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Syndiotactic polystyrene with very high molecular weight produced by sterically and electronically modified catalyst

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Abstract

A new type of the half-metallocene catalysts for the syndiospecific polymerization of styrene was prepared by the reaction of various kinds of trialkanolamine with Cp^*TiCl_3 in the presence of triethylamine. All seven compounds have a highly thermal stability and they show fairly good activities in the presence of cocatalyst MMAO in styrene polymerization. Especially, highly bulky and electronically deficient **7**/MMAO system affords syndiotactic polystyrene with very high molecular weight. © 2002 Published by Elsevier Science B.V.

Keywords: Half-metallocene; Syndiotactic polystyrene; Triethanolamine; High molecular weight; *N*,*N*,*N*-Tris((*R*)-2-phenylethanol)amine; Pentamethylcyclopentadienyl; Chiral ligand; Titanium

1. Introduction

The use of titanium/MAO catalyst system in the first preparation of syndiotactic polystyrene (sPS) by Ishihara et al. has spurred an active search for new types of sPS catalysts [1]. A wide variety of new catalytic systems based on titanium or zirconium organometallic complexes have been reported in the literature [2]. The examples include $Cp'TiX_3$ ($Cp' = C_5H_5$, C_5Me_5 and X = halide, alkyl, alkoxy) [3], (η^5-indenyl)$TiCl_3$ [4] and substituted indenyl derivatives [5]. Recently, we reported that Cp*Ti(TEA) (TEA = triethanolateamine) and their derivatives [6] could electronically and sterically modify the catalytic active site by introducing sterically bulky and electron-rich multidentate ligands in place of monodentate X_3 ligands and those catalysts were active and good syndiospecific catalyst systems for styrene. In addition, Kaminsky et al. and Schellenberg [7] demonstrated that the introduction of electronically deficient fluorine atoms in cyclopentadienyl-based titanium complexes lead a strong increase in the polymerization activity and molecular weight when compared with the corresponding chlorinated titanium complex. In this regard, we reasoned that the introduction of moderately steric-bulky and electronically withdrawing group into TEA ligand system could affect the polymerization activity and the molecular weight of sPS. Herein we report the synthesis, characterization and styrene polymerization study of new titanium compound containing sterically bulky phenyl-substituted TEA ligand. We also report the comparison with catalytic activity for titanium complexes containing less bulky and electron-donating methyl-substituted TEA ligands.

2. Experimental

2.1. General considerations

All reactions were carried out under an Ar atmosphere using standard Schlenk and glove box techniques [8]. Argon was deoxygenated with activated Cu catalyst (regenerated by heating to 300 °C under H_2 gas) and dried with drierite (Aldrich). All solvents were dried by distilling from Na–K alloy/benzophenone ketyl

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($C_6H_5CH_3$ and Et_2O) or CaH_2 (methylene chloride) under a nitrogen atmosphere and stored over the activated molecular sieves (3A) [9]. $CDCl_3$ was obtained from Aldrich and dried over activated molecular sieves (4A), and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve.

2.2. Measurements

^1H- and $^{13}C\{^1H\}$ FT-NMR spectra were recorded on a Bruker AM 300 spectrometer. The chemical shifts are referenced to the residual peaks of the $CDCl_3$ (7.24 ppm in ^1H-NMR, 77.0 ppm in $^{13}C\{^1H\}$-NMR). EIMS and exact mass spectra were obtained by VG Auto Spectrometer. Elemental analyzes were performed by Korea Basic Science Center, Seoul, Korea. The thermal properties of sPS were investigated by Thermal Analyst 200 DSC system under nitrogen atmosphere at a heating rate of 20 °C min^{-1}. Molecular weights of polymers were determined at 140 °C in 1,2,4-trichlorobenzene by PL 220+220R GPC calibrated with standard polystyrenes.

2.3. Syntheses

All chemicals were purchased from Aldrich. MMAO was purchased in Akzo (MMAO-3A type, Al content = 5.9 wt.%, $d = 0.89$ g ml^{-1}, solvent = $C_6H_5CH_3$). Cp^*TiCl_3 [10], *N*,*N*,*N*-tris((*R*)-2-phenylethanol)amine (**7a**) [11] and precatalysts **1**–**6** were synthesized by literature procedures [6d].

2.3.1. (Pentamethylcyclopentadienyl)titanium(-tris((R)-2-phenylethanolate)amine) (7)

A reddish solution of Cp^*TiCl_3 (2 mmol, 0.58 g) in 40 ml of CH_2Cl_2 was added dropwise to a stirred solution of **7a** (2 mmol, 0.76 g) and Et_3N (6 mmol, 0.84 ml) in 40 ml of CH_2Cl_2 at −78 °C. After the completion of the addition, the reaction mixture was warmed to room temperature and stirred for 12 h. The residue, obtained by removing the solvent under vacuum, was redissolved in $C_6H_5CH_3$ and the resulting mixture was filtered through a Celite bed. The removal of solvent from the yellow filtrate gave the desired product **7** in 80% (0.89 g).

^1H-NMR (300.13 MHz, $CDCl_3$, ppm): $\delta = 7.37$–7.23 (m, 15H, C_6H_5), 5.55 (dd, 3H, $J = 4.1$, 10.4 Hz, OCH), 3.05–2.91 (m, 6H, NCH_2), 2.00 (s, 15H, $C_5(CH_3)_5$).

$^{13}C\{^1H\}$-NMR (75.1 MHz, $CDCl_3$, ppm): $\delta = 144.9$, 128.2, 127.1, 125.6 (C_6H_5), 123.5 ($C_5(CH_3)_5$), 81.87 (OCH), 64.60 (NCH_2), 11.65 ($C_5(CH_3)_5$).

EIMS (% intensity): $m/z = 557$ [80%, M^+], 451 [100%, $M^+ - OCHPh$], 422 [22%, $M^+ - Cp^*$], 345 [98%, $M^+ - 2OCHPh$], 302 [56%, $M^+ - N(CH_2CHPhO)_2$], 241 [56%, $M^+ - 3OCHPh$], 198 (85%, $3OCHPhCH_2$), 182 (71%, Cp^*Ti^+).

Exact mass calc. for $C_{34}H_{39}NO_3Ti$: 557.2409. Found: 557.2401. Anal. Calc. for $(C_{34}H_{39}O_3NTi)_n$ $(557.5)_n$: C, 73.24; H, 7.05; N, 2.51. Found: C, 73.39; H, 7.15; N, 2.22%.

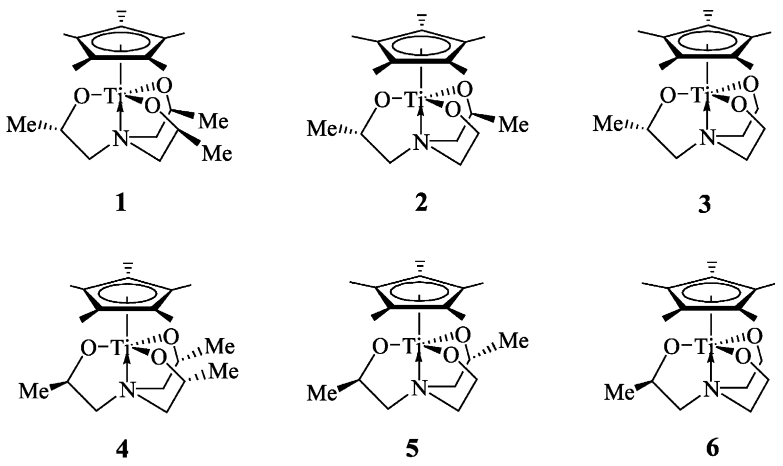
2.4. Polymerization procedure

Styrene polymerizations were carried out in 250 ml Schlenk flask with magnetic stirring. Toluene, the polymerization solvent, was distilled from Na–K alloy under Ar atmosphere just before use. Styrene monomer was distilled from CaH_2 and stored in the refrigerator. Polymerizations were carried out as following: $C_6H_5CH_3$, styrene, MMAO and the Ti compound were injected into a 250 ml Schlenk flask with magnetic stirring in that order at the desired polymerization temperature. After the desired reaction time was reached, reaction was terminated by the addition of 50 ml of MeOH and the addition of 50 ml of 10% HCl in MeOH was followed. The resulting precipitated polymer was collected, washed three times each with 500 ml of MeOH and dried in vacuo at 70 °C for 12 h. The polymer was extracted with refluxing 2-butanone for 12 h and the resulting insoluble portion was determined as the sPS portion (SI) of the polymer obtained. Syndiotacticity of the insoluble portion was confirmed by measuring ^{13}C-NMR spectra at 100 °C in 1,1,2,2-tetrachloroethane-d_2.

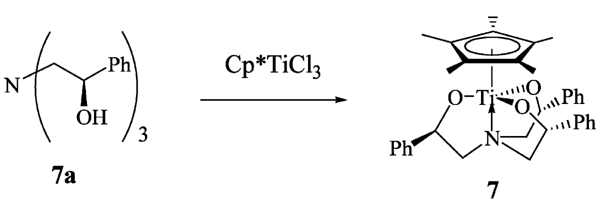
3. Results and discussion

Compounds **1**–**6** were prepared by literature procedure [6d] and they were outlined in Scheme 1. Likewise, the reaction of Cp^*TiCl_3 with **7a** in the presence of triethylamine in CH_2Cl_2 afforded crystalline solids **7** in a yield of 80% (See Scheme 2). Attempted use of trilithiated species instead of neutral *N*,*N*,*N*-tris((*R*)-2-phenylethanol)amine in toluene or diethylether was not successful and a mixture of several unidentified compounds was obtained, suggesting that mild reaction condition of HCl elimination is essential and required for the synthesis of **7**. Yellow crystalline solids **1**–**7** are freely soluble in toluene and methylene chloride but insoluble in hydrocarbon solvents such as hexane and pentane. In addition, they are air-stable for the extended period in the solid state and thermally stable below 100 °C. Like other compounds **1**–**6**, compound **7** has some volatile nature and the EIMS spectra of the compound exhibits molecular peaks for the corresponding complex.

Owing to the failure in obtaining single crystals for **7**, its structural nature was established by NMR spectroscopy, EIMS, exact mass and elemental analyzes. The ^1H- and $^{13}C\{^1H\}$-NMR spectra of **7** show the presence of only one pure compound. The stoichiometry of the



Scheme 1. The structures of compounds **1**–**6**.



Scheme 2. Synthetic route for compound **7**.

reaction was ascertained from the integral ratio of ^{1}H-NMR (See Fig. 1). The NMR spectra of the compound **7** were consistent with the trigonal bipyramidal structure of C_3 symmetry. Its three arms of the trialkanolamine ligand were magnetically equivalent by both ^{1}H- and ^{13}C{^{1}H}-NMR. In comparison to the free *N*,*N*,*N*-tris((*R*)-2-phenylethanol)amine precursor, all signals are shifted to downfield, which is a consequence of the complexation with Lewis acidic titanium metal. The greater extent of downfield shifts of OCH resonance than those of NCH_2 resonance suggests a strong bond between O atom and Ti atom and a weak interaction between the N atom and the Ti atom upon complexation. The NMR signals were sharp and variable-temperature studies showed no evidence of inter- or intramolecular ligand exchange at ambient temperature. In addition, the ^{1}H- and ^{13}C{^{1}H}-NMR indicate that complexes show monomeric structural feature in solution. Thus, the ligand *N*,*N*,*N*-tris((*R*)-2-phenylethanol)

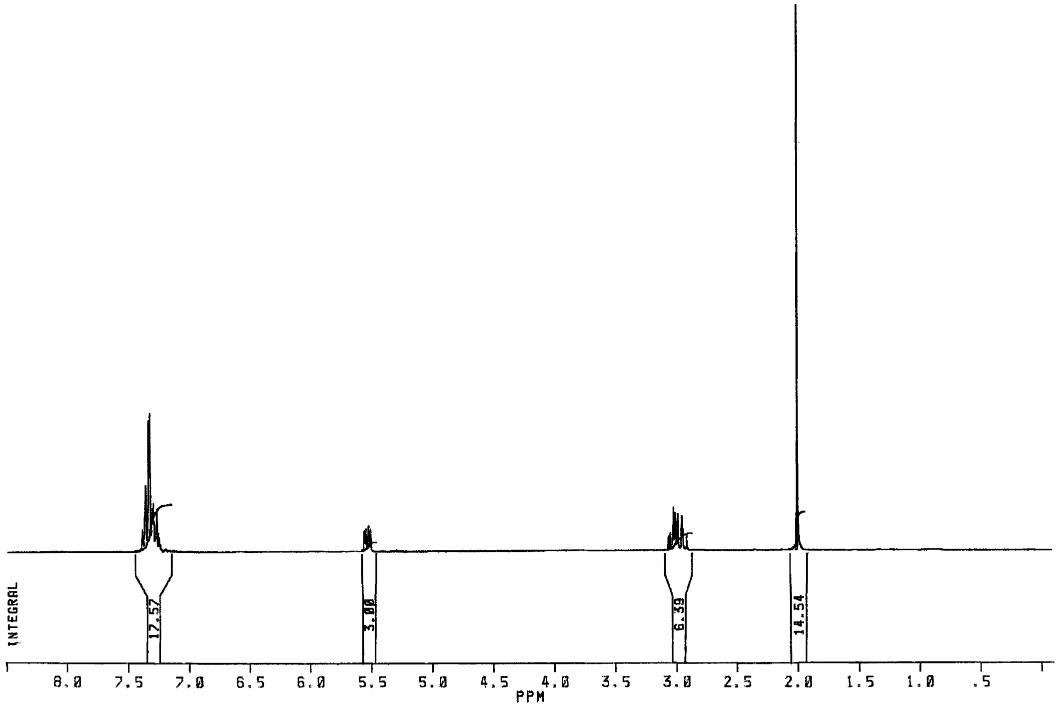


Fig. 1. ^{1}H-NMR spectrum for compound **7**.

Table 1
Syndiospecific polymerization data using **1**–**7**/MMAO [a]

Catalyst	Tp (°C)	PS (g)	*A* [b] (× 10^{-7})	Yield (%)	Tm [c]	SI [d] (%)	Mw [e]	Mn [e]	Mw/Mn [e]
1	30	0.352	0.25	7.73	275.2	99.2	41,000	14,600	2.81
	50	1.30	0.92	28.6	277.0	99.0	31,900	15,700	1.96
	70	2.23	1.57	50.0	273.9	98.7	31,400	17,100	1.84
	90	2.41	1.70	52.9	269.1	97.2	19,400	9,900	1.96
2	30	0.46	0.32	10.1	273.5	98.5	48,800	19,500	2.5
	50	1.25	0.88	27.5	277.9	99.7	45,200	22,300	2.03
	70	2.31	1.63	50.7	273.6	98.4	33,700	18,500	1.82
	90	2.42	1.71	53.2	268.4	97.0	19,100	9,600	1.99
3	30	0.26	0.18	5.71	274.2	98.7	46,400	18,600	2.49
	50	0.99	0.70	21.7	272.5	98.5	40,600	19,700	2.06
	70	1.92	1.35	42.2	273.3	98.5	34,000	18,900	1.80
	90	2.41	1.70	52.9	267.8	96.8	19,800	10,200	1.94
4	30	0.26	0.18	5.71	273.7	98.5	41,800	14,100	2.97
	50	1.29	0.91	28.3	275.0	99.0	44,700	23,000	1.94
	70	2.61	1.84	57.3	274.8	98.8	31,600	17,200	1.84
	90	2.71	1.91	59.5	270.1	97.9	20,300	10,100	2.01
5	30	0.51	0.36	11.2	273.5	98.5	51,600	19,900	2.59
	50	1.48	1.04	32.5	277.6	99.4	49,000	24,100	2.04
	70	2.29	1.61	50.3	275.4	99.0	33,400	17,900	1.86
	90	2.50	1.76	54.9	270.7	98.5	20,200	10,700	1.88
6	30	0.28	0.20	6.15	271.5	98.6	43,500	15,700	2.78
	50	0.95	0.67	20.9	277.7	99.5	44,820	21,260	2.11
	70	1.83	1.29	40.2	273.6	98.8	34,100	17,200	1.98
	90	2.49	1.76	54.7	269.7	97.9	20,000	9,700	2.07
7	30	1.49	1.05	32.7	277.0	99.4	872,000	443,000	1.97
	50	1.93	1.36	42.4	275.4	99.0	520,800	263,400	1.98
	70	3.54	2.50	77.8	273.1	98.4	179,800	96,100	1.87
	90	3.8	2.69	83.7	271.8	98.0	73,000	39,200	1.86
Cp*$TiCl_3$	30	0.88	0.62	19.3	274.6	97.7	231,000	136,000	1.70
	50	2.62	1.84	57.6	272.9	96.0	197,000	114,000	1.73
	70	3.00	2.12	65.9	272.7	95.4	182,300	87,000	2.09
	90	1.36	0.96	29.9	272.5	95.0	23,200	11,000	2.11

[a] Polymerization condition: [styrene] = 0.436 M (5 ml); [Ti] = 0.195 mM; Al/Ti = 1000; time = 10 min.
[b] Activity = g sPS/(mol Ti mol styrene h).
[c] Determined by DSC.
[d] SI, 2-butanone insoluble portion whose tacticity was established by ^{13}C-NMR in 1,1,2,2-tetrachloroethane-d_2.
[e] Determined by GPC.

amine is coordinated to the titanium atom in a tetradentate manner.

Compounds **1**–**7** are examined as catalysts for styrene polymerization in the presence of MMAO as a cocatalyst. The polymerization results are summarized in Table 1 in terms of the activity of the catalyst, yield, Tm, syndiotacticity, Mn, Mw and Mw/Mn. To probe the nature of the polymerization reaction, the polymerizations at various temperatures were carried out. In order to assess the significance of the quoted activity values, we also carried out the control polymerization experiment using by Cp*$TiCl_3$/MMAO system in the same polymerization condition. The polymerization data, summarized in Table 1, reveal that **1**–**7**/MMAO systems are fairly good catalysts in producing sPS in terms of activity, conversion, syndiotacticity and Tm at all polymerization temperatures even though the polymerization time is fixed to 10 min. The sPS samples were analyzed by GPC and DSC. It is interesting to note that the catalytic activity increases as the polymerization temperature Tp increases even up to 90 °C. In general, the well-known good catalysts for sPS had maximum catalytic activity at somewhat low polymerization temperature. For example, (η^5-indenyl)$TiCl_3$/MAO [4] and Cp*$TiCl_3$/MAO [6] showed maximum catalytic activity at 50 and 70 °C, respectively. The catalysts with high activity at high polymerization temperature should be needed in the aspect of industrial application. The optimum activity for **1**–**7**/MMAO systems is observed at 90 °C under the same polymerization condition, indicating that the precatalysts **1**–**7** have the high thermal stability and also the chelating trialkanolamine ligand with the unique steric bulkiness seems to play an important role in stabilizing the active species generated

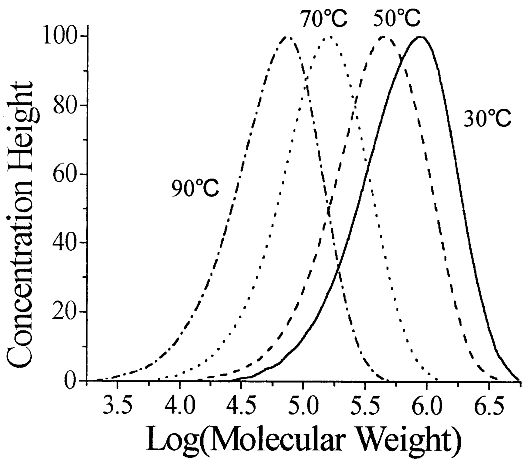


Fig. 2. The molecular weight distribution of sPS obtained by **7**/MMAO system as a function of the polymerization temperature.

from the reaction between the precursor and MMAO. In addition, **1**–**7**/MMAO systems afford polystyrenes with high stereospecificity of greater than 96.8% and high Tm value of 268.4–277.9 °C over the entire Tp range studied. As many homogeneous metallocene catalysts based on pentahapto ligands, **1**–**7**/MMAO systems also show a somewhat lowering of Tm value with increasing Tp [12].

The molecular weight distributions and polydispersity indices for sPS produced by **1**–**6**/MMAO show quite different tendency from those yielded by **7**/MMAO. **1**–**6**/MMAO systems afford polystyrenes whose Mw falls in the range of 19,100–51,600 with Mw/Mn = 1.8–2.97, whereas sPS made by **7**/MMAO system shows Mw in the range of 73,000–872,000 with Mw/Mn = 1.86–1.97. In case of the catalyst systems **1**–**6**/MMAO, lowering the polymerization temperature Tp from 90 to 30 °C resulted in two or two-and-half times increases of Mw value. Surprisingly, **7**/MMAO system shows a precipitous lowering of Mw value with raising polymerization temperature Tp. However, it is interesting to note that polystyrenes yielded by **7**/MMAO system have higher molecular weight than polymers produced by **1**–**6**/MMAO and Cp*$TiCl_3$/MMAO systems (See Fig. 2). Especially in the case of the polymerization temperature of 30 °C, **7**/MMAO system affords polystyrene with Mw = 872,000 and 20 times higher Mw than **1**–**6**/MMAO systems do. We believe at this stage that those tremendous increases of molecular weight are attributable to the steric bulkiness and electronic effect of phenyl substituents, which make the termination process such as β-hydride elimination or chain transfer reaction by $AlMe_3$ less affordable. As far as the polydispersity index concerns, the minimum value of the polydisperisty index for **1**–**6**/MMAO systems is observed at 70 °C as increasing the polymerization temperature, while the polydispersity index for **7**/MMAO system is narrowing as Tp increases. Furthermore, Table 2 compares some

Table 2

Typical examples of titanium catalysts generating sPS with high molecular weight [a]

Catalyst system	Tp (°C)	Time (min)	$10^5 \times$ [Ti] (mol)	[Sty] (ml)	Al/Ti	$10^{-7} \times A$ [b]	Tm	$10^{-3} \times$ Mw	PDI	Lit.
(1,3-ph_2Ind)$TiCl_3$/MAO	50	10	250	5	400	3.6	262.0	496	n.d. [c]	[5a]
(C_6H_5Me)Ti(Cl_2AlCl_2)$_2$/MAO	30	40	1350	15	700	3.7×10^{-6}	269.0	2353	2.93	[13]
Cp*$TiMe_3$/$Ph_3CB(C_6F_5)_4$	25	5	4.38	5	1 [d]	0.59	n.d. [c]	832	3.2	[14]
Cp*TiF_3/MAO	30	40	0.25	20	300	0.17	277.0	700	1.8	[7a]
(MeCp)TiF_3/MAO	10	40	0.25	20	300	0.26	272.0	1420	About 2	[7a]
7/MMAO	30	10	195	5	1000	1.05	277.0	872	1.97	This work

[a] Tp, polymerization temperature; [Ti], amount of catalyst used; [Sty], amount of styrene used; Al/Ti, molar ratio; Tm, melting point of sPS; Mw, weight average molecular weight; PDI, polydispersity index; lit, literature.

[b] Activity = g sPS/(mol Ti mol styrene h).

[c] n.d., not described.

[d] B/Ti = 1.

typical examples for sPS catalysts producing high molecular weight polymer in the literature and our work. $(C_6H_5Me)Ti(Cl_2AlCl_2)_2$/MAO system [13] shows the highest molecular weight but the catalytic activity is somewhat low. In the case of $Cp^*TiMe_3/Ph_3CB(C_6F_5)_4$ system [14], the obtained polymer has the broad molecular weight distribution in spite of short polymerization time and the least used amount of cocatalyst. Cp^*TiF_3/MAO and $(MeCp)TiF_3$/MAO system [7a] could produce high molecular weight polymer but the catalytic activity is slight lower than other catalysts. In this regard, our catalyst system **7**/MMAO is one of the most valuable catalysts producing sPS with the high molecular weight in the aspect of catalytic activity, Mw, PDI and Tm among all parameters of polymerization condition.

4. Conclusion

In this paper, we have demonstrated the highly thermal stable catalyst system in generating sPS. Especially, **7**/MMAO system could give syndiotactic polystyrene with very high molecular weight. Further studies on ethylene-homopolymerization and copolymerization of ethylene with styrene are now in progress.

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References

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

[2] (a) N. Ishihara, M. Kuramoto, M. Uoi, Macromolecules 21 (1988) 3356;
(b) A. Kucht, H. Kucht, S. Barry, J.C.W. Chien, M.D. Rausch, Organometallics 12 (1993) 3075;
(c) F.C. Flores, J.C.W. Chien, M.D. Rausch, Macromolecules 29 (1996) 8030;
(d) Y. Kim, Y. Han, M.H. Lee, S.W. Yoon, K.H. Choi, B.G. Song, Y. Do, Macromol. Rapid Commun. 22 (2001) 573.

[3] N. Ishihara, M. Kuramoto, Syntheses and properties of syndiotactic polystyrene, in: K. Soga, M. Terano (Eds.), Catalyst Design for Tailor-Made Polyolefins, Kodansha, Tokyo, 1994, p. 339.

[4] T.E. Ready, R.O. Day, J.C.W. Chien, M.D. Rausch, Macromolecules 26 (1993) 5822.

[5] (a) P. Foster, J.C.W. Chien, M.D. Rausch, Organometallics 15 (1996) 2404;
(b) Y. Kim, B.H. Koo, Y. Do, J. Organomet. Chem. 527 (1997) 155.

[6] (a) Y. Kim, E. Hong, M.H. Lee, J. Kim, Y. Han, Y. Do, Organometallics 18 (1999) 36;
(b) Y. Kim, Y. Do, Macromol. Rapid Commun. 21 (2000) 1148;
(c) Y. Kim, Y. Han, Y. Do, J. Organomet. Chem. 634 (2001) 19;
(d) Y. Kim, Y. Han, J.W. Hwang, M.W. Kim, Y. Do, Organometallics 21 (2002) 1127.

[7] (a) W. Kaminsky, S. Lenk, V. Scholz, H.W. Roesky, A. Herzog, Macromolecules 30 (1997) 7647;
(b) J. Schellenberg, J. Polym. Sci.: Part A: Polym. Chem. 38 (2000) 2428.

[8] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, Butterworth-Heineman, Boston, 1996, pp. 176, 215, 342.

[9] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, The Purification of Laboratory Chemicals, Pergamon, New York, 1980.

[10] G.H. Llinas, M. Mena, F. Palacios, P. Royo, R. Serrano, J. Organomet. Chem. 340 (1988) 37.

[11] W.A. Nugent, R.L. Harlow, J. Am. Chem. Soc. 116 (1994) 6142.

[12] (a) B. Rieger, X. Mu, D.T. Mallin, M.D. Rausch, J.C.W. Chien, Macromolecules 23 (1990) 3559;
(b) J.C.W. Chien, R. Sugimoto, J. Polym. Sci. Part A 29 (1991) 459.

[13] W. Kaminsky, Y.W. Park, Macromol. Rapid Commun. 16 (1995) 343.

[14] A. Grassi, C. Lamberti, A. Zambelli, I. Mingozzi, Macromolecules 30 (1997) 1884.