

Nonisothermal Crystallization Behavior of Poly (butylene terephthalate)–Poly (ethylene terephthalate-co-isophthalate-co-sebacate) Segmented Copolyesters

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ABSTRACT: In this paper, two different analytical methods were applied to investigate nonisothermal crystallization behavior of copolyesters prepared by melting transesterification processing from bulk polyesters involving poly (butylene terephthalate) (PBT) and ternary amorphous random copolyester poly(ethylene terephthalate-co-isophthalate-co-sebacate) (PETIS). The results show that the half-time of crystallization of copolyesters depended on the reaction time and decreased with the content of ternary polyesters in the amorphous segment. The modified Avrami model describes the nonisothermal crystallization kinetics very well.

The values of the Avrami exponent range from 2.2503 to 3.7632, and the crystallization kinetics constant ranges from 0.0690 to 0.9358, presenting a mechanism of three-dimensional spherulitic growth with heterogeneous nucleation. Ozawa analysis, however, failed to describe the nonisothermal crystallization behavior of copolyesters, especially at higher cooling rate. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1232–1238, 2003

Key words: crystallization; polyesters; kinetics (polym.)

INTRODUCTION

The most available semicrystalline thermoplastic polyesters, namely, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), are very important because they have been widely used as film and fiber. The use of their copolyesters has drawn much attention because of their low price and versatile properties for application. Most of them are binary or ternary random copolymers, and have been studied extensively by many researchers.^{1–3} In practice, synthesis of segmented copolyesters with crystallizing segments is an effective way to obtain new polyester material because regulation of the crystal structure offers an additional possibility of optimizing their properties.⁴

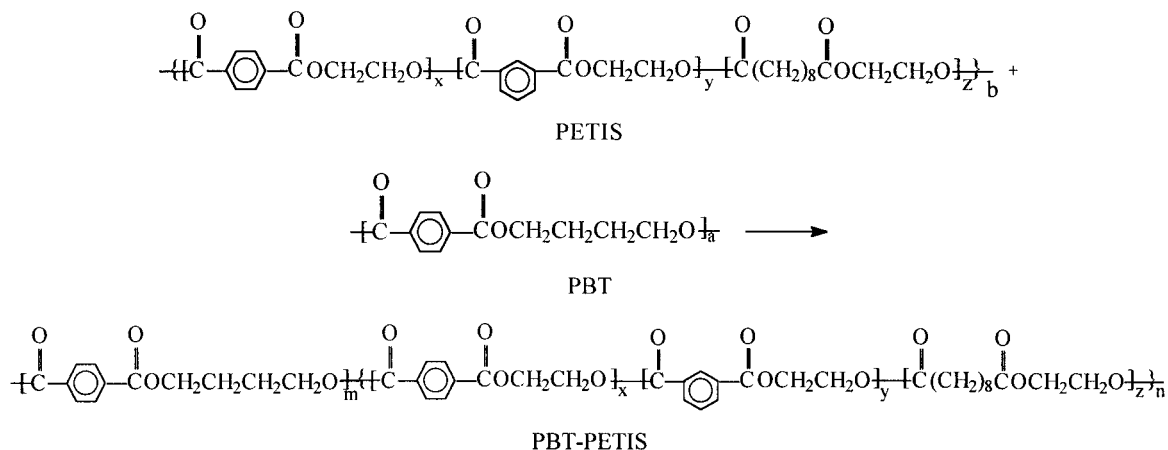
Recently, in our laboratory, we synthesized a series of segmented copolyesters employing bulk polyester produced on large scale poly (butylene terephthalate) (PBT) and ternary amorphous random copolyester poly(ethylene terephthalate-co-isophthalate-co-sebacate) (PETIS) by melting transesterification processing. The fraction of PETIS random copolymers ranged from 70 to 80 wt % (with the contents of aliphatic

polyester poly(ethylene sebacate) ranging from 28 to 32 wt %). The composition suggests the formation of copolyesters with moderate elasticity.

Because interchange reactions between different polyesters give rise to different sequence distribution according to reaction time,⁵ dependence of copolyester properties on reaction time is important during melting processing. To check the role of reaction time, polymerization experiments were carried out at different time.

For applications, crystallization behavior is of technological importance. Nonisothermal crystallization kinetics is therefore required to obtain parameters for real industrial processing conditions. The process of nonisothermal crystallization is relatively complex for segmented copolyesters synthesized by melting transesterification. No attention has been paid to the influence of reaction time on noncrystallization behavior of segmented copolyesters, which is one of the major objectives in this work. Investigations of nonisothermal crystallization behaviors of PBT–PETIS segmented copolyesters samples with both varying composition and different reaction time were undertaken by differential scanning calorimetry (DSC). The interest in this subject was mainly focused on quantitative evaluations of nonisothermal crystallization kinetics of PBT–PETIS, using the modified Avrami and Ozawa equations as analytical approaches.

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Scheme 1

EXPERIMENTAL

Materials

The chips of PBT were kindly supplied by Yi Zheng Chemical Fiber Company, China. PETIS ternary random copolyester was synthesized in our laboratory by melting polycondensation under vacuum conditions.

Synthesis of PBT-PETIS segmented copolyesters

Melting transesterification between PBT and PETIS was conducted in a four-necked flask equipped with a mechanically sealed stirrer and condenser under nitrogen atmosphere and vacuum conditions of <133Pa. The melting processing proceeded isothermally at $255 \pm 2^\circ\text{C}$ for 20 and 40 min, respectively. The synthesis of segmented copolyesters is given in Scheme 1.

Measurement of intrinsic viscosity

The intrinsic viscosity of segmented copolyesters was determined at $25 \pm 0.1^\circ\text{C}$ in a phenol/1,1,2,2-tetrachloroethane (50/50, w/w) solution with a concentration of 0.5 g/100 mL by a Ubbelohde viscometer.

Designated segmented copolyester samples with their intrinsic viscosity are shown in Table I.

DSC procedures

DSC measurements were carried out on a SHIMADZU-50 apparatus following the ASTM - D3418 method⁶ and using samples of ~5 mg. After the sample was completely melted, it was cooled at rates (R) of 2.5, 5.0, 10.0, and $20.0^\circ\text{C}/\text{min}$, respectively. The melting and crystallization thermograms were recorded by a computer. Two specimens of each sample were tested and the mean values and standard deviations were calculated.

The dependence of relative crystallinity on time [$X(t)$] was determined by integration of cooling curves:

$$X(t) = \int_{t_0}^t \frac{dH}{dt} / \Delta H_c \quad (1)$$

in which t_0 is the initial time when crystallization begins, $\int dH/dt$ is the heat evolution rate at time t ; and ΔH_c is the overall heat of crystallization.

TABLE I
Designated Samples and Intrinsic Viscosity

Sample	Feed Ratio (wt %)		Reaction Time (min)	Intrinsic Viscosity (dL/g)
	PBT	PBT/(PET/PEI/PES)		
PBT	100	0	—	0.8000
20PBT-20	20	20/(32/16/32)	20	0.5860
20PBT-40	20	20/(32/16/32)	40	0.6231
30PBT-20	30	30/(28/14/28)	20	0.5647
30PBT-40	30	30/(28/14/28)	40	0.6074
PETIS	0	0/(40/20/40)	150	0.4866

TABLE II
Characteristic Data of Heating Run for Segmented Copolyesters

Sample	T_{m1} (°C)	T_{m2} (°C)	$T_{m, onset}$ (°C)	$T_{m, endset}$ (°C)	ΔH_m (J/g)
PBT	— ^a	225.76 ± 0.28	205.89 ± 0.68	238.28 ± 0.29	43.20 ± 0.56
20PBT-20	—	221.09 ± 0.21	200.23 ± 0.10	229.96 ± 0.77	13.50 ± 0.20
20PBT-40	—	214.27 ± 0.12	148.78 ± 1.23	226.54 ± 1.39	14.73 ± 1.07
30PBT-20	186.00 ± 0.72	199.97 ± 0.12	158.50 ± 0.61	214.91 ± 0.02	16.28 ± 0.18
30PBT-40	175.57 ± 0.01	187.27 ± 0.25	136.15 ± 0.82	206.47 ± 0.03	16.30 ± 0.30

^a Not detected.

RESULTS AND DISCUSSION

Melting behavior

In DSC curves, multiple melting peaks are presented in sample 30PBT-20 and sample 30PBT-40, which is the most widespread observation that has been reported in the literature.^{7,8} Park and Kang⁹ pointed out that the lower temperature peak can be attributed to the melting of the PBT crystal related to the ternary random copolyester, and the other peak to that of the pure PBT crystal. The double peaks are marked T_{m1} and T_{m2} in Table II respectively, and ΔH_m is the heat of fusion. From the data in Table II it can be seen that all DSC curves in the heating run show melting peaks whose location depends on both composition and reaction time. Firstly, melting temperatures gradually move to lower temperature regions when the content of PBT segment is increased, but vary proportionally with the content of amorphous copolyester PETIS. Relatively short amorphous random copolyester segments, which during melting transesterification are generated from the low feed fraction of amorphous polyester, might act as a crystal imperfection. As a result, the melting temperatures are depressed.

Secondly, for a chosen composition, samples with shorter reaction time reveal higher melting temperatures than those of with longer reaction time. There is a tendency that sequence length of polyesters is shortened as the reaction time is prolonged, and what is worse, randomness may occur.⁵ Consequently, segmented copolyesters tend to be random ones, leading to lower melting temperatures. Moreover, the broad distribution of sequence length caused by prolonged reaction time is the reason for wide range of melting temperatures.

Nonisothermal crystallization behavior

The crystallization exotherms of sample 20PBT-20 from the melt with four different cooling rates over the range 2.5–20.0 °C/min are shown in Figure 1. The exothermic peaks shift to lower temperature region as the cooling rate increases. This observation is a typical of other samples and a common phenomenon for semicrystalline polymer crystallized nonisothermally.^{10–13} When polymer was undergoing crystalli-

zation at lower cooling rate, it had relatively long time lying within the temperature range that promoted sufficient mobility of segments for the growth of crystallites; but when cooled down at a relatively rapid rate, segments were frozen before the formation of regular crystallite, thereby decreasing the crystallization temperature. Moreover, for a chosen cooling rate, the crystallization exotherm moves to lower temperature as the content of amorphous copolyester decreases. In spite of this phenomenon, the crystallization exotherms reveal higher peak temperatures (T_p) for samples with short reaction time. The DSC cooling curves of segmented copolyesters that were cooled down at rate of 5.0°C/min are presented in Figure 2. The shift of crystallization temperatures is in agreement with the change of melting temperatures, because of the incorporation of short sequence length of amorphous polyester segments induced by decreased amorphous ternary polyester content and prolonged reaction time during melting processing. The characteristic data of nonisothermal crystallization exotherms for the samples investigated are summarized in Table III.

Modified Avrami analysis

The well-known Avrami equation for describing isothermal crystallization kinetics of polymers is given as follows:^{14–16}

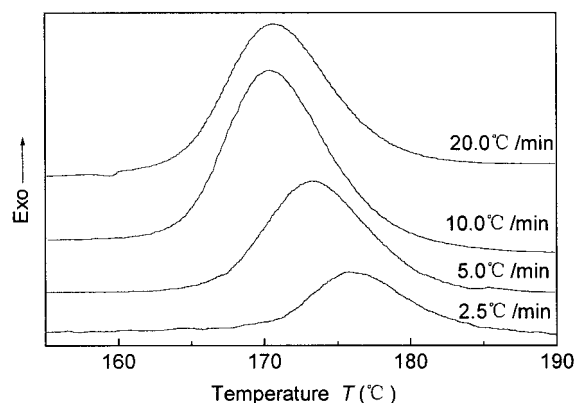


Figure 1 Nonisothermal crystallization exotherms of sample 20PBT-20 measured at different cooling rates.

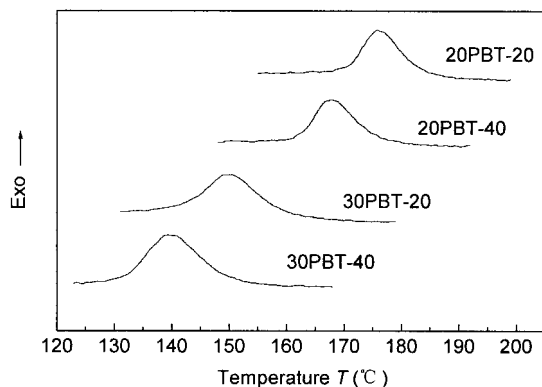


Figure 2 Nonisothermal crystallization exotherms of samples measured at a cooling rate of 5.0°C/min.

$$1 - X(t) = \exp(-Z_t t^n) \quad (2)$$

where n is the Avrami exponent whose value depends on the mechanism of nucleation and on the form of crystal growth, and Z_t is the crystallization kinetics constant containing the nucleation and the growth parameters.¹⁷

The Avrami approach is reasonably established when relative crystallinity is a function of time for nonisothermal crystallization at a chosen cooling rate, and the modified Avrami equation gives essentially the same expression. The plots of relative crystallinity as a function of time for sample 20PBT-20 are shown in Figure 3. All curves have sigmoidal shapes, which is the typical crystallization behavior of polymers. The half-time of crystallization, $t_{1/2}$ can also be determined from Figure 3 and is denoted as the time when the development of crystallization is complete by 50%.

Avrami lines obtained from following double logarithmic equation are presented in Figure 4:

$$\log \{-\ln[1 - X(t)]\} = \log Z_t + n \lg t \quad (3)$$

The slope of the straight line at the early stage (n) and the antilogarithmic value of the intersection with the y-axis (Z_t) can be calculated. Assuming the cooling rate to be a constant or approximately constant, Jezi-

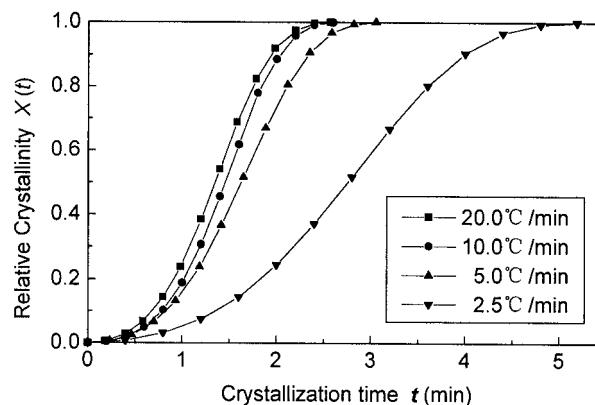


Figure 3 Development of relative crystallinity with time for sample 20PBT-20.

orny¹⁸ corrected the crystallization rate constant (Z_t) as follows:

$$\log Z_c = \log Z_t / R \quad (4)$$

in which Z_c , the final form of crystallization rate constant, is an important parameter because it is the true characteristic for the nonisothermal crystallization process.

Results of Avrami exponent (n) and Avrami crystallization kinetics constant (Z_c) as well as the half-time of crystallization ($t_{1/2}$) are collected in Table IV. The Avrami exponents range from 2.2503 to 3.7632. Similar values of n were obtained for the shorter reaction time samples and the longer reaction time samples, but these values are slightly influenced by the content of amorphous ternary random polyester.

As mentioned early, the Avrami exponent n refers to the specific mechanism of nucleation and the geometry and the kinetics of crystallite growth. For the crystallization of PBT homopolymer, the Avrami exponent n ranges from 2.0911 to 2.5768, depending on the cooling rate. From the values it can be speculated that spherulitic development arises from heterogeneous nucleation for which the literature provided an earlier indication.¹⁹ Comparing the Avrami exponents of segmented copolyesters with those of PBT ho-

TABLE III
Characteristic Data of Nonisothermal Crystallization Exotherms for Segmented Copolyester Samples

Sample	-2.5°C/min			-5.0°C/min			-10.0°C/min			-20.0°C/min		
	T_p (°C)	ΔH_c (J/g)	t_p^a (min)	T_p (°C)	ΔH_c (J/g)	t_p (min)	T_p (°C)	ΔH_c (J/g)	t_p (min)	T_p (°C)	ΔH_c (J/g)	t_p (min)
PBT	190.36	39.50	5.60	186.36	40.19	3.17	183.43	42.51	2.45	184.21	43.07	2.40
20PBT-20	175.77	9.11	3.00	173.30	9.02	1.68	170.70	11.23	1.52	170.61	10.46	1.40
20PBT-40	167.86	10.95	6.40	162.45	10.82	3.73	160.29	10.83	2.89	161.06	10.26	2.90
30PBT-20	150.36	10.20	3.85	145.30	15.94	2.25	145.70	13.31	2.00	145.32	14.34	1.88
30PBT-40	139.40	12.36	6.22	133.19	11.86	4.47	132.36	13.72	3.70	131.92	12.77	3.58

^a t_p is the time to reach maximum degree of crystalline order.

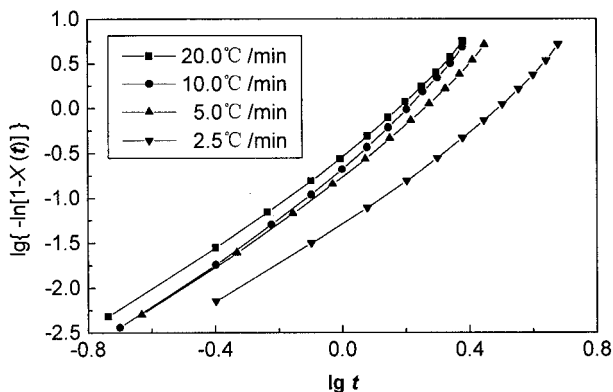


Figure 4 Avrami analysis based on the nonisothermal crystallization data for sample 20PBT-20.

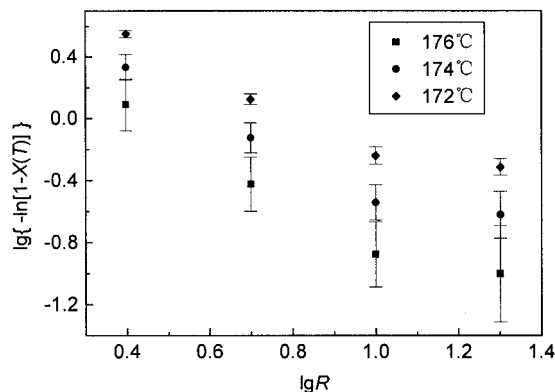


Figure 5 Ozawa analysis based on the nonisothermal crystallization data for sample 20PBT-20.

mopolymer, we found that these values of copolyesters approximate those of PBT. The results indicate a mechanism of three-dimensional spherulitic growth with heterogeneous nucleation.

All Z_c values increase with increasing cooling rate, whereas the reciprocal value of half-crystallization time ($1/t_{1/2}$) is shortened, which indicates that the nonisothermal crystallization rate is accelerated by increasing the cooling rate. More specially, Z_c ranges from 0.9358 to 0.3117 for sample 20PBT-20 and from 0.9069 to 0.2304 for sample 30PBT-20. Similar results were determined for other samples. Because the nucleating capability of samples is enhanced at a rapid cooling rate, the increased nucleation density leads to the increase of crystallization rate and a little time is needed for the development of crystalline entities.

In comparison, the trend appears significant for PETIS-content-rich copolyesters. Moreover, all of the shorter reaction time samples crystallized more quickly than the longer reaction time samples. Both cases are partially due to the appropriateness of polyester sequence length, because crystallization is accompanied by a selection of sequence according to their length. Reasonable sequence length of polyester segments that should favor chain aggregation and give rise to regular crystals might be present in samples with shorter reaction time and higher ternary polyester content. In this respect, the results of kinetics

parameters confirm our previous study on melting behaviors.

Ozawa analysis

The Ozawa approach²⁰ derived from Avrami theory for describing the nonisothermal crystallization kinetics of polymers takes the effect of cooling rate on crystallization into account by assuming R is a constant:

$$X(T) = 1 - \exp(k(T)/R^m) \quad (5)$$

where m is the Ozawa exponent whose value also depends on the mechanism of nucleation and growth just as the Avrami exponent does, $k(T)$ is the Ozawa kinetics crystallization rate constant, and $X(T)$ is the relative crystallinity as a function of temperature.

From the double logarithmic form of Ozawa equation, eq. 6 can be derived:

$$\log\{-\ln[1 - X(T)]\} = \log k(T) - m \log R \quad (6)$$

where the exponent m can be obtained from the negative value of slope and $k(T)$ can be obtained from the intercept of the straight line at different temperatures.

The Ozawa approach described the nonisothermal behavior well for several polymers,²⁰⁻²³ including bi-

TABLE IV
Kinetic Parameters from the Modified Avrami Analysis of Nonisothermal Crystallization

Sample	-2.5°C/min			-5.0°C/min			-10.0°C/min			-20.0°C/min		
	$t_{1/2}$ (min)	n	Z_c (min ⁻ⁿ)	$t_{1/2}$ (min)	n	Z_c (min ⁻ⁿ)	$t_{1/2}$ (min)	n	Z_c (min ⁻ⁿ)	$t_{1/2}$ (min)	n	Z_c (min ⁻ⁿ)
PBT	5.2916	2.0911	0.1251	3.0351	2.2708	0.4182	2.3840	2.5768	0.6700	2.2925	2.3515	0.8278
20PBT-20	2.7790	2.2682	0.3177	1.6322	2.4539	0.7001	1.4557	2.5099	0.8484	1.3564	2.3933	0.9358
20PBT-40	6.1210	3.7632	0.0690	3.5662	2.6155	0.4159	2.7713	2.8400	0.6527	2.7408	2.7179	0.8183
30PBT-20	3.8302	2.2503	0.2304	2.2478	2.3491	0.6108	1.9627	2.4143	0.8073	1.8333	2.4381	0.9069
30PBT-40	5.8809	2.5537	0.1189	4.2280	2.5342	0.3969	3.5424	2.5747	0.6633	3.4341	2.5347	0.8194

TABLE V
Kinetic Parameters from the Ozawa Analysis of Nonisothermal Crystallization

Temperature (°C)	20PBT-20 (three data points) ^a			20PBT-20 (four data points) ^b		
	<i>m</i>	<i>k</i> (<i>T</i>)(min ^{-<i>m</i>)}	<i>r</i> ²	<i>m</i>	<i>k</i> (<i>T</i>)(min ^{-<i>m</i>)}	<i>r</i> ²
176	1.6042 ± 0.0651	5.4728 ± 1.7308	0.99901 ± 0.00091	1.2365 ± 0.1457	3.2011 ± 0.6823	0.96632 ± 0.01955
174	1.4552 ± 0.0537	8.0964 ± 1.1092	0.99963 ± 0.00003	1.0902 ± 0.0734	4.8785 ± 0.5360	0.96339 ± 0.00829
172	1.1539 ± 0.0227	11.6248 ± 1.9023	0.99890 ± 0.00089	0.9814 ± 0.0854	7.3198 ± 0.7156	0.96402 ± 0.00468

^a Cooling rates: 2.5°C/min, 5.0°C/min, and 10.0°C/min.

^b Cooling rates: 2.5°C/min, 5.0°C/min, 10.0°C/min, and 20.0°C/min.

nary copolyesters.^{12,13} The plot in Figure 5, however, shows a finer fit for straight line at slow cooling rate and deviates significantly at rapid cooling rate.

The application is limited because of the later section of crystallization in which secondary crystallization was reported to occur. The introducing of polyesters gives rise to very complex nucleation and growth, which is significant in the case of rapid cooling rate. The latter may be another reason why the Ozawa approach is unfit for describing nonisothermal crystallization behavior of copolyesters. Based on the observation of the nonisothermally crystallized samples, Sajkiewicz²⁴ thought that the deviation from the linearity of the Ozawa plot is caused by spatial constraints during the growth of the crystallites.

The parameters from Ozawa analysis for sample 20PBT-20 with the corresponding correlation coefficient *r*² as a comparison are shown in Table V. Two groups of kinetics parameters arise and come from different selections of data points. Segmented copolyesters crystallize faster at lower temperature. This result can be deduced from Table V where the value of the Ozawa kinetics crystallization rate constant [*k*(*T*)] is inversely proportional to that of temperature. The change in tendency of the Ozawa exponent is similar with temperature but the increase is not sharp. In fact, the integer value of *m* is equal to the dimensionality of crystal growth. The change in trend of the Ozawa exponent confirms that the development of crystallization at elevated temperature results in more perfect crystals. The other conclusion of the analysis is that, although temperature has intensive influence on both nucleation and growth, nucleating is evidently predominant at higher temperature.

Kinetic crystallizability

Kinetic crystallizability (*G*) proposed and developed by Ziabicki²⁵ and Jeziorny¹⁸ characterizes the degree of crystallinity obtained at unit cooling rate within the range from the melting temperature (*T*_m) to the glass transition temperature (*T*_g). Jeziorny considered that the crystallization rate function *K*(*T*) can be rewritten by using Gaussian function. The expression of kinetic crystallizability is given as follows:

$$G = \int_{T_g}^{T_m} K(T) = (\pi/\ln 2)^{1/2} K_{\max} D/2 \approx 1.064 K_{\max} D \quad (7)$$

where *D* is the half-width of exothermic peak. The maximum crystallization rate *K*_{max} is related to both relative crystallinity at the maximum crystallization rate *X*(*t*)_{max} and the crystallization time at the maximum crystallization rate *t*_{max}. The relationship is expressed as follows:¹⁷

$$K_{\max} = \frac{1}{1 - X(t)_{\max}} \cdot \frac{X(t)_{\max}}{t_{\max}} \quad (8)$$

where *G* can be taken as a parameter for comparing the crystallization ability of different polymers. The equation obtained was corrected by considering the influence of *R*:

$$G_c = G/R \quad (9)$$

The values shown in Table VI reveal that kinetic crys-

TABLE VI
Kinetic Crystallizability of Segmented Copolyesters

Sample	-2.5°C/min			-5.0°C/min			-10.0°C/min			-20.0°C/min		
	<i>D</i> (°C)	<i>X</i> (<i>t</i>) _{max}	<i>G</i> _c	<i>D</i> (°C)	<i>X</i> (<i>t</i>) _{max}	<i>G</i> _c	<i>D</i> (°C)	<i>X</i> (<i>t</i>) _{max}	<i>G</i> _c	<i>D</i> (°C)	<i>X</i> (<i>t</i>) _{max}	<i>G</i> _c
PBT	5.5480	0.6181	0.6416	6.3947	0.6000	0.6446	6.6750	0.5752	0.3786	6.5381	0.5852	0.2045
20PBT-20	6.5355	0.5916	1.3893	7.3524	0.5485	1.1290	7.6320	0.5502	0.6550	7.2881	0.5418	0.3275
20PBT-40	7.7709	0.5824	0.7207	9.0264	0.5895	0.7387	8.8729	0.5676	0.3275	8.7173	0.5757	0.2169
30PBT-20	8.8419	0.5021	0.9857	10.4608	0.4994	0.9870	8.8542	0.5193	0.5089	9.0909	0.5309	0.2906
30PBT-40	10.4608	0.5802	0.9740	11.2578	0.5813	0.7446	11.0710	0.5576	0.4013	11.4571	0.5508	0.2086

tallizability (G_c) is influenced by the feed ratio; that is, at a chosen cooling rate, the value is proportional to the content of amorphous random copolyester PETIS. The crystallization ability of segmented copolyester is enhanced by the introduction of ternary random copolyester segments. In spite of this enhancement, the longer the reaction proceeds, the lower is the G_c value. The kinetic crystallizability decreases at rapid cooling rate.

CONCLUSIONS

DSC measurement were performed to investigate the nonisothermal crystallization behavior of segmented copolyesters, using modified Avrami and Ozawa equations as analytical methods. The data obtained from the experiments agree with the modified Avrami model fairly well. The Avrami exponents show a variation in range of 2.2503 to 3.7632. The final form of crystallization rate constant (Z_c) lies within the range of 0.0690 to 0.9358. The values of crystallization rate constant increase as cooling rate increases or reaction time decreases. Applying Ozawa analysis, we found that derivation from the straight line occurs in the case of a rapid cooling rate. Nevertheless, we can obtain the Ozawa exponent and kinetics constant within reasonable corresponding correlation coefficient range for sample 20PBT-20. The value of the Ozawa kinetics crystallization rate constant [$k(T)$] is inversely proportional to that of temperature, which indicates that segmented copolyesters crystallize faster at lower temperatures. Kinetic crystallizability varies reversibly

with both cooling rate and reaction time, which is directly related to the feed ratio. The trend appears notable for the PETIS-rich copolyesters.

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