X-ray Diffraction Study of Disorder in Allied Spectra-1000 Polyethylene Fibers†

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ABSTRACT: Full-pattern refinement based on X-ray diffractometer data from Allied Spectra-1000 polyethylene reveals a crystallite structure including disordered atoms that can be interpreted as indicating a wandering of the polymer chain from one ordered site to the next in the *b*-axis direction. Parameters of the model that were determined include the unit cell, disorientation, crystallite size and paracrystallinity, atomic coordinates, anisotropic temperature factors, the setting angle, and interatomic distances and angles.

Introduction

Recently in this laboratory we began a program to try to improve the precision of X-ray diffraction analysis of the structures of crystalline polymer fibers. We hoped that by using a diffractometer we could obtain more accurate data than those estimated in the past by photographic techniques. We have also written a computer program for full-pattern least-squares (Rietveld) refinement of the structure based on the two-dimensional data thus obtained.

A sample of Allied Spectra-1000 polyethylene fibers[1] was used in the course of testing these methods, because the basic crystal structure of polyethylene is well-known from several X-ray[2,3] and electron[4,5] diffraction studies. The purpose of this report is to describe an apparent disorder that we observed as a result of this analysis and to discuss the parameters of the model that was used to fit the data.

Experimental Section

Individual fibers were pulled from a sample of Spectra-1000 yarn[6,7] and wrapped on a C-shaped support to produce a 170-strand sample with diameters of 0.4–0.6 mm. This sample was mounted on a four-circle diffractometer and aligned with the fibers (the crystallographic *c* axis) along the ϕ axis. Mo Kα X-rays were used with a graphite monochromator. A 2-mm square counter aperture was located 28 cm from the sample. All data were collected at room temperature.

Scattering from any region of two-dimensional reciprocal space could be measured in the bisecting mode by setting the diffractometer angles, χ, ω, and 2θ. Several types of scans were made, but the results reported here are based on 25 scans made parallel to the layer lines, five centered on each layer, at *l* values of −0.04, −0.02, 0.00, 0.02, 0.04, ..., 3.96, 3.98, 4.00, 4.02, 4.04. For each scan individual counts were measured for 240 s at steps 0.005 Å^{-1} apart in reciprocal space. Every 80 min a count was made at a reference position to verify that the beam intensity did not vary significantly. The "+" signs of Figure 1 show the measured data for the five scans that were centered on the layer lines. A list of the observed counts is available as supplementary material.

Full-Pattern Refinement Program. Structure refinement was done by using program FIBLS, a full-pattern fiber-diffraction least-squares program that we are developing. A complete description of this program will be published elsewhere; the following provides only a brief summary.

FIBLS uses as its observations the counts measured at specified positions in two-dimensional reciprocal space corresponding to a particular setting of the diffractometer. Usually these observations are grouped into scans made either parallel to the layer lines or parallel to the fiber-axis or meridional direction.

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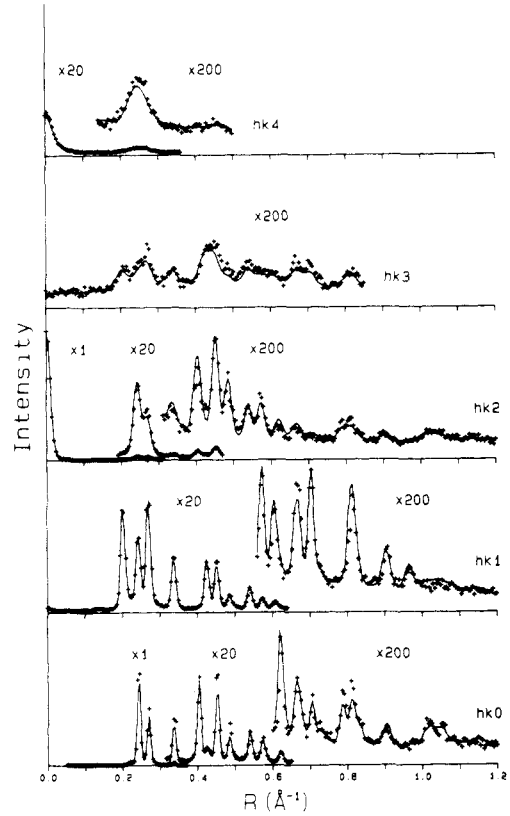

Figure 1. Diffractometer scans along the layer lines of Allied Spectra-1000 polyethylene. The "+" signs are the observations and the solid curves are calculated. The data are plotted on three different scales, as indicated on the figure.

Variables can be categorized as those which primarily affect the peak positions, the peak shapes, or the peak intensities. Peak positions depend upon the crystal lattice parameters and on the fiber-axis direction vector.

Peak shapes are determined by anisotropic particle-size parameters and by the fiber mosaic spread or disorientation that measures the width of the distribution of crystallite orientations from the fiber axis. Paracrystallinity parameters cause the peaks to broaden anisotropically as a function of their axial or radial distance from the origin.[8] The width of the observed peaks may also depend on the size of the counter aperture.

Peak intensities depend upon atomic coordinates, occupancy factors, and isotropic or anisotropic temperature factors. At present the amorphous contribution to the intensity is represented by straight-line segments between specified points. The background values at these points are parameters that may be adjusted. Future versions of the program may be improved to treat background as the Fourier transform of oriented amorphous material.[9]

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All of these parameters can be easily constrained by the user by simply writing a subroutine to set certain parameters in terms of others. The correct derivatives are determined automatically by using a procedure described by Busing.[10]

Also available to the user is a subroutine to set atomic coordinates in terms of rigid groups, interatomic distances, bond angles, and torsion angles. These distances and angles can be equated to extra parameters that can be adjusted by least squares, if desired.

When the refinement is underway but there are still discrepancies between some of the observed and calculated peaks, program FIBLS permits the addition of structure-factor increments as least-squares variables. The refined values of these increments can then be used to produce a difference Fourier map that should give clues as to how the model needs to be improved.

At the start of each cycle, the structure factors and derivatives for all possible reflections are calculated and saved. Then at each data point, corresponding to a diffractometer setting, the intensity is calculated by integrating over the counter aperture the contributions of the reflections that are accessible. Each such reflection is treated as a Gaussian distribution in reciprocal space with coefficients that depend on the peak-shape parameters described above.

Analytical derivatives are used to set up the matrix of normal equations, and parameter shifts are computed in the usual way. Principal-component analysis is available as a diagnostic tool to identify poorly determined or redundant groups of variables.

The observed and calculated patterns can be plotted as part of the printed output or by means of a separate pen-plotter program. The contributions of individual reflections to the calculated intensities can be identified by means of an auxiliary output file.

Polyethylene Refinement

Refinements were made keeping the methylene groups rigid with C–H distances set at the typical X-ray value[11] of 0.95 Å and an H–C–H angle of 106.1° as reported for propane.[12] The distance of the C atom from the *c* axis and the setting angle[3,13,14] were adjusted while maintaining the *Pnam* symmetry.[15] Anisotropic temperature factors for the hydrogen atoms were constrained to be the same as those for carbon. Variables included a scale factor, values of the background at specified points, orthorhombic lattice parameters, crystallite disorientation, and anisotropic crystallite size and paracrystallinity parameters.

Any contribution of the triclinic phase was ignored. A small equatorial peak at 0.220 $Å^{-1}$ is probably the triclinic 010 reflection described as very strong by Turner-Jones,[16] but its intensity is much less than other discrepancies in this region of the pattern.

The structure and its thermal ellipsoids after an initial refinement are shown in Figure 2. The apparent thermal motion shows marked elongation in the *b*-axis direction, indicating the possibility of some kind of disorder. The pattern calculated from this model exhibited significant discrepancies, especially in the 200, 201, and 202 reflections, which calculate weaker than they are observed.

The elongated thermal motion was eliminated by constraining the thermal displacements to be the same in the *a* and *b* directions. Structure-factor increments were refined for 32 reflections, and a difference Fourier map was calculated. The three strongest peaks from this map are located between the chain sites in the *b*-axis direction, as shown in Figure 3. Further refinement yields occupancies of 0.1 or less for these disordered atoms. The parameters of this final model are listed in Table I. The resulting calculated pattern, shown as solid curves in Figure 1, is in fair agreement with the observations. A comparison of the observed and calculated counts is available as supplementary material.

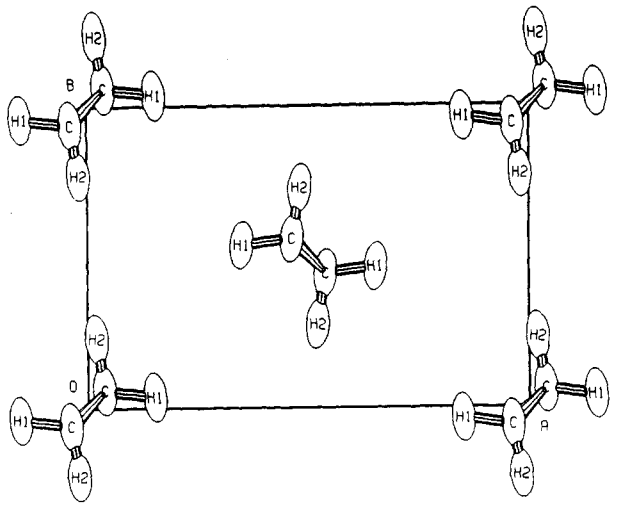

Figure 2. Thermal ellipsoids (30% probability) after a preliminary refinement of Allied Spectra-1000 polyethylene with hydrogen atoms constrained to have the same anisotropic temperature factors as the carbon atoms. The view is down the fiber axis.

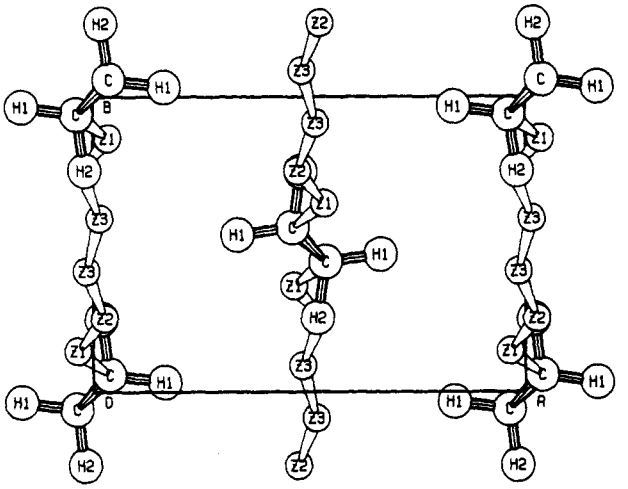

Figure 3. Structure of Allied Spectra-1000 polyethylene showing the disordered peaks, Z1, Z2, and Z3, found in a difference Fourier map. The bonds drawn between these peaks represent a possible interpretation in which the chain wanders from one ordered site to the next.

Discussion

It is clear that the properties of Allied Spectra-1000 polyethylene are very different from those of the melt-crystallized material. The lattice parameters found here differ significantly from those reported by Swan[17] or by Zugenmaier and Cantow[18] for highly linear polyethylene samples, the *a* axis being shorter and the *b* and *c* axes being longer.

Bunn[2] described as "serious discrepancies" the fact that his calculated intensities for the *hk*1 reflections were smaller than those observed. There is no evidence for these discrepancies from the present study.

The crystallites are highly oriented, the disorientation given in Table I being equivalent to an orientation function[19,20] of 0.999565 (7). The crystallite size is somewhat smaller than that reported by Kavesh and Schultz.[3] The mean-square atomic displacements (measuring disorder of the first kind) are considerably smaller than those found by these authors[3] or those assumed by Hu and Dorset[5] in their electron diffraction work. The setting angle is similar to that reported by others.[3,13]

Table I
Final Parameters of the Model after Full-Pattern Refinement of Allied Spectra-1000 Polyethylene

space group: *Pnam*, $Z = 4$ (for formula unit CH_2)
lattice: $a = 7.4069$ (12), $b = 4.9491$ (8), $c = 2.55117$ (9) Å
X-ray wavelength: 0.71073 Å
disorientation:[a] 0.690 (5)°
crystallite size:[b] $L_1 = L_2 = 121.0$ (9), $L_3 = 110.4$ (6) Å
paracrystallinity:[b] $T_{11} = T_{22} = T_{12} = T_{21} = 0.0174$ (8), $T_{31} = T_{32} = 0.0042$ (6), $T_{13} = T_{23} = 0.0055$ (5), $T_{33} = 0.00110$ (5) Å²
setting angle:[c] 45.9 (3)°
distance of C atom from c axis: 0.403 (2) Å
bond distances: C–C = 1.509, C–H = 0.950 Å
bond angles: C–C–C = 115.4, C–C–H = 108.7, H–C–H = 106.1°
weighting scheme: $\sigma(C)^2 = C + 0.0001C^2$, $w = 1/\sigma(C)^2$

Crystal Structure Parameters[d]

atom	occup	x	y	z	$U_{11} = U_{22}$	U_{33}
C	1.000	0.03906	0.05674	0.25	0.0255 (8)	0.0132 (3)
H1	1.000	0.16578	0.02703	0.25	0.0255	0.0132
H2	1.000	0.02300	0.24719	0.25	0.0255	0.0132
Z1	0.093 (5)	0.03500	0.86020	0.25	0.0760[e]	
Z2	0.109 (6)	0.02630	0.25010	0.25	0.0760[e]	
Z3	0.050 (4)	0.01490	0.58900	0.25	0.0760[e]	

[a] σ for the angular distribution $\exp(-\theta^2/2\sigma^2)$. [b] See ref 8. [c] angle between the b axis and the carbon atom plane. See ref 3, 13, and 14. [d] Standard errors are given for the independent variables; other parameters are derived or assumed. Coordinates are fractional, and the U's are mean-square atomic displacements, Å². [e] For the disordered atoms U corresponds to an assumed Debye–Waller B of 6.

The mean distance of the C atom from the c axis and the C–C distance derived from this parameter must be longer than the refined values reported in Table I, because the latter are reduced by thermal motion.[21] Neglecting the effects of internal bond-stretching and bond-angle-bending vibrations, corrected values of these quantities are 0.435 and 1.544 Å, respectively. These should be regarded as upper limits based on the assumption that the observed thermal motion is the result of translational displacements along the fiber axis and librations about this axis. If translations perpendicular to the carbon atom plane make significant contributions, then the corrected mean values will be smaller. This upper limit on the C–C distance is close to the expected value[22] of 1.541 Å for paraffin molecules. The calculated lower limit on the C–C–C bond angle is 111.4°, somewhat less than the 112.4° found in propane.[12]

The difference Fourier maxima are rather diffuse, and their exact locations depend on various assumptions of the model. In general, they are found on the mirror planes at $z = 0.25$ or 0.75, but this is not particularly significant. Density maxima on symmetry elements are often the result of the overlap of disordered peaks somewhat displaced from these elements.

One possible interpretation of the disorder corresponds to a wandering of the polymer chains from one site to the next, as is illustrated by the bonds drawn in Figure 3. The lengths of these bonds range from 1.44 to 1.56 Å, and they can therefore be reasonably accepted as C–C distances. It should be emphasized, however, that this interpretation is by no means unique. It is entirely possible that the observed extra density between pairs of sites in the b direction is the result of chain folding or some other deviation from the basic crystal structure.

It will be of interest to study other samples of polyethylene fibers to understand the relationship between this apparent disorder and the manufacturing process.

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Supplementary Material Available: Table of observed and calculated X-ray diffraction intensities (29 pages). Ordering information is given on any current masthead page.

References and Notes

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Registry No. Polyethylene, 9002-88-4.