# Direct Determination of Polymer Crystal Structures by Electron Crystallography – Isotactic Poly(1-butene), Form (III)

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## Abstract

Three-dimensional electron diffraction intensity data from form (III) of isotactic poly(1-butene) have been collected by tilting solution- and epitaxially grown thin microcrystals. The orthorhombic space group is $P2_12_12_1$ with cell constants $a = 12.38$, $b = 8.88$ and $c = 7.56$ Å, the latter being the chain repeat. The crystal structure was determined by direct methods, employing the tangent formula ($QTAN$) and initially 106 phase values were found for 125 unique observed reflections. Refinement by Fourier techniques gave a structure very similar to that proposed in an earlier powder X-ray diffraction study. After rejecting three reflections during the refinement process, the final $R$ factor for 122 reflections is 0.26 and the r.m.s. phase error to the earlier model is only 4°, with no deviations found for the centrosymmetric reflections. The structure consists of infinite chains, each having approximate $4_1$-helical symmetry with the chains coiled about the true crystallographic $2_1$ axes at $(\frac{1}{4},0,z)$ and $(\frac{3}{4},\frac{1}{2},z)$.

## Introduction

Polymer physics is the main area of organic materials research where quantitative electron crystallographic techniques have been most often employed for *ab initio* crystal structure determination. Typically, these analyses often rely on separate X-ray crystal structure determinations to elucidate the geometry of monomeric or oligomeric segments. Such results are used to decide which parts of the polymer chain can be held conformationally rigid so that 'linkage bonds' can be defined. The ensuing chain model is then twisted around these linkages in a search for minimal non-bonded potential energy (Brisse, 1989). Also, if one has a zonal electron diffraction data set in a projection down the chan axis (*i.e.* for crystals grown from solution), a simultaneous minimum of the crystallographic $R$ factor calculated using the measured intensity data can also be sought (Brisse, 1989; Pérez & Chanzy, 1989). This procedure, which is adapted from fiber X-ray analysis, often yields reasonable crystal structures for linear polymers. On the other hand, such a use for electron diffraction intensities implies an underlying suspicion that they may not represent a simple Fourier transform of the unit cell, a mistrust possibly justified by early attempts to use such data for quantitative structure determinations. Recent successful uses of direct phasing methods for analyses of such data sets (Dorset, 1992a), however, demonstrate that this overly cautious viewpoint is unwarranted, as long as the theoretical constraints to data collection (Cowley, 1981) are recognized and respected so that intensities adequately near the kinematical approximation can be measured.

Since goniometer stages exist for electron microscopes, it is also possible to collect three-dimensional data from solution-crystallized samples and such data have been utilized for conformational structure analyses (Brisse, Rémillard & Chanzy, 1984; Chanzy, Pérez, Miller, Paradossi & Winter, 1987; Guizard, Chanzy & Sarko, 1985; Meille, Brückner & Lando, 1989). However, direct phasing techniques, based on the probabilistic estimates of phase invariant sums, have been found to be just as effective for *ab initio* structure determinations, wherein no previous assumptions regarding chain geometry are made. Using a previously published tilt series of intensities from a solution-grown crystal (Brisse, Rémillard & Chanzy, 1984), the structure of poly(*trans*-1,4-cyclohexanediyldimethylene succinate) was redetermined by evaluation of three- and four-phase structure invariants (Dorset, 1991a) and the model was subsequently refined by Fourier methods. Because of the well known 'missing cone' of diffraction data resulting from a limited goniometer tile range (thus excluding details of the Fiber axis repeat if only solution-grown crystals are used), supplementary intensity data from epitaxially oriented samples (Wittmann, Hodge & Lotz, 1983) have been found to be invaluable in enabling a more complete sampling of reciprocal space to be made for data collection.

Direct phase analysis of such combined data sets include the determinations of poly(ethylene) (Dorset, 1991b) and poly(ε-caprolactone) (Dorset, 1991c). The latter structure is non-centrosymmetric and was solved by finding phase values for some non-restricted intensities (via an algebraic unknown) after two zonal sets were assigned phase values.

Although these initial results are encouraging, it is of particular interest to determine how far these techniques can be extended to general, non-centrosymmetric polymer structures which do not have a pseudo-cell repeat to aid in the construction of a molecular phasing model [e.g. the case of poly-(ε-caprolactone)]. For this purpose, we have chosen the non-centrosymmetric form (III) conformation of poly(1-butene) as a suitable test of the direct phasing approach. This polymorph is unstable to mechanical stresses. It has not been obtained in fiber form and, therefore, is not amenable to classical fiber X-ray diffraction analysis. As a consequence, the only previous structural characterization utilized powder X-ray diffraction data (Cojazzi, Malta, Celotti & Zannetti, 1976) and was carried out by conformational refinement of a chain model with idealized bond distances and angles. However, the limited number (21) of measured intensities and the overlap of numerous relections for most of the previously measured X-ray maxima make an independent ab initio analysis, based on single crystal data, particularly important. The following electron diffraction structure analysis, therefore, is also the first single crystal determination reported for this polymer and actually defines a methodology for determining the structures of such unstable polymer crystal forms.
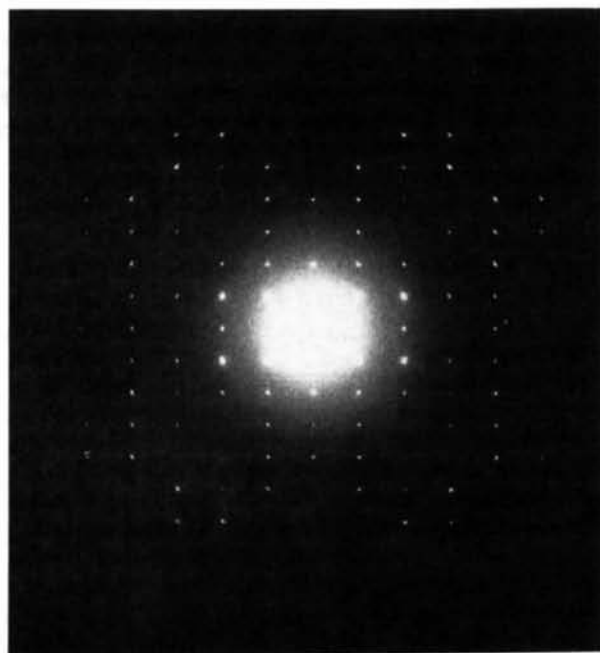
## Materials and methods

### Data collection

High molecular weight ($M_r$ = 180 000 or 750 000), isotactic poly(1-butene) (Aldrich Chemical Co., Inc., Milwaukee, WI) (tacticity > 99%) was solution-crystallized as form (III). Preparation methods for single crystals and epitaxially oriented film followed two different procedures, both, however, utilizing the organic compound 2-quinoxalinol (2-QUIN), which was found to initiate the crystallization of form (III). When 2-QUIN was used in a small quantity as a nucleating agent for growth from thin molten films, it prevented the spontaneous crystallization of poly(1-butene) in form (II). [Note that form (III) crystals can also be obtained by solution-crystallization, but are curled and hence inappropriate for the current investigation.] For single crystals, a hot concentrated solution of 20% polymer and 80% $n$-$C_{32}H_{66}$ in $CHCl_3$ was prepared, which was evaporated on a glass slide to form a thin film. The 2-QUIN was then sublimed and condensed onto the polymer/$n$-paraffin thin film to form small crystals. The paraffin and poly(1-butene) were then melted at 413 K and slowly cooled (0.1 K min$^{-1}$) to ambient temperature. The poly(1-butene) crystallization, nucleated by crystals of 2-QUIN, occurs for form (III) at ca 363 K in molten paraffin, which crystallizes at ca 333 K. 2-QUIN and the paraffin diluent are then washed away with ethanol and chloroform to leave thin, fairly large crystals of the polymer (20–50 mm lateral diameter). Using techniques developed in the Strasbourg laboratory several years ago (see Wittmann & Lotz, 1990), epitaxial growth of the same molecular conformer was effected by the use of 2-quinoxalinol as a substrate (Kopp, Wittmann & Lotz, 1993). For this purpose, a thin polymer film (10–20 nm) was produced on a glass slide by evaporation of a $CHCl_3$ solution. 2-QUIN crystals form on this film by controlled evaporation of a saturated $CHCl_3$ solution. Epitaxial crystallization is then induced by melting the poly(1-butene) film on a Kofler stage and cooling to ambience. Again, the substrate crystals are washed away with $CHCl_3$ to leave the epitaxially oriented polymer film.
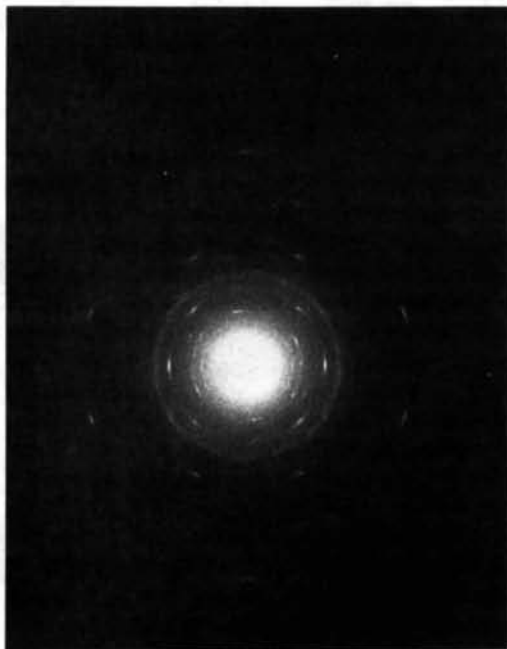
Electron diffraction patterns were recorded at 120 kV on Kodak DEF-5 film using a Philips CM-12 electron microscope equipped with a goniometer stage. For solution-grown crystals, the $hk0$ diffraction pattern (Fig. 1a) is found at 0° tilt and other three-dimensional data are accessed by tilting the microcrystals around the $a^*$ and $b^*$ axes of this reciprocal net. Epitaxial crystals give ($2h$, $h$, $l$) patterns from the untilted samples (Fig. 1b), which means that the (110) plane is the contact plane with the 2-QUIN substrate, i.e. normal to the electron beam. This means that the $a^*c^*$ and $b^*c^*$ planes are within reach of the ± 60° tilt limits of the goniometer stage when $c^*$ is the tilt axis. Hence, combining the data from both types of crystal means all the reciprocal space is accessible for data collection. From observed systematic absences, the orthorhombic space group is identified to be $P2_12_12_1$. Occasionally, violations of the forbidden (300) reflection are seen, probably due to some secondary scattering (Cowley, Rees & Spink, 1951), but its absence is justified by the numerous $hk0$ diffraction patterns observed and noting its disappearance as crystals are rotated around the $a^*$ axis. The unit cell constants are measured consistent with the parameters given earlier by Cojazzi et al. (1976), viz. $a$ = 12.38, $b$ = 8.88, $c$ = 7.56 Å.

Intensity data were measured by integration of the scans obtained from a Joyce Loebl Mk III C flat-bed microdensitometer. For data measured from solution-crystallized samples, no Lorentz correction was applied, as established earlier (Dorset, 1976). However, since the reflections in films from epitax-

ially crystallized samples are arced and extend over a extensive tilt range at considerable intensity, a Lorentz correction, suggested earlier by Vainshtein (1956) and used later to correct data from similar curvilinearly deformed microcrystals (Dorset, Massalski & Fryer, 1987), was employed, viz. $|F_{hkl}| = (I_{hkl}d_{hkl}^*)^{1/2}$, where $d_{hkl}^*$ is the reciprocal spacing for a given reflection hkl. To assemble a three-dimensional data set, the constantly excited reflections on a reciprocal lattice row are used to scale intensities for any given tilt around a particular reciprocal axis. Data from separate tilt series are scaled with reflections common to both sets, as described earlier (Hu & Dorset, 1989). It is encouraging to note that there are no major variations of continuously excited relative intensities as a crystal is rotated around a reciprocal axis. Despite the low estimate of $B_{iso}$ (0.0 Å$^2$) from the Wilson plot, this suggests that the data are reasonably close to the kinematical limits required for ab initio structure analysis (Cowley & Kuwabara, 1962; Dorset, 1980). In all, 125 non-zero intensity data were collected from these films. An additional zero value for $|F_{002}^{obs}|$ was retained in structure-factor calculations, for reasons which will be made apparent. After evaluation of an overall temperature factor from a Wilson (1942) plot, normalized structure-factor magnitudes, $|E_{hkl}|$, were calculated in the usual way from the observed $|F_{hkl}|$ with electron scattering factors (Doyle & Turner, 1968).



(a)



(b)

Fig. 1. Electron diffraction pattern from poly(1-butene), form (III): (a) hk0 pattern from a solution-grown crystal. Goniometric tilts were around the $a^*$ and $b^*$ axes for three-dimensional data collection. (b) (2h,h,l) pattern from epitaxially oriented crystals. Tilts were made around the $c^*$ axis to collect three-dimensional data.

### Direct phasing procedure

Since evaluation of three- and four-phase invariants would not be sufficient, by itself, for solving this structure from a limited data set, the tangent formula (Karle & Hauptman, 1956) was employed for this purpose in the QTAN version of Langs & DeTitta (1975). This requires the calculation of three-phase invariants (1883 $\Sigma_2$-triples were generated for $A > 0.2$) and negative quartets (72 were generated for $B \le -0.05$). As has been shown in other work to be published elsewhere, NQEST (DeTitta, Edmonds, Langs & Hauptman, 1975) may not be the most suitable figure of merit for electron diffraction determinations but, on the other hand, it is the only one found to be of any use at all for some applications (Dorset, 1992b). Thus, 20 phase values were independently determined by origin and enantiomorph identification, followed by evaluation of zonal triples and quartets and a fit to this separate group was used to identify the most probable phase set from the tangent formula.

### Structure determination

The Wilson (1942) plot for the observed $|F_h|$ data indicates that the overall temperature factor appears to be $B = 0.0$ Å$^2$, probably indicating the difficulty in fitting a line to an intensity distribution dominated by effects of a molecular transform rather than the approximately Gaussian fall-off of single atomic

Table 1. *'Hand-phasing' with $\Sigma_1$ and $\Sigma_2$ triples*

| hkl | Phase | Source | hkl | Phase | Source |
|---|---|---|---|---|---|
| 400 | $\pi$ | $\Sigma_1$ | 440 | $\pi$ | $\Sigma_2$ |
| 110 | $\pi/2$ | $\Sigma_2$ | 540 | $\pi/2$ | $\Sigma_2$ |
| 10,1,0 | 0 | $\Sigma_2$ | 840 | 0 | $\Sigma_1$ |
| 120 | $\pi/2$ | $\Sigma_2$ | 350 | $\pi/2$ | $\Sigma_2$ |
| 620 | 0 | $\Sigma_2$ | 450 | 0 | $\Sigma_2$ |
| 920 | $-\pi/2$ | $\Sigma_2$ | 550 | $\pi/2$ | $\Sigma_2$ |
| 10,2,0 | $\pi$ | $\Sigma_2$ | 170 | $\pi/2$ | $\Sigma_2$ |
| 530 | $-\pi/2$ | Origin | 270 | $\pi$ | Origin |
| 630 | 0 | $\Sigma_2$ | 201 | $-\pi/2$ | Origin |
| 340 | $-\pi/2$ | $\Sigma_2$ | 301 | $\pi/2$ | Enantiomorph |

scatterers. The average values for this normalized structure factor,

$$\langle |E|^2 \rangle = 1.000, \langle |E^2 - 1| \rangle = 0.876, \langle |E| \rangle = 0.889$$

$$\%|E|\rangle3.0{:}0.0; \quad \%|R|\rangle2.0{:}4.0, \quad \%|E|\rangle1.0{:}29.4,$$

are consistent with the theoretical estimates (Karle, Dragonette & Brenner, 1965) for a non-centrosymmetric distribution, despite the small number of measured data. In order for a direct
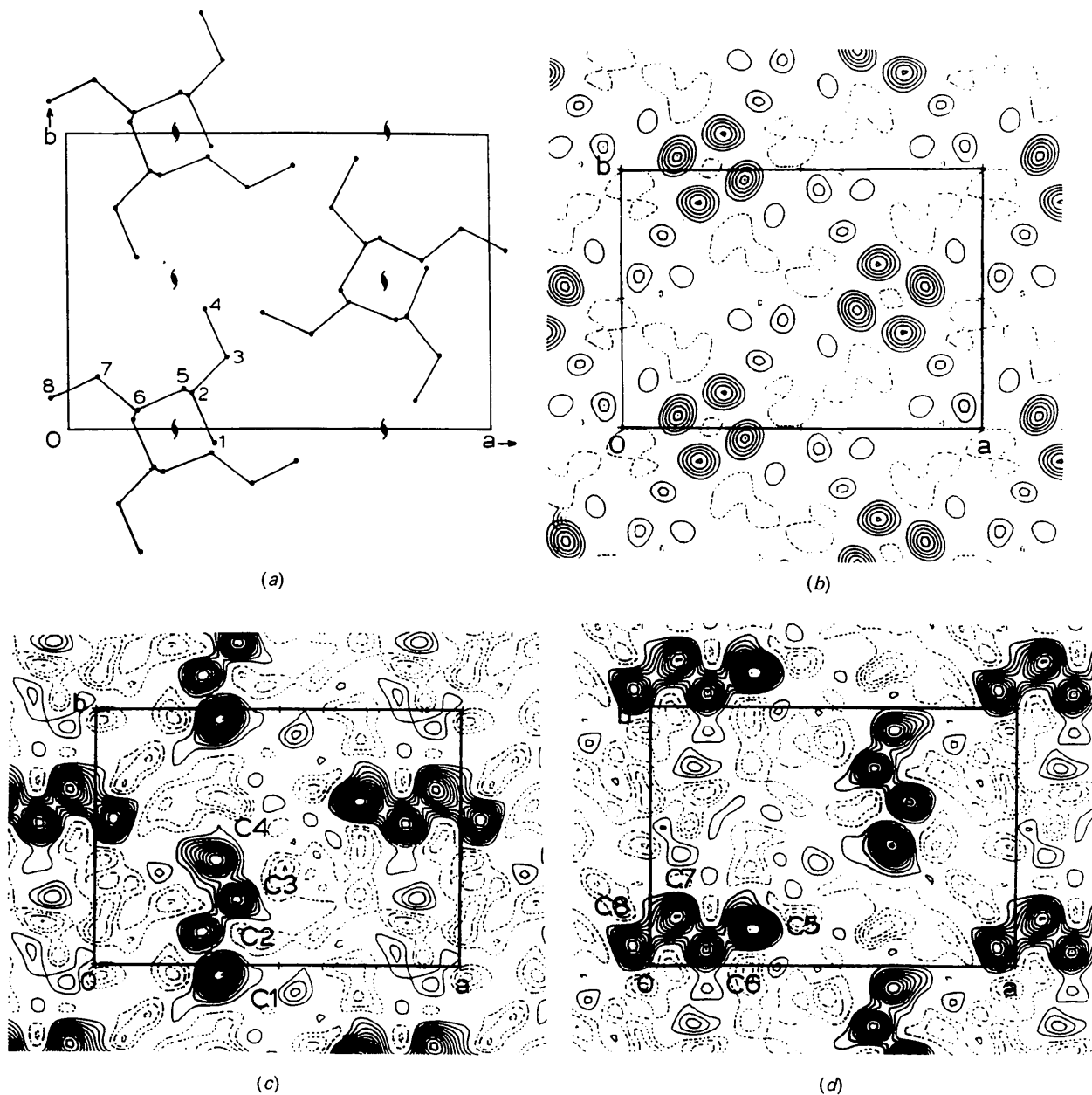


(a)



(b)



(c)



(d)

Fig. 2. (a) Molecular packing in the projection down c, showing the pseudo-fourfold symmetry; (b) electrostatic potential in the projection down c; (c) electrostatic potential in the section $z = 0.12$; (d) electrostatic potential in the section $z = 0.35$ (indicating that density persists somewhat beyond the $z \pm 0.25$ required by the pseudo-$4_1$ symmetry operation).

comparison to the X-ray results to be made, the origin was defined by the following assignments, using reflections among the highest $|E_{hkl}|$ values: $\varphi_{201} = -\pi/2$, $\varphi_{270} = \pi$, $\varphi_{530} = -\pi/2$. Although its value could be permuted by $QTAN$, the enantiomorph was selected in the subsequent list of solutions by setting $\varphi_{301} = \pi/2$. For use in the basis set for the tangent formula, algebraic values were given to the following additional phases: $\varphi_{004}$, $\varphi_{421}$, $\varphi_{541}$, $\varphi_{620}$, $\varphi_{440}$. Centrosymmetric phases were started at 0 and permuted over the two possible values; noncentrosymmetric phases were started at $\pi/4$ and permuted over four values incremented by $\pi/2$. For all the variable phases used in $QTAN$, this generates 128 possible solutions. The correct phase solution is found among the 38 lowest values of $NQEST$, but does not, by any means, correspond to the lowest value. For this reason, 20 phases determined separately from zonal three-phase structure invariants (Table 1) were compared with the trial solutions generated by the tangent formula for each permutation and this was used finally to decide on the best solution, containing 106 phase values.

In potential maps obtained from this initial set of phased $F_{hkl}$, all eight C atoms in the asymmetric unit were located (Fig. 2). The initial $R$ value for this model compared with all the data was 0.33. An isotropic temperature factor of $B = 4.0$ Å$^2$ was used for all structure-factor calculations, which used Doyle & Turner (1968) atomic scattering factors for electrons.

A full-matrix least squares refinement was attempted, starting with fixed $B = 4.0$ Å$^2$ and then allowing the atomic positions to vary (but constrained by a dampening factor for shifts). No geometrically reasonable model could be realized by this process, even though lower $R$ factors were produced. Because of poor correlation, three large intensities (110, 021 and 421) were revised by remeasuring the diffraction films. Intensity data were selected from patterns where the Ewald sphere surface is most reliably near the reflection center (*i.e.* in cases where there are multiple measurements of the same reflection for various crystal orientations). Three other values from somewhat less intense reflections (550, 011, 851), which may have been perturbed significantly by multiple scattering, were removed to produce a revised intensity data set with 122 non-zero reflections.

Subsequent Fourier refinement (including one map based on $2|F_o| - |F_c|$) led to atomic positions which were similar to those of Cojazzi *et al.* (1976) (Table 2). We note that these derived valence parameters (Fig. 3a) were found directly by Fourier refinement, whereas idealized values (Fig. 3b) had been assumed in the earlier conformational refinement against powder X-ray data. As shown in Table 3, the match

Table 2. *Fractional coordinates for poly(1-butene)* $(\times 10^3)$

|  | This determination | | | Cojazzi *et al.* (1976) | | |
|---|---|---|---|---|---|---|
|  | x | y | z | x | y | z |
| C1 | 346 | −38 | 108 | 348 | −34 | 107 |
| C2 | 298 | 125 | 163 | 301 | 121 | 159 |
| C3 | 381 | 248 | 103 | 379 | 247 | 102 |
| C4 | 325 | 402 | 120 | 324 | 401 | 123 |
| C5 | 279 | 134 | 358 | 274 | 136 | 357 |
| C6 | 160 | 67 | 413 | 163 | 71 | 409 |
| C7 | 72 | 183 | 353 | 73 | 180 | 352 |
| C8 | −38 | 105 | 370 | −38 | 104 | 373 |

Table 3. *Conformational angles (°) for the poly(1-butene) chain*

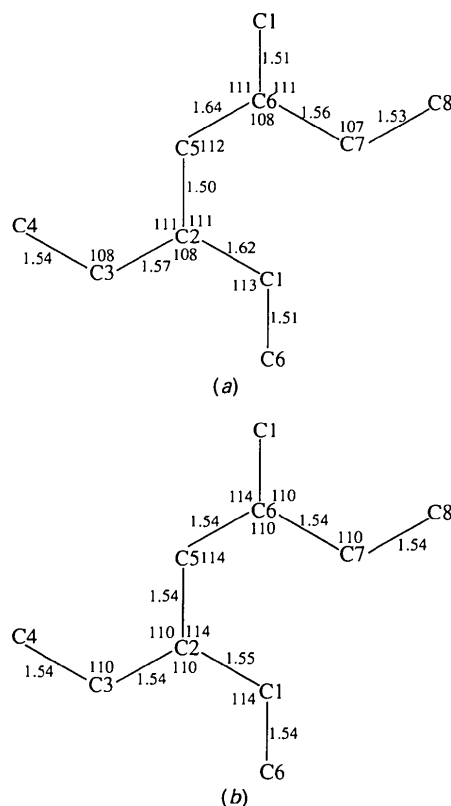|  | This determination | Cojazzi *et al.* (1976) |
|---|---|---|
| C1—C2—C3—C4 | 168.4 | 169.9 |
| C4—C3—C2—C5 | −70.0 | −63.7 |
| C3—C2—C5—C6 | 154.4 | 152.8 |
| C2—C5—C6—C7 | −73.1 | −76.6 |
| C5—C6—C7—C8 | 168.5 | 169.9 |
| C5—C2—C1—C6* | 165.4 | 159.1 |
| C3—C2—C1—C6* | −73.3 | −76.6 |

\* From next subunit



Fig. 3. (a) Calculated bond distances and angles for poly(1-butene) from the final coordinates in Table 2. Although some of the values are somewhat distorted, the average values are in good agreement with accepted values. (b) Bond distances (Å) and angles (°) from the idealized model of Cojazzi *et al.* (1976) used for conformational refinement.

Table 4. *Closest intermolecular contacts* (Å)

| | Symmetry operation | This determination | Cojazzi et al. (1976) |
|---|---|---|---|
| C8···C4 | 45503 | 4.08 | 4.12 |
| C8···C4 | 54504 | 3.98 | 3.92 |
| C8···C3 | 45503 | 3.94 | 3.96 |
| C7···C8 | 55504 | 4.13 | 4.16 |

Symmetry based on 5550N, where '555' refers to an untranslated unit-cell origin and where, for example, 455 denotes a shift along $-a$ by one unit cell repeat. Symmetry operators in the cell are O1, O2,... in the sequence given in *International Tables for X-ray Crystallography* (1952, Vol. 1).

between chain conformational angles is very good. Finally, the closest intermolecular distances for the two determinations are also in good agreement (Table 4). The final structure then has a chain backbone linked along atoms C6—C1—C2—C5— C6—C1 with the ethyl branches —C3—C4 and —C7—C8 linked to C2 and C6 atoms, respectively. The structure consists of infinite chains, each having approximate $4_1$-helical symmetry, with the chains coiled around the true crystallographic $2_1$-axes at $(\frac{1}{4},0,z)$ and $(\frac{3}{4},\frac{1}{2},z)$ (Fig. 2a). The chain packing is shown in Fig. 4. The final $R$ factor for these coordinates is 0.26. It is interesting to note that the structure proposed by Cojazzi et al. (1976) actually gives a higher crystallographic residual to our measured election diffraction data (0.28) when $B = 4.0$ Å$^2$ is assigned to all atoms. If these coordinates are fixed and the temperature factors are refined by least-squares, the C atoms of the polymer backbone have an average value $B = 3.1$ Å$^2$, whereas the outer ethylene carbons have an average $B = 3.9$ Å$^2$, resulting in $R = 0.26$. The structural solutions cannot be distinguished by refinement, in other words, and it is also apparent that the structure suggested in the original model refinement against the powder X-ray data can again be justified by our much larger set of single crystal data. This can be shown in another way by the fit of the model constructed by Cojazzi et al.
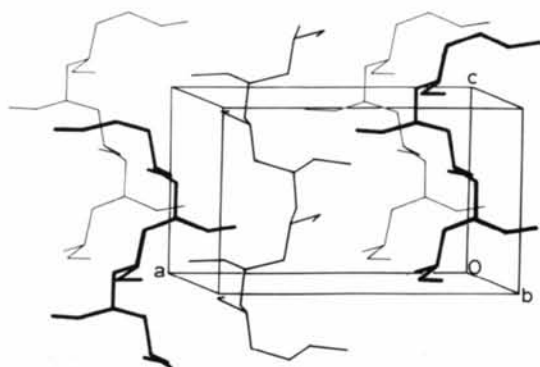
(1976) to the three-dimensional electrostatic potential map resulting from this analysis (Fig. 5). The final observed and calculated structure-factor magnitudes from our Fourier refinement model have been deposited.*

## Discussion

On comparing the above procedure to the powder X-ray determination performed earlier (Cojazzi et al., 1976), the advantages of single-crystal electron diffraction methods over powder or fiber techniques for *ab initio* polymer structure analyses are clear. First, the unit-cell constants and space-group symmetry can be determined unequivocally from the data (Fig. 1). For this structure, 125 non-zero individual reflections were measured from the single-

(a)

(b)

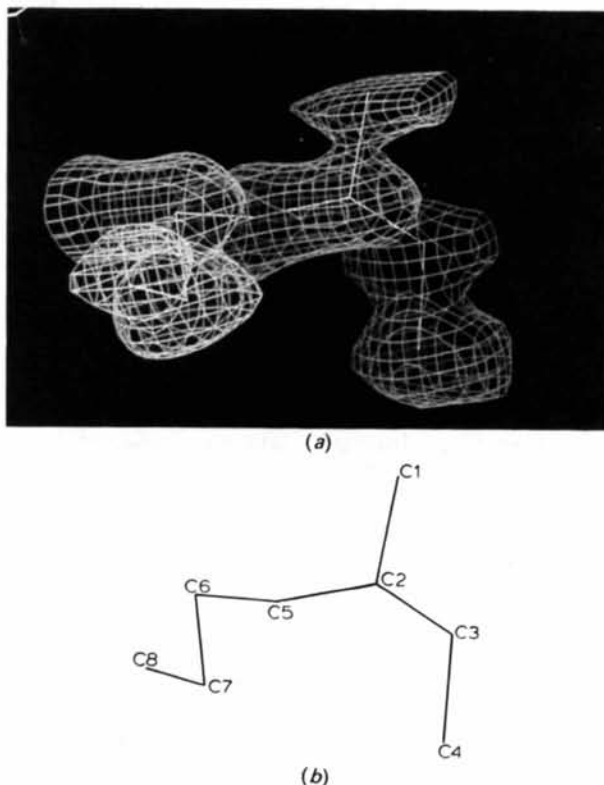Fig. 5. Fit of the model of Cojazzi et al. (1976) to the three-dimensional electrostatic potential map found in this direct electron crystallographic determination is indicated in (a), where the optimized model is shown within the continuous potential envelope. Atomic positions in the dimer unit are labeled in a separate drawing of the molecular skeleton (b) in the same orientation as shown in (a).



Fig. 4. Drawing of the poly(1-butene) chain packing, with the unit-cell axes indicated. The axis of the chain is parallel to the unit-cell c axis.

crystal diffraction patterns compared with 21 used in the powder X-ray determination. Moreover, in the latter analysis, only three peaks were free of reflection overlap and some had as many as 15 possible contributors to a single maximum. The electron diffraction data were also measured to higher resolution, *i.e.* 1.1 compared with 1.6 Å. The analysis could be carried out directly, with individual atomic positions visualized on a potential map. Finally, the isotropic temperature values are somewhat lower for the electron diffraction determination, denoting some possible static disorder expressed in the powder X-ray data [a similar case was observed when comparing the electron diffraction and fiber X-ray determinations of poly($\varepsilon$-caprolactone) (Dorset, 1991*c*)]. Most importantly, however, no chain model was assumed for this structure analysis, which, nevertheless, resulted in a structure very close to that found with a conformational fit starting from an idealized chain geometry.

The success of the tangent formula for solving such a non-centrosymmetric structure, even for a data set which is quite limited in size compared with normal, small molecule X-ray determinations, is quite impressive. We find that the application of the tangent formula resulted in an initial phase set of 106 reflections, for which the r.m.s. phase deviation to the X-ray model is only 16° (compared with the calculated values from the earlier X-ray model). At the end of the Fourier refinement, this figure is only 4° for 122 reflections, with no discrepancies observed for the 68 centrosymmetric zonal reflections. The final crystallographic *R* factor is also in the range expected for such determinations (Dorset, 1991*b*,*c*).

This analysis is the first independent single-crystal structure analysis of this polymer. However, some difficulties were encountered in this work: although the tangent formula is effective for electron diffraction data [as also shown in our earlier analysis of a non-centrosymmetric thiourea structure (Dorset, 1992*b*)], the figure of merit used to identify the correct structure is unreliable. This was previously indicated in a re-analysis of the diketopiperazine structure with the tangent formula (D. L. Dorset & M. P. McCourt, unpublished data). In an earlier, more favorable case, it was shown (Dorset, 1992*b*) that *NQEST* was a reliable indicator of the correct solution. However, the use of negative quartet invariants (Hauptman & Green, 1976) requires a reliable estimate of weak 'cross-terms', $|E_{h+k}|$, $|E_{k+h}|$ and $|E_{l+h}|$, given the four strong magnitudes $|E_h|$, $|E_k|$, $|E_l|$ and $|E_m|$. Here, we experience a complete breakdown of the *NQEST* reliability. Thus, when *NQEST* could at least be used to minimize the number of trial maps to be generated, there was an appreciable recurrence of the same *hkl* reflections for $|E_h| \leq 0.5$ in respective experimental and theoretical

(kinematical) data sets (*e.g.* room-temperature thiourea 73% overlap; for diketopiperazine 79% overlap). For this determination, in terms of $|E_h|$ values with magnitude $\leq 0.60$, there is only 35% overlap of reflection indices for the two data sets. Hence, the cross-terms for the quartets will not correctly predict which should be negative, making the use of *NQEST* questionable. Another factor to be considered here is the small number of negative quartet invariants generated for a relatively small data set, such that the statistical relevance of this figure is even more questionable. Despite these difficulties, it is gratifying that the tangent formula, which relies on triple phase invariants, itself predicts correct phase values. As we have seen before, this seems to be due, in part, to the preservation of kinematical phases by the convolution of phased structure factors, $F_{hkl}*F_{hkl}$, found in mathematical models for *n*-beam dynamical scattering (Cowley & Moodie, 1959), which, as pointed out by Moodie (1965), closely resembles the operation of the Sayre (1952) equation.

Another problem in these *ab initio* electron diffraction determinations is in the method used for structure refinement. For all the examples we have considered so far, Fourier techniques are the most effective device for refining such a structure, even in the case where the structure contains some heavy atoms (Dorset, Tivol & Turner, 1992). On the other hand, slight deviations from ideal kinematical structure-factor magnitudes, either due to multiple scattering contributions or mismeasurement of some intensities, can affect the position of some atomic peaks in the potential maps, as we have shown previously (Dorset, 1991*a*). Ideally, one would like to perform an unconstrained least-squares refinement. Given enough intensity data per atom, this is indeed possible, as we shall demonstrate in another publication. For this polymer structure, however, this did not lead to a useful result, despite the fact that there are approximately five reflections for each refineable parameter (assuming an overall temperature factor). In such cases, of course, an optimized chain geometry can be fitted to a detailed three-dimensional potential map, calculated from the derived phase set, so that such an optimization is much less equivocal than those performed in fiber X-ray crystallography.

We conclude by reiterating that the present investigation indicates *direct* routes to solving crystal structures of certain kinds of unstable polymer phases. Among the unstable crystalline phases, some are actually induced by stretching, *e.g.* when forming oriented samples for X-ray fiber analysis, and hence, X-ray techniques might be optimally suited for determining their structure. On the other hand, crystalline forms unstable to stresses require 'quiescent' crystallization conditions, *i.e.* solution-crystalli-

zation to produce chain-folded single crystals and, as illustrated in the present study, epitaxial crystallization to orient a projection normal to the chain axis. Electron diffraction is required in this latter case due to the small size of chain-folded single crystals and also because the thickness of epitaxial layers (ca 30 nm) must be limited to avoid disorientation mechanisms linked with bulk polymer growth (e.g. lamellar twisting).

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# X-ray Diffraction Studies of Oriented Dilauroyl Phosphatidylcholine Bilayers in the $L_\delta$ and $L_\alpha$ Phases

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## Abstract

X-ray diffraction studies on oriented multilayers of dilauroyl phosphatidylcholine in the lyotropic liquid-crystalline $L_\alpha$ phase and a not previously reported mono-domain three-dimensional $L_\delta$ phase at two temperatures (293 and 343 K) and various relative humidities (0–100%) are described. Absolute one-dimensional electron-density profiles of the different structural phase bilayers were constructed to a resolution of 4 Å using direct methods (e.g. swelling and triplet structure-invariant relationships) to solve for the phase problem. The absolute electron-density distributions clearly demonstrate differences between the two structural phases of dilauroyl phosphatidyl-choline bilayers. In addition, the various structural properties of the two different phases have been quantified. In the case of the $L_\delta$ phase, the structural quantities (e.g. volumes of the terminal methyl group and headgroup, and the number of waters) are examined for the first time.

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