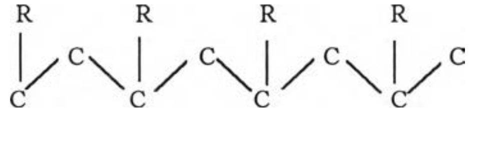
# CHAPTER I

# INTRODUCTION

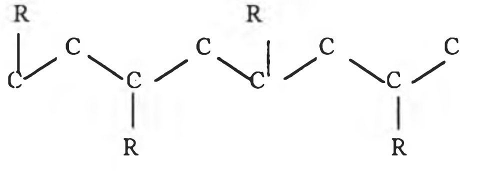
Ziegler catalysis involves rapid polymerizaton of ethylene and α-olefins with the aid of catalysts based on transition element compounds, normally formed by reaction of a transition element halide or alkoxide or alkyl or aryl derivative with a main-group element alkyl or alkyl halide (Ziegler, 1955), (Kissin, 1975). Catalysts of this type operate at low pressures (up to 30 atm, often at 8-10 atm at temperature up to 120 °C, often as low as 20-50°C).

Using such α-olefins as monomers, Natta (Natta,1955; Sinn and Kaminsky, 1980) found that most of the product had a stereoregular structure. Three types of steric arrangement of polypropylene are possible:

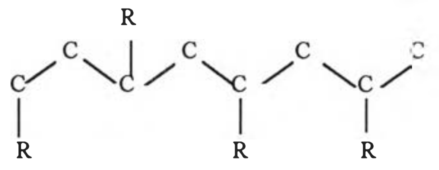
1. Same steric arrangement of monomer units by a head-to-tail chain arrangement, referred to *isotactic*




2. Alternately opposite steric arrangement of monomers, referred to as *syndiotactic*



3. *Atactic*, or at-random arrangement of monomer units



The characteristics between the different forms of polypropylene produced (assuming equal molecular weight distribution, equal percentage of branching, etc.) are remarkable, as shown in table 1.1 .

**Table 1.1** Some characteristics of polypropylene

| Characteristics | Polypropylene | | |
|---|---|---|---|
| | Isotactic | Syndiotactic | Atactic |
| Melting Point (°C) | 165-171 | 125-131 | < 0 |
| Crystallinity (%) | 55-65 | 50-75 | 0 |
| Tensile Strength (kP/cm$^2$) | 320-350 | - | - |

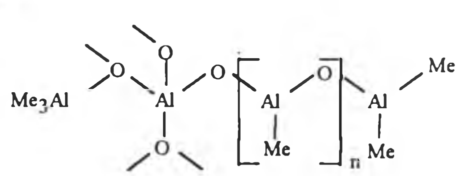
Most Ziegler catalyst systems are heterogeneous, but some homogeneous systems are known. It is not clear at present that stereoregulation and stereoselectivity are the results of heterogeneity.

Homogeneous Ziegler-Natta catalysis has been limited to the field of diene polymerization and ethylene-propylene copolymerization. Nevertheless, many of these catalysts and polymerization systems have received considerably academic attention in the hope that they might provide models for heterogeneous systems since it was believed that problems associated with surface properties and particle sizes could be avoided (Tait, 1982).

Among a great number of known Ziegler-type catalysts, homogeneous systems have been preferentially investigated in order to understand elementary steps of the polymerization, which is simpler in solution than in heterogeneous systems. Table 1.2 summarizes important homogeneous Ziegler catalysts. The best known systems are based on bis(cyclopentadienyl) zirconium (IV) dichloride.

Much work has been performed using homogeneous Ziegler-Natta catalyst systems with the aim of establishing a general mechanistic scheme. Such systems are easier to study than heterogeneous systems in that each metal atom is supposed to form an active center.

These generation of catalysts, sometimes refered to as "single-site" catalysts, are based upon modifications of $Cp_2ZrCl_2$ combined with methylaluminoxane, **I** : MAO,

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The simple complex $Cp_2ZrCl_2$ is an extremely active ethylene polymerization catalyst. Because there is a single type of active species in solution, a high degree of control over polymer properties is possible. Narrow molecular weight distributions are possible, they can be controlled by ligand and process variations. Greatly improved control of comonomer incorporation is also possible, for instance, the comonomer can be incorporated specifically into one region of the molecular weight distribution.

**Table 1.2** Homogeneous Ziegler Catalyst System

| System | Transition metal (M) : aluminium compound | monomer | Temp (°C) | Activity (g/mmole metal·hr) | Reference |
| --- | --- | --- | --- | --- | --- |
| [a]$Cp_2Zr(Ph)_2$ / MAO | 450 | propylene | 50 | 47.09 | John A.Ewen (1984) |
| $Cp_2ZrCl_2$ / MAO | 500 | propylene | 20 | 1,680 | T.Tsutsui et al. (1989) |
| $Et(Ind)_2HfCl_2$ /MAO | 2,000 | 1-butene | 20 | 2,500 | M.Kioka (1986) |
| $Et(Ind)_2ZrCl_2$ /MAO | 4,000 | 1-butene | 20 | 9,700 | M.Kioka (1986) |
| [b]$Et(Ind)_2ZrCl_2$ /MAO | 10,000 | propylene | 30 | 67,500 | N.Kashiwa (1989) |

[a] Cp = $\eta^5$-$C^5H^5$

The single-site catalysts give interesting results when applied to propylene polymerization. The complex $Cp_2ZrCl_2$ is not chiral and gives polypropylene with pure atacticity.