#### Polymer Process Engineering Prof. Shishir Sinha Department of Chemical Engineering Indian Institute of Technology-Roorkee Lecture – 01 Introduction to polymers

Welcome to the Polymer Process Engineering. Hello friends. This is the first lecture of the Polymer Process Engineering where we will deal with the different aspect of the polymers, what are the polymers. I mean you can say this is a brief introduction about the polymers. So, let us see that what different type of topics we are going to cover in this particular lecture. That is the introduction of polymers, that is the brief anatomy of the polymers.

Then we will discuss about the monomers, their functionalities, how they are joining with other monomers and other chains to get a bigger chain. Then we will discuss about the nomenclature of the polymers. Now polymers they cover all aspects of our day to day life. So it is necessary to have a classification of these polymers.



We will discuss about this in the section of classification of polymers. And then we will discuss about the short history of polymerization process. Now see what are the polymers? In itself we can say that we cannot avoid polymers in our day to day life. Like when we start our day from toothbrush and we go to the bed with the cloths or linen etc. Everywhere you will find the role of polymer in our daily affairs.

It also play a very vital role in various industrial applications. It also play a very vital role in different type of aspects which are very closely related to our day to day affairs. So now it is a duty of me to have a brief introduction about polymers. Now basically the polymers are macromolecules and they are caused by the joining several small molecules they are called monomers. Now this joining of these monomers is again a very cumbersome process and it is a very technical process.

We will discuss all these things. Now the high molecular weight substance that results from the single repeating unit is known as polymer. So if you say that we are joining 1 monomer, 2 monomer, 3 monomer. So if you see the different masses in that particular mass then you will see that the mass is having a high molecular weight substance. And the large molecules with the large molecular masses make up polymers.

# **Introduction to polymers**

- Polymers are macromolecules created by joining several tiny molecules known as monomers.
- The high molecular weight substance that results from a single repeating unit is known as a polymer.
- Large molecules with large molecular masses make up polymers. For instance, polyethylene is created when several ethylene molecules join as monomers.
- The starting point for creating a polymer is a monomer. "Polymerization" is the process of combining monomers to create a giant molecule.

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For instance the polyethylene is created when several ethylene molecules they join together as a monomer and they form a long polyethylene chain. So how we can designate this particular process and this particular process of creation of a polymer like example of ethylene monomer they joined together to form the polyethylene. This process is called the polymerization. So in a very scientific language we can say polymerization is a process of combining monomers to create a giant molecule. Now based on the various physical characteristics like you see we will find some hard polymers, some soft polymers, some flexible polymers all these things.

So based on their physical characteristics high polymers they are defined having the high degree of polymerization where oligopolymers they are defined as a relatively low degree of polymerization. We will discuss all these things in due course of time because see when we see from toothbrush to the linen there are variety of spectrums like what we are using here in the computer the hard polymers. So different type of polymers they are coming across our day to day life. So therefore different type of a polymerization process are there. Now then when we are talking about the degree of polymerization the question arises that what is the degree of polymerization? So the degree of polymerization is a total number of single monomer units that are joined together to form a polymer.

# **Introduction to polymers**

- Based on this physical characteristic, high polymers are defined as having a high degree of polymerization, whereas oligopolymers are defined as having a relatively low degree of polymerization.
- Degree of polymerization is the total number (n) of single monomer units that are joined together to form a polymer.
- By dividing the word monomer into its two constituent partsmono, which stands for one, and mer, which stands for part—it can be understood.

So by dividing the word monomer into its two constituents parts mono which stands for one and mer which stands for part so it can be understood. So monomer and then monomer, monomer, monomer they form the polymer. So let us have a brief discussion about the monomer. This is the smallest unit of a polymer or you can say the building dock of polymer which is called the monomer. They are bonded together by covalent bond in repeating unit to form a complex structure that is known as polymer.

#### Monomer

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- The smallest unit of a polymer is called a monomer. Monomers are bonded together by covalent bonds in repeating units to form a complex structure known as a polymer.
- Monomers are building blocks of the polymer structure, and they have ability to bond with each other to form a long chain.
- To produce the lengthy chain, the monomer must have at least two reactive groups at both ends.

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Now by this way you can predict that there must be some specific things should be there in monomer so that they can form a bond maybe unsaturation, maybe some other speciality things. This gives enough opportunity to form the different type of polymers. So to produce the lengthy chain obviously the monomer must have at least two reactive groups at both ends. So definitely it is a very you can say very specialized type of a thing. Every chemical component cannot become the monomer must have some specialized things maybe such unsaturation, maybe the reactive groups something like this so that they can form a reaction and then they can build up the chain over the period of time.

So when we are talking about the functionality of monomer because one functional group should be there in the monomer to form the polymeric chain then question arises that what is functionality? So the monomers functionality is usually determined by the number of bonding sites it has with other molecules under the circumstances of the polymerization process so that the reaction can take place over those functional sites. Now therefore, say a bi-functional monomer is a monomer with the functionality of two and it can link to other molecules under the suitable condition. We will discuss about the suitable condition in due course of time. Now a monomer that may interact with more than two molecules during the polymerization event is said to be the poly function. Now let us take an example of vinyl monomer.

#### **Functionality of a monomer**

- A monomer's functionality is determined by the number of bonding sites it has with other monomers under the circumstances of the polymerization procedure.
- Thus, a bifunctional monomer is a monomer with functionality two, and can link to two other molecules under suitable conditions.
- A monomer that may interact with more than two molecules during polymerization events is said to be polyfunctional.
- Using vinyl monomers as an example, the double bond (CH<sub>2</sub> = CHX) can be thought of as a location for two free valencies.



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Now this is our vinyl monomer. Here you see that this is the double bond. Now which is a reactive site? So the double bond can be thought of as a location of two free valencies. So one can be joined over here and other can be joined over here. So this can be a building block.

So when we call about the polyvinyl then again a monomer can join with this. By this way another double bond may act as a functional site. Now usually when we talk about the different type of a polymers then obviously there are several questions arises like what are the nomenclature of the polymers, what are the polymers, how we can classify them so that we can use those polymers in a different aspect. So usually the polymers are classified into four groups. Now based on the use, based on the variety of the reasons, applications, chemistry, and engineering, polymers can be classified in the variety of scopes like thermoset polymers, thermoplast polymers but here we are discussing about the chemistry aspect that how we can classify the polymers.

So one is the homopolymer. The polymer that is created from just one kind of a monomer or one kind of a structural unit and the homopolymer these characteristics are mainly specified by the monomer. For example, if you say that styrene or propylene. Now when we form the polypropylene from the propylene this is called the homopolymer. So at room temperature for example, a room temperature polystyrene is a rigid solid where the polybutyl acetate is flexible and sticky.

#### **Nomenclature of Polymers**

Polymers are classified into four types **Homo-Polymer** 

The polymer that is created from just one kind of monomer, or one kind of structural unit. The homo-polymers' characteristics are mainly specified by the monomer. At room temperature, polystyrene, for instance, is a rigid solid, whereas poly (butyl acrylate) is flexible and sticky. Example;

Neoprene, PVC, polystyrene, polypropylene, polyethylene etc. are examples of the homo polymer.

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So, you see that this all depends on the nature of the monomer. How this thing like vinyl chloride polyvinyl chloride it all depend on their basic nature and that is why they are clubbed under the head of a homopolymer. Now let us talk about another classification that is copolymer. These copolymers are polymers made from two or more different types of monomers. Many of the commercially significant polymers are copolymers, and in copolymers, the order in which the monomers are arranged is varied you can say the start of engineering is involved in the creation of these copolymers, and it is just like the art of developing different type of copolymers for the variety of the end uses.

Now the different type of monomers and their arrangement usually they affect the copolymers quality so because it is quite obvious you are having the different monomer and you are having the different arrangement it is just like that here you are having like this or like this linear or branched. Now there are two homopolymers they can join to create a single polymer chain to create a block polymer. So there are different type of copolymers including statistical random alternative block gradient graft copolymers all these things based on the sequential distribution of all monomers. So if you have any structural analysis or if you have any kind of structure then definitely you will find another different type of copolymer. Another is the statistical or random copolymer.

# **Nomenclature of Polymers**

#### Copolymers

- Copolymers are polymers made from two or more different types of monomers. Many of the commercially significant polymers are copolymers. In copolymers, the order in which the monomers are arranged is varied.
- The different types of monomers and their arrangements affect the copolymer's qualities. Two homo-polymers are joined to create a single polymer chain to create a block copolymer.
  - There are several different types of copolymers, including statistical/random, alternative, block, gradient, and graft copolymers, based on the sequential distribution of the monomers.

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Now the sequential distribution of monomer in these copolymers complies with the statistical law and usually these monomers are bonded at a random in the polymer chain to form the random copolymer. There are different type of methods used to produce the random copolymer like nearby units sometimes do not affect the likelihood of finding a single monomeric unit at any given a place in the chain. So you see that this is a permutation combination type of a thing. Now random copolymer structures of polymer depends upon the random attachment of monomer into the backbone of polymer. So again this is you see purely mathematical aspect in this aspect.

# Nomenclature of Polymers

#### Statistical/random copolymer

- The sequential distribution of monomers in these copolymers complies with the statistical law. Monomers are bonded at random in polymer chains to form random copolymers. The Markovian zero-order method is used to produce the random copolymer. since the nearby units do not affect the likelihood of finding a single monomeric unit at any given place in the chain.
- Random copolymer structure of polymer depends upon the random attachment of the monomers into the backbone of the polymers.

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For example, like PMMA polymethyl methacrylate butyl acrylate this is formed with a random copolymerization of methyl methacrylate and butyl acrylate monomer by free radical polymerization. Alternate copolymers like copolymers they are made up of two monomeric unit types dispersed in alternate series it is known as alternate copolymer. So one may be like this another may be like this,

this is y like this. Example is that polystyrene, malleic and hydride this is formed by the alternative attachment of monomer such as styrene and malleic and hydride by the free radical polymerization. So we are using different type of a terminology like called free radical polymerization etcetera.

Nomenclatu	re of Polymers
Example;	
Poly(methyl methacrylate-stat-butylacrylate) is formed by random	
copolymerization of methyl methacryl	ate and butyl acrylate monomers by
free radical polymerization process.	
Alternate co-polymers	
A copolymer made up of two monomeric unit types dispersed in alternate	
series is known as an alternating copolymer.	
Example;	$\times \to \times \to$
Poly(styrene-alt-meleic anhydride) is for	rmed by
alternatively attachment of monomers (s	uch as styrene
and maleic anhydride) by free radical po	lymerization
method.	-
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Now these are the different polymerization techniques. Now let us have a discussion about the block copolymer. Now in these copolymers the building blocks of varied monomer compositions they are linearly organized. Now see when we talk about the linearly organized there may be certain type of polymers like this is the linearly organized sometimes another you can say the backbone is connected then this may be called as a branch type of a thing. Now these blocks are mixed with homopolymer and copolymer with a different composition.

# Nomenclature of Polymers

#### **Block co-polymers**

In these copolymers, the building blocks of varied monomer compositions are linearly organized. The blocks are mixes of homo-polymers and copolymers with different compositions.

#### Example;

Polystyrene-block-polybutadiene-block-polystyrene copolymer having the linear arrangement of monomer blocks of different components such as styrene and butadiene synthesized by ionic polymerization method.

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One example is that polystyrene, polybutadiene block polymerization of the polystyrene copolymer is having the linear arrangement of the monomer block of a different component like styrene and butadiene. They are synthesized by the ionic polymerization method. So you see that we can join the two monomer in different aspects and how they are joining this determines the classification or the class of polymers. Another classification of polymer that is based on the source. You see that when we discuss about the use of polymer you will find that variety of uses are there and these polymers are embedded in every aspect of our day to day life.



So you see that there are certain natural polymers, there are certain synthetic polymers, nature has given so many type of a polymers. So based on the source of the polymer that is what is the different sources of polymer they can be classified into the synthetic or a natural. Now there are variety of natural polymers. Now these polymers are found in the plant, animal, examples are protein, cellulose like cotton you are using the natural cotton these are the natural polymers, starch, raisins, rubbers all these are the natural polymers.

#### Synthetic Polymers:

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Synthetic polymers are made from lower molecular weight molecules derived from natural feedstock and petroleum.Man-made polymers include a wide range of synthetic materials including plastic (polythene), synthetic fibres (nylon 6) and synthetic rubbers (Buna-S).



Svnthtetic Polymers

Now these are the cellulosic derivatives like cellulose, acetate, rayon that is very common name and the cellulose nitrate so these are the semi synthetic polymers. Another is the synthetic polymers. Now synthetic polymers they are made from a lower molecule derived from the natural feedstock and you see the petroleum or the crude oil is the backbone of this particular synthetic polymer source. So manmade polymers they include a wide range of synthetic materials including the polyethylene synthetic fibers, nylon 6, 6 synthetic rubbers all these things they are attributed in the synthetic polymer. You see that almost 60, 70 percent of the polymer mass chunk is attributed to the synthetic polymers.

Another classification is based on the backbone of the polymer chain. One example is that organic polymers. The organic polymers they are defined as those with the backbone chain primarily composed of carbon atoms. But you see that typically atoms of hydrogen, oxygen, nitrogen all these they are connected to the side valencies of the backbone carbon atom and the most artificial polymers are made of organic compounds.

Another form is the inorganic polymers. Now organic, inorganic polymers they are those who typically chain backbone does not contain any kind of a carbon atom. It is quite obvious by the name, name implies organic and inorganic. So carbon atom represents an absence of carbon atom plays a very vital role. So this the example of inorganic polymers are silicon rubber, glass all these are the thing. Then another classification is based on the structure of polymers.

# Based on Backbone of the polymer chain: Organic Polymers: Organic polymers are defined as those with a backbone chain primarily composed of carbon atoms. But typically, atoms of hydrogen, oxygen, nitrogen, etc. are connected to the side valencies of the backbone carbon atoms. Most artificial polymers are made of organic compounds. Inorganic polymers: On the other hand, inorganic polymers are those whose typical chain backbone does not contain a carbon atom. Examples of it include silicone rubber and glass.

So in the previous slides we discussed about the linear branch all those things. Now it is a time to have a discussion about all those things. Now the linear polymers, these polymers are made up of a lengthy chains. For example, the polyvinyl chloride and high density polyethylene. You see that here these are the linear chains and they are performing with the secondary bonding.

# **Classification of polymers**

#### Classification Based on the Structure of Polymers:

#### Linear Polymers:

These polymers are made up of lengthy, erect chains. Examples include PVC and high-density polythene.



So primary bonding is this one and this one is the secondary bonding. So this is the linear one. Another is the branched polymers. There are certain polymers such as LDPE or low density polyethylene or high density polyethylene or linear low density polyethylene or low density polyethylene. This comprises of linear chains with some branching. Here you see that these are the typical examples of HDPE, LDPE, LLDPE. Here you see this is the HDPE. You can clearly see that these are the small spherical shapes. They are the monomers and they are clubbed together and some sort of this branching is there.



These are the branched polymers. Similarly, here you see that this is LLDPE. You see these are the monomers, these are spherical shapes there and these monomer chain, they are branched together to give a branched linear low density polyethylene. So in a more you can say anatomically way, this is the way here they can form the branched polymers. Another this is again very important polymers.



These are the cross-linked polymers. They typically consist of strong covalent connections between the several linear polymer chains. Here you see that there may be certain V covalent bonds may form among these chains, but herein the cross-linked you see that these are the strong covalent bonds. So they form the network and sometimes they are referred as a network polymers. So the basic backbone of these cross-linked polymers are the strong covalent bond and presence of a linear polymer chain. Now these chains and the best example is the vulcanized rubber urea formaldehyde.

You see that all different kind of switches, electrical switches which you are using in your officially office or the domestic purpose, they are form of the urea formaldehyde resins and other linear polymers they are made from bi-tri-functional monomers. And under the most circumstances these cross-linked polymers are either solid and they do not melt, soft or dissolve. So you see the disposal of these polymers again very burning issue. Another stream of classification is based on the mode of polymerization and this is more engineered classification. This can be classified based on the polymerization mode into two different subgroups, addition polymerization and condensation polymerization.

Now let us talk about the addition polymerization first. Now the repetitive addition of monomer molecule with double or triple bonds in the production of addition polymerizations like polyethylene from ethane and polypropylene from propane. Now here you see that this is a monomer. Now if you add on, add on, add on this is from the addition polymerization. Condensation polymerization, they are formed by repeated condensation reaction between the two different bi-functional or trifunctional monomeric units.



In these polymerization reaction the elimination of small molecules may be water, may be alcohol, may be HCL, these take place. So that the bonding can be created in between these monomers. So example is terylene or sometimes it is referred as a dekron, nylon 6, nylon 6, 6, etc. This is the example is nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipic acid.

**Condensation Polymers:** The condensation polymers are formed by repeated condensation reaction between two different bi- functional or tri-functional monomeric units.

In these polymerization reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place. The examples are terylene

(dacron), nylon 6, 6, nylon 6, etc. For e.g., nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipic acid.



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So water can be eliminated from this. Another example of classification is based on the molecular forces. So the mechanical properties of the polymers they are governed by intermolecular forces, Van der Waal forces and hydrogen bonds they are present in the polymers. Now these forces also bind the polymer chains so that the interaction among the either chain or monomer can be intact. Now under this category the polymers they are classified into different groups that is based on the magnitude of intermolecular forces present in them. Typically they are clubbed as elastomers, it is a very common name, fibers, liquid resins and plastics.

# **Classification of polymers**

#### Based on Molecular Forces:

The mechanical properties of polymers are governed by intermolecular forces, e.g., van der Waals forces and hydrogen bonds, present in the polymer. These forces also bind the polymer chains.

- Under this category, the polymers are classified into the following groups on the basis of magnitude of intermolecular forces present in them. They are
  - (i) Elastomers
- (ii) Fibers
- (iii) Liquid resins
- (iv) Plastics

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Let us take the example of elastomers. Now these the rubbers, rubber obviously we have discussed can be found in two ways, one is natural rubber and the second one is a synthetic rubber. These are the elastomers or the rubbers, they are like solids with elastic properties. Now in these elastomers, the polymers, the polymer chain they are held together by the weakest intermolecular forces. Now

you see when we talk about the linking of the monomer or the chain, then there must be some molecular forces like this.

# **Classification of polymers**

#### **Elastomers:**

- These are rubber like solids with elastic properties.
- In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the
- polymer to be stretched. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanized rubber.
- The examples are buna-S, buna-N, neoprene, etc.

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These forces may be strong like this, or some may be weak. So this all depends on the chain structure. So these elastomers are joined together by weak intermolecular forces and these weak binding forces permit the polymer to be stretched like here. You see that this is stretched. A few cross-linked they are introduced in between the chain which help the polymer to retract to its original position after the force is released as in the vulcanized rubber. Now the thing is that these forces can be triggered by various factors, maybe mechanical force, maybe thermal force or maybe the chemical force.

Another example is the fibers. Now if drawn from the long filament like material, its length is at least 100 times its diameter, the polymer set to be covered into the fibers. Fibers are the threat forming solids which possesses the high tensile strength and high molecules. Now these characteristics can be attributed to the strong intermolecular forces like hydrogen bonding and these strong forces also lead to close packing of chains and thus impart the crystalline structure or the crystalline nature. Example is terra-line, nylon 6-6 all those things and you see that it is a very co

#### Fibers:

- If drawn into long filament like material whose length is at least 100 tim its diameter, polymers are said to have been converted into 'fibre'.
- Fibres are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also le to close packing of chains and thus impart crystalline nature.
- Examples are polyamides (nylon 6, 6), polyesters (terylene), etc.

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mmon thing all the clothings etcetera they are attributed to these man-made or synthetic fibers.

Let us talk about the liquid resins. The polymers used as adhesive, potting compound, sealants etcetera the liquid form and they are clubbed under the liquid resin. So when you flow the liquid to the atmosphere they may form, they may get polymerized by either atmospheric oxygen or air or atmospheric moisture. So the best example in this category is epoxy adhesive or polysulfide sealants. Now plastics, it is a very common thing. Now a polymer can be shaped into the hard and tough utility items by the application of heat and pressure.

#### Liquid Resins:

- Polymers used as adhesives, potting compound sealants, etc. in a liquid form are described liquid resins.
- · Examples are epoxy adhesives and polysulphide sealants.

#### **Plastics**:

- A polymer is shaped into hard and tough utility articles by the application of heat and pressure; it is used as a 'plastic'.
- Typical examples are polystyrene, PVC and polymethyl methacrylate. They are two types (a) thermoplastic and (b) thermosetting plastic.

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Now it is used as a plastic. Many may say that this plasticity is the behavior and in the polymers we are utilizing this particular behavior. The typical example are polystyrene, PVC, polymethane, methacrylate. Now when we talk about these plastics again they can be sub classified into two ways. One is the thermoplastic and second one is the thermosets.

Let us have a brief outlook about the thermoplastic polymers. Some polymers they used to get or they used to acquire a soft character upon heating. This can be converted into the thermoplastic classification and they can regain their original shape upon cooling. Now this process of heating or reshaping and retaining the same, this can be repeated several times and such polymers that can be softened on the heating or stiffened on the cooling they are termed as thermoplastic. Now it is a beautiful property because when the any kind of commodity plastic it completes its life cycle then by utilizing this particular property it can form, you can melt these thermoplastic polymers to shape another one utility item. So this is a very very essential and a very beautiful property of these thermoplastic polymers.

Now these thermoplastic polymers they are linear or slightly branched long chain molecule. They are capable of repeatedly softening and heating and hardening on cooling subjected to the breakage of their bonds. Polyethylene, PVC, nylon all these sealing wax they are best example of thermoplastic polymers. Let us talk about the thermosetting polymers. Some polymers they undergo some chemical changes upon heating and convert themselves into infusible mass.

#### Thermoplastic Polymers:

- Some polymers soften on heating and can be converted they can retain on cooling.
- The process of heating, reshaping and retaining the san can be repeated several times. Such polymers, that
- soften on heating and stiffen on cooling, are termed thermoplastics.
- These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling.
- Polyethylene, PVC, nylon and sealing wax are examples of thermoplastic polymers.

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They are like yoke of air which on heating sets into the mass and one set cannot be reshaped or you cannot revert to its original condition. Now these polymers that become the insoluble mass on the heating they are called the thermosetting polymers. Its mechanical strength is on the higher side.

# **Classification of polymers**

#### Thermosetting Polymers:

- Some polymers undergo some chemical change on heating and convert themselves into an infusible mass. They are like the yolk of egg, which on heating sets into a mass, and, once set, cannot be reshaped. Such polymers, that become and insoluble mass on
- heating, are called 'thermosetting" polymers.
- These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible.
- Some common examples are <u>bakelite</u>, urea- <u>formaldelyde</u>

Cesins, etc. (

This is a beautiful property. Now these polymers are cross-linked. We discussed this cross-linking behavior in a couple of slides before. And they are heavily branched molecules that on heating undergo extensive cross-linking molds and again become infusible. Some of the examples like bacalite urea formaldehyde. Now the advantage or disadvantage of these polymers are they are once configured into any shape they cannot be reconfigured. So that is an important thing and by this way the recycling of these polymers is the biggest challenge.



Thermosetting





Thermoplastic

#### Thermosetting Polymers:

- On heating, some polymers go through a chemical shift and transform into an infusible mass. They are similar to the way that an egg yolk solidifies when heated and cannot be reconfigured once it has done so. Thermosetting polymers are those that solidify
  - into an insoluble mass when heated.
- These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible.
- Some common examples are bakelite, urea- formaldelyde resins, etc

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Thermosetting

Now, let us talk about the short history of the polymerization process. Now, the reason is that because there is a process, a set process covered triggered by various kinds of aspects like maybe initiator, maybe the application of the temperature, maybe the application of the pressure, and this triggers the polymerization process because the joining of different molecules is an art. So, in the early 1830s, several scientists created a semi-synthetic cellulose derivative like celluloid and cellulosic acetate. Now natural polymers are generated by our mother nature, and they were processed in the 19th century to make valuable products like cellulose, starch, natural rubbers, etc. Later in 1840, there were several scientists discovered that the addition of sulfur to the raw material raw natural rubber helps to prevent the material from becoming sticky, and that gives an idea about synthetic rubber. Charles Goodyear, who was born in New Haven, Connecticut, in December 29, 1800 he invented the vulcanization cycle in 1839.

# A short history of polymerization process

- In the 1830s, Henri Braconnot and Christian Schonbein created semisynthetic cellulose derivatives like celluloid and cellulose acetate.
- Natural polymers generated by Mother Nature were processed in the 19th century to make valuable products, including cellulose, starch, and natural rubber from Hevea brasiliensis.

• In1840s, Friedrich Ludersdorf and Nathaniel Hayward discovered that on the addition of sulfur to raw natural rubber it helps to prevent material from becoming sticky.

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Now in the 1830s he discovered the sulphur vulcanization of a natural rubber by accident and in 1844 received the US patent for this particular work. The process of vulcanization of the rubber makes it heat resistant without a change in the flexibility, and it is the first successful and commercialized product in the polymer science. Now you see that this is the backbone of your tires. Now you see that from cycle tire to aircraft tires, you see what the importance of this particular process is. Now by treating the cellulose with nitric acid in 1847, the Christians created the cellulosic nitrate which was utilized in 1860 to make the celluloid a synthetic thermoplastic and sometimes go back to the history of celluloid films.

# A short history of polymerization process

- Charles Goodyear born in New Haven, Connecticut on 29 December 1800, invented the vulcanization cycle in 1839.
- In the 1830s, he discovered the sulfur vulcanization of natural rubber by accident and in 1844 received U.S patent for this work.
- The process of vulcanization of rubber makes it heat resistant without a change in the flexibility. It is the first successful

and commercialized product in polymer science.

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They were very much popular in 1884 the coordinate they developed the first artificial fiber plant which was based on the viscous rayon or regenerated cellulose. Then, Thomas Graham they proposed in 1861 that collides an aggregated form of tiny molecules such as cellulose and other polymers were held together by unidentified intermolecular interaction. Then Herman this was a German organic chemist who demonstrated the presence of polymers this can he characterize the macromolecules although these the macromolecules they are the another term of polymers and he received the Nobel Prize in 1953 for this particular work. He is also known as for his discovery of strong reaction and the ketenes and Stodinger considers the macromolecules as a pure aggregates of a smaller molecule that were closely connected. And the next year the polypropylene joined the list of commercially available polymers and right after polyethylene, polystyrene and polyvinyl chloride.

# A short history of polymerization process

- By treating cellulose with nitric acid in 1847, Christian F. Schonbein created cellulose nitrate, which was <u>utilised</u> in the 1860s to make celluloid, a synthetic thermoplastic.
- In 1884 Hilaire de Chardonnet developed the first artificial fibre plant which was based on the viscous rayon or regenerated cellulose.
- Thomas Graham proposed in 1861 that colloids and aggregated forms of tiny molecules, such as cellulose and other polymers, were held together by unidentified intermolecular interactions.

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Further, Staudinger he proposed the polymers are composed of a long chain of atom together with the covalent bond. So, this is the basic chemistry. Then Staudinger this gave the first empirical description of a macromolecule in the beginning of the 20th century and the new technique were developed at the same time to evaluate particular material with the special properties. Now, Leo Baekeland created the Bakelite, the thermosetting material used in electric and home appliances everywhere you will find this Bakelite is there the cross-link polymer where you need you can see the barrier between the heat and your hands.

You will see that there is some thermoset polymer. So, in 1907 by the polymerization of phenol and formaldehyde they created the phenol formaldehyde resin. DuPont in 1930 they produced a new variety of polymers such as synthetic rubber, nylon and Teflon. A very interesting story about the nylon it was invented in New York and London simultaneously that is why it is named even the nylon. In 1930 the research group developed the models for the distribution of chain length in the batch reactor from different polymer chemistries and which was further in 1940s refined to more complex and systematic model which is still used today. The emergence when we discover the nylon and polyethylene they began in 1940 with the development of a novel synthetic polymer because everybody was engaged in developing the novel materials.

# A short history of polymerization process

- Leo Baekeland created Bakelite, a thermosetting material used in electric and home appliances, in 1907 by polymerizing phenol and formaldehyde to create phenol-formaldehyde resin
- Du Pont in 1930s produced a new variety of polymers such as synthetic rubber, Nylon and Teflon.
- In the 1930s, the research groups developed models for the distribution of chain length in the batch reactors from different

polymer chemistries, which was further in 1940s

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are still used today.

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Now this includes the synthetic rubber, synthetic fiber from the limited natural resources. So, Hermann Mauck they found a polymer research center at Brooklyn Polytechnic in US in 1946 which sets the standards for disciplines, pedagogy and curriculum. The Breton Chemical Society, the premier in the chemical research, the Poly Division, this was established in 1950 and since expanded to become the association of the second largest division with 8000 members. Professor Danbeck the founder of Breton Chemical Works in Wakefield, he was born in Luton in 30th May 1911. Professor Danbeck was among the first to apply the principle of chemical reaction engineering to the polymer reaction engineering at the same time because some reaction engineering need to be addressed the problem so that we can develop more and more different polymers for utility application.

# A short history of polymerization process

- The emergence of Nylon and polyethylene began in the 1940s with the development of novel synthetic polymer materials including synthetic rubbers and synthetic fibres made from limited natural resources.
- Herman Mark founded a polymer research centre at Brooklyn Polytechnic in the United States in 1946, which set the standards for the discipline's
- pedagogy and curriculum.
- The American Chemical Society's POLY division was established in the 1950s and has since expanded to become the

association's second-largest division with 8000

members.

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This was considering the polymerization reaction to both the chemical and process level. These processes were graded as a homo continuous and hetero continuous on the basis of degree of mixing.

Similarly, Ziegler, Ziegler was a German chemist who together with Nata, both of them they received the Nobel Prize in the chemistry in 1963 in the polymer research by the Ziegler-Nata process. So, the single polymer crystals they were discovered and stereospecific propylene and ethylene polymerization methods. This was developed in 1950 and thanks to the Ziegler-Nata catalyst based on the transition metal.

# A short history of polymerization process

- Giulio Natta is an Italian chemist and Nobel Prize recipient. He shared a 1963 Nobel Prize in Chemistry for the work on strong polymers with Karl Ziegler.
- He began studying the polymerisation of olefins and the kinetics of subsequent parallel reactions in 1938.
- He expanded Ziegler 's work on organometallic catalysts to stereospecific polymerisation.

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Now, the development of polycarbonates from the polymerization of a phosgene and bisphenol A. Now the groundbreaking research on organometallic compounds was triggered and honored by the Nobel committee because it triggered the unique polymerization reaction and led to the deployment of the cutting edge, highly effective industrial process. Now, Natta, he was an Italian chemist and a Nobel Prize recipient, he shared this Nobel Prize with Ziegler and they worked and they formed a Ziegler-Natta catalyst, Ziegler-Natta Reaction scheme and many things they have developed Now they began studying of polymerization of olefins and kinetics of subsequent parallel reactions in 1938. Now discovering the novel polymer groups, they are having sterically ordered structure such as atactic polymers, isotactic and non-linear nonbranched olefinic polymers. So, in the laboratory of Montecatini, Isotactic polypropylene manufactured first on industrial scale in 1957 and the product successfully marked as a plastic fiber.

# A short history of polymerization process

- Discovering novel polymer groups having a sterically ordered structure, such as atactic copolymers, isotactic polymers, and linear non-branched olefinic polymers.
- In the laboratories of Montecatini, isotactic polypropylene manufactured first on an industrial scale in 1957 and the product successfully marketed as plastic fibre.



So, by employing the inert solvent as a heat sink and the flashing the monomer after condensation outside the reactor, the heat of polymerization problem was resolved because sometimes it creates a problem during the polymerization process. So, the production of a polypropylene oxide and polycarbonates occurred simultaneously. In 70s liquid crystalline polymers led to the development of aramid, Kevlar, polyethylene, the super strong fiber and this is the backbone of bulletproof jackets. This was originally created by the DuPont liquid crystalline polymer with 40 percent glass fiber filler, this several uses in the electronic packing, housing and solar cell applications.

# A short history of polymerization process

 By employing an inert solvent as a heat sink and flashing the monomer after condensation outside the reactor, the heat of polymerization problem was resolved. The production of polypropylene oxide and polycarbonates occurred simultaneously.

In 1970s liquid crystalline polymers led to the development of

- Aramid/Kevlar and polyethylene a super-strong fibre.
- Originally created by DuPont, liquid crystalline polymer with 40% glass fibre filler has several uses in electronic packing and housing and is also employed in solar cell applications.



So, in this particular lecture we discussed about the different aspects of polymers. We discussed that how these polymers are formed through from monomers, what should be the basic characteristics of the monomer so that they can form the polymers, what different kind of the classification stream of the polymers, rather based on the source, based on the use, based on the basic chemistry and we

discussed about the short history of polymerization process and discuss that how this utility product or utility aspect emerged over the period of time. For your convenience, we have included several differences. Thank you very much.