Crystalline Bilayers in the Very Long Chain *n*-Alkanoic Acid $C_{191}H_{383}COOH$

Goran Ungar* and Xiangbing Zeng

Department of Engineering Materials and Centre for Molecular Materials, University of Sheffield, Sheffield S1 4DU, U.K.

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Pure monodisperse normal alkanes containing several hundred C atoms, like their shorter chain counterparts, crystallize in layers.[1,2] While shorter alkanes always adopt the extended-chain conformation, those with more than 120−150 C atoms can also crystallize as folded chains, with the fold length being an integer fraction of the chain length.[1,3] Recent work has indicated that even in the "noninteger form" (NIF) the fold length is exactly half the full chain length.[4,5]

In the present paper we announce the first results of a study of a long *n*-alkane derivative, 1-*n*-dononacontahectanoic acid, $C_{191}H_{383}COOH$. The compound was kindly supplied by Dr. Gerald Brooke of Durham University, and the synthesis has been described in ref 6.

The sample was packed in a thin-wall glass capillary and investigated by simultaneous powder small- and wide-angle X-ray scattering (SAXS and WAXS) at the Synchrotron Radiation Source at Daresbury. A quadrant multiwire proportional detector was used for SAXS and a curved 1-d position-sensitive detector for WAXS.

In many aspects of crystallization and chain folding the behavior of the carboxylic acid is similar to that of *n*-alkanes in the same range of chain lengths which we have studied, e.g., $C_{194}H_{390}$ or $C_{198}H_{398}$. Extended-chain, once-folded chain and NIF forms[7] were all found under different conditions of melt crystallization. However, in addition to these lamellar forms, we have also observed a new structure in $C_{191}H_{383}COOH$, on which we now report briefly. The full account of this work, including the analysis of electron density profiles, surface disorder, and thermodynamic stability of this structure, will be published elsewhere.[7]

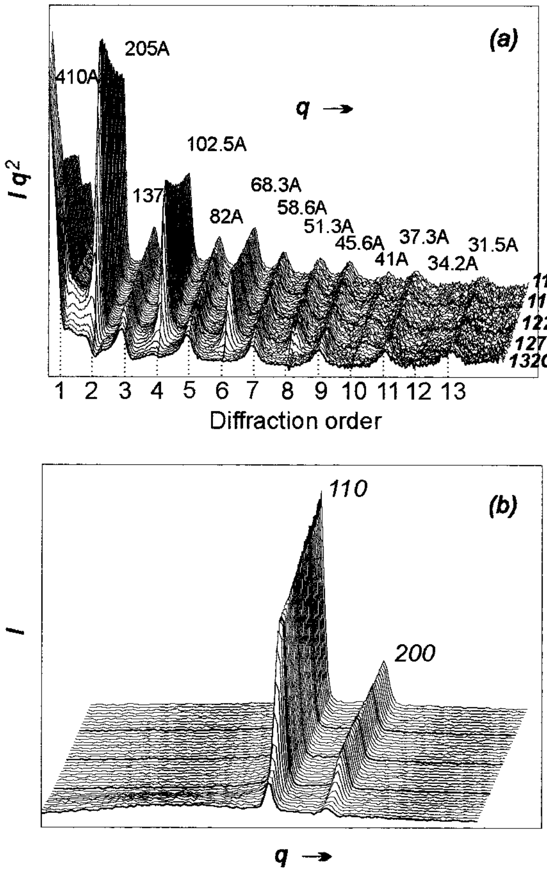

Figure 1. (a) SAXS traces (Lorentz-corrected intensities vs *q*) of $C_{191}H_{385}COOH$ recorded during cooling a partially crystallized sample at 0.3 °C/min from 132 to 112 °C. Bragg spacings corresponding to the observed peak positions, recording temperatures, and diffraction orders of the bilayer phase are marked. (b) Wide-angle diffractograms recorded simultaneously with those in (a). Orthorhombic 110 and 200 reflections are shown.

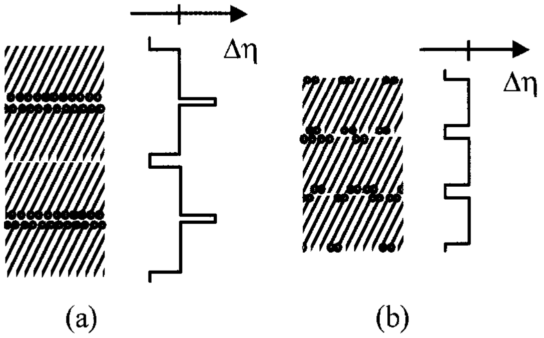

Figure 2. Schematic sketches of the double-layer (a) and monolayer (b) structure. Circles represent carboxylic groups. Deviation from average electron density, $\Delta\eta(x)$, is shown schematically on the right.

The new phase appears when the carboxylic acid is crystallized from the melt at a supercooling not exceeding 2 °C. Figure 1 shows a series of SAXS traces recorded during cooling the sample at 0.3 °C/min between 132 and 112 °C. Prior to the cooling run the sample had already been allowed to crystallize isothermally at 132 °C for 30 min. The phase that had developed at 132 °C, represented by the first three or four SAXS traces, has a lamellar periodicity of 410 Å, and the odd diffraction orders are much stronger than the even ones. The value 410 Å corresponds to twice the length of the extended chain molecule inclined at 32° to the layer normal, i.e., to the value $2 \times (192 \times 1.272 + 3) \times \cos 32°$, derived from molecular model based on the data for short-chain analogues.[8,9] The spacing and intensity distribution all suggest that this lamellar form has a double-layer structure that is made up of extended alkanoic acid molecules paired by their −COOH end groups, as illustrated in Figure 2a. The tilt angle of 32° is somewhat lower than the usual angle of 35°, characteristic of {201} basal, or layer, planes found both in the high-temperature structure of long-chain alkanes[10] (and polyethylene) and in the ordered structure of saturated fatty acids.[11]

The wide-angle diffractograms recorded simultaneously with the SAXS traces are shown in Figure 1b. The angular range shown contains the strongest peaks,

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* Corresponding author.

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which are the 110 and 200 reflections of the orthorhombic lattice of polyethylene and long alkanes and which also correspond to the sublattice in most of the ordered phases of shorter *n*-alkanes.[12,13] Thus, the crystallographic subcell of the alkane moiety is not changed significantly by the presence of the carboxylic group.

While a quantitative analysis of diffraction peak intensities and reconstruction of the electron density profile of the different phases in $C_{191}H_{383}COOH$ will be reported elsewhere,[7] already a qualitative assessment of the SAXS curve can be shown to be compatible with the bilayer structure of antiparallel molecules depicted in Figure 2a. First we make the usual assumption that the structure is centrosymmetric and not ferroelectric. Hence, the electron density deviation from average, $\Delta\eta$, is an even function of the coordinate x along layer normal with the origin at the center or the edge of the bilayer of periodicity L:

$$\Delta\eta(x) = \Delta\eta(-x) \tag{1}$$

Since the intercrystalline gap in these highly crystalline phases is small compared to L, we can safely assume that the structure factors of first few odd diffraction orders will all have the same sign.[14] Now if in the bilayer structure only odd diffraction orders had nonzero intensities, then $\Delta\eta(x)$ would be an odd function relative to the origin at $x = L/4$ or $x = 3L/4$, i.e.

$$\Delta\eta(x) = -\Delta\eta\left(\frac{L}{2} - x\right) \tag{2}$$

Thus, if only odd orders were present, the dip (negative fluctuation) in $\Delta\eta(x)$ at the boundary between two bilayers would be matched exactly by its opposite (positive fluctuation) in the center of the bilayer, as shown schematically on the right of Figure 2a. Such a symmetrical $\Delta\eta(x)$ distribution makes sense if we consider that there is an excess of electrons in a $-COOH$ group over that in an equivalent volume occupied by $-CH_2-$ groups. On the other hand, the dip in $\Delta\eta(x)$ at the methyl end is the common feature of all crystalline alkanes.[5,14] In fact, a profile similar to that in Figure 2a is obtained[7] using crystallographic data for a representative of shorter-chain *n*-alkanoic acids, such as $C_{11}H_{23}COOH$ in the C- or α-form,[9] which also show bilayer structures. The presence of weak even-order diffraction peaks (second and very weak fourth) in the SAXS traces of bilayer $C_{191}H_{383}COOH$ is a measure of asymmetry of the $\Delta\eta(x)$ distribution, i.e., of departure from eq 2.

The reason for the formation of the bilayer structure in $C_{191}H_{383}COOH$ must be the same as in short-chain acids, i.e., pairing of molecules through hydrogen bonding of the carboxylic groups. However, it may not have been expected a priori that a structure as ordered as this would form in such long-chain molecules. During crystallization chains with the COOH group at the wrong end must be selectively rejected if bilayers are to form. A H-bonded pair of $C_{191}H_{383}COOH$ molecules can be regarded as a supramolecular chain with a length close to that of the longest pure alkane synthesized, *n*-$C_{390}H_{782}$.[6,15] It is interesting to note that we have not succeeded in crystallizing this alkane in the extended-chain form directly from the melt at atmospheric pressure; rather, it was obtained by annealing of chain-folded crystals. In contrast, the bilayer phase of $C_{191}H_{383}COOH$, which is the extended-chain form of the supramolecular dimer, forms comparatively readily from the melt and very readily upon heating of the monolayer crystal (see below).

The bilayer phase of $C_{191}H_{383}COOH$ is notable for the sharpness of the diffraction peaks and for the fact that intensity diminishes very slowly up to high diffraction orders (a strong 13th order is still visible at the edge of the detector range). These features point to both high regularity in lamellar stacking and to a thin interface (methyl and carboxyl) between the crystal layers.

WAXS traces (Figure 1b) show that only about 12% of the material crystallizes in the bilayer form. On continued cooling, irrespective of the cooling rate, further crystallization takes place in a more conventional “monolayer” form, i.e., one in which a molecular layer is a complete repeat unit—see the schematic drawing in Figure 2b. The layer periodicity of this form is 202 Å, which corresponds accurately to the length of extended chains tilted at 35° ({201}/{001} angle) and projected onto the layer normal. The positions of the small-angle diffraction orders (Figure 1a) correspond closely to those of even orders of the bilayer phase.

Theoretically, for 100% pure material, it should be possible to crystallize the whole sample at one temperature and in only one polymorph. The reason that this is not the case here is not entirely clear. Since the melting point of the monolayer form is only 2 °C lower than that of the bilayer form, broadening of the melting range beyond 2 °C due to impurities would allow the formation of the kinetically favored monolayer phase. Impurities may in fact be degradation products as some degradation has been noticed to occur during the experiment, despite efforts to minimize the sample’s exposure to elevated temperature and the X-ray beam.

In the monolayer form $C_{191}H_{383}COOH$ molecules are oriented up and down with equal probability. It is not known at this stage what fraction of molecules are paired through H-bonding, and to that end IR spectroscopy will be used. Considering that the lamellae grow independently from each other, the bonding is likely to be to a large extent intralamellar, i.e., between adjacent molecules within a layer. In this case the carboxyl chain ends would have to be bent toward each other in order to allow the establishment of directed H-bonds. Such a conformation may thus be regarded as a once-folded supramolecular chain.

There is some support for the “folded supermolecule”, i.e., intralamellar H-bonding, from the melting behavior: the melting point difference between bilayer and monolayer forms is 1.6−2.6 °C. If both forms were made up of extended dimers and differred only in the degree of longitudinal ordering (carboxylic and methyl groups separated or mixed, respectively, on successive layer interfaces), then their molar configurational entropy difference would be equal to $R \ln 2$. This would mean a melting point difference of only 0.7 °C. The excess melting point difference measured is believed to come from the work of bending of the carboxylic ends. In comparison, the melting point difference between extended and once-folded forms of *n*-alkane $C_{390}H_{782}$ is 3.0 °C. The above argument is of course only valid if the alkanoic acid molecules are completely dimerized in both the solid and the melt.

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