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Unexpected Thermally Stable, Cholesteric Liquid-Crystalline Helical Polyisocyanides with Memory of Macromolecular Helicity

Yoko Hase,[a] Yuuki Mitsutsuji,[a] Masayoshi Ishikawa,[a] Katsuhiro Maeda,[a] Kento Okoshi,[b] and Eiji Yashima*[a, b]

Abstract: The achiral sodium salt of poly(4-carboxyphenyl isocyanide) (poly-**1**–Na) folds into a one-handed helix induced by optically active amines in water. The induced helicity remains when the optically active amines are completely removed, and further modification of the side groups to amide residues is possible without loss of memory of macromolecular helicity. Although the helical poly-**1**–Na loses its chiral memory at high temperature, helical polyisocyanides modified with achiral primary amines, which no longer have any chiral components, keep their memory perfectly even at 100 °C in *N*,*N*-dimethylformamide in some cases and exhibit cholesteric liquid-crystalline phases, thus providing a robust scaffold with heat resistance to which a variety of functional groups can be introduced.

Keywords: chirality · helical structures · helicity memory · liquid crystals · polyisocyanides

Introduction

The design and synthesis of artificial helical polymers[1] and supramolecular helical assemblies[1h,2] has become an attractive challenge with implications for biological helicity, superstructures, and functions.[1,2] Fully synthetic helical polymers with a controlled helical sense have been prepared either by the polymerization of optically active monomers[1b,e,f] or by the helix-sense selective polymerization of achiral bulky monomers with chiral catalysts or initiators.[1a,c,d,f] Although helical polymers are themselves of particular interest because of their possible application as chiral materials, such as liquid crystals[3] and enantioselective adsorbents,[4] only a limited number of artificial helical polymers stable in solution are available. Their synthesis requires the polymerization of diligently designed chiral or bulky monomers; therefore, further modification of the helical polymers with the desired functional groups while maintaining their one-handed helical conformations after polymerization is virtually impossible.[1,5]

Recently, we reported an unexplored approach that produced a helical polyisocyanide with a controlled helix sense, based on the noncovalent "helicity induction and chiral memory effect".[1f,h,6] An achiral sodium salt of poly(4-carboxyphenyl isocyanide) (poly-**1**–Na) was found to fold into a one-handed helix through configurational isomerization (*syn*/*anti* isomerization) around the C=N backbones by noncovalent interactions with optically active amines in water. The helix remained after complete removal of the chiral amines and further conversion of the pendant group into the carboxy and methyl ester, although these helical polyisocyanides were thermally unstable and lost their chiral memory at high temperature, probably due to a helix-to-coil transition through the *syn*/*anti* isomerization.[7] We now found that the helical poly-**1**–Na (*h*-poly-**1**–Na) can be further modified with a variety of achiral amines, including glycine oligomers and aza-crown ethers, through an amide linkage, while maintaining the macromolecular helicity memory (Figure 1). Surprisingly, the helical polyisocyanides modified with primary amines kept their memory perfectly even at 100 °C in *N*,*N*-dimethylformamide (DMF),[8] and some of them exhibited lyotropic cholesteric liquid-crystalline (LC) phases. Nolte and co-workers developed a series of helical poly(isocyanopeptide)s with cholesteric liquid crystallinity

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[a] Y. Hase, Y. Mitsutsuji, M. Ishikawa, Dr. K. Maeda,
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] Dr. K. Okoshi, Prof. Dr. E. Yashima
Yashima Super-Structured Helix Project
Exploratory Research for Advanced Technology (ERATO)
Japan Science and Technology Agency (JST)
101 Creation Core Nagoya, Shimoshidami
Moriyama-ku, Nagoya 463-0003 (Japan)

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stabilized by well-defined arrays of intramolecular hydrogen bonds in which the helix-sense excess and handedness are determined by the amino acid chirality of the pendant.[1d,3d,9,10]

Results and Discussion

h-Poly-**1**–Na was prepared by a previously reported method.[7] Achiral poly-**1**–Na (the number-average molecular weight as the methyl ester form was 3.3×10^4, as determined by size-exclusion chromatography (SEC) with polystyrene standards in chloroform ($CHCl_3$)) or poly-**1**–H was annealed with (*S*)-phenylalaninol ((*S*)-**2**) or (*R*)-phenylglycinol ((*R*)-**3**) in water or water/acetonitrile (1:1 *v*/*v*) at 50°C for 30 or 15 days, respectively ([**2**]/[poly-**1**–Na] = 10, [**3**]/[poly-**1**–H] = 20).[7] During this process of helicity induction, the helical structure of poly-**1**–Na was automatically memorized, probably through configurational isomerization around the C=N double bonds (*syn*/*anti* isomerization),[7a] so that the isolated *h*-poly-**1**–Na and *h*-poly-**1**–H after removal of the chiral amines exhibited optical activity due only to the one-handed helicity; the molar ellipticities at about 360 nm ($\Delta\varepsilon_{360}$) of the polyisocyanides after isolation were −8.29 (Table 1, run 1) and −10.6 $\text{M}^{-1}\,\text{cm}^{-1}$ (Table 1, run 2) in water and alkaline water, respectively.[7]

The reaction of *h*-poly-**1**–Na and *h*-poly-**1**–H with a wide variety of primary and secondary amines was then performed as outlined in Figure 1. 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM)[11] was used as a condensing agent. The reactivity of amines **8**–**12** were relatively low; therefore, the reaction with DMT-MM was repeated twice under the same experimental conditions, and the amphiphilic or hydrophobic helical poly-**1** polymers with NH- or N-substituted amide residues (*h*-poly-**1**–**4** to *h*-poly-**1**–**12**) were obtained in high yields without loss of memory of the macromolecular helicity (see Experimental Section). The glycine-oligomer-modified polymers (*h*-poly-**1**–**5** to *h*-poly-**1**–**7**) were soluble in organic solvents such as DMF, but not soluble in water, so the pendant methyl esters were further hydrolyzed with sodium hydroxide in water to afford water-soluble sodium salts (*h*-poly-**1**–**5**–Na to *h*-poly-**1**–**7**–Na) (Table 1). The reaction of *h*-poly-**1**–H with diazomethane was also performed to obtain the corresponding ester (*h*-poly-**1**–Me) according to the previously reported method (Table 1, run 20).[7a] The chiroptical properties of the modified *h*-poly-**1** polymers are summarized in Table 1. The obtained polymers with memory of macromolecular helicity exhibited an intense induced circular dichroism (ICD) with large optical rotations ($[\alpha]_D^{20} = -750$ to $-1780°$) (Table 1).

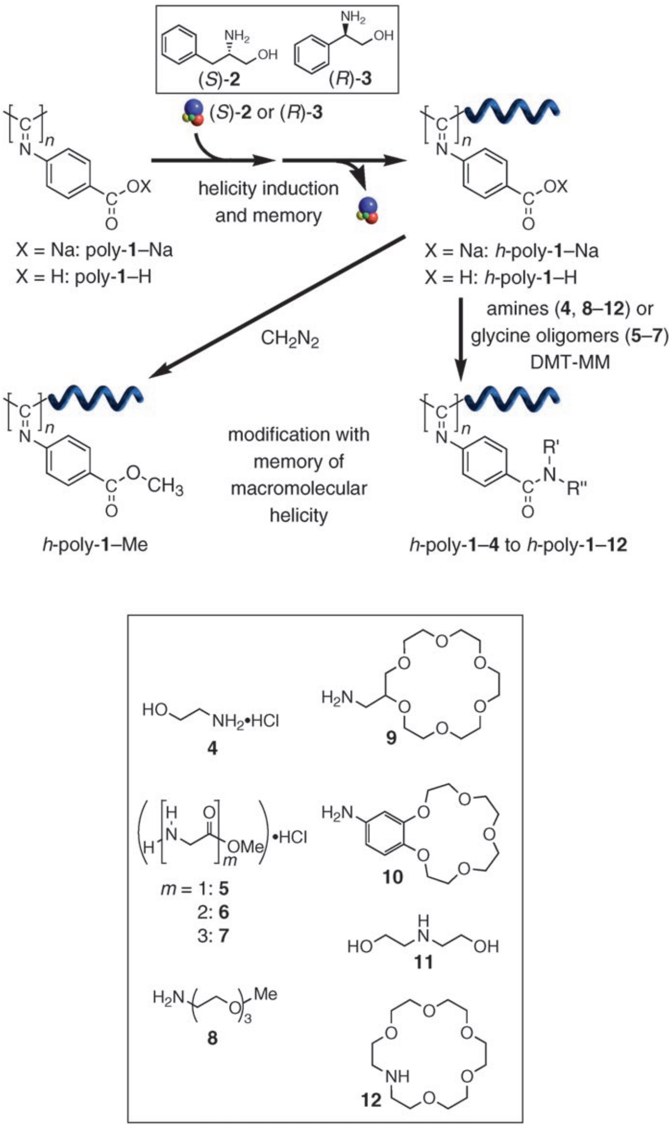
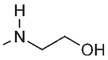
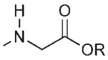
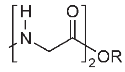
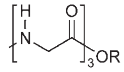
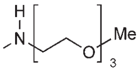
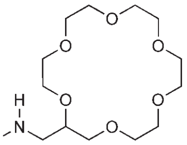
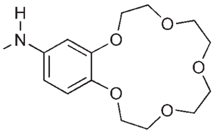
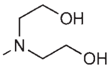
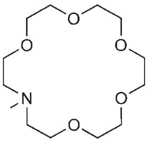
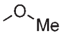


Figure 1. Schematic illustration of one-handed helicity induction and memory in poly-**1**–Na and poly-**1**–H and the modification of the side groups of the polymer with memory of macromolecular helicity. A one-handed helix is induced in poly-**1**–Na and poly-**1**–H with (*S*)-**2** in water and (*R*)-**3** in water/acetonitrile (1:1 *v*/*v*), respectively, and is memorized after complete removal of the chiral amines. The side groups of helical poly-**1**–Na or poly-**1**–H can be modified with optically inactive amines (**4**, **8**–**12**) or glycine oligomers (**5**–**7**) in the presence of DMT-MM or by esterification with diazomethane (CH_2N_2). The helix sense of the *h*-poly-**1** polymers that show a negative first Cotton effect was assigned to be left-handed on the basis of the signs of the Cotton effect of analogous helical polyisocyanides determined by atomic force microscopy measurements.[9j]

Abstract in Japanese:

誘起らせん構造を記憶として保持したポリ(4-カルボキシフェニルイソシアニド)の側鎖を、らせんキラリティーを保持したまま様々の１級および２級アミンを用いて化学修飾できることを見出した。アミド水素を有するポリマーは DMF 中 100 °C で加熱後も CD 強度がほとんど変化しなかったのに対し、アミド水素を持たないポリマーの CD 強度は著しく減少した。らせん構造の安定化には側鎖の嵩高さとアミド水素による分子内水素結合が大きく寄与していることが示唆された。また、得られたポリマーの一部は濃厚溶液中で剛直主鎖型液晶を形成し、コレステリック液晶相に特徴的な縞状組織を示した。

Table 1. Chiroptical properties of helical poly(phenyl isocyanide) derivatives.

Run	Polymer	Substituent	Solvent	$\Delta\varepsilon$ [$\mathrm{M^{-1}\,cm^{-1}}$] (λ [nm])[a]	$[\alpha]_D^{20}$ [b]	$t_{1/2}$ [h][c]
1	*h*-poly-**1**–Na[d]	–	water	−8.29 (360)	−1380	0.16
2	*h*-poly-**1**–H[e]	–	alkaline water[f]	−10.6 (357)	−1700	0.20
3	*h*-poly-**1**–**4**[g]		water	−9.10 (354)	−1130	0.42
4	*h*-poly-**1**–**4**[h]		DMF	−5.98 (364)[i]	−1030[i]	–[j]
5	*h*-poly-**1**–**5**–Na[h]	 R = Na	water	−9.63 (355)	−1100	1.0
6	*h*-poly-**1**–**5**[h]	R = Me	DMF	−11.7 (364)	−1640	–[j]
7	*h*-poly-**1**–**6**–Na[h]	 R = Na	water	−8.71 (357)	−840	2.5
8	*h*-poly-**1**–**6**[h]	R = Me	DMF	−11.2 (363)	−1130	–[j]
9	*h*-poly-**1**–**7**–Na[h]	 R = Na	water	−9.72 (357)	−770	4.2
10	*h*-poly-**1**–**7**[h]	R = Me	DMF	−10.7 (363)	−950	–[j]
11	*h*-poly-**1**–**8**[g]		water	−13.7 (356)	−1250	1.7
12	*h*-poly-**1**–**8**[g]		DMF	−13.8 (364)[k]	−1470[k]	–[k,l]
13	*h*-poly-**1**–**9**[g]		water	−13.9 (359)	−910	40.9
14	*h*-poly-**1**–**9**[h]		DMF	−9.87 (365)	−750	–[j]
15	*h*-poly-**1**–**10**[g]		DMF	−12.5 (374)	−950	–[j]
16	*h*-poly-**1**–**11**[g]		water	−9.66 (357)	−1170	7.8
17	*h*-poly-**1**–**11**[g]		DMF	−9.42 (361)	−1160	1.3
18	*h*-poly-**1**–**12**[g]		water	−13.7 (360)	−960	19.1
19	*h*-poly-**1**–**12**[g]		DMF	−14.1 (362)	−960	3.7
20	*h*-poly-**1**–Me[g]		$\mathrm{CHCl_3}$	−11.9 (361)	−1780	3.7[m]

[a] Measured at ambient temperature with a polymer concentration of 1.0 mg mL^{-1}; $\Delta\varepsilon$ of the first Cotton effect and the indicated λ. [b] $c = 0.1$ g dL^{-1}. [c] Half-life of the helicity memory at 80 °C in DMF or water. [d] Induced by the use of (*S*)-**2**. [e] Induced by the use of (*R*)-**3**. [f] [Polymer]/[NaOH] = 1.0. [g] Derived from *h*-poly-**1**–H (run 2). [h] Derived from *h*-poly-**1**–Na (run 1). [i] DMF-soluble part. [j] ICD intensity showed almost no decrease at 100 °C for 1 h. [k] Measured in DMF containing 1 vol % of water. [l] ICD intensity decreased by about 6 % after annealing at 100 °C for 1 h, probably because of water (1 vol %) in DMF used as solvent. [m] Measured in 1,1,2,2-tetrachloroethane.

Figure 2 shows the typical absorption and CD spectra of the modified *h*-poly-**1** polymers together with those of the original *h*-poly-**1**–H in water or alkaline water. The polymers exhibited similar ICD patterns in the imino chromophore regions of the polymer backbones (280–450 nm) as well as in the pendant aromatic regions (200–280 nm). These results clearly demonstrate that the side chains of *h*-poly-**1**–Na or *h*-poly-**1**–H can be converted into a variety of functional groups while keeping the one-handed helicity of the original com-

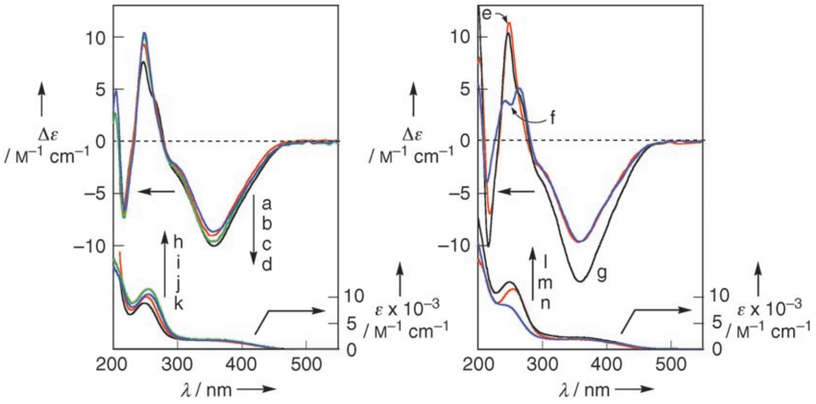


Figure 2. a)–g) CD and h)–n) UV/Vis spectra of *h*-poly-**1**–H (d, k) in alkaline water ([polymer]/[NaOH] = 1.0) and *h*-poly-**1**–**4** (b, j), *h*-poly-**1**–**5**–Na (c, h), *h*-poly-**1**–**6**–Na (a, i), *h*-poly-**1**–**7**–Na (e, m), *h*-poly-**1**–**9** (g, l), and *h*-poly-**1**–**11** (f, n) in water at ambient temperature. Concentration of polymer = 1.0 mg mL^{-1}. The CD and UV/Vis spectra of *h*-poly-**1**–**8**, *h*-poly-**1**–**10**, and *h*-poly-**1**–**12** are shown in Figure S1 in the Supporting Information.

pound. The observed exciton-coupled ICD patterns in the aromatic region suggest that the pendant aromatic functional groups are aligned in a one-handed helical array. Although the optical activity of *h*-poly-**1**–Na and *h*-poly-**1**–H changed after modification (Table 1), we observed an almost-linear relationship between the molar rotation (Φ) and the molar ellipticity of the first Cotton effect ($\Delta\varepsilon_{1st}$) of the *h*-poly-**1** polymers that is independent of solvent (Figure S2 in the Supporting Information).

Next, we investigated the thermal stability of the modified *h*-poly-**1** polymers in water and organic solvent to explore the effects of hydrogen bonding of the amide residues and steric hindrance of the pendant groups on their helical structures. As reported previously, the carboxy (*h*-poly-**1**–H) and methyl ester (*h*-poly-**1**–Me) derived from *h*-poly-**1**–Na were thermally unstable, and their optical activity completely disappeared at high temperature (Figure 3 A, line a for *h*-poly-**1**–Na) due to *syn*/*anti* isomerization around the C=N double bonds, as evidenced by significant changes in the ^{1}H and ^{13}C NMR spectra of *h*-poly-**1**–Na,[7a] thus giving a half-life ($t_{1/2}$) of 0.20 and 3.7 h at 80 °C in alkaline water and 1,1,2,2-tetrachloroethane, respectively (Table 1, runs 2 and 20). However, modification with achiral amines effectively improved the thermal stability of the helix as the size of the amide unit and steric congestion increased (Figure 3 and Table 1). The thermal stability was measured by monitoring the decrease in the CD intensity of the first Cotton effect in the polymer backbone region with time at different temperatures (Figure 3) or at 80 °C (Table 1).[12] Specifically, *h*-poly-**1**–**4** modified with achiral amine **4** and *h*-poly-**1**–**5**–Na to *h*-poly-**1**–**7**–Na bearing glycine oligomers showed considerable improvement in thermal stability in water as the size of the NH amide unit increased (Figure 3 A, lines b–d and f), and the half-life in water at 80 °C also increased in this order (0.42, 1.0, 2.5, and 4.2 h, respectively). Furthermore, *h*-poly-**1**–**9** with bulky [18]crown-6 as the pendant did not lose its memory even at 90 °C in water (Figure 3 A, line g) (for thermal stabilities of other *h*-poly-**1** polymers at 80 °C in water, see Table 1).[13]

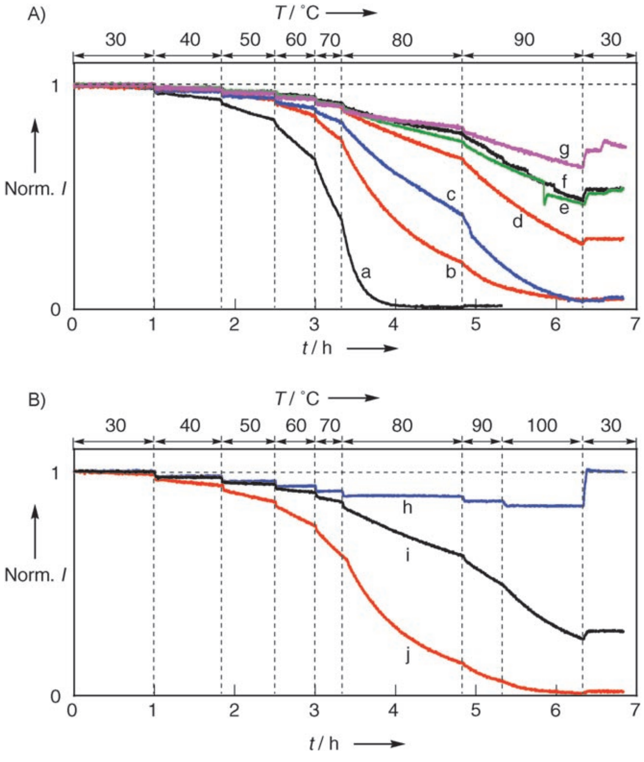


Figure 3. Stability of the memory of macromolecular helicity of *h*-poly-**1**–Na (a), *h*-poly-**1**–**4** (b), *h*-poly-**1**–**5**–Na (c), *h*-poly-**1**–**6**–Na (d), *h*-poly-**1**–**7**–Na (f), *h*-poly-**1**–**9** (g), and *h*-poly-**1**–**11** (e) in water (A), and of *h*-poly-**1**–**6** (h), *h*-poly-**1**–**11** (j), and *h*-poly-**1**–**12** (i) in DMF (B) studied by CD following jumps in temperature. The changes in CD signal intensity at the first Cotton effect were followed and normalized.

Interestingly, the NH amide modified polymers (*h*-poly-**1**–**4** to *h*-poly-**1**–**10**) are unexpectedly stable in DMF irrespective of the size of NH amide units and perfectly preserve their helicity at 100 °C (Table 1) (for *h*-poly-**1**–**6**, see Figure 3 B, line h). Although the intensity of CD of *h*-poly-**1**–**6** showed a decrease of about 5 % at 100 °C in DMF when the temperature-dependent volume change of DMF was taken into consideration, it recovered its original value at 30 °C. The cooperative intramolecular hydrogen bonding between neighboring NH amide pendants must facilitate this remarkable stability of the helix and its interesting "helix-breathing" behavior in DMF.[14] During the helix-breathing process, we observed a small red shift of less than 5 nm in the CD spectra. Similar hydrogen-bonding-assisted helix formation and stabilization was reported by Nolte and co-workers for poly(isocyanopeptide)s, although the helices unfold irreversibly at high temperature.[3d,9a,b,15]

The formation of intramolecular hydrogen bonds was proved by the IR spectra of *h*-poly-**1**–**5** and *h*-poly-**1**–**10** (Figure S3 in the Supporting Information). These two compounds showed the amide NH and carbonyl stretching (amide I) bands at 3313 and 1645 cm^{-1} and at 3277 and 1641 cm^{-1}, respectively, in [D_7]DMF and/or as a film. These band positions suggest that the *h*-poly-**1** polymers form an intramolecular-hydrogen-bonding network through the neighboring amide groups. *h*-Poly-**1**–**10** was soluble in chloroform and showed similar bands, whereas the model compound of *h*-poly-**1**–**5**, benzoylglycine methyl ester (model **5**), exhibited the NH and amide I bands significantly shifted to higher wavenumbers (3323 and 3442 cm^{-1} in [D_7]DMF and $CDCl_3$, respectively, and 1664 cm^{-1} in $CDCl_3$) due to free or solvated NH and amide residues (for the IR data of other *h*-poly-**1** polymers, see Table S1 in the Supporting Information).

Additional evidence for the intramolecular hydrogen bonds of the NH amide modified polyisocyanides in DMF was obtained from amide H/D exchange experiments (Figure 4). The half-lives of the H/D exchange for the amide protons of *h*-poly-**1**–**5**, model **5**, and *h*-poly-**1**–**9** in [D_7]DMF containing 3.68 mM D_2O at 30 °C, estimated by Arrhenius analysis, are 4.2 h, 2.9 min, and 15.7 h, respectively, indicating the significantly enhanced stability of *h*-poly-**1**–**5** and *h*-

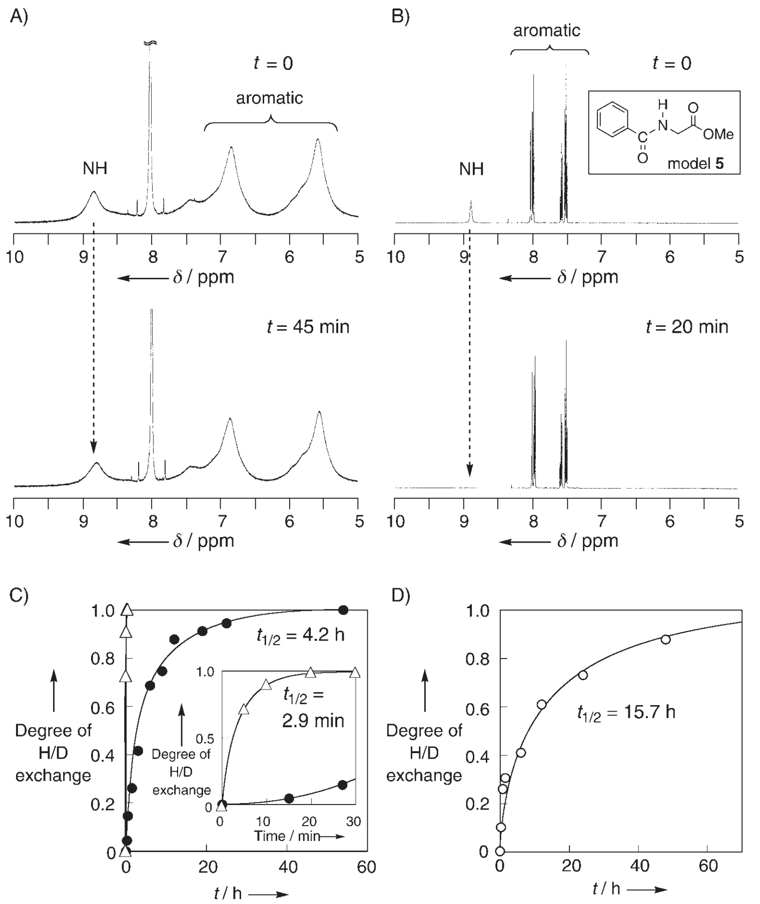


Figure 4. ^{1}H NMR spectral changes with time of *h*-poly-**1**–**5** (A) and its model compound model **5** (B) in [D$_7$]DMF (700 μL) after the addition of D_2O (50 μL) at 30 °C. Plots of the changes in degree of H/D exchange of the amide NH protons of *h*-poly-**1**–**5** (●), model **5** (△) (C), and *h*-poly-**1**–**9** (○) (D) with time at 30 °C are shown. The inset in C shows the expanded detail of the plots.

poly-**1**–**9** that results from the intramolecular-hydrogen-bonding arrays (Figure 5).

To explore further the synergic effects (intramolecular hydrogen bonding and steric and hydrophobic effects) of the pendant amide moieties on the remarkable thermal stability of the helical polyisocyanides, those that bear N-substituted pendants of different bulk (*h*-poly-**1**–**11** and *h*-poly-**1**–**12**) were prepared in the same way, and their thermal stabilities in water and DMF at high temperature were measured; the results were then compared with those of the NH amide modified polyisocyanides (Figure 3 and Table 1). The N-substituted *h*-poly-**1**–**11** was much more stable than the analogous NH amide modified polyisocyanide, *h*-poly-**1**–**4**, in water and showed a similar thermal stability to *h*-poly-**7**–Na, which bears a glycine trimer as the pendant (Figure 3 A, lines b, e, and f); however, their chiral memory was gradually lost at 80 °C in water. On the other hand, the more-bulky N-substituted *h*-poly-**1**–**12** preserved its helical structure; the half-life at 80 °C in water was 19.1 h (Table 1, run 18), which is longer than those of *h*-poly-**1**–**7**–Na (4.2 h) and *h*-poly-**1**–**11** (7.8 h) (Table 1, runs 9 and 16), but significantly shorter than that of the NH amide *h*-poly-**1**–**9** with a bulky crown ether residue (40.9 h) (Table 1, run 13). In stark contrast to the NH amide modified polyisocyanides, these N-substituted polyisocyanides gradually lost their optical activity in DMF at high temperatures (Figure 3 B, lines i and j); their half-lives at 80 °C in DMF were 1.3 (*h*-poly-**1**–**11**) and 3.7 h (*h*-poly-**1**-**12**) (Table 1, runs 17 and 19). These results support our assumption that intramolecular hydrogen bonding plays a critical role in the remarkable thermal stabilities of the NH amide modified polyisocyanides in DMF, whereas steric and hydrophobic effects combined with intramolecular hydrogen bonding play a dominant role in the thermal stabilities of the NH- and N-substituted amide modified polyisocyanides in water.[16]

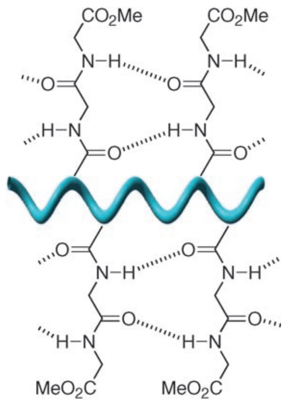


Figure 5. Schematic illustration of hydrogen-bond formation in *h*-poly-**1**–**6** between the side chains.

Interestingly, some modified helical polyisocyanides, such as *h*-poly-**1**–**8**, *h*-poly-**1**–**9**, *h*-poly-**1**–**10**, and *h*-poly-**1**–**12** were found to form lyotropic cholesteric LC phases in concentrated aqueous solution (*h*-poly-**1**–**8**, –**9**, and –**12**) and $CHCl_3$ (*h*-poly-**1**–**10**) owing to the stiffness of their main chains, thus showing a fingerprint texture (Figure 6), although the original polyisocyanide *h*-poly-**1**–Na did not show an LC phase in concentrated aqueous solution (<20 wt %). The spacings of the fringes that correspond to the half-pitch of the cholesteric helical structure were 3.9 (*h*-

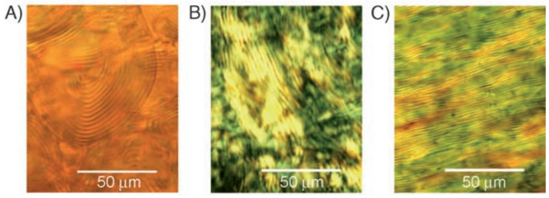


Figure 6. Polarized optical micrographs of cholesteric LC phases of *h*-poly-**1**–**8** (A) and *h*-poly-**1**–**12** (C) in water and *h*-poly-**1**–**10** (B) in $CHCl_3$. The concentrations of the polymers were 35, 35, and 40 wt %, respectively.

poly-**1**–**8** in water), 2.0 (*h*-poly-**1**–**12** in water), and 5.0 μm (*h*-poly-**1**–**10** in $CHCl_3$). To date, several synthetic helical polymers are known to show cholesteric LC phases, but the present LC helical polyisocyanides are different from the helical polymers previously reported: the helical polyisocyanides have no stereogenic centers in the main chain and the pendant groups, and their cholesteric LC phases are solely derived from memory of macromolecular helicity with a preferred helical sense.[17] Furthermore, the helical LC polyisocyanides have an unexpected thermal stability even at 100 °C in DMF, and the helical conformation is maintained without loss of macromolecular helicity.

Conclusions

In summary, we have demonstrated that a helical polyisocyanide with memory of macromolecular helicity can be further modified with various achiral amines without loss of optical activity to result in designer helical polyisocyanides with outstanding thermal stability in solution, although the original polymer loses its chiral memory at high temperature. Furthermore, some modified helical polyisocyanides exhibit cholesteric LC phases, thus providing a robust scaffold with heat resistance and liquid crystallinity to which a variety of functional groups can be introduced for further application as enantioselective catalysts and in chiral recognition.[4,5b]

Experimental Section

Instruments

Solution pH was measured with a B-211 pH meter (Horiba, Japan). NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300 MHz for ^1H, a Varian VXR-500S spectrometer operating at 500 MHz for ^1H and 125 MHz for ^{13}C, or a Varian Innova 700 spectrometer operating at 700 MHz for ^1H, with tetramethylsilane (TMS) (for $CDCl_3$), CH_3CN or acetone (for D_2O, ^1H NMR), dioxane (for D_2O, ^{13}C NMR), or the solvent residual peak (for [D_6]dimethyl sulfoxide ([D_6]DMSO) and [D_7]DMF) as the internal standards. Elemental analysis was performed by the Nagoya University Analytical Laboratory in the School of Engineering. SEC measurements were performed with a Jasco PU-980 liquid chromatograph (Jasco, Hachioji, Japan) equipped with a UV (254 nm; Jasco UV-970) detector and a Tosoh (Tokyo, Japan) TSKgel MultiporeH$_{XL}$-M SEC column (30 cm), and $CHCl_3$ was used as the eluent at a flow rate of 1.0 mL min^{-1}. The molecular-weight calibration curve was obtained with polystyrene standards (Tosoh). IR spectra were recorded on a Jasco Fourier Transform IR-620 spectrometer. UV/Vis and CD spectra were recorded in 0.2- or 1.0-mm quartz cells on a Jasco V-560 spectrophotometer and a Jasco J-820 spectropolarimeter, respectively. The temperature was controlled with a Jasco PTC-423L apparatus (−10 to 100 °C). The concentration of polymers was calculated on the basis of the monomer units and 1 mg mL^{-1} unless otherwise stated. Temperature-jump experiments were performed in 1.0-mm quartz cells by using the same CD system. The change in temperature was achieved within about 5 s. Optical rotation was measured in a 5-cm quartz cell equipped with a temperature controller (EYELA NCB-2100) on a Jasco P-1030 polarimeter.

Materials

All starting materials were obtained from commercial suppliers and were used as received. L-Phenylalaninol ((*S*)-**2**), (*R*)-phenylglycinol ((*R*)-**3**), and aza[18]crown-6 (**12**) were purchased from Tokyo Kasei (TCI, Tokyo, Japan). 2-Aminoethanol hydrochloride (**4**), 4′-aminobenzo[15]crown-5 (**10**), and *N*,*N*-diethanolamine (**11**) were obtained from Wako (Osaka, Japan). Glycine methyl ester hydrochloride (**5**) and glycylglycine methyl ester hydrochloride (**6**) were obtained from Acros Organics (Geel, Belgium) and Research Organics Inc. (Cleveland, OH), respectively. 2-(Aminomethyl)[18]crown-6 (**9**) was purchased from Aldrich. Glycylglycylglycine methyl ester hydrochloride (**7**),[18] 4-(ethoxycarbonyl)phenyl isocyanide (**1**–Et),[7,19] sodium 4-isocyanobenzoate (**1**–Na),[7] and DMT-MM[11] were prepared according to the reported methods. 3,6,9-Trioxadecylamine (**8**) was prepared from triethyleneglycol monomethyl ether (TCI) via *N*-(3,6,9-trioxadecyl)phthalimide.[20] *N*-Benzoylglycine methyl ester (model **5**) was prepared by condensation of benzoyl chloride with **5**. Anhydrous DMF and acetonitrile (CH_3CN) (water content < 0.005 %) were purchased from Wako and stored under nitrogen. Dichloromethane (CH_2Cl_2) was dried over calcium hydride, distilled, and stored under nitrogen. Methanol was dried over turning magnesium and iodine and distilled under nitrogen. D_2O (99.9 atom % D, Isotec Inc.) was stored under nitrogen. $CDCl_3$ (99.8 atom % D, Merck), [D_6]DMSO (99.9 atom % D, Isotec Inc.), and [D_7]DMF (99.5 atom % D, Merck) were dried over 4-Å molecular sieves (Nacalai Tesque, Kyoto, Japan) and stored under nitrogen. All solvents used for CD, NMR spectroscopy, and measurement of optical rotation were purged with nitrogen prior to use. Deionized, distilled water was degassed with nitrogen before use for all experiments.

Syntheses

Poly-**1**–Na: Prepared by the polymerization of sodium 4-isocyanobenzoate (**1**–Na) with $NiCl_2 \cdot 6H_2O$ (Kishida, Osaka, Japan) in water at ambient temperature for 24 h according to a previously reported method.[7,19] The number-average molecular weight (M_n) and molecular-weight distribution (M_w/M_n) were 3.3×10^4 and 3.2, respectively, as its methyl esters determined by SEC with polystyrene standards and $CHCl_3$ eluent at a flow rate of 1.0 mL min^{-1}.

Helicity induction in poly-**1**–Na and isolation of *h*-poly-**1**–Na: *h*-Poly-**1**–Na (100 mg) was annealed with (*S*)-**2** ([(*S*)-**2**]/[poly-**1**–Na] = 10) in water at a polymer concentration of 1.0 mg mL^{-1} at 50 °C. The intensity of the CD signals increased with time and reached an almost-constant value ($\Delta\varepsilon_{360} = -9.31\ \mathrm{M^{-1}\,cm^{-1}}$) after 25 days. After the sample was allowed to stand at 50 °C for 30 days, the solution was lyophilized. The recovered polymer complexed with (*S*)-**2** was dissolved in a small amount of water, and the solution was poured into a large amount of THF to remove (*S*)-**2**. The precipitated *h*-poly-**1**–Na was collected by centrifugation, washed with THF and diethyl ether, and then dried in vacuo at room temperature overnight. Conversion of poly-**1**–Na into poly-**1**–H was carried out by treatment of poly-**1**–Na in aqueous HCl (1 N). The resulting poly-**1**–H was further converted into the methyl ester (poly-**1**–Me) with CH_2N_2 in diethyl ether according to the method reported previously.[19] Caution: CH_2N_2 is hazardous and potentially explosive.

Helicity induction in poly-**1**–H and isolation of *h*-poly-**1**–H:[7] Poly-**1**–H (100 mg), derived from poly-**1**–Na, and (*R*)-**3** (1.86 g) were placed in a 100-mL flask equipped with a stopcock ([(*R*)-**3**]/[poly-**1**–H] = 20), and water (50 mL) was added by syringe to dissolve them completely. The solution was diluted with CH_3CN (water/CH_3CN = 1:1 *v*/*v*) to keep the polymer concentration at 1.0 mg mL^{-1}, and the initial UV/Vis and CD spectra were recorded. The solution was transferred to an ampoule, which was then degassed with nitrogen and sealed. The ampoule was kept at 50 °C on an oil bath under shielded light. A 0.3-mL aliquot of the solution was withdrawn by pipette at appropriate time intervals, and UV/Vis and CD spectra were recorded at ambient temperature (20–25 °C). The CD signal intensity increased with time and reached an almost-constant value after 15 days. After the sample was allowed to stand at 50 °C for 15 days, the CH_3CN was removed by evaporation, and the aqueous solution was lyophilized. The recovered polymer complexed with (*R*)-**3** was dissolved in a small amount of water, and the solution was poured into a large amount of THF. The precipitated *h*-poly-**1**–H complexed with (*R*)-**3** was dissolved in a small amount of water, and the solution was poured into a large amount of aqueous HCl (1 N) to remove (*R*)-**3** completely. The *h*-poly-**1**–H was collected by centrifugation, washed with water, methanol, and diethyl ether, and then dried in vacuo at room temperature overnight. The conversion of *h*-poly-**1**–H into *h*-poly-**1**–Me was carried out in the same way.

h-Poly-**1**–H: $[\alpha]_D^{20}=-1700$ ($c=0.1$ g dL^{-1}, alkaline water ([polymer]/[NaOH] = 1.0)); IR (KBr): $\tilde{\nu}=1701$ (C=O), 1655 cm^{-1} (C=N); ^{1}H NMR (500 MHz, soluble part in [D$_6$]DMSO, 30 °C): $\delta=5.2$–7.8 ppm (br, 4H; aromatic); elemental analysis: calcd (%) for $(C_8H_5NO_2\cdot{}^1/_2H_2O)_n$: C 61.54, H 3.87, N 8.97; found: C 61.44, H 3.95, N 8.76.

h-Poly-**1**–Me: $[\alpha]_D^{20}=-1780$ ($c=0.1$ g dL^{-1}, $CHCl_3$); IR ($CHCl_3$): $\tilde{\nu}=1718$ (C=O), 1647 cm^{-1} (C=N); ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C): $\delta=3.2$–4.2 (br, 3H; CH_3), 5.0–7.8 ppm (br, 4H; aromatic); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C): $\delta=52.0$ (br, CH_3), 117.3, 126.9, 129.5, 150.6 (br, aromatic), 160.6, 162.4 (br, C=N), 165.8 ppm (br, C=O).

General procedure for the derivatization of *h*-poly-**1**–Na or *h*-poly-**1**–H with achiral amines: The reactions of *h*-poly-**1**–Na and *h*-poly-**1**–H with glycine oligomers (**5**–**7**) and optically inactive amines (**4**, **8**–**12**), respectively, were carried out with DMT-MM as the condensing agent.

The typical experimental procedure for the reaction of *h*-poly-**1**–Na with glycine oligomers is described here. DMT-MM (54 mg, 0.20 mmol) was added to a solution of **5** (45 mg, 0.35 mmol) and *h*-poly-**1**–Na (30 mg, 0.18 mmol) in degassed water (15 mL). The pH of the solution was adjusted to 6.4 with aqueous NaOH (2 N), and the reaction mixture was stirred at room temperature under nitrogen. After 1 day, the resulting polymer was precipitated into a large amount of acetone, collected by centrifugation, washed with acetone, and then dried in vacuo at room temperature overnight to yield *h*-poly-**1**–**5** (29 mg, 74 %). The content of residues of **5** in *h*-poly-**1**–**5** was determined to be approximately 100 % by ^{1}H NMR spectroscopy and elemental analysis. In the same way, *h*-poly-**1**–**6** and *h*-poly-**1**–**7** were prepared in 73 and 86 % yield, respectively.

The reactivities of amines **8**–**12** are relatively low; therefore, the reaction with DMT-MM was repeated twice under the same experimental conditions. DMT-MM (41 mg, 0.15 mmol) was added to a solution of **12** (72 mg, 0.27 mmol) and *h*-poly-**1**–H (20 mg, 0.14 mmol) in degassed water (9.0 mL) and aqueous NaOH (1 N, 0.1 mL). The reaction mixture was stirred at room temperature under nitrogen. After 1 day, the resulting polymer was precipitated into a large amount of acetone, collected by centrifugation, washed with acetone, and then dried in vacuo at room temperature overnight to yield the polymer (35 mg). The recovered polymer was found to contain 80 mol % of **12** as the pendant group to each monomer unit. The reaction was then repeated with the recovered polymer (35 mg) in the same manner. The content of the residues of **12** in *h*-poly-**1**–**12** was approximately 100 % as determined by ^{1}H NMR spectroscopy and elemental analysis. Similarly, *h*-poly-**1**–**4**, *h*-poly-**1**–**8**, *h*-poly-**1**–**9**, *h*-poly-**1**–**10**, and *h*-poly-**1**–**11** were prepared in 89, 80, 75, 89, and 82 % yield, respectively.

h-Poly-**1**–**5** to *h*-poly-**1**–**7** are not soluble in water, and the pendant methyl esters were further hydrolyzed with NaOH in water to give the corresponding sodium carboxylates (*h*-poly-**1**–**5**–Na to *h*-poly-**1**–**7**–Na).

h-Poly-**1**–**4**: $[\alpha]_D^{20}=-1130$ ($c=0.1$ g dL^{-1}, water); IR (film): $\tilde{\nu}=1642$ cm^{-1} (amide I); ^{1}H NMR (500 MHz, D_2O containing 5 mM NaOD, 30 °C): $\delta=2.5$–4.5 (br, 4H; ethylene), 5.2–7.8 ppm (br, 4H; aromatic); elemental analysis: calcd (%) for $(C_{10}H_{10}N_2O_2\cdot H_2O)_n$: C 57.68, H 5.81, N 13.45; found: C 58.02, H 5.45, N 13.11.

h-Poly-**1**–**5**: $[\alpha]_D^{20}=-1640$ ($c=0.1$ g dL^{-1}, DMF); IR (film): $\tilde{\nu}=1645$ cm^{-1} (amide I); ^{1}H NMR (500 MHz, [D$_7$]DMF, 30 °C): $\delta=3.5$–4.3 (br, 5H; CH_2 and CH_3), 5.1–7.8 ppm (br, 4H; aromatic); elemental analysis: calcd (%) for $(C_{11}H_{10}N_2O_3\cdot{}^6/_5H_2O)_n$: C 55.09, H 5.21, N 11.68; found: C 55.59, H 4.70, N 11.19.

h-Poly-**1**–**6**: $[\alpha]_D^{20}=-1130$ ($c=0.1$ g dL^{-1}, DMF); IR (film): $\tilde{\nu}=1651$ cm^{-1} (amide I); ^{1}H NMR (500 MHz, [D$_7$]DMF, 30 °C): $\delta=3.5$–4.3 (br, 7H; CH_2 and CH_3), 5.1–7.8 ppm (br, 4H; aromatic); elemental analysis: calcd (%) for $(C_{13}H_{13}N_3O_4\cdot{}^8/_5H_2O)_n$: C 51.35, H 5.37, N 13.82; found: C 51.21, H 4.97, N 13.79.

h-Poly-**1**–**7**: $[\alpha]_D^{20}=-950$ ($c=0.1$ g dL^{-1}, DMF); IR (film): $\tilde{\nu}=1653$ cm^{-1} (amide I); ^{1}H NMR (500 MHz, [D$_7$]DMF, 30 °C): $\delta=3.5$–4.5 (br, 9H; CH_2 and CH_3), 5.2–7.8 ppm (br, 4H; aromatic); elemental analysis: calcd (%) for $(C_{15}H_{16}N_4O_5\cdot 2H_2O)_n$: C 48.91, H 5.47, N 15.21; found: C 49.51, H 5.00, N 14.58 (functionality ≈ 92 %).

h-Poly-**1**–**8**: $[\alpha]_D^{20}=-1250$ ($c=0.1$ g dL^{-1}, water); IR (film): $\tilde{\nu}=1633$ cm^{-1} (amide I); ^{1}H NMR (500 MHz, D_2O, 30 °C): $\delta=2.8$–4.2 (br m, 15H; CH_2 and CH_3), 5.2–7.8 ppm (br m, 4H; aromatic); elemental analysis: calcd (%) for $(C_{15}H_{20}N_2O_4\cdot{}^8/_7H_2O)_n$: C 57.57, H 7.18, N 8.95; found: C 57.42, H 6.69, N 9.05.

h-Poly-**1**–**9**: $[\alpha]_D^{20}=-910$ ($c=0.1$ g dL^{-1}, water); IR (film): $\tilde{\nu}=1651$ cm^{-1} (amide I); ^{1}H NMR (500 MHz, D_2O, 30 °C): $\delta=2.4$–4.5 (br m, 25H; CH and CH_2), 5.1–7.8 ppm (br m, 4H; aromatic); elemental analysis: calcd (%) for $(C_{21}H_{30}N_2O_7\cdot{}^3/_2H_2O)_n$: C 56.11, H 7.40, N 6.23; found: C 55.37, H 6.89, N 7.05 (functionality ≈ 95 %).

h-Poly-**1**–**10**: $[\alpha]_D^{20}=-950$ ($c=0.1$ g dL^{-1}, DMF); IR (film): $\tilde{\nu}=1641$ cm^{-1} (amide I); ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C): $\delta=2.6$–4.5 (br m, 8H; ethylene), 5.2–8.0 ppm (br m, 4H; aromatic); elemental analysis: calcd (%) for $(C_{22}H_{24}N_2O_6\cdot{}^3/_2H_2O)_n$: C 60.13, H 6.19, N 6.37; found: C 59.78, H 6.01, N 6.40.

h-Poly-**1**–**11**: $[\alpha]_D^{20}=-1170$ ($c=0.1$ g dL^{-1}, water); IR (film): $\tilde{\nu}=1603$ cm^{-1} (amide I); ^{1}H NMR (500 MHz, D_2O containing 5 mM NaOD, 30 °C): $\delta=2.5$–4.4 (br m, 8H; ethylene), 5.2–7.8 ppm (br m, 4H; aromatic); elemental analysis: calcd (%) for $(C_{12}H_{14}N_2O_3\cdot{}^6/_5H_2O)_n$: C 56.33, H 6.46, N 10.95; found: C 55.71, H 5.84, N 10.57 (functionality ≈ 97 %).

h-Poly-**1**–**12**: $[\alpha]_D^{20}=-960$ ($c=0.1$ g dL^{-1}, water); IR (film): $\tilde{\nu}=1633$ cm^{-1} (amide I); ^{1}H NMR (500 MHz, D_2O, 30 °C): $\delta=2.5$–4.5 (br m, 24H; ethylene), 5.1–7.8 ppm (br m, 4H; aromatic); elemental analysis: calcd (%) for $(C_{20}H_{28}N_2O_6\cdot{}^1/_2H_2O)_n$: C 59.84, H 7.28, N 6.98; found: C 60.13, H 7.21, N 6.73.

The CD and UV/Vis spectra of *h*-poly-**1**–**8**, *h*-poly-**1**–**10**, and *h*-poly-**1**–**12** are shown in Figure S1 in the Supporting Information.

Polarized Microscopy Studies

Concentrated solutions of *h*-poly-**1**–**8**, *h*-poly-**1**–**9**, and *h*-poly-**1**–**12** in water and *h*-poly-**1**–**10** in $CHCl_3$ were prepared in separate 2-mL test tubes. After the polymers were completely dissolved to give clear homogeneous solutions, they were transferred to a 1.0-mm (internal diameter) glass capillary by pipette, and the ends were sealed. The samples were left at ambient temperature (23–25 °C) until stable fingerprint textures were obtained. The fingerprint textures showing the retardation lines for the cholesteric liquid crystals were observed with a NIKON E600POL polarized microscope. The fingerprint spacings, which are equal to half of the cholesteric helical pitch, were measured by comparing them to a photograph of a standard microscopic ruler.

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[13] During the decrease in intensity of the CD signals of the *h*-poly-**1** polymers in water, we observed an increase in the absorption intensity (hyperchromic effect) in the aromatic region ($\lambda_{max}\approx 250$ nm) relative to that before heat treatment, which may provide evidence for the intramolecular stacking of the aromatic pendants of *h*-poly-**1** polymers that are favored in water after helicity induction and memory, as previously reported for *h*-poly-**1**–Na.[7a]

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amide residues should be taken into consideration on the basis of the difference in thermal stability in DMF and water.

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