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## Lecture - 49 Batch Polymerization

Welcome to the batch polymerization concept under the head of emulsion polymerization. So, we are going to start another chapter pertaining to this batch polymerization with the emulsion polymerization concept. Now, if you recall that in the previous lectures under the head of the radical polymerization, we discussed emulsion polymerization in a very short note.

So, in this particular segment, we are going to discuss the concept of emulsion polymerization in detail with the various segmentations. Now, before we start, let us have looked at what different topics we have covered previously.

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We discussed about the population balance modelling and if you recall that in the population balance modelling, we discussed about the different chain molecular weight distribution and how the mathematical modelling can help you to predict the various molecular weight distribution concepts as well as the in-situ property of the polymers.

Then, we discussed about the physical properties and phase equilibrium calculation of all those emulsion polymerization and radical polymerization concept. Now, we discussed a brief about the emulsion polymerization.

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Now, in this particular chapter, we are going to discuss about the emulsion polymerization. What is the basics of these emulsion polymerization? Then we will discuss about the microstructural features of the emulsion polymerization and we will have knowledge about some factors those who are affecting the emulsion polymerization and last, we will discuss about the process of emulsion polymerization in line with the batch emulsion polymerization.

So, let us have a brief look about what is the emulsion polymerization that is in line with the concept which we discussed earlier. Now, emulsion polymerization is, you can say that another form of radical polymerization, it usually starts with an emulsion consisting of water, monomer and surfactant. So, all 3 factors are having their own importance. Water is the dispersion media; monomer is quite obvious that you require the monomer and surfactant is used to alter the surface energy of any dispersion media.

So, in other words, it is a free radical polymerization in which a monomer or a mixture of monomers is polymerized in aqueous surfactant solution to form a polymer chain. Now, it all depends on the mechanism of polymerization, whether you have a water surfactant combination with monomer or you may have monomer surfactant combination with water. So, it all depends on the mechanism whatever you are going to start.

Now, the important features of emulsion polymerization is the micro-structural formation. So, micro-structural formation, this is the unique characteristics of polymer dispersion.

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Now, here you can see that in this particular figure, you can see that the molecular weight distribution as we agreed upon that plays a very vital role. So, the control of molecular weight or the control of the chain size or the chain length is the utmost important during this emulsion polymerization. So, whenever we talk about this molecular weight distribution, then the particle size distribution is also playing a very vital role, because both the things are supplement to each other.

Now, when we talk about this particle size distribution, then obviously, the particle diameter and weight, these concerts plays a very vital role. Apart from this, the particle morphology, particle morphology plays a very vital role, what is the surface morphology, what is the porosity etcetera. So, these things are playing a very vital role and when we discuss about the characteristics of polymer dispersion that influence the product property.

Then you can design your polymer maybe with the help of a branching, maybe with the help of cross linking or gel formation. So, all these things play a very vital role. Apart from this, the polymer composition or polymer or monomer sequencing distribution, if you see that we discussed about the randomness and branching etcetera, in the previous lecture. So, all these factors play a very vital role. Apart from this, the surface composition is extremely crucial to play to develop all these polymeric particles.

Now, you see that all these things, especially, when we discuss the polymerization process or especially the emulsion polymerization. So, all these factors play a very vital role in characterising the polymer what you are going to develop in due course of time with the help

of emulsion polymerization, whether it is a branching cross linking, polymer composition, molecular weight distribution, particle morphology etcetera.

So, based on this particular concept, you may decide the concentration of monomer, you may decide the concentration of surfactant, you may decide the concentration of other ingredients in the polymerization mass. So, these are the several factors which are influencing the characteristics of polymer and especially when we talk about the emulsion polymerization, then the crucial part is the polymer dispersion.

Polymer dispersion, there are only a couple of media through which you can disperse the things. One is the water and other one is the surfactant solution.

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So, when we talk about the micro-structural feature of the emulsion polymers, now, they includes copolymer composition, they include the monomer sequence distribution as we see in this particular figure, they include the molecular weight distribution, as we have discussed in this particular figure, then they are very much crucial with respect to the polymer architecture, maybe the branching, grafting, cross linking, gel content etcetera and the polymer surface functionality.

So, in just what we discussed in the previous figure, we have already enlisted these particular points, which are important for the micro-structural feature of the emulsion polymerization. Now, a couple of things, we need to remember during this emulsion polymerization. One is

that the copolymer composition has a direct effect on the glass transition temperature of the polymer.

As we agreeing upon that the molecular weight distribution or the molecule rate, it is directly related with the glass transition temperature. So, the glass transition temperature as we know that it determines the minimum film forming temperature that is MFFT of any kind of latexes, which is the emulsion polymeric product and the application.

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So, in other words, you can say that molecular weight distribution is directly interlinked with the glass transition temperature and this is directly linked with the MFFT which is directly linked with the processing part or application part of your volume developed polymer. Now, sometimes, we need to take several examples to explain the thing. So, if we take an example of a butyl acrylate, methyl methacrylate 95: 5 (w/w) weight percent mixture is an adhesive whereas 50:50 copolymer of the same monomer act as a binder for paint and coating.

So, you can see the hairline difference between these 2 things like butyl acetate if you increase the quantity of methyl methacrylate in this combination, then it can be used as a binder for various type of things. So, ultimately the composition, the copolymer composition plays a very vital role. So, sometimes, you may use that copolymer as an adhesive and sometimes, you may use as a paint or coating.

So, drastically, there will be a change when you change these copolymer composition. It also affects the properties such as resistance to hydrolysis, weather-ability etcetera. So, this

composition plays a very crucial role during the polymerization. The conventional free radical polymerization, which is the process used to manufacture almost all commercial emulsion polymers do not allow the production of block and gradient copolymer, usually accessible by means of controlled radical polymerization.

So, again this particular aspect, while you design any polymerization process, this particular concept you need to look into, nevertheless, graft copolymers, they are frequently formed and the extension of grafting largely determines the application property. So, these small points, we need to address while we are looking for proper process of emulsion polymerization as well as in see to their application properties.

So, the grafting in case of emulsion polymerization, this determines the size of rubber domain. This is again one of the example. So, if we are looking for the rubber domain in ABS polymer, the toughness of these polymer increases with the rubber size. Now, molecular weight distribution strongly affects the application properties that is in people quoted with the styrene, acrylate copolymer or the dry pick strength increases and the blister resistance decreases as the molecular weight of polymer increases.

So, in other words, you may require appropriate molecular weight distribution for those polymers for a specific use as we discussed in this particular example. Sometimes, if we take the adhesive, now, there are several other associated parameters or associated properties are required in the adhesive application; one is tack, then the peel resistance, then the shear resistance.

#### In adhesives,

- Tack: is determined and is maximum for low molecular weights,
- peel resistance: is mainly determined by the intermediate molecular weights, and
- **shear resistance**: by the high molecular weights.

So, when we discuss the end use of those adhesive especially when we discussed the epoxy adhesive etcetera, then the tack is determined and is maximum for low molecular weight. So, whenever you design the polymerization process, you are always looking for small chain polymers, so, that you may maintain the low molecular weight distribution.

For the peel resistance, it is mainly determined by the intermediate molecular weights. So, you can again set the range accordingly, then, if you go for the last one that is the shear resistance, that is attributed to the high molecular weight. Now, if this is the high molecular weight, then again during the process designing process, you may look into the things that you may go for prolong polymerization, so, that there may be enough opportunity for monomer and polymer to combine together to form the larger chain.

Now, sometimes, we talk about the gel content in polymer. So, the polymer architecture plays an important role in defining the properties. For example, in papers coated with carboxylated styrene-butadiene latexes;

- blister resistance decreases with increase in gel content, while
- dry pick increases with the gel content, and
- wet pick will obviously increase with low gel contents
- Maxima for binding strength found at relatively high gel contents

Hence, optimal gel content needs to be determined

Therefore, whenever we designed the polymer to be used in the paper coating industry, they need an optimum gel content which needs to be determined. It may be through experimental or maybe some other methodology through which you can determine those gel contents.

Sometimes, we may look into the modification of the surface properties. Now, these surface property is of polymer need to be altered with respect to the bulk polymer. The effect of some external mediums such as air, humidity, it can be balanced by providing additional strength to the surface polymer. For example, a minute amount like 1 to 2% based on monomer in the acidic monomer like acrylic acid, acetic acid etcetera, usually added during the manufacturing of latexes.

So, it just triggered the entire polymerization process. Now, due to the water soluble nature, most of the acetic acid rich polymer chain moves towards the surface after the polymerization. So, that it facilitates the desired property or desired modification which one person is looking for.

The availability of acetic acid at the surface usually increases the stability of latexes, increases the shear strength of the adhesive, and it increases the picky strength of the coated paper. So, the form and quantity of surfactant, it influences the application property such as colloidal stability and the water sensitivity of all those films.

Now, as we were discussing in the different points that we will look into the particle morphology. Now, usually the particle morphology explains various properties of synthetic polymers or synthetic latexes, the rubbery core and hard shell polymer or latexes, they can be used to increase the toughness of plastics such as poly-vinyl chloride or poly-methyl methacrylate or epoxy resins or poly-carbonate. So, you can use this appropriate to alter the particle morphology. Other applications, these may include that as pigment in the coating, sometimes, you need to formulate the hybrid polymers or latexes, then another issue which is related to the characterization of those emulsion polymerization is the effect of rheology.

Understanding the rheology is important during emulsion polymerization as

- it panels mixing and heat transfer
- it determines the maximum solids content attainable
- It plays a vital role in the applications of the dispersion

So, sometimes, with the other mechanical approaches during the polymerization process under the head of any reactor, it plays a very vital role.

Now, sometimes, the high solid content latex having molecular weight greater than 55 wt%, have several commercial advantages like it maximises the capacity of the reactor during the production. It minimises the cost of transportation because of the rheological effect. It offers the flexible product formulation, it usually faster the drying rates. So, however, if we talk about the small particle size, usually the small particle size is required for better quality of the polymer film because the smaller the particle.

And if you deposit over the surface or if you utilise the polymer film, then you will get the desired property in a better form. Now, let us have a discussion about the process of emulsion polymerization. So, usually the emulsion polymerization is carried out in a stirred tank reactors, they usually operated in a semi-continuous fashion. So, the continuous tank reactors are sometimes referred as a CSTR.

They are used to for the production of some high demand emulsion polymers like styrene butadiene rubber. Batch process one can use to polymerize monomer with a comparable reactivity and low heat generation rates. Let us take the example in acrylic fluorinated copolymer for clotting application. So, this is one of the example. Now, sometimes, we look into the parts of coating formulation usually that what are the significant segments of those coating formulation because every segment plays a very vital role in designing the polymerization process. So, first thing is that we can look into the polymer dispersion. It may act as a binder, then the pigments, they are used for the colouring, brightness, modifying these reflectivity of the coating. Another aspect is the fillers such as calcium carbonate, tar, clay, non-bentonite or bentonite clays etc. are being used for this purpose. These clays are used to modify the opacity and to reduce the cost of additional pigments.

Sometimes, they play a very vital role in the economics also. So, wetting agent, surfactants, they reduce the surface tension or alter the surface energy and they increases the adhesion to the surface. Another point is the thickness. They used to improvise the rheology for the coating or sometimes, during the reaction or sometimes, during the application, they alter the viscosity, so, that it can apply to the various surfaces being in question.

Then coalescent that is to accelerate the film formation, then another part is the deformer, this is usually used for to reduce the forming because sometimes, form you can say the undesired phenomena in the emulsion polymerization, then biocides to avoid the formation of any kind of microorganism growth maybe because of the humidity maybe because of some other water content because water is an integral part of this emulsion polymerization.

So, it may create a problem for the problem. So, that is why the biocides are added to these processes. Now, this emulsion polymerization usually as we described that it can be carried out either in the continuous or a batch mode. So, as we discussed that commercially stirred tank reactor or CSTR in the semi-continuous mode, they are frequently being used to carry out these emulsion polymerization.

And the CSTRs, they are used like to produce the high molecular weight polymers like styrene butadiene rubber (SBR).

The batch reactor are only applied to polymerize the monomer with the comparability activities and small rate of heat generation because sometimes, the exothermicity of these reaction play a very vital role in designing the reactors.

So, let us have a discussion about the semi-continuous process.

So, a fraction of monomer, emulsifier, initiator and water is usually fed into the reactor. If you recall that all 4 are the integral part of emulsion polymerization like water is the dispersion media. Monomer is a prerequisite for this polymerization process. Emulsifier and initiator both

are to initiate the polymerization process. Now, this fraction is first polymerize for sometime and then the remaining formulation is usually fed over a certain period of time, maybe for 3 to 4 hours.

Now, this particular step is essential to impart certain the mechanical improvisation of polymer being developed in due course of time. Now, monomer can be provided either as in the aqueous pre-emulsion stabiliser with any kind of emulsifier or as a virgin monomer that is the predesigned aspect of this particular process and that is based on the chemistry behind this particular polymerization process.

Sometimes, monomers are pre-treated with inhibitors to allow the surface storage, but it can be used directly without any purification. Now, see, this is again a very crucial part which giving a minute to describe because, sometimes, monomers, they are having some un-saturation maybe, sometimes, they are having the free radicals inside etcetera. So, sometimes, they may start to the polymerization process in situ, now, to prevent during maybe during the storage maybe during the transportation etcetera.

So, to prevent this particular approach, there are certain inhibitors are being added to these monomers. So, that these in-situ polymerization can be prevented. Now, whenever you are using these monomers which are pre-treated, then obviously, you need to look into this particular concept because these inhibitors sometimes, may play a crucial role during the polymerization and even they can stop the further polymerization.

So, there are 2 type of pre-treated monomers available one with you can use a directly without any purification and some are required the purification is step a priori. So, this particular concept, one need to look during this particular polymerization process. Now, the initiator is usually fed into the reactor through a separate stream and sometimes, it is quite obvious because this is the demand of the reaction process.

Now, the specified reason behind this polymerization that the small fraction of feed is to neatly the desired amount of polymer particles. So, if you recall that in previous we discussed that for the nucleation, we require a very small quantity of initiator, it is not as by the stoichiometric demand of this polymerization process. So, that is why the initiator is having very limited role in this polymerization process.

Now, the particle nucleation step, this determines the rate and the quality of the polymer, but, it is difficult to reproduce similar results in each run because of the variety of reasons, maybe the process parameter play, maybe some inhibitors, maybe some sort of because, the growth of all these chains are random in nature. So, the seeded semi-continuous emulsion polymerization is sometimes, being used for the desired property.

Now, this particular process initiates with the feeding of previously synthesised latex seed and a fraction of formulation sometimes, being used in the semi-continuous mode. Now, the nucleation of a new particle is usually minimised, leading to the better reproducibility. Now, although this process is usually not commercialised, but it is easy to understand the concept of a batch mode.

So, emulsion polymerization usually contains a hybrid mixture, variety of different monomers and the typical formulation of monomer composition may be attributed to the pre-cast monomer, may be pre-functionalized monomer. So, they are first determined according to the final product requirements, sometimes, you will require the higher mechanical history and sometime you may require the flexibility; sometimes, may require very specific application.

So, it all depends on that what kind of final product you require. So, based on this, you can change the recipe of these ingredients in the emulsion polymerization. Now, broadly if we talk about the monomers, then broadly it can be defined as the principal monomer, maybe hard monomers like styrene, methyl methacrylate, vinyl chloride monomers, vinyl acetate etcetera, sometimes, they are referred as the soft monomers butadiene and butyl acetate, acrylate etcetera.

Some minor monomers are also being used like acrylic acid, methacrylate, acrylamide etcetera. Now, whenever we require this type of thing, then glass transition temperature plays a vital role. So, the ratio between the hard that is high glass transition temperature; high glass transition temperature means, you require more and more energy or more and more temperature in part and the polymer to make them to allow them to flow and the soft that meets the requirement of a Tg is on the lower side.

Then the principle monomers those who are having the low water solubility is usually chosen for that particular application. Now, minor functional monomers, they are used to afford the various special features like enhanced stability, better adhesion etcetera. Cross linking agent, chain transfer agents, they are also used in the formulation to control either the chain architecture or the molecular weight distribution.

Like in the previous lectures, we discussed about those chain architecture and the importance of cross linking agent in deciding the fate of the molecular weight distribution of the polymer which we are producing. So, we are not going to discuss in deep at this juncture. Surfactants are used to disperse the monomer in water. Thereby, these surfactants are usually alter the surface energy. So, they can disperse the monomer in the water adequately.

The surfactants usually stabilises the monomer droplets by absorbing on the surface and it can be either ionic, non-ionic, cationic etcetera. So, ionic surfactant, these stabilisers through the electrostatic repulsion and non-ionic surfactant, they provided by steric stabilisation. Now, the use of surfactant in excess, this may lead to the micelle formation that swells with the monomer.

So, sometimes, you may experience that the size of monomer may grow drastically. So, sometimes, it is advisable and sometimes, it is not. So, the thermal stabilisers sometimes, are used to for the polymerization to carry out the high temperature range may be around 75 to 90 degree Celsius whereas, Redox system, they are applied to for the low temperature and the high rate of initiation applications.

So, generally those initiators are dissolved in water or any other solvent which may deem to be fit for that particular process. So, they generate radicals in that particular phase. Now, sometimes, due to very high hydrophilicity of the generated radical, it does not directly enter into the organic phase. The generated radicals, they react with the dissolved monomer in the aqueous phase and then form the oligo radicals.

So, by this way, they initiate the formation of chains. Now, due to the low concentration of monomer in aqueous phase, the formed oligo radicals, they start expanding slowly thereby, the size of chain keep on increasing. Now, when monomer groups, they are added to the aqueous phase, the oligo radicals, they start to become the hydrophobic and they start joining the organic phase. So, by this way, the chain starts, propagation starts.

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# **Batch Emulsion Polymerization**



- As micelles usually contain greater surface area (in order of three times in magnitude), the chances of penetration of radicals into micelles increases
- Thus oligoradicals find a monomer rich environment within the micelles, and starts growing speedily in the form of polymer chain.

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And as micelle usually contained greater surface area like this, which we discussed that swelling or something like this. So, usually it contains the greater surface area, maybe sometimes, in the order of 3 times of the magnitude, the chances of penetration of those radical into those micelle is usually increases. So, the oligo radicals, they find a monomer rich environment within the micelle and it starts going speedily to form the polymer chain. So, this is the propagation step of those polymerization processes.

Now, the process of formation of polymer particles by entry of those radicals into the micelle is called the heterogeneous nucleation.

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Because, with the help of those micelle, these chains are start growing. The oligomers, they can also be converted into the polymer particle and if they start growing in hydrophilic ways,

and increases its length up to a limit that is starts precipitating. So, this is the foremost required phenomena in the emulsion polymerization. The emulsifier strengthens the precipitated polymer chains.

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So, whatever the polymer chains are precipitated during the course of polymerization, the emulsifier strengthens these polymer chains and the monomer diffuses to form a new organic phase which grows to form the polymer chain. So, that by this way, you increase the size of polymer chain. The process of this formation of polymer particle by the precipitation of these oligo radicals is called the homogeneous nucleation.

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So, this usually occurs in monomer with the high water solubility that is, sometimes, like if you say that methyl methacrylate, it may be referred as 1.5 grams per 100 gram of water and

heterogeneous nucleation is usually find in the way where the water insoluble monomers are present like styrene 0.045 grams per 100 gram of water. Now, sometimes, we need to encounter the issues of related to the coagulative nucleation.

Now, the regardless of the mechanism involved in the particle nucleation, the freshly formed polymer particles are very small and they can undergo a rapid increase in the surface area during the particular growth. Now, this rapid increase in the surface area sometimes, desirable and sometimes, disadvantageous, because if you are increasing the surface area, then sometimes, the situation may arise when you may not be able to control the polymer chain.

So, therefore, monomer may not be able to diffuse to the surface of these particles. So, this particular deficiency or we can say the uncertainity in the stabilisation of the growing particles may create a future problem during the course of polymerization process. So, the specie is producing the homogeneous and heterogeneous nucleation; these can be considered as a precursor that is stabilised only after the coagulation and polymerization.

The process is combined and there is termed as the coagulative nucleation. So, during the nucleation in the batch reactor, 3 kinds of particles can be seen together. One is quite obvious that is the monomer droplet. Another one is that monomer those swell in the micelles or monomer swelling micelles, monomers swollen polymer particles. So, the 3 things, you can see all together and whenever you truncate the polymerization process, you need to address these 3 particles or 3 recipes in the polymer mass while during the control of the chain size.

Now, the monomer is consumed by the free radical, which is then replaced by the monomer that diffuses from the monomer droplets through the aqueous phase. So, therefore, the particle size increases with the decrease in the monomer droplet that is quite obvious because the monomer is continuously being consumed in due course of the formation of polymer chains.

The amount of micelles reduces as they become the polymer particles upon the entry of radical because this triggers the propagation step. Thereafter, the micelles are destroyed to provide the surfactant to stabilise. So, the polymer chain that precipitate in the aqueous phase and the increasing surface area of a growing polymer particles. So, after sometimes, all micelles are disappeared, that means you can say that this is the start of your termination or a truncation process.

Now, the nucleation stage is considered to end after this particular point as a very little amount, a small amount of new particles can form because of heterogeneous nucleation. It cannot be possible after this particular point because all micelles are disappear in due course of time. Now, as surfactants are not available to stabilise the particle formed by the homogeneous nucleation, the process cannot be proceed in this way. That is why the termination either starts or termination process achieved.

So, the region where the nucleation stage hence, the batch emulsion polymerization is called the interval 1. Monomer conversion about 5 to 10% depending on the surfactant monomer ratio occur till the end of interval 1. That means it is the in between step that is the interval 1. (Refer Slide Time: 37:22)



At the end of interval 1, almost  $10^{17}$  to  $10^{18}$  particles per litre are formed. Now, unless coagulation occurs, the number of particles remain constant during the rest of the batch process. This is because all the micelles are already disappeared in due course of time.

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# **Batch Emulsion Polymerization**

- In Interval II, the reactor system contains monomer droplets and polymer particles.
- The monomer that diffuses from the monomer droplet through the aqueous phase is only present in the system.
- In the presence of the monomer droplet, the concentration of the monomer in the polymer particles, reaches a maximum value that remains approximately constant during Interval II.

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Now, interval 2, the reactor system contains monomer droplets and polymer particles. So, the monomer that diffuses from the monomer droplet through the aqueous phase is only present in the system. Now, in the presence of monomer droplet, the concentration of the monomer in the polymer particle reaches a maximum value that remains approximately constant during the interval 2. So, that is a crucial point in this regard.

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Now, as the polymerization proceeds further with the monomer transport, the size of polymer particles gradually increases and finally, after sometime, the monomer droplet vanishes and marking the end of interval 2. So, the conversion of monomer at which the interval 2 ends decided with the extent to which the polymer particles were swelling by the monomer. So, the higher the maximum swelling the earlier the monomer droplet disappears, so, that it gives you an opportunity to control the size of the polymer chain.

So, in general, the water soluble monomer, this is possesses a superior amount of the maximum swelling therefore, reduces the monomer conversion at the end of interval 2. So, most of the monomer polymerizes during the interval 3. And interval 3, the monomer concentration in the polymer particle decreases continuously. For example, the styrene, the interval 3 starts about 40% conversion and the vinyl acetate about 15% conversion.

So, these are the crucial point or sometimes, referred as the critical point for the batch emulsion polymerization. So, you need to look and you need to find out those percentage conversion so, that you can design your polymerization process accordingly.

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So, in this particular lecture, we have discussed about the batch polymerization concept under the edges of emulsion polymerization and if you wish to have further readings, we have enlisted several differences for your convenience. You may go through all those references and do your future work related to these emulsion polymerization. Thank you very much.