The setting angle of polyethylene—A critique of powder X-ray determinations

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(*Received 1 November 1985*)

A critique is given of three determinations of melt-crystallized polyethylene crystal structures from powder X-ray data, one of which proposes a change in chain setting angle with hydrostatic pressure. Based on the use of Hamilton's statistics, which evaluates the significance of the crystallographic R-factor for a structural model in a refinement, and also the calculation of electron density maps from observed structure factor magnitudes and calculated phases, it is shown that the precision of two structure analyses is poor—mainly because of the paucity of diffraction data. Refinement of a model with a larger data set enables one to define the setting angle to lie somewhere between 44° and 48°.

(Keywords: polyethylene; X-ray diffraction; setting angle)

INTRODUCTION

The crystal structure of lamellar polyethylene has been known since 1939 to be basically similar to the orthorhombic form of n-paraffins[1]. However, the effect of chain folds on the 'setting angle', i.e. the angle the chain zig-zag makes to the $b \cong 5.0$ Å unit cell axis, is less well established, even though attempts have been made to determine this parameter with X-ray and electron diffraction intensity data[2-4]. Single crystal X-ray crystal structure analyses of an even-chain paraffin[5,6] have shown that this value is in the range 41°–42° for the two polymorphic forms, a result consistent with the electron diffraction structure analysis of the same material[7]. However, earlier electron diffraction analyses of other paraffins[4,8] have been found to give values between 42° and 48°. The value 46° has been found in X-ray crystal structure analysis of shorter odd-chain paraffins[9] and polyethylene[2], but 48° is also quoted as the value for melt-crystallized linear high molecular weight polyethylene at room temperature[4] and atmospheric pressure[3].

As discussed in various studies, including a recent review of the technique[10], the interpretation of electron diffraction intensity data from thin microcrystals for quantitative crystal structure analysis can be hampered by at least three perturbations of these data, which are exclusive of beam-induced radiation damage. An apparent diffraction incoherence caused by elastic bend deformations to the specimen is especially important for projections down a long unit cell axis and, as shown[7,11], would undoubtedly affect the earliest crystal structure analysis on paraffin, which gave only an incomplete (single layer) representation of the unit cell contents. Although the effect is subtle, n-beam dynamical diffraction has also been shown to affect the diffracted intensities with increasing chain length[11]. Finally, data from rather thick crystals include the errors due to incoherent multiple scattering, especially if the space group forbidden reflections are included in the Fourier transform[12] and thus some reported electron diffraction determinations have been shown[13] to be of questionable worth. An additional problem with such zonal data is that the determination is made only on a projection down the chain.

Presumably, a number of these difficulties would be overcome with a set of three-dimensional kinematical intensity data, e.g. as obtained from X-ray Debye–Scherrer diagrams. Such determinations have also been published[1-4], one of which[3], interestingly, describes a change of this setting angle with hydrostatic pressure and two others describe a temperature dependence[2,4]. Unfortunately, however, the analyses, as presented, are incomplete. Because these results are important for the understanding of polyethylene crystallization, they are evaluated further here in terms of their statistical significance and self-consistency and also used to determine experimental valence parameters for the carbon chain.

EXPERIMENTAL

Diffraction data

Powder X-ray data sets used in this analysis are published intensities from melt-crystallized Marlex 6002[2], Sholex 6050[4] (described as being similar to Marlex 50), and Du Pont Sclair[3]. The diffraction data from the latter material is of particular interest since a correlation is made between setting angles and hydrostatic pressure on the sample. In one experiment[4], 28 unique *hkl* diffraction intensities were measured with a scintillation counter from a drawn fibre specimen irradiated with Ni-filtered CuKα radiation. These were subsequently corrected for the Lorentz-factor, beam polarization and absorption. The details of the X-ray experiments on the other specimens are less specific but there were only 9 or 12 *hkl* intensities used in the respective analyses[2,3]. The unit cell constants for the melt-crystallized sample giving most intensity data are[4]: $a = 7.40$, $b = 4.93$, $c = 2.54$ Å, which are similar to the average values found for the sample subjected to various pressures[3], i.e. $a = 7.41 \pm 0.02$; $b = 4.92 \pm 0.01$; $c = 2.55$ Å or the values given by Kavesh

0032-3861/86/091349$03.00

and Schultz[2]: $a=7.39$; $b=4.93$; $c=2.54$ Å. The space group is Pnam or Pca2$_1$ (equivalent for $Z=4$ and a fixed atom $z/c=0.25$, as shown in ref. 14).

Computations

Structure factor calculations were carried out in the usual way, i.e.

$$F_{hkl}=\sum_h\sum_k\sum_l f_i \exp 2\pi i\left(h\frac{x}{a}+k\frac{y}{b}+l\frac{z}{c}\right)\exp(-B\sin^2\theta/\lambda^2)$$

where the isotropic temperature factor for rigid body refinement is defined as $B=6.0$ Å^2 for both atoms, which is similar to the value (5.8 Å^2) used by Kawaguchi *et al.*[4]. Scattering factor values were obtained from ref. 15. For analyses of setting angles a rotation function[16] is used, i.e.

$$\begin{vmatrix} x' \\ y' \end{vmatrix} = \begin{vmatrix} \cos\psi \sin\psi \\ -\sin\psi \cos\psi \end{vmatrix} \begin{vmatrix} x \\ y \end{vmatrix}$$

where ψ is the angular deviation from the 41.2° setting angle from carbon and hydrogen positions given by Abrahamsson *et al.*[17] for the $O_\perp$-methylene subcell. The rotation matrix thus generates new atomic coordinates for the structure factor expression above and the resulting experimental data are compared with observed data with the usual crystallographic R-value

$$R=\frac{\sum||F_{\text{obs}}|-k|F_{\text{calc}}||}{\sum|F_{\text{obs}}|}$$

where the data sets are normalized so that $\Sigma|F_{\text{obs}}|=k\Sigma|F_{\text{calc}}|$.

Electron density maps are also calculated in the usual way (either for (001) projections or as sections through the unit cell at $z/c=0.25$) i.e.

$$\rho(x,y,z)=\frac{1}{v}\sum_h\sum_k\sum_l\left|F_{hkl}\right|\exp i\phi$$

$$\times\exp-2\pi i\left(h\frac{x}{a}+k\frac{y}{b}+l\frac{z}{c}\right)$$

Statistical analysis

As shown by Hamilton[18], the significance of a R-factor minimum for establishing the validity of an improved structural model within a confidence level α is based on the ratio $\mathscr{R}=R_1/R_0$ where R_1 and R_0 are the values for (adjacent) models. That is, if $\mathscr{R}$ exceeds a value $\mathscr{R}_{p,n-p,\alpha}$ then the hypothetical model R_1 can be rejected as being less satisfactory at significance level α if $R_1 \geqslant R_0 R_{p,n-p,\alpha}$. For a greater degree of freedom, $n-p$, the quantity $\mathscr{R}$ is defined for p refined parameters and n data as

$$\mathscr{R}_{p,n-p,\alpha}\cong\left[\frac{\chi^2_{n-p}}{n-p}+1\right]^{1/2}$$

where values of χ^2_{n-p} are found in Table III in Hamilton's book[18]. For lesser degrees of freedom, values of $\mathscr{R}_{p,n-p,\alpha}$ are found in Table V of ref. 18 or are calculated from the relationship

$$\mathscr{R}_{p,n-p,\alpha}\equiv\left[\frac{\mathrm{p}}{\mathrm{n}-\mathrm{p}}F_{p,n-p,\alpha}+1\right]^{1/2}$$

where values of the distribution $F_{p,n-p,\alpha}$ are found in Table IV of this work (ref. 18). In this study $p=1$ and $n-p=27$, 11 and 8, respectively, for the data sets of Kawaguchi *et al.*[4], Phillips and Tseng[3], and Kavesh and Schultz[2].

For these tests it is usually assumed that the R-values are appropriately weighted. The weights given to R-values from powder X-ray analyses are usually based on reflection multiplicity[19]. Here we assume that the R-values are based on unit weights (as given above), which, although not exact, is not a bad approximation for a structure which is well refined[18] (here meaning that the valence parameters and temperature factor are reasonable).

RESULTS

Rigid body analysis

Values of $\mathscr{R}=R_i/R_{\text{min}}$ are given in *Table 1* for chain rotation refinements of the setting angle for data sets listed in three cited works. Using the significance level $\alpha=0.05$ (or one chance in twenty of the selected structure being incorrect) the computed value of $\mathscr{R}_{1,27,0.05}=1.075$ indicates that the data of Kawaguchi *et al.*[4] support structures within the range 44°–48°. The situation is even worse with the data of Phillips and Tseng[3]. Although the R-value minima correspond more or less to the values reported in their paper, the value $\mathscr{R}_{1,11,0.05}=1.200$ indicates that any setting angle between 41° and 56° can be accepted, e.g. for the data at 1 bar. Even for a probability of one chance in four that the structure may be false, i.e. $\mathscr{R}_{1,11,0.25}\simeq 1.07$, the range of acceptable structural models is rather large (e.g. 8°) for many pressures and again is not sufficient to pinpoint values within a 10° range expected for these setting angles.

Table 1 Values of $\mathscr{R}=R_i/R_{\text{min}}$ for published X-ray powder diffraction data from melt-crystallized linear polyethylene

Setting angle (deg)	Kawaguchi *et al.*[4]	Kavesh and Schultz[2]	Phillips and Tseng[3] 1 bar	1 kbar	2 kbar	3 kbar	4 kbar	5 kbar	6 kbar
34	–	2.22	1.45	1.45	1.47	1.45	1.32	1.23	1.23
38	1.40	1.46	1.28	1.27	1.28	1.26	1.12	1.09	1.10
41	1.14	1.00	1.15	1.14	1.15	1.11	1.03	1.03	1.03
44	1.00	1.17	1.09	1.07	1.06	1.02	1.00	1.00	1.00
48	1.06	1.63	1.02	1.00	1.00	1.00	1.01	1.03	1.08
52	1.31	2.11	1.00	1.04	1.02	1.01	1.15	1.18	1.22
56	–	2.78	1.07	1.12	1.11	1.09	1.36	1.39	1.38
R_{min}	0.112	0.054	0.163	0.162	0.159	0.164	0.146	0.147	0.145

Analysis of data from Kavesh and Schultz[2] ($\mathscr{R}_{1,8,0.05} \simeq 1.29$) constrains the setting angle to lie somewhere between 41 and 44°, if only one parameter is refined.

Electron density calculations

Within the angular limits of the above rigid body refinement and also the resolution limit of the X-ray diffraction data, it is found that no changes in calculated crystallographic phases occur. The features of the electron density map, therefore, are dependent upon the structure factor amplitudes, given the phases based on a carbon zigzag chain projection with a dyad at the C–C bond centre in the pgg projection. Electron density maps were calculated with observed structure factors and calculated phases at the level $z/c = 0.25$ (defined by unit cell symmetry) to locate the carbon atoms (see *Figure 1*). (Because of the small number of intensities, the data of Kavesh and Schultz[2] were not used.) These positions were used to calculate a setting angle and also C–C valence parameters (compare to $d_{cc} = 1.54$ Å, $\mathrm{C}\overset{\mathrm{C}}{\frown}\mathrm{C} = 111.8°$). These values are tabulated in *Table 2* and are compared with reported values and allowed ranges found from the above rigid body analysis.

From the values in *Table 2* it is readily seen that no justification can be found for the claimed dependence of setting angle on barometric pressure, since the data are not self-consistent. The computed C–C bond length deviates 0.11 to 0.16 Å from the actual and the bond angle 14.4° to 23.2°. Using the data of Kawaguchi *et al.*[4], a setting angle of 42° is found and a value for the valence parameter which differs 0.08 Å in bond length and 8.0° in bond angle.

Least-squares refinement

Using the most complete data set[4], a least-squares refinement of the polyethylene crystal structure was attempted starting from the known $O_\perp$ subcell atomic coordinates[17]. If only the carbon atom position is refined, valence parameters similar to those reported in *Table 2* are obtained ($d_{cc} = 1.60$ Å, $\mathrm{C}\overset{\mathrm{C}}{\frown}\mathrm{C} = 105.6°$) at $R = 0.18$ with a chain setting angle of 46°. If the carbon atom positions are refined in the presence of hydrogen atoms (which have fixed values), the resulting setting angle is 47.6° and valence parameters are very close to ideal values ($d_{cc} = 1.56$ Å, $\mathrm{C}\overset{\mathrm{C}}{\frown}\mathrm{C} = 109.8°$). If one generates theoretical hydrogen atoms for this carbon position and then refines on isotropic temperature factors, the final R value is 0.11, with final parameters as given in *Table 3*.

DISCUSSION

It is not difficult to demonstrate the transition of crystalline properties from that of a molecular crystal to that of a polymer as one proceeds from the lower paraffins through monodisperse higher paraffins[20,21], through polydisperse low molecular weight polyethylene[22] to very

Table 3 Final atomic positions and thermal parameters after constrained least-squares refinement with X-ray data from Kawaguchi *et al.*[4]

Atom	x/a	y/b	z/c	B_{iso} (Å^2)
C	0.045	0.061	0.25	6.4
H-1	0.181	0.020	0.25	4.5
H-2	0.017	0.269	0.25	9.0

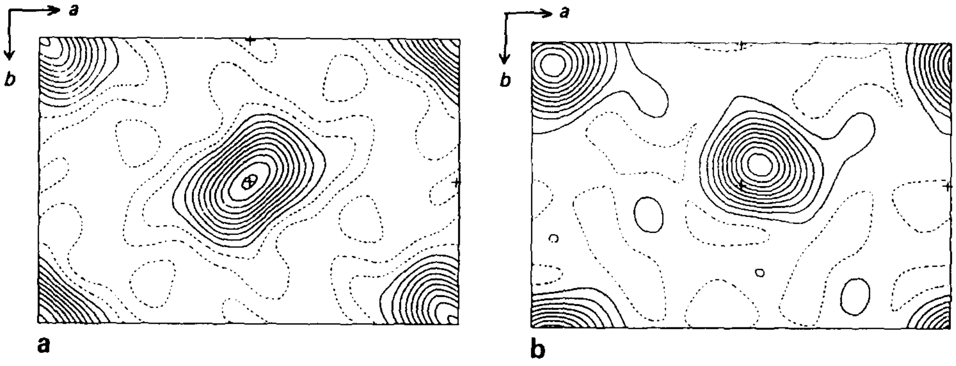

Figure 1 Electron density maps for polyethylene calculated from observed structure factor magnitudes of Kawaguchi *et al.*[4] and phases from structure factor calculation (see test). (a) Zonal projection from F_{hk0}, (b) section through three-dimensional map at $z/c = 0.25$ showing position of carbon atom

Table 2 Calculated valence parameters and setting angle determined from computed electron density maps

Data	Fourier map	Setting angle reported	Rigid body range ($\alpha = 0.05$)	$d_{\mathrm{C-C}}$ (Å)	$\mathrm{C}\overset{\mathrm{C}}{\frown}\mathrm{C}$
Kawaguchi *et al.*[4]	42.0°	44°–46°	44 to 48°	1.62	103.8°
Phillips and Tseng[3]:					
1 bar	48.2°	48°	41° to >56°	1.43	126.2°
1 kbar	41.8°	47°	41° to >56°	1.40	131.2°
2 kbar	48.9°	48°	41° to >56°	1.43	126.2°
3 kbar	45.2°	47°	41° to >56°	1.42	127.8°
4 kbar	41.4°	45°	38° to 52°	1.42	127.8°
5 kbar	43.6°	44°	38° to 52°	1.38	135.0°
6 kbar	40.3°	43°	38° to 48°	1.40	103.8°

long chain polymers. During these intermediate steps occur sectorization with ⟨130⟩ striations[20], then chain folding[21], with sectorization with ⟨1$\bar{3}$0⟩ striations[22] to give the texture of the infinite chain polymer. It is curious, however, that such a simple quantity as the chain setting angle has so far eluded crystallographic analyses for various reasons.

The problems encountered here are characteristic of systems where too few diffraction data are acquired to adequately define a crystal structure. Even though the asymmetric unit of polyethylene contains one 'heavy' atom, using the rule of thumb which suggests that 4 diffraction intensities be present for each refineable parameter[23]—e.g. two orthogonal directions, a scale factor and an isotropic temperature factor—then 16 data are required compared to 9 in the smallest data set. When using such limited data sets, then, a realistic view must be kept about the expected precision of the analysis and the fact that a mere R-value minimum is not the sole determinant of a structure. It is shown here that for the high pressure experiment[3], no claim can be made about a setting angle dependence, no matter how reasonable the experimental model may seem, simply because of the paucity of data. This insufficiency is not only expressed by the wide range of setting angles which are equally permitted by the analysis but also by the inaccuracy of the valence parameters determined from the electron density map. A similar comment can be made for the analysis made by Kavesh and Schultz[2]. Although a very small R-factor minimum (0.054) is found by rigid body refinement, if four parameters are being refined by least-squares then, because there are only nine data, any value 2.27 times larger would indicate an equally probable model. The structure analysis made with the larger data set is undoubtedly more precise. As shown above however, there are still not enough data to allow unconstrained refinement. Least-squares refinement for the carbon coordinates gives a setting angle in the range allowed by the rigid body refinement on the whole chain with the same R-value minimum. Although the significance test at $\alpha = 0.05$ is suitably small ($\mathcal{R} = 1.07$), the residual minimum is nevertheless still too insensitive to allow one to pinpoint a setting angle. Moreover, small variations in isotropic temperature factors are probably not significant but there is no indication of the anisotropy suggested by other workers[1,2].

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