

PS13.01.09 ELECTRON CRYSTALLOGRAPHIC ANALYSIS OF POLY (p-OXYBENZOATE): A COMBINED MODEL AND DIRECT PHASING APPROACH. D. L. Dorset, Electron Diffraction Department, Hauptman-Woodward Institute, Buffalo, NY 14203; J. Liu, B.-L. Yuan and P. H. Geil, Department of Materials Science and Engineering, and Materials Research Laboratory, University of Illinois, Urbana, IL 61801

Electron diffraction patterns from phase I of poly(p-oxybenzoate) were collected from ca. 100 Å thick single crystal lamellae (hk0 data) grown by confined thin film melt polymerization. Alternative orientations (e. g. 0kl data) were obtained from high molecular weight whiskers grown (polymerized) from dilute solution. The quality of the intensity data were ascertained by a R_{merge} criterion using various patterns for any given orientation. The orthorhombic unit cell has dimensions: $a = 7.42$, $b = 5.70$, $c = 12.45$ Å and the crystal structure was determined in two orthogonal projections, [001] and [100] by direct methods. In the former case, the centrosymmetric projection down the chains (plane group pgm) was easily determined as a molecular profile by symbolic addition. The latter, noncentrosymmetric projection (pg), was found via a multiresolution approach using the Sayre equation. After location of all atomic positions (via Fourier refinement) in the latter projection, the final solution was within 0.2 Å deviation from the model found independently using the Cerius² program, where the chains were packed to match the observed diffraction patterns qualitatively. The chain packing is found to be polar, with two staggered monomer units in the asymmetric unit. This study, among other things, demonstrates the facility of innovative crystallization techniques, in addition to the epitaxial orientation procedures often used, for providing essential single crystal diffraction data from a projection onto the polymer chain axis.

Supported, in part by the NSF Polymer and Physical Chemistry Programs.

PS13.01.10 KEVLAR FIBRE S IN THERMAL ENVIRONMENTS. Kalyani Vijayan, R. V. Iyer, Materials Science Division, National Aerospace Laboratories, Bangalore 560 017, India

Kevlar fibres are found to undergo isothermal decomposition. Features which are typical of decomposition at 500°C are found to be introduced at much lower temperatures. The parameter which critically controls such behavior is the duration of the cumulative exposure to any temperature. On the basis of X-ray diffraction data, optical and scanning electron micrographs, weight loss and tensile data, detailed characterization of isothermal decomposition occurring in the temperature range of 250 to 500°C has been carried out. It is found that decomposition is preceded by damage to the surface of individual filaments. Presence of surface impurities enhance the damage. There is also evidence for evolution of volatile components via the surface. Progressive changes in crystal structural and tensile characteristics and the weight of the fibre have also been observed. Based on data collected at various stages of isothermal ageing at different temperatures, a structural model has been proposed to explain the decomposition behavior of Kevlar fibres.

The effect of thermal spikes, each of 10s duration, on Kevlar fibres has also been examined. Fibres were exposed to cumulative spikes, upto 60s duration, in the temperature range 100 to 700°C. Above a threshold temperature, the spikes are found to leave a detectable impression on the tensile as well as the structural characteristics of the fibre.

PS13.01.11 CRYSTAL STRUCTURE AND CRYSTAL TRANSITION OF POLY(TETRAMETHYLENE SUCCINATE) Y. Ichikawa, H. Kondo, K. Noguchi and K. Okuyama, Faculty of Technology, Tokyo University of Agriculture and Technology, Kaganei Tokyo 184, Japan.

Recently, biodegradable polymers have been receiving special attention especially from the ecological viewpoint. It is well known that some of synthetic crystalline aliphatic polyesters, such as poly(tetramethylene succinate) (PTMS), poly(ethylene succinate) and their copolymers, show excellent biodegradability. Physical properties of crystalline polymers, in general, depend strongly on their crystal structure.

The molecular conformation and crystal structure of PTMS (α -form) was first investigated by Chatani and coworkers (Chatani, Y., Hasegawa, R., & Tadokoro, H., *A Meet., Soc. Polym. Sci. (Japan)*, 1971, page 420). Recently, we found that a new crystal modification of PTMS (β -form) was induced by strain (Ichikawa, Y., Suzuki, J., Washiyama, J., Moteki, Y., Noguchi, K., & Okuyama, K., *Polymer*, 1994, **35**, 3338-3339). We have already reported that the thermodynamic first-order phase transition was the operative mechanism in the transition from a to β -form (Ichikawa, Y., Washiyama, J., Moteki, Y., Noguchi, K., & Okuyama, K., *Polym. J.*, 1995, **27**, 1230-1238). In order to obtain a deep insight in the crystal transition mechanisms of PTMS, the two crystal structures have been investigated. The resulting structures of both crystal forms are summarized in the table.

Table. Crystal data of two crystal forms of PTMS

| | α -form | β -form |
|---------------------------------|--------------------|--------------------|
| Crystal system | monoclinic | monoclinic |
| Space group | P2 ₁ /n | P2 ₁ /n |
| Cell dimensions | | |
| $a/\text{Å}$ | 5.23(2) | 5.84(5) |
| $b/\text{Å}$ | 9.12(3) | 8.32(11) |
| $c(\text{fiber axis})/\text{Å}$ | 10.90(5) | 11.89(7) |
| β° | 123.9(2) | 131.6(5) |
| No. of chains per unit cell | 2 | 2 |

Fiber II Methods of Structure Determination

MS13.02.01 ULTRA-FINE STRUCTURES IN CRYSTALLINE POLYMERS FROM HIGH-RESOLUTION TEM. Masaki Tsuji, Institute for Chemical Research, Kyoto University

High-resolution TEM has become a conventional approach to clarify ultra-fine structures even in crystalline solids of radiation-sensitive polymers. In this presentation, we will show our high-resolution TEM studies mainly on fiber structure of flexible linear polymers. The specimens used here are uniaxially oriented crystalline thin films of isotactic polystyrene [i-PS](1), poly(aryl-ether-ether-ketone) [PEEK](2), polyethylene [PE](3) and poly(4-methyl-1-pentene) [P4M1P](3). For PE and P4M1P, their high-resolution images were taken at 4.2K by cryogenic TEM.

The films of PE, P4M1P and PEEK revealed stacked lamellar structure. Lattice images of PE showed (110) and/or (200) lattice fringes running in the fiber-axis [FA] direction. Each of the domains in which the fringes are observed corresponds to a so-called crystallite within a lamella, revealing crystallite size, shape and orientation. The images accordingly clarified the relationship between the lamellar structure and such domains. In some of the images, a tiny crystalline region, "tie-crystallite"(2), was identified, which connects adjacent lamellae in the FA direction. Such tie-crystallites were also recognized in the lattice images of P4M1P and PEEK films.

The i-PS film used here has basically fibrillar structure. Lattice images of the film showed (110) fringes running in the FA