Polymeric Materials of Different Kind
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Lecture - 26
Copolymers 1

Hello, let us continue our journey into learning about polymers and polymeric systems of different kind is the topic for this week that we are trying to focus on. And I hope by the end of this week, you will get convinced about the excellent tunability and the wide variety of polymeric systems that we can use. And it should be no surprise to us therefore, that polymers are being used in so many different diverse applications.

Concomitant with this of course, we have to worry about the sustainability aspects which also we are discussing in this course. So, today, we will continue looking at these different kinds of systems by looking at copolymers and our focus will still be in this lecture related to the applications point of view and where some of these copolymeric systems are used. In the next lecture on copolymers, we will also look at the properties of these copolymer systems and how they can be related to let us say the properties of the homopolymers which are already known.

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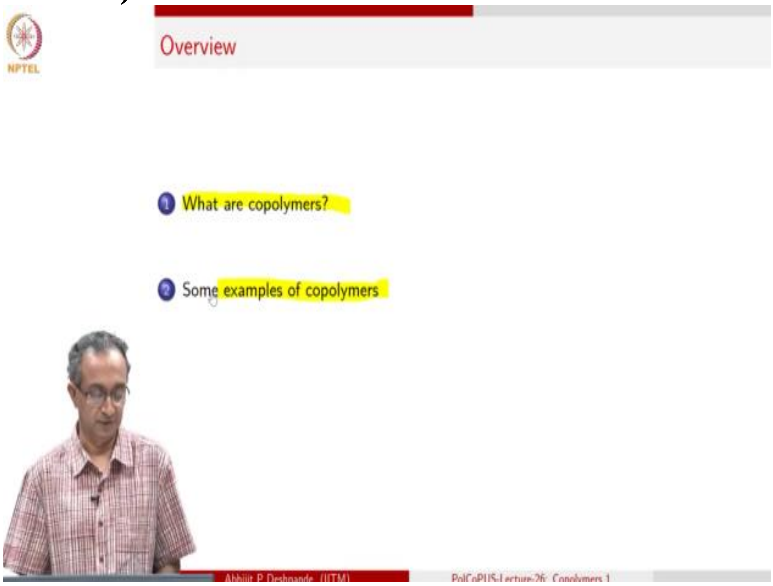

Overview

1. What are copolymers?
2. Some examples of copolymers

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So, we will begin this lecture by looking at quickly defining what are the copolymers and different types of copolymers which are present? And then we will finish this lecture by quickly looking at 2, 3 examples of these copolymer systems which are commercially used.

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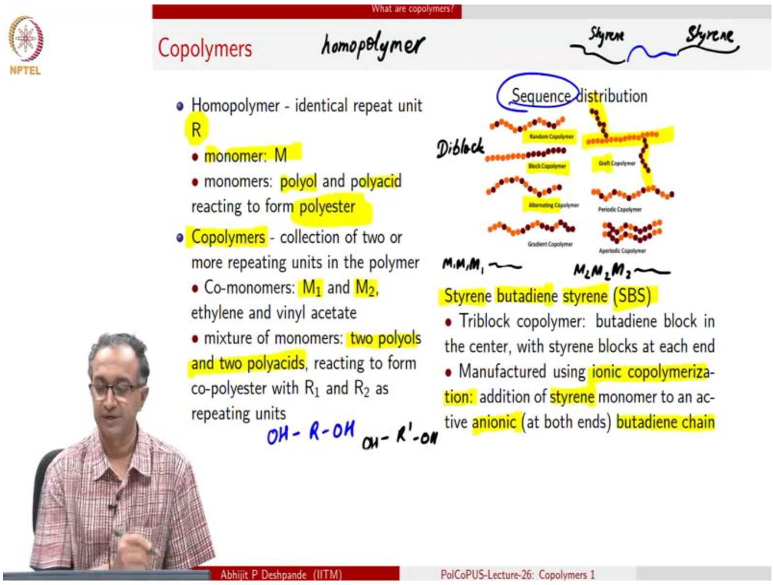

What are copolymers?

Copolymers

- Homopolymer - identical repeat unit R
  - monomer: M
  - monomers: polyol and polyacid reacting to form polyester
- Copolymers - collection of two or more repeating units in the polymer
  - Co-monomers: M_1 and M_2, ethylene and vinyl acetate
  - mixture of monomers: two polyols and two polyacids, reacting to form co-polyester with R_1 and R_2 as repeating units

Sequence distribution

Styrene butadiene styrene (SBS)

- Triblock copolymer: butadiene block in the center, with styrene blocks at each end
- Manufactured using ionic copolymerization: addition of styrene monomer to an active anionic (at both ends) butadiene chain

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So, copolymers are the polymeric materials, which have repeating units or monomers, which themselves can also form polymer. So, therefore, copolymer generally is contrasted with homopolymer and so, for a homopolymer basically we have monomer M or if we let us say have polyester, then we just have a polyol and polyacid giving us polyester, and in this case, the repeating unit will be R.

So, this is a homopolymer in which case you have a monomer itself attaching itself like polystyrene or you can have monomers reacting themselves to give you a repeating unit which is a polyester repeating unit. Now, when we say we are forming copolymer, we can do it therefore, in ways where we can let us say, 2 monomers which can form polymers by themselves.

So, you can form a polymer which is let us say M_1, M_1, M_1. So, basically a chain like this or we also have another homopolymer possible which is with the second monomer instead of that, now, we can combine the 2 monomers and this is what is shown here in this picture, where therefore, how M_1 and M_2 attach with respect to each other, there are very different possibilities.

Similarly, if we will continue with this example of polyester, then we can have 2 polyols and 2 poly acids. So, when I say 2 polyols basically, we are looking at polyols is nothing but let us say this is 1 example of diol 2 hydroxyl acid groups. So, we can have this or we can have another. So, clearly if we individually use them we can get a homopolymer with R prime as one case and R in the other case, and, but when we combine them together, we will get basically a copolymer.

And so, the sequence of R_1, R_2 or M_1, M_2 is what is different and so, we can have them randomly distributed, we can have them alternating so, M_1, M_2, M_1, M_2 and so, on. We can also have blocks of them or we can make one of them as backbone chain and the other one as graft these are the most common, but of course, there are other varieties of copolymers also exist and depending on our synthetic capability, we can make any or all of these different copolymers and just 1 commercial example of triblock copolymer.

So, what I have here is shown is a diblock copolymer because you can see that there are 2 blocks, but we also have triblock copolymer where there is a styrene block, then a butadiene block and another styrene block. And the way this is synthesized is using ionic copolymerization which we already looked at during our lectures, the 6th and 9th lectures on polymerization, depolymerization.

And so, how we do this is first we grow butadiene chain and both of those ends have anionic group and that anionic group can be used by styrene to start polymerization. So, we have a block of butadiene and then on both ends of this block we will get styrene. So, that is why this is styrene on one side styrene on another side and butadiene in between.

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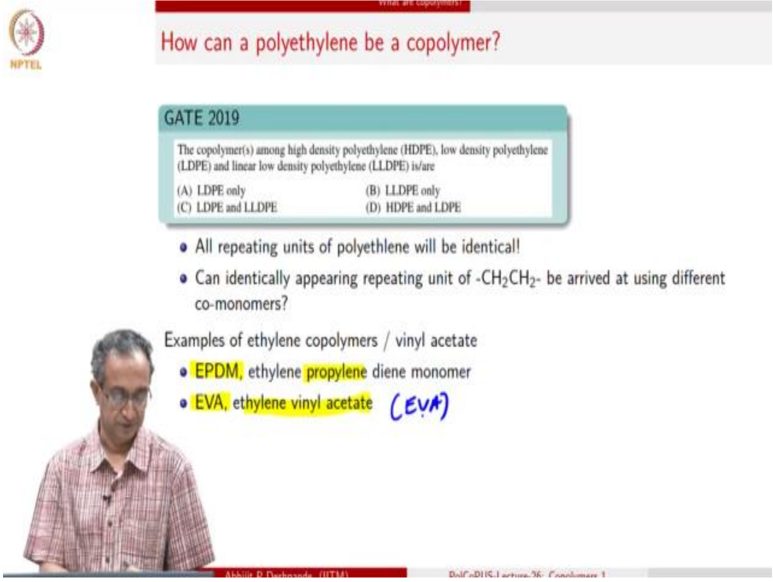

How can a polyethylene be a copolymer?

GATE 2019

The copolymer(s) among high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) is/are

(A) LDPE only
(B) LLDPE only
(C) LDPE and LLDPE
(D) HDPE and LDPE

- All repeating units of polyethlene will be identical!
- Can identically appearing repeating unit of -CH_2CH_2- be arrived at using different co-monomers?

Examples of ethylene copolymers / vinyl acetate

- EPDM, ethylene propylene diene monomer
- EVA, ethylene vinyl acetate (EVA)

So, let us continue looking at this copolymer system by just looking at this exam question where the highlight is that these are all polyethylenes. Now, but the question says that you know, which among the following polyethylene is a copolymer. So, when we say polyethylene of course, the repeating unit is going to be this $(CH\ 2\ CH\ 2\ )_N$ and so, clearly all of these polymers have these, this essential structure of course.

There can be branching as we have seen, we know that LDPE has significant amount of branching and LLDPE has controlled amount of branching. So, where does copolymerization come into this? So, the question is all repeating units of polyethylene of course, are just CH 2 CH 2, but, even though it appears that they are all this repeating unit of CH 2 CH 2 can be they be arrived using different co monomers so, that is the key.

So, we can use while doing the polymerization we can use ethylene and other sets of co monomers to still get repeating unit which is CH 2 CH 2 and that if you can think of then you can answer this question .Of course, ethylene and polyethylene is by far the largest volume polymer as we saw in our lecture also on states in the environment in the 25th lecture, but, ethylene is also used with other co monomers not just in branched polyethylenes but also for example, ethylene propylene diene monomer.

So, in this case, these are both rubber like systems ethylene vinyl acetate and so, co polymers here are either propylene or EVA as it is called. So, therefore, why do we do this? Why are copolymers common? And the answer is of course, exploiting and tuning the properties the way we want and ethylene polyethylene will give us one property vinyl acetate will give us another property we combine both of them together and more importantly, we can control the amount of ethylene and amount of vinyl acetate that is there in a macro molecular chain.

And so, the flexibility of macromolecules the size of the macro molecule and therefore, any other bulk properties in terms of mechanical or other response can be controlled.

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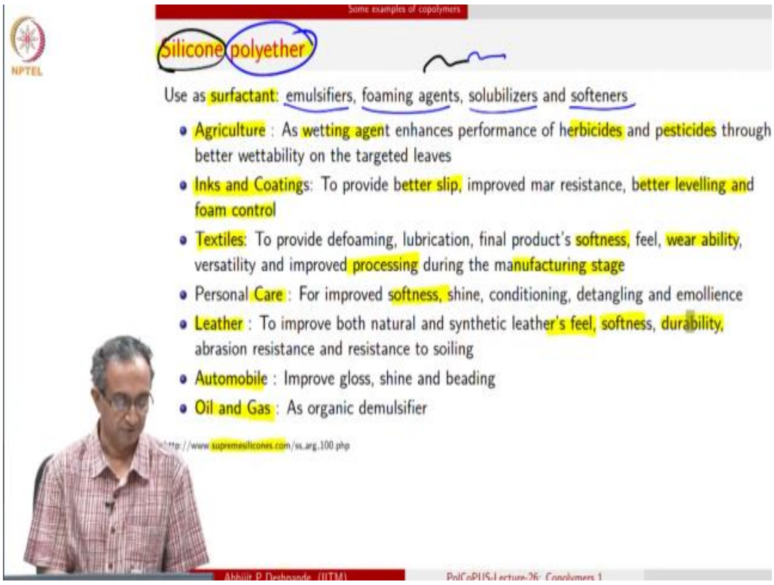

Some examples of copolymers

Silicone polyether

Use as surfactant: emulsifiers, foaming agents, solubilizers and softeners

- Agriculture : As wetting agent enhances performance of herbicides and pesticides through better wettability on the targeted leaves
- Inks and Coatings: To provide better slip, improved mar resistance, better levelling and foam control
- Textiles: To provide defoaming, lubrication, final product's softness, feel, wear ability, versatility and improved processing during the manufacturing stage
- Personal Care : For improved softness, shine, conditioning, detangling and emollience
- Leather : To improve both natural and synthetic leather's feel, softness, durability, abrasion resistance and resistance to soiling
- Automobile : Improve gloss, shine and beading
- Oil and Gas : As organic demulsifier

http://www.supremesilicones.com/ss.arg.100.php

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And so, generally these copolymers will also be available in variety of grades. And 1 example of these polymeric material systems which are co polymers is where we combine silicones and polyether. So, these are 2 different distinct we can get polyether itself by also we have polyethylene oxide or variety of other examples of these being present. And then we also have silicones which are very important rubber like materials for their thermal stability and they are used in wide ranging application.

But if we combine these 2 then we get materials, which are in fact, surface active agents, because we have the ether components which are hydrophilic and water loving and then silicon components which are hydrophobic or water hating. So, we get a molecule which has silicon segment and then it will also have polyether segment. And so, therefore, they can be used as emulsifiers, foaming agents, solubilizers, softeners.

And just see the mind boggling variety of applications that are there and this is from a company website which makes supreme silicones which make many of these things and they are trying to highlight how many different applications are there for such polymers and this is true for any other silicon polyethers that we you can look up. So, the applications are from agriculture to coatings to textiles, personal care, leather, automobile, oil and gas look at the range.

But if you look at where it is being used, you can see that the property which is being exploited is the surface active agent nature of it. So, for example, it is a wetting agent, herbicide or pesticide when it is applied, we would like to, it to be applied on the leaves instead of falling all over because then the efficacy of the active ingredient is not good. So what you need to do in these systems when you are applying these herbicides or pesticides, you also need to add a wetting agent.

So that leaves get wet and herbicide actually coats the leaf and so, things like that. So, there is an improved slip, better levelling, foam control in inks and coatings for textiles, there is a final product softness, wear ability, improved processing during manufacturing stage improved softness. So, you can see all of these are related to the surface modification that is possible through these copolymeric systems.

So, individually of course, silicones are popular individually polyether also have their own applications, but when we combine these 2 in a copolymer form, they open up a new vista of applications in terms of surface modification.

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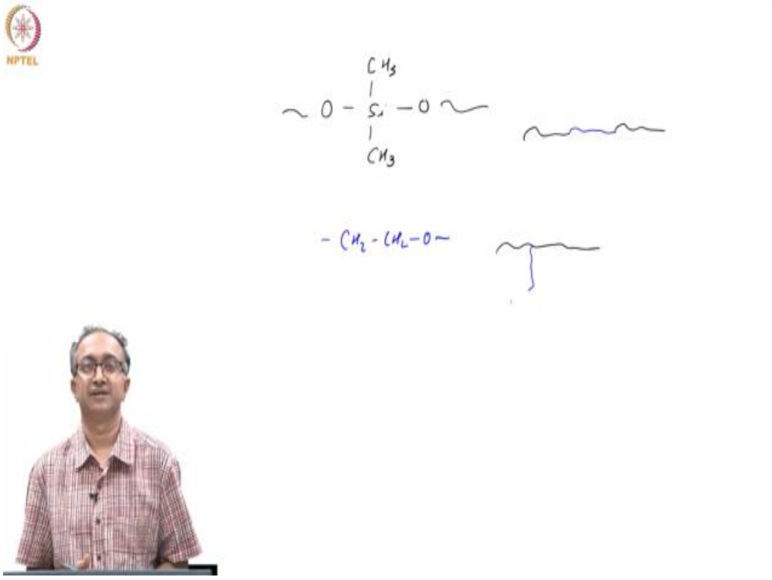

So, having seen the overall applications of this system, I can just quickly look at how the 2 systems are and this is the silicon entity and then we also have the ether entity. Polyethylene oxide or also polyethylene glycol, and now, these 2 have to be combined together. So, we could do combination as part of the backbone itself, where we have some blocks of silicone and some blocks of polyether.

We could also have an option where commercial systems are available, where the polyether is added as a side chain and by doing these things, you can see that how you can get an amphiphilic molecule which means with both hydrophilic hydrophobic characteristics, and it can be beautifully exploited as a surface active agent.

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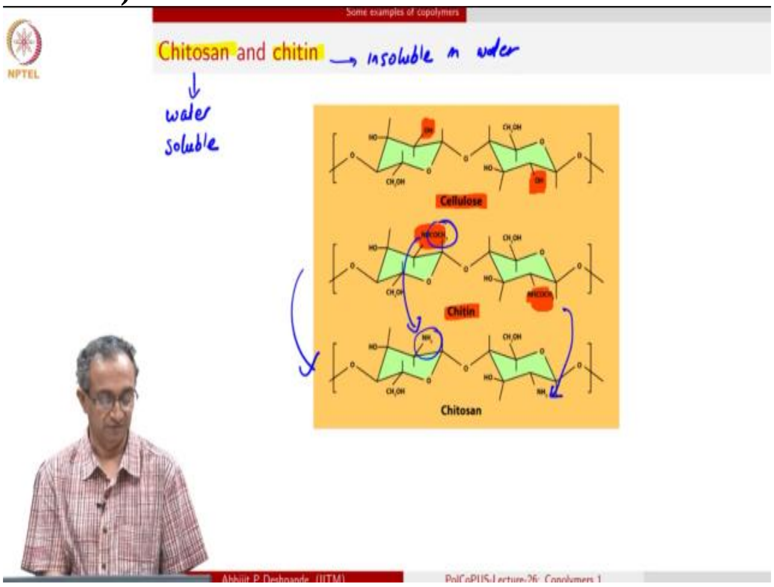

Some examples of copolymers

Chitosan and chitin → insoluble in water

↓ water soluble

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The other example that I want to give you is related to natural biopolymer and chitin is of animal origin and it is a very hardy polymer with very strong mechanical properties and hydrogen bonding and we can modify it by modifying a group on the chitin molecule and then it becomes water soluble. So chitosan for example, is therefore hydrophilic and water soluble. And again, chitin is insoluble in water.

So, you can again see that what we are exploiting in these copolymers is different molecular interactions. Therefore, we get a macro molecule with different properties. And then the arrangement of how these different macro molecular segments can organize with respect to each other gives us excellent mechanical or other properties. And just to highlight how small modifications to group can make huge difference in terms of interactions and therefore, the organizing ability of the macromolecule, look at here cellulose and chitin.

So, both of them are very similar, except the hydroxyl groups is different in compared to chitin and this is the group which is modified to amine group when we carry out a transformation from chitin to chitosan and because of this amine group hydrophilicity is present while in this case, because of the organic moiety the hydrophobicity is stronger. So, now, instead of doing this conversion for each and every repeating unit, if we do it selectively, then essentially we have effectively a copolymer of chitin and chitosan.

And by doing effective amount of this transformation to amine I can get it more hydrophilic or less hydrophilic. And therefore, what this allows me to do is basically get a variety of engineering materials by suitable tuning of the chemistry that I am carrying out to carry this transformation, I can get a controlled amount of hydrophilicity or hydrophobicity on a polymer chain and therefore chitosan with these different degree of modifications is being thought of as an applications in biomedical and variety of applications wherever we can exploit such complex characteristics of these molecular systems.

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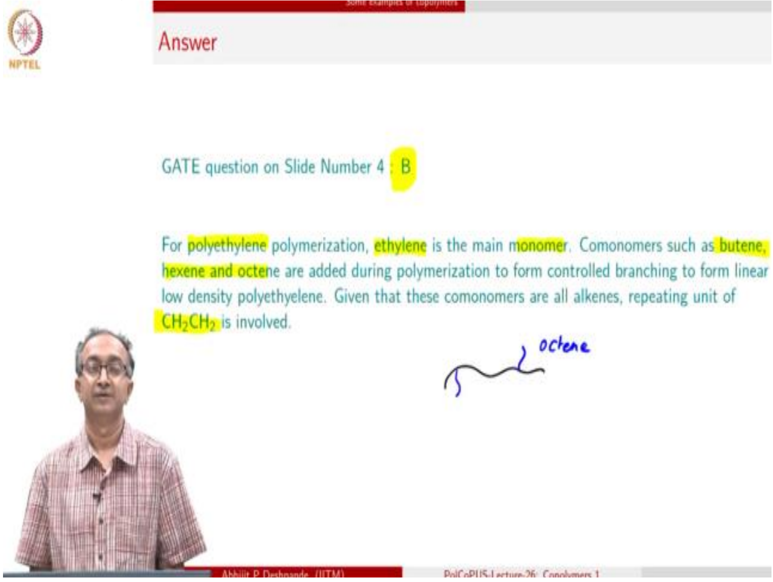

Some Examples of Copolymers

Answer

GATE question on Slide Number 4 : B

For polyethylene polymerization, ethylene is the main monomer. Comonomers such as butene, hexene and octene are added during polymerization to form controlled branching to form linear low density polyethyelene. Given that these comonomers are all alkenes, repeating unit of CH_2CH_2 is involved.

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So, with this, we will close this lecture on some examples of commercially interest copolymer systems. And you might have guessed that for polyethylene, ethylene is of course, the monomer. But if you want to control the branching, then we actually use a co monomer and these co monomers also have the same CH 2 CH 2 repeating unit. So, once the polymerization is done and let us say octene gets attached to a backbone chain, so what we will have is the polyethylene backbone and then on which octene is attached.

So therefore, if you look at the repeating units are still CH 2 CH 2, but it is in fact it is a copolymerization that has been effected to arrive at control level of branching. Thank you.