Introduction to Polymer Science

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Lecture - 02
Definitions/Terminologies, Classifications

Welcome back. In last lecture, we introduced the polymer science and also discussed briefly about the history of development of polymer science.

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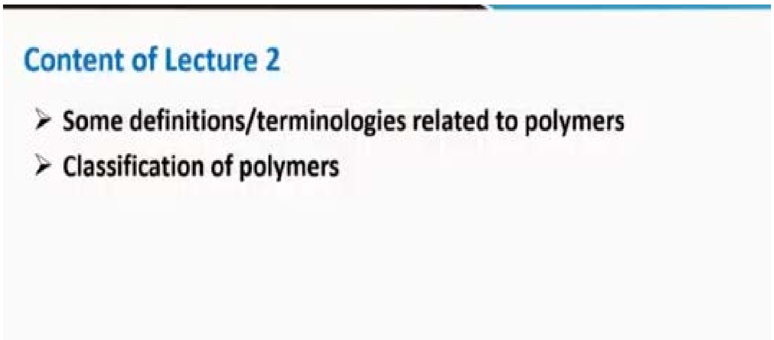

In this lecture, we will discuss some definition and terminologies related to polymers and also start the discussion of the classification of polymers.

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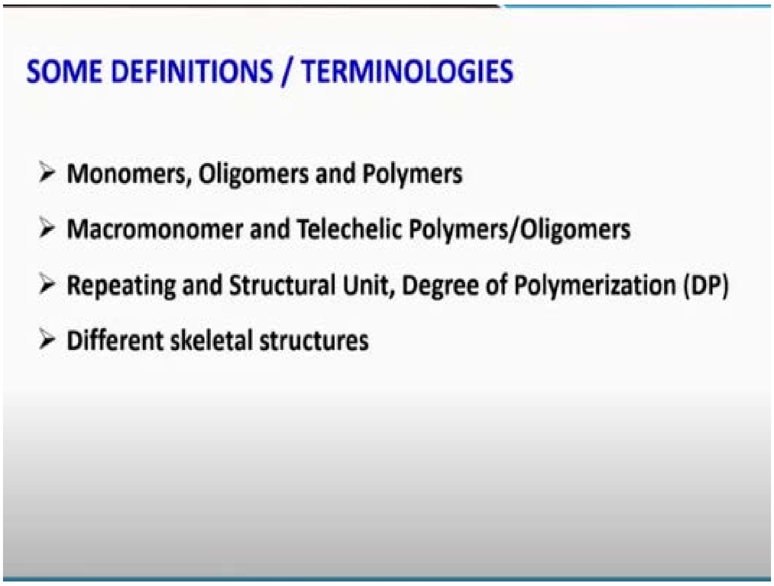

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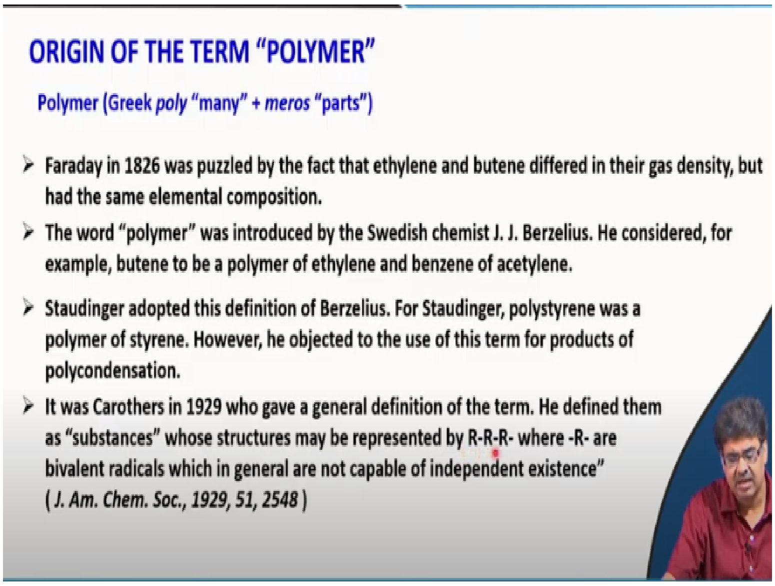

What does the term polymer mean? The word 'polymer' originated from the Greek words 'polys' which means many and 'meros' which means parts. Simply it means that a polymer has many parts. In 1826, Faraday was puzzled by the fact that ethylene and butene differed in their gas densities, but they have the same elemental composition. Then, the word polymer was first introduced by Swedish chemist J.J. Berzelius. He considered, for example, butene to be a polymer of ethylene and benzene to be a polymer of acetylene. Staudinger adopted this definition of Berzelius and he described polystyrene as a polymer of styrene but he did not accept this definition for the products of polycondensation. So later, Carothers in 1929, gave a general definition of the term. He defined them as 'substances' with a collection of molecules whose structures may be represented by a generic structure R-R-R- where –R are bivalent radicals, which in general are not capable of independent existence.

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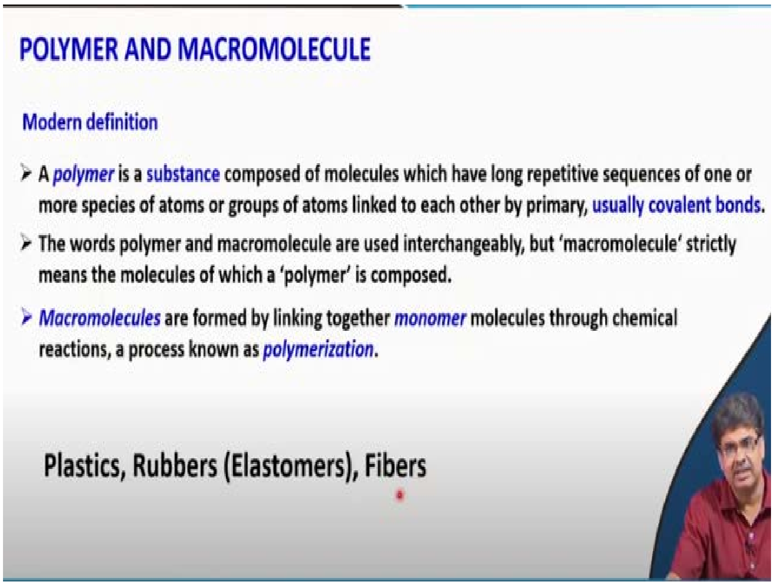

Later, the modern definition of polymers came and you will always hear the term macromolecules which is somewhat related to polymers. Though they are almost similar, there is a subtle difference between the general understanding of these two terms, polymer and macromolecule. The modern definition of a polymer is that it is a collection of molecules or simply it is composed of molecules, which have large repetitive sequences of one or more species of atoms linked to each other by primary, usually covalent bonds. Nowadays, several researchers also call them macrostructures, which are developed through non-covalent bonds like hydrogen bonding, π-π interactions, and so on. However, in the sense of polymer chemistry or polymer industry what we generally describe is that the molecules are formed by covalent bonds and that is typically what we call 'polymer'. So again, the polymer is a sample or a substance composed of molecules, which are large molecules or macromolecules. The words polymer and macromolecules are used interchangeably, but macromolecules strictly mean the molecules to which a polymer is composed.

Polymer is referred to as a collection of macromolecules that are formed by linking together monomer molecules through chemical reaction processes known as polymerization. Now several terms like plastics, rubbers or elastomers, fibers are very common and the term 'plastic' is very commonly used for describing polymers. When people talk about polymers, they generally refer to plastics. Are all plastics made of polymers? Yes, but the reverse is not true. Not that all polymers are plastics. Now this term plastics, rubbers, fibers they have different meanings and they are defined based on their properties. They are based on their behaviors, mechanical behaviors.

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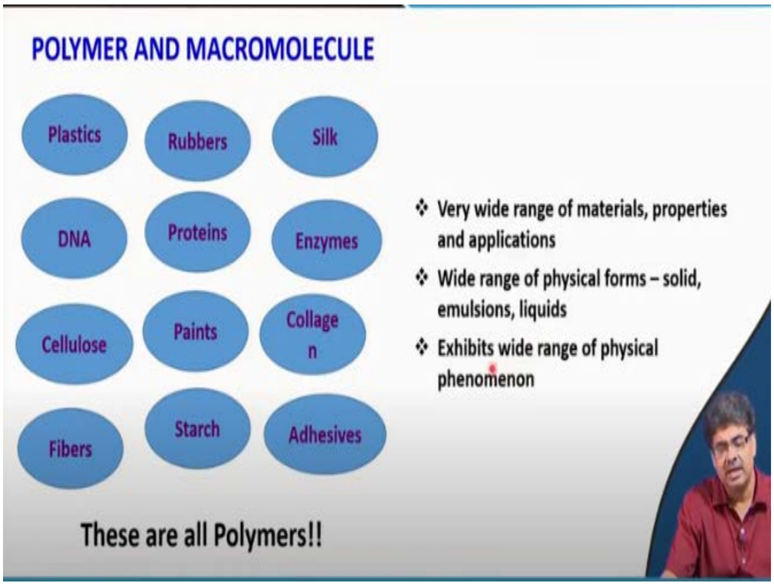

Now, there are so many things we can describe as polymers like plastics, rubber, silk, DNA, proteins, enzyme, cellulose, these are all polymers. Polymers have a very wide range of materials properties and applications, a wide range of physical forms, solid emulsions, foams, liquids, and they exhibit a wide range of physical phenomena.

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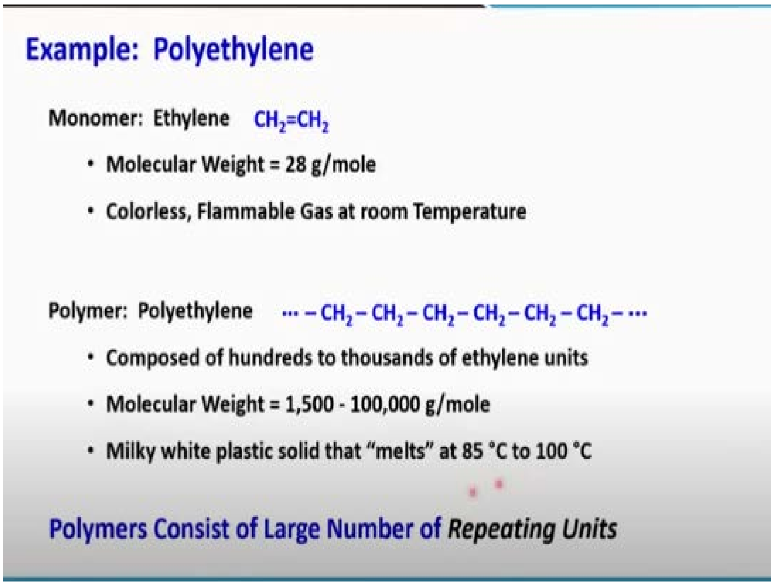

For example, polyethylene, the most commonly used polymer which is used in our daily life, is prepared from the monomer ethylene, which is a colorless, flammable gas at room temperature. Whereas, the polymer polyethylene, is composed of hundreds to thousands of ethylene units and the molecular weight is 1500 to typically one lakh or more. It is a milky white plastic solid that melts or softens at 85 ^{o}C to 100 ^{o}C. So polymer consists of a large number of monomer repeat units.

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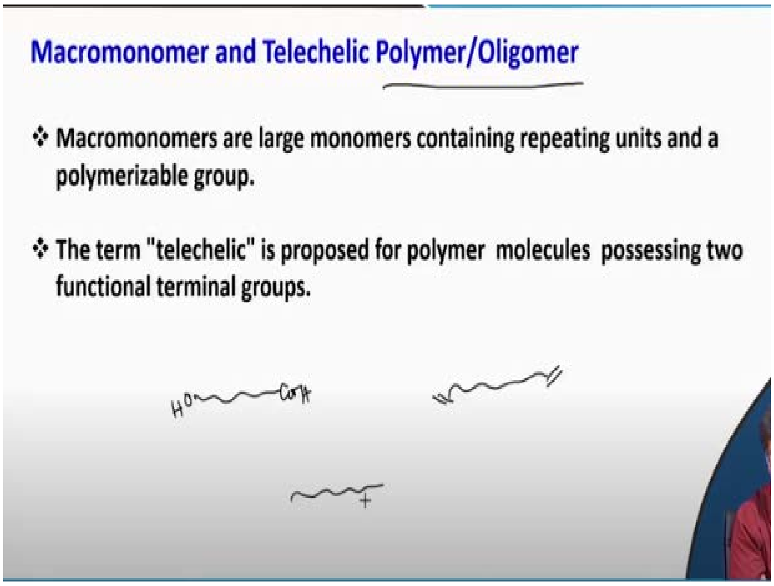

Two more terms should be remembered, that is macromonomer and telechelic polymer or oligomer. Macromonomers are large monomers containing repeating units and a polymerizable group. So if we write a polymer structure and at the end, there is a double bond or a functional group like COOH, then this is a macromolecule but it is polymerizable because of the presence of this polymerizable end-group or functional. So it is a macromolecular monomer, or in short, it is a macromonomer. The term telechelic is proposed for the polymer molecules or oligomer molecules possessing two functional groups at the end. So if there is an oligomer in which COOH on one end and OH on the other end, or something else like a double bond on both the ends then we call this as a telechelic polymer or depending on the size we call this as an oligomer.

Now we are always hearing these two terms, polymers and oligomers. The polymers or the chains which are not very high molecule weight are oligomers. So the cutoff for deciding the fact that a chain is a polymer or an oligomer depends on the specific polymer. In order to have a useful property for a polymer sample, we need to have a minimum length of the polymer chain or minimum molecular weight. If we can achieve a sample with that molecular weight, then we call it polymer and if the sample has molecular weight of polymer chain less than that molecular weight, the sample is not useful. It does not have required properties and we call this as an oligomer.

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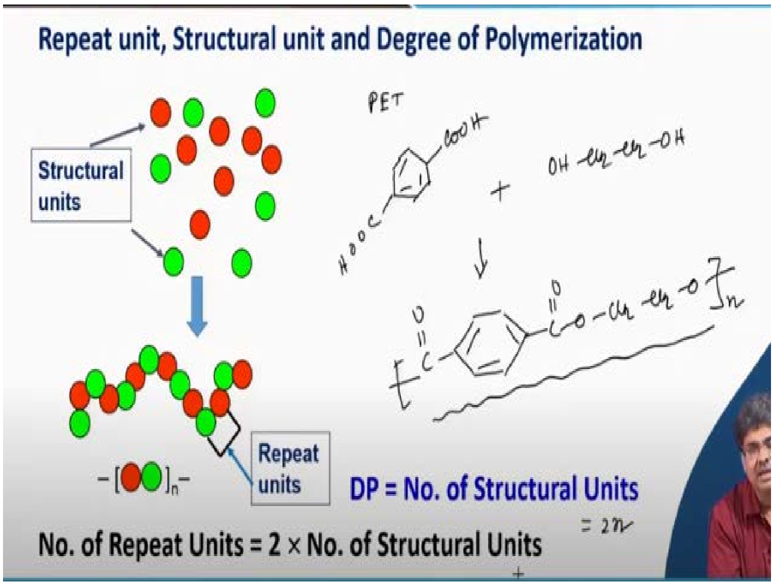

Now there are some more important concepts like repeat unit, structural unit, and degree of polymerization. The degree of polymerization is very important to understand. If we have a polymer synthesized from two monomers, which are represented by two colors, red and green, then the polymer is usually presented like this. Giving a specific example, if we want to make polyethylene terephthalate (PET), we must have a reaction between terephthalic acid and ethylene glycol. The polymer PET forms and ‘n’ is the number of repeat units. Now, in this case, the repeat unit contain two structural units, one structural unit from terephthalic acid, another structural unit from ethylene glycol. We have the number of repeat units ‘n’ is twice the number of structural units. So in this particular case, the number of structural units would be 2n and we call that number of structural units as the degree of polymerization or DP. In this particular case, ‘n’ is not the degree of polymerization, ‘2n’ is the degree of polymerization, where ‘n’ is the number of repeat units. So the number of repeat units is not the number of degrees of polymerization. But the number of structural units is the degree of polymerization.

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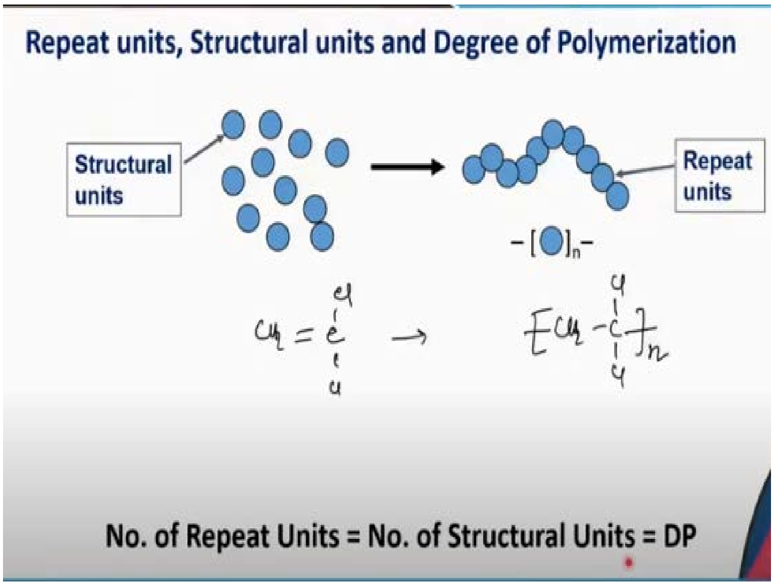

We take a simple polymer, which is synthesized from a single monomer like CH_2=CHCl or vinyl chloride In this case, 'n' is the number of degrees of polymerization, number of structural units as well as number of repeat units. So in this particular case, when a polymer is synthesized from a single monomer then the number of repeat units equals the number of structural units, equals the degree of polymerization. So in this case that is equal to 'n'.

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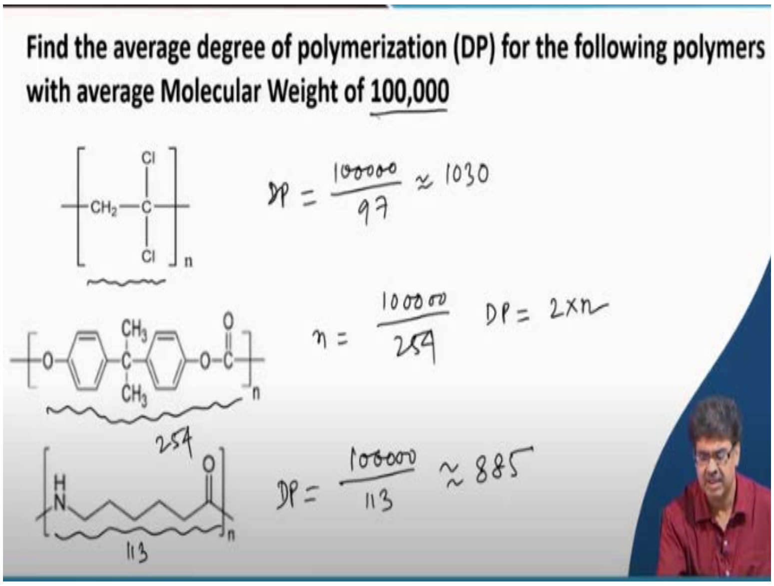

Now giving a few examples like if we have a molecular weight of one lakh then what would be the degree of polymerization for the first case. The average molecular weight is 100,000 in this case, where the molecular weight of the repeat unit is 97. So in this case degree of polymerization is 100,000 divided by 97 which turns out to be 1030 approximately. But in the second case, this repeat unit has a molecular weight of 254. So in this case, ‘n’ would be 100,000 divided by 254. The degree of polymerization would be 2n. Now in the third case, this is synthesized from a single monomer. So the degree of polymerization would be 100,000 divided by the molecular weight of the repeat unit, i.e. 113, which turns out to be 885.

Now, these are the examples to clarify the concept of calculation of the degree of polymerization.

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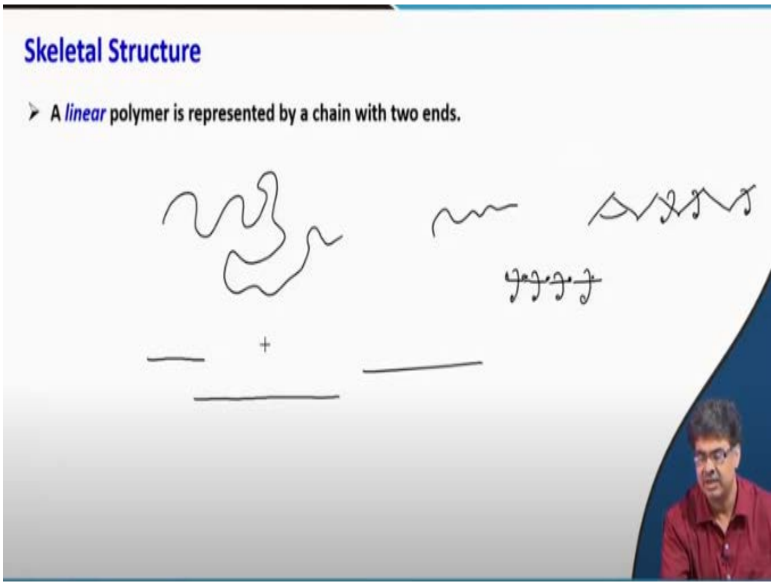

Now we will talk about skeletal structure. What do we mean by skeletal structure? It could be a linear polymer, which is represented by a chain with two chain ends. Now generally, we write polymers like it is having simple two ends because, most of the polymers are formed by atoms, which are linked by a single bond. Now, because these bonds can rotate, we can hardly write the polymers as a straigth. Also, carbon-carbon bonds have a particular bond angle and these bonds can rorate. As a result of this rotation, we get a flexible polymer chain. So that is why we do not represent the polymers by stiff chains.

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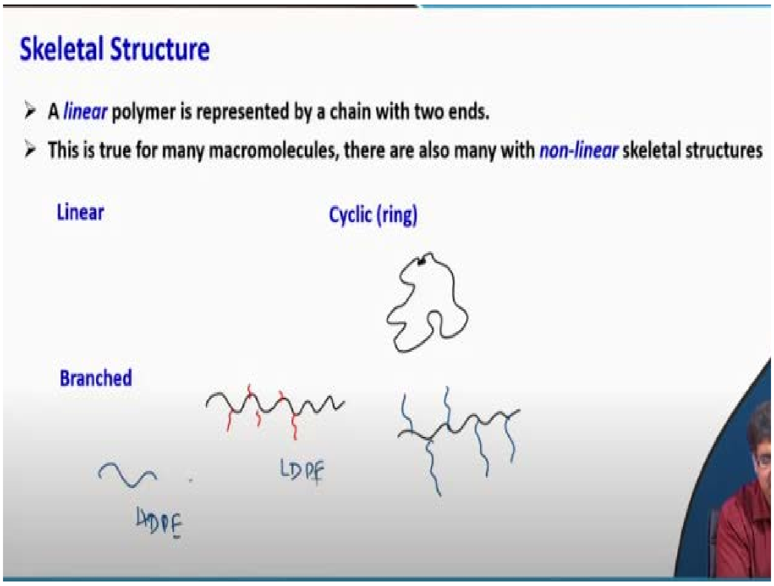

Now, linear polymers are represented by a chain with two ends and this is true for many macromolecules but there are also some non-linear skeletal structures e.g. we can get also cyclic rings where we have a polymer chain that is linked at the ends. So we get a ring structure for this. We can also get a branched structure e.g we have one long polymer chain and second another small branch coming out, or we can have a chain and have long branches. Now branches can be placed uniformly. Sometimes branches are generated because of some side reaction and that happens randomly and we can also do post-polymerization to place these branches in a very orderly fashion.

Now obviously, it can be understood that the properties of these branched structures and the linear polymers will be different, since linear polymers can come close and make ordered structures very easily whereas, for the long branched polymer chains, it will be difficult for them to come closer and make an orderly structure or crystal structure.

So basically that is why, when we talk about polyethylene, the high-density polyethylene HDPE are linear, whereas low-density LDPE polymers cannot pack well as they have branched structure in the polymer chain.

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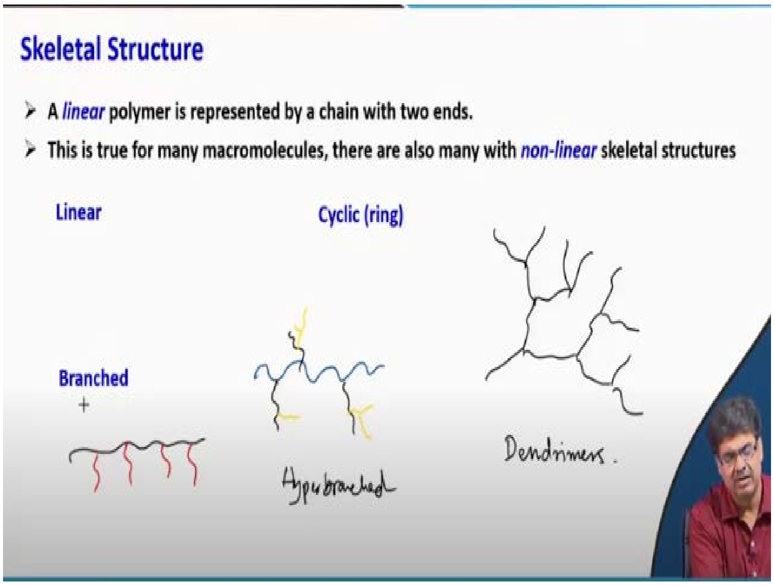

Now, we can also have this branched in a way that there is a sub-branch formed. So, a molecule can have further branches. They can have branches that can form branches from a sub-branch and which can branch further.

Branches can come out from the branches and in that case, we call these hyperbranched structures. And some cases these branches are placed in a very orderly fashion. Like if we start from one branch and then two and this goes further to another two, this goes into another two; if this is done in a very orderly fashion we get a nice ordered macromolecular structure and we get in this case, dendrimers.

When we have a simple branch, we also call it is a graft. They are called graft polymers.

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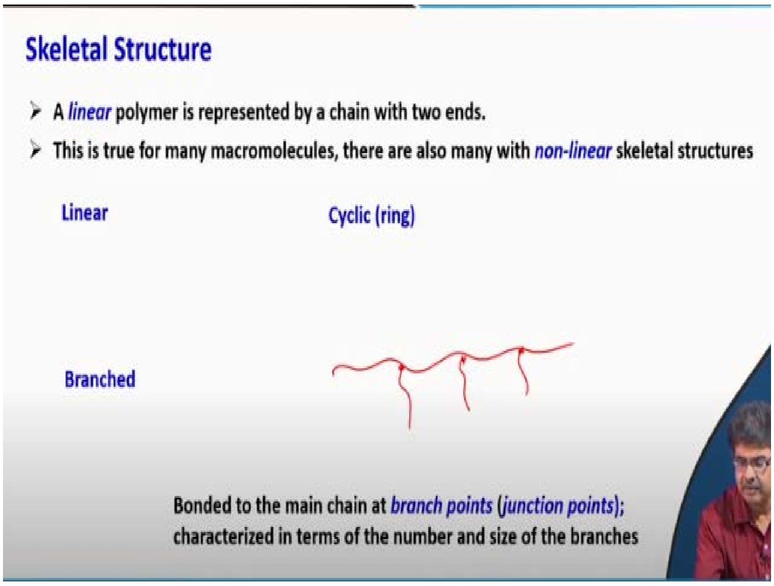

And then we can also have other brush-type polymers, in which, branches are bonded to the main chain at the branch points. And these branched polymers are characterized in terms of the number of branches or size of the branches whether it is a short branch or a long branch and so on.

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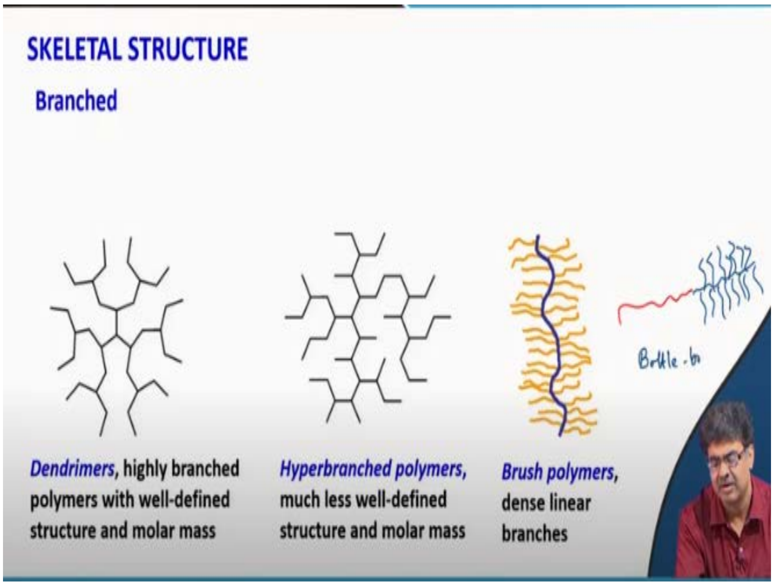

As it is already explained that, we can have a kind of random branching of the molecule, we call this hyperbranched polymer. This has a poorly-defined structure and molar masses. The dendrimers are highly branched polymers with well-defined structures and molar masses. Similarly, we can have brush polymers in which, there is one main chain and then there is a very densely populated branched structure. So we call it a brush polymer that has dense linear branches. We can also have one linear chain and then another chain with a lot, densely populated branches. It is like the brush we typically use for cleaning the feeding bottles for babies. So, we call this type as brush polymer due to bottle brush type shape. So depending upon the shape, we call these structures differently.

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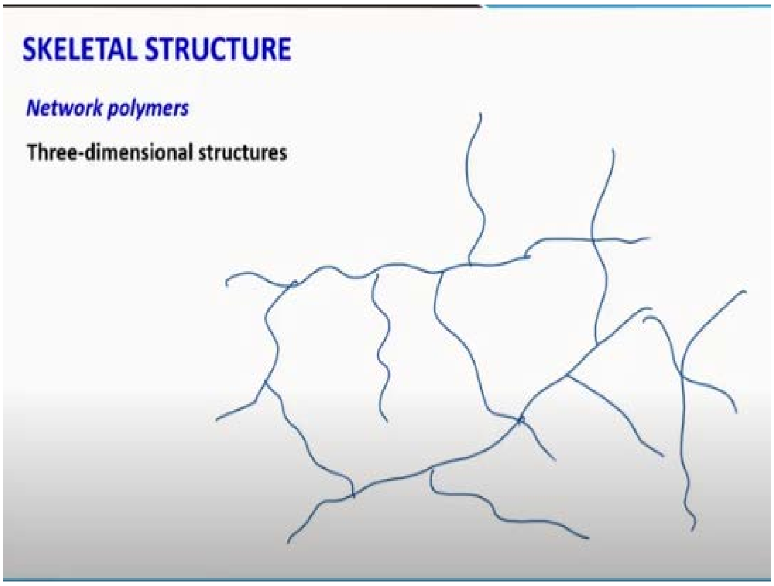

We can also have three-dimensional structures, if these branches link between two polymer chains, then what happens? We get a network structure where all the polymer chains are linked to each other. There are branches and the main polymer chain. So in that case, we are getting almost all the chains are linked with each other. As a result, we are getting a network polymer. In that case, the molecular weight of the polymer is infinity because all the chains are linked with each other.

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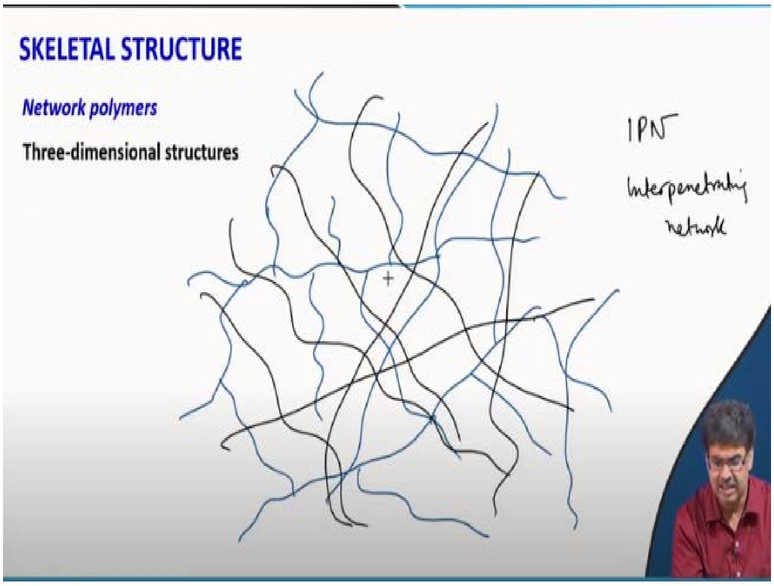

Now if we have one network and mixed with another network. Then, we call this an interpenetrating network. Two networks are interpenetrated with each other. So we call this an IPN, interpenetrating network. In this case, as it is drawn with two different colors, that two networks that are interlinked with each other. Sometimes this is very useful, we can get the properties of two networks together.

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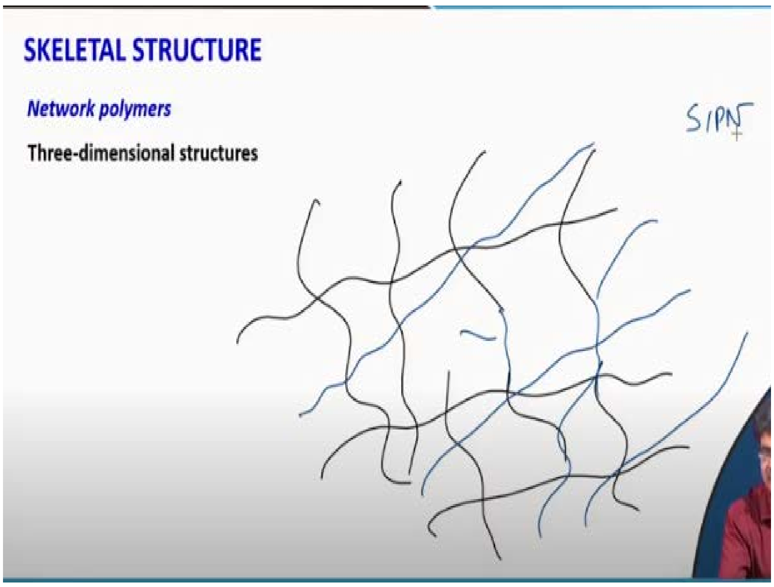

Sometimes one of the networks is not cross-linked with another network polymer. So one set of polymer chains is mixed with another set of polymers, but those are not linked to each other but rather intermingled with one another. So we call this a SIPN or semi-interpenetrating network.

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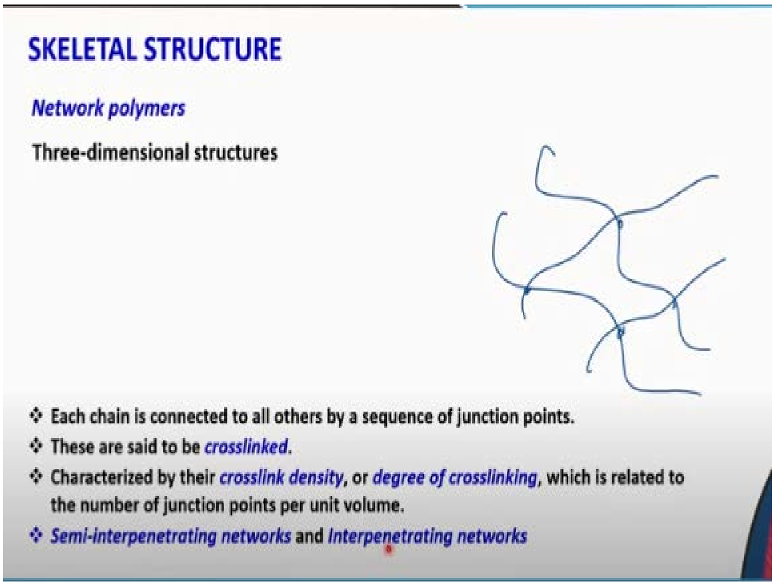

So, in the case of the network polymers, each chain is connected to all other chains by a sequence of junction points as we have seen. These points are called junction points. Also these middle portions are called cross-links and the polymer chains are called cross-linked. These are characterized by the cross-link density which means the number of cross-links per gram of polymer chain or per mole of the polymer chain. We also call that degree of cross-linking which is related to the number of junction points per unit volume. We just described what is a semi-interpenetrating network and an interpenetrating network.

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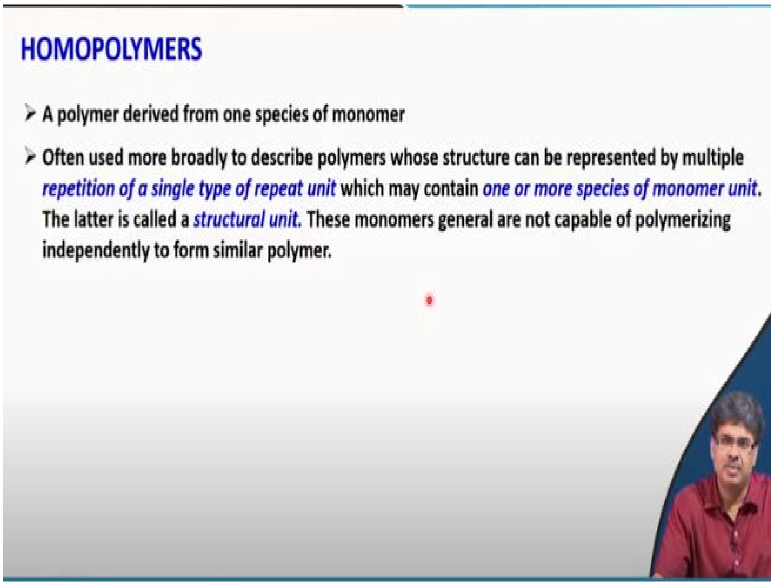

Now, we will go to the next classification which is homopolymer and copolymer. Homopolymers are a polymers derived from one species of monomer and are often used more broadly to describe polymers whose structure can be represented by multiple repeat units or a single type of repeat unit. If we have a polymer like PET, that is also a homopolymer because I cannot make a polyester molecule just from either ethylene glycol or terephthalic acid. So in this case we should call polyethylene terephthalate as a homopolymer, not a copolymer because we cannot make a polymer independently either from terephthalic acid or from ethylene glycol. If we use terephthalic acid and half of ethylene glycol and half of butylene glycol and make a polyester, then it can be called as a copolymer. So there is a little difference between this copolymer and homopolymer. In case of PET type polymer, we call that ethylene glycol or terephthalic acid as structural units when they are in the polymer structure.

Okay with this we should end this and then, next lecture we will talk about copolymers.