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Properties and Crystalline Structures of Syndiotactic Poly(propylene-*co*-1-butene)

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Syndiotactic polypropylene was originally prepared at a very low polymerization temperature of −78 °C[1] with a conventional Ziegler−Natta catalyst, such as the tris(2-methyl-1,3-butanedionato)vanadium/$AlEt_2Cl$ catalyst system. However, the polymer obtained had a relatively low molecular weight and poor stereoregularity. Therefore, the properties of highly syndiotactic polypropylene have not yet been examined in detail. In the past few years, development in metallocene catalysts, particularly by Ewen and co-workers, has enabled us to synthesize highly syndiotactic polypropylene in good yield at a conventional polymerization temperature of 25−70 °C. Highly syndiotactic polypropylene obtained by using isopropyl(cyclopentadienyl)(1-fluorenyl)zirconium dichloride (i-Pr(Cp)(Flu)$ZrCl_2$)[2] showed good stiffness, impact strength, and heat resistance. It also had a good transparency because of the small size of spherulites and low crystallinity in comparison with isotactic polypropylene. Many analyses of crystalline structures and properties inherent in syndiotactic polypropylene have been reported,[3−9] but few reports have been presented on propylene−based copolymers prepared with a syndiospecific catalyst.[10,11] In the present report, we examine the structures and properties of several poly(propylene-*co*-olefin) copolymers (ethylene to 1-hexene olefins) obtained with a syndiospecific catalyst and find that syndiotactic poly(propylene-*co*-1-butene) crystallizes in a whole comonomer composition, different from other poly(propylene-*co*-olefins).

Results and Discussion. Five kinds of syndiotactic poly(propylene-*co*-olefin) (olefin = ethylene, 1-butene, 1-pentene, 1-hexene, or 4-methyl-1-pentene) were examined by GPC, DSC, and X-ray diffraction. The structures and properties of the polymers obtained are summarized in Table 1. The molecular weight of each copolymer decreases with increasing comonomer content. However, the M_w/M_n values of the copolymers were kept within 1.8−2.2

Figure 1 shows the relationship between the melting point (T_m) and the comonomer content in the copolymers. The copolymers, other than poly(propylene-*co*-1-butene), showed a steep melting point depression with increasing olefin content. On the contrary, poly(propylene-*co*-1-butene) showed a small depression and, furthermore, had a melting point in the whole range of 1-butene content.

The dependence of T_m on the comonomer content was analyzed according to the Flory theory describing the melting point depression in copolymers.[12] When a propylene unit is a crystallizable component and the other olefin unit a noncrystallizable component, Flory's equation is represented as follows.

$$1/T_m - 1/T_m^\circ = -(R/\Delta H_u) \ln N_{pr}$$

where T_m° is the equilibrium melting temperature for a completely syndiotactic polypropylene, T_m is the equilibrium melting temperature of copolymers, and N_{pr} is the mole fraction of propylene units in a random copolymer. It is adequate to apply the equilibrium melting point for Flory's equation. The exact equilibrium melting point of syndiotactic propylene-based copolymers has not yet been obtained, because the slower crystallization rate at isothermal conditions (especially at higher crystallization temperature) and phase transfer during the melting state complicate determination of them. The T_m obtained at a constant cooling rate was applied instead of the equilibrium melting point in the limited sense. In the region below 10 mol %, $1/T_m$ is plotted against $-\ln N_{pr}$ in Figure 2. From the slope, one can estimate the values of ΔH_u. Even if any uncertainty remains about the quantity ΔH_u, it is clear that the ΔH_u of syndiotactic poly(propylene-*co*-1-butene) is larger than the ΔH_u for the other copolymers. The ΔH_u, for reference, of poly(propylene-*co*-1-butene) was 4.4 kJ/mol, which is larger than the ΔH_u for the other copolymers (2.9 kJ/mol).

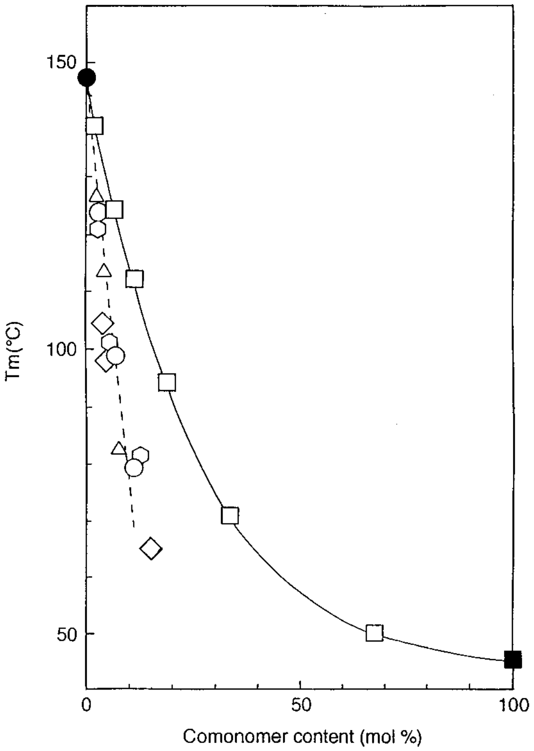

Figure 1. Relationship between the T_m and comonomer content of syndiotactic poly(propylene-*co*-olefins): (○) propylene−ethylene; (□) propylene−1-butene; (◇) propylene−1-pentene; (⬡) propylene−1-hexene; (△) propylene−4-methyl-1-pentene; (●) syndiotactic polypropylene; (■) syndiotactic poly(1-butene).

The crystallinity of the copolymers was determined from the X-ray diffraction pattern according to the method described in a previous paper.[13] The relationship between crystallinity and the comonomer content is shown in Figure 3. Similar to the behavior of the melting temperature, poly(propylene-*co*-1-butene) exhibited a lower decrease of crystallinity than the other copolymers and maintained crystallinity over the whole range of 1-butene content. In the case of the other poly(propylene-*co*-olefins), copolymers containing more than 20 mol % of comonomer have no more crystalline structure. To understand the peculiarity of poly(propylene-*co*-1-butene) mentioned above, we examined the crystalline structure of the copolymers in detail by X-ray diffractometry.

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Table 1. Properties and Structures of Syndiotactic Poly(propylene-*co*-olefins) Obtained with *i*-Pr(Cp)(Flu)ZrCl$_2$/MAO[a]

							axial length (Å)[f]	
run no.	comonomer	(mol %)[b]	M_w[c] ($\times 10^{-4}$)	M_w/M_n	T_m[d] (°C)	X_c[e] (%)	*a* axis	*b* axis
(a)		0	26.6	2.1	147.1	38.1	14.42	11.18
(b)-(1)	ethylene	3.1	10.9	2.2	123.9	26.1	14.42	11.12
(b)-(2)		7.2	9.3	2.0	98.8	18.2	14.36	11.10
(b)-(3)		11.2	6.3	2.2	79.4	15.6	14.42	10.48
(c)-(1)	1-butene	2.1			139.4			
(c)-(2)		6.6	24.4	1.9	124.7	29.8	14.60	11.08
(c)-(3)		11.5			112.4			
(c)-(4)		19.1	19.7	2.0	94.5	25.2	14.86	11.24
(c)-(5)		33.7			72.1			
(c)-(6)		67.8	11.1	2.2	50.0	17.1	16.34	11.30
(c)-(7)		100	7.6	2.2	45.1	24.5	16.90	11.56
(d)-(1)	1-pentene	3.9			114.4			
(d)-(2)		5.1	24.7	2.0	108.4	21.4	14.52	11.14
(d)-(3)		15.1	21.0	2.0	65.0	10.9	14.64	11.22
(d)-(4)		21.1	19.1	1.8				
(d)-(5)		100	9.0	2.1	37.3			
(e)-(1)	1-hexene	2.8			120.6			
(e)-(2)		5.6	25.7	2.0	101.2	17.3	14.56	11.14
(e)-(3)		12.7	23.5	2.3	81.5	10.1	14.62	11.10
(e)-(4)		21.7	16.6	1.8				
(f)-(1)	4-MPT-1[g]	2.4			126.5			
(f)-(2)		4.2	23.3	1.9	113.4	21.9	14.56	11.14
(f)-(3)		7.4	19.3	2.0	82.7	13.1	14.54	11.18
(f)-(4)		17.5	15.4	1.8				
(f)-(5)		100	5.0	2.3				

[a] See experimental section for polymerization conditions. [b] Content of comonomer in copolymers by ^{13}C NMR spectroscopy. [c] The weight-average molecular weights of the polymers were determined from by GPC using polystyrene standards. [d] Melting temperature obtained from the fully crystallized sample under the conditions described in the experimental section. [e] X_c denotes the polymer crystallinity, which was determined by WAXD. [f] Calculated from the (200) and (010) reflections from WAXD. [g] 4-Methyl-1-pentene.

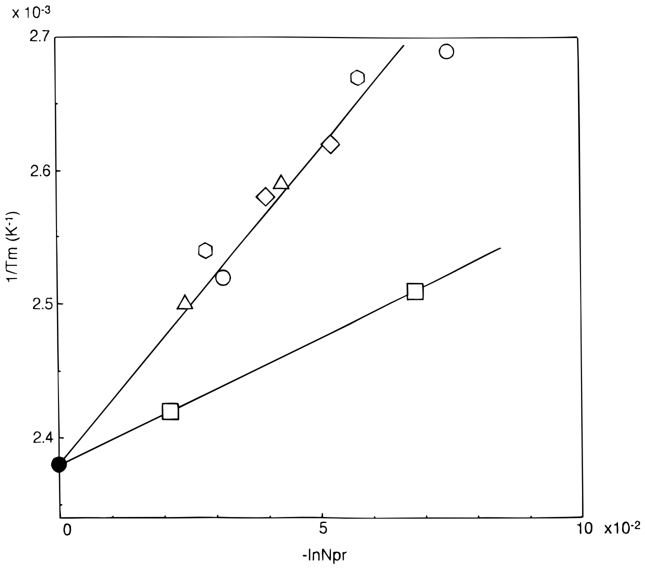

Figure 2. Plots of $1/T_m$ against $-\ln N_{pr}$ of syndiotactic poly(propylene-*co*-olefins) according to the Flory equation: (○) propylene–ethylene; (□) propylene–1-butene; (◇) propylene–1-pentene; (⬡) propylene–1-hexene; (△) propylene–4-methyl-1-pentene; (●) syndiotactic polypropylene.

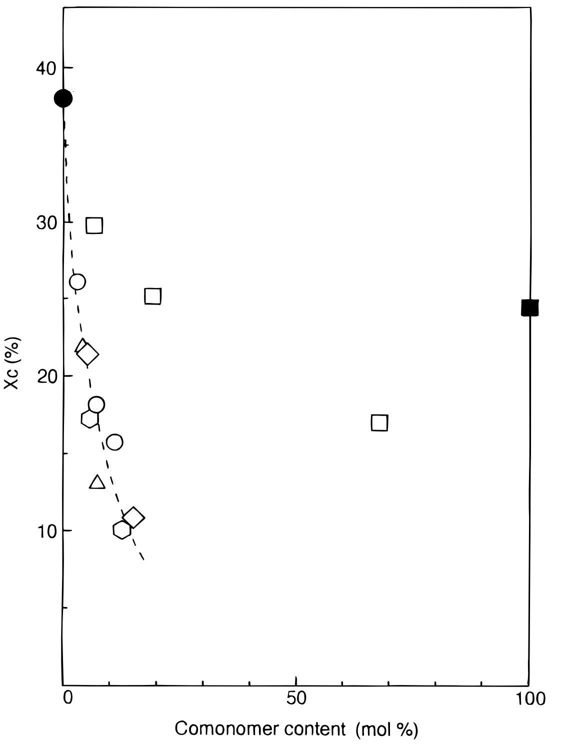

Figure 3. Relationship between the crystallinity and comonomer content of syndiotactic poly(propylene-*co*-olefins): (○) propylene–ethylene; (□) propylene–1-butene; (◇) propylene–1-pentene; (⬡) propylene–1-hexene; (△) propylene–4-methyl-1-pentene; (●) syndiotactic polypropylene; (■) syndiotactic poly(1-butene).

The *a*-axial length of the unit cell and the *b*-axial length were calculated from the (200) reflections and the (010) or (020) reflections, respectively.[14–16] The data are listed in Table 1. Copolymers besides poly(propylene-*co*-1-butene) exhibited no significant change in the length of the *a*- and *b*-axes. In contrast, as shown in Figure 4, the *a*-axis of poly(propylene-*co*-1-butene) expanded linearly with an increase in 1-butene content; the *b*-axis showed, however, little change. Isotactic poly(propylene-*co*-1-butene) prepared with an isospecific Ziegler–Natta catalyst is known to have crystallinity over the whole range of 1-butene content, but the axial length changes drastically when the 1-butene content is more than 45 mol %.[17] Both syndiotactic polypropylene and poly(1-butene) have the (t_2g_2) conformation in the crystals.[18] Projections along the *c*-axis are shown in Figure 5a. Syndiotactic polypropylene has three kinds of unit cells differing in the packing manner of left (L) and right (R) helicals of the polymer chains.

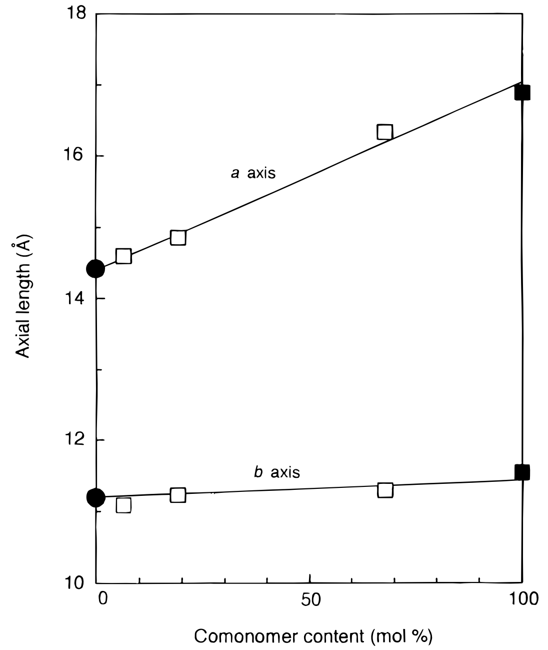

Figure 4. Axial length of the unit cell of syndiotactic poly(propylene-*co*-1-butene): (□) propylene–1-butene; (●) syndiotactic polypropylene; (■) syndiotactic poly(1-butene).

When 1-butene units enter into the unit cells, the ethyl groups of the 1-butene unit should be directed along the *a*-axis in any unit cell as shown in Figure 5b. As a result, 1-butene units lead to the expansion of the *a*-axis, whereas they have only a slight effect on the *b*-axis.

Experimental Section. The detailed preparation method of *i*-Pr(Cp)(Flu)ZrCl$_2$ is described in the literature.[2] MAO was purchased from Tosoh Akzo Co., Ltd., and used without further purification. 1-Pentene, 1-hexene, and 4-methyl-1-pentene were commercially obtained and dried over 13A molecular sieves.

Copolymerization of propylene with ethylene was carried out in an agitated 1 L autoclave at 25 °C. Propylene–ethylene mixed gas was fed to the autoclave containing 300 mL of toluene, and the pressure was kept at 8 kg/cm^{2}G. Toluene (10 mL), MAO, and the catalyst (1.5×10^{-3} mol) were mixed in a 100 mL glass flask at 25 °C for 5 min in advance. The Al/Zr molar ratio was adjusted to 1000. Polymerization was started by adding the catalyst solution to the autoclave. The temperature and monomer gas pressure were kept constant during polymerization. After 1 h, the polymerization was terminated by adding isobutyl alcohol. The polymer obtained was dissolved in xylene at 130 °C, and catalyst residues were removed by filtration at 130 °C. The polymer was precipitated by pouring the solution into a large excess of methanol and dried *in vacuo* at 60 °C for 4 h.

Copolymerizations of propylene with other α-olefins were carried out in a 1 L autoclave. Measured amounts of liquid α-olefin and liquid propylene were introduced into the autoclave. Further experiments proceeded as described in the copolymerization of propylene with ethylene.

^{13}C NMR spectra of polymers were measured at 67.8 MHz in *o*-dichlorobenzene at 135 °C with a JEOL EX-270 spectrometer. The weight-average molecular weight (M_w) and molecular weight distribution of the polymers were determined by gel permeation chromatography (Waters 150CV) at 140 °C using *o*-dichlorobenzene as solvent. DSC measurements were made with a Perkin-Elmer DSC-VII under the following conditions. A sample (10 mg) in an aluminum pan was kept at 220 °C in an atmosphere of nitrogen for 5 min and then cooled at a rate of 3 °C/min to room temperature. The sample pan was kept at 23 °C for 1 week. The sample was analyzed by heating at a rate of 10 °C/min from room temperature to 220 °C, and the temperature at the maximum peak of the endothermic curve obtained was designated as the melting point. The sample for the X-ray diffraction measurements was crystallized

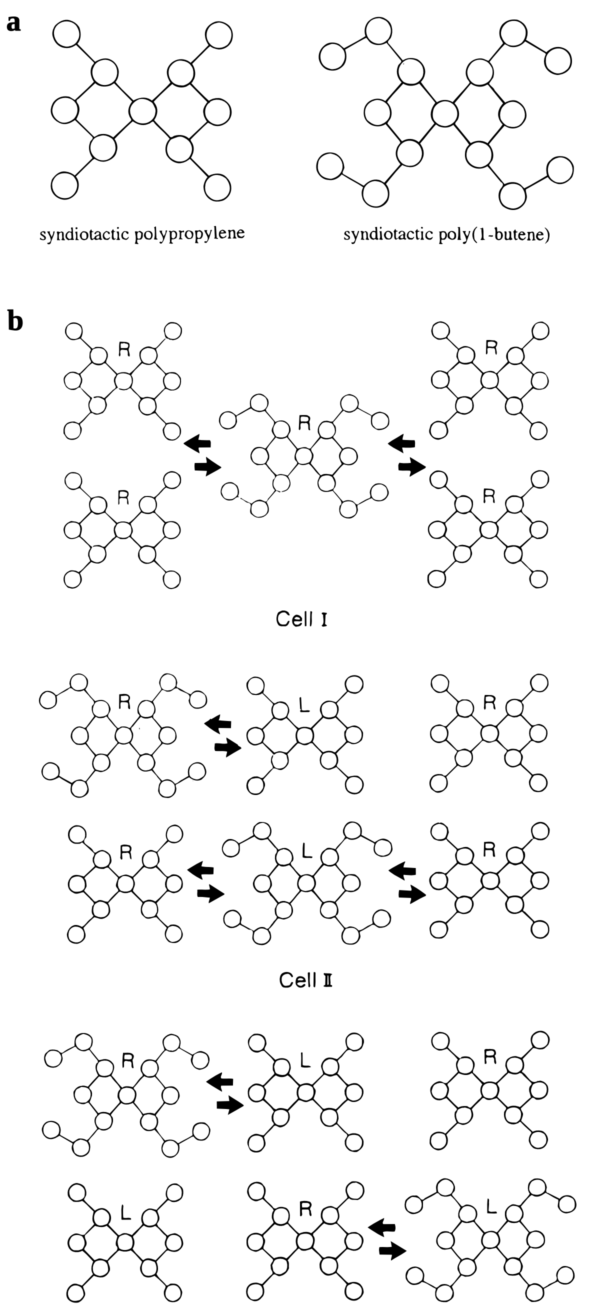

Figure 5. (a) Molecular-axis projections of syndiotactic polypropylene and syndiotactic poly(1-butene) in the crystal. (b) Plausible unit cells for the stable $(t_2g_2)_2$ form of syndiotactic poly(propylene-*co*-1-butene). Right- and left-handed helical molecules are identified by R and L, respectively.

from 230 °C to room temperature and kept at 23 °C for 1 week. Wide-angle X-ray diffraction patterns were acquired on an automatic Rigaku-RU200B diffractometer in the transmission mode using Cu Kα radiation.

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