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Helicity Induction in a Poly(4-carboxyphenyl isocyanide) with Chiral Amines and Memory of the Macromolecular Helicity in Aqueous Solution

Yoko Hase, Masayoshi Ishikawa, Reiko Muraki, Katsuhiro Maeda, and Eiji Yashima*

Department of Molecular Design and Engineering, Graduate School of Engineering,
Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan

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ABSTRACT: Poly(4-carboxyphenyl isocyanide) (poly-**1**-**H**) and its sodium salt (poly-**1**-**Na**) show an induced circular dichroism (ICD) in the n−π* transition region of the imino chromophores upon complexation with chiral amines in dimethyl sulfoxide (DMSO) and water, respectively, due to the prevailing one-handed helix formation of the polymers. The helical structure of poly-**1**-**Na** induced in water can be further memorized after complete removal of the chiral amines. We now report that poly-**1**-**Na** also forms an induced helical structure and exhibits a similar ICD in the presence of an optically active quaternary ammonium salt, various chiral amines, and L-amino acids in water. Poly-**1**-**H** was insoluble in water, but became soluble in the presence of chiral amines, and the complexes also showed similar ICDs. The effects of the water content in various aqueous organic solutions on the ICDs and the memory of the induced macromolecular helicity were also investigated.

Introduction

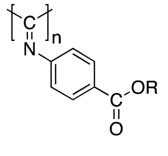
Poly(alkyl or aralkyl isocyanide)s having a bulky side group have been postulated to adopt a stable 4_1 helical conformation even in solution.[1] Nolte et al.,[2] and later Novak et al.,[3] succeeded in preparing optically active helical polyisocyanides by the helix-sense selective polymerization of achiral, bulky *tert*-butyl isocyanide and diphenylmethyl isocyanide, respectively, with optically active catalysts or initiators. The helical structures were kinetically controlled during the polymerization. On the other hand, Euler and Rosen et al. claimed that poly(phenyl isocyanide) (PPI) might not have a stable 4_1 helical conformation, but a nonhelical, linear s-trans or zigzag conformation in solution,[4] whereas Takahashi et al.[5] and Veciana et al.[6] independently reported that the helical conformations of PPIs having bulky chiral substituents were quite stable in solution even at high temperatures.[7]

Recently, we found that an optically inactive poly(4-carboxyphenyl isocyanide) (poly-**1**-**H**) and its sodium salt (poly-**1**-**Na**) changed their structures into the prevailing one-handed helical conformation upon complexation with chiral amines in dimethyl sulfoxide (DMSO)[8] and water,[9] respectively, and the complexes showed a characteristic induced circular dichroism (ICD) in the UV−visible region of the polymer backbones. Moreover, the induced helical structure of poly-**1**-**Na** could be memorized in water even after the chiral amines were completely removed.[9] We considered that hydrophobic and chiral ionic interactions between the poly-**1**-**Na** and chiral amines in water might be essential for this helicity memory effect because the helical poly-**1**-**H** induced by chiral amines in DMSO could not maintain the helicity after removal of the chiral amines.[9a] A similar helicity induction and memory of the helical chirality have been reported for optically inactive poly((4-carboxylphenyl)acetylene)[10] and poly((4-phosphonophenyl)acetylene)[11] with chiral amines through the noncovalent acid−base interactions in DMSO. However, in sharp contrast to the helical memory of poly-**1**-**Na** in water, replacement of the chiral amines by achiral amines was necessary for the memory of the induced helical polyacetylenes.[10,11]

We now show that poly-**1**-**Na** also exhibits a characteristic ICD in the UV−visible region due to the predominantly one-handed helix formation of the polymer upon complexation with an optically active quaternary ammonium salt, various amines, and L-amino acids in water. We also investigated the effects of the pH, the salt concentration, and organic solvents on the ICDs of poly-**1**-**H**− or poly-**1**-**Na**−chiral amine complexes in water and subsequent memory of the induced helicity in various aqueous organic solutions.

Results and Discussion

Helicity Induction in Poly-1-Na with Chiral Amines and Amino Acids. Poly(4-carboxyphenyl isocyanide) (poly-**1**-**H**) was prepared by a previously reported method.[8] The number-average molecular weight (M_n) and its distribution (M_w/M_n) were estimated as its ethyl ester to be 3.0×10^4 and 2.0, respectively, as determined by size exclusion chromatography (SEC) with polystyrene standards using chloroform as the eluent. The sodium salt of poly-**1**-**H** (poly-**1**-**Na**) was prepared by the polymerization of sodium 4-isocyanobenzoate with $NiCl_2{\cdot}6H_2O$ in water[9] ($M_n = 3.3 \times 10^4$ and $M_w/M_n = 3.2$ as its methyl ester by SEC) or by dissolving poly-**1**-**H** in an aqueous NaOH solution, followed by dialysis and precipitation into acetone.



R = H: poly-**1**-**H**

R = Na: poly-**1**-**Na**

Figure 1 shows the typical CD and absorption spectra of poly-**1**-**Na** in the presence of a water-soluble chiral quaternary ammonium salt ((*R*)-**3** in Chart 1) ([(*R*)-**3**]/[poly-**1**-**Na**] = 10) in water. The poly-**1**-**Na**−(*R*)-**3** complex exhibited a very weak ICD in the n−π* transition region of the imino chromophores just after

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* To whom correspondence should be addressed. E-mail: yashima@apchem.nagoya-u.ac.jp.

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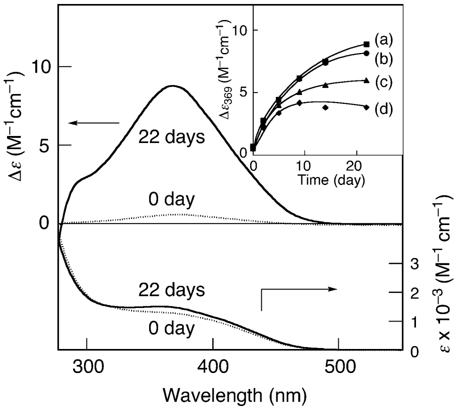
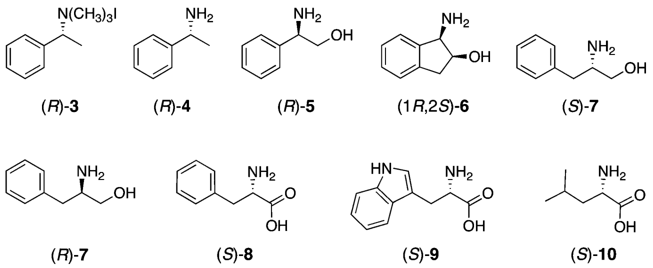


Figure 1. CD and absorption spectral changes of poly-**1-Na** with (*R*)-**3** in water (pH 7.2) at 30 °C after 0 and 22 days with a poly-**1-Na** concentration of 1.0 mg (5.9 μmol monomer units)/mL; molar ratio of (*R*)-**3** to monomeric units of poly-**1-Na** is 10. Inset shows the changes in the CD intensities of the complexes of poly-**1-Na** with (*R*)-**3** at 369 nm; molar ratios of (*R*)-**3** to poly-**1-Na** are 10 (a), 5 (b), 1 (c), and 0.5 (d), and the pHs are 7.2, 7.3, 7.4, and 7.6, respectively.

Chart 1. Structures of Chiral Quaternary Ammonium Salt (3), Amines (4−7), and Amino Acids (8−10)



(*R*)-**3** (*R*)-**4** (*R*)-**5** (1*R*,2*S*)-**6** (*S*)-**7**

(*R*)-**7** (*S*)-**8** (*S*)-**9** (*S*)-**10**

the sample preparation. However, the CD intensity increased very slowly with time at 30 °C depending on the concentration of the chiral ammonium and reached $\Delta\epsilon_{369} = 8.82$ after 22 days when 10 equiv of (*R*)-**3** to the monomer units of poly-**1**-**Na** was used (see inset (a) in Figure 1), but the ICD magnitude had not reached a constant value after this time period. This indicates that the complexation involves an equilibrium in the ion-exchange reaction[12] between the bound sodium ions of poly-**1**-**Na** and the chiral ammonium ions, and the polymer can form a helical conformation with a predominant screw-sense by ionically interacting with the bound ammonium ions in water. This helicity induction process might be the rate-determining step involved in the configurational isomerization around the C═N double bonds (syn−anti isomerization), so that it requires a rather long time as previously reported.[9] The ICD pattern and λ_{max} (369 nm) of the Cotton effect are very similar to those of poly-**1**-**H** complexed with chiral amines in DMSO[8] and the reported optically active PPI derivatives.[5,6] A similar ICD induction in an optically inactive polyelectrolyte through intermolecular chiral ionic interactions in water has been reported for water-soluble polyacetylene derivatives, although they showed no time-dependent ICD changes, and the helicity induction process is regarded as a change in the population of the right- and left-handed helical conformations of the dynamically racemic helical polyacetylenes.[13,14]

Table 1. Signs of Cotton Effects and Differential Molar Absorptivities ($\Delta\epsilon$) for Poly-1-Na−Quaternary Ammonium, −Amine, and −Amino Acid Complexes in Water[a]

			30 °C	50 °C
chiral compound	pH	$\Delta\epsilon$ (λ)[b]	$\Delta\epsilon$ (λ, time)[c]	$\Delta\epsilon$ (λ, time)[d]
(*R*)-**3**	7.2	+0.57 (367)	+8.82 (369, 22)	+9.41 (369, 21)
(*R*)-**4**	11.1	ca. 0	+1.94 (367, 58)	+8.55 (367, 20)
(*R*)-**5**	10.3	ca. 0	−4.67 (360, 71)	−12.0 (361, 36)
(1*R*,2*S*)-**6**	10.5	ca. 0	+3.88 (364, 62)	+3.32 (363, 23)
(*S*)-**7**	10.2	ca. 0	−3.51 (360, 27)	−9.25 (360, 27)
(*R*)-**7**	10.4	ca. 0	+3.68 (360, 30)	+9.74 (360, 29)
(*S*)-**8**	7.4	ca. 0	+0.12 (360, 36)	+0.03 (360, 20)
(*S*)-**9**[e]	7.6	ca. 0	+1.43 (360, 36)	+0.30 (360, 20)
(*S*)-**10**	7.6	ca. 0	−0.13 (360, 36)	

[a] CD spectra were measured in water at 30 °C with poly-**1**-**Na** (1.0 mg/mL); molar ratio of a chiral compound to monomeric units of poly-**1**-**Na** is 10. The pH was measured for poly-**1**-**Na**−chiral compound complexes in water and not further adjusted in order to avoid further increase in the salt concentration. [b] Measured immediately after the preparation of samples; $\Delta\epsilon$ (M^{-1} cm^{-1}) and λ (nm). [c] Measured after the samples had been allowed to stand at 30 °C for days; $\Delta\epsilon$ (M^{-1} cm^{-1}), λ (nm), and time (days). [d] Measured after the samples had been allowed to stand at 50 °C for days; $\Delta\epsilon$ (M^{-1} cm^{-1}), λ (nm), and time (days). [e] Molar ratio of a chiral compound to poly-**1**-**Na** is 5.

The appearance of the ICD was accompanied with a slight change in the UV−visible spectra in the imino chromophore region (Figure 1); the molar absorptivity (ϵ) of the poly-**1**-**Na**−(*R*)-**3** complex at 354 nm increased by 14% after ca. 22 days. Such a hyperchromism was not observed for the helicity induction in poly-**1**-**H** with chiral amines in DMSO at 30 °C, which implies that the helical conformation of the poly-**1**-**Na** induced by (*R*)-**3** in water may be different from that of poly-**1**-**H** with chiral amines in DMSO.

Poly-**1**-**Na** responded to other chiral amines (**4**−**7**) and amino acids (**8**−**10**) (Chart 1) in water, and the complexes exhibited similar ICDs in their patterns after the samples had been allowed to stand at 30 °C for days (Table 1), although the complexes showed almost no ICD just after the preparation of the sample solutions. The enantiomers of **7** induced the ICDs of the mirror images (Table 1). The magnitude of the ICD was influenced by the pH and the salt (NaCl) concentration, which is consistent with the ionic nature of the interaction for the helicity induction (Figures S1 and S2 in Supporting Information).[14] The primary amine (*R*)-**4** and amino acids (**8**−**10**) produced rather weak ICDs and showed a small change with time at 30 °C. A bulky amino acid (**9**) exhibited a moderate ICD. As for the sign for the induced Cotton effects with respect to the absolute configurations of the chiral compounds, there was no clear relationship. The poly-**1**-**Na** complexed with chiral amines (**4**−**7**) in water showed the same Cotton effect signs as those for the poly-**1**-**H** complexed with the same amines in DMSO if the absolute configurations were the same, except for **7** ($\Delta\epsilon_{372}$ of poly-**1**-**H**−(*S*)-**7** = 1.46 in DMSO after 88 days at 30 °C).[8] This suggests that the predominant helix-sense of the polymer induced by (*S*)-**7** may be opposite in DMSO and water.

We then investigated the temperature effect on the macromolecular helicity induction for the poly-**1**-**Na**−chiral amine complexes and found that the ICD intensities tended to rapidly increase at higher temperatures (Figure 2 and Table 1). The poly-**1**-**Na**−(*R*)-**5** complex, for example, showed a gradual increase in the ICD intensity at higher temperatures during the initial stage and the ICD intensity ($\Delta\epsilon$) reached an almost constant value ($\Delta\epsilon_{360} = 12$) after 42 days at 50 °C, but the ICD value at 60 °C was rather weak when compared to that observed at 50 °C over 20 days (Figure 2). At 90 °C, it decreased ($\Delta\epsilon_{360} = 6.2$ after 7 days) (data not shown). This indicates that an equilibrium may lie between the folding and unfolding process, and at temperatures over 90 °C, the induced helical poly-**1**-**Na** may be collapsed. This folding and unfolding process may be accom-

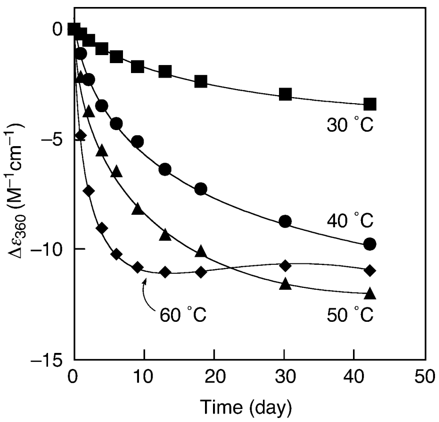


Figure 2. Changes in the CD intensity of the complex of poly-**1-Na** with (*R*)-**5** (360 nm) in water (pH 10.3) at 30, 40, 50, and 60 °C with a poly-**1-Na** concentration of 1.0 mg/mL; molar ratio of (*R*)-**5** to monomeric units of poly-**1-Na** is 10.

panied by the configurational isomerization of the polymer backbone.[9]

Effect of Water on Helicity Induction in Poly-1-H−Amine Complexes in DMSO and Other Various Organic Solvents. As previously reported, poly-**1-H** exhibited an ICD in the UV−visible region in DMSO due to the predominantly one-handed helix formation of the polymer upon complexation with chiral amines, and the ICD intensities gradually increased with time.[8] However, the helical poly-**1-H** almost completely lost its induced helicity after removal of the chiral amines.[9a] Poly-**1-H** is not soluble in water but becomes soluble in the presence of amines, therefore, we then investigated the effect of water on the ICDs of poly-**1-H** with chiral amines and subsequent memory of the induced helicity in DMSO−water mixtures. Table 2 and Figure 3 show the changes in the ICD intensity of the poly-**1**−(1*R*,2*S*)-**6** complex in DMSO−water mixtures at 50 °C. (1*R*,2*S*)-**6** was selected because the amine was an effective helicity inducer for poly-**1-H** in DMSO[8] as well as in water (Table 1). The poly-**1**−(1*R*,2*S*)-**6** complex showed relatively intense ICDs over a short period of time (3 days) in aqueous DMSO containing less than 50 vol % water (runs 1−6 in Table 2). However, in high water-containing solvents (water content ≥ 70%), it required a long time for the helicity induction (runs 7−9 in Table 2). The ICD intensities and their changes with time, however, highly depended on the structures of the chiral amines used in DMSO−water mixtures; for instance, the poly-**1-Na**−(*R*)-**5** complex produced a weaker ICD in pure DMSO ($\Delta\epsilon_{358} = -1.6$) and water ($\Delta\epsilon_{358} = -1.6$) after ca. 40 days, but the ICD intensity significantly increased in 45 and 50 vol % water in DMSO, thus exhibiting an intense ICD ($\Delta\epsilon_{358} = -7$ and -11 after 33 and 107 days, respectively) (Figure S3 in Supporting Information).

As recently reported, the induced helical structure of poly-**1-Na** in water can be memorized after complete removal of the chiral amines.[9] In addition, the helical poly-**1-Na** can be converted into the corresponding carboxylic acid without loss of the macromolecular helicity.[9] We then isolated the helical poly-**1-H**s induced by (1*R*,2*S*)-**6** in DMSO−water mixtures to completely remove the chiral amine (see Experimental Section), and their CD spectra were then measured (Table 2 and Figure 3). The isolated poly-**1-H**s from the pure DMSO and 10−30 vol % water in DMSO could not maintain their induced helical structures after removal of the chiral amine and exhibited negligibly weak ICDs and, hence, very low memory efficiencies (runs 1−4 in Table 2 and Figure 3) as reported previously.[9a] However, the relative ICD intensities of poly-**1-H**s before and after the isolation dramatically increased with the further increase in the amount of water. The memory efficiency significantly increased from 4% (30 vol % water) to 49% (40 vol % water) and reached almost 100% (70−100 vol % water) (runs 4−9 in Table 2 and Figure 3). This sudden onset and remarkable increase in the memory efficiency in the DMSO−water mixtures (≥40 vol %) was accompanied by a gradual increase in the molar absorptivity at 354 nm of the isolated helical poly-**1-H**s (Table 2), but the reasons for these changes are not clear at present, and we need further experiments including the NMR and IR measurements of the poly-**1-H**−chiral amine complexes during the helicity induction and helical poly-**1-H**s after isolation to follow the changes in the C═N double bonds of the polymers.

We note that the helical poly-**1-H** and poly-**1-Na** induced by the same chiral amine (*R*)-**5** in water kept their helicity with almost the same memory efficiency after isolation, indicating that the countercation (Na^+) hardly affects the maintenance of the helicity in the polymers (runs 10 and 11 in Table 2).

We next examined the effect of other wide varieties of organic solvents on the helicity induction in poly-**1-H** with (*R*)-**5** in water and the memory of the helicity in order to develop a more efficient helicity induction and subsequent memory of the helicity system; the water content was fixed at 50 vol % and the changes in the ICD intensity at the first Cotton effect of poly-**1-H** were followed at 50 °C (Table 3). Among a series of organic solvents used including protic (alcohols) and aprotic (DMSO, *N*,*N*-dimethylacetamide (DMA), 1,2-dimethoxyethane (DME), and acetonitrile) polar solvents, alcohols except for methanol, acetonitrile, and DME were found to be very good organic solvents for the effective helicity induction in poly-**1-H**, judging from the ICD intensity values and the time required for the intense ICDs (Table 3 and Figures S4 and S5 in Supporting Information); the highest $\Delta\epsilon_{360}$ value of poly-**1-H** (−16.0) was obtained in the water−2-propanol mixture after 40 days at 50 °C. There seems to be no general relation between the relative permittivity of the organic solvents and the efficiency in the helicity induction. We then isolated the helical poly-**1-H**s induced in these organic solvents−water mixtures according to the reported method,[9] and their CD spectra were measured (Table 3). All the poly-**1-H**s maintained their induced helical structures after complete removal of the chiral amine ((*R*)-**5**). The memory efficiencies thus estimated on the basis of the $\Delta\epsilon$ values of the polymers before isolation were greater than 75%. However, we have no concrete evidence for the helix-sense excess and the exact structure of the obtained helical poly-**1-H**. A further detailed structural analysis including X-ray diffraction and NMR is necessary.

In conclusion, a helical poly-**1-H** with the macromolecular helicity memory showing a larger Cotton effect intensity than before[9] could be obtained through the helicity induction with chiral amines in water−organic solvent mixtures. We expect that the resulting optically active helical polyisocyanides may be used as a more effective template for helicity induction in dynamically helical, charged polyacetylenes with opposite charges in water[16] and also as novel chiral materials for enantiomer separation and catalysts.

Experimental Section

Materials. Deionized, distilled water was degassed with nitrogen and used throughout for all experiments. D_2O (99.9 atom % D, Isotec Inc.) was stored under nitrogen. All solvents used for measurements of CD and NMR spectra were purged with nitrogen prior to use. (*R*)-**4** was kindly supplied from Yamakawa Chemical (Tokyo, Japan). (*R*)-**3** was prepared by the reaction of (*R*)-*N*,*N*-

Table 2. Signs of Cotton Effects and Differential Molar Absorptivities (Δϵ) for Poly-1−Amine Complexes in DMSO−Water Mixtures and Memory of the Induced Macromolecular Helicity[a]

				***h*-poly-1-H** after removal of chiral amines		
run	chiral amine	water content (%)	Δϵ (λ, time)[b]	Δϵ (λ)[c,d]	$\epsilon_{354} \times 10^{-3}$[c]	memory efficiency (%)[e]
1	(1*R*,2*S*)-**6**	0	+6.36 (360, 3)[f]	+0.14 (358)	1.34	2
2	(1*R*,2*S*)-**6**	10	+8.53 (362, 3)	+0.04 (358)	1.32	0.5
3	(1*R*,2*S*)-**6**	20	+8.46 (362, 3)	+0.09 (362)	1.30	1
4	(1*R*,2*S*)-**6**	30	+8.13 (361, 3)	+0.35 (355)	1.32	4
5	(1*R*,2*S*)-**6**	40	+6.25 (363, 3)	+3.05 (357)	1.49	49
6	(1*R*,2*S*)-**6**	50	+8.26 (363, 3)	+6.63 (357)	1.61	80
7	(1*R*,2*S*)-**6**	70	+4.09 (362, 23)[g]	+3.96 (356)	1.70	97
8	(1*R*,2*S*)-**6**	90	+3.46 (364, 23)[g]	+3.43 (355)	1.68	99
9	(1*R*,2*S*)-**6**	100	+3.32 (363, 23)[g]	+3.22 (356)	1.63	97
10	(*R*)-**5**	100	−5.61 (359, 3)[h]	−5.12 (357)	1.77	91
11	(*R*)-**5**	100	−12.0 (361, 36)[g]	−11.2 (357)	1.79	93

[a] CD spectra were measured in water at ambient temperature with poly-**1**-**H** (1.0 mg/mL). [b] Measured after the samples had been allowed to stand at 50 °C for days; molar ratio of an amine to monomeric units of poly-**1**-**H** is 10; Δϵ (M^{-1} cm^{-1}), λ (nm), and time (days). [c] Measured in alkaline water ([NaOH]/[poly-**1**-**H**] = 1 and [poly-**1**-**H**] = 1.0 mg/mL). [d] Δϵ (M^{-1} cm^{-1}) and λ (nm). The concentration of the polymers was corrected on the basis of $\epsilon_{302} = 1930$ M^{-1} cm^{-1} because helical and nonhelical poly-**1**s have the same ϵ_{302} value in alkaline water irrespective of their optical activity. [e] Estimated on the basis of the ICD values of poly-**1**−amine complexes before isolation. [f] Molar ratio of an amine to poly-**1**-**H** is 50. [g] Poly-**1**-**Na** (1.0 mg/mL) was used because of solubility limit of poly-**1**-**H** in water with 10 equiv of chiral amines. [h] Molar ratio of an amine to poly-**1**-**H** is 20.

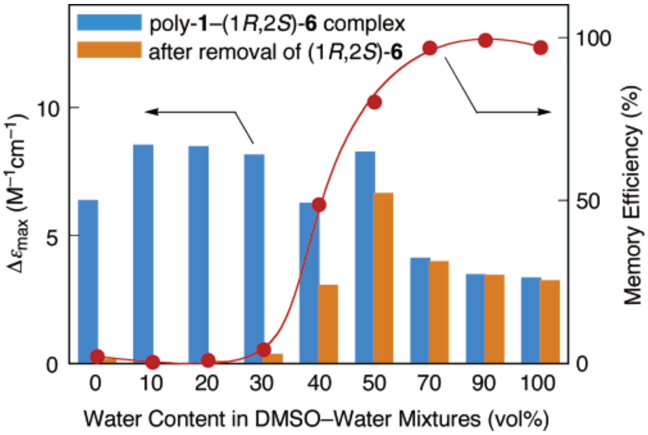


Figure 3. Effect of the water content on helicity induction in poly-**1** with (1*R*,2*S*)-**6** in DMSO−water mixtures at 50 °C and memory of the induced helicity of poly-**1**. Shown are ICD intensities of poly-**1** with (1*R*,2*S*)-**6** in DMSO−water mixtures at 50 °C (blue bars) and helical poly-**1**-**H** with macromolecular helicity memory (orange bars) in alkaline water ([NaOH]/[poly-**1**-**H**] = 1 and [poly-**1**-**H**] = 1.0 mg/mL) after removal of (1*R*,2*S*)-**6**. Memory efficiency (red filled circles) was estimated on the basis of the ICD values of the poly-**1**−(1*R*,2*S*)-**6** complexes before isolation. For more detailed experimental conditions, see Table 2.

Table 3. CD Spectral Data of Induced Helical Poly-1-H with (*R*)-5 in Organic Solvents−Water Mixtures (1:1, v/v) and Isolated Helical Poly-1-H with Macromolecular Helicity Memory[a]

			***h*-poly-1-H** after removal of (*R*)-**5**	
organic solvent	ϵ_r (25 °C)[b]	Δϵ (time)[c]	Δϵ (λ)[d]	memory efficiency (%)[e]
none[f]	78.30	−12.0 (36)	−11.2 (357)	93
methanol	32.66	−9.04 (20)	−7.38 (357)	82
ethanol	24.55	−14.4 (21)	−12.2 (356)	85
1-propanol	20.45	−14.6 (40)	−12.9 (356)	88
2-propanol	19.92	−16.0 (40)	−12.0 (357)[g]	75
DMSO	46.45	−7.94 (14)	−7.18 (356)[h]	90
DMA	37.78	−8.70 (7)	−6.65 (358)	76
acetonitrile	35.94	−13.5 (21)	−11.7 (357)	87
DME	7.20	−14.8 (28)	−12.6 (358)	85

[a] The concentration of poly-**1**-**H** is 1.0 mg/mL and the molar ratio of (*R*)-**5** to monomeric units of poly-**1**-**H** is 20. [b] Relative permittivity (dielectric constant) for the pure liquid at 25 °C. The values are cited from ref 15. [c] Measured at 22−24 °C after the samples had been allowed to stand with (*R*)-**5** at 50 °C for days; Δϵ (M^{-1} cm^{-1}) and time (days) at ca. 360 nm (see Figures S4 and S5 in Supporting Information). [d] Measured in alkaline water ([NaOH]/[poly-**1**-**H**] = 1 and [poly-**1**-**H**] = 1.0 mg/mL); Δϵ (M^{-1} cm^{-1}) and λ (nm). The concentration of the polymers was corrected on the basis of $\epsilon_{302} = 1930$ M^{-1} cm^{-1} because helical and nonhelical poly-**1**s have the same ϵ_{302} value in alkaline water irrespective of their optical activity. [e] Estimated on the basis of the ICD values of poly-**1**-**H**−(*R*)-**5** complexes before isolation. [f] Poly-**1**-**Na** (1.0 mg/mL) in pure water was used and the molar ratio of (*R*)-**5** to monomeric units of poly-**1**-**Na** is 10. [g] The Δϵ value (M^{-1} cm^{-1}) at 357 nm in 2-propanol−water mixture (1:1, v/v) in the presence of *n*-butylamine ([*n*-butylamine]/[poly-**1**-**H**] = 1.1) was −11.2. [h] The Δϵ value (M^{-1} cm^{-1}) at 356 nm in DMSO−water mixture (1:1, v/v) in the presence of *n*-butylamine ([*n*-butylamine]/[poly-**1**-**H**] = 1.1) was −7.13.

dimethyl-1-phenylethylamine (Aldrich) with methyl iodide. Other optically active amino alcohols and amino acids were purchased from Aldrich, Sigma, or Tokyo Kasei (TCI, Tokyo, Japan). Poly-**1**-**H** was prepared according to the previously reported method.[8] Poly-**1**-**Na** was prepared by the polymerization of sodium 4-isocyanobenzoate with $NiCl_2 \cdot 6H_2O$ in water according to the reported method[9] or by dissolving poly-**1**-**H** in an aqueous NaOH solution, followed by dialysis and precipitation into acetone. Conversion of poly-**1**-**H** into the methyl ester was carried out using diazomethane in diethyl ether solution according to the previously reported method.[17]

Instruments. NMR spectra were measured on a Varian VXR-500S spectrometer operating at 500 MHz for ^1H and 125 MHz for ^{13}C, respectively, using dioxane as the internal standard. IR spectra were recorded using a JASCO Fourier transform IR-620 spectrophotometer. Absorption spectra were taken on a JASCO V-570 spectrophotometer. CD spectra were measured in a 0.1 cm quartz cell unless otherwise noted using a JASCO J-725-L spectropolarimeter. Temperature was controlled with JASCO PTC-348WI and ETC-505T apparatuses for CD and absorption measurements, respectively. SEC was performed using a JASCO PU-980 liquid chromatograph equipped with a UV−visible (254 nm; JASCO UV-970) detector. A Tosoh TSKgel H_{XL}-M SEC column (30 cm) was connected and chloroform was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained with standard polystyrenes (Tosoh).

Helicity Induction in Water. Deionized, distilled water was degassed with nitrogen and used throughout for all measurements. The concentration of poly-**1**-**Na** or poly-**1**-**H** was calculated on the basis of the monomer units. A typical experimental procedure is described below. A stock solution of poly-**1**-**Na** (2 mg/mL) in water was prepared in a 10 mL flask equipped with a stopcock. A 1 mL aliquot of the stock solution of poly-**1-Na** was transferred using a transfer pipet to a 2 mL flask equipped with a stopcock, and an appropriate amount of a chiral compound was added to the flask. The solution was immediately mixed with a vibrator (Iuchi, Japan) and finally diluted with water to maintain the poly-**1-Na** concentration of 1.0 mg/mL in order to measure the UV−visible and CD spectra. The solution pH was measured with a B-211 pH meter (Horiba).

Helicity Induction in Organic Solvent−Water Mixtures. A typical experimental procedure is described below. A stock solution of poly-**1-H** (2 mg/mL) in DMSO was prepared in a 10 mL flask equipped with a stopcock. A 1 mL aliquot of the stock solution of poly-**1-H** was transferred to a 2 mL flask equipped with a stopcock, and an appropriate amount of a chiral amine was added to the flask. The solution was mixed with a vibrator and an appropriate amount of water was added to the flask using a Hamilton microsyringe. The resulting solution was finally diluted with DMSO to maintain the poly-**1-H** concentration of 1.0 mg/mL in order to measure the UV−visible and CD spectra.

Isolation of Helical Poly-1-H Induced by (*R*)-5 in Water. The isolation of an induced helical poly-**1-H** was performed using a previously reported method.[9] After the solution of poly-**1-H** with (*R*)-**5** had been allowed to stand at 50 °C for days (see Tables 2 and 3), the solution was lyophilized. The recovered polymer complexed with (*R*)-**5** was dissolved in a small amount of water and then 1 N aq NaOH was added ([NaOH]/[monomeric units of poly-**1-H**] = 10). The solution was poured into a large amount of THF to remove (*R*)-**5**. The aqueous layer was separated and acidified with 1 N aq HCl. The precipitated poly-**1-H** was then collected by centrifugation, washed with methanol, and dried in vacuo at room temperature overnight. The complete removal of (*R*)-**5** was confirmed by the ^{1}H NMR measurement of the recovered polymer. UV−visible and CD spectra of isolated polymers were measured in alkaline water ([NaOH]/[monomeric units of poly-**1-H**] = 1.0). The concentration of the polymers was corrected on the basis of $\epsilon_{302} = 1930\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ because helical and nonhelical poly-**1-H**s have the same ϵ_{302} value in alkaline water irrespective of their optical activity.

Isolation of Helical Poly-1-H Induced by (1*R*,2*S*)-6 or (*R*)-5 in Organic Solvent−Water Mixtures. A typical experimental procedure is described below. After the solution of poly-**1-H** with (1*R*,2*S*)-**6** in organic solvent−water mixtures had been allowed to stand at 50 °C for days (see Table 2), 1 N NaOH in methanol was added to the solution ([NaOH]/[monomeric units of poly-**1-H**] = 10). The solution was poured into a large amount of methanol to remove (1*R*,2*S*)-**6**. The precipitated poly-**1-Na** was collected by centrifugation, and the recovered polymer was dissolved in a small amount of water to maintain the poly-**1-Na** concentration of 0.5 mg/mL. The solution was then acidified with 1 N aq HCl and the precipitated poly-**1-H** was collected by centrifugation, washed with methanol, and dried in vacuo at room temperature overnight. The complete removal of (1*R*,2*S*)-**6** was confirmed by the ^{1}H NMR measurement of the recovered polymer. UV−visible and CD spectra of isolated polymers were measured in alkaline water ([NaOH]/[monomeric units of poly-**1-H**] = 1.0). The concentration of the polymers was corrected on the basis of $\epsilon_{302} = 1930\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ because helical and nonhelical poly-**1-H**s have the same ϵ_{302} value in alkaline water irrespective of their optical activity.

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Supporting Information Available: Effects of the pH and NaCl concentration on the ICD intensity changes of the poly-**1-Na**−(*S*)-**7** complex in water with time, and changes in the ICD intensity of the poly-**1-H**−(*R*)-**5** complex in various organic solvent−water mixtures with time. This material is available free of charge via the Internet at http://pubs.acs.org.

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