Synthesis and Properties of Poly(alkylene p,p'-bibenzoate-co-adipate)s

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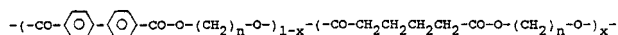
ABSTRACT: Various poly(alkylene p,p'-bibenzoate-co-adipate)s were prepared by melt polycondensation of dimethyl-p,p'-bibenzoate, adipic acid, and an alkylene glycol. The copolyesters were characterized by inherent viscosity, FTIR, proton NMR, DSC, polarized microscopy, and X-ray diffraction. The polymer composition and sequence distribution of the copolyesters can be seen from NMR spectra. The copolyesters exhibit a degree of randomness of about 1, indicating that they are random copolymers. From the DSC data, the glass transition temperature (T_g) and melting point (T_m) of the copolyesters can be detected. When the content of the flexible adipate unit increases, the T_g of copolyesters decreases significantly. The type of alkylene glycol used also affects the T_g to some extent. The copolymerization effect decreases crystallinity and the T_m of the copolyesters. The DSC, polarized microscopy, and X-ray diffraction data show that some copolyesters derived from 1,6-hexanediol exhibit a monotropic smectic phase. As the molar fraction of adipate unit in diacid units, x, is more than 0.4, the liquid crystallinity is completely destroyed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65**: 893–900, 1997

INTRODUCTION

Various copolyesters can be 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 polycaprolactone.[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.

In this article, the synthesis and properties of the copolyesters of p,p'-bibenzoic acid, adipic acid, and an alkylene glycol are described. The general formula of the copolyesters is shown below:

$$-(-CO-\langle\bigcirc\rangle-\langle\bigcirc\rangle-CO-O-(CH_2)_n-O-)_{1-x}-(-CO-CH_2CH_2CH_2CH_2-CO-O-(CH_2)_n-O-)_x-$$

where x is the charge molar fraction of adipic acid in the diacid monomers, n is the carbon number of the alkylene glycol, and each copolyester is denoted as BB/AA-$n(x)$.

EXPERIMENTAL

Dimethyl p,p'-bibenzoate was supplied by Ihara Chemical Industry Co. (Japan). All other re-

agents were Merck reagent grade and used as received. The copolyesters were prepared by melt polycondensation of dimethyl p,p'-bibenzoate, adipic acid, and an alkylene glycol similar to a method described previously.[6]

The inherent viscosity of the copolyesters in phenol/1,1,2,2-tetrachloroethane (60/40 wt/wt) was determined using an Ubbelohde viscometer at 30°C. The IR spectra of the copolyesters were measured by a Perkin-Elmer 1600 FTIR. The characteristic peaks of the copolyesters are at 2926 and 2855 cm^{-1} (C—H stretching), 1709 cm^{-1} (C=O stretching), and 1608 and 1559 cm^{-1} (aromatic). The ^{1}H-NMR spectra of the copolyesters in d-trifluoroacetic acid were determined using a Bruker AM 400 NMR with TMS as the internal standard. The DSC heating curves from -100 to 250°C were determined by a DuPont 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-Elmer DSC7 at a cooling rate of 20°C/min under nitrogen. Optical textures were observed using a Leitz polarizing microscope equipped with a heating stage. The X-ray diffraction patterns were recorded on a Mac Science diffractometer equipped with a Laue camera with an exposure time of 3 h.

RESULTS AND DISCUSSION

The charge compositions used to prepare the copolyesters are shown in Table I. In the prepara-tion of the copolyesters, the molar ratio of diacid monomers to alkylene glycol was held at 1.0 : 1.4. At first, transesterification occurred between dimethyl p,p'-bibenzoate and the alkylene glycol and esterification occurred between the adipic acid and the alkylene glycol at 210°C, and methanol and water were distilled off. After most of the methanol and water were distilled off, the reaction temperature was increased to 240°C and a low vacuum was applied. The excess alkylene glycol was distilled off. Then, a high vacuum (0.5 mmHg) was applied for a long enough period to obtain high molecular weight copolyesters.

It should be noted that the excess alkylene glycol would be evacuated out. This can be verified by the ^{1}H-NMR spectra. Figure 1 shows a typical ^{1}H-NMR spectrum of BB/AA-6(0.3). The assignments of the protons are shown in the figure. From the ratio of integrated intensities of $(H_1/2)$: $H_4 : (H_2 + H_3)$ of the ^{1}H-NMR spectra, the polymer compositions of the BB/AA-6(x) copolyesters can be determined. The composition of other copolyesters can be calculated similarly. The results of the measured polymer composition are listed in Table I. Considering a typical example, BB/AA-6(0.5), the charge molar ratio of BB : AA : 1,6-hexanediol is 0.5 : 0.5 : 1.4. The calculated molar ratio of the BB : AA : hexamethylene unit in the polymer is 0.58 : 0.42 : 1.00. Thus, most of the excess 1,6-hexanediol was distilled off. However, the molar ratio of the p,p'-bibenzoate unit to adipate (0.58 : 0.42) is greater than the charge molar ratio of dimethyl p,p'-bibenzoate to adipic acid. This indi-

Table I   Charge Composition, Measured Polymer Composition, and Inherent Viscosity of the Copolyesters

Sample	Type of Alkylene Glycol	Charge Composition[a]	Polymer Composition[a]	η_{inh} (dL/g)
BB/AA-2 (0.5)	Ethylene glycol	0.5 : 0.5 : 1.4	0.54 : 0.46 : 1.00	0.48
BB/AA-3 (0.5)	1,3-Propanediol	0.5 : 0.5 : 1.4	0.51 : 0.49 : 1.00	0.71
BB/AA-4 (0.5)	1,4-Butanediol	0.5 : 0.5 : 1.4	0.52 : 0.50 : 1.00	0.78
BB/AA-5 (0.5)	1,5-Pentanediol	0.5 : 0.5 : 1.4	0.54 : 0.47 : 1.00	0.56
BB/AA-6 (0.1)	1,6-Hexanediol	0.9 : 0.1 : 1.4	0.88 : 0.09 : 1.00	1.11
BB/AA-6 (0.2)	1,6-Hexanediol	0.8 : 0.2 : 1.4	0.81 : 0.17 : 1.00	1.19
BB/AA-6 (0.3)	1,6-Hexanediol	0.7 : 0.3 : 1.4	0.73 : 0.24 : 1.00	0.71
BB/AA-6 (0.4)	1,6-Hexanediol	0.6 : 0.4 : 1.4	0.66 : 0.33 : 1.00	1.25
BB/AA-6 (0.5)	1,6-Hexanediol	0.5 : 0.5 : 1.4	0.58 : 0.42 : 1.00	1.13
BB/AA-6 (0.6)	1,6-Hexanediol	0.4 : 0.6 : 1.4	0.48 : 0.51 : 1.00	1.22
BB/AA-6 (0.8)	1,6-Hexanediol	0.2 : 0.8 : 1.4	0.22 : 0.77 : 1.00	0.71
BB/AA-6 (1.0)	1,6-Hexanediol	0.0 : 1.0 : 1.4	0.00 : 0.99 : 1.00	0.69

[a] Molar ratio of dimethyl p,p'-bibenzoate : adipic acid : alkylene glycol.

$$-(-CO-\langle O \rangle-\langle O \rangle-CO-O-CH_2CH_2CH_2CH_2CH_2CH_2-O-)-$$

$$11255552or3$$

$$-(-CO-CH_2CH_2CH_2CH_2-CO-O-CH_2CH_2CH_2CH_2CH_2CH_2-O-)-$$

$$4554355553or2$$

Figure 1 ¹H-NMR spectrum of BB/AA-6(0.3).

cates that there might be some adducts of adipic acid evacuated out during synthesis.

The sequence distribution of BB/AA-2(0.5), BB/AA-3(0.5), and BB/AA-4(0.5) can be determined by ¹H-NMR. The ¹H-NMR spectrum of BB/AA-3(0.5) is shown in Figure 2. The copolyesters have four possible sequences: BGB, BGA, AGB, and AGA. It can be seen from the ¹H-NMR spectra that the α-methylene protons of these three copolyesters and the β-methylene protons of BB/AA-3(0.5) and BB/AA-4(0.5) can distinguish the different sequences. The chemical shift of α-meth-

ylene protons of different sequences and the sequence distribution for these three copolyesters are listed in Table II. Inspecting a polymer from one end to the other, the probability of finding an AA unit next to a BB unit is

$$P_{BA} = I_{BGA}/(I_{BGB} + I_{BGA})$$

and the probability of finding a BB unit next to an AA unit is

$$P_{AB} = I_{AGB}/(I_{AGA} + I_{AGB})$$

The degree of randomness is defined as[14]

$$-(-CO-\langle O \rangle-\langle O \rangle-CO-O-CH_2CH_2CH_2-O-)-$$

$$11242$$

$$-(-CO-CH_2CH_2CH_2CH_2-CO-O-CH_2CH_2CH_2-O-)-$$

$$3553232$$

Figure 2 ¹H-NMR spectrum of BB/AA-3(0.5).

Table II Sequence Distribution and Degree of Randomness of BB/AA-2 (0.5), BB/AA-3 (0.5), and BB/AA-4 (0.5)

Sample	Sequence	Chemical Shift (ppm)	Sequence Fraction	B
BB/AA-2 (0.5)	BGB	4.95	0.27	
	BGA	4.72	0.25	1.00
	AGB	4.72	0.25	
	AGA	4.51	0.23	
BB/AA-3 (0.5)	BGB	4.78	0.27	
	BGA	4.64	0.24	0.96
	AGB	4.51	0.24	
	AGA	4.38	0.26	
BB/AA-4 (0.5)	BGB	4.66	0.26	
	BGA	4.58	0.25	1.00
	AGB	4.40	0.25	
	AGA	4.33	0.24	

$$B = P_{AB} + P_{BA}$$

For random copolymers, B = 1; for alternative polymers, B = 2; and for block copolymers, B is close to 0.

The B values for the BB/AA-n(0.5)'s with n = 2–4 are shown in Table II. B is about 1 for these three copolyesters. This indicates that the obtained copolyesters are random copolymers. Even though the reactivity may be different for the diacid monomers, the transesterification reaction renders a random distribution. Thus, random copolyesters are obtained by melt polycondensation.
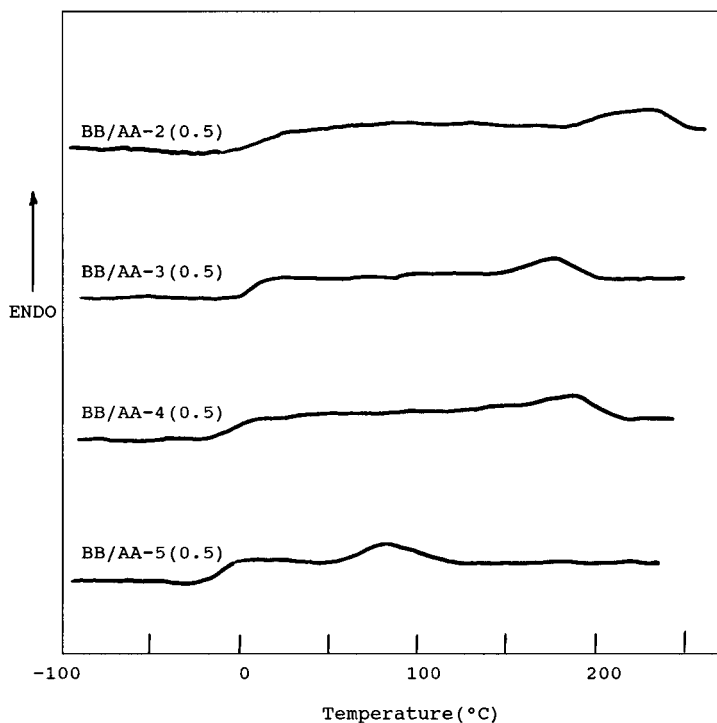
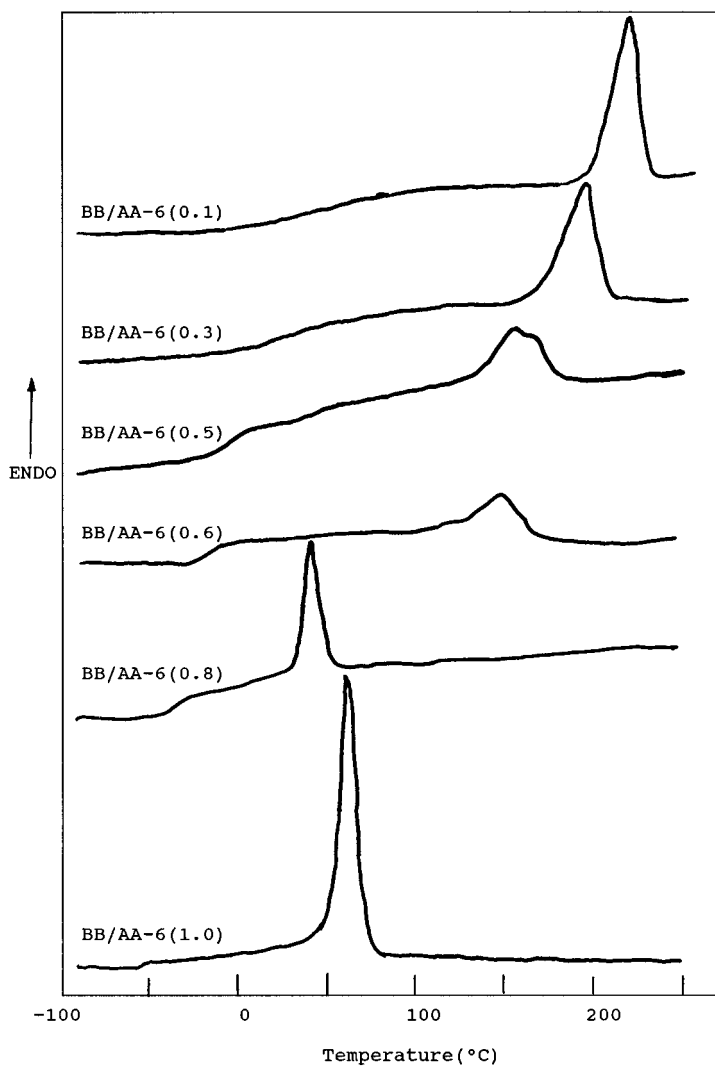**Figure 3** DSC heating curves of BB/AA-n(0.5)'s (n = 2–5).

Figure 4 DSC heating curves of BB/AA-6(*x*) copolyesters.

The DSC heating curves from -100 to 250°C of the copolyesters are shown in Figures 3 and 4. It can be seen that the DSC heating curves exhibit a step inflection and a main endothermic peak. The midpoint of the inflection is taken as the T_g, and the peak temperature is taken as T_m. The T_g, T_m, and ΔH_m of the copolyesters are summarized in Table III.

The BB/AA-*n*(0.5)'s exhibit a T_g of 9 to -13°C. It can be seen that the T_g follows a decreasing trend as *n* increases. Thus, the type of the alkylene glycol affects the T_g to some extent. The content of the flexible adipate unit affects the T_g significantly. As shown in Table III, the T_g decreases significantly as *x* increases for BB/AA-6(*x*) copolyesters.

Table III T_g, T_m, and ΔH_m of the Copolyesters

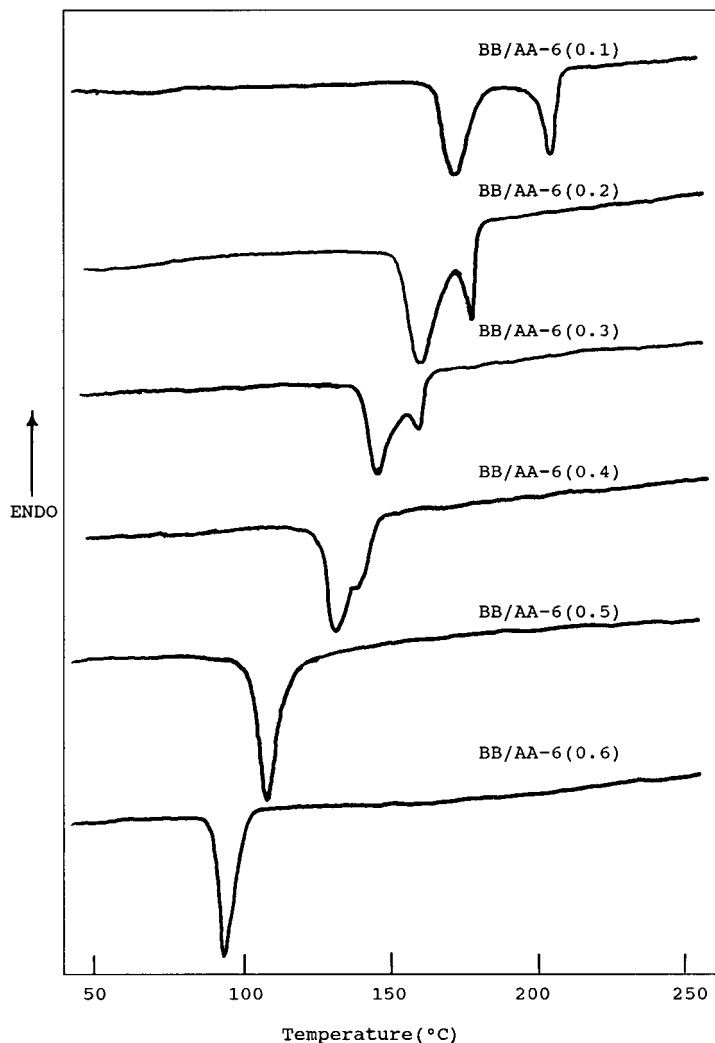| Sample	T_g (°C)	T_m (°C)	ΔH_m (J/g)
BB/AA-2 (0.5)	9	235	12.6
BB/AA-3 (0.5)	−5	172	10.1
BB/AA-4 (0.5)	−11	185	13.4
BB/AA-5 (0.5)	−13	80	10.7
BB/AA-6 (0.1)	60	218	55.2
BB/AA-6 (0.2)	50	203	42.8
BB/AA-6 (0.3)	19	193	33.7
BB/AA-6 (0.4)	1	179	25.6
BB/AA-6 (0.5)	−10	154	19.8
BB/AA-6 (0.6)	−18	144	15.0
BB/AA-6 (0.8)	−37	41	24.6
BB/AA-6 (1.0)	−55	52	80.1

Figure 5 DSC cooling curves of BB/AA-6(x) copolyesters.

As shown in Table III, the composition has a significant effect on the T_m of the copolyesters. For the copolyesters with $x = 0.5$, BB/AA-n(0.5)'s, as n increases, the T_m follows a decreasing zigzag trend. BB/AA-n(0.5) with an even n shows a relatively higher T_m than that with an odd n. Thus, the T_m of these copolyesters exhibits an even–odd effect. As shown in Table III, the BB/AA-6(x) copolyesters exhibit a minimum T_m at $x = 0.8$. For the BB/AA-6(x) copolyesters with $x < 0.8$, the T_m and ΔH_m decrease as x increases due to a copolymerization effect. The copolyesters with x of about 0.5–0.6 show a lower ΔH_m and thus exhibit lower crystallinity due to the copolymerization effect.

Both the second run DSC heating curve and cooling curve of a poly(hexamethylene p,p'-bibenzoate), BB6, exhibit two peaks.[15] BB6 exhibits two endotherms at 219°C (T_I) and 241°C (T_{II}) upon heating and two exotherms at 222°C (T_a) and 154°C (T_b) upon cooling. BB6 exhibits a fan-like texture at about 200°C when observed under the polarized microscope. In combination with the presence of an inner ring of the X-ray diffraction pattern, BB6 exhibits a smectic phase. BB6 is enantiotropic, T_I is a crystalline–smectic transition, and T_{II}, a smectic–isotropic transition, and T_a and T_b are the isotropic–smectic and smectic–crystalline transitions, respectively.

It can be seen from Figure 4 that the thermal properties of the BB/AA-6(x) copolyesters are different from the homopolyester, BB6, and dependent on their composition. From the DSC heating curves, we cannot distinguish the mesogenic transition. However, the DSC cooling curves of some
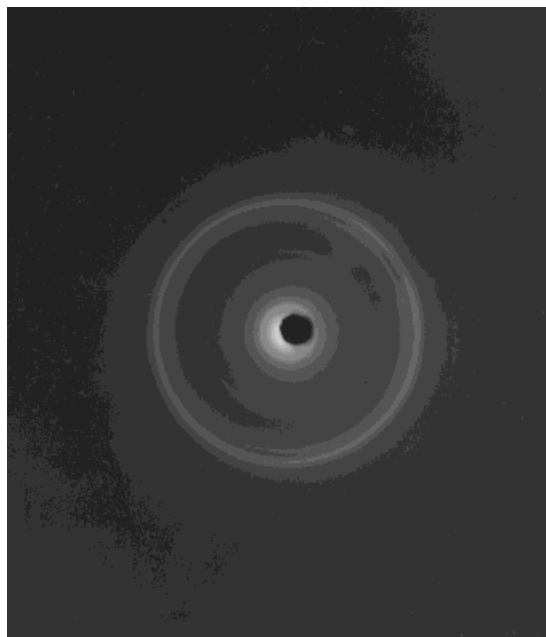
Figure 6 Photograph of X-ray diffraction pattern of BB/AA-6(0.1).

BB/AA-6(x) copolyesters exhibit two exotherms, indicating the appearance of smectic transition. Figure 5 shows DSC cooling curves of the BB/AA-6(x) copolyesters. The DSC cooling curve of BB/AA-6(0.1) exhibits two obvious exotherms. The X-ray diffraction pattern of BB/AA-6(0.1) shows a sharp inner ring similar to BB6 as shown in Figure 6. Thus, the first appearing exotherm (T_a) at 201°C corresponds to an isotropic–smectic transition and the latter appearing exotherm (T_b) at 168°C corresponds to a smectic–crystalline transition. The DSC cooling curves of BB/AA-6(0.2) and BB/AA-6(0.3) exhibit two somewhat overlapped exotherms. The two exotherms of BB/

AA-6(0.4) almost cannot be distinguished due to severe peak overlap. The aforementioned four polymers show no smectic transition upon heating but exhibit a smectic phase upon cooling; thus, they exhibit monotropic smectic liquid crystallinity. The DSC cooling curves of other copolyesters show only one exotherm and no explicit liquid crystallinity can be found. BB/AA-6(0.5), BB/AA-6(0.6), and BB/AA-6(0.8) exhibit only an exotherm (denoted as T_a) corresponding to an isotropic–crystalline transition. The thermal transitions of the copolyesters are summarized in Table IV.

The effect of the composition on the thermotropic transitions of the copolyesters can be described as the effects of the sequence length of the poly(hexamethylene *p,p*′-bibenzoate) segments. As the content of adipic acid increases, the average sequence length of the poly(hexamethylene *p,p*′-bibenzoate) decreases, and the isotropic–smectic transition temperature and the transition heat decrease accordingly. When the charge molar fraction of adipic acid in diacid monomers is 0.5 or more, the copolyesters show no liquid crystallinity owing to not enough average sequence length of the poly(hexamethylene *p,p*′-bibenzoate) segments.

CONCLUSIONS

^{1}H-NMR spectra can be used to determine the sequence distribution of the BB/AA-n(0.5) copolyesters with $n = 2–4$. The copolyesters exhibit a degree of randomness of about 1, indicating that the copolyesters obtained by melt polycondensation are random copolymers. The T_g and T_m of the copolyesters measured by DSC are dependent on

Table IV T_a, T_b, and the Corresponding Transition Heats of BB/AA-6 (x) Copolyesters

Sample	T_a (°C)	ΔH_a (J/g)	T_b (°C)	ΔH_b (J/g)
BB/AA-6 (0.1)	201	18.0	168	33.9
BB/AA-6 (0.2)	176	9.5	159	28.5
BB/AA-6 (0.3)	159	5.7	145	23.4
BB/AA-6 (0.4)	138	[a]	131	28.6
BB/AA-6 (0.5)	107	19.6		—
BB/AA-6 (0.6)	94	15.8		—
BB/AA-6 (0.8)	10	24.2		—
BB/AA-6 (1.0)	36	79.3		—

[a] Cannot be obtained due to peak overlap.

the composition. When the content of the flexible adipate unit increases, the T_g of the copolyesters decreases significantly. The type of alkylene glycol used also affects the T_g to some extent. The copolymerization effect significantly 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 BB/AA-6(x) copolyesters exhibit a monotropic smectic phase. The smectic order decreases with increasing x. When x is more than 0.4, the liquid crystallinity is completely destroyed.

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