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Lamellar Order and the Crystallization of Linear Chain Solid Solutions

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ABSTRACT: Single crystals have been grown from binary *n*-paraffin solid solutions and from multicomponent waxes and low molecular weight polyethylenes. Although conformational and longitudinal disorder must affect the lamellar interface in multilamellar crystals, the interlamellar interaction still must remain regular enough to account for the observed long-range correlation, over large distances (e.g. 10 μm), of successive stacked lamellae. Surface decoration experiments on mixed chain monolamellae with polymethylene fragments as well as atomic force microscopy verify this assertion that the lamellar surface is still flat and well-ordered.

Introduction

Linear chain solid solutions are frequently found in commercially and naturally derived substances. For example, linear polymers are never obtained as a monodisperse molecular species but as a distribution of molecular weights.[1] Petroleum waxes are composed of a Gaussian distribution of chain lengths,[2] and the composition of natural waxes, e.g. from insects, is an even more complicated distribution.[3] Neutral and amphiphilic lipids also include an array of chain lengths and unsaturation sites.[4] In homogeneous multicomponent solutions, the distribution of ingredients determines the physical properties of the mass, which may be important for the function of the polydisperse assembly, as a material or as a component of a living organism.

It is only fairly recently that the solid-state structure of multicomponent linear chain assemblies has begun to be understood. The paradigm for these materials has often been the *n*-paraffins. Crystal structures of binary solid solutions have recently been reported from electron[5] and X-ray[6] diffraction studies, in which the most important effect of copacking of dissimilar chain lengths has been found to occur at a lamellar interface. This is because the effective minimization of molecular volume differences is expressed by longitudinal chain disorder within the lamellae, observed in crystallographic studies as an average falloff of atomic occupancy near the lamellar surface. Vibrational spectroscopy[7] and NMR spectroscopy[8] indicate that conformational disorder at this interface is also an important mechanism for stabilization of such structures. Polydisperse waxes have only recently been characterized by single-crystal diffraction techniques[9] but are found to have quite similar structures. More complex linear molecules such as the cholesteryl esters have also been studied in the binary solid state by X-ray crystallography.[10] Here, because of a static packing domain for the sterol nucleus, the effect of different chain lengths is more acutely felt. Recourse to microfractionation, as observed also for metastable paraffin solid solutions,[11,12] is found to occur at a much smaller molecular volume difference than observed for molecules with approximate cylindrical symmetry.

The importance of disorder in binary and multicomponent crystals for the stabilization of molecular volume differences leads to an apparent paradox when considering the overall *ordering* of the lamellar packing into single crystals large enough for electron or X-ray diffraction data collection. Just how does this long-range ordering occur, given that substantial disorder is expressed at the very interface that would account for ordered growth along the longest unit cell axial direction?

Materials and Methods

Materials. Several *n*-paraffins were used to construct binary solids to be examined in this study. The physical constants and purities of these compounds, as well as the manufacturers, were reported in an earlier paper.[11] Also, a petroleum-based candle wax (obtained in Shannon, Ireland) was examined in one part of the study. Finally, a commercial low molecular weight ($M_n = 535$) polyethylene standard with narrow chain length distribution ($M_w/M_n = 1.11$) was purchased from Scientific Polymer Products, Inc. (Ontario, NY).

Crystallization. Single crystals of binary and polydisperse combinations of paraffin chains were prepared in two ways. For solution growth, expressing the (001) face as the major surface,[13] dilute solutions of the materials were made up in petroleum ether or *p*-xylene. Monolayer crystals could then be formed by evaporation onto a substrate, e.g. a carbon-film-covered electron microscope grid, or onto a cleaved sheet of graphite (for AFM measurements; see below). The paraffin chain axes are oriented perpendicular to the best developed crystal face.

In order to examine the orthogonal view onto the molecular chains, samples could also be epitaxially oriented on benzoic acid. As described earlier,[14] this directional growth requires a very dilute solution of the linear molecule to be made up in the molten carboxylic acid. Since the two components form a eutectic solid, eptiaxial orientation is found to occur at the interface between the two phase-separated components. After removal of the nucleating substance in vacuo, the structure of the oriented paraffin crystals can then be determined by electron microscopy or electron diffraction.

Decoration Experiments. As shown by Wittmann and Lotz,[15] polymethylene fragments, when deposited onto a sample from the vapor phase, can be used as an anisotropic surface probe for polymer and oligomer crystals. The experi-

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ment is sensitive to the crystalline order of the surface being examined, since a dimensional matching of the surface lattice with the lateral packing of the polymethylene chain will cause the deposited material to be epitaxially oriented.

The procedure is rather easy to carry out. Thin crystals of the paraffins are placed on a support and held 13−16 cm below a tungsten filament screened by a metal sheet with a hole drilled through to allow the filament tip to be positioned over it. (This screen acts to shield the specimen from radiative warming when the filament is resistively heated.) This assembly is set up in a vacuum chamber which is then evacuated to about 10^{-5} Torr. A blob of polyethylene (M_w near 35 000), which had been melted onto the filament tip, is then heated to cause smaller (ca. $C_{60}H_{122}$) chain length fragments to be driven off as a vapor. These chain fragments collect at the lower surface where the crystals are held to form crystalline masses. When the substrate is noncrystalline, these deposits have no specific shape, whereas the chain fragments form anisotropic crystalline rods when there is an epitaxial lattice match to a crystalline substrate. In some cases, to enhance visibility of the surface decoration, the sample was then shadowed with C−Pt before removal from the vacuum chamber.

Electron Microscopy and Diffraction. All experiments were carried out at 100 kV on JEOL JEM 100B-7 or JEM 100CX II transmission electron microscopes. For electron diffraction studies, low beam dose conditions were used and patterns were photographed on Kodak DEF-5 film. The camera length was calibrated with the powder pattern from gold films deposited onto the grid surface. Higher beam doses were used in the electron microscopy of metal-shadowed specimens. In this case, exposures (at magnifications in the range 5−20 kX) were photographed on Kodak SO-163 electron imaging film.

Atomic Force Microscopy. Atomic force microscopy (AFM) was done with a contact mode Nanoscope II made by Digital Instruments, Inc. Standard Si_3N_4 Nanoprobe tips, mounted on 200 μm long cantilevers with a specified force constant of 0.12 N/m, were used. Generally, the measurements were made in air with a 15 μm scan range. Typical forces were 10^{-7}−10^{-8} N. Since this resulted in considerable damage to the n-$C_{30}H_{62}$/n-$C_{36}H_{74}$ samples, these were scanned again under water or ethanol. The samples were prepared by evaporating drops of dilute solutions of the paraffin samples in petroleum ether on substrates of highly oriented pyrolytic graphite. This resulted in surfaces which ranged from bare graphite to terraced regions with heights of one to several paraffin chain layers.

Results

An $hk0$ electron diffraction pattern (Figure 1) was obtained from all lozenge crystals grown from solution that is characteristic[16] of the rectangular layer packing in the $O_\perp$ methylene subcell[17] with cell constants near $a_s = 7.42$ and $b_s = 4.96$ Å (also matching the lateral unit cell spacings). When the polydisperse combinations are epitaxially oriented on benzoic acid, it is possible to obtain diffraction patterns with well-resolved peaks and at high resolution. For example, a pattern from a nearly 1:1 n-$C_{32}H_{66}$/n-$C_{36}H_{74}$ solid solution is shown in Figure 2a. The crystal structure (in a form similar to n-$C_{34}H_{70}$) has been reported earlier, based on the electron diffraction intensities.[5] Another diffraction pattern from the candle wax, a multicomponent solution, is shown in Figure 2b. From the indexing rule given previously,[9] this crystallizes with an average lamellar chain length, as if it were n-$C_{31}H_{64}$ in space group $A2_1am$ or n-$C_{32}H_{66}$ in space group $Pca2_1$. The respective average lamellar spacings are 41.1 ± 0.6 Å (41.3 Å) and 42.1 ± 0.3 Å (42.5 Å) (where the numbers in parentheses are the values for pure n-paraffins in the orthorhombic form predicted by Nyburg and Potworowski[18]). Quantitative crystal structure analyses of candle wax, composed of shorter chain components, and of an artificial "flat" wax, made up of equimolar compositions of all even-chain paraffins from n-$C_{26}H_{54}$ to n-$C_{36}H_{74}$, will be reported elsewhere.[9] Both diffract to very high resolution, e.g. the flat wax to 0.75 Å. Finally, in Figure 2c is a diffraction pattern from polyethylene $M_n = 535$. The mean lamellar spacing is 48.0 ± 1.0 Å, which is similar to the value for n-$C_{36}H_{74}$ (47.6 Å).

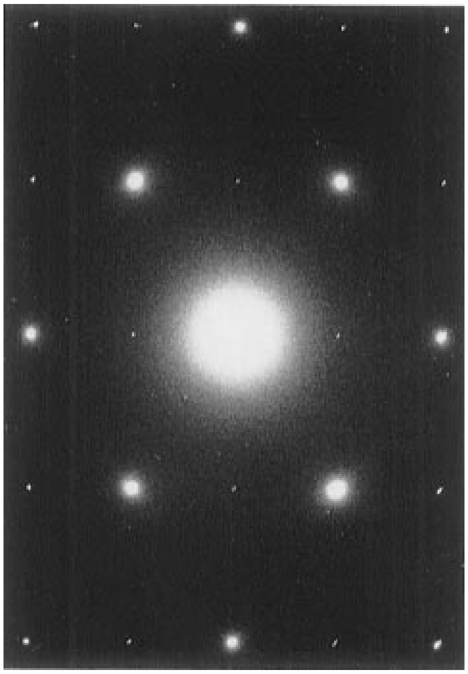

Figure 1. Electron diffraction pattern ($hk0$) from a solution-crystallized paraffin lamella (here, a 1:1 solid solution of n-$C_{32}H_{66}$/n-$C_{36}H_{74}$).

The polymethylene decoration of pure paraffins has already been described by Wittmann and Lotz.[15] As illustrated in Figure 3a for a pure alkane (see further description in terms of the lamellar sectorization in an earlier paper[19]), the chain fragments recrystallize from the vapor phase onto the lamellar surface, which epitaxially nucleates them so that the chain axes are nearly perpendicular to the {110} growth faces. There are two equivalent orientations which are randomly nucleated across the monolayer (001) face. Similar decoration motifs are found for nearly 1:1 combinations of n-paraffins—e.g. if the chain length difference is only one methylene group, as in n-$C_{40}H_{82}$/n-$C_{41}H_{84}$, two methylene groups, as in n-$C_{44}H_{90}$/n-$C_{46}H_{94}$, three methylene groups, as in n-$C_{41}H_{84}$/n-$C_{44}H_{90}$, or four methylene groups, as in n-$C_{32}H_{66}$/n-$C_{36}H_{74}$ or n-$C_{40}H_{82}$/n-$C_{44}H_{90}$. Even the low molecular weight polyethylene has evidence of surface order (Figure 3b).

The lattice ordering at the lamellar surface indicated by these decoration experiments was substantiated by atomic force microscopy. As a control experiment, surface images from n-$C_{36}H_{74}$ lamellae (Figure 4a) can be obtained at molecular resolution to reveal the order of the methyl groups terminating at the lamellar surface. Spacings of the surface lattice 0.47(5) nm by 0.78(5) nm correspond to $hk0$ electron diffraction measurements (see Figure 1) and are in reasonable accord with the earlier AFM work of Stocker et al.[20] Similar quality images can be obtained from n-$C_{35}H_{72}$/n-$C_{36}H_{74}$ solid solutions (Figure 4b) wherein the chains differ by one methylene group. The measured lattice spacings are 0.46(6) nm by 0.76(11) nm, again in accord with the

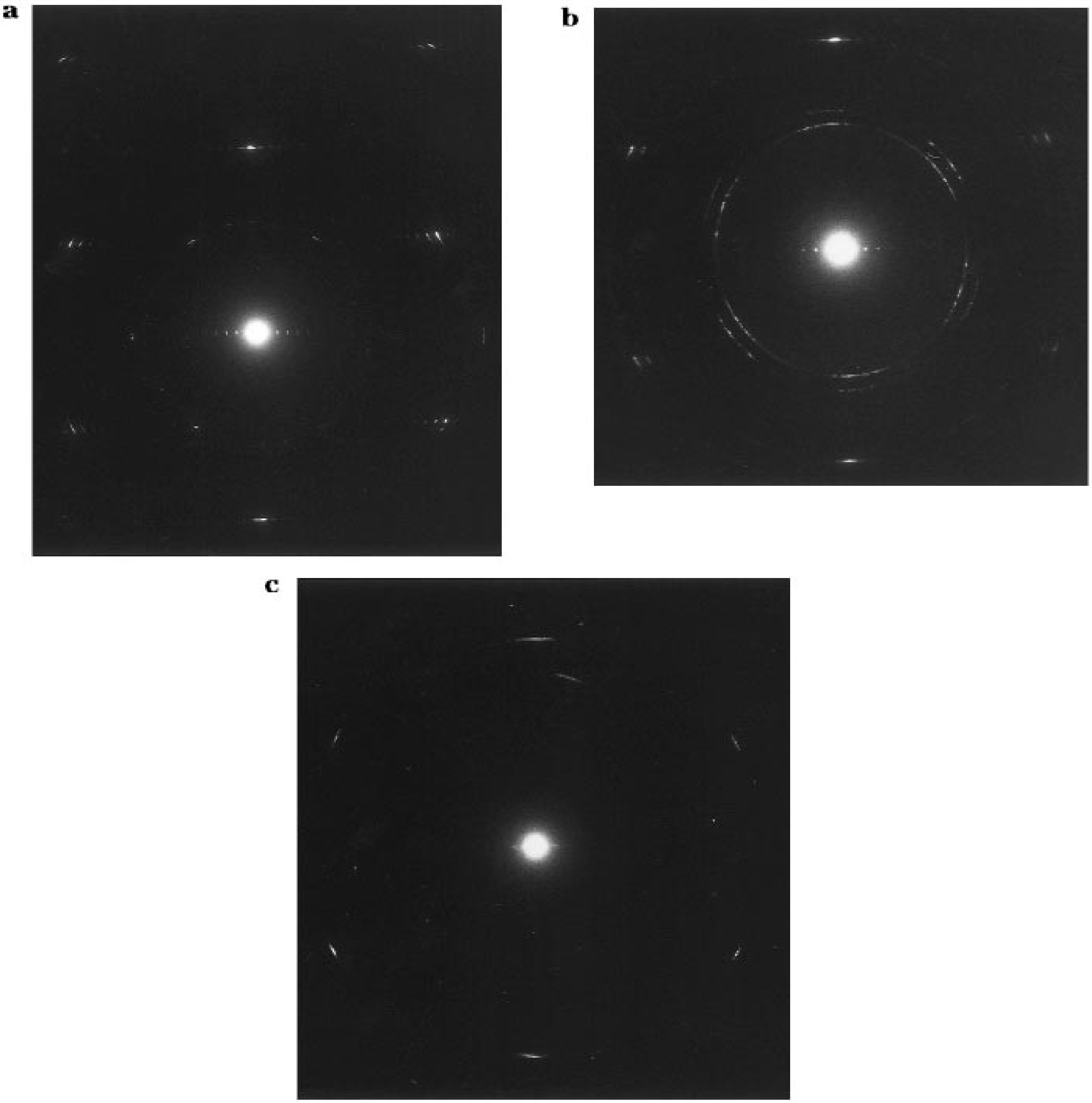

Figure 2. Electron diffraction patterns (0*kl*) from epitaxially oriented paraffin solid solutions: (a) 1:1 n-$C_{32}H_{66}$/n-$C_{36}H_{74}$; (b) multicomponent candle wax; (c) low molecular weight polyethylene.

orthorhombic sublattice. More surprising, perhaps, is that even the n-$C_{32}H_{66}$/n-$C_{36}H_{74}$ lamellae show signs of a surface lattice (Figure 4c) with spacings 0.59(5) nm by 0.78(5) nm. Although it is not so well resolved as the other ones, the surface structure may well be regular enough to explain decoration results, as shown in Figure 3. On the other hand, n-$C_{30}H_{62}$/n-$C_{36}H_{74}$ samples gave no indication of surface order at the atomic level.

Discussion

As discussed at great length by Kitaigorodskii,[21] crystal growth of van der Waals molecules is well approximated by a repulsive hard sphere model for the atom−atom nonbonded potential functions. The resultant molecular packing scheme is a matter of efficiently matching shapes, so that protrusions from one molecular layer will fit into hollows left by another. Recently, the concept of a van der Waals surface has been justified again,[22] after some adverse criticism. Paraffins have always been convenient subjects for studies of crystal growth since the greater fraction of the intermolecular interactions are involved in the formation of a single lamellar layer, whereas the stacking of lamellae accounts for a smaller interactive component.[23] In further theoretical developments, Boistelle and his co-workers[24,25] have shown that the (001) face of linear molecules is convenient to study, not only for the stacking of adjacent layers in the formation of a perfect crystal[26] but also for the formation of polytypes[24] (when the energetic differences between rotationally disordered layer stackings are very small) and even the epitaxial deposition of long chain axes from the vapor phase,[25] predicting the decoration growth mechanism used by Wittmann and Lotz[15] (and also in this study). In all

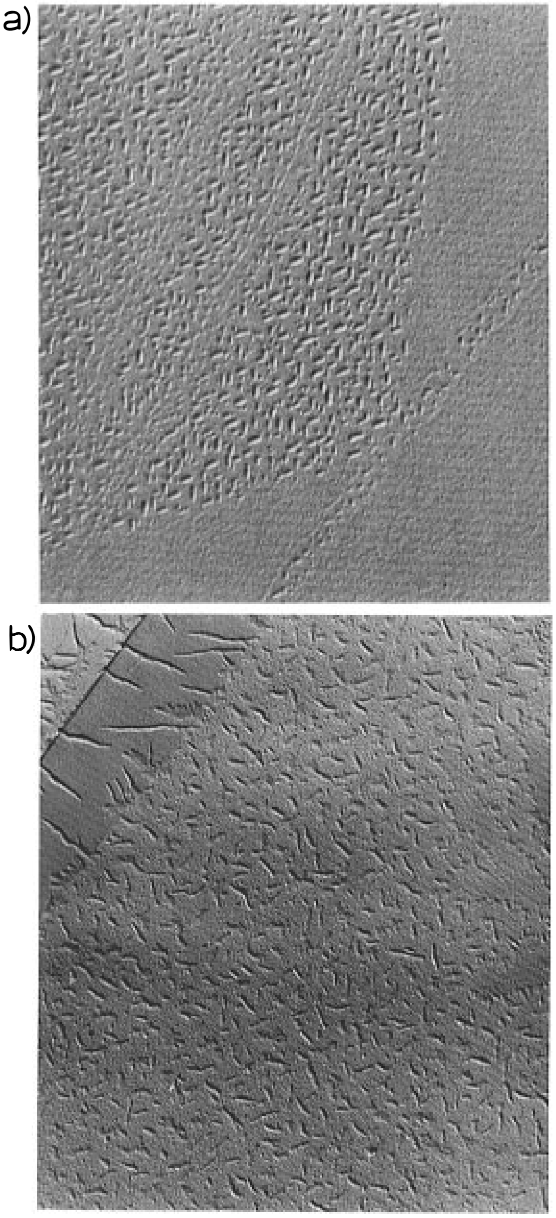

Figure 3. Decoration of paraffin lamellae with polymethylene fragments: (a) pure n-$C_{36}H_{74}$ (a similar decoration motif has been found for single crystals of n-$C_{60}H_{122}$ and for some binary paraffin solid solutions); (b) low molecular weight polyethylene.

cases, favorable interactions between atomically flat crystallographic planes, i.e. a form of epitaxy, is tacitly understood.

The existence of solid solution single crystals for such molecules has been known at least since 1974 when Lüth et al.[27] made their first qualitative description of a structure, based on single-crystal X-ray data. We have demonstrated (e.g. Figure 2) the growth of single crystals for a wide variety of binary and multicomponent solid solutions. Also Bennema et al.[28] have published micrographs of multilamellar crystals from diesel fuel wax. (The ordering of such samples was studied subsequently in unpublished electron diffraction studies of solution and epitaxially crystallized diesel wax samples.) Electron diffraction patterns are found with a very high resolution, not only for stable solid solutions[5,9,11,29] but also for metastable solid solutions[11,30] that grow into an incommensurate solid, and also a sequence of eutectic solids.[11,30] Multicomponent paraffin waxes also crystallize as if they are perfect crystals and can diffract even

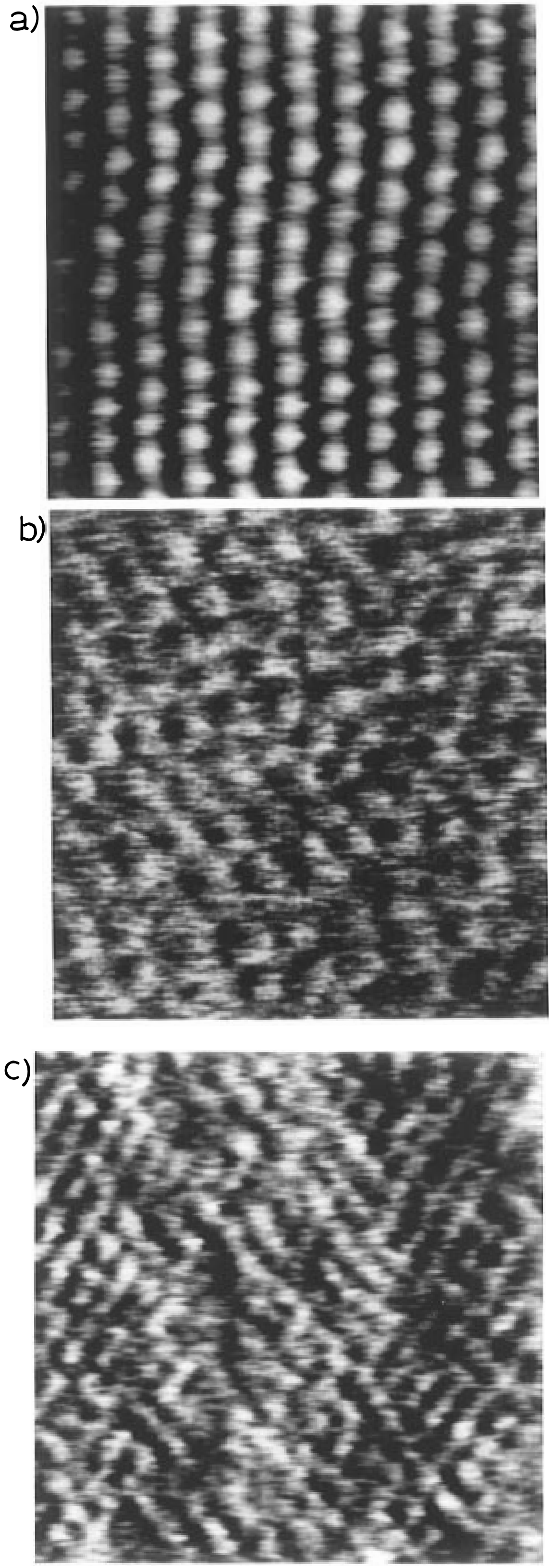

Figure 4. AFM images of paraffin lamellar surfaces: (a) pure n-$C_{36}H_{74}$; (b) n-$C_{35}H_{72}$/n-$C_{36}H_{74}$ solid solution; (c) n-$C_{32}H_{66}$/n-$C_{36}H_{74}$ solid solution.

to 0.75 Å resolution.[9] Yet, at the same time, the structures are disordered, precisely at the lamellar surface where the growth into a multilamellar single crystal should take place. Diffraction experiments[5,6] indicate that the outer carbon positions have only fractional occupancies. Spectroscopic measurements[7,8] reveal an increasing amount of conformational disorder as this lamellar surface is approached.

How can this paradox of a disordered surface giving rise to a highly ordered crystal be resolved? Surface decoration with polymethylene chain segments indicates that, even though there are different chain lengths in the lamellae, the surface is still ordered and regular enough to epitaxially nucleate these chains. AFM experiments also verify the essential flatness of this surface, even when the chains differ by four methylene units. The only conclusion that can be drawn from these observations, then, is that, in the attempts to minimize the volume difference among the component molecular species, by either translational or conformational disorder, the resulting surface must be left as a plane, with very few ciliar protrusions and with a good average lattice repeat. Only then can the next lamella be nucleated so that a three-dimensional crystal can be grown, yielding diffraction patterns with very high resolution and sharp maxima.

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