Strain-induced crystal modification in poly(tetramethylene succinate)

Yasushi Ichikawa*, June Suzuki, Junichiro Washiyama and Yoshihiro Moteki
Showa Denko K. K. Kawasaki Plastics Laboratory, Bionolle Project, 3-2 Chidori-cho, Kawasaki-ku, Kawasaki 210, Japan

and Keiichi Noguchi and Kenji Okuyama
Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan
(Received 8 April 1994)

A new crystal modification induced by strain was found in uniaxially oriented fibres of poly(tetramethylene succinate). This new modification (β form) had a planar zigzag conformation of T_{10} (all *trans*) and a fibre identity period of 11.90 Å, while the conventional α form had a $T_7GT\bar{G}$ conformation and fibre identity period of 10.90 Å. The solid-state crystal transition between α and β forms was reversible with respect to the successive application and release of strain.

(Keywords: crystal modification; strain; poly(tetramethylene succinnate))

Introduction

Recently, biodegradable polymers have received much attention from industry, particularly from the ecological viewpoint. It is well known that some synthetic aliphatic polyesters, such as poly(tetramethylene succinate) (PTMS), poly(ethylene succinate) (PES) and their copolymers[1,2], show excellent biodegradability. These are crystalline polymers. The mechanical properties of crystalline polymers, in general, depend strongly on their crystal structures as well as on the crystallinity of the polymers. Crystal structures can be controlled by pressure, temperature and strain. In poly(butylene terephthalate) (PBT), for instance, two kinds of crystal modifications (α and β form) have been reported[3–7]; the β form appeared under strain. Despite many investigations on the crystal modification in PBT, little work has been done on PTMS. Chatani *et al.* reported the crystal structure (α form) of PTMS in a uniaxially oriented fibre[8]. In this paper, we show the existence of a new crystal modification of PTMS.

Experimental

Commercial grade PTMS (tradename Bionolle) was supplied in pellet form from Showa High Polymer Co., Ltd. No further purification was performed on the polymer. The melting point and the glass transition temperature of PTMS are 114°C and −32°C (by d.s.c.), respectively. Uniaxially oriented specimens were fabricated by melt spinning at 200°C, followed by drawing up to 10 times at room temperature; specimens were then annealed at 80°C in vacuum under a constant length. These specimens are hereafter referred to as original fibres. Nickel-filtered CuKα radiation operated at 50 kV and 140 mA was used throughout this investigation. X-ray fibre photographs were taken for both the original and strained (by 14%) fibres, by means of a cylindrical camera (diameter 100 mm) at room temperature. The fibre identity periods were calculated from the X-ray photographs.

Results and discussion

Figures 1a and *b* show the X-ray fibre photographs for the original and strained fibre of PTMS. In

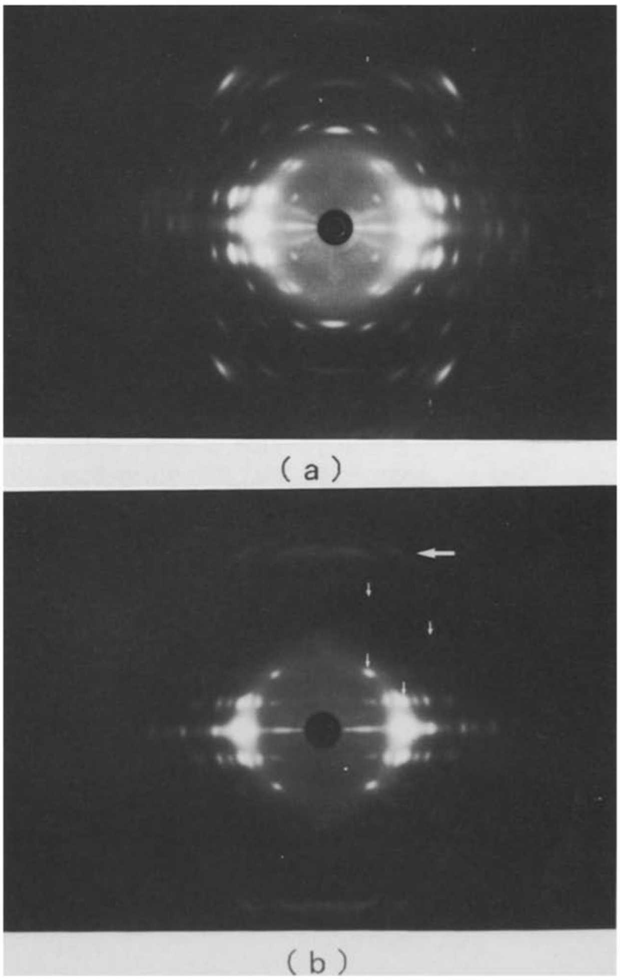

Figure 1 X-ray fibre photographs of poly(tetramethylene succinate): (a) original fibre and (b) strained (14%) fibre. Note that new diffraction spots, indicated by arrows, appear in the strained fibre

---

* To whom correspondence should be addressed

0032-3861/94/15/3338–02

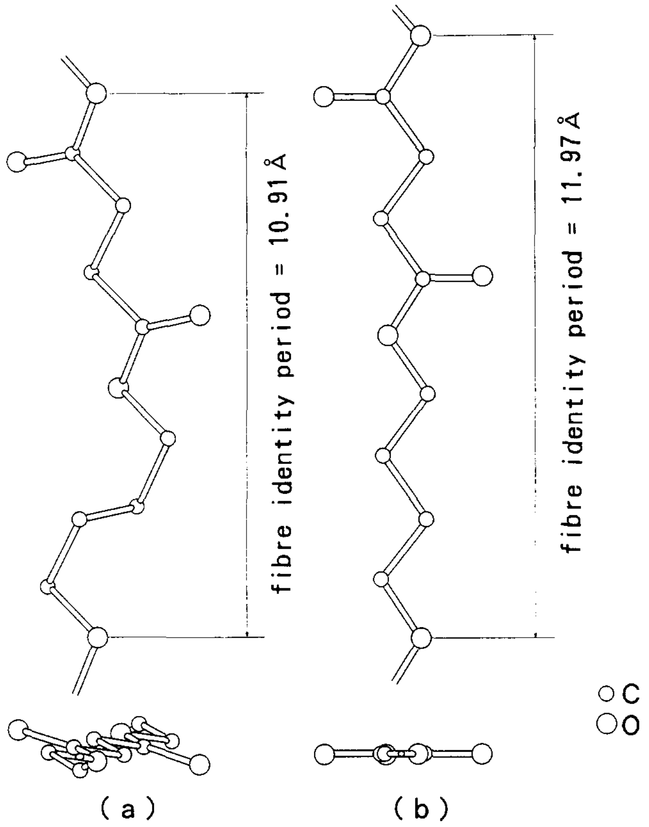

Figure 2 Molecular structure of poly(tetramethylene succinate): (a) α form ($T_7GT\bar{G}$) and (b) β form (T_{10})

Figure 1b new diffraction spots, indicated by arrows, can be clearly seen together with the same diffractions as seen in the photograph from the original fibre (*Figure 1a*). This observation indicates that the strained fibre contains two distinct crystal forms. We term the crystal form observed in the original fibre the α form and the new form that appears in the strained fibre the β form. The fibre identity period of the α form was found to be 10.90 Å, which is close to the reported value of 10.94 Å (ref. 8). The fibre identity period of the β form was observed to be 11.90 Å.

The molecular conformation of the α form is $T_7GT\bar{G}$ (*Figure 2a*), where *T*, *G* and $\bar{G}$ denote *trans*, *gauche* and *minus gauche*, respectively[8]. On the other hand, the molecular conformation of the β form is planar zigzag (all *trans* T_{10}) (*Figure 2b*). Such an all-*trans* conformation under strain has been reported in PBT[3–7] as well as in poly(butylene terephthalate)–poly(tetramethylene oxide) block copolymer[9]. These structures are constructed so as to reproduce the fibre identity periods for each crystal form. The observed (and calculated) fibre identity periods for the α and β form are 10.90 Å (10.91 Å) and 11.90 Å (11.97 Å), respectively, both of which are in good agreement. The bond lengths and bond angles employed in this calculation are taken from those for PES[10] and are as follows: C–C = 1.52 Å; C(O)–C = 1.48 Å; C(O)–O = 1.33 Å; C–O = 1.42 Å; C=O = 1.20 Å; ∠C–C–C = ∠C–C–O = 109.5°; ∠C–C(O)–O = ∠C(O)–O–C = 113.0°; ∠O–C=O = 125.0°; the internal rotation angles for *T*, *G* and $\bar{G}$ are 180°, 60° and −60°, respectively.

The solid-state crystal transition from the α form to the β form and *vice versa* was found to be reversible with respect to the repeated application and removal of strain; this feature is similar to the crystal transition reported in PBT[3–7]. Under the current experimental conditions, both the α and β form of PTMS were observed, while Yokouchi *et al.*[3] have shown that in PBT a pure β form is obtained at a large strain regime. Future work will be aimed at obtaining a pure β form and more detailed crystal structure determination.

References

1 Yokota, Y., Ishioka, R. and Watanabe, N. 3rd International Scientific Workshop on Biodegradable Plastics and Polymers, Osaka, 1993, Abstracts p. 96
2 Nishioka, M., Tuzuki, T., Wanajyo, Y., Oonami, F. and Horiuchi, T. 3rd International Scientific Workshop on Biodegradable Plastics and Polymers, Osaka, 1993, Abstracts p. 97
3 Yokouchi, M., Sakakibara, Y., Chatani, Y., Tadokoro, H., Tanaka, T. and Yoda, K. *Macromolecules* 1976, **9**, 266
4 Boye, C. A. and Overton, J. R. *Bull. Am. Phys. Soc.* 1974, **19**, 352
5 Jakeways, R., Ward, I. M., Wilding, M. A., Hall, I. H., Desborough, I. J. and Pass, M. G. *J. Polym. Sci., Polym. Phys. Edn* 1975, **13**, 799
6 Tashiro, K., Nakai, Y., Kobayashi, M. and Tadokoro, H. *Macromolecules* 1980, **13**, 137
7 Roebuck, J., Jakeways, R. and Ward, I. M. *Polymer* 1992, **33**, 227
8 Chatani, Y., Hasegawa, R. and Tadokoro, H. Meeting of the Society of Polymer Science (Japan), 1971, p. 420
9 Tashiro, K., Hiramatsu, M., Ii, T., Kobayashi, M. and Tadokoro, H. *Seni Gakkaishi* (*Japan*) 1986, **42**, 597
10 Ueda, A. S., Chatani, Y. and Tadokoro, H. *Polym. J.* 1971, **2**, 387