Communication

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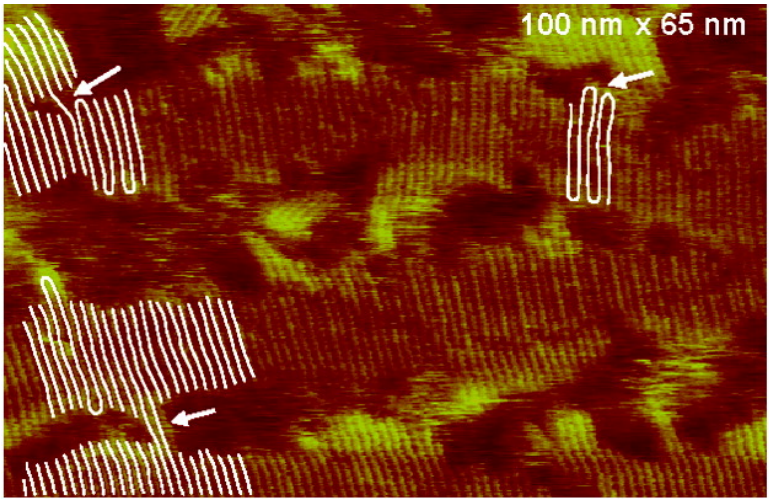

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Two-Dimensional Folded Chain Crystals of a Synthetic Polymer in a Langmuir−Blodgett Film

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Folded chain crystals are the most common crystalline structures of flexible polymer chains and have been one of the major subjects of intensive investigations in the area of polymer science. However, the exact nature of the chain folding in the crystals is still unresolved and is a topic of continuing controversy.[1] Direct observation of the folded chain crystals by scanning probe microscopy including atomic force microscopy (AFM) should be one of the promising methods to settle this problem and has been extensively studied.[2] Although the ordered crystalline structures have been visualized at a molecular level by AFM, it is still challenging to observe somewhat irregular structures, such as chain folding and tie-chains; these structures are particularly important to understand the crystalline structures and the folding mechanism. The difficulty comes from the fact that AFM cannot clearly resolve these somewhat irregular chains when they stack three-dimensionally; this is the case for the bulk samples usually used in the previous AFM studies.[2]

Polymer monolayers spread on a water surface is an ideal model for polymer chains in two dimensions (2D).[3] For example, isotactic poly(methyl methacrylate) (*it*-PMMA) is known to spread on the water surface as a monolayer, which further crystallizes under compression.[4] However, clear AFM imaging has been achieved for neither the crystalline structures nor the structures in a dilute state.

We now show the first clear observations of *it*-PMMA monolayers deposited on mica at different surface pressures and the 2D folded chain crystals assembled from single chains by AFM. Furthermore, gentle crystallization of the monolayer by an extremely slow compression on the water surface enables us to observe the crystals at the molecular level, thus visualizing the chain foldings and tie-chains. We emphasize that the structures observed here are the 2D structures, but the resulting molecular level information will provide an important clue toward the understanding of the polymer crystals and their 3D formations.

Figure 1a shows the surface pressure−area ($\pi-A$) curves for an *it*-PMMA (the number average molecular weight (M_n) of 175 700, a polydispersity index (PI) of 1.21, and [*mm*] = 98%) and a syndiotactic (*st*)-PMMA (M_n: 178 700, PI: 1.16, and [*rr*] = 79%). The *it*-PMMA exhibits a typical expanded $\pi-A$ curve with a transition at around 10 mN/m, corresponding to its crystallization. On the other hand, the *st*-PMMA shows a compressed $\pi-A$ curve without any apparent transition. The scaling analysis of the $\pi-A$ curves of polymers in a semidilute regime can be expressed as $\pi \approx C^{2\nu/(2\nu-1)}$, where π and C represent the surface pressure and the surface concentration, respectively, and ν is the critical exponent to express the relation between the radius of gyration (R) and the molecular weight (M) in the form of $R \approx M^{\nu}$.[5] In two dimensions, the ν value is still in criticism, but is expected to be around 0.57 and 0.75 for θ and good solvents, respectively.[6] The ν values estimated from the $\pi-A$ curves in Figure 1a are 0.79 (*it*-PMMA) and 0.55 (*st*-PMMA), which indicates that the *it*- and *st*-PMMAs exist in close to a good solvent condition and θ state, respectively, showing a good agreement with a previous study.[7] Previously, de Gennes pointed out that an isolated single polymer chain in the 2D θ state could have a 2D bulk density; in other words, it exists in highly aggregated conformations.[8] The AFM tapping mode height images of the monolayers of the *it*- and *st*-PMMAs deposited on mica at different surface pressures and areas are shown in Figure 1, parts b and c, respectively. The AFM images clearly indicate that the *it*-PMMA deposited at the 1.3 nm^2/repeating unit (ru), which is wider than the onset of the $\pi - A$ curve (ca. 0.6 nm^2/ru), exists as single chains on mica (thickness: ca. 0.3 nm). However, the individual *it*-PMMA chains became a continuous film when the surface pressure was increased at the deposition (1 mN/m; the data not shown here) and finally formed lamella crystals at 10 mN/m (thickness: ca. 0.6 nm) (Figure 1b). On the other hand, the *st*-PMMA showed aggregated structures (thickness: ca. 0.6 nm) even deposited from a dilute state, thus forming a continuous film under compression (Figure 1c). These AFM images observed here are in good agreement with the behaviors of the $\pi-A$ curves of the *it*- and *st*-PMMAs.[9]

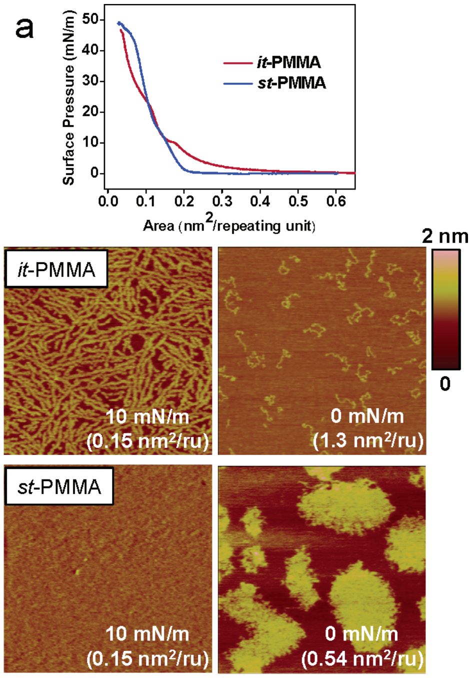

Figure 1. $\pi-A$ curves of *it*-PMMA and *st*-PMMA on water (a). AFM height images of the monolayers of *it*-PMMA (b) and *st*-PMMA (c) deposited on mica at different surface pressures and areas. The compression rate was 4.1×10^{-2} nm^2·ru^{-1}·min^{-1}. Scale = 1 × 1 μm.

We next focused on the lamella crystals of *it*-PMMA. Initial attempts to observe such lamella crystals under high magnification

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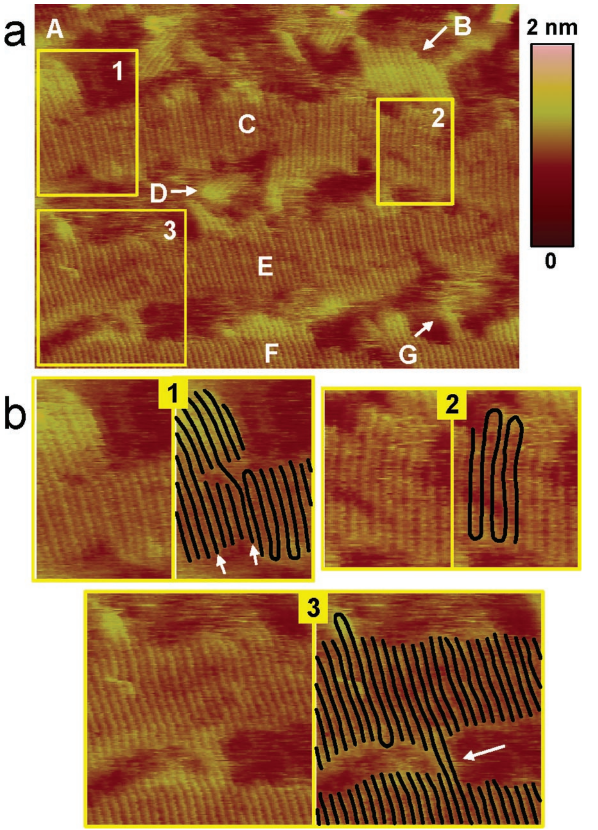

Figure 2. High-magnification AFM height image of *it*-PMMA deposited on mica at 10 mN/m. The compression rate was 8.2×10^{-4} nm^2•ru^{-1}•min^{-1}. Scale = 100 × 75 nm. (b) Zoomed images of the areas indicated in (a) (left). Schematic representations of possible chain conformations are also shown in (b) (right) as black lines.

were not successful, but we could successfully observe clear molecular level images of the lamella structures when the samples were compressed at a slower compression rate. Figure 2 shows high-magnification AFM images of the *it*-PMMA lamella obtained by compressing at a rate of 8.2×10^{-4} nm^2•ru^{-1}•min^{-1}; we note that the compression rate was 1/50 of the normal conditions, and it took about 13 h for it to be compressed to 10 mN/m. The higher regularity with better resolution might be due to the slow crystallization. Large lamella crystals with stripes perpendicular to the long axis of the lamella are clearly shown in Figure 2a (C, E, F). As mentioned below, we believe that these are folded-chain crystals of the *it*-PMMA chains. In some areas, chain foldings are visible (see the zoomed images and the schematic representations of a possible chain packing in Figure 2b). However, chain foldings are not perfectly observed in all areas. Annealing of the film further improved the crystallinity, resulting in a better visualization of the folding chains. Figure S1 is an AFM image of the *it*-PMMA lamellas after annealing at 50 °C; in some areas, regular chain foldings are clearly visible (see Supporting Information).[10] Tie-chains are also clearly seen (see two tie-chains combining lamellas E and F in the zoomed image **3** in Figure 2b). We could also observe a defect in the crystal; for example, in image **1** of Figure 2b, different numbers of short chains (upper: two, lower: three) are sandwiched between the two long chains indicated by the arrows. Between the lamellas, there are small crystals (for example, see B and D). There are also vague areas between the lamellas such as that indicated by G; these are probably amorphous chains existing as loose tie-chains or hair chains (chains emanating from crystals) or floating chains (free chains). Under high magnification, the outlines of the lamellas are not smooth, and significant variations in their widths are noticeable; these somewhat irregular structures may be specific in the 2D crystals due to the absence of 3D packing interactions.

2D fast Fourier transforms of the images showed a specific spot corresponding to the stripe−stripe distance of 1.29 nm. Several different models have been proposed for the bulk crystals of *it*-PMMA;[11] one of the most plausible models may be the double-stranded helix model proposed by Kusanagi and Tadokoro.[11,12] The model shows that two 10_1 helices of *it*-PMMA chains are intertwined to form a double helix, which packs in an orthorhombic unit cell with the parameters $a = 2.098$, $b = 1.217$, and c (fiber axis) = 1.05 nm. The distances between the double-helix strands in their model are 1.213 and 1.217 nm in the (110) and (100) planes, respectively, which is in fair agreement with the distance between the stripes of the *it*-PMMA observed here.[13] The length of a double-stranded helix of the *it*-PMMA used in this study was estimated from the molecular weight and found to be 365 or 185 nm, depending on the assumption as to whether the double-stranded helix is made of two chains or a single chain. The average width of the present 2D *it*-PMMA lamella was ca. 17 nm, thus the double helix of the *it*-PMMA chains is expected to be folded 22 or 11 times on average.

In summary, we have succeeded in observing the 2D folded-chain crystals of *it*-PMMA, and the foldings and tie-chains have been clearly visualized for the first time. The molecular level visualization using 2D crystals should be one of the promising ways to improve our understanding of the self-assembly of polymer chains.

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Supporting Information Available: Experimental details and AFM images of an annealed lamella crystal. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) An atactic PMMA showed a compressed type $\pi - A$ curve and also formed an aggregated structure even when deposited from a dilute state, similar to *st*-PMMA. See: (a) Kumaki, J.; Nishikawa, Y.; Hashimoto, T. *J. Am. Chem. Soc.* **1996**, *118*, 3321. (b) Kumaki, J.; Hashimoto, T. *J. Am. Chem. Soc.* **2003**, *125*, 4907.
(10) The difficulty in observing chain foldings in all areas is probably due to the movements of the chains as a result of their amorphous nature and/or possible irregular structures. The regular sharp foldings observed here may be better visualized than irregular foldings due to the restricted motions and the regular structures. However, the exact structures of the chain folding in the invisible regions, including their regularity, are not clear at present. This characterization will be the objective of future studies.
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(13) Possible explanations for the agreement of the crystal parameter between the 2D and 3D crystals are (1) the chain−chain interaction is superior to the chain−substrate and chain−air interactions and (2) the 3D crystal of *it*-PMMA is close to ideal hexagonally closed-packed double helices. If a chain in a 3D crystal interacted in a different manner with the adjacent chains in the different crystal planes, the structure of the 2D crystal might be different from the 3D crystal; this might not be the present case.

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