

ISOTHERMAL CRYSTALLIZATION OF PROPYLENE-1-DECENE COPOLYMERS

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Abstract

The isothermal crystallization and subsequent melting behavior of one propylene homopolymer and three propylene-1-decene copolymers with different comonomer contents prepared by metallocene catalyst were studied using differential scanning calorimetry (DSC). It is found that the Avrami exponent of the propylene copolymers decreases gradually with the increase of comonomer content, from 3.0 for the propylene homopolymer to 1.4 for the copolymer with 7.83 mol% 1-decene units. Higher comonomer content also weakens the dependence of crystallization rate constant and crystallization half-time on temperature. Double melting peaks, which correspond to α and γ crystal phases, respectively, are observed for all copolymers under isothermal crystallization. The result shows that higher crystallization temperature is favorable to the segregation of α and γ crystal phases, resulting in higher proportion of γ crystal phase.

Keywords: isothermal crystallization, melting, propylene-1-decene copolymer

Introduction

Copolymerization is one of the useful methods to improve polymer properties. The synthesis, structure and properties of ethylene- α -olefin copolymers have been extensively studied. By contrast, there are few reports on propylene- α -olefin copolymers [1–15], especially on the properties (such as crystallization) of this type copolymer [16–18]. The invention of metallocene catalyst makes it possible to prepare propylene copolymers with narrow molecular mass distribution and chemical composition distribution due to its characteristic of single active species. This leads to a promising perspective of propylene- α -olefin copolymers in application. We have previously synthesized a series of propylene – higher α -olefin copolymers [19]. In this paper, isothermal crystallization behavior of propylene-1-decene copolymers with various comonomer contents is reported.

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Experimental

Materials

Propylene homopolymerization and copolymerization with 1-decene were carried out at various feed ratios using $(\text{Ind})_2\text{SiZrCl}_2$ /methylaluminoxane (MAO) as catalyst. The details of the polymerization process were described elsewhere [19]. Structural characteristic of the polymers is given in Table 1.

Table 1 Structural characteristic of propylene-1-decene copolymers

Samples	[1-decene] in feed	D/mol% in copolymers	[<i>mmmm</i>]/%	$\overline{M}_w \cdot 10^{-4}$	$\overline{M}_w/\overline{M}_n$
PP	0	0	86.3	3.36	2.18
PD1	0.025	2.25	83.7	3.32	2.05
PD2	0.05	3.92	85.0	3.23	2.12
PD3	0.1	7.83	85.9	3.17	2.03

Isothermal crystallization

The isothermal crystallization experiments were carried out on a Perkin Elmer Pyris-1 calorimeter. About 3~4 mg of polymer samples were encapsulated in aluminum pans and heated to 180°C at a rate of 10°C min⁻¹ and maintained for 10 min, then the samples were quickly cooled to the desired crystallization temperature (100°C min⁻¹) and held until the crystallization was completed. The samples prepared by this way were heated immediately from the crystallization temperature at a rate of 10°C min⁻¹.

The isothermal crystallization kinetics was analyzed with Avrami equation [20].

$$1-X(t) = \frac{\Delta H_{t=\infty}^c - \Delta H_t^c}{\Delta H_{t=\infty}^c - \Delta H_{t=0}^c} = \exp(Kt^n) \quad (1)$$

where $X(t)$ is the relative crystallinity at time t , $\Delta H_{t=\infty}^c$ and ΔH_t^c are the heats of crystallization on complete crystallization and after time t . Thus:

$$\log[-\ln(1-X(t))] = \log K + n \log t \quad (2)$$

The crystallization rate constant K and Avrami exponent n can be determined from the interception and slope in the plot of $\log[-\ln(1-X(t))]$ vs. $\log(t)$.

Wide angle X-ray diffraction (WAXD)

X-ray diffraction experiments were performed on a Bruker D8 X-ray diffractometer (40 kV, 40 mA) using Ni-filtered CuK_α radiation in a step of 0.02° from 5° to 45°.

Results and discussion

Isothermal crystallization kinetics

The Avrami plots of the four samples crystallized at different temperatures are shown in Fig. 1 and the obtained parameters are summarized in Table 2. It is found that the Avrami exponents for propylene homopolymer are close to 3, which is a typical Avrami exponent of polymer with heterogeneous nucleation mechanism in case of spherulite growth. An interesting finding is that the Avrami exponent of the copolymers decreases gradually as the comonomer content in the copolymers increases. The Avrami exponent for PD1 is about 2, and it is only 1.4 for PD3. Since Avrami exponent also reflects the growth dimension of the crystals, this shows that the introduction of comonomer units into the PP chains leads to a more planar structure of the crystallites formed. Such a result is accordance with the absence of spherulite in the copolymers when observed with a polarized light microscope.

Table 2 Isothermal crystallization data

Sample	Crystallization temperature/ °C	$T_m/$ °C	$\Delta H_f/$ J g ⁻¹	Avrami exponen/ n	$\log K/$ s ⁻¹	$T_{1/2}/$ s
PP	110	129.7/137.2	29.8	2.6	-4.86	64.5
	112	130.0/138.3	28.4	2.7	-5.64	113.7
	114	130.7/139.0	26.5	2.6	-6.13	188.4
	116	131.7/139.7	26.3	2.7	-6.98	302.2
PD1	92	99.44/120.0	21.5	1.8	-3.47	75.2
	94	101.4/120.7	20.2	1.8	-3.80	114.1
	96	103.7/121.7	19.9	1.9	-4.29	141.0
	98	105.4/122.7	15.5	1.9	-4.60	199.2
PD2	84	92.2/110.4	19.2	1.7	-4.10	184.3
	86	93.5/111.4	17.0	1.7	-4.19	227.4
	88	95.2/112.4	15.7	1.7	-4.28	280.5
	90	97.4/113.7	13.8	1.7	-4.35	319.0
PD3	40	51.3/75.0	16.2	1.4	-2.99	97.0
	42	52.6/75.7	15.4	1.4	-3.07	117.2
	46	57.0/78.0	14.0	1.4	-3.19	149.6
	48	59.3/79.4	12.0	1.4	-3.30	170.6

When $\log K$ is plotted vs. $1/T$, the slope is activation energy of the crystallization. This plot is shown in Fig. 2. It is found that the slope decreases in the following order: PP>PD1>PD2>PD3, indicating a smaller activation energy for the copolymer with higher 1-decene content. This indicates that the crystallization rate of propylene homopolymer has a stronger dependence on temperature, when compared to the copolymers. The crystallization half-time is also plotted vs. temperature (Fig. 3). Again a similar variation for the slope is observed, which is in accordance with the result of crystallization rate constant.

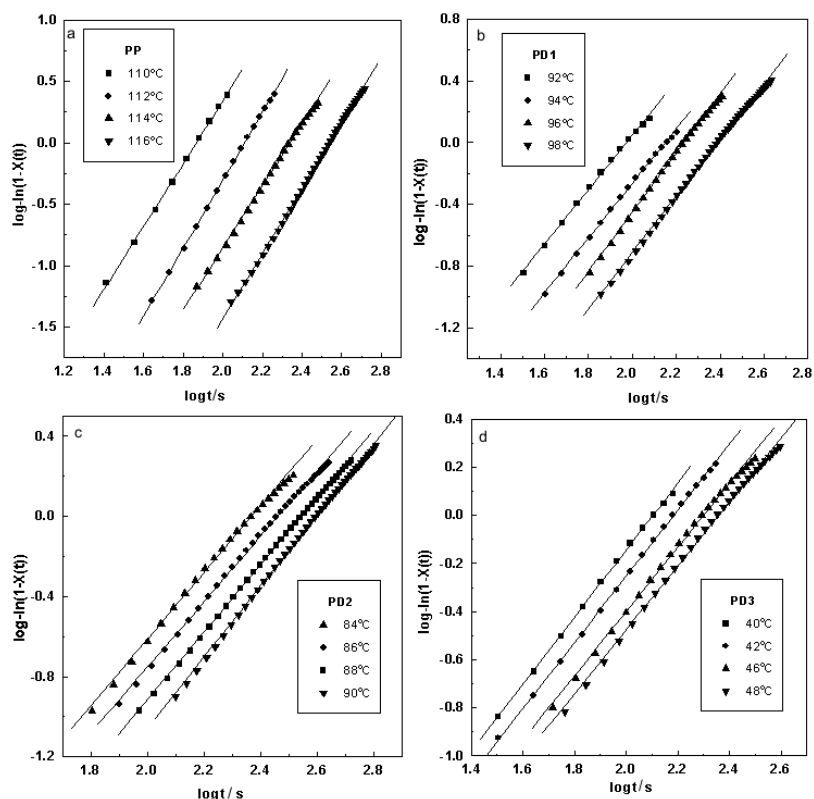


Fig. 1 Avrami plots of various samples crystallized at different temperatures a – PP; b – PD1; c – PD2; d – PD3

Melting behavior

After isothermal crystallization was completed, all the polymers were immediately heated to 170°C and the melting traces were recorded (Fig. 4). A striking feature in Fig. 4 is that double melting peaks are observed for all polymers crystallized. Figure 5 is the WAXD pattern of PD1 after isothermal crystallization at 94°C. Apart from the reflections of α crystal phase, a characteristic reflection of γ crystal phase is also observed at $2\theta=19.7^\circ$ in Fig. 5 [21]. This indicates that the double melting peaks correspond to α and γ crystal phases, respectively. One author suggested that α phase is produced by longer propylene sequences with stronger crystallizability and γ phase by shorter propylene sequences with weaker crystallizability [22]. Therefore, the appearance of double peak shows that there still exist propylene sequences of different lengths in the propylene-1-decene copolymers, though metallocene catalysts are believed to have single type of active site. These sequences separate and form different crystalline populations during isothermal crystallization. The observation of inhomogeneous distribution of polymer chains in the melt of PD2 and PD3 by synchrotron small-angle X-ray scattering (SAXS)

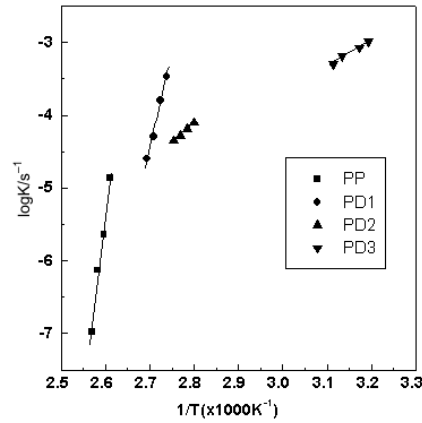


Fig. 2 Plots of $\log(K)$ vs. $1/T$

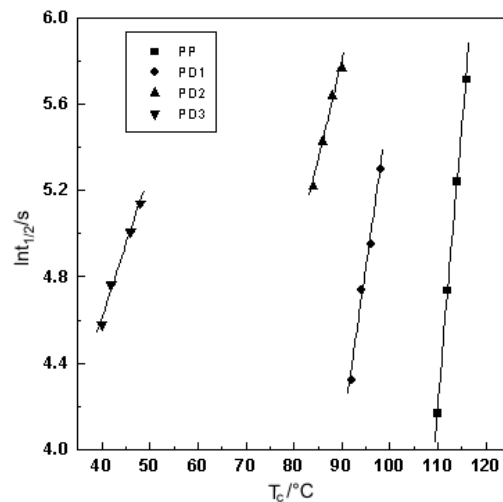


Fig. 3 Dependence of crystallization half-time on temperature

supports this viewpoint [23]. This is highly similar to the inhomogeneous composition distribution observed in metallocene-based ethylene copolymers [24–26]. With increasing in comonomer content in the polymer chains, the percentage of short propylene sequences becomes higher and the proportion of γ crystal phase increases accordingly, as shown by WAXD [23]. Comparing the different curves in Fig. 4, one can see that the proportion of the low temperature peak increases with the crystallization temperature except for PD3. Bond *et al.* observed similar phenomenon in metallocene-based propylene homopolymer [27]. The propylene sequences with different lengths are easier to segregate at higher temperature, while they tend to crystallize in the same crystals at lower temperature because of kinetic trap. In the quickly quenched propylene copolymers, only α crystal phase can be observed and γ crystal phase disappears completely. The anomalous change for PD3 may be due to partial melting of γ crystal phase at higher crystalliza-

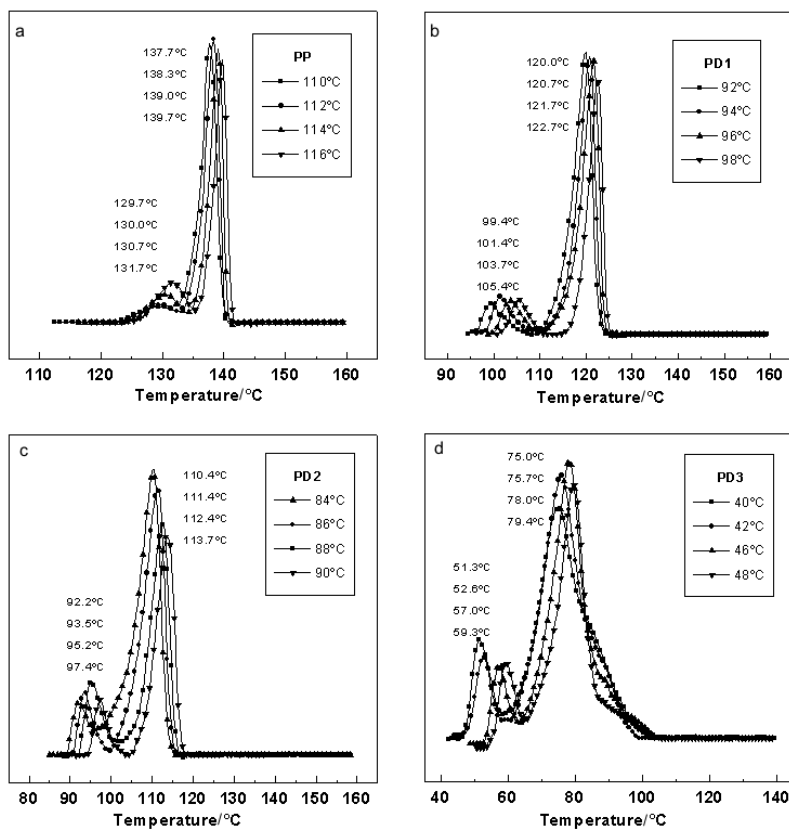


Fig. 4 Melting behavior of propylene-1-decene copolymers after isothermal crystallization a – PP; b – PD1; c – PD2; d – PD3

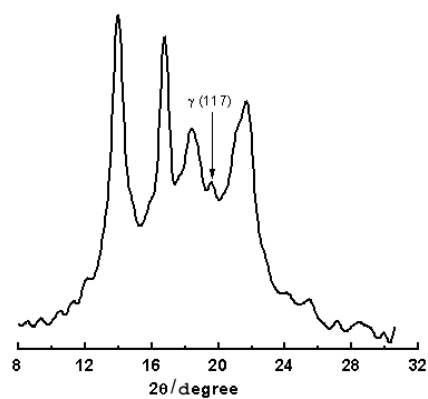


Fig. 5 WAXD pattern of PD1 after crystallization at 94°C

tion temperature and due to the low melting temperature of γ crystal phase. It is also noticed that the melting temperatures of both peaks shift to higher temperatures as crystallization temperature increases, showing that the lamellar thickness of both α and γ crystal phases increases as crystallization temperature increases.

Conclusions

The isothermal crystallization kinetics analyzed by Avrami equation shows that the Avrami exponent decreases as comonomer content in the copolymers increases. The crystallization rate of the copolymers with higher comonomer content has weaker dependence on crystallization temperature. Double melting peaks originating from α and γ crystal phases are observed in the polymers after isothermal crystallization. The proportion of γ crystal phase increases with crystallization temperature and comonomer content.

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