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Communications to the Editor

Synthesis of Isotactic Polypropene-*block*-Poly(methyl methacrylate) Using Magnesium Bromide-Terminated Isotactic Polypropene

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Introduction. Block copolymers containing polypropene (PP) segments seem to be very important to the improvement of the compatibility with other materials. Various syndiotactic PP-based block copolymers can be synthesized by using a living polymerization system composed of $V(acac)_3$ and $Al(C_2H_5)_2Cl$ at −78 °C.[1] It has been recently reported that syndiotactic PP-*block*-poly(methyl methacrylate) (PMMA) improves the mechanical property of the blend of isotactic PP and PMMA.[2] From the industrial point of view, it seems more important to synthesize the block copolymers containing the isotactic PP segment. A few isotactic PP-based block copolymers were synthesized by utilizing chain transfer reactions. Isotactic PP-*block*-poly(methyl vinyl ketone) was synthesized by using the Al-terminated isotactic PP as an initiator,[3] which was formed by the chain transfer with $Al(C_2H_5)_3$. Isotactic PP-*block*-polystyrene and -poly(styrene-*co*-acrylonitrile) were synthesized by using thiol-terminated isotactic PP as a chain transfer reagent in radical polymerization;[4] the thiol-terminated polymer was synthesized from the vinylidene-terminated PP obtained by a *rac*-dimethylsilylenebis(indenyl)zirconium–methylaluminoxane (MAO) catalyst.

In this paper, an attempt was made to prepare isotactic PP-*block*-PMMA by using magnesium bromide (MgBr)-terminated isotactic PP as an initiator, which was prepared from the vinylidene-terminated polymer obtained with the *rac*-ethylenebis(tetrahydroindenyl)zirconium dichloride ($Et[H_4Ind]_2ZrCl_2$)–MAO catalyst.

Results and Discussion. We have already reported that chlorine-, bromine-, and iodine-terminated isotactic PPs were obtained in high yields (>80%) by halogenolysis of Zn-terminated[5] or Al-terminated[6] polymer. However, such halogen-terminated isotactic PPs cannot be used as precursors of the Grignard reagent due to their poor solubility in polar solvents. Therefore, in this paper, the MgBr-terminated isotactic PP was prepared by transmetalation of the B-terminated PP prepared from the vinylidene-terminated PP. It is reported that trialkylborane is quantitatively converted to the corresponding Grignard reagent by reaction with pentane-1,5-diyldi(magnesium bromide) in benzene or toluene according to the following scheme.[7]

$$R_3B + 2BrMg(CH_2)_5MgBr \longrightarrow 3RMgBr + [(H_2C)_5B(CH_2)_5]^{+}MgBr^{-}$$

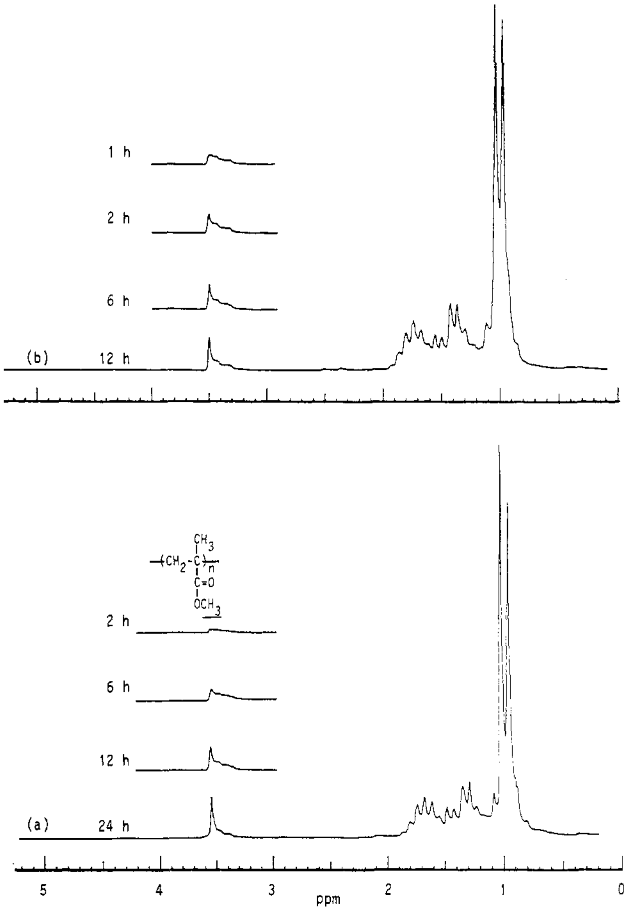

Figure 1. 100-MHz ^1H NMR spectra of isotactic PP-*block*-PMMA obtained at (a) −78 and (b) 0 °C.

The formation of a relatively stable bicyclic borate might cause a shift of the equilibrium to the right.

The MgBr-terminated isotactic PP synthesized according to the procedure described in the Experimental Section was subjected to polymerization of MMA as an anionic initiator. The polymerization was conducted at −78, 0, and +45 °C by changing the polymerization time. The produced polymers were extracted with boiling acetone to remove homo-PMMA. The ^1H NMR spectra of the acetone-insoluble fractions obtained at −78 and 0 °C are displayed in Figure 1. The absence of the resonance of vinylidene protons (at around 4.8 ppm) indicated that the hydroboration proceeded quantitatively. Besides the strong resonances of PP, the resonance of methoxy protons was observed at around 3.5 ppm, the intensity of which was increased with an increase in the polymerization time. The methoxy protons were also observed in the polymers obtained at 45 °C, the intensity of which was, however, very weak and independent of polymerization time. The ratios of monomer units (MMA/propene) in the copolymers were estimated from the relative intensity of the methoxy and hydrocarbon protons. The results are shown in Figure 2, which clearly shows that the MMA content in the copolymer increased with an increase in the polymerization time. The number-average molecular weight determined by GPC also increased with prolonging

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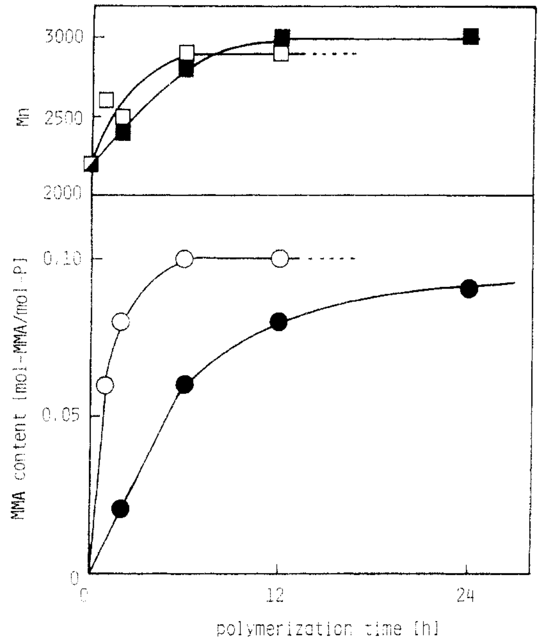


Figure 2. PMMA content and number-average molecular weight of isotactic PP-*block*-PMMA against polymerization time: (●, ■) −78 °C; (○, □) 0 °C.

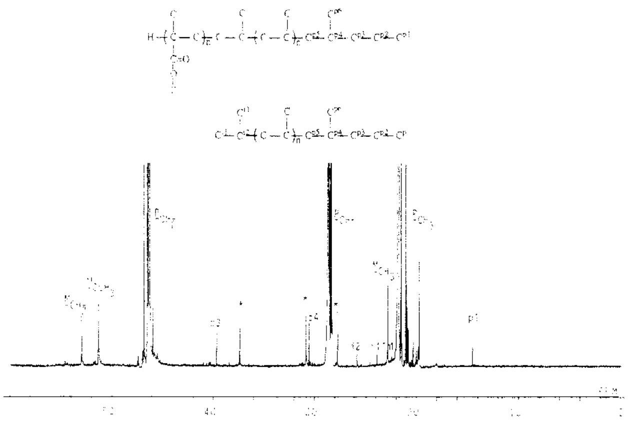


Figure 3. 125-MHz ^{13}C NMR spectrum of isotactic PP-*block*-PMMA obtained at 0 °C for 12 h.

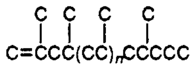
the polymerization time to reach a steady value, which indicates the formation of the block copolymer.

To investigate the polymer structure in more detail, the ^{13}C NMR spectrum was measured for the block copolymer obtained at 0 °C for 12 h (Figure 3). Besides the strong resonances of the main chain carbons of PP, the resonances of PMMA are observed at 22.80, 51.31, 52.95, and 176.36 ppm. These chemical shifts indicate that the PMMA sequences have an isotactic structure.[8] Several other weak resonances can be attributed to 2-methylpentyl and 2-methylpropyl end groups. The former is produced by the insertion of propene into a Zr–H bond, and the latter is produced by hydrometalation of the vinylidene group followed by hydrolysis. In the present polymer, the intensity of the 2-methylpropyl group is weaker than that of the 2-methylpentyl group. The relative intensity of these groups suggests that approximately 70% of the polymer chains reacted with MMA under the present conditions.

In conclusion, the MgBr-terminated isotactic PP was synthesized by the hydroboration of vinylidene-terminated polymer followed by transformation of B–C bonds with pentane-1,5-diyldi(magnesium bromide). The MgBr-terminated polymer was found to initiate the polymerization of MMA to produce the isotactic PP-*block*-PMMA copolymer.

Experimental Section. Materials. Propene (Mitsubishi Petrochemical Co.) was purified by passing through columns of $CaCl_2$, P_2O_5, and molecular sieves (3 Å). Et[H_4-Ind]$_2$ZrCl_2 was prepared according to the literature.[9] Methylaluminoxane (Tosoh Akzo Chemicals Co.) and a borane–dimethylsulfide complex (Aldrich Chemical Co.) were used without further purification. Research grade benzene and toluene (commercially obtained) were dried over calcium hydride under reflux for 24 h and distilled on a molecular sieve (4 Å). Methyl methacrylate (MMA; extra pure grade) was dried over calcium hydride and distilled before use. Argon (99.9995%) was used without further purification. Pentane-1,5-diyldi(magnesium bromide) in tetrahydrofuran (0.6 M) was synthesized from magnesium tunings (for Grignard reagent, Wako Chemical Co.) and 1,5-dibromopentane (Aldrich Chemicals Co.; dried over molecular sieves (4 Å)).

Preparation of Isotactic PP. The vinylidene-terminated isotactic PP was synthesized at 30 °C by the Et[H_4Ind]$_2$ZrCl_2–MAO catalyst as reported previously.[10] The produced polymer was extracted with boiling acetone, and the boiling-acetone insoluble fraction (about 90 wt %) was used as a starting material. The structure of the polymer was confirmed as **I** by ^{13}C NMR and ^1H NMR.[10]



$$\mathrm{C{=}\overset{C}{\overset{|}{C}}C\overset{C}{\overset{|}{C}}(C\overset{C}{\overset{|}{C}})_{n}C\overset{C}{\overset{|}{C}}CCC}$$

I

The properties of the polymer used in the present study were characterized as follows: melting point = 114 °C, isotactic triad = 0.82, number-average molecular weight (M_n) determined by chain end analysis = 5300, M_n by GPC = 2200 (polydispersity = 2.0). The discrepancy of M_n may be due to the limitation of GPC in the low molecular weight range. The vinylidene content in the polymer was calculated by M_n (5300) to be 0.19 mmol/g of polymer.

Synthesis of MgBr-Terminated PP. The terminal C=C bond of the polymer was hydroborated by a borane–dimethylsulfide complex.[11] After about 1 g of the PP was placed in a 50-mL Schlenk tube equipped with a magnetic stirrer, the tube was evacuated and replaced with argon. Toluene (10 mL) and a borane–dimethylsulfide complex (0.086 mmol) were added to the tube, and the mixture was heated at 70–80 °C for 2 h. After pentane-1,5-diyldi(magnesium bromide) in tetrahydrofuran solution (0.173 mmol) was added, the mixture was continually stirred for 2 h to obtain MgBr-terminated PP.[7]

Synthesis of PP-*block*-PMMA Copolymer. MMA polymerization with the MgBr-terminated PP was conducted at −78, 0, and +45 °C. When the polymerization was conducted at 0 or +45 °C, MMA (9.4 mmol) was added into the MgBr-terminated PP in toluene at the polymerization temperature. When the polymerization was conducted at −78 °C, MMA was added at 0 °C and the mixture was quickly cooled in a dry ice–ethanol bath. The polymerization was quenched by pouring the polymerization mixture into ethanol containing hydrochloric acid. The precipitate was collected and dried under vacuum at 60 °C for 6 h. The obtained polymer was extracted with boiling acetone, and the acetone-insoluble fraction was supplied for analyses.

Analytical Procedures. The ^1H spectra of samples were recorded on a JEOL FX-100 spectrometer operated at 99.45 MHz in the pulse Fourier transform (FT) mode.

The ^{13}C NMR spectrum was recorded on a JEOL GX-500 spectrometer operated at 125.65 MHz in the pulsed FT mode. In ^{1}H 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 $^{13}C-^{1}H$ couplings. The pulse angle was 45°, and about 8000 scans were accumulated in 8 s of pulse repetition. The spectra were obtained at 80 °C in a C_6D_6 solution using C_6H_6 as an internal reference (7.15 ppm for ^{1}H NMR and 128.0 ppm for ^{13}C NMR, respectively).

The gel permeation chromatograms (GPC) of the polymers were recorded on Sensyu SSC-7100 equipped with a Shodex GPC UT-806L column at 145 °C and *o*-dichlorobenzene as the solvent. The molecular weights were determined by a universal calibration technique.

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