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# Reactive graphite etch and the structure of an adsorbed organic monolayer—a scanning tunneling microscopy study

Jürgen P. Rabe, Stefan Buchholz, and Anna M. Ritcey

Max Planck Institut für Polymerforschung, Postfach 3148, D-6500 Mainz, Federal Republic of Germany

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Two types of surface interactions of the basal plane of graphite with an organic ambient have been investigated with the scanning tunneling microscope: (1) At the bulk interphase between octylcyanobiphenyl and graphite local surface reactions have been observed with a threshold tip bias of  $-1.7$  V and lifetimes of the reaction products on the order of 1 s. At more negative bias between  $-2.5$  and  $-4$  V the reactions become more intense resulting in localized graphite etch. While a crystalline adsorbate phase of octylcyanobiphenyl is very rarely observed on the flat graphite surface, it occurs more readily after the etching procedure, indicating a lack of nucleation sites on the pristine graphite. (2) A monolayer of a mixed cellulose ether (laurylmethyl) transferred onto graphite by the Langmuir–Blodgett technique has been imaged in the tip bias range of  $+10$  mV to  $+1$  V with a resolution of better than 1 nm. From the images one can determine the conformation of the individual polymer molecule. The polymer is found to be extended over several tens of nanometers and characteristic kinks along the chain are observed, indicative of a conformation which results from the adsorption of a twisted ribbon.

## I. INTRODUCTION

Atomic resolution is a common feature in scanning tunneling microscopy (STM) of inorganic semiconductor surfaces.<sup>1</sup> However, only few high resolution images of organic adsorbates have been reported in the literature, among them adsorbate layers of a class of low molecular weight liquid crystalline materials on graphite<sup>2,3</sup> and individual phthalocyanine molecules on copper.<sup>4</sup> Also STM images of DNA<sup>5</sup> and some synthetic polymers<sup>6–8</sup> on graphite have been obtained, however at lower resolution. The major problems in imaging such systems are, firstly, a lack of electronic conductivity of the adsorbate and, secondly, their molecular mobility. Because of these difficulties, few systems have been successfully imaged to date by STM and it is this lack of experimental data which contributes to a third problem, namely the lack of a good understanding of the contrast mechanism in STM imaging of organics.

In order to minimize the problem of conductivity, thin organic molecules lying flat on graphite have been chosen for this study. The first system investigated is the interphase between graphite and octylcyanobiphenyl, a material which undergoes a bulk phase transition from crystalline to smectic near room temperature. It had been shown previously<sup>2</sup> that a highly ordered adsorbate layer may be imaged at the interphase, which is very stable and extends over macroscopic distances on the sample. From the fact that the image does not necessarily occur spontaneously after preparation but may take several hours before it emerges, one may conclude that crystallization needs to be initialized. It will be shown below that graphite can be etched in octylcyanobiphenyl ambient with the STM and that the crystallization may be initialized by the etch.

The second system investigated is a cellulose derivative on graphite. A rather stiff polymer was chosen, since in this case even a weak interaction energy per monomer may sum sufficiently to permit an individual molecule to stick stably to the

substrate. Cellulose is the  $\beta$  (1,4) linked homopolymer of *D*-glucose. x-ray data reveal a repeat unit of 1.03 nm, as well as a two-fold symmetry.<sup>9</sup> The corresponding molecular conformation is an extended ribbon with a  $2_1$  screw axis coincident with the chain. The exact nature of the packing of the polymer chains into the various observed polymorphic forms remains unclear.<sup>10</sup> One of the difficulties in studying cellulose is its insolubility in common solvents. Ester- and ether-derivations render cellulose soluble and the derivatives have been classified as semirigid polymers with a persistence length on the order of 10 nm.<sup>11</sup> However, many derivatives form lyotropic liquid crystalline phases at polymer concentrations which imply a greater chain stiffness.<sup>12</sup> While it has been shown that several cellulose derivatives exist as extended helices in the solid crystalline state,<sup>13</sup> little is known about the chain conformation in the liquid crystalline phase. It will be demonstrated below that the conformation of a cellulose derivative in a Langmuir–Blodgett monolayer as well as of an isolated molecule can be determined from direct imaging with the STM.

## II. EXPERIMENTAL

Highly oriented pyrolytic graphite (HOPG) was obtained from Union Carbide, USA. Octylcyanobiphenyl (Merck, FRG), silicone oil (1,1,2,3,3-Pentaphenyl-1,2,3-Trimethyl-trisiloxane; Petrarch Systems, USA) and ethyl cellulose (Aldrich; 100 cp) were obtained commercially and used without any further purification. Laurylmethyl cellulose was prepared by the alkylation of remaining hydroxyl groups on methyl cellulose (Henkel, FRG; degree of substitution: 1.9).<sup>14</sup> Analysis indicates complete substitution and a molecular weight of 150 000. Monolayer films were prepared on HOPG substrates using Langmuir–Blodgett and Langmuir–Schäfer techniques as described previously.<sup>6</sup> Details of the transfer behavior will be given elsewhere.<sup>14</sup> The STM<sup>6</sup> was operated at room temperature with Pt/Ir and W

tips in air, if not specified otherwise. The tunneling current was generally 2 nA. Variable Current (or so called "constant height") images were obtained with the tip scanning at 1 kHz in the  $x$  direction and 40 Hz in the  $y$  direction, corresponding to 10 images per s at a resolution of 100 lines. These current images were stored in real time on video tape. Digital image processing was performed with the software package MIMPS<sup>tm</sup> licensed from Stanford University. It was used primarily to remove some high frequency noise and to generate quasi three-dimensional images.

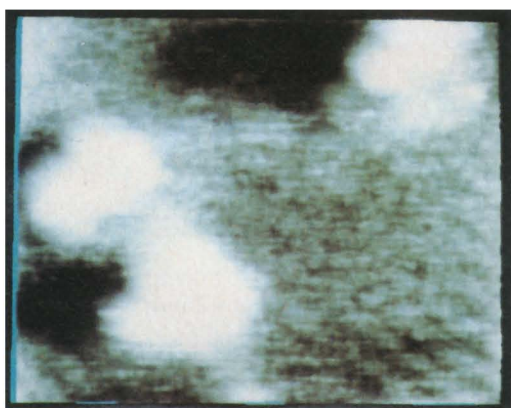
### III. RESULTS AND DISCUSSION

#### A. Octylcyanobiphenyl on graphite

At the interphase between octylcyanobiphenyl and graphite generally only graphite was observed at atomic resolution with the occasional exception of an ordered adsorbate phase similar to the one reported before.<sup>2</sup> The graphite images remain stable upon raising the tip bias to  $-1.7 \pm 0.1$  V. At this threshold the tunneling current becomes noisy and features like the ones shown in Fig. 1 appear consistently in the variable current images on a time scale of several seconds.



(a)



(b)

FIG. 1. Initial stage of graphite etch under octylcyanobiphenyl ambient in air, showing individual adsorbates on graphite. Top view STM image, obtained in the variable current mode. The brightness is proportional to the current. Scan range  $3.2 \text{ nm} \times 2.5 \text{ nm}$ ; acquisition time  $< 1$  s. (a)  $V_{\text{tip}} = -1.6$  V (single adsorbate); (b)  $V_{\text{tip}} = -1.7$  V (several adsorbates simultaneously).

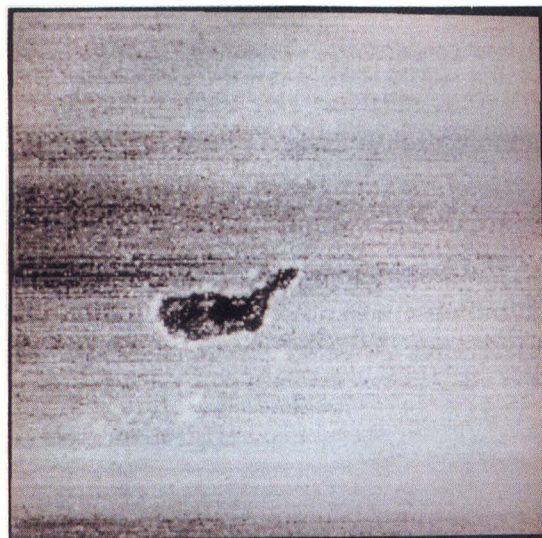
However, they are only stable for less than 1 s and, therefore, the fast variable current mode is required to observe them. They disappear totally if one lowers the tip bias to values less negative than  $-1.6$  V. We interpret the features in Fig. 1 as metastable reaction products of the ambient fluid with the graphite surface. The reaction is localized at the position of the tunneling gap. As the tip bias is increased to about  $-2$  V the tunneling current becomes more unstable and several adsorbates occur simultaneously. If one lowers the bias now again to values less negative than  $-1.6$  V, adsorbate features may remain with a longer lifetime on the order of minutes. These features are similar to the ones found after bias pulses on graphite in dimethylphthalate<sup>15</sup> or also air.<sup>16</sup> It should be mentioned that the molecules could not be identified by their shape. Also, a higher bias is necessary for 100 ns or  $1 \mu\text{s}$  pulses to cause reliably an effect. The latter can be attributed to the finite excitation and/or reaction probability of the molecules, since at the threshold voltage the adsorbate appears on a time scale as slow as seconds. If one increases the bias to even more negative values, one can observe the onset of localized reactive etching of graphite. Given in Fig. 2 are the STM images of a small hole, etched during 2 min at  $-2.5$  V and a big hole, etched at  $-3$  V, respectively. The diameter is of the order of 10 nm and the holes are surrounded by walls which are below 1 nm in height. The small hole is about one monolayer deep, while the big hole extends several monolayers deep. Even larger holes are formed during 2 min at a bias of  $-4$  V. At a positive tip bias no stable imaging was possible after operating at about  $+3$  V for 1 min. Etch effects similar to the ones described above are found in air, water vapor (10 mbar) and silicone oil, where, however, the adsorbate images are less clear. No etch up to  $\pm 4$  V bias was found in helium gas (1 atm) and dry toluene (10 mbar).

The observations given above demonstrate that in the ambients as different as air, water, octylcyanobiphenyl, and silicone oil always highly reactive species are formed at a tip voltage around  $-2$  V or more negative indicating that a similar reaction is involved. At this threshold voltage the adsorbate is bonded metastably to the surface while at more negative bias mobile reaction products are formed which lead to the graphite etch. Since dry toluene does not show this reaction, it may be speculated that rest water present in octylcyanobiphenyl and silicone oil is involved in the reaction. It should be noted that after etching graphite in octylcyanobiphenyl at a bias of  $-4$  V for several minutes also the ordered monolayer<sup>2</sup> has been repeatedly found, indicating that the etched hole may act as a nucleation site for the crystallization.

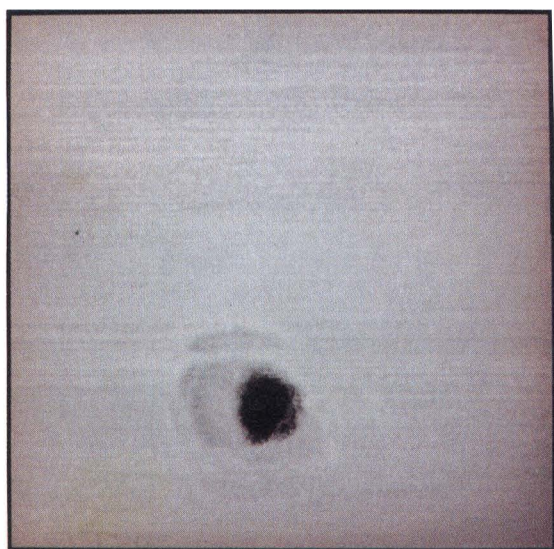
#### B. Cellulose derivatives on graphite

Laurylmethyl- and ethyl cellulose monolayers were transferred onto graphite by the Langmuir-Blodgett technique with a transfer ratio smaller than unity and varying somewhat from experiment to experiment. This is similar to what has been observed previously for other Langmuir-Blodgett monolayers on graphite.<sup>6</sup> Accordingly with the STM (i) bare graphite, (ii) islands of a monolayer of mostly parallel rods (Fig. 3), or (iii) single isolated polymer molecules like





(a)



(b)

FIG. 2. Holes etched into graphite under octylcyanobiphenyl ambient in air. Top view STM image, obtained in the constant current mode. The brightness is proportional to the height. Scan range  $100\text{ nm} \times 100\text{ nm}$ ;  $V_{\text{tip}}$  (during scanning) =  $-1\text{ V}$ . (a) Etch at  $V_{\text{tip}} = -2.5$  for 2 min. (b) Etch at  $V_{\text{tip}} = -3.0\text{ V}$  for 2 min.

the one shown in Fig. 4 were observed at a tip bias between  $+10\text{ mV}$  and  $+1\text{ V}$ . Both images, Figs. 3 and 4, were obtained in the variable current mode. In order to distinguish the polymer chain in Fig. 4 from a graphite step, also the back scan in  $x$  direction has been recorded. As it is expected for an adsorbate the typical electronic “shadow” next to pronounced features in variable current images flips symmetrically around the object upon reversing the scan direction.

Figure 4 shows that the polymer is extended over tens of nanometers. Perfectly straight segments are displaced by characteristic kinks. Clearly, single kinks as well as double kinks can be identified, with variable separation between them. The stability of these images is such that the same individual molecule can be imaged over at least an entire day. It

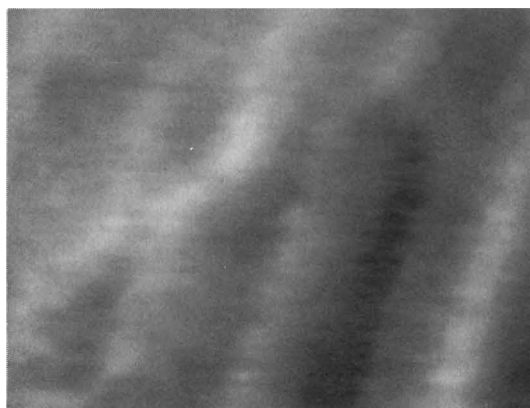


FIG. 3. Langmuir-Blodgett film of laurylmethyl cellulose on graphite, showing mainly parallel rods with characteristic kinks. Top view STM image obtained in the variable current mode. Bright and dark means high and low current, respectively. The width of the image is  $9.5\text{ nm}$ .

should be mentioned, however, that occasionally a sudden motion of a particular segment is observed. This, incidentally, may allow the investigation of very slow ( $>0.1\text{ s}$ ) segmental motion at the surface. The reproducibility of the given images is such that for all samples investigated, parallel extended rods with characteristic kinks were found somewhere in our typically accessed scan area of  $1.5 \times 1.5\ \mu\text{m}^2$ . The investigated samples include different pieces of graphite, different monolayer preparations and, for comparison, two different cellulose derivatives, laurylmethyl- and ethyl-ethers. The fact that both, laurylmethyl- and ethyl cellulose molecules are found to be highly extended is consistent with the lyotropic behavior of many cellulose derivatives.<sup>17</sup> However, it must be remembered that for the STM samples the polymers have been applied to graphite by the Langmuir-Blodgett technique, which involves particular surface and orientation forces. The highly extended chain can, therefore, only be attributed to the adsorbed molecule.

Characteristic for all images are the kinks mentioned above. The separation between them shows a fairly narrow distribution for one particular section of a molecule, as can be judged from Fig. 4. However, this separation varies more widely between individual molecules even within the same monolayer preparation. It should be further noted that in all molecules observed, the chain is preferentially displaced to the right of the kink, as evident in Fig. 4. This can be explained as follows: The cellulosic ribbon in solution may be assumed to be somewhat twisted around its axis. Upon adsorption to a flat surface, energy is minimized for a particular orientation of the anhydroglucose rings relative to the graphite surface; the polymer does not, however, untwist perfectly prior to adsorption. Each kink would correspond then to a twist of the ribbon, and the direction of the chain displacement may be related to the chirality of the molecule.

In terms of contrast of STM images, the results described above show that the current through the adsorbed cellulose backbone is considerably enhanced over the current into “bare” graphite, i.e., through other highly mobile contaminants from the air, independent of the applied tip voltage in

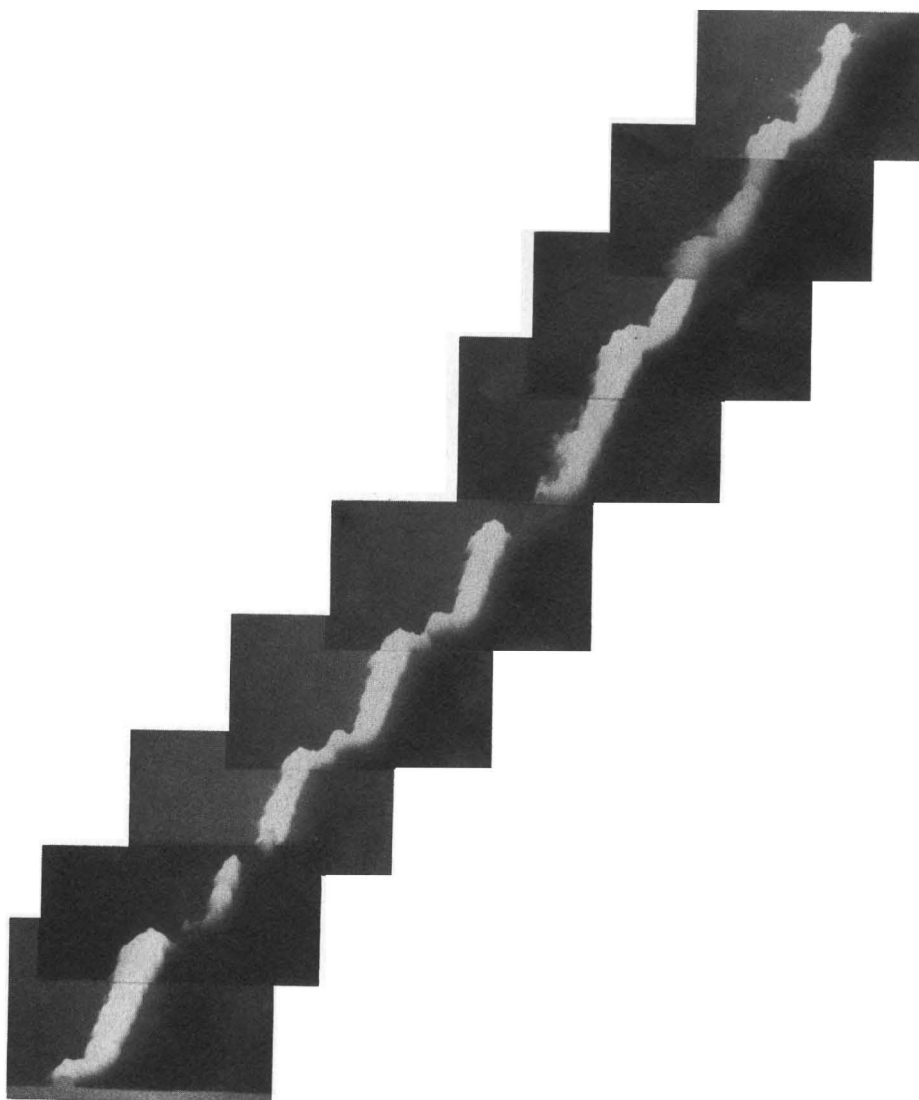


FIG. 4. Single laurylmethyl cellulose molecule on graphite, which is extended over about 50 nm. Characteristic single and double kinks can be identified. Top view STM image, obtained in the variable current mode. Bright and dark means high and low current, respectively. The image is composed from smaller overlapping images taken subsequently while moving the field of view of the STM along the chain. The width of a single image is 9.5 nm.

the range investigated. The fact that the lauryl sidechains are probably also oriented partially flat on the graphite, indicates that the current through hydrocarbons is less than through the adsorbed anhydroglucose residues. Furthermore, the cellulose chain at the kink barely alters the current. These findings agree with what has been observed for a number of low molecular weight liquid crystalline materials adsorbed on graphite,<sup>2,3</sup> where hydrocarbon covered graphite was found to have a much higher impedance than graphite covered by several different more polarizable organic entities. The explanation given for these cases was the reduction in local barrier height due to the intrinsic or induced dipole moment of an adsorbate.<sup>3</sup> Applied to cellulose, this means more specifically that the local barrier height of graphite is reduced differently, depending on the orientation of the anhydroglucose ring, allowing STM to distinguish between the rings in the straight parts and at the kink.

In summary, local surface reactions of the basal plane of graphite under a number of fluid ambients have been observed at the tip position and at a threshold tip bias of  $-1.7$  V. Metastable adsorbate products with lifetimes on the order of 1 s have been observed. At more negative bias

between  $-2.5$  and  $-4$  V the reactions become more intense resulting in localized graphite etch. The etched holes may act as nucleation sites for an organic ambient.

Furthermore, stable STM images of polymer monolayers and isolated polymer molecules, transferred by the Langmuir-Blodgett technique, have been obtained with unprecedented resolution. For the particular cellulose derivative discussed above it was found that the backbone of the adsorbed polymer is highly extended. Moreover, characteristic kinks have been found which can be attributed to a twisted ribbon adsorbed on the surface. In addition the data obtained demonstrate that monolayers from stiff polymers are well suited for STM imaging since (i) they can be thin enough to pass a sufficient tunneling current, and (ii) even small interaction energies per monomer may add up for the polymer to be strongly enough adsorbed for stable imaging. The data also contribute to our understanding of contrast mechanism in STM imaging of organics.

With these imaging capabilities it becomes possible now to investigate details of the adsorption phenomena of cellulose derivatives. For example, the question of epitaxy and side-chain dependence of the conformation should be further ex-

amined in order to elucidate the surface forces involved. Moreover, it appears feasible that cellulose derivations will render more molecular entities accessible for STM imaging. Finally, slow molecular dynamics of polymers at surfaces may become experimentally accessible.

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