

Crystal structure analysis of polyethylene with electron diffraction intensity data: Deconvolution of multiple scattering effects

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Recent determinations of n-paraffin and polyethylene crystal structures from electron diffraction data have claimed chain setting angles different from those reported for n-hexatriacontane. Re-evaluation of these data show that these determinations must be questioned because the intensities used were badly marred by multiple scattering. Due to the complexity of this phenomenon, efforts to deconvolute this error source are only partially successful. An independent structure determination for mostly unilamellar crystals of very low molecular weight polyethylene with data less affected by multiple scattering indicates that the atomic coordinates originally proposed for polyethylene in the earliest X-ray structure can still be justified.

Keywords Electron diffraction; polyethylene; multiple scattering; crystal structure

INTRODUCTION

For the typical microcrystalline preparations commonly encountered in polymer physics, electron diffraction data have been gainfully used to elucidate crystal structures. The availability of spot patterns from single microcrystals, for example, enables a facile determination of unit cell symmetry. It also removes the ambiguities found in powder X-ray diffraction studies of microcrystalline aggregates or fibres which are caused by the overlap of reflections with nearly the same reciprocal spacing. A number of polymer crystal structure determinations representing various complex repeating units have used electron diffraction intensity data¹⁻⁵.

Since good single crystal electron diffraction data have long been available⁶, it is rather surprising that there is currently a controversy over the structure of linear polyethylene. Recent analyses of such data have been in apparent conflict with the earliest X-ray structure determination reported by Bunn⁷. Electron diffraction studies⁸⁻¹⁰ were reported to give a chain 'setting angle' (i.e., angle to the orthorhombic $b \approx 4.95 \text{ \AA}$ axis) different (e.g. 5°) from the *ca.* 42° found by X-ray studies of orthorhombic even-chain n-paraffins¹¹ or polyethylene⁷ and, furthermore, a dependence of this angle on chain length was claimed⁹.

Extensive studies on the utility of electron diffraction intensities for quantitative crystal structure analysis of organic materials, while showing great promise for the technique, have also demonstrated the occurrence of data perturbations not commonly encountered in X-ray crystallography. The importance of n-beam dynamical scattering is well documented¹²⁻¹⁴, and its implications for the success of crystallographic phasing procedures such as 'direct methods' have been discussed in detail¹⁵. Furthermore, elastic crystal bending is shown to have a significant

effect on diffraction intensities, particularly if the unit cell length along the incident beam direction is large¹⁶. The effect of this data perturbation for paraffinic materials and other organics has been extensively considered in terms of successful crystal structure analysis^{14,17,18}. In light of these effects, procedures have evolved for defining optimal diffraction conditions and for appropriate structure refinement¹⁹. Full cognizance of error sources allowed the first application of direct phasing procedures to electron diffraction data²⁰; the resulting structure of an n-paraffin was in full agreement with the earlier X-ray determination^{12,20}.

This paper shows that the discrepant results of electron and X-ray diffraction studies on polyethylene are due to yet another data perturbation, i.e., the multiple scatter first noted for paraffins by Cowley *et al.*²¹ Although the reported procedure⁸⁻¹⁰ for polyethylene structure analysis using optical transformation of masks related to the electron diffraction patterns is certainly a valid means to obtain a Patterson function²², the intensity data used for these analyses are demonstrated to be so badly affected by this multiple scatter that a correct structure, in fact, could not be derived.

EXPERIMENTAL

Electron diffraction data

Two sources of electron diffraction data were used in this work. One is taken from Figure 4b of ref 10 in which the radii of spots in the depicted diffraction pattern mask are proportional to the observed structure factor magnitudes from unfractionated linear polyethylene. The lamellar thickness was reported to be 120 \AA .

Thin (mostly unilamellar) crystals of a low molecular weight (1000 daltons) polyethylene (Polyscience, Inc.,

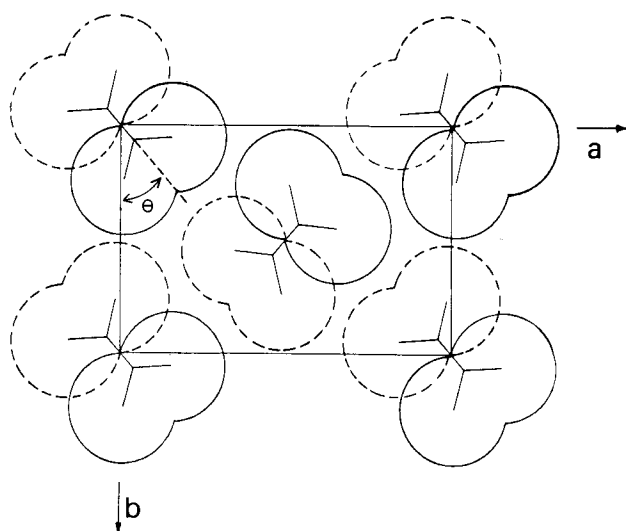


Figure 1 Projection of the polyethylene crystal structure down the c -axis defining the setting angle as the angle between the projected C—C bond and the b -axis

Warrington, PA) were grown from dilute solutions in warm *n*-hexane onto carbon-film covered 400-mesh Cu electron microscope grids. Selected area electron diffraction patterns and bright field images (6.7 K magnification) obtained at 100 kV on a JEOL JEM-100B electron microscope were recorded on Kodak NS5T No-Screen X-ray film. This very fast photographic emulsion combined with low incident beam currents ensures that the sample is virtually unaffected by radiation damage¹². A low angle X-ray diffraction measurement on bulk material gives a lamellar 'long spacing' (117 Å) similar to that found for the linear polyethylene used in the cited study, and is somewhat longer than predicted by the molecular weight estimate provided by the manufacturer.

After the diffraction films were scanned by a Joyce-Loebl MkIIIIC flat-bed microdensitometer, the areas under the diffraction peaks were used directly as the recorded intensities. No Lorentz correction of the type used in the previous study^{9,10} was employed. Although this is justified elsewhere^{12,23}, it should be reiterated that such microcrystals are largely perfect and not the sort of mosaic that would be modelled by the Lorentz correction. The principal smearing of diffraction intensities along reciprocal lattice rods is due to elastic crystal bending and, therefore, it is found that a direct use of the measured intensities is a more correct treatment of the data.

Computations

A starting structural model for polyethylene is represented by the chain packing found in X-ray crystal structures of several representative paraffins and paraffinic derivatives²⁴. In this orthorhombic structure with *pgg* plane group symmetry in the projection down the chain c -axis (Figure 1), the fractional atomic coordinates are:

	x/a	y/b	z/c
C(1)	0.p38	0.065	0.25
H(1)	0.179	0.049	0.25
H(2)	0.010	0.273	0.25

with representative unit cell edges: $a = 7.478$ Å, $b = 4.970$ Å, $c = 2.549$ Å. This structure has a chain setting angle of

41.3°. Using the projected C—C and C—H bond distances found after transformation to polar coordinates, the atomic coordinates for chain setting angles from 30° to 55° were generated at 1° intervals. These were used for calculation of kinematical structure factors utilizing Doyle-Turner²⁵ atomic scattering factors. The rotationally varied model structure was compared to experimental data by the usual crystallographic R factor, i.e.

$$R = \frac{\sum ||F_0| - k|F_c||}{\sum |F_c|}$$

with data sets scaled such that $k\sum |F_c| = \sum |F_0|$.

Incoherent secondary scattering was modelled by calculation of the convolution products I'_{hk}

$$I'_{h_1 k_1} = \sum_{h_2 k_2} I_{h_2 k_2} I_{h_1 - h_2, k_1 - k_2} \quad (1)$$

These intensities were combined with the kinematical intensities from the zone I_{hk} to give

$$J_{hk} = I_{hk} + mI'_{hk} \quad (2)$$

where J_{hk} represents the total intensities from the crystal. The weight of the self-convolution contribution m is determined by the relative intensities of the plane group forbidden reflections I_{h00} and I_{0k0} (where h and k are odd) as shown by Cowley *et al.*²¹; i.e. in this work, $m = (I_{100} + I_{300} + I_{010}) / (I_{020} + I_{110} + I_{200} + I_{310} + I_{400})$ is used to determine the contribution from multiple scattering.

All major calculations were carried out on a PDP VAX 11/780 computer.

RESULTS

Reference calculations

Kinematical diffraction data were generated to resolution $\sin \theta/\lambda = 0.80$ Å⁻¹ for a polyethylene structure with setting angle of 42°. The behaviour of the R value is shown in Figure 2A for the comparison of diffraction data from structures having setting angles other than 42°. As expected, the minimum is seen to be very sharp.

When secondary scattering effects are included in the calculated diffraction data, the behaviour of the R value changes. A self-convolution of intensities (see equation (1)) at weight $m = 0.06$ (see equation (2)) based on the relative forbidden intensity sum calculated from the diffraction mask in ref 10, was added to the kinematical intensities of the structure with 42° setting angle. In this calculation, crystallographic intensities to resolution $\sin \theta/\lambda = 0.40$ Å⁻¹ were self-convoluted to give an artificially extended intensity set with resolution $\sin \theta/\lambda = 0.80$ Å⁻¹. In other words the data at resolution < 0.4 Å contains true intensities contaminated by a self-convolution while the data at > 0.4 Å resolution is only due to the multiple scattering. This set was compared to true higher resolution ($\sin \theta/\lambda = 0.80$ Å⁻¹) crystallographic intensities derived from structure models with different setting angles. As shown in Figure 2C, there is no well-defined R value minimum. Definition of an exact setting angle with such data is therefore impossible.

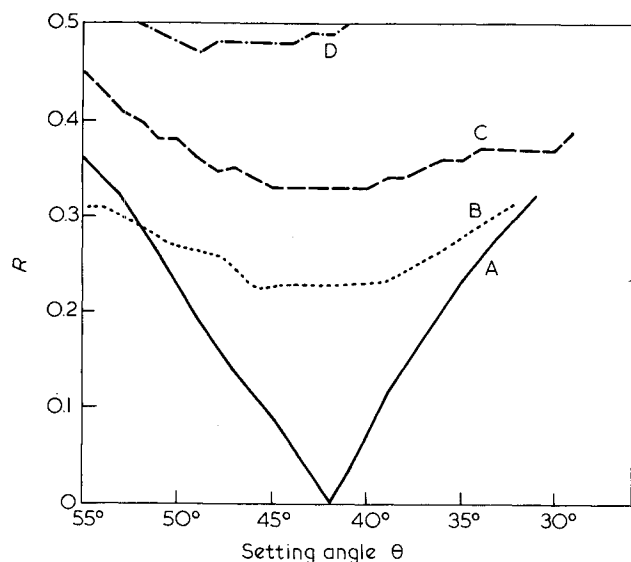


Figure 2 Behaviour of R value with change of polyethylene chain setting angle. (A) Comparison of rotated structures with a structure at setting angle 42° ; (B) comparison of model structures of different setting angles to observed diffraction data from a short chain polyethylene; (C) comparison of model structures with 42° setting angle structure diffraction data including multiple scattering (I^* only); (D) comparison of model structures using previously published data¹⁰ from multilamellar polyethylene microcrystals



Figure 3 Electron diffraction pattern (hko) from thin crystal of short chain polyethylene showing small contribution due to multiple scattering

Data from earlier polyethylene structure analysis¹⁰

Agreement of calculated kinematical diffraction data for structure models with different setting angles with diffraction data given for polyethylene¹⁰ is universally poor (Figure 2D). There is a very slight minimum at a setting angle of 49° but it is impossible to deduce a correct structure. When the unnecessary Lorentz correction²⁶ of the form d^*_{hkl}/α is removed from this data set the agreement with all structure models is even worse.

Electron diffraction data from a shorter chain polyethylene

Electron diffraction intensities were recorded from monolamellar crystals of a shorter chain polyethylene which have lamellar thickness near that of the polymer

considered by the previous workers (see above). As shown in Figure 3 it is possible to record diffraction patterns with a small contribution from secondary scattering. Although the data resolution ($\sin \theta/\lambda = 0.50 \text{ \AA}^{-1}$) is somewhat lower than considered above, it should be sufficient to define a correct structure. In Figure 2B we again see some flattening of the R value minimum, allowing any structure with setting angles between 42° and 46° to be equally likely. However, correction for secondary scattering using the 42° structural model and an m -value of 0.02 determined from the intensities of the space group forbidden reflections (see above) lowers the R value from 0.23 to 0.17 (Table 1).

DISCUSSION

The presence of multiple elastic electron scattering from microcrystals is favoured by the existence of a layered structure²⁶. Multilamellar crystals of *n*-paraffins or polyethylene are good examples of such structures, and, accordingly, will give electron diffraction patterns with very intense space group forbidden reflections. In paraffins this separation of layers may be due to occasional mismatches of methyl end planes since this is the site of least van der Waals attraction in the crystal. For the latter case of polyethylene, the lamellar surface structure is undefined, but probably is not so well-ordered as the paraffin crystal structure²⁷.

The salient effect of multiple scattering, besides the concealment of actual space group symmetry, is the spurious increase of data resolution. Use of such electron diffraction data in previous studies of polyethylene and *n*-paraffins⁸⁻¹⁰ has led to crystal structures which cannot be substantiated. That an attempt to correct for multiple scattering by mere removal of space group forbidden reflections from the diffraction mask¹⁰ had little effect on the appearance of the resulting Patterson map is not

Table 1 Comparison of observed diffraction data to kinematical data $|F_{\text{calc}}|$ from structure with setting angle 41.3° ²⁴, and with data $|F'_{\text{calc}}|$ corrected for multiple scattering. $|F'_{\text{calc}}| = J_{hk} I_{hk}^{1/2}$; $J_{hk} = I_{hk} + m I_{hk}^* I_{hk}$, where m is adjusted to reflect the relative weight of forbidden intensities in Figure 3

hko	$ F_{\text{obs}} $	$ F_{\text{calc}} $	$ F'_{\text{calc}} $
200	6.76	8.77	8.04
400	2.60	3.80	3.73
600	1.06	1.51	1.64
110	8.33	9.03	8.25
210	2.22	2.07	1.99
310	3.25	2.90	3.32
410	1.96	1.48	1.52
510	1.77	1.67	1.83
610	1.06	1.36	1.20
020	4.15	4.53	4.50
120	1.99	1.82	1.88
220	3.19	1.71	2.37
320	2.09	2.10	2.08
420	1.55	0.61	1.07
520	1.84	1.74	1.68
620	0.89	0.10	0.49
720	1.06	1.56	1.30
130	1.84	2.02	2.11
230	2.16	2.11	2.02
330	1.48	0.73	0.94
430	1.99	1.57	1.58
530	1.12	0.73	0.68
630	1.00	1.82	1.53

surprising. Multiple scattering involves self-convolution of intensities such that *all* reflections in the diffraction pattern are affected. To correct for this would involve a deconvolution of the whole data set. This is a very difficult task indeed. Not only are single convolutions $I*I$ contributing to this perturbation (single scatter) but also multiple convolutions $I*I*I$, $I*I*I*I$, etc., each with its own weight²¹. Moreover the increased number of layers in a multilamellar structure increases the weight of higher order terms. To adequately correct for this scattering would entail a detailed knowledge of the total crystal defect structure, a task which is beyond present capabilities; since this also changes from crystal to crystal.

The best correction for multiple scattering is its avoidance. Use of unilamellar paraffin or polyethylene crystals favours this although the presence of a point defect (kink) along a chain may cause it to appear. Diffraction patterns used for crystal structure analysis should contain minimal multiple scattering contribution. Although the actual diffraction resolution seen in such patterns may disallow definition of subtle structural details, such as small variations of chain setting angle, there is no merit to exacerbate an already difficult experiment with poor data.

The analysis presented here indicates that the setting angle found for n-hexatriacontane is equally appropriate for polyethylene. Although higher resolution data are desirable, there is no crystallographic reason at present to propose structures different from n-paraffins.

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