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Crystallizations of poly(ethylene terephthalate co ethylene isophthalate)

Baozhong Li*, Jiayan Yu, Seungwoo Lee, Moonhor Ree

Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, South Korea

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Abstract

Crystallization behaviors of crystallizable poly(ethylene terephthalate co ethylene isophthalate) with different molar ratios of polyethylene terephthalate (PET) to polyethylene isophthalate (PEI) were studied both non-isothermally and isothermally by differential scanning calorimetry (DSC). Avrami and Ozawa plots were used to describe the non-isothermal crystallizations. However, the Avrami treatment cannot predict the mechanisms of non-isothermal crystallizations for the above copolyesters, while the Ozawa explanation can be taken to reveal that the non-isothermal crystallization is dominated by heterogeneous nucleation. The activation energies of crystallization were calculated from the Kissinger equation. The copolyester 90/10 shows synergistic effects on non-isothermal crystallization, in that it has the lowest activation energy of crystallization. Isothermal crystallizations were explained by Avrami plots. From lower degrees of supercooling to higher ones, the crystals of the copolyesters grow from low dimension to multidimensions, but the crystallization rates become lower. The percentage of spherulite growth of the copolyester 100/0 (PET homopolymer) is higher than that of the other copolyesters under the same degree of supercooling. Equilibrium crystallization temperatures (T_c^0) and melting temperatures (T_m^0) were postulated respectively. T_c^0 and T_m^0 decrease with the increasing composition of PEI, indicating that the equilibrium crystals of the copolyesters become imperfect. With involvement of PEI, the copolyester is not likely crystallizable perfectly and the crystal becomes less perfect. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Copolyesters; Non-isothermal crystallization; Isothermal crystallization

1. Introduction

Crystallization behaviors are a permanent topic in the field of polymer science. A recent review [1] concerning crystallizations of polymers has been published. In our previous paper [2], the natures of crystallization of a series of copolyesters based on different ratios of polyethylene terephthalate (PET) to polyethylene isophthalate (PEI) have been qualitatively explored, the results showed that only the copolyesters containing polyethylene isophthalate below 15% are crystallizable [2]. In this study, the crystallizations of the crystallizable copolyesters were studied isothermally and non-isothermally, quantitatively to unveil the effect of PEI on the crystallization behaviors of the copolyesters.

2. Experimental

The molar ratios of PET to PEI of the copolyesters in this study are 100/0, 90/10 and 85/15. PET homopolymer is regarded as a special copolyester with 0% PEI. In the following sections, the copolyesters are denoted as the ratios of PET to PEI, e.g. 100/0 is used to refer to PET homopolymer, and so on.

DSC measurements were conducted on a Seiko differential scanning calorimeter (Model DSC-220CU). The specimens were weighted in the range 4 to 6 mg. During the measurement, dried N_2 gas was purged at a constant flow rate. For the cases of non-isothermal crystallization, the specimens were heated to 300°C at a rate of 20°C/min and held for 10 min to remove residual crystals, which may be seeds for the crystallization. The first cooling runs at rates of 1, 2, 5, 10, 20 and 30°C/min from 290°C to room temperature were recorded.

For isothermal crystallizations, the specimens were also heated to 290°C at a rate of 20°C/min and held for 10 min to remove the residual crystals, then they were quickly cooled to the proposed crystallization temperatures. Heat fusion versus time was recorded. The specimens isothermally crystallized at the crystallization temperatures were heated from room temperature to 290°C at a rate of 20°C/min to check out the melting temperature and heat fusions of the crystals thus formed.

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* Corresponding author. Tel: + 81-273-46-9414; fax: + 81-273-46-9687.

E-mail address: < bz_li@hotmail.com > (B. Li)

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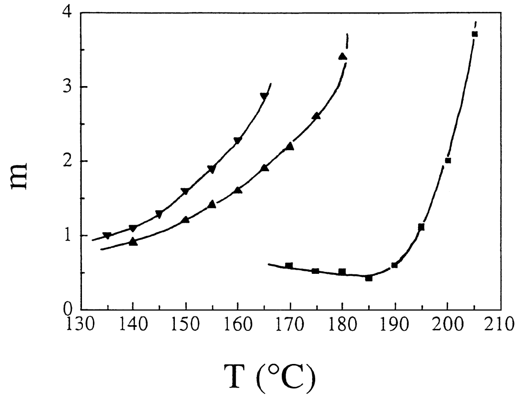

Fig. 1. Dependence of Ozawa exponents on the temperature of the copolyesters (■, ▲ and ▼ for the copolyesters 100/0, 90/10 and 85/15, respectively).

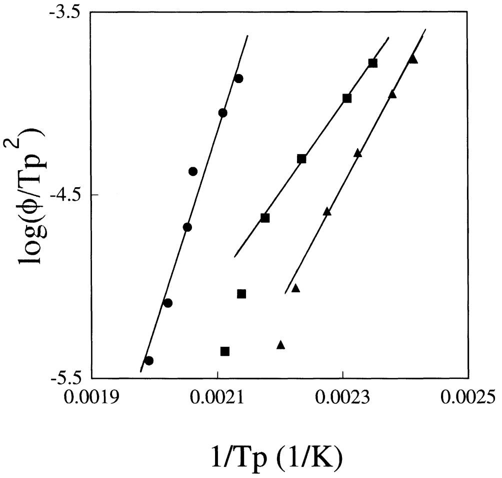

Fig. 3. Plot of $\log(\Phi/T_p^2)$ versus $1/T_p$ for the copolyesters.

3. Results and discussion

The relative crystallinity (X_t) is defined as follows:

$$X_t = \frac{\int_{\xi_0}^{\xi} \left(\frac{dH_c}{d\xi}\right) d\xi}{\int_{\xi_0}^{\xi_\infty} \left(\frac{dH_c}{d\xi}\right) d\xi} \tag{1}$$

where H_c is the heat fusion during crystallization. For non-isothermal crystallization, ξ_0 and ξ_∞ refer to the onset and end temperatures of crystallization, respectively. ξ_0 and ξ_∞ stand for the onset and end times of crystallization, in the case of isothermal crystallization.

According to the relationship between time (t) and temperature (T), as illustrated in Eq. (2), the dependence of relative crystallinity on time for the copolyester can be obtained. It is noted that the relative crystallinity increases with time but decreases with temperature:

$$t_x = \frac{T_i - T_x}{\Phi} \tag{2}$$

where T_i and T_x are the temperature at the initial time and a certain time x during the cooling run, respectively; Φ is the cooling rate.

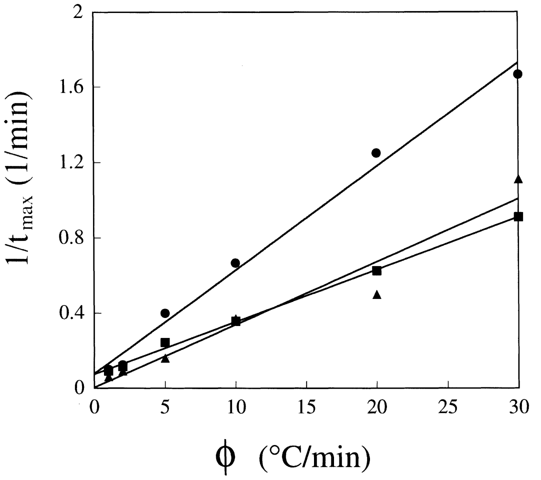

Fig. 2. The rate of non-isothermal crystallization changing with the cooling rate for the copolyesters (●, ■ and ▲ for the copolyesters 100/0, 90/10 and 85/15 in turn, as is the case for Figs. 3, 4, 6–8).

Non-isothermal crystallization of polymers [3,4] has been described by the Avrami equation:

$$1 - X_t = \exp(-kt^n) \tag{3}$$

where k is a constant, n is the Avrami exponent, depending on the modes of nucleation and crystal growth.

It is concluded that Avrami plots cannot depict the crystallization behaviors, in that non-linearity of Avrami plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ for non-isothermal crystallization of the copolyesters was shown. On the other hand, Ozawa plots [5] of the linear relationship between $\log[-\ln(1 - X_t)]$ and $\log \phi$ show their priority to explain the non-isothermal crystallizations of the above polymers. The Ozawa exponent (m) can be obtained from the slopes in the Ozawa plots. Ozawa exponents for the copolymers increase with temperature, as depicted in Fig. 1. The average values of Ozawa exponents of the copolyesters (about 1.5) indicate that the so-called predetermined nuclei already exist prior to non-isothermal crystallization according to Ozawa's explanation [5], as the synthesis of the

Table 1
Activation energies of crystallization for the copolyesters

Copolyester	E (kJ/mol)
100/0	90.6
90/10	40.2
85/15	49.6

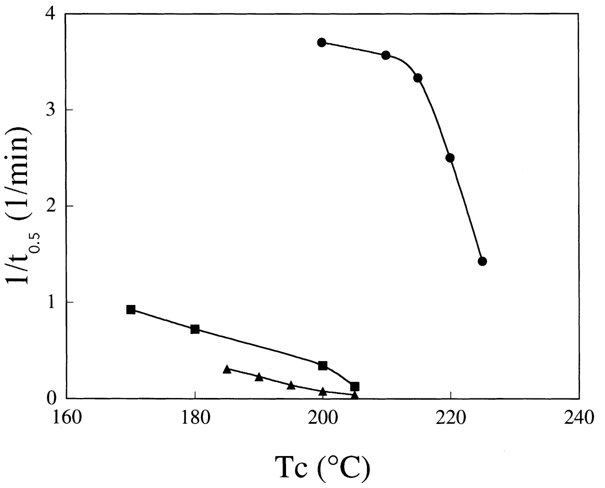

Fig. 4. The relationship between the crystallization rates and isothermal crystallization temperature for the copolyesters.

copolyesters was conducted under the catalysts $Zn(OAc)_2$ and $Sb(OAc)_2$, which cannot be removed from the polymeric systems, so that they played a role as heterogeneous nuclei for the crystallization. t_{max} is the time when the peak of crystallization appears. $1/t_{max}$ had been proposed [6] to characterize the rate of non-isothermal crystallizations. Fig. 2 illustrates the rates of non-isothermal crystallization changing with cooling rate for the copolyesters. It can be seen that the rate of crystallization increases with cooling rate, because of the higher degree of supercooling (the higher the cooling rate, the higher the degree of supercooling).

In order to investigate the effect of composition of PEI on crystallization behaviors, some physical aspects, such as the activation energy (E_c), the equilibrium melting temperature (T_m^0) and crystallization temperature (T_c^0) are concerned.

The activation energy of crystallization for the copolyesters can be obtained by the Kissinger equation [7]:

$$\log\left(\frac{\Phi}{T_p^2}\right) = \log C + \left(\frac{E_c}{RT_p}\right) \qquad (4)$$

where T_p (K) is the peak during the crystallization run, different from the crystallization temperature in isothermal crystallization; C is a constant coefficient; R is the gas constant.

Fig. 3 shows the plots of $\log(\Phi/T_p^2)$ versus $1/T_p$ for the copolyesters. At lower cooling rates, deviation happens. The data of the activation of crystallization for the copolyesters (listed in Table 1) show that the crystal of the copolyester 90/10 may easily be kinetically formed from the disorder amorphous region. The copolyester 90/10 shows a synergistic effect on non-isothermal crystallization.

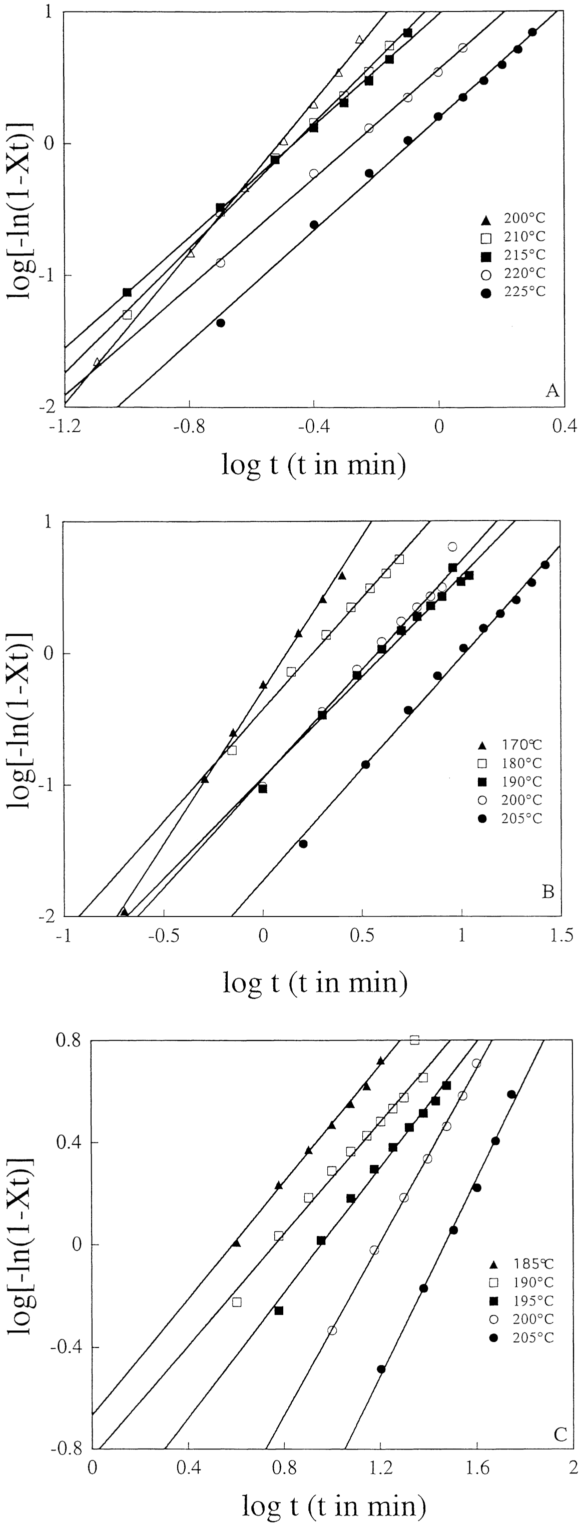

Fig. 5. Avrami plots for isothermal crystallizations of the copolyesters. (A, B and C refer to the copolyesters 100/0, 90/10 and 85/15, respectively).

Isothermal crystallizations of the copolyester were also included in this study. It is common that the relative crystallinity increases with time at different crystallization temperatures (T_c) for the copolyesters. The time ($t_{0.5}$), at which half crystallization happens, can be postulated. The isothermal crystallization rates of the copolyesters conducted are expressed by $1/t_{0.5}$. Fig. 4 represents the crystallization rates at the crystallization temperatures of the

Table 2
Avrami exponents at different crystallization temperatures and degrees of supercooling for isothermal crystallization of copolyesters

100/0			90/10			85/15		
T_c (°C)	ΔT (°C)[a]	n	T_c (°C)	ΔT (°C)[a]	n	T_c (°C)	ΔT (°C)[a]	n
200	76	2.9	170	93.2	2.7	185	70.7	1.8
210	66	2.4	180	83.2	1.9	190	65.7	1.7
215	61	2.1	190	73.2	1.9	195	60.7	1.9
220	56	2.1	200	63.2	1.9	200	55.7	1.9
225	51	2.2	205	58.2	1.7	205	50.7	1.8

[a] ΔT (°C): degree of supercooling.

copolyesters. The rates of the copolyesters 90/10 and 85/15 increase mildly, while that of the copolyester 100/0 increases rapidly and then slightly. This indicates that PET homopolymer is distinguished from the copolyesters containing PEI, in other words, the involvement of PEI does affect the crystallization behaviors of the copolyesters.

The Avrami equation [8,9] has been widely used to explain isothermal crystallizations of polymers. Avrami plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ of the copolyesters are shown in Fig. 5. Table 2 lists Avrami exponents at different crystallization temperatures for the copolyesters. If the crystals of the copolyesters, formed at the isothermal crystallization temperatures, are heated, the heat fusion (ΔH_m) increases with crystallization temperature, as shown in Fig. 6. The results imply that the crystals become perfect under higher crystallization temperatures.

To study isothermal crystallization, the equilibrium melting temperature (T_m^0) is of great interest. T_m^0 can be speculated from the modified Gibbs–Thomson equation [10]. A linear extrapolation in the plot of T_m versus T_c to $T_m = T_c$ leads to T_m^0 (see Fig. 7). With determination of T_m^0, the degree of supercooling ($\Delta T = T_m^0 - T_c$) can be obtained. Consequently, isothermal crystallizations of the copolyesters can be compared under the same ΔT. The comparison has been listed in Table 2. The Avrami exponent of PET homopolymer is higher than that of either of the copolyesters 90/10 and 85/15 at the same supercooling. It can imply that the percentage of multidimensional growth of the crystals is prevailingly higher than those of the copolyesters 90/10 and 85/15. It can be inferred that PEI prevents the copolyesters 90/10 and 85/15 from the growth of the crystals at multidimensions. Certainly, the crystals grow multidimensionally at lower degree of supercooling (higher crystallization temperature).

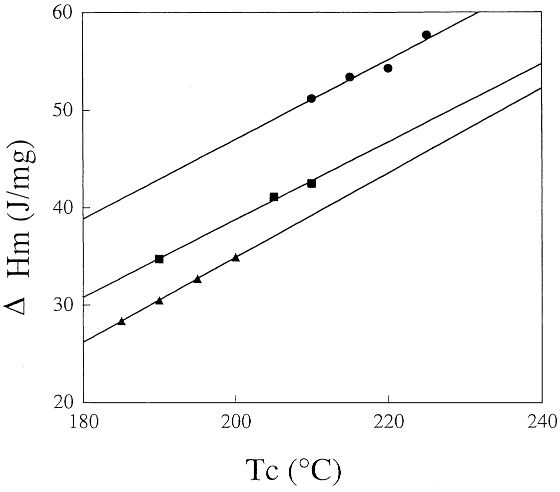

Fig. 6. The heat fusion changing with the isothermal crystallization temperatures for the copolyesters.

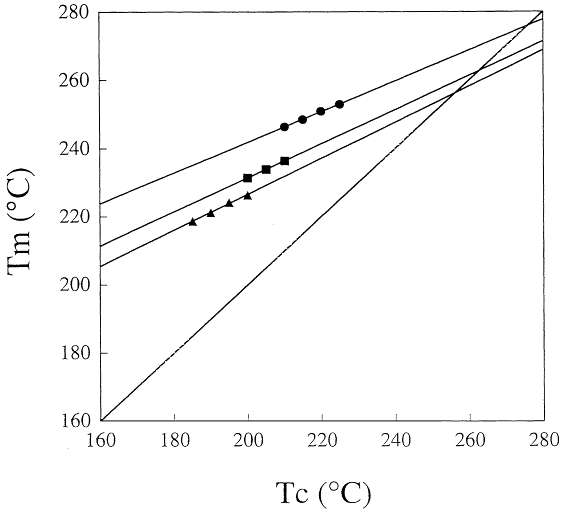

Fig. 7. The linear relation between T_m and T_c for the copolyesters.

As mentioned previously, during non-isothermal crystallization, the peak in the cooling run was called T_p. For comparison, T_c^0 is taken as the equilibrium crystallization temperature. Fig. 8 illustrates the profiles of T_p at different cooling rates for the copolyesters. T_c^0 can be postulated from Fig. 8, when the cooling rate is zero. Both T_m^0 and T_c^0

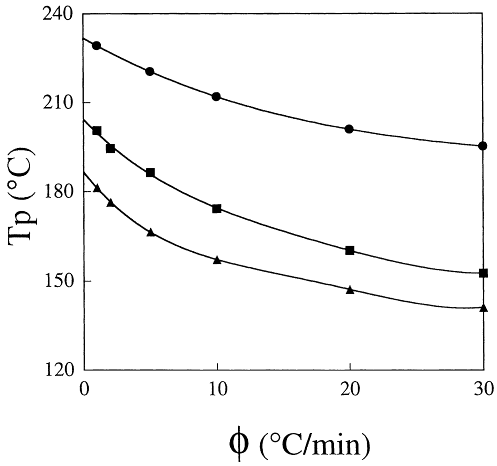

Fig. 8. Profiles of T_p at different cooling rates for the copolyesters.

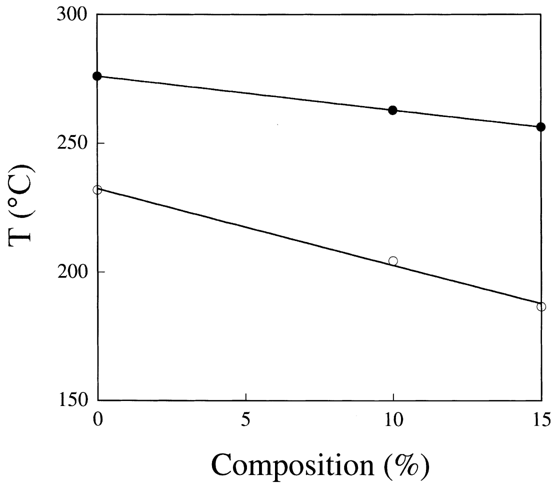

Fig. 9. Dependence of equilibrium crystallization temperature and melting temperature on the composition of PEI (● and ○ for T_c^0 and T_m^0, respectively).

decrease with increasing the composition of PEI, as referred to in Fig. 9, which indicates that the ideal crystals of the copolyesters become imperfect when the composition of PEI increases.

4. Conclusion

Non-isothermal crystallization of copolyesters cannot be predicted by the Avrami equation, but can be described by Ozawa plots. It is revealed that nuclei exist before non-isothermal crystallization. Isothermal crystallization behaviors indicate that the crystals grow at multidimensional scales. Poly(ethylene isophthalate) in the copolymers does hinder the crystallization of the copolyesters, as compared with the equilibrium melting and crystallization temperatures for the copolyesters.

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