Isothermal Crystallization of Metallocene-Based Propylene/α-Olefin Copolymers

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ABSTRACT: Isothermal crystallization and subsequent melting behavior of two propylene/hexene-1 copolymers and two propylene/octene-1 copolymers prepared with metallocene catalyst were investigated. It is found that γ-modification is predominant in all copolymers. The Avrami exponent shows a weak dependency on comonomer content and comonomer type. At higher crystallization temperatures (T_c) the crystallization rate constant changes more rapidly with T_c and the crystallization half-time substantially increases. Double melting peaks were also observed at high T_c, which is attributed to the inhomogeneous distribution of comonomer units along the polymer chains and the existence of crystals with different lamellar thicknesses. The equilibrium melting temperatures (T_m°) of the copolymers were obtained by Hoffman–Weeks extrapolation. It was found that the T_m° decreases with increasing comonomer content, but are independent of comonomer type, implying that comonomer units are excluded from the crystal lattice. Dilation of the crystal lattice was also observed, which depends on crystallization, comonomer content, and comonomer type. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 240–247, 2005

Key words: crystallization; copolymerization; kinetics (polym.); WAXD; comonomer inclusion

INTRODUCTION

Copolymerization is one of the most useful methods to modify the properties of polymers. Copolymers of propylene with higher α-olefins, such as butene-1, hexene-1, and octene-1, have been prepared with both conventional Ziegler–Natta catalysts and metallocene catalysts.[1–9] However, crystallization behavior of propylene/α-olefin copolymers has thus far rarely been reported,[10–15] when compared with the vast literature dealing with crystallization of ethylene copolymers.

There are three crystal modifications, monoclinic α-modification, hexagonal β-modification, and orthorhombic γ-modification, in isotactic polypropylene.[16–18] The α- and γ-crystal modifications can be formed under the same crystallization conditions. In propylene copolymers, comonomer units, like stereo- and regio-defects, interrupt the polypropylene chain. The shorter propylene sequences are favorable to the formation of γ-modification.[10] Because the formation of α- and γ-crystal modifications is competitive, study of the crystallization kinetics of both modifications is very important, which can help us understand the metastability of α- and γ-modifications from the perspective of kinetics.[19] Moreover, the partition of the comonomer unit between the crystalline region and amorphous region is also an interesting topic in propylene copolymers. Some authors have observed that parts of stereo-defects, regio-defects, and small comonomer units such as ethylene and butene-1 can be partially included in the crystal lattice.[14,15,20–24]

This article reports the investigation of isothermal crystallization of two propylene/hexene-1 copolymers and two propylene/octene-1 copolymers, prepared with metallocene catalyst. The isothermal crystallization kinetics and subsequent melting behavior were studied. The inclusion of the comonomer units in the crystal lattice and dilation of the crystal lattice are discussed as well.

EXPERIMENTAL

Preparation of propylene copolymers

Propylene/hexene-1 and propylene/octene-1 copolymers were prepared by copolymerization of propylene with comonomers at 30°C, using *rac*-$(CH_3)_2Si[(2,4,6\text{-}CH_3)_3Ind]_2ZrCl_2$ as catalyst and methylaluminoxane (MAO) as cocatalyst. The polymerization procedure was described elsewhere.[8] The copolymerization of propylene with α-olefinic comonomers was carried out in a 250-mL glass reactor, equipped with a propylene inlet and a magnetic stirrer. After the reactor was flushed

TABLE I
Comonomer Content and M_η of Propylene Copolymers

Sample	Comonomer	Comonomer content (mol %)	M_η
PH1	Hexene-1	2.21	35,400
PH2	Hexene-1	3.16	40,200
PO1	Octene-1	1.16	36,100
PO2	Octene-1	2.69	41,400

with argon, toluene (100 mL) and octene-1 or hexene-1 were injected into the reactor with syringes at the set temperature, and then propylene gas was introduced to saturate the solution. Copolymerization was conducted at two different comonomer concentrations, 0.025 and 0.05M, for both comonomers. The propylene pressure was kept at a constant value of 0.1 MPa. Appropriate amounts of MAO and triisobutylaluminum (TIBA) solutions were injected into the reactor, and copolymerization was initiated by the addition of the toluene solution of metallocene catalyst. Propylene was continuously supplied to the reactor to maintain constant pressure. Copolymerization was terminated by acidified ethanol, and the product was poured into an excess of ethanol. The conversion of the comonomers was less than 10%. The polymer was separated by filtration, washed, and dried under vacuum.

Characterization of propylene copolymers

The comonomer contents in the copolymers were determined using ^{13}C-NMR, which was carried out on a DMX 500 spectrometer (Bruker, Darmstadt, Germany) at 100°C with o-$C_6D_4Cl_2$ as solvent. The concentration of polymer was 20% w/v, delay time was 10 s, and scanning time was 3000 s. The viscosity-average molecular weight ([η]) of the polymers was measured by viscometry with a Ubbelohde-type viscometer using decahydronaphthalene as solvent at 135 $\pm$ 0.1°C. The concentration of the solution was about 0.1% g/mL and a small amount of antioxidant (4,6-di-t-butyl-p-cresol) was added to the solution. The viscosity-average molecular weight was calculated according to the relationship[25] [η] $= KM_\eta^\alpha$ ($K = 1.10 \times 10^{-4}$, $\alpha = 0.80$). Values of comonomer content and viscosity-average molecular weight of the copolymers are given in Table I.

DSC experiments

The isothermal crystallization kinetics of propylene/α-olefin copolymers was carried out on a Perkin–Elmer Pyris-1 calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT). About 3–4 mg of samples were sealed in aluminum pans and heated to 200°C, held for 5 min, and then cooled, at a rate of 100°C/min, to the crystallization temperatures and held until crys-

tallization was completed. The change of heat flow with time was recorded upon crystallization. After isothermal crystallization was completed, the samples were immediately heated to 180°C from the crystallization temperature at a rate of 10°C/min.

Wide-angle X-ray diffraction (WAXD)

X-ray diffraction experiments were performed on a Bruker D8 X-ray diffractometer (40 kV, 40 mA) (Cheshire, UK) using Ni-filtered Cu–K$_\alpha$ radiation (wavelength: 0.1542 nm) from 5 to 45°, in increments of 0.02°. The samples were quenched with ice water after isothermal crystallization and then WAXD experiments were carried out immediately.
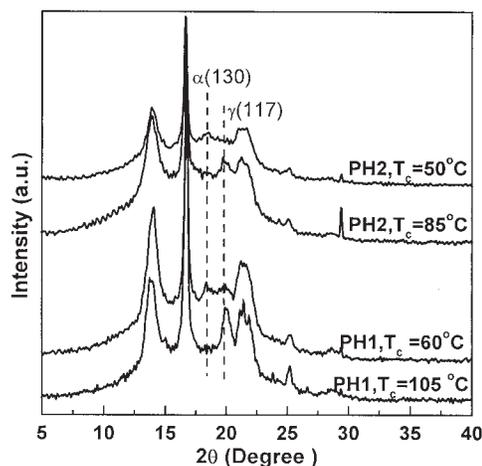
(a)
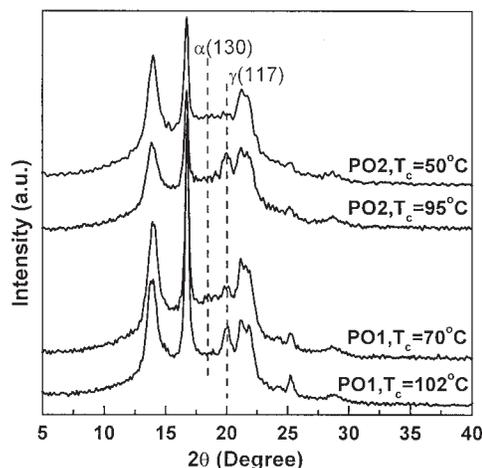
(b)

Figure 1 WAXD patterns of propylene copolymers after crystallization at different temperatures: (a) PH1 and PH2; (b) PO1 and PO2.
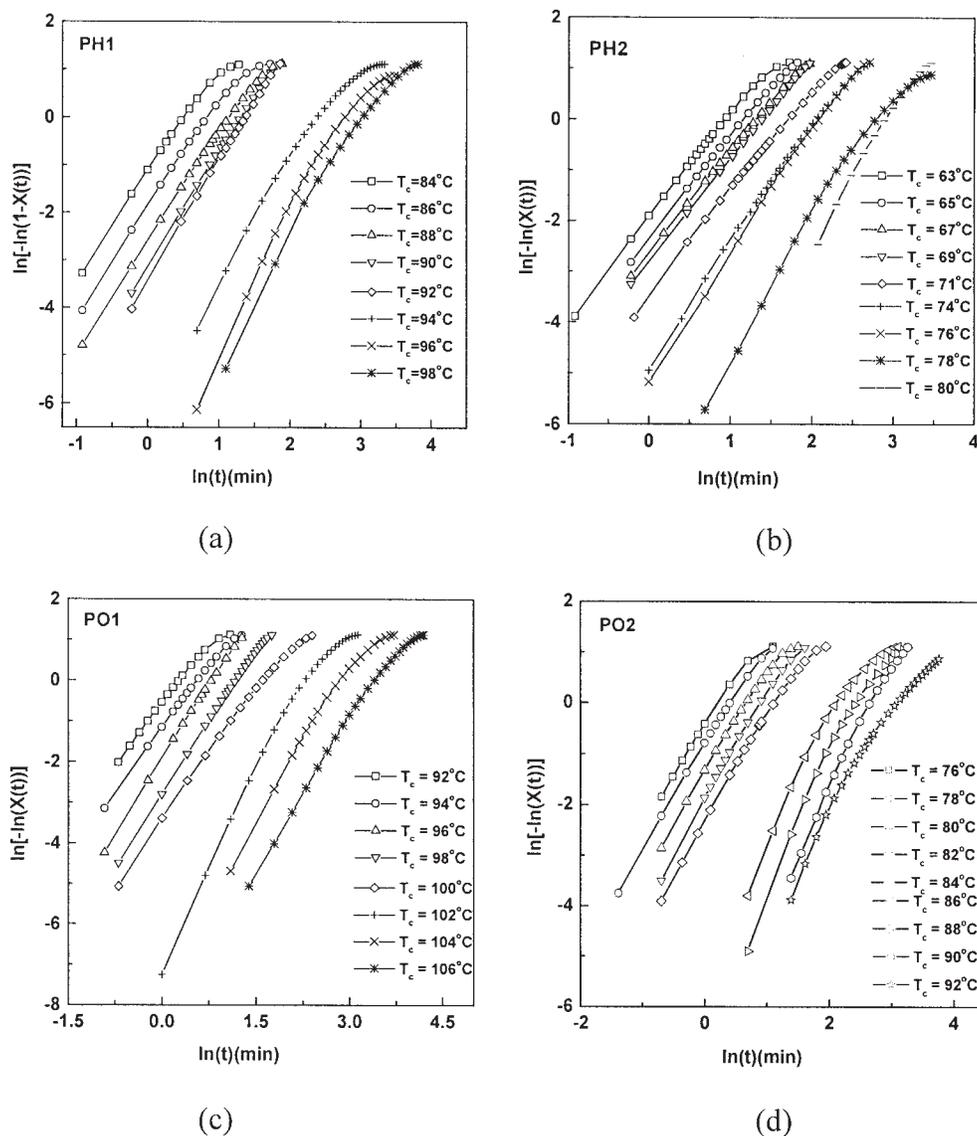
Figure 2   Avrami plots of PH1 (a), PH2 (b), PO1 (c), and PO2 (d) at different crystallization temperatures.

RESULTS AND DISCUSSION

WAXD results

Figure 1 shows the WAXD patterns of propylene copolymers after crystallization at two different temperatures (T_c). At lower T_c both the characteristic (130) reflection of α-crystal modification and the characteristic (117) reflection of γ-crystal modification appear at $2\theta = 18.6°$ and $2\theta = 20.1°$, respectively, in all the copolymers. Comparing the relative intensity of these two characteristic reflections, one can see from Figure 1 that both α- and γ-modifications are not obvious at lower T_c, indicating lower crystallinity. At higher T_c, γ-modification becomes more evident, although the intensity of the characteristic reflection of the α-modification becomes weaker, showing that γ-modification is the predominant crystal. Such a tendency is

common in these four propylene copolymers, irrespective of comonomer type and comonomer content. Increase of relative content of γ-modification with crystallization temperature has been reported by other authors.[15,23] The γ-modification is generally formed by the short propylene sequences.[10] The comonomer units incorporated reduce the length of propylene sequences and interfere with crystallization of polypropylene, leading to formation of γ-modification in these four copolymers. The favorable formation of γ-modification at higher T_c is determined by the metastability of α- and γ-modifications and crystallization kinetics of these two crystal modifications.[19] The γ-modification becomes stable at high temperature and has a faster crystallization rate than that of the α-modification.[26–28] The intensity of characteristic reflections of both α- and γ-modifications decreases as the comono-

mer content increases, showing that crystallinity is reduced by the enchained comonomer units.

Isothermal crystallization kinetics

The isothermal crystallization kinetics of the polypropylenes can be interpreted in terms of the following Avrami equation[29]:

$$1 - X(t) = \frac{\Delta H^c_{t=\infty} - \Delta H^c_t}{\Delta H^c_{t=\infty} - \Delta H^c_{t=0}} = \exp(-kt^n) \qquad (1)$$

where $X(t)$ is the relative crystallinity at time t, and $\Delta H^c_{t=\infty}$, $\Delta H^c_{t=0}$, and ΔH^c_t are the crystallization enthalpies on complete crystallization, at $t = 0$, and after time t, respectively. Therefore, we have

$$\ln\{-\ln[1 - X(t)]\} = \ln k + n \ln t \qquad (2)$$

The crystallization rate constant k and Avrami exponent n can be determined from the intercept and slope in the plot of $\ln\{-\ln[1 - X(t)]\}$ versus $\ln(t)$, respectively.

The Avrami plots of PH1, PH2, PO1, and PO2, at various crystallization temperatures, are shown in Figure 2. Because γ-modification is predominant in all copolymers, the obtained parameters mainly reflect the characteristics of γ-modification. It is found that the Avrami exponents of these four propylene copolymers scatter in the range of 2.0–3.0, indicating imperfect spherulite morphology. Comonomer content and comonomer type have no obvious effect on the Avrami exponent. With increasing crystallization temperature, the Avrami exponents tend to become slightly higher. It is noticed that there is a gap between some lines at intermediate crystallization tempera-
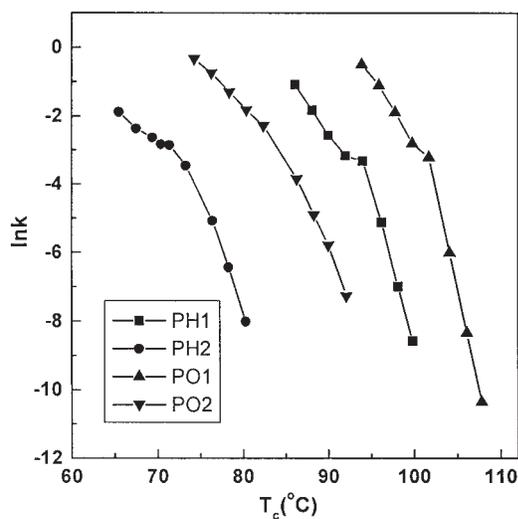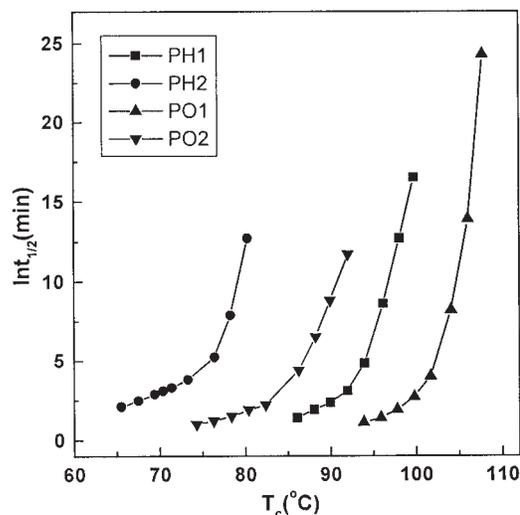
Figure 4 Changes of crystallization half-time with crystallization temperature.

tures in Figure 1 for all samples, implying a sudden change in crystallization rate constant. Figure 3 shows the changes of logarithmic crystallization rate constant ($\ln k$) with crystallization temperature. It is also observed that, after a certain crystallization temperature, $\ln k$ changes more sharply with T_c. Given that crystallization rate constant (k) in the Avrami equation is related with the linear growth rate of spherulites (G), $\ln G$ will show a similar dependency on crystallization temperature. Based on the change of $\ln G$ with T_c, the crystallization temperature of polymer usually can be classified as three regimes.[30] As a result, we believe that the different dependencies of $\ln k$ on crystallization temperature result from different crystallization temperature regimes. The changes of crystallization half-time ($t_{1/2}$), with crystallization temperature, for these four samples are depicted in Figure 4. At lower crystallization temperature, crystallization half-time changes slowly with T_c, but increases rapidly with T_c at higher crystallization temperatures.

Melting behavior

The melting traces of propylene copolymers after isothermal crystallization are illustrated in Figure 5. It is found that the melting temperatures of the copolymers increase with crystallization temperatures. Another phenomenon that should be noted is the double melting peaks at higher crystallization temperatures. The double melting peak phenomenon is observed in all four of these copolymers, irrespective of comonomer content and comonomer type. There are many potentialities that can result in double melting peaks: reorganization, existence of different crystal phases, or crystals with different lamellar thicknesses. The possibility of reorganization can be excluded for the fol-

Figure 3 Plots of $\ln k$ versus T_c for propylene copolymers.
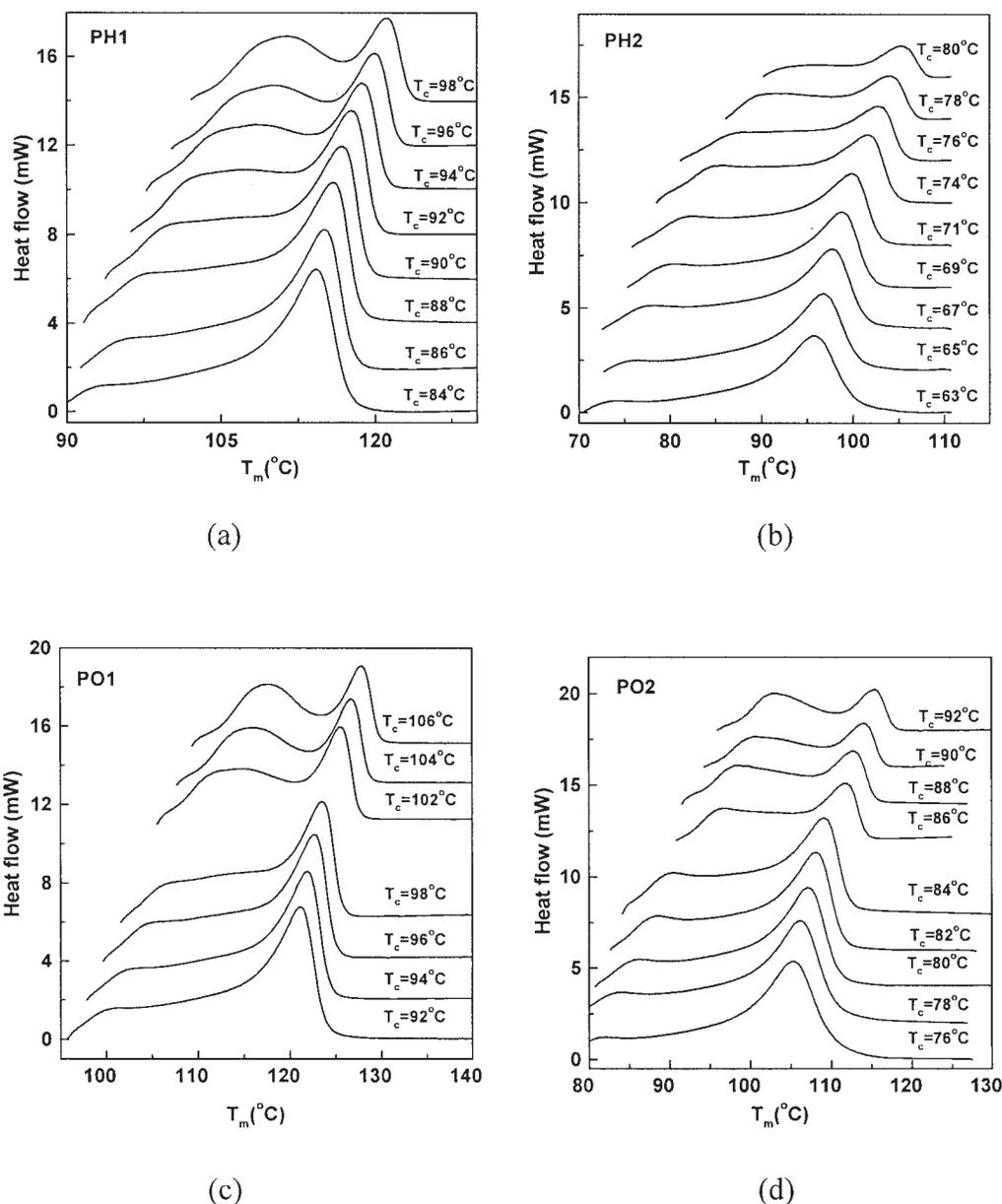
Figure 5 Melting traces of PH1 (a), PH2 (b), PO1 (c), and PO2 (d) after isothermal crystallization at a heating rate of 10°C/min.

lowing reasons: (1) the melting temperature of the low-temperature peaks is just slightly above the crystallization temperatures, and thus any possible reorganization will be completed at the applied crystallization temperature; (2) a higher crystallization temperature leads to more perfect crystals and the possibility of reorganization is reduced, which is contradiction to the observation that double melting peaks become more evident at higher crystallization temperatures. Such a phenomenon also cannot be attributed to melting of different crystal phases because γ-modification is exclusively formed at higher T_c.

We believe that the double melting peaks at high T_c are attributable to the presence of γ-crystals with dif-

ferent lamellar thicknesses, produced by the propylene sequences of different lengths distributed in the same polymer chains or different polymer chains, although these propylene copolymers were prepared with single-site metallocene catalyst and at low conversion of comonomer. The propylene sequences of different lengths tend to segregate and form discrete crystals. A higher T_c facilitates the separation of various propylene sequences, leading to more obvious double melting peaks. At lower T_c propylene sequences of different lengths can cocrystallize. The inhomogeneous distribution of comonomer units is observed in metallocene-based propylene/decene-1 copolymers[31] and in ethylene/α-olefin copolymers
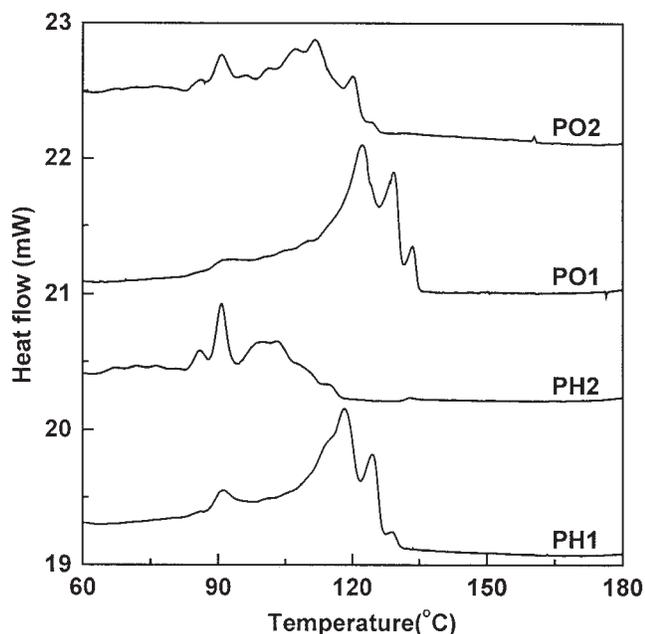
Figure 6 Melting traces of propylene copolymer after stepwise crystallization.

prepared by metallocene catalysts and by hydrogenation of polybutadiene from living anionic polymerization as well.[32–36] These facts show that, although metallocene-based olefinic copolymers have a comparatively more homogeneous comonomer distribution than that of conventional copolymers, there still exists inhomogeneous comonomer distribution to some extent.

To further confirm this speculation, stepwise crystallization, which was frequently used to characterize composition heterogeneity of ethylene copolymers,[37–39] was conducted for these four propylene copolymers. The samples were stepwise cooled from 140 to 50°C, at an interval of 5°C, and were held at each temperature for 12 h under nitrogen. The melting traces of propylene copolymer after stepwise crystallization are shown in Figure 6. A common feature in Figure 6 is that all the samples exhibit multiple melting peaks after stepwise crystallization. Because these samples underwent stepwise crystallization at each temperature for a long time, any possible reorganization procedure should have been completed during crystallization and the multiple melting peaks reflect the melting of crystals with different lamellar thicknesses. Moreover, the propylene sequences of different lengths are most likely to segregate, to form discrete crystals under stepwise crystallization conditions. As a result, we can correlate the multiple melting peaks with sequence distribution in the propylene copolymers. These propylene sequences of different lengths can be distributed in the same polymer chains and/or different polymer chains.[40,41] These two

situations are not identified because it is not the objective of the present work. It is also observed that propylene copolymers with high comonomer content exhibit more melting peaks and the melting peaks are poorly separated. This shows that the composition distribution is more inhomogeneous in the propylene copolymers with high comonomer content.

Equilibrium melting temperature ($T_m^°$)

Figure 7 shows the plot of T_c versus T_m. Based on the Hoffman–Weeks equation the equilibrium melting temperature ($T_m^°$) of the polymers can be obtained by extrapolating this plot to $T_c = T_m = T_m^°$ [42]:

$$T_m = (1 - 1/\gamma)T_m^° + T_c/\gamma \qquad (3)$$

where γ is the ratio of the crystal thickness to the thickness of the initial nucleus at crystallization temperature T_c. The obtained equilibrium melting temperatures for PH1, PH2, PO1, and PO2 are 162.6, 152.9, 173.5, and 157.6°C, respectively. The $T_m^°$ decreases as comonomer content increases. In our previous work we examined the effect of isotacticity on $T_m^°$ and found that polypropylenes with different isotacticities have similar equilibrium melting temperatures, 186°C,[28] and other authors reported the same findings.[43] This shows that isotacticity and comonomer content have different effects on $T_m^°$. Isotacticity does not affect $T_m^°$, although comonomer reduces $T_m^°$. The more comonomer units enchained, the lower the $T_m^°$. The change of $T_m^°$ with comonomer content is shown in Figure 8. One
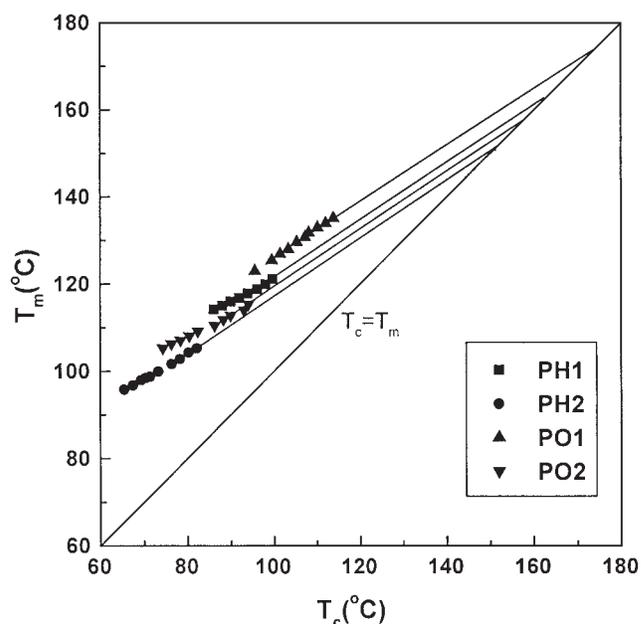
Figure 7 Hoffman–Weeks extrapolation of propylene copolymers.

can see that the equilibrium melting temperatures of propylene/hexene-1 copolymers and propylene/octene-1 copolymers fall into the same line, indicating that these two types of copolymers have the same T_m° as long as they have the same comonomer content. When the plot of T_m° versus comonomer content is extrapolated to zero comonomer content, the T_m° obtained is 186°C, which is similar to the equilibrium melting temperature of propylene homopolymer. From the effects of isotacticity and comonomer content on equilibrium melting temperature, we can infer that in the equilibrium state the comonomer units, such as hexene-1 and octene-1, are excluded from the crystal lattice of polypropylene, whereas stereo-irregularities can be included in the crystal lattice of polypropylene.

Dilation of crystal lattice

Table II summarizes the position of (117) reflection in γ-modification and corresponding d-spacing calculated from the Bragg equation. The degree of dilation of the crystal lattice can be seen from the d-spacing of the (117) reflection. It is found that the d-spacing of the (117) reflection in all the propylene copolymers is larger than that reported for propylene homopolymer, 4.380 Å.[44] At lower T_c the copolymers have relatively larger d-spacing than that of those at higher T_c. Moreover, comparing the d-spacing of propylene/hexene-1 copolymers and that of propylene/octene-1 copolymers, one can see that propylene/hexene-1 copoly-
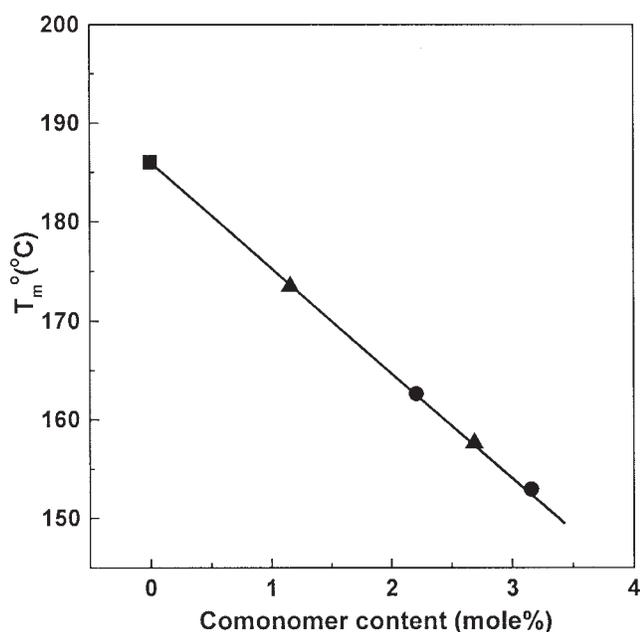
TABLE II
Position and d of (117) Reflection at Various Crystallization Temperatures

Sample	T_c (°C)	2θ of (117) reflection (°)	$d_{(117)}$ (Å)
PH1	105	19.92	4.458
	60	19.70	4.507
PH2	85	19.72	4.502
	50	—	—
PO1	102	20.10	4.418
	70	19.84	4.475
PO2	95	20.02	4.436
	50	19.74	4.498

mers have larger d-spacing. With increasing comonomer content, the d-spacing also becomes larger.

CONCLUSION

Isothermal crystallization kinetics shows that all of the investigated propylene copolymers have Avrami exponents between 2.0 and 3.0. Comonomer content and comonomer type have no effect on the Avrami exponent. Double melting peaks are observed for the propylene copolymers at higher crystallization temperatures, which can be attributed to the inhomogeneous distribution of comonomer units along the polymer chains and the existence of crystals with different lamellar thicknesses. The equilibrium melting temperatures of the copolymers decrease with increasing comonomer content, but are independent of comonomer type. This shows that comonomer units are excluded from the crystal lattice in the equilibrium state. Dilation of the crystal lattice was also observed, which depends on crystallization, comonomer content, and comonomer type.

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Figure 8 Change of equilibrium melting temperature with comonomer content. ■: polypropylene; ●: propylene-hexene-1 copolymers; ▲: propylene-octene-1 copolymers.

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