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Dipole-Driven Ferroelectric Assembly of Styrene on Au{111}

Ashleigh E. Baber, Stephen C. Jensen, and E. Charles H. Sykes*

Department of Chemistry, Tufts University, Medford, Massachusetts 02155-5813

Received February 9, 2007; E-mail: charles.sykes@tufts.edu

Ferroelectric materials have an interesting set of properties such as controllable polarization, piezoelectricity, and nonlinear optical and dielectric activity.[1−3] As such, they have been utilized for many applications such as nonvolatile random access memories, sensors, capacitors, microactuators, and optical components.[1−4] In recent years, device miniaturization has led to an interest in the development of smaller ferroelectric materials with even faster switching rates. This has raised questions about the relevant size effects that lead to deviations from bulk properties and ultimately cessation of ferroelectric properties.[2,3] Despite this, functional ferroelectric films with thicknesses in the nanometer range have been successfully synthesized. Perovskite films as thin as 1.2 nm have been produced and shown to be ferroelectric.[5] Also, copolymer films have displayed ferroelectricity in 1 nm thick layers.[6] There is, however, a current lack of understanding of the finite domain size required for ordering to occur, the mechanism of ordering, and the effect of the supporting surface on the ordering.[2,3] Understanding the fundamental nanoscale mechanisms of ferroelectric ordering and transitions is crucial for the continued development of smaller and faster ferroelectric devices.

Herein we report on a study in which the ferroelectric properties of styrene, a simple hydrocarbon molecule with a weak dipole moment supported on a Au{111} surface, are investigated. The excellent resolution of low-temperature scanning tunneling microscopy (STM) allows us to readout the orientation of each individual molecule in an array and to investigate ferroelectric ordering and ferroelectric transitions at the single-molecule level.

It is useful at this point to provide a brief description of common types of dipole ordering exhibited by ferroelectric materials. Parallel alignment of the individual dipoles leads to the formation of a domain with a net electric field and is referred to as ferroelectric ordering. Antiparallel alignment yields a domain with no net polarization and is called antiferroelectric ordering. Randomly arranged dipoles with no long-range order also yield structures with no net field and are referred to as paraelectric structures.

Au{111} has a unique structure commonly referred to as the *herringbone*, or technically, the $23 \times \sqrt{3}$ reconstruction.[7,8] The lower coordination of the Au surface atoms, as compared to that in the bulk, leads to a 4.4% contraction of the top layer with 23 gold atoms stacking along the $[1\bar{1}0]$ direction that would normally contain 22 atoms in the bulk. This results in the formation of domains of surface atoms with both hcp and fcc packing separated by soliton walls with an intermediate packing structure. These three domains all have slightly different electronic properties[9] and also different adsorption strengths.[10,11] Molecules have been shown to bind preferentially to hcp and fcc regions of the surface and typically bind very weakly or not at all to the soliton walls.[10] We use this effect to our advantage in these experiments to corral styrene molecules into small regions and study their local ordering as well as long-range interactions between these regions.

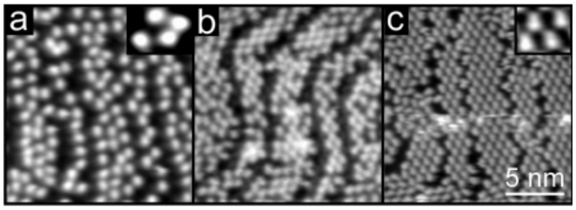

Figure 1. Coverage-dependent STM images of styrene on Au{111} at 7 K. The depressed lines are the soliton walls of the Au herringbone reconstruction. Insets show high-resolution images of individual styrene molecules at the different coverages that appear as "pear-shaped" protrusions. At coverages >0.5 ML, the styrene molecules orient in ferroelectric domains in the hcp and fcc regions of the surface. Styrene coverages are 0.3 ML (a), 0.6 ML (b), and 0.9 ML (c). Image conditions: $V_{\mathrm{Tip}} = 0.5$ V, $I = 2$ pA.

Figure 1 shows STM images of a range of surface coverages of styrene on a Au{111} surface at 7 K. The depressions (dark lines) running through the images are soliton walls that separate the narrower hcp and wider fcc regions of the herringbone reconstruction. Figure 1a shows that, at a coverage of 0.3 monolayers (ML), the styrene molecules preferentially adsorb in the hcp and fcc regions, but not on the soliton walls. The inset of Figure 1 shows a high-resolution image of four individual styrene molecules in the fcc region. Each molecule appears pear-shaped, and the molecules point in random orientations. Figure 1b shows that, upon increasing the coverage to 0.6 ML, a few ordered structures begin to form in the hcp and fcc regions. Figure 1c shows that at 0.9 ML coverage all of the hcp and fcc regions of the surface are covered with an ordered array of styrene molecules and that adsorption on the soliton walls is still not favored. The inset of Figure 1c shows a high-resolution image of four styrene molecules in the fcc region. The molecules again appear pear-shaped, and it is obvious that all four molecules are orientated in the same direction.

Further STM imaging of the 0.9 ML surface coverage revealed that the styrene molecules within fcc and hcp regions align with their long axes parallel to one another and that the majority of the molecules in each region point in the same direction. Analysis of 1117 molecules revealed that 74 ± 4% of the molecules in fcc regions are orientated in the same direction and similarly 68 ± 5% in the hcp regions. These results indicate that dipole-driven ferroelectric ordering of styrene is occurring within each region. A simple Boltzmann distribution calculation reveals that the energy difference between a styrene molecule aligned parallel and antiparallel to its neighbors is 70 ± 15 J/mol in the fcc domains and 50 ± 15 J/mol in the hcp domains. This small interaction energy is consistent with the small dipole moment of styrene (0.1 D) that points toward the vinyl group.[12] The possibility that the ordering could be a consequence of the intrinsic strain field of the Au{111} surface,[7,8,13] and not dipole−dipole interactions, was also considered. However, if this was the case, then one would expect to observe styrene molecules orienting in preferential directions at all surface coverages, as opposed to our experimental finding that molecular ordering only occurs at coverages >0.5 ML.

Figure 2 shows an STM image of 0.9 ML styrene on Au{111} on which the direction of each styrene molecule has been labeled

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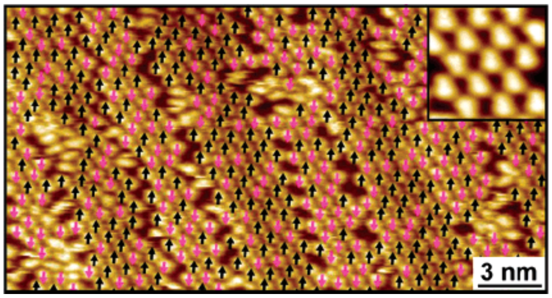

Figure 2. STM image of 0.9 ML of styrene on Au{111} at 7 K. The inset shows the internal structure of the molecules from which their orientations are labeled with black or red arrows, denoting upward or downward pointing molecules, respectively. It is clear that most of the molecules orient in one preferred direction (ferroelectrically) within each hcp and fcc domain, and that the polarization of neighboring domains alternate antiferroelectrically. Image conditions: $V_{\mathrm{Tip}} = 0.5$ V, $I = 1$ pA.

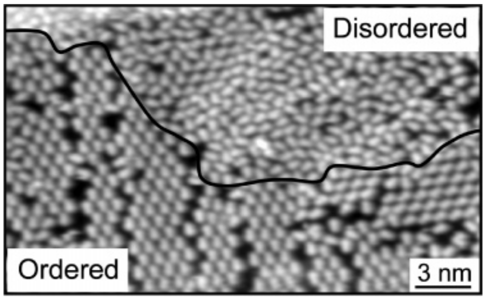

Figure 3. STM image of an area of the surface with two local coverages of styrene on Au{111} at 7 K. The lower part of the figure shows an area of 0.9 ML coverage with local ferroelectric and long-range antiferroelectric ordering. The upper part of the image shows an area where a higher local coverage (~1 ML) has forced the molecules into random orientations. Image conditions: $V_{\mathrm{Tip}} = 0.5$ V, $I = 1$ pA.

with an arrow. Black arrows indicate upward pointing molecules, and red arrows indicate downward pointing molecules. The inset shows an expanded view of an fcc domain in which the orientation of each molecule can be seen. It is obvious from these data that not only do styrene molecules order ferroelectrically within hcp and fcc regions, but long-range antiferroelectric ordering of the domains is also present. An explanation of this phenomenon requires an understanding of the growth mechanism of the domains. As we discussed, low coverages of styrene molecules orient randomly. As the coverage increases, small ferroelectric domains form within the hcp and fcc regions. In the far-field, the net dipoles of these domains would be completely screened by the image charge of the metal surface. However, due to the small distance between the hcp and fcc regions (~1 nm), the styrene molecules in each domain experience asymmetric fields, and as the domains grow, they order with their net dipoles antiparallel to their neighboring domains. This leads to a surface structure with small domains of ferroelectrically ordered molecules. Adjacent domains orient antiparallel and give rise to a long-range antiferroelectric structure.

The effect of further increasing surface coverage is demonstrated in Figure 3, in which two areas of different local coverages are present in the same STM image. The lower part of the image shows a typical area of 0.9 ML coverage with local ferroelectric and long-range antiferroelectric ordering of the domains. The upper part of the image has a higher local coverage close to 1 ML, in which the orientations of all the styrene molecules are randomized in a paraelectric structure. This is an example of a piezoelectric transition in which the polarization of a material is changed by an applied force. The higher local coverage of styrene molecules has crowded the surface, and the styrene molecules can no longer adopt their energetically preferred orientations with respect to one another. This is analogous to the transition of flat-lying to tilted benzene in densely packed monolayers caused by short-range repulsive interactions.[14] In the present case, crowding has led to a disordered array of molecules with no net dipole.

We also investigated the effect of the STM tip on the ordering of styrene by recording STM “movies”, which consist of a series of images of the same area taken ~3 min apart (see Supporting Information). These data revealed that the tip has a randomizing effect on the ferroelectric structures. Scanning an area, such as that shown in Figure 3, induces small motions of the individual molecules that subsequently “refreeze” in a different, random orientation. These results demonstrate that the ferroelectric ordering is an intrinsic property of the styrene/Au{111} system, not an effect of the tip.

To summarize, our findings indicate that complex ferroelectric ordering can occur in a simple system of weakly polar molecules on a metal surface and that STM can be used to investigate molecular-scale ordering processes and transitions between different structures. This type of system represents a robust setup with which to study dipole−dipole interactions and ferroelectric assembly. By adding functional groups to styrene, we hope to alter its dipole moment and thus tune the dipole−dipole interaction energy. This will allow investigation of the effect of dipole strength on the aforementioned phenomena. We also plan on investigating the effect of external electric fields parallel to the surface in an effort to switch the polarization of the ferroelectric domains externally and to study the dynamics of the switching process at the molecular level.

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Supporting Information Available: STM movie showing the effect of the tip in randomizing an ordered ferroelectric structure and sample preparation methods are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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