Macromolecules **1993,** *26,* 6664-6666

Polymerization of Styrene with the TiCl$_3$/Methylaluminoxane Catalyst System

Marcos Lopes Dias,[†] Antonino Giarrusso, and Lido Porri*

Dipartimento di Chimica Industriale e Ingegneria Chimica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

Received July 8, 1993
Revised Manuscript Received September 13, 1993

Introduction

The polymerization of styrene with catalyst systems derived from methylaluminoxanes (MAO) and soluble transition-metal compounds produces polystyrene with different stereochemical structures. Syndiotactic (sPS),[1-9] isotactic (iPS),[10] and atactic polystyrene (aPS)[5] have been obtained using different catalyst systems. Soluble Ti compounds (e.g., (η^5-C$_5$H$_5$)TiCl$_3$, Ti(OR)$_4$) give, in combination with MAO, highly syndiotactic PS. TiCl$_3$ (violet modification) has also been used, in combination with MAO, but different results have been reported: isotactic PS was obtained using aluminum activated (AA) TiCl$_3$,[11] while a mixture of isotactic and syndiotactic PS was obtained using δ-TiCl$_3$.[7] In order to clarify this problem, we have examined the polymerization of styrene with catalysts derived from AA TiCl$_3$, from hydrogen-activated (HA) TiCl$_3$, and from the soluble complex TiCl$_3$·3THF, respectively. We present in this paper the results of our investigations.

Experimental Section

All the operations were carried out under dry argon. Toluene, used as the polymerization solvent, was dried by refluxing over potassium-benzophenone for 8 h, then distilled, and stored over molecular sieves. Styrene (Aldrich, 99%+) was distilled over CaH$_2$ immediately before use. HA TiCl$_3$ and AA TiCl$_3$ were supplied by Enichem Polimeri. TiCl$_3$·3THF was prepared by extracting HA TiCl$_3$ with boiling THF.[12] MAO (Schering, 30 wt % solution in toluene) was used as received. CpTiCl$_3$ (Aldrich, 97%) was purified by vacuum sublimation, and Ti(O-nBu)$_4$ (Aldrich, 99%) was distilled under vacuum. CpTiCl$_2$·2THF was prepared according to the literature.[13]

The polymerizations were carried out in a 100-mL glass cylindrical reactor. Toluene and MAO were first introduced, and then the Ti compound, as a solution or suspension in toluene, was added under stirring; the mixture was brought to the polymerization temperature, and then styrene was introduced. The polymerization was terminated with CH$_3$OH, and the polymer was coagulated with an excess of methanol containing aqueous HCl, thoroughly washed with pure CH$_3$OH, and then dried under vacuum, at room temperature.

In one run, MAO (12.5 mL, 21.3 mmol) and AA TiCl$_3$ (16 mg, 0.082 mmol) were reacted for 30 min in toluene (10 mL) under stirring, and then the suspension was filtered through a glass filter into the reactor containing styrene (10 mL). In another run the solid phase of the suspension prepared as above was separated by decantation and washed with toluene. Fresh toluene (10 mL) and styrene (10 mL) were then added.

The crude polymerization products were fractionated with boiling acetone in a Kumagava extractor, for 12 h, to remove the amorphous fraction. ^{13}C NMR spectra were recorded on a Bruker AM-200 instrument operating at 50.32-MHz frequency, using *o*-dichlorobenzene (85 °C) as solvent, or on a Bruker AM-270 instrument operating at 67.93 MHz, using CDCl$_3$ as solvent (room temperature) and TMS as internal standard. DSC analyses were made with a Mettler TA 3000 system; curves were recorded on a heating scan at 10 K/min. Intrinsic viscosities were determined in tetralin at 100 °C using a Desreux-Bishof viscometer.

Table I. Polymerization of Styrene with TiCl$_3$/MAO[a]

	TiCl$_3$[b]			polymer[c]	
run	type	mmol	MAO (mmol)	yield (g)	T_m (°C)[d]
1	AA	0.082	3.06	0.24	216, 267
2	AA	0.082	21.3	0.38	263
3	HA	0.1	3.06	0.22	
4	HA	0.1	21.3	0.24	259
5	AA	0.082[e]	21.3	0.44	270
6	AA	0.082[f]	21.3	0.01	221

[a] Polymerization conditions: styrene, 10 mL (87.4 mmol); solvent, toluene, runs 1–4, 40 mL, run 5, 20 mL, run 6, 10 mL; 20 h, room temperature. [b] TiCl$_3$ content of AA TiCl$_3$ was calculated on the basis of the formula 3TiCl$_3$·1AlCl$_3$. [c] Crude polymerization product. [d] Determined by DSC. [e] The filtered solution of the MAO/AA TiCl$_3$ suspension was used (see the Experimental Section). [f] The solid phase of the MAO/AA TiCl$_3$ suspension was used (see the Experimental Section).

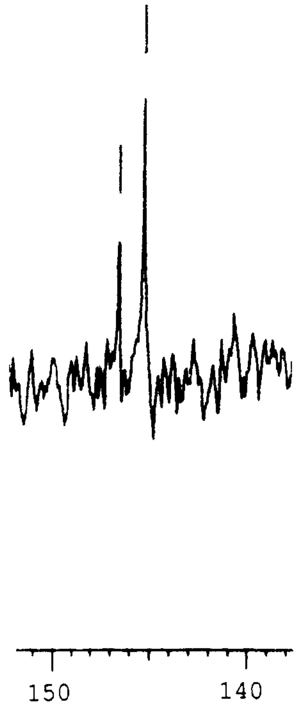

Figure 1. Aromatic C1 region of the ^{13}C NMR spectrum of polystyrene obtained with MAO/TiCl$_3$ at an Al/Ti molar ratio of 270 (*o*-dichlorobenzene + 10% C$_6$D$_6$; 85 °C; δ in ppm from TMS).

Results and Discussion

Some results of polymerization runs carried out with MAO/AA TiCl$_3$ and MAO/HA TiCl$_3$, at different Al/Ti molar ratios, are reported in Table I. DSC curves of the polymers obtained at an Al/Ti ratio of ca. 40 (acetone-insoluble fraction) showed the presence of two endothermic peaks, one at 210–220 °C, corresponding to the melting point of iPS, and the other at 260–270 °C, corresponding to the melting point of sPS. The peak at 210–220 °C was much less intense in the polymers obtained at an Al/Ti ratio of ca. 270.

DSC data are consistent with the ^{13}C NMR spectra (*o*-dichlorobenzene + 10% C$_6$D$_6$, 85 °C) which show two rather broad peaks in the aromatic C1 region, at 145.2 and 146.5 ppm (δ from TMS), which are typical of syndiotactic and isotactic sequences, respectively.[1] The broadness of the two peaks is indicative of the presence of aPS (Figure 1).

[†] On leave from the Instituto de Macromoleculas, Universitade Federal do Rio De Janeiro.

0024-9297/93/2226-6664$04.00/0

Table II. Polymerization of Styrene with Soluble Ti Catalysts[a]

run	Ti compd type	Ti compd μmol	MAO (mmol)	temp (°C)	time (h)	yield (g)	polymer insoluble fraction[b] %	polymer insoluble fraction[b] T_m (°C)[c]	polymer insoluble fraction[b] [η] (dL/g)
1	$TiCl_3 \cdot 3THF$	7	7	50	1	0.13		269.8	0.44
2	$TiCl_3 \cdot 3THF$	20	10.0	50	1.5	0.27	88		
3	$TiCl_3 \cdot 3THF$	25	12.5	rt	20	0.65	83		
4	$TiCl_3 \cdot 3THF$	20	10	rt	24	0.75			
5	$CpTiCl_3$	3	3	50	1	0.98	95	259.9	0.29
6	$CpTiCl_3$	3.3	3.1	0	2	0.25		267.8	0.51
7	$CpTiCl_2 \cdot THF$	3	3.1	50	1	0.80	80	257.9	0.34

[a] Polymerization conditions: styrene, 5 mL (run 3, 10 mL); solvent, toluene, 20 mL (run 3, 40 mL; runs 2 and 4, 10 mL). [b] Residue to acetone extraction. [c] Determined by DSC.

In conclusion, $TiCl_3$/MAO was found to give a mixture of aPS, iPS, and sPS, with the proportion of sPS increasing with the Al/Ti ratio.

In other runs, MAO was reacted with AA $TiCl_3$ in toluene for about 30 min and then the suspension was filtered or decanted to separate the liquid from the solid phase (see the Experimental Section). Both the liquid and the solid phase polymerized styrene, giving products consisting of a fraction soluble in boiling acetone (amorphous PS) and an acetone-insoluble fraction, crystalline by X-ray. The ^{13}C NMR spectrum (Figure 2) of the crystalline fraction of the polymer obtained with the homogeneous catalyst shows a peak at 145.2 ppm (δ from TMS), typical of syndiotactic sequences, while that of the polymer obtained with the heterogeneous catalyst shows a peak at 146.3 ppm, typical of isotactic sequences.

These results indicate that the crystals of $TiCl_3$ are partially solubilized on reaction with MAO, to give a soluble catalytic species that polymerizes styrene to sPS. The amount of $TiCl_3$ that goes into solution likely depends on the amount of MAO and probably also on the size of the $TiCl_3$ crystals.

A more convenient method to obtain a soluble catalyst from $TiCl_3$ is to use the complex $TiCl_3 \cdot 3THF$ in combination with MAO. This system (Table II) gives a product consisting of sPS, along with minor amounts (ca. 15%) of amorphous polymer. The activity of MAO/$TiCl_3 \cdot 3THF$ is lower than that of $CpTiCl_3$/MAO or $CpTiCl_2 \cdot 2THF$/MAO (Table II) but is comparable with that of other Ti systems reported in the literature, e.g., $Ti(O\text{-}nBu)_4$/MAO[6,7] and $Ti(benzyl)_4$/MAO.[2] The main reason for the different activity of the various soluble Ti catalyst systems is probably the fact that a different percentage of Ti is active in each system; it has been reported that this is the case for $CpTi(OR)_3$/MAO and $Ti(benzyl)_4$/MAO.[8]

Styrene has recently been polymerized[14] with heterogeneous catalysts based on $Ti(OR)_4$ deposited on different supports: $Mg(OH)_2$, Mg(OH)Cl, or $MgCl_2$. Isotactic PS has been obtained using Mg(OH)Cl or $MgCl_2$, while atactic PS was obtained using $Mg(OH)_2$. In light of the results of this paper, the formation of isotactic PS with chlorine-containing supports may be attributed to the formation of $TiCl_3$ as a result of ligand exchange between $Ti(OR)_4$ and the support and subsequent reaction with MAO.

Conclusions

(1) Crystalline $TiCl_3$ gives, on reaction with MAO in toluene, two types of catalyst systems: a soluble one, which polymerizes styrene to syndiotactic polymer, and an insoluble one, which polymerizes styrene to isotactic polymer.

(2) A soluble catalyst for the syndiotactic polymerization of styrene can be obtained from $TiCl_3 \cdot 3THF$ and MAO. The fact that catalysts for sPS can be obtained from different Ti compounds ($TiCl_3$, $Ti(OR)_4$, $CpTi(OR)_3$,

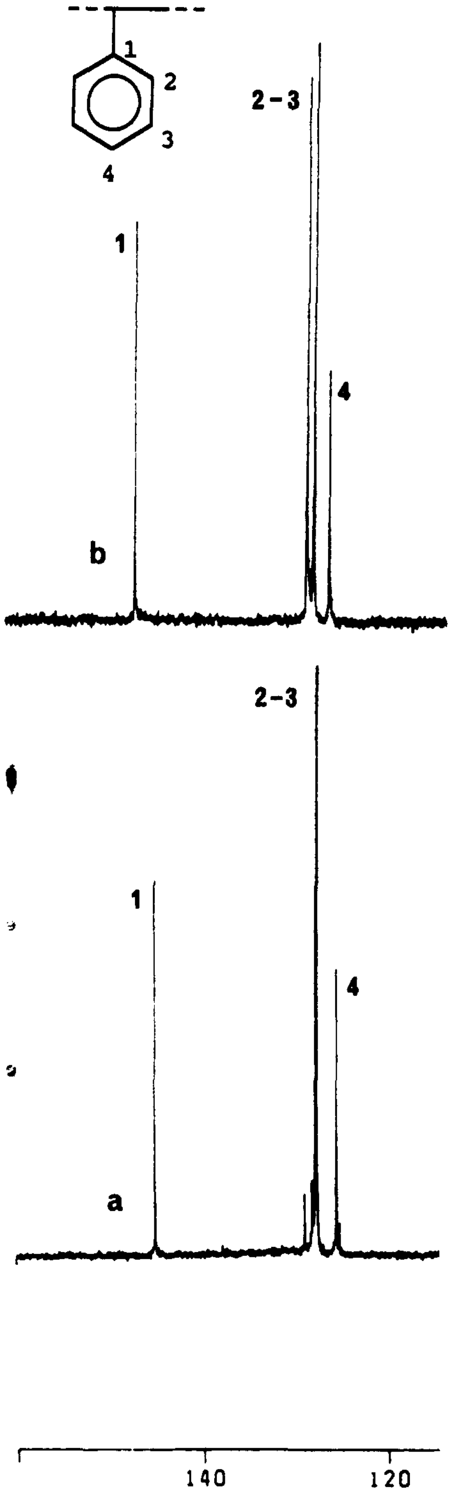

Figure 2. Aromatic region of the ^{13}C NMR spectrum of polystyrene obtained with MAO/$TiCl_3$ at an Al/Ti molar ratio of 270: (a) soluble catalyst, (b) insoluble catalyst ($CDCl_3$; 25 °C; δ in ppm from TMS).

$CpTiCl_3$, $CpTiCl_2$) indicates that the type of anionic ligand bonded to Ti does not have a determining influence on the stereospecificity.

Acknowledgment. This work has been carried out with the financial support of Consiglio Nazionale delle Ricerche, "Programma Finalizzato Chimica Fine II", and of Ministero Università e Ricerca Scientifica e Tecnologica, Rome, Italy. We thank the Conselho Nacional de Desenvolvimento Cientifico e Technologico (CNPq) of Brazil for a fellowship to M.L.D.

References and Notes

(1) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464.
(2) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277.
(3) Ammendola, P.; Pellecchia, C.; Longo, P.; Zambelli, A. *Gazz. Chim. Ital.* **1987**, *117*, 65.
(4) Grassi, A.; Pellecchia, C.: Longo, P.; Zambelli, A. *Gazz. Chim. Ital.* **1987**, *117*, 249.
(5) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356.
(6) Zambelli, A.; Oliva, L.; Pellecchia, C. *Macromolecules* **1989**, *22*, 2129.
(7) Zambelli, A.; Pellecchia, C.; Oliva, L.; Longo, P.; Grassi, A. *Makromol. Chem.* **1991**, *192*, 223.
(8) Chien, J. C. W.; Salajka, Z. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1243, 1253.
(9) Chien, J. C. W.; Salajka, Z.; Dong, S. *Macromolecules* **1992**, *25*, 3199.
(10) Longo, P.; Grassi, A.; Oliva, L.; Ammendola, P. *Makromol. Chem.* **1990**, *191*, 237.
(11) Mani, R.; Burns, C. M. *Macromolecules* **1991**, *24*, 5476.
(12) Clark, R. J. H.; Lewis, J.; Machin, D. J.; Nyholm, R. S. *J. Chem. Soc.* **1963**, 379.
(13) Lucas, C. R.; Green, M. L. H. *Inorg. Synth.* **1976**, XVI, 238.
(14) Soga, K.; Monoi, T. *Macromolecules* **1990**, *23*, 1560.