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# Morphology of a Self-Assembled Monolayer of a Polymer

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The formation of monolayers that form spontaneously by adsorption from solution has found increasing attention in the last years.[1–7] Experiments with such self-assembled monolayers are often performed with gold as substrate, due to its unique resistance toward oxidation under atmospheric conditions. Most investigations deal with low molecular weight compounds, and only a few articles describe self-assembled polymer layers.[8,9] However, the morphology of such a polymer layer has never been observed, although several atomic force microscopy (AFM) studies on polymers deposited on inorganic surfaces by solvent evaporation and the Langmuir–Blodgett technique have already been successfully performed[10] and self-assembled monolayers of low molecular weight compounds have also been described.[5,6,11] Here, we report on the first direct observation of the morphology of a self-assembled monolayer of a polymer. These observations provide a direct observation of the rigidity of "rigid-rod" polymers.

The polymer used in this work consists of a main chain of poly(*p*-phenylene), regularly substituted with flexible side chains, as shown in Figure 1. This substance belongs to the class of rigid-rod polymers, the side chains providing the polymer with a certain solubility. Preparation and characterization have been described previously,[12,13] and the material used for this study consists of chains of 90 phenylene rings on the average; i.e., the average length of the molecule is ca. 35 nm.

Scanning electron microscopy and AFM revealed that the gold films consisted of flat grains of 30–600-nm diameter, as already reported for gold films prepared under similar conditions.[5,6] Furthermore, in agreement with descriptions of gold samples prepared in a similar manner,[5,14] we observed the (111) face on the grains of the pure samples. The surface roughness of the gold substrates was 2 nm and that of the underlying silicon wafers was 0.5 nm, over horizontal distances of 200 nm.

The polymer was adsorbed from a $CH_2Cl_2$ solution during 6 h onto freshly evaporated gold slides, procedurally analogous to systems involving low-molecular-weight compounds.[7,15,16] The adsorption was confirmed by infrared spectroscopy at grazing incidence reflection and X-ray photoelectron spectroscopy. The layer thickness is ca. 20 Å, as determined by ellipsometry. The advancing contact angle of water on these layers is 72° and, therefore, about 20° below that expected for a compact alkane layer.[7,17] Also, the advancing contact angle of water on a monolayer of an aromatic rigid-rod polymer with alkyl side chains on gold and copper is expected to be ca. 90°.[18] The advancing contact angle of water on pure gold substrates was 60 ± 2°. Hence, the gold substrate is probably not covered completely and perfectly.

The surface morphology was investigated with AFM. All images were collected on a Nanoscope III (Digital Instruments, Santa Barbara, CA) in air in constant force mode, where the force between the AFM tip (Si cantilever, Nanoprobe) and the organic surface is held constant. The vertical displacements of the sample, needed for keeping the preselected force constant, are recorded as the tip scans across the surface. The imaging force was ≈10 nN. Forces in the range of ca. 20–50 nN gave no pictures. Images (512 × 512 pixels) were acquired at a rate of 30 lines/s, requiring ≈17 s/image. The images thus obtained reveal structured islands in unstructured surroundings. The size of these structured domains is on the order of dozens of nanometers, i.e., comparable to the length of the macromolecules. In the following we focus on these structured domains.

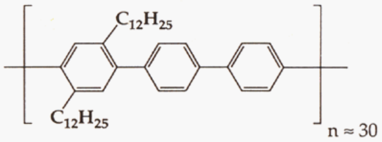

**Figure 1.** Poly(2,5-didodecyl-*p*-terphenyl-4,4″-diyl).

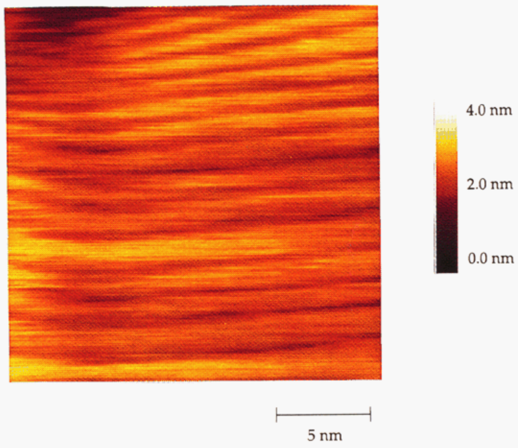

**Figure 2.** AFM top-view image of a 20 × 20 nm section of a thermally evaporated Au film on Si(111) coated with poly(2,5-didodecyl-*p*-terphenyl-4,4″-diyl).

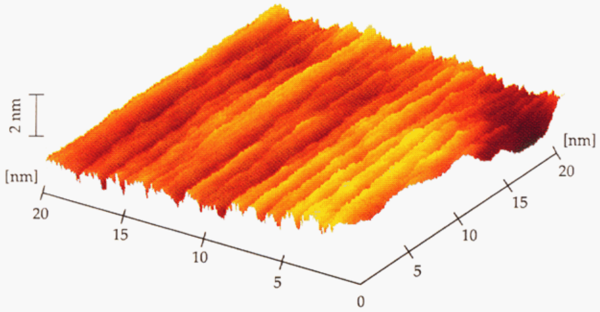

**Figure 3.** Surface plot of Figure 2.

Figures 2 and 3 display unfiltered AFM pictures of a gold surface after treatment with the polymer. They show slightly bent striae separated by distances of 1–1.5 nm. The lateral dimensions of these stripes are in agreement with the molecular dimensions of the macromolecules involved, and they are assumed to represent the polymer chains. The variation in distances between neighboring striae indicates imperfect packing of molecules, as suggested by the results of contact angle measurements. The fact that the molecules appear bent is in accord with the expected flexibility of such polymer chains.[19] In blank experiments, we never have observed striations after solvent evaporation but instead were able to observe the (111) face of gold in atomic resolution.

Figure 4 displays a profile perpendicular to the chain directions. The vertical corrugation appears to be ca. 0.5

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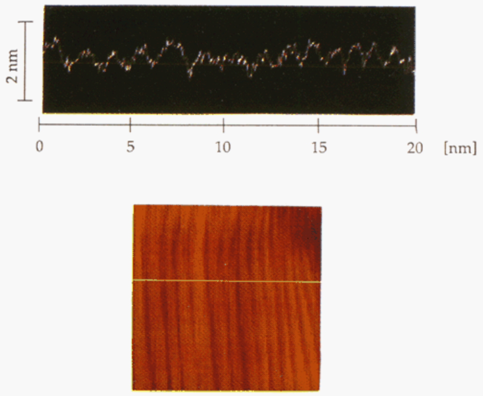

**Figure 4.** (a, top) Contour of the surface for the white line drawn in image b. (b, bottom) Top-view image (20 × 20 nm) of the polymer layer on gold.

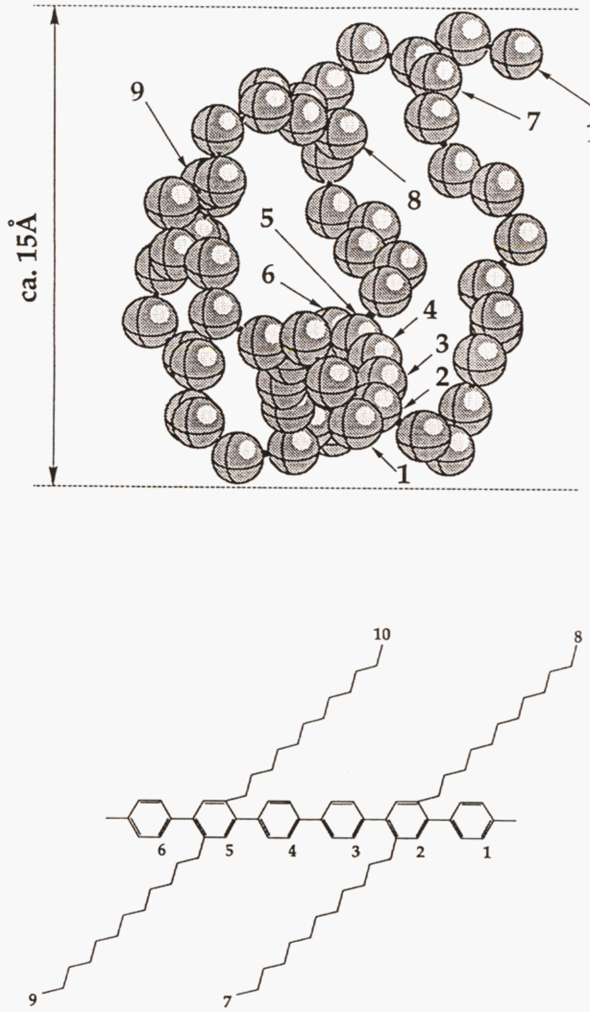

**Figure 5.** Attempt at visualization of a possible conformation of poly(2,5-didodecyl-*p*-terphenyl-4,4″-diyl) on gold (front view).

nm. It is not evident if the AFM tip touches the blank gold surface between two neighboring stripes. Since neighboring rings are most likely twisted against each other,[20–23] the macromolecule's habit is roughly cylindrical with a diameter of ca. 1–2 nm (Figure 5), in harmony with the ellipsometric measurements (the refractive index used for the determination of film thickness was 1.45 as determined by measurement on a thick polymer film; a refractive index difference of ±0.1 leads to an error of ±1 Å in the calculated layer thickness). The dimensions and shape of the striae suggest the self-assembled monolayer to have the structure of a 2-dimensional liquid crystal.

These AFM pictures not only show the first direct observation of a self-assembled polymer layer but they also belong to the rare examples of an imaging of a nonperiodic organic surface with molecular resolution. The reason for the high resolution might be found in the strongly restricted mobility of the segments of the rather rigid polymer backbone; i.e., the movements of the polymer backbone are very slow compared to the time required for an AFM picture and, as a consequence, the picture does not "smear" as is commonly observed for flexible polymers. The highly mobile *n*-alkyl groups provide a "liquid" coat for the rigid backbone. It is anticipated that layers of other rigid-rod polymers are also suitable subjects for AFM studies.

Besides the direct observation of the film structure, the AFM pictures confirm the hypothesis that polymers on the base of poly(*p*-phenylene) exhibit relatively small persistence lengths at the surfaces investigated here. The persistence length is on the order of 10 nm, judging from Figures 2 and 3 and others. This is, of course, not identical with equilibrium conformational characteristics in solution or melt but provides a convenient basis for comparison. Studies of other adsorbed rigid-rod polymers, e.g., aromatic polyesters or aromatic polyamides, seem promising.

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