Polymers: Concepts, Properties, Uses and Sustainability
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Lecture - 02
Polymers - Molecular Structure

Hello and welcome to this lecture on introductory course on polymers. We are into week one and the questions we are trying to address are what is a polymer and how do we describe these polymers and what are their unique features. So in this second lecture, we will learn some basic nomenclature related to polymers and what is their chemical structure.

We will look at many of the lectures in this in four broad modules and this is associated with concepts module of the course.

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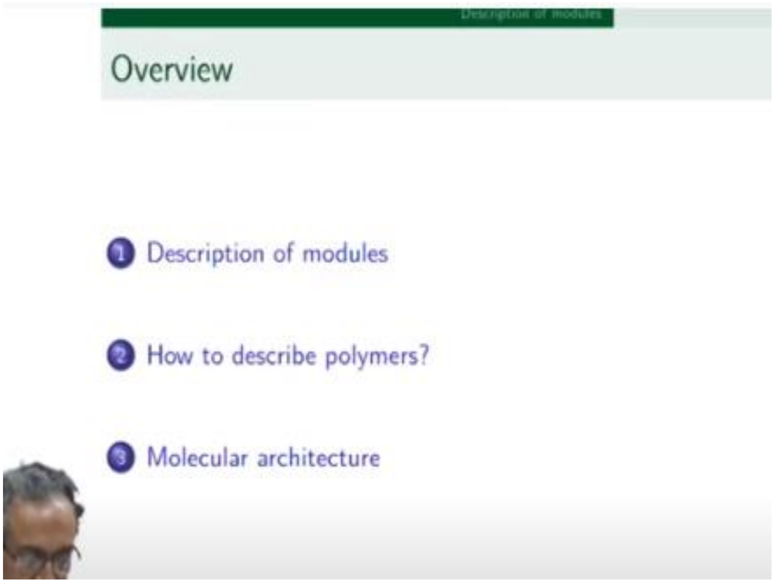

What we will do in this lecture is first look at little bit more about the modules that we will follow in this course and then look at molecular structure and how do we describe these polymers.

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So just continuing on from where ever I left off in the first lecture, the modules are associated with four broad issues. The first one is related to concepts, where we will learn scientific and engineering concepts related to polymers. An important aspect of usage of these polymers in scientific and engineering applications is their properties.

And here as people working with polymers, we must be able to estimate and calculate properties, have numbers, play around with numbers, use the numbers. So that will be an important component of the course, where we will look at quantitative and calculations associated with these polymers and their properties. Of course, these are important class of materials because they have present as well as future applications.

So not only do we need to worry about how to estimate or calculate, we also have to worry about how to apply or what is the application of these materials and the sustainability of polymers.

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So the questions that if you look at associated with the different modules in concepts we will try to learn why and how of polymers, why is its mechanical property? Why can strain be very high before it breaks? In terms of properties, how much? How much does the rubber extend before it breaks? Is it 10%? No, in fact, it can be as high as 600%, 800% strain. So which means it can become eight times its length.

Of course, it is not surprising. You have always used a rubber band which can extend five to six times its original size. Now also where is the application? What property mix makes it very suitable for a given application? And if an application is not there can I think of a given material and then apply it in a new situation? And of course, finally what do we do given the questions associated with sustainable use of polymers.

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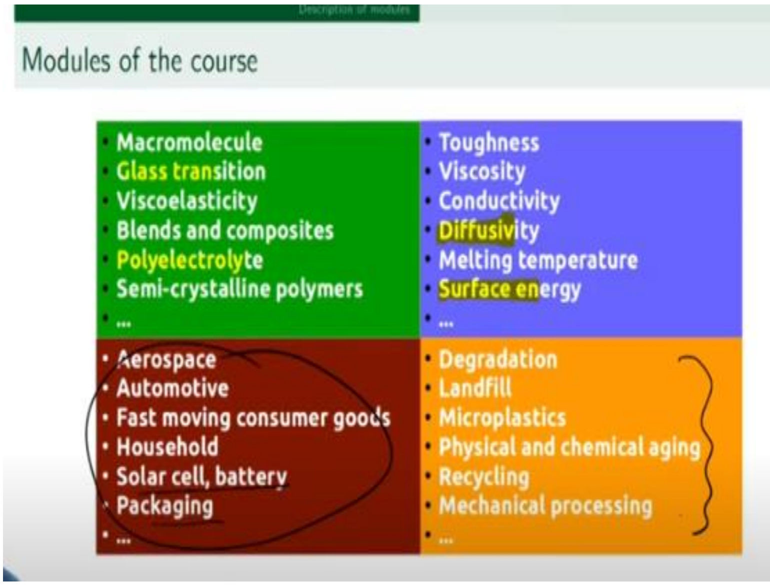

So when we go down several lectures in this course, these are the kinds of things that we will be discussing in each of the module. So in concept related things we may discuss things related to for example, an important concept called glass transition, which makes the material very soft above glass transition and very hard below glass transition.

The fact that PET bottle at room temperature is good enough to store soda, but at 70, 80 degrees it will not at all be able to store the carbon dioxide and carbon dioxide will permeate from it, is a very important concept associated with glass transition. Or for example, polymers with ionic groups. In fact, many of the macromolecules that are there in our body, whether it is protein or DNA, they are all examples of polyelectrolyte.

So what happens when you have a macromolecule, a giant molecule with charges on it? The second set of lectures are associated with properties and there we will look at properties such as conductivity in terms of diffusion of small molecules like I mentioned carbon dioxide diffusing out of a PET bottle. If we are using several materials together then their surface energies.

So many of these properties. What are the numbers? How why is it that a polymer has a given surface energy or why does it have a given conducting property or a resisting property and so on. So here we will look at very specific number based calculations for evaluating theoretically as well as from a practical consideration.

And in terms of applications, we will look at various different classes of applications from sophisticated applications like energy storage and energy generation to something which is more mundane in terms of day-to-day use packaging applications and so on. And of course, we will also spend a significant amount of time looking at sustainable use of these polymers and what makes these polymers challenging in terms of their sustainable use.

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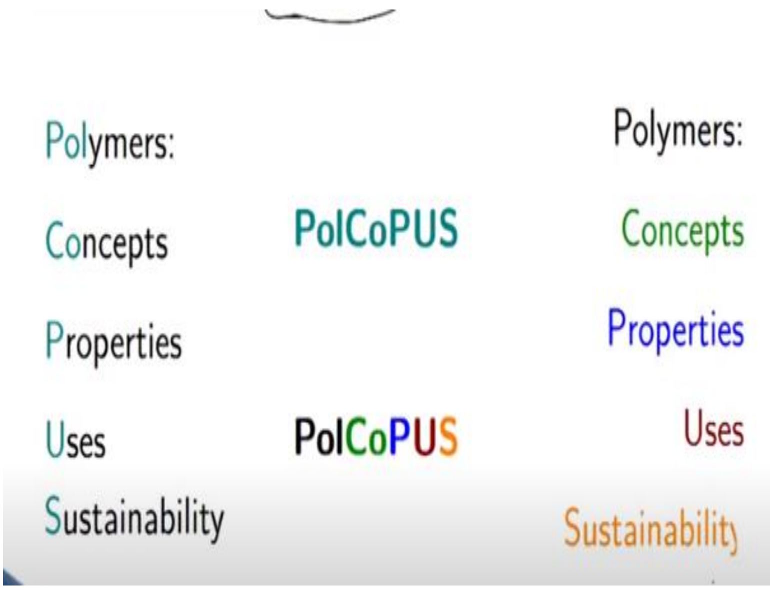

So therefore, the lectures in this course will be as you can notice, the current lecture is always mentioned here. The section which is being discussed is on the screen and the slide number is also mentioned. And so you can follow all the lectures by focusing on some of the messages which are there on the slide in a very standard format.

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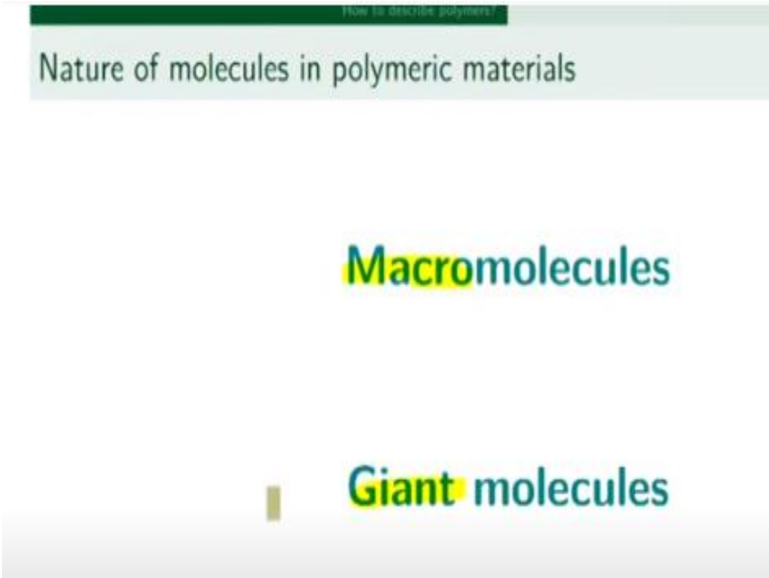

And just to remind ourselves again, and this is something which cannot be overemphasized while learning about polymers is the fact that they are macromolecules or they are very giant molecules. And given that this is their nature, one of the first things we will start doing is learning about what is meant by a polymer, what is a polymer made up of?

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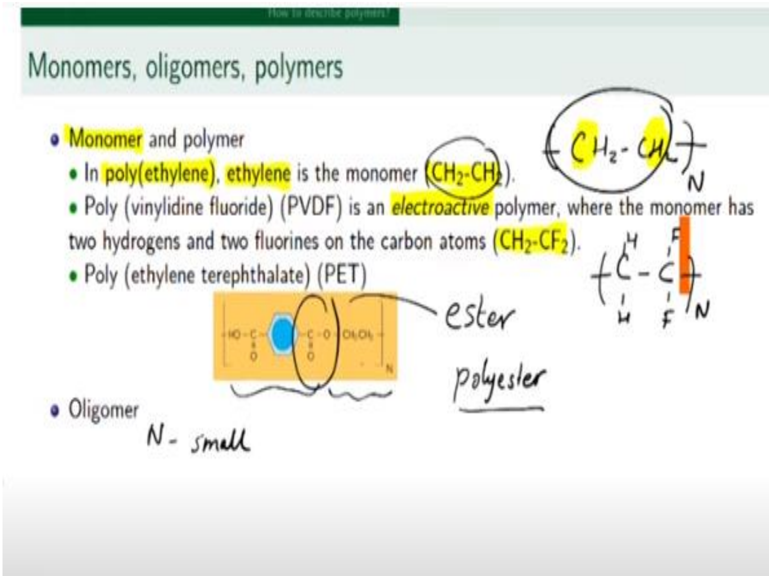

So generally, the monomers is a single molecular unit, which combines together to make a polymer. And so for example, ethylene is the monomer for polyethylene and ethylene as most of you know is just CH_2-CH_2. So polymer or polyethylene would be written as CH_2-CH_2 repeating itself several times.

So this is one nomenclature which we will have to get used to where we say the, what is a polymer? This is polyethylene because CH_2-CH_2 is repeated N times and so this is a chain of polymer. This is a macromolecule in which ethylene units have reacted with each other and N no of ethylene units have reacted. Another example of a molecule is PVDF.

This is a very important polymer for making strain gauge. That is why I have referred to it as an electroactive polymer. Just search what is meant by electroactive polymer. In fact it is a very important class of materials, which is being researched as well as applied in the last two decades or so. So in this case, if you look at the monomer it is very similar to ethylene, except that instead of C and hydrogens, you now have C and fluorine repeated.

And of course, you can clearly now notice that from ethylene to PVDF, there is some similarity, but there are important differences. And the reason PVDF is an electroactive polymer is because of this C-F bond which is there. And this is very polar and all the electroactive properties associated with this polymer are related to this C-F. And clearly that is absent in case of polyethylene where it is only carbon and hydrogen bonds.

Another example of a repeating unit for a polymer is PET, which I have already mentioned as a PET bottle that we are very familiar with. This looks somewhat different compared to the polymers that I described already. In case of ethylene, we had the ethylene unit and the polymer looked very similar. So monomer and repeating unit looked very similar. In this case in fact, monomers have been combined, two monomers.

And to form this ester bond. So polyethylene terephthalate is a polyester. This you would have heard. In fact, a lot of our clothing if it is not cotton we call it polycot, is mainly polyester and cotton or just polyester. And again, so polyester not PET, but family of polyester wherever this ester bond is there, because you can change many of these chemicals. In this case this is CH_2-CH_2 you can have different units.

In this case there is a benzyl ring that can also be different. So you can get variety of polyesters. So in this case monomers are diacids and diols. We will look at this again in the course to come. If you have N small then we call it oligomer. You can look at various words wherever oligo is the prefix to it. It means a smaller number.

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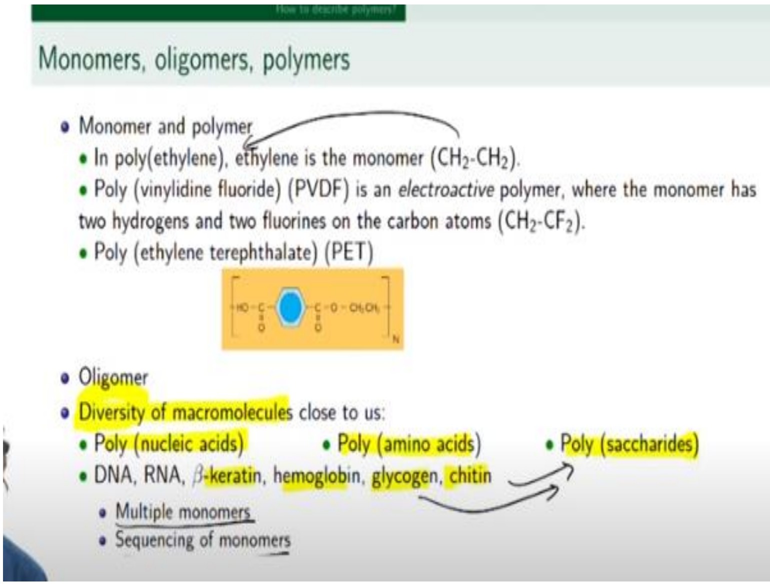

If you look at the natural macromolecules, macromolecules within us. What we notice is really diverse nature of these macromolecules. It is mindboggling in fact. Because if you look at how the repeating units and monomers of either of these proteins, polysaccharides or molecules, nucleotides, which make up as poly nucleotides as DNA, RNA. This many of you must be familiar with.

It is there in our hair, keratin. It is a protein. You can look at what are the monomers that make up keratin and you will be surprised to see how diverse range. Hemoglobin all of us are familiar with. You can look up also glycogen and chitin. These are two examples of polysaccharides. And what you will notice is unlike simple case where I talked about polyethylene being made up of ethylene, in this case the monomers and repeating units are actually complex.

So you have quite often multiple monomers and therefore the sequencing of monomers is very important. So question you can ask yourself is why does nature have such a, such diversity? Why is sequencing of monomer so crucial? And if you remember, many of the biochemical reactions which are going on which are underlying feature of life, they are very specific.

Each of these reaction is in response to a specific condition. And this is something can be achieved if you have this diversity. And so something related to macromolecules in nature is very different compared to macromolecules of synthetic polymers that we talk about.

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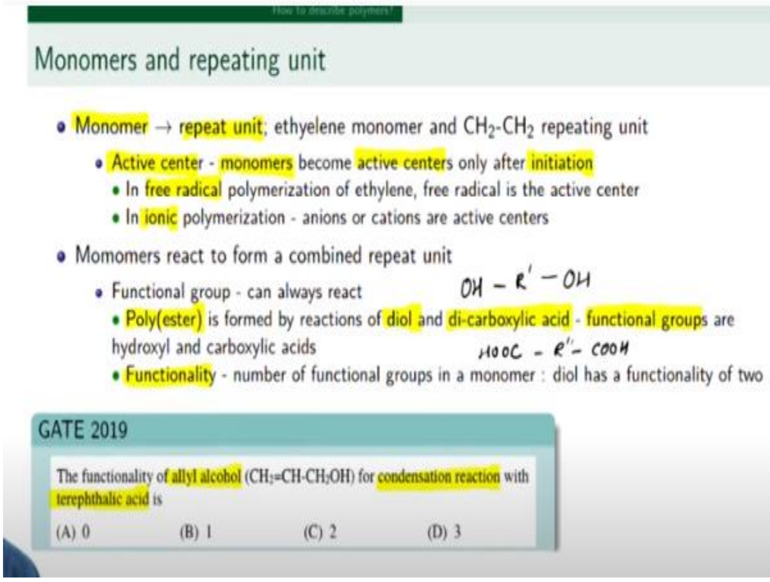

Let us continue looking at this nomenclature. So monomer as we say is building unit of a polymer. And once the polymer is built, there is something which keeps on getting repeated. And in case of polyethylene, the monomer and the repeating unit are same. And in these type of polymers, what there is an active center. So ethylene which cannot really react with itself will have to be activated.

So monomers become active centers due to initiation. So when we add an initiator, which can be a free radical or it can be an ion. Once this is added, then monomer becomes activated and then this activated monomer can start combining with other monomers. But in such a set of polymers, the monomers and repeating units are identical.

But in other cases like we saw in for PET or other polyesters for example, polyester is formed with a molecule which looks like a diol. Diol means two hydroxyl groups. And a di-carboxylic acid, which implies a molecule which has some group and then carboxylic acid, but two of them. And so these are called functional groups.

And in this case, the monomers are this diol and di-carboxylic acid, when they react, you have a polyester bond formation and the repeating unit. Because the reaction happens and water gets eliminated in this case the repeating unit looks different compared to the monomer itself. But again as we saw earlier so the repeating unit is continued to be repeated throughout the polymer chain.

So important thing to note in all of this is functionality. The monomer which is being added or the reacting species, which is being added, how many times can it react? So we saw that diol and di-carboxylic acid can react two times. So these are examples of bifunctional materials. And here you can ponder over this question. For example, what is the functionality of allyl alcohol?

But look at the other part of it. The question is also asking specific. So clearly functionality is a concept where you have to think of how many different ways can a molecule react? You just think over this question before you go any further, just pause and think as to what your answer is for allyl alcohol functionality.

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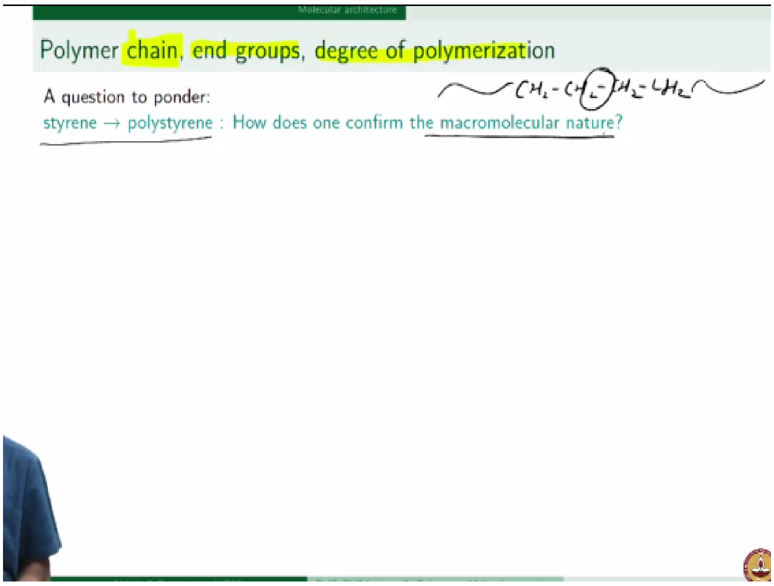

Let us continue on our journey to define some of the nomenclature associated with polymers. So polymers we will refer to as a chain because it is one building block keeps on repeating itself. It is like chained together, monomers are chained together. And of course, the end of the polymer is the either an initiator molecule or it is either a carboxylic or hydroxyl group in case of polyester.

So end groups are important. And then we will also define what is called the degree of polymerization, what is the length of polymer basically. And while we are doing this, a question that you can think of is how we really establish that there is a chemical reaction and a polymer is being formed due to a covalent bond formation.

So for example, in case of polyethylene, we have CH_2-CH_2 repeated itself and between two ethylene molecules this covalent bond is being formed. And we will also soon become familiar with drawing polymers like this implying that it is a long chain of polymers and I have just shown two repeating units here.

So the question you can think of is if I have styrene, going to polystyrene, how I establish that styrene has indeed covalently bonded with another set of styrenes and I have got a linear chain of styrene, which are all together covalently bonded. And in fact, this question is very important, because this was what scientists and engineers grappled with 100 years ago while trying to establish concept of macromolecule.

And it is nontrivial. In fact, you can try to read the history and see how some people try to argue that you know styrene molecules just agglomerate with each other and therefore, the solid styrene which looks like is a colloidal form of aggregated solid. And then came along other set of scientists and technologists saying no styrene molecule is reacting with another styrene molecule to form a macromolecule.

And therefore liquid styrene becomes solid styrene due to macromolecule formation. And it is a very exciting story as to how people went back and forth and established the macromolecular nature of these polymeric systems.

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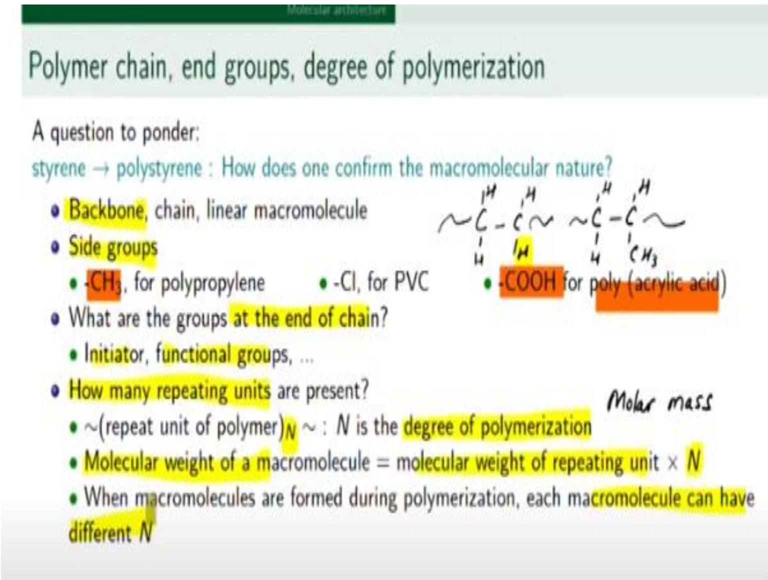

So let us continue in terms of looking at the further terminology. So given that the polymer chain is going to be our central concern, the chain itself we will refer to as backbone also. And we will call it backbone because around these backbones several other things can be talked about. One example is side group on a polymer chain. For example, we saw that for polyethylene the groups were only hydrogens.

But if instead of a hydrogen I replace it with a methyl, then that becomes propylene. Rest are all still hydrogen. So then this is polypropylene I can make out of propylene. So you can see that there are several different possibilities with very similar double bond associated molecules. Let me just draw this to indicate that this is a polymer part of repeating chain, because the monomer itself will have double bond.

Because the chain is formed, now the double bond is not there and there is single bond in a polymer chain. So if instead of methyl if I have carboxylic acid, then I get polyacrylic acid, which is an example of an ionic polymer or a poly electrolyte. Because we have an acidic group which is there reacted on the backbone of the polymer chain itself. And as I mentioned earlier, the question is what could be at the end of the chain.

So end of the chain could be an initiator, it could be a functional group. And so many times to measure molecular weights using chemical means, these end groups are very useful because we can count the number of end groups and then we can see, we can find out how many macromolecules are there in the system.

One of the important things related to macromolecules is its degree of polymerization or how many repeating units are there in a polymer and we will denote in this course using capital N and it is also called the degree of polymerization. So molecular weight of a macromolecule is basically the molecular weight of repeating units time this N. And in this course, we will refer to this molecular weight according to the current scientific terminology as molar mass.

But in industries or in many common parlance, you will use molecular weight also. So molar mass is what is formally now it is called, but molecular weight is also used by several users. One important feature which we will have to become very familiar with is the fact that there will be a distribution of molecular weights or molar masses in a polymer.

When I take a bulk sample and look at different macromolecules each macromolecule will have or can have different N. And this is again where synthetic polymer differ from many of the natural polymers. And so because if you look at a protein its molecular weight is fixed. And if I take a bulk sample of protein solution, all the proteins will have same molecular weights, protein molecules will have the same molecular weight.

But in case of polyethylene when I make, each macromolecule of polyethylene may have a different molecular weight.

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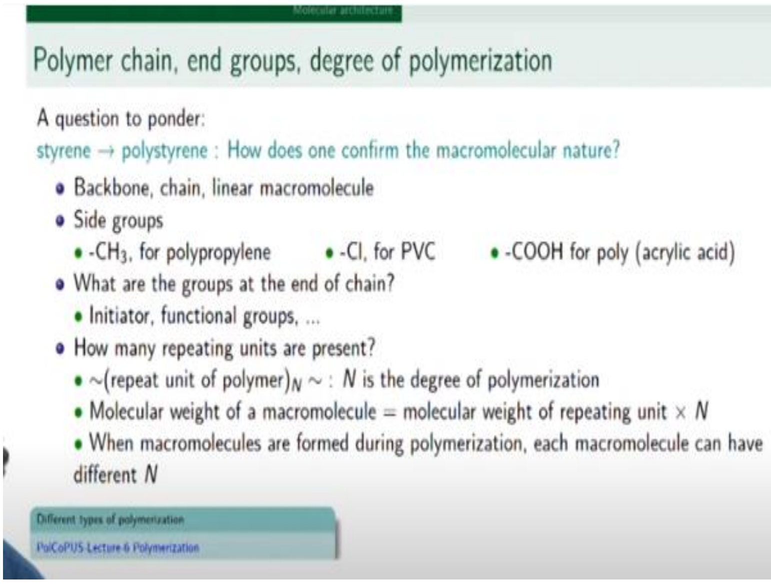

And so of course, some of this we will learn as to why there is a distribution of molecular weight by looking at polymerization techniques, and the statistics of polymer formation in case of polymerizations.

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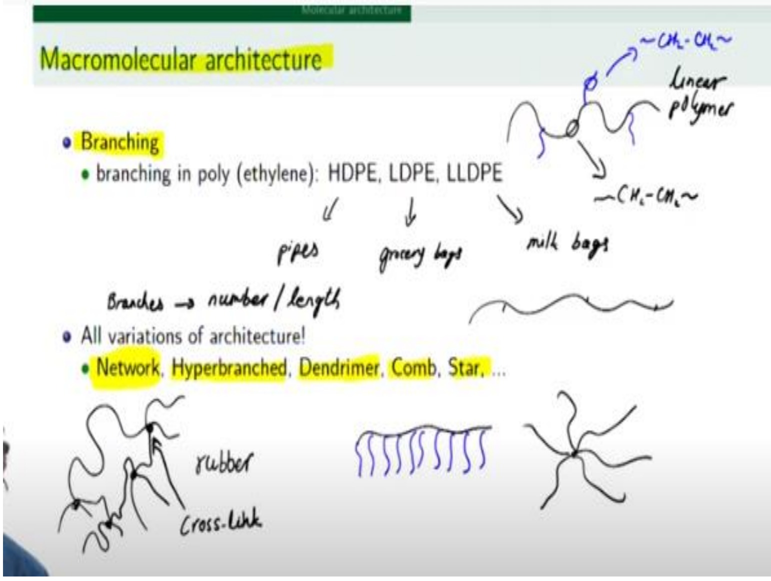

One important structural feature which these macromolecules have is what is called molecular architecture. If we just have a single room, then it is just going to be square block, cubicle block. But if we have a building, then we can talk of architecture. How are rooms arranged? What is the accessibility from one room to the other? What is the, how is the utilities available from one room to the other.

And that is the architecture. How what is the appearance of. And so same way in polymer, monomers are the building blocks through which a polymer chain is made.

Now what is the architecture for this particular macromolecule? So one important architectural variety is in terms of branching. So one thing which we will continuously do in this course is start drawing curves like this.

And then understand from them that this is a polymer chain being drawn. And what I have drawn here is a linear polymer chain, which implies that it is possible to get a branched polymer chain. What will that look like? There will be branches which are growing from the backbone. Now you can also see why something is called the backbone. So in this case the black curve which indicates the backbone while the blue curves indicate the branches, which are there.

And of course, if you zoom in to any one small segment you might see, so for example if this is a polyethylene chain, then somewhere very up close you will be able to see all the molecular details. And similarly, if it even the branches are polyethylene, then if you zoom in you will see that again the same repeating unit. So branching in polyethylene is one of the most important structural features.

In fact, you can make storage vessels or pipes out of polyethylene. You can make very flexible grocery bag kind of things. Or you can also make stronger bags which are for example, milk bags. And so the same polymer can be used in a variety of applications depending on whether it is branched or not branched and what kind of branching does it have? The D here refers to density.

So we have high density polyethylene, low density polyethylene and linear low density polyethylene. If you look at poly HDPE itself, it will look something like this, which is a linear polymer with maybe some small branches on it. If you look at LDPE, it has long as well as lots of branches.

While LLDPE has controlled set of branches. The number of branches is also controlled, and the length of each and every branch is also controlled. So clearly when we try talking about branching and backbone in the material for branching, we need to know the number of branches as well as length of branches. And then depending on what these features are, we can see different types of polymers being generated.

Not just branching, there are various types of architecture possible in polymers. And for example, you can have the polymers in a network. So a macromolecular chain can be covalently bonded to another polymer chain. And so what you can generate therefore is a network. In fact rubber looks like this. It is a cross-linked network of macromolecules.

And in fact its elastic properties, the fact that we can stretch a rubber band and we leave it, it comes back is because of this cross-link network. So network is an important aspect. The other key word that I used is cross-link. So whenever we say something is cross-linked, it implies that a network is formed. Cross-link is nothing, but wherever the molecules, macromolecules have joined together.

We can also have hyperbranched polymer, which means the number of branches is just too much. In fact, I leave this as an exercise to you to just search on the internet, if you search in hyperbranched polymer or if you look for LLDPE, you will clearly see how the molecular architecture is very different compared to a linear macromolecule or HDPE let us say. And other aspect, we can have very different, comb for example.

And can you guess as to how a comb macromolecule may look? And you should be able to guess that because as the name suggests, there may be a backbone and then on this backbone, there will be branches but arranged in such a nice manner that it looks like a comb. Now I have drawn them in two different colors to indicate that they could be two different monomers.

The black ones could be one set of monomers, the blue ones could be another set of monomers. Or they could also be both same monomers, It can also have star. Again what does star mean? Basically macromolecules growing out like a star from a single point. So you can see there is a very rich variety of molecular architecture which is present.

And through polyethylene we already know that this molecular architecture is very important, because it determines what the properties of these polymers will be and where can they be used.

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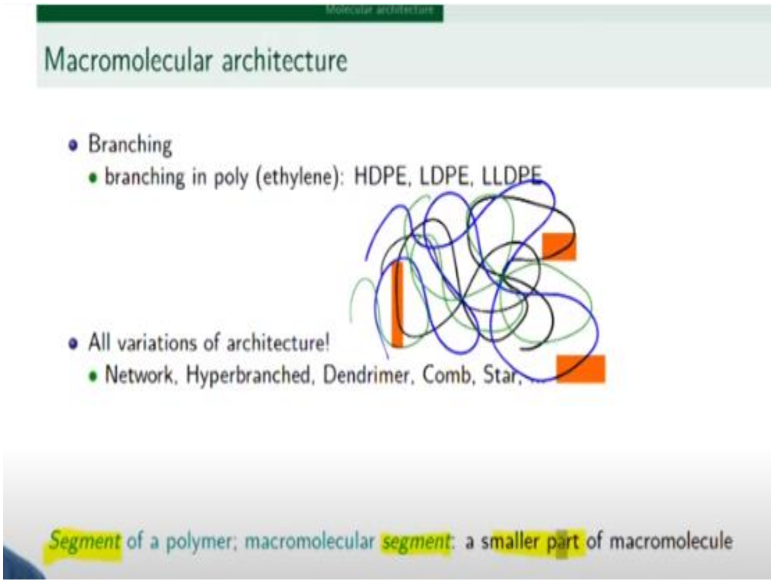

And other feature given that we have such long macromolecules that we need to remember, is many times the overall macromolecule may not be able to move or its properties as a whole macromolecule may not be important. So soon we will also start looking at macromolecules like this, where there is one macro molecule. Then there is another macromolecule. There are all entangled like bowl of noodles.

And in such cases, what we will see is what is important is not the overall macromolecule and what it is doing, but maybe some small part of the macromolecules and what it is doing. And an important therefore phrase, which we should remember, is what is called a segment of a polymer. Basically, it is a small unit of macromolecule which can move. So the fact that cross-linked rubber can stretch is because what segments can stretch and so on.

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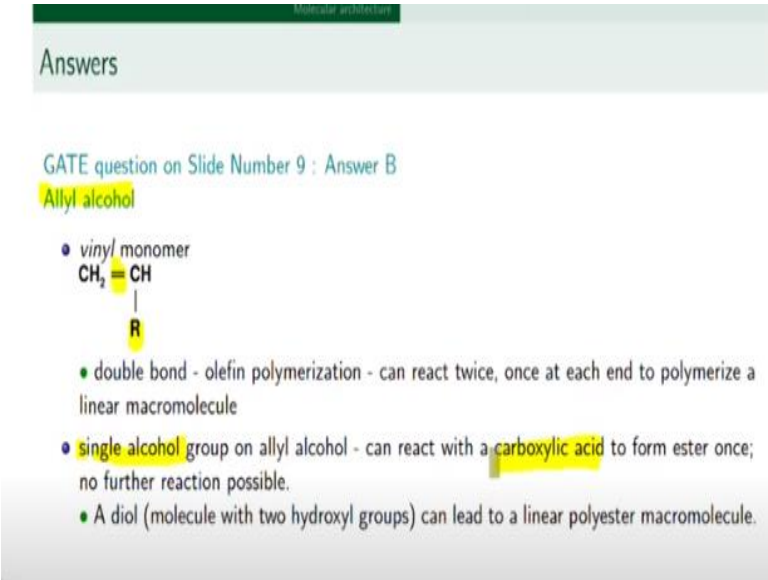

So with this, we come to the close of this particular lecture on the structure of polymer molecules. Just to talk about the question which was posed on slide number 9, you know allyl alcohol what is its functionality? And if you see it is a vinyl monomer with double bond. So just like ethylene, it can react at both ends and form a chain. At the same time, this R group also has an alcohol group. It is a single alcohol group.

So therefore, it can react with acid. So now you can go back and look at the question carefully, and then see what the functionality is as far as reaction with carboxylic acid is concerned. So clearly, this molecule has functionality of different kinds. If you think of this double bond reacting, there is a functionality. If you think of this R reacting, then there is functionality.

And so that is a trick question in trying to ask as to what is the functionality of allyl alcohol? The question that you should be asking is tell me with respect to what? And so the second part of the question was with respect to reaction with carboxylic acid. And so the answer you can find out. So thank you and we will meet again in the third lecture of the series. Thank you.