

Helical Structures

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Control of Main-Chain Stiffness of a Helical Poly(phenylacetylene) by Switching On and Off the Intramolecular Hydrogen Bonding through Macromolecular Helicity Inversion**

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Rodlike helical polymers with an excess of one-handedness arising from an optically active component incorporated into

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the main chain or at the pendants often show chiral liquid-crystalline (LC) phases in concentrated solutions or in a melt.^[1] Since the 1980s, such LC helical polymers have been extensively studied with much interest. Typical biological macromolecules, such as DNA,^[2] polysaccharides,^[3] and polypeptides,^[4] which adopt an ordered structure such as a helical structure, with a controlled helix sense stabilized by intra- and/or intermolecular hydrogen-bonding networks, also exhibit chiral LC phases resulting from the rigid-rod characteristics of the polymer main chains. Intramolecular hydrogen bonding has been used to construct synthetic helical polymers, such as polyisocyanopeptides,^[5] and amino acid bound polyacetylenes.^[6] The former helical polymers showed a clear cholesteric LC phase.

Recently, we reported the first helical poly(phenylacetylene)s bearing L- or D-alanine pendants with a long alkyl chain (poly-L-1 and poly-D-1, respectively) that showed cholesteric LC phases in organic solvents owing to their main-chain stiffness assisted by intramolecular hydrogen bonds; their persistence lengths were determined to be approximately 40 nm in chloroform,^[7] whereas the previously prepared monosubstituted polyacetylenes appear to be too flexible to exhibit LC phases.^[6a-c,8] We also found inversion of the helicity of poly-L-1 and poly-D-1 in response to the solvent polarity; the Cotton effect signs corresponding to the helix sense of poly-1 in benzene were inverted to the opposite signs in polar solvents such as THF and chloroform.^[9] Furthermore, the macromolecular helicity inversion process could be directly visualized by atomic force microscopy (AFM), which revealed their diastereomeric helical conformations and enabled the determination of the helical sense.^[9,10]

We now show a dramatic change in the main-chain stiffness of poly-L-1^[11] accompanied with inversion of the helical sense of the polymer (Figure 1), resulting from the “on

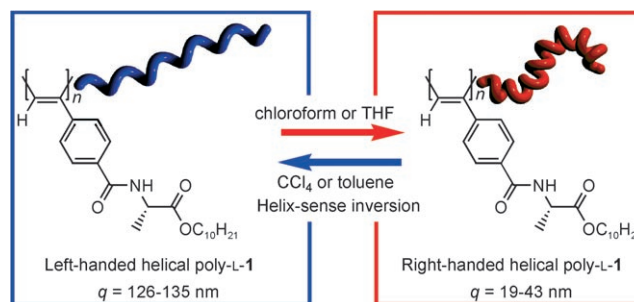


Figure 1. Illustration of the helix-sense inversion of poly-L-1 regulated by solvents with different polarities, leading to diastereomeric helical poly-L-1s with extremely different main-chain stiffnesses. The helical senses of the diastereomeric poly-L-1s were determined by AFM.^[9]

and off” fashion of the intramolecular hydrogen-bonding networks in polar and nonpolar solvents as revealed by the changes in their circular dichroism (CD) and IR spectra, persistence lengths, and rheological properties.

Figure 2a shows the CD spectra of poly-L-1 in polar and nonpolar solvents. Poly-L-1 exhibited split-type intense induced circular dichroisms (ICDs) in the conjugated polyene chromophore region. The ICD patterns measured in nonpolar

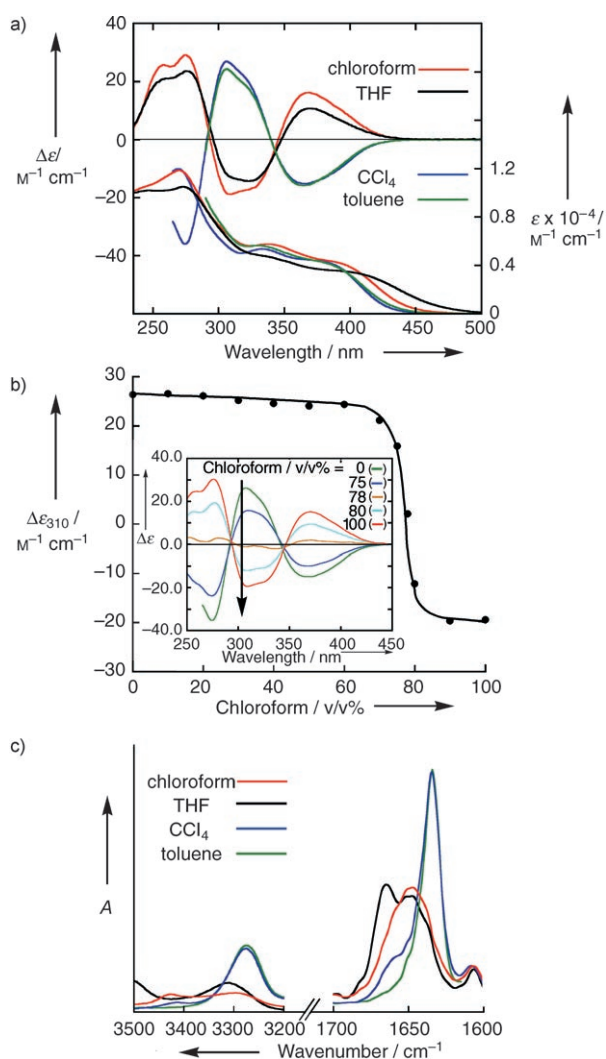


Figure 2. a) CD and absorption spectra of poly-L-1 taken in CCl₄ at 25 °C (blue line), toluene at 0 °C (green line), chloroform at 25 °C (red line), and THF at 0 °C (black line) in dilute solution (0.2 mg mL⁻¹) in a 1.0-mm quartz cell. b) Changes in the CD intensity (second Cotton effect) of poly-L-1 (0.2 mg mL⁻¹) in chloroform 25 °C. Inset: effect of the different chloroform concentrations. c) FTIR spectra of poly-L-1 (5 mg mL⁻¹) taken in CCl₄ (blue line), toluene (green line), chloroform (red line), and THF (black line) at ambient temperatures.

solvents such as CCl₄, toluene, and benzene are almost mirror images of those in polar solvents, such as chloroform and THF, indicating inversion of the helicity of poly-L-1 induced by solvent polarity as reported previously.^[9] The changes in the ICD patterns were accompanied by a slight red shift in the absorption spectra in polar solvents probably owing to the difference in their diastereomeric right- and left-handed helical conformations.^[12] As expected, the preferred helical sense of poly-L-1 can be controlled by the composition of the polar and nonpolar solvents. Figure 2b shows the changes in the second Cotton intensity of poly-L-1 at approximately 310 nm in CCl₄/CHCl₃ mixtures at 25 °C. In sharp contrast to the previously reported solvent-induced helicity inversion in synthetic helical polymers,^[6c,13] the ICD intensity suddenly changed and the sign became inverted from the positive to

negative direction, yielding almost mirror images in the presence of about 80 vol % chloroform.

The IR spectra of poly-L-1 were then measured in the polar and nonpolar solvents showing opposite Cotton effect signs to investigate the origin of the helicity inversion (Figure 2c). Poly-L-1 showed sharp amide NH and carbonyl stretching (amide I) bands at approximately 3275 and 1635 cm⁻¹, respectively, in nonpolar solvents such as CCl₄ and toluene, whereas in the polar chloroform and THF, the NH and amide I bands significantly shifted to higher wavenumbers accompanied by significant band broadening and/or splitting (see the Supporting Information). These band positions imply that poly-L-1 forms an intramolecular hydrogen-bonding network through the neighboring amide groups in nonpolar solvents, whereas in polar solvents, such hydrogen bonding is weakened or switched off,^[14] resulting in the formation of a different helical conformation, in this particular case, the opposite helical conformation, thus showing inversion of the Cotton effect signs.

We anticipated that such solvent-induced on–off switching of the intramolecular hydrogen-bonding networks in the pendant amide residues of poly-L-1 might lead to a significant change not only in the main-chain stiffness, resulting in a change in the persistence length (q), but also in the rheological property of the polymer fluids. The q values of poly-L-1 in polar and nonpolar solvents were then estimated on the basis of the wormlike chain model. This model can be described as an analytical function of the molecular weight (M_w) and the radius of gyration (S) if the q values and the molar mass per unit contour length (M_L), which eventually leads to the monomer unit height (h), are given.^[15] In this way, the dependence of the molecular weight on the radius of gyration of poly-L-1 in polar and nonpolar solvents was explored by using a size-exclusion chromatography (SEC) system equipped with multiangle light scattering (MALS) and refractive-index detectors in a series (Figure 3a). This series is a powerful method to evaluate the q value of polymers in a facile way in conjunction with the wormlike chain model.^[16] The solid curves in the plots were calculated by using the parameters determined from the fits of the unperturbed wormlike chain model over the entire M_w studied range, and are represented by the theoretical values of $\langle S^2 \rangle^{0.5}$.

The calculated h values of poly-L-1 in polar and nonpolar solvents almost coincide with the reported value (0.22 nm) of poly(4-carboxyphenylacetylene) (PCPA),^[8] indicating that poly-L-1 appears to take a similar helical conformation irrespective of the solvent polarity.^[7] The calculated q values of poly-L-1 in nonpolar CCl₄ and toluene are 134.5 and 126.3 nm, respectively; these values are the highest among all synthetic helical polymers reported so far, including the polyisocyanates, polyisocyanides, and polysilanes,^[17] and are even stiffer than double-helical DNA (< 60 nm).^[20] In sharp contrast, poly-L-1 showed a dramatic decrease in its persistence length to 42.9 and 19.2 nm in the polar solvents chloroform^[7] and THF, respectively, leading to a rather semirigid polymer. These results clearly demonstrate that the main-chain stiffness of poly-L-1 can be readily controlled by the on–off switching of the intramolecular hydrogen-bonding networks of the pendant amide groups as generated

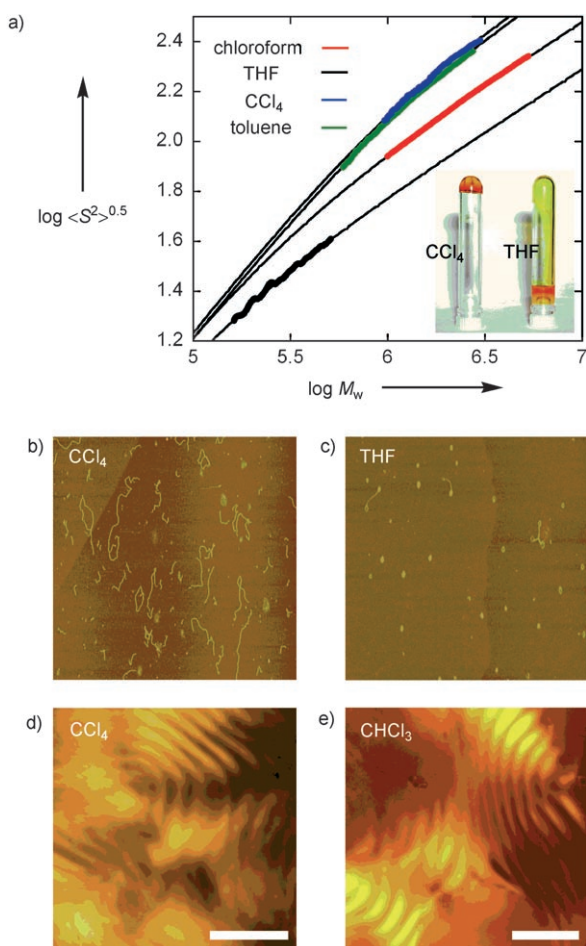


Figure 3. a) Double-logarithmic plots of the radius of gyration versus the molecular weight of poly-L-1 in CCl_4 (blue points), toluene (green points), chloroform (red points), and THF (black points) obtained by SEC-MALS measurements at 25 °C. Solid curves (black lines) were obtained on the basis of the wormlike chain theory and fit well with the experimental data. The evaluated parameters are as follows: In CCl_4 , $q = 134.5$ nm, $M_L = 1613.0$ nm $^{-1}$, $h = 0.22$ nm; in toluene, $q = 126.3$ nm, $M_L = 1699.6$ nm $^{-1}$, $h = 0.21$ nm; in chloroform, $q = 42.9$ nm, $M_L = 1537.7$ nm $^{-1}$, $h = 0.23$ nm; in THF, $q = 19.2$ nm, $M_L = 1663.8$ nm $^{-1}$, $h = 0.21$ nm. The inset shows the visible difference in poly-L-1 ($M_w = 166.2 \times 10^4$ and $M_w/M_n = 2.12$) in CCl_4 and THF, taken at ambient temperature (10 mg/100 μL). b, c) AFM height images (5.0×5.0 μm^2) of poly-L-1 cast from a dilute solution in CCl_4 (b) and THF (c) on mica modified with trimethoxypropylsilane. d, e) Polarized optical micrographs of poly-L-1 in 15 wt% CCl_4 (d) and chloroform (e) solutions in glass capillary tubes taken at ambient temperature (20–25 °C). Scale bars: 50 μm .

by solvent polarity, which also induces inversion of the helicity of poly-L-1 simultaneously.^[21]

Additional strong evidence of the change in the main-chain stiffness of the polymer depending on the solvent polarity was obtained from AFM measurements. Figure 3b and c show typical AFM images of isolated poly-L-1 chains on mica modified with trimethoxypropylsilane prepared by spin-casting a dilute solution of poly-L-1 in CCl_4 and THF (0.2 mg mL $^{-1}$), respectively. Individual poly-L-1 chains with an extended structure can be directly visualized on the mica prepared from a nonpolar CCl_4 solution, indicating the stiff

main-chain conformation. On the contrary, the polymer cast from polar THF appears highly tangled on the AFM images as a result of the flexible main-chain conformation.

As expected, the on–off switching of intramolecular hydrogen bonds brought about a change in the rheological property of poly-L-1, which can be visibly observed as a viscosity change in solution (Figure 3a, inset). A solution of poly-L-1 in polar THF (10 % w/v) is highly viscous but still fluid, whereas in nonpolar CCl_4 , the solution became a viscous liquid and subsequently gelled. These visible changes are in good agreement with the difference in their persistence lengths in each solvent assisted by the on–off switching of the intramolecular hydrogen bonds.

Another interesting and unique feature of rigid rodlike helical polymers is the formation of chiral LC phases. Combined with a specific property of inversion of the helicity of poly-L-1 regulated by solvent polarity, cholesteric LC phases of poly-L-1 with an opposite twist sense to each other can be produced by using nonpolar and polar solvents (Figure 3d and e). We then estimated the q values of poly-L-1 in different solvents by measuring their isotropic–cholesteric LC phase boundary concentrations (see the Supporting Information).^[22] The q values calculated by the theory of Khokhlov and Semenov^[22a,b] in CCl_4 , toluene, chloroform, and THF were 175.3, 163.9, 70.5, and 33.5 nm, respectively; these values are in rough agreement with those estimated by the SEC-MALS measurement.

In conclusion, we have demonstrated that the macromolecular helicity and main-chain stiffness of poly-L-1 can be controlled simultaneously by solvent polarity, resulting from the “on and off” fashion of the intramolecular hydrogen-bonding networks, which further results in a change in the rheological property of the polymer solutions. Changing the solvent polarity also allows one to control the mesoscopic cholesteric states of the opposite twist sense derived from inversion of the macromolecular helicity of the polymer chain. The present results will provide a novel approach for the rational design of chiral materials with inversion of the macromolecular helicity-based rheology switching.

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