Ziegler-Natta catalyst

Kurl Ziegler (of Germany) and Giulio Natta (of Italy) developed the catalysts which permit stereo ~~chemical~~ regular polymerization of alkenes of the type $RCH=CH_2$ (where R = H, alkyl or aryl).

Ziegler-Natta catalysts are a combination of organometallics which consists of a complex of triethylaluminium, Et_3Al and a transition metal chloride, $TiCl_4$. When these are mixed in a hydrocarbon solvent (benzene, Toluene, etc), a heterogeneous precipitate develops which catalyses polymerization of alkenes at low temp. and pressure.

Eg:

$$n(CH_3-CH=CH_2) \xrightarrow[100^\circ C,\ 10\ atm]{Z\text{-}N.\ catalyst} -(CH(CH_3)-CH_2-CH(CH_3)-CH_2)_n-$$

propylene → polypropylene

$$n(CH_2=C(CH_3)-CH=CH_2) \xrightarrow[100^\circ C,\ 10\ atm.]{Z\text{-}N.\ catalyst} -(CH_2-C(CH_3)=CH-CH_2)_n-$$

isoprene → cis-1,4-Poly isoprene (Rubber).

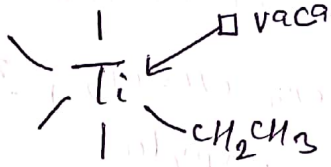
* The polymerization by the use of Ziegler catalysts under mild conditions produces unbranched polyethylene and stereoregular (isotactic) polystyrene or polypropylene.

Mechanism of polymerization using Ziegler-Natta catalysts:

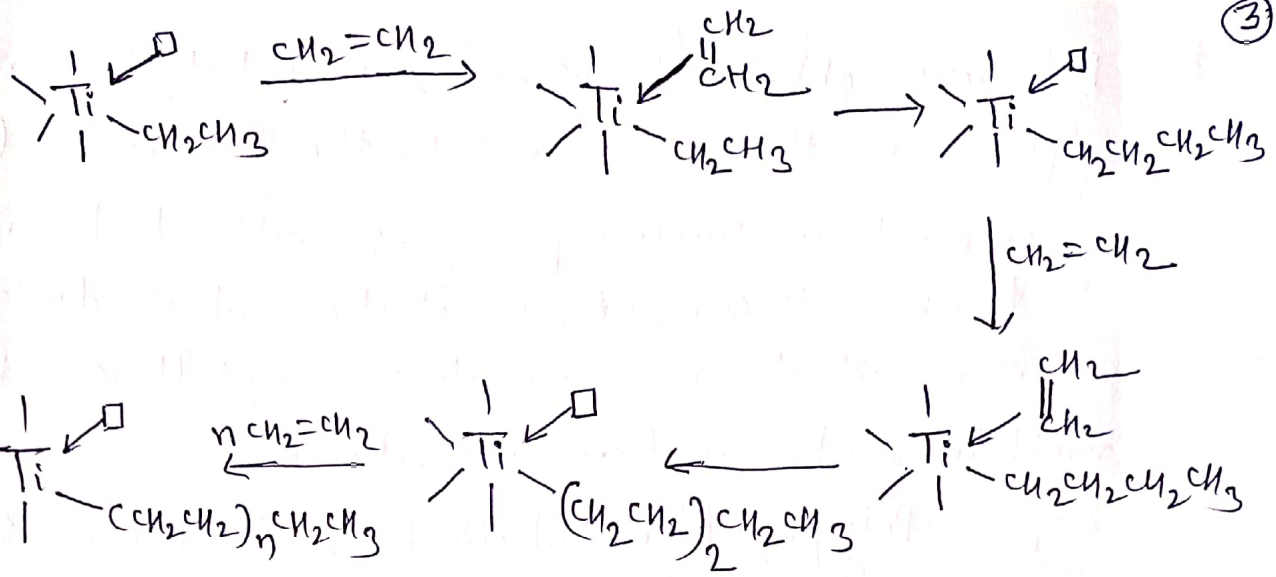
Mechanism:

Polymerization by Z-N. catalysts is neither free radical nor ionic types. It is probably a coordination polymerization.

* Probably, triethylaluminium reduces the transition metal to a lower valence state producing titanium trichloride, diethyl aluminium chloride and an ethyl-free radical which combine to form the complex, the active catalysts. The active catalysts (heterogeneous precipitate) is suggested to be an octahedral complex of titanium with a vacant coordination site and an ethyl group bonded to Ti.



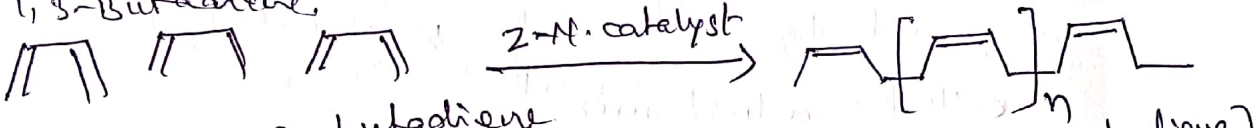
* It is suggested that the monomer coordinates at the vacant site of the metal with its ~~π-bonds~~ π-clouds to form a π-bond.
* Now, that both the monomer and the ethyl group are held very close to each other by Ti, the monomer inserts itself between the metal and the ethyl group to form a four-carbon chain.
* The coordination site is now vacant for the coordination of another monomer unit and the process is repeated.
* The metal complex with the growing chain probably influences the incoming monomer molecules to fall in the pattern and hence the stereoregularity.
* The growing chain of the polymer separates from the metal probably through the insertion of a hydrogen.



Applications:

1. Synthesis of synthetic rubbers:
Synthetic rubbers have been made by polymerizing dienes other than isoprene.

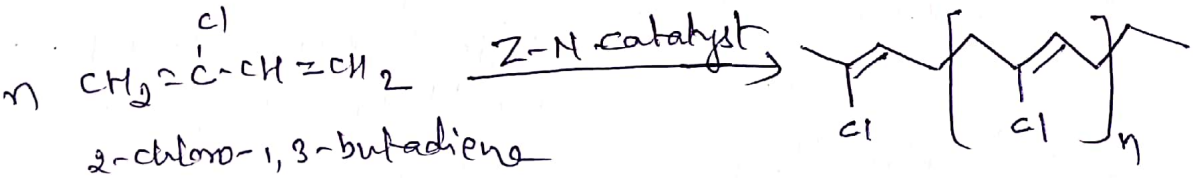
(a) 1,3-Butadiene



1,3-butadiene

cis-poly(1,3-butadiene)
a synthetic rubber.

2. (b) 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 shoe soles, tires, hoses, and coated fabrics.



2-chloro-1,3-butadiene
(Chloroprene)

neoprene

1. Polymers obtained using Z-N. catalysts are superior to those obtained by the free radical process.

2. It produces linear polymers without branching and gives stereoregular (isotactic and syndiotactic) polymers which are more dense, crystalline, high melting and mechanically strong.

   eg: Polypropylene obtained by the use of Z-N. catalyst is ~~an excellent~~ extensively used for the preparation of sheets, pipes, synthetic fibres, domestic articles for everyday use, etc.

3. The copolymer of ethylene and propylene prepared by the use of Z-N catalyst is an excellent elastomer.

4. Metal alkyls, obtained in the process on heating in the presence of ethylene and nickel catalyst give straight chain 1-alkenes of even number of carbons.

$$M-(CH_2-CH_2)_n-CH_2CH_3 \xrightarrow[\text{heat}]{CH_2=CH_2,\ Ni} H_2C=CH-(CH_2-CH_2)_{n-1}-CH_2CH_3$$

   These alkenes are used for the manufacture of detergents on a commercial scale.