

Combination System of Fluorine-containing Phenoxy-imine Ti Complex and Chain Transfer Agent: A New Methodology for Multiple Production of Monodisperse Polymers

Makoto Mitani, Jun-ichi Mohri, Rieko Furuyama, Seiichi Ishii, and Terunori Fujita*
Catalysis Science Laboratory, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba 299-0265

(Received October 18, 2002; CL-020889)

Multiple production of Zn-terminated polyethylene with narrow molecular weight distribution was attempted using the combination of fluorine-containing phenoxy-imine Ti complexes and Et_2Zn . One of the two complexes promotes living polymerization in the presence of ethylene and Et_2Zn and, moreover, undergoes chain transfer with Et_2Zn in the absence of ethylene, resulting in a rare example of multiple production of nearly monodisperse Zn-terminated polyethylenes which are valuable intermediates for functional polymers and block copolymers.

Living olefin polymerization techniques allow the synthesis of a wide variety of precisely-controlled polymers, such as monodisperse polymers, end-functionalized polymers and block copolymers, all of which are potentially high-performance polymers. Recent advances in the rational design of well-defined transition metal complexes for olefin polymerization have resulted in the introduction of fairly high performance catalysts for living olefin polymerization.^{1,4,5}

Despite the great progress made with the living polymerization catalysts, one fundamental limitation remains: a living polymerization catalyst can only make one polymer chain during the course of the polymerization, resulting in an extremely low productivity compared with an existing olefin polymerization catalyst. Although using a chain transfer agent can increase the productivity of a living polymerization system, the system loses its living nature and no longer provides the precisely-controlled polymers. One solution to this problem is to develop catalysts that incorporate monomers without termination even in the presence of a chain transfer agent² and undergo chain transfer only in the absence of a reacting monomer. Such catalysts will provide a new methodology for the multiple production of the aforementioned precisely-controlled polymers.

Recently, we discovered a new series of Ti complexes with fluorine-containing phenoxy-imine chelate ligands (fluorinated Ti-FI Catalysts)³ which are capable of initiating living polymerization of propylene as well as ethylene.^{4,5} With these results, we have tried the multiple production of the precisely-controlled polymers using fluorinated Ti-FI Catalysts and chain transfer agents. Here, we

describe the multiple production of nearly monodisperse Zn-terminated polyethylenes using these systems.

In this study, we employed Et_2Zn as a chain transfer agent^{2c,d} since Zn-terminated polyolefins can be transformed to various functional polymers and block copolymers. Ti-FI Catalysts used in this research⁶ and polymerization methods⁷ are summarized in Figure 1. Firstly, the living nature of complex **1**/MAO system under the given conditions was confirmed. Thus, polymerization results with **1**/MAO using ethylene-saturated toluene for 10 min (Table 1, run 1), and those with the same polymerization followed by stirring under nitrogen for 30 min and then ethylene feed to the system (runs 2, 3) indicated the linear relationship between M_n and polymer yield. These results showed that no spontaneous chain transfer and/or termination occurred despite the absence of monomer (runs 1–3 and Figure 2, left), and in the second polymerization, the polyethylene successfully grew in a living fashion. With these baseline results established, the multiple production of narrow molecular weight distribution polymers using Et_2Zn as a chain transfer agent was attempted. The same polymerization experiment was run, and then Et_2Zn (80:1 ratio of Zn:Ti) was added to the reaction mixture and stirred for 5 min under N_2 . Additional ethylene was fed (20 L/h, 5 min) to the resulting mixture. The effects of the chain transfer reaction are clearly revealed by the decrease of polymer molecular weight in the presence of Et_2Zn . A comparison of GPC curves (runs 3, 4 and Figure 3, left) indicated that the

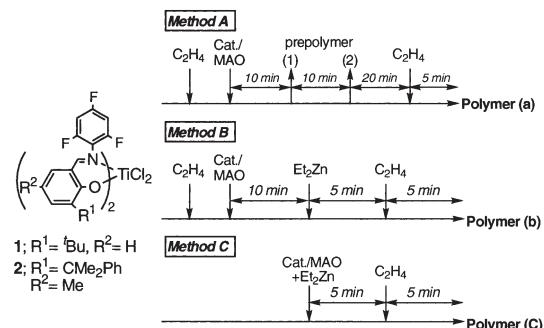


Figure 1. Complexes **1**, **2** and polymerization methods A–C.

Table 1. Results of ethylene polymerization with complexes **1** and **2**/MAO^a

Run	Complex	Polym. method	Polymer	Et_2Zn /mmol	Polymer yield/g	$M_n^b /10^3$	M_w/M_n^b
1	1	A	(1) ^c	—	0.816	37.5	1.07
2	1	A	(2) ^c	—	0.801	37.0	1.08
3	1	A	(a)	—	1.537	67.7	1.13
4	1	B	(b)	1.6	1.411	23.8	1.57
5	1	C	(c)	1.6	0.762	7.8	1.83
6	2	A	(1) ^c	—	0.721	36.7	1.20
7	2	A	(a)	—	1.559	70.1	1.14
8	2	B	(b)	1.6	1.638	37.1	1.31
9	2	C	(c)	1.6	0.945	32.5	1.26

^aConditions: complex (0.02 μmol), cocat. MAO (2.5 mmol), 1 atm, toluene 250 mL. ^bDetermined by GPC using polyethylene calibration. ^cPrepolymer.

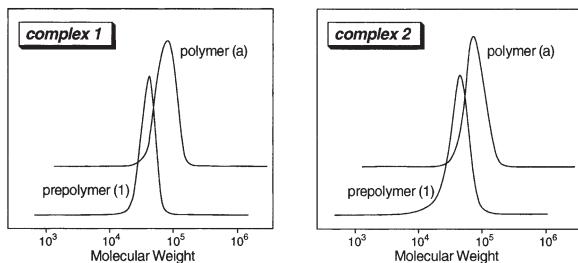


Figure 2. GPC profile of the polyethylenes obtained by complexes **1** and **2** (method A).

resultant polymer (b) does not contain higher molecular weight polymer chains, suggesting that quantitative chain transfer occurred with Et_2Zn . However, the GPC curve for (b) was broadened towards low molecular weight region, which showed that the second polymerization proceeded accompanied by considerable chain transfers by residual Et_2Zn , and thus the **1**/MAO catalyst system lost its living nature under the conditions employed.

Alternatively, complex **2** having a cumyl group instead of the *tert*-butyl group at the R^1 position was also investigated as a catalyst for the multiple production of narrow molecular weight distribution polymers. The living nature of the polymerization for **2**/MAO was demonstrated by the linear increase in M_n with polymer yield (runs 6, 7 and Figure 2, right). The multiple production of Zn-terminated polyethylenes with narrow molecular weight distributions was performed by **2**/MAO using the same procedures as **1**/MAO.

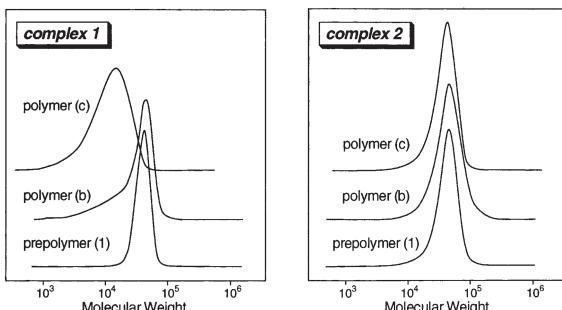


Figure 3. GPC profile of the polyethylenes obtained by complexes **1** and **2** (method B and C).

Surprisingly, the GPC curve of the resulting polymer (b) is unimodal and, at the same time, M_n and M_w/M_n values are substantially the same as the prepolymer. Moreover, no peak broadening and no low molecular weight tail were detected (run 8 and Figure 3, right). These results indicate that the **2**/MAO system undergoes chain transfer with Et_2Zn in the absence of ethylene and promotes living polymerization in the presence of ethylene and Et_2Zn .⁸ The unique living polymerization nature of **2**/MAO was further confirmed by polymerization using method C. Thus, polymerization conducted by passing ethylene over a mixture of **2**, MAO, and Et_2Zn produced narrow M_w/M_n (1.26) polymer having practically the same M_n as the prepolymer, confirming that the **2**/MAO system promotes living ethylene polymerization in the presence of Et_2Zn (run 9 and Figure 3, right). These results are in stark contrast to those found for the **1**/MAO/ Et_2Zn system, which provided broadened M_w/M_n (1.83) polymer with a low M_n of 7800 (run 5 and Figure 3, left). These results suggest that **2**/MAO/ Et_2Zn system is capable of catalytically producing nearly monodisperse Zn-terminated polyethylenes using alternate reactions of living

polymerization and chain transfer, which can be realized by an intermittent monomer feed.

The differences in polymerization behavior in the presence of Et_2Zn suggest that the steric bulk of the R^1 position plays a key role in the mechanism of the multiple production of Zn-terminated polyethylenes with narrow molecular weight distributions. The sterically larger cumyl group (compared to the *tert*-butyl group) at the R^1 position may give sufficient steric protection to a living polymer from Et_2Zn .

In summary, the multiple production of nearly monodisperse Zn-terminated polyethylenes using the combination of complex **2**/MAO and Et_2Zn has been introduced, which represents a rare example of the multiple production of narrow molecular weight distribution polymers. This chemistry will provide a convenient and efficient route to prepare Zn-terminated polyolefins which are valuable intermediates for producing functionalized polyolefins and block copolymers containing a polyolefin and a polar polymer segment. Efforts to expand the scope and define the limitations of the chemistry introduced are in progress, and results will be reported in due course.

We would like to thank Dr. M. Mullins for his fruitful discussions and suggestions.

References and Notes

- 1 For a recent review see; G. W. Coates, P. D. Hustad, and S. Reinartz, *Angew. Chem., Int. Ed.*, **41**, 2236 (2002).
- 2 For example; a) K. Koo and T. J. Marks, *CHEMTECH*, **29**, 13 (1999). b) T. C. Chung, G. Xu, Y. Lu, and Y. Hu, *Macromolecules*, **34**, 8040 (2001). c) H. Kuroawa, T. Shiono, and K. Soga, *Macromol. Chem. Phys.*, **195**, 1381 (1994). d) T. Shiono, H. Kuroawa, and K. Soga, *Macromolecules*, **28**, 437 (1995). e) S. Kojo, M. Kioka, and N. Kashiwa, *Polymer*, **36**, 5015 (1995).
- 3 a) S. Matsui, M. Mitani, J. Saito, Y. Tohri, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, and T. Fujita, *J. Am. Chem. Soc.*, **123**, 6847 (2001). b) H. Makio, N. Kashiwa, and T. Fujita, *Adv. Synth. Catal.*, **344**, 477 (2002).
- 4 a) J. Saito, M. Mitani, J. Mohri, Y. Yoshida, S. Matsui, S. Ishii, S. Kojo, N. Kashiwa, and T. Fujita, *Angew. Chem., Int. Ed.*, **40**, 2918 (2001). b) J. Saito, M. Mitani, J. Mohri, S. Ishii, Y. Yoshida, T. Matsugi, S. Kojo, N. Kashiwa, and T. Fujita, *Chem. Lett.*, **2001**, 576. c) S. Kojo, T. Matsugi, J. Saito, M. Mitani, T. Fujita, and N. Kashiwa, *Chem. Lett.*, **2001**, 822. d) J. Saito, M. Mitani, M. Onda, J. Mohri, S. Ishii, Y. Yoshida, T. Nakano, H. Tanaka, T. Matsugi, S. Kojo, N. Kashiwa, and T. Fujita, *Macromol. Rapid Commun.*, **22**, 1072 (2001). e) M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojo, T. Matsugi, N. Kashiwa, and T. Fujita, *J. Am. Chem. Soc.*, **124**, 3327 (2002). f) M. Mitani, R. Furuyama, J. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa, and T. Fujita, *J. Am. Chem. Soc.*, **124**, 7888 (2002).
- 5 a) J. Tian, P. D. Hustad, and G. W. Coates, *J. Am. Chem. Soc.*, **123**, 5134 (2001). b) P. D. Hustad, J. Tian, and G. W. Coates, *J. Am. Chem. Soc.*, **124**, 3614 (2002). c) M. Lamberti, D. Pappalardo, A. Zambelli, and C. Pellecchia, *Macromolecules*, **35**, 658 (2002).
- 6 Spectral data of the complexes: Complex **1**; see Ref. 4e. Complex **2**: $\text{TiC}_{46}\text{H}_{38}\text{N}_2\text{O}_2\text{F}_6\text{Cl}_2$, ^1H NMR (270 MHz, CDCl_3 , TMS): δ 1.52 (s, 3H, cumyl-Me), 1.76 (s, 3H, cumyl-Me), 2.18 (s, 3H, aromatic-Me), 6.28–6.37 (m, 1H, aromatic-H), 6.67–6.74 (m, 1H, aromatic-H), 6.87 (d, 1H, J = 2.4 Hz, aromatic-H), 6.99 (d, 1H, J = 1.6 Hz, aromatic-H), 7.16–7.33 (m, 5H, aromatic-H), 8.08 (d, 1H, J = 1.4 Hz, CHN); Anal. Found: C, 61.83; H, 4.00; N, 2.83%; Calcd for $\text{TiC}_{46}\text{H}_{38}\text{N}_2\text{O}_2\text{F}_6\text{Cl}_2$: C, 62.53; H, 4.33; N, 3.17%.
- 7 **General polymerization procedure:** Flow of ethylene gas (100 L/h) was charged into 250 mL of toluene at 25 °C. After 5 min, the ethylene gas feed was stopped, and the toluene solution was kept under N_2 at 25 °C. To the resulting solution, toluene solutions of MAO (1.0 M, 2.5 mL) and complex **1** or **2** (4 mM, 5.0 mL) were added to start polymerization. Subsequent operations are as follows. **Prepolymer synthesis:** After 10 min {prepolymer (1)} or 20 min {prepolymer (2)}, *s*-butyl alcohol (10 mL) was added to terminate the polymerization. **Method A:** After 40 min, the ethylene gas feed (20 L/h) was initiated to start postpolymerization (5 min), and then *s*-butyl alcohol (10 mL) was added to terminate the polymerization. **Method B:** After 10 min, a 1.0 M *n*-hexane solution of diethylzinc (1.60 mL, 1.60 mmol) was added and stirred for 5 min. To the resulting mixture, the ethylene gas feed (20 L/h) was initiated to start re-polymerization (5 min), and then *s*-butyl alcohol (10 mL) was added to terminate the polymerization.
- 8 The possibility cannot be ruled out that some chain transfer reactions occur during the course of the re-polymerization. Detailed studies concerning polymerization and chain transfer reactions are under way.