Macromolecules **1992,** *25,* 4425–4430

Electron Crystallography of Linear Polymers: Direct Phase Determination for Zonal Data Sets

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Received January 23, 1992; Revised Manuscript Received April 29, 1992

ABSTRACT: To facilitate fitting a conformational chain model to two-dimensional electron diffraction intensity data, the zonal crystal structures of five representative linear polymers have been determined by the probabilistic estimate of three- and four-phase structure invariant sums. For two examples where individual atomic positions can be resolved in projection (i.e., poly(ethylene sulfide) and γ-poly(pivalolactone)), the structures can be refined further by Fourier techniques. In another example, α-poly[3,3-bis(chloromethyl)-oxacyclobutane], on the other hand, one fails to find the position of a linkage methylene group in difference Fourier maps, even though the initial phase set is mostly correct. Two polysaccharide structures, mannan and anhydrous nigeran, can only be visualized as a molecular density envelope, undoubtedly due to the overlap of many projected atomic positions. In all cases the phase determination is best carried out as a multisolution technique, via one or two algebraic unknowns in phase, to circumvent false indications given by incorrectly predicted invariant sums.

Introduction

Electron diffraction techniques have been frequently employed in polymer science since the enhanced scattering cross-section of matter for electrons (vs X-rays) permits the study of chain-folded lamellae as single crystals.[1] Of all the organic materials investigated by electron diffraction, linear polymers represent the most frequent case where the diffraction intensities are used for quantitative structure analyses, as recently reviewed.[2] Most frequently, zonal data from untilted lamellar crystals have been analyzed, although a few three-dimensional determinations have been reported more recently.[2]

When zonal electron diffraction intensities are used for structure analyses, the techniques employed to find the best structural model are very similar to the ones used for fiber X-ray diffraction data.[3,4] For a complicated repeat structure, the complete X-ray crystal structures of monomer and oligomer sequences can be elucidated to determine what portions of the polymer repeat can be held conformationally rigid. These rigid units are concatenated via "linkage bonds" around which rotational freedom is permitted. Hence, two figures of merit, the crystallographic R factor and the internal energy (calculated from nonbonded atom–atom potential functions), are simultaneously minimized during the course of the analysis.

Although there is no reason to expect that this analytical procedure should not be successful, one wonders if a more direct analysis is possible, at the very least to guide the course of the conformational refinement. Recently, we have reported that so-called direct-phasing procedures, of the kind employed in X-ray crystallography, can be very successful for the ab initio analysis of three-dimensional electron diffraction intensities from thin polymer microcrystals.[5–7] After Fourier refinement, these analyses lead to bond distances and angles in good agreement with the values expected in X-ray determination. However, it is not yet known how useful direct-phasing techniques will be for the analysis of two-dimensional data, particularly since many atoms are overlapped in a view down the molecular chain axis. In an initial attempt to explore the possibilities for the direct analysis of zonal electron diffraction data, results from five representative polymer structures reported in this paper demonstrate that the dimensional limitation is not, in itself, a significant impediment to structure determination.

Data and Methods

Electron diffraction intensity data from five chain-folded polymer samples have been chosen from the literature[8–12] based on the success of the structure analysis by more conventional methods. These are summarized in Table I. (For three of these materials, three-dimensional diffraction intensities had been collected but only the $hk0$ data are used here.) Although, by coincidence, all of the polymer samples crystallize with orthorhombic unit cells (three with space group $P2_12_12_1$), there is no reason to expect that monoclinic or triclinic structures could not be analyzed with equal facility, as evidenced by suitable examples using other polymer and small organic crystal data.[7]

As discussed elsewhere,[7,13] direct determination of crystallographic phases can be made by the probabilistic estimate of a structure invariant phase sum, e.g.

$$\psi = \phi_{h_1} + \phi_{h_2} + \phi_{h_3} + \ldots = 0, \pi$$

subject to the constraint $\Sigma_i h_i \equiv 0$, where $h_i = (h_i k_i l_i)$, the Miller indices of reflections contributing to the phase invariant. When three phases are included in the sum, the invariant is called a "triple", and when four are included, it is termed a "quartet". For a triple, if $\vec{h}_1 = \vec{h}_2 = -{}^1/_2\vec{h}_3$, the invariant is termed Σ_1 and the probability of the correct estimate of $\psi = 0,\pi$ depends on the quantity $A_1 = (|E_h|^2 - 1)|E_{2h}|/N^{1/2}$, where $|E_h|$ is a normalized structure factor and N is the number of atoms in the unit cell. When $\vec{h}_1 \neq \vec{h}_2 \neq \vec{h}_3$ the triple is termed Σ_2 and the probability of correctly estimating $\psi = 0$ depends on the magnitude $A_2 = (2/N^{1/2})|E_{h_1}E_{h_2}E_{h_3}|$. Finally, the prediction of the quartet sum depends on the quantity $B = (2/N)|E_{h_1}E_{h_2}E_{h_3}E_{h_4}|(|E_{h_1+h_2}|^2 + |E_{h_2+h_3}|^2 + |E_{h_1+h_3}|^2 - 2)$.

The above statements mean that phase values of certain reflections h_i can be determined according to the magnitudes of normalized structure factors $|E_h|$ calculated using

$$|E_h|^2 = |F_h|^2/\epsilon\sum_i f_i'^{\,2}$$

Here $|F_h|$ is the measured structure factor, f_i' are the atomic scattering factors[14] corrected for thermal motion (an overall

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Table I
Data for Polymers Using Direct Phase Determination of Electron Diffraction Intensities

polymer	space group	unit cell constants	no. of obsd $hk0$ reflections	atoms in asymmetric unit
poly(ethylene sulfide)	$Pbcn$	$a = 8.51$, $b = 4.94$, $c = 6.69$ Å	22	2
α-poly[3,3-bis(chloromethyl)-oxacyclobutane]	$Pna2_1$	$a = 17.85$, $b = 8.15$, $c = 4.82$ Å	29	8
γ-poly(pivalolactone)	$P2_12_12_1$	$a = 8.23$, $b = 11.28$, $c = 6.02$ Å	45	7
mannan	$P2_12_12_1$	$a = 8.92$, $b = 7.21$, $c = 10.27$ Å	34	12
anhydrous nigeran	$P2_12_12_1$	$a = 17.76$, $b = 6.00$, $c = 14.62$ Å	43	22

Table II
Phase Determination for Zonal Electron Diffraction Data

polymer	no. of Σ_1 phases	no. of Σ_2 triples	no. of quartets	origin	no. in initial phase set
poly(ethylene sulfide)	3	26 (3)[a]	11 (1)	$\phi_{130} = 0$	17 (1)
α-poly[3,3-bis(chloromethyl)-oxacyclobutane]	0	27 (2)	9 (2)	$\phi_{610} = 0$ $\phi_{530} = 0$	19 (0)
γ-poly(pivalolactone)	1	30 (5)	3 (0)	$\phi_{110} = -\pi/2$ $\phi_{360} = -\pi/2$	22 (7)
mannan	3	47 (5)	43 (6)	$\phi_{110} = \pi/2$ $\phi_{210} = 0$	24 (0)
anhydrous nigeran	4	25 (8)	9 (3)	$\phi_{130} = \pi/2$ $\phi_{610} = 0$	21 (2)

[a] Numbers in parentheses indicate erroneous phase predictions either for invariant sum ψ or individual values ϕ.

Table III
Initial Phase Set for Poly(ethylene sulfide)

$hk0$	ϕ(dir meth)[a]	ϕ(cryst struct)	$hk0$	ϕ(dir meth)[a]	ϕ(cryst struct)
020	a	π	350	a	π
040	0	0	400	0	0
110	0	0	420	a	π
130	0	0	510	a	π
150	a	π	530	0	0
200	0	0	620	a	π
220	a	π	710	a	π
240	a[b]	0	820	a	π
330	0	0			

[a] $a = \pi$. [b] Erroneous.

thermal motion can be estimated from a Wilson plot[15]), and ϵ is a scaling factor to account for certain classes of reflections which contain systematic absences. One has, therefore, a set of simultaneous equations in phase, ranked according to A_1, A_2, or B so that the invariants with larger values are most probable. To solve these simultaneous equations and, hence, to determine phase values for enough reflections to a allow computation of an *interpretable* potential map, one needs a set of starting phase values.

All of the space groups[16] considered in this study have centrosymmetric projections. (However, note that the shifted pgg plane group origin for $P2_12_12_1$ leads to $hk0$ phase values $0,\pi$ when h is even and $\pm\pi/2$ when h is odd.) For a primitive unit cell projection such as (001), one is permitted to set arbitrarily the phase values of two reflections to define the unit cell origin, so long that, e.g., $hk0 \neq gg0$ or $\Sigma_i h_i k_i 0 \neq gg0$, where g is an even integer. (For space group $Pbcn$, the plane group is cmm in the (001) projection; hence only one reflection can be used from the $hk0$ set.[13]) These can be used to evaluate the three- and four-phase invariants to find other phase values. It is generally helpful to use reflections where $|E_h|$ is suitably large. If not enough phases can be determined by the partial origin definition, then one can use algebraic unknowns, e.g., $\phi_{hk0} = a, b, ...,$ to establish the phase relationships between reflections. Depending on the number n of unknowns, one is required to compute 2^n potential maps to look for a structure solution.

Analyses

Poly(ethylene sulfide).[8] Data for the phase determination are reviewed in Table II. To interpret the entry for this and other polymer samples, one can state that 3 phase values were found from Σ_1 triples and the remainder of the 17 values after partially defining the origin, by specifying $\phi_{130} = 0$, were determined from 26 Σ_2 triples and 11 quartets. These phase invariant sums selected above threshold values for A_2 and B, respectively, included three triples and one quartet with erroneous predictions. An algebraic unknown was needed to find phase relationships among certain reflections, as shown in Table III, requiring the calculation of two maps. Errors in the triples and quartets can lead to a false definition $a = 0$ via the ϕ_{150} determination. It was beneficial to retain this ambiguity, and the initial phase set of 17 reflections contained one error ($\phi_{240} = \pi$) when a was set to its correct value.

The incorrect and correct phase choices are immediately apparent by inspection of the calculated potential maps (Figure 1). When $a = \pi$, the map resembles the one calculated in the earlier determination (made after the $|F_{hk0}|$ were corrected for an inappropriate Lorentz factor used in the first analysis[17]). From this map one can obtain the x,y coordinates of the sulfur atom and, using geometry, locate appropriate coordinates for the C atom. Using these to calculate structure factors, there are no disagreements in phase assignments with the earlier determination for all 22 $hk0$ data. The correct density map (Figure 1c) is then compared to the ones calculated from the partial phase set. This can be interpreted in terms of all atom positions in Figure 1d.

α-Poly[3,3-bis(chloromethyl)oxacyclobutane].[9] As outlined in Table II, phase determination of this polyether makes use of Σ_2 triples and quartets. After origin definition, phase values are found for 19 reflections. However, due to erroneous phase invariants, contradictory phase values are found for ϕ_{130}, ϕ_{230}, and ϕ_{420}, and these are assigned an algebraic quantity a, requiring computations of two maps (Figure 2a,b). In either map, the positions of the Cl atoms are correctly specified. Since the ether oxygen is nearly eclipsed with a chain methylene and two other methylenes of the backbone are also nearly eclipsed, the centers of these projected atom positions cannot be resolved in a rather large peak between

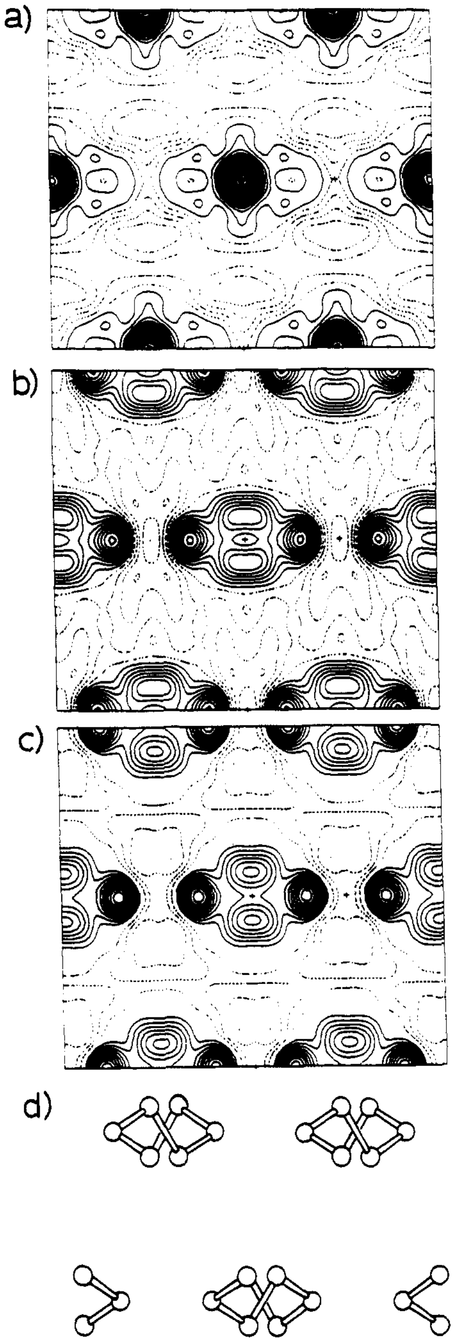

Figure 1. Potential maps for poly(ethylene sulfide). (a) Calculated from phases in Table III with $a = 0$; (b) calculated from phases in Table III with $a = \pi$; (c) calculated from $hk0$ phases determined from crystal structure (and/or Fourier refinement); (d) molecular packing.

the Cl positions. When the unknown is assigned the value $a = \pi$, a position for one of the methylenes linking the Cl to the backbone is suggested but the other methylene is not seen (Figure 2b). The initial phase assignments are given in Table IV.

Attempts were made to refine the structure with difference Fourier syntheses based on $|F_o| - |F_c|$. In no case can the missing linkage atom be found. In fact, when C atomic positions from the crystal structure analysis[9] are used to calculate the potential map (Figure 2c), its position remains unresolved. If, on the other hand, a geometrically reasonable structure is fit to the observed density and the atomic positions (Figure 2d) are used to calculate structure factors, the phases for all 29 $hk0$ reflections agree with the earlier model.[9]

γ-Poly(pivalolactone).[10] Despite the large number of $hk0$ data, this was not an easy structure to determine by direct methods. After origin definition, one Σ_1 triple phase as well as numerous Σ_2 triples and quartets were used to assign phase values to 22 reflections. Of these, it was clear that three reflections were giving contradictory phase values. Since two algebraic unknowns were needed to produce a suitably large phase set, this required the calculation of four potential maps. (The initial phase list is given in Table V. Note that seven phases are incorrect.)

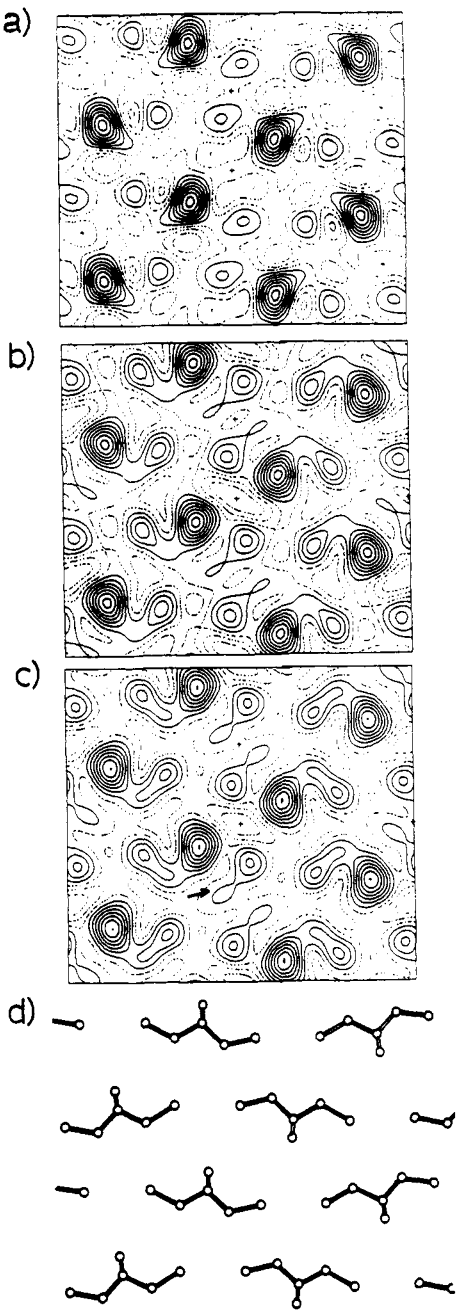

Figure 2. Potential maps for α-poly[3,3-bis(chloromethyl)oxacyclobutane]. (a) Calculated from phases in Table IV with $a = 0$; (b) calculated from phases in Table IV with $a = \pi$; (c) calculated from complete $hk0$ phases determined in the earlier crystal structure analysis (an arrow points to the position of the missing methylene group); (d) molecular packing.

Potential maps are not easily interpreted. The best map (Figure 3a) does not clearly show individual atom positions but a trial structure, suggested by a hypothetical asymmetric unit, was fit to the density, using the linkage oxygen and the five unique carbons. After this assignment, it was then possible to find the remaining oxygen position, as well as to clearly define the carbon positions, by Fourier refinement (including the use of a difference synthesis). The final map (Figure 3b) closely resembles the one

Table IV
Initial Phase Set for α-Poly[3,3-bis(chloromethyl)oxacyclobutane]

$hk0$	ϕ(dir meth)[a]	ϕ(cryst struct)	$hk0$	ϕ(dir meth)[a]	ϕ(cryst struct)
020	π	π	510	π	π
120	π	π	530	0	0
130	a^b	0	610	0	0
210	π	π	630	π	π
230	a	π	710	0	0
310	π	π	720	0	0
320	π	π	730	π	π
400	π	π	800	0	0
420	a	π	820	π	π
430	π	π			

[a] $a = \pi$. [b] Erroneous.

Table V
Initial Phase Set for γ-Poly(pivalolactone)

$hk0$	ϕ(dir meth)[a]	ϕ(cryst struct)	$hk0$	ϕ(dir meth)[a]	ϕ(cryst struct)
020	0	0	380	$-\pi/2$	$-\pi/2$
110	$-\pi/2$	$-\pi/2$	400	b^b	0
120	$b + \pi/2$	$-\pi/2$	430	π^b	0
160	$\pi/2^b$	$-\pi/2$	440	b	π
250	0	0	470	π^b	0
260	b	π	510	$\pi/2^b$	$-\pi/2$
270	0	0	540	$a + \pi/2$	$\pi/2$
280	a^b	π	610	$\pi - a$	π
350	$\pi/2 - a$	$\pi/2$	620	0^b	π
360	$-\pi/2$	$-\pi/2$	630	$\pi - a$	π
370	$\pi/2 - a$	$\pi/2$			

[a] $a = 0$, $b = \pi$. [b] Erroneous.

calculated from the coordinates (Figure 3d) listed by Meille et al. (Figure 3c), except that there is an origin shift for the mass distribution in the unit cell. When the projected atom positions are used to calculate structure factors, only four phase errors remain for 45 $hk0$ data, and these correspond to rather weak reflections.

Mannan.[11] After finding three phases from Σ_1 triples and origin definition, evaluation of Σ_2 triples and quartets (Table II) enables one to determine phase values for 24 reflections. Only one phase, ϕ_{120}, is uncertain, but the most frequent assignment is the correct value $-\pi/2$. The initial phase set is compared to the values calculated from the crystal analysis in Table VI. There are no errors.

On the basis of the partial phase set, one can calculate a (001) potential map (Figure 4a) In this it is not possible to resolve most of the atomic positions. Using atomic coordinates for this structure (Figure 4c) to generate a complete $hk0$ phase set, it is possible to calculate a similar potential map (Figure 4b).

Anhydrous Nigeran.[12] Electron diffraction data from a second polysaccharide, the anhydrous form of nigeran, were also analyzed. Two reflections are used for partial origin definition, and four more phases are picked up from Σ_1 triples. After evaluation of Σ_2 triples and quartets, a total of 23 phases are assigned (Table VII). However, two reflections are ambiguously defined, as indicated by contradictory results from the phase invariants. These are omitted from the initial phase set used to calculate the first potential map (Figure 5a), a set which contains two further errors. Again, individual atomic positions are not resolved for much of the structure. Using the coordinates published by Pérez et al. (Figure 5c) to generate a complete set of ϕ_{hk0}, the resulting F_o potential map is found to resemble the previous one (Figure 5b).

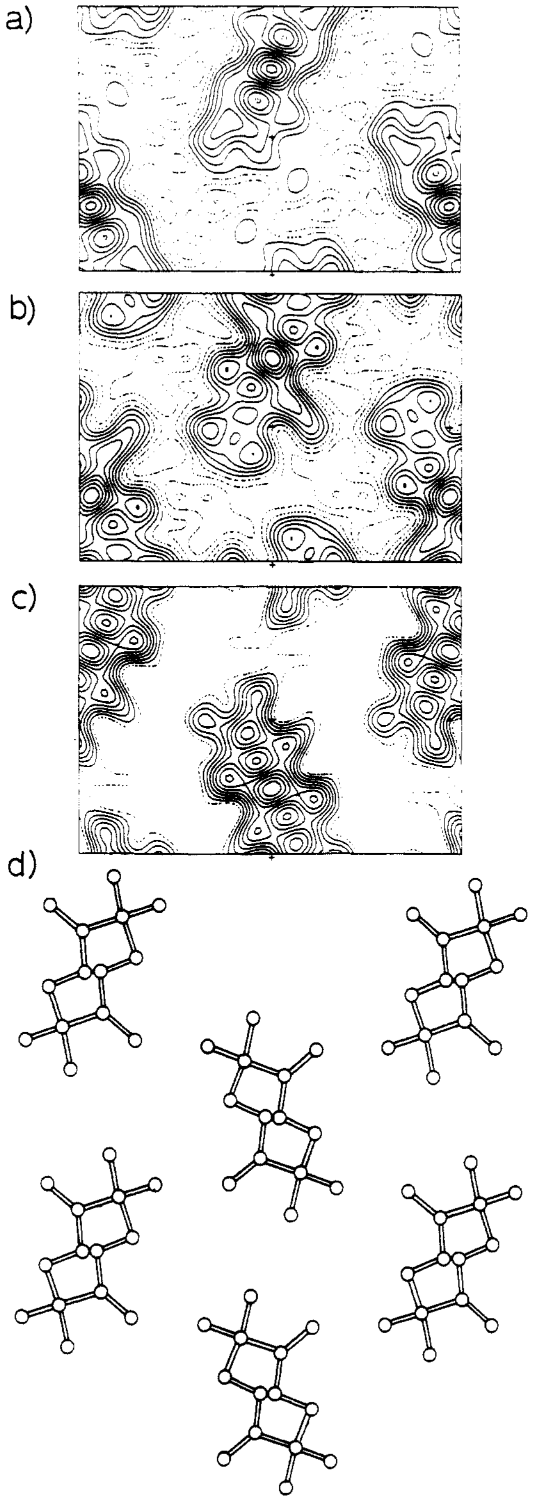

Figure 3. Potential maps for γ-poly(pivalolactone). (a) Calculated from phases in Table V with $a = 0$, $b = \pi$; (b) after Fourier refinement; (c) computed from $hk0$ phases from crystal structure coordinates (note the origin shift of this structure); (d) molecular packing.

Discussion

It is interesting that direct-phasing methods based on the probabilistic estimate of triple and quartet structure invariant sums can be an effective means for determining zonal structural projections of linear polymers from electron diffraction intensity data, despite the fact that the number of measured reflections is rather small. Although the intensities are obviously changed somewhat by multiple scattering, they are close enough to their kinematical values to permit a nearly correct ranking of phase invariants in terms of probability. Hence, within a threshold value of A or B, most of these sums are correct, allowing enough phase determinations to be made to permit calculation of a potential map which can often be

Table VI
Initial Phase Set for Mannan

*hk*0	ϕ(dir meth)	ϕ(cryst struct)	*hk*0	ϕ(dir meth)	ϕ(cryst struct)
020	0	0	320	$\pi/2$	$\pi/2$
040	π	π	340	$-\pi/2$	$-\pi/2$
110	$\pi/2$	$\pi/2$	350	$\pi/2$	$\pi/2$
120	$-\pi/2$	$-\pi/2$	400	0	0
130	$-\pi/2$	$-\pi/2$	410	π	π
140	$\pi/2$	$\pi/2$	420	0	0
200	π	π	430	π	π
210	0	0	440	π	π
220	π	π	450	0	0
230	0	0	510	$\pi/2$	$\pi/2$
240	0	0	520	$-\pi/2$	$-\pi/2$
310	$-\pi/2$	$-\pi/2$	550	$-\pi/2$	$-\pi/2$

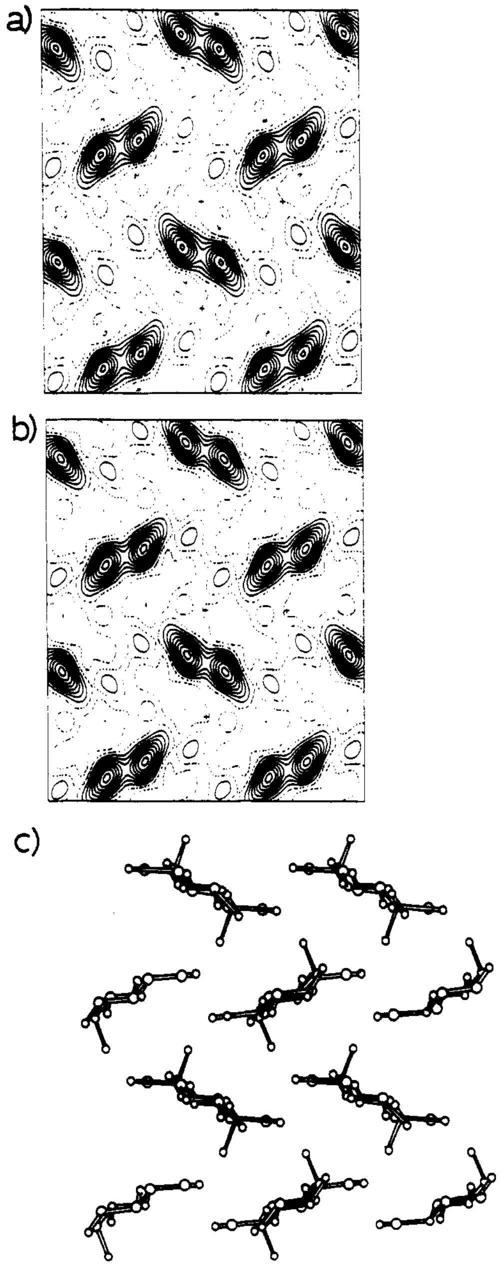

Figure 4. Potential maps for mannan. (a) Calculated from phases in Table VI; (b) calculated from complete *hk*0 phases based on atomic coordinates found in the earlier crystal structure analysis; (c) molecular packing.

interpreted directly in terms of a reasonable molecular packing.

Table VII
Initial Phase Set for Anhydrous Nigeran

*hk*0	ϕ(dir meth)[a]	ϕ(cryst struct)	*hk*0	ϕ(dir meth)[a]	ϕ(cryst struct)
200	π	π	13,1,0	$2a - \pi/2$	$\pi/2$
400	π	π	020	π	π
800	$a - \pi/2$	0	220	0	0
10,0,0	$a + \pi/2$	π	520	$\pi/2$	$\pi/2$
12,0,0	π	π	620	$a - \pi/2$	0
14,0,0	$2a$[b]	0	820	$a + \pi/2$[b]	0
110	$-\pi/2$	$-\pi/2$	130	$\pi/2$	$\pi/2$
310	$\pi/2$	$\pi/2$	330	$-\pi/2$	$-\pi/2$
610	0	0	830	0	0
710	a	$\pi/2$	930	a	$\pi/2$
910	a	$\pi/2$			

[a] $a = \pi/2$. [b] Erroneous.

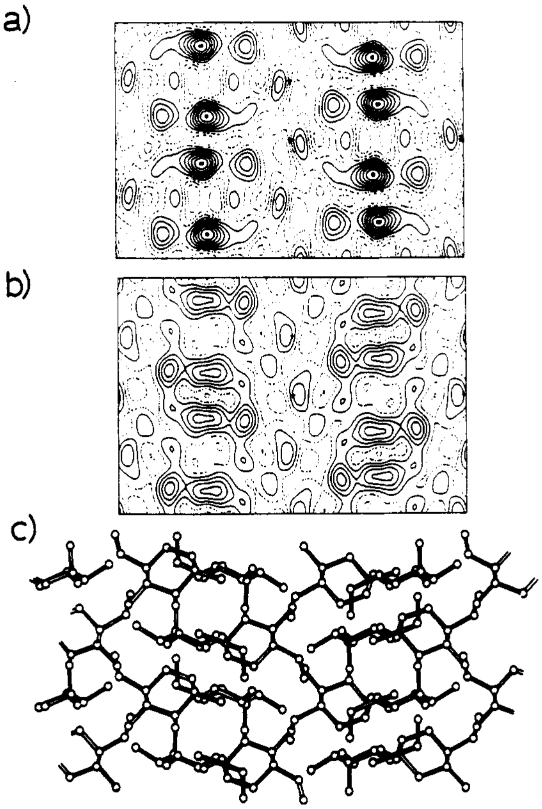

Figure 5. Potential maps for anhydrous nigeran. (a) Calculated from phases in Table VII with $a = \pi/2$; (b) calculated from complete *hk*0 phases based on atomic coordinates found in the earlier crystal structure analysis; (c) molecular packing.

The presence of incorrectly predicted phase sums must always be anticipated for such data sets, however. Since the determination of individual phases follows a logic "tree", the presence of a few such errors can lead to a false structure, if the solution of the simultaneous equations is made without due caution. Sometimes the presence of erroneous phase invariant sums is manifested by conflicting phase assignments for certain reflections, as demonstrated by some of the examples considered in this study. If the number of affected reflections is small, the ambiguity might be settled statistically by the number of indications favoring one phase choice instead of another. (One such phase was found for the mannan structure.) In other cases, there may be enough reflections affected that it is worthwhile to assign an algebraic quantity (consistent with their interrelationship) to their phase values and thus settle the problem by the appearance of the computed potential maps. In fact, the multisolution approach via unknowns, in general, seems to be the safest way to proceed with such data sets. Another caution can be given for the use of Σ_1 triples. It is best to accept phase values from these invariants only if there are numerous indications for a given reflection, and this assignment should always be tested for internal consistency with Σ_2 triples and quartets.

With these caveats in mind it is, nevertheless, clear that crystal structures can be determined ab initio by this method for a variety of polymer structures. In the simplest examples, individual atomic positions can be found and the structure can be refined in projection by Fourier techniques. An independent determination of a polymer structure in projection would be of considerable assistance to constraining further the refinement of a chain model.

When insufficient data resolution and/or considerable overlap of projected atomic positions disallows the determination of individual atomic coordinates, the density distribution of the molecule in the projection map still would serve as a constraint for refinement of a conformational model, e.g., the two polysaccharide structures shown above. More recently, another successful direct analysis was carried out for cellulose triacetate II, using data published originally by Roche et al.[18] This structure has 20 atoms per asymmetric unit, and the phase determination identifies values for 14 of 22 unique *hk*0 reflections with no errors. Additionally, an unknown polysaccharide structure was solved, finding 11 phase values for 22 *hk*0 data. A single phase ambiguity necessitated calculation of two maps (details to be published elsewhere), one of which matches the independently determined atomic model very closely. Given such phase ambiguities, however, it may be difficult to decide which map is most likely in a multisolution approach without necessary atomic resolution which permits the choice to be made from chemical knowledge. One method, which needs to be tested in future work, would be to use various moment calculations which test the "peakness" of the map by computing the average of the density raised to some power—a device that has succeeded for some X-ray determinations.[19] Another method might be to use a figure of merit based on the concept of maximum entropy.[20]

Acknowledgment. This research was supported in part by grants from the National Science Foundation (Grant CHE91-13899) and the National Institutes of Health (Grant GM46733), which are gratefully acknowledged. I thank Dr. M. P. McCourt for helping to prepare the molecular packing diagrams.

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Registry No. Poly(ethylene sulfide), 24980-34-5; α-poly[3,3′-bis(chloromethyl)oxacyclobutane], 26917-50-0; γ-poly(pivalolactone) (homopolymer), 24969-13-9; γ-poly(pivalolactone) (SRU), 24937-51-7; anhydrous nigera, 31799-84-5; mannan, 9036-88-8.