

Synthesis, Structure, and Properties of Syndiotactic Polystyrene Catalyzed by Cp*Ti(OBz)₃/MAO/TIBA

Qigu Huang, Yaping Sheng, Wantai Yang

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029

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ABSTRACT: The synthesis of syndiotactic polystyrene (sPS) catalyzed with Cp*Ti(OBz)₃/MAO/TIBA and toluene as the solvent and the effects of polymerization temperature and the external addition of TIBA on polymerization behavior were investigated. The study revealed that catalytic activity increased with polymerization temperature. The greatest activity, 619 kg sPS mol⁻¹ Ti h⁻¹, was exhibited up to 90°C. TIBA also improved catalytic activity. The molecular weight of the polymer obtained decreased with polymerization temperature and the

amount of TIBA. The structure and properties of syndiotactic polystyrene were characterized by ¹³C-NMR, FTIR, DSC, and GPC methods. It was confirmed that the sPS obtained featured all-trans planar zigzag conformation and higher syndiotacticity, molecular weight, and melting point. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 501–505, 2007

Key words: metallocene catalyst; syndiotactic polystyrene; structure

INTRODUCTION

Syndiotactic polystyrene (sPS) from abundant inexpensive monomer catalyzed with metallocene catalysts,^{1–14} compared with iPS produced by Ziegler–Natta catalyst, had a fast crystallization rate, a high degree of crystallizability, a high melting point, superior thermostability and chemical resistance, high modulus of elasticity, and excellent mechanical properties, as well as a low specific gravity and dielectric constant.

The catalytic activity of styrene polymerization increased in this order: CpTiCl₂H < Cp*TiCl₃ (Cp* = η⁵-pentamethylcyclopentadienyl) ~ CpTiCl₃ (Cp = cyclopentadienyl). Half-titanocene exhibited good stereocontrol in the syndiotactic polymerization of styrene.^{1–9,15–18} However, the activity of these catalysts in polymerization of styrene was much lower than that in polymerization of olefins. So there has been a lot of research into improving the catalytic activity as well as the stereospecificity properties of polymers. Many recent studies^{8,9,15–18,19} have demonstrated that even subtle structural modifications of a given ligand framework leads to dramatically increased catalytic activity, syndiotacticity, and molecular weight. Chien and Campbell^{20–22} also found that the catalyst CpTiCl₃ was

converted into CpTi(OMe)₃, CpTi(OEt)₃, and CpTi(OBu)₃ and that their catalytic activity and polymerization behavior showed considerable change. Chien and Salajka²² and Xu¹¹ confirmed organo-Lewis acids used as cocatalysts in cationic metallocene polymerization catalysts for styrene polymerization and investigated their polymerization mechanism, catalytic activity, and behavior. Those results showed that the polymer obtained had excellent properties and that the polymerization behavior was considerably different from that of other homogeneous catalyst systems. So any change in a component of a catalyst system could result in a dramatic difference in catalytic activity and polymerization performance. However, little work has been reported on TIBA as a cocatalyst instead of MAO partially in the catalyst system of Cp*Ti(OBz)₃. In the present work, to understand the influence of cocatalyst components on the polymerization behavior and properties of polymers obtained for further perfecting of the design of styrene syndiotactic polymerization, TIBA was added as a cocatalyst for styrene polymerization. The performance of the catalyst in the presence of MAO (solid) and TIBA and the properties of the polymer obtained were investigated.

EXPERIMENTAL

Materials

All operations of air- and moisture-sensitive materials were performed using the rigorous repellence of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line under a nitrogen atmosphere. Toluene, benzene, and *n*-hexane were fur-

Correspondence to: Q. Huang (qgh96@yahoo.com.cn).

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ther purified by refluxing over metal sodium under nitrogen for 48 h and distilled before use. Triethylamine was dried using a molecular sieve. The chemical reagents were from Yong De Chemical Reagent Co. (Tianjing, China) styrene, purchased from SINOPEC (Beijing), was treated over calcium hydride (CaH_2) for 48 h, stirred in the presence of an $\text{Al}(\text{i-Bu})_3$ solution (2.6M in *n*-hexane) for 24 h, distilled under reduced pressure, and then kept in a refrigerator under nitrogen atmosphere. The $\text{Al}(\text{i-Bu})_3$ (TIBA) solution (2.6M in *n*-hexane) was purchased from Aldrich (Milwaukee, WI). Methylaluminoxane (MAO) containing 25 mol % AlMe_3 was prepared as previously described.^{23,24}

Titanium oxidation states

The manipulations for determining titanium oxidation states [Ti(II), Ti(III), and Ti(IV)] were done as described previously.²⁵ Two redox titrations, A and B, were carried out. The Ti(II) ion was titrated as two electron-redoxing species in A, with the titer equal to $2[\text{Ti(II)}] + [\text{Ti(III)}]$. And in B the Ti(II) ion was first oxidized to the Ti(III) ion by a proton and subsequently titrated as a one-electron-reducing species. So titer B was the sum of $[\text{Ti(II)}] + [\text{Ti(III)}]$. The total Ti concentration was determined by atomic absorption. Sodium diphenylamine sulfonate was used as the indicator, and the titrimetric end point showed a sharp color change from purple to green within ± 2 drops of 0.1000N $\text{K}_2\text{Cr}_2\text{O}_7$.

Polymerization procedure

All polymerizations were carried out in a 150-mL glass reactor equipped with a magnetic stirrer. After purging all moisture and oxygen by a high-vacuum pump, the reactor was sealed under a nitrogen atmosphere. Freshly distilled toluene (20 mL), styrene (20 mL), and the desired amounts of methylaluminoxane (MAO) and TIBA were added in that order. The reactor was put in an oil bath at the selected temperature and stirred. Finally, the preactivated half-titanocene catalyst (15–20 μmol) with MAO ($\text{Al}/\text{Ti} = 200$) in toluene was syringed (preactivation time about 15 min). After a selected reaction time, the polymerization was terminated with 150 mL of 10 wt % HCl in alcohol. The polymer obtained was filtered and washed with alcohol three times, then dried overnight in a vacuum oven at 80°C. The polymer was extracted with 2-butanone at a boiling temperature for 24 h in a Soxhlet extractor to remove atactic polystyrene. The syndiotactic polystyrene was determined as the amount of polymer insoluble in boiling 2-butanone.

Characterization

^{13}C -NMR spectra were determined with INOVA500 in 1,2,4-trichlorobenzene(d_3) solvent at 130°C. The

pulse interval was 5.2 s, and the acquisition time was 0.8 s. The polymer solution was prepared by dissolving polymer in solvent up to 10 wt %. Chemical shifts were referenced using internal solvent resonance and reported related to tetramethylsilane. The average molecular weight and molecular weight distribution were measured by PL-GPC200 instrument using standard polystyrene as the reference and 1,2,4-trichlorobenzene as the solvent at 150°C. Fourier-transform infrared spectroscopy (FTIR; Bruker EQUINOX55) was used for investigating crystal types in the sPS. Spectra were obtained at a 2 cm^{-1} resolution, and averages were obtained from at least 64 scans in the standard wave number range of 500–2000 cm^{-1} . Thin films for FTIR studies were obtained by casting the sPS melting solution on a metal oven at 240°C after melting at 300°C. DSC thermograms were recorded with a Perkin-Elmer DSC-7 instrument at 10 K/min. The instrument was calibrated with an indium standard at 10°C/min. The melting temperature of the syndiotactic polystyrene (5–10 mg) was determined as the second heating scanning under a nitrogen flow of 20 cm^3/min . Elemental analyses were performed on a PE-2400 spectrometer.

RESULTS AND DISCUSSION

Synthesis of catalyst precursors

The catalyst was synthesized as described previously.^{26–28} 1,2,3,4,5-Pentamethylcyclopentadiene (12.4 mL, 79.4 mmol) was treated with a metal, K (3.1 g, 79.5 mmol) and then with trimethylchlorosilane (10.1 mL, 80.0 mmol) to form a trimethylsilyl derivative according to a convenient method. 1,2,3,4,5-Pentamethylcyclopentadienyltrichlorotitanium (Cp^*TiCl_3) was prepared by the reaction of trimethylsilyl derivative with TiCl_4 in a hexane solution. The crude product was sublimated at 115°C–120°C under vacuum to get red needle crystals, that is, Cp^*TiCl_3 (15.5 g, 68%, $^1\text{H-NMR}$: $\delta = 2.06$, s, 15H, Cp^* ; ANAL. Calcd: C, 41.59%; H, 5.19%; found: C, 41.81%; H, 5.32%). Cp^*TiCl_3 (0.81 g, 28 mmol) was esterified with benzyl alcohol (8.8 mL, 84.5 mmol) in benzene (20 mL) solution in the presence of triethylamine (1.2 mL, 84.5 mmol) at ambient temperature for 24 h to obtain the metallocene catalyst. 1,2,3,4,5-Pentamethylcyclopentadienyltribenzoyloxide-titanium, $\text{Cp}^*\text{Ti}(\text{OBz})_3$, $^1\text{H-NMR}$ (CDCl_3): δ 7.21 (s, 15H, Ph_3), 4.54 (s, 6H, O-CH_2), 1.88 (s, 15H, Cp^*). ANAL. Calcd. for $\text{Cp}^*\text{Ti}(\text{O-CH}_2-\text{Ph})_3$: C, 73.81%; H, 7.14%. Found: C, 73.40%, H, 7.25%.

Polymerization behaviors

One newly synthesized half-titanocene catalyst using methylaluminoxane (MAO solid or solution) and TIBA as cocatalysts for syndiotactic polymerization of

TABLE I
Effect of Temperature on Styrene Syndiospecific Polymerization Catalyzed by Cp*Ti(OBz)₃/MAO/TIBA

Run	T_p (°C)	Yield (g)	Activity (kg PS mol ⁻¹ Ti h ⁻¹)	SI (%)	sPS fraction	
					$M_w \times 10^{-5}$	T_m (°C)
1	70	8.12	381.6	97.8	3.11	273.2
2	80	11.63	546.6	96.7	2.96	272.8
3	90	13.17	619.0	96.1	2.57	272.3
4	100	10.89	511.8	95.1	2.13	269.5
5	110	9.27	435.7	88.6	1.82	268.1
6 ^a	90	1.78	83.5	94.3	1.56	268.5
7 ^b	90	8.63	405.6	95.0	1.33	261.8
8 ^c	90	3.18	149.5	95.1	0.91	259.3

Polymerization conditions: Al(MAO)/Ti = 200 (mol/mol), [Ti] = 5.0×10^{-4} mol/L, TIBA = 2.6×10^{-2} mol/L; solvent: 20 mL of toluene, 20 mL of styrene; time: 1 h.

^a Catalyst system, Cp*TiCl₃/MAO/TIBA.

^b Commercial solution of MAO in toluene [10% (w/v)].

^c Al(MAO)/Ti = 252 (mol/mol), commercial solution of MAO in toluene [10% (w/v)].

SI, insoluble weight in boiling 2-butanone (g)/total weight (g).

styrene was investigated. The catalytic activity of the catalyst and the properties of the polymer obtained are compiled in Table I, which shows that for the Cp*Ti(OBz)₃/MAO/TIBA catalyst system, the catalytic activity of styrene polymerization increased with polymerization temperature, T_p . The highest catalytic activity, 619.0 kg sPS mol⁻¹ Ti h⁻¹, was obtained up to 90°C. Further enhancing T_p to 110°C, a small reduction in catalytic activity and syndiotacticity of polystyrene obtained were observed. On the other hand, the molecular weight (M_w) of the polymer obtained decreased with increasing polymerization temperature. This was because the average molecular weight of polymer was predominantly decided by the Kp/Ktr ratio, where Kp increased with temperatures below Ktr, which results in the decreasing of M_w as temperature increased. It was very remarkable that this catalyst system resulted in a high molecular weight of $M_w = 2.57 \times 10^5$, high syndiotacticity of 96.1%, and a melting point temperature of 272.3°C, even at polymerization temperatures as high as 90°C, which indicates that the complex was extremely stable, compared to those reported in the literature.^{8,9}

The titanocene complex, which had phenyl ring ligands and used MAO/TIBA as a cocatalyst, exhibited much higher catalytic activity than complexes without phenyl ring ligands (runs 3 and 6 in Table I). This discovery indicates that the presence of a phenyl ring ligand moiety met the electronic coordination requirements for high activity. In addition, because of the charge of active site of the complex could be effectively delocalized over all the phenyl rings, electron donation and resonance stabilization increased from phenyl ring substituents would stabilize the active species and make a monomer styrene with a high order to access the coordination site more easily, which increased the number of active species or made it have a longer life. Therefore, overall activity was

enhanced. The high molecular weight of syndiotactic polystyrene thus obtained could mainly have been a result of the electron effect caused by the presence of the electron-releasing Cp* and phenyl ring moiety, resulting in an increase in electron density at the metal center and also at the β -carbon. Consequently, the β -hydrogen elimination and chain transfer to monomer reactions would be diminished during the course of polymerization.²⁶⁻²⁸ On the other hand, the phenyl ring substituent in the complex might have made the titanium center diminish detrimental β -agostic interactions during propagation.²⁹ This steric advantage made monomer styrene insertion relative to chain termination mainly by β -hydrogen elimination or sterically stabilize the active species. We studied the kinetics of styrene polymerization catalyzed by the half-titanocenes examined.³⁰ It was found that complexes with ligands of phenyl ring substituents were more stable and had higher catalytic activity than did complexes with no phenyl ring substituents.

The relationship between polymerization behavior and details of the ligand structure of titanocene was also observed in the melting temperature and molecular weight of the polymers thus obtained, which revealed the stereospecificity and typical chain propagation/chain termination ratios of this titanocene. Table I also shows that all the melting points and syndiotacticity of the polymers obtained with the catalyst system were higher. The melting point ranged from 268.1°C to 273.2°C and syndiotacticity from 88.6% to 97.8%, suggesting that the aromatic ring substituent titanocene catalyst activated by MAO and TIBA did not bring about regioerrors or stereoerrors of monomer insertion. On the other hand, for this titanocene, a high rate of propagation was almost associated with an increased molar mass of the polymers thus obtained. It seemed that improved control over the rates of both chain propagation (R_p) and chain termi-

TABLE II
Effects of TIBA on Syndiospecific Polymerization of Styrene
with Cp*Ti(OBz)₃/MAO/TIBA

Run	TIBA ($\times 10^{-2}$ M)	Activity (kg PS mol ⁻¹ Ti h ⁻¹)	SI (%)	[Ti(III)] ^a (mol %)	sPS fraction	
					$M_w \times 10^{-5}$	T_m (°C)
9	0	trace	—	19.3		
10	1.3	385.6	92.8	47.6	2.83	271.2
3	2.6	619.0	96.1	71.2	2.57	272.3
11	5.2	474.8	94.3	68.7	1.76	266.1
12 ^b	0	trace	—	16.6		

Polymerization conditions: Al(MAO)/Ti = 200 (mol/mol), [Ti] = 5.0×10^{-4} mol/L; solvent: toluene 20 mL, styrene 20 mL; time: 1 h.

^a Ti(III) fraction (mol)/total Ti [Ti(II), Ti(III), and Ti(IV)] (mol); SI, insoluble weight in boiling 2-butanone (g)/total weight (g).

^b Commercial solution of MAO in toluene [10 % (w/v)], Al(MAO)/Ti = 200 (mol/mol).

nation or chain transfer (R_T or R_{tr}) could become true by designing the ligand structure of metallocene catalysts. However, a commercial solution of MAO was used as cocatalyst, instead of solid MAO, and so catalytic activity was obviously decreased (runs 8 and 9 in Table I). It was possible that the ligands, OBz, of the complex, were substituted by alkyl, which resulted in complexes with no phenyl ring ligands.

From Table II it can be seen that the catalytic activity depended on the concentration of TIBA when the amount of MAO was not changed [Al(MAO)/Ti = 200 mol/mol]. The highest activity, 619.0 kg sPS mol⁻¹ Ti h⁻¹, was shown at a TIBA concentration of 2.6×10^{-2} M, at which the Ti(III) fraction was highest, 71.2 mol % of the total Ti concentration. Ti(III) favors styrene polymerization.⁸ However, when no TIBA was added, the Ti(III) fraction was lowest, 19.3 mol %, which led to much lower catalytic activity (run 9 in Table II). Only a trace amount of polymer was observed. We also found that an overabundant amount of TIBA resulted in decreasing catalytic activity and Ti(III) fraction. When the amount of TIBA was as high as 5.2×10^{-2} M, the catalytic activity and Ti(III) fraction decreased to 474.8 kg PS mol⁻¹ Ti h⁻¹ and 68.7 mol %, respectively (run 11 in Table II). In addition, when a commercial solution of MAO was used as cocatalyst at the same Al/Ti mole ratio, very low catalytic activity was shown, only trace polymer was obtained. This catalyst system was interesting for industrial uses because of its high catalytic activity at a fairly low Al(MAO)/Ti ratio of 200, which would result in lower production costs. But the molecular weights of all the polymers thus obtained obviously changed with an increasing amount of TIBA (runs 10, 3, and 11 in Table II). The results suggested that TIBA acts as a chain transfer agent to some extent.

Characterization and properties of sPS

The stereostructure of the polymer insoluble in 2-butanone was determined by ¹³C-NMR (Fig. 1). The

presence of a sharp single signal for the quaternary C carbon in the phenyl ring at $\delta = 145.2$ ppm showed that the polymer was highly syndiotactic.¹ The other two singlets of phenyl ring were at $\delta = 125.6$ and 127.8 ppm. Two sharp peaks at $\delta = 43.93$ and 40.62 ppm were attributed to methylene and methine carbon, respectively, in the backbone chain.

Infrared spectra of syndiotactic polystyrene–cast film annealed at 240°C from an sPS melting solution at 300°C were studied. One signal was observed at 1222 cm⁻¹, assigned to the all-*trans* planar zigzag conformation.^{31,32}

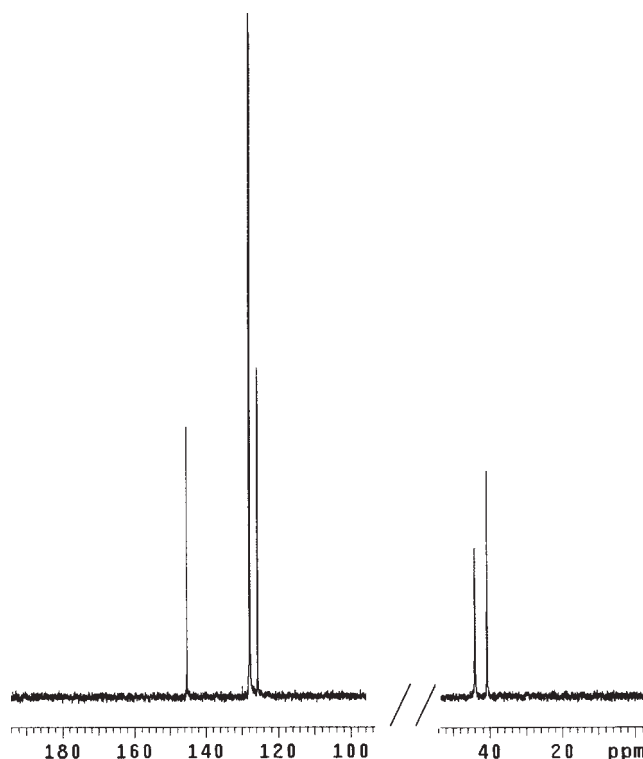


Figure 1 ¹³C-NMR spectrum of syndiopolystyrene of boiling 2-butanone-insoluble fraction from run 3 in Table I.

CONCLUSIONS

A novel syndiotactic polystyrene featuring high molecular weight, melting point, and syndiotacticity by a simply structured half-titanocene catalyst, Cp*Ti(OCH₂-C₆H₅)₃, with MAO and TIBA as cocatalysts was obtained. The catalyst system showed the highest catalytic activity, 619 kg sPS/mol⁻¹ Ti h⁻¹, under typical conditions. The polymer obtained even with a polymerization temperature as high as 90°C featured an all-*trans* planar zigzag conformation and a higher melting point, 272.3°C.

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