Direct Introduction of Primary Amine into Nonpolar Polyolefins Mediated by a New Metallocene IFZ Catalyst. A New Synthetic Approach for One-pot Synthesis of Allyl Amine-capped Polyolefins

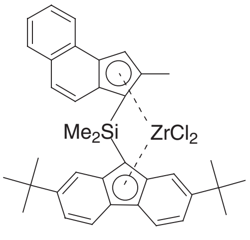
Jun-ichi Imuta,* Yoshihisa Toda,[†] Tomoaki Matsugi, Hideyuki Kaneko, Shingo Matsuo, Shin-ichi Kojoh, and Norio Kashiwa
R&D Center, Organo-metal Complexes Catalyzation Laboratory, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura 299-0265
[†]*Analytical Research Laboratory, Mitsui Chemical Analysis and Service, Inc., 6-1-2 Waki, Kuga-Gun, Yamaguchi 740-0061*

(Received February 25, 2003; CL-030155)

We report on the first example of metallocene-catalyzed allyl amine incorporation having only one CH_2 chain spacer into the nonpolar polymer backbone using new metallocene **1** and methylaluminoxane with high activity at high temperature. This is the first example of predominant chain end site-selective introduction of amine group into the polyolefins.

The incorporation of polar groups, especially having highly reactive hydrogen such as OH or NH_2, into an otherwise nonpolar material is desired as a substantial way for modifying the properties of polyolefins to broaden the polyolefin applications. Promising catalysts containing group 10 transition metals[2] or organolanthanide[3] have succeeded in the controlled copolymerization of simple olefins with polar monomers. Zirconocene/MAO catalysts were also successful in copolymerizing ethylene with 10-undecen-1-ol[4] or other polar monomers,[5] having long CH_2 spacers between polar and vinyl groups, although Ziegler–Natta catalysts containing group 4 transition metals are known for their highly oxophilic nature.[6]

In recent research, we discovered a novel stereorigid bridged metallocene having an indenyl ligand, a fluorenyl ligand, and a zirconium ion named IFZ catalyst **1** exhibiting unique catalytic performance for olefin polymerization[7] and ethylene/10-undecen-1-ol[8] or allyl alcohol[9] copolymerization.



1

Concerning amino groups, tertiary amine-functionalized olefins are easy to copolymerize with group IV catalysts, provided that sufficient steric hindrance is present around the nitrogen atom.[10] However, direct polymerization of primary or secondary amines have not been successfully carried out, with one exception, that is in a secondary amine having a long chain spacer, namely the copolymerization of *N*-phenyl-10-undecenamine with 1-hexene using $TiCl_3/Et_2AlCl$ catalyst system.[11] Now we here report that the use of IFZ catalyst **1** and MAO as a cocatalyst has successfully enabled the first copolymerization of ethylene with a masked primary allyl amine having two reactive hydrogens and one CH_2 chain spacer.[12]

In our polymerization system, the copolymerizations of ethylene with allyl amine using IFZ catalyst **1**/MAO cocatalyst were conducted as follows: Subjection of the toluene solution of IFZ catalyst **1** and MAO to the solution of allyl amine masked by triethylaluminum (TEA) or tri-*iso*-butylaluminum (TIBA) and ethylene, led to the predominant production of **2**. The results are shown in Table 1. By use of TEA, allyl amine was incorporated into the chain end, although the concomitant incorporation to the inner site also occurred (Entry 1) (Figure 1). The ^{13}C NMR assignment of the copolymer presented in Figure 1 showed an ambiguous absorption band at 31.9 ppm (peak No. 7), which were interpreted by DEPT editing to CH (peak No. 7a) and CH_2 (peak No. 7b). Furthermore, analysis of end groups by ^{13}C NMR revealed signals of α, ω-end groups due to aminomethyl and Et(Me) groups only, while signals which were attributable to the carbon of vinyl or vinylidene (114.4, 39.1 ppm) were not detected. This result implies that the chain termination predominantly occurred at the incorporated masked allyl amine unit by alkylaluminums (TEA, MAO).

The use of TIBA relatively increased the incorporation of allyl amine into the inner site (entry 2). Analysis of this copolymer by ^{13}C NMR showed that one chain end group was aminomethyl (94%) and the other end group was alkyl (methyl: 62% and iso-butyl: 44%) due to the predominant chain termination by alkylaluminum (Figure 2). This result of chain termination indicates that both alkylaluminums (MAO, TIBA) act almost comparably as chain transfer reagents in the chain transfer reaction. The relative increase of inner aminomethyl group in a polymer chain and the increased molecular weight ($M_n = 25000$)

Table 1. Ethylene/Allyl amine polymerization using IFZ catalyst **1**/MAO catalyst system

Entry	1	MAO	R_3Al^a	Ethylene	Temp.	Time	Yield	Activ.^{b}	M_n^{c}	MD^c		Number of NH_2 group^e	
	mmol	mmol		L/h	°C	min	g				mol%^{d}	end	in
1	0.025	1.57	TEA	2	50	60	4.98	0.20	6,500	2.41	0.57	0.86	0.33
2	0.025	1.57	TIBA	2	50	75	1.26	0.043	25,000	2.49	0.22	0.94	1.17
3	0.250	7.90	TEA	>5	100	180	43.5	0.053	3,700	2.39	0.30	0.19	n.d.

Conditions: 0.1 MPa pressure, toluene; 500 mL, R_3Al; 48 mmol, Allyl amine 40 mmol. [a]Allyl amine was treated with R_3Al before adding toluene solution of MAO and **1**. [b]kg-polymer·mmol-Zr^{-1}·h^{-1}·atm^{-1}. [c]Mw/Mn by GPC analysis. [d]Comonomer content in polymer determined by ^1H-NMR analysis. [e]This value is based on one polymer chain determined by ^{13}C-NMR analysis.

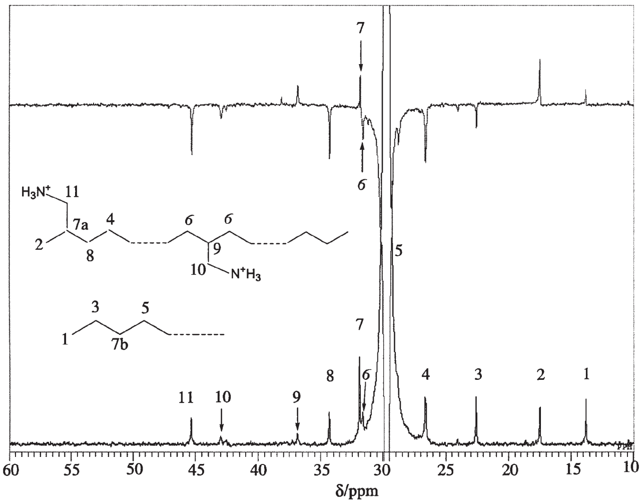
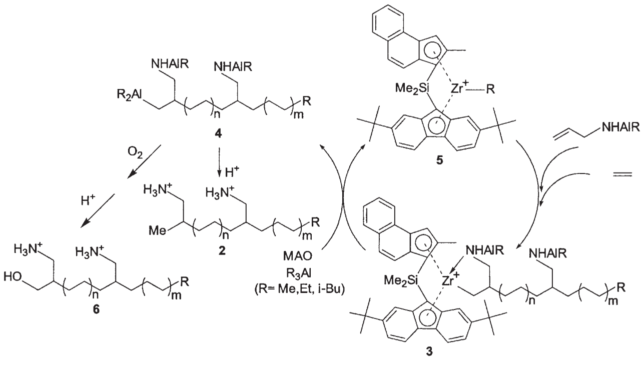


Figure 1. ^{13}C NMR spectra (270 MHz) of a copolymer (Entry 1 in Table 1).

of this copolymer may be caused by the lower chain transfer rate compared to Entry 1. In contrast the result of copolymerizing masked allyl alcohol with ethylene,[9] the numbers of incorporated allyl amine were different, 10 for allyl alcohol, 1 for allyl amine, respectively when TIBA was used as masking alkylaluminums. A sequence analysis of the copolymer revealed that incorporated amine into a polyethylene backbone was isolated. It is intriguing that the numbers of incorporated polar monomer are significantly lower than those cases in allyl alcohol under similar reaction condition. The degree of electronic interactions between Zr cation and oxygen or nitrogen atoms of inserted polar monomers may determine the reaction pathway going to the chain transfer reaction or successive ethylene insertion when the steric hindrance of alkyl aluminum is the same (Scheme 1). Direct observation of the intermediate **3** by using NMR technique was unsuccessful. These unique regioselectivities would be caused by the combination of IFZ catalyst 1 and alkylaluminums having different steric hindrance.

Polymerization under the condition of IFZ catalyst **1**/MAO = 0.25 mmol/7.90 mmol at higher ethylene supply and temperature (>5 L/h. and 100 °C) for longer polymerization time (3 h) was conducted (Entry 3) to obtain a large amount of polymer. The obtained polymers, however, resulted in the mixtures of allyl amine functionalized polyethylene (10%) and homo-polyethylene (90%) having lower molecular weight ($M_n = 3700$) probably due to more frequent chain transfer to alkylaluminums at the activated bond between Zr and ethylene units, unlike the polymerization behavior in Entry 1 or 2. Thus, this active polymer mixture before quenching was subjected to the aerobic oxidation followed by an acid hydrolysis, and we have obtained the mixtures consisting of aminohydroxyl-capped polyethylene **6** (7%), amino-capped polyethylene **2** (3%), and hydroxyl-capped polyethylene (60%) besides homo-polyethylene (30%). The assignment of **6** (-CH_2OH: 64.2 ppm, -$CH_2NH_3{}^+$: 43.5 ppm, -CH-: 38.7 ppm), **2** (-$CH_2NH_3{}^+$: 45.5 ppm), and hydroxyl-capped polyethylene (-CH_2OH: 62.7 ppm) was determined by ^{13}C NMR analysis. The chemical yield of **6** obtained by aerobic oxidation from **4** was estimated reasonable from the literature[13] at 70% using ^{13}C NMR technique. This is a one-pot synthesis of regioselective A,B-functionalized polyolefin **6**. Moreover this polyolefin **6** is a new polymer structure in which polyethylene polymer chain was specifically end capped by different functional groups (amino and hydroxyl group).



Scheme 1. Proposed reaction pathway in this catalyst system.

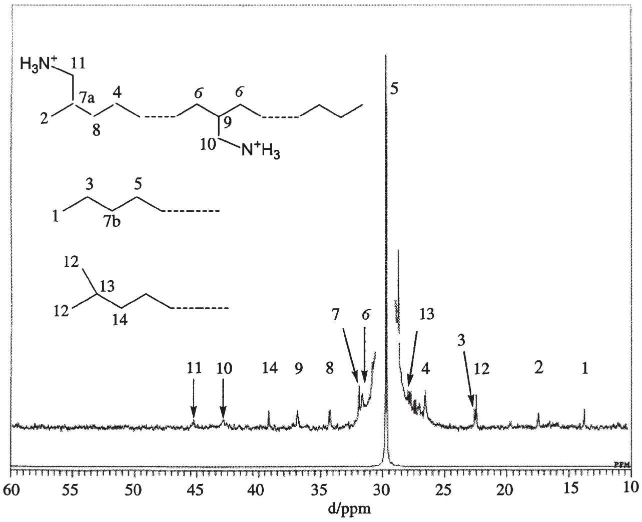


Figure 2. ^{13}C NMR spectra (270 MHz) of a copolymer (Entry 2 in Table 1).

References

1 L. S. Boffa and B. M. Novak, *Chem. Rev.*, **100**, 1481 (2000).

2 S. D. Ittel, L. K. Johnson, and M. Brookhart, *Chem. Rev.*, **100**, 1169 (2000).

3 G. Desurmont, M. Tanaka, Y. Li, and H. Yasuda, *J. Polym. Sci., Polym. Chem.*, **38**, 4095 (2000).

4 S. Tsubaki, J. Jin, T. Sano, T. Uozumi, and K. Soga, *Macromol. Chem. Phys.*, **202**, 1757 (2001).

5 a) M. J. Schneider, R. Schäfer, and R. Mülhaupt, *Polymer*, **38**, 2455 (1997). b) H. Hagihara, M. Murata, and T. Uozumi, *Macromol. Rapid Commun.*, **22**, 353 (2001).

6 U. Giannini, G. Brückner, E. Pellino, and A. Cassata, *J. Polym. Sci., Part C*, **22**, 157 (1968).

7 J. Imuta, M. Yoshida, and Y. Tohi, Eur. Patent 754698 (1999); U. S. Patent 6004897 (1999); *Chem. Abstr.*, **126**, 186525 (1999).

8 J. Imuta, Y. Toda, and N. Kashiwa, *Chem. Lett.*, **2001**, 710.

9 J. Imuta, Y. Toda, and N. Kashiwa, *J. Am. Chem. Soc.*, **124**, 1176 (2002).

10 U. M. Stehling, K. M. Stein, D. Fisher, and R. M. Waymouth, *Macromolecules*, **32**, 14 (1999).

11 H. V. Holler and E. A. Youngman, U. S. Patent 3761458 (1983); *Chem. Abstr.*, **80**, 15684 (1983).

12 J. Imuta, Y. Toda, and N. Kashiwa, Jpn. Kokai Tokkyo Koho 2002-155109A (2002).

13 a) A. L. Mogstad and R. M. Waymouth, *Macromolecules*, **25**, 2282 (1992). b) D. R. Burfield, *Polymer*, **25**, 1817 (1984).

Published on the web (Advance View) June 27, 2003; DOI 10.1246/cl.2003.656