Introduction to Polymer Science

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Lecture - 03
Classifications, Nomenclature

Okay, welcome back to this course on Introduction to Polymer Science.

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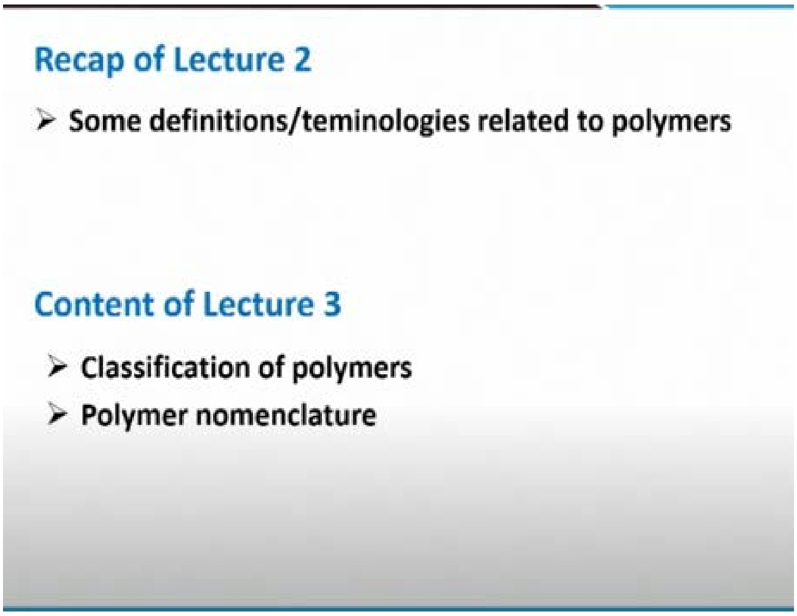

Recap of Lecture 2

- Some definitions/teminologies related to polymers

Content of Lecture 3

- Classification of polymers
- Polymer nomenclature

In the last lecture, we had discussed about some definitions and terminologies related to polymers. For example, degrees of polymerization, repeating units, structural units and the term polymers and macromolecules, and so on. In this lecture, we will divide the polymers into different classes based on some parameters, and also we will introduce how to name polymer molecules.

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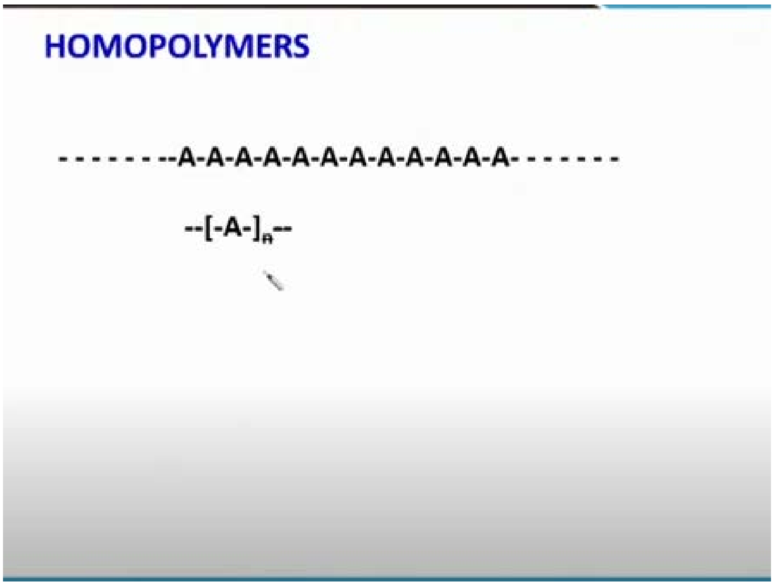

HOMOPOLYMERS

- - - - - - - --A-A-A-A-A-A-A-A-A-A-A-A- - - - - - -

--[-A-]$_n$--

We talked about homopolymers, which are made from a single monomer. And typically we can represent homopolymer, just like A being any representative monomer, and typically it is written in a third bracket or a single bracket [-A-]$_n$ with subscript ‘n’ where ‘n’ is the number of repeat units.

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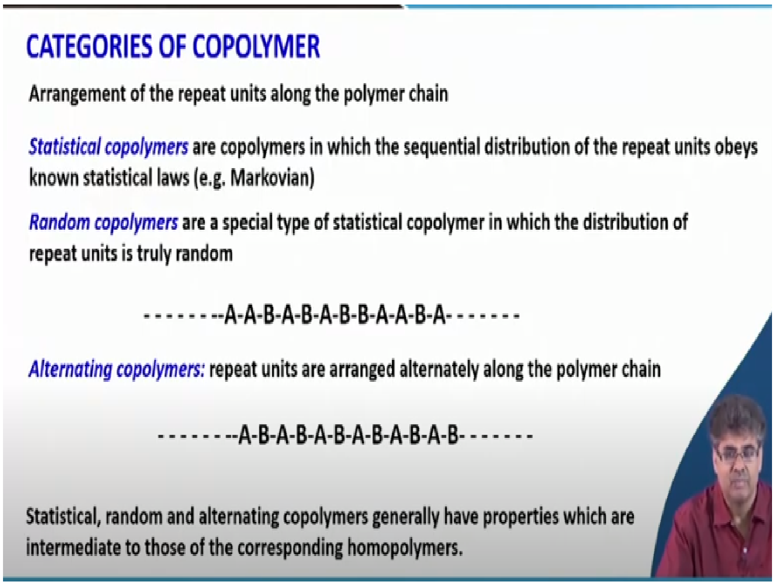

CATEGORIES OF COPOLYMER

Arrangement of the repeat units along the polymer chain

Statistical copolymers are copolymers in which the sequential distribution of the repeat units obeys known statistical laws (e.g. Markovian)

Random copolymers are a special type of statistical copolymer in which the distribution of repeat units is truly random

- - - - - - - --A-A-B-A-B-A-B-B-A-A-B-A- - - - - - -

Alternating copolymers: repeat units are arranged alternately along the polymer chain

- - - - - - - --A-B-A-B-A-B-A-B-A-B-A-B- - - - - - -

Statistical, random and alternating copolymers generally have properties which are intermediate to those of the corresponding homopolymers.

When we talk about copolymers, they can be divided based on the arrangement of the repeat units along the polymer chain. For example, if the repeating units are arranged statistically, following a known statistical law for example Markovian, then they will be called a statistical copolymer. One special case of the statistical copolymer is the random copolymer where the monomers are incorporated in the growing chain in completely random manner. In most cases when we talk about statistical copolymer it generally means random copolymer. In this case, the monomers which are reacting and forming polymers are just getting incorporated randomly in the copolymer chain. Just to represent, A and B are written randomly without any bias between two monomers.

We can also have alternating copolymer where two monomers must be in A-B-A-B-A-B-A-B form i.e. two monomers are sitting one after another. So, if the monomers are arranged perfectly in an alternative way, we call these copolymers as an alternating copolymers. Now, in all the statistical copolymer, random copolymer, and alternating copolymer, the property of the final copolymer is an average of the two monomers, which are present in this polymer and it also depends upon the weight or mass of the individual constituent monomers.

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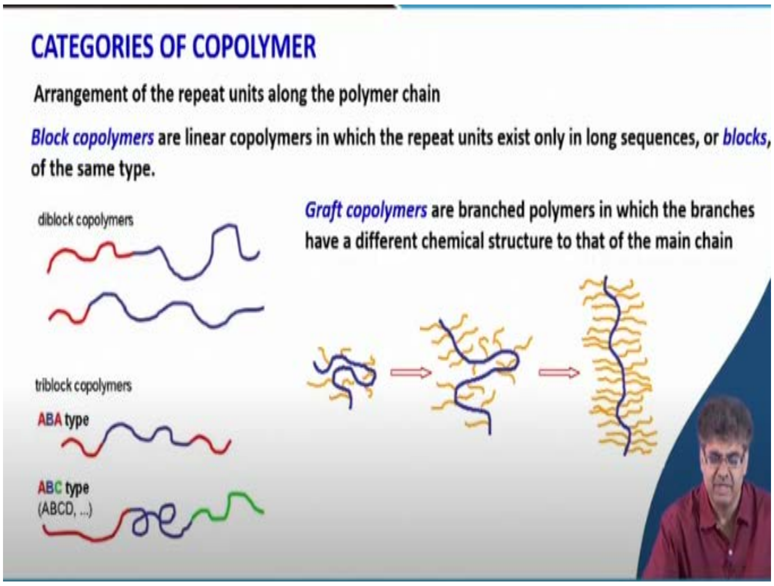

CATEGORIES OF COPOLYMER

Arrangement of the repeat units along the polymer chain

Block copolymers are linear copolymers in which the repeat units exist only in long sequences, or *blocks*, of the same type.

Graft copolymers are branched polymers in which the branches have a different chemical structure to that of the main chain

We can also have another arrangement of the monomers which is called block copolymer. Block copolymers are linear copolymers in which the repeating units exist only in long sequences or blocks of a similar type of monomer. For example, in this case, it is schematically shown as a diblock copolymer. One block is red color is and another block is blue in color. In the scheme, there are two different block copolymers in which, the block lengths are varying. We can also have a triblock copolymer. For example, in ABA type triblock, there is block A and B and then again A. There may be also ABC type block copolymer where A, B, and C are different. So, there are many types of the blocks as per the arrangement of the monomer units. We can have also graft copolymers. Graft copolymers are branched polymers in which the branches have a different chemical structure to that of the main chain. So in this case, there is one main chain and branches. So according to the scheme, we have blue color which represents the backbone and there are different branches in yellow. The graft copolymer can vary with the number of branches or the length of branches present. As we increase the number of branches or the branching density, then it lands up in a brush polymer. Thus, copolymers depending upon the different structural arrangements of the monomers, are classified as random copolymers, statistical copolymers, and alternating copolymers, and also we can have block copolymers and graft copolymers.

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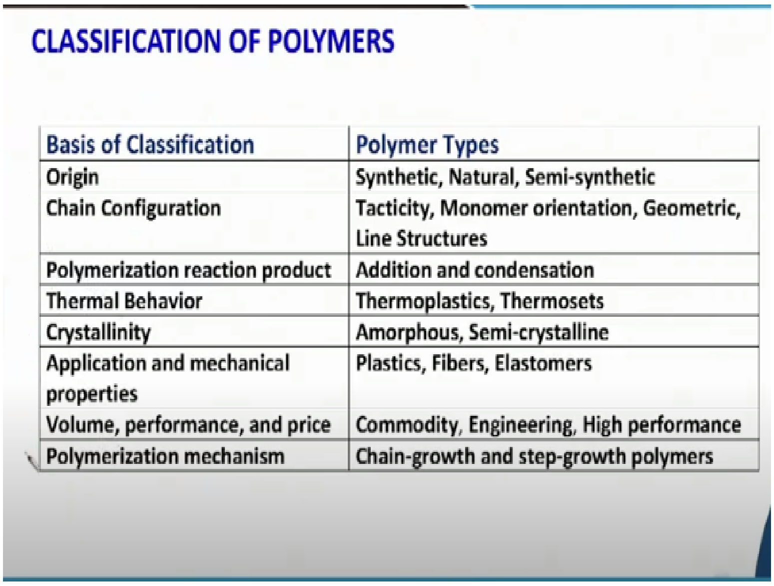

CLASSIFICATION OF POLYMERS

Basis of Classification	Polymer Types
Origin	Synthetic, Natural, Semi-synthetic
Chain Configuration	Tacticity, Monomer orientation, Geometric, Line Structures
Polymerization reaction product	Addition and condensation
Thermal Behavior	Thermoplastics, Thermosets
Crystallinity	Amorphous, Semi-crystalline
Application and mechanical properties	Plastics, Fibers, Elastomers
Volume, performance, and price	Commodity, Engineering, High performance
Polymerization mechanism	Chain-growth and step-growth polymers

Different parameters are used to classify the polymers. However, it is not necessary to remember all the types of classification but remembering the meaning of the polymers types as shown in this right column should be sufficient.

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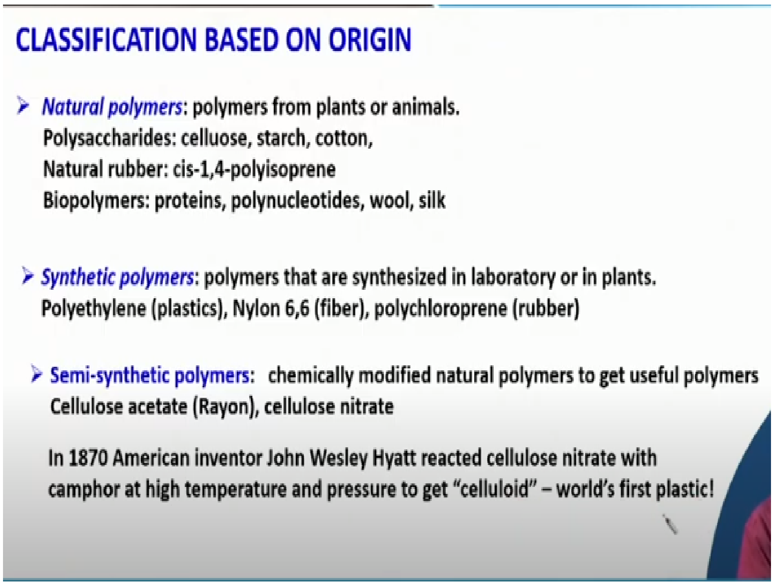

CLASSIFICATION BASED ON ORIGIN

- *Natural polymers*: polymers from plants or animals.
  Polysaccharides: celluose, starch, cotton,
  Natural rubber: cis-1,4-polyisoprene
  Biopolymers: proteins, polynucleotides, wool, silk

- *Synthetic polymers*: polymers that are synthesized in laboratory or in plants.
  Polyethylene (plastics), Nylon 6,6 (fiber), polychloroprene (rubber)

- Semi-synthetic polymers: chemically modified natural polymers to get useful polymers
  Cellulose acetate (Rayon), cellulose nitrate

  In 1870 American inventor John Wesley Hyatt reacted cellulose nitrate with camphor at high temperature and pressure to get "celluloid" – world's first plastic!

First, we will discuss about the different types of classification and different polymers based on different classification parameters. In the first case, we talked about classification based on origin. As we discussed that polymers can be obtained naturally from plant or animal-based materials for example polysaccharides like cellulose, starch, cotton, and natural rubber or cis1,4-polyisoprene, and then biopolymers like proteins, nucleic acids, wool, silk. We can also have completely synthetic polymers. In 1907 Baekeland was the first to make completely synthetic polymers 'Bakelite', but after that many polymers have been produced and nowadays most of the useful polymers in commercialized products are made of synthetic polymers. The polymers are synthesized in the laboratory or in plants and the monomers eare from synthetic origins like petroleum products or natural gtc. So those are synthetic polymers.

There may be a mixture of natural and synthetic polymers, which implies taking the natural polymers and then modifying them in the laboratory or in the plant and doing some chemical reactions. These polymers are called semi-synthetic polymers. So, semi-synthetic polymers are chemically modified natural polymers to get useful polymers like cellulose acetate and cellulose nitrate. Now in 1870, American inventor John Wesley Hyatt reacted cellulose nitrate with camphor at high temperature and pressure to get celluloid which was eventually the world's first plastic material. So world's first plastic material was a semi-synthetic polymer.

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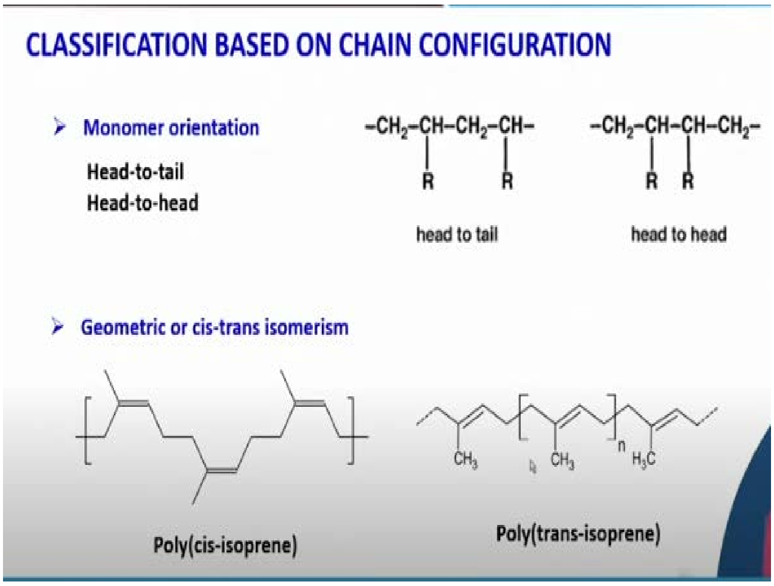

CLASSIFICATION BASED ON CHAIN CONFIGURATION

- Monomer orientation
  - Head-to-tail
  - Head-to-head

$-CH_2-CH(R)-CH_2-CH(R)-$

head to tail

$-CH_2-CH(R)-CH(R)-CH_2-$

head to head

- Geometric or cis-trans isomerism

Poly(cis-isoprene)

Poly(trans-isoprene)

Depending on the chain configuration, we can define or classify polymers in different ways like, how the monomers are oriented in a polymer chain i.e. can be either head to tail or head to head. For example, in the polymeric structure, we can call one part as a head or tail. So basically it is a head-to-tail arrangement. It may be called head to head or tail to tail. Either it is a head to head arrangement or tail to tail arrangement. And in most cases, almost exclusively we found head to tail arrangement during reaction from reactivity point of view. We generally do not get head to head. Of course, there are some special cases where we can synthesize head to head polymers, but in almost every case we get head to tail polymers.

There may be other arrangements like cis-trans isomerization. For example, if we take an isoprene molecule to get polyisoprene, the polyisoprene is completely in cis form. So basically the arrangement across this double bond is completely cis and wherein in the other case, we have all trans polymer. So we can have different geometric polymer isomerization. For example, poly cis-isoprene and poly trans-isoprene.

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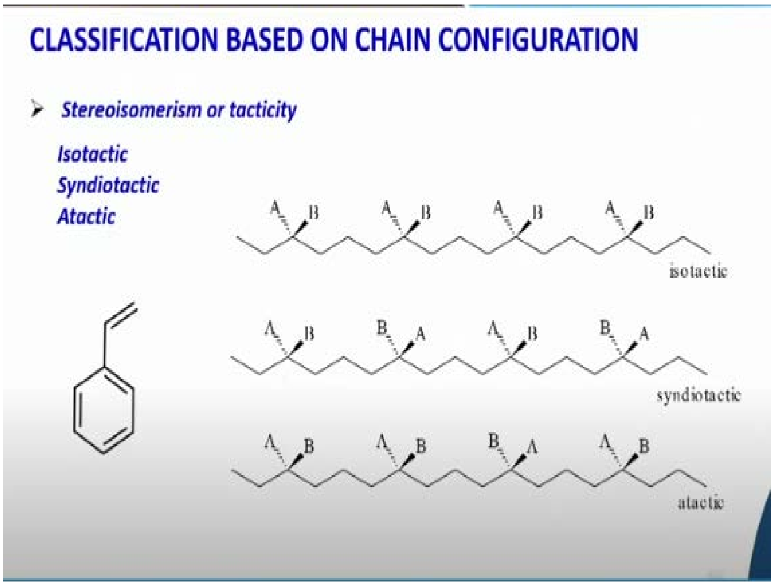

CLASSIFICATION BASED ON CHAIN CONFIGURATION

- *Stereoisomerism or tacticity*

Isotactic
Syndiotactic
Atactic

There is also stereoisomerism or tacticity and depending upon the arrangement of the monomers, it can be isotactic, syndiotactic or atactic molecules. The arrangement is very important in terms of the properties of these polymers. When an asymmetric carbon is in the monomer, the stereoarrangement across the asymmetric carbons in the polymer chain determines its tacticity. For example, in polystyrene, A and B is a methyl and hydrogen group respectively. So in this case, if all the elements are in the same arrangement then we call this an isotactic molecule. If they are in alternate arrangements it is called Syndiotactic, and if the configuration around the chiral or asymmetry carbon atoms is randomly oriented, these polymers are called atactic polymers.

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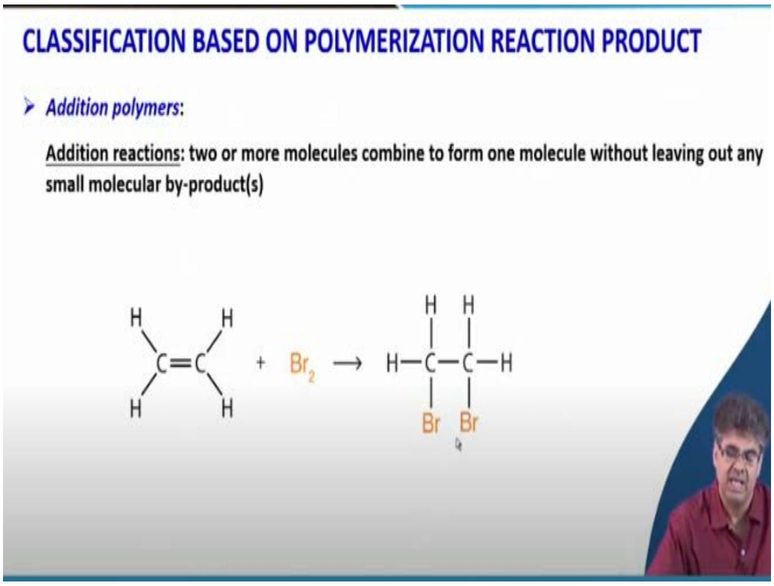

CLASSIFICATION BASED ON POLYMERIZATION REACTION PRODUCT

- *Addition polymers*:

Addition reactions: two or more molecules combine to form one molecule without leaving out any small molecular by-product(s)

Now based on the polymerization reaction product, there are also addition polymers or condensation polymers. Now, in organic chemistry, the standard definition of addition reaction is, addition reactions are the reactions where two or more molecules combine to form one molecule without elimination of any small molecule as byproduct. For example, if we consider this reaction between ethylene and bromine, this is a simple example of an addition reaction where two molecules are reacting and forming a product without any small molecular byproduct. We can have the same type of reaction for making polymers.

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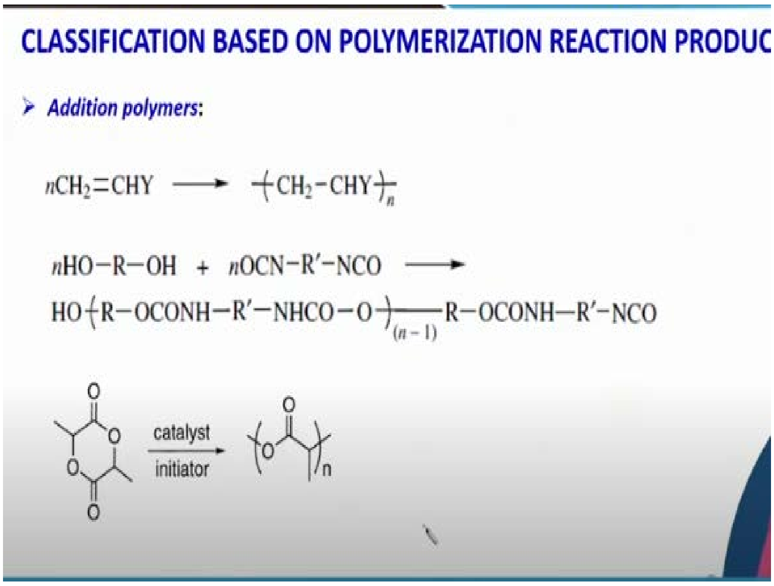

CLASSIFICATION BASED ON POLYMERIZATION REACTION PRODUC

- *Addition polymers*:

$$n\mathrm{CH_2{=}CHY} \longrightarrow \left(\mathrm{CH_2{-}CHY}\right)_n$$

$$n\mathrm{HO{-}R{-}OH} + n\mathrm{OCN{-}R'{-}NCO} \longrightarrow$$

$$\mathrm{HO}\left(\mathrm{R{-}OCONH{-}R'{-}NHCO{-}O}\right)_{(n-1)}\mathrm{R{-}OCONH{-}R'{-}NCO}$$

When there is one monomer used to make the polymer, it is considered that just addition of monomers make the polymer molecule. So, it is called an addition polymer. For example, polyethylene, polystyrene, and many other polyvinyl chlorides, etc. According to definition of an addition reaction, polyurethane should be also an addition polymer. Similarly, this ring-opening polymerization of the lactide also should be considered as an addition polymer. In this case, the monomers are getting added up to make the polymer. In all these cases, no small molecule is coming out from the reaction mixture.

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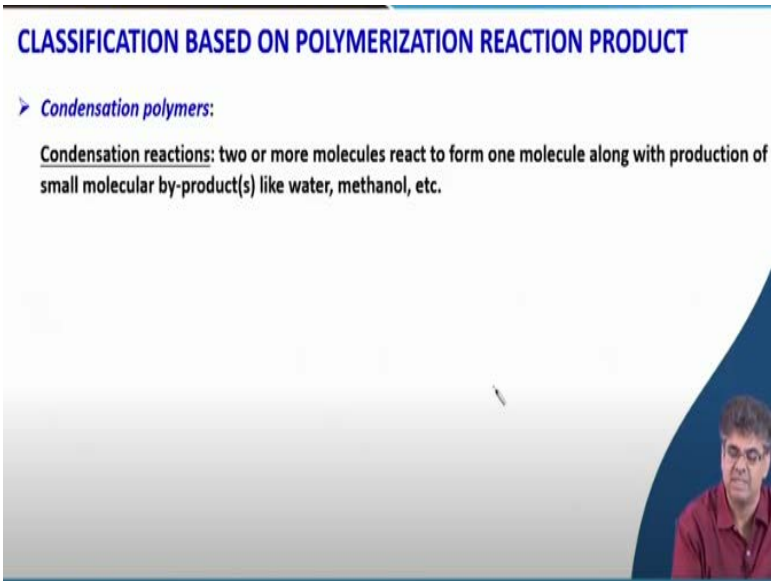

CLASSIFICATION BASED ON POLYMERIZATION REACTION PRODUCT

- *Condensation polymers*:

Condensation reactions: two or more molecules react to form one molecule along with production of small molecular by-product(s) like water, methanol, etc.

The next type of polymer is condensation polymer. From organic chemistry, the definition of condensation reaction is that, if two or more molecules react to form one molecule along with the production of small molecular byproducts like water, methanol, etc. then we call this a condensation reaction. So, the polymer which will form the product along with some byproducts like water or methanol, or some other small molecule, is called condensation polymers.

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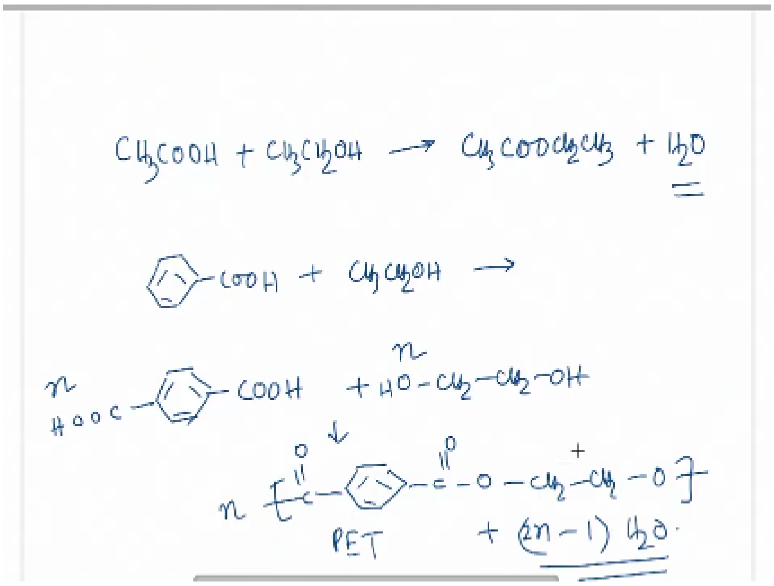

Now, for example, a standard condensation reaction like, the reaction between acetic acid and ethanol will give ethyl acetate and H_2O. So in this reaction, as water is coming out as a molecule byproduct we call it a condensation reaction. Now when there is benzoic acid instead of acetic acid we get ethyl benzoate and water.

But if there is both bifunctional acid and bifunctional alcohol, for example, the reaction between terephthalic acid and ethylene glycol. If we considered there are ‘n’ number of terephthalic acid and ‘n’ number of ethylene glycol, then we get n number of PET polymer and (2n – 1) number of H_2O molecule. So in this case, we call it a condensation polymer.

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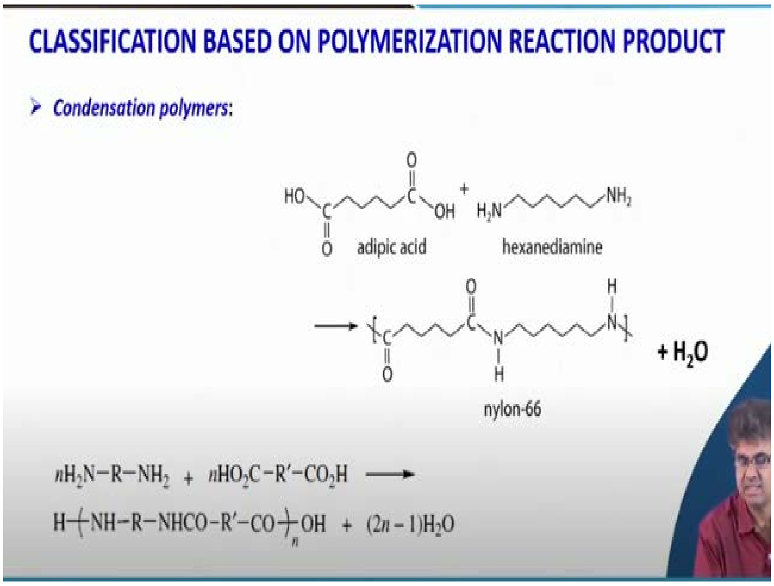

CLASSIFICATION BASED ON POLYMERIZATION REACTION PRODUCT

- *Condensation polymers:*

$n H_2N{-}R{-}NH_2 + n HO_2C{-}R'{-}CO_2H \longrightarrow$

$H{+}NH{-}R{-}NHCO{-}R'{-}CO{+}_n OH + (2n-1)H_2O$

Another example is a reaction between adipic acid and hexane diamine to produce a polyamide which is commonly known as nylon. Depending upon the number of carbon atoms in the acid and diamine the name changes. In both cases, there are 6 carbons, so it is called nylon-66. A general reaction between a diamine and a diacid forms these kinds of products. So this is a general example of condensation polymers.

There are also chain growth polymerization and step growth polymerization, which depend on the mechanism of polymerization. And these two classifications are related. For example, condensation polymers are related to step growth polymerization and chain growth polymerization is related to the addition polymers. But they are not 100% related to each other. There is some difference as well.

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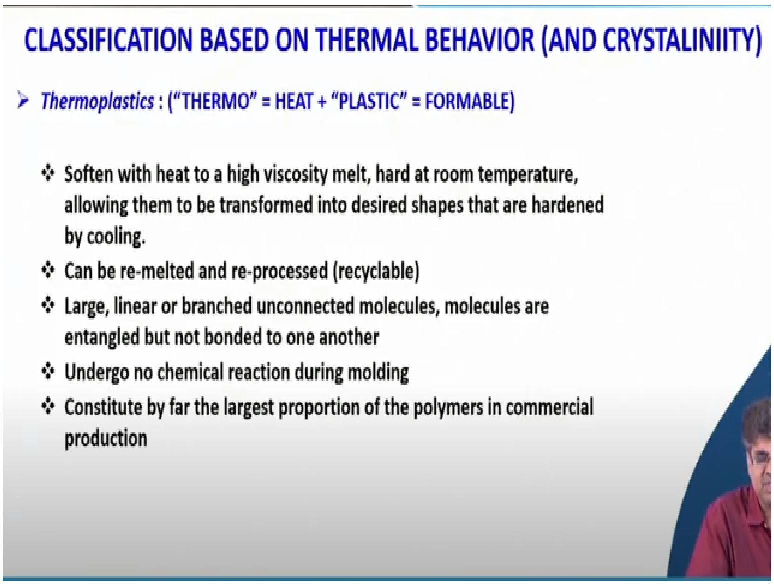

CLASSIFICATION BASED ON THERMAL BEHAVIOR (AND CRYSTALINIITY)

- *Thermoplastics* : ("THERMO" = HEAT + "PLASTIC" = FORMABLE)
  - Soften with heat to a high viscosity melt, hard at room temperature, allowing them to be transformed into desired shapes that are hardened by cooling.
  - Can be re-melted and re-processed (recyclable)
  - Large, linear or branched unconnected molecules, molecules are entangled but not bonded to one another
  - Undergo no chemical reaction during molding
  - Constitute by far the largest proportion of the polymers in commercial production

Now, to discuss the classification of polymers based on thermal behavior and crystallinity, we will talk about thermoplastics. As the name suggests that 'thermo' means 'heat' and 'plastics' means 'formable'. So, thermoplastics are formed after heating. On heating, the material becomes soft, and once it becomes soft, it can be given a shape as per requirement. The plastics which are very commonly used in our everyday livelihood are basically thermoplastic. So, thermoplastics are materials that we can heat, soften and then make whatever design we want. Basically it softens with heat to a high viscosity melt and becomes hard when it is cooled to room temperature. So, the process is called the molding. So, it can be remelted and reprocessed. So it is recyclable. Thermoplastics are formed from large linear or branched unconnected molecules. The large molecules are entangled, otherwise we will not get this high viscosity, but they are not bonded to each other. And during the melting process or cooling process, these polymer molecules do not undergo any chemical reaction.

This is the process that is called the molding process. As thermoplastics or plastics constitute the largest portion of the polymers in commercial production. So all the commercial polymers are mainly thermoplastics material.

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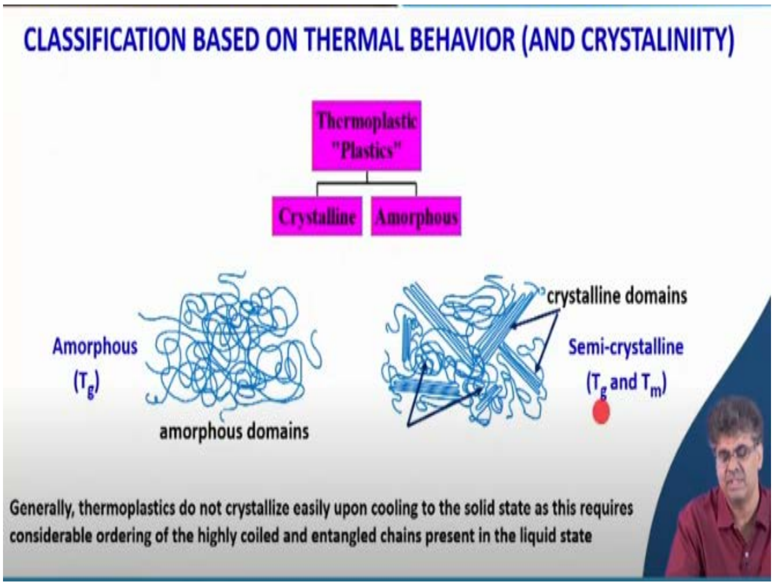

CLASSIFICATION BASED ON THERMAL BEHAVIOR (AND CRYSTALINIITY)

Thermoplastic "Plastics"

Crystalline

Amorphous

Amorphous (T_g)

amorphous domains

crystalline domains

Semi-crystalline (T_g and T_m)

Generally, thermoplastics do not crystallize easily upon cooling to the solid state as this requires considerable ordering of the highly coiled and entangled chains present in the liquid state

Thermoplastics can be either crystalline or amorphous depending upon the crystallinity. In this case, crystallinity means it is not 100% crystalline as we cannot make a 100% crystalline polymer. So it is kind of semi-crystalline. So, here a crystalline polymer means a semi-crystalline polymer. Amorphous, as I discussed, consist of large polymer molecules and they are not linked to each other, but because they are large, they entangle with each other. When the sample is heated above a certain temperature, it becomes soft with high viscosity melt. After cooling, it becomes hard again. The temperature, above which it becomes soft, that temperature is called glass transition temperature or T_g. Glass transition temperature is the softening temperature and the plastic materials are processed much above this temperature, and to give it a particular shape we have to cool down to room temperature. In the amorphous polymer, there are no crystalline domains. These domains are all amorphous. To have a crystal, long-range order of molecules are needed, but in this case, none of these polymers have any ordered structure.

Now, there is also a semi-crystalline polymer. So, in this polymer, there is a partly crystalline domain. In this polymer, some chains are nicely arranged in order. So these regions are crystalline. The crystallinity can vary from a low number to a quite high number. But it is never can reach 100% crystalline as the polymer molecules are large entangled polymer. So it is very difficult almost impossible for all the chains to come and align themselves parallel so that they can make crystalline.

So, the thermoplastics do not crystallize easily upon cooling to the solid state and this requires considerable ordering of the highly coiled entangled chains present in the liquid state. So some attributes need to be present in polymer structure to form this crystalline material. So, the glass transition temperature (T_g) is there for amorphous material and semi-crystalline material for the amorphous region, but for the crystalline materials crystalline regions we have T_m or melting point. The crystalline polymers form a melt above this temperature. So semi-crystalline material has two transitions. The glassy region or amorphous region will become soft above the glass transition temperature and the crystallines will become melt above the melting temperature.

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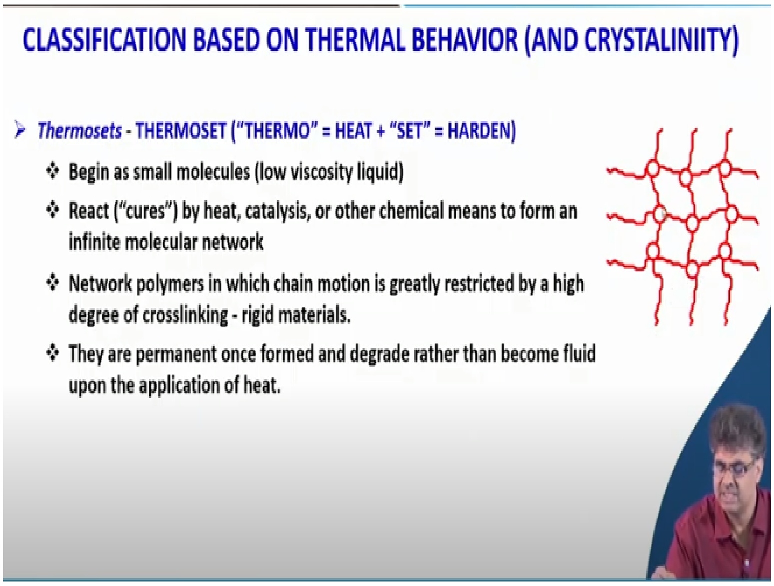

CLASSIFICATION BASED ON THERMAL BEHAVIOR (AND CRYSTALINIITY)

- *Thermosets* - THERMOSET ("THERMO" = HEAT + "SET" = HARDEN)
  - Begin as small molecules (low viscosity liquid)
  - React ("cures") by heat, catalysis, or other chemical means to form an infinite molecular network
  - Network polymers in which chain motion is greatly restricted by a high degree of crosslinking - rigid materials.
  - They are permanent once formed and degrade rather than become fluid upon the application of heat.

There is another set of polymers which we call thermosets and as the name suggests, ‘thermo’ is heat and ‘set’ means hardened. So in this case, the polymers on heating become hard. Before heating at room temperature, it is a small molecule or oligomer type molecule which has low viscosity. On heating, they react with each other and form interlinked polymer molecules which gives cross-linking between the polymer chains in presence of a catalyst or without catalyst and forms an infinite molecular network. In network polymers, if there is a high degree of cross linking, then the chain motions are greatly restricted and we have a rigid material. Now if there is less cross linking, then there could be a possibility of some amount of motion between the polymer chains within the network. So it can be a little bit softened, elastic type material. As they are chemically cross-linked, so once they are formed they are permanent and if we heat it further, it will degrade rather than become fluid again. So basically thermosets are not recyclable material. So, thermoset material cannot be reused like thermoplastic

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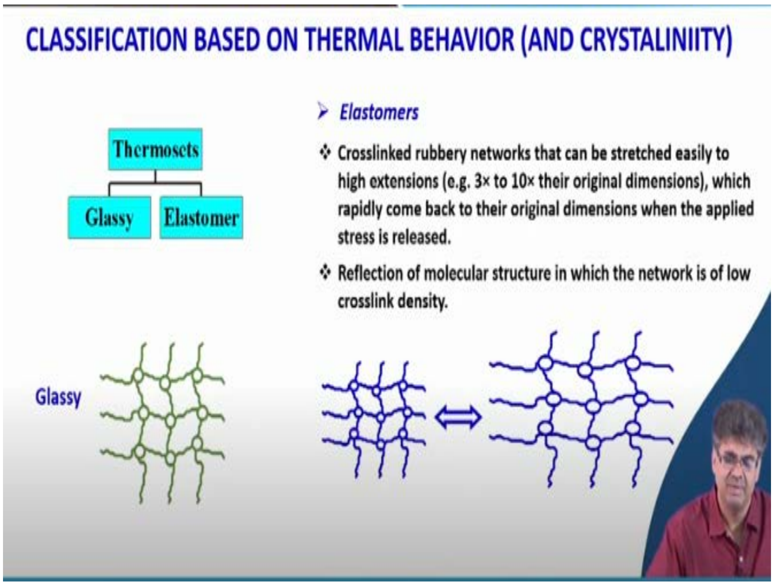

CLASSIFICATION BASED ON THERMAL BEHAVIOR (AND CRYSTALINIITY)

Thermosets

Glassy Elastomer

- *Elastomers*
  - Crosslinked rubbery networks that can be stretched easily to high extensions (e.g. 3× to 10× their original dimensions), which rapidly come back to their original dimensions when the applied stress is released.
  - Reflection of molecular structure in which the network is of low crosslink density.

Glassy

There are two different types of thermosets. If the crosslinking is less, and the polymer chains are above their glass transition temperature, they have the mobility to move around. Then it can be stretched like a rubber band, it can extend 3 to 10 times to its original dimension and if the applied stress is removed it can come back to its original dimension. This is called an elastomer.

Now, glassy means if the temperature of the polymer is below the glass transition temperature, then these polymer chains are stiff. These intermediate polymer chains have not much mobility. As well as if we have a high crosslink density, the mobility also gets restricted. So in that case, this becomes very hard material and we cannot stretch them. So they are called glassy thermoset material.

So basically in terms of thermal behavior, we have two classes of materials, thermoplastics, which are again subdivided two cases – amorphous and semicrystalline. Thermosets are also subdivided - one is glassy and another is elastomer type thermosets.

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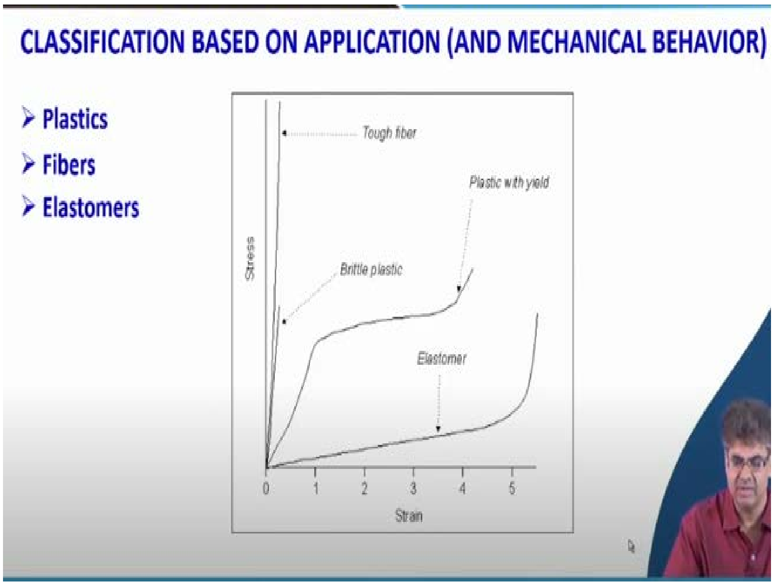

CLASSIFICATION BASED ON APPLICATION (AND MECHANICAL BEHAVIOR)

- Plastics
- Fibers
- Elastomers

There is a classification based on application and mechanical behavior. Now, what is called stress? Stress is the applied force per unit area and strain is the change in length divided by the original length.

Now in the case of elastomer, by applying a very small amount of stress one can stretch this polymer to a high extent. So basically strain is high on a given very small amount of stress.

On the other side, tough rubber like the fibers which are used for making clothes and materials needs very high stress to have a very small extension of their length over their original length. So in this case, very high stress is needed for a small amount of strain.

The ratio of stress by strain is the modulus. So in the elastomer modulus is very low and in fiber, the modulus is very high. And in intermediates, there are plastics and brittle plastics which can show yield behavior. So we have two extremes, elastomer, and fiber and then in between, we can have different types of plastic behavior.

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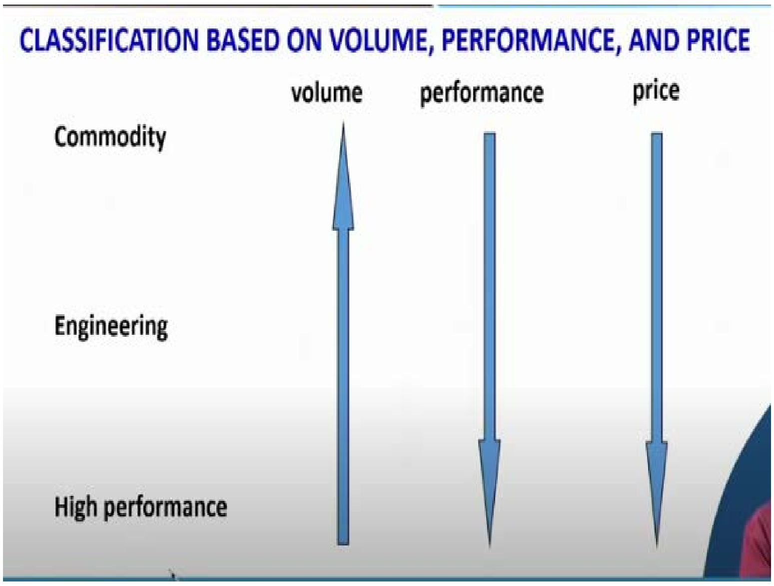
CLASSIFICATION BASED ON VOLUME, PERFORMANCE, AND PRICE

There is a classification based on the amount volume of the material which is used in the market. So when we talk about this very commonly used plastic material which we use for making, buckets and bottles which are very commonly used, we can anticipate that the volume of this plastic material will be very large and the price should be very low as well because the volume is high. So we call those materials commodity plastics. On the other hand, some plastics used for very high end applications like medical applications or space applications, which are in less volume and price is high. Then there are some applications where plastics are in engineering applications like in the car and in the structural applications, in which the volume is intermediate. So price is also intermediate and performance also intermediate.

So based on the volume of the plastics or the polymer used in the total market, performance and price, we can also classify polymers in commodity engineering and high performance.

The final classification where there is a classification of polymers in terms of their mechanism of polymerization, the step-growth polymerization and chain-growth polymerization will be done in the next class.