Syndiospecific Living Polymerization of Propene with [*t*-BuNSiMe$_2$Flu]TiMe$_2$ Using MAO as Cocatalyst

Tariqul Hasan, Atau Ioku, Kei Nishii, Takeshi Shiono,* and Tomiki Ikeda

Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama 226-8503, Japan

Received October 10, 2000; Revised Manuscript Received February 21, 2001

ABSTRACT: Propene polymerization was conducted at 0 °C by [*t*-BuNSiMe$_2$Flu]TiMe$_2$ combined with B(C$_6$F$_5$)$_3$, MAO, or the MAO which had been dried in a vacuum and washed with hexane before use. The effect of cocatalyst was investigated under atmospheric pressure of propene in a semibatch system where polymerization rate was followed by the amount of propene consumed. The B(C$_6$F$_5$)$_3$ system was deactivated within 30 min, while the MAO system showed steady polymerization rate. On the other hand, the activity of the dried MAO system was so high that the kinetic profile could not be evaluated precisely. The MAO system gave the low molecular weight polymer, and the number of polymer chains was more than 10 times higher than the amount of titanium complex employed. In the dried MAO system, however, the produced polymer showed the highest molecular weight and narrowest molecular weight distributions of about 1.2. The batchwise polymerization with the dried MAO system indicated that propene polymerization proceeded quantitatively regardless of the monomer charged, and the number-average molecular weight of the polymer obtained increased linearly against the polymer yield with keeping the molecular weight distribution narrow and the number of polymer chains constant. The results of postpolymerization testified that living polymerization proceeded under these conditions. The ^{13}C NMR measurement indicated that syndiotactic-rich polypropenes were produced in a highly regiospecific manner by this catalyst system.

Introduction

Since the discovery of metallocene catalyst, a great number of organometallic compounds have been applied for olefin polymerization as a so-called single-site catalyst from both the academic and the industrial points of view.[1] Living polymerization system has also attracted much attention for precise control of polymer structure. V(acac)$_3$/AlEt$_2$Cl (acac = acetyl acetonate and its analogues) had been the only catalyst for living polymerization of propene until just recently.[2]

The recent development of single-site catalyst has enabled living polymerization of α-olefins by various transition metal compounds. Brookhart et al. reported that the living polymerization of α-olefins (propene, 1-hexene, and 1-octadecene) proceeded at −10 °C with Ni−diimine catalysts combined with methylaluminoxane (MAO), and the poly(α-olefin)s obtained had less branches than those expected from 1,2-insertion of α-olefins.[3] McConville et al. reported living polymerization of higher α-olefins (1-hexene, 1-octene, and 1-decene) with [ArN(CH$_2$)$_3$NAr]TiMe$_2$ using trispentafluorophenylborane (B(C$_6$F$_5$)$_3$) as cocatalyst at 23 °C to produce regioregular polymers.[4] Schrock et al. also reported living polymerization of 1-hexene by zirconium complexes containing tridentate diamido ligand.[5] Kim et al. reported that 2,2′-ethylenebis[*N,N*′-(triisopropylsilyl)anilinido]dimethylzirconium/B(C$_6$F$_5$)$_3$ catalyst gave atactic poly(1-hexene) in a living nature at −10 °C[6] in which the molecular weight distribution (MWD) of polymer obtained was relatively broad when MAO was used as cocatalyst. Fukui et al. reported living polymerization for propene with Cp$_2$ZrMe$_2$ at −78 °C and Cp$_2$HfMe$_2$ at −50 °C activated by B(C$_6$F$_5$)$_3$ in the presence of trioctylaluminum (Oct$_3$Al).[7] They also succeeded in isospecific living polymerization of 1-hexene with *rac*-Et(Ind)$_2$ZrMe$_2$ at −78 °C. Sita et al. have recently reported that Cp*ZrMe$_2$[RNC(Me)NR] catalyst using [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] as cocatalyst conducted the living polymerization of 1-hexene at −10 °C and gave highly isotactic poly(1-hexene).[8] Although several papers have reported on living polymerization of α-olefin, there are only a few reports on living polymerization of propene, which generally require more severe conditions.

We have recently found that the [*t*-BuNSiMe$_2$Flu]TiMe$_2$/B(C$_6$F$_5$)$_3$ system promoted the living polymerization of propene at −50 °C in a highly regiospecific manner, whereas the catalytic system was deactivated even at 0 °C.[9] McConville et al. proposed the deactivation mechanism induced by [MeB(C$_6$F$_5$)$_3$]$^-$ in the [ArN(CH$_2$)$_3$NAr]TiMe$_2$/B(C$_6$F$_5$)$_3$ system.[10] On the other hand, low molecular weight polypropene terminated with Al−C bonds was produced in high yield at 40 °C by [*t*-BuNSiMe$_2$Flu]TiMe$_2$ when MAO was used in place of B(C$_6$F$_5$)$_3$, because trimethylaluminum (Me$_3$Al) in MAO acted effectively as a chain transfer reagent.[11] These results suggest that the living polymerization might proceed with [*t*-BuNSiMe$_2$Flu]TiMe$_2$ at higher temperatures if Me$_3$Al-free MAO is used as cocatalyst.

In this point of view, we have investigated propene polymerization with [*t*-BuNSiMe$_2$Flu]TiMe$_2$ using Me$_3$Al-free MAO as cocatalyst.

Experimental Section

Materials. All operations were carried out under nitrogen atmosphere using standard Schlenk techniques. [*t*-BuNSiMe$_2$Flu]TiMe$_2$ was synthesized according to the literature.[9] Organoaluminum compounds (MAO and Oct$_3$Al) donated from Tosoh-Finechem Co., Ltd., and B(C$_6$F$_5$)$_3$ donated from Nippon Shokubai Co., Ltd., were used without further purification. Me$_3$Al was removed from the toluene solution of MAO (Al = 9.4 wt %, 200 mL) by evaporation of solvent and volatile Me$_3$Al under vacuum for 4 h. The remaining Me$_3$Al was removed by means of washing with hexane (100 mL × 4), and the solid

10.1021/ma0017438 CCC: $20.00

part was dried under vacuum to obtain white powder (3.5 g), which is hereafter called dried MAO. Research grade propene (98%, purchased from Takachiho Chemicals Co.) was purified by passing through columns of NaOH, P_2O_5, and molecular sieves 3A, followed by bubbling through a $NaAlH_2Et_2$/1,2,3,4-tetrahydronaphthalene solution. All solvents were commercially obtained and dried with standard methods.

Polymerization Procedure. Polymerization was performed in a 100 mL glass reactor equipped with a magnetic stirrer and conducted by the following two methods. (i) Semibatch method: Gaseous propene was introduced in the reactor under atmospheric pressure. After the solvent was saturated with propene, polymerization was started by successive addition of prescribed amounts of cocatalyst and catalyst. Propene pressure and temperature were kept constant during the polymerization, and consumption rate of propene was monitored by a gas flow meter. (ii) Batch-type method: After a certain amount of propene measured by a gas flow meter was dissolved in the solvent, polymerization was started by successive addition of prescribed amounts of cocatalyst and catalyst. Polymerization was conducted for 1 h and terminated with acidic methanol. The polymers obtained were adequately washed with methanol and dried under vacuum at 60 °C for 6 h.

Analytical Procedure. Molecular weight and molecular weight distribution of polypropenes obtained were determined by gel permeation chromatography with a Waters 150CV at 140 °C using *o*-dichlorobenzene as a solvent. The following parameters were used for universal calibration: $K = 7.36 \times 10^{-5}$ and $\alpha = 0.75$ for polystyrene standards; $K = 1.03 \times 10^{-4}$ and $\alpha = 0.78$ for polypropene samples. ^{1}H NMR spectra of MAO were measured at room temperature on a JEOL GX300 spectrometer operated at 300.40 MHz in pulse Fourier transform mode. The pulse angle was 45°, and 16 scans were accumulated in pulse repetition of 7.0 s. Sample solution was prepared by addition of benzene-d_6 in toluene up to 10%. The methyl peak of toluene (2.09 ppm) was used as internal reference. ^{13}C NMR spectra of polypropene were measured at 120 °C on a JEOL GX 500 spectrometer operated at 125.65 MHz in pulse Fourier transform mode. The pulse angle was 45°, and about 10 000 scans were accumulated in pulse repetition of 5.0 s. Sample solution was prepared in 1,1,2,2-tetrachloroethane-d_2 up to 10 wt %. The central peak of 1,1,2,2-tetrachloroethane (74.47 ppm) was used as internal reference.

Results and Discussion

To check whether Me_3Al was removed from MAO or not with the procedure described in the Experimental Section, we measured ^{1}H NMR spectra of MAO before and after the treatment. The ^{1}H NMR spectrum before the treatment showed strong resonance assignable to Me_3Al. After the treatment, however, the resonance perfectly disappeared, and only a broad peak derived from MAO was observed very weakly. These results indicate that the dried MAO prepared did not contain free Me_3Al.

Propene polymerization was then conducted by [*t*-BuNSiMe$_2$Flu]TiMe$_2$ combined with $B(C_6F_5)_3/Oct_3Al$, MAO, and dried MAO using a semibatch system, and the kinetic profiles are shown in Figure 2. The $B(C_6F_5)_3/Oct_3Al$ system showed the high activity in initial several minutes while the activity dropped immediately with increasing polymerization time. On the other hand, the steady polymerization rate was observed in the MAO system. When dried MAO was used as cocatalyst, [*t*-BuNSiMe$_2$Flu]TiMe$_2$ showed the highest polymerization rate. The production of a large amount of polymer, however, increased the viscosity in polymerization media and prohibited effective stirring, which caused the apparent decrease in polymerization rate.

The results of polymerization and GPC analysis are summarized in Table 1. In the absence of Oct_3Al, the $B(C_6F_5)_3$ system showed very low activity (entry 1). On the other hand, the high molecular weight polymer was produced with narrow MWD in the presence of Oct_3Al (entry 2). We have previously investigated the effects of Oct_3Al in this system at −50 °C, which conducted living polymerization of propene, and found Oct_3Al acted not only as a scavenger but also as a promoter for propagation.[12] Although the number of polymer chain (*N*) was almost the same with the number of titanium complex employed in the $B(C_6F_5)_3/Oct_3Al$ system, the rate−time profile indicated that this catalyst system was deactivated. The *N* value in the MAO system was more than 10 times higher than the number of titanium

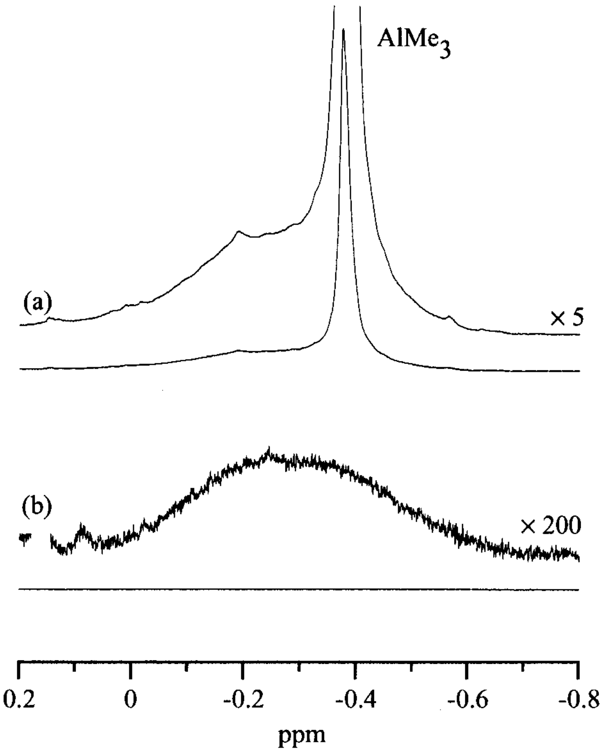

Figure 1. The 300 MHz ^{1}H NMR spectra of methyl region of MAO: before (a) and after (b) the treatment of MAO.

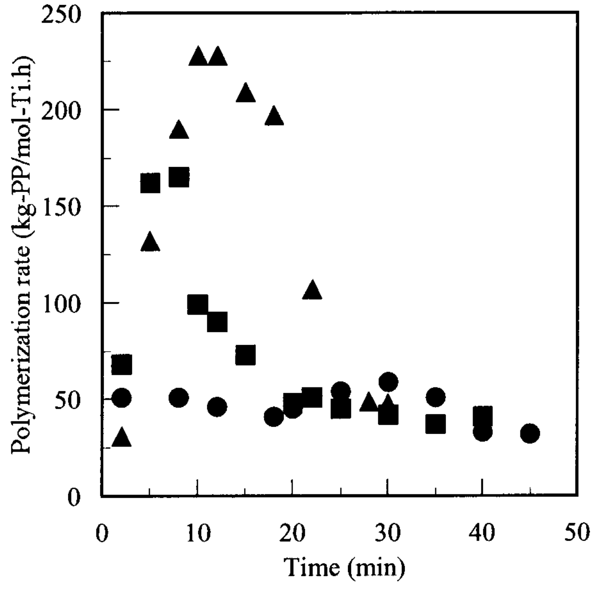

Figure 2. Rate−time profiles of propene polymerization with [*t*-BuNSiMe$_2$Flu]TiMe$_2$ using various cocatalysts: (a) $B(C_6F_5)_3$/Oct_3Al (■), (b) MAO (●), (c) dried MAO (▲).

Table 1. Effect of Cocatalyst on Propene Polymerization with [*t*-BuNSiMe$_2$Flu]TiMe$_2$[a]

entry	cocatalyst	time (min)	yield (g)	activity (kg of PP/mol of Ti h)	M_n[b] ($\times 10^{-4}$)	M_w/M_n[b]	N[c] (μmol)
1[d]	B(C$_6$F$_5$)$_3$	60	trace				
2[e]	B(C$_6$F$_5$)$_3$/Oct$_3$Al	60	1.20	59.8	6.0	1.39	20
3[f]	MAO	60	0.63	31.3	0.24	1.36	260
4[f]	dried MAO	30	2.57	256.6	15.7	1.22	16

[a] Polymerization conditions: toluene = 30 mL, Ti = 20 μmol, propene = 1 atm, 0 °C. [b] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) determined by GPC using universal calibration. [c] Number of polymer chain calculated from yield and M_n. [d] B = 20 μmol. [e] B = 20 μmol, Oct$_3$Al = 400 μmol. [f] MAO = 8.0 mmol.

Table 2. Effect of Monomer Concentration on Propene Polymerization with [*t*-BuNSiMe$_2$Flu]TiMe$_2$/Dried MAO[a]

entry	propene (mol/L)	yield (g)	conv (%)	M_n[b] ($\times 10^{-4}$)	M_w/M_n[b]	N[c] (μmol)
5	1.00	1.22	97	10.1	1.35	12
6	1.25	1.55	98	14.2	1.42	11
7	1.58	1.91	96	15.5	1.31	12
8	1.0 + 1.0[d]	2.40	95	18.1	1.42	13

[a] Polymerization conditions: toluene = 30 mL, Ti = 20 μmol, MAO = 8.0 mmol, 0 °C. [b] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) determined by GPC using universal calibration. [c] Number of polymer chain calculated from yield and M_n. [d] After 1 h polymerization, 1.0 mol/L propene was added, and the polymerization was conducted for further 1 h.

complex although the steady polymerization rate was observed. We have already reported that the [*t*-BuNSiMe$_2$Flu]TiMe$_2$/MAO system predominantly gave low molecular weight Al-terminated polypropene at 40 °C.[11,13] This result indicate that the chain transfer reaction occurred in the MAO system even at 0 °C. On the other hand, the dried MAO system showed the highest activity and gave the polymer with the highest molecular weight. Since the *N* value was less than the number of titanium complex employed and MWD was narrow, the dried MAO system probably conducted the living polymerization.

To investigate the living nature of [*t*-BuNSiMe$_2$Flu]TiMe$_2$/dried MAO system, we conducted propene polymerization at 0 °C with batchwise operation by changing the amount of monomer in feed. The results are summarized in Table 2. Regardless of the amount of monomer in feed, the conversion reached over 96%, and the *N* value was constant with relatively narrow MWD. These results imply that no chain transfer reactions occurred in this catalyst system.

Postpolymerization was then conducted in entry 8, where the same amount of propene (1 mol/L) was added after 1 h polymerization of entry 5, and the polymerization was continued for further 1 h. The GPC curves of entries 5 and 8 are illustrated in Figure 3. The GPC curve of entry 8 shifted to higher molecular weight range, and no peak or shoulders were observed in the range of that of entry 5, although the M_w/M_n value slightly increased. In addition, the polymer yield and the M_n value became almost double with that of entry 5, and the *N* value was constant. These results indicate that the Ti−polymer bond was not deactivated even in the absence of propene and initiated the successive polymerization quantitatively.

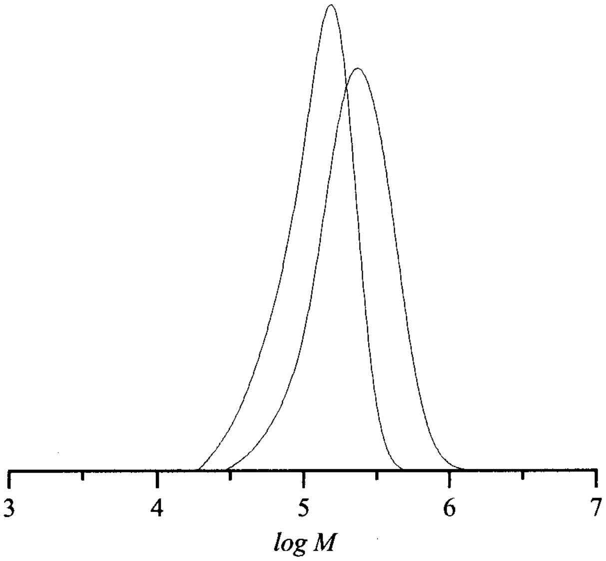

Figure 3. GPC curves of polypropene obtained with [*t*-BuNSiMe$_2$Flu]TiMe$_2$/dried MAO at 0 °C: before (a) and after (b) the postpolymerization.

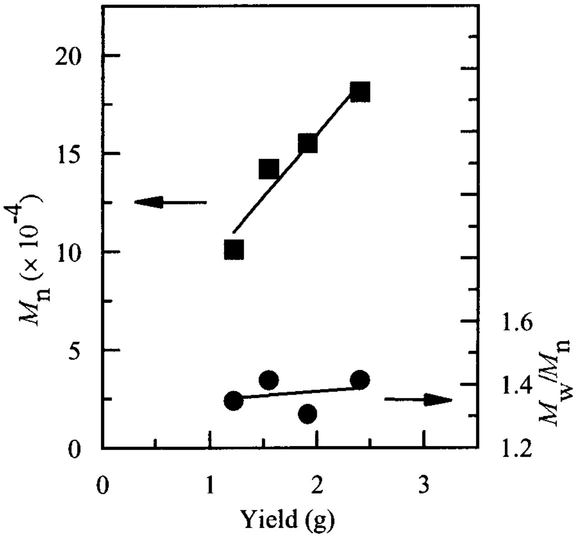

Figure 4. M_n and M_w/M_n of polypropene obtained with [*t*-BuNSiMe$_2$Flu]TiMe$_2$/dried MAO at 0 °C as a function of yield.

In Figure 4, M_n and M_w/M_n values are plotted against the polymer yield based on data summarized in Table 2. The M_n value linearly increased against the polymer yield, although the M_w/M_n values were slightly larger than that of an ideal living system. The results described above indicated that the [*t*-BuNSiMe$_2$Flu]TiMe$_2$/dried MAO system practically conducted the living polymerization of propene at 0 °C.

We have previously reported the living polymerization of propene with [*t*-BuNSiMe$_2$Flu]TiMe$_2$/B(C$_6$F$_5$)$_3$ at −50 °C.[9] The catalyst system was, however, deactivated at 0 °C or even at −50 °C when Ph$_3$B(C$_6$F$_5$)$_4$ was used in place of B(C$_6$F$_5$)$_3$. The active species of [*t*-BuNSiMe$_2$Flu]TiMe$_2$-based catalysts should be the coordinatively unsaturated cationic titanium species, [*t*-BuNSiMe$_2$Flu]TiMe$^+$. These results indicate that the counteranion

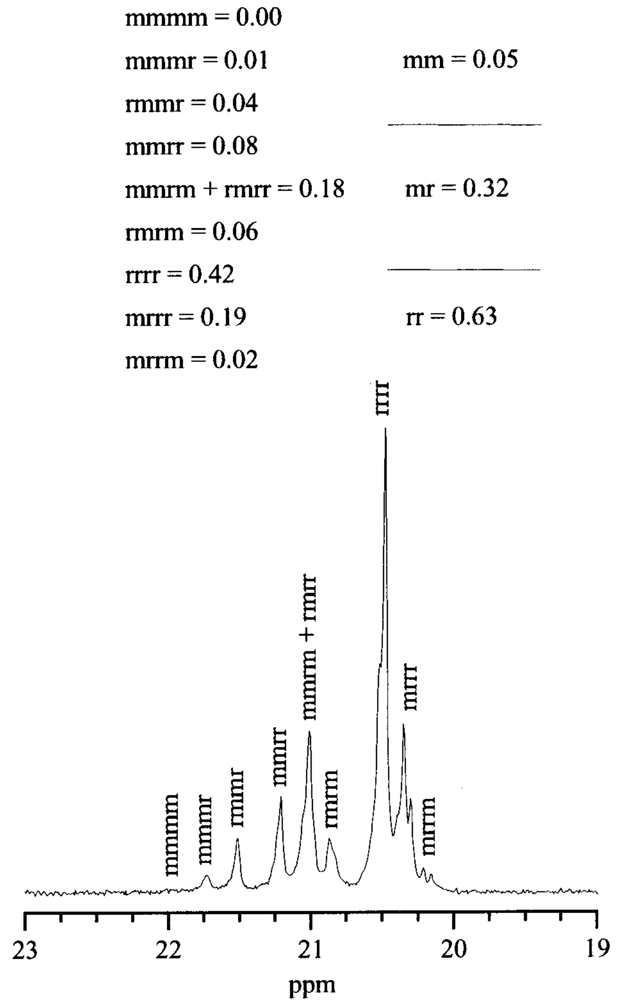

Figure 5. The 125 MHz ^{13}C NMR spectrum of methyl region of polypropene obtained with [*t*-BuNSiMe$_2$Flu]TiMe$_2$/dried MAO (entry 5).

derived from MAO is most effective to stabilize the [*t*-BuNSiMe$_2$Flu]TiMe$^+$ cation, although the structure of MAO is still controversial.[14]

Molecular Structure of Polypropene. The ^{13}C NMR spectrum of the methyl region of the living polypropene obtained in entry 5 is shown in Figure 5. The triad analysis showed that the produced polymer was syndiotactic-rich (rr = 63%, mr = 32%, mm = 5%). The syndiospecificity of the dried MAO system at 0 °C was almost the same with that of V(acac)/Et$_2$AlCl system at −78 °C (rr = 63%, mr = 31%, mm = 6%).[2] In addition, any resonance assignable to the regioirregular unit was not observed, which indicates that this living polymerization proceeded in a highly regiospecific manner.

Conclusion

Living polymerization of propene proceeded with [*t*-BuNSiMe$_2$Flu]TiMe$_2$ catalyst at 0 °C when dried MAO which was free from Me$_3$Al was used as cocatalyst. The postpolymerization experiment proved that the catalyst system was not deactivated even in the absence of propene and conducted the successive polymerization quantitatively to afford high molecular weight polymer ($M_n = 1.8 \times 10^5$). The ^{13}C NMR spectrum of polypropene obtained indicated that this living polymerization proceeded in syndiospecific and highly regiospecific manner. The results obtained in this paper suggest the potentiality of dried MAO as cocatalyst for the living polymerization with transition-metal alkyls.

Acknowledgment. This work was supported by the New Energy and Development Organization (NEDO) for the project on Technology for Novel High-Functional Materials in Industrial Science and Technology Frontier Program, Agency of Industrial Science and Technology (AIST).

References and Notes

(1) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98,* 2587.
(2) Doi, Y.; Suzuki, S.; Soga, K. *Macromolecules* **1986**, *19,* 2896. and references therein.
(3) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118,* 11664.
(4) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118,* 10008.
(5) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119,* 3830.
(6) Kim, K.; Jeon, M. Y.; Park, J. S.; Heo, J. *Organometallics* **1998**, *17,* 3161.
(7) Fukui, Y.; Murata, M.; Soga, K. *Macromol. Rapid Commun.* **1999**, *20,* 637.
(8) Sita, L. R.; Jayaratne, C. K. *J. Am. Chem. Soc.* **2000**, *122,* 958.
(9) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31,* 3184.
(10) McConville, H. D.; Rettig, J. S.; Scollard, D. J. *Organometallics* **1997**, *16,* 1810.
(11) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1997**, *30,* 4713.
(12) Shiono, T.; Hagihara, H.; Ikeda, T. In *Metalorganic Catalysts for Synthesis and Polymerization: Recent Results by Ziegler–Natta and Metallocene Investigations*; Kaminsky, W., Ed.; Springer-Verlag: Berlin, 1999; p 264.
(13) Shiono, T.; Yoshida, S.; Hagihara, H.; Ikeda, T. *Appl. Catal. A* **2000**, *145,* 200.
(14) The interactions between tetravalent cationic group 4 species and counteranions are reviewed by: Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100,* 1391.

MA0017438