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Styrene Polymerization Behavior of Phenoxy−Imine Ligated Ti Complexes/MAO: Formation of Highly Isotactic and Syndiotactic PS

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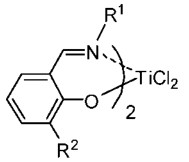
ABSTRACT: Unique styrene polymerization behavior of bis(phenoxy−imine) Ti complexes (Ti−FI catalysts) combined with dried MAO (DMAO) was revealed. Upon activation with DMAO at 20 °C, non-fluorinated Ti−FI catalysts **1** and **2** produce highly syndiotactic polystyrene (sPS, T_m 275 °C (**1**), 279 °C (**2**)), whereas fluorinated Ti−FI catalysts **3** and **4** form highly isotactic PS (iPS, T_m 224 °C (**3**), 213 °C (**4**)). Interestingly, the fluorinated Ti−FI catalysts can produce an iPS/sPS mixture by varying polymerization conditions.

Study of the synthesis of stereoregular polymers of olefinic monomers yields useful information about catalysis and mechanisms for polymerization. For polystyrene (PS), researchers at Idemitsu reported on the first synthesis of highly syndiotactic PS (sPS) (T_m ca. 265 °C) using $CpTiCl_3$/methylaluminoxane (MAO) in the mid-1980s.[1] This report has stimulated extensive investigations into molecular catalysts for sPS, resulting in the introduction of a number of high-performance catalysts.[2,3] The syndiospecific polymerizations are normally promoted by Ti(III) species via a chain-end control mechanism. As for isotactic PS (iPS), while some 50 years ago Natta prepared this polymer (T_m ca. 230 °C) using a heterogeneous catalyst, the development of molecular catalysts for iPS was slower and first reported in 1998. Thus, the catalysts for iPS are still limited to only a few examples,[4] all of which possess a bridged ligand framework and C_2 symmetry, capable of mediating isospecific polymerization via a site-control mechanism.

In our own work, we have developed bis(phenoxy−imine) group 4 transition metal complexes (now known as FI catalysts), for the controlled (co)polymerization of olefinic monomers, as a result of ligand oriented catalyst design.[5] FI catalysts with appropriate activators display unique and versatile polymerization catalysis, including highly syndiospecific (living) propylene polymerizations with Ti−FI catalysts despite their C_2 symmetric nature.[6,7] The syndiospecific polymerizations proceed via a chain-end control mechanism featuring unusual 2,1-insertion though syndioselectivity is evidently governed by the ligand structures.[7,8] Well-established experimental results together with theoretical calculations suggest a mechanism which involves chiral site inversion driven by a stereocenter at α-carbon of the growing polymer chain.[8] These unique propylene polymerization characteristics have motivated us to examine the polymerization of styrene with Ti−FI catalysts.

Styrene polymerizations using four Ti−FI catalysts, complexes **1**−**4** (Figure 1),[8b,c] combined with dried MAO (DMAO) revealed marked differences in polymerization behavior between non-fluorinated and fluorinated versions (Table 1). Non-fluorinated complexes **1** and **2** gave high molecular weight crystalline PS that is insoluble in methyl ethyl ketone (MEK), with moderate activity. We confirmed that the MEK-soluble part (atactic PS) was made with DMAO. ^{1}H and ^{13}C NMR analyses along with T_ms (275 and 279 °C) demonstrated the production of highly syndiotactic PS (entries 1−3). No iPS formation was indicated by the NMR analyses. Conversely, fluorinated complexes **3** and **4** afforded lower molecular weight crystalline PS that is insoluble in MEK, with much higher activity (entries 4−6). To our surprise, the PS formed with these complexes exhibited T_ms ranging from 213 to 224 °C, indicative of the formation of iPS. ^{1}H and ^{13}C NMR analyses confirmed that the PS is indeed isotactic (Figure 2).



complex	R^1	R^2
1	C_6H_5	^{t}Bu
2	C_6H_5	$SiMe_3$
3	C_6F_5	^{t}Bu
4	C_6F_5	$SiMe_3$

Figure 1. Ti−FI catalysts employed in this study.

Table 1. Styrene Polymerization with Complexes 1−4/DMAO[a,b]

entry	complex	A^c	$M_n{}^d$ ($\times 10^3$)	$M_w/M_n{}^d$	$T_m{}^e$ (°C)	tacticity^f
1	**1**	0.56	215	7.5	275	syn
2	**1**^{g}	0.12	779	2.4	275	syn
3	**2**	0.64	132	9.0	279	syn
4	**3**	5.21	10	4.4	224	iso
5	**4**	10.15	8	2.3	213	iso
6	**4**^{g}	1.37	10	2.4	217	iso

[a] Conditions: toluene 30 mL, styrene 100 mL, Ti 0.2 mmol, DMAO 50 mmol as Al, 20 °C, 60 min. [b] Results are based on MEK-insoluble polymers. [c] In g of polymer/(mmol of Ti·h). [d] Determined by GPC using PS calibration. [e] Determined by DSC. [f] Determined by ^{13}C NMR (syn, syndiotactic; iso, isotactic). [g] 0 °C, 360 min.

Although the iPS obtained with **3** (entry 4) showed a somewhat broadened molecular weight distribution, the iPS produced with **4** displayed a unimodal molecular weight distribution (M_w/M_n 2.3, 2.4) in a manner consistent with single-site catalysis. It should be noted that complexes **3** and **4** are not merely a notable addition to the limited list of molecular catalysts for iPS, but also the first examples of a catalyst with a nonbridged ligand that polymerizes styrene in an isospecific fashion.

^{13}C NMR analyses for the sPS (entries 1 and 3) and iPS (entries 4 and 5) indicated virtually perfect tacticity, which made

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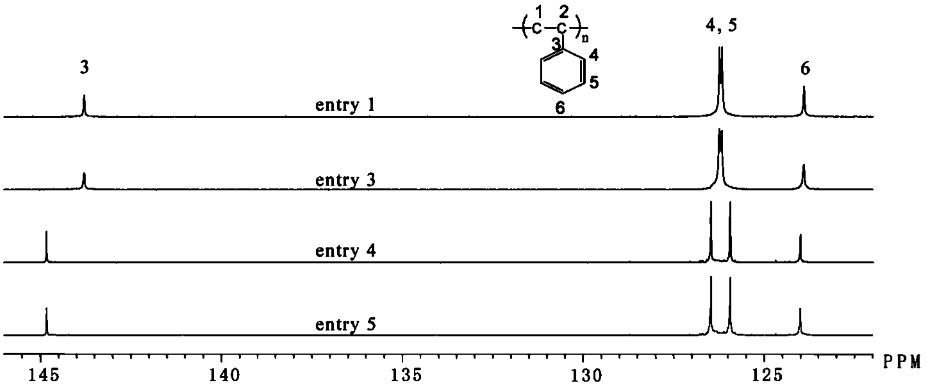

Figure 2. ^{13}C NMR spectra of the aromatic region for the PS obtained with complexes **1**−**4**/DMAO (Table 1).

Table 2. Styrene Polymerizations Using Complexes 1 and 4 with DMAO under Various Conditions[a,b]

entry	complex	premix (min)	T (°C)	A[c]	M_n[d] (×10^3)	M_w/M_n[d]	T_m[e] (°C)	iPS/sPS[f]
7	**1**	0	20	0.17	[g]	[g]	269	[g]
8	**1**	0	40	0.22	100	6.9	271	0/100
9	**1**	13	40	13.26	109	2.9	271	0/100
10	**1**	13	60	16.04	101	2.9	271	0/100
11	**4**	0	20	1.76	13[h]	1.5[h]	220[i]	99/1
12	**4**	0	40	2.65	564/14[j]	2.1/2.0[j]	216/268	47/53
13	**4**	13	40	17.20	117	2.8	270	0/100
14	**4**	13	60	29.57	97	3.1	271	0/100

[a] Conditions: toluene 10 mL, styrene 20 mL, Ti 0.02 mmol, DMAO 5 mmol as Al, 60 min. [b] Results are based on MEK-insoluble polymers. [c] In g of polymer/(mmol of Ti·h). [d] Determined by GPC using PS calibration. [e] Determined by DSC. [f] Determined by ^{1}H NMR. [g] Polymer yield was insufficient for characterization. [h] A small peak (M_n 2050 × 10^3, M_w/M_n 1.7) was also observed. [i] A very small peak was observed at 269 °C. [j] The GPC trace was bimodal.

it impracticable to discuss stereoregulating mechanisms based on stereoerrors. Hence, an sPS sample with a higher portion of stereoerrors was prepared with **1**/DMAO at a higher temperature of 80 °C. Microstructural analysis of the sPS using ^{13}C NMR suggested the operation of a chain-end control mechanism,[9] which is generally accepted for styrene polymerizations with CpTiX$_3$.[2,10] Unfortunately, regiochemistry and the stereoregulating mechanism for the iPS could not be determined because stereoerrors and chain-end structures were below the NMR detection level.[11]

To gain insight into the marked differences observed between the fluorinated and the non-fluorinated complexes, styrene polymerizations with complexes **1** and **4** were performed under various conditions (Table 2).

In the case of **1**/DMAO, raising polymerization temperature to 40 °C led to a small activity increase (entry 8). With the intention of expediting the activation process, complex **1** was treated with DMAO at 20 °C prior to a polymerization reaction (premix procedure), resulting in a dramatic activity increase for sPS formation (entries 9 and 10). Alternatively, while complex **4** practically gave iPS at 20 °C (entry 11), at 40 °C **4** formed an iPS/sPS mixture at a ratio of 47/53, which was indicated by ^{1}H NMR (entry 12). The PS arising from **4** at 40 °C displayed two discrete T_ms at 216 and 268 °C. Additionally, the GPC trace showed conspicuous bimodal peaks, and each peak is consistent with single-site catalysis (M_w/M_n ca. 2). The ratio of iPS/sPS can be varied by polymerization conditions. Surprisingly, with the premix procedure, complex **4** at 40 and 60 °C exclusively yielded sPS (entries 13 and 14).

All the observations described above are consistent with the proposal that iPS and sPS were produced with two distinctive active species generated from a single catalyst precursor, i.e., complex **4**.

We previously described that, upon activation with DMAO, complex **3** formed a cationic methyl Ti(IV) species (L$_2$TiMe$^+$, L: FI ligand) and that the cationic species slowly decomposed to LAlMe$_2$ (inactive toward styrene polymerization) and an NMR silent compound(s), which is most likely a paramagnetic Ti(III) species.[12] This particular decomposition pathway was also demonstrated for complexes **1** and **4**, suggesting that such decomposition is common for Ti−FI catalysts.[9] Therefore, under the higher polymerization temperatures and/or premix conditions, the Ti(IV) species is probably transformed to the Ti(III) species, which is active for syndiospecific styrene polymerization as is the case for most of the reported catalysts for sPS.[2,10,13]

Altogether, it would be reasonable to attribute the isospecific styrene polymerization to the C_2 symmetric cationic Ti(IV) species and the syndiospecific polymerization to the assumed Ti(III) species. The inactivity of non-fluorinated Ti(IV) species derived from complexes **1** and **2** toward styrene probably stems from their less electrophilic nature compared to those originating from fluorinated complexes **3** and **4**.[5]

Judging from the polymerization results described so far, the proposed site inversion between Δ and Λ for propylene polymerization seems not to take place for styrene polymerization with complexes **3** and **4** combined with DMAO.[7,8] Considering that the site inversion for propylene polymerization with fluorinated Ti−FI catalysts is promoted by the presence of a secondary polypropylene growing chain, styrene polymerization with fluorinated Ti−FI catalysts presumably proceeds via a 1,2-insertion.[7] Indeed, our preliminary DFT calculations suggested that catalytically active species stemming from complex **3** may favor 1,2-insertion.[9] On the basis of the results described above, we believe that the isospecific styrene polymerization with fluorinated Ti−FI catalysts **3** and **4** proceeded via a site-control mechanism with 1,2-insertion without the site-inversion process. Further studies, including a more detailed mechanistic investigation, are underway.

In summary, the pronounced effects of phenoxy−imine ligand structures on styrene polymerization behavior of Ti−FI catalysts have herein been revealed. It is highly significant that the fluorinated Ti−FI catalyst selectively produces both iPS and sPS. The catalyst can form an iPS/sPS mixture by varying polymerization conditions.

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Supporting Information Available: Experimental details, including NMR spectra of PSs, ^{1}H NMR spectra of complexes **1**

and **4**/DMAO, and DFT calculation results. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464.

(2) For a review: Schellenberg, J.; Tomotsu, N. *Prog. Polym. Sci.* **2002**, *27*, 1925.

(3) (a) Kirillov, E.; Lehmann, C. W.; Razavi, A.; Carpentier, J.-F. *J. Am. Chem. Soc.* **2004**, *126*, 12240. (b) Luo, Y.; Baldamus, J.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 13910. (c) Pellecchia, C.; Pappalardo, D.; Oliva, L.; Zambelli, A. *J. Am. Chem. Soc.* **1995**, *117*, 6593.

(4) (a) Beckerle, K.; Manivannan, R.; Lian, B.; Meppelder, G.-J. M.; Raabe, G.; Spaniol, T. P.; Ebeling, H.; Pelascini, F.; Mülhaupt, R.; Okuda, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 4790. (b) Capacchione, C.; Proto, A.; Ebeling, H.; Mülhaupt, R.; Möller, K.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964. (c) Arai, T.; Ohtsu, T.; Suzuki, S. *Macromol. Rapid Commun.* **1998**, *19*, 327. (d) Caporaso, L.; Izzo, L.; Sisti, I.; Oliva, L. *Macromolecules* **2002**, *35*, 4866. (e) Izzo, L.; Napoli, M.; Oliva, L. *Macromolecules* **2003**, *36*, 9340. (f) Rodrigues, A.-S.; Kirillov, E.; Roisnel, T.; Razavi, A.; Vuillemin, B.; Carpentier, J.-F. *Angew. Chem., Int. Ed.* **2007**, *46*, 7240.

(5) For reviews: (a) Matsugi, T.; Fujita, T. *Chem. Soc. Rev.* **2008**, *37*, 1264. (b) Mitani, M.; Saito, J.; Ishii, S.; Nakayama, Y.; Makio, H.; Matsukawa, N.; Matsui, S.; Mohri, J.; Furuyama, R.; Terao, H.; Bando, H.; Tanaka, H.; Fujita, T. *Chem. Rec.* **2004**, *4*, 137.

(6) For the first report on syndiospecific propylene polymerization, living ethylene and propylene polymerizations with bis(phenoxy−imine) Ti complexes: Mitani, M.; Yoshida, Y.; Mohri, J.; Tsuru, K.; Ishii, S.; Kojoh, S.; Matsugi, T.; Saito, J.; Matsukawa, N.; Matsui, S.; Nakano, T.; Tanaka, H.; Kashiwa, N.; Fujita, T. WO Patent 01/55231, Jan 26, 2000.

(7) (a) Makio, H.; Fujita, T. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 52. (b) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30. (c) Sakuma, A.; Weiser, M.-S.; Fujita, T. *Polym. J.* **2007**, *39*, 193. (d) Corradini, P.; Guerra, G.; Cavallo, L. *Acc. Chem. Res.* **2004**, *37*, 231. (e) Talarico, G.; Busico, V.; Cavallo, L. *J. Am. Chem. Soc.* **2003**, *125*, 7172.

(8) (a) Milano, G.; Cavallo, L.; Guerra, G. *J. Am. Chem. Soc.* **2002**, *124*, 13368. (b) Furuyama, R.; Saito, J.; Ishii, S.; Mitani, M.; Matsui, S.; Tohi, Y.; Makio, H.; Matsukawa, N.; Tanaka, H.; Fujita, T. *J. Mol. Catal. A* **2003**, *200*, 31. (c) Mitani, M.; Furuyama, R.; Mohri, J.; Saito, J.; Ishii, S.; Terao, H.; Nakano, T.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc.* **2003**, *125*, 4293.

(9) See Supporting Information for more details.

(10) Pellecchia, C.; Grassi, A. *Top. Catal.* **1999**, *7*, 125.

(11) To gain insight into the regiochemistry of iPS, we performed styrene polymerization in the presence of ^{13}C-enriched $Al(CH_3)_3$. We obtained, however, ^{13}C-enriched polyethylene, which displays a resonance at 28.04 ppm (1,1,2,2-tetrachloroethane-d_2). Similar observations were reported by Zambelli and co-workers; see: Ammendola, P.; Tancredi, T.; Zambelli, A. *Macromolecules* **1986**, *19*, 307.

(12) (a) Makio, H.; Fujita, T. *Macromol. Symp.* **2004**, *213*, 221. (b) Makio, H.; Oshiki, T.; Takai, K.; Fujita, T. *Chem. Lett.* **2005**, *34*, 1382.

(13) Mahanthappa, M. K.; Waymouth, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 12093, and references therein.

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