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LB-Deposited, Side-Chain Substituted Polyaniline, Polypyrrole and  
the Corresponding Monomers, Studied by STM

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13. ABSTRACT (Maximum 200 words)  STM investigations were carried out on monolayers of two conducting polymers and the corresponding monomers. 2-pentadecyl-aniline, poly-2-pentadecyl-aniline, 3-hexadecyl-pyrrole and poly-3-hexadecyl-pyrrole which were transferred from the liquid/air interface on a MoS <sub>2</sub> substrate by the Langmuir-Blodgett technique. The polymers were polymerized at the liquid/air interface with ammonium persulfate in the sub phase as the oxidizing agent. All compounds showed high orientational and positional order on the substrate surface. Two different structures were observable, rows and rod like structures. The distance between the rods were found for all compounds =4.3A. The row distances were found to be different for every substance. We think that the rods are the alkyl side chains and the rows represent the polymer chain or molecular monomer aggregates.	
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# LB-DEPOSITED, SIDE-CHAIN SUBSTITUTED POLYANILINE, POLYPYRROLE AND THE CORRESPONDING MONOMERS, STUDIED BY STM

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## Introduction

Conductive polymers, such as polyaniline and polypyrrole are of great interest in the view of possible future applications. While the polymerization reaction and the phenomena of conductivity of these two compounds and their derivatives are well investigated<sup>1-4</sup>, there is relatively little structural data available in the literature.

By using the LB-technique, it is possible to prepare ultra thin films of the polymers and the corresponding monomers on solid support. The polymerization reaction can be performed at the water/air interface on an oxidative reagent containing sub phase. In this case the LB-trough works like a 2-dimensional dilatometer, monitoring the progress of the reaction by moving the barriers and holding a constant desired surface pressure ( $\pi$ ). After the monolayer is transferred onto a molybdenum disulfide (MoS<sub>2</sub>) substrate by the Langmuir-Blodgett technique, it should be possible to obtain structural information of the molecules in the monolayer.

Scanning Tunneling Microscopy (STM) is a well suited technique<sup>5-8</sup> to investigate surface structures of such conducting organic molecules. In this note we report the results about STM investigations of poly-2-pentadecyl-aniline, poly-3-hexadecyl-pyrrole and the corresponding monomers. The monolayers on the substrate were subsequently annealed after the LB-transfer. We did not try to control lateral packing in the transferred films by the LB-technique.

## Experimental

2-pentadecyl-aniline and 3-hexadecyl-pyrrole were synthesized by published methods<sup>9,10</sup>. Spreading solutions were made in Chloroform (99% Naclai-Tesque, Japan) Sub phase solutions were prepared with Millipore water and ACS reagent grade chemicals (Aldrich and Naclai). All polymerization reactions and LB-transfers were performed at 25°C with a KSV LB5000 Langmuir trough, using a Wilhelmy plate to detect the surface pressure. Aniline was polymerized

on a 0.1M sulfuric acid sub phase, the pyrrole on a Millipore water sub phase, both containing 0.03M Ammonium persulfate as the oxidizing reagent. The polymerization reactions were monitored by the barrier movement and said to be finished when no further movement was observable. Freshly cleaved MoS<sub>2</sub> was used as the conductive substrate. For the monomer samples, the substrate was dipped into the sub phase before spreading; for the polymers, after the polymerization reaction was finished. The dipping speed was 1 mm/min in both cases. All samples were annealed above the individual melting point for at least 12 h. The STM system used in this study was a commercially available NanoScope II (Digital Instruments Inc., U.S.A.) with a platinum/iridium tip. The reproducibility of the preparations and the measurements was proofed by preparing at least 2 different samples of every compound.

## Results and Discussion

### 1.) 2-pentadecyl-aniline

Figure 1 shows at the right side a STM image of poly-2-pentadecyl-aniline and on the left side an image of the corresponding monomer, both with the same scan size of 5 nm. One can see that in both cases an ordered structure is observable. All images show ordered rows which are covered by an orientationally ordered periodic rod like sub structure. The distance determination with an image processing system shows for the polymer 7.9Å between the rows and 4.3Å between the rods. For the monomer the distances were found as 6.8Å and 4.3Å respectively. We think that the rows correspond to the polymer chains and the rods are established by the alkyl side chains, since the distance between the rods agrees well with the known spacing of alkyl chains in the free rotator phase<sup>11</sup>. From the above data, the surface area of a repeating unit of the polymer was calculated as 33.5Å<sup>2</sup>. This value is comparable to the mean molecular area at the liquid/air-interface, which was determined from a  $\pi$ /area isotherm as about 32Å<sup>2</sup>. Table 1 compares the measured distance values and surface areas for all compounds described in this note.

For the monomer, the surface area of one repeating unit on the substrate was calculated as 29.3Å<sup>2</sup> compared to 45Å<sup>2</sup> from the  $\pi$ /area isotherm at the transfer pressure. Therefore the occupied area at the MoS<sub>2</sub>-surface is 15Å<sup>2</sup> less than at the liquid/air-interface. This finding can be interpreted by considering the level of hydration of the aniline amine groups at the water surface and at the substrate. The molecules on the solid surface are dehydrated and therefore they can arrange with a higher packing density than on the water surface.

The above data for the polymer is consistent with a model of the backbone conformation in which the benzene rings are lying flat on the substrate with the alkyl side chains pointing away from the substrate, covering the backbone. The monomer

data would fit to a model in which the benzene rings are standing perpendicular at the surface, connected to it via the amine groups and aggregated along an imaginary line through the centers of the benzene rings. The alkyl side chains should be tilted and interdigitated with adjacent rows.



Figure 1: STM images of 2-pentadecyl-aniline  
left side: Monomer, scan size 5nm, upstroke, constant current mode. Tip bias voltage: 1848 mV setpoint current: 0.11 nA  
right side: Polymer, scan size 5nm, downstroke const. current mode. Tip bias voltage: 1998 mV setpoint current: 0.31 nA

## 2.) 3-hexadecyl-pyrrole

Figure 2 shows the STM images of poly-3-hexadecyl-pyrrole (right) and 3-hexadecyl-pyrrole monomer (left), both with a scan size of 10nm x 10nm. As in the aniline measurements, ordered rows and rod like structures are observable, indicating high orientational and positional order. Manual distance determination for the rod-to-rod distance yield  $4.2 \pm 0.4 \text{ \AA}$  and a row-to-row distance of  $6.2 \pm 0.4 \text{ \AA}$ . With this data, interpreted as in the aniline case, the surface area covered by one polymer repeating unit was calculated as  $26.04 \pm 1.6 \text{ \AA}^2$ . This result fits very well with the value, determined from the  $\pi$ /area isotherm at the transfer pressure, which was  $27.4 \text{ \AA}^2$ . For the monomer we found a rod-to-rod distance of  $4.0 \pm 0.5 \text{ \AA}$  and a row-to-row distance of  $15 \pm 1.5 \text{ \AA}$ . Since the value for the rods can be interpreted with the distance between the alkyl side chains, a distance of  $15 \text{ \AA}$  between the rows is difficult to explain. One model which would fit the data, shows the rings standing on the substrate with a tilt angle and overlapping with each other, attached to the surface via the nitrogen atoms. The alkyl side chains are in the air partly covering the rings and forming a low energy surface. In the case of the polymer, a model with the polymer backbone in an all anti nitrogen configuration and outward "floating" alkyl side chains would fit the measured data.

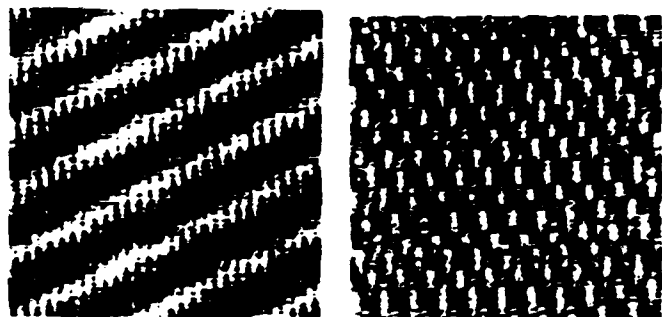


Figure 2: STM images of 3-hexadecyl-pyrrole  
left side: Monomer, scan size 10nm, constant current mode. Tip bias voltage: 1320 mV setpoint current: 0.31 nA  
right side: Polymer, scan size 10nm, constant current mode. Tip bias voltage: -1400 mV setpoint current: 0.20 nA

	rod dist. [Å]	row dist. [Å]	mMa sol. [Å <sup>2</sup> ]	mMa liqu. [Å <sup>2</sup> ]
P2PAN	4.26±0.07	7.80±0.04	33.5	32
2PAN	4.32±0.11	6.83±0.24	29.5	45
P3HPY	4.2±0.4	6.2±0.4	26	27.4
3HPY	4.0±0.5	15±1.5	--	24.8

Table 1: Distances between observable rows and rods, as well as calculated (solid/air-interface) and measured (liquid/air-interface) mean molecular areas of repeating units, for poly-2-pentadecyl-aniline (P2PAN), 2-pentadecyl-aniline (2PAN), poly-3-hexadecyl-pyrrole (P3HPY) and 3-hexadecyl-pyrrole (3HPY).

## Conclusions

The monolayers of poly-2-pentadecyl-aniline, poly-3-hexadecyl-pyrrole and the corresponding monomers show, after LB-transfer and annealing, high orientational and positional order. The polymers show nearly the same mean molecular area per repeating unit at the liquid/air-interface and on solid support, the monomers require less area on the substrate in the case of the aniline and a larger area in the case of the pyrrole monomer. The behavior of the aniline can be explained by dehydration during transfer and annealing.

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## References

1. A.G.,MacDiarmid; A.J.,Epstein; Macromol.Chem Macromol.Symp., 1991, 51, 217-234
2. MacDiarmid, A.G.; Chiang J.C.; Halpern, M.; Huang, W.S.; Mu, S.L.; Somasiri, N.L.D.; Wu, W.; Yaniger, S I.; Mol. Cryst. Liq. Cryst. 1985, 121, 173.
3. MacDiarmid, A.G.; Chiang, J.C.; Richter, A.F.; Somasiri, N.L.D.; Epstein, A.J.; Conducting Polymers Alcazer, L.; Ed.; Reidel Publication, Dordrecht, Holland. 1987; pp 105-120.
4. Genies, E.M.; Boyle, A.; Lapkowski, M.; Tsintavis, C Synth. Met. 1990, 36, 139-182. and refs therein
5. Othani, H.; Wilson, R.J.; Chiang, S.; Mate C.M.; Phys. Rev. Lett. 1988, 60, 2398
6. Frommer, J.E.; Foster, J.S.; Nature 1988, 333, 502.
7. Yang, R.; Yang, R.X.; Evans, D.F.; Hendrickson, W.A.; Baker, J.; J. Phys. Chem. 1990, 94, 6123-6125
8. Smith, D.P.E.; Hörber, H.; Gerber, Ch.; Binnig, G. Science 1989, 245, 43.
9. Rùhe, J.; Ezquerra, T.A.; Wegner, G.; Macromol Chem. Rapid. Commun., 1989,5,1
10. Bodalia, R.; Stern, R.; Batich, C.; Duran, R.; J. Poly. Sci. Chem. Ed. 1993, 31, 2123
11. Helm, C.A.; Tippmann-Krayer, P.; Möhwald, H., Kjaer, K.; Als-Nielsen, J.; Biophys. J. 1991, 60, 1454

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