Single-Molecule Imaging of a Micro-Brownian Motion of a Chiral Helical π-Conjugated Polymer as a Molecular Spring Driven by Thermal Fluctuations

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We observed a micro-Brownian motion of single molecules of a chiral helical π-conjugated polymer as a molecular spring on mica substrate under *n*-octylbenzene at room temperature using high-speed (rapid scan) AFM. The average velocity at the chain end of the polymer was 67 nm s^{-1} at the observation point. The analytical result shows that the mean square displacement in a single polymer chain is proportional to the time and, hence, complies with Einstein's law of Brownian motion. The diffusion constant (*D*) is measured to be 8.2×10^{-15} $m^2 s^{-1}$ at the solid/liquid interface.

Polymers are ubiquitous materials that display many excellent properties, and they have become indispensable in maintaining and developing our current way of life. In particular, π-conjugated polymers are recognised as being part of the next generation of functional polymers for photonic and electronic applications.[1–3] Nevertheless, it is difficult to discuss the correlation between their structures and properties at a molecular level, since these are diverse, dynamic, and, in general, very complex. If the structure and properties of a polymer could be directly observed, with minimal inferences or hypotheses, the relationship between polymer structures and functions could be clarified. Consequently, molecular devices of a polymer might be created based on new design concepts and new working principles, may be the soft nanomachines. Recently, we have achieved the direct observation of single molecules in a π-conjugated polymer at room temperature using a scanning tunneling microscope (STM)[4] and an atomic force microscope (AFM)[5] to measure the chiral helical structure. In addition, we succeeded in using a total internal reflection fluorescence microscope (TIRFM) to image single-molecule dynamic fluorescence[6,7] and a combination of an AFM and an objective-type TIRFM to simultaneous image the molecular structure and a novel fluorescent phenomenon.[8]

In this study, we observed micro-Brownian motion of a single molecule of a chiral helical π-conjugated polymer (Figure 1),[4,5,9] which has a structure of a molecular machine, namely a molecular spring, using a high-speed (rapid-scan) AFM at a solid/liquid interface. A high-speed AFM offers outstanding performance for observing the movement of single molecules in aqueous solution at room temperature.[10–12] However, we modified the specifications of this high-speed AFM in order to use even in the organic solvent, allowing successful imaging of the movement of a single molecule of a chiral helical π-conjugated polymer at room temperature. In addition, we measured the flexibility of a single polymer chain as a fundamental property of a molecular spring.

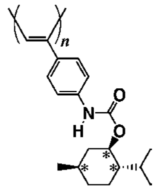

Figure 1. Chemical structure of (−)-poly(MtOCAPA). The appearance is a yellow solid. $M_w = 1.05 \times 10^6$, $M_w/M_n = 3.30$ (GPC), *cis* % >90 (^{1}H NMR), $[\alpha]_D^{25} = -499°$ (*c* 0.0183, $CHCl_3$), (see Supporting Information[14]).

We cast tetrahydrofuran (THF, 50 µL × 3) on freshly cleaved mica for removing water and cast *n*-octylbenzene (5 µL) immediately. This allowed us to cast a dilute tetrahydrofuran (THF) solution (10^{-6} mol L^{-1}, 5 µL) of a chiral helical π-conjugated substituted phenylacetylene polymer [(−)-poly(MtOCAPA)] (Figure 1) on a mica substrate for single-molecule imaging. Afterward, we conducted high-speed AFM observations in *n*-octylbenzene at room temperature[13] and measured the flexible motion of a string-like substance 2 nm in height and 200 nm long (Figures 2a and 2b). The average velocity at the chain end of the polymer was 67 nm s^{-1} at the observation point. Because the size of the string-type substance corresponds to the value of the molecular model calculation (Figure 2c), we concluded that the observed substance is a single molecule of the chiral helical π-conjugated polymer. In particular, the zigzag structure is confirmed in the 48th frame in Figure 2a with a structural period, measured to be 24.0 ± 4.0 nm, based on the coarse and dense (compressional) helical structure of a polymer chain.[5] When several molecules are simultaneously observed, their motion is not synchronous but rather random (Figure 2d). We directly observed the reversible motion of elongation, curvatures, and folding of a single polymer chain. It was found that single molecules of (−)-poly(MtOCAPA) have suitable flexibility of their π-conjugated main chain to serve as a molecular spring. In addition, this polymer chain was difficult to form a molecular globule, because it has π-conjugated main chain. Furthermore, most of the polymer chains were not detached from the substrate surface which would otherwise lead to diffusion in the solvent but rather were rolled onto the substrate surface (Figures 2a and 2d). This dynamic behavior can be explained by the energy state of a single polymer chain adsorbed to a mica surface in *n*-octylbenzene at room temperature.

We hypothesize that this behavior is due to thermal motion, which reflects a compensation of energy of solvation and adsorption onto the substrate surface. To validate this conclusion, we conducted a detailed motional analysis. We measured the dimensional displacements of a single polymer chain in the *X*-direction and fitted it to a Gaussian curve (Figure 3a). The standard devi-

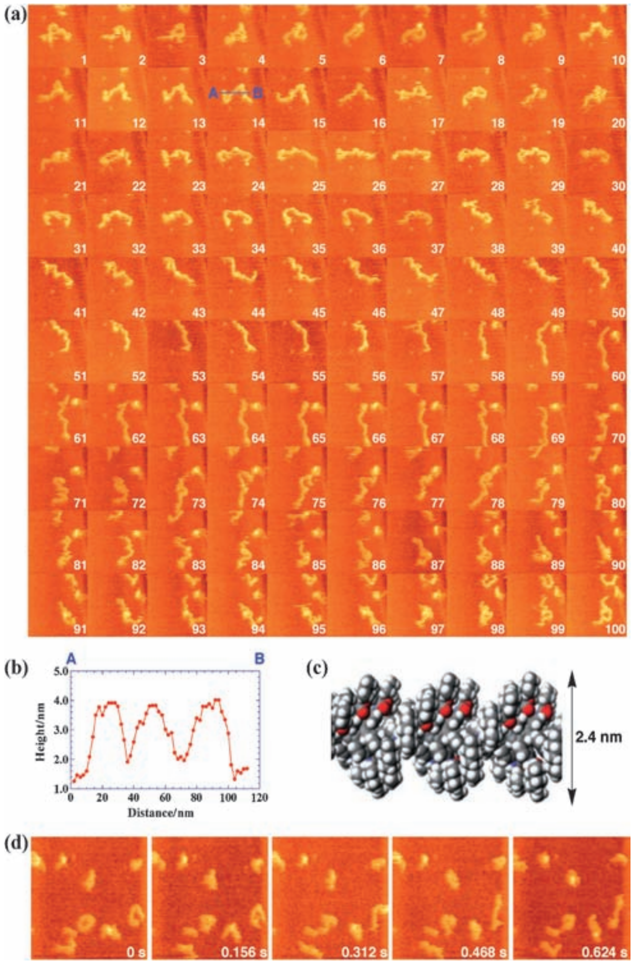

Figure 2. High-speed AFM images in continuous scanning mode of a chiral helical π-conjugated polymer [(−)-poly(MtOCAPA)] on mica in *n*-octylbenzene at room temperature. (a) The observation area is 200 × 200 nm^2. The frame rate is 252 ms per frame. Pixel: 100 × 100. (b) Analytical result of a line profile in an AFM image of the 14th frame in (a). (c) An optimized molecular model of a polymer. (d) The area is 300 × 300 nm^2. The frame rate is 156 ms per frame. Pixel: 100 × 100. Dynamic images of a single molecule of (−)-poly(MtOCAPA) in a Supporting Information.[14]

ation values were the time-average displacements at each observation time. The result shows that the mean-square displacement in a single polymer chain is proportional to time and, hence, complies with Einstein's law of Brownian motion (Figure 3b). The diffusion constant (D) is measured to be 8.2×10^{-15} m^2 s^{-1}. Though the diffusion constant is low, this is the effect of the adsorption of a molecule on the substrate. This result demonstrates that the motion of a single polymer chain is micro-Brownian motion at a mica/*n*-octylbenzene interface.

This polymer chain has a flexible π-conjugated chiral helix, which serves as a structure of a molecular spring. A study of high-speed AFM imaging of dynamical structural change of the coarse and dense (compressional) helix[5] inside the single chain is in progress. We anticipate that our studies will form the basis for creating innovative molecular devices such as molecular motors or molecular electronics/photonics materials that utilize thermal stochastic energy as one of the driving sources.

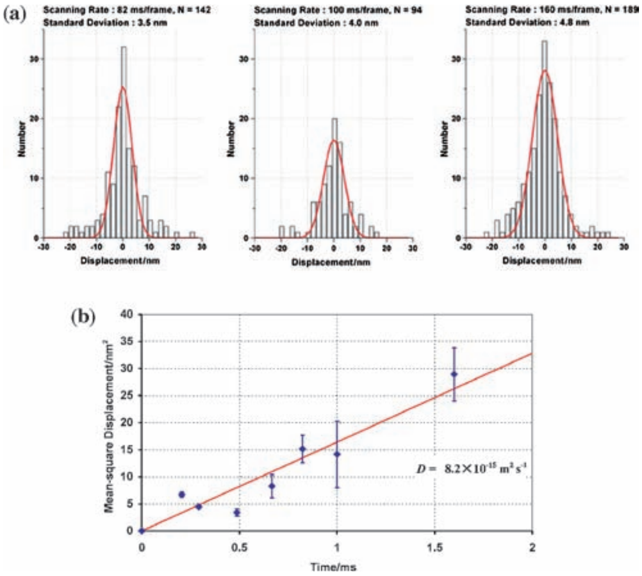

Figure 3. (a) Typical analytical results of the dimensional displacement in a single polymer chain of (−)-poly(MtOCAPA) in the X-direction at scanning rates of 82, 100, and 160 ms per frame in high-speed AFM imaging at a solid/liquid interface. Lines are the best fits of the data to a Gaussian curve; the standard deviations are 3.5, 4.0, and 4.8 nm, respectively. (b) Mean-square displacement as a function of time of tip-scanning cycle in the direction of the X axis. The mean-square displacements were obtained from the standard deviation in (a). The plots were fitted to the diffusion equation, $\langle x^2 \rangle = 2Dt$.

This work was supported partly by Gtant-in-Aid for Young Scientists (A) from MEXT, Japan (No. 1568007) (to K.S.), and also by SENTAN, JST (to K.S. and T.A.).

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13 Amplitude of cantilever oscillation ($A_{\text{p-p}}$) is 5 nm (free), and a set point is 0.9. Although THF is a good solvent for this polymer, *n*-octylbenzene has low miscibility.
14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) June 6, 2009; doi:10.1246/cl.2009.690