Polymer Chemistry
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Lecture - 16
Radical Chain Polymerization (Contd.)

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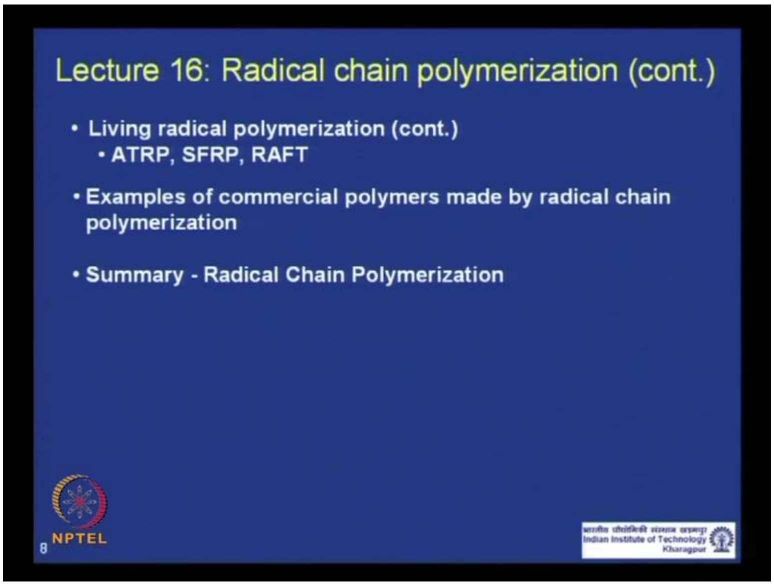

Lecture 16: Radical chain polymerization (cont.)

- Living radical polymerization (cont.)
  - ATRP, SFRP, RAFT
- Examples of commercial polymers made by radical chain polymerization
- Summary - Radical Chain Polymerization

Welcome back to this course on polymer chemistry and in this lecture, this is lecture 16. We will discuss lecture on living radical polymerization; and we will talk about three different type of living radical polymerization, ATRP, SFRP and RAFT. We will talk about the full forms, time; and I planned to just give you examples of commercial polymers, which are made use of this radical polymerization technique and then, we will conclude this module of radical chain polymerization at the end by giving you a brief summary of what we have learnt in radical chain polymerization.

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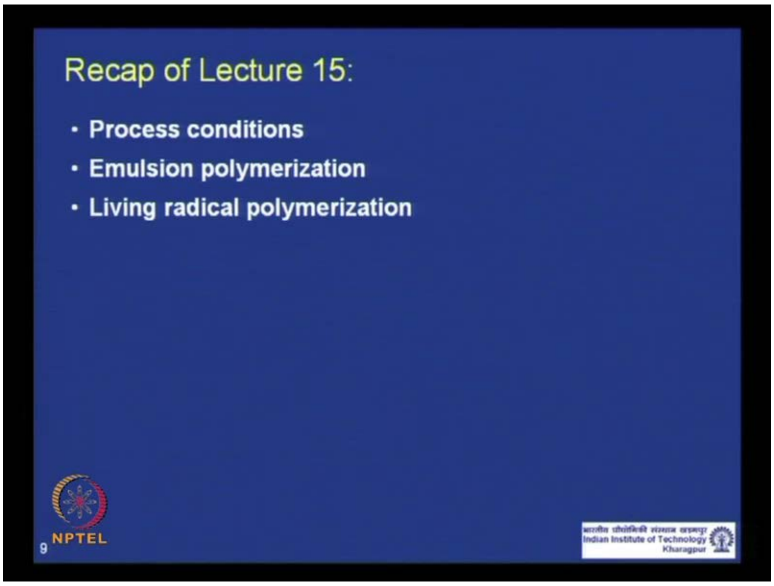

Recap of Lecture 15:

- Process conditions
- Emulsion polymerization
- Living radical polymerization

This recap in the last lecture, we discussed in detailed a different polymerization processes, and we spent lot of time on emulsion polymerization. And we discussed, we just introduced the concept of living polymerization and let us begin from the same page, we left in the last lecture.

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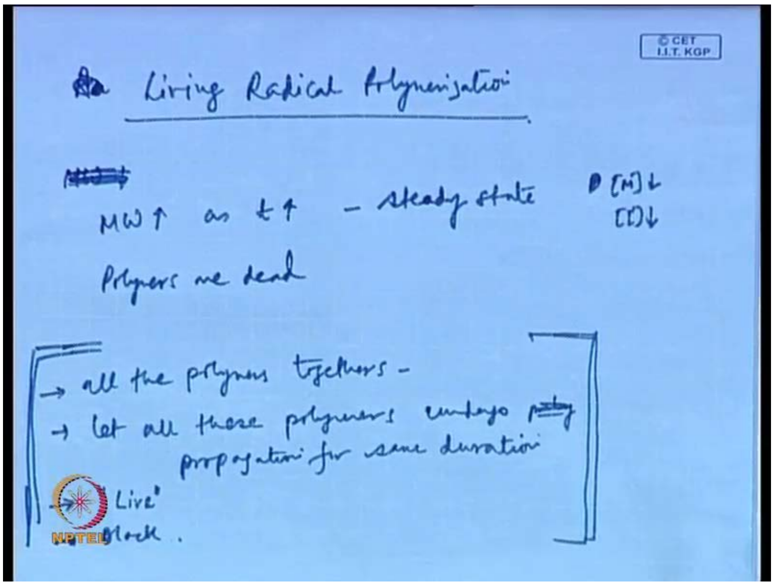

Living Radical Polymerization

MW ↑ as t ↑ – steady state $[M]\downarrow$ $[I]\downarrow$

Polymers are dead

→ all the polymers together –

→ let all these polymers undergo propagation for same duration

'Live'

Block ..

Now, as we were discussing that in a normal chain polymerization process, as soon as the initiation reaction is slower, as we know initiation reaction is slower. So, the chain initiation takes place leaving a time during almost during inter polymerization time and the propagations step is faster. So, as an agent, a radical generates its undergo propagation reaction and at the end by molecular termination reaction have, and the polymers become dead with time you generate different molecular weight polymers and of course, these polymers are not live or dead. So, you have much larger or broader molecular weight polymers.

Now, if we can by any means start almost all the chains at more or less same time; that means, initiation must be faster and then, let the polymers, all these chains we just started let them under go polymerization reaction or propagation reaction for same deviation. Then, what happen on that has to happen. This propagation has to be much lower compared to initiation first of all and if that happen or if that has to happen, then all these polymers should be live. That means they are reactive to the monomer. So, they can undergo polymerization reaction, say the live you can add a second monomer and form block polymer at the end of the polymerization.

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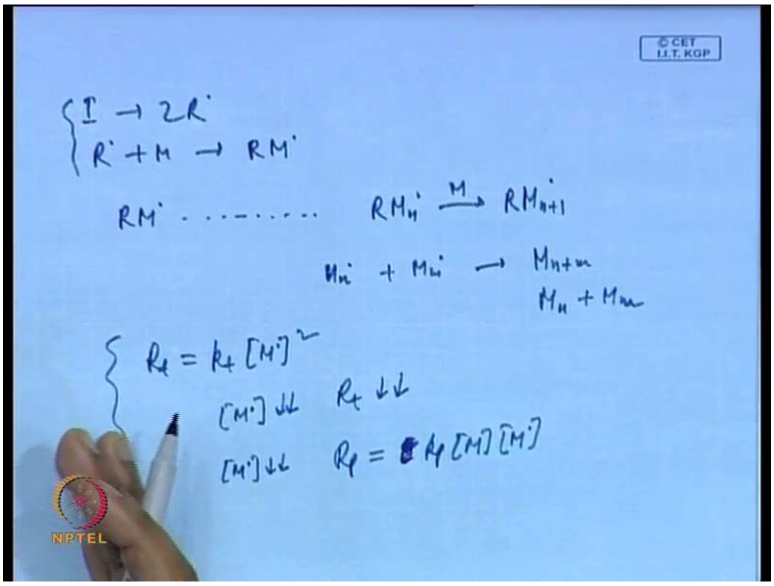

Now, how can we achieve this? All this point we just talked about in a normal radical reaction. What happen is you get a radical which immediately reacts with a monomer to start the chain, and you have this, all this reaction forming RM n dot and propagation continued RM n plus 1 dot and so on and this initiation process is lower. So, as soon as this radical generates, they undergo polymerization reaction and these two reactions n M dot plus M n dot did undergo by molecular reaction forming either M n M plus n depending upon which type of termination reaction they are undergoing. So, at the end, you get a dead polymer. Now, if by any means if you can know what is the rate of termination reaction? Rate of termination reaction we know k t M dot square, where M dot is the concentration of total radical, total propagating radical.

So, this is summation of all the concentration, of all the propagating radical present. Now, if you can reduce this M dot, then what happens is RT comes down much lower. If you are by any means if you can reduce this M dot, then RT comes down. So, if you can bring down such a level that RT is insignificant, then there practically no termination reaction would happen. In this case that will in suit that the polymers which are forming, they are not killed or the chains which has getting initiated, they are not killed. That is one thing. How do we achieve is M dot is very low, then what is R p? R P also you know this k P MM dot. This is very slow. Then, rate of polymerization also will be lower compared to a normal radical polymerization. So, that ensures if you can bring down the conception of this, that ensures that the termination reaction is much low or if is basically insignificant.

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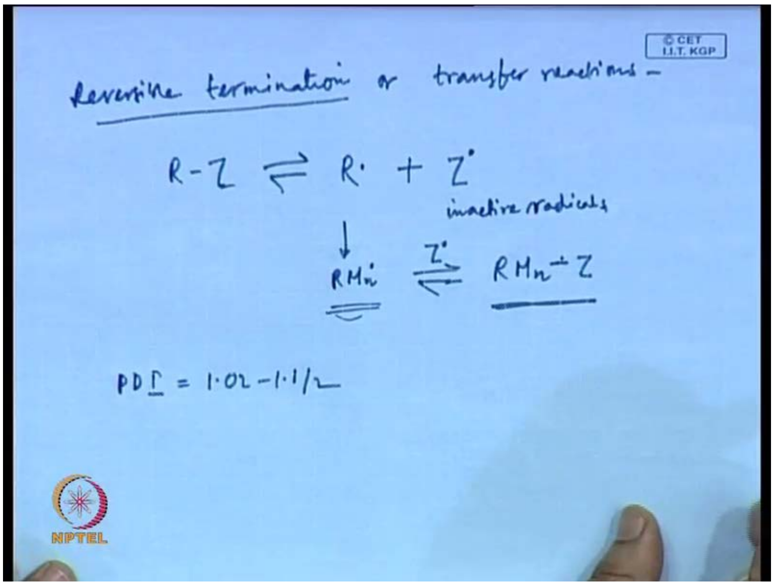

Now, how do you achieve the condition where you let all the polymers, all the chains react for the same duration? Now, that is achieved by reversible termination or reversible transfer reaction, say I have an initiator molecule which is R z. Typically, all time in normal reaction, we write a single arrow which means any reversible reaction. Now, in this case we are writing double arrow which means this reversible reaction. Now, if the structure of Z is such that its inactive radical, then this would not take part in propagating, radical propagating step. So, only this will take part in propagation step. Now, this will again react with the monomers and form different chain length.

Now, because this is radical, it will be again part of the equilibrium process with Z. So, this is a case we are talking about reversible termination. So, if this happened in normal case, if this bimolecular reaction happen, you get a termination step dead polymer, but in this case because this is reversible, this can again come back and give you back this active radical and inactive radical. Now, if the structure of this is such that here if this equilibrium is shifted mostly towards right hand side, then what happened is this radical stays or spend most of its time in a dormant form. This is a dormant form. This does not take part in the polymerization reaction, where for a small fraction of their lifetime, they are present in this active form.

So, what happen in this way you are reducing the concentration of the radical active radical present and that will ensure that your termination reaction are negligible because this is a reversible termination reaction. This radical is not under if it do not undergo any termination reaction. It can react with a monomer and again go back to the domain form because is equilibration process or reversible process, so that all the radicals, all the propagating radicals we generate from the initial initiation reaction, they will spend more or less same amount of time in as active form and as a domain form which will ensure that all the polymer chains are progressing or reacting during or for a same number, same amount of time or same duration.

So, one more time if you have a initiator which reversibly form this R dot and z dot, where R dot is an active radical and z is inactive radical because of its structure, then what happen is only these undergo polymerization of propagation reaction and at the very beginning, the concentration of R dot is quite highest. They will undergo some termination reaction till the concentration of z dot is much higher at very beginning and this forms, this might undergo bimolecular termination reaction.

So, you get drop in R dot concentration and you get more and more z dot at beginning once the concentration of z dot is sufficiently higher compared to R dot and also f chosen this equilibrium such a way that the equilibrium constant is towards this side. Then, what happens is this equilibrium is shifted mainly towards this sight. So, the average time radical, a propagating radical spend in this form which is active form which can react with the monomer and propagate much lower compared to the time, an average radical spend in dormant form or inactive form. By this way, you are ensuring this.

After the initial period of time, the concentration of radical are small which will ensure the termination reaction is negligible and also because these are equilibrium process, every radical is coming out and going in the dormant form. This is all. All this time, all this propagating radical is spending same amount of time in this form. So, they are undergoing the propagating radical for same duration which ensures that the chain length of the polymer produced is almost similar size. So, p d I would be very narrow. So, 1.02 to 1.1 1.2 something like this. So, they are very close and at that the end of the reaction, again they will remain in this form. So, you can add a second monomer to form a block polymer.

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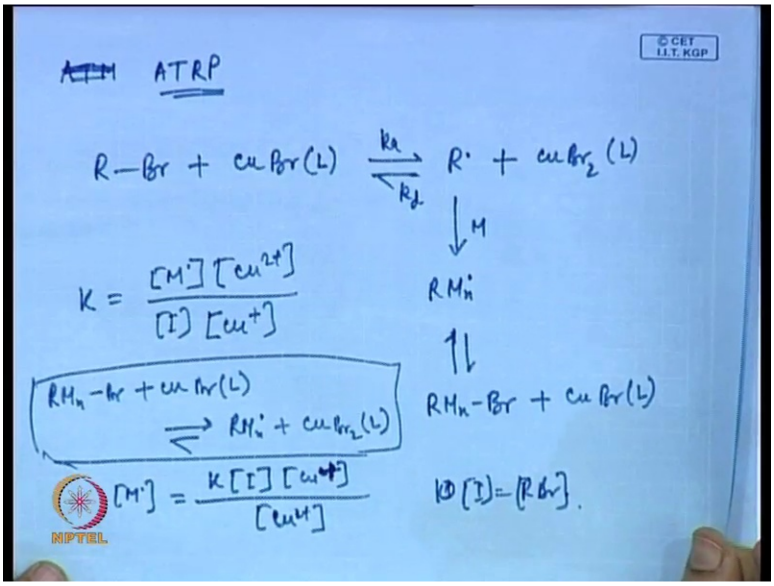

~~ATM~~ ATRP

$$R{-}Br + CuBr(L) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} R^{\cdot} + CuBr_2(L)$$

$$\downarrow M$$

$$RM_n^{\cdot}$$

$$\uparrow\downarrow$$

$$RM_n{-}Br + CuBr(L)$$

$$K = \frac{[M^{\cdot}][Cu^{2+}]}{[I][Cu^{+}]}$$

$$\boxed{RM_n{-}Br + CuBr(L) \rightleftharpoons RM_n^{\cdot} + CuBr_2(L)}$$

$$[M^{\cdot}] = \frac{K[I][Cu^{+}]}{[Cu^{2+}]}$$

$$[I] = [RBr].$$

The three types of living radical polymerization. First one is ATRP, atom transfer radical polymerization. In this case, your initiator is a halide and you have redox reaction, where you have a q plus halide. It can undergo reversible atom transfer reduction process, where you get R dot plus Cu Br 2 L. L is an organic (( )) which basically complex with this copper salt, so that the copper salt remain insoluble, remain soluble in the organic solvent. So, this now again can react with M from R M n dot, it can M 1, M 2 and so on.

So, it happens, this happens to all the radicals and this again goes to the same reaction form, R M n Br plus Cu at l. So, at any moment of time, the concentration of this is very small which means the termination reaction is very less because this is a part of the equilibrium. So, one more radical it is coming out capturing a monomer, increasing the chain length, going into the equilibrium. Second monomer, second radical is coming out reacting with the monomer and going to reaction. So, average time this spends in terms of active form is same for all the propagating radicals. So, chain length, all the propagating radicals are same. Now, if I write equilibrium is constant for this reaction, this is M dot.

So, let us write this. For this reaction, M n dot we are writing M dot and copper 2 plus. I initiated this side is initiator which is this initiator is this and Cu plus which is this. I am writing if you confuse. I am writing this equilibrium reaction for. So, this reaction, this K K of this reaction would be given by this. So, the concentration of this propagating radical is given by K I Cu 2 plus k I plus k I Cu plus by Cu 2 plus I is R Br. Concentration of I R is the concentration of R Br.

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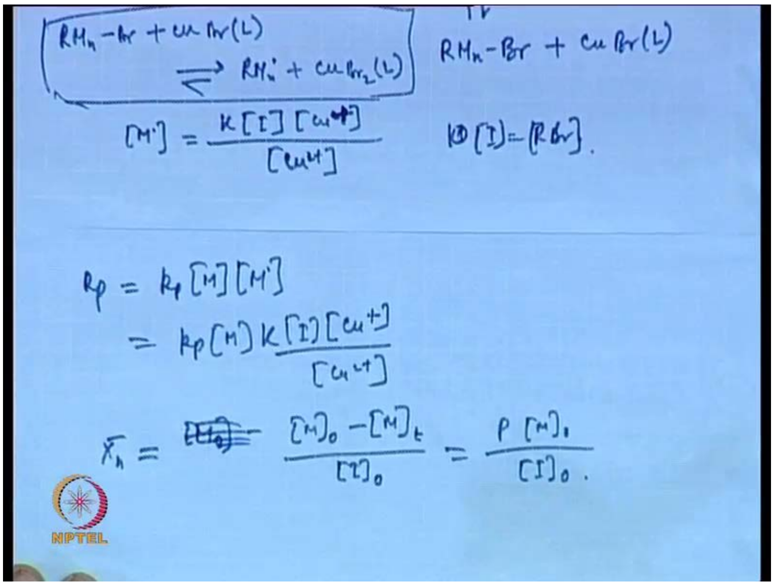

$$RM_n-Br + CuBr(L) \rightleftharpoons RM_n^{\bullet} + CuBr_2(L)$$

$RM_n-Br + CuBr(L)$

$$[M^{\bullet}] = \frac{K[I][Cu^{+}]}{[Cu^{2+}]}$$

$[I] = [RBr].$

$$R_p = k_p[M][M^{\bullet}]$$

$$= k_p[M]K\frac{[I][Cu^{+}]}{[Cu^{2+}]}$$

$$\bar{X}_n = \frac{[M]_0 - [M]_t}{[I]_0} = \frac{p[M]_0}{[I]_0}.$$

So, what is R p? Rate of polymerization will be given by k p M and concentration of the radical which is given by k p M k I Cu plus by Cu 2 plus. So, that is the rate equation and the molecular weight would be given by the total number of monomers is reacted. So, M 0 is the initial. The concentration of your monomer by M t is a monomer present in time t divided by total initiator concentration which is given by the conversion M 0 by I 0, each initiator by one radical and one radical produces one chain. So, if you have monomer polymerized with two chains, then total decrease of polymerization will be 100 by 2 is 50.

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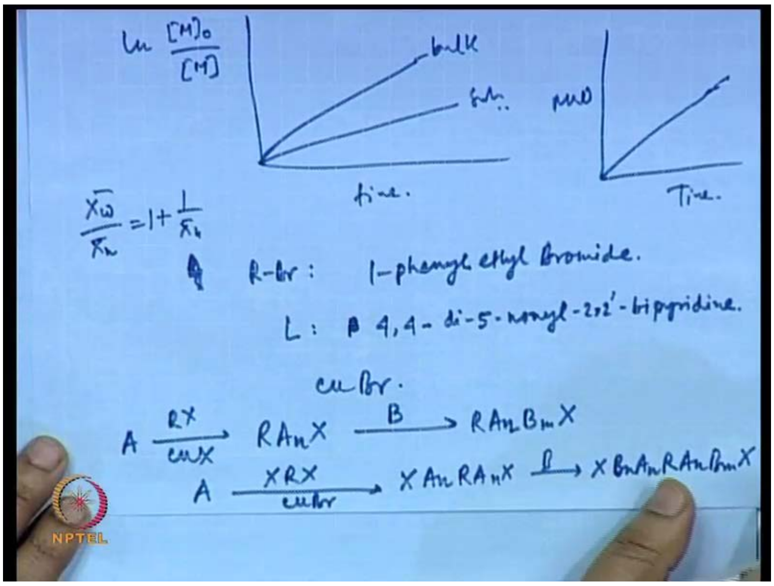

Now, if you plot with time, see this is experimental plot. You get same for bulk and say if a solution you get a slower rate because this is straight line, which means that this is a first order reaction. Example of R Br is 1 phenyl ethyl bromide and l is 4, 4 di 5 nonyl 2 2 dash by pyridine. So, if you have these, all the three plus styrene bulk solution, you get experimentally this.

So, what happens to the molecular weight if you plot molecular weight versus time? What will you get? Again, it is a straight line. As time goes, no reaction forward. So, more propagation happen. So, the reaction molecular rate increases linearly, where in case of normal chain polymerization, you can get very high molecular even at beginning of the polymerization and in such case, the molecular rate is small at the beginning and it increases slowly after. As the time goes, you can take a monomer and do a reaction like this, R n X a polymer and then, you can add a second monomer. You can form a block polymer like this. You can take a dihalide and then, you can make tri block polymer as well and for a simple case, the PDI for this sort of reaction given by this.

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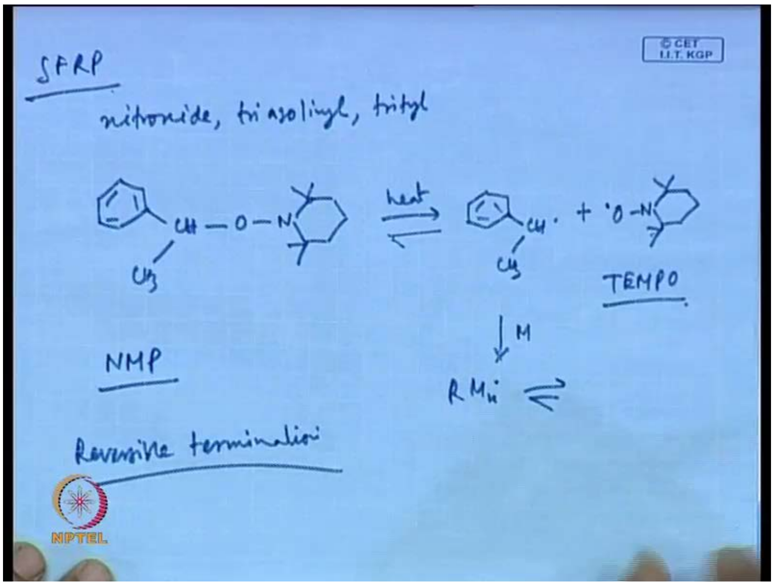

SFRP

nitroxide, triazolinyl, trityl

NMP

Reversible termination

So, higher the molecular weight, lower is the PDI. A second type of living radical polymer is stable free radical polymerization. In this case, the same thing you can generate the z dot which is very stable like nitroxide triazolinyl trityl radical. For example, I have initiator like this. When it forms two radicals, this radical commonly known as tempo. This is very stable. Because of these two large groups, they cannot take part in bimolecular termination reaction among themselves.

So, that is why this radical is very stable and that can be stored for days in a container which can be used later on. So, same thing happens in this case because you have a stable radical and this can react with same form RM n dot which again undergoes reversible reaction and form the same logic, which you discuss ATIP and do the living chain polymerization. When this stable free radical polymerization is done through nitroxide, it is often called NM p nitroxide mediated polymerization. So, logic, all the arguments remains similar as in the case of ATIP. Again, this is a case of reversible termination like ATIP.

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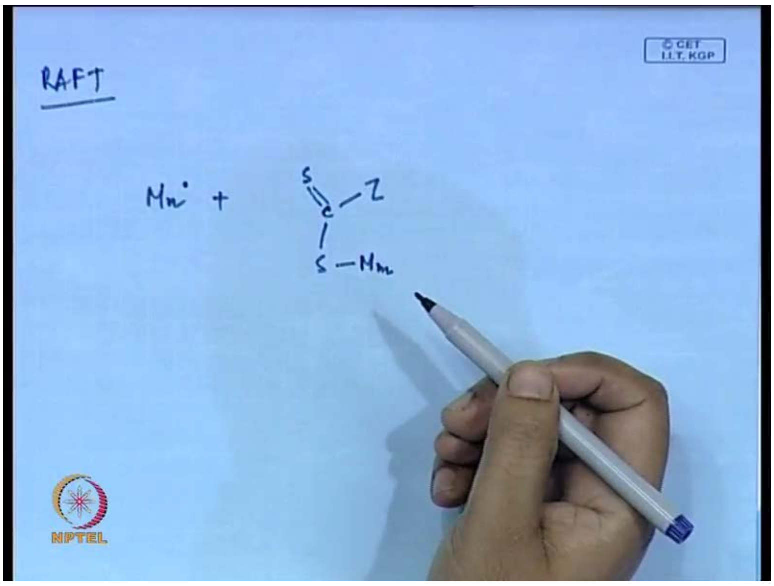

Now, the third case which is RAFT, reversible addition fragmentation transfer. The name suggests that it take advantageous advantage of reversible transfer reaction. Now, in this case what happens, you have the same way you have h n come to that.

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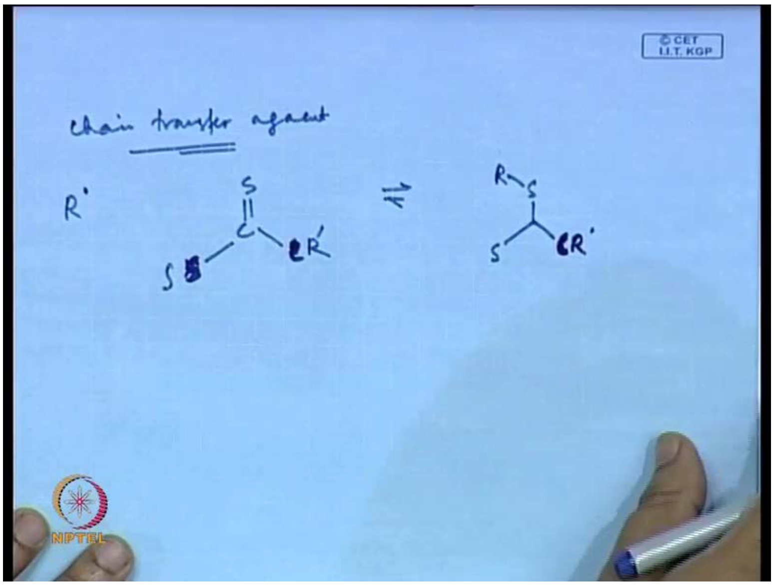

You have a chain transfer agent here which is having general structure or something and gives you the more common, most common structure. It could be something else as well, but for time being, I will just give you the most common example. It is a dithio ester.

Now, if you have a radical which can undergo reversible addition to this S is a form R S, this is let us put at carbon. Let us take one more time. Getting little confused.

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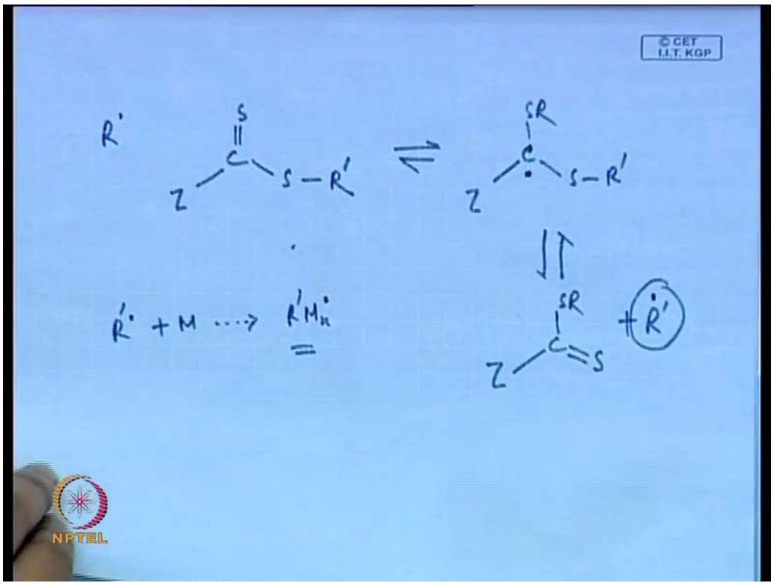

So, I have the chain transfer agent which has generic structure life. It is dithio ester and I have a radical produced by normal thermal initiation of some other reactions, like thermal initiations AIVN (( )) of peroxide. Then, it can undergo reversible addition and form this differentiate make R star, this radical. Now, if this bond if chosen in such a way, in this case, it is higher bond that this can again reversibly fragment by homolitic cleveage. Then, this is found, this radical can react with monomer forming M n dot. So, this initial reaction as well as, now this can undergo similar reversible addition and common fragmentation reaction.

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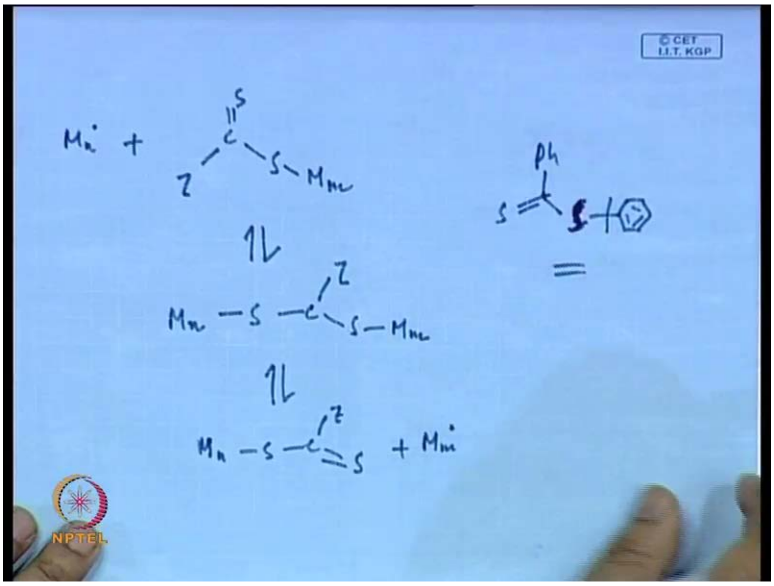

So, in general, we can write that it general. So, you have a reversible, addition reversible fragmentation and this is a transfer reaction because the original radical is getting transferred and getting terminated in forming in a new radical which is a transferred reaction. For example, a raft transfer agent is, we can give as simple example of transfer reaction. See in case of raft reaction, what is the molecular weight?

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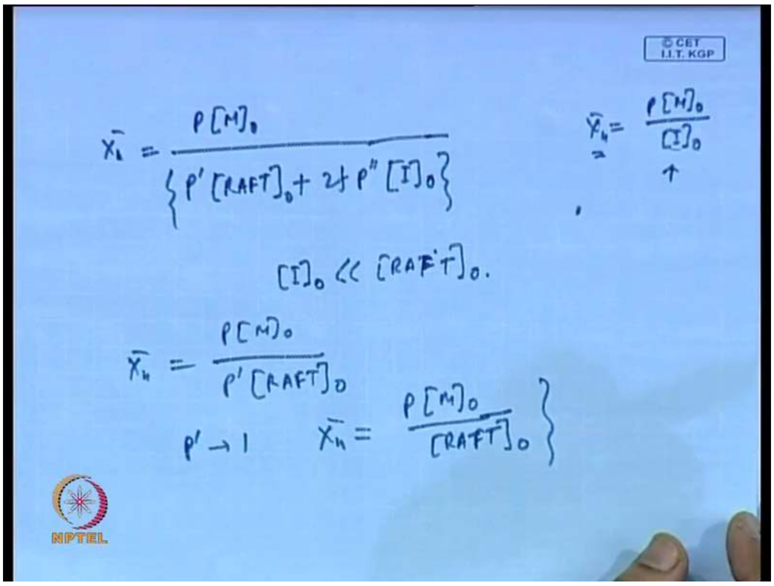

$$\bar{X}_n = \frac{p[M]_0}{\{p'[RAFT]_0 + 2f p''[I]_0\}}$$

$$\bar{X}_n = \frac{p[M]_0}{[I]_0} \quad \uparrow$$

$$[I]_0 \ll [RAFT]_0.$$

$$\bar{X}_n = \frac{p[M]_0}{p'[RAFT]_0}$$

$$p' \to 1 \qquad \bar{X}_n = \frac{p[M]_0}{[RAFT]_0} \Big\}$$

Again like earlier, it is the conversion multiplied by the initial mole of the monomer, and the conversion of the raft reagent plus the conversion of the initiator. This gives you the number of chains form in case of ATIP or other reactions. See we discussed that this is by the total initiator molecule. Remember the expression for the ATIP? We had P M 0 by I 0. Physically, each I 0 was forming one radical and that radical was participating in a propagating chain. So, this gives the number of monomers reacted divided by the number of chains formed which gives you the degree of polymerization and in this case, this is the transfer reaction. So, to include the number of radicals form, the initiator molecules which is given by if it is thermal polymerization is to 5, this is your deficiency factor and the conversion of this. Because each raft agent forms one radical, so we have to come include the concentration of the raft agent as well as initiator concentration. So, total like the case of transfer reaction, chain transfer reaction, we have included this. In this case also, we have to include both these.

Now, because typically we use the I0 concentration much lower than the raft concentration, we can use N 0. This is the conversion of raft region. Now, if we do reaction such a way that all the RAFT regions or did take part in the polymerization reaction, we choose the raft region such as, such a way that every raft reagent is participating in the transfer reaction. The chain transfer position for the raft reagent we use is very high, so that all raft agents can actually be participating in the chain transfer reaction. So, P dash becomes close to 1. So, finally, this becomes the raft agent concentration.

So, in this case, the molecular weight depends upon the chain transfer reagent and the chain transfer constant is much higher compared, much higher, so that all the raft agent is taking part in the chain transfer reagent and also because the concentration of the initial raft agent is much higher than original initiator radical, we can simply write the average degrees of polymerization, end of the polymerization is. Similarly, as in case of ATIP reaction or (()) reaction, where I 0 can be replaced by the raft reagent concentration and the beginning and again try other cases, we can utilize this raft reaction reversible addition, fragmentation transfer reaction for making block polymer at the end of the polymerization if we add a second monomer.

Now, with this, we will in this discussion living radical polymerization, what you will do is quickly go through different commercial polymerization. Now, we will do this and go little faster because this is just information, nothing more to understand.

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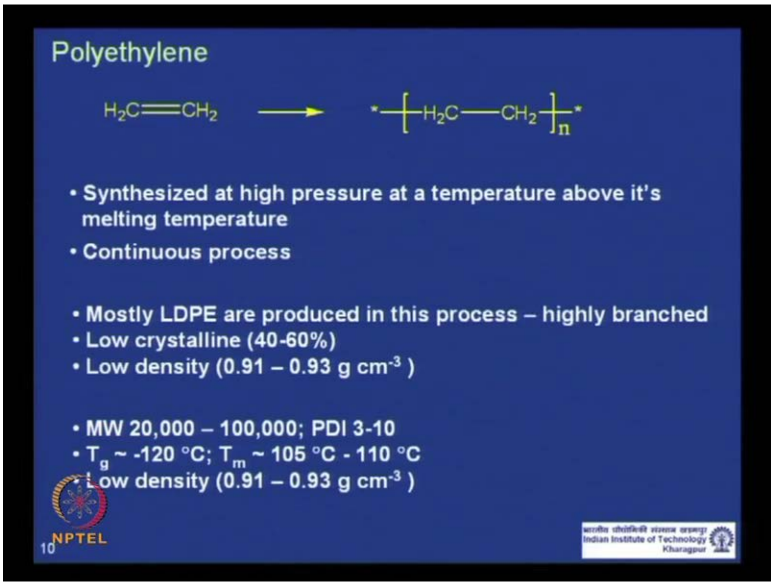

Polyethylene

$$H_2C{=}CH_2 \longrightarrow {*}\!\left[H_2C{-}CH_2\right]_n\!{*}$$

- Synthesized at high pressure at a temperature above it's melting temperature
- Continuous process

- Mostly LDPE are produced in this process – highly branched
- Low crystalline (40-60%)
- Low density (0.91 – 0.93 g cm^{-3})

- MW 20,000 – 100,000; PDI 3-10
- T_g ~ -120 °C; T_m ~ 105 °C - 110 °C
- Low density (0.91 – 0.93 g cm^{-3})

So, we will spend little time on these examples and if you want, you can get more information of any text book or some other literature. This is just to complete your knowledge on the radical chain polymers. You have studied for last 5-6 lectures, what is radical polymerization, radical chain polymerization and have talked about different monomer structures, but finally, it matters or it is useful if some commercial polymers have made using these techniques. So, once you know that there are several polymers which are made using this technique, then your learning will be complete in that sense.

Now, the simple monomer is all polyethylene and polyethylene is synthesized at high pressures and temperature above the melting temperature, its melting temperature. Now, remember this is a gaseous reaction to polyethylene is a gas to solid form, solid polymers. The volume change is significant. Now, remember we talked about the effect of pressure briefly that in that reaction, in the polymerization reaction, if the volume change is higher, then it is increasing pressure. You can increase the reaction rate or we can make the reaction more feasible. So, that is why in this case, the high pressure is used.

As I said that you have to keep your reaction temperature above of melting temperature in this case, so that the polymers have mobility, so that they can undergo further propagation reaction. So, this reaction is done about the melting temperature, its continuous process and while talking about the chain transfer to the polymers, we gave examples of polyethylene because indeed chain transfer reaction happens to polymers in this case. So, branches are produced. So, this is a highly branched polymer and mostly, LDPL is low density polyethylenes are produced in this case and because this is the branched structure, it is low crystalline because the polymers cannot align each other parallely. If they are branched, they cannot align all that time.

So, the crystalline come down and once the crystalline come down, the density of polymers also come down. So, it is also low density. Typical molecular for the commercial polymers are 20000 to 100000 PDI, 3 to 10 and T g of these polymers are about 120 degree of centigrade. T m is from 105 to 110 degree centigrade and density as a set, it is in low density one more time.

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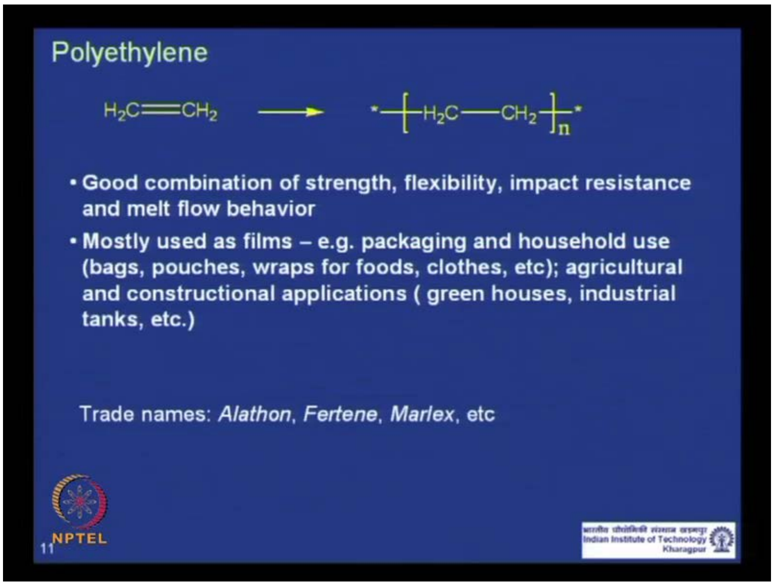

Polyethylene

$$H_2C{=}CH_2 \longrightarrow *\!-\!\left[H_2C{-}CH_2\right]_n\!-\!*$$

- Good combination of strength, flexibility, impact resistance and melt flow behavior
- Mostly used as films – e.g. packaging and household use (bags, pouches, wraps for foods, clothes, etc); agricultural and constructional applications (green houses, industrial tanks, etc.)

Trade names: *Alathon*, *Fertene*, *Marlex*, etc

Applications are in the most of this has very good strength, flexibility in packed resistance and these are good melt flow behavior. If you have good melt flow behavior, then you can do the processing easily. The melt processing becomes easier and in this case because we talked about application of this polymers in playing. So, blow molding, basically the molding is done by blowing higher through a molten polymers, so that thin flames that can be done easily if you have a good melt flow behavior and polyethylene’s are used mostly as films for packaging materials, for house hold and agricultural construction application. For example, whatever we commonly talked about, say polyethenes, these bags, pouches, food wraps or cloth wraps and all these things, they are made up of polyethylene. The other examples now in this slide and the coming few slide where we are talking about other polymers, I will just mention few examples.

Now, there are 100 of other examples, other applications, these polymers are applied. So, for this class, it is not possible to cover all the examples. I will try to give the most common application of these polymers, but this and for this and for the coming polymers and there are trade names, where you by it this name, these polymers get sold in the market. Again there are companies sell these polymers in different trade names and this is not expressively. This is a very few of trade names covered in this slide.

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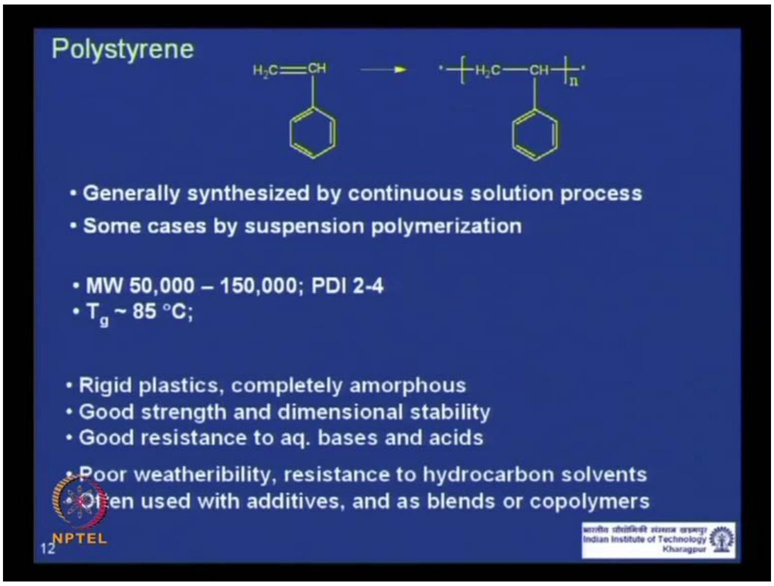

Polystyrene

- Generally synthesized by continuous solution process
- Some cases by suspension polymerization

- MW 50,000 – 150,000; PDI 2-4
- T_g ~ 85 °C;

- Rigid plastics, completely amorphous
- Good strength and dimensional stability
- Good resistance to aq. bases and acids
- Poor weatheribility, resistance to hydrocarbon solvents
- Often used with additives, and as blends or copolymers

Polystyrene, generally this is synthesized by continuous solution process. Some cases where you need polystyrene beads and if you are giving the suspension polymers, some cross linker (()) vinyl benzene type compound, then you can actually make cross linked bib, polystyrene bead by suspension polymerization. The linear polymerization, typically useful commercial applications have molecular weight, it is 50000 to 150000, PDI 2 to 4 and T g is around 85 degree centigrade and it is very rigid polymers because backbones is having aromatic structures. If it is the chain is not difficult to rotate, the single (()) becomes difficult. So, it is rigid plastics. So, it cannot come off.

So, it cannot crystallize. If you want to crystallize polymer, then you have to align them next to each other parallely. If you have rigid backbone, then it is very difficult because that is why its polystyrene is a completely amorphous polymer. It has good strength and dimensional stability. It has only elongation from 1 to 3 percent. It has very good resistance to aqueous basis and acids, but there is some problem, disadvantage in polystyrene structure too because it is an aromatic structure. It has poor weatheribility, it absorbs UV light and becomes yellow and it is soluble in hydrocarbon solvents. So, its resistance to hydrocarbon solvent is poor. So, often polystyrene is used with these stabilizers, UV stabilizer and also as a component or as a blend with other polymers or a co-polymer, with other monomers. For example, in the beginning, we talked about (()) butylenes styrene rubber lower or in the butylenes styrene rubber as such this is the example of co polymer, very common applications of polystyrene.

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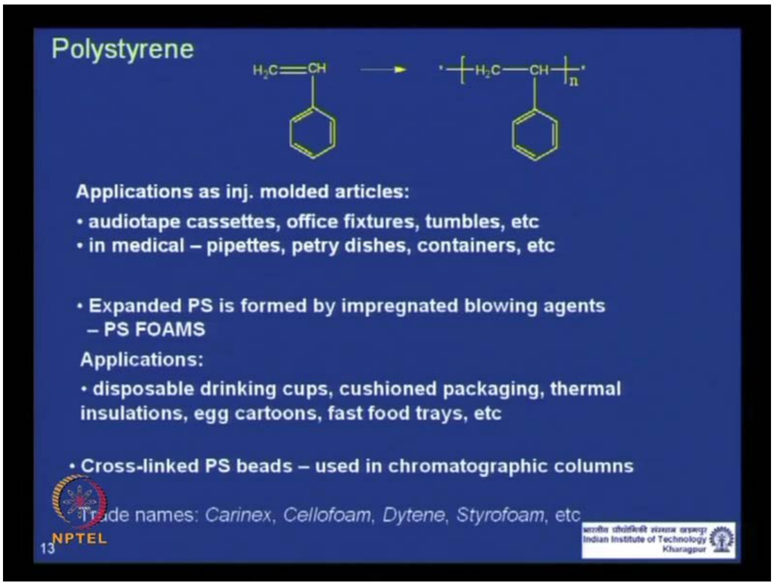

Polystyrene

Applications as inj. molded articles:
- audiotape cassettes, office fixtures, tumbles, etc
- in medical – pipettes, petry dishes, containers, etc

- Expanded PS is formed by impregnated blowing agents – PS FOAMS

Applications:
- disposable drinking cups, cushioned packaging, thermal insulations, egg cartoons, fast food trays, etc

- Cross-linked PS beads – used in chromatographic columns

Trade names: *Carinex, Cellofoam, Dytene, Styrofoam, etc*

This is audiotape cassettes, office fixtures, tumbles and in medical because this styrene has an aromatic backbone. This is stable on a (()). So, if you want is medical equipment that typically sterilize by high energy radiation by like gamma rays, so these polymer polystyrene is in use. Medical applications like pipettes, petry dishes and medical containers and so on. Lot of applications of polystyrene goes as FOAM. Foam of polymer polystyrene is found by impregnating and blowing agents, and we have seen yourself many applications of polystyrene founds like disposable drinking cups, the cushions, cushioned packaging and thermal insulator and sometimes, these cushions packaging like your labeled reagent bottles comes with some packing outside or some boxes made up of polyester in foams. They are also used for thermal insulations. If they were ever the unit to protect the brittle material inside like a cartoon, fast food, trays.

These are the cheep polymers. So, you can use this for very common applications and cross linked PS beads which can by for the suspension polymer, they can be used for chromatographic materials.

In a chromatographic poly, these polystyrene columns are made by these, this cross linked polystyrene beads. So, polystyrenes have also some high end applications. In that sense, from the trade names by which polystyrene is sold is mentioned here Styrofoam, cellofoam, dytene and so on.

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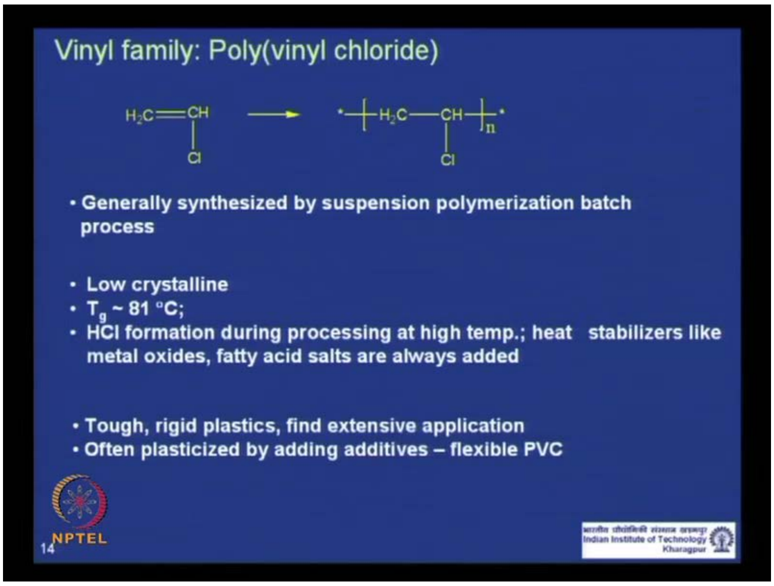

Vinyl family: Poly(vinyl chloride)

$$H_2C{=}\underset{\displaystyle Cl}{\underset{|}{CH}} \longrightarrow \cdot\!\!\left[H_2C-\underset{\displaystyle Cl}{\underset{|}{CH}} \right]_n\!\!\cdot$$

- Generally synthesized by suspension polymerization batch process

- Low crystalline
- T_g ~ 81 °C;
- HCl formation during processing at high temp.; heat stabilizers like metal oxides, fatty acid salts are always added

- Tough, rigid plastics, find extensive application
- Often plasticized by adding additives – flexible PVC

These are very few lists of the trade names we are talking about. Next, we talk about the vinyl families and most important polymer in the vinyl family is poly vinyl chloride as generally synthesized by suspension polymerization batch process. It has low crystallinelity; it has T g around 81 degrees centigrade to 80 degree centigrade. Now, when process this polymer at high temperature is actually evolved or produced hcl and that is very detrimental for several applications.

So, almost every applications of poly vinyl alcohol, one need to add degrees, stabilize metal oxide, fatty acids salt to basically minimize the hcl production. Otherwise there is no practical application of PVC of polyvinyl chloride also, though it has a rigid back bone. It has rigid plastics and also it finds several applications and there are lots of applications and in most of the applications are PVC plasticized. PVC plasticized means it by adding some additives which are called as plasticized T g is brought down.

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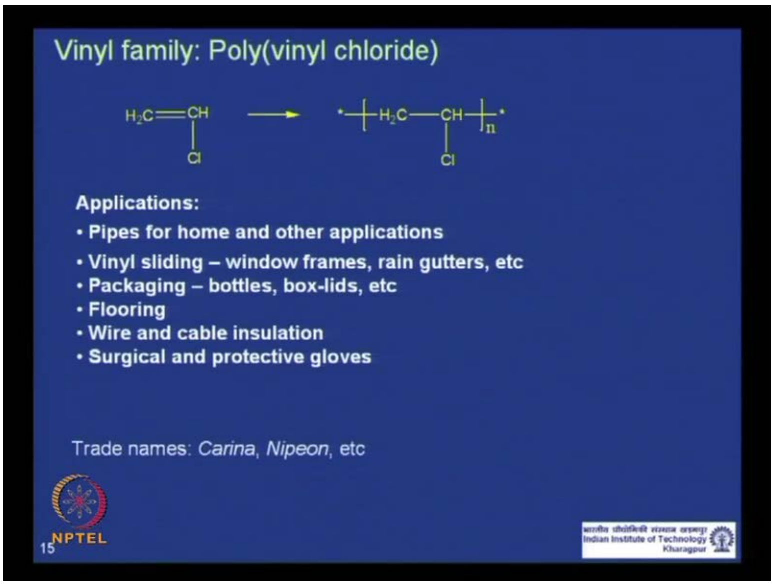

Vinyl family: Poly(vinyl chloride)

$$H_2C{=}CH(Cl) \longrightarrow \cdot\!\left[H_2C{-}CH(Cl)\right]_n\!\cdot$$

Applications:

- **Pipes for home and other applications**
- **Vinyl sliding – window frames, rain gutters, etc**
- **Packaging – bottles, box-lids, etc**
- **Flooring**
- **Wire and cable insulation**
- **Surgical and protective gloves**

Trade names: *Carina*, *Nipeon*, etc

So, at room temperature, at the main temperature with PVC becomes flexible and the applications of flexible PVC are lot. All the pipes, most of the pipes you see in the home or other applications are made of PVC, their applications vinyl sliding like window frames, rain gutters. They are also used in packaging material as like bottles, box-lids and they are also used in wire and cable insulations for electrical valve and they are also used in some of other uses of surgical and protective gloves. Some trade names are mentioned here.

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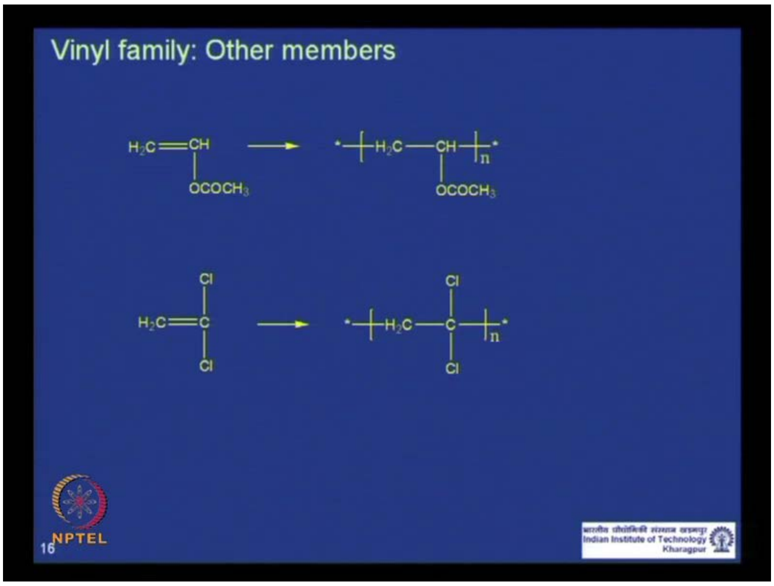

Vinyl family: Other members

$$H_2C{=}CH(OCOCH_3) \longrightarrow \cdot\!\left[H_2C{-}CH(OCOCH_3)\right]_n\!\cdot$$

$$H_2C{=}CCl_2 \longrightarrow \cdot\!\left[H_2C{-}CCl_2\right]_n\!\cdot$$

Other families of vinyl members will not be discussed. I will not discuss in detail, but these are also important vinyl polymers like vinyl acetate. Vinyl acetate utilized to vinyl alcohol to make poly vinyl alcohols. Polyvinyl alcohols are not produced from poly vinyl alcohol because vinyl alcohol does not exist in that. So, poly vinyl alcohols are produced from the hydrolysis of poly vinyl acetates. The other important polymers in this family is poly (()) chloride. The structure is mentioned in the bottom.

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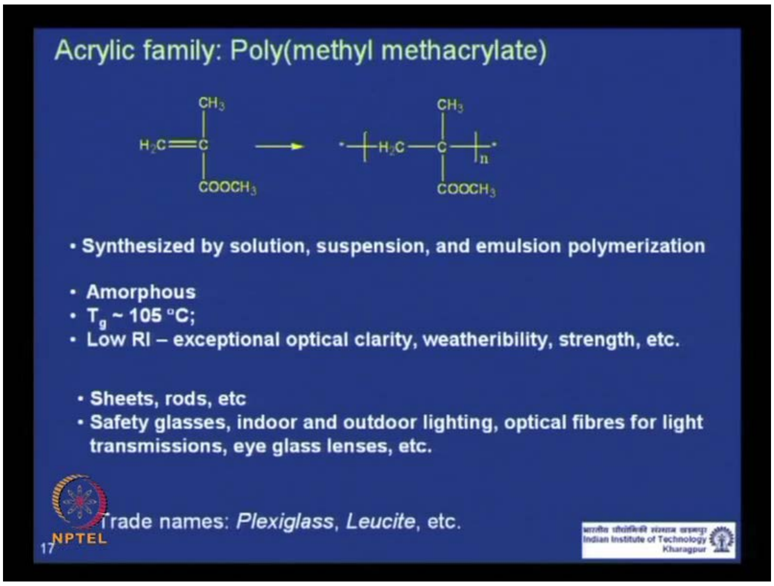

Acrylic family: Poly(methyl methacrylate)

- Synthesized by solution, suspension, and emulsion polymerization

- Amorphous
- T_g ~ 105 °C;
- Low RI – exceptional optical clarity, weatheribility, strength, etc.

- Sheets, rods, etc
- Safety glasses, indoor and outdoor lighting, optical fibres for light transmissions, eye glass lenses, etc.

Trade names: *Plexiglass*, *Leucite*, etc.

So, move to the next set of polymers is acrylic families and the most important is poly methyl methaculate. That actually covers most of the volume of acrylic polymers and the poly methyl PM is actually synthesized by solution suspension or by emulsion polymerization. It is (()) of as you can see the structure that it is having the bulky side group. So, it is very difficult to align the chains. These are difficult to align. So, they are perfectly, they are completely amorphous nor crystality. They are Tg weather 105 degree centigrade. They are very low refracting index which makes them exceptional having optical clarity because no aromatic group containing, so they have good weatheribility. They have good strength and some of the applications are in rods, safety glasses, indoor and outer lightings and optical fibres. They are effectively slow. So, they are used in optical fibres for light transmission, eye goggles and cd. The cheap cd’s are manufactured by compact divisional. Though they are very (()), they are brittle. Some of the trade names are shown here.

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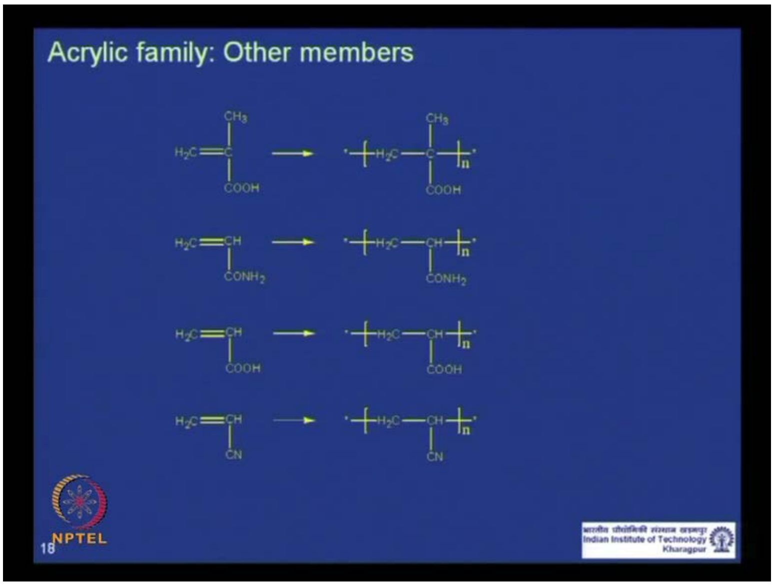

Acrylic family: Other members

The other acrylitic families are poly methyl acrylitic acids, polyacrolomite poly acrylic acid and poly acronitral. They also have produced commercially and find several applications and some other monomers which are also used or polymerized by radical chain. Polymerization is slight like vinyl carbozole and in vinyl phirilidin phirilidone.

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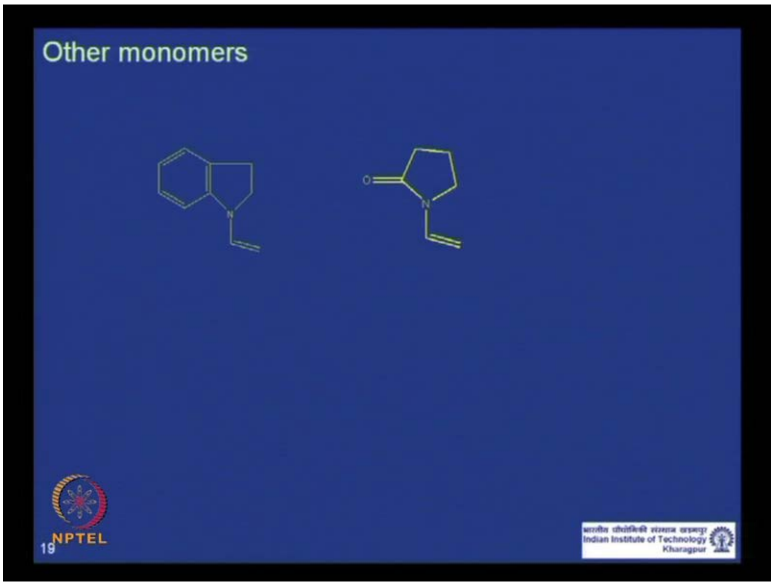

Other monomers

So, they are also used by the monomers which are also polymerized by radical polymerization. So, with this, what we come to the end of this module on radical polymerization. Now, what we will do in next 5-10 minutes is just to give the summary or recollect your memory, basically the most important points of the radical chain polymerization which we discussed in that 5-6-7 class lectures.

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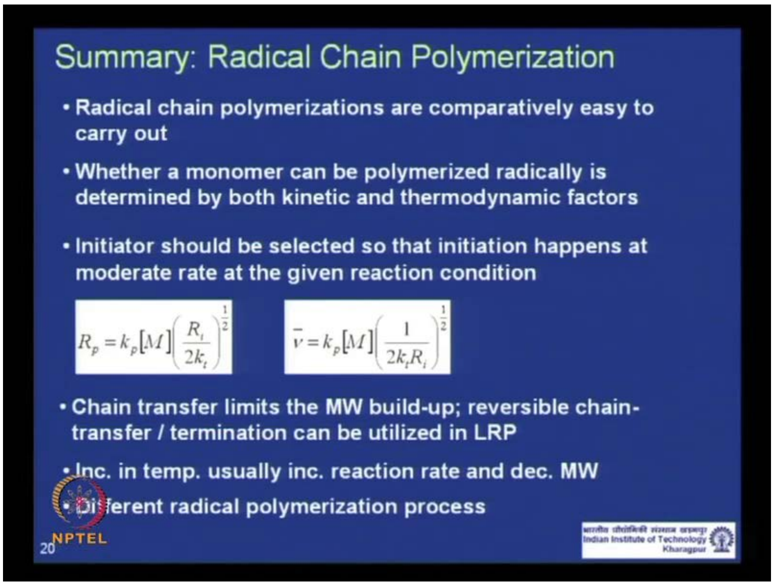

Summary: Radical Chain Polymerization

- Radical chain polymerizations are comparatively easy to carry out
- Whether a monomer can be polymerized radically is determined by both kinetic and thermodynamic factors
- Initiator should be selected so that initiation happens at moderate rate at the given reaction condition

$$R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}} \qquad \bar{\nu} = k_p[M]\left(\frac{1}{2k_t R_i}\right)^{\frac{1}{2}}$$

- Chain transfer limits the MW build-up; reversible chain-transfer / termination can be utilized in LRP
- Inc. in temp. usually inc. reaction rate and dec. MW
- Different radical polymerization process

So, radical chain polymerization as we can see from our discussion that radical chain polymerizations are comparatively easiest to carry out in respect or in comparison to the step-growth polymerization; provided you take care of the solvent, if you are using a solvent and any impurity which can terminate the radicals or any impurities which can act as a chain transfer agent. So, if you can minimize these impurities, the chain transfer agent or any vital which actually kills the radicals, then you can have this radical polymerization process done easily.

Now, as you have seen we discussed the radical polymerization is done mostly for the double bond containing monomers, but not all the monomers which contain the double bond can be polymerized radically, and that depends on both the thermo dynamic and kinetic factor. Thermeric factor we discussed two lectures back that if polymerizability of a monomer in radical chain, polymerization is mainly governed by the enthalpy value, deluge value, not deluge value, and the deluge value, it depends on whether the monomer is stabilized, whether it is electronically or (()) hypercongication or resonance. If it is stabilized, then the deluge value comes down. If the polymer produced from this molecule is strained, highly strained, then also deluge value comes down.

So, we showed the examples of alpha methyl styrene or 1 1 1 2 or 1 1 2 di substrate monomers like a mallian hydrie, where these radical polymerization becomes difficult and that is all any factor, kinetic factor also plays if the resulting radicals cannot approach each other, radicals produced or propagating radicals cannot approach a monomer. For example, in case of 1 2 di substitute reaction, then the polymerization becomes difficult. The (()) hydrie initiator you should choose such a way that the reactions happened in the model rate, so that the temperature which you are planning to reaction or rather you choose your polymerization reaction temperature such a way that the half life of your initiator is somewhat between, say your reaction time frame. It should be too low.

So, the reaction is too fast or it should not be too slow. That reaction is very slow and we have talked about these equations several times and the rate of polymerization and the kinetic chain length which is related to the molecular weight or number of (()) decreases the polymerization. In both cases, if you increase the volume molecular concentration of the monomer, the molecules weight as well as the rate of the polymerization increases, but when we try to do that, while that by carrying out the reaction is the bulk condition where you get a maximum concentration of the monomer.

The other complication arises like increasing a viscosity or lot of heat generation. So, it is not always possible to increase the monomer concentration. If you want to increase the reaction rate by increasing temperature, we have found out that it does increase the reaction rate in most cases, but in the simultaneous, it also decreases the molecular weight. If you have the chain transfer reagents are present, chain transfer reaction actually limit the molecular built and more the amount of chain transformation, lower is the molecular weight and we have seen that. You can actually take advantage if you can do this chain transfer or chain termination by reversible way, where you can utilize this reversible chain transfer termination reaction and carryout leaving reaction and carryout a leaving radical polymerization, where your poly dispersity index is much lower compared to the normal polymer radical.

Polymerization has also the polymers remain leaving at the end of the polymers. So, we can utilize this by making block co-polymers by design of the second monomer at the end of the reaction and also, we talked about the different polymerization process like bulk suspension, emulsion, dispersion solution, different types of processes and the advantages and disadvantages of all these processes and at the beginning of your requirement, you should choose the polymerization process which suit you the most and at the end, we discussed few examples of the commercial polymers which is synthesized using this radical chain polymerization technique.

So, with this, we conclude our module on radical chain polymerization and what we will do, what we will start in the next lecture is ionic polymerization. Why? Basically, in state of radical, this chain polymerization will be initiated by ionic species whether it is an ion cationic or an anionic species. So, with this, we will end this lecture today and will begin our discussion on ionic chain polymerization in the next class, next lecture.