

Synthesis and Melt Spinning of Fully Aromatic Thermotropic Liquid Crystalline Copolyesters Containing *m*-Hydroxybenzoic Acid Units

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ABSTRACT: Fibers of fully aromatic thermotropic copolyesters based on *p*-acetoxybenzoic acid (*p*-ABA), hydroquinone diacetate (HQDA), terephthalic acid (TPA), and *m*-acetoxybenzoic acid (*m*-ABA) were prepared by a high-temperature melt-spinning technique. Two types of the copolyesters were prepared by a high-temperature melt polycondensation reaction using 33 mol % of kink (*m*-ABA) and 67 mol % linear monomer units (*p*-ABA, TPA, HQDA), and characterized by differential scanning calorimetry (DSC), polarized optical microscopy, wide-angle X-ray diffraction (WAXD), and intrinsic viscosity measurements. The mechanical properties and the morphology of the fibers were also determined by tensile tester, WAXD, and scanning electron microscopy (SEM). The copolyesters exhibited phase-separated nematic liquid crystalline morphology within a broad temperature range in an isotropic matrix. DSC analysis of the copolyesters revealed broad endotherms associated with the nematic phases. The melting and spinning temperatures were in a processable region. Fibers exhibit well-developed fibrillar structure parallel to the fiber axis. The highly oriented morphology of the fibrils is slightly dependent on the type of the linear monomer. The strength and modulus values determined for the fibers that contain equal molar composition of the linear *p*-ABA, HQDA/TPA units are comparable to other reported rigid systems containing fully aromatic species. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2580–2587, 2002

Key words: liquid-crystalline polymers; copolymerization; fibers; morphology; mechanical properties

INTRODUCTION

In the last three decades, thermotropic liquid crystalline polymers (TLCPs), which can form thermally stable nematic mesophase, have been of considerable interest because of their attractive prop-

erties as high-performance engineering materials for high strength and high modulus fibers and films.^{1–10} The anisotropic nature of these systems leads to a high degree of molecular orientation during processing in the melt state. The ordered phase can be achieved by different routes, depending on whether the polymer chains are rigid or flexible. The ability of form anisotropic and ordered phases is exploited and, because of the long relaxation time, this anisotropy is maintained during solidification.

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On the other hand, for flexible or semirigid chains, the ordered phase is mechanically induced with some assistance from the flow field.^{11–16}

Melt processing techniques are generally preferred over the corresponding solution processes because of the relative simplicity and minimum environmental risk. The macroscopic orientation of the domains of the thermotropic melt is easily achieved in shear flow and/or elongational flow field, and the chain orientation develops very rapidly with the increasing draw-down ratios.^{17–19} Many general techniques to lower the melt temperature and to increase the solubility of the rigid systems have been reported.^{2–5,20–23} One of the techniques employed for achieving the processability is partial replacement of the rod-like units in rigid polyester by angular disruptor units containing *m*-phenylene groups.^{5,7,24,25} In recent years, many thermotropic liquid crystalline aromatic copolyesters capable of forming high strength–high modulus fibers have been reported.^{9,10,15,26–28} Among totally aromatic thermotropic copolyesters, those based on *p*-hydroxybenzoic acid (*p*-HBA) and *m*-hydroxybenzoic acid (*m*-HBA) are especially attractive, however, the processing and the technological applications of this class of polymers have been rarely reported in terms of fiber formation and properties.

In our previous study,²⁹ a series of melt processable, totally aromatic thermotropic liquid crystalline copolyesters containing four different monomer units [*p*-acetoxybenzoic acid (*p*-ABA), terephthalic acid (TPA), hydroquinone diacetate (HQDA), and *m*-acetoxybenzoic acid (*m*-ABA)] were prepared and characterized in detail. Nematogenic copolyesters with a composition of 33 mol % kink units are suitable for potential applications as high strength–high modulus fibers. This paper is concerned with the preparation of thermotropic liquid crystalline copolyesters containing 33 mol % *m*-ABA and 67 mol % linear *p*-ABA/HQDA/TPA units, melt spinning of the copolyesters, and subsequent characterization of the fibers. The variation of the properties of copolyesters and fibers with type of the linear monomers is also discussed.

EXPERIMENTAL

Monomer Synthesis

TPA, *p*-HBA, *m*-HBA, and hydroquinone (HQ) were obtained commercially from Merck and used

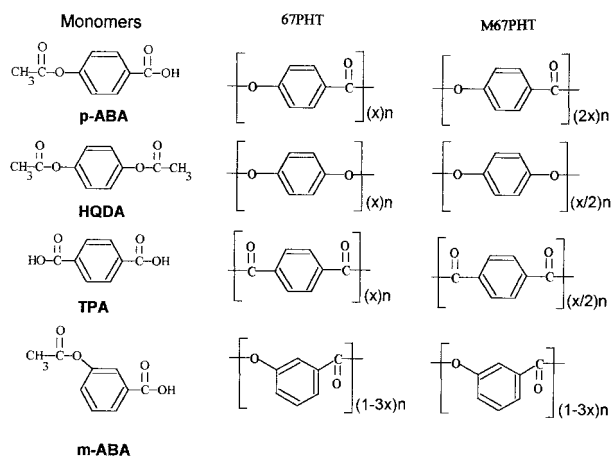


Figure 1 Structure of monomers and compositions of monomeric units in copolyesters based on *p*-acetoxybenzoic acid (*p*-ABA), hydroquinone diacetate (HQDA), terephthalic acid (TPA), and *m*-acetoxybenzoic acid (*m*-ABA) (*x*: mol fraction that is equal to 0.223; *n*: degree of polymerization).

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 sulfuric acid catalyst (Figure 1). Each product was recrystallized from ethanol–water mixture (25:75 v/v) and dried under vacuum at 60 °C for 24 h.

Copolyester Synthesis

All the copolyesters were prepared according to the procedure reported in our previous study.¹⁹ Two types of copolyesters were prepared from 33 mol % kinked *m*-ABA and 67 mol % linear *p*-ABA/HQDA/TPA monomers (Figure 1). The copolyester that is coded as 67PHT contains equimolar amounts of linear monomers. The other copolyester that is coded as M67PHT contains 50 mol % higher content of *p*-ABA and 50 mol % lower content of HQDA/TPA compared with 67PHT copolyester (Table I). A typical procedure is described as follows: Monomers (0.25 mol in total) and acetic acid (80 mL) were charged into a cylindrical glass reactor (diameter 35 mm and length 250 mm) fitted with a stainless stirrer, nitrogen inlet, vacuum outlet, and a tube connected via a condenser to a condensate collector. The reaction flask was evacuated and purged with nitrogen gas three times to remove all air. The temperature of silicone oil bath was increased to 280 °C, and then the reactor was placed in oil bath while the reac-

Table I Charged Composition and Intrinsic Viscosity Values of the Copolyesters Prepared by Melt Polycondensation Reaction

Polymer Code	Charged Composition (mol %) <i>p</i> -ABA/ HQDA/TPA/ <i>m</i> -ABA	$[\eta]$ (dL/g) ^a	$[\eta]$ (dL/g) ^b
67PHT	22.3:22.3:22.3:33.0	0.34	0.46
M67PHT	44.6:11.2:11.2:33.0	0.55	0.63

^a Intrinsic viscosity values for the copolyesters prepared under 60 min vacuum application.²⁹

^b Intrinsic viscosity values for the copolyesters prepared under 120 min vacuum application (this work).

tants were stirred with a dry nitrogen flow of ~50 mL/min. Excess acetic acid incorporated into reaction mixture was collected in 10 min. The homogeneous reaction mixture was then maintained at 280 °C under nitrogen flow for 45 min, and at this point, most of the acetic acid as reaction byproduct had been collected. The next stage was carried out under vacuum for an additional 120 min. During this period, vacuum was gradually applied and reached 0.05 mmHg at the end of the reaction period. The reaction was stopped by introducing 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 dried at 60 °C in vacuum oven overnight.

Fiber Spinning

To establish optimum melt spinning temperature for the polymer prepared under 60 min²⁹ and 120 min vacuum application, dried polymer granules were melted under nitrogen and the melt temperature was then gradually raised within nematic region until fine, flexible, even, and long (at least 1.0 m long) fibers could be drawn from the melt with a fine stainless-steel hook. Only the copolyesters prepared by polycondensation under 120 min vacuum application were drawn easily. Fibers from 67PHT and M67PHT copolyesters were melt spun with free-fall extrusion on a home-made fiber extrusion and spinning set-up at temperatures of 300 and 310 °C, established by the procedure already described above. A spinneret with 8 holes with diameters 0.508 mm and length 1.52 mm was employed. The filaments were quenched in air and collected with a wind-up equipment placed 1.0 m from the bottom of the spinneret.

Characterization

The intrinsic viscosity of the copolyesters dissolved in dichloromethane/trifluoroacetic acid

(70:30 v/v) solution was determined by an Ubbelohde viscometer, at 25 °C and at the concentration of 0.5 g/dL.

The optical texture of the copolyesters was studied with a polarizing microscope equipped with a hot-stage (temperature limit: 430 °C). The sample was prepared by heating a piece on a glass plate (200–300 °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 [i.e., the crystal-to-nematic (T_{cn}) and nematic-to-isotropic (T_{ni}) transitions] were noted. The photomicrographs of the typical nematic textures and isotropic transitions were taken under the polarizing microscope.

The differential scanning calorimetry (DSC) measurements of the copolyesters and the fibers were performed on a Du Pont DSC 910, under a nitrogen flow to determine melting temperatures (T_m) and glass transition temperatures (T_g). First DSC scans were run between 40 and 390 °C at 30 °C/min. The samples then cooled in 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. The T_g s were assumed to be at the mid-point of the change in the heat capacity data.

Wide-angle X-ray diffraction (WAXD) patterns of the powder copolyesters and the spun fibers were obtained at room temperature, with a flat-plate camera, by Huber-Guinier G600 powder diffractometer on Enfaf-Nonius 550 generator with Ni-filtered CuK α radiation (36 kV, 18 mA) of the wavelength of 1.54 Å. Film-to-substance distance was 4 cm, and exposure time was 4 h.

A Lloyd's tensile tester (Lloyd LR 5K) was used to determine the fiber tensile properties. The extension rate used in all experiments was 2 mm/min. Single fibers were mounted and glued over a longitudinal slot, cut from the center of the tab.

The average of five determinations was reported for each sample. Cross-sectional areas were determined with an optical microscope.

A scanning electron microscope (SEM), model JEOL JSM-6400, was used to investigate the morphology or structure of the fibers. The samples were fractured or peeled parallel to the fiber axis at room temperature and the fractured/peeled surfaces were mounted on holders with a conductive epoxy and sputtered with gold in a vacuum chamber to give a conductive surface prior to SEM observations.

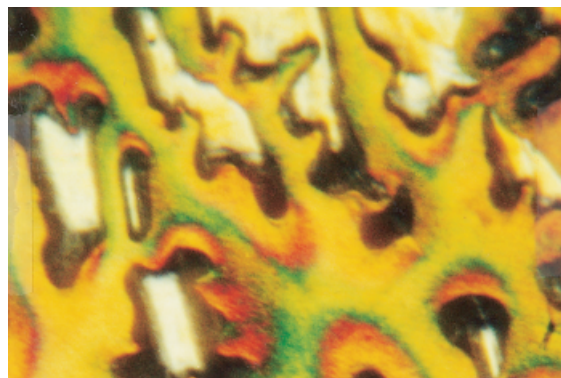
RESULTS AND DISCUSSION

Polymer Characterization

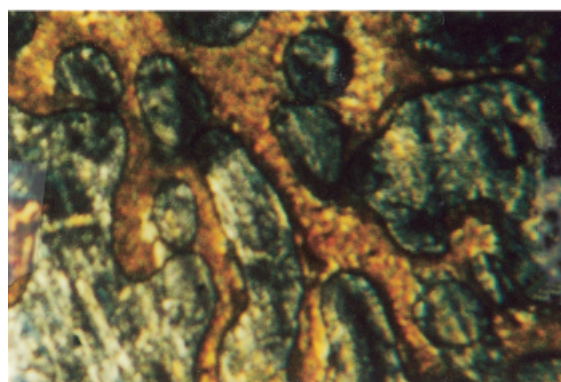
The intrinsic viscosities of the 67PHT and M67PHT copolyesters are shown in Table I. Compared with the copolyesters prepared in our previous study,²⁹ increasing copolycondensation time at vacuum stage from 60 to 120 min leads to an increase in intrinsic viscosity values of the copolyesters (from 0.34 to 0.46 g/dL for 67PHT and from 0.55 to 0.63 g/dL for M67PHT) that assure spinnability.

The morphological textures of copolyesters were studied as a function of temperature in a hot-stage polarizing optical microscope. Photomicrographs of nematic phase and nematic-to-isotropic phase transitions are shown in Figures 2 and 3. The data on T_{cn} and T_{ni} transition temperatures of liquid crystalline copolyesters are given in Table II. Both 67PHT and M67PHT copolyesters produced turbid melts and exhibited nematic mesophases in the ranges 210–360 and 210–370 °C, respectively, that are apparent from the high birefringences under crossed polarizers. The nematic phase exists over a broad temperature range. Both samples exhibit phase separated anisotropy and isotropic domains. Compared with 67PHT copolyester, bisphasic fluid structure is observed more clearly at 320 °C for M67PHT copolyester, displaying isotropic droplets dispersed in the anisotropic medium (Figure 3a).

The DSC thermograms of the copolyesters in the first and second heating cycles are shown in Figure 4. The endothermic peaks observed in the first heating cycle are very weak and broad (Figures 4a and 4c, Table II). The melting temperatures observed for 67PHT and M67PHT copolyesters are at 227 and 246 °C, respectively. The broad endotherms of the copolyesters are consis-



(a)

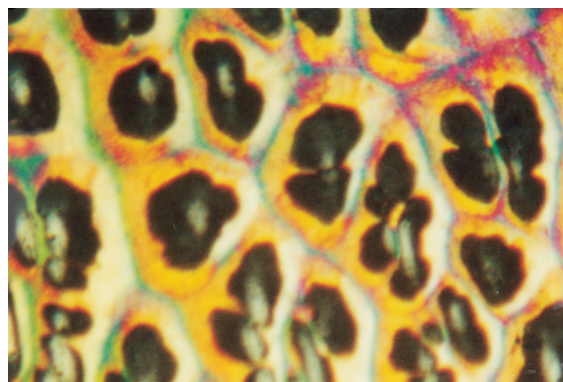


(b)

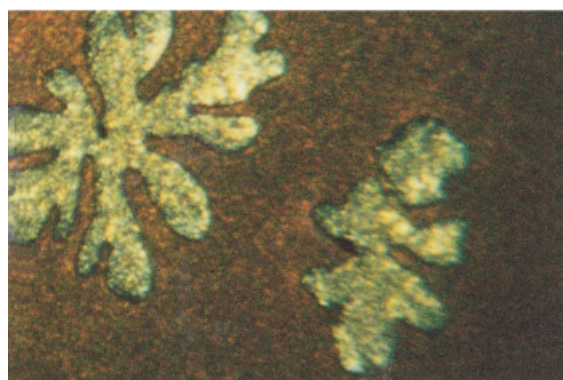
Figure 2 Polarizing optical photomicrographs ($\times 100$) of 67PHT copolyester: (a) nematic phase at 320 °C, (b) isotropic phase at 360 °C.

tent with the flow temperatures obtained by hot-stage polarized light microscopy. The mesophase that is the continuous phase exhibits a broad peak, which is characteristic of the softening process of liquid crystalline polymers. The second heating DSC thermograms showed no distinct melting endotherms, implying that they have either lost their structural regularity or crystallization may be extremely slow during the cooling process (Figures 4b and 4d). The structural irregularities caused by the random sequence distribution of the four different monomers, together with the existence of bent structure in *m*-ABA units may hinder crystallization. Endothermic steps assignable to the glass transition were present in the second heating cycle.

Typical WAXD patterns of powder 67PHT and M67PHT copolyesters are shown in Figures 5a and 5c. Each of the virgin powder copolyesters



(a)



(b)

Figure 3 Polarizing optical photomicrographs ($\times 100$) of M67PHT copolyester: (a) nematic phase at 320 °C, (b) isotropic phase at 370 °C.

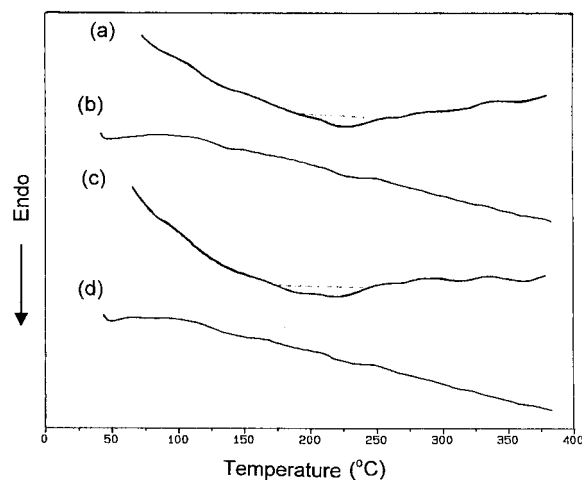


Figure 4 DSC thermograms of the copolyesters: (a) first heating of 67PHT, (b) second heating of 67PHT, (c) first heating of M67PHT, (d) second heating of M67PHT.

showed diffraction pattern with only one ring, with a d -spacing of 4.14 Å for 67PHT and 4.16 Å for M67PHT, typical of a low crystalline polymer. The results of the WAXD studies are in good agreement with the DSC measurements in terms of low crystallinities observed for the copolyesters prepared.

Fiber Characterization

The first and second heating cycles the DSC thermograms of the fiber samples that are melt spun

Table II Thermal, Optical, and Mechanical Properties of the Copolyesters and the Copolyester Fibers

Polymer Code	DSC				Polarized Microscopy		Mechanical Properties		
	First Scan ^a		Second Scan ^b		T_{cn} (°C)	T_{ni} (°C)	Tensile Strength (GPa)	Initial Modulus (GPa)	Elongation to Break (%)
	T_g (°C)	T_m (°C)	T_g (°C)	T_m^c (°C)					
67PHT	114	227	121	—	210	360	—	—	—
M67PHT	115	223	122	—	210	370	—	—	—
67PHT Fiber	114	226	121	—	—	—	0.34	22.7	1.9
M67PHT Fiber	114	235;265	116	—	—	—	0.06	5.46	1.2

^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 Not observed.

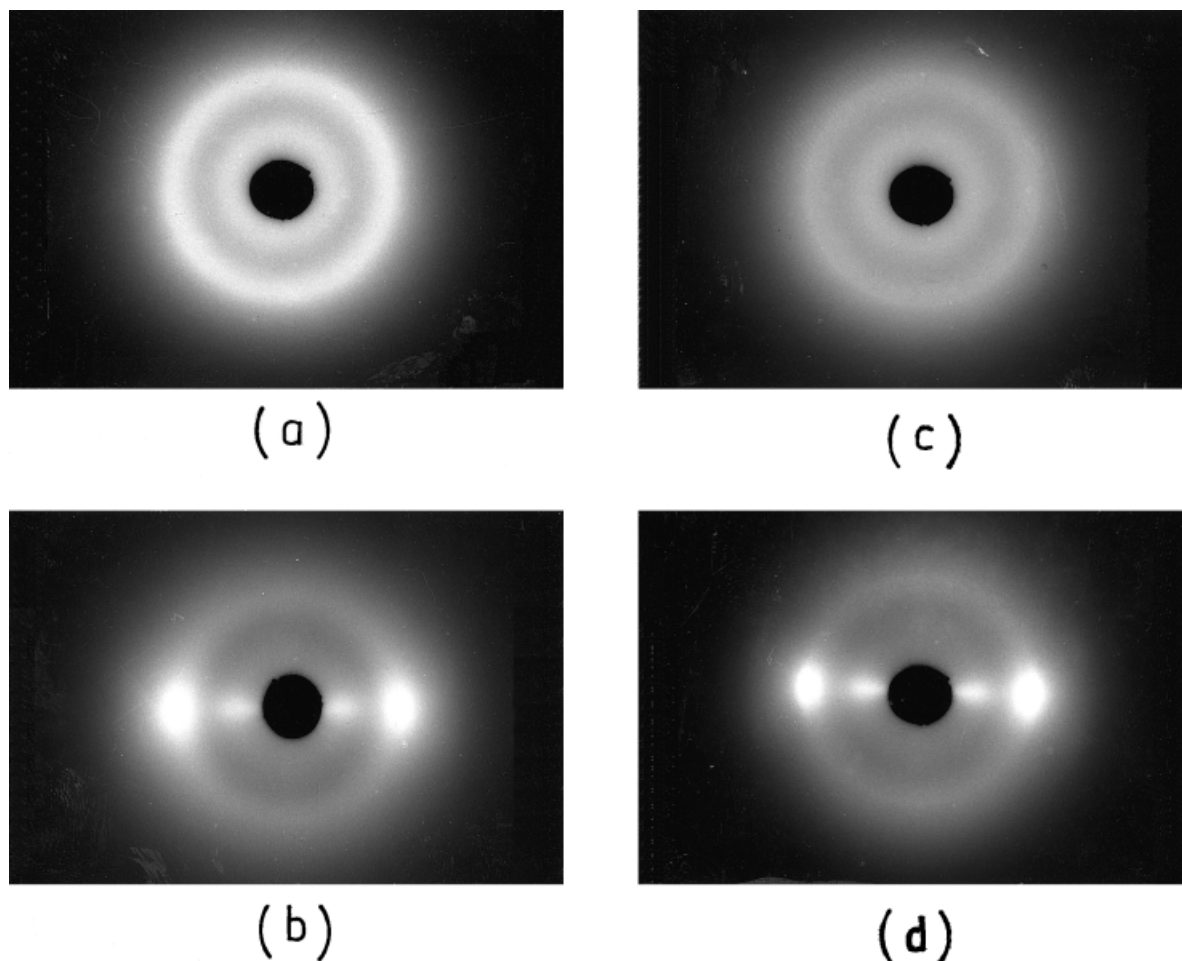


Figure 5 Wide-angle X-ray diffractograms of the copolyesters: (a) 67PHT copolyester, (b) 67PHT fiber, (c) M67PHT copolyester, (d) M67PHT fiber.

from the nematic mesophase are shown in Figure 6. After spinning of the copolyesters, the area of the melting endotherms become larger and more distinguishable because of the high degree of molecular orientation during processing. The endothermic peaks at 226 °C for 67PHT fibers, and double peaks at 235 and 265 °C for M67PHT fibers are intensified (Table II). The T_g values of the fibers observed in the first heating cycle are in agreement with those of the copolyesters (Figures 6a and 6c). The second heating DSC thermograms of the fibers are similar to those of the powder copolyester that showed no distinct melting endotherms (Figures 6b and 6d).

WAXD diffraction patterns of 67PHT and M67PHT fibers samples are shown in Figures 5b and 5d, respectively. It can be clearly recognized that the chains in the fluid are highly oriented in the flow direction at the initial state of spin draw-

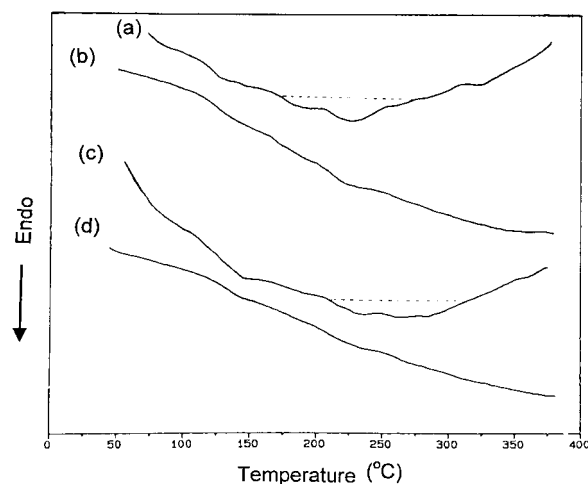
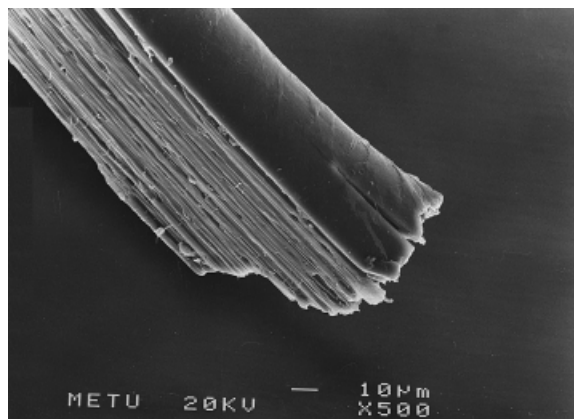
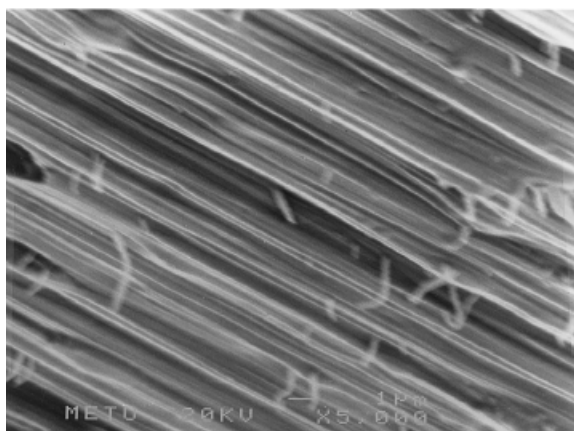


Figure 6 DSC thermograms of the fibers: (a) first heating of 67PHT fiber, (b) second heating of 67PHT fiber, (c) first heating of M67PHT fiber, (d) second heating of M67PHT fiber.



(a)



(b)

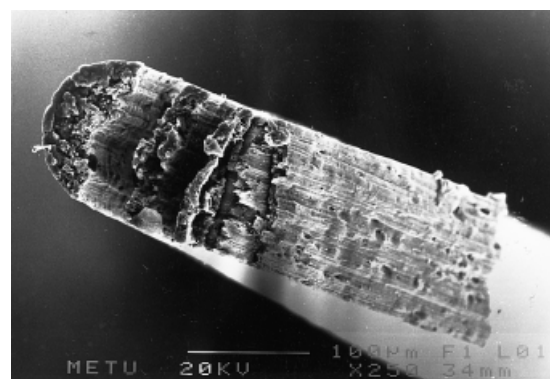
Figure 7 SEM photomicrographs of 67PHT fibers at different magnifications. The fibers were fractured or peeled parallel to the fiber axis at room temperature.

ing. In both diffraction patterns, fibers are clearly anisotropic, which is characteristic of an oriented nematic phase.

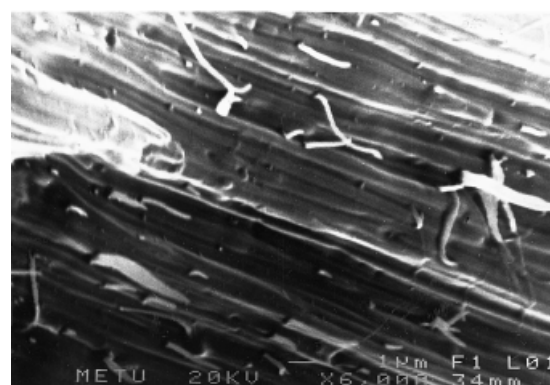
The SEM photomicrographs of 67PHT (Figure 7) and M67PHT fiber samples (Figure 8) show that fibers exhibit well-developed fibrillar structure parallel to the fiber axis. The orientational structures observed by X-ray diffraction are confirmed by the SEM technique. Axial orientation of the fibrillar texture in Figures 7a and 8a is readily visible to the naked eye and is clearly demonstrated at higher magnification (Figures 7b and 8b). The highly oriented morphology of the fibrils is slightly dependent on the type of the linear monomers. It seems that unoriented regions within the material are present, and the fibrils become less fine and less oriented as the

p-ABA content increases and HQDA/TPA content decreases (Fig. 8b).

The average tensile strength, initial modulus, and elongation to break of the fibers are 0.34 GPa, 22.7 GPa, and 1.9% for 67PHT fibers and 0.06 GPa, 5.46 GPa, and 1.2% for M67PHT fibers, respectively (Table II). Compared with 67PHT fibers, the less pronounced orientation within the M67PHT fibers severely limited the mechanical properties. According to Nakai et al.,^{30, 31} the mechanical properties of the LCPs and their mixtures depend on the phase separation. Undesirable macroscopic phase separation of the M67PHT copolyester and poor adhesion among the phases may result also in a lowering of the mechanical properties of M67PHT fiber compared with the 67PHT fiber. The strength and modulus values determined for 67PHT fibers are comparable to



(a)



(b)

Figure 8 SEM photomicrographs of 67PHT fibers at different magnifications. The fibers were fractured or peeled parallel to the fiber axis at room temperature.

those of rigid systems containing totally aromatic spacers.^{7,9,12,19,28}

CONCLUSION

The copolyesters showed nematic mesophases in a very broad temperature range. The melting or flow temperatures were in the processable region. WAXD diffraction patterns of 67PHT and M67PHT fibers samples showed that the polymer chains are highly oriented in the flow direction. The SEM photomicrographs of 67PHT and M67PHT fiber samples of copolyesters show that fibers exhibit well-developed fibrillar structure parallel to the fiber axis. The highly oriented morphology of the fibrils is also dependent on the type of the linear monomers. Compared with 67PHT fibers, less oriented fibrillar structures in M67PHT fibers severely limited the mechanical properties of the fibers. M67PHT copolyester, as seen in a polarized microscope, has higher amount of phase separation than 67PHT copolyester, and poor adhesion is thought to be the low mechanical performance of M67PHT. The mechanical properties determined for 67PHT fibers are comparable to those of rigid systems containing totally aromatic spacers. The nature of the linear unit (*p*-ABA or TPA/HQDA) clearly has an effect on the orientation and phase separation behavior of totally aromatic copolyesters and on the mechanical properties of the fibers formed.

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