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Anomalous Periodic Structure of Polypropylene Chains Observed with Scanning Tunneling Microscopy

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Using low-current scanning tunneling microscopy (STM), isolated strands of the insulating polymer isotactic polypropylene (*i*PP) supported on highly oriented pyrolytic graphite (HOPG) have been studied. STM imaging can clearly identify a 2.0 nm periodicity along the strand, which indicates an aggregation of polymer chains, known to exist in the α and β crystalline forms for *i*PP, which both exhibit a lattice constant in one dimension near 2.0 nm. However, a structural conformation with repeat units of 4.0 nm is more commonly found. Tunneling spectroscopy on this conformation finds variations in the electronic structure across the repeat units which can be associated with specific structural features on the chain. We suggest that this conformation derives from substrate–polymer interactions and is a modification of the 3–1 helix.

Generally, the bulk optical and electronic characteristics of a polymeric material are attributed to some ensemble average of the electronic structure of individual molecular strands of the polymer, modified by the effects of molecular conformation, doping, steric order, and so forth. Thus, a detailed understanding of the electronic structure of individual molecules, independent of bulk measurements, is a necessary step in any predictive polymer physics. Further, an understanding of specific polymer–surface interface interactions is necessary for many applications. However, by their very nature, studies of individual or isolated clusters of several molecules are exceedingly difficult.

It has been thought for some time that scanning tunneling microscopy (STM) and spectroscopy (STS) could provide a unique insight into such systems because of their ability to both image at the atomic scale and collect spatially resolved electronic information.¹ Due to difficulties of strand isolation and perturbative effects in the imaging process, most scanning probe studies have been limited to large-scale crystalline states, gross self-assembly, or disordered thin films. Moreover, early attempts at STM imaging of individual macromolecular species were fraught with imaging artifacts.² In this work, strands of polypropylene have been isolated and studied using low-current STM/STS techniques. This has allowed electronic characterization of polymer–substrate interactions, chain electronics, and long range ordering of the molecule.

Dilute polymer–solvent mixtures were prepared by desolving a small amount of high-molecular-weight isotactic polypropylene (*i*PP) in tetrahydrofuran (THF). We note that, generally, *i*PP is quite resistant to THF. However, by roughening the surface of extruded *i*PP ($M_w = 202\,000$) and “washing” the surface with THF, it was found that the low-molecular-weight species from the

surface would wash into the solution. This solution was then deposited on freshly cleaved, highly oriented pyrolytic graphite (HOPG). The sample was put into a turbopumped prechamber where the pressure was lowered to $>10^{-6}$ Torr to allow the THF to be pumped away. After 1 h in the prechamber, the sample was introduced into ultrahigh vacuum (UHV, $<10^{-10}$ Torr), where it was imaged using a custom-designed (RHK Technology) scanning tunneling microscope. The microscope is equipped with a heating stage to allow gentle heating of the substrate ($<200\text{ }^\circ\text{C}$) for removal of remaining solvent. All imaging and spectroscopy experiments were carried out at room temperature. Stable imaging was established in the voltage range 100–500 mV and 10–20 pA. Atomic resolution of the support substrate was used as a quick test of the quality of the tunneling tips before imaging the polymers. All imaging was performed with mechanically formed Pt–Ir tips (Digital Instruments).

Naturally, the density of molecules within the deposition solution was low; therefore, large terraces of the HOPG were observed with strands of polymer found randomly scattered across the substrate, as shown in Figure 1a. Most of the deposited polymer strands observed were tangled and twisted with an occasional straight strand observed (Figure 1a, right). These “straight” molecules were quite long and appear to have a “string of pearls” structure with a repeat segment along the axis. These can be found following the contours of the HOPG surface and draped across steps of the substrate. The surprising fact that they lie flat on the surface of HOPG suggests that there exists some interaction between the substrate and the polymer molecule. We note that on Au substrates these long flat chains are not usually observed as expected but rather aggregated globules or twisted strands are seen. Because of the numerous reports of artifacts caused by solvent–substrate interactions and HOPG cleaving, extensive studies were performed to determine the effects of the solvent on imaging.³ The strands shown in Figure 1 were *only* observed when *i*PP was present. Such structures were not observed with freshly cleaved HOPG or with THF-washed HOPG. Further, the surface heights on either side of the strands were compared to ensure that these were not associated with HOPG steps. As

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(1) See, for example, Tsukruk, V. V. *Scanning Probe Microscopy of Polymer Surfaces*. In *Rubber Chemistry and Technology*; Vol. 70, pp 430–467, for an excellent review of scanning probe studies in soft materials.

(2) Chang, H.; Bard, A. *Langmuir* **1991**, 7, 1143–1153. This is an excellent general reference to the artifacts and pitfalls that can come with the use of HOPG substrates in STM studies of macromolecules. There are, however, some striking differences between these artifacts and the structures reported here, as discussed in the text.

(3) Chang, H.; Bard, A. *Langmuir* **1991**, 7, 1143–1153.

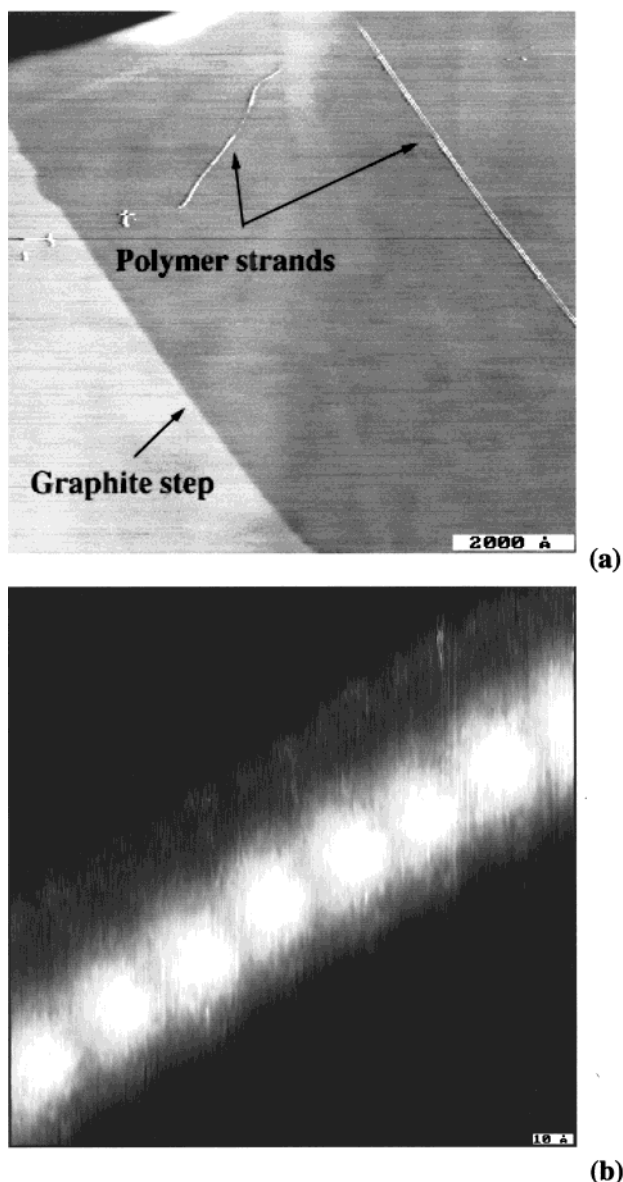


Figure 1. (a) STM micrograph of isolated polymer strands on HOPG. (b) Close-up view of a typical isolated strand.

discussed later in the paper, tunneling spectroscopy further suggests that these are not graphitic ribbons resulting from the cleaving process. From these observations, we conclude that the strands observed are macromolecules of *i*PP.

Figure 1b shows an enlarged STM image of one of the chains on HOPG. The observed repeat segments are approximately 2.0 nm in length. The strand is symmetric about the axis with a width of 2.0 nm and height of around 0.5 nm at 100 mV. The height was found to be somewhat voltage dependent. The width in this case may be convoluted with the tip of the scanning tunneling microscope as the image is collected and therefore may not represent the actual width of the polymer chains. The repeating segments shown correspond well to the known 3/1 helical unit cell dimensions of several α -PP chains crystallized in the α or β polymorph. It is important to note that the extreme length of the observed strands indicates that they cannot be individual polymer strands,

since their expected contour lengths are significantly shorter. However, recent reports of self-organized PPV (poly(phenylene vinylene)) have suggested that "artificial" alignment of macromolecules can occur at the edge of evaporating solvent bubbles.⁴

Isotactic polypropylene, $(-\text{CH}_2\text{CH}(\text{CH}_3)-)_n$, is known to crystallize in at least three different polymorphs, each of which exists as a 3/1 helix with three "mers" per 360 pitch.⁵ The most common form, the α form, consists of a monoclinic unit cell containing four chains with lattice constants $a = 0.665$ nm, $b = 2.096$ nm, and $c = 0.650$ nm (Figure 2).⁶ The hexagonal β form unit cell contains nine chains with similar constants, $a = 1.908$ nm and $c = 0.649$ nm. A structural model is shown in Figure 2.

While the repeating dimension of Figure 1b is observed in many images, the most commonly found structure, shown in Figure 3, exhibits a repeat unit of approximately 4.0 nm (2.0 nm in width). This morphology seems to be oriented completely to one side of the chain (left and right orientations have been observed). The height of the object in these images is around 0.2 nm at 100 mV, much smaller than the sample–tip separation in typical STM imaging. Thus, it is expected that tip convolution in the image is minimal. The occurrence of this dimension is surprising and may represent a new substrate-induced morphology or unit cell distortion not previously observed. We suggest that such organization of strand morphology may originate from selective orientation which the *i*PP strand can adopt commensurately on the HOPG lattice.

To further probe the origins of the anomalous strand morphology, we used tunneling spectroscopy to characterize the electronic structure of the strand. Spatially resolved tunneling spectroscopy was performed with a fixed tunneling gap on a preselected grid during image acquisition. This ensures that drift during each measurement was minimal, since each spectrum can be associated with a specific pixel of the image. Tunneling $I-V$ curves were converted to a differential conductivity through numerical differentiation of the tunneling spectra.⁷ In Figure 3, the letters A and B mark the positions of tunneling spectra taken on this strand of the polymer. The graph below the image in Figure 3 compares differential conductivity, as indicated with arrows. The features within the spectra are quite typical of the various positions within the substructure and repeatable down the strand. Subtle variations of the spectra are found locally (within 1.0 nm or so) around each marked position. We note that graphitic structures should have typical graphitic tunneling spectroscopic signatures or at least features similar to those of graphite step edges.⁸ However, the general features of these spectra fall into the two categories shown in Figure 3, quite different from those of tunneling spectroscopy on HOPG.

The simplest interpretation of the differential conductivity curves is in terms of polymer–substrate interactions according to the diagram of Figure 4.⁹ In this model, the molecular states of the polymer and molecular states formed by polymer–substrate interactions provide enhanced tunneling at specific energies. This can be illustrated by considering a positively biased substrate

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(5) Brueckner, S.; Meille, S. In *Polypropylene: An A–Z Reference*; Karger-Kocsis, J., Ed.; Kluwer Academic Publishing: Dordrecht, 1999; pp 606–614.

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(8) Fuchs, H. *Fesenius' Z. Anal. Chem.* **1987**, *329*, 113.

(9) This interpretation of tunneling spectroscopy is discussed in detail in the above reference.

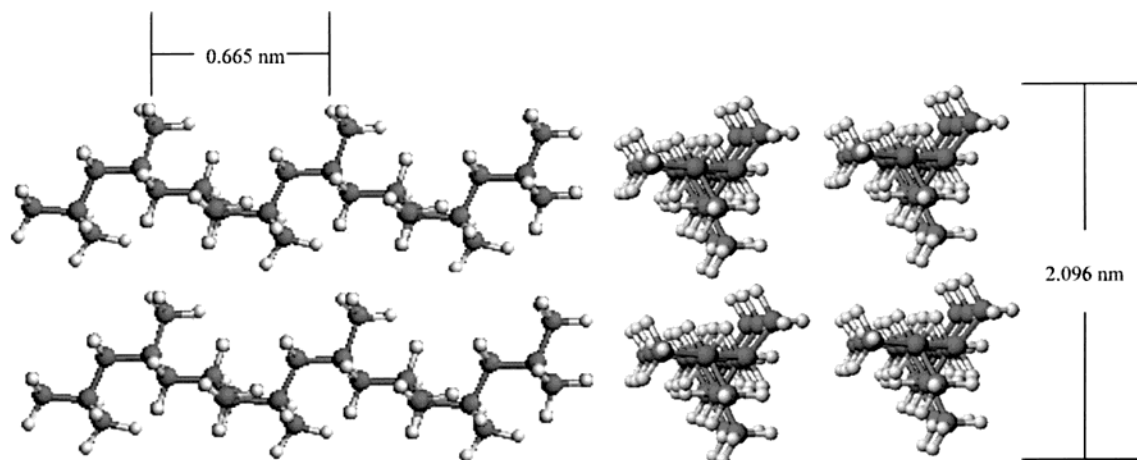


Figure 2. Side (a) and end (b) α form unit cell views of an isotactic polypropylene 3/1 helical arrangement.

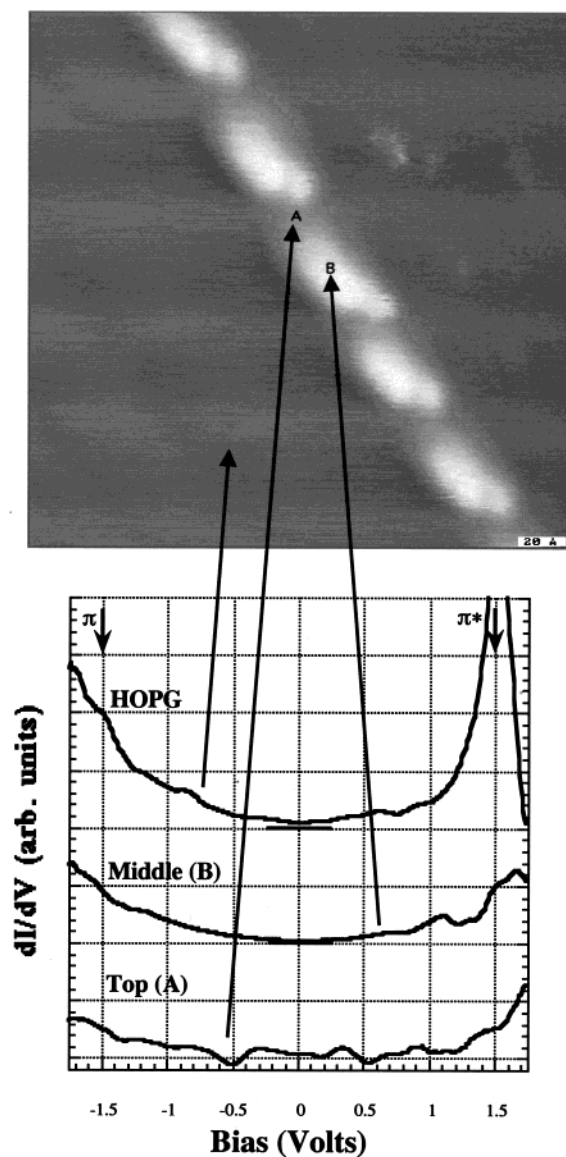


Figure 3. (top) Most commonly found configuration of *i*PP on HOPG. Points A and B mark where spectra have been collected. (bottom) Comparison of HOPG and polymer tunneling spectra. The polymer spectra were taken as indicated by the arrows. These are presented as differential conductivity dI/dV .

relative to the STM tip, as shown in Figure 4. Electrons from the filled tip states will flow through the polymer

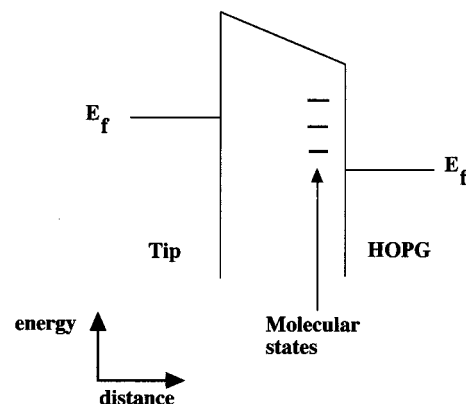


Figure 4. Energy diagram of the tunneling gap between the substrate and the tip. States within the polymer allow enhanced electron transfer between the substrate and the tip when the Fermi level is aligned with an empty state in the gap.

and into the substrate if there are no unfilled states available within the polymer. Available states are those with energies equal to or below the Fermi level of the tip. However, when a state is available and the electrons can tunnel into the polymer, the distance that the electron must tunnel is less and therefore a substantial increase in the tunneling current is observed. In Figure 4 this means that electrons from the tip will tunnel into the tunneling gap states shown of equal or lower energy and then into the HOPG. As the bias is changed relative to the substrate, the position of the tip Fermi level changes relative to the gap states, resulting in the features observed in the tunneling spectra. In this interpretation we expect, at higher tunneling voltages, the differential conductivity should be dominated by contributions which arise from ballistic electron transport between HOPG and the STM tip. Notice, in both of the tunneling spectra shown, common features are observed around ± 1.5 eV and are most likely derived from the $\pi-\pi^*$ states of the HOPG.¹⁰

Spectra taken at B, on top of the polymer "ball" or repeat unit, exhibit several features not seen in the graphitic spectra. Specifically, resonances in the tunneling current occur around ± 1.25 eV (along with the ± 1.5 eV features). These states must be associated with the molecular states of the *i*PP or with interactions between the substrate and the polymer, which allow for resonant tunneling, as described above. Spectra acquired at position A, however,

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show the same features as those found at B and an additional state at 0.25 eV. Spectra collected at similar positions on other repeat units along the chain show very similar features. Thus, this position is related to a very different set of electronic states in the polymer strand from those found further into the repeat unit. These states are extremely small in energy compared to energies typically associated with strand electronics. Interestingly for binding energies, we expect a little more than approximately 0.15 eV/mer on the basis of simple dispersion interactions. Thus, a possible origin of this feature in the tunneling spectra is that this position along the strand is related to binding the strand to the substrate.

It is interesting to note the total energy to remove a section of the polymer from the substrate must be extraordinarily high. We attempted to manipulate the polymer strand by positioning the tip over the center of a repeat unit and then pulsing the voltage. In carbon nanotubes this has been shown to result in cutting the molecule or manipulating it.¹¹ Graphitic structures have been reported to be weakly bound to the surface of HOPG, and certainly, one would expect that they would be as easily manipulated as carbon nanotubes.¹² However, in the case of the polymer, severe distortion of the underlying

HOPG surface resulted. No removal of the polymer units could be achieved at any value of the pulse magnitude, and pulse rates up to 10 μ s were used. Since it is known that the HOPG surface is disturbed by voltage pulses above approximately 8.0 V, the total energy of the polymer binding to this surface presumably lies above 8.0 eV. This would necessarily include intrastrand strain as well as the polymer–interface energy, since both the C–C bonds of the polymer and the polymer–HOPG bonding would have to be broken to remove any element of the chain.

In conclusion, tunneling spectroscopy results and manipulation results strongly suggest that we have demonstrated imaging and spatially resolved electronic structure in isolated polymeric strands of *i*PP. We have measured dimensions consistent with either of two common crystalline morphologies when the polymer is supported on HOPG. However, the most common feature observed represents an anomalous form of *i*PP, and specific electronic signatures have been identified which may be related to previously undetected distortion of the morphology and/or interactions with the substrate.

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