

Synthesis and Non-Isothermal Crystallization Behavior of Poly(ethylene-co-1,4-butylene terephthalate)s

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Abstract: A series of random poly(ethylene-co-1,4-butylene terephthalate)s (PEBTs), as well as poly(ethylene terephthalate) (PET) and poly(1,4-butylene terephthalate) (PBT), were synthesized by the bulk polycondensation. Their composition, molecular weight, and thermal properties were determined. All the copolymers are crystallizable, regardless of the compositions, which may originate from both even-atomic-numbered ethylene terephthalate and butylenes terephthalate units that undergo inherently crystallization. Non-isothermal crystallization exotherms were measured over the cooling rate of 2.5-20.0 K/min by calorimetry and then analyzed reasonably by the modified Avrami method rather than the Ozawa method. The results suggest that the primary crystallizations in the copolymers and the homopolymers follow a heterogeneous nucleation and spherulitic growth mechanism. However, when the cooling rate increases and the content of comonomer unit (ethylene glycol or 1,4-butylene glycol) increases, the crystallization behavior still becomes deviated slightly from the prediction of the modified Avrami analysis, which is due to the involvement of secondary crystallization and the formation of relatively low crystallinity. Overall, the crystallization rate is accelerated by increasing cooling rate but still depended on the composition. In addition, the activation energy in the non-isothermal crystallization was estimated.

Keywords: aromatic copolyesters, non-isothermal crystallization, crystallization mechanism, activation energy of crystallization, equilibrium melting point, effect of composition.

Introduction

Poly(ethylene terephthalate) (PET) is widely used as fibers, films, bottles, and molding plastic because of its excellent thermal and mechanical properties, high chemical resistance, and low gas permeability.¹⁻³ Poly(1,4-butylene terephthalate) (PBT) is also rapidly gaining importance as an engineering thermoplastic due to its attractive mechanical properties, rapid crystallization rate, and good moldability.⁴ However, both of the homopolymers still have some undesirable properties, such as poor dyeability, pilling, poor adhesion (to metals), and high molding temperature.^{5,6}

Copolymerization can provide a means of tailoring the characteristics of polyesters to desirable values or confer specific chemical properties not present in the major component as a homopolymer, although the use of copolymer-

ization to modify a particular property may also alter other properties, is not always desirable.

For polymers, isothermal process has been studied thoroughly. However, in industry polymers are practically processed under dynamic and non-isothermal conditions. Thus, the non-isothermal behavior from the melt is of increasing technological importance. Moreover, it is necessary to investigate non-isothermal crystallization behavior for optimizing the process and understanding properties of processed products.

In this study, a series of random copolymers containing ethylene terephthalate and 1,4-butylene terephthalate units were synthesized by the conventional bulk polycondensation of dimethyl terephthalate with ethylene glycol and 1,4-butylene glycol in various compositions. Their composition and molecular weight were determined by proton nuclear magnetic resonance (¹H-NMR) spectroscopy and viscometry, respectively. The non-isothermal crystallization behaviors were investigated by calorimetry in complement of the modified Avrami and the Ozawa analysis in regard with the

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effect of chemical composition.

Experimental

Materials and Polymerization. Ethylene glycol (EG) and 1,4-butylene glycol (BD) were supplied from LG Chemical Company (Korea) and dimethyl terephthalate (DMT) was obtained from SKC Limited (Korea). The other chemicals were purchased from Aldrich Chemical Company (USA). All the chemicals were used as received without further purification.

A random copolymer, poly(ethylene-*co*-butylene terephthalate) was synthesized by a two-step reaction sequence as follows (see Figure 1). In the first step, DMT of 1.0 equivalent was added into the mixture of 1.1 equivalent EG and 1.1 equivalent BD in a two-neck flask equipped with a mechanically sealed stirrer and a motor. Then, zinc acetate dihydrate (2.7×10^{-4} wt% of the loaded DMT), as an ester interchange reaction catalyst, was added to the mixture. After the addition was completed, the flask was equipped with a condenser. Then, the ester interchange reaction was conducted under stirring for 2.0-2.5 h at 180-210°C. Methanol byproduct was removed with a yield of 92% from the reaction mixture through the reaction. In the second step, titanium butylate (9.9×10^{-4} wt% of the loaded DMT) and trimethyl phosphate (1.5×10^{-3} wt% of the loaded DMT) were added into the reaction mixture as a polycondensation catalyst and a thermal stabilizer, respectively. The polymerization was carried out with stirring for 2.5-3.5 h at 260-280°C under a vacuum of ca. 1×10^{-2} torr as described elsewhere.^{5,6} In the same manner, a series of poly(ethylene-*co*-1,4-butylene terephthalate)s (PEBTs) were prepared by varying the feed ratio of EG and BG monomers. In addition, homopolyesters [namely, poly(ethylene terephthalate) (PET) and poly(1,4-

butylene terephthalate) (PBT)] were synthesized.

Measurements. Compositions of the synthesized copolymers were determined in a mixture of CF_3COOD and CDCl_3 (3:1 in volume) by $^1\text{H-NMR}$ spectroscopy (Bruker ASPECT 300 MHz). Intrinsic viscosity $[\eta]$ was measured in CF_3COOH at 30 ± 0.1 °C using an Ubbelohde suspended level capillary viscometer.^{5,7} From the measured $[\eta]$, weight average molecular weight (\bar{M}_w) was estimated using the Mark-Houwink-Sakurada equation with constants $a = 0.68$ and $k = 4.33 \times 10^{-4}$ which were determined previously for PET homopolymer.^{5,6,8}

Thermal characterization was performed for all the polymers by differential scanning calorimetry (DSC) (Seiko DSC 220CU). Both temperature and heat flow were calibrated using indium and tin standards. The weight of all samples employed was in the range of 4.0-6.0 mg. In the DSC measurement, polymer sample was preheated at 290°C for 10 min in order to remove its thermal history and then cooled down to 0°C with a rate of 10.0 K/min. Then, the cooled sample was again heated up to 300°C with a rate of 5.0 K/min. The melting point (T_m) of crystals in the sample was chosen as the temperature at the peak maximum of melting transition measured in the heating run and the heat of fusion (ΔH_f) was additionally estimated. The glass transition temperature (T_g) was chosen as the temperature at the middle point of glass transition obtained in the heating run.

For all the crystallizable polymers, non-isothermal crystallization was conducted with varying cooling rate over 2.5-20.0 K/min. Each polymer sample was heated up to 290°C with a rate of 20 K/min and then dwelled at 290°C for 10 min in order to remove its thermal history, subsequently cooled down to 0°C with a chosen cooling rate. Crystallization peak temperature (T_p) was estimated from the peak maximum of DSC exotherm measured during the crystallization.

In addition, isothermal crystallization was performed in order to determine equilibrium melting temperature. All the samples were heated up to 290°C with a heating rate of 20°C and dwelled at 290°C for 10 min, followed by quenching to a certain crystallization temperature. The isothermal crystallization was conducted at that temperature for 40 min, then re-heated to 290°C with a heating rate of 10 K/min. Melting point was determined as the temperature at the peak maximum in the measured endotherm.

Analysis of Non-isothermal Crystallization. Non-isothermal exotherms measured in the DSC measurement were analyzed by the modified Avrami method as follows. For non-isothermal crystallization with a chosen cooling rate, the relative crystallinity X_t is expressed to be a function of crystallization temperature:^{5,6,9-11}

$$X_t = \frac{\int_{T_o}^T \left(\frac{dH_c}{dT} \right) dT}{\int_{T_o}^{T_\infty} \left(\frac{dH_c}{dT} \right) dT} \quad (1)$$

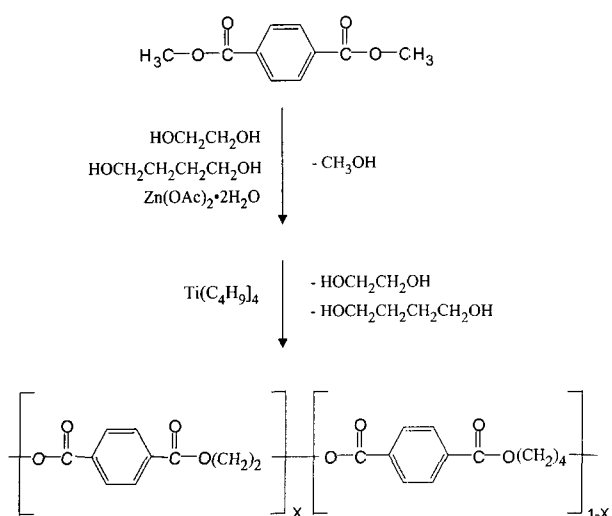


Figure 1. Synthetic scheme of poly(ethylene-*co*-1,4-butylene terephthalate)s.

where T is the crystallization temperature and T_o and T_∞ represent the onset and end temperature of crystallization, respectively.

Here, the X_t can be expressed again as a function of crystallization time t , according to the Avrami equation:^{5,6,9-11}

$$1 - X_t = \exp(-kt^n) \quad (2)$$

where n is the Avrami exponent, and k is the growth rate constant. The crystallization time t is converted from the cooling rate C and the crystallization temperatures T and T_o as follows:

$$t = \frac{T_o - T}{C} \quad (3)$$

The rate of non-isothermal crystallization depends upon the cooling rate employed, so that the k should be corrected adequately as follows:

$$\log k' = \frac{\log k}{C} \quad (4)$$

And, the crystallization half time $t_{1/2}$, that is defined as the time at which the development of crystallization is complete by 50%, can be determined from the corrected crystallization rate constant k' :

$$t_{1/2} = \left(\frac{\ln 2}{k'} \right)^{1/n} \quad (5)$$

The non-isothermal exotherms were analyzed further by the Ozawa method as follows. According to the Ozawa approach,^{5,6,12,13} the crystallization time t in the Avrami equation (2) is replaced by the cooling rate C . Therefore, the X_t in the non-isothermal crystallization can be expressed to be a function of the cooling rate C :

$$X_t = 1 - \exp\left(\frac{-K(T)}{C^m}\right) \quad (6)$$

where $K(T)$ is the cooling function at temperature T and m is the Ozawa exponent.

In addition, the activation energy E_a in the non-isothermal crystallization was estimated from the variation of crystallization peak temperature T_p with cooling rate C :^{5,6,14,15}

$$\frac{d(\ln(C/T_p^2))}{d(1/T_p)} = -\frac{E_a}{R} \quad (7)$$

where R is the universal gas constant.

Results and Discussion

Polymerization. A series of PEBTs, including PET and PBT homopolymers, were synthesized by varying the feed ratio of EG and BG comonomers with respect to the DMT monomer in the bulk polymerization. Their chemical com-

positions were determined by ¹H-NMR spectroscopy. A typical ¹H-NMR spectrum is presented in Figure 2, which was measured from the BD30 copolymer. This copolymer has been made from the feed ratio of 20 mol% BG and 80 mol% EG in the polymerization but characterized to contain 30.3 mol% BG and 69.7 mol% EG unit on the backbone from the integrations of its specific chemical shifts denoted in the ¹H-NMR spectrum. All other polymers are characterized in the same manner, and their results are summarized in Table I.

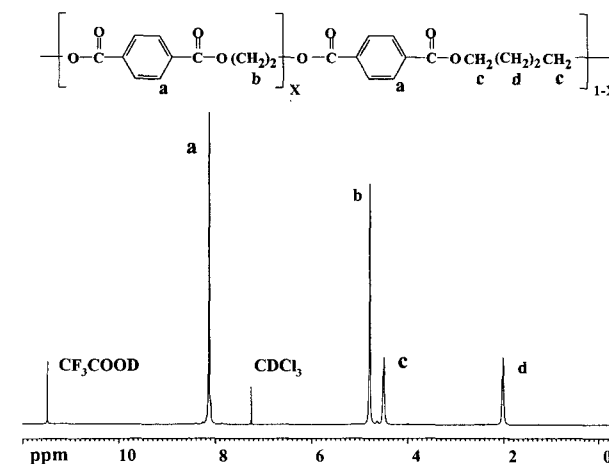


Figure 2. ¹H-NMR spectrum of BD30 copolymer dissolved in a mixture solvent.

Table I. Composition, Intrinsic Viscosity $[\eta]$, and Weight \overline{M}_w^c Average Molecular Weight of PET, PBT, and Their Copolymers

Polymer	Feed Ratio in Polymerization ^a (BG/EG)	Composition in Polymer ^b (BG/EG)	$[\eta]$ (dL/g)	\overline{M}_w^c
PET	0/100	0/100	0.545	36,000
BD8	5/95	7.5/92.5	0.523	34,000
BD16	10/90	15.6/84.4	0.510	33,000
BD22	14/86	21.5/78.5	0.468	29,000
BD30	20/80	30.3/69.7	0.480	30,000
BD44	30/70	44.2/55.8	0.550	37,000
BD57	40/60	56.6/43.4	0.454	28,000
BD69	50/50	68.5/31.5	0.369	20,000
BD82	60/40	81.5/18.5	0.414	24,000
BD84	70/30	84.0/16.0	0.310	16,000
BD90	80/20	90.2/9.8	0.323	17,000
PBT	100/0	100/0	0.350	19,000

^a Molar ratio of BG and EG monomers fed in the polymerization.

^b Measured by ¹H-NMR spectroscopy.

^c Estimated from the measured intrinsic viscosity using the Mark-Houwink-Sakurada equation with constants $a = 0.68$ and $k = 4.33 \times 10^{-4}$ which were determined previously for PET homopolymer.^{5,6,8}

Overall, the content of BG monomer unit incorporated into the polymer is always larger than that fed in the polymerization. This result might come mainly from the differences in their chemical and physical natures. The BG monomer has two methylene units more than EG. Such methylene units possess an electron donor-ability, so that the oxygen atoms in BG become more electronegative than those in EG. Due to the relatively high electronegativity, the hydroxyl groups of BG monomer become a relatively strong nucleophile that can attack the carbonyl carbons of DMT. Consequently, BG reacts more favorably with the DMT monomer than EG in the ester exchange reaction, leading to a relatively high content of BG unit in the resultant copolymer. In addition, the BG has a relatively high boiling point (230°C) than that (197°C) of EG. Thus, EG is more volatile than BG, so that EG component is removed more easily than BG in the polycondensation under reduced pressure, resulting in a high content of BG unit in the polymer backbone.

In addition, such oxydiethylene unit, which is known to form in the bulk polymerization of EG and DMT,¹⁶⁻¹⁸ is not detected spectroscopically for all the polymers synthesized in this study. Therefore, the dimerization of EG monomers may be negligible in the synthesis of PET and its copolymers containing BG units.

Weight average molecular weights (\overline{M}_w 's) have been estimated from the measured $[\eta]$'s and listed together in Table I. The \overline{M}_w is in the range of 16,000-37,000. In particular, the relative low \overline{M}_w 's of the PBT homopolymer and its copolymer rich with BD units may be associated partially with the improper constants a and k in the Mark-Houwink-Sakurada equation, which were found originally for PET homopolymer.

Phase Transition Behavior and Equilibrium Melting Temperature. The measured DSC endotherms are shown Figure 3 and their analyzed results are listed together in Table II. In the measurement, all the polymers were crystallized

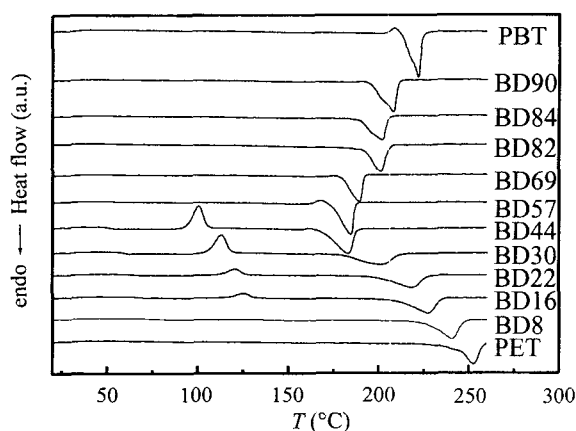


Figure 3. DSC thermograms of PET, PBT, and their copolymers measured during heating run with 5.0 K/min after cooled with 10.0 K/min from the melt.

with a cooling rate of 10.0 K/min from the melt and then reheated with a rate of 5.0 K/min.

All the copolymers exhibit a melting endotherm, regardless of the composition, indicating that they all are crystallizable. This is the unique feature of the PEPT polymers, which could not achieve from other copolyesters composed of ethylene terephthalate units.^{5,6,19} PET and PBT homopolymers exhibit $T_m = 258.6^\circ\text{C}$ and $T_m = 222.3^\circ\text{C}$, respectively. T_m of the copolymer is in the range of 183-258°C, depending on the composition. The BD44 polymer containing 44.2 mol% BD unit shows the lowest T_m (183.2°C). From the endothermic peaks, crystallinities X_c 's of PET and its copolymers rich with EG unit were estimated using $\Delta H_f^\circ = 117.7 \text{ J/g}$ for PET²⁰ while those of PBT and its copolymers rich with BG unit were estimated using $\Delta H_f^\circ = 98.5 \text{ J/g}$ of PBT.²¹ The results are summarized in Table II. All the polymers reveal a X_c in the range of 28.6-51.2%, depending on the composition. The PBT has a relatively larger X_c than that of PET. Overall, the BG rich copolymer exhibits a larger X_c than that of the corresponding EG rich copolymer.

In particular, the copolymers containing BD unit of 15.6-44.2 mol% show additionally an exothermic peak over 80-140°C, depending on the composition, which is associated with recrystallization occurred during the heating run.

T_g was also obtained from the measured DSC endotherms. PET and its copolymers rich with EG unit show a single

Table II. Glass Transition Temperature (T_g), Melting Temperature (T_m), Heat of Fusion (ΔH_f), and Crystallinity (X_c) of PET, PBT, and Their Copolymers^a

Polymer	T_g (°C)	T_m (°C)	ΔH_f (J/g)	X_c (%) ^b
PET	76.1	258.6	43.98	37.4
BD8	69.2	240.5	35.41	30.1
BD16	67.0	226.9	34.02	28.9
BD22	65.3	218.4	34.07	30.0
BD30	60.1	201.6	33.63	28.6
BD44	52.4	183.2	36.08	30.7
BD57	- ^c	184.7	39.07	39.7
BD69	-	189.5	32.09	32.6
BD82	-	201.1	32.61	33.1
BD84	-	202.0	31.47	31.9
BD90	-	208.5	39.08	39.7
PBT	-	222.3	50.41	51.2

^aMeasured by DSC with a heating rate of 5.0 K/min after crystallized with a cooling rate of 10.0 K/min from the molten state.

^bEstimated from the heat of fusion measured in the PET and its copolymers rich with EG unit using the heat of fusion (117.6 J/g) of the fully crystallized PET polymer but from the heat of fusion measured in the PBT and its copolymers rich with BG unit using the heat of fusion (98.5 J/g) of the fully crystallized PBT polymer.

^cNot detected.

T_g : T_g decreases with increasing the content of BG unit. However, such glass transition behavior could not be detected for PBT and its copolymers rich with BG unit. This might come from their relatively large X_c . Even quenched samples of theirs show no glass transition, suggesting that PBT and its copolymers crystallize rapidly even through the quenching process.

As described above, the copolymers reveal a single T_g rather than two T_g s corresponding to those of PET and PBT homopolymers. Further, the copolymers reveal a single T_m rather than two T_m of the ethylene terephthalate and butylenes terephthalate blocks. These results suggest that they are a random copolymer.

In addition, equilibrium melting temperature T_m^o was determined as follows. All the polymers were crystallized isothermally at various temperatures T_c s for 40 min, subsequently reheated to measure T_m . A representative result is presented in Figure 4, which were measured from the BD69 polymers crystallized isothermally at various T_c s. The polymer exhibits a multiple melting behavior, regardless of T_c s. The melting peak A is relatively very broad but becomes strong and shifts sensitively to the high temperature region as T_c increases. Thus, this peak is considered as the melting of crystals formed secondarily in the crystallization. The peak B appears with less broadness, and becomes intensive and shifts gradually to the high temperature region as T_c increases. This peak is confirmed to correspond to the melting of lamellar crystals formed primarily through the isothermal crystallization by time-resolved small-angle x-ray scattering.²² Finally, the third melting peak C appears in the high temperature region. The position of this peak varies very little with the crystallization history. However, this peak becomes weak as T_c increases. This behavior is in contrast to that of the peak B (namely, the melting of primarily formed lamellar

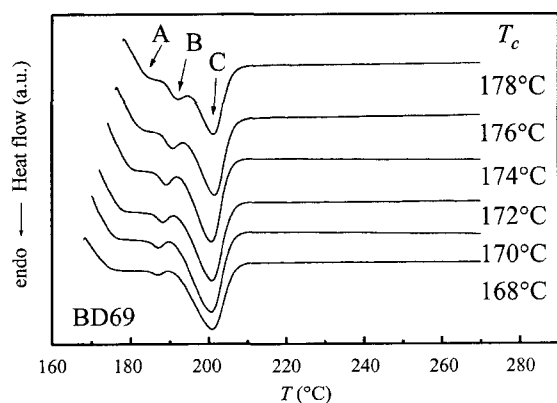


Figure 4. DSC thermograms of BD69 copolymer measured on the subsequent heating run with 10.0 K/min after isothermally crystallized for 40 min at chosen temperatures: (A) melting of secondarily formed crystals; (B) melting of primarily formed crystals; (C) melting of crystals recrystallized during heating run. The denoted temperatures are the crystallization temperatures.

crystals). This fact suggests that the population of crystals corresponding to the peak C is dependent upon that of the primarily formed crystals: That is, the crystals, which are corresponding to the peak C, form in low population when the population of primarily formed crystals is large. For these facts, the peak C is assigned to the melting of crystals recrystallized during the subsequent heating run after crystallized at a chosen T_c . Such multiple melting behaviors are observed in the other copolymers as well as the homopolymers.

From the DSC thermograms of each polymer, the T_m of primarily formed crystals is determined and then plotted with T_c in accordance to the Hoffman-Weeks method,²³ giving its equilibrium melting temperature T_m^o . A typical Hoffman-Weeks plot of T_m s and T_c s is shown in Figure 5(a). The determined T_m^o s are plotted in Figure 5(b) as a function of composition. The T_m^o s of PET polymer decreases as the content of BG unit increases: 275.4°C for PET, 263.2°C for BD8, 259.7°C for BG16, 253.7°C for BG22, 212.9°C for BG30, and 203.5°C for BG44. The T_m^o s of PBT polymer also decreases as the content of EG unit increases: 230.6°C for PBT, 228.7°C for BG90, 213.1°C for BG82, and 203.2°C for BG69. The lowest (=194.0°C) is determined

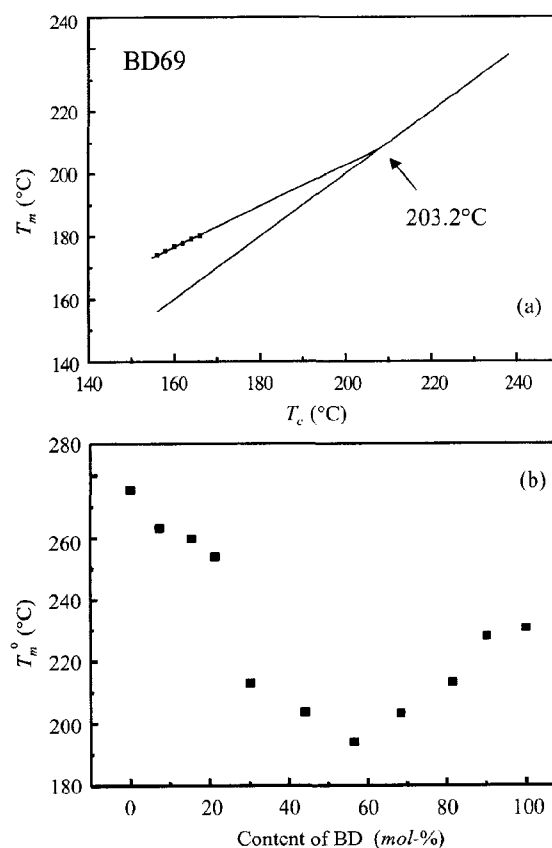


Figure 5. (a) Hoffman-Weeks plots of T_m s and T_c s measured from BD69 copolymer. (b) Plots of T_m^o s versus composition in the PEBT: Here, T_m^o was estimated by the Hoffman-Weeks plot of T_m s and T_c s measured from each polymer.

from the BD57 polymer containing BG unit of 56.6 mol%.

Non-isothermal Crystallization Behavior. Non-isothermal crystallization behaviors in the PEBT copolymers, as well as PET and PBT homopolymers, were investigated with varying cooling rate by DSC. All the polymers always exhibit exothermic peaks arising from their crystallization. Some of the measured DSC exotherms are shown in Figure 6. For a given polymer sample, the exothermic peak becomes broad and shifts to the low temperature region as the cooling rate increases, regardless of the composition. From the DSC thermograms, there are estimated the crystallization peak temperature T_p , heat of crystallization ΔH_c , and crystallinity X_c . The results are listed in Table III. For all the polymers, more rapid cooling rate causes lower T_p , ΔH_c ,

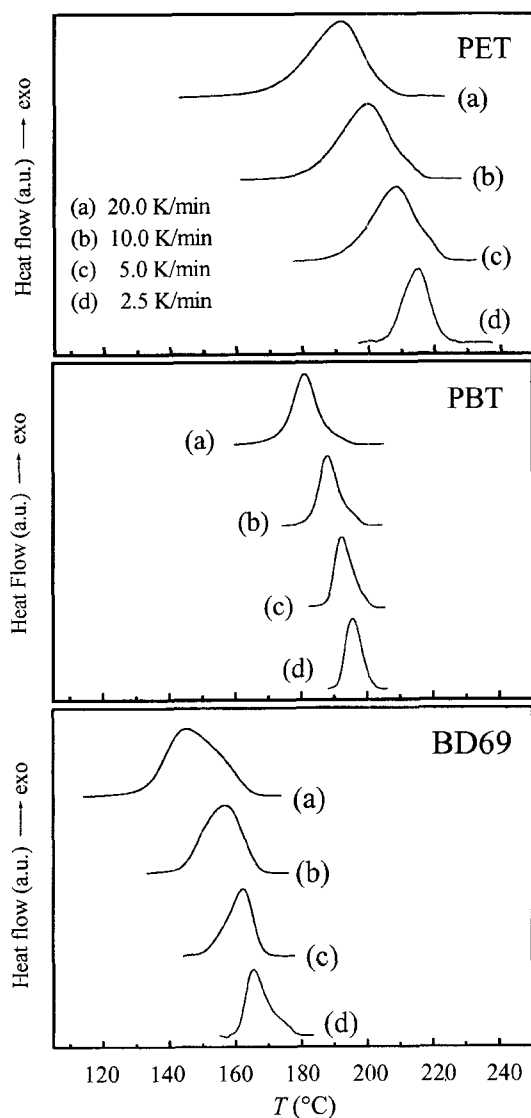


Figure 6. DSC thermograms of PET, PBT, and BD69 copolymer measured during non-isothermal crystallization with various cooling rates from the melt.

Table III. Crystallization Peak Temperature (T_p), Heat of Crystallization (ΔH_c), and Crystallinity (X_c) of PET, PBT, and Their Copolymers^a

Polymer	Cooling Rate (K/min)	T_p (°C)	H_c (J/g)	X_c^b (%)
PET	20	191.7	-45.41	38.6
	10	199.5	-45.84	39.0
	5	208.4	-47.22	40.2
	2.5	216.9	-47.34	40.3
BD8	20	154.8	-40.93	34.8
	10	170.6	-42.41	36.1
	5	186.5	-43.04	36.6
	2.5	196.6	-46.46	39.5
BD16	20	162.7	-37.97	32.3
	10	164.8	-40.02	34.0
	5	173.4	-41.63	35.4
	2.5	184.1	-42.99	36.6
BD22	20	153.3	-36.00	30.6
	10	158.5	-43.41	36.9
	5	172.9	-43.45	36.9
	2.5	179.7	-43.47	37.0
BD30	20	144.8	-35.43	30.1
	10	149.3	-38.88	33.1
	5	153.4	-43.50	37.0
	2.5	156.3	-45.50	38.7
BD44	20	132.1	-33.32	28.3
	10	139.9	-45.60	38.8
	5	146.7	-48.11	40.9
	2.5	145.0	-49.63	42.2
BD57	20	126.0	-37.02	37.6
	10	145.6	-45.89	46.6
	5	151.7	-46.54	47.3
	2.5	155.0	-47.71	48.4
BD69	20	145.3	-51.95	52.7
	10	157.0	-52.11	52.9
	5	162.1	-52.77	53.6
	2.5	162.3	-53.27	54.1
BD82	20	162.5	-51.79	52.6
	10	171.5	-52.14	52.9
	5	176.4	-55.35	56.2
	2.5	178.8	-56.79	57.7
BD84	20	166.0	-43.05	43.7
	10	174.7	-44.68	45.4
	5	178.0	-45.25	45.9
	2.5	180.0	-48.68	49.4

Table III. (continued)

Polymer	Cooling Rate (K/min)	T_p (°C)	H_c (J/g)	X_c^b (%)
BD90	20	168.2	-48.89	49.6
	10	173.7	-49.23	50.0
	5	179.1	-51.34	52.1
	2.5	184.5	-53.69	54.5
PBT	20	181.1	-57.49	58.4
	10	187.9	-55.14	56.0
	5	192.2	-54.54	55.4
	2.5	195.3	-54.73	55.6

^a Measured with a cooling rate of 10.0 K/min by DSC.

^b Estimated from the heat of fusion measured in the PET and its copolymers rich with EG unit using the heat of fusion (117.6 J/g) of the fully crystallized PET polymer but from the heat of fusion measured in the PBT and its copolymers rich with BG unit using the heat of fusion (98.5 J/g) of the fully crystallized PBT polymer.

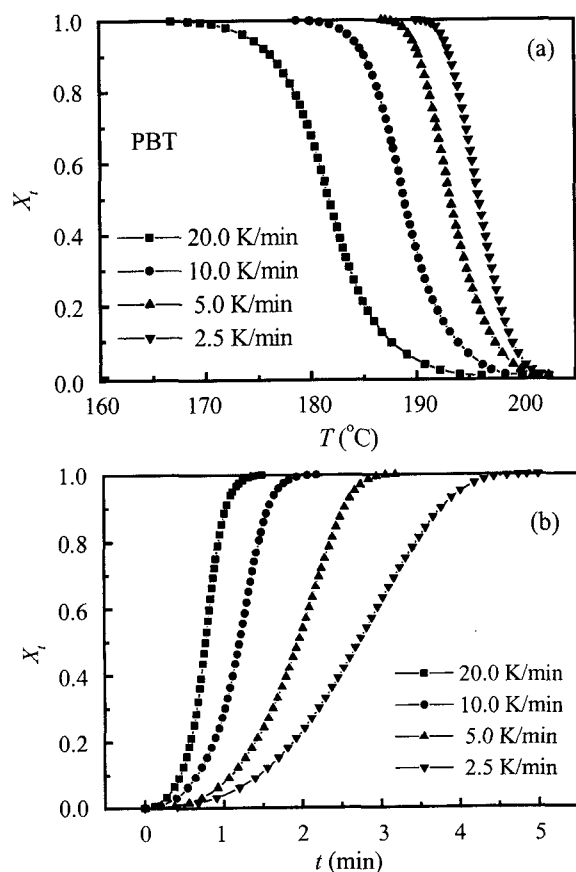


Figure 7. (a) Plots of relative crystallinities X_t s versus crystallization temperature T_c for PBT homopolymer crystallized non-isothermally at various cooling rates. (b) Plots of relative crystallinities X_t s versus crystallization time t for PBT homopolymer crystallized non-isothermally at various cooling rates.

and X_c . However, the X_c in PBT homopolymer exceptionally increases with cooling rate. This result may be associated with its rapid crystallization characteristic.

The relative crystallinities X_t s, which were obtained from the measured DSC exotherms, were analyzed in detail using Eqs. (1), (2), (3), (4), and (5) in the modified Avrami method. Figure 7 shows typical plots of X_t versus T and plots of X_t versus t . Figure 8 displays typical double-logarithmic plots of X_t versus $\log t$. The analyzed results are listed in Table IV.

For all the polymers, the crystallization rate constant k' increases with increasing cooling rate; the crystallization half-time $t_{1/2}$ shortens with increasing cooling rate. Conclusively, the non-isothermal crystallization is accelerated by

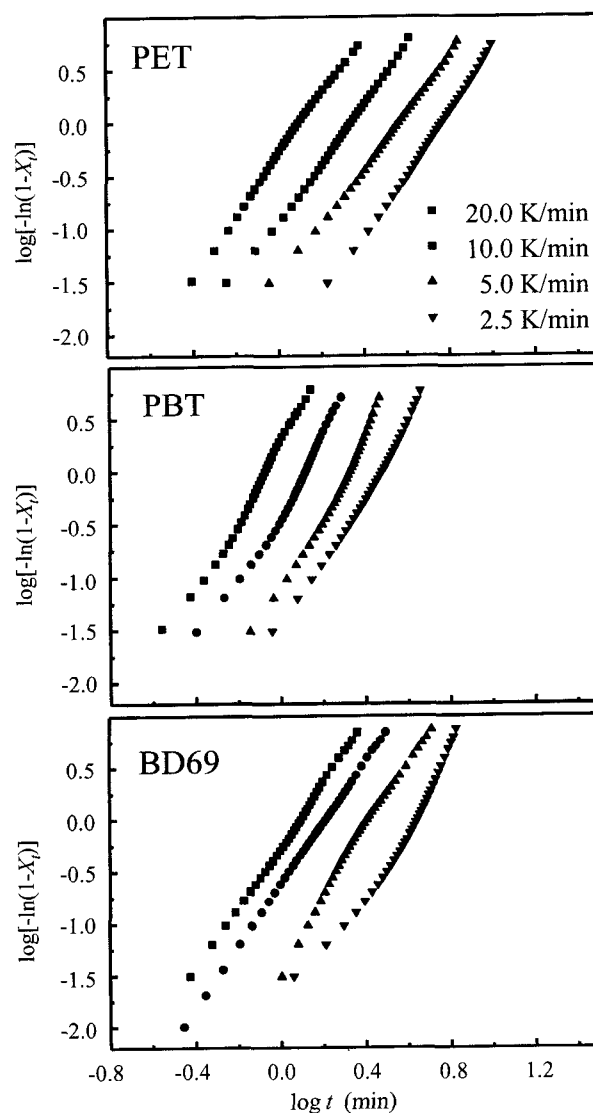


Figure 8. Avrami plots of relative crystallinities X_t s for PET, PBT, and BD69 copolymer crystallized non-isothermally at various cooling rates.

Table IV. Avrami Parameters of PET, PBT, and Their Copolymers

Polymer	Avrami Parameters	Cooling Rate (K/min)			
		2.5	5.0	10.0	20.0
PET	n	3.0	2.6	2.7	2.9
	k'	0.1229	0.5051	0.8066	1.0345
	$t_{1/2}$	1.79	1.13	0.95	0.87
BD8	n	3.2	3.2	2.8	3.0
	k'	0.2746	0.5180	0.7616	0.8565
	$t_{1/2}$	1.34	1.09	0.97	0.9328
BD16	n	3.4	3.4	2.8	2.5
	k'	0.0682	0.3317	0.7172	0.9035
	$t_{1/2}$	1.98	1.25	0.99	0.90
BD22	n	2.3	2.2	2.1	2.3
	k'	0.2230	0.5464	0.8041	0.9755
	$t_{1/2}$	1.65	1.12	0.93	0.86
BD30	n	2.4	2.1	2.2	2.2
	k'	0.1082	0.5417	0.7879	0.9539
	$t_{1/2}$	2.17	1.12	0.94	0.86
BD44	n	2.4	2.4	2.4	2.4
	k'	0.0711	0.5987	0.8528	1.0006
	$t_{1/2}$	2.57	1.06	0.92	0.86
BD57	n	2.8	3.0	2.7	2.3
	k'	0.2500	0.5938	0.8307	0.9364
	$t_{1/2}$	1.43	1.05	0.93	0.89
BD69	n	3.3	3.2	3.0	3.0
	k'	0.1527	0.5342	0.8660	0.9704
	$t_{1/2}$	1.59	1.08	0.93	0.89
BD82	n	3.4	3.1	3.0	2.9
	k'	0.2110	0.6588	0.9281	0.9971
	$t_{1/2}$	1.43	1.02	0.91	0.88
BD84	n	2.8	2.8	2.6	2.7
	k'	0.2538	0.7837	1.0461	1.0604
	$t_{1/2}$	1.43	0.96	0.85	0.85
BD90	n	3.0	3.0	2.9	2.7
	k'	0.1772	0.6013	0.9188	1.0379
	$t_{1/2}$	1.59	1.05	0.91	0.86
PBT	n	3.0	3.4	3.2	3.2
	k'	0.2753	0.6098	0.9215	1.0272
	$t_{1/2}$	1.36	1.04	0.91	0.88

increasing cooling rate. In contrast, the increasing of cooling rate causes a reduction in the X_c generated in the polymer as mentioned above.

In comparison, PBT homopolymer has relatively lower T_p and T_m (or T_m^o) than those of PET polymer. From the facts, one expects that PET polymer crystallizes more rapidly than

PBT polymer because the PET polymer having a relatively high T_m is always experienced to a relatively large degree of supercooling through the whole cooling process. However, PBT polymer crystallizes more rapidly and generates larger X_c than PET homopolymer when they crystallize under a same cooling rate. This suggests that PBT polymer owns a

rapid crystallization rate enough to overcome its disadvantage in the degree of supercooling due to the relatively low T_p and T_m , compared to PET polymer.

Based on the crystallization characteristics, the copolymers can be classified into two groups as follows. The first group includes BD16, BD30, and BD44 polymers that reveal a slower crystallization rate than that of PET polymer. In fact, the results are opposite to the expectation because they are composed of butylenes terephthalate units which have a tendency to crystallize rapidly. On the other hand, the other copolymers belong to the second group, which exhibit a rapid crystallization rate, compared to PET polymer: of course, these copolymers have a relatively slower crystallization rate than that of PBT polymer. Here, the relatively rapid crystallization behaviors in the second group of copolymers are understandable with counting the crystallization characteristic observed from PBT homopolymer. However, their crystallization rates are fluctuated with varying composition. That is, they do not show an exact correlation between crystallization rate and composition. This may result from a competition of ethylene terephthalate and butylenes terephthalate units in the crystallization. Such competitive crystallizabilities may be originated from the characteristic of both even-atomic-numbered ethylene terephthalate and butylenes terephthalate units in the polymer backbone which are inherently crystallizable.

The Avrami exponent n is found to vary over the range of 2.1-3.4, depending on the composition as well as the cooling rate. Overall, their n decreases slightly with increasing cooling rate except for PBT homopolymer. The variations in the estimated n are, perhaps, associated to some factors in the DSC measurement as follows. First, the n may depend highly on the overall volume of crystals (namely, overall crystallinity X_c) made through the crystallization process. When a polymer specimen is filled with a very small population of crystals through the crystallization process, there is a large uncertainty in the DSC measurement, consequently causing a relatively large error in the estimation of n value. As shown in Table III, rapid cooling rate can allow relatively low X_c in the non-isothermal crystallization, so that the rapid crystallization process has some possibility to cause an error in estimating n value. Second, rapid cooling rate causes high crystallization rate but also allows the secondary crystallization to occur. In general, the secondary crystallization takes place in complicate ways and its possibility becomes large as the degree of supercooling increases.²⁴ The involvement of such secondary crystallization always causes a reduction in the n value.

In particular, for the crystallization process with a relatively slow cooling rate such as 2.5 K/min, the n is estimated to be in the range of 2.9-3.4, depending on the composition, except for BD22, BD30, and BD44 copolymers. The n values are comparable with those reported for PET homopolymer and its copolymers containing either ethylene isophthalate or

oxydiethylene terephthalate unit which proceed crystallization through three-dimensional spherulitic growth with a predominant heterogeneous nucleation.^{5,6,25} And, the polymers made in this study contain a small amount of catalyst residue which was used in the bulk polymerization. Such catalyst residue may play as nuclei, so that the crystallization in all the used polymers might be initiated via heterogeneous nucleation mechanism. Therefore, PET and PBT homopolymers, as well as their copolymers might follow a heterogeneous nucleation and three-dimensional spherulitic growth in the non-isothermal crystallization.

The measured X_c s were analyzed further using Eq.(6) in the Ozawa method. Some of Ozawa plots are illustrated in Figure 9. And, some of the analyzed results are listed in Table V. In fact, when Ozawa analysis is done properly for a polymer crystallized at various cooling rates, its Ozawa plots should give a series of parallel lines with a same slope m . However, such Ozawa plots are not obtained for all the polymers studied in the present work. For each polymer

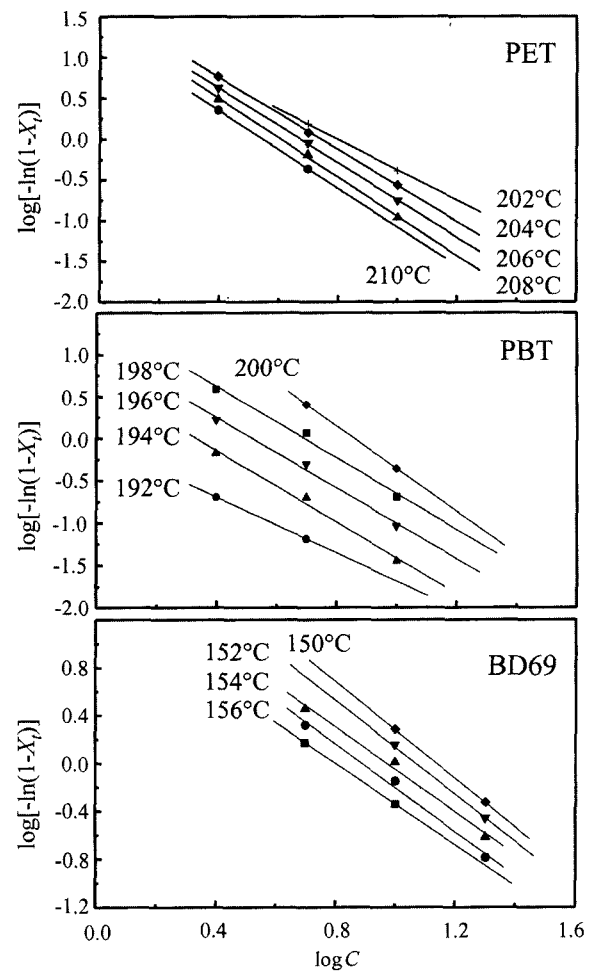


Figure 9. Ozawa plots of relative crystallinities X_c s for PET, PBT, and BD69 copolymer crystallized non-isothermally at various cooling rates.

Table V. Ozawa Exponent (*m*) and Cooling Function [*K*] (*T*) of PET, PBT, and Their Copolymers

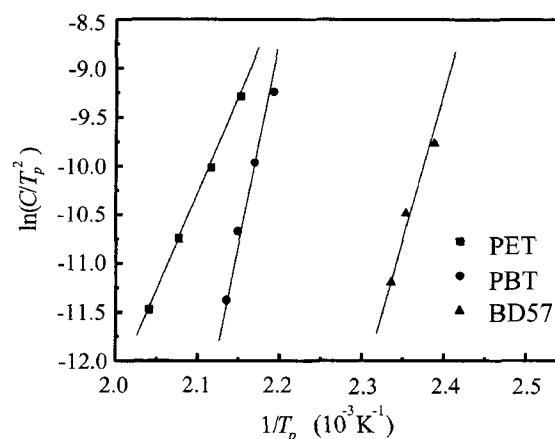
<i>T</i> (°C)	PET Homopolymer		PBT Homopolymer		BD69 Copolymer	
	log <i>K</i> (<i>T</i>)	<i>m</i>	log <i>K</i> (<i>T</i>)	<i>m</i>	log <i>K</i> (<i>T</i>)	<i>m</i>
210	1.296	2.4				
208	1.459	2.4				
206	1.537	2.3				
204	1.637	2.2				
202	1.521	1.9				
198			-0.041	2.5		
196			0.696	2.1		
194			1.083	2.1		
192			1.468	2.1		
190			2.171	2.5		
158					1.362	1.7
156					1.633	1.8
154					1.730	1.8
152					2.183	2.0
150					2.316	2.0

composition, the *m* varies with temperature rather than be constant. Overall, the *m* changes in the range of 1.9-2.5, depending on the composition as well as the temperature. These exponent *m* values are unrealistically too small, compared to those determined by the modified Avrami method. Conclusively, these results suggest that Ozawa method is not applicable to PET, PBT, and their copolymers undergone non-isothermal crystallization.

Limits in the application of Ozawa method have been also reported previously for PET, poly(trimethylene terephthalate), poly(ethylene-*co*-oxydiethylene terephthalate)s, poly(ethylene isophthalate-*co*-terephthalate)s, polyethylenes, poly(ether ether ketone)s (PEEKs), and poly(ether ether ketone ketone)s (PEEKKs).^{5,6,19,26,27}

Such limits of Ozawa analysis in the applications may be associated to several reasons as follows. First, Ozawa analysis does not count any secondary crystallization although it covers a relatively wide range of crystallization temperature in which the secondary crystallization occurs in a certain portion not to be negligible. Second, The Ozawa exponent *m* may be characteristic to change rather than have a fixed value, depending on the crystallization temperature, the cooling rate, and the transformed volume function. Third, Ozawa plot, in practice, is limited to only two or three data points, consequently leading to a relatively large error in determining Ozawa parameters.

In addition, the Kissinger plot was performed further for PET, PBT, and BD57 copolymer. The results are presented in Figure 10. For these polymers the Kissinger plots exhibit

**Figure 10.** Kissinger plots of PET, PBT, and BD57 copolymer crystallized at various cooling rates.

a relatively good linearity. From the slope in the plot, the crystallization activation energy E_a is estimated: 163.2 kJ/mol for PET, 260.4 kJ/mol for PBT, and 220.1 kJ/mol for BD57. Here, the ΔE_a in the melt crystallization is negative since the transforming the molten fluid into the crystalline state has to release energy. In the view of kinetics, the activation energy can correlate to the crystallization rate. As described earlier, the crystallization rate constant k' , which was estimated by the modified Avrami analysis, decreases relatively in the order PBT > BD57 > PET. Conclusively, the lower activation energy of crystallization drives the more

rapid crystallization rate.

Conclusions

A series of PEBT copolymers, as well as PET and PBT homopolymers, were synthesized by conventional bulk polycondensation. The compositions and molecular weights were determined. Their thermal properties were also measured: T_g , T_m , T_m^o , and T_p . The copolymers were evident to be a random copolymer from their single T_g behavior. The copolymer consisting of both even-atomic-numbered EG unit and BG units is crystallizable over the whole composition. However, their crystallizability still depends on the composition.

The non-isothermal crystallization behavior was investigated with varying cooling rate. The crystallizations are fitted better by the modified Avrami analysis than the Ozawa analysis. The results suggest that the copolymers, as well as the homopolymers follow a heterogeneous nucleation and spherulitic growth mechanism in the crystallization. However, the crystallization behaviors are still deviated slightly from the prediction of the modified Avrami analysis because of the involvement of secondary crystallization and the reduction of X_c caused under rapid cooling rate. The crystallization rate is accelerated by increasing cooling rate. PBT exhibits a more rapid crystallization rate than PET, so that the crystallization rate of PBT polymer is reduced by incorporating EG unit in the backbone, whereas that of PET is accelerated by incorporating BG unit. In addition, the activation energy in the crystallization was estimated by the Kissinger method. Overall, in the crystallization lower activation energy leads to more rapid crystallization rate.

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