Electron-Diffraction Structure Analysis of Polyethylene. A Direct Phase Determination

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ABSTRACT: Direct determination of crystallographic phases based on estimates of triplet and quartet structure invariants is used to solve the crystal structure of polyethylene using three-dimensional electron-diffraction intensity data from solution-crystallized and epitaxially crystallized specimens. In this analysis, the phase values of 40 out of 50 reflections are assigned ab initio. Valence parameters for the carbon zigzag chain, computed from the carbon atomic positions in the electrostatic potential map, are consistent with X-ray determination of alkane crystal structures. The chain setting angle calculated from the carbon atom position in the potential map is close to the value found for orthorhombic even-chain *n*-paraffins. A somewhat larger value is found when a zigzag chain model is rotated to find a minimum of the crystallographic residual, consistent with an earlier X-ray analysis.

Introduction

Because of the capability for obtaining single-crystal diffraction patterns from microcrystalline samples of linear polymers, electron diffraction has been often employed for deriving unit cell dimensions and space group symmetry to facilitate quantitative structure analyses with fiber X-ray diffraction data. In optimal cases, electron-diffraction intensity data have been used by themselves for quantitative crystal structure determination by a limited number of laboratories. The polymer structures have ranged from rather simple linear chains[1] to complex polysaccharides,[2] and, generally, the analyses are made from zonal data, although an increasing number of three-dimensional determinations have appeared in the literature in recent years.[3]

Unlike typical X-ray crystal structure analyses of small molecules, the number of observed intensity data from polymer microcrystals is rather small, even though the intensity data are distinct and the crystallographic symmetry easily discerned from the intensity-weighted reciprocal lattice. For this reason it has been fruitless, apparently, to carry out an ab initio structure determination where no preconceived notions about the molecular geometry are imposed upon this analysis. Models based on three-dimensional X-ray crystal structures of oligomers can be constructed, which are allowed to rotate about defined "linkage bonds" while the rest of the unit remains rigid.[1,2] During the structure search, two functions are simultaneously minimized. One is the crystallographic residual, which, by itself, can be an imprecise figure of merit when the number of refineable parameters approaches in order of magnitude the number of observed data. The other parameter is the internal energy of the molecule and/or packing array based on known nonbonded potential functions between the constituent atoms.

Although such structure analyses have proven to be very useful, they unfortunately can also be criticized for being subject to an assumed constrained conformation for the chain monomer. One possible way of overcoming such constraints is to attempt a direct analysis based on probabilistic estimates of Hauptman–Karle structure-invariant relationships of three- and four-phase combinations.[4,5] This methodology is almost unknown in electron crystallography although the first actual use of it[6] with zonal *hk*0 diffraction data from an *n*-paraffin was shown to produce a structure almost identical with the one elucidated by interpretation of a Patterson map. In this paper, the first application of the direct phase determination to electron-diffraction intensity data from a linear polymer is described by using polyethylene as an example.

Materials and Methods

Electron Diffraction. The intensity data used in this determination are the ones published by Hu and Dorset[7] that were obtained from polyethylene ($M_n = 2015$, $M_w = 2306$), which had been epitaxially oriented on benzoic acid and annealed in the presence of this substrate to improve the sample crystallinity. These data, which represent a projection onto the chain axes and also *hk*0 data from solution-crystallized samples, had been obtained at 100 kV with a JEOL JEM-100B7 electron microscope equipped with a goniometer stage allowing different regions of reciprocal space to be sampled. After integration of peaks from scans with a flat-bed microdensitometer and scaling between zones to produce a 3D set, some 50 unique intensity data had been obtained with a value appreciably above background. There was no Lorentz correction required. Minor perturbations of the intensity data due to dynamical scattering and incoherent multiple scattering were shown earlier[7] not to cause significant deviations from the kinematical condition.

With use of the orientation found in the *International Tables for X-ray Crystallography*,[8] the centrosymmetric space group is *Pnma* (No. 62) with $a = 7.48$ Å, $b = 2.55$ Å, $c = 4.97$ Å where *b* corresponds to the chain direction. For this space group, the phases of related equal-magnitude structure factors from several octants of reciprocal space are interrelated differently according to whether single or combined Miller index values are even or odd. Hence

$$F_{hkl} = F_{\bar{h}\bar{k}\bar{l}} = F_{\bar{h}kl} = F_{h\bar{k}l} = F_{hk\bar{l}}$$

$$h + l = 2n, \quad k = 2n$$

$$F_{hkl} = F_{\bar{h}\bar{k}\bar{l}} = -F_{\bar{h}kl} = -F_{h\bar{k}l} = F_{hk\bar{l}}$$

$$h + l = 2n, \quad k = 2n + 1$$

$$F_{hkl} = F_{\bar{h}\bar{k}\bar{l}} = -F_{\bar{h}kl} = F_{h\bar{k}l} = -F_{hk\bar{l}}$$

$$h + l = 2n + 1, \quad k = 2n$$

$$F_{hkl} = F_{\bar{h}\bar{k}\bar{l}} = F_{\bar{h}kl} = -F_{h\bar{k}l} = -F_{hk\bar{l}}$$

$$h + l = 2n + 1, \quad k = 2n + 1 \tag{1}$$

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Table I
Normalized Structure Factors for Polyethylene and a Comparison of Phases Determined in This Study (DP) with Those Found from a Model Calculation (M)

hkl	$\|E\|$	ϕ_{DP}	ϕ_M	*hkl*	$\|E\|$	ϕ_{DP}	ϕ_M
101	2.96	0	0	314	0.82	π	π
502	1.81	π	π	111	0.81	π	π
200	1.76	0	0	503	0.81	0	0
203	1.49	π	π	202	0.77	0	0
403	1.49	π	π	413	0.74	π	π
020	1.38	π	π	123	0.72	π	π
114	1.38	π	π	223	0.72	0	0
112	1.16	π	π	022	0.66	π	π
302	1.16	π	π	312	0.66	π	π
002	1.16	0	0	006	0.60		π
220	1.14	π	π	221	0.59		0
011	1.13	π	π	213	0.58	π	π
121	1.12	π	π	313	0.54		π
603	1.09	π	π	321	0.51	π	π
702	1.09	π	π	113	0.46		π
401	1.02	π	π	212	0.45		π
301	0.96	0	0	402	0.45	0	0
013	0.94	π	π	015	0.44	π	π
201	0.92	π	π	303	0.44	0	0
400	0.87	0	0	211	0.44	π	π
601	0.87	π	π	422	0.39		π
501	0.83	0	0	600	0.35		0
102	0.82	π	π	004	0.28		0
103	0.82	0	0	404	0.21		0
115	0.82	0	0	323	0.14		π

If $F_{hkl} = -F_{\bar{h}kl}$, for example, the phases of the two reflections differ by π.

Direct Phase Determination. Subject to the phase restrictions specified by the space group *Pnma*, certain linear combinations of phases can be identified as structure invariants in the subgroup $P\bar{1}$. The three-phase ("triple") invariant[5]

$$\psi = \phi_{\mathbf{h}_1} + \phi_{\mathbf{h}_2} + \phi_{\mathbf{h}_3}$$

is defined when $\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = 0$ where $\mathbf{h}_n$ are Miller indices. When $\mathbf{h}_1 \neq \mathbf{h}_2 \neq \mathbf{h}_3$, this is known as a sigma 2 (Σ_2) triple. The probability of $\psi = 0$ is estimated from the magnitude of

$$A_2 = k|E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}|$$

where

$$k = 2\sigma_3/\sigma_2^{3/2}$$

and

$$\sigma_n = \sum_{j=1}^{N} Z_j^n$$

The quantity Z_j is the value of the electron scattering factor for atom j at $\sin\theta/\lambda = 0$, and N is the total number of atoms in the unit cell. When $\mathbf{h}_1 = \mathbf{h}_2$ and $\mathbf{h}_3 = -2\mathbf{h}_1$, the probability of the resultant sigma 1 (Σ_1) triple predicting $\psi = 0$, π depends on the sign and magnitude of

$$A_1 = (|E_{\mathbf{h}}|^2 - 1)|E_{2\mathbf{h}}|/\sqrt{N}$$

The four-phase (quartet) structure invariant is similarly defined by

$$\psi = \phi_{\mathbf{h}_1} + \phi_{\mathbf{h}_2} + \phi_{\mathbf{h}_3} + \phi_{\mathbf{h}_4}$$

where

$$\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 + \mathbf{h}_4 = 0$$

The probability of $\psi = 0$ is based on the magnitude of

$$B = \frac{2}{N}|E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}E_{\mathbf{h}_4}|(|E_{\mathbf{h}_1+\mathbf{h}_2}|^2 + |E_{\mathbf{h}_2+\mathbf{h}_3}|^2 + |E_{\mathbf{h}_1+\mathbf{h}_3}|^2 - 2)$$

It is apparent, therefore, that the magnitudes of the normalized structure factors $E_{\mathbf{h}}$ are important for estimating the phase of the invariant linear combinations given above. These normalized values are calculated from the measured structure factors $|F_{\mathbf{h}}|$ by

$$E_{\mathbf{h}}^2 = |F_{\mathbf{h}}|^2/\epsilon\sum_{i=1}^{N} f_i^2$$

Here f_i is the electron scattering factor of atom i and ϵ is a multiplicity factor to account for zones containing translational symmetry elements for this space group.[9]

One is therefore left with numerous simultaneous equations based on the phases of the measured reflections. In order to evaluate their values algebraically, one is permitted to specify the phases of three noninvariant reflections ($h_ik_il_i$) so that the Miller indices obey the rule that neither $h_ik_il_i = eee$ nor

$$\sum_i h_ik_il_i = eee$$

where *eee* is a triple of even numbers. This specification thus defines the unit cell origin.[10] For this purpose, it is obviously advantageous to chose reflections that appear often in structure invariants with suitably large *A* or *B* values.

Results

The hierarchy of three-dimensional normalized structure factor values for polyethylene calculated from the data published earlier[7] is indicated in Table I. Based mainly on their presence in the Σ_2 triples formed from reflections with highest A_2 values, the phases of two *h0l* reflections and one *hkl* reflection are specified to define the origin, as shown in Table II. Four additional phase values are obtained from Σ_1 relationships for which $A_1 \geq 0.74$. With these seven phases, it is possible to work through Σ_2 triples to find the phase values for other reflections. Note that two groups of normalized structure factors are found that have phase relationships amongst them, as indicated initially by the algebraic quantities *a* and *b*. The value $b = \pi$ is determined as one works down the Σ_2 triples with decreasing A_2 value, but the value $a = \pi$ is found only after evaluating quartet relationships. Eventually, a value of $A_2 = 1.41$ is reached where a false phase assignment is made, inconsistent with the determination made from triples at higher A_2. This is found to be due to an erroneous π compensation for the space group related phases indicated above in (1). If all such relationships requiring an addition of π are ignored, the succeeding Σ_2 triples remain to be reliable at least to A_2

Table II
Sequence of Phases Determined from Structure Invariants: Origin Definition $\phi_{101} = 0$, $\phi_{112} = \pi$, $\phi_{403} = \pi$

$\sum_1$ Triples

$\phi_{202} = \phi_{002} = \phi_{200} = \phi_{400} = 0$

$\sum_2$ Triples

$\phi_{502} = \pi$
$\phi_{603} = \pi$
$\phi_{401} = \pi$
$\phi_{302} = \pi$
$\phi_{203} = \pi$
$\phi_{301} = 0$
$\phi_{601} = \pi$
$\phi_{020} = a$
$\phi_{121} = a$
$\phi_{011} = \pi$
$\phi_{013} = b$
$\phi_{114} = b$
$\phi_{220} = a$
$\phi_{102} = \pi$
$\phi_{702} = \pi$
$\phi_{201} = \pi$
$\phi_{103} = 0$
$\phi_{213} = \pi$
$\phi_{022} = \pi$
$\phi_{501} = 0$
$\phi_{314} = \pi$
$\phi_{015} = \pi$
$\phi_{413} = \pi$
$\phi_{321} = a$
$\phi_{111} = \pi$
$\phi_{223} = 0$
$\phi_{402} = 0$
$\phi_{123} = \pi$
$\phi_{312} = \pi$
$\phi_{115} = 0$

from triple at $A = 3.00$, $\phi_{013} = \pi = b$

Quartets

$\phi_{121} = \pi = a$
$\phi_{211} = \pi$
$\phi_{303} = 0$
$\phi_{503} = 0$

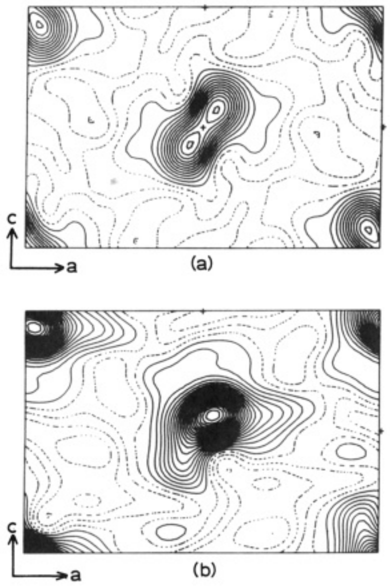

Figure 1. Electrostatic potential maps for polyethylene calculated from 40 phased $|F_o|$ magnitudes after direct-phase determination: (a) view down chains, calculated from $(h0l)$ data alone; (b) section at $y/b = {}^1/_4$.

$= 1.20$. Similarly, quartets become unreliable when $B = 5.54$ for the same reason. If we ignore structure invariants below this value for which a π-compensation is specified to make $\psi = 0$, the quartets can be used to $B = 4.00$. For these regions of lower probability, it is useful to confirm new phase assignments by comparing determinations made individually from Σ_2 triples and quartets.

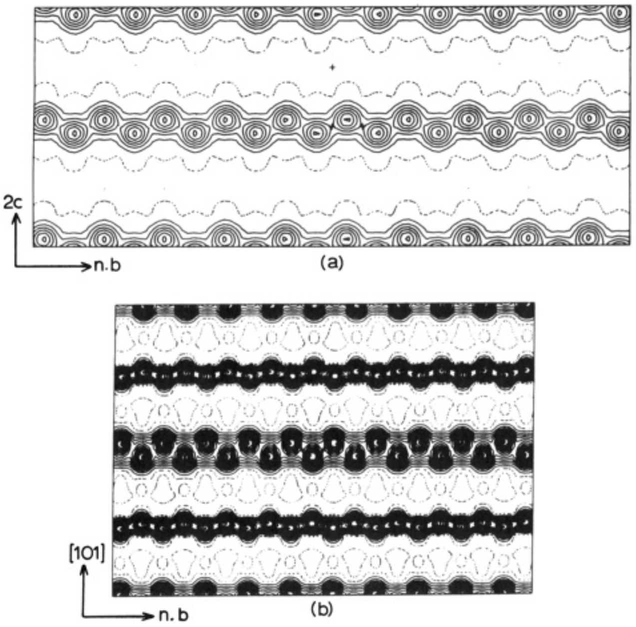

Figure 2. Electrostatic potential maps in views onto the chain axis calculated after direct-phase determination: (a) (100) plane; (b) (101) plane.

As shown in Table II, the direct phasing sequence assigns value to 40 out of 50 reflections. The values, moreover, are entirely consistent with the phases calculated using a model based on the orthorhombic layer packing of an n-paraffin[11] (Table I). The electrostatic potential maps calculated from the 40 phased $|F_o|$ values resemble electron density maps calculated from phase X-ray diffraction data.[12] For example, the projection down the chain axes (Figure 1a) and the density section at $y/b = {}^1/_4$ (Figure 1b) can be compared directly to our previously published maps for this polymer[12] based on X-ray data from another laboratory.[13] It is not possible to visualize the hydrogen atom positions clearly. For the projected structure in Figure 1a, the carbon atom positions are found at $x/a = 0.037$ and $z/c = 0.065$. The space group requires $y/b = 0.25$ when $Z = 4$. Thus, the calculated C–C bond distance is 1.54 Å, and the C–C–C bond angle is 112.3°. For the carbon atom position ($x/a = 0.033$, $z/c = 0.066$) found at the section at $y/b = 0.25$ (Figure 1b), the valence parameters are $d_{C-C} = 1.52$ Å and C–C–C = 114.3°. These values are typical of alkyl chain derivatives.[14]

It is also possible to visualize the chain packing in a projection onto the long axes. For example, a view down the [100] axis resolves the atomic positions of the carbon in the zigzag chain (Figure 2a). A projection onto the (101) plane (Figure 2b) shows one carbon zigzag, which is nearly viewed edge-on, and its neighbor where the line of sight is nearly normal to the zigzag plane, consistent with the nearly orthogonal arrangement of these planes in the crystal.

Discussion

It is clear from this analysis that traditional direct phasing techniques based on estimates of structure invariants could be useful for the determination of other polymer crystal structures. The electron-diffraction intensity data observed from lamellar polymer single crystals, which can be obtained from both solution-crystallized and epitaxially crystallized samples, can be close enough to the kinematical diffraction conditions to allow this ab initio analysis to be successful, as demonstrated in the study described here. The derived valence parameters are close to the values obtained from X-ray crystallography, and, thus, such analyses may be of use when molecular models lead to an ambiguity in the structure determination, e.g., when two distinct R-factor minima are found that cannot be distinguished by a statistical analysis. Admittedly, the example considered here is a rather simple one in terms of the number of atoms in the asymmetric unit. Nevertheless, similar use of direct methods recently to solve the 3D structure of a paraffin[15] and the lamellar packing of a phospholipid[16] from electron-diffraction intensity data indicates that this technique may also have further applications for more complex polymer structures.

The phase value for reflections in Table I that are not directly determined from the structure invariants can be found by a subsequent structure factor calculation using the carbon atom position located in the electrostatic potential maps in Figure 1. Alternatively, it may be possible to use the phase set by itself via the Sayre equation[17] to determine the missing values, a possibility that should be considered in future work.

It is also interesting to note that a rigid-body structure refinement will progress in a way similar to the one carried out earlier for polyethylene with fiber X-ray data.[12] Using the projected carbon atom position in Figure 1a, a calculated setting angle of 40.5° is similar to the 42.1° value found for the *n*-paraffin *n*-$C_{36}H_{74}$ using electron-diffraction data[18] or 42° for polyethylene determined from phased X-ray data.[12] Rotating a rigid zigzag chain about its axis, however, leads to a minimum of the crystallographic *R*-factor at a somewhat higher value, i.e., 46.7°, just as found with the X-ray data. Even given the uncertainty of this measurement[7,12] due to the imprecision of the crystallographic residual as a figure of merit,[19] the setting angle, nevertheless, may, in fact, be somewhat larger than the value found for orthorhombic even-chain paraffins.

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