Science and Technology of Polymers
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Lecture - 3
Basic Concepts on Polymers (Contd.)

Yes, the next scheme of classification is on the basis of thermal response, response to high temperature, low temperature, how the polymers behaves.

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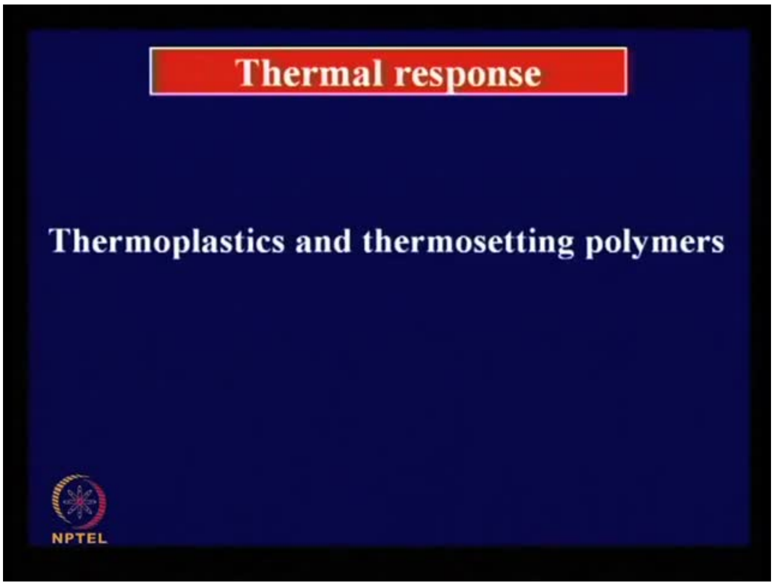

Thermal response

Thermoplastics and thermosetting polymers

The two major classis are thermoplastics and thermosetting. Thermoplastic polymers and thermosetting polymers, we have seen the examples of synthetic polymers, semi synthetic polymers and natural polymers, all of them can be categorized into these two classis thermoplastic polymers, thermosetting polymers. Thermoplastic polymers are those, which softens on application of heat again hardens on cooling, this is a reversible change, if a polymer shows reversible change from soft to hard, hard to soft by heating and cooling in vice versa, we get thermoplastic response.

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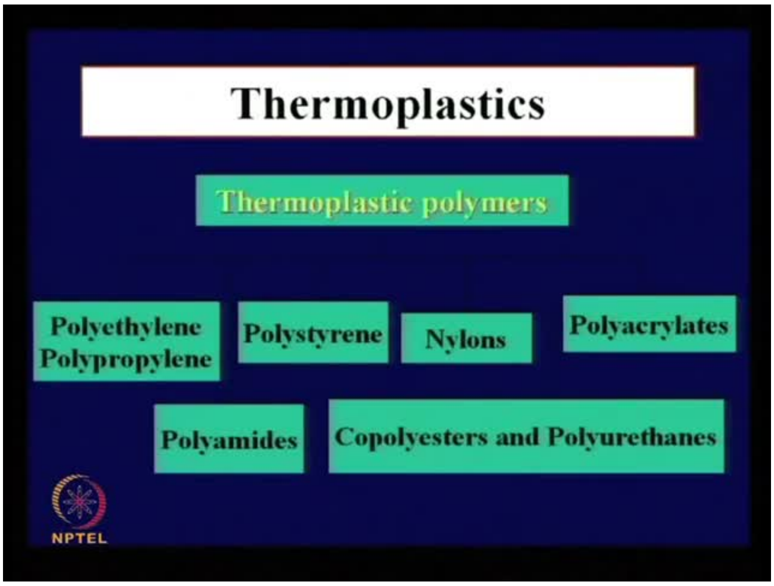

Thermoplastics

Thermoplastic polymers

Polyethylene
Polypropylene

Polystyrene

Nylons

Polyacrylates

Polyamides

Copolyesters and Polyurethanes

Polyethylene, polypropylene, polyesters, of course saturated polyesters, polyamides, polycarbonates, polystyrenes, nylons, polyacrylates, polyurethanes, these are all thermoplastic polymers. These polymers are recyclable, once a product is made from this thermoplastic polymers after use of the polymer, when it is disposed it can be managed by collecting, those disposed polymer. After cleaning, washing and drying again those polymers can be reprocessed, for making new set of products known as recycling or recycle products. So, thermoplastics can respond to recycling of oldest plastic, oldest polymers.

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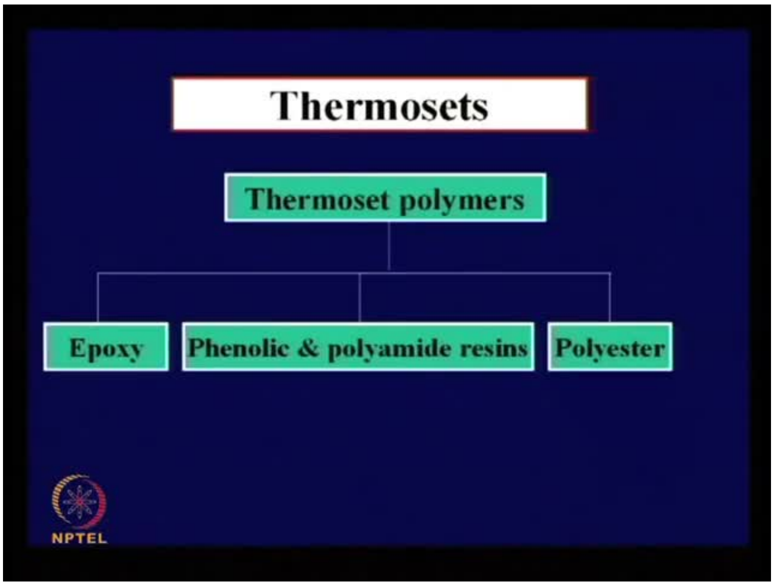

Thermosets

Thermoset polymers

Epoxy

Phenolic & polyamide resins

Polyester

Whereas, thermo set polymers behave differently, you have seen in case of that phenol polyamide resins synthesis, area of polyamide resin synthesis, phenol polyamide resins synthesis.

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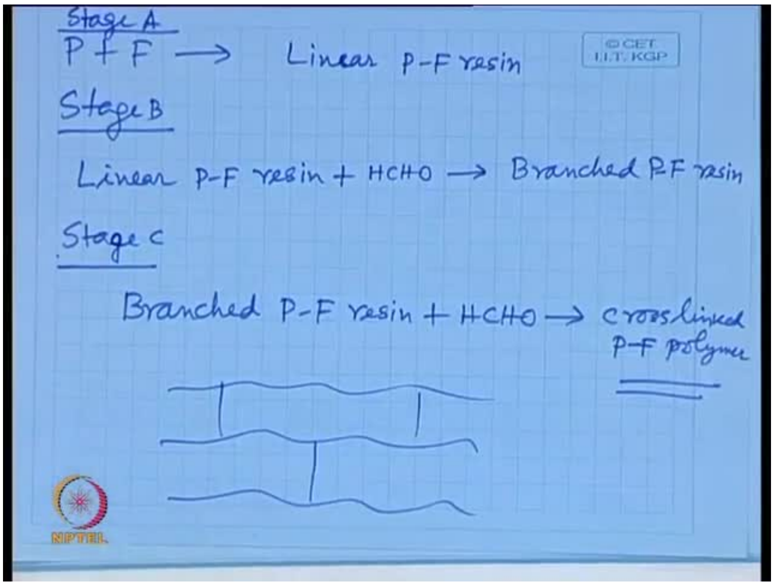

Stage A

P + F → Linear P-F resin

Stage B

Linear P-F resin + HCHO → Branched P-F resin

Stage C

Branched P-F resin + HCHO → cross linked P-F polymer

There we saw that, that this polymers initially remains in thermoplastic stage linear, than when it is branched steel it is in the thermoplastic stage, but on further heating that leads to a stage c polymer, a c stage polymer, which are thermo set. Means, this is a universal change. This thermo set polymers are infusible by heating, it cannot be fused, cannot be melted by heating and there also insoluble in insolvents. Because of a three dimensional network of polymer molecules, they form a three dimensional network of polymer chains.

That is why these polymers are insoluble and infusible, because to make them fusible, melt able or solvable this inter molecular bonds are to broken. Whereas, thermo plastic molecules are polymers are linear molecules. Examples, again may be large only few examples are shown over here, epoxied polymers, epoxy polymers, phenolic polymers, polyamide resins can lead to thermo set also thermo in addition to thermoplastic polyesters, you can have thermoplastic polyesters.

Whereas, in I can have thermo set polyesters also, if you take unsaturated polyester. Then unsaturated polyester undergo inter molecular cross linking reactions to form a three dimensional network of polymer chains, which is insoluble and infusible. Say if you take example of cellulose cotton. Now, we have got the definition of thermoplastic and thermo set polymers, linear polymers, branched polymers and crosslink polymers, three dimensional network polymers. Now, if I ask you a question, what about cellulose cotton, is it solvable in water? Have you found, have you seen any solvent for cellulose cotton, no.

So, we can call it thermo set polymer, can you melt cotton you can melt for polyesters, polyester fibre, can you melt cotton? Why the question is why? We cannot melt cotton, we cannot dissolve cotton why? There must be some reason, what is that reason? Can anybody answer any of you hurry, from commonsense you can answer. Yes I am not getting. What kind of three d network. Through primary bond, primary bond, sorry you are wrong, cellulose is a thermoplastic polymer, cotton is a thermoplastic polymer, but it cannot be dissolved in solvent it cannot be melted.

Fine if you want to melt it by heating it will degrade, because of extensive hydrogen bonding between, hydroxide groups of anhydride glucose units. There are three hydroxide anhydride glucose unit, cotton cellulose is a polymer of anhydride glucose units, cottons cellulose is a polymer of anhydride glucose ring, containing three hydroxide groups one primary hydroxide groups and two secondary hydroxide groups, please look at this cellulose molecular structure. That enter into extensive inter molecular hydrogen bonding, now the chemical bonding aspect is coming you see. Here, we can compare discreet molecular compounds with a polymeric compounds, polymeric materials.

You have to think of primary bond and secondary bonds, what are primary bonds, primary bonds can be covalent, ionic, coordinate covalent bond, metallic metallic bond, secondary bond, hydrogen bonding, hydrogen bonding minerals bonding, minerals bonding. What is the genesis of Van Der Waals bonding? Differentiate electronic negativity between atoms that is an induced effect. So, think of ethylene, it is gas (( )) condition is it not?.

Ethylene is a gas on, when ethylene is converted to polyethylene it becomes tough, hard, solid, plastic materials where from this strength has come. Van Der Waals bond, random desperation force, random desperation force that constitutes this Van Der Waals bonds, whose magnitude around 1 to 3 kilocalories is per mole, hydrogen bond 1 to 5 kilocalories is per mole bond energy. So, here this hydrogen bond huge, hydrogen bonding is bonding is the inter molecular hydrogen bonding is there, so it is insolvable.

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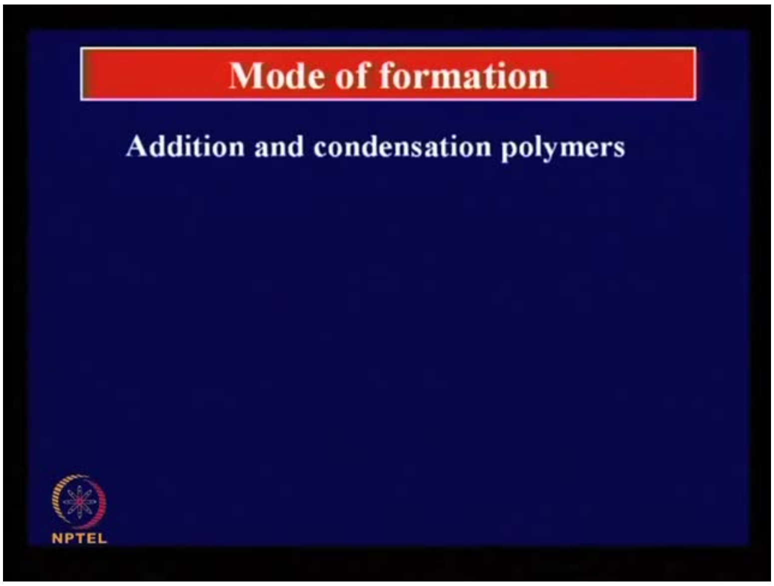

Mode of formation

Addition and condensation polymers

Then next categorise polymers can be of two types; condensation polymers and addition chain polymers, based on the principle of formation. Now, ethylene when converted to polyethylene, it is made by addition chain reaction. I was talking about functional groups in ethylene, there is no such functions as is found in case of are diacid, dialcohol, doils, diamines. That means, there is no I mean hydroxy acid function of groups available in ethylene molecule, but it undergoes polymerisation to polyethylene.

Where is that bond? What is the functional groups? Then the phi bond the phi electronics, the phi phi bond opens up by homolytic cleavage the two free electronics on each carbon and that, those free electronics help in combining with one another forming the polyethylene molecular, that addition chain polymerisation. So, all this polymers all the monomers having all finicky double bond, can undergo addition chain polymerisation or ring monomers, can also undergo addition chain polymerisation.

Whereas, condensation polymerisation that needs functional groups like hydroxyl group, carboxyl group, amen group or acetyl group, acyl groups like this. That condenses to from a polymer chain eliminating a small molecule of say, it may be water, it may be hydrogen chloride, it may be sodium chloride depending on the functional groups, which have been reacted to from this polymer. So, we can have addition and condensation polymers.

So, if you look in to this synthesis of polyester, if you look into the synthesis of polyamide, if you look into the synthesis of polyamides, if you look into the synthesis of phenol and formaldehyde phenol and formaldehyde reaction product, polycarbonate synthesis, epoxies synthesis will find that some small molecule is eliminated and that means, is a condensations reaction. This condensation reaction occurs in steps multistep reaction step one, forming a dimer.

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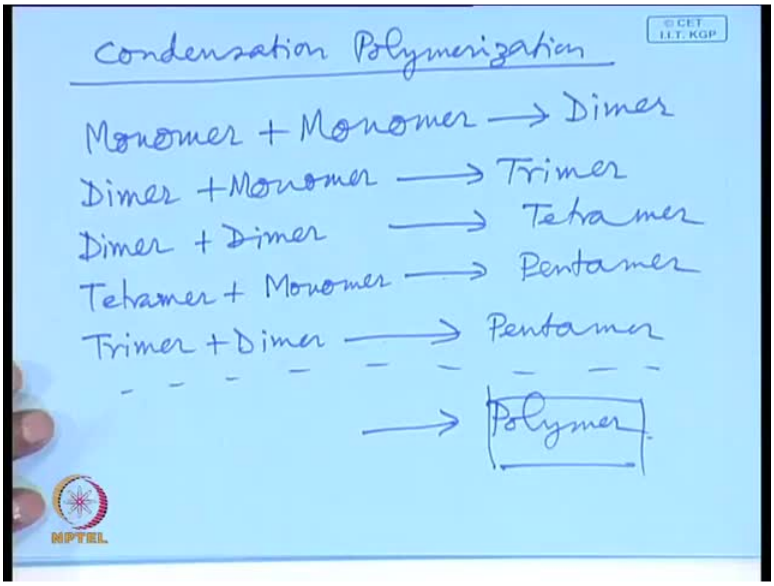

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Condensation Polymerization

Monomer + Monomer → Dimer
Dimer + Monomer → Trimer
Dimer + Dimer → Tetramer
Tetramer + Monomer → Pentamer
Trimer + Dimer → Pentamer
- - - - - - - - - - -
→ Polymer

So, various steps, so it is a slow process, first dimer is formed, formed trimer is formed tetramer is formed, pentamer is formed, hexamer is formed, heptamer is formed, octamer is formed, nonomer is formed, dodecamer is formed. This way it proceeds in steps and these are called intermediates. In each and every step, there is condensation reaction between two functional groups, either one hydroxide group and a carboxyl group or carboxyl group or carboxyl group or amino group like this, okay?

Slowly and slowly these intermediates growing in length bigger and bigger and bigger and bigger. So, this is a slow process, condensation polymerisation is a slow process whereas, addition chain polymerisation is a very fast process. Once a monomer is initiated by opening a phi bond, eventually it finishes its growth to a very big molecular weight molecular size polymer. Say time taken for completion of promotion of, one addition chain polymer way fraction of a second minus seven second time minus seven second time a polymer molecules, from the in the addition chain polymer, whereas step polymer he is takes hours of time. Now, you can you understand the examples of this polymers additions, what are the addition chain polymer, what are the condensation polymer, you understand from the this thing example, we can get the examples synthesis principles.

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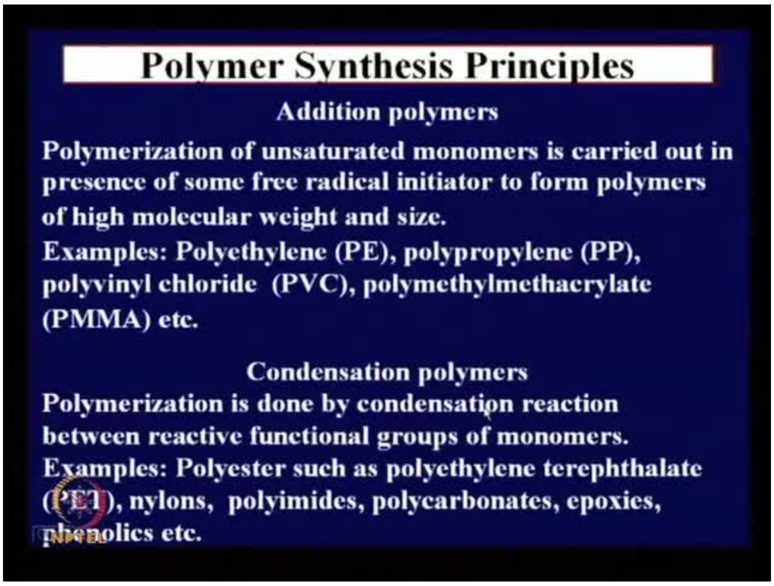

Polymer Synthesis Principles

Addition polymers

Polymerization of unsaturated monomers is carried out in presence of some free radical initiator to form polymers of high molecular weight and size.

Examples: Polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polymethylmethacrylate (PMMA) etc.

Condensation polymers

Polymerization is done by condensation reaction between reactive functional groups of monomers.

Examples: Polyester such as polyethylene terephthalate (PET), nylons, polyimides, polycarbonates, epoxies, phenolics etc.

I have already told, what is addition chain, addition polymers examples, polyethylene polypropylene, polyvinyl chloride, polymethylmethacrylate, polystyrene, polyacralites, styrene between rubber, poly between rubber, promo pine rubber. All these are main point addition chain polymerisation principle, condensation polymerisation principle done by condensation reaction, between reactive functional groups of monomers. Examples are polyester such as, polyethylene terephthalate, nylons, polyimides, polycarbonates, epoxiex, phenolics, that means amino polymers etcetera.

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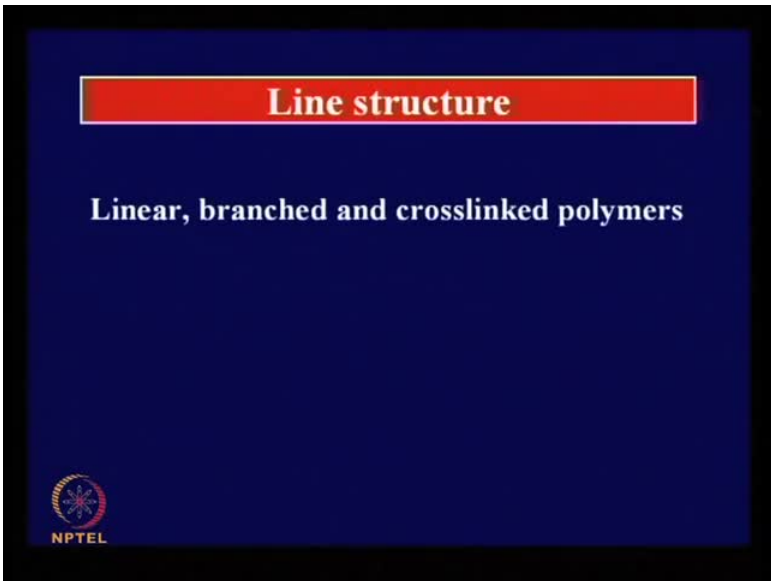

Line structure

Linear, branched and crosslinked polymers

Then classification on the basis of line structure the polymer, can be linear structure branched structure and crosslink polymer, you have seen. I already explained, what are the classes of polymers, linear polymer, branched polymer and crosslink polymers? For example, polyethylene. If you take the polyethylene example polyethylene.

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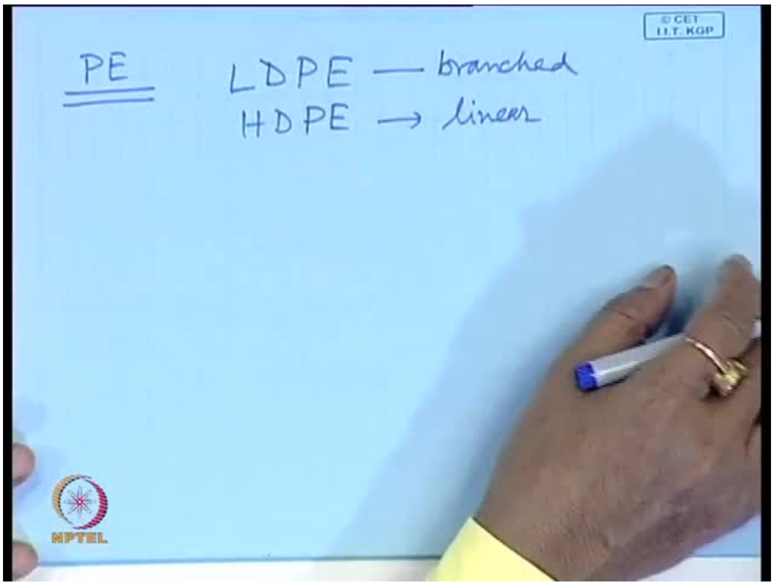

PE

LDPE — branched
HDPE → linear

I told you L D P E and H P P E two grades example, the low density, high density, this is a branched polymer, this is linear polymer. Then may be very small branches or lit some short branches is there, but engineer we can say we can say that L D P E is branched, because of this branch it is of low density have you got the concept of low density due to having branch low density means, was packing packing efficiency. Now, if there are branches, then the branch will hinder closer approach of the neighbouring molecules. Your you have cut your hair, now how do you feel? If you place your thumb over here, is it not pricking your skin, place your is it not pricking your skin? No, you are wrong. You ask your friend to touch it is pricking.

Student: Yes sir

Now, as this hairs grows bigger and bigger and bigger, it would become uncomfortable. Actually, my teacher used to tell story like this, there was a student in the class, he named Raghu, every day he comes to the class without preparing lesson and teachers become very angry, why he had not come prepare with your lesson every day?

So, you are not studying, you will have not be able to good result in the exam, you must study and come to the class. Everyday this same thing is happening and since teacher become's angry used to hold is hair like this, give shacking on the head that means, every next day he was just expecting that, if gives this kind of some your pain to the student.

So, next day he will come preparing is lesson, than no result, but on this contrary, so student also getting angry, sir well next day I will give you lesson, I will teach you lesson. So, you came cutting his hair like that, so he could not hold his hair. So, days onwards he got pricking on this teacher he just after touching, he was getting a shock like. So, again the teacher was well, we have taken this kind of measure, let me right for few days again, your hair will grow and then I will able to catch like that. So, this a this is a case of branching and we see a effect of branch.

So, if there is the length of branch is longer, then the affect on densities is minimum, if they length of branch is order effect of density is the is a one more on density is more. So, this is the situation so low density you understand, so low density polyethylene how it is made actually, so low density polyethylene, it is it is a co polymer of it is a co polymer ethylene and 1 hexene or 1 pentene.

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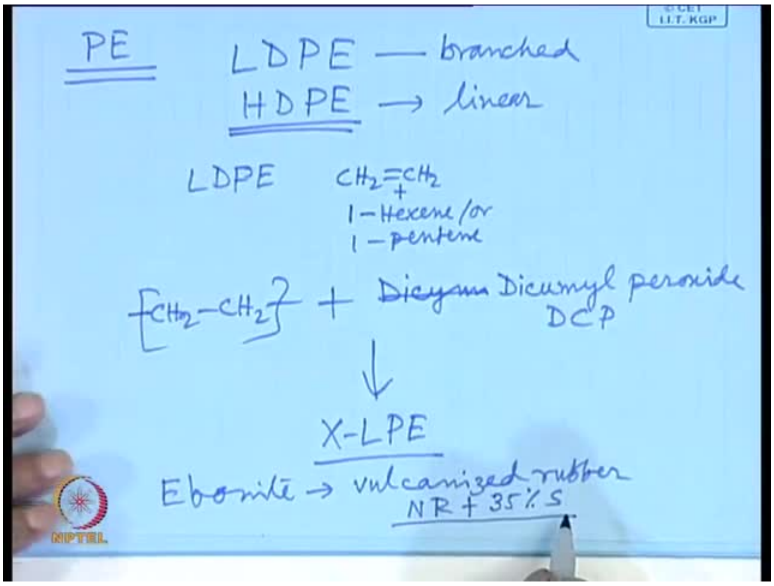

PE

LDPE — branched

HDPE → linear

LDPE $CH_2=CH_2$ + 1-Hexene/or 1-pentene

$\left[CH_2-CH_2\right]$ + ~~Dicyan~~ Dicumyl peroxide DCP

↓

X-LPE

Ebonite → vulcanized rubber

NR + 35% S

So, this will you will have four or five carbon atom branch, the regulated regulated polymer chain structure in order to develop low density polymer, for making frames or very low profile products. Whereas, high density polymer, there is no branch such branches and this this linear polymer can also crosslink. So, even if you take polyethylene use some peroxide sorry D C P crosslink polyethylene, X L P E vulcanise rubber.

Since, one from poly as supreme is a thermoplastic polymer from you get latex, you coagulate the latex, isolate the solid rubber wash it and dry, we get dried our that is thermo plastic. When you add sulphur to it, along with other chemicals auxiliary chemicals, we get crosslink vulcanized rubber is a tier is a vulcanized rubber ebonite, ebonite it is a rubber. Another vulcanized rubber, natural rubber plus 35 percent sulphur ebonite used in usedt in making a battery case ebonite, ebonite is a balkanise rubber use for making battery case ceasing, battery container, storage battery.

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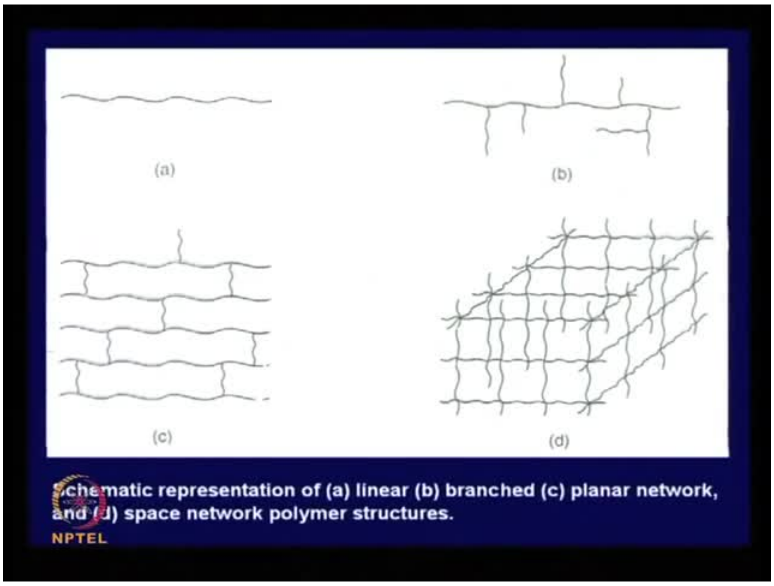

Schematic representation of (a) linear (b) branched (c) planar network, and (d) space network polymer structures.

This is schematic representation of, this is a linear polymer, this a branch polymer. Branches can be of different types long branch, long branch short branch like this. c is a planar network structure configuration and this is three dimensional network polymer or known as, space network polymer. When first concrete there is also a three dimensional network structure, all those that is not a polymer of the concept comes from there, three dimensional network polymer. Now, if I ask you a question, now here we seen in case of linear polymer, there is a limit of molecular, this length is from here to here, it may be say 1000 kilo dell tone or 10 kilo dell tone 100 kilo dell tone like this.

Here, molecular is little bigger, because of this branches here molecular is little bigger, what is the molecular at of this system? Cross link system this one, three dimensional network system, who can say? What would be the molecular weight of this three dimensional space network polymer system? Is there anybody to answer, is this molecular size finite, is this molecular size finite yes or no?

Student: Yes, yes.

Is this finite? Is this also finite? Infinite on cross linking inter molecular linkage of linear molecules lead to infinite molecular weight, infinite molecular size.

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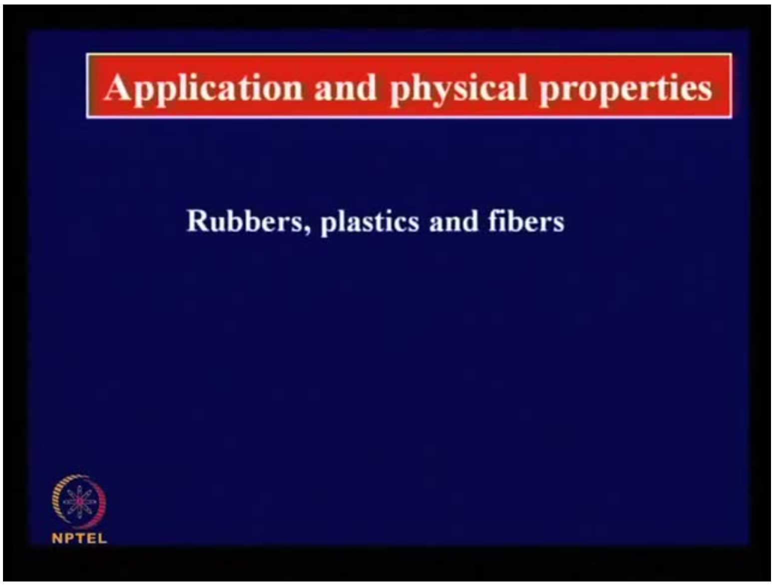
Application and physical properties

Rubbers, plastics and fibers

Then classification is application on physical properties, rubber plastics and fiber is same polymer, can be available in any of this three different forms. Either plastic or fiber or rubber, you take polyethylene, we can you can have you can have polyethylene plastic, you can have polyethylene fiber, you can have polyethylene rubber, what is the difference among this three?

The difference is the matter of degree of alignment, it is an matter of degree alien matter of degree, extent of alignment, molecular alignment, molecular order, molecular organization. If the organization is highest, it will lead to a fiber suppose, this is one molecule this is another molecule. If they remain side by side lateral in this way and there is contact to each other. So, this is very strong, but if it is vertices like this only contact in one point.

So, this is in aligned maximum aligned stages alien situation minimum alien situation, so molecular segmental order alignment, crystalline alignment, crystallinity. So, fibers are maximum crystalline, then plastics minimum crystallinity, minimum or no crystalline order amorphous. So, from the degree of alignment from the concept of molecular order, we can categorise polymers as a rubber, amorphous, fibers, maximum crystalline and plastics intermediate crestallinity and tacticity.

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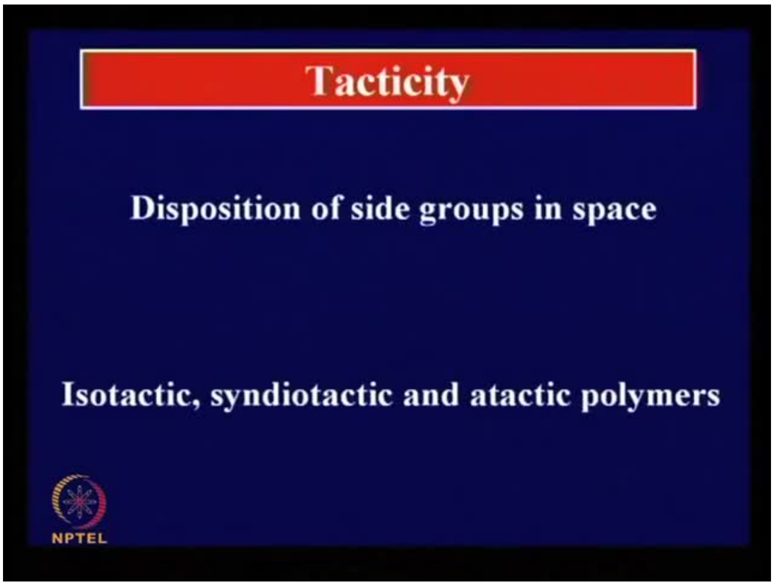

Tacticity

Disposition of side groups in space

Isotactic, syndiotactic and atactic polymers

Tacticity. Disposition of side groups in space through that disposition, we get three different geometric configurations, isotactic configuration, syndiotactic configuration and atactic configurations. Then what are the examples of polymers, which can, so such type of configurations, can this polymer show such type of configuration?

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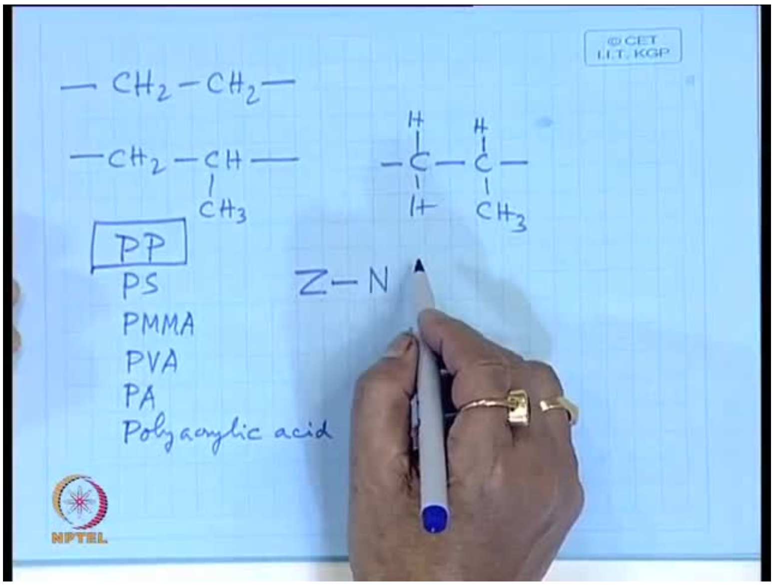

No, because this is a symmetric, this molecule this is non symmetric means, there is some asymmetric centre. This centre is a asymmetric known as, (( )) centre that means, is an every carbon is different from others. So, this leads to such type of isotactic syndiotactic and atactic configurations. So, this way poly propylene, polystyrene, P M M A poly phenol alcohol, polyacrylates, polyacrylic acid, this can lead to the atactic configuration atactic structure atacticsity.

Now, before the discovery of Zinc larine nat Catalyst, you know have you heard, this name zinc larine nat. Orginomentlic Catalyst the developed this catalyst and for, which there owned double prise in 1963 based on their work technology was developed in 1970 for preparing, this polyethylene polypropylene using stereo specific orginomentlic catalyst, for stereo specific polymerisation. So, isotactic polyethylene, a polypropylene syndiotactic polyethylene, prior to development of this technology, when polypropylene was manufactured around 30 to 40 percent of the product become atactic, then what is atactic? Then what is isotactic? What is syndiotactic? Look at this structure.

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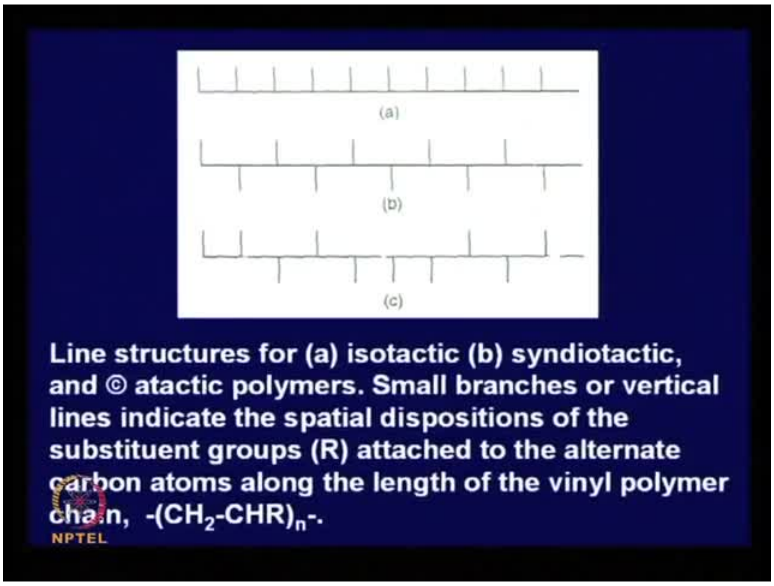

Line structures for (a) isotactic (b) syndiotactic, and © atactic polymers. Small branches or vertical lines indicate the spatial dispositions of the substituent groups (R) attached to the alternate carbon atoms along the length of the vinyl polymer chain, -(CH$_2$-CHR)$_n$-.

Here, you see this is on configuration, this is an another configuration, this is an another configurations. Now, this two configurations symmetric configuratios, this is isotactic, this is isotactic this is syndiotactic configuration and where you see, there is no symmetry there is no regularity in dispositions of the side groups this one. So, this is a atactic configuration, now atactic polypropylene is an is useless product, it is this steaky, soft, weak, polymer in mass, oxeye mass no product can be made from this atactic polypropylene whereas, isotactic and syndiotactic polypropylene is strong and tough polymer.

So, 30 to 40 percent of atactic prop propylene, would have to be separated from this isotactic and syndiotactic polymers and that was loss and because of, that reason the cost of polypropylene was very high. That cost was reduced to large extent using, this stereo specific catalyst say aluminium alkyl titanium chloride combination, titanium chloride and aluminium alkyl, titanium chloride aluminium alkyl, this combination orginomentlic combination leads to hundred percent conversion to either syndiotactic or isotactic with no atactic variety. So, today the cost of polypropylene is the, is very low is a lowest cost polymer, cheapest polymer cheapest polymer available in the market as, commodity polymer is a commodity polymer.

Commodity polymer is such, which is available at low cost, if it finds large volume consumption for making products this are known as, commodity product general purpose use polypropylene, polyethylene. This is also commodity polymer, polyethylene, polypropylene, polypropylene, chloride. These are the three polymers, three polymering members, which are used most among all other products available.

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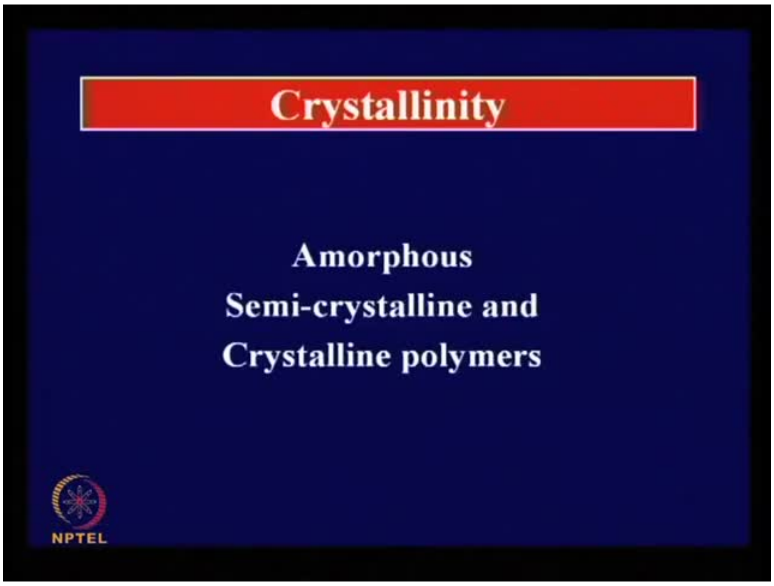

Crystallinity

Amorphous
Semi-crystalline and
Crystalline polymers

Crystallinity, I told you amorphous semi crystalline and crystalline polymers. Now, this crystallinity or concept of crystalline structure in polymers little different from the concept of crystallinity metals and in other discreet molecules, in metals and discreet molecules find crystllinity. If you say crystallinity crystalline there is 100 percent crystalline material with little defect, but polymers although, we call it crystalline polymer but the crystallinity percent crystsllinity is not 100 it is less than that, it may be 60 percent, it may be 40 percent, it may be 50 percent, it may be 20 percent like this. What is this? That means there are certain zones are domains in a polymer example, having crystalline region, crystalline order followed by amorphous regions.

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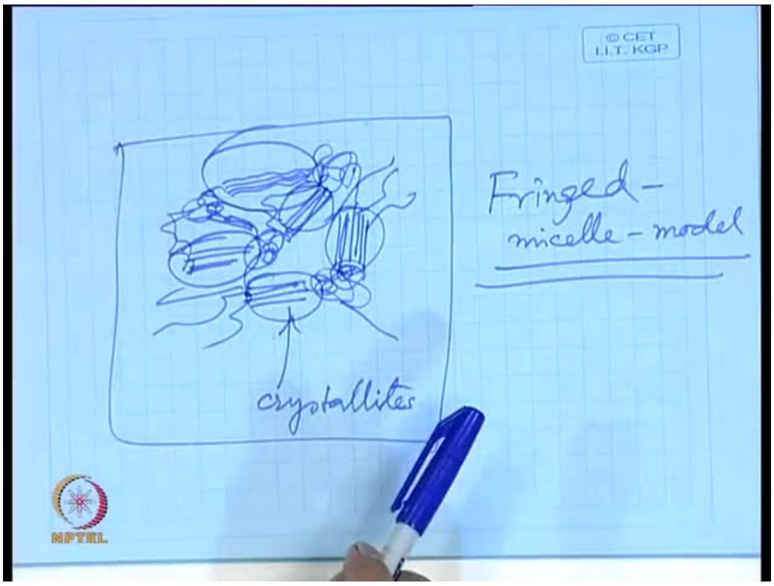

So, it may look like this, these are crystalline regions that means, one molecule can pass from pass through amorphous regions, two crystalline region through crystalline region to another amorphous regions. So, these are known as crystallites actually, this is a fringed model fringed model were crystallites remain dispersion amorphous matrix is a semi crystalline or quasi crystalline polymer.

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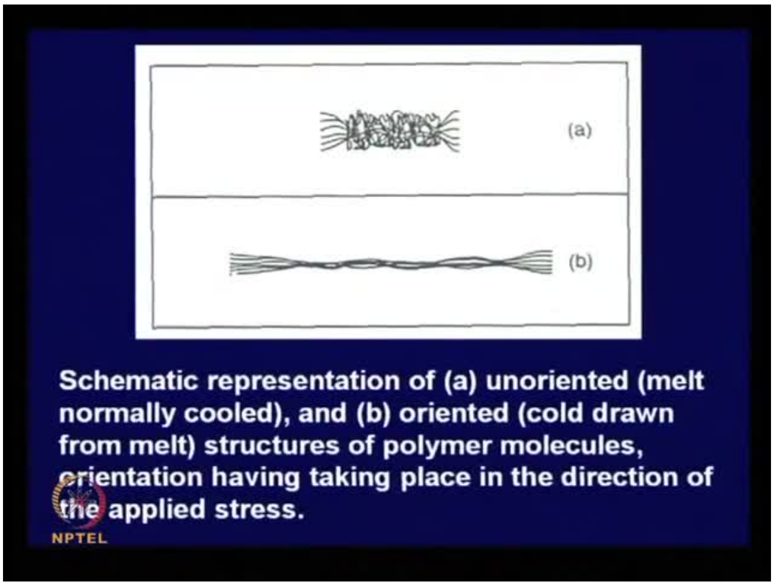

Schematic representation of (a) unoriented (melt normally cooled), and (b) oriented (cold drawn from melt) structures of polymer molecules, orientation having taking place in the direction of the applied stress.

Now, this is a schematic representation of unoriented melt disposition, unoriented melt polymer melt, if you melt it look like this zig zag, zig zag. That means, there is segments polymer segments of cold it, cooled in cooled it and cold configuration. I taken this from a book, for you have understanding that is science and technology of polymers, plastics, rubbers and fibers written by professor Pigou that day I told you to by this book. This figure is oriented cold drawn from melt, if you heat a polymer towards, melting than if having place on stressing force molecules gets aligned it become crystalline. So, this is this is more crystalline, than this one. This is a one first this is a crystalline, structure property relationship, why this is necessary?

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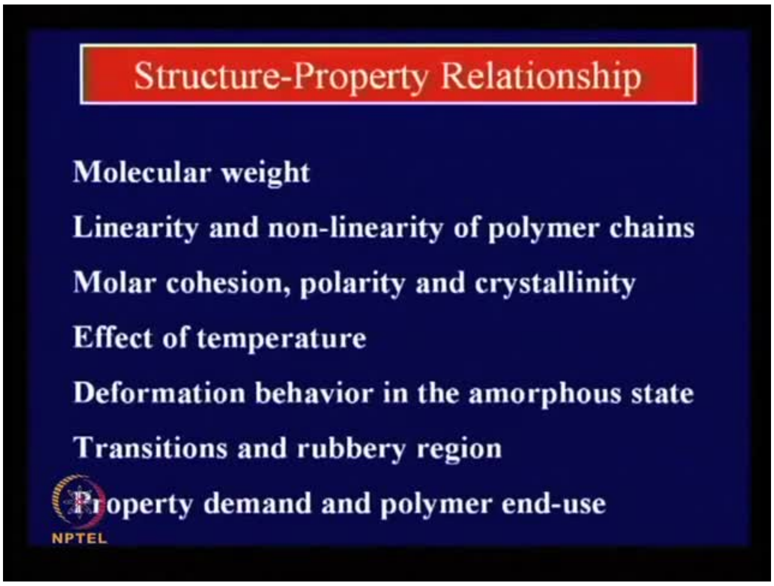

Structure-Property Relationship

Molecular weight

Linearity and non-linearity of polymer chains

Molar cohesion, polarity and crystallinity

Effect of temperature

Deformation behavior in the amorphous state

Transitions and rubbery region

Property demand and polymer end-use

Because we have to look into the polymer structure than correlate, this structure with properties, if you want to make a product for selection of a suitable polymer, then you you must know the properties. Then you have to make correlation, between in the properties with the molecular formula, chemical formula of the polymer structure of the polymer.

So, these are there are few points molecular weight, you have to know the molecular weight, you have to know know the linearity and non-linearity of polymer chains, molar cohesion, molar cohesions secondary balance process, secondary bonds, polarity in the molecule, crystallinity, then effect of temperature on the polymer sample, how it behaves? Then deformation behaviour of the polymer under load in a amorphous condition, amorphous state in crystalline state.

Then on application of temperature a heat that means, if you the temperature of the polymer, then there are a certain transactions of faze from last see to rubbery faze to melt faze last transaction is melting transaction. Then property based this structural features, you know the properties of the polymer, which can be exploited, for end use of the polymer for making product. Well let us stop here, next you will see.

Thank you.