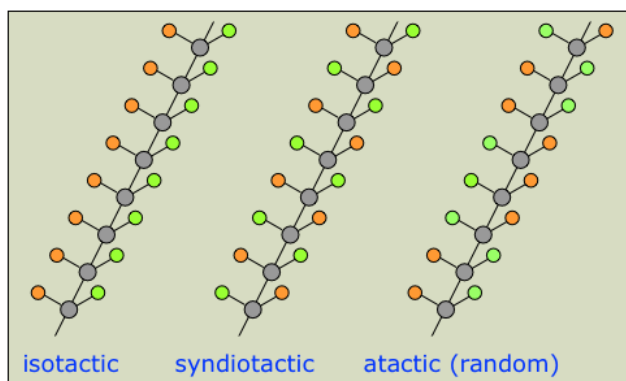
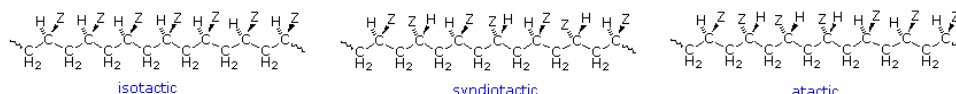


30.2: STEREOCHEMISTRY OF POLYMERIZATION - ZIEGLER-NATTA CATALYSTS

ZIEGLER-NATTA CATALYTIC POLYMERIZATION

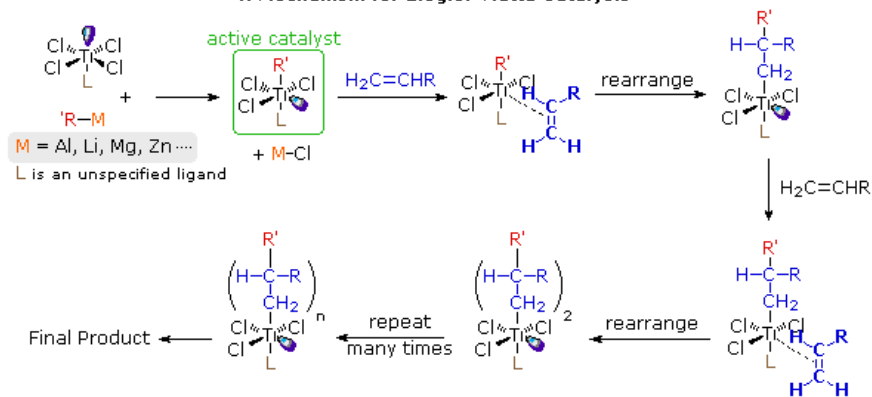
When propene is enchainned into a polymer, a new chiral center is formed at every position where a methyl group branches from the backbone. Rather than trying to assign each of these chiral centers with stereochemical configurations (*R*) or (*S*), we instead describe the relative stereochemical relationships along the backbone. The term used to describe these relationships is "**tacticity**". If there is no apparent relationship between the projection of the methyl groups along the backbone, the polymer is termed "**atactic**". If the methyl groups alternate, pointing first one direction, then the other, all the way along the chain, then the polymer is termed "**syndiotactic**". If the methyl groups all project the same direction, the polymer is described as "isotactic".



An efficient and stereospecific catalytic polymerization procedure was developed by Karl Ziegler (Germany) and Giulio Natta (Italy) in the 1950's. Ziegler-Natta catalysts are prepared by reacting certain transition metal halides with organometallic reagents such as alkyl aluminum, lithium and zinc reagents. The catalyst formed by reaction of triethylaluminum with titanium tetrachloride is commonly used. Ziegler-Natta catalysts allowed for the first time, the stereochemically controlled synthesis of polymers with virtually no branching. By changing the catalyst, pure isotactic, syndiotactic, or atactic polymers could be created. For this important discovery, Ziegler and Natta received the 1963 Nobel Prize in chemistry. For example, the polymerization of ethylene, using a Ziegler-Natta catalyst produces a stronger (more crystalline) and more heat resistant product, called high-density polyethylene (HDPE), than typical radical polymerizations which produces low-density polyethylene (LDPE). HDPE is normally produced with molecular weights in the range of 200,000 to 500,000, but it can be made even higher. Polyethylene with molecular weights of three to six million is referred to as ultra-high molecular weight polyethylene, or UHMWPE. UHMWPE can be used to make fibers which are so strong they replaced Kevlar for use in bullet proof vests. Large sheets of it can be used instead of ice for skating rinks.

The following diagram presents one mechanism of the Ziegler-Natta polymerization. Formation of the Ziegler-Natta catalyst, adds an alkyl group ligand to create an organo transition metal compound with a vacant coordination site. An alkene ligand is then coordinated to the transition metal which is followed by a 1,2-insertion of the alkene into the metal-carbon bond. The insertion creates a vacant coordination site which can react with another alkene. These same elementary steps continue to occur to provide the polymerization.

A Mechanism for Ziegler-Natta Catalysis



? EXERCISE 30.2.1

When the monomer vinylidene fluoride, $\text{H}_2\text{C=CF}_2$, is polymerized it does not create isotactic, syndiotactic, and atactic forms. Please explain

Answer

When vinylidene fluoride is polymerized it does not create a chiral center due to the symmetry created by the two fluorides. Chirality is necessary to create isotactic, syndiotactic, and atactic polymer forms.

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