Science and Technology of Polymers

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Lecture - 9

Principles of Polymer Synthesis (Contd.)

Well, this polymer growth can be either totally stopped or can be carried out at a slow speed. Now, there are other aspects also which is known as gel effect or auto acceleration. During the growth of polymer, during the polymer synthesis, polymer manufacture, this is a situation it can lead to a catastrophic failure of polymer growth. It can lead to a serious accident; it can lead to explosion of the polymerization reactor due to auto acceleration. What is that auto acceleration? In order to understand that auto acceleration, you need to imagine the synthesis of polymer, synthesis of polymer from monomer at different rates.

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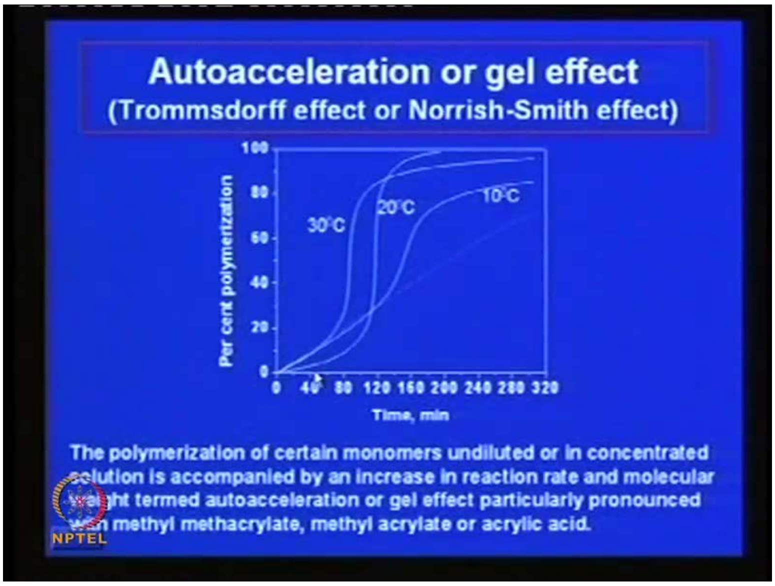

Autoacceleration or gel effect
(Trommsdorff effect or Norrish-Smith effect)

The polymerization of certain monomers undiluted or in concentrated solution is accompanied by an increase in reaction rate and molecular weight termed autoacceleration or gel effect particularly pronounced with methyl methacrylate, methyl acrylate or acrylic acid.

Here, you see the growth of polymer with time as shown in three cases, at 10 degree Celsius temperature, at 20 degree Celsius temperature and 30 degree Celsius temperature. During polymer synthesis, what happens you think of starting from initiation to termination. Although, there may be a limited number of initiator free radicals, primary free radicals produced during initiation. As soon as it produces primary free radicals, that initiates monomer to form to start the growth of quite a good number of polymer chains that continue to grow, ultimately they terminate with each other for being a dead polymer chain.

What happens here? Try to understand the physical situation in a polymerization reactor. Once this initiation starts and initiated monomer chains grow to bigger and bigger size, in case of a liquid system, it will increase the viscosity of the mass. So, it can be understood that it is a diffusion control process. That means, growing chains are diffusing within the system from one place to the other and before termination event, two growing chains should diffuse close to each other, so that they can collide and terminate to form a dead polymer chain or else a growing chain can interact with a primary free radical for termination also, although, I have not mentioned that thing previously, but it also can happen. That is also again a diffusion process. So, when this polymer chain becomes very big, the system becomes highly viscous. If they cannot come closer, then they cannot terminate. That means, there is a continuous increase in rate of polymerization whereas, termination rate is decreased once again.

You try to understand the situation propagation rate goes on increasing, whereas termination is not able to occur because of increase in viscosity of the system. So, R T is less than R P. There can be a sudden acceleration of the polymerization rate. This is a situation where you see after, say after say 65 or 70 minutes of growth polymerization, there is sudden rise of polymer growth at this temperature. A case where it is shown for three cases of polymerization carried out at 10 degree, 20 degree and 30 degree. It can also happen in case of monomers polymerized in bulk without using any solvent bulk polymerization.

There is no solvent, there is no separate solvent added, where the monomer itself can act as a solvent for the polymer. The polymer chains which are being formed, that remains dissolved in the monomer phase. Gradually what happens with the progress of time is this polymer chain will increase the viscosity of the polymer solution. The viscosity goes on increasing and then the diffusability of the growing chains for termination that is decreased, that leads towards acceleration of this rate. Now, if you carry out using a solvent solution there, solvent actually prevents, solvent does not allow the viscosity to increase that much. Even then it is a solution polymerization depending on the monomer concentration taken per in that solution case. This happen, this acceleration of rate can happen.

So, this phenomenon is known as auto acceleration, but sometimes it is known as Trommsdorff effect or Norrish-smith effect and other way also, it is called gel effect. That means entire mass gels looks like a cross linked system. Those who are synthesizing polymethyl methacrylate, those who are doing lab class, they can experience. It is not that true. It can always happen, but sometimes it happens all of a sudden. You are just, what you do you take a conical flask or a RB flask where you take a certain quantity of monomer, add specified quantity and dissolve it. Then, you with nitrogen gas to remove this oxygen from this system, then you close it in nitrogen condition. Then, you stir this continuous in a thermostatic bath polymer. During that process, you can ask your supervisor there.

Sir, I am not getting any polymer. So, I do not see that the viscosity of the solution is increased. So, in my case, polymer growth is not there. In another case, in some other case, one can find that the viscosity is gradually increasing. In some other case, one can find all of a sudden the mass within the flask sets to solid and starts boiling inside. So, these effects can be visualized.

Why it happens? Because if there is auto acceleration, if there is auto acceleration like this, so it is highly exothermic reaction. That means, the propagation rate had become very high. So, many monomer molecules are adding to the growing chain and liberating huge quantity of heat. That is increasing the temperature as well as that is decomposing, that is helping to decompose the initiator present over there.

So, a complicated situation can happen there and inter mass gels and that polymer mass becomes waste or useless. Now, in a small system, the point of danger is not that much, but in case of a huge container, say a batch of few tons in a big reactor there, just imagine the quantity of heat that is involved over there that will explode the reactor like huge bomb. So, that is the danger situation. So, this occurs due to auto acceleration of rate. So, that is known as auto acceleration effect or gel effect or Tromsdorff effect or Norrish-smith effect.

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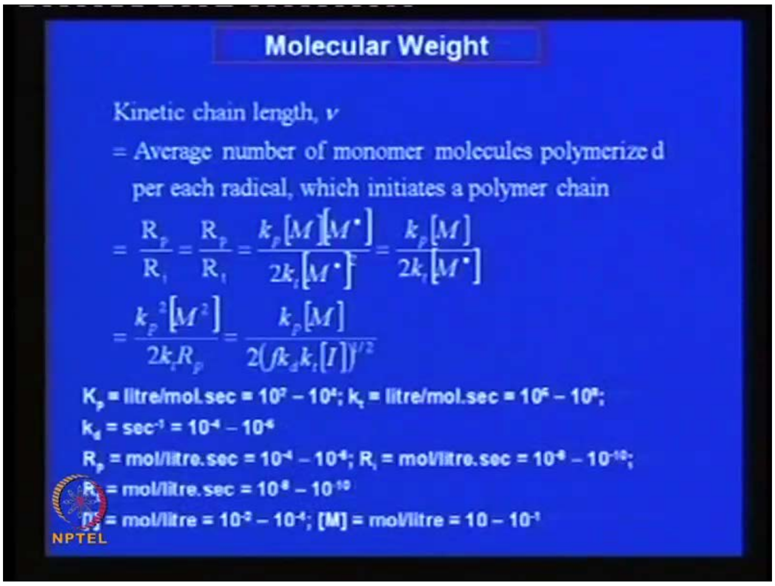

Molecular Weight

Kinetic chain length, v

= Average number of monomer molecules polymerized per each radical, which initiates a polymer chain

$$= \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[M][M^\bullet]}{2k_t[M^\bullet]^2} = \frac{k_p[M]}{2k_t[M^\bullet]}$$

$$= \frac{k_p^2[M^2]}{2k_t R_p} = \frac{k_p[M]}{2(fk_d k_t[I])^{1/2}}$$

K_p = litre/mol.sec = $10^2 - 10^4$; k_t = litre/mol.sec = $10^6 - 10^8$;

k_d = sec^{-1} = $10^{-4} - 10^{-6}$

R_p = mol/litre.sec = $10^{-4} - 10^{-6}$; R_i = mol/litre.sec = $10^{-8} - 10^{-10}$;

R_t = mol/litre.sec = $10^{-8} - 10^{-10}$

$[I]$ = mol/litre = $10^{-2} - 10^{-4}$; [M] = mol/litre = $10 - 10^{-1}$

Now, let us see what happens to the molecular weight of the polymer formed by this addition chain in case of condensation polymerization. You have seen the effect of rate on molecular weight number of arrays degree with the extent of as well as rate of all those things. You have seen there. Now, let us see the situation in case of addition chain. Now, here to understand or to explain the effect of this rate of polymerization or rate of the molecular size on parameter has been considered here, that is kinetic chain length. What is the concept of kinetic chain length? It means that the length of the polymer chain or growing chain prior to termination, it remains kinetic.

So long it remains alive; so long a growing polymer chain remains alive. It is called kinetic. So, length of the polymer chain prior to termination is known as kinetic chain length. So, you can have the relation of this kinetic chain length with the rate of termination. This kinetic chain length can be expressed as the ratio of R p and R i or R p on R t rate of and rate of termination ratio of these two rates ratio are R p and R t gives a measure of kinetic chain length.

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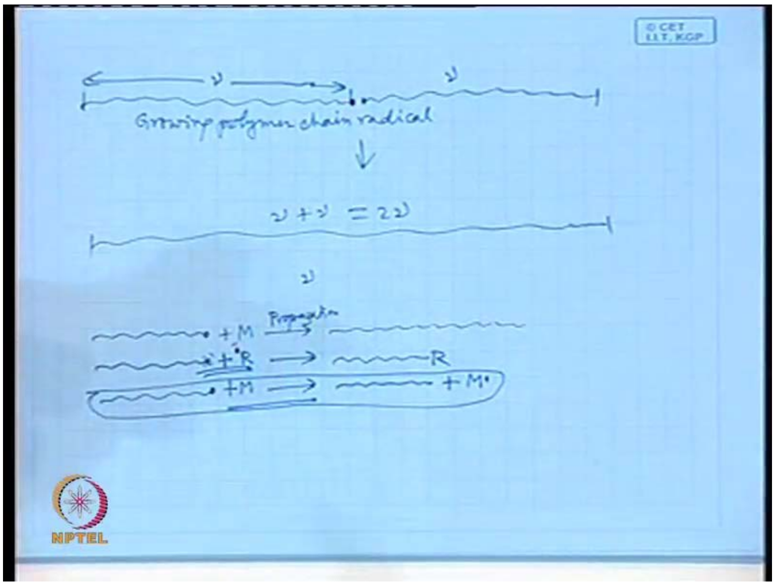

That means a polymer chain is growing. It has initiated over here and it is growing at the end. It bears a, so this is a growing polymer chain radical. So, length of this polymer chain from here to here is known as the kinetic chain length prior to termination. Now, if there are two such growing chains terminated by complete process, the length of the polymer chain after termination will be this much. So, it will be mu plus mu equal to 2 mu.

So, if it is by coupling, if it is by disproportionation, the molecular weight will be equal to mu, either mu or (( )). Now, by substituting these values of R p and R t here can get a relation K p M by twice K t M dot (( )) again. This M dot concentration if that can be obtained by the steady state concept and after substitution, you can get this relation. So, this is equal mu is equal to K p M by twice f K D K t i to the power half and these for your idea, for your information, the values of various rate constants and rates of termination, rate of initiation, etcetera. This K p unit is unit of your propagation rate constant unit of decomposition, unit of rate constant, unit of termination rate, constant rate. So, please do not ignore the rate constant values and values as well as their units. Looking at these rates or taking these values, you can go for calculation of various parameters in this addition chain case.

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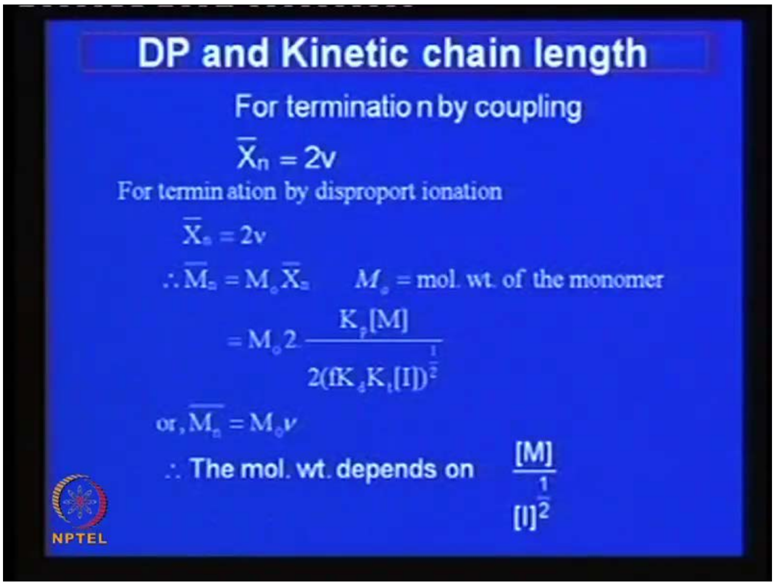

DP and Kinetic chain length

For terminatio n by coupling

$\overline{X}_n = 2v$

For termin ation by disproport ionation

$\overline{X}_n = 2v$

$\therefore \overline{M}_n = M_0 \overline{X}_n$ $\quad M_0$ = mol. wt. of the monomer

$$= M_0 2 \frac{K_p[M]}{2(fK_d K_t[I])^{\frac{1}{2}}}$$

or, $\overline{M}_n = M_0 v$

$\therefore$ The mol. wt. depends on $\dfrac{[M]}{[I]^{\frac{1}{2}}}$

Now, the degree of number average, degree of kinetic relation between number, average degree of and kinetic chain length, I am sorry. One thing I forgot to mention. I just told you that before it needs nitrogen, none of you asked me the reason. You know the reason why oxygen is first? Why nitrogen is first to remove oxygen? Oxygen acts as if you carry out this addition chain in presence of air and in presence of oxygen, you will not get a polymer. Polymer will not be formed. So, oxygen should be removed because oxygen acts as that, inhibits for that reason oxygen is removed.

Anyway, let us comeback this degree of and kinetic chain length. As I mentioned this number of degree of may be equal to twice mu, if the termination is by coupling process, if it is by disproportionation process, it would be equal to X n bar will be equal to mu. So, by putting those values, this is the molecular weight. If the molecular weight of the monomer is M 0 M 0 into X n bar is equal to M 0 into 2 into this K p M by twice f K D K t i to the power half, so it indicates that the molecular weight depends on the concentration of monomer and the initiator concentration, the ratio of these two parameters, monomer concentration and initiator concentration molecular weight. So, if the initiator concentration is high, you see if the initiator concentration is high, the molecular weight will be low. This is mathematical clear from here but physical concept.

So, if the concentration of the initiator is very high, why the molecular weight will be low? More number of polymer chains will be initiated, started, but the quantity of the available monomer is less. So, the total length of the polymer will be less. This is one thing. Another thing is if there are more number of initiated free radicals present in t, the system there are many more possibilities that can happen. So, this is a growing chain that is provocating as it gets more and more monomer. It will continue to increase in length. Now, if instead of getting reacting with interacting with monomer, if it interacts with a primary radical or impurity which can act as initiator or a radical like this, its growth is arrested over here. Not only that, if there are many more chains present in the system that can interact with monomer, even in this case of interaction with the monomer may not be propagation, but it can stop over here.

That means, it will stop over here plus new chain can be initiated. So, this is propagation, but this is not propagation. This step is not propagation. This is different situation. So, in order to get high productivity, high rate, one can use higher concentration of initiator, but the problem will be at the cost of, you can do it at the cost of molecular weight. Molecule will be lower not only that it can act as, it can transfer this radical activity to this initiator. So, those things we are coming to discuss. So, the molecular weight of the polymer depends on the ratio of the monomer concentration to that of the initiator concentration.

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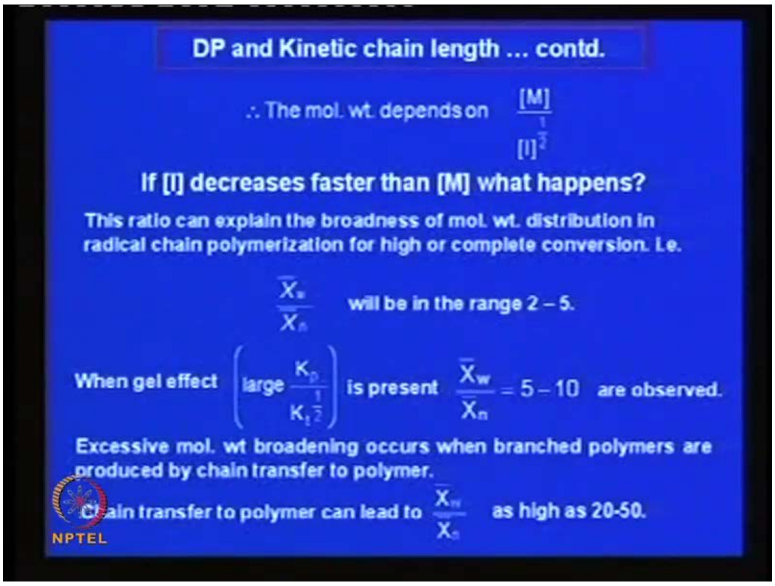

DP and Kinetic chain length ... contd.

∴ The mol. wt. depends on $\frac{[M]}{[I]^{\frac{1}{2}}}$

If [I] decreases faster than [M] what happens?

This ratio can explain the broadness of mol. wt. distribution in radical chain polymerization for high or complete conversion. I.e.

$\frac{\overline{X}_w}{\overline{X}_n}$ will be in the range 2 – 5.

When gel effect $\left(\text{large } \frac{K_p}{K_t^{\frac{1}{2}}}\right)$ is present $\frac{\overline{X}_w}{\overline{X}_n} = 5 - 10$ are observed.

Excessive mol. wt broadening occurs when branched polymers are produced by chain transfer to polymer.

Chain transfer to polymer can lead to $\frac{\overline{X}_w}{\overline{X}_n}$ as high as 20-50.

Now, here let us consider one parameter. You have been acquainted with a parameter number is degree of polymerization. You can have another parameter weight array degree of what is number of arrays, what is weight of arrays.

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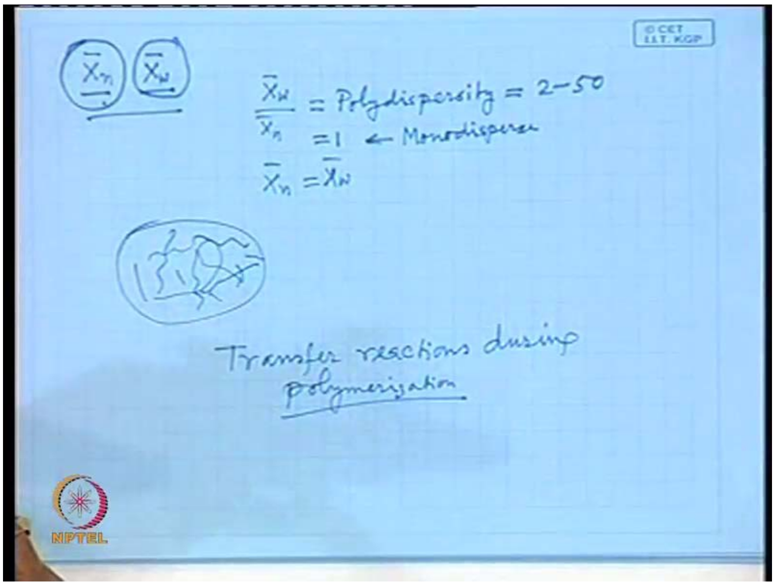

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$\bar{X}_n$ $\bar{X}_w$

$$\frac{\bar{X}_w}{\bar{X}_n} = \text{Polydispersity} = 2\text{–}50$$

$= 1$ ← Monodisperse

$$\bar{X}_n = \bar{X}_w$$

Transfer reactions during polymerization

This is based on number count, this is based on weight count, number of species, this is based on the weight of different species present that actually concludes the molecular weight distribution. Distribution of the various molecules of different sizes, say if you take a ratio of these two, this is known as polydispersity. Now, if this is equal to 1, it is a case known as monodisperse. It means, X w X n bar is equal to X w bar. All this small discrete, small molecules are monodisperse. The polymers are not that monodisperse, although you can have monodisperse polymer.

What is the polydispersity value? It can raise from 2 to 50 or even more. That means, you can have a sample of polymer having different sized molecules present in this thing, large molecular chains, smaller molecular chains. So, there is a distribution of molecular sizes in a sample of polymer that is expressed in terms of this polydispersity index that is shown over here. Now, this monodisperse polymer, sometimes it is required for specific purposes like molecular standards or standard polymer molecules which will have standard set of properties. So, we need sometimes monodisperse polymers, otherwise polydisperse polymer samples are produced during this polymer synthesis. Now, if the sample of polymer contents large distribution, mechanical properties, thermal properties, optical properties, all these properties will be influenced by this dispersity of molecular sizes, we will discuss those things while when we shall discuss the structure property polymers.

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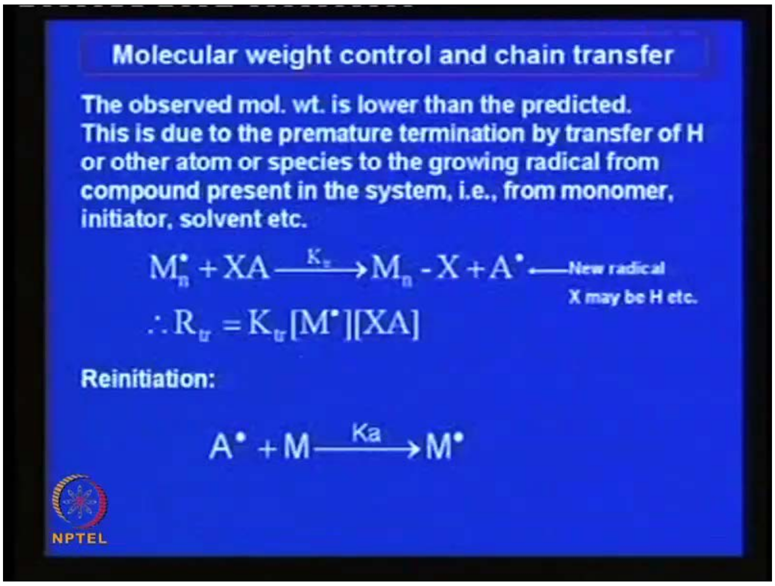

Molecular weight control and chain transfer

The observed mol. wt. is lower than the predicted. This is due to the premature termination by transfer of H or other atom or species to the growing radical from compound present in the system, i.e., from monomer, initiator, solvent etc.

$$M_n^\bullet + XA \xrightarrow{K_{tr}} M_n\text{-}X + A^\bullet \longleftarrow \text{New radical}$$

X may be H etc.

$$\therefore R_{tr} = K_{tr}[M^\bullet][XA]$$

Reinitiation:

$$A^\bullet + M \xrightarrow{Ka} M^\bullet$$

Now, here in this case of addition chain, how to control the polymer molecular weight in case of condensation polymerization? You saw that molecular weight can be controlled by deliberate addition of monofunctional reagents or you can stop by chilling or by some other means. Those are the techniques of controlling over there, but in case of addition chain which is so fast, so rapid, how to control it or sometimes if I want a very high molecular rate product, I may not get it, you may not get it. You may not get that high molecular weight. So, what is influencing, what parameters influences comes on the way to reduce the molecular weight or which becomes to achieve a high molecular weight that those things can be understood by considering parameter known as transfer reactions.

Let me give you a concept of transfer reactions. See you have taken a system of monomer and initiator for polymerization by supplying sufficient energy. Initiator decomposes to initiate a monomer for starting a polymer chain. It propagates by adding more and more number of monomer molecules. Ultimately, two growing chains interact with each other forming a dead polymer molecule. During these events of reactions, what happens is that initiator radical may not perform its normal function; monomer may not perform its proper function. It can sometimes behave abnormally. Sometimes the monomer system we have taken or initiator system, we have taken may not be pure as is required. Sometimes, the need to be carried out in the bulk without using any solvent, sometimes need to be carried out in presence of a solvent solution, sometimes need to be carried out in suspension and as well as emulsion technique. Now, during those situations, the monomer, initiator polymer chain, radicals, solvents, etcetera behave in abnormal fashion that leads to transfer reaction.

What is transfer reaction? Transfer reaction is a process when the activity of a growing free radical chain is transferred to some other species other than monomer. That means any activity other than propagation, any activity of growing chain other than propagation is known as transfer reaction. That means, its activity is transferred to some other species and it becomes dead and it cannot help growth of higher molecular weight that is transfer reaction as I was showing.

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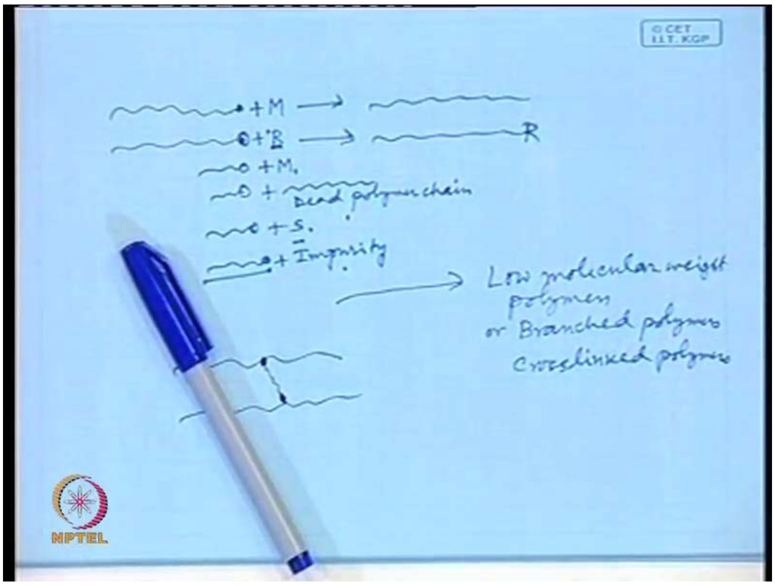

The chain is growing when it is supposed to add to monomer giving bigger chains, but it interacts with R radical. So, it can stop over here that is a transfer. That means this activity is transferred to this primary radical. Now, this activity can be transferred to a monomer. Not only that, this activity can be transferred to a polymer chain, a dead polymer chain, this activity can be transferred to a solvent, so the present monomer, dead polymer chain, solvent and some impurity.

So, if this activity or active site of these growing chains are killed, if the activity of the growing chains are transferred from these active sides to agencies like impurity, solvent, dead polymer monomer, such type of events are known as transfer reactions and result is low molecular weight polymers or branched polymers and sometimes cross linked polymers. People have experienced of presence of gel in a thermoplastic linear polymer system, say those who are working with polyethylene, low density polyethylene or high density polyethylene for injection molding or film blowing techniques in the (( )) blowing the gel content of the polymer is a parameter which should be taken care of the gel content affects. The (( )) of the polymer during the manufacture of films, the quality of the films during the manufacture of the films depend on the gel content of the polymer means a polyethylene granule that may contain some polymeric gel.

How to justify that those polymer contents, polymer gels thermoplastic, no cross linking agent is added there during manufacture? Where it comes from? These transfer reactions because once that radical activity of a growing chain is transferred to a dead polymer, some activities created on the polymer backbone chain. This is a dead polymer. So, some active site is created over here. Now, it is surrounded by monomer molecules. So, a site chain can start growing from here, again it contains active site over here. Now, if this is capable of extracting one hydrogen from another polymer chain, so (( )) gel.

So, what are the effects of these transfer reactions? These effects are apparent. It leads to low molecular weight chain, it leads to branched polymer structure, it leads to gel structure, it affects the polymer kinetics to a large extent. In practical case situation, it is not possible because the system is very high, viscous and the gel content is not very high. Gel content may be say 1 or 2 percent or less than 1 percent.

So, in order to separate that gel, that will not be economic expensive one and there is a high viscous system. How to separate it? So, these are the side reactions. Transfer reactions are kind of side reactions or adverse reactions which affects the polymer kinetics, which affects the polymer qualities, etcetera. So, the influence of transfer reactions should be given proper care, proper attention polymer manufacture. So, here you see it is shown schematically shown with the help of this relation. See, growing chain radical having n number of monomer units at the end, active side and active radical. So, this is an agent. It might be a solvent, it might be polymer, it might be a monomer, it might be an initiator, it might be an impurity anything.

So, what happens is this transfer, its radical side radical activity to this molecule by attaching X with this one and producing a new active side, new radical. Now, this new radical may or may not be capable of initiating. There is no guarantee that it will initiate, but it can initiate that is called reinitiation K a, reinitiation rate constant K a. Now, its kinetics of growth is totally different from the normal kinetics, normal propagation reactions. You understand? So, this is the situation. If there is transfer reaction, if that occurs during that should be minimized, but in order to have a proper control over the molecular weight as well as the molecular weight distribution as you have seen earlier, this X w bar by, sorry X n bar. This ratio can be controlled by deliberate addition of transfer agents, deliberate addition of chain transfer agent. Why that is necessary?

Why we need a polydisperse polymer, not monodisperse? Because you think of a polydisperse polymers being a mixture of molecules of different sizes. It contains low molecular weight, high molecular weight as well as medium molecular weight, that is if the molecular distribution is broad, the presence of low molecular weight spaces in the polymer sample helps in better processing, easy processing of the polymer by melt processing techniques or solution processing technique. So, these things (( )) mentioning for your reference, it may be necessary in later stages.

So, molecular weight distribution can be controlled by deliberate addition of chain transfer agent. That is different thing that you are deliberately adding some chain transfer agent to control the polymer molecular weight as well as molecular weight distribution, but these effects of transfer reactions on to monomer, on to a dead polymer chain, on to an impurity, on to solvent, these are not always recommended because these reactions become unaccounted for unknown things. That means, if you do not have any control over them, so while you are going to synthesize or manufacture a polymer in a solution technique or bulk technique, you select a suitable monomer initiator system, suitable monomer initiator solvent system, so that there are minimum transfer reactions.

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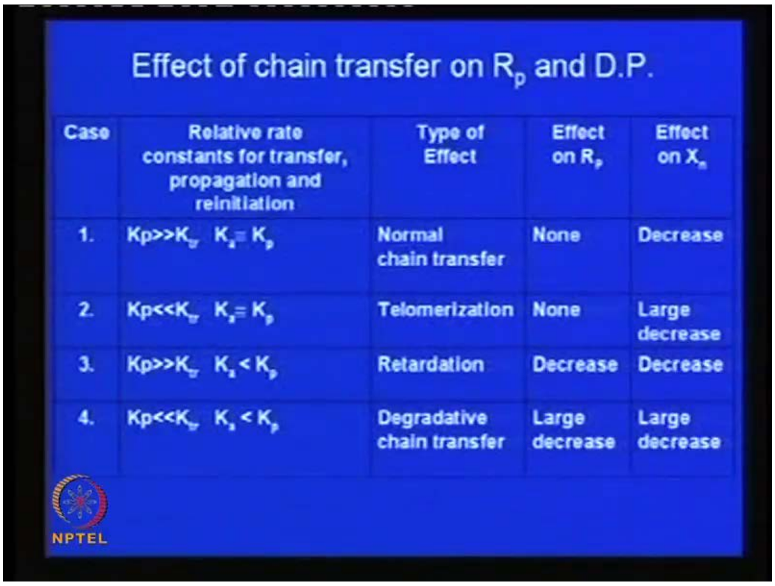

Effect of chain transfer on R_p and D.P.

Case	Relative rate constants for transfer, propagation and reinitiation	Type of Effect	Effect on R_p	Effect on X_n
1.	$Kp >> K_{tr}$ $K_a = K_p$	Normal chain transfer	None	Decrease
2.	$Kp << K_{tr}$ $K_a = K_p$	Telomerization	None	Large decrease
3.	$Kp >> K_{tr}$ $K_a < K_p$	Retardation	Decrease	Decrease
4.	$Kp << K_{tr}$ $K_a < K_p$	Degradative chain transfer	Large decrease	Large decrease

Look at the effect of chain transfer on rate of, and degree of. There are various cases based on these rate constant values. You know K p is rate propagation, K t R is the rate of transfer reaction, not termination transfer reaction, it is also a kind of termination killing activity, but its activity is transferred to some other space which is not accounted for. Its growth is annihilated premature. Annihilation transfer reaction is a kind of premature termination. Premature termination is not a desire situation. So, that is a transfer reaction. So, if the rate of propagation is, sorry rate constant propagation is greater than termination rate constant, that is normal chain transfer and effect on molecular weight, polymer molecular weight decreases.

Now, if this rate of propagation is very less than transfer constant, it leads to telomerization. Telomers means low molecular spaces oligomers, telomers means low molecular weight olygomers that will lead to a broad molecular weight distribution and there is large decrease in number of degree of is K p is greater than transfer constant, but initiation rate, initiator reinitiation rate constant is less than rate constant of propagation retardation effect of retardation. So, this needs a thorough analysis, critical analysis thinking on the rate constant, values of propagation, transfer reinitiation, all these things. So, you put some time, devote some time on this table is available in book. Also, you devote some time on this table and critically analyze the situations. What can happen is your concept will be clear, all right.

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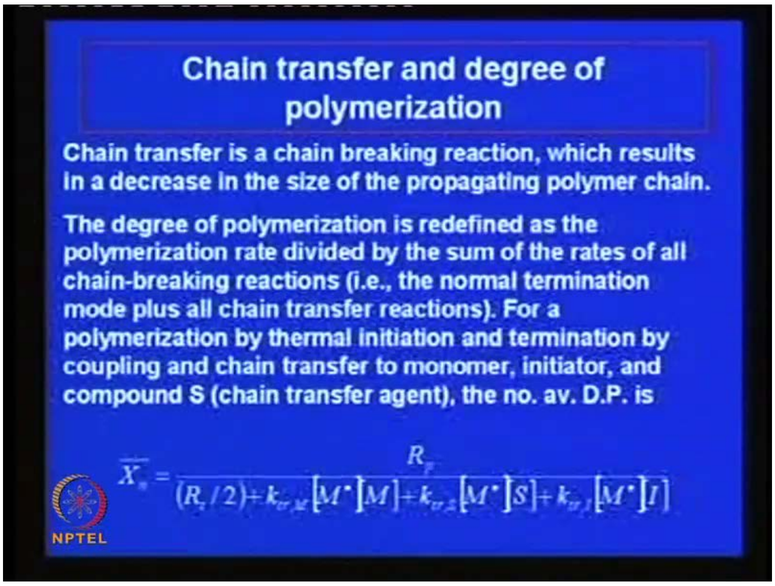

Chain transfer and degree of polymerization

Chain transfer is a chain breaking reaction, which results in a decrease in the size of the propagating polymer chain.

The degree of polymerization is redefined as the polymerization rate divided by the sum of the rates of all chain-breaking reactions (i.e., the normal termination mode plus all chain transfer reactions). For a polymerization by thermal initiation and termination by coupling and chain transfer to monomer, initiator, and compound S (chain transfer agent), the no. av. D.P. is

$$\overline{X}_n = \frac{R_p}{(R_t/2) + k_{tr,M}[M^\bullet][M] + k_{tr,S}[M^\bullet][S] + k_{tr,I}[M^\bullet][I]}$$

Now, let us see how to calculate the influence of those various transfer reactions on the number of arrays, degree of polymerization chain. Now, you know these numbers of arrays degree of polymerization of the kinetic chain length, you saw is the ratio of R p by R t rate of propagation divide by rate of termination. Now, if this rate of termination is combination of normal termination reaction, as well as various transfer reactions because those transfer reactions lead to termination of the polymer growth.

So, if you take a sum of different rates of termination reactions beyond normal termination, then if you sum up those different termination rates, then the ratio of rate of propagation and the rate of those terminations, some of those rates of terminations give you an account of number of arrays degree of. That means, in order to have a calculation of number of arrays degree of polymerization involving various transfer reactions. You have to consider this relation. It seems very complicated or clumsy. It is that not at all this is very simple thing. You just could not see in this screen, it is not visible.

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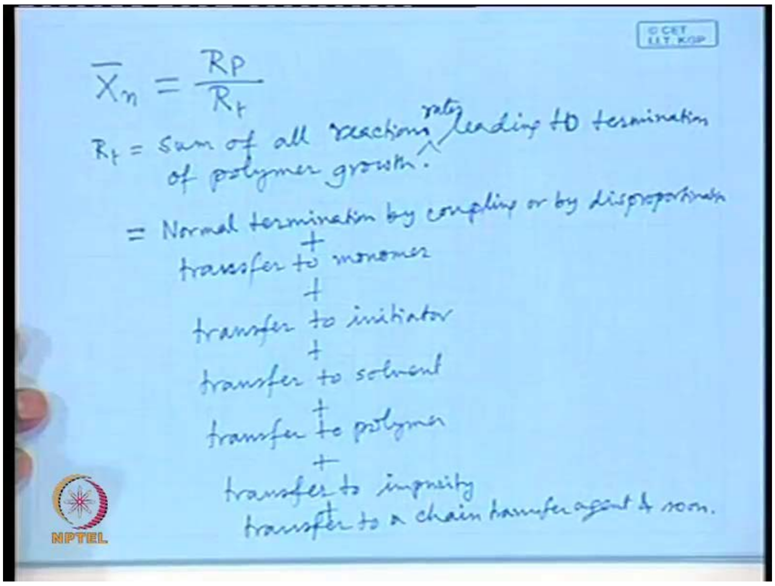

$$\overline{X}_n = \frac{R_P}{R_t}$$

R_t = Sum of all reactions rates leading to termination of polymer growth.

= Normal termination by coupling or by disproportionation

\+

transfer to monomer

\+

transfer to initiator

\+

transfer to solvent

\+

transfer to polymer

\+

transfer to impurity

\+

transfer to a chain transfer agent & soon.

Then, I am writing X n bar is equal to R p by R t. What is R t? Sum of all reactions leading to all reaction rates leading to termination of polymer growth. What are those? Normal termination by coupling or by disproportionation plus transfer to monomer plus transfer to initiator plus transfer to solvent plus transfer to polymer plus transfer to impurity plus transfer to a chain transfer agent and so on. Those expressions for their rates, expressions of their rates, rate expression for normal termination expressions for normal termination.

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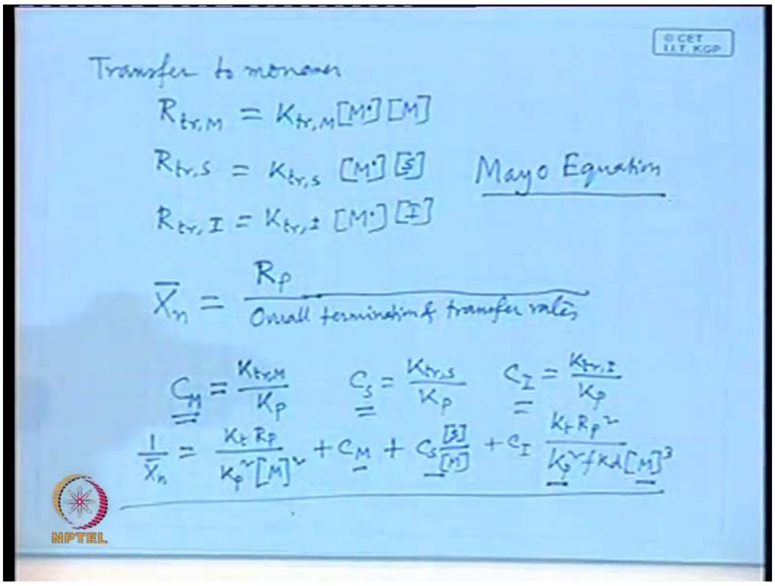

Transfer to monomer

$$R_{tr,M} = K_{tr,M}[M^{\cdot}][M]$$

$$R_{tr,S} = K_{tr,S}[M^{\cdot}][S]$$

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

Mayo Equation

$$\overline{X}_n = \frac{R_p}{\text{Overall termination \& transfer rates}}$$

$$\underline{\underline{C_M}} = \frac{K_{tr,M}}{K_p} \qquad \underline{\underline{C_S}} = \frac{K_{tr,S}}{K_p} \qquad \underline{\underline{C_I}} = \frac{K_{tr,I}}{K_p}$$

$$\frac{1}{\overline{X}_n} = \frac{K_t R_p}{K_p^2[M]^2} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{K_t R_p^2}{K_p^2 f K_d [M]^3}$$

You know R t by 2 for this normal termination. Then, the second term is K t R M M dot M. This is transfer to monomer. Transfer to monomer rate, say R t r M is equal to K t r M transfer to monomer. It is like this where a growing chain is there, monomer and transfer to solvent R t M and transfer to solvent R t s. Here, K t R s growing chain concentration of solvent. Similarly, R t R initiator transfer to monomer transfer to solvent transfer to initiator K t R initiator M i like this. Similarly, we can have transfer to polymer impurity, transfer to gen, transfer agent. So, these are varies ratio. So, some of these rates are returned. Is it too difficult to remember? Very simply. Of course, the oral expression shows over all degree of polymerization become equal to Rp by overall termination and transfer ratio.

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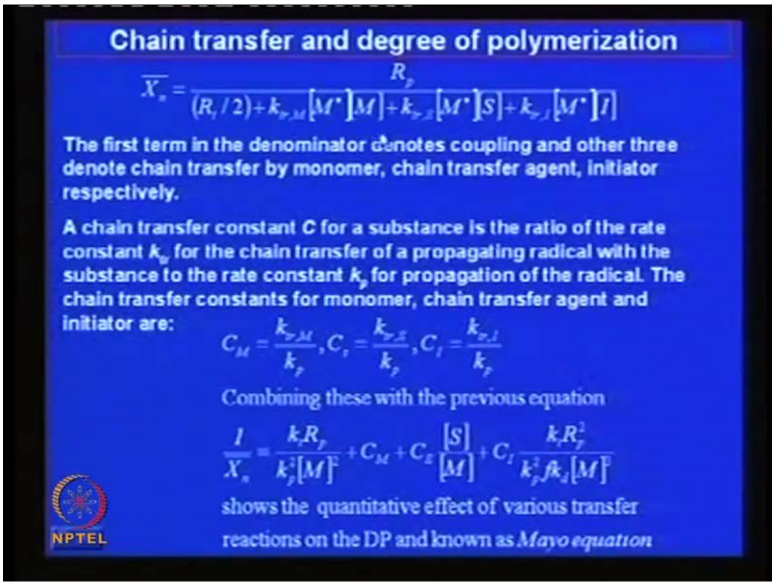

Chain transfer and degree of polymerization

$$\overline{X}_n = \frac{R_p}{(R_t/2) + k_{tr,M}[M^\bullet][M] + k_{tr,S}[M^\bullet][S] + k_{tr,I}[M^\bullet][I]}$$

The first term in the denominator denotes coupling and other three denote chain transfer by monomer, chain transfer agent, initiator respectively.

A chain transfer constant *C* for a substance is the ratio of the rate constant k_{tr} for the chain transfer of a propagating radical with the substance to the rate constant k_p for propagation of the radical. The chain transfer constants for monomer, chain transfer agent and initiator are:

$$C_M = \frac{k_{tr,M}}{k_p}, C_s = \frac{k_{tr,S}}{k_p}, C_I = \frac{k_{tr,I}}{k_p}$$

Combining these with the previous equation

$$\frac{1}{\overline{X}_n} = \frac{k_t R_p}{k_p^2[M]^2} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{k_t R_p^2}{k_p^2 f k_d [M]^3}$$

shows the quantitative effect of various transfer reactions on the DP and known as *Mayo equation*

Again shown here, same expression has shown here. You just read the first. The denominator denotes coupling and other three denote chain transfer by monomer, solvent chain transfer, agent initiator respectively. A chain transfer constant C for a substance is the ratio of another terminology is another parameter is introduced. Chain transfer constant addition and chain transfer constant is the ratio of the transfer rate, constant transfer rate. What is this? Suppose, if you want to evaluate, if you want to know this gel transfer to monomer, transfer constant for monomer C M, that is K t R M divided by K p normal propagation that this is the transfer R to monomer, this is the gel transfer constant to monomer. Similarly, C s would be equal to K t R s divided by K p. Similarly, C i would be is equal to K t R i divided by K p.

So, by substituting this transfer constants to this equation, this equation you can get relation 1 by X n bar is equal to Kt Rp divided by K p square M square plus C M plus C s concentration solvent divided by concentration of monomer plus C i K t R p square by K p square f K D M cube. If you proceed systematically, you can easily derive this relation. So, this transfer constants and this transfer constants or monomer red concentration for termination propagation and monomer concentration S H R, all this have influence on the degree of polymerization. So, this relation shows quantitative effect of varies transfer reaction on the degree of polymerization and known as Mayo equation. This equation or this top equation, this equation or these equations is known as Mayo equation.

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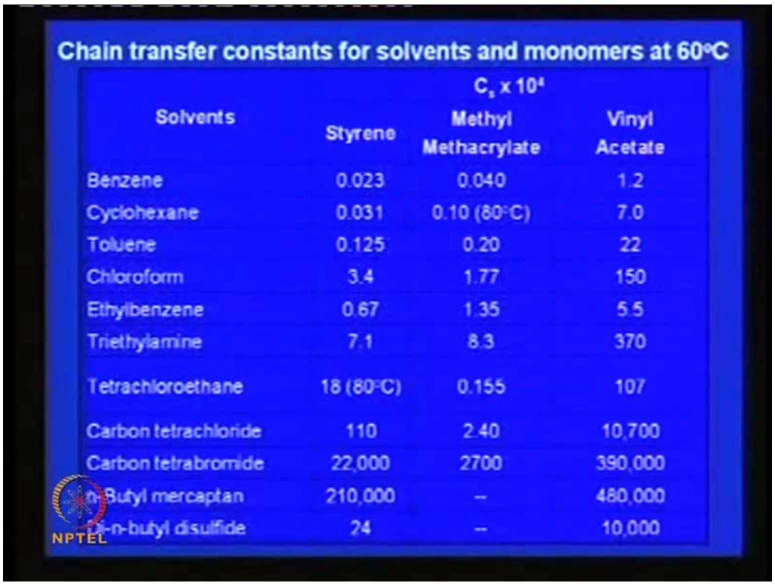

Chain transfer constants for solvents and monomers at 60°C

Solvents	Styrene	$C_s \times 10^4$ Methyl Methacrylate	Vinyl Acetate
Benzene	0.023	0.040	1.2
Cyclohexane	0.031	0.10 (80°C)	7.0
Toluene	0.125	0.20	22
Chloroform	3.4	1.77	150
Ethylbenzene	0.67	1.35	5.5
Triethylamine	7.1	8.3	370
Tetrachloroethane	18 (80°C)	0.155	107
Carbon tetrachloride	110	2.40	10,700
Carbon tetrabromide	22,000	2700	390,000
n-Butyl mercaptan	210,000	--	480,000
Di-n-butyl disulfide	24	--	10,000

Here I am writing mayo equation underlined with pen kept on the table. Look at some data. Chain transfer constant for solvent and monomer at specific temperature. So, if you take system of styrene as a monomer and benzene as the solvent, this is the transfer constant for solvent Ktr, CS value this one, this is one. How this is evaluated polymerization involving those monomers and solvents should be converted and those parameters like Kp Kt monomer, constant initiator, monomer constant, solvent constant. If those are known, then by making a flat of this something to be taken as constant portion, then you can evaluate these values constant for CS, same CI all these things. Now, here you see for benzene and styrene is 0.023. Look at this nangal butyl marcaptan transfer constant is very high for this styrene and for this acetate. That means what small quantity of methacrylate butyl octal during polymerization would be immediately stopped.

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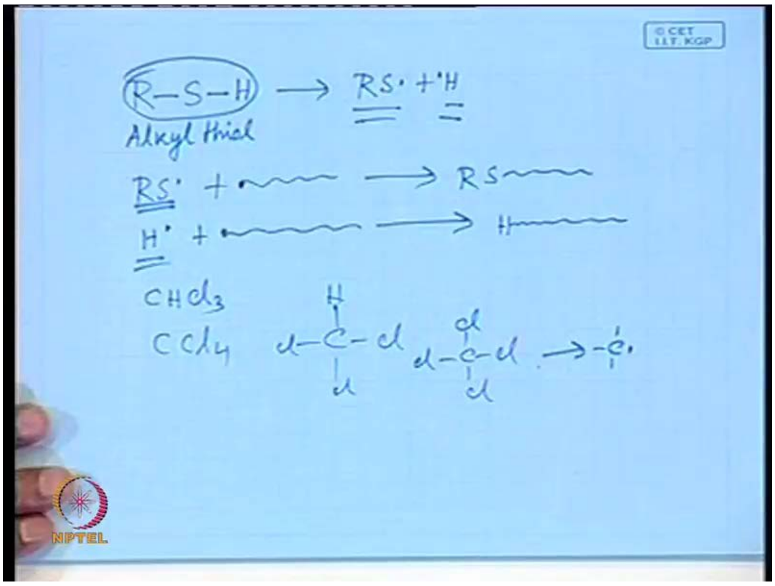

That is radical activity of those gray chain will be stopped by this butyl marcaptan. What is marcaptan? Say suppose alchoradical S and H marcaptan is a thiol. This in general, this is known as alkyl thiol regrets into radical and h radical, both are active, highly active radical. Now, these active radicals reaction is going down, so that you stop the growth of this thing, like this or H. So, activities of polymer chain transfer to this or this that will make the growth stop. Sometimes these are known as radical.

Now, here we can say how these are actually the energy available within the polymorphism system. The temperature and the environment, this molecule sufficiently will break into RS dot and H dot. Not only that, if you take chloroform or carbon red oxide, some of it depends on the energy of the cl or in case of carbon tetra chloride, C cl C cl C cl C cl. This bond can break the band id break and leave to radical. That means, in the system id, there is a chance of radical formation other than the monomer.

Then, that can effect polymer growth by such via radical, activity radical stopping activity which is known as transfer reaction. So, the ability of this monomer polymer system, every of this monomer and solvent system, student asked question of different monomers, that means different monomer solvent systems. That is why you see the value here, nubutyl marcaptan for styrene is ha 2 10 1480 1000. This value, these two monomers is different at hey, say triethytamine for this monomer styrene 7.1 and vinyl acetate 370. The transfer activity does not act as a transfer for this styrene polymerization and here acts as for agent for vinyl acetate polymerization. Understand? Student asked question here. You see chloroform is not a transfer agent for this styrene or methyl methacrytate, but it is transfer agent for vinyl acetate chain transfer constants for solvents. Actually, solvent in that use for polymerization for solution polymerization case, these shows the activity or (( )) from the growing chain of styrene, growing chain of methyl methacrytate or polymer vinyl acetate.

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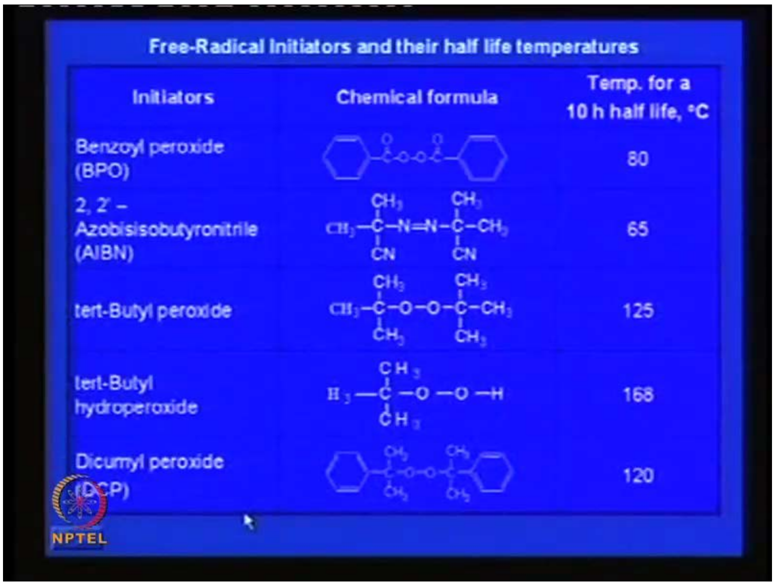

Free-Radical Initiators and their half life temperatures

Initiators	Chemical formula	Temp. for a 10 h half life, °C
Benzoyl peroxide (BPO)		80
2, 2' – Azobisisobutyronitrile (AIBN)	$CH_3-\underset{CN}{\overset{CH_3}{C}}-N{=}N-\underset{CN}{\overset{CH_3}{C}}-CH_3$	65
tert-Butyl peroxide	$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	125
tert-Butyl hydroperoxide	$H_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-H$	168
Dicumyl peroxide (DCP)		120

This same thing in another way it is shown effect of initiation radical initiators and their half life temperatures. Half life temperatures are given over here. The formulas are shown over here and half life temperatures are shown. You can see in the net. That is all.

Thank you.