

Notes

Scanning Tunneling Microscopy Studies of Langmuir–Blodgett-Deposited Alkyl-Substituted Polyaniline and Its Corresponding Monomer

P. Quint,[†] W. Knoll,^{‡§} M. Hara,[‡] H. Sasabe,[‡] and R. S. Duran^{*,†}

Department of Chemistry, University of Florida, Gainesville, Florida 32611, and Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako-shi, Saitama 351-01, Japan

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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,^{1–7} 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.^{8–16}

We use a Langmuir trough to polymerize functionalized anilines at the liquid/air interface.¹⁷ By moving the barriers and working at different surface pressures (π), it is possible to manipulate the distance and order between monomer molecules during the polymerization reaction. The reaction rate can also be monitored by using the trough as a two-dimensional dilatometer.¹⁷

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 two-dimensional films. By transferring the polymer and the corresponding monomer onto a solid support, structural data of both preordered molecules should be available and can be compared.

Scanning tunneling microscopy (STM) is a very powerful tool for investigating surface structures of organic molecules.^{18–21} In this paper we report the results of STM investigations of a 2D polymerized, side chain substituted aniline and its corresponding monomer, both transferred from the liquid/air interface to a molybdenum disulfide (MoS_2) 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 2D, control intermolecular distances during polymerization, and establish film thickness on MoS_2 . We did not try to control lateral packing in the transferred films by the LB technique.

Experimental Section

The *o*-pentadecylaniline was synthesized by a published method,²² *p*-hexadecylaniline was purchased from Aldrich

[†] University of Florida.

[‡] RIKEN.

[§] Permanent address: Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55124 Mainz, Germany.

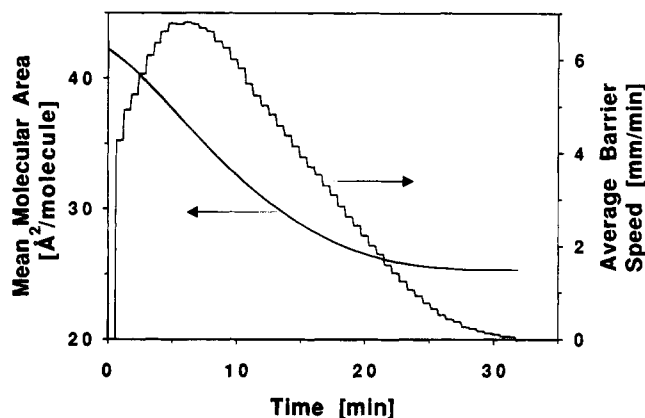


Figure 1. Typical results from the Langmuir film polymerization of *o*-pentadecylaniline at room temperature (see also ref 17). Surface pressure (30 mN/m) was held constant during the reaction; arrows indicate ordinate scales for mean molecular area and average barrier speed vs reaction time. The subphase was a mixture of 0.1 M H_2SO_4 and 0.03 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

(97%) and used as received. The monomers were spread from chloroform (99.9%; Nacalai, Tesque, Japan) solutions. Subphase solutions were prepared with Millipore water (Millipore, $\geq 18 \text{ M}\Omega$ 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 subphase was considered free of surfactants when no surface pressure change was detectable by quickly moving the barriers toward the platinum Wilhelmy plate.

Fresh cleaved MoS_2 was used as the conductive substrate. For the monomer samples, the substrate was dipped into the Millipore water subphase before spreading. The monomers were spread onto the subphase surface and compressed at $1.56 \text{ Å}^2 \text{ molecule}^{-1} \text{ min}^{-1}$ to a pressure of 20 mN/m, after allowing the chloroform to evaporate for 15 min. For deposition, the substrate was raised from the subphase at a speed of 1 mm/min. For the polymerization, the *o*-pentadecylaniline 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 $14.5 \text{ Å}^2 \text{ molecule}^{-1} \text{ min}^{-1}$ 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.¹⁷ 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 subphase with the MoS_2 surface, polymer deposition was started outside the subphase. The substrates were dipped into the subphase at 1 mm/min and pulled out at 50 mm/min. Transfer ratios were typically 1 ± 0.15 . All samples were annealed above the individual melting point for at least 12 h and slowly cooled down to ambient temperature at a rate of $5^\circ\text{C}/15 \text{ min}$.

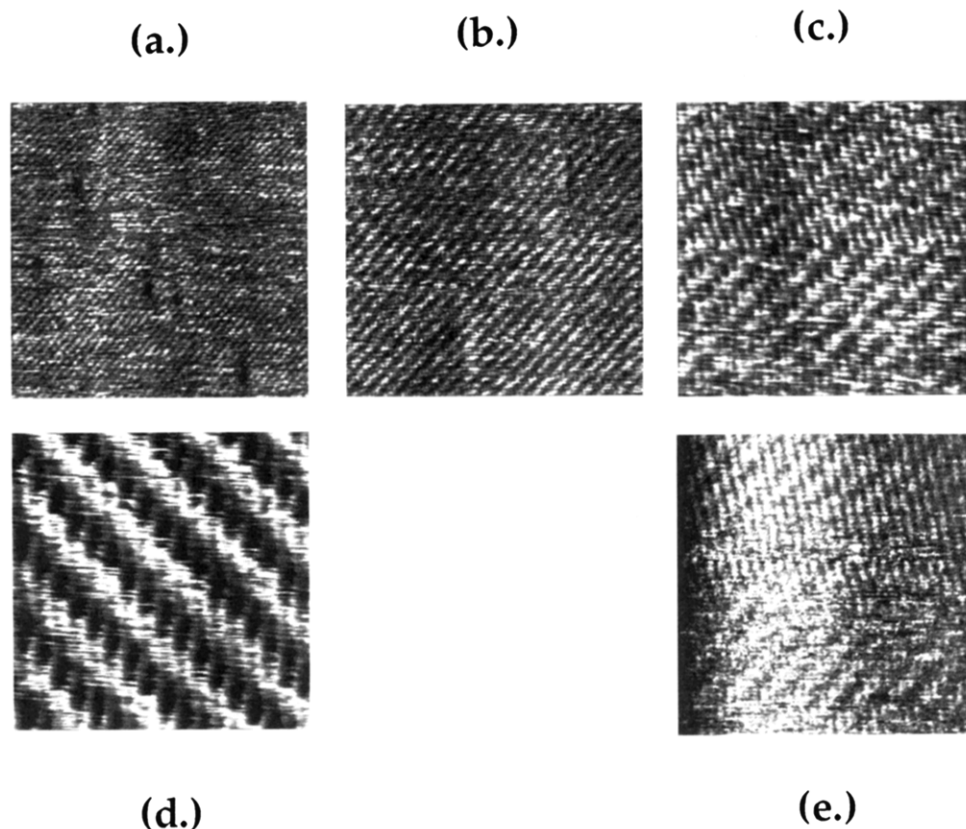


Figure 2. Images of poly(*o*-pentadecylaniline), recorded under different scanning conditions: (a) scan size 40 nm, upstroke, constant current mode, tip bias voltage -1498 mV, setpoint current 0.13 nA; (b) scan size 20 nm, upstroke, constant current mode, tip bias voltage -1498 mV, setpoint current 0.13 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.

Table 1. Data Obtained from Distance Determinations of the Structures in the STM Images of Poly(*o*-pentadecylaniline), *o*-Pentadecylaniline Monomer, and *p*-Hexadecylaniline Monomer (Area of Repeating Units Calculated for the Substances at the Substrate Surface and Measured at the Liquid/Air Interface)

	poly- (<i>o</i> -pentadecylaniline)	<i>o</i> -pentadecylaniline monomer	<i>p</i> -hexadecylaniline monomer
row distance (Å)	7.9	6.8	8.4
rod distance (Å)	4.3	4.3	
area of repeating units on substrate surface (Å ²)	34	29	
area of repeating units at liquid/air interface (Å ²)	32	45	23.5 ¹⁷

A Nanoscope II instrument (Digital Instruments, Santa Barbara, CA) and commercially available Pt-Ir scanning tips were used for the measurements. For the polymer, the images shown are representative of structures observed on several areas, each of three different MoS₂ samples, while for the monomer two different samples were studied. Unless otherwise noted, all measurements were performed in the constant current mode and images were flattened and low-pass filtered. 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. Parts a–d of Figure 2 show STM images of poly(*o*-pentadecylaniline) monolayers, scanned in the constant current mode with different xy scales. In this mode, the tunneling current is held constant and the tip movement up and down perpendicular to the surface structure is recorded. It should be noted that parts a and b of Figure 2 were scanned in the upward direction, while parts c and d of Figure 2 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 rodlike substructure. 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.²³ From the STM image, the surface area of one repeating unit was calculated as 34 Å²; this value is very close to the mean molecular area of a monomer repeat unit at the liquid/air interface, determined from the polymer π /area isotherm as about 32 Å². Table 1 compares the measured distance values and surface areas of the repeating units for the polymer and monomer.

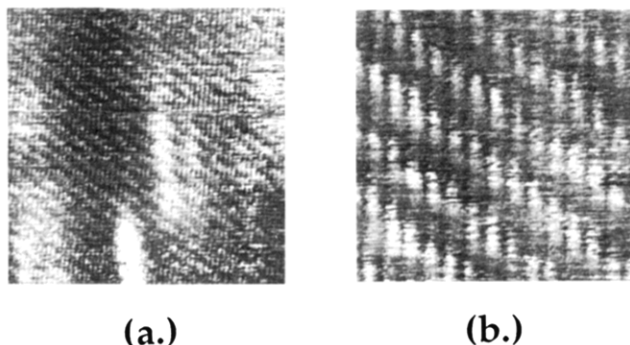


Figure 3. Images of *o*-pentadecylaniline: (a) scan size 20 nm, upstroke, constant current mode, tip bias voltage 1745 mV, setpoint current 0.11 nA; (b) scan size 5 nm, upstroke, constant current mode, tip bias voltage 1848 mV, setpoint current 0.11 nA.

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 cannot 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 alkyl chains act as insulators, 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 ca. 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*-pentadecylaniline 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 rodlike structures tilted at an angle of about 30° with respect to the rows. The distance between the rows is 6.8 Å, and that between rods was found to be 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 Å². At the liquid/air interface, however, the mean molecular area at the transfer pressure was about 45 Å² from the π /area isotherm. Therefore, a difference of about 15 Å² exists between the occupied area of the molecules at the liquid/air interface and that at the MoS₂ surface. This result can be explained by the fact that the amine group of the aniline is hydrated at the water surface, but not necessarily at the substrate. Therefore, between deposition and scanning, probably during annealing, the aniline molecules lose the water molecules associated with the hydration shell 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 at 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 tip contamination rate was high and molecules were easily scraped from the surface by the STM tip to the edges of the scanned area. Though unintentional, this allowed us to frequently image the underlying MoS₂ lattice and verify that it was not affected by the LB deposition process. Also the fact that the monomer is not conductive resulted in difficult tunneling conditions.

We also made STM measurements of *p*-hexadecylaniline monomer but did not succeed to get high-resolution images over an entire field of view; at high resolution the tip was often contaminated within half of a 10 × 10 nm scan. Nevertheless, we reproducibly 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 rodlike ordered substructure. 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 danger 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 electrooptical applications.

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