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SYNDIOTACTIC POLYSTYRENE POLYMERIZATION RESULTS USING A TITANIUM(III) COMPLEX, $Cp^*Ti(OMe)_2$ AND IMPLICATIONS TO THE MECHANISM OF POLYMERIZATION

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INTRODUCTION

Syndiotactic polystyrene (SPS) is a new semi-crystalline engineering thermoplastic synthesized via homogeneous Ziegler/Natta type catalysis. The polymer was first prepared in 1985 by Idemitsu Kosan Co. Ltd. [1] and has been under joint product and process development by Idemitsu Petrochemical Co. Ltd. and Dow Plastics since 1988. Recently, Dow and Idemitsu announced that they will complete semicommercial plant construction in 1996 utilizing a unique continuous polymerization process.

The high syndiospecific stereoregularity of SPS produced via homogeneous catalysis gives rise to its functional values of high heat resistance and excellent chemical resistance. The melting point of SPS is 270 °C and the typical level of crystallinity of SPS following melt processing is approximately 50% based on DSC results. The rate of crystallization of SPS is several orders of magnitude higher than isotactic polystyrene and similar to polyethylene terephthalate. The maximum crystallization rate occurs near 160 °C, however, the crystallization rate of SPS can be enhanced through the use of nucleators. The quiescent crystallization rate is great enough to allow for the use of SPS in injection molding processes, and the material can be reinforced with glass or other fibers to gain full advantage of the high melting temperature in engineering applications. The crystallinity of SPS, as well as its hydrocarbon nature, yields excellent resistance toward moisture, steam and various chemicals including automotive fluids. SPS can also be quenched into the amorphous state and subsequently strain induced to crystallize allowing for processing into film and fiber forms as well.

The syndiospecificity of SPS, which is responsible for the crystallinity of SPS and consequently its heat and chemical resistance, results from the homogeneous coordinative polymerization. Typically, a Group IVB transition metal complex is utilized with a cocatalyst such as methylaluminoxane (MAO) or a cation forming cocatalyst comprising a noncoordinating counter ion, such as N,N-dimethylanilinium tetrakisperfluorophenylborate. Initial evaluations of various titanium compounds with methylaluminoxane (MAO) cocatalyst were published by Ishihara, *et al.* [1] Their polymerization activities indicated that titanium metallocene complexes with one cyclopentadienyl ligand yield the highest activity for SPS polymerization.

The oxidation state of the transition metal active species in Ziegler/Natta polymerization of olefins has been a subject of debate since the discovery of coordinative polymerization of polyolefins. [2-4] Titanium, which has been used extensively for the polymerization of SPS, can exist in the +4, +3 and +2 oxidation states. However, generally, the starting titanium complex for SPS polymerization has been in the +4 state, e.g. $Ti(OC_2H_5)_4$, $Cp^*Ti(OCH_3)_3$ or $Cp^*Ti(CH_3)_3$. Recent work, [5,6] using ESR spectroscopy, has shown the presence of significant amounts of Ti(III) in the active catalyst solutions. Furthermore, the active site for SPS polymerization has been proposed to be a Ti(III) cationic species [7]. Identification of the oxidation state of the active titanium species in SPS polymerization is important for the design of more efficient catalysts.

In order to address the question of the influence of the titanium oxidation state on the polymerization of SPS, we have synthesized the titanium(III) metallocene, $Cp^*Ti(OMe)_2$, via reduction of $Cp^*Ti(OMe)_3$ with t-butyllithium and characterized the complex via X-ray crystallography. The polymerization results for $Cp^*Ti(OMe)_2$ with either MAO cocatalyst or N,N-dimethyl-anilinium tetrakisperfluorophenylborate cocatalyst will be compared with the analogous titanium(IV) complex, $Cp^*Ti(OMe)_3$.

EXPERIMENTAL

Synthesis of $Cp^*Ti(OMe)_2$

A 100 ml Schlenk flask was charged with 1.05 g of $Cp^*Ti(OMe)_3$ and 35 ml of anhydrous tetrahydrofuran. The flask was cooled to -78°C and 2.4 ml of 1.7

molar t-butyllithium added. After stirring for one hour at -78°C, a solution of 0.5 g of trimethylchlorosilane in 15 ml of anhydrous tetrahydrofuran was added. After slowly warming to room temperature, the volatiles were removed under vacuum. The product was extracted in hexane, filtered and recrystallized at -10°C. Deep-reddish colored crystals were isolated (52% yield) and used for this study.

Polymerizations

Catalyst solutions were prepared in volumetric flasks using toluene solvent. The required amounts of cocatalyst, aluminum alkyl and titanium complex were added and diluted to a final concentration of 0.003 molar in titanium. Polymerizations were carried out in septum capped, crimp sealed ampoules. The ampoules were charged with 10 ml of styrene, equilibrated at temperature and initiated with various amounts of catalyst solution as indicated in the tables. The polymerizations were quenched with addition of methanol after the desired time. The polymer was isolated and dried under vacuum in order to determine the percent conversion.

RESULTS AND DISCUSSION

The titanium(III) complex, $Cp^*Ti(OMe)_2$, was prepared via reduction of $Cp^*Ti(OMe)_3$ with t-butyllithium. Suitable crystals for X-ray crystallography were obtained from hexane. Successful structure solution and refinement showed that the space group assignment was C2. Final cell parameters were a = 15.219(3) Å, b= 8.714(1) Å, c= 11.488(1) Å, β= 118.47(1)°, α = γ = 90°. V = 1334.7(4) Å^3. The complex is dimeric with two bridging methoxide groups, two terminal methoxide groups and two Cp* rings trans to each other with respect to the Ti-Ti vector (Figure 1). The two halves of the dimer are related by a 2-fold symmetry axis. The bond lengths and angles are comparable to other organotitanium complexes. The Ti - Ti contact distance is 3.117(2) Å which is comparable to other organotitanium dimers. [8, 9] The Ti - Cp(carbon) distance averages 2.37(3) Å with the individual values ranging from 2.29(1) Å through 2.44(2) Å. The Ti to Cp centroid distance is 2.045 Å. These Cp - titanium distances are consistent with other metallocene titanium systems. The C(Cp) - Ti - O bond angles are all very close to 120°. The crystal is held together by van der Waals forces between adjacent dimer molecules. No hydrogen bonds are present between adjacent dimers.

Table 1 shows a comparison of the percent conversion for $Cp^*Ti(OMe)_2$ and $Cp^*Ti(OMe)_3$ with varying MAO ratio in the MAO cocatalyst system. At very low MAO ratio, both catalysts yield very little SPS. However, Cp*Ti(OMe)2 gives

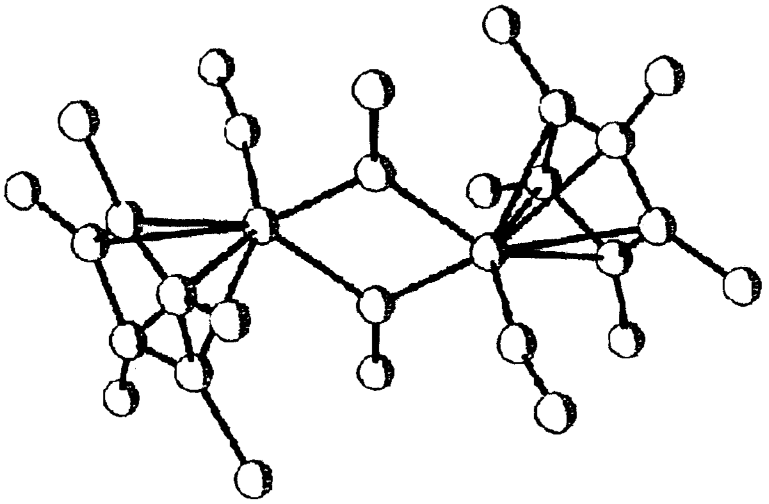

Figure 1. Projection Showing the Dimeric Nature of $Cp^*Ti(OMe)_2$. Hydrogens omitted for clarity.

TABLE 1. Percent Conversion to SPS with MAO Content Molar Ratios Styrene: MAO:Ti 233,333:MAO:1; 70°C for 1 hour

Catalyst	MAO:Ti	% Conversion
$Cp^*Ti(OMe)_2$	25	10
	50	32
	100	55
	200	63
$Cp^*Ti(OMe)_3$	25	2
	50	22
	100	33
	200	41

a higher conversion at lower MAO ratio than $Cp^*Ti(OMe)_3$. Table 2 shows a comparison of percent conversion for $Cp^*Ti(OMe)_2$ and $Cp^*Ti(OMe)_3$ with the addition of triisobutylaluminum (TIBA) in the MAO cocatalyst system.

The trend of increasing conversion with TIBA content is observed in Table 2 for $Cp^*Ti(OMe)_3$ and relatively low conversion is observed with no TIBA.

However, for $Cp^*Ti(OMe)_2$, high conversion is obtained even with no TIBA and the conversion is higher than for $Cp^*Ti(OMe)_3$. This suggests the

TABLE 2. Percent Conversion to SPS with TIBA Content Molar ratios Styrene:MAO:TIBA:Ti 233,333:200:TIBA:1; 70°C for 1 hour

Catalyst	TIBA:Ti	% Conversion
$Cp^*Ti(OMe)_2$	0	58
	6	62
	10	64
	50	66
$Cp^*Ti(OMe)_3$	0	30
	6	47
	10	53
	50	62

TABLE 3. Percent Conversion to SPS with TNPA Content Molar Ratios Styrene: TNPA:Borate:Ti 200,000:TNPA:1:1; 70°C for 2 hours

TNPA:Ti	% Conversion
0	1
3	31
5	49
10	48
15	54
30	55

function of the aluminum alkyl is reduction of the Ti(IV) species while the MAO cocatalyst generates the active Ti(III) cationic site. Thus, the titanium (III) complex requires less aluminum alkyl overall, i.e. less MAO and no TIBA.

Polymerization results with $Cp^*Ti(OMe)_2$ and N,N-dimethyl-anilinium tetrakisperfluorophenylborate cocatalyst are shown in Table 3. The tri-*n*-propylaluminum (TNPA) content in the catalyst solution was varied and 2 hour polymerizations run at 70°C at a ratio of 200,000:X:1:1 (S:TNPA:Borate:Ti). Essentially no polymerization is observed in the absence of TNPA. However, at X=5, high conversion was obtained and there was very little subsequent increase in conversion at higher values of TNPA. These results again suggest aluminum alkyl is necessary for alkylation of the $Cp^*Ti(OMe)_2$ but not required for reduction. This is unlike Ti(IV) complexes which require aluminum alkyl for both the alkylation and reduction step to the active Ti(III) cation.

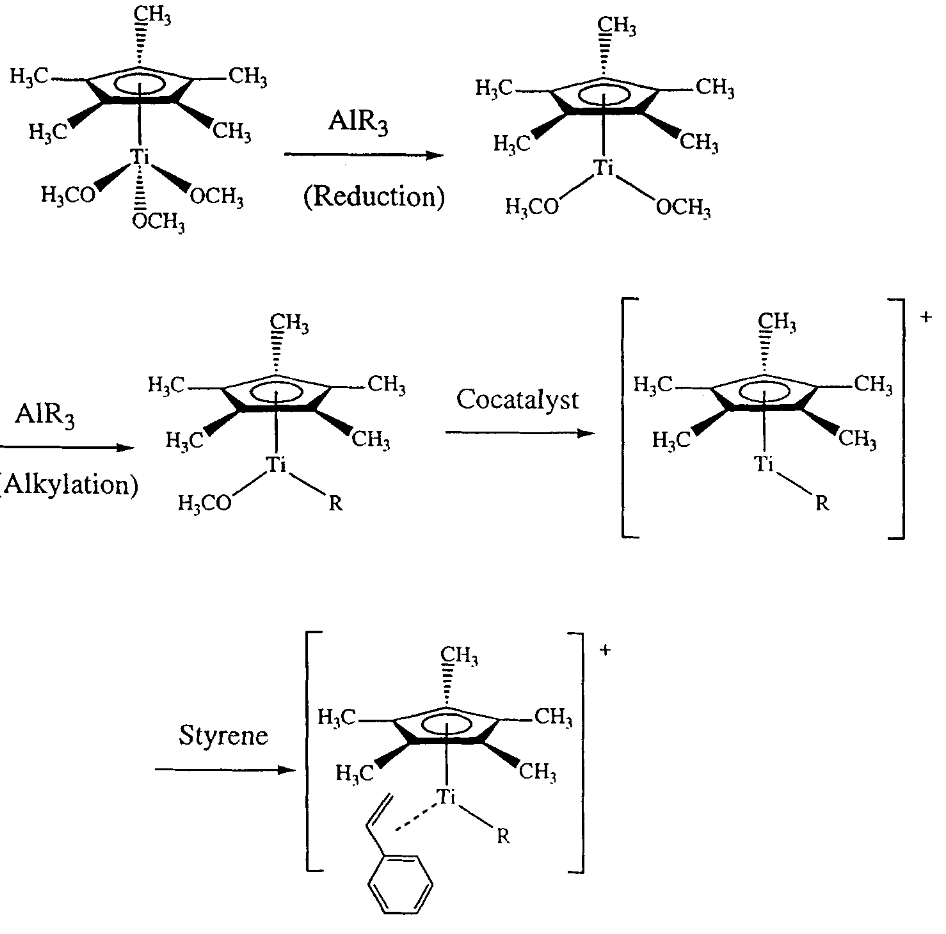

Figure 2. Proposed Mechanism for Active Site Formation for SPS Polymerization.

CONCLUSIONS

A titanium (III) metallocene complex, Cp*Ti(OMe)$_2$, has been synthesized and characterized via X-ray crystallography. It is a highly active catalyst for SPS polymerization in the presence of a cocatalyst, either MAO or N,N-dimethylanilinium tetrakisperfluorophenylborate (Figure 2). The polymerization results support the polymer-ization mechanism recently proposed by Gassi, Zambelli and Laschi [7] involving a Ti(III) cationic active site. A titanium (IV) complex is reduced with aluminum alkyl, either MAO or AlR$_3$, to a titanium (III) species. The titanium (III) complex is then alkylated, again either by MAO or AlR_3, and reaction with the cocatalyst forms the active titanium (III) cationic species. Our results, starting with $Cp^*Ti(OMe)_2$, demonstrate a significant reduction in the amount of aluminum alkyl required for optimum polymerization activity. In this case, aluminum alkyl for the Ti(IV) to Ti(III) reduction is not necessary.

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