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Notes

Uniaxial Orientation of a Rodlike Helical Poly(phenylacetylene) in an Electric Field

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Introduction

The orientational organization of polymers generally arises through liquid crystal formation in concentrated solutions. The orientation direction of randomly positioned rodlike polymers in a liquid crystalline (LC) solution continuously changes by location in which the polymers are preferentially oriented along an axis called the "director". The uniform alignment of rodlike polymers is of great interest because the alignments of the polymer main chains give rise to remarkable improvements in the electrical, optical, and mechanical properties.[1] It has been revealed that the uniform orientation of LC polymers can be achieved by applying a magnetic field, an electric field, and spinning.[2] To our knowledge, however, previous studies on the electric-field-induced alignments of rodlike polymers based on the electric dipole along the main chain have been confined to the α-helical polypeptides,[3] whereas electric-field-induced alignments of side-chain LC polymers with semirigid backbones have been reported.[4] The cholesteric phase formed by the α-helical polypeptides in helicogenic solvents is presumably unwound by the applied electric field and changes to a nematic phase with the director more or less parallel to the applied field.[3] The structure of the α-helical polypeptides is such that the polar amide residues linked to each other by intramolecular hydrogen bonding regularly align in one direction, parallel to the helical axis, so that a large electric dipole moment as the vector sum of all the dipole moments can be generated along the helical axis.[5] However, an analogous dipole accumulation in fully synthetic helical polymers has not yet been reported.

We now show that a helical poly(phenylacetylene) bearing L-alanine residues with a long alkyl chain as the pendants (poly-L-**1**) forms a highly aligned cast film in an electric field, as illustrated in Figure 1a. The structural analyses based on the polarized optical microscopy, polarized IR spectroscopy, and X-ray diffraction as well as the molecular modeling suggest that two sets of extended intramolecular hydrogen-bonded arrays of the pendant amide groups are helically arranged in a parallel fashion so as to accumulate the large dipole moment along the helical axis. Although the antiparallel arrangement of the two sets of hydrogen-bonded helical arrays of the pendant amide groups was proposed as a plausible form in analogous helical polyacetylenes, i.e., the poly(*N*-propargylamide)s[6] based on semiempirical molecular orbital calculations, it could accordingly be ruled out for poly-L-**1**.

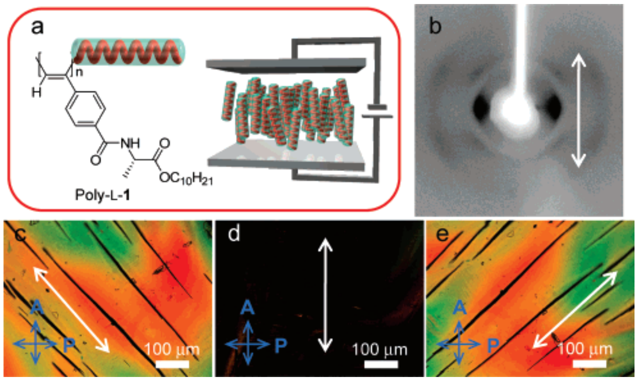

Figure 1. Alignment of a helical poly(phenylacetylene) in the electric field. (a) Structure of helical poly-L-**1** and schematic illustration of the electric-field-induced alignment of poly-L-**1** molecules. (b) Through-view WAXD pattern (the incident beam was normal to the film surface) of a highly oriented poly-L-**1** film prepared from a cholesteric LC benzene solution of poly-L-**1** (10.4 mg/mL) in an electric field (6000 V/cm). The electric field direction is vertical as indicated by the white arrow. (c−e) Polarized optical micrographs of oriented poly-L-**1** film under crossed polarizers. The horizontal and vertical blue arrows represent the transmission axes of the polarizer (P) and analyzer (A), respectively. The film was tilted at −45° (c, counterclockwise), 0° (d, parallel), and +45° (e, clockwise) to the transmission axis of the analyzer. The white arrows indicate the direction of the applied electric field.

Results and Discussion

Stereoregular (*cis*−*transoidal*) poly(phenylacetylene), poly-L-**1**, was prepared according to a previously reported method.[7] In our previous studies, the circular dichroism (CD) spectra with characteristic Cotton effects in the polymer backbone region (250−450 nm) and the direct atomic force microscopy (AFM) observations of poly-L-**1** chains at molecular resolution combined with X-ray diffraction revealed that the poly-L-**1** has a right-handed 11 units per 5 turns (11/5) main-chain helical conformation with a helical pitch of ca. 2.4 nm in nonpolar solvents.[8] Two series of pendant helical arrays firmly linked to each other by intramolecular hydrogen bonding allow the polymer to form an unprecedented rigid main-chain conformation with a very long persistence length of over 100 nm in nonpolar solvents like benzene, so that the polymer forms a cholesteric LC phase in concentrated solutions.[9]

On the basis of the AFM and X-ray structural analysis results, a computer-generated plausible model for a helical poly-L-**1** can be proposed (see Figure 3a), which shows that all the amide carbonyl groups are specifically oriented in one direction so

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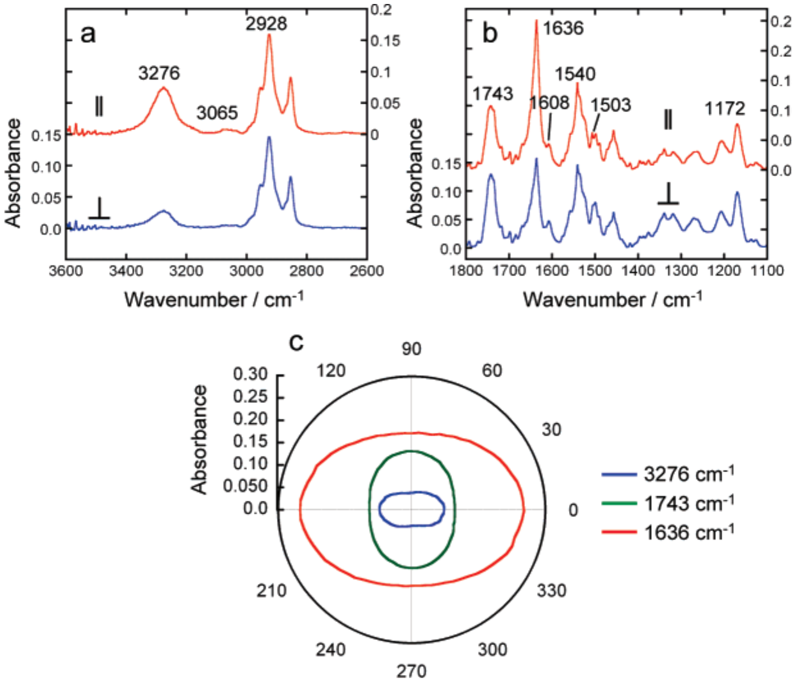

Figure 2. Polarized IR spectra of an oriented poly-L-**1** film. The film was prepared on a CaF_2 substrate from a concentrated LC benzene solution (5.0 mg/mL) in an electric field (6000 V/cm). (a, b) IR spectra with the incident light polarized parallel (∥, red line) and perpendicular (⊥, blue line) to the applied electric field. (c) Polar plots of the absorbance against polarization angles with respect to the applied electric field direction for the N−H stretching at 3276 cm^{-1} (blue line) of the amide group, the C═O stretching of the ester group at 1743 cm^{-1} (green line), and the C═O stretching of the amide group (amide I) at 1636 cm^{-1} (red line).

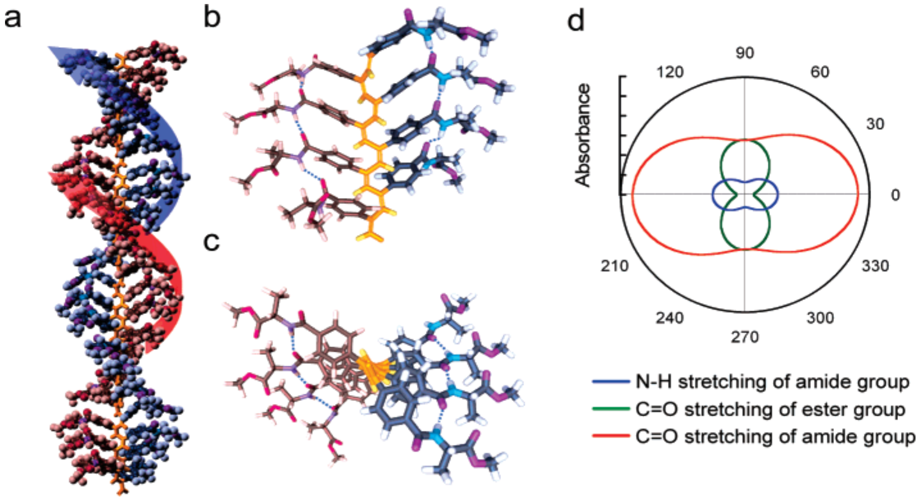

Figure 3. (a) Optimized 11/5 helical structure of poly-L-**1** (40-mer) on the basis of WAXD and polarized IR structural analyses followed by molecular mechanics calculations (see Supporting Information). The structure is represented by ball-and-stick models; two sets of hydrogen-bonded helical arrays (*n* and *n* + 2) of the pendants and the main-chain carbon and hydrogen atoms (stick model) are shown in different colors for clarity. When the main chain of poly-L-**1** has a right-handed helical structure, the polymer has the opposite, left-handed helical array of the pendants. (b, c) The detailed structure (8-mer) taken from (a) is also shown by a stick model in (b) (side view) and (c) (top view). The hydrogen bonds between the neighboring side chains are indicated by the dotted lines. In these models (a−c), the pendant decyl ester groups of poly-L-**1** are replaced by the methyl ester groups for clarity. (d) Calculated polar plots of the relative IR absorbance vs polarization angle with respect to the main-chain helical axis for the N−H stretching of the amide group (blue line), the C═O stretching of the ester group (green line), and the C═O stretching of the amide group (red line) on the basis of the optimized structure of poly-L-**1**. The absorbance intensities are arbitrarily chosen.

that they can form intramolecular hydrogen bonds to the neighboring amide N−H groups, resulting in two sets of parallel hydrogen-bonded helical arrays; an alternative antiparallel arrangement of the hydrogen-bond arrays[6] could be sterically impossible for poly-L-**1** to form the hydrogen-bonded arrays. The IR spectra support the formation of such intramolecular hydrogen bonds between the pendant amide residues of poly-L-**1**.[9]

The parallel arrangement of the polar amide residues of poly-L-**1** may generate a large dipole moment along the main-chain helical axis of the polymer. We then investigated the electric-field-induced macromolecular alignment of poly-L-**1**. The oriented poly-L-**1** film was prepared by gradual solvent evaporation of a concentrated LC benzene solution of poly-L-**1** in a benzene vapor atmosphere on a CaF_2 substrate in an electric field of 6000 V/cm (Figure S1, Supporting Information).

Figure 1c−e shows the polarized optical micrographs of the oriented poly-L-**1** film observed under crossed polarizers. The poly-L-**1** film is oriented parallel to the applied electric field direction, as evidenced by the fact that the counterclockwise (Figure 1c) and clockwise (Figure 1e) images tilted at −45° and +45° with respect to the transmission axis of the analyzer,

Table 1. IR Absorption Bands and Dichroic Ratio (*R*) for Selected Functional Groups of Oriented Poly-L-1 Film[a]

wave-number (cm^{-1})	assignment	dichroic ratio[b] R ($A_{\parallel}/A_{\perp}$)
3276	N−H stretching of amide group	1.94
3065	C−H stretching of disubstituted benzene	2.28
2928	C−H stretch of aliphatic group	1.01
1743	C=O stretching of ester group	0.73
1636	amide I	1.46
1608	C−C stretching of benzene	0.83
1540	amide II	0.87
1172	C−O stretching of ester group	0.80

[a] The film was prepared on a CaF_2 substrate from a concentrated LC benzene solution in an electric field (6000 V/cm). [b] Dichroic ratio R ($A_{\parallel}/A_{\perp}$) of designated absorption bands, in which the incident infrared radiation is polarized parallel (||) and perpendicular (⊥) to the direction of the electric field.

respectively, showed a clear birefringence, whereas the upright image (Figure 1d) showed complete extinction. The oriented poly-L-**1** film also exhibited a highly birefringent optical texture with a characteristic banded pattern perpendicular to the applied electric field. The average bandwidth was ca. 10−20 μm (Figure S2, Supporting Information), in which the dark lines turned into bright ones when the sample was properly rotated between crossed polarizers. These observations also support the orientation of the polymer along the electric field direction, since a similar shear-induced banding has been frequently observed perpendicular to the shearing direction for a wide range of main-chain LC polymers.[10]

A through-view pattern of the wide-angle X-ray diffraction (WAXD) for the uniaxially oriented poly-L-**1** film revealed the exact direction of the orientation of the polymer main chains (Figure 1b). A diffuse, but apparent, equatorial reflection with a spacing of 1.95 nm is attributed to the lateral packing of the polymer molecules; thus, the polymer chains likely align in the meridional direction corresponding to the applied electric field direction because the electric field direction in the film was placed parallel to the meridional direction.

The orientation of each functional group in the monomer units of poly-L-**1** was further elucidated by polarized IR spectroscopy (Table 1 and Figure 2a,b). The polarized IR spectra of the oriented poly-L-**1** film showed sharp signals assigned to the amide NH and carbonyl stretching (amide I) bands at 3276 and 1636 cm^{-1}, respectively, which suggested the formation of intramolecular hydrogen-bonding networks.[8,9]

Since poly-L-**1** has a one-handed helical structure,[7,8] the static orientational distribution of the functional groups must be symmetrical about the helical axis, and therefore, the orientation of the vibrational transition moment can be described in terms of an angle between the particular vibrational transition moment and the helical axis. To elucidate the orientation directions of the vibrational transition moments for selected functional groups of poly-L-**1**, the IR absorbance ellipsoids of each functional group in the film plane were drawn in the polar plots, which were generated by rotating the polarizer in 5° increments during the polarized IR measurements (Figure 2c). The polarization angle $\theta = 0°$ corresponds to the direction of the applied electric field, and the dichroic ratios (R) ($A_{\parallel}(\theta = 0°)/A_{\perp}(\theta = 90°)$) for selected functional groups of poly-L-**1** were then calculated (Table 1). The results indicate that the vibrational transition moments of the amide N−H and carbonyl groups of poly-L-**1** appear to lie parallel to the electric field applied to the film, whereas the ester carbonyl groups tend to be oriented perpendicular to the applied electric field.

A polymer model of poly-L-**1** (70-mer) (70 repeating monomer units) (Figure 3a) was then constructed on the basis of the X-ray structural analysis[8b] and molecular mechanics calculations (see Supporting Information). Since the IR absorption is proportional to the squared scalar product of the projected electric vector of the incident light on the vibrational transition moment, the relative IR absorption of a particular functional group in the model is given by

$$A \propto \sum_{i=1}^{n} \cos^2 \alpha_i$$

where α_i denotes the angle between the vibrational transition moment of the functional group in the i th monomer unit and the polarization axis which was rotated in the plane containing the main-chain helical axis in increments of 5°.[11] The relative IR absorptions for selected functional groups were then calculated using the central part of the optimized poly-L-**1** (50-mer), and the calculated values were plotted vs the polarization angles with respect to the direction of the main-chain helical axis (Figure 3d). The calculated polar plots are roughly identical to the observed ones (Figure 2c).

In summary, we have demonstrated that a poly(phenylacetylene) bearing L-alanine residues with a long alkyl chain as the pendants could be highly aligned in the electric field due to the large electric dipole moment along the main-chain helical axis. The molecular modeling based on the polarized IR spectroscopy combined with an X-ray structural analysis revealed that all the amide groups were unidirectionally oriented in large part so as to form helically arranged intramolecular hydrogen-bonding networks, resulting in the accumulation of a large electric dipole moment along the helical axis. To the best of our knowledge, this may be the first example of the hydrogen-bonding-driven spontaneous formation of a large electric dipole based on a fully artificial helical polymer, leading to an electric-field-induced alignment of the polymers. The present results including the uniformly aligned rodlike helical polymers with a large electric dipole will contribute to developing a novel nonlinear optical device due to its polar structure.

Supporting Information Available: Full experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Donald, A. M.; Windle, A. H.; Hanna, S. In *Liquid Crystalline Polymers*, 2nd ed.; Cambridge University Press: Cambridge, 2006; Chapters 9 and 10.

(2) (a) Moore, R. C.; Denn, M. M. In *High Modulus Polymers*; Zachariades, A. E., Porter, R. S., Eds.; Dekker: New York, 1988; pp 169−193. (b) Calundann, G.; Jaffe, M.; Jones, R. S.; Yoon, H. N. In *Fibre Reinforcements for Composite Materials*; Bunsell, A. R., Ed.; Elsevier: Amsterdam, 1988; pp 211−248. (c) Haase, W. In *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Blackie: Glasgow, 1989; pp 309−329.

(3) (a) Yen, C.-C.; Tokita, M.; Park, B.; Takezoe, H.; Watanabe, J. *Macromolecules* **2006**, *39*, 1313−1315. (b) Monzen, K.; Hiraoka, K.; Uematsu, Y.; Date, M. *Polym. J.* **1998**, *30*, 499−507. (c) Watanabe, T.; Miyata, S.; Furukawa, T.; Takezoe, H.; Nishi, T.; Sone, M.; Migita, A.; Watanabe, J. *Jpn. J. Appl. Phys.* **1998**, *37*, L136−L138. (d) Iizuka, E. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1985**, *41*, 131−147. (e) Iizuka, E. *Adv. Polym. Sci.* **1976**, *20*, 79−109.

(4) (a) Geng, J.; Zhou, E.; Li, G.; Lam, J. W. P.; Tang, B. Z. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 1333−1341. (b) Findlay, R. B. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1993**, *231*, 137−151. (c) Nazemi, A.; Williams, G.; Attard, G. S.; Karasz, F. E. *Polym. Adv. Technol.* **1992**, *3*, 157−168.

(5) Wada, A. *Adv. Biophys.* **1976**, *9*, 1−63.

(6) Nomura, R.; Tabei, J.; Nishiura, S.; Masuda, T. *Macromolecules* **2003**, *36*, 561−564.

(7) Okoshi, K.; Sakajiri, K.; Kumaki, J.; Yashima, E. *Macromolecules* **2005**, *38*, 4061−4064.

(8) (a) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 5650−5651. (b) Sakurai, S.-i.; Okoshi, K.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 1245−1248.

(9) Okoshi, K.; Sakurai, S.-i.; Ohsawa, S.; Kumaki, J.; Yashima, E. *Angew. Chem., Int. Ed.* **2006**, *45*, 8173−8176.

(10) The banded texture has often been observed for both lyotropic and thermotropic main-chain LC polymers, such as hydroxypropylcellulose and poly(γ-benzyl-L-glutamate) under crossed polarizers, and their morphological features and mechanism have been investigated in detail, but the exact mechanism of the band formation remains unsolved. For reviews, see: (a) Donald, A. M.; Windle, A. H.; Hanna, S. *Liquid Crystalline Polymers*, 2nd ed.; Cambridge University Press: Cambridge, 2006; Chapter 9. (b) Viney, C.; Putnam, W. S. *Polymer* **1995**, *36*, 1731−1741. (c) Kiss, G.; Porter, R. G. *Mol. Cryst. Liq. Cryst.* **1980**, *60*, 267−280.

(11) It is generally accepted that the transition moment directions of the C═O stretching vibrations in an amide group and an ester group are inclined at 20° and 19° from the C═O bond direction toward the C−N and C−C bond directions, respectively.[12] The transition moment of the N−H stretching vibration is nearly identical to the direction of the N−H bond. For more detailed calculation procedures, see Supporting Information and: Wool, R. P. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1921−1929.

(12) (a) Bradbury, E. M.; Elliott, A.; Fraser, R. D. B. *Trans. Faraday. Soc.* **1960**, *56*, 1117−1124. (b) Fraser, R. D. B. *J. Chem. Phys.* **1958**, *28*, 1113−1115. (c) Fraser, R. D. B. *J. Chem. Phys.* **1953**, *21*, 1511−1515.

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