Coexisting Lattice Structures in a Langmuir–Blodgett Film: Identified by Atomic Force Microscopy

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Molecular resolution atomic force microscope images of the surface of barium arachidate Langmuir–Blodgett (LB) multilayers show coexisting domains of three different structures, two of which have previously unknown crystal lattices. The most prevalent structure is a tilted (26°) triclinic packing of unit cell area 61.1 Å² (20.4 Å³/molecule) with a 3X1 superstructure causing a sawtooth height modulation. Also present is a tilted (19°) rectangular herringbone packing with alternating molecular pairs displaced vertically by a single methylene group having a unit cell area of 80.6 Å² (20.1 Å³/molecule). Untilted, molecularly disordered regions with an area per molecule virtually identical to the other two packings are also seen, all within the same molecular layer. Although the alkane packing is quite distinct between the three domains, the area per molecule is essentially constant, and is substantially greater than that observed when cadmium is used as the counterion. This suggests that the barium counterion determines the area per molecule of the LB film and that the alkane packing adjusts to find the optimal structure given this constraint. Although the three structures do not occupy similar area fractions of the LB film, all three are found on each film we have examined. The submicrometer extent of each region, the extent of twinning and defects, and the complexity of the lateral and vertical molecular packing make the determination of the lattice structure of these films impossible by any technique other than atomic force microscopy.

Introduction

Langmuir–Blodgett (LB) films have many potential applications in the areas of electronics, nonlinear optics, cell membrane models, and biosensors. Many of these applications of LB films are based on the premise of perfect molecular layering and orientation. There is also the general belief that the structure of the monolayer at the air–water interface is simply related to the structure of the monolayer and multilayer after transfer to a substrate. Hence, studies of the degree and type of order of these molecularly layered films are of critical importance.

In addition, LB films are model systems for the crossover between two and three dimensions and may demonstrate aspects of the physics of two dimensions including hexatic phases. Ordering in LB films has been studied by several techniques, including electron diffraction, X-ray diffraction, X-ray reflectivity, near-edge X-ray adsorption fine structure (NEXAFS), the surface force apparatus, and various spectroscopies. These experiments have given information about molecular order and orientation averaged over areas from square micrometers to square millimeters and, typically, averaged over all of the layers of the LB film. However, as is the case here, the features of interest are often smaller than the minimum areas these probes can resolve, and the averaging can make analysis difficult, if not impossible. For this reason, local probes, such as the atomic force microscope (AFM), have emerged as essential techniques for structural characterization because of their ability to identify lattice structure and defects in LB films on length scales ranging from molecular resolution to many micrometers.

Several recent papers have shown that LB films of cadmium arachidate (CdA) as thin as two molecular layers show features reminiscent of bulk crystals, such as long-range order and periodicity at the submicron scale. The following experiments have given information about molecular order and orientation averaged over areas from square micrometers to square millimeters and, typically, averaged over all of the layers of the LB film. However, as is the case here, the features of interest are often smaller than the minimum areas these probes can resolve, and the averaging can make analysis difficult, if not impossible. For this reason, local probes, such as the atomic force microscope (AFM), have emerged as essential techniques for structural characterization because of their ability to identify lattice structure and defects in LB films on length scales ranging from molecular resolution to many micrometers.

range order\textsuperscript{12-20} and grain boundaries.\textsuperscript{19} However, they also have distinctive features, such as an incommensurate undulating height modulation,\textsuperscript{12} and can be quite sensitive to the number of layers,\textsuperscript{20,22} pH during deposition,\textsuperscript{21} or type of cation as we show here. This is intriguing since the molecular packing symmetry and lattice dimensions of such systems has not always been shown to correspond to one or another of the well-known packings of long-chain alkanes,\textsuperscript{20,23} wherein the zigzag chains of neighboring hydrocarbon molecules fit into each other one of several distinct ways.\textsuperscript{24} In this paper we show that by the simple substitution of Ba\textsuperscript{2+} for Cd\textsuperscript{2+} in LB films virtually all of the structural parameters of the molecular organization change dramatically. The local packing changes from a uniform, untitled, nearly-centered rectangular lattice (with the two molecules in the unit cell having the familiar “herringbone” arrangement) in the case of CdA\textsuperscript{20} to three different packing arrangements in the case of barium arachidate (BaA).

The predominant structure (\textasciitilde70\% of the surface area in the films we have examined) in BaA, in described locally by a well-known, tilted, triclinic packing.\textsuperscript{24} However, a regular commensurate superstructure of packing defects is introduced into the normal triclinic lattice, resulting in a “sawtooth” surface modulation and a previously unknown structural phase with a three-molecule unit cell of area 61.1 Å\textsuperscript{2} or 20.4 Å\textsuperscript{2}/molecule. The effect of the packing defects is to reduce the overall tilt of the triclinic packing from 36° to 26°, thereby increasing the packing density by 4\%, resulting in a smaller area per molecule. The minority structure (<10\%) is a four-molecule unit cell in which pairs of molecules are packed in a tilted (19°) rectangular herringbone lattice, but adjacent pairs alternate vertically up and down by a single methylene group. The molecular area of the 2×2 lattice is 80.6 Å\textsuperscript{2} or 20.1 Å\textsuperscript{2}/molecule. The difference in molecular area between the two lattices is only 1\%, although the details of the packing arrangement are completely different. The third structure, which occupies 20–30\% of the area of the film, is disordered in comparison to the other two areas, but still presents diffuse spots in the Fourier transforms and some evidence of röllike patterns in the images. These disordered areas are found to be untitled by comparing the bilayer thickness of the three regions, and have roughly the same area per molecule as both lattice structures.

We speculate that the molecular areas of the various arrangements, which are all close to the same, are dictated by the size and bonding requirements of the barium counterion. The alkane packing is then forced to adopt one or more optimal configurations compatible with that area per molecule. Such an arrangement is yet another example of the concept of packing “frustration” where local and global packing structures are incompatible. Such frustrated structures occur often in phospholipid–water bilayers,\textsuperscript{25,26} Langmuir–Blandgett films,\textsuperscript{27,28} thermotropic blue phases,\textsuperscript{29-32} and smectic-A* phases.\textsuperscript{33,34} The structure of these materials are often theoretically related to a frustration in molecular packing due to some internal anisotropy of the molecule.\textsuperscript{35-38} In particular, there can be a competition between the packing of the head and tail groups due to different size or symmetry or between local packing and long-range order that necessitates structural defects to ensure the proper global ordering.\textsuperscript{39-43}

Scanning probe microscopies, i.e., atomic force microscopy and scanning tunneling microscopy (AFM and STM), have been used increasingly to image LB and other thin organic films.17–23 The AFM can routinely achieve molecular resolution lattice images on a variety of nonconductive surfaces\textsuperscript{17-20} and has been shown to be able to identify local defects and inhomogeneities in ordered surfaces.\textsuperscript{19,20} The scanning tunneling microscope has also been applied to structural studies of organic molecules either adsorbed or deposited on substrates,\textsuperscript{36-38} but the technique is limited to conductive substrates and layers less than a few nanometers thick, so it is of limited use for studies of LB monolayers and cannot be used for multilayers.\textsuperscript{38} The AFM is extremely surface sensitive, probing only the atoms located directly at the interface with a lateral resolution of \textasciitilde1 Å. With proper attention to experimental details, lattice parameters can be measured with reproducibility and an overall precision of \textasciitilde1\%. Difficulties that must be considered include damage to the sample by the AFM tip, image drift due to thermal variations and hysteresis of the piezoelectric scanners, and both gross and subtle variations between AFM tips. We show here that the lattice symmetry and repeat distances of barium arachidate multilayer films can be determined with the AFM with a precision equivalent to that of high-resolution X-ray diffraction.\textsuperscript{40} The combination of high-precision lattice measurements and three-dimensional, molecular resolution images greatly simplifies the determination of complex lattice structures in thin organic films. In fact, the complexity and small domain sizes of the barium arachidate lattices make this work impossible by any presently available technique other than AFM.

**Experimental Section**

Arachidic acid (CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{17}COOH, Aldrich, 99\%) was spread from chloroform (Fisher spectranaalyzed solution (1.85 mg/mL) onto an aqueous (water from a Milli-Q\textsuperscript{29} water system was used) subphase with 5 × 10\textsuperscript{-4} M BaCl\textsubscript{2} (Aldrich, 99.99\%) added and adjusted to pH 6.9 by addition of NaHCO\textsubscript{3} (Aldrich, 99.9\%) or pH 9.5 by addition of NaOH (Fisher, 99\%). Muscovite mica substrates were cleaned by continuous rinsing with ethanol for 5 min and cleaved using ordinary adhesive tape immediately before use. Isotherms and film deposition were done on an automated Nima\textsuperscript{42} trough at 22.0 ± 0.5 °C and a surface pressure of \(\pi = 30 \pm 0.1\) dyn/cm with a vertical dipping speed of approximately 1.6 mm/min. Transfer ratios for the three-layer films used in this study were approximately unity. We were not able to deposit multilayers at surface pressures of 10 and 20


(39) Millipore Corp., Bedford, MA.

(40) NIMA Technology Ltd., Warwick Science Park, Coventry CV4 7EZ, England.
mN/m at either pH, although in previous work with CdA, we observed identical lattice structures regardless of the transfer pressure.\textsuperscript{20,22} Mono- and trilayer films deposited on a hydrophilic substrate and imaged in air had the methyl end of the alkyl chain at the interface. The length of storage time (<2 weeks in closed containers) did not affect the images. AFM measurements were performed with a Nanoscope II\textsuperscript{44} FM in air at room temperature, using a 1 \textmu m \times 1 \textmu m scan head and a silicon nitride tip on a cantilever with a spring constant of 0.12 N/m. The best molecular resolution was achieved by using the so-called "force mode"; i.e., scanning the tip at approximately constant height and measuring spring deflection. Typical forces used were on the order of 10 nN.

We have shown elsewhere that the AFM may be used to determine lattice parameters of LB films in a quantitative manner.\textsuperscript{20} Special attention must be paid to calibration, elimination of image drift, and variation between AFM tips. The x and y (lateral) dimensions of the AFM were calibrated using six images of areas from 30 to 40 nm on a side obtained from different regions (within 100 nm of each other) on a mica surface. This procedure was repeated with six different AFM tips. For each tip, the reciprocal lattice vectors (riv), determined from Fourier transforms, were averaged to reduce statistical fluctuations. The resulting wave vectors were parameterized by their magnitude and the angle between them. The six data sets were fit to find the best overall linear calibration constants in x and y directions. The standard deviations from the expected values for mica of 60° and 0.450 nm (adjusted with the best fit calibration) were \sigma_x = 0.9° and \sigma_y = 0.005 nm. This shows that the absolute precision of our m independent calibrations to be \sigma_m^{-1} = 0.005/\sqrt{(6/0.450)} \approx 0.5%. The vertical calibration was done by measuring the known, 5.8-nm height of cadmium arachidate bilayers deposited by Langmuir–Blodgett deposition.\textsuperscript{20} In general, the precision of the vertical calibrations was less than the lateral calibration, with \sigma_z = 0.1 nm and an absolute precision of \approx 1 %.

Good quality images of the LB film lattice must be obtained over large areas in order to determine lattice parameters with sufficient precision to evaluate lattice details. This requires that both thermal and mechanical drift be eliminated for best results. The degree of drift in the image was evaluated by comparing Fourier transforms of images scanned in opposite directions (up and down). The initial variations between spot positions from up and down scans were often as large as 0.03 nm in amplitude and 3° in angle. However, after scanning times on a single area ranging from 0.5 to 2 h, Fourier spots from the two scan directions were in the same location within our ability to measure them given the digitization of the data on the display (0.01 nm, 0.8°).

There was no damage done to the sample even after hours of continuous imaging in the AFM, except where noted. In addition, great care must be taken in the crystallographic analysis of images; the combination of high-resolution, three-dimensional images and autocorrelation functions can simplify the determination of even especially difficult, multiple-molecule unit cells, as is shown here.

Results

Low-magnification images of the films showed distinct inhomogeneities on the surface of all multilayer films examined. Figure 1a shows a 600-nm region which contains holes one bilayer deep as well as other, more subtle, features. Figure 1b shows a region containing many of the shallower features having a depth of only a few angstroms. By analyzing approximately 15 images of this type, we have identified 3 distinct regions on the basis of surface height. The 3 regions are at heights of 5.0 \pm 0.1, 5.2 \pm 0.1, and 5.5 \pm 0.1 nm, respectively, when measured from the bottom of the bilayer holes. The surface on the bottom of such holes is a flat, molecularly disordered monolayer surface similar to that seen on CdA monolayers.\textsuperscript{20} A fully extended, untitled bilayer has a height of 5.5 nm.\textsuperscript{20} Approximately 60 well-calibrated, drift-free molecular resolution images (30-40 nm on a side) were obtained on 4 LB films (2 each at pH 6.9 and 9.2) using 7 different AFM tips.

Although BaA films made at pH 6.9 contain only 50-60% of the possible Ba and those made at pH > 9 have 100% Ba,\textsuperscript{42} we noticed no significant difference in our results for the two types of films. This is consistent with IR measurements that show that the alkane chains in multilayer barium stearate are arranged in a triclinic

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{(a, top) Low-magnification image (0.5 \mu m \times 0.5 \mu m) of a three-layer LB film of barium arachidate. Lighter colors correspond to higher regions. The surface has several regions of varying height which are labeled T for tilted, U for untitled, and 1 for a one-layer region at the bottom of a bilayer hole. (b, bottom) A region of the surface containing fewer bilayer holes, allowing better observation of the contrast between tilted and untitled regions.}
\end{figure}

\textsuperscript{41} Nanoscope II FM, Digital Instruments, Inc., Goleta, CA 93117.
packing that is invariant with pH from 7 to 9.5. Surface potential measurements suggest that the Ba ion interacts with fatty acids electrostatically by screening negative charges in a nonspecific way, while Cd interacts more specifically via covalent bonding. Hence, BaA films are a mixture of protonated and deprotonated fatty acids with Ba over the entire pH range, while cadmium forms specific complexes with deprotonated fatty acids with a well-defined stoichiometry.

There was, however, perfect correlation between the molecular structures observed and the height of the region. The 5.0-nm high regions had what we shall call the 3×1 structure (~70% of the surface), the 5.2-nm high regions had the 2×2 structure (~5%), and the 5.5-nm high regions had the disordered structure (~25%). Figure 2a shows high and low regions that were found to correspond to the 2×2 and 3×1 structures, respectively. The cross section shown in Figure 2b shows that the difference in height between the two types of regions is 0.4–0.5 nm. Similarly, Figure 3a shows high and low regions that were found to correspond to 2×2 and 3×1 structures, respectively, and the cross section in Figure 3b shows a height difference of about 0.15 nm.

**Figure 2.** (a, top) Region containing high and low areas corresponding to disordered (marked D) and 3×1 (marked 3) structures, respectively. Indistinct horizontal streaks are electronic noise from the raster pattern and the height leveling software and are not indicative of any surface structures. (b, bottom) The height cross section along the line marked in (a) shows the height difference between the disordered and 3×1 regions to be 0.4–0.5 nm.

**Figure 3.** (a, top) Region containing high and low areas corresponding to 2×2 (marked 2) and 3×1 (marked 3) structures, respectively. (b, bottom) The height cross section along the line marked in (a) shows the height difference between 2×2 and 3×1 regions to be 0.1–0.2 nm.

Representative molecular resolution images of the 3×1, 2×2, and disordered structures are shown in Figure 4a–c. The respective two-dimensional Fourier transforms (FT) are shown in Figure 4d–f, respectively. The FT’s of the disordered images varied from location to location so no particular lattice structure was determined. However, positional correlations typically extended 5–6 repeat distances even in the disordered regions. Figure 5 shows a comparison of the positional correlation function (along a lattice direction) of the 3×1 and disordered structures. The 3×1 correlations (solid line) have a gradual decay but are still substantial at 10 nm (in fact the correlations extend as far as we can measure with our instrument, ~40 nm) while the correlations of the disordered structure (dashed line) die out by 4 nm. In order to determine the unit cell dimensions of a given lattice structure, it was first necessary to determine accurately the basis of the reciprocal lattice, 
in. The choices of b₁ and b₂ for each structure are labeled in Figure 4d,e. In the 3×1 structure b₁ corresponds to a distance suggestive of one molecular row; however, b₂ corresponds to a distance about 3 times as large, hence the 3×1 nomenclature and the three-molecule unit cell. Figure 6a shows the Fourier amplitude (with background subtracted) along the b₂ direction for an image which shows 14 harmonics. By fitting the peak positions versus harmonic number to a line, we show explicitly that the peaks are actually harmonics of b₂ and therefore b₂ is a basis vector. Analogously, the 2×2 structure has b₁ and b₂ of equal length corresponding to two molecular rows each. The names we have given the two structures are by
Figure 4. Unprocessed molecular resolution image and Fourier transforms of the various structures seen: (a, top left) 3×1, individual molecules can be seen as well as the sawtooth superstructure every three rows (running from lower left to upper right); (b, middle left) 2×2, alternating rows of high and low molecules can be clearly seen; (c, bottom left) disordered, isolated areas of molecular order are visible but without long-range correlation; (d, top right) Fourier transform (FT) of (a) with the basis of the reciprocal lattice labeled (many high-order peaks are visible); (e, middle right) FT of (b) with the basis of the reciprocal lattice labeled; (f, bottom right) FT of (c). Only diffuse peaks can be seen corresponding to short-range order.
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Figure 5. One-dimensional autocorrelation functions (normalized to 1) along a lattice direction of the 3×1 structure (solid line) and the disordered structure (dashed line). Although the 3×1 structure has oscillating correlations that continue well past the plotted range of 10 nm (we have measured ≥40 nm), the positional correlations of the disordered structure die out after 5–6 lattice repeat distances or ~4 nm.

Figure 6. (a, top) Intensity of a FFT along the b2 direction with the intensity along the perpendicular direction (which is featureless) subtracted as background. Fourteen peaks are visible. (b, bottom) In order to demonstrate explicitly that the peaks are harmonics of the first, we have fit the center position of each peak versus its harmonic number to a straight line. The inset plot of the residuals from the fit show that any deviation is not systematic and is due to fluctuations.

Figure 7. (a) Unit cell diagram of the 3×1 structure showing the three-molecule unit cell dimensions a1 and a2 (determined from the position of the Fourier spots) as well as the positions of molecules within the unit cell given by translations of ±u (determined from analysis of autocorrelation functions). (b) Explicit demonstration of how the unit cell can be constructed by simply inverting every third "local cell." This remarkable coincidence implies that a simple packing defect may be inserted every three molecules. (c) Unit cell diagram of the 2×2 structure showing the unit cell dimensions a1 and a2, as well as the centered rectangular packing (defined by u1 and u2) of which the lattice is constructed. The dashed figures represent the hydrocarbon skeleton of each molecule and demonstrate the herringbone nature of local packing. The circles represent the position of the terminal methyl groups, with the light ones being displaced vertically by a chain repeat distance (2.54 Å) relative to the dark ones.

Figure 8. (a, top) A detail from the two-dimensional autocorrelation function of the image shown in Figure 4a. Note the packing defects separating every three rows of local packing. (b, bottom) Height cross section taken in the (01) direction. The sawtooth pattern is most easily observed by noting the modulation of the depth of the troughs between molecules.

8a, which contains information from all the Fourier spots, and the height modulation of the image along the 01 direction (Figure 8b). Analysis of many autocorrelation functions tells us that the local packing (within the unit...
Figure 9. Structural model of the packing of alkyl chains in the 3×1 structure, viewed along the chain axis. The black lines represent the projected hydrocarbon backbone of the chain, while the circles represent the hard-sphere radius of the hydrogen atoms. The hashed circles represent the hydrogen atoms belonging to a particular carbon atom in the chain (say, the tenth) while the unfilled circles represent the hydrogen atoms belonging to the carbon atom directly below on the chain (e.g., the ninth). Tangential circles from neighboring molecules represent close packing and demonstrate which atoms are at the same height. The figure shows two regions of tilted triclinic packing separated by a packing defect which causes a jump in the structure both vertically and in the plane. In the LB film, such defects occur exactly every three rows.

The cell can be defined by a1 and a second vector (u) as shown in Figure 7a. The positions of the three molecules within the unit cell are therefore defined by translations of ±u. The three-molecule unit cell area is 61.1 Å², corresponding to 20.4 Å²/molecule. Figure 7b serves to point out a remarkable concidence: the lattice vectors of the unit cell can be exactly reconstructed from the local packing vectors simply by inverting every third local cell. This inversion corresponds to a particular packing defect. Figure 6b shows a height cross section taken in the (01) direction. The individual oscillations correspond to terminal methyl groups; however, a regular sawtooth pattern with a period of three molecules is apparent by examining the depths of the troughs between molecules. Hence, this tells us that the packing defect includes a displacement in the z direction. Putting the images, height modulation, and Fourier transform information together, we can construct a molecular packing model consistent with all of the data. This model, shown in Figure 9, shows that tilted layered structures can be formed by displacing a neighboring molecule along its axis by the repeat distance along the chain. (Where solid lines touch, the methylene groups are in the same horizontal plane; overlap of solid lines indicates a vertical displacement.) The view in Figure 9 is along the axes of the chains and shows one way in which such chains can be packed (the “T” subcell according to Kitagorodskii24). The uniformly tilted regions on top and bottom are joined by a very specific sort of defect, similar to a stacking fault in three dimensions, which is consistent with the inversion of the local cell illustrated in Figure 7b. If we project the lattice dimensions deduced from our experiments onto the plane perpendicular to the alkane chains, we obtain the chain packing dimensions a1(cb) = 0.42 ± 0.01 nm and a2(cb) = 0.45 ± 0.01 nm, with the angle between them γ(cb) = 76 ± 1°. This compares favorably with Kitagorodskii’s24 ideal values of 0.412 nm, 0.445 nm, and 77° for this type of packing. The packing defect reduces the tilt to 26° from a value of 36° in the uniformly tilted structure. This calculated tilt angle is consistent with the measured bilayer heights (5.0 ± 0.1 nm) of these regions as (5.5 nm) cos(26°) = 5.05 nm.

Figure 10a shows a remarkably high resolution image of the 2×2 structure. By inspection of the image and the cross section along the a2 direction (Figure 10b), one can see that there are alternating rows of low and high molecules. In addition, there is a zigzag pattern along the rows. These features and the particular lattice distances and symmetry are perfectly consistent with the type of structure shown in Figures 7c and 11 which show the familiar centered rectangular herringbone structure15 tilted 19° along the a1 direction (Kitagorodskii24 R(01)). In addition, however, every other (a1) row of molecules is displaced vertically by a repeat distance (2.54 Å) along the chain. The local packing dimensions deduced from this structure (Figure 7c) of u1 = 0.51 ± 0.01 nm and u2 = 0.79 ± 0.01 nm compare favorably with the “ideal” chain packing dimensions for the tilted rectangular structure24 of 0.496 and 0.785 nm. The calculated tilt angle is also consistent with the measured bilayer height of 5.2 ± 0.1 nm as (5.5 nm) cos(19°) = 5.26 nm. The molecular area of the 2×2 lattice is 80.6 Å² or 20.1 Å²/molecule. The difference in molecular area between the 2×2 and 3×1 structures is only 1%, although the details of the packing arrangement are quite different.

The third structure, which occupies 20–30% of the area of the film, is disordered in comparison to the other two areas, but still presents diffuse spots in the Fourier transforms and some evidence of rowlike patterns in the
Figure 11. Structural model of the packing of alkyl chains in the 2×2 structure, viewed along the chain axis. The black lines represent the projected hydrocarbon backbone of the chain, while the circles represent the radius of the hydrogen atoms. The circles filled with darker colors represent molecules in rows that are displaced vertically by a chain repeat distance relative to the lighter molecules. Along each row the herringbone pattern can be seen.

images. These disordered areas are found to be untitled by comparing the bilayer thickness of the three regions. This observation shows that this region is not a mixture of the two types of crystal lattices observed in other regions. A rough estimate of the molecular area gives a value close to that of the two lattice structures. The location of the Fourier transform spots also changes with time, indicating that some sort of molecular rearrangements or lateral diffusion is occurring. This is not surprising as an untitled lattice with an area per molecule of 20 Å² is not close packed which would allow for greater molecular motion.

Discussion

The bulk crystal structures of fatty acids display a rich polymorphism. Crystals of the same material often appear to have different crystal symmetries when prepared by different methods. At least three types of symmetry are known, A, B, and C. The nearly-centered rectangular structure of the 2×2 regions is related to the B and C types, while the triclinic 3×1 structure is locally similar to the A type. Clearly the cation, in association with the headgroup, must play a role in deciding which of the several alkane packings will be favored. In the case of barium the packing has been further adjusted by the addition of two commensurate defect superstructures.

To accommodate the Ba²⁺ ion, the alkane lattice must be more loosely packed than the close-packed untitled herringbone structure observed in CdA (18 Å²/molecule), and so must tilt by introducing a regular offset of one or more methylene groups per chain, or by giving up the close packing entirely. This leads to a reduction in the alkane-alkane contact, and a consequent reduction in the van der Waals interaction energy. The appearance of regular defects may be a compromise between the two driving forces. The 3×1 structure appears to be favored, perhaps because it allows more alkane contact, but not sufficiently to eliminate the appearance of other structures entirely. It is unknown whether the structures we have observed are present in the interior of thick BaAA LB films (or crystalline BaA for that matter) or if they are present only by virtue of the extra freedom given by the free surface, in which case they would be analogous to crystalline surface reconstructions. Clearly, this is an interesting avenue for further research. Kato and Oshima have observed that annealing barium arachidate monolayers on the water surface at temperatures near the melting point of the alkane results in fewer macroscopic defects in films transferred to substrates.

Conclusions

We have determined that the surface of barium arachidate LB films contains three types of regions, untitled somewhat disordered regions which cover about 25% of the surface, tilted (26°) regions with local triclinic packing and a 3×1 superstructure which cover ~70% of the surface, and a tilted (16°) centered rectangular lattice with a 2×2 unit cell constructed by molecular rotation in one direction and vertical translation in the other. These results show that the molecular tilt in Langmuir–Blodgett films is significantly more complicated than that predicted by molecular dynamics simulations, in that for a given area per molecule, there can exist multiple lattice structures of varied symmetry. Because of the detailed, local, three-dimensional information given by the AFM, we have been able to construct molecular packing models which are based on known ways of packing hydrocarbon chains and are consistent with the data in every detail. No other technique would have permitted such an analysis, given the coexistence of submicrometer regions, and the complex three-dimensional structures on the surface of extremely thin films (three molecular layers). Although there have been many cases in which the AFM has verified surface structures known from other techniques, this study demonstrates the unique abilities of the AFM as a tool for determining new surface structures on molecular length scales.

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