Effect of Polycondensation Reaction Conditions on the Properties of Thermotropic Liquid-Crystalline Copolyester

Meryem Yikici[a]; Zekeriya Yerlikaya[b]; Serpl Aksoy[a]; Haydar Altinok[c]

[a] Department of Chemistry, Gazi University, Teknikokullar, Ankara, Turkey [b] Faculty of Education, Department of Science Education, Kastamonu University, Kastamonu, Turkey [c] Department of Chemistry, Kırıkkale University, Yahşihan Kırıkkale, Turkey

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MERYEM YIKICI,[1] ZEKERIYA YERLIKAYA,[2] SERPİL AKSOY,[1] and HAYDAR ALTINOK[3]

[1]*Department of Chemistry, Gazi University, Teknikokullar, Ankara, Turkey*
[2]*Faculty of Education, Department of Science Education, Kastamonu University, Kastamonu, Turkey*
[3]*Kırıkkale University, Department of Chemistry, Yahşihan Kırıkkale, Turkey*

In this study a range of wholly aromatic copolyesters based on kink m-acetoxybenzoic acid (m-ABA) monomer (33 mol%) and equi-molar-linear p-acetoxybenzoic acid (p-ABA), hydroquinone diacetate (HQDA) and terephthalic acid (TPA) monomers (67 mol%) have been synthesized by melt polycondensation reaction process at 280°C and 260°C for different time intervals. Characterization of copolyesters were performed by solution viscosity measurement, wide−angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), hot-stage polarized light microscopy, proton-nuclear magnetic resonance analysis (^{1}H-NMR). According to the results obtained, copolyesters showed thermotropic liquid crystalline behavior in an appropriate temperature range. The copolyesters were prepared in high yields. It was observed that the intrinsic viscosities of the copolyesters are increased regularly with increasing polymerization time and temperature. All the copolyesters were soluble in a trifluoroacetic acid/dichloromethane (30:70 v/v) except the copolyesters which were synthesized at 280°C in 5 h. According to the WAXD results; the degree of crystallinity of copolyesters were found to be between 5−15%. DSC and hot stage polarized light microscopy results showed that all the copolyesters are melt processable and a significant molecular interaction exist in a very broad temperature range (160°C and 165°C) in the nematic mesophase. The T_g values are increased with an increasing polycondensation reaction time and temperature and they were observed between 93−126°C. Fibers prepared by a hand-spinning technique from the polymer melt exhibit well-developed fibrillar structure parallel to the fiber axis.

Keywords: thermotropic; liquid crystalline; copolyester; polycondensation; melt spinning; fiber

1 Introduction

Totally stiff-chain aromatic polyesters that form thermally stable nematic mesophase are of considerable interest due to their attractive properties as high performance engineering materials for high strength and high modulus fibers and films (1−11). The anisotropic nature of these systems lead to a high degree of molecular orientation during processing in the melt state (12−16). Many thermotropic liquid-crystalline polyesters (TLCPs) that are melt-processable in a broad temperature range have been synthesized and characterized in detail through the use of different types of structural modifications (1−5, 11, 17−26). The liquid-crystalline behavior and the transition temperatures were dependent on the copolymerization of different mesogen-forming monomers, use

of rod-like arylene moieties of different lengths, use of kink units, and the incorporation of flexible spacers.

In our previous studies (21, 22), a series of melt-processable totally aromatic thermotropic liquid crystalline copolyesters containing four different monomer units [m-acetoxybenzoic acid (m-ABA), p-acetoxybenzoic acid (p-ABA), hydroquinone diacetate (HQDA) and terephthalic acid (TPA)] were prepared and characterized in detail. Nematogenic copolyesters with a composition of 33 mol% kink units are found to be suitable for potential applications as high strength-high modulus fibers. Though, the effect of monomer structure and monomer composition on the liquid crystalline behavior of copolyesters have been well documented in these studies, no work has been reported in an open literature on the systematic investigation of the effect of polycondensation reaction conditions (i.e., temperature and time) on morphology and thermal transition of such copolyesters, as yet.

This study is concerned with the preparation, characterization and melt spinning of thermotropic liquid crystalline copolyesters containing 33 mol% m-ABA units and

Address correspondence to: Zekeriya Yerlikaya, Faculty of Education, Department of Science Education, Kastamonu University, Kastamonu 37200, Turkey. Tel: 90 366 214 2312-195; Fax: 90 366-212 3353. E-mail: y.zekeriya@gmail.com

67 mol% linear p-ABA/HQDA/TPA units at different polycondensation reaction temperatures and time intervals.

2 Experimental

2.1 Monomer Synthesis

p-Hydroxybenzoic acid (p-HBA), m-hydroxybenzoic acid (m-HBA), hydroquinone (HQ) and TPA were obtained commercially from Merck and used without 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 sulphuric acid catalyst (21). Each product was crystallized from an ethanol-water mixture (25:75 v/v) and dried under a vacuum at 60°C for 24 h.

2.2 Copolyesters Synthesis

All the copolyesters were prepared by the high-temperature melt polycondensation method on a 0,1 mol scale without any catalyst as described in our previous study (21). Copolyesters were synthesized in two series for 2 different polycondensation reaction temperatures (260 and 280°C) and 4 different polycondensation reaction time (1, 2, 3, and 5 h). The stoichiometric details of the copolyesters, and the polymer abbreviations used are summarized in Table 1.

A typical procedure is summarized as follows: The monomers (0.1 mol in total) and acetic acid (35 mL) were charged in to a cylindrical glass reactor (diameter 35 mm and length 250 mm) fitted with a stainless stirrer, a nitrogen inlet, a vacuum outlet and a tube connected via condenser to a condensate collector. After the reaction flask was evacuated and purged with nitrogen 3 times to remove all air, the temperature of the silicone oil bath was increased to 260 or 280°C. Then the reactor was placed in oil bath while the reactants were stirred with a dry nitrogen flow. Excess acetic acid was incorporated into the reaction mixture to obtain more homogeneous mixture and to prevent the sublimation of the monomers. This excess acid was collected in 10 min. The homogeneous reaction mixture was maintained at 280°C or 260°C under nitrogen flow for 45 min, and at this point, most of the acetic acid as reaction by product had been collected. The next stage was carried out under vacuum for different time intervals (1, 2, 3, and 5 h.). 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 dried at 60°C in vacuum oven overnight.

2.3 Fiber Spinning

In order to investigate the spinning properties and to establish optimum melt spinning temperature for the copolyesters prepared; dried polymer granules were melted under nitrogen and the temperature was then gradually raised within the nematic region until fine, flexible, even and long (at least 50.0 cm long) fibers could be prepared by a hand-spinning technique from a polymer melt with a fine stainless-steel hook. The copolyesters that were spun easily are S67PHT2 (melt spinning temperature: 290°C), S67PHT3 (melt spinning temperature: 290°C) and 67PHT3 (melt spinning temperature: 310°C).

2.4 Characterization

The intrinsic viscosity of the copolyesters dissolved in dichloromethane/trifluoroacetic acid (70:30 v/v) solution was determinated by an Ubbelohde Viscometer, at 25°C and at the concentration of 0.5 g/dL.

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 (200–300°C) and then pressing the melt with another piece of hot glass plate so that it was formed in to a sandwich with a thin film inside. The mesomorphic transition temperatures and disappearance of birefringence, that are, the crystal-to-nematic (T_{cn}) and nematic-to-isotropic (T_{ni}) transitions, were noted.

Table 1. Stoichiometric details, polycondensation reaction time and temperature, and the yield of copolyesters

Series	Charged composition (mol%) p-ABA/HQDA/TPA/m-ABA	Abbreviation	Time (hour)	Temperature (°C)	Conversion[a] (%)
I	22.3: 22.3: 22.3: 33.0	S67PHT1	1	260	88
	22.3: 22.3: 22.3: 33.0	S67PHT2	2	260	90
	22.3: 22.3: 22.3: 33.0	S67PHT3	3	260	86
	22.3: 22.3: 22.3: 33.0	S67PHT5	5	260	85
II	22.3: 22.3: 22.3: 33.0	67PHT1	1	280	86
	22.3: 22.3: 22.3: 33.0	67PHT2	2	280	85
	22.3: 22.3: 22.3: 33.0	67PHT3	3	280	83
	22.3: 22.3: 22.3: 33.0	67PHT5	5	280	80

[a]The percentage yield do not include the amount of product wasted with the broken glass reactor.

Table 2. Transition temperatures, optical properties and intrinsic viscosity values of Series I and Series II copolyesters

Series	Polymer Code	DSC		Polarized microscopy		$[\eta]$d
		T_g (°C)[a]	T_m (°C)[a]	Tcn[b] (°C)	T_{ni} (°C)[c]	(dL/g)
I	S67PHT1	93	330	190	360	0.13
	S67PHT2	96	—[e]	190	360	0.18
	S67PHT3	96	—[e]	190	360	0.21
	S67PHT5	106	—[e]	200	360	0.36
II	67PHT1	108	—[e]	205	370	0.26
	67PHT2	109	—[e]	205	370	0.34
	67PHT3	124	—[e]	210	370	0.43
	67PHT5	126	—[e]	210	370	—[f]

[a]From DSC measurements at a heating rate of 10°C/min.
[b]The onset of crystal (c) to nematic (n) transition.
[c]The onset of nematic (n) to isotropic (i) transition.
[d]Intrinsic viscosity measured in dichloromethane/trifluoroacetic acid solution (70:30 v/v) at 25°C.
[e]Not observed.
[f]Insoluble.

The differential scanning calorimetry (DSC) measurements of the copolyesters were performed on a Du Pont DSC 910, under a nitrogen flow to determine transition temperatures. DSC scans were run between 40 and 390°C at 10°C/min. The weight of 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 patterns of the powder copolyesters were obtained at room temperature by Rigalum Miniflex with Ni- filtere CuK$_\alpha$ radiation (38 kV, 18 mA) of the wavelength of 1.54 Å. The crystallinities of the samples were calculated using the following equation (27, 28):

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

The ^{1}H-NMR of the 67PHT2 and S67PHT2 copolyesters were recorded on a Bruker AM-400 NMR spectrometer. A mixture of trifluoroacetic acid-d and chloroform-d (50:50 v/v)
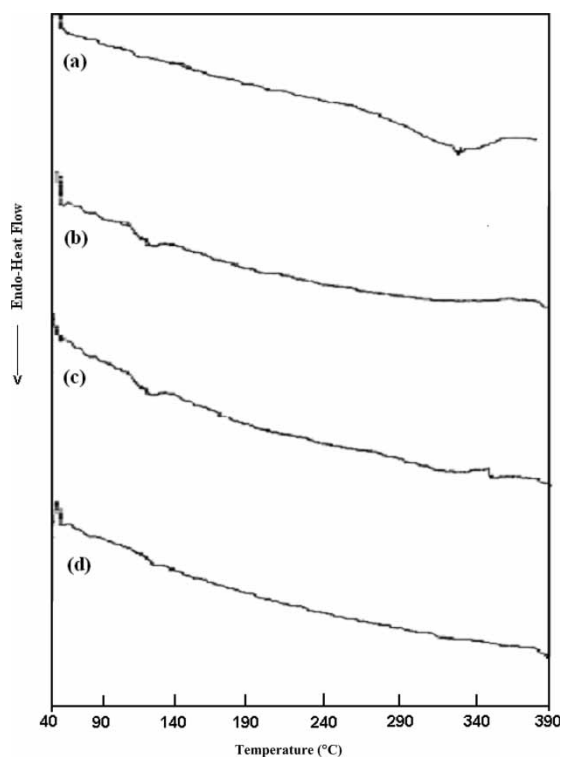

Fig. 1. DSC thermograms of Series I copolyesters; (a) S67PHT1, (b) S67PHT2, (c) S67PHT3, (d) S67PHT5.
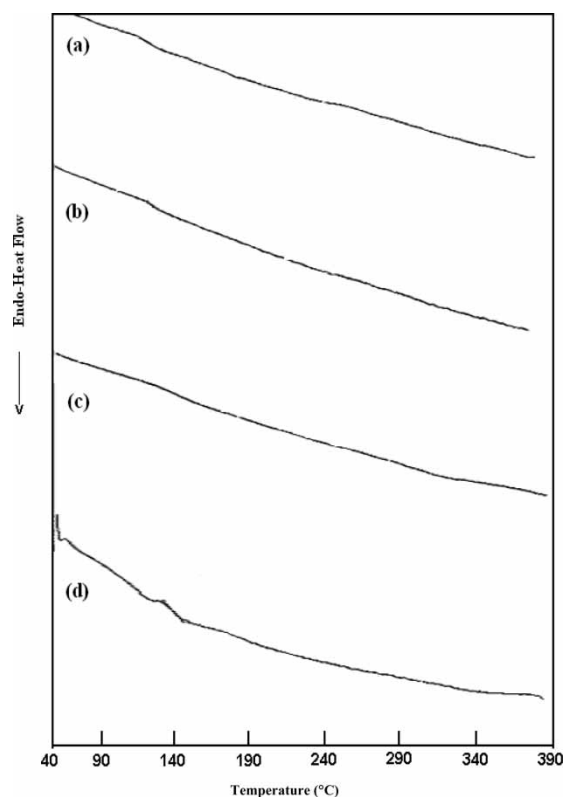

Fig. 2. DSC thermograms of Series II copolyesters; (a) 67PHT1, (b) 67PHT2, (c) 67PHT3, (d) 67PHT5.
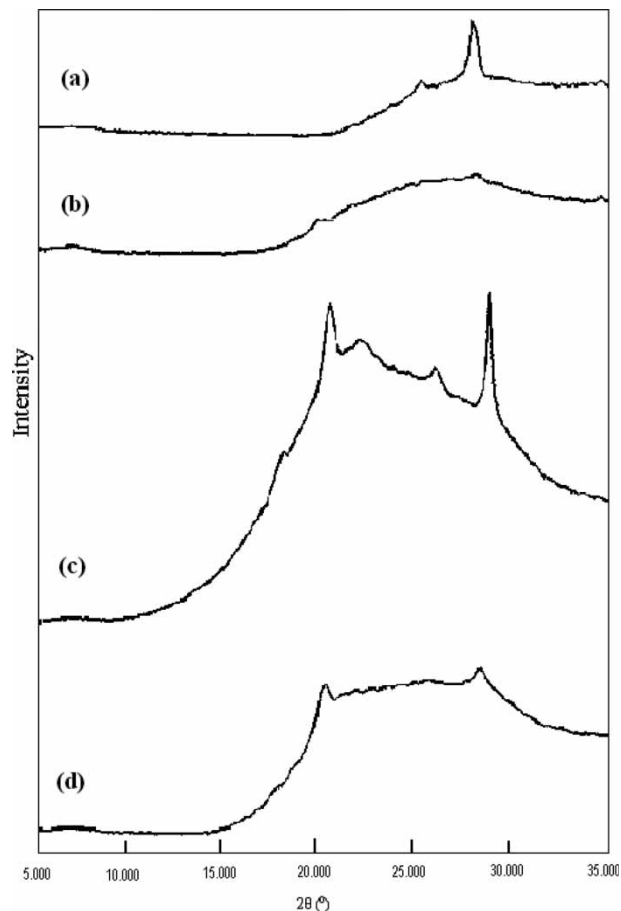
Fig. 3. WAXD difractograms of Series I copolyesters (a) S67PHT1, (b) S67PHT2, (c) S67PHT3 and (d) S67PHT5.
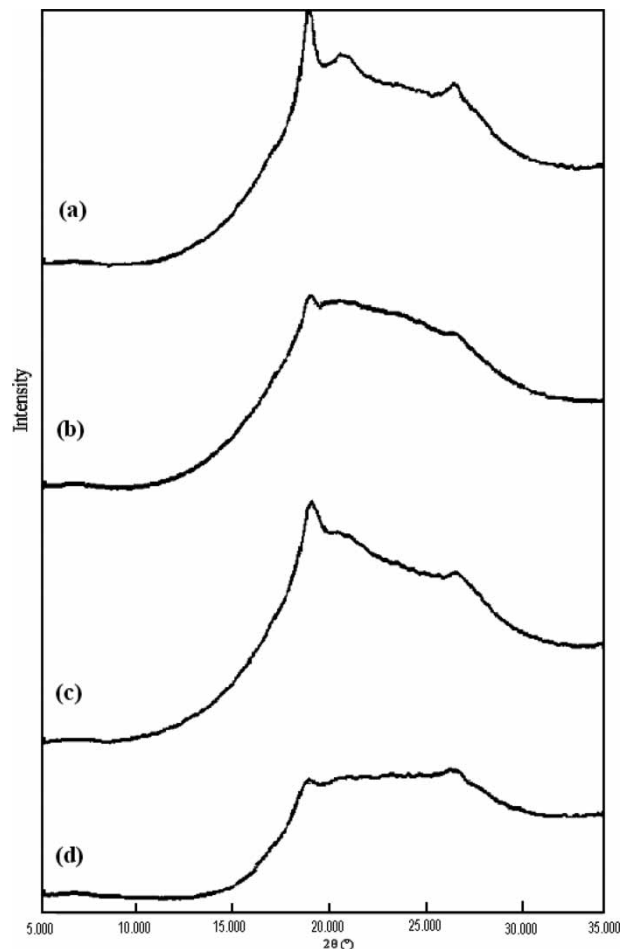

Fig. 4. WAXD difractograms of Series I copolyesters (a) 67PHT1, (b) 67PHT2, (c) 67PHT3 and (d) 67PHT5.

was used as a solvent. The chemical shifts were measured with respect to chloroform (7.28 ppm).

A scanning electron microscope (SEM), model Jeol JSM-6360LV was used to investigate the morphology or structure of the fibers prepared by a hand-spinning technique. The samples were fractured or peeled parallel to the fiber axis at room temperature and the fracture/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.

3 Results and Discussion

3.1 Synthesis

The totally aromatic copolyesters were prepared in high yields by high temperature melt polycondensation between four different monomer units. Monomers have been polymerized at 280°C and 260°C for different time intervals. In Series I and II coding, the total molar percentages of linear units are followed by the initials of the linear monomers: P stands for p-ABA, H stands for HQDA and T stands for TPA (67PHT).

Numerical value (i.e. 67) before the codes refer to the total amount (in mol%) of linear monomers and these at the end of the codes (i.e., 1, 2, 3, or 5) refers to the polycondensation time (in hour) under vacuum. In Series I coding; the S character that placed before 67PHT denotes the polycondensation temperature at 260°C. For example; while 67PHT2 in Series II refers to the copolyester prepared under 280°C and 2 h under vacuum, S67PHT2 refers to the copolyester prepared at 260°C and 2 h under vacuum.

The polycondensation reaction was performed by placing the reactor to the preheated oil bath at 260°C or 280°C to increase the probability of obtaining random copolyesters. It was reported that (14, 21), a rapid heating of the reaction mixture from ambient temperature up to the polycondensation temperature and charging acetic acid to the reaction medium are essential to reduce the sublimation of monomers and increase the probability of obtaining random copolyesters.

3.2 Thermal Properties of Copolyesters

The morphological textures of copolyesters were studied as a function of temperature in a hot stage polarizing

Table 3. Wide-angle X-Ray diffraction results for Series I and Series II copolyesters

Series	Polymer code	2θ (°)	d-Spacing (Å)	Intensity[a]	Degree of crystallinity (%)
I	S67PHT1	25.0	3.49	wB	15.0
		28.2	3.16	sS	
	S67PHT2	20.1	4.27	wB	5.0
		28.4	3.14	wB	
	S67PHT3	20.8	4.00	sS	13.0
		22.5	3.95	wB	
		26.1	3.41	wB	
		29.3	3.05	sS	
	S67PHT5	21.0	4.56	wB	10.0
		28.4	3.14	wB	
II	67PHT1	19.2	4.62	sS	13.0
		22.2	3.67	wB	
		26.6	3.35	wB	
	67PHT2	19.2	4.62	wB	7.0
		26.6	3.35	wB	
	67PHT3	19.4	4.57	mB	12.0
		20.5	4.32	wB	
		26.8	3.32	wB	
	S67PHT5	19.2	4.62	wB	9.0
		26.6	3.35	wB	

[a]Key: w, weak; vw, very weak; m, medium; s, strong; vs, very strong; B, broad; S, sharp.

microscope. Crystal-to-nematic (T_{cn}), nematic-to-isotropic (T_{ni}) phase transition temperatures are shown in Table 2. In the nematic mesophase, a significant molecular interaction exist in a very broad temperature range for both Series I (170°C) and for Series II (165°C) copolyesters, apparent from the high birefringences under crossed polarizers. In general, the liquid crystalline behavior of the copolyesters depends greatly on the composition, content of linear units or content of kinked units in the polymer chains (2−6, 14, 21). T_{cn}'s observed for S67PHT and 67PHT copolyesters are between 190 and 210°C. A comparison between Series I and Series II copolyesters indicates the effect of the polycondensation temperature on the T_{cn} and T_{ni} transitions. For instance, T_{cn} temperatures were rised up about 10 or 15°C by increasing polycondensation temperatures from 260°C to 280°C.

The DSC thermograms of copolyesters are illustrated in Figures 1 and 2. All the copolyesters are melt processable. The melting or the flow temperatures observed by hot-stage polarized ligth microscopy were found to be almost equal to the T_{cn}'s transition temperatures. The copolyesters showed very weak-broad or any detectable melting endotherms, characteristic of the softening process of liquid-crystalline polymers. 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 in these type polymers (2, 3, 14, 19, 21). The more detectable broad endotherm of the S67PHT1 copolyester observed at 330°C may be due to the fact that, this copolyester might has gained an additional structural regularity during polycondensation reaction due to the insufficient stirring of the

polymer melt or inhomogeneous reaction mixture that lead to a blocky structure mainly between p-ABA units that have higher reactivity, as reported in previous studies (21, 29).

The T_g values of the copolyesters are increased in each Series with an increasing polycondensation reaction time (Table 2). These results might be related to the effect of the increased molecular weight of the copolyesters with increasing reaction time as evidenced by viscosity measurements given below.

3.3 Viscosity Measurement

The intrinsic viscosities of the copolyesters prepared in two series are listed in Table 2. Except 67PHT5 copolyester synthesized at 280°C in 5 h, all other copolyesters were soluble in a trifluoroacetic acid/dichloromethane (30:70 v/v) mixture.

In general, the viscosity values of the copolyesters in Series I and II were increased with increasing polycondensation reaction temperature and time. When the polycondensation temperature was reduced from 280 to 260°C; it was observed that the viscosity values were decreased almost by 50%, when a comparison are performed between the copolyesters synthesized at the same time intervals. On the other hand, the calculated intrinsic viscosity values for Series II copolyester prepared at 280°C might be lower than the expected values, since small amount of HQDA monomer is lost by sublimation, as it is supported by ^{1}H-NMR results given below.

3.4 WAXD Analysis

WAXD patterns and the degree of crystallinities of the Series I and Series II copolyesters are shown in Figures 3 and 4,
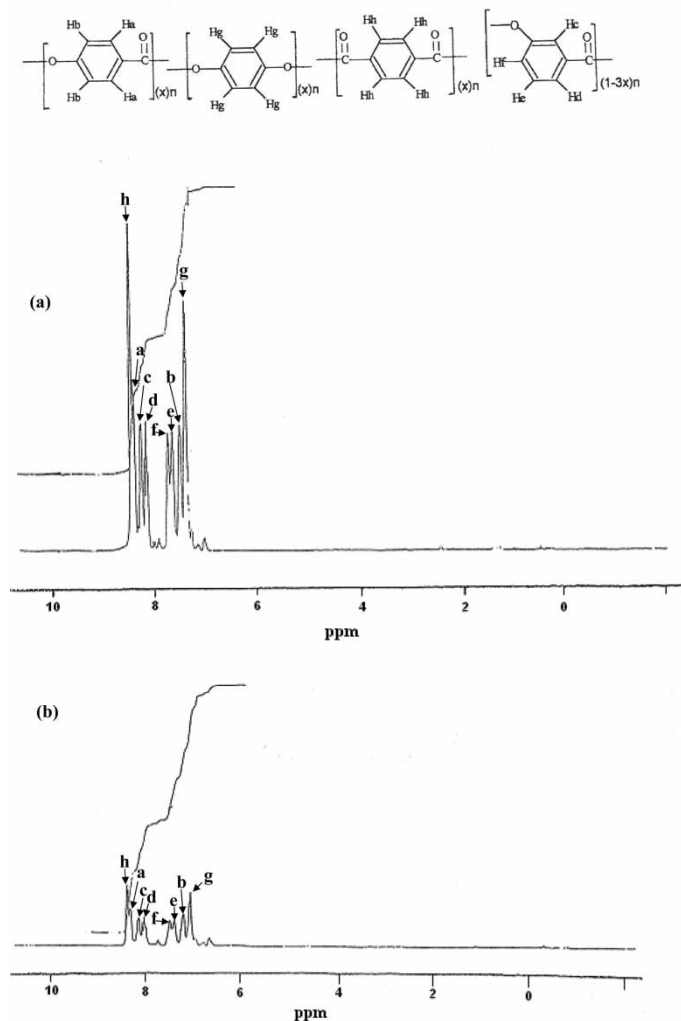
Fig. 5. ^{1}H-NMR spectra of S67PHT2 (a) and 67PHT2 (b) copolyesters (the degree of polymerization is given by n, and the mole fraction of the polymers are designated as x).

Fig. 6. SEM microphotographs of S67PHT2 fiber; 600X (a) and 2500X (b).

respectively. d-Spacings, Bragg angles and degree of the crystallinity of the copolyesters are given in Table 3. The physical and mechanical properties of polymers are profoundly dependent on the degree of crystallinity. The percentage of crystallinities in Series I and II were obtained between 5−15% and 7−13%, respectively. The S67PHT1 that has the highest degree of crystallinity (15%) showed two main

Table 4. Calculated copolyester compositions determined by ^{1}H-NMR spectroscopy for S67PHT2 and 67PHT2 copolyesters

Polymer code	Monomer feed ratio (mol %) [(p-ABA/ HQDA/TPA)/m-ABA]	Copolyester composition (mol%) [(p-ABA/ HQDA/TPA)/m-ABA]
S67PHT2	67/33	67.5/32.5
67PHT2	67/33	64.5/35.5

diffraction peaks at $2\theta = 28.2°$, $d = 3.16$ Å, and $2\theta = 25.0°$, $d = 3.49$ Å. On the other hand, the 67PHT1 copolyester in Series II with a degree of crystallinity of 13% showed three main diffraction peaks, at $2\theta = 19.2°$, $d = 4.62$ Å, $2\theta = 22.2°$, $d = 3.67$ Å, and $2\theta = 26.6°$, $d = 3.35$ Å.

According to these results; although, polycondensation reaction temperature has no considerable influence on the degree of crystallinity of these type polymers, the polycondensation reaction time influenced the degree of the molecular rearrangement. By increasing polycondensation time from 1 to 5 h, the degree of crystallinity for both series I and II were decreased by 5 and 4%, respectively. Consequently, it is possible to prepare these type of polymers with different degree of crystallinity and thus, physical and mechanical properties by controlling the polycondensation reaction time and temperature.

3.5 ¹H-NMR Analysis

Figure 5 shows typical expanded regions of the ¹H-NMR spectra of the soluble copolyesters S67PHT2 and 67PHT2 with chemical shifts evident between 7.38 and 8.55 ppm. According to the integrated areas of the peaks, the composition of the copolyesters that are calculated for the kink and linear units were very close to the feed ratios for S67PHT copolyester prepared at 260°C (Table 4). However, 67PHT2 copolyesters prepared at 280°C, contain somewhat less linear units (2.5 mol%) than expected from the feed ratios. This result is almost in accordance with the results given in our previous study (21) performed for 67PHT copolyester (mol% of (p-ABA/HQDA/ TPA) = 65.5; mol% of m-ABA = 34, 5) and it indicates the effect of high temperature on the sublimation of the monomers. Small amounts of monomers, probably HQDA were lost by sublimation during the high-temperature melt-polycondensation reaction. These results also support the outcomes reported in early studies (14, 21), related to the sublimation of the monomers during high-temperature melt-polycondensation reaction.

3.6 SEM Analysis of Fibers

SEM microphotographs of S67PHT2 (Fig. 6), 67PHT3 (Fig. 7) and S67PHT3 (Fig. 8) handspun fiber samples showed that the polymer chains were oriented in the flow direction, characteristic of the fibers drawn in the nematic state. Although, no additional drawing or heating processe was applied to increase the orientation, fibers still exhibit well-developed fibrillar structure parallel to the fiber axis. Highly oriented morphology of the fibrillar texture in Figs. 7(a) and 8(a) is readily visible to the naked eye and is clearly demonstrated even with lower magnification. This situation is probably due to the high degree of crystallinity of 67PHT3 (12%) and S67PHT3 (13%) compared to S67PHT (5%).
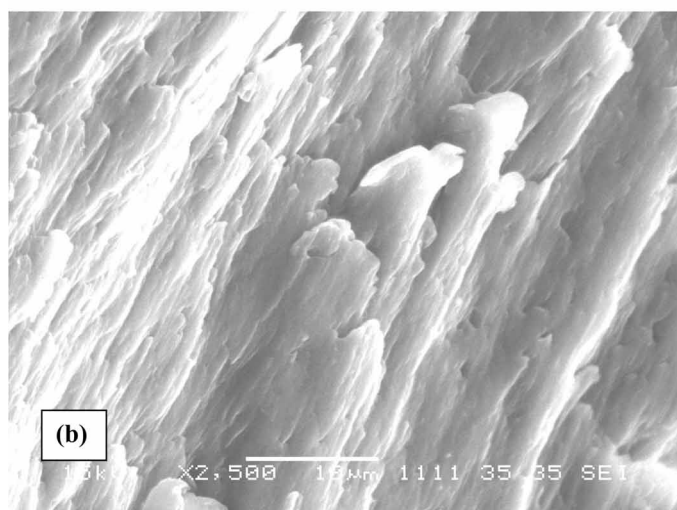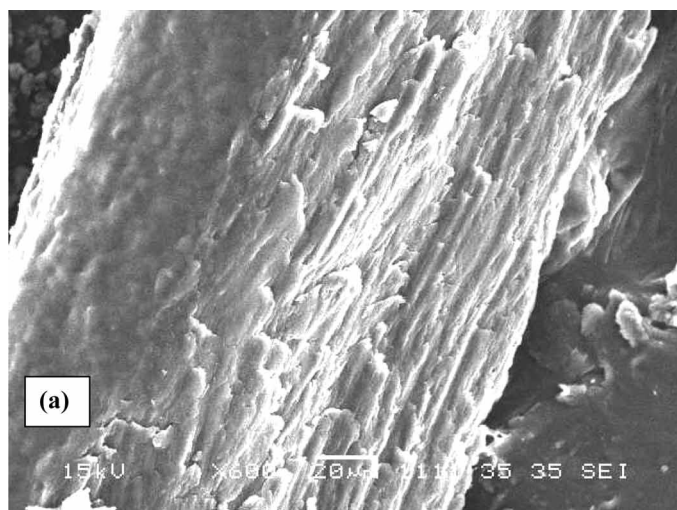

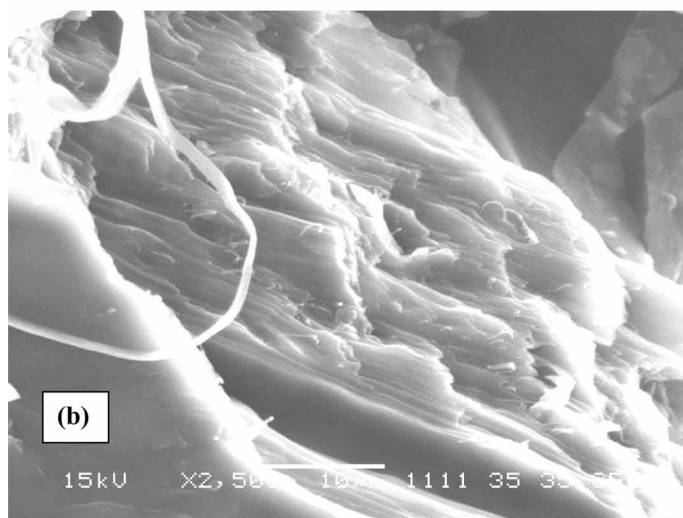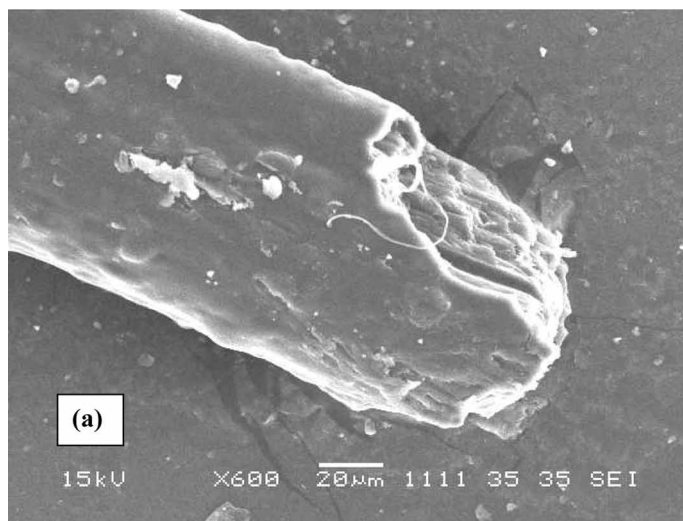**Fig. 7.** SEM microphotographs of 67PHT3 fiber; 600X (a) and 2500X (b).

Fig. 8. SEM microphotographs of S67PHT3 fiber; 600X (a) and 2500X (b).

4 Conclusions

A series of copolyesters were prepared by high temperature melt polycondensation reaction. All the copolyesters had the same monomer composition, but the polycondensation reaction conditions were changed in each case in terms of temperature and time. The influence of reaction temperature and time on the thermal properties, liquid-crystalline behaviors, solubility, viscosity, and degree of crystallinity of the copolyesters were investigated.

All the copolyesters showed nematic mesophase in a broad temperature range. The flow or melting temperatures were found to be in the processable region for all the copolyesters. In general, the T_g values of the copolyesters and the intrinsic viscosity values of the copolyesters in Series I and II increased with increasing polycondensation temperature and time. From the ^{1}H-NMR spectra, the compositions of the S67PHT2 and 67PHT2 copolyesters were calculated to be almost equal to the feed ratios. SEM microphotographs of the handspun fibers prepared from S67PHT2, S67PHT3, and 67PHT3 copolyesters showed that the polymer chains were oriented in the flow direction and fibers exhibit well-developed fibrillar structure parallel to the fiber axis. Finally, for various industrial applications, it is possible to control some properties of these type of high-performance engineering materials, such as degree of crystallinity, transition temperatures and viscosity or molecular weight by adjusting the reaction conditions.

5 Acknowledgments

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