Non - Metallic Materials
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Module – 01
Polymer materials
Lecture – 02
Understanding of polymer structures

Welcome back to the second lecture of the course entitled Non-Metallic Materials. And in today's lecture, we will Understand the polymer structure. So, one of the major non-metallic materials include various types of polymer. So, we need to understand the structure of the polymers. So, we will start the lecture with understanding on polymer structure.

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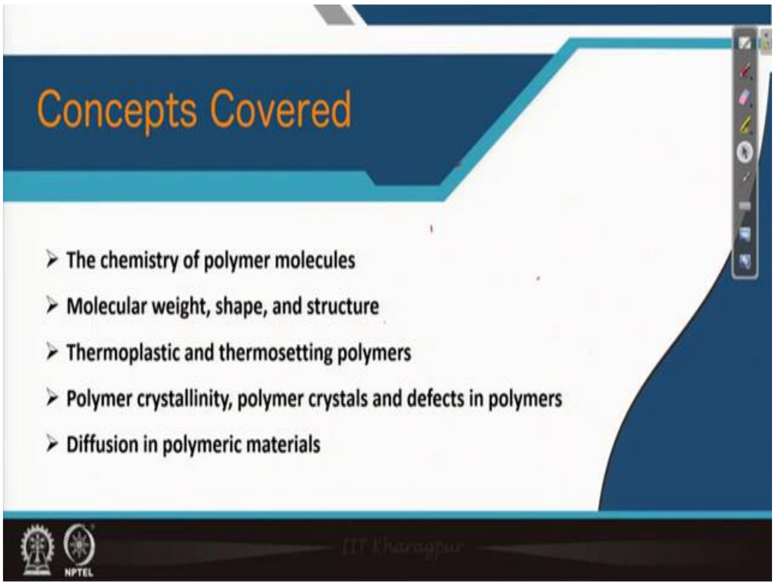

Concepts Covered

- The chemistry of polymer molecules
- Molecular weight, shape, and structure
- Thermoplastic and thermosetting polymers
- Polymer crystallinity, polymer crystals and defects in polymers
- Diffusion in polymeric materials

Now, first the coverage of this particular lecture is having the chemistry of the polymer molecules, you need to understand the chemistry how it forms, and how the properties are changed across a set of polymeric materials. And molecular weight, which is very important in case of polymer materials its shape, its structure that we will be describing.

Then two important set of polymer – one is thermoplastic which can be processed at high temperature, and thermosetting polymers. One is recyclable and other one is not, you will understand. It basically it is amorphous material, but certain polymer crystallinity is there.

So, we will talk about crystalline polymers, polymer crystals, we will examine and different types of defects in the polymers we will talk about. And finally, the diffusion of the polymer materials that is also an important aspect. So, I will shed light on that.

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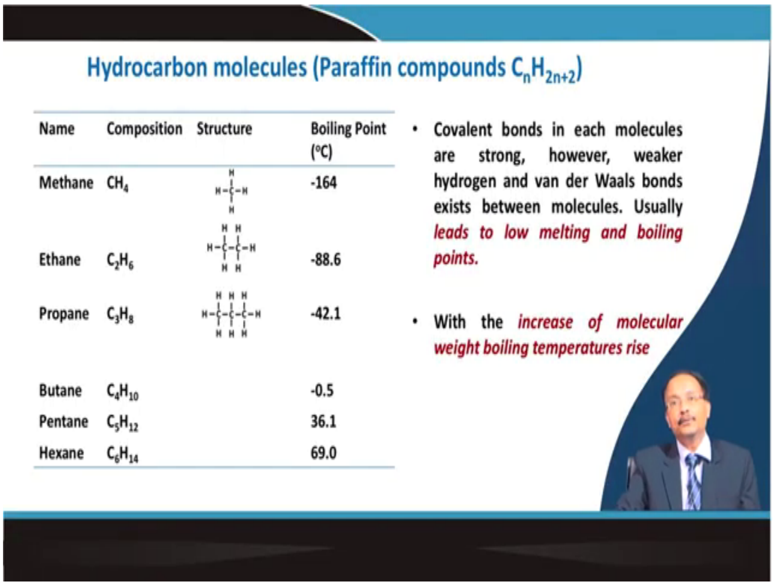

Hydrocarbon molecules (Paraffin compounds C_nH_{2n+2})

Name	Composition	Structure	Boiling Point (°C)
Methane	CH_4		-164
Ethane	C_2H_6		-88.6
Propane	C_3H_8		-42.1
Butane	C_4H_{10}		-0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

- Covalent bonds in each molecules are strong, however, weaker hydrogen and van der Waals bonds exists between molecules. Usually *leads to low melting and boiling points.*
- With the *increase of molecular weight boiling temperatures rise*

So, we will start from hydrocarbon molecules, which is well-known to you. You know that they these are all paraffin compounds having a general formula C n H 2 n plus 2. So, if C is, sorry n is 1, then it is CH 4 methane, like that you have ethane, then propane, butane, pentane, hexane, you can go on. So, it is higher order structure. And you can see the structure here that is drawn carbon is having 4 valence states.

So, it is taking a 4 hydrogen to satisfy it is covalency and they have covalent bond. And as you can go to higher order of this organic molecules, you see that the boiling point is progressively increased. So, methane it is a basically a gas. The boiling point is minus 164 degree Celsius; and in case of hexane, it is 69 degree Celsius positive.

So, basically this materials are strong, but between molecules weaker hydrogen or van der Waals bond that exists, so that leads to relatively lower melting point as well as boiling point. And as I said with the increase of molecular weight the boiling temperature keeps on rising.

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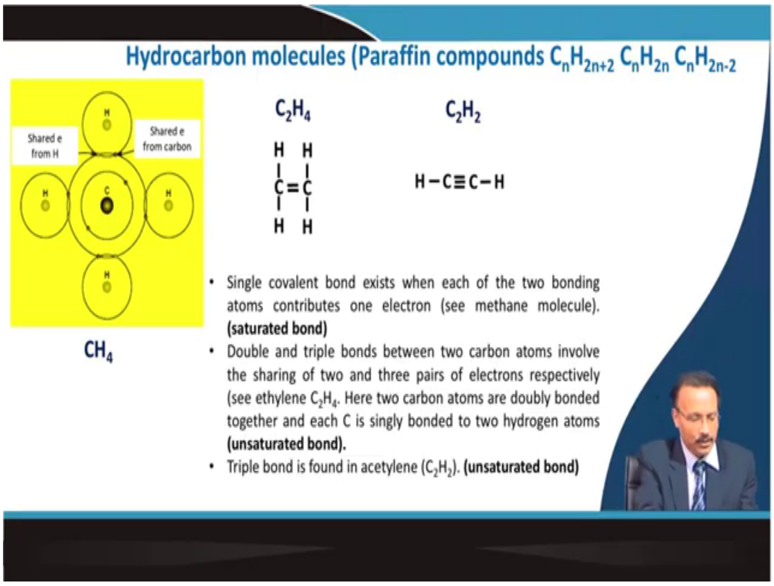

Hydrocarbon molecules (Paraffin compounds C_nH_{2n+2} C_nH_{2n} C_nH_{2n-2}

$H-C\equiv C-H$

- Single covalent bond exists when each of the two bonding atoms contributes one electron (see methane molecule). **(saturated bond)**
- Double and triple bonds between two carbon atoms involve the sharing of two and three pairs of electrons respectively (see ethylene C_2H_4. Here two carbon atoms are doubly bonded together and each C is singly bonded to two hydrogen atoms **(unsaturated bond).**
- Triple bond is found in acetylene (C_2H_2). **(unsaturated bond)**

So, this is the typical structure of methane as you can see, and the intermolecular bonds are covalent. And once you have a single covalent bond, two bonding atoms they contributes one electron just like your methane, so then we call it is a saturated bond. But in certain organic material like ethylene, you have double bond; and acetylene, you have triple bond. So, they are unsaturated bonds.

And in the second case, two carbon atoms are doubly bonded together. And each carbon is singly bonded to two hydrogen as you can see. So, it is in between carbon, it is double bond, and single bond in case of this hydrogen. So, in case of acetylene, you have a triple bond exists between two carbon atom and then single bond with hydrogen.

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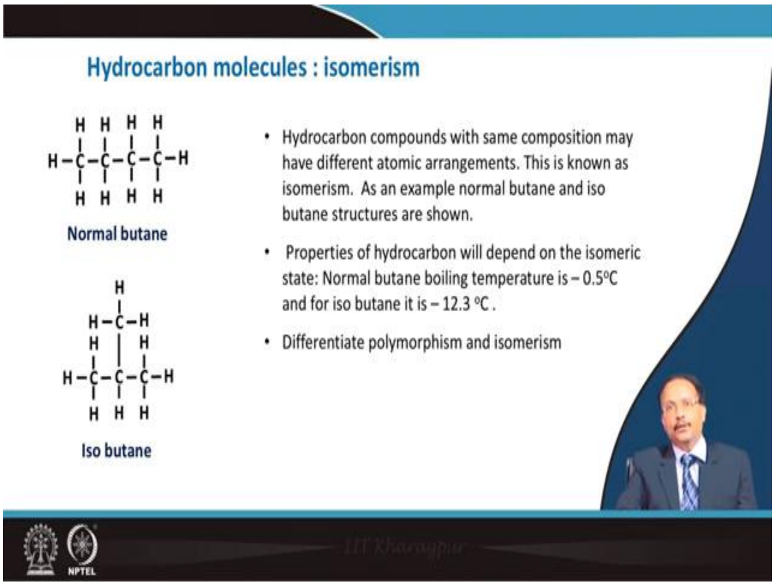

Hydrocarbon molecules : isomerism

- Hydrocarbon compounds with same composition may have different atomic arrangements. This is known as isomerism. As an example normal butane and iso butane structures are shown.
- Properties of hydrocarbon will depend on the isomeric state: Normal butane boiling temperature is – 0.5°C and for iso butane it is – 12.3 °C .
- Differentiate polymorphism and isomerism

So, in this hydrocarbon molecule, we have isomerism. And in case of isomerism, as you can see the composition remain same, but they have different atomic arrangement. And this is something similar to polymorphism in case of ceramic material. And later try to explain that in what way it is similar, and in what way it is different from isomerism.

So, as an example, I have shown this normal butane and iso butane. And the property of this hydrocarbon, they certainly depends on this isomeric state. For example, normal butane you have a boiling temperature which is minus 0.5 degree Celsius, and for iso butane it is minus 12.3 degree Celsius. So, it depends on the isomeric merism. And therefore, the structure of the hydrocarbons.

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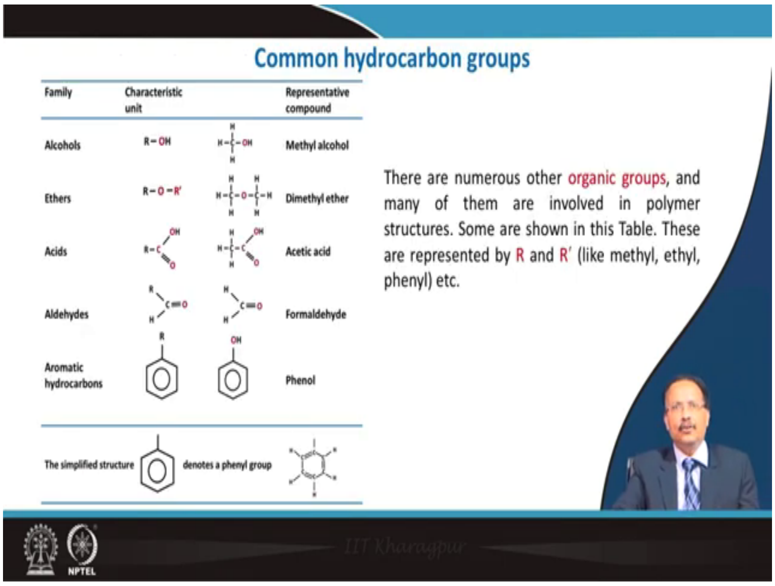

Common hydrocarbon groups

Family	Characteristic unit		Representative compound
Alcohols	$R-OH$		Methyl alcohol
Ethers	$R-O-R'$		Dimethyl ether
Acids			Acetic acid
Aldehydes			Formaldehyde
Aromatic hydrocarbons			Phenol

The simplified structure denotes a phenyl group

There are numerous other organic groups, and many of them are involved in polymer structures. Some are shown in this Table. These are represented by R and R′ (like methyl, ethyl, phenyl) etc.

So, there are various organic groups that is available, it is denoted either by R in this these slides or R dash. So, you can have methyl, ethyl, phenyl group. So, depending on this group, you have representative compound. Say for example, here it is methyl alcohol or you can have a dimethyl ether, you can have acid like organic acid, acetic acid, you have aldehydes which is having CHO group or aromatic, various types of hydrocarbons that is there.

And the structure is a bit complicated in case of phenol as you can see. And this is a simplified structure, but actual structure is ring like structure with the alternate double and single bonds.

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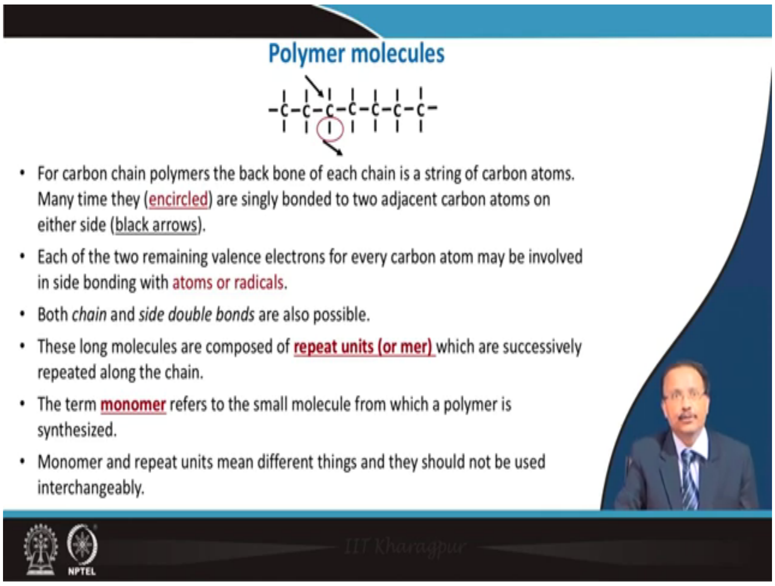

Polymer molecules

- For carbon chain polymers the back bone of each chain is a string of carbon atoms. Many time they (encircled) are singly bonded to two adjacent carbon atoms on either side (black arrows).
- Each of the two remaining valence electrons for every carbon atom may be involved in side bonding with atoms or radicals.
- Both *chain* and *side double bonds* are also possible.
- These long molecules are composed of **repeat units (or mer)** which are successively repeated along the chain.
- The term **monomer** refers to the small molecule from which a polymer is synthesized.
- Monomer and repeat units mean different things and they should not be used interchangeably.

Now, this polymer molecules, the carbon chain of this polymer they form the backbone of the structure. So, it is, this string of carbon atoms. And usually this carbon is bonded with two other carbon, so they are very strong. And the other bonds, they are free. So, two remaining valence electron of every carbon, they are not bonded.

So, a side bonding is possible. Whatever I have marked with this arrow, you can see the side bonding is possible. And this chain side bonded double chain is also possible. So, all types of complicated structure one can form for particular polymer molecules. Now, these long molecules, they are basically composed of repeat units we call me r, so poly mer.

So, various mers are attached together to form a long molecules. We call this is polymer. And the term which is monomer which refers to the small molecule, where from the polymer is synthesized. This large polymeric chain is formed. So, monomer and repeat units mean different things, and they should not be used interchangeably. So, you cannot use monomer and repeat units, they are not similar things or same things, so that you can use like the same way.

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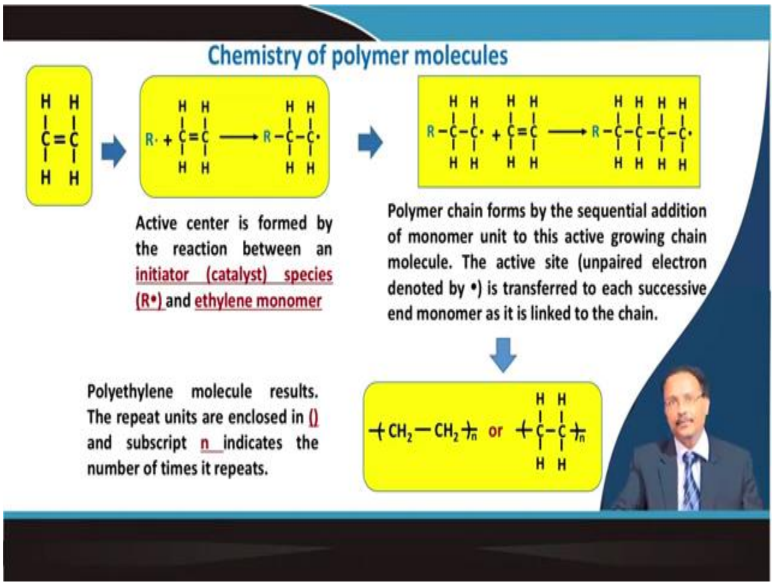

Chemistry of polymer molecules

Active center is formed by the reaction between an initiator (catalyst) species (R•) and ethylene monomer

Polymer chain forms by the sequential addition of monomer unit to this active growing chain molecule. The active site (unpaired electron denoted by •) is transferred to each successive end monomer as it is linked to the chain.

Polyethylene molecule results. The repeat units are enclosed in () and subscript n indicates the number of times it repeats.

$-\!\!\left(CH_2-CH_2\right)\!\!-_n$ or

Now, how exactly it is formed? So, as you can see in this new slide, we have this organic molecules. And here you will have to put a active center. And therefore, an initiator which we call catalyst also catalyst species, and the ethylene monomer, so these two are reacted right to make the polymerization.

So, this reaction you can see. And for this reaction, R, this group this organic group is attached. And this double bond of ethylene monomer this is broken. And again it is ready to take another monomer. So, this reaction continues.

We will talk about the polymer reaction two different types of reactions are there. And it forms this monomer with the help of this active center, they form actually the polymer polymeric structure. And keep on increasing. So, there must be a limit it cannot be extended infinitely.

So, number of this monomer which is accommodated in the so called polymer which is forming after this reaction this is denoted like this. So, it is still basically CH 2 and CH 2. So, that n times, this is increased.

So, we result is from the ethylene monomer, you are creating what we call a polythene, polyethylene molecule, so that is results. The repeat unit actually is encapsulated I mean inside the bracket. And the subscript n that denotes that how many times it is repeated. So, this is how it is differentiated.

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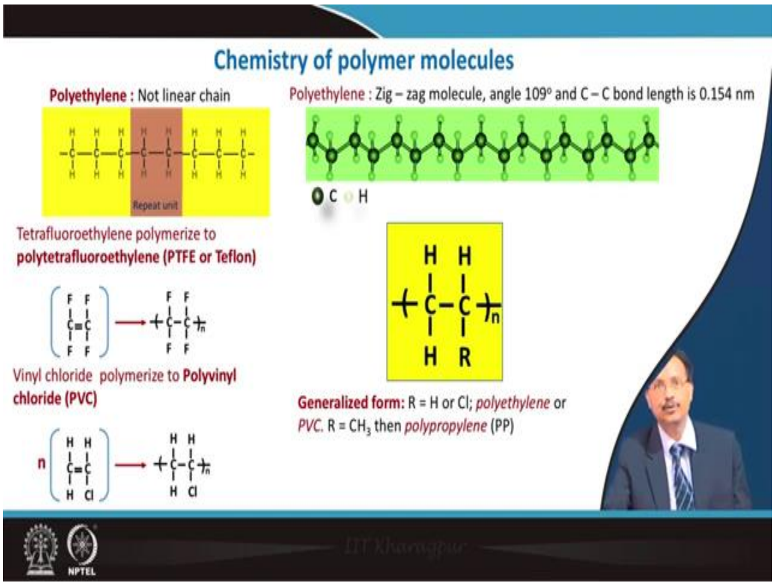

Chemistry of polymer molecules

Polyethylene : Not linear chain

Polyethylene : Zig – zag molecule, angle 109° and C – C bond length is 0.154 nm

Tetrafluoroethylene polymerize to **polytetrafluoroethylene (PTFE or Teflon)**

Vinyl chloride polymerize to **Polyvinyl chloride (PVC)**

Generalized form: R = H or Cl; *polyethylene* or *PVC*. R = CH_3 then *polypropylene* (PP)

So, polythene is a although I have shown, but it is not a linear chain. The actual polythene chain is zig-zag one and the angle is ah about 109, 109 degree; and carbon-carbon bond length is about 0.154 Angstrom. So, similar reaction is possible for other monomer as well. So, you can make what we call Teflon polytetrafluoroethylene. So, the formula is given by this or you have polymerization after polymerization you get polyvinyl chloride – PVC.

So, the general form generalized form is some kind of R is there. So, R is different in each cases. If it is H or chloride, then you will have polyethylene or PVC or CH 3 is also possible, then the polymer will termed as polypropylene. So, they are all commodity polymers and used very commonly.

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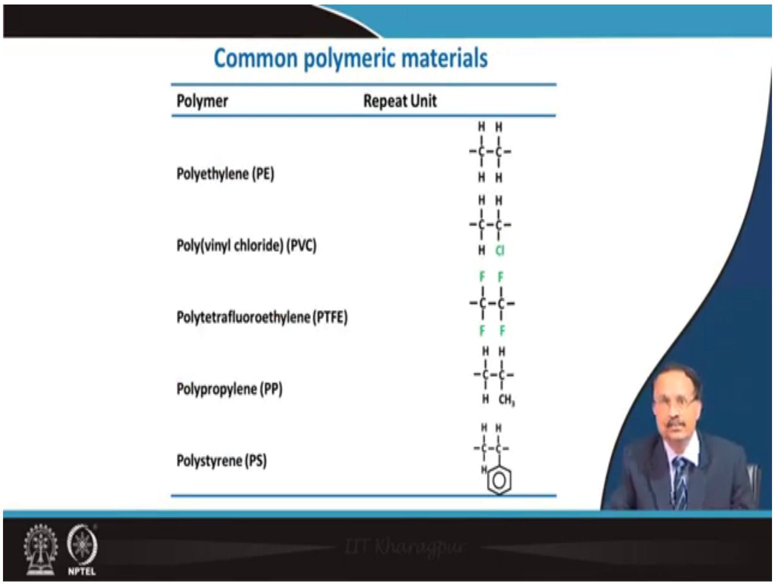

Common polymeric materials

Polymer	Repeat Unit
Polyethylene (PE)	
Poly(vinyl chloride) (PVC)	
Polytetrafluoroethylene (PTFE)	
Polypropylene (PP)	
Polystyrene (PS)	

So, these are common polymeric material. And repeat unit, I have tabulated starting from polyethylene abbreviated as PE, then you have polyvinyl chloride – PVC, then polytetrafluoroethylene – PTFE, then polypropylene, and then polystyrene. So, progressively it may be simpler like this common polymers or it could be little bit more complicated.

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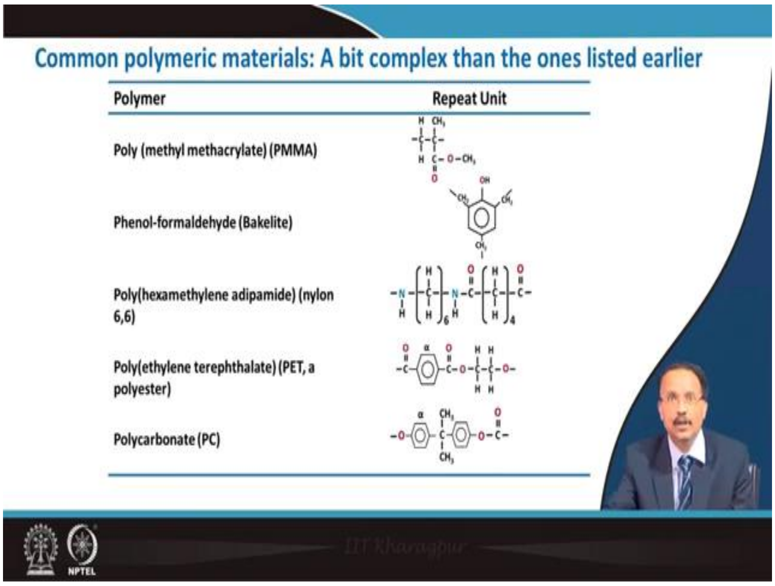

Common polymeric materials: A bit complex than the ones listed earlier

Polymer	Repeat Unit
Poly (methyl methacrylate) (PMMA)	
Phenol-formaldehyde (Bakelite)	
Poly(hexamethylene adipamide) (nylon 6,6)	
Poly(ethylene terephthalate) (PET, a polyester)	
Polycarbonate (PC)	

So, we have poly methyl, methacrylate, the same principle it forms. And as I have said this side group, they are not always single group, but they are having double bonds here. Then phenol formaldehyde which we call Bakelite. Then nylon is another example.

Then polyethylene terephthalate PET, PET made bottle and polycarbonate, these are all ah complex, but in the same principle it occurs you have a monomer, you have a active center in the form of a catalyst. And first the catalyst set up the monomer, and then there is a chain reaction, and the polymerization takes place.

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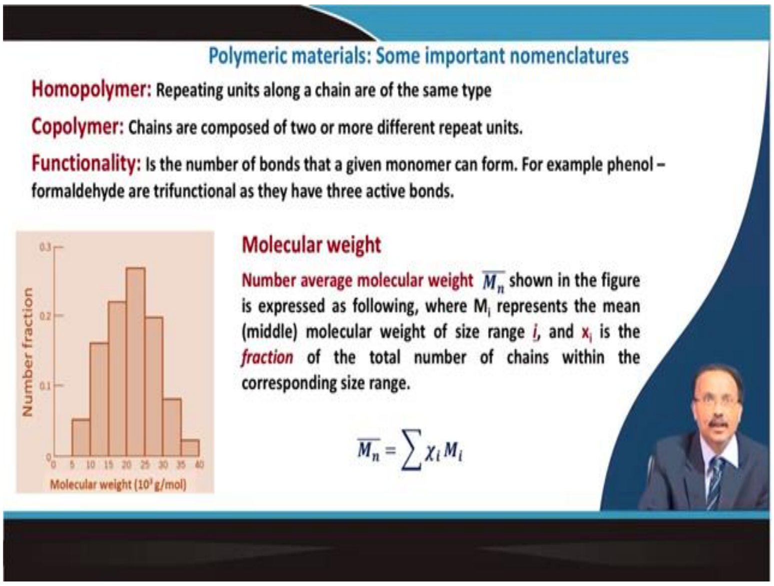

Polymeric materials: Some important nomenclatures

Homopolymer: Repeating units along a chain are of the same type

Copolymer: Chains are composed of two or more different repeat units.

Functionality: Is the number of bonds that a given monomer can form. For example phenol – formaldehyde are trifunctional as they have three active bonds.

Molecular weight

Number average molecular weight $\overline{M_n}$ shown in the figure is expressed as following, where M_i represents the mean (middle) molecular weight of size range *i*, and x_i is the *fraction* of the total number of chains within the corresponding size range.

$$\overline{M_n} = \sum \chi_i M_i$$

So, some important nomenclature of this polymeric material is first one is homopolymer that repeating units along a chain are of same type, so then we call it is a homopolymer. Then we have copolymer – the chains are composed of two different types of repeat unit, then we call it is a copolymer. Functionality is the number of bonds that a given monomer can form. For example, if you take phenol formaldehyde, they are trifunctional and they have three active bonds.

So, based on that, you have different types of polymeric material. In order to characterize the polymeric material, you need to characterize it in terms of its molecular weight. So, the first molecular weight is number average molecular weight. This is shown in this figure. Here the term this M i that represent the mean the middle molecular weight is having a size. I will explain it later on with a certain example.

And x i is a fraction of the total number. So, now, you want to calculate the molecular weight which is number average molecular weight, then it is a summation of x i and M i. So, corresponding size range, you know and fraction you know, so we added up and come up with number average molecular weight.

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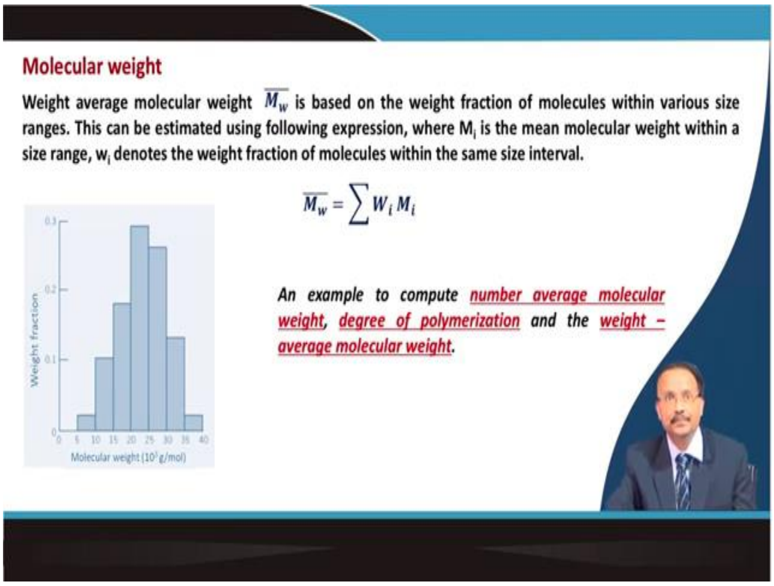

Molecular weight

Weight average molecular weight $\overline{M_w}$ is based on the weight fraction of molecules within various size ranges. This can be estimated using following expression, where M_i is the mean molecular weight within a size range, w_i denotes the weight fraction of molecules within the same size interval.

$$\overline{M_w} = \sum W_i M_i$$

An example to compute number average molecular weight, degree of polymerization and the weight – average molecular weight.

And the second one is based on the weight fraction of the molecules within again various size range. So, here it is defined as M w bar, and it is the weight fraction and the M i the mean molecular weight within a particular size range in that particular average that will give you the weight average molecular weight.

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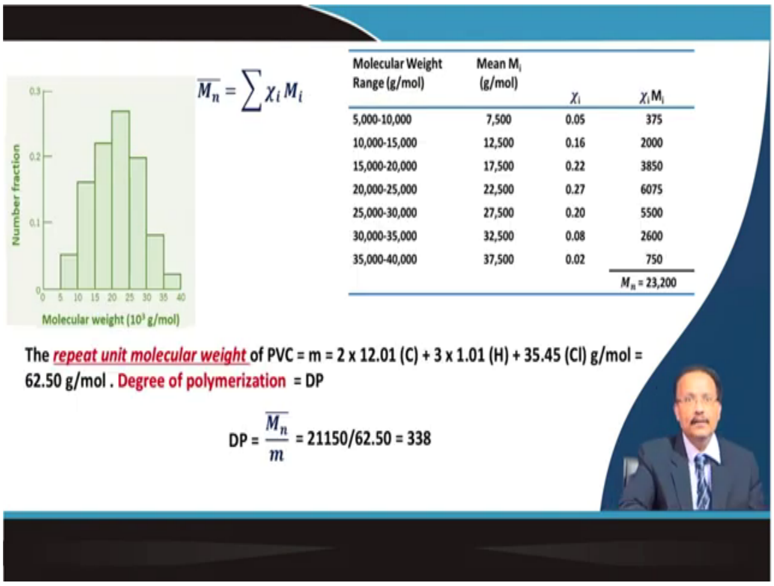

$$\overline{M_n} = \sum \chi_i M_i$$

Molecular Weight Range (g/mol)	Mean M_i (g/mol)	χ_i	$\chi_i M_i$
5,000-10,000	7,500	0.05	375
10,000-15,000	12,500	0.16	2000
15,000-20,000	17,500	0.22	3850
20,000-25,000	22,500	0.27	6075
25,000-30,000	27,500	0.20	5500
30,000-35,000	32,500	0.08	2600
35,000-40,000	37,500	0.02	750
			M_n = 23,200

The *repeat unit molecular weight* of PVC = m = 2 x 12.01 (C) + 3 x 1.01 (H) + 35.45 (Cl) g/mol = 62.50 g/mol . Degree of polymerization = DP

$$DP = \frac{\overline{M_n}}{m} = 21150/62.50 = 338$$

So, number average molecular weight, degree of polymerization, and weight average molecular weight, these three things you can basically estimate. And I will try to explain that how exactly it is done. So, you can see the molecular weight range is given for this particular view graph is in between 5,000 to 10,000; and slowly it is increasing to 35,000 and 40,000.

And the mean you can calculate 5,000 and 10,000. So, mean will come 7,500. And similarly for this case, the mean will come 37,500. The fraction you need to know for each of these size range this fraction is known. So, now, you multiply the mean one with the fraction, you get this number. You add it up and you get the number average molecular weight.

The repeat unit molecular weight of PVC that you can calculate it is two then for carbon it is 12.01; and 3 into for hydrogen it is 1.01; and for chlorine, it is 35.45. So, then it is coming 62.50 gram per mole.

So, once you can calculate this repeat unit molecular weight, molecular weight of the unit which is repeating, and you know this number average molecular weight divide this. So, M n bar m subscript n bar divided by this repeat unit molecular weight that will give you the degree of polymerization. And in this case the degree of polymerization is 338.

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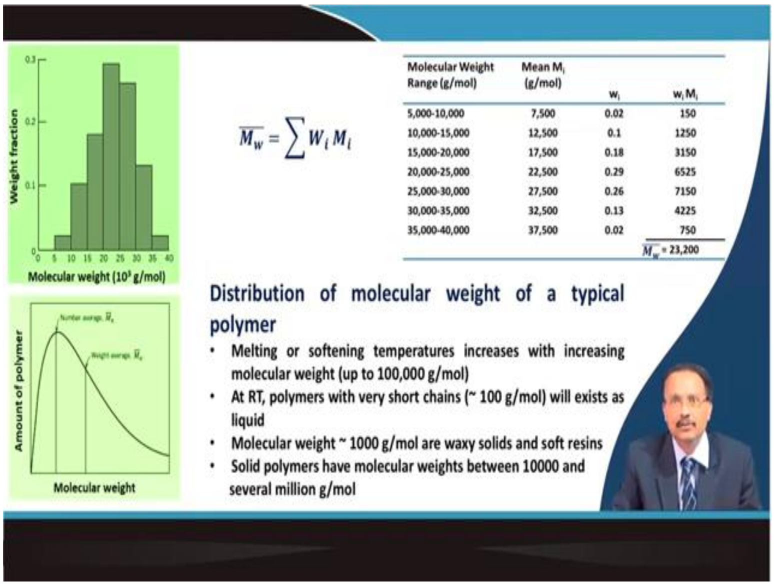

$$\overline{M_w} = \sum W_i M_i$$

Molecular Weight Range (g/mol)	Mean M_i (g/mol)	w_i	$w_i M_i$
5,000-10,000	7,500	0.02	150
10,000-15,000	12,500	0.1	1250
15,000-20,000	17,500	0.18	3150
20,000-25,000	22,500	0.29	6525
25,000-30,000	27,500	0.26	7150
30,000-35,000	32,500	0.13	4225
35,000-40,000	37,500	0.02	750
			$\overline{M_w}$ = 23,200

Distribution of molecular weight of a typical polymer

- Melting or softening temperatures increases with increasing molecular weight (up to 100,000 g/mol)
- At RT, polymers with very short chains (~ 100 g/mol) will exists as liquid
- Molecular weight ~ 1000 g/mol are waxy solids and soft resins
- Solid polymers have molecular weights between 10000 and several million g/mol

Similarly, you can also calculate the weight average molecular weight in the same way the way we have calculated the number average molecular weight. So, instead of this number fraction, here we have weight fraction and we can calculate this. So, there is a distribution of molecular weight for a typical polymer. Melting or softening temperature usually increases with the increase of the molecular weight. So, up to 100,000 gram per mole you can get.

At room temperature, polymers are with very short chains will exists as a liquid. The molecular weight if it is around 1000 gram per mole, then it is a waxy solids and soft resin. And solid polymers have molecular weight which is in between 10,000 to several millions gram per mole.

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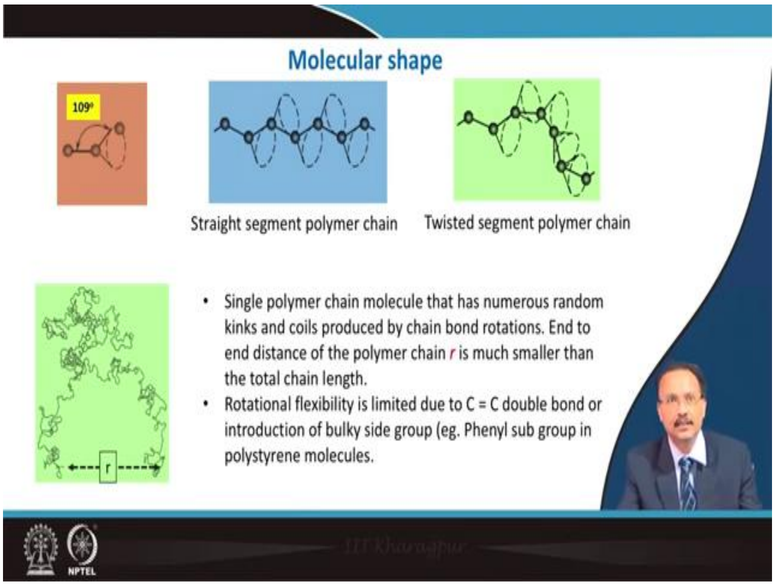

Molecular shape

Straight segment polymer chain

Twisted segment polymer chain

- Single polymer chain molecule that has numerous random kinks and coils produced by chain bond rotations. End to end distance of the polymer chain *r* is much smaller than the total chain length.
- Rotational flexibility is limited due to C = C double bond or introduction of bulky side group (eg. Phenyl sub group in polystyrene molecules.

So, molecular shape either it could be straight, it could be zinged like this, this already I have explained. And straight segment polymer chain or it can be twisted. So, the actual polymer molecules will be something like this.

It is a macromolecules that has numerous random kink coil due to this chain bond rotation; end-to-end distance is important which is demarcated by R. And this rotational flexibility is limited because if it is having carbon-carbon double bond or introduction of a bulky side group like phenyl, then it is the flexibility of the polymer is reduced.

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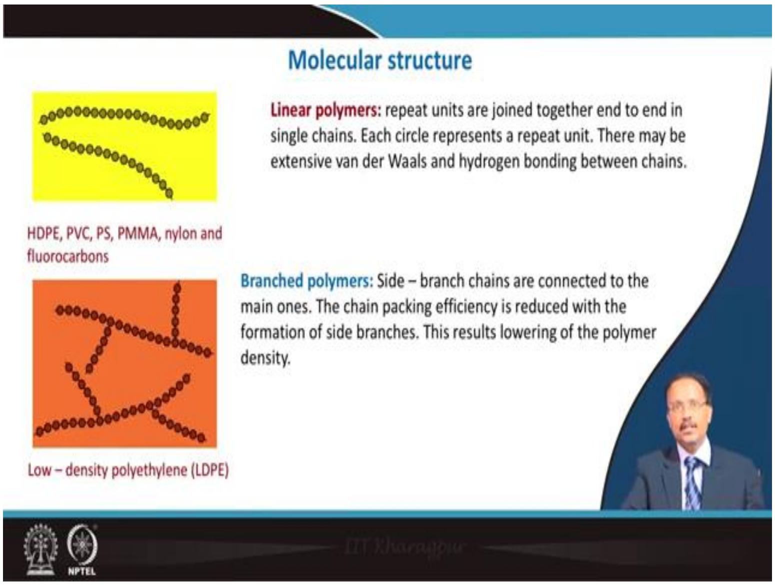

Molecular structure

Linear polymers: repeat units are joined together end to end in single chains. Each circle represents a repeat unit. There may be extensive van der Waals and hydrogen bonding between chains.

HDPE, PVC, PS, PMMA, nylon and fluorocarbons

Branched polymers: Side – branch chains are connected to the main ones. The chain packing efficiency is reduced with the formation of side branches. This results lowering of the polymer density.

Low – density polyethylene (LDPE)

As far as the molecular structure is concerned, you have a linear polymer. So, repeat unit just joined end-to-end to form a single chain, or it could be a branched polymer like this. The far more example is nylon or high density polyethylene, low density polyethylene they are branched polymer.

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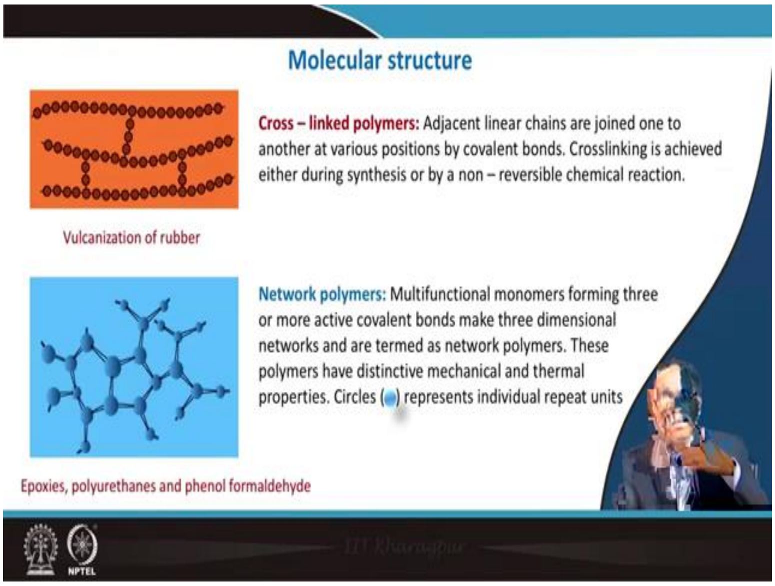

Molecular structure

Cross – linked polymers: Adjacent linear chains are joined one to another at various positions by covalent bonds. Crosslinking is achieved either during synthesis or by a non – reversible chemical reaction.

Vulcanization of rubber

Network polymers: Multifunctional monomers forming three or more active covalent bonds make three dimensional networks and are termed as network polymers. These polymers have distinctive mechanical and thermal properties. Circles (●) represents individual repeat units

Epoxies, polyurethanes and phenol formaldehyde

You can have a cross linked polymer. So, adjacent linear chain they are joined at various position by covalent bonding, and it is either achieved during processing or a non-reversible chemical reaction.

Or you have network polymers, this is multifunctional monomers forming three or more active covalent bonds that make a three-dimensional network. This polymers have distinct mechanical and thermal properties and the individual repeat unit that is demarcated by this spheres. Examples are epoxies, polyurethanes, or phenol formaldehyde.

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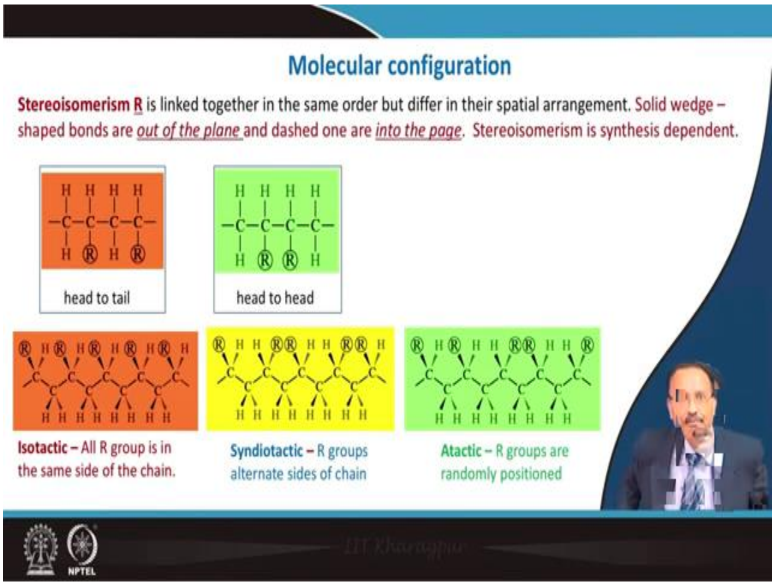

Molecular configuration

Stereoisomerism **R** is linked together in the same order but differ in their spatial arrangement. Solid wedge – shaped bonds are *out of the plane* and dashed one are *into the page*. Stereoisomerism is synthesis dependent.

head to tail

head to head

Isotactic – All R group is in the same side of the chain.

Syndiotactic – R groups alternate sides of chain

Atactic – R groups are randomly positioned

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Molecular configuration ah we have stereoisomerism where this R group linked in the same order, but in different spatial arrangement. So, what is this solid wedge is out of the plane bonds, and dashed one is inside the plane. So, based on its position either head to head or head to tail kind of orientation, you have isotactic. All R groups are in the same side of the chain, or you have syndiotactic groups R groups are alternate sides of the chain, or you can have atactic groups the R groups are random.

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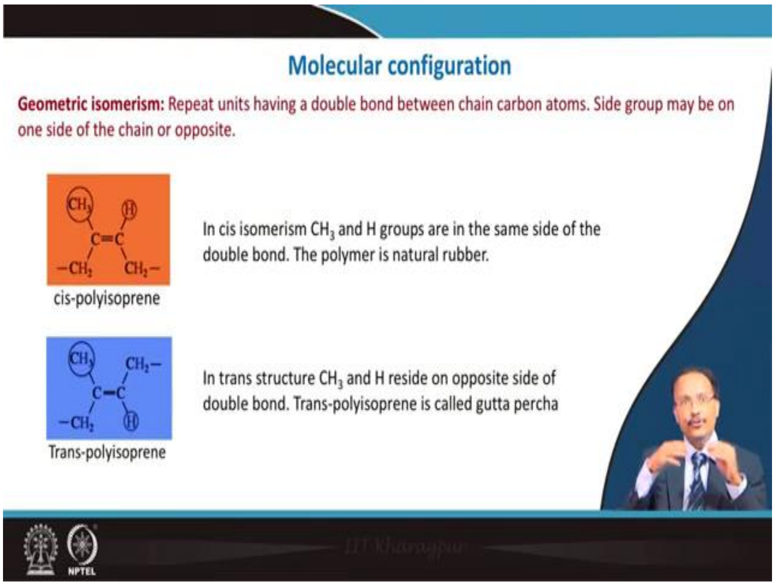

Molecular configuration

Geometric isomerism: Repeat units having a double bond between chain carbon atoms. Side group may be on one side of the chain or opposite.

cis-polyisoprene

In cis isomerism CH_3 and H groups are in the same side of the double bond. The polymer is natural rubber.

Trans-polyisoprene

In trans structure CH_3 and H reside on opposite side of double bond. Trans-polyisoprene is called gutta percha

You can also have geometric isomerism. Particularly in this kind of side the repeat units having a double bond between the chain as it is shown, side groups may be one side of the chain or in the opposite side. So, there are cis isomerism where for example the CH 3 and H are in the same side, or you can have trans structures. So, trans polyisoprene a particular type of rubber where they are in the different types, different sides of the group.

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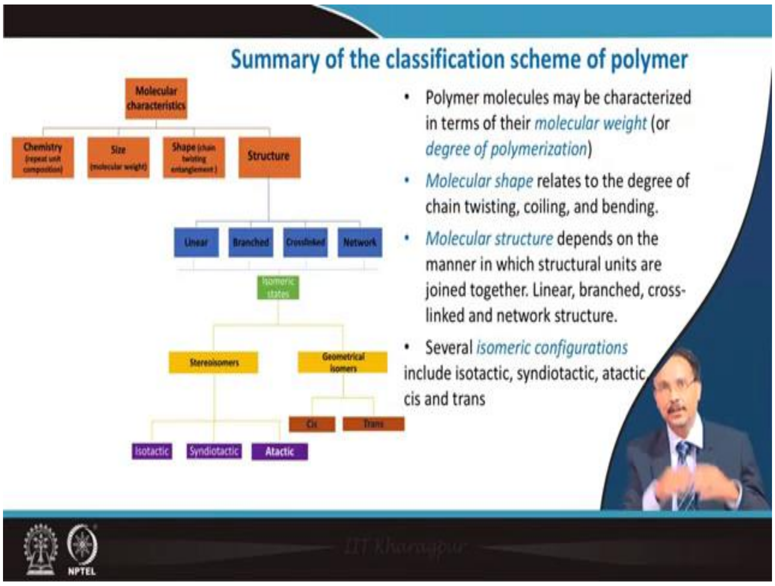

Summary of the classification scheme of polymer

Molecular characteristics
Chemistry (repeat unit composition)
Size (molecular weight)
Shape (chain twisting entanglement)
Structure
Linear
Branched
Crosslinked
Network
Isomeric states
Stereoisomers
Geometrical isomers
Cis
Trans
Isotactic
Syndiotactic
Atactic

- Polymer molecules may be characterized in terms of their *molecular weight* (or *degree of polymerization*)
- *Molecular shape* relates to the degree of chain twisting, coiling, and bending.
- *Molecular structure* depends on the manner in which structural units are joined together. Linear, branched, cross-linked and network structure.
- Several *isomeric configurations* include isotactic, syndiotactic, atactic, cis and trans

So, we can classify the summary of the scheme of the polymer whatever I have explained. Based on the chemistry, size, shape and structure, the structure could be either linear, branched, cross-link or network type. Or the isomeric structure could be stereoisomers or geometric isomers. Then stereoisomers could be three different types; and geometric isomers will be two different types – cis and trans.

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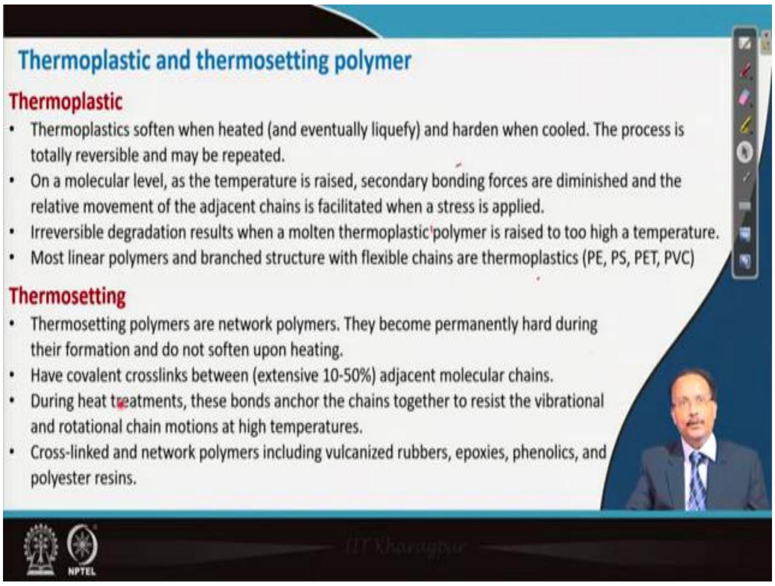

Thermoplastic and thermosetting polymer

Thermoplastic

- Thermoplastics soften when heated (and eventually liquefy) and harden when cooled. The process is totally reversible and may be repeated.
- On a molecular level, as the temperature is raised, secondary bonding forces are diminished and the relative movement of the adjacent chains is facilitated when a stress is applied.
- Irreversible degradation results when a molten thermoplastic polymer is raised to too high a temperature.
- Most linear polymers and branched structure with flexible chains are thermoplastics (PE, PS, PET, PVC)

Thermosetting

- Thermosetting polymers are network polymers. They become permanently hard during their formation and do not soften upon heating.
- Have covalent crosslinks between (extensive 10-50%) adjacent molecular chains.
- During heat treatments, these bonds anchor the chains together to resist the vibrational and rotational chain motions at high temperatures.
- Cross-linked and network polymers including vulcanized rubbers, epoxies, phenolics, and polyester resins.

The thermoplastic polymers soften when you heat it; and harden when you cool. And this is a totally reversible process. When the temperature is raised, the secondary bond forces are diminished; and relative movement of the adjacent chains is facilitated when the stress is applied. Irreversible degradation results when molten thermoplastic polymer is raised to too high a temperature, and most linear chain polymers they are having flexible chains with the thermoplastics.

And thermosetting polymers are known as network polymers, they become permanently hard, you cannot recycle it. And there is covalent cross-linking exists about 10 to 50 percent adjacent to the molecular chain. And cross-link network polymers that includes vulcanized rubber. Rubber treated with sulfur, or epoxies, or phenolics, and polyester resins.

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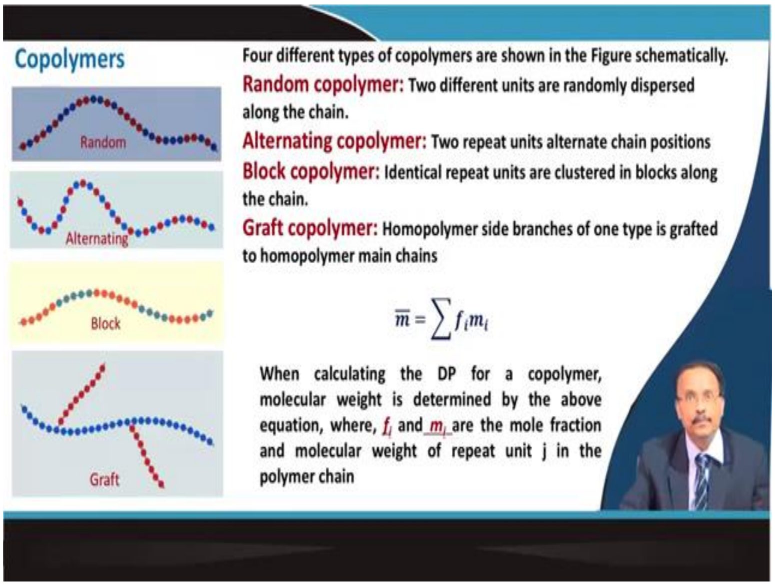

Copolymers

Four different types of copolymers are shown in the Figure schematically.

Random copolymer: Two different units are randomly dispersed along the chain.

Alternating copolymer: Two repeat units alternate chain positions

Block copolymer: Identical repeat units are clustered in blocks along the chain.

Graft copolymer: Homopolymer side branches of one type is grafted to homopolymer main chains

$$\overline{m} = \sum f_i m_i$$

When calculating the DP for a copolymer, molecular weight is determined by the above equation, where, f_i and m_i are the mole fraction and molecular weight of repeat unit j in the polymer chain

So, these are the two different types of polymers. Also you have copolymers four different types. One is random copolymer the two different units which are different colors. You can see they are alternating randomly occupied and forming this copolymers, two different types of polymers.

You can have alternating copolymers where it is quite regular red comes after blue and so on repeatedly. You can have a block of red and block of blue, we call it is a block copolymer. And finally, it is a graft copolymer which is a homopolymer side braches of one type is grafted to another type of homo homopolymer chain.

So, when we calculate the degree of polymerization for a copolymer, the molecular weight determined by the equation that is shown here, where this is the fraction and m i is the mole fraction of the molecular weight of the repeat unit of the polymer chain. So, you can calculate the DP.

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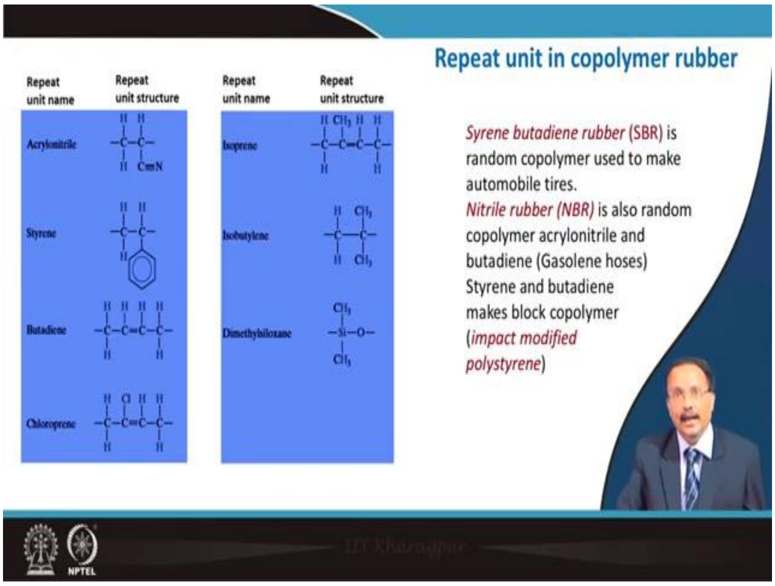

Repeat unit in copolymer rubber

Syrene butadiene rubber (SBR) is random copolymer used to make automobile tires.
Nitrile rubber (NBR) is also random copolymer acrylonitrile and butadiene (Gasolene hoses)
Styrene and butadiene makes block copolymer (*impact modified polystyrene*)

And for the rubber, I have listed the different copolymer rubbers. And this is very important this syrene butadiene rubber, it is a random copolymer. Nitrile rubber is also a random copolymer. And styrene and butadiene makes the block copolymer impact modified polystyrene.

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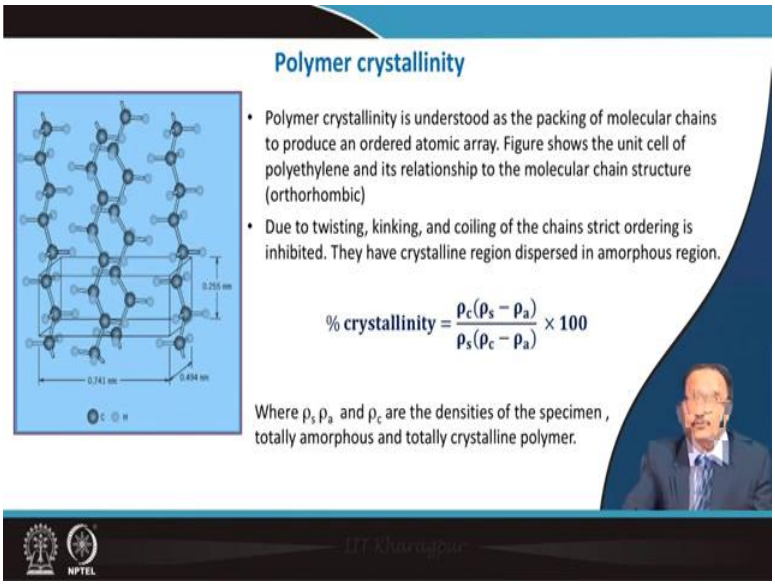

Polymer crystallinity

- Polymer crystallinity is understood as the packing of molecular chains to produce an ordered atomic array. Figure shows the unit cell of polyethylene and its relationship to the molecular chain structure (orthorhombic)
- Due to twisting, kinking, and coiling of the chains strict ordering is inhibited. They have crystalline region dispersed in amorphous region.

$$\%\ \text{crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

Where ρ_s ρ_a and ρ_c are the densities of the specimen , totally amorphous and totally crystalline polymer.

So, various types of copolymer exists in rubbery material. You can calculate the polymer crystallinity. And this is understandable that these chains which are regularly arranged the molecular chain to produce a ordered structure. This is shown here. And you can always construct some kind of unit cell, and it is shown for polyethylene.

And due to the twisting, or kinking, coiling, etcetera, the chain strictly ordering is inhabited. So, they have certain crystalline region which is embedded in a an amorphous region. So, you can calculate the percent crystallinity of the specimen which is totally amorphous and totally crystalline polymer by this relation.

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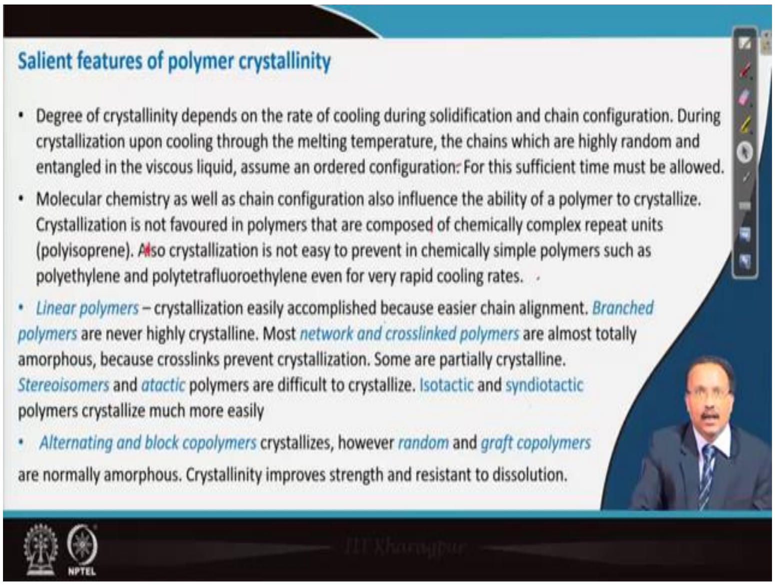

Salient features of polymer crystallinity

- Degree of crystallinity depends on the rate of cooling during solidification and chain configuration. During crystallization upon cooling through the melting temperature, the chains which are highly random and entangled in the viscous liquid, assume an ordered configuration. For this sufficient time must be allowed.
- Molecular chemistry as well as chain configuration also influence the ability of a polymer to crystallize. Crystallization is not favoured in polymers that are composed of chemically complex repeat units (polyisoprene). Also crystallization is not easy to prevent in chemically simple polymers such as polyethylene and polytetrafluoroethylene even for very rapid cooling rates.
- *Linear polymers* – crystallization easily accomplished because easier chain alignment. *Branched polymers* are never highly crystalline. Most *network and crosslinked polymers* are almost totally amorphous, because crosslinks prevent crystallization. Some are partially crystalline. *Stereoisomers* and *atactic* polymers are difficult to crystallize. Isotactic and syndiotactic polymers crystallize much more easily
- *Alternating and block copolymers* crystallizes, however *random* and *graft copolymers* are normally amorphous. Crystallinity improves strength and resistant to dissolution.

And polymer crystallinity is basically dependent on the cooling through the solidification. We will come to this point during crystallization upon cooling through the melting point the chains which are highly random and entangled in the viscous liquid assume a ordered configuration. And molecular chemistry as well as the chain configuration also influences the ability of polymer to crystallize.

Actually the linear polymers crystallization is easy. Branched polymers are never highly crystalline and most network and cross linked polymers are almost totally amorphous because the cross links prevent crystallization. Alternate and block copolymer crystallizes. However, they are quite random and graft copolymers are normally amorphous. So, this is the classification that is made based on its structure.

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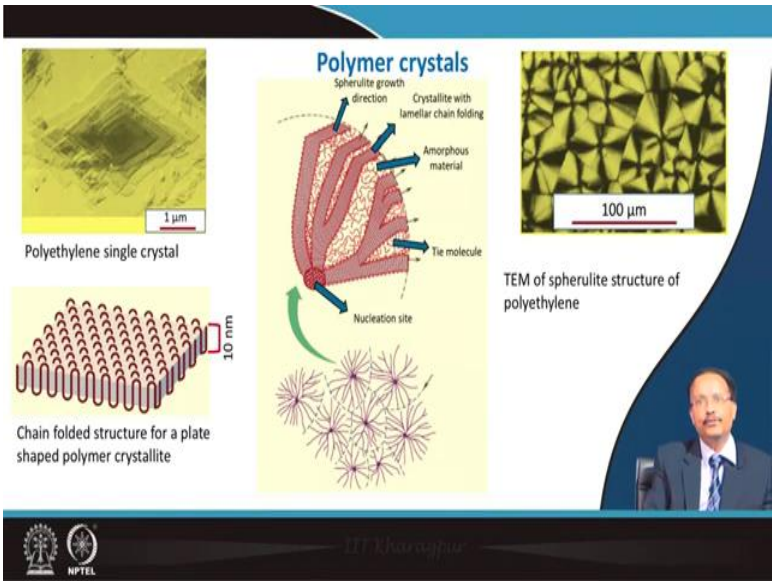

Polymer crystals

Polyethylene single crystal

Chain folded structure for a plate shaped polymer crystallite

TEM of spherulite structure of polyethylene

So, typical polymer crystals look like this. As you can see the first one is a single crystalline structure. And otherwise it is having a spherulite structure, where the direction of the spherulite growth which is crystalline in nature which is spatially oriented like this. And in between this crystalline structure, you have amorphous region. And this is a typical micrograph for polyethylene. And this is schematically shown, it is a crystalline structure embedded in amorphous structure materials.

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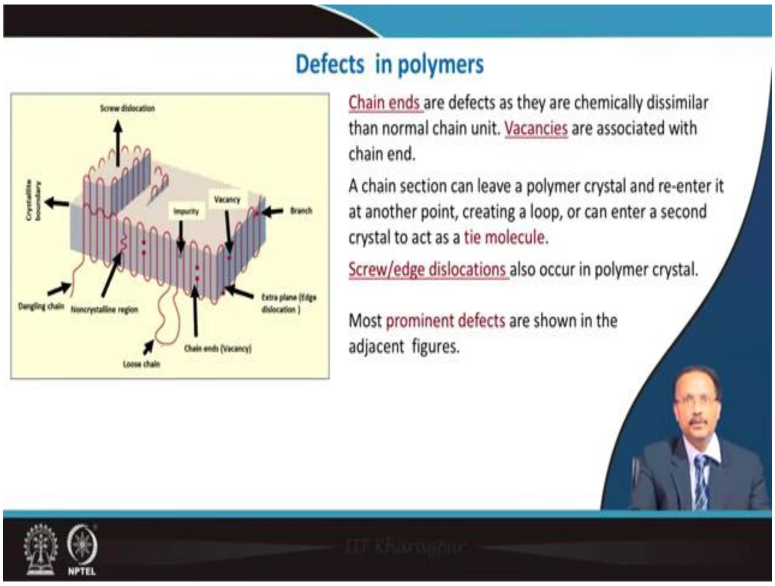

Defects in polymers

Chain ends are defects as they are chemically dissimilar than normal chain unit. Vacancies are associated with chain end.

A chain section can leave a polymer crystal and re-enter it at another point, creating a loop, or can enter a second crystal to act as a tie molecule.

Screw/edge dislocations also occur in polymer crystal.

Most prominent defects are shown in the adjacent figures.

Defects they are having vacancy associated with their chain ends or you can have a screw and edge dislocation also possible in this material. Most prominent defects are shown here – the impurity, vacancy, dangling chain, so these are the common defects in the polymer.

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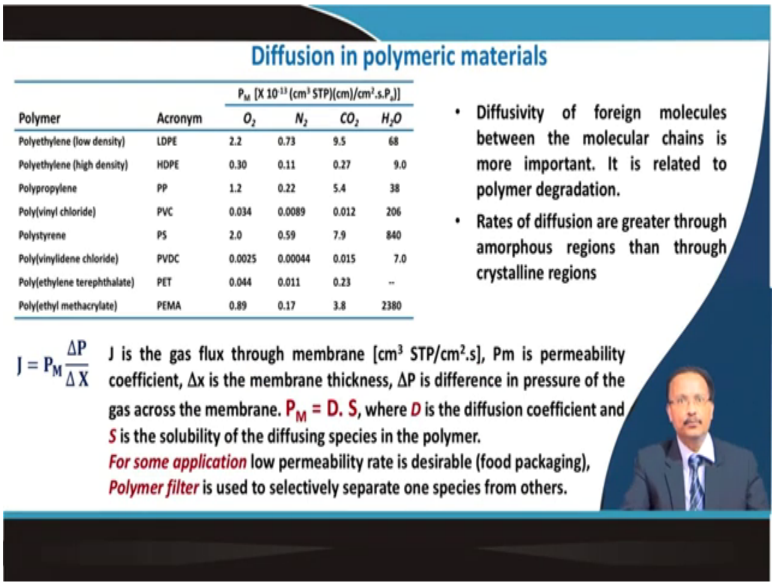

Diffusion in polymeric materials

Polymer	Acronym	P_M [X 10^{-13} (cm^3 STP)(cm)/cm^2.s.P$_a$)] O_2	N_2	CO_2	H_2O
Polyethylene (low density)	LDPE	2.2	0.73	9.5	68
Polyethylene (high density)	HDPE	0.30	0.11	0.27	9.0
Polypropylene	PP	1.2	0.22	5.4	38
Poly(vinyl chloride)	PVC	0.034	0.0089	0.012	206
Polystyrene	PS	2.0	0.59	7.9	840
Poly(vinylidene chloride)	PVDC	0.0025	0.00044	0.015	7.0
Poly(ethylene terephthalate)	PET	0.044	0.011	0.23	--
Poly(ethyl methacrylate)	PEMA	0.89	0.17	3.8	2380

- Diffusivity of foreign molecules between the molecular chains is more important. It is related to polymer degradation.
- Rates of diffusion are greater through amorphous regions than through crystalline regions

$$J = P_M \frac{\Delta P}{\Delta X}$$

J is the gas flux through membrane [cm^3 STP/cm^2.s], Pm is permeability coefficient, Δx is the membrane thickness, ΔP is difference in pressure of the gas across the membrane. $P_M = D. S$, where *D* is the diffusion coefficient and *S* is the solubility of the diffusing species in the polymer.
For some application low permeability rate is desirable (food packaging),
Polymer filter is used to selectively separate one species from others.

And finally, diffusivity of the foreign molecules between the molecular chain is very important, and that diffusivity usually is determined by this relation. So, this is the gas flux through the membrane. And PM is the permeability. And the pressure difference and distance is there. So, you can calculate the diffusion coefficient if it is known.

And then PM is given by this relation. So, some application of this polymer, low permeability rate is desirable, for example, in food packaging. And polymer filter is used for selectively separate out the species from each other. So, they are the diffusion of the impurity or the saline in order to increase a salinity, reduce the salinity of the water the polymer membrane is used where the diffusion concept is important.

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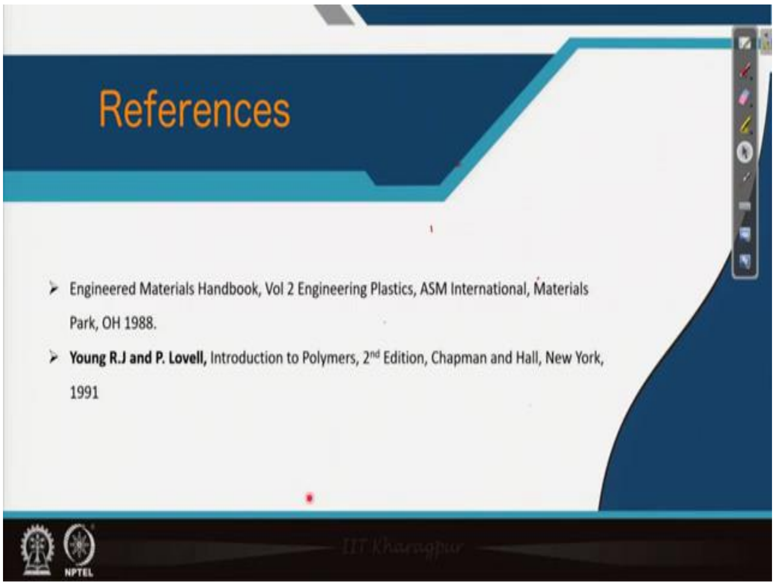

References

- Engineered Materials Handbook, Vol 2 Engineering Plastics, ASM International, Materials Park, OH 1988.
- **Young R.J and P. Lovell,** Introduction to Polymers, 2nd Edition, Chapman and Hall, New York, 1991

So, that defines what we call the polymer structure in a nutshell, and these are the two books that one can consider.

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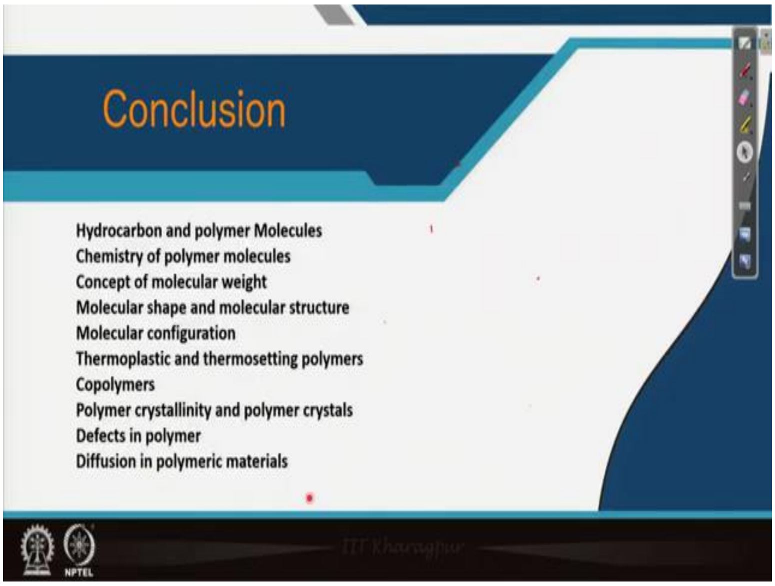

Conclusion

Hydrocarbon and polymer Molecules
Chemistry of polymer molecules
Concept of molecular weight
Molecular shape and molecular structure
Molecular configuration
Thermoplastic and thermosetting polymers
Copolymers
Polymer crystallinity and polymer crystals
Defects in polymer
Diffusion in polymeric materials

And we have defined this hydrocarbons and polymer molecules, then chemistry, then concept of molecular weight, then molecular shape and structure, molecular configuration, two types of polymer – thermoplastic and thermosetting, copolymers, and polymer crystallinity, brief introduction about different types of defect, and diffusion in polymeric materials.

Thank you for your attention.