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Two-Dimensional Surface Chirality Control by Solvent-Induced Helicity Inversion of a Helical Polyacetylene on Graphite

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The development of two-dimensional (2D) chiral surfaces has attracted considerable interest because of possible applications in electrochemical sensors for chiral molecules and enantioselective catalysis and adsorbents for producing and separating chiral molecules, respectively.[1] The supramolecular self-assembly concept has been intensively applied to create 2D chiral surfaces through epitaxial adsorptions and alignments of chiral small molecules on crystalline graphite and metals, as evidenced by scanning probe microscopy (SPM) observations of their enantiomorphic 2D arrangements at the atomic or molecular level.[1,2] Although biological polymers, such as DNA and proteins, have been utilized to create helical architectures of patterned 2D assembled polymers,[3] it still remains difficult, but a great challenge, to create 2D chiral surfaces using fully synthetic helical polymers on the substrates.[4]

Recently, we reported that rigid and rodlike, helical poly(phenylacetylene)s bearing L- or D-alanine residues with a long alkyl chain as the pendants (poly-**1D** and poly-**1L**, respectively) (Figure 1) self-assembled hierarchically on highly oriented pyrolytic graphite (HOPG) upon exposure to organic solvent vapors; flat poly(phenylacetylene) monolayers formed epitaxially on the basal plane of the graphite, on which helical poly(phenylacetylene) further self-assembled into chiral 2D bundles of helices.[5] High-resolution atomic force microscopy (AFM) revealed their helical conformations in the 2D crystals and enabled the determination of the molecular packing, helical pitch, and handedness. Here we show the unprecedented switchable 2D chiral surfaces based on inversion of the helicity of helical poly(phenylacetylene)s upon exposure of a specific organic solvent (Figure 1), which can be directly visualized by AFM with molecular resolution.

The *cis-transoidal* helical poly-**1D** and poly-**1L** prepared by the reported method showed characteristic Cotton effect signs due to a predominant one-handed helical conformation in nonpolar solvents, such as benzene.[6] However, we found that the Cotton effect signs corresponding to the helix-sense of the polymers in benzene inverted to the opposite signs in polar solvents, such as tetrahydrofuran (THF) and chloroform (Figures 1A and S1). This suggests that the helix-sense of the polymers may be inverted by changing the solvent polarity. We then measured the AFM images of the polymers deposited on HOPG from a dilute THF solution (0.1 mg/mL) after THF vapor exposure in the same way[4b,5] in order to get the first convincing evidence for the inversion of helicity.[7]

As shown in the AFM images of poly-**1D** (Figure 2A) and poly-**1L** (Figure S2), poly-**1**s self-assembled into well-defined 2D helix bundles with an average height of 1.76 ± 0.14 nm for poly-**1D** and 1.68 ± 0.08 nm for poly-**1L** after 11 h of THF vapor exposure. The high-resolution AFM-zoomed images (Figure 2B) revealed a number of periodic oblique stripes (blue and green lines in Figure 2B), probably originating from a one-handed helical array of the pendants that were tilted anticlockwise (poly-**1D**) or clockwise (poly-**1L**) at −75 ± 8 and +75 ± 7°, respectively, with respect to the axis of the polymer main chain (white arrows in Figure 2B). This remarkable 2D mirror-image relationship suggests that poly-**1D** and poly-**1L** have enantiomeric left- and right-handed helical structures with respect to the pendant arrangements, respectively, upon exposure of THF vapor;[8] the helicity of poly-**1**s prepared from THF appears to be opposite that of benzene.[5] These results are consistent with the CD results as evidenced by their opposite Cotton effect signs in each solution (Figures 1A and S1). The AFM images of poly-**1D** and poly-**1L** are different from those prepared from benzene vapor exposure;[5] individual polymer chains with a clear chain−chain lateral spacing could not be clearly visualized in the images, however regular arrangements of the enantiomerically tilted stripes provide particularly useful information for a possible helical pitch and enantiomorphic 2D molecular packing. The average distance between each stripe shown in Figure 2B may reflect the helical pitch of poly-**1D** (2.19 ± 0.20 nm) and poly-**1L** (2.15 ± 0.15 nm). These values agree well with the half-pitch of the helical arrangements of the pendants as determined by the wide-angle X-ray diffraction (WAXD) analysis of the polymers (2.11 nm),[9] but are shorter than the helical pitch of the same polymers with the opposite helix-sense prepared from benzene (2.47 ± 0.18 and 2.34 ± 0.21 nm, respectively) (see ref 5 and Table S1).

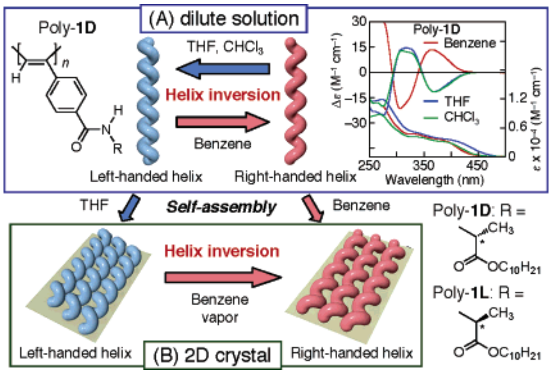

Figure 1. Schematic illustration of the macromolecular helicity inversion in dilute solution and 2D crystal state. (A) CD and absorption spectra of poly-**1D** measured in THF, chloroform, and benzene at 5 °C, room temperature, and 6 °C, respectively ([poly-**1D**] = 1.5 mg/mL). The helix-sense of poly-**1** in benzene inverts to the opposite helix-sense in THF and chloroform. (B) Rodlike helical poly-**1D** self-assembles into 2D helix bundles with the controlled helicity upon exposure of each organic solvent vapor. The one-handed 2D helix bundles of poly-**1D** further invert to the opposite handedness by exposure to benzene vapor on the substrates.

On the basis of these AFM observations, possible enantiomorphic 2D arrangements of helical poly-**1D** and poly-**1L** with an opposite handedness can be drawn (Figure 2B). The individual one-handed

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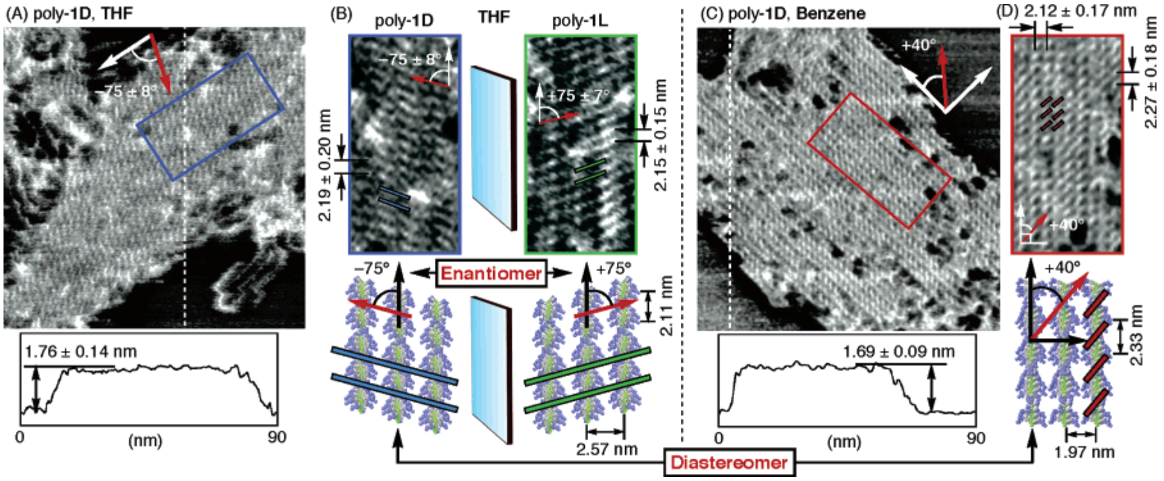

Figure 2. AFM images of 2D self-assembled poly-**1** on HOPG and helical structures of poly-**1** proposed by AFM and X-ray analyses. (A) AFM phase image of self-assembled poly-**1D** spin cast on HOPG from a dilute THF solution (0.1 mg/mL). Scale = 90 × 90 nm. The white arrow indicates the direction of the polymer main-chain axes. The cross-section profile shown by the white dashed line is also shown. (B) Magnified AFM phase images of self-assembled poly-**1D** (left) and poly-**1L** (right), which correspond to the area indicated by the squares in (A) and Figure S2, respectively. Scale = 20 × 40 nm. Schematic drawings of the mirror-image relationship of helical poly-**1D** (left) and poly-**1L** (right) 2D crystals with antipodal oblique pendant arrangements (blue and green lines, respectively) are also shown. Possible models were constructed based on the X-ray structural analysis results. Decyl side groups were replaced by methyl groups for clarity. (C) AFM phase image of poly-**1D** 2D crystals after helicity inversion by benzene vapor (for the corresponding height image, see Figure S5 in Supporting Information). Scale = 90 × 90 nm. The cross-section profile shown by the white dashed line is also shown. (D) Magnified AFM phase image of self-assembled poly-**1D** (see the red square in (C)). Scale = 20 × 40 nm. Schematic drawing of helical poly-**1D** 2D crystals with oblique pendant arrangements is also shown. Possible models were constructed based on the X-ray structural analysis results.

helical polymer chains aligned with an almost extended structure, but shifted to one-third helical pitch to each other with respect to the main-chain axis, as estimated from the constant tilt angle of the oblique stripes and the lateral spacing from the X-ray analysis.

Finally, we demonstrate that the surface chirality can be switched based on the helicity inversion of the poly-**1D** upon exposure of a different solvent vapor. First, 2D left-handed helix bundles were prepared by spin casting a dilute solution of poly-**1D** in THF (0.1 mg/mL) on HOPG, followed by THF vapor exposure for 11 h in the same way as shown in Figure 2A. After drying in vacuo, the sample was exposed to benzene vapor for 12 h, and the AFM measurements were performed. A left-handed 2D helix bundle of poly-**1D** on HOPG prepared from THF changed to the opposite right-handed helix bundles by subsequent exposure to benzene vapor (Figure 2C).[10] The periodic oblique stripes (red lines in Figure 2D) were tilted clockwise at +40° with respect to the main-chain axis. The 2D molecular ordering of each polymer consists of right-handed helical polymer chains arranged in parallel, with chain-to-chain spacing (2.12 ± 0.17 nm) and helical pitch (2.27 ± 0.18 nm). The structure of the 2D chiral crystal is almost the same as that prepared from a benzene solution, indicating that the surface chirality generated by the self-assembled helical poly-**1D** can be simply controlled by a specific solvent vapor based on the helicity inversion on the surface.[11] Consequently, the present results not only demonstrate the direct evidence of the inversion of macromolecular helicity of a dynamic helical poly(phenylacetylene) in different solvents but also provide a unique 2D switchable chiral surface based on the inversion of helicity. Further application of this system toward controlling chiral recognition is now in progress in our laboratory.

Supporting Information Available: Full experimental details (PDF). This material is available free of charge via the Internet at http://pubs.ac.org.

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(8) We note that, when poly-**1D** has a left-handed helical array of the pendants, the main chain has an opposite, right-handed helical structure.

(9) For more details, see Supporting Information.

(10) Both the height (Figure S5) and phase (Figure 2C) AFM images showed identical structures. The phase images are presented here for better clarity. For the changes in the AFM images with time, see Figure S7.

(11) The sample (Figure 2C) was further exposed to THF vapor for 12 h, but we could not clearly observe 2D helix bundles with the opposite handedness. The reason for this irreversible helicity inversion on HOPG is not clear, but the high affinity of aromatic benzene toward the substrate graphite may be involved. To achieve reversible surface chirality control based on inversion of the helicity, exposures by solvent combinations with different polarities should be worth investigating.

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