B.Sc. Semester-VI Organic Chemistry Paper-XIV

2. Synthetic Polymers

Coverage:

6. (i) Ziegler-Natta Polymerization



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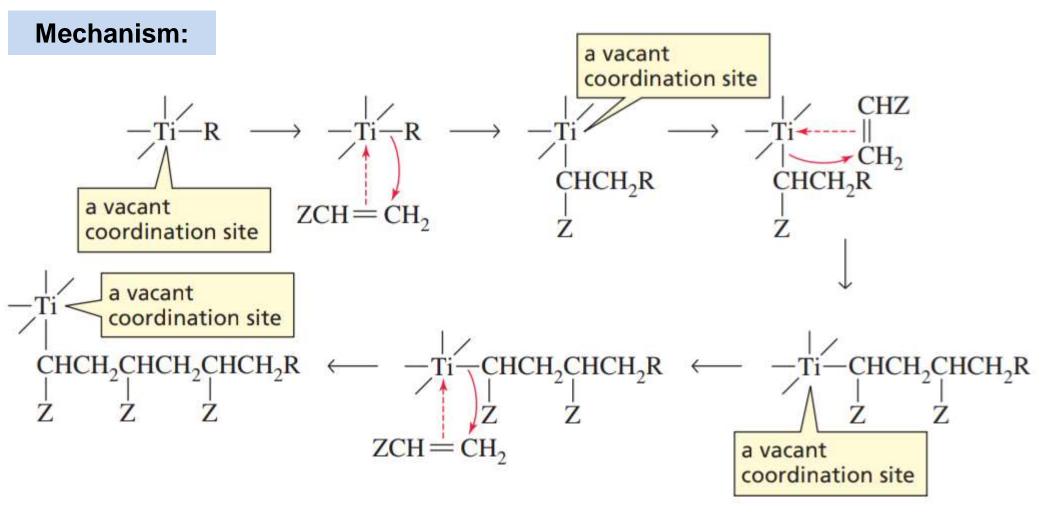
In 1953, Karl Ziegler and Giulio Natta found that the structure of a polymer could be controlled if the growing end of the chain and the incoming monomer were coordinated with an aluminum—titanium initiator. These initiators are now called **Ziegler–Natta catalysts**. Long, unbranched polymers with either the isotactic or the syndiotactic configuration can be prepared using Ziegler–Natta catalysts. Whether the chain is isotactic or syndiotactic depends on the particular Ziegler–Natta catalyst used. These catalysts revolutionized the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers that have greater resistance to cracking and heat. High-density polyethylene is prepared using a Ziegler–Natta process.

The mechanism of the Ziegler–Natta-catalyzed polymerization of a substituted ethylene is shown in Figure The monomer forms a π complex (previously), with titanium at an open coordination site (i.e., a site available to accept electrons) and the coordinated alkene is inserted between the titanium and the growing polymer, thereby extending the polymer chain. Because a new coordination site opens up during insertion of the monomer, the process can be repeated over and over.

Polyacetylene is another polymer prepared by a Ziegler–Natta process. It is a **conducting polymer** because the conjugated double bonds in polyacetylene make it possible to conduct electricity down its backbone after several electrons are removed from or added to the backbone.

Ziegler-Natta Polymerization

Or,
$$nCH_2 = CH_2 \xrightarrow{TiCl_4/Al(CH_2CH_3)_2Cl} \xrightarrow{MgCl_2} \nearrow n$$
Ethylene Polyethylene



The mechanism of the Ziegler–Natta-catalyzed polymerization of a substituted ethylene. A monomer forms a π complex with an open coordination site of titanium and then is inserted between the titanium and the growing polymer.

Ziegler-Natta Polymerization

Neoprene is a synthetic rubber made by polymerizing 2-chloro-1,3-butadiene in the presence of a Ziegler–Natta catalyst that causes all the double bonds in the polymer to have the trans configuration. Neoprene is used to make wet suits, shoe soles, tires, hoses, and coated fabrics.

Karl Ziegler (1898–1973), the son of a minister, was born in Germany. He was a professor at the University of Frankfurt and then at the University of Heidelberg.

Karl Ziegler and Giulio Natta did not work together, but each independently developed the catalyst system used in polymerization. They shared the 1963 Nobel Prize in chemistry. Giulio Natta (1903–1979) was the son of an Italian judge. He was a professor at the Polytechnic Institute in Milan, where he became the director of the Industrial Chemistry Research Center.

Ziegler-Natta Polymerization

Isotactic polymerization

TiCl₄ / AIR₃

1-4 atm, rt

$$Cl_3Ti \longrightarrow R + Cl \longrightarrow AIR_2$$

$$Cl_3Ti \longrightarrow R - Complex$$

$$Cl_3Ti \longrightarrow R - Cl_3Ti \longrightarrow R$$

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