

4. DIFFUSE SCATTERING AND RELATED TOPICS

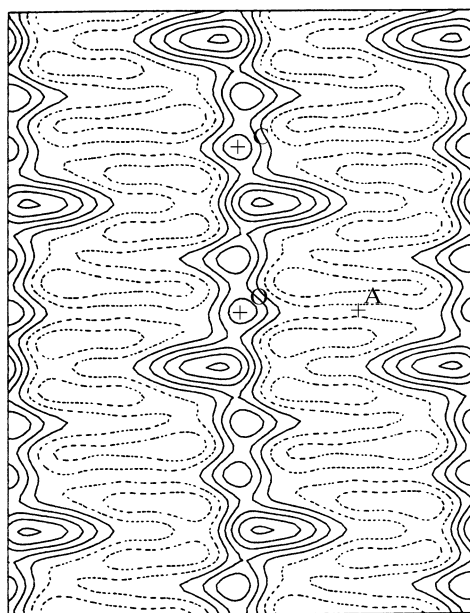


Fig. 4.5.3.1. Initial potential map for poly- γ -methyl-L-glutamate (plane group pg) found with phases generated by the Sayre equation.

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 (Brisse *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 orthogonal projections of the same polymer polymorph can be obtained, respectively, by self-seeding and epitaxial orientation. While tilting these specimens, all of reciprocal space can be sampled for intensity data collection.

Polyethylene crystals were used to collect 50 unique maxima (Hu & Dorset, 1989) and, *via* symbolic addition, the centrosymmetric phases of 40 reflections (space group $Pnma$) could be readily determined (Dorset, 1991b). The structural features were readily observed in the three-dimensional potential maps (Fig. 4.5.3.2a), and atomic coordinates (with estimated values for hydrogen-atom positions) could be refined by least squares (Dorset, 1995b) to give a final R value of 0.19.

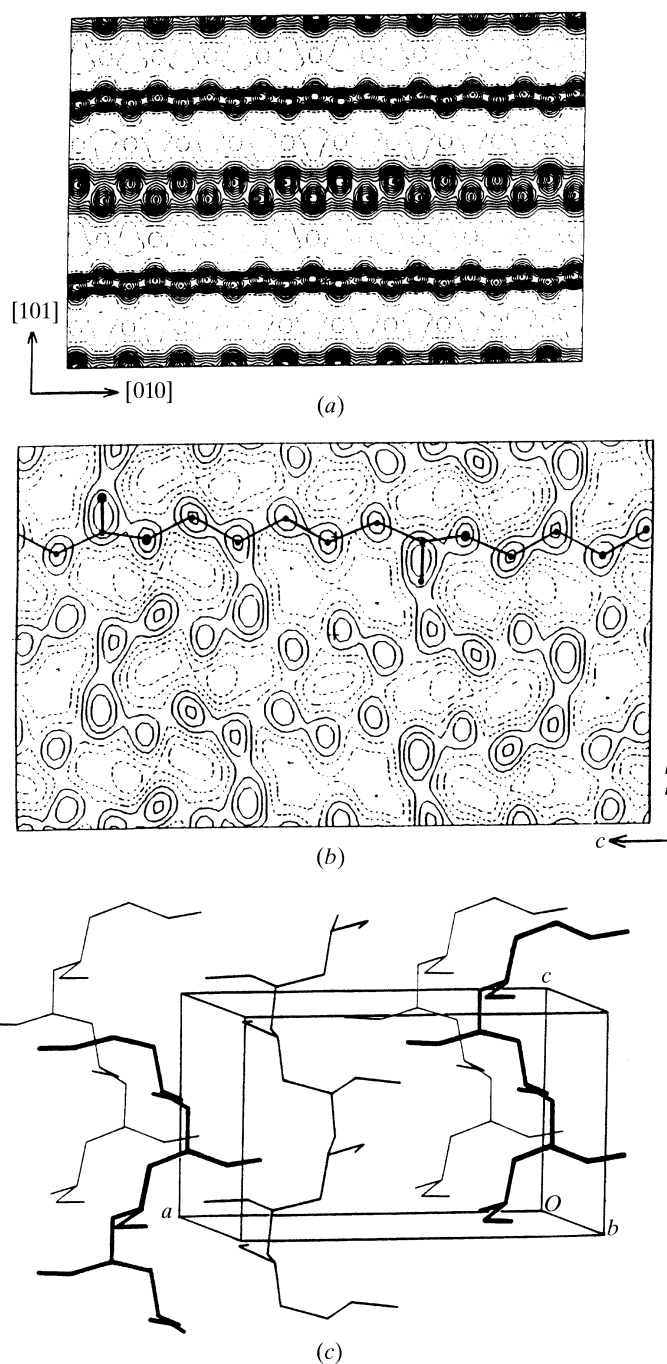


Fig. 4.5.3.2. Crystal structures of linear polymers determined from three-dimensional data. (a) Polyethylene; (b) poly(ϵ -caprolactone); (c) poly(1-butene), form (III).

Poly(ϵ -caprolactone) was epitaxially crystallized on benzoic acid and, with $hk0$ data from solution-crystallized samples, a unique set of 47 intensities was collected for the noncentrosymmetric orthorhombic unit cell (space group $P2_12_12_1$) (Hu & Dorset, 1990). Direct phase determination was achieved *via* symbolic addition, using one algebraic unknown to assign values to 30 reflections (Dorset, 1991c). Atomic positions along the chain repeat, including the carbonyl position, were clearly discerned in the [100] projection (Fig. 4.5.3.2b) and the three-dimensional model was constructed to fit to the map calculated from all phased data, yielding a final crystallographic residual $R = 0.21$. This independent determination was able to distinguish between two rival fibre X-ray structures, in favour of the one that predicted a non-planar chain conformation.