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The morphology and electronic structure of ordered polyimide monolayers

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Abstract. Monolayers of two different polyimides (PMDA-ODA and PMDA-PDA) have been prepared on graphite and oxidized silicon surfaces using the Langmuir–Blodgett (LB) technique of Kakimoto and co-workers. Scanning tunnelling microscopy indicates that both the rod-like PMDA-PDA and the zig-zag PMDA-ODA are characterized by a high degree of two-dimensional order on graphite. X-ray absorption spectroscopy at the carbon, nitrogen and oxygen K-edges has been used to obtain information on the orientation of the different sections in the polymer chain. With the help of corresponding spectra from the model compounds pyromellitic diimide and diphenyl ether some insight can be gained into the origin of the resonances at the C and N K-edges.

1. Introduction

Recently, Kakimoto *et al* [1] have shown that monolayers and multilayers of PMDA-ODA polyimide can be prepared on solid surfaces using a Langmuir–Blodgett (LB) technique which allows subsequent removal of the long alkyl chains. (PMDA-ODA \equiv pyromellitic dianhydride/oxydianiline.) In a recent study [2] we have shown with core and valence level photoemission that such layers adsorbed on highly oriented pyrolytic graphite (HOPG) are imidized to a similar extent as thicker samples prepared by spin-coating or by the molecular co-deposition method. Further, studies with scanning tunnelling microscopy (STM) indicated that the monolayers are characterized by a high degree of two-dimensional order over areas as large as 100 nm \times 100 nm [3]. There was, however, still some doubt as to the exact interpretation of the STM pictures, particularly as to the polymer chain conformation. The purpose of the present study has been to address the problem of the STM images by extending the investigation to the rod-like PMDA-PDA polyimide and to assign the resonances in the x-ray absorption spectrum of the PMDA-ODA polyimide by measuring the spectra of model compounds (PMDA-PDA \equiv pyromellitic dianhydride/*p*-phenylene diamine). The extended chain conformation of the PMDA-PDA polyimide is characterized by a simple rod-like structure (figure 1(a)), whereas the extended chain conformation of the PMDA-ODA polyimide has a bent C–O–C bond at the ether oxygen giving rise to a zig-zag structure (figure 1(b)), in addition to a possible rotation about the C–N bond linking the PMDA and ODA sections [4].

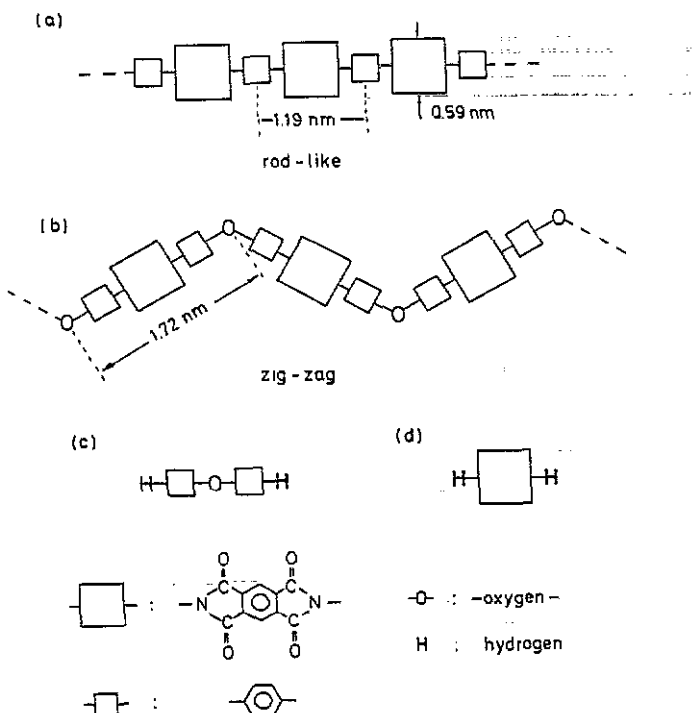


Figure 1. Molecular structure of two polyimides and related model compounds: (a) PMDA-PDA (pyromellitic dianhydride/p-phenylene diamine), (b) PMDA-ODA (pyromellitic dianhydride/oxydianiline), (c) DPE (diphenyl ether) and (d) PMDI (pyromellitic diimide). The dimensions have been calculated with the Chem-X set of molecular modelling programs.

2. Experimental details

The monolayers were prepared using a circular LB trough and transferred at a constant film pressure of 25 mN m^{-1} , a transfer speed of 7 mm min^{-1} and a constant temperature of approximately 25°C . The details of the subsequent procedure have been given earlier [3]. Both graphite (HOPG) and silicon covered with a thin native oxide film, which provide hydrophobic and hydrophilic surfaces, respectively, were used as substrates. A commercial STM (Nanoscope II; Digital Instruments Inc.) with a $0.5 \mu\text{m}$ scan head was used for imaging the layers on graphite. These experiments were performed in the constant current mode with a Ni tip or a Pt-Ir tip in air. X-ray absorption spectra were measured in a double-chamber UHV system (base pressure less than 2×10^{-10} mbar in both chambers) on two different grazing incidence monochromators (SX-700 IV and HE-TGM 1) at the Berlin synchrotron radiation source BESSY. Spectra were recorded in the partial yield mode at a resolution of approximately 0.3 eV (1.0 eV) at the C K-edge, and of approximately 0.6 eV (1.4 eV) at the N K-edge. (The values in brackets refer to the HE-TGM.) After preparation of the monolayers on graphite and introduction into the UHV system, the samples were heated to $\sim 400^\circ\text{C}$ for 10 min in order to drive-off fully the remaining water. The monolayers on oxidized silicon were only heated to 200°C because of evidence of full imidization. Thick films of the model compounds pyromellitic diimide (PMDI) and diphenyl ether (DPE) were prepared by evaporation onto a cold Cu substrate.

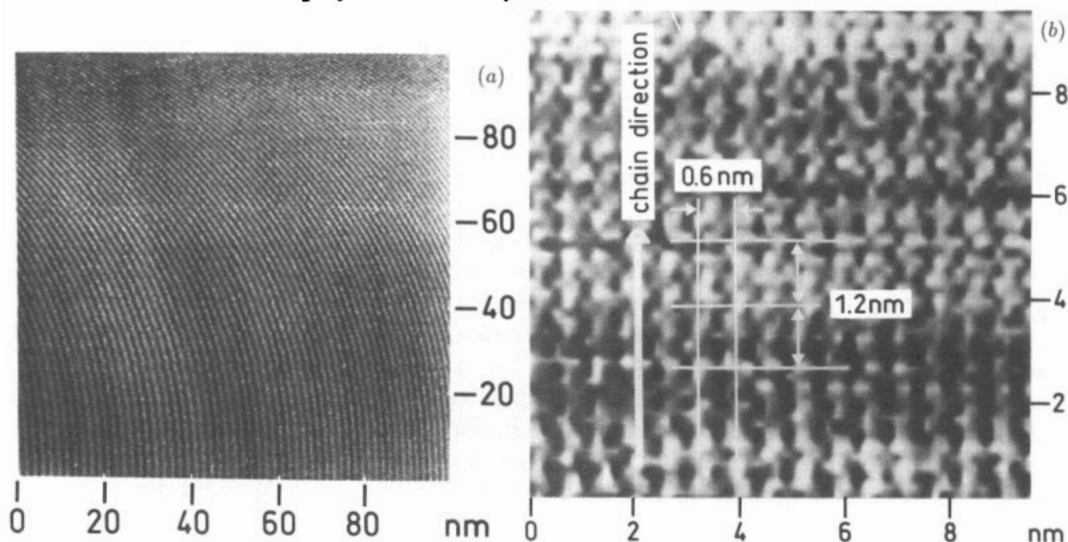


Figure 2. (a) Raw topographical STM image of a monolayer of PMDA-ODA polyimide on a HOPG substrate in air in the constant-current mode; area $100\text{ nm} \times 100\text{ nm}$; current setting 3 nA ; sample bias -12.2 mV . (b) Raw topographical STM image of a monolayer of PMDA-PDA polyimide on a HOPG substrate in air in the constant-current mode; area $10\text{ nm} \times 10\text{ nm}$; current setting 2.0 nA ; sample bias, 10.1 mV .

3. Scanning tunnelling microscopy

In our previous work we were unable to interpret satisfactorily the STM images obtained from PMDA-ODA monolayers on graphite [3]. Figure 2(a) shows a raw topographic image for a field of view of $100\text{ nm} \times 100\text{ nm}$. The micrograph differs slightly from the one published previously due to different film preparation and different tunnelling conditions. Nonetheless, it shows a considerable degree of two-dimensional order which is found over large areas of the substrate. We thus obtain the remarkable result that the two-dimensional order established in the LB trough is transferred to the polyimide film despite deposition on the substrate, subsequent imidization and removal of the long alkyl chains. As in the earlier work, smaller field-of-view images show more detailed structural features, but these are difficult to interpret satisfactorily. In contrast, figure 2(b) shows a raw topographic image ($10\text{ nm} \times 10\text{ nm}$) of a monolayer of the rod-like PMDA-PDA on a HOPG substrate. It shows a regular array structure with periodicities of approximately 1.2 and 0.6 nm in two orthogonal directions over areas as large as $30\text{ nm} \times 30\text{ nm}$. On the basis of the molecular dimensions shown in figure 1, we suggest that the direction of the polymer backbone is coincident with the axis showing approximately 1.2 nm periodicity and that the distance between the chains is approximately 0.6 nm . The chain direction corresponds roughly to the transfer direction. Note also a certain degree of 'smearing' of the image perpendicular to the chains which is in the scan direction and indicates some interaction between the tip and the film. The observation of this more or less regular pattern which is consistent with both the conformation and molecular dimensions of the polymer is quite significant. The data reinforce our view that STM studies are capable of identifying ordered structures in such layers and that the images are consistent with the molecular dimensions. However, this result does not help us to understand the details of the PMDA-ODA images such as that of figure 2(a). This particular problem is made even more difficult by the conclusions drawn from the x-ray absorption spectra

reported later which indicate that the ring planes of the PMDA and ODA sections are parallel to the graphite surface.

4. Near-edge x-ray absorption spectroscopy

X-ray absorption spectroscopy in the near-edge region is not only a probe of unoccupied valence states but also a useful tool for determining molecular orientation [5]. This is due to the polarization dependence of the various resonances, i.e. the variation in their intensity as a function of the orientation of the E vector relative to some symmetry element of the molecule [6]. In a simple model, the transitions at the carbon, nitrogen and oxygen edges of polyimide can be grouped into two types: π^* resonances normally below the ionization limit, which are polarized perpendicular to the ring planes of the polymer unit, and σ^* resonances occurring above the threshold which are polarized parallel to those planes. In the case of polyimides we might expect that the π orbitals associated with the carbonyl and phenylene groups in both PMDA and ODA units interact via the nitrogen lone pair and are delocalized over the whole monomer unit if the ring systems are co-planar. An interruption of the conjugation would occur if there is torsion about the C–N bond between the PMDA and the ODA or PDA ring planes.

The carbon K-edge of a single PMDA-ODA polyimide monolayer on oxidized silicon is shown in figure 3(c) for an angle between the E vector of the light and the surface normal of $\theta_E = 25^\circ$. The sharp resonances (features 1 to 7) are assigned to transitions to the π system, in general agreement with calculation [7]. They exhibit relatively small changes in intensity as a function of θ_E (spectra not shown), indicating that the polymer is adsorbed such that the PMDA and ODA moieties have fixed, but possibly different, orientations relative to the surface or, alternatively, that the orientation of both is random. In both cases a twisting about the C–N bond could therefore occur. The monolayer spectrum of figure 3(c) is virtually identical to the corresponding spectrum from a thick spin-coated film (figure 3(d)) reproduced from [8]. The assignment of the observed resonances is aided by the spectra of the model compounds DPE and PMDI shown in figures 3(a) and (b), respectively. These were taken for thick ($\sim 30 \text{ \AA}$) films evaporated onto a single-crystal copper substrate. There is almost a 1:1 correspondence between the features in the DPE and PMDI spectra and all eleven resonances identified in the C 1s spectrum of the monolayer. The sharpest, most intense peak at 285.3 is assigned to C 1s $\rightarrow \pi^*$ transitions in both the ODA part (DPE: peak at 285.7 eV designated 2) and the PMDA part (PMDI: peak at 285.1 eV designated 1). The latter appears to constitute the low energy shoulder. The second peak (designated 3, 4) also arises from transitions in both π^* systems, as does the next peak which is designated as 5. The shoulder (6) at approximately 291.0 eV is assigned to ODA and the next peak (7) at 292.1 eV to PMDA. The broad features (8, 9) and (10, 11) can be attributed to both the ODA part and the PMDA part and are almost certainly due to σ -type resonances. The fact that the spectrum (c) is given by the sum of spectra (a) and (b) in figure 3 suggests that there is very little interaction between the two moieties in the polyimide monolayer. It may also mean that there is a torsional angle about the C–N bond, which in turn would be compatible with the polarization dependence. However, it will be seen from the data for a PMDA-ODA monolayer on graphite reported below that such a conclusion cannot be drawn with certainty.

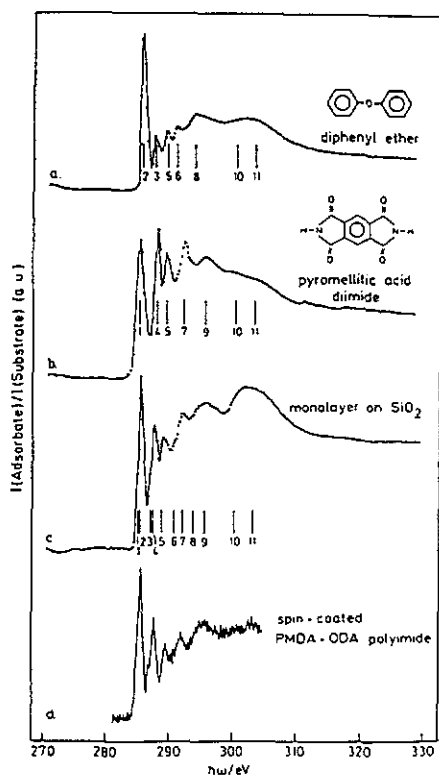


Figure 3. The carbon K-edge spectra of (a) multilayers of DPE on Cu{110} at ~ 130 K, (b) multilayers of PMDI on Cu{110}, (c) a monolayer of PMDA-ODA polyimide on oxidized silicon prepared using the LB technique, and (d) a thick PMDA-ODA polyimide film prepared using the spin-coating method (after [8]).

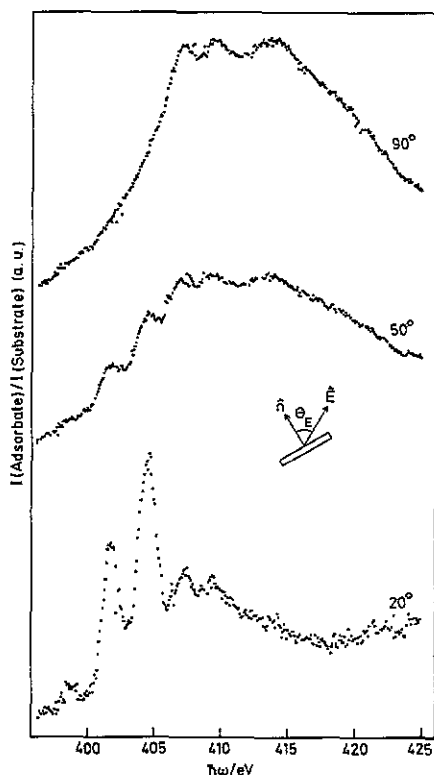


Figure 4. The nitrogen K-edge spectra of a single monolayer of PMDA-ODA polyimide on HOPG for angles between the E vector and the surface normal, θ_E of 20° , 50° and 90° .

The measurement of carbon K-edge absorption spectra for polyimides on HOPG is not possible due to the very strong, polarization-dependent resonances of the substrate. Figure 4 thus shows *nitrogen* K-edge spectra for a monolayer of PMDA-ODA polyimide on HOPG as a function of θ_E . (We note that there is a discrepancy between [2] and the present data in that a third, strong resonance at lower energy was found in our earlier work. This may have been related to incomplete imidization; some indication for a low energy resonance is still seen in the $\theta = 20^\circ$ spectrum of figure 4.) Two important observations can be made, the first of which is only apparent by comparison with the corresponding N K-edge spectrum of the model compound PMDI which cannot be shown here for reasons of space. There is a striking similarity between the spectra and, as in the case of figure 3, a 1:1 correspondence is found between the resonances of the monolayer and of the model compound. The second observation concerns the variation in intensity as θ_E is varied: there is a strong polarization dependence with the π^* resonances exhibiting a maximum at high

angles of incidence. The sharp, most intense peak in the O K-edge spectra (also not shown), which is assigned to the O 1s \rightarrow π^* transition at the carbonyl group, shows a similar polarization dependence. These results indicate that the PMDA and ODA moieties in the monolayer are co-planar and oriented parallel to the HOPG surface. Thus for $\theta_E = 90^\circ$, i.e. for the E vector parallel to the surface, the intensity of the π^* resonances which are polarized perpendicular to the ring planes, goes to zero. Furthermore, the strong similarity to the model compound spectra indicates that—despite the co-planar configuration—there is little or no interaction of the two ring systems, i.e. no π^* delocalization across the N atom. Although the observation of a high degree of orientational order in the PMDA-ODA monolayer on graphite is an interesting result in itself (and a convincing application of near-edge spectroscopy in such studies), it is difficult to reconcile the parallel adsorption geometry thus obtained with the STM data of figure 2(a) and [3]. At present we can offer no explanation for this discrepancy.

5. Conclusions

STM studies reveal that monolayers of both PMDA-PDA and PMDA-ODA on graphite are characterized by a high degree of two-dimensional order. In the case of PMDA-PDA we suggest that the direction of the polymer backbone is coincident with the axis showing approximately 1.2 nm periodicity and that the intermolecular distance is approximately 0.6 nm. These data provide confirmation of the simple interpretation of such STM images in terms of molecular models. The corresponding images for PMDA-ODA are, however, still difficult to interpret. Using the polarization dependence of x-ray absorption spectra the ring planes of the PMDA-ODA monolayer are found to be orientated parallel to the graphite substrate.

Acknowledgments

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