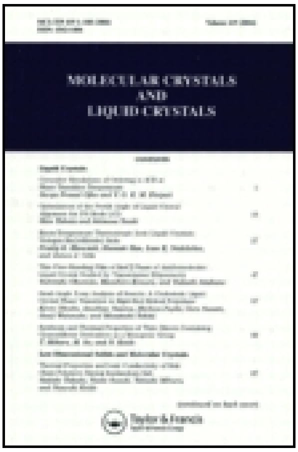

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Segregation of Liquid Crystalline Mesophases During the Transesterification of PET with Sebacic Acid, Hydroquinone and 4-Hydroxybenzoic Acid

Rossana Miliè [a] , Lilia Minkova [b] , Sara Filippi [a] , Giovanni Polacco [a] & Pierluigi Magagnini [a]

[a] Dept. of Chemical Engineering, University of Pisa, via Diotisalvi, Pisa, 256126, Italy

[b] Institute of Polymers, Bulgarian Academy of Sciences, Sofia, 1113, Bulgaria

To cite this article: Rossana Miliè, Lilia Minkova, Sara Filippi, Giovanni Polacco & Pierluigi Magagnini (2002): Segregation of Liquid Crystalline Mesophases During the Transesterification of PET with Sebacic Acid, Hydroquinone and 4-Hydroxybenzoic Acid, Molecular Crystals and Liquid Crystals, 372:1, 37-50

To link to this article: http://dx.doi.org/10.1080/713738187

Mol. Cryst. and Liq. Cryst., 2001, Vol. 372, pp. 37-50

Segregation of Liquid Crystalline Mesophases During the Transesterification of PET with Sebacic Acid, Hydroquinone and 4-Hydroxybenzoic Acid

ROSSANA MILIÈ[1], LILIA MINKOVA[2], SARA FILIPPI[1],
GIOVANNI POLACCO[1] and PIERLUIGI MAGAGNINI[1]

[1]*Dept. of Chemical Engineering, University of Pisa, via Diotisalvi,*
256126 Pisa, Italy and
[2]*Institute of Polymers, Bulgarian Academy of Sciences,*
1113 Sofia, Bulgaria

Abstract The phase behavior and the morphology of PET-based copolyesters have been studied by DSC, optical and electron microscopy and WAXS. The materials 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 that, though appearing as a homogeneous liquid-crystalline copolymer when characterized by conventional calorimetric and microscopic techniques, was shown by solvent fractionation and X-ray analysis to contain a segregated phase, probably 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 favor the segregation phenomena. The results confirm that an enthalpy-driven compositional differentiation of the two phases of the investigated copolyesters takes place during synthesis.

Keywords Liquid Crystalline Polymers; Phase Segregation; PET; Transesterification reactions.

INTRODUCTION

Exchange reactions taking place between condensation polymers, or between a condensation polymer and one or more monomers, have been studied extensively in the last decades[1, 2]. As a rule, these reactions are known to lead to block copolymers, at first, and then, gradually, to copolymers having the most probable molar mass distribution, random sequence distribution, and compositional homogeneity. They can therefore be used either for the production of new materials with enhanced properties, or for the compatibilization of immiscible polymers. However, several examples have been provided, recently, showing that sequence ordering can in fact take place as a result of interchain exchange reactions when the reaction medium is not homogeneous in the thermodynamic sense[2]. Thus, the segregation of a crystalline[3], or liquid-crystalline[4] (LC) phase within the medium can provide the enthalpic driving force for the reactions to run toward sequential reorganization and compositional differentiation, rather than toward the expected entropy-driven randomization. In particular, the transesterification reaction of poly(ethylene terephthalate) (PET) with a mixture of sebacic acid (S), 4,4'-diacetoxybiphenyl (B), and 4-acetoxybenzoic acid (H) in the molar ratio 1/1/2, was shown to produce "synthetic blends" consisting of an aromatic-rich LC phase dispersed in an isotropic matrix of aliphatic-rich copolyester[4-6].

In a previous work[7], the reactive blending of equimolar amounts of PET and poly(phenylene sebacate) (PQS) at temperatures higher than the melting points of the two polyesters was studied. The products were characterized by differential scanning calorimetry and by optical and electron microscopy, and it was found that blending did in fact cause the gradual transformation of the biphasic blend, until an apparently homogeneous LC copolyester was obtained after 180 min. A product having the same overall composition, prepared by transesterification of PET with an equimolar mixture of S and Q, showed very similar characteristics. However, the X-ray diffraction analysis of both products provided evidence indicating that a crystalline phase, probably formed by chain segments rich of Q and T units, was developing, though rather slowly, in these systems.

In order to get further evidence demonstrating that phase segregation followed by compositional differentiation takes place in systems where transreactions occur between PET and appropriate monomer mixtures, the transesterification of PET with S, Q, and varying amounts of 4-hydroxybenzoic acid (H) has been studied in this work.

EXPERIMENTAL

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 and hydroquinone were supplied by Merck; 4-hydroxybenzoic acid was supplied by Aldrich. All monomers were used as received. The hydroxylated monomers (Q and H) were acetylated and purified by crystallization as described elsewhere[8, 9]. The molecular structure of PET and those of the monomers in the acetylated form are reported in figure 1.

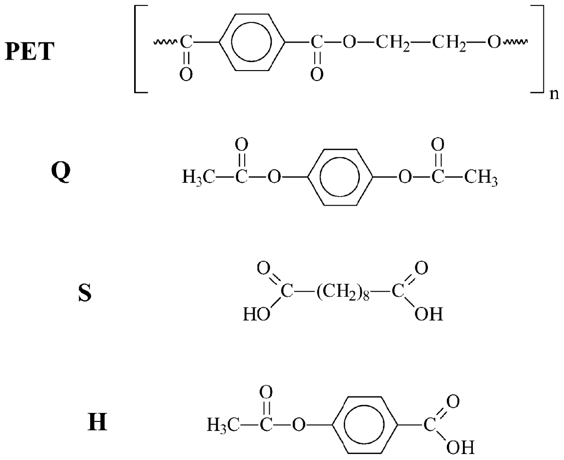

FIGURE 1 Chemical structures of PET, Q, S and H.

Techniques

Polycondensations

The copolyesters PET-Q-S and PET-Q-S-H were prepared by reacting PET with the monomers in a Pyrex round-bottomed reactor equipped with a helicoidal stainless steel stirrer. The reaction was carried out at 290°C and a rotational speed of 100 rpm for 3-4 hours during which the pressure was reduced gradually to about 0.1 mm Hg. The procedure is described in detail elsewhere for similar systems[4].

Thermal properties

Differential Scanning Calorimetry (DSC) was performed with a Perkin Elmer DSC-4 apparatus with a heating/cooling rate of 10°C/min. The measurements were made under a nitrogen atmosphere.

Morphology

The morphology of the samples was examined by Polarizing Optical Microscopy (POM), using a Leitz Ortholux-BK apparatus equipped with a hot stage, and by Scanning Electron Microscopy (SEM), with a Jeol T300 apparatus.

Structure

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

Solvent extraction

The solvents employed for 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 fractions were taken out of the hot toluene or chloroform suspensions by centrifugation or, respectively, filtration. The accuracy of separation was generally poor because the insoluble fraction consisted either of particles that were too fine to be reliably filtered/decanted, or of large porous globules that might prevent complete extraction of the soluble material. The toluene, or chloroform, insoluble fractions mentioned below are referred to as TI or CI fractions, respectively.

RESULTS AND DISCUSSION

The first copolymer, referred to herein as R1, was synthesized from PET, Q and S in the 1/1/1 molar ratio. The nominal composition of this polymer is equal to that of the materials described in a previous paper[7]. Copolymers R2 to R5 were prepared with the same PET/Q/S molar ratio using different amounts of added H. Figure 2 shows, in a ternary diagram, the nominal composition of these copolymers. Their degree of aromaticity, calculated as the percent ratio of the number of aromatic carbons to the total number of atoms in the backbone[10] increases from 30.8 for R1 to 42.1 for R5. The degree of aromaticity is commonly used to qualitatively measure the stiffness (anisotropy) of the molecules of liquid-crystalline polymers.

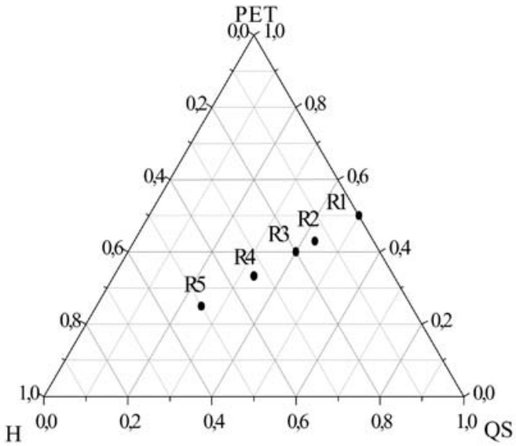

FIGURE 2 Nominal composition of the copolyesters.

As already discussed in the previous article[7], R1 behaves as a homogeneous random copolymer when studied by calorimetric and microscopic analysis. As an example of this, the SEM micrograph of the surface of a freeze fractured R1 sample is shown in Figure 3.

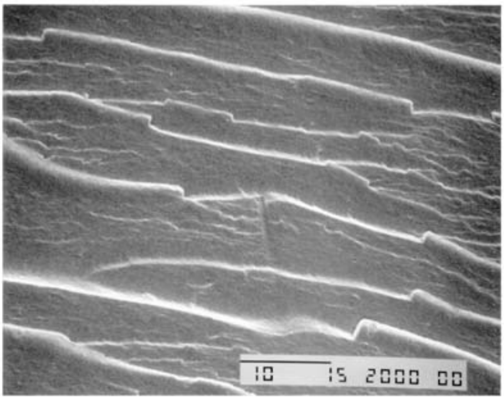

FIGURE 3 SEM micrograph of the fracture surface of R1.

It should be emphasized, however, that the POM analysis of R1, as well as that of the reactive blend prepared previously[7] with 180 min blending, shows that these materials are mesomorphic. Therefore, the average length of the aromatic sequences present in the macromolecules is probably higher than expected for a random copolymer. Moreover, the X-ray diffraction patterns of the two products show an intense, composite reflection at $2\theta \approx 20\text{-}22.5°$, plus a few other ill-resolved reflections at $2\theta \approx 23$, 28 and 30°. The latter weak reflections suggest that the (initial) segregation of a crystalline phase may have taken place in these materials. If this were so, one might conclude that the system does in fact show a thermodynamic tendency to evolve toward the formation of the two other related homopolyesters poly(phenylene terephthalate) (PQT) and poly(ethylene sebacate) (PES), whose chemical structure is shown in Figure 4. In fact, it is expected that, compared to a random copolyester with equal overall composition, an equimolar mixture of PQT and PES would contain less free energy, under the conditions employed for the synthesis of R1, as PQT would be in the crystalline state.

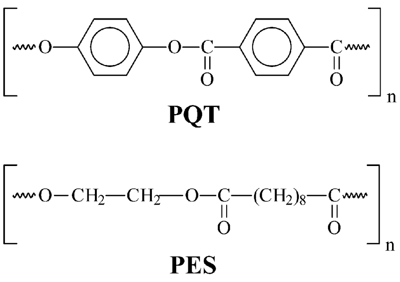

FIGURE 4 Chemical structures of PQT, and PES.

In order to demonstrate that a segregated crystalline phase is actually present in the apparently homogeneous R1 copolyester, a sample of the latter was treated with boiling toluene, which should be a non-solvent for this (supposedly aromatic-rich) phase. After a number of trials, we did succeed in separating by centrifugation an insoluble fraction that was observed on the electron microscope. The SEM micrograph of the toluene-insoluble (TI) fraction, shown in Figure 5, demonstrates definitely the biphasic nature of R1. The TI fraction is composed of droplets of less than 1 μm diameter, embedded in a continuous phase.

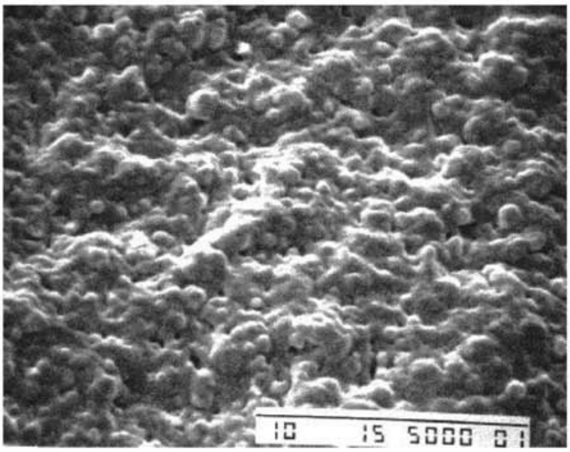

FIGURE 5 SEM micrograph of the TI fraction of R1.

The presence of these dispersed droplets couldn't be reliably inferred in the micrograph of R1 (Figure 3) probably because they are too small to induce significant deviations in the fracture surface of this material. However, the morphology of the TI fraction strongly suggests that phase separation due to sequential reordering has actually taken place during the R1 synthesis. The behavior of this material with respect to solvents seems to indicate that its chemical composition obeys a bimodal distribution with no strong separation of the two maxima. The insoluble material acting as a cement for the microspheres of the TI fraction (cf. Figure 5) is supposed to be an interphase of intermediate composition, and this is in line with its strong adhesion to the droplets. The reason why the transreactions have not led to a stronger differentiation of the phases has been tentatively attributed to the fairly low overall degree of aromaticity of the reaction mixture.

In order to test this hypothesis, a number of copolymers in which the degree of aromaticity was enhanced by the addition of increasing amounts of H to the starting mixture were synthesized, as shown in Figure 2. The products, R2 to R5, were also fractionated with solvents and characterized as described for R1. The results seem to confirm that an increased overall aromaticity of the charge does actually enhance segregation.

The SEM micrograph of the TI fraction of copolyester R3 is shown in Figure 6.

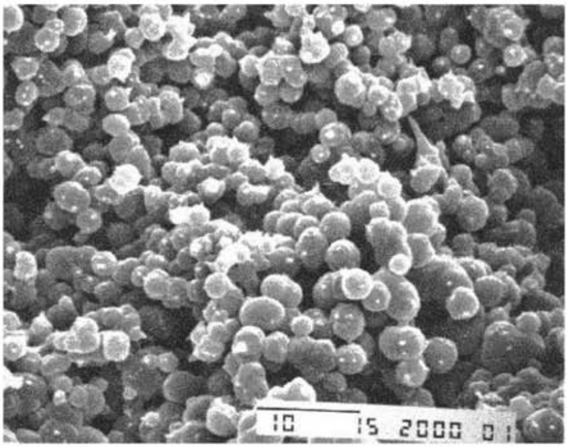

FIGURE 6 SEM micrograph of the TI fraction of R3.

It is readily observed that the TI phase is composed of "clean" microspheres with diameters in the 2-4 μm range, thus demonstrating that fractionation with boiling toluene was much more efficient in this case. This must clearly be attributed to enhanced differentiation of the chemical composition of the two phases of this material.

Copolyesters R4 and R5, characterized by still higher aromaticity, were shown to be biphasic even from a macroscopic point of view. For both materials the SEM analysis did in fact reveal very clearly the presence of a dispersed phase, consisting of large globules, through which the fracture surface goes with no appreciable deviation. The micrograph taken on a freeze-fractured sample of R5 is presented in Figure 7. Clearly, solvent fractionation was easier for these materials, not only because the composition and the properties of the two relevant phases are mutually farther, but also because the insoluble droplets have much larger dimensions (up to 200-400 μm). In Figure 8, the chloroform insoluble (CI) fraction of the R4 copolyester is shown. The picture clearly reveals that the globules are formed by the aggregation of much smaller particles (droplets and fibrils), as already found in a previous study of similar systems[4].

From the morphological characterization of PET-Q-S-H copolyesters containing different concentrations of H monomer units, it may be concluded that an increase of the overall degree of aromaticity of these materials greatly favors the phase segregation phenomena.

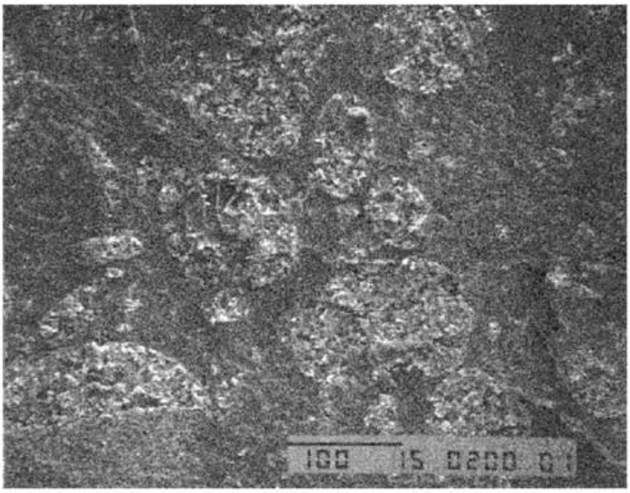

FIGURE 7 SEM micrograph of the fracture surface of R5.

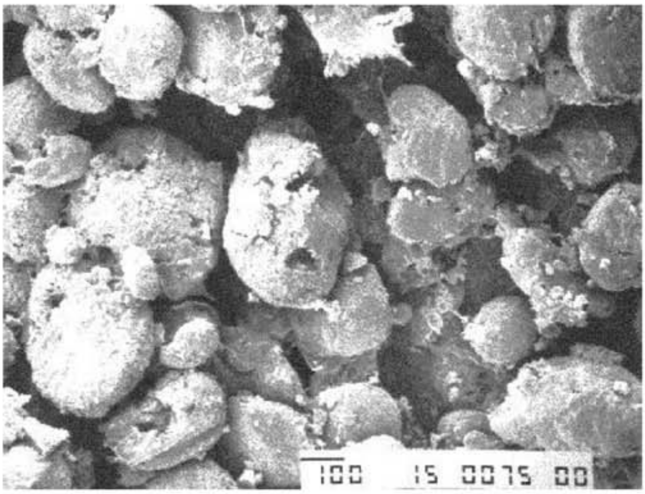

FIGURE 8 SEM micrograph of the CI fraction of R4.

A differential scanning calorimetry investigation of the copolyesters and of their soluble and insoluble fractions failed to provide reliable information on their thermal properties: in fact, the DSC scans of most samples did not show clear transitions associated with the fusion of the crystalline phases, in a temperature range between 25 and 300°C. This result is not surprising because most of the insoluble fractions of the copolyesters were shown by POM not to melt in this range. On the other hand, the soluble fractions are probably characterized by very low structural order in the crystalline state, as it is expected for copolyester chains with statistical distribution of the monomer units.

The POM observations, carried out by placing small polymer particles between microscope slides on the hot stage and heating them at 10°C/min with occasional compression of the cover slip, provided more detailed information. Copolyesters R1, R2 and R3 produced an apparently homogeneous nematic texture at 200-230°C, which remained practically unchanged either upon heating to over 280°C, and on subsequent cooling down to room temperature. Due to the strong birefringence of the mesophase, the presence of the dispersed phase of these materials couldn't be demonstrated by POM. In agreement with results of the SEM investigation, the biphasic morphology of R4 and R5 was readily observed on the optical microscope, when the aliphatic-rich matrix melted at about 170°C, and a slight pressure on the cover slip reduced the sample to a thin film. Bright domains, apparently solid, though being slightly deformed under pressure, could be clearly distinguished from the less birefringent matrix, and remained practically unchanged even at 330°C.

The X-ray diffraction patterns of the copolyesters are reported in Figure 9. As already mentioned, the spectrum of R1 displays a main reflection at $2\theta \approx 20°$, which is due to the lateral packing of the copolyester chains and is typical for polymers with liquid-crystalline order. The peak is accompanied by a number of ill-resolved reflections at $2\theta \approx 23$, 28 and 30°, probably ascribable to the crystalline TI phase. The X-ray patterns of the R2-R5 polymers demonstrate very clearly that the addition of varying amounts of H to the charge leads to strong disruption of the longitudinal order of the copolyester macromolecules. In fact, the spectrum of R2 shows that the weak reflections attributed to crystalline order are almost absent, while the main reflection at $2\theta = 20.5°$ due to liquid-crystallinity has become considerably sharper and more intense. The disordering effect induced by the addition of the third monomer (H) is probably maximum for R3 or R4 copolyesters: in fact, the secondary reflections at 2θ=19.7 and 22-23° are hardly visible in the spectra of these materials. They are practically consisting of a single, very strong and sharp reflection due to the mesomorphic organization of the macromolecules.

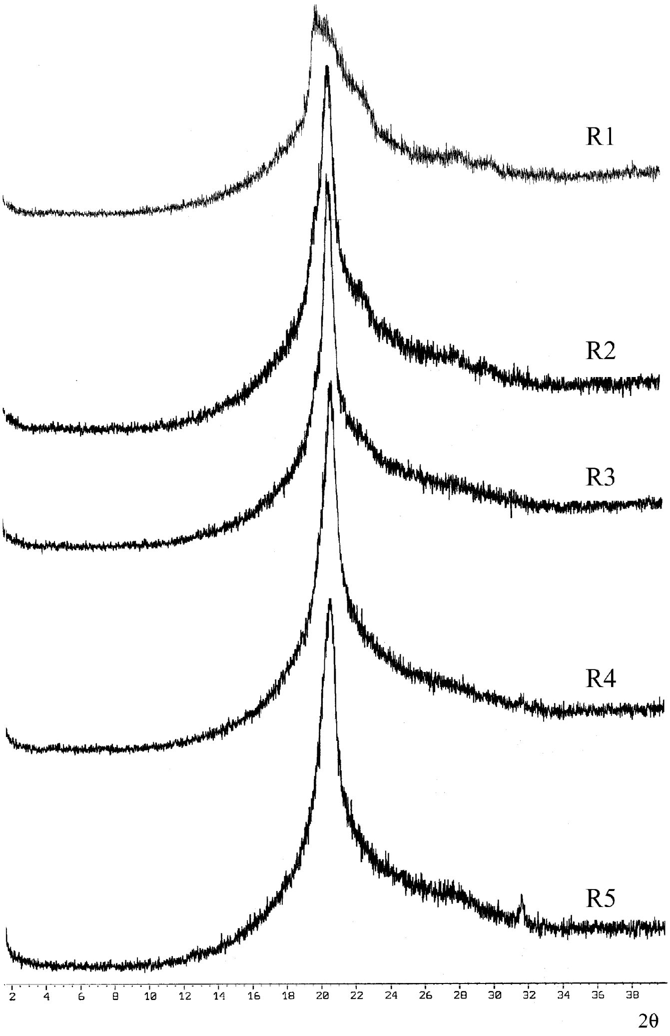

FIGURE 9 X-ray diffraction patterns of the copolyesters.

The spectra of the R4 and R5 copolyesters, which contain fairly high concentrations of H units, show a progressive broadening of the main peak, and the appearance, especially in the spectrum of R5, of other secondary wide angle reflections: one broad at $2\theta \approx 28°$, and one at $2\theta \approx 31.7°$. The first effect is certainly due to the increased concentration of aromatic units in the chains, which makes them stiffer and reduces their packing ability. The presence of new secondary reflections, different from those of the spectrum of R1, is attributed to the formation of crystalline regions arising from the organization of chain segments rich of H units.

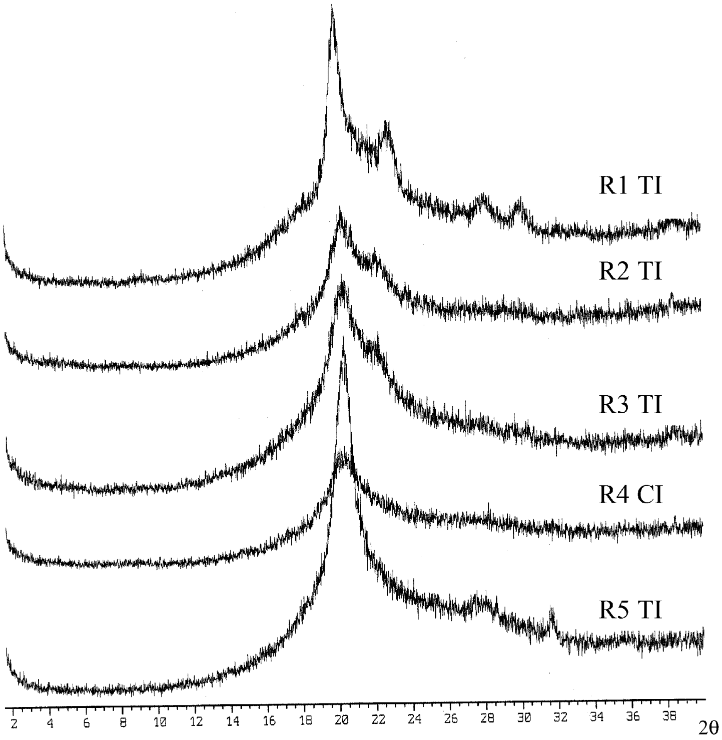

FIGURE 10 X-ray diffraction patterns of the insoluble fractions.

The above conclusions are convincingly supported by the X-ray diffraction patterns of the insoluble fractions of the copolyesters, shown in Figure 10. Let's start from the spectrum of the insoluble fraction of R5, which is very similar to that of the whole copolymer, except for the secondary reflections that appear slightly more intense. This finding is not surprising because this highly aromatic copolyester is only slightly soluble in boiling toluene. All other spectra differ appreciably from those of the copolyesters, especially in that the reflection close to $2\theta \approx 20°$ is much less intense. Moreover, except perhaps for the CI fraction of R4, a number of additional reflections are clearly visible in the X-ray diagrams, indicating some type of crystalline order. The TI fraction of R1, in particular, shows a strong sharp reflection at $2\theta \approx 19.6°$ and the other reflections at $2\theta \approx 23$, 28, and 30°, whereas the intensity is rather weak at $2\theta \approx 20.5°$, where the typical reflection of the liquid-crystalline structure of these copolyesters appears. This confirms that the crystalline order displayed by R1 is concentrated in the toluene insoluble phase, which is rich of aromatic TQ units. The soluble fraction of this copolyester possesses weak liquid-crystalline order.

A comparison of the spectra of the TI fractions of R2 and R3 with that of the analogous fraction of R1 confirms that the addition of H to the polymerization feed reduces drastically the longitudinal order of the copolyester chains, even within the segregated phase. Thus, the type of order present in the insoluble fractions gradually changes from crystalline to liquid-crystalline as the concentration of added H increases. In particular, R4 can be considered as a "synthetic blend" of two statistical copolyesters forming separate liquid-crystalline phases that differ from each other for the composition: the insoluble, high-melting, dispersed phase is rich of aromatic units, whereas the lower melting, soluble one is rich of aliphatic units. It is only when the concentration of H units exceeds a certain limit, as it happens for R5, that a new crystalline order, probably arising from the organization of H-rich sequences, is observed in the X-ray spectrum of the insoluble fraction, as discussed before.

CONCLUSIONS

In a previous paper[7], it had been shown that the transesterification reactions taking place in the melt in a blend composed of equimolar amounts of PET and PQS produce an apparently homogeneous, random copolyester. Similar results were found when PET was reacted with a mixture of the two monomers Q and S to give a product with the same overall composition. The present results demonstrate that these products do in fact contain a segregated phase rich of aromatic units (T and Q), which is responsible for the presence of weak X-ray diffraction peaks indicative of a three-dimensional crystalline structure. Crystallizable polyester chains rich of QT sequences can only be formed, in this system, by enthalpy-driven ester exchange reactions running toward compositional differentiation, rather than toward phase homogenization.

Even more evident segregation phenomena leading to the formation of true "synthetic blends", in place of the expected homogeneous copolyesters with random sequence distribution, take place when the content of aromatic units in the system is increased by the addition of H to the mixture of monomers.

Acknowledgments

This work was carried out with the financial support of C.N.R., of the Italian Ministry of University (MURST), and of the Bulgarian Academy of Sciences.

References

1. A.M. Kotliar, J. Polym. Sci., Macromol. Rev. **16**, 367 (1981)
2. S. Fakirov, Transreactions in Condensation Polymers, Wiley-VCH, Weinheim, (1999)
3. R.W. Lenz, E. Martin, and A.N. Schuler, J. Polym. Sci., Polym. Chem. Ed., **11**, 2265 (1973)
4. M.S. Tonti, M. Masseti, G. Poli, M. Paci, P.L. Magagnini, C. Forte, and C.A. Veracini, Polym. Eng. Sci., **39**, 1891 (1999)
5. G. Poli, M. Paci, P.L. Magagnini, R. Scaffaro, and F.P. La Mantia, Polym. Eng. Sci. **36**, 1244 (1996)
6. P.L. Magagnini, M. Paci, G. Poli, M.S. Tonti, and P. Narducci, Polym. Eng. Sci., **39**, 1891 (1999)
7. L. Minkova, S. Filippi, G. Polacco, M. Paci, P.L. Magagnini, Macromol. Chem. Phys., in press
8. B. Tsai, C. Lee, N.S. Chang, M.S. Chen, and S.J. Chang, J. Appl. Polym. Sci., **40**, 1499 (1990)
9. P.L. Magagnini, B. Bresci, M. Paci, A. Roggero, and F.P. La Mantia, in Recent Advances in Chemical Engineering, p.541, D.N. Saraf, and D. Kunzru, ed.s., Tata-McGraw-Hill, New Delhi (1990)
10. G.W. Calundann and M. Jaffe, in Proc. Robert A. Welch Conf. on Chem. Res., XXVI, Synthetic Polymers, 247 (1982)