Introduction to Polymer Science

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Lecture – 20
Polymer Stereochemistry and Zeigler - Natta coordination Polymerization

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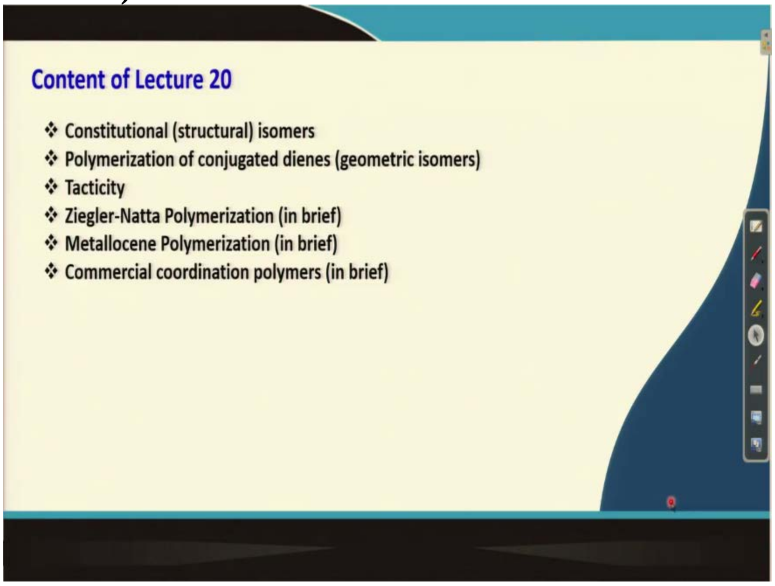

Content of Lecture 20

- Constitutional (structural) isomers
- Polymerization of conjugated dienes (geometric isomers)
- Tacticity
- Ziegler-Natta Polymerization (in brief)
- Metallocene Polymerization (in brief)
- Commercial coordination polymers (in brief)

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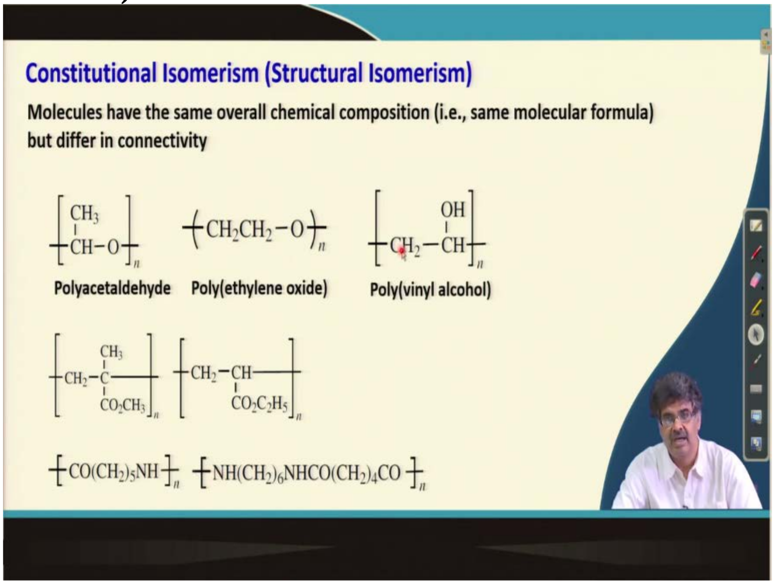

Constitutional Isomerism (Structural Isomerism)

Molecules have the same overall chemical composition (i.e., same molecular formula) but differ in connectivity

Polyacetaldehyde Poly(ethylene oxide) Poly(vinyl alcohol)

$-\!\!\left[CO(CH_2)_5NH\right]\!\!-_n$ $-\!\!\left[NH(CH_2)_6NHCO(CH_2)_4CO\right]\!\!-_n$

Welcome back, in this lecture 20 we will discuss about polymer stereochemistry and Zeigler-Natta coordination polymerization. Let us understand constitutional isomerism which was previously called structural isomerism. Molecules that have the same overall chemical composition, that is the same molecular formula, but differ in bonding structure or connectivity are called constitutional isomerism. Look at these three structures. They have same molecular formula C_2H_4O but their connectivity is different in each molecule. These are examples of constitutional isomerism which were previously called structural isomerism. Other examples like poly(methyl acrylate) and poly(ethyl acrylate) and other polymers as shown in the slide. So, these are the examples of constitution isomers.

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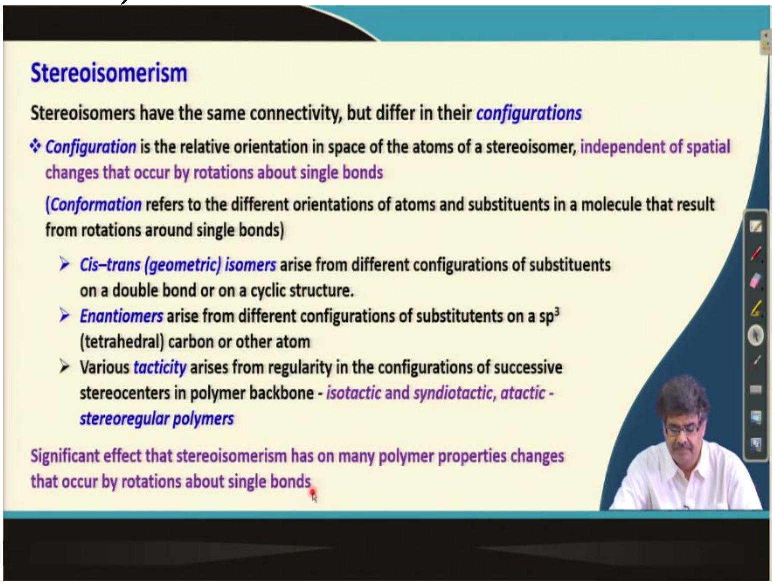

Stereoisomerism

Stereoisomers have the same connectivity, but differ in their *configurations*

- *Configuration* is the relative orientation in space of the atoms of a stereoisomer, independent of spatial changes that occur by rotations about single bonds

(*Conformation* refers to the different orientations of atoms and substituents in a molecule that result from rotations around single bonds)

- *Cis–trans (geometric) isomers* arise from different configurations of substituents on a double bond or on a cyclic structure.
- *Enantiomers* arise from different configurations of substitutents on a sp^3 (tetrahedral) carbon or other atom
- Various *tacticity* arises from regularity in the configurations of successive stereocenters in polymer backbone - *isotactic* and *syndiotactic, atactic* - *stereoregular polymers*

Significant effect that stereoisomerism has on many polymer properties changes that occur by rotations about single bonds

Next, we will talk about stereoisomers. Stereoisomers have the same connectivity, but they differ in their configurations. What are configurations? If you recall from your early chemistry knowledge, that configurations are the relative orientation of atoms in space which can be achieved independent of the spatial change or changes that can occur by rotation about single bond. So, if we can get different spatial arrangements, by rotating the single bonds, then we do not call them as different configurations. Configurations are the relative orientation in the space of the atoms. When we get different orientations, just by rotating the single bond, we call those structures as conformations. Different types of configurations can be possible, for example, cis-trans configuration or cis-trans isomer or geometric isomers, which arise from the different configurations of substituents on a double bond or a cyclic structure. We can have different configuration or stereoisomers in this case. For example, we know that enantiomers arise from different configurations of substituents on sp^3 or tetrahedral carbon atom or other atom. So, these are the examples of stereoisomers because they have different configurations. Specially in case of polymers, we can have various tacticity as we discussed earlier in the beginning, which arises from the regularity in the configurations of successive stereocenters in polymer backbone.

We gave examples like isotactic and syndiotactic polymers, where isotactic means the orientation of the groups in the stereocenters are same when we go one after one. Whereas, in case of syndiotactic, we got alternate arrangements of the groups, around stereocenters, and atactic where there was no particular arrangement of these stereocenters, and these are examples of stereoregular polymers. Stereoregularity in polymers actually have significant effect on their property.

If we compare for example, isotactic polystyrene, syndiotactic polystyrene or atactic polystyrene, the properties of the resulting polymers would be quite different from each other.

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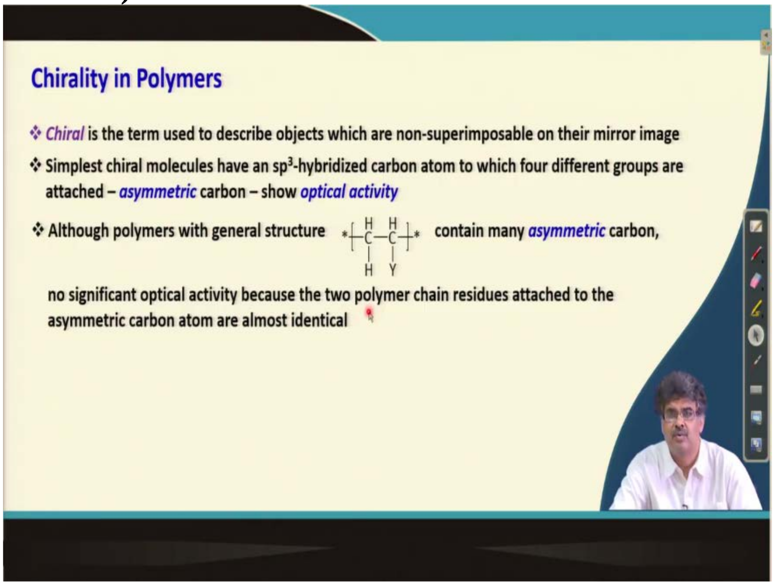

Chirality in Polymers

- *Chiral* is the term used to describe objects which are non-superimposable on their mirror image
- Simplest chiral molecules have an sp^3-hybridized carbon atom to which four different groups are attached – *asymmetric* carbon – show *optical activity*
- Although polymers with general structure $*\!\left[\begin{array}{c}H\\|\\C\\|\\H\end{array}\!-\!\begin{array}{c}H\\|\\C\\|\\Y\end{array}\right]\!*$ contain many *asymmetric* carbon, no significant optical activity because the two polymer chain residues attached to the asymmetric carbon atom are almost identical

We know if a small organic molecule has chiral center, it shows optical activity. Just to bring chirality in polymers in this perspective, chiral is a term used to describe objects which are non-superimposable on their mirror image. Simplest chiral molecules that have a SP^3-hybridized carbon atom to which four different groups are attached, we call that particular carbon as asymmetric carbon and they show optical activity.

In case of polymers, if we look at this carbon actually, this carbon has all the four substituents different i.e. four groups which are attached to the carbon atom, they are all different. So, they are in true sense asymmetric because the four substituents are different, but, in reality polymers do not show optical activity.

This is because, effectively the substituents from both are effectively almost same specially the first 2 atoms or first 2 groups are same on both sides. No significant optical activity is shown by this type of polymers as the polymer chain residues attached to the asymmetric carbon atom are almost identical. We can have optical activity from polymers, but that is a special case because of different conformational arrangements, which is beyond the scope of this course.

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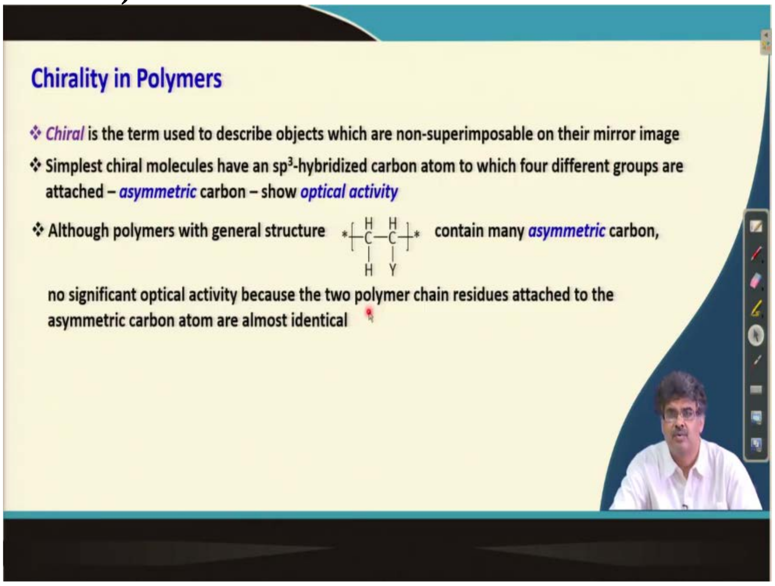

Chirality in Polymers

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- Although polymers with general structure $*\!-\!\left[\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Y}{C}}\right]\!-\!*$ contain many *asymmetric* carbon, no significant optical activity because the two polymer chain residues attached to the asymmetric carbon atom are almost identical

Now, let me move to next topic on polymerization of 1, 3-butadiene and substituted butadienes. For example, let us have substituted 1,3-butadiene. If you recall your organic chemistry knowledge, this is the carbon number 1, this is 2, this is 3 and this is 4. If we polymerize we can either polymerize the double bond at C1 and C2 which will lead to 1, 2- polymerization, or we can polymerize the double bond at C3 and C4 that will lead to 3, 4 polymerization or we can actually have another 1, 4 type polymerization as well. Now, there is more chance of 1,4-polybutadiene forming more because an active center, either a cation, radical or anion can actually participate in resonance conjugation and proceed the polymerization in this fashion. Now, this 1, 4 polymers can also have 2 stereoisomers. For example, this is a double bond and we know that at across the double bond we can have cis arrangement or trans arrangement. So, basically we can have cis 1, 4 polyisoprene. This is the structure of natural rubber which, as you can see is not very regular. Hence, this polymer cannot actually form orderly crystalline structures and as a result they are amorphous rubbery materials.

Whereas, Gutta percha or balata are predominantly trans-1, 4 isoprene, which actually have very orderly structure. So, many polymer chains actually come close and get ordered one after another to form crystalline domains. As a result, these trans-1, 4 polyisoprene are hard and rigid material. You can see the different stereoisomers from the same polymer can have different morphologies and as a result they can have different properties all together as we have seen for natural rubber and Gutta percha and balata.

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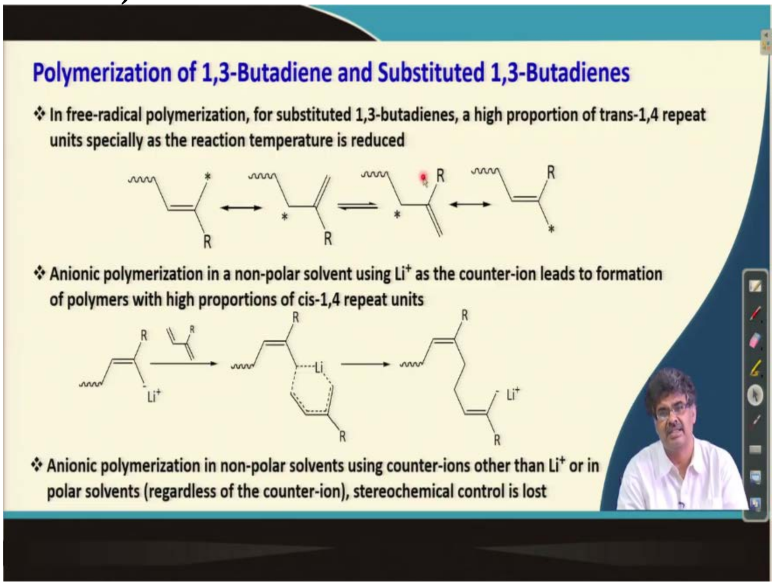

Polymerization of 1,3-Butadiene and Substituted 1,3-Butadienes

- ❖ In free-radical polymerization, for substituted 1,3-butadienes, a high proportion of trans-1,4 repeat units specially as the reaction temperature is reduced
- ❖ Anionic polymerization in a non-polar solvent using Li^+ as the counter-ion leads to formation of polymers with high proportions of cis-1,4 repeat units
- ❖ Anionic polymerization in non-polar solvents using counter-ions other than Li^+ or in polar solvents (regardless of the counter-ion), stereochemical control is lost

Now, in free radical polymerization for substituted 1, 3-butadiene, there is a high portion of trans-1, 4 repeat units specially as the reaction happens at reduced temperature. That is because, if we look at the propagation step, since at the active center is planner, the next attack on this carbon atom could be from the other side because of steric hindrance, and as a result, trans-isomers are formed preferentially. If we increase temperature, then there is a possibility of rotation around this single bond and as a result this loss of preference of trans-isomers are kind of lost. As a result, we get cis form if we increase the temperature. So, basically if we do this reaction at lower temperature, we are likely to get trans isomer but if we do at higher temperature, we can get a mixture of both trans and cis isomer.

If we do anionic polymerization of this monomer in non-polar solvent, with lithium ion as the counter-ion then this lithium ion will be tightly bound with this anionic propagating center and the incoming monomer will actually coordinate with this like this and forming a 6 membered ring and as a result, there is a similar arrangement around this double one and thus we get cis 1, 4 repeat units in this case.

Now, if instead of non-polar solvent if we use polar solvent or if you use a larger cation other than lithium and then this tight ion-pair formation is lost and as a result, this will be separated and the chances of forming or trans 1, 4 repeat unit will be much higher. So, in anionic polymerization using non-polar solvent and counter-ions other than lithium or otherwise in polar solvents, regardless of the counter-ion, the stereochemical control is lost. We are likely to get more trans- isomer.

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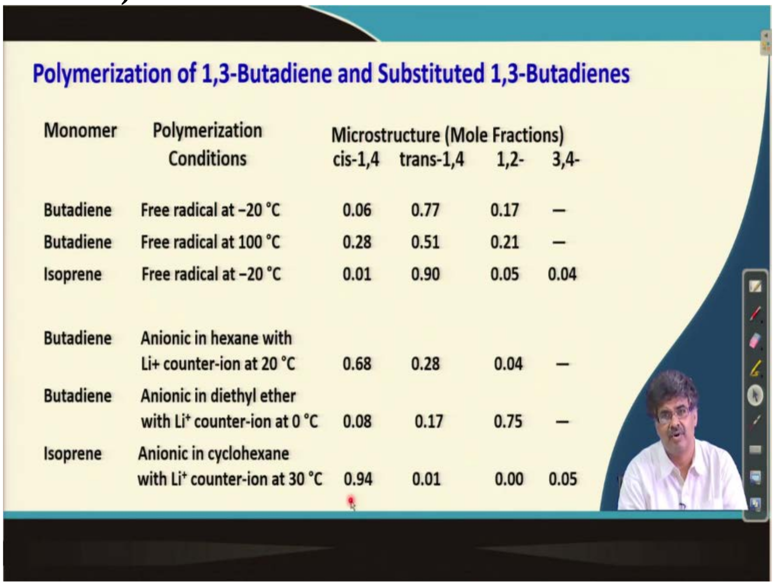

Polymerization of 1,3-Butadiene and Substituted 1,3-Butadienes

Monomer	Polymerization Conditions	Microstructure (Mole Fractions) cis-1,4	trans-1,4	1,2-	3,4-
Butadiene	Free radical at −20 °C	0.06	0.77	0.17	—
Butadiene	Free radical at 100 °C	0.28	0.51	0.21	—
Isoprene	Free radical at −20 °C	0.01	0.90	0.05	0.04
Butadiene	Anionic in hexane with Li+ counter-ion at 20 °C	0.68	0.28	0.04	—
Butadiene	Anionic in diethyl ether with Li^+ counter-ion at 0 °C	0.08	0.17	0.75	—
Isoprene	Anionic in cyclohexane with Li^+ counter-ion at 30 °C	0.94	0.01	0.00	0.05

For example, if you look at this table where butadiene was used for free radical polymerization at lower temperature, we are getting more trans-isomer. If we increase the temperature some cis-isomer is also forming. The extent of trans-isomer is coming down as we explained because of rotation around the single one, but if we increase the substituent size is from butadiene to isoprene then this steric preference increases.

So, at this same temperature now you can see we are generating more trans-isomer because the attack from the other side is more favorable because of the presence of higher sized substituent. If you increase the size of this substituent and if you do reaction at lower temperature, we are likely to get more trans-isomer. Look at the data for anionic polymerization of butadiene using lithium ion. When you use a non-polar solvent at 20°C, mostly cis-isomers are formed but when we use a polar solvent like dimethyl ether, then this is lost. Then we get 1, 2 isomerization. Then this preference or stereocontrol is lost, but, if we increase the size of the substituent and again we do reaction in a non-polar solvent, then even higher amount of cis-1,4 isomer is produced. If you want to use trans-1, 3 butadiene then we should use a radical polymerization at lower temperature and if you want to use cis product then you should use anionic polymerization with lithium ion as counter-ion in a nonpolar solvent and so on. So, this gives you an idea about what we should do if we want a specific type of polymer from 1,3 butadiene and substituted 1,3 butadiene.

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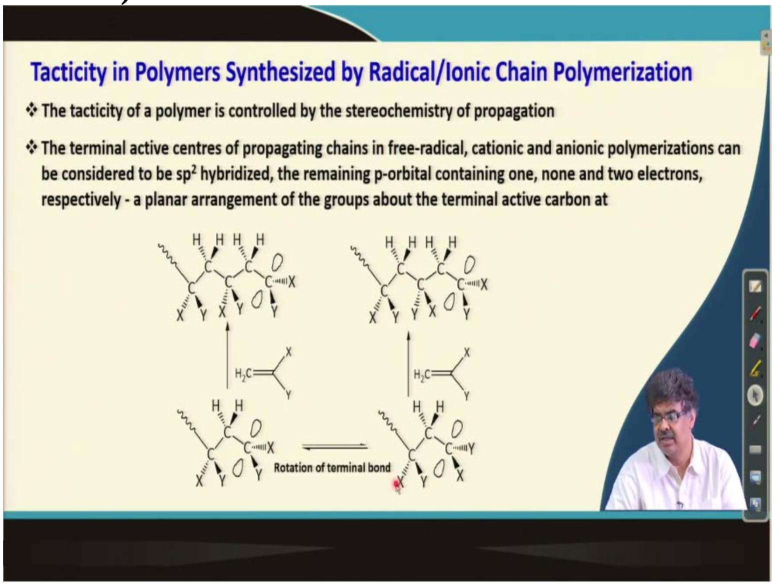

Tacticity in Polymers Synthesized by Radical/Ionic Chain Polymerization

- The tacticity of a polymer is controlled by the stereochemistry of propagation
- The terminal active centres of propagating chains in free-radical, cationic and anionic polymerizations can be considered to be sp^2 hybridized, the remaining p-orbital containing one, none and two electrons, respectively - a planar arrangement of the groups about the terminal active carbon at

We will discuss now about tacticity of polymers synthesized by radical or ionic chain polymerization. The tacticity of polymers is controlled by the stereochemistry of propagation center basically. Now, in case of a chain polymerization for radical, the propagating center is a radical and for cationic polymerization the propagating center is a cation and for anionic polymerization it is an anion. When these propagating center is radical or cation, then this is a sp2 hybridized carbon, so, this is a planar molecule, and in case of anionic although it is sp3 hybridized, but because of the presence of substituent, we remember that anionic polymerization is only possible when the anion is stabilized by resonating substituent. As a result, you effectively get a double bond with the substituent and we get a sp^2 hybridized carbon atom.

Thus, in all these three cases, we have a planar structure. As a result, when the next monomer attacks, generally it attacks on the opposite side of the existing substitution. As a result, we generally have a tendency to form syndiotactic isomers but again, if we increase temperature, then because of this rotation of this single bond as is shown here, then this stereo control is lost, then we are likely to get a random arrangement of these stereocenters. So, we are more likely to get atactic polymerization. Again if we do a polymerization at very low temperature, we might get a trans or syndiotactic whereas, if we do at a moderate to high temperature, we are likely to get atactic polymers. For isotactic we cannot probably make with these simple radical polymerizations, we need special technique we will discuss later.

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Zeigler-Natta Polymerization

(Coordination Polymerizations)

Now, as we said that we cannot make various stereo specific or stereo regular polymers using radical or ionic polymerization and that is overcome by this Ziegler-Natta polymerization we which uses coordination as a step and we also call these Ziegler-Natta polymerization as coordination polymerization.

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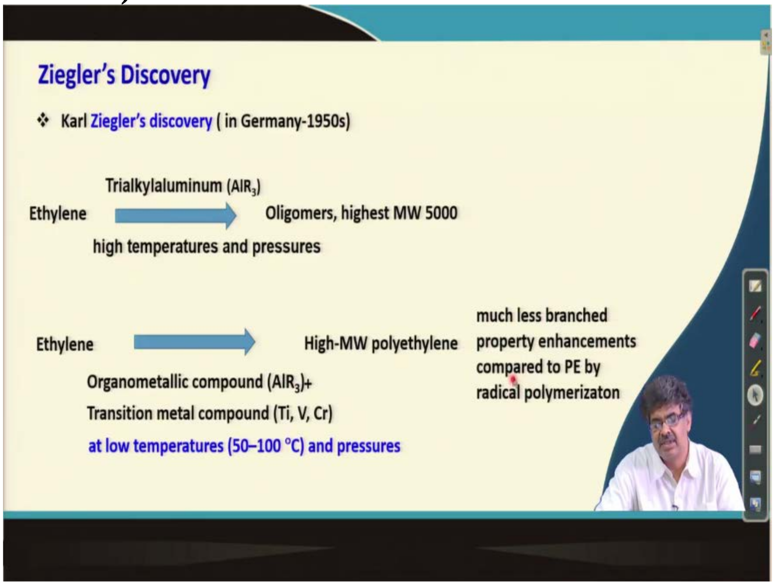

Ziegler's Discovery

❖ Karl Ziegler's discovery (in Germany-1950s)

Trialkylaluminum (AlR_3)

Ethylene → Oligomers, highest MW 5000

high temperatures and pressures

Ethylene → High-MW polyethylene

Organometallic compound (AlR_3)+

Transition metal compound (Ti, V, Cr)

at low temperatures (50–100 °C) and pressures

much less branched

property enhancements compared to PE by radical polymerizaton

It was first discovered by Ziegler in 1950s in Germany. He polymerized ethylene in presence of trialkylaluminum at high temperature and pressure to get an oligomer type molecule whose highest molecular weight was about 5000. This is not a useful polymer because this does not have a proper enough or required amount of mechanical properties for polyethylene to be applicable. When it used along with this organometallic compound, like transition metal compounds either titanium, vanadium or chromium, then this polymerization can be done at lower temperature and pressure in yielding high molecular polyethylene. This polyethylene also much less branched and compared to the polyethylene synthesized by radical polymerization. As the result these polymers can actually crystallize and form more highly useful polymers polyethylene. So, this actually was a very giant discovery, which actually enables syntheses of high molecular weight polyethylene, which is a very important and commonly used polymer.

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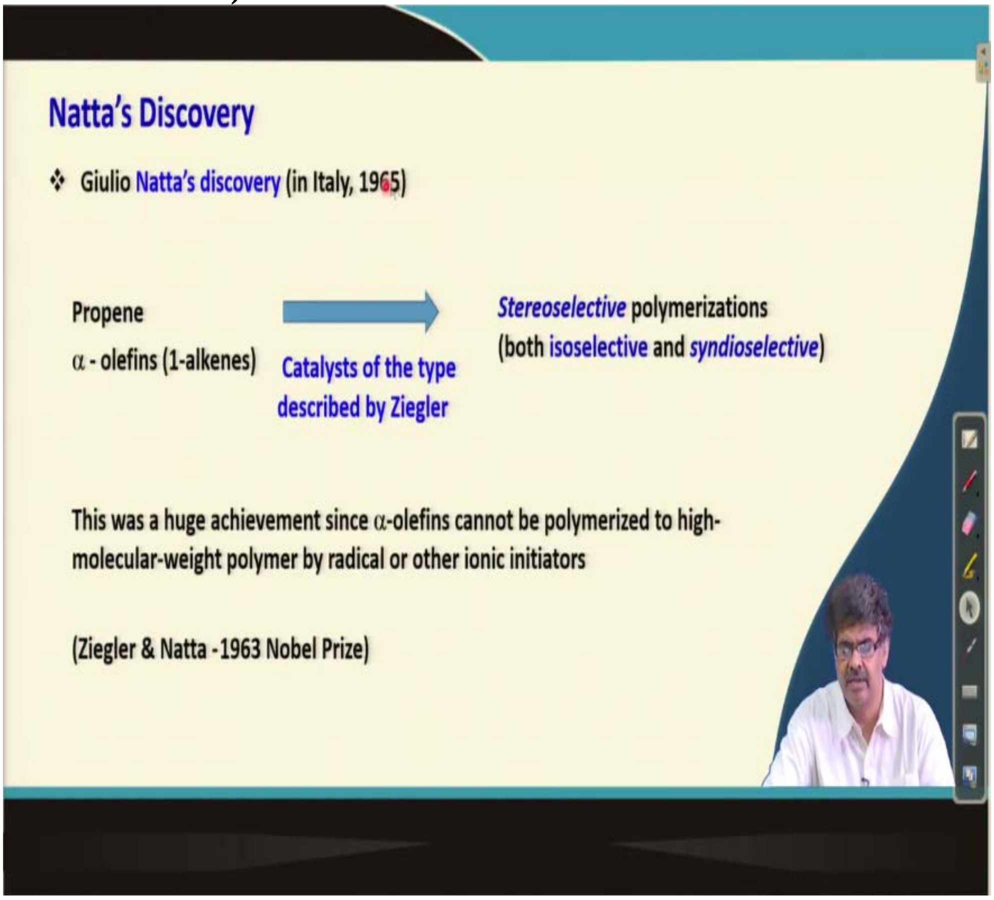

Natta's Discovery

- Giulio Natta's discovery (in Italy, 1965)

Propene
α - olefins (1-alkenes)

Catalysts of the type described by Ziegler

Stereoselective polymerizations
(both isoselective and *syndioselective*)

This was a huge achievement since α-olefins cannot be polymerized to high-molecular-weight polymer by radical or other ionic initiators

(Ziegler & Natta - 1963 Nobel Prize)

Later on Natta in Italy 1954 used similar catalyst system, but instead of ethylene he showed that it can be actually used for alpha olefins like propylene and using same catalyst described by Ziegler, he actually succeeded to get stereoselective polymerization, both isoselective as well as syndioselective. This was a huge achievement since, as we just discussed that alpha olefins cannot be polymerized to high molecular weight polymers by radical and other ionic initiators specially with stereoselectivity, like if you want isoselective and syndioselective polymers. As a result, Ziegler and Natta was combinedly awarded the Nobel Prize in 1963.

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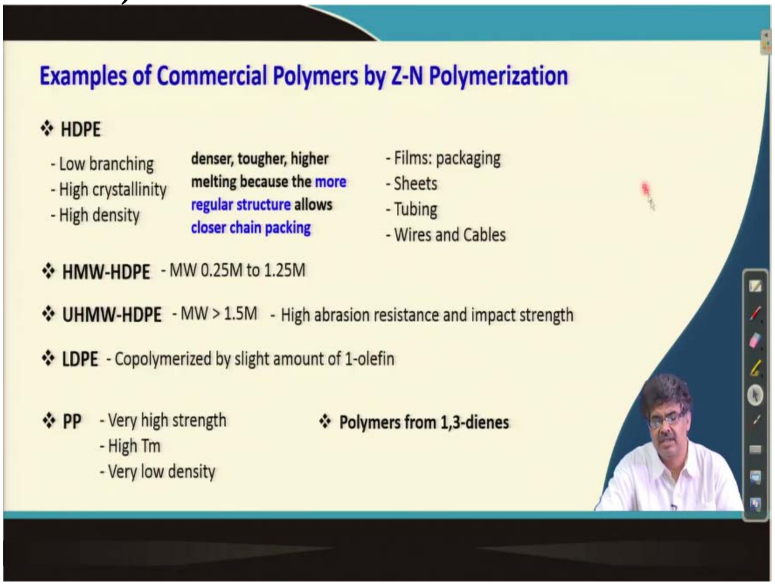

Examples of Commercial Polymers by Z-N Polymerization

- **HDPE**
  - Low branching
  - High crystallinity
  - High density

  denser, tougher, higher melting because the more regular structure allows closer chain packing

  - Films: packaging
  - Sheets
  - Tubing
  - Wires and Cables
- **HMW-HDPE** - MW 0.25M to 1.25M
- **UHMW-HDPE** - MW > 1.5M - High abrasion resistance and impact strength
- **LDPE** - Copolymerized by slight amount of 1-olefin
- **PP**
  - Very high strength
  - High Tm
  - Very low density
- **Polymers from 1,3-dienes**

There is a common example of commercial polymers by Ziegler-Natta polymerization, i.e. high density polyethylene. As the name suggests, high density that means it is highly crystalline. It is a less branched, highly crystalline, high density and it is denser, tougher, with higher melting point because of more regular structure which allows closer chain packing and its applications are in films, packaging sheets, tubing, wires and cables.

High molecular weight HDPE has molecular weight in the range of 0.25 million to 1.25 million. Ultra-high molecular weight UHMWPE has molecular higher than 1.5 million and has high abrasive resistance and high impact strength. Some of these ultra-high molecular HDPE are used for knee replacement. LDPE, low density polyethylene, which is copolymerized with small amount of 1-olefin and as a result some branching might happen and we get low density polypropylene which has very high strength, high melting point, very low density. These are the common examples of commercial polymers which are regularly synthesized by Ziegler-Natta polymerization.

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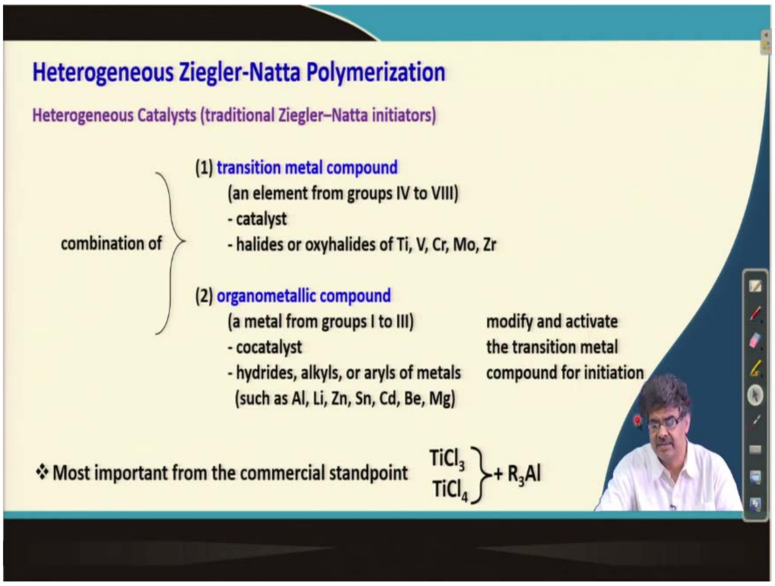

Heterogeneous Ziegler-Natta Polymerization

Heterogeneous Catalysts (traditional Ziegler–Natta initiators)

combination of

(1) transition metal compound
(an element from groups IV to VIII)
- catalyst
- halides or oxyhalides of Ti, V, Cr, Mo, Zr

(2) organometallic compound
(a metal from groups I to III)
- cocatalyst
- hydrides, alkyls, or aryls of metals
(such as Al, Li, Zn, Sn, Cd, Be, Mg)

modify and activate the transition metal compound for initiation

❖ Most important from the commercial standpoint $\left.\begin{matrix} TiCl_3 \\ TiCl_4 \end{matrix}\right\} + R_3Al$

There are 2 types of catalysts which are used for Ziegler-Natta polymerization, one is heterogeneous and another is homogeneous. The heterogeneous catalyst is a traditional Ziegler-Natta initiator, which was originally used by Ziegler and Natta which actually is combination of 2 catalysts. There are 2 compounds, one is a transition metal compounds of elements from groups 4 to group 8, used as catalyst and in general it is halide or oxyhalide of titanium, vanadium, chromium, zirconium and so on. The second one is organometallic compound, alkyl aluminium and this is actually cocatalyst. The most important from a commercial standpoint is either $TiCl_3$ plus alkyl aluminum or $TiCl_4$ and alkyl aluminum and these organometallic compounds actually modify and activate the transition metal compounds for initiation.

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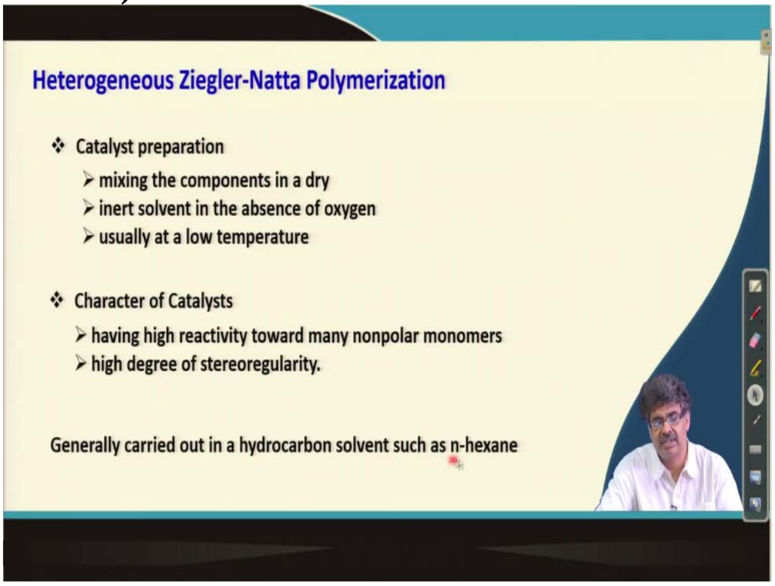

Heterogeneous Ziegler-Natta Polymerization

❖ Catalyst preparation
  - mixing the components in a dry
  - inert solvent in the absence of oxygen
  - usually at a low temperature

❖ Character of Catalysts
  - having high reactivity toward many nonpolar monomers
  - high degree of stereoregularity.

Generally carried out in a hydrocarbon solvent such as n-hexane

Now, for Ziegler-Natta polymerization, the catalyst preparation, for catalyst preparation we basically mix the components in dry condition and inert solvents are used. In absence of oxygen, usually done at low temperature and the catalyst tray having high reactivity towards many nonpolar monomers, high degree of steady regularity and the polymerization is generally carried out in a hydrocarbon solvent such as n-hexane.

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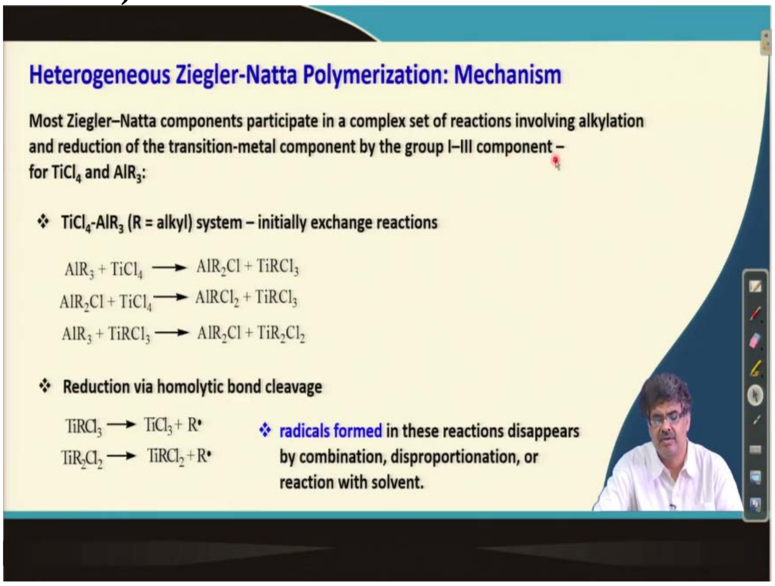

Heterogeneous Ziegler-Natta Polymerization: Mechanism

Most Ziegler–Natta components participate in a complex set of reactions involving alkylation and reduction of the transition-metal component by the group I–III component – for $TiCl_4$ and AlR_3:

- $TiCl_4$-AlR_3 (R = alkyl) system – initially exchange reactions

$$AlR_3 + TiCl_4 \longrightarrow AlR_2Cl + TiRCl_3$$
$$AlR_2Cl + TiCl_4 \longrightarrow AlRCl_2 + TiRCl_3$$
$$AlR_3 + TiRCl_3 \longrightarrow AlR_2Cl + TiR_2Cl_2$$

- Reduction via homolytic bond cleavage

$$TiRCl_3 \longrightarrow TiCl_3 + R^\bullet$$
$$TiR_2Cl_2 \longrightarrow TiRCl_2 + R^\bullet$$

- radicals formed in these reactions disappears by combination, disproportionation, or reaction with solvent.

Now, in heterogeneous polymerization, most of the Ziegler-Natta components participate in a complex set of reactions involving alkylation and reduction of transition metal components by group 1 to 3 components like $TiCl_3$ and for AIR_2. It happens in 2 steps, initially there is exchange reaction between the 2 components we described, for example, alkyl aluminium with $TiCl_4$, which is a very complex reaction setup but this is what generally happens. $TiRCl_3$ can also generate radical by homolytic cleavage, which are quenched by combinations or disproportionation with themselves or reaction with solvent. The top three combinations, as shown in the slide, are generally used for catalysts in Ziegler-Natta polymerization.

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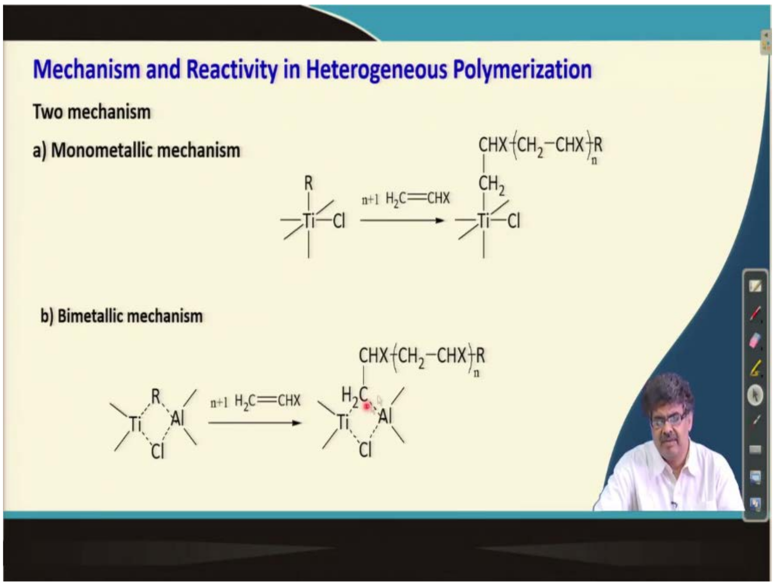

Mechanism and Reactivity in Heterogeneous Polymerization

Two mechanism

a) Monometallic mechanism

b) Bimetallic mechanism

There are mainly 2 mechanism by which is Ziegler-Natta polymerization happens, one is monometallic mechanism and other is bimetallic mechanism that will be discussed briefly in the coming slide.

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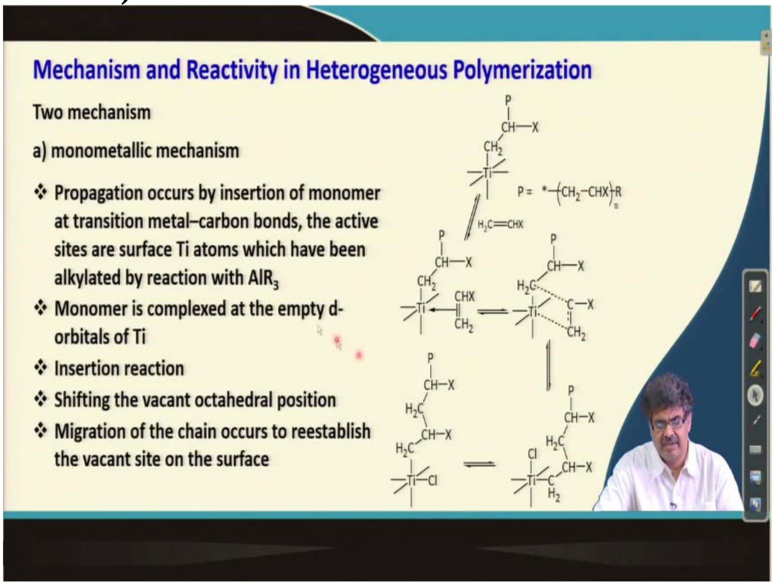

Mechanism and Reactivity in Heterogeneous Polymerization

Two mechanism

a) monometallic mechanism

- ❖ Propagation occurs by insertion of monomer at transition metal–carbon bonds, the active sites are surface Ti atoms which have been alkylated by reaction with AlR_3
- ❖ Monomer is complexed at the empty d-orbitals of Ti
- ❖ Insertion reaction
- ❖ Shifting the vacant octahedral position
- ❖ Migration of the chain occurs to reestablish the vacant site on the surface

In monometallic mechanism, one of the chlorine atoms is removed. A vacant d orbital is generated on titanium which actually coordinates with the incoming monomer and forms a complex and as a result there is an insertion of this new monomer between titanium and carbon center. Later, but because of the migration of this chain to this original place, the stereo regularity is maintained. So, propagation occurs by insertion of monomer at the transition metal carbon bond and the migration is basically to reestablish the vacant site on the surface of the catalyst.

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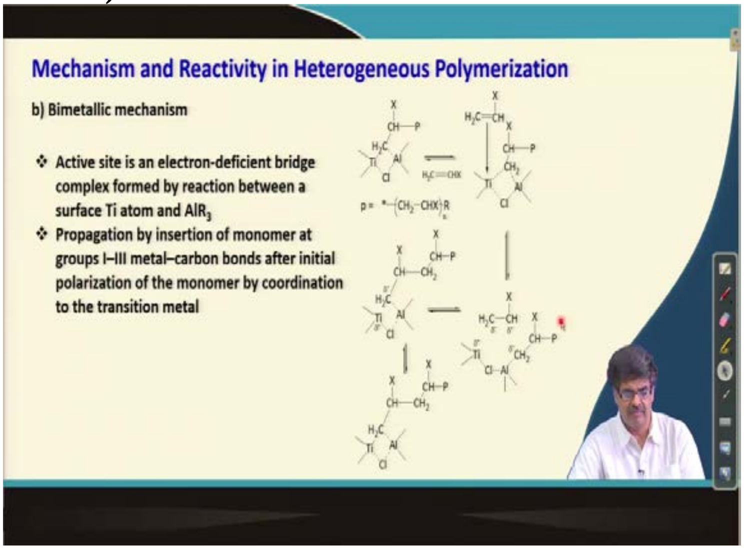

Mechanism and Reactivity in Heterogeneous Polymerization

b) Bimetallic mechanism

- Active site is an electron-deficient bridge complex formed by reaction between a surface Ti atom and AlR_3
- Propagation by insertion of monomer at groups I–III metal–carbon bonds after initial polarization of the monomer by coordination to the transition metal

In case of bimetallic mechanism, the active site is an electron-deficient bridge complex formed between titanium atom and this alkyl aluminum, and in this case propagation happens by insertion of the monomer at the group III metal - carbon atoms. Once the coordination happens, there is a partial charge which gives kind of a 6 membered complex intermediate formation and results in insertion of new monomer between aluminum and carbon center which is quite complicated reaction mechanism.

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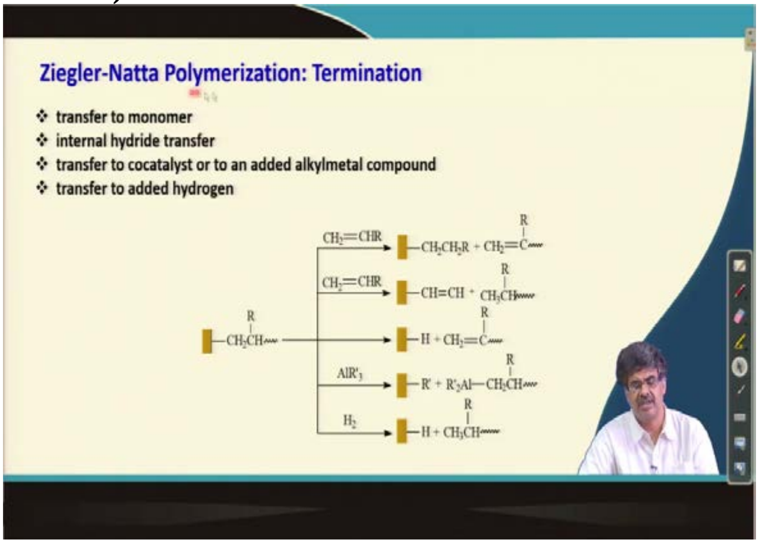

Ziegler-Natta Polymerization: Termination

- transfer to monomer
- internal hydride transfer
- transfer to cocatalyst or to an added alkylmetal compound
- transfer to added hydrogen

Let us just talk about the termination step. The termination can happen in case of Ziegler-Natta polymerization like we had discussed for regular chain polymerization. Transfer can happen to monomers or internal hydride transfer or transfer to cocatalyst or it can be quenched by addition of hydrogen.

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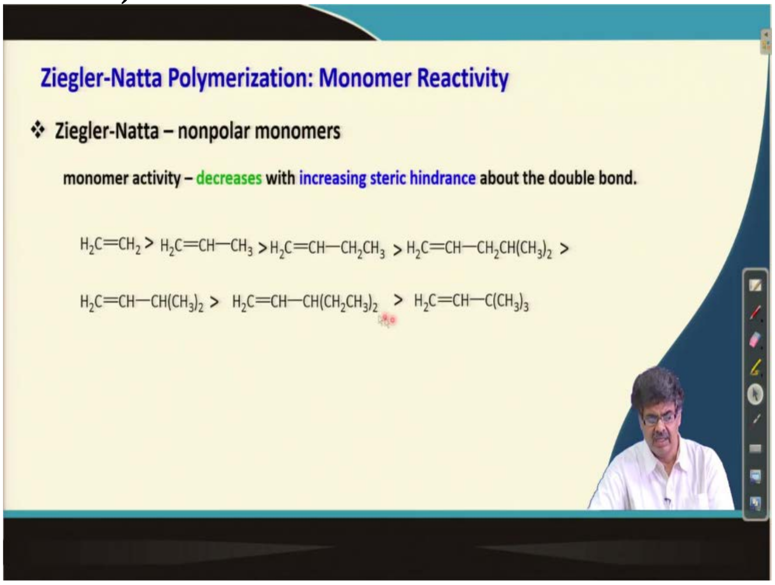

Ziegler-Natta Polymerization: Monomer Reactivity

- Ziegler-Natta – nonpolar monomers

monomer activity – decreases with increasing steric hindrance about the double bond.

$H_2C{=}CH_2 > H_2C{=}CH{-}CH_3 > H_2C{=}CH{-}CH_2CH_3 > H_2C{=}CH{-}CH_2CH(CH_3)_2 >$

$H_2C{=}CH{-}CH(CH_3)_2 > H_2C{=}CH{-}CH(CH_2CH_3)_2 > H_2C{=}CH{-}C(CH_3)_3$

In case of nonpolar monomers, the reactivity of the monomers actually decreases with increasing the steric hindrance about the double bond. This is the order, as we increase more and more steric hindrance of the monomer, the coordination possibility with the titanium actually decreases because of the steric hindrance. So, the reactivity of the monomers for Ziegler-Natta polymerization decreases as we increase the steric hindrance about the double bond.

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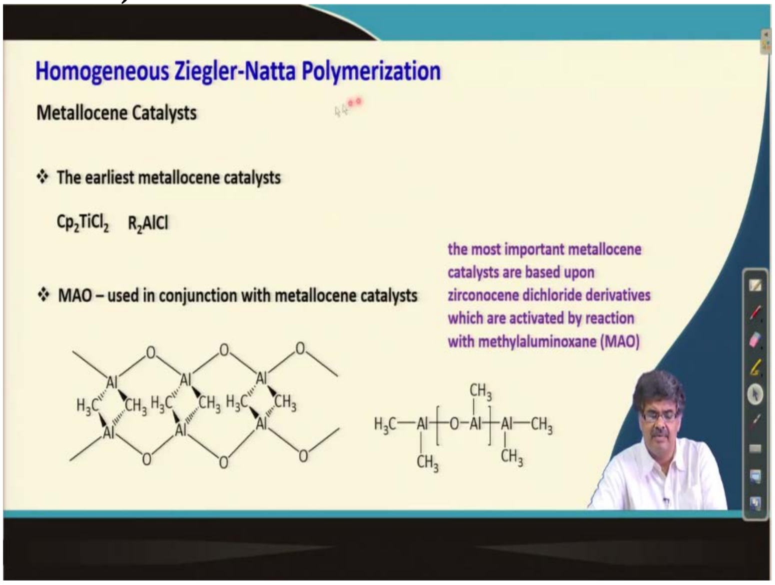

Homogeneous Ziegler-Natta Polymerization

Metallocene Catalysts

- The earliest metallocene catalysts

Cp_2TiCl_2 R_2AlCl

- MAO – used in conjunction with metallocene catalysts

the most important metallocene catalysts are based upon zirconocene dichloride derivatives which are activated by reaction with methylaluminoxane (MAO)

Homogeneous Ziegler-Natta polymerization happens in presence of metallocenes as catalyst. Nowadays, the most important metallocene catalysts are based upon zirconocene dichloride derivatives which are activated by reaction with methylaluminoxane or in short MAO, this is the structure of methylaluminoxane MAO and this is actually main catalysts is zirconium. This is activated by this cocatalyst MAO.

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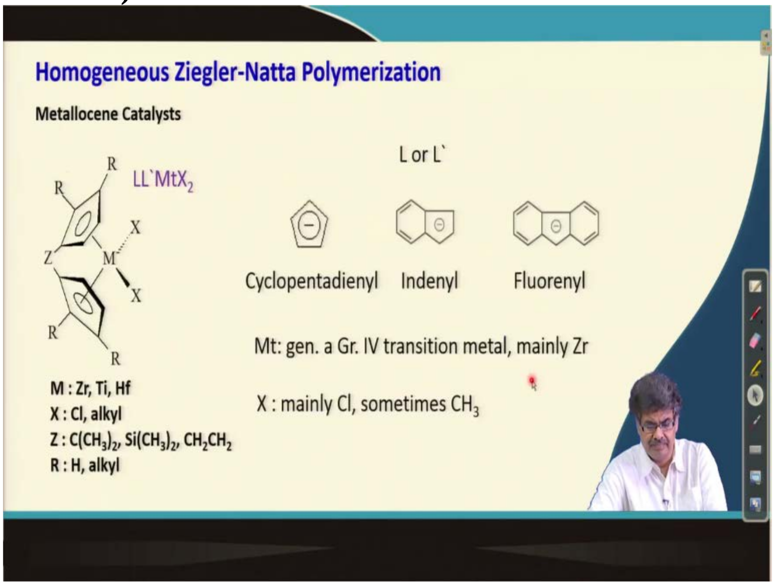

Homogeneous Ziegler-Natta Polymerization

Metallocene Catalysts

$LL^`MtX_2$

L or L`

Cyclopentadienyl Indenyl Fluorenyl

Mt: gen. a Gr. IV transition metal, mainly Zr

X : mainly Cl, sometimes CH_3

M : Zr, Ti, Hf
X : Cl, alkyl
Z : $C(CH_3)_2$, $Si(CH_3)_2$, CH_2CH_2
R : H, alkyl

This is the typical or general structure of metallocene catalysts where M is zirconium, titanium, hafnium and the X are chlorine or alkyl and rest of the terms are shown in the slide.

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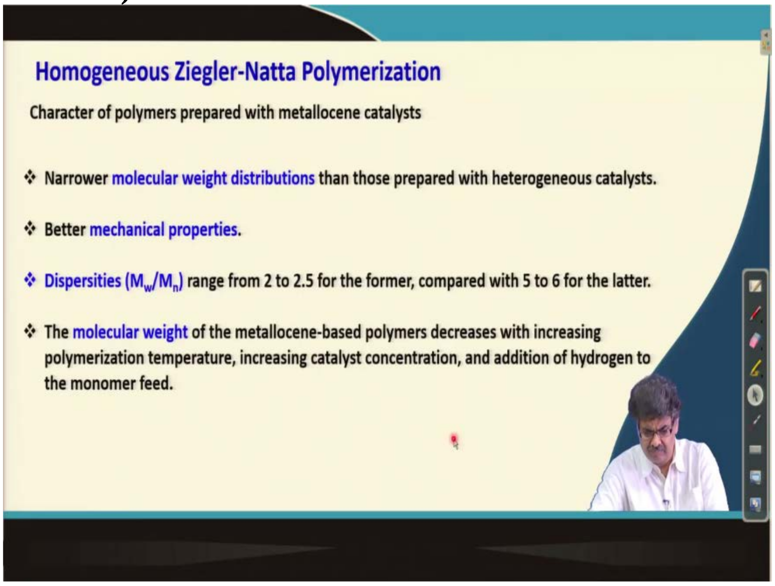

Homogeneous Ziegler-Natta Polymerization

Character of polymers prepared with metallocene catalysts

- Narrower molecular weight distributions than those prepared with heterogeneous catalysts.
- Better mechanical properties.
- Dispersities (M_w/M_n) range from 2 to 2.5 for the former, compared with 5 to 6 for the latter.
- The molecular weight of the metallocene-based polymers decreases with increasing polymerization temperature, increasing catalyst concentration, and addition of hydrogen to the monomer feed.

The metallocene catalysts are homogeneous Ziegler-Natta catalysts. They have some advantages for example, narrow molecular weight distribution compared to those prepared with homogeneous catalysis, with better mechanical properties. Generally, dispersities range from 2 to 2.5 compared to the heterogeneous catalysts which have a much higher, dispersity value, 5 to 6 and the molecular weight of metallocene based polymers decreases with increasing polymerization temperature, increasing catalyst concentration and addition of hydrogen to monomer feed.

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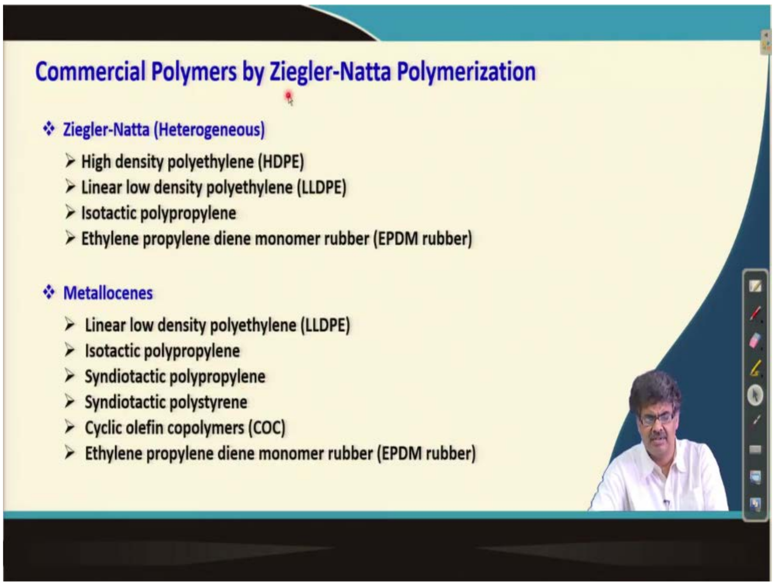

Commercial Polymers by Ziegler-Natta Polymerization

- Ziegler-Natta (Heterogeneous)
  - High density polyethylene (HDPE)
  - Linear low density polyethylene (LLDPE)
  - Isotactic polypropylene
  - Ethylene propylene diene monomer rubber (EPDM rubber)
- Metallocenes
  - Linear low density polyethylene (LLDPE)
  - Isotactic polypropylene
  - Syndiotactic polypropylene
  - Syndiotactic polystyrene
  - Cyclic olefin copolymers (COC)
  - Ethylene propylene diene monomer rubber (EPDM rubber)

These are some commercial polymers made using heterogeneous Ziegler-Natta and metallocene catalysts or homogeneous Ziegler-Natta polymerization which we discussed at the beginning. For example, using metallocene, we can synthesize syndiotactic polypropylene or syndiotactic polystyrene, isotactic polypropylene, so on. So, with this I conclude our discussion on Ziegler-Natta polymerization or coordination polymerization. Next I will talk about some ring opening polymerization.