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Chiral Stimuli-Responsive Gels: Helicity Induction in Poly(phenylacetylene) Gels Bearing a Carboxyl Group with Chiral Amines

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Abstract: Poly(phenylacetylene) gels (gel-**1**-H and gel-**2**-H) bearing a carboxy pendant were synthesized either by the copolymerization of (4-carboxyphenyl)acetylene (gel-**1**-H) with a bis(phenylacetylene) derivative as the cross-linking reagent using a rhodium complex ($[Rh(cod)_2]BF_4$: cod = 1,5-cyclooctadiene) as the catalyst or by the cross-linking of poly[(4-carboxyphenyl)acetylene] with diamines (gel-**2**-H). The obtained gels were found to swell in DMSO and exhibited an induced circular dichroism (ICD) in the long absorption region of the main chain in the presence of optically active amines. These results indicate that a predominantly one-handed helix can be induced in the polymer network of the gels through chiral acid−base interactions. The swelling properties and the Cotton effect intensities of the gels depend on the cross-linking ratio and the chiral amines. Gel-**1**-Na and gel-**2**-Na prepared from gel-**1**-H and gel-**2**-H, respectively, also significantly swelled in water and showed ICDs characteristic of chiral amino alcohols and free amino acids in water.

Introduction

Stimuli-responsive gels have recently received much attention as novel soft materials because their swelling properties and morphology drastically change in response to external physical and chemical stimuli[1] such as temperature,[2] electric and magnetic fields,[3] light,[4] pH,[2b,d,g] and solvent composition.[2a−c] Such stimuli-responsive gels, called smart gels, intelligent gels, or biomimetic gels, have extensively been studied in view of their potential applications to actuators,[5] shape memories,[6] drug delivery devices,[7] sensors,[8] and displays.[9] In addition, a variety of molecularly imprinted gels (MI gels) that exhibit molecular and chiral recognition abilities for the target imprinted molecules have also been designed and prepared not only as model polymers for enzymes, but also as chiral stationary phases in high-performance liquid chromatography (HPLC).[10] However, these MI gels are highly crosslinked and are too hard to undergo the swelling and shrinking in response to guest molecules. Recently, a few MI hydrogels have been reported to show significant volume changes (phase transitions) in the presence of the imprinted molecules used in the formation of hydrogels.[11] Although these MI hydrogels showed specific swelling changes in the presence of guest molecules, to the best of our knowledge, polymer gels that exhibit changes in morphology or conformation in response to chiral stimuli have not yet been reported.

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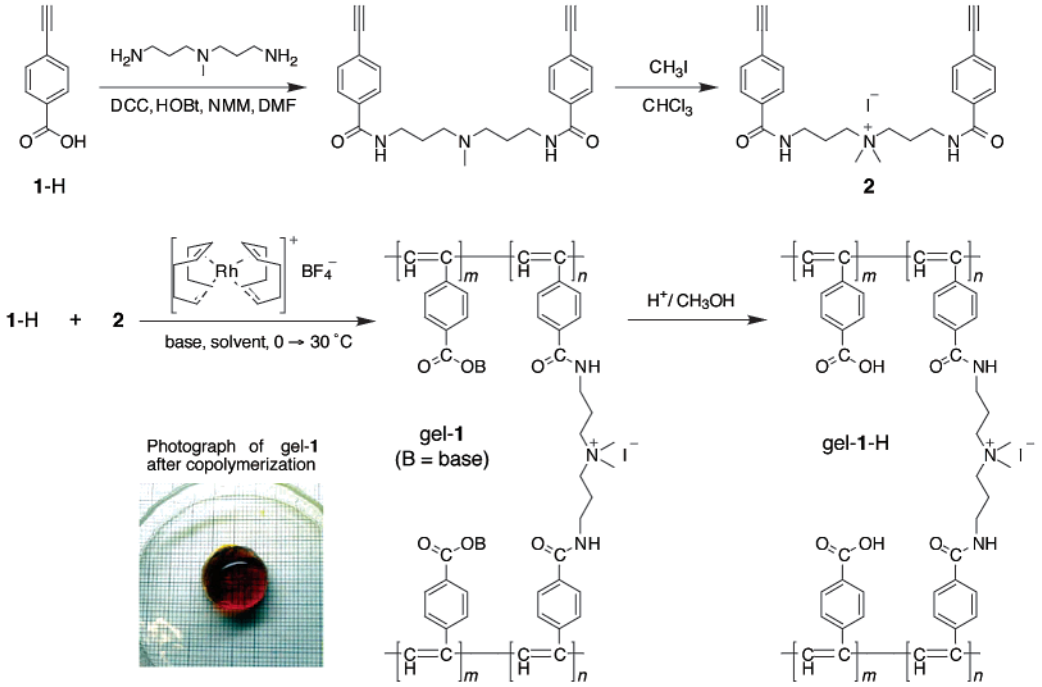
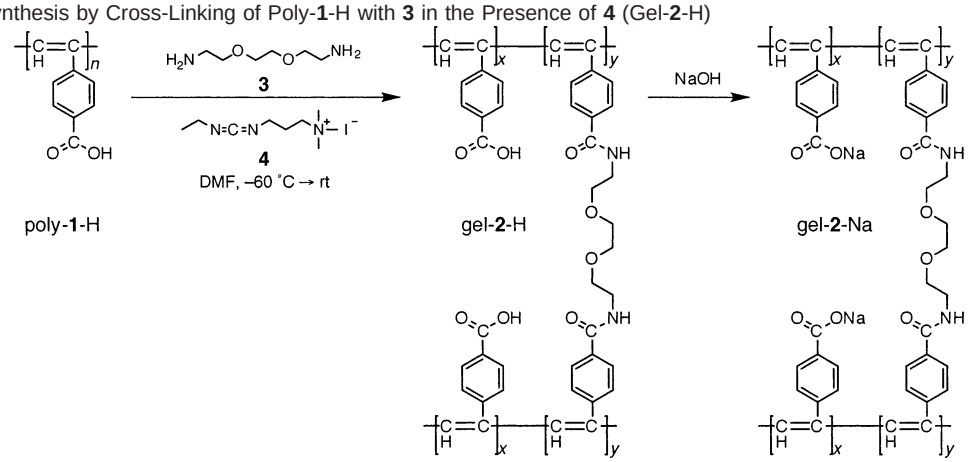
10.1021/ja029036c CCC: $25.00

Scheme 1. Gel Synthesis by Copolymerization of **1**-H and **2** (Gel-**1**-H)



Scheme 2. Gel Synthesis by Cross-Linking of Poly-**1**-H with **3** in the Presence of **4** (Gel-**2**-H)



We previously reported that an optically inactive, cis-transoidal poly[(4-carboxyphenyl)acetylene] (poly-**1**-H) showed an induced circular dichroism (ICD) based on a predominantly one-handed helix formation in the presence of optically active amines in solution.[12] We also found that the induced macromolecular helicity could be memorized even after the replacement of the chiral amines used for the helicity induction on poly-**1**-H with achiral amines.[13] Moreover, we have recently developed a novel method for the direct polymerization of (4-carboxy)phenylacetylene (**1**-H) in water using water-soluble Rh complexes; the sodium salt of poly-**1**-H (poly-**1**-Na) was quantitatively obtained and showed an ICD characteristic of natural, free amino acids in water.[14] In this study, we prepared poly(phenylacetylene) gels bearing a carboxy group either by the copolymerization of **1**-H with a novel bis(phenylacetylene) monomer as the cross-linking reagent using a water-soluble Rh complex or by the cross-linking (condensation) of poly-**1**-H with diamines and investigated if a one-handed helical conformation could be induced on the obtained gels in the presence of optically active compounds using CD spectroscopy.

Results and Discussion

Syntheses and Structures of Gel-1-H and Gel-2-H. Poly-[(4-carboxyphenyl)acetylene] gels (gel-**1**-H and gel-**2**-H) were synthesized either by the cross-linking polymerization or by the cross-linking of poly-**1**-H with diamines as schematically illustrated in Schemes 1 and 2. Their structures and helicity induction in the gels were then investigated. A novel cross-linking acetylene monomer (**2**) was prepared according to Scheme 1; a quaternary ammonium residue was introduced to the middle part of the spacer for improving the solubility in polar solvents. Gel-**1**-H was prepared by the copolymerization of **1**-H with a small amount of **2** using a water-soluble Rh complex, bis(1,5-cyclooctadiene)rhodium tetrafluoroborate ([Rh(cod)$_2$]BF$_4$) (Scheme 1).[14] Table 1 summarizes the results of the copolymerization of **1**-H and **2** with [Rh(cod)$_2$]BF$_4$ in the presence of various bases. When the copolymerization was

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Table 1. Copolymerization of **1**-H and **2** in the Presence of Various Bases with $[Rh(cod)_2]BF_4$ at 30 °C for 24 h[a]

run	base	solvent	**2** in feed (mol %)	gel-**1**-H[b] yield (%)	gel-**1**-H[b] color
1	NaOH	H_2O[c]	0.5	36	yellow-orange
2	(*S*)-**5**	MeOH	0.5	17	yellow-orange
3	(*S*)-**5**	DMSO	0.5	*d*	
4	2-aminoethanol	MeOH	0.5	50	yellow-orange
5	Et_2NH	MeOH	0.5	62	deep red
6	Et_2NH	MeOH	1.0	75	deep red
7	Et_2NH	MeOH	2.0	79	deep red
8	Et_2NH	MeOH	5.0	85	deep red

[a] Polymerized under nitrogen; [monomer (**1**-H + **2**)] = 0.5 M, [monomer]/[Rh] = 200, [base]/[monomer] = 1.5 (run 1) and 2 (runs 2−8). Polymerization was initiated at 0 °C, and the temperature was raised to 30 °C. [b] DMSO insoluble fraction; yields were calculated by the weight of dried gel. [c] DMSO (5 vol %) was used to dissolve **2** in aqueous media. [d] Soluble in DMSO.

performed in the presence of diethylamine (Et_2NH) ([Et_2NH]/[**1**-H] = 2) in methanol, the polymerization rapidly and homogeneously proceeded to give deep red transparent gels in moderate yields (runs 5−8 in Table 1). Other bases such as NaOH, (*S*)-phenylalaninol ((*S*)-**5**), and 2-aminoethanol were also employed to examine the effect of the bases on the copolymerization. NaOH afforded a transparent gel (run 1) in water similar to that prepared with Et_2NH in methanol, while (*S*)-**5** and 2-aminoethanol gave yellow-orange opaque gels in methanol because small and large yellow-orange particles were produced during the copolymerization (runs 2 and 4). Although optically active amines such as (*S*)-**5** instead of Et_2NH may afford an optically active gel derived from the helical structure formed during the copolymerization even after the removal of the chiral amines,[13] the obtained gel-**1**-H swollen in dimethyl sulfoxide (DMSO) exhibited no ICD based on the induced helical conformation of the main chain. The reason for this is not clear at present, but the network formation does disturb the maintenance of the induced helical structure. On the other hand, gelation could not take place in DMSO (run 3) because of the poor polymerizability of **1**-H in DMSO as reported previously.[14] The molar ratios of **2** to **1**-H (0.5−5 mol %) also influenced the properties of gel-**2**-H. Gel-**2**-H prepared using a higher content of **2** in the feed became hard and brittle, and in the case of 5 mol % **2** in feed, the gel gradually became turbid during the copolymerization. These results suggest that bases, solvents, and the molar ratio of the cross-linking reagent in the feed strongly influence the properties of the gels.

Gel-**1**-H's prepared by the copolymerization were stable for a day, but not stable over a longer period, and part of the gels very slowly dissolved in DMSO or the DMSO solution containing amines with time probably because of decomposition of the polymer's main chain.[16] We then prepared gel-**2**-H through cross-linking of a prepolymer (poly-**1**-H) with a diamine (**3**) in the presence of a condensation reagent (**4**)[15] in *N*,*N*-dimethylformamide (DMF) at −60 °C according to Scheme 2. The results of the cross-linking are summarized in Table 2. When the molar ratio of **3** to the monomer units of poly-**1**-H in the feed was from 3 to 7 (mol %), yellow-orange homogeneous gels insoluble in DMSO were successfully obtained. The gel

Table 2. Cross-Linking of Poly-**1**-H with Diamine (**3**) in the Presence of Condensation Reagent (**4**) in DMF[a]

run	**3** in feed (mol %)	**4** in feed (mol %)	gel-**2**-H yield (%)[b]	gel-**2**-H color
1	2	4	*c*	
2	3	6	57	yellow-orange
3	4	8	65	yellow-orange
4	5	10	81	yellow-orange
5	6	12	89	yellow-orange
6	7	14	92	yellow-orange

[a] Cross-linked under nitrogen; [monomer units of poly-**1**-H] = 0.05 M. Condensation was initiated at −60 °C, and the reaction mixture was allowed to stand at room temperature. [b] DMSO insoluble fraction; yields were calculated by the weight of dried gel. [c] Soluble in DMSO.

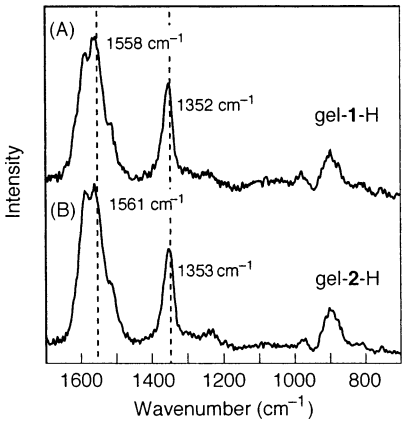

Figure 1. Laser Raman spectra of gel-**1**-H (A) (run 5 in Table 1) and gel-**2**-H (B) (run 4 in Table 2).

yields also increased with an increase in the molar ratio of **3** in the feed. On the contrary, under a dilute concentration of poly-**1**-H (less than 0.01 M), at higher temperatures, or using 3,3′-diamino-*N*-methyldipropylamine instead of **3** as the cross-linking reagent, gel-**2**-H insoluble in DMSO could not be obtained.

To gain information on the stereoregularity of the gels, the laser Raman spectra of the dried gels in the solid state were measured.[17,18] ^1H NMR spectroscopy is frequently used to estimate the stereoregularity of linear poly(phenylacetylene)s[12,16,19] but cannot be applied to gels (Figure 1). Gel-**1**-H (A, run 5 in Table 1) showed well-defined peaks at 1558 and 1352 cm^{-1} that can be assigned to the C=C and C−C bond vibrations for the cis polyacetylenes, respectively, according to the literature.[17] Under the same conditions, the peaks derived from the C−H bond vibration for the cis or trans form could not be clearly detected because the peak around 900 cm^{-1} is weak and very broad. Gel-**2**-H (B, run 4 in Table 2) prepared from cis-

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(18) It is necessary to observe the measured laser Raman spectra of the solid poly(phenylacetylene) samples because they may deteriorate or isomerize from the cis to trans form in the presence of a strong laser light; in addition, the S/N ratio becomes worse due to the fluorescence when the exposure time is too long.
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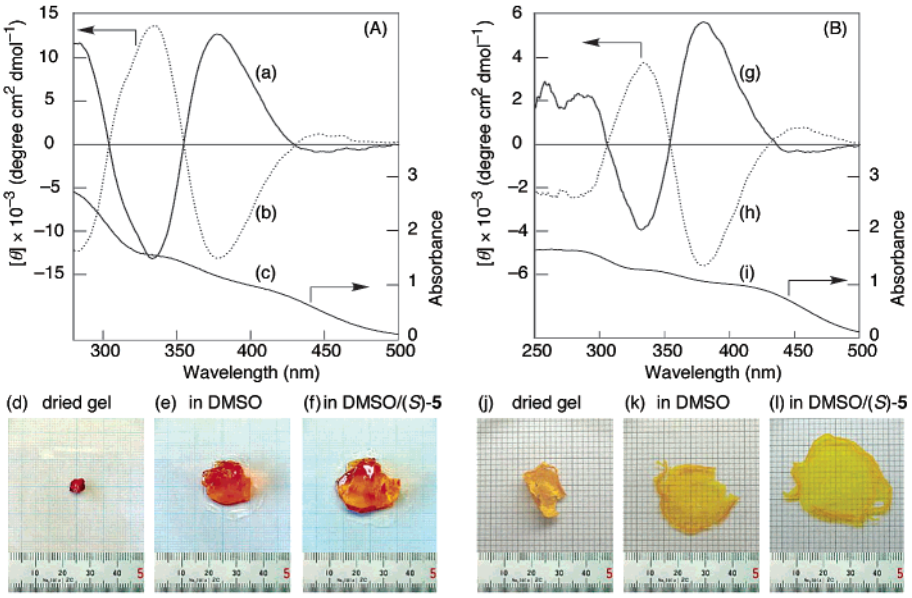
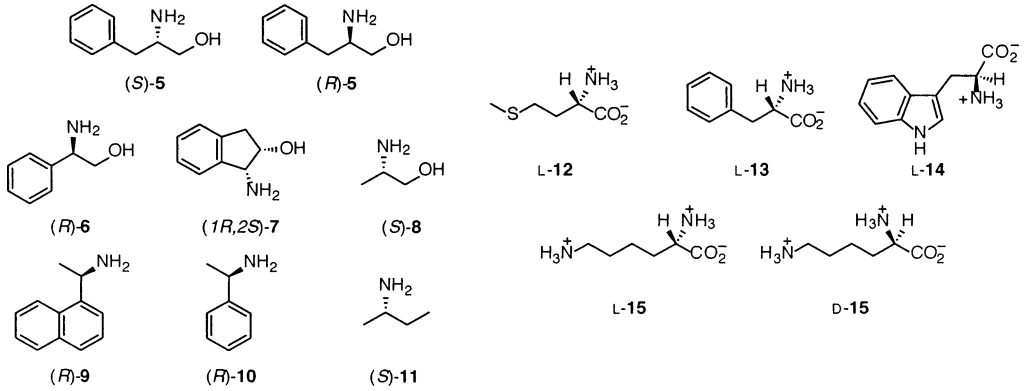


Figure 2. CD spectra of gel-**1**-H (A) (run 5 in Table 1) and gel-**2**-H (B) (run 4 in Table 2) swollen in DMSO with (*S*)-**5** (a and g) and (*R*)-**5** (b and h) at room temperature. Absorption spectra with (*S*)-**5** are also shown (c and i). The CD intensities were normalized using molar absorptivity at 400 nm (ϵ_{400} = 2860). The molar ratio of **5** to monomer units of the gels is 50. Photographs of the dried (d and j) and swollen state in DMSO in the absence (e and k) and presence (f and l) of (*S*)-**5** of gel-**1**-H (d−f) and gel-**2**-H (j−l) are shown below.

Chart 1. Structures of Optically Active Amines (**5**−**11**) and Natural Amino Acids (**12**−**15**)



transoidal poly-**1**-H also exhibited the peaks (1561 and 1353 cm^{-1}) characteristic for the cis form, while the peaks due to the trans form (1220 cm^{-1}) were negligible similar to that of the gel-**1**-H. These results indicate that both gels probably have a stereoregular cis-transoidal structure.

Swelling Properties and Helicity Induction of the Gels in DMSO. Gel-**1**-H (run 5 in Table 1) and gel-**2**-H (run 4 in Table 2) swelled in DMSO, which is a good solvent for the helicity induction and memory of the macromolecular helicity of poly-**1**-H;[12,13] the swelling ratio in DMSO reached 11 and 9, respectively (e and k in Figure 2). Upon the addition of optically active amines such as (*S*)-phenylalaninol ((*S*)-**5** in Chart 1) to the swollen gels in DMSO, these gels further swelled; the swelling ratios of gel-**1**-H and gel-**2**-H increased to 66 and 22, respectively (f and l). These volume changes were accompanied by the induction of CD in the absorption region of the polymer main chains. Figure 2 (A and B) shows the typical CD and absorption spectra of gel-**1**-H and gel-**2**-H swollen in DMSO containing (*S*)- and (*R*)-**5**. Both gels formed complexes with the optically active amines through an acid−base interaction in DMSO and exhibited split-type ICDs of the mirror images in the UV−visible region. The differences in the ICD intensities and the swelling ratios between the gels may be due to the lower cross-linking density of gel-**1**-H than that of gel-**2**-H. The ICD intensities of these gels were lower than that of poly-**1**-H induced by the same chiral amines in DMSO, although the Cotton effect signs were the same if the absolute configurations of the amines were the same. This may be due to the difficulty in the conformational change of the polymer network between the cross-linking points. We also measured the LD spectra of the gels in the presence of optically active amines in DMSO and found that the LD contributions caused by macroscopic anisotropy are negligible. On the basis of these results, it is concluded that a one-handed helical conformation can be induced even in the gels with a lower cross-linking density upon complexation with optically active amines as schematically shown in Scheme 3. The Cotton effect signs of gel-**1**-H (run 5 in Table 1) and gel-**2**-H (run 4 in Table 2) swollen in DMSO with 10 equiv of (*S*)-**5** inverted slowly with time upon the addition of 50 equiv of (*R*)-**5**, which indicates that the polymer backbone in the gels

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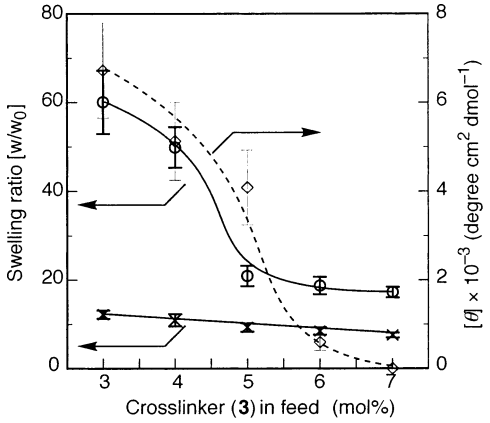
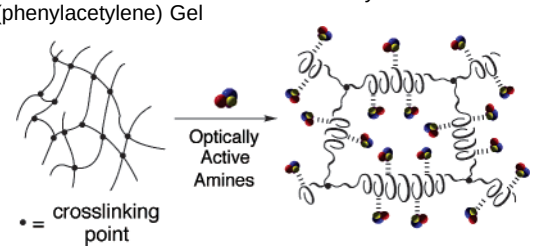


Figure 3. Effects of the amount of cross-linking reagent (**3**) on the swelling ratio of gel-**2**-H (Table 2) in DMSO in the absence (×) and presence (○) of (*S*)-**5** at room temperature; [(*S*)-**5**]/[gel-**2**-H] = 50. The CD intensities of gel-**2**-H in DMSO with (*S*)-**5** are also shown (◇). The error bars represent the standard deviation estimated by three measurements of the swelling ratios and CD spectra.

Scheme 3. Schematic Illustration of Helicity Induction in the Poly(phenylacetylene) Gel



switches the helix-sense by responding to the chirality of the amine (see the Supporting Information).

The changes in the swelling ratio and ICD intensity of gel-**2**-H in DMSO with (*S*)-**5** versus the molar ratio of the cross-linking reagent (**3**) were investigated (Figure 3). The gel-**2**-H hardly changed the volume in DMSO in the absence of the chiral amine ((*S*)-**5**) irrespective of the amount of **3** in the feed, whereas in the presence of (*S*)-**5**, a significant change in the swelling ratios (○) was observed in the vicinity of ca. 5 mol % **3**. According to the changes in the swelling ratio, the ICD intensities (◇) also similarly changed; the ICD intensities and swelling ratios decreased as the cross-linking density of the gels increased. However, the gels prepared with an amount less than 3 mol % cross-linking reagent were too soft to handle, and, therefore, an adequate amount of the cross-linking reagent (5 mol % for gel-**2**-H) is necessary to obtain stable gels. On the other hand, highly cross-linked gel-**1**-H's (runs 6−8 in Table 1) also swelled in DMSO and exhibited ICDs, but the volume changes in the DMSO decreased as the amount of **2** in the feed increased, as expected; w/w_0 and $[\theta] \times 10^{-3} = 60$ and +12.9 (run 6), 43 and +9.4 (run 7), and 13 and +0.7 (run 8), respectively.

To investigate the effect of the chiral amines (Chart 1) on the helix formation and the swelling properties of the gels, the CD spectra and swelling ratios of the gels in the presence of various optically active amines were measured in DMSO (Table 3).[12] The gels underwent a distinct swelling behavior in response to different chiral amines. The gels swelled greater with relatively bulky chiral amino alcohols (**5**−**7**) including **5** and showed ICDs, while a less bulky amino alcohol (**8**) and primary amines (**9**−**11**) prevented swelling or caused shrinking of the gels, so that the CD spectra of the gels could not be measured because the gels became turbid after the addition of the chiral amines. These swelling and shrinking changes in the gels may be controlled by a balance of the intermolecular forces such as electrostatic, ionic, and hydrophobic forces together with the hydrogen bonding interaction between the gels with chiral amines. It is known that acid−amine complexes partly dissociate into free ions (carboxylate and ammonium ions) which may be dependent on the structures of the amines in DMSO. Such a dissociation ability may affect the swelling properties, and thus the ICD intensities.[20] Because the ICD intensities of poly-**1**-H were remarkably dependent on the kinds of chiral amines, the CD intensities induced on these gels were normalized as values relative to those of the original polymer (Table 3). Although the ICD intensities of the homopolymer increased as the

Table 3. Swelling Ratios and Cotton Effects of Gel-**1**-H and Gel-**2**-H in DMSO with Various Optically Active Amines (**5**−**11**) at ca. 22−24 °C[a]

			second Cotton effect[c,d]				
			gel-**1**-H or gel-**2**-H		poly-**1**-H[e]		
gel	amine	swelling ratio[b,c]	sign	$[\theta]_{second}$	sign	$[\theta]_{second}$	relative intensity[f] (%)
gel-**1**-H	none	11 ± 1					
	(*S*)-**5**	66 ± 6	+	14.9 ± 1.3	+	17.4	86 ± 8
	(*R*)-**5**	56 ± 6	−	13.0 ± 1.2			
	(*R*)-**6**	61 ± 4	−	8.7 ± 0.8	−	21.7	40 ± 4
	(1*R*,2*S*)-**7**	47 ± 3	−	20.1 ± 1.8	−	34.1	59 ± 5
	(*S*)-**8**	10 ± 1		*g*			
	(*R*)-**9**	12 ± 2		*g*	−	30.6	
	(*R*)-**10**	9 ± 1		*g*	−	12.6	
gel-**2**-H	none	9 ± 1					
	(*S*)-**5**	22 ± 2	+	4.1 ± 0.8	+	17.4	24 ± 5
	(*R*)-**5**	21 ± 1	−	4.8 ± 0.5			
	(*R*)-**6**	24 ± 2	−	1.0 ± 0.1	−	21.7	4 ± 1
	(1*R*,2*S*)-**7**	22 ± 3	−	2.0 ± 0.6	−	34.1	6 ± 2
	(*S*)-**8**	10 ± 2		*g*			
	(*R*)-**9**	12 ± 1		*g*	−	30.6	
	(*R*)-**10**	8 ± 1		*g*	−	12.6	
	(*S*)-**11**	13 ± 1		*g*	+	1.4	

[a] Gel-**1**-H (run 5 in Table 1) and gel-**2**-H (run 4 in Table 2) were used, and the molar ratio of chiral amines to monomer units of dried gels was 50. [b] The swelling ratios were estimated using the following equation: swelling ratio = w/w_0, where w_0 and w represent the weights of dried and swollen gel, respectively.[2g] [c] The CD and swelling ratio measurements were repeated three times under the same conditions to calculate the mean and standard deviations. [d] The sign and CD intensity (10^3 deg cm^2 dmol^{-1}) of the second Cotton effect. [e] The sign and CD intensity of linear poly-**1**-H with chiral amines in DMSO. Data were taken from ref 12. [f] Relative second Cotton intensity of gels to poly-**1**-H. [g] Not detected because the gel became turbid.

(20) One may expect that the helicity induction in the gels may lead to deswelling of the gels, because the end-to-end distance of a polymer chain between cross-linking points seems to decrease by helix formation with chiral amines in DMSO. However, recent viscometric studies on a conformational change of poly((4-carboxyphenyl)acetylene) (poly-**1**-H) in DMSO before and after complexation with an optically active amine ((*R*)-**9**) indicate that poly-**1**-H behaves as a weak polyelectrolyte in the presence of the amine; the poly-**1**-H−(*R*)-**9** complex partly dissociates into carboxylate and ammonium ions. This feature might cause swelling of the gels because of repulsive electrostatic interactions between the carboxylate ions. Another important result obtained from the viscometric study is that the chain stiffness parameter (the persistent length) of poly-**1**-H in DMSO becomes longer in the presence of the chiral amine, from 4.2 nm in pure DMSO to 8.6 nm in DMSO with (*R*)-**9**. This means that the polymer becomes stiff, but the change in the poly-**1**-H conformation upon complexation with the amine is not as drastic as the coil to helix transition of polypeptides (Sato, T.; Ashida, Y.; Morino, K.; Maeda, K.; Okamoto, Y.; Yashima, E., unpublished results). On the basis of these results, we think that the helicity induction may not lead to a drastic change of the swelling ratio of the gels, but the formation of carboxylate ions may be responsible for the swelling behavior of the gels in the presence of chiral amines. However, it is not clear at present why the less bulky amino alcohol (**8**) and primary amines (**9**−**11**) prevent swelling or caused shrinking of the gels in DMSO.

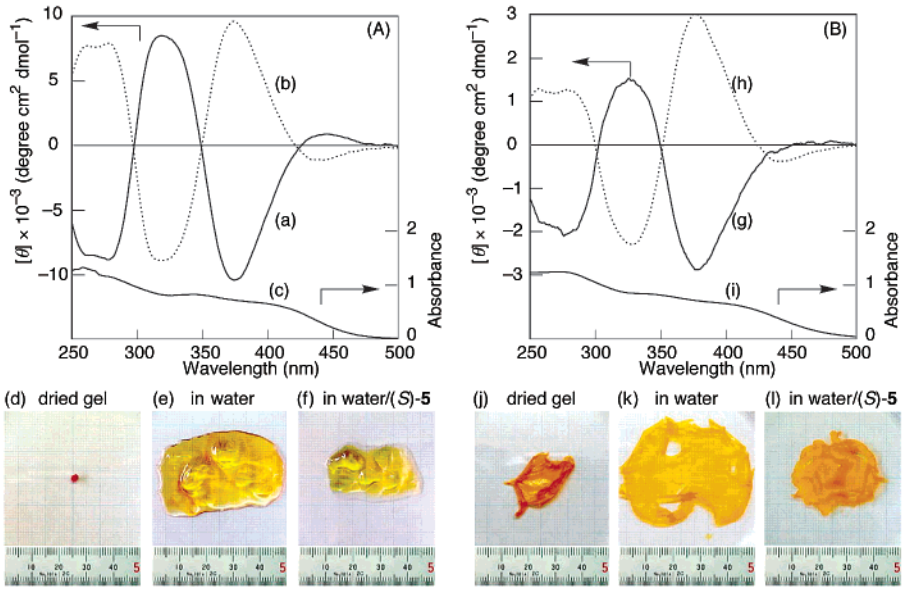


Figure 4. CD spectra of gel-**1**-Na (A) and gel-**2**-Na (B) derived from gel-**1**-H (run 5 in Table 1) and gel-**2**-H (run 4 in Table 2) swollen in water with (*S*)-**5** (a and g) and (*R*)-**5** (b and h) at room temperature. Absorption spectra with (*S*)-**5** are also shown (c and i). The CD intensities were normalized using molar absorptivity at 400 nm ($\epsilon_{400} = 2300$). The molar ratio of **5** to monomer units of the gels is 10. Photographs of the dried (d and j) and swollen state in water in the absence (e and k) and presence (f and l) of (*S*)-**5** of gel-**1**-Na (d−f) and gel-**2**-Na (j−l) are shown below.

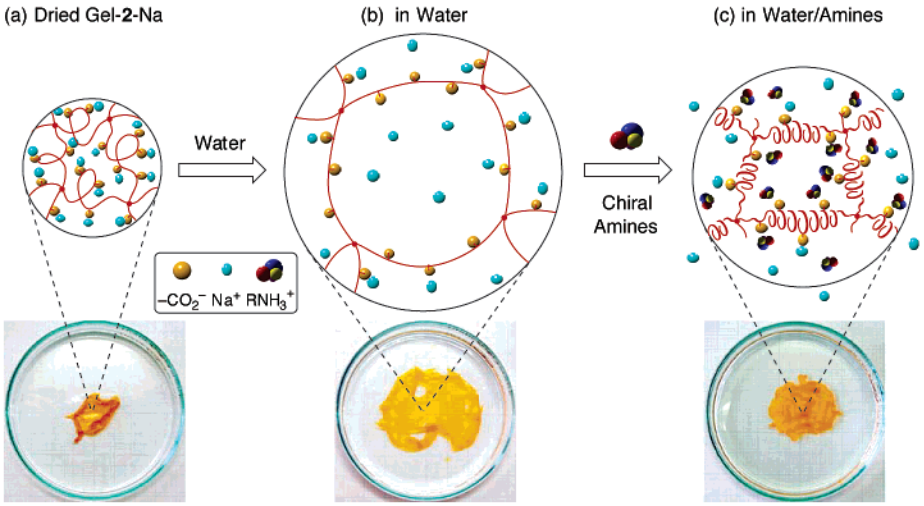


Figure 5. Schematic illustration of swelling and shrinking of gel-**2**-Na derived from gel-**2**-H (run 4 in Table 2) in water after the addition of chiral amines (top). The changes in volume of gel-**2**-Na with (*S*)-**5** in water are also shown (bottom).

bulkiness of the chiral amines increased,[12] the relative intensities of the gels did not show such a clear tendency, while the amine **5** induced a larger CD on the gel than did **6** and **7**. The steric effect between the chiral amines and the gel matrix may influence the helicity induction.

Swelling Properties and Helicity Induction of the Gels in Water. Gel-**1**-H and gel-**2**-H do not swell in water, but after conversion of the carboxy groups of the gels into the sodium carboxylate groups (gel-**1**-Na and gel-**2**-Na, respectively), both gels behaved as hydrogels and swelled in water. The hydrogels, gel-**1**-Na and gel-**2**-Na prepared by soaking gel-**1**-H and gel-**2**-H in aqueous NaOH (0.1 N), significantly swelled in pure water by a factor of 910 and 46, respectively (Figure 4e and k), due to the electrostatic repulsion between the intramolecular carboxylate anions generated by the dissociation of the sodium salts as illustrated in Figure 5b. In particular, the drastically swollen gel-**1**-Na in water was quite soft to handle. Figure 4A and B shows the CD and absorption spectra of gel-**1**-Na and gel-**2**-Na in the presence of (*S*)- and (*R*)-**5** in water; the gels exhibited similar ICD patterns as those of the homopolymer, poly-**1**-Na in water,[14] but the ICD intensities of the gels were weak as compared to that of poly-**1**-Na. Not only chiral amines including (*S*)-**5** but also some natural, free amino acids brought about ICDs in the gels (Table 4). Although the ICD intensities were dependent on the kinds of chiral compounds used, the signs of the Cotton effects of the gels were in accordance with those of poly-**1**-Na with the same chiral compounds,[14] which suggests that the present gels can be applicable to a novel soft material for chirality sensing. However, the ICD intensities of the gels were relatively weak; particularly, those of the gels induced by free amino acids are weak due to the electrostatic repulsion between the carboxylate anions of the gels and free amino acids.

Contrary to the swelling properties of gel-**1**-H and gel-**2**-H in DMSO, most optically active compounds caused similar swelling in the gels; gel-**1**-Na and gel-**2**-Na shrunk to one-third and one-half, respectively, in pure water when compared to the

Table 4. Swelling Ratios and Cotton Effects of Gel-**1**-Na and Gel-**2**-Na in Water with Various Optically Active Amines (**5**−**11**) and Amino Acids (**12**−**15**) at ca. 22−24 °C[a]

			second Cotton effect[c,d]				
			gel-**1**-Na or gel-**2**-Na		poly-**1**-Na[e]		
gel	additive	swelling ratio[b,c]	sign	$[\theta]_{second}$	sign	$[\theta]_{second}$	relative intensity[f] (%)
gel-**1**-Na	none	910 ± 130					
	(*S*)-**5**	330 ± 40	−	10.5 ± 0.2	−	18.9	56 ± 1
	(*R*)-**5**	310 ± 30	+	9.4 ± 0.3	+	17.9	52 ± 2
	(*R*)-**6**	230 ± 30	+	1.2 ± 0.3	+	3.1	37 ± 9
	(1*R*,2*S*)-**7**	240 ± 20	−	5.9 ± 0.6	−	10.4	57 ± 6
	(*S*)-**8**	290 ± 30	−	4.0 ± 0.7	−	3.9	100 ± 20
gel-**2**-Na	none	46 ± 2					
	(*S*)-**5**	29 ± 3	−	3.0 ± 0.4	−	18.9	16 ± 2
	(*R*)-**5**	23 ± 2	+	3.0 ± 0.4	+	17.9	17 ± 2
	(*R*)-**6**	25 ± 3	+	0.18 ± 0.09	+	3.1	6 ± 3
	(1*R*,2*S*)-**7**	30 ± 3	−	0.62 ± 0.0	−	10.4	6 ± 1
	(*S*)-**8**	34 ± 3	−	0.7 ± 30.16	−	3.9	19 ± 4
	(*R*)-**9**	23 ± 3	−	0.39 ± 0.11			
	(*R*)-**10**	31 ± 2	−	1.3 ± 0.2			
	(*S*)-**11**	28 ± 3	+	0.31 ± 0.10			
	L-**12**	27 ± 2	+	0.25 ± 0.08	+	7.0	4 ± 1
	L-**13**	20 ± 1	−	0.14 ± 0.05	−	2.4	6 ± 2
	L-**14**	39 ± 2	+	0.53 ± 0.14	+	14.7	4 ± 1
	L-**15**	23 ± 2	+	0.77 ± 0.24	+	8.3	9 ± 3
	D-**15**	22 ± 2	−	0.60 ± 0.10			

[a] The gels (gel-**1**-Na and gel-**2**-Na) derived from gel-**1**-H (run 5 in Table 1) and gel-**2**-H (run 4 in Table 2) were used, and the molar ratio of chiral amines to monomer units of dried gels was 10. [b] The swelling ratios were estimated using the following equation: swelling ratio = w/w_0, where w_0 and w represent the weights of dried and swollen gel, respectively.[2g] [c] The CD and swelling ratio measurements were repeated three times under the same conditions to calculate the mean and standard deviations. [d] The sign and CD intensity (10^3 deg cm^2 dmol^{-1}) of the second Cotton effect. [e] The sign and CD intensity of linear poly-**1**-Na with chiral amines in water. Data were taken from ref 14. [f] Relative second Cotton intensity of gels to poly-**1**-H.

swelling ratios. The swelling and shrinking of the gels in water before and after the addition of optically active compounds are probably determined by the repulsive electrostatic interactions of the ionized gels associated with the sodium and ammonium cations as shown in Figure 5. The changes in the volume of gel-**2**-Na in water after the addition of (*S*)-**5** are also shown in Figure 5 (bottom). The gels drastically swell in pure water due to the intramolecular Coulomb repulsion between the carboxylate anions because the sodium ions of the carboxylates tend to dissociate in pure water (Figure 5b). Upon the addition of chiral amines such as (*S*)-**5**, the amines dissociate into the quaternary ammonium ions in aqueous media, which can interact with the carboxylate groups to induce helical conformation on the gels. However, because of the common ion effect[21] (Figure 5c), the gels slightly shrunk.

Conclusions

We have successfully prepared two types of poly(phenylacetylene)-based gels that respond to chiral stimuli and change their volumes in DMSO and water. These gels exhibited ICDs due to helix formation in the gels. Although a large number of stimuli-responsive gels have been reported, this may be the first example of a chirality-responsive gel. The present strategy can be applicable for designing and synthesizing other various chirality- and chiral-responsive gels bearing other various achiral functional groups[22−25] and chiral pendants,[26] respectively. The latter will undergo a different volume change accompanied by a helix−helix transition in the gel in response to chiral stimuli. We believe that the macromolecular helicity induced in the gels can be memorized when the chiral amine is replaced with achiral amines.[13,27] This work is now in progress in our laboratory.

Experimental Section

Materials. **1**-H, poly-**1**-H, and $[Rh(cod)_2]BF_4$ were prepared according to the previously reported methods.[14] The molecular weight (M_n) of poly-**1**-H was estimated as its methyl ester by size exclusion chromatography (SEC) (polystyrene standards) using tetrahydrofuran (THF) as the eluent: $M_n = 3.2 \times 10^4$ (DP = 200) and $M_w/M_n = 3.2$. DMF and DMSO were dried over CaH_2, distilled under reduced pressure, and stored under nitrogen. Chloroform was dried over CaH_2, distilled under nitrogen, and stored under nitrogen. Methanol was dried over turning magnesium and iodine, distilled onto molecular sieves 4 Å (Nacalai Tesque, Tokyo, Japan) under nitrogen, and then distilled again under high vacuum just before use. Et_2NH was dried over KOH pellets, distilled under nitrogen, and stored under nitrogen. Dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt), and 1-{3-(dimethylamino)propyl}-3-ethylcarbodiimide methiiodide (**4**) were purchased from Aldrich. 3,3′-Diamino-*N*-methyldipropylamine, methyl iodide, and 2,2′-(ethylenedioxy)bis(ethylamine) (**3**) were obtained from Tokyo Kasei (TCI, Tokyo, Japan). *N*-Methylmorphorine (NMM) was purchased from Kishida Chemicals (Osaka, Japan). These reagents were used as received.

Measurements. NMR spectra were taken on a Varian Mercury 300 operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C with tetramethylsilane (TMS) as the internal standard. IR and Raman spectra were recorded on a Jasco Fourier Transform IR-620 spectrophotometer and a Jasco RMS-200 spectrophotometer using the 532 nm exciting line at 100 mW (exposure time: 5 s × 2), respectively. CD and absorption spectra were taken on a Jasco J-725L spectropolarimeter and a Jasco V-570 spectrophotometer, respectively. Linear dichroism (LD) spectra were measured using a Jasco J-725 spectropolarimeter with an LD attachment.

***N*,*N*-Bis{*N*-(4-ethynylbenzoyl)-3-aminopropyl}dimethylammonium Iodide (2).** The cross-linking reagent (**2**) was prepared according to Scheme 1. To a solution of **1**-H (7.2 g, 49 mmol) in DMF (200 mL) were added DCC (6.2 g, 30 mmol) and HOBt (4.2 g, 31 mmol) at 0 °C under nitrogen. After the reaction mixture was stirred at 0 °C for 1 h and at room temperature for 1 h, NMM (3.0 mL, 23 mmol) and 3,3′-diamino-*N*-methyldipropylamine (2.0 mL, 12 mmol) were then added. The mixture was stirred for 18 h and filtered. The solvent was removed by evaporation, and the residue was extracted with diethyl ether (200 mL). The etheral layer was then washed with 0.01 N NaOH (100 mL) and water (100 mL × 2) and dried over $MgSO_4$. After filtration, the solvent was evaporated to give 5.0 g of an amide intermediate. The purity was ca. 80% on the basis of its ^{1}H NMR spectrum. The crude product was used without further purification. The obtained amide

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(27) When achiral amines, for instance, 2-aminoethanol and *n*-butylamine, were added to the optically active gels in DMSO induced by (*S*)-**5**, the gels shrunk and became turbid, so that the CD measurements of the gels were difficult. We believe that an appropriate combination of chiral and achiral amines should make it possible to memorize the induced helicity in the gels.

derivative (2.0 g) was dissolved in chloroform (40 mL), and to this was added dropwise methyl iodide (1.6 mL, 10 mmol) under nitrogen at room temperature. The reaction mixture was stirred for 1 h. After filtration, the precipitate was washed with chloroform, and the crude product was purified by recrystallization from ethanol to give 1.9 g of **2** (3.5 mmol) as slight brown crystals in 70% yield; mp > 156 °C (decomposition). IR (KBr, cm^{-1}): 3293 ($\nu_{\equiv C-H}$), 1628 ($\nu_{C=O}$). ^1H NMR (DMSO-d_6): δ 1.94 (m, $CH_2CH_2CH_2$, 4H), 3.02 (m, CH_3, 6H), 3.30−3.36 (m, CH_2N and CH_2N^+, 8H), 4.37 (s, ≡CH, 2H), 7.57 (d, aromatic, 4H), 7.85 (d, aromatic, 4H), 8.65 (m, NH, 2H). ^{13}C NMR (DMSO-d_6): δ 22.47, 36.30, 50.30, 61.37, 82.78, 82.83, 124.43, 127.48, 131.59, 134.24, 165.62. Anal. Calcd for $C_{26}H_{30}IN_3O_2 \cdot 0.5H_2O$: C, 56.53; H, 5.66; N, 7.61, Found: C, 56.79; H, 5.61; N, 7.38.

Copolymerization of 1-H and 2 (Gel-1-H). Polymerization was conducted using a water-soluble Rh complex, $[Rh(cod)_2]BF_4$, in a way similar to that previously reported (Scheme 1).[14] **1**-H (2.0 g, 14 mmol) and **2** (37 mg, 68 μmol) were placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated three times, a three-way stopcock was attached to the ampule. Methanol (20 mL) and Et_2NH (0.29 mL, 2.1 mmol) were then added to dissolve **1**-H and **2**. A 2.8 mL of $[Rh(cod)_2]BF_4$ solution in methanol (0.025 M) was added to the solution at 0 °C, and the temperature was raised to 30 °C. The molar ratios of **1**-H to **2** and the Rh complex were 20 and 200, respectively. The color of the solution immediately changed to dark red, and the solution coagulated within 1 min. After 24 h, the resulting gel was immersed in methanol for 1 day, followed by DMSO, methanol, and methanol/acetic acid (9/1, v/v) for 1 day, several days, and 1 day, respectively, to remove unreacted monomer, catalysts, amines, and oligomers. The gel was finally washed with methanol and dried in vacuo at room temperature overnight to give a deep red gel (gel-**1**-H) in 65% yield. IR (KBr, cm^{-1}): 1701 ($\nu_{C=O}$), 1605 ($\nu_{C=C}$). Raman (solid, cm^{-1}): 1558 ($\nu_{cis\ C=C}$), 1352 ($\nu_{cis\ C-C}$).

Gel-**1**-Na was prepared according to the following procedure: gel-**1**-H was immersed in 0.1 N aqueous NaOH for 1 h, and the resulting gel-**1**-Na was washed with water and methanol and dried in vacuo at room temperature overnight. IR (KBr, cm^{-1}): 1586, 1391 (ν_{COO^-}).

Cross-Linking of Poly-1-H with 3 (Gel-2-H). Cross-linking of poly-**1**-H was performed using **3** and **4** as a cross-linking and condensing reagent, respectively, according to Scheme 2.[15] Poly-**1**-H (20 mg, 0.14 mmol) was placed in an ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated three times, a three-way stopcock was attached to the ampule, and DMF (2.0 mL) was added to dissolve the polymer. Stock solutions of **3** (2.0 μL/mL) and **4** (20 mg/mL) in DMF were prepared, and the stock solutions of **3** (0.51 mL, 7.0 μmol) and **4** (0.20 mL, 14 μmol) were added to the poly-**1**-H solution at −60 °C. A 2.8 mL aliquot of the reaction mixture was transferred to a Petri dish (3 cm i.d.) in a desiccator using a syringe at room temperature. The cross-linking reaction immediately occurred, and the solvent was then evaporated under high vacuum to obtain a cross-linked gel. The molar ratios of the monomer units of poly-**1**-H to **3** and **4** were 10 and 20, respectively. The resulting crude gel was washed with water, DMSO, and methanol and dried in vacuo at room temperature overnight to give a yellow-orange filmlike gel (gel-**2**-H) in 81% yield. IR (KBr, cm^{-1}): 1698 ($\nu_{C=O}$), 1609 ($\nu_{C=C}$). Raman (film, cm^{-1}): 1561 ($\nu_{cis\ C=C}$), 1353 ($\nu_{cis\ C-C}$). Gel-**2**-Na was prepared using the same procedure as for gel-**1**-Na. IR (KBr, cm^{-1}): 1588, 1387 (ν_{COO^-}).

CD and Swelling Ratio Measurements of Gels. A typical experimental procedure is described below. A stock solution of (*S*)-**5** (3.1 g, 21 mmol) in DMSO was prepared in a 30 mL flask equipped with a stopcock, and then 2.8 mL of the stock solution was transferred to a Petri dish (8 cm i.d.). A piece of gel-**1**-H (5.6 mg, 38 μmol) was placed in the Petri dish, and the gel was allowed to stand for an appropriate time until the gel showed no further swelling. After several hours, the area surrounding the gel was wiped with a soft cloth, and the swollen gel was weighed. The swelling ratio was calculated using the following equation; [swelling ratio] = w/w_0, where w_0 and w represent the weights of the dried and swollen gels, respectively.[2g] The swollen gel was sandwiched between quartz plates (2 cm diameter), and the CD and absorption spectra were measured. The CD intensities were normalized using the molar absorptivity at 400 nm ($\epsilon_{400} = 2860$). The CD and swelling ratio measurements were repeated three times under the same conditions, and the mean and standard deviations were then calculated. The same procedure was performed for the CD and swelling ratio measurements of gel-**2**-H, gel-**1**-Na, and gel-**2**-Na. For gel-**1**-Na and gel-**2**-Na, the CD intensities were normalized using the molar absorptivity at 400 nm ($\epsilon_{400} = 2300$).

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Supporting Information Available: Changes in the CD intensity of gel-**1**-H and gel-**2**-H swollen in DMSO with 10 equiv of (*S*)-**5** upon the addition of 10 and 50 equiv of (*R*)-**5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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