

## CHAPTER I

### INTRODUCTION

Polystyrene (PS) has been known since 1925, commercialised by IG Farben and it is now one of the most widespread polymeric material, appreciated for its excellent stiffness and transparency and its good processability. It is an amorphous polymer with a softening temperature of about 100°C. Brittleness and poor thermal and chemical resistances are its main faults from an applicative point of view. The polymerization of styrene with radical initiators either in bulk, in solution, in suspension or in emulsion afford atactic polystyrene (APS). Cationic and anionic initiated polymerizations also afford atactic polystyrenes. In the course of radical or ionic polymerizations, the growing polymer chain can move freely. This freedom may be decreased in the presence of tight ion pairs. Partially stereoregular polystyrene were obtained in anionic polymerizations by changing reaction conditions [1-3]. Usually the chain end needs to be covalently linked to a metal co-ordination complex to have substantial stereochemical control on polymerization.

In 1955, Natta *et al.* obtained isotactic polystyrene (IPS) by using a Ziegler-Natta catalytic system  $\text{TiCl}_4/\text{Al}(\text{CH}_2\text{CH}_3)_3$ . The isotactic polymer is highly crystalline, with a melting temperature of 240°C. However, its crystallization rate is too slow to make any commercial application of this material viable.

In 1985, Ishihara *et al.* [4-6] (Idemitsu Kosan Co., Ltd.) were able to obtain syndiotactic polystyrene (SPS) by using homogeneous organometallic catalytic system based on titanium compounds and methylaluminoxane (MAO). SPS is a highly crystalline polymer, with a melting temperature of about 270°C and a glass transition temperature similar to atactic polystyrene (Table 1). The relatively fast crystallization rate, the low specific gravity, low dielectric constant, high modulus of elasticity and

excellent resistance to chemicals make SPS a promising material for a large number of applications in the automotive, electronic and packaging industries.

**Table 1.1.** Structure and thermal properties of atactic, isotactic and syndiotactic polystyrene.

	Atactic PS (APS)	Isotactic PS (IPS)	Syndiotactic PS (SPS)
Structure	Amorphous	Crystalline	Crystalline
Crystallization rate	-	Slow	Fast
Glass temperature( $T_g$ )/ °C	100	99	100
Melting point( $T_m$ )/ °C	-	240	270

The discovery of the homogeneous catalytic system metallocene/MAO, able to produce highly linear and stereoregular polyolefins, represented an important breakthrough in alkene polymerization. Similar catalytic system based on group 4A metal compounds, especially titanium, and MAO (or *tris*(pentafluorophenyl) borate derivatives) were successfully used to produce polystyrene and its copolymer with a high degree of syndiotacticity. To replace the conventional Ziegler-Natta catalysts used in industrial slurry and gas-phase processes with metallocene catalysts (drop-in technology), metallocene catalysts have to be immobilized on supports. Supported metallocene catalysts are prepared by the reaction of supports and metallocenes. There are many publications describing the heterogenation of metallocenes onto supports such as silica, alumina, magnesium chloride, starch, zeolites, cyclodextrin, and synthetic polymer [7-11]. The supported catalysts can overcome some disadvantages of homogeneous metallocene catalysts such as poor polymer morphology, reaction fouling, and low bulk density of the polymer.

In general, supported metallocenes have a lower catalytic activity than their corresponding homogeneous metallocene systems. The reasons for this poor catalytic activity may include (1) significant steric hindrance around the active site due to the large

support surface and (2) deactivation of catalytic sites or inefficient production of active sites during the supporting process.

To overcome the preparation complexity of traditionally supported metallocene catalysts, metallocene can be supported *in situ*, which eliminates the need for a supported step before polymerization. These catalysts have a good catalytic activity, produce polymers with a good morphology and high bulk density, and do not cause reactor fouling.

## **1.1 The objectives of the thesis**

- 1.1.1 Synthesis of polymer-supported titanocene catalysts.
- 1.1.2 Study of influence of parameters affecting polymerization of styrene.

## **1.2 The scope of the thesis**

Polymer-supported titanocene catalysts are synthesized and used for the polymerization of styrene. The corresponding homogeneous catalysts are also tested for activity comparison. The polymerization conditions are investigated to obtain optimum condition. The synthesized polystyrenes are characterized spectroscopically and with other techniques.

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