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Role of ligands in metallocene catalyst in PP polymerization tacticity

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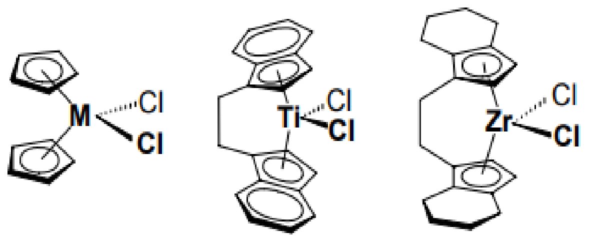
ABSTRACT

This paper focuses on ligands and its role in metallocene PP polymerization. This paper will cover section of Ligands effect and measurement of size of ligands. The major drawback of such catalysts is the cost of their synthesis. Many efforts are being made to reduce the cost of synthesis so that process can be carried out on large scale. Ligands play a key role in tacticity of PP polymers. An increase in the production of metallocene catalyst has brought a revolution in the polymer industry.

1. Introduction

Cyclopentadienyl ligands or cyclopentadienyl complexes are substituted derivatives of C2H5 parent ligand.C2H5 C5H5(C5H5)mMLm is the formulae used for cyclopentadienyl ligands used in metallocene catalysts(Kuklin et al., 2015). Metallocene catalysts which are mostly zirconocene derivatives in which zieconocene chloride is the parent ligand. In the olefin polymerization by zirconocene catalyst elucidation of ligand effects was discovered. Polymer parameters can be altered through a rational ligand strip at the center of transition metal.

Metallocene catalyst are also known as homogenous catalyst because of their solubility and single-site character. These developments have also helped in development of chiral metallocenes(Laine et al., 2015). Such metallocenes not only remain specified to a certain group of metals but also in rest of transition metals. These catalysts consist of cyclopentadienyl ligands.



M=Ti 1
=Zr 2
3
4

Figure 1: Ligand modifications in the metallocene catalyst

2. Metallocene Symmetry and Polymer Tacticity

Some monomers are prochiral in nature and their ends facing the metals help in determining the stereo regularity of the polymers. The repeating units of monomer in a polymer chain is known as it's stereoregularity.

Sometimes the methyl groups in the polymer chain are randomly distributed either on one side or different sides. Based on the kind of distribution polymer can be termed as

- Atactic
- Isotactic
- Syndiotactic
- Stereo-Block
- Hemi-isotactic

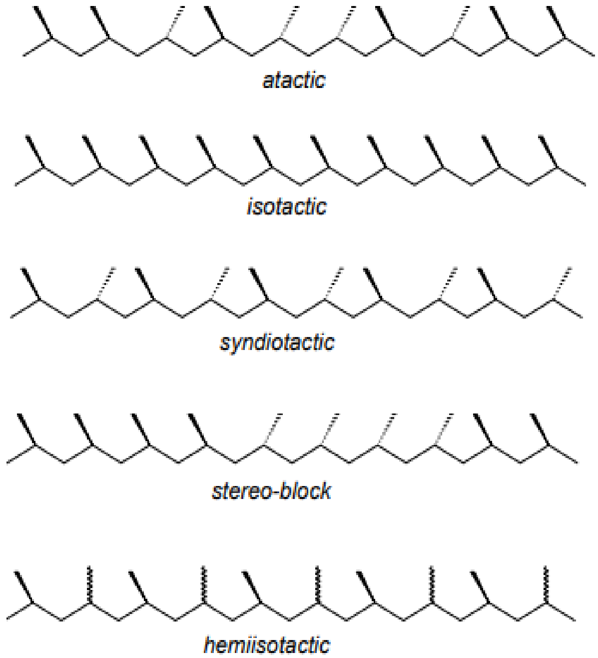


Figure 2: Different Stereo structures of ligands in metallocenes

Chain end control and active site control are the two processes which are widely used to induce polymer tacticity. The symmetry of the last monomer will depict the tacticity the whole polymer in the case of chain end control method where as the binding on active site depicts tacticity in the case of active site control method. If a unit is placed incorrectly, it will be rectified and placed correctly when next unit is place to form a pure polymer.

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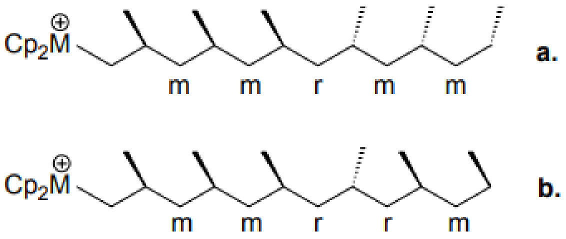


Figure 3: Unit insertion in a catalytic site

The last inserted unit in a chain end controlled catalysts (a) defines the orientation of the next inserted unit whereas for a catalytic-site controlled catalyst (b), any errors are corrected by the chirality of the catalyst(Resconi et al., 2000b).

3. Ligand Strategies

Π ligands can be used to solve racmeso polymer problem. These ligands can be connected to the metal to produce only one diastomer. Formation of the ligand plays a key role in this. An example of this is provided in the below figure, the route that Halterman followed to synthesise rac-bis-indenyl titanium and zirconium dichlorides (Nakanishi et al., 2016).The ligand is designed in such a way that only one isomer can be formed when ligand attaches to the metal.

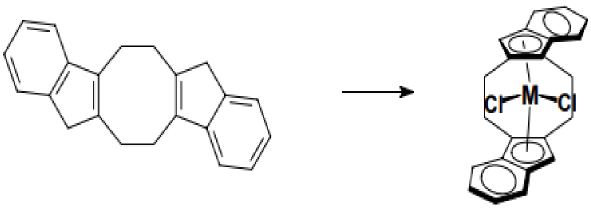


Figure 4: Ligand Strategies

The separation procedures can be carried out swiftly by using double-bridged ligands. These ligands can be used to produce only one diastereomer.

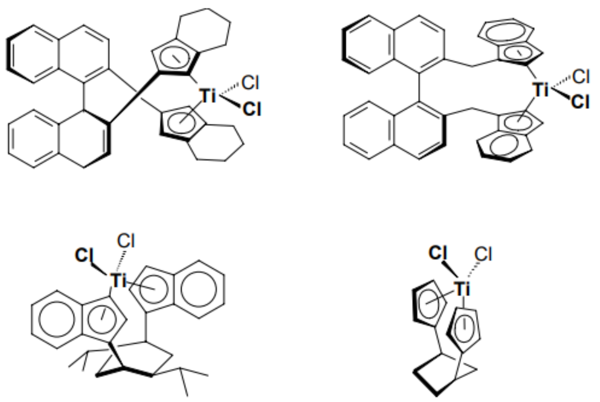


Figure 5: Doubly Bridged Ligands

Chiral ligands are used in the synthesis of ansa-metallocenes in the production of single diastereomer.

Ligand size measurements:

The size of ligand is required in measuring the impact of ligand on polymer formation. To measure the size of a ligand there are three ideologies that are followed:

- Tolman cone angle
- Analytical solid angle
- Numerical solid angle

The Tolman cone angle (θ) is the sum of half un symmetrical vertex group in a ligand multiplied by two. Largest angle from the metal to the outer radius is calculated using half-vertex angle.

$$\theta = \frac{2}{n}\sum_{i=1}^{n}\theta_i/2$$

Equation 1: used for tolman angle.

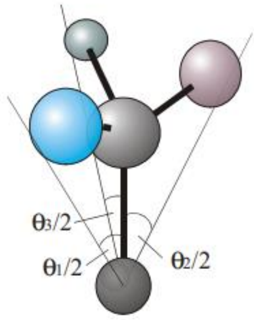


Figure 6: Tolman Cone angle Methodology

Half vertex angle in a polymer is measured for every unsymmetrical ligand.

A vector r is subtended from the point of origin to a point on the surface whose area is dS to calculate Analytical solid angle.

$$\Omega = \int_S \frac{r \cdot dS}{r^3}$$

$$\theta/^{\circ} = 2\arccos\left[1 - \frac{\Omega(\mathrm{sr})}{2\pi}\right]$$

Equation 2: Used for measuring analytical solid angle.

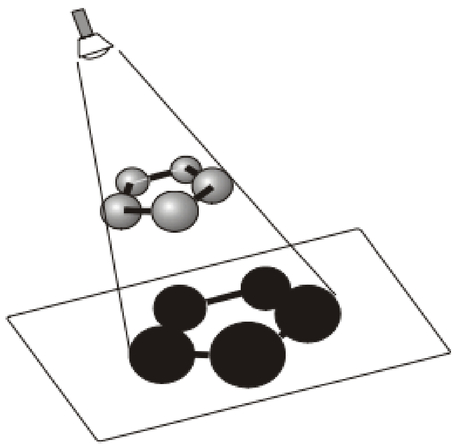


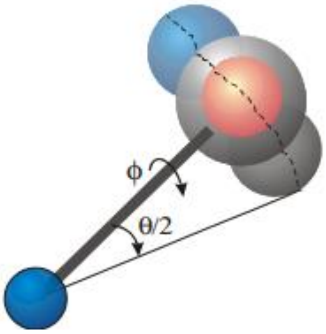
Figure 7: Analytical solid angle

The shape of the ligand is reflected and the size of the shadow is measured to calculate the size of Analytical solid angle.

The numerical solid angle (ΩN) can be considered as a compromise between θ and Ω measurements. In this calculation a non-circular cone is traced around the outer van der Waals radius of the ligand being measured.

$$\Omega_N = \int_{\phi=0}^{2\pi} (1-\cos\frac{1}{2}\theta)d\phi$$

Equation 3: for measuring numerical solid angle.



Ligand regular profile used to create non-circular cone.

4. Conclusion

The metallocene catalyst are the most advanced form of catalyst being used in Tacticity of pp polymers. The ligands are key components of such catalysts. These ligands are known as cyclopentadienyl ligands. Metallocene catalysts have also been successfully engaged in catalytic organic reactions, such as enantioselective C–C and C–H bond formations.

Polymer tacticity can be carried out through two mechanisms 1) chain end control and 2) Catalytic site control. Ligands are constructed in such a way that only one diastereomer is formed. Other major concept involved in polymer tacticity is measuring ligand size. Ligand size measured using three ideologies: Tolman cone angle, analytical solid angle and numerical solid angle. By trying to understand the details of how 165 these polymerisation reactions occur new rules for the synthesis of better catalysts have been discovered. Overall, we can say metallocene catalyst are the best form of catalyst used in tacticity control of pp polymers.

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