Polymer Chemistry

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Lecture - 11
Radical Chain Polymerization (Contd.)

Welcome back to this course on Polymer Chemistry and today we will continue our discussion on Radical Chain Polymerization.

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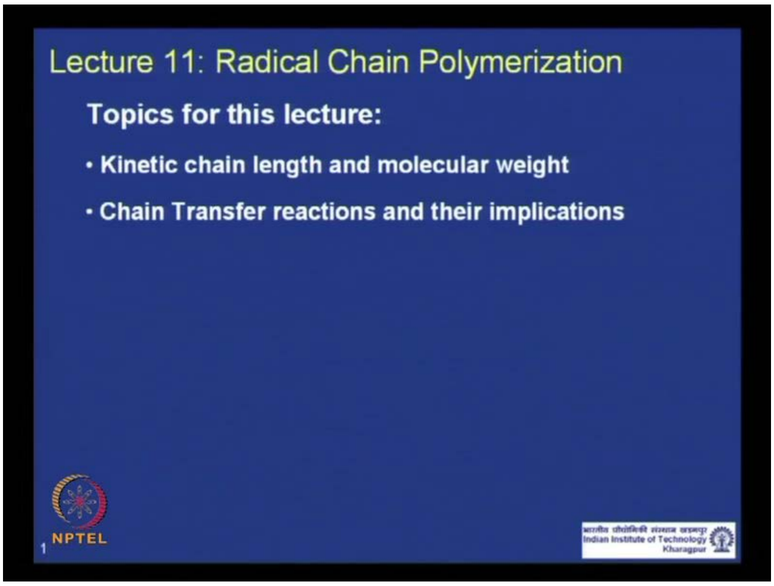

Lecture 11: Radical Chain Polymerization

Topics for this lecture:

- Kinetic chain length and molecular weight
- Chain Transfer reactions and their implications

In this lecture, I planned to cover kinetic chain length and the molecular weight of the polymer produced in radical chain polymerization. And then I will discuss several or several different possible chain transfer reactions and their implications in terms of molecular weight and rate of polymerization.

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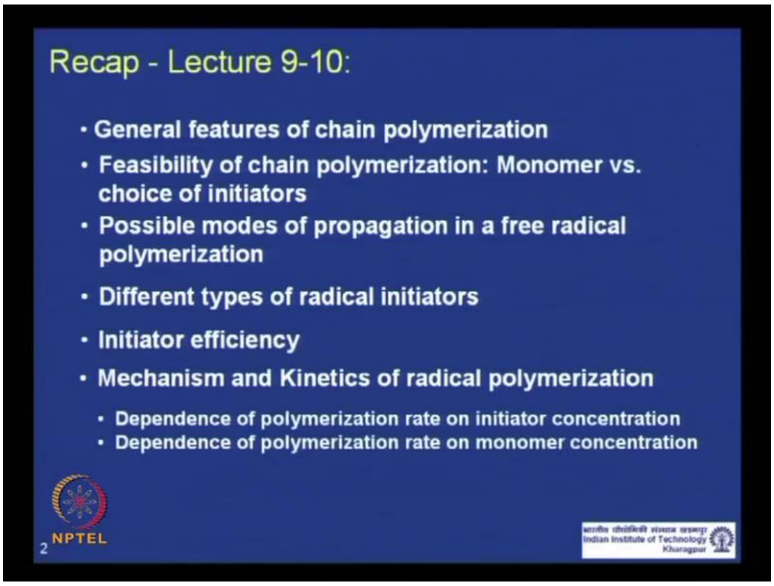

Recap - Lecture 9-10:

- General features of chain polymerization
- Feasibility of chain polymerization: Monomer vs. choice of initiators
- Possible modes of propagation in a free radical polymerization
- Different types of radical initiators
- Initiator efficiency
- Mechanism and Kinetics of radical polymerization
  - Dependence of polymerization rate on initiator concentration
  - Dependence of polymerization rate on monomer concentration

Before I begin, just let us recap the discussion we had on radical chain polymerization in last two lectures, lecture 9 and 10. We begin our discussion with a general feature of chain polymerization, how chain polymerization compares with step polymerization. And then we discussed how a monomer structures determines it is feasibility towards undergoing polymerization, polymerization reactions towards a initiator, different kind of initiator radical cationic or anionic.

And then we found out that during chain polymerization it is always head tail arrangement, head tail head tail type arrangements is always exclusively preferred. We discussed different types of radical initiators, thermal initiators, photochemical initiators, redox initiators. We also discussed different types of monomers or types of monomers, which can be polymerized in radical chain polymerization mechanism and which are the types of monomers, which cannot be polymerized or it will difficultly polymerized in radical chain polymerization.

And we talked about that, not all the radicals generated either by redox reaction or by thermal decomposition of any initiator species or by some other means, actually initiate a polymer chain part of which get lost due to some side reactions. So, the fraction of the initiators produced during the decomposition of the thermal initiator or some other process, which actually initiate the radicals, we call the terms initiator efficiency.

And, you also discussed different steps involved in a radical chain polymerization and kinetics of radical chain polymerization. And in that way, we found the dependency of polymerization rate on initiator concentration as well as dependency of polymer rate on monomer concentration.

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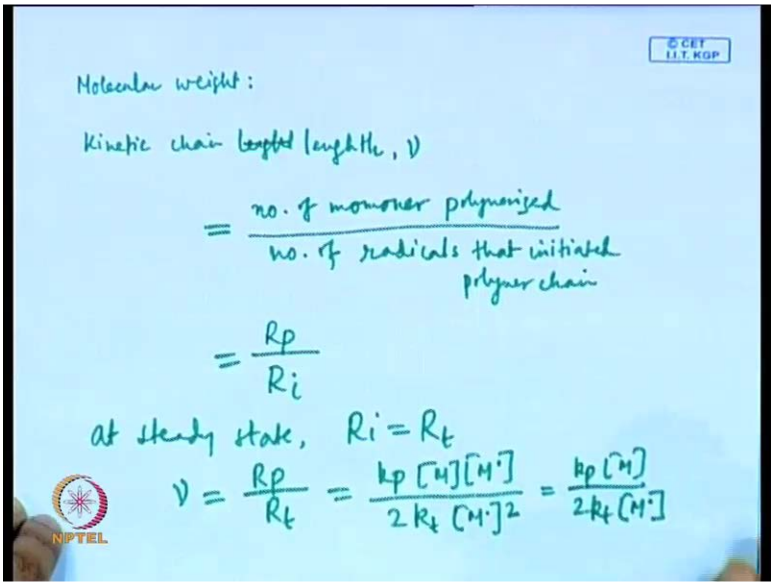

Molecular weight:

Kinetic chain ~~length~~ length, ν

$$= \frac{\text{no. of monomer polymerized}}{\text{no. of radicals that initiated polymer chain}}$$

$$= \frac{R_p}{R_i}$$

at steady state, $R_i = R_t$

$$\nu = \frac{R_p}{R_t} = \frac{k_p[M][M^\cdot]}{2k_t[M^\cdot]^2} = \frac{k_p[M]}{2k_t[M^\cdot]}$$

Now, let us begin or continue our discussion on molecular weight, molecular weight of the polymer produced in radical chain polymerization. Now, to start the discussion on molecular weight, we defined a term called kinetic chain length nu, which is which is the number of monomers polymerized per each radicals, that initiated the polymer chain. We can write number of monomer that polymerized, divided by the number of radicals that initiated polymer chain.

Considering the time, we can say that, the top one is the rate of polymerization, rate of disappearance of monomers and the denominator is rate of formation of the radicals, which is nothing but rate of initiation reaction. So, we can write rate of polymerization divided by rate of initiation, now at steady state we knew that we know by this time, that R i is equals to the rate of termination.

So, we can write nu as R p rate of polymerization by rate of termination, rate of polymerization given by k p M dot. M dot is the concentration of all the radical species present, all the summation of the concentration, all the propagating radical and this is k t M dot square, or I can write simply it is.

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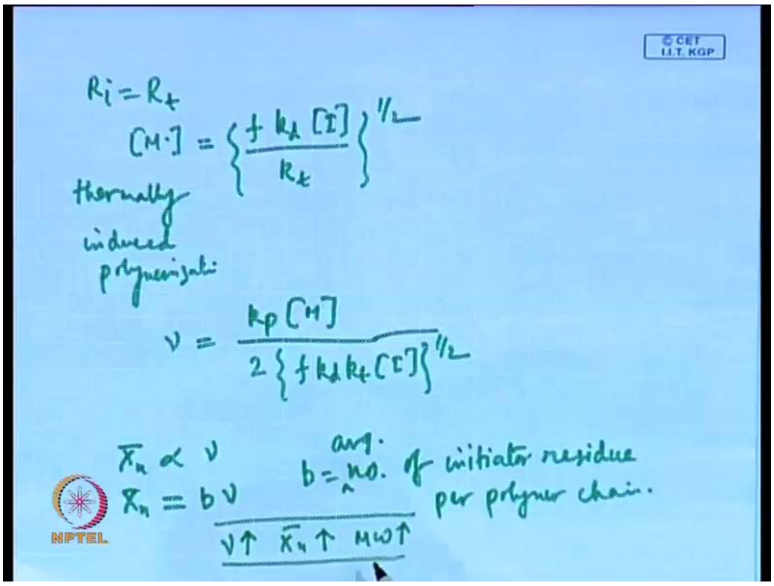

$R_i = R_t$

$[M\cdot] = \left\{\frac{f\,k_d\,[I]}{k_t}\right\}^{1/2}$

thermally induced polymerizati

$\nu = \frac{k_p[M]}{2\{f\,k_d\,k_t\,[I]\}^{1/2}}$

$\bar{X}_n \propto \nu$

$\bar{X}_n = b\nu$ $\quad b = \overset{\text{avg.}}{\text{no.}}$ of initiator residue per polymer chain.

$\nu\uparrow \quad \bar{X}_n\uparrow \quad MW\uparrow$

Now, we know from that steady state condition, where R i is R t. In the last lecture we found, that the value of M dot in case of a thermally induced polymerization, is given by f k d I by k t to the power half. So, we can now write nu k p M k d k t to the power half from the last expression. The what is the importance of kinetic chain, why we are discussing or defining a term kinetic chain length nu, we will now know that, degrees of polymerization is directly proportional to nu.

Exactly we will know that, degree average number average degrees of polymerization is equals to b nu, where b is the number of initiator residue average number of initiator residue per polymer chain. So, if we if kinetic chain length goes up, which means number average degrees of polymerization will go up, hence the molecular weight will also will go up. So, that is a importance of kinetic chain length, that if it is goes up or goes down, then accordingly the molecular weight goes up or goes down.

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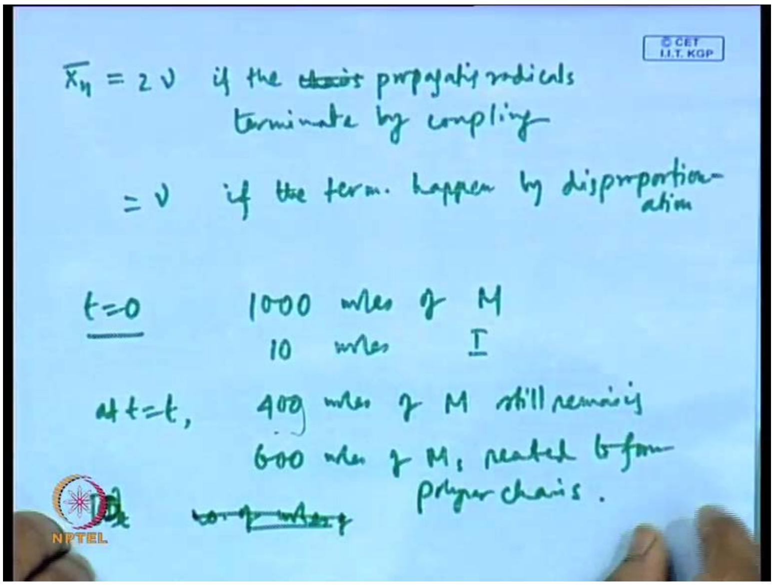

$\overline{X}_n = 2\nu$ if the ~~chains~~ propagating radicals terminate by coupling

$= \nu$ if the term. happen by disproportionation

t=0 1000 moles of M

10 moles I

at t=t, 400 moles of M still remaining

600 moles of M, reacted to form polymer chains.

Now, how the molecular weight or degrees of average number average degrees of polymerization related to nu, it is twice nu, if the chains or the propagating radical terminates by coupling and it goes to nu, if the termination happen by disproportionation. Now, I hope you can you can get this, if we just look at this, that if I have a if I have a propagating radical having a active species here, if I have a if I have a radical here at the end of a propagating chain, I have another radical at the end of the propagating chain.

This has a average number of molecules nu, this also have average number of monomer molecules nu. Now, if they gets terminated by coupling reaction, the polymer which is formed here, that will have number of degrees of polymerization or total number of monomer present in that chain, will be twice nu. Now, if this two propagating radical collide, interact and get terminated of a deformed dead polymer by this propagation reaction, then you get two polymer chain.

Two dead polymer chain, which will have again the same number of monomer molecules, which were present in the chain before the termination reactions. Let us take a example, you know simple example and see whether we can visualize this more. Now, let us we start a reaction at t is equal to 0, I have a say 1000 mole of 1000 moles of monomer M and say 10 moles of I, initiator molecules. Now at time t, we stop the reaction and we found that, there are 400 moles of monomer still remaining.

So, how many moles of monomers has reacted to form polymers, is basically 600 moles of monomers reacted to form polymer chains. Now, if I consider that I t, the consideration of or the number of moles of number of moles of let us do it in the next page.

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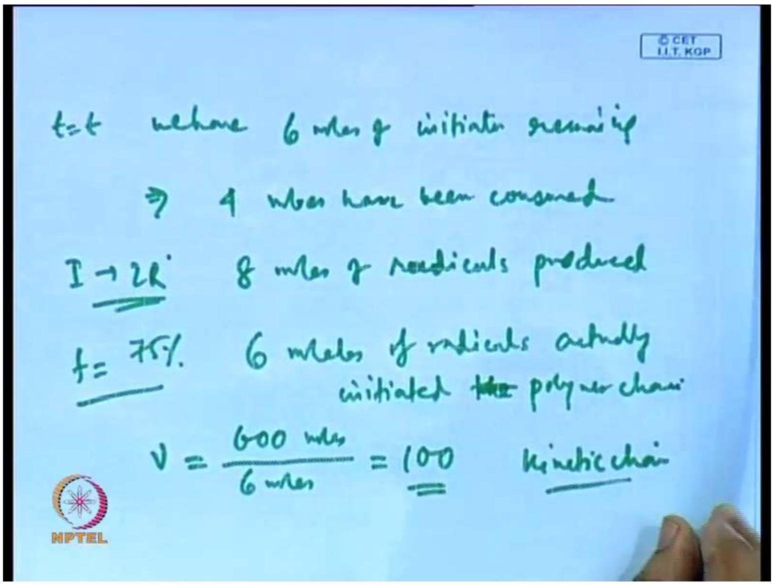

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t=t we have 6 moles of initiator remaining

$\Rightarrow$ 4 moles have been consumed

$I \rightarrow 2R^{\cdot}$ 8 moles of radicals produced

f = 75% 6 moles of radicals actually initiated ~~the~~ polymer chain

$\nu = \frac{600 \text{ moles}}{6 \text{ moles}} = 100$ kinetic chain

At time t, we have 6 moles initiator remaining, which means four moles have been consumed. Each initiator molecule produces, if we consider a thermally initiated polymerization, each I produce 2 R dot. So, there are 8 moles of radicals produced during this time frame, during the polymerization reaction. Now, if say 75 percent of this radical has initiated a polymer chain, so efficiency f is 75 percent that means, 6 moles of radical actually initiated polymer chain.

So, number of, what is nu? Total number of monomers polymerized, which is 600 moles that is a number of monomers polymerized. How many number of radicals has initiated polymer chains, that 6 moles so that is 100. So, 100 is the value of kinetic chain length that means, 100 monomers has, in a average every chain before termination on average every chain before it undergoes termination reaction, which we call kinetic chains has a number of monomer units of 100.

So, is clear, 100 means the number of monomers on average, which is present in a polymer chain before it undergoes termination reaction. We call that chain as a kinetic chain, kinetic chain have 100 monomers.

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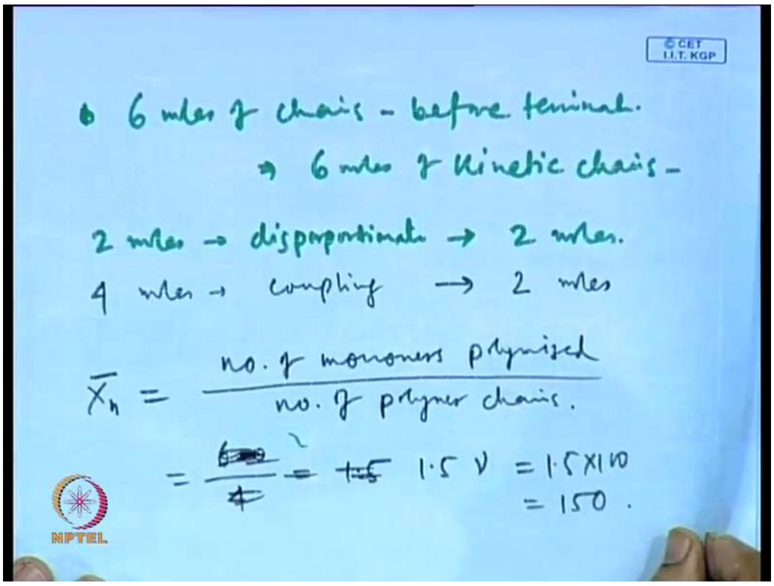

- 6 moles of chains - before terminat.

→ 6 moles of kinetic chains -

2 moles → disproportionate → 2 moles.

4 moles → coupling → 2 moles

$$\bar{X}_n = \frac{\text{no. of monomers polymerised}}{\text{no. of polymer chains.}}$$

$$= \frac{600}{4} = 1.5\,\nu = 1.5 \times 100$$

$$= 150.$$

Now, what will happen this 6 moles of, there are 6 moles of chains before termination before termination or otherwise 6 moles of kinetic chains. Now they will get terminated and form polymer molecules, dead polymer molecules. Let us assume that, two moles of this, become dead or on the weight termination reaction by disproportionation reaction. So, how many molecules, how many chains polymer chains, 2 moles because each kinetic chain 2 of 2 of the chain to 2 chains will come and react and form 2 dead chains.

So, 2 moles kinetic chain will produce 2 moles, now rest of the 4 moles, if I consider that they undergo coupling to get terminated, then they will also form 2 moles of polymers. Because, each 2 mole kinetic chain will come and interact and form one polymer so it get 4 4 moles of polymers. So, what is the average degrees of polymerization, number of monomers polymerized divided by number of polymer chains.

Because, this is a total number of monomers polymerized and this is the number of chains formed so that will give the number of average number of monomers present in a single chain. So, that is 600 by 4 1.5 so that is nu is. So, that is 1.5 nu, which is 1.5 multiplied by 100, 150 600 by 4.

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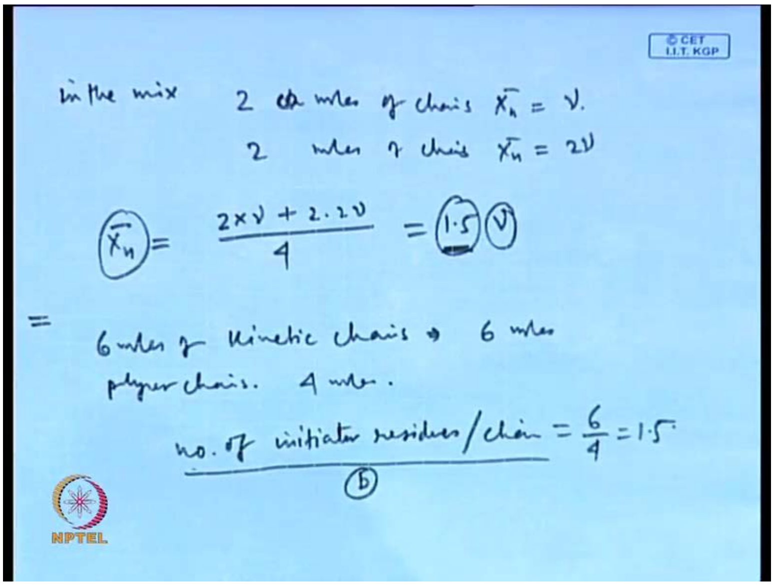

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in the mix   2 ~~ch~~ moles of chains $\bar{X}_n = \nu$.

2 moles of chains $\bar{X}_n = 2\nu$

$$\boxed{\bar{X}_n} = \frac{2\times\nu + 2.2\nu}{4} = \boxed{1.5}\,\boxed{\nu}$$

=

6 moles of kinetic chains → 6 moles
polymer chains. 4 moles.

no. of initiator residues/chain $= \frac{6}{4} = 1.5$

(b)

You can get same number, if I consider how many number of, we have in the mixture. In the mixture, we have 2 chains or 2 moles of chains, X n bar with nu and 2 moles of chains with X n bar of 2 nu. So, again on average, we have 2 chains or 2 moles of chains with nu degrees of polymerization, 2 into 2 nu divided total number of chains is 4. So, 1.5 nu again you get this same number so fine so you will know how the average degrees of polymerization is related to the kinetic chain.

Now, what is 1.5, if you we can get this number, if we consider the number of, how many number of initiator residue present per chain. Now, if I have one kinetic chain like this, the one end, this end you have a one initiator residue, which initiated the chain. If I react with another kinetic chain, and form a dead polymer by coupling reaction, then you have a polymer chain, which have two residues. So, a polymer formed by coupling of two kinetic chains will have two initiator residues whereas, if this undergo disproportion and form two different polymer chain, then each polymer will have one initiator residues.

So, in this case, this two moles of chain which underwent disproportionation reaction, you have total number of, this has each one has one residues initiator residues and this has two initiator residues. You have 6 moles of kinetic chains so initiator residues will have 6 moles, each kinetic residues have 1 moles and you have chains polymer chains, 4 moles. So, number of initiator residues per chain, per polymer chain is (()) 6 by 4 is 1.5.

So, this number is nothing but the number of initiator residues per chain, which we call or term as b. Now, we can get a more general expression of b, if we consider a more general example.

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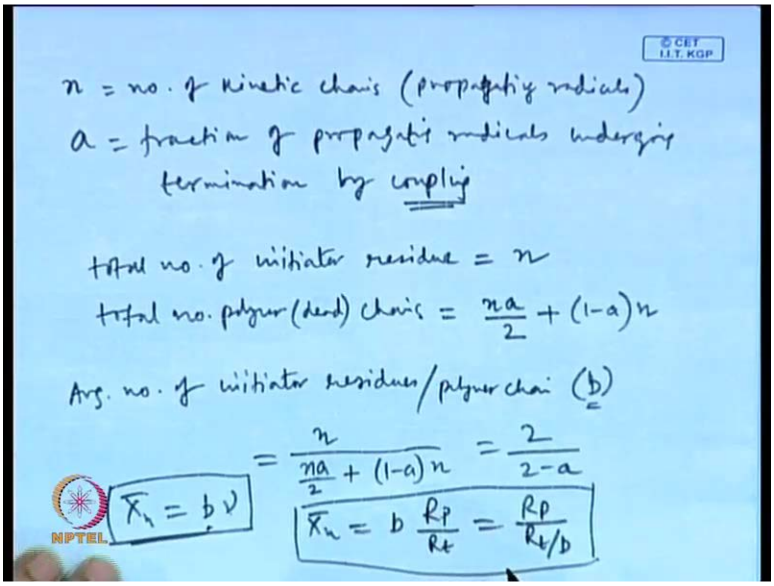

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n = no. of kinetic chains (propagating radicals)
a = fraction of propagating radicals undergoing termination by coupling

total no. of initiator residue $= n$
total no. polymer (dead) chains $= \frac{na}{2} + (1-a)n$

Avg. no. of initiator residues/polymer chain (b)

$$= \frac{n}{\frac{na}{2} + (1-a)n} = \frac{2}{2-a}$$

$$\boxed{\bar{X}_n = b\nu}$$

$$\boxed{\bar{X}_n = b\frac{R_p}{R_t} = \frac{R_p}{R_t/b}}$$

See, if I have n is the number of kinetic chains, which means propagating radicals and of this a n, a is the fraction of this propagating radicals, undergoing termination by coupling. So, total number of initiator residues in the polymer sample is, n is the number of kinetic chain so each kinetic chain will have one initiator residues. So, total number of initiator residues in the sample is n and total number of chains, polymer chains, polymer means dead chains is, a is the fraction.

So, n a is the number and if they are going termination by coupling so it is two of them produce one chain. So, n a will produce n a by two chains and rest (1 minus a), which is undergoing termination by disproportionation, they will form one minus a by n chain. So, average number of initiator residues for polymer chain is given by, n n a by 2 plus (1 minus a) n 2 by 2 by a, this is we term as b.

So, if I know if I know X n and X n is given by b nu so from experiment if I know the molecular weight above sample, if I know the molecular weight and total total amount total gram, then we know number of chains as well. And if we get the concentration of the initiator residues, then you can divide by the number of chains to get b. So, we from that, we can know or experiment the determine b and if we know b, we can find out a or number of fractional chain, which are undergoing termination by coupling.

And 1 minus a are the number of chains, which kinetic chains, which has undergone termination reaction by the disproportionation reaction. Now, in this case, we go back and see how we define the average degrees of polymerization, x n in this chain polymerization is a number of monomer polymerized by the number of polymer chain. What is the definition of X n, is the number of monomer units present average number of monomer unit present per chain, which is obviously will given by number of monomer unit consumed or polymerized divided by number of polymer chain, simple.

Now, remember in the step polymerization case, what was a X n bar or average degrees of polymerization, again it was number of monomer molecules polymerized divided by the number of molecules present at the end of the reaction. We have used that formula, number of molecules present at the end of the reaction that means, in the step polymerization case, we have considered every molecules present at the end of the polymerization is part of the polymer sample.

Because, there is no distinct no boundary between, you know in this case chain we have monomers and high molecular polymers, there is nothing intermediate. So, we can easily remove the monomer molecules, which we can discuss the monomer molecules and we can only count the polymer chains. But, in case of step of polymerization, we are talking about number of molecular present that means, each one each molecules whether it is a monomer or dimmer or trimmer, that also are in those are also included part of polymer polymer sample.

So, when we talking about polymer distribution, it contains the monomer, dimmer, trimmer sample as well. So, in case, we find in a step polymerization, that our polydispersity is less than 2, in spite of having a high molecular weight. What could be the reason, we have found that in case of step polymerization, the polydispersity index is always two. Theoretical polydispersity is always two, if we get a high enough molecular weight because that given by 1 plus p, p should be almost one to get a high molecular weight.

So, ideal theoretical polydispersity index should be two but if we find some time, that even in spite of getting large molecular weight, our polydispersity index is lower. That could be because if we do the reaction in the solution and during the precipitation of the polymers, the monomer or the low molecular weight fractions remain in the solution. So, what you finally measuring, what we finally measuring the polydispersity of the sample, which is the void of the monomer, dimmer, trimmer, which are suppose to be part of the polymer mixture, that is the reason we might get a narrower distribution.

So, that is the fundamental one fundamental difference between chain polymers and step polymers, how do we calculate or how do you understand, what the average degrees of polymerization is or the average molecular weight average number average molecular weight is. In this case chain case, we do not consider the monomers, whether in the step polymers case, we consider every molecule present at the end of the reaction.

So, if we got this, and you can write b R p by R t or R p by R t by b. So, this is the average number of (( )), we can get it from this and you know, unless the monomer is the monomer is sterically crowed. If we are talking about a coupling reaction, then two radical chain ends has to come and collide each other. Now, unless the monomers is sterically crowded or they have a easily abstractable beta hydrogen, in majority cases they undergo termination by coupling reaction like styrene, acrylonitrile, methyl acrylate.

They are not very sterically hindered and either they have a beta hydrogen for elimination whereas, in case of methyl methacrylate because it has a beta hydrogen, which can be easily eliminated. It undergoes termination reaction both by coupling as well as by disproportionation reaction, and as we increase the temperature, the fraction of termination fraction of disproportionation termination increases as we increase we increase the temperature.

So, till now, we have been considering the termination of this propagating radical by bi molecular interaction between two propagating radical, either by coupling (( )). Now, there could be another type of reactions, by which propagating radical or a kinetic chain can get terminated, which is transfer reactions.

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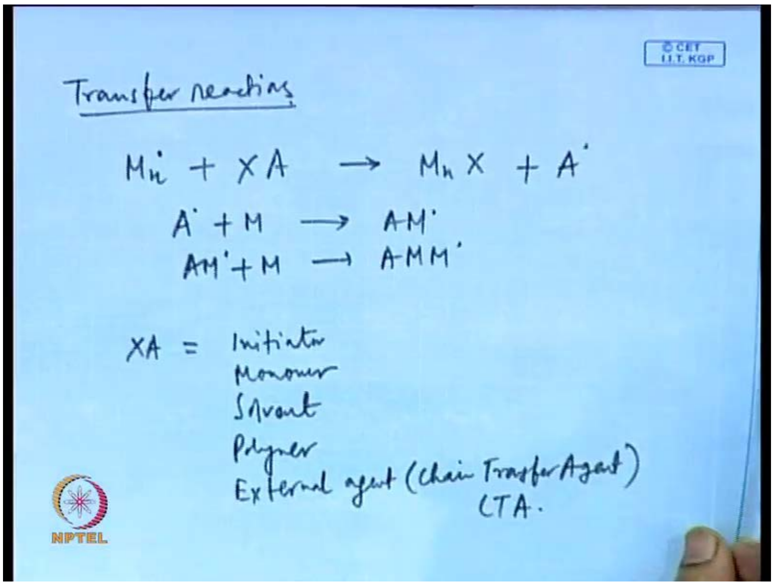

Transfer reactions

$$M_n^{\cdot} + XA \rightarrow M_nX + A^{\cdot}$$

$$A^{\cdot} + M \rightarrow AM^{\cdot}$$

$$AM^{\cdot} + M \rightarrow AMM^{\cdot}$$

XA = Initiator
Monomer
Solvent
Polymer
External agent (Chain Transfer Agent)
CTA.

So, now, let us discuss transfer reaction so if I have a propagating radical M n dot. It can react with the third molecule and form M n X plus A dot so here one kinetic chain, which was suppose to continue one chain is getting broken by reacting with X A and forming a new radical, now this new radical can initiate another chain like this. So, from one radical you have be discussing that, we had one kinetic chain, in this case from one radical, we have 1 dead polymer plus 1 another kinetic chain.

So, basically for a given number of monomers polymerized, the number of chains at the end of the polymerization is no more. Because, 1 kinetic chain is getting broken down to 1 dead polymer and a another kinetic chain, which means, this is a chain breaking reaction. As a result of this, the average number average degrees of polymerization or the molecular weight will definitely come down.

What are X A is, X A could be the initiator molecules, it could be the monomer itself to the solvent molecules, it could be the polymer itself or it could be any external agent. External agent, which are could be added added deliberately from outside or it could be present as a impurities and we call some time call as this chain transfer agent or CTA.

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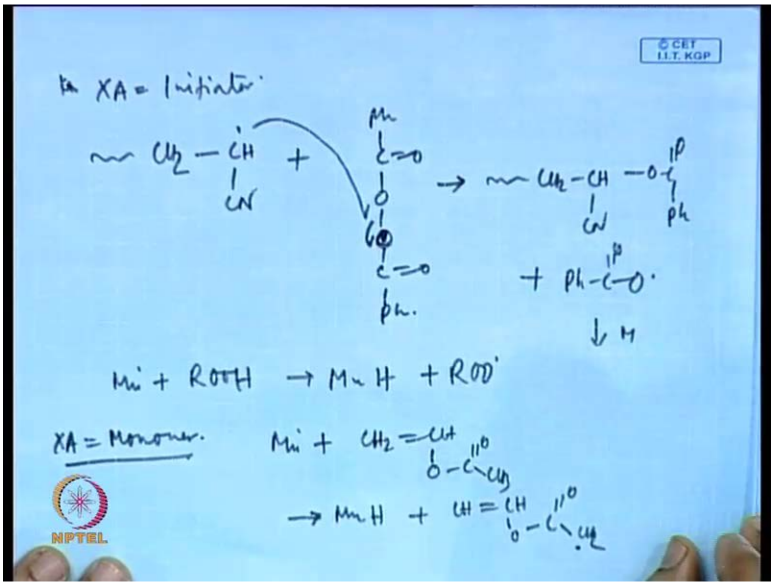

So, give let us give some examples of this transfer reaction, when X A is initiator say, I have a reaction of acrylonitrile. It can react with say, this case the benzoyl peroxide is initiator and it can check up this and from now, this can again react with the monomer and initiate another kinetic chain. There could be some peroxides or hydro peroxides, which also when act as a initiator, they participated in chain transfer reaction and resulting decrease of molecular weight, example of X A is monomer methyl methacrylate dot, it is not the methyl methacrylate.

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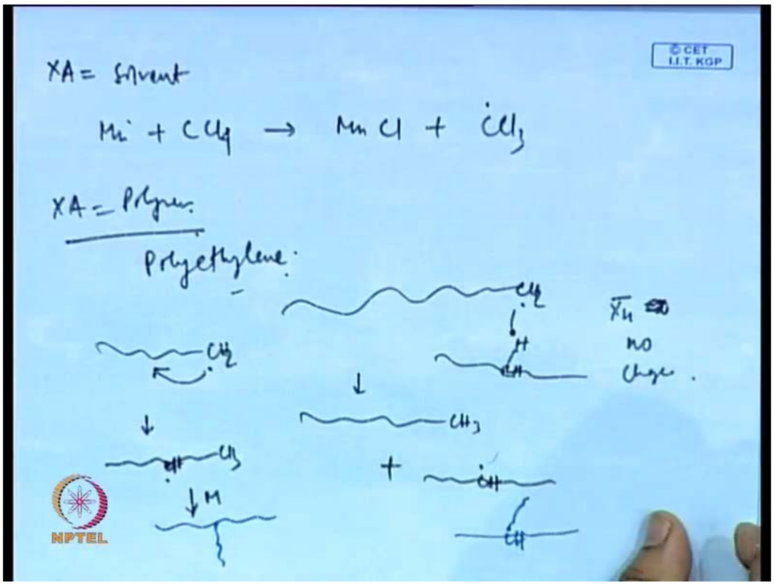

So, this is example of, where you are getting a chain transfer by the monomer itself. Examples, where X A is solvent, if I take carbon tetrachloride, then it can take up chloride and form CCl 3 dot. X A being polymer, consider poly ethylene, you have another chain, it could be dead chain dead polymer. Now, it can abstract this hydrogen and form these dead chain, and you have a new polymer, where you have a radical generated in between not the end.

Now, it can undergo further polymerization from here and form a chain here so it can undergo here and form a chain. So, you may have a branching here so if transfer happen within polymer, you get branching. Similarly, if this can back bite this can back bite and abstract 1 hydrogen from here, producing C C and a CH dot here, now this can react with monomer giving branches.

So, in this case, if the chain transfer happen with another polymer molecule the two thing happening is, one you are getting branches and another important thing particularly for this case is that, X n bar does not change here, no change. You have started with 2 polymer chain when a transfer happened, you have same 1 kinetic chain and 1 polymer dead polymer chain.

In this case, you have 1 kinetic chain, intra molecular back biting you are resulting it, one kinetic chain so the number of chains in this case does not change. This is a special case of chain transfer, where because of chain transfer, the molecular weight does not change but it results in branching of the linear polymers.

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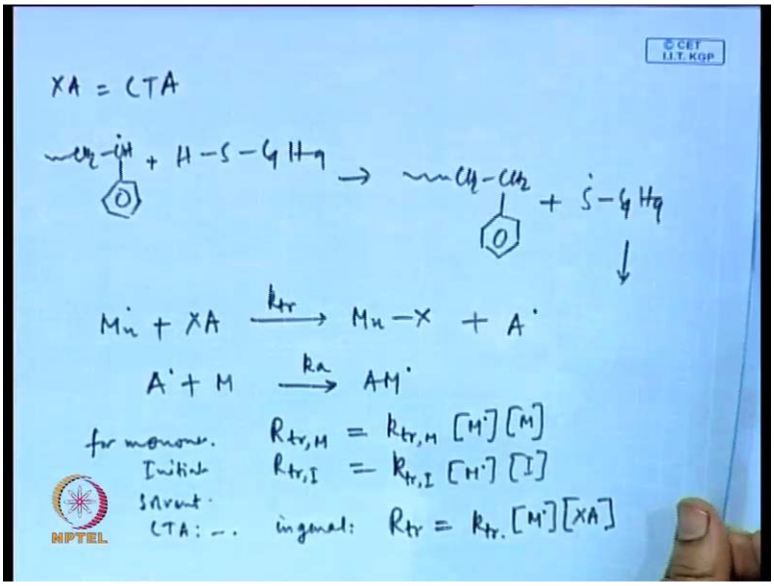

$XA = CTA$

$M_n^{\cdot} + XA \xrightarrow{k_{tr}} M_n{-}X + A^{\cdot}$

$A^{\cdot} + M \xrightarrow{k_a} AM^{\cdot}$

for monomer. $R_{tr,M} = k_{tr,M}[M^{\cdot}][M]$

Initiator $R_{tr,I} = k_{tr,I}[M^{\cdot}][I]$

Solvent.

CTA: --. in general: $R_{tr} = k_{tr.}[M^{\cdot}][XA]$

Examples of deliberately added chain transfer agent is like H S C 4 H 9, if you are considering a reaction with styrene, this can initiate further chain. So, what we just now learned we have learned what are chain what are chain transfer reaction and what are the different types of chain transfer agent could be possible, it could be initiator, it could be monomer, it could be a transfer agent, to be solvent in all this case, except the chain transfer to the polymers.

You are generating more chains at the end of the polymerization, which means that you are breaking a chain and as a result the molecular weight or the number average degrees of a polymers, polymerization is lower than, if there was no transfer reaction present. If I can write a general reaction like this , this is the rate constant for transfer reaction and this is rate constant for the subsequent initiation a propagation reaction with the a dot molecule.

So, we can write for monomer, we can write rate of transfer monomer given by, k transfer monomer M dot M. For initiator, we can write similar transfer initiator, k transfer initiator m dot I similarly, we can write for solvent, CTA and so.

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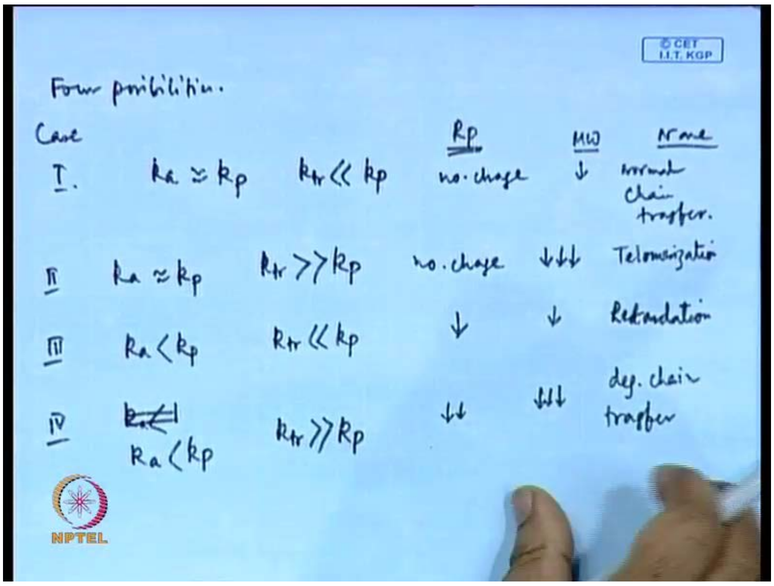

Four possibilities.

Case			R_p	MW	Name
I.	$k_a \simeq k_p$	$k_{tr} \ll k_p$	no. change	↓	normal chain transfer.
II	$k_a \simeq k_p$	$k_{tr} \gg k_p$	no. change	↓↓↓	Telomerization
III	$k_a < k_p$	$k_{tr} \ll k_p$	↓	↓	Retardation
IV	~~$k_a \neq$~~ $k_a < k_p$	$k_{tr} \gg k_p$	↓↓	↓↓↓	deg. chain transfer

So, in general, we can write rate of chain transfer is rate constant for transfer M dot X A, now there could be 4 possibilities 4 possibilities, this is the rate constant for the transfer reaction. Now a radical propagating radical can react with the monomer, which corresponds to k p, rate of polymerization and it can react with a transfer agent, which is your rate constant for transfer reaction. And when this is new radical is formed, this initiate a another new chain polymerization, with rate polymerization rate of rate constant k a.

Now, case 1 k to k p and k transfer transfers much lower than the propagation so what happen, what is the effect on rate of polymerization. Rate of polymerization nothing but rate of disappearance or rate of consumption of monomers, now if this new radical formed for transfer reaction, they also consuming monomer in the same rate. Obliviously, rate of polymers polymerization does not change so no change, what happen to molecular weight, obviously decreased. Because, chain transfer always breaks the chain and the name we gave for this type of reaction is normal normal chain transfer.

Now, case 2 is again, k is similar to k p and k transfer is much higher than k p so R p rate of polymerization, again no change. Because, new radical form is also consume in monomer in same rate molecular weight because the number of transfer reactions rate constant for transfer reaction, is much higher than the chain propagation reaction. So, the number of chains undergoing transfer reaction is much more many more so the molecular weight drop significantly, it large decrease in the molecular weight and we call this as telomerization.

The third case is, k the new rate of polymerization with the radical form due to transfer reaction is lower than k p but rate of transferring rate constant for transfer reaction is much lower than the rate constant for the original polymerization reaction. In this case we got, this rate is lower than chain polymerization, rate of polymerization come down. So, as the molecular weight and we call this as retardation, whether is fourth case thus the worst case, where k is lower than k p and k transfer is higher than k p. In this case, because of this, rate comes down and because of this, molecular weight has large drop.

So, both large decrease in the molecular weight as well as the decrease the large decrease in the rate of polymerization and this we term as degradative chain transfer. So, basically under reaction, you get extremely low molecular weight polymers are oligomers and that to the rate of consumption rate of reaction of the monomers happen must lower. In this case, in the telomerization case, rate of polymerization is fast the monomer is reacted much at the same rate, as if there was no transfer reaction but the molecular weight drops.

So, for a given time, you are getting illed, number of polymers you are getting more but the rate at which polymers monomers is reacting is similar as the original rate, for the molecular weight drop significantly.

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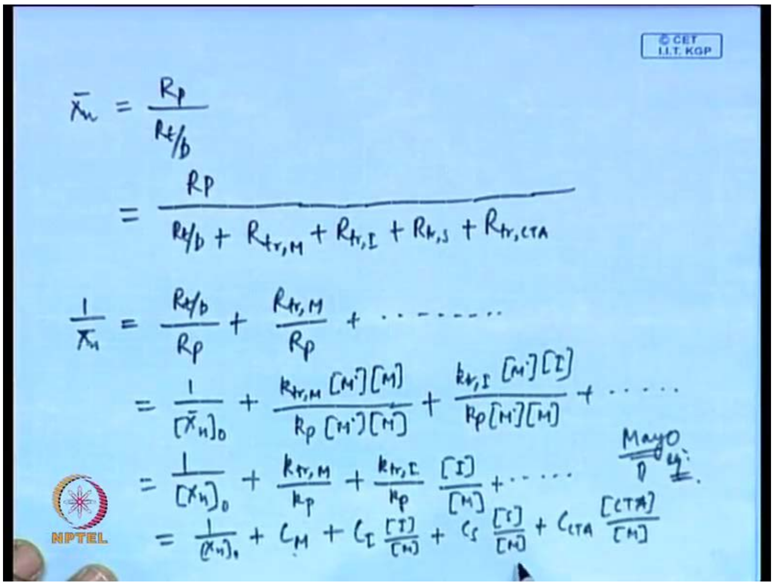

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$$\bar{X}_n = \frac{R_p}{R_t/b}$$

$$= \frac{R_p}{R_t/b + R_{tr,M} + R_{tr,I} + R_{tr,S} + R_{tr,CTA}}$$

$$\frac{1}{\bar{X}_n} = \frac{R_t/b}{R_p} + \frac{R_{tr,M}}{R_p} + \cdots\cdots$$

$$= \frac{1}{[\bar{X}_n]_0} + \frac{k_{tr,M}[M^\cdot][M]}{k_p[M^\cdot][M]} + \frac{k_{tr,I}[M^\cdot][I]}{k_p[M^\cdot][M]} + \cdots$$

$$= \frac{1}{[\bar{X}_n]_0} + \frac{k_{tr,M}}{k_p} + \frac{k_{tr,I}}{k_p}\frac{[I]}{[M]} + \cdots$$

Mayo eq.

$$= \frac{1}{(\bar{X}_n)_0} + C_M + C_I\frac{[I]}{[M]} + C_S\frac{[S]}{[M]} + C_{CTA}\frac{[CTA]}{[M]}$$

So, now, write the kinetic expressions, now we are found that, this is the this is the expressions gives the average degrees of polymerization without any transfer reaction, where only the termination is due to either coupling or this propagation. And b is the number average number of initiated residues per polymer chain at the end of the reaction. So, if a talk about transfer reaction, that include the other reactions, which by which termination takes place, which are other rates, that transfer by the monomer rate of transfer, by initiated rate of transfer, by solvent or rate of transfer by the C T H, chain transfer.

Now we are not writing rate of transfer by polymers because as you seen that polymers, they do not contribute in terms of decreasing the number of molecular weight of the polymer. So, we are not considering the rate for chain transfer in polymers case, so if I can write 1 over X bar, I can write R t by b by R p, similarly R transfer mono by R p and so on, other terms.

This is 1 over X n 0, which means, that have number average degrees of polymerization reactions of any transfer reaction and you can write the rate expression for individual rates. So, k transfer is given by rate constant transfer monomer, M dot M by k p M dot M plus, if I talk about the initiated then, k transfer initiated M dot I k p M dot M plus others, 1 over X n 0 n by k p plus k transfer I by k p I by M so on.

Now, this is the rate of transfer rate constant for transfer by the original rate of propagation is, we are writing transfer coefficient or transfer coil constant. So, this is the transfer constant for chain transfer constant for monomer, this is chain transfer constant for the initiator, similarly for solvent, we can write C S solvent by M plus C CTA, CTA by M. Now, this is mayo equation so any increase in the right hand side, anything which increases the value of right hand side, will decrease the molecular weight.

So, any absence of any transfer reaction, you get the highest molecular weight, which is basically the molecular weight we get in absence of transfer reactions. Now, just look at this transfer once, typically in normal cases, the transfer to monomer and initiator are very negligible. They did they generally do not take place and unless we had a transfer agent from outside deliberately all the impurities present, this also does not contribute too much.

So, actually the main contribution for chain transformations chain transfer reaction is, the solvent so whether this might be significant for some particular cases, for this is very important for majority of the radical chain polymerization reactions. So, let us discuss little more about this terms S and so basically for a given concentration monomer and solvent this is the value of C S will determine the chains transfer reactions in terms, which will determine the value of the molecular weight of the chains getting produced in this reactions.

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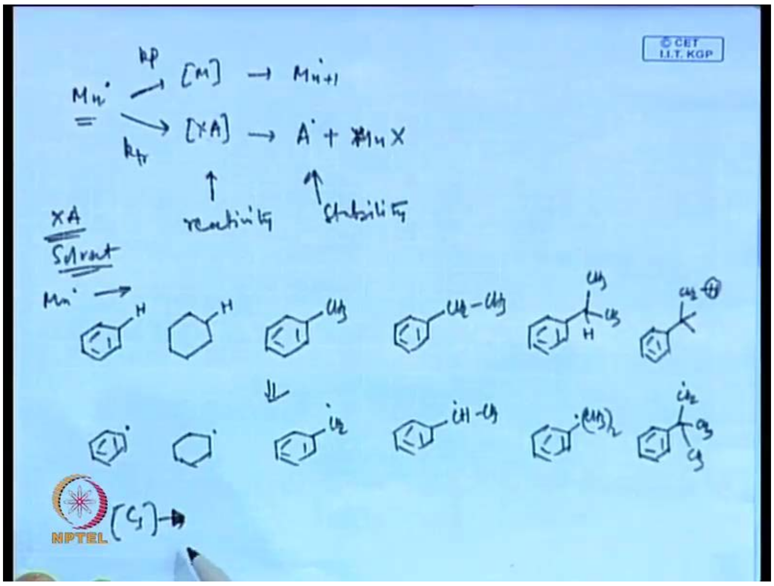

Now, if I go and look this M n M n dot chain one propagating radical, they can react with a monomer, which is k p and it can react with X X A it could be solvent in others, which is basically the transfer. Now, this produces again M n bar M n 1 plus if we write, and this produce A bar plus X M n X. Now, whether a chain transfer will happen and if it is happen how extent, it will determine by the reactivity compression between the monomer and the chain transfer agent of the solvent here.

And also, the stability of this M n dot or A dot, if it is more stable, then it will be this reaction will be dominating over the original propagation reaction. If it is this M n dot, which is the original propagations radical is more stabile, then obviously, this will be more preferred reaction over transfer reaction. If the reactivity of the original radical propagating radical is very high, then it cannot distinguish that extent and other weight, even if there is a difference in the reactivity of these two molecules towards this.

Because, this is highly reactive, it will react both m and this, if it is less reactive, then the more reactive between this two will react with this. If it is very reactive, then both of them will react, if it is low react less reactive, then between this two which is more reactive, that will react with this. So, that reaction will be prominent preferred, let us take example and see whether we can grass this. Let us consider examples like benzene, we are talking about solvent.

Let us consider X A as solvent so benzene cyclohexane, toluene, Methyl benzene, isopropyl benzene and tertiary butyl benzene. Now, it just react with M n dot and undergo a transfer reaction obviously, this is a hydrogen, which will abstract, Slide this is the hydrogen it will abstract from here. And between this case, this is the hydrogen is more recently abstractable and in this case, it is this hydrogen is abstractable and this case, this hydrogen is abstract able and this case, there is no hydrogen here so this hydrogen, which is more abstractable.

So, what is the resulting radicals form in this case, this radical, this radical dot now, from your basic knowledge of organic chemistry, you know which what is the order of stability of this radical. Now, the most stable radical is, it will participate in the transfer reaction in more extent, the lower is the if it is lower, then it will participate in the transfer reaction in lower extent. So, what is the value if I.

So, what we will do in the next lecture, let us start from this page and look at the value of this C S transfer constant and is know, the higher the value of C S, the more the solvent participate in the transfer reaction so lower would be the molecular weight of the resulting polymer. So, let us stop for this class this lecture now, and we will start from this page in the next lecture immediately.