Science and Technology of Polymers

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Module - 3
Lecture - 8
Principles of Polymer Synthesis

Well, in the last class I discussed about the sequences of various events, that happen during the course of polymerization of an often allophenic monomer of an allophenic monomer. In presence of some initiator I discussed that initiator needs breaking of breaking into three radicals.

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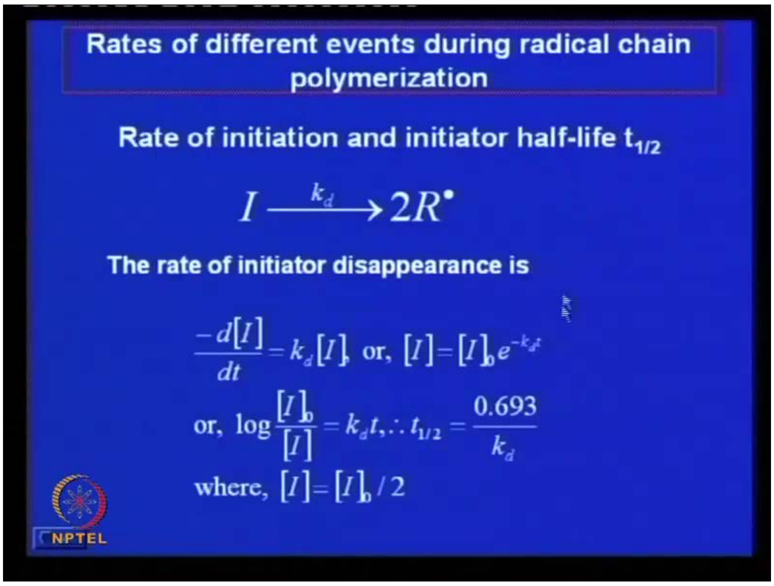

Rates of different events during radical chain polymerization

Rate of initiation and initiator half-life $t_{1/2}$

$$I \xrightarrow{k_d} 2R^{\bullet}$$

The rate of initiator disappearance is

$$\frac{-d[I]}{dt} = k_d[I], \text{ or, } [I] = [I]_0 e^{-k_d t}$$

$$\text{or, } \log\frac{[I]_0}{[I]} = k_d t, \therefore t_{1/2} = \frac{0.693}{k_d}$$

$$\text{where, } [I] = [I]_0/2$$

And those radicals initiate the monomer at continuing propagation after propagation next step is termination of the propagating free radical, which is known as growing chain radical. So, you have seen sequences of events like initiator decomposition followed by initiation of monomers or polymerization. Once the monomer once a monomer molecule is initiated, then it starts propagation to form bigger chain molecules. A time comes when those bigger macro molecular chain radicals combine at any rate with each other to form a dead polymer molecule. So, there are events like initiator decomposition, initiation, propagation and termination of the growing chain free radicals.

Of course, each and every step in this process of polymerization has its own kinetics each is guided by its own rate constant. So, if you want to evaluate the kinetics of polymerization involving allophenic monomers for addition chain polymerization. You have to consider the rates of decomposition of initiator, rate of initiation, rate of propagation and rate of termination. So, if we see here that rate of initiation and initiator half-life. Let us, discuss today you know what is half-life of initiator? That means time required for 50 percent decomposition of the initiator that is half-life. We have seen one initiator molecule decomposes to form 2 free radicals and decomposition rate constant is designated by k d.

So, from here we see the rate of initiator disappearance is expressed as minus d I by d t is equal k d into initiator concentration, I 0 I or I is equal to I 0 e to the power minus k d t applying limiting and boundary conditions at d is equal to 0 I b is I 0 and at any instant of time. What is the initiator concentration? That can be evaluated from this relation. Now, by the setting the initiated concentration at any instant of time, when the initiator molecules 50 percent of the initiator molecules have been decomposed that is the, if that is put in this equation we get half-life of the initiator at a particular temperature. Of course, that is equal to 0.693 by k d this is a quiet known relation in every case of this decomposition reactions.

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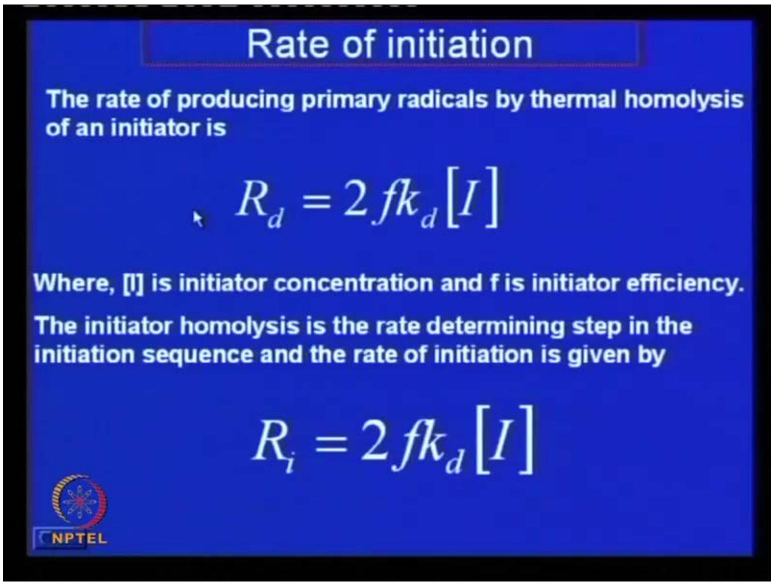

Rate of initiation

The rate of producing primary radicals by thermal homolysis of an initiator is

$$R_d = 2fk_d[I]$$

Where, [I] is initiator concentration and f is initiator efficiency.

The initiator homolysis is the rate determining step in the initiation sequence and the rate of initiation is given by

$$R_i = 2fk_d[I]$$

Now, the rate of initiation the rate of when the primary radicals are formed from the decomposition of an initiator molecule, those primary radicals interact with monomer to initiate the polymer chain. Now, the rate of that initiation is expressed as R i is equal to 2 into f k d into initiator concentration. Now, here f is the factor is a factor of efficiency factor. What is why this efficiency factor is included in this equation in this rate equation because once an initiator molecule is thermally decomposed.

Now, their thermal decomposition efficiency comes into play at the same time. It is not always true that once a radical is produced, free radical is produced that free radical is capable of initiating polymerization. So, two things efficiency of decomposition of initiator molecule as well as efficiency of initiation of monomer molecules by the generated primary free radicals these two things please do not confuse. So, in the decomposition step there is one efficiency parameter in the initiations initiations stage that is also another efficiency parameter.

So, when a polymerization is started is it not that true always that all the initiator molecules, which have been taken used for the polymerization that decompose. Initially that slowly decomposes the take time depending on its half-life and temperature if it decomposes. As soon as it decomposes it is not true that all the preprimary free radicals produced from the decomposition of the initiator will initiate the polymerization 100 percent so this efficiency parameter comes. So, here the rate of decomposition of initiator that is equal to 2 f k d I and that is equal to rate of initiation is the same 2 f k d I.

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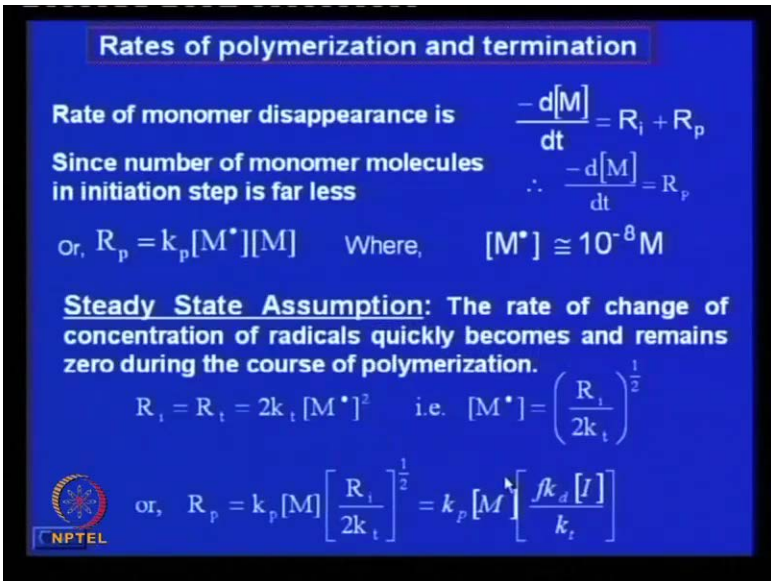

Rates of polymerization and termination

Rate of monomer disappearance is $\frac{-d[M]}{dt} = R_i + R_p$

Since number of monomer molecules in initiation step is far less $\therefore \frac{-d[M]}{dt} = R_p$

Or, $R_p = k_p[M^\bullet][M]$ Where, $[M^\bullet] \cong 10^{-8} M$

Steady State Assumption: The rate of change of concentration of radicals quickly becomes and remains zero during the course of polymerization.

$$R_i = R_t = 2k_t[M^\bullet]^2 \quad \text{i.e.} \quad [M^\bullet] = \left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}$$

$$\text{or,} \quad R_p = k_p[M]\left[\frac{R_i}{2k_t}\right]^{\frac{1}{2}} = k_p[M]\left[\frac{fk_d[I]}{k_t}\right]$$

So, what will be the rate of polymerization, now the rate of polymerization depends on this monomer disappearance. So, the monomer disappearance rate is expressed as minus d M d t where M is concentration term that is the sum of two rates, rate of initiation of monomers as well as the rate of propagation you have seen the propagation steps.

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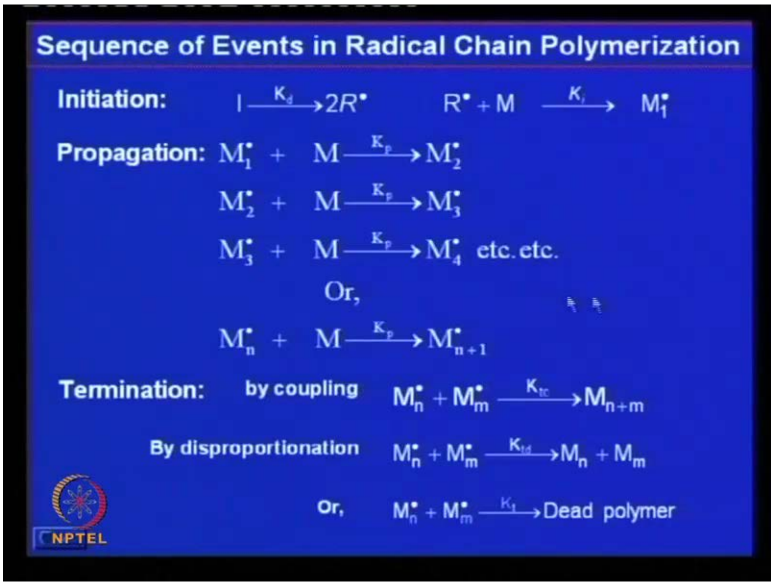

Sequence of Events in Radical Chain Polymerization

Initiation: $I \xrightarrow{K_d} 2R^\bullet \qquad R^\bullet + M \xrightarrow{K_i} M_1^\bullet$

Propagation:

$$M_1^\bullet + M \xrightarrow{K_p} M_2^\bullet$$

$$M_2^\bullet + M \xrightarrow{K_p} M_3^\bullet$$

$$M_3^\bullet + M \xrightarrow{K_p} M_4^\bullet \text{ etc. etc.}$$

Or,

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

Termination: by coupling $M_n^\bullet + M_m^\bullet \xrightarrow{K_{tc}} M_{n+m}$

By disproportionation $M_n^\bullet + M_m^\bullet \xrightarrow{K_{td}} M_n + M_m$

Or, $M_n^\bullet + M_m^\bullet \xrightarrow{K_t} \text{Dead polymer}$

Let, me go back to this here you see this is decomposition step, initiator decomposition step, this is the initiation step, this are the propagation steps all these propagation steps proceed the same rate. So, in every case you see only one red constant is included here as

K p. Then termination where we turn this termination constant as K t c if it is terminated by coupling reaction coupling of two growing free radicals or if it terminates by this proportionate reaction. So, we term it as denote it as K t d here the molecular weight is lower in this case at the molecular rate of the polymer is bigger. And ultimately overall if we consider the overall termination involving two growing chain free radicals, we call it a dead polymer molecule.

So, this is the termination step is a death activity, killing activity of the propagating polymer chains from propagating polymer free radical chains. So, here you see the since the number of monomer molecules in initiation step is far less here. I have shown this is rate of disappearance of monomer can be considered as the rate of polymerization because here monomer is disappeared to form a polymer. So, if we measure the rate of disappearance of monomer, then we can find out the rate of polymerization. Now, as it is shown that this rate is the sum of two different rates, rate of initiation because in the initiation step monomer is also disappeared. And in the propagation step monomer is also disappeared, but since in the monomer initiation step. The consumption of the monomer is far and far less than the consumption of monomer in the propagation steps.

The physical significance is like this once an initiate once a initiator molecules are decomposed producing primary free radicals. So, at any instant of time there may be plenty of primary free radicals in the system. So, simultaneously one can expect initiation of many polymer chains. In those initiation steps only one monomer is involved whereas, in all those initiated monomer chains starts consuming monomer in the propagation step. So, the consumption of monomers overall consumption of monomers in the propagation step is far and far ahead of this monomer consumption in the initial stage.

So, that R i in this expression in this rate expression if it is neglected that is nothing wrong. So, overall rate of polymerization R p can expressed as overall disappearance of the monomer minus d M by d t. So, it can also be expressed as R p is equal to rate constant of propagation k p growing chain radical concentration into monomer concentration. Where the concentration of the monomer is very less concentration of this growing chain is very less it is so trangient it is. So, trangient that if you once it is initiated within a very short period it completes its growth and gets terminated becomes dead. So, in the any at any instant of time if one measures the concentration of the growing chain radicals it is very less, although it is very difficult to measure again. There is no experimental technique availability left that such strange concentration of such trangient intermediate species can be evaluated.

Now, in order to calculator evaluate this rate of propagation you have to know this parameters k p M dot and M, that means concentration of monomer at an instant of time unreacted monomer remaining and M. Now, this is this can be this can be estimated, the quantity of monomer present at any instant of time can be estimated there are procedures, but how to estimate this thing as I mentioned this concentration is very less. So, trangient that it is very difficult to receive an almost impossible, but although I have said it is not so stable, but it has got it must have adequate stability for colliding with a monomer molecule for the growth activity for the propagation.

You should not confuse with that although it is very fast that is why its concentration is very less, but it has got sufficient stability. That means stability of the growing chain radical through the resonance stabilization. Hyper concentration things I have shown earlier that way it are stable adequately. So, that an incoming monomer can collide with this growing chain free radical site and add on to it. Otherwise one cannot get a polymer chain one cannot get a polymerization product.

In order to evaluate this concentration a steady state assumption has been taken done, what is that? That is the rate of change of concentration of growing chain radicals quickly becomes 0 and remains 0. During the course of polymerization rate of change of concentration rate of change of concentration of radicals quickly becomes 0 as well as remains 0 during the course of polymerization. If it is elaborated in this way that, once a growing chain is initiated eventually it is converted to a macro molecular chain and it is terminated.

So, if you assume that rate of initiation is equal to the rate of termination, in other way you can take this concept of steady state. At the steady state rate of initiation becomes equal to rate of termination. Now, let us see what the rates of initiation rate of termination. Now, the rate of termination is 2 k t M dot square this factor of 2 here is due to the fact, that during this termination two growing free radical are involved in this termination process there is a concept convention.

Since, two radicals are involved in the termination step so this factor of two has come and this is here M dot into M dot M dot square. So, from this relation one can take one can get the concentration of this growing free radical chain is equal to R i 2 k t under square root. Since, R i is equal to 2 f k d I one can after substituting this concentration of M dot square growing chain radical concentration here in this equation. In this equation you can get this expression after substituting of this expression by this efficiency factor has been included in the rate equation.

So, this is the overall rate of propagation, overall rate of polymerization you should not forget this thing. So, R p is equal to rate constant into the monomer concentration term into efficiency factor into rate of decomposition of the initiator into initiator concentration divided by a rate of termination rate constant should be half over here. It cannot be turned now somehow it was there do not worry for these things these minor things it is square is there R i by 2 k t k d I by f. So, this is overall rate of propagation overall rate of polymerization one second I repeat R p is equal to k p M k p M if k d I by I k t to the power half.

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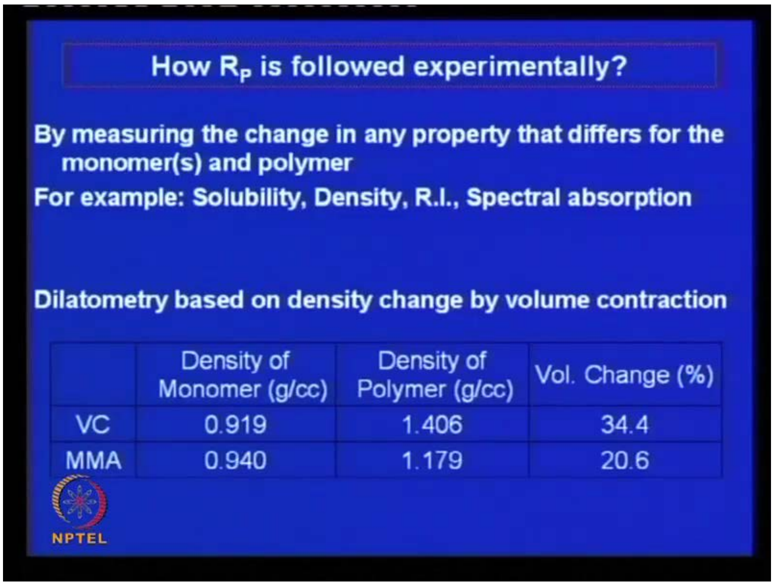

How R_P is followed experimentally?

By measuring the change in any property that differs for the monomer(s) and polymer

For example: Solubility, Density, R.I., Spectral absorption

Dilatometry based on density change by volume contraction

	Density of Monomer (g/cc)	Density of Polymer (g/cc)	Vol. Change (%)
VC	0.919	1.406	34.4
MMA	0.940	1.179	20.6

Now, the question is how this rate of this polymerization is experimentally followed how it is evaluated well. You can say sir, you are showing us with the help of these expressions or equations that this is the way to get this rate of polymerization, but how to experimentally evaluated. Suppose you are given this assignment of synthesizing poly methyl, methyl acrylate or poly phenyl chloride or poly phenyl acetate in the laboratory. If I ask you to evaluate the rate of such polymerization how to evaluate, that means you have to go through by measuring the change in any of the property that differs for the monomers and polymers.

Now, that property may be solubility, that property may be density, that property may be refractive index, that property may be specific volume. So, there are instruments like very simple instruments if in you can fabricate it your laboratory. If you prepared the dilatometer or dilatometer is nothing but a very small bulb, glass bulb connected with a capillary. You know you have seen this glass thermometer in the glass thermometer there is bulb filled with mercury connected to a capillary. So, this rise of this mercury three through the capillary helps us to measure the temperature of a system, it is simply like a same it is similar kind of thing.

So, you can prepare a dilatometer you fill the dilatometer with the monomer and initiator or monomer initiator solution or you can take in a solvent also. Then you place dilatometer and close it and then place the dilatometer in thermostatic bath, which can maintain a constant temperature. Then raise the temperature of this thermostatic bath to the decomposition temperature of the initiator say 80 degree Celsius for benzoyl peroxide.

What will happen benzoyl peroxide will decompose and will initiate polymerization, as soon as it starts polymerization initiate polymerization it will convert the monomer to polymer. Once it converts monomer is converted into polymer there will be volume sinkage, sinkage in volume. So, that volume sinkage can be read from the capillary scale of the capillary, that can help you to measure the change in volume or as well as the change in density like that. You can say you carry on this polymerization in silt ampoules, you have seen medicines liquid medicines for hypodermic or interferon injections are available in silt ampoules. What do you do? You break over the ampoule and suck the liquid by hypodermic syringe then we inject in the body.

Similarly, here also you feel take this monomer initiator and in an ampoule and evacuate it by facing in liquid nitrogen temperature. It will frozen after it is frozen liquid is frozen then you connect it to a vacuum line evacuate the oxygen here, then in that evacuated condition you seal it. So, you can have several sealed monomer and sealed ampoules evacuated sealed ampoules in many numbers, then you place all those ampoules monomer ampoules monomer filled ampoules in a thermostatic bath. It is the temperature of bath to the decomposition temperature of the initiator. Then you take out the sealed ampoules time to time after some specific time intervals of about 5 minute or 10 minute or 20 minute intervals take out it and freeze it.

So, that you stop arrest the reaction by freezing open the break the ampoule and pour the liquid in non-solvent. What you will see? The polymer which has been formed within the ampoule it remained soluble in the mono un reacted monomer. When you pour that polymer solution in non-solvent like methyl I suppose. So, you are polymerizing methyl methyl acrylate into poly methyl methyl acrylate, which poly methyl methyl acrylate remains dissolved in methyl acrylate poly methyl methyl acryl ate monomer.

So, you are pouring a polymer solution in methyl methyl acrylate into a non-solvent like methanol as soon as you pour it immediately, it will precipitate out it will solidify. This show a see in the first after the first interval of 20 minute you have taken the first ampoule. You have poured in this non-solvent you have got a solid precipitator polymer then you filter it quantitatively. Wash it with solvent plus solvent to remove the un reacted monomer then you dry it and take the wet.

You know the quantity of monomer take was taken has contained in that ampoule from that you can calculate how much monomer has been converted to this solid polymer then you take the second ampoule. You take out the second ampoule, which is grown further to that of the first one do the repeat the same process isolate the solid polymer by putting in non-solvent wash it, dry it take the wet this time. You will have samples like ten samples suppose and you will find that starting from sample one to sample ten you will find that the amount of polymer you have got will be different, you will be casually more and more and more.

So, that can also help you how much polymer that will give you a conversion percent conversion and that percent conversion you know the time at what after what time you have taken out the ampoule from thermostatic bath. You know the time so amount of polymer you have got after that times from that you can calculate the rate of polymerization.

So, that is the way another way if you do not have any sophisticated instrument this is the simplest way available to you in the laboratory. You can carry out the you can evaluate the rate of polymerization of that particular monomer or if you have some instruments like say UV or other spectroscopic instrument, with the help of the spectroscopic instrument you can also evaluate the rate.

Now, in a dilatometeric experiment with the taking the help of the dilatometer based on density change by volume contraction cases of vinyl acrylate polymerization and methyl methyl acrylate polymerization, this was the density of the monomer, then density of the polymer. So, volume change is this from this volume change, which is propositional to the growth that way one can calculate the rate of polymerization.

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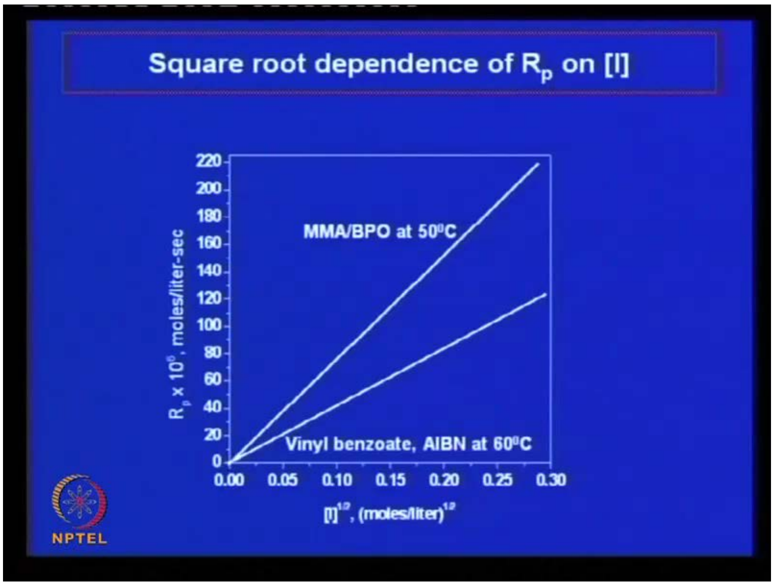

Square root dependence of R_p on [I]

This shows a square root dependence of rate of polymerization on initiative contraceptive. Now, many people have done extensively research on this effect of initiator concentration on the polymerization rate, effect of monomer concentration on the polymerization rate, effect of temperature on the polymerization rate, effect of different initiators on the polymerization rate, effect of presence of different solvents in the polymerization all these things. We do not have that much of scope for discussion of those details in this particular course, but just I mention you that question should automatically come.

Sir, what would be the optimum concentration of initiator, which should we taken for polymerization of one particular monomer either one particular initiator will be suitable for all the monomers for polymerization. So, these questions automatically comes the answer is no. It is specific to a specific system of monomer and initiator an initiator used for polymerization of phenyl chloride may not be efficient for polymerization of methyl methyl acrylate may not be so effective for polymerization of styrene, may not be so effective for polymerization of acryl amide.

So, this is the situation not only that what is the effect of temperature of polymerization? What is effect of initiator concentration if in if one initiator is selected as a as an efficient initiator for one polymerization of one monomer to get a polymer of that monomer. That what is the optimum concentration of that initiator, which gives you maximum conversion as well as deserved molecular weight or highest molecular weight as well as highest rate that is to be evaluated? And those works have already been done or many monomers, but for your understanding for your information.

Just I mentioning here a case where monomer methyl methyl acrylate was polymerized in presence of benzoyl peroxide at 50 degree Celsius and vinyl benzoate another monomer was polymerized. Using as iso diisobutyl trio nitrite as an initiator, iso diisobutyl trio nitrite at 60 degree Celsius. So, this is the rate behavior this is the schematic drawing all the scales are there this is not to the scale let be of like this.

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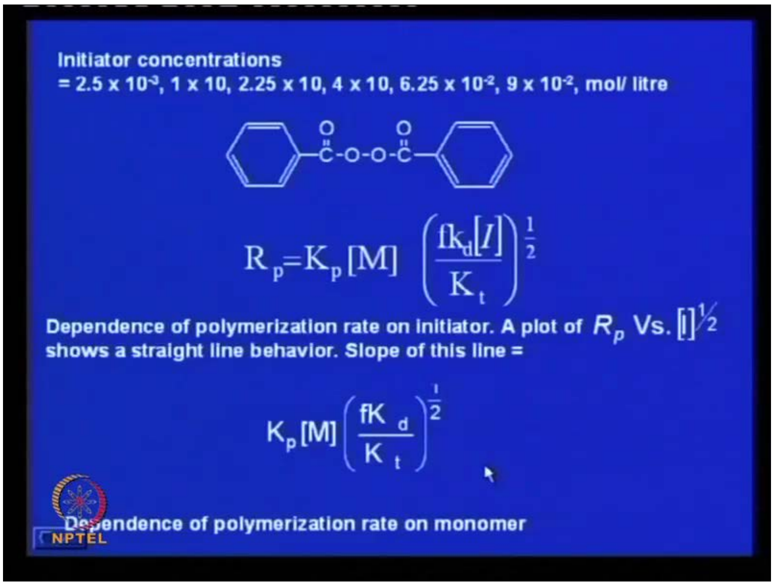

Initiator concentrations
= 2.5×10^{-3}, 1×10, 2.25×10, 4×10, 6.25×10^{-2}, 9×10^{-2}, mol/ litre

$$R_p = K_p[M]\left(\frac{fk_d[I]}{K_t}\right)^{\frac{1}{2}}$$

Dependence of polymerization rate on initiator. A plot of R_p Vs. $[I]^{1/2}$ shows a straight line behavior. Slope of this line =

$$K_p[M]\left(\frac{fK_d}{K_t}\right)^{\frac{1}{2}}$$

Dependence of polymerization rate on monomer

Now, in order to evaluate this thing rate as well as other parameters just you see. You take select different concentration of initiators you say this is another one concentration this another concentration this is another concentration like this. So, different concentrations are selected of this initiator, this is benzoyl peroxide, its break over here and ultimately what happens carbon dioxide is released and some phenyl radical is produced. So, both this radical as well as this phenyl radical initiate the polymerization and this is the overall rate of polymerization.

Now, in order to know the dependency of polymerization rate on initiator a plot of R p as such initiator concentration as you have shown earlier, you have seen earlier that is plotted. Then this is the slope of curve. So, if you know this parameters K d K t monomer concentration and K p, so you can calculate the initiator efficiency factor a factor value of a factor, if you know this f K d K t M. Then you can evaluate this K p. So, this is the way by just measuring the rate of polymerization and if some other parameters are known some unknown parameter can be calculated from this polymerization.

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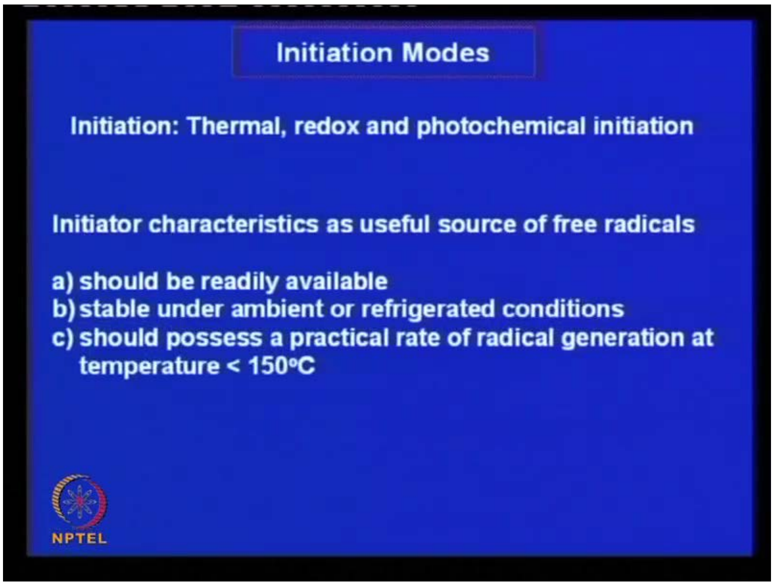

Initiation Modes

Initiation: Thermal, redox and photochemical initiation

Initiator characteristics as useful source of free radicals

a) should be readily available
b) stable under ambient or refrigerated conditions
c) should possess a practical rate of radical generation at temperature < 150°C

Just I have mentioned that in general that an initiator decomposes to produce two primary free radicals. What is that initiator and how they are decomposed that means they must be excited by different forms energy may be thermal energy, may be light energy or may be chemical energy. So, here only three cases are mentioned say thermal initiation by thermal excitation of the monomers by initiators, those initiators decompose to form primary free radicals. Those primary free radicals initiate a monomer to form a polymer if you should ask a question, but you are not asking question that. If we do not use initiator what can happen can you get a polymer is there any real necessity of initiator can only this monomers form polymer without using an initiate answer yes or no, if you do not use an initiator can we get polymer from a monomer that is one stimulation you are giving.

I am telling that if you do not use any initiator yes that is one way other than radiation. Here, is given some clue can allophenic monomers undergo polymerization without using any initiator how? Of course, by homolysis of double bonds how? By supplying of energy (( )) what is that form of energy as he told that either radiation electromagnetic radiation or thermal stimulation. Both can initiate the polymerization and can help getting a polymer, but that polymerization is not easy to control that polymerization kinetics.

Say, if you keep a monomer within a bottle within a container at an ambient condition for a long period that monomer can start polymerization within the container. Now, after sometime you will find that entire monomer has been converted to polymer solid polymer it happens. In the laboratory if you keep methyl methy acrylate or styrene in a bottle on the rack you will find after 6 months of time that entire monomer has converted to a solid material that is polymer. Polystyrene or poly methyl methyl acrylate for that reason that monomer needs stabilization by putting innovator.

Why that happens, because in this ambient ambient condition the temperature that is from 20 degrees to 40 degree 44 degree like that, so that temperature can slowly initiate the monomer as simple as you told that thermal homolysis of the allophenic double bond. Once a double bond is opened that will initiate the polymerization the so many monomer as radical monomer chains polymer chains (( )). Of course, if the monomer is not pure if there is impurity that impurity can also start polymerization. So, monomers should be start stored in a pure condition as well as it should be stored with the help of the innovator. That means you have to add such innovator for example, these monomers are stored with hydroquinone. Hydroquinone is a innovator molecule what is role of initiator innovator.

Now, if there is a possibility of breaking monomer molecule thermolysis homilies thermal homilies of the monomer polyphonic monomer double bond that free radical will be scavenged stopped I directing with this hydroquinone radical. So, that innovates unit that is initiation that innovator will innovate its growth that is called initiation. So, thermal initiation is possible photochemical initiative is possible. So, if electromagnetic radiation if a monomer is exposed to electromagnet radiation. That means energy should be sufficient enough to break that allophenic double bond, which may be in the form of heat, may be in the form of chemical energy or may be in the form of electromagnetic radiation energy.

Now, initiative characteristics are should be readily available should be stable under ambient or refrigerated conditions. So, that this initiator starts decomposition should possess a practical rate of radical generation at temperature less than 50 degree Celsius. Otherwise, if the polymerization needs to be carried out at high temperature then the cost of the polymer will be high.

It is convenient it will be economic, it will be convenient as well as it is an economic. If the polymerization can be carried out at lower temperature there are various reasons. We can save energy if a polymerization at lower temperature. At the same if we carry out the polymerization at the higher temperature, what will happen it can give you higher productivity. Although, at the higher cost it can give you higher productivity, but that will lead to random kinetics, uncontrollable kinetics of the polymerization what can happen during polymerization. A polymer reactor polymerization reactor can explode because such polymerization reactions are highly exothermic in nature. If there is acceleration of rate of polymerization at any instant of time, eventually at any moment there will be huge accumulation of huge quantity of heat accumulation of huge quantity of heat within the reactor.

If that heat could not be dissipated from the reactor, that reactor will explode so those are the problems and difficulties. So, in order to avoid all these problems it is better to polymerize at lower temperature which can be controlled that will remain at your control in entire polymerization kinetics. So, it is advisable or it is better if the polymerization is carried out at lower temperature. Although, polymerizations are carried out at higher temperature for some cases say in the gas phase allophenic polymerization of ethylene propylene etcetera. If you look into literature you will find that that your technology of manufacture of polyethylene poly propylene at high temperature gas phase polymerization.

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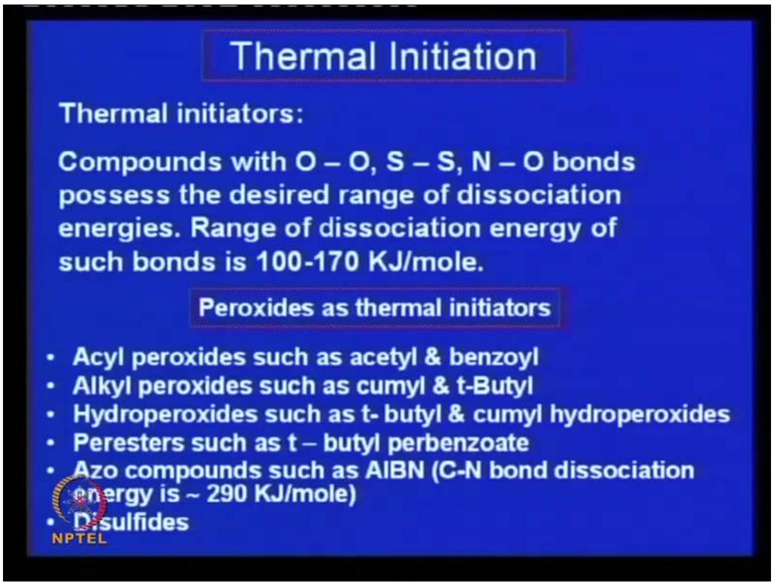

Thermal Initiation

Thermal initiators:

Compounds with O – O, S – S, N – O bonds possess the desired range of dissociation energies. Range of dissociation energy of such bonds is 100-170 KJ/mole.

Peroxides as thermal initiators

- Acyl peroxides such as acetyl & benzoyl
- Alkyl peroxides such as cumyl & t-Butyl
- Hydroperoxides such as t- butyl & cumyl hydroperoxides
- Peresters such as t – butyl perbenzoate
- Azo compounds such as AIBN (C-N bond dissociation energy is ~ 290 KJ/mole)
- Disulfides

Thermal initiators contains O O bonds, S S bond, N O bonds that possess desired range of dissociation energies, which lie within this value 100 to 170 kilo joule per mole. So, a compounds chemical compound having such bonds can act as initiator thermal initiators. Now, if you take peroxide compounds as thermal initiator or as a compound of thermal initiator are acyl peroxide and acetyl and benzoyl peroxides alkyl peroxides such as cumyl and tertiary butyl peroxides.

Hydro peroxides such as tertiary butyl and cumyl hydroxides peresters such as tertiary butyl perbenzoate as a compound such as isobutyl nitrite 2 2 dash, 2 2 prime isodiis isobutyl nitride, where it contains C N bond that is… This energy is C N bond energy is quiet high, but in a bonds breaks and disulphide disulphides or thiols thiols organic thiols that can also be used as initiators for polymerization of allophenic monomers.

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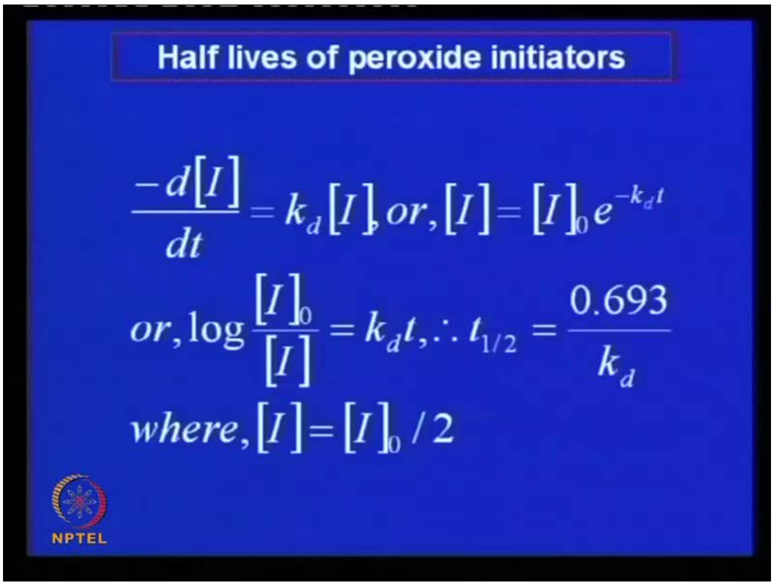

Half lives of peroxide initiators

$$\frac{-d[I]}{dt} = k_d[I]\, or, [I] = [I]_0 e^{-k_d t}$$

$$or, \log\frac{[I]_0}{[I]} = k_d t, \therefore t_{1/2} = \frac{0.693}{k_d}$$

$$where, [I] = [I]_0/2$$

Half-lives of peroxide initiators we have already seen, how that can be calculated knowing half-lives of initiators helps to select suitable initiator for one particular system of polymerization.

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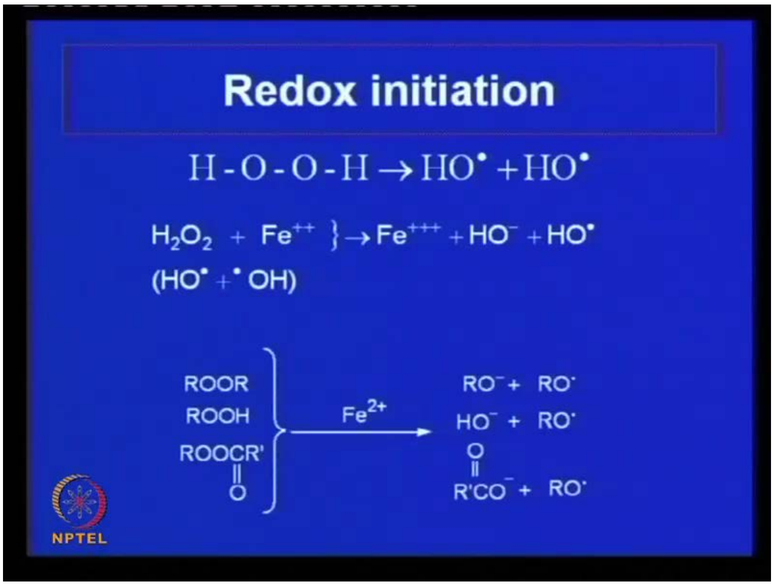

Redox initiation

$$\mathrm{H\text{-}O\text{-}O\text{-}H \rightarrow HO^{\bullet} + HO^{\bullet}}$$

$$\mathrm{H_2O_2 + Fe^{++}} \}\rightarrow \mathrm{Fe^{+++} + HO^{-} + HO^{\bullet}}$$

$$\mathrm{(HO^{\bullet} + {}^{\bullet}OH)}$$

$$\left.\begin{matrix}\mathrm{ROOR}\\ \mathrm{ROOH}\\ \mathrm{ROO\overset{}{C}R'} \\ \mathrm{\;\;\;\;\;\;\; \| \;\;} \\ \mathrm{\;\;\;\;\;\;\;O\;\;}\end{matrix}\right\} \xrightarrow{\mathrm{Fe^{2+}}} \begin{matrix}\mathrm{RO^{-} + RO^{\cdot}}\\ \mathrm{HO^{-} + RO^{\cdot}}\\ \mathrm{\;O}\\ \mathrm{\;\|}\\ \mathrm{R'CO^{-} + RO^{\cdot}}\end{matrix}$$

Redox initiation what is redox initiation? That redox initiation is more advantageous than thermal initiation because redox initiation can be carried out at very lower temperature lower than ambient temperature. Even say if you take hydrogen peroxide and ferrous system ferrous salt and hydrogen peroxide that produce on as well as free radical.

Because the hydrogen peroxide homiletic decomposition on two radicals and that interacts with ferrasion. So, it is oxidized to ferric and an ion and a free radical will be produced that free radical in said polymerization and that is done at very low temperature at ambient temperature. That means from 0 to 50 degree Celsius temperature at 0 to 50 degree Celsius temperature this redox system can occur or say partial per sulphate aluminum per sulphate, this can be used as oxidant instead of ferrous ferric that is also a free radical polymerization. Let, me give you an example of polymerization of styrene and butadiene copolymerization of styrene and butadiene. The styrene butadiene can be done in solution again the demands of polymerization copolymerization can be done in bulk, can be done in solution, can be done in emulsion.

Again that emulsion polymerization can be done at higher temperature can be done at lower temperature and we will find later not now. We will cover in this course that styrene butadiene rubber that is manufactured by two major techniques cold technique and hot technique, hot polymerization is carried out at 50 degree Celsius temperature using this redox initiation system.

As well as that cold polymerization of copolymerization of styrene butadiene that is carried out at lower temperature, say 5 to 10 degree Celsius temperature cold polymerization and hot polymerization. Now, it has been found that polymer obtained through cold polymerization carried out at 5 to 10 degree Celsius gives better quality of rubber. Better quality of styrene butadiene rubber cold polymer is better gives high molecular rate at higher rate as well as excellent molecular rate distribution, this gives the same thing a general system of peroxides exile peroxide etcetera.

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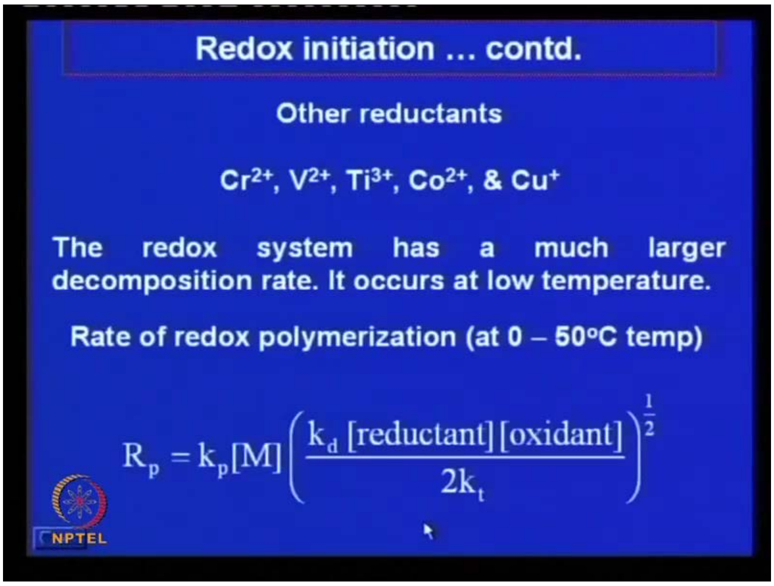

Redox initiation … contd.

Other reductants

Cr^{2+}, V^{2+}, Ti^{3+}, Co^{2+}, & Cu^{+}

The redox system has a much larger decomposition rate. It occurs at low temperature.

Rate of redox polymerization (at 0 – 50°C temp)

$$R_p = k_p[M]\left(\frac{k_d\,[\text{reductant}]\,[\text{oxidant}]}{2k_t}\right)^{\frac{1}{2}}$$

Decomposition into free radicals and ions, other reductant, which can also be used say chromium, vanadium, titanium, cobalt and copper in the ready state. The redox system has a much larger decomposition rate it occurs at low temperature and the rate of redox polymerization gives you very good rate. At this temperature range and this rate of this redox polymerization can be calculated can be evaluated with the help of this expression. You can compare why I have shown this thing you can compare the rate of polymerization using thermal initiation as you have seen R p is equal to k p M f k d I by 2 k t to the power half. Here, you see k p M as efficiency factor is not there k d reductant concentration, oxidant concentration by 2 k t to the power half as the efficiency factor the decomposition factor that is not included here. That is the difference between that rate expression with this redox polymerization rate expression.

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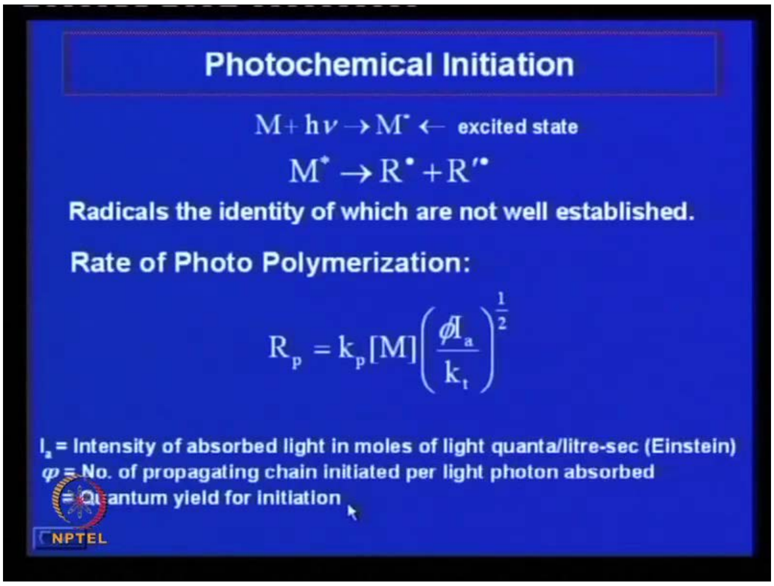

Photochemical Initiation

$M + h\nu \rightarrow M^{*} \leftarrow$ excited state

$M^{*} \rightarrow R^{\bullet} + R'^{\bullet}$

Radicals the identity of which are not well established.

Rate of Photo Polymerization:

$$R_p = k_p[M]\left(\frac{\phi I_a}{k_t}\right)^{\frac{1}{2}}$$

I_a = Intensity of absorbed light in moles of light quanta/litre-sec (Einstein)

φ = No. of propagating chain initiated per light photon absorbed

= Quantum yield for initiation

Photochemical initiation monomer the monomer and this is the light h v and this is the excited state of the monomer, when it absorbs the light of a suitable wave length. Now, this once this monomer is excited by light the disassociation the bond of that monomer by bond that disassociates producing free radical, R dot and R prime dot and that initiates polymerization. Now, there are other considerations too.

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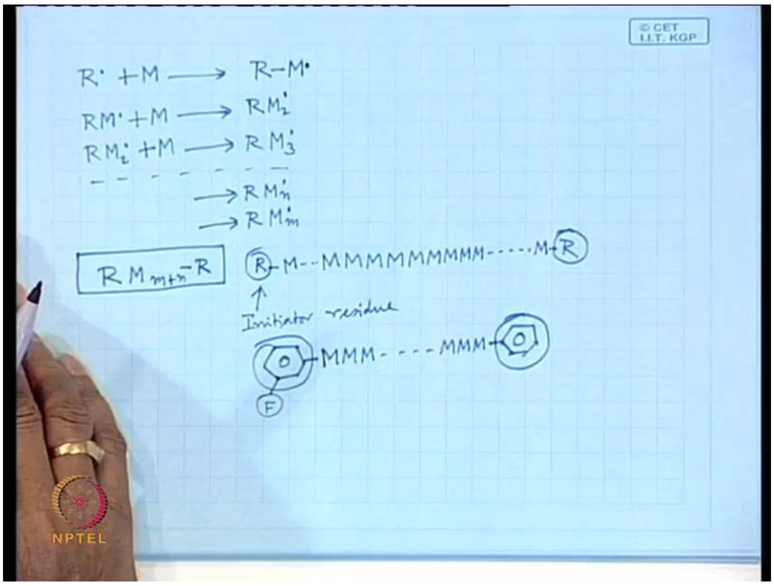

You have seen in case of thermal initiation that sequences of events, that you have seen that primary radical R that adds to the monomer at the initiation step for being an initiative radical, this R M dot adds two another monomer for being R M 2 dot. R M 2 dot plus M R M 3 dot this shows a it continues till we get R M n dot likewise. We can get R M m dot and in this in the termination step we get R M m plus n R. So, look at the chemical nature of this polymer here M M you are having a chain of M at the end on R group are at the end another R group. What is this R? This is these are initiator residue initiator residue that remains attached to this polymer chain say if you take benzoyl peroxide, that benzoyl peroxide will give a polymer product with this. What if it is done by photochemical initiation, this initiator residue will not be there of course, this can be in one way advantageous in order to study the course of polymerization.

If it contains one isotropic level or a functional group, which can be estimated say functional group F suppose, which can be estimated then that can help you to count the number polymer chains that has been produced. So, there are various considerations which can automatically arise. Now, here in this case of photochemical initiation as before you can compute the rate of polymerization. A similar fashion as monomer term is there polymerization is there and phi I a by k t to the power half, where I a is intensity of absorbed light in moles of light quanta per liter second or Einstein.

This phi is number of propagating chain initiated per light photon absorbed or quantum yield for initiation of polymerization. There is another way of polymerization polymerization principle that is plasma polymerization. Now, this plasma polymerization today has become very important to the semi-conductor or electronic industries semi-conductor or electronic people for making devices. Plasma polymerization why? Now, in a way of producing fabricating device semi-conductor device or micro electronic device there, if you want to use a polymer then the processing of that polymer leading to that microelectronic chips or semiconductor device.

Then you have a very thin film involving very small quantity of polymer, which is very difficult to fabricate by taking a polymer synthesized in this fashion. So, people try to deposit that polymer on the electrode or on a substrate in a very thin film form the thin thickness may be in the nanometer range, nanometer scale. Suppose, it may be 10 nanometer or 5 nanometer or 20 nanometer like that to make a such a thin film using this polymer polymer produced by this fashion is very difficult the sophisticated may not be achieved for that purpose, so people go for plasma polymerization.

What is plasma polymerization? The principle is same now you take the monomer raise that polymer to the plasma state, that means it is taken to such excited stage monomer is raised to that excited state under a low pressure. Low pressure by creating plasma what happens that plasma excites the monomer to form a polymer say, what happens if you start with a liquid monomer or a gaseous monomer that liquid or gaseous monomer will form a solid polymer molecule?

That will be deposited on a substrate in an in a very organized way very organized way say one can get hepitextual growth type of thing monolayer double layer perfectly crystalline thin film so that can be done by plasma polymerization. There that you can say kind of photochemical polymerization plasma polymerization by photo chemical initiations that can that is also possible. So, those things those who are interested literature is available I have told you the basic principle you can go through the literature and you can get the details from there.

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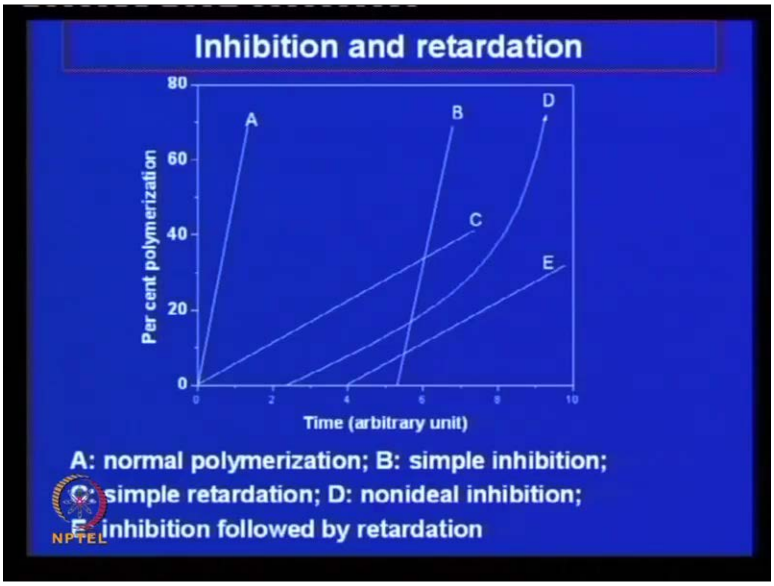

Inhibition and retardation

A: normal polymerization; B: simple inhibition;
C: simple retardation; D: nonideal inhibition;
E: inhibition followed by retardation

Now, I just mentioned you what is called inhibition of polymerization. What is inhibition of polymerization? Here you see this plot of polymer growth verses time rate of polymerization nothing but rate of polymerization. So, in this case normal in case of normal polymerization you see the rate is very high that in percent conversion is say 70 percent conversion can be achieved within say 1 minute time. Suppose, 70 percent conversion that means 30 percent of monomer will remain un reacted and 70 percent of monomer will be converted to polymer. Now, this curves look at the curves it starts the polymerization from the very beginning, but the rate is not that high as in case of A.

That means the polymer growth is retarded polymer growth is retarded that means free radicals are produced, that starts polymerization polymer growth occurs, but at a slower speed that is called retardation. Now, when this polymerization starts once the initiation is occurred, if there is no initiation no polymerization the growth may be different growth rate may be different. Now, one can one case can happen so in this case E inhibition B. B is simply inhibition B is a simple inhibition rate is same, but polymerization was not allowed to start say in case of hydroquinone you add hydroquinone to a monomer store in a bottle that polymer will not grow.

So, to have stopped just in order to start the polymerization you have to remove the innovator. After removal of the innovator it starts polymerization and this case c inhibition occurs in this time, then retarded growth is retarded. So, inhibition followed by retardation and this, a non-ideal inhibition non-ideal inhibition, so this is what is called inhibition and retardation.

Thank you.