Introduction to Polymer Science
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Lecture - 18
Reversible - Deactivation Radical Polymerizations (RDRP)

Welcome back in this lecture 18, I will discuss Reversible-Deactivation Radical Polymerizations or in short RDRP.

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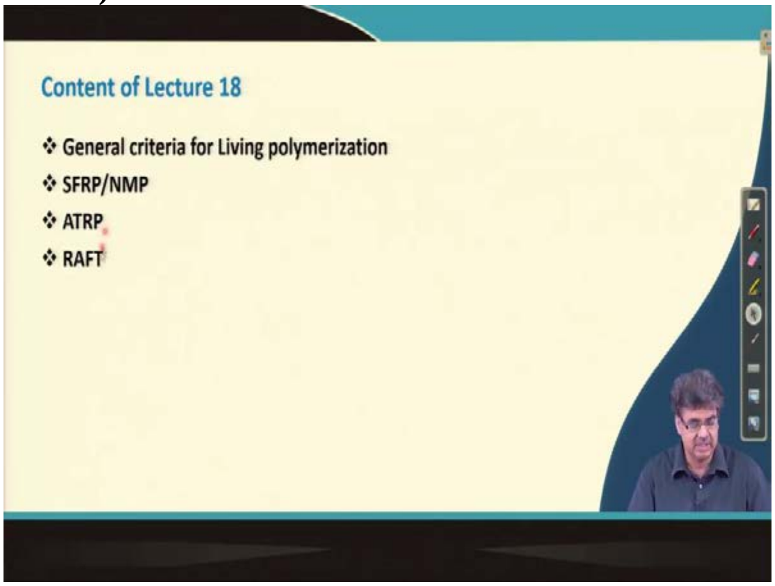

Content of Lecture 18

- General criteria for Living polymerization
- SFRP/NMP
- ATRP
- RAFT

Let us start with RDRP polymerization, Reversible-Deactivation Radical Polymerization. Earlier this polymerization used to be known as living radical polymerization or control radical polymerization. All three names i.e. living radical polymerization or control radical polymerization or RDRP are basically the same type of polymerization.

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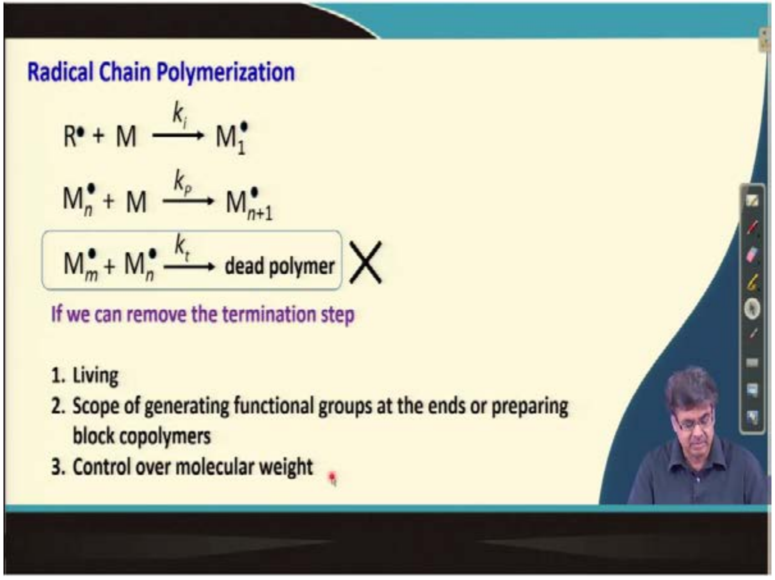

Radical Chain Polymerization

$$R^\bullet + M \xrightarrow{k_i} M_1^\bullet$$

$$M_n^\bullet + M \xrightarrow{k_p} M_{n+1}^\bullet$$

$$\boxed{M_m^\bullet + M_n^\bullet \xrightarrow{k_t} \text{dead polymer}} \times$$

If we can remove the termination step

1. Living
2. Scope of generating functional groups at the ends or preparing block copolymers
3. Control over molecular weight

Now, let us go back and discuss what was the kinetics of radical chain polymerization. We have learned that the chain polymerization consists of 3 steps, first one is initiation, second one is propagation and third one is termination. Now, in case, somehow we can remove this termination step which produced dead polymers, then what happens ? Then the propagating radical will continue to propagate without undergoing any termination reaction and let us also assume that there is no chain transfer reaction in the system.

In absence of any termination and chain transfer reaction, these propagating radicals will continue to polymerize as long as monomers are present in the system. Unlike in conventional radical polymerization where lifetime of a radical is about 0.1 second to 10 seconds, in this case the lifetime of the radical may be increased to hours or even higher, as long as there is no termination reaction.

As a result, what will happen is, the chains will remain living and, at end of the polymerization when all the monomers are consumed, we can actually do some reaction on the active radical and generate functional groups and also we add a second batch of monomer and restart the polymerization reaction forming a block copolymer. Now, if we know how many number of radicals were initially produced which initiated the polymerization chain, then by knowing how many polymer chains are actually produced at the end of polymerization we will be able to estimate the molecular weight values for the resulting polymers. If necessary, we can control the molecular weight.

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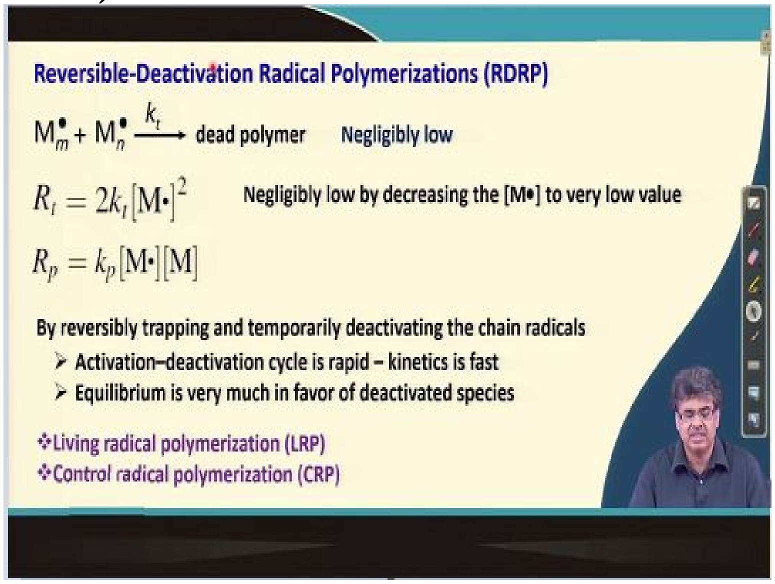

Reversible-Deactivation Radical Polymerizations (RDRP)

$M_m^\bullet + M_n^\bullet \xrightarrow{k_t}$ dead polymer   Negligibly low

$R_t = 2k_t[\mathrm{M}\cdot]^2$ Negligibly low by decreasing the [M•] to very low value

$R_p = k_p[\mathrm{M}\cdot][\mathrm{M}]$

By reversibly trapping and temporarily deactivating the chain radicals

- ➢ Activation–deactivation cycle is rapid – kinetics is fast
- ➢ Equilibrium is very much in favor of deactivated species

❖Living radical polymerization (LRP)
❖Control radical polymerization (CRP)

But, in practice, it is very difficult to remove or completely eliminate this bimolecular interaction between 2 radicals because they are very reactive with each other. So, in practice, we can actually bring these termination reactions to a negligibly low value. How can you do that? We know the termination reaction is proportional to square of the concentration of this radical. So, if you somehow decrease the concentration of this radicals in the system, then the termination reaction will come down drastically.

$$M_m^{\cdot} + M_n^{\cdot} \overset{k_t}{\rightarrow} dead\ polymer$$

$$R_t = 2k_t[M^{\cdot}]^2$$

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

So, we can bring down the termination reaction by decreasing the concentration of $\mathrm{M}^{\cdot}$ to a very low value. However, we also know that the rate of polymerization is given by this expression, which is directly proportional to the concentration of propagating radicals and if we reduce this concentration, then obviously, the polymerization reaction or polymerization rate also will come down.

So, you can ask that if we use a small amount of initiator molecules, so that when they dissociate completely, they generate small amount of this initiating radical, then we can get a low amount or low concentration of $M^{\cdot}$ in that case, but in that case, of course, the termination reaction will come down because your number of radicals in the systems is low.

What happens at the end of polymerization? Once the monomers are over, the propagating radicals will definitely interact with each other and form the dead polymer chains. So, there is no scope of further using that radical for making block copolymer. They will form dead chains and not living chains. Secondly, because the radicals are generated with time, there will be chains which are produced of different length since the starting point of each chain will be different as the initiator or radicals generates, and as a result the distribution of molecular weight will be also very high. So, to avoid that problem, especially if we want to have an acceptable polymerization rate, we cannot use a very small amount of initiator and suppress the radical concentration. We have to use a definite acceptable amount of initiator, so that this rate also increases.

So, what is the way out? The way out is by reversibly trapping and temporarily deactivating these chain radicals. Using reversible trapping and temporarily deactivating the chain radicals we can actually decrease the concentration of these propagating radicals and this reversible activation deactivation cycle must be very rapid. So, the kinetics must be very fast and at any point of time the equilibrium should be towards the deactivated species so that effectively a radical spends more time as a deactivated species rather than active species. As I mentioned earlier, this used to be known as living radical polymerization, but as I explained it now, it is actually not truly living because there will be some bimolecular termination reaction. So, we cannot say that it is a completely living radical polymerization, we can say quasi or pseudo living polymerization. Then, researchers used to call this as controlled radical polymerization, because you can control the polymerization but to avoid all these terminologies, in 2009, IUPAC came with this nomenclature, which actually captured the mechanistic aspects of these polymerization which talked about reversible deactivation of the propagating radical.

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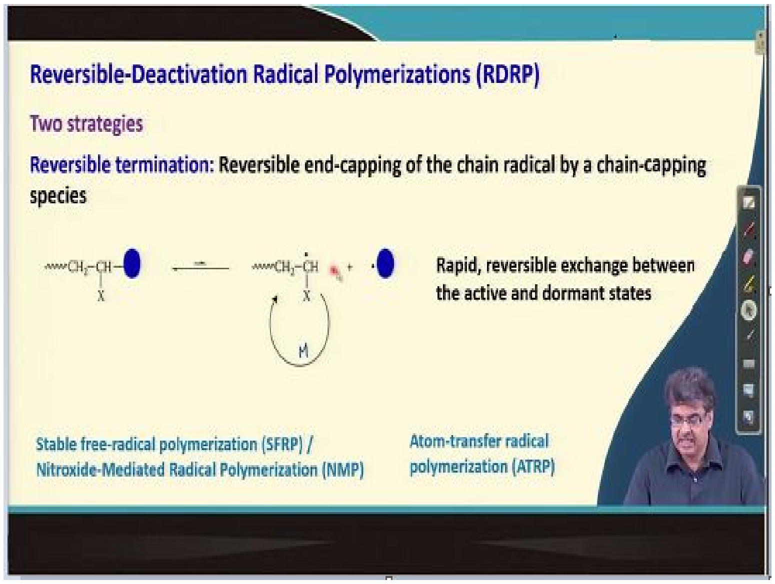

Reversible-Deactivation Radical Polymerizations (RDRP)

Two strategies

Reversible termination: Reversible end-capping of the chain radical by a chain-capping species

Rapid, reversible exchange between the active and dormant states

Stable free-radical polymerization (SFRP) / Nitroxide-Mediated Radical Polymerization (NMP)

Atom-transfer radical polymerization (ATRP)

There are 2 strategies by which we can actually do this reversible deactivation, one is by reversible termination. This process is reversible end-capping of the chain radicals by a chain capping species. For example, this is a propagating chain and this chain is capped with a chain capping species, which is shown here with the blue circle. Now, it can dissociate and produce radicals. Now, here, the radical cannot react with the monomer and start a polymerization chain, it can only react with the propagating radical and make a dormant species that means, this does not do any polymerization reaction, and this is chosen in such a way there is this equilibrium is more towards this dormant species. Now, once these radicals generate, the time it is spending as a radical species it can capture another monomer or more few monomers and propagate the chain and again it can react with this radical to make the dominant species. So in this case, these radical captures monomers from the medium and propagate the chain, but other propagating radicals spend most of the time in dormant state. It shows that the effective concentration of this propagating radical comes down in the medium, and as you can see at the end of the polymerization.

We can have this molecule capped with this and we can use these further for making a block copolymer or we can do some reaction at the chain end to make functional polymers as well. Also if we start most of the chains at the same time, then all the resulting polymers will be of nearly same molecular weight and the molecular weight distribution would be also narrow. So, this is rapid reversible exchange between the active and dormant states.

Then I will give you example of stable free radical polymerization is SFRP or it is also called Nitroxide-mediated radical polymerization (NMP) and Atom Transfer Radical Polymerization (ATRP). These are the polymerization techniques which follow this reversible termination strategy.

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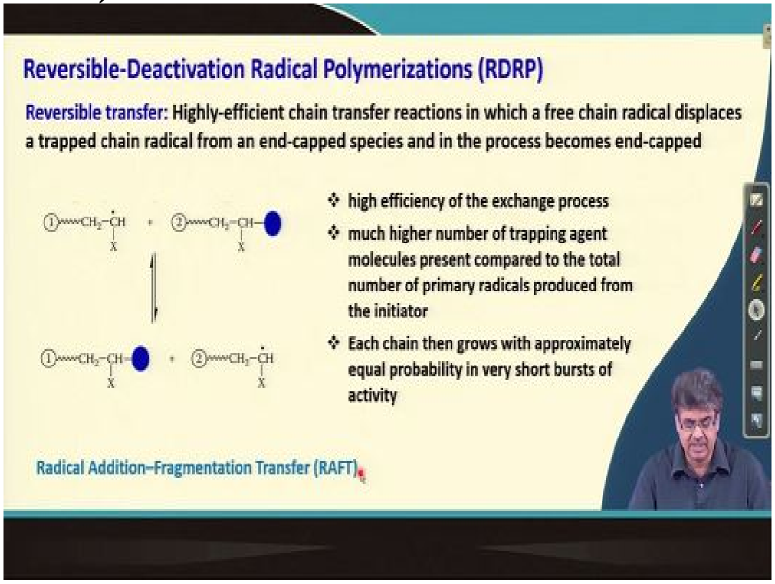

Reversible-Deactivation Radical Polymerizations (RDRP)

Reversible transfer: Highly-efficient chain transfer reactions in which a free chain radical displaces a trapped chain radical from an end-capped species and in the process becomes end-capped

- ❖ high efficiency of the exchange process
- ❖ much higher number of trapping agent molecules present compared to the total number of primary radicals produced from the initiator
- ❖ Each chain then grows with approximately equal probability in very short bursts of activity

Radical Addition–Fragmentation Transfer (RAFT)

There could be another strategy where reversible transfer strategy is applied. In this case, we have a propagating polymer chain and it reacts with another dormant chain, which has a propagating polymer chain capped with a trapping species and knock out the capping species to generate a new radical. The produced new radical do the reverse reaction as shown in the slide and there is an equilibrium between these two. This will be discussed when we talk about RAFT polymerization in more detail. Therefore, in this case, the numbers of chains that are propagating are actually determined by the number of the end capping species present in the medium in most cases, and the exchange reaction is highly efficient reaction. If we use the trapping agents in much higher number than the original or the primary initiators then each chain can actually grow approximately with equal probability so that we can get a narrow polydispersity. We will give you an example of Radical Addition-Fragmentation Transfer polymerization or RAFT polymerization.

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Reversible-Deactivation Radical Polymerizations (RDRP): General Features

- ❖ Irreversible chain transfer and chain termination reactions are minimized
- ❖ The rate of chain initiation is also much larger than the rate of chain propagation
- ❖ Chains grow at a more constant rate than seen in traditional chain polymerization
- ❖ Both yield and molecular weight of the polymers produced increase with reaction time (conversion)
- ❖ Polymer chain lengths are nearly equal (very low dipersity)
- ❖ Predetermined molar mass
- ❖ Polymer can be synthesized in stages, each stage containing a different monomer that is added to the reaction system, yielding a block copolymer
- ❖ Control over end groups

Now, there are some general features for this RDRP process; there is no irreversible chain transfer and chain termination, the rate of chain initiation is much higher compared to rate of chain propagation and chain grows at a more constant rate than seen in the radical chain polymerization and both yield and molecular weight of the polymers produced increases with reaction time or conversion.

This is unlike conventional radical chain polymerization where it is seen that with conversion or time the molecular weight of the resulting polymers initially goes up, then remain nearly same and then and slowly it comes down. In case of conventional radical polymerization from beginning itself, because the lifetime of these propagating radicals is 0.1 second to 10 seconds, so these radicals stay live for this small duration and they propagate and then they react with each other and form the polymer chains. We can get high molecular weight polymer chains from the beginning itself and with time as the concentration of monomer and concentration of initiator comes down, this molecular weight actually comes down. In case of RDRP process, this molecular weight and the yield actually continues to increase linearly with conversion. Polymer chains, which are produced by this process are nearly equal. So, we have very low dispersity and we can actually predict the molar mass before the reaction and we can actually target a particular molar mass or molecular weight of polymer. As we explained that we can synthesize polymers in different stages so that we can make block copolymers and we can have control over end groups. So, once the reaction is over, we can do some chemical reaction to modify the end group.

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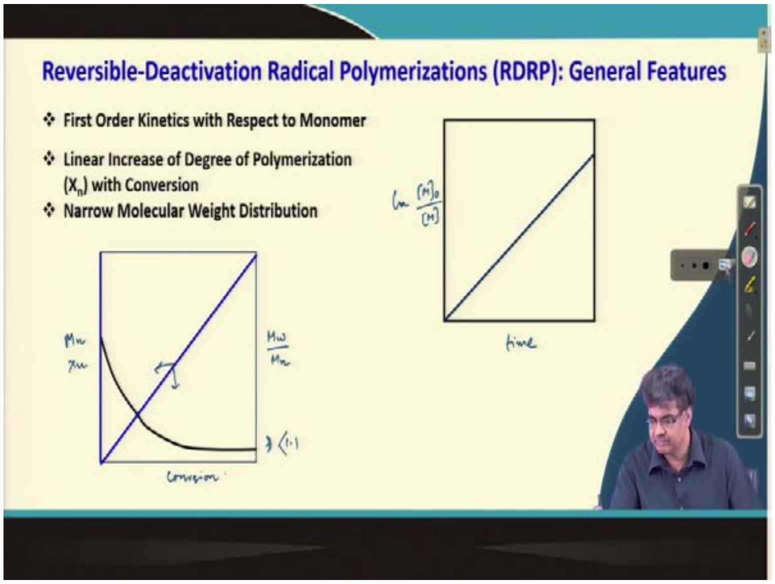

Reversible-Deactivation Radical Polymerizations (RDRP): General Features

- First Order Kinetics with Respect to Monomer
- Linear Increase of Degree of Polymerization (X_n) with Conversion
- Narrow Molecular Weight Distribution

Some more general features is first order kinetics is followed with respect to monomer. So, if we plot $\ln[M]_0/M$, where $[M]_0$ is the initial monomer concentration, this is monomer concentration at time t, with time we get a linear increase. So, this is a conversion because this linearly increases with time as we explained that the degree or polymerization or the molecular weight actually increases linearly with conversion and the molecular distribution is also very narrow.

If we plot molecular weight, M_n, or X_n or degree of polymerization with conversion then we get a linear curve. So, molecular weight increases with conversion. These are the parameters which we can monitor to prove that whatever you are doing, the polymerization is actually following this mechanism and this is what is polydispersity.

So, polydispersity index or dispersity actually comes down as we increase conversion or as we increase the molecular weight, but finally, we can get very narrow polydispersity even less than 1.1 because the polymers which we are generating are very close in their size.

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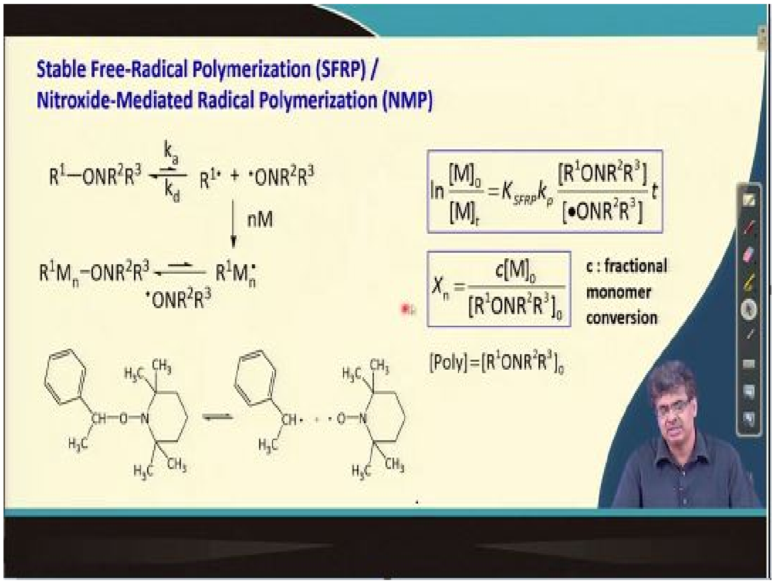

Stable Free-Radical Polymerization (SFRP) /
Nitroxide-Mediated Radical Polymerization (NMP)

$$R^1\text{—}ONR^2R^3 \underset{k_d}{\overset{k_a}{\rightleftharpoons}} R^{1\bullet} + {}^{\bullet}ONR^2R^3 \xrightarrow{nM} R^1M_n^{\bullet} \rightleftharpoons R^1M_n\text{—}ONR^2R^3$$

$$\boxed{\ln\frac{[M]_0}{[M]_t} = K_{SFRP}k_p\frac{[R^1ONR^2R^3]}{[\bullet ONR^2R^3]}t}$$

$$\boxed{X_n = \frac{c[M]_0}{[R^1ONR^2R^3]_0}}$$

c : fractional monomer conversion

$[Poly]=[R^1ONR^2R^3]_0$

We will talk about the first example where we talk about stable free radical polymerization SFRP or nitroxide mediated radical polymerization. Basically this can dissociate under certain conditions producing a radical and nitroxide. Now, this is a very stable radical, this does not react with itself or with monomers. It actually reacts only with the original radicals from which it is produced to form the original initiating species.

$$ln\frac{[M]_0}{[M]_t} = k_{SFRP}k_p\frac{[R^1ONR^2R^3]}{[^{\cdot}ONR^2R^3]}t$$

$$X_n = \frac{c[M]_0}{[R^1ONR^2R^3]_0}$$

$$[poly] = [R^1ONR^2R^3]_0$$

This equilibrium, this is chosen in such a way that this is mostly on the left hand side. Non-radical species are present mainly in the medium, radical concentration is very low. Now, once this is formed, it can react with a few monomers and basically propagate the polymer chain and which again can react with this stable radical. This is the stable radical and generate the dormant species which again can dissociate like this step and this cycle can go on.

So, basically the cycle can go on and we can generate longer and longer polymer chains and with time, the molecular weight increase. This is TEMPO radical which is a very stable radical. Originally, it was used for synthesis of polystyrene at 125 ^{o}C, bulk method. Originally it was added externally and some other radical initiator was used but later on, this was found to be more effective way to do polymerization, where the stable radical can be produced from the adduct with the monomer species. In terms of conversion, here also conversion is linearly related to time and, we can actually predict the molecular weight by dividing the monomer which is converted. So, if $[M]_0$ is my initial monomer concentration and *c* is the fractional monomer conversion so, out of 100 if 90% of monomer is consumed, then *c* will be 0.9 and if all the monomers are consumed, *c* will be 1. So, if we actually do the reaction to the completion level, *c* will be 1. So, we can just directly divide the initial monomer concentration with ratio of these species to find out what is the expected degree of polymerization, as this gives the initial concentration of these molecules, i.e. the number of polymer chains which are produced at the end of this polymerization. So, if you divide the number of monomers with the number of polymer chains produced can get the degree of polymerization.

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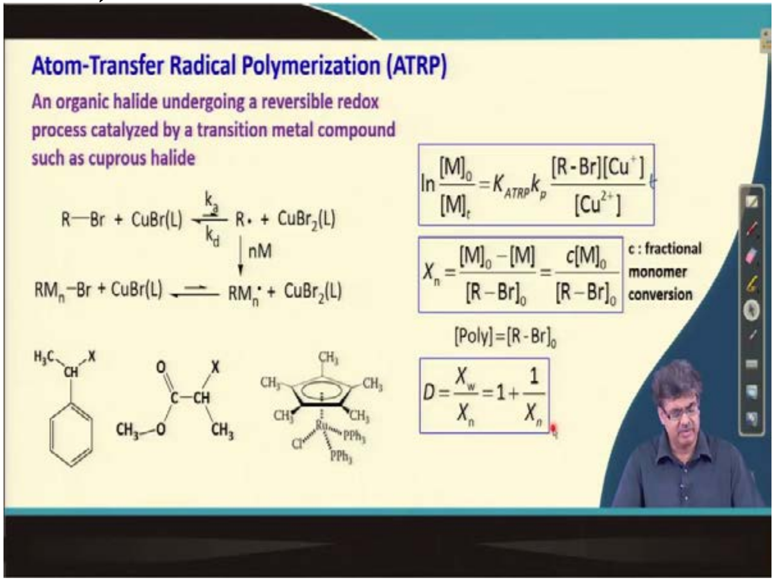

Atom-Transfer Radical Polymerization (ATRP)

An organic halide undergoing a reversible redox process catalyzed by a transition metal compound such as cuprous halide

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

$$\downarrow nM$$

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

$$\ln\frac{[M]_0}{[M]_t} = K_{ATRP}k_p\frac{[R\text{-}Br][Cu^{+}]}{[Cu^{2+}]}t$$

$$X_n = \frac{[M]_0-[M]}{[R-Br]_0} = \frac{c[M]_0}{[R-Br]_0}$$

c : fractional monomer conversion

$$[Poly] = [R\text{-}Br]_0$$

$$D = \frac{X_w}{X_n} = 1 + \frac{1}{X_n}$$

Let us talk about the second method, atom transfer radical polymerization. So, in this case an organic halide undergoes a reversible redox process catalyzed by a transition metal compound such as cuprous halide. In this case we have an organic halide and a transition metal compound which has a ligand associated with it. For example if we take a Cu compound, CuBr, which react with the organic halide to produce a radical, and CuBr is oxidized to form cupric bromide. Ligands are present with the Cu compounds all along these reactions

This is a very fast exchange process. This dynamic equilibrium is very fast and it is more towards the dormant species. So, the equilibrium is such that, at any point of time, the number of radicals or the tendency of being in radical form will be lower compared to this dormant form, which does not propagate a polymer chain. Now, once this radical is formed, it can react with monomers and continue propagation. They can react with the cupric bromide and are reduced to form alkyl halide. As this cyclic process is repeated, we can get higher chain length. Some of these alkyl halides, are shown here and some of the ligand which are used for this purpose are shown here and in this case also the conversion is related to the time linearly also we can estimate the degree of polymerization by dividing the fractional monomer conversion with the initial concentration of alkyl bromide, because this is what determines how many number of polymer chain will be produced at the end of the polymerization. This is how we can get the polydispersity which is given one by the following equations.

$$\ln \frac{[M]_0}{[M]_t} = k_{ATRP} k_p \frac{[R - Br][Cu^{+}]}{[Cu^{2+}]} t$$

$$X_n = \frac{[M]_0 - [M]}{[R - Br]_0} = \frac{c[M]_0}{[R - Br]_0}$$

$$[poly] = [R - Br]_0$$

$$Đ = \frac{X_w}{X_n} = 1 + \frac{1}{X_n}$$

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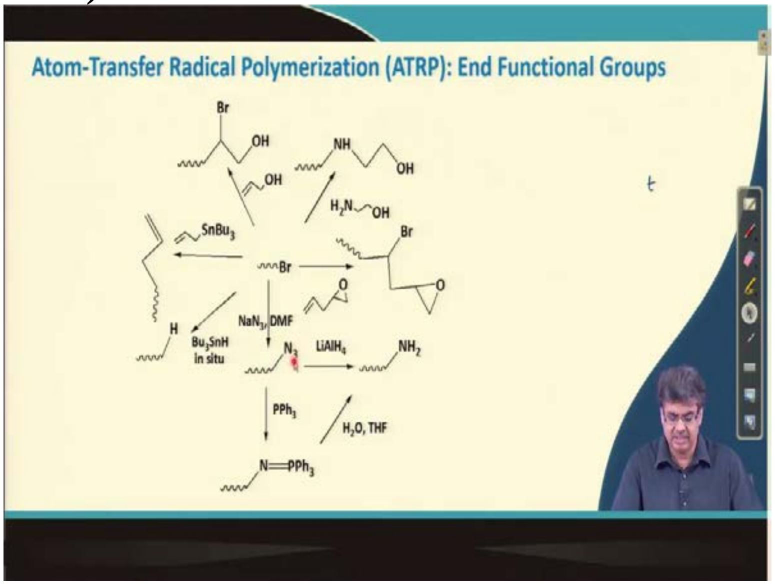

Atom-Transfer Radical Polymerization (ATRP): End Functional Groups

Now, at the end of the polymerization we will have this alkyl halide with this bromide or other halides at the end of the polymer chain and we can actually use these for synthesizing lots of functional polymers and some examples are given. One example is that by reacting with this molecule we can even generate macromonomer. So, basically we have a long polymer chain and we have a polymerizable group at the end of the polymer chain. So, now we can actually polymerize this polymer, or this group and so it is called macro-monomer. So, there are other ways like you can generate azide functionalized polymers which can be further reacted with many other reagents, to make other functional groups like amine and so on.

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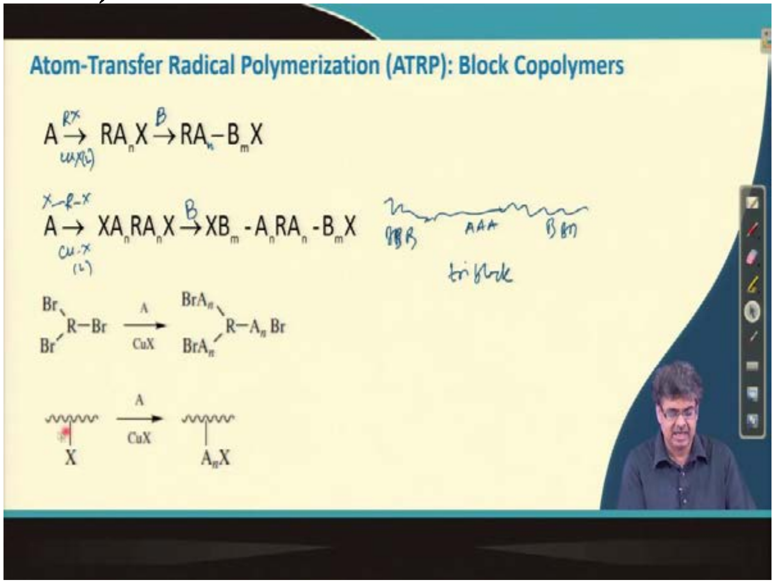

Atom-Transfer Radical Polymerization (ATRP): Block Copolymers

$A \xrightarrow[CuX(L)]{RX} RA_nX \xrightarrow{B} RA_n-B_mX$

$A \xrightarrow[Cu\text{-}X\,(L)]{X\text{-}R\text{-}X} XA_nRA_nX \xrightarrow{B} XB_m\text{-}A_nRA_n\text{-}B_mX$

We can actually generate block copolymers, like if we use R-X and a copper halide then we can generate first block and then we can again add the second monomer to make the block copolymer of A and then B. Similarly, we can use a molecule having bromide or halide in both the sides then we can actually make block copolymer from both the sides and then we can add B so, we make a middle block with A, we can actually make a tri block with polyA in the middle and polyB in bothe the sides. We can also take a tribromide, we can make a star polymer like shown in the slide, and we can actually use this to functionalize or make a graph copolymer more like this, which is shown here.

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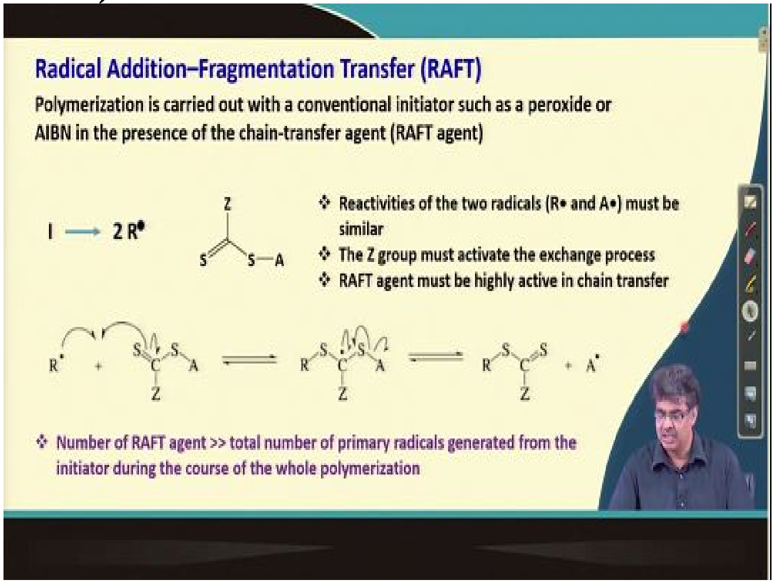

Radical Addition–Fragmentation Transfer (RAFT)

Polymerization is carried out with a conventional initiator such as a peroxide or AIBN in the presence of the chain-transfer agent (RAFT agent)

$I \longrightarrow 2R^{\bullet}$

- ❖ Reactivities of the two radicals (R• and A•) must be similar
- ❖ The Z group must activate the exchange process
- ❖ RAFT agent must be highly active in chain transfer

- ❖ Number of RAFT agent >> total number of primary radicals generated from the initiator during the course of the whole polymerization

So, we will come to the last example of this RDLP where we are talking about the radical addition fragmentation, transfer polymerization. Now, in this case, polymerization is carried out with conventional initiators such as peroxide or AIBN. So, basically the radicals are generated in more conventional way like thermal initiation of peroxide or AIBN is used in presence of a chain transfer agent, which is also called RAFT agent. We can have a conventional way of generating these radicals in presence of these RAFT agents.

Now, what is the characteristics of these RAFT agent? This initial initiating radical and when we homolytically cleave this bond, it will generate $A^{\cdot}$ or A radical. The reactivity of this original $R^{\cdot}$ and $A^{\cdot}$ must be similar, so, that the reaction rate is not hampered, and there will be a dynamic equilibrium between the propagating radical and dormant radical. We will come to that. The Z group must be activating these exchange processes and the RAFT agent must be highly reactive in chain transfer.

So, basically the RAFT agent must be very highly active in chain transfer process. When initially these radical generates, it can actually react with the RAFT agent. It can attack this and generate intermediate radicals. So, it is an addition step and then this S-A bond can homolytically split and generate this fragment. Thus, we are talking about addition and then fragmentation and all these steps are reversible.

That is why we are calling this as a reversible addition fragmentation. These are transforming the original radical to a new radical. Now, initially, this can also react with some monomers to generate or propagate a radical or the propagating chain and which can react with this chain transfer agent as well, but at the beginning, this concentration of these RAFT agents is used much higher than the original radical. Once this generates, it reacts more with monomer, but it also reacts mostly with this chain transfer agent and forms adduct with $A^{\cdot}$, which now can react again with the monomer to generate propagating chain. So, immediately after some time when some percentages of monomer are used up or consumed, most of these chain transfer regions will be consumed and we will have some propagating chain which will have the RAFT agent at the end.

After we start the polymerization, immediately after 1 or 2% of monomers conversion, all these chain transfer agents will react and will be consumed and we get some oligomeric chain with the end as RAFT agent. Now, once we have these RAFT agents, and as we said that total number of RAFT agent is much more than total number of primary radicals, so the number of chains which gets produced at the end of the polymerization is mainly determined by this number of RAFT agents which is used since this determines the number of polymers chains which are produced at the end of the polymerization.Like if I start with one R, it is giving another A, if it react with a new chain transfer reagent then it will produce another radical. So, number of radicals remain same during the reaction, which is given by the number of primary radicals but number of polymer chains is given by the number of RAFT agents which are produced. There will be few more because of the presence this propagating radical terminate among themselves.

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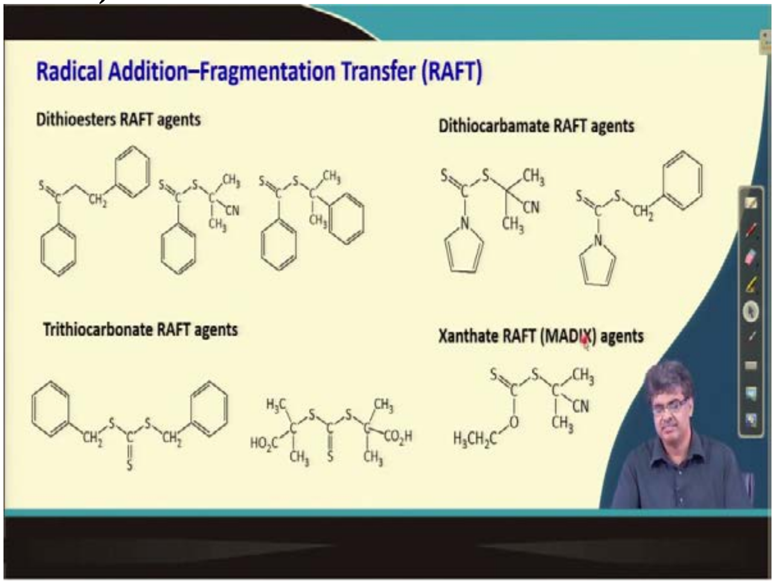

Radical Addition–Fragmentation Transfer (RAFT)

Dithioesters RAFT agents

Dithiocarbamate RAFT agents

Trithiocarbonate RAFT agents

Xanthate RAFT (MADIX) agents

So, these are the some of the RAFT agents which are typically used in laboratories e.g. dithioesters, We can have a trithioesters to prepare tri-block copolymer. We can also have dithiocarbonate, xanthate type RAFT agents also. When you use xanthate type we call these as a MADIX polymerization.

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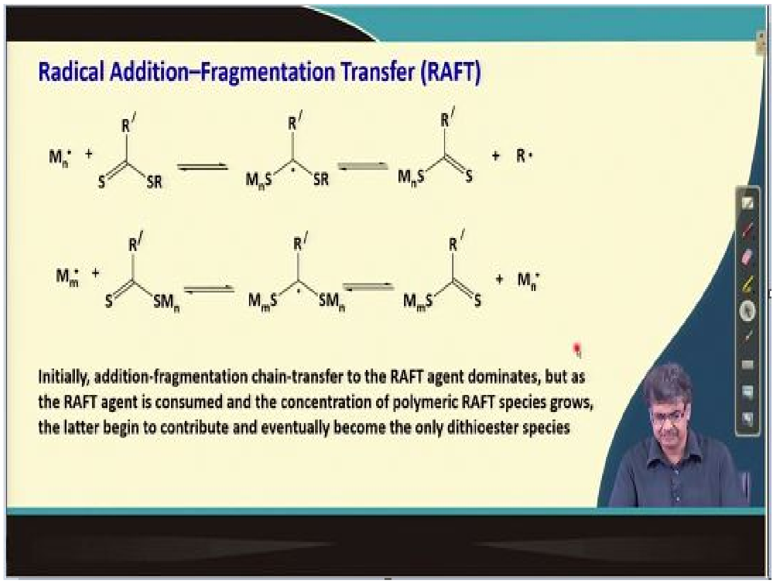

Radical Addition–Fragmentation Transfer (RAFT)

Initially, addition-fragmentation chain-transfer to the RAFT agent dominates, but as the RAFT agent is consumed and the concentration of polymeric RAFT species grows, the latter begin to contribute and eventually become the only dithioester species

In the next lecture, I will start from this page and talk little more about this radical RAFT addition fragmentation transfer reaction.