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SURFACE MOLECULAR STRUCTURE DETERMINATION OF LITHIUM SALT OF 10,12-NONACOSADIYNOIC ACID MONOMER AND POLYMER LANGMUIR-BLODGETT FILMS BY SCANNING FORCE MICROSCOPY COMPARED TO ELECTRON DIFFRACTION RESULTS

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SURFACE MOLECULAR STRUCTURE DETERMINATION OF LITHIUM SALT OF 10,12-NONACOSADIYNOIC ACID MONOMER AND POLYMER LANGMUIR-BLODGETT FILMS BY SCANNING FORCE MICROSCOPY COMPARED TO ELECTRON DIFFRACTION RESULTS

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

Langmuir-Blodgett films of lithium salts of 10,12-nonacosadiynoic acid monomer (Li/16-8 DA) and polymer (Li/16-8 PDA) were characterized by scanning force microscopy (SFM or AFM) to study their surface molecular structure. Based on analysis of these images, a two-dimensional oblique unit mesh is assigned for Li/16-8 DA monomer LB film with unit mesh parameter c = 0.549 ± 0.040 nm and b = 0.541 ± 0.060 nm with an angle of 113°. A hexagonal unit mesh is assigned for Li/16-8 PDA with unit mesh parameter c = 0.497 ± 0.052 nm and b = 0.497 ± 0.060 nm. We then report the comparison of two-dimensional, fast Fourier transform (FFT) of SFM images to the electron diffraction images. From the viewpoint of a three-dimensional structure projected onto a plane, centered rectangular nets can be assigned for both Li/16-8 DA and Li/16-8 PDA. The monomer unit cell parameters are c = 0.460

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± 0.040 nm and b = 1.020 ± 0.060 nm. The polymer cell parameters are c = 0.485 ± 0.080 nm and b = 0.820 ± 0.010 nm. The correlation between the two very different methods of surface structure determination is excellent. However, care must be taken in assigning the unit net (two-dimensional representation) and the projected unit cell (three-dimensional) vectors.

Key Words: Surface molecular structure; Lithium salt of 10,12-nonacosadiynoic acid monomer and polymer; LB film

INTRODUCTION

In a series of papers [1-5], we have examined the structure of various diacetylene monolayers and multilayers deposited by the Langmuir Blodgett technique or one of its variations. Various experimental techniques were used including X-ray diffraction, electron diffraction and scanning force microscopy (SFM), nee AFM. In particular salts of the monomers $CH_3\text{-}(CH_2)_{n-1}\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}(CH_2)_m\text{-}COOH$ (designated as n-m DA) were deposited and polymerized by exposure to UV light (the polymer form is designated as n-m PDA). There are strong geometric constraints that must be met for substantial conversion to occur [3]. Moreover, while the monolayers formed at the air/water interface are solids (the monolayer compressibility is small), after polymerization the films are rigid. It is possible to transfer bilayers of the polymerized lithium salt of 16-8 DA so as to span the openings in grids suitable for electron diffraction [3]. The cadmium salt of 12-8 DA can be deposited by the Langmuir Blodgett technique to form multilayers of sufficient thickness to allow X-ray diffraction spots to be collected for analysis [4, 6]. In a separate series of experiments [1, 2], multilayers of the cadmium salt of 12-8 DA were deposited on various substrates as steps and analyzed by scanning force microscopy (SFM). We note that of the structures techniques for LB films, only SFM does not cause polymerization of m-n DA. Moreover, the molecule is polymerized by normal laboratory light; in the Polymer Microdevice Laboratory (PML) illumination is filtered to avoid this problem.

The various deposition techniques necessarily stress the monolayer during the process. The question is whether such stress causes reconstruction of the monolayer possibly into a different 2d crystal class or perhaps the structure would lose range of order. The n-m DA system is close to ideal since it can be polymerized *in situ* either as a Langmuir film before deposition or after deposition as a LB film. Determining the structure by several techniques including SFM provides an example for comparison of the diffraction and SFM techniques and the character of the data analyzed in each case.

The purpose of this paper is to compare the information obtained by electron diffraction and SFM for determining structure of LB deposited 16-8 DA and 16-8 PDA molecules.

EXPERIMENT

The 10,12-nonacosadiynoic acid (16-8 DA) monomer, $CH_3(CH_2)_{15}$-C≡C-C≡C-$(CH_2)_8$COOH was synthesized via an asymmetric coupling method with copper (I) chloride as catalyst [2]. Chloroform (HPLC grade) was purchased from Fisher and used as received. 1 mM 16-8 DA chloroform solution was used to spread the monolayer. The solution was stored in a refrigerator under a nitrogen atmosphere. The 16-8 DA monomer was purified by recrystallization with either warm methanol or hexane and filtered with 0.2-μm particle filter so as to remove oligomers. The build up of oligomers is slow when the samples are stored carefully; samples were filtered and recrystallized before use.

The processing window of 21°C and 25 mN/m was used for 16-8 DA LB vertical deposition with a subphase of 1 mM LiOH aqueous solution. The processing window [3] is relatively narrower for Li/16-8 DA system than 16-8 DA system and is more sensitive to the existence of oligomers. Polymerization was initiated by UV-light incident on Li/16-8 DA LB films under nitrogen atmosphere for 30 minutes to obtain the Li/16-8 PDA LB films.

In addition to vertical deposition, horizontal deposition was also used to obtain uniform Li/16-8 PDA LB films. See Reference [4] for details for coating SFM tips.

The Nanoscope III Digital Multi-Mode Scanning Probe Microscope (SPM) system from Digital Instrument was used to obtain surface information with nanometer-scale resolution. “A” type scanner and silicon nitrate (Si_3N_4) pyramidal tips with spring constant of 0.58 N/m were used. The substrate used was mica because of its molecular smoothness. A scanning rate of 61 Hz was used. A very small contact force about 0.1 nN was used in the contact mode in order to minimize the scratching effect. The images reported herein were not affected by changing the direction of scan, imperfections that are expected in true 2d crystallization were observed, the pattern did not change with tapping mode.

RESULTS AND DISCUSSION

Isotherms

Figure 1 shows the isotherm of Li/16-8 DA at 21°C with a subphase of 1 mM of lithium hydroxide aqueous solution. The co-area is 0.195 nm^2/molecule and the collapse pressure is about 60 mN/m. This suggests that the Langmuir film of Li/16-8 DA monolayer is extremely stable at the air-water interface. It is also true that the equilibrium spreading pressure for these systems is below 1 mN/m.

The temperature effect on isotherm of Li/16-8 DA Langmuir monolayer was studied. The co-area changed to 0.23 nm^2/molecule and the collapse pressure dropped to 48 mN/m at a temperature of 32 C. When the temperature was lowered to 12°C, the co-area was 0.20 nm^2/molecule but the collapse pressure dropped to

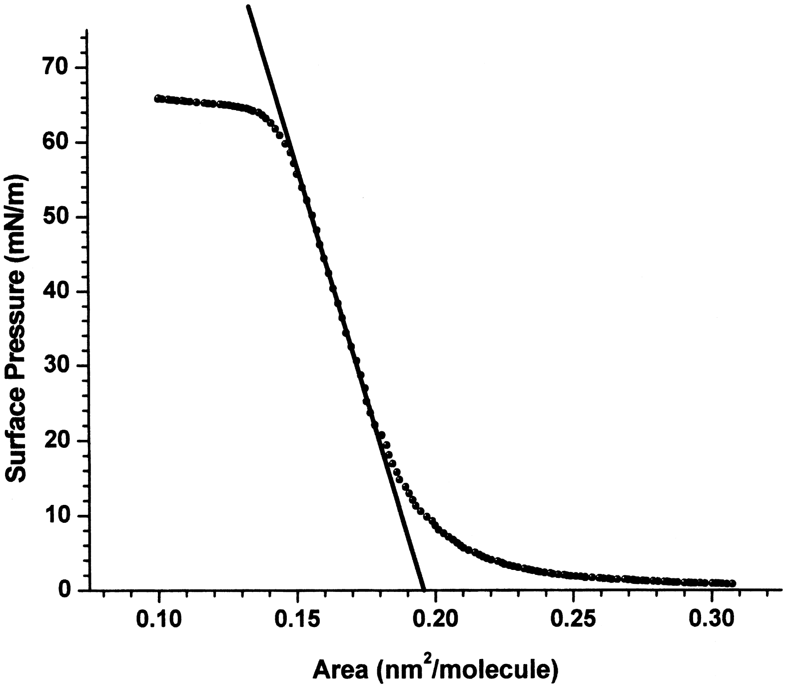

Figure 1. Surface pressure-area isotherm for Li/16-8 DA Langmuir monolayer.

49 mN/m. These Langmuir films at 12°C and 32°C are not as stable as that at 21°C, but are relatively stable when they are compared to stearic acid monolayer.

In a third set of experiments at 20°C, we studied the effect of subphase composition on the isotherms. For pure water as the subphase; the isotherm had a co-area 0.25 nm^2/molecule and a collapse pressure of 35 mN/m. When a 1 mM LiOH aqueous solution was used as the subphase the isotherm had a co-area of 0.20 nm^2/molecule and a collapse pressure of 60 mN/m. Obviously, the 16-8 DA monolayer associated with the Li ion is more stable. When the Langmuir films were allowed 10 additional minutes of annealing time at the constant pressure of 10 mN/m, small deviations in the isotherm were noted. Indeed, the annealing process provides time for the molecules to relax and pack better at the air-water interface. The annealing process improved the film stability since the slope of the isotherm was larger (elastic modulus is larger) and the collapse pressure is increased to 40 mN/m from 35 mN/m.

Stability Investigation (Creep Test)

A creep test was run on a Li/16-8 DA Langmuir monolayer at the air-water interface with a subphase of 1 mM LiOH aqueous solution at 21°C and a constant pressure of 25 mN/m. We found only a 1% surface area change after one hour. This confirms that the Li/16-8 DA monolayer is very stable, even though is was compressed to at least 25 times the equilibrium spreading pressure.

Scanning Force Microscopy (SFM)

We studied the surface morphology of these LB films in the scale range of nanometers to micrometers. To analyze the surface morphology of the Li/16-8 DA and Li/16-8 PDA, Langmuir-Blodgett films in the nanometer scale, a five-layer Li/16-8 DA monomer LB film was vertically deposited onto a freshly peeled mica substrate. Li/16-8 PDA polymer LB films were prepared from the Li/16-8 DA monomer LB films by exposure to 30 minutes of UV-radiation under a nitrogen atmosphere. Contact mode SFM images of the Li/16-8 DA and the Li/16-8 PDA LB films are shown in Figures 2 and 3, respectively. The software provided by Digital Instrument, Nanoscope III^{TM} v4.23, was used to analyze the images.

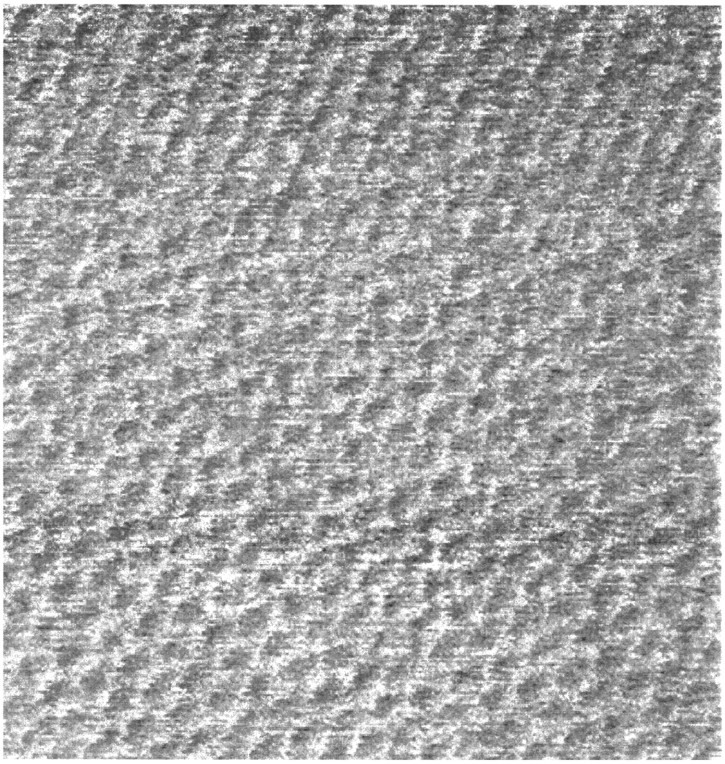

Figure 2. SFM image of monomer monolayer surface (10 nm by 10 nm) of Li/16-8 DA.

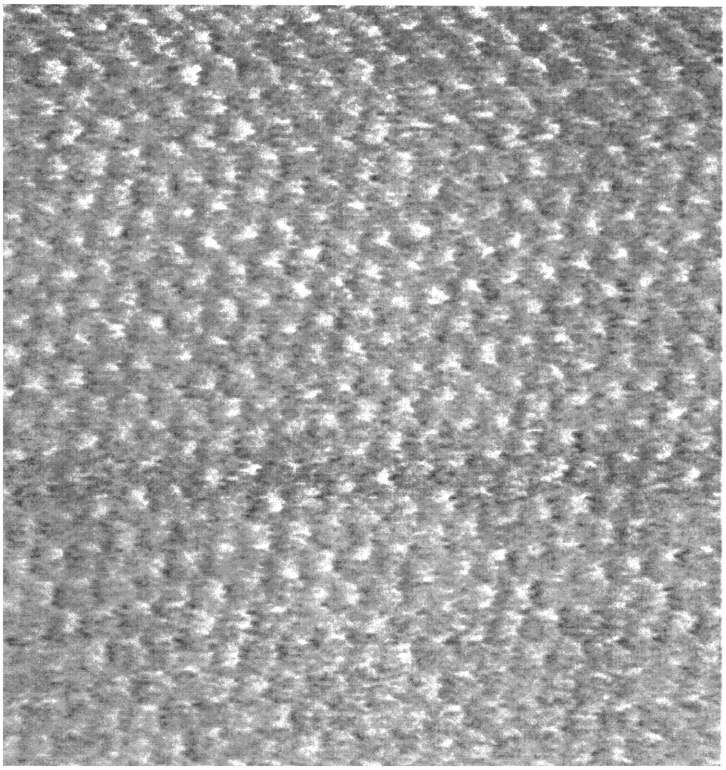

Figure 3. SFM image of polymer monolayer surface (10 nm by 10 nm) of Li/16-8 PDA.

Before further image analysis, the SFM images were flattened and image edges were cut off.

Roughness Analysis

AFM images in Figures 2 and 3 was used for an area roughness analysis. Image areas of 5 × 5 and 8 × 8 nm^2, taken as patches from the 10 nm × 10 nm images, were analyzed. Information obtained from the area roughness analysis is listed in Table 1, where the "image Z range" is the height range recorded (highest to lowest points) and the average roughness (R_a) is calculated using

$$Ra = \frac{1}{L_x L_y} \int_0^{Ly} \int_0^{Lx} |f(x,y)|\, dx dy \tag{1}$$

Table 1. Roughness Analysis of the AFM Images

	Li/16-8 DA LB Films		Li/16-8 PDA LB Films	
Image size (nm^2)	5 × 5	8 × 8	5 × 5	8 × 8
Image Z range (nm)	0.249	0.264	0.420	0.421
Mean roughness (Ra, nm)	0.028	0.029	0.051	0.050
Ra/Z range	0.112	0.110	0.121	0.119
Surface roughness (Rms or Rq , nm)	0.035	0.036	0.064	0.063
Rms (Rq)/Z range	0.141	0.136	0.152	0.150

where L_x and L_y are the dimensions of the reference surface, Z = 0, and Z = f(x,y) is the surface elevation relative to the reference. The RMS elevation, (R_q), is the standard deviation of the Z values within the given area and is calculated by:

$$R_q = \sqrt{\frac{\sum (Z_i - <Z>)^2}{N-1}} \tag{2}$$

where N is the number of points (pixels) within the area.

As shown in Table 1, surface roughness, for both the monomer and polymer LB films, does not depend on the chosen image sizes. The surface roughness is 0.028 nm for the monomer and 0.050 nm for the polymer LB films. It showed that both surfaces of the monomer and the polymer LB films are very smooth. However, the surface of the Li/16-8 PDA LB films is rougher than that of the Li/16-8 DA LB films. The Z ranges for the PDA LB film and DA LB film are 0.420 nm and 0.249 nm, respectively. This indicates that the image contrast of the PDA polymer image is better than that of the DA monomer image. One reasonable explanation is that the PDA LB films are tougher than that of the DA LB films and the images of the PDA LB films should be less affected by contact mode AFM probe scanning. One-dimensional roughness can also be analyzed by section analysis. It is a good indication of the image resolution; again, the result confirmed that the image resolution for Li/16-8 PDA image is better than that of Li/16-8 DA image. However, the roughness calculation for one dimension is not as precise as the area roughness since it will depend on the line chosen.

2D Unit Cell Analysis

A 2-Dimensional fast Fourier transform (FFT) filtering process was used to remove low frequency acoustic noise and high frequency electronic noise that might affect the image analysis. Figures 4 and 5 show the FFT reciprocal space images from Figures 2 and 3. Clearer images were obtained after filtration.

In Figures 2 and 3, net lines were drawn on the centroids of the high patterns from which unit mesh parameters can be calculated by direct measurement. Alternately, the average peak distance or can be read from the position of the centroids in the power spectral density (PSD) spectrum, Figures 4 and 5. However, there are two ways to construct the representation of the patterns. We show the reciprocal space vectors for the second method, which was based on the analysis of the electron diffraction image, Figure 6. In Table 2, we list the unit mesh parameters measured to give a vector set ($\vec{R} = n\vec{b} + m\vec{c}$) that covers the centroids of Figures 2 and 3 and are consistent with reciprocal space vectors measured on Figures 4 and 5 (these net vectors are not shown). Another unit mesh analysis without FFT filtering was performed on the original images; the same unit mesh parameters were obtained. This indicates that FFT filtering has insignificant effects on the locations of the centroids; such image analysis should be used for precise determination of the net.

The 2D unit net for Li/16-8 DA LB films is oblique and from the AFM images the parameters are c = 0.514 nm, b = 0.414 nm and θ equal to 114°. The surface area per molecule is 0.195 nm^2 (a·b·sinθ). The surface area for Li/16-8 DA monomer monolayer calculated from the isotherm at surface pressure of 25 mN/m is about 0.190 nm^2 (the co-area is 0.195 nm^2/molecule). These two values are within experimental error. Moreover, it indicates that the packing of Li/16-8 DA monomer monolayers does not change during deposition.

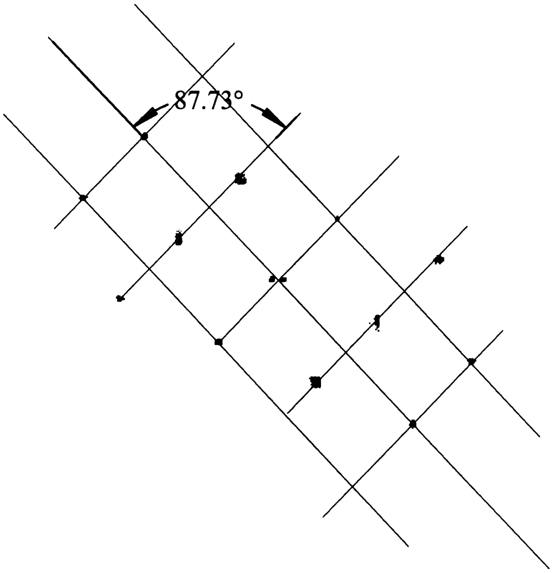

Figure 4. Representation of Fourier transform image of Li/16-8 DA (monomer).

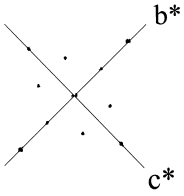

Figure 5. Representation of Fourier transform image of Li/16-8 PDA (polymer).

The 2D unit cell of Li/16-8 PDA LB films appears to be hexagonal in the direct AFM image and the lattice parameters c = 0.439 nm, b = 0.439 nm and $\alpha = 120°$. The area per molecule is 0.167 nm^2 (a·b·sinθ). It indicates that the surface structure was changed and the area per molecule changed from 0.195 nm^2 to 0.167 nm^2 due to the photopolymerization process. However, as can be seen in Table 2, the repacking of the sidechains, demonstrated by X-ray diffraction relieve this approximately 15% mismatch, the volumes per molecule being almost identical. We now turn to an analysis of the same images and select a net consistent with the electron diffraction data determined by Day and Lando [3].

Comparison Between Atomic Force Microscopy and Electron Diffractometry

A comparison was made between the information obtained from SFM images and electron diffraction (ED) patterns for Li/16-8 DA and Li/16-8 PDA LB films. The lattice parameters are listed in Table 3. The information provided by ED is three-dimensional, $R^* = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$, even though the geometry of the ED experiments limits data collection that determines only $\vec{b}^*, \vec{c}^*$ in reciprocal space. In contrast, SFM reports the physical profile of the upper surface of groups of atoms around the terminal CH$_3$ group of the diacetylene molecules; inner structure of the monolayer cannot be obtained. Note that it is possible to obtain data to determine $\vec{a}^*$ by tilting the sample. This was not done in the Day experiments but was accomplished by X-ray diffraction.

The ED pattern is shown in Figure 9 [1] and the lattice parameters were calculated by Day and Lando [3]. In order to compare these two results, different coordinate systems were chosen as demonstrated in the SFM FFT patterns shown

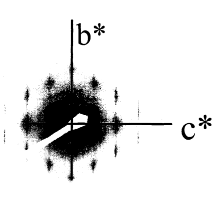

Figure 6. Electron diffraction image of Li/16-8 PDA (polymer) (from reference 3).

Table 2. 2D Lattice Parameters for Li/16-8DA and Li/16-8PDA LB Films

	Lattice Type	Lattice Parameters
Li/16-8 DA monomer unit mesh	Oblique	a = 0.549 ± 0.05 nm b = 0.541 ± 0.05 nm 0 = 113º area per molecule −0.274 nm^2
Li/16-8 PDA polymer unit mesh	Hexagonal	a = 0.497 ± 0.052 nm b = 0.497 ± 0.060 nm 0 = 120º area per molecule =0.212 nm2

in Figures 4 and 5. In Figure 4, 16-8 DA, a nearly orthogonal net was constructed. The angle of 88 deg is within the experimental uncertainty of 90 deg. Similarly, a new coordinate system is assigned in Figure 5, which are orthogonal. It is interesting to note that the (odds, 0) and (0, odds) diffraction points are missing. This dynamic absence [5] is due to the symmetry of the system and is also seen in the diffraction patterns in the three-dimensional electron diffraction experiment. Please note that neither the smearing on maxima within the smears (see reference 3) are present in the FFT of the SFM images. These nuances are lost in the SFM experiment.

As shown in Table 3, the orthogonal lattice parameters b and c determined from the ED patterns were found to correspond to the AFM FFT. The lattice parameters are somewhat different in the case of monomer, but they are the same within the experimental error in the case of polymer. The similarities of the lattice parameters for the polymer from AFM and ED experiments strongly suggest that no tip scratching occurred in these AFM images. A reasonable explanation is that Li/16-8 PDA LB films are tough enough to stand scratching from Contact-Mode scanning tips and no scratching artifacts were shown in these images [6]. The difference in the lattice parameters for the Li/16-8 DA LB films between ED and

Table 3. Comparison of Unit Cell Parameters from Electron Diffraction and SFM Fourier Transform

	b*-axis	c*-axis
Polymer (Li/16-8 PDA) by		
x-ray a = 7.1 ± 0.005 nm		
ED	0.311 ± 0.005 nm	0.409 ± 0.005 nm
SFM	0.820 ± 0.05 nm	0.485 ± 0.05 nm
Monomer (Li/16-8 DA) by		
x-ray a = 6.2 ± 0.005 nm		
ED	0.920 ± 0.005 nm	0.483 ± 0.005 nm
SFM	1.020[a] ± 0.05 nm	0.0460 ± 0.05 nm

[a] This probably corresponds to *b* sin γ in the monoclinic unit cell in which *c* is the unique axis and γ = 123 deg. The value for the *b* axis is probably 1.216 nm.

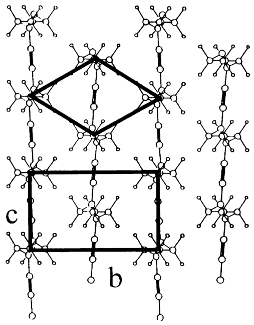

Figure 7. Structure of Li/16-8 PDA (polymer) determined from electron diffraction intensity data (see reference 3) compared to a hexagonal unit mesh determined by SFM.

AFM experiments arises from the nature of the solid-state polymerization. The values of the lattice parameters b and c obtained from ED experiment for Li/16-8 DA and knowledge of the monoclinic γ are between that of monomer and polymer LB films obtained from AFM. This fact indicates that the electron beam used in ED experiment polymerized the 16-8 DA monomer films and the diffraction pattern is of the known solid solution of polymer in monomer. Please note that the monomer unit cell is actually monoclinic with $\vec{c}\,^*$, as the unique axis (see a values for monomer and polymer in Table 3 ($\gamma = 123$ deg).

Although oblique and hexagonal unit nets can describe the surface structure of the Li/16-8 DA and PDA LB film, the rectangular (nets) obtained from the FFT surface structure are similar to the unit cell determined by electron diffraction. It was clear that the human eye sees only the main features of the AFM image and that the FFT is required for unit cell determination that is consistent with the ED data. It should be noted that the relative intensities of the AFM FFT and the electron diffraction do not completely correspond. This should be expected, because the Fourier Transform of the electron diffraction relative intensity data is the Patterson function (a vector map) not the AFM map. Fortunately, the Patterson projection and the electron density projection are sufficiently similar to give lattice constant from the two methods that agree.

Figure 7 shows the probable structure and an outline of the 3D unit cell and an indication of what the 2D assignment is representing.

CONCLUSION

The two-dimensional unit cells of the Li/16-8 DA and Li/16-8 PDA LB films were determined by contact-mode atomic force microscope. The PDA image showed the same surface structure as the results from electron microscopy when FFTs of the AFM images are used to obtain lattice constants in agreement with ED.

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