Stereochemistry of Polymerisation

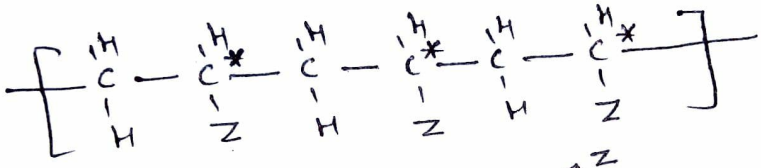
When a monomer of the type $CH_2 = CH-Z$ ($Z = CH_3, CN, Cl$ etc.) polymerises, the carbon atom bearing substituent Z becomes asymmetric (chiral centre). Due to this, the polymer can have any of the three possible stereoisomeric polymers. ~~the differences in~~ They differ in configuration (tacticity).

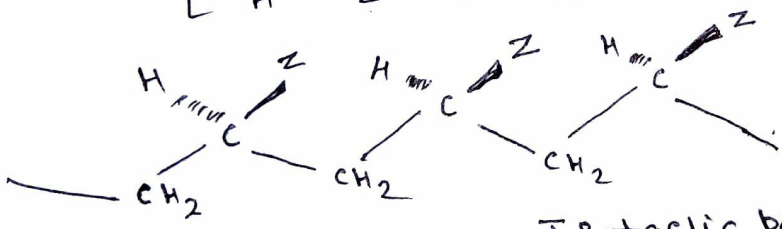
Due to differences in configuration (tacticity), polymers have different physical properties.

1 - **Isotactic polymer** : The polymer in which all the substituent are oriented on the same side of the zig zag backbone carbon chain is called isotactic polymer.

Greek
iso = same
tactic = order

$CH_2 = \underset{Z}{CH} + CH_2 = \underset{Z}{CH} + CH_2 = \underset{Z}{CH} \longrightarrow$





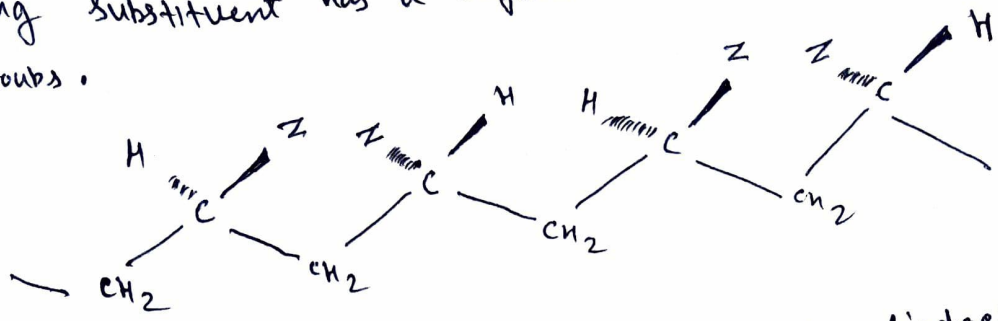
If $Z = -CH_3$ then Isotactic polypropylene (all $-CH_3$ (Z) groups are oriented on the same side

i.e. all the asymmetric carbon atoms of the repeating units have the same configuration.

The polymerisation of propylene using Ziegler-Natta catalyst yields isotactic polypropylene which has a linear structure. Linear polymeric chains pack together closely. As a result, they have high density, tensile strength, ~~crystalline~~ and melting point. Linear polymers are crystalline i.e. polymers with greater crystallinity (i.e. a more regular packing arrangement). Linear polymers are called as high density polyethylene (HDPE).

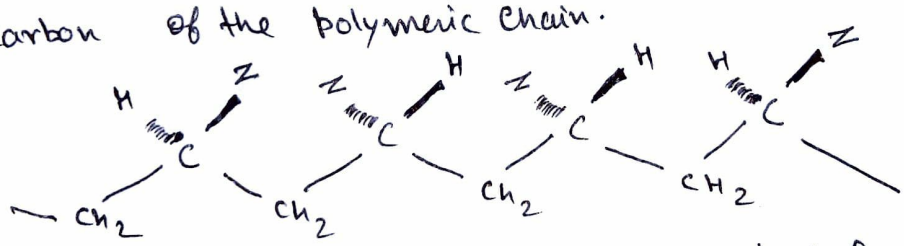
2- Syndiotactic polymer [Syn = alternate tactic = order]

In this polymer, asymmetric carbon atom having substituent has a regular alternation of H and Z groups.



It has crystalline structure. Syndiotactic polymer can be prepared by modifying the Ziegler-Natta catalyst.

3. Atactic polymer :- It has random arrangement of H and Z group on the asymmetric carbon of the polymeric chain.
(Atactic = no order)



— Z groups are randomly oriented.

Polypropylene produced by free radical polymerisation is atactic and has branched chain. Branched chain polymers are amorphous, soft and elastic and is not very useful. Branched polymer is known as low density polyethylene (LDPE).

Ziegler-Natta polymerisation

Anionic & cationic polymerisation, give iso and syndiotactic polymer whereas free-radical polymerisation give atactic polymer.