Introduction to Polymer Science
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Lecture - 04
Classification by Polymerization Mechanism, Nomenclature

Welcome back. In this lecture, we are going to discuss the classification by polymerization mechanism and nomenclature of polymers.

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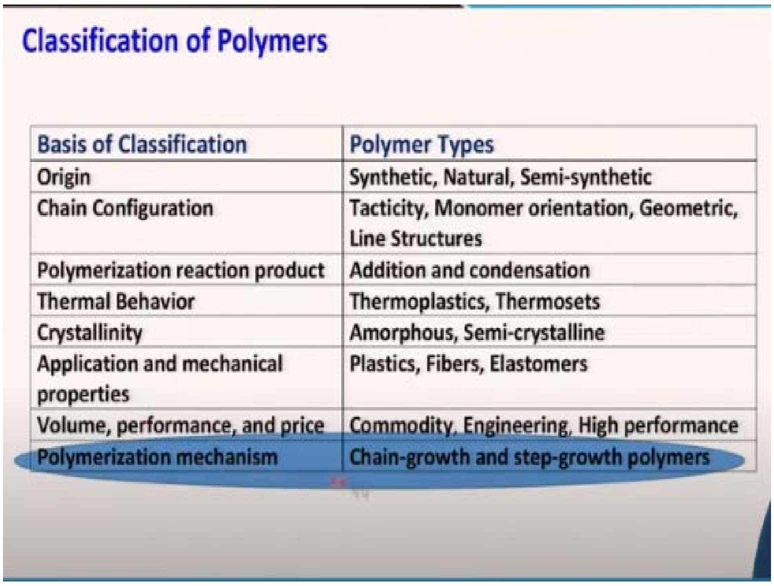

Classification of Polymers

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

We had discussed different classification methods and we are just left with the only one which is the polymerization mechanism.

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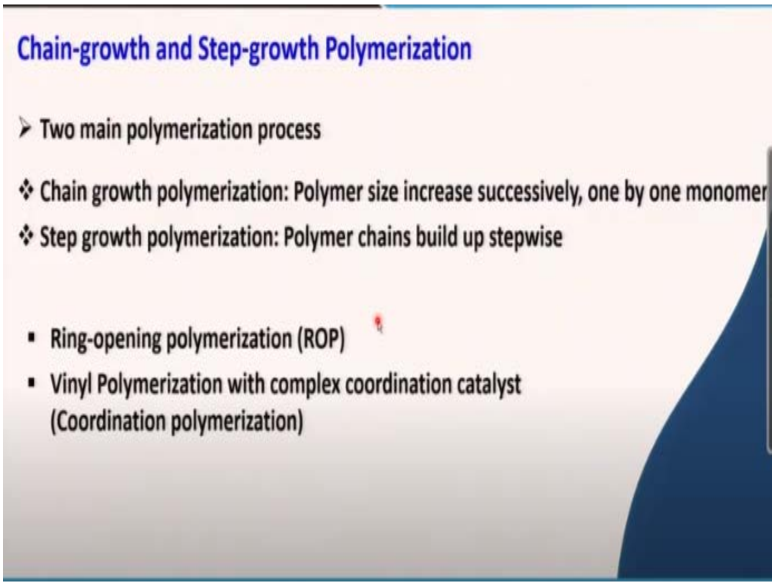

Chain-growth and Step-growth Polymerization

- Two main polymerization process
- Chain growth polymerization: Polymer size increase successively, one by one monomer
- Step growth polymerization: Polymer chains build up stepwise

- Ring-opening polymerization (ROP)
- Vinyl Polymerization with complex coordination catalyst (Coordination polymerization)

Polymerization mechanisms are classified mainly into two processes. One is chain-growth polymerization and another is step-growth polymerization. In chain-growth polymerization, polymer size increases by successive addition of one monomer after one, and in step-growth polymerization, polymer chains build up stepwise.

Now there are few other specialized polymerization techniques like ring-opening polymerization, coordination polymerization but these follow either chain-growth polymerization technique or step-growth polymerization techniques may be of a different mechanism.

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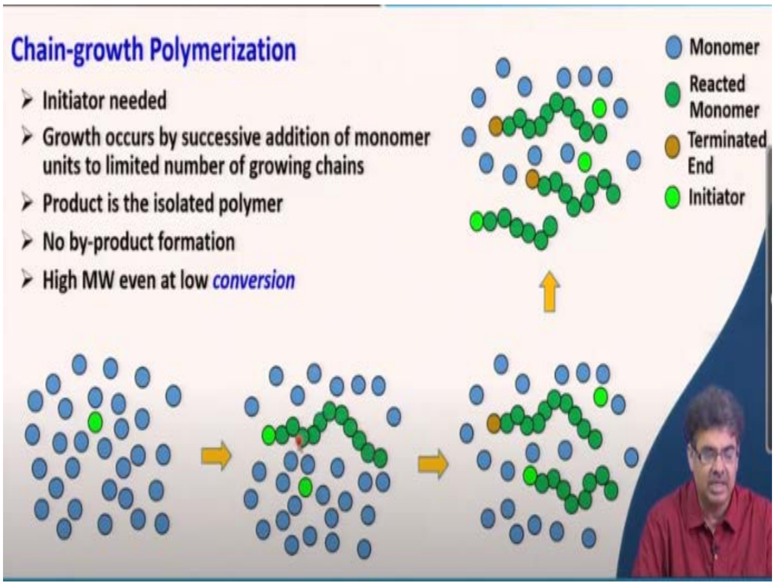

Chain-growth Polymerization

- Initiator needed
- Growth occurs by successive addition of monomer units to limited number of growing chains
- Product is the isolated polymer
- No by-product formation
- High MW even at low *conversion*

Now, what is chain-growth polymerization? If we have a cluster of monomers, which is shown here with these blue spheres, one initiator is activated either by heating the solution or by shining light or some other means. Then as soon as this radical or anion or cation generates, it reacts with the monomer and initiates a chain, which then reacts with another monomer and third monomer, and so on.

So eventually the monomers react with the growing chains of the polymer and polymer chains keep increasing in size. Now with time, more and more initiators will generate, and as a result, more and more polymers will be produced. Of course, some of these propagating radical or propagating cations or anions will terminate the chain by some statistical methods. At the end of the reaction if all the monomers get reacted, then we will have many such chains. So, if you go back and look at the characteristics of chain-growth polymerization, we know that we need an initiator otherwise the chain cannot start.

The growth of the polymer chain occurs by successive addition of monomer units to the limited number of growing chains. In this mechanism of polymerization, the final isolated product is the polymer chains. If we take this mixture and then do some fractionation either by precipitation or some other method, we will take out these polymer chains. Unreacted monomers or initiators or small molecular chains are not part of the polymer product.

As you can see, high molecular weight polymer chains can form even at low conversion. Conversion is the percentage of monomers which reacted. So with time more and more monomers react and conversion goes up. Even at low conversions, we see that high molecular weight polymer chains occur. It may happen when the reaction of radicals or ions is very fast. Actually, even at low conversion, we get high molecular weight polymer chains.

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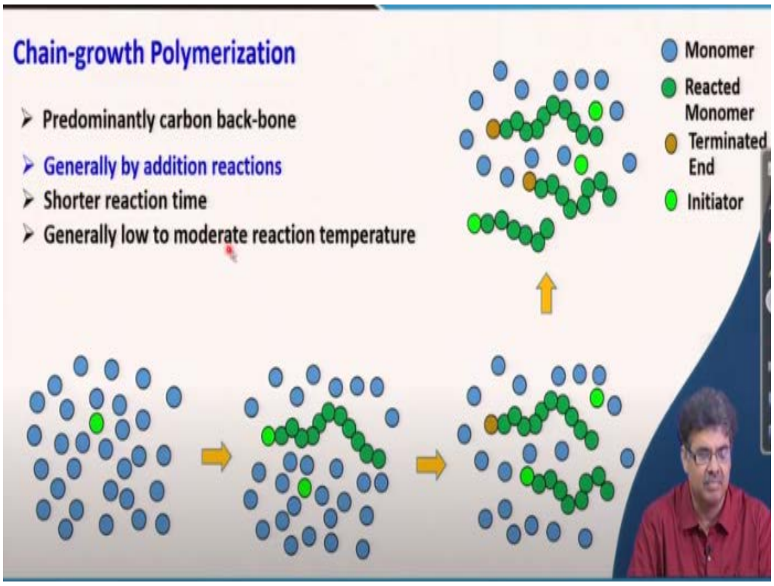

Chain-growth Polymerization

- Predominantly carbon back-bone
- Generally by addition reactions
- Shorter reaction time
- Generally low to moderate reaction temperature

The chain-growth polymerization predominantly happens for the carbon backbone and generally, this happens by addition reactions. Generally, no byproduct formation takes place. Since the reaction is fast, the reaction time is generally short and we need to have the temperature such that this initiator gets activated which can be done by using low to moderate reaction temperature. Most of these reactions are done in solution. So, the temperature anyway will be restricted by the solvent boiling point. For example, if we are doing a reaction in an aqueous medium, then obviously we can go up to 70-80 ^{o}C.

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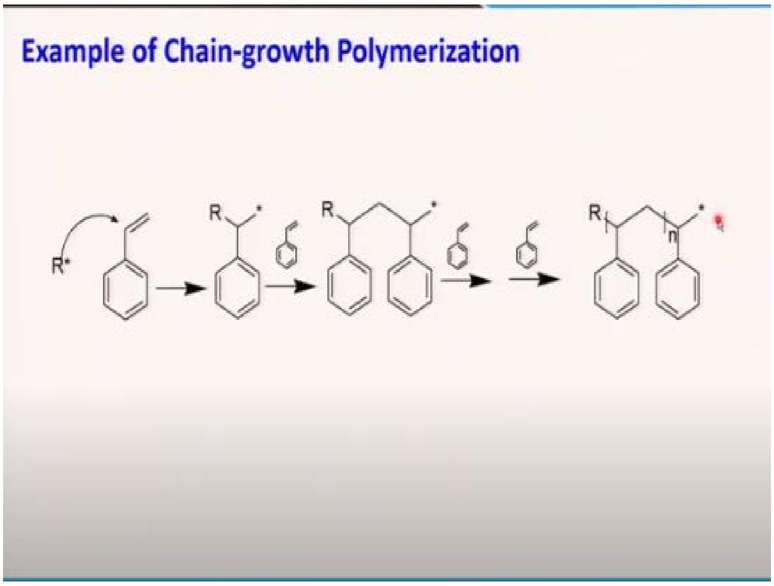

Example of Chain-growth Polymerization

This is one example of synthesizing polystyrene. R^* could be radical, or cation or anion. So this is the initiation step. And once this initiation happened, more and more styrene molecules get added to the chain end and we get a long polymer chain and these polymers will ultimately get terminated by some mechanism. The statistical mechanism will be discussed later.

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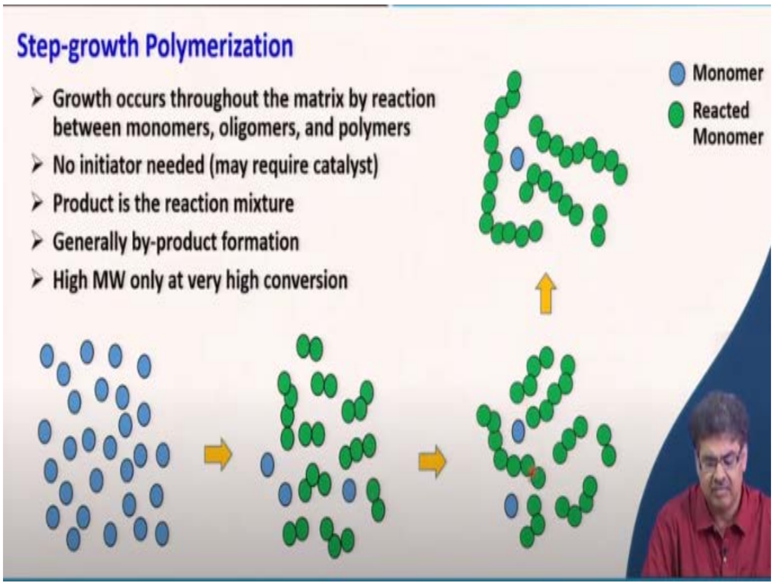

Step-growth Polymerization

- Growth occurs throughout the matrix by reaction between monomers, oligomers, and polymers
- No initiator needed (may require catalyst)
- Product is the reaction mixture
- Generally by-product formation
- High MW only at very high conversion

In the case of step-growth polymerization, the initiator molecule is not required but sometimes a catalyst is required to make the reaction faster. Once the reaction starts with these monomers which typically have functional groups, they can react with each other resulting in formation of dimer, trimer, tetramer, and so on. When the dimer reacts with another monomer it gives a trimer. If trimer reacts with another dimer gives pentamer. If the timer reacts with the monomer, gives tetramer, and so on. With time, these oligomeric chains get longer and longer. But there are always a bit of monomer or dimers left in the polymerization medium. So, with time, the average number of monomer units in a polymer chain goes up. And for that, average molecular weight goes up. And finally, we can stop the reaction whenever we want.

In this mechanism, no initiator is needed usually, but sometimes we need a catalyst to make the reaction feasible. The product is not isolated by using a solvent extraction method or something. If we can dissolve this polymer and isolate the polymer from a non-solvent, then monomers and small molecules generally do not precipitate along with the polymer chains. Here, the entire mixture i.e. everything present in the mixture is the product. In this case, due to reaction between two functional groups, by-product formation takes place. It is also important that high molecular weight polymers are only formed when most of the monomers have reacted i.e. at high conversion. When there is low conversion, only small molecules like dimer, trimer, tetramer, oligomer are formed. To have a high molecular weight, the conversion must be very high in case of step-growth polymerization.

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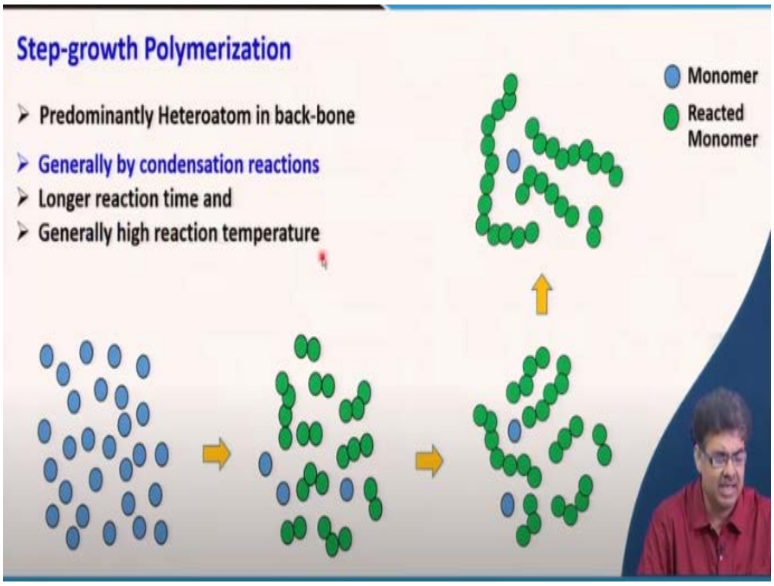

Step-growth Polymerization

- Predominantly Heteroatom in back-bone
- Generally by condensation reactions
- Longer reaction time and
- Generally high reaction temperature

Now, this polymerization mechanism is typically for heteroatom backbone, and these reactions between functional groups happen by condensation reaction. So many people correlate that condensation means step-growth and chain-growth means addition. In most cases, they are true. Condensation polymers are actually made using step-growth polymerization and chain-growth polymerization is used for making addition polymers, though this is not true for every case. If we need to have a high conversion, the reaction time should be longer and the temperature should be high.

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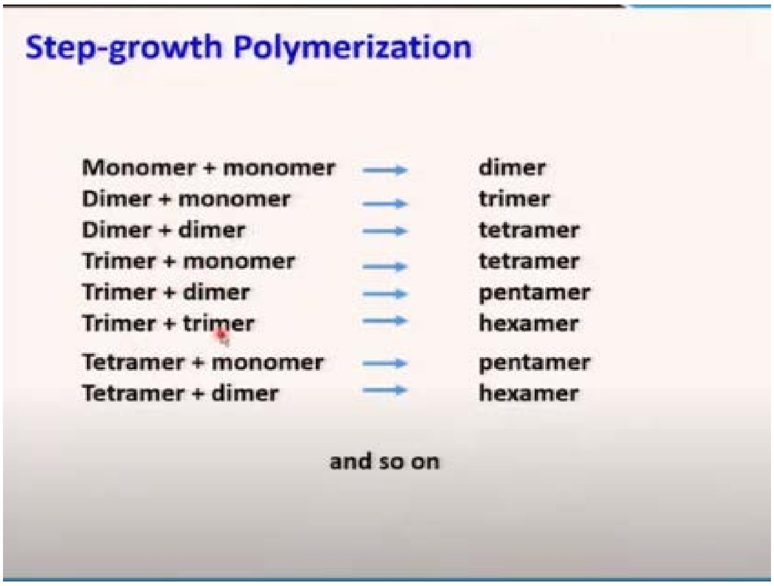

Step-growth Polymerization

Monomer + monomer → dimer
Dimer + monomer → trimer
Dimer + dimer → tetramer
Trimer + monomer → tetramer
Trimer + dimer → pentamer
Trimer + trimer → hexamer
Tetramer + monomer → pentamer
Tetramer + dimer → hexamer

and so on

Reactions happen between chains of different mass like dimer, trimer, tetramer and slowly these polymer chains grow with time.

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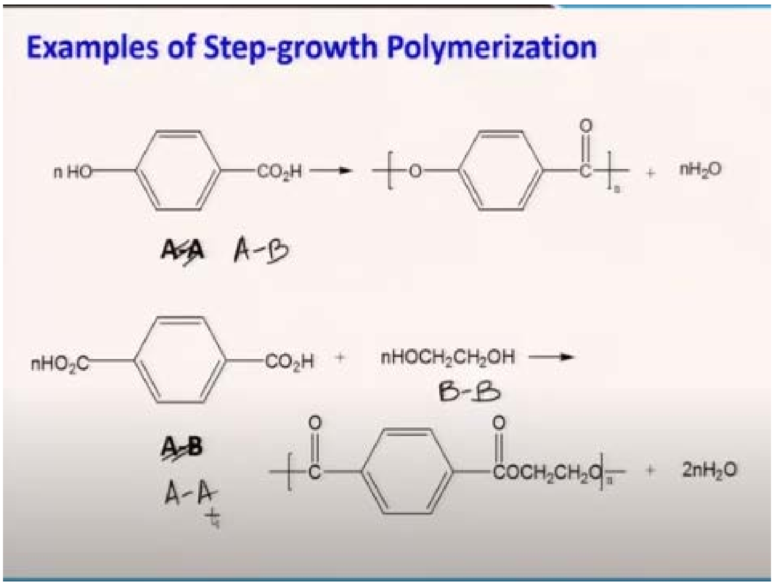

Examples of Step-growth Polymerization

For example, a condensation step needs two functional groups as discussed earlier. One example is, hydroxycarboxylic acid and typically we call this as A-B. There are two different functional groups. Since we have H_2O as a byproduct, so, this is a condensation reaction. Another example is where the two functional groups are in two different monomers. We have two carboxylic groups in one monomer and two alcohol groups in different another monomer. With this, it should be called an A-A and B-B type molecule. So, there may be reaction between the A-B type monomers or between A-A and B-B type monomers.

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Chain-growth	Step-growth
➤ Initiator needed	➤ No initiator needed
➤ Growth occurs by successive addition of monomer units to limited number of growing chains	➤ Growth occurs throughout matrix by reaction between monomers, oligomers, and polymers
➤ Product is the isolated polymer	➤ Product is the reaction mixture
➤ No by-product formation	➤ Generally by-product formation
➤ High MW even at low conversion	➤ High MW only at very high conversion
➤ Generally by addition reactions	➤ Generally by ~~addition~~ condensation reactions
➤ Predominantly carbon back-bone	➤ Predominantly Heteroatom in back-bone
➤ Shorter reaction time	➤ Longer reaction time
➤ Generally low to moderate reaction temperature	

There is a comparison between the two polymerization methods. In the case of chain growth, an initiator is needed and the chain is growing by the addition of monomers at the chain ends. Product is the isolated product and no byproduct formation occurs. High molecular weight polymer can form even at low conversion. This is generally an addition reaction, with polymers having predominantly carbon back-bone. The reaction time is shorter and low to moderate temperature is required.

In the case of step-growth, there is no requirement of an initiator. Growth occurs throughout the matrix by reaction between monomers, oligomers, and polymers. Byproduct formation takes place and the product is the reaction mixture itself. In this case, high molecular weight polymers are formed at very high conversions. This happens by condensation reaction and is predominantly with heteroatom backbone. This takes comparatively longer time and generally, high temperature is required for this case.

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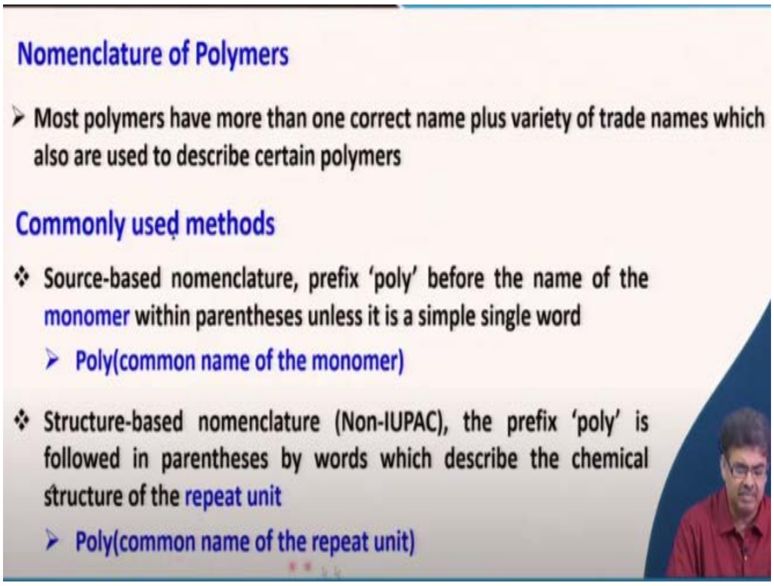

Nomenclature of Polymers

- Most polymers have more than one correct name plus variety of trade names which also are used to describe certain polymers

Commonly used methods

- Source-based nomenclature, prefix 'poly' before the name of the monomer within parentheses unless it is a simple single word
  - Poly(common name of the monomer)
- Structure-based nomenclature (Non-IUPAC), the prefix 'poly' is followed in parentheses by words which describe the chemical structure of the repeat unit
  - Poly(common name of the repeat unit)

Regarding nomenclature of polymers, most polymers have more than one correct name and a variety of trade names. There are mainly two methods used very commonly for naming polymers. One is source-based nomenclature, where we add a prefix before the name of the monomer from which it is synthesized. So basically, it is written as, poly (common name of the monomer). It does not always need to use this bracket if the monomer is a simple single word. If it is a multi-worded monomer name or there are numbers or others, like Greek letters are involved or some isomer name or a stereochemistry are involved then we must put bracket within. It is always safe to put bracket, the name of the monomer from which this is sourced or synthesized.

The second method is based on the structure of the repeat unit. So, in this case, the common name of the repeat unit is in the bracket and poly is before that. Now, this is a structure-based nomenclature (non-IUPAC).

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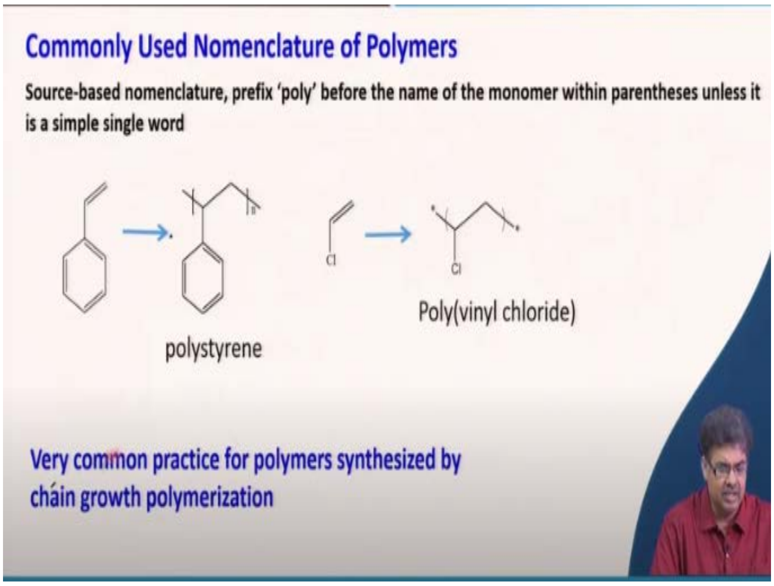

Commonly Used Nomenclature of Polymers

Source-based nomenclature, prefix 'poly' before the name of the monomer within parentheses unless it is a simple single word

Very common practice for polymers synthesized by chain growth polymerization

For example, this polymer is synthesized from the monomer which is named styrene. So, we write the name of this polymer as polystyrene. In another case, the polymer is synthesized from this monomer whose name is vinyl chloride. So, we write this polymer name is poly (vinyl chloride). We are putting the name of the monomer within a bracket. That should be the standard practice. Even if we would put the name styrene within the bracket that also is not a problem but if we do not put a bracket in vinyl chloride, then it actually a problem. So, this is a very common practice for polymers synthesized by chain-growth polymerization.

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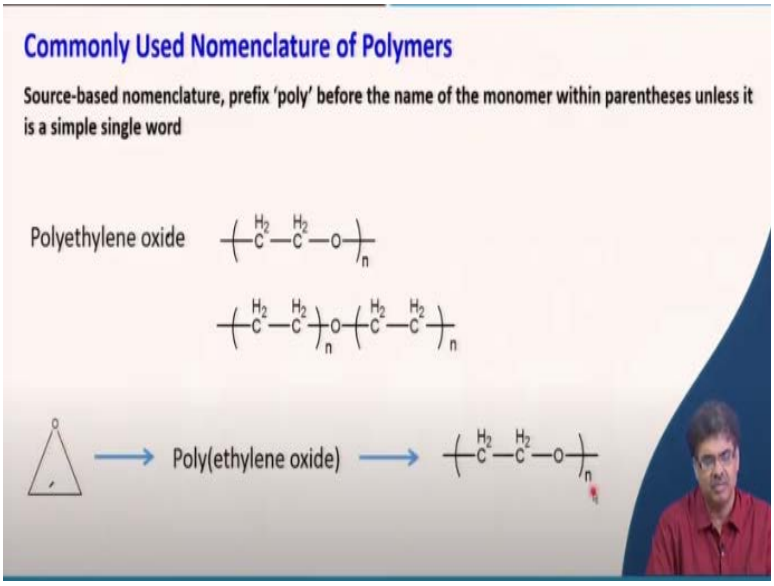

Commonly Used Nomenclature of Polymers

Source-based nomenclature, prefix 'poly' before the name of the monomer within parentheses unless it is a simple single word

Polyethylene oxide $\left[\overset{H_2}{C}-\overset{H_2}{C}-O \right]_n$

$\left[\overset{H_2}{C}-\overset{H_2}{C} \right]_n O \left[\overset{H_2}{C}-\overset{H_2}{C} \right]_n$

$\longrightarrow$ Poly(ethylene oxide) $\longrightarrow \left[\overset{H_2}{C}-\overset{H_2}{C}-O \right]_n$

Now, why we required to put multi-worded names within brackets? In the case of poly (ethylene oxide), if we write polyethylene oxide like this. then it is polyethylene and oxide two are seems different molecule. The polymer is synthesized from a monomer, named ethylene oxide. So, if we put the ethylene oxide within a bracket, then we can certainly say that this is a polymer that is synthesized from a monomer named ethylene oxide.

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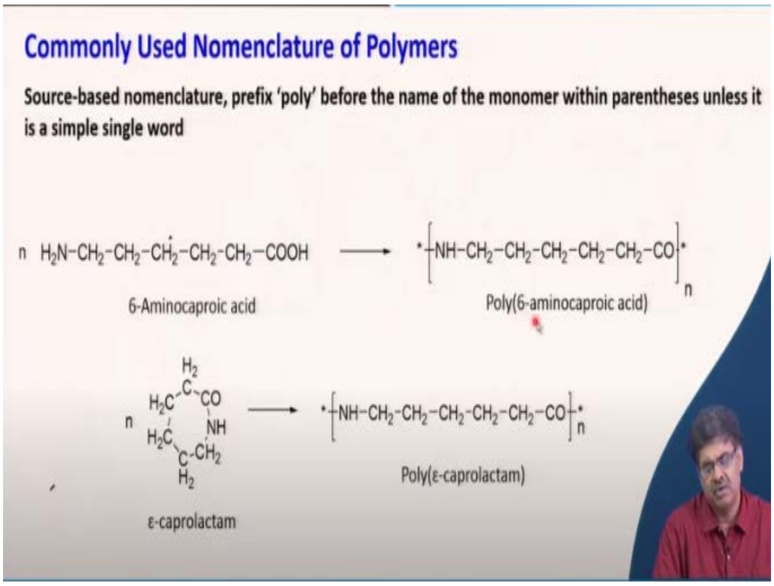

Commonly Used Nomenclature of Polymers

Source-based nomenclature, prefix 'poly' before the name of the monomer within parentheses unless it is a simple single word

$$n\ H_2N-CH_2-CH_2-CH_2-CH_2-CH_2-COOH \longrightarrow *\!\left[NH-CH_2-CH_2-CH_2-CH_2-CH_2-CO\right]_n\!*$$

6-Aminocaproic acid

Poly(6-aminocaproic acid)

$$n\ \text{ε-caprolactam} \longrightarrow *\!\left[NH-CH_2-CH_2-CH_2-CH_2-CH_2-CO\right]_n\!*$$

ε-caprolactam

Poly(ε-caprolactam)

In this case, this polymer can be sourced from 6-aminocaproic acid by a condensation reaction. So, it is called poly (6-aminocaproic acid) and by a ring-opening polymerization reaction poly(ε-caprolactam) is formed from ε-caprolactam.

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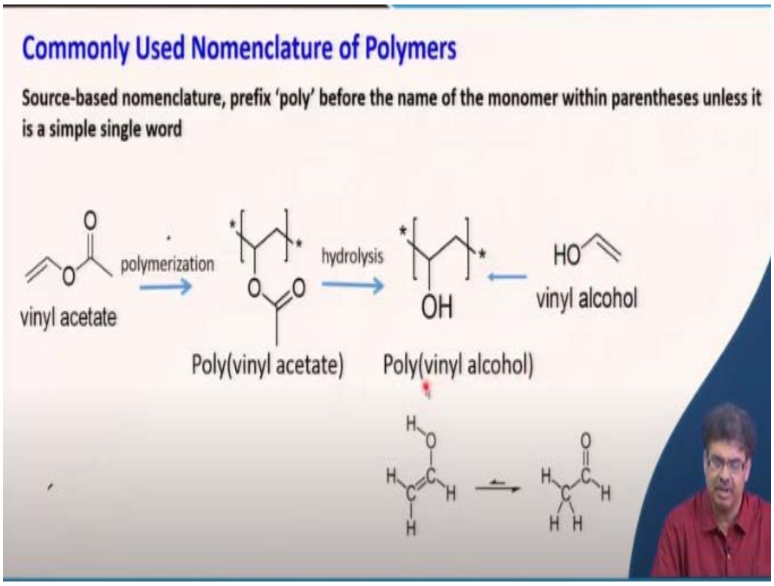

Commonly Used Nomenclature of Polymers

Source-based nomenclature, prefix 'poly' before the name of the monomer within parentheses unless it is a simple single word

Now sometimes what happens, the name of the polymer is such that the monomer name does not exist and it seems like it is a sort of hypothetical monomer from which it is synthesized. If we look at the chemical structure of the polymer poly(vinyl alcohol), it is apparent that this is synthesized from a monomer whose name is vinyl alcohol from the name of this polymer. However, from the structure of vinyl alcohol, it is understandable that it is not stable at room temperature because it tautomerizes and forms acetaldehyde. In fact, we cannot take vinyl alcohol and polymerize it to make poly(vinyl alcohol). It always stays as acetaldehyde. So how the polymer poly (vinyl alcohol) is synthesized? It is synthesized from a monomer vinyl acetate, which polymerizes to make poly (vinyl acetate), and then it is hydrolyzed to make a poly (vinyl alcohol). So that is why poly (vinyl alcohol) does not always contain 100% OH group, few percentages of the substituents are acetate group, still exist. So that is why when you buy polyethylene alcohol you will see that percentage of hydrolyses like 98% or 95%. It means that 95% of the vinyl acetate group has been hydrolyzed to the alcohol group and so on. So, although the name looks like it is synthesized from vinyl alcohol as it is named poly (vinyl alcohol). But it may not be synthesized from that monomer.

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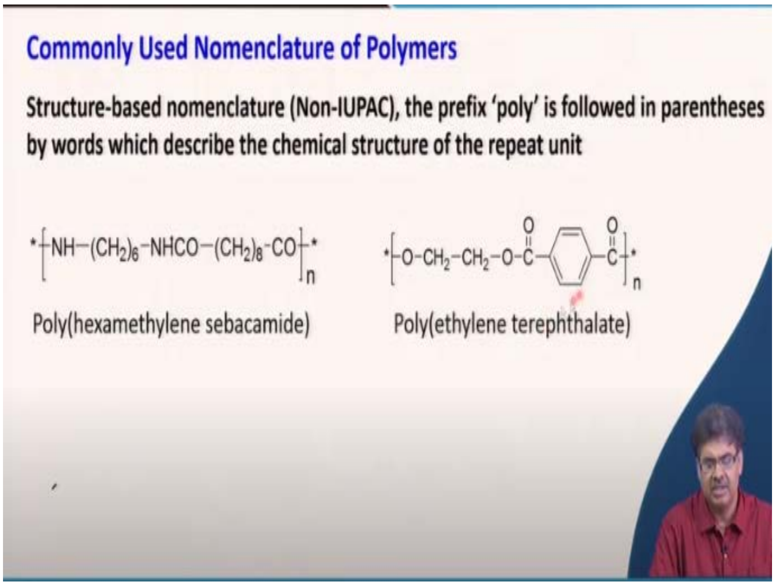

Commonly Used Nomenclature of Polymers

Structure-based nomenclature (Non-IUPAC), the prefix 'poly' is followed in parentheses by words which describe the chemical structure of the repeat unit

$*\!-\!\left[\text{NH}-(\text{CH}_2)_6-\text{NHCO}-(\text{CH}_2)_8-\text{CO}\right]_n\!-\!*$

Poly(hexamethylene sebacamide)

Poly(ethylene terephthalate)

This is a structure-based nomenclature that is very commonly used. For example, in the case of poly (hexamethylene sebacamide), the name of the repeat unit is hexamethylene sebacamide, which is synthesized from hexamethylene diamine and sebacic acid. So, it is an amide. We put the name of this repeat unit within the bracket and put poly before that. That is a structure-based nomenclature and non-IUPAC nomenclature which is commonly used.

Another example for poly(ethylene terephthalate). It is synthesized from ethylene glycol and terephthalic acid. So, it is an ester. There should be 'ate' at the end. It is written as the name of this repeat unit ethylene terephthalate. So we put poly before that and named as poly (ethylene terephthalate). Now, this is a very common practice for polymers synthesized by step-growth polymerization.

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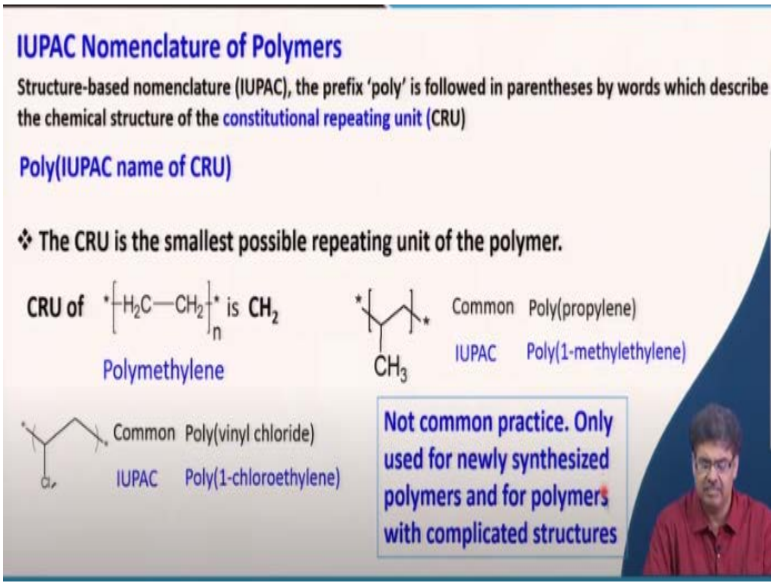

IUPAC Nomenclature of Polymers

Structure-based nomenclature (IUPAC), the prefix 'poly' is followed in parentheses by words which describe the chemical structure of the constitutional repeating unit (CRU)

Poly(IUPAC name of CRU)

❖ The CRU is the smallest possible repeating unit of the polymer.

CRU of $*\left[H_2C-CH_2\right]_n*$ is CH_2

Polymethylene

Common Poly(propylene)

IUPAC Poly(1-methylethylene)

Common Poly(vinyl chloride)

IUPAC Poly(1-chloroethylene)

Not common practice. Only used for newly synthesized polymers and for polymers with complicated structures

In case of the recommended nomenclature system by IUPAC, we have to put the IUPAC name of the constitutional repeat unit and within the bracket and poly before that. The constitutional repeat unit is the smallest possible repeat unit of the polymer. For example, in polyethylene, the smallest part is CH_2. That means, we should name this polymer by putting the IUPAC name of this repeat unit and put poly before that. The name is polymethylene. Similarly, poly(propylene) is commonly known so because the monomer is propylene, but the IUPAC name of this repeat unit is 1-methylethylene. We put the IUPAC name as poly (1- methylethylene). Similarly, in the case of poly(vinyl chloride), the IUPAC name is poly(1-chloroethylene). In practice, the IUPAC naming of polymer is not common. It is used generally in newly synthesized polymers and polymers with complicated structures. But if anyone chooses to name a polymer using the IUPAC name, there is no harm, but it is not a standard practice. Commonly in research, literature, and industries to report polymer, these common names are generally used.

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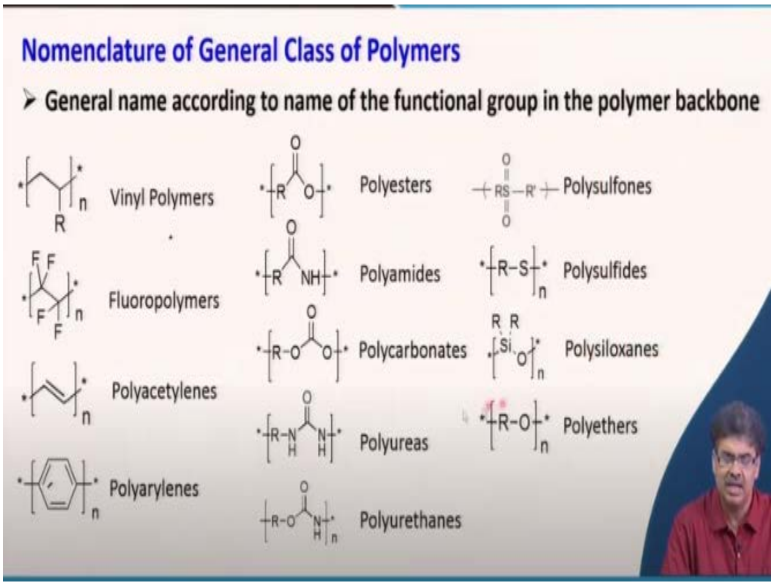

Nomenclature of General Class of Polymers

- General name according to name of the functional group in the polymer backbone

There is another type of nomenclature that is the nomenclature of the general class of polymers and that depends upon the functional group of the polymer backbone. For example, a vinyl polymer containing fluorine groups is called fluoropolymer. There are polyacetylene, polyarenes, polyester, polyamides, polycarbonate, polyureas, polyurethanes, polysulfones, polysulfides, polysiloxane, polyethers, and so on. So, these are named for not any particular polymer, but ares used to represent a general class of similar polymers. We say that polycarbonates are good for making water bottles, polysulfones are making good structural material, polysiloxanes are good for making some rubber and elastomers, and so on.

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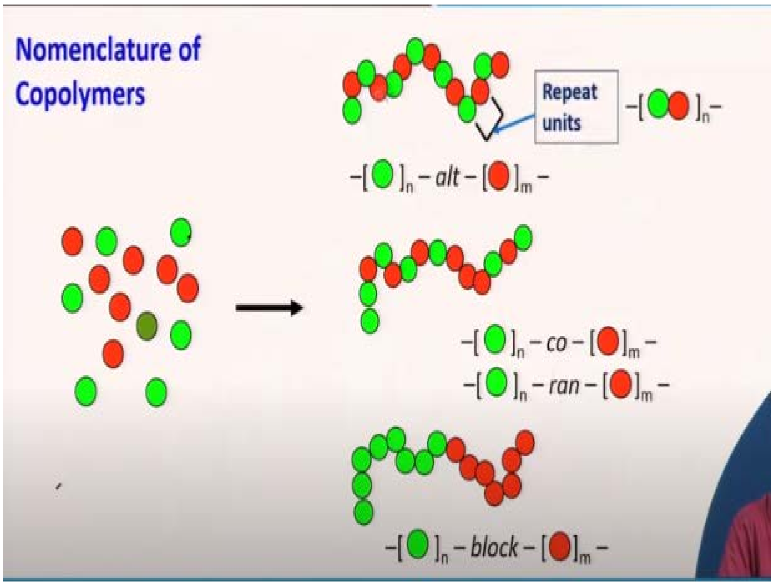

Nomenclature of Copolymers

Now in the case of the nomenclature of copolymers, there is shown schematically that copolymers are synthesized from two monomers. So commonly, the name of the repeat unit is placed within the bracket with n as the number of repeat units and put poly before that. We may also have the copolymer structure where these two monomers are randomly distributed. Also we can have blocks of two monomers. Then we write the name of structures like this; the name of the first monomer and as this is a copolymer we write as a ‘co’ to represent a copolymer and if the comonomers randomly distributed, then we can write it as ‘ran’, to show that this is a random copolymer. In case the monomers form blocks, then we have to write ‘block’ in this.

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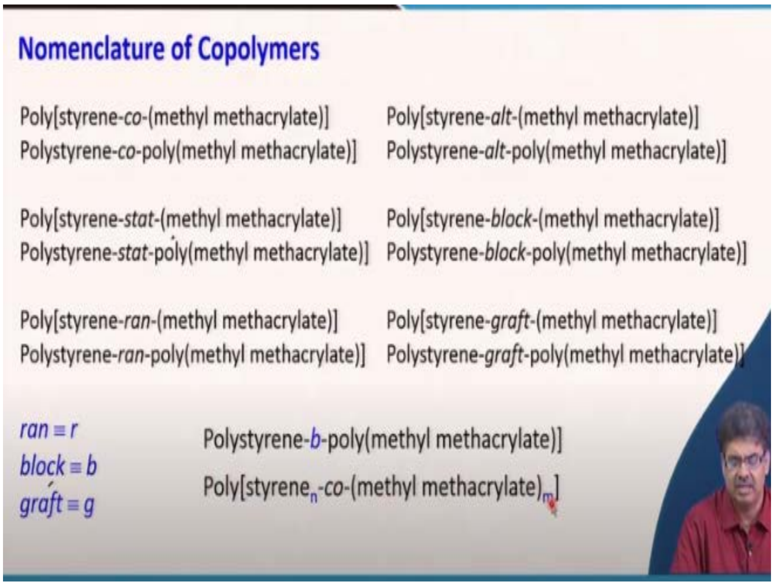

Nomenclature of Copolymers

Poly[styrene-*co*-(methyl methacrylate)]
Polystyrene-*co*-poly(methyl methacrylate)]

Poly[styrene-*stat*-(methyl methacrylate)]
Polystyrene-*stat*-poly(methyl methacrylate)]

Poly[styrene-*ran*-(methyl methacrylate)]
Polystyrene-*ran*-poly(methyl methacrylate)]

Poly[styrene-*alt*-(methyl methacrylate)]
Polystyrene-*alt*-poly(methyl methacrylate)]

Poly[styrene-*block*-(methyl methacrylate)]
Polystyrene-*block*-poly(methyl methacrylate)]

Poly[styrene-*graft*-(methyl methacrylate)]
Polystyrene-*graft*-poly(methyl methacrylate)]

ran ≡ *r*
block ≡ *b*
graft ≡ *g*

Polystyrene-*b*-poly(methyl methacrylate)]
Poly[styrene$_n$-*co*-(methyl methacrylate)$_m$]

For example, we can write poly, and then within a bracket, [styrene-*co*-(methyl methacrylate)] to make it clear that it is just a copolymer of styrene and methyl methacrylate. We can also write this as polystyrene-co-poly(methyl-methacrylate). Both are correct and both are used very frequently. Now if the copolymer is a statistical copolymer, i.e. a statistical distribution of styrene and methyl methacrylate exists within the polymer then we write it as poly [styrene-*stat*-(methyl methacrylate)]. If it is the statistics are a random distribution then we write it as poly [styrene-*ran*-(methyl methacrylate)]. If the monomers are distributed alternatively then we write it as poly [styrene-*alt*-(methyl methacrylate)]. If they are a distributed like blocks, then we write poly [styrene-*block*-(methyl methacrylate)]. And if they are graft then we write it as poly [styrene-*graft*-(methyl methacrylate)]. Now sometimes, we do not write the full word *ran* or *graft* or *block*. We may write '*r*' for random, '*b*' for block, and '*g*' for graft like polystyrene-*b*-poly(methyl methacrylate). And sometimes to specify how many monomers are present within each copolymer fraction, we can put the number 'n' to represent how many styrenes are there in the polymer chain and this 'm' represents how many methyl methacrylates. This is optional, we can write it or if we do not know exactly it does not need to write this thing.

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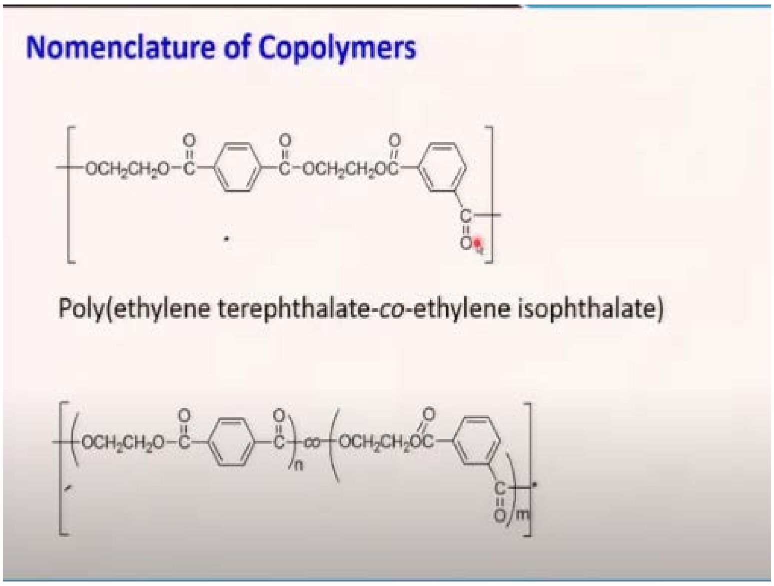

Nomenclature of Copolymers

Poly(ethylene terephthalate-*co*-ethylene isophthalate)

So, in this copolymer, a step-growth polymerization occurs. In this case, ethylene glycol is common, but there are terephthalic acid and isophthalic acid. So, we can write as poly (ethylene terephthalate-co-ethylene isophthalate). It is a better way to represent as ethylene terephthalate, and ethylene isophthalate in two different copolymer residues and then put ‘n’ and ‘m’ to represent how many of such these copolymer units are there.

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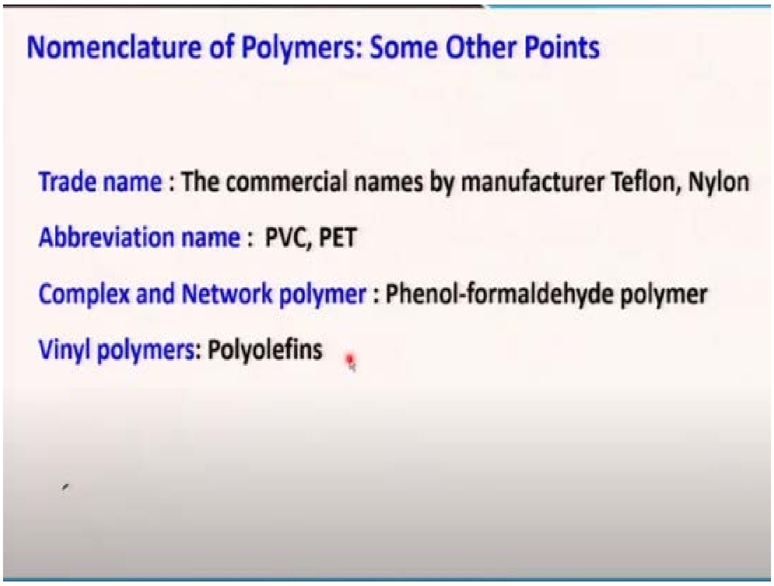

Nomenclature of Polymers: Some Other Points

Trade name : The commercial names by manufacturer Teflon, Nylon

Abbreviation name : PVC, PET

Complex and Network polymer : Phenol-formaldehyde polymer

Vinyl polymers: Polyolefins

Some other interesting points; polymers have trade names in the commercial market e.g. Teflon, or polytetrafluoroethylene that are used for nonstick coating for our cookware. Nylon is very commonly used is the trade name for polyamides. And also, there is a very common abbreviation like poly(ethylene terephthalate), it is so commonly called PET. Bottles are often made from PET, even in a TV advertisement, it is notified as PET material. As it is very common, so it has become a name by itself. So, PET means PET polymer. PVC means polyvinyl chloride. People actually write PVC, and not write poly(vinyl chloride).

And if the polymer is very complex or network polymer then we just write the names of the two monomers, phenol-formaldehyde polymer without just putting any structure for copolymer. It is a network, then we just write phenol-formaldehyde polymer and generally, vinyl polymers are also called polyolefins.

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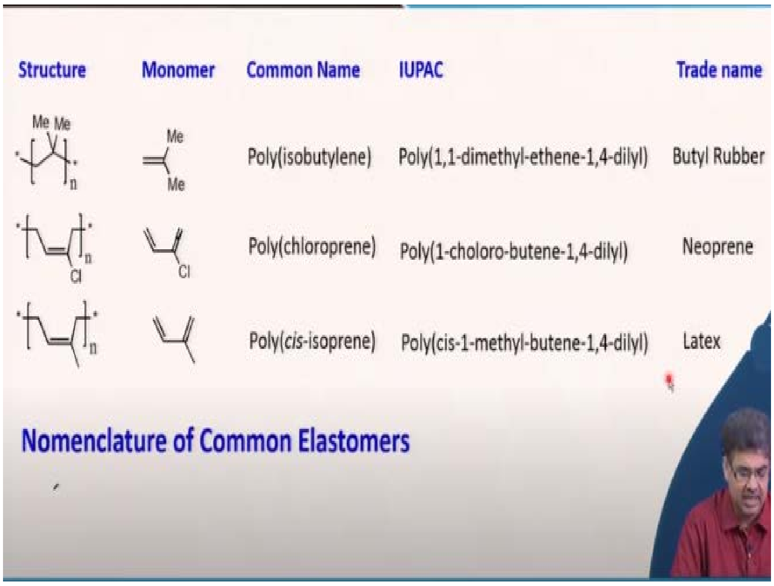

Structure	Monomer	Common Name	IUPAC	Trade name
		Poly(isobutylene)	Poly(1,1-dimethyl-ethene-1,4-dilyl)	Butyl Rubber
		Poly(chloroprene)	Poly(1-choloro-butene-1,4-dilyl)	Neoprene
		Poly(*cis*-isoprene)	Poly(cis-1-methyl-butene-1,4-dilyl)	Latex

Nomenclature of Common Elastomers

Examples of some nomenclature for common elastomers are shown here. There is also the name of monomer from which it is synthesized. In the first case, the common name of the monomer is isobutylene. The IUPAC name is the IUPAC name of this repeat unit, which is 1,1 -dimethyl ethene-1,4-dilyl. So this is the IUPAC name and the trade name for this polymer butyl rubber. So if anyone says butyl rubber, it is not needed to mention that because it is very common. Similarly, if we talk about the polymer in which the monomer is chloroprene, a common name, the IUPAC name is poly and within bracket 1-chloro-butene-1,4-diene i.e. the IUPAC name of the repeat unit. The common name is neoprene from which the neoprene gloves are made. Similarly, latex is a natural polymer and it is the polymer of monomer cis-isoprene.

We will talk about the molecular weight of polymers in the next lecture.