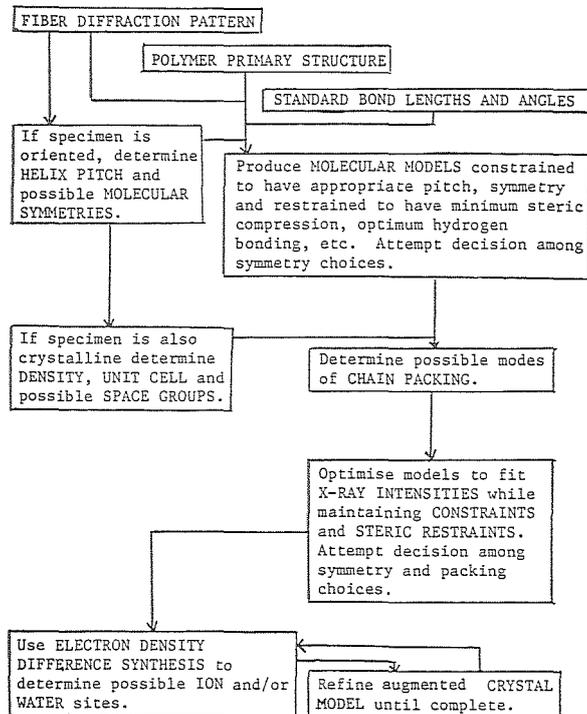


**10.X-01** ORDERED STRUCTURES OF POLYPEPTIDES AND PROTEINS. By H. A. Scheraga, Baker Laboratory of Chemistry, Cornell University, Ithaca, N. Y. 14853.

The structures and lattice energies of crystals of small molecules are used to parameterize empirical potential energy functions; the latter are employed in conformational energy calculations on polypeptides and proteins in solution and in the crystalline state. Such calculations provide insights into the types of structures adopted by low-molecular-weight oligopeptides, synthetic polymers and copolymers of amino acids, and fibrous and globular proteins, in response to intra- and inter-molecular interactions. For example, they can account for structures of open-chain and cyclic oligopeptides, for polymorphism in crystals of polyamino acids (and the temperature-induced interconversion between various crystal forms), for inter-strand complex formation in a fibrous protein such as collagen [using synthetic polytripeptides (containing a glycine residue in each tripeptide unit) as models of collagen], and for the nature of ordered ( $\alpha$  and  $\beta$ ) structures in globular proteins (i.e. the stabilities of left or right-handed  $\alpha$ -helices, and of left- or right-handed  $\beta$  sheets). Each of these examples will be discussed as illustrations of the applicability of conformational energy calculations.

X-ray diffraction can be used to help determine the molecular architecture of the many biologically or industrially important macromolecules (such as DNA, collagen, cellulose, pectin) which are linear polymers that prefer to be long helices rather than more complexly folded structures. It is usually possible to prepare uniaxially oriented specimens in which such helical molecules are aligned with their long axes parallel. Often further lateral organisation occurs but rarely to the degree of a three-dimensionally ordered single crystal. Nevertheless, the modern version (Smith and Arnott, *Acta Cryst.* (1978), A34, 3-11) of the linked-atom least-squares method (Arnott and Wonacott, *Polymer* (1966) 7, 157-166) provides a means of augmenting the relatively sparse X-ray data from fibers with non-controversial stereochemical information as outlined in the chart above. The result can be quite detailed, accurate visualisations of (for example) DNA interacting with an intercalating drug (Arnott *et al.*, *Nature* (1980) 287, 561-3) or of specific cations acting as conformational determinants of connective tissue polysaccharide molecules (Cael *et al.*, *J. Mol. Biol.* (1978) 125, 21-42).

**10.X-02** X-RAY DIFFRACTION ANALYSIS OF FIBROUS POLYMERS. By Struther Arnott, Department of Biological Sciences, Purdue University, West Lafayette, IN 47907, U.S.A.



**10.1-01** CRYSTAL BENDING EFFECTS IN LINEAR POLYMERS. Barbara Moss and Douglas L. Dorset, Medical Foundation of Buffalo, Inc., 73 High St., Buffalo, NY 14203, U.S.A.

Electron diffraction data are usually assigned considerably lower thermal parameters than X-ray data obtained at the same temperature, presumably due to some systematic error in one of the data sets. Using the model proposed by Cowley (*Acta Cryst.* (1961) 14, 920), crystal bending may be simulated through the smearing-out of Patterson peaks. The diffraction intensities calculated from the Patterson map are then modified through a term somewhat like a temperature factor. The extent of the bend effects depends on the unit cell orientation. Zones where the electron beam is parallel to a long crystallographic axis will exhibit the largest effects. Neglect of bending may be a major cause of the large discrepancies between electron and X-ray temperature factors.

The available experimental electron diffraction data for alpha-poly(3,3-bis(chloromethyl)oxacyclobutane), referred to as BCMO (Claffey *et al.*, *Phil. Mag.* (1974) 30, 1223), nigeran (Pérez *et al.*, *J. Med. Biol.* (1979) 129, 113) and poly(trimethylene terephthalate), denoted TMTP (Poulin-Dandurand *et al.*, *Polymer* (1979) 20, 419) have been re-investigated to determine the extent of bending and dynamical effects. The microcrystals of these materials are characteristically very thin (100Å), and calculations based on the Cowley-Moodie N-beam theory (*Acta Cryst.* (1957) 10, 609) confirm that dynamical scattering effects are small.

The polymers display varying characteristics. BCMO forms thin (60Å) rigid crystals. No bend contours were observed (Claffey *et al.*) and calculations confirm the lack of bending. Allowance for crystal bending of 2° and realistic temperature factors leads to considerably improved agreement between observed and calculated structure factors for nigeran. Similar results are obtained for

TMP, where bending of  $8^\circ$  is indicated.

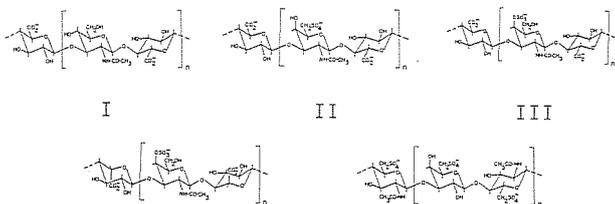
Crystal bending may seriously modify electron diffraction data and should be included in the analysis of these materials. This will generally lead to more realistic temperature factors and considerably improved agreement with experiment, facilitating crystal structure determinations.

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### 10.3-02 THE UNIT CELL OF THE LOW TEMPERATURE FORM (PHASE II) OF POLYTETRAFLUOROETHYLENE by J. Weeks, E. S. Clark\*, and R. K. Eby, National Bureau of Standards, Washington, DC

The crystal structure of Phase II PTFE has been determined from X-ray and electron diffraction data. Remarkable electron diffraction patterns giving highly resolved spots to the 26th layer were obtained from fibers of nearly 100% crystallinity. The layer line heights do not correspond to small integers for the layer line numbers. This nonuniformity is interpreted in terms of a regular but incommensurate helical conformation close to the previously assigned  $13/6 = 2.1667$   $\text{CF}_2$  groups per turn. Refinement of the layer line data gives a conformation of  $2.1598$   $\text{CF}_2$  groups per turn or a helix of  $473/219$  conformation. Quantitative evaluation of the lattice parameters as well as intensity estimates were made from X-ray diffraction data. The unit cell is triclinic and contains two chain stems of opposite handedness with repeat distance of  $c = 614.9$  Å (chain axis). The cross section of the cell is  $a' = 9.6478$  Å,  $b' = 5.6490$  Å,  $\gamma' = 90^\circ$ . The calculated density is  $2.344$   $\text{g/cm}^3$  for a cell containing 2838 atoms. Several trial structures are proposed based on intensity fit of X-ray data. Because of the unusual nature of this structure, very similar structures, differing in only small details of packing give radically different cell constants. The problems of unit cell specification and space group determination (P1 or P1̄) will be presented in the poster session. \*Polymer Engineering, The University of Tennessee, Knoxville, TN 37916, USA

### 10.3-01 CONNECTIVE TISSUE POLYSACCHARIDES: CATIONS AS DETERMINANTS OF CONFORMATIONS. By Struther Arnott and A. K. Mitra, Department of Biological Sciences, Purdue University, West Lafayette, IN 47907, U.S.A.



The glycosaminoglycans, hyaluronate (I), chondroitin 6-sulfate (II) and 4-sulfate (III), dermatan sulfate (IV), keratan sulfate (V), found in connective tissues are linear, polyanionic polydisaccharides in which successive sugar units are linked alternately 1 $\rightarrow$ 3 and 1 $\rightarrow$ 4 diequatorially. Similar  $2_7$  helices have been observed for all. Similar  $3_2$  helices have been trapped for all except (V).  $3_3$  helices have been found in (II) and (IV). Hyaluronate is unique in having  $4_3$  allomorphs of two distinctive kinds. Common intra and inter-cellular cations ( $\text{K}^+$ ,  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ) influence the polyanion conformation quite specifically. How they do this has been visualized in detailed fiber diffraction studies in which the polyanion conformations and the sites of water molecules and cations have all been defined.

### 10.3-03 CORRELATIONS STRUCTURALES ENTRE LES POLY (n-METHYLENE TEREPHTHALATES) ET LEURS COMPOSES MODELES, n = 2 à 6. A. Palmer & F. Brisse, Département de Chimie, Université de Montréal, Montréal, H3C 3V1.

Les structures cristallines des poly(n-méthylène téréphtalates), (nGT), ont été généralement établies par analyse conformationnelle. Dans le cas du 3GT on fit aussi usage de composés modèles apparentés. Afin de confirmer la relation entre la conformation de la partie méthylénique de ces polyesters et celle de la séquence correspondante dans les composés modèles, nous avons synthétisé et déterminé les structures cristallines du dibenzoate de butylène-1,4 ( $R = 5,4$ ) et du di(*para*-nitrobenzoate) de pentylène-1,5 ( $R = 6,9$ ) composés apparentés au 4GT et 5GT respectivement. Il existe deux polymorphes du 5GT: une forme  $\alpha$ , relâchée et une forme  $\beta$ , tendue. La conformation de la séquence méthylénique du di(*para*-nitrobenzoate) de pentylène-1,5 se compare favorablement à celle de la forme  $\beta$  du polyester parent. Contrairement à la molécule étudiée plus haut celle de dibenzoate de butylène-1,4 ne présente aucun élément de symétrie alors que les deux formes ( $\alpha$  relâchée et  $\beta$  étirée) du 4GT possèdent un centre de symétrie au milieu de la séquence méthylénique. Toutefois il est possible de considérer deux régions distinctes dans la molécule de dibenzoate de butylène-1,4. L'une d'entre elle s'apparente à la forme  $\alpha$  4GT et l'autre à la forme  $\beta$  4GT. La comparaison systématique des conformations de polyesters du type nGT avec celles des composés modèles apparentés sera présentée pour  $n = 2$  à 6.