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STM Studies of LB Deposited Alkyl Substituted  
Polyaniline and Its Corresponding Monomer

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Enclosure

# STM Studies of LB Deposited alkyl substituted Polyaniline and its corresponding Monomer

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## Abstract

STM investigations were carried out on monolayers of poly(*o*-pentadecyl aniline), *o*-pentadecyl aniline monomer and *p*-hexadecyl aniline. The polymer was prepared by Langmuir polymerization on a 0.1 M H<sub>2</sub>SO<sub>4</sub> sub phase, containing ammonium persulfate as the oxidizing agent. Monolayers of all the compounds were transferred by the LB technique from the air/liquid interface to a MoS<sub>2</sub> substrate. After annealing, molecular resolution images were obtained for all three compounds. The *o*-pentadecyl aniline monomer showed a decreased mean molecular area on the MoS<sub>2</sub> surface, compared to that at the liquid/air interface, while the polymer images showed similar packing at both interfaces. The *p*-hexadecyl aniline showed similar ordering on the substrate as the ortho substituted monomer. The polymer images showed evidence of backbone connectivity. After annealing all monolayers showed high positional and orientational order.

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## Introduction

Polyaniline is one of the most promising conductive polymers with a number of possible future applications. Its excellent stability in the presence of oxygen and moisture, its optoelectronic features<sup>1-4</sup>, and the possibility to prepare thin conductive films have aroused much scientific interest in this compound. Thus, many methods of polymerization and doping have been reported<sup>5-11</sup>.

We use a Langmuir trough to polymerize functionalized anilines at the liquid/air interface. By moving the barriers and working at different surface pressure ( $\pi$ ), it is possible to manipulate the distance and order between the monomer molecules during the polymerization reaction. The reaction rate can also be monitored by using the trough as a 2-dimensional dilatometer<sup>12</sup>.

In spite of the above, there is little structural data in the literature about polyaniline and its derivatives. It was therefore of great interest for us to obtain data about the configurational, orientational and positional order in the above-mentioned 2-dimensional films. By transferring the polymer and the corresponding monomer onto a solid support, structural information of both preordered molecules should be available and can be compared.

Scanning tunneling microscopy (STM) is a very powerful tool for the investigation of surface structures of organic molecules<sup>13-17</sup>. In this note we report the results of STM investigations of a 2-D polymerized, side chain substituted aniline and its corresponding monomer, both transferred from the liquid/air interface to a molybdenum disulfide (MoS<sub>2</sub>) substrate by the Langmuir Blodgett (LB) technique and subsequently annealed. It should be noted that the Langmuir trough was used as a means to confine the reaction to 2-D, control intermolecular

distances during polymerization, and establish film thickness on MoS<sub>2</sub>. We did not try and control lateral packing in the transferred films by the LB technique.

## Experimental

The o-pentadecyl aniline was synthesized by a published method<sup>18</sup>; p-hexadecyl aniline was purchased from Aldrich (97%) and used as received. The monomers were spread from chloroform (99.9%, Nacalai-Tesque, Kyoto, Japan) solutions. Sub phase solutions were prepared with Millipore water (Millipore™, ≥18MΩ resistivity) and ACS reagent grade chemicals (Aldrich and Nacalai).

A commercially available Teflon trough, equipped with two Teflon barriers, and a Wilhelmy surface pressure measurement system (KSV, Finland) was used to prepare samples. Before spreading, the trough was carefully cleaned with Ethanol and Millipore water. The sub phase was considered free of surfactants when no surface pressure change was detectable by quickly moving the barriers towards the platinum Wilhelmy plate.

Freshly cleaved MoS<sub>2</sub> was used as the conductive substrate. For the monomer samples, the substrate was dipped into the Millipore water sub phase before spreading. The monomers were spread onto the sub phase surface and compressed at 1.56 Å<sup>2</sup>molecule<sup>-1</sup>min<sup>-1</sup> to a pressure of 20mN/m, after allowing the Chloroform to evaporate for 15 min. For deposition, the substrate was raised from the sub phase at a speed of 1 mm/min.

For the polymerization, the o-pentadecyl aniline monomer was spread onto 0.1 M sulfuric acid, containing 0.03 M ammonium persulfate as the oxidizing agent. Chloroform was allowed to

evaporate for 2 min. and the monomer was compressed at  $14.5 \text{ \AA}^2 \text{ molecule}^{-1} \text{ min}^{-1}$  to a pressure of 20 mN/m, which was held constant during the polymerization. The reaction was monitored by the barrier movement and said to be finished when no further movement was observable. Figure 1 shows a typical graph, measured during the polymerization. During the reaction, the mean molecular area decreases due to the formation of covalent bonds and concurrent molecular rearrangement<sup>12</sup>. Molecular weights, as measured by GPC with polystyrene standards, for these conditions are typically around 20,000, with a polydispersity of about 2.5. Since no information was available about the interaction of the sub phase with the MoS<sub>2</sub> surface, polymer deposition was started outside the sub phase. The substrates were dipped into the sub phase at 1 mm/min and pulled out at 50 mm/min. All samples were annealed above the individual melting point for at least 12 h and slowly cooled down to ambient temperature with a rate of 5°C/15 min.

The STM system used in this study was a commercially available NanoScope II (Digital Instruments Inc., Santa Barbara, U.S.A.) with a sharp platinum/iridium tip. For the polymer, the images shown are representative of structures observed on several areas each of 3 different MoS<sub>2</sub> samples, while for the monomer, 2 different samples were studied. Unless otherwise noted, all images were obtained in the constant current mode and digitally filtered, only to remove high frequency noise. Measurement reproducibility from sample to sample was better than 0.2 Å. Quoted distance measurements, therefore are relative, not absolute and are obtained from averaging many representative values.

## STM Results

### a.) Polymer

Figure 2 a-d shows STM images of poly-o-pentadecyl aniline monolayers, scanned in the constant current mode with different scanning scales. In this mode, the tunneling current is held constant and the tip movement perpendicular to the surface structure is recorded. It should be noted that Figure 2 a-b were scanned in the upward direction, while Figure 2 c-d were downstroke scans. Additionally Figure 2e is a polymer image which was scanned in constant height mode. In this mode the tip scans at a constant height and the differences in tunneling current are recorded. Clearly the images measured at different scales, as upstrokes and downstrokes, and in both constant height and current modes show the same features.

All images in Figure 2 show ordered rows which are covered by an orientationally ordered periodic rod-like sub structure. The distance between the rows was found to be 7.9 Å, and that between rods was 4.3 Å. We think the rows are established by the polymer chains. While the distance between the rods corresponds very well to the known spacing between alkyl chains in the free rotator phase<sup>19</sup>. From the STM image, the surface area of one repeating unit was calculated as 33.5 Å<sup>2</sup>; this value is very close to the mean molecular area of a monomer repeat unit at the liquid/air interface, determined from the polymer  $\pi$ /area isotherm as about 32 Å<sup>2</sup>. Table 1 compares the measured distance values and surface areas of the repeating units for the polymer and monomer.

The above considerations lead us to believe that the rods correspond to the alkyl side chains. From Figure 2d it is also clear that the rods interdigitate slightly with those in adjacent rows. One would expect the extended side chain to be about 19 Å long, however the rod length measured by STM was found to be approximately 9 Å, therefore the side chains can not lie flat on the surface. The low value of the measured rod length can also be explained by tilting the side chains with respect to the layer plane. Because of the insulating nature of the alkyl



chains, the tunneling conditions did not allow for the polymer backbone to become visible at atomic resolution. Nonetheless, significant connectivity due to the polymer backbone is observed along the row direction in all images. The STM results are consistent with a model of the backbone conformation with aniline rings lying flat on the substrate surface and the alkyl side chains pointing away from the plane of the surface. The above conformation is also thermodynamically favorable in that the polar backbone is down, while the lower energy alkyl side chains are up and minimize the surface energy. Since it was possible to get high resolution images over a broad range of setpoint currents (0.1 to about 0.3 nA) and scanning voltages (1.3 - 2 V, positive or negative tip bias voltage), the polymer seems to be stable and well fixed to the substrate surface after annealing.

#### b.) Monomers

Figure 3 shows STM images of o-pentadecyl aniline monomer monolayers at different scales. Individual molecules are clearly arranged in an ordered pattern. In the case of the monomer, two periodicities are also observable. Parallel rows are covered with periodic rod-like structures tilted at an angle of about 30 degrees with respect to the rows. The distance between the rows is 6.8 Å, and that between rods found as 4.3 Å. Since the distance between the rods is comparable to the polymer measurements, they also correspond to the alkyl side chains. The surface area of one repeating unit was calculated as 29.3 Å<sup>2</sup>. At the liquid/air interface however, the mean molecular area at the transfer pressure was about 45 Å<sup>2</sup> from the  $\pi$ /area isotherm. Therefore a difference of about 15 Å<sup>2</sup> exists between the occupied area of the molecules at the liquid/air interface and that at the MoS<sub>2</sub> surface. This result can be interpreted by considering the level of hydration of the aniline amine groups at the water surface and at the substrate. Therefore between deposition and scanning, probably during

annealing, the molecules are dehydrated and can arrange at the substrate as molecular aggregates with a higher packing density. The measured distances would fit to a model with the benzene rings standing perpendicular on the surface, connected to it via physisorption of the amine groups and aggregated along an imaginary line through the centers of the benzene rings. Also for the monomer, the measured STM rod length does not reach the expected value of about 19 Å for fully extended alkyl chains. It is expected that the side chains of the aggregate rows are both tilted with respect to the substrate plane and interdigitated with adjacent rows. In contrast to the polymer, the monomer aggregates were found to be "soft" during STM scanning. It was only possible to get images with a very low setpoint current (0.11 nA). Even under these conditions, the molecules were easily scraped from the surface by the STM tip to the edges of the scanned area. Also the fact that the monomer is not conductive resulted in difficult tunneling conditions.

We also made STM measurements of p-hexadecyl aniline monomer, but did not succeed to get high resolution images. Nevertheless we found rows of molecular aggregates, similar to the ortho monomer, which showed row periodicities of 8.4 Å and no connectivity. With the obtained data it is not possible to discuss a model for the molecular arrangement of this monolayer.

## Conclusion

All investigated compounds showed ordered rows and a rod-like ordered sub structure. The area of the repeating units was calculated and found to be nearly the same on the substrate, compared with the liquid/air interface, for the polymer, but very different for the monomer. A possible interpretation for the observed structures was discussed. Since the area of the

repeating units is the same before deposition and after annealing in the case of the polymer, multilayer deposition should be possible without the risk of further molecular rearrangement. On the other hand for the monomer, the mismatch of packing between that on the solid substrate and the water surface should lead to unstable or metastable transferred LB films. For the monomer no connectivity between molecules was observed, while the polymer clearly showed high connectivity within the rows and was very stable under the scanning conditions. If the kind of order and stability observed for the polymer could be demonstrated on other substrate surfaces as well, it would be a very interesting candidate for liquid crystal alignment and other electro-optical applications.

### **Acknowledgment**

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## Figure captions

Figure 1: Typical results from the Langmuir film polymerization of *o*-pentadecyl aniline at room temperature. 30mN/m surface pressure, was held constant during reaction, Arrows indicate ordinate scales for mean molecular area and average barrier speed vs reaction time. The sub phase was a mixture of 0.1 M H<sub>2</sub>SO<sub>4</sub> and 0.03 M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

Figure 2: Images of poly-*o*-pentadecyl aniline, recorded under different scanning conditions:

- (a.) scan size 40 nm, upstroke, constant current mode. Tip bias voltage: -1498 mV      Setpoint current: 0.13 nA
- (b.) scan size 20 nm, upstroke, constant current mode. Tip bias voltage: -1498 mV      Setpoint current: 0.13 nA
- (c.) scan size 10 nm, downstroke, constant current mode. Tip bias voltage: 1268 mV      Setpoint current: 0.16 nA
- (d.) scan size 5 nm, downstroke, constant current mode. Tip bias voltage: 1998 mV      Setpoint current: 0.31 nA
- (e.) scan size 10 nm, upstroke, constant height mode. Tip bias voltage: 1648 mV      Setpoint current: 0.13 nA

Figure 3: Images of *o*-pentadecyl aniline:

- (a.) scan size 20 nm, upstroke, constant current mode. Tip bias voltage: 1745 mV      Setpoint current: 0.11 nA
- (b.) scan size 5 nm, upstroke, constant current mode. Tip bias voltage: 1848 mV      Setpoint current: 0.11 nA

Table 1: Data obtained from distance determinations of the structures in the STM images of poly-*o*-pentadecyl aniline, *o*-pentadecyl aniline monomer and *p*-hexadecyl aniline monomer. Area of repeating units, calculated for the

substances at the substrate surface and measured at the liquid/air interface.

	Poly-o-pentadecyl-aniline	o-pentadecyl-aniline monomer	p-hexadecyl-aniline monomer
row distance	7.86 ± 0.04 Å	6.83 ± 0.24 Å	8.4 Å
rod distance	4.26 ± 0.07 Å	4.32 ± 0.11 Å	-
area of repeating units on substrate surface	33.5 Å <sup>2</sup>	29.5 Å <sup>2</sup>	-
area of repeating units at liquid/air interface	32 Å <sup>2</sup>	45 Å <sup>2</sup>	23.5 Å <sup>2</sup> (Ref. 12)

Table 1



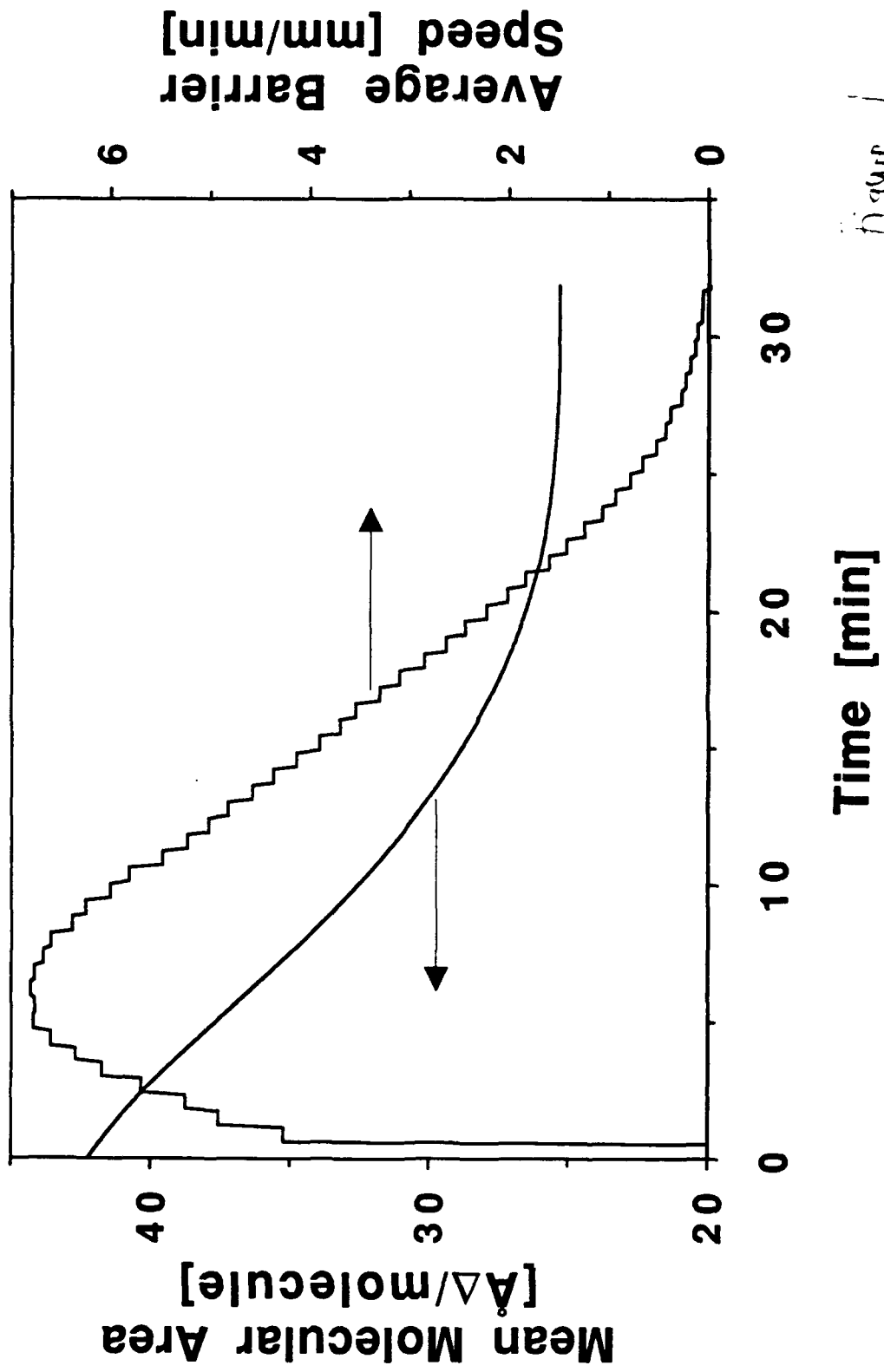
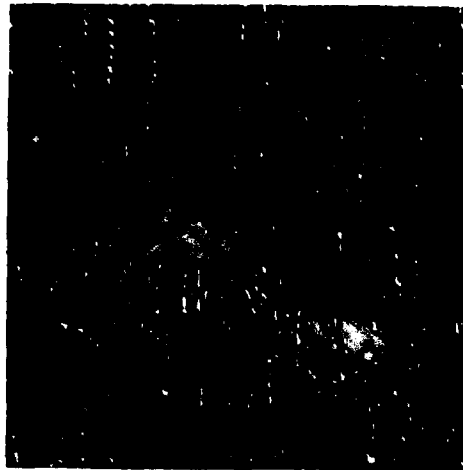
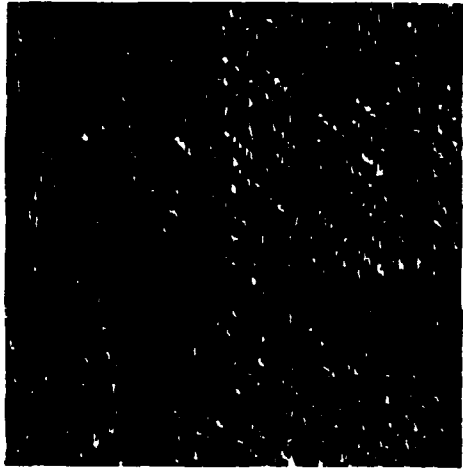


Figure 1

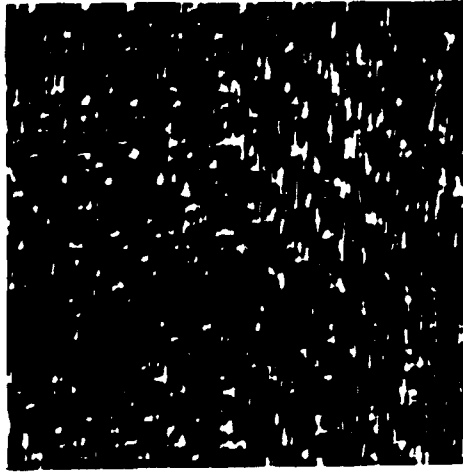
(a.)



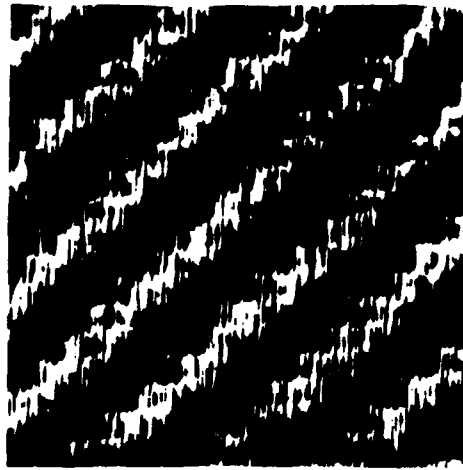
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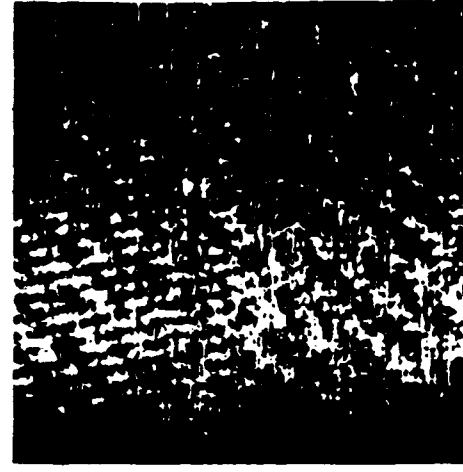
(c.)



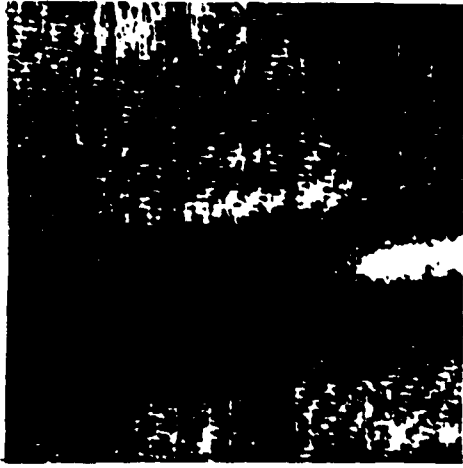
(d.)



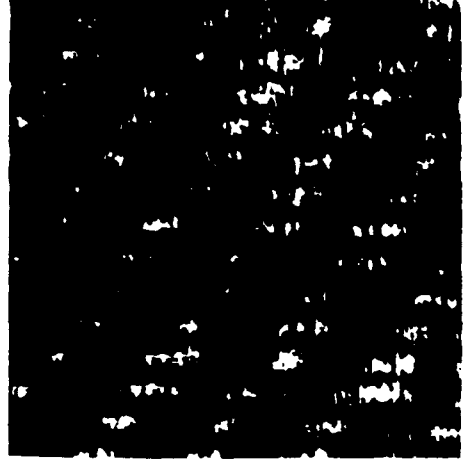
(e.)



*ρ*  $\approx$  1.15  $\times$  10<sup>3</sup> kg/m<sup>3</sup>



(a.)



(b.)

Figure 2

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