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# Isospecific Polymerization of Propene over $TiCl_3$ Combined with Bis($\omega$-alkenyl)zinc Compounds

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ABSTRACT: Bis(3-butenyl)zinc (BBZ) and bis(7-octenyl)zinc (BOZ) were synthesized from $ZnCl_2$ and the Grignard reagent prepared from the corresponding bromide. Propene polymerization was conducted with $TiCl_3$ using those compounds as cocatalyst. The activity strongly depended on the kind of cocatalyst and increased in the following order BBZ < BOZ < $AlEt_2Cl$. These catalyst systems gave isotactic polypropylenes whose melting points were around 160 °C. The bis($\omega$-alkenyl)zinc compounds acted as a chain transfer reagent to give zinc-terminated polymers with low molecular weights. IR, $^1H$ NMR, and $^{13}C$ NMR analyses of the produced polymers indicated incorporation of the 7-octenyl group at the initiation chain end, whereas the 3-butenyl group was not observed, probably due to back-biting cyclization. BOZ copolymerized with propene to give PP having hexylzinc groups as side chains, while BBZ did not. The zinc−carbon bonds at the termination end as well as the side chain were converted to vinyl groups by coupling with allyl bromide to give $\alpha,\omega$-divinyl isotactic polypropylene with pendant 8-nonenyl groups.

## Introduction

Functionalization of isotactic polypropylene (PP), which is one of the most important plastics, is highly expected to improve the compatibility with other materials. It is possible to obtain some terminally functionalized PP using living polymerization methods[1] and also utilizing chain transfer reactions.[2] Carrying out propene polymerization with a $TiCl_3-AlEt_2Cl$ catalyst containing a large amount of $ZnEt_2$, we found that almost all polymer chain ends are terminated by metals (mainly by Zn). These metal−polymer bonds were then subjected to oxygen, carbon dioxide, halogen, or allyl bromide to obtain hydroxyl-, carboxyl-, halogen-, or vinyl-terminated isotactic PP.[3−5]

Functionalization at the initiation chain end was also achieved by using functionalized alkylzinc compounds as cocatalyst and/or chain transfer reagent combined with $TiCl_3$. For example, bis(3-aminopropyl)zinc, whose amino groups are protected with ethylene-1,2-bis(dimethylsilyl), was effective as cocatalyst to give isotactic PP having the amino group at the initiation end.[6] Bis(4-methyl-3-pentenyl)zinc (BMP) was effective not only as cocatalyst but also as a chain transfer reagent.[7] Therefore, most of the produced polymer possessed a 2,6-dimethyl-5-heptenyl group and a Zn-PP bond at the initiation and termination ends, respectively. The Zn-terminated end could be converted to a vinyl group, which gives isotactic PP with the alkenyl groups both at the initiation and at the termination chain ends.

Functionalization of the side chain is another method to improve the properties of isotactic PP. Copolymerization of propene with a functionalized monomer seems to be one of the best methods. However, most organic compounds having active protons or heteroatoms are liable to cause a deactivation of the polymerization centers. Recently, Chung et al. prepared 5-hexenyl-9-BBN (BNN = borabicyclo[3.3.1]nonane) and copolymerized it with $\alpha$-olefin by the $TiCl_3-AlEt_2Cl$ catalyst.

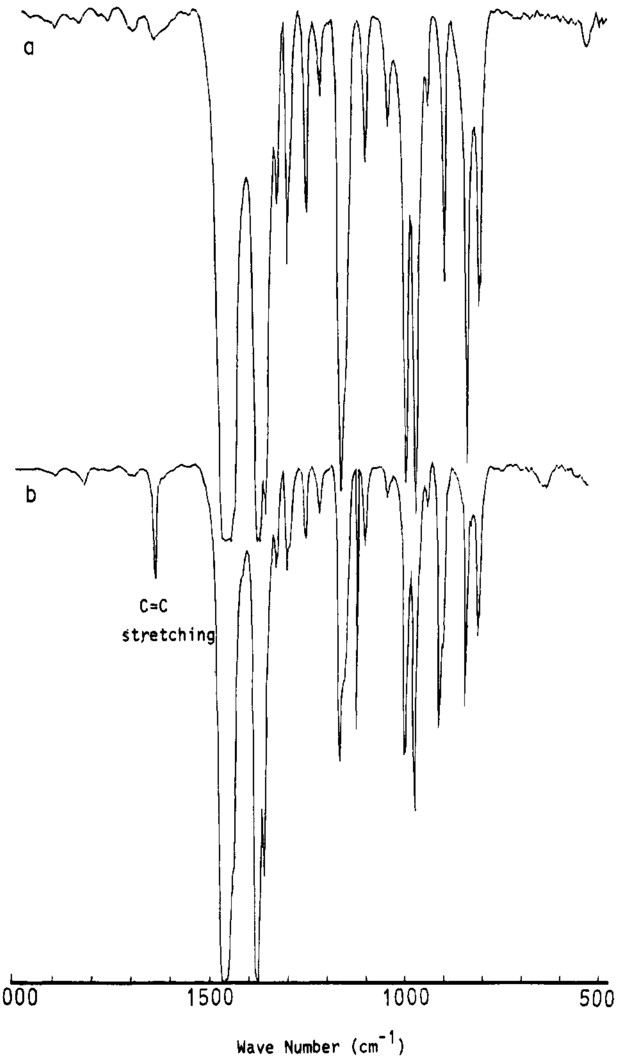

**Figure 1.** IR spectra of PP obtained with the $TiCl_3$−BBZ catalyst: (a) ethanol-quenced; (b) allyl bromide-quenched.

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**Table 1. Results of Propene Polymerization with $TiCl_3$–Bis(3-butenyl)zinc–($AlEt_2Cl$)[a]**

| run no. | Zn (Al) [mmol/L] | yield [g/mmol-Ti] | $M_n$[b] × $10^{-3}$ | $N$[c] [mol/mol-Ti] | $T_m$[d] [°C] | $\Delta H$[e] [J/g] | terminator | $-CH=CH_2$,[f,g] [mmol/g-PP] |
|---|---|---|---|---|---|---|---|---|
| 1 | 40 | 0.38 | 7.9 | 0.048 | 162 | 90.9 | EtOH/HCl | nd[h] |
| 2 | 120 | 0.46 | 6.7 | 0.069 | 162 | 92.5 | EtOH/HCl | nd |
| | | | | | | | Br–C–C=C | 0.12–0.13[f] |
| 3 | 240 | 0.69 | 5.0 | 0.14 | 159 | 81.6 | Br–C–C=C | 0.18–0.41[f] |
| 4 | 240 (20) | 0.62 | 4.9 | 0.13 | 158 | 69.4 | EtOH/HCl | nd |
| 5 | 240 (20) | 0.85 | 4.2 | 0.20 | | | Br–C–C=C | 0.25–0.45[f] (0.24[g]) |
| 10 | 0 (20) | 5.7 | 210 | 0.027 | 161 | 89.7 | EtOH/HCl | |
| 11 | 0 (240) | 6.1 | 190 | 0.032 | 161 | 89.0 | EtOH/HCl | |

[a] Polymerization conditions: 50-mL stainless steel autoclave, $TiCl_3$ = 0.6–0.8 mmol, heptane = 25 mL, propene = 3 L (STP), 40 °C, 1 h. [b] Number-average molecular weight. [c] Number of polymer chains. [d] Melting point determined by DSC. [e] Heat of fusion determined by DSC. [f] Determined by IR. [g] Determined by $^1H$ NMR. [h] Not detected.

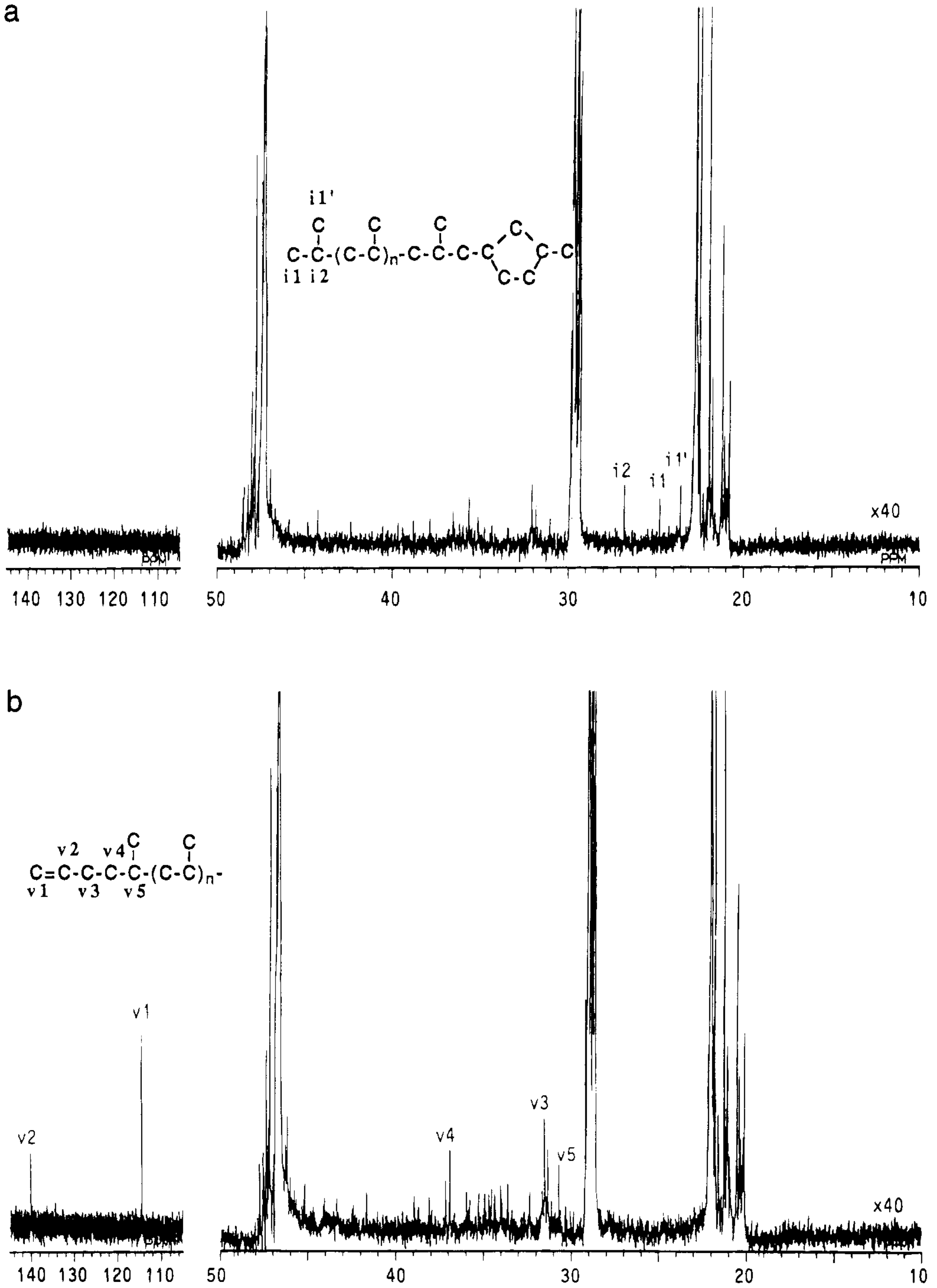
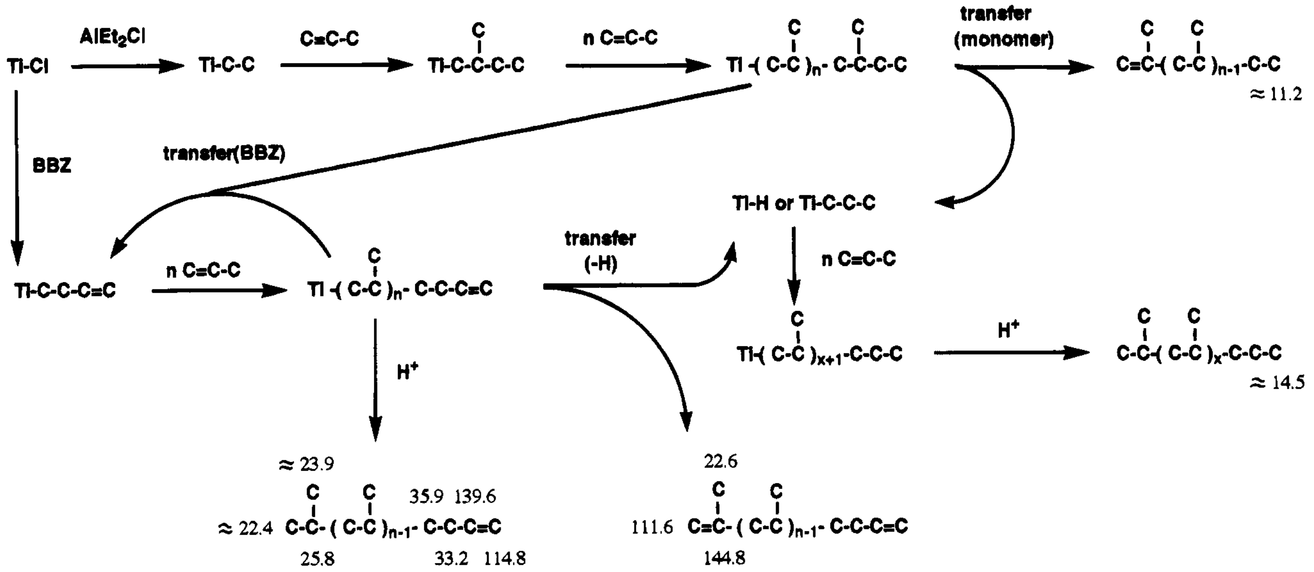


**Figure 2.** 125-MHz $^{13}C$ NMR spectra of PP obtained with the $TiCl_3$–BBZ–$AlEt_2Cl$ catalyst: (a) ethanol-quenched; (b) allyl bromide-quenched.

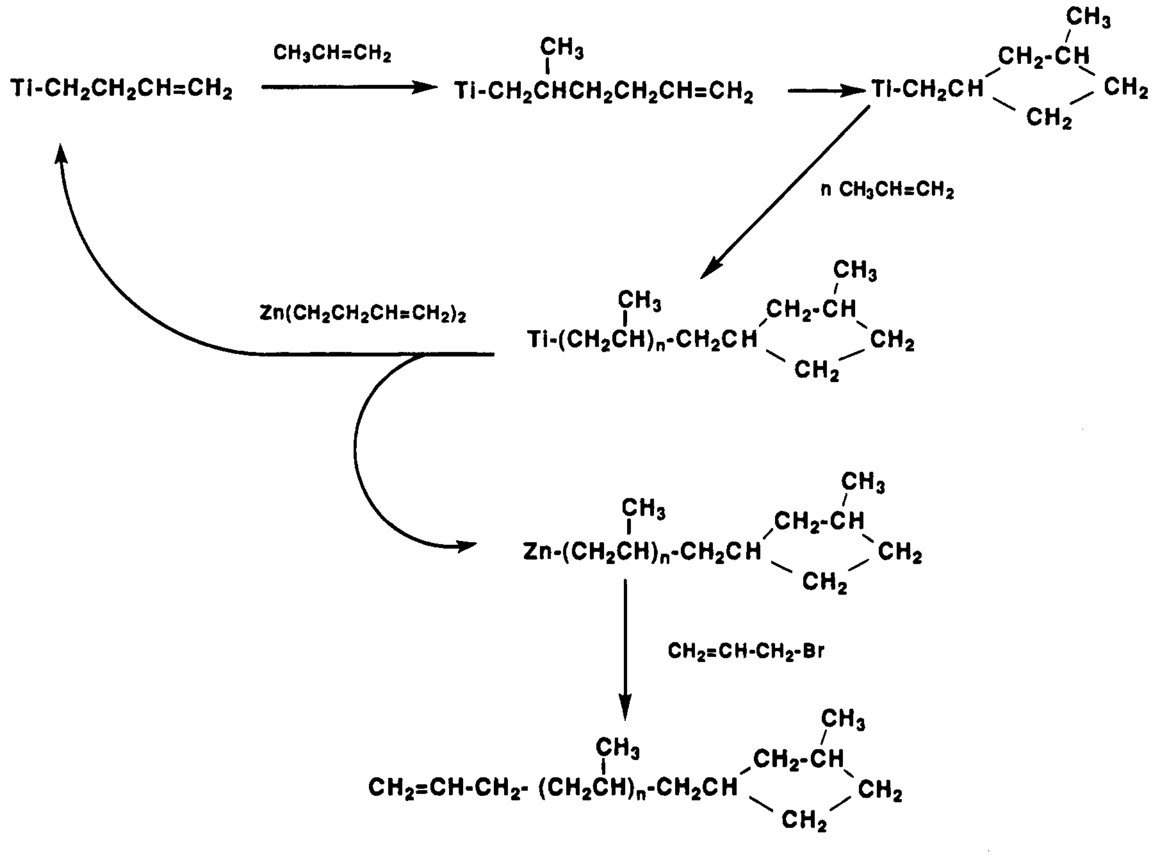
9-BBN at the side chain of the copolymer was converted to hydroxyl, iodine, or poly(methyl methacrylate) groups.[8-10]

In this paper, we prepared some bis(ω-alkenyl)zinc compounds and conducted propene polymerization using them as cocatalyst combined with $TiCl_3$, because these

**Scheme 1. Plausible Structures of Chain End Groups and Their Chemical Shifts (ppm from Tetramethylsilane)**



**Scheme 2. A Plausible Mechanism of Propene Polymerization with the $TiCl_3$–BBZ–$AlEt_2Cl$ Catalyst**



zinc compounds are expected to act not only as chain transfer reagent like BPZ to give α,ω-divinyl-PP but also as a comonomer like 5-hexenyl-9-BBN to introduce the zinc–carbon bond at the side chain.

## Results and Discussion

Bis(3-butenyl)zinc (BBZ) was synthesized according to the procedure described in the Experimental Section. Propene polymerizating was conducted with the $TiCl_3$–BBZ catalyst at 40 °C for 1 h, the results of which are summarized in Table 1 (run nos. 1–3). The increase in the concentration of BBZ increased the polymer yield and decreased the number-average molecular weight ($M_n$). As a result, the number of polymer chains increased with increasing concentration of BBZ, which suggests that BBZ acts as a chain transfer reagent as well as a cocatalyst. Propene polymerization was also conducted with a conventional $TiCl_3$–$AlEt_2Cl$ catalyst for reference. $AlEt_2Cl$ gave a higher activity than BBZ but had a very low ability as a chain transfer reagent (run nos. 10 and 11). The addition of $AlEt_2Cl$ to the $TiCl_3$–BBZ did not affect the polymer yield and the $M_n$ value (run nos. 4 and 5).

The thermal property of PP obtained with these catalysts was investigated by differential scanning calorimetry (DSC). The melting point ($T_m$) and heat of fusion ($\Delta H$) of the produced polymers are shown in Table 1. $T_m$ and $\Delta H$ do not differ much between the two catalyst systems, indicating that the isotacticity of

**Table 2. Results of Propene Polymerization with $TiCl_3$–Bis(7-Octenyl)zinc–($AlEt_2Cl$)[a]**

| run no. | Zn (Al) [mmol/L] | yield [g/mmol-Ti] | Mn[b] × $10^{-3}$ | $N$[c] [mol/mol-Ti] | $T_m$[d] [°C] | $\Delta H$[e] [J/g] | terminator | $-CH=CH_2$[f] [mmol/g-PP] |
|---|---|---|---|---|---|---|---|---|
| 6 | 40 | 0.43 | 9.7 | 0.044 | 161 | 88.2 | EtOH/HCl | nd[g] |
| 7 | 240 | 1.1 | 4.2 | 0.26 | 159 | 77.3 | EtOH/HCl | 0.09 |
| | | | | | | | Br–C–C=C | 0.32 |
| 8 | 240 (20) | 2.9 | 6.1 | 0.48 | 159 | 80.6 | EtOH/HCl | |
| 9 | 240 | 0.55 | 2.1 | 0.26 | 159 | 42.3 | EtOH/HCl | 0.17 |
| | | | | | | | Br–C–C=C | 1.5 |
| 10 | 0 (20) | 5.7 | 210 | 0.027 | 161 | 89.7 | EtOH/HCl | |

[a] Polymerization conditions: run nos. 6–8 and 10, 50-mL stainless steel autoclave, $TiCl_3$ = 0.5–0.9 mmol, heptane = 25 mL, propene = 3 L (STP), 40 °C, 1 h; run no. 9, $TiCl_3$ = 0.5 mmol, 50-mL glass reactor, heptane = 25 mL, propene = 1 atm, 40 °C, 24 h. [b] Number-average molecular weight. [c] Number of polymer chains. [d] Melting point determined by DSC. [e] Heat of fusion determined by DSC. [f] Determined by $^1$H NMR. [g] Not detected.

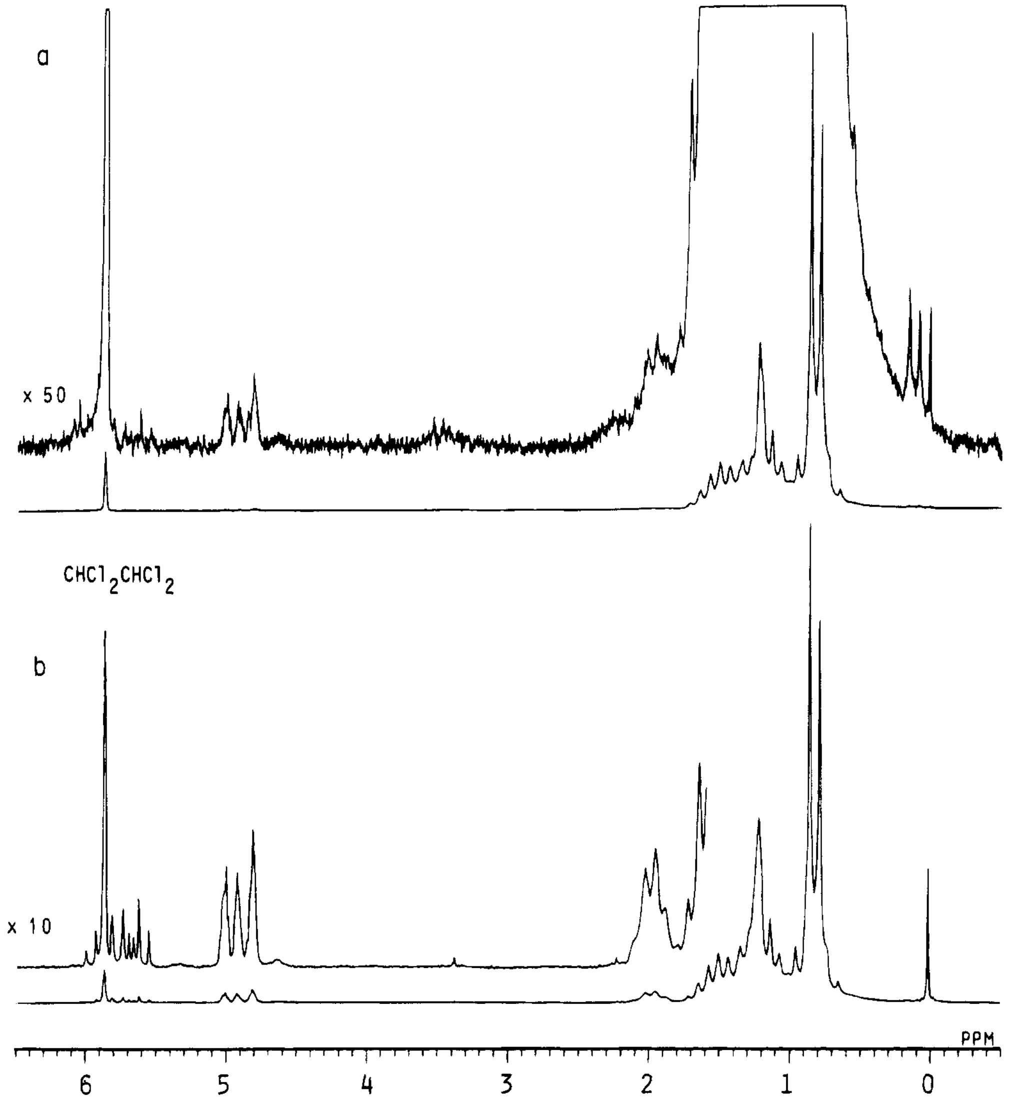


**Figure 3.** 90-MHz $^1$H NMR spectra of PP obtained with the $TiCl_3$–BOZ catalyst: (a) ethanol-quenched; (b) allyl bromide-quenched.

the present PP is comparable to that produced with the conventional catalyst.

It was thus proved that BBZ initiates and chain-transfers the isospecific polymerization of propene. Therefore, it is expected that the initiation end of the produced polymers is at least partly functionalized by the vinyl group. The IR and $^1$H NMR spectra of typical polymers were measured to characterize the microstructure of the polymers obtained with the $TiCl_3$–BBZ and $TiCl_3$–BBZ–$AlEt_2Cl$ catalysts. However, the corresponding vinyl group could not be detected in the IR and $^1$H NMR spectra. We have previously reported that the metal–polymer bonds of PP obtained with the $TiCl_3$–$AlEt_2Cl$–$ZnEt_2$ catalyst can be converted to vinyl groups in fairly good yield by the coupling reaction with allyl bromide in the presence of *N*-methylimidazole.[5] Therefore, the method was applied also to the present system.

Figure 1 shows the IR spectra of the polymers before and after the coupling reaction (run no. 5). After the coupling reaction, the absorption attributable to C=C stretching of the vinyl group newly appeared at 1643 cm$^{-1}$. The contents of the vinyl group in PP were determined from the IR spectra according to the method described in the Experimental Section and are shown in Table 1. The vinyl content increased with increasing concentration of BBZ, suggesting that BBZ acts as a

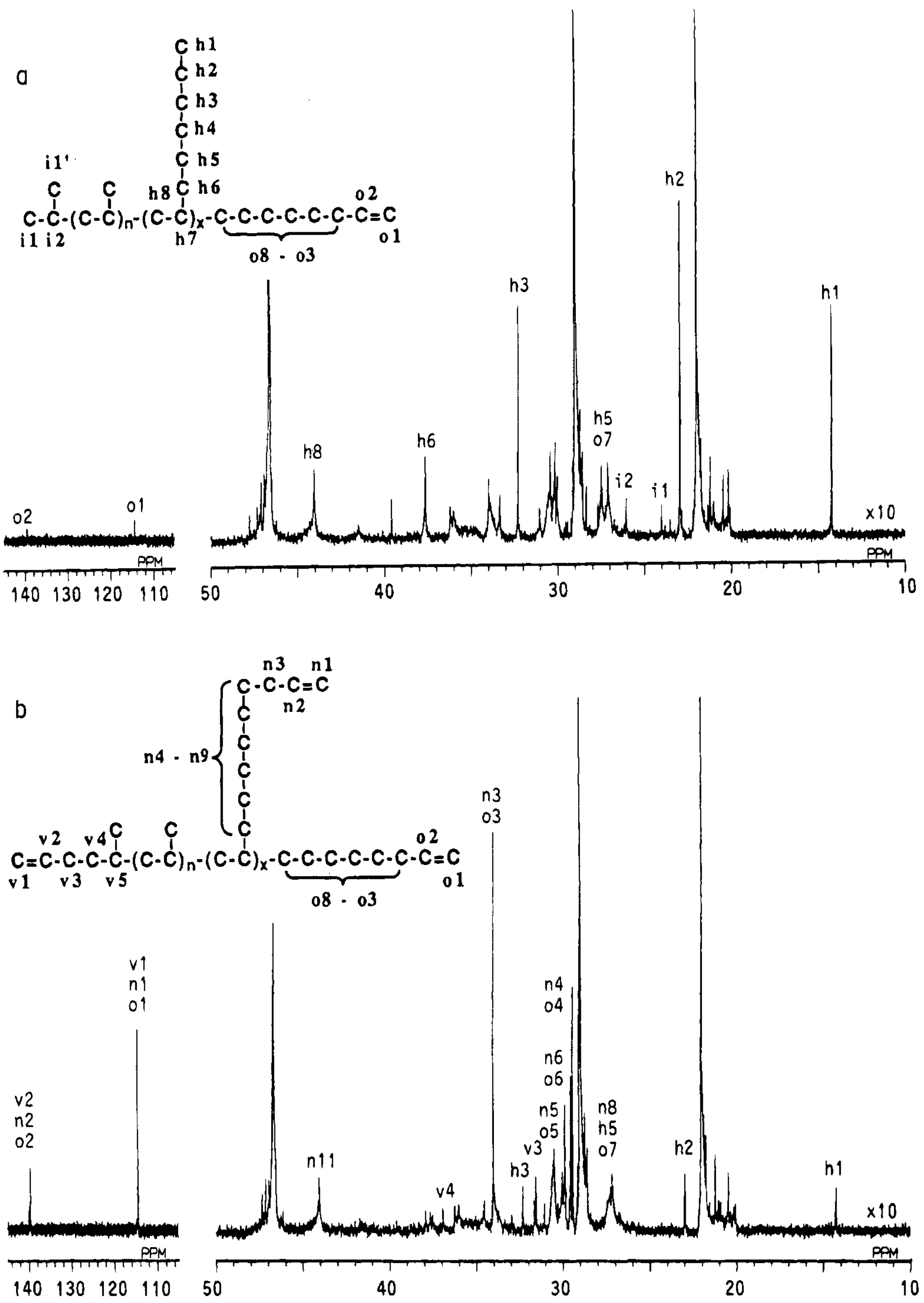


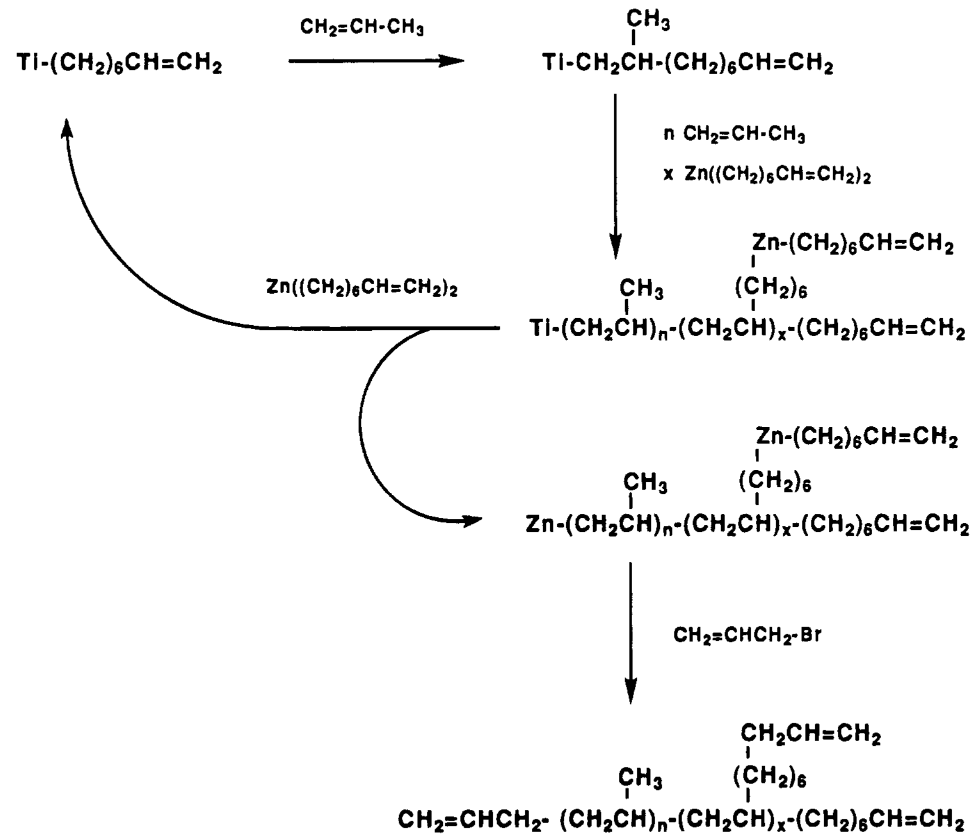
**Figure 4.** 125-MHz $^{13}C$ NMR spectra of PP obtained with the $TiCl_3$−BOZ catalyst: (a) ethanol-quenched; (b) allyl bromide-quenched.

chain transfer reagent. It is not clear, however, why the vinyl group is not introduced at the initiation chain end.

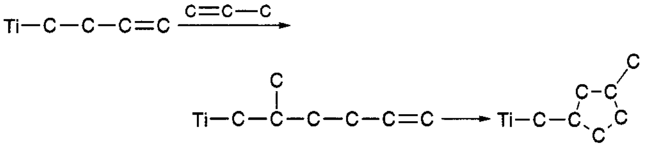
To investigate the structure of the chain ends in more detail, $^{13}C$ NMR spectra of the polymers obtained with the $TiCl_3$−BBZ−$AlEt_2Cl$ catalyst were measured before and after the coupling reaction (run nos. 4 and 5). Figure 2 shows the $^{13}C$ NMR spectrum of the ethanol-quenched PP. Besides the three strong resonances derived from the main-chain carbons, weak resonances attributable to the 2-methylpropyl end group can be observed, which is derived from the hydrolysis of the metal−PP bonds formed by 1,2-insertion of propene. However, the spectrum does not display any resonance assignable to the ethyl, vinyl, propyl, and vinylidene end groups, which should be formed by the initiation and/or chain transfer with $AlEt_2Cl$ and BBZ, and the chain transfer via β-hydrogen subtraction or by monomer, respectively (Scheme 1).

After the coupling reaction with allyl bromide, the resonances due to the 2-methylpropyl end group disappeared completely and those assignable to the vinyl end group newly appeared, suggesting that the 2-methylpropyl group derived from the metal−PP bonds is quantitatively converted to the vinyl group (Figure 2b). The absence of the vinyl group at the initiation chain end may be explained as follows (Scheme 2). BBZ acts as cocatalyst (alkylation of the Ti−Cl bond) as well as a chain transfer reagent. After the first propene monomer inserts into the Ti−(3-butenyl) bond, however, a five-membered ring end group is formed as shown below. The weak resonances between 30 and 40 ppm might be assigned to the cyclic structure. Formation of a similar five-membered ring has been confirmed in

**Scheme 3. A Plausible Mechanism of Propene Polymerization with the $TiCl_3$–BOZ Catalyst**



the 1,5-hexadiene polymerization with the $V(acac)_3$–$AlEt_2Cl$, $TiCl_3$–$AlEt_2Cl$, or zirconocene–methylaluminoxane catalyst systems.[11–15] The absence of ethyl, propyl, and vinylidene end groups suggests that the chain transfer reaction was mainly caused by BBZ.



Such a cyclization might be prevented by changing the 3-butenyl group to a longer one. From such a viewpoint, bis(7-octenyl)zinc (BOZ) was synthesized and supplied as cocatalyst. Propene polymerization was conducted with the $TiCl_3$–BOZ catalyst under high pressure (run nos. 6–8) or low pressure (run no. 9) of propene, the results of which are summarized in Table 2. Addition of more BOZ caused an increase in the polymer yield with a decrease in the $M_n$ value, which indicates that BOZ acts as a chain transfer reagent as well as a cocatalyst. Addition of $AlEt_2Cl$ increased the polymer yield without changing the $M_n$ value and thermal properties of the produced polymer. Contrary to the polymer obtained with BBZ, the polymers obtained in a higher concentration of BOZ contained vinyl groups (Figure 3a). The vinyl contents determined by $^1H$ NMR are shown in Table 2. The decrease in propene pressure decreased the $M_n$ value and increased the vinyl content, which supports that chain transfer mainly occurs by BOZ.

Then the produced polymers were brought into contact with allyl bromide in the presence of *N*-methylimidazole. After the reaction, the vinyl content of the polymer obtained under high propene pressure increased more than 3 times and those under low propene pressure increased more than 10 times, respectively. This result suggests that Zn–carbon bonds are present not only at the termination end formed by chain transfer with BOZ but also at side chains formed by copolymerization of BOZ with propene. The decrease in the heat of fusion with the decrease in propene pressure also supports the copolymerization, since the propene polymerization was conducted under the same concentration of BOZ independent of the propene pressure.

The $^{13}C$ NMR spectra of the polymers before and after the coupling reaction were measured to investigate the polymer structure in more detail (Figure 4). Besides the three strong resonances derived from main-chain carbons, weak resonances attributable to the 2-methylpropyl and vinyl ($(CH_2)_6CH{=}CH_2$) end groups are observed with similar intensities. In addition, some stronger resonances are observed, which can be assigned to the pendant hexyl group according to the literature[16] as shown in Figure 4. This result indicates that BOZ can copolymerize with propene to form the pendant hexylzinc group. The content of the pendant group was calculated from the intensities of the propene and 1-octene units in the $^{13}C$ NMR, which indicates about 5 mol % of 1-octene was incorporated in the produced polymer. After the coupling reaction, the intensities of the carbons in the 2-methylpropyl and hexyl groups were significantly weakened, and those in the vinyl group were strengthened. A plausible model of propene polymerization with the $TiCl_3$–BOZ catalyst is shown in Scheme 3.

On the other hand, there was no evidence of copolymerization of BBZ with propene. Such a difference between BOZ and BBZ may result from the fact that the butenyl groups of BBZ are intramolecularly coordinated to zinc to form the stable cyclic structure in nonpolar solvents.[17]

In conclusion, it is proved that an adequate bis($\omega$-alkenyl)zinc compound is effective not only as a cocatalyst and/or chain transfer reagent but also as a functionalized comonomer. The produced polymer can be converted to isotactic α,ω-divinyl-PP having pendant ω-alkenyl groups by the coupling reaction with allyl bromide.

## Experimental Section

**Materials.** Propene (Mitsubishi Petrochemical Co.) was purified by passing through columns of $CaCl_2$, $P_2O_5$, and molecular sieves 3A. $TiCl_3$ (AA type, Toho Titanium Co.) and $AlEt_2Cl$ (Tosoh Akuzo Chemical Co.) were used without further purification. Research grade pentane and heptane commerically obtained were dried over $CaH_2$ under reflux for 24 h and distilled before use. Diethyl ether was successively dried over $CaH_2$ and sodium metal under reflux for 12 h and distilled before use. Magnesium (turnings for Grignard reagent, from Wako Pure Chemical Industries, Ltd.) was dried under vacuum. $ZnCl_2$ (10 g) was treated with 25 mL of thionyl chloride under reflux for 2 h. After decantation, the remaining thionyl chloride was removed under vacuum. 4-Bromo-1-butene and 8-bromo-1-octene (Aldrich Chemical Co., Inc.) were dried over molecular sieves 4A. Argon (99.9995%) and nitrogen (99.9995%) were used without further purification.

**Synthesis of Bis(3-butenyl)zinc (BBZ).** It is reported by Denis et al. that BBZ can be synthesized using exchange of zinc metal with bis(3-butenyl)mercury.[18] In this paper, however, BBZ was prepared from (3-butenyl)magnesium bromide and $ZnCl_2$ as follows. In a 500 mL three-necked flask equipped with a mechanical stirrer were placed 9 g of magnesium and 170 mL of ether under an argon atmosphere. 4-Bromo-1-butene (50 g) in 50 mL of diethyl ether was added dropwise to the mixture at room temperature, followed by raising the temperature to the reflux temperature. After stirring for 2 h, a small portion of the reaction mixture was hydrolyzed and titrated with hydrochloric acid to estimate the concentration of (3-butenyl)magnesium bromide. $ZnCl_2$ (21 g) in 200 mL of ether was then added dropwise to the Grignard reagent, and the mixture was stirred for 12 h at 30 °C. The reaction mixture was filtered, and the filtrate was concentrated by evacuating diethyl ether. The product was dissolved in pentane to precipitate magnesium halides. After filtration, the pentane was evaporated and the residue was dried under vacuum to obtain BBZ in a 90% yield as a reddish brown liquid. Analytical data: 90-MHz $^1$H NMR ($C_6D_6$) 0.2–0.4 (2H, t, $CH_2Zn$), 2.0–2.4 (2H, q, $CH_2$), 4.8–5.2 (2H, t, $=CH_2$), 5.8–6.2 (1H, m, $-CH=$); 22.4-MHz $^{13}$C NMR ($C_6D_6$) 14.7 ($CH_2Zn$), 30.7 ($CH_2$), 112.1 ($=CH_2$), 144.8 ($-CH=$). These values are in good agreement with those reported previously.[17]

**Synthesis of Bis(7-octenyl)zinc (BOZ).** BOZ was prepared by the reaction of (7-octenyl)magnesium bromide and $ZnCl_2$ according to a procedure similar to that described above. BOZ was obtained in an 80% yield. Analytical data: 90-MHz $^1$H NMR ($C_6D_6$) 0.2–0.5 (2H, t, $CH_2Zn$), 1.1–1.7 (8H, m, $-CH_2-$), 1.8–2.2 (2H, q, $-CH_2-$), 4.8–5.2 (2H, t, $=CH_2$), 5.5–6.1 (1H, m, $-CH=$); 22.4-MHz $^{13}$C NMR ($C_6D_6$) 16.4 ($CH_2Zn$), 26.9, 29.4, 29.5, 34.3, 36.7, 114.5 ($=CH_2$), 139.3 ($-CH=$).

**Polymerization Procedure.** Propene polymerization was conducted with a 50 mL glass reactor or a 50 mL stainless steel autoclave equipped with a magnetic stirrer according to the procedures reported previously.[5] The polymerization was terminated by pouring the mixture into a dilute solution of hydrochloric acid in ethanol (ca. 500 mL) and stirred overnight. The precipitated polymer was washed with plenty of water and ethanol successively and dried under vacuum at 60 °C for 8 h.

**Coupling Reaction with Allyl Bromide.** After the polymerization, the remaining propene monomer was evacuated and nitrogen was introduced. A small portion of the reaction mixture was taken out, if necessary, and the hydrolyzed polymer was purified as described above for reference. The coupling reaction with allyl bromide was conducted in the presence of *N*-methylimidazole at around 130 °C for 3 h as reported previously.[5]

**Analytical Procedure.** $^1$H NMR spectra of samples were recorded on a JEOL EX-90 spectrometer operated at 89.45 MHz in the pulse Fourier transfer (FT) mode. $^{13}$C NMR spectra were recorded on a JEOL GX-500 spectrometer operated at 125.65 MHz in the pulse FT mode. In the $^1$H NMR measurements, the pulse angle was 45 °C, and 100–500 scans were accumulated in 9 s of pulse repetition. In the $^{13}$C NMR measurements, broad-band decoupling was used to remove the $^{13}$C–$^1$H coupling. The pulse angle was 45°, and 6000–8000 scans were accumulated in 8 s of pulse repetition. The spectra were obtained at 130 °C in 1,1,2,2-tetrachloroethane-$d_2$ solution (2 wt % for $^1$H NMR and 15 wt % for $^{13}$C NMR in a 5 mm o.d. tube). Hexamethyldisiloxane was used as an internal reference (0 ppm for $^1$H NMR; 2.03 ppm for $^{13}$C NMR, respectively).

Differential scanning calorimetry (DSC) measurements were made on a Seiko DSC-220. Polymer samples (ca. 4 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. Sample films were made with a hotpress at 160 °C under 100 kg/cm$^2$ of pressure.

The content of the vinyl group in the polymer was estimated with IR spectra from the absorbance ratios of the C=C stretching band (1643 cm$^{-1}$) of the vinyl group and the C–H deformation bands (1303, 1256, 1220, 1167, and 973 cm$^{-1}$). Calibration curves were obtained with vinyl-terminated isotactic PPs containing 0.076, 0.12, and 0.18 mmol of vinyl groups per gram of PP, which were prepared by the coupling reaction between Zn–polymer bonds and allyl bromide and characterized by $^1$H and $^{13}$C NMR.[5] Gel-permeation chromatography of the polymers was performed on a Waters 150C at 140 °C in *o*-dichlorobenzene as solvent.

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