6760 *Macromolecules* **2002,** *35,* 6760−6762

Propene Polymerization with Stereospecific Metallocene Dichloride−$[Ph_3C][B(C_6F_5)_4]$ Using ω-Alkenylaluminum as an Alkylation Reagent and as a Functional Comonomer

Young-Gon Nam, Takeshi Shiono,* and Tomiki Ikeda

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

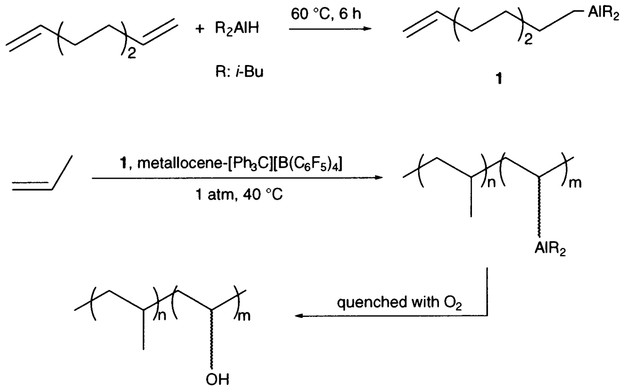
Received April 1, 2002
Revised Manuscript Received July 2, 2002

Introduction. Recent development of single site catalysts for olefin polymerization has enabled us to control the microstructure of polyolefin precisely.[1] An unsolved and unsurmountable task in this field is to copolymerize functional monomers with olefins because highly oxophilic active species of catalyst are intolerant toward the polar group of comonomer.[2] Brookhart et al. reported the first example of copolymerization of olefins and alkyl acrylates by less oxophilic Pd(II)-based catalysts.[3] The neutral salycyladiminato Ni(II) catalysts developed by Grubbs et al., which required no cocatalyst, are conspicuously active systems for the synthesis of functional polyethene.[4]

In the case of functionalization of polypropene (PP), however, direct copolymerization of propene and polar monomers seems to be very difficult because stereospecificity and copolymerizability should be controlled simultaneously. Copolymerization of propene and α-olefin that has a precursor of functional group is one of the most promising methods to functionalize PP. For that purpose, diolefin is used to prepare reactive PP, in which the remaining olefinic group at side chain is applied for functionalization. PP with pendant vinyl groups can be prepared by copolymerization of propene with α,ω-diolefins such as 1,5-hexadiene, whereas cyclic copolymerization or cross-linking reaction of α,ω-diolefins prevents the introduction of vinyl group with keeping original properties of PP.[5] We have recently reported that isotactic PP with pendant vinyl group was obtained in a good yield when propene polymerization was conducted with a $MgCl_2$-supported $TiCl_4$ catalyst in trivinylcyclohexane as a comonomer.[6] The pendant vinyl groups of PP obtained were transferred to hydroxyl groups via hydroalumination very easily.[7] Another method to functionalize PP using α,ω-diolefins has been well investigated by Chung et al.; they prepared borane-containing monomers from α,ω-diolefins and 9-borabicyclo[3.3.1]nonane and conducted copolymerization of propene and the synthesized monomer with $TiCl_3$-based catalysts.[8] The obtained isotactic polymer containing pendant alkyl borane was converted to functional PP.

In this communication, we synthesized 7-octenyldiisobutylaluminum (ODIBA) derived from hydroalumination of 1,7-octadiene with diisobutylaluminum hydride, because ODIBA should act as a protected comonomer as well as a cocatalyst. Propene polymerization was then conducted by stereospecific metallocene dichlorides−$[Ph_3C][B(C_6F_5)_4]$ in the presence of ODIBA, and the pendant Al group of the produced polymer was converted to a hydroxyl group by O_2 at ambient temperature (Scheme 1).

Scheme 1. Synthesis of ODIBA and Propene Polymerization with ODIBA



Experimental Section. a. Materials. Propene (Takachiho Chemical Co.) was purified by passing it through MnO and molecular sieves 4A in stainless steel columns at 60 °C. *rac*-Dimethylsilylbis(2-methylindenyl)zirconium dichloride (*rac*-$Me_2Si[2\text{-}Me(Ind)_2]ZrCl_2$) and diphenylmethylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride ($Ph_2C[(Cp)(9\text{-}Flu)]ZrCl_2$) obtained from Boulder Scientific Co. were used without further purification. Triphenylcarbenium tetrakis(pentafluorophenyl)borate ($[Ph_3C][B(C_6F_5)_4]$) and diisobutylaluminum hydride donated from Asahi Glass Co., Ltd., and Tosoh Finechem Co. Ltd., respectively, were used without further purification. 1,7-Octadiene and toluene commercially obtained were dried with CaH_2 and distilled before use.

b. Synthesis of 7-Octenyldiisobutylaluminum. ODIBA was synthesized by hydroalumination of excess 1,7-octadiene with diisobutylaluminum hydride at 60 °C for 6 h in a 50 mL Schlenk flask equipped with a magnetic stirrer. After the hydroalumination, the remaining 1,7-octadiene was removed by evacuation. The product was analyzed by ^1H and ^{13}C NMR. For the analysis of gas chromatography (GC), 0.5 mL of product was diluted with 2 mL of *m*-xylene as an internal reference and decomposed by successive addition of distilled water and hydrochloric acid.

c. Polymerization Procedure. Propene polymerization with ODIBA was conducted in a 200 mL glass reactor equipped with a magnetic stirrer. After toluene and ODIBA (toluene + ODIBA = 100 mL) were added to the reactor, an atmospheric pressure of propene was introduced at 40 °C until the solvent was saturated with propene. Polymerization was started by successive addition of the borate and the zirconocene complex. After the polymerization for 30 min, the reaction mixture was divided into two parts under a N_2 atmosphere. One part was quenched directly with a dilute solution of hydrochloric acid in methanol. The other was brought into contact with O_2 gas at room temperature for 1.5 h before quenching with the hydrochloric acid solution in methanol. The precipitated polymers were filtered out and dried under vacuum at 60 °C for 6 h.

d. Analytical Procedures. ^{13}C NMR spectra of polymers were recorded at 120 °C on a JEOL GX-500

---

* To whom correspondence should be addressed: Tel 045-924-5242, Fax 045-924-5276, e-mail tshiono@res.titech.ac.jp.

10.1021/ma025528y CCC: $22.00

Table 1. Polymerization of Propene with ODIBA by Stereospecific Metallocene Catalysts Combined with $[Ph_3C][B(C_6F_5)_4]$[a]

no.	catalysts	ODIBA in feed (M)	R_p ($\times 10^4$)[b]	M_n ($\times 10^4$)[c]	M_w/M_n[c]	T_m (°C)[d]	ΔH (J/g)[d]	hexyl content (mol %)[e]	hydroxyl content (mol %)[e]
1[f]	*rac*-$Me_2Si[2\text{-}Me(Ind)]_2ZrCl_2$		130	12.5	1.6	148	84		
2		0.031	74.7	9.4	2.6	133	57	0.4	0.8
3		0.062	32.5	4.3	2.9	110	43	1.7	5.1
4		0.124	21.4	2.4	3.1	99	25	2.4	9.6
5[f]	$Ph_2C[(Cp)(9\text{-}Flu)]ZrCl_2$		60.2	6.5	2.4	121	43		
6		0.031	39.3	6.4	2.3	110	32	0.3	1.3
7		0.062	29.0	6.4	2.1	103	29	0.4	3.9
8		0.124	16.6	7.0	2.8			2.0	7.1

[a] Polymerization conditions: Zr = B = 12 μmol; time = 30 min; temperature = 40 °C; propene = 1 atm. [b] In g of polymer/mol of Zr h. [c] Determined by GPC using polystyrene standards. [d] Determined by DSC. [e] Determined by ^{13}C NMR. [f] Polymerization was conducted with triisobutylaluminum (0.017 M) in place of ODIBA.

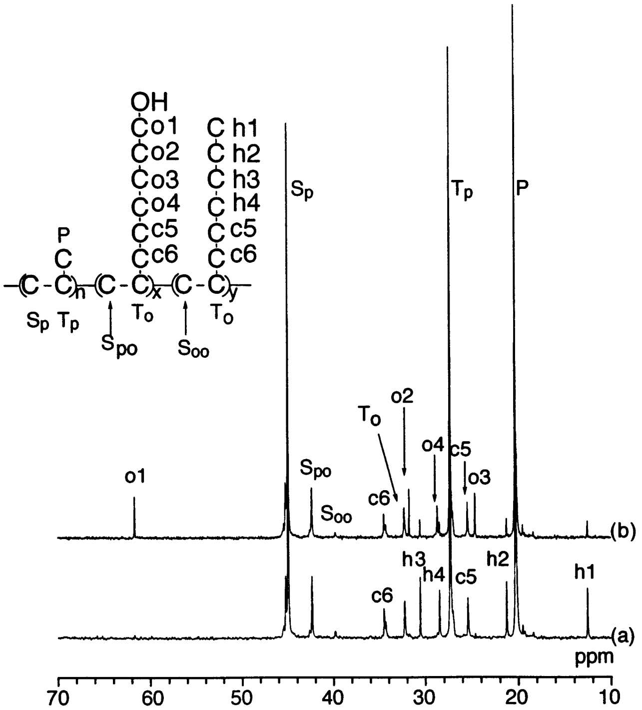


Figure 1. 125.65 MHz ^{13}C NMR spectra of PPs obtained with an isospecific metallocene catalyst (Table 1, no. 3): (a) quenched with MeOH; (b) quenched with O_2.

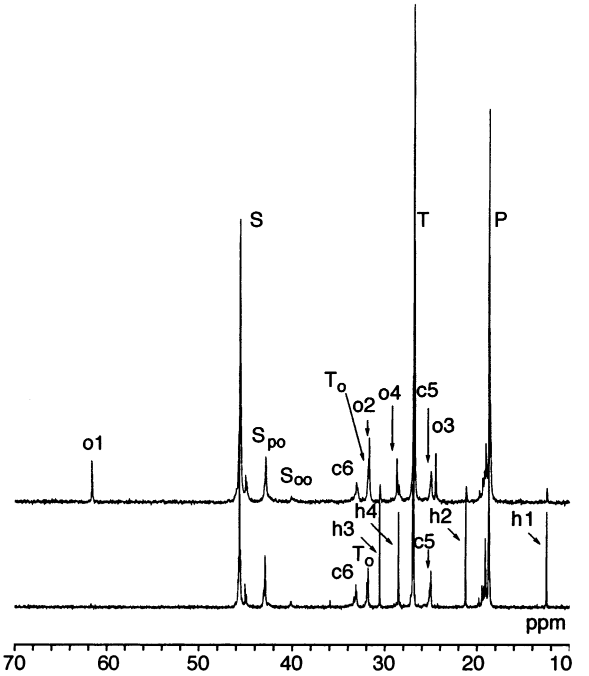


Figure 2. 125.65 MHz ^{13}C NMR spectra of PPs obtained with a syndiospecific metallocene catalyst (Table 1, no. 7): (a) quenched with MeOH; (b) quenched with O_2.

spectrometer in pulse Fourier transform (FT) mode. The pulse angle was 45°, and 10 000 scans were accumulated in 7 s of pulse repetition. A sample solution was made in 1,1,2,2-tetrachloroethane-d_2 as solvent, and the resonance of tetrachloroethane was used as an internal reference (74.47 ppm). Differential scanning calorimetry (DSC) measurements were made on a Seiko DSC-220. Polymer sample (ca. 4 mg) was encapsulated in an aluminum pan, and the third scanning curve was recorded at a heating rate of 10 °C/min after previous heating to 220 °C followed by cooling to −40 °C. Gel permeation chromatograms (GPC) of the polymers were recorded on a Waters 150 C equipped with two Shodex 80M/S columns at 140 °C using *o*-dichlorobenzene as solvent and calibrated with standard polystyrene samples.

Results and Discussion. We carried out propene polymerization in the presence of ODIBA by isospecific and syndiospecific metallocene dichlorides paired with $[Ph_3C][B(C_6F_5)_4]$. For comparison, propene polymerization was conducted with $(i\text{-}Bu)_3Al$ in place of ODIBA (Table 1). The activities with ODIBA were about half of those with $(i\text{-}Bu)_3Al$ irrespective of the zirconocene compounds and decreased with increasing the concentration of ODIBA. The results indicate that ODIBA was effective as an alkylation reagent. The number-average molecular weights (M_n) and molecular weight distribution (M_w/M_n) of the polymers obtained were determined by GPC, the results of which are also shown in Table 1.

The M_n value of the polymer obtained with the isospecific catalyst decreased according to the concentration of ODIBA, whereas that with the syndiospecific catalyst was independent of the ODIBA concentration. The results indicate that chain transfer by ODIBA is predominant in the isospecific catalyst but negligible in the syndiospecific one.

The incorporation of ODIBA as a comonomer was then investigated by ^{13}C NMR. Figures 1 and 2 show the spectra of isotactic and syndiotactic PPs quenched with MeOH and O_2, respectively. In the spectra of PPs quenched with MeOH (Figures 1a and 2a), the characteristic methyl carbon of pendant hexyl group is observed at 12 ppm, and the other carbons in the hexyl group are assigned to each resonance shown in Figures 1 and 2 on the basis of the relative intensities and the calculated chemical shifts of poly(propene-*ran*-1-octene).[9] The methylene carbons in the main chain split into three resonances because of the diad sequence of propene (P) and 1-octene (O), and the resonances can be assigned to PP, PO, and OO diads according to the literature.[10]

On the other hand, in the spectra of the polymer quenched with O_2 (Figures 1b and 2b), the methylene carbon connected to a hydroxyl group appears at 61.9 ppm accompanied by the decrease of the pendant hexyl group.[9] These ^{13}C NMR spectra clearly indicate that ODIBA was chemically incorporated to the PP main chain, and the pendant Al groups were successively converted to hydroxyl groups by quenching with O_2. The relative intensities of the hydroxymethylene to the hexyl groups give the conversion of Al−C to HO−C to be 68−81%. The contents of hydroxyl group in the copolymers determined by ^{13}C NMR were from 0.8 to 9.6 mol % for isotactic and from 1.3 to 7.1 mol % for the syndiotactic PPs in the present conditions (Table 1).

The thermal properties of the produced polymers were investigated by DSC. Both the melting points and heat of fusion of the copolymers decreased with an increase in the ODIBA concentration. These results also support the incorporation of ODIBA in stereoregular PP chains.

In conclusion, stereoregular PPs having a hydroxyl group at the side chain were easily synthesized by the very simple and clean method, that is, stereospecific propene polymerization by zirconocene dichlorides−$[Ph_3C][B(C_6F_5)_4]$ combined with ODIBA, in place of usual trialkylaluminum, followed by quenching with O_2.

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

References and Notes

(1) For recent reviews, see: (a) Lee, D. H.; Noh, S. K. *Korea Polym. J.* **2001**, *9*, 71−83. (b) Chum, P. S.; Kruper, W. J.; Guest, M. J. *Adv. Mater.* **2000**, *12*, 1759−1767. (c) Gladysz, J. A. *Chem. Rev.* **2000**, *100*, 1167−1682. (d) Marks, T. J., Stevens, J. C., Eds. *Top. Catal.* **1999**, *7*, 1−208. (e) Britovsek, G. J. P.; Gibson, V. C.; Wass, D, F. *Angew. Chem., Int. Ed.* . **1999**, *38*, 428−447. (f) Jordan, R. F. *J. Mol. Catal.* **1998**, *128*, 1−337. (g) Mcknight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587−2598. (h) Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 13−18. (i) Soga, K.; Shiono, T. *Prog. Polym. Sci.* **1997**, *22*, 1503−1546. (j) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 144−187. (k) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907−3945. (l) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270. (m) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170.

(2) For a recent review, see: (a) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479−1493. (b) Yanjarappa, M. J.; Sivaram, S. *Prog. Polym. Sci.* **2002**, *27*, 1347−1398.

(3) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267−268.

(4) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460−462.

(5) Knorr, J.; Bornemann, S.; Schimmel, T.; Arnold, M. *Polym. Prepr.* **2000**, *41*, 468−469. (b) Naga, N.; Shiono, T.; Ikeda, T. *Macromolecules* **1999**, *32*, 1348−1355. (c) Dassaud, J. P.; Guyot, A.; Spitz, R. *Polym. Mater. Sci. Eng.* **1992**, *67*, 100−101.

(6) Nam, Y.-G.; Murayama, S.; Shiono, T.; Ikeda, T. *Macromolecules* **2001**, *34*, 6533−6535.

(7) Nam, Y.-G.; Murayama, S.; Shiono, T.; Ikeda, T. *Future Technology for Polyolefin and Olefin Polymerization Catalysis*; Technology and Education Publishers: Tokyo, 2001; pp 339−344.

(8) Chung, T. C. *Prog. Polym. Sci.* **2002**, *27*, 39−85 and references therein.

(9) The carbons of hydroxyhexyl group were assigned by the relative intensities and calculated chemical shifts as follows: 61.9 ppm, o1; 31.8 ppm, o2; 24.5 ppm, o3. The resonances of 25.5 and 34.5 ppm were assignable to c5 and c6 of hydroxyhexyl and hexyl groups.

(10) Uozumi, T.; Soga, K. *Makromol. Chem.* **1992**, *193*, 823−831.

MA025528Y