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, *Gazz. 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 2ϑ–constant lines (τ– lines) and the ones orthogonal (ρ– lines).
The X-ray fiber diffraction pattern of vulcanized poly-isobutylene (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:

$$f_{H,m,s}(z) = \frac{C_{ms}}{H}[2^{-s} \cdot (2^{1/m} - 1) + |z|^s]^{-m}$$

which is a generalization of the Pearson–VII function (C_{ms} = normalization factor; for $s = 2$ $f(z)$ is Pearson–VII, for $s = 2$ and $m = \infty$ $f(z)$ is Gauss function). In the above expression z is either $(\rho_i - \rho_k)/H_\rho$ or $(\tau_i - \tau_k)/H_\tau$ being ρ_k τ_k referred to centre of the spot (Bragg position) and ρ_i τ_i to any point close to k. The $3 + 3$ paramters H, m, and s were adjusted by a l.s. procedure independently for each Bragg peak. s values close to 2 and high m values were obtained indicating that Gauss profiles are substantially appropriate. The two H 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 (Lagrange 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 CMe$_2$—CH$_2$—CMe$_2$ and one for all CH$_2$—CMe$_2$—CH$_2$ 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 109.9° 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. Deguire and F. Brisse, 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, [-O-(CH$_2$)$_x$-O-CO-(CH$_2$)$_y$-CO-]$_n$ for x = 2,4,6,8,10 and 12 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 interchain 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 methylenic 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 of these structures with respect to those obtained for polyesters with x= 2 and y = 0,2,4 and 6.

10.2-2   POLYMORPHISM IN THE FIBER STRUCTURE OF POLY-BIS (4-4'DICYCLOHEXYLMETHANE) n-DODECANEDIAMIDE. R. Barton, Jr., E. I. duPont de Nemours and Co., Textile Fibers Dept., Experimental Station - E302/126, Wilmington DE 19807, U.S.A.

Structure of the title polymer has been studied by X-ray diffraction analysis of fibers spun from the polymer. Polymorphism is observed in this system, with structure dependent primarily on the temperature-tension history of the fiber. The most stable allomorph, obtained via relaxed annealing, consists of chains packed such that: (a) laterally, dicyclohexylmethane moieties are side-by-side, each hydrogen-bonded via amide groups in the a direction with similar neighboring groups related by a glide plane; the packing allows for perfect hydrogen bonding, is stereochemically efficient, and is consistent with the experimental unit-cell parameters ($a = 9.30$ Å, $b = 6.06$ Å); (b) longitudinally, there is a 2$_1$ helix with two chemical repeats per crystallographic repeat ($c = 45.0$ Å), and the observed fiber axis repeat is shorter than the calculated length (22.5 Å vs. 27.4 Å). Proposed space group is Pca2$_1$; calculated density is 1.060 g·cm^{-3} vs. 1.05 g·cm^{-3} measured. The structure, based on 100% trans-trans isomer in the dicyclohexylmethane moiety, can also accommodate the cis-trans isomer without serious distortion, explaining why high crystallinity can be developed in fibers with only 55% trans- trans isomer. When fibers are subjected to high tension and temperature, a monoclinic allomorph is developed ($a = 9.57$ Å, $b = 5.32$ Å, $c = 52.6$ Å, $\gamma = 100°$, probable space group P2$_1$/m) together with a disordered intermediate structure. This form, while only partially defined, must contain a fully extended chain and an unfavorable conformation in the dicyclohexylmethane moiety. Disordered structures are also described.