Living Polymerization of Propene with a Chelating (Diamide)dimethyltitanium Complex Using Silica-Supported Methylaluminoxane

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A living polymerization system, in which neither chain transfer reaction nor deactivation occurs, affords polymers with predictable molecular weights and narrow molecular weight distribution. The living polymerization, therefore, has attracted much attention for synthesizing terminally functionalized polymers and block copolymers. Several papers have reported on the living polymerization of propene in a homogeneous catalytic system.[1−7] There is, however, a few examples for living polymerization of propene with the supported catalysts.[8,9] The supported catalysts are important for modern polyolefin process using gas phase, advanced slurry, or bulk polymerization technology.[10−12] The heterogenization of the single-site catalyst is necessary to produce polymer particles of a desired morphology and to avoid reactor fouling with finely dispersed swelling of polymers. The integration of the living and supported catalytic systems is expected in the present fields of polyolefins.

We have recently found that living polymerization of propene proceeded in heptane at 0 °C by a chelating (diamide)dimethyltitanium complex ([ArN(CH_2)$_3$NAr]-$TiMe_2$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), which was reported as a living polymerization catalyst for higher α-olefins combined with B(C_6F_5)$_3$,[13] when dried modified methylaluminoxane (dried MMAO) was used as a cocatalyst.[14] In this paper, we focused our effort on the heterogenization of this system to achieve a well-defined supported catalyst for living polymerization of propene.

Propene polymerization was conducted at 0 °C with [ArN(CH_2)$_3$NAr]$TiMe_2$ using MMAO/SiO_2 and dried MMAO/SiO_2[15] as a cocatalyst, and the rates of propene consumption against polymerization are plotted in Figure 1. When 0.67 mM of [Ti] was used, the MMAO/SiO_2 system showed a low steady rate. On the other hand, the dried MMAO/SiO_2 system showed a high consumption rate in the initial stage, but the rate gradually decreased because a large amount of produced polymer prohibited effective stirring. We, therefore, investigated the rate−time profile of the dried MMAO/SiO_2 system with a half amount of [Ti] (0.33 mM) and found that the system showed a steady rate.

To investigate the living nature of this system, we investigated the time dependence of molecular weight (M_n) and molecular weight distribution (M_w/M_n) with 0.33 mM of [Ti]. The results are plotted in Figure 2. We have previously reported the living polymerization of propene with the corresponding homogeneous system,[14]

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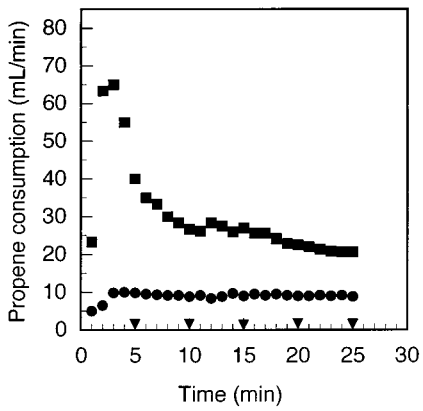

Figure 1. Rate−time profiles of propene polymerization with [ArN(CH_2)$_3$NAr]$TiMe_2$−SiO_2 MMAO: MMAO/SiO_2 system ([Ti] = 0.67 mM) (▼), dried MMAO/SiO_2 system ([Ti] = 0.67 mM) (■), dried MMAO/SiO_2 system ([Ti] = 0.33 mM) (●).

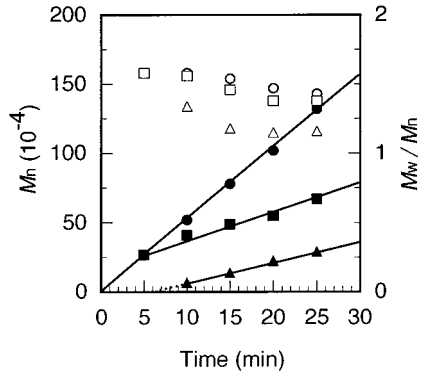

Figure 2. Plots of M_n and M_w/M_n against polymerization time in propene polymerization with [ArN(CH_2)$_3$NAr]$TiMe_2$: dried MMAO/SiO_2 system ([Ti] = 0.67 mM), M_n (■), M_w/M_n (□); dried MMAO/SiO_2 system ([Ti] = 0.33 mM), M_n (●), M_w/M_n (○); corresponding homogeneous system ([Ti] = 0.67 mM), M_n (▲), M_w/M_n (△).

the results of which are also shown in Figure 2. In the initial stage, the dried MMAO/SiO_2 system gave a high molecular weight polypropene even for 5 min although the homogeneous system showed the induction period. The M_n values of 0.33 mM of [Ti] increased almost linearly with increasing polymerization time accompanied by narrowing the M_w/M_n values, which were slightly broader than that of the homogeneous system, and the straight line on M_n against the polymerization time went through the origin. These results indicate the living nature of the dried MMAO/SiO_2 system.

To confirm the living character of this system, we conducted postpolymerization with the dried MMAO/SiO_2 system using 0.33 and 0.67 mM of [Ti]: the same amount of propene was added after 1 h of polymerization, and the polymerization was continued for another 1 h. These results are summarized in Table 1. After the postpolymerization, the polymer yield and the M_n value became almost double those of the prepolymer, keeping the N value constant regardless of the amount of Ti used. Therefore, there is no doubt that the [ArN(CH_2)$_3$-NAr]$TiMe_2$−dried MMAO/SiO_2 system practically conducted living polymerization of propene although the M_w/M_n value was slightly broader than that expected for perfect living polymerization. Since the living po-

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Table 1. Postpolymerization of Propene with [ArN(CH$_2$)$_3$NAr]TiMe$_2$−Dried MMAO/SiO$_2$[a]

entry	[Ti] (mM)	propene (g)	yield (g)	conv (%)	M_n[b] ($\times 10^{-4}$)	M_w/M_n[b]	N[c] (mol/(mol of Ti))
1	0.67	0.63	0.60	95	32.6	1.50	0.09
2	0.67	0.63 + 0.63[d]	1.15	91	57.0	1.40	0.10
3	0.33	0.20	0.19	95	59.1	1.56	0.03
4	0.33	0.20 + 0.20[d]	0.36	90	115.0	1.44	0.03

[a] Polymerization conditions: heptane = 30 mL, [Al] = 0.13 M, 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 chains calculated from yield and M_n. [d] After propene polymerization for 1 h, propene was again added, and the polymerization was conducted for another 1 h.

Table 2. Effect of Cocatalysts on Propene Polymerization with [ArN(CH$_2$)$_3$NAr]TiMe$_2$[a]

entry	cocatalyst	yield (g)	activity (kg of PP/(mol of Ti h))	M_n[b] ($\times 10^{-4}$)	M_w/M_n[b]	N[c] (mol/(mol of Ti))
5[d]	MMAO/SiO$_2$	0.07	8	51.2	1.41	0.01
6[d]	dried MMAO/ SiO$_2$	1.96	235	66.1	1.34	0.15
7[e]	dried MMAO/ SiO$_2$	0.37	89	124.0	1.43	0.03
8[f]	dried MMAO	2.68	321	29.2	1.16	0.46

[a] Polymerization conditions: heptane = 30 mL, propene = 1 atm, temperature = 0 °C, time = 25 min. [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 chains calculated from yield and M_n. [d] [Ti] = 0.67 mM, [Al] = 0.13 M. [e] [Ti] = 0.33 mM, [Al] = 0.13 M. [f] [Ti] = 0.67 mM, [Al] = 0.27 M: corresponding homogeneous system.

lymerization was confirmed in the dried MMAO/SiO$_2$ system, the declined slope around 5 min in the dried MMAO/SiO$_2$ system with 0.67 mM of [Ti] is then ascribed to the decrease in the monomer concentration caused by ineffective stirring but not to the deactivation of active species.

The results obtained with different cocatalysts are summarized in Table 2, which clearly shows that polymerization features strongly depended on the kind of cocatalysts. Although the MMAO/SiO$_2$ and dried MMAO/SiO$_2$ systems gave polyporopene, the dried MMAO/SiO$_2$ system showed a higher activity than the MMAO/SiO$_2$ system. When the same amount of titanium complex was used, the M_n and M_w/M_n values of polymers obtained in both systems were almost the same. Consequently, the number of polymer chains per Ti (N) in the dried MMAO/SiO$_2$ system was higher than that in the MMAO/SiO$_2$ system. The difference in the cocatalyst ability between MMAO/SiO$_2$ and dried MMAO/SiO$_2$ can be interpreted as follows. When MMAO is used, free trialkylaluminums in MMAO competitively react with surface silanol to reduce the amount of MMAO supported on SiO$_2$. On the other hand, dried MMAO contains less trialkylaluminums and is effectively supported on SiO$_2$, and the N value becomes larger than that of the MMAO/SiO$_2$ system. The low N value of the dried MMAO/SiO$_2$ system with 0.33 mM of [Ti] is probably due to impurities in the system. The homogeneous system shows the highest N value, namely the highest initiation efficiency.

The microtacticity of polypropene determined by ^{13}C NMR showed that the produced polymer was statistically atactic, irrespective of the cocatalyst employed.

In summary, the [ArN(CH$_2$)$_3$NAr]TiMe$_2$−dried MMAO/SiO$_2$ system conducted living polymerization of propene at 0 °C. The results obtained in this paper show the potentiality of dried MMAO/SiO$_2$ as a cocatalyst for living polymerization of olefins with supported single-site catalysts.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Doi, Y.; Suzuki, S.; Soga, K. *Macromolecules* **1986**, *19*, 9, 2896−2900.
(2) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664−11665.
(3) Fukui, Y.; Murata, M.; Soga, K. *Macromol. Rapid Commun.* **1999**, *20*, 637−640.
(4) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134−5135.
(5) Saito, J.; Mitani, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Matsugi, T.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2001**, 566−576.
(6) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 3184−3188.
(7) Hasan, T.; Ioku, A.; Nishii, K.; Shiono, T.; Ikeda, T. *Macromolecules* **2001**, *34*, 3142−3145.
(8) Liu, B.; Matsuoka, H.; Terano, M. *Macromol. Rapid Commun.* **2001**, *22*, 1−24.
(9) Blunt, H. W. (Hercules Inc.), US 4408019, **1983**; *Chem. Abstr.* **1984**, *100*, 7417h.
(10) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347−1376.
(11) Fink, G.; Steinmetz, B.; Zechilin, J.; Przbyla, C.; Tesche, B. *Chem. Rev.* **2000**, *100*, 1377−1390.
(12) Corradini, P.; Busico, V.; Cipullo, R. In *Catalyst Design For Tailor-Made Polyolefins;* Soga, K., Terano, M., Eds.; Kodansya: Tokyo, 1994; p 21.
(13) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008−10009.
(14) Hagimoto, H.; Shiono, T.; Ikeda, T. *Macromol. Rapid Commun.* **2002**, *23*, 73−76.
(15) Complete details are given in the Supporting Information.

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