

Single Molecular Imaging of a micro-Brownian Motion and a Bond Scission of a Supramolecular Chiral π -Conjugated Polymer as a Molecular Bearing Driven by Thermal Fluctuations

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The micro-Brownian motion of a single polymer chain was directly measured by high-speed (rapid-scan) AFM on a mica substrate under an aqueous solution at room temperature. The diffusion constant was $1.3 \times 10^{-14} \text{ m}^2/\text{s}$, which is a basic property of a molecular bearing at a solid-liquid interface. The molecule was a micrometer-long supramolecular chain in which π -conjugated polyrotaxane was coupled by a π - π interaction. Bond scission of this supramolecular chain was directly observed, and the dynamic folding behavior of a single polymer chain was also imaged.

Polymers are very useful materials that display many excellent properties and have become indispensable in maintaining and developing our current way of life. Especially, π -conjugated polymers are recognized as 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 the molecular level because polymers are diverse, dynamic and can be very complex. If the structure and properties of a polymer could be directly observed, then with minimal inferences or hypotheses, the relationship between polymer structures and functions could be clarified. Consequently, molecular devices of a polymer might be created on the basis of new design concepts and new working principles, which may lead to soft nanomachines. Recently, we have directly observed 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 a chiral helical structure and a total internal reflection fluorescence microscope (TIRFM) to image single molecular dynamic fluorescence.^{6,7}

π -Conjugated polymers may be flexible because they are organic molecules. We have used high-speed (rapid-scan) AFM⁸ to observe their flexibility and motion driven by thermal fluctuations. The observed polymer is the same as those in previous research where the molecular structure and functions were simultaneously observed using a combination of an AFM and an objective-type TIRFM.⁹ Figures 1a and 1b show the chemical structure and optimized molecular model, respectively. This π -conjugated polymer has a molecular bearing structure, which is a kind of soft nanomachines. Figure 1c shows the flexible motion of a single chain of the supramolecular π -conjugated polymer on mica under an aqueous solution at room temperature. Because its height, which is ca. 1.5 nm, corresponds to the height of α -cyclodextrin, the polymer chain is clearly a single molecule as shown in Figure 1d. Various studies have been trying to apply rigid rod-like π -conjugated polymers to a molecular wire for molecular electronics devices, but it is troublesome if the wire

moves. While conducting an experiment, we envisioned a new design concept for a molecular device that has the flexibility of a single molecule. We collected images for a total of 14.08 s and irradiated with an ultraviolet (UV) pulsed laser during the last 5.6 s as shown in Figure 1c. During the pulsed laser irradiation, the cantilever was bent owing to the light pressure of the laser beam. Thus, the probe pressed the observation surface for an instant. The scanning line, which looks like a scratch, showed this state from 8.48 s to 14.08 s. Hence, we observed the probe pressing onto a single polymer chain with a high probe

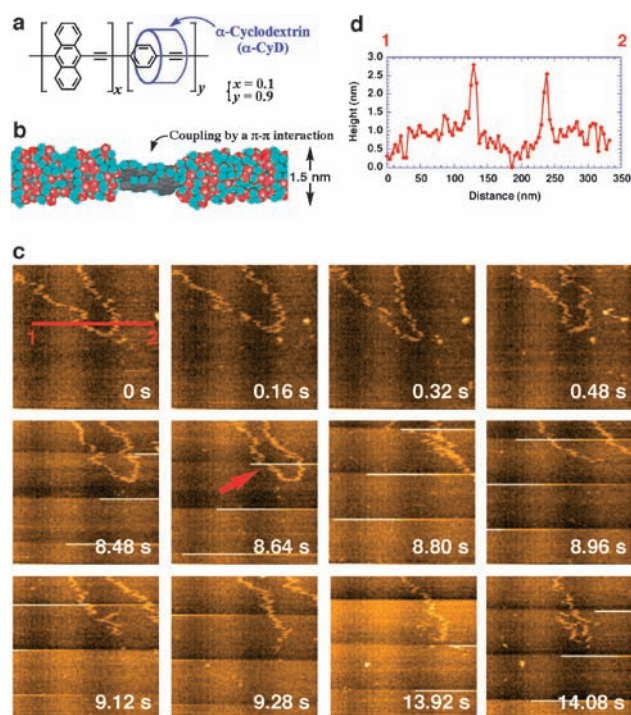


Figure 1. (a) Chemical structure of a polyrotaxane: (+)-poly[AEPE-rotaxa-(α -CyD)]. (b) A molecular mechanics calculation optimized model of a supramolecular polymer. (c) High-speed AFM images of a single molecule of a supramolecular chiral π -conjugated polymer on mica under aqueous solution at room temperature. (8.48–14.08 s) UV pulsed laser of 355 nm irradiating 20 nJ at 20 Hz. (13.92–14.08 s) The dynamic folding behavior of the cut end in a single polymer chain. (8.64 s) The imaging of chain scission in a single molecule. The point of a scission is indicated by a red arrow. XY range: 400 nm \times 400 nm. Z range: 5.0 nm. Scan rate: 160 ms per frame. Pixel: 100 \times 100. Dynamic images of single molecular (+)-poly[AEPE-rotaxa-(α -CyD)] as a Supporting Information.¹⁰ (d) A cross sectional result of single polymer chain on the red line indicated in a high-speed AFM image at 0 s as shown in Figure 1c.

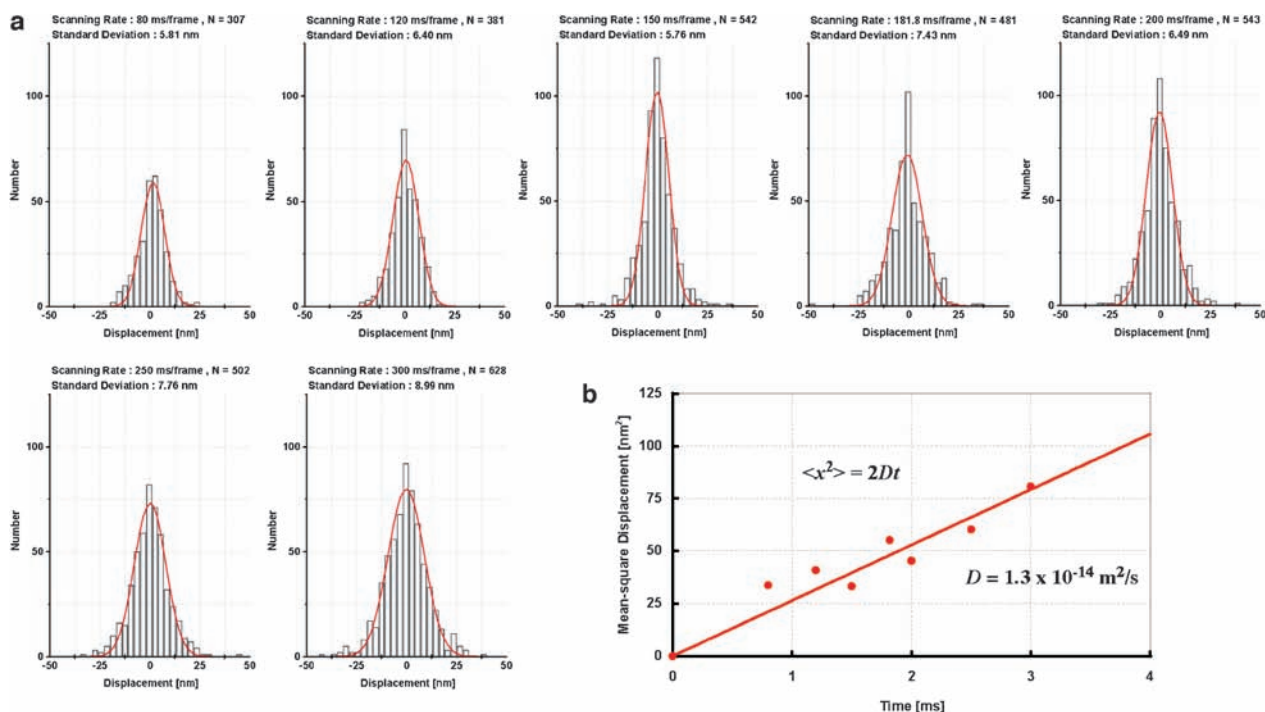


Figure 2. (a) Analytical results of the displacement in a single polymer chain of (+)-poly[AEPE-rotaxa-(α -CyD)] at scanning rates of 80, 120, 150, 181.8, 200, 250, and 300 ms per frame in high-speed AFM imaging (without UV pulsed laser irradiation). Lines are the best fits of the data to a gaussian curve; the standard deviations are 5.81, 6.40, 5.76, 7.43, 6.49, 7.76, and 8.99 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 deviations in Figure 2a. The plots were fitted to equation, $\langle x^2 \rangle = 2Dt$. A diffusion constant of a micro-Brownian motion is $1.3 \times 10^{-14} \text{ m}^2/\text{s}$.

tip pressure while irradiating, which subsequently cut the single polymer molecule as shown in the image at 8.64 s. We also observed a folding phenomenon, i.e., the cut end folded dynamically (from 13.92 to 14.08 s). The fact that the probe tip pressure cut the polymer chain supports our conclusion that the polymer is a supramolecular polymer coupled by molecular interaction because molecular interaction force is weaker than a covalent bond. Thus, information in terms of structural chemistry can be obtained. Figure 1c shows the images under an aqueous solution at room temperature. We consider that this is a micro-Brownian motion, which is excited by the Brownian motion of water molecules at room temperature. Unlike STM, AFM uses the AC (tapping) mode and the probe touches the surface. It is speculated that molecules move mainly owing to the touching probe tip, although there may also be Brownian motion. Hence, we conducted a detailed analysis. We changed the probe scanning speed and analyzed the one-dimensional displacement of a single polymer molecule in the probe scanning direction. In practice, we changed the frame rate to 80, 120, 150, 181.8, 200, 250, and 300 ms per frame, collected images under the seven different conditions, and analyzed the displacement. We made a histogram of these analysis results with the displacement as the horizontal axis and the observation number as the vertical axis, and fitted the data to the Gaussian curve as shown in Figure 2a. Finally, we plotted the square of the standard deviation of this distribution (i.e., mean-square displacement, $\langle x^2 \rangle$) and the probe scanning cycle time (t) as shown in Figure 2b. The result shows that the mean-square displacement in a single supramolecular polymer chain is proportional to the time and, hence, complies with Einstein's Law of Brownian motion.

$$\langle x^2 \rangle = 2Dt \quad (1)$$

Here, D is the diffusion coefficient. In this result, the D value is calculated as $1.3 \times 10^{-14} \text{ m}^2/\text{s}$ in the one-dimensional motion. Hence, this motion is a Brownian motion at solid-liquid interface, and the motion in a single polymer chain is a micro-Brownian motion, i.e., thermal motion.

We anticipate that our studies will be the basis for creating innovative molecular devices such as molecular motors or molecular electronics/photonics materials, which utilize thermal stochastic energy as the driving source.

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