Macromolecules **2004,** *37,* 5145−5148

Articles

Copolymerization of Propylene and Polar Allyl Monomer with Zirconocene/Methylaluminoxane Catalyst: Catalytic Synthesis of Amino-Terminated Isotactic Polypropylene

Hideaki Hagihara,*,† Kenji Tsuchihara,† Junichi Sugiyama,†
Kazuhiko Takeuchi,† and Takeshi Shiono*,‡

Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Central 5-1, 1-1-1 Higashi, Tsukuba 305-8565, Japan, and Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Yokohama 226-8503, Japan

Received August 21, 2003; Revised Manuscript Received April 9, 2004

ABSTRACT: The copolymerizations of propylene with allyl monomers carrying alcohol or amine were conducted by the *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride/methylaluminoxane catalyst system. The allyl monomers were pretreated by alkylaluminum before the polymerization. Although the efficiency of the introduction of allyl alcohol-based comonomer was extraordinary low (0.04−0.08 mol % in polymer), the trimethylaluminum-treated allylamine was found to be introduced more effectively (0.65 mol % in polymer). The ^{13}C NMR study indicated that the position of allylamine unit in the copolymer was influenced by the kind of alkylaluminum used at the polymerization. In the presence of trimethylaluminum, the terminally aminated polypropylene was obtained ([amino end polymer]/[whole polymer] = 0.83). In the presence of triisobutylaluminum, however, the allylamine unit is located both on the main chain and at the chain end. The end-aminated polymer was probably obtained due to the formation of dormant species after the insertion of the comonomer followed by the chain transfer to alkylaluminum.

Introduction

Recently, the introduction of a functional group into polyolefin by means of copolymerization has become one of the most important subjects of the olefin polymerization. It is well-known that α-olefins containing a polar group with long methylene spacers (such as 5-hexen-1-ol and 10-undecen-1-ol) could be applicable for the copolymerization with olefins (ethylene, propylene, and so on) by the traditional olefin polymerization catalyst systems (Ziegler−Natta and metallocene), in general, although the additional alkylaluminum is required in order to mask the polar group. So far, numerous studies on the spacer monomers having long CH_2 chain were reported.[1−18] However, there are few investigations about the copolymerization with α-olefin having only one CH_2 spacer (allyl monomer) although several allyl monomers having a useful polar group (such as allyl alcohol and allylamine) are more commercially available than the long spacer monomer.

In 1983, Arit et al. first reported the copolymerization of allyl monomer and olefin.[19] The copolymerization of allyl alcohol and propylene was conducted with the $TiCl_3/AlEt_2Cl$ catalyst. Although the activity was very low, isotactic propylene containing 4 wt % of allyl alcohol unit was obtained. Recently, Imuta et al. reported the copolymerization of ethylene and allyl alcohol with the bulky metallocene/methylaluminoxane/trialkylaluminum catalyst system.[20] In that case, the kind of alkylaluminum greatly influenced the structure of copolymer produced. In the presence of trimethylaluminum, for instance, terminally hydroxylated polyethylene was obtained due to the formation of dormant species by the insertion of trimethylaluminum-treated allyl alcohol, followed by the chain transfer to free trimethylaluminum. However, research on copolymerization of olefin and polar allyl monomer is insufficient at present. In this report, we investigated the copolymerization of propylene and two kinds of allyl monomers (allyl alcohol and allylamine) with isospecific zirconocene catalyst.

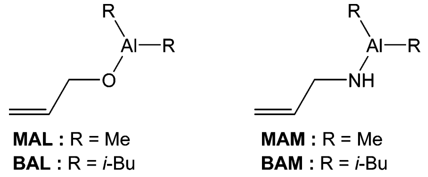


Figure 1. Allyl monomers treated by alkylaluminums.

Experimental Section

Allyl alcohol and allylamine were pretreated with 1 mol equiv of alkylaluminum (trimethyl- or triisobutyl-) at room temperature for 3 h−3 days (Figure 1, see Supporting Information). Commercially obtained methylaluminoxane (MAO, contaminated by 30% trialkylaluminum), trimethylaluminum (TMA), triisobutylaluminum (TIBA), and tri-*n*-octylaluminum (TOA) were used without further purification. The alkylaluminum-free MAO (d-MAO) was prepared by the vacuum-

---

[†] National Institute of Advanced Industrial Science and Technology.
[‡] Tokyo Institute of Technology.
* Authors to whom correspondence should be addressed.

10.1021/ma030436+ CCC: $27.50 © 2004 American Chemical Society
Published on Web 06/10/2004

Table 1. Copolymerization of Propylene and Allyl Monomer[a]

run	monomer	MAO	AlR_3[b]	time (min)	yield (g)	M_n[c] (× 10^{-3})	M_w/M_n[c]	content[d] (mol %)	mmmm[e] (%)	T_m[f] (°C)	ΔH[f] (cal/g)
1	MAL	MAO		30	0.15	7.4	2.00	0.04	84.0	142.8	20.6
2	BAL	MAO		10	0.95	15.8	1.71	0.08	83.9	142.3	19.4
3	MAM	MAO		30	0.19	7.4	1.67	0.65	83.3	141.7	17.7
4	BAM	MAO		30	0.05	7.7	1.70	0			
5	MAM	d-MAO		30	0						
6	MAM	d-MAO	$AlMe_3$	30	0.31	6.5	1.76	0.45	83.6	141.5	18.1
7	MAM	d-MAO	$Al\textit{i}\text{-}Bu_3$	30	0.48	7.4	1.60	0.63	83.8	141.0	16.8
8	MAM	d-MAO	$AlOct_3$	30	trace						
9[g]		MAO		10	6.64	9.9	2.73	0	81.0	138.7	18.2

[a] Conditions: Zr = 0.01 mmol, Al(MAO)/Zr = 300, comonomer = 48 mmol, toluene = 30 mL, RT. [b] Additional alkylaluminum (24 mmol) at the polymerization. [c] Determined by GPC using PS standard. [d] Determined by ^1H NMR. [e] Isotactic pentad determined by ^{13}C NMR. [f] Melting point and heat of fusion determined by DSC (second run). [g] Control run.

drying according to the literature.[21] Copolymerization conducted by the semibatch wise method in the atmospheric pressure of propylene by the *rac*-dimethylsilylbis(1-indenyl)-zirconium dichloride [*rac*-$Me_2Si(1\text{-}Ind)_2ZrCl_2$]/ethylaluminoxane catalyst. The general procedure is as follows: To a 50 mL glass reactor were added the prescribed amounts of MAO/toluene suspension and alkylaluminum-protected allyl monomer, as described above. After addition of trialkylaluminum if necessary, gaseous propylene was introduced to the reactor at room temperature. Polymerization was started by addition of zirconocene/toluene solution. After the polymerization, the reactant was quenched by isopropyl alcohol and then slowly poured into dilute HCl/methanol. The precipitated polymer was filtered and washed with methanol and then dried under vacuum at 60 °C.

Molecular weights (M_n) and molecular weight distributions (M_w/M_n) of copolymers were measured using a PL GPC-220 with a DRI detector at 140 °C using trichlorobenzene as the solvent. The ^1H and ^{13}C NMR spectra were recorded at 120 °C on a JEOL GSX-270 using tetrachloroethane-d_2 as the solvent. The resonances observed were assigned according to the literature.[22−25] Melting points and heats of fusion were determined by SII DSC6200. DSC samples were encapsulated in aluminum pans and scanned at 10 °C/min, and data of the second heating were used for analysis.

Results and Discussion

The results for the copolymerizations are summarized in Table 1. Values of M_n and M_w/M_n determined by GPC and contents of allyl monomers determined by ^1H NMR are also listed. Efficiencies of the introduction of allyl alcohol-based comonomers (MAL and BAL) were extraordinarily low (runs 1 and 2, 0.04−0.08 mol %). It was not enough to analyze the microstructure of copolymer precisely. On the other hand, it was found that the allylamine-based comonomer (MAM) was introduced into the copolymer more effectively (run 3, 0.65 mol %). These results indicate that the efficiency of the introduction of comonomer was greatly influenced by electronic nature of polar group. However, in the case of similar comonomer BAM, the activity was very low and the allylamine units were not introduced (run 4). It indicates that the deactivation occurred in this system. One of the plausible explanations is that BAM was contaminated by slight unprotected allylamine that caused deactivation of active center. Unfortunately, viscous oily property of BAM did not allowed effective purifications. The other explanation is that the lone pair electrons on the nitrogen give rise to a major fulfillment of electron deficiency with active center. However, this explanation might be inadequate in this case because we previously found that the TIBA was more effective protective reagent than TMA in the copolymerization of olefin and 5-hexen-1-ol.

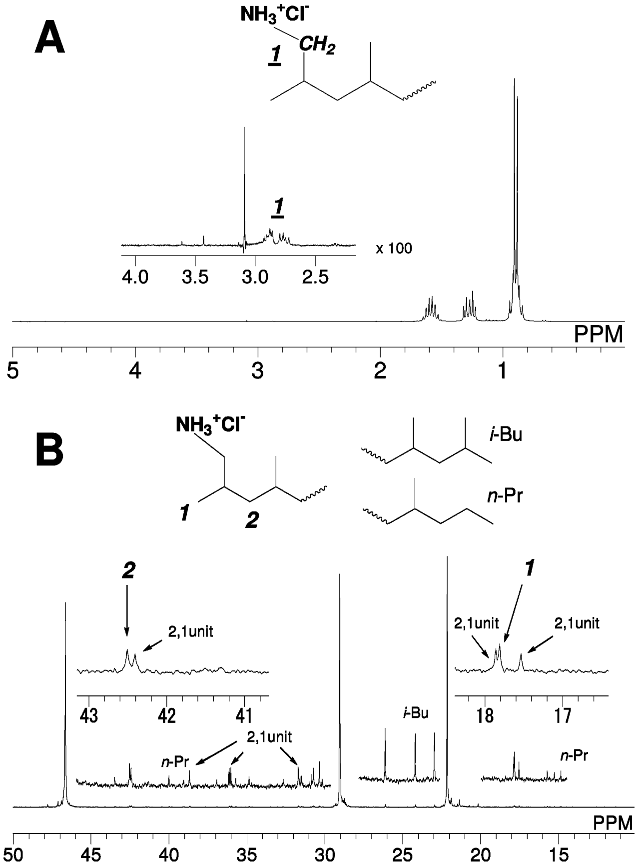
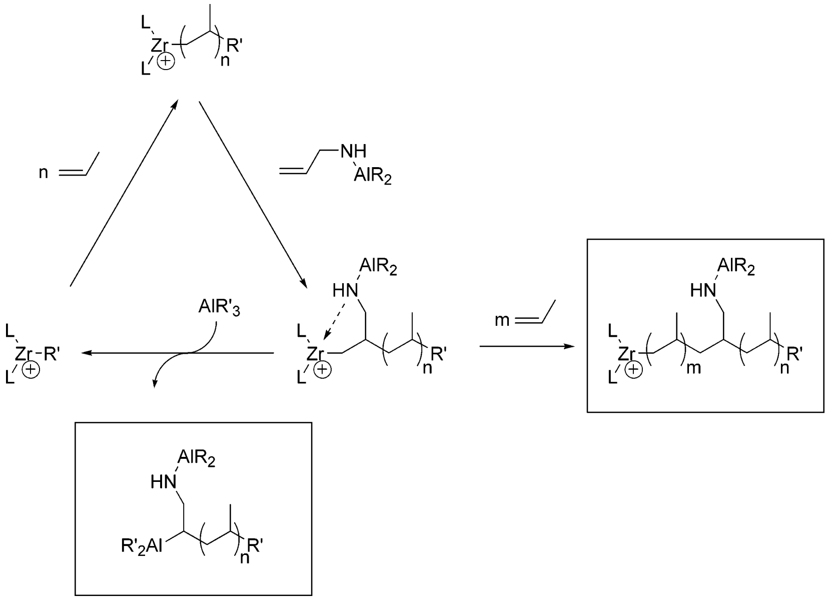


Figure 2. ^1H and ^{13}C NMR spectra of poly(allylamine-*co*-propylene) obtained in run 3.

The microstructures of the obtained poly(propylene-*co*-allylamine) were investigated by NMR study in detail. Figure 2 shows the ^1H (A) and ^{13}C (B) NMR spectra of polymer obtained in run 3. In the ^1H NMR spectrum, a resonance assignable to methylene protons adjacent to the amino group (hydrochloride) was observed at 2.7−2.9 ppm. A split pattern of the resonance indicated that two protons of the methylene were not equivalent. In the ^{13}C NMR spectrum, in addition to the main chain and inversion structure (2,1 insertion unit), several chain end structures were observed. The peaks at 26.12, 24.20, and 22.95 ppm were assigned to isopropyl chain end. The peaks at 39.99 and 14.86 ppm were also assigned to *n*-propyl chain end. In addition, other new resonances appeared at 42.53 and 17.81 ppm. These peaks may be assignable to the chain end structure containing a amino group, $-\mathbf{C}H_2(CH_2NH_2)CHCH_3$ and $-CH_2(CH_2NH_2)CH\mathbf{C}H_3$, respectively. (The chemical shifts for these calculated by CS ChemNMR

Scheme 1. A Plausible Mechanism of Allylamine−Propylene Copolymerization



Pro 6.0 were 41.5 and 17.5 ppm, respectively.) Unfortunately, the resonance of methylene carbon adjacent to amino group could not be observed. The ^{13}C NMR study of the 2-methylbutylamine hydrochloride as a model compound implied that the peak of it should appear at about 46 ppm, which must be overlapped by the peak of methylene carbon of the main chain (see Supporting Information). The ratio of [amino end polymer]/[whole polymer] calculated by the intensities of resonances described above was 0.83. On the other hand, it was hard to observe any other structures containing amino group (e.g., allylamine unit in the main chain) in this spectrum. It is also hard to detect the unsaturated end group, although the existence of the *n*-propyl chain end implied formation of unsaturated $CH_2{=}CH(CH_3)-$ chain end by β-H elimination of the propagating chain. It seems appropriate that the unsaturated end structures were very minor in this product. The "amino" terminally functionalized polypropylene was probably formed due to the formation of dormant species after the insertion of MAM followed by the chain transfer reaction with free TMA in the MAO (Scheme 1). Similar mechanisms of chain transfer to trialkylaluminum were described in our previous paper and the paper of Imuta et al.[17,20]

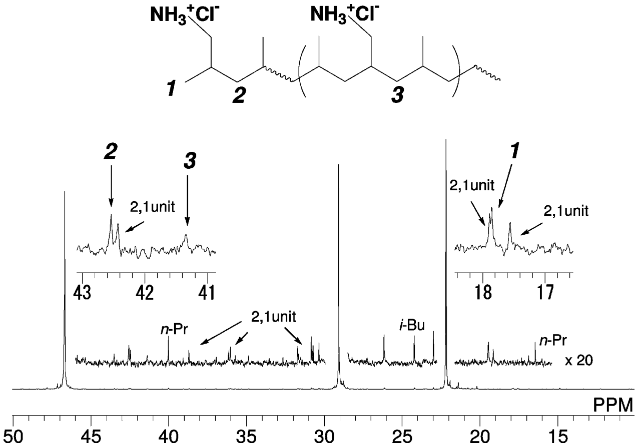


Figure 3. ^{13}C NMR spectrum of poly(allylamine-*co*-propylene) obtained in run 7.

We expected that the allylamine unit could be introduced in the main chain of polypropylene, if the chain transfer to aluminum was depressed by removal of TMA from the polymerization system. Therefore, the copolymerization with the alkylaluminum-free MAO (d-MAO) was examined. The polymerization did not proceed with only d-MAO (run 5), probably due to the deactivation of catalyst and/or formation of dormant species. However, the extra addition of trialkylaluminum at the polymerization made it possible to obtain the polymer (runs 6−8).

The ^{13}C NMR analysis revealed that the position of allylamine unit was influenced by the kind of additional alkylaluminum. Similar to the MAO system, the end amination polypropylene was obtained with the addition of TMA (run 6). On the other hand, the polymer obtained with the addition of TIBA included not only the chain end allylamine unit but also the allylamine unit that was located in the main chain (run 7). Figure 3 shows the spectrum of polymer obtained in run 7. The new resonance assignable to the inner allylamine unit, $-\mathbf{C}H_2CH(CH_2NH_2)\boldsymbol{C}H_2-$, was observed at 41.33 ppm (the chemical shift calculated by CS ChemNMR Pro 6.0 was 39.6 ppm). The ratio of terminal amino group and inner amino group estimated from the intensities of ^{13}C NMR resonances was terminal:inner = 0.7:0.3. The results revealed that positions of the allylamine units were dependent upon the kind of trialkylaluminum. However, it seemed strange that the contents of allylamine and the molecular weight of run 7 were very similar to those of run 3. The polymer obtained in run 7 might be a mixture of copolymer and homo-polypropylene, which was produced due to the chain transfer to TIBA from the normal polypropylene propagating chain.

The thermal properties of copolymers are also listed in Table 1. It was found the melting point (T_m) and the heat of fusion (ΔH) of copolymers obtained were similar to the isospecific homo-polypropylene, although the values seemed to be slightly decreased with increasing contents of allyl monomers. The isotactic pentad (mmmm) and T_m of the control run were lower than the others. The reason for that was probably due to reaction heat of homo-polymerization, which demonstrated very high activity. Therefore, functionalization of polypropylene was achieved without deterioration of thermal properties.

Consequently, it was found that the TMA-pretreated allylamine was useful for the synthesis of amino-functionalized polypropylene and that the microstructure of the copolymer can be controlled by the polymerization conditions. In particular, it was noteworthy that the terminally aminated isotactic polypropylene could be obtained effectively in the presence of TMA.

Acknowledgment. This work was supported by the New Energy and Development Organization (NEDO) for the Project on Nanostructured Polymeric Materials.

Supporting Information Available: Details of comonomer (MAL, BAL, MAM, and BAM) preparation and ^{1}H NMR analysis; supplementary ^{1}H spectra of copolymer obtained in runs 1, 2, 6, and 7; supplementary ^{13}C NMR spectrum of copolymer obtained in run 6; ^{1}H and ^{13}C NMR spectra of 2-methylbutylamine hydrochloride as a model compound for end-aminated polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.
(2) Aaltonen, P.; Lofgren, B. *Macromolecules* **1995**, *28*, 5353.
(3) Aaltonen, P.; Fink, G.; Lofgren, B.; Seppala, J. *Macromolecules* **1996**, *29*, 5255.
(4) Hakala, K.; Helaja, T.; Lofgren, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1966.
(5) Aaltonen, P.; Lofgren, B. *Eur. Polym. J.* **1997**, *33*, 1187.
(6) Hakala, K.; Lofgren, B.; Helaja, T. *Eur. Polym. J.* **1998**, *34*, 1093.
(7) Marques, M. M.; Correia, S. G.; Ascenso, J. R.; Ribeiro, A. F. G.; Gomes, P. T.; Dias, A. R.; Foster, P.; Rausch, M. D.; Chien, J. C. W. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2457.
(8) Vogl, O. *J. Macromol. Sci., Chem.* **1985**, *A22*, 541.
(9) Purgett, M. D.; Xie, S.; Bansleben, D. A.; Vogl, O. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 657.
(10) Purgett, M. D.; Vogl, O. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 2051.
(11) Datta, S.; Ver Strate, G.; Kresge, E. N. *ACS Div. Polym. Chem: Polym. Prepr.* **1992**, *33*, 899.
(12) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679.
(13) Schulz, D. N.; Bock, J. *J. Macromol. Sci., Chem.* **1991**, *A28*, 1235.
(14) Wilén, C. E.; Luttikhedde, H.; Hjertberg, T.; Näsman, J. H. *Macromolecules* **1996**, *29*, 8569.
(15) Tsuchida, A.; Bollen, C.; Sernetz, F. G.; Frey, H.; Mülhaupt, R. *Macromolecules* **1997**, *30*, 2818.
(16) Ramakrishnan, S.; Berluche, E.; Chung, T. C. *Macromolecules* **1990**, *23*, 378.
(17) Hagihara, H.; Murata, M.; Uozumi, *T. Macromol. Rapid Commun.* **2001**, *22*, 353.
(18) Hagihara, H.; Tsuchihara, K.; Takeuchi, K.; Murata, M.; Ozaki, H.; Shiono, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 52.
(19) Arit, K. P.; Binsack, R.; Grogo, U.; Neuray, D. U.S. Patent 4423196, 1983; *Chem. Abstr.* **1984**, *100*, 139804.
(20) Imuta, J.; Kashiwa, N.; Toda, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1176.
(21) Hasan, T.; Ioku, A.; Nishii, K.; Shiono, T.; Ikeda, T. *Macromolecules* **2001**, *34*, 3142.
(22) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617.
(23) Hayashi, T.; Inoue, Y.; Chujo, R.; Asakura, T. *Macromolecules* **1988**, *21*, 2675.
(24) Tsutsui, T.; Ishimaru, N.; Mizuno, A.; Toyota, A.; Kashiwa, N. *Polymer* **1989**, *30*, 1350.
(25) Shiono, T.; Soga, K. *Macromolecules* **1992**, *25*, 3356.

MA030436+