Polymer Chemistry
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Lecture - 15
Radical Chain Polymerization (Contd.)

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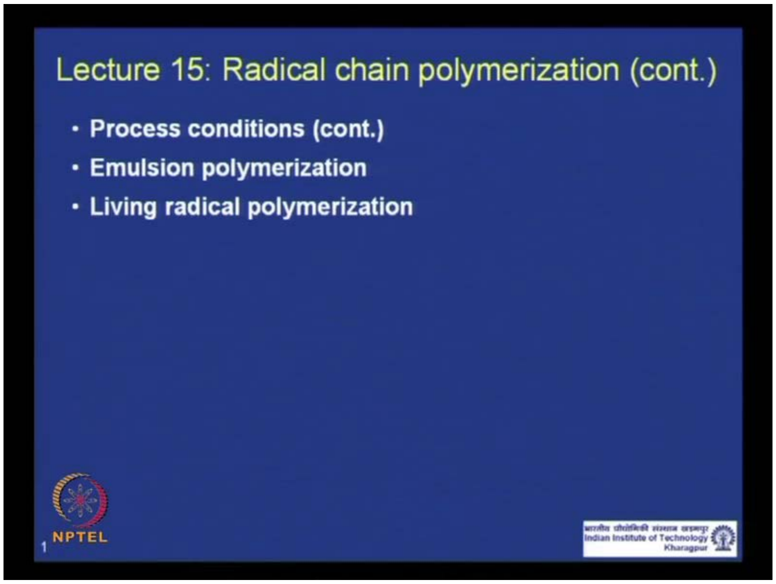

Lecture 15: Radical chain polymerization (cont.)

- Process conditions (cont.)
- Emulsion polymerization
- Living radical polymerization

Welcome back to this 15th lecture of the Polymer Chemistry course. I should say that, welcome to the 15th lecture of this polymer chemistry course, and in this course in this lecture today, we will continue our discussion on polymer polymerization processes, different processes we start discussing in the last lecture. And then we will talk about in little detail about emulsion polymerization, and then we will begin in this lecture or sort of introduce the concept of living radical polymerization in this lecture.

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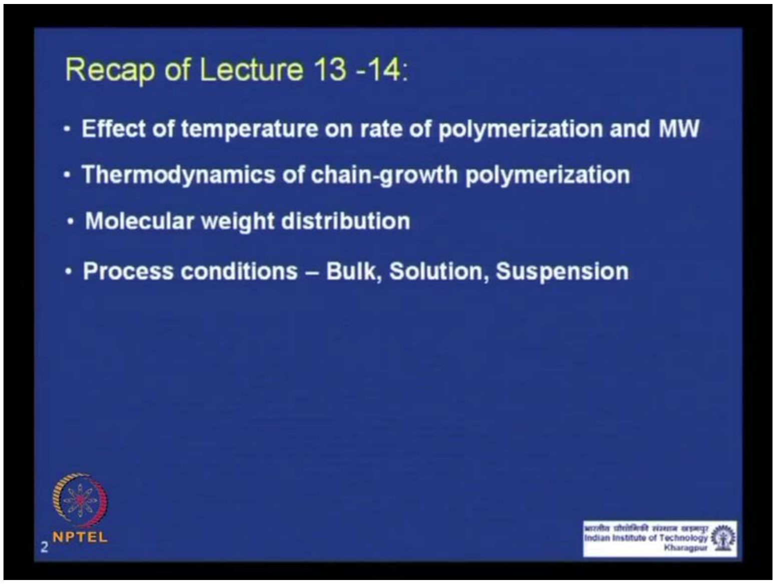

Recap of Lecture 13 -14:

- Effect of temperature on rate of polymerization and MW
- Thermodynamics of chain-growth polymerization
- Molecular weight distribution
- Process conditions – Bulk, Solution, Suspension

So, just recap last 2 lectures, we discussed in detail effect of temperature on the rate of polymerization and molecular weight. And we found that in most cases it will increase the temperature, the polymerization rate goes up and thermal molecular weight also comes down, except the case of growth of polymerization. And we discussed the effect of pressure, on the rate of polymerization molecular weight in very briefly, and we talked about thermodynamics of chain growth polymers, we talked about the ceiling temperature, and relations between ceiling temperature and the monomer concentration at equilibrium.

And then we talked about the dependence of monomer structure on the value or the values of the del h and del s, the enthalpy change and the entropy change, how that those values depend on the structure of the monomer depending upon how the double bond in a monomer is stabilized or the polymer is strained or not. And then we just began with different processes of making polymers, by radical chain polymerization, and we talked about bulk and solutions solution polymerization in last lecture. We also talked about suspension polymerization, in last lecture we will let us start with suspension polymerization once again in this lecture.

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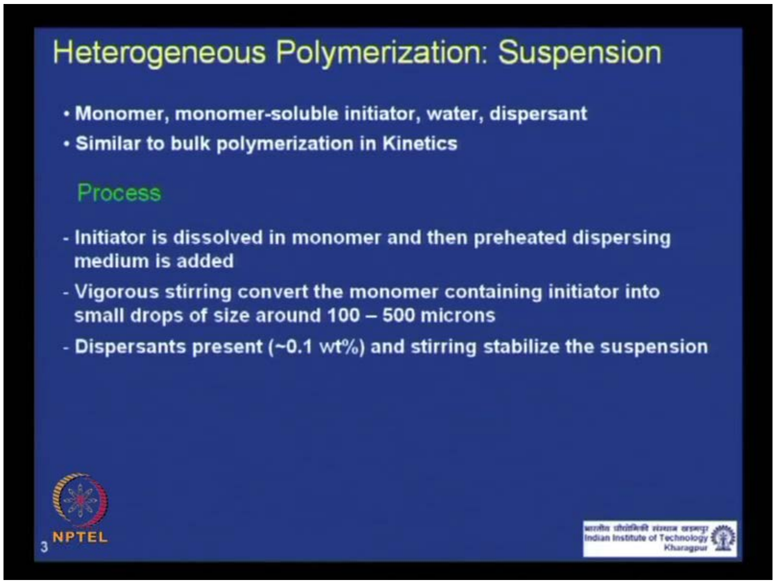

Heterogeneous Polymerization: Suspension

- Monomer, monomer-soluble initiator, water, dispersant
- Similar to bulk polymerization in Kinetics

Process

- Initiator is dissolved in monomer and then preheated dispersing medium is added
- Vigorous stirring convert the monomer containing initiator into small drops of size around 100 – 500 microns
- Dispersants present (~0.1 wt%) and stirring stabilize the suspension

Now, suspension polymerization as we talked about in last lecture that it is a heterogeneous polymerization, where you have monomer and monomer soluble initiator, and you have aqueous medium, and dispersions which actually absorbed on the monomer droplets. And prevent them sterically to collide each other, and aqueous and make larger particles, and this dispersions are typically water soluble polymers like polyethylene, polyvinyl alcohols or polyaniline pyrrolidone and so on. And it could be some inorganic particles as well which we which can absorb on the monomer particle size.

Now, depression a suspension polymers is similar to the bulk polymerization except that in this case, you have this tiny droplets which are dispersed in the aqueous medium, whereas in the bulk bulk polymerization, there was no such case. So, in this case as we discussed in the last lecture, what you do we actually dissolve the initiator in monomer, and then heat it to the required temperature, or the temperature we are planning to do the polymerization reaction. Then the dispersion medium which is a aqueous solution with the with the dispersions or added and stirred vigorously.

Now, vigorous stirring form this monomer droplets into small size, which is around this 100 to 500 microns and they are remain they remains stable, because they are surrounded or absorbed by the dispersion molecules. So, they actually, this dispersion molecule prevent this droplets to collide each other, and form a large particles.

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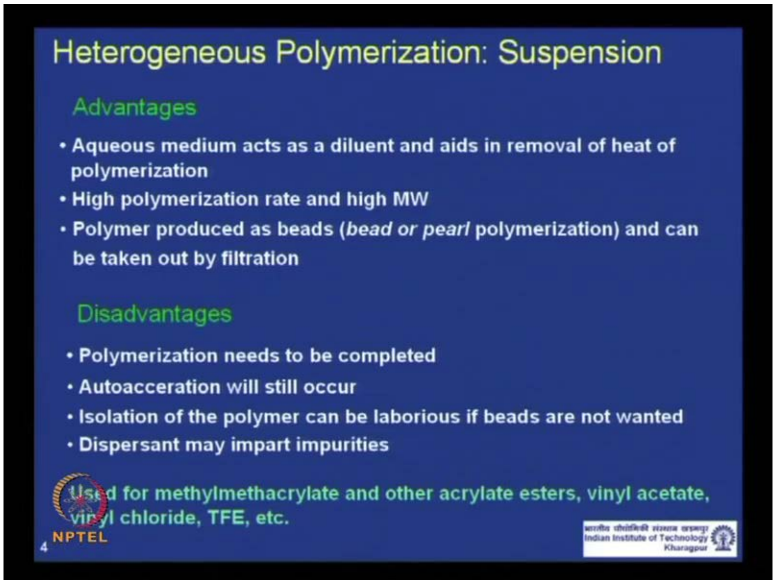

Heterogeneous Polymerization: Suspension

Advantages

- Aqueous medium acts as a diluent and aids in removal of heat of polymerization
- High polymerization rate and high MW
- Polymer produced as beads (*bead or pearl* polymerization) and can be taken out by filtration

Disadvantages

- Polymerization needs to be completed
- Autoacceration will still occur
- Isolation of the polymer can be laborious if beads are not wanted
- Dispersant may impart impurities

Used for methylmethacrylate and other acrylate esters, vinyl acetate, vinyl chloride, TFE, etc.

And this kinetics of suspension polymerization is same as the bulk polymerization, the advantage is because you have this aqueous medium present as diluents, so it is the heat dissipation which that heat which formed due to the polymerization reaction. You can easily take out the heat, because of the dispersing medium, so no such problem in case of, as in the case of bulk polymerization. And because the concentration in those monomer droplets, the concentration of monomer in those monomer droplets is high, similar to bulk polymerization, so the rate of polymerization as well as molecular weights is also high.

And polymers produced in this case are in the form of beads droplets, so you can simply at the end of the polymerization you can just separate out the beads by filtering process. And these beads should not stick to each other, if you are planning to filter the beads from the reaction medium, so it should be such that the beads should not stick to each other. And it happens if the polymer you have synthesized or you have produced is rigid, so that and also there the temperature at which is below their glass transition temperature, so that they are not soft either, so basically they do not stick to each other.

So, these polymerization procedures are mainly for applied mainly for the polymers where glass transition temperature is well above the room temperature, room temperature like PMMA polymethylmethacrylate and so on. But not everything is good in this case, also there are disadvantages as well, now because you are planning to take out the polymerization at the end of the reaction in the form of beads, and take it to the application, the polymerization must complete. So, you should be able to take the polymerization till the equilibrium, it should be such a way that it should be able to complete the reaction as much as possible.

And auto acceleration, because it is a bulk polymerization auto acceleration will also happen, but that is not, in this case this is not that much problematic like the case of pure bulk polymerization. And if you do not want the polymers in bead shape, you want the polymer as such in a powder shape or (( )) shape whatever, and then because the polymers are formed in beads bead form, it is very sometimes it becomes very difficult, if you want to isolate the polymers in the form other than beads.

And of course this beads are absorbed, beginning they are absorbed with this dispersions like water soluble, polymer of the inorganic, particles we have to make sure you watch this beads thoroughly several times, to get rid of this dispersion. But even though there could be possibilities of this dispersion remaining in the polymer beads as impurities, so these are the disadvantages. And as I said these are used for the polymers that whose glass transition temperature is way above room temperature, like methylmethacrylate other acrylate esters, vinyl acetate, vinyl chloride, and so on.

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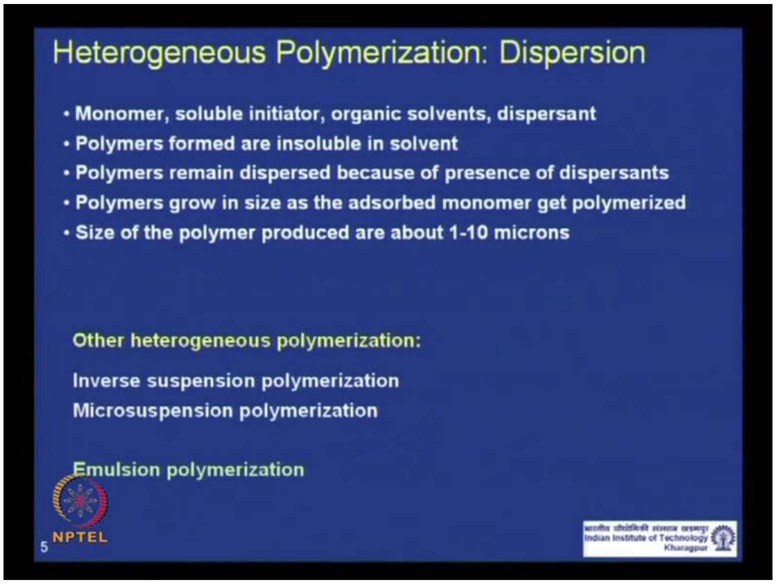

Heterogeneous Polymerization: Dispersion

- Monomer, soluble initiator, organic solvents, dispersant
- Polymers formed are insoluble in solvent
- Polymers remain dispersed because of presence of dispersants
- Polymers grow in size as the adsorbed monomer get polymerized
- Size of the polymer produced are about 1-10 microns

Other heterogeneous polymerization:

Inverse suspension polymerization
Microsuspension polymerization

Emulsion polymerization

Another type of heterogeneous polymerization is dispersion polymerization, in this case you have monomer dissolved in organic solvent, and the initiator is also dissolved in organic solvent and in this case also you have organic soluble dispersion. Now, in this case the polymers which form they are in soluble in the solvent, so in absence of dispersion they would have precipitated from the solution. But because you have dispersion present in the medium, this polymer polymers will remain, they will the dispersion will get absorbed on the surface of this polymer, and the polymers should remain as dispersion in the polymerization medium.

Now, new monomers will get absorbed on to this polymer particles, and the polymerization will take place on that monomer, so polymer remains dispersed, because the present of dispersions. And polymers grow in size as the absorbed monomers on this polymer molecules they get polymerized, and in this case the size of polymers are below of the size, what we achieved for a suspension polymers, say about 1 to 10 microns. Other is heterogeneous polymers like inversion suspension polymerization, is exactly the opposite inverse of suspension polymers, where the monomer is water soluble, and the dispersion medium is organic solvent.

For example, acrylamide the polymerization in acrylamide in organic solvent, the other polymer type like microsuspension polymerization where the size of the beads are in much smaller micro domain, so the name microsuspension polymers are used. And it could be the polymerization could be done in an emulsion, now we will talk in more detail about this emulsion polymerization now.

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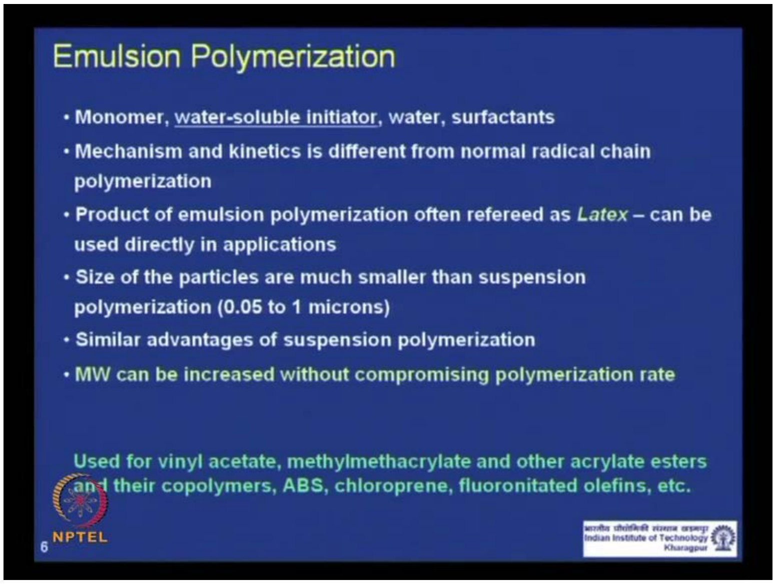

Emulsion Polymerization

- Monomer, water-soluble initiator, water, surfactants
- Mechanism and kinetics is different from normal radical chain polymerization
- Product of emulsion polymerization often refereed as *Latex* – can be used directly in applications
- Size of the particles are much smaller than suspension polymerization (0.05 to 1 microns)
- Similar advantages of suspension polymerization
- MW can be increased without compromising polymerization rate

Used for vinyl acetate, methylmethacrylate and other acrylate esters and their copolymers, ABS, chloroprene, fluoronitated olefins, etc.

Now, in case in emulsion polymerization, you have apparently singular composition, monomer water has a medium, surfactants has a dispersions, but the only difference in this case is that in this case you have water soluble initiator. In this suspension case you have monomer soluble initiator; you have water soluble initiator, now apparently its looks that this is small difference, but this has very far reaching implications in terms of the mechanism and the kinetics of the polymerization process in emulsion.

The mechanism and the kinetics in case of emulsion polymerization do not follow a normal chain reaction polymerization kinetics or mechanism, as was the case for the earlier 4, 5 process, we just talked about this mechanism and kinetics for emulsion process are quiet different and complex, and still not completely understood. So, research was still under way to understand the mechanism of the emulsion polymerization process. Now, the product of at the end of the polymerization, you get the product, the polymer product as dispersed particles not a bead not a large beads like suspension polymers, that there is a much smaller size about say 0.05 to 1 micron size, particles which are dispersed in a aqueous medium.

Now, often this product of emulsion polymerization are termed as latex, and this latex can be directly used in several applications like paint, coatings and many other applications where you can directly take the you can directly take the polymer product at the end of the emulsion, and apply is as a as a painting or coatings. Of course, you have to have add the required pigment for or additives other additives for painting applications or so on, so as I said the size of the particles are much smaller than suspensions polymers, is about 0.05 to 1 micron. And of course, the similar type of advantages are there as in the case of suspension polymers, the heat removal is not a problem, viscosity build up is also not a problem in this case.

One of the major advantages, one of the distinct advantage for emulsion polymerization which is highlighted here is that unlike other radical polymerization, for a fixed monomer concentration the molecular weight can be increased without compromising the polymerization rate. We know from our discussion from last few lectures that, if you want to increase the polymerization rate either by increasing the temperature, or by increasing the initiator concentration what happen, polymerization rate goes up, but simultaneously the molecular weight comes down.

But, this is the case where keeping the monomer concentration fixed, you can increase the polymerization rate without compromising the molecular weight, or you can increase the molecular weight without compromising the compromising the polymerization. Now, we will discuss more on the mechanistic part in a minute, and then we will understand this point, with little more clarity. And it are used for monomers at acetate, methylmethacrylate and other acrylate polymers, and it also applied for that copolymers like (( )) styrene, ABS and rubber and fluoronitated to the olefins.

Now, this emulsion polymerization is of great industrial importance, in lot of industrial polymers are made by this process, and it started at the time of world war two. When this first example of emulsion polymerization was done, which was emulsion polymerization was used to synthesize, used to synthesize a rubber, synthetic rubber or styrene and butadiene, which was first example of synthetic rubber. And that was synthesized during the world war two by emulsion polymerization, and that that had a great importance in the outcome of the result of the war. So, of the process we discussed emulsion polymerization is of great importance industrially, you should remember that.

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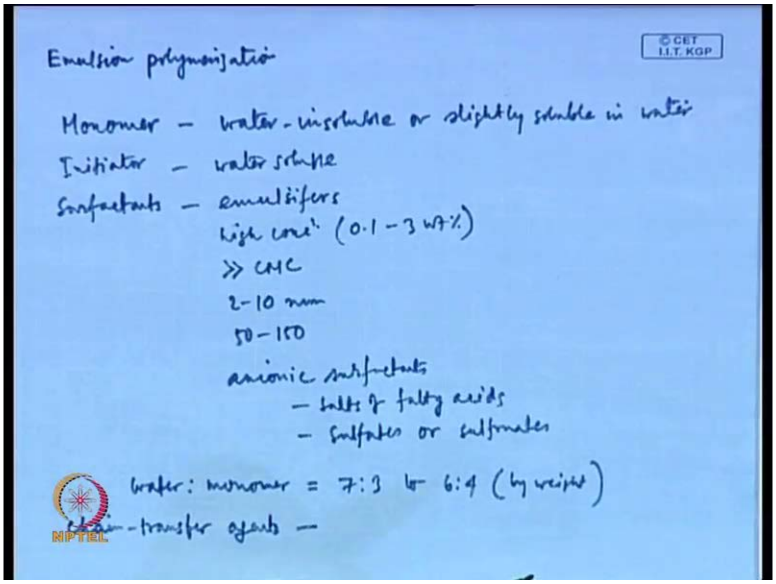

Emulsion polymerization

Monomer – water-insoluble or slightly soluble in water
Initiator – water soluble
Surfactants – emulsifiers
high conc^n (0.1 – 3 wt%)
≫ CMC
2 – 10 nm
50 – 150
anionic surfactants
– salts of fatty acids
– sulfates or sulfonates

water : monomer = 7:3 to 6:4 (by weight)
chain-transfer agents –

Now, let us let us go back and look at the mechanism of the emulsion polymerization, now what are the constitutes, now say at the beginning what are the constitutions we have, we have monomers which is water insoluble or slightly soluble, very slightly soluble in water. Now, we have initiator which is water soluble, these are typically thus the per sulfate potassium or sodium per sulfate or redox initiators we talked about, when you talked about different types of initiators. And we have surfactant, now surfactants act as a dispersant stabilizer of the large monomer droplets will come to that, and it also act as a solubilizer of the monomers molecules in it is core.

And it is also called emulsifier, because it is responsible for emulsifying the medium, so it is also calls emulsifier, and it is used at quite high concentration, if we remember the concentration of the dispersant in suspension polymers, it was around 0.01 weight percent. But in this case it is much higher, so 0.1 to 3 weight percent and of course, this concentration are quite high, and it is far greater than the critical micelle aggregation critical micelle aggregation concentration, CMC of the surfactant. So, most of the surfactant molecules present at in this water medium as micelles, as you can appreciate that, because the surfactant concentration is quite high and CMC of the surfactants are quite low.

So, the most of the surfactant molecules are present as or present in, micelles, and micelles if you are not aware micelles are aggregation of surfactants which because it has surfactant has about hydrophobic and hydrophilic components by forming micelles. This molecule can hide the hydrophobic parts from aqueous environment, and they form aggregates, and typically this aggregate are of size of 2 to 10 nanometer. And they have aggregation numbers which means the number of surfactants per micelle is around 50 to 150, this numbers depends on the different kinds of surfactants.

Now, generally anionic surfactants are used for emulsion polymerization, and typically these are salts of fatty acids, salt of salts of fatty acids, like sodium or potassium salts of palmitic or stearate or laurateo or it has sulfates like sodium lauryl sulphates or sodium dodecyl sulfate or sulfonate, like sodium benzene, (( )) benzene sulfonate. So, these are typical anionic surfactant used in this emulsion polymerization process, and typical concentration of are the ratio of water is to monomer is taken as say about 70 30 to 60 40 by weight. Now, of course if you require the control of molecular weight chain transfer, agent, origins can be added if you require or as required by the scientist; so you know what are the ingredients are there in a emulsion polymerization system.

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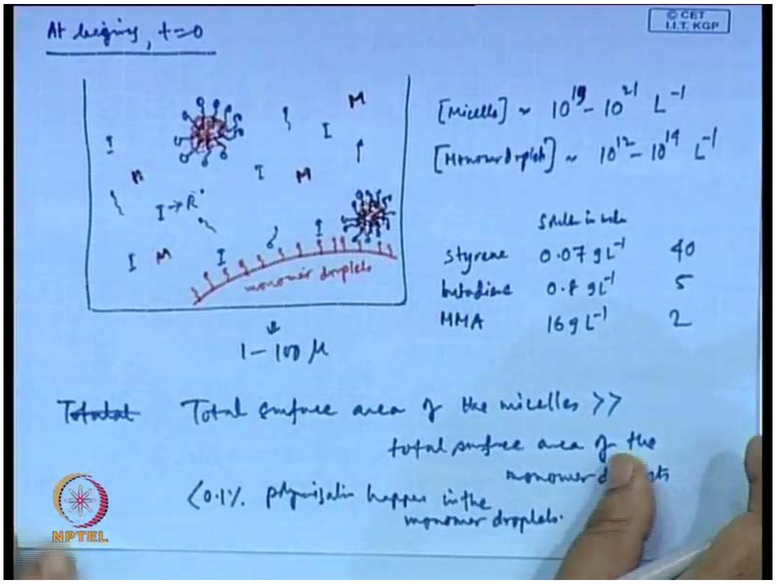

At beginning, t = 0

$[\text{Micelle}] \sim 10^{19} - 10^{21}\ L^{-1}$

$[\text{Monomer droplet}] \sim 10^{12} - 10^{14}\ L^{-1}$

	Soluble in water	
styrene	$0.07\ g\,L^{-1}$	40
butadine	$0.8\ g\,L^{-1}$	5
MMA	$16\ g\,L^{-1}$	2

~~Totatat~~ Total surface area of the micelles >> total surface area of the monomer d[illegible]ts

<0.1% polymerization happens in the monomer droplets.

Now, let us see what happens at the beginning at the beginning t is equal to 0, you have water with initiator, so I let us draw something like this, so this is a inside is a water medium, so you have initiator molecules dissolved in the water molecule, when you add surfactants, surfactants will form micelles. Now, I am just drawing this cartoons, they could mean they will be many micelles, so let us let me draw through here, now I am drawing a spherical micelle that does not mean that all the micelles or spherical or all the time micelles are spherical.

Micelles are this surfactant aggregates can be other types as well depending up on the concentration of the surfactant, or the or the composition of the aqueous medium, whether there are salt present or not, it could be cylindrical or lamellar or other aggregates can be possible. So, in this case lets draw for simplistic spherical micelles, so you have surfactants mainly as micelles, but also you have free surfactant in the water medium; the concentration of this surfactants are CMC.

Now, if you add monomer, now obviously there will be slight solubility, very slight solubility, so you have I write M for the monomer, so you have few monomer molecules, very small amount of monomer I write M, they are dissolved in water. A small amount of monomer are are will be present or will be solubilized in the surfactant core, because we know that surfactant cores are hydrophobic in nature, which means they can this like (()) core; so they can solubilize any non polar or hydrophobic molecules inside.

So, when you add monomers there are very small fractions of monomer present in a soluble, in a water medium, is very a small fraction of present as as a soluble inside the surfactant micelle. And a large amount of monomer present as monomers droplets which are stabilized by the surfactant, so let me tell you one more time that at beginning we dissolved the initiator in the water, and then when we add the surfactants surfactant form micelles, many micelles; and there will be some surfactant as a free molecules in the water medium. Now, when you add the monomers a very small fraction of monomer would be soluble in the aqueous medium, there will be small fraction of the monomer inside the micelle core as a soluble.

And large fraction actually is greater 95 percent of the fraction of the monomers will be present as large droplets. Now, let me tell you few numbers, the concentration of surfactant micelle say micelle and around 10 to the power 19 to 10 to the power 21 liter inverse, so per liter of this you have this many micelles. And concentration of monomer droplets droplets, they are of the order of 10 to the power 12 to 10 to the power of 14 liter inverse, now they are all this monomer droplet are stabilized, again by absorption of the surfactants.

Now, the this the solubility of the monomer or the partition of the monomer outside micelle, and in the aqueous medium would depend on the solubility of the monomer in aqueous solution. For example, if you consider three monomers like styrene, butadiene, and methylmethacrylate, the solubility in water of these free monomers are gram per liter, butadiene 0.8 gram per liter, whereas MMA is 16 gram per liter. Obviously, the less the soluble, the monomer is in the aqueous medium they will try to partition more inside the micelles.

So, the factor, the amount of monomer inside the micelle by the amount of monomer outside the micelle in aqueous solution are of this order 40, 5 and 2 this numbers is the ratio of the amount of monomer inside the micelle, and outside, outside means as a dissolved monomer. Obviously, styrene has a minimum solubility in the water, so they will it will partition more inside the micelles, so it has the amount of monomer inside the micelles much more compared to MMA which has a higher solubility in water.

So, as I said 95 percent, more than 95 percent of the monomer present as large droplets, now large droplet size, this droplet size is about say 1 to 100 micron which has quite large compared to the sizes of the surfactant micelle. So, if you will compare this number and the size, then total surface area total surface area of the micelles which will be much greater than the total surface area of the monomer droplets. Because, the number of micelles are much more huge compared to the monomer droplets, obviously even though the sizes of the micelles are smaller than the monomer droplets, the total surface area or the micelles are considerably higher compared to the total surface area of the monomer droplets.

So, this is the situation, I hope you are clear what at the beginning of the emulsion polymerization, now you start a polymerization that mean initiator is forming say radical. Now, what happened if initiator forms radical, initiator is forming radical, now this radical will react with the monomer present in the aqueous medium and form. Because, the concentration of this monomers is quite low, so they can only form oligomeric species, and also this oligomeric species oligomeric species or oligomeric radical, propagating radical they are also not soluble in water.

So, they will try to find a place to go, are you clear I is forming giving rise to initiator radical say R dot, now R dot will react with M the concentration of M is very small, so R dot will react with M and form oligomeric propagating radical. Now, because M itself is very insoluble, you know slightly soluble in water, so obviously the oligomeric radical will be even more insoluble in water. So, it will try to find space to go, now it can go inside micelle or it can go the monomer droplets, because that is the place where you have hydrophobic environment.

Now, because the surface area of the micelles are much more, it is always 99 percent plus or even more, time radical or a primary radical or a propagating radical, oligomeric propagating radical will move into a surfactant micelle containing the monomer molecules; rather than moving into a monomer droplets. Now, that is very important concept and here the primary radical or the propagating radical, they will move into the micelle core, and start the reaction immediately the polymerization reaction, rather than entering this monomer droplets.

So, polymerization does not take place in the monomer droplet, actually if you stop the reaction after sometime, you will find that less than 1 percent, actually less than 0.01 percent polymerization polymerization happens in the monomer droplet. Most of the polymerization happens inside this surfactant micelles, now what happened once the polymer on the propagating radical or the primary radical gets into this micellar core, they will start the polymerization reaction. Now, once they start the polymers reaction, the monomer concentration will be lower because monomer is getting converted into polymer.

So, monomer will be supplied from the bulk via or monomer will be supplied again inside the micellar core and to maintain the equilibrium, this monomer droplet will supply the monomer in the solution, are you clear. Polymerization happening inside the miceller core, monomer concentration get depleted, so (( )) the monomers inside the micelle, this monomer droplets will become smaller by supplying micelle, supplying monomer to the miceller core via, this aqueous medium.

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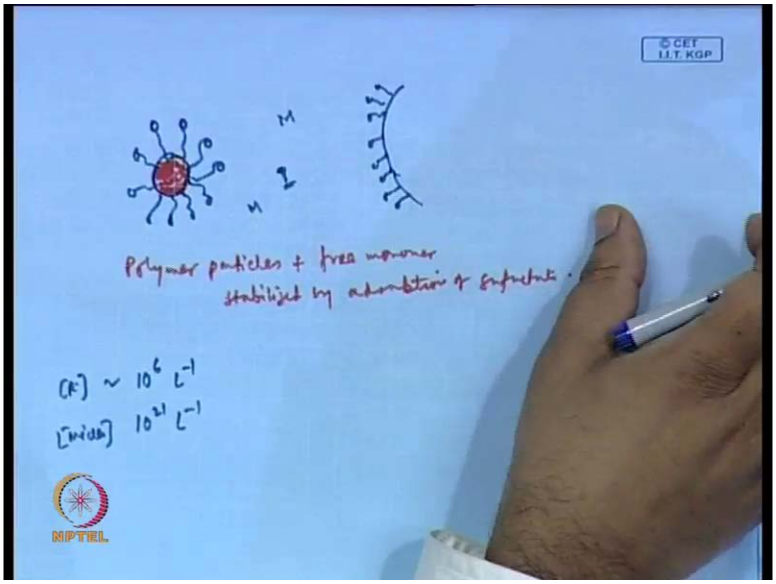

So, what happen slowly this micelle core will become something like this is larger, so after some time you have this is say polymer particle, and this concern polymer particle and free monomer, and your surfactant micelle grows in size. Now, you cannot call this as a surfactant micelle in more is basically, now you can have to name polymer particle plus free monomer stabilized by absorption of surfactant, you got it. So, more and more of this will generate and to stabilize this, you require more and more surfactant, the number of surfactant which was originally present; in the micelle they are not sufficient to stabilize this.

Where from they will get they will get this surfactant micelle, they will get this surfactant, there are other micelle where the polymerization is not started, when you start this polymerization this radical will not go in all the micelle containing monomer. Because, this number is much higher compared to the number of primary radicals, for example the radical concentration typically at the beginning is R dot, beginning is 10 to the power 16 liter inverse, whereas we know that concentration of micelle around 10 to power 21; so it is basically 10 to the power of 5 times number of micelles.

So, what happen that the radical will go in small number of micelles which will grow, and form particles surrounded by the surfactant. Now, as this particles form more and more, the this requires more and more surfactant molecules to get stabilized, which will be supplied by the micelle, which are not taking part in polymerization reaction or the inactive micelles. This is the micelles where polymerization is taking place we call them active micelles, and the micelles where polymerization is not taking place we call inactive micelle.

So, inactive micelles will slowly break releasing the monomer in the solution, and the they will supply the surfactant through the growing polymer particles. So, what happened soon as situation will come where the all the surfactant actually consumed, and you have a fixed number of particles which are active, where the polymerization is going on.

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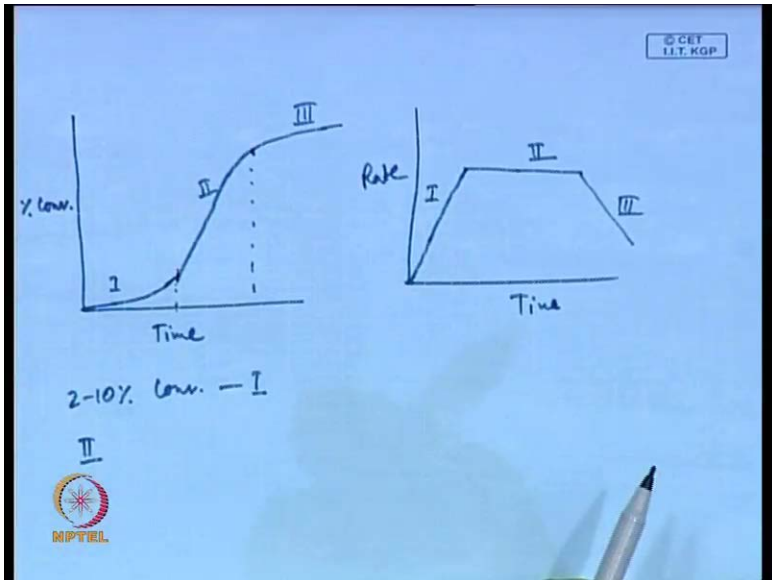

So, if you plot the conversion, we plot the conversion with time as more and more active micelle form or the polymerization takes place in more and micelle more and more my micelles. The rate or conversion goes up to a certain one point, where all the micelle are all the the inactive micelles they are broken down realizing all the surfactant. So, every surfactant, every micelle which are present, they all active micelle or they have already turned into the polymer particle surrounded by the surfactant molecules.

So, that is this happens within 2 to 10 percent of conversion, and we call this part as a stage I, so if you plot the rate of the polymer, polymerization rate with time as more and more and more this active micelles or the more and more micelles take part in the polymerization rate goes up. At the end of this stage I, the surfactant are consumed, so you have fixed number of particles, particles I mean polymer particles plus free monomer surround by the surfactant molecules, so they have now fixed in number. So, no more increase in the number of particles, hence no more increase in the rate of polymerization, so that is the end of stage II a stage I.

Now, what happened stage II, now you have what you have now, you have large monomer droplets still present of course, the size is sunk from the beginning and you have the initiator molecules, and you have such particles, particles means monomer plus polymer surrounded by the surfactant molecules, that is a stage at the end of the stage I. So, at the one more time, at the end of stage I you have large monomer droplets stabilized by the absorption of surfactant molecules of course, the this size has sunk from the beginning, you have the initiator molecules still present in the in the solution, you have monomer molecules as well.

And you have polymer particles, which are polymer particles plus free monomers surrounded by or stabilized by the absorption of the surfactant molecules, this has formed by the polymerization in the surfactant micelles, there are no free micelle in this time. Now, what happened here as more and more reaction happen, the monomer concentration get depleted, so to supply more monomers this size of this, monomer droplets comes down, and it is supplied to this reacting polymer particles. And because the monomer concentration inside these particle are almost remain constant, so the polymerization rate remain almost constant, throughout this stage II.

So, what happen in this stage II, what is happing in stage II one more time, monomer is getting into as the polymerization progress, monomer is getting depleted and that is relinquished by the supply of monomer from this droplet via the aqueous medium. So, the size of this monomer is becoming smaller and smaller, and will vanish at the end of stage II, so at the stage II you have only this particles, no surfactant, free surfactant micelles, neither you have free droplets.

So, what happen now, now this will continue the reaction till you have the monomer present in this reaction, so the monomer concentration inside this polymerization reactor comes down. So, the reaction rate also comes down, and till the reaction is over, so that is stage III, stage III gets completed when this reactions gets completed. So, you I hope you understand all this stage I, stage II, and stage III, one more time stage I is completed when all this inactive size surfactant micelles gets broken, into for supplying surfactants to the active micelles.

Stage II, at the end of stage II all the monomer droplets disappeared, because the monomer has been supplied to the reacting polymer particle, surrounded by the surfactant molecules, and stage III is basically the completion of the polymerization reaction inside those reacting, or active polymer particles.

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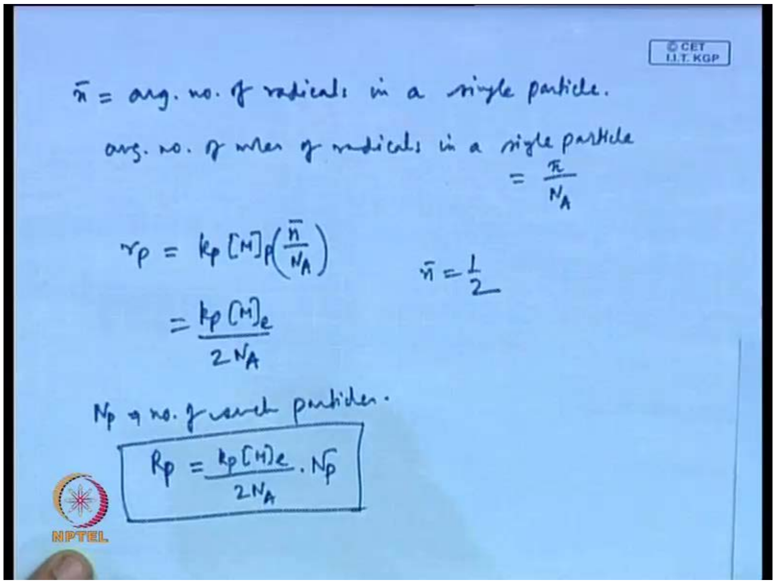

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$\bar{n}$ = avg. no. of radicals in a single particle.

avg. no. of moles of radicals in a single particle $= \frac{\bar{n}}{N_A}$

$$r_p = k_p [M]_p \left(\frac{\bar{n}}{N_A}\right) \qquad \bar{n} = \frac{1}{2}$$

$$= \frac{k_p [M]_e}{2 N_A}$$

N_p is no. of such particles.

$$\boxed{R_p = \frac{k_p [M]_e}{2 N_A} . N_p}$$

Now, if we want to look at the kinetics part for this emulsion process, let us call define n bar which is the average number of radicals in a single particle, there are many such particles. So, average number of moles of radical in a single particle is n bar by N A, N A is the abogados number. So, the rate of polymerization inside one particle, one polymer particle is given by we know the expression, K p M p where this is the monomer concentration inside one particle, and the radical concentration which is given by this that is from our knowledge.

Now, let us imagine what happened inside this particle, you have a polymerization reaction going on at beginning you have a micelle at the beginning you had this micelles, with solon with this monomers one of this R dot or a oligomeric propagating radical gets into this thing, they start polymerization. Now, this polymerization continue till second radical gets into this reactor, because the size is very small, so if the second radical gets in the effective radical concentration goes high, so the immediately the bimolecular termination reaction happen.

So, at any point of time it could be 1 radical or it could be 0 radical, it can ever have more than 1 radical, because as soon as the second radical gets into the this medium or this polymer particle, they will the 2 radicals will terminate will do the bimolecular reaction and terminate. So, at any point of time there are two possibilities, either you can have 1 polymerization is progressing with 1 propagating radical, or it have a 0 polymer radical polymer, 0 radicals in this.

Now, because the radical are entering into this micelles or the particles randomly, the probability that at any point of time the probability that any point of time a particle have a 1 or 0 radical is same, you understand that can it can have either 1 radical or a 0 radical, it cannot have more than 1 radical. And that is because the this radicals are entering into this micelles or the polymer particles randomly, the probability that you will find at any point of time, the chances or the probability of finding at any point of time 1 radical or 0 radical is same.

That means the average number of radicals in 1 particle is half, because the probability of finding 1 radical and no radical is same, so probability of finding 1 radical is or the average number of radical is half. So, n bar is half, so we can write M p by twice N A, now you have, if you have N p is a number of such particles, then total this is the total reaction rate will given the by the rates in individual particle multiplied by the total number of particles. So, that is the rate of polymerization, and this can be increased by increasing N p which is the number of such particle, which is taking part in the reaction, that can be increased by increasing the surfactant concentration or by increasing the number of micelles.

If you increase the number of micelles, then it is likely that number of micelles is taking part in polymerization is more compared to a situation, we you have less number of micelle. So if we increase the number of micelles by increasing the surfactant concentration, you will increase a N p, and then you will increase the rate of polymerization, what is the molecular weight.

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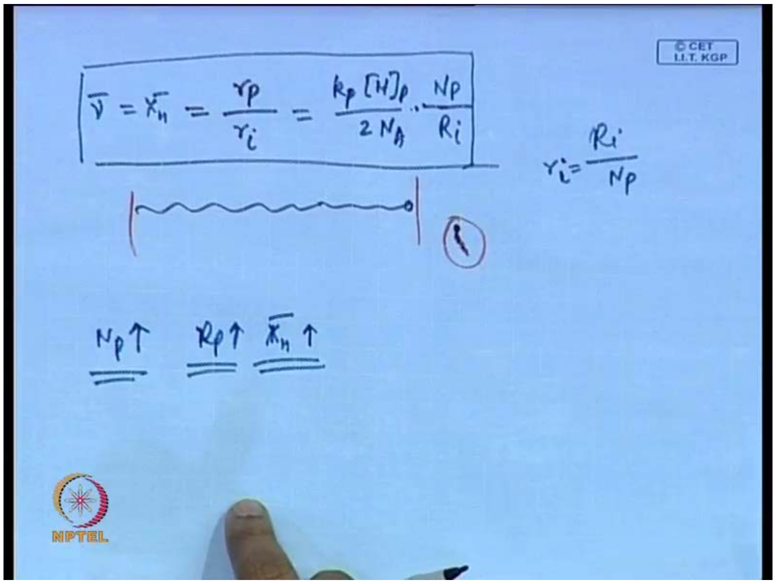

$$\boxed{\bar{\nu} = \bar{X}_n = \frac{r_p}{r_i} = \frac{k_p[M]_p}{2N_A} \cdot \frac{N_p}{R_i}}$$

$$r_i = \frac{R_i}{N_p}$$

$$\underline{\underline{N_p \uparrow}} \quad \underline{\underline{R_p \uparrow}} \quad \underline{\underline{\bar{X}_n \uparrow}}$$

Now, kinetic chain length in this case is same as degrees of polymerization, we talked about this before that, if you have two kinetic chain, and if they are if they are terminating by a combination reaction, then the molecular weights double. Then the length of the kinetic chain or if they are doing a termination by this propagation, then they are the X n is same as the kinetic chain length. But in this case, because the how does it terminate termination happens, it happens as soon as the second one gets in, so if you have a polymer particle of this size which was undergoing the propagation, now you have some second radical comes in and they will undergo immediately termination reaction.

Now, this size, the size of this radicals or size of this oligomeric propagating radical is much smaller, very oligomeric in nature, so whether they terminate by this propagation or they terminate by a combination, the size of the final dead chain is same as a size of this kinetic chain length. You can ignore or this size of size contribution due to this entering propagating radical is insignificant, so we can write chain degrees of polymerization that is in, and the polymerization is forming in a particle.

So, we can write the rate of polymerization by rate of initiation in a particle, so r p we know we have just now deduced, this is M p by 2 A N A that is r p.

Now, r i is what, is given by N p by R I, where R i is the total initiation rate, total number of initiator is generating and N p is the number of particle where they are going, so for one particle the initiation would be given by R i by N p. So, R i which is initiation rate for single particle will be total of initiator rate by the number of particles, so I just putting this R i here to get this, so you get the molecular weight as this. So, if you fix or if you do not change the initiation reaction, the molecular weight again goes up with N p, so with single handle by just increasing N p, you can now increase the molecular weight of the polymer.

And at the same time you can increase the polymerization rate, which is not happened in earlier case, where if you increase the initiation rate the polymer molecular weight comes down at the same, where the polymerization rate goes up. So, this is one very advantages advantage of your emulsion polymerization where N p as N p goes up, which you can achieve by increasing the surfactant concentration and increasing the number of micelle. Or miceller concentration with both the R p rate of polymerization goes up; as well as the number average degrees of polymerization.

Now, at any point of time you can find out the size of this emulsion polymer, the particles like miceller particles or the droplets by help of this electron microscopic or light scattering or inter centrifugation. If you want to prove in a reaction, if you promote the reaction, you know find out what is the size of this your polymer particles or so on, so I hope you understood this emulsion polymerization part.

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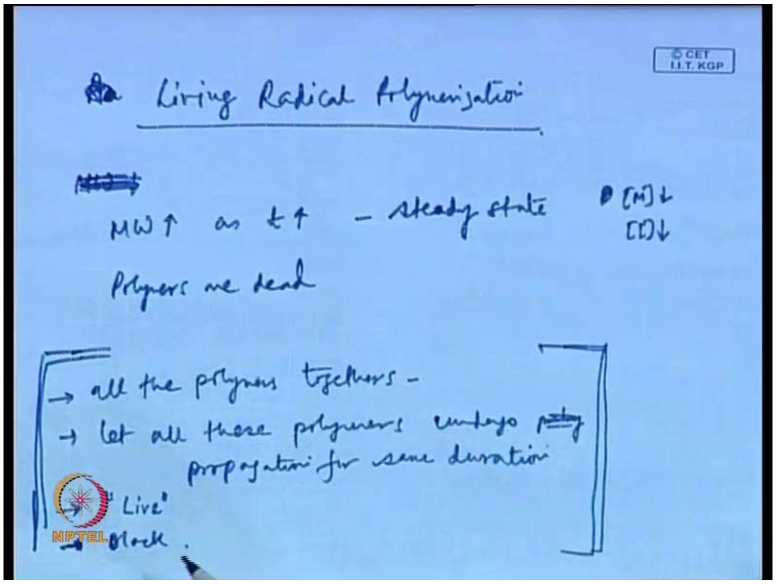

Living Radical Polymerization

MW ↑ as t ↑ – steady state [M]↓ [I]↓

Polymers are dead

→ all the polymers together –

→ let all these polymers undergo ~~poly~~ propagation for same duration

'Live'

→ Block.

And what we will do we will next move to the discussion on living radical polymerization, now we by this time we know that molecular weight in a normal polymerization, radical polymerization comes down. In a steady state the molecular weight comes down as time goes, sorry it is the other way round, molecular goes up and as time progresses or time increases. I am talking about steady state, because most of the time reaction happens in a steady state, if gel effect or other complication happen, then the situation is more complicated to simply conclude.

So, the polymers form at the beginning will have low molecular weight, whereas if you increase or when the polymers is producing later on during the reaction, the size increases that we have we have rationalized. Because, the concentration of monomer also goes down, concentration on initiator also goes down, but as the concentration initiator goes down faster than the monomer, so effectively the monomer molecular weight increases. It also true for normal radical polymerization that that the polymers are dead, which means that you, once the polymerization is complete you cannot take this polymers and add the second monomer to make a black copolymer, or something like rather that.

So, if you design a mechanism by which you can start all the polymers together, so if you design, can design a mechanism or you can start all the polymer together, and let all this polymer all this polymers undergo polymerization or propagation for same duration. For you have you have initiator lot of polymers together, all the polymers together and you have continuing all this polymers all this polymers is undergoing polymer propagation reaction, this during the same duration.

Now, that is the only possible, if this polymers are live that means they do not undergo this bimolecular termination reaction, if they undergo bimolecular termination reaction they will be dead immediately, and they will not be able to continue the propagation chain. So, what we will do and if they are live, they will remain live at the end of the polymerization as well, if they can live all this time, which is quite a longer time compared to a termination reaction. Then there is no reason why they will be dead at the end of the polymerization, so they will be still be live at the end of the polymerization, so you can use this and make the block copolymers.

So, what we will do in the next lecture, we will talk about the strategies by which we can achieve this situation this situations, so that we can make all the polymer chains of similar size, because they are started from same time, and continue it for same time. So, all the polymers should be of similar size the (()) will be lower, and they will be live all the time, so say the at the end of the polymerization, they will also be live. So, we will see what are the strategies we can take to make such a requirement fulfilled, so we will talk we will start from this slide in the next lecture.