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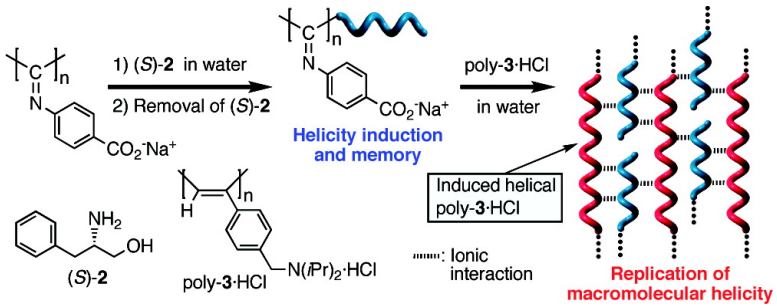

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Macromolecular Helicity Induction in a Cationic Polyacetylene Assisted by an Anionic Polyisocyanide with Helicity Memory in Water: Replication of Macromolecular Helicity

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Abstract: We report the first example of the replication of macromolecular helicity. An optically active helical and anionic polyelectrolyte, the sodium salt of poly(4-carboxyphenyl isocyanide), was found to serve as the template for further helicity induction in a different polyelectrolyte with opposite charges in water, resulting in interpolymer helical assemblies with controlled helicity. The effects of the pH and salt concentration on the helicity induction were investigated.

Introduction

Biological macromolecules such as DNA and proteins possess a characteristic one-handed helical structure and further assemble into three-dimensional, predetermined higher-order structures which are responsible for their elaborate biological functions.[1] Therefore, the syntheses and applications of artificial helical polymers and supramolecular helical assemblies with controlled helicity have been attracting great interest with implications for biological helicity, superstructures, and functions.[2] We recently reported that a macromolecular helicity with an excess of one helical sense can be induced in an achiral anionic polyelectrolyte, the sodium salt of poly(4-carboxyphenyl isocyanide) (poly-**1**-**Na**), with chiral amines, such as (*S*)- or (*R*)-phenylalaninol ((*S*)- or (*R*)-**2**), in water. The induced helicity of the polymer (***h***-poly-**1**-**Na**) can be "memorized" after complete removal of the chiral amines (Figure 1).[3] A similar macromolecular helicity induction and memory is possible in optically inactive but dynamically racemic helical polyacetylenes bearing various functional groups, such as a carboxy and a phosphonate group.[4] However, in sharp contrast to the helical memory of the present polyisocyanide, replacement of chiral amines by achiral amines is essential for the memory of the induced helical polyacetylenes.[4] We now show that this anionic helical polyisocyanide with a helicity memory, which no longer has any chiral components and stereogenic centers, can serve as the template for further helicity induction in a different polyelectrolyte with opposite charges (poly-**3**·HCl) through an electrostatic interaction in water. This results in helical assemblies with controlled helicity (Figure 1). This unique chiral amplification process through a noncovalent bonding interaction between the polymers ("helicity-replication"[5]) may be linked to the polyelectrolyte complexes with opposite charges from each other[6] and the biomimetic coiled coil (helix bundle) superstructures in proteins[7] that will provide useful layered helical assemblies[8] as chiral materials for enantioselective separation and catalysis.[9]

[†] Department of Molecular Design and Engineering.
[‡] Institute for Advanced Research.

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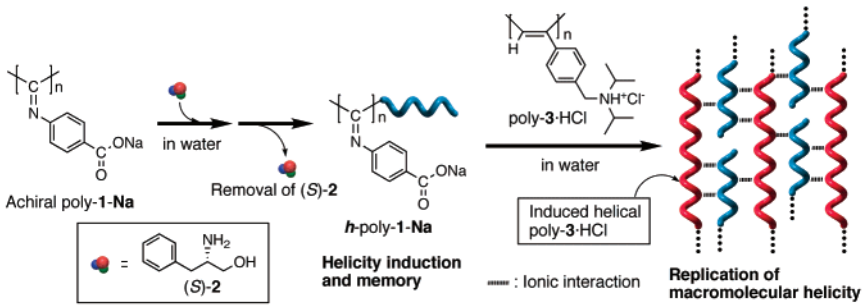

Figure 1. Schematic illustration of one-handed helicity induction and memory in poly-**1**-**Na** and the replication of the macromolecular helicity. A one-handed helix is induced in poly-**1**-**Na** with (*S*)-**2** and memorized in water after complete removal of (*S*)-**2** (left). The helical poly-**1**-**Na** (***h***-poly-**1**-**Na**) further induces macromolecular helicity in optically inactive poly-**3**·HCl in water (right). The helix senses of ***h***-poly-**1**-**Na** prepared by (*S*)-**2** and poly-**3** induced by the ***h***-poly-**1**-**Na** are tentative but probably left-handed (see text).

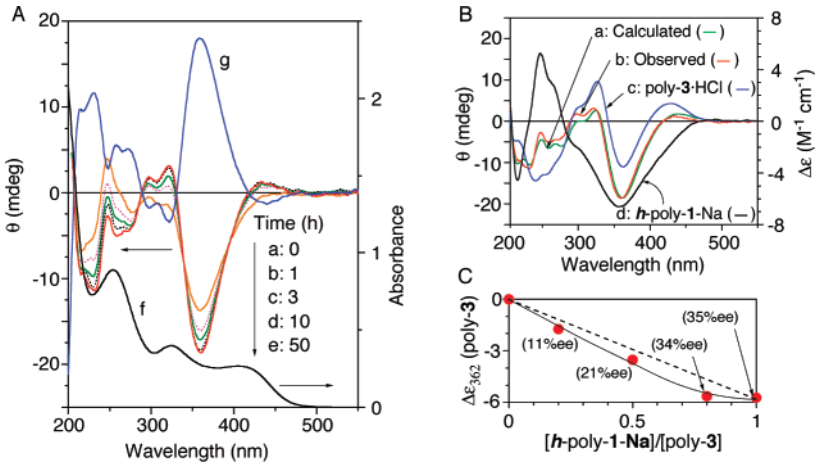

Figure 2. Replication of the macromolecular helicity of ***h***-poly-**1**-**Na** to poly-**3**·HCl in water. (A) Time-dependent CD spectral changes of poly-**3**·HCl with ***h***-poly-**1**-**Na** obtained by (*S*)-**2** after keeping the sample at ca. 25 °C for (a) 0, (b) 1, (c) 3, (d) 10, and (e) 50 h in water (pH 1.7); molar ratio of monomer units of ***h***-poly-**1**-**Na** to poly-**3**·HCl is 0.5. Contributions from linear dichroism are negligible. Absorption spectrum of poly-**3**·HCl with ***h***-poly-**1**-**Na** after 50 h is shown in trace f. CD spectrum of poly-**3**·HCl with ***h***-poly-**1**-**Na** obtained by (*R*)-**2** after keeping the sample at ca. 25 °C for 50 h in water (pH 1.7) is also shown in trace g. The concentration of poly-**3**·HCl is 1.0 mg/mL. (B) The observed and calculated CD spectra of the ***h***-poly-**1**-**Na**−poly-**3**·HCl complex after 50 h: (a) calculated CD spectrum of the complex; (b) observed CD spectrum of the complex (from e in Figure 2A); (c) calculated CD spectrum of poly-**3**·HCl based on the CD of poly-**3**·HCl-(*S*)-PL-Na complex in water at 25 °C (pH 5.4); (d) calculated CD spectrum of ***h***-poly-**1**-**Na**. (C) Titration curves of poly-**3**·HCl with ***h***-poly-**1**-**Na** in water at 25 °C after 50 h. $\Delta\epsilon_{362}$ indicates the calculated CD intensity at the second Cotton (362 nm) of poly-**3**·HCl as shown in Figure 2B. Enantiomeric excess (ee) of induced helical poly-**3**·HCl was estimated using $\Delta\epsilon_{362} = -16.5$ as the base value.

Results and Discussion

Helicity Induction in a Cationic Polyacetylene by an Anionic Helical Polyisocyanide with Helicity Memory. The ***h***-poly-**1**-**Na** was prepared according to a previously reported method.[3a] The achiral poly-**1**-**Na** (the number-average molecular weight was 3.3×10^4) was first annealed with (*S*)- or (*R*)-**2** in water at 50 °C for 29 days ([**2**]/[poly-**1**-**Na**] = 10). During this annealing process the helical structure of the polyisocyanide was induced and memorized at the same time.[3a] Therefore, the isolated ***h***-poly-**1**-**Na** without any trace amount of the chiral amines exhibited an induced circular dichroism (ICD) in the polymer backbone (280−450 nm) as well as in the pendant aromatic regions (200−280 nm).[3a] We then investigated if the ***h***-poly-**1**-**Na** having a one-handed helical array of the pendant carboxy groups could induce a helicity in an oppositely charged, dynamic helical polyacetylene, the HCl salt of poly((4-*N*,*N*-diisopropylaminomethylphenyl)acetylene) (poly-**3**·HCl in Figure 1) (the number-average molecular weight was 3.4×10^5)[10] in water. This was done by following the changes in the CD spectra of ***h***-poly-**1**-**Na** in the presence of poly-**3**·HCl in water.

Upon addition of ***h***-poly-**1**-**Na** ($\Delta\epsilon_{360} = -8.60$ at pH 8.8) obtained by (*S*)-**2** to poly-**3**·HCl in water at pH 5.0, random interpolymer aggregates of the ***h***-poly-**1**−poly-**3** ion complex were immediately precipitated as anticipated at pH 5.5. During the precipitation helicity induction on poly-**3** could not be expected because the polyion complexes appear to be tightly bound together in the insoluble matrix before helicity induction on the poly-**3**. However, the complex became soluble with further addition of aqueous 1.0 or 0.5 N HCl in response to the change in the pH value, resulting in loosely networked assemblies. The initial CD spectrum of the slightly viscous solution at pH 1.7 (molar ratio of monomer units of ***h***-poly-**1**-**Na** to poly-**3** is 0.5) was almost the same as that of the original ***h***-poly-**1**-**Na**. However, we observed remarkable changes in the CD pattern and intensity with time (0−50 h) (Figure 2A, traces

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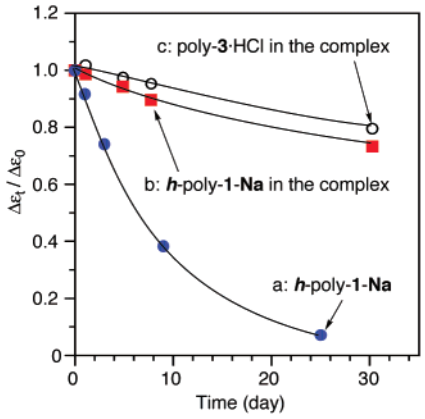

Figure 3. Changes in the ICD intensities ($\Delta\epsilon_t/\Delta\epsilon_0$) of ***h***-poly-**1-Na** (a) and ***h***-poly-**1-Na** (b) and induced helical poly-**3**·HCl (c) in the polyelectrolyte complexes in water at pH 8.8 (a) and 1.7 (b and c) at room temperature (ca. 23−25 °C), where $\Delta\epsilon_t$ represents the ICD intensity at ca. 360 nm after days. The concentration of poly-**3**·HCl is 1.0 mg/mL, and the molar ratio of monomer units of ***h***-poly-**1-Na** to poly-**3**·HCl is 0.5.

a−e) accompanied with negligible changes in their absorption spectra. We found that the CD difference spectra during this time period are identical to that of an induced helical poly-**3**·HCl. The observed CD spectrum of the complex, for instance, after 50 h (Figure 2B, trace b), can be resolved into two components corresponding to the ***h***-poly-**1-Na** (trace d) and separately prepared helical poly-**3**·HCl induced by the sodium salt of (*S*)-phenyllactic acid ((*S*)-PL-Na) in water (trace c); the calculated CD spectrum (trace a) is in fair agreement with the observed one (trace b), indicating that the conformation of poly-**3** trapped by the ***h***-poly-**1** slowly changed into a one-handed helical conformation, resulting in helical assemblies, which requires a rather long time for relaxation of the polymers. The effects of the pH and salt (NaCl) concentration on this helicity-replication process will be discussed later in detail.

We note that the soluble helical assemblies are quite stable in water at pH 1.7 and do not lose their optical activity even after 1 month (Figure 3b and c). On the other hand, the original ***h***-poly-**1-Na** (pH 8.8) lost its optical activity within 1 month in water (Figure 3a), probably due to a helix-to-coil transition through *syn*−*anti* isomerization around the C═N double bonds of the polymer backbone.[3a] The intermolecular ionic interactions between the polyelectrolytes with opposite charges must facilitate this stability of the helical conformations of the ***h***-poly-**1** and poly-**3** in water.

When poly-**3**·HCl was complexed with (*S*)-PL-Na, it resulted in a large helical induction in the polymer at pH 5.4 and the complex exhibited the maximum $\Delta\epsilon_{362}$ value of −16.5. On the basis of this $\Delta\epsilon_{362}$ value, the helix sense excess of poly-**3**·HCl induced by the ***h***-poly-**1-Na** was estimated to be 21%. However, the helicity induction on poly-**3**·HCl with (*S*)-PL-Na decreased sharply when the pH was lowered to 1.8 and the $\Delta\epsilon_{362}$ value of the poly-**3**·HCl-(*S*)-PL-Na complex decreased to −1.2. On the basis of these observations one may think that if the ***h***-poly-**1-Na**−poly-**3**·HCl complex were soluble at a higher pH (ca 5) in the presence of salt, it would occur a large helical induction in the poly-**3**·HCl associated with the ***h***-poly-**1-Na**. Actually, the ***h***-poly-**1-Na**−poly-**3**·HCl complex became soluble in the presence of 2.0 M NaCl (pH 5.5), but the complex showed no ICD in the poly-**3**·HCl chromophore region after 3 days, and then the ion complex precipitated. This suggests that interpolymer complexations appear to be more difficult to control compared to the complexation between a polymer and small molecules.

The ***h***-poly-**1-Na** may have a left-handed helix,[11] which induced the same left-handed helicity in poly-**3**·HCl[4c,12] based on their Cotton effect signs. When ***h***-poly-**1-Na** ($\Delta\epsilon_{360} = 8.59$) obtained by (*R*)-**2** is used instead, poly-**3** with the opposite macromolecular helicity is induced (Figure 2A, trace g). Poly-((4-carboxyphenyl)acetylene) with a helicity memory[4a,c] cannot be used as the template for this helicity replication since the polymer preserves the helicity only when complexed with achiral amines; therefore, the memory in water is lost.

The further addition of ***h***-poly-**1-Na** induces an increased excess of the single-handed helix of poly-**3** up to 35%, as evidenced by the increase in the optical activity derived from the helical poly-**3** at pH 1.7 (Figure 2C).

Atomic force microscopy (AFM) analyses of ***h***-poly-**1-Na**, poly-**3**·HCl, and the ***h***-poly-**1-Na**−poly-**3**·HCl complexes on a freshly cleaved mica surface were then conducted to observe changes in the morphology of the polymer main chains and the helical assemblies. Figure 4a and b shows typical AFM images of ***h***-poly-**1-Na** and poly-**3**·HCl, respectively. Individual ***h***-poly-**1-Na** and poly-**3**·HCl chains can be directly visualized on mica prepared from dilute polymer solutions (0.03 and 0.01 mg/mL, respectively), which indicates that the molecular weight (length) of poly-**3**·HCl was greater than that of ***h***-poly-**1-Na** as expected from the SEC results.

AFM images of the ***h***-poly-**1-Na**−poly-**3**·HCl complex of different concentrations (Figure 5) suggest nanostructured network assemblies at a relatively high concentration of the complex (0.1−0.05 mg/mL), while single-like polymer chains and bundle-like polymer complexes could be visualized on mica prepared from a dilute solution (0.01 mg/mL). We note that the CD intensity of the ***h***-poly-**1-Na**−poly-**3**·HCl complex in water (pH 1.8) remained constant over the examined concentration range (1.0−0.01 mg/mL).

Effects of pH and Salt and Polymer Concentrations on Replication of Macromolecular Helicity. It is well known that polyelectrolyte complexations are highly dependent on the external conditions such as the pH, ionic strength, and concentration of the polyelectrolytes.[6] We then carefully investigated the effects of the pH and salt (NaCl) and polymer concentrations on the helicity induction in poly-**3**·HCl upon complexation with ***h***-poly-**1-Na**. As previously mentioned, upon addition of ***h***-poly-**1-Na** at pH 8.8 to poly-**3**·HCl (1.0 mg/mL and [poly-**1**]/[poly-**3**] = 0.5) at pH 5.0 in water, highly aggregated interpolymer complexes precipitated at pH 5.5. However, when diluted polymer solutions ([poly-**3**·HCl] = 0.1 and 0.01 mg/mL and [poly-**1**]/[poly-**3**] = 0.5) were mixed, the complexes became soluble in water at pH 5.2 and 6.2, respectively. We then followed the changes in the CD of the solutions, but the solutions did not show any apparent ICD in the poly-**3**·HCl chromophore region after 3 days, indicating that in a highly dilute solution significant interpolymer interactions did not occur, so that helicity induction in the poly-**3**·HCl could not be attained.

The polyelectrolyte complexes ([poly-**3**·HCl] = 1.0 mg/mL and [poly-**1**]/[poly-**3**] = 0.5) also became soluble in response

(11) The helix sense of the helical poly(phenyl isocyanide)s was determined by the exciton-coupled CD method; the negative $\Delta\epsilon_{364}$ band was found to be a left-handed helix. Takei, F.; Hayashi, H.; Onitsuka, K.; Kobayashi, N.; Takahashi, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 4092−4094.
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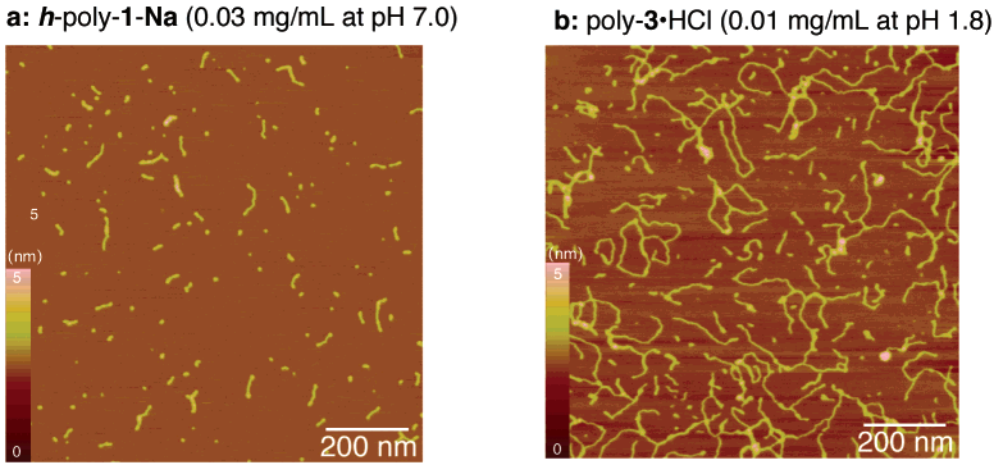

Figure 4. AFM tapping-mode images ($1 \times 1\ \mu m^2$) of ***h***-poly-**1**-**Na** (a) and poly-**3**·HCl (b) on mica. The concentrations of ***h***-poly-**1**-**Na** and poly-**3**·HCl in water are 0.03 and 0.01 mg/mL, respectively.

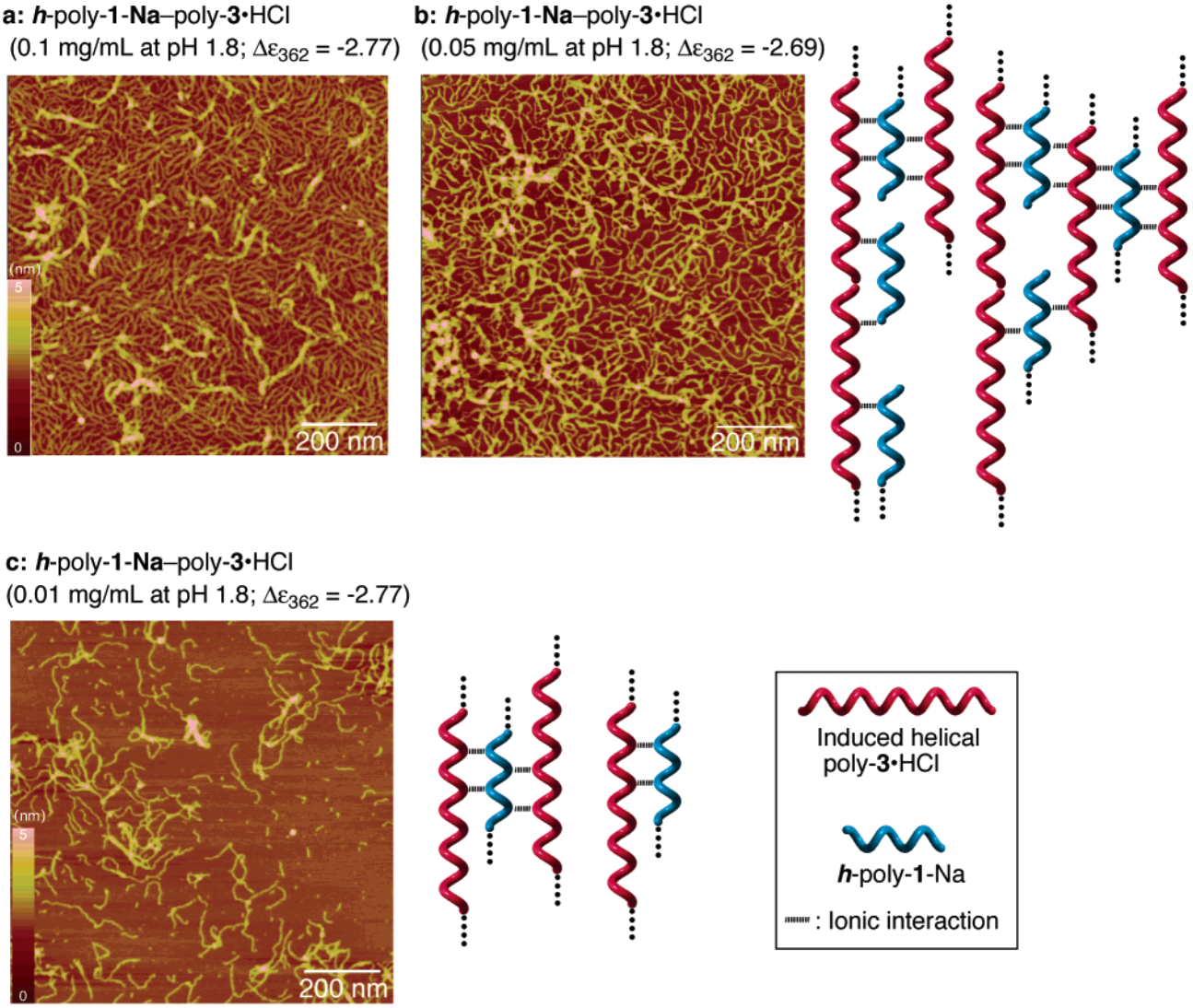

Figure 5. AFM tapping-mode images ($1 \times 1\ \mu m^2$) of the ***h***-poly-**1**-**Na**−poly-**3**·HCl complexes at a different concentration on mica, and schematic illustrations of nanostructured assemblies of low and high molecular weight ***h***-poly-**1** and poly-**3** species, respectively; molar ratio of monomer units of ***h***-poly-**1** to poly-**3** is 0.5. In the model assemblies the actual ***h***-poly-**1** molecules should be shorter. These dilute complex solutions showed a full ICD as that shown in Figure 2A (trace e).

to the change in the pH values ranging from 2.5 to 1.0, and the changes in their CD spectra were followed. Figure 6 shows the ICD intensity changes (second Cotton) of poly-**3**·HCl upon complexation with ***h***-poly-**1**-**Na** in water at different pHs with time. The solution pH was adjusted with 1.0 or 0.5 N HCl after mixing the polyelectrolyte solutions. The helicity induction

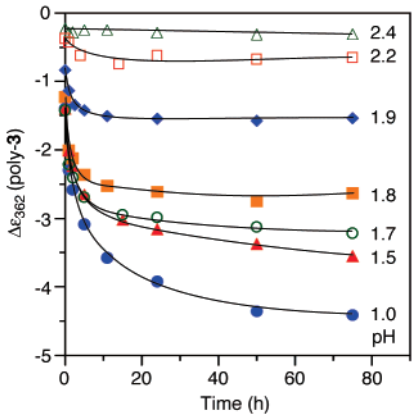

Figure 6. Changes in ICD intensities (second Cotton) of poly-**3**·HCl (1 mg/mL) upon complexation with ***h***-poly-**1-Na** in water at different pHs with time. The molar ratio of monomer units of ***h***-poly-**1-Na** to poly-**3**·HCl is 0.5.

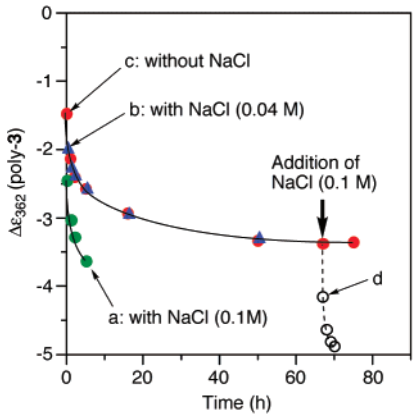

Figure 7. Changes in ICD intensities (second Cotton) of poly-**3**·HCl (1 mg/mL) upon complexation with ***h***-poly-**1-Na** in water at pH 1.7 with time in the absence (c) and presence of 0.04 (b) and 0.1 M (a) NaCl. The ICD changes of poly-**3**·HCl by the addition of NaCl to (c) after 67 h are also shown in (d). The molar ratio of monomer units of ***h***-poly-**1-Na** to poly-**3**·HCl is 0.5.

process was highly sensitive to the solution pH. At higher pHs (>2.0), the helical chirality of ***h***-poly-**1-Na** could not be effectively transferred to poly-**3**·HCl because the interpolymer ionic complexation appears to be too strong to induce a conformational change in the bound poly-**3**·HCl chains, and the complexes showed almost no further increase in the ICD intensity even after the samples had been allowed to stand for 75 h at ambient temperature. The polyelectrolyte complex solution at pH 2.4 was then diluted 10 and 50 times with acidic water to maintain the pH at 2.4, but we could not detect any increase in the ICD intensity after 162 h. On the other hand, the ICD intensity of poly-**3**·HCl significantly increased with time while lowering the solution pH (pH < 2.0). In particular, the increment was remarkable at pH 1.0; the $\Delta\epsilon_{362}$ value of poly-**3**·HCl increased from −1.4 to −4.4 after 75 h (Figure 6). At lower pHs (<2.0), the charge density of ***h***-poly-**1** and the number of ion pairings between the polyelectrolytes might be diminished; therefore, the bound poly-**3**·HCl could form an induced helical conformation. We note that ***h***-poly-**1** precipitated in acidic water below pH 5 without poly-**3**·HCl with the opposite charges. This may provide tentative evidence that ion pairing between the polyelectrolytes with opposite charges is a major component in stabilizing such specific polyelectrolyte complexes with macromolecular helicity.

The effect of the salt (NaCl) concentration on the helicity induction in poly-**3**·HCl upon complexation with ***h***-poly-**1-Na** was then investigated. The polyelectrolyte complex solutions at pH 1.7 and 2.4 were selected on the basis of the previously found pH effect on the helicity induction in poly-**3**·HCl (Figure 6). The presence of a salt is expected to attenuate the electrostatic interactions because of the charge-shielding effect of the salt. In the presence of NaCl at pH 2.4, the ICD intensity of the poly-**3**·HCl (1 mg/mL) complexed with ***h***-poly-**1-Na** ([poly-**1**]/[poly-**3**] = 0.5) gradually increased with time depending on the salt concentration; the $\Delta\epsilon_{362}$ value increased from −0.29 to −0.46 and −0.62 after 42 h in 0.04 and 0.1 M NaCl, respectively. The addition of salt to the ***h***-poly-**1**−poly-**3** complex solutions may enhance freedom of the bound poly-**3**·HCl chains trapped by the ***h***-poly-**1-Na** chains, resulting in a further induction of the helical conformation in the poly-**3**·HCl chains, because the charges on the polyelectrolytes are shielded in the presence of a salt. However, the increments are not significant (see Figure 6 for comparison). At a high salt concentration (0.2 M), the solution became turbid and further CD measurements were difficult.

Upon addition of NaCl (0.1 M) to a freshly prepared polyelectrolyte complex solution at pH 1.7 (poly-**3**·HCl = 1 mg/mL and [poly-**1**]/[poly-**3**] = 0.5), the $\Delta\epsilon_{362}$ value of the poly-**3**·HCl increased with time and reached a maximum of −3.7 after 5 h (Figure 7a). The increasing rate was significantly accelerated as compared with those at a low salt concentration (0.04 M) and without salt (Figure 7b and c). After 5 h, however, the solution became turbid and the ICD changes could not be completely followed. We then added NaCl (0.1 M) to the optically active ***h***-poly-**1-Na**−poly-**3**·HCl complex at pH 1.7, which was prepared by mixing the polyelectrolyte solution, and the solution had been allowed to stand for 67 h (marked by an arrow in Figure 7c). The ICD intensity of the helical poly-**3**·HCl induced by ***h***-poly-**1-Na** further increased with time ($\Delta\epsilon_{362}$ = −4.9) before precipitation of the polyelectrolyte complexes.

These results clearly indicate that replication of the macromolecular helicity process is governed by a delicate balance of the ionic interaction forces regulated by the external conditions including the pH and salt and the polyelectrolyte concentrations.

Conclusions

In summary, we found that the optically active, helical polyelectrolyte with helicity memory, the sodium salt of poly(4-carboxyphenyl isocyanide), could serve as a novel template for the helicity induction in a different polyelectrolyte with opposite charges in water. These helical polyelectrolytes are held together by the simple attraction of opposite charges, but their interpolymer complexations were more difficult to control compared to the complexation between a polymer and small molecules and highly influenced by external conditions such as the pH and salt concentration. However, we believe that a further increase in the helix sense excess of the bound poly-**3**·HCl may be possible by better control of the external conditions and also by changing the molecular weights of the polyelectrolytes as well as the functional groups.[13] This helicity-

(13) (a)Saito, M. A.; Maeda, K.; Onouchi, H.; Yashima, E. *Macromolecules* **2000**, *33*, 4616−4618. (b) Maeda, K.; Goto, H.; Yashima, E. *Macromolecules* **2001**, *34*, 1160−1164. (c) Onouchi, H.; Maeda, K.; Yashima, E. *J. Am. Chem. Soc.* **2001**, *123*, 7441−7442.

replication strategy will offer hierarchical growth of an ordered helical assembly with a controlled helix sense. Research along this line is now in progress in our laboratory.

Experimental Section

Full experimental details are available in the Supporting Information.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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