

## Hierarchical Amplification of Macromolecular Helicity of Dynamic Helical Poly(phenylacetylene)s Composed of Chiral and Achiral Phenylacetylenes in Dilute Solution, Liquid Crystal, and Two-Dimensional Crystal

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**Abstract:** Optically active poly(phenylacetylene) copolymers consisting of optically active and achiral phenylacetylenes bearing L-alanine decyl esters (**1L**) and 2-aminoisobutylic acid decyl esters (**Aib**) as the pendant groups (poly(**1L**<sub>m</sub>-co-**Aib**<sub>n</sub>)) with various compositions were synthesized by the copolymerization of the optically active **1L** with achiral **Aib** using a rhodium catalyst, and their chiral amplification of the macromolecular helicity in a dilute solution, a lyotropic liquid crystalline (LC) state, and a two-dimensional (2D) crystal on the substrate was investigated by measuring the circular dichroism of the copolymers, mesoscopic cholesteric twist in the LC state (cholesteric helical pitch), and high-resolution atomic force microscopy (AFM) images of the self-assembled 2D helix-bundles of the copolymer chains. We found that the macromolecular helicity of poly(**1L**<sub>m</sub>-co-**Aib**<sub>n</sub>)s could be hierarchically amplified in the order of the dilute solution, LC state, and 2D crystal. In sharp contrast, almost no chiral amplification of the macromolecular helicity was observed for the homopolymer mixtures of **1L** and **Aib** in the LC state and 2D crystal on graphite.

### Introduction

Chiral amplification is a unique and significantly interesting phenomenon in connection with not only the origin of homochirality in biological macromolecules<sup>1</sup> but also the development of ideal methods to produce optically active compounds.<sup>2</sup> Pioneering work on the chiral amplification of synthetic helical polymers in dilute solutions was achieved using polyisocyanates

by Green and co-workers.<sup>1a,b,3</sup> Polyisocyanates are typically stiff and dynamic helical polymers,<sup>1a,b,3,4</sup> consisting of interconvertible right- and left-handed helical conformations separated by rarely occurring helical reversals. Because of very small helix inversion barriers in dynamic helical polyisocyanates, the copolymerization of achiral isocyanates with a small amount of optically active ones or the copolymerization of nonracemic isocyanates with a small enantiomeric excess (ee) can produce

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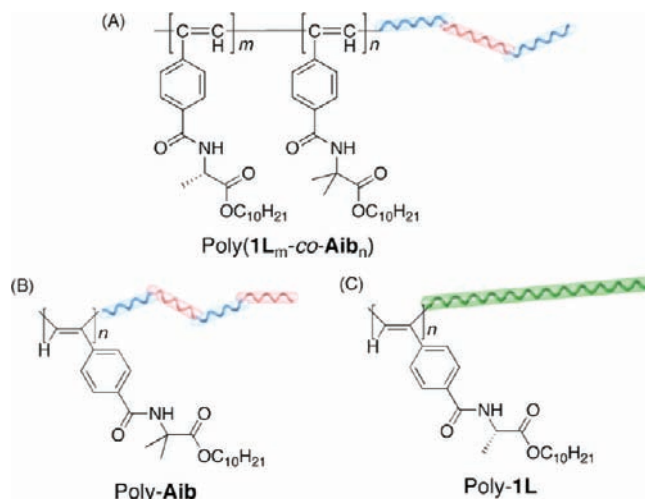
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optically active polyisocyanates with a greater excess of single-handed helical conformation. Green et al. termed these highly cooperative processes the “sergeants and soldiers effect”<sup>3a</sup> and “majority rule”,<sup>3b</sup> respectively. They extended the chiral amplification principle to liquid crystalline (LC) systems, and discovered the chiral amplification of helical polyisocyanates in liquid crystals, resulting in a further increase in the helical sense excess of the polyisocyanates than that in a dilute solution due to the reduction in population of the energetically unfavorable, kinked helical reversals in the LC state.<sup>3c</sup>

We previously reported a similar, but noncovalent, hierarchical amplification of the macromolecular helicity of a positively charged poly(phenylacetylene), the hydrochloride of poly(4-(*N,N*-diisopropylaminomethyl)phenylacetylene), in water. The macromolecular helicity with an excess single-handed helix was first induced in the positively charged poly(phenylacetylene) upon complexation with an oppositely charged nonracemic acid as a dopant through electrostatic interaction in dilute water, thus showing an induced circular dichroism (ICD) in the polymer backbone region.<sup>5</sup> Subsequently, the macromolecular helicity was further amplified in the polymer backbone as a greater excess of a single-handed helix through self-assembly into a lyotropic cholesteric liquid crystal<sup>5a,c</sup> as observed in the polyisocyanates by Green et al.<sup>3c</sup>

We also reported the first helical poly(phenylacetylene)s bearing L- or D-alanine pendants with a long *n*-decyl chain as the pendants (poly-**1L** and poly-**1D**, respectively) that showed cholesteric LC phases in organic solvents.<sup>6</sup> Interestingly, the cholesteric twist sense in the LC phases of the polymers was inverted in response to the solvent polarity derived from inversion of the macromolecular helicity of the polymer chain, resulting from the “on and off” fashion of the intramolecular hydrogen bonding networks in nonpolar and polar solvents, respectively.<sup>6,7</sup> In addition, we recently found that the rigid rodlike helical poly-**1L** and poly-**1D** hierarchically self-assembled on highly oriented pyrolytic graphite (HOPG) upon exposure to organic solvent vapors such as benzene; flat poly(phenylacetylene) monolayers epitaxially formed on the basal plane of the graphite, on which the helical poly(phenylacetylene)s further self-assembled into chiral two-dimensional



**Figure 1.** Structures of poly(**1L<sub>m</sub>-co-Aib<sub>n</sub>**) (A), poly-**Aib** (B) (left- (blue) and right-handed (red) helical segments), and poly-**1L** (C) (left-handed helix (green)).

(2D) helix-bundles with a controlled helicity.<sup>8</sup> High-resolution atomic force microscopy (AFM) revealed their helical conformations in the 2D crystals and enabled us to determine the molecular packing, helical pitch, and handedness.<sup>8,9</sup>

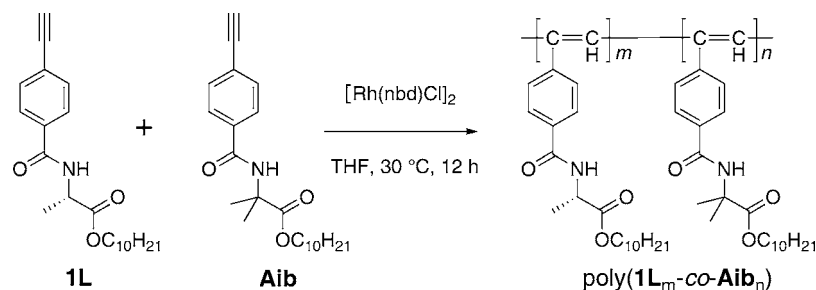
On the basis of these observations, we report the synthesis of a series of dynamic helical poly(phenylacetylene) copolymers (poly(**1L<sub>m</sub>-co-Aib<sub>n</sub>**)) consisting of optically active and achiral phenylacetylenes with L-alanine decyl esters (**1L**) and 2-aminoisobutylic acid decyl esters (**Aib**) as the pendant groups, and their chiral amplification of macromolecular helicity in a dilute solution, a lyotropic LC state, and a 2D crystal on a substrate was investigated by measuring the circular dichroism (CD) of the copolymer backbones, mesoscopic cholesteric twist in the LC state, and high-resolution AFM images of the self-assembled 2D helix-bundles of the copolymer chains (Figure 1A). The chiral amplification of macromolecular helicity for the mixtures of the homopolymers of **Aib** (poly-**Aib**) and **1L** (poly-**1L**) in the LC state and 2D crystal on graphite was also investigated (Figure 1B and 1C, respectively) and the mechanism of hierarchical amplification of the macromolecular helicity was discussed.

## Results and Discussion

The optically active poly(phenylacetylene) copolymers (poly(**1L<sub>m</sub>-co-Aib<sub>n</sub>**)) with various compositions were prepared by the

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Scheme 1. Synthesis of Poly( $\mathbf{1L}_m$ -co- $\mathbf{Aib}_n$ )

copolymerization of the enantiomerically pure  $\mathbf{1L}$  and achiral  $\mathbf{Aib}$  with different feed monomer ratios using a rhodium complex  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  (nbd = norbornadiene) in tetrahydrofuran (THF) according to a previously reported method (Scheme 1).<sup>6,9b</sup> All copolymers were obtained in high yield (>80%) with relatively high molecular weights ( $M_n = 9.3\text{--}18.1 \times 10^4$ ) and were soluble in most common organic solvents, such as benzene, toluene, THF,  $\text{CHCl}_3$ , and  $\text{CCl}_4$ . The copolymer compositions were estimated by their  $^1\text{H}$  NMR spectra, which were nearly in accordance with those in feed. Their stereoregularities were confirmed to be predominantly cis–transoidal on the basis of their characteristic laser Raman spectra (Figure S1, Supporting Information).<sup>10</sup> The copolymerization results are summarized in Table 1. The homopolymers poly- $\mathbf{Aib}$  and poly- $\mathbf{1L}$  were also synthesized in the same way (runs 1 and 8 in Table 1, respectively).<sup>6,9b</sup>

The chiroptical properties of poly( $\mathbf{1L}_m$ -co- $\mathbf{Aib}_n$ ) and poly- $\mathbf{1L}$  were first investigated in dilute toluene and benzene solutions at different temperatures. Figure 2A shows the CD and absorption spectra of poly( $\mathbf{1L}_m$ -co- $\mathbf{Aib}_n$ ) and poly- $\mathbf{1L}$  in toluene at  $-20$  °C. Unexpectedly, the copolymers exhibited a very weak ICD independent of the content of the  $\mathbf{1L}$  units in the copolymers in the  $\pi$ -conjugated polymer backbone regions at  $-20$  °C and even at  $-60$  °C (Figure S2B, Supporting Information). Moreover, the absorption and CD spectral patterns were completely different from those of the previously prepared, analogous helical poly(phenylacetylene)s bearing chiral bulky substituents.<sup>11</sup> In contrast, poly- $\mathbf{1L}$  showed a significant increase of the ICD intensity with the decreasing temperature accompanied by a large red-shift in the absorption spectra (Figure S2A, Supporting Information). Similar unusual variable-temperature CD and absorption spectra were observed for poly( $\mathbf{1L}_m$ -co- $\mathbf{Aib}_n$ ) and poly- $\mathbf{1L}$  in benzene (Figure S3, Supporting Information). These results suggested that the chirality of the pendant L-alanine residues ( $\mathbf{1L}$  units) may not be transferred in dynamically racemic helical segments composed of achiral  $\mathbf{Aib}$  units in dilute toluene and benzene solutions even at low

temperatures, resulting in poor amplification of the helical chirality (Figure 2C (red line) and Figure S3B (green and red lines)).

First, we anticipated a significant amplification of the helical chirality (positive nonlinear effect) that would take place in poly( $\mathbf{1L}_m$ -co- $\mathbf{Aib}_n$ ) because the homopolymer of  $\mathbf{Aib}$  (poly- $\mathbf{Aib}$ ) is a rigid rodlike helical polymer and showed a lyotropic nematic LC phase in concentrated toluene solution (see below) and its persistent length estimated in a dilute toluene solution was extremely high (89.6 nm) at 25 °C.<sup>9b</sup> In addition, the number-average length of the helical blocks (right- or left-handed helical segments) estimated by direct AFM observations of individual polymer chains was 60 nm, which corresponds to 287 monomer units.<sup>9b</sup> Therefore, unexpectedly, no chiral amplification in the poly( $\mathbf{1L}_m$ -co- $\mathbf{Aib}_n$ ) may be ascribed to the L-alanine residues whose helical sense bias may be too weak to induce an excess of the one-handed helix in the neighboring achiral  $\mathbf{Aib}$  units in dilute benzene and toluene solutions.<sup>12</sup>

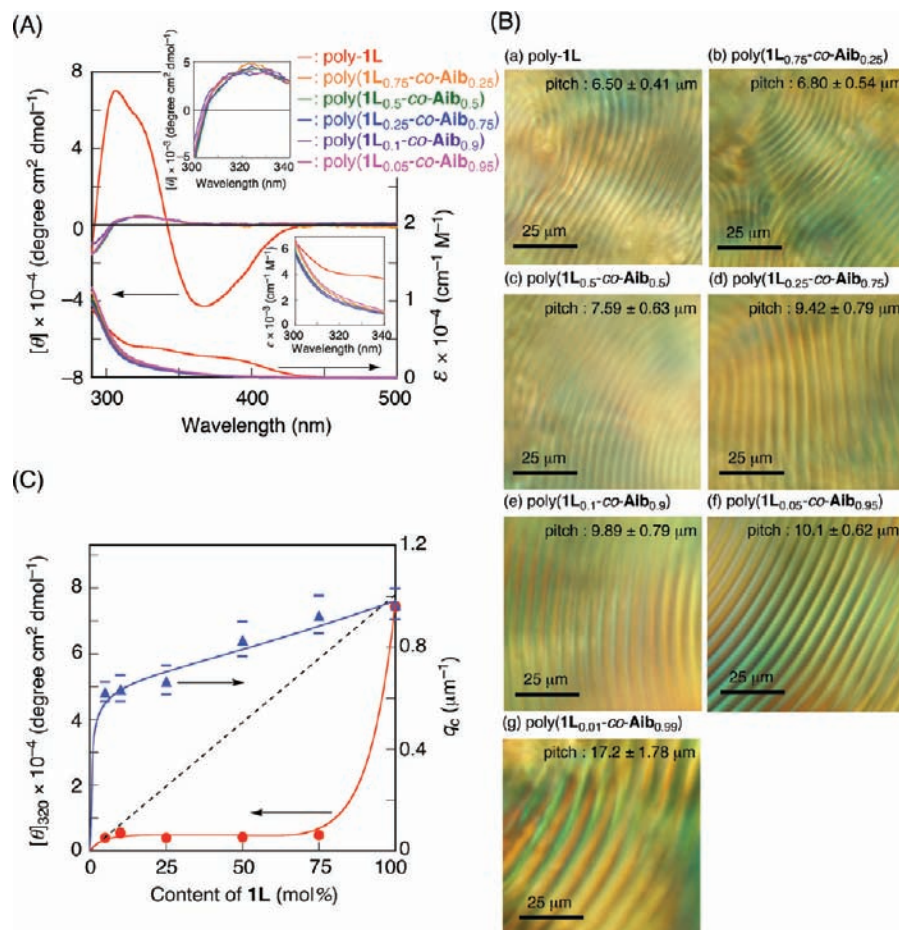
We then further investigated the effects of the solvent and temperature on the chiroptical properties of poly( $\mathbf{1L}_m$ -co- $\mathbf{Aib}_n$ ) and poly- $\mathbf{1L}$ , because as previously reported, the homopolymer poly- $\mathbf{1L}$  is sensitive to the solvent polarity and showed inversion of the helical sense of the polymer backbone resulting from the “on and off” fashion of the intramolecular hydrogen bonding networks in polar and nonpolar solvents. These changes in the helical sense inversion were accompanied by a remarkable change in the main-chain stiffness (persistent length).<sup>6b</sup> In nonpolar  $\text{CCl}_4$  and polar THF at 25 °C, a similar tendency was observed, but poly( $\mathbf{1L}_{0.75}$ -co- $\mathbf{Aib}_{0.25}$ ) showed as an intense CD as that of poly- $\mathbf{1L}$  in  $\text{CCl}_4$  at 0 and  $-10$  °C (Figure S4A–C, Supporting Information) and further dramatic increases in the ICD intensities were observed for most of the copolymers in THF at lower temperatures (Figure S5A–D, Supporting Information), leading to a positive nonlinear effect at  $-60$  and  $-100$  °C (Figure S5E). These variable-temperature CD spectral changes were accompanied by a significant change in their absorption spectra as observed for poly- $\mathbf{1L}$  in toluene (Figure

Table 1. Copolymerization Results of  $\mathbf{1L}$  and  $\mathbf{Aib}$  with  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  in THF at 30 °C for 12 h<sup>a</sup>

run	$\mathbf{1L}$ (mol %)	$\mathbf{Aib}$ (mol %)	copolymer				
			sample code	yield (%) <sup>b</sup>	$\mathbf{1L}$ (mol %) <sup>c</sup>	$M_n \times 10^{-4}$ <sup>d</sup>	$M_w/M_n$ <sup>d</sup>
1	0	100	poly- $\mathbf{Aib}$	98	0	28.9	3.8
2	1	99	poly( $\mathbf{1L}_{0.01}$ -co- $\mathbf{Aib}_{0.99}$ )	83	—	9.3	6.6
3	5	95	poly( $\mathbf{1L}_{0.05}$ -co- $\mathbf{Aib}_{0.95}$ )	83	4.7	9.6	6.5
4	10	90	poly( $\mathbf{1L}_{0.1}$ -co- $\mathbf{Aib}_{0.9}$ )	88	7.7	13.4	5.3
5	25	75	poly( $\mathbf{1L}_{0.25}$ -co- $\mathbf{Aib}_{0.75}$ )	83	30	16.2	5.1
6	50	50	poly( $\mathbf{1L}_{0.5}$ -co- $\mathbf{Aib}_{0.5}$ )	91	43	18.1	4.4
7	75	25	poly( $\mathbf{1L}_{0.75}$ -co- $\mathbf{Aib}_{0.25}$ )	90	76	15.7	6.8
8	100	0	poly- $\mathbf{1L}$	98	100	43.7	4.1

<sup>a</sup> [Monomer] = 0.5 M,  $[\text{Rh}(\text{nbd})\text{Cl}]_2$  = 0.0025 M. <sup>b</sup> Methanol-insoluble fraction. <sup>c</sup> Estimated by  $^1\text{H}$  NMR. <sup>d</sup> Determined by SEC using polystyrene standards.





**Figure 2.** (A) CD and absorption spectra of poly(**1L**<sub>0.05</sub>-co-**Aib**<sub>0.95</sub>) (pink lines), poly(**1L**<sub>0.1</sub>-co-**Aib**<sub>0.9</sub>) (purple lines), poly(**1L**<sub>0.25</sub>-co-**Aib**<sub>0.75</sub>) (blue lines), poly(**1L**<sub>0.5</sub>-co-**Aib**<sub>0.5</sub>) (green lines), poly(**1L**<sub>0.75</sub>-co-**Aib**<sub>0.25</sub>) (orange lines), and poly-**1L** (red lines) in dilute toluene solutions (0.06 mg/mL) at  $-20^{\circ}\text{C}$ . (B) Polarized optical micrographs of cholesteric LC phases of poly-**1L** (a), poly(**1L**<sub>0.75</sub>-co-**Aib**<sub>0.25</sub>) (b), poly(**1L**<sub>0.5</sub>-co-**Aib**<sub>0.5</sub>) (c), poly(**1L**<sub>0.25</sub>-co-**Aib**<sub>0.75</sub>) (d), poly(**1L**<sub>0.1</sub>-co-**Aib**<sub>0.9</sub>) (e), poly(**1L**<sub>0.05</sub>-co-**Aib**<sub>0.95</sub>) (f), and poly(**1L**<sub>0.01</sub>-co-**Aib**<sub>0.99</sub>) (g) in 20 wt % toluene solutions taken at ambient temperature (ca.  $25^{\circ}\text{C}$ ). (C) Changes in the CD intensity at ca. 320 nm and the cholesteric wavenumber ( $q_c$ ) of poly(**1L**<sub>*m*</sub>-co-**Aib**<sub>*n*</sub>) versus the content of **1L** units in dilute toluene solutions at  $-20^{\circ}\text{C}$  and concentrated toluene solutions at  $25^{\circ}\text{C}$ , respectively. The error bars represent the standard deviation estimated by an evaluation of ca. 30 fingerprint spacings.

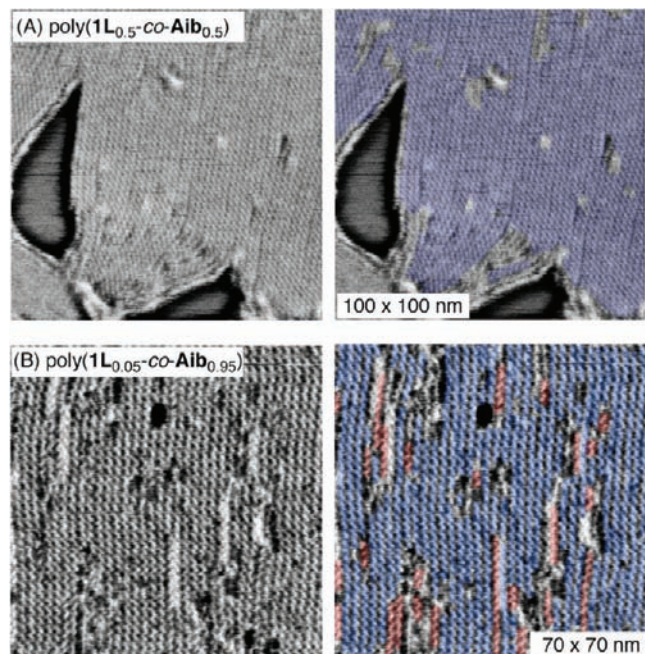
S2A). In addition, the Cotton effect patterns of poly(**1L**<sub>*m*</sub>-co-**Aib**<sub>*n*</sub>) in  $\text{CCl}_4$  at 0 and  $-10^{\circ}\text{C}$  are almost mirror images to those in THF at low temperatures, indicating the inversion of the helicity of the copolymer backbones that took place induced by the solvent polarity as reported previously for poly-**1L**.<sup>6b,7</sup>

These results suggest that the dynamic helical conformations of poly(**1L**<sub>*m*</sub>-co-**Aib**<sub>*n*</sub>) and their predominant helical senses are very sensitive to the solvent polarity and temperature and are most likely governed by delicate interactions between the chiral and achiral pendant groups and also with the solvent molecules.<sup>11c</sup>

We next investigated if the macromolecular helicity of poly(**1L**<sub>*m*</sub>-co-**Aib**<sub>*n*</sub>) in a dilute solution could be amplified in the lyotropic cholesteric LC state as observed for polyisocyanates consisting of chiral and achiral isocyanates. As previously reported, the poly-**1L** and poly-**Aib** homopolymers formed cholesteric and nematic LC phases in concentrated solutions, respectively.<sup>6,9b</sup> We found that poly(**1L**<sub>*m*</sub>-co-**Aib**<sub>*n*</sub>) also formed similar cholesteric LC phases in concentrated toluene and  $\text{CCl}_4$  solutions. Figure 2B shows the optical micrographs of poly(**1L**<sub>*m*</sub>-co-**Aib**<sub>*n*</sub>) and poly-**1L** in concentrated toluene solutions (20 wt %) at ca.  $25^{\circ}\text{C}$ . All copolymers and homopolymers showed a fingerprint texture typical of the cholesteric LC phases, in which the spacing of the fringes defines half of the cholesteric pitch ( $p$ ) and a smaller pitch represents an increased preference of the one helical sense in the cholesteric phase.<sup>3c,13</sup> The plots of

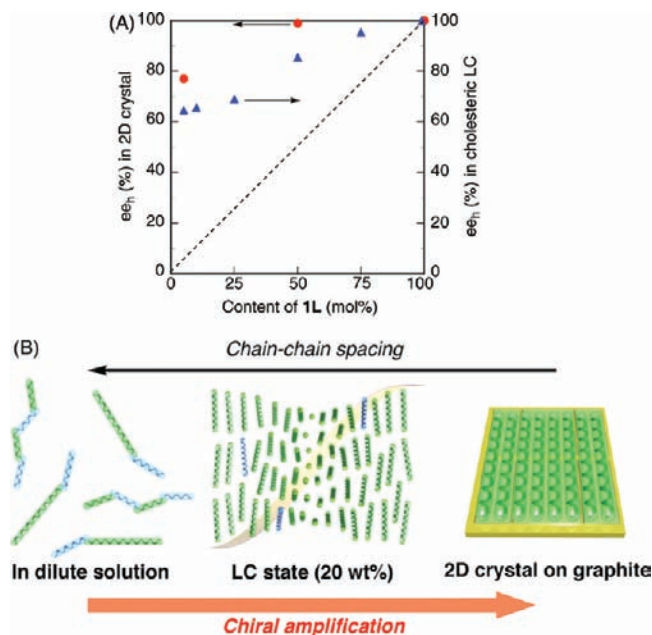
- (11) (a) Yashima, E.; Huang, S.; Matsushima, T.; Okamoto, Y. *Macromolecules* **1995**, *28*, 4184–4193. (b) Nomura, R.; Fukushima, Y.; Nakako, H.; Masuda, T. *J. Am. Chem. Soc.* **2000**, *122*, 8830–8836. (c) Morino, K.; Maeda, K.; Okamoto, Y.; Yashima, E.; Sato, T. *Chem.—Eur. J.* **2002**, *8*, 5112–5120. (d) Percec, V.; Aqad, E.; Peterca, M.; Rudick, J. G.; Lemon, L.; Ronda, J. C.; De, B. B.; Heiney, P. A.; Meijer, E. W. *J. Am. Chem. Soc.* **2006**, *128*, 16365–16372. (e) Rudick, J. G.; Percec, V. *New J. Chem.* **2007**, *31*, 1083–1096. (f) Jia, H.; Teraguchi, M.; Aoki, T.; Abe, Y.; Kaneko, T.; Hadano, S.; Namikoshi, T.; Marwanta, E. *Macromolecules* **2009**, *42*, 17–19.
- (12) In general, if chiral/achiral helical copolymers exhibit a measurable absorption and CD spectral change depending on the content of the chiral units resulting from a conformational change, it is difficult to determine their handedness and to quantify their helical sense excesses on the basis of the Cotton effect intensity of the optically pure homopolymer. In the present case, we presume that the copolymers, poly(**1L**<sub>*m*</sub>-co-**Aib**<sub>*n*</sub>), may possess a helical conformation different from that of the poly-**1L** in toluene and benzene at low temperatures, but with a negligibly small helical sense excess, thus showing very weak ICDs. This speculation is supported by the facts that the poly-**Aib** and poly-**1L** possess rigid rodlike features in dilute toluene because their persistent lengths estimated in dilute toluene are extremely high, 126 and 89.6 nm at  $25^{\circ}\text{C}$ , respectively.<sup>6b,9b</sup>

- (13) Chandrasekaran, S. *Liquid Crystals*, 2nd ed.; Cambridge University Press: Cambridge, 1992; Chapter 4.



**Figure 3.** AFM phase images of 2D self-assembled poly( $\mathbf{1L}_{0.5}\text{-co-Aib}_{0.5}$ ) (A) and poly( $\mathbf{1L}_{0.05}\text{-co-Aib}_{0.95}$ ) (B) cast from dilute toluene solutions on HOPG [copolymer] = 0.005 mg/mL). The polymer strands with clearly identifiable left- and right-handed helical blocks are shown in blue and red colors, respectively (right). Unidentifiable strands are uncolored (black and white).

the cholesteric wavenumber  $q_c$ , defined by  $2\pi/p$  versus the content of the  $\mathbf{1L}$  units in the copolymers are shown in Figure 2C (blue line). The  $q_c$  value of the helical polymer solutions strongly depends on the polymer concentration, temperature, and the solvent. If the solution contains enantiomers, i.e., the right- and left-handed helices,  $q_c$  also depends on the excess of the one helical sense.<sup>3c,5a,c</sup> Under the constant polymer concentration of 20 wt % in toluene at ca. 25 °C, the  $q_c$  value of the copolymers was found to increase with the increasing  $\mathbf{1L}$  units of the copolymers, in which a larger  $q_c$  value indicates an increased preference of the one helical sense, and the copolymers with  $\mathbf{1L}$  unit contents lower than 75% exhibited a  $q_c$  value larger than that expected from the content of the  $\mathbf{1L}$  units, resulting in a positive nonlinear effect (see the blue line in Figure 2C). This noticeable positive nonlinear effect indicates a significant amplification of the helical sense excess in the LC state, whereas in the dilute toluene solution, chiral information of the pendant  $\mathbf{1L}$  units covalently bonded to the copolymer backbone was hardly transformed into a polymer chain (Figure 2C, red line). This remarkable chiral amplification in the LC state over a dilute toluene solution may be caused by favorable interchain interactions between the poly( $\mathbf{1L}_m\text{-co-Aib}_n$ ) chains or the reduction in population of the helical reversals along the copolymer chains accompanied by a conformation change, because the kinked helical reversals likely disturb the close parallel packing of the dynamic helical copolymer chains in the LC state as proposed for the chiral amplification of polyisocyanates in the LC state,<sup>3c,e,5c</sup> although the reason for such a unique solvent effect observed in toluene on the chiral amplification phenomena in the LC and dilute solutions remains unsolved. Using the maximum  $q_c$  value of  $0.94 \mu\text{m}^{-1}$  for the poly- $\mathbf{1L}$  as the base value, the helical sense excess ( $ee_h$ ) of poly( $\mathbf{1L}_m\text{-co-Aib}_n$ ) in concentrated LC toluene solutions can be calculated (Figure 4A). A similar strong amplification of the macromolecular helicity



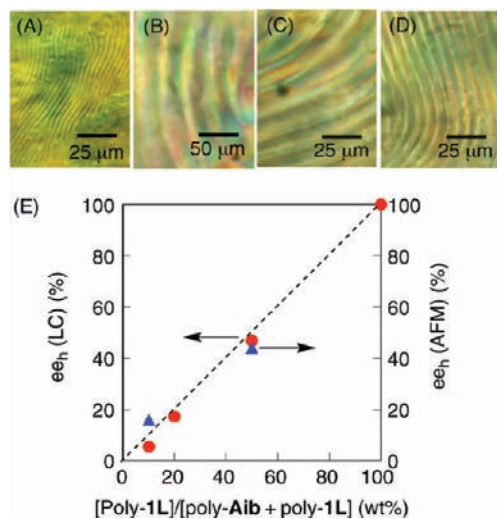
**Figure 4.** (A) Plots of the  $ee_h$  values of poly( $\mathbf{1L}_m\text{-co-Aib}_n$ ) versus the content of  $\mathbf{1L}$  units in the cholesteric LC state in toluene (triangles) and 2D crystals (circles). The  $ee_h$  values of poly( $\mathbf{1L}_m\text{-co-Aib}_n$ ) in concentrated LC solutions were calculated using the maximum  $q_c$  value of  $0.94 \mu\text{m}^{-1}$  as the base value. On the basis of an evaluation of ca. 1000 helical blocks, the  $ee_h$  values of poly( $\mathbf{1L}_m\text{-co-Aib}_n$ ) in the 2D crystals were estimated by AFM. (B) Schematic illustration of hierarchical chiral amplification of macromolecular helicity of poly( $\mathbf{1L}_m\text{-co-Aib}_n$ ). Excess of one-handed helical sense (right- or left-handed helix) of poly( $\mathbf{1L}_m\text{-co-Aib}_n$ ) is significantly amplified in the LC state and further amplified in the 2D crystal, resulting from a cholesteric LC and 2D helix-bundle formation, respectively.

of poly( $\mathbf{1L}_m\text{-co-Aib}_n$ ) in the LC state over that in a dilute solution was observed in concentrated  $\text{CCl}_4$  solutions (Figures S4D and S4E).

We then investigated the  $ee_h$  values of poly( $\mathbf{1L}_m\text{-co-Aib}_n$ ) by directly measuring the AFM images of the self-assembled 2D helix-bundles of the copolymer chains on HOPG. Figure 3 shows the AFM phase images of poly( $\mathbf{1L}_{0.5}\text{-co-Aib}_{0.5}$ ) and poly( $\mathbf{1L}_{0.05}\text{-co-Aib}_{0.95}$ ) deposited on HOPG from a dilute toluene solution (0.005 mg/mL), followed by toluene vapor exposure at ca. 25 °C for 12 h in a way similar to that previously reported.<sup>8,9</sup> The copolymers self-assembled into well-defined 2D helix-bundles with a constant height (ca. 1.6 nm), and the copolymer chains were closely packed parallel to each other. These AFM images provide the possible helical pitch, helical sense, and molecular arrangements of the copolymers. Unfortunately, the helical structures of the other copolymers could not be clearly observed by AFM. Careful observations of the AFM images of the copolymers in Figure 3 indicated that the copolymers predominantly possess the left-handed helical array of the pendants, which fairly agreed with the previous AFM observation results of the poly- $\mathbf{1L}$ , although the opposite right-handed helical segments were visualized in part in the AFM image of poly( $\mathbf{1L}_{0.05}\text{-co-Aib}_{0.95}$ ) (red colors in Figure 3B (right)). On the basis of an evaluation of ca. 1000 helical blocks, the helical sense excess (%  $ee_h$ ) of poly( $\mathbf{1L}_{0.5}\text{-co-Aib}_{0.5}$ ) and poly( $\mathbf{1L}_{0.05}\text{-co-Aib}_{0.95}$ ) were estimated to be >99% and 77%, respectively.

Figure 4A shows the relationships between the  $ee_h$  values of poly( $\mathbf{1L}_m\text{-co-Aib}_n$ ) estimated in the cholesteric LC state and 2D crystals versus the content of the  $\mathbf{1L}$  units of the copolymers. The helical sense excesses of the copolymers in the 2D crystals



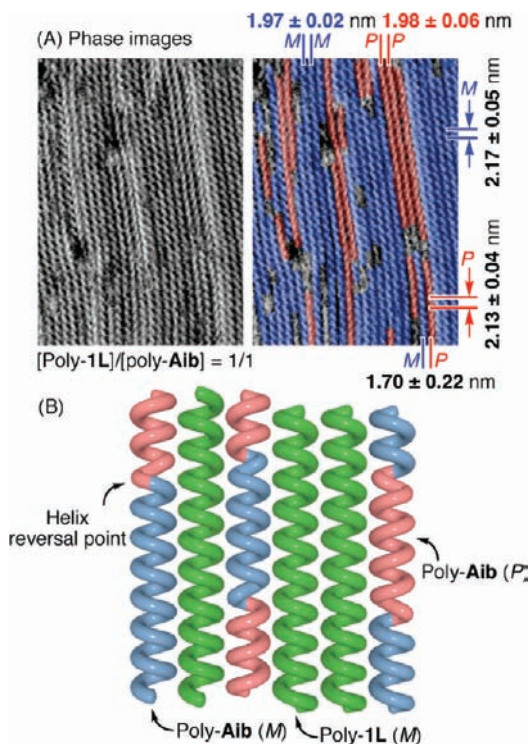


**Figure 5.** Polarized optical micrographs of cholesteric LC phases of poly-1L (A) and poly-Aib-poly-1L mixtures (B–D) in benzene. [Polymer] = 20 wt %; [poly-1L]/[poly-Aib] = 1/9 (B), 2/8 (C), and 1/1 (D) (w/w). (E) Changes in the calculated and observed  $ee_h$  values of the mixtures of poly-1L and poly-Aib in the cholesteric LC state (circles) and 2D crystal state (triangles), respectively, versus the wt% of poly-1L. The  $ee_h$  values in the cholesteric LC state were calculated using the maximum  $q_c$  value of 1.12 for poly-1L in benzene (20 wt %) (A) as the base value. The  $ee_h$  values in the 2D crystal state were estimated based on the helical sense excesses of helical blocks on HOPG observed in the high-resolution AFM images (see Figures 6 and S7).

are significantly out of proportion to the content of the 1L units, showing a greater excess of a single-handed helix through self-assemblies in the 2D crystals (“sergeants and soldiers effect”) over those in the cholesteric LC state. This additional chiral amplification in the 2D crystals may be ascribed to the further close interchain interactions between the poly(1L<sub>m</sub>-co-Aib<sub>n</sub>) chains or further reduction in the population of the helical reversals between the interconvertible right- and left-handed helical blocks of the poly(1L<sub>m</sub>-co-Aib<sub>n</sub>) chains over the LC state.

In order to elucidate the hierarchical chiral amplification mechanism of poly(1L<sub>m</sub>-co-Aib<sub>n</sub>), we investigated if a similar chiral amplification of the macromolecular helicity was possible for the mixtures of the corresponding homopolymers poly-1L and poly-Aib in the cholesteric LC state and 2D crystal. As previously mentioned, poly-Aib forms a lyotropic nematic LC phase in concentrated benzene solution.<sup>9b</sup> We anticipated that the nematic LC poly-Aib phase would convert to the cholesteric counterpart by doping with the optically active, cholesteric LC poly-1L in solution, since the dynamically racemic helical poly-Aib may be transformed into an excess of the one helical sense in the cholesteric state, which can be visible and quantified by the change in its helical pitch in the cholesteric LC state and further visualized by high-resolution AFM.

Figure 5A–D shows the polarized optical micrographs of the poly-1L-poly-Aib mixtures with different ratios in concentrated benzene solutions (20 wt %) at ca. 25 °C. All of the homopolymer mixtures also showed a fingerprint texture typical of the cholesteric LC phases in concentrated benzene solutions. The plots of the  $ee_h$  values of the poly-1L-poly-Aib mixtures estimated from the cholesteric wavenumbers ( $q_c$ ) of the mixtures versus the amounts of poly-1L in the mixtures (wt%) showed a linear relationship between them (Figure 5E, red circles), indicating that almost no chiral amplification of the macromolecular helicity took place for the homopolymer mixtures in the



**Figure 6.** (A) AFM phase images of a poly-Aib-poly-1L mixture cast from a dilute benzene solution on HOPG ([polymer] = 0.005 mg/mL, [poly-1L]/[poly-Aib] = 1/1 (w/w)). The polymer strands with clearly identifiable right- and left-handed helices are shown in red and blue, respectively (right). Unidentifiable strands are uncolored (black and white). Scale = 50 × 70 nm. (B) Schematic drawings of the possible arrangements of right- and left-handed helical segments of a poly-Aib and poly-1L mixture in the 2D crystals. Red and blue helical segments represent the right- (P) and left-handed (M) helical poly-Aib and green helical segments stand for the left-handed helical poly-1L. For AFM height and phase images of a poly-Aib-poly-1L mixture ([poly-1L]/[poly-Aib] = 1/1), see Figure S8.

LC state. A similar tendency was also observed in toluene (Figure S6, Supporting Information).

The helical structures of the poly-1L-poly-Aib mixtures in the 2D crystals on HOPG were then observed by AFM. Figures 6A and S7 show the typical AFM images of the poly-1L-poly-Aib mixtures ([poly-1L]/[poly-Aib] = 1/1 or 1/9 (w/w)) deposited on HOPG from dilute benzene solutions (0.005 mg/mL), followed by benzene vapor exposure at ca. 25 °C for 12 h. The polymer strands with right- (red) and left-handed (blue) helices are clearly visualized by AFM, and the left-handed helices were found to be predominant in the 2D crystals of the homopolymer mixtures (Figures 6A and S7 (right)). On the basis of these high-resolution AFM images, the  $ee_h$  values of the poly-1L-poly-Aib mixtures were then estimated in the same way (see Figure 4A), and these values were plotted versus the amounts of poly-1L (blue triangles in Figure 5E). The observed linear relationship between the helical sense excesses of the poly-1L-poly-Aib mixtures and the amounts of poly-1L clearly indicated that no chiral amplification of the macromolecular helicity occurred in the 2D crystals nor in the LC state. In other words, the chiral information of poly-1L with a preferred-handed helix-sense was hardly transferred to the neighboring dynamically racemic helical poly-Aib strands even in the 2D crystals as well as in the LC state. Therefore, it is reasonable to conclude that the left-handed helical segments observed in the 2D crystals likely consist of left-handed helical poly-1L and poly-Aib blocks, and the opposite right-handed helical segments are

mainly composed of right-handed helical poly-**Aib** blocks (Figure 6). This conclusion is supported by the fact that poly-**1L** formed left-handed helix-bundles on HOPG as deposited from a dilute benzene solution.<sup>8</sup> These results indicate that the dominant driving force behind the hierarchical amplification of the helical chirality observed for the copolymers poly(**1L<sub>m</sub>-co-Aib<sub>n</sub>**) in the LC and 2D crystal states is most likely the reduction in population of the helical reversals along the polymer chains.<sup>5c,5e</sup> The long decyl alkyl chains attached at the pendant groups of the copolymers and also of the homopolymers may interfere with the favorable close packing of neighboring helical polymer chains with a specific handedness, so that the helical chirality could not be efficiently transferred through interchain interactions.

In summary, we have demonstrated the hierarchical amplification of the macromolecular helicity of dynamic helical poly(phenylacetylene)s bearing optically active and achiral residues as the pendants groups in the cholesteric LC state and 2D crystals. It was found that the macromolecular helicity of the poly(**1L<sub>m</sub>-co-Aib<sub>n</sub>**)s was more efficiently amplified in the LC state than in a dilute solution and further in the 2D crystals. In sharp contrast, however, almost no chiral amplification in the macromolecular helicity was observed for the mixtures of

the corresponding homopolymers of **1L** and **Aib** in the LC state and 2D crystal on graphite. We emphasize that the hierarchical amplification of the macromolecular helicity is, for the first time, unambiguously revealed by the direct observations of helical structures by high-resolution AFM. The present results will provide useful information for understanding the amplification mechanism of the macromolecular helicity in other dynamic helical polymers at the molecular level not only in solution but also in the LC and solid states,<sup>14</sup> as well as for designing novel liquid crystalline helical poly(phenylacetylene)s with a controlled helix-sense together with specific functions.

**Supporting Information Available:** Experimental details, laser Raman spectra of poly(**1L<sub>m</sub>-co-Aib<sub>n</sub>**) and poly-**1L**, CD and absorption spectra of poly(**1L<sub>m</sub>-co-1D<sub>n</sub>**) and poly-**1L** in toluene, benzene, CCl<sub>4</sub>, and THF at various temperatures, changes in the CD intensity of poly(**1L<sub>m</sub>-co-1D<sub>n</sub>**) in CCl<sub>4</sub> and THF at various temperatures, polarized optical micrographs of cholesteric LC phases of poly-**1L** and poly(**1L<sub>m</sub>-co-1D<sub>n</sub>**) in CCl<sub>4</sub> and poly-**1L**–poly-**Aib** mixtures in toluene, changes in the cholesteric wavenumber ( $q_c$ ) of poly(**1L<sub>m</sub>-co-1D<sub>n</sub>**) in CCl<sub>4</sub> and poly-**1L**–poly-**Aib** mixtures in toluene, and AFM images of poly-**1L**–poly-**Aib** mixtures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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