PS13.01.09 ELECTRON CRYSTALLOGRAPHIC ANALYSIS OF POLY(POXYBENZOATE)-A COMBINED MODLAND DIRECT PHASING APPROACH. D. L. Dorsett, Electronics Department, Hauptman-Woodward Institute, Buffalo, NY 14203; J. Liu, B.-L. Yuan and P. H. Gei, Department of Materials Science and Engineering, and Materials Research Laboratory, University of Illinois, Urbana, IL 61801

Electron diffraction patterns from phase I of poly(poxymethylene) were collected from ca. 100 A thick single crystal lamellae (hk0 data) grown by confined thin film melt polymerization. Alternative orientations (e.g. (010) data) were obtained from high molecular weight whiskers grown (polymerized) from dilute solution. The quality of the intensity data were ascertained by a Rmerge criterion using various patterns for any given orientation. The orthorhombic unit cell has dimensions: a = 7.42, b = 5.70, c = 12.45 A 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 multishot 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 A 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 such domains via the surface. Progressive changes in crystal structure 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 TGA analysis, it is shown 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.

Fiber II

PS13.01.10 KEVLAR FIBRES 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, up to 60 s duration, in the temperature range 100 to 700°C. A threshold temperature, the spikes are found to leave a detectable impression on the tensile as well as the structural characteristics of the fibre.

Fiber II

Methods of Structure Determination

PS13.01.11 CRYSTAL STRUCTURE AND CRYSTAL TRANSITION OF POLY(4-TETRAMETHYLENE SUCCINATE) Y. Ichikawa, H. Kondo, K. Noguchi and K. Okuyama, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei 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(4-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 (a-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 (b-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 a 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

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>a-form</th>
<th>b-form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Cell dimensions a/A</td>
<td>5.23(2)</td>
<td>5.24(5)</td>
</tr>
<tr>
<td>b/A</td>
<td>9.12(3)</td>
<td>8.32(11)</td>
</tr>
<tr>
<td>c/fiber axis/A</td>
<td>10.50(5)</td>
<td>11.89(7)</td>
</tr>
<tr>
<td>β°</td>
<td>123.9(2)</td>
<td>131.6(5)</td>
</tr>
<tr>
<td>No. of chains per unit cell</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

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Electron diffraction patterns from phase I of poly(poxymethylene) were collected from ca. 100 A thick single crystal lamellae (hk0 data) grown by confined thin film melt polymerization. Alternative orientations (e.g. (010) data) were obtained from high molecular weight whiskers grown (polymerized) from dilute solution. The quality of the intensity data were ascertained by a Rmerge criterion using various patterns for any given orientation. The orthorhombic unit cell has dimensions: a = 7.42, b = 5.70, c = 12.45 A 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 multishot 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 A 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 such domains via the surface. Progressive changes in crystal structure 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 TGA analysis, it is shown 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.

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Fiber II

Methods of Structure Determination

MS13.02.01 ULTRA-FINE STRUCTURES IN CRYSTALLINE POLYMERS FROM HIGH-RESOLUTION TEM. Masaki Tsuchi, 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 PE, P4M1P, 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

MS13.02.02 STRUCTURE DETERMINATION BY ELECTRON CRYSTALLOGRAPHY USING BOTH MAXIMUM ENTROPY AND SIMULATION APPROACHES. I. G. Voigt-Martin, Institut für Physikalische Chemie der Universität Mainz, Germany

Electron crystallography is gaining importance for the investigation of polymers and their monomeric analogs due to the small dimensions of their crystals and the limited number of reflections. Our aim is to give chemists essential information at a molecular level to aid the directed synthesis of suitable molecules for ferroelectric and nonlinear optical applications. Using the information from electron diffraction patterns, both simulation and ab initio maximum entropy approaches were used to obtain detailed information about magnitude and direction of dipoles and hyperpolarisability components of three newly synthesised organic materials.

MS13.02.03 ELECTRON DIFFRACTION IN POLYMER CRYSTAL STRUCTURE ANALYSIS: SOME RECENT EXAMPLES. Stefano Valdo Meille, Dipartimento di Chimica, Politecnico di Milano, via Mancinelli 7, 20131 Milano, Italy

It is normally assumed that X-ray fiber patterns provide the more readily accessible and reliable diffraction data for polymers. Essential geometric information like the fiber repeat and the probable helical symmetry are immediate results with this technique. It is however inapplicable to low molecular weight or infusible polymers and to phases present in small proportion or else unstable to elongation. Even in favorable cases the determination of lattice constants and of integrated intensities may be problematic because of polymorphism and overlapping of diffraction maxima.

Experience in our laboratory shows that often the key problem in the structural analysis of polymers is the determination of the unit cell and, the space group, even with relatively simple asymmetric units. Electron diffraction (E.D.) represents the most reliable technique for this purpose and examples involving the β- and γ-polymorphs of isotactic polypropylene and other recent structural investigations will be discussed. Lattice parameters even more so than the space group can hardly be predicted by packing analysis while on the other hand molecular modeling is often adequate to determine molecular conformation also in the crystal.

There is also increasing evidence that with appropriate precautions E.D. intensities are adequate for polymer crystal structure solution and refinement. It appears that the negative impact of dynamic effects and of radiation damage on E.D. data have been overemphasized while background and peak shape problems in fiber diffraction are often underestimated. Combined approaches using parallel structural refinements with E.D. and X-ray powder diffraction data may represent an efficient alternative to traditional refinements based on fiber data.

MS13.02.04 THE ROLE OF DIRECT METHODS IN POLYMER CRYSTALLOGRAPHY. D. L. Dorset, Electron Diffraction Department, Hauptman-Woodward Institute, 73 High Street, Buffalo, NY 14203-1196 USA

Because of the sparse sampling of the reciprocal lattice in electron or polymer diffraction studies of linear polymers, most structural analyses have relied on model-based trial and error searches for simultaneous minima of the crystallographic residual and the lattice packing energy. Recently, however, true ab initio structure determinations, using direct phasing methods, have proven to be very effective. For single crystal electron diffraction data, these determinations are facilitated if care is taken to collect intensities from a complete reciprocal lattice, requiring observation of data from two orthogonal crystal orientations in the tilt experiments. If only one crystal orientation is available for tilting (e.g. a chainfolded lamella), then the missing information in the unsampled "dead zone" may degrade details along the polymer chain axis. In this case, prediction of the missing information by the Sayre equation may be useful. An alternative approach is to combine data from fibers with the lamellar single crystal data, when epitaxial orientation is not possible for achieving the orthogonal orientation of the chain packing in a single crystal form. Tests with fiber x-ray data from polyethylene and poly (e-caprolactone) demonstrate that the structure can be determined ab initio, and also that a reasonably good approximation deconvolution of overlapped intensities can be made without assumption of a molecular model a priori. Such procedures have been repeated with electron diffraction intensities (lamella and fiber) from poly (ethylene sulfide) with good success. Numerous direct methods approaches have been evaluated but the most powerful techniques found so far seem to be the Sayre equation in a multisolution approach or the SnB technique based on the minimal principle.

Supported by grants from the NSF (CHE-94-17833) and NIGMS (GM-46733)

MS13.02.05 MODEL FITTING: A CRITERION FOR POLYMER STRUCTURE IDENTIFICATION AFTER DIRECT METHODS. Mary P. McCourt, Department of Mathematics and Natural Sciences, D’Youville College & Electron Diffraction Department, Hauptman-Woodward Institute, Buffalo, NY

Although direct phasing methods have been found to be effective for determining polymer crystal structures from electron diffraction or x-ray diffraction data sets, there can be instances where the resultant potential or electron density maps cannot be interpreted directly in terms of atomic positions. For example, there may be algebraic ambiguities due to poor connectivity of Miller indices (e. g. undersampled reciprocal lattice) or insufficient resolution to visualize the positions themselves. Fitting of polymer chain models to the resultant can be quite useful, therefore, for identification of a structure and derivation of atomic coordinates to permit calculation of an R-factor. Examples of electron diffraction data sets from single crystal orientations, e. g. Mannan I and poly (pivalolactone) will be discussed in this context, where the model compensates for unmeasured data in the "missing cone". In another example, poly (ethylene sulfide), where data from lamellar crystals and fibers are combined to sample all of reciprocal space, model fitting overcomes bond length distortions due to dynamical scattering. In fiber x-ray determination, direct methods have been used to solve the crystal structure of poly (e-caprolactone). Despite the high resolution of the data set, the non-planar chain conformation is best visualized when a chain is fit to the electron density profile. Finally in the analysis of poly (trimethyl-p-silsphylene), the low resolution of the x-ray data requires the correct space group and phase set to be chosen on the basis of the chain skeleton. In all of these applications, the construction is used as a figure of merit for ab initio analysis rather than as the basis for a trial and error search.

Research supported by a grant from the NSF (CHE-94-17835)