

Novel Monotitanocene and Methylaluminoxane Catalyst for Syndiospecific Polymerization of Styrene

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ABSTRACT: Syndiotactic polystyrene (sPS) was synthesized with a novel monotitanocene complex of η^5 -pentamethylcyclopentadienyltri-4-methoxyphenoxy titanium [$\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3$] activated by methylaluminoxane (MAO) in different polymerization media, including heptane, toluene, chlorobenzene, and neat styrene. In all cases bulk polymerization produced sPS with the highest activity and molecular weight. Solution polymerization produced much better activity in heptane than in the other solvents. Using a solvent with a higher dipole moment, such as chlorobenzene resulted in lower activity and syndiotacticity because of the stronger coordination of solvent with the Ti(III) active species, which controlled syndiospecific polymerization of styrene. With bulk polymerization at a higher polymerization temperature the $\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3$ -MAO catalyst produced sPS with high catalytic activity and molecular weight. The external addition of triisobutylaluminum (TIBA) to the $\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3$ -MAO system catalyzing styrene polymerization led to significant improvement of activity at a lower Al:Ti molar ratio, while the syndiotacticity and molecular weight of the yields were little affected. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1243–1248, 2001

Key words: Monotitanocene catalyst; methylaluminoxane; polystyrene; syndiotactic polystyrene; syndiospecific polymerization of styrene

INTRODUCTION

Synthesis of syndiotactic polystyrene (sPS) has generated much interest because of its properties and applications.^{1,2} Monotitanocene–methylaluminoxane (MAO) catalysts have been found to be the most favorable for syndiospecific polymerization of styrene.^{3–10} Because the component of MAO used as cocatalyst is rather complicated, many efforts have been made to discover the role of each part in olefin polymerization.^{11–13} During preparation it was found that MAO always contains some amount of unreacted trimethylalumi-

num (TMA), which cannot be removed easily by vacuum distillation. The residual TMA in MAO has been known to have an important influence on promoting the activity of monotitanocene catalysts for syndiospecific polymerization of styrene.^{14,15} It has been suggested that the TMA reduces Ti(IV) complexes to Ti(III) and Ti(II) states and that Ti(III) active species catalyze the syndiospecific polymerization of styrene with a higher catalytic activity.^{16–18}

The activity and syndiospecificity of the catalysts are sensitive to various polymerization conditions, such as the polymerization temperature, the concentrations of catalyst and cocatalyst and their molar ratio, polymerization time, monomer concentration, and so on.^{19–22} However, relatively little work has been carried out to investigate the

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influences of the solvent used as the polymerization medium. Good yields and syndiotacticity of sPS were obtained in some aromatic solvents such as toluene, mesitylene, *m*- and *p*-xylene, and neat styrene, but reactions performed in benzene and anisole produced lower yields.²³ Toluene is always selected as the common solvent for syndio-specific polymerization of styrene with homogeneous monotitanocene–MAO catalyst systems, as reported in many articles.

This article describes the use of a novel monotitanocene η^5 -pentamethylcyclopentadienyltri-4-methoxyphenoxy titanium [$\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3$] complex activated by MAO for syndiospecific polymerization of styrene. The investigation of the influence of different polymerization media (aliphatic and aromatic solvents) on the activity and syndiospecificity of polymerization products is also reported. Under the adopted conditions, activity enhancement was observed when external triisobutylaluminum (TIBA) was added to the $\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3/\text{MAO}$ catalyst system at a lower Al:Ti molar ratio.

EXPERIMENTAL

Materials

Toluene, heptane, and chlorobenzene were refluxed over metallic sodium for 24 h and distilled in a nitrogen atmosphere before use. Styrene was purified by distillation under reduced pressure over CaH_2 and was finally stored in a nitrogen atmosphere.

η^5 -Pentamethylcyclopentadienyltri-4-methoxyphenoxy titanium [$\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3$] was prepared by the reaction of η^5 -pentamethylcyclopentadienyl trichloride titanium (Cp^*TiCl_3) with 4-methoxyphenol in the presence of an absorbent of HCl such as $\text{N}(\text{Et})_3$. A yellow liquid product (yield 89%) was obtained.

ANAL. Calcd for $\text{C}_{31}\text{H}_{36}\text{O}_6\text{Ti}$: C, 64.44%; H, 8.47%. Found: C, 64.13%; H, 8.24%.

Methylaluminoxane (MAO) was prepared by the controlled reaction of trimethylaluminum (TMA) with H_2O from $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ dispersed in toluene for several hours. The final solid product was obtained after evaporation.

Polymerization of Styrene

Polymerization runs were carried out under an extra-pure-grade nitrogen atmosphere in 100-mL

glass flasks equipped with a magnetic stirrer. The MAO, solvent, or styrene, TIBA (needed), and $\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3$ were introduced in that order into the reactor. The temperature was kept constant during polymerization and terminated by the addition of 10 wt % HCl in ethanol. The polymers were washed with ethanol and dried in vacuum at 80°C to a constant weight. The syndiotactic index (SI) of polystyrene was determined as the weight percentage of the insoluble fraction after the obtained polymer was extracted for 12 h with boiling butanone.

Characterization

The viscosity-average molecular weights (M_v) of the polymers were calculated from $[\eta]$ measured in *o*-dichlorobenzene at 135°C for sPS. Differential scanning calorimetry (DSC) analysis was conducted with a Perkin-Elmer DCS-7 system at 10°C/min. Infrared spectra were obtained with a Nicolet 205 Fourier transform infrared spectrometer.

RESULTS AND DISCUSSION

The results of styrene polymerization with η^5 -pentamethylcyclopentadienyltri-4-methoxyphenoxy titanium [$\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3$]–MAO catalyst in heptane, toluene, and chlorobenzene solutions and neat styrene are summarized in Table I. The order of polarity of the three solvents is chlorobenzene > toluene > heptane, while with the corresponding activity of the styrene solution, polymerization is in the opposite order: heptane > toluene > chlorobenzene. The syndiotacticity of polystyrene prepared in high-polar solvent of chlorobenzene is even less, only 31.7 wt % and 62.6 wt %, and the molecular weight is also the lowest. It should be noted that bulk polymerization is the best choice in all cases for preparing sPS with high activity and molecular weight using $\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3$ –MAO catalyst.

It is well known^{16–18} that the reaction of monocyclopentadienyl titanium complexes CpTi-L_3 ($\text{Cp} = \eta^5$ -cyclopentadienyl, η^5 -pentamethylcyclopentadienyl, or substituted η^5 -cyclopentadienyl and $\text{L} = \text{halide, alkyl, alkoxy}$) with MAO produces mainly CpTi-MeL_2 and CpTi-MeL active species. Because MAO is a strong Lewis acid, previous reports^{24–26} described the cationic active species of $[\text{CpTi-Me}]^+$, which catalyze syndiospecific stereoregular polymerization of styrene, are

Table I Effect of Solvent Polarity on Styrene Polymerization with Novel Cp*Ti(OC₆H₄OCH₃)₃-MAO Catalyst

Run No.	Solvent Sample	^a D. M. μ	$V_{\text{sol.}} : V_{\text{st.}}$ (ml : ml)	[St.] (mol/L)	^b S. C. (wt %)	^c A $\times 10^{-5}$ (gPS/molTi h)	^d S. I. (wt %)	Pure sPS	
								$M_v \times 10^{-5}$	T _m (°C)
1	Heptane	0	1:1	4.3	34.4	12.9	96.0	1.8	267
2	Heptane	0	1:3	6.5	50.0	28.1	96.8	3.2	269
3	Toluene	0.37	1:1	4.3	16.1	6.0	97.5	2.5	268
4	Toluene	0.37	1:3	6.5	44.6	25.1	97.8	4.3	270
5	Chlorobenzene	1.54	1:1	4.3	2.6	1.5	31.7	0.9	263
6	Chlorobenzene	1.54	1:3	6.5	5.8	3.3	62.6	2.6	269
7	Bulk	0.13(st.)	/	8.6	78.7	59.0	96.8	5.5	271

Polymerization conditions: [Ti] = 1.2×10^{-4} mol/L, Al_{MAO}/Ti = 400 mol/mol, Al_{TIBA}/Ti = 200 mol/mol, T_p = 90°C, t_p = 1 h;

^aDipole moment of solvent.

^bStyrene conversion.

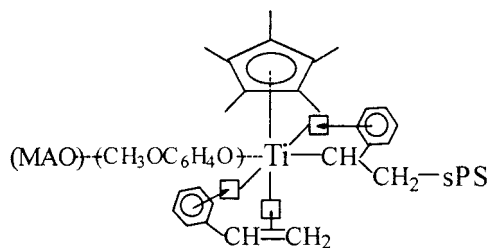
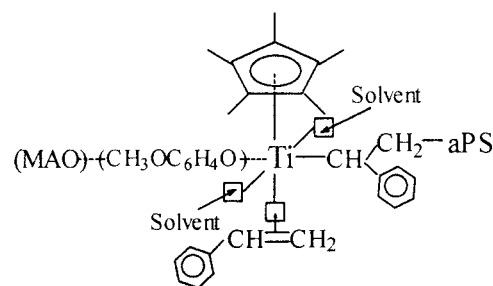
^cActivity of catalyst.

^dSyndiotactic index.

possibly formed as a result of an abstraction of the L ligand from CpTi-MeL complex by MAO. However, this conclusion cannot explain why¹⁰ the activities are affected by the L ancillary ligand of monotitanocene complexes. Consequently, in this article we suggest that syndiospecific polymerization of styrene is performed by an active species of Cp*Ti-Me(OC₆H₄OCH₃)-MAO through a coordination polymerization mechanism, as shown in Scheme 1. This is why various monotitanocene catalysts for styrene polymerization with distinct ancillary ligands and in different media have different properties with respect to activity and stereospecificity. Indeed, high-polar solvents can also coordinate with the Ti of Cp*Ti-Me(OC₆H₄OCH₃)-MAO, as shown in Scheme 2. The result causes a breakage of the mechanism of syndiospecific polymerization of styrene and produces atactic polystyrene (aPS).

Syndiotactic polystyrene has been reported to possess several crystalline structures depending on the specific crystallization condition.²⁷⁻²⁹ In-

frared spectroscopy was applied to determine characterization of the sPS crystalline structures.³⁰ Several infrared bands have been assigned for characterization of the different chain conformations. The 548 cm⁻¹ and 571 cm⁻¹ bands and the 934/943 cm⁻¹ doublet are indicative of the presence of a helical crystalline phase, while the 1222 cm⁻¹ band is associated with a long planar zigzag sPS chain structure with an all-*trans* conformation. For the sPS sample obtained using the Cp*Ti(OC₆H₄OCH₃)₃-MAO catalyst with bulk polymerization, the infrared spectrum only shows a helical crystalline structure [Fig. 1(a)]. The 1222 cm⁻¹ band can be observed and has been assigned to the all-*trans* planar zigzag crystalline structures in Figure 1(b), which show the infrared spectrum of sPS produced from Run 2 in the heptane solvent. Figure 2 exhibits the DSC curves of sPS obtained from Run 2 [Fig. 2(b)], with heptane used as the solvent, and from

**Scheme 1** Mechanism of syndiospecific polymerization of styrene**Scheme 2** Mechanism of atactic polymerization of styrene.

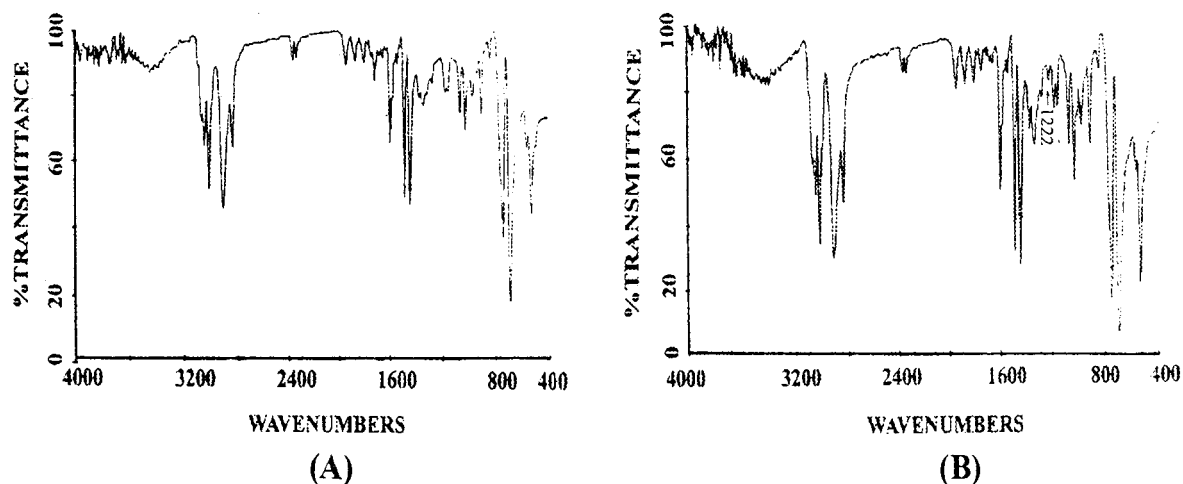


Figure 1 Infrared spectra of sPS samples: (a) Run 7 prepared with the bulk polymerization method; (b) Run 2 prepared in heptane medium.

Run 7 [Fig. 2(a)], which utilized the bulk polymerization method. The former displays a distinct bimodal shape, from which both corresponding crystalline structures of sPS can be assumed, while the latter only shows a unimodal shape.

Data for the syndiospecific polymerization of styrene at various temperatures are presented in Table II. In most cases catalytic activity is higher at high temperatures compared to low ones, while the highest activity is displayed at 90°C. This highlights another unique feature of the $\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3\text{-MAO}$ catalyst—that high-catalytic-activity and molecular-weight sPS was generated largely because of its higher stability at the polymerization temperature

than was another catalyst (such as $\text{Cp}^*\text{TiCl}_3\text{-MAO}$).³¹ However, the consequent elevation of temperature also deactivates the catalyst and enhances the acceleration of the chain-transferring reaction; therefore, the activity and the molecular weight decrease at 100°C (Run 10) or 110°C (Run 11).

As shown in Table III, under the adopted conditions, preliminary tests performed with TIBA as cocatalyst to promote the $\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3$ complex for styrene polymerization indicate the production of only trace atactic polystyrene (aPS) and no sPS. The external addition of triisobutylaluminum (TIBA) to $\text{Cp}^*\text{Ti}(\text{OC}_6\text{H}_4\text{OCH}_3)_3\text{-MAO}$ catalyst system causes an increase of catalytic ac-

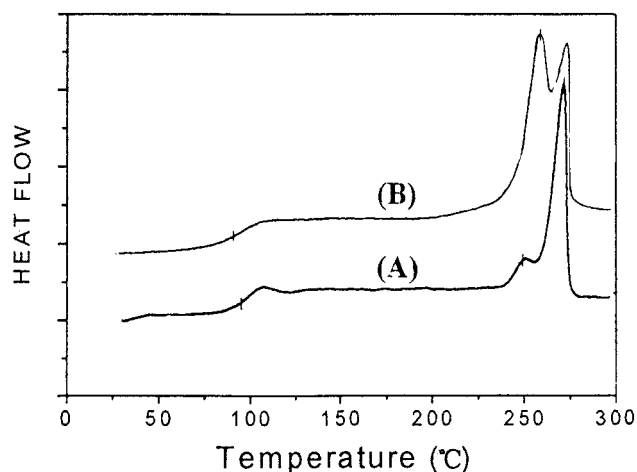


Figure 2 DSC curves of sPS samples: (a) Run 7 prepared with the bulk polymerization method; (b) Run 2 prepared in heptane medium.

Table II Influence of Temperature on Bulk Syndiospecific Polymerization of Styrene with Cp*Ti(OC₆H₄OCH₃)₃-MAO Catalyst

Run No.	Temperature (°C)	S. C. (wt %)	A × 10 ⁻⁵ (gPS/molTi h)	S. I. (wt %)	Pure sPS	
					M _v × 10 ⁻⁵	T _m (°C)
8	70	46.5	35.4	96.3	6.8	270
9	80	65.3	47.8	97.0	6.1	272
7	90	78.7	59.0	96.8	5.5	271
10	100	70.4	54.2	96.5	3.2	270
11	110	55.8	42.3	95.6	1.8	267

Polymerization condition: [Ti] = 1.2 × 10⁻⁴ mol/L, Al_{MAO}/Ti = 400 mol/mol, Al_{TIBA}/Ti = 200 mol/mol, t_p = 1 h.

tivity, compared with the system without TIBA. The activity in Run 7 is threefold higher than that in Run 13, with nearly the same syndiotactic index (SI), while the molecular weight of sPS from Run 7 is slightly lower than that from Run 13. According to our previous works,³² with the Cp*Ti(OC₆H₄OCH₃)₃-MAO catalyst the best Al:Ti molar ratio to assure higher activity is about 800 (Run 14). It is obvious that using TIBA decreases the amount of MAO to one-half, while activity is unaltered. However, the activity for the polymerization of Run 16 is lower than that of Run 7 because of an overdose of added TIBA, which causes more Ti(III) species to be reduced sequentially to Ti(II) species and the apparent chain-transferring effect of TIBA.

CONCLUSION

This article has reported on the use of a rather heat-stable novel monotitanocene catalyst composed of η⁵-pentamethylcyclopentadienyltri-4-methoxyphenoxy titanium [Cp*Ti(OC₆H₄OCH₃)₃] and

methylaluminoxane (MAO) for syndiospecific polymerization of styrene reported herein shows several unique properties compared with other catalysts. In bulk polymerization at 90°C, this catalyst exhibits the highest activity and produces a higher molecular weight of syndiotactic polystyrene. In solution polymerization, higher activity has been seen in heptane compared to toluene. Both active species were generated in a polar solvent such as chlorobenzene. One of them prepares sPS, and the other prepares atactic polystyrene because of coordination of the solvent with the Ti of Cp*Ti-MeL/MAO active species. In bulk polymerization the external addition of triisobutylaluminum (TIBA) to the catalyst system leads to a reduction of MAO dosage and enhances catalytic activity, while the syndiotacticity and molecular weight of the polymerization product are hardly influenced.

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Table III Effects of External Addition of TIBA on Styrene Bulk Polymerization with Cp*Ti(OC₆H₄OCH₃)₃-MAO Catalyst

Run No.	Al _{MAO} /Ti (mol/mol)	Al _{TIBA} /Ti (mol/mol)	S. C. (wt %)	A × 10 ⁻⁵ (gPS/molTi h)	S. I. (wt %)	M _v × 10 ⁻⁵	T _m (°C)
12	0	400	trace	trace	/	/	/
13	400	0	33.8	25.3	95.8	6.3	272
14	800	0	77.8	58.3	96.4	6.1	272
15	400	100	48.6	36.4	96.2	5.8	271
7	400	200	78.7	59.0	96.8	5.5	271
16	400	400	68.2	51.1	94.2	4.2	269

Polymerization conditions: [Ti] = 1.2 × 10⁻⁴ mol/L, T_p = 90°C, t_p = 1 h.

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