Membrane Technology
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Lecture No 3
Polymer Basics, Polymers used in Membrane Preparation and their Properties

Good morning, students. Today the lecture 3 of module 1. In today's lecture will cover basics of polymers than polymers used in membrane preparation.

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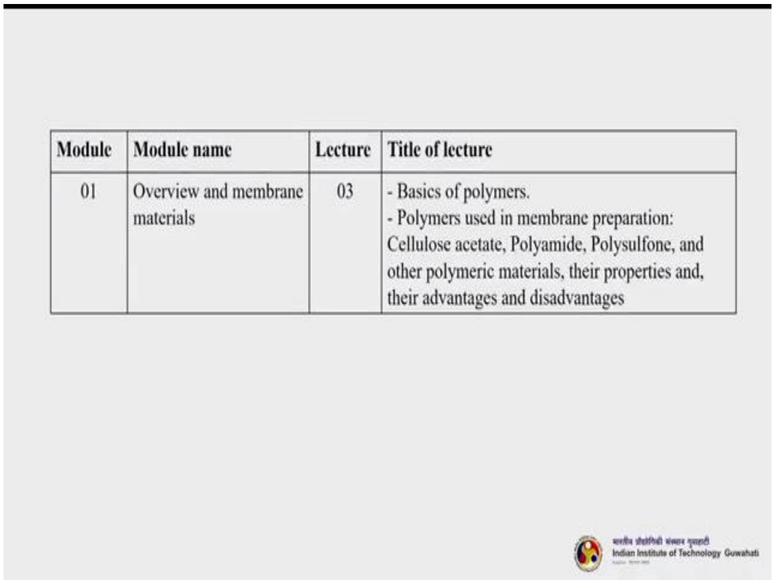

Module	Module name	Lecture	Title of lecture
01	Overview and membrane materials	03	- Basics of polymers. - Polymers used in membrane preparation: Cellulose acetate, Polyamide, Polysulfone, and other polymeric materials, their properties and, their advantages and disadvantages

And few polymers will discuss, which are the most widely used in industries to prepare polymeric membranes, such as cellulose acetate, polyamide. polysulfone, and other polymeric materials that will try to understand their basic properties, advantages and disadvantages of using such polymers, for membrane and preparation. So, why I'm trying to cover polymers, basics of polymers.

Is that one need to understand the various properties of the polymers how the polymers, actually manufacture, what is their source, what are their different advantages and disadvantages, so that when somebody. Try to prepare a membrane in a lab scale. Using polymeric materials, this knowledge will help you to understand and to fix the which polymer to be utilized for preparing a particular membrane for a particular targeted desert separation of course.

So, more than 130 materials have been identified to lead to prepare members. However, only very few have a to commercial status and lesser than that have obtained a regulatory approval for using food, pharmaceutical and other Kindred applications. Now the reason is that most of the polymers have their diverse among even white to talk about polymers, today's lecture, of course, we're talking about polymers.

Next lecture will cover our inorganic ceramic materials. So let us restrict our discussion to polymers.

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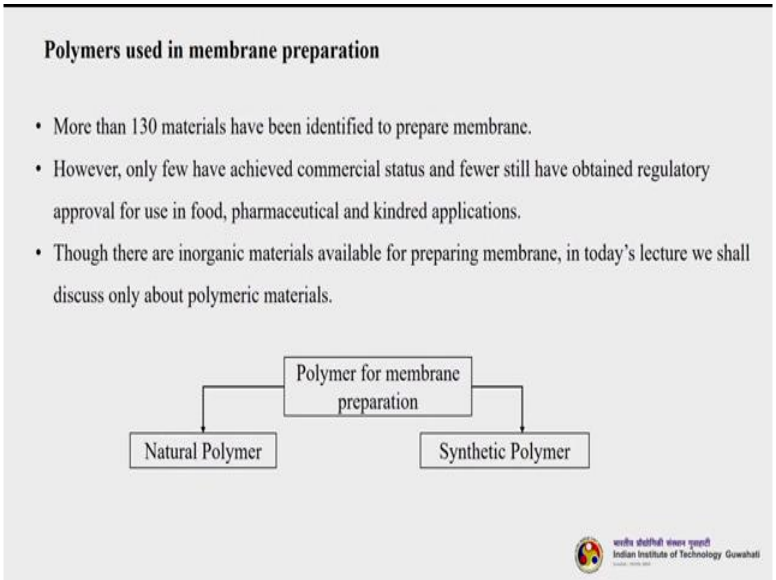

Polymers used in membrane preparation

- More than 130 materials have been identified to prepare membrane.
- However, only few have achieved commercial status and fewer still have obtained regulatory approval for use in food, pharmaceutical and kindred applications.
- Though there are inorganic materials available for preparing membrane, in today's lecture we shall discuss only about polymeric materials.

So, I was telling that why only very few were used commercially, and only very few has obtained regulatory approval. The reason is that every polymer is very unique by nature of their inherent properties. So, to suit a particular application, one particular polymer properties has to meet the standards of the separation which you want to actually use. So there are inorganic materials also preparing member and.

So, today's lecture as I told you will only focus about polymeric materials. So there are two types of different polymers take this one is natural polymer and other is synthetic Polymer. So we will discuss about

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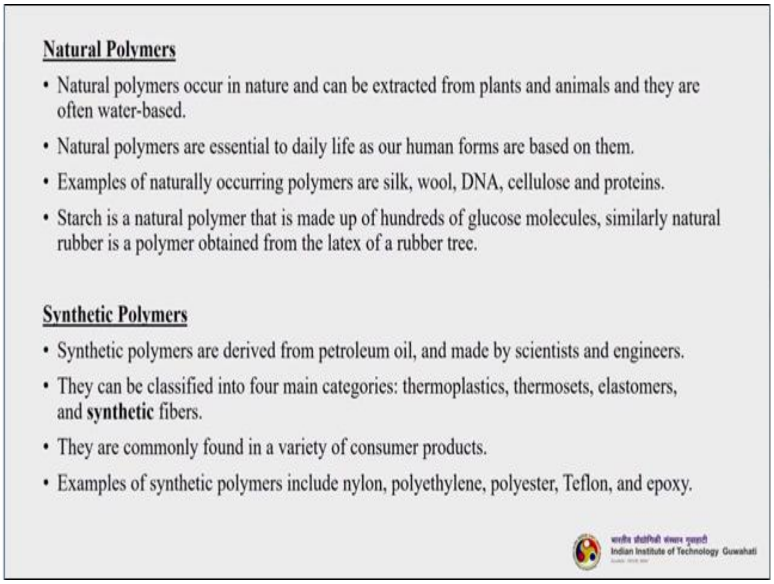

Natural Polymers

- Natural polymers occur in nature and can be extracted from plants and animals and they are often water-based.
- Natural polymers are essential to daily life as our human forms are based on them.
- Examples of naturally occurring polymers are silk, wool, DNA, cellulose and proteins.
- Starch is a natural polymer that is made up of hundreds of glucose molecules, similarly natural rubber is a polymer obtained from the latex of a rubber tree.

Synthetic Polymers

- Synthetic polymers are derived from petroleum oil, and made by scientists and engineers.
- They can be classified into four main categories: thermoplastics, thermosets, elastomers, and **synthetic** fibers.
- They are commonly found in a variety of consumer products.
- Examples of synthetic polymers include nylon, polyethylene, polyester, Teflon, and epoxy.

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These things slowly so natural polymers are natural polymers occur in nature, as the name suggests itself, and can be extracted from plants and animals and mostly they're often water based so natural polymers you know they are essential to daily life, as our as our body. Usually, and the human forms all sorts of human and even animal forms are based on them. So some of the examples are silk, wool, DNA ,cellulose and proteins.

So starch is a natural polymer that is made up of 100’s of glucose molecules. Similarly natural rubber is a polymer often from the latex of the rubber tree. You may be aware that rubber is also made synthetically. So, Then synthetic polymer synthetic polymers are derived from petroleum oil and made by scientists and engineers, so they can be classified into four different categories.

So, thermoplastics thermo sets elastomers and synthetic fibers. So they are commonly found in a variety of consumer products and use them in our daily life everyday. Examples are nylon polyethylene, polyester, Teflon and epoxy.

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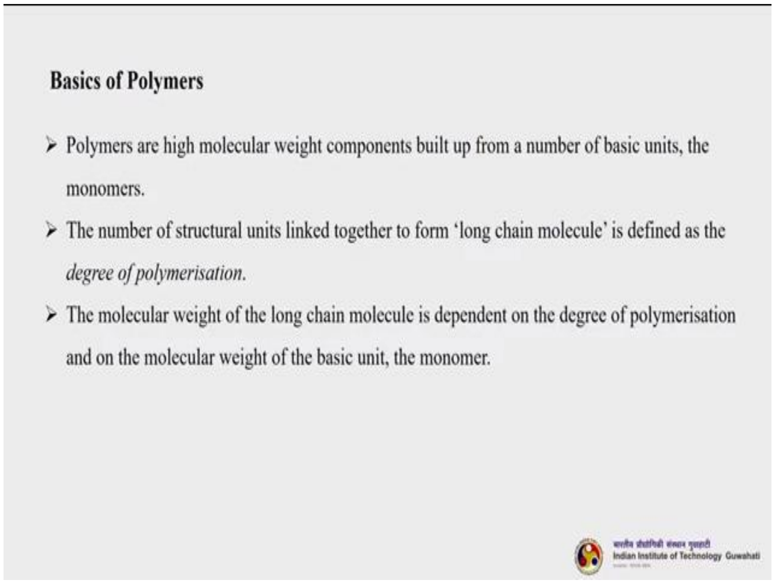

Basics of Polymers

- Polymers are high molecular weight components built up from a number of basic units, the monomers.
- The number of structural units linked together to form 'long chain molecule' is defined as the *degree of polymerisation.*
- The molecular weight of the long chain molecule is dependent on the degree of polymerisation and on the molecular weight of the basic unit, the monomer.

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So let us discuss some of the basics of the polymers. So, polymers are high molecular weight components, built up from a number of basic units the monomers, the number of structural units linked together to form a long chain molecule is defined as the degree of polymerization, the molecular weight of long chain molecule is dependent on the degree of polymerization, and under molecular weight of the basic unit that is the monomer.

So, in a nutshell we can understand that when several monomers joined together, it becomes a polymer. Of course, how they join how they use each other, whether it's a single monomer, There are different types of monomer that are fused together to get a polymer. So these are, of course, different issues to be addressed and dealt differently.

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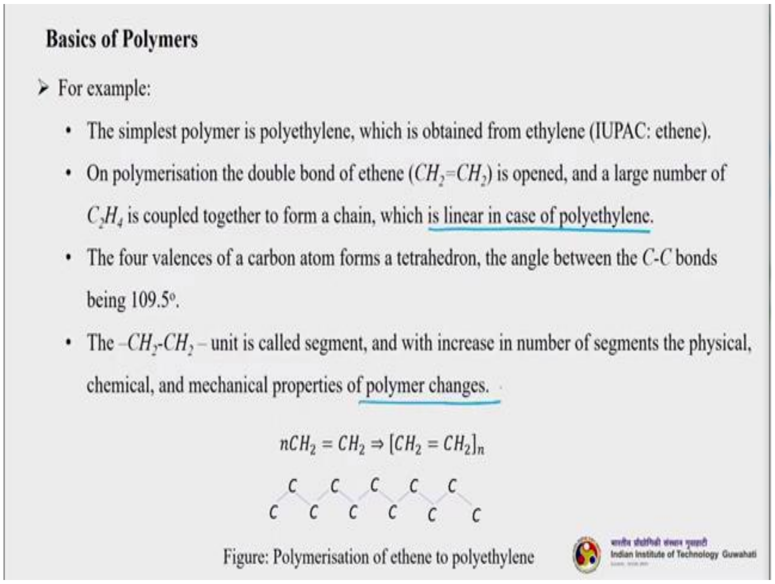

Basics of Polymers

- For example:
  - The simplest polymer is polyethylene, which is obtained from ethylene (IUPAC: ethene).
  - On polymerisation the double bond of ethene (CH_2=CH_2) is opened, and a large number of C_2H_4 is coupled together to form a chain, which is linear in case of polyethylene.
  - The four valences of a carbon atom forms a tetrahedron, the angle between the C-C bonds being 109.5°.
  - The $-CH_2$-CH_2- unit is called segment, and with increase in number of segments the physical, chemical, and mechanical properties of polymer changes.

$$nCH_2 = CH_2 \Rightarrow [CH_2 = CH_2]_n$$

Figure: Polymerisation of ethene to polyethylene

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So, for example the simplest polymer is polyethylene so all of us knows this and we use it in our everyday life. So, which is obtained from the ethylene, or ethane, the IUPC name is actually ethene. So on polymerization that double bond of the ethane that CH2 double bond CH2 is opened up. And the last number of C2H4 is coupled together to form a chain, which is linear in case of a polyethlyne.

So, it is a linear molecule, polyethlyne, and 4 valences of a carbon atom forms a tetrahedron, the angle between the CC bonds is easily 109.5 degree. The CH2 CH2 unit is called the segment, and with increasing number of segments the physical, chemical and mechanical properties of the polymer changes. So when we increase the number of segments, so the properties of the polymer changes.

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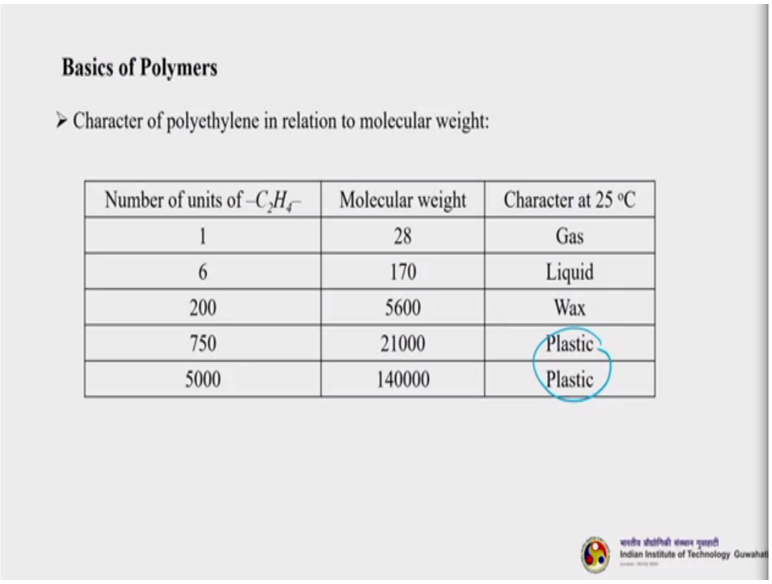

Basics of Polymers

- Character of polyethylene in relation to molecular weight:

Number of units of $-C_2H_4-$	Molecular weight	Character at 25 °C
1	28	Gas
6	170	Liquid
200	5600	Wax
750	21000	Plastic
5000	140000	Plastic

So we will see how it actually. So, let us see this, polyethlyne, when the number of units is only 1 its molecular weight is 28, and the characters. Each characteristic features at 25 degrees, behaves as gas when we increase the number of units to 6, the molecular rate increases to 170, and it behaves as liquid quarter when we increase the number of pennies to 200.

So the molecular weight jumps to 5600, and its characteristics features becomes like wax them again we increase to 750 or 5000 or, more than that. So their molecular weight, just keep on increasing okay and they become plastics. So as you can understand from this particular table. When the number of units are increasing the number of units per particular polymer, so their molecular weight is increasing.

As well as their properties are also changing. So from gas to liquid, liquid to wax, and then wax to plastic.

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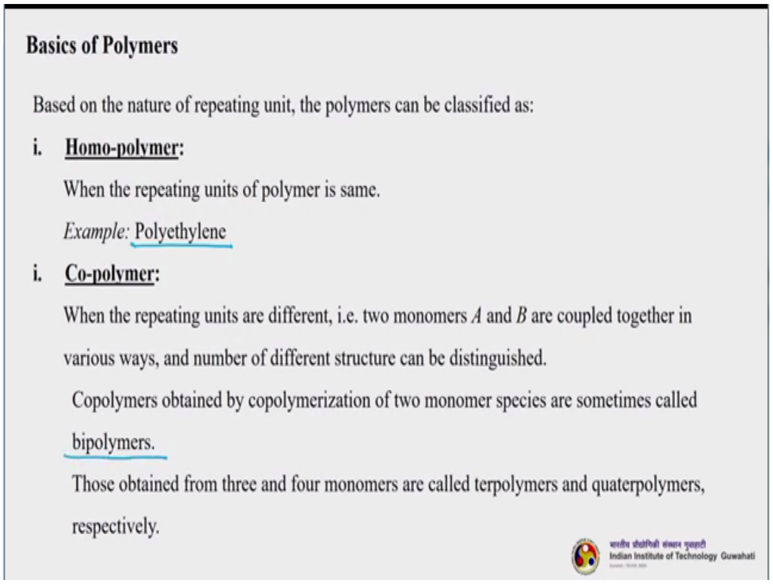

Basics of Polymers

Based on the nature of repeating unit, the polymers can be classified as:

i. **Homo-polymer:**

When the repeating units of polymer is same.

Example: Polyethylene

i. **Co-polymer:**

When the repeating units are different, i.e. two monomers *A* and *B* are coupled together in various ways, and number of different structure can be distinguished.

Copolymers obtained by copolymerization of two monomer species are sometimes called bipolymers.

Those obtained from three and four monomers are called terpolymers and quaterpolymers, respectively.

So, based on the nature of repeating unit polymers can be classified as homo polymer and co-polymer. So, when repeating units of the polymer of same, then it is the homo polymer so polyethylene is the best example of this thing. So, all the monomers of the same nature are and origin. So co-polymer when the repeating units are different. So that means two more monomers.

A and B are coupled together in various ways, and number of different structure can be distinguished so co polymers are often by co polymerization of two monomers spieces are sometimes called biopolymers. When the monomers species are two. So those obtained from 3 or 4 1 numbers are called terpolymers and quarterpolymers, respectively.

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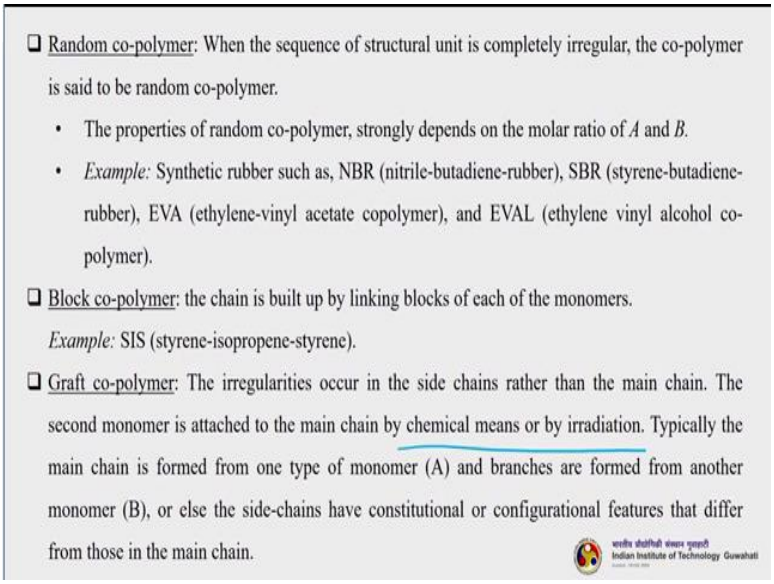

- ☐ Random co-polymer: When the sequence of structural unit is completely irregular, the co-polymer is said to be random co-polymer.
  - The properties of random co-polymer, strongly depends on the molar ratio of *A* and *B*.
  - *Example:* Synthetic rubber such as, NBR (nitrile-butadiene-rubber), SBR (styrene-butadiene-rubber), EVA (ethylene-vinyl acetate copolymer), and EVAL (ethylene vinyl alcohol co-polymer).
- ☐ Block co-polymer: the chain is built up by linking blocks of each of the monomers.
  Example: SIS (styrene-isopropene-styrene).
- ☐ Graft co-polymer: The irregularities occur in the side chains rather than the main chain. The second monomer is attached to the main chain by chemical means or by irradiation. Typically the main chain is formed from one type of monomer (A) and branches are formed from another monomer (B), or else the side-chains have constitutional or configurational features that differ from those in the main chain.

There are different types of copolymer suggest. The first one is random co-polymer, the second one is block co-polymer. And the third one is graft co-polymer. So what is random copolymer? So when the sequence of structural unit is completely irregular. The co-polymer he said to me random co-polymer. So the properties of random co-polymer strongly depends on the molar ratio both the monomer units A and B.

So, a classic example is the synthetic rubber, which is NBR the nitrile-butadine-rubber or SBR styrene-butadiene-rubber EVA ethlyne-vinyl acetate co-polymer or EVAL ethylene vinyl alchohol co-polymer. So, the next type of co-polymer is a Block co-polymer, here the chain is built up by linking blocks of each of the monomers. So one example is SIS which is styrene-isopropene-styrene.

So, the next is graft co-polymer here, the irregularities occur in the side chain rather than the main chain. So the second monomer is attached to the mentioned by chemical means, or irradiation. So, typically the main chain is formed from one of the monomer and branches or from from another monomer. And the side or else the side himself constitutional or configurational features that differ from those in the main chain. So basically two different nature of monomers are fused together to get a graft co-polymer.

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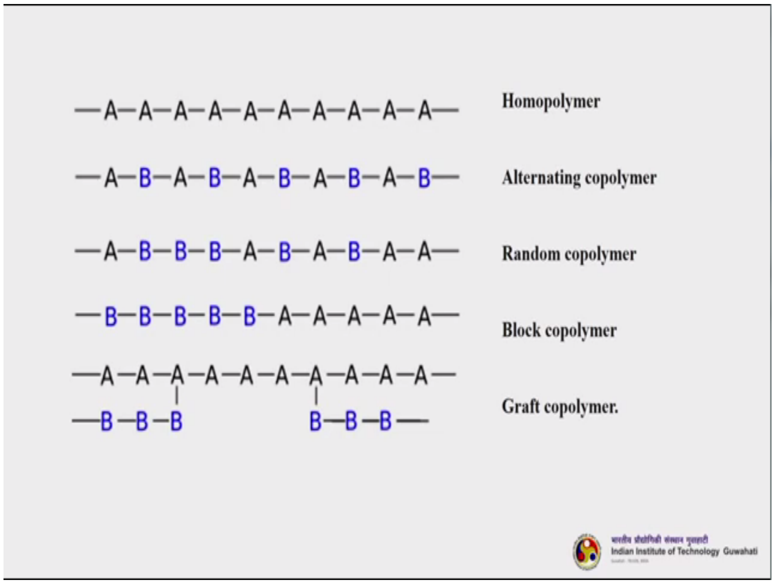

—A—A—A—A—A—A—A—A—A—A— Homopolymer

—A—B—A—B—A—B—A—B—A—B— Alternating copolymer

—A—B—B—B—A—B—A—B—A—A— Random copolymer

—B—B—B—B—B—A—A—A—A—A— Block copolymer

—A—A—A—A—A—A—A—A—A—A—
—B—B—B B—B—B—
Graft copolymer.

So, let us have a look to this particular image, where you can see that the different structures of polymers. So the homo polymer you can see the only single monomer type or that single, single type of monomer. In alternating co-polymer. So we have one type of monomer which is A, followed by a different type of monomer which is B. Then again, A again B. So it goes in in a sequence. So it is a random cooperation.

So, A and B are fused to get them randomly, so there is no particular sequence that is followed here in this particular case you can see there are five monomers of B fused together, followed by 5 monomers of A. So, again this sequence will repeat so this is called block co-polymer, and in graft polymer, you can see the two different types of monomers are fused together. How about they are joined by grafting. So here, the B monomers are grafted. Okay, to the monomeric chain of A

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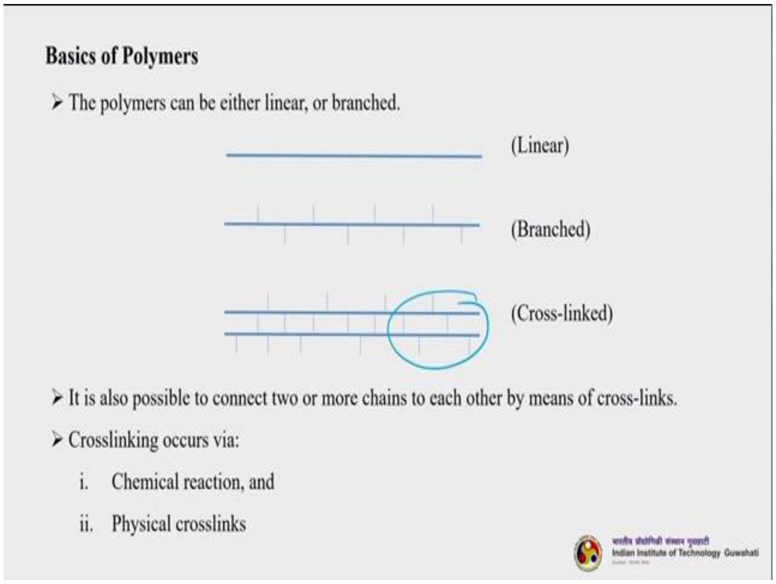

Basics of Polymers

- The polymers can be either linear, or branched.

- It is also possible to connect two or more chains to each other by means of cross-links.
- Crosslinking occurs via:
  i. Chemical reaction, and
  ii. Physical crosslinks

So the polymers can be either linear, or they can be branched the linear looks something like this. And if it is branched, then they can be grafted to both me any one of the side of the monomeric chain. And when it is crosslinkd. So the structures look something like this. It is also possible to connect two or more chains to each other by means of cross linking so cross linking of course by two methods. One by chemical reaction, another by physical cross linking

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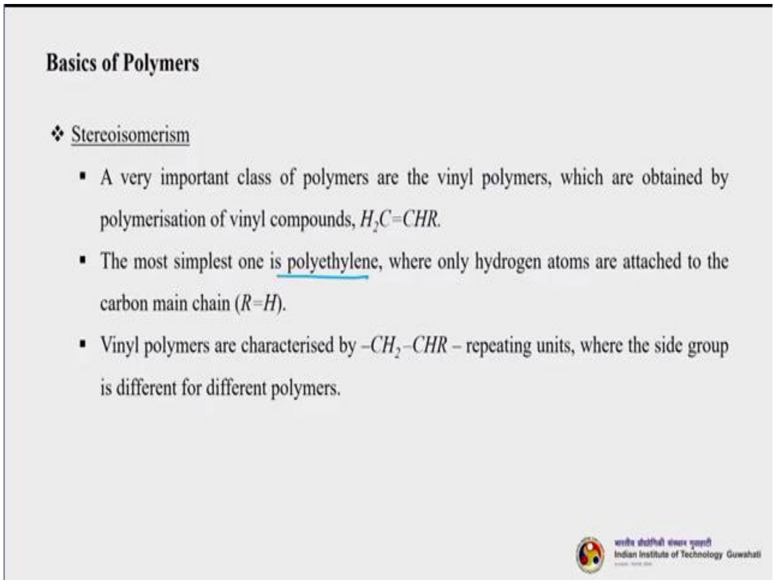

Basics of Polymers

- Stereoisomerism
  - A very important class of polymers are the vinyl polymers, which are obtained by polymerisation of vinyl compounds, $H_2C{=}CHR$.
  - The most simplest one is polyethylene, where only hydrogen atoms are attached to the carbon main chain ($R{=}H$).
  - Vinyl polymers are characterised by $-CH_2-CHR-$ repeating units, where the side group is different for different polymers.

Will discuss little more about the basics of polymers. So, let us understand what is stereoisomerisam. So a very important class of polymers are vinyl polymers, which are obtained by polymerization of vinyl components that is CH2 CHR. the most simplest one is polyethylene.

Okay, were only hydrogen atoms of carbon main chain. So vinyl polymers are characterized by CH2 CHR repeating units. We have the side group is different from the different polymers.

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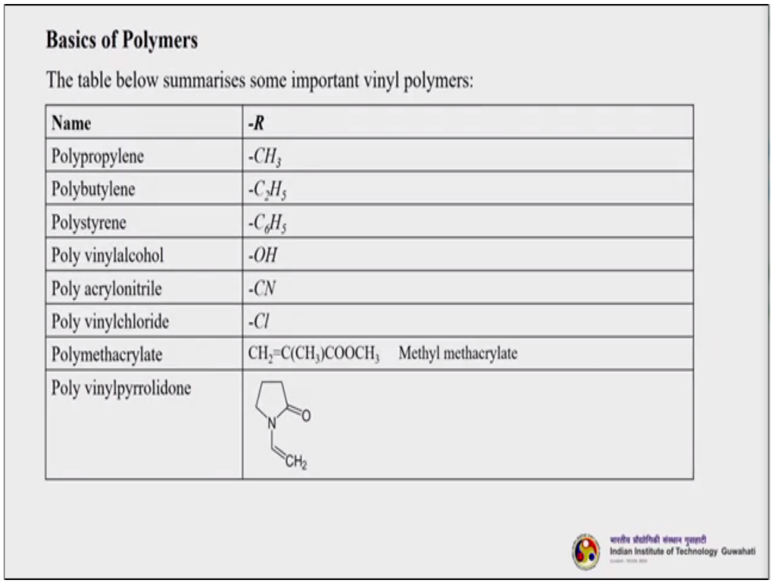

Basics of Polymers

The table below summarises some important vinyl polymers:

Name	***-R***
Polypropylene	$-CH_3$
Polybutylene	$-C_2H_5$
Polystyrene	$-C_6H_5$
Poly vinylalcohol	$-OH$
Poly acrylonitrile	$-CN$
Poly vinylchloride	$-Cl$
Polymethacrylate	$CH_2=C(CH_3)COOCH_3$ Methyl methacrylate
Poly vinylpyrrolidone	

Let us look at this table, this is telling us about different vinyl polymers. So, polypropylene. The R group is CH3 poly butylene the R group is C 2H5 for polystyrene. It is C6H5 imilarly for poly vinylalcohol it is OH for vinylchloride it is CL so polymethacrylate it is CH2 this is C CH3 COOCH3, which is methyl methacrylate. Okay for polyvinylpyrrolidone this is the repeating unit.

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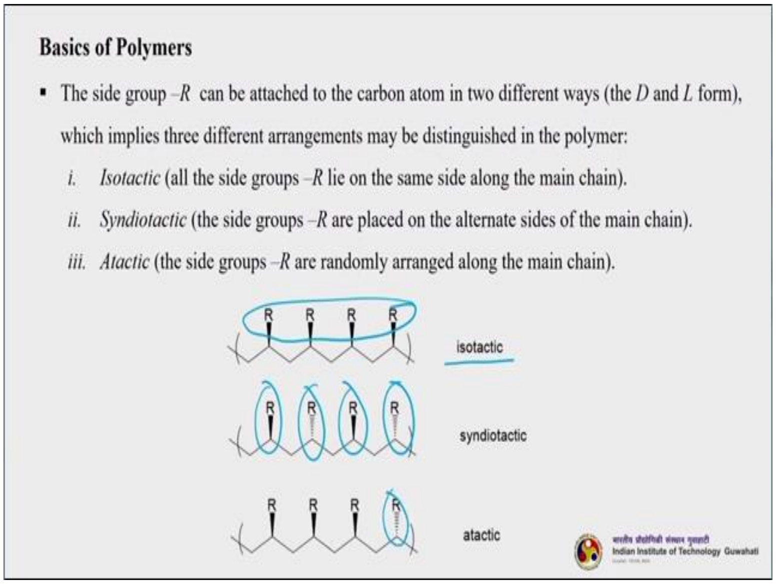

Basics of Polymers

- The side group *–R* can be attached to the carbon atom in two different ways (the *D* and *L* form), which implies three different arrangements may be distinguished in the polymer:
  - *i.* *Isotactic* (all the side groups *–R* lie on the same side along the main chain).
  - *ii.* *Syndiotactic* (the side groups *–R* are placed on the alternate sides of the main chain).
  - *iii.* *Atactic* (the side groups *–R* are randomly arranged along the main chain).

So, the side group R can be attached to the carbon atom in two different ways, either in the form of D or L form. So, you can read little more about this verse six from any polymer textbook. And here we will just, I'm trying to just give you a little understanding about the six fundamental of polymers, then we will quickly move to different types of polymers which are utilized for the preparation of membranes.

So, three different elements may be distinguished in the Polymer. So the first is called isostatic. The second one is syndiotactic. And the third one is called atactic. So what is isostatic. So here all the side groups are lie on the same side of the main cha, you can see all the R’s are lying on the same side of the main chain. Nothing is lying here on the bottom side so this is a certainty in syndiotactic that R groups are placed on the alternate sides of the main chan.

So one, one here, followed by one here. Okay, then one here, again, followed by one here so this is alternate arrangements. And in atactic, the side groups are randomly arranged along the main chain. So there is actually no proper sequencing polar. So you can see here the three arragments followed by another one. So it can be anything so it is basically random, they don't follow any proper sequence.

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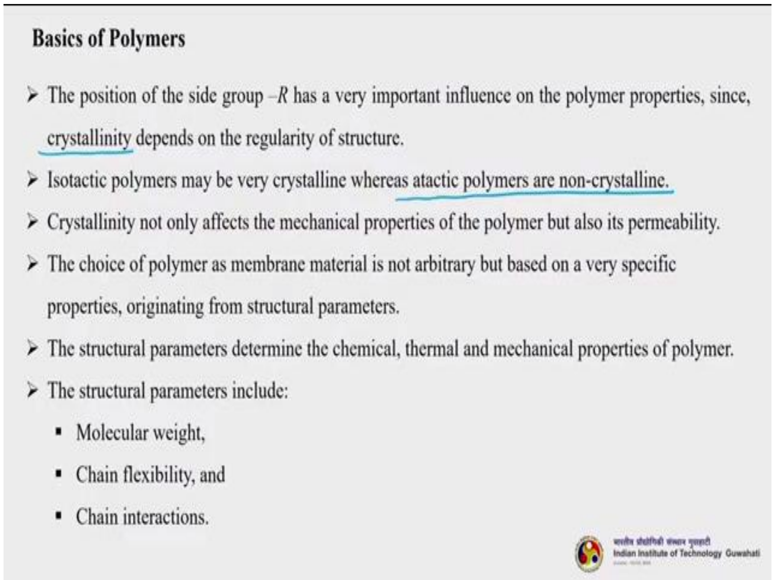

Basics of Polymers

- The position of the side group –*R* has a very important influence on the polymer properties, since, crystallinity depends on the regularity of structure.
- Isotactic polymers may be very crystalline whereas atactic polymers are non-crystalline.
- Crystallinity not only affects the mechanical properties of the polymer but also its permeability.
- The choice of polymer as membrane material is not arbitrary but based on a very specific properties, originating from structural parameters.
- The structural parameters determine the chemical, thermal and mechanical properties of polymer.
- The structural parameters include:
  - Molecular weight,
  - Chain flexibility, and
  - Chain interactions.

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So the position of the side group -R has a very important influence on the polymer properties, since crystallinity and it depends on the regularity of structure. So, Crystallinity It is a very important feature of the polymers, isotactic polymers may be very crystallines whereas atactic polymers are non crystalline and so most of them atactic polymers are non crystalline. So crystallinity not only affects the mechanical properties of the polymer, but also aperitifs permeability.

As you know, the permeability is one of the most important feature of the membranes. So crystallinity, and permeability both are very important for polymeric material. So the choice of polymers, as membrane material is not arbitrary but based on a very specific properties are originating from the structural parameters. So that is what I was telling in the beginning of the class that which polymer to be the chooser.

Or a particular separatism or a particular targeted application. It is to be decided based on so many things first is you are going to separate the solute physically or the solvent, and what type of membrane material, you will decide, so that there will be more interaction between the membrane and the solute or solvent that is going to be separated and how the properties of the membrane will affect the separation.

So that is why we're trying to understand the deeper properties of the different polymeric materials, and in the next class will understand the properties of the ceramic materials. So the structural parameters determine the chemical thermal and mechanical properties of polymer structural parameters or molecular weight, chain flexibility and chain interactions, this three.

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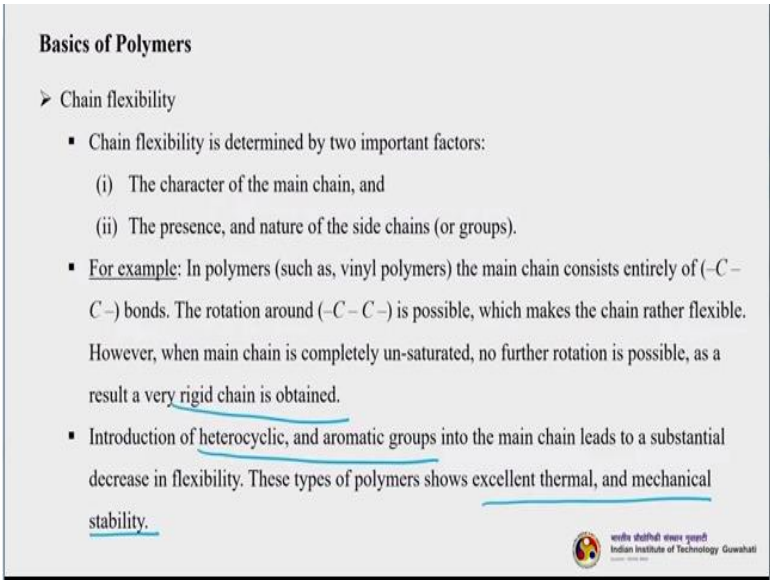

Basics of Polymers

- Chain flexibility
  - Chain flexibility is determined by two important factors:
    - (i) The character of the main chain, and
    - (ii) The presence, and nature of the side chains (or groups).
  - For example: In polymers (such as, vinyl polymers) the main chain consists entirely of $(-C-C-)$ bonds. The rotation around $(-C-C-)$ is possible, which makes the chain rather flexible. However, when main chain is completely un-saturated, no further rotation is possible, as a result a very rigid chain is obtained.
  - Introduction of heterocyclic, and aromatic groups into the main chain leads to a substantial decrease in flexibility. These types of polymers shows excellent thermal, and mechanical stability.

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Let us Understand production flexibility. So chain flexibility is determined by two important factors. The first one is the character of the mentioned, the second one is the presence and the nature of the side chain so group so basically two things. The first one the, first monomer. The main, which consists of the main chain, and the second one is the another monomer which we're going to grab.

Or getting cross linked to the main chain, which is called a sides chains basically, for example in polymer such as vinyl polymers. The main chain consistent entirely of C C bonds. Okay, the rotation arround CC is possible, which makes the chain rather that flexible. However, when main chain its completely un saturated, no further the rotation is possible. As a result a very rigid chain is obtaind, when the rotation is possible.

The chain becomes flexible, rotation of CC bond. When the main chain becomes completely unsaturated so no more rotation can be possible, so as a result very rigid structure is often so introduction of heterocyclic and aromatic groups into the mentioned list a substantial decrease in flexibility. So how you increase the flexibility of the particular polymer so you can introduce some of heterocyclic or aromatic groups to the main chain.

So the degree of flexibility increases. So this type of polymer so excellent thermal and mechanical stability. For certain, a membrane in America, you need to have excellent thermal and mechanical stability. Okay, support this, you can imagine some of the heterocyclic and getting close to the main chain. So it is to increase the flexibility,

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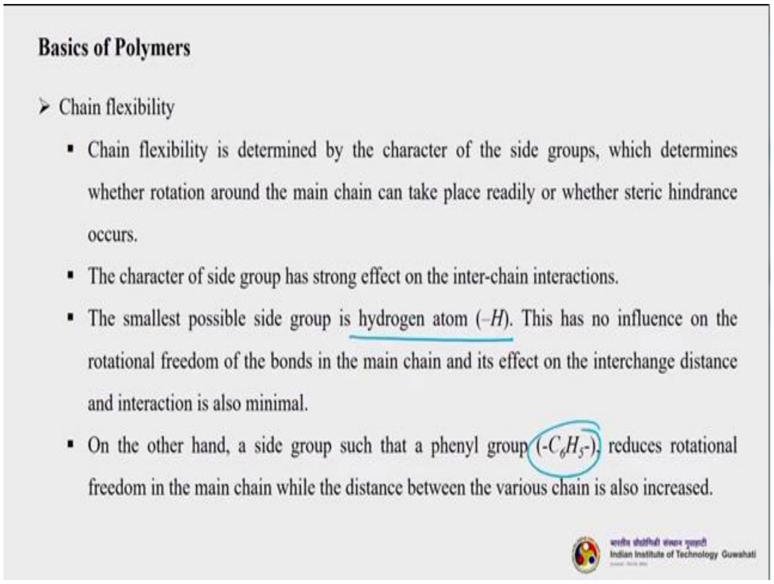

Basics of Polymers

➢ Chain flexibility

- Chain flexibility is determined by the character of the side groups, which determines whether rotation around the main chain can take place readily or whether steric hindrance occurs.
- The character of side group has strong effect on the inter-chain interactions.
- The smallest possible side group is hydrogen atom ($-H$). This has no influence on the rotational freedom of the bonds in the main chain and its effect on the interchange distance and interaction is also minimal.
- On the other hand, a side group such that a phenyl group ($-C_6H_5-$), reduces rotational freedom in the main chain while the distance between the various chain is also increased.

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So chain flexibility is determined by the character of the side groups, which determines wether rotation around the main chain can take place readly or whether steric hindrance occures, so the side chain actually deciding whether rotation is possible or not. The character of the side group is strong effect on the inter chain interactions. The smallest possible side group is the hydrogen atom. the hydrogen, is the smallest possible size group that can be imparted to the main chain.

So this is no influence in the rotational freedom of the bonds in the main chain, and it depends on the interchange distance and interaction is also very very minimal. So, on the other hand, if there is a phenyl group C6H5 then it reduces the rotational freedom of the main chain, while the distance between the various chain is also increased. So the next parameter is molecular weight.

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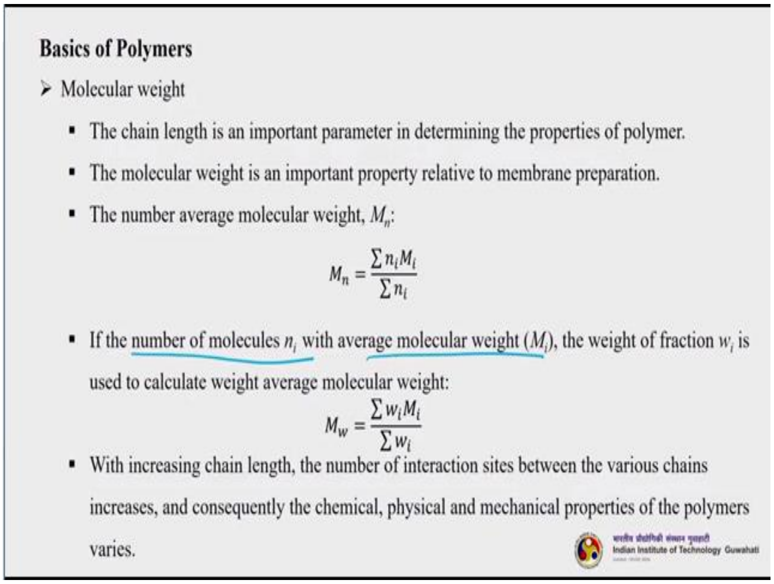

Basics of Polymers

- Molecular weight
  - The chain length is an important parameter in determining the properties of polymer.
  - The molecular weight is an important property relative to membrane preparation.
  - The number average molecular weight, M_n:

$$M_n = \frac{\sum n_i M_i}{\sum n_i}$$

  - If the number of molecules n_i with average molecular weight (M_i), the weight of fraction w_i is used to calculate weight average molecular weight:

$$M_w = \frac{\sum w_i M_i}{\sum w_i}$$

  - With increasing chain length, the number of interaction sites between the various chains increases, and consequently the chemical, physical and mechanical properties of the polymers varies.

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So the chain length is an important parameter in determining the properties of a polymer, the molecular weight is an important property relative to membrane preparation, the membrane molecular weight is given by Mn = ni summation of niMi/ summation of ni . So ni is the number of molecules, with the average molecular weight. Mi the weight of fraction wi is used to calculate the average molecular weight.

So molecular weight is the summation of wiMi/ summation of wi. So with increasing chain length and number of interaction sides between various chains increases, and consequently the chemical, physical and mechanical properties of the polyworks varies, so this would have seen in one of the table when I was showing you. When the chain numbers increases when the number of units increases, how the properties and the molecular weights are different.

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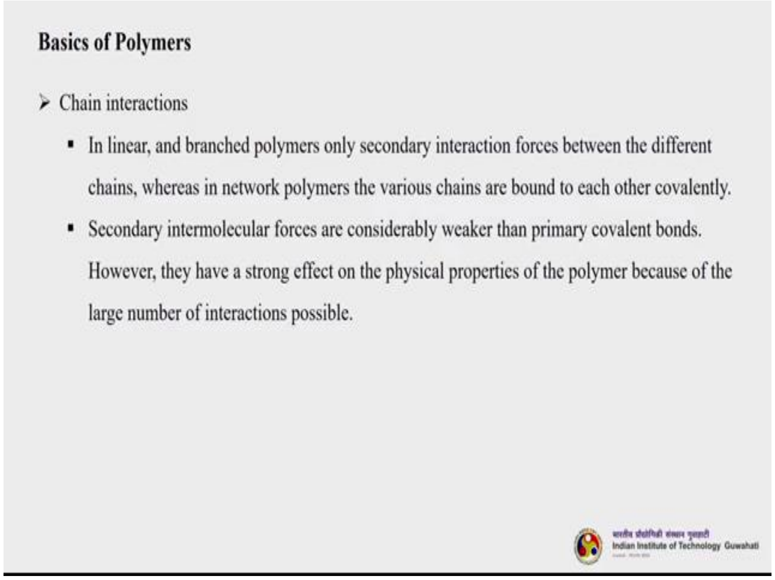

Basics of Polymers

- Chain interactions
  - In linear, and branched polymers only secondary interaction forces between the different chains, whereas in network polymers the various chains are bound to each other covalently.
  - Secondary intermolecular forces are considerably weaker than primary covalent bonds. However, they have a strong effect on the physical properties of the polymer because of the large number of interactions possible.

So, in linear and branched polymers only secondary interaction forces between the different chain lengths exist, whereas in network polymers the various chain lengths are bound to each other covalently secondary intermolecular forces are considerably weaker than the primary coven and opponents, however they have a strong effect on the physical properties of the polymer because of the last number of interactions that is actually possible.

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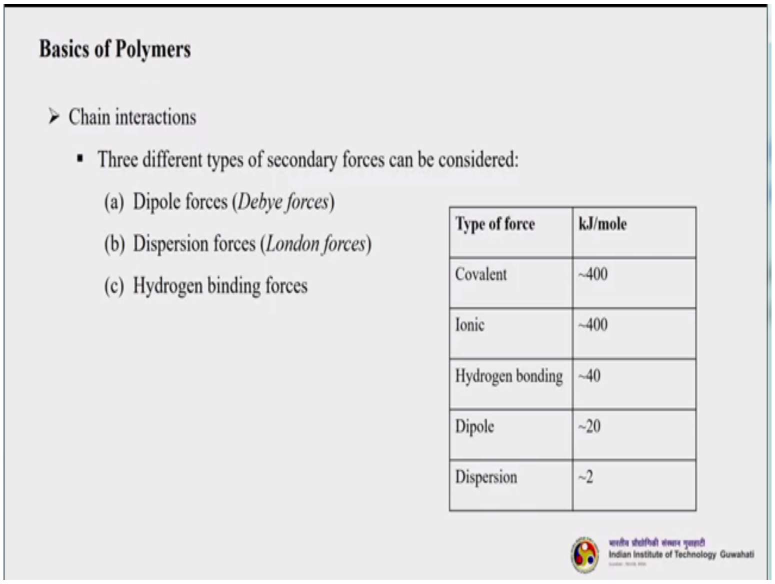

Basics of Polymers

- Chain interactions
  - Three different types of secondary forces can be considered:
    (a) Dipole forces (*Debye forces*)
    (b) Dispersion forces (*London forces*)
    (c) Hydrogen binding forces

Type of force	kJ/mole
Covalent	~400
Ionic	~400
Hydrogen bonding	~40
Dipole	~20
Dispersion	~2

So three types of secondary forces can be considered. The first one is dipole forces which are also called a debye forces. The second one is called dispersion forces, also known as London forces and the third one is the hydrogen binding forces. Here in the table you can see there are different types of forces and their kilojoules per mole is also given the energy so covalent ionic hydrogen bonding dipole and dispersal you can see, currently the strongest in terms of the energy, and dispersion is that smallest.

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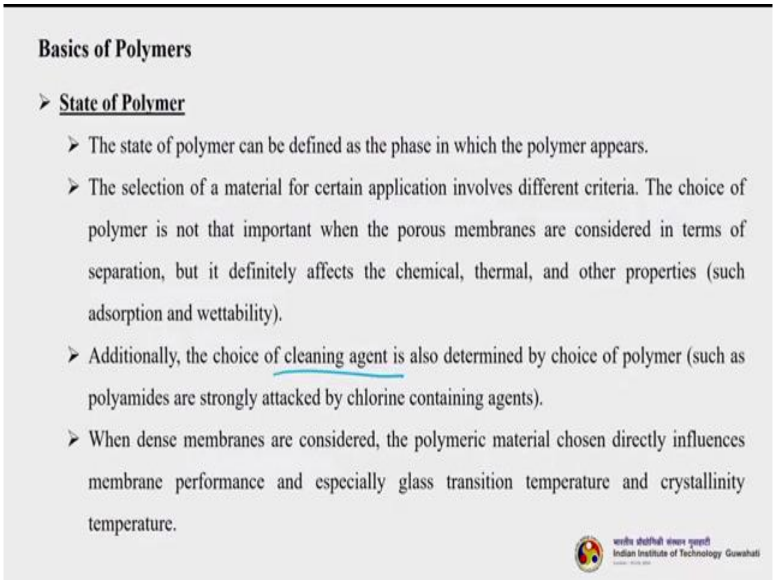

Basics of Polymers

- State of Polymer
  - The state of polymer can be defined as the phase in which the polymer appears.
  - The selection of a material for certain application involves different criteria. The choice of polymer is not that important when the porous membranes are considered in terms of separation, but it definitely affects the chemical, thermal, and other properties (such adsorption and wettability).
  - Additionally, the choice of cleaning agent is also determined by choice of polymer (such as polyamides are strongly attacked by chlorine containing agents).
  - When dense membranes are considered, the polymeric material chosen directly influences membrane performance and especially glass transition temperature and crystallinity temperature.

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So a student let us try to understand what is the state of polymer that the state of polymer can be defined as the phase, in which the polymer appears. The selection of materials for certain application elements different criteria. The choice of polymer is not that important when porous membranes are actually considered in terms of separation but it certainly affects its chemical thermal and other properties such as the absorption and wettability.

Additionally, the choice of cleaning agent is also determined by the choice of Polymer. So what is the meaning of that. So, in one of the classes I told you know, when the controller separation is happening, then the solutes are getting deposited on the surface of the membrane. So when this is increasing the concentration polarization increases, the layer becomes scarce, and some of the solutes gets inside the membrane inputs.

So there by, making two types of fouling possible one is external fouling and internal fouling. So in the membrane gets fouled we need to clean it. So the easiest way of cleaning is by backflushing. So you use water and backflush the membrane, from the back side of the membrane you flush it. So the pores will get clean, but many times it happens there.

And the pores are not getting cleaned, due to strong interaction of the solut molecules, along with the membrane material, so you need to use some organic solvents, some acids dilute a sip some alkalis or some other solvents to clean it. So, these type of solvents mess with their membrane material. So that is why it is very important that the choice of polymer also determines or governs the choice of cleaning agent.

So when dense membranes are considerd the polymeric materials to chain directly influences the membrane performance in a specific glass transition temperature and crysllinity temperature, especially when there are no pores, non porous membranes.

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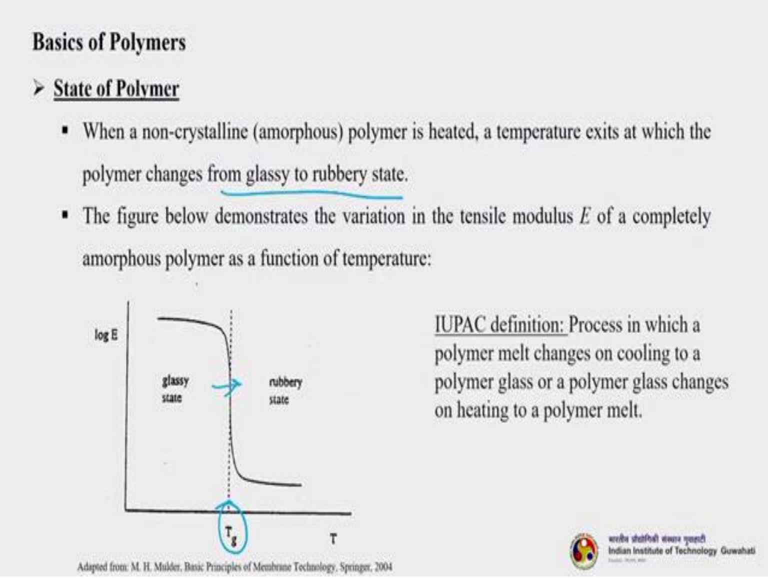

Basics of Polymers

- State of Polymer
  - When a non-crystalline (amorphous) polymer is heated, a temperature exits at which the polymer changes from glassy to rubbery state.
  - The figure below demonstrates the variation in the tensile modulus E of a completely amorphous polymer as a function of temperature:

IUPAC definition: Process in which a polymer melt changes on cooling to a polymer glass or a polymer glass changes on heating to a polymer melt.

Adapted from: M. H. Mulder, Basic Principles of Membrane Technology, Springer, 2004

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So let us understand what is actually here this one, glass transition temperature is. So it is one of the most important properties of the polymeric materials. So in a non crystalline or amorphous polymer is heated, a temperature exist, okay, at which polymer changes from glassy to rubber state. Okay. So the figure below demonstrate the variation in the tensile model E of a completely amorphous polymer as a function of temperature. You can see Tg. Okay.

This is actually the glass transition temperature and glasses states. The change of glass state to rubber state is happening at which temperature is known as the glass transition temperature. So the IUPC definition suggest that the process in which a polymer melt changes from cooling to a polymer glass or a polymer glass changes on heating to a polymer melt.

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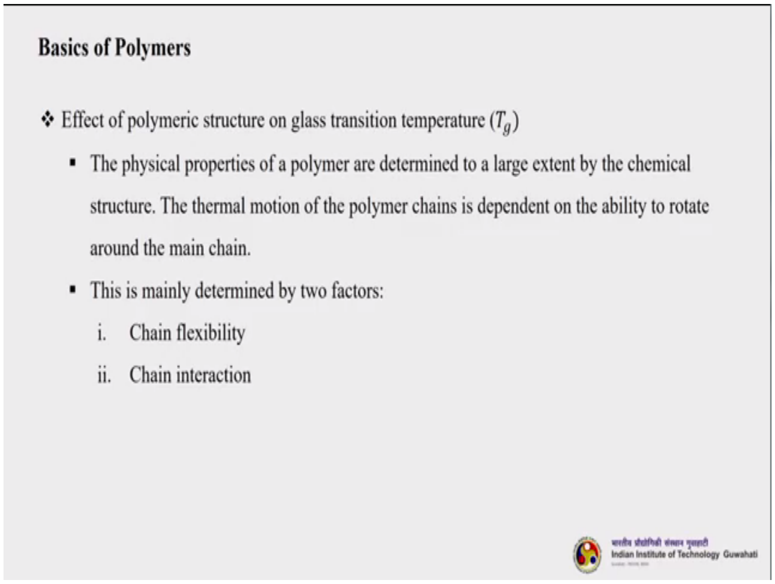

Basics of Polymers

❖ Effect of polymeric structure on glass transition temperature (T_g)
  - The physical properties of a polymer are determined to a large extent by the chemical structure. The thermal motion of the polymer chains is dependent on the ability to rotate around the main chain.
  - This is mainly determined by two factors:
    1. Chain flexibility
    2. Chain interaction

So, effect of polymeric structural glass transition temperature, but the physical properties of the polymer are determined to a large extent by the chemical structure. So the thermal rotate motion of the polymer chance is dependent on the ability to rotate around the main chain. So this is mainly determined by two factors. Chain flexibility and chain interaction.

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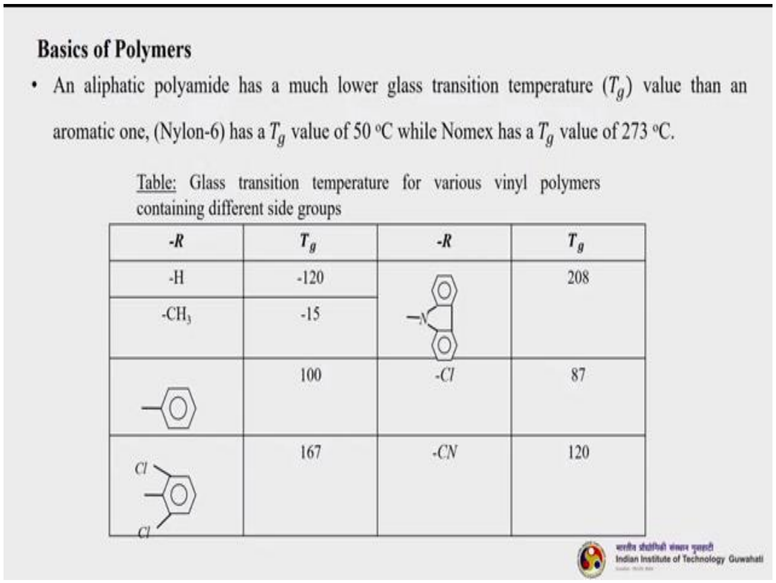

Basics of Polymers

- An aliphatic polyamide has a much lower glass transition temperature (T_g) value than an aromatic one, (Nylon-6) has a T_g value of 50 °C while Nomex has a T_g value of 273 °C.

Table: Glass transition temperature for various vinyl polymers containing different side groups

-R	T_g	-R	T_g
-H	-120		208
$-CH_3$	-15		
	100	-Cl	87
	167	-CN	120

So, an aliphatic polyamide has a much lower glass transition temperature than that of a aromatic one. For example Nylon-6 has a glass transition temperature of 50 degree while Nomex has a temperature of 273 degree centigrade so this table gives the glass transition temperature of various polymers containing different side groups

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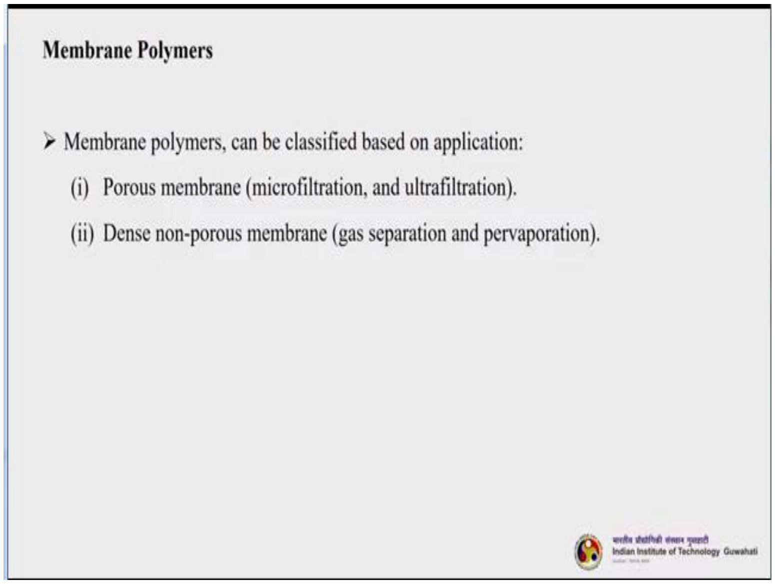

Membrane Polymers

- Membrane polymers, can be classified based on application:
  - (i) Porous membrane (microfiltration, and ultrafiltration).
  - (ii) Dense non-porous membrane (gas separation and pervaporation).

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Now let us discuss about the membrane polymers. So there are two different types of membrane polymers can be classified. One is based on porous membrane structures and other is dense non porous membrane structures. So porous are basically are microfiltration ,ultrafiltration. And non porous is that is used for gas separation and pervaporation.

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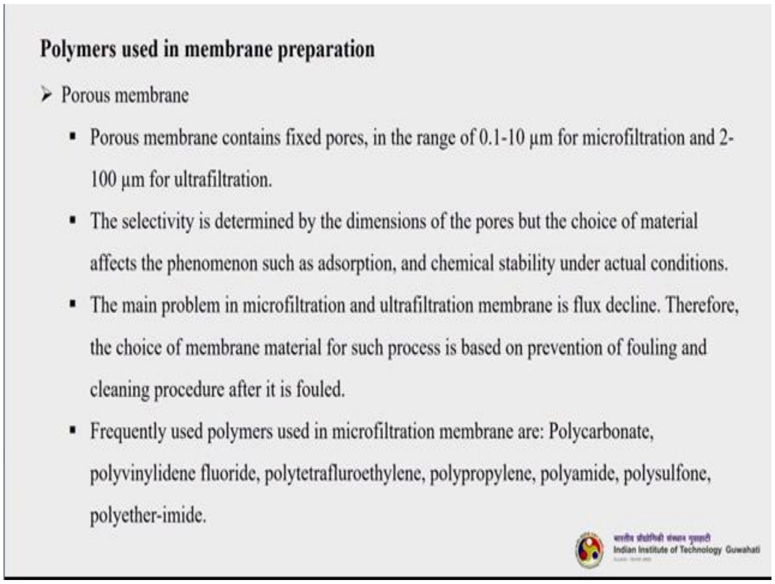

Polymers used in membrane preparation

- Porous membrane
  - Porous membrane contains fixed pores, in the range of 0.1-10 μm for microfiltration and 2-100 μm for ultrafiltration.
  - The selectivity is determined by the dimensions of the pores but the choice of material affects the phenomenon such as adsorption, and chemical stability under actual conditions.
  - The main problem in microfiltration and ultrafiltration membrane is flux decline. Therefore, the choice of membrane material for such process is based on prevention of fouling and cleaning procedure after it is fouled.
  - Frequently used polymers used in microfiltration membrane are: Polycarbonate, polyvinylidene fluoride, polytetrafluroethylene, polypropylene, polyamide, polysulfone, polyether-imide.

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So porous membrane, so porous membrane contains fixed pores in the range of 0.1-10 micron for microfiltration and 2-100 micron ultrafiltration. Now the selectivity is determined by the diamensions of the pores, but the choice of material effects of the phenomena such as adsorbtion and chemical stability under certain actual conditions. Now the main problem in microfiltration and ultrafiltration is the flux decline.

This we have discussed in last class. Therefore the choice of membrane for such process is based on prevention of fouling and cleaning procedure, after it is fouled, so frequently used polymers used in microfiltration membrane are polycarbonate, polyvinylidene fluoride, which is PPDF,Then PTFE, polytetrafluroethlyne, polypropylene, polyamide,polysulfone and polyether-imide. So there are many other sources so these are some of the polymers which are actually commercially been used.

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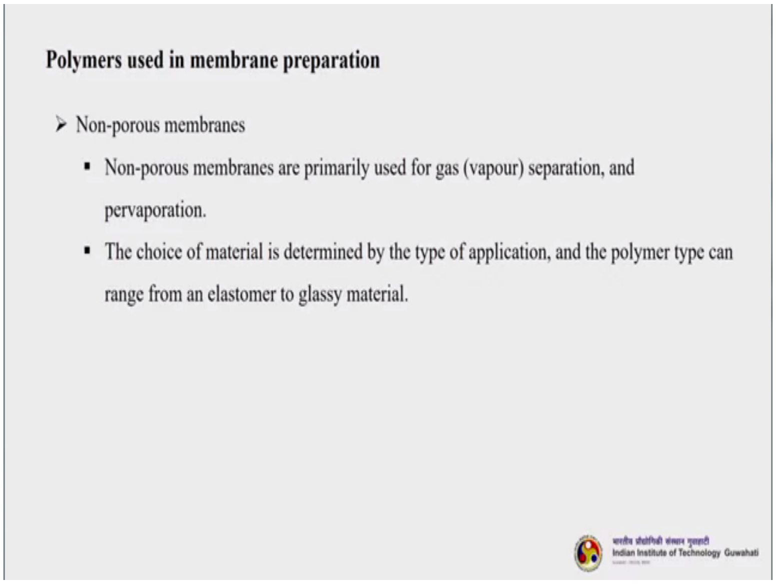

Polymers used in membrane preparation

- Non-porous membranes
  - Non-porous membranes are primarily used for gas (vapour) separation, and pervaporation.
  - The choice of material is determined by the type of application, and the polymer type can range from an elastomer to glassy material.

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And let us see about non porous membranes. So non porous membranes are primarily used for gas separation and pervaporation. So the choice of material is determined by the type of application, and the polymer type can range from an elastomer to glassy material.

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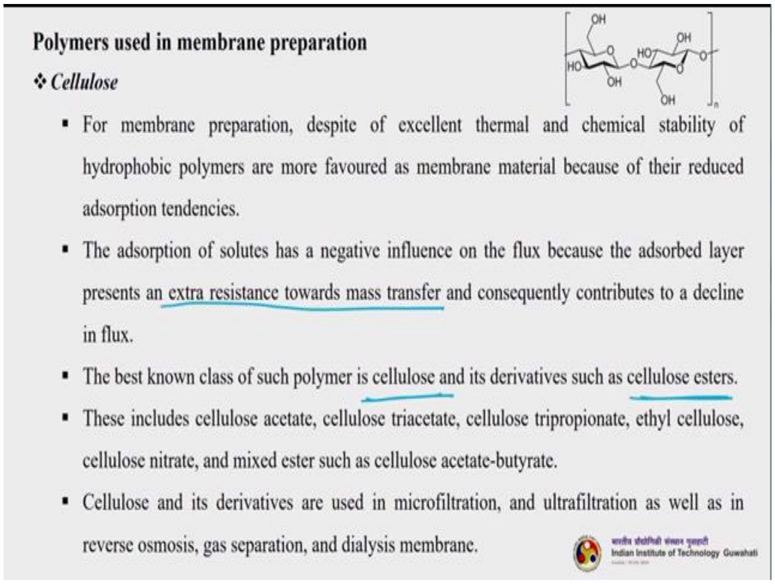

Polymers used in membrane preparation

❖ *Cellulose*

- For membrane preparation, despite of excellent thermal and chemical stability of hydrophobic polymers are more favoured as membrane material because of their reduced adsorption tendencies.
- The adsorption of solutes has a negative influence on the flux because the adsorbed layer presents an extra resistance towards mass transfer and consequently contributes to a decline in flux.
- The best known class of such polymer is cellulose and its derivatives such as cellulose esters.
- These includes cellulose acetate, cellulose triacetate, cellulose tripropionate, ethyl cellulose, cellulose nitrate, and mixed ester such as cellulose acetate-butyrate.
- Cellulose and its derivatives are used in microfiltration, and ultrafiltration as well as in reverse osmosis, gas separation, and dialysis membrane.

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So now we will see, and discuss about the few polymeric materials which are widely used for preparing a membranes. So let us start with cellulose which is the most evidently available natural material on Earth. For membrane preparation, despite of excellent thermal and chemical stability hydrophobic polymers are more favoured as membrane material because of their reduced adsorption tendencies.

So hydrophobic materials polymers are more widely used, because their adsorption tendencies towards solute will be very less so that the deposition of the solutes on the surface of the membrane, as well as the consequent fouling will be less. So the adsorbtion of solutes has a negative influence on the flux, because the adsorbed layer presents and extra resistance towards mass transfer, and consequently contributes to a decline in flux.

So the another resistance which we have discussed earlier also one resistance, the that is inherent is due to the membrane thickness. The second resistence is coming due to the adsorb layer on the surface of the solute. Lesser is the thickness of the adsorption lesser will be the resistance towards mass transfer. So the best known class of such polymer is cellulose, and its derivatives such as cellulose easters, so these include cellulose acetate

Cellulose triacetate cellulose triproportionate, ethyl cellulose, cellulose nitrate and mix esters, such as cellulose acetate butrate. So cellulose and its derivatives are used in microfiltration and ultrafiltration as well as in reverse osmosis, gas seperation and dialysis membrane.

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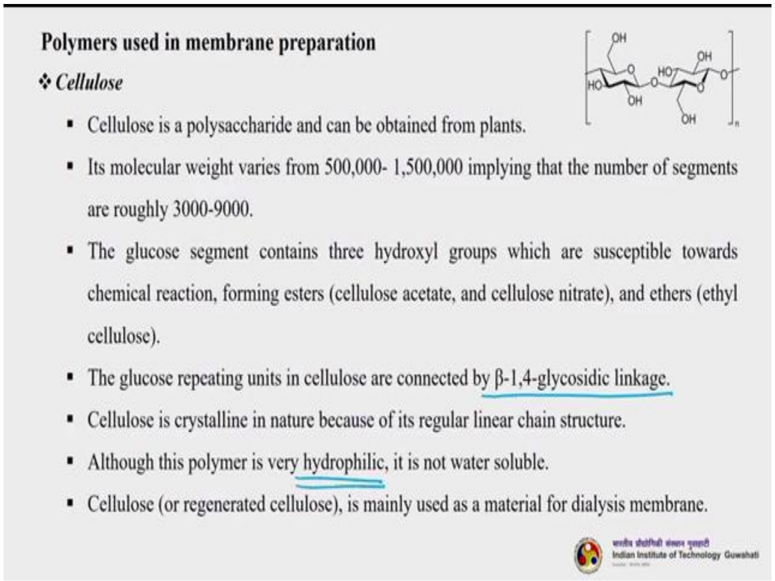

Polymers used in membrane preparation

❖ *Cellulose*

- Cellulose is a polysaccharide and can be obtained from plants.
- Its molecular weight varies from 500,000- 1,500,000 implying that the number of segments are roughly 3000-9000.
- The glucose segment contains three hydroxyl groups which are susceptible towards chemical reaction, forming esters (cellulose acetate, and cellulose nitrate), and ethers (ethyl cellulose).
- The glucose repeating units in cellulose are connected by β-1,4-glycosidic linkage.
- Cellulose is crystalline in nature because of its regular linear chain structure.
- Although this polymer is very hydrophilic, it is not water soluble.
- Cellulose (or regenerated cellulose), is mainly used as a material for dialysis membrane.

So what is cellulose, cellulose is a polysaccharide and can be obtained from plants. Its molecular weight usually ranges from 500,000 to 1,50,000, implying that the number of segments are roughly between 3000 to 9000. So, as you understand the number of units increase the molecular weight also increases the glucose segment contents three hydroxyl groups who have susceptible towards chemical reaction.

So and forming easters so cellulose acetate and cellulose nitrate and ethers, ethyl cellulose, the glucose repeating units are connected by the beta-1,4-glycosidic linkage, cellulose is crystalline in nature, because of its regular linear chain structure, although this polymer is hydrophilic, it is not water soluble. So cellulose or regenerated cellulose is mainly used as a material for dialysis membrane.

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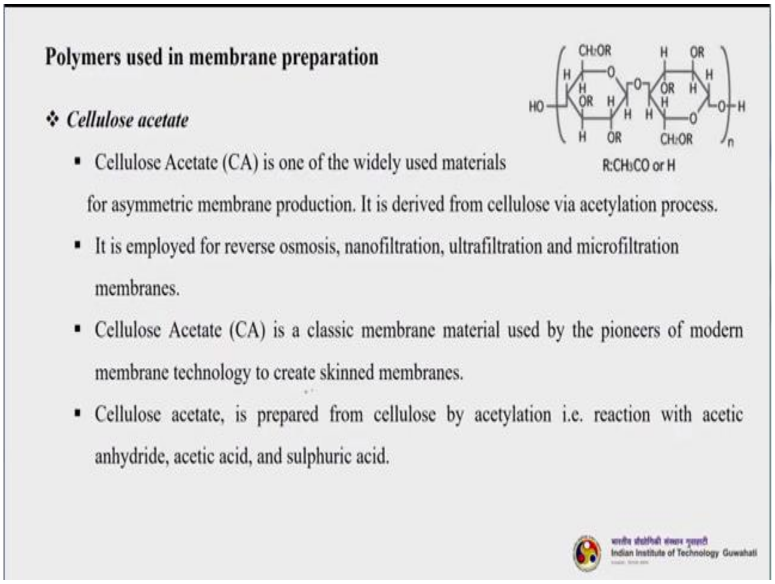

Polymers used in membrane preparation

- ***Cellulose acetate***
  - Cellulose Acetate (CA) is one of the widely used materials for asymmetric membrane production. It is derived from cellulose via acetylation process.
  - It is employed for reverse osmosis, nanofiltration, ultrafiltration and microfiltration membranes.
  - Cellulose Acetate (CA) is a classic membrane material used by the pioneers of modern membrane technology to create skinned membranes.
  - Cellulose acetate, is prepared from cellulose by acetylation i.e. reaction with acetic anhydride, acetic acid, and sulphuric acid.

The next one is cellulose acetate, so you can see the structure of cellulose acetate here in the top corner cellulose acetate is one of the widely used materials for asymmetric membrane production. It is derived from cellulose via a acetylation process. It is employed for reverse osmosis nanofiltration and microfiltration and ultrafiltration membranes. So cellulose acetate is a classic membrane material used by pioneers of modern membrane technology to create skinned membranes.

So, as you know, we have discussed what is skin membranes. So, one top layer that is fused, along with a porous layer, and the top layer is actually called skin membranes, mostly the asymmetric membranes. So cellulose acetate is prepared from cellulose by acetatylation. That is reaction with acetic anhydride acetic acid and sulfuric acid.

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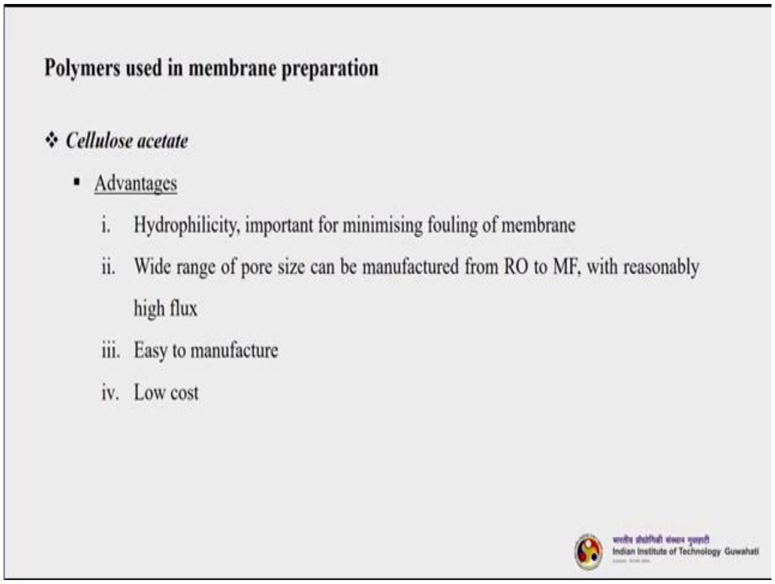

Polymers used in membrane preparation

❖ *Cellulose acetate*

- Advantages
    1. Hydrophilicity, important for minimising fouling of membrane
    2. Wide range of pore size can be manufactured from RO to MF, with reasonably high flux
    3. Easy to manufacture
    4. Low cost

So let us understand what are the different advantages and disadvantages of cellulose acetate. Now, the advantages it hydrophilicity. So, the more the material we hydrophilic the fouling will be less. Okay. So, a wide range of pore size can be manufactured from RO to microfiltration with reasonably higher flux. It is very easy to manufacture and the cost is, of course, low,

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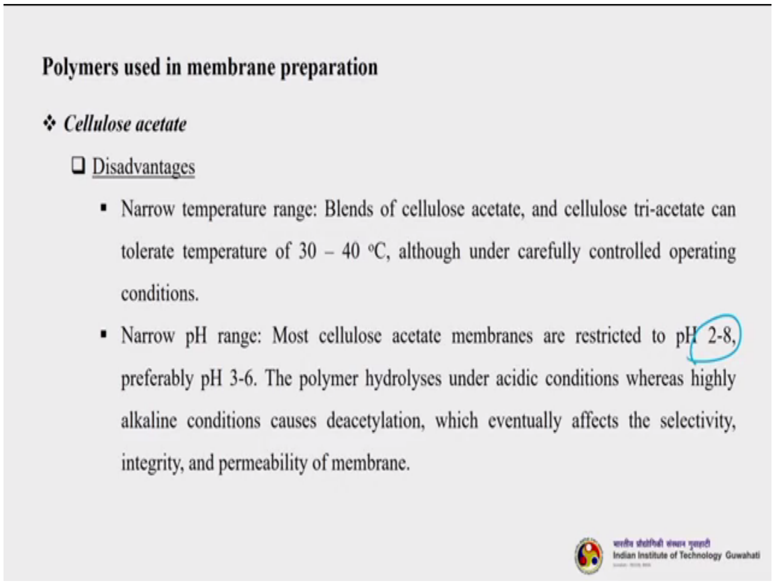

Polymers used in membrane preparation

❖ *Cellulose acetate*

❑ Disadvantages

- Narrow temperature range: Blends of cellulose acetate, and cellulose tri-acetate can tolerate temperature of 30 – 40 °C, although under carefully controlled operating conditions.
- Narrow pH range: Most cellulose acetate membranes are restricted to pH 2-8, preferably pH 3-6. The polymer hydrolyses under acidic conditions whereas highly alkaline conditions causes deacetylation, which eventually affects the selectivity, integrity, and permeability of membrane.

But it has certain disadvantages also the first disadvantage is that it has narrowed temperature range, it cannot withstand high temperature, the temperature which can be utilized using this membrane is between 30 to 40 degrees centigrade. Although under carefully controlled operating conditions, you can go little beyond that. And another disadvantage is that narrow pH range. So most of the cellulose acetate membranes are restricted to pH 2-8.

And few can go, 3-6, the polymer hydrolyzes under acidic conditions. Whereas highly alkaline condition causes deacetylation. So, then the cellulose acetate will go back to cellulose actually, and which eventually affect the selectivity integrity and permeability of the membrane.

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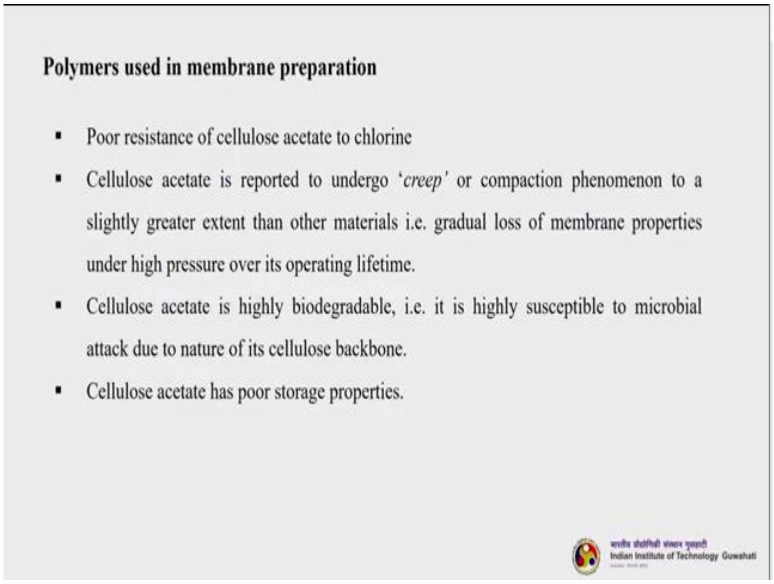

Polymers used in membrane preparation

- Poor resistance of cellulose acetate to chlorine
- Cellulose acetate is reported to undergo '*creep*' or compaction phenomenon to a slightly greater extent than other materials i.e. gradual loss of membrane properties under high pressure over its operating lifetime.
- Cellulose acetate is highly biodegradable, i.e. it is highly susceptible to microbial attack due to nature of its cellulose backbone.
- Cellulose acetate has poor storage properties.

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So other disadvantages of cellulose acetate is that, it is poor resistance to chlorine. So many times chlorine is present in water in wastewater so and they are using a cellulose acetate for such treatment water or wastewater treatment, then the presence of chlorine actually will create problem for this type of membranes and cellulose acetate is reputed to undergo creep so creep is a compaction phenomenon. Okay.

And the compaction of creeping is greater is slightly greater than other polymeric materials. So, that is the gradual loss of membrane properties under high pressure over its operating lifetime. Cellulose acetate highly biodegradable This is another big problem. When if at all you are using this type of membrane. For some, by revelation or wastewater treatment process on in using it from some production of some biopharmaceutical drugs.

So it is highly susceptible to microbial attack. Due to the nature of which cellulose backbone, so microbes will actually try to eat the cellulose as a source of glucose for them. So cellulose acetate has poor storage properties.

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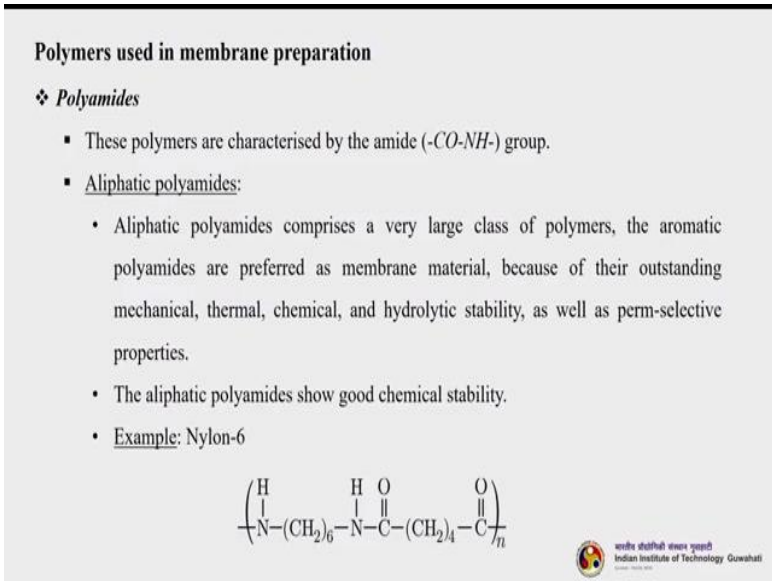

Polymers used in membrane preparation

❖ ***Polyamides***

- These polymers are characterised by the amide (-*CO-NH*-) group.
- Aliphatic polyamides:
  - Aliphatic polyamides comprises a very large class of polymers, the aromatic polyamides are preferred as membrane material, because of their outstanding mechanical, thermal, chemical, and hydrolytic stability, as well as perm-selective properties.
  - The aliphatic polyamides show good chemical stability.
  - Example: Nylon-6

$$\left(\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right)_n$$

So the next class of membrane which is widely which is called polyamides PA. So these polymers are characterized by the CONH group, so the repeating unit is CONH. So, aliphatic polyamides comprise a very large class of polymers, and the aromatic polyamides are preferred as a membrane and material, because of the outstanding mechanical thermal chemical and hydro lytic stability as well as perm-selective properties.

And the aliphatic polyamide so good chemical stability for example Nylon-6, Nylon-6 is a very good material for preparing membranes

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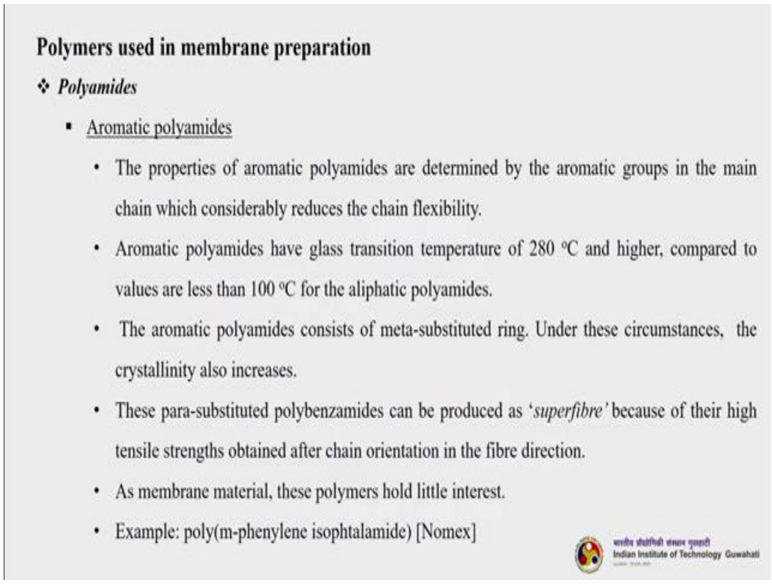

Polymers used in membrane preparation

- ***Polyamides***
  - Aromatic polyamides
    - The properties of aromatic polyamides are determined by the aromatic groups in the main chain which considerably reduces the chain flexibility.
    - Aromatic polyamides have glass transition temperature of 280 ^{o}C and higher, compared to values are less than 100 ^{o}C for the aliphatic polyamides.
    - The aromatic polyamides consists of meta-substituted ring. Under these circumstances, the crystallinity also increases.
    - These para-substituted polybenzamides can be produced as '*superfibre*' because of their high tensile strengths obtained after chain orientation in the fibre direction.
    - As membrane material, these polymers hold little interest.
    - Example: poly(m-phenylene isophtalamide) [Nomex]

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And the properties of aromatic polyamide are determined by the aromatic groups in the main chain, which considerably reduces the chain flexibility. So aromatic polyamide have glass transition temperature of 280 degrees centigrade, and even higher than this, compared to the values less than hundred degrees. For the, aliphatic polyamides, so aromatic polyamide consist of meta-substituted ring.

Under these circumstances the crystallinity also increases for the polymer. So this para-substituted polybenzamides, can be produced as superfiber, because of their high tensile strength obtaind after chain orientation in the fiber direction. As membrane material this polymer hold little interest example is Nomex which is polym-phenylene isophtalamide.

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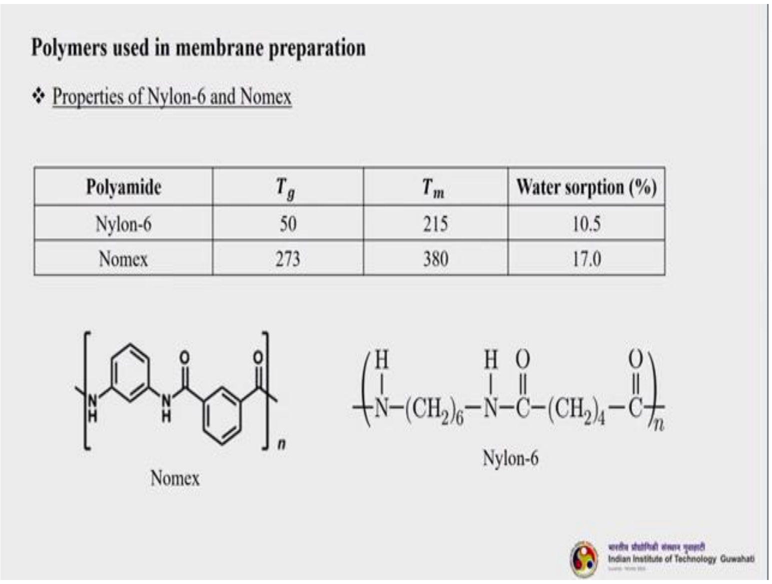

Polymers used in membrane preparation

- Properties of Nylon-6 and Nomex

Polyamide	T_g	T_m	Water sorption (%)
Nylon-6	50	215	10.5
Nomex	273	380	17.0

Nomex

$\left(\overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} \right)_n$

Nylon-6

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So, let us look the properties of Nylon-6 and Nomex. You can see that Nomex has a higher glass transition temperature than Nylon-6, and it is melting temperature is also higher than that of the Nylon-6 and its waters sorption capacity is also higher. So these are the structurs of Nomex Nylon-6.

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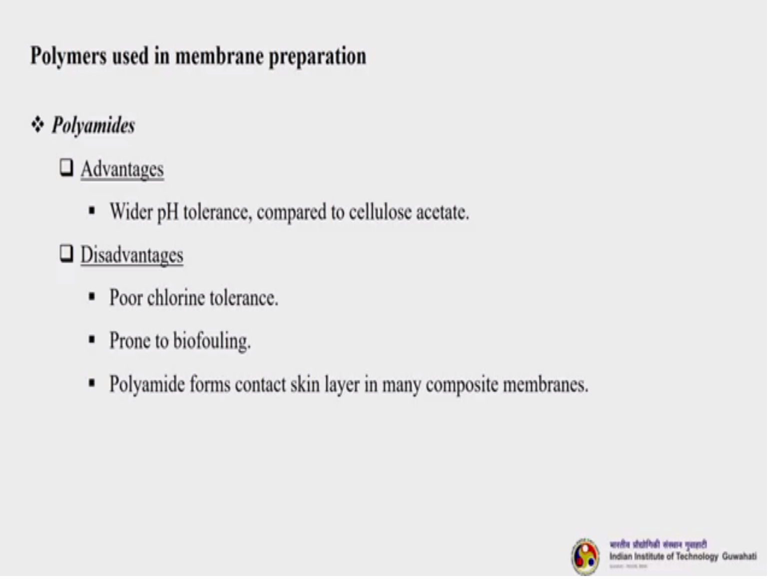

Polymers used in membrane preparation

- *Polyamides*
  - Advantages
    - Wider pH tolerance, compared to cellulose acetate.
  - Disadvantages
    - Poor chlorine tolerance.
    - Prone to biofouling.
    - Polyamide forms contact skin layer in many composite membranes.

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And let us understand what are the advantages and disadvantages of polyamides. So the advantage is wide pH tolerance compared to cellulose acetate, so you can use it without any hindrance for different water wastewater treatment processes and disadvantage is, again, poor chlorine, tolerance, and it is prone to prone to bio fouling and polyamide forms. Contact skin layer in many composite membranes.

So, actually, when we are preparing a composite number and using a polyamide, so it will form and other types of skin layer in the composite membrane itself, thereby providing an additional resistance to already existing resistance.

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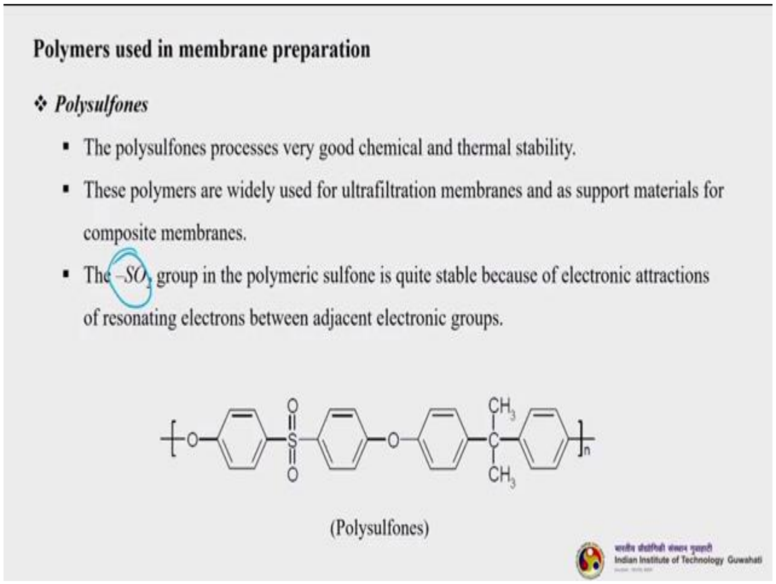

Polymers used in membrane preparation

❖ ***Polysulfones***

- The polysulfones processes very good chemical and thermal stability.
- These polymers are widely used for ultrafiltration membranes and as support materials for composite membranes.
- The $-SO_2$ group in the polymeric sulfone is quite stable because of electronic attractions of resonating electrons between adjacent electronic groups.

(Polysulfones)

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So the next class is widely used in membrane preparation is polysulfones, or its derivatives which is polyethersulfones, PS or PES. So the polysulfones posesses very good chemical and thermal stability. So these polymers are widely used for ultrafiltraation membranes and its support materials for composite membranes, so most of the ceramic based composite membranes uses polysulfones.

Or polyethersulfones to impact the top or skill layer on the surface of the ceramic membranes, whereas the ceramic mumbling is used as the support SO2 group. Okay, in the polymer itself one is quite stable, because of the electronic attractions of regenerating electrons, adjacent electronic groups. So this is the polysulfones structure.

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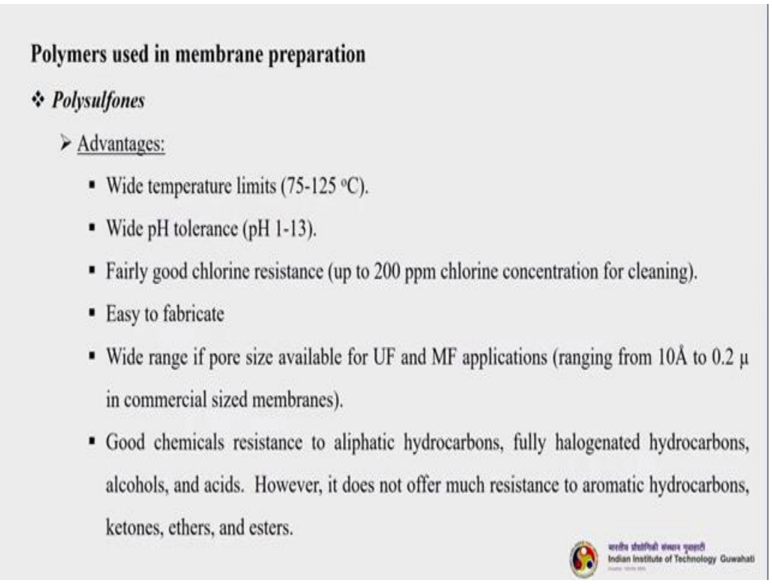

Polymers used in membrane preparation

- ***Polysulfones***
  - Advantages:
    - Wide temperature limits (75-125 °C).
    - Wide pH tolerance (pH 1-13).
    - Fairly good chlorine resistance (up to 200 ppm chlorine concentration for cleaning).
    - Easy to fabricate
    - Wide range if pore size available for UF and MF applications (ranging from 10Å to 0.2 μ in commercial sized membranes).
    - Good chemicals resistance to aliphatic hydrocarbons, fully halogenated hydrocarbons, alcohols, and acids. However, it does not offer much resistance to aromatic hydrocarbons, ketones, ethers, and esters.

And the advantages is, is that it can withstand wide temperature limits almost up to 125 degrees centigrade. And the tolerance limit of the polysulfone membranes and put pH is very wide 1- 13. Fairly good chlorine resistance up to 200 ppm chlorine, it can withstand. So, for cleaning purposes, this type of membranes who have no problem. While it deals with chlorine, and it is easy to fabricate wide range if pore size available for ultrafiltration and microfiltration applications.

So, we can easily prepare either microfiltration or ultrafiltration and membranes, using polysulfones material, so good chemical resistance to aliphatic hydrocarbons fully halogenated hydrocarbons alcohols and acids. So this means that polysulfones have extreme good chemical stability towards most of the chemicals and solvents. However, it does not much upon much resistance to aromatic hydrocarbons, such as ketones,ethers and easters.

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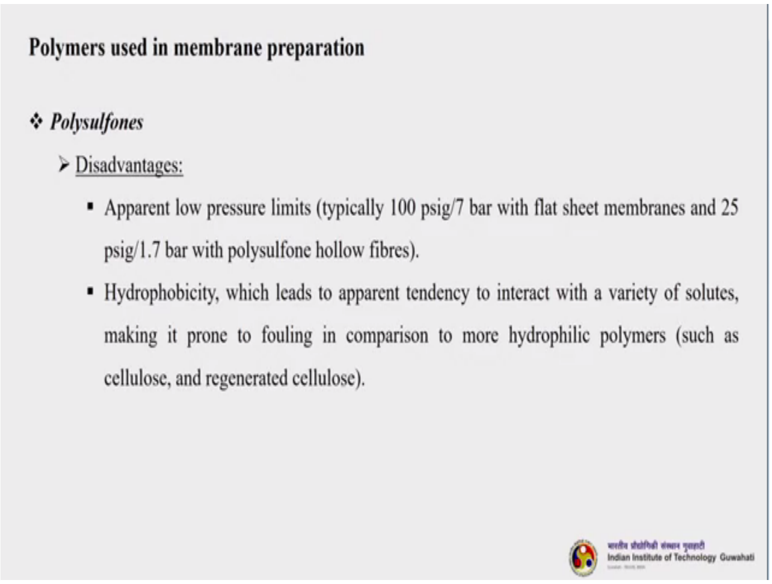

Polymers used in membrane preparation

❖ ***Polysulfones***

- ➢ Disadvantages:
  - Apparent low pressure limits (typically 100 psig/7 bar with flat sheet membranes and 25 psig/1.7 bar with polysulfone hollow fibres).
  - Hydrophobicity, which leads to apparent tendency to interact with a variety of solutes, making it prone to fouling in comparison to more hydrophilic polymers (such as cellulose, and regenerated cellulose).

Its disadvantage is that it has very low pressure limits. So typically around 700 bar when you use polysulfone membrane and as a flat sheet membrane, or 25, bar when you use them as hollow fiber membranes, so many upon it happens that we use preserved much higher than 25 or 30 bars. So in that those applications. It is difficult to use polysulfone membranes. So another disadvantage is hydrophobicity.

So, which leads to apparent tendency to interact with a variety of solutes, making it prone to fouling in competition to more hydrophilic polymers such as cellulose and regenerated cellulose.

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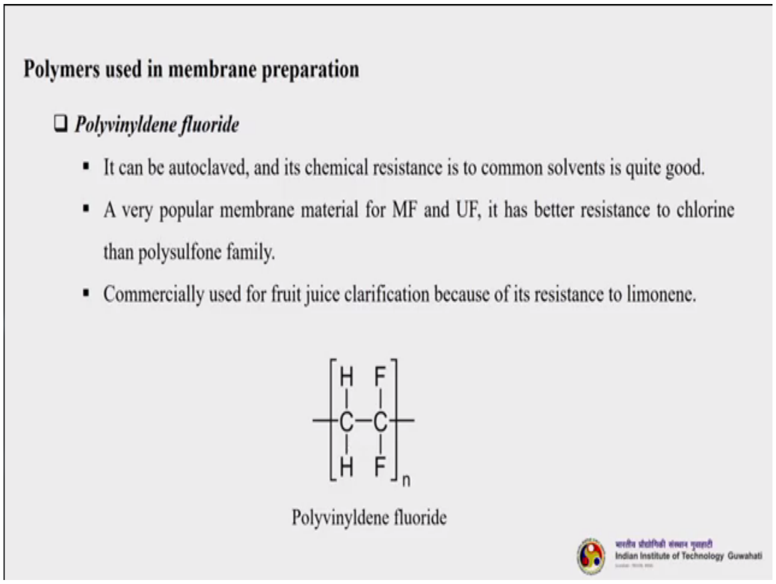

Polymers used in membrane preparation

❑ ***Polyvinyldene fluoride***

- It can be autoclaved, and its chemical resistance is to common solvents is quite good.
- A very popular membrane material for MF and UF, it has better resistance to chlorine than polysulfone family.
- Commercially used for fruit juice clarification because of its resistance to limonene.

Polyvinyldene fluoride

So the next classes. PVDF so polyvinyldene fluoride, so it can be autoclave so this is the beauty of PVDF membrane and its chemical resistance is to common solvents is extremely good, so it is a very popular number in for manufacturing of microfilteration and ultrafiltration, and it is better resistance to chlorine than all other polymeric materials. So commercially used for fruit juice clarification, because of its resistance to limonene, limonene is the substance which is present in. Most of the fruit juices. So, this is the structure of PVDF.

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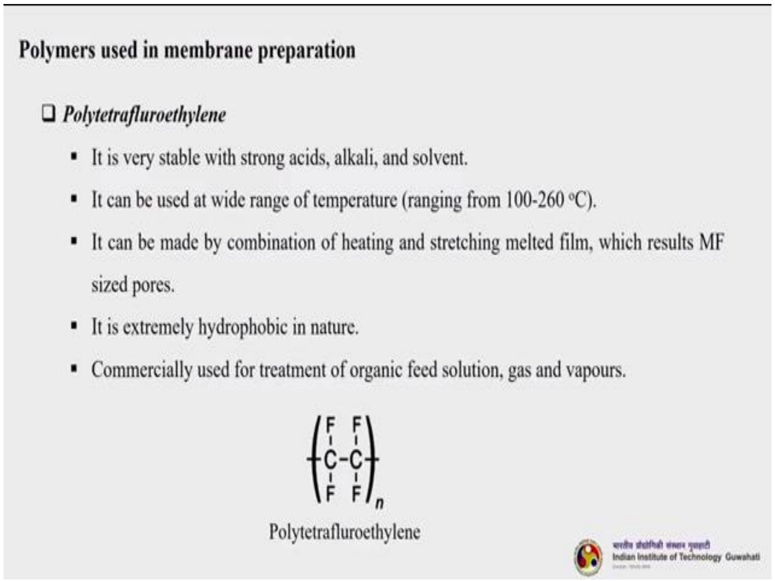

Polymers used in membrane preparation

❑ ***Polytetrafluroethylene***

- It is very stable with strong acids, alkali, and solvent.
- It can be used at wide range of temperature (ranging from 100-260 °C).
- It can be made by combination of heating and stretching melted film, which results MF sized pores.
- It is extremely hydrophobic in nature.
- Commercially used for treatment of organic feed solution, gas and vapours.

$$\left(\begin{array}{cc} F & F \\ | & | \\ -C & -C- \\ | & | \\ F & F \end{array}\right)_n$$

Polytetrafluroethylene

The next class is PTFE, which is called polytetrafluoroethylene, so it is also very stable with strong acids, alkalis and solvents, it can be used at a wide range of temperature usally, it can withstand up to 60 degrees in centigrade, temperature, it can be made by a combination of heating and streching melted filim, which results microfiltration sized pores, it is easy to fabricate also.

It is extremely hydrophobic in nature. So the adsorbtion of solutes due to hydrophobic nature will be more and commercial use for treatment of organic feed solution gas and vapors.

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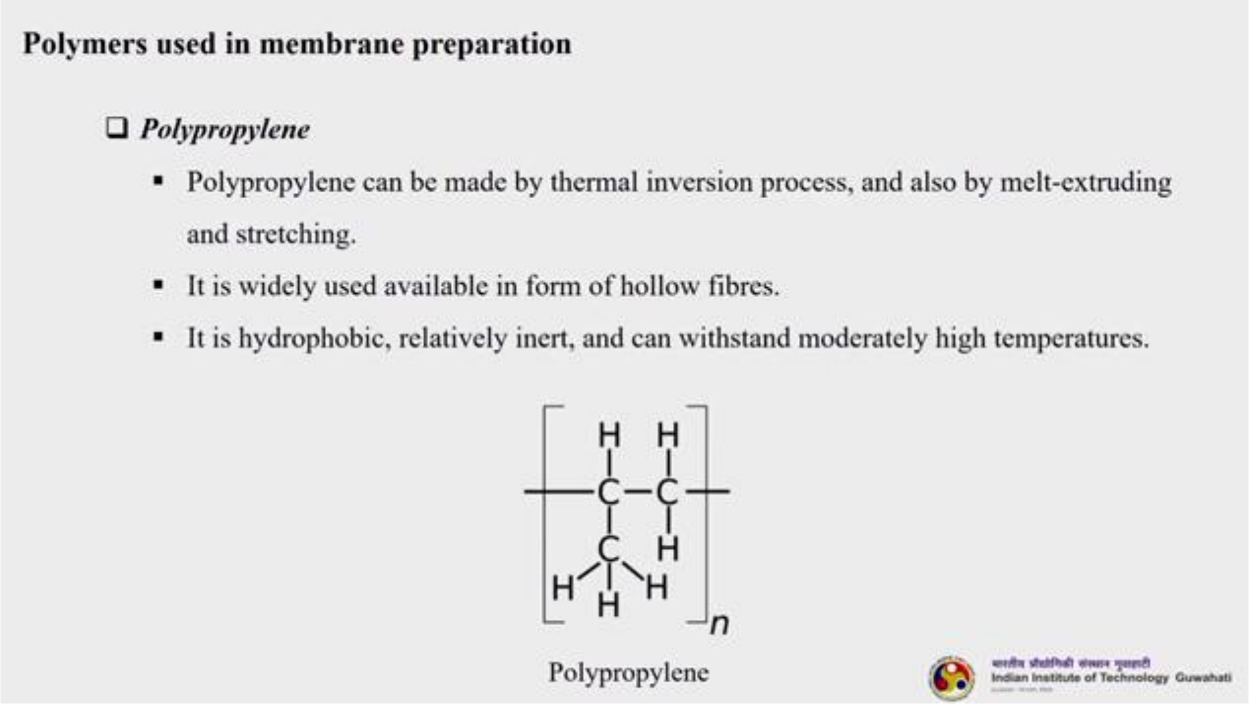

Polymers used in membrane preparation

❑ ***Polypropylene***

- Polypropylene can be made by thermal inversion process, and also by melt-extruding and stretching.
- It is widely used available in form of hollow fibres.
- It is hydrophobic, relatively inert, and can withstand moderately high temperatures.

Polypropylene

The next class is polypropylene PP. The polypropylene can be made by thermal inversion process, and also by melt extruding and streching. It is widely available in the form of hollow fibers. And it is hydrophobic relatively inert and can withstand moderately high temperatures.

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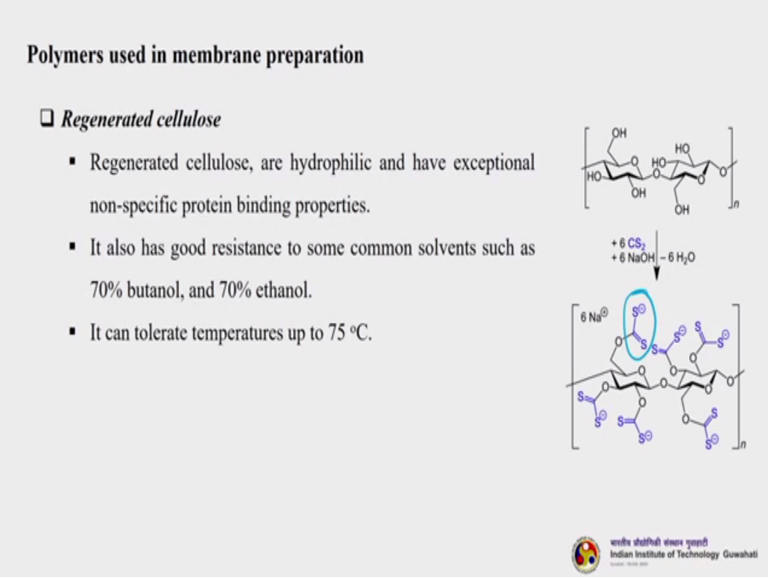

Polymers used in membrane preparation

❑ *Regenerated cellulose*

- Regenerated cellulose, are hydrophilic and have exceptional non-specific protein binding properties.
- It also has good resistance to some common solvents such as 70% butanol, and 70% ethanol.
- It can tolerate temperatures up to 75 °C.

So the next class is regenerated cellulose. So these, you can see the regenerated structures here. So this is actually the structure of the cellulose, to which we are adding CH to sodium hydroxide, and water is getting out of this reaction. So their by we are impacting different types of this sulpher groups here. Okay, to increase its different properties of the cellulose. So that is why it is called regenerated cellulose.

So they are extremely hydrophilic and have exceptional non specific protein binding properties. So this class of membrane material is extremely good to prepare membranes of microfiltration or ultrafiltration range where the application is protein separation. So it is also good resistant to some common elements such as butanol and ethanol so it can almost 70% of both butanol and ethanol concentration.

So it can tolerate temperature up to 75 degrees centigrade which is actually lower as compared to other polymeric materials.

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Text/References

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You can refer these at the text and references books as every after every lecture I am showing this so Mulder is the most important textbook for this particular course, so you can refer to that apart from other books also. So, thank you very much. And in the next class will be discussing about the inorganic materials for membrane preparation, their properties advantages and disadvantages.

So it is that in the next class will wind up our different membrane materials, and the next class will start how membrane can be prepared, using different techniques. So thank you very much.

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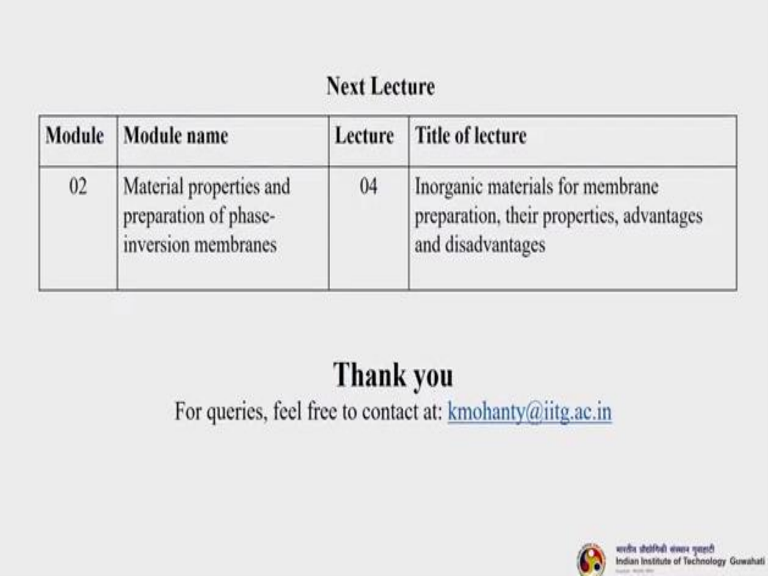

Next Lecture

Module	Module name	Lecture	Title of lecture
02	Material properties and preparation of phase-inversion membranes	04	Inorganic materials for membrane preparation, their properties, advantages and disadvantages

Thank you

For queries, feel free to contact at: kmohanty@iitg.ac.in

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