DOI: 10.1002/ange.200701546

**Helical Structures**

# Two-Dimensional Helix-Bundle Formation of a Dynamic Helical Poly(phenylacetylene) with Achiral Pendant Groups on Graphite

*Shin-ichiro Sakurai,* Sousuke Ohsawa, Kanji Nagai, Kento Okoshi, Jiro Kumaki,* and Eiji Yashima**

The design and synthesis of helical polymers with a controlled helix sense[1] have been attracting great interest because of the wide variety of possible applications in materials science, chemical sensing, separation of enantiomers, and enantioselective catalysis.[2] The detailed structural characterizations of the helical polymers are essential to explore the relationships between their structures and properties and to further develop more sophisticated chiral materials. However, the determination of helical structures including helical pitch and handedness still remains very difficult. Conventional spectroscopic methods in dilute solution are not straightforward, and X-ray analysis in the solid state is a laborious task; these methods may not provide unambiguous helical structural information, and in particular, the helical sense. The direct observation of the helical polymers by atomic force microscopy (AFM) on solid substrates should be one of the most promising methods to settle this problem and has been extensively studied.[3] Recently, we reported that rigid rodlike helical poly(phenylacetylene)s bearing L- or D-alanine residues with a long *n*-decyl chain as the pendants (poly-L-Ala in Figure 1 a) hierarchically self-assembled on highly oriented pyrolytic graphite (HOPG) upon exposure to organic solvent vapors, such as benzene; flat poly(phenylacetylene) monolayers losing helical structures epitaxially formed on the basal plane of the graphite, on which helical poly(phenylacetylene)s further self-assembled into chiral two-dimensional (2D) helix-bundles with a controlled helicity.[4] High-resolution AFM revealed their helical conformations in the 2D crystals and enabled us to determine the molecular packing, helical pitch, and handedness.[5] Herein we show that an optically inactive but dynamically racemic helical poly(phenylacetylene) bearing achiral α-aminoisobutyric acid (Aib) residues with the same *n*-decyl chain as the pendants (poly-Aib in Figure 1 a)[6] also crystallizes under an organic solvent vapor atmosphere on HOPG, resulting in 2D helix-bundle formation (Figure 1 c). Poly-Aib no longer has any stereogenic centers, but likely consists of an equal mixture of interconvertible right- and left-handed helical segments separated by rarely occurring helical reversals in solution (Figure 1 c, left), as do polyisocyanates and polysilanes, and therefore, poly-Aib in dynamic equilibrium is a chiral or dynamically racemic helical polymer.[1a,h,j,2e,8] We could successfully visualize such enantiomeric right- and left-handed helical segments and the helical reversals of poly-Aib on HOPG by high-resolution AFM, and the results were quantified by X-ray diffraction of the oriented liquid crystalline (LC) poly-Aib film.

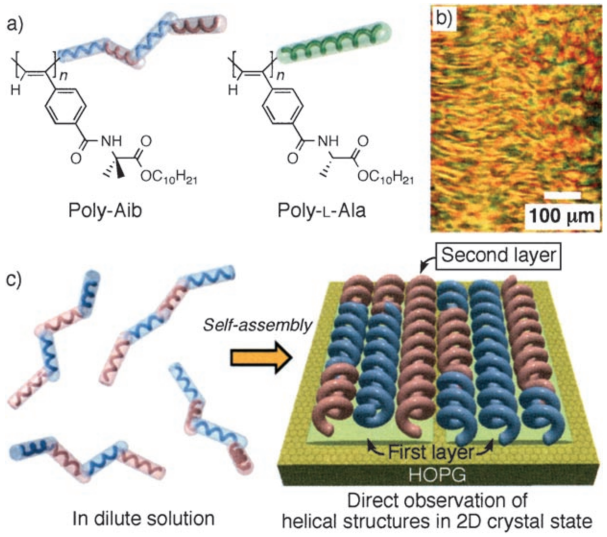

***Figure 1.*** a) Structures of poly-Aib (red: right-handed, blue: left-handed helical segments) and poly-L-Ala. b) Polarized optical micrograph of a nematic LC phase of poly-Aib in 15 wt% benzene solution taken at ambient temperature (ca. 25 °C). c) Schematic representation of 2D crystallization of helical poly-Aib on HOPG.

Poly-Aib formed a lyotropic nematic LC phase in a concentrated benzene solution (above 10 wt%) as seen in its polarized optical micrograph (Figure 1 b), indicating that poly-Aib is a rigid-rod helical polymer. This assumption is supported by its extremely long persistence length of 89.6 nm in toluene[9] assisted by intramolecular hydrogen bonds as observed for an analogous helical poly-L-Ala.[12]

The typical high-resolution AFM height images of poly-Aib deposited on HOPG from a dilute benzene solution (0.01 mg mL$^{-1}$) at approximately 25 °C, followed by benzene vapor exposure at about 25 °C for 12 h, can be seen in Figure 2 a. Poly-Aib self-assembles into well-defined 2D

---

[*] Dr. S.-i. Sakurai, Dr. K. Okoshi, Dr. J. Kumaki, Prof. E. Yashima
Yashima Super-structured Helix Project, Exploratory Research for Advanced Technology (ERATO)
Japan Science and Technology Agency, 101 Creation Core Nagoya
Shimoshidami, Moriyama-ku, Nagoya 463-0003 (Japan)
Fax: (+81) 52-739-2083
E-mail: sakurai@yp-jst.jp
kumaki@yp-jst.jp
yashima@apchem.nagoya-u.ac.jp
Homepage: http://www.yashimapj.com/

S. Ohsawa, K. Nagai, Prof. E. Yashima
Department of Molecular Design and Engineering
Graduate School of Engineering, Nagoya University
Chikusa-ku, Nagoya 464-8603 (Japan)
Fax: (+81) 52-789-3185

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

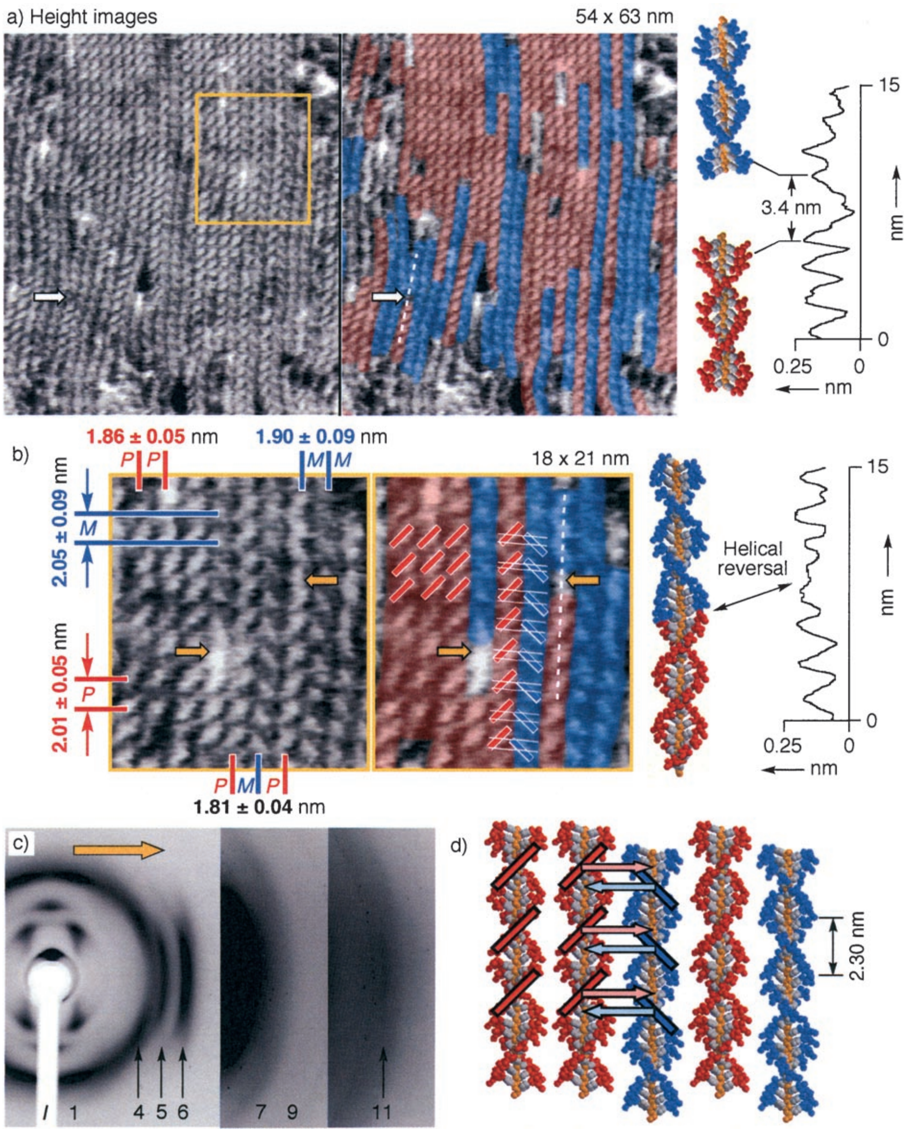

***Figure 2.*** a) AFM height images of 2D self-assembled poly-Aib cast on HOPG. The polymer strands with clearly identifiable right- and left-handed helical blocks are shown in red and blue, respectively (right). The cross-section height profile, taken along the white dashed line, and right- (red) and left-handed (blue) helical polymer models constructed on the basis of the X-ray analysis are also shown. Unidentifiable strands are uncolored. b) Magnified AFM height images of poly-Aib, corresponding to the yellow square in (a). The cross-section height profile taken along the white dashed line and a polymer model with right- and left-handed helical blocks separated by a helical reversal (yellow arrows) constructed by molecular modeling and molecular mechanics calculations on the basis of the X-ray analysis are also shown. See text for more details. c) WAXD pattern of an oriented poly-Aib film. The horizontal direction, which nearly corresponds to the helical axis, is shown by a yellow arrow. See text for more details. d) Schematic drawings of right- and left-handed helix bundles of poly-Aib in 2D crystals constructed on the basis of the AFM results and X-ray structural analysis.

helix-bundles with a constant height of 1.53 ± 0.05 nm, most of which are clearly resolved into individual right- and left-handed helical blocks packed parallel to each other (Figure 2a; right).[14] These AFM images, and in particular the enlarged images (Figure 2b), provide possible helical pitch, helical sense, and molecular arrangements of poly-Aib. The periodic oblique stripes observed in each helical block (red and blue colors in Figure 2b (right)), which originated from a one-handed helical array of the pendants, were tilted clockwise or counterclockwise at +43 and −45°, respectively, with respect to the main-chain axis. This remarkable 2D mirror-image relationship suggests that poly-Aib molecules most likely consist of right- and left-handed enantiomeric helical blocks with a helical pitch of 2.01 ± 0.05 (*P*) and 2.05 ± 0.09 nm (*M*), respectively, estimated from the average distance between each stripe (Figure 2b). The average chain-to-chain distance between the right-handed helical blocks (*PP*; 1.86 ± 0.05 nm) is in good agreement with that of the left-handed helical blocks (*MM*; 1.90 ± 0.09 nm). The chain-to-chain distance between the helical blocks of opposite sense was estimated to be 1.81 ± 0.04 nm (*PMP*, Figure 2b; left), which agreed fairly well with those between the helical blocks of the same sense. The helical blocks of the same sense (Figure 2b, red bars only) packed parallel to each other, while those of the opposite sense (Figure 2b, red and blue bars) shifted to one-third helical pitch relative to each other with respect to the main-chain axis (see thin white solid lines in Figure 2b (right) and the arrows in Figure 2d). These observations indicate a difference in packing structures and energy between homochiral helices and heterochiral helices in the 2D crystals; if homochiral chain–chain interactions are favored over heterochiral counterparts,[15] chiral domain formations (preferential resolution) will be expected (discussed below).

The three-dimensional solid-state structure of poly-Aib was investigated by X-ray analysis. In Figure 2c, a wide-angle X-ray diffraction (WAXD) pattern is shown of a unidirectionally oriented poly-Aib film prepared by casting a concentrated nematic LC benzene solution in an electric field. The WAXD pattern of the highly oriented film shows diffuse but apparent meridional reflections on the 5th and 11th layer lines, which are assignable to the turn-layer line and the unit height, respectively, giving an 11-unit/5-turn helix with a 0.209 nm translational length per unit (for more details, see the Supporting Information, Table S1).[16] The helical pitch estimated by AFM is almost identical to the half pitch of the pendant helical arrangements as determined by the X-ray analysis (2.30 nm; for comparison between the AFM and X-ray results, see the Supporting Information, Table S2).

The right- and left-handed helical block segments separated by helical reversals in individual polymer chains could also be visualized in the 2D crystals (Figure 2b). The cross-section height profile denoted by a white dashed line in Figure 2b clearly shows a unidentifiable plateau section with virtually the same height along with the block segments of the helices of opposite sense, which is assumed to be a helical reversal in the polymer chain. Force-field calculations suggest that a poly-Aib chain having a helical reversal can be constructed so as to maintain its rodlike structure (Figure 2b; right). In contrast, in the height profile indicated in Figure 2a, there is a gap between helical blocks of opposite sense (Figure 2a, white arrows) which is different from the helical reversal; in this case, two poly-Aib chains align with a distance between them of 3.4 nm.[17]

Statistical analysis of a series of high-resolution AFM images of poly-Aib helix bundles and height profiles along with each polymer chain may provide the average lengths of right- and left-handed helical blocks and the population of helical reversals. According to Lifson, Green, and co-workers,[1a,18] the length of the helical-sense blocks ($L$), in other words, the number of monomer units between the helical reversals, can be calculated as a function of the free-energy difference between the helical ($\Delta G_h$) and the helical reversal states ($\Delta G_r$), the most important thermodynamic stability parameters for representing a unique feature of dynamic helical polymers, $L = \exp(\Delta G_r/RT)$ ($R$ and $T$ are the gas constant and the absolute temperature, respectively). Poly-Aib is an equal mixture of right- and left-handed helices, and therefore, $\Delta G_h = 0$. This fact suggests that if the helical sense blocks of poly-Aib could be measured with certainty by the AFM, the $\Delta G_r$ value for poly-Aib in the 2D crystal state could be calculated. However, the average molecular length of poly-Aib determined by single-molecular AFM measurements (216 nm which corresponds to 1034 monomer units) (Supporting Information, Figure S7)[10d,19] is longer than each side of the high-resolution AFM images (ca. 60 nm; Figure 2a), and it was difficult to determine the average lengths of helical blocks ($L$) between the helical reversals in individual polymer chains in such a limited area. We measured the sequential high-resolution AFM images of poly-Aib deposited on HOPG such that each AFM image partially overlapped with the scan area (100 × 100 nm) in which the helical structures of poly-Aib could be clearly observed. The four or five sequential high-resolution AFM images thus obtained were then overlapped to reconstruct the whole images covering a wider area with maintaining the high-resolution (Supporting Information, Figure S3 and S4).

On the basis of an evaluation of 375 helical-sense blocks between the helical reversals and those between the polymer end and the helical reversal in individual polymer chains in the AFM images including the images in the Supporting Information, Figure S3 and S4, the number-average length of helical blocks ($L_n$) was estimated to be 60 nm, which corresponds to 287 monomer units (Supporting Information, Figure S5). Based on the $L_n$ value, the free energy difference between the helical reversal states ($\Delta G_r$) of poly-Aib was calculated to be approximately 3.4 kcal mol$^{-1}$. Previously, this key free energy ($\Delta G_r$) was experimentally determined to be about 2.5–3.7 kcal mol$^{-1}$ on a monomer-unit basis for helical poly(phenylacetylene)s with different chiral or achiral pendant groups in bulkiness on the basis of the temperature-dependent changes in their CD (circular dichroism) intensities in solution.[20] The estimated $\Delta G_r$ value of poly-Aib in the 2D crystalline state is in fair agreement with those of helical poly(phenylacetylene)s determined in solution. As a consequence, the results revealed a rarely occurring helical reversal along with the long helical blocks with the opposite sense which appeared only once in every 287 monomer units on average in dynamic helical poly-Aib.

We investigated a possibility of spontaneous resolution of dynamically racemic poly-Aib helices into homochiral domains with the same helical sense in the 2D crystals prepared at different temperatures.[21] Careful observations of the AFM images (Figure 2a; Supporting Information S3, S4, and S6) reveal that poly-Aib tends to self-assemble into small domains composed of several helical blocks of the same sense under benzene vapor exposure. However, the average homochiral domain size appears to be small at the macroscopic level.

In conclusion, we have successfully and directly observed the unique structure of a dynamically racemic helical poly(phenylacetylene) on HOPG upon exposure to organic solvent vapors. In particular, the helical reversals along with the long helical blocks with the opposite sense as well as the helical pitch and handedness were clearly visualized for the first time based on the 2D self-assembled helix-bundle formation using AFM with molecular resolution. Poly-Aib forms a lyotropic nematic LC phase in concentrated benzene solution. We anticipate that the nematic LC poly-Aib phase will convert into the cholesteric counterpart by doping with optically active small molecules or helical poly(phenylacetylene)s, such as cholesteric liquid-crystalline poly-L-Ala in solution. The dynamically racemic helical poly-Aib may be transformed into an excess of one helical sense in the cholesteric state, which can be visible and quantified by the change in its helical pitch in the cholesteric liquid crystal and further visualized by high-resolution AFM.[22] The work along this line is now in progress.

Received: April 9, 2007

**Keywords:** chirality · helical structures · scanning probe microscopy · self-assembly · surface analysis

---

[1] a) M. M. Green, N. C. Peterson, T. Sato, A. Teramoto, R. Cook, S. Lifson, *Science* **1995**, *268*, 1860–1866; b) S. H. Gellman, *Acc. Chem. Res.* **1998**, *31*, 173–180; c) P. E. Nielsen, *Acc. Chem. Res.* **1999**, *32*, 624–630; d) T. Nakano, Y. Okamoto, *Chem. Rev.* **2001**, *101*, 4013–4038; e) D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes, J. S. Moore, *Chem. Rev.* **2001**, *101*, 3893–4011; f) J. J. L. M. Cornelissen, A. E. Rowan, R. J. M. Nolte, N. A. J. M. Sommerdijk, *Chem. Rev.* **2001**, *101*, 4039–4070; g) R. Nomura, H. Nakako, T. Masuda, *J. Mol. Catal. A* **2002**, *190*, 197–205; h) M. Fujiki, J. R. Koe, K. Terao, T. Sato, A. Teramoto, J. Watanabe, *Polym. J.* **2003**, *35*, 297–344; i) I. Huc, *Eur. J. Org. Chem.* **2004**, 17–29; j) K. Maeda, E. Yashima, *Top. Curr. Chem.* **2006**, *265*, 47–88.

[2] a) Y. Okamoto, T. Nakano, *Chem. Rev.* **1994**, *94*, 349–372; b) Y. Okamoto, E. Yashima, *Angew. Chem.* **1998**, *110*, 1072–1095; *Angew. Chem. Int. Ed.* **1998**, *37*, 1020–1043; c) E. Yashima, *J. Chromatogr. A* **2001**, *906*, 105–125; d) C. Yamamoto, Y. Okamoto, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 227–257; e) E. Yashima, K. Maeda, T. Nishimura, *Chem. Eur. J.* **2004**, *10*, 42–51; f) M. Reggelin, S. Doerr, M. Klussmann, M. Schultz, M. Holbach, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5461–5466.

[3] a) T. Kanno, H. Tanaka, T. Nakamura, H. Tabata, T. Kawai, *Jpn. J. Appl. Phys.* **1999**, *38*, L606–L607; b) K. Furukawa, K. Ebata, M. Fujiki, *Adv. Mater.* **2000**, *12*, 1033–1036; c) J. J. L. M. Cornelissen, J. J. J. M. Donners, R. de Gelder, W. S. Graswinckel, G. A. Metselaar, A. E. Rowan, N. A. J. M. Sommerdijk, R. J. M. Nolte, *Science* **2001**, *293*, 676–680; d) K. Shinohara, S. Yasuda, G. Kato, M. Fujita, H. Shigekawa, *J. Am. Chem. Soc.* **2001**, *123*, 3619–3620; e) B. S. Li, K. K. L. Cheuk, D. Yang, J. W. Y. Lam, L. J. Wan, C. Bai, B. Z. Tang, *Macromolecules* **2003**, *36*, 5447–5450; f) S.-i. Sakurai, A. Ohira, Y. Suzuki, R. Fujito, T. Nishimura, M. Kunitake, E. Yashima, *J. Polym. Sci. Part A* **2004**, *42*, 4621–4640; g) P. Samorí, H. Engelkamp, P. A. J. de Witte, A. E. Rowan, R. J. M. Nolte, J. P. Rabe, *Adv. Mater.* **2005**, *17*, 1265–1268; h) V. Percec, J. G. Rudick, M. Wagner, M. Obata, C. M. Mitchell, W.-D. Cho, S. N. Magonov, *Macromolecules* **2006**, *39*, 7342–7351. For reviews of single-macromolecule observations by AFM, see: i) A. D. Schlüter, J. P. Rabe, *Angew. Chem.* **2000**, *112*, 860–880; *Angew. Chem. Int. Ed.* **2000**, *39*, 864–883; j) S. S. Sheiko, M. Möller, *Chem. Rev.* **2001**, *101*, 4099–4123; k) S. Minko, Y. Roiter, *Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 9–15; l) P. Samorí, M. Surin, V. Palermo, R. Lazzaroni, P. Leclère, *Phys. Chem. Chem. Phys.* **2006**, *8*, 3927–3938.

[4] a) S.-i. Sakurai, K. Okoshi, J. Kumaki, E. Yashima, *Angew. Chem.* **2006**, *118*, 1267–1270; *Angew. Chem. Int. Ed.* **2006**, *45*, 1245–1248; b) S.-i. Sakurai, K. Okoshi, J. Kumaki, E. Yashima, *J. Am. Chem. Soc.* **2006**, *128*, 5650–5651.

[5] This method is also very useful for constructing highly ordered 2D helix bundles with a controlled helicity for helical polyisocyanides on HOPG; their helical structures were visualized by AFM. T. Kajitani, K. Okoshi, S.-i. Sakurai, J. Kumaki, E. Yashima, *J. Am. Chem. Soc.* **2006**, *128*, 708–709.

[6] Stereoregular (*cis-transoid*) poly-Aib was prepared by the polymerization of the corresponding monomer with a rhodium catalyst in a method similar to that previously reported.[7] The number-average molecular weight ($M_n$) and its molecular weight distribution ($M_w/M_n$; $M_w$ is the weight-average molecular weight) of poly-Aib were $9.05\times10^5$ and 1.48, respectively, as determined by size exclusion chromatography (SEC) equipped with multi-angle light scattering (MALS) and refractive-index detectors in series with polystyrene standards using toluene as the eluent. The *cis-transoidal* structure of poly-Aib was confirmed by laser Raman spectroscopy (Supporting Information).

[7] K. Okoshi, K. Sakajiri, J. Kumaki, E. Yashima, *Macromolecules* **2005**, *38*, 4061–4064.

[8] We also synthesized a copolymer composed of achiral Aib monomer and an optically active L-Ala (the corresponding monomer of poly-L-Ala) by the copolymerization with a rhodium catalyst in THF at 30 °C ([Aib]/[L-Ala] = 75/25 (mol/mol) in feed), and the temperature dependence of the CD spectral changes of the copolymer in THF was preliminary investigated (Figure S8). The magnitude of the CD of the copolymer increased with decreasing temperature, which is consistent with the dynamic helical behavior observed in reported helical poly(phenylacetylene)s,[1j] polyisocyanates,[1a] and polysilanes.[1h]

[9] Although the persistence length is a useful measure to evaluate the stiffness of rodlike helical polymers, published examples are limited to biopolymers,[10a] polyisocyanates,[1a,10b] polysilanes,[1h,10c] and polyisocyanopeptides.[1f,10d] The few reported lengths for helical polyacetylenes are too short to exhibit an LC phase[11] except for poly-L-Ala (126 nm in toluene)[12] and the hydrochloride of poly(4-(*N*,*N*-diisopropylaminomethyl)phenylacetylene; 28 nm in water).[13]

[10] a) T. Sato, A. Teramoto, *Adv. Polym. Sci.* **1996**, *126*, 85–161; b) H. Gu, Y. Nakamura, T. Sato, A. Teramoto, M. M. Green, C. Andreola, *Polymer* **1999**, *40*, 849–856; c) T. Sato, K. Terao, A. Teramoto, M. Fujiki, *Polymer* **2003**, *44*, 5477–5495; d) P. Samorí, C. Ecker, I. Gössl, P. A. J. de Witte, J. J. L. M. Cornelissen, G. A. Metselaar, M. B. J. Otten, A. E. Rowan, R. J. M. Nolte, J. P. Rabe, *Macromolecules* **2002**, *35*, 5290–5294.

[11] a) R. Nomura, J. Tabei, S. Nishiura, T. Masuda, *Macromolecules* **2003**, *36*, 561–564; b) Y. Ashida, T. Sato, K. Morino, K. Maeda, Y. Okamoto, E. Yashima, *Macromolecules* **2003**, *36*, 3345–3350.

[12] K. Okoshi, S.-i. Sakurai, S. Ohsawa, J. Kumaki, E. Yashima, *Angew. Chem.* **2006**, *118*, 8353–8356; *Angew. Chem. Int. Ed.* **2006**, *45*, 8173–8176.

[13] K. Nagai, K. Sakajiri, K. Maeda, K. Okoshi, T. Sato, E. Yashima, *Macromolecules* **2006**, *39*, 5371–5380.

[14] As previously reported for the 2D hierarchical self assembly of analogous poly-L-Ala on HOPG, flat poly-Aib monolayers first form epitaxially on the basal plane of the graphite, on which poly-Aib self-assembles into 2D helix bundles. We note that when poly-Aib has a left-handed helical array of the pendants, the main chain has an opposite, right-handed helical structure.[4]

[15] a) J. L. Baumgarten, *Macromol. Rapid Commun.* **1994**, *15*, 175–182; b) M. M. Green, S. Zanella, H. Gu, T. Sato, G. Gottarelli, S. K. Jha, G. P. Spada, A. M. Schoevaars, B. Feringa, A. Teramoto, *J. Am. Chem. Soc.* **1998**, *120*, 9810–9817.

[16] For helical structures of other polyacetylenes proposed from X-ray analysis, see refs. [4] and [13]. Percec and co-workers recently reported helical structures of cylindrical polyacetylenes with bulky dendrons as the pendants based on X-ray analysis. V. Percec, E. Aqad, M. Peterca, J. G. Rudick, L. Lemon, J. C. Ronda, B. B. De, P. A. Heiney, E. W. Meijer, *J. Am. Chem. Soc.* **2006**, *128*, 16365–16372.

[17] In this way, the helical reversals of poly-Aib can be discriminated from the gap of the two polymer ends (see Supporting Information, Figure S2).

[18] a) S. Lifson, C. Andreola, N. C. Peterson, M. M. Green, *J. Am. Chem. Soc.* **1989**, *111*, 8850–8858; b) M. M. Green, J.-W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger, J. V. Selinger, *Angew. Chem.* **1999**, *111*, 3329–3345; *Angew. Chem. Int. Ed.* **1999**, *38*, 3138–3154.

[19] a) S. A. Prokhorova, S. S. Sheiko, M. Möller, C.-H. Ahn, V. Percec, *Macromol. Rapid Commun.* **1998**, *19*, 359–366; b) H. G. Börner, K. Beers, K. Matyjaszewski, S. S. Sheiko, M. Möller, *Macromolecules* **2001**, *34*, 4375–4383.

[20] K. Morino, K. Maeda, Y. Okamoto, E. Yashima, T. Sato, *Chem. Eur. J.* **2002**, *8*, 5112–5120.

[21] For recent reviews of 2D spontaneous resolution on substrates, see: a) L. C. Giancarlo, G. W. Flynn, *Acc. Chem. Res.* **2000**, *33*, 491–501; b) S. De Feyter, A. Gesquière, M. M. Abdel-Mottaleb, P. C. M. Grim, F. C. De Schryver, C. Meiners, M. Sieffert, S. Valiyaveettil, K. Müllen, *Acc. Chem. Res.* **2000**, *33*, 520–531; c) L. P. -García, D. B. Amabilino, *Chem. Soc. Rev.* **2002**, *31*, 342–356; d) S. De Feyter, F. C. De Schryver, *Chem. Soc. Rev.* **2003**, *32*, 139–150; e) S. M. Barlow, R. Raval, *Surf. Sci. Rep.* **2003**, *50*, 201–341.

[22] Preliminary experiments showed that a concentrated nematic poly-Aib solution in benzene brought about a fingerprint texture typical of the cholesteric LC state in the presence of poly-L-Ala (total polymer concentration = 20 wt% and [poly-L-Ala]/[poly-L-Ala + poly-Aib] = 10 wt/wt).