

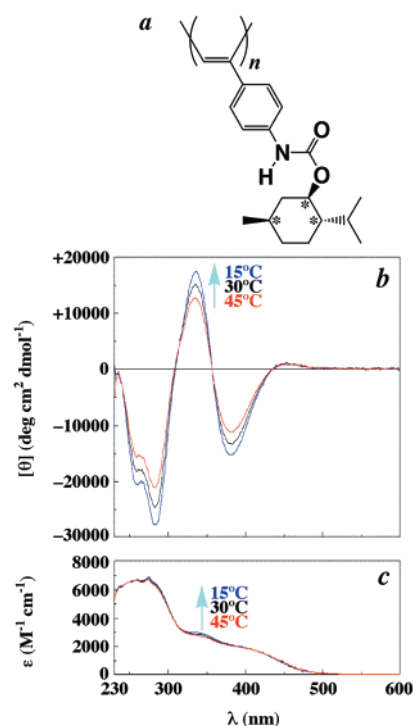
## Direct Measurement of the Chiral Quaternary Structure in a $\pi$ -Conjugated Polymer at Room Temperature

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$\pi$ -Conjugated polymers have been developed as advanced materials for photonic or electronic applications. If the  $\pi$ -conjugated polymer chain can be controlled in the higher order structure, novel functions at the molecular level will become available due to the unique  $\pi$ -electron system. Many studies confirming the fact that a  $\pi$ -conjugated polymer has a helical structure have already been completed.<sup>1–6</sup> Most of these studies have provided us with data on molecular aggregates or data on the average of many molecules. Although we now understand that the main chain of the polymer takes the form of a helix, does one chain have both right- and left-handed helices? What is the ratio of the right-handed helices to the left-handed ones? What about the regions where the helix is reversed, and how does it dynamically change? The answers already provided to all these fundamental questions have been based only on conjecture. Therefore, it is necessary to establish a technique that can determine the structure at the single-molecule level in order to achieve the above-mentioned objective. Here we show that a scanning tunneling microscope (STM)<sup>7,8</sup> allows us to see the  $\pi$ -electron orbital of a chiral quaternary structure, where it was directly observed and its size was even measured with high resolution.

We synthesized a  $\pi$ -conjugated polymer, an optically active polyphenylacetylene bearing menthoxy-carbonylamino groups [(–)-Poly(MtOCAPA), Figure 1a]. It was found that (–)-poly(MtOCAPA) has a high molecular weight, that is, its molecular weight is of an order of  $1 \times 10^6$  Da, that the *cis* content of the polymer is 90 mol %, and the main chain has a *cis*–*transoidal* high stereo-regularity.<sup>6,9</sup> The primary structure of this polymer was examined using a nuclear magnetic resonance spectrometer (<sup>1</sup>H NMR). As is apparent from the spectrum of this polymer observed using a circular dichroism spectrometer [CD, Figure 1b] and an ultraviolet–visible absorption spectrometer [UV–vis, Figure 1c], chirality was detected not only in the side group but



**Figure 1.** (a) Chemical structure of (–)-poly(MtOCAPA). (b) Circular dichroism and (c) UV–vis spectra of (–)-poly(MtOCAPA) in tetrahydrofuran solution at 15 (blue line), 30 (black line), and 45 °C (red line), respectively.

also in the main chain, which had expanded  $\pi$ -conjugation. It was found from these observations that the optically active menthyl in the side group induced chirality in the  $\pi$ -conjugated system of the main chain. This CD spectrum shows that the main chain of (–)-poly(MtOCAPA) has a secondary structure having an excess of the one-sense helix structure, which is stabilized by the bulky substituent. Because the intensity of this CD signal increased in reverse proportion to the temperature of the polymer solution, it is presumed that this main chain has a flexible helix structure.

Scanning probe microscope imaging was used to directly observe the structure of a single polymer chain. We initially tried to use an atomic force microscope (AFM) image of a polymer placed on a mica substrate under ambient conditions. Each single polymer molecule that formed a chain could be distinguished, and intertwined polymer chains could also be observed. An overall image of the polymer molecules could be directly observed using the AFM, but the  $\pi$ -conjugated system in the main chain could not be observed by AFM since this polymer had a bulky menthyl group and the main chain was hidden behind the side groups on the front. To observe the main chain without being obstructed by the bulky menthyl group, STM was used, since this allows us to see molecular orbitals having the low-energy gap of the HOMO–LUMO on which a tunneling current flows.<sup>10–12</sup> Figure 2a shows a typical low magnification image of the low current STM of (–)-poly(MtOCAPA) placed on a highly oriented pyrolytic graphite (HOPG) substrate under ambient conditions.<sup>13</sup> During our observation, the sample bias voltage and the tunneling current were maintained at +20.0 mV and 30.5 pA, respectively, and an STM probe using a Pt/Ir tip was operated at a 3.05 Hz scanning rate.<sup>14</sup> In Figure 2a, it can be observed that the two  $\pi$ -conjugated polymer chains are intertwined to form a right-

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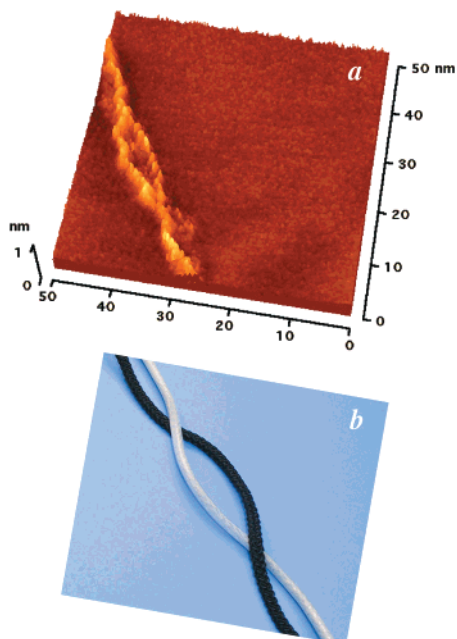
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**Figure 2.** (a) Low current STM height image of intertwined two (-)-poly(MtOCAPA) chains on HOPG at room temperature ( $V_s = +20.0$  mV and  $I_t = 30.5$  pA). (b) String model of the intertwining polymer chains.

handed double helix structure, as in the case of the model shown in Figure 2b, and the right-handed helix structure can also be observed. The analytical result is shown in Figures 3 and 4. The width of one right-handed helix chain was 0.9 nm [Figure 3a]. This width of 0.9 nm matched the width of the main chain backbone of polyphenylacetylene in the  $\pi$ -electronic system of the cis-transoidal<sup>6</sup> main chain structure 20-mer which was obtained by optimization using the molecular mechanics calculation [Figure 3b]. This corroborated the observations that the STM image displays the  $\pi$ -electron orbital of the main chain of a polymer and that the helix of the secondary structure is a super-helix tertiary structure [Figure 4a]. As a result of the analyses [Figure 4b], the pitch of this super-helix is 2 nm.<sup>15</sup> It is shown to be a super-helix with a close-packed structure, because the pitch agrees with the width of the model in Figure 3b. In addition, it was shown in Figure 4b that the super-helix width is 2 nm, that the helix sense is right-handed, and that this precisely controlled super-helix tertiary structure extends over a range of more than 10 nm. When the polymer structure in Figure 2a was turned over, it could be observed that the two  $\pi$ -conjugated polymer chains are intertwined to form a right-handed double helix structure, as in the case of the model shown in Figure 2b. This substantiated the presence of a quaternary structure, which is much higher in the chiral hierarchical structure. It was also found that the quaternary structure is so soft that its form can be changed during probe scanning. That is, we proved that the main chain of the (-)-poly(MtOCAPA) was flexible despite the  $\pi$ -conjugated system.

In the present study, it was shown that it was possible to determine the structure of a single polymer chain using STM. We observed that it has a higher-order structure, and the fine

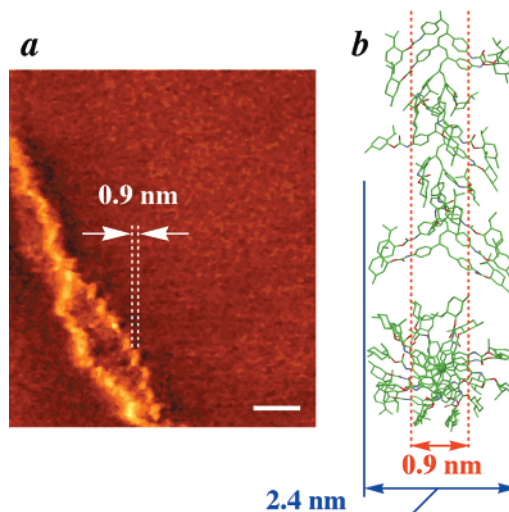
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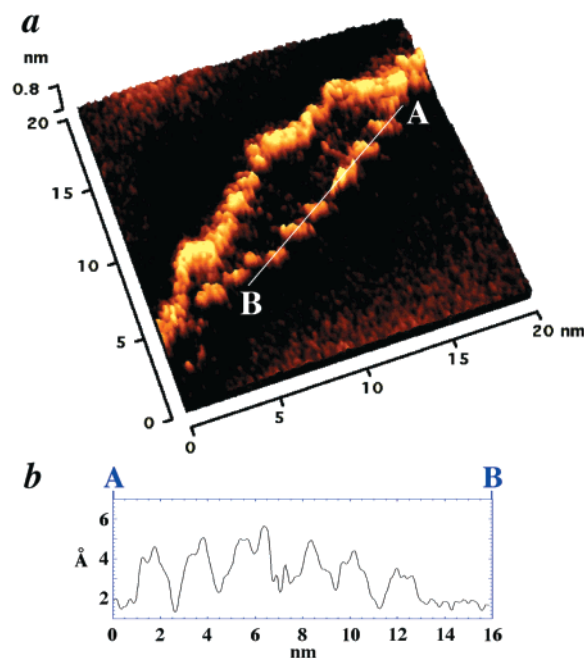
(13) Although the single polymer chains were also observed in part, the double helix structure shown in Figure 2 were observed mostly in many places.

(14) Molecules on HOPG substrate were easy to move by the effect of probe scanning. In this study, STM parameters were chosen as to obtain the mostly stable STM imaging condition. Moving of the object under the effect of the STM probing shows that it is not the well-known artifact image observed on HOPG surface. Because the artifacts are the modulated structure of the HOPG surface, they never move even if they are scanned repeatedly.

(15) These values showed high-reproducibility in the stably obtained STM images of the polymer chains.



**Figure 3.** (a) STM height image of (-)-poly(MtOCAPA), Bar: 5.0 nm,  $V_s = +20.0$  mV and  $I_t = 30.5$  pA. (b) Molecular mechanics calculated optimized model of 20-mer of cis-transoidal (-)-poly(MtOCAPA). Side-view (upper). Top-view (bottom).



**Figure 4.** (a) A close-up view of STM height image of (-)-poly(MtOCAPA) ( $V_s = +20.0$  mV and  $I_t = 30.5$  pA), (b) Analytical result of super-helix pitch in the cross section of the STM image.

structure of the single  $\pi$ -conjugated polymer chains was confirmed for the first time. However, in our current method, the molecule itself is changed by the STM measurement, and the helical structure becomes loosened. Therefore, to determine the electronic structures and the ratio of the two different helical-senses by the effect of the chiral pendant groups, we need to take an approach where we stabilize the STM measurements by fixing the molecules on the substrate, which is currently in progress. Finally, this unique higher-order structure of the  $\pi$ -electronic system is expected to provide novel photonic or electronic functions that will lead us toward molecular devices.

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**Supporting Information Available:** Experimental details of GPC, CD, STM, molecular mechanics (MM) calculation, and synthesis of the polymer (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.