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Synthesis and Properties of Thermotropic Liquid Crystalline Copolyesters Containing *p*-Hydroxyphenylacetic Acid and *m*-Hydroxybenzoic Acid Units

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*A series of copolyesters based on *p*-acetoxybenzoic acid (*p*-ABA), *m*-acetoxybenzoic acid (*m*-ABA), and *p*-acetoxyphenylacetic acid (*p*-APAA) were prepared by a modified melt polycondensation reaction. The effect of linear *p*-ABA structure, kink *m*-ABA and flexible *p*-APAA moiety on the properties of copolyesters were systematically investigated. The copolyesters were characterized by DSC, thermogravimetric analysis, ¹H-NMR, polarized optical microscopy, X-ray diffraction, and intrinsic viscosity measurements. The copolyesters exhibited nematic liquid-crystalline phases in a broad temperature range of about 110°C, when the content of linear *p*-ABA units was over 55 mol%. DSC analysis of the anisotropic copolyesters revealed broad and weak endotherms associated with the nematic phases, and the melting temperatures were found to be in the processable region. The degree of crystallinity, thermal decomposition temperatures, crystal-to-nematic and nematic-to-isotropic transitions depend on the type of monomer units, and these transitions increased as the content of the rigid-linear *p*-ABA units increased, or as the content of the flexible/kink *p*-APAA/*m*-ABA units decreased.*

Keywords liquid-crystalline polymers, thermal properties, polycondensation, flexible units, X-ray

Introduction

Thermotropic liquid-crystalline polymers (TLCs) are an important class of structural polymers. In the last three decades, they have received considerable attention because of their excellent mechanical properties, thermal stability and chemical resistance with easy processability (1–6). The objective of designing melt-processable nematogenic

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polymers is to reduce the melting temperature to at least 50°C below the thermal stability limit and to obtain a melt that remains nematic until the onset of decomposition. Many melt-processable nematogenic copolyesters have been synthesized and characterized (7–10). The liquid-crystalline behavior and the transition temperatures were dependent on the copolymerization of the ester groups, use of rodlike arylene moieties of different lengths, use of kink units, and the incorporation of flexible spacers (22). A majority of the commercially important or academically interesting TLCs are random, wholly or partially aromatic polymers with p-oxybenzoate residues in the main chain (23). The systems based on the rigid rod-flexible spacer concept have the virtue of thermally processable polymers that can be manipulated by the nature and mole fraction of flexible spacers. For this purpose, a wide range of polymers containing rigid rods and flexible spacers with different lengths containing two or more $-\text{CH}_2-$ aliphatic groups in the backbone were prepared and characterized (16, 19, 23–26).

This study deals with the synthesis and a systematic characterization of a new type of copolyester modified with p-acetoxyphenylacetic acid (p-APAA). For this purpose, p-acetoxybenzoic acid (p-ABA-linear), m-acetoxybenzoic acid (m-ABA-kink), and p-APAA (semiflexible with one $-\text{CH}_2-$ group in the backbone) monomer units were used in different compositions. In addition, a homopolymer of p-APAA and a copolyester based on two monomers (p-ABA/p-APAA) were prepared and used for comparison. The homopolymers of p-ABA (100P), and m-ABA (100M), together with the copolyesters of p-ABA/m-ABA (50PM) prepared in our previous study were also used for comparison (21).

Experimental

Monomer Synthesis

p-Hydroxybenzoic acid (p-HBA), m-hydroxybenzoic acid (m-HBA), and p-hydroxyphenyl acetic acid (p-HPAA), were obtained commercially from Merck and used without further purification. p-ABA (mp: 187–192°C), m-ABA (mp: 130–135°C) and p-APAA (mp: 90–95°C) (Figure 1) were prepared from p-HBA, m-HBA, and p-HPAA, respectively as described previously (20).

Copolyester Synthesis

All the copolyesters and homopolyesters of p-ABA [p-poly(oxybenzoate)] coded as 100P, m-ABA [m-poly(oxybenzoate)] coded as 100M, and p-APAA [p-poly(oxyphenyleneacetate)] coded as 100F were prepared by a high-temperature melt-polycondensation method on a 0.1 mol scale without any added catalyst as described in our previous study (20). Stoichiometric details of the copolyesters prepared in two series and the polymer abbreviations that are used are summarized in Table 1 and, a typical procedure is summarized as follows: Monomers (0.1 mol in total) and acetic acid (35 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. After the reaction flask was evacuated and purged with nitrogen gas three times to remove all air, the temperature of the silicone oil bath was increased to 280°C, and then the reactor was placed in an oil bath while the reactants were stirred with a dry nitrogen flow. Excess acetic acid incorporated into a reaction mixture was collected in 10 min. The homogeneous reaction mixture was then maintained at 280°C

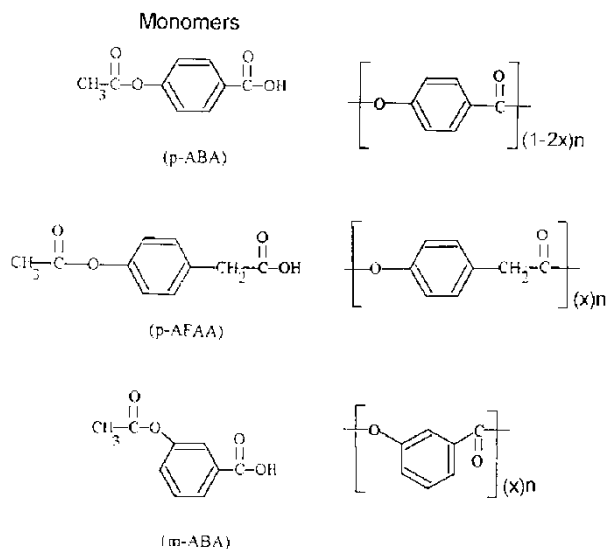


Figure 1. Structure of monomers and compositions of monomeric units in copolyesters based on p-acetoxybenzoic acid (p-ABA), m-acetoxybenzoic acid (m-ABA), and p-acetoxyphenylacetic acid (p-AFAA) (x: mol fraction; n: degree of polymerization).

under a nitrogen flow for 45 min. The next stage was carried out under 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 recovered by breaking the glass container and dried at 60°C in a vacuum oven overnight.

Table 1
Stoichiometric details and abbreviations of the polyesters prepared by melt-polycondensation reaction

| Series | Charged composition (mol%) | | Abbreviation |
|--------|----------------------------|-------|-------------------|
| | p-ABA/m-ABA/p-AFAA | p-ABA | |
| I | 50.0:50.0:0.00 | 50 | 50PM ^a |
| | 50.0:0.00:50.0 | 50 | 50PF |
| II | 70.0:15.0:15.0 | 70 | 70PMF |
| | 60.0:20.0:20.0 | 60 | 60PMF |
| | 55.0:22.5:22.5 | 55 | 55PMF |
| | 50.0:25.0:25.0 | 50 | 50PMF |
| | 40.0:30.0:30.0 | 40 | 40PMF |
| III | 100:0.00:0.00 | 100 | 100P ^a |
| | 0.00:100:0.00 | 0.00 | 100M ^a |
| | 0.00:0.00:100 | 0.00 | 100F |

^aFrom Reference no: 21.

Characterization

The optical texture 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 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, 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 a polarizing microscope.

The differential scanning calorimetry (DSC) measurements were performed on a Du Pont DSC 910 under a nitrogen flow. DSC scans were run between 30–390°C at 10°C/min. The weight of all samples was kept between 5–10 mg. The glass transition temperatures (T_g) were assumed to be at the mid-point of the change in the heat capacity.

Thermogravimetric analysis (TGA) for all samples was performed by a TGA system (Shimadzu TGA-50 Instrument) under a nitrogen flow between 20–700°C at a heating rate of 20°C/min.

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 the concentration of 0.5 g/dL.

Wide-angle X-ray diffraction (WAXD) patterns for 100F and 50PF polyesters were obtained by Philips PW 1050/25 Goniometer with $\text{CoK}\alpha$ radiation of the wavelength of 1.79 Å, and for other polyesters obtained by a Huber-Guinier G600 powder diffractometer on a Enfaf-Nonius 550 generator with $\text{CuK}\alpha$ radiation of the 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 (27, 28):

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

Where I_c is the intensity of the crystalline component, and I_a is the intensity of the amorphous component that are the values obtained from the areas of the X-ray diffraction curve.

$^1\text{H-NMR}$ 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 copolyesters and homopolyesters were prepared by high temperature melt-polycondensation. In Series I and Series II coding, the composition of the copolyesters is defined by the letters P, M, F and by the molar percentages of p-ABA units. P stands for p-acetoxybenzoic acid, M stands for m-acetoxybenzoic acid and F stands for p-acetoxyphenyl acetic acid. For example, 60PMF (Series II) copolyester include three different monomer units and 60 molar percentage of p-ABA in the polymer chains. In Series II copolyesters, the molar percentage of m-ABA and p-APAA units are equimolar in each.

Excess acetic acid was added to the reaction medium to obtain a more homogeneous mixture and prevent the sublimation of monomers. The polycondensation was performed

Table 2
Thermal properties of homopolyesters and copolyesters

| Series | Polymer code | DSC | | | Polarized microscopy | | TGA ^b | [η] ^c |
|--------|-------------------|----------------------------------|----------------------------------|---------------------------------|-----------------------------------|----------------------|---------------------|-------------------------|
| | | T _g (°C) ^a | T _m (°C) ^a | ΔH_f (J/g) ^a | T _{cn} (°C) ^h | T _{ni} (°C) | T _d (°C) | (dL/g) |
| I | 50PM ^e | 123 | 175 | — ^d | — ^d | — ^d | 432 | — ^f |
| | 50PF | 108 | 247 | 12.5 | — ^d | — ^d | 345 | 0,63 |
| II | 70PMF | — ^d | 247;306 | 5.55 | 240 | 340 | 384 | — ^f |
| | 60PMF | 136 | 246 | 6.15 | 220 | 330 | 376 | — ^f |
| | 55PMF | 142 | 246 | 5.17 | 210 | 320 | 371 | — ^f |
| | 50PMF | 135 | 246 | 4.07 | — ^d | — ^d | 358 | — ^f |
| III | 40PMF | 123 | 248 | 9.17 | — ^d | — ^d | 368 | 0.75 |
| | 100P ^e | — ^d | — ^d | — ^d | — ^d | — ^d | 476 | — ^f |
| | 100M ^e | 129 | 210 ^g | — ^d | — ^d | — ^d | 405 | 0.20 |
| | 100F | 117 | 246 | 55.2 | — ^d | — ^d | 267 | 0.10 |

^aFrom DSC measurements at a heating rate of 10°C/min.

^bThermal stability was determined from TGA in nitrogen, at a heating rate of 20°C/min (T_d: Initial decomposition temperature).

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

^dNot observed.

^eFrom reference no: 21

^fInsoluble.

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

^hThe onset of crystal (c) to nematic (n) transition.

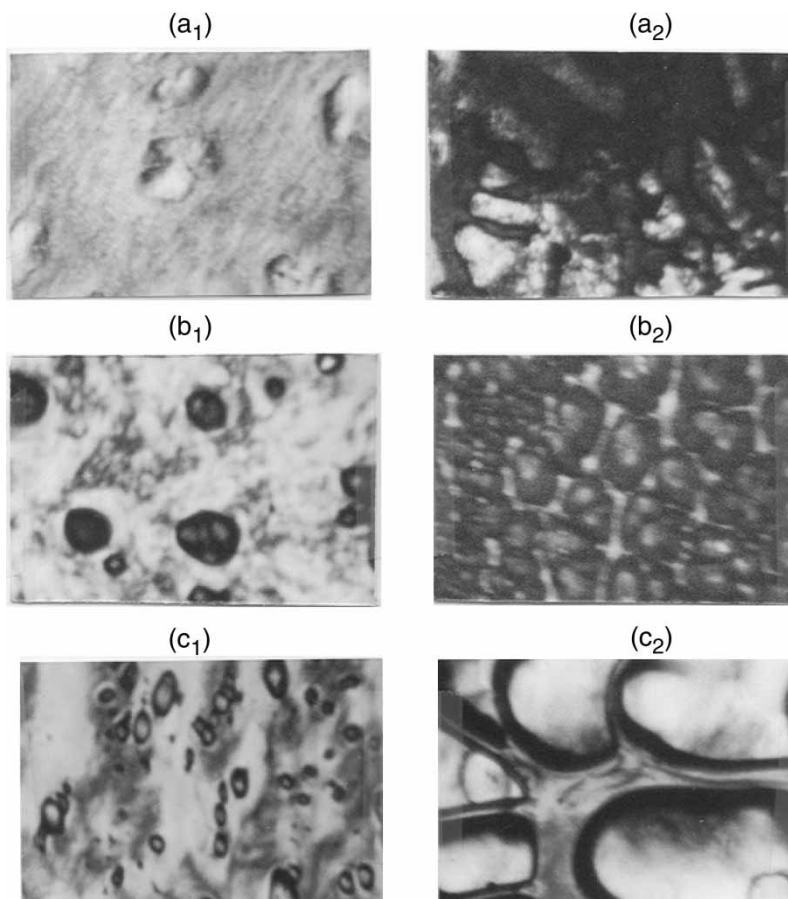


Figure 2. Polarizing optical photomicrographs ($\times 100$) of 70PMF, 60PMF and 55PMF copolyesters; (a₁) 70PMF at 315°C, (a₂) 70PMF at 340°C, (b₁) 60PMF at 305°C, (b₂) 60PMF at 330°C, (c₁) 55PMF at 300°C, (c₂) 55PMF at 320°C.

by placing the reactor to the preheated oil bath at 280°C to increase the probability of obtaining random copolyesters (14, 20). In fact, sublimation of monomers was not observed during the polymerization period. The conclusive evidence on the product stoichiometry is given subsequently with the analysis of the $^1\text{H-NMR}$ data.

The intrinsic viscosities of the 40PMF, 50PF, 100F, and 100M polyesters are listed in Table 2. All other polyesters were insoluble in the dichloromethane/trifluoroacetic acid (70:30 v/v) mixture. When the solubility of these copolyesters were compared with the four monomer (p-ABA/HQDA/TPA/m-ABA) systems, (20) considerable solubility decrease was observed for three comparable (Series II) monomer systems.

Thermal Properties of Copolyesters

The morphological textures of the 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(a₁,b₁,c₁) and 2(a₂,b₂,c₂), respectively. The copolyesters in Series II containing 70, 60, and 55 mol% linear

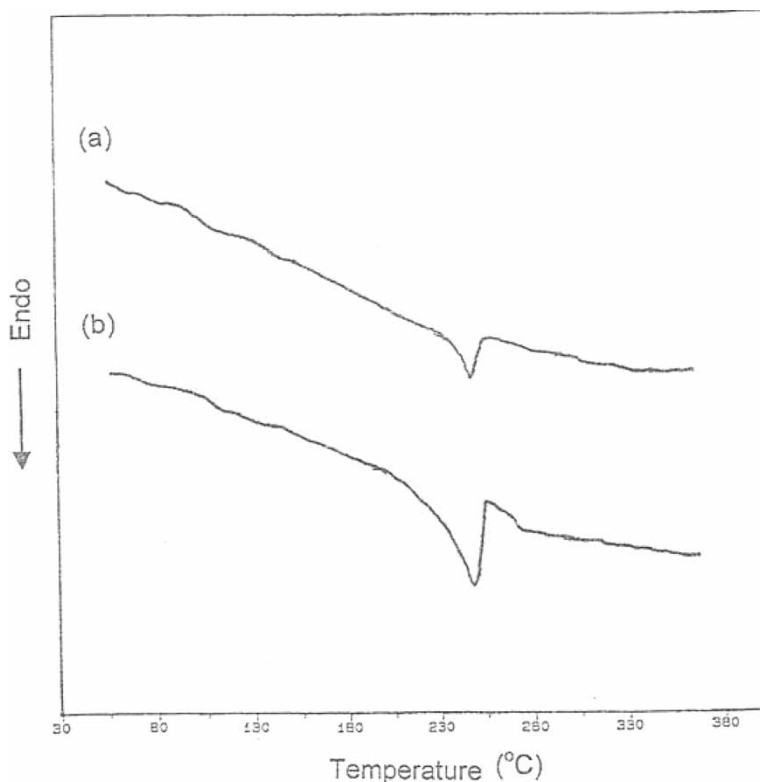


Figure 3. DSC thermograms of 50PF copolyester (a), and 100F homopolyesters (b).

p-ABA units produced turbid melts and exhibited nematic mesophases. In the nematic mesophase, a significant molecular interaction exists in a very broad temperature range (110°C) for the copolyesters, apparent from the high birefringences under crossed polarizers. The data of T_{cn} and T_{ni} transition temperatures of liquid-crystalline copolyesters are given in Table 2. In general, the liquid-crystalline behavior of the copolyesters depends greatly on the composition, content of p-ABA units, or content of m-ABA/p-APAA units in the polymer chains. The ability of these polymers to form liquid-crystalline melts was reduced at high m-ABA/p-APAA unit contents.

The DSC thermograms of the copolyesters are illustrated in Figures 3 and 4. The endothermic peaks observed are weak and broad for thermotropic liquid-crystalline copolyesters that contain 55 mol% or higher p-ABA units (Figure 4). The broad endotherms of the Series II copolyesters are consistent with the flow temperatures obtained by hot-stage polarized light microscopy. The mesophase that is the continuous phase exhibits broad peaks, characteristic of the softening process of liquid-crystalline polymers. The DSC thermogram of the 70PMF copolyester showed two distinct and broad melting endotherms at 247 and 306°C. The one at 247°C is the melting temperature of p-APAA crystalline units, which is the same temperature observed for pure p-APAA polyester (Figure 3(b)). The crystallinities that melt at 307°C could be a doublet repeating unit composed of p-ABA and p-APAA monomeric units.

Another interesting point is that for five compositions in Series II, 247°C is found as the major melting temperature. Apparently, p-ABA crystallites do not melt at these

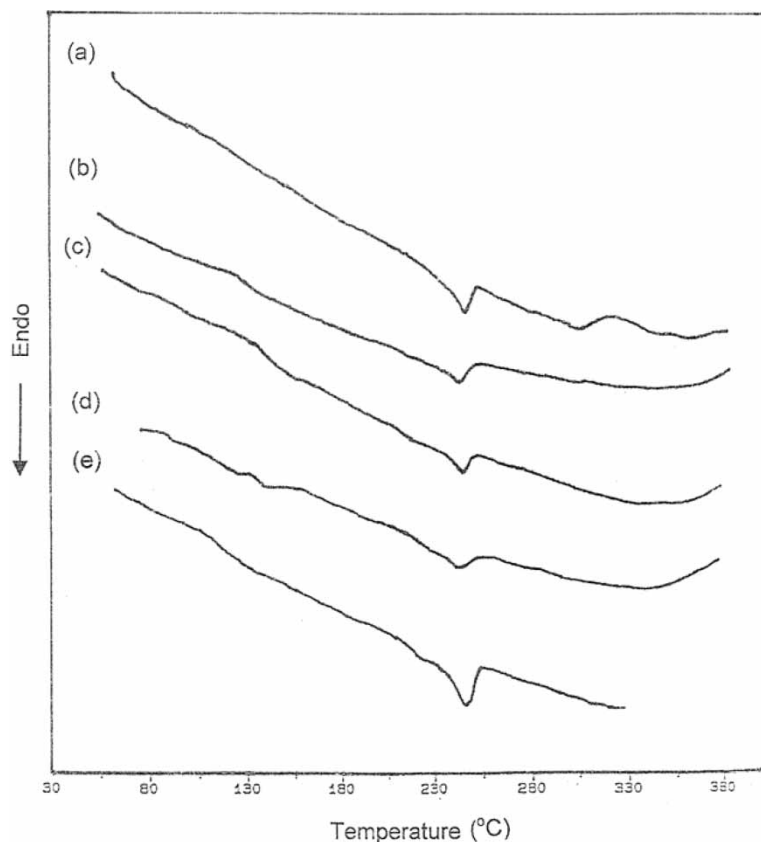


Figure 4. DSC thermograms of Series II copolyesters; (a) 70PMF, (b) 60PMF, (c) 55PMF, (d) 50PMF, (e) 40PMF.

temperatures and its homopolymer is thought to decompose before T_m is reached (23). Compared to the liquid-crystalline copolyesters in Series II, the isotropic samples of 100F and 50PF polyesters showed sharper melting endotherms with higher ΔH_f values in DSC thermograms, implying a more crystalline structure as evidenced also by the WAXD data discussed below. As expected, the isotropic crystalline structures give rise to a high value of enthalpy of fusion, while liquid-crystalline structures give a small value of enthalpy of fusion (Table 2). The extreme case is the homopolymer 100F, which has a comparatively high crystallinity and no liquid crystalline behavior with an extremely high ΔH_f value of $55.2 \text{ J} \cdot \text{g}^{-1}$. Also, isotropic 40PMF copolyester with a lower level of crystallinity has higher ΔH_f value than anisotropic 70PMF copolyester.

The T_g values of the Series II copolyesters are shown in (Table 2). The T_g 's were lowest for 40PMF and highest for 55PMF copolyesters at 123°C and 142°C , respectively. The T_g values are decreased when the mol% of m-ABA/p-APAA units in the polymer composition is higher than 55%. In general, T_g 's for this series of polymers are approximately defined by the content of p-APAA units in the structure. This result is in accordance with earlier studies on the effect of flexible segments on T_g of semicrystalline copolyesters such as poly(ethylene terephthalate) (PET) and isophthalic acid substituted PET (14, 16). In contrast, earlier studies related to the totally aromatic systems containing

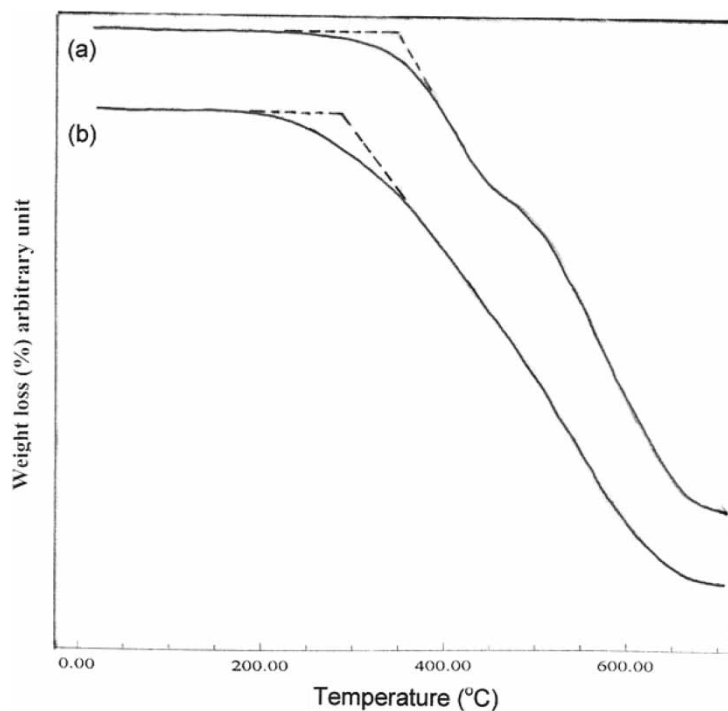


Figure 5. TGA thermograms of 50PF copolyester (a), and 100F homopolyesters (b).

nonlinear (i.e., *m*-ABA) systems showed exactly opposite behavior as a result of an increase of nonlinear segments in the polymer composition or a decrease in crystallinity (5, 20, 29, 30).

The initial decomposition (T_d) temperatures estimated from the TGA thermograms for Series II copolyesters (Figure 6), and for 50PF and 100F polyesters (Figure 5) under nitrogen are given in Table 2. All the copolyesters and homopolyester of *p*-APAA (100F) exhibit a similar pattern of decomposition with no significant weight loss below the initial decomposition. The T_d 's of the copolyesters were found in the 358–384°C range for Series II copolyesters, indicating good thermal stability at elevated temperatures. Thermal stabilities were found to depend upon the content of *p*-APAA and T_d 's were decreased as the content of *p*-APAA units in the polymer chain increased.

WAXD Analysis

WAXD patterns of 100F homopolyesters and 50PF copolyester are shown in Figure 7, and those of Series II copolyesters are shown in Figure 8. *d*-Spacing, Bragg angles and degree of crystallinity of the all polyesters are given in Table 3. The physical and mechanical properties of polymers are profoundly dependent on the degree of crystallinity. Among the degree of crystallinities calculated for polyesters prepared in this study, 100F polyester attains the highest crystallinity (40%) and showed two main diffraction peaks (Figure 7(b)). The peak at $2\theta = 23.10^\circ$, $d = 4.47 \text{ \AA}$ is the most intense peak compared

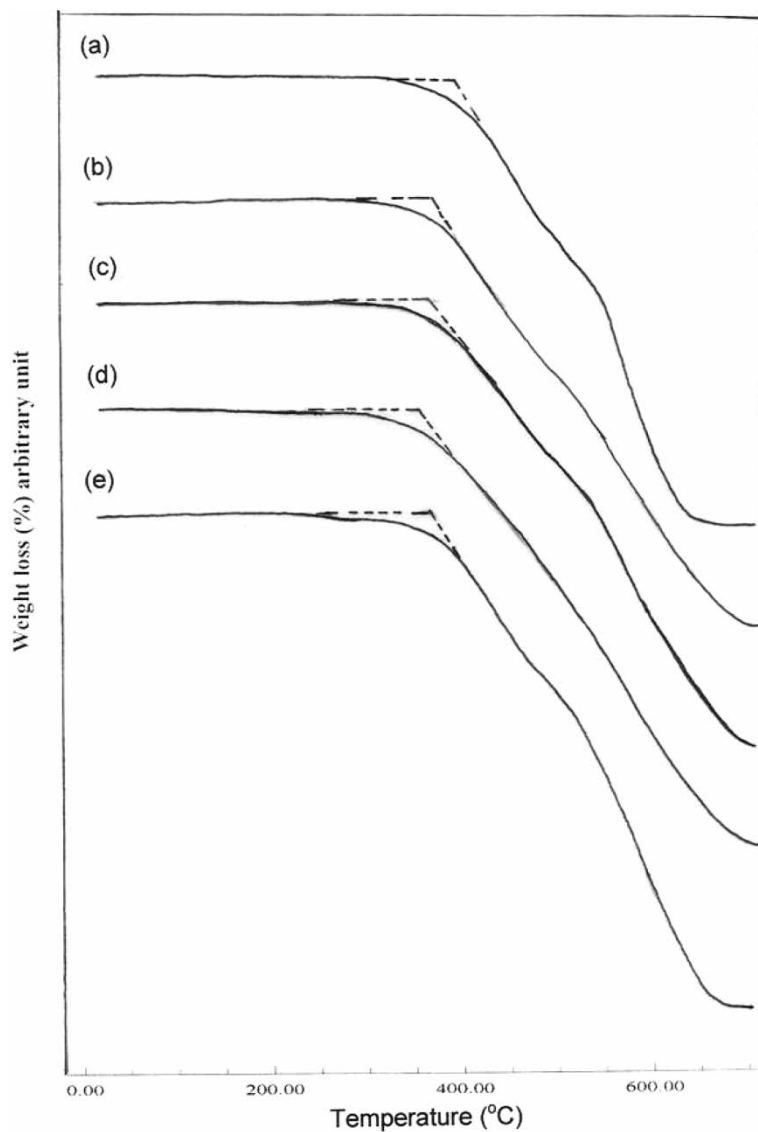


Figure 6. TGA thermograms of Series II copolyesters; (a) 70PMF, (b) 60PMF, (c) 55PMF, (d) 50PMF, (e) 40PMF.

to the other broad and moderate peak. Due to the effect of random copolymerization, the degree of crystallinity determined from the diffractogram of 50PF (Figure 7(a)) is 34.5% that is lower than the homopolyester of 100F, as expected.

With the increasing content of p-APAA/m-ABA units in the polymer chains of Series II copolyesters, the degree of crystallinity of the copolyesters and the intensity of original four main diffraction peaks for 100P mentioned in our previous study (21) decreased and became broader [Figure 8(a–e)]. Compared to the results obtained for 50PF copolyester prepared in this study or two and three-monomer systems (p-ABA/m-ABA or HQDA/TPA/m-ABA) prepared in our earlier study (21) incorporation of

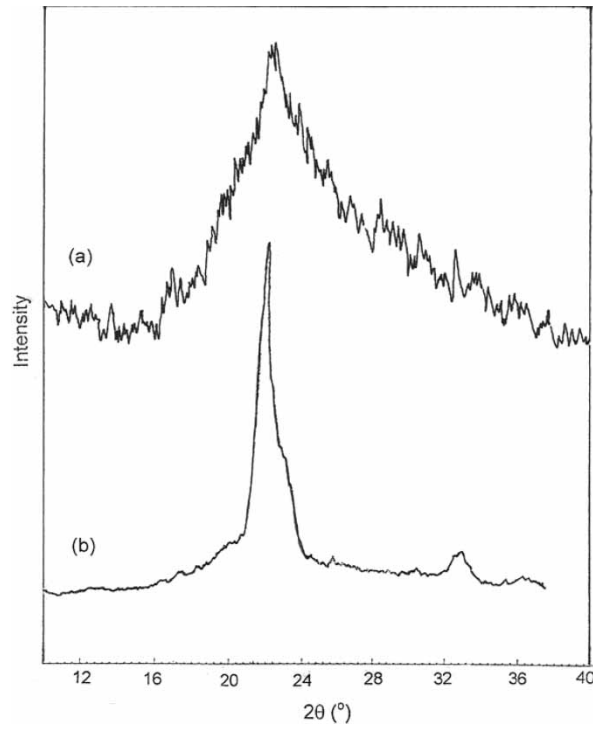


Figure 7. Wide-angle X-ray diffractograms of 50PF copolyester (a), and 100F homopolyesters (b).

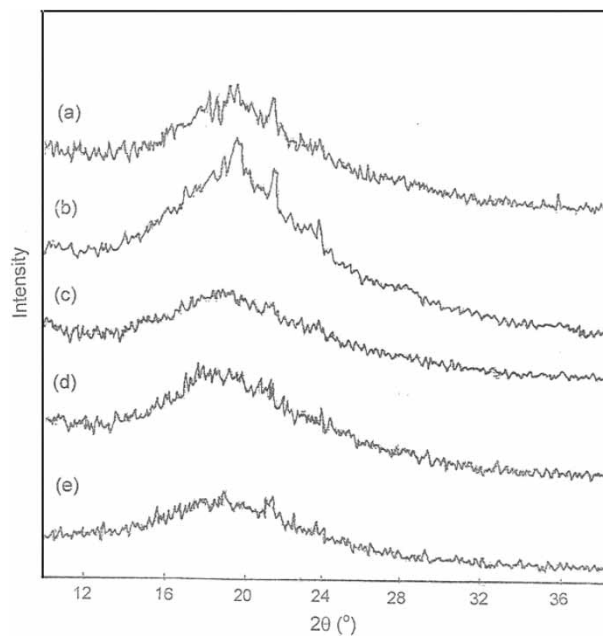


Figure 8. Wide-angle X-ray diffractograms of Series II copolyesters; (a) 70PMF, (b) 60PMF, (c) 55PMF, (d) 50PMF, (e) 40PMF.

Table 3
Observed X-ray diffraction data for homopolyesters and copolyesters

| Polymer code | 2θ ($^\circ$) | d-Spacing (\AA) | Intensity ^a | Degree of crystallinity (%) |
|-------------------|------------------------|----------------------------|------------------------|-----------------------------|
| 50PM ^c | 19.22 | 4.61 | wB | 6.5 |
| | 21.42 | 4.15 | sS | |
| | 23.78 | 3.74 | wB | |
| 50PF ^b | 23.40 | 4.41 | vsS | 34.5 |
| | 28.80 | 4.00 | wB | |
| | 30.80 | 3.37 | wB | |
| | 32.80 | 3.17 | wS | |
| | 18.10 | 4.89 | wS | |
| 70PMF | 18.50 | 4.79 | mB | 11.0 |
| | 19.14 | 4.63 | wS | |
| | 19.52 | 4.54 | wS | |
| | 21.32 | 4.16 | sB | |
| | 18.88 | 4.71 | wS | |
| 60PMF | 19.44 | 4.56 | sB | 7.0 |
| | 21.36 | 4.17 | sB | |
| | 23.76 | 3.74 | wB | |
| 55PMF | 21.36 | 4.15 | wB | <5 |
| | 23.84 | 3.73 | wB | |
| 50PMF | 20.88 | 4.14 | wB | <5 |
| | 21.36 | 4.17 | wS | |
| | 24.02 | 3.70 | wS | |
| 40PMF | 19.04 | 4.67 | wS | <5 |
| | 21.44 | 4.14 | wB | |
| 100P ^c | 19.74 | 4.49 | vsS | 42.0 |
| | 21.00 | 4.23 | mB | |
| | 23.63 | 3.76 | mB | |
| | 29.44 | 3.03 | mB | |
| 100M ^c | 21.34 | 4.16 | sS | 10.5 |
| | 23.74 | 3.75 | wB | |
| 100F ^b | 23.10 | 4.47 | vsS | 40.0 |
| | 32.30 | 3.22 | wB | |
| | 35.70 | 2.92 | wB | |

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

^bWAXD patterns were obtained by Philips PW 1050/25 Goniometer with CoK α radiation of the wavelength of 1.79 \AA .

^cFrom reference no: 21

30 mol% or more p-APAA/m-ABA units into the copolyesters, together with the random copolymerization considerably reduced the degree of crystallinity. This may be explained by the fact that, chain orientation or packing was prevented to some degree by kink m-ABA units together with the random copolymerization of three different monomer units.

¹H-NMR Analysis

Figure 9 shows typical expanded regions of the ¹H-NMR spectra of the soluble polyesters (100F, 50PF, and 40PMF) with the chemical shifts evident between 6.97 and 8.45 ppm for aromatic protons, 3.80 and 4.11 ppm for aliphatic protons. According to the integrated areas of the peaks, the compositions of the copolyesters which are calculated for the total aliphatic or total aromatic units were very close to the feed ratios (Table 4). However, the 50PF (Figure 9(b)) copolyester contains somewhat less aromatic units (4.0 mol%) than expected from the feed ratios. This may indicate that a small amount of p-ABA monomer is lost by sublimation during the high temperature melt

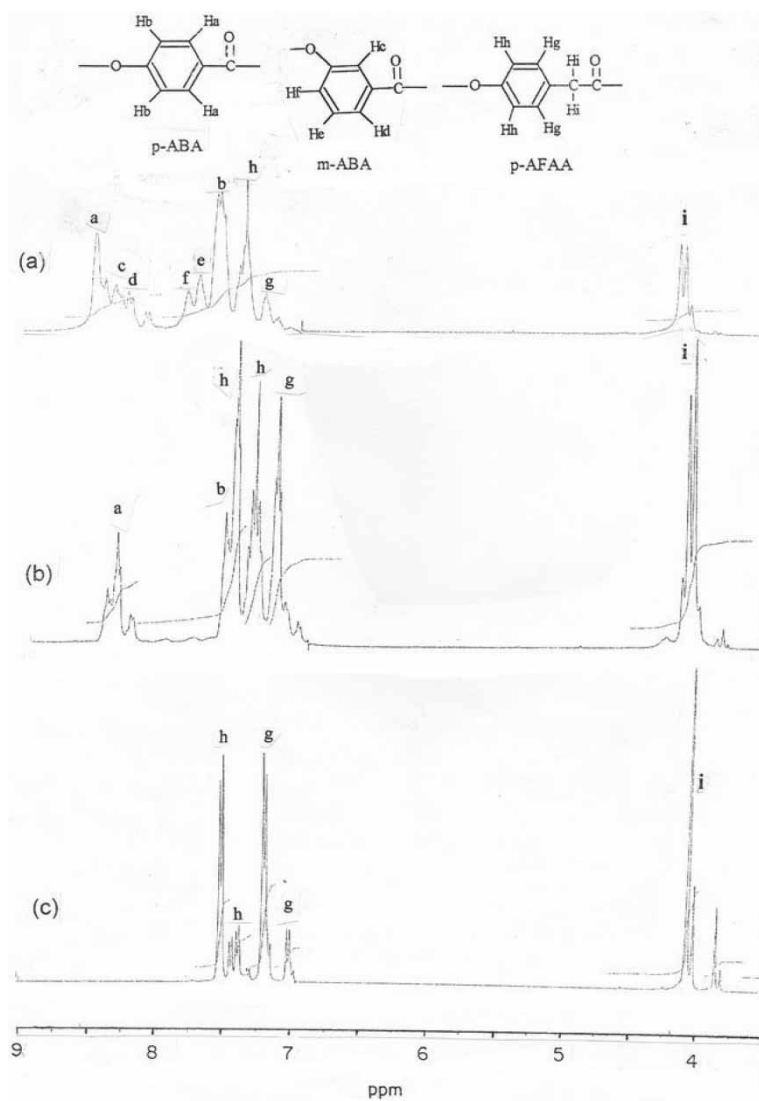


Figure 9. ¹H-NMR spectra of 40PMF copolyesters (a), 50PF copolyester (b), and 100F homopolymer (c).

Table 4
Calculated copolyester compositions determined by $^1\text{H-NMR}$ spectroscopy

| Polymer code | Monomer feed ratio (mol%) [(aliphatic/aromatic) protons] | Polyester composition (mol%) [(aliphatic/aromatic) protons] |
|--------------|--|---|
| 50PF | 20.0/80.0 | 24.0/76.0 |
| 40PMF | 13.0/87.0 | 12.8/87.2 |
| 100F | 33.3/66.7 | 33.1/66.9 |

polycondensation reaction. Nevertheless, the molar ratios are within the accuracy of quantitative $^1\text{H-NMR}$ spectrometry.

Conclusions

A series of homopolyesters or copolyesters with different p-ABA/m-ABA/p-APAA comonomer compositions were prepared by high temperature melt polycondensation. The influence of linear, kink and flexible-aliphatic monomer units on the thermal properties, liquid crystalline behaviors, solubility, viscosity and degree of crystallinity were investigated. The copolyesters containing 70, 60, and 55 mol% of linear p-ABA units showed nematic mesophases in a broad temperature range. The melting or flow temperatures were found to be in the processable region. The T_g values of the copolyesters containing three different monomer units (p-ABA/m-ABA/p-APAA) were decreased, when the content of m-ABA/p-APAA units in the polymer composition is equal or higher than 50%. All the polyesters were thermally stable and they can be processed without degradation above the melting temperatures. According to the results obtained from WAXD patterns, the copolyesters, prepared from three monomer system have semicrystalline or amorphous structure. The degree of crystallinity is decreased as a result of the incorporation of m-ABA/p-APAA units in polymers. From the $^1\text{H-NMR}$ spectra, the compositions of the soluble polyesters were calculated to be almost equal to the feed ratios.

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