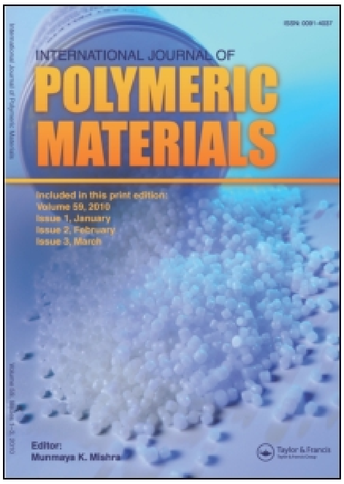

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Liliya I. Minkova[a]; Rossana Milié[b]; Sara Filippi[b]; Giovanni Polacco[b]
[a] Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria [b] Dipartimento di ingegneria Chimica, Universltà di Pisa, via Diotisalvi 2, Pisa, Italy

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Synthesis of PET-based Liquid Crystalline Copolyesters: Influence of the Overall Degree of Aromaticity on Phase Segregation

LILIYA I. MINKOVA[a,*], ROSSANA MILIÉ[b], SARA FILIPPI[b]
and GIOVANNI POLACCO[b]

[a]*Institute of Polymers, Bulgarian Academy of Sciences,*
Acad. G. Bontchev str., 1113 Sofia, Bulgaria; [b]*Dipartimento di Ingegneria*
Chimica, Università di Pisa, via Diotisalvi 2, 56126 Pisa, Italy

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Novel PET-based copolyesters have been synthesised by transesterification of PET with equimolar amounts of sebacic acid (S) and 4,4′-diacetoxybiphenyl (B) and with varying amounts of 4-acetoxybenzoic acid (H). The structure, the morphology, and the thermal properties of the PET-S-B-H copolyesters have been studied by scanning electron microscopy (SEM), polarized optical microscopy (POM), differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXS). It has been demonstrated that segregation of a liquid-crystalline phase, during polycondensation, provides the driving force for compositional differentiation, with the result that the final products are "synthetic polymer blends". The characteristics of PET-S-B-H copolymers have been compared with those of PET-S-Q-H copolyesters having the same molar composition (Q-hydroquinone). It has been shown that the phase segregation is more prominent in PET-S-B-H copolyesters than in PET-S-Q-H polymers of similar molar composition. The influence of the overall degree of aromaticity of the copolyesters on the segregation phenomenon has been discussed.

Keywords: PET-based liquid crystalline copolyesters; Segregation phenomenon; Degree of aromaticity

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[*] Address for correspondence: Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bontchev str. bl. 103A, 1113 Sofia, Bulgaria. Tel.: +359 2 757145, Fax: +359 2 707523, e-mail: minkova@polymer.bas.bg

1. INTRODUCTION

Thermotropic liquid crystalline polymers are one of the most interesting classes of polymeric materials. Among the well known thermotropic liquid crystalline polymers (LCP) such as Vectra®, Xydar®, Ultrax®, Rodrun®, *etc.*, the polymers based upon poly(ethylene terephthalate) (PET) are considered to be the cheapest and the easiest to process since they require relatively low temperatures. The latter LCPs were intensively investigated during the last twenty years in view of their potential as high performance resins. The preparation of different LCPs through the high temperature cleavage of preformed PET with selected monomers, such as 4-hydroxybenzoic acid (H), terephthalic acid (T), hydroquinone (Q), 4,4′-dihydroxybiphenyl (B), *etc.*, followed by polycondensation of the resulting oligomers, was performed [1–13].

It is well known that the liquid-crystalline copolyesters synthesised by the transesterification of PET with H are compositionally heterogeneous; they consist of two phases, one rich in H units, and the other rich in ethylene terephthalate (ET) units. Even after the improvement recently brought by Suenaga *et al.* [4] to the synthetic technique, the copolyester with the trade name Rodrun LC5000 with the highest H content (80 mol%) is still heterogeneous. Only that with 60 mol% H (Rodrun LC3000) is practically homogeneous, but shows fairly low thermal resistance. Even more heterogeneous is the product of the transesterification of PET with a mixture of sebacic acid (S), B and H in the molar ratio 1/1/2 that was in fact a "synthetic blend" consisting of an aromatic-rich LC phase dispersed in an isotropic matrix of aliphatic-rich copolyester [8–10]. The compositional heterogeneity of these LCPs shows that sequence ordering takes place as a result of interchain exchange reactions when the reaction medium is not homogeneous in the thermodynamic sense [14]. Thus, the segregation of a crystalline [15] or liquid-crystalline [9] phase within the medium can provide the enthalpic driving force for the reactions to run toward sequential reorganisation and compositional differentiation, rather than toward the expected entropy-driven randomisation.

In a previous work [12] PET-based copolyesters were prepared by transesterification of PET with equimolar amounts of sebacic acid (S) and hydroquinone (Q), and with varying amounts of

4-hydroxybenzoic acid (H). In no case a compositionally homogeneous random copolyester was obtained; even the synthesis carried out in the absence of H gave a product containing a segregated phase formed by aromatic-rich copolyester chains. An increase of the amount of added H and, thereby, of the overall degree of aromaticity of the mixture, was shown to favour the segregation phenomena. It should be noted, too, that a reactive blend of equimolar amounts of PET and poly(phenylene sebacate) (PQS) [16], prepared at temperatures higher than the melting points of the two polyesters, contains a segregated phase rich in aromatic units (T and Q).

In this work, novel PET-based copolyesters have been synthesised by transesterification of PET with equimolar amounts of sebacic acid (S) and 4,4′-diacetoxybiphenyl (B) and with varying amounts of 4-acetoxybenzoic acid (H). The composition of the copolyesters has been chosen to be equal to that of the products previously prepared from PET, S, Q and H [12]. The aim was to investigate the influence of the substitution of Q with B on the morphology and the characteristics of the copolyesters.

2. EXPERIMENTAL PART

2.1. Materials

A commercial grade of PET, kindly provided by Shell, was used for the copolyester syntheses. The polymer had an intrinsic viscosity of 0.63 dL/g, in a 60/40 w/w phenol/tetrachloroethane mixture at 25°C.

Sebacic acid (S) and 4,4′-dihydroxybiphenyl (B) were supplied by Merck; 4-hydroxybenzoic acid (H) was supplied by Aldrich. The hydroxylated monomers (B and H) were acetylated and purified by crystallization.

2.2. Copolyester Synthesis

The copolyesters PET-B-S and PET-B-S-H were prepared by reaction of PET with the monomers in a Pyrex round-bottomed reactor equipped with a helicoidal stainless steel stirrer and attached to a vacuum line. The reaction was carried out at 290°C and a rotational speed of 100 rpm for 3 – 4 hours; during the last polymerisation stage the pressure was reduced gradually to about 0.1 mm Hg. The procedure is described in detail elsewhere [8 – 10]. Copolyesters with different nominal composition were prepared.

2.3. Solvent Extraction

The solvents employed for the extractive fractionation were toluene or chloroform. Weighed amounts of the powdered polymers were treated with boiling solvent in a magnetically stirred glass flask for 15 h. The insoluble fractions were taken out of the hot toluene or chloroform suspensions by centrifugation or filtration. The toluene or chloroform insoluble fractions were referred to as TI or CI fractions, respectively.

2.4. Characterisation of the Polycondensation Products

The thermal properties of the copolymers were determined with a Perkin Elmer DSC-4 apparatus with a heating/cooling rate of 10°C/min. The measurements were made under a nitrogen atmosphere.

The morphology of the samples was examined by polarising optical microscopy (POM) using a Leitz Ortholux-BK-Pol apparatus equipped with a hot stage, and by scanning electron microscopy (SEM), with a Jeol T300 apparatus.

The X-ray diffraction patterns of the products were recorded with a Siemens D-500 diffractometer using the Ni-filtered CuKα radiation.

3. RESULTS AND DISCUSSION

The nominal composition of the copolyesters prepared is presented on a ternary diagram (Fig. 1), whose edges correspond to the three parent homopolymers PET, poly(4,4′-biphenylene sebacate) (PBS), and poly-4-oxybenzoate (PH). The investigated polymers are referred to herein as B-40.0, B-41.6, B-44.4, and B-47.6. The figures indicate the degree of aromaticity of the copolyesters. The degree of aromaticity is commonly used to qualitatively measure the stiffness (anisotropy) of

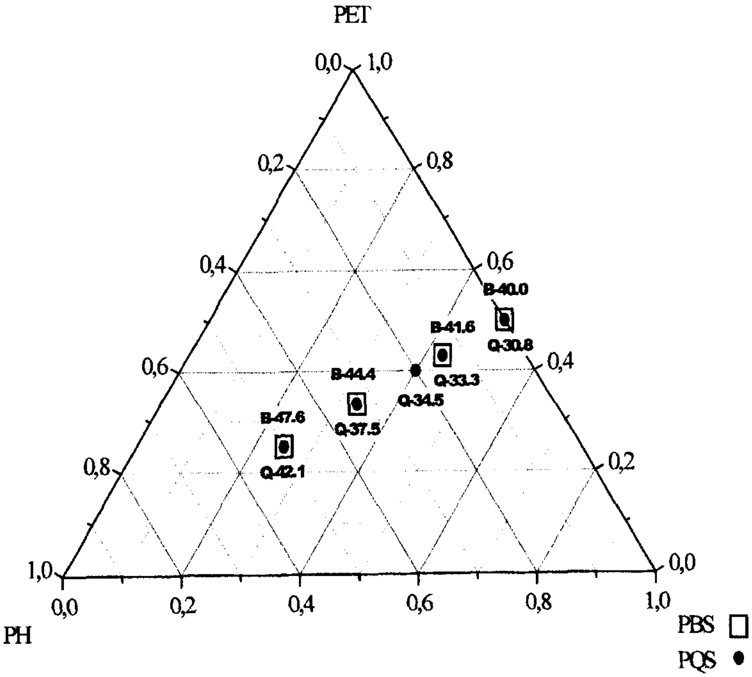

FIGURE 1 Ternary diagram of the nominal composition of the PET-S-B-H (□) and PET-S-Q-H (•) copolyesters. The figures indicate the degree of aromaticity of the samples.

the LCP macromolecules. It is calculated as the percent ratio of the number of aromatic carbons to the total number of atoms in the backbone [17]. The first copolymer (B-40.0) was synthesised from PET, B and S in the 1/1/1 molar ratio. Copolymers B-41.6, B-44.4 and B-47.6 were prepared with the same PET/B/S molar ratio, using different amounts of added H. The nominal composition of the copolyesters prepared in this work is equal to that of the materials synthesised from PET, Q, S and H in a previous work [12]. The latter copolymers, also reported in Figure 1 for comparison, are referred to herein as Q-30.8, Q-33.3, Q-34.5, Q-37.5, and Q-42.1, where the figures have the same meaning indicated above. It is clearly observed that the degree of aromaticity of the copolyesters containing B is always higher than that of the copolyesters based on Q, with equal molar composition.

The phase state of the copolyesters prepared was investigated by SEM. In Figure 2 the SEM micrographs of the fracture surfaces of the as obtained copolyesters are presented. The morphology of the

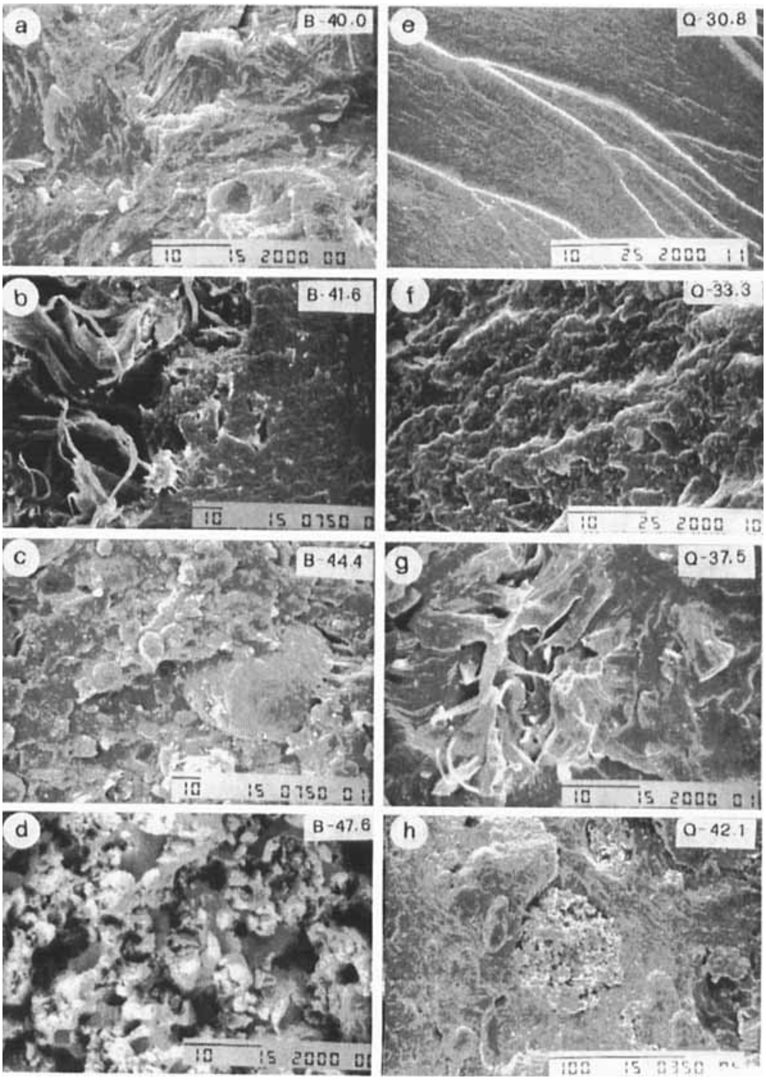

FIGURE 2 SEM micrographs of the fracture surfaces of: (a–d) PET-S-B-H copolyesters; (e–h) PET-S-Q-H copolyesters.

PET-B-S-H copolyesters (Figs. 2a, b, c, d) is compared here with that of the corresponding PET-Q-S-H copolyesters (Figs. 2e, f, g, h). The aim was to evaluate the influence of two factors on the phase state of the samples, namely, that of an increase of the H content, and that of an increase of the degree of aromaticity.

The SEM micrograph of the B-40.0 shows no clear sign of heterogeneity (Fig. 2a). The fracture surface of the sample is fibrous, and this suggests that the product has liquid-crystalline properties. This indication is supported by optical microscopic observations, as discussed below. The morphology of the analogous copolyester Q-30.8 also appears homogeneous (Fig. 2e), as already discussed in a previous work [12]. The addition of an equal amount of H (14 mol%) to the two above copolyesters leads to products (B-41.6 and Q-33.3) displaying quite different morphology (Figs. 2b and 2f). In fact, while the SEM micrograph of the sample having lower degree of aromaticity (Q-33.3) is typical for a heterogeneous material with phase segregation on a microscopic scale, that of B-41.6 clearly demonstrates the gross separation of fairly large fibrous domains dispersed in a almost homogeneous matrix. The interfacial adhesion between matrix and LC domains is extremely strong, and this is an indication that the chemical compositions of the two phases cannot be very different. It can also be observed that the fibrils forming the dispersed phase droplets are oriented perpendicular to the interface, thus indicating that the mesomorphic domains have an axial configuration of the nematic vector [10]. Although other parameters, such as the structure and shape of the two monomer units may have a role in the morphological changes undergone by the system as a result of the substitution of Q with B, it is thought that the clear segregation of a liquid-crystalline phase within the mass of the B-41.6 copolyester is predominantly due to the overall increase of aromaticity and stiffness of the polymer chains.

A further increase of the H content up to 33.3 mol% leads to an even more pronounced phase separation, as it is shown in Figure 2c for the B-44.4 copolyester. The dispersed phase appears mainly as non-fractured globules with a wide dimensions distribution; moreover the adhesion between the dispersed phase and the matrix seems to be slightly lower than that found for the B-41.6 sample, as demonstrated by the fact that the majority of the droplets are not fractured. This is probably due to an increased difference in the composition of the two phases. The dispersed phase is thought to be rich of H, B and T units, whereas the matrix possesses a much lower degree of aromaticity. A comparison of the micrograph of B-44.4 (Fig. 2c) with that of the analogous copolyester Q-37.5 (Fig. 2g) clearly demonstrates that the two polymers have quite different morphology. The fracture surface of Q-37.5 displays morphological characteristics that make it resemble that of B-41.6 (Fig. 2b), especially with respect to the dispersed phase, and that of B-40.0 (Fig. 2a), with respect to the matrix. These observations again suggest that the degree of aromaticity of the copolyesters is the main factor that determines their morphology.

The degree of aromaticity of copolyester B-44.4 is not far from that of Q-42.1, and the morphology of the two materials is also similar, in that the minor phase consists of globular particles imbedded in a quasi-homogeneous matrix. However, the cohesion within the globules is much stronger for B-44.4, as demonstrated by the fracture propagating along the interface whereas for Q-42.1 it runs across the minor phase particles without deviation. This is probably due to the inner morphology of the dispersed particles, which consist of liquid-crystalline monodomains for B-44.4, and of less coherent aggregates of smaller particles (fibrils and droplets) for Q-42.1. Such different morphology of the LCP droplets had already been observed for PET-B-S-H copolyesters in a previous work [9, 10]. It was shown that small LCP droplets and fibrils aggregate into poorly coherent glomerules, already during the last stage of the polycondensation, if their composition has become so rich of aromatic units to cause the melting point to exceed the temperature of the reaction medium. We believe that this explanation holds for the copolyesters under study, too. Thus, the minor phase of Q-42.1 is thought to possess a melting point higher than 290°C, whereas this is not so for B-44.4. This is not surprising because, as it was demonstrated elsewhere [11, 13], highly aromatic copolyesters made up of E, T, B and H units have melting points appreciably lower than those containing Q in place of B.

The morphology of copolyester B-47.6 (Fig. 2d) is typical for a polymer/LCP blend having a composition close to phase inversion. The LCP phase is thought to be rich of H, B and T units, whereas the matrix contains the majority of the E and S units. Here, compositional differentiation between the two phases is probably maximum.

Solvent fractionation of the PET-B-S-H copolyesters was performed using boiling toluene or chloroform as described in the experimental section. The aim was to separate the soluble fraction, containing the aliphatic-rich macromolecules, from the insoluble fraction, containing the aromatic-rich ones. The results show that B-40.0 is completely soluble in the solvents as it could be expected from its morphology, and this supports the hypothesis that this product is a quasi-random copolymer. On the contrary, for the copolyesters demonstrating two-phase morphology, an insoluble fraction can be separated by solvent treatment. Moreover, the amount of the insoluble fraction increases with an increase of the degree of aromaticity. An example of the morphology of the insoluble fraction is presented in Figure 3 for copolyester B-44.4. The results confirm that the two phases of B-41.6, B-44.4 and B-47.6 have different chemical structure, and, thereafter, different solubility.

The PET-B-S-H copolyesters were also investigated by optical microscopy under polarised light in order to estimate the structure organisation of the samples. Small pieces of the samples were placed on the object glass and covered with a cover glass. The samples were heated using the hot stage of the microscope from room temperature up to 340°C with a heating rate of 10°C/min. At higher temperatures polymer degradation started. Thin films of the samples were prepared by gently pressing the cover glass as soon as polymer deformation became possible. The samples were then cooled from 340°C to room

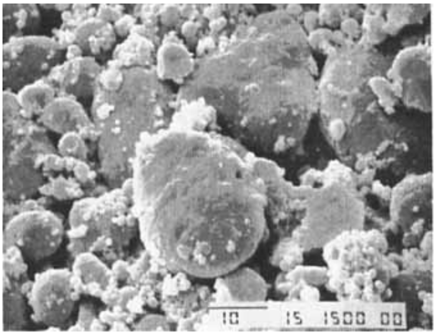

FIGURE 3 SEM micrograph of the fracture surface of the insoluble fraction of B-44.4.

temperature at the same rate. Micrographs were taken during the thermal treatment, and at room temperature as well.

The crystal-nematic transition was clearly observed in copolyester B-40.0 at about 200°C. The liquid-crystalline mesophase displays the typical nematic texture which is preserved until 340°C. The LCP texture does not change during subsequent cooling. Copolyester B-41.6 also melts at about 210°C, giving rise to an apparently homogeneous birefringent film upon sample compression. However, the micrograph taken at room temperature, after cooling, shows the presence of bright liquid-crystalline domains dispersed in a darker liquid-crystalline matrix. This shows that separation of two liquid-crystalline phases has taken place in this sample. Copolyester B-44.4 also melts in the same temperature range (about 200°C) and transforms into an apparently homogeneous nematic mesophase. Upon further heating, however, the sample separates into two phases that become clearly visible at about 280°C; one of the phases soon becomes isotropic, while the other preserves its nematic texture up to the maximum temperature of 340°C. A micrograph showing the texture of B-44.4 at 340°C is presented in Figure 4a. Upon cooling, the

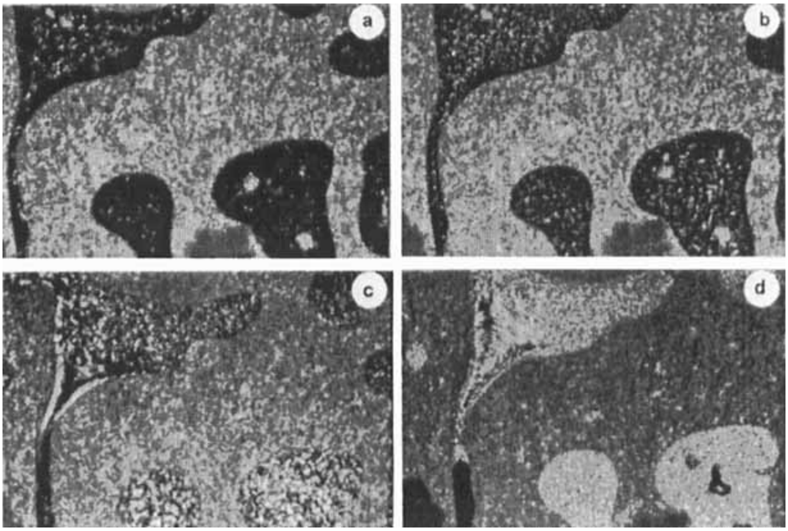

FIGURE 4 Optical micrographs of the texture of B-44.4 at different temperatures: (a) 340°C; (b) 280°C; (c) 180°C; (d) room temperature. (See Color Plate I).

isotropic phase transforms into a nematic mesophase at about 280°C, while the second liquid-crystalline phase does not change significantly (Fig. 4b). On further cooling, the first phase crystallises over a wide temperature range (Figs. 4c and 4d). Figure 4d shows the phase state of the sample at room temperature. Optical microscopic observation confirms very clearly that copolyester B-44.4 consist of two segregated liquid-crystalline phases, the aromatic-rich one has a nematic-isotropic transition higher than 340°C, while the aliphatic-rich mesophase becomes isotropic at about 280°C. The behaviour of copolyester B-47.6 is qualitatively similar to that discussed for B-44.4.

The thermal properties of the synthesized copolyesters were also studied by DSC in the 60–330°C temperature range with a heating/cooling rate of 10°C/min. Unfortunately, however, the crystal-nematic transitions could hardly be detected, due to their very low enthalpy changes. As an example, the DSC heating and cooling scans of B-44.4 are presented on Figure 5. Polymer softening, that was clearly seen to occur at about 200°C by optical microscopy (indicated by an arrow on the heating trace) could hardly be observed by DSC. On the contrary, the cooling scan displays a weak but definite exothermic transition at 280°C, that was identified by POM as the isotropic-nematic transition of the matrix phase.

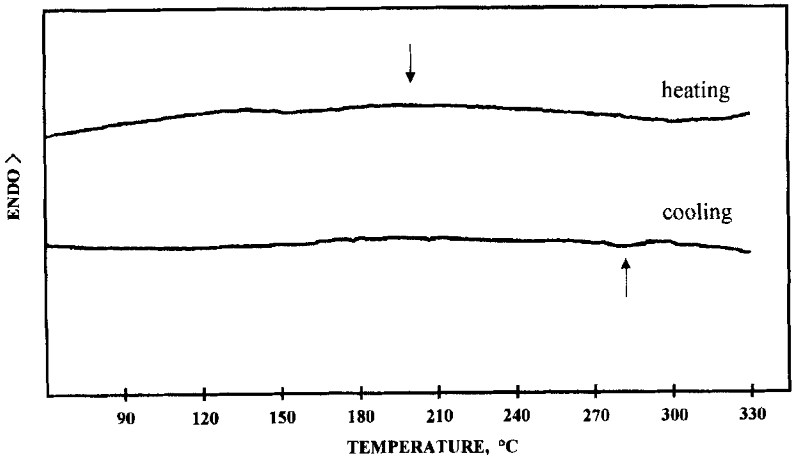

FIGURE 5 DCS heating and cooling scans of B-44.4. The arrows indicate the phase transitions.

The crystal structure of the copolyesters was studied by WAXS. The X-ray diffraction patterns of the copolyesters, taken at room temperature, are reported in Figure 6. The main reflection at $2\theta \approx 20°$, which is due to the lateral packing of copolyester chains having longitudinal disorder, is typical for polymers with liquid-crystalline properties. This confirms the optical microscopic observation showing that both phases of the samples posses mesomorphic character. It should be mentioned, also, that the weak reflections at $2\theta \approx 23°$ and 28° which can be detected in some of the diffractograms are slightly more expressed for the samples with lower degree of aromaticity. Moreover, a weak shoulder at about 19° can be observed for sample B-40.0. The WAXS patterns of the copolyesters indicate that the liquid-crystalline character of the samples increases with the increase of the degree of aromaticity, and that an increase of the concentration

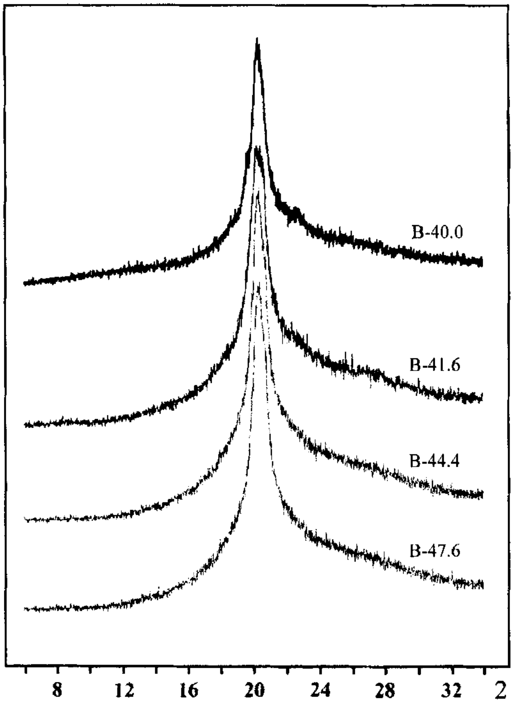

FIGURE 6 X-ray diffraction patterns of PET-S-B-H copolyesters.

of H does not lead, in this case, to the formation of long H sequences that would otherwise lead to the appearance of high angle crystalline peaks. The latter conclusion is confirmed by the finding that the diffractograms of the insoluble fractions of the samples are almost similar to those presented in Figure 6.

4. CONCLUSION

The present study of the structure, the morphology, and the thermal properties of a series of copolyesters synthesised by transesterification of PET with mixtures of equimolar amounts of B and S and different amounts of H demonstrates that segregation of a liquid-crystalline phase, during polycondensation, provides the driving force for compositional differentiation, with the result that the final products are in fact "synthetic polymer blends". A comparison of the PET-B-S-H copolymers studied here with PET-Q-S-H copolyesters having the same molar composition has provided convincing evidence that the overall degree of aromaticity of the mixtures is an important parameter that helps the observed segregation phenomena. Thus, for the PET-B-S-H copolyesters, that possess higher aromaticity than the PET-Q-S-H polymers of similar molar composition, phase segregation was shown to be more prominent. It should be emphasised, however, that the segregation of an aromatic-rich liquid crystalline phase and the subsequent compositional differentiation of the two phases of the system are strongly encouraged by the presence of aliphatic monomer units, such as E and S, that concentrate in the copolyester chains forming the matrix. In fact, as it was demonstrated recently [13], substitution of the S units of the PET-B-S-H copolyesters studied here with terephthalic acid monomer units (T) leads to practically homogeneous, highly aromatic p(E-T-B-H) copolyesters with very good thermal and mechanical properties.

Acknowledgments

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