Synthesis and Properties of Copolyesters of p,p'-Bibenzoic Acid, Dimer Acid, and Alkylene Glycol

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ABSTRACT: Copolyesters of p,p'-bibenzoic acid, dimer acid, and an alkylene glycol are prepared by melt polycondensation of of dimethyl p,p'-bibenzoate, dimer acid, and an alkylene glycol. The copolyesters are characterized by the inherent viscosity, FTIR, proton NMR, DSC, polarized microscopy, and X-ray diffraction. The polymer composition and sequence distribution of the copolyesters can be seen from the NMR spectra. The copolyesters exhibit a degree of randomness of about 1, indicating that they are random copolymers. The glass-transition temperature (T_g) and the melting point (T_m) of the copolyesters are found from the DSC heating curves. When the content of the flexible dimer acid unit increases, the T_g of the copolyesters decreases significantly. The copolymerization effect decreases the crystallinity and the T_m of the copolyesters. It can be seen from the DSC, polarized microscopy, and X-ray diffraction data that some copolyesters derived from 1,6-hexanediol and 1,5-pentanediol exhibit a monotropic smectic phase. As the molar content of the dimer acid unit increases, the isotropic–mectic transition temperature and the smectic order decreases significantly. The liquid crystallinity is completely destroyed at certain molar contents of the dimer acid unit. The smectic order of the copolyesters derived from 1,6-hexanediol is significantly higher than that of the copolyesters derived from 1,5-pentanediol, and it is described as an odd–even effect. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 750–758, 2003

Key words: copolyesters; p,p'-bibenzoic; dimer acid; thermotropic; smectic; thermal transition

INTRODUCTION

Various copolyesters are used as hot melt adhesives. Typical examples are copolyesters of terephthalic acid, adipic acid, and 1,4-butanediol or ethylene glycol; copolyesters of terephthalic acid, isophthalic acid, and 1,4-butanediol or ethylene glycol; copolyesters of terephthalic acid, isophthalic acid, adipic acid; and 1,4-butanediol; and copolyesters of poly(butylene terephthalate) and poly(caprolactone).[1–10] The use of a more rigid diacid such as p,p'-bibenzoic acid may improve the heat resistance. Furthermore, various poly(alkylene p,p'-bibenzoate)s exhibit thermotropic liquid crystallinity.[11–14] The incorporation of the p,p'-bibenzoate into the copolyesters may render interesting properties such as liquid crystalline behavior. Copolyesters of p,p'-bibenzoic acid, adipic acid, and an alkylene glycol were prepared and studied previously.[15] The use of p,p'-bibenzoic acid has been found to raise the glass-transition temperature of the copolyesters significantly. If a more flexible aliphatic diacid is used instead of adipic acid, the flexibility of the copolyesters is increased. Dimer acid has been widely used to design hot melt adhesives.[16,17] The incorporation of the dimer acid unit into the copolyesters will render better flexibility.

This article describes the synthesis and properties of the copolyesters of p,p'-bibenzoic acid, dimer acid, and an alkylene glycol. The general formula of the copolyesters is shown below:

$$—(—CO—C_6H_4—C_6H_4—CO—O—(CH_2)_n—O—)_{1-x}$$
$$—(—CO—C_{34}H_{68}—CO—O—(CH_2)_n—O—)_x—$$
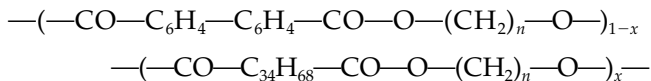
where x is the charge molar fraction of dimer acid in the diacid monomers, n is the carbon number of the alkylene glycol, and each copolyester is denoted as BDn(x).

EXPERIMENTAL

Dimethyl p,p'-bibenzoate was supplied by Ihara Chemical Industry Co., Ltd. A saturated dimer acid (PRIPOL 1009) with an acid value of 195–200 was supplied by Unichema. All other reagents were Merck reagent grade, and they were used as received.

The copolyesters were prepared by melt polycondensation of dimethyl p,p'-bibenzoate, dimer acid, and

TABLE I
Charge Composition, Measured Polymer Composition, and
Inherent Viscosity (η_{inh}) of Copolyesters

Sample	Type of alkylene glycol	Charge composition[a]	Polymer composition[a]	η_{inh} (dL/g)
BD2(0.5)	Ethylene glycol	0.5:0.5:1.4	0.46:0.52:1.00	0.32
BD3(0.5)	1,3-Propanediol	0.5:0.5:1.4	0.46:0.53:1.00	0.48
BD4(0.5)	1,4-Butanediol	0.5:0.5:1.4	0.47:0.51:1.00	0.38
BD5(0.1)	1,5-Petanediol	0.9:0.1:1.4	0.83:0.16:1.00	0.94
BD5(0.2)	1,5-Petanediol	0.8:0.2:1.4	0.76:0.22:1.00	0.68
BD5(0.3)	1,5-Petanediol	0.7:0.3:1.4	0.67:0.32:1.00	0.59
BD5(0.4)	1,5-Petanediol	0.6:0.4:1.4	0.56:0.47:1.00	0.54
BD5(0.5)	1,5-Petanediol	0.5:0.5:1.4	0.49:0.53:1.00	0.48
BD6(0.1)	1,6-Hexanediol	0.9:0.1:1.4	0.84:0.15:1.00	0.61
BD6(0.2)	1,6-Hexanediol	0.8:0.2:1.4	0.77:0.21:1.00	0.86
BD6(0.3)	1,6-Hexanediol	0.7:0.3:1.4	0.67:0.33:1.00	0.87
BD6(0.4)	1,6-Hexanediol	0.6:0.4:1.4	0.57:0.40:1.00	0.55
BD6(0.5)	1,6-Hexanediol	0.5:0.5:1.4	0.46:0.52:1.00	0.49
BD6(0.6)	1,6-Hexanediol	0.4:0.6:1.4	0.37:0.59:1.00	0.47
BD6(0.8)	1,6-Hexanediol	0.2:0.8:1.4	0.20:0.82:1.00	0.39

[a] The molar ratio of dimethyl p,p'-bibenzoate dimer acid alkylene glycol.

an alkylene glycol (carbon number = 2–6) similar to a method described previously.[6]

The inherent viscosity (η_{inh}) of the copolyesters in phenol/1,10,2,2 tetrachloroethane (60/40 w/w) at a concentration of 0.5 g/dL was determined with an Ubbelohde viscometer at 30°C. The IR spectra of the copolyesters were measured by a Perkin Elmer 1600 FTIR. Their characteristic peaks are at 3066, 2926, 2855 (C—H stretching), 1709 (C=O stretching), and 1608 and 1559 cm^{-1} (aromatic). The proton NMR spectra of the copolyesters in d-trifluoroacetic acid were determined by a Bruker AM 400 NMR. The DSC heating curves from −100 to 250°C were determined by a Du Pont DSC 910 at a heating rate of 20°C/min under nitrogen. The DSC cooling curves from 260 to 40°C were determined by a Perkin
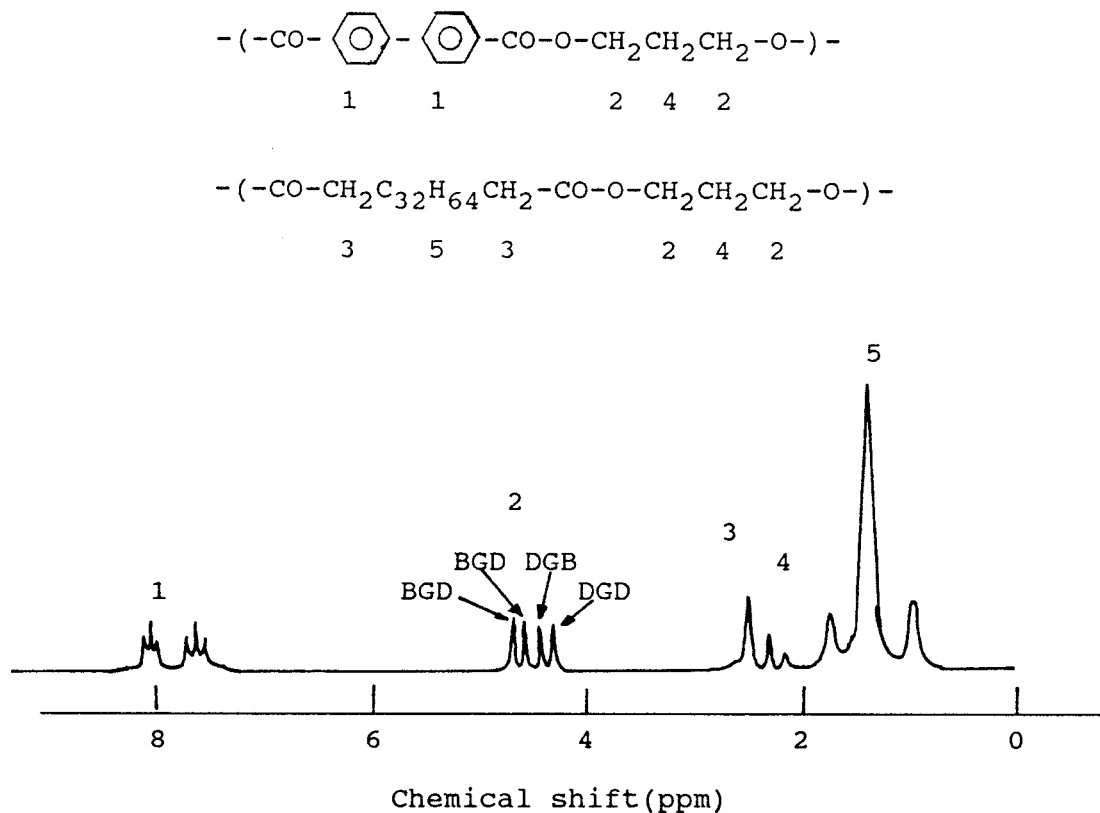

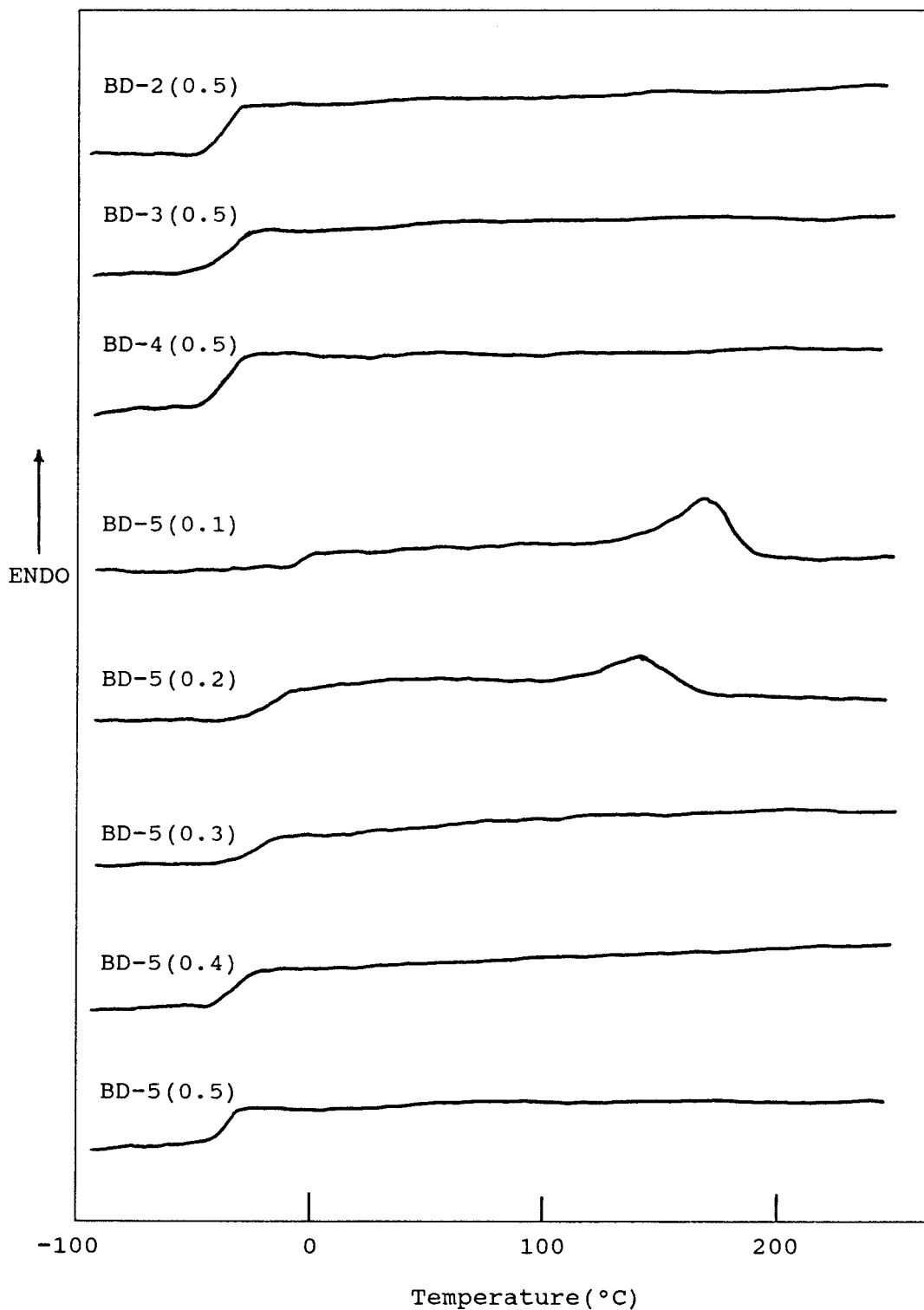**Figure 1** The proton NMR spectrum of BD3(0.5).

Figure 2 The DSC heating curves of BD2(0.5), BD3(0.5), BD4(0.5), and BD5(x) copolyesters.

Elmer DSC7 at a cooling rate of 20°C/min under nitrogen. The X-ray diffraction patterns were recorded on a Shimadzu XD-5 X-ray diffractometer using Cu Kα radiation. The liquid crystalline texture was investigated on a Leitz polarizing microscope equipped with a hot stage.

RESULTS AND DISCUSSION

The charge compositions used to prepare the copolyesters are summarized in Table I. In the preparation of the copolyesters, the molar ratio of diacid monomers to alkylene glycol was held at 1.0:1.4. First, transesteri-
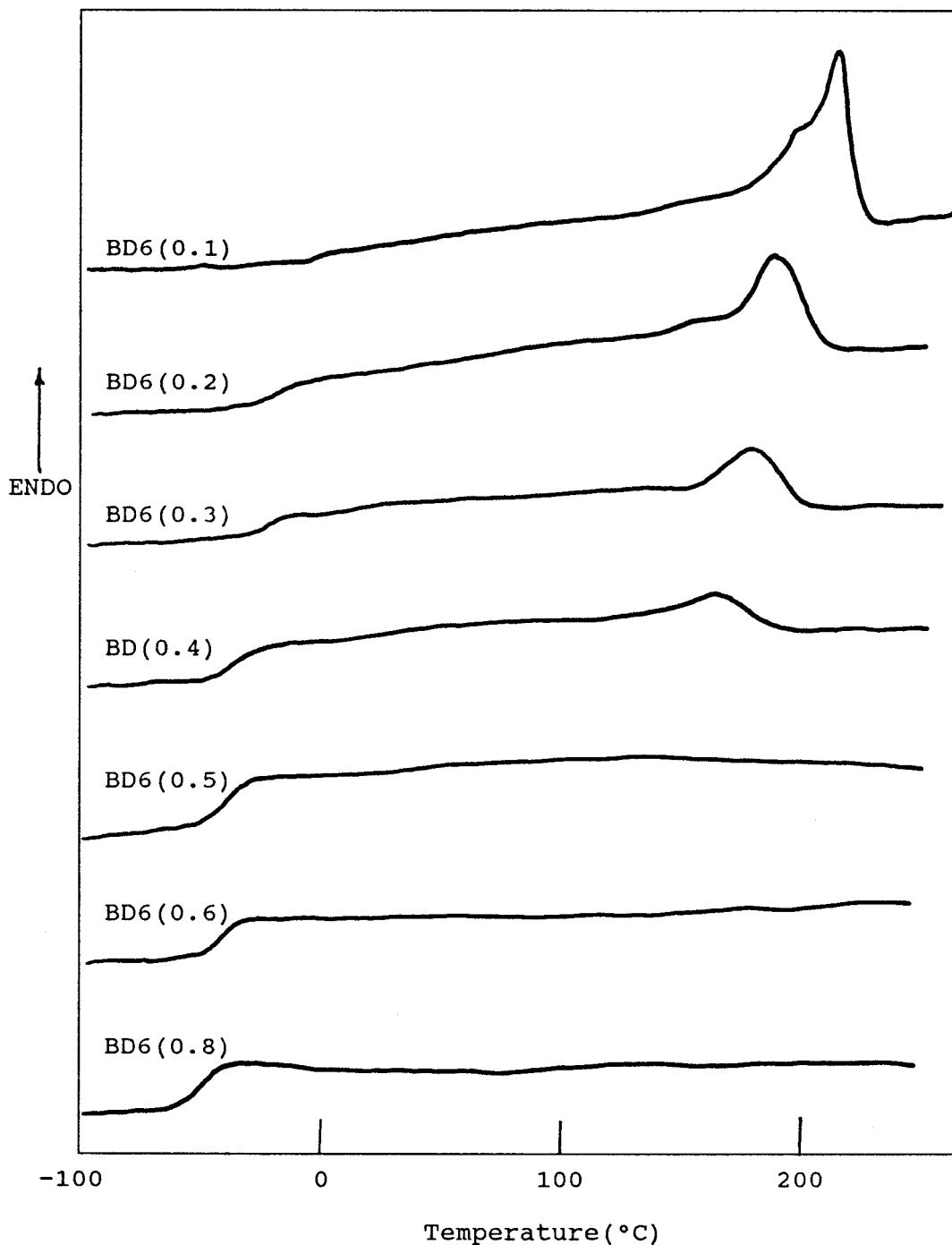
Figure 3 The DSC heating curves of BD6(x) copolyesters.

fication occurred between dimethyl p,p'-bibenzoate and the alkylene glycol, and esterification occurred between the dimer acid and the alkylene glycol at 220°C. The by-products (methanol and water) were distilled off. After most of the methanol and water were distilled off, the reaction temperature was raised to 240° and a vacuum was applied. The excess alkylene glycol was distilled off. A high vacuum (0.5 mmHg) was applied for a long enough period to obtain high molecular weight copolyesters. The inher-

ent viscosity values of the copolyesters are shown in Table I.

The copolyesters show similar IR spectra. Their characteristic peaks are at 3066, 2926, 2855 (C—H stretching), 1708 (C=O stretching), and 1608 and 1559 cm^{-1} (aromatic). For the BD5(x) and BD6(x) copolyesters, the ratio of the absorbance of the aromatic peak at 1608 cm^{-1} to that of the carbonyl peak at 1708 cm^{-1} decreases as the content of dimer acid increases, as expected.

The proton NMR spectra reveal more information about the composition and structure of the copolyesters. Figure 1 shows a typical proton NMR spectrum of BD3(0.5). The assignments of the protons are also shown in Figure 1. It can be seen that the resonance of the α-methylene protons (H2) of the alkylene glycol unit exhibits a quartet for BD3(0.5). The copolyesters have four possible sequences: BGB, BGD, DGB, and DGD, where B, G, and D represent the units of p,p'-bibenzoic acid, alkylene glycol, and dimer acid, respectively. Clearly, the proton NMR spectrum of the H2 of BD3(0.5) can distinguish these four different sequences, and the sequence distribution can be determined as described previously.[6,15] Also, the sequence distribution of BD2(0.5) and BD4(0.5) can be determined by the proton NMR spectra through the analysis of their resonance peaks of the α-methylene protons of the glycol unit. The degree of randomness is $[I_{BGD}/(I_{BGB} + I_{BGD})] + [I_{DGB}/(I_{DGD} + I_{DGB})]$, where I denotes the integrated intensity of each sequence. For random copolymers, B = 1; for alternative polymers, B = 2; and for block copolymers, B ~ 0. The degree of randomness values of BD2(0.5), BD3(0.5), and BD4(0.5) are close to 1, indicating a random structure. Thus, the copolyesters that are obtained are random copolymers. Even though the reactivity may be different for the two diacid monomers, the transesterification reaction renders a random distribution.

The proton NMR spectra can be used to determine the polymer composition of the copolyesters. For example, the polymer composition of BD3(0.5) can be calculated from the ratio of integrated intensities of H1:H3:H2. The polymer composition of other copolyesters can be determined similarly. The results are shown in Table I.

Considering a typical example, BD6(0.5), the charge molar ratio of dimethyl p,p'-bibenzoate/dimer acid/1,6-hexanediol was 0.5:0.5:1.4. The calculated molar ratio of p,p'-bibenzoate units/dimer acid units/hexamethylene units in the polymer is 0.46:0.52:1.00. Thus, most of the excess 1,6-hexanediol was distilled off during the preparation of BD6(0.5). The molar ratio of the p,p'-bibenzoate unit to the dimer acid unit of the copolyesters is somewhat smaller than the charge molar ratio as shown in Table I. This is different than the case of the copolyesters of p,p'-bibenzoic acid, adipic acid, and an alkylene glycol in which the molar ratio of p,p'-bibenzoate to adipate was found to be higher than the charge molar ratio of dimethyl p,p'-bibenzoate to adipic acid.[15] This would be due to the very high boiling point of the dimer acid and related adducts, and more adducts of p,p'-bibenzoate have been distilled off during synthesis.

The DSC heating curves from -100 to $250°C$ of the copolyesters are shown in Figures 2 and 3. It can be seen that the thermal properties are significantly affected by the composition. The DSC heating curves of

TABLE II
Glass-Transition and Melting Temperatures (T_g, T_m and Melting Enthalpy (ΔH_m) of Copolyesters

Sample	T_g (°C)	T_m (°C)	ΔH_m (cal/g)
BD2(0.5)	−39	—	—
BD3(0.5)	−37	—	—
BD4(0.5)	−42	—	—
BD5(0.1)	−10	173	4.87
BD5(0.2)	−17	144	2.04
BD5(0.3)	−32	—	—
BD5(0.4)	−34	—	—
BD5(0.5)	−38	—	—
BD6(0.1)	−4	212	10.9
BD6(0.2)	−20	188	6.71
BD6(0.3)	−27	178	3.15
BD6(0.4)	−39	168	2.12
BD6(0.5)	−40	—	—
BD6(0.6)	−43	—	—
BD6(0.8)	−46	—	—

some copolyesters exhibit only a step inflection, and those of other copolyesters exhibit a step inflection and a main endothermic peak. The midpoint of the inflection is taken as the glass-transition temperature (T_g) and the peak temperature of the endotherm is taken as the melting temperature (T_m). The T_g, T_m, and ΔH_m values of the copolyesters are summarized in Table II.

It can be seen that the content of the dimer acid unit (x) is a major factor influencing the T_g of the copolyesters, as shown in Table II. For the BD5(x) and BD6(x) copolyesters, the T_g decrease as x increases, as expected. The T_g values of BDn(0.5)s are around $-40°C$, which is about 30°C lower than those of the copolyesters of p,p'-bibenzoic acid, adipic acid, and an alkylene glycol with similar molar composition. The enhancement of the flexibility by the incorporation of the dimer acid is obvious. Because the copolyesters are random copolymers, the T_g would be attributed to the weight average of the constructed units. The molecular weight of the dimer acid (566) is considerably higher than that of adipic acid (146). The weight percentage of the dimer acid unit in the copolyesters is also higher than that of the adipate unit in the copolyesters of p,p'-bibenzoic acid, adipic acid, and an alkylene glycol with similar molar composition. In combination with the more flexible nature of the dimer acid unit, the T_g of the copolyesters is lowered significantly.

As shown in Table II, the composition has a significant effect on the T_m of the copolyesters. For BD5(x) copolyesters with $x \geq 0.3$ and other copolyesters with $x \geq 0.5$, no melting endotherm was found by DSC, indicating that they are amorphous. This is different than the case of the copolyesters of p,p'-bibenzoic acid, adipic acid, and an alkylene glycol, which were found to be crystalline with an obvious DSC endothermic peak.[15] Because the structure of the dimer acid unit is
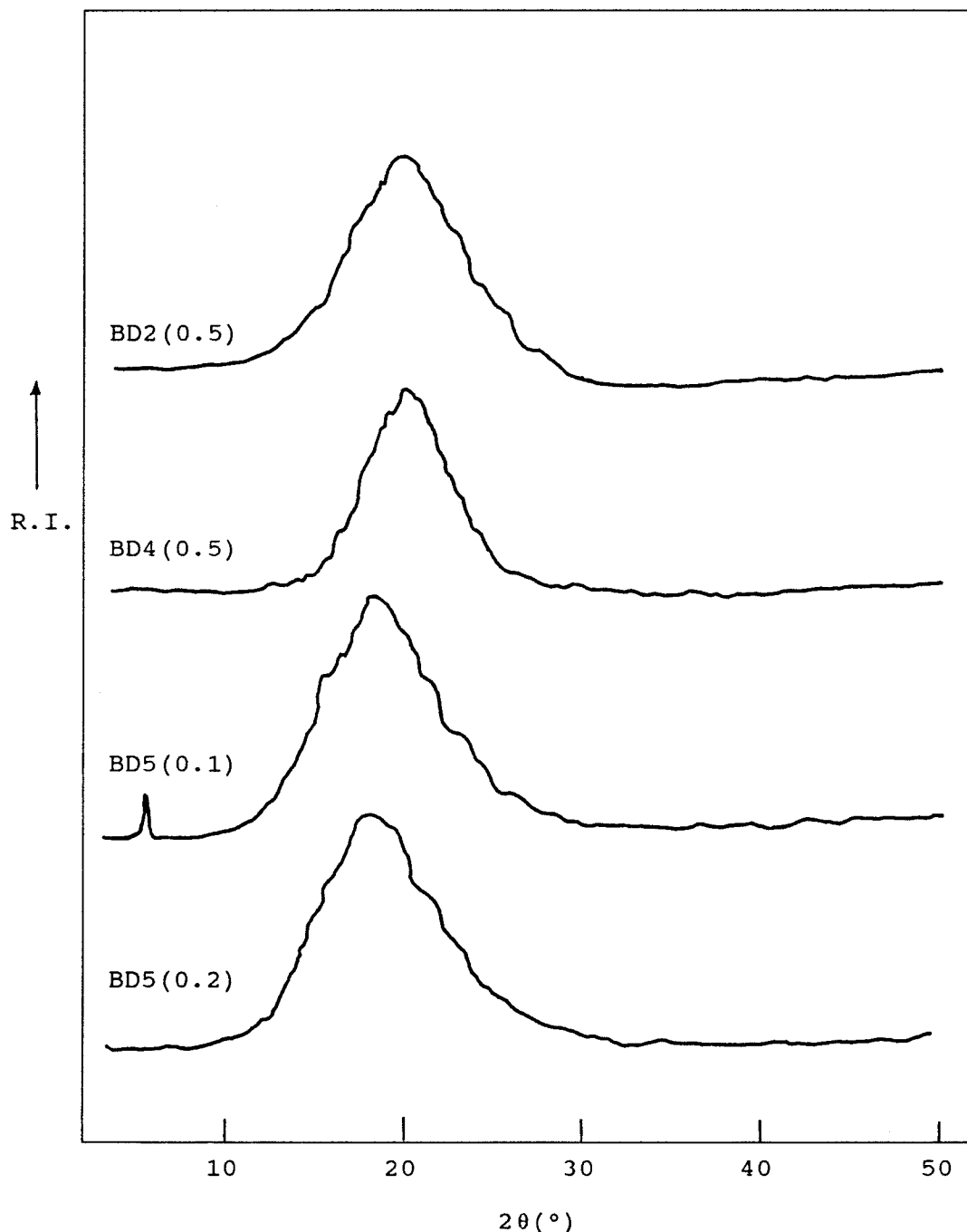
Figure 4 The X-ray diffraction pattern of BD2(0.5), BD4(0.5), and some BD5(x) copolyesters.

nonlinear and the length of the dimer acid unit ($-CO-C_{34}H_{68}-CO-$) is considerably different than that of the p,p'-bibenzoate unit ($-CO-C_6H_4-C_6H_4-CO-$), the copolyesters tend to form amorphous materials as the content of the dimer acid unit increases. BD6(x) copolyesters with x = 0.1–0.4 and BD5(x) copolyesters with x = 0.1–0.2 are crystalline, and their T_m and ΔH_m decreases as x increases, as shown in Table II.

The X-ray diffraction patterns of some typical copolyesters are shown in Figures 4 and 5. All the amorphous copolyesters exhibit a broad scattering peak. Although no obvious crystalline diffraction peak has been found for BD5(0.1) and BD5(0.2), some BD6(x) copolyesters do show obvious crystalline diffraction peaks at 2θ = 18.9, 20.6, and 23.4° as shown in Figure 5. As x increases, the diffraction peaks of BD6(x) copolyesters tend to become broader and even disappear for BD6(0.4), indicating a decreasing trend in the crystallinity. Thus, the trend obtained from the X-ray diffraction patterns is qualitatively consistent with the DSC data.
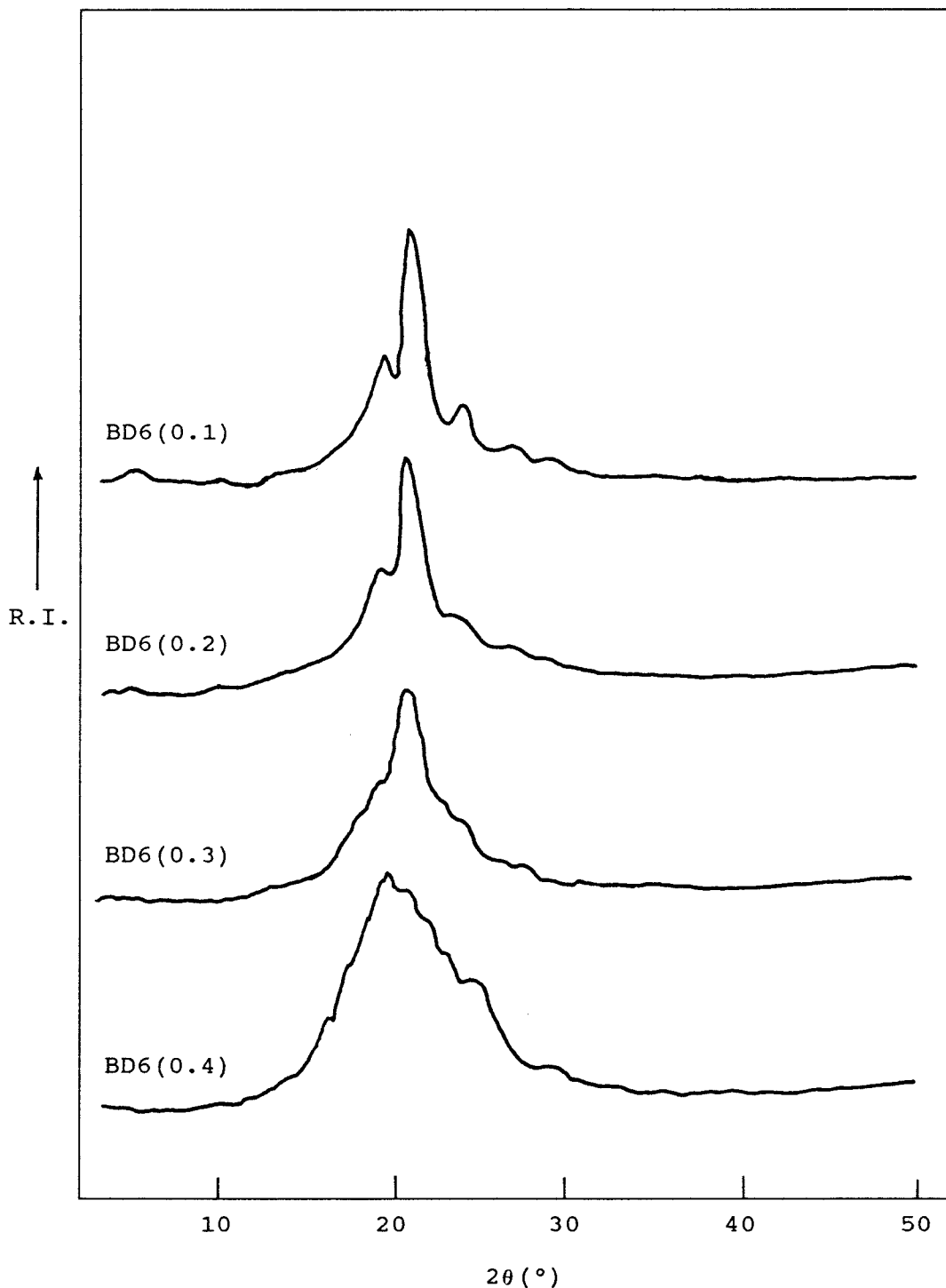
Figure 5 The X-ray diffraction pattern of some BD6(x) copolyesters.

Both poly(hexamethylene p,p'-bibenzoate) and poly(pentamethylene p,p'-bibenzoate) have been shown to form a smectic phase.[11–13] The DSC heating and cooling curves of high molecular weight poly-(hexamethylene p,p'-bibenzoate) and poly(pentamethylene p,p'-bibenzoate) have been found to exhibit two obvious endotherms and exotherms, respectively, indicating the formation of an enantiotropic smectic phase.[18] BD5(x) and BD6(x) copolyesters contain segments that may form a smectic phase. However, we cannot distinguish the liquid crystalline transitions from the DSC heating curves for the BD5(x) and BD6(x) copolymers.

The DSC cooling curves from 260 to 40°C of some BD5(x) and BD6(x) copolyesters are shown in Figure 6. Some of these copolyesters exhibit two exotherms
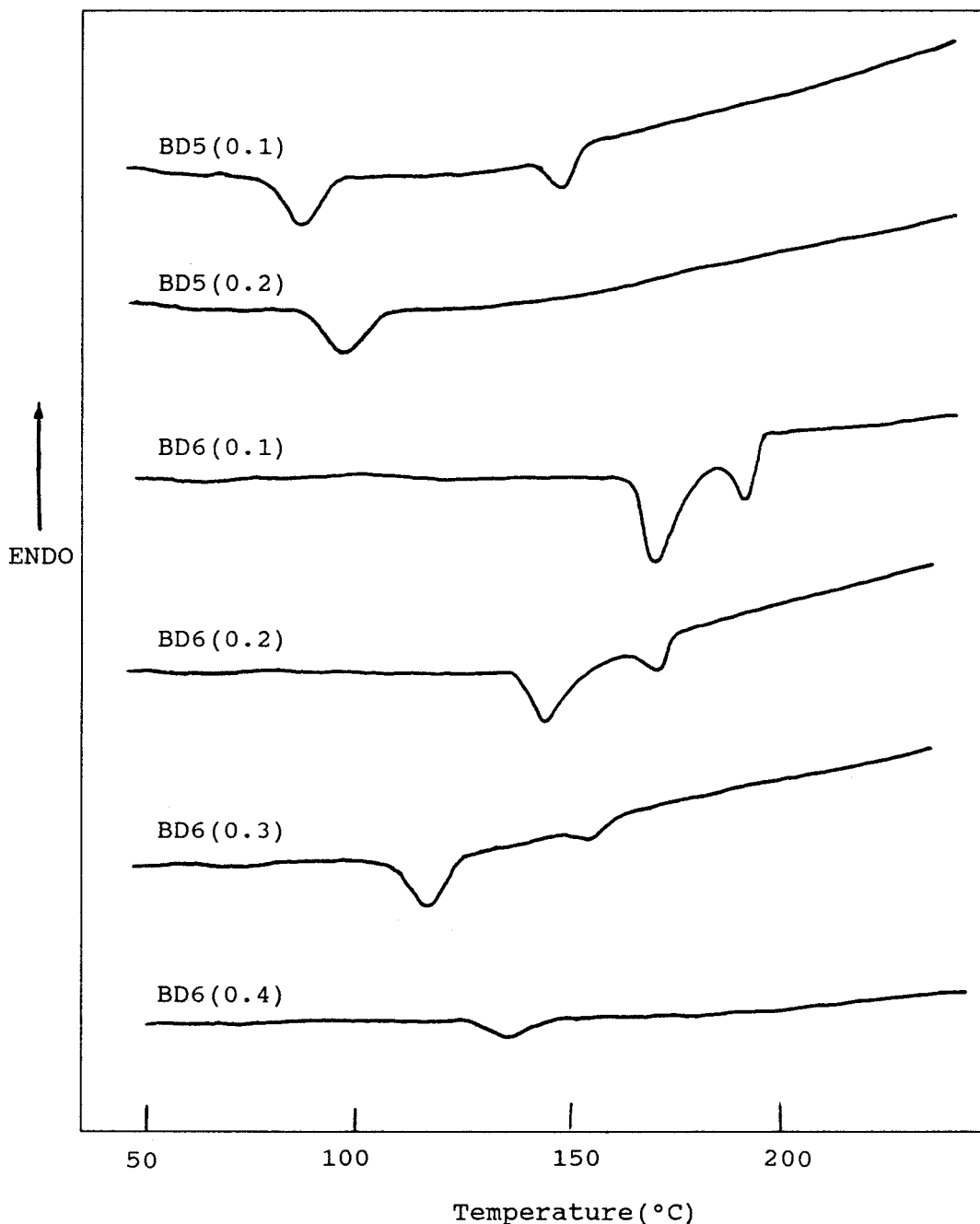
Figure 6 The DSC cooling curves of some BD5(x) and BD6(x) copolyesters.

upon cooling, indicating the possible existence of a liquid crystalline phase. The first appearing exotherm at higher temperature is taken as T_a and the latter appearing exotherm is taken as T_b. The transition temperature and the corresponding transition heats are tabulated in Table III. As shown in Figure 4, the X-ray diffraction pattern of BD5(0.1) exhibits an obvious peak at $2\theta = 5.8°$, corresponding to a layered spacing of 1.52 nm. The observed layered spacing is slightly shorter than the fully extended length of the repeat unit of poly(pentamethylene p,p'-bibenzoate) (1.72 nm), indicating the possible existence of a smectic

phase.[13] As shown in Figure 5, the X-ray diffraction patterns of BD6(0.1) and BD6(0.2) exhibit a layered spacing peak of 1.75 nm, which is also slightly shorter than the fully extended length (1.96 nm) of the repeat unit of poly(hexamethylene p,p'-bibenzoate). In combination with the two exotherms exhibited by the copolyesters upon cooling, which is a fanlike texture observed on the polarized microscope between T_a and T_b, the copolyesters would display a monotropic smectic phase. The T_a value corresponds to an isotropic–smectic transition, and T_b corresponds to a smectic–crystalline transition.

TABLE III
First and Second Exotherm Temperatures (T_a, T_b) and Corresponding Transition Heats (ΔH_a, ΔH_b) of BD5(x) and BD6(x) Copolyesters

Sample	T_a (°C)	ΔH_a (cal/g)	T_b (°C)	ΔH_b (cal/g)
BD5(0.1)	148	1.69	86	2.97
BD5(0.2)	94	1.89	—	—
BD6(0.1)	191	2.42	170	6.80
BD6(0.2)	170	0.78	144	5.63
BD6(0.3)	153	0.26	117	2.94
BD6(0.4)	133	1.64	—	—

As shown in Table III, the composition and type of alkylene glycol used significantly affected the smectic transition temperatures and transition heats. BD6(x) copolyesters with x = 0.1–0.3 exhibit a monotropic smectic phase, but BD6(0.4) shows no liquid crystallinity. The effect of the composition on the smectic transitions of the BD6(x) copolyesters can be described as the effect of the sequence length of the poly(hexamethylene p,p'-bibenzoate) segments. Because the copolyesters are random copolymers, as the dimer acid unit content or increases, the average sequence length of the poly(hexamethylene p,p'-bibenzoate) segments decreases. Accordingly, the isotropic–smectic transition temperature and the transition heat decrease. When $x \geq 0.4$, the smectic order is completely destroyed. The effect of the composition on the smectic transitions of the BD5(x) copolyesters follows a similar trend as shown in Table III. But the smectic order is completely destroyed at a lower dimer acid unit content (x = 0.2). The ΔH_b (the smectic order) of BD5(x) copolyesters is also significantly lower than that of BD6(x) copolyesters at a similar composition. This would be due to the odd–even effect. The carbon number of the alkylene unit of BD5(x) copolyesters is odd, and it is more difficult for the mesogenic unit to pack in an ordered phase. Thus, BD6(x) copolyesters with an even carbon number of alkylene units exhibit higher smectic order.

CONCLUSION

Copolyesters of p,p'-bibenzoic acid, dimer acid, and an alkylene glycol have been prepared by melt polycondensation. The polymer composition and sequence distribution of the copolyesters can be determined from the proton NMR spectra. The copolyesters ex-hibit a degree of randomness of about one, indicating that they are random copolymers. The T_g and T_m values of the copolyesters can be seen from the DSC heating curves. When the content of the flexible dimer acid unit increases, the T_g of the copolyesters decreases significantly. The copolymerization effect decreases the crystallinity and T_m of the copolyesters. BD5(x) copolyesters with $x \geq 0.3$ and other copolyesters with $x \geq 0.5$ are amorphous. BD5(0.1) and BD6(x) copolyesters with x = 0.1–0.3 exhibit a monotropic smectic phase. As the molar content of the dimer acid unit increases, the isotropic–smectic transition temperature and the smectic order decrease significantly. The smectic order is completely destroyed at x = 0.2 for BD5(x) copolyesters or 0.4 for BD6(x) copolyesters. The smectic order of the BD6(x) copolyesters is significantly higher than that of the BD5(x) copolyesters, and this is described as an odd–even effect.

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