

SHORT COMMUNICATIONS

Crystal Modification in Poly(ethylene succinate)

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(Received July 13, 1995)

KEY WORDS Poly(ethylene succinate) / Crystal Structure / Crystal
Modification / X-Ray Diffraction /

Mechanical properties of crystalline polymers, in general, depend strongly on their crystal structures as well as on the crystallinity and orientation of the polymers¹. Crystal structures can be controlled by pressure, temperature, and strain. Strain induced crystal modifications have been reported in some polyesters and polyethers, such as in poly(butylene terephthalate) (PBT)²⁻¹⁰ and poly(ethylene oxide) (PEO)¹¹ as well as in poly(oxacyclobutane) (POCB).¹² In addition, the authors have recently discovered a new crystal modification in poly(tetramethylene succinate) (PTMS),^{13,14} which is a biodegradable aliphatic polyester. In these cases, the conformation changes from *gauche* to *trans* in the $(\text{CH}_2)_x\text{O}$ unit ($x=2, 3, \text{ and } 4$) cause such crystal modifications, which result in a change of mechanical characteristics. Chatani *et al.* have determined the skeletal conformation of poly(ethylene succinate) (PES) to be $T_3GT_3\bar{G}$, where *T*, *G*, and \bar{G} denote *trans*, *gauche*, and *minus gauche*, respectively,¹⁵ suggesting a possibility of a new crystal modification by an application of strain. Despite many investigations on the crystal modification in PBT and polyethers,²⁻¹² few works have been made on aliphatic polyesters.^{13,14} In this paper, we show

the existence of a new crystal modification in PES.

EXPERIMENTAL

PES utilized in this work was commercially available and supplied in a pellet form from Showa Highpolymer Co., Ltd., so-called "Bionolle"¹⁶; no further purification was performed on the polymer. The melting point and the glass transition temperature of PES are 99°C and -11°C (by DSC), respectively. Uniaxially oriented fiber specimens were obtained by melt spinning at 190°C, followed by drawing up to 5.5 times at room temperature. The resulting fibers were then annealed at 80°C in vacuum under a constant length; we referred them original fibers hereafter. One of the original fiber was stretched up to 30%, under which a small plastic strain is incorporated, by means of a conventional stretching device; we referred it strained fiber. The applied strain was determined based on the ratio of the strained fiber length to that of the original one. X-Ray fiber photographs were taken for both the original and strained fibers, using a cylindrical camera (diameter of 100 mm) at room temperature as reported before.^{13,14} The fiber

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identity periods were then calculated from the X-ray photographs.

RESULTS AND DISCUSSION

Figures 1a and 1b show the X-ray fiber photographs for the original and strained fiber of PES, respectively. In Figure 1b, new diffraction spots with strong streak can be seen together with the same diffraction spots as seen in the photograph from the original fiber (Figure 1a). This observation indicates that the strained fiber contains two distinct crystal forms. We term the crystal form observed in the original fiber as the " α -form" and the new form appeared in the strained fiber as the " β -form". The solid-state crystal transition from the α -form to the β -form and *vice versa*

is found to be reversible with respect to the repeated application and removal of strain, the feature of which is similar to the crystal transition reported in PBT²⁻¹⁰ and PTMS.^{13,14} The streaks appear on every layer line, while discrete reflections are observed on the equatorial line as reported in many polymers.^{12,17,18} It is hence conceivable that the β -form of PES in this work contains disorder along the fiber axis. Similarity of the size and symmetry of the methylene and the carbonyl groups might result in such a disorder in the molecular arrangements.¹⁸

The fiber identity period (FP) of the α form is found to be 8.40 Å, which is close to the reported value of 8.33 Å.¹⁵ On the other hand, the FP of the β -form is found to be 9.50 Å, which is somewhat smaller than the calculated FP for the all *trans* T_8 (9.70 Å) conformation. Such a shortening in FP has been reported in a series of polyesters of $[-O(CH_2)_2O-CO-(CH_2)_x-CO-]_n$ with $x \geq 4$, which have no *G* and \bar{G} in the skeletal conformations, and is explained in terms of the introduction of *skew* (*S*) conformation in the ethylene glycol unit.^{15,19} We thus expect that the β -form of PES also contains *S* in the ethylene glycol units, although a definite conclusion cannot be derived at present. The determination of the crystal structure of the β -form as well as the detailed study of the crystal transition mechanisms will be the future projects.

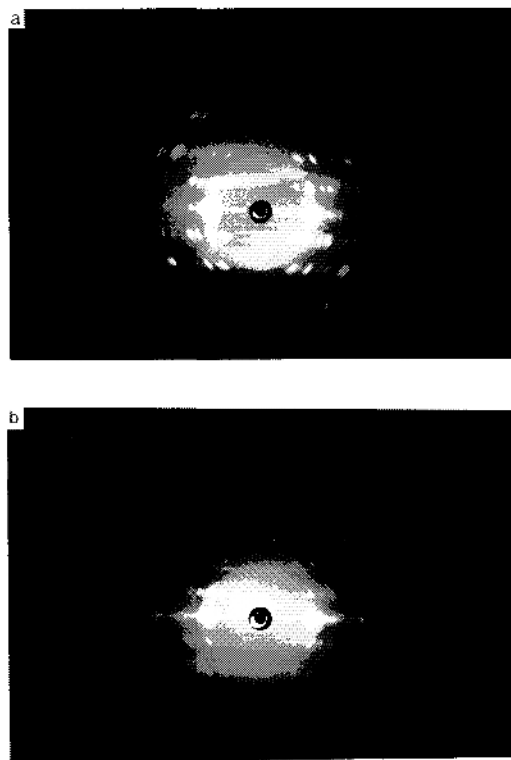


Figure 1. X-Ray fiber photograph of PES: (a) original fiber and (b) for a strained (30%) fiber. Note that new diffraction spots with streaks appear in the strained fiber.

REFERENCES

1. L. E. Nielsen, "Mechanical Properties of Polymers and Composites," Marcel Dekker Inc., New York, N.Y., 1975.
2. C. A. Boyle and J. R. Overton, *Bull. Am. Phys. Soc.*, **19**, 352 (1974).
3. R. Jakeways, M. A. Wilding, I. M. Ward, I. H. Hall, I. J. Desborough, and M. G. Pass, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 799 (1975).
4. F. M. Lu and J. E. Spruiell, *J. Appl. Polym. Sci.*, **21**, 1595 (1986).
5. M. Yokouchi, Y. Sakakibara, Y. Chatani, H. Tadokoro, Y. Tanaka, and K. Yoda, *Macromolecules*, **9**, 266 (1976).

6. H. W. Siesler, *J. Polym. Sci., Polym. Lett. Ed.*, **17**, 453 (1979).
7. K. Tashiro, Y. Nakai, M. Kobayashi, and H. Tadokoro, *Macromolecules*, **13**, 137 (1980).
8. K. Tashiro, M. Iiramatsu, T. Ii, M. Kobayashi, and H. Tadokoro, *Seni Gakkaishi (Japan)*, **42**, T-597 (1986).
9. K. Tashiro, M. Iiramatsu, T. Ii, M. Kobayashi, and H. Tadokoro, *Seni Gakkaishi (Japan)*, **42**, T-659 (1986).
10. I. H. Hall and M. G. Pass, *Polymer*, **17**, 807 (1976).
11. K. Tashiro and H. Tadokoro, *Rep. Prog. Polym. Phys. Jpn.*, **21**, 417 (1978).
12. Y. Takahashi, Y. Osaki, and H. Tadokoro, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1153 (1981).
13. Y. Ichikawa, J. Suzuki, J. Washiyama, Y. Moteki, K. Noguchi, and K. Okuyama, *Polymer*, **35**, 3338 (1994).
14. Y. Ichikawa, J. Washiyama, Y. Moteki, K. Noguchi, and K. Okuyama, *Polym. J.*, **27**, 1230 (1995).
15. A. S. Ueda, Y. Chatani, and H. Tadokoro, *Polym. J.*, **2**, 387 (1971).
16. USP, 5306787.
17. K. Suchiro, Y. Chatani, and H. Tadokoro, *Polym. J.*, **7**, 352 (1975).
18. Y. Chatani, Y. Okita, H. Tadokoro, and Y. Yamashita, *Polym. J.*, **1**, 555 (1970).
19. A. Turner-Jones and C. W. Bunn, *Acta. Cryst.*, **15**, 105 (1962).