Helicity Induction and Chiral Amplification in a Poly(phenylacetylene) Bearing *N*,*N*-Diisopropylaminomethyl Groups with Chiral Acids in Water

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ABSTRACT: A water-soluble, hydrochloride of a stereoregular poly(phenylacetylene) bearing an *N*,*N*-diisopropylaminomethyl group (poly-**1**-HCl) as the pendant was found to form a predominantly one-handed helix upon complexation with various chiral acids including aromatic and aliphatic carboxylic acids, phosphoric and sulfonic acids, and amino acids through noncovalent bonding interactions in water. The complexes exhibited an induced circular dichroism (ICD) in the UV−vis region of the polymer backbone. The Cotton effect signs were the same when chiral carboxylic acids with the same absolute configurations were used. In sharp contrast to the helix induction in the neutral poly-**1** with chiral acids in organic solvents, the charged poly-**1**-HCl is highly sensitive to the chirality of the acids and can detect a small enantiomeric imbalance in the chiral acids in water.

Introduction

Chiral acids including phosphoric and sulfonic acids as well as carboxylic acids and amino acids are the particularly common and important structural units in many natural products and drug molecules,[1] and therefore, the development of convenient and accurate methodologies for the detection and assignments of the chirality of chiral acids and determination of their enantiomeric compositions have attracted significant interest. Various types of chiral[2,3] or achiral[4] host molecules, in particular for chiral carboxylic acids, have been prepared. Chiral host molecules composed of optically active and fluorescent receptor units are often used to sense the chiral carboxylic acids because of the high sensitivity inherent to fluorescence spectroscopy.[2] Circular dichroism (CD) spectroscopy is also a powerful tool for chirality sensing, particularly when a host molecule is achiral and chromophoric. The noncovalent bonding to a chiral, nonracemic guest provides a characteristic induced CD (ICD) in the absorption region of the achiral receptors; the Cotton effect sign can be used to determine the absolute configuration of the guest molecules.[4,5]

In a series of studies, we reported the helicity induction in optically inactive, stereoregular *cis*−*transoidal*-poly(phenylacetylene)s bearing functional groups such as carboxy,[6] phosphonate,[7] boronate,[8] and amino groups[9] or bulky crown ethers as the pendants,[10] which can change their structures into the prevailing, dynamic one-handed helices upon complexation with specific chiral guests, and their complexes show a characteristic ICD in the UV−vis region of the polymer backbones. The Cotton effect signs corresponding to the helical sense can be used as a novel probe for the chirality assignments of the guest molecules.[11] Helical polyacetylenes are very sensitive to chiral stimuli and exhibit optical activity due to a one-handed helicity of the polymer main chains through a significant amplification of chirality with high cooperativity, which is a unique feature of dynamic helical polyacetylenes.[12,13] For instance, the introduction of bulky crown ethers as the pendants in poly(phenylacetylene)s backbones produced dynamic helical polymers which can respond to the chirality of nearly racemic amino acids and amino alcohols in organic solvents with high sensitivity without derivatization.[10]

On the other hand, a number of chiral receptor molecules have been prepared for chiral or chirality recognition, but almost all host molecules prepared so far work in organic solvents, and the chiral recognition of charged chiral molecules in water with charged, water-soluble chiral hosts remains very difficult.[14] Because small electrolytes completely dissociate into free ions in water by hydration, attractive electrostatic and hydrogen-bonding interactions are hindered in water.[15] In sharp contrast, polyelectrolytes, such as nucleic acids, are completely different from small electrolytes; that is, a portion of the counterions are bound to polyelectrolytes with a sufficiently high charge density, and therefore, polyelectrolytes can effectively interact with small charged biomolecules even in water.[16] On the basis of these considerations, we recently found that a charged polyelectrolyte consisting of a chromophoric polyacetylene backbone and benzoic acid or phenylphosphonic acid as the pendant could interact with a variety of charged chiral biomolecules including amines, amino alcohols, amino acids, amino sugars, and peptides in water.[17] The complexes form supramolecular assemblies with a controlled helicity and exhibit a characteristic ICD without derivatization in water. These polyelectrolytes possess negatively charged functional groups as the pendants and can efficiently detect the chirality of positively charged chiral guest molecules.

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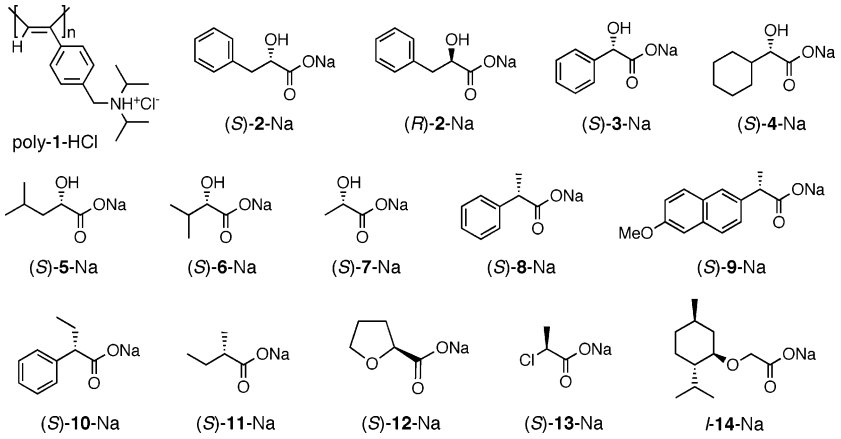
Chart 1. Structures of Poly-1-HCl and Chiral Carboxylates



In the present study, we investigated the helicity induction and chiral amplification of an optically inactive, positively charged polyacetylene, the hydrochloride of poly(4-(*N,N*-diisopropylaminomethyl)phenylacetylene) (poly-**1**-HCl) (Chart 1), in water with various chiral acids including phosphoric and sulfonic acids and amino acids as well as carboxylic acids by CD spectroscopy to develop a novel helical polymer capable of sensing chiral acids in water. The neutral poly-**1** was already reported to show an ICD in the UV−vis region due to the helix formation in the presence of chiral carboxylic acids in organic solvents.[9a,b] However, the neutral poly-**1** is not sensitive to the chirality of chiral acids in organic solvents and requires a large excess amount of chiral acids to exhibit a full ICD. Very recently, we also found that poly-**1**-HCl formed a predominantly one-handed helix induced by a small amount of a chiral acid as the dopant in water, thus showing a characteristic ICD in the UV−vis region. Moreover, the complex was found to form a lyotropic cholesteric liquid crystalline phase in concentrated water solutions, and the helix-sense excess of the polymer backbone was significantly amplified through interchain interactions in a lyotropic cholesteric state compared to that in a dilute solution.[18] However, a detailed investigation of the helix induction and chiral amplification of poly-**1**-HCl with various chiral acids in dilute water solution has not yet been reported.

Results and Discussion

CD Studies on Helix Induction of Poly-1-HCl with Chiral Acids in Water. Figure 1 shows the typical CD and absorption spectra of poly-**1**-HCl in the presence of sodium salts of (*R*)- and (*S*)-phenyllactic acid (**2**-Na) (0.5 equiv to monomer units of poly-**1**-HCl) in water. The complexes showed mirror images of the split-type intense ICDs in the polymer backbone region. A similar helicity induction on optically inactive polymers and oligomers through intermolecular chiral interactions has been reported.[19] The ICD magnitude slightly increased with the decreasing temperature (Table 1). These results indicate that poly-**1**-HCl can form a predominantly one-handed helix upon noncovalent complexation with the chiral acids in water. The CD titration experiments using (*S*)-**2**-Na in water (pH 4.9−5.4) at 25 and 0 °C were then carried out. The ICD intensities of the second Cotton ($\Delta\epsilon_{2nd}$) increased with the increasing concentration of (*S*)-**2**-Na and reached an almost constant value at [(*S*)-**2**-Na]/[poly-**1**-HCl] = 0.3 (Figure 2). The CD titration data were then analyzed

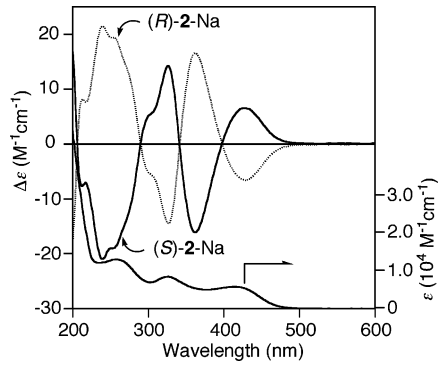


Figure 1. CD spectra of poly-**1**-HCl with (*S*)- and (*R*)-**2**-Na in water at room temperature. The absorption spectrum of poly-**1**-HCl with (*S*)-**2**-Na at room temperature is also shown. The concentration of poly-**1**-HCl is 1.0 mg (4.0 μmol monomer units)/mL. [**2**-Na]/[poly-**1**-HCl] = 0.5.

Table 1. Signs and Difference in Exciton Coefficient of the Second Cotton ($\Delta\epsilon_{2nd}$) for the Complexes of Poly-1-HCl with Chiral Carboxylates in Water[a]

		second Cotton [λ (nm) and $\Delta\epsilon_{2nd}$ ($M^{-1}\,cm^{-1}$)]			
guest	pH	sign	25 °C, $\Delta\epsilon$ (λ)	10 °C, $\Delta\epsilon$ (λ)	0 °C, $\Delta\epsilon$ (λ)
(*S*)-**2**-Na	5.1	−	15.04 (361)	15.63 (361)	15.88 (361)
(*R*)-**2**-Na	5.2	+	14.75 (361)	15.45 (361)	15.67 (361)
(*S*)-**3**-Na	5.3	−	14.38 (361)	15.19 (361)	15.42 (362)
(*S*)-**4**-Na	5.4	−	15.85 (361)	16.30 (361)	16.42 (361)
(*S*)-**5**-Na	5.3	−	13.49 (361)	14.29(362)	14.50 (362)
(*S*)-**6**-Na	5.3	−	7.33 (361)	8.87 (361)	9.20 (361)
(*S*)-**7**-Na	5.3	−	4.23 (361)	5.14 (361)	5.38 (361)
(*S*)-**8**-Na	5.1	−	10.43 (362)	11.73 (362)	11.93 (362)
(*S*)-**9**-Na	5.0	−	3.99 (362)	8.60 (363)	10.91 (364)
(*S*)-**10**-Na	5.1	−	13.17 (362)	14.48 (363)	14.83 (363)
(*S*)-**11**-Na	5.4	−	3.04 (361)	3.88 (360)	3.92 (361)
(*S*)-**12**-Na	5.5	−	1.08 (362)	1.27 (362)	1.29 (362)
(*S*)-**13**-Na	5.3	−	11.83 (361)	12.88 (361)	13.23 (362)
l-**14**-Na	4.9	+	14.93 (362)	15.20 (362)	15.02 (362)

[a] The concentration of poly-**1**-HCl is 1.0 mg/mL, and [guest]/[poly-**1**-HCl] = 0.1.

to estimate the binding constant (*K*). Plots of the $\Delta\epsilon_{2nd}$ values of poly-**1**-HCl as a function of the concentrations of (*S*)-**2**-Na gave a saturation binding isotherm. The Hill plot analysis of the data resulted in apparent binding constants (*K*s) of 1.9×10^4 and 2.9×10^4 M^{-1} at 25 and 0 °C, respectively.[20] Poly-**1**-HCl exhibited apparent ICDs even with 0.001 equiv of (*S*)-**2**-Na (Figure 2, inset). A very small chiral bias in the monomeric diisopropylammoniomethyl units of poly-**1**-HCl complexed with (*S*)-**2**-Na is significantly amplified to induce the same helix sense on the major free monomeric units. In sharp

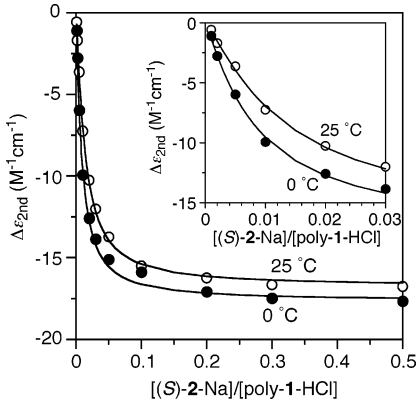


Figure 2. Titration curves of poly-**1**-HCl ($\Delta\epsilon_{2nd}$) with (*S*)-**2**-Na in water (pH 4.9−5.4) at 25 and 0 °C. Inset shows expanded detail of the titration curves. Curves in the plots were the calculated ones using $K = 1.9 \times 10^4$ and 3.0×10^4 at 25 and 0 °C, respectively.

contrast, the neutral poly-**1** required a large amount of chiral acids (>500 equiv) to induce a full ICD in organic solvents, such as tetrahydrofuran (THF).[9a,b] A similar and strong chiral amplification was observed for crown ether-bound poly(phenylacetylene)s in organic solvents.[10] However, the neutral polyacetylenes were not sensitive to the chirality in water,[21] suggesting that the polyelectrolyte function of the poly-**1**-HCl is essential for a powerful chirality-sensing probe with a high sensitivity in water.

The magnitude of the ICDs was influenced by the pH and salt (NaCl) concentration (see Supporting Information). The ICD magnitude dramatically decreased with a decrease in the pH in the region of pH < 4. Moreover, the addition of a small amount of aqueous 0.1 N NaOH resulted in precipitation of the polymer (pH > 6), which means that the generation of free diisopropylaminomethyl pendants remarkably reduces the solubility of the polymer in water due to the highly hydrophobic nature of the pendant. The addition of an achiral salt, such as NaCl, caused a decrease in the ICD magnitude. These results indicate that the nature of the interaction between poly-**1**-HCl and chiral acids may be mainly ionic rather than hydrophobic in water.

The results of the ICD studies for the complexes with other chiral aromatic and aliphatic carboxylates as well as α-hydroxy acid salts (Chart 1) are summarized in Table 1. The charged poly-**1**-HCl showed split-type ICDs in the presence of a very small amount of chiral α-hydroxy acid salts (**2**-Na−**7**-Na) ([α-hydroxy acid salt]/[poly-**1**-HCl] = 0.1) in water. The magnitude of the Cotton effects appears to reflect the bulkiness of the α-hydroxy acids and likely increased with an increase in the bulkiness of the chiral acids in the order of **2**-Na, **3**-Na, **4**-Na > **5**-Na > **6**-Na > **7**-Na. As we previously reported, the neutral poly-**1** exhibited almost no or very weak ICDs in the presence of an excess of chiral carboxylic acids in organic solvents such as THF, whereas it showed moderate or weak ICDs in the presence of an excess of chiral α-hydroxy acids such as (*S*)-**3**.[9b] In organic solvents, the chelation-type complexation of the hydroxy group of the α-hydroxy acids to the amino group of poly-**1** together with the acid−base interaction was considered to be important for the appearance of the ICDs.[9] In water, however, poly-**1**-HCl showed ICDs in the presence of a small amount of chiral carboxylates without an α-hydroxy group (**8**-Na−**14**-Na) ([carboxylate]/[poly-**1**-HCl] = 0.1). These results suggest that the additional intermolecular hydrogen bonding of the hydroxy group seems to be no longer essential for the helicity induction on the charged poly-**1**-HCl with chiral acids in water. The ICD magnitude of the poly-**1**-HCl−chiral carboxylate complexes also tends to increase with an increase in the bulkiness of the carboxylates at 25 °C, except for **9**-Na and **13**-Na. There was a good relation between the Cotton effect signs of the complexes and the absolute configurations of the chiral acids. The complexes showed the same Cotton effect signs if the absolute configurations of the chiral acids (**2**−**13**) are the same. Therefore, the induced Cotton effect signs corresponding to the helix sense of poly-**1**-HCl can be utilized for the chirality assignments of chiral carboxylic acids in water.

Poly-**1**-HCl also responded to other chiral acids, such as phosphoric (**15**-Na−**20**-Na, **21**-K, DNA) and sulfonic acids ((*R*)-**22**) and a bile acid (**23**-Na) (Chart 2), in water, and exhibited similar ICDs in their patterns in the UV−vis region (Table 2). As for chiral phosphoric acids, four ribonucleotides (**15**-Na−**18**-Na) with the same D-ribofuranoside residue were used in order to investigate whether poly-**1**-HCl could exhibit an ICD reflecting the difference in the nucleobases. Interestingly, poly-**1**-HCl complexed with guanosine 5′-monophosphate (**16**-Na) exhibited an opposite ICD pattern compared with those of the complexes with other nucleotides (**15**-Na, **17**-Na, and **18**-Na). A similar nucleobase-specific CD inversion has also been observed for the complexation of poly((4-dihydroxyborophenyl)acetylene) with **16**-Na among four ribonucleotides in water,[8b] although the mechanism for the nucleobase-selective inversion of the ICD is not clear. Among four ribonucleotides, **17**-Na showed a relatively weak ICD. These results indicate that the ribonucleotide bases play a critical role in the helix-sense control of poly-**1**-HCl, and poly-**1**-HCl may be used as a probe for a sensory system of ribonucleotide base recognition by using CD spectroscopy.

Nucleotides exist as di- and triphosphate types in nature. For example, adenosine can be isolated as 5′-diphosphate (ADP **19**-Na) and 5′-triphosphate (ATP **20**-Na) as well as 5′-monophosphate (AMP, **15**-Na), and ATP−ADP interconversion plays an important role in biological processes as a major energy source. We then investigated the effect of the type of anionic phosphate residues on the helicity induction in the cationic poly-**1**-HCl using **15**-Na, **19**-Na, and **20**-Na as the helix inducer (Table 2). The magnitude of the observed ICDs increased in the following order: triphosphate (**20**-Na) > diphosphate (**19**-Na) > monophosphate (**15**-Na), indicating that the multiple interactions between the phosphoric acid residues and the positively charged pendants of poly-**1**-HCl appear to be favorable for the induction of helicity with an excess one-handedness in poly-**1**-HCl. The positively charged poly-**1**-HCl can also interact with the negatively charged DNA from salmon testes to give an apparent ICD without precipitation of the complex at a low DNA concentration ([DNA] < 0.01 mg/mL). A bile acid **23**-Na with remote stereogenic centers also produced a weak ICD (Table 2).

Amino acids are also important optically active biomolecules and can complex with poly-**1**-HCl, thus showing characteristic ICDs. The ICD results for the complexes of poly-**1**-HCl with several amino acids and its derivatives and some chiral alcohols (Chart 3) are summarized in Table 3. The complexes with amino acids exhibited rather weak ICDs, except for tryptophan (Trp)

Chart 2. Structures of Various Chiral Acids

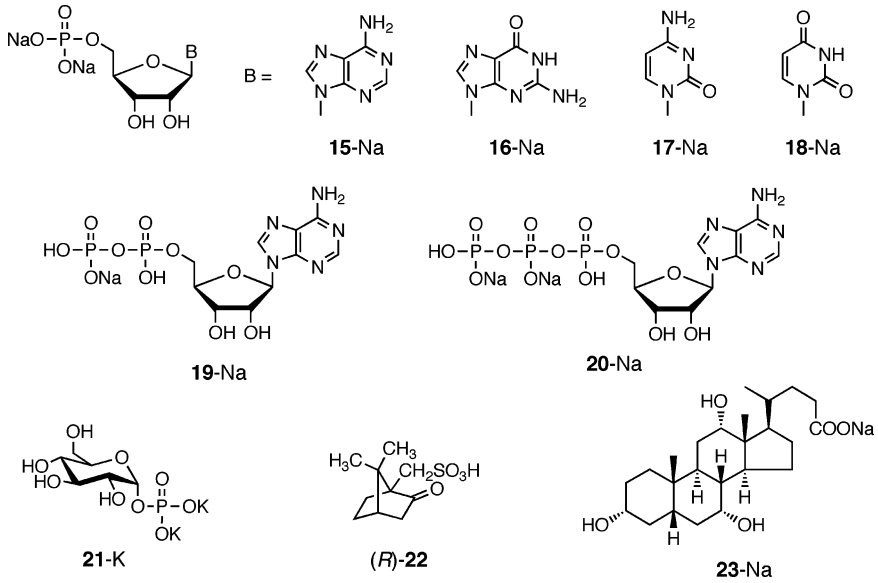


Table 2. Signs and Difference in Exciton Coefficient of the Second Cotton ($\Delta\epsilon_{2nd}$) for the Complexes of Poly-1-HCl with Chiral Phosphoric and Sulfonic Acids in Water[a]

		second Cotton [λ (nm) and $\Delta\epsilon_{2nd}$ (M^{-1} cm^{-1})]			
guest	pH	sign	25 °C, $\Delta\epsilon$ (λ)	10 °C, $\Delta\epsilon$ (λ)	0 °C, $\Delta\epsilon$ (λ)
phosphoric acid					
15-Na	5.3	+	8.09 (361)	9.67 (361)	10.17 (361)
16-Na	5.3	−	12.41 (361)	12.49 (362)	12.17 (362)
17-Na	5.6	+	5.36 (363)	7.39 (362)	8.13 (362)
18-Na	5.6	+	10.27 (362)	12.34 (362)	12.87 (362)
19-Na	4.9	+	13.66 (361)	14.81 (361)	15.14 (361)
20-Na	4.2	+	13.90 (361)	15.40 (361)	15.62 (361)
21-K	5.5	+	0.49 (361)	0.69 (364)	0.75 (361)
DNA[b]	5.7	−	0.12 (360)	0.13 (360)	0.14 (361)
sulfonic acid					
(*R*)-**22**	4.4	−	15.42 (359)	15.87 (360)	15.87 (360)
bile acid					
23-Na	5.8	−	0.19 (357)	0.14 (357)	0.12 (363)

[a] The concentration of poly-**1**-HCl is 1.0 mg/mL, and [guest]/[poly-**1**-HCl] = 0.1. [b] The concentration of salmon DNA is 0.01 mg/mL.

and phenylalanine (Phe) bearing bulky aromatic substituents compared with those with chiral carboxylic acids even at 0 °C. The electrostatic repulsions between the positively charged pendants of poly-**1**-HCl and the ammonium ion of the amino acids may disturb the attractive interaction because amino acids exist in the twitter ionic form in the pH region where the CD measurements were performed (3.7 < pH < 5.3). Therefore, N-protected amino acids with Boc groups resulted in a dramatic increase in the ICD intensities. As for the relationship between the observed Cotton effect signs and the absolute configurations of the amino acids, there is a good relationship for the *N*-Boc amino acids, although such a relationship could not be observed for the free amino acids. For L-Phe, the Cotton effect sign became inverted from positive to negative at 0 °C, but the reason for this change is not clear at present.

Aromatic amino acids, such as Trp and Phe, induced a particularly intense ICD among the tested amino acids without protection of the amino group. In this case, not only the electrostatic attractive interaction but also the hydrophobic interaction might play an important role in the helicity induction on poly-**1**-HCl in water. Recently, we reported that poly(phenylacetylene)s bearing crown ether pendants also exhibited intense ICDs in the presence of aromatic amino acids, Trp and Phe, as well as an aromatic alcohol **25** in water, and the hydrophobic interaction between the polymers and these chiral guests functions as a chiral bias for inducing an excess one-handed helicity in water.[21] We then investigated the importance of the hydrophobic interaction for helicity induction in poly-**1**-HCl using chiral neutral alcohols (L-**24**, (*S*)-**25**, and (*S*)-**26** in Chart 3) having no negatively charged groups capable of interacting with poly-**1**-HCl through electrostatic interactions as a helix inducer. Among these chiral alcohols, an aromatic alcohol (*S*)-**25** gave an intense ICD, which suggests that poly-**1**-HCl can also be used to detect the chirality of chiral neutral molecules through hydrophobic interactions in water.

Chiral Amplification and Nonlinear Effects in Water. Previously, we reported that the complex formation of poly(phenylacetylene)s bearing carboxy, phosphonate, or crown ether residues as the pendants with partially resolved chiral compounds, such as amines and amino acids, showed a unique positive nonlinear relationship (chiral amplification or "majority rule") between the enantiomeric excess (ee) of the chiral compounds and the observed ICD intensities in water as well as in organic solvents.[6b,7,10,22] We then investigated if a similar chiral amplification could be possible for poly-**1**-HCl in water. The chiral carboxylate **2**-Na was selected as a helix inducer because it produced the most intense ICD in water among the chiral acids used in this study as **4**-Na did (Table 1). The changes in the ICD intensity of poly-**1**-HCl with respect to the ee's of **2**-Na in water are depicted in Figure 3. The CD intensities of poly-**1**-HCl, corresponding to the helical sense excesses, were out of proportion to the ee's of **2**-Na, showing a convex deviation from the linearity in water. The extent of the departure from linearity slightly increased with the decreasing temperature. When poly-**1**-HCl was dissolved in water with an only 0.1-fold excess **2**-Na of 60% ee ((*S*) rich), the complex showed the full ICD as induced by 100% ee of **2**-Na (Figure 3A). The excess enantiomer bound to the polymer induces

Chart 3. Structures of Amino Acids and Chiral Alcohols

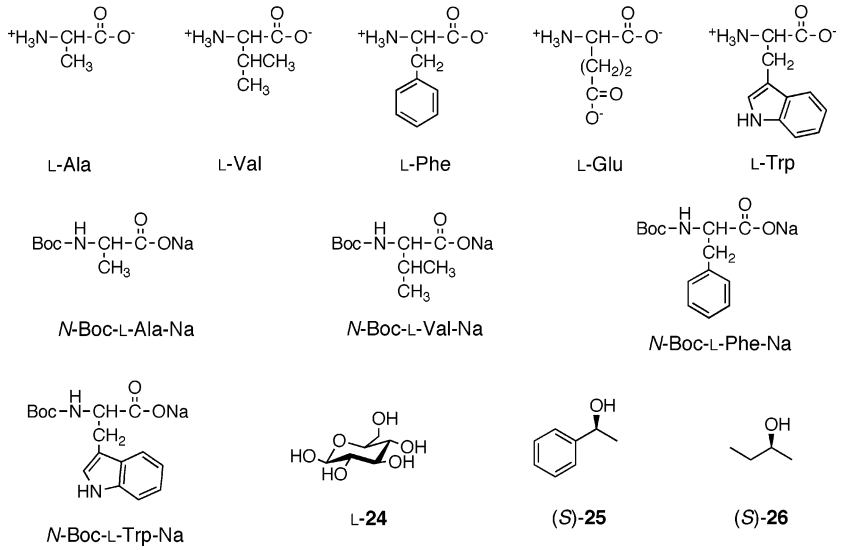


Table 3. Signs and Difference in Exciton Coefficient of the Second Cotton ($\Delta\epsilon_{2nd}$) for the Complexes of Poly-1-HCl with L-Amino Acids and Chiral Alcohols in Water[a]

			second Cotton [λ (nm) and $\Delta\epsilon_{2nd}$ (M^{-1} cm^{-1})]			
guest	[guest]/[poly-**1**-HCl]	pH	sign	25 °C, $\Delta\epsilon$ (λ)	10 °C, $\Delta\epsilon$ (λ)	0 °C, $\Delta\epsilon$ (λ)
amino acid						
L-Ala	100	5.3	−	0.37 (363)	0.46 (361)	0.48 (363)
	0.1	5.1	−	*b*	*b*	0.10 (358)
L-Phe	40	5.1	c	+5.08 (362)	+0.64 (361)	−4.55 (361)
	0.1	5.2	+	*b*	*b*	0.095 (360)
L-Glu	5	3.7	−	*b*	*b*	0.10 (365)
L-Val	0.1	5.1	−	*b*	*b*	0.076 (367)
L-Trp	7	5.2	+	9.13 (362)	11.1 (362)	12.1 (362)
	0.1	5.2	+	0.22 (360)	0.41 (360)	0.46 (359)
N-Boc-L-Ala	0.1	4.7	−	3.81 (362)	4.27 (362)	4.25 (362)
N-Boc-L-Val-Na	0.1	5.1	−	0.69 (361)	1.44 (361)	1.77 (361)
N-Boc-L-Phe-Na	0.1	5.0	−	9.84 (361)	11.72 (361)	12.38 (361)
N-Boc-L-Trp-Na	0.1	5.3	−	12.56 (361)	12.73 (361)	12.53 (361)
alcohol						
L-**24**	10	5.3	−	0.061 (363)	0.070 (367)	0.076 (364)
(*S*)-**25**	10	5.3	−	10.25 (362)	11.01 (362)	11.01 (362)
	1	4.0	−	1.71 (363)	2.36 (363)	2.48 (363)
(*S*)-**26**	10	5.6	−	0.93 (361)	1.11 (360)	1.11 (360)

[a] The concentration of poly-**1**-HCl is 1.0 mg/mL. [b] No distinctive CD. [c] The Cotton effect sign was inverted depending on temperatures.

an excess of a single-handed helix despite its proportion, which will result in a more intense ICD than that expected from the ee of **2**-Na. The positive nonlinear effect of poly-**1**-HCl vs the ee of **2**-Na increased with an increase in the amount of **2**-Na. As shown in Figure 3B, the extent of the departure from linearity increased, especially in the low ee region of **2**-Na (<60% ee) when poly-**1**-HCl was dissolved in water with a 0.5-fold excess **2**-Na. Therefore, a stronger nonlinear effect would be expected for poly-**1**-HCl in the presence of greater amounts of the chiral acid. However, the further addition of (*S*)-**2**-Na (>0.5 equiv) resulted in precipitation of the polymer because the solution pH became higher with the increasing amount of (*S*)-**2**-Na, and therefore, further experiments were difficult.

Conclusions

In summary, we have found that a positively charged poly(phenylacetylene) derivative bearing the hydrochloride of the diisopropylaminomethyl group as the pendants formed a predominantly one-handed helical conformation induced by a noncovalent interaction with various chiral acids in water, and the complexes exhibited characteristic ICDs in the UV−vis region even in the presence of a small amount of chiral acids with a low optical activity. Poly-**1**-HCl was highly sensitive to the chirality of the carboxylic acids and showed the same Cotton effect signs if the configurations were the same. The present results demonstrate that the poly-**1**-HCl can be utilized as a chirality sensing probe for chiral acids in water. On the other hand, the neutral poly-**1** was not sensitive to the chirality of chiral acids in organic solvents, and other noncharged neutral polyacetylenes also showed a weak chiral amplification in water. These results suggest that the polyelectrolyte function of the poly-**1**-HCl may play an important role in the high chiral amplification property in water. This finding will contribute to the design and construction of more sensitive helical polyacetylenes for the detection of chirality of target molecules in water.

Experimental Section

Materials. Deionized, distilled water was degassed with nitrogen before use for all experiments. Optically active acids and alcohols were obtained from Aldrich or Tokyo Kasei (TCI, Tokyo, Japan). The sodium salt of **2** was prepared by neutralization of **2** with aqueous 1 N NaOH, followed by precipitation

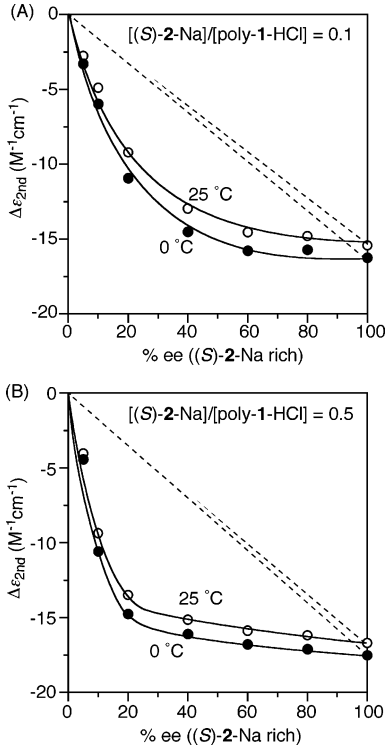


Figure 3. Changes in ICD intensity ($\Delta\epsilon_{2nd}$) of poly-**1**-HCl (1.0 mg/mL) vs the % ee of **2**-Na ([**2**-Na]/[poly-**1**-HCl] = 0.1; pH 5.1−5.4) (A), ([**2**-Na]/[poly-**1**-HCl] = 0.5; pH 5.4−5.5) (B) in water at 25 and 0 °C during the complexation with poly-**1**-HCl.

into a large amount of acetone. The other sodium salts of optically active carboxylic acids (**3**−**14**) were prepared by mixing the solution of the corresponding acids in water or ethanol with aqueous 1 N NaOH ([acids]/[NaOH] = 1.0 (mol/mol)), followed by lyophilization. Nucleotides (**15**−**20**-Na) and DNA from salmon testes were purchased from Sigma and used as received.

Cis-transoidal poly-**1** was prepared by polymerization of 4-(*N*,*N*-diisopropylaminomethyl)phenylacetylene with $[Rh(nbd)Cl]_2$ (nbd = norbornadiene) in THF according to the previously reported method.[9a,b] Poly-**1** was quantitatively converted to its HCl salt (poly-**1**-HCl) by dissolving poly-**1** in aqueous 1 N HCl, followed by precipitation into acetone and filtration. The recovered polymer was dissolved in water, and the solution was lyophilized. The stereoregularity of the poly-**1**-HCl was investigated by NMR spectroscopy.[23] However, we could not estimate the stereoregularity of the poly-**1**-HCl by its ^{1}H NMR spectrum in D_2O because of the broadening of the main chain protons even at 80 °C, which may be due to the rigidity of the polymers' main chains. The Raman spectrum of poly-**1**-HCl gave useful information and showed intense peaks at 1580, 1353, and 974 cm^{-1}, which can be assigned to the C=C, C−C, and C−H bond vibrations in the *cis*-polyacetylenes, while those in the *trans*-polyacetylene were not observed, indicating that the poly-**1**-HCl possesses a highly *cis-transoidal* structure (Figure S-2).[24] The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly-**1**−HCl are 3.4×10^5 and 2.2, respectively, as determined by SEC using poly(ethylene oxide) and poly(ethylene glycol) standards in water containing 9 mM tartaric acid and the 0.1 mM tartaric acid disodium salt as the eluent at a flow rate of 0.6 mL/min.

Spectroscopic data of poly-**1**-HCl: ^{1}H NMR (D_2O, 80 °C): δ 1.34 (br, CH_3, 12H), 3.76 (br, CH × 2 and CH_2, 4H), 5.75 (br, =CH, 1H), 6.0−9.6 (br, aromatic, 4H). Anal. Calcd for $(C_{15}H_{22}ClN)_n$: C, 71.55; H, 8.81; N, 5.56. Found: C, 71.55; H, 8.93; N, 5.75.

Instruments. Melting point was measured on a Yanakao melting point apparatus and is uncorrected. The solution pH was measured with a B-211 pH meter (Horiba, Japan). NMR spectra were taken on a Varian Mercury 300 operating at 300 MHz for ^{1}H and a Varian VXR-500S operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C in D_2O using acetonitrile as the internal standard. Elemental analyses were performed by the Nagoya University Analytical Laboratory in School of Engineering. SEC measurements were performed with a Jasco PU-980 liquid chromatograph (Jasco, Hachioji, Japan) equipped with a UV (254 nm; Jasco UV-970) detector. A Tosoh (Tokyo, Japan) TSK-GEL SuperAWM-H column (30 cm) was connected, and a water solution containing 9 mM tartaric acid and the 0.1 mM tartaric acid sodium salt was used as the eluent at a flow rate of 0.6 mL/min. The molecular weight calibration curve was obtained with poly(ethylene oxide) and poly(ethylene glycol) standards (Tosoh). IR spectra were recorded with a Jasco Fourier transform IR-620 spectrophotometer. Laser Raman spectra were taken on a Jasco RMP-200 spectrophotometer. The absorption and CD spectra were measured in a 0.1, 0.5, 1.0, or 10 mm quartz cell on a Jasco V-570 spectrophotometer and a Jasco J-725 or J-820 spectropolarimeter, respectively. The temperature (0−25 °C) was controlled with a Jasco ETC 505T (for absorption spectral measurements) and a Jasco PTC-423L apparatus (for CD spectral measurements).

CD Measurements. The concentration of poly-**1**-HCl was calculated on the basis of the monomer units and was 1 mg/mL (4.0 mM monomer units) unless otherwise stated. In the complexation of poly-**1**-HCl with optically active acids, a stock solution of poly-**1**-HCl (2 mg/mL) in water was prepared in a 5 mL flask equipped with a stopcock. A 500 μL aliquot of the poly-**1**-HCl solution was transferred to a 1 mL flask equipped with a stopcock using a micropipet (Mettler-Toledo GmbH, Switzerland). An appropriate amount of sodium salts of optically active acids was added to the flask, and the solution was diluted with water to keep the poly-**1**-HCl concentration at 1.0 mg/mL and absorption and CD spectra were taken.

CD Titrations of Poly-1-HCl with (*S*)-2-Na and Hill Plots. A stock solution of poly-**1**-HCl (2.0 mg/mL, 7.9 mM) in water was prepared in a 5 mL flask equipped with a stopcock. Stock solutions of (*S*)-**2**-Na (0.20, 0.40, 1.99, and 7.94 mM) in water were also prepared in 100, 100, 25, and 5 mL flasks, respectively. The 0.50 mL aliquots of the poly-**1**-HCl solution were transferred to eleven 1 mL flasks equipped with stopcocks, and increasing amounts of the stock solutions of the (*S*)-**2**-Na were added to the flasks; the molar ratios of (*S*)-**2**-Na to poly-**1**-HCl were 0.001, 0.002, 0.005 (0.20 mM (*S*)-**2**-Na), 0.01, 0.02, 0.03 (0.40 mM (*S*)-**2**-Na), 0.05, 0.1 (1.99 mM (*S*)-**2**-Na), and 0.2, 0.3, 0.5 (7.94 mM (*S*)-**2**-Na), and the resulting solutions were diluted with water to keep the poly-**1** concentrations at 1.0 mg/mL (4.0 mM). The absorption and CD spectra were then taken for each flask to determine the changes in the CD spectra (Figure 2). Plots of the CD intensities of the second Cotton ($\Delta\epsilon_{2nd}$) of poly-**1**-HCl as a function of concentration of (*S*)-**2**-Na gave a saturation binding isotherm at 25 and 0 °C. The Hill plot analysis of the data resulted in apparent binding constants (*K*s) according to the Hill equation, $\log(Y/(1-Y)) = n \log[G] + n \log K$, where Y, n, and [G] represent the fractional saturation, the Hill coefficient, and the concentration of the guest, respectively.[20] The n values were 1.20 and 1.14 with a correlation coefficient $r > 0.999$ at 25 and 0 °C, respectively.

Nonlinear Effects. The nonlinear effect between intensities of ICD and percent ee of **2**-Na in the complexation with poly-**1**-HCl was investigated in water. The molar ratio of **2**-Na to the monomer units of poly-**1**-HCl ([**2**-Na]/[poly-**1**-HCl]) was held constant at 0.1 or 0.5 (mol/mol). A typical experimental procedure using **2**-Na ([**2**-Na]/[poly-**1**-HCl] = 0.5) is described below. Stock solutions of poly-**1**-HCl (2 mg/mL, 10 mL), (*S*)-**2**-Na (5 mM, 25 mL), and (*R*)-**2**-Na (5 mM, 25 mL) were prepared. Aliquots of the stock solutions of (*S*)- and (*R*)-**2**-Na were placed into seven 1 mL flasks so that the percent ee of the mixtures (*S* rich) became 5, 10, 20, 40, 60, 80, and 100. To the flasks was added a 0.50 mL aliquot of the stock solution of poly-**1**-HCl, and the resulting solutions were diluted with water to keep the poly-**1**-HCl concentration at 1.0 mg/mL (4.0

mM). The absorption and CD spectra were then taken for each flask to determine the changes in the CD spectra (Figure 3B). The same procedure was performed in the experiment with poly-**1**-HCl and **2**-Na ([**2**-Na]/[poly-**1**-HCl] = 0.1).

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Supporting Information Available: ICD intensity changes in the pH and salt concentration for the complex of poly-**1**-HCl with (*S*)-**2**-Na and the laser Raman spectrum of poly-**1**-HCl. This material is available free of charge via the Internet at http://pubs.acs.org.

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