Investigation of spatial configuration of Polypropylene and the influence of Molecular Weight Distribution, Catalyst type and Tacticity on mechanical, Thermal and optical properties of polymers

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Abstract: *Polypropylene is considered as one of the most important plastic types because of its substantial supreme properties such as high melting temperature, good chemical resistance and desirable mechanical properties, and achieving desired properties of Polypropylene is a significant activity, besides, gaining this properties is the most important economical factor in reactor polymerization which gives a considerable curve for performance cost polypropylene. In this paper, polypropylene properties, finding physical factor_ the form, and other factors such as molecular weight _ the type of used catalyst and molecular mass which would be expanded to properties of final polypropylene application, are all described. The state of mechanical changes _thermal and photic changes of polymer which are closely dependant to foresaid factors_ is also discussed in present paper, and this indicates the path toward achieving desired quality.*
Keyword: *Polypropylene ¸ Stereo specificity Stereochemistry ،Ziegler-Natta catalysts، Atacticity*
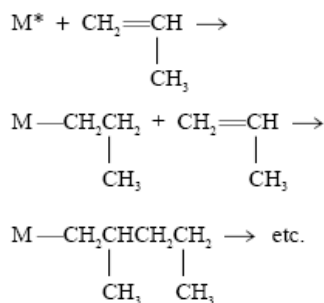
I. Introduction

1.1 Polymerization reaction

Polypropylene is prepared by polymerizing propylene, a gaseous byproduct of petroleum refining, in the presence of a catalyst under carefully controlled heat and pressure Propylene is an unsaturated hydrocarbon, containing only carbon and hydrogen atoms:

$$CH_2 = CH$$
$$|$$
$$CH_3$$
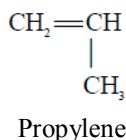
Propylene

In the polymerization reaction, many propylene molecules (monomers) are joined together to form one large molecule of polypropylene. Propylene is reacted with an organometallic, transition metal catalyst (see 1.4 Catalysts for a description of catalysts used in the reaction) to provide a site for the reaction to occur, and propylene molecules are added sequentially through a reaction between the metallic functional group on the growing polymer chain and the unsaturated bond of the propylene monomer:

$$M^* + CH_2 = CH \rightarrow$$
$$|$$
$$CH_3$$

$$M - CH_2CH_2 + CH_2 = CH \rightarrow$$
$$| \qquad\qquad |$$
$$CH_3 \qquad\quad CH_3$$

$$M - CH_2CHCH_2CH_2 \rightarrow \text{ etc.}$$
$$| \qquad |$$
$$CH_3 \quad CH_3$$

One of the double-bonded carbon atoms of the incoming propylene molecule inserts itself into the bond between the metal catalyst (M in the above reaction) and the last carbon atom of the polypropylene chain. A long, linear polymer chain of carbon atoms is formed, with methyl (CHJ groups attached to every other carbon atom of the chain (Figure 1.1). Thousands of propylene molecules can be added sequentially until the chain reaction is terminated.

1.2 Stereospecificity

With Ziegler-Natta or metallocene catalysts, the polymerization reaction is highly stereospecific. Propylene molecules add to the polymer chain only in a particular orientation, depending on the chemical and crystal structure of the catalyst, and a regular, repeating three-dimensional structure is produced in the polymer chain Propylene molecules are added to the main polymer chain, increasing the chain length, and not to one of the methyl groups attached to alternating carbon atoms (the pendant methyl groups), which would result in branching. Propylene molecules are usually added head-to-tail and not tail-to-tail or head-to-head. Head-to-tail addition results in a polypropylene chain with pendant methyl groups attached to alternating carbons; in tail-to-tail or head-to head addition, this alternating arrangement is disrupted.
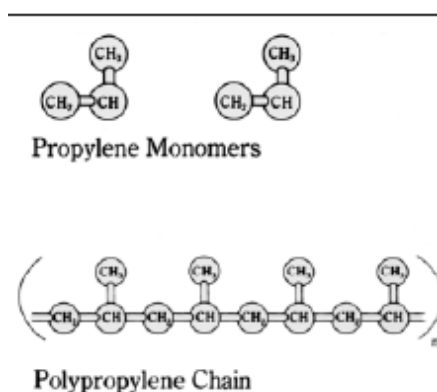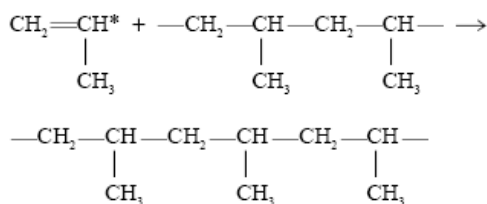

Figure 1.1 Molecules of propylene and polypropylene. In the polymerization reaction, propylene monomers (top) are added sequentially to the growing polymer chain (bottom), to form a long, linear polymer chain composed of thousands of propylene monomers. The portion of the chain shown in parentheses is repeated n number of times to form the polymer.
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Head-to-tail addition of propylene to the growing polypropylene chain
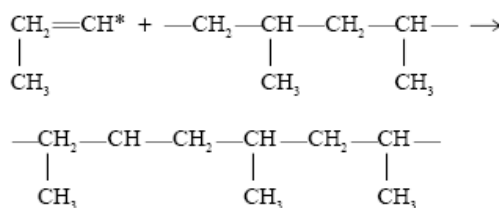
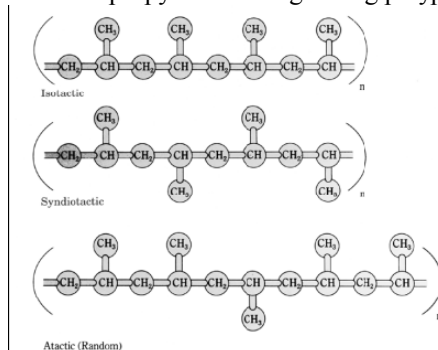Tail-to-tail addition of propylene to the growing polypropylene chain

Figure 1.2 Stereochemical configurations of polypropylene. In isotactic polypropylene, top, the pendant methyl groups branching off from the polymer backb?ne are all on the same side of the polymer backbone, with identical configurations relative to the main chain. In syndiotactic polypropylene, middle, consecutive pendant methyl groups are on opposite sides of the polymer backbone chain. In atactic polypropylene, bottom, pendant methyl groups are oriented randomly with respect to the polymer backbone. The portion of the chain shown is repeated n number of times to form the polymer.

Occasional tail-to-tail or head-to-tail additions of polypropylene to the growing polymer chain disrupt the crystalline structure and lower the meltmg pomt of the polymer; formulations in which this occurs are used in thermoforming or blow molding.

Polypropylene can be isotactic, syndiotactic, or atactic, depending on the orientation of the pendant methyl groups attached to alternate carbon atoms. In isotactic polypropylene (Figure 1.2), the most common commercial form, pendant methyl groups are all in the same configuration and are on the same side of the polymer chain. Due to this regular, repeating arrangement, isotactic polypropylene has a high degree of crystallinity. In syndiotactic polypropylene, alternate pendant methyl groups are on opposite sides of the polymer backbone, with exactly opposite configurations relative to the polymer chain. Syndiotactic polypropylene is now being produced commercially using metallocene catalysts. In atactic polypropylene, pendant methyl groups have a random orientation with respect to the polymer backbone. Amounts of isotactic, atactic, and syndiotactic segments in a formulation are determined by the catalyst used and the polymerization conditions. Most polymers are predominantly .isotactic, with small amounts of atactic polymer. New metallocene catalysts make possible other stereochemical configurations, such as hemi-isotactic polypropylene. In this configuration, most pendant 'methyl groups are on the same side of the polypropylene chain, as in isotactic polypropylene; however, other methyl groups are inserted at regular intervals on the opposite side of the chain.

1.3 Effect on characteristics of polypropylene
The structure and stereochemistry of polypropylene affect its properties.

1.3.1 Stereochemistry
Because of its structure, isotactic polypropylene has the highest crystallinity, resulting in good mechanical properties such as stiffness and tensile strength. Syndiotactic polypropylene is less stiff than isotactic but has better impact strength and clarity. Due to its irregular structure, the atactic form has low crystallinity, resulting in a sticky, amorphous material used mainly for adhesives and roofing tars. Increasing the amount of atactic polypropylene in a predominantly isotactic formulation increases the room temperature impact resistance and stretchability but decreases the stiffness, haze, and color quality.

The amount of atactic polypropylene in a polypropylene formulation is indicated by the level of room temperature xylene solubles; levels range from about 1-20%. Polypropylenes generally have higher tensile, flexural, and compressive strength and higher moduli than polyethylenes due to the steric interaction of the pendant methyl groups, which result in a more rigid and stiff polymer chain than in polyethylene. General effects of atactic level on the properties of polypropylene are listed in Table 1.1.

1.3.2 Molecular weight and melt flow index Longer polypropylene chain lengths result in a higher molecular weight for the polymer. The weight-average molecular weight of polypropylene generally ranges from 220,000-700,000 glmol, with melt flow indices from less than 0.3 gil 0 min. to over 1000 gil 0 min. The melt flow index (MFI) provides an estimate of the average molecular weight of the polymer, in an inverse relationship; high melt flow indicates a lower molecular weight.

Viscous materials with low MFI values (2) are used in extrusion processes, such as sheet and blow molding, that require high melt strength. Resins with MFI values of 2-8 are used in film and fiber applications, and materials with MFI values of 8-35 or more are used in extrusion coating, injection molding of thin-walled parts that requires rapid mold filling, and fiber spinning

Table 1.1 Effect of Atacticity on Polypropylene Weight Properties

Property	With Increasing Atacticity
Stiffness	Decreases
Moduli	Decreases
Strength	Decreases
Room Temperature Impact Resistance	Increases
Stretchability	Increases
Elongation	Increases
Shear Rheology	Increases
Long Term Heat Aging (LTHA) Resistance	Decreases
Heat Distortion Temperature	Decreases
Heat Seal Strength	Increases
Haze in Films	Decreases
Blocking in Films	Increases
Irradiation Tolerance	Increases
Extractables(solubility)	Increases
Smoke and Fume Generation	Increases
Color Quality	Decreases
General Optical Properties	Increases
Melting Temperature	Decreases
Heat of Fusion	Decreases
Crystallization Temperature	Decreases

Table 1.2 Effect of Increasing Molecular on Properties of Polypropylene

Property	With Increasing Atacticity
Impact Resistance	Increases
Elonfation	Increases
Moduli	Decreases
Strength	Decreases
Die Awell	Increases
Shear Rheology	Increases
Melt Strength	Increases
Heat seal Strength	Increases
Heat Distortion Temperature	Decreases
Irradiation Tolerance	Decreases
Haze	Decreases
Extractavles(solubility)	Decreases
Crystallization Temperature	Decreases

The toughness of a grade of polypropylene is directly related' to molecular weight: higher molecular weights provide greater toughness. As a result, higher molecular weight polypropylenes have greater impact resistance and elongation and less brittleness. General effects of increasing molecular weight on polypropylene properties are summarized in Table 1.2.

1.3.3 Molecular weight distribution

A polypropylene resin is composed of numerous chains of varying lengths, with varying molecular weights. The molecular weight distribution (MWD) indicates the variation of molecular weight in a particular formulation; the MWD is narrow if most molecular chains are approximately the same length and broad if the chains vary widely in length (Figure 1.3).

Molecular weight distribution, measured as the ratio of weight-average molecular weight to number-average molecular weight (Mw/Mn) can vary from 2.1 to over 11.0. The number-average molecular weight is related to the number of polymer chain molecules at a particular molecular weight, while the weight-average molecular weight relates to the mass (or weight) of the polymer chain molecules at a particular molecular weight.

The MWD influences the processability of a resin due to the shear sensitivity of molten polypropy - the apparent viscosity decreases as the applied pressure increases. Because a polypropylene resin with a broad MWD is more shear sensitive than a narrow MWD formulation (Figure 1.4), materials with broad MWD's are processed more easily in applications such as injection molding. Polypropylene resins with narrow MWD's are used m extrusion, in which a narrower MWD generally results in a higher achievable extrusion output rate or in applications such as fibers.
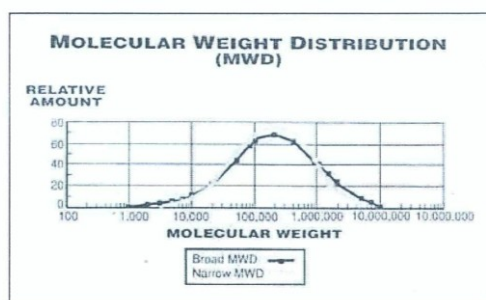
Figure 1.3 Graph of broad and narrow molecular weight distributions in polypropylene. In a resin with a narrow molecular weight distribution, polymer chains have approximately the same length and therefore the same molecular weight. The frequency of occurrence of these molecular weight chains is high, resulting in a narrow, high peak. A resin with a broad molecular weight distribution consists of polymer chains of varying lengths and molecular weights, resulting in a broad molecular weight distribution. The frequency of occurrence of any particular molecular weight is low, producing a low, broad peak.
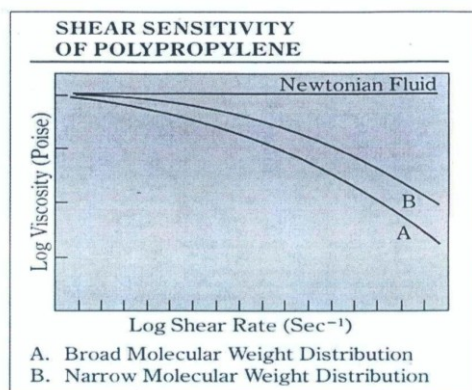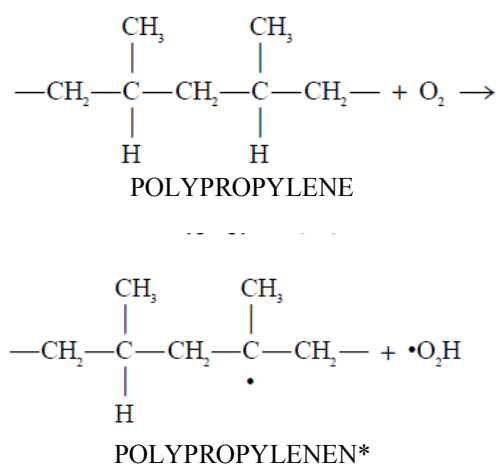
SHEAR SENSITIVITY OF POLYPROPYLENE

Newtonian Fluid

Log Viscosity (Poise)

B
A

Log Shear Rate (Sec⁻¹)

A. Broad Molecular Weight Distribution
B. Narrow Molecular Weight Distribution

Figure 1.4 Influence of the molecular weight .distribution of a polypropylene resin on shear sensitivity. In a Newtonian fluid, such as water, the viscosity of the fluid is constant with varying shear strain. In molten polypropylene, a shear sensitive material, the viscosity varies with the rate of shearing strain. A polypropylene resin with a broad molecular weight distribution, A, is more shear sensitive than a resin with a narrow molecular weight distribution, B.
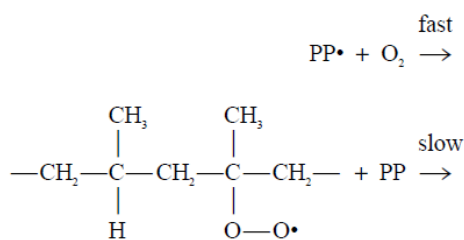
1.3.4 Oxidation

Polypropylene is highly susceptible to oxidation due to the presence of the tertiary hydrogen on the carbon atom bonded to the pendant methyl group. Polypropylene undergoes oxidation more readily than polyethylene, and oxidative chain scission, which reduces the molecular weight, occurs under normal processing conditions if the resin is not stabilized.
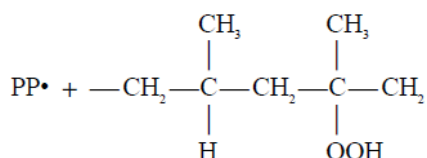
Polymer oxidation occurs through a free radical chain reaction. Mechanical stress, heat, or the presence of oxygen or metal catalyst residues results in homolytic cleavage of the carbon hydrogen or carbon-carbon covalent bond in the polypropylene chain; each atom receives one electron from the two-electron covalent bond, producing two free radicals, each with an unpaired electron. An example of a chain initiation reaction in the presence of oxygen is given below:

$$
\begin{array}{ccc}
CH_3 & & CH_3 \\
| & & | \\
-CH_2-C-CH_2-C-CH_2- & + & O_2 \rightarrow \\
| & & | \\
H & & H
\end{array}
$$

POLYPROPYLENE

$$
\begin{array}{ccc}
CH_3 & & CH_3 \\
| & & | \\
-CH_2-C-CH_2-C-CH_2- & + & \bullet O_2H \\
| & & \bullet \\
H & &
\end{array}
$$

POLYPROPYLENEN*

The chain reaction is propagated through the formation of a hydroperoxide, accompanied by the formation of another free radical:

$$PP\bullet + O_2 \xrightarrow{\text{fast}}$$

$$-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{O-O\bullet}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2- + PP \xrightarrow{\text{slow}}$$

PEROXIDE FREE RADICAL

$$PP\bullet + -CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{OOH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2$$
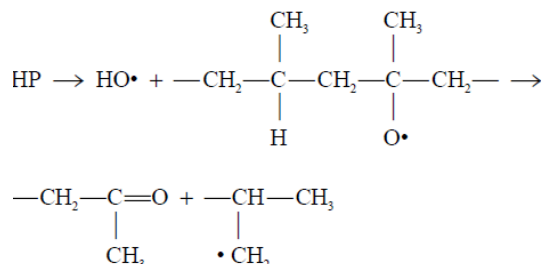
HYDROPEROXIDE

The oxidation rate is determined by the rate of the slow step in the chain propagation reactions. Due to the presence of the pendant methyl group, polypropylene contains tertiary hydrogen atoms, in which the carbon atom covalently bonded to the hydrogen is also bonded to three other carbon atoms. The free radical (PP·) formed from abstraction of a tertiary hydrogen is more stable than those formed from abstraction of a primary carbon atom attached to one other carbon) or secondary carbon atom attached to two other carbons) hydrogen, due to the tendency of carbon atoms along the chain to electronically donate electrons to the electron-deficient radical. The higher probability of reaction with the tertiary hydrogen considerably increases the susceptibility of polypropylene to oxidation.

$$-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-$$
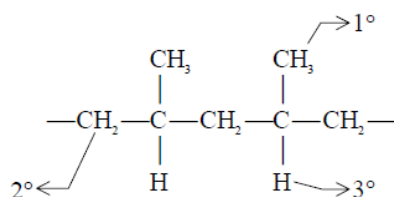
In further reactions (chain branching reactions that increase the amount of free radicals), the hydroperoxide decomposes in the presence of heat or metal catalyst residues to form an alkoxy radical. Oxidative chain scission is believed to occur through disintegration of this alkoxy radical:

$$HP \rightarrow HO\bullet + -CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{O\bullet}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2- \rightarrow$$

$$-CH_2-\underset{\underset{CH_3}{|}}{C}=O + -CH-CH_3$$
$$\underset{\bullet CH_2}{|}$$

The decrease in molecular weight resulting from chain scission produces a gradual loss in mechanical properties. Crosslinking, which is common in polyethylene oxidation, producing an increase in viscosity, does not occur frequently in polypropylene due to preferential oxidative attack at the tertiary hydrogen, which leads to chain scission. Compounds such as carboxylic acids, lactones, aldehydes, and esters are also produced during oxidation reactions, resulting in chemical modifications such as yellowing. Chain reactions are terminated when two radicals combine to form an inactive species.

1.3.5 Electrical conductivity
Electrically conductive materials, such as metals, have delocalized electrons that can easily move along a potential gradient. Electrons in the covalent bonds of organic molecules such as polypropylene must remain

near their host atoms and are not free to move through the material; as a result, they are poor conductors of electricity. The high dielectric strength and low dielectric constant and dissipation factor of polypropylene make it useful as an insulating material. Conductive materials such as carbon black can be added to a polypropylene formulation for applications requiring electrical conductivity.

1.3.6 Chemical resistance
Because it is composed of only carbon and hydrogen atoms, and not polar atoms such as oxygen or nitrogen, polypropylene is nonpolar. Nonpolar molecules are generally soluble in nonpolar solvents, while polar molecules are more soluble in polar solvents ("like dissolves like"); as a result, nonpolar molecules are more easily absorbed by polypropylene than polar molecules. Polypropylene is resistant to attack by polar chemicals such as soaps, wetting agents, and alcohols but can swell, soften, or undergo surface crazing in the presence of liquid hydrocarbons or chlorinated solvents. Strong oxidizing agents such as fuming nitric acid or hot, concentrated sulfuric acid can cause swelling and polypropylene degradation. A large degree of absorption can cause a loss of physical properties.

1.4 Catalysts
The development of catalysts for polypropylene polymerization in the 1950's made the production of stereospecific polypropylene possible and led to the rapid growth rate of polypropylene that is still occurring today. Catalysts are substances that increase the rate of a reaction but undergo no pennanent chemical change themselves. In polypropylene polymerization, catalysts are organometallic transition metal complexes. They provide active sites or polymerization sites where the polymerization reaction occurs, by holding the growing polymer chain and the propylene monomer in close proximity to each other so that they can react. With commercial catalysts, a high yield of stereospecific polypropylene is produced.

1.4.1 Ziegler-Natta catalysts
Ziegler-Natta catalysts are the most common commercial catalysts. Karl Ziegler and Guilio Natta jointly received the Nobel Prize in 1963 for the development of polyolefin polymerization catalysts with high yield and a high degree of stereospecificity. The original Ziegler-Natta catalysts were a complex of transition metal halides, usually titanium trichloride (TiCl}), with an organometallic compound, typically triethylaluminum, as cocatalyst to initiate the polymerization. Yield of isotactic polypropylene in these original catalysts was low, 30-40%, but was rapidly increased to over 80% with further development. [768, 788] Due to the low isotacticity, postreactor treatment was necessary in order to remove catalyst residues and atactic material.

Catalyst improvements have led to increased stereospecificity and productivity. The low surface areas of early TiCI) catalysts resulted in low catalyst activity; since only titanium atoms on the catalyst surface are accessible to the organometallic compound, few active sites were formed, and the amount of polypropylene produced per gram of catalyst used was low. TiCI) catalysts with increased surface areas resulted in increased productivity and isotacticity (-95%).

Supported heterogeneous Ziegler-Natta catalysts were developed in the 1960's, with magnesium chloride (MgCIJ used as the inert support material. Heterogeneous catalysts are present in a different phase (solid, liquid, gas) from the reaction mixture; they are fixed onto the surface of a support material for feeding into the reactor during processing and for control of polymer growth. Addition of a Lewis base, typically a benzoic acid ester, as an electron donor (internal donor) and a second Lewis base (methyl-p-toluate) as an external donor to the $MgCl_2$-supported catalyst increased catalyst activity and stereospecificity and eliminated the necessity of post reactor removal of catalyst residues.

Catalyst systems using newer Lewis bases (alkylphthalates and alkoxysilanes as internal and external donors, respectively) further increased isotacticity and activity and are currently used in the industrial production of polypropylene. Catalyst systems using new internal electron donors, developed in the latter part of the 1980's, result in very high activity and isotacticity without use of an external electron donor. They are not yet in industrial use.

1.4.2 Characteristics of polypropylene produced using Ziegler-Natta catalysts
Zeigler-Natta catalysts are multi-sited catalysts, containing several reactive sites. As a result, the polypropylene produced can include polymer molecules with a broad range of molecular weights and some branching off from the main polymer chain. For film and fiber applications and for injection molding of thin walls or parts with intricate structures, a narrower molecular weight distribution and increased melt flow rate may be required. For these applications, the polypropylene produced must be chemically or thermally broken down in post-reactor extrusion.

Chemical breakdown of the polymer chains is accomplished by oxidative chain degradation initiated by a peroxide, a process called controlled rheology (CR) or visbreaking. This process shortens the average length of the polymer chains, lowers the molecular weight, and narrows the molecular weight distribution, resulting in lower melt viscosity, increased flow rates, and slightly enhanced impact strength. Molding cycles can be up to 15% faster than with conventional grades, and warpage and shrinkage are reduced.

Metal catalyst residues that remain in the polypropylene resin may affect the opacity of the resin, and resins made using different catalysts may have different levels of clarity. In addition, additives can interact with catalyst residues to produce yellowness.

1.4.3 Metallocene catalysts

Metallocene catalysts have recently been developed for industrial use, and metallocene-produced polypropylene is now available. In contrast to Zeiger-Natta catalysts, metallocene catalysts are single-sited - they have identical active sites - and properties such as molecular weight and stereostructure can be tailored to meet the needs of the application. Syndiotactic polypropylene is now being produced commercially using metallocenes; commercial production was not possible with Ziegler-Natta catalysts.

Metallocenes are organometallic compounds with a sandwich-like spatial arrangement, consisting of a transition metal (iron, titanium, zirconium) situated between two cyclic organic compounds (Figure 1.5). Geoffrey Wilkinson and Ernst O. Fischer received the Nobel Prize in chemistry for elucidation of the structure of ferrocene, one of the first metallocenes discovered. The first metallocenes used for polymerization, titanocenedichloride and an aluminum alkyl such as trimethylaluminum, showed poor activity and were used only in scientific studies. However, in 1975, accidental introduction of water into a test tube containing a metallocene catalyst system and ethylene increased the polymerization rate 1000 times and led to the development of methylalumoxane (MAO), a product of the partial hydrolysis of trimethylaluminum, as a catalyst activator or co catalyst
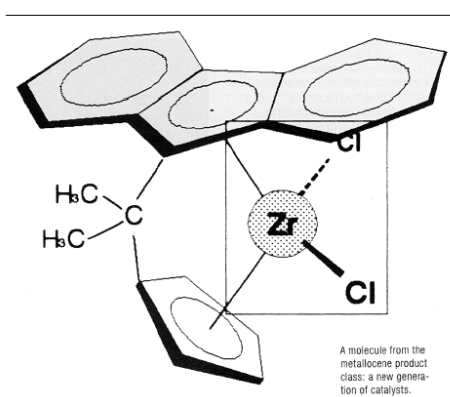

Figure 1.5 Structure of one type of metallocene catalyst. A zirconium atom is bound to two chlor!ne atoms and to a bridged alkyl group. The ZrCI2 complex IS located in a cleft formed by the alkyl group; the polymerization reaction occurs in the cleft. The molecule is represented in three dimensions - the dotted line indicates that one chlorine is located behind the plane of the paper, while the heavy bold line to the other chlorine indicates that it is located in front of the plane of the paper.

The introduction of chiral, bridged metallocenes using first titanium, then zirconium, in the 1980's allowed the stereoselective polymerization of propylene to isotactic polypropylene. In bridged metallocenes, a molecular "bridge" connects the two organic compounds of the metallocene "sandwich". A chiral molecule is one that, in its three dimensional configuration, cannot be superimposed on its mirror image. In 1988, syndiotactic polypropylene was synthesized using zirconiumcontaining metallocenes.

Current metallocene catalyst systems commonly use zirconium chloride ($ZrCI_2$) as the transition metal complex, with - a cyclopendadiene as the organic compound and an aluminoxane such as MAO as cocatalyst. Polypropylene resins with varying micro structures, molecular weights, and other properties can be produced by varying the transition metal and organic compound used.

Metallocene polymerization in the laboratory makes use of homogeneous catalysis; catalysts and reacting materials are in solution. For large-scale industrial processes, metallocenes must be fixed or supported on powdery, insoluble substrates; $Si0_2$, Alp], or $MgCI_2$, are generally used. A polypropylene chain is synthesized on each grain of powder, and because active sites on each grain are identical, the chains grow to a uniform length.

1.4.4 Characteristics of polypropylene produced using metallocene catalysts

Polypropylenes made using metallocene catalysts exhibit increased rigidity and transparency, higher heat distortion temperatures, improved impact strength and toughness even at subambient temperatures, and low extractables. Due to the uniformity of the polypropylene chains, metallocene-catalyzed propylene has a very narrow molecular weight distribution (Mw/Mn of 2.0) compared to conventional polypropylene (minimum Mw/Mn of 3-6). The narrow MWD results in lower shear sensitivity of the polypropylene resin and provides low melt elasticity and elongational viscosity in extrusion processes.

The melting point (l47-158°C; 297-3 16°F) of metallocene polypropylene currently produced is generally lower than that of conventional polypropylene (160-170°C; 320-338°F) and can be tailored to a specific application by using the appropriate metallocene as catalyst. As with Ziegler-Natta catalysts, resin color is affected by the type and amount of catalyst residue present, and interaction with additives may cause yellowing.

II. Conclusion

Studies and tests show that structure and Spatial arrangement of polypropylene molecules and type of used catalyst are effective on its properties and changes in tacticity and molecular mass cause to changes in polymer properties as follow. Because of high crystalline structure of polypropylene isotactic, it has good mechanical properties such as stiffness and tensile strength. Syndiotactic polypropylene has less stiffness but more resistance to impact and better transparency than polypropylene isotactic. Increasing the little amount of polypropylene atactic cause to enhance impact resistance in ambient temperature and tensile strength, but Stiffness, opacity and color quality is reduced and higher mass molecular polypropylene is tougher and has impact resistance and more length increasing and less frangibility, meantime researches demonstrated that residual metal catalyst in polypropylene resin is effective on opalescence of resin, and resins made with different catalysts have different transparency.

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