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Hierarchical Amplification of Macromolecular Helicity in a Lyotropic Liquid Crystalline Charged Poly(phenylacetylene) by Nonracemic Dopants in Water and Its Helical Structure

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ABSTRACT: We report a unique hierarchical amplification of chiral information from a nonracemic guest to macromolecular helicity, followed by a mesoscopic, supramolecular cholesteric twist in water. This remarkable chiral amplification involves two-step chirality transfer processes, which enable the detection and sensing of an extremely small imbalance in chiral guest molecules. The macromolecular helicity with an excess single-handed helix was first induced in the positively charged, chromophoric poly(phenylacetylene), the hydrochloride of poly(4-(*N*,*N*-diisopropylaminomethyl)phenylacetylene) (poly-**1**-HCl) upon complexation with an oppositely charged nonracemic acid as a dopant through electrostatic interaction in dilute water. 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 (LC). Direct evidence for the hierarchical amplification process of the helical sense excess of the polymer during the cholesteric LC formation was demonstrated by direct comparison of the excess of the one helical sense of the polymer in dilute solution with that in the cholesteric LC state. Poly-**1**-HCl formed a lyotropic nematic LC in water in the absence of chiral acids, indicating its rigid-rod characteristic regardless of the lack of a single-handed helix, as evidenced by the long persistence lengths before (26 nm) and after (28 nm) the one-handed helicity induction in the polymer. X-ray diffraction of the oriented films of the nematic and cholesteric liquid crystalline poly-**1**-HCls exhibited almost the same diffraction pattern, suggesting that both polymers may have the same helical structure despite the substantial difference in their helical characteristics, dynamically racemic and one-handed helices in dilute solution, respectively. On the basis of the X-ray analyses, the most plausible helical structure of poly-**1**-HCl is proposed to be a 23 unit/10 turn (23/10) helix.

Introduction

Biological macromolecules, such as DNA and proteins, adopt an elaborate one-handed helical structure, which further self-assembles into lyotropic cholesteric liquid crystals (LCs) in water because of their stiff helical backbones.[1] Since the discovery of their biological helices and liquid crystallinities, significant attention has been paid to developing artificial helical polymers with a controlled helix sense[2] and liquid crystallinity because of the great interest from fundamental and biological viewpoints as well as for attractive applications in chiral materials science.[3] Several synthetic polymers bearing optically active pendants through covalent bonding also exhibit cholesteric LCs due to their rigid helical backbones in organic solvents or in the melt.[2a,4] However, aqueous cholesteric LCs derived from synthetic helical polymers are rare[1b] despite their potential for a wide range of applications, including biomimetic composite materials and electric-field responsive materials.[5]

In a series of studies, we reported the unique feature of dynamic helical, chromophoric poly(phenylacetylene)s with various functional groups as the pendants for the chirality detection and sensing of chiral small molecules in dilute solution. The poly(phenylacetylene)s formed an excess of one helical sense induced by noncovalent specific interactions with chiral guests, and the complexes exhibited a characteristic induced circular dichroism (ICD) in the polymer backbone regions in dilute solution.[2j,6] The interactions that occurred in the remote pendants are highly cooperative so that the molecular chirality of the guests transforms into dynamic helical poly(phenylacetylene)s, resulting in the generation of an easily measurable excess of the one helical sense as detected by circular dichroism (CD) because the complexation with chiral guests remarkably alters the population of the right- and left-handed helices of the dynamically racemic helical polymers separated by helical reversals.[7,8] However, the induced helical poly(phenylacetylene)s prepared so far showed no LC phase in organic solvents, probably because of their rather flexible backbones.

Recently, we have found that a positively charged poly(phenylacetylene), the hydrochloride of poly(4-(*N*,*N*-diisopropylaminomethyl)phenylacetylene) (poly-**1**-HCl; Chart 1) also

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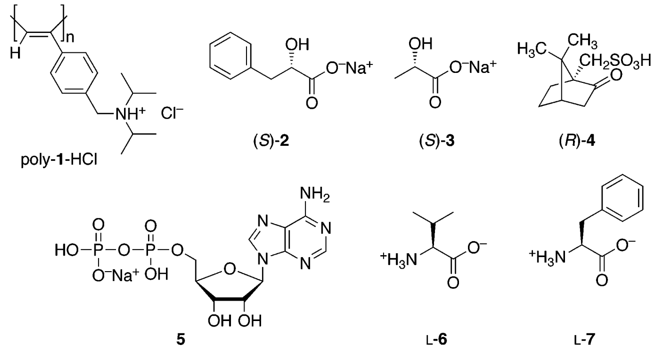
Chart 1



forms a predominantly one-handed helix upon complexation with various chiral acids, including carboxylic acids, phosphonic and sulfonic acids, and amino acids, and exhibits similar ICDs through the significant amplification of chirality in water.[9] The polymer is very sensitive to the chirality of chiral acids, as evidenced by the appearance of an ICD in the presence of a tiny amount of chiral carboxylic acids such as the sodium salt of phenyl lactic acid ((*S*)-**2** in Chart 1) as the dopant and even with **2** of a low enantiomeric excess (ee) in dilute water solution.[9] Moreover, the poly-**1**-HCl formed a lyotropic LC phase in concentrated water solutions, resulting in the first polyacetylene-based aqueous LC.[9a,10]

Interestingly, the helix-sense excess of poly-**1**-HCl was further amplified in the cholesteric LC phase in the presence of the nonracemic **2** than that in dilute solution.[9a,11,12] This concept of the amplification of the helical chirality in the LC state was first demonstrated by Green et al. using the optically inactive poly(*n*-hexyl isocyanate), a typical stiff dynamic helical polymer.[2a,b] They found that the lyotropic nematic liquid crystalline polyisocyanate converted to the cholesteric counterpart by doping with optically active polyisocyanates in organic solvents and discovered the amplification of the helical sense excess of the polyisocyanate by the LC state over that in dilute solutions.[4e] This is called the “bad neighbors” rule. These precedent observations together with our preliminary results prompted us to explore if the poly-**1**-HCl could work as a general-purpose chirality sensing probe for other various chiral acids, including important biomolecules such as amino acids and nucleotides, in an aqueous LC state, and the results were compared with those in a dilute water system reported previously.[9]

In addition, the fact that dynamically racemic and preferred-sense helical poly-**1**-HCls form nematic and cholesteric LCs makes possible the analysis of their helical structures by X-ray diffraction because we can make shear-oriented films from the LC samples. Although a large number of stereoregular cis−transoidal polyacetylenes with aliphatic and aromatic pendants have been synthesized with much interest,[6,10,13] their exact structures have not yet been determined. Previous X-ray studies of cis−transoidal aliphatic and aromatic polyacetylenes revealed their lateral packing of the polymer molecules, and a pseudohexagonal columnar packing structure composed of helical polyacetylenes in the solid state was proposed based on the X-ray diffraction results.[10c−e,g,14] Computational studies suggested that the most energetically preferred conformation of the cis−transoidal helical polyacetylenes was a nearly 7/3 helix.[6e,15]

In sharp contrast to the other stiff rodlike helical polymers, such as polyisocyanates and polysilanes, with a long persistence length (*q*), which stands for the backbone stiffness (20−45[16] and ca. 70 nm,[17] respectively) and a very large helical domain,[2a,b,f] the previously prepared substituted polyacetylenes appear to be rather flexible with a low population of such a helical domain.[7,18] As a result, there has been no structural information available to define the main chain helical structures of the polyacetylenes.

In this study, we report convincing evidence for the hierarchical amplification of the helicity of poly-**1**-HCl in the LC state, that is, the strong enhancement of preferred handedness through the cholesteric twist. We also demonstrate that the lyotropic solution can be used as a simple indicator of enantiomeric excess of various small chiral molecules. To more quantitatively analyze the helicity induction in poly-**1**-HCl with chiral amplification in the LC state, the persistence length of poly-**1**-HCl before and after the single-handed helicity induction with chiral acids was determined. Finally, we show the X-ray data of the oriented poly-**1**-HCl films prepared from nematic and cholesteric LC samples and propose the possible helical structures of the poly-**1**-HCls. On the basis of these results, the mechanism of the preferred-sense helicity induction in poly-**1**-HCl with chiral acids in dilute solution, followed by amplification of the macromolecular helicity process in the LC state, is discussed.

Results and Discussion

Helicity Induction in Dilute Solution and Cholesteric Liquid Crystal Formation in Concentrated Solution. As previously reported,[9,19] poly-**1**-HCl was highly sensitive to the chirality of various acids, as already demonstrated by the appearance of ICDs in the presence of an extremely small amount of chiral acids, such as (*S*)-**2** and **2** of low ee, in dilute aqueous solution.[9] Figure 1A shows the typical CD and absorption spectra of poly-**1**-HCl with (*S*)- and (*R*)-**2** in water. In a concentrated water solution (above 8 wt %), poly-**1**-HCl formed a birefringent nematic phase (Figure 1D). The addition of nonracemic acids to a concentrated poly-**1**-HCl solution brought about the LC state, with a fingerprint texture typical of the cholesteric LC, where the spacing of the fringes defines half of the cholesteric pitch and a smaller pitch represents an increased preference of the one helical sense in the cholesteric phase[3a,9a] (for the typical textures, see Figure 1E−I).

We previously performed titration experiments with (*S*)-**2** and **2** of different ee’s by following either the changes in the CD intensity of the second Cotton effect ($\Delta\epsilon_{2nd}$) in dilute solution and the cholesteric pitch (*p*) in the LC state in order to explore if the macromolecular helicity induced in poly-**1**-HCl by chiral **2** in dilute solution would be further amplified in the LC state by comparing their nonlinear responses to the chirality of **2** in each pair of titrations.[9a] In parts B and C of Figure 1, the previously reported titration experiment results using (*S*)-**2** and **2** of different ee’s in the LC state[9a] are shown, along with additional experiments, in the plot of the cholesteric wavenumber q_c (defined by $2\pi/p$) versus the concentration of (*S*)-**2** and the % ee of **2**, respectively; the CD titration results in a dilute water solution[9a] are also shown for comparison. A remarkable chiral amplification in the LC state over that in the dilute solution was observed during the titrations with (*S*)-**2** and nonracemic **2**; for instance, the q_c value increased with the increasing ee and reached a constant value at about 40−50% ee, while in dilute solution, the $\Delta\epsilon_{2nd}$ value became constant at over 75% ee (Figure 1C). The sudden onset and more rapid increase in the q_c value over that in the $\Delta\epsilon_{2nd}$ value in dilute solution suggest a subsequent amplification of the helical sense excess in the LC state. In the titrations with (*S*)-**2** in dilute and concentrated solutions, the difference in their increments is also significant (Figure 1B).

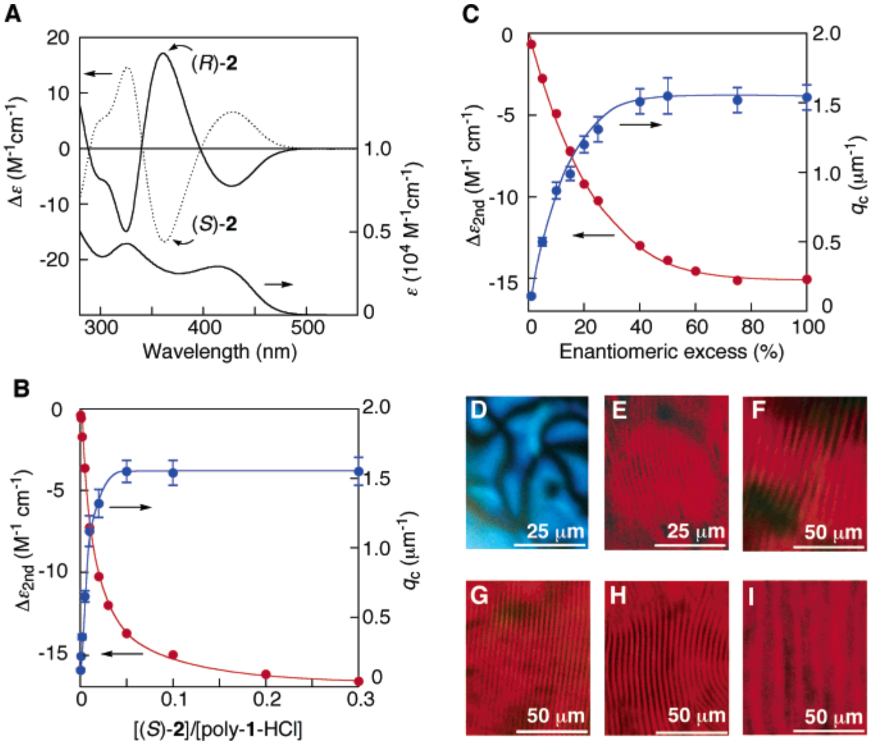


Figure 1. (A) CD spectra of poly-**1**-HCl with (*S*)- and (*R*)-**2** in water at 25 °C. Absorption spectrum of poly-**1**-HCl with (*R*)-**2** at 25 °C is also shown. The concentration of poly-**1**-HCl is 1.0 mg (4.0 μmol monomer units)/mL. [**2**]/[poly-**1**-HCl] = 0.5. (B) Changes in the ICD intensity ($\Delta\epsilon_{2nd}$) (red filled circles) and the cholesteric wavenumber (q_c) (blue filled circles) of poly-**1**-HCl vs the concentration of (*S*)-**2** in dilute (1 mg/mL) and concentrated (20 wt %) water solutions, respectively. (C) Changes in the ICD intensity (red filled circles) and q_c (blue filled circles) of poly-**1**-HCl vs the % ee of **2** (*S*-rich) in dilute (1 mg/mL) and concentrated (20 wt %) water solutions, respectively. The molar ratio of **2** to the monomeric units of poly-**1**-HCl is 0.1 equiv. (D−I) Polarized optical micrographs of a nematic LC phase of poly-**1**-HCl (20 wt %) (D) and cholesteric LC phases of poly-**1**-HCl (20 wt %) in the presence of 50 (E) and 5% ee (F) (*S*-rich) of **2** (0.1 equiv), (*S*)-**3** (0.1 equiv) (G), (*R*)-**4** (0.01 equiv) (H), and L-**6** (0.1 equiv) (I) in water. The error bars in B and C represent the standard deviation estimated by an evaluation of ca. 30 fingerprint spacings (see Table 1).

The cholesteric wavenumber q_c of helical polymer solutions strongly depends on the polymer concentration, temperature, and the solvent.[4d,e] If the solution contains enantiomers, i.e., the right- and left-handed helices, q_c also depends on the excess of one helical sense. It can be theoretically shown that q_c of such a solution is given by[20]

$$q_c = q_{c,max}(f_M - f_P) \qquad (1)$$

where f_M (f_P) is the fraction of the left-handed (right-handed) helix component, and $q_{c,max}$ is q_c at $f_M = 1$ and $f_P = 0$. For the cholesteric LC solution of a helical poly-**1**-HCl induced by a chiral acid, $q_{c,max}$ is experimentally available from the titration experiments under the fixed polymer concentration and temperature, if the chiral acid used as a dopant only acts to change the population of the right- and left-handed helices of the dynamically racemic helical poly-**1**-HCl chain through complexation in water, and dissociated acid ions do not directly contribute to the twisting of the helical polymer chains at all. Thus, we can estimate the excess of one helical sense ee$_h$ (= $f_M - f_P$) of the poly-**1**-HCl in a particular cholesteric LC solution showing a different cholesteric pitch under the conditions from eq 1 or by

$$\text{ee}_h \text{ (in the LC state)} = q_c/q_{c,max} \qquad (2)$$

while the ee$_h$ in the dilute solution is estimated from $\Delta\epsilon_{2nd}$ by

$$\text{ee}_h \text{ (in the dilute solution)} = \Delta\epsilon_{2nd}/\Delta\epsilon_{2nd,max} \qquad (3)$$

along with the maximum value of $\Delta\epsilon_{2nd}$ ($\Delta\epsilon_{2nd,max}$).

The titration experiments with (*S*)-**2** in the aqueous LC state under the constant polymer concentration of 20 wt % at ca. 25 °C gave the minimum cholesteric pitch of 4.06 μm (maximum $q_c = 1.55\ \mu\text{m}^{-1}$) in the presence of 0.3 equiv of (*S*)-**2**, at which the polymer has a single-handed helix in the LC state (see Figure S4 in the Supporting Information).[21] In the same way, the maximum $\Delta\epsilon_{2nd}$ value could be determined to be −17.2 from the CD titration results using (*S*)-**2** in a dilute water solution, at which the polymer is anticipated to have a complete single-handed helix (see Figure S3 in the Supporting Information).[21] On the basis of these values as the base ones, the ee$_h$ values of poly-**1**-HCl induced by chiral acids in a dilute solution and in the LC state can be separately estimated from eqs 3 and 2, respectively, leading to the direct evaluation for the amplification of the intrinsic helical sense excess of the poly(phenylacetylene) by the LC state that can be demonstrated by comparing the ee$_h$ values.[22]

As chiral acids, we selected different functional acids (**2**−**7**, Chart 1) as excellent (**2**, **4**, and **5**), moderate (**3**), and poor (**6** and **7**) helicity inducers in dilute water according to the recently reported results,[9b] and the ee$_h$ values of poly-**1**-HCl in dilute and concentrated liquid crystalline water solutions were calculated using the maximum $\Delta\epsilon_{2nd}$ and q_c values of −17.2 M^{-1} cm^{-1} and 1.55 μm^{-1} as the base values, respectively, as described above. These results are summarized in Table 1 and the calculated ee$_h$ values of poly-**1**-HCl in the cholesteric LC state are plotted versus those in dilute water (Figure 2). If the helical sense ratio of the poly-**1**-HCl induced by the chiral acids in dilute water remained in the LC state, we should observe a linear relation between the ee$_h$ values in dilute solution and cholesteric LC. However, we found a positive nonlinear

Table 1. Signs and $\Delta\epsilon_{2nd}$ Values in Dilute Solution, Cholesteric Helical Pitch (p) and Cholesteric Wavenumber (q_c) in Concentrated Solution, and Excess of One Helical Sense (ee_h) of Poly-1-HCl Induced by Chiral Dopants in Dilute and Concentrated LC Solutions

			dilute solution (1 mg/mL)		lyotropic LC (20 wt %)		
run	chiral dopant	[dopant]/[poly-**1**-HCl]	$\Delta\epsilon_{2nd}$ (M^{-1} cm^{-1}) [λ (nm)]	ee_h (%)[a]	p (μm)[b]	q_c (μm^{-1})[b]	ee_h (%)[c]
1	(*S*)-**2**	0.3	−16.7 (361)	97	4.06 ± 0.25	1.55 ± 0.10	100 ± 6
2	(*S*)-**2**	0.1	−15.0 (361)[d]	87	4.10 ± 0.25	1.54 ± 0.09	99 ± 6
3	(*S*)-**2**	0.05	−13.7 (361)	80	4.06 ± 0.22	1.55 ± 0.08	100 ± 5
4	(*S*)-**2**	0.02	−10.3 (361)	60	4.79 ± 0.38	1.32 ± 0.10	85 ± 6
5	(*S*)-**2**	0.01	−7.26 (361)	42	5.66 ± 0.54	1.12 ± 0.11	72 ± 7
6	(*S*)-**2**	0.005	−3.63 (361)	21	9.64 ± 0.62	0.65 ± 0.04	42 ± 3
7	(*S*)-**2**	0.002	−1.70 (361)	10	17.5 ± 1.0	0.36 ± 0.02	23 ± 1
8	(*S*)-**2**	0.001	−0.58 (361)	3	28.9 ± 1.9	0.22 ± 0.01	14 ± 1
9	(*S*)-**2**	0.0005	−0.39 (358)	2	53.6 ± 3.3	0.12 ± 0.01	8 ± 1
10	**2** (75% ee)[e]	0.1	−15.1 (361)	88	4.15 ± 0.25	1.52 ± 0.09	98 ± 6
11	**2** (50% ee)[e]	0.1	−13.9 (360)	81	4.06 ± 0.36	1.55 ± 0.13	100 ± 8
12	**2** (40% ee)[e]	0.1	−13.0 (361)	76	4.19 ± 0.24	1.51 ± 0.09	97 ± 6
13	**2** (25% ee)[e]	0.1	−10.2 (361)	59	4.82 ± 0.32	1.31 ± 0.09	85 ± 6
14	**2** (20% ee)[e]	0.1	−9.22 (361)[f]	54	5.25 ± 0.25	1.20 ± 0.06	77 ± 4
15	**2** (15% ee)[e]	0.1	−7.20 (361)	42	6.35 ± 0.34	0.99 ± 0.05	64 ± 3
16	**2** (10% ee)[e]	0.1	−4.90 (361)	28	7.27 ± 0.50	0.87 ± 0.06	56 ± 4
17	**2** (5% ee)[e]	0.1	−2.76 (361)	16	12.5 ± 0.6	0.50 ± 0.03	32 ± 2
18	**2** (1% ee)[e]	0.1	−0.65 (359)	4	58.0 ± 2.8	0.11 ± 0.01	7 ± 1
19	(*S*)-**3**	0.1	−4.23 (361)[d]	25	7.42 ± 0.37	0.85 ± 0.04	55 ± 3
20	(*S*)-**3**	0.01	−0.56 (361)	3	12.5 ± 0.6	0.51 ± 0.02	33 ± 1
21	(*R*)-**4**	0.1	−15.4 (359)[d]	90			
22	(*R*)-**4**	0.01	−4.39 (360)	26	8.21 ± 0.16	0.77 ± 0.02	50 ± 1
23	**5**	0.1	+13.7(361)[d]	80			
24	**5**	0.001	+ 0.32 (361)	2	52.2 ± 3.4	0.12 ± 0.01	8 ± 1
25	L-**6**	0.1	*d, g*	~0	27.3 ± 0.9	0.23 ± 0.01	15 ± 1
26	L-**7**	0.1	*d, g*	~0	29.4 ± 1.2	0.21 ± 0.01	14 ± 1

[a] Estimated using $\Delta\epsilon_{2nd} = -17.2$ as the base value. [b] Estimated on the basis of an evaluation of ca. 30 fingerprint spacings. [c] Estimated using the maximum $q_c = 1.55$ as the base value. [d] Cited from ref 9b. [e] (*S*)-Isomer rich. [f] Almost no change in the $\Delta\epsilon_{2nd}$ value was observed when the concentration of poly-**1**-HCl was 1, 5, 10, and 50 mg/mL (0.1, 0.5, 1.0, and 5 wt %). [g] No distinctive CD was observed even when the concentration of poly-**1**-HCl was 1 and 50 mg/mL (0.1 and 5 wt %).

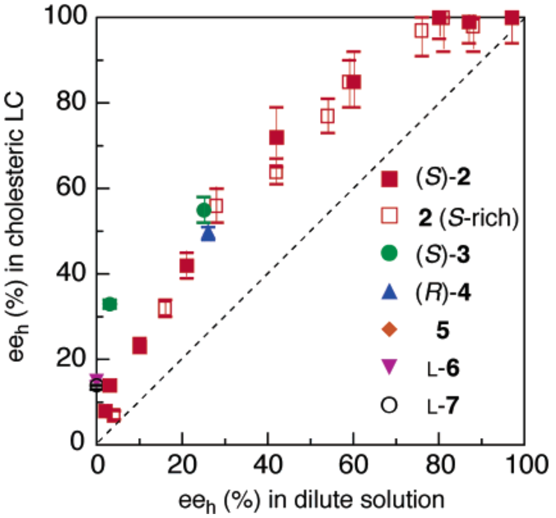


Figure 2. Plots of the calculated ee_h values of poly-**1**-HCl in the presence of chiral dopants ((*S*)-**2** (red filled squares), **2** (*S*-rich) (red open squares), (*S*)-**3** (green filled circles), (*R*)-**4** (blue solid upward triangle), **5** (orange filled diamond), L-**6** (violet solid downward triangle), and L-**7** (black open circle)) in the cholesteric LC state vs those in dilute water (see Table 1). The ee_h values of poly-**1**-HCl in dilute and concentrated liquid crystalline water solutions were calculated using the maximum $\Delta\epsilon_{2nd}$ and q_c values of −17.2 and 1.55 as the base values, respectively.

relationship between the helix-sense excesses of poly-**1**-HCl in dilute solution and those in the cholesteric LC state, which clearly demonstrates the amplification of the helical sense excess in the LC state (Figure 2). As well as **2**, a chiral aliphatic carboxylic acid (**3**), sulfonic and phosphoric acids (**4** and the sodium salt of adenosine diphosphate (ADP, **5**), respectively), and amino acids (**6** and **7**) were found to assist in the cholesteric LC formation in the concentrated aqueous poly-**1**-HCl solutions.

Poly-**1**-HCl formed an excess one helical sense over of 80% ee_h in the presence of (*S*)-**2** equal to or greater than 0.05 equiv and **2** of more than 50% ee in a dilute solution (runs 1−3, 10, and 11 in Table 1). In the LC state, however, the ee_h value became slightly higher, resulting in the almost perfect single-handed helix in the LC state. A noticeable chiral amplification of poly-**1**-HCl in the LC state was observed when smaller amounts of (*S*)-**2** and **2** of low ee were used (runs 4−9 and 12−18 in Table 1). The excess of a one helical sense induction in poly-**1**-HCl through a noncovalent bonding interaction with chiral acids such as (*S*)-**2** involves an equilibrium, so that one may think that the ICD intensity may depend on the concentration of the polymer. However, the ICD intensity scarcely changed in the polymer concentrations ranging from 0.1 to 5.0 wt % in the presence of 0.1 equiv of a 20% ee of (*S*)-**2** (run 14 in Table 1).[23] The chiral sulfonic and phosphoric acids ((*R*)-**4** and **5**) could also induce an excess of a one helical sense in poly-**1**-HCl with 0.1 equiv of the acids in dilute solution (runs 21 and 23 in Table 1). However, 0.01 equiv (*R*)-**4** and 0.001 equiv **5** induced an only slightly excess of the one-helical sense and an almost racemic helix in the poly-**1**-HCl, respectively, in dilute solution (runs 22 and 24 in Table 1). In the LC state, however, the helicity was amplified, resulting in the larger helical sense excess in the polymer. We note that the L-amino acids **6** and **7** (0.1 equiv) are poor helicity inducers and could not induce an ICD in poly-**1**-HCl at all in the dilute (0.1 wt %) and more concentrated polymer solutions (5 wt %) (runs 25 and 26 in Table 1). However, in the LC state (20 wt %), the chirality is in fact amplified, leading to a cholesteric LC, where the polymer has an excess helical sense of 14−15% ee_h. These convincing results provide a direct evidence for the amplification

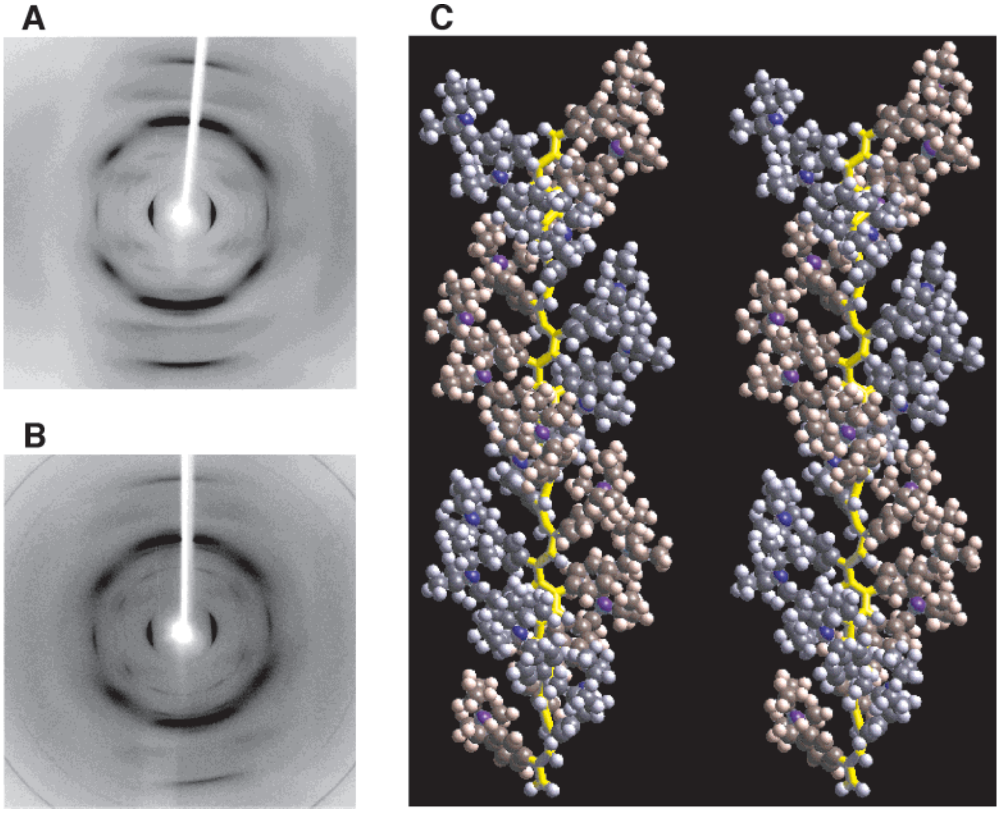


Figure 3. X-ray diffraction patterns of oriented optically inactive poly-**1**-HCl film (A) and optically active poly-**1**-HCl−(*S*)-**2** film (B) taken from the edge-view position with a beam parallel to the film surface; the vertical direction is nearly corresponding to the helical axis.[32] The two Debye−Scherrer rings that appeared on the higher angle side in B are assigned to the 111 (3.26 Å) and 200 (2.82 Å) reflections from the precipitated NaCl during the sample preparation. Stereoview of a possible 23/10 helical structure of poly-**1** (23-mer) is shown in (C) using the space-filling model. The main chain carbon atoms are shown in yellow using the cylinder model for clarity. The 4-(*N*,*N*-diisopropylaminomethyl)phenyl substituents, represented by light blue and red for clarity, arrange in a helical array with a predominant screw-sense along the polymer backbone.

of chirality in the LC state and demonstrate a highly sensitive chirality sensing system.

Persistence Length Measurements. We next estimated the backbone stiffness (persistence length (q)) of poly-**1**-HCl before and after the single-handed helicity induction, thus showing nematic and cholesteric LC phases in concentrated water solutions, respectively, by measuring their isotropic−LC phase boundary concentrations.[25] The cholesteric and nematic LC poly-**1**-HCl solutions were prepared in water (10 wt %) in the presence of 0.1 equiv of (*S*)-**2** and NaCl, respectively. NaCl was used to reduce the effect of the salt concentration on the phase boundary concentration measurements for the nematic LC poly-**1**-HCl. These solutions were gradually diluted with water until the birefringence disappeared during polarizing optical microscopy. The concentration at which the birefringence disappeared was taken as the isotropic−LC phase boundary concentration C_i. The q values can be calculated by the theory of Khokhlov and Semenov[25] combined with the theory of Stroobants et al.[25c] when the molar mass per unit contour length (M_L), the C_i, and the isotropically averaged effective molecular diameter d_{eff}[26] are given (see the Supporting Information). The determined q values thus obtained for an optically inactive poly-**1**-HCl and a single-handed helical poly-**1**-HCl in the nematic and cholesteric LC states were 26.2 and 28.0 nm, respectively. These large q values indicate that both the poly-**1**-HCls are rigid and their LC formations are definitely based on their main chain stiffness.[27] We note that the q values are almost the same for both the optically active and inactive poly-**1**-HCls or the latter is only a little smaller than the former.

We first considered that the optically inactive poly-**1**-HCl might have a shorter persistence length than the single-handed helical poly-**1**-HCl because the former poly-**1**-HCl chain is expected to have more helical reversals. However, the optically active and inactive poly-**1**-HCls actually have similar q values, indicating that kinks due to the helical reversal in the polymer chain are too few to contribute to the chain flexibility and the alternative contribution of the torsional fluctuation in the polyacetylene chain may be predominant.[7] Consequently, the dynamically racemic poly-**1**-HCl helices may have a long helical sequence with few helical reversals. Such a stiff helical polyacetylene is expected to form a regular helical structure over long distance so that the helical conformation may be determined from the X-ray analysis. In fact, the helical structures of the liquid crystalline polyisocyanates and polysilanes having a large persistence length have been determined by the X-ray analyses of the corresponding oriented films to be an 8 unit/3 turn helix (8/3)[28] and a 7 unit/3 turn helix (7/3), respectively.[4g,29]

Helical Structure. Cis−transoidal poly(phenylacetylene)s have been considered to have a helical conformation because of the steric effect between the main chain protons and the phenyl substituents at the vicinal units that may cause a deviation from planarity,[6,7,10c−e,g,13−15] although their exact helical structures have not yet been determined.[30] The three-dimensional solid-state structures of the optically inactive and active poly-**1**-HCls were then investigated by X-ray analysis. Parts A and B of Figure 3 show the wide-angle X-ray diffraction (WAXD) patterns of the uniaxially oriented poly-**1**-HCl and poly-**1**-HCl−(*S*)-**2** films prepared from concentrated nematic and cholesteric LC water solutions, respectively. X-ray photographs were taken from the edge-view position with a beam parallel to the film surface at ambient temperature (20−25 °C).[31]

Table 2. X-ray Diffraction Data of Optically Inactive (Poly-1-HCl) and Optically Active (Poly-1-HCl−(*S*)-2) Oriented Films

	optically inactive poly-**1**-HCl				optically active poly-**1**-HCl−(*S*)-**2**			
layer line *l*	d_{obs}/Å[a]	d_{cal}/Å[b]	*h k*[b]	I_{obs}[c]	d_{obs}/Å[a]	d_{cal}/Å[d]	*h k*[d]	I_{obs}[c]
0	17.23	17.18	11, 20	vs	16.64	16.64	11, 20	vs
	9.92	9.92	02, 31	vw	9.61	9.61	02, 31	vw
	8.59	8.59	22, 40	m	8.32	8.32	22, 40	m
	6.50	6.49	13, 42, 51	s	6.31	6.29	13, 42, 51	s
2	9.29	9.21	02, 31	w	8.93	8.96	02, 31	w
3					11.79	11.74	11, 20	vw
	10.19	10.22	21	m				
					8.31	8.31	02, 31	m
	8.12	8.26	12	m				
					7.50	7.44	22, 40	w
5	8.67	8.61	11, 20	w	8.59	8.54	11, 20	m
	6.10	6.18	41	vs	6.07	6.06	41	s
6	8.19	8.29	nm[e]	vw				
7	7.12	7.10	nm[e]	m				
					6.56	6.53	11, 20	m
8	6.12	6.22	streak	vs	6.11	6.22	streak	vs
9	5.55	5.53	nm[e]	m	5.57	5.53	nm[e]	m
10	4.83	4.82	01	m				
	4.63	4.64	21	w	4.58	4.62	21	w
					4.27	4.27	22, 40	vw
13	3.83	3.83	nm[e]	s	3.83	3.83	nm[e]	s
23	*f*	2.16	00		*f*	2.16	00	

[a] Spacings observed in X-ray diffraction patterns of poly-**1**-HCl oriented films. [b] Spacings calculated and indexed on the basis of an orthorhombic unit cell with parameters, $a = 34.36$, $b = 19.84$, and $c = 49.74$ Å. [c] Observed intensities; vs = very strong, s = strong, m = medium, w = weak, and vw = very weak. [d] Spacings calculated and indexed on the basis of an orthorhombic unit cell with parameters $a = 33.29$, $b = 19.21$, and $c = 49.74$ Å. [e] Near meridional reflections. These reflections may be indexed as 10*l*, which should be split across the meridian. However, the imperfect orientation of the films may result in such arclike reflections linked at the meridian, and their calculated *d* values were estimated as the 00*l* reflections because these reflections were read along the meridian. [f] Not observed.

Surprisingly, the X-ray diffractions of an oriented optically inactive poly-**1**-HCl film (Figure 3A) and an optically active, single-handed helical poly-**1**-HCl−(*S*)-**2** film ([(*S*)-**2**]/[poly-**1**-HCl] = 0.1) (Figure 3B) showed essentially the same pattern, exhibiting diffuse, but apparent equatorial and near- and off-meridional reflections (for the WAXD patterns with different ranges of sensitivities, see Figure S6 in the Supporting Information).[32] The four equatorial reflections, 17.23, 9.92, 8.59, and 6.50 Å for poly-**1**-HCl and 16.64, 9.61, 8.32, and 6.31 Å for poly-**1**-HCl−(*S*)-**2**, can be visually indexed with a two-dimensional hexagonal lattice of $a = 19.84$ and 19.21 Å, respectively, and the observed *d*-spacings are listed in Table 2. We then determined the fiber periods to be 49.74 Å (= *c*) from the layer lines and attempted to index the reflections based on the hexagonal unit cell, but the third and fifth layer line reflections could not be indexed.

Next, we used a larger orthogonal lattice with the hexagonal symmetry and found that all the reflections, including a series of equally spaced layer line reflections (1/49.74 $Å^{-1}$ apart) attributed to the helical poly-**1**-HCl and poly-**1**-HCl−(*S*)-**2** structures, can be reasonably indexed to an orthorhombic unit cell with $a = 34.36$, $b = 19.84$, and $c = 49.74$ Å for poly-**1**-HCl and $a = 33.29$, $b = 19.21$, and $c = 49.74$ Å for poly-**1**-HCl−(*S*)-**2**, respectively, where the reflections on the third and fifth layer lines can also be reasonably indexed to (213) and (123), and (415), respectively (Table 2).[33] Although we could not observe a meridional reflection on the 23rd layer line (2.16 Å) (see Table 2) corresponding to the unit height (*h*) of the helical structures even when the X-ray measurements were performed using a cylindrical camera with the samples tilted ca. 21° normal to the beam, the most plausible structure of the helical poly-**1**-HCl and poly-**1**-HCl−(*S*)-**2** can be proposed to be a 23 unit/10 turn helix (23/10) by considering the density measurement results[34] combined with the layer lines observed in the X-ray diffraction patterns.[36] The validity of the 23/10 helical structure has been confirmed by Miyazawa's equation, as shown in the Supporting Information.

Figure 3C illustrates the molecular structure of the 23/10 helix of the right-handed helical poly-**1** model (23-mer), where the bond lengths (C═C: 1.374 Å and C−C: 1.466 Å), the bond angles (C−C═C: 128.8° and C═C−C: 124.8°), and the dihedral angles (C−C═C−C: 0° (cis), C═C−C═C: transoid (140.3°)) were used as the internal coordinates (see the Supporting Information). We noted that when the poly-**1** main chain has a right-handed helical structure, poly-**1** has the opposite left-handed helical array of the pendants (23 unit/1.5 turn helix with a helical pitch of 33.16 Å).[38]

Although the packing-mode has not been elucidated yet, these X-ray results suggest that the poly-**1**-HCls before and after the preferred-sense helicity induction may possess the same helical conformation (23/10 helix) independent of their helical sense ratio, specifically in the solid state prepared from the liquid crystalline water solutions, as evidenced by their essentially same layer reflections. We first thought that the poly-**1**-HCl might show rather broad and different X-ray diffractions from those of the single-handed helical poly-**1**-HCl−(*S*)-**2** because the poly-**1**-HCl consists of equal amounts of interconvertible right- and left-handed helical conformations separated by helix reversals in dilute solution, and the kink due to the helix reversal may cause more or less disordered packing of the polymer chains. However, the present X-ray results together with the fact that both polymers have almost the same persistence length support our speculation that poly-**1**-HCl may have a stiff helical polymer with long alternating left- and right-handed helical segments (long helical persistence length) separated by rarely occurring helix reversals even in dilute solution, the population

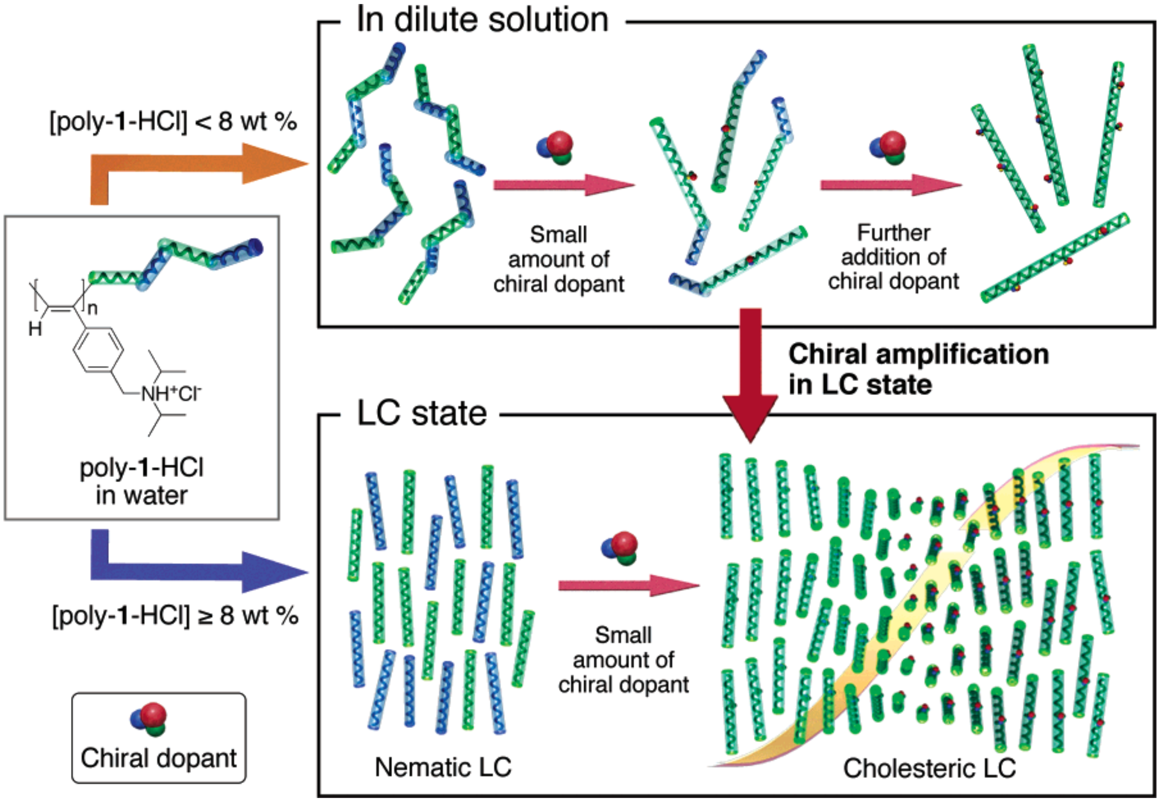


Figure 4. A possible mechanism of the hierarchical amplification process of the macromolecular helicity of poly-**1**-HCl mediated by a nonracemic dopant in dilute and concentrated water solutions. Poly-**1**-HCl has interconvertible, right- (green) and left-handed (blue) dynamic helical conformations separated by rarely occurring helix reversals in dilute solution. Excess of preferred-sense helical sense (right- or left-handed helix) of poly-**1**-HCl is induced with a small amount of chiral dopant, and further addition of the chiral dopant is required for a complete single-handed helix formation in poly-**1**-HCl in dilute solution (upper). In LC state, the population of helix reversals may be reduced even in the nematic LC state to form the racemic single-handed helices. In the presence of a small amount of chiral dopant, chirality is significantly amplified, resulting in a single-handed helical supramolecular assembly, thus showing a cholesteric LC phase (bottom).

of which may be further reduced even in the nematic LC state to form the racemic single-handed helices (see Figure 4). As a result, the poly-**1**-HCl exhibited the same X-ray diffraction pattern as that of the single-handed helical poly-**1**-HCl.[40] This, however, may be the first unambiguous evidence that poly(phenylacetylene)s are in fact a dynamically racemic helical polymer composed of interconvertible right- and left-handed helical segments, and this unique helical characteristic is responsible for their remarkable amplification of the chirality in dilute solution and further in the LC state.

On the basis of these results, we propose a possible mechanism for the hierarchical amplification process of the macromolecular helicity of poly-**1**-HCl mediated by a nonracemic dopant in dilute and concentrated water solutions (Figure 4). The original poly-**1**-HCl is a rigid-rod dynamic helical polymer with interconvertible long right- and left-handed helical segments separated by rarely occurring helix reversals in dilute solution. Therefore, upon complexation with a small amount nonracemic acid or even with that of a low ee, a greater excess one helical sense than that expected from the amount or ee of the acid is induced in the polymer ("sergeants and soldiers"[42] and "majority" effects[43]),[2a,b,j] thus showing an ICD, whereby the chiral information of the nonracemic acid transfers to the polymer backbone as an excess of a single-handed helix with high cooperativity in dilute solution. The macromolecular helicity induced in the polymer is further amplified in the LC matrix, resulting in the increase in the helical sense excess of the polymer, probably by the reduction in population of the helical reversals as observed in the polyisocyanates by Green et al.[4e]

Conclusions

In summary, we have demonstrated a novel hierarchical amplification of chirality during the transfer of chiral information from nonracemic guests to the helical systems either at macromolecular and subsequent supramolecular mesoscopic levels, leading to an easily measurable excess of one helical sense in a dynamic helical polyacetylene, which can be detected by measuring the CD of the polymer or the mesoscopic cholesteric twist in the LC state if the CD is not available. The main chain stiffness with a dynamic helical characteristic that allows a formation of the LC phase is essential for realizing this hierarchical amplification of the chirality system for detecting and sensing a small chiral bias of the guest molecules. The present results including the helical structure (23/10 helix) proposed by the X-ray diffraction studies will contribute to developing a more efficient chirality-sensing system based on liquid crystalline helical polyacetylenes through the hierarchical amplification of chirality in the LC state.

Experimental Section

Full experimental details are available in the Supporting Information.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) The maximum q_c and $\Delta\epsilon_{2nd}$ values were determined from the titration results. The q_c and $\Delta\epsilon_{2nd}$ values were plotted versus the inverse [(S)-**2**]/[poly-**1**-HCl], and the maximum q_c and $\Delta\epsilon_{2nd}$ values were estimated from their intercepts (see Figures S3 and S4 in the Supporting Information).

(22) Green et al. demonstrated the amplification of the helical sense excess of a dynamically racemic helical polyisocyanate in the LC state doped with two different optically active polyisocyanates in their helical characteristics, one of which has a single-handed helix and the other, unequal interconverting right- and left-handed helical senses. They observed a nonlinear relationship between their dilute solution optical activities and cholesteric properties in the latter system, giving rise to higher q_c values than the former system. Green et al. proposed the amplification mechanism that is driven by the reduction in population of the mobile kinked helical reversals.[4e]

(23) We further estimated the degree of complexation (f_c) of poly-**1**-HCl with **2** of 20% ee (S-rich) by potentiometric pH titration according to the reported procedure[24] because the amino group of poly-**1**-HCl must take one of the two following forms: the complex form with **2** (20% ee) and the free ammonium ion in an aqueous solution. The determined f_c value thus obtained for the solutions with the polymer concentrations ranging from 0.1 to 1.0 wt % in the presence of 0.1 equiv **2** (20% ee) was almost 0.1 irrespective of the polymer concentration. This indicates that all the **2** (20% ee) in the polymer solution is complexed with the amino groups of the polymer. Because we can expect that the degree of complexation maintains this value with the further increasing polymer concentration under the condition of [**2** (20% ee)]/[poly-**1**-HCl] = 0.1, we concluded that the content of the complexed monomer units in the poly-**1**-HCl does not depend on the polymer concentration. This is consistent with the polymer concentration independence of the ICD intensity, and furthermore, verifies that the chiral amplification in the LC phase takes place at the constant content of the complexed monomer units in the poly-**1**-HCl.

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(31) Any heat treatment of the samples was not performed because the poly-**1**-HCl is thermally unstable and cis-to-trans isomerization took place at high temperature (>100 °C), although the poly-**1**-HCl is quite stable in solution and in the solid state at ambient temperature (20−25 °C) for a long time and the diffraction patterns did not change after ca. one month at ambient temperature (20−25 °C).

(32) In Figure 3A and B, the WAXD intensities were not perfectly symmetrical and the meridian directions in both the WAXD patterns are not perfectly vertical-aligned. Because the samples were made by piling up several uniaxially oriented, thin, and rectangle-shaped films of ca. 10 mm length, 1.5 mm width, and 0.02 mm thickness (Supporting Information), it was difficult to align perfectly the samples with the orientation axes in each film. In addition, the samples were so soft and flexible and had a slightly arclike shape, which made it difficult to set the oriented samples perfectly normal to the beam, that is, the helical axes of the films were not perfectly parallel to the

meridian direction, which may also cause the different pass lengths in the top and bottom half, resulting in slightly dissymmetrical WAXD intensities. Similar dissymmetrical WAXD patterns were reported. For example, see: Miller, R. D.; Farmer, B. L.; Fleming, W.; Sooriyakumaran, R.; Rabolt, J. *J. Am. Chem. Soc.* **1987**, *109*, 2509−2510.

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(34) The orthorhombic unit cell of the poly-**1**-HCl is assumed to contain four helices or two double helices of the polymer chain, which requires the density of 1.135 g/cm^3, which is in good agreement with the observed value (1.142 g/cm^3).[35] In addition, when the number of repeating units per the fiber period is assumed to be other than 23, the observed density was considerably different from the calculated density (see the Supporting Information). On the other hand, the observed density of the poly-**1**-HCl−(*S*)-**2** ([(*S*)-**2**]/[poly-**1**-HCl] = 0.1) film (1.178 g/cm^3)[35] was different from the calculated value (1.272 g/cm^3) for this unit cell containing four helices of the poly-**1**-HCl chain complexed with 0.1 equiv (*S*)-**2**. The reason is not clear at the present, but highly disordered location of the 0.1 equiv (*S*)-**2** molecules in the film and NaCl precipitation during the sample preparation, resulting in the formation of defects and giving rise to voids between polymer films and NaCl particles, respectively, should be taken into consideration for the lower observed density of the poly-**1**-HCl−(*S*)-**2** film.

(35) The densities of the poly-**1**-HCl and poly-**1**-HCl−(*S*)-**2** ([(*S*)-**2**]/[poly-**1**-HCl] = 0.1) films were measured by the standard flotation method in a carbon tetrachloride/*n*-heptane mixture at ambient temperature (20−25 °C).

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