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Copolymerization of Propene and 1,2,4-Trivinylcyclohexane by a $MgCl_2$-Supported $TiCl_4$ Catalyst

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Introduction. Polypropene (PP) is one of the most important polymeric materials, whose excellent physical properties and high cost performance have resulted from the development of catalyst and production systems.[1]

Recently, much effort has been paid to functionalize PP. Terminal functionalization of PP has been achieved via vinylidene-terminated or metal-terminated group produced by chain transfer reactions.[2] Several terminally functionalized PPs can be transformed to PP-based block copolymers.[2c,i,j] We have previously reported that a $MgCl_2$-supported $TiCl_4$ catalyst was also available for chain-end functionalization of PP.[3]

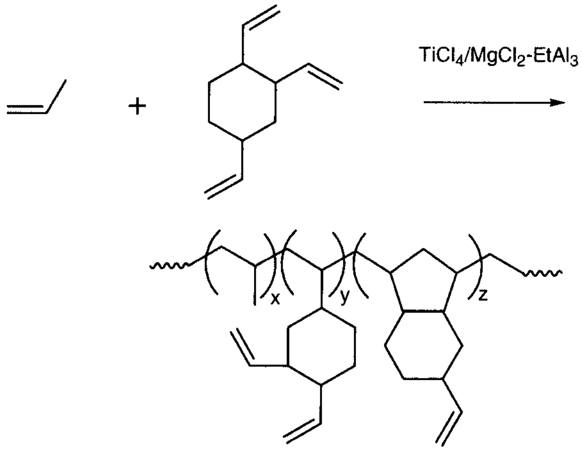
Functionalization of side chain is another method to modify the properties of poly(α-olefin)s.[4] Although direct copolymerization of propene with a functionalized monomer is the best way for the synthesis of PP with pendant functional groups, a simultaneous control of copolymerization ability and stereospecificity seems to be very difficult at present. Only a few functional comonomers were copolymerized with propene, because oxophilic active species of Ziegler−Natta catalysts are intolerant toward polar groups.[5]

Copolymerization with diolefin is another way to prepare reactive PP, in which the remained olefinic group at side chain is applied for functionalization.[6] PP with pendant vinyl groups can be prepared by copolymerization of propene with α,ω-diolefins such as 1,5-hexadiene, while cyclic copolymerization of α,ω-diolefins prevents the introduction of high vinyl contents while keeping original properties of PP, which demonstrates the disadvantage of this method.[9]

From these points of view, we have chosen 1, 2, 4-trivinylcyclohexane (TVCH) as comonomer, because one vinyl group remains even after the cyclopolymerization as shown in Scheme 1. In this study, TVCH was copolymerized with propene by using a $MgCl_2$-supported $TiCl_4$ catalyst, because $MgCl_2$-supported $TiCl_4$ catalysts are widely used in the industrial processes for isotatic PP.

Experiment. Materials. Propene (Takachiho Chemical Co.) was purified by passing it through MnO and molecular sieves 4A in stainless steel columns at 60 °C. TVCH from Aldrich Co. was dried over CaH_2 and distilled at 85−88 °C under a reduced pressure of 20 mmHg. $TiCl_4$ (Wako Chemical Co.), $MgCl_2$ donated from Toho Titanium Co. (surface area, 80 m^2/g), and $AlEt_3$ donated from Tosoh-Finechem Co. were used without further purification. Toluene was dried over CaH_2 under refluxing for 24 h and distilled under N_2 prior to use. Nitrogen and argon were purified by passing them through MnO and molecular sieves 4A for removing the traces of oxygen and water. A $MgCl_2$-supported $TiCl_4$ catalyst was prepared according to usual procedure.[8]

Scheme 1. Copolymerization of Propene with TVCH



Polymerization Procedures. Copolymerization of propene and TVCH was conducted in a 100-mL glass reactor equipped with a magnetic stirrer. After measured amounts of TVCH and $AlEt_3$ were placed in the reactor under nitrogen atmosphere, propene was introduced at 40 °C until TVCH was saturated with propene. Polymerization was started by adding the catalyst into the reactor and terminated by addition of a dilute solution of hydrochloric acid in methanol. The precipitated polymers were filtered out and dried under vacuum at 60 °C for 6 h. Atactic and isotactic polymers were fractionated as follows. About 1 g of obtained polymer was placed in a 200-mL, round-bottomed glass flask with 100 mL of dry xylene, and the mixture was heated at 120 °C under N_2 until the copolymer was dissolved. Then, the solution was slowly cooled to room temperature, and the solid product (cold-xylene insoluble fraction, isotactic polymer) was isolated by filtration, washed several times with hexane to completely remove cold-xylene soluble fraction (atactic polymer). Atactic copolymer was precipitated in excess methanol. Both fractions were dried under vacuum at 60 °C for 6 h.

Analytical Procedures. ^1H NMR spectra of samples were recorded at 120 °C on a JEOL GX-500 spectrometer in pulse Fourier transform (FT) mode. The pulse angle was 45°, and 1000 scans were accumulated in 7 s of pulse repetition. The sample solution was made in 1,1,2,2-tetrachloroethane-d_2 as a solvent and the resonance of tetrachloroethane was used as an internal reference (5.91 ppm). Differential scanning calorimetry (DSC) measurements were made on a Seiko DSC-220. The 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 a solvent and calibrated with standard polystyrene samples.

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Table 1. Copolymerization of Propene with TVCH by $TiCl_4/MgCl_2-Et_3Al$ Using TVCH as a Solvent[a]

no.	amt of propene (M)	solvent	time (min)	activity[b]	I.I. (%)	$M_n \times 10^4$ (M_w/M_n)[c] isotactic[d]	$M_n \times 10^4$ (M_w/M_n)[c] atactic[e]	T_m[f] (°C)	ΔH[g] (J/g)	T_g[h] (°C)	isotactic[d] vinyl	isotactic[d] vinylidene[i]	atactic[e] vinyl	atactic[e] vinylidene[i]
1	0.98	heptane	10	13.0	64	3.0 (9.1)	0.8 (6.3)	154	104	−10.1		0.04		0.1
2	0.64	TVCH	10	9.1	68	6.2 (6.5)	1.5 (6.6)	156	69	−1.8	1.3	0.02	4.4	0.08
3	1.03	heptane	60	6.6	65			154	120	−7.0				
4	0.65	TVCH	60	4.0	72			155	52	−0.4				

[a] Polymerization conditions: Ti = 0.19 mmol, Al/Ti = 100 mol/mol, solvent = 10 mL, 40 °C, and 10 min. [b] kg of polymer/(mol of Ti·h·[propene]). [c] Determined by GPC using polystyrene standard. [d] Cold-xylene insoluble fractions. [e] Cold-xylene soluble fractions. [f] Melting points of isotactic polymers. [g] The heat of fusion of isotactic polymer. [h] Glass transition temperatures of atactic polymer. [i] Chain-end groups by β-hydrogen transfer.

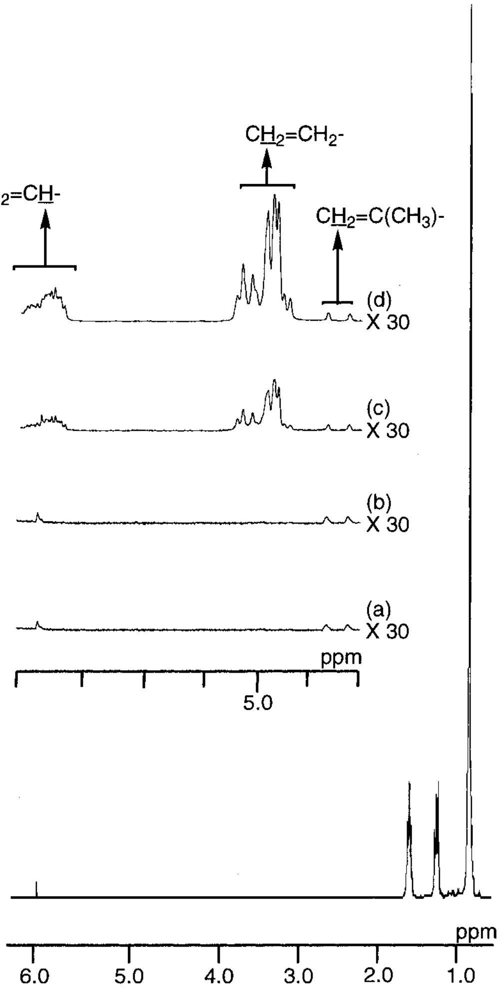

Figure 1. 500 MHz ^1H NMR spectra of polypropene (a, isotactic; b, atactic) and poly(propene-*co*-TVCH) (c, isotactic; d, atacic).

Results and Discussion. We carried out copolymerization of propene and TVCH using TVCH as a solvent. The results are summarized in Table 1. The activity of propene polymerization in TVCH was approximately two-thirds of that in heptane, irrespective of the polymerization time (Table 1), which suggests that TVCH did not affect the deactivation process.

Incorporation of vinyl group was then investigated by means of ^1H NMR. In the expanded spectra of olefinic region, only vinylidene protons, which were formed by β-hydrogen transfer, appear around 4.6−4.7 ppm in isotactic and atactic PPs (Figure 1, parts a and b). In the spectra of the copolymers, vinyl protons arising from TVCH are observed at 4.8−5.1 ppm together with the vinylidene protons in both isotactic and atactic copolymers (Figure 1, parts c and d). The contents of vinyl groups in the copolymers determined from the ^1H NMR spectra were 1.3 mol % for isotactic and 4.4 mol % for atactic copolymers, respectively (Table 1, no. 2).

The thermal properties of produced polymers were investigated by DSC. Concerning the isotactic fractions, the T_m value of the copolymer was slightly higher than that of isotactic PP, while the ΔH value of isotactic copolymer was almost half of that of isotactic polypropene. On the other hand, the T_g value of atactic copolymer was increased in ca. 8 °C compared with that of atactic PP. The introduction of rigid cycloaliphatic units would result in a higher T_g value. The increase of T_g was also observed in the copolymerization of propene with α, ω-diolefins[7] and cycloolefins.[9]

The molecular weights of isotactic and atactic copolymers determined by GPC were found to be higher than those of corresponding polypropenes (Table 1). Since the concentrations of vinylidene chain end that resulted from β-hydrogen elimination to monomer or active center were lower both in isotactic and atactic copolymers compared with polypropenes, the higher molecular weights of isotactic and atactic fractions are, partly, ascribed to the suppression of β-hydrogen chain transfer in TVCH. The other plausible reason is copolymerization of propene with pendant vinyl groups in the produced copolymers. The higher I.I. value of copolymer in keeping with a higher T_m accompanied by a decrease of the ΔH value could be explained by copolymerization of propene with atactic copolymer, which is soluble in TVCH and hence could be more easily copolymerized, on isospecific sites.

These results indicate that TVCH was adequately incorporated into PP when TVCH was used as a solvent. Furthermore, nonstereospecific sites of the $MgCl_2$-supported $TiCl_4$ were more reactive for copolymerization of propene and TVCH than isospecific sites.

In conclusion, atactic and isotactic PP having vinyl group at side chain were synthesized by a $MgCl_2$-supported $TiCl_4$ catalyst with a reasonable activity using TVCH as solvent. A more detailed study is now being carried out, the results of which will be reported elsewhere.

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(8) Catalyst preparation was conducted in a 0.5-L three-necked flask equipped with a condenser and a mechanical stirrer. First, 17.2 g (0.18 mol, 80 m^2/g) of $MgCl_2$ was placed in the reactor, and 43 mL (0.31 mol) of $TiCl_4$ was added to the solid. The reaction was allowed to continue at 100 °C for 2 h with vigorous stirring. After the supernatant was decanted, the solid product was isolated by filtration, washed several times with 250 mL of hexane to remove $TiCl_4$, and dried under vacuum at room temperature for 4 h. The Ti content in the catalyst determined by UV−vis spectrometry was 0.9 wt %.

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