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Well-Defined Lyotropic Liquid Crystalline Properties of Rigid-Rod Helical Polyacetylenes

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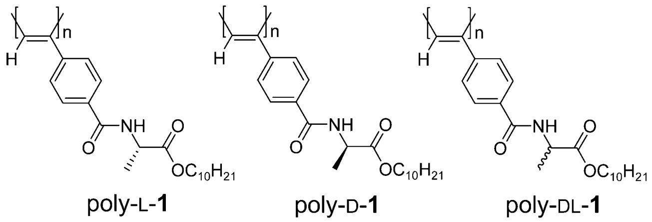
Liquid crystalline (LC) phases formed by rigid and semirigid helical polymers have been extensively studied with much interest since the 1980s. Typical examples are biological macromolecules, such as DNA,[1] polysaccharides,[2] polypeptides,[3] and some viruses,[4] which chiefly form cholesteric LC phases in water due to their stiff backbones composed of their homochiral components. Fully synthetic optically active helical polymers, such as polyisocyanates,[5] polysilanes,[6] and polyguanidines,[7] also form LC phases in organic solvents or in the melt, when their backbones are stiff enough with an excess one-handedness to self-assemble into supramolecular helical arrays in the LC state or solid state, resulting in a cholesteric or a twist grain boundary phase.[8] Optically active components incorporated into the main chain or at the pendants control the helix-sense excess and the handedness in these dynamic helical polymers, leading to further macroscopic chirality in the LC phase. Therefore, a mixture of equal amounts of helical polymers with the opposite helical senses results in the achiral nematic LC. However, an optically inactive, dynamic helical polymer composed of racemic monomer units may not show such a clearly identified nematic phase because the polymer appears to have a number of helical reversals between the interconverting right- and left-handed helical segments, which may destabilize the rigidity of the polymer backbone, so that close parallel packing of the polymer chains may not be possible.

Recently, we reported the first example of a helical polyacetylene consisting of a chromophoric polyacetylene backbone and the hydrochloride of the 4-(*N*,*N*-diisopropylaminomethyl)phenyl group as the pendant that formed a cholesteric LC in aqueous solution based on the main-chain stiffness with an excess of one helical sense of the polymer induced by a small amount of a nonracemic chiral dopant.[9] The polyelectrolyte function accompanied by the hydrophobic pendants of this polymer may be essential for the appearance of the LC phase in water because the neutral polymer showed no LC phase in organic solvents.[9]

In this study, we synthesized novel sets of stereoregular (cis−transoidal) poly(phenylacetylene)s bearing L-, D-, or racemic DL-alanine residues with a long alkyl chain as the pendants (poly-L-**1**, poly-D-**1**, and poly-DL-**1**, respectively; Chart 1) and found that these polyacetylenes form well-defined lyotropic cholesteric or nematic LCs depending on the chiral nature in the pendants in organic solvents as evidenced by their indisputably clear fingerprint and Schlieren textures. Although a number of LC polyacetylenes have been prepared, in most cases, their liquid crystallinities have originated from the mesogenic pendants covalently bonded to the main chain.[10] The poly-**1**'s are the first well-defined lyotropic LC polyacetylenes in organic solvents based on the main-chain stiffness with a macromolecular helicity.

Chart 1. Structures of Polymers



All polymers were prepared by the polymerization of the corresponding optically pure and racemic monomers (L-**1**, D-**1**, and DL-**1**) with a rhodium catalyst in tetrahydrofuran (THF) according to previously reported methods.[11] The molecular weight (M_w) and its distribution (M_w/M_n) are 498 000 and 2.18 for poly-L-**1**, 465 000 and 2.30 for poly-D-**1**, and 774 000 and 1.81 for poly-DL-**1**, respectively, as estimated by size exclusion chromatography (SEC). All the polymers have a highly cis−transoidal structure based on their ^{1}H NMR spectra.[11,12]

The typical CD and absorption spectra of poly-L-**1**, poly-D-**1**, and poly-DL-**1** in chloroform are shown in Figure 1. Poly-L-**1** and poly-D-**1** exhibited mirror images of split-type intense induced circular dichroisms (ICDs) assigned to the $\pi-\pi^*$ electronic transition of the conjugated polyene chromophore regions, indicating that the polymers have a predominantly one-handed helical structure, while poly-DL-**1** showed no ICD at all.

To investigate the global conformational properties of these polymers, the relationship between the intrinsic viscosity $[\eta]$ and the absolute molecular weight of the polymers was explored in chloroform by SEC equipped with refractive index and light scattering detectors and a viscometer, and the results were analyzed using the wormlike cylinder theory (Figure 2).

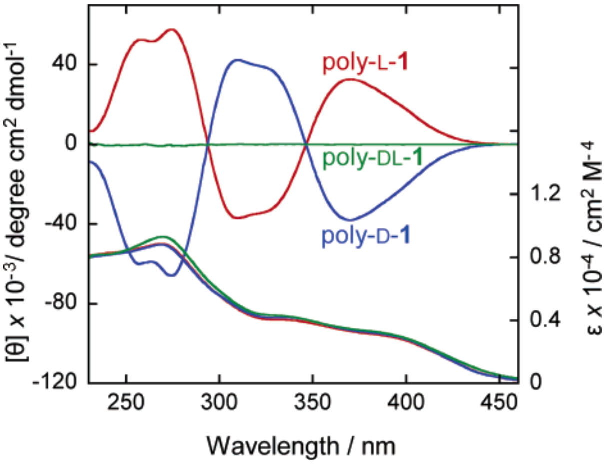


Figure 1. CD and UV−vis spectra of the polymers (poly-L-**1**, poly-D-**1**, and poly-DL-**1**) taken at ambient temperature in dilute chloroform solution (1.5 mg/mL) in a 0.2 mm quartz cell.

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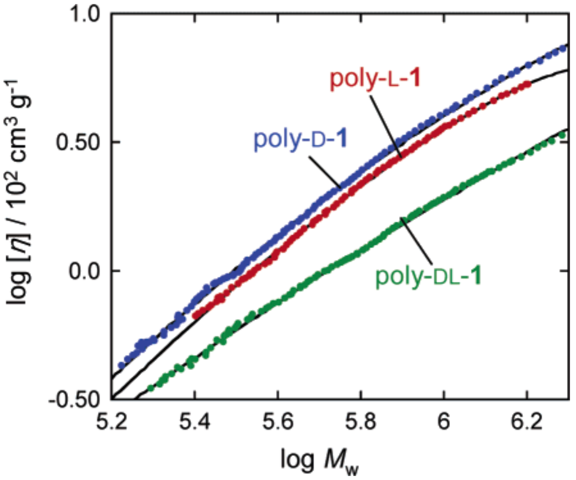

Figure 2. Double-logarithmic plots of the intrinsic viscosity vs molecular weight of poly-L-**1** (red points), poly-D-**1** (blue points), and poly-DL-**1** (green points), taken at 40 °C in chloroform. Solid curves (black lines) were obtained from the wormlike cylinder theory and fit well with the experimental data. The evaluated parameters are $q = 36.9$ nm, $d = 1.63$ nm, $M_L = 1577.4$ nm^{-1}, $h = 0.23$ nm for poly-L-**1**, $q = 40.9$ nm, $d = 1.49$ nm, $M_L = 1487.1$ nm^{-1}, $h = 0.24$ nm for poly-D-**1**, and $q = 16.1$ nm, $d = 1.24$ nm, $M_L = 1710.1$ nm^{-1}, $h = 0.21$ nm for poly-DL-**1**.

The viscosity index (α) can be roughly estimated by the slope of the plots (log [η]/log M_w) and was 1.18, 1.14, and 0.96 for poly-L-**1**, poly-D-**1**, and poly-DL-**1**, respectively, indicating that these polymers have an entirely stiff-rod conformation. According to Bushin et al.[13] and Bohdanecky,[14] the intrinsic viscosity [η] in the unperturbed wormlike cylinder model of the Yamakawa–Fujii–Yoshizaki theory[15] can be described as an analytical function of the molecular weight if the persistence length (q), the diameter of the cylinder (d), and the molar mass per unit contour length (M_L), which eventually leads to the monomer unit height (h), are given. The solid curves in the plots were calculated using the parameters determined from the fits between the theoretical and experimental [η] values (Figure 2).

The calculated monomer unit height (h) values almost coincide with the reported value (0.22 nm) of poly(4-carboxyphenylacetylene) (PCPA),[16] indicating that these polymers take almost the same helical pitch in their main-chain conformations irrespective of the pendant chirality. The calculated q values of poly-L-**1**, poly-D-**1**, and poly-DL-**1** are 36.9, 40.9, and 16.1 nm, respectively; these values are significantly longer than that of the reported value of a helical PCPA induced by chiral amines (8.6 nm).[16] These results indicate that not only poly-L-**1** and poly-D-**1** composed of optically pure monomers but also optically inactive poly-DL-**1** bearing the racemic pendants have stiff main-chain conformations. The origin of the main-chain rigidity of poly-**1**'s may be largely ascribed to the intramolecular hydrogen bonding between the amide groups in the neighboring side chains as well as the steric effect of the adjacent side chains. Intramolecular hydrogen bonding has been used to construct synthetic helical polymers such as polyisocyanopeptides[17] and polypropargylamides.[18,19] In these cases, the persistence lengths were found to be 76 ± 6[17b] and 13.5 nm,[18b] respectively, and a clear cholesteric LC phase was observed in the former case.[17a,20]

Figure 3 shows the polarized optical micrographs of poly-L-**1** (a) and poly-DL-**1** (b) in concentrated solutions of 1,2-dichloroethane. Poly-L-**1** forms a cholesteric phase as evidenced by its indisputably clear fingerprint texture (Figure 3a), while poly-DL-**1** forms a nematic phase which shows a typical Schlieren texture (Figure 3b). As far as we know, such a clear Schlieren texture has not been observed in nematic phases derived from a "racemic" helical polymer composed of racemic monomer units based on the main-chain stiffness. Consequently, the poly-**1**'s are the first liquid crystal polyacetylenes in organic solvents based on the main-chain stiffness. Similar clear microscopic textures were also observed in concentrated solutions of nonpolar solvents, such as benzene, chloroform, 1,1,2,2-tetrachloroethane, and carbon tetrachloride, but not observed in polar solvents such as THF. These results indicate that the main-chain stiffness of the polymers may be maintained through intramolecular hydrogen bonds between the neighboring pendant amide residues because an aprotic solvent like THF is supposed to hamper the hydrogen bonding.[21]

Moreover, transmission electron microscopy (TEM) observations showed that the helicoidal structure of the cholesteric phase formed in poly-L-**1** solution could be successfully solidified into a cast film by gradual evaporation of the solvent. Figure 4 shows a typical bright-field TEM image of a cross section of the poly-L-**1** cast film. A clear banded texture was observed due to the thickness variations of the sample. This sinusoidal surface topology may be produced due to the preferential crack propagation along the twist of the director field.[8,22] The observed banding repeat distance was ca. 150 nm, which also depends on the local contact angle between

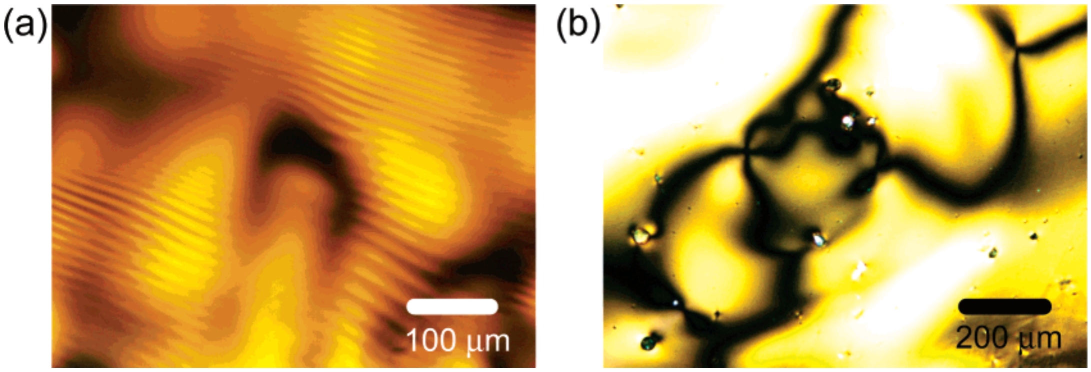

Figure 3. Polarized optical micrographs of poly-L-**1** (a) and poly-DL-**1** (b) in 15 wt % 1,2-dichloroethane solution taken at ambient temperature (20–25 °C). Scale bars in the images represent 100 (a) and 200 μm (b). The solution of poly-L-**1** was sealed in a glass capillary tube, while the solution of poly-DL-**1** was placed on a glass plate without a cover glass to develop the planar structure before observation of the Schlieren texture. The cholesteric LC phase of poly-L-**1** was phase-separated from an isotropic phase in equilibrium, and the poly-L-**1** maintained its cholesteric pitch for over 4 months.

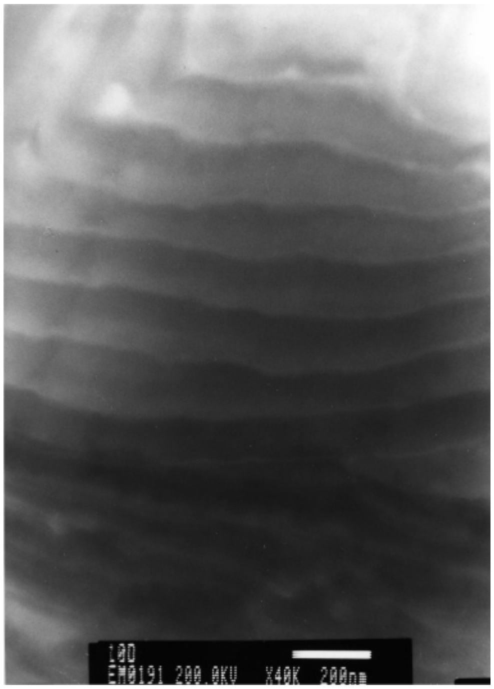

Figure 4. Bright-field TEM image of an ultramicrotomed cast film of a cholesteric LC of poly-L-**1**. The film was cross-sectioned (about 60 nm thickness) at room temperature perpendicular to the surface using a diamond knife and stained in ruthenium tetroxide (RuO_4) vapor for 7 min on a copper microgrid (200 mesh) before the TEM observation. Scale bar represents 200 nm.

the knife and the cholesteric helical axis, corresponding to the half helical pitch of the cholesteric twist. Thus, the pitch should have moved from several microns in the liquid crystal phase in the solution to less than 300 nm in the solid across the visible light region during the solvent evaporation.

In summary, we found that novel poly(phenylacetylene)s bearing L-, D-, and racemic DL-alanine pendants formed lyotropic cholesteric or nematic LCs due to the exceptional stiffness of their polymer backbones. Although the origin of this remarkable stiffness of these polyacetylenes has not yet been clearly elucidated, to the best of our knowledge, the present study is the first observation of well-defined cholesteric and nematic LCs formed in optically active and inactive polyacetylenes based on the main-chain stiffness with a macromolecular helicity in organic solvents.

We expect that related helical polyacetylenes bearing other amino acid residues and functional groups[10,18,20,23] will also form lyotropic and/or thermotropic LC phases, and such LC polyacetylenes may provide novel chiral materials for optical switching, sensors, and display devices.

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Supporting Information Available: Detailed experimental procedures and HPLC chromatograms of the enantioseparation of the monomers (L-**1**, D-**1**, and DL-**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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