Polymer Reaction Engineering
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Lecture - 03
A Short History of Polymerization Process and Monomers & its Distribution

Okay, welcome to this lecture of Polymer Reaction Engineering. In this particular lecture, we will discuss about a brief history of the polymerization processes, monomer and its distribution. Now why we are emphasizing the short history of the polymerization process?

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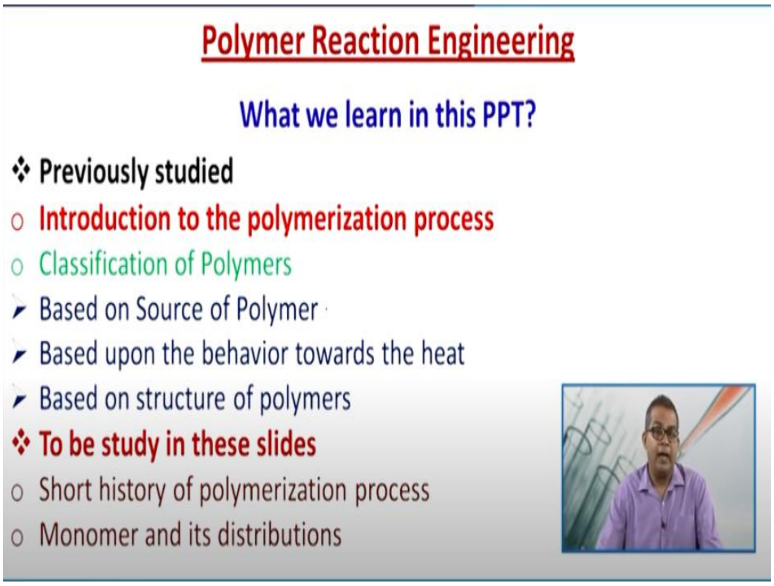

Polymer Reaction Engineering

What we learn in this PPT?

- Previously studied
  - Introduction to the polymerization process
  - Classification of Polymers
    - Based on Source of Polymer
    - Based upon the behavior towards the heat
    - Based on structure of polymers
- To be study in these slides
  - Short history of polymerization process
  - Monomer and its distributions

Now if you recall in the previous lectures, which we have studied about the small amount of polymerization process protocols and different type of classification streams. Now in this lecture, because to synchronize the thing that how this particular polymerization process evolved over the period of time and what are the main genesis behind this evolution process, we have introduced this particular segment to this particular course.

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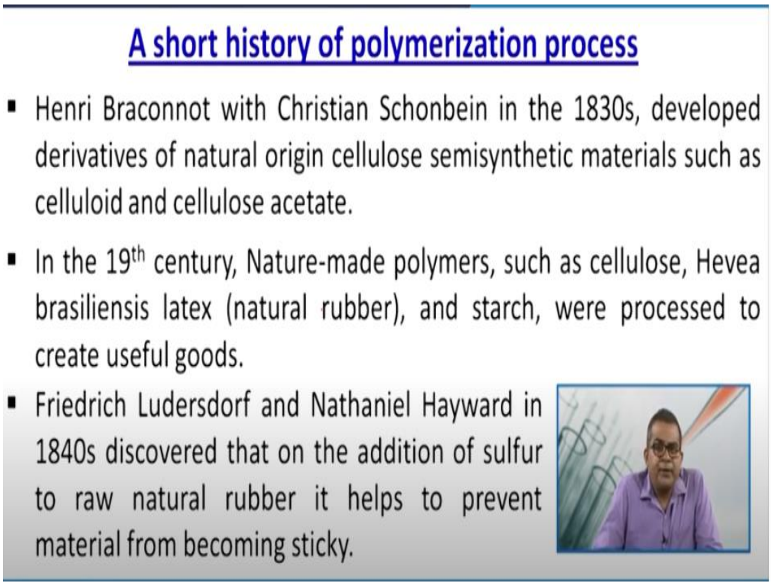

A short history of polymerization process

- Henri Braconnot with Christian Schonbein in the 1830s, developed derivatives of natural origin cellulose semisynthetic materials such as celluloid and cellulose acetate.
- In the 19th century, Nature-made polymers, such as cellulose, Hevea brasiliensis latex (natural rubber), and starch, were processed to create useful goods.
- Friedrich Ludersdorf and Nathaniel Hayward in 1840s discovered that on the addition of sulfur to raw natural rubber it helps to prevent material from becoming sticky.

Now let us have a look about the short history. Now history because, this when we study about any kind of a history process, sometimes we need to learn about the different type of a shortcoming from the past to improvise our products in the future. And the improvisation process always tutored by various kind of a demand from society, various kind of a demand from the environment, various kind of other demands attributed to the need of time.

So based on this particular approach, and this particular concept, various scientist, various engineers, various corporate organization, they gave a major impetus towards the development of all these polymerization process. Now see in the past all these polymeric projects because this polymer polymeric products are very sensitive in nature. Because always the eco friendly polymers, they are the buzzword nowadays.

Similarly, if you go for the industrial protocol operation, the energy efficient process, they are the buzzword. Similarly, if you go to the modern era, where the personal protective equipments, different type of a gears, different type of drug delivery systems etc., they are the need of a time. So based on this approach scientist, engineers, chemist, they were involved themself to develop a new process.

Similarly, if you see that the start of this particular polymerization processes the Henri Braconnot with the Christian in 1830, they developed the derivative of natural origin cellulose semisynthetic material, such as celluloid and cellulose acetate. Now celluloid is a very common or a buzzword in the past era. Last up to last decade you may remember that the celluloid films etc., they were more popular those days.

So they tried to develop this kind of thing product, these things with that help of a naturally origin cellulose recall your classification stream. In 19th century the nature made polymers like cellulose, different type of a latex or natural rubber, starch, they were processed to create a useful goods that is purely the consumer driven approach. Similarly, Fredrich etc., they developed discovered the different type of sulfur to natural rubber to develop automotive tire etc.

In 1840, they initiated the process for the development of this particular thing.

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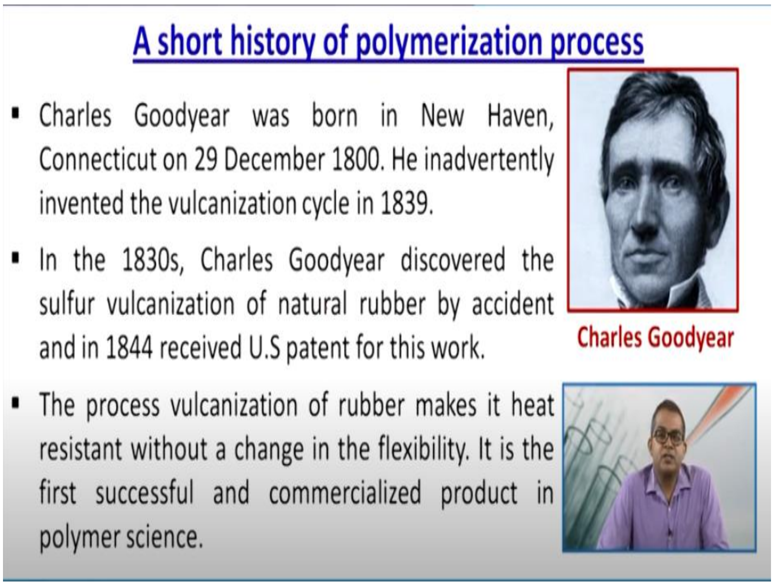

A short history of polymerization process

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

Charles Goodyear

Later on, this, Charles Goodyear he developed because he is you can say sometimes are referred as a father of automotive tire. He was born in New Haven, Connecticut, in December 1800. And inadvertently, he invented the vulcanization process cycle in 1839. Now it is a boon to the automotive tire industry. In 1830, the Goodyear discovered the sulfur vulcanization of national rubber by an accident.

And in 1844 he received the US patent for his work. Now see, the purpose of giving this particular thing to into this slide is that you see that almost you can say more than 175 years ago, that particular technology was developed and is still now from natural rubber to the synthetic rubber to the radial tire to the tubeless tires etc. So, this is the sequential process of development of this automotive tire industry.

So, this process of vulcanization of rubber, come back to this particular process, this makes it heat resistance without the change in its flexibility. See, when the objective of this particular natural rubber vulcanization is that when automotive tire moves into the surface, then there may be generation of a frictional heat. There may be generation of certain other things. So, it should not lose its property.

So, first thing is that they tried that it offers the heat resistant. Now this was the first successful and commercialized product in the polymer history, right.

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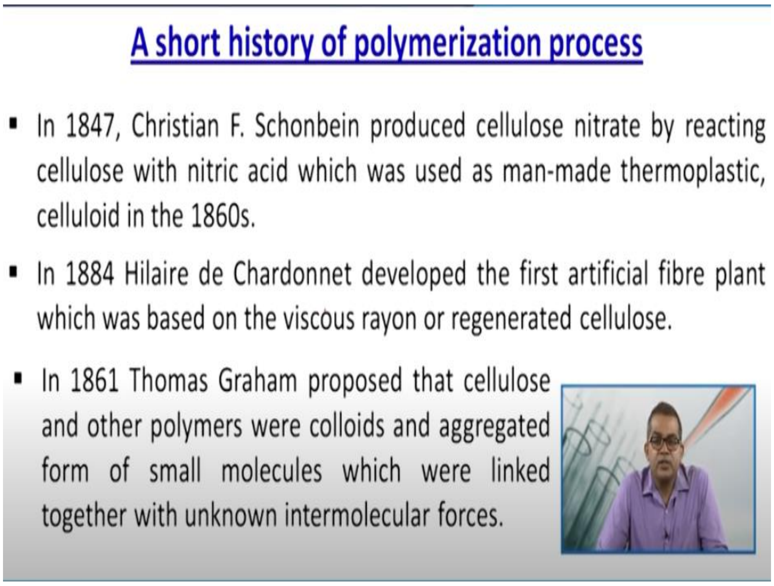

A short history of polymerization process

- In 1847, Christian F. Schonbein produced cellulose nitrate by reacting cellulose with nitric acid which was used as man-made thermoplastic, celluloid in the 1860s.
- In 1884 Hilaire de Chardonnet developed the first artificial fibre plant which was based on the viscous rayon or regenerated cellulose.
- In 1861 Thomas Graham proposed that cellulose and other polymers were colloids and aggregated form of small molecules which were linked together with unknown intermolecular forces.

So just try to synchronize the things that how we develop, what was the starting point, etc. Similarly, in 1847 Christian et al they produced the cellulose nitrate by the reaction of cellulose with the nitric acid and which was used as a manmade thermoplastic celluloid in 1860. Now you can see the application of celluloid, the film industry earlier it was depend on this celluloid thing.

In 1884 the Chardonnet developed the first artificial fiber plant, which was based on the viscous rayon and regenerated cellulose. So that time people were trying to develop the artificial fiber which can supplement the natural fiber because that was a need of a time because the population was growing day by day and the demand of the people were on the various spectrum.

In 1861 the Thomas Graham they proposed that cellulose and other polymers were colloids and aggregated to form small molecules which may be linked together to the unknown intermolecular forces. Though it was starting point, but it gives gave you another opportunity for the development of all those protocols.

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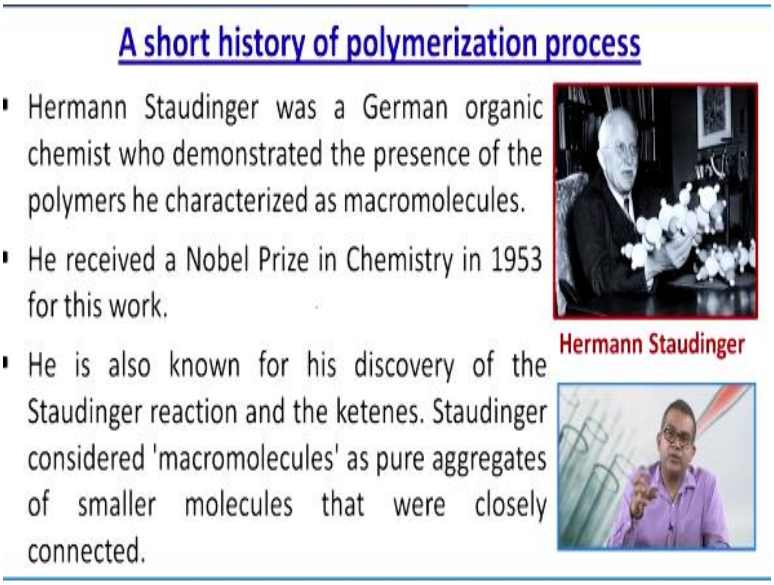

A short history of polymerization process

- Hermann Staudinger was a German organic chemist who demonstrated the presence of the polymers he characterized as macromolecules.
- He received a Nobel Prize in Chemistry in 1953 for this work.
- He is also known for his discovery of the Staudinger reaction and the ketenes. Staudinger considered 'macromolecules' as pure aggregates of smaller molecules that were closely connected.

Hermann Staudinger

Then Hermann Staudinger was, this was a German organic chemist, he demonstrated the presence of the polymer that he characterized as a macromolecule. See different monomers, different molecules they prepared a giant molecule that is referred as a macromolecule. For this, he received the Nobel Prize in Chemistry in 1953. He is also known for his discovery of the Staudinger reaction in the ketene.

Now this Staudinger, reconsidered the macromolecule as a pure aggregate of small molecules that were closely connected. So sometimes in the previous lecture, I told you that these polymeric chains are intermingled with each other, they are the macromolecules.

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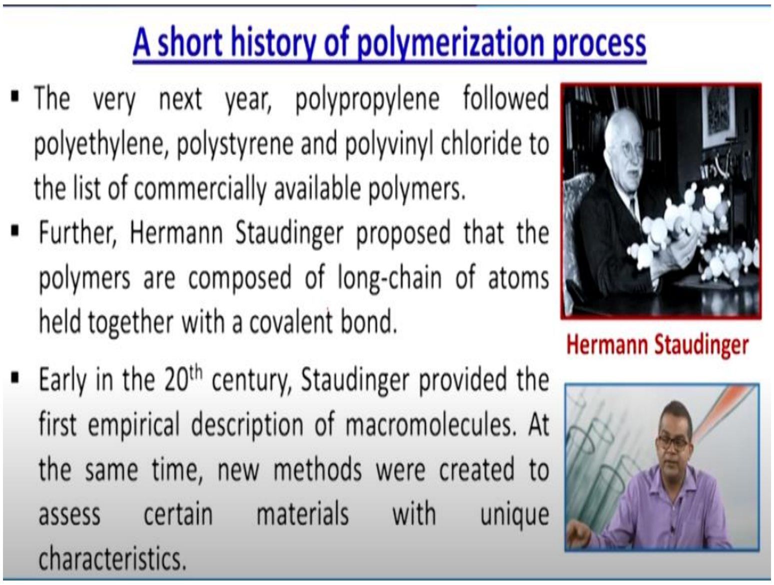

A short history of polymerization process

- The very next year, polypropylene followed polyethylene, polystyrene and polyvinyl chloride to the list of commercially available polymers.
- Further, Hermann Staudinger proposed that the polymers are composed of long-chain of atoms held together with a covalent bond.
- Early in the 20^{th} century, Staudinger provided the first empirical description of macromolecules. At the same time, new methods were created to assess certain materials with unique characteristics.

On the very next year, the polypropylene followed by the polyethylene, polystyrene, polyvinyl chloride to the list of the commercially available polymers. So, it opens a huge spectrum of a product protocols. Then Staudinger proposed that the polymers they are composed of long chain of atom they held together with the covalent bond because he felt that there are certain forces, there are certain things must be attributed for this particular joining.

So early in 20th century, he provided the first empirical description of a molecules, macromolecules. And at the same time, new method they were created to assess the certain materials with a unique characteristic. We will discuss those characteristics in subsequent lectures.

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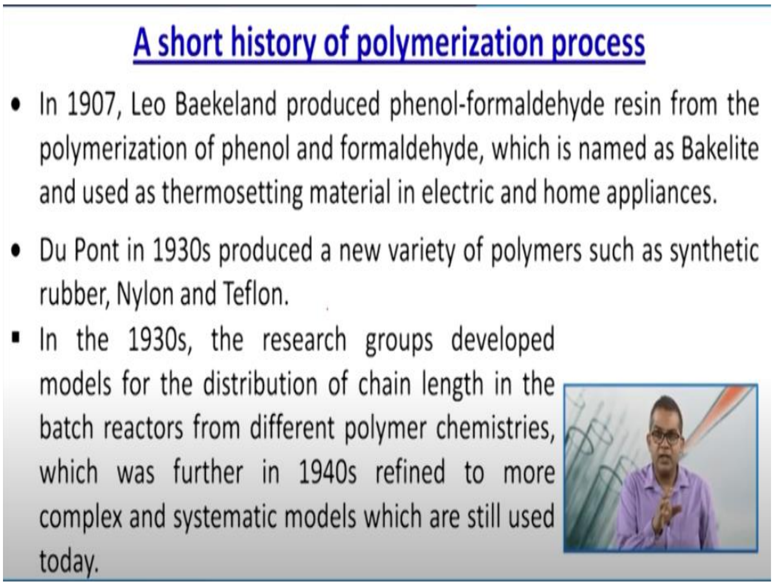

A short history of polymerization process

- In 1907, Leo Baekeland produced phenol-formaldehyde resin from the polymerization of phenol and formaldehyde, which is named as Bakelite and used as thermosetting material in electric and home appliances.
- 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 refined to more complex and systematic models which are still used today.

In 1907 Leo he produced the phenol formaldehyde resin from the polymerization of a phenol and formaldehyde, which is termed as a bakelite and used for the thermosetting material which we discussed in the previous lectures. In 1930, DuPont they produced a new variety of polymer, such as synthetic rubber, nylon and Teflon all of you are aware about the history of a nylon. It was discovered simultaneously in New York and London.

In 1930 the research group developed a model for the distribution of the chain length in the batch reactor from the different polymer chemistries, which was further in 1940 refined to more and more complex and systematic model which are still used today. Now just to recall the previous lecture, we discussed that when a monomer gets polymerized so there are various spectrum of molecules.

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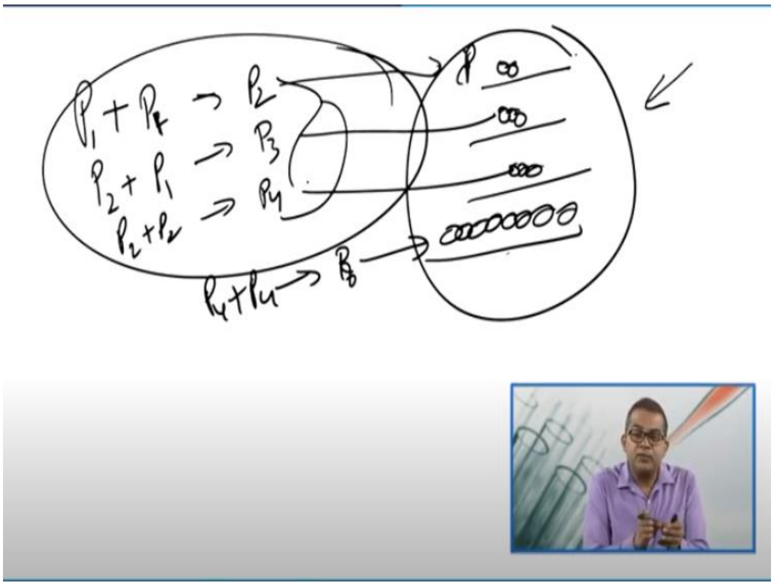

Like, if you recall that I gave you this approach that P_1 that is the monomer may get combined with P_2 sorry P_1 to give you P_2. And this P_2 may get combined with the either P_1 or its P_2 itself to give a different product stream like P_3 and P_4. And simultaneously, they may have an opportunity to combine together. So, these are now if you see if you visualize these things, they are just like these two molecules.

They are three and they are four and if you see that P_4 plus P_4, they are forming P 8. Now by this way, the chain gets extended over the period of time. Now if you consider it is a mass, it is the polymeric mass you will find that P_2, P_3, P_4, P_8 etc. So, you will find that this polymeric mass consists of various chains having the different chain lengths.

So, this particular approach being first considered by this particular research group and they find that this type of a model and they was they were first trying to develop a similar type of systematic model for the prediction of the molecular weight of polymeric system.

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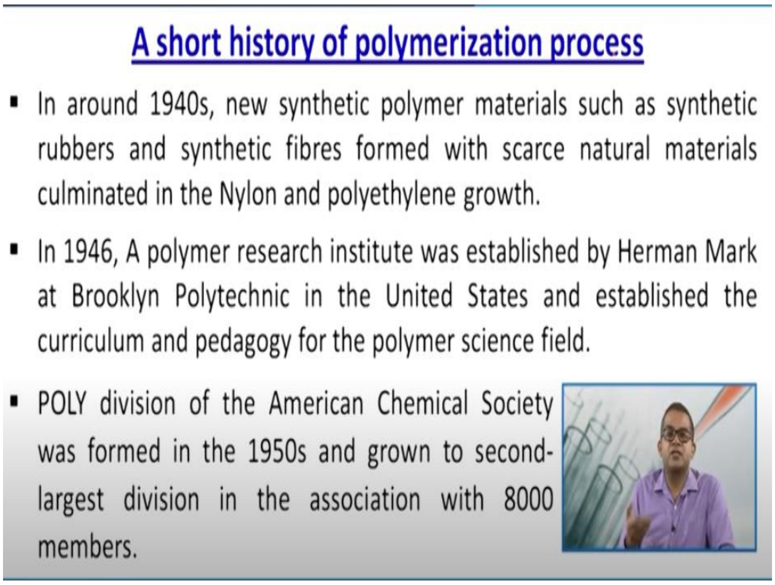

A short history of polymerization process

- In around 1940s, new synthetic polymer materials such as synthetic rubbers and synthetic fibres formed with scarce natural materials culminated in the Nylon and polyethylene growth.
- In 1946, A polymer research institute was established by Herman Mark at Brooklyn Polytechnic in the United States and established the curriculum and pedagogy for the polymer science field.
- POLY division of the American Chemical Society was formed in the 1950s and grown to second-largest division in the association with 8000 members.

In 1946, a polymer research institute was established by Herman Mark in Brooklyn Polytechnic in the United States and established the curriculum and pedagogy for the polymer science field. So, you may see that what we are discussing right now at this juncture, it was initiated by Herman Mark way back in 1946, to channelize, the study of a polymer science, to synchronize the study of the polymer science and to give a seed of or a food for thought in the undergraduates or graduates in their mind.

Now POLY division of American Chemical Society, it was formed in 1950 and grown to the second largest division in the association with almost 8000 members. Now this is just to give a platform for the dissemination of the knowledge to the dissemination of other approaches to among the scientist.

And moreover, it provided a platform for various industrial organization to come forward for their requirement so that the scientific community may share its knowledge and jointly together to develop the various products being useful for the mankind.

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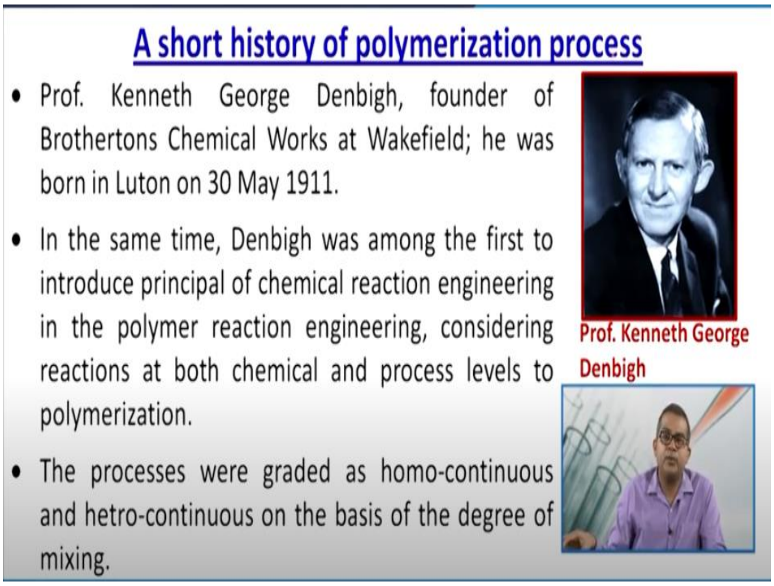

A short history of polymerization process

- Prof. Kenneth George Denbigh, founder of Brothertons Chemical Works at Wakefield; he was born in Luton on 30 May 1911.
- In the same time, Denbigh was among the first to introduce principal of chemical reaction engineering in the polymer reaction engineering, considering reactions at both chemical and process levels to polymerization.
- The processes were graded as homo-continuous and hetro-continuous on the basis of the degree of mixing.

Now Professor Kenneth George, he is the founder of Brotherton Chemicals Work, Wakefield. He was born in Luton in 1911. And he was one of the first person or introduce the principle of a chemical reaction engineering in the polymer reaction engineering concept. See, the chemical reaction engineering concept is a very old concept.

And if you recall in the very first lecture, I discussed about the formation of ammonia through nitrogen and hydrogen to ammonia. Now it is not so simple process that if you mix nitrogen and hydrogen, you will get the ammonia. There are various things involved in that particular approach. This reaction is exothermic. And again, this reaction is a temperature sensitive reaction.

You need to maintain a particular temperature over which beyond that particular temperature, the catalytic activity etc., they may go on depletion etc. So, in case of in case if you are looking for a proper efficiency, in case you are looking for proper eco friendly process, you have to maintain certain conditions of pressure and temperature within the system.

Moreover, there may be certain side reactions, there may be certain and you can say unreacted components, unreacted raw material, which are always the part and parcel of your product stream. So how to separate it out, how to maintain the temperature, how to go for a proper selectivity, how to go for proper efficiency, reaction efficiency, how to make the system eco friendly.

So, these are the part and parcel and what are the different orders of the reaction, what kind of things do you need to incorporate in that particular reactor etc. So, these are the part and parcel of your chemical reaction engineering concept. Now those concepts are equally applicable to the polymer reaction engineering. The reason is that if you recall the previous slide or a handmade slide, where we discussed that the two monomers may combine to form the P_2.

And then P_2 may combine with P_1 or P_2 itself and again whatever product being formed may combine in a sequential manner with the different type of a product available at that juncture. Now if you are looking for a particular product, then always as an engineering perspective, you are looking for a fixed molecular weight, you are looking for a fixed structure etc. So how to control the things?

Because this thing if you maintain the favorable condition, then this polymerization process will go on go on up to it consumes all the raw material etc. But sometimes because it may enhance the molecular weight, so it may become a bulky one and it probably it may not be a useful product for you. So how to control those things? How to get your desired product?

So, the similar application of the chemical reaction engineering are equally applied to certain applications, they are equally applied to polymer reaction engineering. So, the start this the professor Kenneth he they graded the homo-continuous and hetero-continuous reactions on the basis of a degree of a mixing, right.

So just you recall all, just you conceptualize all kind of a different protocols or a different processes or operations applicable for any kind of an application and then you try to correlate the things accordingly.

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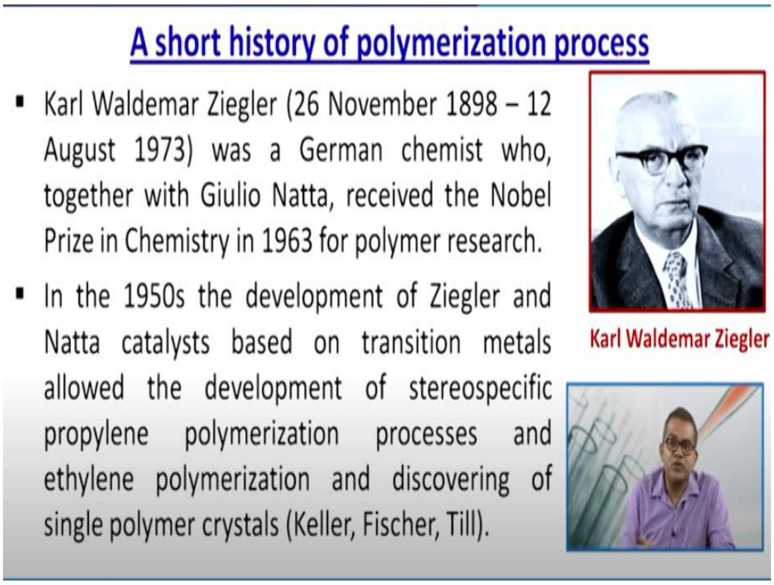

A short history of polymerization process

- Karl Waldemar Ziegler (26 November 1898 – 12 August 1973) was a German chemist who, together with Giulio Natta, received the Nobel Prize in Chemistry in 1963 for polymer research.
- In the 1950s the development of Ziegler and Natta catalysts based on transition metals allowed the development of stereospecific propylene polymerization processes and ethylene polymerization and discovering of single polymer crystals (Keller, Fischer, Till).

Karl Waldemar Ziegler

Then, Karl W Ziegler in, he was a German chemist, who together with the Natta they received the Nobel Prize in Chemistry in 1963 for the polymer research and they gave the very, you can say the popular Ziegler Natta catalyst for the polymeric system. It is a very famous catalyst and you can say the boon for polymer science. So, in 1950, they developed the Ziegler and Natta catalyst.

Based on the transition metal they allowed to development of a stereo specific polypropylene polymerization process and ethylene polymerization process and discovered the single polymer crystal. So, they were the first who introduced this Ziegler Natta catalyst for the polymerization process.

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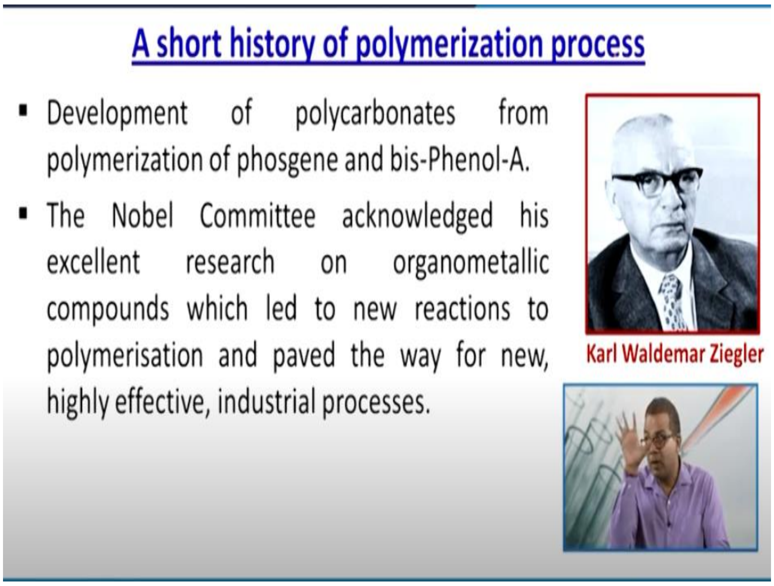

A short history of polymerization process

- Development of polycarbonates from polymerization of phosgene and bis-Phenol-A.
- The Nobel Committee acknowledged his excellent research on organometallic compounds which led to new reactions to polymerisation and paved the way for new, highly effective, industrial processes.

Karl Waldemar Ziegler

Similarly, the development of polycarbonates from polymerization of phosgene and bis-phenol-A. Now the Nobel Committee incidentally they acknowledged this excellent research on organometallic compounds, which led to the new reaction and they opened the new horizon for this polymerization process.

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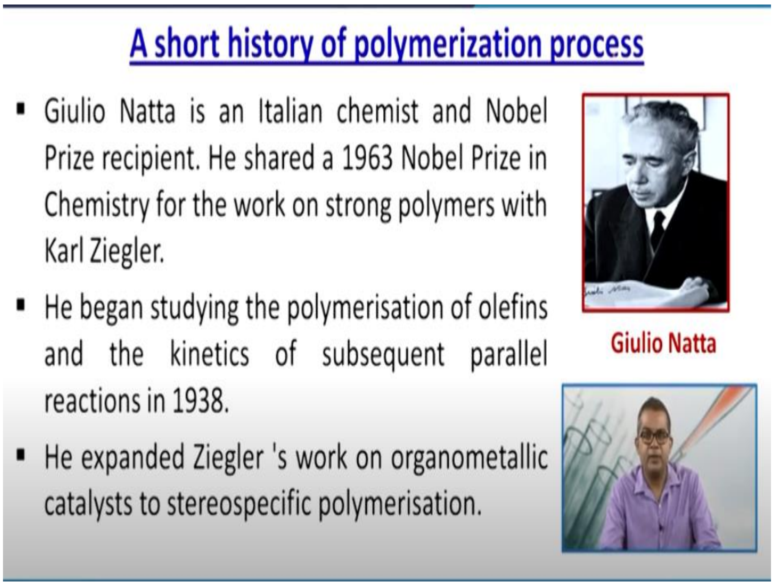

A short history of polymerization process

- 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.

Giulio Natta

This the Natta he was an Italian chemist and a Nobel Prize recipient shared with the Ziegler in 1963. So, he began the studying of the polymerization of olefins and developed the kinetics of subsequent parallel reactions in 1938. So, he expanded this the Ziegler's work on organometallic catalysis to the stereospecific polymerization. So, it was a collective work of both Ziegler and Natta.

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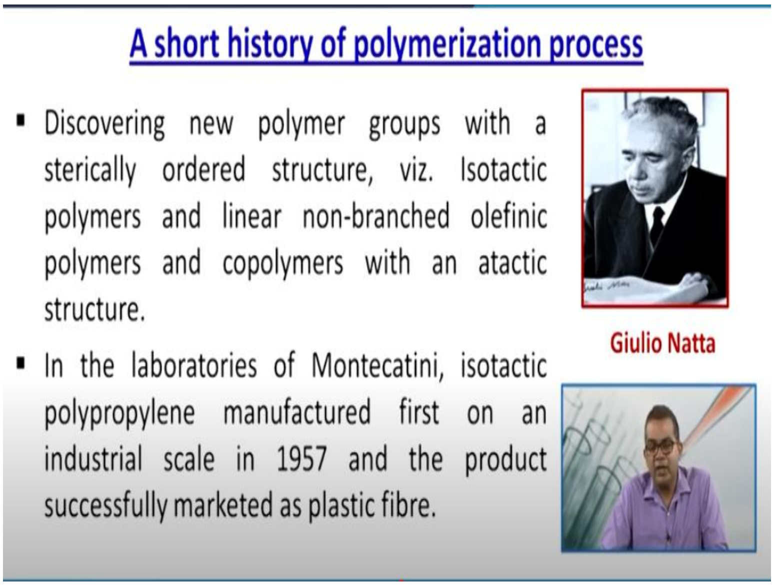

A short history of polymerization process

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

Giulio Natta

Now discovering new polymer group with this the sequentially ordered structure like isotactic polymers or linear or non-branched olefinic polymers and copolymers with different type of atactic structure. So, in the laboratory isotactic polypropylene they manufacture first on the industrial scale way back in 1957. And, this product was successfully marketed as the polymeric fiber or referred as plastic fiber.

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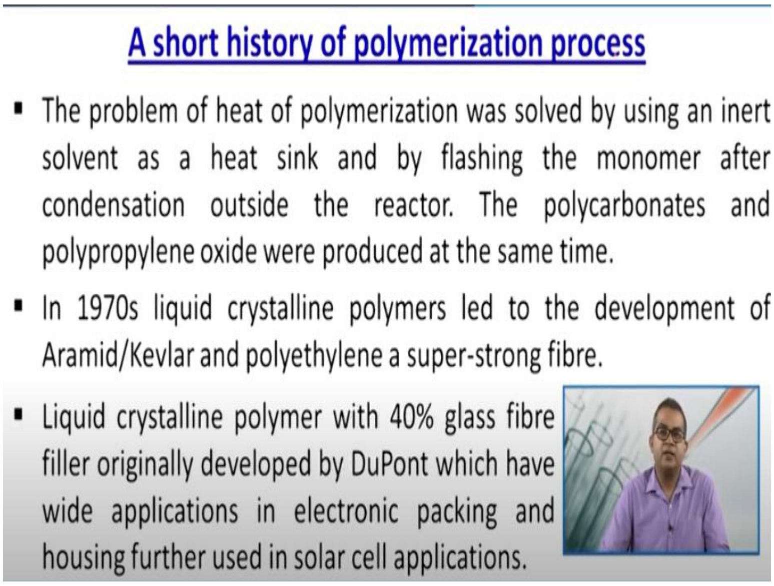

A short history of polymerization process

- The problem of heat of polymerization was solved by using an inert solvent as a heat sink and by flashing the monomer after condensation outside the reactor. The polycarbonates and polypropylene oxide were produced at the same time.
- In 1970s liquid crystalline polymers led to the development of Aramid/Kevlar and polyethylene a super-strong fibre.
- Liquid crystalline polymer with 40% glass fibre filler originally developed by DuPont which have wide applications in electronic packing and housing further used in solar cell applications.

Now sometimes the problem of heating of a polymerization was discussed among all the scientist and this was solved by using an inert solvent as a heat sink. Because this is you can say the foremost problem experienced by various scientist in past. So they used an inert solvent as a heat sink and by flashing the monomer after condensation outside the reactor.

So, the polycarbonate and the polypropylene oxide they were produced first time by this particular reaction stream. In 1970, the liquid crystalline polymers they led to the development of Aramid, Kevlar, Aramid and Kevlar bulletproof jackets etc. It is very popular in that sense. So, polyethylene they form a super strong fiber.

Sometimes the liquid crystalline polymer with say 40% of a glass fiber filler, originally developed by DuPont have wide application in electronic packing, housing, sometimes used in the solar cell applications etc.

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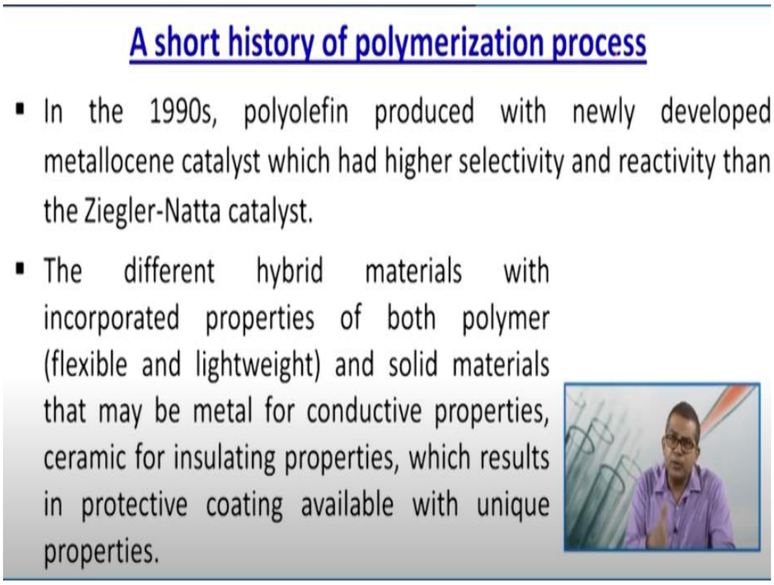

A short history of polymerization process

- In the 1990s, polyolefin produced with newly developed metallocene catalyst which had higher selectivity and reactivity than the Ziegler-Natta catalyst.
- The different hybrid materials with incorporated properties of both polymer (flexible and lightweight) and solid materials that may be metal for conductive properties, ceramic for insulating properties, which results in protective coating available with unique properties.

In 1990 era, the polyolefin produced with the newly developed metallocene catalyst, which had higher selectivity and reactivity than the Ziegler-Natta catalyst. So, you see that from 1963 to 1990, they improvised this particular approach. Now the different hybrid materials they are sometimes incorporated in properties of a both polymers maybe flexible or a lightweight and sometimes to the solid material may be strongly packed etc.

So, there may be metal for the conductive properties, ceramic or sometimes the insulating properties etc. So, this type of approach is sometimes useful for protective coating with different unique properties. Now this coating in a broad spectrum is referred as a barrier between the atmosphere and over which you are applying that particular coat. So, they must possess a specific type of properties, maybe inertness towards the atmosphere.

We all aware that atmosphere may contain the UV radiation, may contain the humidity, may contain heat or a chilling effect etc. So, they must provide the barrier. So, these are the food for thought for development of new material.

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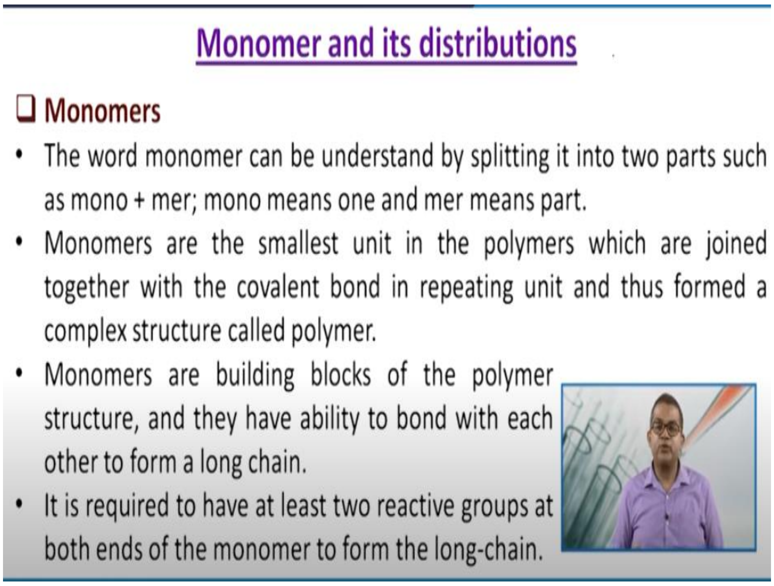

Monomer and its distributions

❑ **Monomers**

- The word monomer can be understand by splitting it into two parts such as mono + mer; mono means one and mer means part.
- Monomers are the smallest unit in the polymers which are joined together with the covalent bond in repeating unit and thus formed a complex structure called polymer.
- Monomers are building blocks of the polymer structure, and they have ability to bond with each other to form a long chain.
- It is required to have at least two reactive groups at both ends of the monomer to form the long-chain.

Now once we discuss this particular approach related to the history of this one, the purpose I told you that the purpose of this history was just to give an idea that how this polymeric process being developed and who contributed more in the development of this polymerization process and what are the school of thoughts for that particular development. Let us have a look about the monomer and its distribution.

Now the distribution part we have already have certain idea about what is monomer. In this particular concept, we will try to discuss about its distribution pattern. So, the word monomer this can we understand by the splitting into the different two different part. One is mono plus mer. Mono means one and mer means the different part.

So, they are the smallest unit in the polymeric system, which are joined together with the help of a different bonding pattern, maybe the covalent bond, maybe other things in the different repeating units, which we discussed in the previous lecture. And thus, they formed by this joining the complex structure that is referred as the polymer.

So, in other words, you can say that they are the building blocks of a polymer structure and they have ability to bond with each other to form a long chain. We discussed this in the lecture two. So just a brief that what is the prerequisite for this particular approach? So, there must have at least two reactive groups or some sort of unsaturation over there to form a long chain.

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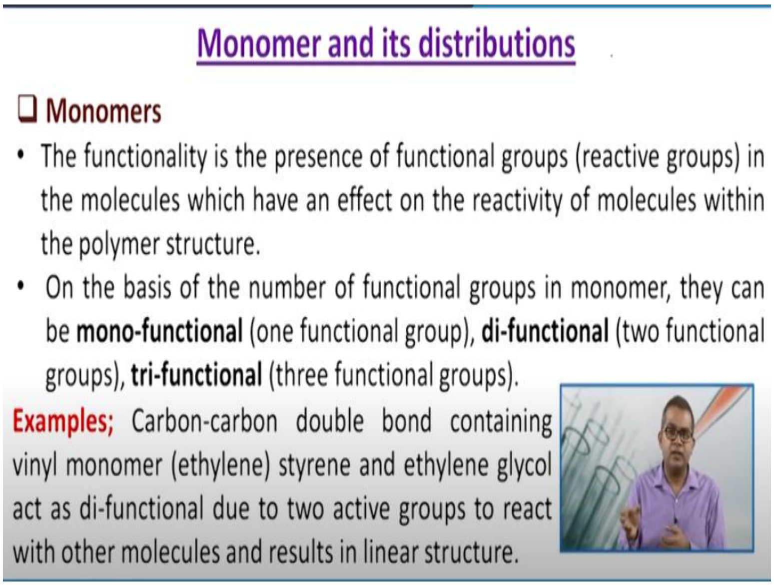

Monomer and its distributions

❑ **Monomers**

- The functionality is the presence of functional groups (reactive groups) in the molecules which have an effect on the reactivity of molecules within the polymer structure.
- On the basis of the number of functional groups in monomer, they can be **mono-functional** (one functional group), **di-functional** (two functional groups), **tri-functional** (three functional groups).

Examples; Carbon-carbon double bond containing vinyl monomer (ethylene) styrene and ethylene glycol act as di-functional due to two active groups to react with other molecules and results in linear structure.

Now the reactive groups they are sometimes referred as the functionality of those monomers. So, the functionality is the presence of a functional group or reactive groups in the molecules which have an effect on the reactivity of a molecules within the polymer structure. You may say that not every molecule is participating molecule in the polymeric system.

So, they must have an efficacy with respect to the functional group so that they can become the part and parcel of the polymeric structure. So, on the basis of a number of functional groups in monomer they can be either mono functional, they may have a one functional group, may have a di-functional. They may have a two functional groups. And they may have a tri-functional, they may have a three functional groups.

I will give you some examples of these mono-functional, di-functional and tri-functional like carbon-carbon double bond. They may contain the vinyl monomer or vinyl monomer styrene. Ethylene glycol, they can act as a di-functional group etc.

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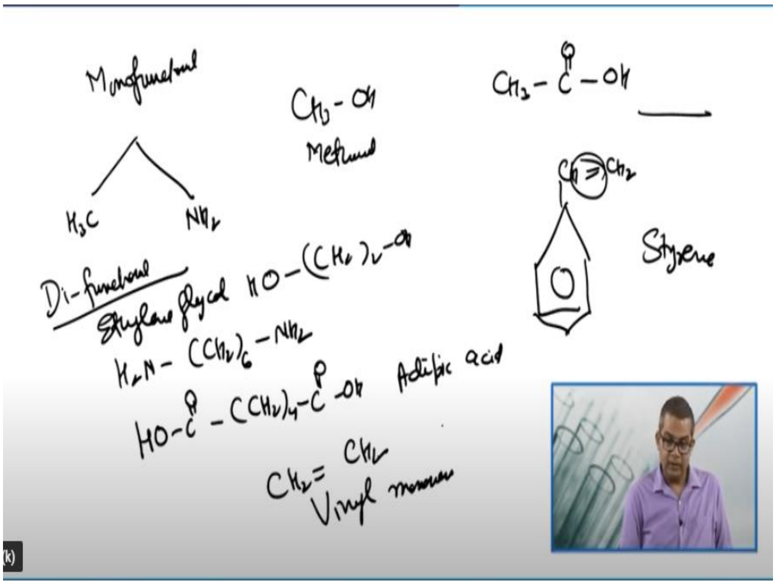

Now let us give you an example of mono-functional. Now this is you can see here you are having some mono functionality like CH_3-OH. This is methanol and CH_3. So, these are the some mono-functional groups. Now let us have some examples of a di-functional. They are ethylene glycol OH, styrene sorry this is styrene. You see here double bond is there. Similarly, H_2 and CH_2. This is hexamethylene diamine.

Similarly, another one is adipic acid and above all this is our favorite vinyl monomer. Now let us have some one example of say tri-functional group.

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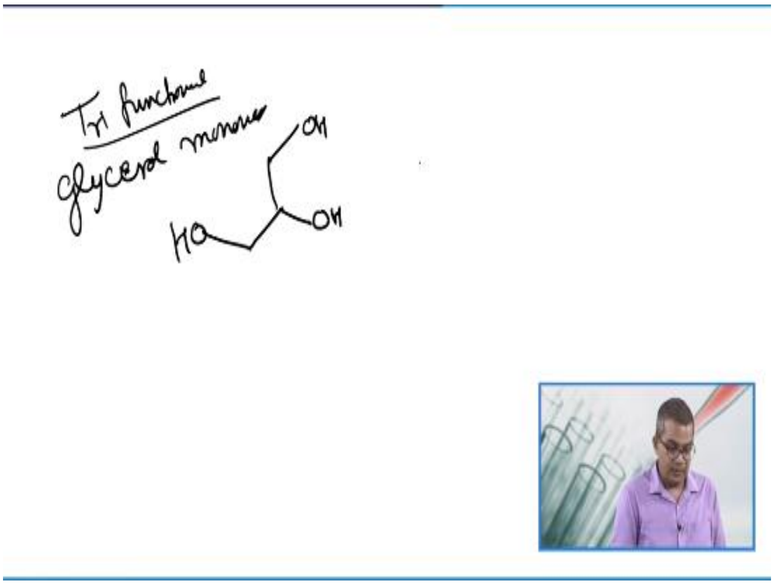

Now this is the glycerol. You see this is the tri-functional one. So, this may offer a wide spectrum of the functionality and that gives you a very good source of various kind of polymerization reactions.

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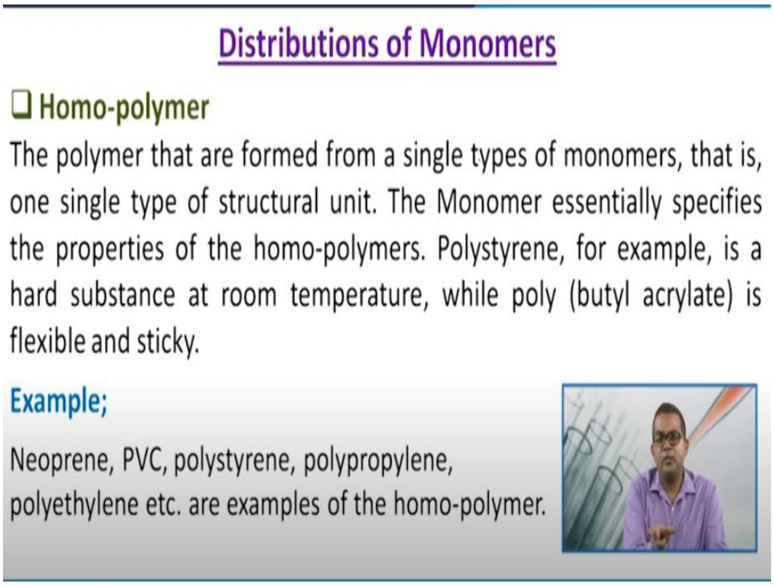

Distributions of Monomers

❑ Homo-polymer

The polymer that are formed from a single types of monomers, that is, one single type of structural unit. The Monomer essentially specifies the properties of the homo-polymers. Polystyrene, for example, is a hard substance at room temperature, while poly (butyl acrylate) is flexible and sticky.

Example;

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

Now another part is that the homo-polymer. Now these the homo-polymers they are formed from a single type of a monomer. They may be different type of monomer. So, and it may be the combination of different monomer to give you different polymer polymeric product. So, they are formed from a single type of monomer and that is a single type of structural unit in other words you may say.

So, these monomers essentially specify the properties for homo-polymer. Polystyrene I gave you an example of polystyrene is a hard substance at room temperature, while poly butyl acrylate is flexible and sticky. So, the best example of these homo-polymer are neoprene, PVC. Neoprene is very common for the sports surfaces.

Polystyrene, polypropylene, polyethylene etc. So, these are the examples of **homo-polymer**. In other words, you can say the homo-polymer the repeating units are same.

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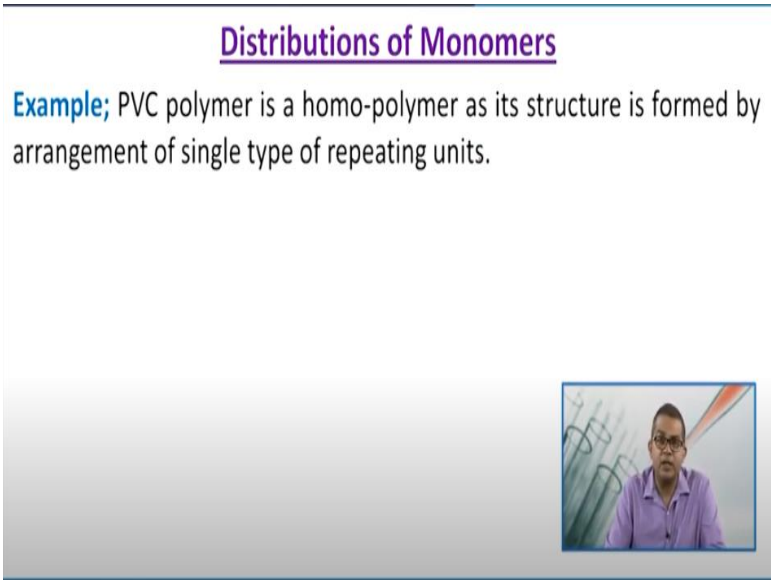

Distributions of Monomers

Example; PVC polymer is a homo-polymer as its structure is formed by arrangement of single type of repeating units.

PVC is again one of the example of the homo-polymer.

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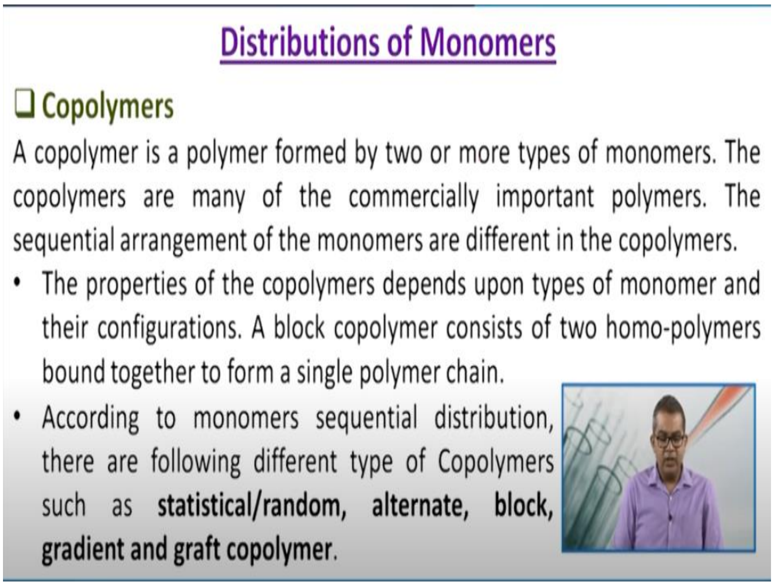

Distributions of Monomers

❑ Copolymers

A copolymer is a polymer formed by two or more types of monomers. The copolymers are many of the commercially important polymers. The sequential arrangement of the monomers are different in the copolymers.

- The properties of the copolymers depends upon types of monomer and their configurations. A block copolymer consists of two homo-polymers bound together to form a single polymer chain.
- According to monomers sequential distribution, there are following different type of Copolymers such as **statistical/random, alternate, block, gradient and graft copolymer.**

There are certain copolymers. Now copolymer is a polymer formed by the two or more type of monomer. Means, if you compare with the homo-polymer here you are using two or more different type of monomer. So, the copolymer they are mainly having the commercial importance with respect to the polymeric application. The sequential arrangement of the monomer they are different in the copolymers.

So, it gives you another opportunity with respect to the engineering perspective that how you can attach those different type of monomer to one of the base polymeric chain. So, the properties of copolymer depends on types of monomer, their configuration. So, a block polymer usually sometimes referred as the base of this copolymer. Block polymer consist of two homo-polymers.

They are bound together to form a single polymer chain. So sometimes according to the monomeric sequential distribution, sometimes there are different type of copolymer configuration and to discuss all those things you may require the statistical and random sometimes they are I mean the block gradient or a graft copolymer. So wide variety of copolymer distributions are given in the literature.

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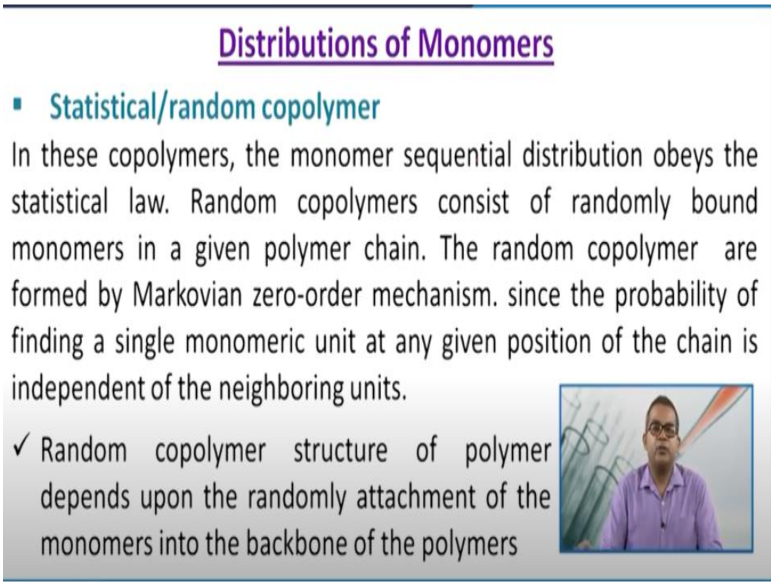

Distributions of Monomers

- Statistical/random copolymer

In these copolymers, the monomer sequential distribution obeys the statistical law. Random copolymers consist of randomly bound monomers in a given polymer chain. The random copolymer are formed by Markovian zero-order mechanism. since the probability of finding a single monomeric unit at any given position of the chain is independent of the neighboring units.

✓ Random copolymer structure of polymer depends upon the randomly attachment of the monomers into the backbone of the polymers

So, let us have a look about the statistical and random copolymer. So, in these types of a copolymer, the monomer sequential distribution always obeys the statistical law. Now the random copolymer consists of a randomly bound monomer in a given polymer chain. So sometimes these random copolymers are formed by Markovian zero-order mechanism. This is again very popular.

We will discuss this Markovian zero-order mechanism in subsequent lectures. So, the sometimes the probability theory applies over here for the prediction of the randomness of all these copolymers etc. So, the random copolymer structure of a polymer usually depend on random attachment of a monomer into the backbone of polymer.

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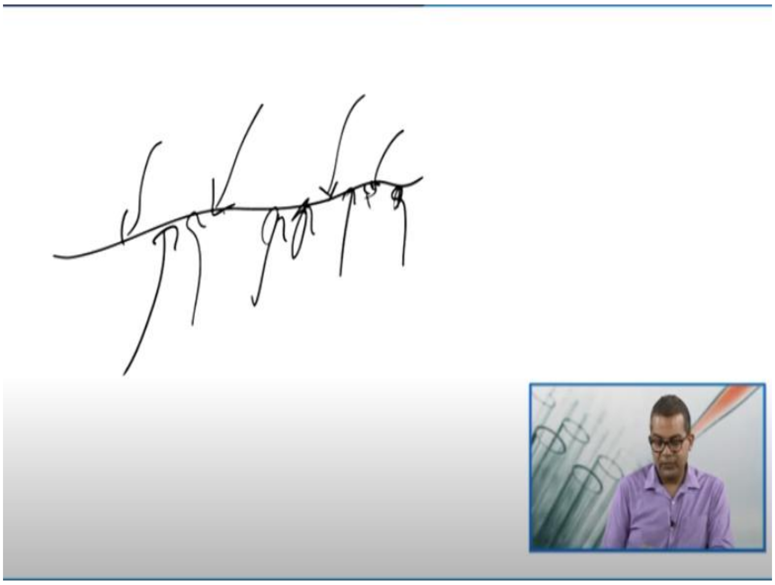

So usually what happen there are a backbone of a polymer and then different type of other polymer systems or monomeric systems they can attach together. It is a different thing and so that you can improvise the property of the polymeric system in due course of time.

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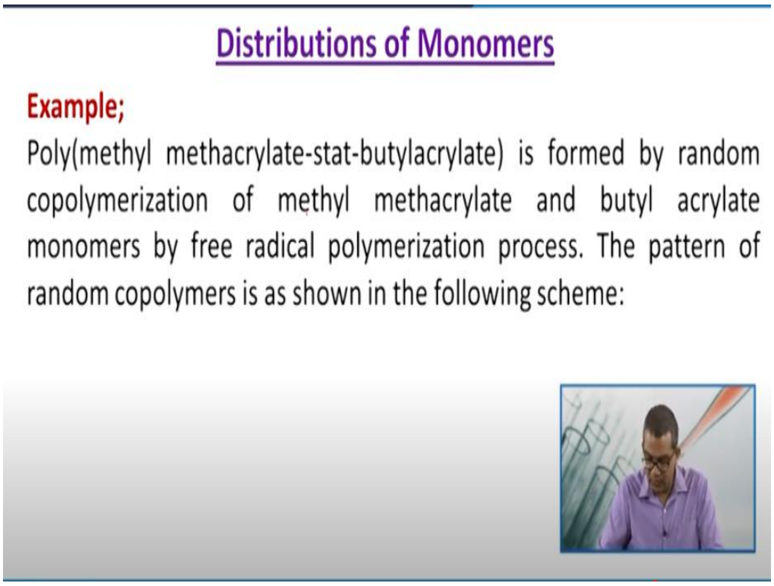

Distributions of Monomers

Example;

Poly(methyl methacrylate-stat-butylacrylate) is formed by random copolymerization of methyl methacrylate and butyl acrylate monomers by free radical polymerization process. The pattern of random copolymers is as shown in the following scheme:

The best example of this type of a copolymer system is poly(methyl methacrylate) sometimes with the butyl acrylate usually formed by the random copolymerization of MMA, that is methyl methacrylate and butyl acrylate monomer. And the mechanism or protocol referred is as the free radical polymerization process. We will discuss this free radical polymerization process in due course of time.

Now the pattern of random copolymer we are going to discuss in this particular slide.

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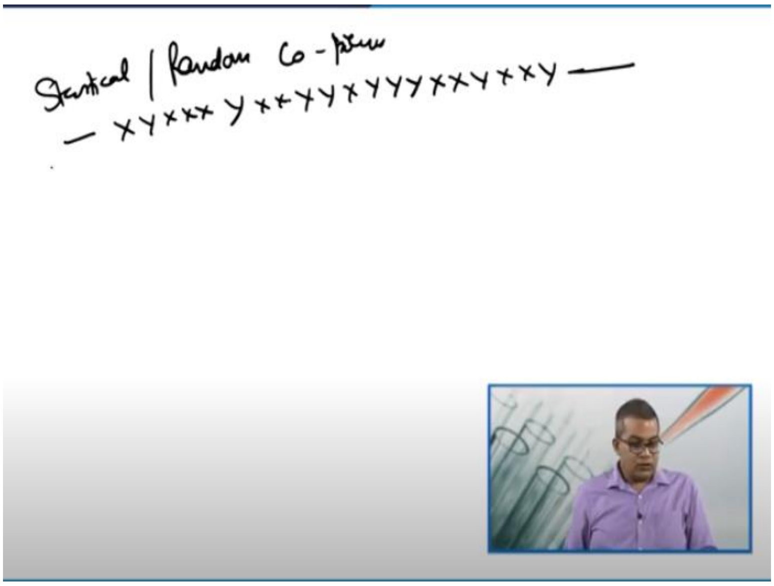

Statical | Random Co-polym

— xyxxx y xxyyxyyyxxyxxy —

Now statistical or random copolymer. Now here xyxxx sometimes y xx. Now here x and y, they are the two different monomer units, which are attached into the main chain randomly like you can see over here like this. So, this is you can say more discrete type of a thing and you see that, there is no fixed pattern. That is why it is called the random pattern of this particular polymerization stream.

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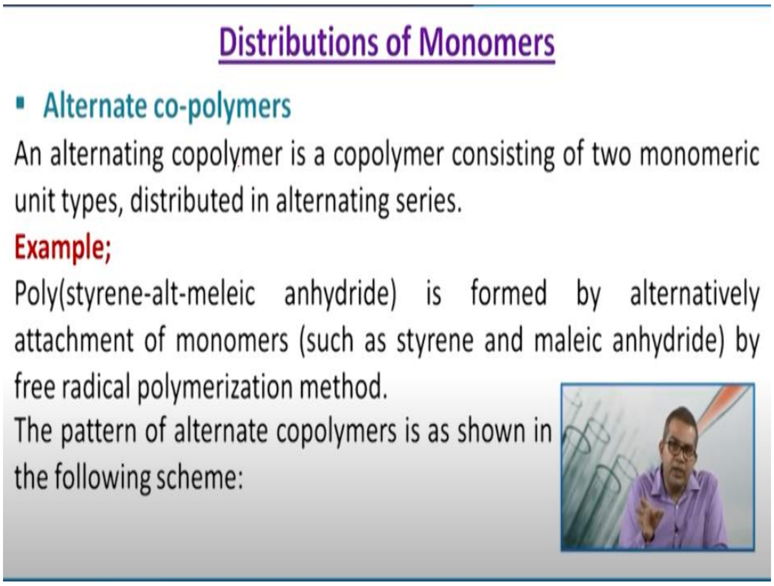

Distributions of Monomers

- Alternate co-polymers

An alternating copolymer is a copolymer consisting of two monomeric unit types, distributed in alternating series.

Example;

Poly(styrene-alt-meleic anhydride) is formed by alternatively attachment of monomers (such as styrene and maleic anhydride) by free radical polymerization method.

The pattern of alternate copolymers is as shown in the following scheme:

There are certain alternate copolymers. Now an alternating copolymer usually a copolymer consists of two monomer unit types, and distributing in alternating series. The best example of this is polystyrene meleic anhydride, usually formed by alternatively attachment of monomers like styrene and meleic anhydride by the free radical polymerization method.

So, we will discuss as I promised that this free radical polymerization in the subsequent lecture. Now you see that what is the generalized pattern of this free radical polymer, this alternate copolymerization.

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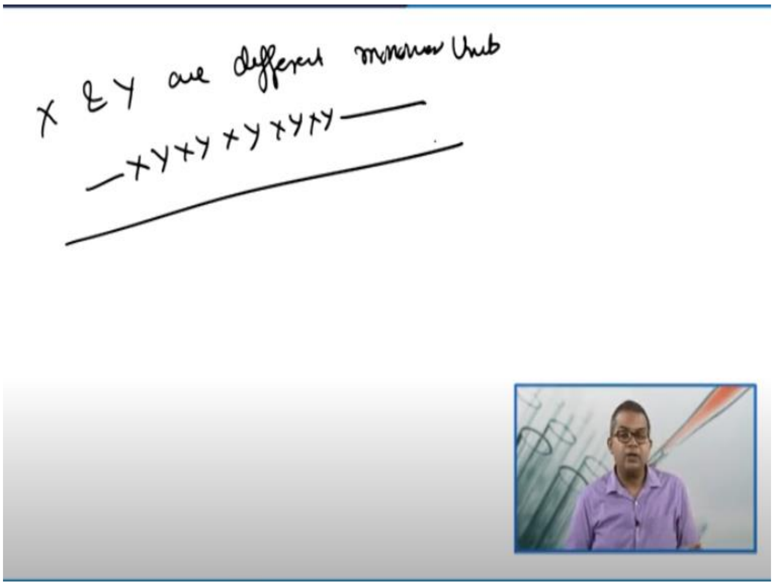

x & Y are different monomer Unit

—xyxy xy xyxy——

Again, take back with this x and y are different monomer units. Now here x y, x y, x y, x y, x y and so on. So, you see that this is the alternate copolymerization arrangement.

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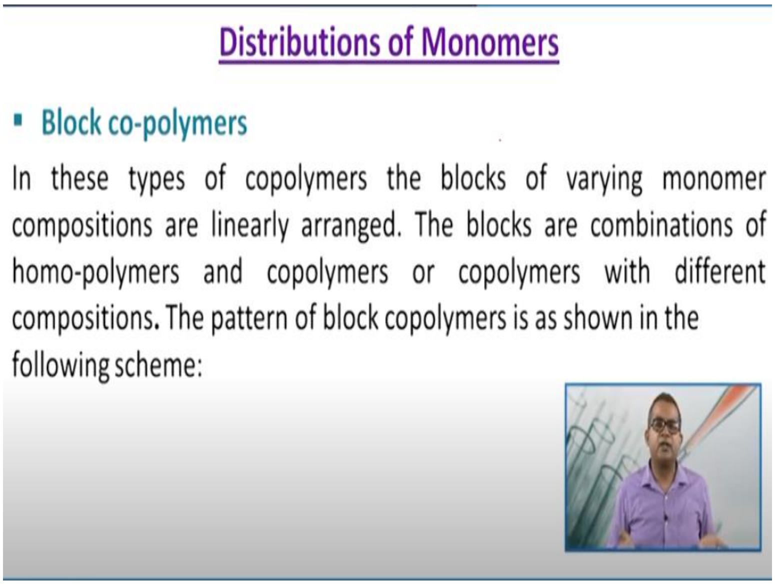

Distributions of Monomers

- Block co-polymers

In these types of copolymers the blocks of varying monomer compositions are linearly arranged. The blocks are combinations of homo-polymers and copolymers or copolymers with different compositions. The pattern of block copolymers is as shown in the following scheme:

Now another part is that **block copolymers**. Now block copolymers in this type of a copolymeric system, the blocks of various monomeric compositions are linearly arranged. So, one block is here, another block is here like this. So, these blocks are the combination of either homo-polymer and a copolymer or copolymer with a different composition. So, the pattern of block copolymers we can discuss like this.

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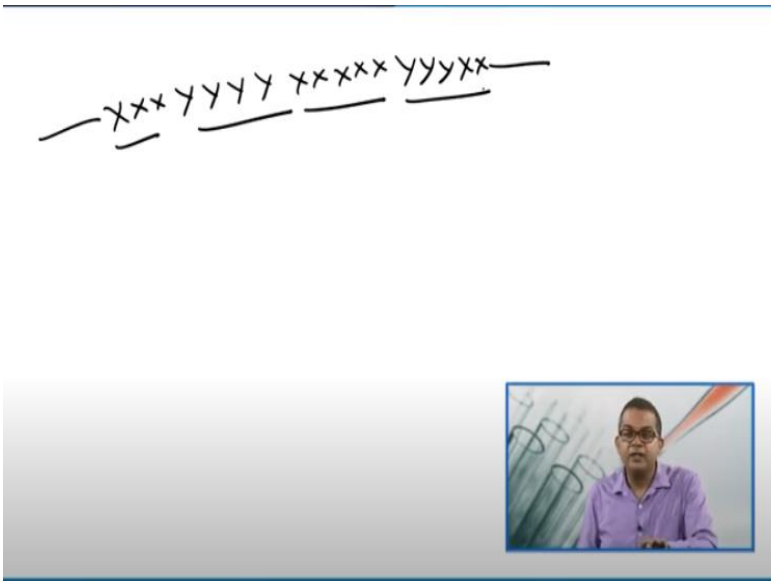

Now here you see that again the same type of monomer. Now see here these are the blocks. So, the blocks of a varying monomer x and y they are arranged linearly. So, this is the you can say the need of a time. Sometimes you may require the different or hybrid property requirement. So, they offer a very good opportunity for this particular product improvisation or process improvisation.

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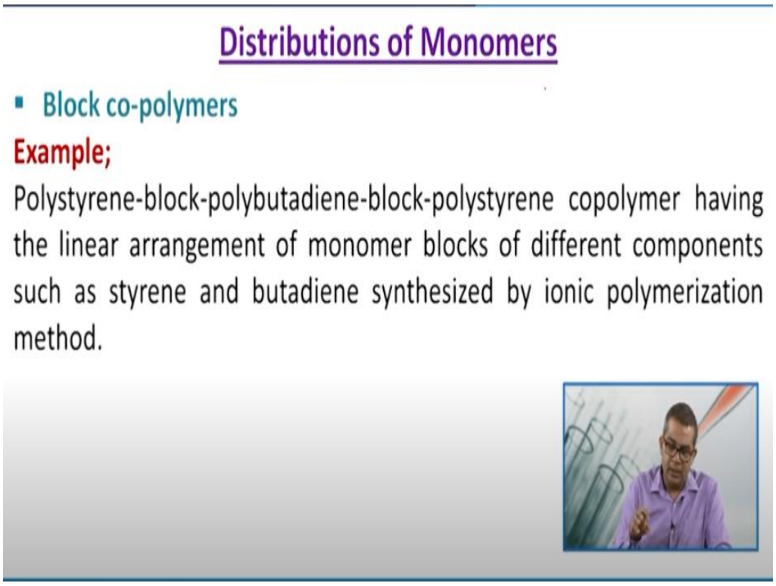

Distributions of Monomers

- Block co-polymers

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.

There are several example of block copolymers like polystyrene-block-polybutadiene-block-polystyrene copolymer. They are having the linear arrangement of monomer blocks of different components such as styrene, butadiene synthesized by ionic polymerization method.

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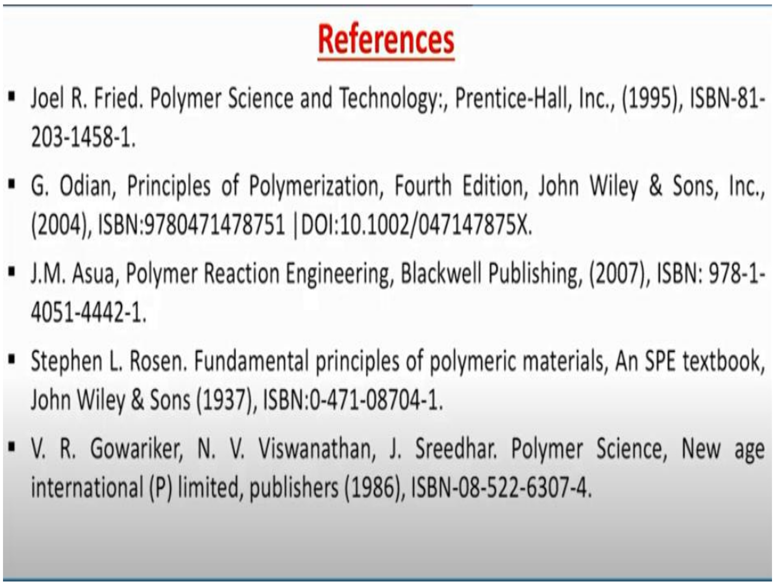

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Now this offers a good option or good protocol or process through which you can either improvise the property or you can develop the things. So, in this particular lecture, we have developed or we have discussed different type of chain arrangement. You can go single or homo-polymer. We can have a different randomly attached monomers. We are having the different type of a blocks of those different monomers.

We can have a wide variety. So, before we go into the deep of this reaction engineering concept, we must be aware about that what kind of things we are looking for and how we can adhere to those particular things so that we can improvise the thing. So, by this way, we are concluding this lecture and in the due course of time we will discuss about the reaction engineering details. Thank you very much.