

direction. One of the coherent regions in which the fringes are observed is about 15nm wide and reaches 200nm long. The fringes are slightly curved and partly faint, but the region seems to have no defects. Taking into account the procedure of specimen preparation, the region in question corresponds to a "shish" in the shish-kebab structure and is considered to be a kind of tie-crystallite mentioned above. Molecular chains of i-PS seem to be more or less extended in such a shish.

The fiber structure of PE, P4M1P and PEEK has two faces of lamellar and fibrillar structure. It is deduced that in ultra-drawn films/fibers of ultra-high molecular weight PE, one face, namely the lamellar structure is lost and the other face, namely the fibrillar structure consisting of a great number of tie-crystallites is enhanced. 1) Tsuji, M. et al., *Sen-i Gakkaishi*, 42, p.T-580 (1986). 2) Kawamura, H. et al., *Bull. Inst. Chem. Res., Kyoto Univ.*, 68, p.41 (1990). 3) Tsuji, M. et al., *Sen-i Gakkaishi*, 48, p.384 (1992).

#### 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 non-linear 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  $\beta$ - and  $\gamma$ -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 chain-folded 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 ( $\epsilon$ -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-94-17835) 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. an 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 ( $\epsilon$ -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 (tetramethyl-p-silphenylene), 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 (CHE94-17835)