

Nonracemic Dopant-Mediated Hierarchical Amplification of Macromolecular Helicity in a Charged Polyacetylene Leading to a Cholesteric Liquid Crystal in Water

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The helix is a central structural motif among the variety of conformational states available in molecular and supramolecular organizations. Chemists have been interested in constructing helical arrays that mimic biological helices, such as the α -helix in proteins and the double helix in DNA.¹ These biological polymers form cholesteric liquid crystals (LCs) in water because of their stiff and one-handed helical backbones composed of their homochiral components (D-sugars and L-amino acids).² The interplay between the homochirality, macromolecular helicity, and the chirality at a macroscopic level is of great interest³ from fundamental and biological viewpoints as well as for attractive applications in materials science.^{1,4} On the other hand, only a few synthetic polymers consisting of nonbiological components via covalent bonding exhibit cholesteric LCs because of their rigid helical backbones in organic solvents or in the melt.^{1b,e,5}

In earlier studies, we reported a series of unique chromophoric polyacetylenes with various functional groups as the pendants that formed a predominantly one-handed helix induced by complexation with specific chiral guests. The complexes exhibited a characteristic induced circular dichroism (ICD) in the UV–visible region of the polymer backbones in dilute solution.⁶ The highly cooperative interactions in the pendants give rise to an easily measurable excess of one helical sense in dynamic helical polyacetylenes since the complexation with chiral guests remarkably alters the population of the right- and left-handed helices of the polymers separated by helical reversals. In the lyotropic LC state, however, each helical polymer chain can interact with others, and a further amplification of the excess helical sense could be produced over that in dilute solution, leading to a tightening of the cholesteric pitch.^{5a,7} Green et al. demonstrated that optically inactive poly(*n*-hexyl isocyanate), a typical wormlike dynamic helical polymer, formed a lyotropic nematic LC phase, which was converted to the cholesteric counterpart by doping with chiral small molecules or optically active polyisocyanates in organic solvents.^{5a} We now find that an optically inactive, positively charged polyacetylene, the hydrochloride of poly(4-(*N,N*-diisopropylaminomethyl)-phenylacetylene) (poly-1-HCl; Figure 1), forms an excess helical sense induced by a small amount of a chiral acid (2) as the dopant even with a low enantiomeric excess (ee) in water. The macromolecular helicity, even though the helix-sense excess is imperfect in dilute solution, is significantly amplified in the LC state and is readily visible and quantified by the helical pitch observed in the cholesteric LC (Figure 1).

In dilute solution, poly-1-HCl (the number-average molecular weight was 3.4×10^5)⁸ formed a predominantly one-handed helix induced by chiral acids such as the sodium salts of (*S*)- and (*R*)-phenyl lactic acid (2). The complexes exhibited mirror images of

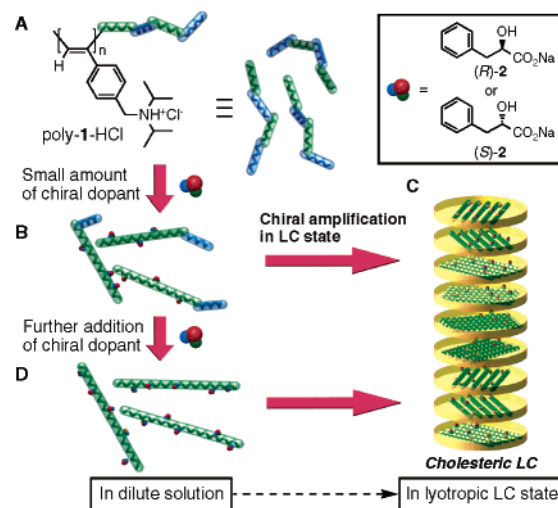


Figure 1. Schematic illustration of chiral amplification in macromolecular helicity in dilute solution and LC state. (A) Poly-1-HCl has interconvertible, right- (green) and left-handed (blue) dynamic helical conformations separated by helical reversals in solution. (B) Excess of one-handed helical sense (right- or left-handed helix) of poly-1-HCl is induced with a small amount of (*S*)- or (*R*)-2 in dilute solution. (C) In LC state, chirality is significantly amplified, resulting in a one-handed helical supramolecular assembly, thus showing a cholesteric LC phase. (D) Further addition of the chiral dopant (2) is required for a complete one-handed helix formation in poly-1-HCl in dilute solution.

split-type intense ICDs in the polymer backbone region (see Supporting Information). The CD titration using (*S*)-2 showed that the CD intensity of the second Cotton effect at 362 nm ($\Delta\epsilon_{362}$) increased with increasing concentration of (*S*)-2 and reached an almost constant value at 0.3 equiv of (*S*)-2 with the apparent binding constant (*K*) of 1.9×10^4 (M^{-1}) (Figure 2A, inset). This indicates that 0.3 equiv of (*S*)-2 induced an almost one-handed helix in poly-1-HCl in dilute solution. In sharp contrast, the neutral poly-1 required a large amount of (*S*)-2 acid (500 equiv) to induce a full ICD in organic solvents.⁸

The chiral amplification of poly-1-HCl in dilute solution was also demonstrated by the appearance of ICDs upon complexation with 2 of low ee (Figure 2B, inset). The changes in the $\Delta\epsilon_{362}$ value of poly-1-HCl with respect to the ee of 2 display a positive nonlinear effect, and a 60–80% ee of 2 gave rise to the full ICD as induced by pure (*S*)-2. Similar and strong chiral amplification has been observed for a poly(phenylacetylene) having a bulky crown ether pendant with amino acids in organic solvents.^{9a} However, the noncharged, neutral polyacetylene was not sensitive to chirality in water and showed a weak chiral amplification.^{9b} These observations suggest that the polyelectrolyte function of the poly-1-HCl appears

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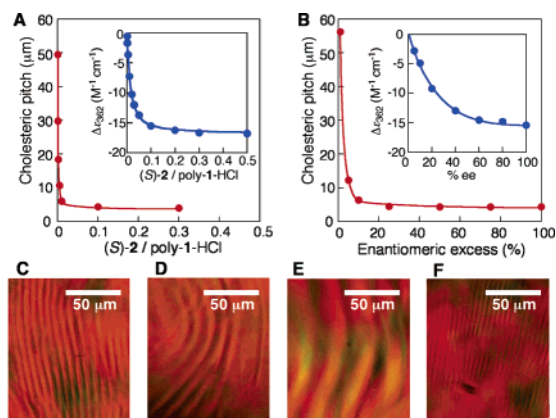


Figure 2. (A) Changes in the cholesteric pitch and ICD intensity ($\Delta\epsilon_{362}$) (inset) of poly-1-HCl versus the concentration of (S)-2 in concentrated (20 wt %) and dilute (inset, 1 mg/mL) water solutions. A curve in the plot (inset) was the calculated one using $K = 1.9 \times 10^4 \text{ (M}^{-1}\text{)}$. (B) Changes in the cholesteric pitch and ICD intensity ($\Delta\epsilon_{362}$) (inset) of poly-1-HCl versus the % ee of **2** (S-rich) in concentrated (20 wt %) and dilute (inset, 1 mg/mL) water solutions. Molar ratio of **2** to the monomeric units of poly-1-HCl is 0.1. (C–F) Polarized optical micrographs of cholesteric liquid crystalline phases of poly-1-HCl (20 wt %) in the presence of 0.002 (C), 0.001 (D), and 0.0005 equiv (E) of (S)-2 and 5% ee (S rich) of **2** (0.1 equiv) (F) in water.

to be essential as a powerful chirality-sensing probe with a high chiral amplification property in water.

During the intensive exploration of the chirality amplification mechanism, we discovered that the poly-1-HCl formed a lyotropic LC state in concentrated water (10–40 wt %), as evidenced by an LC texture. Although a number of liquid crystalline polyacetylenes have been reported, their liquid crystallinities have originated from the mesogenic pendants covalently bonded to the main chain.¹⁰ However, poly-1-HCl is the first liquid crystalline polyacetylene based on main chain stiffness with a macromolecular helicity. We note that the neutral poly-1 showed no LC phase in organic solvents. Again, the polyelectrolyte may allow for the appearance of the LC phase in water.

The addition of (S)-2 to the concentrated solution of the polymer in water brought about a fingerprint texture typical of the cholesteric LC state (Figure 2C–E), where the spacing of the fringes defines the half pitch of the cholesteric helical structure. Our main focus is to know if the macromolecular helicity induced in poly-1-HCl by chiral **2** in dilute solution would be further amplified in the LC state. To explore this possibility, we performed the same titration experiments with (S)-2 and nonracemic **2** of different ee's by following the changes in the cholesteric pitch.

Figure 2C–E shows the changes in the cholesteric pitch as a function of the amount of (S)-2. The cholesteric pitch decreased as the concentration of (S)-2 increased, where a smaller pitch represents an increased preference of the one helical sense, which may differ from the excess helical sense in dilute solution. The helical pitch reached an almost constant value ($4 \mu\text{m}$) at 0.01 to 0.1 equiv of (S)-2 in the LC state (Figure 2), while a higher excess (S)-2 (0.1–0.3 equiv) was required in dilute solution for the appearance of the full ICD (Figure 2A, inset). The sudden onset and rapid decrease in the cholesteric pitch suggest that cooperativity in the polymer significantly increases in the LC phase. Because of its high sensitivity in the LC state, the poly-1-HCl showed an apparent cholesteric LC phase of well-defined fingerprint patterns even in the presence of 0.0005 equiv of (S)-2 (Figure 2E). This means that once an excess of one helical sense is induced in a poly-1-HCl chain with (S)-2, the same helical sense can be induced in the dynamically racemic helical poly-1-HCl chains of the nearest

neighbors through interchain interactions in the LC state, so that the entire polymer chains are transformed into a one-handed helix, resulting in the cholesteric LC phase. Such an amplification of chiral information is not seen in dilute solution.

We then investigated the changes in the cholesteric helical pitch of poly-1-HCl with respect to the ee of **2** (0.1 equiv) (Figure 2B). Again, the poly-1-HCl is highly sensitive to the chirality of **2** and exhibited a cholesteric LC phase in the presence of 1% ee of **2**. The helical pitch decreased with the increasing ee and reached a constant value at about 10% ee (for a typical cholesteric LC texture, see Figure 2F). In dilute solution, however, the $\Delta\epsilon_{362}$ value became constant at over 60% ee (Figure 2B, inset).

Although the mechanism of this remarkable chiral amplification in the LC state has not yet been clearly elucidated, the population of the helical reversals between the interconverting right- and left-handed helical segments of the poly-1-HCl chains may be reduced in the LC state compared to that in dilute solution (see Figure 1), because the kinked helical reversals would likely interfere with the close parallel packing of helical poly-1-HCl chains in the LC state; this effect has one precedent and has been called the “bad neighbors rule”.^{5a,11} In summary, the present results demonstrate that the synthetic chromophoric polyelectrolytes with a dynamic helical characteristic promise to be one of the powerful tools to detect a tiny imbalance in ee of chiral molecules and to be potentially valuable in a variety of areas, including in both materials and biological aspects.¹²

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Supporting Information Available: Experimental details and CD and absorption spectra of poly-1-HCl with (S)- and (R)-**2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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