Science and Technology of Polymers
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Lecture - 10
Principles of Polymer Synthesis (Contd.)

Today, we shall discuss about the polymer synthesis by ionic chain polymerization. Till now, you have seen the addition chain polymer synthesis by initiation with free radicals and those free radicals sources could be different from chemical initiators which can decompose at the polymerization temperature and release free radicals. Those free radicals are highly active those active radicals initiate the monomers and carry out the proper polymerization through various steps of initiation, propagation, and termination.

We have seen there that the molecular weight is controlled by chain transfer reactions, transfer of their radical activity to various species present in the polymer polymerization medium, and it controls the molecular weight. Sometimes, it is necessary that there is deliberate need of addition of chain transfer agent in order to control the molecular weight at keep the molecular weight at a desired level. Also the distribution of molecular sizes, those are also controlled by the chain transfer reaction.

Apart from this, there are possibilities of chain transfer to solvents, chain transfer to monomers, chain transfer to initiators, chain transfer to impurities, all those things that can happen. Those should be avoided and it needs a proper selection of monomer, needs a proper selection of monomer initiator system, a monomer initiator solvent system, control of temperature and also that way one can prevent the prevent preparation of production of polymer branches there, because the chain transfer can also occur to dead polymer molecules.

So, you have heard those things. One should be careful, must have a proper control system, so that one can get well defined polymer properties including molecular weight. And you have seen there that there are chances of auto acceleration. Do you remember what is auto acceleration I told auto acceleration that can occur, that can happen during polymerization; polymerization synthesis as a result of temperature increase, because you know these polymerizations are highly exothermic polymerizations. So, the reactor system should be such that heat generated during polymerization should be properly dissipated, properly removed by with the help of condenser system or through a some coolant through the reactor.

Otherwise, if the polymerization is carried out in bulk also in bulk polymerization since there is no solvent.

Monomer acts as the solvent, might act as the solvent of the polymer that increases the viscosity of the polymerization mass and that increase in viscosity becomes a problem. Once the viscosity of the polymerization increases, there rate of termination decrease and die to decrease in rate of termination. There might be sudden increase in polymerization rate that causes the auto acceleration to affect and other names of auto accelerations are Tromsdorff effect or Norrish-smith effect or gel effect because it actually leads to gelation. That means solidification of the polymerization mass which leads to actually wastage of the polymer batch that cannot be processed or that cannot be handled. The reactor system could damage.

So, there are so many different problems. In order to avoid all those things, one must be careful, so that no acceleration, auto acceleration kind of thing happens. Before polymerization to occur, you have to be careful about the inhibition by other agents. Inhibition means, even if you use adequate quantity of initiator or suitable initiator in the polymerization system, what can happen is this initiator, it may not give that efficient initiation of the monomers and you may not get polymer. So, then you have to think there might have been happening there this inhibition process. What is inhibition? There may be certain free radicals which are stabilized.

So, if there is presence of stabilized free radicals, those stabilized free radicals can scavenge this generated free radicals generated during the polymerization. If those free radicals are scavenged or intermediate your growing chain radical intermediate size, if those are scavenged, then one can get proper growth of the polymer, so that inhibition effect will be removed as well as sometimes, the polymerization is controlled by taking some retarding agent. It may not be polymerization, it may not be inhibited.

That means, inhibition means total stoppage of polymerization, no growth, but one can have, one can control the rate of polymerization by using certain retarded molecules. Those retarded molecules retire the polymerization growth, polymer growth, polymerization rate. That means, the rate of polymerization may get lower, otherwise it may be required in some cases, where due to high rate of polymerization, there may be certain rise of viscosity that may lead to say gel effect due to gelation condition. So, you must have heard that in the initial period of the polymerization, you use some retarder also that initially polymerization rate is under kept under control.

So, these are the things that you have seen there. So, I have summarized the things what you have seen and you can compare the polymerization rate initiated by different means, say free radical initiation, photochemical initiation and redox initiation. You compare the rate, the dependence of the parameters on the molecular weight and molecular weight distribution k and you have seen what kinetic chain is, all these things. How this kinetic chain length is related to various rate constants, rate constant for termination, rate constant for propagation, rate constant for initiation. Those things are included in those equations.

So, you see how they are related. Kinetic chain length mean is equal to, is related to those parameters k p k T k i and as well as what is that called R i and the initiator efficiency factor. So, they are related you have seen. I have shown you. Please go through books I have mentioned. The books, the fundamental books I have mentioned or book by professor P. Ghosh or book by professor (( )) and (( )) or any other book you can. Fundamentally polymer science book, you will get all those things.

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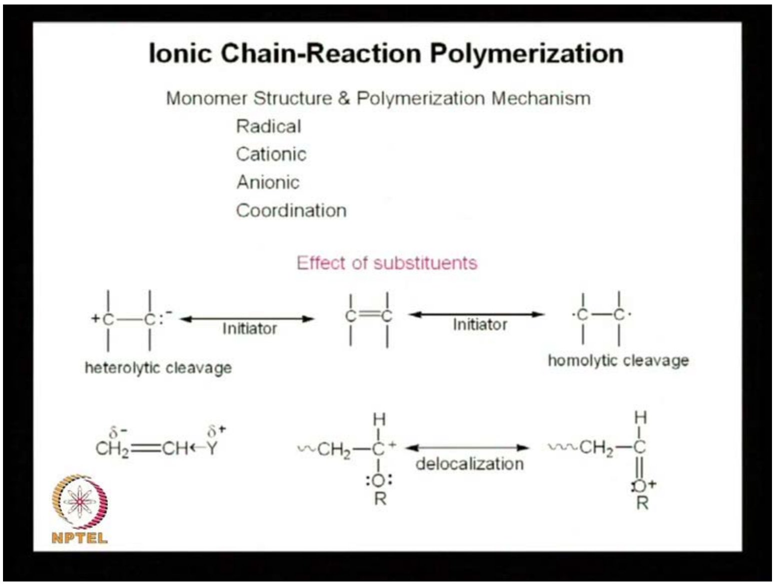

Ionic Chain-Reaction Polymerization

Monomer Structure & Polymerization Mechanism

Radical
Cationic
Anionic
Coordination

Effect of substituents

Now, today let us see how this polymer, the addition chains polymer can be manufactured or synthesized. It is by ionic polymerization technique, ionic polymerization principle. You have seen, it needs polarization of the bond. This is the holyphenic monomer. Now, it can have substituents on these carbons, two carbons. There are two substituents here. Now, the presence of substituents actually influences the pi electron cloud over here. That means, either that can help to break this pi electron, pi bond homolytically or that can polarize this thing. Now, this polarization depends on the electron withdrawing and electron donating nature of the substituent present over here. You see hemolytic cleavage producing free radicals on one side. One initiator free radical can combine leaving behind this free radical for addition of further monomer units.

So, growth of polymer chain by free radical. Here, you see the pi bond is polarized positive side and negative side due to this polarization. This polarization will be effected due to the presence of substituents. Look at this molecule here. Now, this is a substituent y and if it is electron donating type, you see this substituent will be positively charged center and due to increase in electron density, in this pi bond area, what will happen is this carbon will assume negative charge, partial negative charge. So, now if there is some, this will help initiation of a monomer and I told you, it needs the stability of the system. Now, this stabilization can be affected, can be obtained by delocalization of the charge. Over here you can see, this resonance stabilization through delocalization can occur and once this is stabilized and that stabilization depends on the nature of the substituents present over here.

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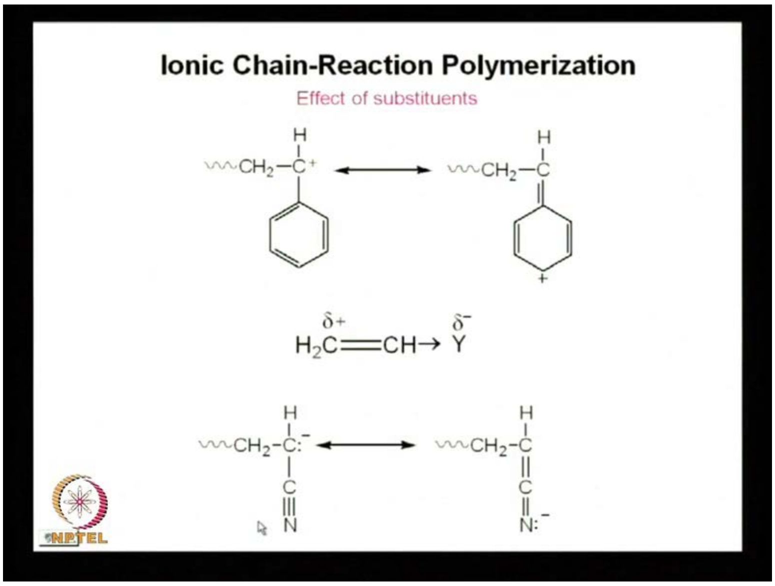

Ionic Chain-Reaction Polymerization

Effect of substituents

$$\overset{\delta+}{H_2C}{=}CH\rightarrow \overset{\delta-}{Y}$$

Here also, you see one example. This styrene forward stabilizes because of this aromatic ring, a delocalized system, and electron system and in this case, you see as opposed to the previous molecule here you see the substituent withdrawing in nature. That means it is electronegative in nature. So, due to that reason, it can actually draw pi electron cloud from this pi bond. So, this carbon will be positively charged and this carbon will be, your substituent will be negatively charged. So, this way you can see if the molecule is like this, say acrylonitrile. Acrylonitrile in the CN group is electron withdrawing nature type electron, withdrawing type group. So, it actually makes this carbon positive and this carbon negative and you see due to delocalization, it can stabilize this chain species.

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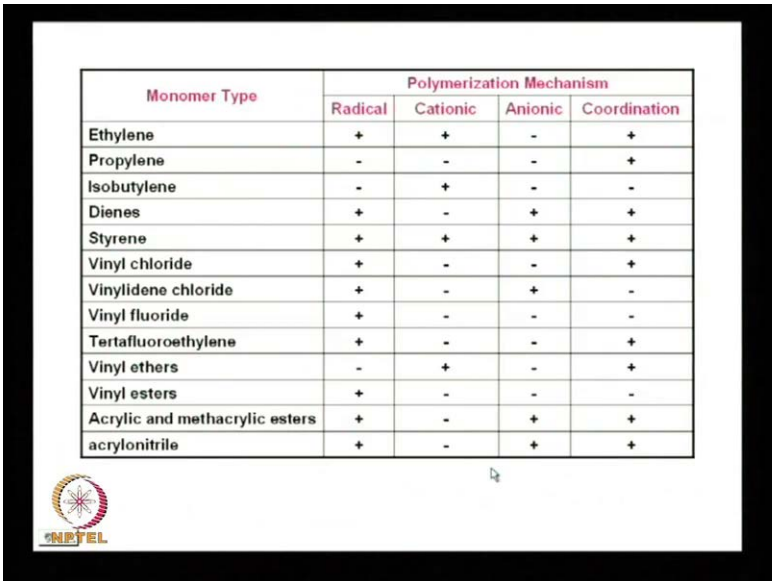

Monomer Type	Polymerization Mechanism			
	Radical	Cationic	Anionic	Coordination
Ethylene	+	+	-	+
Propylene	-	-	-	+
Isobutylene	-	+	-	-
Dienes	+	-	+	+
Styrene	+	+	+	+
Vinyl chloride	+	-	-	+
Vinylidene chloride	+	-	+	-
Vinyl fluoride	+	-	-	-
Tertafluoroethylene	+	-	-	+
Vinyl ethers	-	+	-	+
Vinyl esters	+	-	-	-
Acrylic and methacrylic esters	+	-	+	+
acrylonitrile	+	-	+	+

Now, here is a table. These tables are available in books also. Now, different monomers are there, polyphonic monomers. Ethylene, propylene, isobutylene, dienes, styrene, vinyl chloride, vinylidene chloride, vinyl fluoride, tetrafluoroethylene, vinyl ethers, vinyl esters, acrylic and methacrylic esters, acrylonitrile. Now, the polymerizability of these monomers by various initiation principles, initiation mechanism here is shown positive. That means it is possible by that mechanism. Negative means, it does not respond to that initiation.

So, positive means, it responds to that radical polymerization or cationic polymerization. Negative means coordination polymerization. I won’t be able to cover here because of the time shortage. I have to cover many things. So, if I get time afterwards, the end of the course, I will cover as well as the copolymerization of various monomers, how various monomers enter into copolymer structure in alternating way, in block way, in random way depending on the reactivity ratios of the monomers. So, I will discuss later if I get time, otherwise you have to look into book. It is not very difficult to understand. You have to go through the book and you have to learn from there. If you need my help, you come to me and I will explain you.

Now, here you seem coordination polymerization. What is coordination polymerization? You do not know coordination polymerization. It means the polymerization of these monomers having certain substituents which can lead to isotactic, atactic, syndiotactic structure. I mentioned before that you remember polypropylene. There is a possibility of formation of isotactic, syndiotactic and atactic structure of polypropylene because of this chiral centre present on that carbon atom I explained to you earlier.

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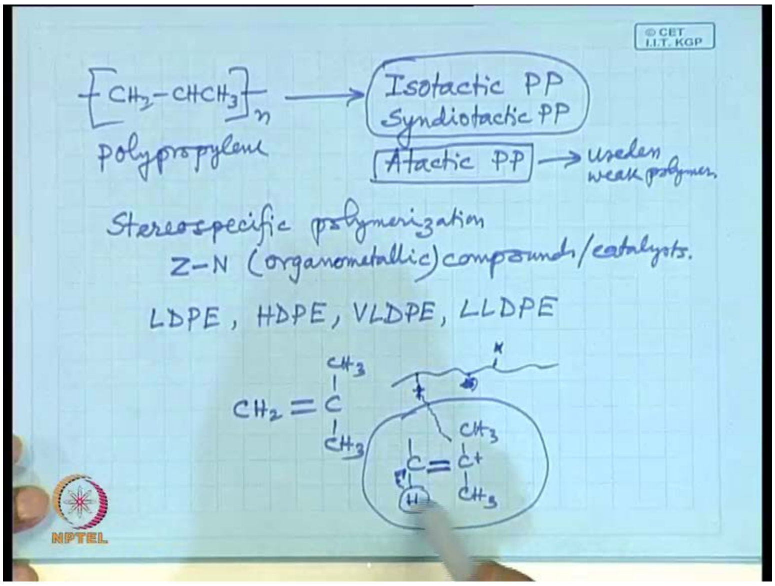

$-[CH_2-CHCH_3]_n- \longrightarrow$ Isotactic PP

Syndiotactic PP

polypropylene

Atactic PP → useless weak polymer.

Stereospecific polymerization

Z-N (organometallic) compounds/catalysts.

LDPE, HDPE, VLDPE, LLDPE

$CH_2=C(CH_3)_2$

So, that polypropylene, it leads to isotactic PP, syndiotactic PP and atactic PP. This is useless polymer. Now, if certain percentage of atactic PP is produced in a batch, so this should, this cannot add to mechanical and other property properties. So, isotactic and syndiotactic is desirable and for that purpose, it needs to be specifically manufactured. So, this polymerization is known as stereo specific polymerization.

Stereo specific polymerization is carried out by Ziggler Nata catalyst, which are organometallic compounds that undergo specifically that specifically produces either isotactic structure or syndiotactic structure with no atactic structure. One can use other initiators for polymerization or other catalyst for polymerization for this polypropylene. Not only that, today the various states of polythene I mentioned, LDPE HDPE very low density polyethenes, LLDPE, etcetera. These have been possible because of this stereo specific polymerization Ziggler Nata catalyst that gives highly specific structure. So, that is actually called coordination polymerization that occurs through coordination mechanism because aluminium trialcyl and titanium tetrachloride, that is a combination of this Ziggler Nata catalyst. Huge numbers of catalyst combinations have been efficient, catalyst combination have been developed and today, so many manufacturer, they are manufacturing these polymers and coming to the competition in the market because of Ziggler Nata catalyst.

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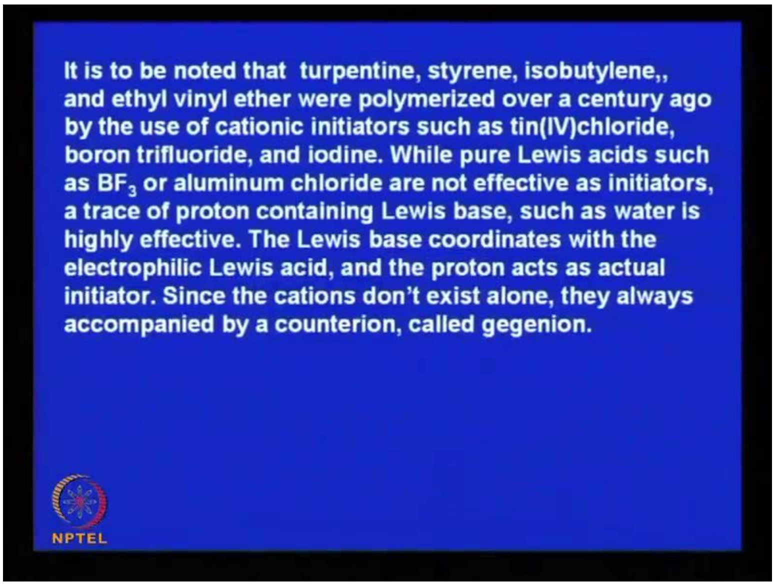

It is to be noted that turpentine, styrene, isobutylene,, and ethyl vinyl ether were polymerized over a century ago by the use of cationic initiators such as tin(IV)chloride, boron trifluoride, and iodine. While pure Lewis acids such as BF$_3$ or aluminum chloride are not effective as initiators, a trace of proton containing Lewis base, such as water is highly effective. The Lewis base coordinates with the electrophilic Lewis acid, and the proton acts as actual initiator. Since the cations don't exist alone, they always accompanied by a counterion, called gegenion.

Here, you see it is to be noted that turpentine, styrene, isobutylene, ethyl vinyl ether were polymerized over a century ago by the use of cationic initiators, such as tin tetrachloride, boron trifluoride and iodine as initiators or catalysts. While pure Lewis acids such as boron trifluoride or aluminium chloride are not effective as initiators, a trace of proton containing Lewis base, such as water is highly effective. The Lewis base coordinates with the electrophilic Lewis acid, and the proton acts as actual initiator. Since the cations don't exist alone, they always accompanied by a counterion called gegenion.

So, now we are going to explain this cationic polymerization and the principles of cationic polymerization. Now, you have seen the kind of monomer; say isobutylene is a monomer which contains two methyl groups which are electron donating in nature to the pi bond. So, it can due to the donating nature of this methyl group molecule isobutylene, due to the electron donating nature of this molecule, it forms a cation, carbocation and that carbocation is very much effective in adding incoming monomers and that cause polymerization. This kind of polymerization is carried out in highly purified condition at very low temperature. It is an advantage.

Now, theoretically you see those are exothermic in nature and if those are free radical, free radical has to be generated. It needs an induction period and time temperature also. At that temperature, the initiator is raised to that temperature for its decomposition. So, it acts efficiently between 70 to 80 degrees celsius. So, raising the temperature of a reaction mass to that temperature level, what happens beyond is that there will be exothermic polymerization, huge heat generation, so that raises the temperature to a very high level and that becomes difficult to control the temperature in polymerization reactor.

Now, if the polymerization could be initiated at much lower temperature, then you can get well defined properties of the polymers. So, here the cationic polymerizations or anionic polymerizations, these are carried out at a very low temperature, although they are exothermic polymerization, but since they are carried out at very low temperature, so thermal control or control over polymerization, it becomes very easy and in very purified system.

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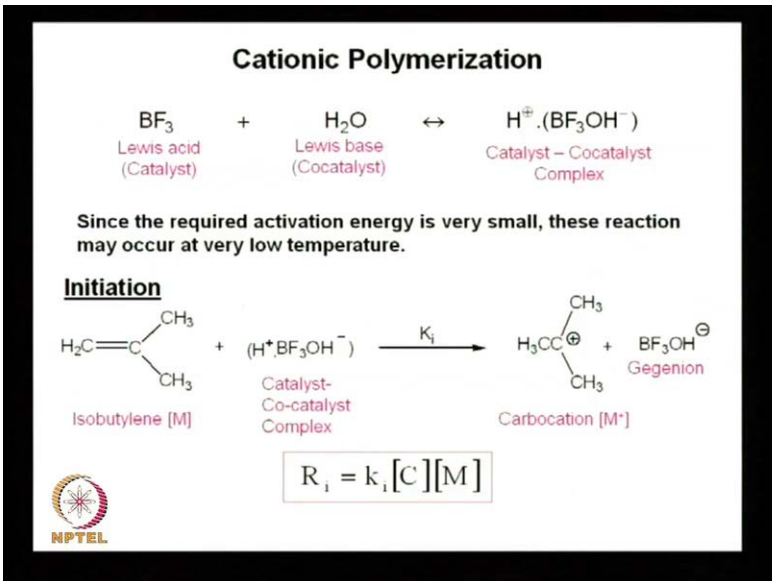

Cationic Polymerization

BF_3 + H_2O ↔ $H^{\oplus}.(BF_3OH^-)$

Lewis acid (Catalyst) | Lewis base (Cocatalyst) | Catalyst – Cocatalyst Complex

Since the required activation energy is very small, these reaction may occur at very low temperature.

Initiation

$R_i = k_i[C][M]$

Let us see now this shows the scheme of polymer synthesis by cationic. This means, as I mentioned, it needs a Lewis acid as a catalyst like, say (( )) chloride or boron trifluoride. This is a Lewis acid and for effectiveness, this Lewis acid alone cannot initiate. I mentioned, so it needs a co-catalyst as a Lewis base proton containing compound. Now, a very trace amount of this proton component containing compound, say here it is water along with this boron tri fluoride, it forms a complex. This complex is known as catalyst, co catalyst, complex catalyst, co catalyst complex H plus B F 3 O H minus. Since, the required activation energy is very small, these reactions may occur at very low.

Now, another important point for this kind of polymerization by cationic mechanism activation energy of this formation of catalyst, co catalyst complex as well as initiation and propagation is very low. So, this polymerization can be carried out at a very low temperature whereas, in case of free radical polymerization, the activation is high for initiation of free radical generation and initiation, both and propagation.

So, there it needs high temperature for carrying out the polymerization. Since the activation is low, this can be carried out at very low temperature. So, look at the initiation step. This is a monomer isobutylene having two methyl group on this, a on this backbone and this is the catalyst, co catalyst complex and this catalyst co catalyst complex initiates this polymerization by donating this proton to this molecule. Donating this proton to this molecule means, here it is S H plus. So, it becomes minus. So, H plus adds to CH2 becoming CH3 and this centre becomes positive.

Now, since this is positive, this is a cation and the other parts of the catalyst that anion that is known as gegenion. That remains very close to this thing, this growing center, cationic center. So, this remains at the vicinity of the cationic center. Now, once another monomer comes in between, so that this adds to (( )). That means it polarizes that. Already it is polarized because of the presence of this thing and can easily initiate that monomer here. You see rate, expression rate of initiation is constant into concentration of the catalyst co catalyst complex and the monomer concentration. As before, you have seen that rate expression is very same to some rate constant concentration of the catalyst and concentration of the monomer. You can say, sir here catalyst is not consumed, why it is then included here? You see it is added to this thin. There you see catalyst concentration is included in this rate expression. You will see later that this kinetic chain length or polymerization that is also that remains independent on catalyst concentration.

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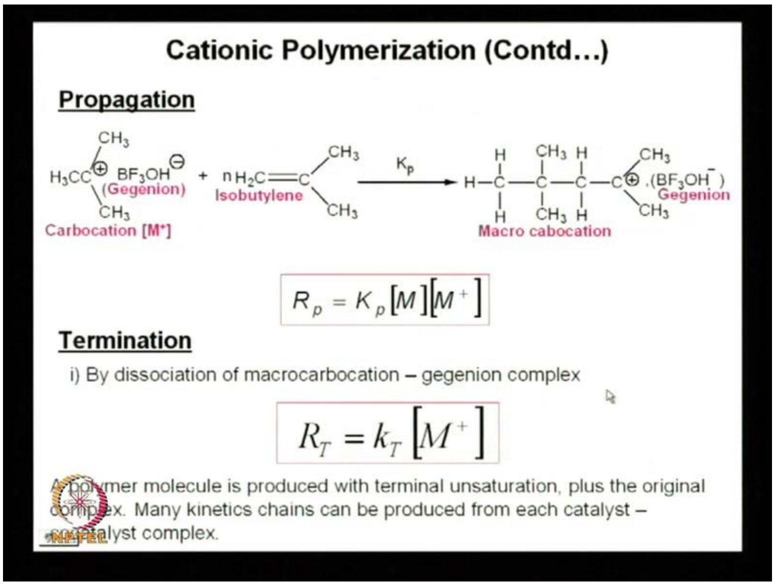

Cationic Polymerization (Contd…)

Propagation

$$R_p = K_p[M][M^+]$$

Termination

i) By dissociation of macrocarbocation – gegenion complex

$$R_T = k_T\left[M^+\right]$$

A polymer molecule is produced with terminal unsaturation, plus the original complex. Many kinetics chains can be produced from each catalyst – cocatalyst complex.

You will see that one event of initiation by this process can lead to large number of polymer chain growth. Look at the propagation, this carbocation and gegenion complex. When it comes close to new phase molecule, then that adds to gradually. It continues addition. This site, cationic site, it increases its length and this is actually known as macro carbocation. Macro carbocation actually here it is not shown in the bracket. It should be shown in number units and then you can say macro carbocation and write that way, macro carbocation, the length of which may be huge.

Now, once this macro carbocation is formed, then it requires to be terminated. That means, for in case of radical chain polymerization, you have seen the sequences, the events, there initiation propagation and termination. Here also, initiation propagation and termination steps are there. Look at the rate of propagation here. As before also, here as that of radical chain polymerization R p was equal to K p into monomer concentration and growing chain free radical chain concentration and instead of growing free radical chain, we have taken the concentration of macro carbocation. As in case of free radical chain polymerization, we have seen the estimation of that. The concentration of the growing free radical chain is very difficult. Because of tangency, because of very fast process here also, it is not possible to determine or to estimate the concentration, this parameter. So, here also, you have to evaluate this carbocation, concentration of carbocation.

Now, let us look at the termination step. Now, termination here can occur by dissociation macro carbocation gegenion complex. You have seen in case of free radical chain concentration there that occur two different processes. What are those processes? Coupling and disproportionation. It is a kind of disproportionation here. So, if a polymer molecule is produced with terminal unsaturation that means this cation has to be killed. So, if some proton is removed as attached to this carbocation carbon, then there will be negative center. So, that negative and positive center will form a double bond and that end of the polymer chain will be unsaturated. So, a polymer molecule is produced with terminal unsaturation plus the original complex. So, original complex is regenerated here and termination step by this macro carbocation, decomposition or disassociation.

So, original complex catalyst co catalyst complex is degenerated and that is still active as it was active in the beginning. So, the conclusion is many kinetics chai chains can be produced from each catalyst co catalyst complex. You read it as many kinetic, not kinetics. It is man kinetic can be produced from each catalyst co catalyst complex. Have you got the beauty of this system? One complex, isolated complex molecule of catalyst co catalyst. If it is formed, that will initiate one polymer chain that will grow to its fullest length. Then it will be terminated at the point of termination that catalyst co catalyst complex is regenerated. That means it will again come back to the initiation step, so only one complex. That means, it says that small concentration of catalyst co catalyst complex can produce large number of polymer chains of very high molecular weight. You understand?

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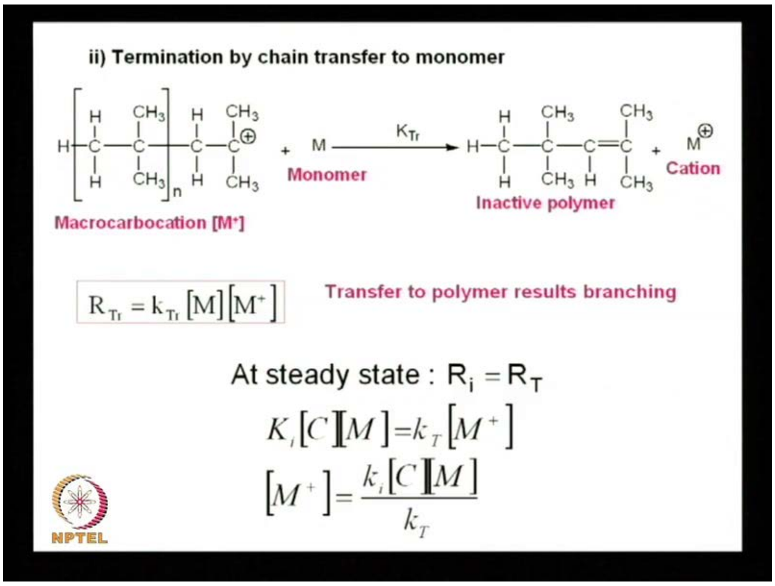

ii) Termination by chain transfer to monomer

$$R_{T_r} = k_{T_r}[M][M^+]$$

Transfer to polymer results branching

At steady state : $R_i = R_T$

$$K_i[C][M] = k_T[M^+]$$

$$[M^+] = \frac{k_i[C][M]}{k_T}$$

Now, there can also be termination by other technique, termination by chain transfer to monomer. Before as in case of chain polymerization, here you see it is macro carbocation in number of units are there and at the terminal unit, this cationic center is there that adds to this monomer. Monomers become initiated and it becomes dead, so it transfers its cationic center to a monomer and producing a newly initiated monomer which can continue to grow producing large number of (( )).

So, here you see there are two ways. Both the processes can occur simultaneously. One catalyst co catalyst complex that initiates large number of polymer chains. At the same time if the termination occurs by transfer reactions to monomer, then that also initiates. It becomes dead and initiates a new chain by starting another process. It is a kind of relay process. It is dead starting another chain to grow relay process here. Also you see rate of transfer is equal to R T i MM plus.

Now, transfer to polymer results in branching a transfer to monomer. There is no chance of branch. How the transfer to polymer results occurs? What happen here is you see at the terminal point, this cationic center is transferred to monomer, but if it interacts with the dead polymer molecule, if this cationic center is transferred at the midpoint of polymer chain or midpoint of any monomer chain to some cationic center will be produced there like this. If some hydrogen mashed from here, it will be this center is cationic. Suppose, cationic or this one cationic center, once this cationic center is produced, it will further add one monomer to this branch. So, this analysis of polymer, one can see what kind of termination access causing this polymerism. Here people are talking in the back ground.

You see in the stem, the active center is present in the center is a very good question. Now, surrounding that center, what the cells are present are monomer and polymer. Now, it is for this kind of transfer, some activation are required for transfer to monomer or to polymer is that activational energy is available to this cationic center. Then it can match or it can leave or what can happen is it can leave this cationic center to other polymer or other monomer or another growing chain or another species catalyst co catalyst complex in this polymer form the carbon.

From here you see, hydrogen can be taken by some other species present surrounding this terminal, cationic terminal, macro cationic center. So, if this is removed, so one proton is removed, so this is negative center. So, what will happen is it produces unsaturation. So, it cannot be specifically said what is the driving force, what is the origin and we can say or you can explain in thermodynamically and activation energy terminology, activation energy may not be sufficient for transferring this activity to monomer or other things or any other presence surrounding or very close to our visiting of this end that can match hydrogen and creating some situation.

This can get terminated. That means, this cationic center is actually broken, destroyed or killed. That is why that is called self-desiccations or self-termination. Here also, you have to assume this steady state as you see, find out green chain carbon radication. So, you have to find out this diameter carbocation concentration. The macro carbocation by steady state concept R i become equal to R T. So, you can get this M plus, this is equal to k i C M by k T concentration term.

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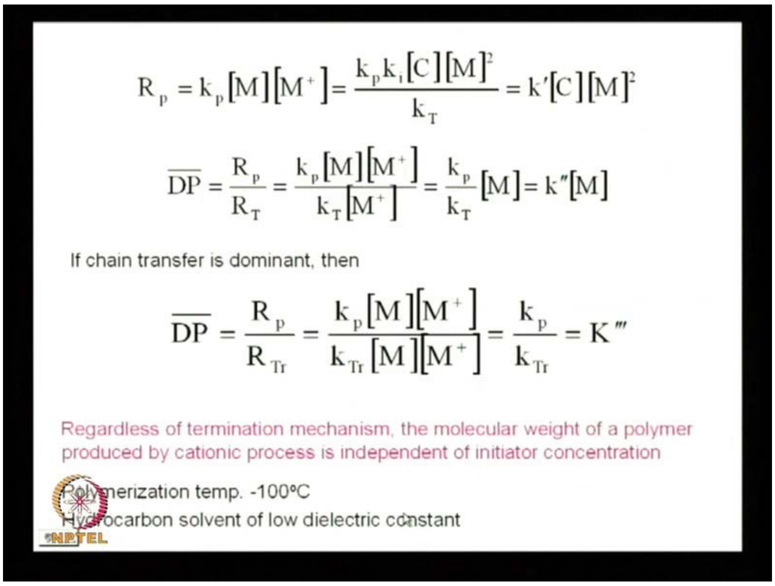

$$R_p = k_p[M][M^+] = \frac{k_p k_i [C][M]^2}{k_T} = k'[C][M]^2$$

$$\overline{DP} = \frac{R_p}{R_T} = \frac{k_p[M][M^+]}{k_T[M^+]} = \frac{k_p}{k_T}[M] = k''[M]$$

If chain transfer is dominant, then

$$\overline{DP} = \frac{R_p}{R_{Tr}} = \frac{k_p[M][M^+]}{k_{Tr}[M][M^+]} = \frac{k_p}{k_{Tr}} = K'''$$

Regardless of termination mechanism, the molecular weight of a polymer produced by cationic process is independent of initiator concentration

Polymerization temp. -100°C

Hydrocarbon solvent of low dielectric constant

This is the dead concentration for termination is substituted the value of M plus carbo concentration of carbocation term to this. Read my equation? No problem. My equation there you can find including these three rate constant within key prime overall net constant and concentration of the co carbon catalyst. So, it is depending on monomer concentration is the R p. So, now what is DP? It is equal to R p by R T. From this R p R T, you find, you see it is independent of degree of polymerization, is independent of catalyst concentration because you have seen this catalyst are regenerated and then goes for reinitiation of poly merchant, but here is little different from that of radical polymerization. It can reinitiate only after it assumes adequate of the poly merchant.

In case of radical polymerization, the linear occurs transfer reactions is premature. Re-transferation here, it does not happen due to premature transferation transfer reactions. You understand? So, premature transfer reactions are not occurring here. That is why many polymerizations are match for effective and gives well defined properties of the polymorphism. Why did one can have those facilities of that control system coming? Because thermal control as it is very difficult to control and your high temperature and it is also equally low temperature, which means you have to maintain the low temperature because these kind of polymerization carried out minus 100 degree celsius. So, there also you have to maintain that low temperature and that is also little expensive polymerization can be continued, obtained here.

If one wants to synthesize polymerization manufacture by cationic, if he has the facilities of that control, that infrastructure for maintaining that low temperature, we can have better control over polymerization because you know any reaction carried out here in high temperature that is difficult to control the kinetics. It becomes complicated. I think you will agree with me. Kinetics of a process, kinetic of polymer here chemical reaction becomes complicated if it is carried out in high temperature because the kinetic energy of the reacting species to be controlled can lead to random pass leaving to random products.

So, for that reason if this reaction can be carried out at low temperature, provided it is so active that it can be carried out at low temperature and one can get very good control over the polymerization as if chain transfer is dominant in the termination process. It is dominated by chain transfer to monomer to polymer. Then you see this DP is independent of either monomer concentration or catalyst concentration, so regardless of termination mechanism, the molecular rate. So, polymer produced by cationic process is independent of initiator. Concentration polymerization temperature is minus 100 degree Celsius. Hydrocarbon solvent of low dielectric constant should be used because that controls polariseability and the activity of the ionic centers in the polymerization. If it is high polar solvent, no cationic polarization.

So cationic polymerization has very strange requirement and probably, you got this one by such cationic process, high molecular weight process and one can get high productivity that is polymerization need also the polymer can be produced at very fast rate. So, productivity of synthesizing manufacturing polymer by ionic polymerization will be higher. At the same time, it will get high molecular weight polymer. At the same time, you will get polymer of well defined properties. I mean properties depended on the molecular weight, molecular size distribution. It gives you very controlled size distribution for this cationic polymerization very good process, provided you have that identity, facilities for carrying out such cationic polymerization.

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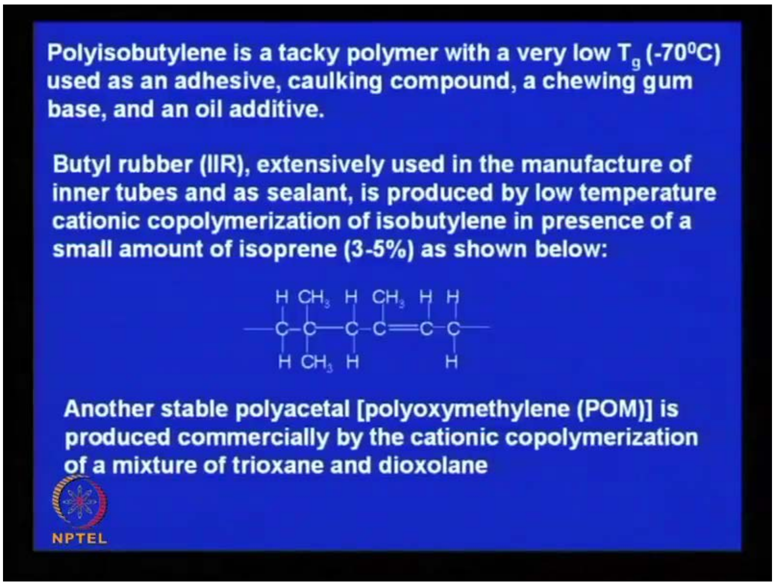

Polyisobutylene is a tacky polymer with a very low T_g (-70⁰C) used as an adhesive, caulking compound, a chewing gum base, and an oil additive.

Butyl rubber (IIR), extensively used in the manufacture of inner tubes and as sealant, is produced by low temperature cationic copolymerization of isobutylene in presence of a small amount of isoprene (3-5%) as shown below:

Another stable polyacetal [polyoxymethylene (POM)] is produced commercially by the cationic copolymerization of a mixture of trioxane and dioxolane

Look at this statement here. Polyisobutylene is a tacky polymer, means tackiness and stickiness. These are the two terminologies, sticky. You know stickiness. What is stickiness? Stickiness means if anything stick to a surface, the surface property that is called stickiness. That means if there is a surface, if the paper will stick to the surface, that is stickiness. This stickiness property, this paper becomes ideate on to the surface if there is some adhesive action. Additive tackiness. Now, if you take two polymer surfaces, we take two polymer surfaces. If the surfaces of those two polymers are sticky, then those two polymer surface added to each other that is called stickiness. Anyway, hey sorry, tackiness. If it is tacky, then only it will be added to this another polymer surface.

So, polymer polyisobutylene is a tacky polymer with a very low glass transition temperature, say of course glass transition temperature of rubber of this kind of polymers lie around, say minus 65 to minus 75 minus 80 like that. For this T g of polymers as isobutylene is minus 70 degree and this becomes tackiness property. This polymer is used as adhesive, caulking compound, a chewing gum base. Similarly, butyl rubber is used as chewing gum base and additive form while property is (( )). So, these are the use of polyisobutylene.

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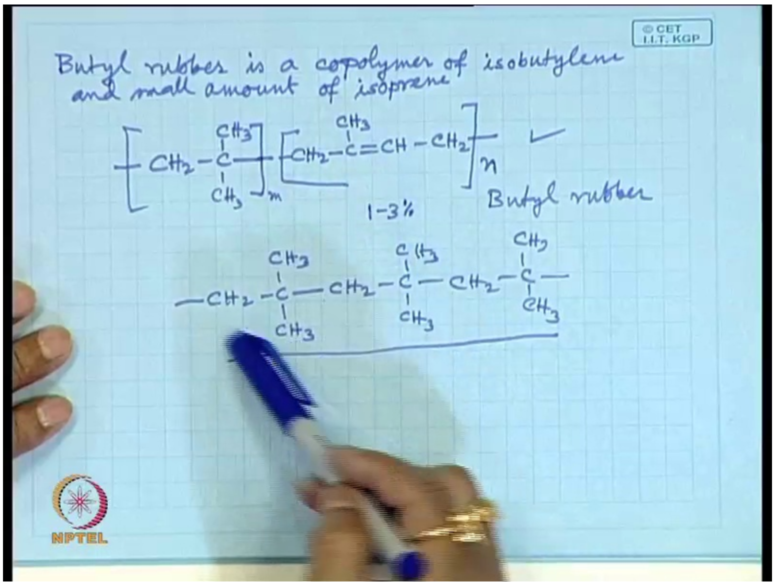

Butyl rubber is a copolymer of isobutylene and small amount of isoprene

There is a very good polymer, no match. Butyl rubber which is a copolymer. We can say butyl rubber, who said me to write. No, butyl rubber is a copolymer of isobutylene and small amount of isoprene. I am drawing this structure. This is isobutylene and this is isoprene. Now, this actually wants to cheaper sell up to 10 percent. So, this is a copolymer of this isoprene for isobutylene polyisobutylene. Why that is required? Now, if you take polymer of this isobutylene, what it indicates is that the backbone is saturated is noted. Its back bone is saturated. This if you continue these numbers of units back bone saturated, so it is a saturated polymer thermoplastic and a very good characteristics of this kinetic polymer. Because of this symmetric structure configuration, this polymer glass (( )) of this polymer is less and this low gas possibility property is exploited in automobile.

Now, in your cycles, any motor cycles, the tyres are used. Inside the tyre, there is a tube. The tube is filled with air at high pressure. So, if the permittivity of the air is very high through that tube, what will happen is everyday probably to fill with air is not economic and convenient also. So, for that, some polymer is used whose gas possibility permeability is very low and air is a polymer. This is known as butyl rubber. Butyl rubber is copolymer of isoprene and butylenes. Now, here the purpose to using this small quantity of isoprene is there to create sides for cross linking alconisation. Here this polymer is not alconisable by tolper, but this polymer is alconised by sulphur. Isoprene you need can react with sulphur into some natural rubber in case of polybutyle rubber or other dying rubbers. The sulphur is used as vocalizing general causing agent. The plastic polymer to thermoset polymer to this polyisobutylene here is used to manufacture or this isobutylene is used to manufacture this butyl rubber by this cationic polymerization.

So, those things let know here another stable polyacetal polyoxymethylene. Polyacetal polyoxymethylene is produced commercially by the cationic copolymerization. Now, here you go through some books will find some monomer varies monomer of how they are polymerized by this cationic copolymerization. Hope you have got this point tic tic tic and not only that, there saturated backbone of very long length. What happens in a butyl polymer chain? So, after 100 to 150 units of isobutylene isoprene unit comes for linking purpose, so enter system symmetric and saturated.

So, this polymer is very stable to high temperature. Now, riding your getting the compute of these wheels, tyres. Do you know how these tyres are manufactured? The tyres are manufactured by completion of molding using tyre curing bladder. Apart from using this butyl rubber for making inner tubes, but this butyl rubber is also used for making bladder which profits pressure to the mold between the mold and the tyre component. Green tier at high temperature of 172-180 degree Celsius.

This at that temperature that bladder remain stable, that bladder made of butyl rubber. So, there are various uses of this butyl rubber which can stand at very high temperature. If you take natural rubber because of the presence of the double bond isoprene, you need it not stable towards that high temperature to break a polymer. Structure will be destroyed, but because of this saturated back bone chain, this polymer is stable to high temperature.

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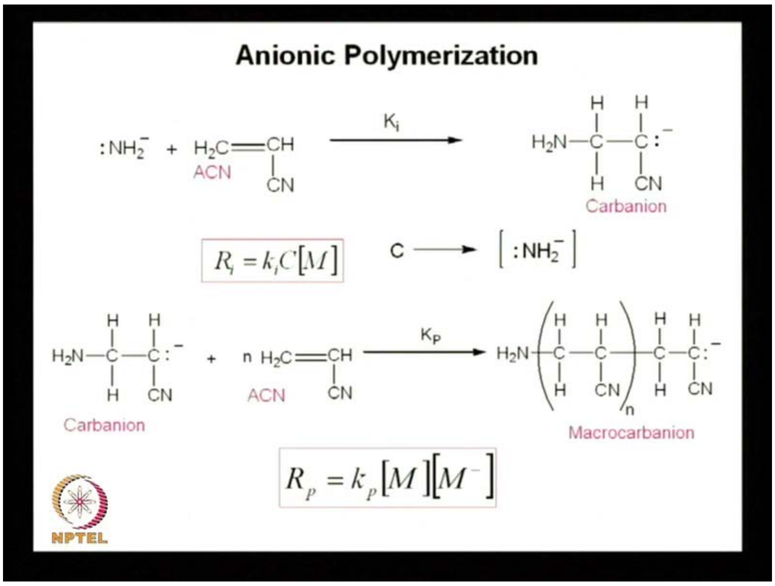

Anionic Polymerization

$$:NH_2^- + H_2C{=}CH(CN) \xrightarrow{K_i} H_2N{-}CH_2{-}\overset{..}{C}H(CN)^-$$

$$R_i = k_i C[M]$$

$$C \longrightarrow [:NH_2^-]$$

$$H_2N{-}CH_2{-}\overset{..}{C}H(CN)^- + n\,H_2C{=}CH(CN) \xrightarrow{K_p} H_2N{+}CH_2{-}CH(CN){+}_n CH_2{-}\overset{..}{C}H(CN)^-$$

$$R_p = k_p[M][M^-]$$

Now, let us come to anionic polymerization. Chain polymerization or anionic polymerization by anionic initiator, this you have seen because of the presence of this CN group C triple band nitrogen nitrite group. Now, this helps polarization of this pi bond. What happens is this is a catalyst NH2 minus, this is a catalyst. This catalyst acts as anionic catalyst say polybutyle is made by anionic polymerization known as living polymerization. This is a terminology living polymerization.

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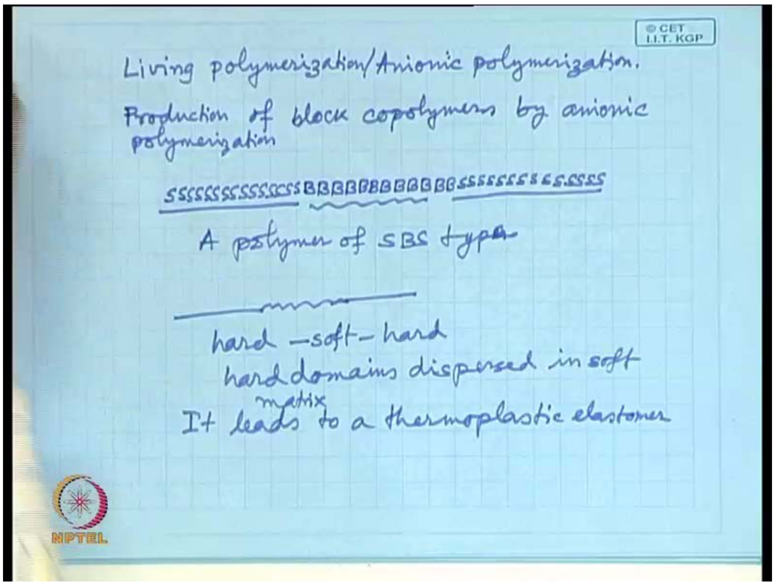

Living polymerization/Anionic polymerization.

Production of block copolymers by anionic polymerization

SSSSSSSSSSSSSSSSBBBBBBBBBBBBBSSSSSSSSSSSSSSS

A polymer of SBS type

hard – soft – hard

hard domains dispersed in soft matrix

It leads to a thermoplastic elastomer

Why it is called living polymerization? You know you can understand this reaction steps here. Nothing difficult. If you go through it as before, you have seen this cationic polymerization, their expressions, all those things and how to calculate all those things. You can easily get it, but few things I am mentioning here is this anionic polymerization or living polymerization here actually anionic initiators like sodium duterine, sodium alkyl or amides. These things actually help in initiation of monomers which are polymerizable by anionic polymerization by these anionic initiators.

Why it is called living polymerization? Once the polymerization starts, so as long the monomer is present in the system, it will not become dead. It will not terminate, it will live alive. How? In case of radical chain polymerization, even if you do not add any chain transfer agent, the polymer molecules will become dead by transfer to monomer initiator, all these things by various chain transfer reactions or by termination reaction or by coupling process, disproportionation process. So, the radical activity of those free radical growing chains becomes dead or killed spontaneously of course after growth of adequate molecular size, but here it will remain live. That is why it is called living polymerization.

Why it will not terminate? This kind of concept or this characteristic behavior has been exploited by producing block co polymers. What are block co polymers? See I am just showing. Suppose, you have taken styrene. The polymer has the styrene to produce a block adequate or desired length, known length block of styrene polystyrene. See, may be this block length may be say 10,000 molecular weight, then this center remains alive. It will not terminate and then you add buteryne. So, as long the buteryne monomer is present, it will continue to form a buteryne block. As soon as the buteryne is exhausted, it remains live and then you once again add styrene.

So, what you are getting is a polymer of SBS type styrene buteryne styrene block of polymer. Now, it is a unique property. Now, styrene is rigid, polyester is rigid because of the presence of phenyl link in the backbone, chain attached in the backbone of every alternate carbon. This is a rigid polymer whereas, polybuterine, that backbone chain contains only hydrogen substituents. So, it is flexible. So, what you are getting? You are getting a chain followed by flexible chain followed by a rigid one. So, what it forms?

A hard block. It forms a hard block followed by soft block. What happens is this hard block assemble at certain domains, regions, hard domains embedded, hard domains dispersed in soft matrix. It gives like a composite. So, it leads to a thermoplastic elastomer. Please remind me later where I shall cover this elastomer to explain or to cover elaborately about this thermoplastic elastomer. Now, here our scope is limited to discuss details of this thermoplastic elastomer, but I have told you the concept by anionic chain polymerization. You can manufacture this hard, soft, hard blocks as thermoplastic customers, since it is living in nature.

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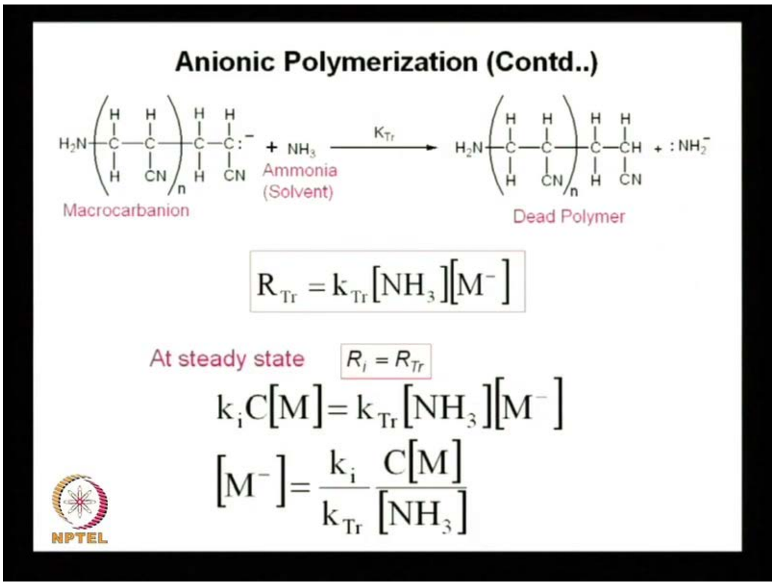

Anionic Polymerization (Contd..)

$$R_{Tr} = k_{Tr}[NH_3][M^-]$$

At steady state $R_i = R_{Tr}$

$$k_i C[M] = k_{Tr}[NH_3][M^-]$$

$$[M^-] = \frac{k_i}{k_{Tr}} \frac{C[M]}{[NH_3]}$$

As before you see different expressions for different rates R p R T R and by steady state concept, you get this from steady state concept, get this concentration and then you get this R p and therefore, DP you can get this is monomer and this is ammonia concentration. Thus, the rate of propagation and molecular weight are both inversely related to the concentration of ammonia and the activation energy for chain transfer is larger than the activation energy for propagation. The overall activation energy is approximately 38 kilo calories per mole. The reaction rate increases and molecular weight decreases as the temperature is increased and then you see there are various other possibilities using various other initiators. You can show, go through the book and read it, you will understand.

Thank you.