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Effect of rod-like imide unit on crystallization of copoly(ethylene terephthalate-imide)

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Abstract

The effect of the imide unit on the isothermal and non-isothermal crystallization, kinetics crystallization of a new family of copoly(ethylene terephthalate-imides) (called copolyesterimides or PETIs) was investigated using differential scanning calorimetry. With a combined Avrami and Ozawa equation, one can describe the non-isothermal crystallization process of copolyesterimides, and the results show the same tendency as that in the isothermal crystallization process. These studies show that the processes of crystal nucleation and growth result in mainly three-dimensional growth with a thermal nucleation. In both isothermal and non-isothermal crystallization processes, the crystallization rate of PETIs, with imide content below 0.5%, is higher than that of neat PET, while PETI-3 (0.3 mol% imide) has the highest crystallization rate. This rate is significantly enhanced over PET homopolymer. It is proposed that imide units precipitate from the melt and act as nucleating agents during the crystallization process of these novel copolyesterimides. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Copolyesterimides; Poly(ethylene terephthalate-imide); Copolymers

1. Introduction

Poly(ethylene terephthalate) (PET), a typical semicrystalline polymer, is an important commercial polymer that is widely used for fibers, films, containers, and engineering plastics [1,2]. However, PET has a low crystallization rate in comparison to other semicrystalline polymers such as polypropylene, or polyethylene (PE). Thus the ultimate degrees of crystallinity for PET are generally lower. It has been reported [3–7] that, the maximum growth of PET crystals is 10 μm/min, a growth rate which is, indeed, very slow when compared, as an example, to that of PE (5000 μm/min). Crystallization kinetics of unmodified PET depended primarily on temperature, M_w, and catalyst residues [8,9]. The low thermal crystallization rate and the slow nucleus formation offer advantages in the manufacture of transparent, partly crystalline containers. However, this slow crystallization rate is a disadvantage for PET in injection-molding applications [7,10]. The crystallization rate can be increased by using high mold temperature (at least 130 °C) attained by oil or electrical heating and long mold cycle. These techniques present economic disadvantages [11,12] and often yield finished parts of low crystallinity that are difficult to remove from the mold or brittle products with a coarse spherulitic texture. A variety of inorganic or organic substances, known as nucleating agents, are commonly added at small concentrations (often <1 wt%) to produce (a) high degrees of crystallinity and (b) a fine spherulitic structure with concomitant improvements in mechanical properties and a faster overall rate of crystallization. Increased rates resulting from the higher nucleus density yield shorter cycles with corresponding economic advantages.

Although, improvement in the crystallization rate of PET has been desired in many applications, approaches of modification based on copolymerization have been difficult to achieve. It is generally considered that the crystallization of polymers is hindered by copolymerization of

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comonomers, because the incorporation of comonomer units of different size and shape into backbone leads to an irregular chain structure and thereby inhibits regular chain packing for crystallization [13,14]. However, incorporation of small amounts of comonomer units in the polymer, such as ionomer units and arylate units in PET copolymers, plays a different role for crystallization, and usually increases the crystallization rate [13,15,16].The mechanism of heterogeneous nucleation was proposed to explain the improvement, though this mechanism is not well understood up to now. It is believed that nucleation occurs more easily in the presence of foreign particles, which reduced the free energy barrier that needs to be overcome in order to form nuclei having required critical size [5].

In our previous papers [17,18], a new family of copolyesterimides, PETIs, were synthesized, which contained rod-like rigid imide units based on *N*,*N*′-diphenylbiphenyl-3,3′,4,4′-tetracarboxydiimide (BMBI) in the main chain of PET segments. The results of thermal and mechanical property analyses showed that these new copolyesterimides have much higher glass transition temperatures (T_g) and tensile strengths than that of unmodified neat PET. The crystallization kinetic studies showed that the incorporation of imide-unit into PET changed the crystallization rate significantly, and the crystallization rate became slower when the content of imide unit in the copolyesterimides increased [19]. However, the crystallization rates were observed to be faster than that of neat PET when the content of imide unit was below 1 mol%. The crystallization rate of copolyesterimides containing 0.2 mol% imide unit was much faster than that of any other copolyesterimides and neat PET. According to these results, a small amount (≤0.5 mol%) of imide unit in PET can significantly increase the crystallization rate.

These observations in our initial study of the crystallization characteristics of these new PETIs led to the work described in this report, which focuses on a finer range of copolymer compositions at low levels of imide group incorporation. Thus, a series of PETIs based on the BMBI imide group with imide contents of ≤0.5 mol% were prepared and their crystallization characteristics studied.

2. Experimental

2.1. Materials

3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA) was purchased from TCI, Inc. (Japan) and purified by vacuum sublimation. Methyl *p*-aminobenzoate (MAB) was commercially available and recrystallized from benzene. Dimethyl terephthalate (DMT) was used after vacuum dried at 60 °C for 12 h. Ethylene glycol was dried by anhydrous $MgSO_4$ and then by vacuum distillation. Dimethylformamide (DMF) was also dried by anhydrous $MgSO_4$ and then vacuum distilled over P_2O_5 under nitrogen atmosphere. Pyridine was distilled over KOH under nitrogen atmosphere, while other reagents were used as received.

Copolyesterimides (PETIs) of various small contents (0–0.5 mol%) of imide unit were synthesized using the method described in our previous paper [17]. PETIs were first dissolved in the mixture of 1,1,2,2-tetrachloroethane and phenol (50/50 v/v), and then precipitated by adding the solution into excess of methanol. The precipitate was then extracted by methanol for 24 h to remove the solvent. After vacuum dried at 80 °C for 12 h, the dried copolyesterimides were used for DSC analysis.

2.2. Characterization and procedures

Infrared spectra were recorded on a Bruker vector series Fourier-transform infrared (FT-IR) spectrometer with KBr pellets. ^{1}H NMR spectra were recorded in CF_3COOD or a mixture solvent $CDCl_3/CF_3COOD$ (3:1 by volume) using a Bruker ARX400 NMR spectrometer. Inherent viscosity (η_{inh}) was measured with an automated Ubbelhode viscometer kept at 25.0 °C. The measurements were performed at a concentration of about 0.5 g dl^{-1} in a mixture of phenol/1,1,2,2-tetrachloroethane (50/50 v/v).

A Perkin–Elmer DSC-7 instrument with cold trap was used for thermal analysis. The instrument was calibrated by indium before the measurements. All measurements were conducted under a high-purity nitrogen atmosphere to minimize the possibility of moisture gain and consequent hydrolytic degradation. The weight of samples were about 5 mg for all copolyesterimides.

For isothermal crystallization kinetic studies [12], the samples sealed in aluminium pan were heated from 20 to 280 °C/min; held at the final temperature for 5 min to eliminate the thermal history or mechanical history, quenched rapidly at 300 °C/min to the desired temperature. The exothermic curves as a function of time were recorded.

For non-isothermal crystallization kinetic studies [12], the samples were measured with procedure similar to that for the isothermal crystallization kinetic study. After annealing at 300 °C, the samples were cooled at different cooling rate to 100 °C. These cooling curves were recorded and used for non-isothermal crystallization kinetics analysis. The cooling rates in this study were 40, 20, 10, 5, or 2.5 °C/min.

3. Results and discussion

3.1. Synthesis of copolyesterimides and thermal properties

Copolyesterimides (PETIs) were prepared according to the procedure described in our previous paper [17], where the chemical structures of PETIs were confirmed by ^{1}H NMR and FT-IR techniques [17]. The results of measured composition, inherent viscosity, and thermal properties of

Table 1
Physical properties of copolyesterimides and PET

Sample	Imide content		$[\eta]^a$ (dl/g)	$T_g{}^b$ (°C)	$T_{cc}{}^c$ (°C)	ΔH_{cc} (J/g)	$T_m{}^d$ (°C)	ΔH_m (J/g)	$T_c{}^e$ (°C)	ΔH_c (J/g)	ΔT^f (°C)
	Feed (%)	Calc (%)									
PET	0	0	0.71	77.2	149.7	22.0	255.0	32.1	183.8	32.5	71.2
PETI-1	0.1	0.11	0.85	76.0	142.8	19.9	254.1	34.3	187.5	34.7	66.6
PETI-2	0.2	0.21	0.90	80.2	132.1	2.92	255.5	28.4	199.2	34.0	56.3
PETI-3	0.3	0.28	0.82	76.9	143.9	26.0	254.9	36.0	202.9	33.6	52.0
PETI-4	0.4	0.40	0.86	75.6	146.4	24.5	254.1	38.0	185.1	36.5	69.0
PETI-5	0.5	0.47	0.80	80.7	150.5	21.0	253.8	28.0	178.0	30.4	75.8

Imide content is calculated by BMBI/(BMBI + DMT) (mol/mol). DSC data was recorded from second cycle of DSC scan at a scan rate of 20 °C/min.

[a] Measurement using TCE/phenol (50/50 v/v) as solvent at 25 °C with concentration of 0.5 g/dl.

[b] T_g detected from the second heating scan at a heating rate of 20 °C/min.

[c] Cold crystallization temperature detected from the second heating scan at a heating rate of 20 °C/min.

[d] Melting temperature detected from the second heating scan at a heating rate of 20 °C/min.

[e] Crystallization temperature detected from the second cooling scan at a cooling rate of 20 °C/min.

[f] Temperature difference between melting temperature and crystallization temperature ($\Delta T = T_m - T_c$).

the synthesized copolyesterimides are listed in Table 1. Table 1 shows that the imide content in the copolyesterimides (PETIs) is close to the feed ratio, and their inherent viscosity was high with the values of 0.8–0.9 dl/g. The glass transition temperature T_g and melting temperature T_m of all PETIs were about the same as that of neat PET. However, the T_c and T_{cc} changed significantly with the imide content in the copolymers. T_{cc} decreased first and then increased, while T_c increased first and then decreased as the imide content in PETIs increased. The change of T_c and T_{cc} indicated that the crystallization rate increased first and then decreased as the imide content increased. It was found that PETI-3 with imide content of 0.3 mol% had the highest crystallization rate. It should be pointed out that the PETIs with imide content below 0.5% had the lower T_{cc} and higher T_c than those for the neat PET. This means that the crystallization rate of these copolyesterimides were higher than that of PET. Furthermore, from the data of ΔH_m and

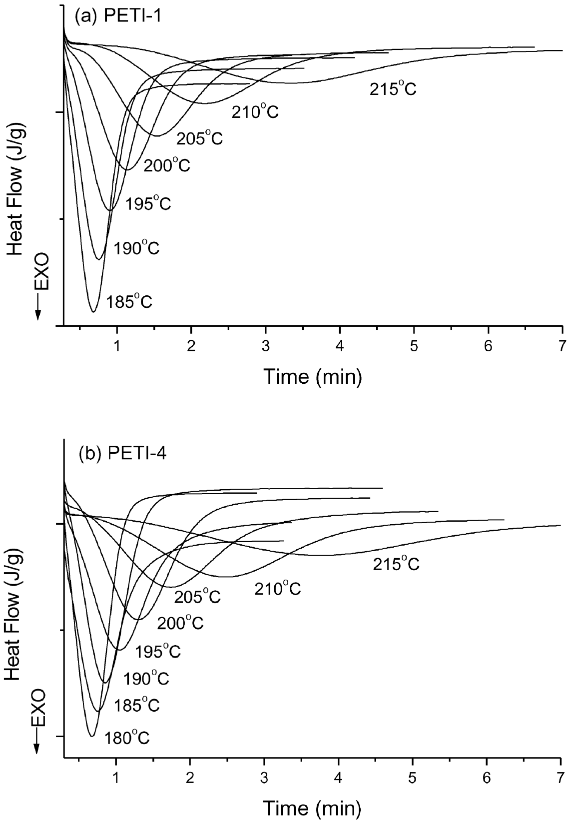


Fig. 1. Typical DSC curves of isothermal crystallization at different temperatures for: (a) PETI-1, (b) PETI-4.

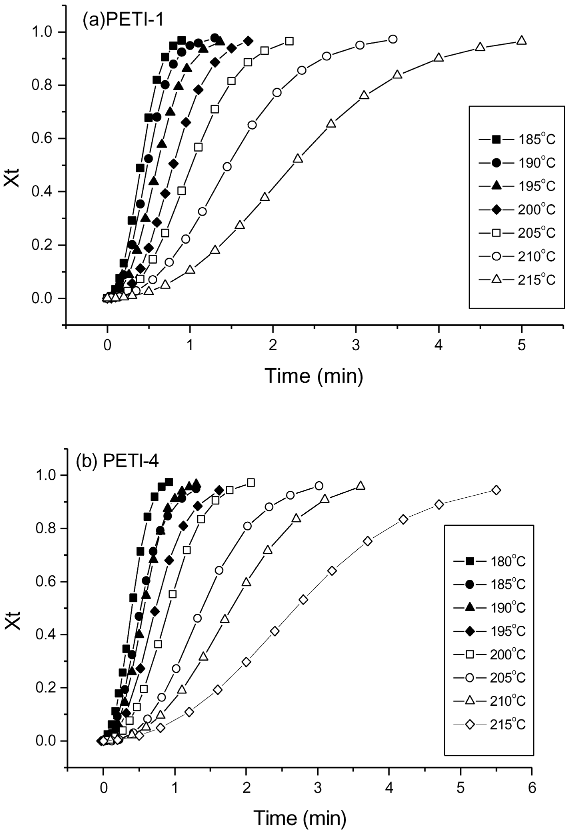


Fig. 2. Relative degree of crystallinity $X(t)$ as a function of time.

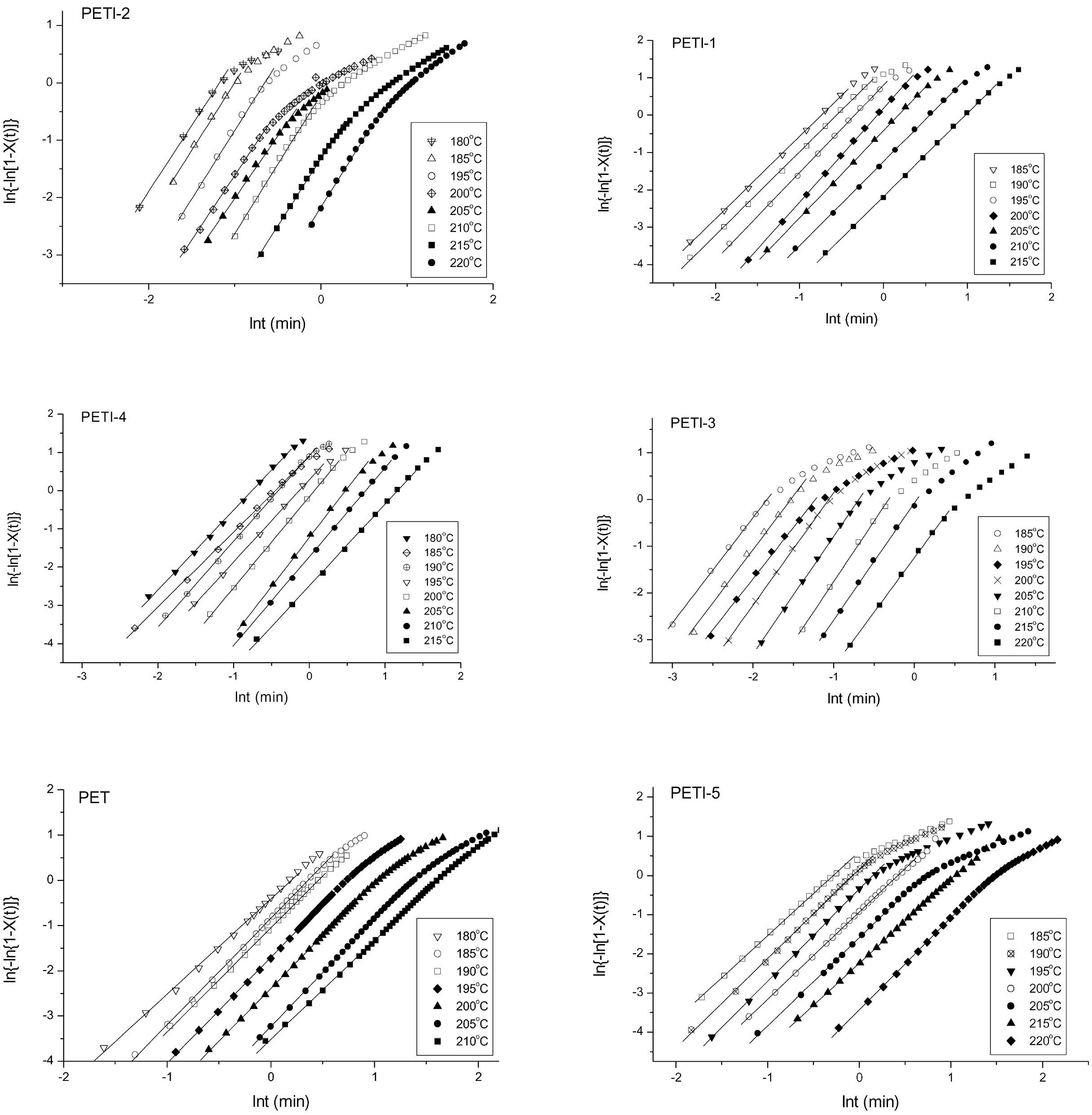
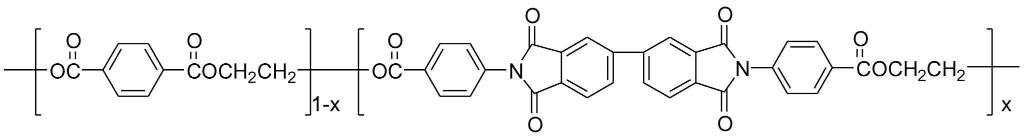


Fig. 3. Plots of $\ln\{-\ln[1-X(t)]\}$ against $\ln t$ for the isothermal crystallization of PETIs and PET.

ΔH_c, it can be found that the crystallinity of these copolyesterimides was also higher than that of PET. The structure of the synthesized copolyesterimides is shown as following:



PETI

3.2. Isothermal crystallization kinetics

Isothermal crystallization from melt was carried out for all copolyesterimides and neat PET at various

Table 2
Isothermal crystallization parameters for PETIs and PET

Code	T_c (°C)	n	k (min^{-n})	$t_{1/2}$ (min)	$\tau_{1/2}$ (min^{-1})
PET	180	2.18	0.63	1.05	0.96
	185	2.35	0.43	1.23	0.82
	190	2.32	0.33	1.37	0.73
	195	2.34	0.18	1.77	0.56
	200	2.47	0.08	2.42	0.41
	205	2.39	0.04	3.33	0.30
	210	2.24	0.03	4.27	0.23
PETI-1	185	2.18	4.94	0.41	2.46
	190	2.27	3.58	0.49	2.06
	195	2.33	2.20	0.61	1.64
	200	2.54	1.23	0.80	1.25
	205	2.33	0.65	1.03	0.97
	210	2.25	0.29	1.48	0.67
	215	2.22	0.11	2.26	0.44
PETI-2	180	2.30	9.28	0.32	3.08
	185	2.48	12.72	0.31	3.23
	195	2.58	6.12	0.43	2.33
	200	2.34	1.30	0.76	1.31
	205	2.34	1.39	0.74	1.35
	210	2.46	0.84	0.93	1.08
	215	2.31	0.27	1.51	0.66
	220	2.37	0.11	2.13	0.47
PETI-3	185	2.31	72.24	0.13	7.44
	190	2.43	45.60	0.18	5.58
	195	2.46	25.41	0.23	4.32
	200	2.47	14.15	0.29	3.39
	205	2.59	6.30	0.43	2.34
	210	2.58	2.34	0.62	1.60
	215	2.47	0.92	0.89	1.12
	220	2.38	0.29	1.44	0.70
PETI-4	180	2.11	4.83	0.40	2.51
	185	2.06	2.63	0.52	1.91
	190	2.27	2.50	0.57	1.76
	195	2.15	1.33	0.74	1.35
	200	2.36	1.19	0.80	1.26
	205	2.61	0.30	1.38	0.72
	210	2.36	0.17	1.80	0.56
	215	2.17	0.08	2.72	0.37
PETI-5	185	2.20	1.95	0.62	1.60
	190	2.34	1.20	0.79	1.27
	195	2.35	0.70	0.99	1.01
	200	2.22	0.40	1.29	0.78
	205	2.26	0.20	1.72	0.58
	210	2.13	0.11	2.40	0.42
	215	2.26	0.04	3.58	0.28
	220	2.15	0.02	5.46	0.18

Table 3
Isothermal crystallization parameters of PETIs and PET

T (°C)	Code	PET	PETI-1	PETI-2	PETI-3	PETI-4	PETI-5
185	$\tau_{1/2}$ (min^{-1})	0.82	2.46	3.23	7.44	1.91	1.6
	k (min^{-n})	0.43	4.94	12.72	72.24	2.63	1.95
200	$\tau_{1/2}$ (min^{-1})	0.41	1.25	1.31	3.39	1.26	0.78
	k (min^{-n})	0.08	1.23	1.30	14.15	1.19	0.40

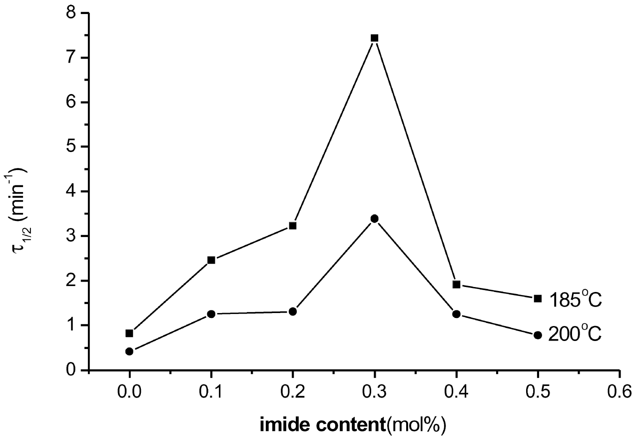


Fig. 4. Plots of $\tau_{1/2}$ versus composition of PETIs and PET at temperature of 185 and 200 °C.

crystallization temperatures. Fig. 1 shows typical DSC curves at the given crystallization temperature. The relative degree of crystallinity, $X(t)$, accumulated at time t can be calculated from the crystallization exotherms recorded by DSC.

The typical plots on the time dependence of the relative degree of crystallinity are shown in Fig. 2. The results can then be used to extract the kinetic information via the well-known Avrami equation [20,21], as follows

$$X(t) = 1 - \exp[-kt^n] \tag{1}$$

or

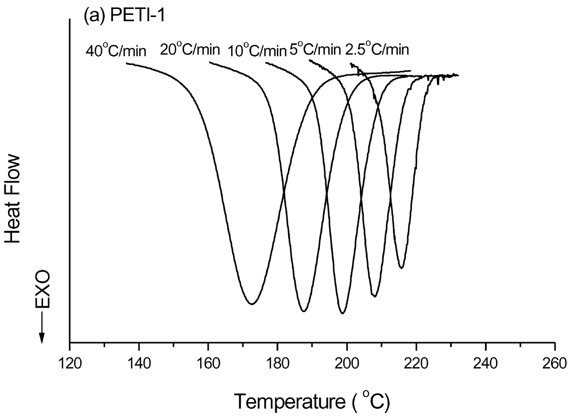
$$\ln\{-\ln[1 - X(t)]\} = n \ln t + \ln k \tag{2}$$

where k is the growth rate constant, and the exponent n in the Eq. (1) represents the nucleation mechanism and the growth dimension. Generally, the value of n varies between 1 and 4, corresponding to growth forms from rod ($n = 1$ or 2) to spherulites ($n = 3$ or 4).

The plots of Avrami analyses are shown in Fig. 3 for all copolyesterimides and neat PET. Each curve in Fig. 3 shows an initial linear portion, and then subsequently levels off. Many crystalline polymers exhibit such a deviation from linearity at the later stage of crystallization, and this deviation has been attributed to secondary crystallization [5,8,22].

Table 2 lists the values of n and k, which were determined from the initial linear portion of straight lines. The Avrami exponent n was about the same regardless of the crystallization temperature T_c and composition, because the Avrami exponent is generally a weak function of temperature [8]. The Avrami exponent near 2.5 is a typical value for PET, which meant that the crystallization mode was three-dimensional with athermal nucleation [3].

The crystallization half-time $t_{1/2}$ is defined as the time at which the extent of crystallization is 50% completed, which can be determined from the measured kinetic parameters



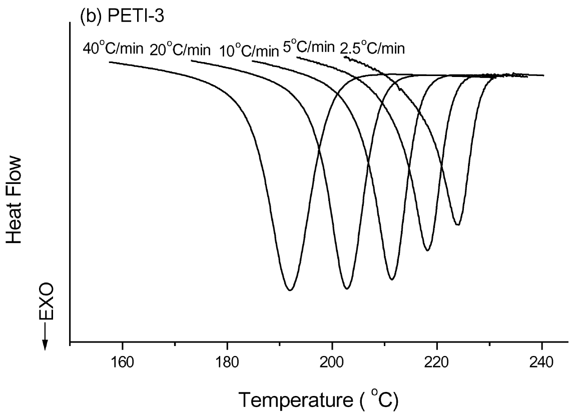


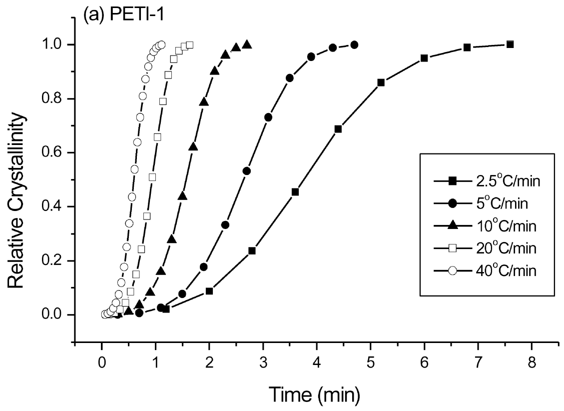
Fig. 5. Typical DSC curves of PETIs at various cooling rate for: (a) PETI-1 (b) PETI-3.

[5,8]. That is,

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \tag{3}$$

Usually the rate of crystallization $\tau_{1/2}$ is described as the reciprocal of $t_{1/2}$; and $\tau_{1/2} = 1/t_{1/2}$. The values of $\tau_{1/2}$ and $t_{1/2}$ are also listed in Table 2.

Table 3 lists the isothermal crystallization rate constant k and crystallization rate $\tau_{1/2}$, which increased with a decrease in the crystallization temperature T_c. Fig. 4 shows that at a certain crystallization temperature T_c, such as 185 and 200 °C, k and $\tau_{1/2}$ first increase and then decrease as the imide content in PETIs increases. This means that the imide unit in PETIs acts as a nucleate agent during the isothermal crystallization process [23], which is further discussed in Section 3.3. The crystallization rate of PETIs is higher than that of PET when the imide content is less than 0.5%, with PETI-3 exhibiting the highest crystallization rate. The k and $\tau_{1/2}$ of PETI-3 at 185 °C are, respectively, 168 and 9.1 times than that of neat PET. At 200 °C, these values became 176 and 8.3 times than that of the neat PET.



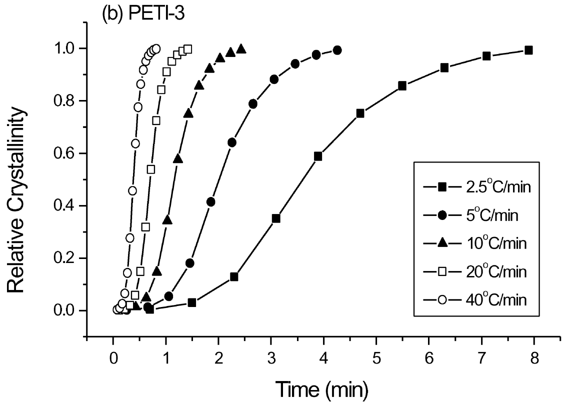


Fig. 6. Relative degree of crystallinity as a function of time for PETI-1 and PETI-3.

3.3. Nucleation mechanism

According to the classical theory of polymer crystallization, the overall crystallization rate, as measured by $\tau_{1/2}$, was determined by both rates of nucleation and linear growth [5,16,22]. Linear growth rate is an inherent character of the polymer and usually depends only on the crystallization temperature. Hence the growth rate is not influenced by the nucleating agents. $\tau_{1/2}$ can therefore be used to compare the nucleating ability of different amount of nucleating agents.

On the other hand, nucleation in polymers may be homogeneous or heterogeneous [5,8,16]. Homogeneous nucleation occurs sporadically in the melting by thermal fluctuation, while the latter starts on the surface of microscopic insoluble particles dispersed randomly in the melting. Such particles can be impurities or arbitrarily added nucleating agents. In the high crystallization region, the overall crystallization rate is controlled by the nucleating rate, so the nucleating agents play the most important role for polymer crystallization at low supercooling.

As discussed in Ref. [18], the imide-containing monomer did not dissolve in the melt very well, when the polymerization temperature was below 270 °C. On the other hand, the morphology showed that imide units separated from the copolyesterimide matrix when the

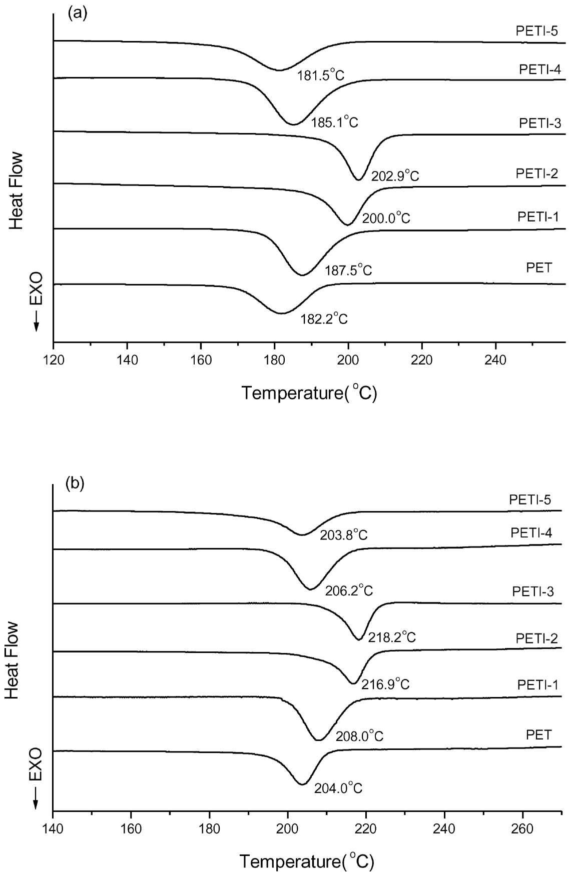


Fig. 7. DSC curves of PETIs and PET at a cooling rate of (a) 20 °C/min, (b) 5 °C/min.

content of imide units in the copolymers was above 7 mol%. So, for the crystallization of PETIs, the increased crystallization rate may be attributed to imide units precipitating from the melt and acting as nucleating agents.

3.4. Non-isothermal crystallization kinetic analysis

3.4.1. Avrami equation analysis in non-isothermal crystallization kinetics

The isothermal crystallization kinetics for copolyesterimides has been discussed above. However, from the practical viewpoint, non-isothermal processes have much more industrial significance because most polymers are processed under non-isothermal condition. The non-isothermal crystallization kinetics are summarized in Figs. 5–7. The typical DSC curves of PETIs at various cooling rates are shown in Fig. 5. The graphs of the relative degree of crystallinity as a function of time were shown in Fig. 6. Fig. 7 shows two series of DSC curves at the cooling rate of 20 and 5 °C/min, respectively. Practically, one can analyze the crystallization rate qualitatively just from the change of crystallization temperature T_c and the degree of supercooling ΔT, when polymers were crystallized from melt at the same cooling rate. It can be seen that the crystallization temperature T_c of PETIs from the melt increases first and then decreases with imide content, and the degree of supercooling ΔT decreases and then increases as the imide content increases. These phenomena indicate that the crystallization rate increases first and then decreases with the increasing imide content. Apparently, PETI-3 has the highest crystallization rate.

Table 4
Non-isothermal crystallization parameter of PETIs and PET

Sample	R (°C/min)	n	Z_t (min^{-n})	$\tau_{1/2}$ (min^{-1})
PET	2.5	3.18	0.01	0.22
	5	3.86	0.02	0.39
	10	3.55	0.18	0.68
	20	3.13	1.21	1.20
	40	2.84	4.11	1.87
PETI-1	2.5	3.12	0.01	0.27
	5	3.36	0.03	0.38
	10	3.16	0.17	0.65
	20	3.43	0.95	1.09
	40	3.16	3.67	1.70
PETI-2	2.5	2.92	0.01	0.22
	5	3.32	0.02	0.36
	10	3.28	0.24	0.73
	20	3.52	1.46	1.24
	40	2.85	4.07	1.86
PETI-3	2.5	3.04	0.01	0.25
	5	3.13	0.06	0.46
	10	3.44	0.31	0.79
	20	3.73	1.96	1.32
	40	3.50	15.50	2.43
PETI-4	2.5	3.11	0.01	0.21
	5	3.39	0.02	0.34
	10	3.38	0.11	0.58
	20	3.42	0.49	0.90
	40	3.02	2.64	1.56
PETI-5	2.5	2.89	0.00	0.18
	5	2.73	0.03	0.33
	10	2.84	0.15	0.58
	20	2.97	0.50	0.90
	40	2.77	1.72	1.39

Mandelkern [24] has considered that the primary stage of non-isothermal crystallization can be described by the Avrami equation, based on the assumption that the crystallization temperature is constant. The following expression results [24,25]

$$X(t) = 1 - \exp(-Z_t t^n) \tag{4}$$

or

$$\ln\{-\ln[1 - X(t)]\} = n \ln t + \ln Z_t \tag{5}$$

where $X(t)$ is the relative degree of crystallinity, Z_t is the rate constant, and n is Avrami exponent in the non-isothermal crystallization process.

By plotting $\ln\{-\ln[1 - X(t)]\}$ versus $\ln t$ by using Eq. (5), we can determine the values of Avrami exponent n and

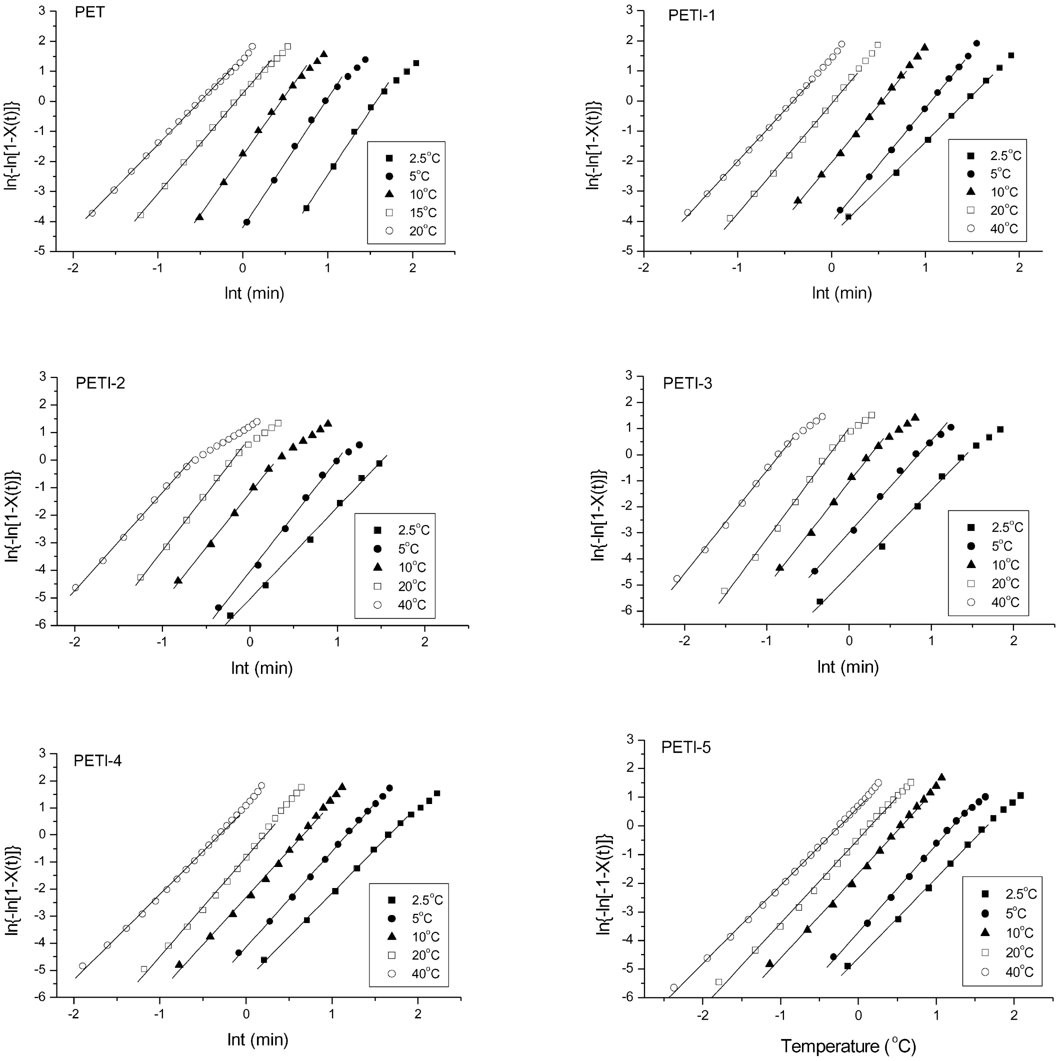


Fig. 8. Plots of $\ln\{-\ln[1-X(t)]\}$ versus $\ln t$ for the non-isothermal crystallization of PETIs and PET.

the rate constant Z_t from the slopes and the intercepts. Fig. 8 shows the Avrami plotting results for the neat PET and five different copolyesterimides (PETI-1–PETI-5). The estimated values of n, Z_t, and $\tau_{1/2}$ are shown in Table 4. The Avrami exponent n was around 3, indicating that the mode of the nucleation and the growth in the primary stage of the non-isothermal crystallization of copolyesterimides were three-dimensional with athermal nucleation [3], which is the same as that in the isothermal crystallization process.

The values of Z_t and $\tau_{1/2}$ of PETIs show the same trend of variation as those for the isotherm crystallization process. The non-isothermal crystallization rate decreases as the content of imide units in copolyesterimides increases. However, the degree of variation was smaller than that in the isothermal crystallization process. This may be attributed to limitation of the Avrami equation in describing the non-isothermal crystallization process of polymers [8,26].

3.4.2. Ozawa analysis of non-isothermal crystallization kinetics

By taking into account the effect of cooling rate R, Ozawa modified the Avrami equation (Eq. (5)) in order to monitor the process of non-isothermal crystallization [27]. The modified Avrami equation is given by

$$1 - C(T) = \exp[-K(T)/R^m] \tag{6}$$

which can be rewritten as

$$\ln\{-\ln[1 - C(T)]\} = -m \ln R + \ln K(T) \tag{7}$$

where $C(T)$ is the fraction of transformed material at temperature T, R is the cooling rate. m is Ozawa exponent, which can be related to, but different from, the Avrami exponent. $K(T)$ was the cooling crystallization function, a kinetic parameter that took into account the geometry and change in nucleation and growth rate.

By drawing plots of $\ln\{-\ln[1-C(T)]\}$ versus $\ln R$ according to Eq. (6), a straight line should yield with a slope

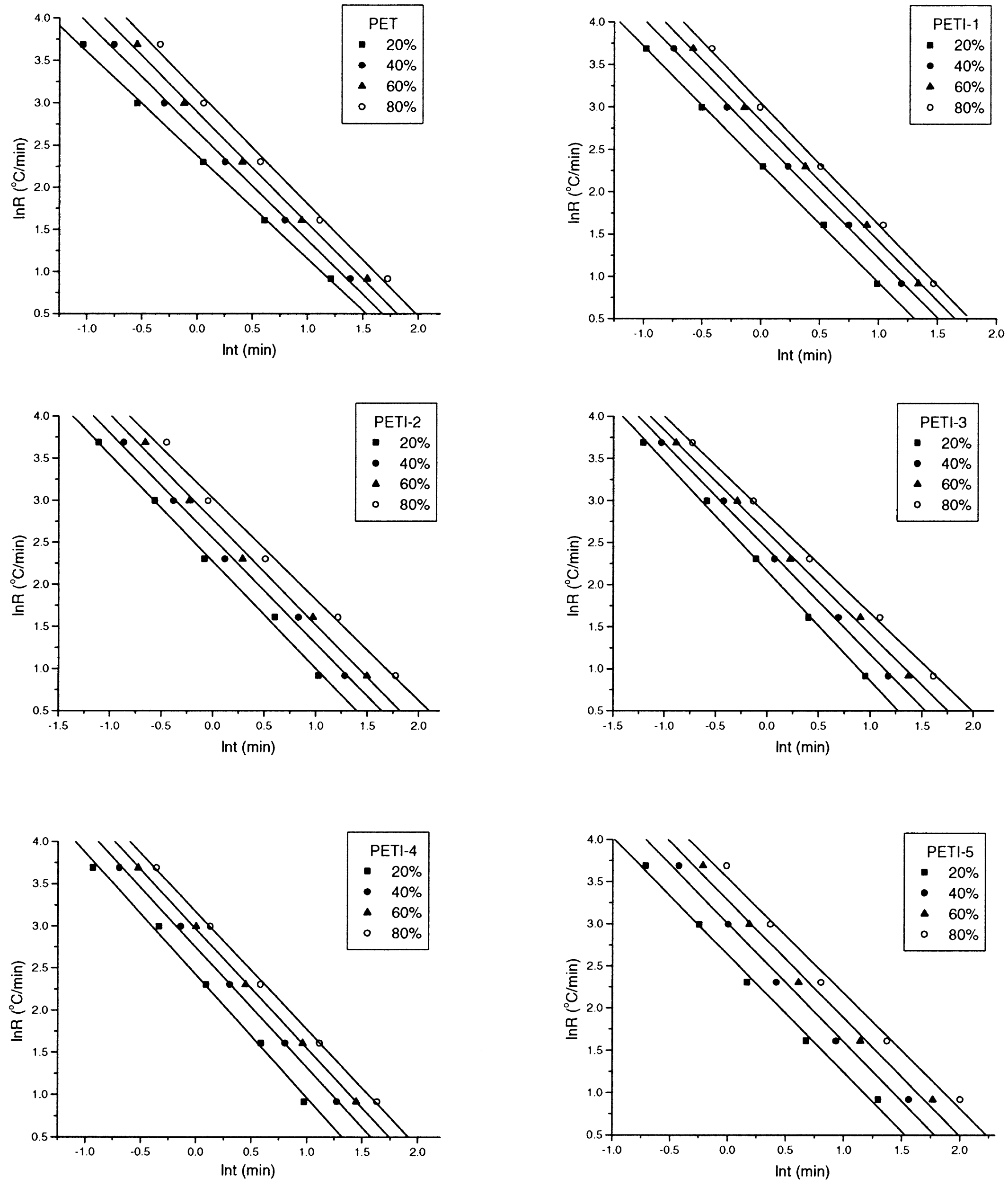


Fig. 9. Plots of ln R versus ln t for PETI at various $X(t)$.

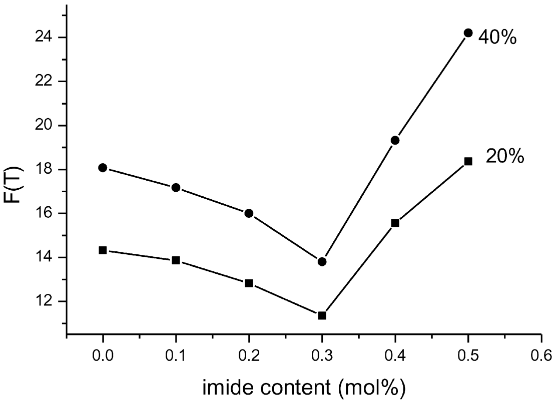


Fig. 10. $F(T)$ as a function of imide content for PETIs and PET.

$-m$ and intercept $\ln K(T)$ for a given temperature. However, no straight lines were obtained in this work by the Ozawa analysis. The experimental results indicated that Eq. (7) was also unable to describe the kinetics of the non-isothermal crystallization of PETIs. This may be attributed to appreciable secondary crystallization existing in the non-isothermal crystallization process of copolyesterimides [8, 26].

3.5. Combined equation of Avrami equation and Ozawa equation

For a better description of non-isothermal crystallization

Table 5
Values of $F(T)$ and a at a certain degree of crystallinity estimated from Eq. (4) for PETIs and PET

Sample	$X(t)$ (%)	a	$F(T)$
PET	20	1.23	10.81
	40	1.28	14.32
	60	1.32	18.07
	80	1.33	23.12
PETI-1	20	1.39	10.20
	40	1.41	13.86
	60	1.42	17.17
	80	1.44	21.13
PETI-2	20	1.27	9.72
	40	1.25	12.82
	60	1.25	15.99
	80	1.20	20.65
PETI-3	20	1.30	8.70
	40	1.25	11.35
	60	1.21	13.80
	80	1.17	17.02
PETI-4	20	1.45	11.22
	40	1.42	15.56
	60	1.41	19.32
	80	1.39	23.71
PETI-5	20	1.41	12.76
	40	1.42	18.36
	60	1.42	24.21
	80	1.39	30.90

process, many models were developed for predicting the time and the amount of solidified polymer or the degree of crystallinity. Liu et al. [26,28] have found a new method for the analysis of non-isothermal crystallization process, which proved to be suitable for the description of a non-isothermal process. By relating Eqs. (5)–(7), the following has been proposed [26,28]:

$$\ln Z_t + n \ln t = \ln K(T) - m \ln R \tag{8}$$

$$\ln R = \frac{1}{m}\ln[K(T)/Z_t] - \frac{n}{m}\ln t \tag{9}$$

Let $F(T) = [K(T)/Z_t]^{1/m}$, and $a = n/m$; the parameter $F(T)$, the cooling rate, which is chosen as a certain degree of crystallization, is achieved in a unit crystallization time. A lower $F(T)$ means a higher crystallization rate. By means of above assumptions,

$$\ln R = \ln F(T) - a \ln t \tag{10}$$

Thus, plotting $\ln R$ against $\ln t$ should yield a straight line of slope, $-a$, and intercept, $\ln F(T)$ for a certain degree of crystallinity. Plots of $\ln R$ versus $\ln t$ according to Eq. (10) for the neat PET and different copolyesterimides (PETI-1–PETI-5) are shown in Fig. 9. By using straight line linear fitting with these data points, slope $-a$ and intercept $\ln F(T)$ were obtained. The values of a and $F(T)$ are listed in Table 5.

Plots of $F(T)$ versus imide content for two $X(t)$ values are shown in Fig. 10. It is obvious that the value of $F(T)$ for PETIs decreases first and then increases with an increase in the imide content, that indicates, the crystallization rate increases first and then decreases as the imide content in the copolyesterimides increases, and the crystallization rate of those PETIs with imide content below 0.5% were higher than that of PET. Among all copolyesterimides and PET, the value of $F(T)$ for PETI-3 (0.3% imide) is the lowest, indicating that PETI-3 has the highest crystallization rate among all PETIs samples.

4. Conclusions

Copolyesterimides with low imide contents ranging from 0.1 to 0.5 mol% were synthesized, and their isothermal and non-isothermal crystallization kinetics were studied by DSC. The Avrami exponent n was found to be around 2.5 for the isothermal crystallization process of copolyesterimides. The processes of crystal nucleation and growth were mainly three-dimensional with athermal nucleation.

In the non-isothermal crystallization process, the Avrami exponent, $n \approx 3$, indicated that the mode of spherulitic nucleation and growth was about the same as that in the isothermal crystallization process of copolyesterimides. The Ozawa equation failed to describe the non-isothermal crystallization process. But with a combined Avrami and Ozawa equation, one can describe the non-isothermal crystallization process, and the result was about the same as that in the isothermal crystallization process. The nucleating mechanism may arise from imide units precipitated from melt and acting as nucleating agent during the crystallization process of the copolyesterimides. The results show that PETI-3 with 0.3% imide has the highest crystallization rate and is much higher than neat PET. In the isothermal crystallization process of copolyesterimides, the crystallization rate constant k and overall crystallization rate $\tau_{1/2}$ for PETI-3 at 185 °C are, respectively, 168 and 9.1 times that of PET; and 176 and 8.3 times at 200 °C.

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