Polymer Reaction Engineering
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Lecture - 05
Gradient and Graft Copolymer, Polymer and its Compositions, Isomerism in Polymers-II

So welcome to this the concluding part of this gradient and graft copolymer, polymer and its composition segment. Here we are going to discuss about the addition polymerization and other approaches which are required for the various polymeric systems. So, if you recall in the previous lecture, we were discussing about condensation polymerization, and we had a discussion about the nylon 6-6 production.

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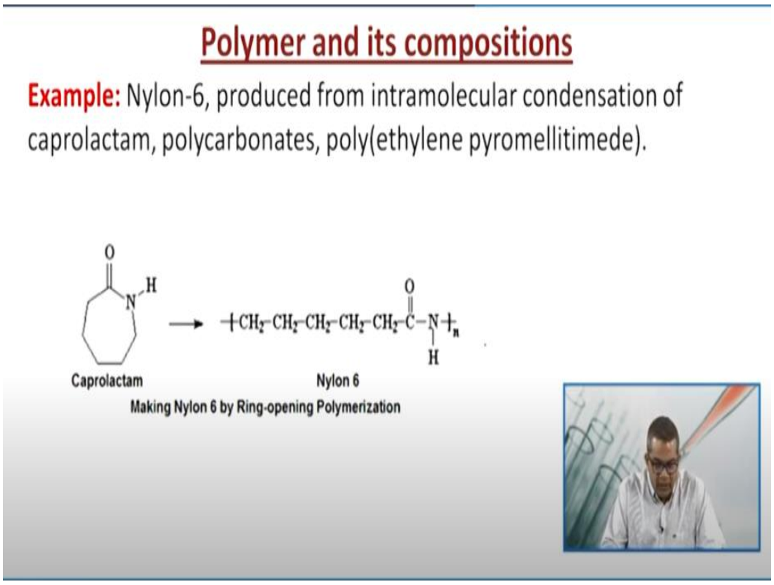

Polymer and its compositions

Example: Nylon-6, produced from intramolecular condensation of caprolactam, polycarbonates, poly(ethylene pyromellitimede).

Making Nylon 6 by Ring-opening Polymerization

Now here we just give you a brief glimpse about and just to refresh your memory about the production of nylon-6. It is usually produced from the intramolecular condensation of caprolactam and polycarbonate etc. You see the importance of this particular condensation polymerization is that this particular reaction deals with the ring opening polymerization. So, it offers a wide spectrum of product profiling etc., the mechanism and the process offer.

So, that is why this particular reaction which is at your screen, it offers a very good opportunity for ring opening because when the ring used to open then there may be enough active sites to carry out the further polymerization process. So, this was all about for the condensation polymerization.

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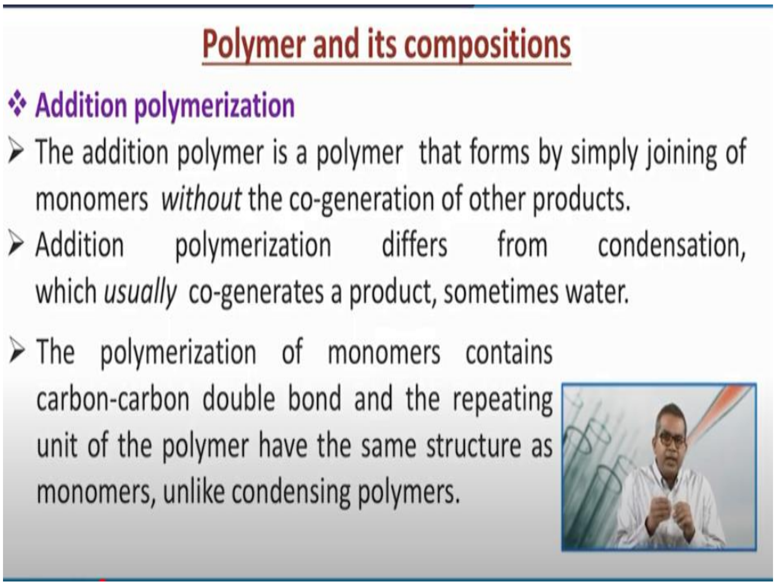

Polymer and its compositions

❖ Addition polymerization

➢ The addition polymer is a polymer that forms by simply joining of monomers *without* the co-generation of other products.

➢ Addition polymerization differs from condensation, which *usually* co-generates a product, sometimes water.

➢ The polymerization of monomers contains carbon-carbon double bond and the repeating unit of the polymer have the same structure as monomers, unlike condensing polymers.

Now let us start with the addition polymerization. Now usually, if you recall this addition polymerization previously, we discussed this addition polymerization is a polymerization process usually formed by simply joining of molecules or monomers without the cogeneration of any other product. If you recall the condensation polymerization, where there was a generation of byproduct.

If you recall the examples, which we discussed previously, the water molecule was produced during the course of polymerization reaction as a byproduct and you need to continuously remove those water molecules to carry out the reaction. But the added benefit to this addition polymerization is that there is no chance of the formation of any kind of allied products and usually they are simply joining.

So sometimes it is referred as other forms. So, this polymerization process they contain sometimes the carbon-carbon double bond and the repeating unit of polymers may have the same structure as monomer unlike the condensing polymers. So, if you recall in the condensing condensation polymerization, we discussed about the formation of nylon 6-6 or PET etc.

In that case, if you see that the structure of the polymer was entirely different from the monomer. But here you may have an opportunity that addition polymerization and the polymer may have the similar type of structure with respect to the repeating unit of that particular polymer.

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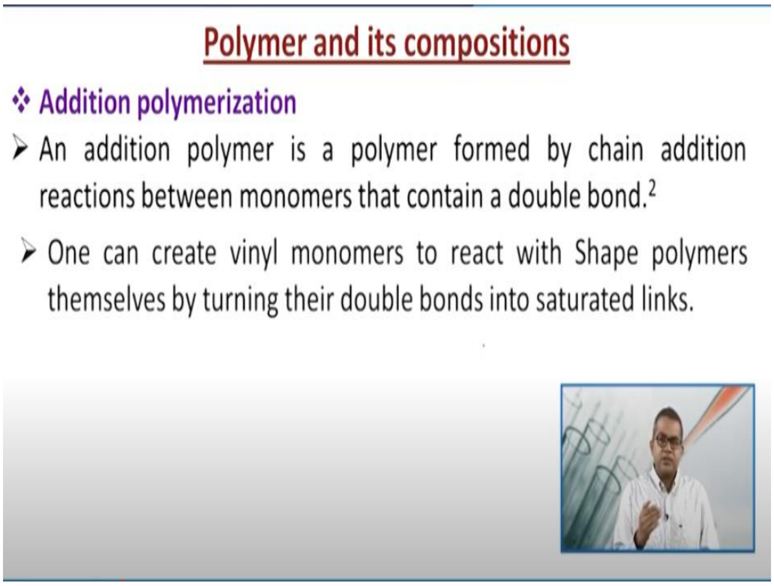

Polymer and its compositions

❖ Addition polymerization

- An addition polymer is a polymer formed by chain addition reactions between monomers that contain a double bond.[2]
- One can create vinyl monomers to react with Shape polymers themselves by turning their double bonds into saturated links.

So usually, in other words, people may say that the addition polymerization or addition polymer is a polymer usually formed by the chain addition of reaction like this between the monomer and that contains a double bond or sometimes any active sites which require. So, one may create any kind of a vinyl monomer to react with the shape polymer etc. So, there are enough opportunities.

There are enough examples like the example of polyethylene, example of formation of polyethylene with respect to the ethylene monomer etc.

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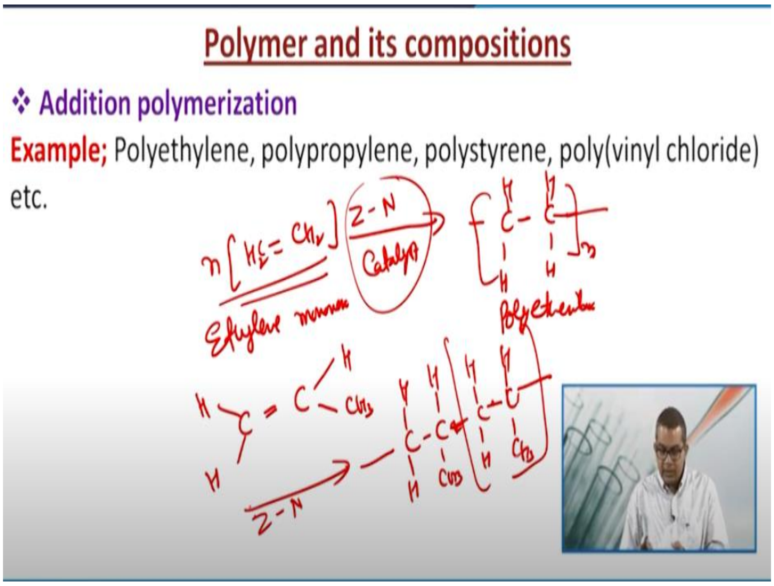

Polymer and its compositions

❖ Addition polymerization

Example; Polyethylene, polypropylene, polystyrene, poly(vinyl chloride) etc.

Now I am giving you couple of examples related to this addition polymerization. The first example related to this is the formation of polyethylene. Now here you see that, this is your ethylene monomer. Now for efficacy of this particular reaction, you may require some catalyst and the best catalyst in this category is your Ziegler-Natta catalyst. And this is your polyethylene.

Now you see that this is your ethylene monomer and this is polyethylene. Now you see that these units these are the repeating units, they are joined together to form this polyethylene. Now this time with the help of a catalyst, so that is the Ziegler-Natta catalyst this. Now sometimes you say that if you develop the polypropylene.

Now here again you see that this is the propylene monomer and if you perform any kind of a polymerization reaction with the help of say like Ziegler-Natta catalyst, then you see that this will form like this sorry. Now this is the repeating unit. So, in some other words you may say that, this is the sequential addition of different type of a monomeric unit.

If you recall the previous lectures where we discussed about the addition of different type of a monomer to form a long chain or a branched chain etc. So, this is one of the best examples of this kind of thing.

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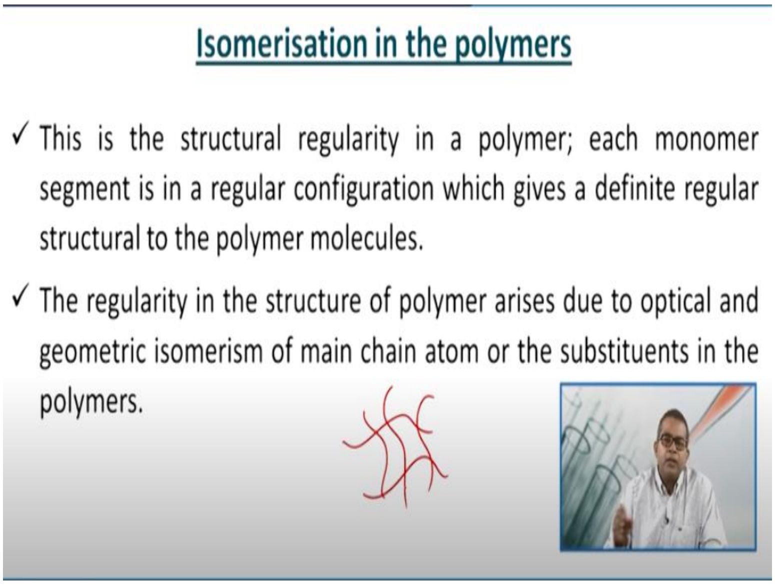

Isomerisation in the polymers

- ✓ This is the structural regularity in a polymer; each monomer segment is in a regular configuration which gives a definite regular structural to the polymer molecules.
- ✓ The regularity in the structure of polymer arises due to optical and geometric isomerism of main chain atom or the substituents in the polymers.

Now when we are discussing about the versatility of this particular polymerization process, we cannot overlook the importance of isomerization process. Because sometimes its demand and if you see in the various petroleum refineries, there is a separate isomerization unit for the product improvisation. So, in the chemistry part, it is already well evident that what is the basic concept of isomerization.

So usually this is the structural regularity in the polymer and each molecule or each monomer segment is in a regular configuration. If you see that the previous example where we were having the polyethylene or polypropylene etc., where each molecule or each polymer system they are having the regular configuration. Now the benefit of this regular configuration, it gives a definite structure to the polymer molecules.

If you recall that we are in the first couple of lectures we discussed that polymer represents in the form of a different chains. So, if you wish to predict the behavior of any kind of a polymeric system, then you must know that what is the structure of that particular polymer molecule like this we have represented.

So, this particular approach always we require that definite we must have the polymers having the regular structure. Now this regularity in the structure of the polymer usually arises due to sometimes optical approach, sometimes the geometric approach and these are clubbed as optical and geometric isomerization of the main atom or the substituent in different type of a polymeric system.

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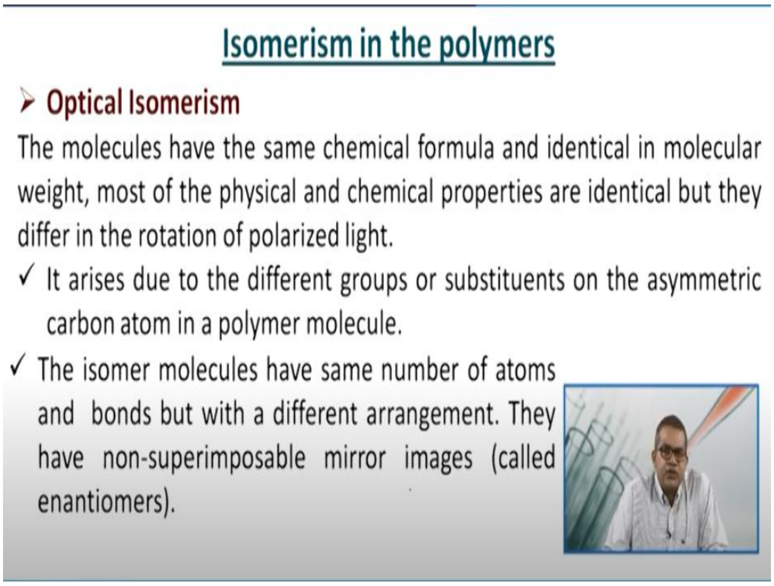

Isomerism in the polymers

- Optical Isomerism

The molecules have the same chemical formula and identical in molecular weight, most of the physical and chemical properties are identical but they differ in the rotation of polarized light.

✓ It arises due to the different groups or substituents on the asymmetric carbon atom in a polymer molecule.

✓ The isomer molecules have same number of atoms and bonds but with a different arrangement. They have non-superimposable mirror images (called enantiomers).

So, let us have a look about different type of isomerization because the product profiling when we consider the product profiling, this kind of knowledge is quite essential. So, the optical isomerization this, the molecules may have the same chemical formula and identical in the molecular weight.

If you recall in the previous lecture, we discussed about the importance, brief importance about the molecular weight because it is the deciding factor of the various properties of polymers. Now these molecules may have sometimes same chemical formula, identical they are in the identical in molecular weight. And most of the physical and chemical properties are identical, but they differ in the rotation of a polarized light.

It is just like that the sugar is available in two forms dextro and levo form. So, this arises due to the different group or substituents on the asymmetric carbon atom in different polymer molecules. So, the isomer molecule may have the same number of atoms bond, but they may have a different arrangement. They have non-superimposable mirrors mirror image that is called the enantiomers.

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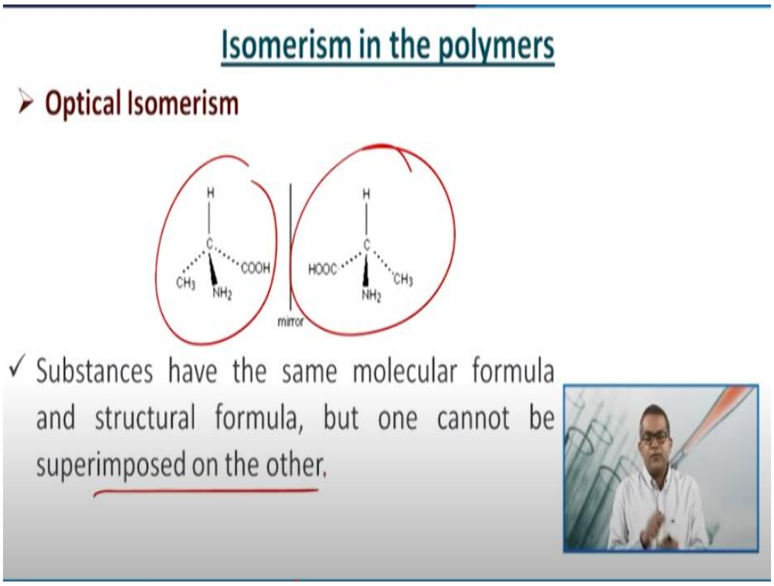

Isomerism in the polymers

- Optical Isomerism

✓ Substances have the same molecular formula and structural formula, but one cannot be superimposed on the other.

If you see that here in this particular photograph or figure, I have given you the mirror image of a particular polymer. Now here you see that although molecular weight is same or kind of functional group, they are same, but still these two polymers are different. So, substance, in other words you may say that the substance may have the same molecular formula, structural formula, but you cannot superimpose them on each other and that is that, that creates the difference in various properties attached to these particular polymeric systems.

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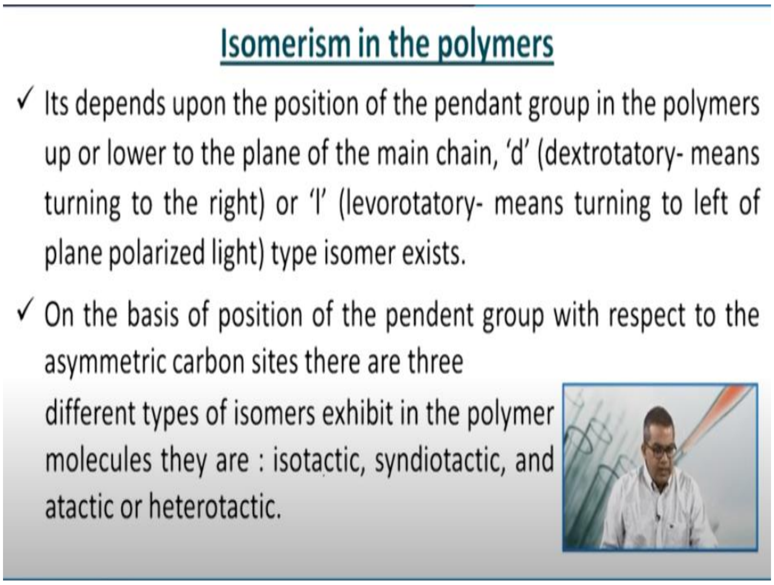

Isomerism in the polymers

- ✓ Its depends upon the position of the pendant group in the polymers up or lower to the plane of the main chain, 'd' (dextrotatory- means turning to the right) or 'l' (levorotatory- means turning to left of plane polarized light) type isomer exists.
- ✓ On the basis of position of the pendent group with respect to the asymmetric carbon sites there are three different types of isomers exhibit in the polymer molecules they are : isotactic, syndiotactic, and atactic or heterotactic.

So usually, it depends on the position of pendant group or the hanging group in the polymer, up or lower that depends on the method of processing. So upper or lower part on the plane of the main chain, sometimes dextrorotatory, sometimes levorotatory etc. So as the name implies that dextrorotatory means turning on the right direction and levorotatory means turning to the left of the plane polarized light.

So, on the basis of this kind of approach or position of the pendant group with respect to asymmetric carbon sites, there are different type of isomers they exhibit in the polymeric system; isotactic, syndiotactic, atactic or heterotactic. So, we are just we will have a brief outline of all these different types of isomers.

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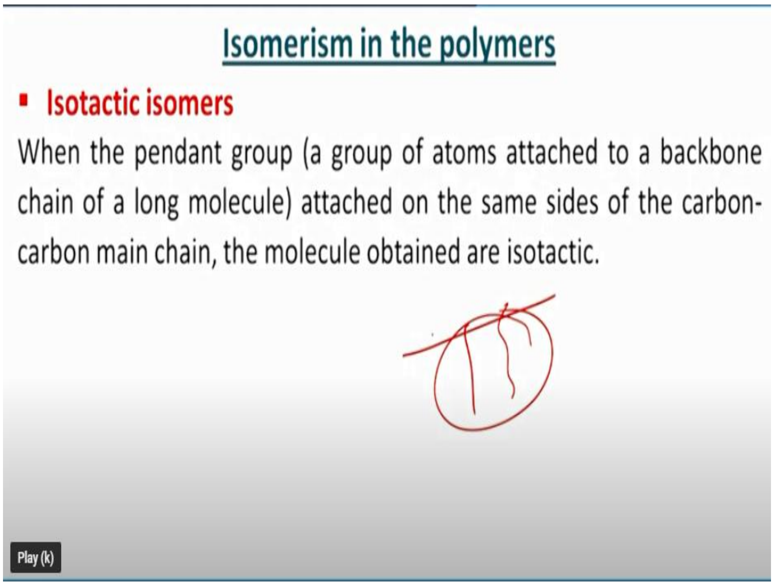

Isomerism in the polymers

- **Isotactic isomers**

When the pendant group (a group of atoms attached to a backbone chain of a long molecule) attached on the same sides of the carbon-carbon main chain, the molecule obtained are isotactic.

Now let us have a look about the isotactic isomers. So, this is that when the pendant group usually, sometimes it is referred as the group of atoms attached to the backbone or a chain of a long molecule like this here. So, if a pendant group is attached on the same side of a carbon main chain, the molecule they are thus obtained is termed as isotactic. It is just like here where this these are the pendant.

They are on the same side of the molecule or the backbone. So, they are termed as isotactic. I am giving you another example of these isotactic isomers.

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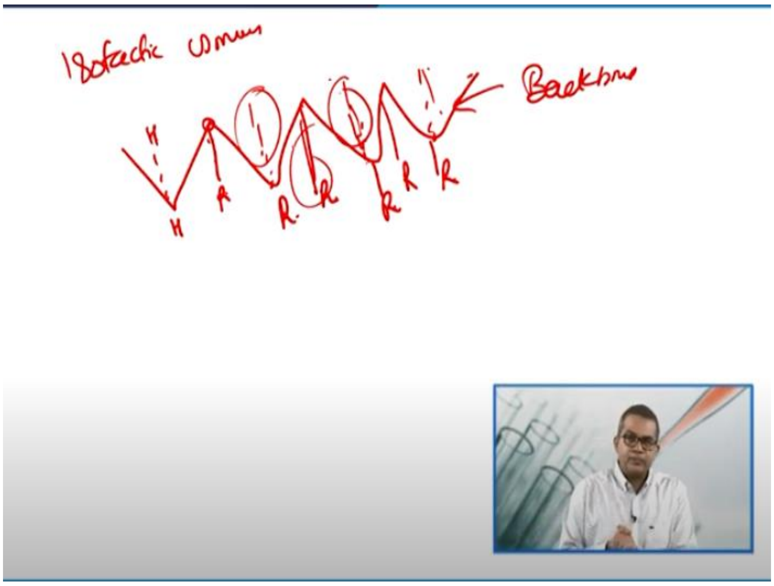

Now here let us see, now here another pendant group see. Now if you see that, this is the backbone of the polymer on the plane of let us assume that it is in the plane of a paper. Now you see that all the dashed-up things are just above the plane of paper and the bold whatever we mentioned over here like this, this and R they are downside of the plain of paper.

So that means, these are the pendant groups like this these dashed. These are the pendant groups and they are having the similar, they occupy the similar side of the backbone. So, they are termed as isotactic.

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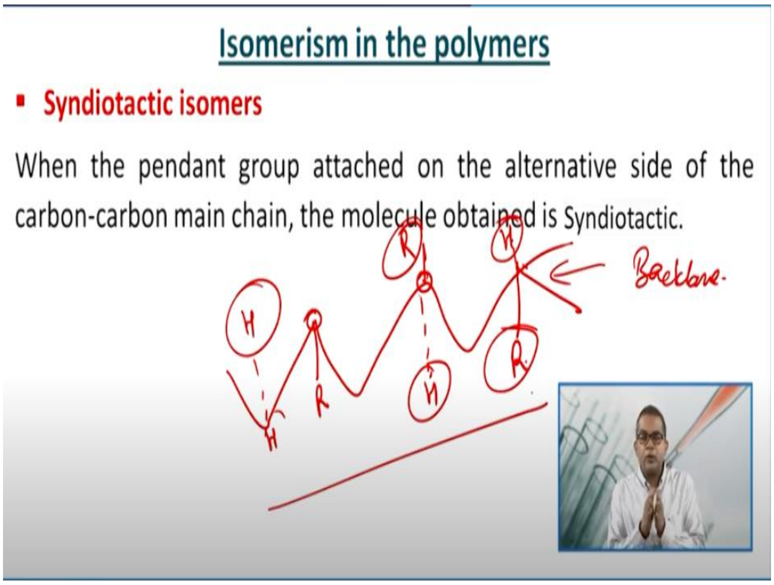

Isomerism in the polymers

- Syndiotactic isomers

When the pendant group attached on the alternative side of the carbon-carbon main chain, the molecule obtained is Syndiotactic.

So, when the pendant group attached on the alternative site of the carbon-carbon main chain, this molecule obtained is referred as syndiotactic. Now I just am giving you the small figure of this to explain that what is this syndiotactic. Now here again I am having a polymeric chain or that is called the backbone chain.

Now here if you see, now here you see that they are these backbones, these pendant groups are on the alternate side like here H. Here you can see H, here H the R, the R etc. So, you can see that they occupies the pendant group they occupies they occupy the alternate arrangement in that particular backbone of polymeric system. So, they are termed as syndiotactic.

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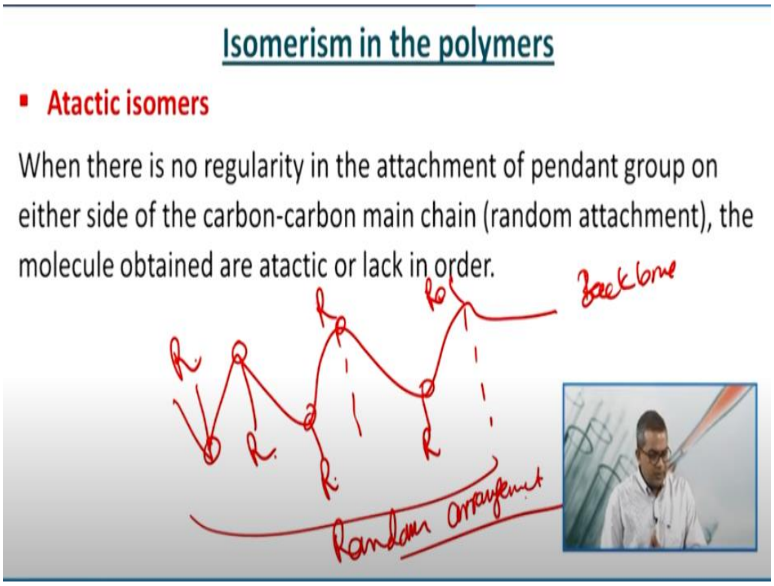

Isomerism in the polymers

- Atactic isomers

When there is no regularity in the attachment of pendant group on either side of the carbon-carbon main chain (random attachment), the molecule obtained are atactic or lack in order.

Another third part of this particular isomeric system is the atactic isomers. So, when there is no regularity in the attachment of a pendant group on either side of the carbon main chain, maybe sometimes you may refer as the random attachment of the pendant group to the polymeric backbone. So, these molecules thus obtained they are atactic isomers or they are lacking in orders etc.

So, you can say that this is the random approach and there is no fixed approach. And if you recall the previous one, when we were discussing about the isotactic, where everything was aligned to a single side of this one. Then we discussed about the syndiotactic when the pendant groups are in the alternate fashion. Now here they are the pendant groups are in random attachment.

Now let us have a look about this one. Again, this is our backbone. Now here different sites are available. Now sometimes you may have R over here. Sometimes again the R over here. Then R then R then R and sometimes here. So, you see that this is the random arrangement. This is the random arrangement of the pendant groups across the backbone.

And sometimes it is you can say it is very feasible and sometimes it is you can say it is a very difficult to orient the things. So that is why based on the requirement and based on the engineering approach, you may go for this type of arrangement.

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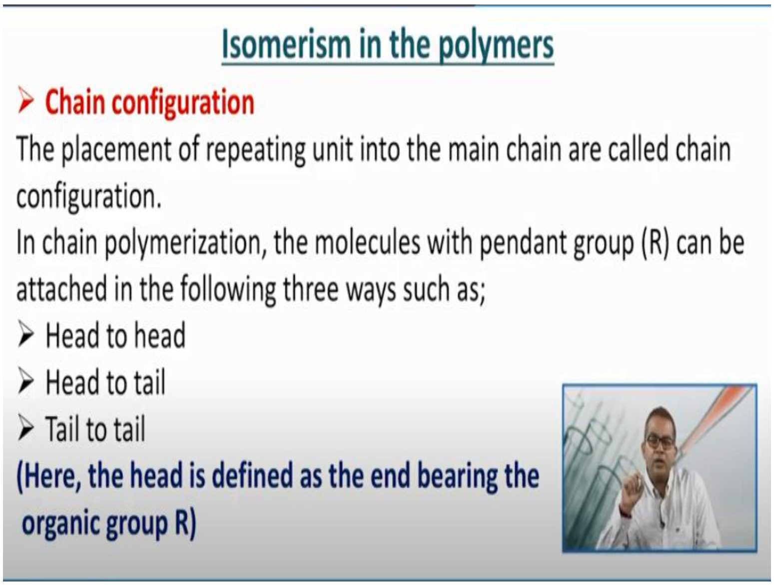

Isomerism in the polymers

- Chain configuration

The placement of repeating unit into the main chain are called chain configuration.

In chain polymerization, the molecules with pendant group (R) can be attached in the following three ways such as;

- Head to head
- Head to tail
- Tail to tail

(Here, the head is defined as the end bearing the organic group R)

Now let us go for the chain-growth and step-growth aspect of classification of polymerization reaction. So, let us have a look about the chain configuration. Now it is quite simple that the placement of repeating unit into the main chain they are called the chain configuration.

Now the in this particular polymerization, the molecules those who are having the pendant group, let us say R in this case can be attached in different ways, maybe head-to-head maybe head to tail or maybe tail to tail. So, this is the three different type of thing.

Now if you see these kinds of a classification or different type of a way for approaching the polymeric system, there are different approaches or different ways through which you can generate more and more different type of tailor-made polymeric system. Now here, when we discuss about that the head is usually defined as the end bearing the organic group R.

Now this organic group R is again having very important because it may have active sites or reactive sites, may have a double bond etc., to carry out the further configuration in due course of time.

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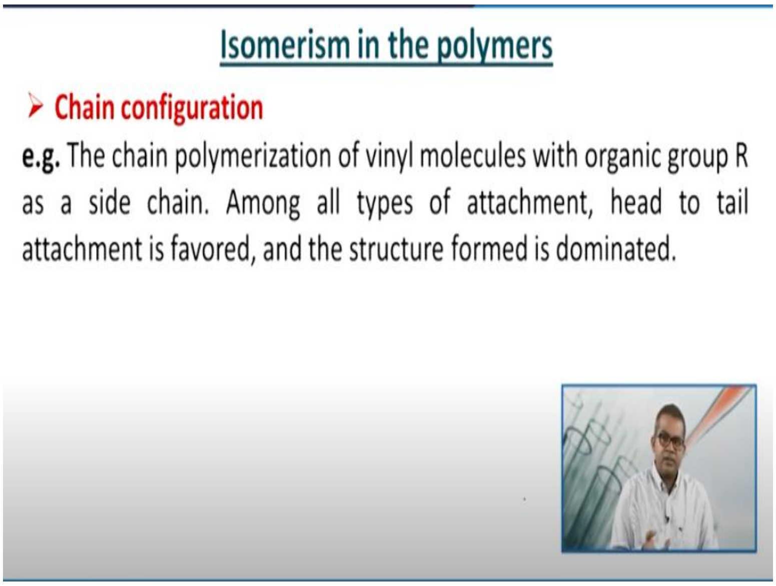

Isomerism in the polymers

- Chain configuration

e.g. The chain polymerization of vinyl molecules with organic group R as a side chain. Among all types of attachment, head to tail attachment is favored, and the structure formed is dominated.

Now just I am giving you an example that the chain polymerization of vinyl molecule with the organic group say R as a side chain. So, among all type of attachment, head to tail attachment is usually favored and usually structure formed is dominating one.

Now here, you see that by this way you can visualize the thing. Now I am using the vinyl monomer.

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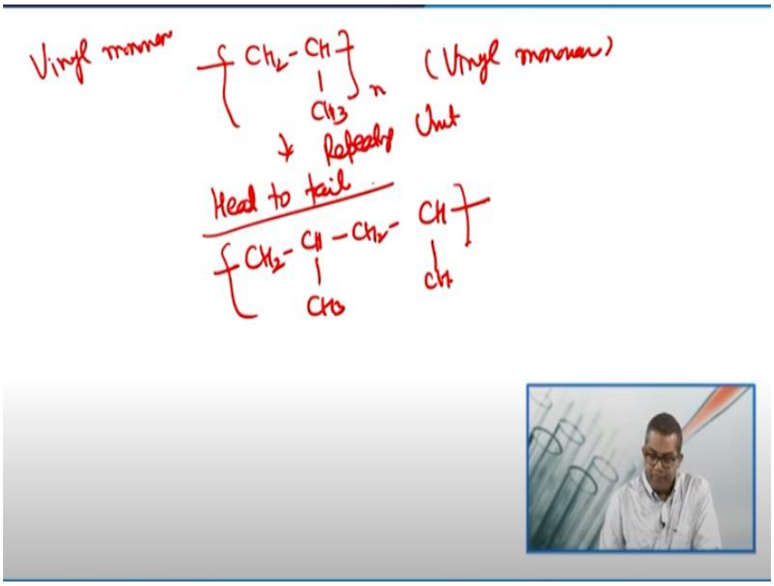

Now this is the structure of vinyl monomer. And if you add this is the, this become the number of, n number, number n is the number of repeating units. This is the repeating unit. Now if I see that we discussed about the head to tail. Now here you see that this is head to tail type of system. Now if you see if you try to compare with the head-to-head, we will discuss in situ.

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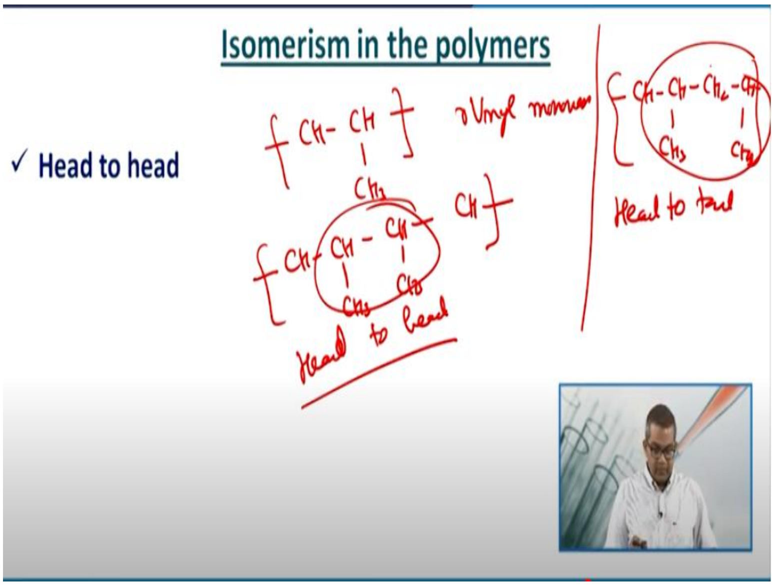

Isomerism in the polymers

✓ Head to head

Now another example of this vinyl monomer is carried with the head-to-head one. Now just see again come back to the monomer side. This is my monomer. Now if talk about the head-to-head. That means, you see that what is the difference. Now this is head-to-head. Now if you recall the head to tail where the configuration was like this.

So, this was head to tail. Now see the difference, here and here. We can clearly visualize that the molecular system is same, molecular weight is same, but the properties of the polymer would be a bit different.

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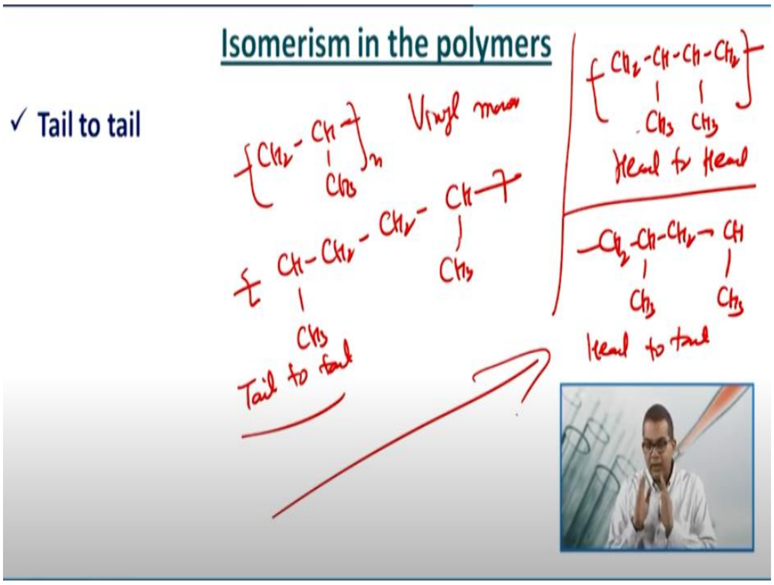

Isomerism in the polymers

- ✓ Tail to tail

Now come back to the tail to tail. Now here you see that the again the same monomer. This is the vinyl monomer and the arrangement is like this. Now this is the tail to tail. Now if you compare with your head-to-head, the head-to-head was CH_2-CH-CH-CH_2 and CH_3. Now this was head-to-head and if you compare with the head to tail, you see this is head to tail.

Now you see the difference among all three approaches and you can see that if we go for the any kind of polymer, the polymer would may have different properties compared to the other one although they are having the same molecular weight, they are having the other things in common, but they will they may have entirely different properties. So, this is just about the chain thing.

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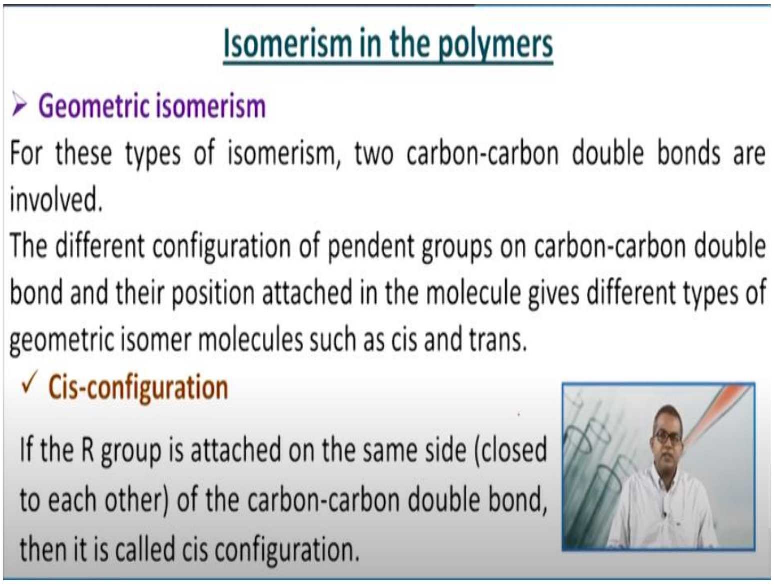

Isomerism in the polymers

- **Geometric isomerism**

For these types of isomerism, two carbon-carbon double bonds are involved.

The different configuration of pendent groups on carbon-carbon double bond and their position attached in the molecule gives different types of geometric isomer molecules such as cis and trans.

- ✓ **Cis-configuration**

If the R group is attached on the same side (closed to each other) of the carbon-carbon double bond, then it is called cis configuration.

Now there are certain geometric type of isomerization process or isomers. So, for these types of isomerism process, there are two carbon-carbon double bonds are usually involved. The different configuration of pendant group on carbon-carbon double bond and their position usually they are attached in the molecule gives different type of a geometric isometric configuration.

It is bit different from the mirror image which we discussed earlier. Now let us have about there are two types of geometric isomerization, cis-configuration and trans configuration. Let us have a look about the cis-configuration. Now if the R group which is our more common group, the R group is attached on the same side that is close to each other of the carbon-carbon double bond then they are called the cis-configuration.

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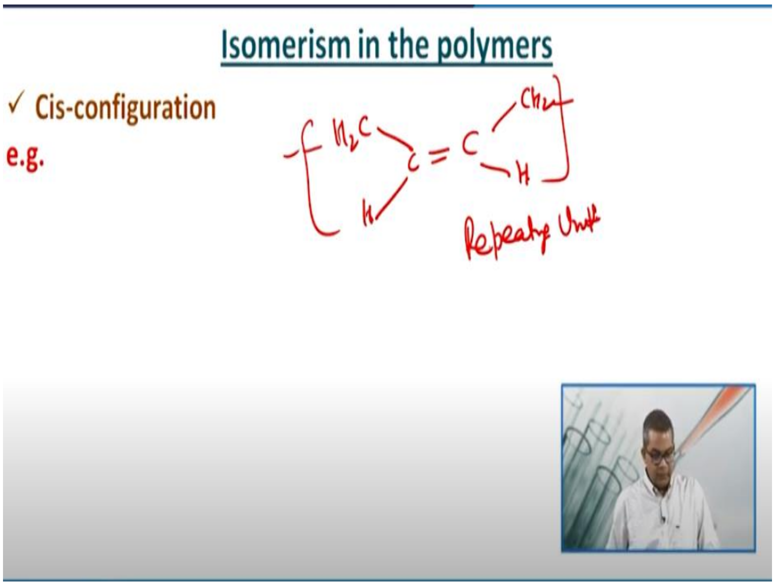

Isomerism in the polymers

✓ Cis-configuration

e.g.

I am giving an example of a cis-configuration. That is, you see that this is the repeating unit. Now this is the example of cis-configuration. Now here if you recall that the repeating unit of this particular approach that the carbon-carbon double bond, they are the R group is attached on the same side of carbon-carbon double bond.

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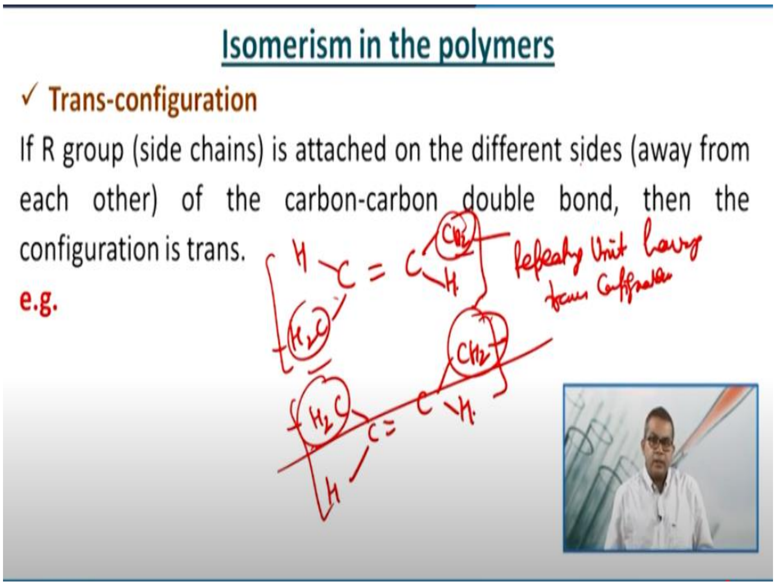

Isomerism in the polymers

✓ Trans-configuration

If R group (side chains) is attached on the different sides (away from each other) of the carbon-carbon double bond, then the configuration is trans.

e.g.

Now if you go for the trans-configuration, now if you see that the R group that is the side chain is attached on the different side of that particular monomer molecule that is away from each other from the carbon-carbon double bond, then the configuration is called as a trans-configuration. Now here you see that this is, now this is the repeating unit having trans-configuration.

Now here you see that the side groups they are away from each other, right. Now if you compare with the cis-configuration, which we discussed in the previous slide, you see that this is more clear picture about this one. Now you see that here, the R groups the position of R group. And here, this one is having the along the side and here you are having this the different side of the things.

So, we have discussed about a brief in brief about the isomerization system and other things related to the development of a polymeric system and these types of things are quite essential, while we try to control the polymerization system, how we can control it because how we can change the molecular weight, how we can have a different type of a polymer with respect to the different the same type of polymeric molecules etc., same type of a molecular weight etc.

So, it provides you a broad spectrum for the development of any kind of a polymeric product.

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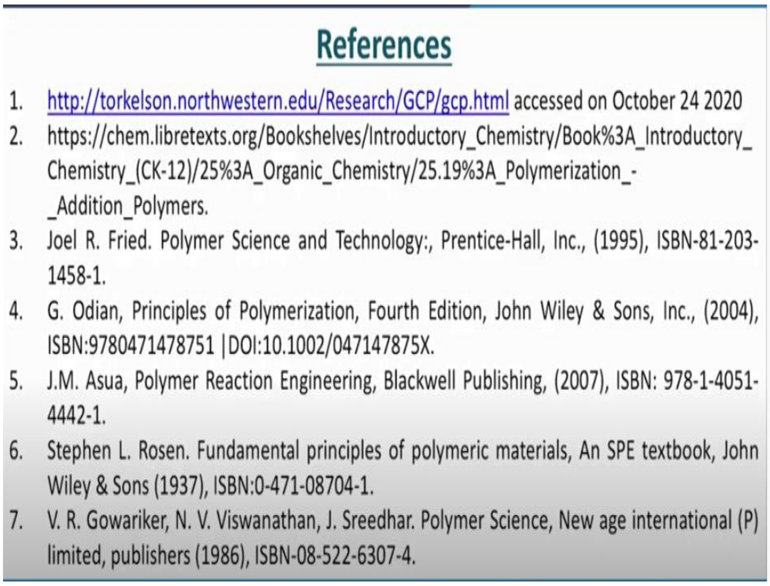

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We have enlisted couple of reference for the knowledge or for the reading etc. So, by this way, we are summing up this particular lecture. Thank you very much.