

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

2. Synthetic Polymers

Coverage:

6. (ii) Stereochemistry of Polymerization : Ziegler-Natta Catalysts

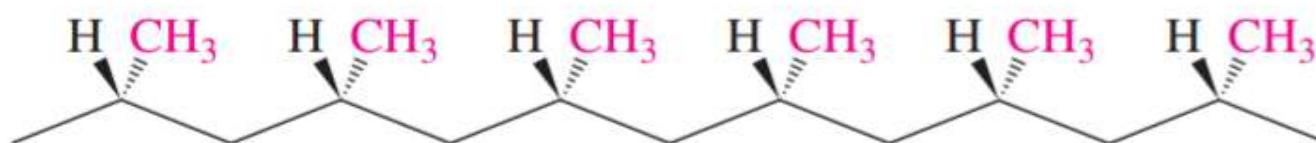


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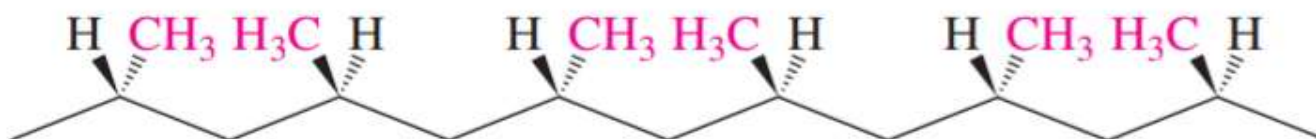
6. (ii) Stereochemistry of Polymerization : Ziegler-Natta Catalysts

Polymers formed from monosubstituted ethylenes can exist in three configurations: isotactic, syndiotactic, and atactic. An **isotactic polymer** has all of its substituents on the same side of the fully extended carbon chain. (*Iso* and *taxis* are Greek for “the same” and “order,” respectively.) In a **syndiotactic polymer** (*syndio* means “alternating”), the substituents regularly alternate on both sides of the carbon chain. The substituents in an **atactic polymer** are randomly oriented.

isotactic configuration (same side)



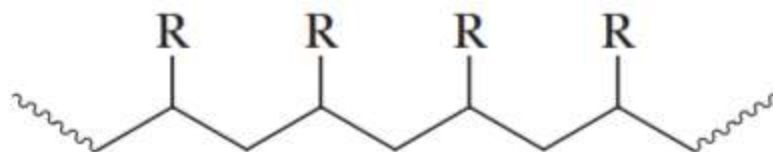
syndiotactic configuration (both sides)



The configuration of the polymer affects its physical properties. Polymers in the isotactic or syndiotactic configuration are more likely to be crystalline solids because positioning the substituents in a regular order allows for a more regular packing arrangement. Polymers in the atactic configuration are more disordered and cannot pack together as well, so these polymers are less rigid and, therefore, softer.

The configuration of the polymer depends on the mechanism by which polymerization occurs. In general, radical polymerization leads primarily to branched polymers in the atactic configuration. Cationic polymerization produces polymers with a considerable fraction of the chains in the isotactic or syndiotactic configuration. Anionic polymerization produces polymers with the most stereoregularity. The percentage of chains in the isotactic or syndiotactic configuration increases as the polymerization temperature decreases.

Stereochemistry of Polymerization : Ziegler-Natta Catalysts



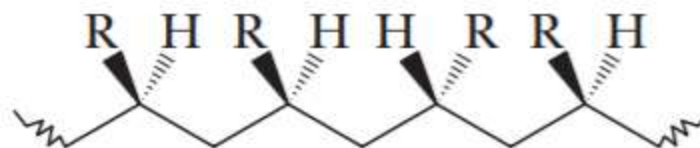
In general, the more stereoregular the chiral centers are, that is, the more highly isotactic or highly syndiotactic the polymer is, the more crystalline it is. A random placement of the substituents, such as in atactic materials, results in a polymer that cannot pack well and is usually highly amorphous. Atactic polystyrene, for



Isotactic polymer
(identical configurations)



Syndiotactic polymer
(alternating configurations)



Atactic polymer
(random configurations)