

The Morphology of the Aromatic Copolyester of Poly(ethylene Terephthalate) and 80 mol % of *p*-Acetoxybenzoic Acid

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Synopsis

The structure of the aromatic copolyester of poly(ethylene terephthalate) and 80 mol % of *p*-acetoxybenzoic acid was investigated by optical and electron microscopy, wide angle X-ray, and thermal analysis. The results of optical (LM) and electron microscopy (TEM and STEM) suggest the existence of ordered domains which appear as large lamellar blocks. These lamellar blocks based on electron diffraction analysis had the same spacings and lamellar thickness (~ 200 Å) as has been described earlier for single crystals of the pure homopolymer of *p*-hydroxybenzoic acid (PHBA). However, the characteristic reversible endotherm at 330–360°C for PHBA could not be obtained. In isolated cases, the lamellar blocks retained their general dimensions up to 535°C whereas the surrounding matrix had degraded severely. An irreversible endotherm was observed at 303°C which suggested the presence of a higher degree of order than expected for a random copolymer. The irreversible nature of the endotherm is consistent with a transition from a semicrystalline structure to a liquid crystalline state. X-ray analysis with as received samples and thermally treated specimen provided additional support for more ordered regions.

INTRODUCTION

Aromatic copolyesters based on polyethylene terephthalate and 60 and 80 mol % of *p*-hydroxybenzoic acid have been made available in experimental quantities from Tennessee Eastman. The copolyester containing 60 mol % of *p*-hydroxybenzoic acid has been characterized by Jackson and Kuhfuss¹ and shown by nmr to have a random distribution. Furthermore, no melting endotherm was observed consistent with the random structure. With respect to the copolyester containing 80 mol % of *p*-hydroxybenzoic acid, data were presented on the mechanical properties, but practically no work has been reported on its structure and thermal behavior other than to note that it displayed liquid crystalline character. Presumably, a detailed characterization was complicated by the relative insolubility of this copolyester composition.

The present study was undertaken to determine whether the structure of the copolyester containing 80 mol % of *p*-hydroxybenzoic acid was random, or, in fact, contained long sequences of *p*-hydroxybenzoic acid units. There were several reasons to suspect this latter possibility since: (1) the acetoxybenzoic acid was known to homopolymerize rapidly at 250–280°C; (2) the relative insolubility of the copolyester composition suggested that in the later stages of the polymerization the reaction was heterogeneous; and (3) in the initial SEM examination of the 80/20 copolyester, it was apparent that the material contained a small amount of a second phase. The irreversible endotherm at 303°C also

suggested the presence of ordered regions similar to those observed in copolymers of *p*-hydroxybenzoic acid and biphenol terephthalate.²

In this report, data are presented to show that the 20/80 copolyester composition is not random. In fact, there is evidence for the presence of small amounts of *p*-hydroxybenzoic acid homopolymer.

EXPERIMENTAL

Materials

The copolyester used in this study was provided kindly by Tennessee Eastman Kodak and consisted of the copolymer of poly(ethylene terephthalate) (PET) and 80 mol % of *p*-hydroxybenzoic acid (PHBA).

Methods

The optical properties of the copolyester were studied with a Zeiss Photomicroscope III equipped with two hot stages useable from room temperature to $\geq 550^\circ\text{C}$. Studies over the 25–300°C temperature range were carried out using a Mettler FP6 hot stage, whereas studies over 300–550°C were carried out using a specially designed hot stage apparatus. Both stages were calibrated with melting point standards over the 25–550°C temperature range.

The morphology of the copolyester was studied by scanning (SEM) and transmission electron microscopy (TEM). Surface morphology was studied using a Hitachi S-500 SEM. The internal morphology was studied using a Phillips 301 equipped with a (S) TEM attachment with microtomed sections ~ 400 Å thick. These were coated with carbon for beam stability in the TEM. Thermal analysis data were obtained with a Perkin Elmer DSC-2 Differential Scanning Calorimeter at a heating rate of 10°C/min. The samples were heated in a nitrogen atmosphere in which they were maintained for 0.5 h before sealing. The X-ray powder determinations were carried out using an X-ray diffractometer and copper radiation. Etching experiments to eliminate polyethylene terephthalate from the copolymer were performed with anhydrous NH_3 in a pressure vessel under 10 atm and at room temperature.

The as received copolyester was first examined microscopically at room temperature. The copolyester appeared as a relatively uniform phase in which ordered regions of varying size (10–50 μ) were embedded. Figure 1 depicts the texture of the 80 mol % PHBA copolyester (as received polymer) at room temperature. When the copolyester was heated from room temperature to 350°C, a nematic mesophase was clearly evident at $\sim 295^\circ\text{C}$ based on the high birefringence under cross polarizers. The rigid aggregates were clearly visible (Fig. 2) up to $\sim 325^\circ\text{C}$, and, on further heating to 328°C, they broke down to small lamellae. At $\sim 334^\circ\text{C}$, the lamellae were no longer visible and merged into the surrounding nematic mesophase. On further heating to 535°C, trace amounts of crystalline material still persisted in the melt. Prolonged standing $>340^\circ\text{C}$ resulted in degradation. The mesophase supercooled without the reformation of the crystal aggregates when it was cooled from $>330^\circ\text{C}$ to room temperature at 10°C/min. Transmission electron microscopy (Fig. 3) also showed the presence of lamellar domains (30–40 μ) embedded in what appeared as an amorphous

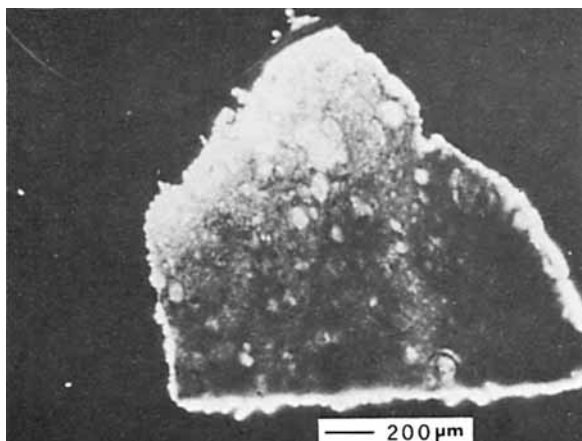


Fig. 1. Optical micrograph of the 80/20 PHBA/PET copolyester at room temperature.

medium. Lamellar thickness ranging from 200 to 400 Å could be observed from the TEM. The electron diffraction pattern of the copolyester domain like regions and amorphous areas are shown in Figure 4. The diffraction pattern of the domain consisted of discrete arcs and yielded d spacings shown in Table I consistent with the diffraction pattern for the homopolymer, whereas the amorphous character of the matrix was evident from the uniform halo. The as-received 80 mol % PHBA/PET copolyester exhibited an endotherm at 303°C which disappeared on cooling to room temperature or on second heating. The difference between the DSC melting point peak (303°C) and the temperature of lamellar break down at ~328°C observed with the optical microscope could be reconciled out if the end of the endotherm rather than the peak was considered.

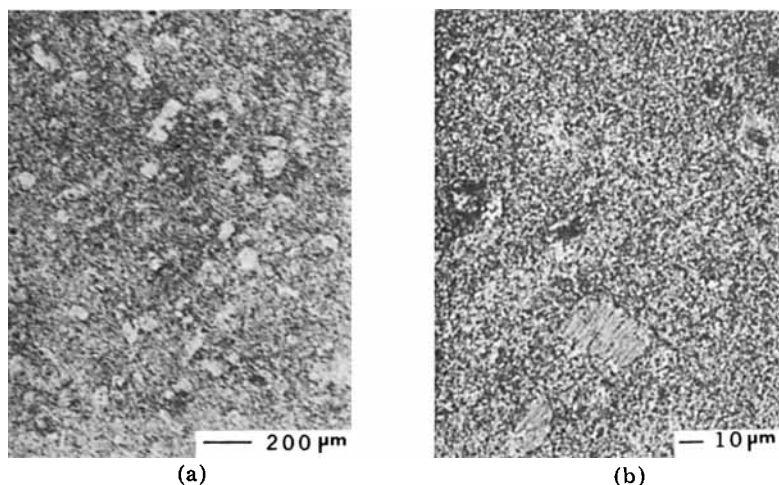


Fig. 2. Optical micrograph of the 80/20 PHBA/PET copolyester at elevated temperatures: (a) 80/20 PHBA/PET at 300°C and (b) 80/20 PHBA/PET at 328°C.

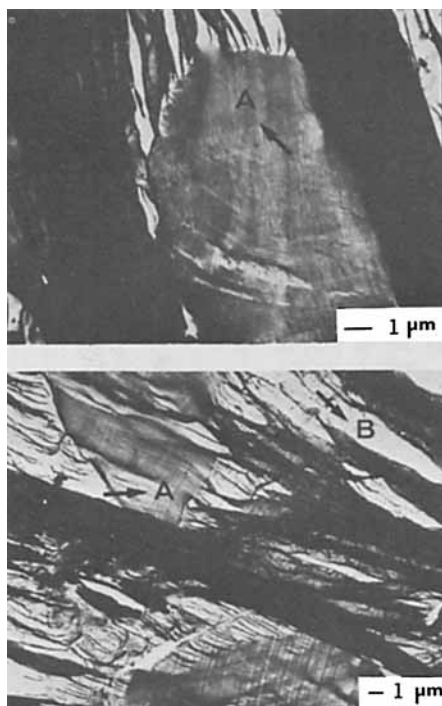


Fig. 3. Transmission electron micrographs of the 80/20 PHBA/PET copolyester: (A) lamellar domain and (B) amorphous region.

DISCUSSION

It has been proposed that the 60 mol % PHBA/PET copolyesters are random copolymers of *p*-oxybenzoic acid units and polyesters terephthalic acid units.^{1,3} This conclusion was reached on the basis of nmr studies of the soluble copolyesters of 60 mol % PET and PHBA (60 mol % PHBA).

Our present results suggest the existence of discrete PHBA domains in the 80% copolymer. These domains have a well defined lamellar structure with average lamellar thickness of 200–400 Å. The electron diffraction pattern from these lamellar blocks consisted of discrete arcs with the same *d* spacings as the pure PHBA homopolymer reported by Economy et al.⁴ The heterogeneous nature of the as-received copolymer is demonstrated by the distinctly different diffraction patterns of the lamellar block vs. the surrounding matrix. Another approach used to indicate the presence of crystalline PHBA was to etch out the noncrystalline regions with ammonia. X-ray analysis of the etched specimen showed a pattern approaching that of the highly crystalline PHBA.

TABLE I
Comparison of Observed Spacings for Pure PHBA and 80 mol % PHBA Copolyester

| Pure PHBA | 80 mol % PHBA copolyester | Relative intensity |
|-----------|---------------------------|--------------------|
| 3.12 | 3.13 | S |
| 4.53 | 4.53 | VS |
| 3.72 | 3.74 | S |
| 6.25 | 6.29 | W |
| 2.58 | 2.27 | VW |

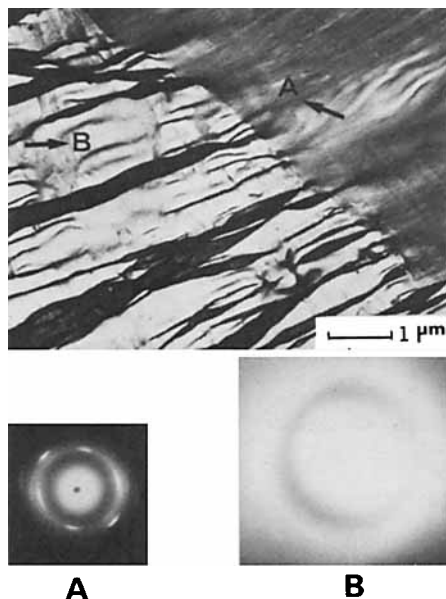


Fig. 4. Electron diffraction patterns of the 80/20 PHBA/PET copolyester from: (A) the lamellar domain and (B) the amorphous region.

The disappearance of the high temperature endotherm at 303°C (heating rate 10°C/min) on cooling or on second heating can best be interpreted as a transition from a semicrystalline state to a liquid crystalline phase. The semicrystalline phase could arise during the later stages of polymerization when the reaction is more likely heterogeneous. The irreversible nature of the transition is consistent with the tendency of the other disordered liquid crystalline structures to supercool. Since no transition is observed at higher temperatures of 330–350°C typical of the PHBA homopolymer, the possibility exists that the endotherm at 303°C is related in some way to the reversible 330°C endotherm of the crystalline PHBA. To test this hypothesis, we performed a DSC analysis of a blend of PET (20%) and PHBA (80%). It was found that the mixture showed a very distinct reversible endotherm at 333°C and that there was no tendency for the endotherm to diminish on repeated recycling. This experiment suggests that the single crystals or stacks of a few single crystals of PHBA present in the copolymer must be less than several percent in light of the absence of any detectable endotherm at 333°C. With respect to the irreversible endotherm at 303°C, it should be noted that a similar kind of behavior has been observed with the aromatic (1/2 and 2/1) copolyesters of PHBA and biphenol terephthalate (BPT). In both cases, the transitions at 430°C and 410°C, respectively, are accompanied by a sharp loss in order as measured by X-ray diffraction techniques.² Further support for the existence of a higher degree of order in the as-received copolymer was obtained from X-ray analysis. X-ray powder scans of the as-received polymer and a sample prepared by heating to 340°C showed significant line broadening and loss in peak heights consistent with loss of order. The presence of adventitious PHBA polymer single crystals in the melt becomes more evident on heating to the much higher temperature of 535°C. Thus, on prolonged heating at that temperature, the matrix degraded extensively and resembled a carbonaceous mesophase pitch in which crystals could be detected.

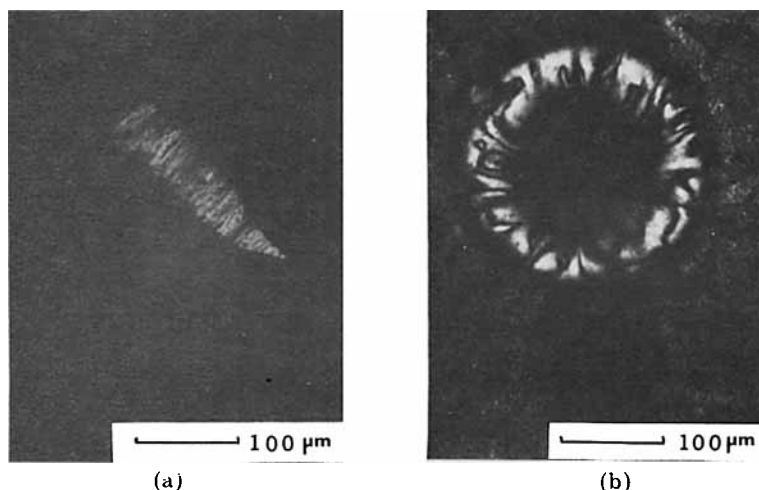


Fig. 5. 80/20 PHBA/PET copolyester at 535°C: PHBA crystal at 535°C (a) next to carbon mesophase (b).

These crystals, presumably of PHBA homopolymer, would be the only structure which could survive this temperature (Fig. 5).

CONCLUSION

Analysis of the as received copolyester of PET/PHBA 20/80 indicates the presence of two major phases, the predominant being a mesophase and the other highly crystalline. Even though diffraction analysis of the highly crystalline phase suggests a strong similarity to the homopolymer of PHBA, it is our feeling that this is a blocky PHBA copolymer with long sequences of PHBA. This is supported by the fact that this phase disappears at 328°C and it is accompanied by loss of order, as suggested from X-ray analysis. One interpretation consistent with the above data is that in the early stages of polymerization, a more random copolymer forms, but in the latter stages blocks with long sequences of PHBA tend to form because of the heterogeneous nature of the latter stages of polymerization. The presence of trace amounts of PHBA single crystals is indicated from thermal cycling to 535°C. The irreversible endotherm at 303°C must be related to a transition of the blocky structure to a mesophase resulting in what appears as a uniform mesophase. It is not clear at present as to the uniformity of this supercooled mesophase.

References

1. W. J. Jackson and H. F. Kuhfuss, *J. Polym. Sci.*, **14**, 2043 (1976).
2. W. Volksen et al., private communication.
3. F. E. McFarlane, V. A. Nicely, and T. G. Davis, *Contemporary Topics in Polymer Science*, Plenum, New York, 1977, Vol. 2, pp. 109-138.
4. J. Economy, R. S. Storm, V. I. Matkovich, S. G. Cottis, and B. E. Nowak, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2207 (1976).

Received September 11, 1981

Accepted November 10, 1981