

4.5. POLYMER CRYSTALLOGRAPHY

the symbolic addition procedure, or in more automated procedures involving the tangent formula (see Chapter 2.2). The Sayre (1952) equation has been found to be particularly effective, where the correct structure is identified *via* some figure of merit after algebraic phase values are used to generate multiple solutions (Stanley, 1986). More recently, maximum-entropy and likelihood methods (Gilmore *et al.*, 1993) have also been effective for solving such structures. After the initial atomic model is found, it can be improved by refinement, generally using Fourier techniques. Least-squares refinement can be carried out under most favourable circumstances (Dorset, 1995a), but requires the availability of a sufficient number of diffraction data. Even so, the refinement of thermal parameters must be uncoupled from that of the atomic positions. Also, positional shifts must be dampened (if X-ray crystallographic software is used) to prevent finding a false minimum, especially if the kinematical *R* factor is used as a figure of merit.

4.5.3.4. Examples of crystal structure analyses

At least four kinds of electron diffraction intensity data sets have been used as tests for direct phase determination *via* the approaches mentioned above.

Case 1: Zonal data sets – view down the chain axis. Such data are from the least optimal projection of the polymer packing, because of extensive atomic overlap along the chain axis. Initially, symbolic addition was used to find phase values for *hk0* data sets from six representative polymers, including three complicated saccharide structures (Dorset, 1992). Most of the determinations were strikingly successful. Later, an unknown data set from the polysaccharide chitosan was obtained from Grenoble (Mazeau *et al.*, 1994) and direct phase determination was able to find a correct model (Dorset, 1995b). More recently, other polymers have been tested [including one case where an electron micrograph provided many of the starting phase terms (Dorset, 1995b)] also comparing favourably with the solution found by energy minimization of a linkage model. For all examples considered so far, the projected symmetry was centrosymmetric.

Later, it was found that a partial phase set provided by symbolic addition could be expanded to the complete zone by the Sayre equation (Dorset *et al.*, 1995). In all of these tests (Dorset, 1995b), there were only one or two examples where there were serious deviations from the phase terms found by other methods. Even in these instances, the potential maps could still be used as envelopes for the actual projection of the chain structure (Dorset, 1992).

Case 2: Zonal data set – view onto the chain axes. Electron diffraction data from a projection onto the polymer chain axes would be more useful if individual atomic positions were to be resolved. An interesting example where such a view can be obtained is an *h0l* data set from the polypeptide poly- γ -methyl-L-glutamate. Electron diffraction data were collected from stretched films by Vainshtein & Tatarinova (1967). In projection, the cell constants are $a = 4.72$, $c = 6.83$ Å with plane-group symmetry *pg*. As shown in Table 4.5.3.1, there were 19 unique intensity data used for the analysis. After initial phase assignment by symbolic addition, a correct solution could be visualized which, after Fourier refinement (Dorset, 1995b), differed from the original one by a mean phase difference of only 6°.

The progress of this structure analysis can be reviewed to give a representative example. Since the *h00* reflections have centrosymmetric phases, the value $\varphi_{100} = 0$ was chosen as a single origin-defining point. From high-probability Σ_1 three-phase invariants (assessed after calculation of normalized structure factors $|E_h|$), one could assign $\varphi_{200} = \varphi_{400} = 0$. Symbolic values were then given to three other phases, *viz.* $\varphi_{106} = a$; $\varphi_{103} = b$; $\varphi_{101} = c$. From this entire basis, other values could be found from highly probable Σ_2

Table 4.5.3.1. Structure analysis of poly- γ -methyl-L-glutamate in the β form

<i>h0l</i>	$ E_h $	$ F_o $	$ F_c $	φ (°) (previous)	φ (°) (this study)
002	0.48	0.72	0.57	−63	−51
004	0.43	0.38	0.31	49	73
006	3.01	1.47	0.88	1	−3
100	1.48	2.12	2.37	0	0
200	1.03	1.04	1.06	0	0
300	0.30	0.65	0.89	0	0
400	0.35	0.15	0.46	0	0
500	0.23	0.07	0.04	180	180
101	0.75	1.02	0.67	−169	−178
201	0.32	0.31	0.42	90	108
102	0.42	0.48	0.56	17	14
202	0.40	0.33	0.64	41	43
103	0.95	0.85	0.77	88	90
203	0.51	0.36	0.42	91	88
303	0.12	0.06	0.31	92	87
403	0.13	0.04	0.54	90	90
104	0.66	0.45	0.27	−22	−13
105	0.55	0.28	0.29	−26	−7
106	1.75	0.69	0.58	5	−5

Fractional coordinates

	This study		Vainshtein & Tatarinova (1967)	
	<i>x</i>	<i>z</i>	<i>x</i>	<i>z</i>
$C_{\alpha, \beta}$	0.048	0.000	0.042	0.000
<i>C'</i>	0.067	0.331	0.092	0.330
<i>O</i>	0.281	0.335	0.300	0.330
<i>N</i>	0.000	0.161	−0.025	0.175

three-phase invariants, as follows:

$$\begin{aligned}\varphi_{006} &= \varphi_{106} + \varphi_{100} \therefore \varphi_{006} = a \\ \varphi_{105} &= \varphi_{006} + \varphi_{101} \therefore \varphi_{105} = a - c + \pi \\ \varphi_{203} &= \varphi_{106} + \varphi_{103} \therefore \varphi_{203} = a - b + \pi \\ \varphi_{300} &= \varphi_{100} + \varphi_{200} \therefore \varphi_{300} = 0 \\ \varphi_{002} &= \varphi_{103} + \varphi_{101} \therefore \varphi_{002} = b - c \\ \varphi_{004} &= \varphi_{006} + \varphi_{002} \therefore \varphi_{004} = a - b + c.\end{aligned}$$

(These invariant relationships include phase interactions among symmetry-related Miller indices characteristic of the plane group.) Additionally $c = \pi$ could be specified to complete origin definition for the zone. It was then possible to permute values of *a* and *b* to arrive at test phase values for this subset, *i.e.* to generate a multiple set of solutions. When $a = 0$, $b = \pi/2$, the map in Fig. 4.5.3.1 was observed. After finding trial atomic positions for Fourier refinement (assuming that two carbon-atom positions were eclipsed in this projection), the final phase set was found as shown in Table 4.5.3.1. Although the crystallographic residual to the observed data, calculated with the model coordinates, was rather large (0.32), there was a close agreement with the earlier determination.

More recently a similar data set, collected from oriented crystal 'whiskers' of poly(*p*-oxybenzoate) in plane group *pg* was analysed. Again the Sayre equation, *via* a multisolution approach, was used to produce a map that contained 13 of 18 possible atomic positions for