Synthesis of Polypropylenes Functionalized with Secondary Amino Groups at the Chain Ends

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Received July 6, 1992; Revised Manuscript Received January 7, 1993

ABSTRACT: Atactic and isotactic polypropylenes having terminal vinylidene groups were prepared with bis(cyclopentadienyl)zirconium dichloride– and ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride–methylaluminoxane catalyst systems. The produced polymers having a vinylidene end group were treated with an excess of borane in benzene, followed by treatment with an excess of 1-hexene. The resulting trialkylboranes were disproportionated with boron trichloride in xylene at 110 °C to obtain alkyldichloroboranes. The products were then brought into contact with 1-butylazide to obtain the polypropylenes having a 1-butylamino group at the chain end in over 80% yield.

Introduction

Terminally functionalized polymers are useful not only for the synthesis of block copolymers but also for the improvement of polymer properties. Terminally functionalized polypropylenes can be produced either by using a living polymerization system[1] or by using chain-transfer reactions.[2] Mülhaupt et al. recently synthesized terminally functionalized polypropylenes and polypropylene-based block copolymers from polypropylene produced with Kaminsky-type catalyst using versatile reactions (including hydrometalation) of the vinylidene groups.[3] We have also prepared terminally aluminated and boronated polypropylenes with hydrometalation of the terminal vinylidene groups and applied them for the synthesis of the terminally hydroxylated and halogenated polymers.[4]

Among terminal functional groups, amino groups are most preferable due to their high reactivity and high affinity with other compounds. In fact, terminally aminated polymers are commercially utilized in some elastomers to improve the dispersity of fillers.[5] In this paper, an attempt was made to prepare terminally aminated polypropylenes using hydroboration.

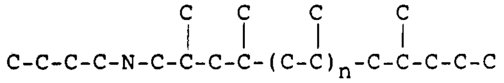
Results and Discussion

Trialkylborane, which shows a versatile reactivity, is very useful to introduce a variety of functional groups at the chain end. However, there are few reactions, such as oxidation to alcohol,[6] in which all three alkyl groups can be utilized. For example, the equimolar reaction of alkylazides with triethylborane gives corresponding alkylethylamines in about 80% yield based on organic azides.[7] The reaction of *N*-chloroamine or hydroxylamineorthosulfonic acid with trialkylboranes gives corresponding amines in about 60% yields based on alkyl groups. Thus, only one or two of the three alkyl groups can be utilized in these reactions. On the other hand, the equimolar reaction of alkyldichloroboranes with alkylazide gives corresponding secondary amines in yields of 84–100%.[8]

From such a viewpoint, in this paper were applied the following procedures to utilize all of the vinylidene groups at the polymer chain ends: (i) perfect conversion of terminal vinylidene groups to boron–carbon bonds with an excess of borane–tetrahydrofuran complex; (ii) hydroboration of 1-hexene with an excess of boron–hydrogen bonds to obtain trialkylboranes; (iii) disproportionation of the trialkylborane with 2-fold of boron trichloride to obtain alkyldichloroborane; and (iv) amination of the alkyldichloroborane with 1-butylazide. Since the concentration of the terminal groups is not so high, borane and 1-butylazide were used in excess in steps i and iv to ensure the conversion of the terminal groups. When step ii was skipped for comparison, the final conversion to the amino group was very low.

Figure 1 shows the 90-MHz ^{1}H NMR spectra of the aminated and original polymers. The original polymers displayed the resonances attributed to vinylidene protons at around 4.8 ppm, which disappeared completely accompanied by an appearance of new resonances at around 2.5 ppm after amination. These new resonances were shifted to approximately 3.0 ppm by the addition of a small amount of trifluoroacetic acid. Accordingly, they can be assigned to the methylene protons connected to amino groups.

The ^{13}C NMR spectra were measured on these polymers to characterize the structures in more detail. Figure 2 shows the 25-MHz ^{13}C NMR spectra of the atactic polymer before and after amination. The original polymer shows the resonances attributed to p1, p3, and p4 carbons of 1-propyl end group as well as those attributed to v4 and v5 carbons of vinylidene group as indicated in the figure.[4b] After amination, the latter resonances disappeared completely and several resonances newly appeared. Since the hydroboration of vinylidene groups by borane–tetrahydrofuran complex is highly regioselective,[9] one may expect to obtain such a polymer having a 1-butylamino group at the chain end as shown below (structure I). The chemical shifts for structure I calculated according to the Lindeman–Adams and substitution rules[10,11] are summarized in Table I, where the chemical shifts of some model compounds are also shown for reference.[12] From the comparison between the calculated and observed values, the new resonances appearing after amination can be assigned to 1-butyl and polypropyl groups connected to nitrogen. The resonances due to the carbons in the polypropyl amino end group (n1, n3, and n4) are broad, and those in the 1-butylamino group are sharp (b1 and b2), which may result from the diastereomeric structures of the polypropylene end.



$$\mathrm{C{-}C{-}C{-}C{-}N{-}C{-}\overset{\overset{C}{|}}{C}{-}C{-}\overset{\overset{C}{|}}{C}{-}(C{-}\overset{\overset{C}{|}}{C})_n{-}C{-}\overset{\overset{C}{|}}{C}{-}C{-}C{-}C} \qquad \mathrm{(I)}$$

In Figure 3 are shown the 125-MHz ^{13}C NMR spectra of the isotactic polymer before and after amination. The spectrum of the aminated polymer does not show any resonance attributable to vinylidene end groups and displays new resonances in similar chemical shift regions

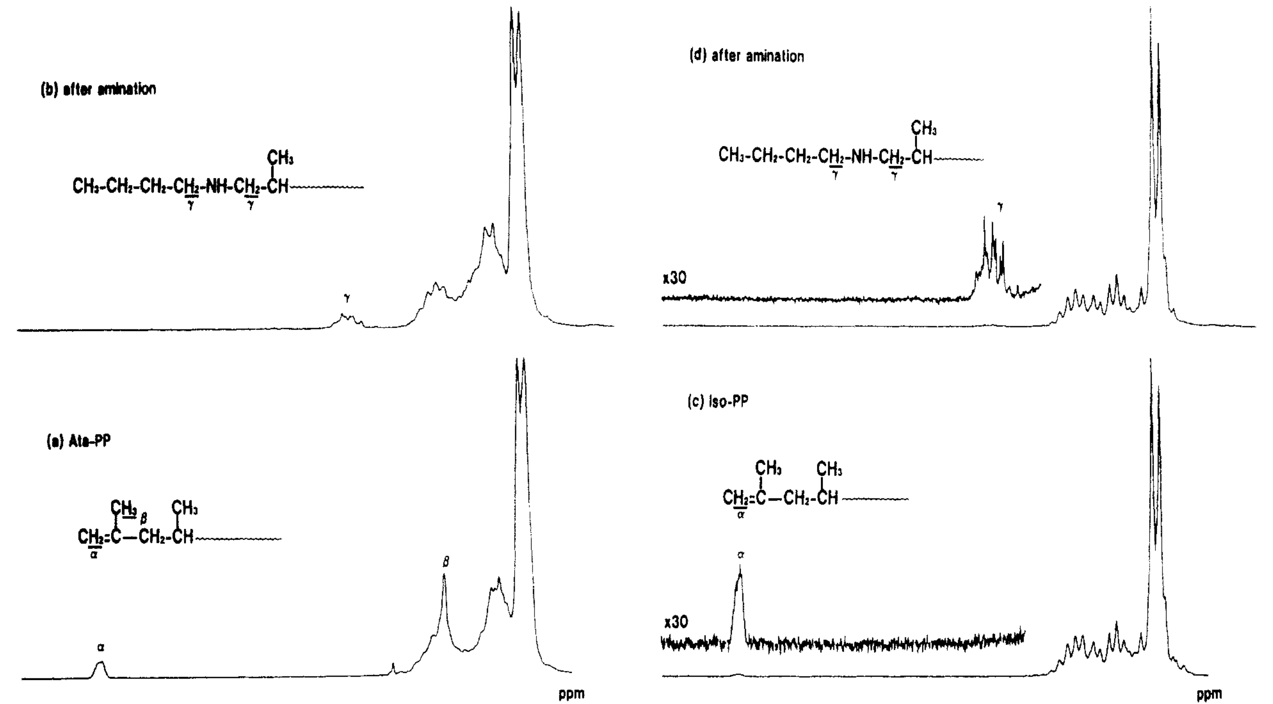


Figure 1. 90-MHz ^{1}H NMR spectra of atactic and isotactic polypropylenes before and after amination: (a) atactic, before amination; (b) isotactic, before amination; (c) atactic, after amination; (d) isotactic, after amination.

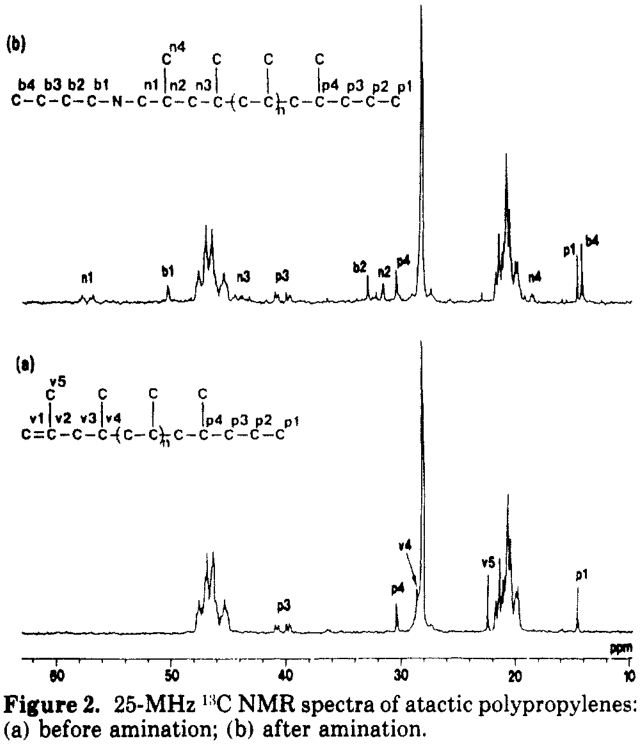
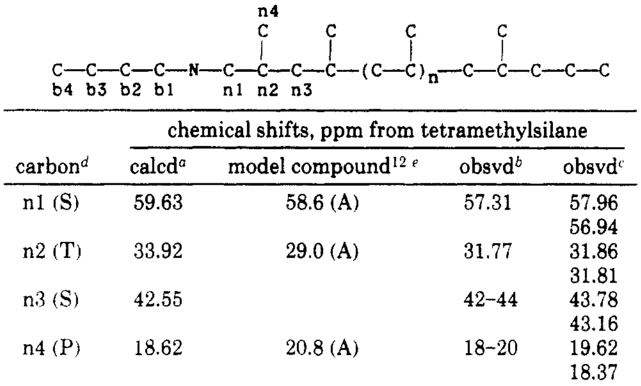


Figure 2. 25-MHz ^{13}C NMR spectra of atactic polypropylenes: (a) before amination; (b) after amination.

Table I
Calculated and Observed Chemical Shifts of Terminally Aminated Atactic and Isotactic Polypropylenes



$$\underset{b4}{C}—\underset{b3}{C}—\underset{b2}{C}—\underset{b1}{C}—N—\underset{n1}{C}—\underset{n2}{\overset{\overset{n4}{C}}{C}}—\underset{n3}{C}—\overset{C}{C}—(C—\overset{C}{C})_n—C—\overset{C}{C}—C—C—C$$

carbon[d]	calcd[a]	model compound[12] [e]	obsvd[b]	obsvd[c]
	chemical shifts, ppm from tetramethylsilane			
n1 (S)	59.63	58.6 (A)	57.31	57.96 56.94
n2 (T)	33.92	29.0 (A)	31.77	31.86 31.81
n3 (S)	42.55		42–44	43.78 43.16
n4 (P)	18.62	20.8 (A)	18–20	19.62 18.37
b1 (S)	50.37	50.1 (B)	49.95	50.39 50.30
b2 (S)	33.09	33.1 (B)	32.26	33.11 33.09
b3 (S)	21.91	20.9 (B)		
b4 (P)	13.37	14.2 (B)	14.03	14.13

[a] Calculated according to the Lindeman–Adams and substitution rules.[10,11] [b] Atactic polypropylene, measured by 25-MHz ^{13}C NMR spectrometer. [c] Isotactic polypropylene, measured by 125-MHz ^{13}C NMR spectrometer. [d] P, primary; S, secondary; T, tertiary. [e] Model compound A: $NH(CH_2CH(CH_3)CH_3)_2$. Model compound B: $NH(CH_2CH_2CH_2CH_3)_2$.

as observed with the aminated atactic polymer. The resonances attributed to the polypropylamine end groups of isotactic polymer are, however, split into doublets with approximately the same intensities. Since the configuration of the methyl groups is highly isotactic even at the chain end (isotactic triad (*mm*) determined from the resonance of C^{i1} is 88%),[4b] the splitting might be caused by the presence of four diastereomers (two enantiomeric pairs) at the chain end (see Chart I). It may be considered, therefore, that hydroboration by the borane–tetrahydrofuran complex can distinguish neither the prochiral faces of the vinylidene groups nor the chiral carbons at the chain end. Such a phenomenon was also observed with the terminally halogenated isotactic polypropylenes which were prepared by hydroalumination of the terminal vinylidene groups followed by halogenolysis.[4c]

The conversions of the vinylidene to the amino group determined by ^{1}H NMR and ^{13}C NMR are summarized in Table II. The conversion based on the ^{1}H NMR spectra was calculated from the relative intensity between the methylene protons connected to the nitrogen and the vinylidene protons of the original polymer, using the intensity of main-chain protons as an internal standard, whereas the conversion based on the ^{13}C NMR spectra was calculated from the relative intensity of the chain-end carbons between the amino and 1-propyl end groups.

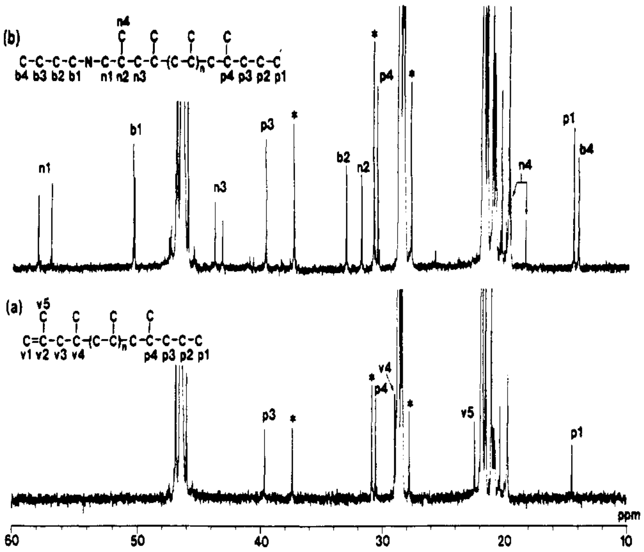
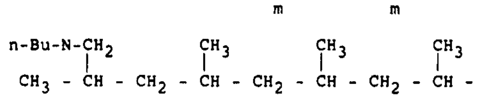


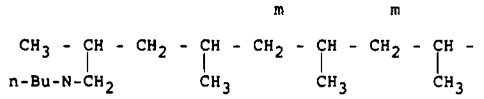
Figure 3. 125-MHz ^{13}C NMR spectra of isotactic polypropylenes: (a) before amination; (b) after amination; (*) resonances from the tetramethylene structure.

Chart I



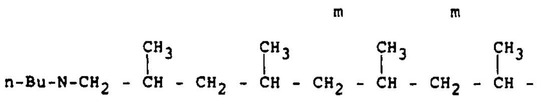
$$CH_3-\overset{\text{n-Bu-N-CH}_2}{CH}-CH_2-\overset{CH_3}{CH}-\overset{m}{CH_2}-\overset{CH_3}{CH}-\overset{m}{CH_2}-\overset{CH_3}{CH}-$$

(II)



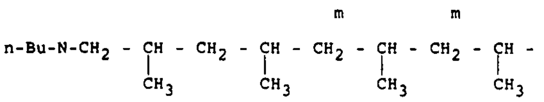
$$CH_3-\underset{\text{n-Bu-N-CH}_2}{CH}-CH_2-\underset{CH_3}{CH}-\overset{m}{CH_2}-\underset{CH_3}{CH}-\overset{m}{CH_2}-\underset{CH_3}{CH}-$$

(III)



$$\text{n-Bu-N-CH}_2-\overset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-\overset{m}{CH_2}-\overset{CH_3}{CH}-\overset{m}{CH_2}-\overset{CH_3}{CH}-$$

(IV)



$$\text{n-Bu-N-CH}_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-\overset{m}{CH_2}-\underset{CH_3}{CH}-\overset{m}{CH_2}-\underset{CH_3}{CH}-$$

(V)

Table II
Conversion of Vinylidene Groups to 1-Butylamino Groups

polymer	conversion, % ^1H NMR	 ^{13}C NMR[a]
atactic PP	87	<85
isotactic PP	86	<83

[a] Minimum value.

Although the conversions determined by ^{13}C NMR seem to be slightly dependent upon the pair of carbons used for calculation, they are in fairly good agreement with those determined by ^1H NMR.

To check the reactivity of the terminal amino group of the isotactic polymer, the polymer was brought into contact with benzoyl chloride. Ionization of the amino group was also conducted by pouring the xylene solution of the polymer into a hydrochloric acid solution in ethanol. The analytical results obtained are summarized in Table III, indicating that chlorine is contained in the ionized polymer. The conversion to hydrochloric acid salt was estimated from the relative content of nitrogen and chlorine to obtain about 90%. In Figure 4b is illustrated the ^1H NMR spectrum of this polymer. The methylene resonance connected to the amino group is broadened and slightly shifted to a lower field.

Table III
Elemental Analyses of Terminally Functionalized Isotactic Polypropylenes[a]

polymer	N content, wt %	Cl content, wt %
calcd[b]	0.40	1.01
after amination	0.37	
after ionization	0.42	0.94
after amidation	0.27 0.26[c] 0.23[d]	

[a] Average values of three measurements. [b] Values calculated on the assumption that vinylidene groups could be completely converted to amino groups. [c] Calculated value based on IR analyses. [d] Calculated value based on ^1H NMR analyses.

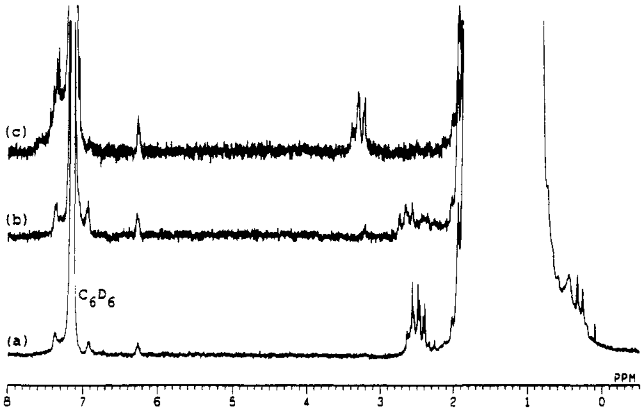


Figure 4. 90-MHz ^1H NMR spectra of isotactic polypropylenes: (a) after amination; (b) after ionization; (c) after amidation.

Figure 4c shows the ^1H NMR spectrum of the amidated polymer, which does not show any resonance assignable to the methylene protons connected to the amino group (at around 2.5 ppm, see Figure 4a) and displays new resonances at around 3.3 and 7.4 ppm. These new resonances can be assigned to the methylene protons connected to the amide group and the aromatic protons of the benzoyl group, respectively, suggesting that amidation of the terminal amino group proceeds quantitatively. The content of nitrogen was calculated from the relative intensity between the methylene protons neighboring the nitrogen and the main-chain protons to obtain 0.23 wt %, which agrees well with the observed value (0.27 wt %).

Figure 5 shows the IR spectrum of the amidated polymer together with that of the original polymer. The amidated polymer displays the carbonyl stretching band at around 1645 cm^{-1}. The molar ratio of the methyl and amide groups was estimated from the intensity ratio of the absorbances at 1165 (C—H deformation band of methyl groups) and 1645 cm^{-1} (C═O stretching band) to obtain 127 mol of CH_3/mol of CO. The molar absorption coefficients employed here, $\epsilon_{1165} = 91.4$ L mol^{-1} cm^{-1} and $\epsilon_{1645} = 995$ L mol^{-1} cm^{-1} were obtained from atactic polypropylene and 1-butyl (2-methylpropyl)benzamide,[13] respectively. The content of nitrogen calculated from this molar ratio is also indicated in Table III. The content of nitrogen in the amidated polymer is lower than those in the aminated and ionized polymers, which might be caused by a loss of low molecular weight fractions in the amidation process.

The effect of these terminal groups on some thermal properties of polymers was briefly examined by means of a differential scanning calorimetry, the results of which are summarized in Table IV. Both the melting point and the heat of fusion did not change, but the glass transition temperature increased to some extent when the functional groups were introduced at the polymer chain end.

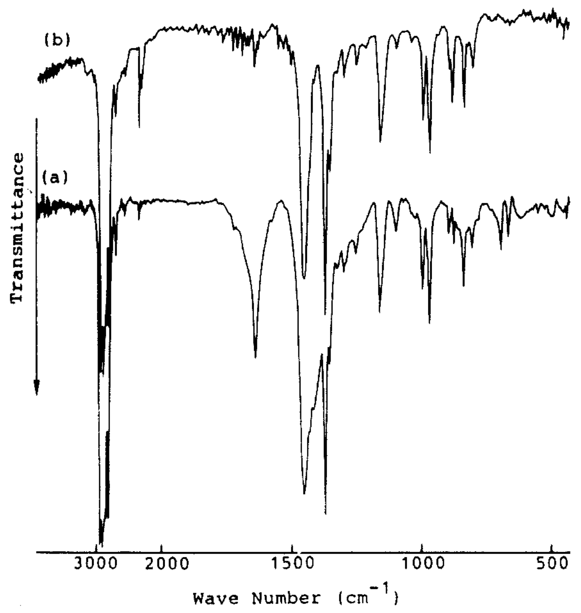


Figure 5. IR spectra of isotactic polypropylenes: (a) after amidation; (b) original.

Table IV
Thermal Analyses of Terminally Functionalized Isotactic Polypropylenes[a]

	T_m, °C	ΔH_f, J/g	T_g,[b] °C	
			i	m
original	116.1	63.0	-21.2	-17.7
after amination	116.4	66.5	-20.4	-15.2
after ionization	115.8	67.8	-16.7	-10.8
after amidation	115.6	51.0	-17.7	-10.4

[a] Obtained from remelted samples. T_m, melting temperature; ΔH_f, heat of fusion; T_g, glss transition temperature. [b] i and m designate the beginning and the middle of the observed transition.

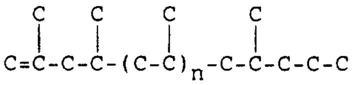
In conclusion, isotactic and atactic polypropylenes having a 1-butylamino group at the chain end have been prepared in over 80% yield.

Experimental Section

Materials. Propene (Mitsubishi Petrochemical Co.) was purified by passing through columns of $CaCl_2$ and P_2O_5 and molecular sieves 3A. $Et[H_4Ind]_2ZrCl_2$ was prepared according to the literature.[14,15] MAO (Tosoh Akzo Chemical Co.) and benzoyl chloride (Wako Pure Chemical Industries, Ltd.) were used without further purification. Research grade benzene, toluene, xylene, and pyridine (commercially obtained) were dried over calcium hydried under refluxing for 24 h and distilled before use. One molar borane solution in tetrahydrofuran and 1.0 M boron trichloride solution in hexane were obtained from Aldrich Chemical Co. Argon (99.9995%) was used without further purification. 1-Butylazide was prepared according to the literature from sodium azide and 1-butyl bromide.[16]

Preparation of Polypropylenes. Propene polymerization was conducted with a 200-mL stainless steel autoclave or a 200-mL glass reactor equipped with a magnetic stirrer. When the glass reactor was used, 100 mL of toluene and 1.8 mmol of MAO were added into the reactor under an argon atmosphere, and then propene was introduced at 20 °C until the solvent was saturated with propene. Polymerization was started by adding 4 mL of toluene solution containing 0.01 mmol of $Et[H_4Ind]_2ZrCl_2$. When the autoclave was used, on the other hand, 9.0 mmol of MAO, 50 mL of toluene, and 3 mL of toluene solution containing 0.03 mmol of Cp_2ZrCl_2 were added into the reactor under an argon atmosphere and then 48 L (STP) of propene monomer was condensed into the reactor at liquid nitrogen temperature. Polymerization was started by setting the reactor at polymerization temperature (0 °C). The polymerization was terminated by the addition of a dilute solution of hydrochloric acid in ethanol. When $Et[H_4Ind]_2ZrCl_2$ was used, the precipitated polymer was filtered and washed with plenty of ethanol. When Cp_2ZrCl_2 was used, on the other hand, the produced polymer (atactic) was extracted with hexane and recovered by evaporation of the solvent because the product was very sticky. Both isotactic and atactic polymers were dried in vacuo at 60 °C for 8 h.

The produced polymers were confirmed to have structure VI from ^{13}C NMR and ^1H NMR as reported previously.[4b,17] The



$$C=\overset{C}{C}-C-\overset{C}{C}-(C-\overset{C}{C})_n-C-\overset{C}{C}-C-C-C$$

(VI)

properties of polymers used in the present study were characterized as follows: isotactic polypropylene, *mm* (isotactic triad) = 0.81, M_n (number-average molecular weight) = 3500, vinylidene content = 0.29 mmol/g of polymer, T_m (melting point) = 121 °C; atactic polypropylene, statistically atactic, M_n = 900, vinylidene content = 1.1 mmol/g of polymer.

Preparation of Terminally Aminated Polypropylenes. The terminal C=C bonds of the polymers were hydroborated by borane–tetrahydrofuran complex.[18] After about 1 g of the isotactic or atactic polymer was placed into a 50-mL Schlenk tube equipped with a condenser and a magnetic stirrer, the tube was evacuated and replaced with argon. Benzene (20 mL) and 1 mL of 1 M tetrahydrofuran solution of borane were added into the tube, and the mixture was heated at 60 (for the atactic polymer) or 80 °C (for the isotactic polymer) for 2 h. After checking the disappearance of vinylidene groups by IR, the remaining B–H was treated with 1 mL of 1-hexene at room temperature for 2 h. The solvent and remaining 1-hexene were evacuated to give trialkylboranes.

The disproportionation of trialkylboranes was conducted with boron trichloride (2 mmol) in 20 mL of xylene at 110 °C for 2 h to give alkyldichloroborane.[19] The product was then brought into contact with an excess amount of 1-butylazide (azide/boron = 5 in molar ratio) at 80 °C for 2 h and at 110 °C for 2 h, successively.[20] The reaction was quenched by adding a small amount of acetic acid at 0 °C, and the product was poured into acidic ethanol. In the case of the isotactic polymer, the precipitated polymer was filtered and washed with an aqueous solution of potassium hydroxide. In the case of the atactic polymer, the produced polymer was extracted with hexane followed by washing with an aqueous solution of potassium hydroxide and recovered by evaporation of the solvent. Both the isotactic and atactic polymers were dried in vacuo at 60 °C for 8 h.

Amidation of Amino Group. Terminally aminated isotactic polypropylene (0.2 g) was placed into a 50-mL Schlenk tube equipped with a condenser and a magnetic stirrer under an argon atmosphere. Xylene (10 mL), pyridine (2 mL), and benzoyl chloride (1 mL) were added into the tube, and the mixture was heated at 140 °C for 6 h. The reaction mixture was poured into ethanol. The precipitate was collected, washed with plenty of ethanol, and dried in vacuo at 60 °C for 8 h.

Hydrochlorination of Amino Group. The terminally aminated isotactic polypropylene was reprecipitated twice from hot xylene into a hydrochloric acid solution (ca. 1 M) in ethanol and dried in vacuo at 60 °C for 8 h.

Analytical Procedures. ^1H spectra of samples were recorded on a JEOL EX-90 spectrometer operated at 89.45 MHz in the pulse Fourier transform (FT) mode. ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer operated at 25.0 MHz or a JEOL GX-500 spectrometer operated at 125.65 MHz in the pulse FT mode. In ^1H NMR measurements, the pulse angle was 45°, and 100–500 scans were accumulated in 9 s of pulse repetition. In ^{13}C NMR measurements, broad band decoupling was used to remove ^{13}C–^1H couplings. The pulse angle was 45°, and 6000–8000 scans were accumulated in 8 s of pulse repetition. The spectra were obtained at room temperature or at 80 °C in $CDCl_3$ or C_6D_6 solution (2 wt % for ^1H NMR and 15 wt % for ^{13}C NMR in a 5 mm o.d. tube), using $CHCl_3$ or C_6H_6 as an internal reference (7.24 and 7.15 ppm for ^1H NMR; 77.0 and 128.0 ppm for ^{13}C NMR, respectively).

Differential scanning calorimetry measurements were made with a Seiko DSC-220. Polymer samples (ca. 3 mg) were encapsulated in aluminum pans. Samples were pretreated at 200 °C for 5 min, chilled with liquid nitrogen, and scanned at 10 °C/min.

IR spectra of the polymers were recorded on a JASCO FT/IR-3 spectrometer. The toluene solution of a polymer sample was cast on a KBr pellet to offer the measurement.

Elemental analyses were carried out by a Yanagimoto CHN Autocorder Type MT-2 and a Yazawa halogen analyzer.

References and Notes

(1) For example: Doi, Y.; Keii, T. *Adv. Polym. Sci.* **1986**, *73/74*, 201.

(2) For example: (a) Agouri, E.; Parlant, C.; Monet, P.; Rideau, J.; Teitgen, J. F. *Makromol. Chem.* **1970**, *137*, 229. (b) Doi, Y.; Soga, K.; Murata, M.; Ono, Y. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 789. (c) Burfield, D. R. *Polymer* **1984**, *25*, 1817. (d) Redina, G.; Albizzati, E. Eur. Pat. Appl. 350059, 1989. (e) Shiono, T.; Yoshida, K.; Soga, K. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 169. (f) Shiono, T.; Kurosawa, H.; Soga, K. *Makromol. Chem.* **1992**, *193*, 2751.

(3) Mülhaupt, R.; Duschek, T.; Rieger, B. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 317.

(4) (a) Shiono, T.; Soga, K. *Polym. Prepr. Jpn.* **1991**, *41*, 2630. (b) Shiono, T.; Soga, K. *Macromolecules* **1992**, *25*, 3356. (c) Shiono, T.; Soga, K. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 371.

(5) Nagata, N.; Kubota, T.; Watanabe, H.; Yoshioka, A. *Rubber Chem. Technol.* **1987**, *60*, 837.

(6) Brown, H. C.; Heydkanp, W. R.; Breuer, E.; Murphy, W. S. *J. Am. Chem. Soc.* **1964**, *86*, 3565.

(7) Suzuki, A.; Sono, S.; Itho, M.; Brown, H. C.; Midland, M. M. *J. Am. Chem. Soc.* **1971**, *93*, 4329.

(8) Brown, H. C.; Midland, M. M.; Kabalka, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 4329.

(9) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988; p 167.

(10) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.

(11) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heyden: London, 1976; p 51.

(12) Kalinowski, H. O.; Berger, S.; Braun, S. Carbon-13 NMR Spectroscopy; Wiley: New York, 1988; p 112.

(13) *n*-Butyl(2-methylpropyl)benzamide was synthesized from (2-methylpropyl)benzamide and n-butyl bromide according to the literature: Isele, G. L.; Luttringhaus, A. *Synthesis* **1971**, 266.

(14) Wild, F. R. W. P.; Zsolerai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233.

(15) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer* **1989**, *30*. 428.

(16) Boyer, J. H.; Hamer, J. *J. Am. Chem. Soc.* **1955**, *77*, 951.

(17) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules* **1988**, *21*, 617.

(18) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 4708.

(19) Brown, H. C.; Levy, A. B. *J. Organomet. Chem.* **1972**, *44*, 233.

(20) Brown, H. C.; Midland, M. M.; Levy, A. B. *J. Am. Chem. Soc.* **1973**, *95*, 2394.