Thermal Properties and Crystallinity of Thermotropic Liquid Crystalline Copolyesters Prepared from Poly(ethylene terephtalate) (PET) and Rigid Aromatic Units

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A series of copolyesters were synthesized by melt-polycondensation reaction of poly(ethylene terephtalate) (PET) with various proportions of equimolar compositions of p-acetoxybenzoic acid (p-ABA), hydroquinone diacetate (HQDA) and terephtalic acid (TPA). Viscosity, liquid crystallinity, thermal properties, degree of crystallinity and thermal stabilitiy of these copolyesters were investigated by Ubbelohde viscometer, hot-stage polarized light microscopy (PLM), differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and thermogravimetric analysis (TGA), respectively. On the basis of viscosity measurement, it was observed that intrinsic viscosity values of the copolyesters are increased regularly with increasing amounts of aromatic units (p-ABA, HQDA and TPA) in the polymer chain. Thermotropic liquid crystalline behavior was observed in the copolyesters containing over 50 mol% of rigid p-ABA/HQDA/TPA aromatic units. 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. As the mol% of PET in the polymer chain increased, the specific enthalpies of fusion and the degree of crystallinity of the copolyesters were also increased regularly.

Keywords: poly(ethylene terephthalate); liquid-crystalline copolyester; thermal properties; crystallinity; copolymerization

1 Introduction

Thermotropic liquid crystalline polymers (TLCPs) are widely used as high-performance engineering materials. In the last three decades, they have received considerable attention because of their excellent mechanical properties, thermal stabilities and chemical resistances with easy processability. Many melt-processable nematogenic copolyesters have been synthesized and characterized through the use of different types of structural modifications (1–23). A number of TLCPs based on poly(ethylene terephtalate) (PET) have drawn attention by many researchers (1, 8, 17, 18). The liquid-crystalline behaviour and the transition temperatures were dependent on the copolymerization of the ester groups, use of rod-like arylene moieties of different length, use of kink units, and incorporation of flexible aliphatic spacers. The systems based on 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 length, containing one or more -CH$_2$-aliphatic groups in the backbone were prepared and characterized (7, 8), (16–18, 21, 22). p-Hydroxybenzoic acid (p-HBA), hydroquinone (HQ), terephthalic acid (TPA), and PET containing copolyesters were synthesized in the same manner and characterized by various thermal, mechanical, morphological investigations (18). However, no work with a systematic investigation related to thermal properties and the liquid crystalline properties has yet been reported in the literature on copolyesters that contain p-HBA, HQ, TPA monomers in equal molar ratios and PET in different compositions.

In our previous studies (13–16), rigid-fully aromatic p-HBA, HQ, TPA monomers were used together with kink m-hydroxybenzoic acid (m-HBA) monomer to synthesize thermotropic liquid crystalline copolyesters. Compared to these studies, by using PET copolyester instead of m-HBA in this work, a series of melt-processable and thermally stable thermotropic liquid crystalline copolyesters were synthesized and characterized in detail.

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2 Experimental

2.1 Monomer Synthesis

TPA, p-HBA, HQ were obtained commercially from Merck and used without further purification. p-Acetoxybenzoic acid (p-ABA) (m.p. $187-192°C$) and hydroquinone diacetate (HQDA) (m.p. $122-124°C$) were prepared by reacting p-HBA, HQ, respectively, with excess acetic anhydride at $60°C$ in the presence of sulphuric acid as catalyst (13) (Figure 1). Each product was recrystallized from ethanol/water mixture (25:75 v/v) and dried under vacuum at $60°C$ for 24 h. PET (SASA, $[\eta] = 0.62$ dL/g) polyester that contains polymer chains end-capped with $-OH$ and $-COOH$ functional groups was used as received.

2.2 Copolyester Synthesis

All the copolyesters were prepared according to the procedure reported in our previous study (13) on a 0.15 mol scale without any added catalyst. Stoichiometric details of the copolyesters and polymer abbrevations are given in Table 1.

p-ABA/HQDA/TPA monomers, PET (0.15 mol total) and acetic acid (35 mL) were charged into a specially designed cylindrical glass reactor (diameter 35 mm and length 250 mm) fitted with a stainless steel 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 oil bath while the reactants were stirred with a dry nitrogen gas that has a flow rate of approximately 50 mL/min. Excess acetic acid incorporated

Fig. 1. Structure and compositions of p-acetoxybenzoic acid (p-ABA), hyroquinone diacetate (HQDA) and terephthalic acid (TPA) monomeric units and PET in copolyesters (x:mol fraction; n: degree of polymerization).

into reaction mixture was collected in 10 min. The homogeneous reaction mixture was then maintained at $280°C$ under nitrogen flow for 50 min. The next stage was carried out under vacuum for a further 5 h at $280°C$. 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 vacuum oven overnight. Since some of the product that adhered to the walls of the broken glass reactor and stirrer was not recovered, the yields reported here are lower than the actual values.

2.3 Characterization

The intrinsic viscosity of the copolyesters dissolved in dichloromethane/triflouroacetic acid (70:30 v/v) solution was determined by a Ubbelohde viscometer, at $25°C$ and at the concentrations of 0.5 g/dL.

The optical observations of the copolyesters were investigated with a polarizing optical 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 formed into a sandwich with a thin film inside. The mesomorphic transition temperatures and disappearance of birefringence, that is, the crystal-to-nematic (T_{cn}) and nematic-to-isotropic (T_{ni}) transitions, were noted.

The differential scanning calorimetry (DSC) measurements were performed under nitrogen flow with a heating rate of $10°C/min$ using a Du Pont DSC 910. DSC scans were run between 30 to $390°C$. The DSC instrument was calibrated using Indium metal as a standard. The molar enthalpies of fusion (ΔH_f) were obtained by integration of the area under melting-endotherm peak. The weight of all the samples was kept between $5-8$ mg. The glass transition temperature (T_g) values 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 (Universal V3.0G 2050 TA Instrument) under a nitrogen flow between $30-800°C$ at a heating rate of $10°C/min$. The derivative thermal gravimetry (DTG) analysis indicates the decomposition rate of samples at a definite heating temperature.

Wide-angle X-ray diffraction (WAXD) patterns of the powder copolyesters were obtained at room temperature on a Rigaku Miniflex X-ray powder diffractometer using CuKα radiation (wavelength of 1.54 Å) operated at 38 kV and 16 mA. 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 that are the values obtained from the areas of the X-ray diffraction curve. All the intensities obtained in this study were
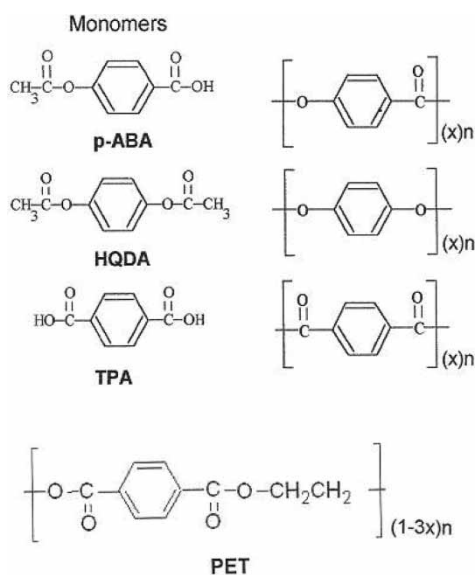
Table 1. Stoichiometric details of the copolyesters prepared by melt polycondensation reaction

Charged composition mol (%) p-ABA/HQDA/TPA/PET	Charged composition of PET units (mol%)	Abbreviation	Conversion[a]
10.0:10.0:10.0:70.0	70.0	30PHT/70PET	90
13.3:13.3:13.3:60.0	60.0	40PHT/60PET	92
16.7:16.7:16.7:50.0	50.0	50PHT/50PET	87
20.0:20.0:20.0:40.0	40.0	60PHT/40PET	89
23.3:23.3:23.3:30.0	30.0	70PHT/30PET	85
33.3:33.3:33.3:0.00	—	100PHT	95

[a]The percentage conversion does not include the amount of product wasted in the broken glass reactor.

integrations between $2\theta = 5°$ and $2\theta = 35°$ as a measure of the degree of crystallinity of samples using WAXD.

3   Results and Discussion

3.1   Synthesis

A series of modified copolyesters based on four different units were synthesized by a melt polycondensation/transesterification reaction process under vacuum at a temperature of 280°C and a reaction time of 5 h, in high yields. In abbreviations, P, H and T stand for linear p-ABA, HQDA and TPA monomers, and they are received in equal molar ratios in the synthesis. Excess acetic acid was added to the reaction medium in order to obtain a more homogeneous mixture and to prevent the sublimation of monomers, especially the sublimation of TPA. The polycondensation was performed by placing the reactor to the preheated oil bath at 280°C to increase the probability of obtaining random copolyesters. It was reported by Erdemir et al. (20) that a rapid heating of the reaction mixture from ambient temperature up to the polycondensation temperature or a preheated oil bath and together with charging acetic acid to the reaction medium are essential to reduce the sublimation of monomers and to increase probability of obtaining random copolyesters. As a matter of fact, sublimation of monomers was not observed during the polymerization period. The stirring procedure during the synthesis is also very important for both obtaining random copolyesters and removing the by-product efficiently.

During the copolymerization period in vacuum, depending on the increase of the viscosity, the shear oppalescence that revealed thermotropic liquid crystalline character of copolyesters was observed at around 280°C for the copolyesters containing PET composition equal or less than 50% or linear p-ABA/HQDA/TPA composition equal or higher than 50 mol%.

3.2   Thermal Properties of Copolyesters

The morphological textures of copolyesters were studied as a function of temperature in a hot-stage polarizing optical microscope. The data of T_{cn} and T_{ni} transition temperatures of liquid crystalline copolyesters are given in Table 2. In general, liquid crystalline behavior of the copolyesters depends greatly on the composition, content of linear units or content of flexible units in polymer chains. The copolyesters containing 50, 60 and 70 mol% of p-ABA/HQDA/TPA units produced turbid melts and thus exhibited liquid crystalline state in a broad temperature range of about 140°C.

The ability of these polymers to form liquid crystalline melts was reduced at high flexible unit contents. Although PET contains linear aromatic TPA units and this brings about and contribute to an increase in total amount af aromaticity in copolyester composition, the effect of the composition of the PET on melting and the liquid crystalline behavior is almost the same as in the copolyesters prepared in our previous studies (13, 15) where the kink m-ABA units were used instead of flexible PET polyester.

When the nematic polymer melts were sheared on glass plates, they exhibited a fine ordered texture of bands perpendicular to the shearing direction which is a very important property for fiber preparation or melt spinning in industrial

**Table 2.** Thermal properties of the copolyesters

Polymer code	T_g (°C)	T_m (°C)	ΔH_f (J/g)	T_{cn} (°C)	T_{ni} (°C)	T_{id} (°C)	T_{max} (°C)	T_{fd} (°C)
30PHT/70PET	64.0	216	39.4	—	—	408	436	448
40PHT/60PET	58.0	208	26.9	—	—	408	440	456
50PHT/50PET	67.0	214	18.8	180	280	386	440	459
60PHT/40PET	52.0	209	10.4	190	310	411	446	473
70PHT/30PET	58.0	220;355	4.16	210	320	416	448	486
100PHT	—	309;359	—	—	—	403	420;445	463
100PET	63.0	250	35.1	—	—	320;520	375;540	382;550

applications. Hence, the stir-opalescence was also clearly evident and this property was appeared under shear as symptom of the liquid crystalline phase. The long period of heating process and the absence of nitrogen atmosphere during the optical microscopy investigations may affect the polymer morphology. For this reason, analysis was performed by using freshly prepared samples for each investigation, and possible industrial application should also be performed under such conditions.
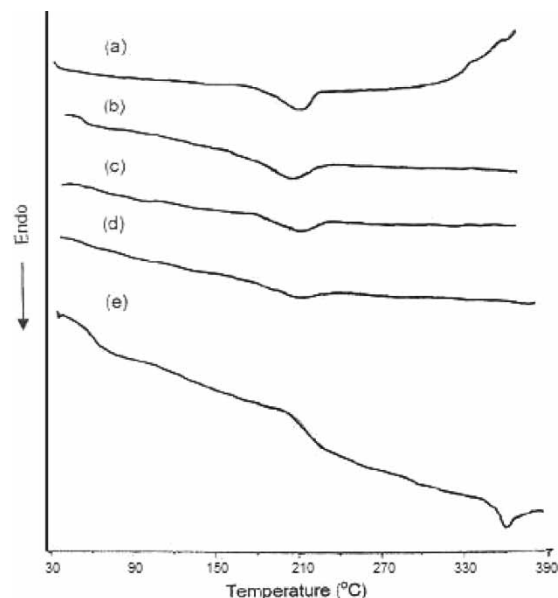
The DSC thermograms of copolyesters are illustrated in Figures 2 and 3, and DSC data are given in Table 2. The DSC data showed that the glass transition temperatures (T_g's) of the polymers ranged from 52 to 67°C. The T_g values obtained are close to each other. In other words, changing the composition of flexible aliphatic groups in the polymer chains has a no significant effect on the T_g values.

In spite of the fact that, no phase transition were detected for 100PHT copolyesters containing fully aromatic units in polarizing optical microscopy analysis up to 400°C, from DSC endotherms, some transitions were observed via two broad and weak endothermic transitions at 309°C and 359°C, respectively. It was reported that, such transitions observed in wholly aromatic rigid polyesters are due to some low molecular weight oligomers or low molecular weight crystalline structures (5). However, 100PHT copolyester is quite crystal and has a rigid structure and the expected melting point(s) for such wholly linear aromatic copolyesters are above the decomposition temperatures (2–5).

All the copolyesters derived from p-ABA/HQDA/TPA and PET are melt processable and the broad endotherms of the nematogenic copolyesters are consistent with the flow
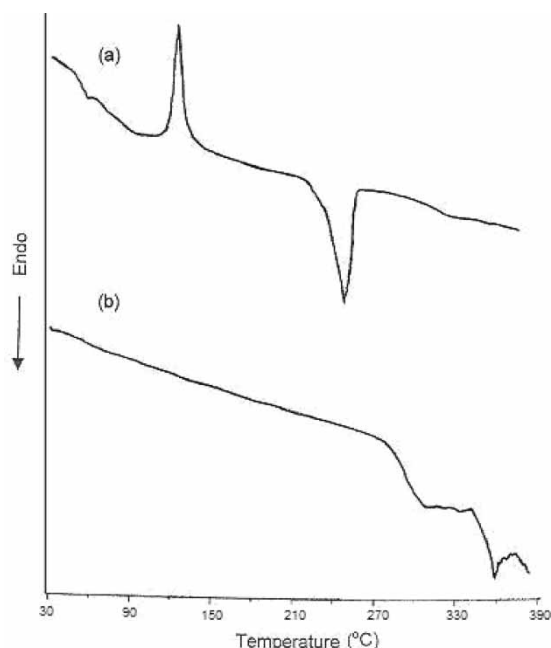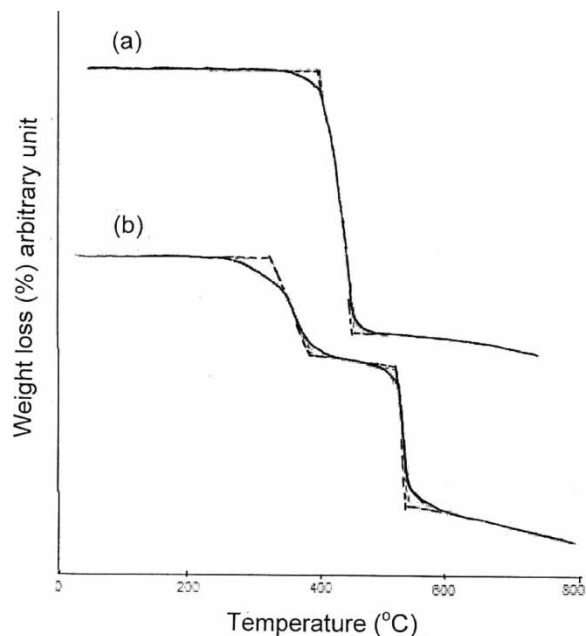

Fig. 3. The DSC thermograms of the copolyesters containing different composition of p-ABA/HQDA/TPA and PET units: a) 30PHT/70PET, b) 40PHT/60PET, c) 50PHT/50PET, d) 60PHT/40PET and e) 70 PHT/30PET.

temperatures obtained by hot-stage polarized light microscopy. As expected, the melting temperatures (T_m's) of the copolyesters observed in this study were lower than PET or PHT because of the copolymerization process. The mesophase, which is the continuous phase, exhibits broad peak, characteristic of the softening process of liquid crystalline polymers.

Some copolyesters showed a more detectable broad endotherm as a result of the more ordered structures and increased crystallinity in the polymer chains. The 70PHT/30PET copolyester showed the dual melting transitions at 220°C and 355°C, respectively. The multiple transitions have been observed and were reported for the copolyesters derived from four monomer units (8, 13–16, 19). We assume that dual endothermic transitions of our polymers are attributed to different morphologies (crystalloids) formed in two stages of crystallization, as well as fast and slow crystallization processes. Furthermore, PET showed a recrystallization exotherm at 129°C that is distinct from other copolyesters.

According to the DSC results, as the PET mol% increases, the specific heat of fusion (ΔH_f) values of the modified copolyesters, that are obtained from the area under the melting endotherms are dramatically increased from 4.36 J.g^{-1} to 39.4 J.g^{-1} (Table 2). The isotropic samples of 30PHT/70PET and 40PHT/60PET polyesters showed broad and sharper melting endotherms with higher ΔH_f values in DSC thermograms, implying a more crystalline structure as evidenced 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.
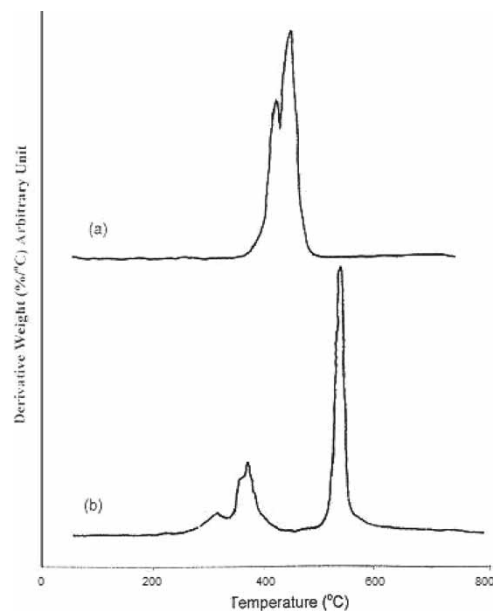

Fig. 2. The DSC thermograms of the a) 100PET and b) 100PHT copolyesters.

Fig. 4. The TGA thermograms of the a) 100PHT and b) 100PET copolyesters.

**Fig. 6.** The DTG Thermograms of the a) 100PHT and b) 100PET copolyesters.

The initial (T_{id}), maximum (T_{max}) and final (T_{fd}) decomposition temperatures estimated from the TGA and DTG thermograms for 100PHT and PET copolyesters (Figures 4 and 6), and for p-ABA/HQDA/TPA/PET copolyesters (Figures 5 and 7) under nitrogen are given in Table 2. All the
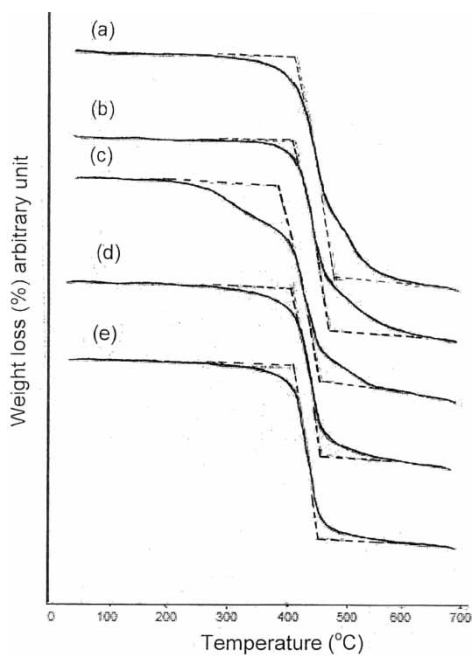
Fig. 5. The TGA Thermograms of the copolyesters containing different composition of p-ABA/HQDA/TPA and PET units: a) 70PHT/30PET, b) 60PHT/40PET, c) 50PHT/50PET, d) 40PHT/60PET and e) 30PHT/70PET.
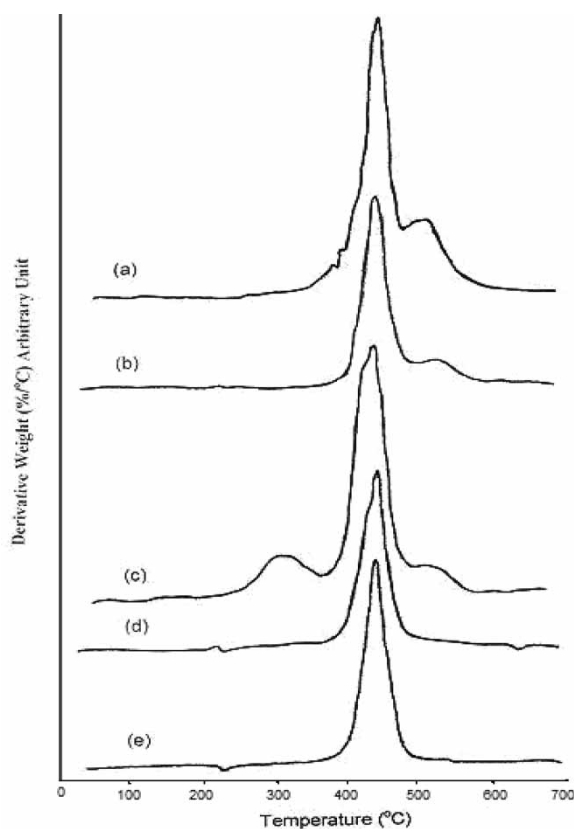
Fig. 7. The DTG thermograms of the copolyesters containing different composition of p-ABA/HQDA/TPA and PET units: a) 70PHT/30PET, b) 60PHT/40PET, c) 50PHT/50PET, d) 40PHT/60PET and e) 30PHT/70PET.

copolyesters exhibit a similar pattern of decomposition with no significant weight loss below the initial decomposition. The T_{id}'s, T_{maxd}'s, and T_{fd}'s were invariably found in the range of 386–416, 436–448, and 448–486°C for copolyesters containing p-ABA/HQDA/TPA/PET units, indicating good thermal stability at elevated temperatures. According to the DSC and optical results obtained, while melting or flow temperatures are depressed to a very efficient melt-processable range, with the exception of the 50PHT/50PET copolyester, the thermal stability of the other copolyesters is still higher than that of 100PHT copolyester (T_{id} is 403°C). In general, with increasing content of rigid-aromatic PHT units in polymer chains, the decomposition temperatures were also increased slightly (Table 2).

3.3 Viscosity Measurement

The intrinsic viscosities ($[\eta]$) of prepared copolyesters and PET are listed in Table 3. With the exception of 100PHT copolyester, all other copolyesters were soluble in a trifluoroacetic acid/dichloro methane (30:70 v/v) mixture. As the amount of PET was increased in the polymer composition, the intrinsic viscosity of the copolyesters was decreased regularly from 0.37 dL/g to 0.17 dL/g. In solubility observations, although PET was dissolved easier than other copolyesters, the 100PHT copolyester was not dissolved due to substantial rigidity. The intrinsic viscosity is a direct characterization of molar mass and refers to reactivity of monomers. In our previous studies, we interpreted to the reactivity of p-ABA,

HQDA and TPA monomers (14–16). When the solubility of these copolyesters was compared with the three monomer (p-ABA/p-APAA/m-ABA) systems (16), considerable solubility increase was observed for PET containing monomer system. For industrial applications, copolymerization time under vacuum can be extended or shortened optionally in order to obtain high or low viscosity products.

3.4 WAXD Analysis

WAXD patterns of copolyesters are shown in Figure 8. The Bragg angles, d-spacings and degree of crystallinity of copolyesters are given in Table 3. The main peak around at $2\theta = 20°$ is typical for all copolyesters. The 30PHT/70PET copolyester showed four main distinct diffraction peaks at $2\theta = 16.6, 17.9, 22.9, 26.1°$ and d = 5.33, 4.96, 3.88, 3.41 Å, respectively (Figure 8(a)). With increasing content of PHT units in polymer chains and due to the effect of random copolymerization, the intensity of the original four main diffraction peaks observed for 30PHT/70PET copolyester decreased and became broader. As a result, the % crystallinity was decreased from 24 to 6%. The physical and mechanical properties of polymers are profoundly dependent on the degree of crystallinity. As compared to the results obtained by the two-monomer (pABA/PET) system (22), incorporation of HQDA and TPA units into copolyesters together with the random copolymerization of four-monomer system, reduced considerably the degree of crystallinity for p-ABA/HQDA/TPA/PET system.

Table 3. The WAXD data and intrinsic viscosities of the copolyesters

Polymer code	2θ (°)	d-Spacing (Å)	Intensity[a]	Degree of crystallinity (%)	$[\eta]^b$ (dL/g)
30PHT/70PET	16.6–17.9	5.33–4.96	mB-sB	24.0	0.17
	21.7–22.9	4.09–3.88	wB-sB		
	26.1–28.2	3.41–3.16	sB-wB		
	32.8	2.73	wB		
40PHT/60PET	15.9–7.4	5.58–5.09	mB-sB	21.5	0.20
	19.5–21.8	4.56–4.07	mB-wB		
	22.4–22.6	3.96–3.92	sB-wS		
	25.6–27.6	3.48–3.23	sB-mB		
	32.5	2.75	wB		
50PHT/50PET	17.1–19.2	5.19–4.61	mB-wS	13.5	0.25
	21.9–25.1	4.06–3.54	mB-mB		
	27.2–31.9	3.27–2.80	wB-mB		
60PHT/40PET	17.3–19.5	5.11–4.55	wB-sB	10.0	0.31
	25.2–27.5	3.53–3.25	mB-mB		
70PHT/30PET	19.7–22.5	4.51–3.95	sB-mB	6.0	0.37
	25.0–27.9	3.56–3.19	wB-mB		
	29.4	3.03	wB		
100PHT	17.4–20.2	5.09–4.39	sB-vsB	46.0	$-^c$
	25.2–28.0	3.53–3.18	sB-vsB		
100PET	–	–	–	–	0.62

[a]Key: w, weak; m, medium; s, strong; vs, very strong; B, broad; S, sharp.
[b]Intrinsic viscosity measured in dicholoromethane/trifluoroacetic acid solution (70:30 v/v) at 25°C.
[c]Insoluble.
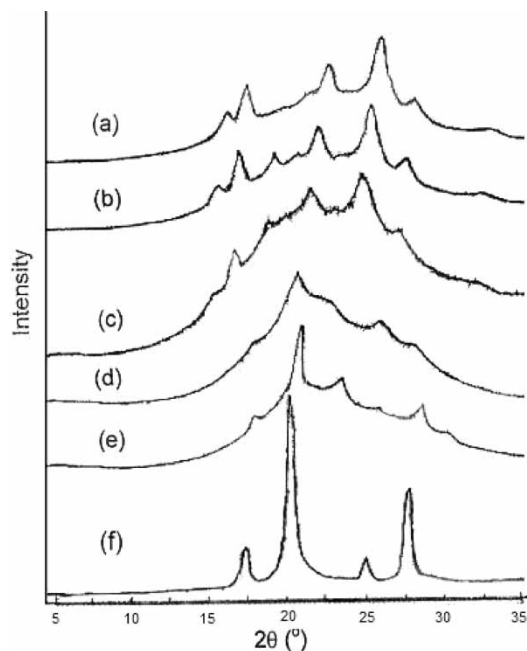
Fig. 8. WAXD patterns of the copolyesters: a) 30PHT/70PET, b) 40PHT/60PET, c) 50PHT/50PET, d) 60PHT/40PET, e) 70PHT/30PET, and f)100PHT.

The 100PHT copolyester has the highest peak intensities and attains a high degree of crystallinity (46%) due to the high packing or chain orientation in the polymer. This value is higher than that calculated for p-poly(oxybenzoate) homo-polyester (42%) prepared from p-ABA monomer (15). The very sharp and strong peaks in 100PHT became broader in PET containing copolyesters.

4 Conclusions

A series of the copolyesters with different p-ABA/HQDA/TPA/PET comonomer compositions were prepared by high temperature melt polycondensation reaction. The influence of linear and flexible aliphatic monomer units on the liquid crystalline behaviors, thermal transition temperatures, thermal stabilities, viscosity and degree of crystallinity were investigated. The copolyesters containing 50, 60, and 70 mol% of linear p-ABA/HQDA/TPA units showed nematic mesophases in a broad temperature range. The melting or flow temperatures were found to be in the proces-sable region. The isotropic samples of 30PHT/70PET and 40PHT/60PET polyesters showed broad and sharper melting endotherms with higher ΔH_f values in DSC thermo-grams, implying a more crystalline structure as evidenced by the WAXD data. All the copolyesters were thermally stable and they can be processed without being degraded above the melting temperatures. Intrinsic viscosities of the copolyesters decreased with further increase in the content PET units. According to the WAXD data, all the copolyesters are semi-crystalline and with an increasing content of PHT

units in polymer chains, the intensity of the original four main diffraction peaks 30PHT/70PET copolyester decreased and became weaker and broader: hence, the degree of crystal-linity was decreased.

5 Acknowledgment

6 References

1. Jackson, W.J. and Kuhfuss, H.F. (1976) *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 2043–2058.
2. Economy, J. (1989) *Mol. Cryst. Liq. Cryst.*, **169**, 1–22.
3. Jackson, W.J. (1989) *Mol. Cryst. Liq. Cryst.*, **169**, 23–49.
4. Noel, C. and Navard, P. (1991) *Prog. Polym. Sci.*, **16**, 55–110.
5. Economy, J. and Goranov, K. (1994) *Adv. Polym. Sci.*, **117**, 221–256.
6. Jin, J.-H. and Kang, C.-S. (1997) *Prog. Polym. Sci.*, **22**, 937–973.
7. Sahoo, N.G., Das, C K., Jeong, H. and Ha, J.S. (2004) *J. Elastom. Plast.*, **36**, 77–91.
8. Liu, Y., Jin, Y., Dai, L., Bu, H. and Luise, R.R. (1999) *J. Polym. Sci., Polym. Chem. Ed.*, **37**, 369–377.
9. Brown, P.J., Karacan, İ, Liu, J., McIntyre, J.E., Milburn, A.H. and Tomka, J.G. (1991) *Polym. Int.*, **24**, 23–32.
10. Garay, R.O., Bhowmik, P.K. and Lenz, R.W. (1993) *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 1001–1006.
11. Han, H., Bhowmik, P.K. and Lenz, R.W. (1994) *J. Polym. Sci. Polym. Chem. Ed.*, **32**, 343–354.
12. Gupta, B., Calundann, G., Charbonneau, L.F., Linstid, H.C., Shepherd, J.P. and Sawyer, L.C. (1994) *J. Appl. Polym. Sci.*, **53**, 575–586.
13. Yerlikaya, Z., Aksoy, S. and Bayramli, E. (2001) *J. Polym. Sci. Polym. Chem. Ed.*, **39**, 3263–3277.
14. Yerlikaya, Z., Aksoy, S. and Bayramli, E. (2002) *J. Appl. Polym. Sci.*, **85**, 2580–2587.
15. Yerlikaya, Z., Aksoy, S. and Bayramli, E. (2003) *J. Appl. Polym. Sci.*, **90**, 3260–3269.
16. Yerlikaya, Z., Aksoy, S. and Bayramli, E. (2006) *J. Mac. Sci. Pure & Appl. Chem.*, **A43(3)**, 433–447.
17. Aly, K.I. and El-Khashef, H. (2001) *J. Mac. Sci. Pure & Appl. Chem.*, **A38(8)**, 785–806.
18. Baroni, D., Romano, R., Fillippi, S., Polacco, G., Paci, M. and Magagnini, P. (2001) *Macromol. Chem. Phys.*, **202**, 2122–2131.
19. Pan, X., Chi, Z., Cheng, D., Jin, M. and Bu, H. (2005) *J. Macromol. Sci. Phys.*, **44**, 249–259.
20. Erdemir, A.B., Johnson, D.J. and Tomka, J.G. (1986) *Polymer*, **27**, 441–447.
21. Kim, H. and Paul, D.R. (1990) *J. Appl. Polym. Sci.*, **40**, 155–181.
22. Kang, T.K. and Ha, C.S. (1999) *J. Appl. Polym. Sci.*, **73**, 1707–1719.
23. Kricheldorf, H.R. and Ruhser, F. (1992) *Polymer*, **33**, 2431–2436.
24. Rabbek, J.F. (1980) Experimental Methods in Polymer Chemistry; Wiley: New York, 508–510.
25. Kasai, N. and Kakudo, M. (1972) *X-Ray Diffraction in Polymer Chemistry*; Elsevier: Amsterdam, 359–367.