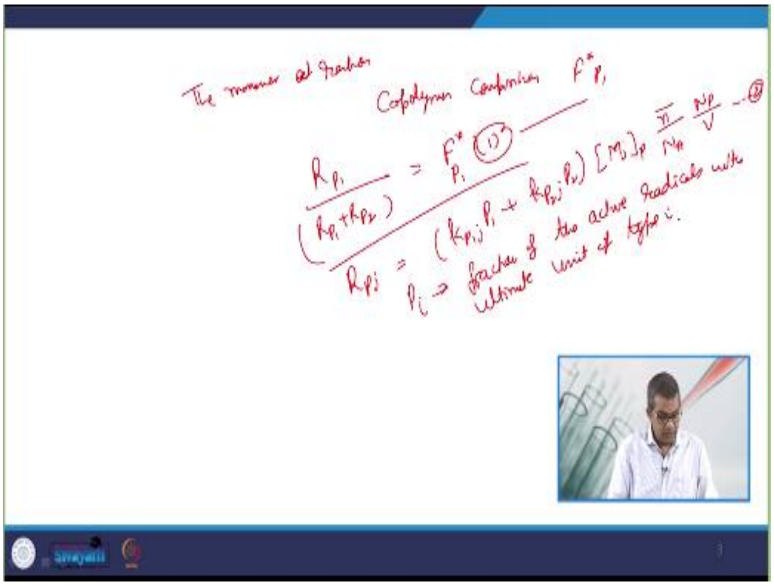

The monomer ratio

Copolymer Composition $F^*_{P_1}$

$\frac{R_{P_1}}{(R_{P_1}+R_{P_2})} = F^*_{P_1}$ ①

$R_{Pj} = (k_{P_{1j}}P_1 + k_{P_{2j}}P_2)[M_j]_P \frac{\bar{n}}{N_A}\frac{N_P}{V}$ -- ②

$P_i \rightarrow$ fraction of the active radicals with ultimate unit of type i.

The total monomer concentration in the reactor is usually chosen to make the rate of heat generation by polymerization equal to the heat transfer rate. The monomer ratio is adjusted so that the ratio of polymerization rates equals the desired copolymer composition, F^*p_1.

$$\frac{R_{p1}}{(R_{p1}+R_{p2})} = F^*_{p1}(1)$$

where R_{pj} is given by

$$R_{pj} = \left(k_{p1j}\,P_1 + k_{p2j}P_2\right)\left[M_j\right]_p \frac{\overline{n}}{N_A}\frac{N_p}{V} \quad (2)$$

and P_i is the fraction of the active radicals with ultimate unit of type i.

$$P_1 = \frac{k_{p21}[M_1]_p}{k_{p21}[M_1]_p + k_{p12}[M_2]_p};\ P_2 = 1 - P_1 \quad (3)$$

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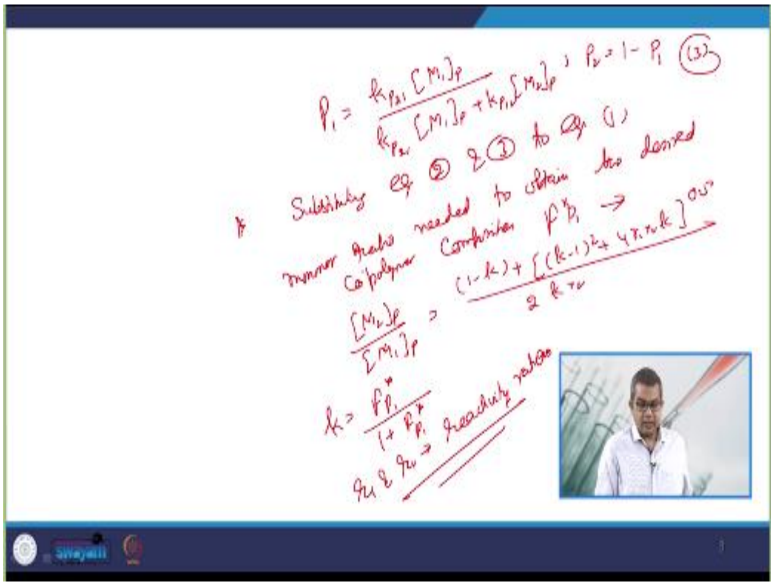

$P_1 = \frac{k_{P_{21}}[M_1]_P}{k_{P_{21}}[M_1]_P + k_{P_{12}}[M_2]_P}$; $P_2 = 1 - P_1$ ③

* Substituting eq ② & ③ to eq (1)

monomer ratio needed to obtain the desired copolymer composition $F^*_{P_1} \rightarrow$

$\frac{[M_2]_P}{[M_1]_P} = \frac{(1-k)+[(k-1)^2+4r_1r_2k]^{0.5}}{2kr_2}$

$k = \frac{F^*_{P_1}}{1+F^*_{P_1}}$

r_1 & r_2 → reactivity ratios

Substituting Equations (2) and (3) into Equation (1), the monomer ratio needed to obtain the desired copolymer composition F^*p_1 is obtained:

$$\frac{[M_2]_p}{[M_1]_p} = \frac{(1 - k) + [(k - 1)^2 + 4r_1r_2k]^{0.5}}{2kr_2}$$

where $k = \frac{F_{p1}^*}{1 + F_{p1}^*}$, and r_1 and r_2 are the reactivity ratios.

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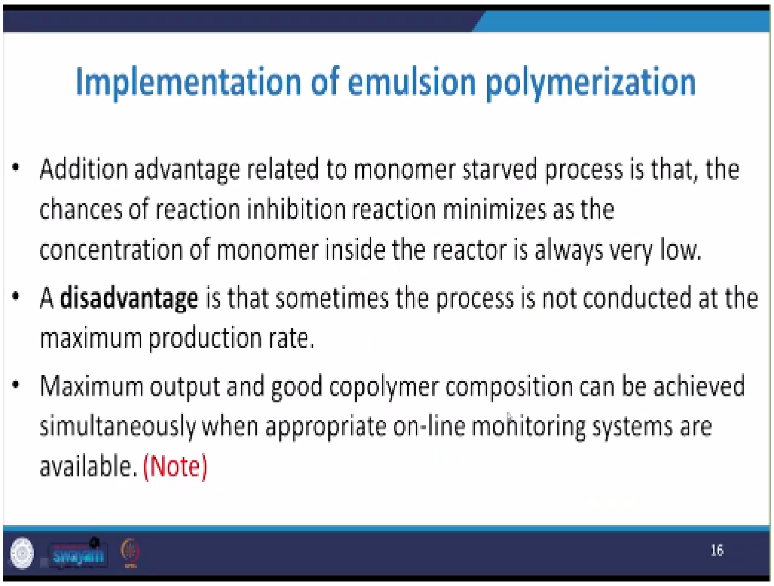

Implementation of emulsion polymerization

- Addition advantage related to monomer starved process is that, the chances of reaction inhibition reaction minimizes as the concentration of monomer inside the reactor is always very low.
- A **disadvantage** is that sometimes the process is not conducted at the maximum production rate.
- Maximum output and good copolymer composition can be achieved simultaneously when appropriate on-line monitoring systems are available. (Note)

another thing is that we have already talked about in detail about the molecular weight distribution. The molecular weight distribution as we know that play a very vital role in deciding the properties of polymer. So, the kinetic length of polymer chain is determined by the competition between the propagation rate and the chain termination rate, because see the initiation step is always there.

So, you need to cut that the or you need to adopt that termination protocol at the appropriate level so that your chain size or in situ the molecular weight distribution should be well in order. So, any process variable affecting these rates has an influence on the molecular weight distribution. That means, the the propagation rate and the chain termination rate. So, both of them they are playing a vital role in deciding the molecular weight distribution.

So, these process variables they are including the initiator type and concentration if you recall that initial term play a very vital role, it not only initiate the things, but also to facilitate the chainration of either free radical or the radical and these radical may combine together to truncate the chain formation chain growth. So, by this way, the the the initiator type and concentration both the things are very much important.

Then the number and size of the polymer particles it is again very crucial with respect to the approach that larger the size, larger the number, then larger the molecular weight, the larger the molecular weight distribution and therefore, the property may affect adversely or sometimes maybe favourably. So, the another aspect is that temperature and monomer concentration.

It is quite obvious, we have already discussed that this play a very vital role in deciding the fate of molecular weight distribution. So, these process variables strongly affect the other kinetic aspect that is the polymerization rate. So, the molecular weight distribution is better control by means of both chain transfer agents CTA and the multifunctional monomers and both the concept we have discussed in the previous lectures.

The presence of chain transfer agent the chain transfer to chain transfer agent is the main chain termination event and instantaneous molecular weight distribution has a number average chain chain length given by this particular mathematical equation.

$$DP_n^{inst} = \frac{k_p[M]_p}{k_{tr}^{CTA}[CTA]_p}$$

with a poly dispersity index (PDI) = 2.

Therefore, the instantaneous MWD can be controlled by **adjusting the monomer/CTA ratio.**

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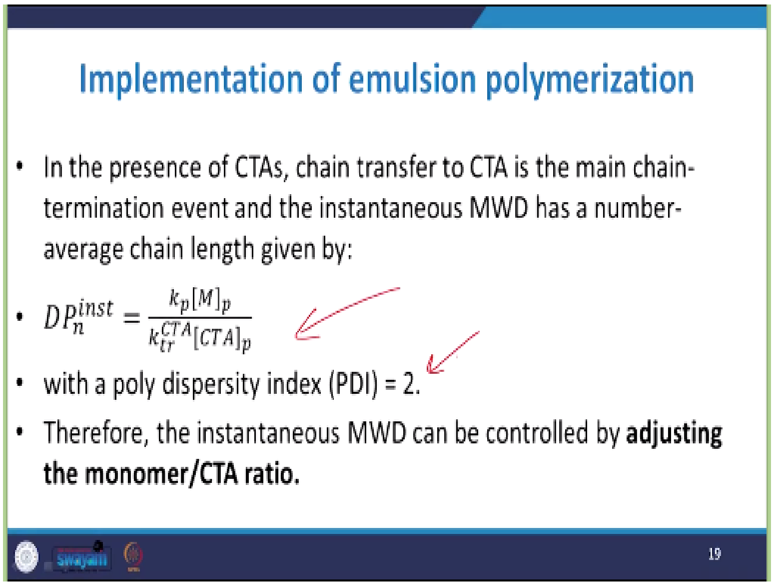

Implementation of emulsion polymerization

- In the presence of CTAs, chain transfer to CTA is the main chain-termination event and the instantaneous MWD has a number-average chain length given by:
- $DP_n^{inst} = \frac{k_p[M]_p}{k_{tr}^{CTA}[CTA]_p}$
- with a poly dispersity index (PDI) = 2.
- Therefore, the instantaneous MWD can be controlled by **adjusting the monomer/CTA ratio.**

The nonlinear polymers they are frequently characterised by their solubility in a given solvent. So, the insoluble part which correspond to high molecular weight heavily branched polymer and the polymer network usually called gel.

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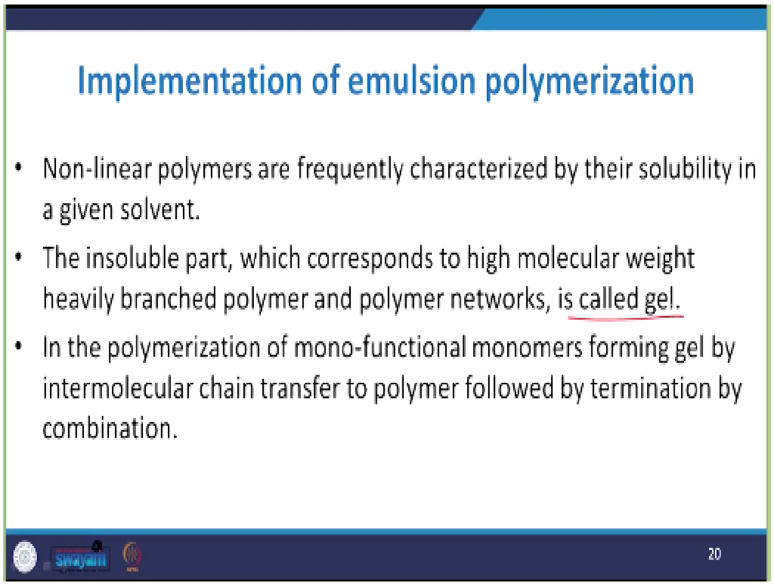

Implementation of emulsion polymerization

- Non-linear polymers are frequently characterized by their solubility in a given solvent.
- The insoluble part, which corresponds to high molecular weight heavily branched polymer and polymer networks, is called gel.
- In the polymerization of mono-functional monomers forming gel by intermolecular chain transfer to polymer followed by termination by combination.

Now in polymerization of mono functional monomer forming gel by intermolecular chain transfer to polymer formed by termination maybe by the combination. So, all kinds of permutation combination theories are applied over here for the formation of these gels. Sometimes multifunctional monomers they are used to create the polymer network. relatively this is the modest approach.

And modest amount of a bifunctional monomer sometimes may be point 5 mole percent, they are enough to obtain a very high gel fraction, it may go up to say 90% sometimes. However, the sole molecular weight decreases severely. So, an independent control of molecular weight distribution and the gel content, this can be achieved by balancing the concentration of chain transfer agent and the multifunctional monomer in the formulation.

So, you may say that the concentration of chain transfer agent and the concentration of multifunctional monomer these can be optimised to get the adequate result as per the desired or full molecular weight distribution concept. sometimes the post treatment of latex is with initiator system they producing very high reactive tertiary butyl radicals in usually a way of modifying the molecular weight distribution.

So, usually it lowers the molecular weight of vinyl acetate rich polymers by hydrogen abstraction usually followed by **β-scission** and led to the **gel formation** in acrylic polymer by hydrogen abstraction usually followed by termination of combination. this represent a possible way or you may term that this is an example to extend the range of properties achievable by given base emulsion polymers.

This particular approach is extremely important while you consider the economics of these emulsion polymerization process. let us have a look about the particle size distribution. Because again, it is the key factor in deciding the polymer properties. the particle size distribution strongly affects the rheology because we always talk about the viscosity we always talk about the processability of those polymers developed in due course of any polymerization process.

So, particle size distribution, it plays a vital role in deciding the fate of rheology. usually this rheology in turns the influences the heat removal rate, mixing, mass transfer and instability of various kinds of polymer being generated. This particle size distribution affects film formation and some application properties and usually it is the result of a competition between the nucleation, particle growth and coagulation.

So, you see that all these three things are the participating parameters in the particle size distribution nucleation, particle growth, because the particle may grow up to any extent then coagulation because two particles or three particles or four particles may combined in-situ or some some other particles to form a coagulant then these things affect the rheological approach of those polymers being developed in the emulsion polymerization.

The particle growth broadens the particle size distribution because of higher number of radicals in the larger particles. particle nucleation usually depends on the availability of emulsifier. If any emulsifier is available, then the nucleation depend is affected by the availability of these emulsify then radical generation rate, how much radical being generated maybe in a positive sense or maybe in the negative sense.

Then the water solubility concept of a monomer, then the number of particles those who are already present within the system. So, these parameters are playing a very vital role in deciding the fate of particle size distribution. easy way of nucleating the new particle is to add enough emulsifier to form micelles. So, that if you recall the figure that micelle will grow up in size.

So, the larger the surface area of polymer particle, the more emulsifier is needed to form the micelles. So, sometimes it may create that depletion of emulsifier within the mass in question, the amount of particles nucleated through the heterogeneous nucleation they genuinely rises through increase in the concentration of the initiator. this is not usually a good practical process for the control of particle size distribution.

Because it usually affects the polymerization rate, molecular weight distribution and the polymer architecture. So, this this thing should be looked into while considering this particular approach. homogeneous nucleation which we discussed earlier, they often yield secondary nucleation in system in which there are no micelles. the homogeneous nucleation rate sometimes increases with the concentration of monomer in the aqueous phase and initiator concentration.

it decreases with the increase in the number of particles. So, in other words, you may say that secondary nucleation sometimes is very difficult to avoid in the larger particle size containing water soluble monomers sometimes, for example, like acrylic acid etcetera. So, irrespective of nucleation mechanism, the newly formed particle sometimes undergo a substantial increase in size maybe because of the polymerization.

So, therefore, they need additional emulsifiers. So, this type of thing mathematically should be performed mathematically should be calculated that how much quantity of additional emulsifier is required to carry out the polymerization process to complete. fast diffusing and ionic emulsifier, they are much more efficient at stabilising the new particle than the slow diffusing non ionic emulsifier.

So, the quality of emulsifier is also play a vital role in deciding the fate of particle size distribution. So, the greater number of polymer particles they are may be generated using the ionic surfactant because they alter the surface energy of the media. coagulation usually is a second order process, therefore, its rate usually increases with the concentration of polymer particles maybe by increasing the solid content and decreasing the particle size.

So, particle stability is the key aspect in controlling the coagulation. the first condition for stability is that they must have a sufficient coverage of the polymer particles. So, that I mean there is a minimum arena requirement and they must cover to form those arena so, that they can form the coagulation, the efficiency of the surfactant may be severely affected by the process condition.

Therefore, the ionic strength sometimes reduces the efficiency of ionic surfactant. deionized water is commonly used in the emulsion polymerization and excess of inorganic initiator may cause coagulation. So, that is why you see that deionized water because there is this minimises the presence of any kind of ions through the water media. The strong agitation may cause the shear induced coagulation.

So, narrow particle size distributions usually are obtained when all the particles are formed during the polymerization of the initial charge and neither secondary nucleation nor coagulation. They occur during the semi continuous operation. Sometimes high solid content may be greater than 55% latex are advantageous, because they maximise the production minimise the transportation cost and sometimes give more flexibility in product formulation.

So, sometimes if you wish to transport the things from one place to another place and if they are having the high density then obviously, they will require less volume for the transportation and that transportation cost may be a bit minimised. So, the maximum solid content is usually limited by the viscosity of the latex. Bimodal particle size distribution with the small particles sometimes accounting for say 28% of the polymer the minimises the latex viscosity.

And bimodal particle size distribution usually they are produced by creating the second crop of polymer particles by adding adding a shot of emulsifier. So, alternatively, another method is given to produce the bimodal particle size distributions are the growth of bimodal seeds and control partial coagulation of monomodal latex. So, in all cases the formation of undesired particle by homogenenous nucleation should be prevented.

So, in this particular chapter, we discussed about the concept of particle size distribution applied to the emulsion polymerization, then we discussed the various parameters essential for the implementation of emulsion polymerization.

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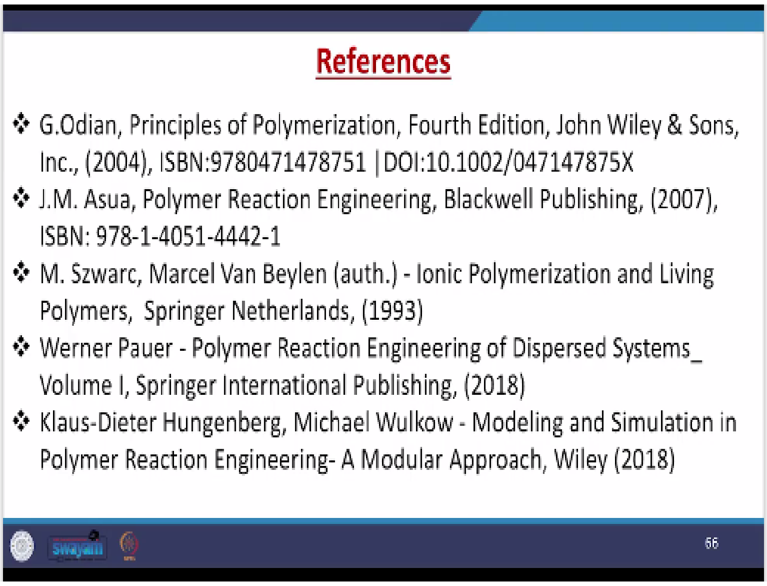

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For ease of your reading we have in listed the couple of references for your further studies. We will continue this implementation aspect in the next lecture. Thank you very much.