

## 4.5. POLYMER CRYSTALLOGRAPHY

Table 4.5.3.1. Structure analysis of poly- $\gamma$ -methyl-L-glutamate in the  $\beta$  form

$h0l$	$ E_h $	$ F_o $	$ F_c $	$\varphi$ ( $^\circ$ ) (previous)	$\varphi$ ( $^\circ$ ) (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)	
	$x$	$z$	$x$	$z$
$\text{Ca}, \beta$	0.048	0.000	0.042	0.000
$\text{C}'$	0.067	0.331	0.092	0.330
$\text{O}$	0.281	0.335	0.300	0.330
$\text{N}$	0.000	0.161	-0.025	0.175

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- $\gamma$ -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  $6^\circ$ .

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  $\Sigma_1$  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  $\Sigma_2$  three-phase invariants, as follows:

$$\begin{aligned}\varphi_{006} &= \varphi_{106} + \varphi_{\bar{1}00} \therefore \varphi_{006} = a \\ \varphi_{105} &= \varphi_{006} + \varphi_{10\bar{1}} \therefore \varphi_{105} = a - c + \pi \\ \varphi_{203} &= \varphi_{106} + \varphi_{10\bar{3}} \therefore \varphi_{203} = a - b + \pi \\ \varphi_{300} &= \varphi_{100} + \varphi_{200} \therefore \varphi_{300} = 0 \\ \varphi_{002} &= \varphi_{103} + \varphi_{\bar{1}0\bar{1}} \therefore \varphi_{002} = b - c \\ \varphi_{004} &= \varphi_{006} + \varphi_{00\bar{2}} \therefore \varphi_{004} = a - b + c.\end{aligned}$$

(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  $a$

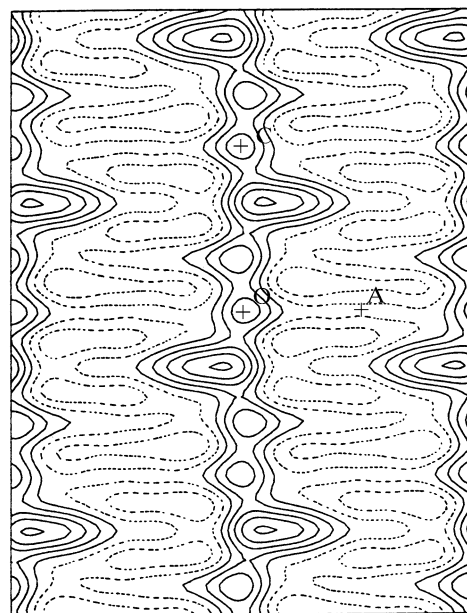


Fig. 4.5.3.1. Initial potential map for poly- $\gamma$ -methyl-L-glutamate (plane group  $pg$ ) found with phases generated by the Sayre equation.

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 the two subunits in the asymmetric unit. The complete structure was observed after the remaining five atom sites were identified in two subsequent cycles of Fourier refinement (Liu *et al.*, 1997) and the average atomic positions were found to be within 0.2 Å of the model derived from an energy minimization.

*Case 3: Three-dimensional data – single crystal orientation.* The first data set from a chain-folded lamella for a direct structure analysis was a centrosymmetric set (space group  $P2_1/n$ ) from poly(1,4-*trans*-cyclohexanediyl dimethylene succinate), composed of 87 reflections (Brissette *et al.*, 1984). The phase determination was quite successful and atomic positions could be found as somewhat blurred density maxima in the three-dimensional maps (Dorset, 1991a). A model was constructed from these positions and the bonding parameters optimized to give the best fit to the data ( $R = 0.29$ ).

Noncentrosymmetric three-dimensional intensity sets (orthorhombic space group  $P2_12_12_1$ ) from the polysaccharides mannan (form I) (Chanzy *et al.*, 1987) and chitosan (Mazeau *et al.*, 1994) were also collected from tilted crystals. In both cases, direct phase determination by symbolic addition via an algebraic unknown was successful, even though the data were not sampled along the chain repeat. For the former polymer, a monomer model could be fitted to the blurred density profile, much as one would fit a polypeptide sequence to a continuous electron-density map (Dorset & McCourt, 1993; Dorset, 1995c). If the Sayre equation were used to predict phases and amplitudes within the 'missing cone' of unsampled data, then the fit of the monomer could be much more highly constrained.

*Case 4: Three-dimensional data – two crystal orientations.* The optimal case for collection of diffraction data is when two