Synthesis of Isotactic Polypropylene Functionalized with a Primary Amino Group at the Initiation Chain End

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Received December 9, 1993
Revised Manuscript Received February 23, 1994

Introduction. Terminally functionalized polymers are useful not only for the synthesis of block polymers but also for the improvement of polymer properties. Functionalization of isotactic polypropylene (iso-PP), which is one of the most important plastics, is expected to improve the property as well as compatibility with other materials. It is possible to obtain some terminally functionalized PP using a living polymerization method[1] as well as utilizing chain-transfer reactions.[2] However, the resulting polymer has a functional group only at the termination end. In this paper, an attempt was made to introduce a functional group at the initiation end of iso-PP.

It is generally accepted that olefin polymerization with Ziegler–Natta catalysts is initiated by alkylation of a transition-metal compound with a cocatalyst like alkylaluminum followed by successive monomer insertion. Therefore, one can expect to obtain a polyolefin with a functional group at the initiation chain end using a cocatalyst having a functional group. In addition, if any other chain-transfer reaction except by the cocatalyst is negligible, the majority of polymer chains may have the functional group at the initiation end and a metal–carbon bond at the termination end. Most organic compounds having active protons or heteroatoms, however, are liable to cause a deactivation of the polymerization centers.

As terminal functional groups, amino groups are most preferable due to their high reactivity with other compounds. In fact, terminally aminated polymers are commercially utilized in some elastomer production to improve the dispersity of fillers.[3] Therefore, in this paper, a dialkylzinc compound with alkylsilyl-protected primary amino groups was synthesized and propene polymerization was conducted over $TiCl_3$ using it as the cocatalyst.

Results and Discussion. Bis[3-(2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl)propyl]zinc (BAZ) was synthesized according to the procedures described in the Experimental Section. Propene polymerization was conducted at 40 °C for 1 h. The typical results are summarized in Table 1. The polymer yield did not depend upon the concentration of BAZ. The number-average molecular weight (M_n) and the number of polymer chains were also found to be independent of the concentration of BAZ, suggesting that BAZ does not act as a chain-transfer reagent. The change in polymerization time from 1 to 3 h did not cause an increase in the polymer yield (run nos. K375 and K388), indicating that the catalyst lifetime is not very long.

Propene polymerization was also conducted with the conventional $TiCl_3$–$AlEt_2Cl$ catalyst system for reference (run nos. K379, K380, and K381). As compared with the conventional catalyst system, the $TiCl_3$–BAZ catalyst system is less active, but the catalyst isospecificity is comparable; i.e., both the isotacticity and melting point of PP do not differ between the two catalyst systems. The structure of PP obtained with the $TiCl_3$–BAZ catalyst system was then investigated by ^1H and ^{13}C NMR. Any resonance attributable to the chain-end structure could not be observed, which may probably be due to a high molecular weight.

Therefore, the terminal amino group was determined by IR after amidation with benzoyl chloride. Figure 1 shows the IR spectra of PP before and after amidation. The amidated PP displayed a new absorption at 1660 cm^{-1} attributable to a carbonyl group. For reference, the IR spectra of a model compound, *n*-butylbenzamide,[4] were measured both in KBr disk and in chloroform solution, which displayed carbonyl absorption at 1640 and 1656 cm^{-1}, respectively. The red shift of the solid sample is ascribed to the association of amido groups. The appearance of the carbonyl group in the amidated polymer at 1660 cm^{-1} suggests that the chain-end amido groups are not associated in the polymer matrix.

The functionality of the polymer (F) is calculated by the following equation:

$$F = (A_{C=O}/A_{C-H})_{obs}/(A_{C=O}/A_{C-H})_{calc}$$

where $(A_{C=O}/A_{C-H})_{obs}$ is the absorbance ratio of amino and methyl groups observed in the IR spectrum, and $(A_{C=O}/A_{C-H})_{calc}$ is the calculated ratio by assuming that every polymer chain has one amido group. The peaks at 972, 1165 (C–H deformation band of the methyl group), and 1656 cm^{-1} (C=O stretching band) were used for the calculation of F, where the molar absorption coefficients $\epsilon_{972} = 104$, $\epsilon_{1165} = 91.4$, and $\epsilon_{1656} = 597$ L mol^{-1} cm^{-1} were estimated from atactic PP and *n*-butylbenzamide in chloroform. The results obtained are summarized in Table 2, indicating the value (0.7–1) to be in fairly good agreement. These results might lead to such a plausible polymerization mechanism as shown in Scheme 1.

In conclusion, iso-PP having a primary amino group at the initiation chain end was synthesized by using BAZ as cocatalyst. A more detailed study is now being carried out, the results of which will be reported elsewhere.

Experimental Section. Materials. 3-Bromopropylamine hydrobromide (from Tokyo Kasei Kogyo Co.), magnesium (turnings for Grignard reagent, from Wako Pure Chemical Ind.), 1,2-bis(dimethylchlorosilyl)ethane (from Sin Etsu Chemical Co.), $TiCl_3$ (aluminum-reduced, from Toho Titanium Co.), $AlEt_2Cl$ (from Tosoh Akzo Chemical Co.), and the other chemicals commercially obtained were used without further purification. Zinc dichloride (from Wako Pure Chemical Ind.) was dried in thionyl chloride under refluxing for 2 h and dried in vacuum. Propene (Mitsubishi Petrochemical Co.) was purified by passing it through columns of sodium hydroxide, phosphorus pentoxide, and molecular sieves of 4 Å. All the solvents were commercially obtained and used after drying according to the usual procedures.

Synthesis of BAZ. BAZ was synthesized according to a procedure similar to that of bis(*N*,*N*-dimethyl-3-aminopropyl)zinc.[5]

(i) Synthesis of 2,2,5,5-Tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopentane (BABR).[6] In a 1-L three-necked flask equipped with a mechanical stirrer were placed 70 g of 3-bromopropylamine hydrobromide, 350 mL of dichloromethane, and 180 mL of triethylamine under an argon atmosphere. The dichloromethane solution of 1,2-bis(dimethylchlorosilyl)ethane (68 g) was added dropwise to the mixture. After stirring for 5 h at 20 °C, the solvent was removed by evaporation and 600 mL of hexane was added. The mixture was filtered, and the filtrate was washed with a 5% aqueous solution of

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Table 1. Results of Propene Polymerization with the $TiCl_3$–BAZ Catalyst System[a]

run no.	BAZ (mmol/L)	yield (g/mmol of Ti)	$M_n \times 10^{-4}$	N (mmol/mmol of Ti)	II[b]	T_m (°C)	ΔH (J/g)
K372	20	0.23	1.4	0.016	0.81	162	72.6
K375	51	1.2	1.5	0.080	0.89	161	69.7
K388[c]	51	1.2					
K376	120	0.97	2.3	0.042	0.83	161	72.4
K367	148	1.3	2.1	0.062	0.85		
K377	260	1.1	1.8	0.061	0.86		
K369	510	0.17	1.3	0.013			
K381[d]	0	trace					
K380[d]	20	5.7	21	0.027	0.86	161	89.7
K379[d]	240	6.1	19	0.032	0.86	161	89.0

[a] Polymerization conditions: 50-mL stainless steel autoclave, heptane = 25 mL, propene = 3 L, $TiCl_3$ = 0.3–0.5 mmol, 40 °C, 1 h. [b] Absorbance ratio of 998 and 973 cm^{-1} determined by FT-IR spectrometry. [c] Polymerization was conducted for 3 h. [d] $AlEt_2Cl$ was used in place of BAZ.

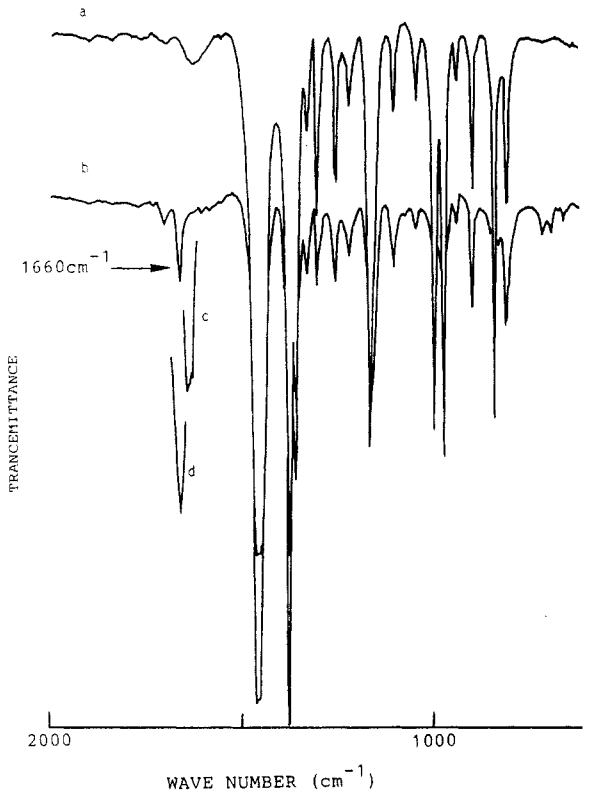


Figure 1. IR spectra of iso-PP obtained with the $TiCl_3$–BAZ catalyst system: (a) before amidation; (b) after amidation; (c) *n*-butylbenzamide in KBr; (d) *n*-butylbenzamide in chloroform.

Table 2. Contents of Amide Group in iso-PP

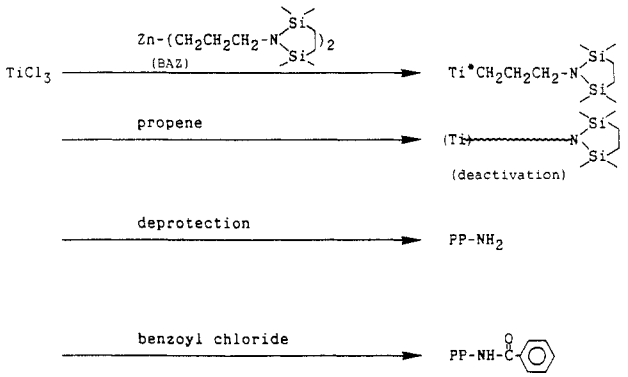
	$A_{C=O}/A_{CH_3}$[b]			$A_{C=O}/A_{CH_3}$[c]		
run no.	obs	calc	$F^{a,b}$	obs	calc	$F^{a,c}$
K372	0.24	0.32	0.75	0.26	0.37	0.70
K375	0.23	0.30	0.77	0.25	0.34	0.74
K376	0.22	0.20	1.1	0.23	0.23	1.0
K367	0.18	0.22	0.82	0.19	0.25	0.76
K377	0.25	0.25	1.0	0.28	0.28	1.0

[a] F = functionality (obs/calc). [b] Estimated from main-chain absorbances at 973 cm^{-1}. [c] Estimated from main-chain absorbances at 1167 cm^{-1}.

sodium hydroxide followed by drying over anhydrous magnesium sulfate. After the hexane was removed by evaporation, the residue was distilled under reduced pressure (5 mmHg, 80 °C) to obtain BABR in a 74% yield.

(ii) Synthesis of BAZ. In a 1-L three-necked flask equipped with a mechanical stirrer were placed 6 g of magnesium and 250 mL of ether under an argon atmosphere. A total of 65 g of BABR in ether was added dropwise to the mixture at 0 °C, and the reaction mixture was slowly warmed up to 30 °C. After stirring for 6 h, 18 g of zinc chloride in 150 mL of ether was added dropwise and the mixture was stirred at 30 °C for 12 h. The reaction mixture was filtered, and the filtrate was concentrated by evacuation. The residue was dissolved in heptane to precipitate magnesium halides. After filtration, the heptane solution was evacuated to obtain BAZ as a viscous liquid in a 79% yield. The analytical data of BAZ are as follows. Elem Anal. Calcd: C, 46.4; H, 9.5; N, 6.0; Zn, 14.0. Found: C, 44.0; H, 9.4; N, 5.6; Zn, 14.7. ^1H NMR ($C_6D_5CD_3$, room temperature): δ 2.75 (t, 2H), 1.80 (q, 2H), 0.80 (d, 4H), 0.35 (t, 2H), 0.15 (s, 12H). ^{13}C NMR ($C_6D_5CD_3$, room temperature): δ 47.99, 32.00, 10.32, 8.15, 0.02. Other resonances were observed at 42.87, 35.09, 27.63, 8.58, and 0.34 ppm in the ^{13}C NMR spectrum, which may be attributed to a coupling byproduct. The byproduct could not be separated, and BAZ was used as obtained.

Scheme 1. Plausible Mechanism of the Production of Aminated PP



Propene Polymerization. Propene polymerization was conducted with a 50-mL stainless steel autoclave equipped with a magnetic stirrer according to the procedure reported previously.[2f]

Amidation of Polypropylene. A total 0.2 g of terminally aminated iso-PP was placed in 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 ethanol, and dried under vacuum at 60 °C for 8 h.

Analytical Procedures. ^1H and ^{13}C NMR spectra of BAZ were recorded on a JEOL EX-90 spectrometer operated at 89.45 and 22.5 MHz, respectively, in the pulse Fourier transform (FT) mode. In ^{13}C NMR measurements, broad-band decoupling was used to remove ^{13}C–^1H decouplings. 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 polymers were recorded on a Jasco FT/IR-3 spectrometer. The zinc content was determined by atomic absorption spectrophotometry (Shimadzu AA-610). Elemental analyses were carried out by a Yanagimoto CHN Autocorder Type MT-2.

References and Notes

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