Molecular Organization of Alkoxy-Substituted Oligo(phenylene-ethynylene)s Studied by Scanning Tunneling Microscopy

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Morphologies and structures of self-assembled monolayers of two conjugated oligo(phenylene-ethynylene)s are observed by scanning tunneling microscopy at submolecular resolution. The cooperative intermolecular and molecular/substrate interactions contribute to long-range order. The influence of endgroups on hydrogen bonding and steric hindrance on the surface patterning is discussed. The different arrangement configuration of the two molecules could be due to the changed endgroups. This control of the two-dimensional self-assembly is promising for future studies on the electronic properties of these molecules.

Introduction

Conjugated polymers are a novel class of semiconductors that combine the optical and electronic properties of semiconductors with the processing advantages and mechanical properties of polymers. They open a wide range of applications in electronic and photonic devices such as emitting layers in electroluminescent devices, polarizers for liquid crystal displays, active media in solid-state plastic lasers and polymer-based photovoltaic cells. In principle, conjugated polymers should be able to pertain to all of the functions an inorganic semiconductor displays. That may include their use in semiconductor diodes and field effect transistors (FETs) and may lead in the future to “molecular electronics”. The conjugated polymers which have attracted the most interest in the past are undoubtedly the poly(p-phenylenevinylene)s (PPVs) since Friend et al. reported on organic polymeric light-emitting diodes (LEDs) in 1990. Contrary to that, the dehydrogenated congeners of PPV, the poly(phenylene-ethynylene)s (PPEs), have attracted much less attention in the polymer community, despite their favorable emission characteristics and high fluorescence quantum yields. Only recently, several groups demonstrated that besides PPE derivatives’ interesting optoelectronic properties, they exhibit a remarkable stiffness and linearity along the conjugated backbone that allow them to self-assemble into well-defined nanostructures and make them candidates for molecular nanowires in molecular-scale electronic devices. For PPEs, Uwe H. F. Bunz also gave a comprehensive review. A fine-tuning of the performance of molecular-based devices depends on the spatial arrangement of the molecules. The morphology of conjugated polymers is of considerable fundamental interest and importance for potential applications insofar as it crucially influences emissive and optical properties. For example, solid-state quantum efficiencies were found to be related to the degree of long-range order in the conjugated polymers and nonemissive orientations are more significant in the materials having a greater degree of long-range order. In this regard, the determination of the nature and degree of order in a self-assembled monolayer can be a prerequisite for its eventual utilization.

In this context, due to their easier processability, oligomers are commonly investigated as excellent models for their corresponding polydisperse macromolecular analogues. These precise models often provide specific information concerning the solution, electronic, photonic, thermal, and morphological properties of their higher homologues. They also serve as useful models for interpreting structural and conformational properties of a polymer.

Scanning tunneling microscopy (STM) has the potential to provide high-resolution imaging and measurement of surface topography and properties on a molecular and even atomic scale due to the very localized nature of the probing. Here we present an STM study on the assembly...
of soluble end-functionalized oligo(phenylene-ethynylene)s (OPEs) 1 and 2 on highly oriented pyrolytic graphite (HOPG). The morphological characteristics of the assemblies are observed, and the interaction mechanisms and origin for different packing arrangements are also discussed.

Experimental Section

A Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) was employed to investigate end-functionalized OPEs monolayers physisorbed on graphite. OPEs 1 and 2 were synthesized as described elsewhere. A drop (~2 μL) of 1 or 2 solution (less than 1 mM, toluene solvent, HPLC grade, Aldrich) was deposited on a freshly cleaved atomically flat surface of HOPG (quality ZYB). STM tips were mechanically cut Pt/Ir wire (90/10). All the STM images presented here were collected using the constant current mode under ambient conditions and without further image processing. The specific tunneling conditions are given in the figure captions.

Results and Discussion

Molecule 1 can physisorb on a graphite substrate with a significant degree of long-range order. The 120°/60° domain angle indicates the registry of alkyl chains to the graphite lattice, as shown in the larger scale STM image (Figure 1). Remarkably bright wires and dark stripes are alternating over the whole viewed area. The bright wires in the image can be assigned to the conjugated backbones, which are characterized by a larger electronic density, and the darker parts can be ascribed to the alkoxyl groups. The spacing (ΔL) between consecutive parallel backbones in Figure 2A amounts to 2.0 ± 0.1 nm, which corresponds to the length of the all-trans dodecyl chains.

Figure 1. A larger scale STM image of molecule 1 recorded with V = 810 mV and I = 679 pA. The molecular structure of molecule 1 is shown on top of the image.

Molecule 2 also forms a well-ordered monolayer when adsorbed on the surface of HOPG. From the STM image (Figure 3) of the 2D monolayer of molecule 2, we can see that the molecular orientation is also determined by the registry of alkyl chains to the graphite lattice. As in the case of molecule 1, noticeably bright rods and dark stripes are alternating over the relatively large area, but with a little staggering between neighboring molecules, compared with the arrangement of molecule 1 which may be directed by the hydrogen bonding between alkoxyl groups. The high-resolution image is resolved in Figure 4A. The alkoxyl side chains with the same length as that of molecule 1 are nearly perpendicular to the conjugated backbone. The spacing ΔL between adjacent parallel backbones also amounts to 2.0 ± 0.1 nm. A slight interdigitation of the trimethylsilyl endgroups in the 2D pattern can be recognized. According to the periodicity of molecular arrangement based on the STM observation, a 2D unit cell with parameters a = 2.3 ± 0.1 nm, b = 4.9 ± 0.1 nm, and α = 78 ± 2° is outlined on the molecular model in Figure 4B. The image displays that the same interdigitation of alkoxyl chains exists over the full length of the chains in the lamella as in the case of molecule 1. In addition, it could be seen from the molecular model that there exists less free space at the position of trimethylsilyl endgroups than in the case of molecule 1, because of the interdigitation of endgroups.

The arrangement of the alkoxyl chains of 1 and 2 belongs to the interdigitated phases, and the observed result obeys Neher’s rule about solid-state ordering of rigid-rod polymers, which states that hairy rigid rods come in different extended parallel to the plane of the substrate plus the diameter of the phenyl ring. The molecular structure is characterized by a 90° angle between the conjugated skeletons and the alkoxyl side chains, which are imaged with submolecular resolution. Due to little difference in electronic density of alternating phenylene and ethynylene groups, they both appear with high contrast and we cannot distinguish one from the other in STM images. The length of one alkoxyl chain is measured to be 1.5 ± 0.1 nm, which is consistent with the length of a molecular chain in its all-trans conformation. The linear packing mode of the conjugated backbone revealed from the STM observation implies that the carboxyl groups possess a head-to-head configuration in the assembling monolayer, and thus hydrogen bonding between carboxyl groups may form. The hydrogen bonding between neighboring carboxyl groups may contribute to the stability of the 2D adlayer on the surface of HOPG. The molecular model in Figure 2B gives a visual representation of the monolayer structure based on the unit cell parameters a = 2.3 ± 0.1 nm, b = 4.9 ± 0.1 nm, and α = 78 ± 2°. The model shows that the alkoxyl chains of the molecules are interdigitated over the full length of the chains in the monolayer. By interdigitation of the alkoxyl chains, a densely packed arrangement of molecule 1 is realized. These space-filling properties of alkoxyl chains and planar conjugated backbones minimize the free space per unit area within the monolayer on the graphite surface. This results in a maximum of the intermolecular and molecule/graphite interactions, thereby stabilizing the film. The high stiffness of the backbone in some aspect favors the close-packing of the alkyl chains, but the packing also suffers from the stiffness of the backbone; we can see from the molecular model that near the position of carboxyl groups, there is some free volume, and the alkoxyl chains have a greater mobility in this area, thereby lowering the resolution, as depicted by the fuzzy scan image (indicated by the black arrow in Figure 2A).

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structural types depending upon the concentration of solubilizing alkoxyl side chains per repeating unit. If the side-chain concentration is very high, a planar arrangement of the polymeric backbone is not accessible. Instead, the polymer chain assumes a cylindrical shape, and no close contacts between the aromatic backbones occur. Decreasing concentration of the side chains results in a lamellar or doubly lamellar morphology in which the structure of the polymer is almost completely dominated by side-chain packing, particularly if long alkyl or alkoxyl groups are present on the rigid backbone. If the side-chain concentration decreases further, efficient interaction between the solubilizing groups of two different polymer chains occurs and an interdigitated phase will result. In our case, due to the low side-chain concentration, efficient interaction between the alkoxyl groups of two oligomers occurs and thus results in an interdigitated phase. Similar structures have been found by Wegner and later by Ringsdorf.22,23

The self-assembly of these two molecules depends on the intermolecular and molecule/substrate interactions. The linearity of the conjugated backbones consisting of alternating triple bonds and phenylene rings contributes to the generation of extremely ordered lamellae in two dimensions.24 This is the case in the physisorbed 2D monolayers on HOPG where the unsaturated main chains tend to adsorb flat on the basal plane of the conductive substrate, maximizing in this way the overlap of its electronic states with those of the graphite, leading to a maximization of the enthalpic gain.25 This latter characterizes the molecular adsorption at surfaces. According to calculations by Hentschke et al.,26 each -CH2 of the alkyl chain on graphite will provide as much as 70 meV adsorption potential for fully commensurate registry. It is obvious that the total desorption barrier of the molecule is greater. Furthermore, the closely assembled alkyl chains surrounding the aromatic cores will substantially enhance the adsorption stability, as well as the diffusion barrier, in all directions within the basal plane.

Besides the common characteristics for these two molecules, we can see that the arrangement of molecule 2 is a little disordered compared to that of molecule 1 in long-range area. The difference is likely attributed to the changed endgroups. For molecule 1, carboxyl endgroups interact with the neighboring molecules through the formation of hydrogen bonding, thus aligning the conjugated molecular backbone and also providing further stabilization to the molecular arrangement. The molecular backbone of molecule 2 is longer than that of molecule 1; the contour length is 2.5 and 2.1 nm for 2 and 1, respectively. If molecule 2 adopts the same aligning arrangement as that of molecule 1, there will be larger free volume in the monolayer, and so by interdigitation

Figure 2. (A) The high-resolution STM image of molecule 1 recorded with V = 900 mV and I = 587 pA. The distance between adjacent parallel backbones is ΔL = 2.0 ± 0.1 nm. (B) Molecular model of the STM image shown in part A. Unit cell parameters: a = 2.3 ± 0.1 nm, b = 4.9 ± 0.1 nm, and α = 75 ± 2°.

Figure 3. A larger scale STM image of molecule 2 recorded with V = 1.06 V and I = 826 pA. The molecular structure of molecule 2 is shown on top of the image.

of trimethylsilyl endgroups, a more close-packed structure has been obtained.

**Conclusion**

In summary, we characterized the morphologies and structures of two conjugated oligo(phenylene-ethynylene)s self-assembled on HOPG by STM. The different arrangement between the two molecules could be due to the changed endgroups: hydrogen bonding is attributed to the arrangement of molecule 1, while for molecule 2, through interdigititation of trimethylsilyl endgroups, a more closely packed structure is obtained. Because many electronic properties of conjugated polymers depend on the degree of order, this structural concept may have importance in the development of molecular electronic devices.

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