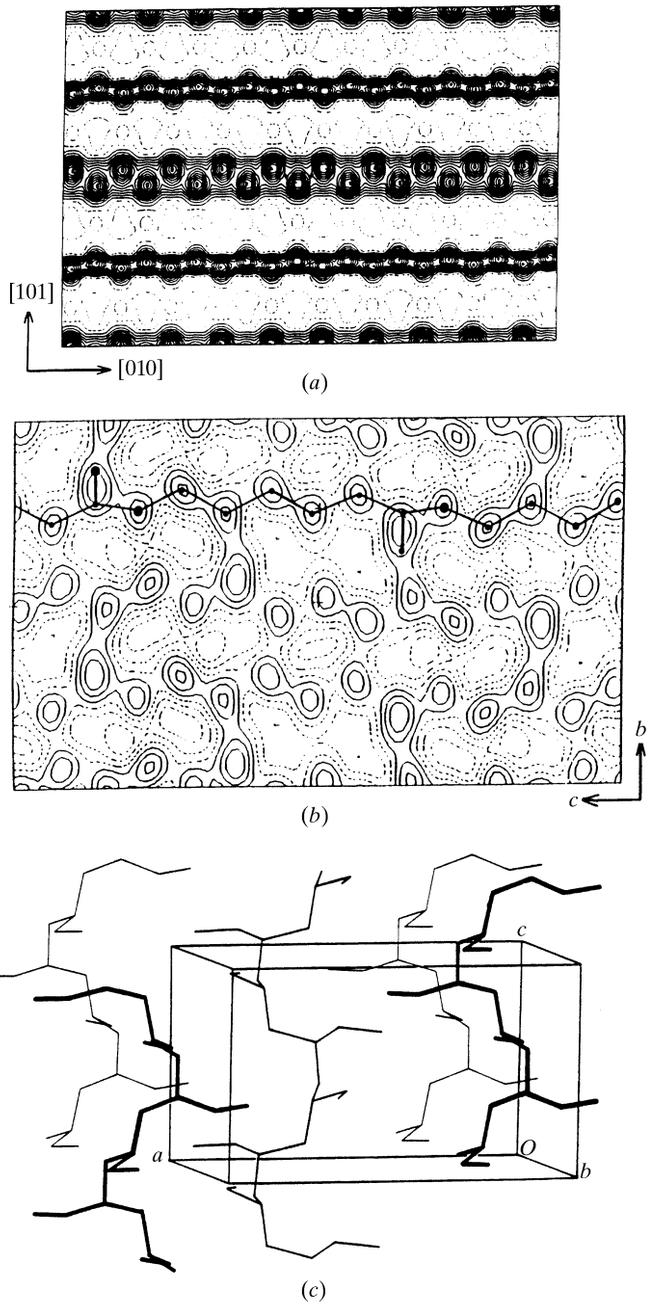

Fig. 4.5.3.2. Crystal structures of linear polymers determined from three-dimensional data. (*a*) Polyethylene; (*b*) poly(ε-caprolactone); (*c*) poly(1-butene), form (III).

orthogonal projections of the same polymer polymorph can be obtained, respectively, by self-seeding and epitaxic 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, 1991*b*). The structural features were readily observed in the three-dimensional potential maps (Fig. 4.5.3.2*a*), and atomic coordinates (with estimated values for hydrogen-atom positions) could be refined by least squares (Dorset, 1995*b*) to give a final R value of 0.19.

Poly(ε-caprolactone) was epitaxically crystallized on benzoic acid and, with *hk*0 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, 1991*c*). Atomic positions along the chain repeat, including the carbonyl position, were clearly discerned in the [100] projection (Fig. 4.5.3.2*b*) 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 nonplanar chain conformation. Because of the methylene repeat, this is actually a difficult structure to solve by automated techniques. For example, the tangent formula and *SnB* (Miller *et al.*, 1993) could only find chain zigzag positions and not the position of the carbonyl oxygen atom (Dorset, 1995*b*).

The most complicated complete polymer crystal structure solved so far by direct methods using electron diffraction data (Dorset *et al.*, 1994) was based on 125 unique data (space group $P2_12_12_1$) from isotactic poly(1-butene), form (III), using orthogonal molecular orientations crystallized in Strasbourg (Kopp *et al.*, 1994). Initially, the standard NQEST figure of merit (FOM) (De Titta *et al.*, 1975) was not suitable for identifying the correct solution among the multiple sets generated with the tangent formula. A solution could only be found when a separate phase determination was carried out with the *hk*0 data to compare with the multiple solutions generated. More recently, the minimal principle (Hauptman, 1993), used as a FOM with the tangent formula or with a multiple random structure generator, *SnB*, correctly identified the structure on the first try (Dorset, 1995*b*). The maps clearly show individual carbon-atom positions in a 4_1 helix that parallels 2_1 helices of the space group (Fig. 4.5.3.2*c*). After Fourier refinement, the crystallographic residual was R = 0.26. The previous powder X-ray diffraction determination was based on only 21 diffraction maxima, some of which had as many as 15 individual contributors.

The work of both RPM and DLD was supported by the US National Science Foundation (grant DBI-9722862 for RPM).

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