

Nonisothermal Crystallization of Metallocene Propylene–Decene-1 Copolymers

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ABSTRACT: The nonisothermal crystallization behavior of one metallocene-based isotactic polypropylene and three propylene–decene-1 copolymers was studied. The effects of comonomer content and cooling rate were investigated. It was found that comonomer units enchain systematically reduce the crystallization temperature (T_c), melting temperature (T_m), fusion enthalpy (ΔH_f), and crystallinity (X_c). Such an effect becomes more evident at a faster cooling rate. With increasing comonomer content, the supercooling required for crystallization increases and the overall crystallization rate is reduced. The Avrami equation is applicable to describe the nonisothermal crystallization kinetics of pro-

pylene–decene-1 copolymer. It was shown that, although the reduced crystallization rate constant Z_c increases with comonomer content, the Avrami exponent decreases with comonomer content and cooling rate, leading to the smaller overall crystallization rate and larger crystallization half-time of the copolymer with higher comonomer content. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1724–1730, 2004

Key words: propylene–decene-1 copolymer; nonisothermal crystallization; metallocene catalysts; kinetics (polym.); copolymerization

INTRODUCTION

Copolymerization of propylene with α -olefins can improve the properties of polypropylene.¹ For example, a film of propylene–butene-1 copolymer offers lower heat-seal initiation temperature and higher clarity.² Copolymers of propylene with α -olefins also have properties that make them candidate materials for special uses: Xu et al. found that propylene–octene-1 copolymers could enrich oxygen from air.³ However, propylene- α -olefin copolymers, prepared from conventional heterogeneous Ziegler–Natta catalysts, usually have a broad composition distribution, attributed to the characteristic of plural active sites of the catalysts,^{4–8} which limits their application. The invention of metallocene catalysts makes it possible to prepare propylene- α -olefin copolymers with relatively homogeneous composition distribution,^{9–11} which broadens the potential application of propylene- α -olefin copolymers. Crystallization behavior and other properties of propylene- α -olefin copolymers, such as formation of γ -crystal form,^{12,13} distribution of comonomer units

between crystalline region and amorphous region,¹⁴ isothermal crystallization kinetics,^{7,15} and dynamic mechanical properties¹⁶ have been studied. It has been shown that both comonomer type and comonomer content have influences on the properties of propylene- α -olefin copolymers.^{17,18} To our knowledge, however, no report on nonisothermal crystallization of propylene- α -olefin copolymers has yet been published. From the perspective of processing, the study of nonisothermal crystallization behavior of a polymer is significant as well as that of isothermal crystallization.¹⁹ For this article, the nonisothermal crystallization behavior of one metallocene-based isotactic polypropylene and three propylene–decene-1 copolymers was studied and the effects of comonomer content and cooling rate were investigated.

EXPERIMENTAL

Materials

Propylene homopolymerization and copolymerization with decene-1 were carried out at various feed ratios using *rac*-Me₂Si(Ind)₂ZrCl₂/methylaluminoxane (MAO) as catalyst. The details of the polymerization process are described elsewhere.²⁰ Structural characteristics of the polymers are given in Table I.

DSC experiments

Nonisothermal crystallization of polypropylene and propylene copolymers was carried out on a Perkin-

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TABLE I
Structural Characteristic of Propylene-Decene-1 Copolymers

Sample	Decene-1 in copolymers mol %	[<i>mmmm</i>] (%)	\bar{M}_w ($\times 10^{-4}$)	\bar{M}_w/\bar{M}_n
PP	0	86.3	3.36	2.18
PD1	2.25	83.7	3.32	2.05
PD2	3.92	85.0	3.23	2.12
PD3	7.83	85.9	3.17	2.03

Elmer Pyris-1 DSC (Perkin Elmer Cetus Instruments, Norwalk, CT). About 2–3 mg of samples were sealed in aluminum pans and heated to 200°C, held for 5 min, and then cooled to –20°C at a prescribed cooling rate. Subsequently the samples were again heated to 180°C 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 α radiation from 5 to 45°, in 0.02° increments.

RESULTS AND DISCUSSION

Nonisothermal crystallization and melting

The nonisothermal crystallization DSC traces of PP, PD1, PD2, and PD3 at various cooling rates and corresponding melting traces are shown in Figures 1 and 2, respectively. It is observed that there is a lower shoulder in the melting traces at the cooling rate of 2°C/min, which is especially evident for PP. This is attributed to the inhomogeneous distribution of stereo/regio defects and comonomer units along the

polymer chains (i.e., existence of propylene segments with various lengths), although these samples were prepared by metallocene catalyst.²¹ At slower cooling rates, the shorter propylene segments can also crystallize and thus a lower shoulder melting peak is observed. By contrast, the shorter propylene sequences are difficult to crystallize at a faster cooling rate. In propylene-decene-1 copolymers, the average length of propylene sequences is not as long as in the homopolymer because of enchainment of decene-1 units and the shorter propylene sequences cannot crystallize, and thus the phenomenon of double melting peaks is not evident.

A series of parameters were obtained, such as crystallization temperature (T_c), melting temperature (T_m), fusion enthalpy (ΔH_f), crystallinity (X_c), the difference between T_m and T_c ($T_m - T_c$), onset crystallization temperature (T_c^{onset}), and end crystallization temperature (T_c^{end}), and are given in Table II. The change of T_m and T_c with comonomer content in the copolymers is illustrated in Figure 3. It is found that the both T_m and T_c linearly decrease with decene-1 content. It is also observed that the cooling rate has less effect on T_m and T_c of propylene homopolymer, but has a greater effect on the copolymer with higher comonomer content, resulting in a larger slope at the cooling rate of –10°C in Figure 3. The fusion enthalpy (ΔH_f) and crystallinity (X_c) decrease with comonomer content as well. PD3 almost loses its crystallinity at the faster cooling rate. As shown in Table II, the difference between T_m and T_c , $T_m - T_c$, depends on both comonomer content and cooling rate. $T_m - T_c$ indicates the supercooling needed for crystallization²²: the smaller the value of $T_m - T_c$, the more easily crystallization takes place. We noticed that, at lower comonomer content such as in PP, PD1, and PD2, the values of $T_m - T_c$ are similar at various cooling rates, but the values of $T_m - T_c$ obvi-

TABLE II
Nonisothermal Crystallization Data

Cooling rate (°C/min)	Sample	T_c (°C)	T_m (°C)	ΔH_f (J/g)	X_c^a	$T_m - T_c$ (°C)	T_c^{onset} (°C)	T_c^{end} (°C)	$T_c^{\text{onset}} - T_c^{\text{end}}$ (°C)	$(T_c^{\text{onset}} - T_c^{\text{end}})/R$ (min)
2	PP	110.2	136.6	65.1	0.311	26.4	114.8	106.8	8.0	4.0
	PD1	94.2	120.7	37.4	0.179	26.5	99.2	87.9	11.3	5.65
	PD2	81.3	108.1	24.2	0.116	26.8	88.4	75.3	13.1	6.55
	PD3	47.9	80.2	12.8	0.061	32.3	55.1	38.8	16.3	8.15
5	PP	106.2	136.2	56.2	0.269	30.0	110.8	102.5	8.3	1.66
	PD1	89.1	119.0	35.7	0.171	29.9	96.2	83.3	12.9	2.58
	PD2	75.9	106.4	23.7	0.113	30.5	87.0	68.7	19.3	3.86
	PD3	41.2	77.2	10.9	0.052	36.0	48.8	23.4	25.4	5.08
10	PP	103.5	136.0	48.9	0.234	32.5	108.1	99.1	9.0	0.90
	PD1	84.8	117.7	33.8	0.162	32.9	90.2	80.4	9.8	0.98
	PD2	69.4	104.6	16.6	0.079	35.2	79.1	63.5	15.6	1.56
	PD3	33.8	75.0	5.9	0.028	41.2	44.4	19.4	25.0	2.50

^a $X_c = \Delta H_f/\Delta H_f^\circ$, where ΔH_f° is the fusion enthalpy of perfect α -crystals. The value of ΔH_f° is 209 J/g.²⁷

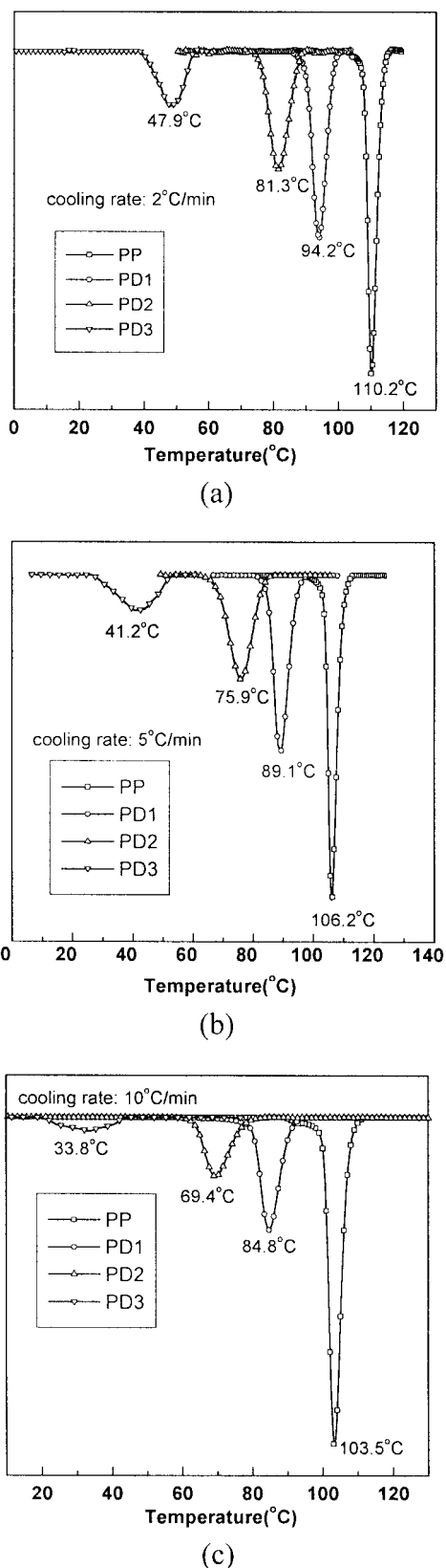


Figure 1 Nonisothermal crystallization DSC traces of PP and propylene-decene-1 copolymers. Cooling rate: (a) 2°C/min; (b) 5°C/min; and (c) 10°C/min.

ously become larger than those of the other three samples.

A possible explanation is that the γ -crystal form is predominant in PD3, whereas the α -crystal form is the major crystalline component in PP, PD1, and PD2, as will be shown in a later section. We have found that γ -crystals have a slower crystallization rate than that of α -crystals in the temperature range studied, although γ -crystals may have a faster crystallization rate at high temperature.²³ As a result, the finding that greater supercooling is needed for nonisothermal crystallization of PD3 is in accordance with the result of isothermal crystallization kinetics. The value of $T_m - T_c$ also becomes larger with the increase of cooling rate, suggesting greater difficulty in crystallization. The difference between the onset crystallization temperature and the end crystallization temperature, $T_c^{\text{onset}} - T_c^{\text{end}}$, is the temperature range of crystallization, and the ratio of $T_c^{\text{onset}} - T_c^{\text{end}}$ to the cooling rate R reflects the overall crystallization rate in nonisothermal crystallization.²⁴ The larger $(T_c^{\text{onset}} - T_c^{\text{end}})/R$ indicates a slower crystallization rate. The variation of $(T_c^{\text{onset}} - T_c^{\text{end}})/R$ with comonomer content is shown in Figure 4. As can be seen from Figure 4, the enchainment of decene-1 units reduce the overall crystallization rate.

Nonisothermal crystallization kinetics

The Avrami equation is used to describe the nonisothermal crystallization of polymers,²⁵ although it is based on the assumption that the crystallization temperature is constant:

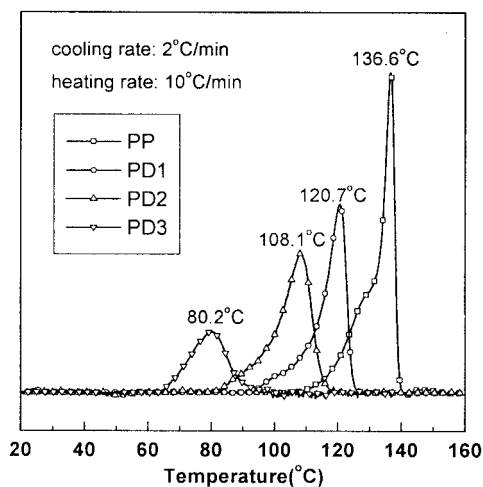
$$1 - X_t = \exp(-Z_t t^n) \quad (1)$$

where the exponent n is a mechanism constant that depends on the type of nucleation and growth process parameters, and Z_t is a composite rate constant involving both nucleation and growth rate parameters. The double-logarithmic form of eq. (2) yields

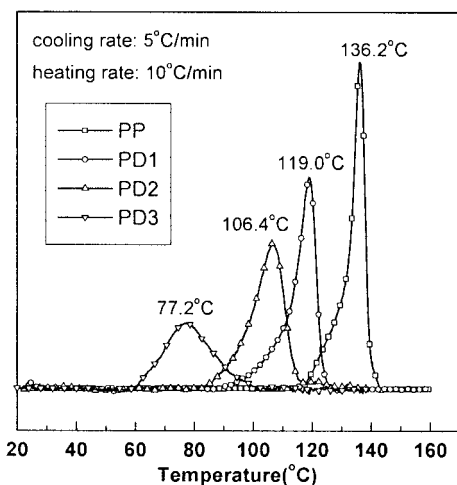
$$\ln[-\ln(1 - X_t)] = \ln Z_t + n \ln t \quad (2)$$

Therefore, the Avrami exponent n and constant Z_t can be obtained from the slope and the interception in the plot of $\ln[-\ln(1 - X_t)]$ against $\ln t$ for each cooling rate, respectively. It should be noted that, in nonisothermal crystallization, Z_t and n do not have the same physical significance as in the isothermal crystallization because, under nonisothermal crystallization, the temperature changes continuously, which affects the rates of both nucleation and spherulite growth.

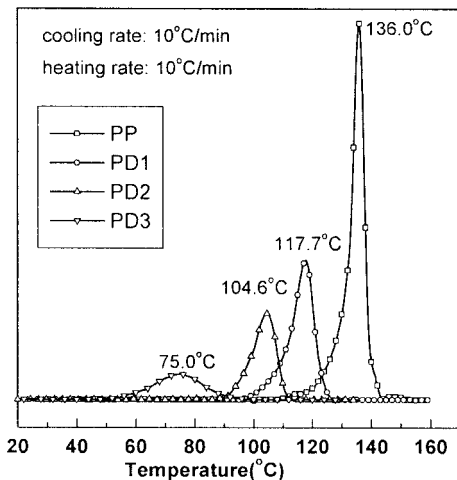
Considering the characteristic of nonisothermal crystallization, the parameter Z_t is corrected by the cooling rate, and the reduced crystallization rate constant Z_c in nonisothermal crystallization is obtained²⁶:



(a)



(b)



(c)

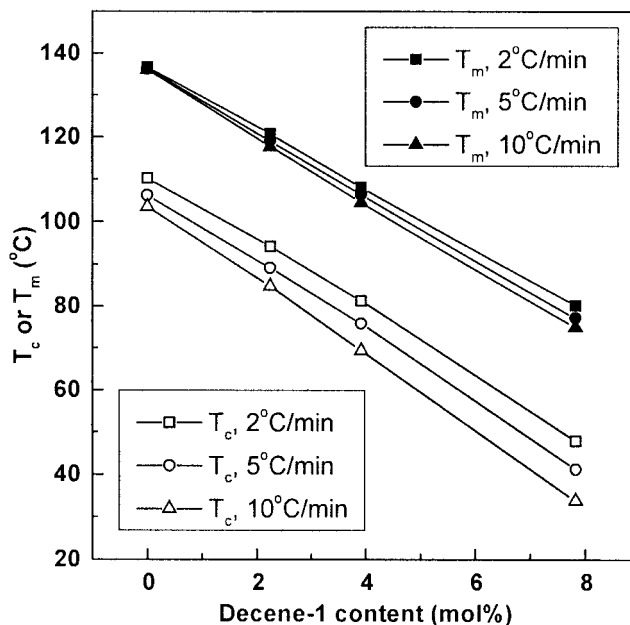


Figure 3 Changes of melting temperature and crystallization temperature with comonomer content.

$$\ln Z_c = \ln Z_t/R \tag{3}$$

The Avrami plots, at various cooling rates, are shown in Figure 5. A linear relationship is observed for all these four samples at various cooling rate, indicating that the Avrami equation is applicable to describe nonisothermal crystallization kinetics of metallocene-based polypropylene and propylene-decene-1 copolymers. It can be seen from Figure 5 that the slope decreases gradually as the comonomer content increases. The plot of Avrami exponent against comonomer content further confirms this point (Fig. 6): the Avrami exponent decreases with increasing comonomer content. When the cooling rate becomes faster, there is a slight decrease in the Avrami exponent. The Avrami exponent derived from crystallization kinetics is usually correlated with the dimension of crystal growth. As a consequence, enchainment of comonomer and a high cooling rate combine to reduce the dimensions of crystal growth, which results in less-perfect crystals. Compared with the Avrami exponents obtained in isothermal crystallization kinetics of the same polymers,¹⁵ it is found that the Avrami exponents, in nonisothermal crystallization, are much larger. The dependency of the crystallization rate constant Z_c on comonomer content and cooling rate is

Figure 2 Melting DSC traces of PP and propylene-decene-1 copolymers after nonisothermal crystallization rate. Cooling rate: (a) 2°C/min; (b) 5°C/min; and (c) 10°C/min. The heating rate is 10°C/min.

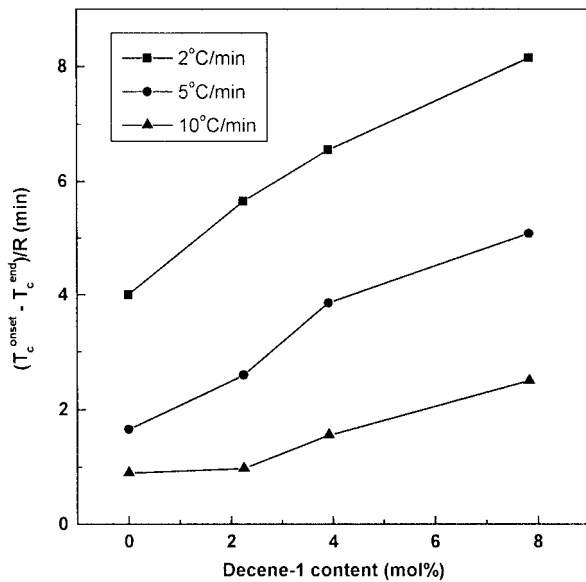


Figure 4 Effect of comonomer content on the overall crystallization rate represented by $(T_c^{\text{onset}} - T_c^{\text{end}})/R$.

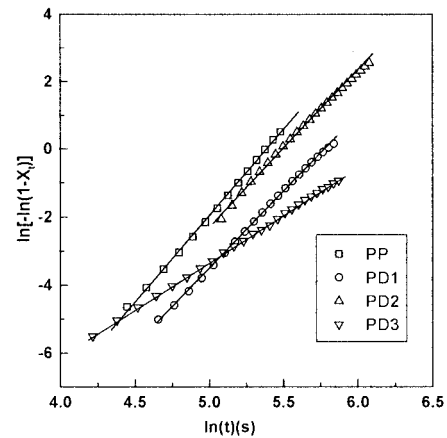
depicted in Figure 7. It is surprising that Z_c increases with comonomer content. At a slower cooling rate, the effect of comonomer content on Z_c becomes more obvious. As a result, the smaller overall crystallization rate of the copolymer with higher comonomer content, as indicated by $(T_c^{\text{onset}} - T_c^{\text{end}})/R$, is not attributed to its smaller crystallization rate constant, but rather to its smaller Avrami exponent. The crystallization half-time can be calculated from the parameters n and Z_t as follows:

$$\ln t_{1/2} = [\ln(\ln 2) - \ln Z_t]/n \quad (4)$$

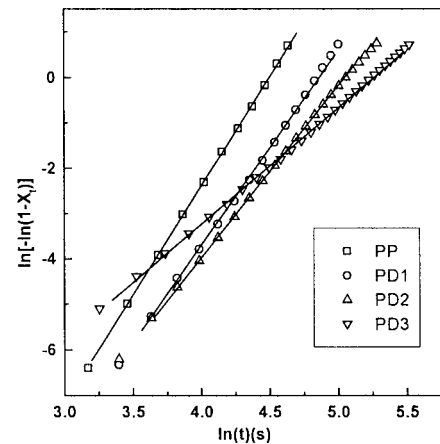
The larger value of $t_{1/2}$ designates the slower crystallization rate. As shown in Figure 8, the value of $\ln t_{1/2}$ increases with comonomer content and decreases with cooling rate, indicating that the copolymer with higher comonomer content, and the polymer at an increasingly slower cooling rate, have slower crystallization rates. This is in accordance with the result of $(T_c^{\text{onset}} - T_c^{\text{end}})/R$.

WAXD patterns

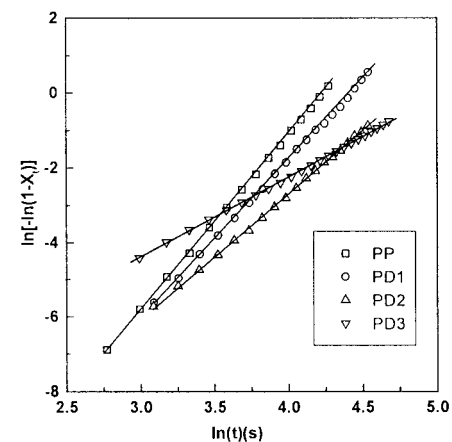
The WAXD patterns of the propylene–decene-1 copolymers, after being cooled in air from 180°C, are shown in Figure 9. Both the α -crystal form with its characteristic (130) reflection at $2\theta = 18.6^\circ$, and the γ -crystal form with its characteristic (117) reflection at $2\theta = 19.6^\circ$, were observed in these four samples. The content of the γ -crystal form, relative to α -crystal form, increases with enchainment of comonomer units, although the overall crystallinity decreases simultaneously with comonomer content. In propylene ho-



(a)



(b)



(c)

Figure 5 Avrami plots for PP and propylene–decene-1 copolymers. Cooling rate: (a) 2°C/min; (b) 5°C/min; and (c) 10°C/min.

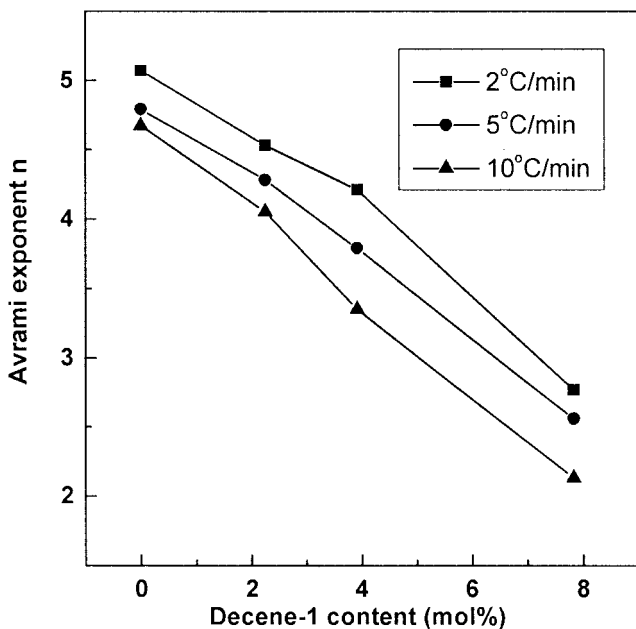


Figure 6 Effect of comonomer content on Avrami exponent.

mopolymer, the amount of γ -crystals is negligible, whereas γ -crystals become the major crystalline content over α -crystals in PD3. The positions of various reflections are listed in Table III. It is found that enchainment of decene-1 units into polypropylene chains does not change the positions of the reflections, showing that the crystal structures of both α - and γ -forms are unaffected by the comonomer units. This is in accordance with the previous finding that the

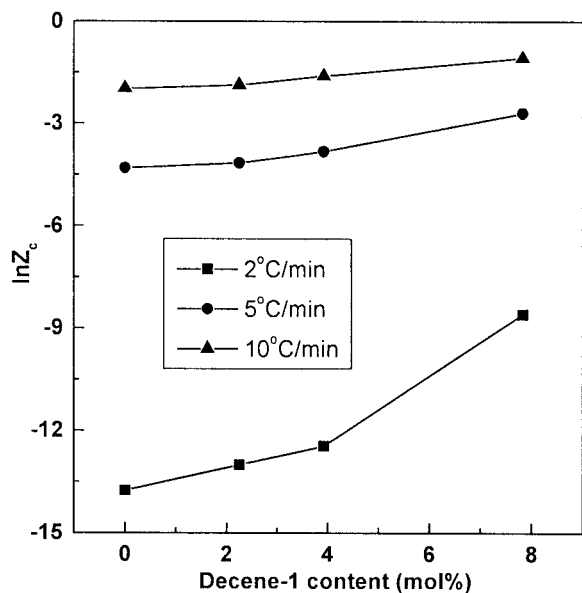


Figure 7 Effect of comonomer content on the reduced crystallization rate constant Z_c .

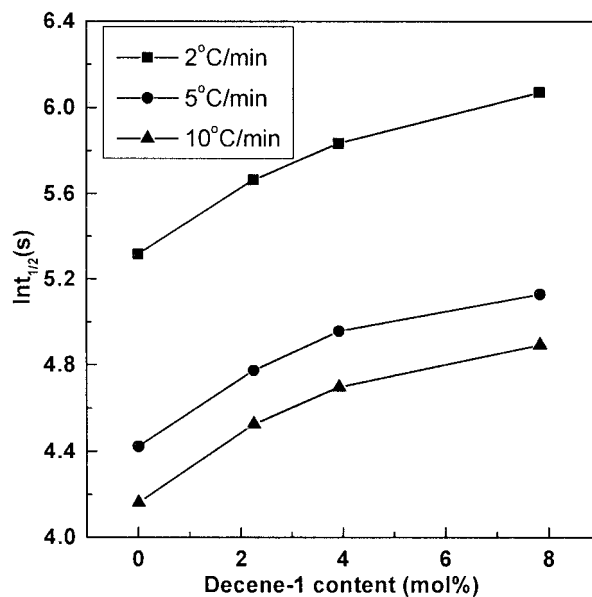


Figure 8 Variation of crystallization half-time with comonomer content.

comonomer units are excluded from the unit cell of the crystals.^{13,14}

CONCLUSIONS

Nonisothermal crystallization and melting behavior of propylene-decene-1 copolymers show that the T_c , T_m , ΔH_f , and X_c are systematically reduced by comonomer units and the degree of reduction becomes higher at a faster cooling rate. As the comonomer content increases, greater supercooling is required for crystallization and the overall crystallization rate is reduced. Avrami analysis of the nonisothermal crystallization

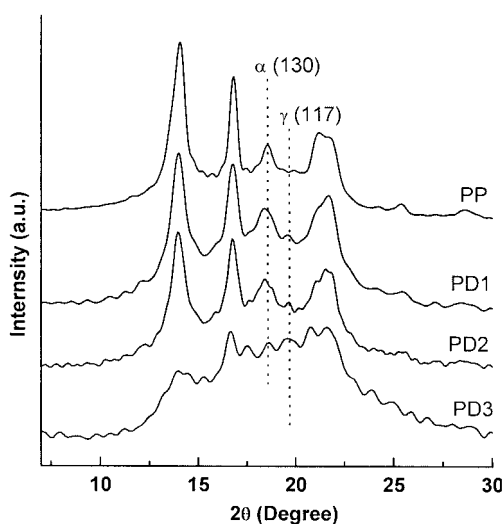


Figure 9 WAXD patterns of PP and propylene-decene-1 copolymers after nonisothermal crystallization.

TABLE III
Positions of Various Reflections in WAXD

Sample	(110)	(040)	(130)	(131 + 041)	(117)
PP	14.06°	16.80°	18.54°	21.70°	—
PD1	14.00°	16.75°	18.40°	21.70°	19.60°
PD2	13.95°	16.75°	18.40°	21.55°	19.65°
PD3	13.95°	16.65°	18.60°	21.60°	19.60°

kinetics reveals that the slower overall crystallization rate for the copolymer with higher comonomer content is attributed to its smaller Avrami exponent instead of the crystallization rate constant.

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References

1. Arnold, M.; Bornemann, S.; Schade, B.; Henschke, O. *Kautsch Gummi Kunstst* 2001, 54, 300.
2. Shell Chemical, Pecten Chem Inc. *Mod Plast Int* 1993, 12, 113.
3. Yang, S. L.; Xu, Z. K.; Feng, L. X. *Makromol Chem Macromol Symp* 1992, 63, 233.
4. Fan, Z. Q.; Forlini, F.; Tritto, I.; Locatelli, P.; Sacchi, M. C. *Macromol Chem Phys* 1994, 195, 3889.
5. Fan, Z. Q.; Feng, L. X.; Yang, S. L. *J Polym Sci Part A: Polym Chem* 1996, 34, 3329.
6. Xu, J. T.; Feng, L. X.; Yang, S. L.; Yang, Y. Q.; Kong, X. M. *Macromolecules* 1997, 30, 7655.
7. Perez, E.; Benavente, R.; Bello, A.; Perena, J. M.; Zucchi, D.; Sacchi, M. C. *Polymer* 1997, 38, 5411.
8. Abiru, T.; Mizuno, A.; Weigand, F. *J Appl Polym Sci* 1998, 68, 1493.
9. Arnold, M.; Henschke, O.; Knorr, J. *Macromol Chem Phys* 1996, 197, 563.
10. Kim, I. *Macromol Rapid Commun* 1998, 19, 299.
11. Kim, I.; Kim, Y. *J Polym Bull* 1998, 40, 415.
12. Turner-Jones, A. *Polymer* 1971, 12, 487.
13. Hosier, I. L.; Alamo, R. G.; Estes, P.; Isasi, J. R.; Mandelkern, L. *Macromolecules* 2003, 36, 5623.
14. Hosoda, S.; Hori, H.; Yada, K.; Nakahara, S.; Tsuji, M. *Polymer* 2002, 43, 7451.
15. Xu, J. T.; Guan, F. X.; Fan, Z. Q. *J Therm Anal Calorim* 2002, 70, 911.
16. Lovisi, H.; Tavares, M. I. B.; da Silva, N. M.; de Menezes, S. M. C.; de Santa Maria, L. C.; Coutinho, F. M. B. *Polymer* 2001, 42, 9791.
17. Brull, R.; Pasch, H.; Raubenheimer, H. G.; Sanderson, R.; van Reenen, A. J.; Wahner, U. M. *Macromol Chem Phys* 2001, 202, 1281.
18. Van Reenen, A. J.; Brull, R.; Wahner, U. M.; Raubenheimer, H. G.; Sanderson, R. D.; Pasch, H. *J Polym Sci Part A: Polym Chem* 2000, 38, 4110.
19. Di Lorenzo, M. L.; Silvestre, C. *Prog Polym Sci* 1999, 24, 917.
20. Xu, J. T.; Zhu, Y. B.; Fan, Z. Q.; Feng, L. X. *J Polym Sci Part A: Polym Chem* 2001, 39, 3294.
21. Xu, J. T.; Wu, F.; Fan, Z. Q.; Ryan, A. J. *J Macromol Sci Phys* 2002, B41, 1331.
22. Roerdink, E.; Warnier, J. M. M. *Polymer* 1985, 26, 1582.
23. Xu, J. T.; Guan, F. X.; Yasin, T.; Fan, Z. Q. *J Appl Polym Sci* 2003, 90, 3215.
24. Gupta, A. K.; Purwar, S. N. *J Appl Polym Sci* 1984, 29, 1595.
25. Avrami, M. *J Chem Phys* 1939, 7, 1103.
26. Jeziorny, A. *Polymer* 1978, 19, 1142.
27. Clark, E. J.; Hoffman, J. D. *Macromolecules* 1984, 17, 878.