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Temperature-Induced Chiroptical Changes in a Helical Poly(phenylacetylene) Bearing *N*,*N*-Diisopropylaminomethyl Groups with Chiral Acids in Water

Kanji Nagai,[a, b] Katsuhiro Maeda,[a] Yoshihisa Takeyama,[a] Takahiro Sato,[c] and Eiji Yashima*[a, b]

Abstract: A stereoregular poly(phenylacetylene) bearing an *N*,*N*-diisopropylaminomethyl group as the pendant (poly-**1**) changed its structure into the prevailing one-handed helical conformation upon complexation with optically active acids in water. The complexes exhibited induced circular dichroism (ICD) in the UV/Vis region of the polymer backbone. Poly-**1** is highly sensitive to the chirality of chiral acids and can detect a small enantiomeric imbalance in these acids, in particular, phenyl lactic acid in water. For example, a 0.005% enantiomeric excess of phenyl lactic acid can be detected by CD spectroscopy. The observed ICD intensity and pattern of poly-**1** were dependent on the temperature and concentration of poly-**1**, probably due to aggregations of the polymer at high temperature as revealed by dynamic light scattering and AFM. On the basis of the temperature-dependent ICD changes, the preferred chiral helical sense of poly-**1** was found to be controlled by noncovalent bonding interactions by using structurally different enantiomeric acids.

Keywords: chirality · circular dichroism · helical structures · induced helices · poly(phenylacetylene)s

Introduction

The helix is an important structural motif among a variety of conformational states observed in molecular and supramolecular organizations as exemplified in DNA and proteins. Therefore, the construction of artificial helical polymers[1] and oligomers (foldamers)[2] or supramolecular helical assemblies[3] with controlled helicity has attracted significant interest in recent years in the fields of polymer and supramolecular chemistry and materials science because of their possible applications in chiroptical devices and chiral materials, which include enantioselective adsorbents and catalysts.[1a,g,4]

In a series of studies, we reported unique helicity induction in optically inactive, stereoregular *cis-transoidal* poly(phenylacetylene)s that bear various functional groups, such as carboxy,[5] phosphonate,[6] boronate,[7] sulfonate,[8] and amine groups,[9,10] or bulky crown ethers[11] as pendants. These poly(phenylacetylene)s change their dynamically racemic helical conformations to that of the preferred sense upon complexation with specific chiral guests in organic solvents[5,6,8,9,11] and water.[7,10,12] Their complexes exhibit characteristic induced circular dichroism (ICD) in the UV/Vis region of the polymer backbones. The signs of the Cotton effect can be used to predict the absolute configurations of the guest molecules.[11p,13]

Among the poly(phenylacetylene)s prepared to date, poly(4-(*N*,*N*-diisopropylaminomethyl)phenylacetylene) (poly-**1**; Scheme 1) is particularly interesting because the hy-

[a] K. Nagai, Dr. K. Maeda, Y. Takeyama, Prof. Dr. E. Yashima
Department of Molecular Design and Engineering
Graduate School of Engineering
Nagoya University
Chikusa-ku, Nagoya 464-8603 (Japan)
Fax: (+81) 52-789-3185
E-mail: yashima@apchem.nagoya-u.ac.jp

[b] K. Nagai, Prof. Dr. E. Yashima
Yashima Super-Structured Helix Project
Exploratory Research for Advanced Technology (ERATO)
Japan Science and Technology Agency (JST)
Creation Core Nagoya 101
2266-22 Shimoshidami, Moriyama-ku
Nagoya 463-0003 (Japan)

[c] Prof. Dr. T. Sato
Department of Macromolecular Science
Osaka University
Machikaneyama-cho, Toyonaka
Osaka 560-0043 (Japan)

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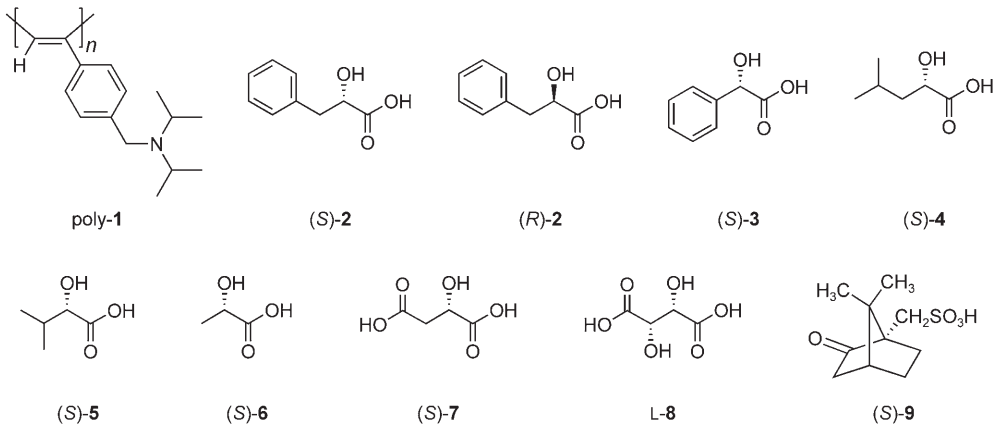

Scheme 1. Structures of poly-**1** and chiral carboxylic and sulfonic acids.

drochloride of poly-**1** (poly-**1**·HCl) is soluble in water and produces an excess in helical sense in the presence of a small amount of various chiral acids, such as the sodium salt of phenyl lactic acid (**2**), of low enantiomeric excess (*ee*) through a significant amplification of chirality in water, thus showing ICD.[10] Moreover, poly-**1**·HCl was, for the first time, found to form a lyotropic nematic liquid crystal (LC) in concentrated aqueous solution because of its stiff helical backbone with a long persistence length of 26 nm. Furthermore, the nematic LC phase converted into the cholesteric counterpart by doping with a tiny amount of chiral acids with low *ee*, and the helix-sense excess of the polymer backbone was further amplified through interchain interactions in the cholesteric LC state relative to that in dilute solution.[10a,c] This liquid-crystalline feature of the induced helical poly-**1**·HCl enabled us to determine its helical structure by X-ray diffraction of oriented films of liquid-crystalline poly-**1**·HCl.[10c] The polyelectrolyte function of poly-**1**·HCl accompanied by the hydrophobic pendants[14] appears to be crucial for such a hierarchical amplification of the macromolecular helicity in dilute and concentrated aqueous solution because the neutral poly-**1** has a low sensitivity to the chirality of the chiral acids[9a,b] and produces no LC phase in organic solvents.[10a]

During the course of our studies, we found that the neutral poly-**1**, which is not soluble in water, became soluble in the presence of excess amounts of free aromatic and aliphatic carboxylic acids ([acid]/[poly-**1**] > 2), which prompted us to investigate the helicity induction and chiral amplification of free poly-**1** with chiral acids in water.

Abstract in Japanese:

側鎖にジイソプロピルアミノメチル基を有するポリフェニルアセチレン誘導体が、水中で光学活性な酸存在下、一方向巻きに片寄ったらせん構造の形成に由来する誘起 CD を示すことを見出した。低温では光学活性な酸のキラリティーに非常に感度良く応答し、0.005%の酸の鏡像体過剰率も CD により検知可能であった。誘起 CD は濃度および温度依存性を示し、AFM や光散乱測定より高温、高濃度では会合体を形成している可能性が高いことが示唆された。誘起 CD の温度応答性を利用して、構造の異なる光学活性な酸存在下、温度による CD 符号の反転が観測された。

Results and Discussion

CD Studies of Helix Induction of Poly-1 with Chiral Acids in Water

Poly-**1** was prepared by the polymerization of the corresponding monomer (**1**) with $[Rh(nbd)Cl]_2$ (nbd = norbornadiene) according to a previously reported method.[9a,b,10] The stereoregularity of poly-**1** was confirmed to be highly *cis-transoidal* (*cis* content = 96%) based on ^{1}H NMR spectroscopy (see Supporting Information, Figure S1).[10c,15] The number-average molecular weight (M_n) and its molecular-weight distribution (M_w/M_n) were 3.4×10^5 and 2.21, respectively, as determined by size-exclusion chromatography (SEC) of its hydrochloride salt (poly-**1**·HCl).[10]

Figure 1a shows typical CD and absorption spectra of poly-**1** in the presence of (*R*)- and (*S*)-**2** (4 equiv with respect to monomer units of poly-**1**) in water at 20 °C (green solid and dotted lines, respectively), as well as the spectral changes at various temperatures.[16] The complexes exhibited mirror images of split-type intense ICD signals in the polymer-backbone region at 20 °C; the CD and absorption spectral patterns and the ICD signal intensity were similar to those of the complex of poly-**1**·HCl with the sodium salt of (*S*)- or (*R*)-**2** ((*S*)- or (*R*)-**2**-Na) in water at 25 °C.[10a] However, in sharp contrast to the poly-**1**·HCl–(*S*)-**2**-Na complex in water, the ICD signal magnitude was sensitive to temperature and increased with a decrease in temperature, although it decreased sharply at around 22–25 °C, and the ICD signal almost completely disappeared at 30 °C.

This remarkable change in the ICD signal intensity was accompanied by a significant change in the absorption spectra. The absorbance maximum (λ_{max}) at 422 nm and 0 °C underwent a red shift to 449 nm at 30–40 °C, the peak at around 320 nm decreased as the temperature increased, with clear isosbestic points at 302 and 375 nm, and the color of the solution changed from yellow to orange (Figure 1a–c).

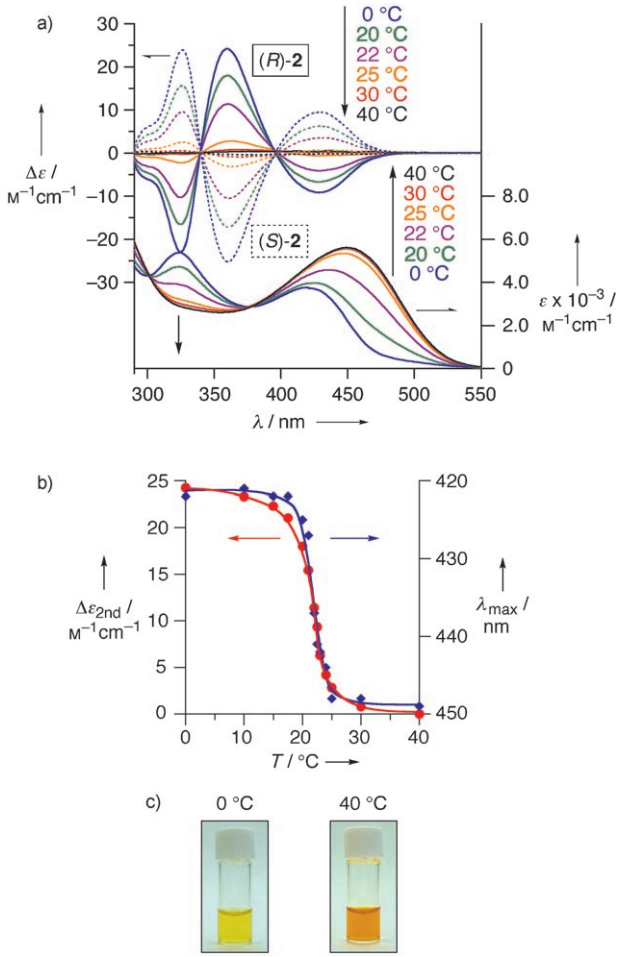

Figure 1. a) CD spectral changes of poly-**1** with (*R*)- and (*S*)-**2** in water (pH 3.1) at various temperatures. Absorption spectral changes of poly-**1** with (*R*)-**2** in water are also shown. b) Temperature-dependent changes in $\Delta\varepsilon_{2nd}$ (red circles) and λ_{max} (blue diamonds) of poly-**1** with (*R*)-**2** in water. c) Visible difference of poly-**1** with (*R*)-**2** in water at 0 and 40 °C. The concentration of poly-**1** was 1.0 mg (4.6 mmol monomer units) mL^{-1}. [**2**]/[poly-**1**] = 4.

These CD and absorption spectral changes were completely reversible and could be repeated at least ten times, which indicates that the helix-sense preference of poly-**1** induced by (*S*)- or (*R*)-**2** increases with decreasing temperature, and the conformation of the polymer backbone may change from a tightly twisted helix at lower temperatures to a rather relaxed, extended one at high temperatures. This speculation is supported by the fact that the CD signal intensity decreased monotonically while maintaining its spectral pattern along with the changes in the absorption maxima (Figure 1 b). A similar thermoreversible change in the absorption spectrum of poly-**1** also took place in the presence of achiral benzoic acid (see Supporting Information, Figure S3). Notably, poly-**1**·HCl complexed with (*S*)- or (*R*)-**2**-Na ([**2**-Na]/[poly-**1**·HCl] = 0.5) did not show such a change in its absorption and CD spectra over the same temperature range (0–40 °C). A similar temperature-dependent CD and absorption spectral change was reported for poly(*N*-propargylamide)s, and this was considered to be due to a transition of the polymer backbones from helix to random coil.[17]

Another possible explanation for the signal shifts in the absorption spectra to longer wavelengths may be due to aggregations of the polymer main chains at high temperature.[18] We next obtained the CD and absorption spectra of poly-**1** at different concentrations ([poly-**1**] = 1–0.01 mg mL^{-1}) in the presence of a constant concentration of (*S*)-**2** at 25 °C (Figure 2). The ICD signal magnitude increased significantly with decreasing poly-**1** concentration and was accompanied by a blue shift in the absorption spectrum. The concentration-dependent changes in the CD and absorption spectra of the poly-**1**–**2** complex suggest the formation of poly-**1** aggregates at high temperature.

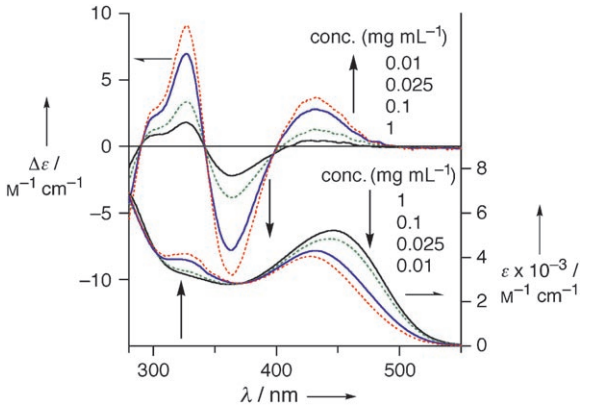

Figure 2. CD and absorption spectral changes of poly-**1** with (*S*)-**2** in water (pH 3.0–2.7) at various concentrations of poly-**1** (0.01–1 mg mL^{-1}) at 25 °C. The concentration of (*S*)-**2** was 3.1 mg (19 mmol) mL^{-1}.

Dynamic light scattering (DLS) of the poly-**1**–(*S*)-**2** complex in water at high (38 °C) and low (3 °C) temperatures was then performed. The values of the hydrodynamic radius (R_h) of the polymer estimated in water at 3 and 38 °C were 43 nm and 2.35 μm, respectively. Furthermore, from the light-intensity-autocorrelation function ($g^2(\tau)$), it was found that the time-correlation delay was much faster at 3 °C than at 38 °C, which indicates that large particles were formed at 38 °C (see Supporting Information, Figure S4).

AFM measurements were also performed to obtain further information with respect to the morphology of the poly-**1**–(*S*)-**2** aggregates at high and low temperatures (Figure 3). Individual poly-**1** chains complexed with (*S*)-**2** were directly observed on mica prepared from a dilute solution at 0 °C, whereas a number of entwined polymer chains were observed when deposited at 40 °C. These results agree with the assumption that the poly-**1**–(*S*)-**2** complex exists as aggregates at high temperature.[19]

Poly-**1** also responded to other optically active free carboxylic and sulfonic acids (**3**–**9** in Scheme 1) in water, and the complexes exhibited similar temperature-dependent ICD signals and signs of the Cotton effect when the absolute configurations of the chiral carboxylic acids were the same (Figure 4 and Table 1); the ICD signal intensities increased significantly with decreasing temperature.

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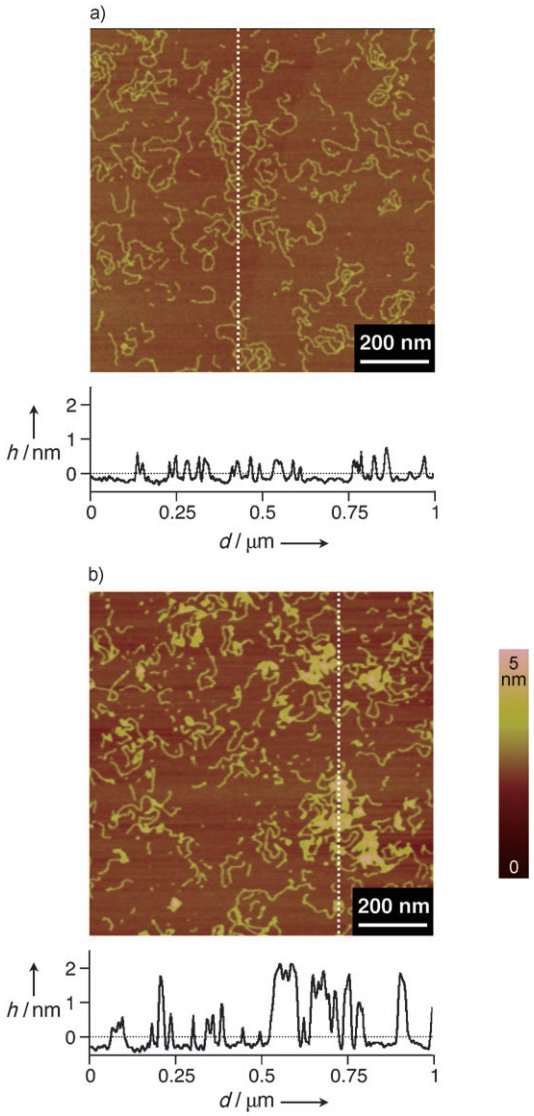

Figure 3. Tapping-mode AFM height images of the poly-**1**–(*S*)-**2** complex on mica prepared at a) 0 and b) 40 °C. The concentrations of poly-**1** and (*S*)-**2** were 0.01 and 3.1 mg mL^{-1} ([**2**]/[poly-**1**] = 400), respectively. The height profiles obtained along the dotted lines in the images are also shown.

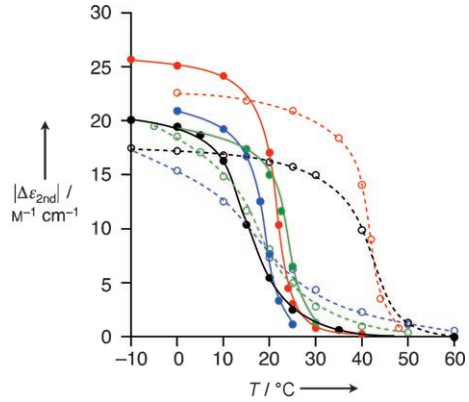

Figure 4. Variation of the $|\Delta\varepsilon_{2nd}|$ values of poly-**1** complexed with (*S*)-**2** (●), (*S*)-**3** (●), (*S*)-**4** (○), (*S*)-**5** (●), (*S*)-**6** (●), (*S*)-**7** (○), L-**8** (○), and (*S*)-**9** (○) in water with temperature. The concentration of poly-**1** was 1.0 mg (4.6 mmol monomer units) mL^{-1}. [(*S*)-**2** or (*S*)-**3**]/[poly-**1**] = 4, [(*S*)-**4**, (*S*)-**5**, or (*S*)-**6**]/[poly-**1**] = 10, and [(*S*)-**7** or L-**8**]/[poly-**1**] = 1.

Table 1. Signs and difference in excitation coefficient of the second Cotton effect ($\Delta\varepsilon_{2nd}$) for the complexes of poly-**1** with chiral carboxylic and sulfonic acids in water.[a]

Chiral acid	[acid]/[poly-**1**]	pH	Sign	Δε [M^{-1}cm^{-1}] (λ [nm]) 25 °C	10 °C	0 °C
(*S*)-**2**	4	3.1	–	3.07 (363)	24.2 (360)	25.1 (360)
(*R*)-**2**	4	3.1	+	2.81 (362)	23.3 (359)	24.2 (360)
(*S*)-**3**	4	3.2	–	2.51 (371)	16.3 (367)	19.4 (368)
(*S*)-**4**	10	2.6	–	20.9 (361)	–	22.6 (361)
(*S*)-**5**	10	2.6	–	1.16 (364)	19.2 (362)	20.9 (362)
(*S*)-**6**	10	2.6	–	6.52 (361)	–	19.4 (362)
(*S*)-**7**	1	3.2	–	15.7 (362)	16.8 (361)	17.2 (361)
L-**8**	1	3.3	–	6.28 (362)	12.5 (361)	15.4 (360)
(*S*)-**9**	4	2.5	+	4.99 (366)	14.8 (364)	18.5 (364)

[a] The concentration of poly-**1** was 1.0 mg mL^{-1}.

Chiral Amplification and Nonlinear Effects in Water

Chiral amplification[20] is one of the most interesting features of dynamic helical polymers as reported for polyisocyanates,[1c,f,21] polysilanes,[1i,k,22] and poly(phenylacetylene)s with functional pendants.[11,p,5b,h,6a,d,e,11] Previously, we reported that the complex formation of poly-**1**·HCl with partially resolved chiral acids showed a strong positive nonlinear relationship (majority rule)[21a] between the *ee* of the chiral acids, such as **2**-Na, and the observed ICD signal intensities in water.[10] The positive nonlinear effect of poly-**1**·HCl increased with an increase in the amount of **2**-Na. However, the addition of **2**-Na (>0.5 equiv) resulted in precipitation of the polymer, and further experiments were difficult.[10c]

We then investigated whether a similar nonlinear effect could be observed for poly-**1** with nonracemic, free carboxylic acids in water. The chiral carboxylic acid **2** was selected as a helix inducer because it produced the most intense ICD signals in water at 0 °C among the chiral acids used in this study (Table 1). Poly-**1** complexed with 4 equivalents of **2** (*S*-rich) exhibited almost no nonlinear effect at 25 °C. However, the extent of the convex deviation from linearity became remarkably greater with decreasing temperature, and below 0 °C even an *ee* of **2** of 5 % gave rise to the full ICD signals as induced by **2** of 100 % *ee* (Figure 5). This noticeable positive nonlinear effect of poly-**1** was superior to that observed for the poly-**1**·HCl–**2**-Na system and enabled the detection of the chirality of **2** of a very small *ee* with an accuracy greater than 0.005 %; an almost-linear relationship between the *ee* (0.1–0.005 %) and the ICD signal intensities of poly-**1** was observed below 0 °C (see Supporting Information, Figure S6). These results indicate that poly-**1** is highly sensitive to the small enantiomeric imbalance of optically active acids in water.

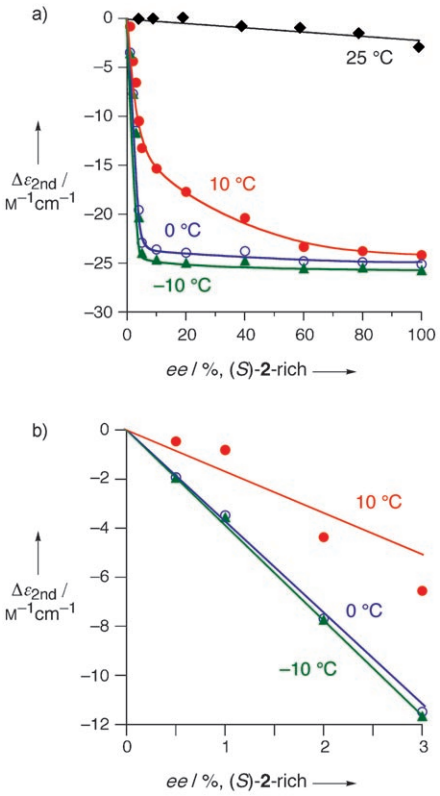

Figure 5. a) Changes in ICD signal intensity ($\Delta\varepsilon_{2nd}$) of poly-**1** (1.0 mg mL^{-1}) versus the *ee* of **2** ([**2**]/[poly-**1**] = 4; pH 3.0–3.2) during complexation with poly-**1** in water at 25, 10, 0, and −10 °C. b) Expanded detail of the ICD signal intensity at 10, 0, and −10 °C.

Chiral Competition: Helix Inversion Controlled by Noncovalent Competition between Structurally Different Enantiomeric Acids

Another interesting feature of dynamic helical polymers is reversible helix inversion between right- and left-handed helices. Biological polymers such as DNA[23] and polypeptides[24] with specific sequences and several synthetic, dynamic helical polymers that bear optically active substituents through covalent bonding are known to undergo inversion of helicity regulated by external stimuli, such as a change in temperature[1g-l,n,p,18,21,25,26] and solvent.[1g-l,n,p,18,26,27] However, inversion of macromolecular helicity induced by chiral stimuli through noncovalent bonding interactions is quite rare,[5i,6e,18,26b,27e,28] but can be used to sense the chirality of chiral guests as well as to produce enantiomeric helices[6e] based on the concept of noncovalent "helicity induction and chiral memory".[11l,p,5c,f,29] Furthermore, Green and co-workers recently reported designer polyisocyanates that showed inversion of helicity at a desired temperature in dilute solution by copolymerization of a pair of structurally different enantiomers, which are in competition with each other in their preference of helical sense.[30]

We then investigated if such an inversion of macromolecular helicity for poly-**1** could be possible by using two different enantiomeric acids in water through noncovalent bonding interactions. We examined a series of combinations of the different enantiomeric acids in Scheme 1 and found that (*S*)-**2** and D-**8**, which showed steep and gentle changes in the ICD signal intensities of poly-**1** versus temperature, respectively, could be used for this purpose.

Figure 6 shows the temperature-dependent changes in the ICD signal intensities of a mixture of poly-**1**, (*S*)-**2**, and D-**8** ([(*S*)-**2**]/[D-**8**]/[poly-**1**] = 0.4:1:1) in water. The sign of the Cotton effect inverted from negative to positive at around 25 °C, a result of the differences in the binding affinity of each enantiomer to poly-**1** and the chiral twisting power between (*S*)-**2** and D-**8**, which may force poly-**1** into either a right- or left-handed helix, depending on the temperature. Consequently, inversion of the helicity of poly-**1** could be controlled by noncovalent chiral competition.[30]

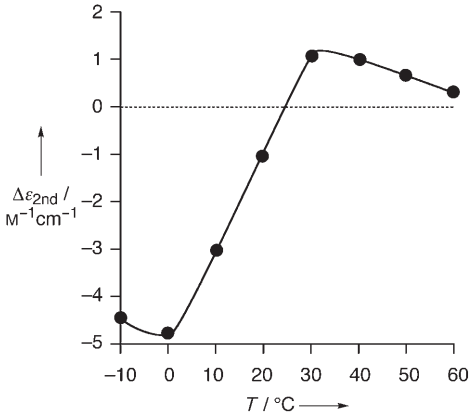

Figure 6. Variation of the $\Delta\varepsilon_{2nd}$ values of poly-**1** complexed with (*S*)-**2** and D-**8** ([(*S*)-**2**]/[D-**8**]/[poly-**1**] = 0.4:1:1) in water with temperature.

Conclusions

In summary, we have found that a poly(phenylacetylene) that bears an *N*,*N*-diisopropylaminomethyl group as the pendant (poly-**1**) is highly sensitive to the chirality of chiral acids through formation of a predominantly one-handed helix in water, particularly at low temperature, and that it can detect an extremely small enantiomeric imbalance in carboxylic acids. The polyelectrolyte function of poly-**1** in the presence of chiral acids appears to be important for its high sensitivity to chirality because poly-**1** shows a weak ICD signal even in the presence of excess chiral acids in organic solvents. Moreover, the preferred helical sense of poly-**1** can be controlled by temperature-dependent, noncovalent chiral competition between structurally different enantiomeric acids.

Experimental Section

Instruments

Solution pH was measured with a B-211 pH meter (Horiba, Japan). NMR spectra were recorded on a Varian INOVA-500 spectrometer oper-

ating at 500 MHz for ^1H in CD_3CN. SEC was 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 an aqueous solution containing tartaric acid (9 mM) and tartaric acid sodium salt (0.1 mM) was used as the eluent at a flow rate of 0.6 mL min^{-1}. The molecular-weight calibration curve was obtained with poly(ethylene oxide) and poly(ethylene glycol) standards (Tosoh). FTIR spectra were obtained in a 0.15-mm CaF_2 cell on a JASCO JV-2001YS spectrophotometer equipped with a temperature controller (EYELA NCB-1200). The concentration of poly-**1** was 5 mg mL^{-1} in D_2O. Laser Raman spectra were obtained on a JASCO RMP-200 spectrophotometer. Absorption and CD spectra were obtained 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 (−10 to 100 °C) was controlled with a JASCO ETC 505T (absorption spectroscopy) and a JASCO PTC-423L apparatus (CD spectroscopy). DLS was performed with a Photal DLS-7070YN instrument (Otsuka Electronics Co., Ltd., Osaka, Japan) equipped with a 10-mW He/Ne laser (632.8 nm) at 3 and 38 °C. AFM was performed with a Nanoscope IIIa microscope (Veeco Instruments, Santa Barbara, CA) in air at ambient temperature with standard silicon cantilevers (NCH, Nanoworld, Neuchâtel, Switzerland) in the tapping mode. AFM images were recorded at the resonance frequency of the tips with 125-μm-long cantilevers (200–300 Hz) and a spring constant of approximately 40 N m^{-1}. All the images were collected with the maximum-available number of pixels (512) in each direction. The scanning speed was at a line frequency of 1.0 Hz. The effective radii of the silicon tips were estimated with Au colloids (5 nm; ICN Biomedicals, Inc., Aurora, OH) as imaging standards and were 5–10 nm.

Materials

Deionized, distilled water was degassed with nitrogen before use in all the experiments. The optically active acids were purchased from Aldrich (Milwaukee, WI) or Tokyo Kasei (TCI, Tokyo, Japan) and used as received.

Cis-transoidal poly-**1** was prepared by the polymerization of 4-(*N*,*N*-diisopropylaminomethyl)phenylacetylene (**1**) with $[Rh(nbd)Cl]_2$ according to a previously reported method.[9a,b,10] The stereoregularity of the obtained poly-**1** was confirmed to be highly *cis-transoidal* (*cis* content = 96 %) based on the ^1H NMR spectrum (see Supporting Information, Figure S1).[10c,15] The M_n and M_w/M_n of poly-**1** were estimated to be 3.4×10^5 and 2.21, respectively, as determined by SEC of its hydrochloride salt (poly-**1**·HCl).[10]

CD: The concentration of poly-**1** was calculated on the basis of monomer units and was 1.0 mg mL^{-1} (4.6 mM monomer units) unless otherwise stated. For the complexation of poly-**1** with optically active acids, poly-**1** (≈1 mg) and an appropriate amount of the chiral acid were dissolved in water in a 2-mL vessel equipped with a screwcap to keep the poly-**1** concentration at 1.0 mg mL^{-1} (4.6 mM), and the absorption and CD spectra were then recorded.

Nonlinear effects of poly-**1** with **2**: The nonlinear effects between the intensities of the ICD signals and the *ee* of **2** during complexation with poly-**1** were investigated in water. The molar ratio of **2** to the monomer units of poly-**1** ([**2**]/[poly-**1**]) was held constant at 4 (mol/mol). In the experiments, stock solutions of **2** were separately prepared for the large ($2 \le ee \le 100$ %) and small ($0.005 \le ee < 2$ %) *ee* values before the CD measurements.

Preparation of **2** with large *ee* and CD measurements with poly-**1**: Stock solutions of (*S*)-**2** (18.6 mM, 10 mL) and (*R*)-**2** (18.6 mM, 10 mL) in acetone were prepared. Aliquots of these stock solutions were placed in 10 vessels so that the *ee* of the mixtures (*S*-rich) were 2, 3, 4, 5, 10, 20, 40, 60, 80, and 100 %. After the acetone was removed under reduced pressure from each vessel, poly-**1** (1.0 mg) was added, and the mixture was dissolved in water to keep the poly-**1** concentration at 1.0 mg mL^{-1} (4.6 mM). The absorption and CD spectra were then recorded for each vessel to determine the changes in the CD spectra.

Preparation of **2** with small *ee* and CD measurements with poly-**1**: The stock solutions of **2** with small *ee* values ($0.005 \le ee < 2$ %) were carefully prepared in a similar way to that in the literature,[11a] and the experimental procedures are described below.

(*S*)-**2** of 1.0 and 0.5 % *ee* (*S*/*R* = 50.5:49.5 and 50.25:49.75): Stock solutions of (*RS*)-**2** (37 mM) and (*S*)-**2** (0.37 mM) in acetone were first prepared as follows: (*RS*)-**2** (61.1 mg) and (*S*)-**2** (15.4 mg) were placed in 10- and 250-mL flasks equipped with stopcocks, respectively. Acetone was then added to make up the solutions of the appropriate volume. Aliquots of the stock solutions of (*RS*)-**2** and (*S*)-**2** were transferred into two 2-mL vessels equipped with screwcaps so that the *ee* of **2** (*S*-rich) was 0.5 and 1.0 %, respectively. After the acetone was removed under reduced pressure, poly-**1** (1.0 mg) was added, and the mixture was dissolved in water to keep the poly-**1** concentration at 1.0 mg mL^{-1} (4.6 mM). The absorption and CD spectra were then recorded for each vessel.

(*S*)-**2** of 0.1 and 0.05 % *ee* (*S*/*R* = 50.05:49.95 and 50.025:49.975): A stock solution of (*S*)-**2** (0.037 mM) was first prepared as follows: The stock solution of (*S*)-**2** (0.50 mL, 0.37 mM) prepared above was transferred into a 5-mL flask equipped with a stopcock and diluted with acetone to the required volume to produce the stock solution of (*S*)-**2** (0.037 mM) in acetone. Aliquots of the stock solutions of (*RS*)-**2** (37 mM) and (*S*)-**2** (0.037 mM) were transferred into two 2-mL vessels equipped with screwcaps so that the *ee* of **2** (*S*-rich) was 0.1 and 0.05 %, respectively. After the acetone was removed under reduced pressure, poly-**1** (1.0 mg) was added, and the mixture was dissolved in water to keep the poly-**1** concentration at 1.0 mg mL^{-1} (4.6 mM). The absorption and CD spectra were then recorded for each vessel.

(*S*)-**2** of 0.01 and 0.005 % *ee* (*S*/*R* = 50.005:49.995 and 50.0025:49.9975): A stock solution of (*S*)-**2** (0.0037 mM) was first prepared as follows: The stock solution of (*S*)-**2** (0.50 mL, 0.37 mM) prepared above was transferred into a 50-mL flask equipped with a stopcock and diluted with acetone to the required volume to produce the stock solution of (*S*)-**2** (0.0037 mM) in acetone. Aliquots of the stock solutions of (*RS*)-**2** (37 mM) and (*S*)-**2** (0.0037 mM) were transferred into two 2-mL vessels equipped with screwcaps so that the *ee* of **2** (*S*-rich) was 0.01 and 0.005 %, respectively. After the acetone was removed under reduced pressure, poly-**1** (1.0 mg) was added, and the mixture was dissolved in water to keep the poly-**1** concentration at 1.0 mg mL^{-1} (4.6 mM). The absorption and CD spectra were then recorded.

DLS: A stock solution of poly-**1** (1.0 mg mL^{-1}, 4.6 mM) complexed with (*S*)-**2** ([(*S*)-**2**]/[poly-**1**] = 4) was prepared in a 5-mL flask equipped with a stopcock in water. The solution was filtered with a 0.45-μm syringe filter (Toyo Roshi Co., Ltd., Japan) below 10 °C, then DLS of the sample was performed at a fixed scattering angle of 90° at 3 and 38 °C. The obtained autocorrelation functions were analyzed by the method of cumulants to give the translational diffusion coefficients (D_s). The corresponding hydrodynamic radius (R_h) was calculated by using the Stokes–Einstein equation: $R_h = k_B T/(6\pi h D)$, in which k_B, h, and T are the Boltzmann constant, the solvent viscosity, and the absolute temperature, respectively. The estimated R_h values for poly-**1** in water at 3 and 38 °C were 43 nm and 2.35 μm, respectively; these values support the formation of aggregates of the polymer main chains at high temperature.

AFM: A stock solution of poly-**1** (0.01 mg mL^{-1}) in an aqueous solution of (*S*)-**2** (0.019 M) was prepared. A 20-μL aliquot of the stock solution was dropped onto freshly cleaved mica, the solution was simultaneously blown off with a stream of argon, and the mica substrate was dried in vacuo overnight for the recording of the AFM images in the tapping mode (Figure 3).

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