

Studies on Co[poly(ethylene terephthalate-*p*-oxybenzoate)] Thermotropic Copolyester (III): Morphological Observation by Polarizing Microscopy

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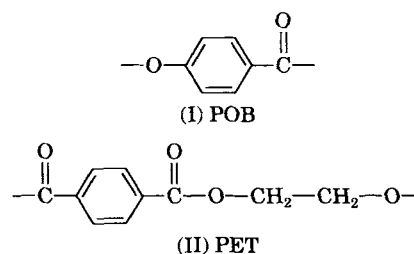
SYNOPSIS

A series of co[poly(ethylene terephthalate-*p*-oxybenzoate)] thermotropic copolyesters with various compositions were prepared by the copolymerization of either poly(ethylene terephthalate) (PET) polymer or its oligomer as moiety (I) and *p*-acetoxybenzoic acid as moiety (II). A detailed description of the crystalline morphology of copolyesters with different compositions as well as under different preparation temperatures is discussed by using a polarized optical micrograph. It is found that the *p*-oxybenzoate (POB)/PET copolyesters with the POB moiety content above 60 mol % were shown to be highly anisotropic. It is also believed that the copolyester made from the PET oligomer (OET) as moiety (II) has shorter repeating units than that of the copolyester made from PET polymer (PET) in the main-chain structure. The solid-state polymerization may cause the randomization of two units due to a transesterification reaction that is examined by NMR spectroscopy analysis. Using the micrographs with different compositions, parallels between before and after the solid-state polymerization are contrasted. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

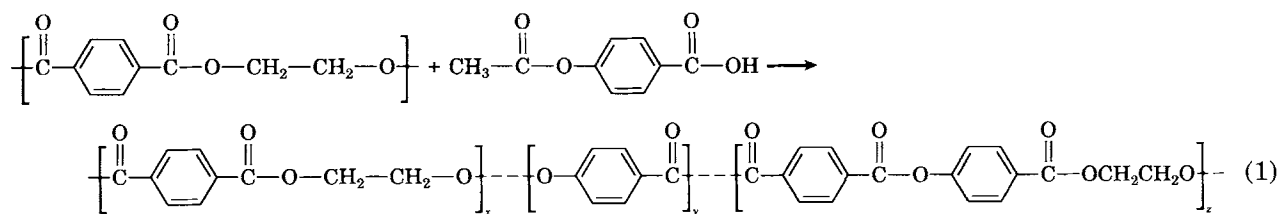
In the last two decades, a new class of thermotropic polymeric material known as liquid crystalline polymers (LCPs) has been developed that received a great attention from both industry and academia.¹ Most of the stiff-chain aromatic polymers that are used as high-strength-high-modulus materials exhibit liquid crystalline behavior. For practical purposes, there is a need for a nematic mesophase at relatively low temperature in regard to processing. A thermotropic aromatic aliphatic copolyester by the polycondensation of *p*-acetoxybenzoic acid

(PAB) and poly(ethylene terephthalate) (PET) has been developed by Tennessee Eastman Co.²⁻⁴ The chemical structure of the kind of *p*-oxybenzoate (POB)/PET copolyesters consists of the following two moieties:



This modification by reacting PET with *p*-acetoxybenzoic acid may proceed according to the following equation:

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Copolyesters thus obtained consist of PPOB, PET, and POB/PET units in the main-chain structure. The POB/PET unit is raised up by the transesterification reaction between POB and PET moieties. We have synthesized this kind of POB/PET copolyesters by using PET having a molecular weight of ca. 20,000 as well as its oligomer having a molecular weight of ca. 2,000 as moiety (II) and have intensively discussed it through thermogravimetric and X-ray diffraction analysis in our previous papers.^{5,6} Zachariades et al. of the IBM Research Laboratory reported a morphological study of the kind of POB/PET copolyester having 80 mol % of POB units⁷ by using optical and electron microscopy. In this paper, we investigated the morphology of the POB/PET copolyester having various POB/PET compositions by using an optical micrograph.

EXPERIMENTAL

Materials

Copolyesters having various POB/PET compositions have been synthesized according to the procedure reported in our previous papers.^{5,6} The Eastman 10109 examined in this study was a commercial thermotropic liquid crystalline copolyester produced by Tennessee Eastman Co.

Method

The morphology of the copolyester was studied with a Zeiss polarized optical microscope (III). The sample was prepared by heating a piece of glass plate, 1 × 2 cm in size, at the temperature 200–350°C, and then pressing the melts with another piece of hot glass plate, so that it was formed into a sandwich, keeping the thin film inside. The sandwich was then rapidly quenched by pouring liquid nitrogen on top of the preparation. The photographs of the films were taken at room temperature under the polarizing microscope with incident polarizing light at 90° (magnification ×320).

In a sequence distribution study using high-field NMR spectra,⁸ 1–5 wt % solutions of the polymer

in deuteriated trifluoroacetic acid were made. With the exception of POB/PET = 80/20, all the solutions were clear and the polymer remained in solution. In this study, the spectra were obtained by using a Varian Unity-300 NMR spectrometer operating at 300 MHz for observing protons.

Code

The codes for each sample examined in this paper are listed in Table I.

RESULTS AND DISCUSSION

Composition Effect

The texture of the film objectives was examined by a polarizing microscope. Figure 1 shows the patterns of PET, OET, PPOB, and Eastman 10109, respectively. It is obvious that the textures of PET and OET indicate the conventional lamellar crystalline. As shown in Figure 1(1) and (2), the typical spherulites are observed. These spherulites are composed of aggregates of lamellar crystals that are radially oriented. However, these are not thermotropic. X-ray diffraction has shown that the crystallinity of OET (25%) is larger than that of PET (17%), as reported in our previous paper.⁶ In fact, the spherulite of OET is seen larger and was much distinguished between cross polaroids. The Eastman product [Fig. 1(4)], in contrast, indicates a typical

Table I Codes of Copolyesters Characterized

POB/PET	Moiety	
	PET Oligomer	PET Polymer
0/100	OET	PET
20/80	O28	P28
40/60	O46	P46
60/40	O64	P64
80/20	O82	P82
100/0		PPOB
Eastman		EAS
PAB		PAB

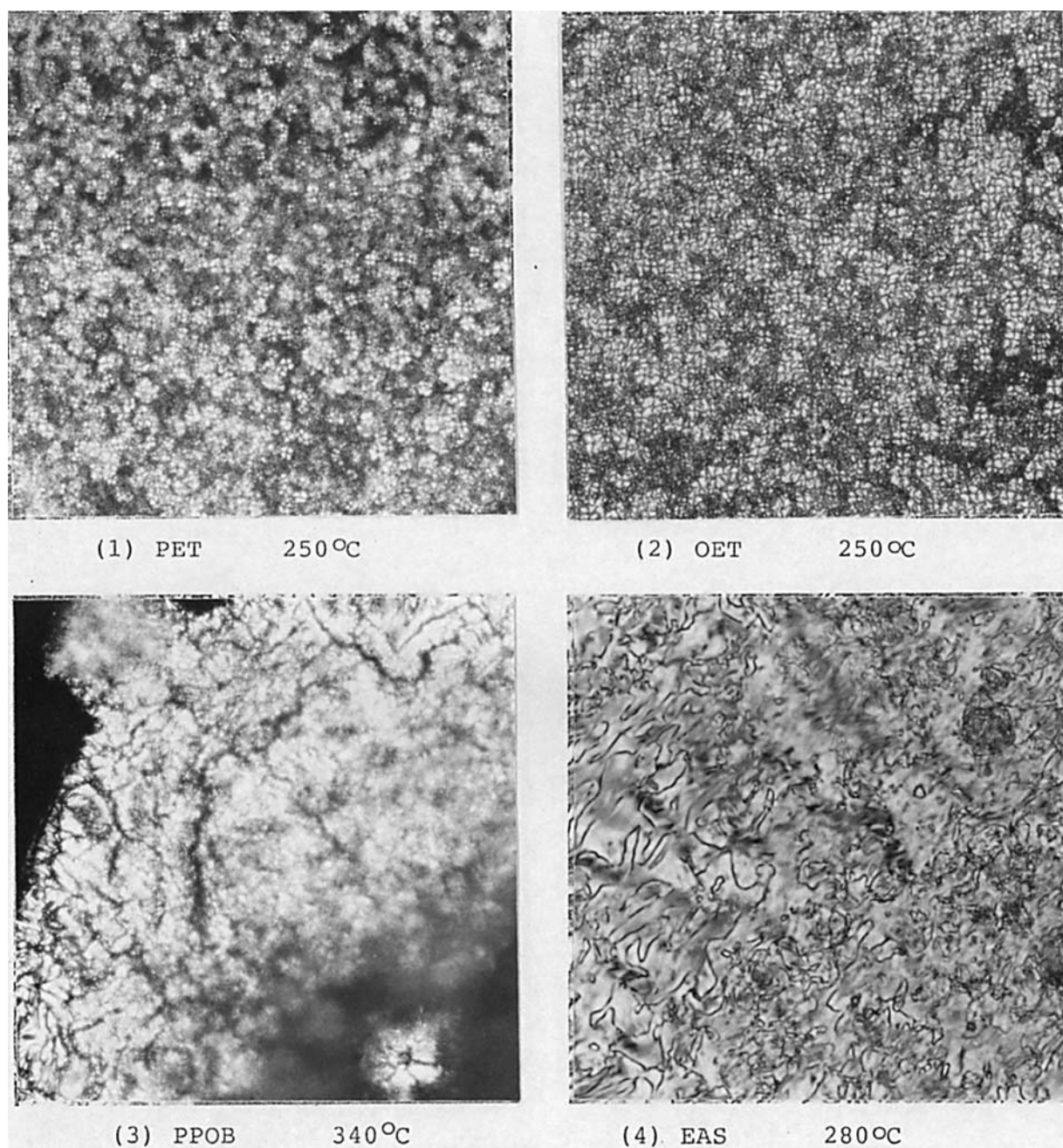


Figure 1 Melt morphology (cross polaroids, $\times 320$): (1) PET; (2) OET; (3) PPOB; (4) EAS.

liquid crystal pattern of colored streak textures that are consistent with the anisotropic mesomorphic phases. On the other hand, for PPOB, the pattern still contains the rigid aggregates of liquid crystalline even prepared under an elevated temperature at 340°C. The structure of PPOB, which exhibits a high melting point at ca. 336°C as reported in the literature,⁹ has long segments of mesogenic units without flexible spacers.

In Figure 2(a) and (b), the parallels of patterns before and after the solid-state polymerization for different POB/PET compositions are shown. For P28, O28, P46, and O46 [see Fig. 2(a)(1)–(4) and (b)(1)–(4)], it is seen that the isotropic crystalline texture becomes obscure [compare with the PET or OET texture in Fig. 1(1) and (2)] but is best appreciated by the appearance of fine mesomorphic domains of anisotropic phases. These domains col-

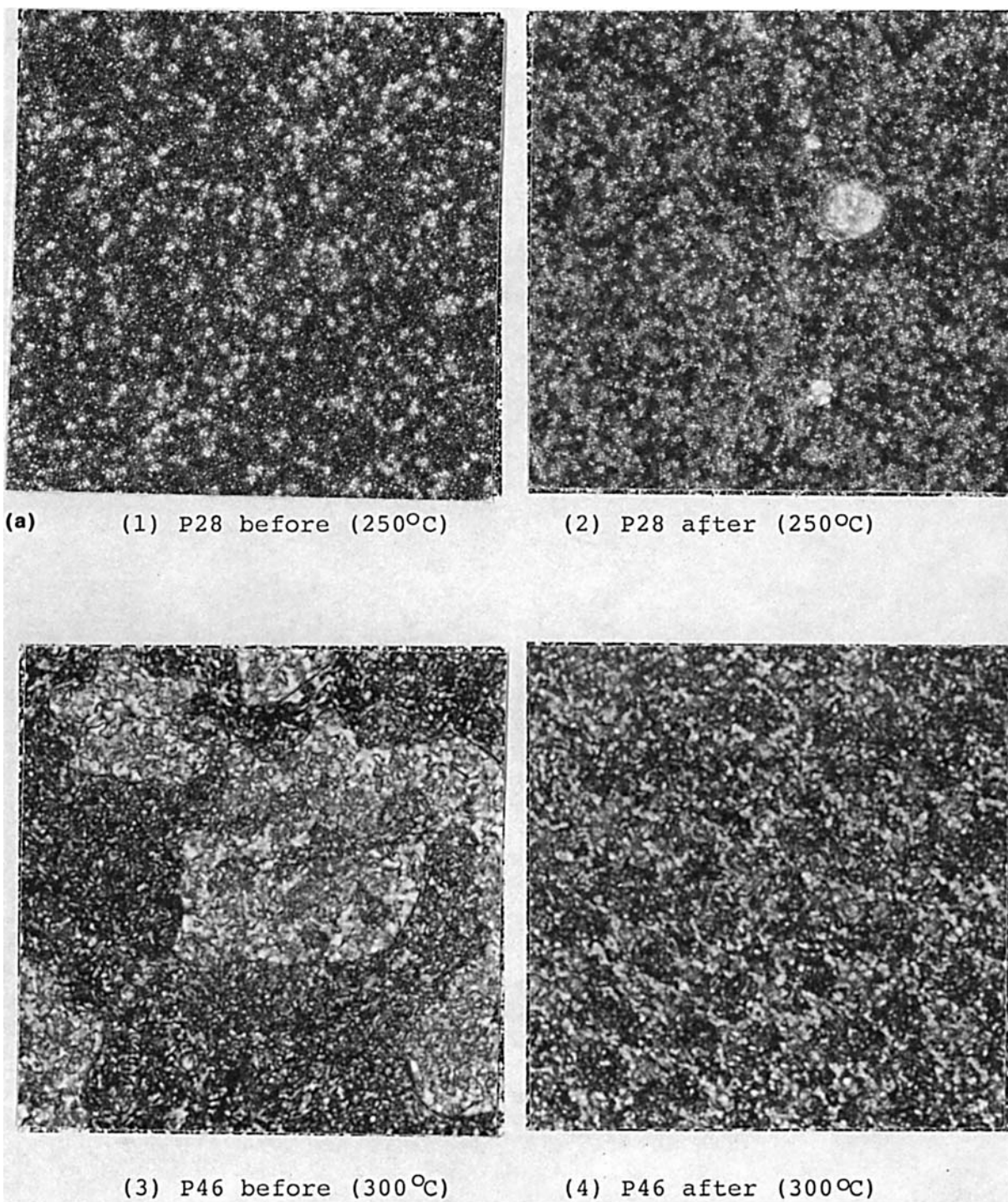
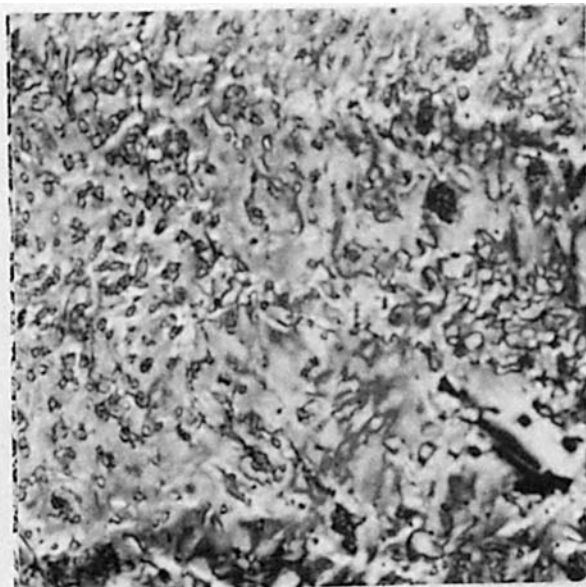


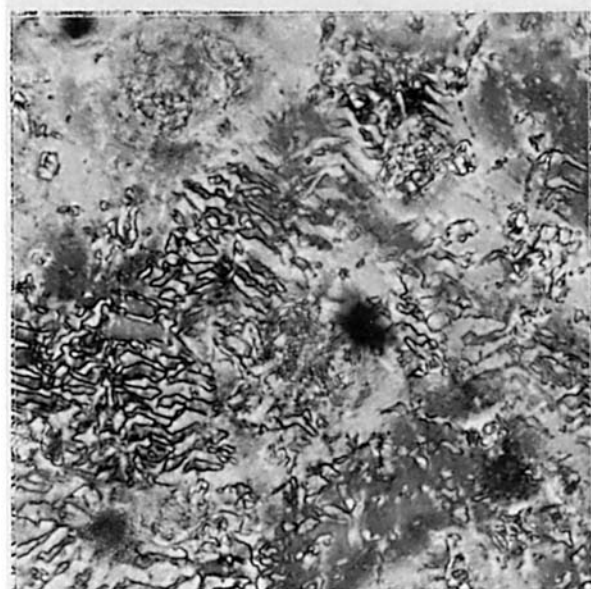
Figure 2 (a) Effects of composition and solid-state polymerization on morphology of POB/PET copolyesters: (1) P28 before; (2) P28 after; (3) P46 before; (4) P46 after; (5) P64 before; (6) P64 after; (7) P82 before; (8) P82 after. (b) Effects of composition and solid-state polymerization on morphology of POB/PET copolyesters: (1) O28 before; (2) O28 after; (3) O46 before; (4) O46 after; (5) O64 before; (6) O64 after; (7) O82 before; (8) O82 after.



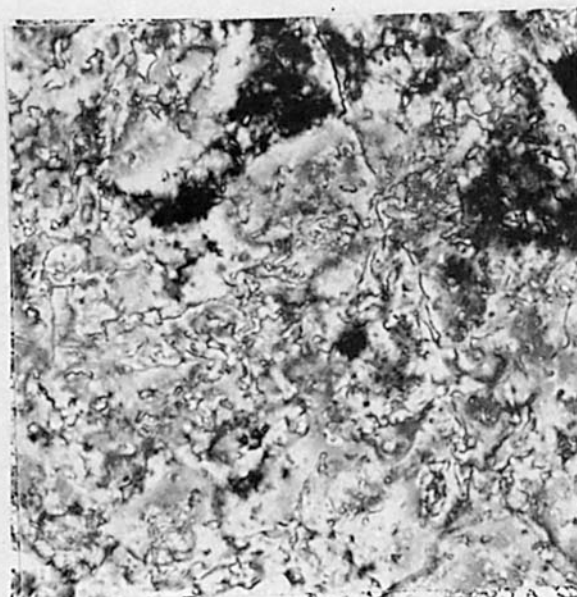
(5) P64 before (300°C)



(6) P64 after (300°C)



(7) P82 before (300°C)



(8) P82 after (300°C)

Figure 2(a) (Continued from the previous page)

ored under birefringence to distinguish between isotropic and anisotropic phases. In general, after solid-state polymerization, the anisotropic phase becomes more precise and dispersed among the matrix.

For P46 and O46, the patterns show an increase in anisotropic phases, yet keep isotropic and aniso-

tropic biphases. Moreover, the isolated larger anisotropic phases appeared especially in the case of P46 [see Fig. 2(a)(3)]. The anisotropic phase is finer and dispersed, however, in the case of O46 [see Fig. 2(b)(3)]. The structure of the copolyester made from OET might be more random with POB and

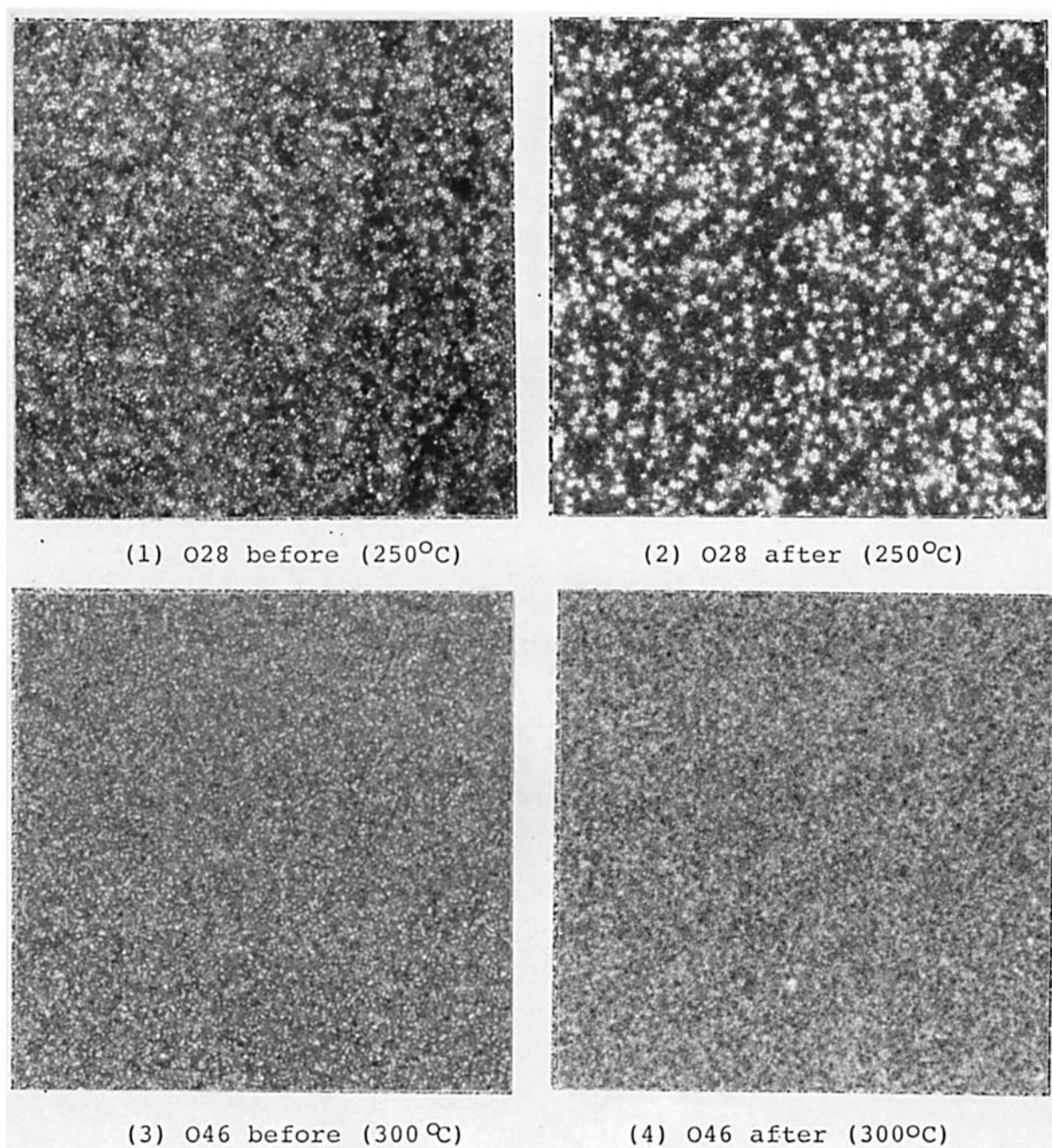


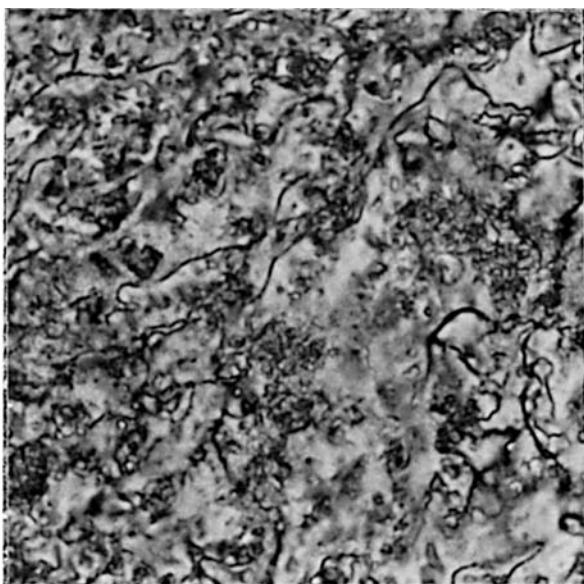
Figure 2 (b) (Continued from the previous page)

PET moieties than that made from PET in this composition.

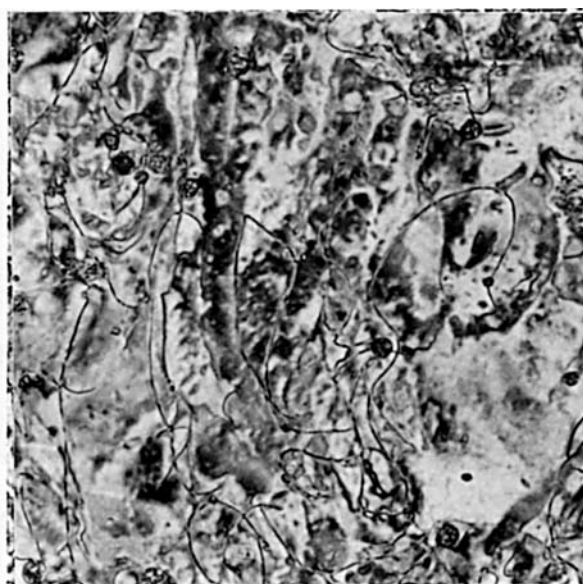
For P64 and O64, the patterns now show the typical threaded texture, which is consistent with a nematic phase [see Fig. 2(a)(5) and (6) and (b)(5) and (6)].

For P82 and O82, the patterns also show strong liquid crystalline structural constitutions. The substantially rigid polymer molecule of POB moiety

with a sufficient addition of flexible polymer molecules of PET moiety is believed to be thermotropic with the nematic mesophase under appropriate temperature. At these compositions, solid-state polymerization causes the randomness of POB/PET units by the effect of transesterification between POB and PET units. These phenomena can be explained by NMR spectroscopy as shown in the last section of this paper. As a result, the structure of



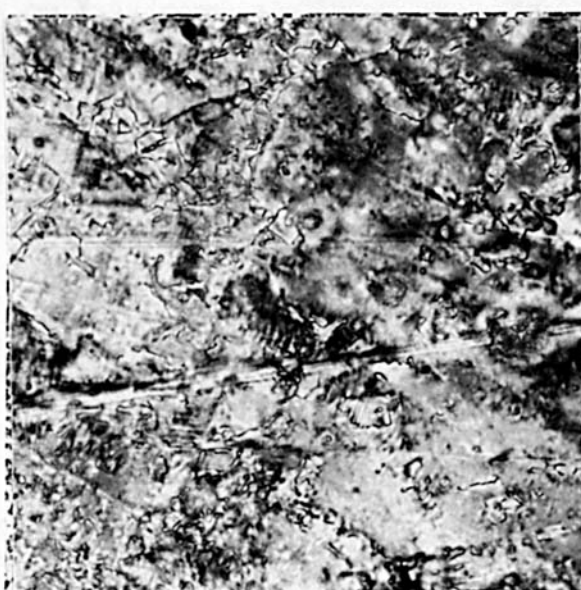
(5) O64 before (300°C)



(6) O64 after (300°C)



(7) O82 before (300°C)



(8) O82 after (300°C)

Figure 2 (b) (Continued from the previous page)

the copolyester that is obtained by more PET spacers in the rigid POB segments shows more birefringence. In general, the copolyester made from OET seems to be relatively uniform compared with the copolyester made from PET, because OET has originally a smaller chain length than that of PET.

Temperature Effect

The morphology of copolyesters depends on the temperature of preparation at which the sample was quenched. Figure 3 shows the temperature effect on the optical micrograph for EAS, whereas Figures 4

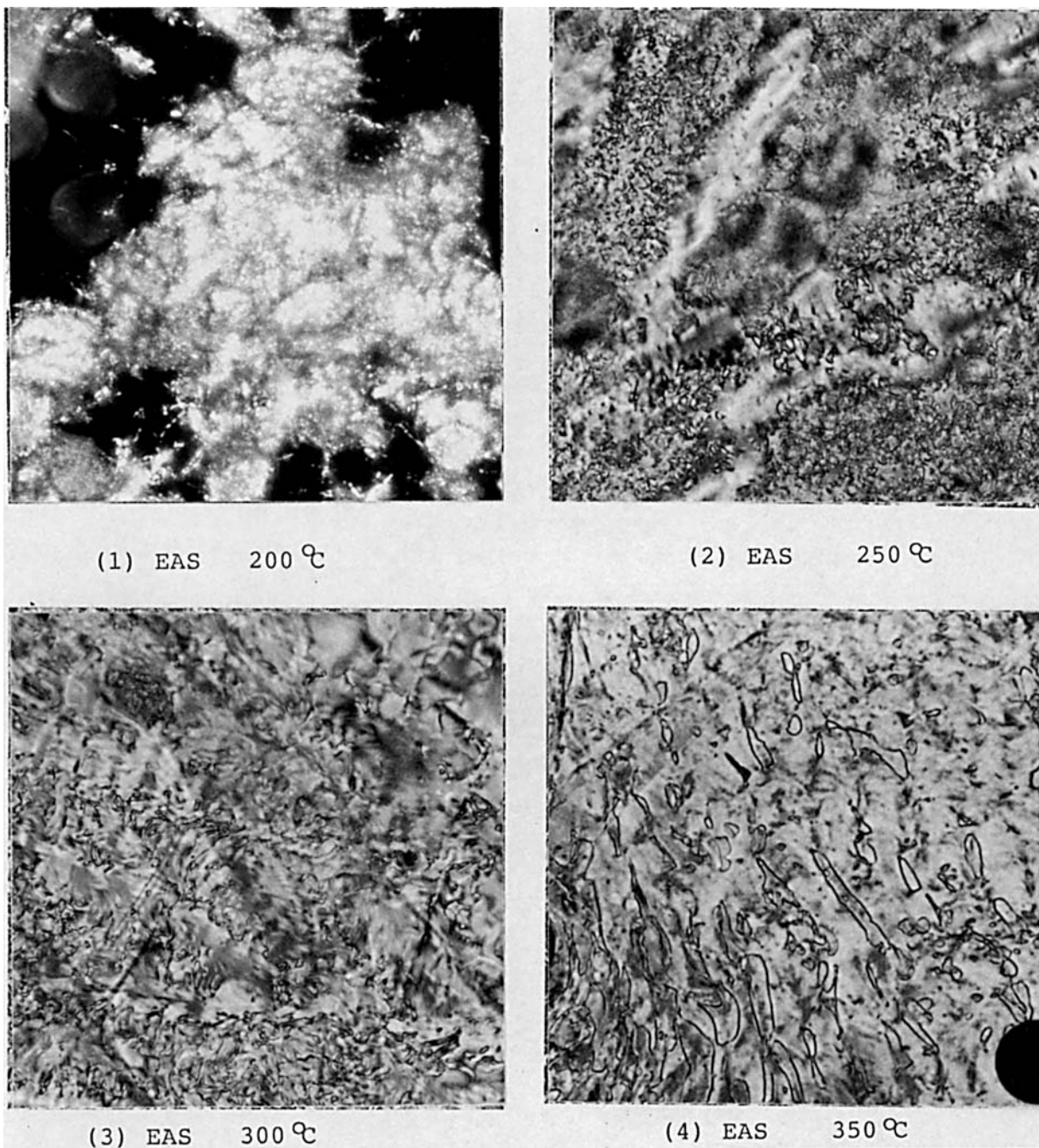


Figure 3 Temperature effect on morphology of EAS cross-polaroids: (1) 200°C; (2) 250°C; (3) 300°C; (4) 350°C.

and 5 show P82 and O82 before and after 4 h solid-state polymerization, respectively. At elevated temperature, evidence of fluidity can be seen and the polymer sample between the glass plates gives rise to an anisotropic fluid that exhibits a typical threaded texture. As temperature increases, the textures of these threads become more obvious and

most of them form closed loops, as illustrated in Figures 3-5. After solid-state polymerization, the structure of threads has a strong tendency to shrink in length and to become finer under the same temperature. If we compare P82 with O82, the texture of O82 prepared at 250°C after solid-state polymerization [i.e., Fig. 4(2)'] shows more characteristics

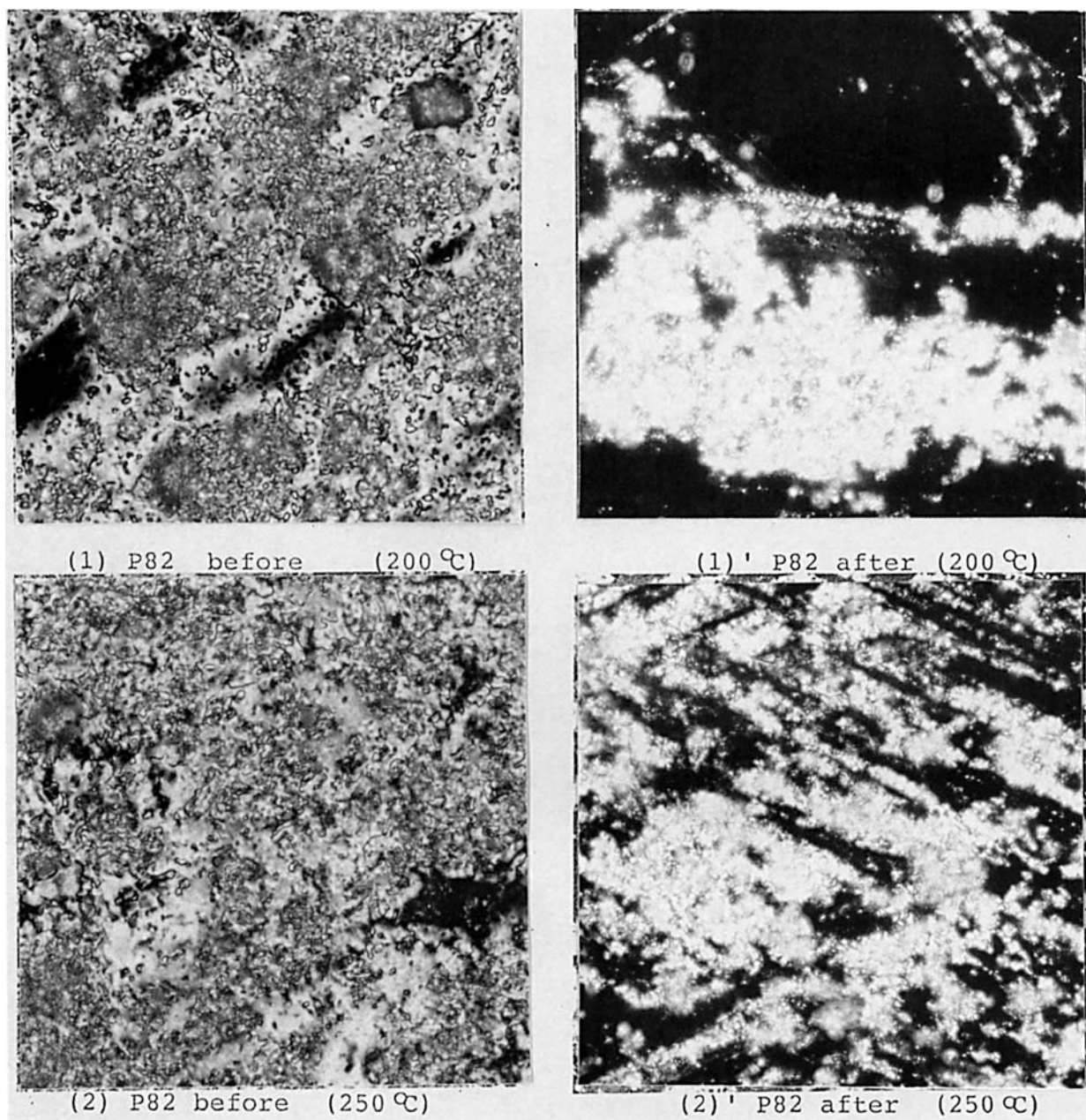


Figure 4 Effect of temperature on morphology of P82 before and after solid-state polymerization: (1) 200°C, before; (1)' 200°C, after; (2) 250°C, before; (2)' 250°C, after; (3) 300°C, before; (3)' 300°C, after; (4) 350°C, before; (4)' 350°C, after.

of birefringence than that of P82 [i.e., Fig. 5(2)'], probably because of its lower softening temperature.

Sequence Distribution Measurements

Nicely et al. studied the sequence distribution of the copolyesters made from PET and PHB by NMR spectroscopy.⁸ Spectra of these types provide direct

measures of the probability of a PHB unit being bonded to another PHB or to a PET unit. Figure 6 shows the proton NMR spectrum at 300 MHz with the assignments of the absorptions for O64 (a) before and (b) after 4 h solid-state polymerizations. The ratio of the peak lengths of the -POB-PET-bond to the -POB-POB-bond is 1.24 for O64 before solid-state polymerization, whereas the ratio is 1.32

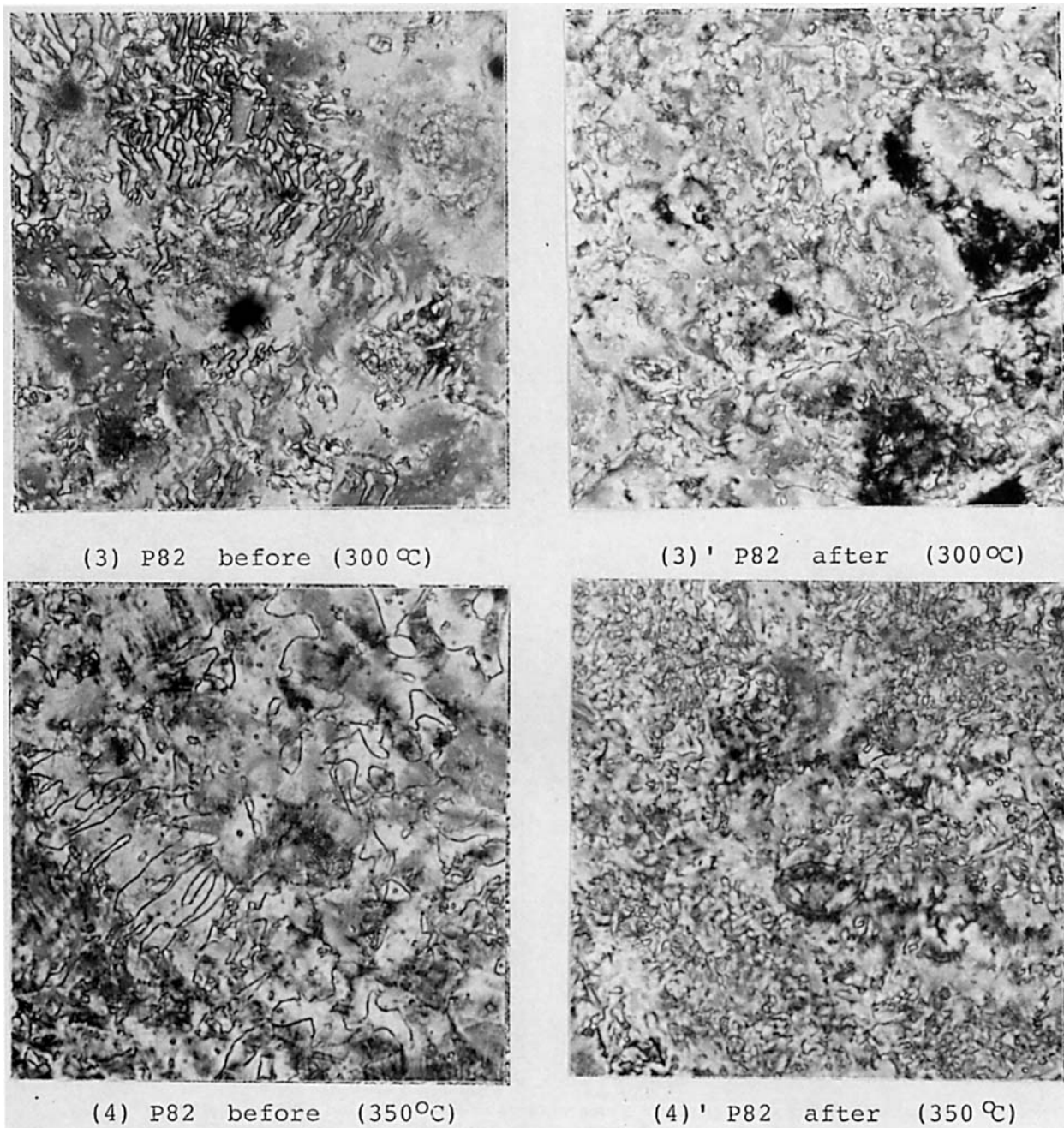


Figure 4 (Continued from the previous page)

for O64 after solid-state polymerization. This means that the random sequence distribution becomes more noticeable due to evidence of transesterification during solid-state polymerization. In other words, the copolyester has shorter sequences of POB units in the structure due to frequent transesterification reactions during the solid-state polymerization.

CONCLUSION

Observation by an optical microscope of the copolyester based on poly(ethylene terephthalate) and *p*-oxybenzoate shows that the copolyester under investigation dominates within the normal isotropic crystallines in the main matrix when the composition of POB/PET is below 60/40 and in the nematic

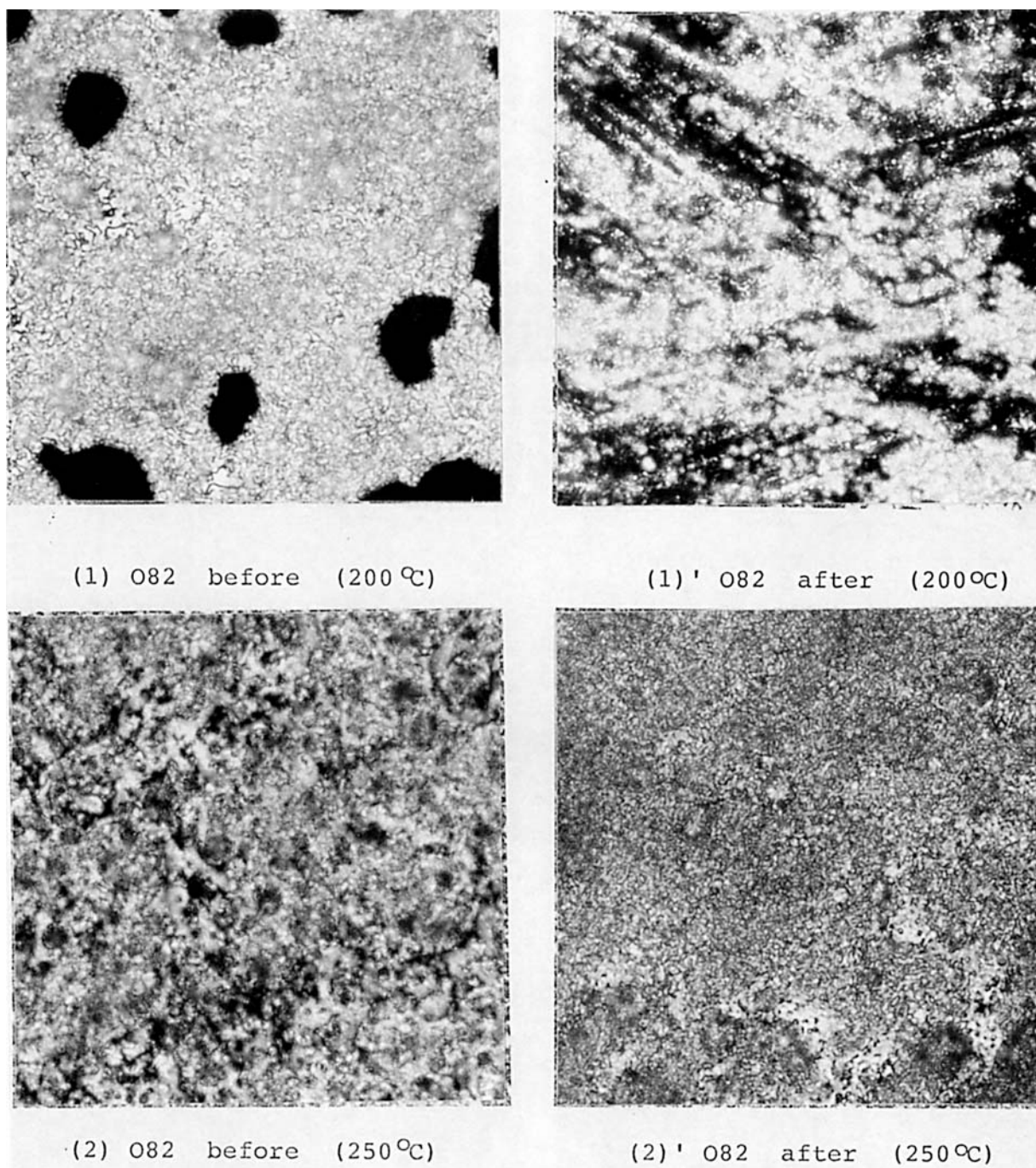
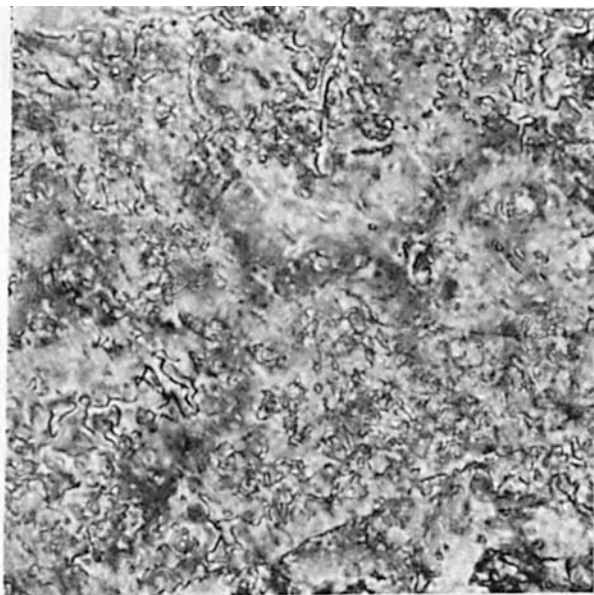


Figure 5 Effect of temperature on morphology of O82 before and after solid-state polymerization: (1) 200°C, before; (1)' 200°C, after; (2) 250°C, before; (2)' 250°C, after; (3) 300°C, before; (3)' 300°C, after; (4) 350°C, before; (4)' 350°C, after.

state of liquid crystallines when the composition of POB/PET is above 60/40. In general, solid-state polymerization of the copolyester causes the randomness in the sequences of two moiety units due to the transesterification reaction. Consequently, the

thread structures become finer in size, as illustrated in the micrograph. Moreover, the copolyester made from OET is more random in structure with two moiety units, illustrating the finer threads of the nematic phase compared with the corresponding co-



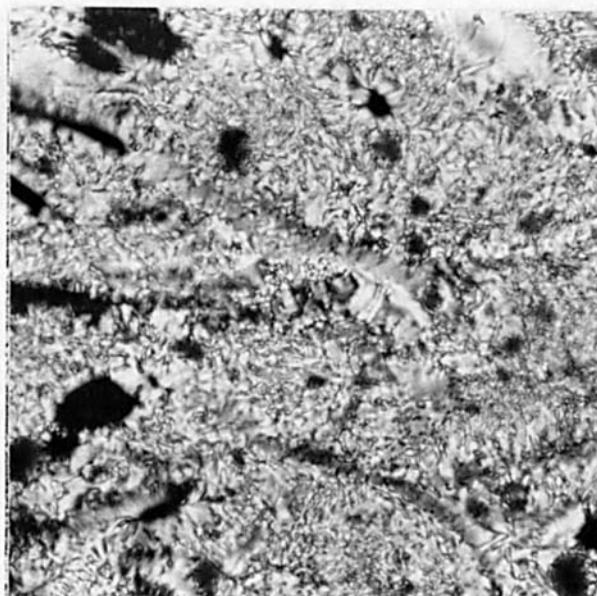
(3) 082 before (300°C)



(3)' 082 after (300°C)



(4) 082 before (350°C)



(4)' 082 after (350°C)

Figure 5 (Continued from the previous page)

polyester made from PET. These finer-threaded nematic phases appeared only at elevated temperature preparation. It is concluded that depending upon composition, temperature of sample preparation,

solid-state polymerization, and source of the PET moiety the series under study shows a complex pattern of crystalline behavior under the polarizing microscope.

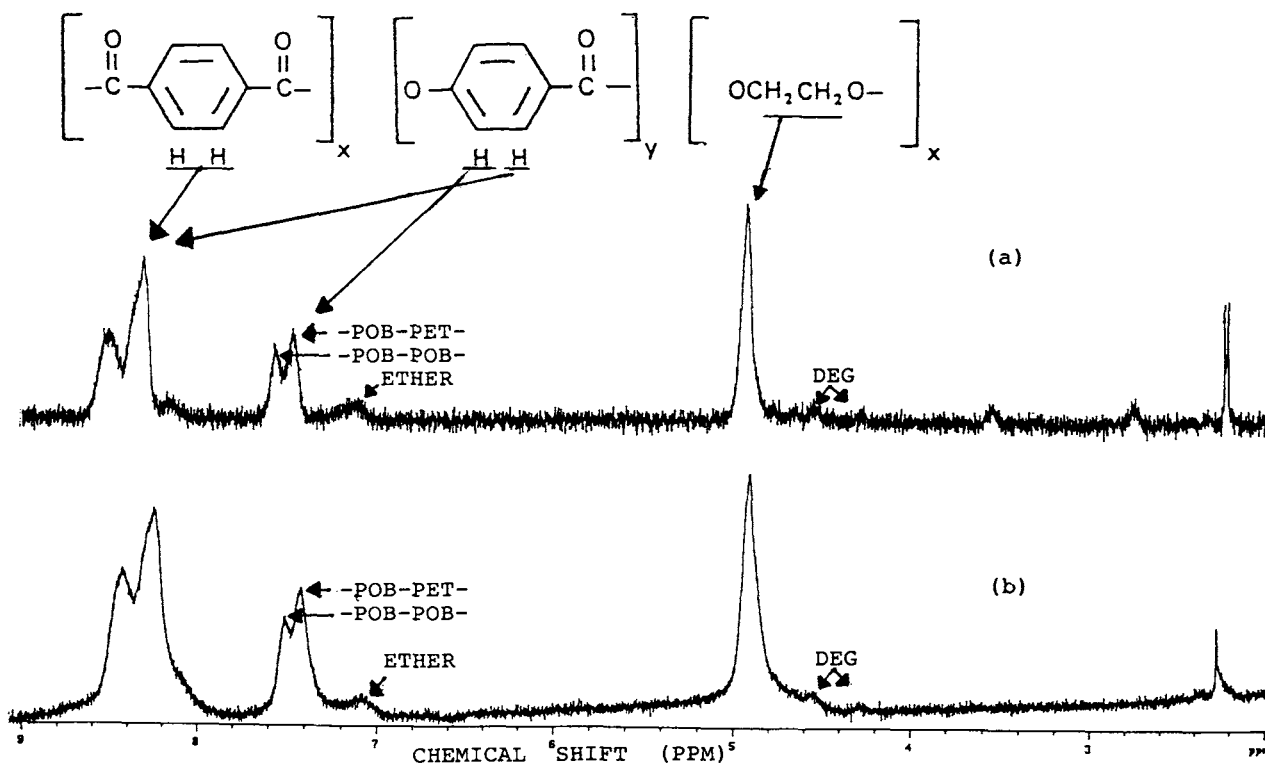


Figure 6 Proton NMR spectrum at 300 MHz with the assignments of the absorptions for O64 dissolved in trifluoroacetic acid: (a) before solid-state polymerization; (b) after 4 h solid-state polymerization.

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