Visualization of Polymer Chain Conformations in Amorphous Polyisocyanide Langmuir−Blodgett Films by Atomic Force Microscopy

Jiro Kumaki,*,[†],[§] Takashi Kajitani,[†] Kanji Nagai,[†] Kento Okoshi,[†] and Eiji Yashima[†],[‡]

Yashima Super-structured Helix Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), Japan, and Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

Received October 3, 2009; E-mail: kumaki@yz.yamagata-u.ac.jp

Polymer Langmuir monolayers have superior mechanical and thermal stability in comparison with monolayers composed of small molecules, and they have been extensively studied for decades for use in possible applications such as optoelectronics and molecular electronics devices.[1] Polymer monolayers are also ideal models for the study of polymer chains in two dimensions, and their structure and properties in their two-dimensional (2D) states have also been the subject of intense study. However, our understanding of polymer monolayers is still limited.[2] For example, it is not clear how 3D polymer chains in a solution dramatically change their conformations in forming 2D chains on the water surface, how they aggregate to form a 2D film, how the chains are packed in the resulting 2D film (i.e., with or without interpenetration into other chains),[3] and whether chain stacking exists in the films at the molecular level (Figure 1A). Direct observation of the polymer chains at the molecular level by microscopy should provide important information concerning these questions. As most polymers have poor stability toward the electron-beam damage inherent in transmission electron microscopy (TEM),[4] atomic force microscopy (AFM) is a more promising approach for these materials, although observation of the molecular-level chain packing is still challenging because of the limited resolution of the method.

Previously, we imaged isotactic poly(methyl methacrylate) (it-PMMA) monolayers deposited on mica at different surface pressures (π). We visualized the aggregation of isolated polymer chains in a dilute state to form an amorphous film and their subsequent crystallization to form 2D folded-chain crystals composed of double-stranded helices of it-PMMA chains.[5] High-resolution AFM resolved the chain packing in the 2D folded-chain crystals along with chain foldings and tie chains. However, the chain packing in the amorphous film could not be resolved because of the disorder and the thinner single chains of it-PMMA in the amorphous state relative to the thicker double-stranded helix in the crystal (diameter ~1.2 nm). Recently, we also reported that rigid rodlike helical polyisocyanide bearing L-alanine residues with long *n*-decyl chains as the pendants (poly-**1** in Figure 1B) spin-cast from a solution onto highly oriented pyrolytic graphite (HOPG) self-assembled into chiral 2D helix bundles upon exposure to an organic solvent vapor. The chain packing (chain-to-chain distance ~2.1 nm) and the pitch and handedness of the helical structures were observed by AFM.[6] As polyisocyanides with an appropriate hydrophilic group are known to spread on a water surface as a monolayer,[7] we expected to be able to visualize the chain packing in these monolayers as a result of the large diameter of the rigid rodlike polyisocyanide molecules. In this study, we have confirmed that the polyisocyanides

spread on a water surface as stable monolayers and successfully used high-resolution AFM to resolve for the first time the chain packing in monolayers deposited on mica. The results show that the long polymer chains, which are partially forced to adopt unusual hairpin-like conformations, are packed in the 2D film without any chain stacking. We have also shown that the persistence lengths of the chains in 2D films depend on their 3D persistence lengths in solution.

The polymers used were poly(phenyl isocyanide)s bearing L-alanine or L-lactic acid residues with long *n*-decyl chains as the pendant groups (poly-**1** and poly-**2**, respectively; see Figure 1B).[8] The number-average molecular weight (M_n), its distribution (M_w/M_n), and the first Cotton effect intensity in the circular dichroism (CD) spectrum in the main-chain absorption region near 360 nm ($\Delta\varepsilon_{1st}$), which reflects the excess of a one-handed helical conformation of the main chain, were 1.9×10^5, 1.92, and −11.0 for poly-**1** and 1.73×10^5, 2.17, and −3.21 for poly-**2**, respectively.[8]

Figure 1B shows surface pressure−area (π−A) isotherms for poly-**1** and poly-**2** spread from benzene solutions. Both polymers form stable, well-defined condensed monolayers on the water surface, as indicated by the good agreement of the limiting area of ~0.28 nm²/repeating unit (ru) with the value of 0.233 nm²/ru calculated for a poly-**1** monolayer on the basis of its reported crystal structure.[9]
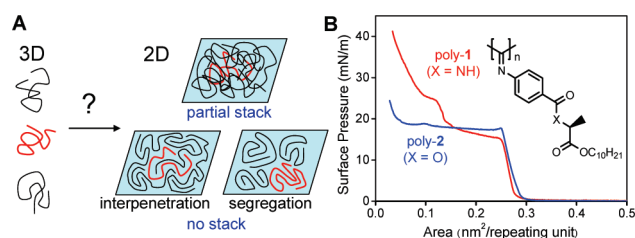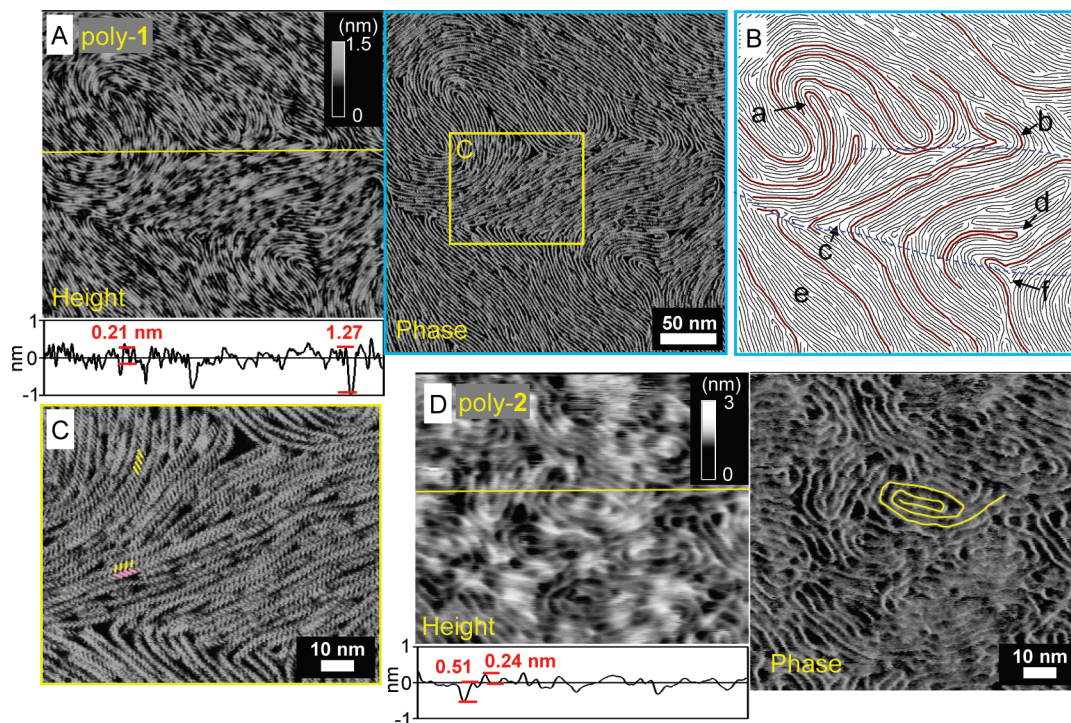

Figure 1. (A) Schematic representation of the molecular packing in a 2D film. (B) π−A isotherms of poly-**1** (red) and poly-**2** (blue) on water.

Figure 2A shows tapping-mode AFM height and phase images of a monolayer of poly-**1** deposited on mica at a surface pressure of 1 mN/m. Long polymer chains closely packed in a 2D film are clearly visualized, and 2D fast Fourier transforms of the image show specific spots corresponding to a chain-to-chain distance of 2.6 ± 0.1 nm, which is in good agreement with that in the (100) plane of the poly-**1** crystal (2.645 nm).[9] The surface undulation of the chains (~0.2 nm), while emphasized in the high-contrast image, is much smaller than the thickness of the film [2.0 ± 0.1 nm, as measured by AFM from the mica surface (data not shown)]; hence, the surface of the monolayer is fairly flat, without any chain stacking. Figure 2B is a schematic representation of the chain packing in Figure 2A; some chains are highlighted in red for clarity. Long flexible

† Japan Science and Technology Agency.
‡ Nagoya University.
§ Present address: Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan.

Figure 2. AFM images of monolayers of poly-**1** and poly-**2**. (A) AFM height (left) and phase (right) images of a monolayer of poly-**1** deposited on mica at 1 mN/m. (B) Schematic representation of the polymer chain packing of the phase image in (A). Some chains are highlighted in red for clarity. (C) Magnified phase image of the area indicated by the yellow square in (A); the yellow and pink lines, respectively, indicate left- and right-handed antipodal oblique pendant helical arrangements with respect to the main-chain axes. (D) AFM height (left) and phase (right) images of a monolayer of poly-**2** deposited on mica at 1 mN/m. The yellow curved line in the phase image indicates a possible conformation of a polymer chain.

polymer chains are packed into the 2D film without any stacking. Such a nonstacking chain packing on substrates has often been proposed without direct evidence, but we for the first time have confirmed it experimentally by high-resolution AFM. Unexpectedly, in some cases, chains are folded into hairpin-like conformation (see a and d in Figure 2B). Also, as indicated by the blue dotted lines, some bundled chains are folded like deformed rock strata. Around these irregularly folded chains, relatively large voids are seen (c, d, f), which cause large defects in the film. These highly forced conformations may be formed during the spontaneous aggregation of the chains spread on the water surface as a result of the condensed nature of the monolayer. Even in a relatively regular area (e.g., e), there are small defects due to the presence of chain ends. We emphasize that the detailed molecular-level information shown here is only available by direct observation of the molecules.

Figure 2C shows a magnified phase image of the area indicated by the yellow square in the right panel of Figure 2A. Similar to the observations of films of the same polymer spin-cast onto HOPG,[6] the clearly observed periodic oblique stripes appear to result from one-handed helical arrays of the pendant groups of individual polymer chains, with predominantly left-handed (yellow lines) and minor right-handed (pink) helices.[6] The observed helical pitch (1.58 ± 0.09 nm) of poly-**1** is slightly larger than the value of 1.30 ± 0.04 nm reported for a spin-cast film on HOPG, indicating that the helical structure might be slightly modified on the hydrophilic mica substrate in comparison with the hydrophobic HOPG substrate. On the other hand, the more flexible poly-**2**, which has no intramolecular hydrogen bonds between the side groups and at room temperature exists in a melted state (in contrast with the solid state of poly-**1**), was difficult to observe at a similar high resolution; however, it was possible to observe chain packing with a chain-to-chain distance of 2.86 ± 0.03 nm, as shown in Figure

2D. The small surface undulation (∼0.24 nm) in comparison with the thickness of the monolayer [0.95 ± 0.08 nm,[10] as measured by AFM from the mica surface (data not shown)] indicates again that there is no stacking of the chains. The yellow curved line indicates a possible packing of a single chain. A comparison of panels C and D of Figure 2, which were taken at the same magnification, reveals a more condensed conformation for poly-**2** than poly-**1**. The *apparent* 2D persistence lengths of the chains were then estimated from the AFM images to be 39 and 6 nm for poly-**1** and poly-**2**, respectively. These values are smaller than those determined for the same polymers in tetrahydrofuran (THF) solutions using size-exclusion chromatography (SEC) with a multiangle laser light-scattering (MALS) detector but clearly reflect the ordering of the persistence lengths in the solution (poly-**1**, 220 nm; poly-**2**, 30.8 nm[8]). The smaller value in the 2D films may be result from the forced conformations of the polymer chains in the condensed monolayers.[11]

In conclusion, we have used AFM to successfully observe the chain packing of long polymer chains in amorphous 2D films for the first time. Our understanding of polymer monolayers will be improved with the help of molecular-level information such as that presented here.

Supporting Information Available: Experimental details, wider views of AFM images, and additional discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience: New York, 1966. (b) Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir–Blodgett to Self-Assembly*; Academic Press: New York, 1991.
(2) Gaines, G. L., Jr. *Langmuir* **1991**, *7*, 834–839.

(3) Recent scanning near-field optical microscopy (SNOM) observations of a PMMA Langmuir−Blodgett (LB) film in which a small amount of the chains were fluorescence-labeled indicated that the polymer chains are highly segregated. See: Aoki, H.; Morita, S.; Sekine, R.; Ito, S. *Polym. J.* **2008**, *40*, 274–280.

(4) Chain images of an LB film composed of phthalocyaninato−polysiloxane oligomers having high stability toward an electron beam have been observed by TEM. See: Yase, K.; Schwiegk, S.; Lieser, G.; Wegner, G. *Thin Solid Films* **1992**, *210/211*, 22–25.

(5) Kumaki, J.; Kawauchi, T.; Yashima, E. *J. Am. Chem. Soc.* **2005**, *127*, 5788–5789.

(6) Kajitani, T.; Okoshi, K.; Sakurai, S.-I.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 708–709.

(7) (a) Teerenstra, M. N.; Vorenkamp, E. J.; Shouten, A. J.; Nolte, R. J. M. *Thin Solid Films* **1991**, *196*, 153–162. (b) Feng, F.; Miyashita, T.; Takei, F.; Onitsuka, K.; Takahashi, S. *Chem. Lett.* **2001**, *30*, 764–765.

(8) Okoshi, K.; Nagai, K.; Kajitani, T.; Sakurai, S.-I.; Yashima, E. *Macromolecules* **2008**, *41*, 7752–7754.

(9) The crystal structure of poly-**1** with an almost perfect single-handed helical structure ($\Delta\varepsilon_{1st} = -20$) prepared by the living μ-ethynediyl Pt−Pd catalyst, has been reported. The polymer forms a crystal with a hexagonal lattice (a = 2.645 nm, c =1.320 nm) and has a 15 units per 4 turns (15/4) helical structure. Thus, the area density in the (100) plane is 0.233 nm²/ru (=2.645 × 1.320/15), which is comparable with the limiting area of the poly-**1** monolayer found here (2.8 nm²/ru). The poly-**1** used in this study forms almost the same crystals (unpublished data). See: Onouchi, H.; Okoshi, K.; Kajitani, T.; Sakurai, S.-I.; Nagai, K.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2008**, *130*, 229–236.

(10) The measured thickness of poly-**2** was underestimated because of penetration of the cantilever into the soft poly-**2** monolayer during the tapping-mode AFM measurements; the thicknesses of the poly-**1** and poly-**2** monolayers should be comparable because of the similar molecular structures and limiting areas of the $\pi-A$ isotherms.

(11) The 2D persistence lengths were determined using the freeware program *2D Single Molecules* provided by Y. Roiter and S. Minko (available for download at http://people.clarkson.edu/~sminko). The chain conformations in the condensed monolayers are expected to be formed out of equilibrium and thus to have unusual hairpinlike conformations and folded bundle chains, resulting in smaller *apparent* persistence length values when estimated by AFM. However, evaluating only the straight parts of the chains and ignoring the parts with these unusual conformations provided a 1 order of magnitude longer *apparent* 2D persistence length of 350 ± 30 nm for poly-**1** (Figure S3 and Table S1), which is comparable with that in the solution (220 nm). For more details, see the Supporting Information.

JA908426U