10. POLYMER CRYSTALLOGRAPHY

10.1-1 WHOLE-PATTERN STRUCTURE REFINEMENT OF CRYSTALLINE FIBROUS POLYMERS. THE POLY-ISOBUTYLENE. By P. Iannelli and A. Immirzi, Dipartimento di Fisica, Università di Salerno, Italy

In a recent work (A. Immirzi, P. Iannelli, Gaz. Chim. Ital. 1987, in press) we have discussed the possibility of refining crystal structures of fibrous materials using a whole-pattern approach, so extending from the one-dimensional to the two-dimensional case the Rietveld’s method. Initially, we have examined the case of the X-ray fiber diffraction pattern recorded on photographic film (either flat or cylindrical camera) and considered the diffraction intensity of each Bragg peak continuously distributed along two mutually orthogonal directions on the film: the 2D-constant lines (r-lines) and the ones orthogonal (p-lines).

The X-ray fiber diffraction pattern of vulcanized polyisobutylene (PIB) (crystallized under stress) has been studied. A number of well resolved Bragg peaks have been examined one-by-one fitting the experimental intensity with a two-dimensional peak function expressed as the product of two one-dimensional distributions of the type:

\[ f_{H,m,s}(z) = \frac{C_{mp}}{H} \rho_{H}^{(a - 1)} \cdot \rho_{m}^{(b - 1)} \cdot \rho_{s}^{(c - 1)} (z) \]

which is a generalization of the Pearson-VII function \( f_{x}(z) \) is Pearson-VII, for \( s = 2 \) \( f(x) = \) Gaussian function. The above expression \( z \) is either \( \rho_{H} \), or \( \rho_{m} \), or \( \rho_{s} \), being \( \rho_{P} \), \( \rho_{m} \), \( \rho_{s} \) referred to centre of the film (Bragg position) and \( \rho_{P} \) to any point close to \( \rho_{P} \). The \( 3 \times 3 \) parameters \( H, m, s \) and \( \rho_{P} \) were adjusted by a least-squares procedure independently for each Bragg peak. The values of \( H, m, s \) close to 2 and high \( m \) values were obtained indicating that Gaussian profiles are substantially appropriate. The two \( Z \) values (half-height peak-widths in the two directions) are regularly variable with the Bragg position on the film.

On these bases structural refinements have been undertaken by means of a computer program which adjusts simultaneously, by minimizing the sum of squared deviations between “observed” and “calculated” intensities, both profile parameters and structural parameters. For the latter “internal” coordinates instead of the usual fractional coordinates have been considered in order to reduce the number of variables and to incorporate the a priori structural information. The program allows also handling constraints among variables (Lagrangian method).

In the case of PIB a preliminary structure refinement based on the model by Tadokoro et al. (J. Polym. Sci. 12, 515, 1974) has been done by considering fixed C–C bond lengths (1.54 Å), only 2 values for the chain angles (one for all CH₂–CH₂–CH₂ and one for all CH₂–CM–CM₂ angles) and 8 independent torsion angles for the four monomeric units contained in the crystallographic asymmetric unit. The values obtained are quite reliable and comparable with Tadokoro’s value. At the present stage of refinement the chain b.a. are 128.6° and 109.5° while the torsion angles are 48.4°, 166.9°, 59.8°, 153.9°, 54.8°, 164.3°, 59.5°, 161.4°.

10.2-1 THE CRYSTAL STRUCTURE OF SOME ALIPHATIC POLYESTERS. By S. Desguise and P. Bristot, Département de Chimie, Université de Montréal, Montréal, Canada.

We have undertaken to establish and/or confirm the crystal structures of a number of aliphatic polyesters: \( \{-(CH_{2})_{x}, \} \cdot \{-(CH_{2})_{y}, -(CH_{2})_{z} \} \) for \( x = 2, 4, 6, 8, 10, 11, \) and \( y = 8 \) using X-ray and electron diffraction. Oriented fibers have been obtained and fiber diffraction patterns have been recorded for poly(hexamethylene sebacate), PE-6,8 and poly(ethylene sebacate), PE-2,8. Both polyesters crystallize in a monoclinic unit cell containing two polymeric chains parallel to the c-axis. The geometrical parameters required for chain building and conformational analyses were obtained from the crystal structure determinations of relevant model compounds. The chains having the lowest energies were positioned and oriented within the unit cell by minimizing the inter-chain interactions. Finally, one discriminates among the various models by a comparison of calculated and observed diffracted intensities. Upon refinement of the scale and temperature factor, the agreement index \( R \) reaches around 0.16 for the PE-6,8. The two methyl-ester sequences are in the fully extended conformation. However, the sebacate group is tilted by 20° with respect to that of the hexamethylene group. PE-2,8 probably adopts the same conformation as PE-6,8. We will discuss these structures with respect to those obtained for polyesters with \( x = 2 \) and \( y = 0, 2, 4, 4,6,8 \)."