

Structure and Properties of Fully Aromatic Thermotropic Liquid-Crystalline Copolyesters Containing *m*-Hydroxybenzoic Acid Units

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ABSTRACT: A series of fully aromatic copolyesters based on *p*-acetoxybenzoic acid (*p*-ABA), hydroquinone diacetate (HQDA), terephthalic acid (TPA), and *m*-acetoxybenzoic acid (*m*-ABA) were prepared by a modified melt-polycondensation reaction. The copolyesters were prepared in two series in which series I is based on a two monomer system (*p*-ABA/*m*-ABA) and series II is based on a three monomer system (HQDA/TPA/*m*-ABA). The effect of different linear structures and kink moiety on the properties of the copolyesters were investigated systematically. The copolyesters were characterized by differential scanning calorimetry, thermogravimetric analysis, ¹H-NMR, polarized optical microscopy, X-ray diffraction, and intrinsic viscosity measurements. It was found that the copolyesters exhibited nematic liquid-crystalline phases when the content of linear (*p*-ABA or HQDA/TPA) units was over 67 mol %. The melting or

flow-transition temperatures were decreased with an increase of the content of kink *m*-ABA units. The copolyesters that contained *p*-ABA as linear units had a significantly higher degree of crystallinity compared to the copolyesters that contain HQDA/TPA as the linear units, implying a higher blockiness in the polymer chains as a result of the higher reactivity of the *p*-ABA units in the *p*-ABA/*m*-ABA system. All the copolyesters had poor solubility except the copolyesters containing at least 40 mol % of *m*-ABA, which were soluble in a dichloromethane/trifluoroacetic acid (70:30 v/v) mixture. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3260–3269, 2003

Key words: liquid-crystalline polymer; thermal properties; polycondensation; structure; X-ray

INTRODUCTION

In recent years, considerable interest has developed in the structure–property relationship of totally aromatic thermotropic liquid-crystalline polyesters (TLCPs). Many melt processable nematogenic copolyesters have been synthesized and characterized through the use of different types of structural modifications.^{1–7}

The liquid-crystalline behavior and transition temperatures were dependent on the copolymerization of the ester groups, use of rodlike arylene moieties of different lengths, use of kink units, and incorporation of flexible aliphatic spacers.^{8–18} To date, there are a few reports of totally aromatic copolyesters containing nonlinear *m*-oxybenzoyl units.^{19–21} Copolyesters containing different amounts of nonlinear *m*-oxybenzoyl units and linear *p*-oxybenzoyl units have been prepared by polycondensation.^{19,20} Although the effect of kink units on the properties of copolyesters have been well documented, no work has yet been reported in

the open literature on a systematic investigation in terms of a type of linear monomer structure.

In our previous reports,^{22,23} we described the preparation and properties of a family of totally aromatic copolyesters based on four different monomer units. Copolyesters from *p*-acetoxybenzoic acid (*p*-ABA)/hydroquinone diacetate (HQDA)/terephthalic acid (TPA)/*m*-acetoxybenzoic acid (*m*-ABA) were random, melt processable, and exhibited a broad nematic liquid-crystalline phase when the polymer composition contained 67 and 75 mol % linear units. A comparison of linear *p*-ABA and HQDA/TPA monomer units was performed in four monomer systems, and it showed that increasing the content of *p*-ABA units and decreasing the content of HQDA/TPA units affects the properties of the copolyesters.

In this study, copolyesters were synthesized in two series, each containing two or three different monomer units, by a melt-polycondensation transesterification technique. The effects of different linear monomer units on the properties of copolyesters were investigated in more detail. Copolyesters containing two monomer units (*p*-ABA/*m*-ABA) and three monomer units (HQDA/TPA/*m*-ABA) were studied in two series with a broad composition range. The effect of linear monomers on the thermal properties and on the

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TABLE I
Stoichiometric Details of Copolyesters Prepared by Melt-Polycondensation Reaction

Series	Charged composition (mol %)		Abbreviation	Polycondensation time under N flow ^a (min)
	<i>p</i> -ABA/HQDA/TPA/ <i>m</i> -ABA	Linear units		
I	100:0.00:0.00:0.00	100	100P	25
	85:0:0.00:0.00:15.0	85	85P	40
	75:0:00.0:0.00:0:25.0	75	75P	45
	67:0:0.00:0.00:33.0	67	67P	45
	50:0:0.00:0.00:50.0	50	50P	45
	40:0:0.00:0.00:60.0	40	40P	45
II	0.00:42.5:42.5:15.0	85	85HT	45
	0.00:37.5:37.5:25.0	75	75HT	45
	0.00:33.5:33.5:33.0	67	67HT	45
	0.00:25.0:25.5:50.0	50	50HT	45
	0.00:20.0:20.0:60.0	40	40HT	45
	0.00:0.00:0.00:100	—	100M	45

^a The polycondensation time under vacuum was 60 min for all polyesters.

degree of crystallinity were investigated systematically. In order to perform a reliable comparison, the method or experimental conditions applied during the melt-polycondensation reaction (i.e., polycondensation time, temperature) for each series in this study were kept similar to those in our previous study related to the four monomer system.²²

EXPERIMENTAL

Monomer synthesis

p-Hydroxybenzoic acid (*p*-HBA), *m*-hydroxybenzoic acid (*m*-HBA), HQ, and TPA were obtained commer-

cially from Merck and used without further purification. *p*-ABA (mp 187–192°C), *m*-ABA (mp 130–135°C), and HQDA (mp 122–124°C) were prepared by reacting *p*-HBA, *m*-HBA, and HQ, respectively, with excess acetic anhydride at 60°C in the presence of a sulfuric acid catalyst. Each product was recrystallized from an ethanol–water mixture (25:75 v/v) and dried under a vacuum at 60°C for 24 h.

Copolyester synthesis

All the copolyesters and homopolyesters of *p*-ABA [*p*-poly(oxybenzoate), coded as 100P] and *m*-ABA

TABLE II
Thermal Properties of Homopolyesters and Series I and II Copolyesters

Series	Polymer code	DSC				Polarized microscopy		TGA ^c			[η] ^d (dL/g)
		First scan ^a		Second scan ^b		T_{ni} (°C)	T_{ni} (°C)	T_{id} (°C)	T_{maxd} (°C)	T_{fd} (°C)	
		T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)						
I	100P	— ^e	— ^e	— ^e	— ^e	—	—	539	550	565	— ^f
	85P	115	323;334	119	276	340	380	487	517	548	— ^f
	75P	112	314;346	111	279;310	320	380	479	507	533	— ^f
	67P	117	296;325	120	311	270	370	477	501	530	— ^f
	50P	123	175	131	— ^e	— ^g	— ^g	476	501	526	— ^f
	40P	124	327	123	240	— ^g	— ^g	461	498	533	0.12
II	85HT	140	343	142	225	330	380	465	524	557	— ^f
	75HT	133	343	136	220	330	370	469	507	535	— ^f
	67HT	141	320	140	— ^e	260	350	485	517	542	— ^f
	50HT	142	236	141	225	— ^g	— ^g	490	517	546	— ^f
	40HT	140	226	139	— ^e	— ^g	— ^g	490	516	542	0.27
	100M	129	210 ^h	130	— ^e	— ^g	— ^g	479	504	522	0.20

^a From DSC measurements at a heating rate of 30°C/min.

^b From DSC measurements at a heating rate of 15°C/min.

^c Thermal stability was determined from TGA in nitrogen at a heating rate of 20°C/min; T_{id} , initial decomposition temperature; T_{maxd} , maximum decomposition temperature; T_{fd} , final decomposition temperature.

^d Intrinsic viscosity measured in dichloromethane/trifluoroacetic acid solution (70:30 v/v) at 25°C.

^e Not observed.

^f Insoluble.

^g Liquid crystalline behavior was not observed.

^h Flow temperature (T_f) determined by hot-stage polarized light microscope.

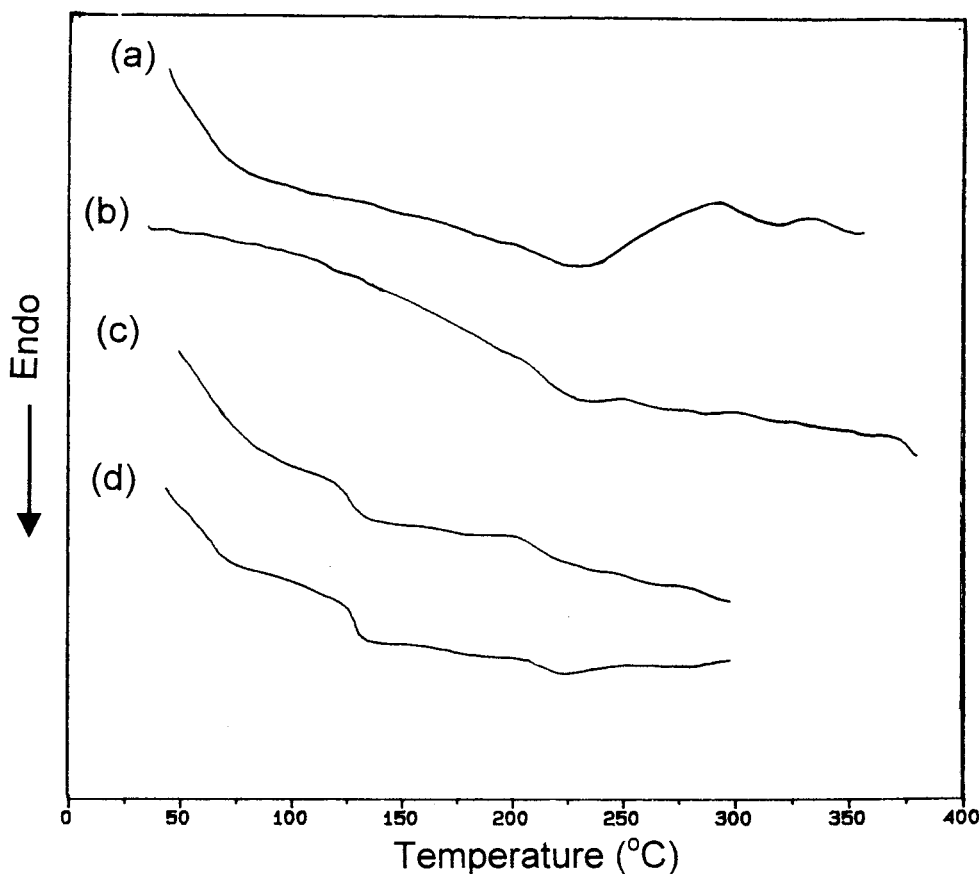


Figure 1 DSC thermograms of homopolymers 100P and 100M: first run for 100P (curve a), second run for 100P (curve b), first run for 100M (curve c), and second run for 100M (curve d).

[*m*-poly(oxybenzoate), coded as 100M] were prepared by the high-temperature melt-polycondensation method on a 0.1 mol scale without any added catalyst as described in our previous study.²² The stoichiometric details of the copolyesters prepared in two series and the polymer abbreviations that are used are summarized in Table I. A typical procedure is summarized as follows: the monomers (0.1 mol in total) and acetic acid (35 mL) were charged into a cylindrical glass reactor (35-mm diameter, 250-mm length) fitted with a stainless stirrer, a nitrogen inlet, a vacuum outlet, and a tube connected via a condenser to a condensate collector. After the reaction flask was evacuated and purged with nitrogen gas 3 times to remove all air, the temperature of the silicone oil bath was increased to 280°C. Then, the reactor was placed in oil bath while the reactants were stirred with a dry nitrogen flow. Excess acetic acid incorporated into the reaction mixture was collected in 10 min. The homogeneous reaction mixture was then maintained at 280°C under a nitrogen flow for 20 or 45 min, depending on the type of polyester (Table I). The next stage was carried out under a vacuum for a further 60 min. The reaction was stopped by introducing the nitrogen gas into the reaction medium and then immersing the flask in a

liquid nitrogen bath. The resulting copolyesters were recovered by breaking the glass container and drying at 60°C in a vacuum oven overnight.

Characterization

The optical textures of the copolyesters were studied with a polarizing microscope equipped with a hot stage (temperature limit = 430°C). The sample was prepared by heating a sample piece on a glass plate (200–350°C) and then pressing the melt with another piece of hot glass plate, so that it was formed into a sandwich with a thin film inside. The mesomorphic transition temperatures and disappearance of birefringence, which are the crystal–nematic (T_{cn}) and nematic–isotropic (T_{ni}) transitions, were noted.

Differential scanning calorimetry (DSC) measurements were performed on a Du Pont DSC 910 under a nitrogen flow. The first DSC scans were run between 40 and 390°C at 30°C/min. The samples were then cooled in the DSC cell from 390 to 40°C at a cooling rate of 20°C/min. Finally, second runs were carried out at a heating rate of 15°C/min. The weight of all samples was kept between 5 and 8 mg.

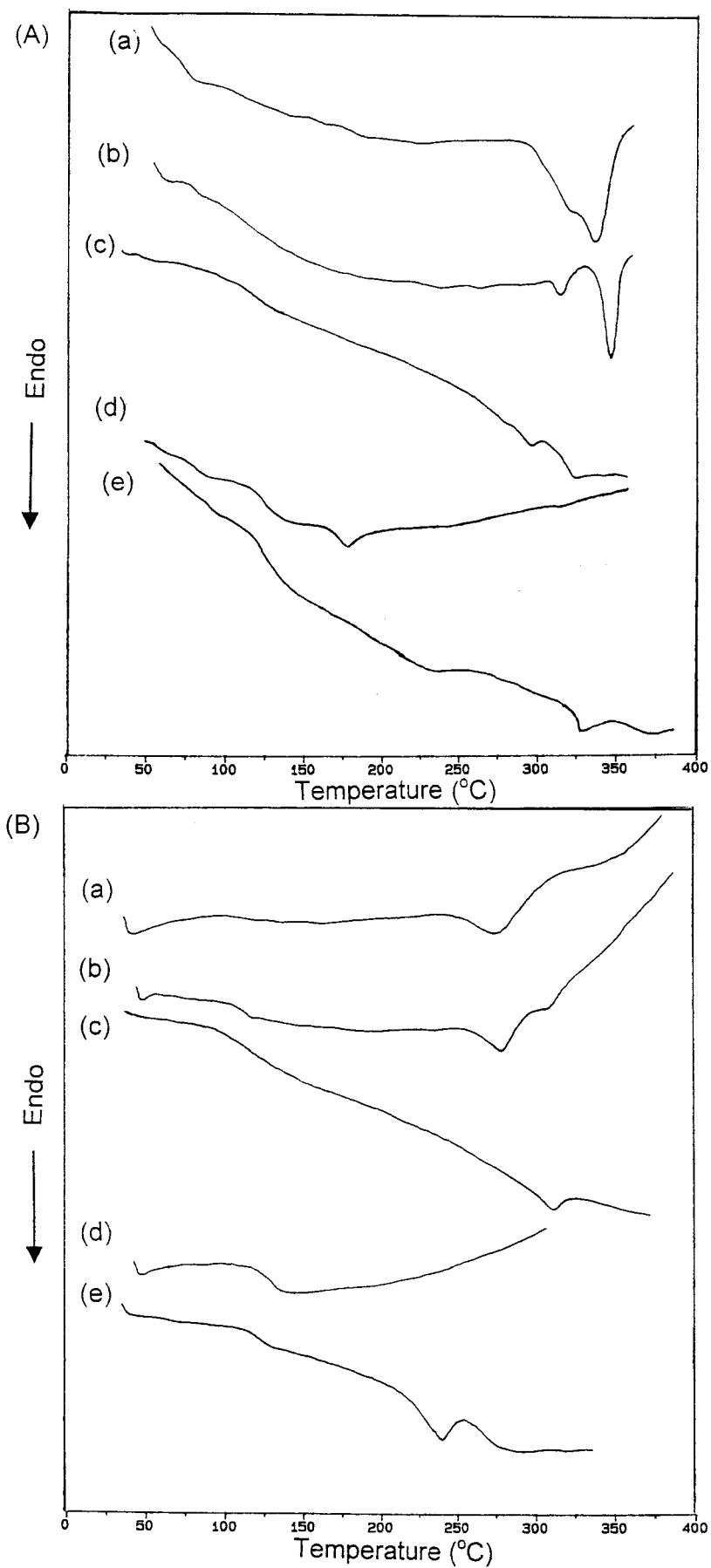


Figure 2 DSC thermograms of series I copolyesters for (A) first heating and (B) second heating for 85P (curve a), 75P (curve b), 67P (curve c), 50P (curve d), and 40P (curve e).

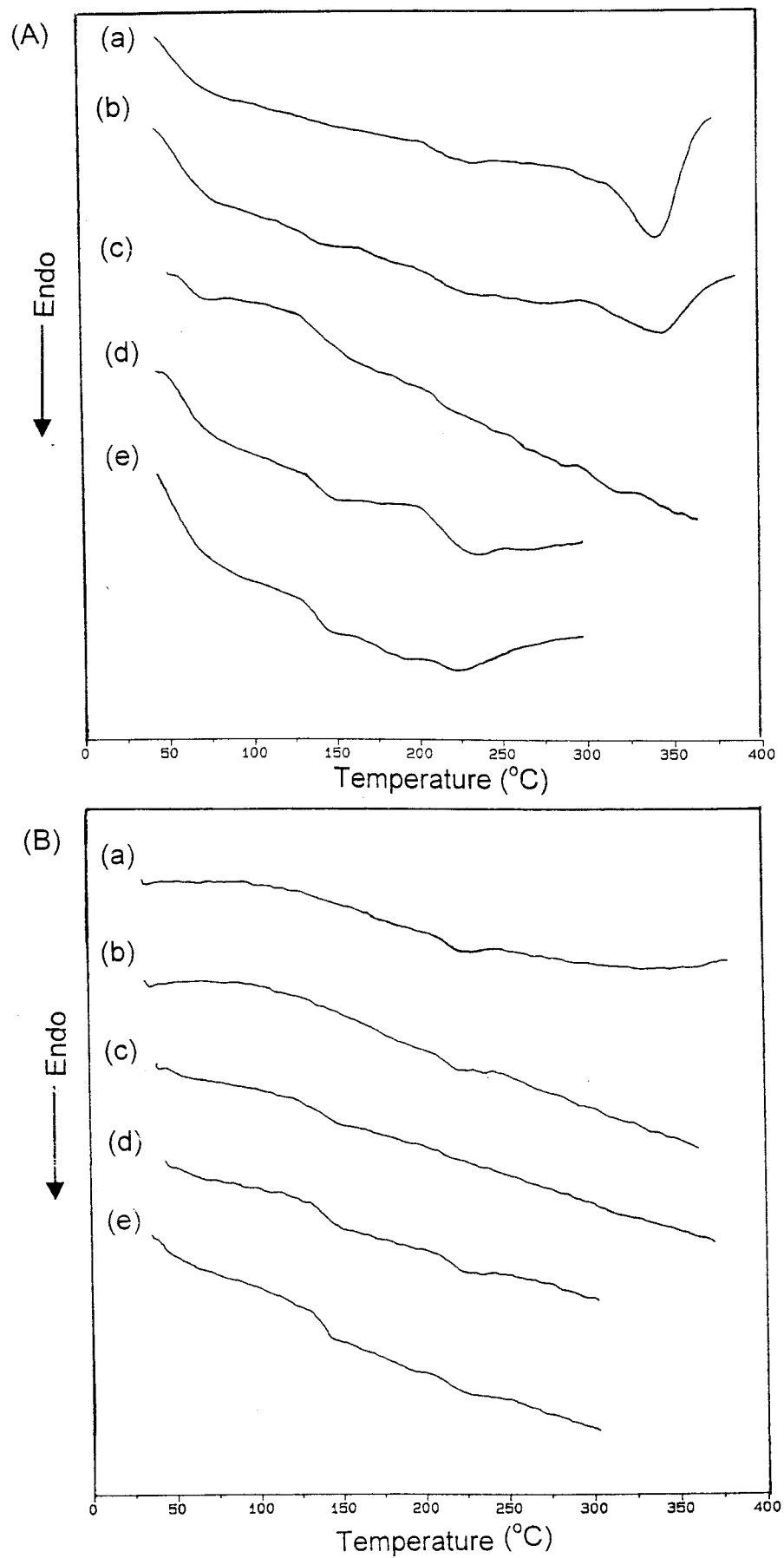


Figure 3 DSC thermograms of series II copolyesters for (A) first heating and (B) second heating for 85HT (curve a), 75HT (curve b), 67HT (curve c), 50HT (curve d), and 40HT (curve e).

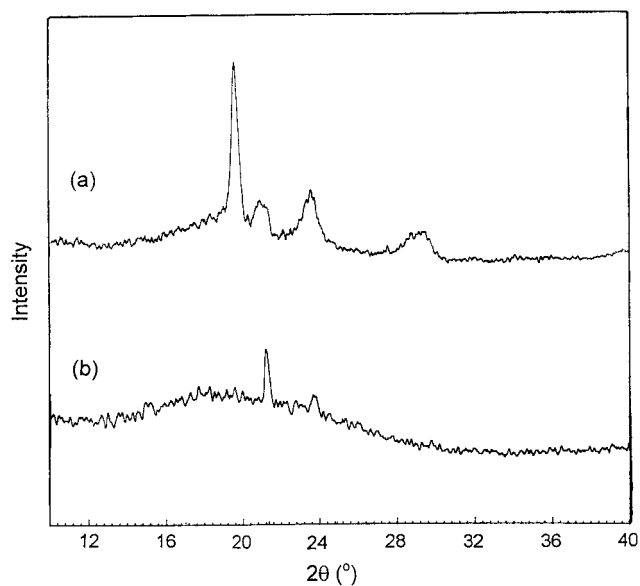


Figure 4 Wide-angle X-ray diffractograms of 100P (curve a) and 100M (curve b) homopolymers.

The glass-transition temperatures (T_g) were assumed to be at the midpoint of the change in the heat capacity.

Thermogravimetric analysis (TGA) for all samples was performed by a TGA system (Universal V3.0G 2050 TA Instrument) under a nitrogen flow between 30 and 800°C at a heating rate of 20°C/min. The derivative TGAs indicate the decomposition rate of samples at a definite heating temperature.

The intrinsic viscosity of the soluble copolyesters in dichloromethane/trifluoroacetic acid (70:30 v/v) solution at 25°C was determined by an Ubbelohde viscometer at a concentration of 0.5 g/dL.

Wide-angle X-ray diffraction (WAXD) patterns were obtained with a Huber-Guinier G600 powder diffractometer on an Enraf-Nonius 550 generator with $\text{CuK}\alpha$ radiation at a wavelength of 1.54 Å. The copolyesters were ground to form a powder sample. The crystallinities of the samples were calculated using the following equation^{24,25}:

$$\% \text{ crystallinity} = \frac{I_c}{I_a + I_c} \times 100$$

where I_c is the intensity of the crystalline component and I_a is the intensity of the amorphous component.

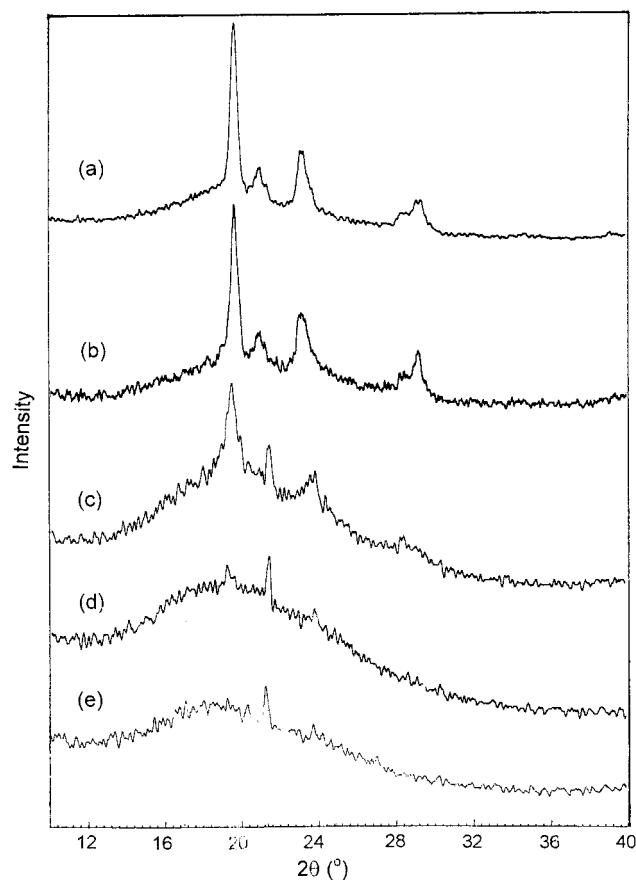


Figure 5 Wide-angle X-ray diffractograms of series I copolyesters 85P (curve a), 75P (curve b), 67P (curve c), 50P (curve d), and 40P (curve e).

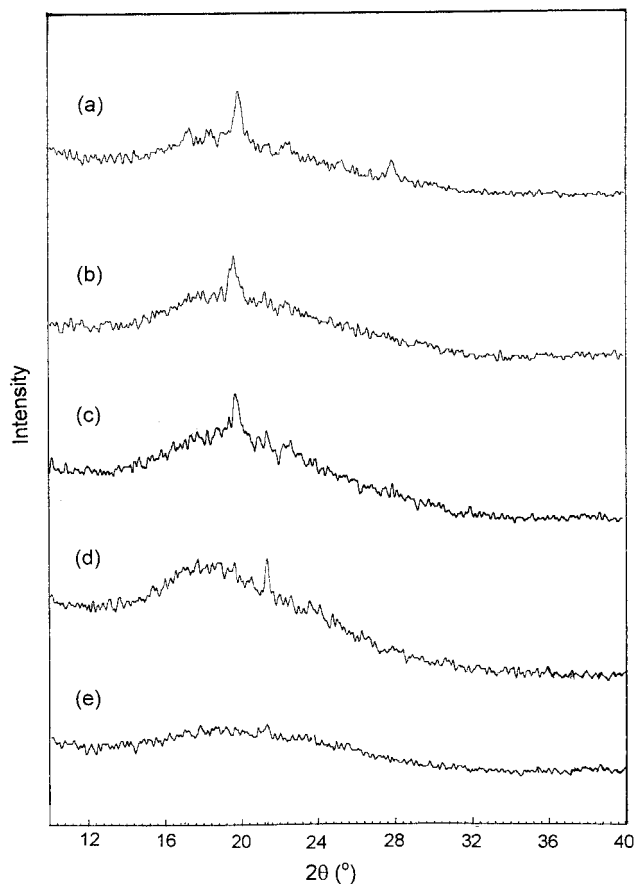


Figure 6 Wide-angle X-ray diffractograms of series II copolyesters 85HT (curve a), 75HT (curve b), 67HT (curve c), 50HT (curve d), and 40HT (curve e).

TABLE III
Observed X-Ray Diffraction Data for Homopolyesters and Series I Copolyesters

Polymer code	2 θ (°)	d Spacing (Å)	Intensity	Degree of crystallinity (%)
100P	19.74	4.49	vs S	42.0
	21.00	4.23	m B	
	23.63	3.76	m B	
85P	29.44	3.03	m B	32.0
	19.76	4.49	vs S	
	21.04	4.22	m B	
	23.24	3.82	m B	
75P	28.36	3.14	w B	25.0
	29.24	3.05	m B	
	19.84	4.47	vs S	
	21.00	4.23	m B	
	23.24	3.82	m B	
67P	28.28	3.15	w B	12.0
	29.20	3.06	m B	
	19.46	4.56	vs B	
	21.40	4.15	m S	
	23.24	3.75	m B	
50P	24.28	3.66	vw S	6.5
	28.28	3.15	vw B	
	19.22	4.61	w B	
40P	21.42	4.15	s S	5.0
	23.78	3.74	vw B	
	21.32	4.16	s S	
100M	23.78	3.74	vw B	10.5
	21.34	4.16	s S	
	23.74	3.75	vw B	

w, weak; vw, very weak; m, medium; s, strong; vs, very strong; B, broad; S, sharp.

The ¹H-NMR spectra of the soluble polyesters were recorded on a Bruker AM-400 NMR spectrometer. A mixture of trifluoroacetic acid-*d* and chloroform-*d* (50:50 v/v) was used as a solvent. The chemical shifts were measured with respect to chloroform (7.28 ppm).

RESULTS AND DISCUSSION

Synthesis

The totally aromatic copolyesters and *p*-poly(oxybenzoate) and *m*-poly(oxybenzoate) homopolyesters were prepared by high temperature melt polycondensation. In series I and II coding, the total molar percentages of linear units are followed by the initials of the linear monomer(s): P stands for *p*-ABA, H stands for HQDA, and T stands for TPA (e.g., 85P is series I or 85HT is series II). During the polycondensation period under nitrogen flow, the homopolyester of *p*-ABA (100P) and copolyester of *p*-ABA/*m*-ABA (85P) were solidified at an early stage and the polycondensation time for these polyesters were noted as 25 and 40 min, respectively (Table II). This may be explained by the higher reactivity of *p*-ABA units.²² The intrinsic viscosities of the 40P, 40HT, and 100M polyesters are listed in Table II. All other copolyesters were insoluble in the dichlo-

romethane/trifluoroacetic acid (70:30 v/v) mixture. When the solubilities of these copolyesters were compared with the four monomer systems (*p*-ABA/HQDQ/TPA/*m*-ABA),²² a considerable solubility decrease was observed for two or three comparable monomer systems.

Thermal properties of copolyesters

The morphological textures of the copolyesters were studied as a function of the temperature in a hot-stage polarizing optical microscope. The copolyesters containing 67, 75, and 85 mol % linear units produced turbid melts and exhibited nematic mesophases. In the nematic mesophase, a significant molecular interaction exists in a broad temperature range (i.e., 90 and 100°C for 67P and 67HT copolyesters, respectively) that is apparent from the high birefringences under crossed polarizers. The data of the T_{en} and T_{ni} transition temperatures of liquid-crystalline copolyesters are given in Table II. The ability of these polymers to form liquid-crystalline melts were reduced at high contents of kinked units.

The DSC thermograms of the *p*-poly(oxybenzoate) and *m*-poly(oxybenzoate) polyesters in the first and second heating cycles are illustrated in Figure 1, and they show no distinct melting endotherms. Because of the highly crystalline structure, the melting point of 100P is very high and it decomposes before the melt.^{1,2,20} The 100M polyester also has a totally amorphous structure that leads to an undetectable melting endotherm. The flow temperature of 100M as deter-

TABLE IV
Observed X-Ray Diffraction Data for Series II Copolyesters

Polymer code	2 θ (°)	d Spacing (Å)	Intensity	Degree of crystallinity (%)
85HT	16.32	5.12	w B	22.0
	18.28	4.85	w B	
	18.86	4.47	s S	
	21.46	4.14	w B	
	22.36	3.97	w B	
75HT	27.82	3.20	w B	12.0
	18.74	4.49	s S	
	21.34	4.16	vw B	
67HT	22.42	3.96	vw B	10.0
	18.66	4.51	s B	
	21.32	4.16	w B	
	22.20	4.00	w B	
50HT	22.58	3.93	w B	6.5
	21.42	4.15	m S	
	23.60	3.77	vw B	
40HT	24.14	3.68	vw B	4.5
	20.86	4.26	vw B	
	21.30	4.17	vw B	

w, weak; vw, very weak; m, medium; s, strong; vs, very strong; B, broad; S, sharp.

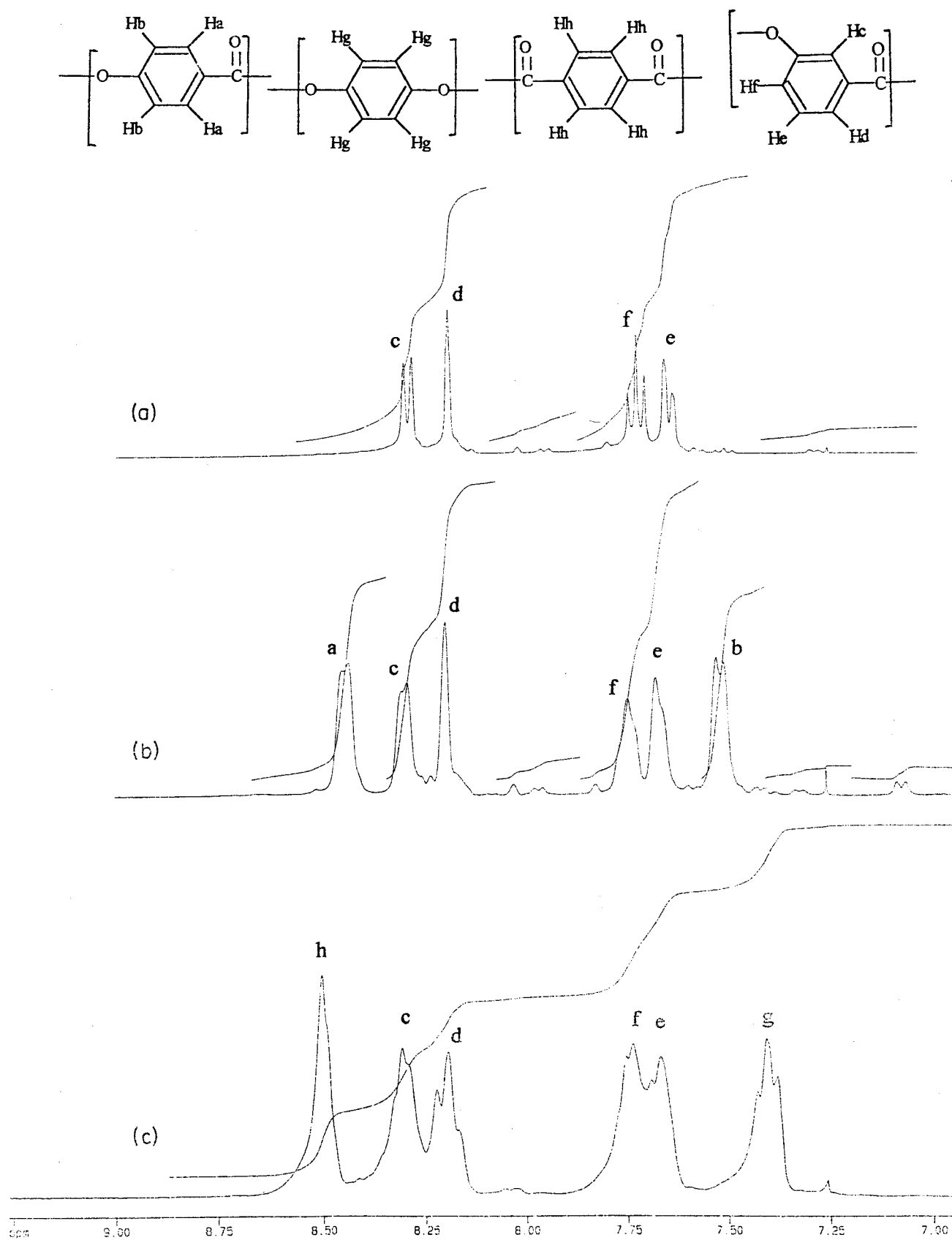


Figure 7 ¹H-NMR spectra of soluble polyesters (a) 100M, (b) 40P, and (c) 40HT.

mined by the hot-stage polarized microscope is 210°C. A more distinct T_g transition was observed at 129 and 130°C for 100M in the first and second heating endotherms, respectively.

The DSC thermograms of the series I and II copolyesters in the first and second heating cycles are illustrated in Figures 2 and 3. The endothermic peaks (Table II) observed in the first heating cycles for the 85P, 75P, 85HT, and 75HT copolyesters [Figs. 2(A), 3(A)] are strong and more detectable. The peaks related to 85P and 75P are stronger and sharper than those of 85HT and 75HT, probably because of the ability of linear *p*-ABA units to form longer and larger oriented regions compared to HQDQ/TPA units. With increasing content of *m*-ABA units, the endothermic peaks became very weak and broad and the melting temperatures were depressed to a more processable region because of the less ordered, amorphous structure of the copolyesters; but the melting temperatures are still high compared to the four monomer system studied earlier.²² A somewhat puzzling point is the higher T_m values for the HT series compared to the P series, although the P series is more crystalline as evidenced by the sharper endotherms and the WAXD data discussed below. When the *p*-ABA units form long sequences in the polymer backbone, the remaining portions of the chains acquire a denser content of the kinked *m*-ABA units by necessity. This so-called stoichiometric effect results in a comparatively easier melting behavior of large portions of the macromolecule, especially for the 85P and 75P copolyesters.

The T_g values of the series I copolyesters increased with increasing content of *m*-ABA units in the polymer composition (Table II). In the first DSC scan, the T_g values were found to be lowest for 85P and highest for 40P copolyesters at 115 and 124°C, respectively. This result is in accordance with earlier studies on the effect of nonlinear segments on the T_g of totally aromatic systems where rotational motion of the nonlinear segments requires a much higher free volume compared to linear segments that can be achieved at relatively higher temperatures.^{21,22} The T_g values for the series II copolyesters in the first and second DSC scans (Table II) are higher than those of the series I copolyesters, and they showed no regular change with the change of the composition. This may be explained by the fact that, because of the two symmetrical carbonyl groups in the TPA units, the rotational motions of the segments requires a much higher free volume compared to the *p*-ABA units in series II.

The second heating DSC thermograms [Figs. 2(B), 3(B)] showed weak melting endotherms compared to the first heating endotherms, implying that they have either lost their structural regularity or the crystallization may be extremely slow during the cooling process. In addition, endothermic steps assignable to the

glass transition were present for each series in the second heating cycle.

The thermal decomposition temperatures estimated from the TGA thermograms under nitrogen are given in Table II. The TGAs give the initial decomposition temperatures (T_{id}), the maximum decomposition temperatures (T_{maxd}), and final decomposition temperatures (T_{fd}). All the copolyesters exhibit a similar pattern of decomposition with no significant weight loss below 461°C. The T_{id} , T_{maxd} , and T_{fd} were invariably found in the range of 461–487, 498–517, and 526–548°C for series I, and 465–490, 507–524, and 535–557°C for series II copolyesters, respectively, indicating good thermal stability at elevated temperatures. The 100P and 100M homopolyesters have initial decomposition temperatures at 539 and 479°C, respectively. This result shows that the highest thermal stability was observed with the homopolyester containing linear *p*-ABA units in the polymer chain. According to the DSC and optical results obtained for both series I and series II copolyesters, although the melting or flow temperatures are depressed to a very efficient melt-processable range, the thermal stability of all the copolyesters was depressed slightly and the lowest decomposition temperature (461°C), even for 40P, is still high for good processability.

WAXD analysis

WAXD patterns and the degree of crystallinities of the homopolyesters and series I and II copolyesters are shown in Figures 4–6. The *d* spacing and Bragg angles of the copolyesters are given in Tables III and IV. The 100P polyester attained the highest crystallinity (42%) and showed four main diffraction peaks (Fig. 4, curve a) as reported by Shinn and Lin.²⁶ The peak at $2\theta = 19.74^\circ$ and $d = 4.49 \text{ \AA}$ is the most intense peak compared to the three other broad and moderate peaks. The 100M polyester showed two peaks (Fig. 4, curve b): the first is moderate and sharp at $2\theta = 21.34^\circ$ and $d = 4.16 \text{ \AA}$, and the second is weak and broad at $2\theta = 23.74^\circ$ and $d = 3.75 \text{ \AA}$. As expected, the crystallinity of the 100M polyester (10.5%) prepared from totally kink units is lower than that of 100P.

With the increasing content of *m*-ABA units in the series I copolyesters, the intensity of the original four main diffraction peaks for 100P mentioned above decreased and became broader (Fig. 5, spectra a–e). The diffractograms of the series I copolyesters with 15 or 25 mol % meta units are very similar to that of the *p*-ABA homopolymer (100P) with the expectation of a somewhat reduced degree of crystallinity. When the linear *p*-ABA units were replaced by linear HQDA/TPA units in series II copolyesters, weaker diffraction peaks were observed for the copolyesters, even with the higher content of linear units (85HT and 75HT). This may be explained by the fact that the reactivity of

TABLE V
Calculated Copolyester Compositions Determined
by ¹H-NMR Spectroscopy

Polymer (code)	Linear/kink monomer feed ratio (mol %)	Copolyester composition (linear/kink) (mol %)
<i>p</i> -ABA/ <i>m</i> -ABA (40P)	40/60	39.7/60.3
HQDA/TPA/ <i>m</i> -ABA (40HT)	40/60	37.9/62.1

p-ABA is higher than that of the HQDA/TPA units, which may result in some blockiness in the polymer chain. In addition, the chain orientation or packing was prevented to some degree by two symmetrical carbonyl groups present in the TPA units. In other words, *p*-ABA has a greater degree of linear symmetry that makes packing in a crystal lattice easier as compared to HQDA/TPA.²²

¹H-NMR analysis

Figure 7 shows typical expanded regions of the ¹H-NMR spectra of the soluble polyesters (100M, 40P, and 40HT) with the chemical shifts observed between 7.38 and 8.47 ppm. According to the integrated areas of the peaks, the compositions of the copolyesters that are calculated for the kink and linear units were very close to the feed ratios (Table V). However, the 40HT copolyester contains somewhat fewer linear units (2.1 mol %) than expected from the feed ratios. This may indicate that a small amount of monomers, probably HQDA, are lost by sublimation during the high temperature melt-polycondensation reaction, as reported by Erdemir et al.⁹ It can also be suggested that the molar ratios are within the accuracy of quantitative ¹H-NMR spectrometry. It can be noted that all the aromatic hydrogens close to the acid groups are observed downfield (peaks h, a, c, and d), those close to the basic groups are observed upfield (peaks f, e, b, and g), and they have about equal areas as expected from the stoichiometry.

CONCLUSION

A series of copolyesters with different *p*-ABA/*m*-ABA or HQDA/TPA/*m*-ABA comonomer compositions were prepared by high temperature melt polycondensation. The influence of linear and kink monomer units on the thermal properties, liquid-crystalline behaviors, solubility, viscosity, and degree of crystallinity were investigated. The copolyesters containing 67 and 75 mol % linear units showed nematic mesophases in a broad temperature range. The melting or flow temperatures were found to be in the processable region for the copolyester composition that contains 33 mol % or higher *m*-ABA units. The T_g values of the copolyesters were increased

with increasing content of *m*-ABA units in the two monomer (*p*-ABA/*m*-ABA) system. A comparison between the linear *p*-ABA and HQDA/TPA units showed that, when the linear *p*-ABA units were replaced by linear HQDA/TPA units, the T_g values of the copolyesters were increased, weaker diffraction peaks were observed, and the degree of crystallinity of the copolyesters was reduced considerably. At the same time, the lower T_m values of the *p*-ABA containing systems compared to the HQDA/TPA systems is explained in terms of a stoichiometric effect where large domains that contain a dense kinked monomer concentration give rise to comparative ease in the melting behavior. All the copolyesters were thermally stable, and they can be processed without degradation above the melting temperatures. From the ¹H-NMR spectra, the compositions of the soluble copolyesters were calculated to be almost equal to the feed ratios.

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