Communications to the Editor

Crystal Phase Transition of Poly(tetramethylene terephthalate) Crystallites in Copolymers with 4,4′-Isopropylidene-bis[(2,6-dibromophenoxy)-ethoxy-2-ethanol]

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Introduction. In a previous paper,[1] an investigation of copolymers of poly(tetramethylene terephthalate) (PTMT) with poly(tetramethyleneglycol) (PTMG) showed that a certain amount of stress is necessary to strain α crystallites of PTMT in the copolymer enough to induce a transition to the β phase. This stress was more readily transferred from the external applied stress for a system with a high modulus than for a system with a relatively low amorphous modulus. The transition between the α and β crystal phases was observed around 800 kg/cm^2 in tensile stress with various copolymers. The transition was not observed in PTMG-rich copolymers in which the amorphous region was too soft to bear this level of tensile stress. The PTMG−PTMT copolymers were used because the tensile modulus varies with PTMG content but contain α crystallites as in the pure PTMT homopolymer. Although copolymerization usually decreases the crystallinity, this fact had little effect on the crystal structure of the crystals.

In this paper PTMT copolymers with 4,4′-isopropylidene-bis[(2,6-dibromophenoxy)ethoxy-2-ethanol] (TBA-EO) were studied to confirm that a high amorphous modulus is necessary to induce the phase change. TBA-EO/PTMT copolymers show comparative tensile strength and tensile modulus to the PTMT homopolymer. However, their crystallinity is lower.[2] If the TBA-EO/PTMT copolymers show an α to β crystalline phase transition similar to the PTMT homopolymer, then it is the amorphous modulus, not crystallinity, that plays the predominant role in the crystalline phase transition of the fibers.

Experimental Section. *Materials.* The PTMT homopolymer and TBA-EO/PTMT copolymers were kindly supplied by Mr. T. Sugita and Mr. T. Katsuura of Mitsubishi Chemical Corp. The preparation of copolymer 1 and copolymer 2 is described by Sugita et al.[3] The comonomer content and the intrinsic viscosity supplied with these samples are compiled in Table 1. The intrinsic viscosity was measured by an Ubbelohde viscometer at 30 °C, using 1,1,2,2-tetrachloroethane and phenol (1 + 1 in weight) as the solvent.

Table 1. Properties of Sample Fibers

sample	TBA-EO content, mol %	Br content, wt %	intrinsic viscosity	sonic modulus, GPa	T_m, °C	H_f, J/g	crystallinity (%)
PTMT homopolymer	0	0	1.40	5.3	229	60.3	42
copolymer 1	4.1	6	0.83	8.6	215	55.2	38
copolymer 2	8.2	12	0.83	6.7	200	36.8	25

Sample Preparation. Sample fibers were prepared according to the method described in the previous paper.[1] The fibers were extruded and stretched 275% to orient and then annealed to crystallize them. An annealing temperature of 200 °C for copolymer 1 and 170 °C for copolymer 2 was utilized. The annealingtemperature was determined relative to the melting point of the copolymers. The annealing time was 20 h under vacuum. The sample fibers were about 1 mm in diameter.

DSC Measurement. A Perkin-Elmer DSC-4 system was used for the measurement of thermal properties. The measurement range was from −15 to 260 °C. The heating rate during measurement was 20 °C/min. About 10 mg of the oriented and annealed fiber was cut and weighted and then sealed in an aluminum pan. The crystallinity of the samples was calculated from the heat of fusion. A heat of fusion of 7.6 kcal/mol (145 J/g) for the PTMT crystal was assumed for the calculation.[4] The normalized crystallinity as homopolymer was calculated according to the copolymer content supplied with the samples.

X-ray Diffraction. Wide-angle X-ray diffraction (WAXS) and the indexing of fiber patterns were performed according to the method described in the previous paper.[1] A toroid camera was used to photograph wide-angle X-ray diffraction patterns using nickel-filtered Cu Kα line radiation (wavelength = 0.154 18 nm).

Mechanical Property. The sonic modulus of sample fibers was measured with an H.M. Morgan Co. Inc. PPM-5R dynamic modulus tester equipped with fiber scanner. A weight of 200 g was applied to exert tension on a sample fiber during measurement. It was measured at an ambient condition of 23 °C and a relative humidity of 50%

Results and Discussion. Results of DSC measurements, crystallinity, and sonic modulus of the sample fibers are compiled in Table 1. Generally crystallinity decreased with increased molar amount of comonomers. The crystallinity that was calculated from the results of the DSC measurement showed the same tendency. Copolymer 2, which contains 8.2 mol % TBA-EO, showed the lowest crystallinity among the sample fibers. Copolymer 1 and copolymer 2 each had a higher sonic modulus than the PTMT homopolymer. This is the effect of the comonomer location in the amorphous phase. The higher modulus of the copolymer samples should support greater stress on the PTMT crystallites embedded

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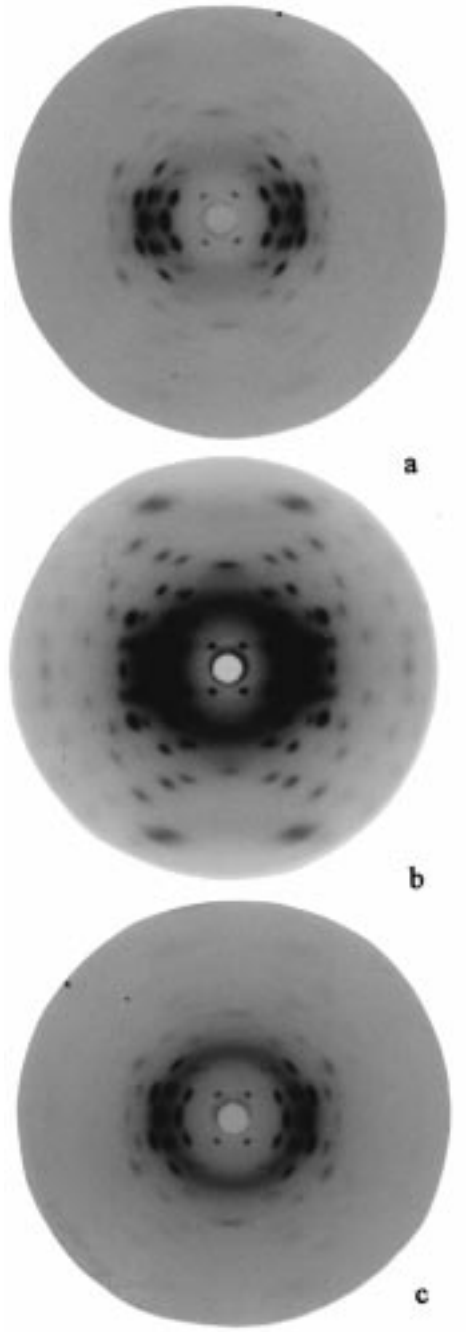

Figure 1. WAXS fiber patterns of PTMT homopolymer (a), copolymer 1 (b), and copolymer 2 (c) without tensile strain.

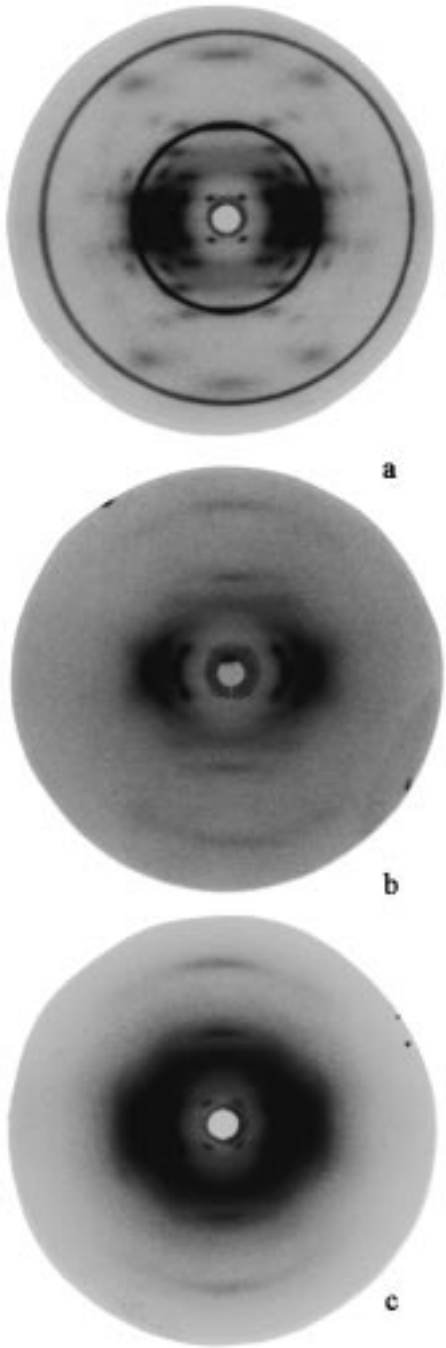

Figure 2. WAXS fiber patterns of PTMT homopolymer strained 30% with CaF_2 (a), copolymer 1 strained 30% (b), and copolymer 2 strained 40% (c).

in the amorphous region of their fibers, resulting in higher strain. Stretching and annealing doubled the sonic modulus of the PTMT homopolymer fiber. The extruded fiber of the PTMT homopolymer showed a sonic modulus of 2.4 GPa, which is similar to the flexural modulus of the bulk sample.[2]

The fiber diffraction pattern of the PTMT homopolymer without tensile strain is shown in Figure 1a. Fiber diffraction patterns of copolymers 1 and 2 without tensile strain are shown in Figure 1b,c. The α crystal structure was observed in both the PTMT homopolymer and PTMT copolymers without tension. Reflections that were assigned to the α phase of the PTMT homopolymer were observed at identical positions on the fiber diffraction patterns of PTMT copolymers. Copolymers 1 and 2 showed stronger amorphous background scatter. This is caused by lower crystallinity and the presence of heavy bromine atoms in the amorphous region of the copolymer samples. The effect is more apparent with copolymer 2. The apparently lower crystallinity of copolymer 2 in Figure 1c agrees with the results of DSC measurements. Since the crystal structures are the same in the PTMT homopolymer, the comonomer should exist primarily in the amorphous regions of the sample fibers. Therefore, heavy bromine atoms scattered X-rays more effectively and made the amorphous scattering much stronger. These effects were more apparent in copolymer 2, which contain 2 times more bromine than copolymer 1. This observation supports this interpretation. Noticeably more reflections on higher layer lines were observed with Figure 1b than in Figure 1a,c due to stronger exposure of X-rays. According to DSC measurement, copolymer 1 is a bit lower in crystallinity

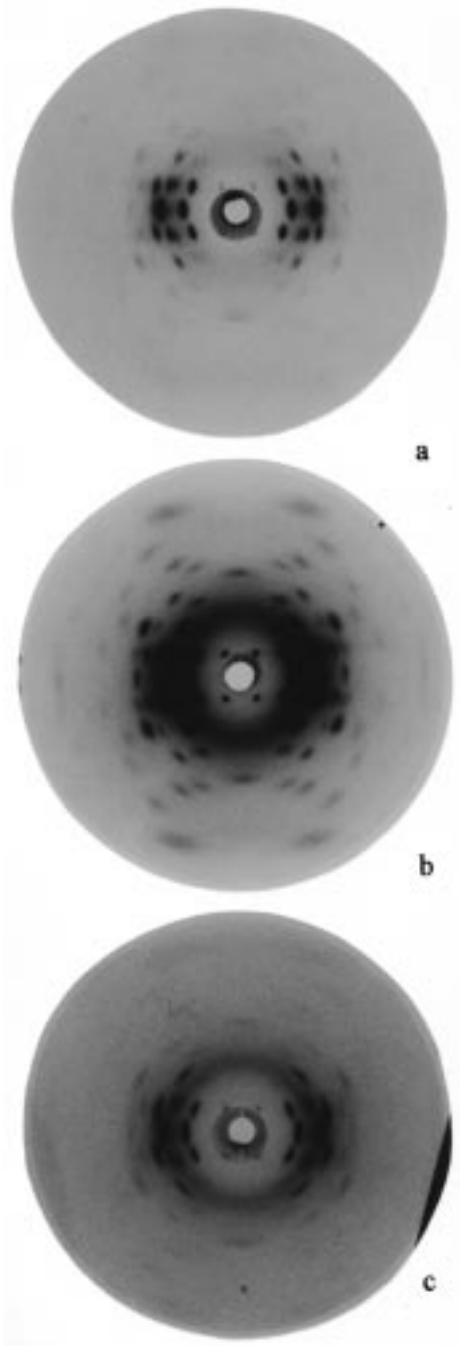

Figure 3. WAXS fiber patterns of PTMT homopolymer (a), copolymer 1 (b), and copolymer 2 (c) strained 30−40% and released.

than the PTMT homopolymer. However, it is still crystalline enough to show higher layer lines when exposed to X-rays for a long time.

Strained fiber diffraction patterns of the PTMT homopolymer, copolymer 1, and copolymer 2 are shown in Figure 2a−c. Fibers of the PTMT homopolymer and copolymer 1 were strained 30%. Fibers of copolymer 2 were strained 40%. These three patterns all show β crystal structure. This result suggests that the stress on the PTMT crystallites is dictated by the overall tensile modulus and not the crystallinity of the sample fibers.

Strained and released fiber diffraction patterns of the PTMT homopolymer, copolymer 1, and copolymer 2 are shown in Figure 3a−c. These three patterns show α

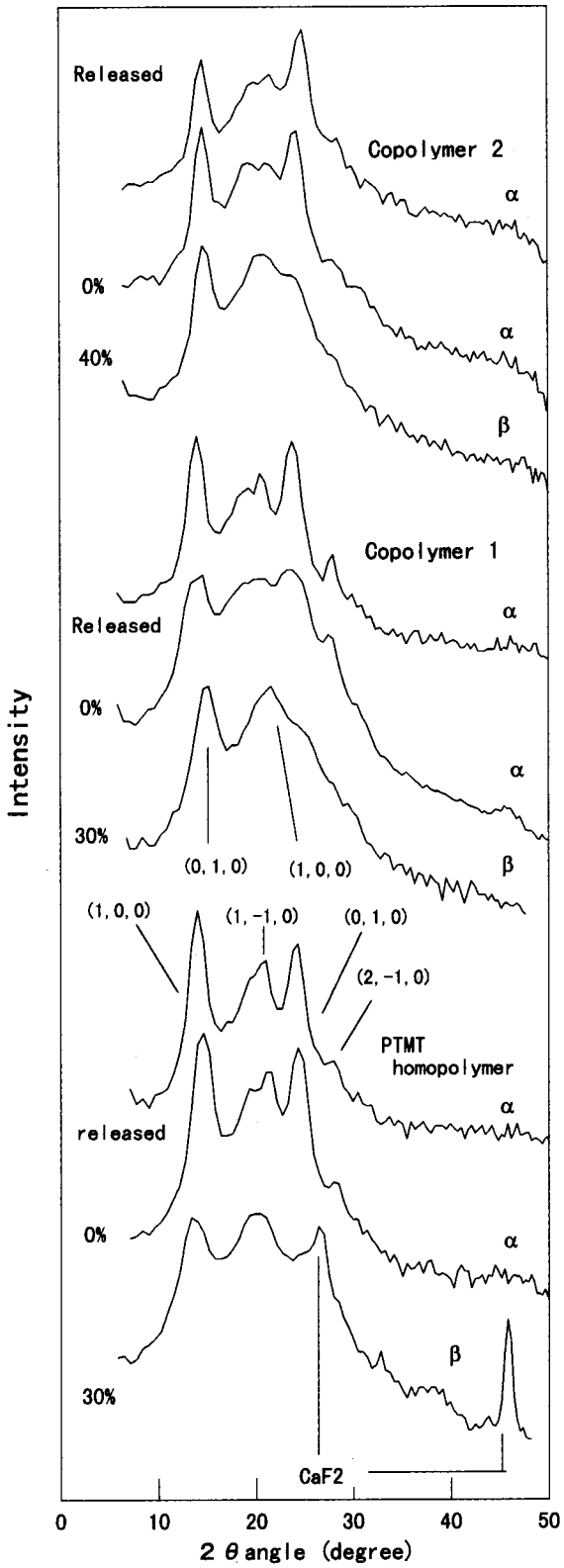

Figure 4. Intensity data on equatorial line.

crystal structure. The copolymer 1 and copolymer 2 showed a reversible crystalline phase transition similar to the PTMT homopolymer. Higher layer lines were observed with copolymer 1 in Figure 3b. It is also the result of longer exposure time and relatively high crystallinity of copolymer 2.

Figure 4 shows a comparison of intensity data on the equatorial line (zeroth layer line). A (1,−1,0) reflection of the α phase was observed in sample fibers without

strain and strained samples after release of the stress. These six samples are in the α phase. The (1,−1,0) reflection is not observed in the β phase. It was not observed in strained sample fibers. These three samples are in the β phase. These assignments agree with the appearance of other reflections on the first (2,−1,0) and fourth layer lines.[1,5,6] Also, positions of the (1,0,0) and (0,1,0) reflection of α crystallites and the (0,1,0) and (1,0,0) reflection of β crystallites support this assignment.

Conclusion. TBA-EO/PTMT copolymers contain the same PTMT crystallites as the PTMT homopolymer. The α to β crystal phase transition of PTMT crystallites is observed in TBA-EO/PTMT copolymers under strain. These copolymers have lower crystallinity and a modulus similar to the PTMT homopolymer. The result supports the idea that a level of tensile strength in amorphous region is necessary to ensure enough stress on PTMT crystallites to induce the crystal phase transition.

References and Notes

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