Science and Technology of Polymers
Prof. Basudam Adhikari
Materials Science Centre
Indian Institute of Technology, Kharagpur

Lecture -7
Principles of Polymer Synthesis (Contd.)

Now, in this maltegene polymerization, what is the necessity of concept of these maltegene polymerization? What is the meaning of this maltegene? If you prepare a polymer using some bi functional monomers, two bi functional monomers, you will get a polymer system having only two chain ends, two ends of the polymer chain. That is termed has exclusively linear polymer or little bit branches may be there, but if it is exclusively bi functional and strict and is maintained then it will be exclusively linear polymer.

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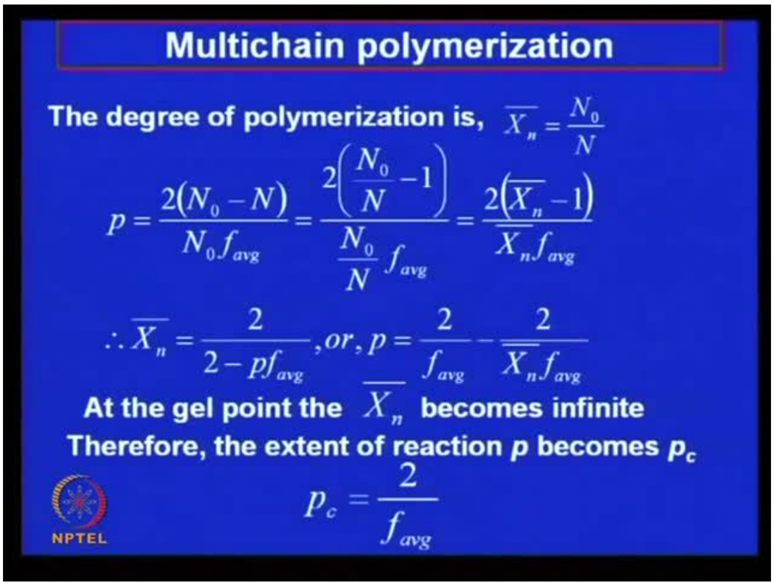

Multichain polymerization

The degree of polymerization is, $\overline{X}_n = \frac{N_0}{N}$

$$p = \frac{2(N_0 - N)}{N_0 f_{avg}} = \frac{2\left(\frac{N_0}{N} - 1\right)}{\frac{N_0}{N} f_{avg}} = \frac{2(\overline{X}_n - 1)}{\overline{X}_n f_{avg}}$$

$$\therefore \overline{X}_n = \frac{2}{2 - p f_{avg}}, or, p = \frac{2}{f_{avg}} - \frac{2}{\overline{X}_n f_{avg}}$$

At the gel point the $\overline{X}_n$ becomes infinite

Therefore, the extent of reaction *p* becomes p_c

$$p_c = \frac{2}{f_{avg}}$$

But along with some bi functional monomer if you take a tri functional polymer or tetra functional monomer, then the polymer product which is obtained from that (( )) will no longer remain as a linear polymer. The polymer molecules will contain more than two ends, more than two chains. That is why it is called multi chain polymerization, am I clear? For the sake of calculation or the amount of reaction to be used for such polymermization this is, you have to consider the average functionality, average number of functional groups present in the reactant system you have taken.

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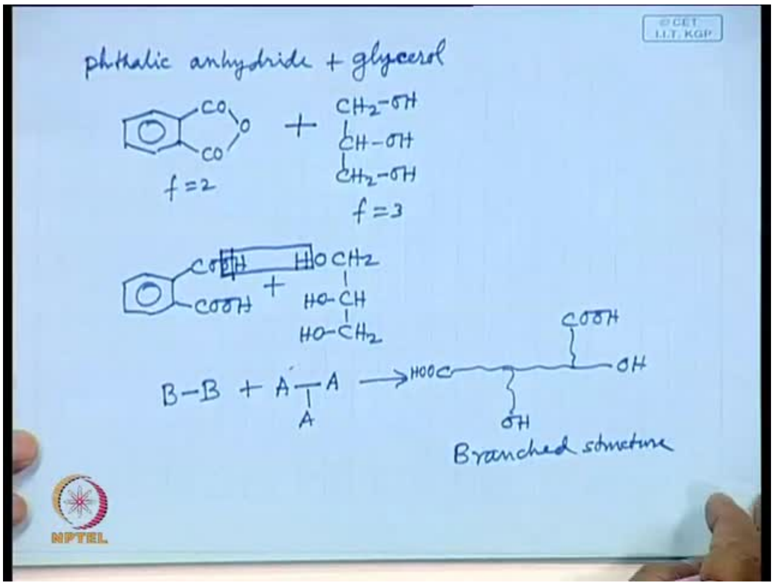

Say for example, if you polymerize phthalic anhydride and glycerol. What is the formula of phthalic anhydride? CO O CO K plus this is a tri functional monomer and f is equal to 3, if a di functional polymer f is equal to 2. This is an phthallic anhydride derived of water, if you add water to this compound this anhydride ring will open for 2 carboxyl groups. In effect you will get glycerol is an alcohol tri functional alcohol, try all. So, these will condense, this will also condense. These are primary arsine group, secondary arsine group. So, what will happen?

As I showed, so if you consider this has a B B having 2 B functional groups with A functional group tri functionary t right like this. So, you will get a polymer system like this branch. Now, the end of this branch or these polymer chain is may contain again OH or… That means mixture of carboxyl functional groups and these ends of these polymer chains. They are further reactive, it can react with another species of this kind. So, what will happen? It will continue to grow bigger in size, so this is a branched structure and these branch structure will lead to since, those groups are reactive as I told hydroxyl and carboxyl reactive groups are there in their ends, so they will lead to intermolecular cross link network structure.

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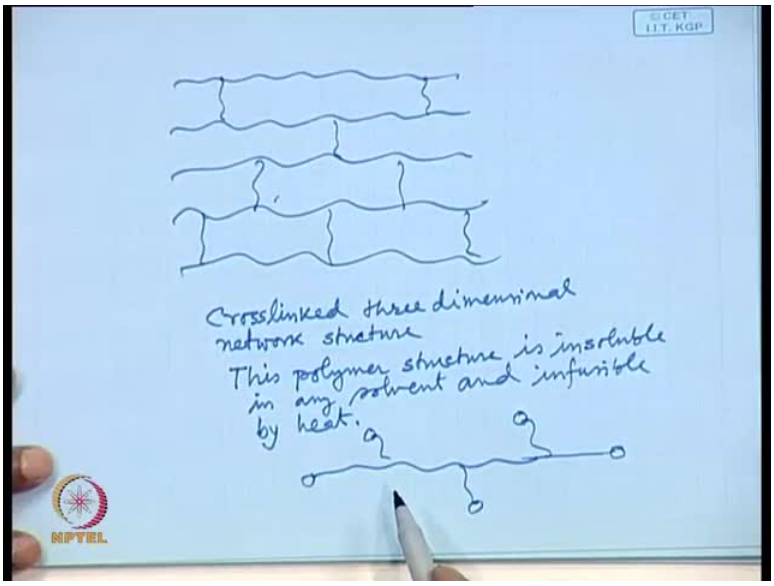

Crosslinked three dimensional network structure

This polymer structure is insoluble in any solvent and infusible by heat.

These are linked by primary valence bonds this is a panel network structure. We can draw a 3 Dimensional network structure. I showed you earlier, so this is a cross linked 3 Dimensional network structure. These polymer 7 structure is insoluble in any solvent and also infusible by heat, do you understand? So, we must have to have a control over such type of growth of polymer structure, once this kind of structure is formed during the polymer synthesis that polymer mass can no longer be used for processing as well as leading to a finished product.

So, what you have to do? You have to stop the polymerization at the branch level like this. If we stop the polymerization here because each of its ends are reactive, you can consider this has a pre polymer. I give you a constructive example of phenol pervindide resin. There are two ways of phenol pervindide resin synthesis. First I told you, I showed you how phenol and pervindide condenses? A stage resin, do u remember?

A stage resin, B stage resin, C stage resin of which A stage is linear and soluble, thermo plastic. B stage is branched soluble, thermo plastic and C stage is the final stage, cross linked thermo setting stage. So, we have to stop the polymerization at B stage, maximum we can go up to the B stage. Then you can take the B stage polymer for making a laminate for making any composite.

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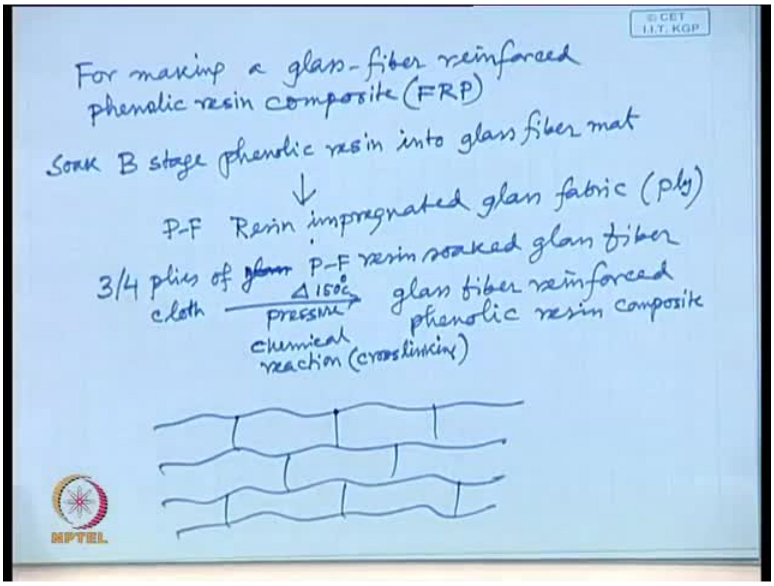

For making a glass-fiber reinforced phenolic resin composite (FRP)

Soak B stage phenolic resin into glass fiber mat

↓

P-F Resin impregnated glass fabric (ply)

3/4 plies of ~~glass~~ P-F resin soaked glass fiber cloth $\xrightarrow[\text{pressure}]{\Delta\ 150^\circ C}$ glass fiber reinforced phenolic resin composite

chemical reaction (crosslinking)

So for making glass fiber reinforced, phenolic resin composite, which is an which is a FRP fibre reinsto plastic, what is done? You have to synthesis phenol forbide resin up to the B stage. That B stage polymer, you take B stage phenolic resin, soak this B stage resin into a glass fiber mat of fabric. Then you will get a glass resign a resin impregnated, glass fabric called a ply. On ply it take this 3 to 4 plies of P F resign soaked glass fiber cloth assembles.

Those 3 4 plies together, then apply heat and pressure. Heat means the temperature should be say around 150 degree Celsius, you will get a glass fiber reinforced phenolic resin composite, do you understand? So, these B stage resin can be consider as a pre polymer up to pre polymer stage. The polymers remain soluble and fusible, that polymer should be used for product fabrication product processing. Final fabrication and final setting final fabrication is given by applying heat and pressure, where some chemical reaction occurs.

These stage, which is known has cross linking and the morphology, you will be a 3 Dimensional network as I mentioned. The cross linked density of this kind type polymer system will depend on, how much cross linking agent is used? How much reactive function is present in the B stage resin? Cross link density means the number of cross links cross links bonds intermolecular cross links bonds present in system or other way around.

We can say, what is the length of the polymer segment between two cross links, molecular weight of the polymer segment between crosslink. That way we can also express the cross link density. To this kind of system a situation can be understood taking account of these calculations and a pre polymer should be prepared considering this critical extend of this action. Then only it will be a useful polymer for fabrication of a suitable product, otherwise that batch of polymer can be discarded. That will be total wastage, understand?

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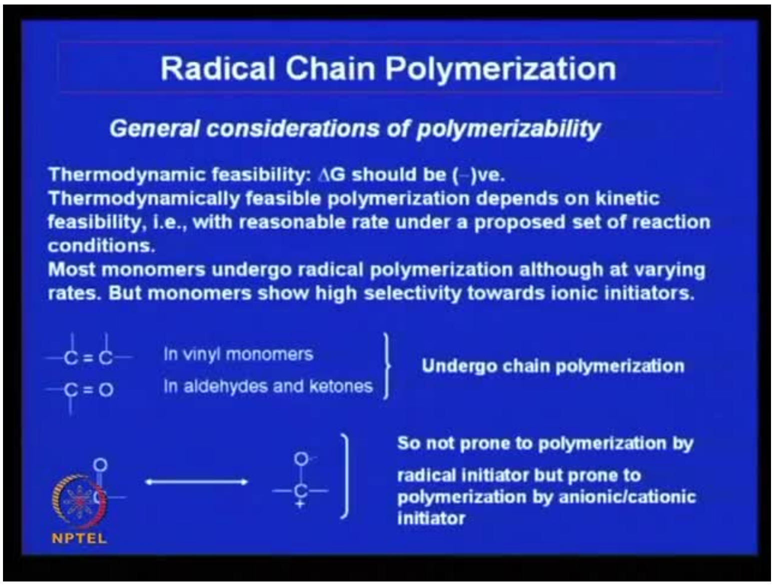

Radical Chain Polymerization

General considerations of polymerizability

Thermodynamic feasibility: ΔG should be (−)ve.
Thermodynamically feasible polymerization depends on kinetic feasibility, i.e., with reasonable rate under a proposed set of reaction conditions.
Most monomers undergo radical polymerization although at varying rates. But monomers show high selectivity towards ionic initiators.

$-C=C-$ In vinyl monomers
$-C=O$ In aldehydes and ketones
Undergo chain polymerization

So not prone to polymerization by radical initiator but prone to polymerization by anionic/cationic initiator

So, this is what about the condensation polymerization or step reaction polymerization leading to polymers like poly ester, poly carbonates, polyamides polyamides poly ethers like this. This is the the principle I have described in brief. Before you you please go through the books, I have referred and please solve the numerical problems given in the exercise problem at the chapter of, at the end of the chapter of those books. Now, let us pass on to radical chain polymerization or chain polymerization rather or polymerization by addition chain reaction principle.

Condensation polymerization principle is reaction in steps, that is why that was a step polymerization. You have seen the characteristics of step reaction polymerization. Now, you will understand characteristics of radical chain polymerization or chain polymerization, additional chain polymerization. Then you can compare the characteristics of step reaction polymer and additional chain polymerization. Now, in case of consideration polymerization, you have seen that minimum requirement for the reactant molecules to be polymerized are bi functionality. The reactants should be bi functional, at least it should be bi functional.

In case of radical chain polymerization, we must have such type of considerations. Although the monomers which undergo addition chain polymerization does not, do not contain in such type of functional groups. What are those things that compounds are available like ethylene, propylene, butadiene, isopine, (( )) methyl acrylayate, methyl with acrylate, acrylic acid. So, each of these compounds contain an oliphinic unsaturation or a double bond in the molecule. These are organic molecule, there contain some double bond alphinic double bond.

Now, that aliphinic double bond supplies this function site for linking up with another for being a large much molecules, macro molecules. So, here sudden consideration should be discussed for polymerisability of such ailphinic monomer. You know for any reaction to happen, it must have certain dynamic feasibility. Once the thermodynamic feasibility to achieved, then we must also consider its kinetic feasibility. That is rate at which that reaction occurs to reduce a polymer. What is thermo dynamic feasibility? That free energy change should be negative for any process, if the free energy change is negative, then only that process can happen that chemical reaction or chemical synthesis process can happen.

Now, let us look into this monomer which undergo radical polymerization or additional chain polymerization, radical polymerization. I mean polymerization involving radical and single electron free radicals available in the monomer that can undergo polymerization. In these monomer some radical is available, that free radical is interactive with a monomer to generate a free radical. Then that will lead to couple for being a bond.

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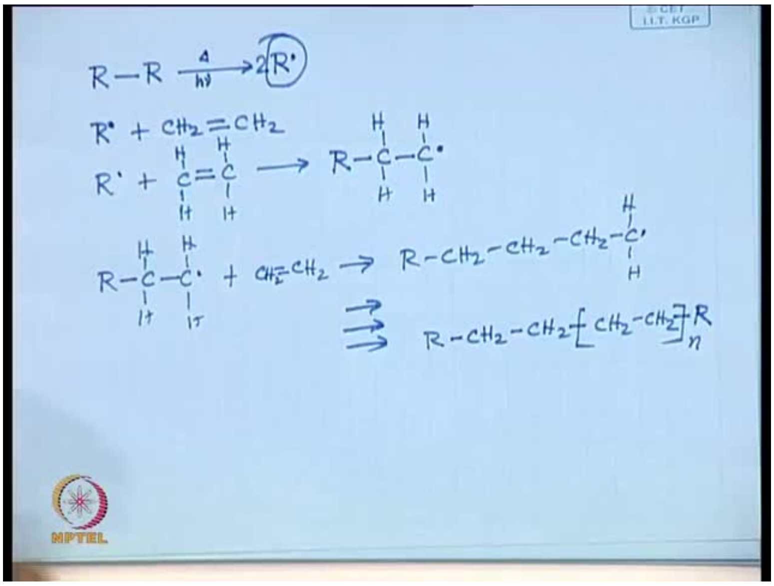

How I am showing you, suppose you take a compound say represented by R R. This is a bond, in these bond they are two electrons involved. Now, if some agency can break these bond say may be heat may be electromagnetic radiation or may be some chemical agency, if there energy if there energy of those agencies, the heat thermal energy electromagnetic radiation or chemical energy, if there energy is more than this bond energy energy of this bond or this an energy, then only it can be broken. If that is sufficient, then it will lead to, for to periodic like this 2 R dot.

Provided these 2 electron is shared by each member are clipped monolithically. That means each of them will take there share, equal share that is called homiletically. Now, these highly reactive, this radical is highly reactive. If that reactive radical comes in contact with an monomer, like this or you can visualize this way. what will happen that will initiate to open this pi bond. For me a bond with this monomer molecule leaving behind a free radical at the end of this carbon, that means 2 electrons present in this pi bond, one of those 2 electrons will be used by this radical to form a bond like this and another radical will be being there, this species is highly reactive.

So, it will further initiate or further add to another monomer like this. So, this process continue at a very very faster rate. And ultimately what happens? If these process continues allowed to continue, ultimately we can get… Actually this is not a right way to show anyway suppose this is n. Now this situation let us examine, where this kind of situation can happen? Let us examine, look at this monomer, it is a vinyl monomer where these instauration is present. Now, these is a ketonic group C double bond O, that means pi electron are present over here.

These kind of molecule can undergo chain polymerization, how? I have shown over here. Now, I told you the agencies here, this free radical, what will be the nature of this free radical? So, that they can attack these molecule to fall a free radical like this. How it happens? You see here is a double bond between a carbon and oxygen that can polarize. That means the incoming agency incoming agency that may be heat, that may be electromagnetic radiation, that may be chemical species, that will disturb the pi electron between this carbon and oxygen or carbon and carbon.

It will disturb in such a way that it can either polarize for being a positive centre as well as a negative center. Positive center carbon and negative center oxygen depending on electro negativitity of the atoms present there. In this case also it can polarize depending on substance present over here. I will see, I will say you later either these can be broken homiletically producing two free electrons, one over here another one over here or it can polarize like this, for being an catonic center and an atomic center. So, (( )) of these pi electron depends on incoming group incoming agency, which will attar the molecules like ethylic propylene vinyl etcetera, then it will continue to add on to each other.

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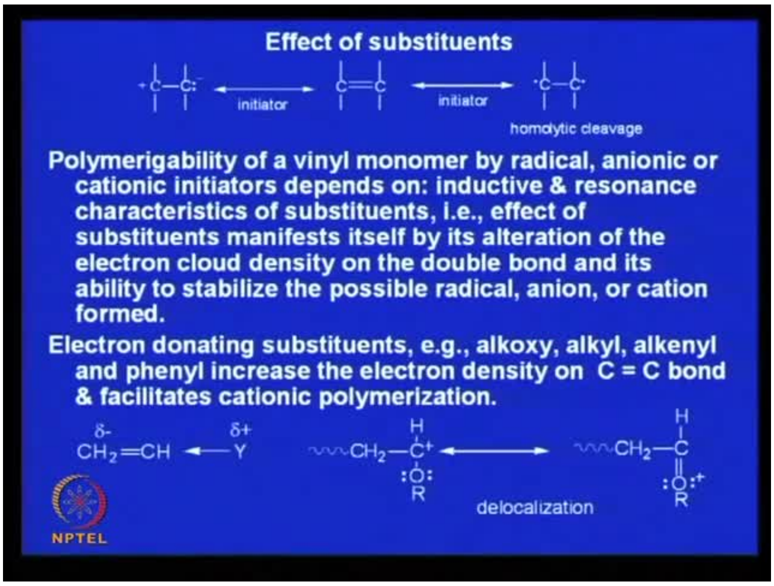

Effect of substituents

Polymerigability of a vinyl monomer by radical, anionic or cationic initiators depends on: inductive & resonance characteristics of substituents, i.e., effect of substituents manifests itself by its alteration of the electron cloud density on the double bond and its ability to stabilize the possible radical, anion, or cation formed.

Electron donating substituents, e.g., alkoxy, alkyl, alkenyl and phenyl increase the electron density on C = C bond & facilitates cationic polymerization.

Here you look, effect of substituence. As I was telling you, now this is the monomer allophonic monomer having this pi bond. Now, if some iniator comes in, comes close to these monomer, can be polarize for being a positive center and a negative center polarization of a monomer pi electrons pi bond. It can break into two free electron hemolytic cleavage or hetrolytic cleavage. That depends on, look at here, suppose a y substitute attached to these carbon, if this is electronic, if these has a capability of electron donating nature to these pi electron, that will increase the electron density with the pi bond between the two carbon or it else decrease the electron density by applying electron.

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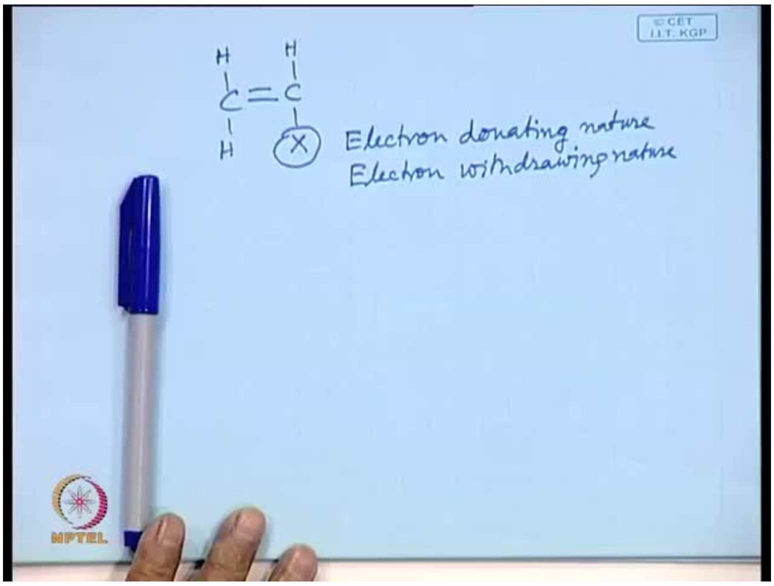

I means to say that this group may be of that makes the monomer its polymers ability. So, you can say what is the necessity of thinking to taking the concept? This concept is there is an necessity, if you want to design a new polymer. If you want to design a new polymer that synthesis a new polymer novel polymer that is a non existing today and you have to start with a monomer. What kind of monomer you should take? For that reason, say if it is of addition chain polymer, you think of a substitution which has is electron, which is electron each, which can donate electron to these system.

If it donates electron to these system to these region, so the electron pi electron cloud will be polarized. So, here these example this y group is electron donating in nature, so what happens? So, different density on this carbon will be more, so it will be delta negative and this side will be delta positive. So, these is the monomer, this is the monomers. It is the inner in nature of the monomers. Now, you think of the attacking species, attacking initiator attacking initiator. If the attacking initiator attacking molecules comes close to this, which is of electron accepting type or the electron donating type, then that can further progress that can attach to these molecules.

Once this happens it can polarize and this electron will be again delocalized by this resonance structures, resonating structures. Again this is a necessary because it needs to be stabilize, once its polarized and some attacking molecules are coming to change its character to start the polymerization, then it must substance stability. Suppose, somebody has entered this room to attack you, for stabbing.

Now, if you run in this room with a high speed, he would not be able to do it. If he is little stable becomes little stationary, then he will find you at some place and he can easily kill you. It is like this, stability. So, stability of this is intermediate the stability of this intermediate should be a parameter should be a criteria. Otherwise you cannot get a polymer. If it is very unstable its existing will not be there for attacking with another or reacting with another species.

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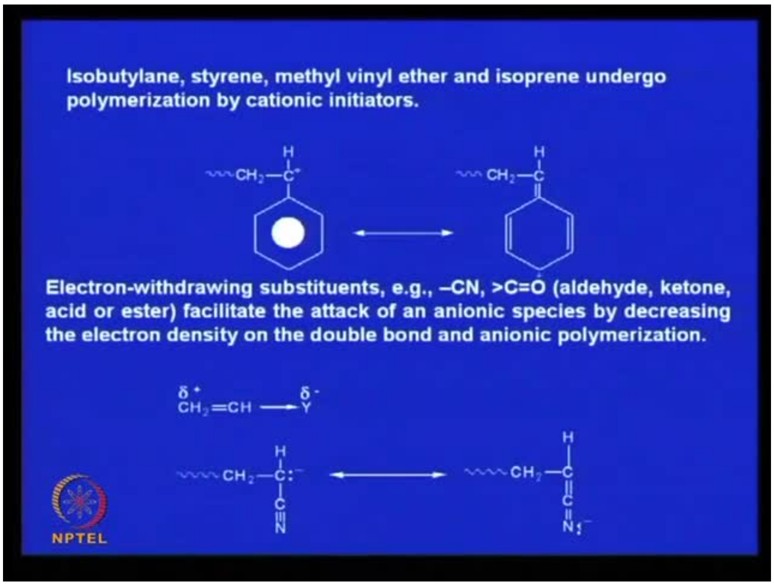

Isobutylane, styrene, methyl vinyl ether and isoprene undergo polymerization by cationic initiators.

Electron-withdrawing substituents, e.g., –CN, >C=O (aldehyde, ketone, acid or ester) facilitate the attack of an anionic species by decreasing the electron density on the double bond and anionic polymerization.

$\overset{\delta+}{CH_2}=CH \longrightarrow \overset{\delta-}{Y}$

What is that group? Electron donating type say ethyl methyl group is electron donating in nature, that will increase the electron density. If it is methyl group CH3 that will increase the electron density over here. This is a case of propylene propylene or you can take a case of isobutylene in propylene in one methyl group, in isobutylene two methyl groups. So, that will further the density in the pi electron pi bond. So, this way we able to see an agency, which is coming to attack the molecule wether it will break the pi bond whole lightyically or hetrolytically.

That depends on the substituent present or the substituent attached to the carbon or to that molecule or the nature of the attacking species, either by the electron donating type or electron withdrawing type. That we will see and we will get free radical polymerization cationic polymerization and anionic polymerization. Free radical polymerization means it is an polymerization initiated by by a free radical, initiated by free radical. Cationic polymerization means is an polymerization initiated by some cationic species, say some seasonal seed say (( )) water combination, boron (( )) water combination that undergoes cationic polymerization or sodium alkyl, some metal alkyl.

That will cause an anile polymerization too. In case of actronitale here you see in these case these C N group is electron, withdrawing type. It is withdrawing electron from this pi bond. So, this carbon will be delta positive and this kind of monomer will under polymerization by an ionic species say butadiene can be polymerized by an ionic species an ionic polymerization. Isobutylene can be polymerized by cationic species cationic polymerization. So, this is the situation.

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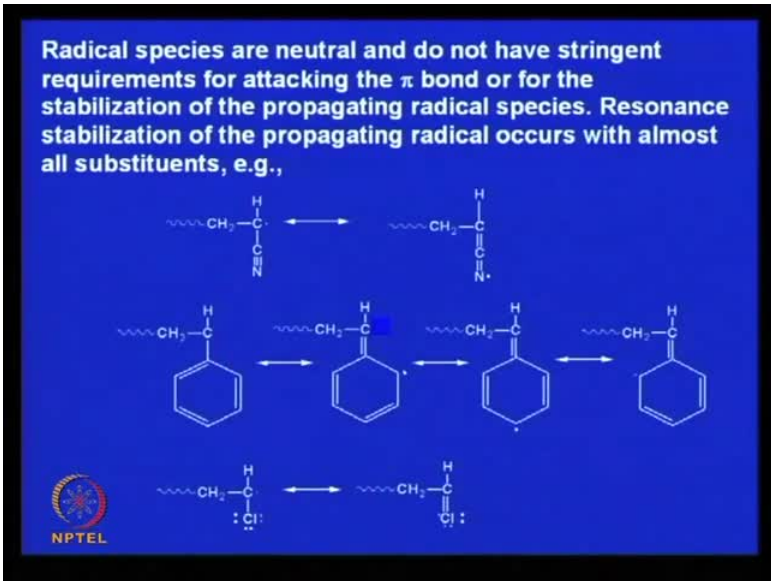

Radical species are neutral and do not have stringent requirements for attacking the π bond or for the stabilization of the propagating radical species. Resonance stabilization of the propagating radical occurs with almost all substituents, e.g., Radical species are neutral and do not have stringent requirements for attacking the pi bond or for the stabilization of the propagation radical species and resonance stabilization of the propagating radical occurs with almost all substituents. Resonance stabilization means the intermediate of the radical species, which has been formed after initiation that should be stable enough for growth of the polymer.

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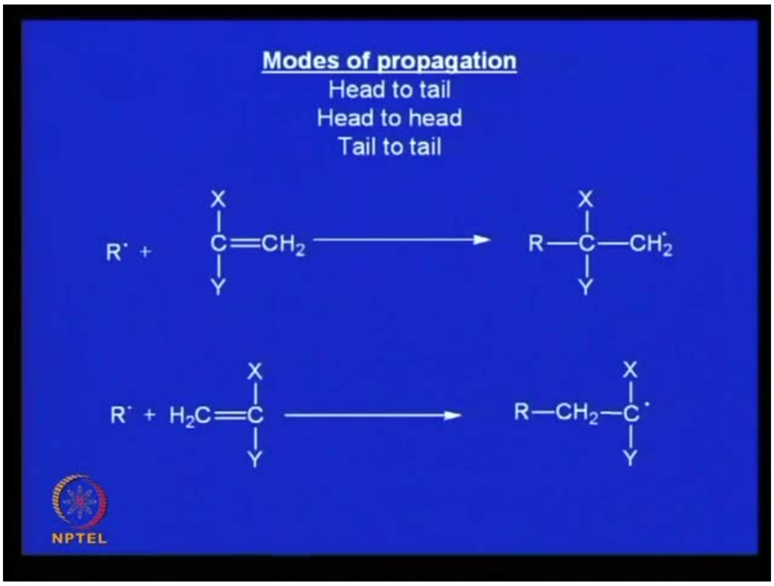

Modes of propagation

Head to tail

Head to head

Tail to tail

$$R^{\cdot} + \overset{X}{\underset{Y}{C}}{=}CH_2 \longrightarrow R{-}\overset{X}{\underset{Y}{C}}{-}\dot{C}H_2$$

$$R^{\cdot} + H_2C{=}\overset{X}{\underset{Y}{C}} \longrightarrow R{-}CH_2{-}\overset{X}{\underset{Y}{C}}{}^{\cdot}$$

Now, modes of propagation. Look into this monomer, alephnic monomer to one carbon two different groups are attached and two other carbon only hydrogen atoms are there. How they will attach with each other?

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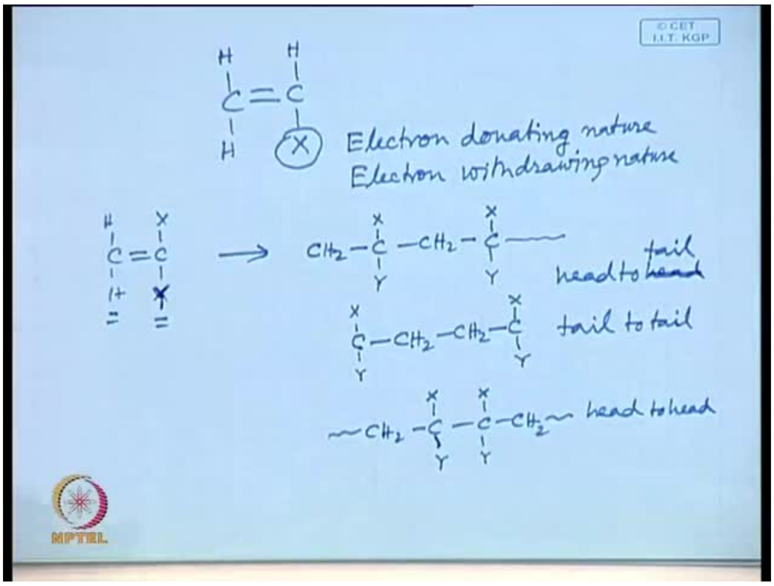

This is a kind of growth or it can swap in that if you consider this as head and if you consider this as tail, then this type of combination during the propagation of the monomers to form a polymers. That is known has head to tail addition, this is head to head addition or else you can get this is tail head to head tail to tail head to head, sorry head to tail. Again it will happen, sit up charge or this radical addition that is different thing, but here you have to constrate the study aspect, studying aspect.

Now, it that depend on its size of this substituents. So, bigger groups will hinder for this kind of addition, bigger substituents it hinders this kind of addition whereas, that will augment this kind of head to tail addition. So, that depends on the size of substituents size of substituents present in the monomer structure.

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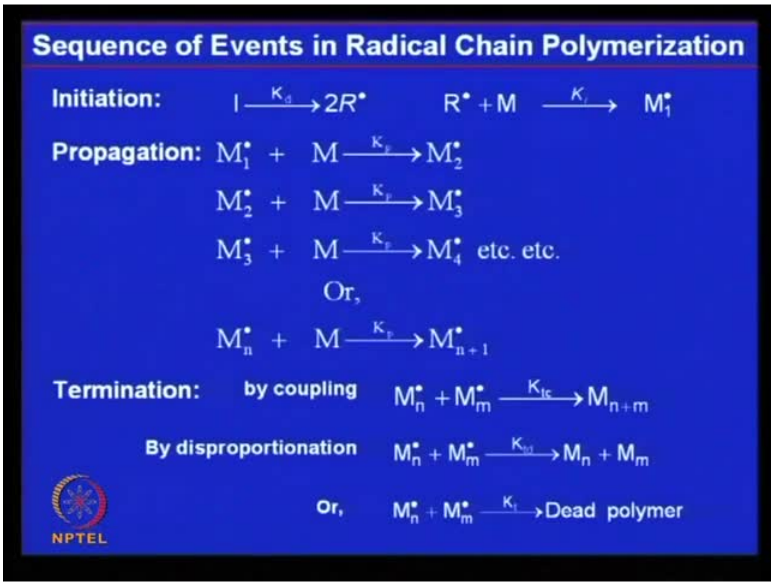

Sequence of Events in Radical Chain Polymerization

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

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

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

$M_3^{\bullet} + M \xrightarrow{K_p} M_4^{\bullet}$ 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, $M_n^{\bullet} + M_m^{\bullet} \xrightarrow{K_t}$ Dead polymer

Now, let us see the sequence of events that occurs in a radical chain polymerization. Now, there are again we must say some steps can be identified as initiation propagation termination of polymer growth. So, in the sequence of synthesis of an polymer from monomer by addition chain reaction principal, it needs an initiator system to initiate the polymerization of an alephenic monomer. Once an alophenic monomer is initiated by initiator molecule for initiator radical, then it propagates that addition reaction propagates, further propagates addition reaction in monomer, to build a very long chain molecule.

Now, there must be a limit of chain growth limit of growth length of the chain, which is formed during such polymerization. In order to control the molecular weight to one extend, it is continued that is say ten 10,000 molecular weight or 5,000 molecular weight or 10,00,000 molecular weight or 60,00,000 molecular weight where we should stop. That means you have to terminate the polymerization at the final step termination.

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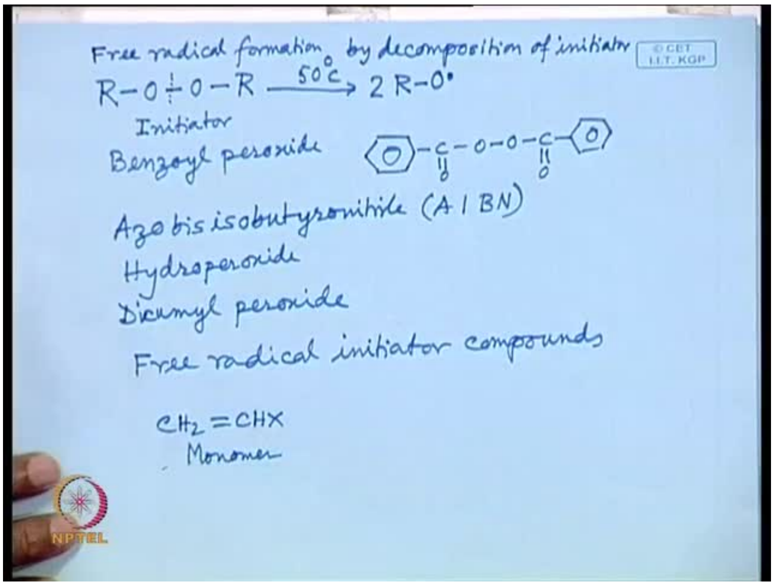

Free radical formation by decomposition of initiator

$R-O \vdots O-R \xrightarrow{50^{\circ}C} 2\,R-O^{\bullet}$

Initiator

Benzoyl peroxide

Azobisisobutyronitrile (AIBN)

Hydroperoxide

Dicumyl peroxide

Free radical initiator compounds

$CH_2=CHX$

Monomer

Let us take a peroxide molecule. You know this peroxide molecules are unstable molecules because this bond is thermally less stable. So, if it is heated say at 50 degree Celsius temperature, it will break into free radicals like this. 2 R radicals, this is a free radical formation reaction. Here this R O O R is an initiator, R O is an initiator. A typical example of this initiator may be benzoyl peroxide, what is the formula of benzoyl peroxide? Is it molecule B PO molecule or you can have, you can have some hydro peroxide say cumin hydro peroxide,

Student: (( ))

Azobisisobutyronitride, azobisisobutyronitride. So, bond nitrogen double bond nitrogen that is unstable, that will break into releasing a free radical hydro peroxide. This hydro peroxide can be cumyl hydro peroxide or di cumyl peroxide. So, these are known as free radical initiator compounds or molecules this initiator molecules are designated by this, i initiator molecule. That decomposes thermally say temperature might be 50 degree, 60 degree, 70 degree, 75 degree, 80 degree.

That decomposition temperatures are different for these compounds and they have certain applibes. So, once this anything initiative decomposes into hemolytic into decomposition of initiator into R radical that R free radical will add on to a monomer designated by m. That monomer may be ethylene monomer, may be methyl acralite monomer, may be phenyl chloride monomer, may be be an acyclic acid monomer, like it like that there you will have a double bond like this. This is a monomer, so this forms a monomer radical initiator.

Radical initiates to form a monomer radical, so this step is known has initiation step. So, this is initiation decomposition step and this is initiation step and both this decomposition and initiation are included in this initiation step. Then propagation of the initiation of the monomer radical to intermediate growing chain radical here. After this first monomer radical react with this second monomer radical. It will increase the length, will be doubled here and this is a growing chain radical and like this it will continue to add more and more number of monomers, m 3, m 4, m 5 and m 10 and MPM, QMN like this.

Depending on number of monomer molecules added to this great chain, these are all growing chain there stability. I was talking of their stability, there stability this of the free radicals are maintained by forming a resonating structures like hyper conjugation. So, they are reasonably stable reasonably stable for a attack of monomer molecule or attacking a another monomer molecule. That means this monomer molecules are coming from this close to the growing chain. This is added, they are added so gradually it is increasing and entire this entire, this step occurs at a fast very very fast rate.

If you look into the rate constant data, you will see how fast it is. Then all these steps intermediate steps are known has propagation steps. How far all propagation of monomers to growing chain are initiated? It is not that only one chain is initiated and only one chain will be formed, one great chain will be formed. Here only a case of one initiation is shown, now in that system there are more number of initiator molecules in a typical polymerization of a finite monomer.

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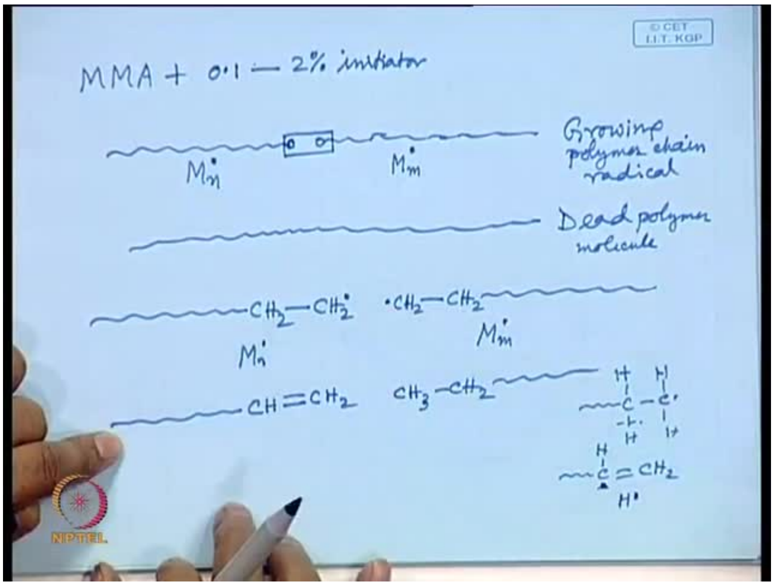

Say methyl metacrylate MMA, here initiator used say 0.1 percent to say say 2 percent initiator concentration is used. That means if you take benzyl peroxide, how much benzyl peroxide is taken? Say if u take 100 gram monomer, so you can take 1 gram of initiator or 0.5 gram of initiator like that. Okay? Now, that 0.5 gram initiator, how many molecules are there?

So, few of those molecules will break initially. If not all at the same time or slowly it can break depending on the availability of your bond breaking energy from the thermal source. So, simultaneously they can be large number of initiator molecules decomposed into free radicals and large number of initiated monomers will be formed, okay?

Student: (( ))

Please wait for some time keep your patience, first you see this is the initiation step, this is the propagation step, propagation continues. Then these radicals are lives. This growing chain radicals are lives. Live in the sense, they have the capability of adding more monomers. If they are monomers available in the reactor in the container, it will go on continuing the addition of the monomer, till it becomes dad. This is a live radicals, this radicals are the live radicals, these are not dead.

Now, in order to kill these growing polymer chains, they need to be terminated. Their growths needs to be terminated, now that termination occurs by two ways. Now, in the system they are many growing chain radicals. This is one growing chain radicals, it is represented by M n dot means n number of monomer molecules are there in the chain. It may be 5000 at one, there is a free radical. Similarly, we can have another chain bearing this free radical at one end having M number of molecules. So, we can visualize this way. Suppose, this is M n dot, this is M m dot, these two radicals can couple.

Student: (( ))

I am keeping your question in mind, I will explain later here this two radicals couple forming a covalent bond because two free radicals can react. So, in a effect for what we are getting? So, these are, this a dead polymer molecule. It is no longer capable of adding more monomers to it. It did, their radical that grown growth activity is anilated is talked or terminated. This is kind of termination is known by terminated by coupling of growing chains.

Now, there can be another case where two growing chain radicals can dispropassionate interact through dispropagination for stopping there growth activity. How that occurs? If I show this a showing only one monomer in it, at the end of the growing chain radicals, what can happen? Now, these species suppose this is M m dot, this is M n dot, this M m dot can abstract one hydrogen from this carbon. So, what will happen? If it does that it will be CH, here one radical will be created.

So, a pi bond will be created over here and there is no longer free radical present. In these case what will happen? This species this species has taken, this hydrogen from here. So, that hydrogen radical hydrogen means not hydrogen atom, hydrogen radical hydrogen radical. That looks like that is CH. So, if it breaks it will form, I am sorry and one hydrogen will be hydrogen radical will be formed, that hydrogen radical will react with this carbon forming CH 3, CH 2, CH 3 CH 2. Look at the peculiarity, in these case these these species becomes saturated, these species become unsaturated.

Here the length becomes doubled, if they are of same size here. The length of the polymer chain remains equal to the length of the growing chain. This is known has termination by decomposition. There are three steps initiation propagation and termination in these polymerization, additional chain polymerization. Thank you very much.