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Isothermal crystallization of syndiotactic poly(propylene-*co*-olefin)s

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Abstract

Isothermal crystallization of syndiotactic poly(propylene-*co*-olefin)s (olefin = ethylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene) was studied. The melting behavior of isothermally crystallized polymers was investigated by differential scanning calorimetry, and the equilibrium melting temperature (T_m^0) was determined by Hoffman–Week's plot. Crystallization rate and Avrami exponent of isothermally crystallized copolymers from the melt were measured by depolarized light intensity technique. The half time of crystallization ($t_{1/2}$) was found to be dependent on the degree of supercooling (ΔT), but independent of the comonomer. The Avrami exponents (n) of copolymers were detected by the Avrami plot and the average n ranged from 2.0 to 2.8 for the primary crystallization process in any copolymer. The effect of isothermal crystallization temperature (T_c) on the crystalline structure of copolymers was studied by wide-angle X-ray diffraction (WAXD). The WAXD patterns of all the copolymers were similar to the pattern of Cell II in the syndiotactic polypropylene. The WAXD pattern of 1-butene copolymer with small amount of 1-butene indicated the existence of Cell III. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Syndiotactic poly(propylene-*co*-olefin); Isothermal crystallization; Crystallization behavior

1. Introduction

In the past few years, development in metallocene catalysts, particularly by Ewen and co-workers, has enabled us to synthesize highly syndiotactic polypropylene with isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (iPr(Cp)(Flu)ZrCl$_2$) in good yield at conventional polymerization temperature [1]. After the finding, a number of studies have been carried out on the crystalline structure, morphology and properties of highly syndiotactic polypropylene.

For the helical $(t_2g_2)_2$ conformation of syndiotactic polypropylene, three types of unit cells differing in the packing arrangement of the polymer chain were reported [2–5]. The crystallization conditions (crystallization temperature and time, etc.) were found to affect the crystallization behavior, crystalline structure and morphology of syndiotactic polypropylene. The effects of the crystallization temperature on the melting behavior of syndiotactic polypropylene have been studied by differential scanning calorimetry (DSC) [6–13]. When the crystallization was carried out at low temperature, a double melting peak was observed in the DSC patterns. The first melting peak (low-melting peak) showed a clear dependence on the crystallization temperature. Furthermore, the effect of crystallization conditions on the crystalline structure was investigated by wide-angle X-ray diffraction (WAXD), and small-angle X-ray scattering (SAXS), electron diffraction (ED) and solid state ^{13}C NMR spectroscopy [6–25]. Ordinary WAXD pattern of syndiotactic polypropylene showed three major diffraction peaks at $2\theta = 12.1$, 15.9 and 20.6° derived from (200), (010) or (020) and (220,121) reflection planes, respectively [4,8–17,19,21,24,25]. When the isothermal crystallization was carried out at a higher temperature (more than 120°C), the reflection peak at $2\theta = 18.8°$ was observed, and assigned to the reflection from (211) planes. Polarizing microscope, transmission electron micrograph (TEM) and atomic force microscopy (AFM) were applied to the observation to determine the effect of crystallization conditions on the crystalline morphology [7,8,18,20,26–28].

However, some reports have been presented about the syndiotactic propylene-based copolymers prepared with syndiospecific metallocene catalyst [29–35]. We studied the properties and structures of syndiotactic poly(propylene-*co*-olefin)s (olefin = ethylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene) and found the peculiar crystalline structures of syndiotactic poly(propylene-*co*-1-butene) [31]. The syndiotactic poly(propylene-*co*-1-butene) showed a higher melting temperature and crystallinity compared to the other copolymers having the same comonomer content. Furthermore, this copolymer showed

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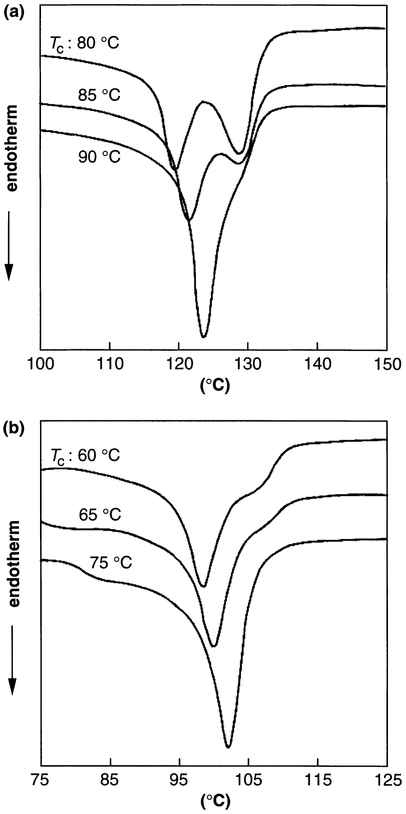

Fig. 1. DSC melting curves of syndiotactic poly(propylene-*co*-ethylene): (a) sample P-E3; and (b) sample P-E7.

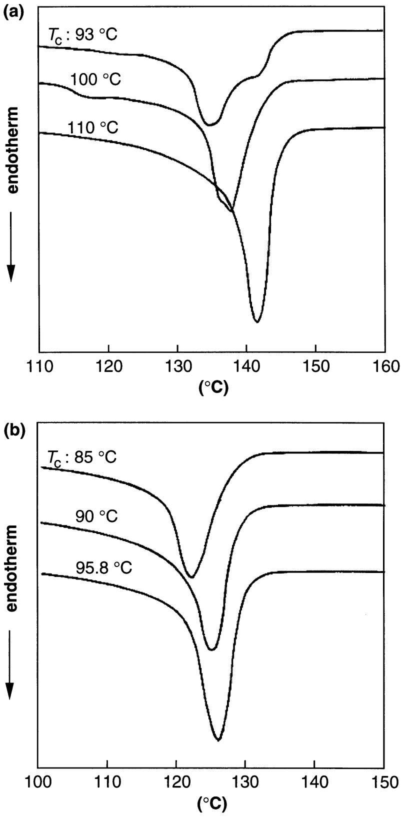

Fig. 2. DSC melting curves of syndiotactic poly(propylene-*co*-1-butene): (a) sample P-B2; and (b) sample P-B7.

the expansion of unit cell along the *a*-axis with an increase of 1-butene content. These phenomena suggested isomorphism of syndiotactic poly(propylene-*co*-1-butene).

Analysis of syndiotactic poly(propylene-*co*-olefin)s is still not complete as compared to the syndiotactic polypropylene.

In this work, we carried out the isothermal crystallization of syndiotactic poly(propylene-*co*-olefin)s and studied the effect of the crystallization temperature on the crystallization behavior and crystalline structure of the copolymers.

2. Experimental

2.1. Materials

The syndiotactic poly(propylene-*co*-olefin)s (olefin = ethylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene) were prepared using isopropyl-(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (*i*Pr(Cp)(Flu)$ZrCl_2$)/methylaluminoxane (MAO) (molar ratio of Al/Zr = 1000) at 25°C in bulk polymerization, and in toluene in the case of propylene–ethylene copolymerization [31].

2.2. Characterization of copolymers

^{13}C NMR spectra of copolymers 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 (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC, Waters 150CV) at 140°C using *o*-dichlorobenzene as solvent. DSC measurements were made on a Seiko DSC-220 under the following conditions. A sample (ca. 5 mg) in an aluminum pan was kept at 180°C for 15 min and then quenched to the crystallization temperature (T_c) in oil bath. The sample was analyzed by heating at a rate of 10°C/min from room temperature to 200°C. WAXD patterns were obtained on an automatic Rigaku-RU200B diffractometer in the transmission mode using CuKα radiation.

2.3. Kinetic study of isothermal crystallization

The depolarized light intensity (DLI) technique was used to follow the crystallization of copolymers [36–38]. Isothermal crystallization was carried out with the Kotaki MK-701 by measuring the intensity of the depolarized light passing through the specimens during isothermal treatment. The thin film of the polymer (about 100 μm) was fused between the glass cover slips in the furnace at 230°C for 5 min and then rapidly transferred to the crystallization bath, maintained at a selected temperature in the range of 80–120°C, until the crystallization was completed.

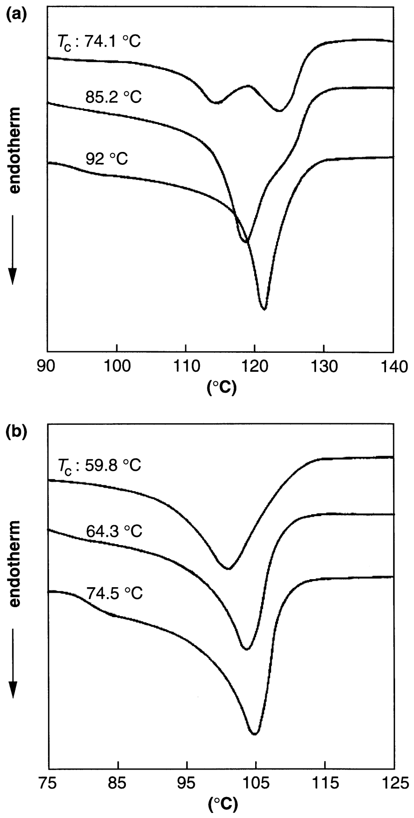

Fig. 3. DSC melting curves of syndiotactic poly(propylene-*co*-1-hexene): (a) sample P-H3; and (b) sample P-H6.

Table 1
Composition and properties of syndiotactic(propylene-*co*-olefin)s obtained with *i*Pr(Cp)(Flu)ZrCl$_2$/MAO

Sample	Comonomer	(mol%)[a]	M_w[b] ($\times 10^{-4}$)	M_w/M_n[b]	T_m^0[c] (°C)
PP	–	0	26.6	2.1	166.7
P-E3	Ethylene	3.1	10.9	2.2	143.5
P-E7		7.2	9.3	2.0	117.8
P-B2	1-Butene	2.1			158.0
P-B7		6.6	24.4	1.9	144.4
P-B12		11.5			132.0
P-PN4	1-Pentene	3.9			132.2
P-PN5		5.1	24.7	2.0	122.7
P-HX3	1-Hexene	2.8			140.2
P-HX6		5.6	25.7	2.0	117.2
P-MP2	4-MPT-1[d]	2.4			142.4
P-MP4		4.2	23.3	1.9	131.5

[a] Content of comonomer in copolymers determined by ^{13}C NMR.

[b] The weight-average molecular weight of polymers were determined from GPC using polystyrene standards.

[c] Equilibrium melting temperature determined by Hoffman–Week's plot.

[d] 4-Methyl-1-pentene.

3. Results and discussion

3.1. Melting behavior and melting temperature of copolymers

The melting behavior and the melting temperature of isothermally crystallized polymers were investigated by DSC at a heating rate of 10°C/min. The DSC melting curves of typical copolymers (ethylene, 1-butene and 1-hexene copolymers) are shown in Figs. 1–3, respectively. Double melting peak or single melting peak with a shoulder are observed in the DSC patterns of copolymers with low comonomer content when the crystallization was carried out at comparatively low T_c, while a single peak occurs in the copolymers crystallized at high T_c (Figs. 1(a), 2(a) and 3(a)). These phenomena were observed in the isothermally crystallized syndiotactic polypropylene (homopolymer) [6–13]. The double melting peak could be explained by the reason that the sample melts at a temperature varying with the crystallization conditions (first peak), recrystallizes from the melt and completely melts (second peak). The second peak almost disappears in the copolymer whose comonomer content is more than ca. 5 mol.% (Figs. 1(b), 2(b) and 3(b)). This result indicates that the recrystallization during the melting cannot occur due to the slow recrystallization at a heating rate 10°C/min in the copolymers with high comonomer content (more than ca. 5 mol.%). A similar tendency was reported in syndiotactic poly(propylene-*co*-1-octene) by Kressler et al. [33].

The equilibrium melting point (T_m^0) was determined by Hoffman–Week's plot. The first melting peak in the DSC melting curves was assigned to T_m at T_c. The results are summarized in Table 1 with the structures of polymers. The heat of fusion per mole of repeating unit (ΔH_u) of copolymers was determined by Flory's equation represented as follows:

$$1/T_m^0(C) - 1/T_m^0(H) = -(R/\Delta H_u)\ln N_{pr},$$

where $T_m^0(C)$, $T_m^0(H)$ and N_{pr} are the equilibrium melting temperature of the copolymer, the equilibrium melting temperature of the syndiotactic polypropylene (homopolymer) and the molar fraction of the propylene units in a copolymer, respectively. In the previous report, we have not determined the T_m^0 of polymers and hence, could not calculate the accurate value of ΔH_u [31]. The $1/T_m^0$ is plotted against $-\ln N_{pr}$ in Fig. 4. The ΔH_u values of the copolymers can be determined by the slope of the plots, and a value of 5.2 kJ/mol for 1-butene copolymer and 1.9 kJ/mol for the other copolymers are obtained.

3.2. Crystallization kinetics

Crystallization kinetics was studied on the basis of the T_m^0. The half time of crystallization ($t_{1/2}$) was determined from the relative DLI technique at various crystallization temperatures (T_c). The $t_{1/2}$ values of copolymers are

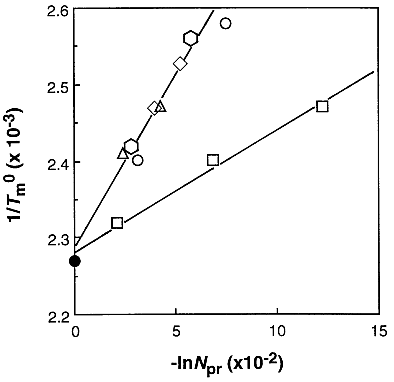

Fig. 4. Plots of $1/T_m^0$ against $-\ln N_{pr}$ of syndiotactic poly(propylene-*co*-olefin)s according to the Flory equation: propylene–ethylene (○), propylene-1-butene (□), propylene-1-pentene (◇), propylene-1-hexene (⬡), propylene-4-methyl-1-pentene (△), and syndiotactic polypropylene (●).

Table 2
Kinetic parameters for isothermal crystallization of syndiotactic polypropylene and syndiotactic poly(propylene-*co*-olefin)s

Sample	T_c[a] (°C)	ΔT[b]	$t_{1/2}$[c] (s)	n[d]	n[e]	K_n[f] (s^{-1})
PP	80	86.7	11	2.30	2.55	2.79×10^{-3}
	90	76.7	14	2.12		2.58×10^{-3}
	100	66.7	30	2.79		5.24×10^{-5}
	110	56.7	85	2.78		3.00×10^{-6}
	120	46.7	298	2.76		1.03×10^{-7}
P-E3	80	63.5	36	2.11	2.38	3.61×10^{-4}
	90	53.5	91	2.70		3.56×10^{-6}
	100	43.5	294	2.34		1.16×10^{-6}
P-E7	80	37.8	1072	2.54	2.54	1.39×10^{-8}
P-B2	80	78.0	13	2.38	2.31	1.55×10^{-3}
	90	68.0	22	2.15		9.01×10^{-4}
	100	58.0	60	2.58		1.79×10^{-5}
	110	48.0	192	2.14		9.01×10^{-6}
P-B7	80	64.4	45	2.48	2.58	5.51×10^{-5}
	90	54.4	97	2.52		6.83×10^{-6}
	100	44.4	432	2.74		4.16×10^{-8}
P-B12	80	52.0	82	2.10	2.23	6.63×10^{-5}
	90	42.0	479	2.35		3.48×10^{-7}
P-PN4	80	52.2	91	2.16	2.16	4.07×10^{-5}
	90	42.2	384	2.15		1.93×10^{-6}
P-PN5	80	42.7	475	2.45	2.45	1.92×10^{-7}
P-HX3	80	60.2	88	2.48	2.50	1.05×10^{-5}
	90	50.2	208	2.51		1.05×10^{-6}
P-HX6	80	37.2	1152	2.02	2.02	4.54×10^{-7}
P-MP2	80	62.4	37	2.24	2.52	2.13×10^{-4}
	90	52.4	79	2.57		9.20×10^{-6}
	100	42.4	246	2.75		1.84×10^{-7}
P-MP4	80	51.5	203	2.08	2.20	1.10×10^{-5}
	90	41.5	470	2.31		4.66×10^{-7}

[a] Crystallization temperature.
[b] $T_m^0 - T_c$ (K).
[c] Half time of crystallization.
[d] Avrami exponent.
[e] Average of Avrami exponent.
[f] Kinetic constant.

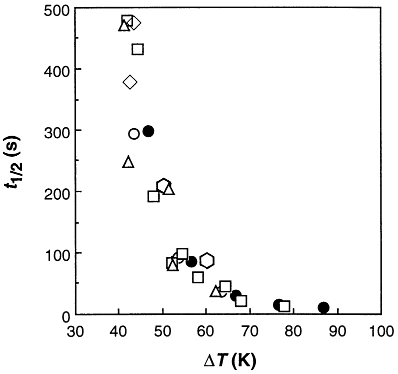

Fig. 5. Plots of $t_{1/2}$ against ΔT of syndiotactic poly(propylene-*co*-olefin)s: propylene–ethylene (○), propylene-1-butene (□), propylene-1-pentene (◇), propylene-1-hexene (⬡), propylene-4-methyl-1-pentene (△), and syndiotactic polypropylene (●).

summarized in Table 2 and the plots of $t_{1/2}$ against the degree of supercooling ($\Delta T = T_m^0 - T_c$) are shown in Fig. 5. The $t_{1/2}$ markedly increased at ΔT less than 55 K. The plots of $t_{1/2}$ against ΔT were located on almost a same curved line.

Isothermal crystallization behavior of polymers can be analyzed by means of the Avrami equation [39–44]:

$$(1 - X_t) = \exp(-K_n t^n), \tag{1}$$

where X_t is the weight fraction of the crystallizable polymer crystallized at time t, K_n is the kinetic rate constant and n is the Avrami exponent, respectively. Eq. (1) can be written as:

$$\log[-\log(1 - X_t)] = n \log t + \log(K_n/2.3). \tag{2}$$

By plotting the quantity $\log[-\log(1 - X_t)]$ against $\log t$, it is possible to determine the value of the Avrami exponent (n) from the slope of the curve. The Avrami plots of syndiotactic poly(propylene-*co*-1-butene) is shown in Fig. 6 and Avrami exponents are summarized in Table 2. The value of Avrami exponent of copolymers ranged from 2.0 to 2.8 for primary crystallization. The transition of crystallization process from primary to secondary crystallization process was observed at $X_t = 0.7$–0.8 in any polymers. Balbontin et al. and Cheng et al. measured the Avrami exponent of

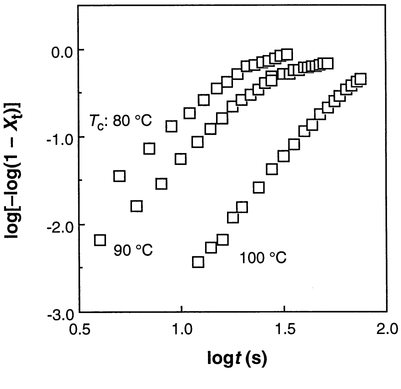

Fig. 6. Plots of $\log[-\log(1 - X_t)]$ against $\log t$ of syndiotactic poly(propylene-*co*-1-butene) (sample P-B2).

Table 3
Crystalline structure of isothermally crystallized syndiotactic poly(propylene-*co*-olefin)s

Sample	T_c[a] (°C)	ΔT[b]	X_c[c] (%)	Axial length[d] (Å)	
				a axis	*b* axis
PP	90	76.7	24.5	14.62	5.58
	100	66.7	25.9	14.56	5.58
	110	56.7	26.7	14.56	11.20, 5.60
	120	46.7	34.4	14.36	11.12, 5.56
	130	36.7	26.7	14.52	5.57
P-E3	70	73.5	23.1	14.56	5.56
	80	63.5	23.1	14.62	5.58
	90	53.5	23.8	14.58	5.59
	100	43.5	25.5	14.50	5.56
P-B2	80	78.0	24.6	14.66	5.60
	90	68.0	24.8	14.56	5.56
	100	58.0	27.4	14.60	5.56
	110	48.0	30.5	14.56	5.57
	120	38.0	27.3	14.64	5.60
P-B7	70	74.4	22.9	14.76	5.60
	80	64.4	23.5	14.76	5.60
	90	54.4	23.8	14.66	5.58
	100	44.4	26.4	14.72	5.59
P-HX3	70	70.2	20.1	14.60	5.57
	80	60.2	20.6	14.64	5.57
	90	50.2	22.0	14.60	5.57
	100	40.2	22.1	14.64	5.58

[a] Crystallization temperature.
[b] $T_m^0 - T_c$.
[c] Polymer crystallinity determined by WAXD.
[d] Calculated from the (200) and (010) or (020) reflections from WAXD.

syndiotactic polypropylene with various molecular weights and syndiotacticities, and reported the values for the Avrami exponent $n = 1.8$–3.9 and 1.9–3.0, respectively ($n = 2.6$ was obtained in our experiment) [10,45]. The three-dimensional (3D) crystal growth of syndiotactic polypropylene was suggested by the Avrami exponent in the earlier report. Lovinger et al. described a transition between 3D (spherulitic) and 2D (axialitic, rectangular single crystal) structures in thin melt crystallized films as the crystallization temperature increased [3,5]. Cheng et al. studied the morphology of syndiotactic polypropylene in the crystallization process by polarized light microscopy observations and indicated that a heterogeneous nucleation was the main process in this crystallization [10,26]. The Avrami exponents of syndiotactic poly(propylene-*co*-olefin)s are within the limits of previously reported value. It seems reasonable to consider that the crystallization behavior (nucleation and growth) of syndiotactic poly(propylene-*co*-olefin)s is almost the same as that of syndiotactic polypropylene.

The rate constant (K_n) was calculated from $t_{1/2}$ using the following relation:

$$K_n = \ln 2/t_{1/2}^n. \qquad (3)$$

The K_n values are summarized in Table 2 and the effect of the comonomer on the K_n could not be found.

Judging from the results, the crystallization rate of copolymers depended on not the kind of comonomer, but on ΔT.

3.3. Crystalline structure

Three kinds of unit cells were proposed for syndiotactic polypropylene. The first one is the *C*-centered orthorhombic unit cell (space group $C222_1$, Cell I) [2]. The second one contains two chain segments in an orthorhombic cell (space group $Pca2_1$, Cell II) [3–5] and the third one involves the doubling of the cell along the *b* axis and corresponding to an *Ibca* space group (Cell III) [3–5].

Crystalline structure of syndiotactic poly(propylene-*co*-olefin)s was studied by WAXD. The crystalline structures of the copolymers are summarized in Table 3. The WAXD patterns of typical copolymers (ethylene, 1-butene and 1-hexene copolymers) are shown in Fig. 7(a)–(d). The weak peak at $2\theta = 18.8°$ from (211), which was derived from the Cell III is observed in the poly(propylene-*co*-1-butene) with a low content of 1-butene (sample P-B2) isothermally crystallized at $\Delta T = 48$ K ($T_c = 110$°C) (Fig. 7(b)) [3,5]. This result indicates that this copolymer (sample P-B2) includes the crystalline structure of Cell III. By contrast, the peak derived from (211) cannot be observed in the WAXD patterns of other copolymers independent of ΔT. The WAXD patterns of these copolymers are similar to the pattern of Cell II in the syndiotactic polypropylene [9]. This result suggests that these copolymers have crystalline structures based on the unit Cell II of syndiotactic polypropylene.

Comparing the WAXD patterns of copolymers, the broadening at $2\theta = 17$–$18°$ could be found in the ethylene, 1-hexene copolymers (Fig. 7(a) and (d)), while the peak could not be observed in 1-butene copolymers (Fig. 7(b) and (c)). Lovinger et al. observed the peak at about $2\theta = 17°$ derived from (110) and (201) reflections in the syndiotactic polypropylene of Cell II [4]. Zannetti et al. calculated the WAXD of Cell II and reported the peak at $2\theta = 17°$ in both the calculated and observed WAXD patterns [9]. These results suggest that the crystalline structure of poly(propylene-*co*-1-butene) is slightly different from Cell II as shown in other copolymers. This difference could cause the peculiar properties of poly(propylene-*co*-1-butene) as reported previously [31].

4. Conclusion

It is clear that the kind of comonomer in the syndiotactic poly(propylene-*co*-olefin)s does not affect the behavior of isothermal crystallization. The Avrami exponent (n) of the copolymers ranged from 2.0 to 2.8. These values were almost similar to that of the syndiotactic polypropylene. The $t_{1/2}$ and K_n values depended on the ΔT value in any copolymer. The WAXD pattern of poly(propylene-*co*-1-butene) showed a sharper peak of (010) reflection than other copolymers. The WAXD patterns of copolymers

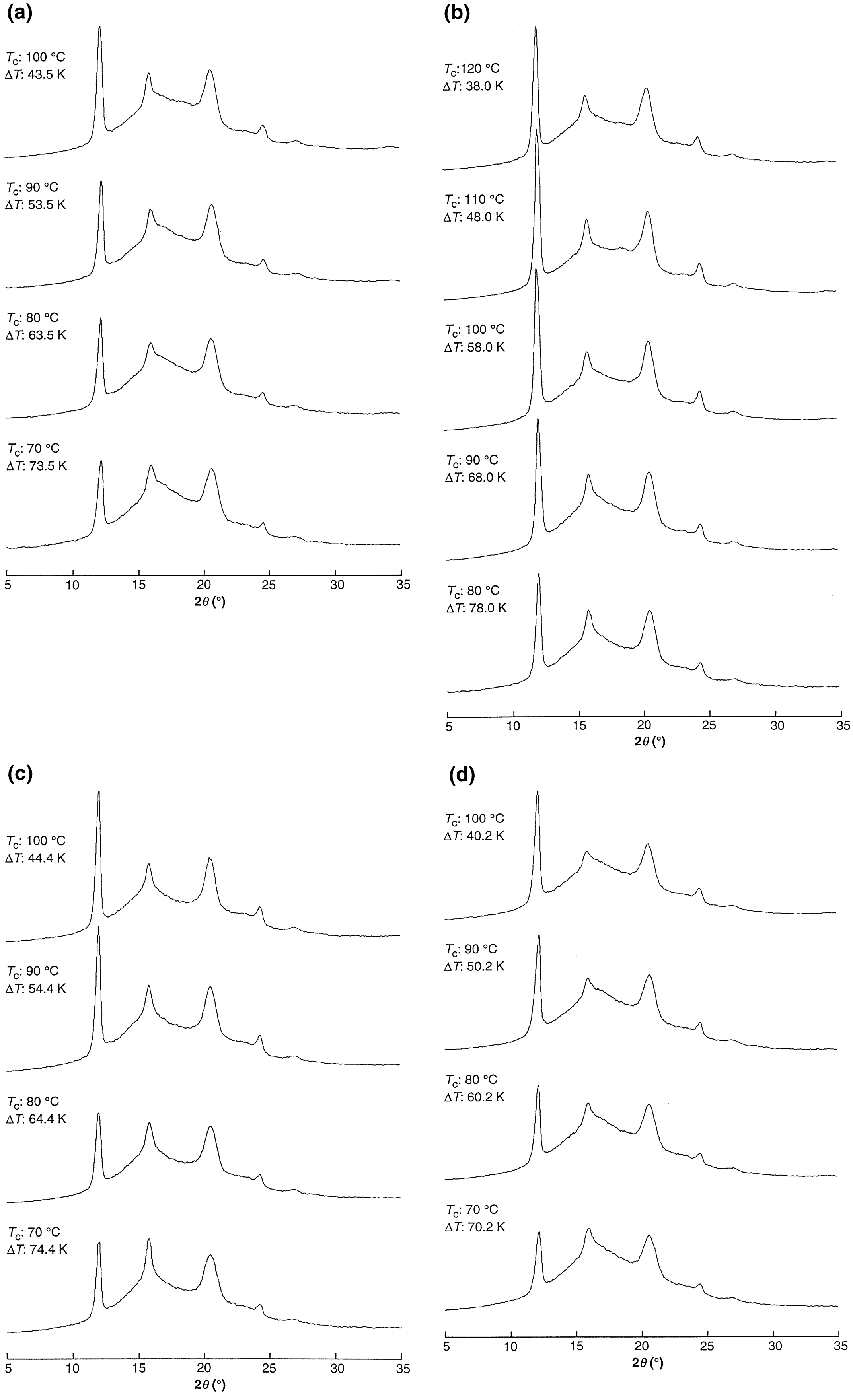

Fig. 7. WAXD patterns of isothermally crystallized syndiotactic poly(propylene-*co*-olefin)s: (a) propylene–ethylene (sample P-E3); (b) propylene-1-butene (sample P-B2); (c) propylene-1-butene (sample P-B7); and (d) propylene-1-hexene (sample P-H3).

indicate the crystalline structure of Cell II, while poly(propylene-*co*-1-butene) with low 1-butene content showed the peak of (211) reflection derived from Cell III.

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