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# *Cis*-Rich Helical Polyacetylene Synthesized in Low-Temperature Chiral Nematic Liquid Crystal

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**Introduction.** Polyacetylene (PA) is a representative one-dimensional conjugated polymer with high conductivity.[1] Polymerization of acetylene is known to proceed through a *cis* insertion of acetylene monomer into a Ti−C bond of a catalytic species composed of Ti(O-*n*-Bu)$_4$ and AlEt$_3$, resulting in a *cis* form.[1b,2] The *cis* form is maintained at low polymerization temperature, but it is thermally isomerized into the *trans* form at high polymerization temperature.[2−4] Thus, when polymerization temperature becomes high, the thermal isomerization proceeds to give a high content of the *trans* form. It has been generally accepted that the most stable structure of PA is a planar structure, irrespective of *cis* and *trans* forms, because of the strong $\pi$-conjugations between sp$^2$-hybridized carbon atoms in the polymer chain.[3] Recently, helical polyacetylene (H-PA) with hierarchical spiral morphology was synthesized in chiral nematic liquid crystal (N*-LC).[5] H-PA is anticipated to be a prototype of a molecular solenoid because of its helical structure and high electrical conductivity.[6] Besides, the development of morphology-retaining carbonization has demonstrated that the H-PA is a promising precursor to produce a helical graphite film with peculiar spiral morphology and a helical graphite fiber.[7]

The N*-LC is useful as an asymmetric reaction field because it enables us to synthesize helical conjugate polymers from achiral monomers and also to prepare helical forms of the polymers without chiroptical substituents in side chains.[8] However, because the N*-LCs used so far have a phase transition temperature from 0 to 30 °C, the polymerization temperatures in the N*-LCs have been restricted to room temperature. Thus, only *trans*-rich H-PA films have been synthesized so far.[5] It is known that the *trans* form of PA is a thermally stable isomer, a thermodynamic product, and is prepared by polymerization around room temperature. On the other hand, the *cis* form of PA is a kinetic product, not thermally stable, and tends to change into the *trans* form by thermal heating or chemical doping.[9] In order to elucidate the chemical and electrical properties of *cis*-rich H-PAs, a so-called low-temperature N*-LC needs to be prepared that can produce *cis*-rich H-PAs. In this work, we developed two kinds of low-temperature N*-LCs for synthesis of *cis*-rich H-PAs and investigated the behavior of *cis*-rich H-PAs during thermal isomerization from *cis* to *trans* form.

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**Experimental Section.** *Preparation of Low-Temperature N*-LC.* The following five kinds of nematic LCs (N-LCs) of phenylcyclohexane derivatives, shown in Figure 1a, were synthesized for use as parent low-temperature N-LCs: 4-(*trans*-4-*n*-propylcyclohexyl)methoxybenzene [PCH301], 4-(*trans*-4-*n*-propylcyclohexyl)ethoxybenzene [PCH302], 4-(*trans*-4-*n*-propylcyclohexyl)butoxybenzene [PCH304], 4-(*trans*-4-*n*-propylcyclohexyl)ethylbenzene [PCH32], and 4-(*trans*-4-*n*-pentylcyclohexyl)propylbenzene [PCH53]. Two kinds of N*-LCs, abbreviated as system 1 and system 2, were prepared by adding a small amount of chiral dopants into the mixtures of N-LCs. System 1 included three kinds of N-LCs and the chiral dopant {PCH302:PCH304:PCH32:chiral dopant = 30:20:50:1 (mole ratio)}, and system 2 included five kinds of N-LCs and the chiral dopant {PCH301:PCH302:PCH304:PCH32:PCH52:chiral dopant = 10:20:20:20:30:1 (mole ratio)}. Through polarized optical microscope (POM) observations, the mesophase temperature regions of system 1 and system 2 were found to be −70 to −35 °C and −49 to −11 °C, respectively. Parts c and d of Figure 1 show the POM images of system 1 and system 2, respectively. Fingerprint textures were observed at −60 °C (system 1) and −35 °C (system 2) in cooling processes. The helical pitches of system 1 and system 2 were evaluated to be 1.3 and 2.5 $\mu$m, respectively. System 1 and system 2 containing catalyst were confirmed to be available for the low-temperature polymerizations ranging from −65 to −40 °C and from −35 to −15 °C, respectively.

*Polymerization of Acetylene.* Acetylene gas of six-nine grade and triethylaluminum, AlEt$_3$, were used without further purification. Tetra-*n*-butoxytitanium, Ti(O-*n*-Bu)$_4$, was distilled under argon gas prior to use. The concentration of the catalyst was 0.05 mol/L of Ti(O-*n*-Bu)$_4$, and the ratio of AlEt$_3$ to Ti(O-*n*-Bu)$_4$ was 4.0. The catalyst solution was aged for 30 min at room temperature. The apparatus and procedure employed were the same as those of the previous work except for the polymerization temperature.[5] The polymerization temperature was controlled by covering a Schlenk flask with an appropriate amount of crushed dry ice and by circulating nonfreezing ethanol through an outer flask which enveloped the Schlenk flask. The temperature was monitored through a thermometer located under the flat-bottom container for the catalyst solution. The initial acetylene pressure was 500−600 Torr, and polymerization time was 5 min. After the polymerization, the H-PA film was carefully stripped away from the container and washed with toluene several times under argon gas and then dried on a Teflon sheet under vacuum for 2 h at room temperature. Note that the toluene used for washing the film was cooled by dry ice to prevent the thermal isomerization of H-PA. The dried film was kept under argon in a refrigerator at −20 °C before measurements.

**Results and Discussion.** *SEM Image and Cis Content of H-PA.* H-PAs were synthesized in N*-LCs containing the chiral dopants (*R*)- and (*S*)-2,2′-PCH506-binaphthyl. These will be abbreviated as (*R*)-H-PA and (*S*)-H-PA, respectively. Figure 2 shows the SEM image of *cis*-rich (*S*)-H-PA (*cis* content: 70%) synthesized in system 2 at −30 °C. Spiral fibril morphology with right-handed screw structure was observed. It was confirmed that the screw direction of the fibrils was the same as that of H-PAs synthesized in the previous work.[5]

*Cis* and *trans* contents of the PA film were evaluated from infrared (IR) absorption peaks of *cis* and *trans* C−H

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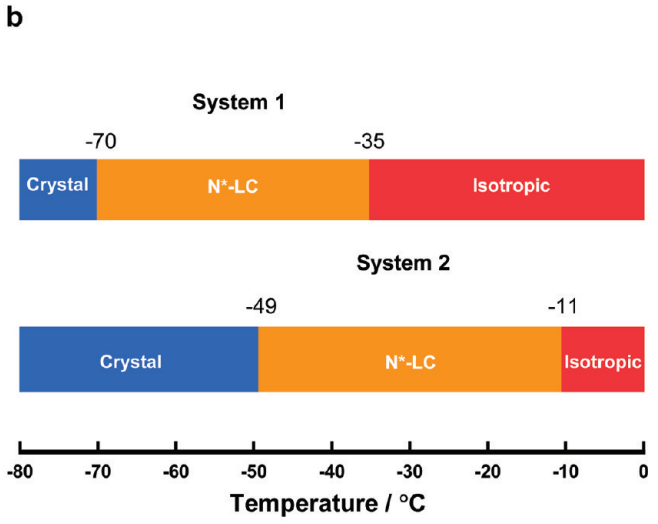
| | |
|---|---|
| N-LCs | PCH301, PCH302, PCH304, PCH32, PCH53 |
| Chiral dopant | (*R*)- or (*S*)-2,2'-PCH506-binaphthyl |
| System 1 | PCH302 : PCH304 : PCH32 : Chiral dopant = 30 : 20 : 50 : 1 (in mol ratio) |
| System 2 | PCH301 : PCH302 : PCH304 : PCH32 : PCH53 : Chiral dopant = 10 : 20 : 20 : 20 : 30 : 1 (in mol ratio) |





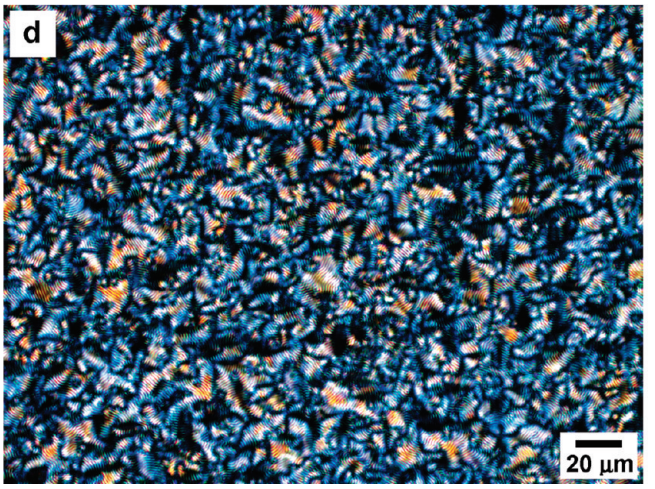



**Figure 1.** Mixing ratios between the parent N-LCs and the chiral dopants in N*-LCs, system 1 and 2 (a), phase transition temperatures (b), and POM images (c, d) of low-temperature N*-LCs:
(c) −60 °C in cooling process (system 1), helical pitch of 1.3 μm; (d) −35 °C in cooling process (system 2), helical pitch of 2.5 μm.

out-of-plane vibrations of H-PA.[2] For instance, the *cis* content was calculated by the following equation:

$$cis\ \text{content}\ (\%) = 100[1.30 \times A_{cis}/(1.30 \times A_{cis} + A_{trans})]$$

where $A_{cis}$ and $A_{trans}$ represent the absorbances of the IR peaks at 740 and 1015 $cm^{-1}$, respectively. The *cis* contents of H-PA were controlled from 63 to 93% by adjusting the polymerization temperature from −5 to −60 °C, as shown in Table 1.

*Thermal Isomerization of Cis-Rich H-PA.* H-PA thin films were synthesized on the surface of a 1 cm quartz cell. UV−vis absorption and circular dichroism (CD) spectra of the films were measured before and after the thermal isomerization. The thermal isomerization was carried out *in vacuo* by heating the films at 150 °C (which corresponds to the isomerization temperature for the transition from *cis* to *trans* form) for 30 min. The H-PA thin film prepared at −60 °C showed a reddish color, and it became blue on heating. The color change was well-explained by differences in absorption bands between the *cis* and *trans* forms. The *cis* and *trans* forms showed $\pi-\pi^*$ transition bands at 400−600 and 600−800 nm, respectively.[10] Figure 3a shows UV−vis spectra of the H-PAs. Intense and weak absorption bands were observed in the regions from 400 to 600 nm and from 600 to 800 nm, respectively, indicating formation of *cis* PA segments. However, upon heating the *cis*-rich film at 150 °C, the band ranging from 600 to 800 nm became more intense, while that from 400 to 600 nm began to disappear. This result implies that the *cis*-rich H-PA changed into *trans*-rich H-PA upon the thermal isomerization. Figure 3b shows CD spectra of (*R*)- and (*S*)-H-PA, which exhibit positive and negative Cotton effects, respectively. This implies that the *cis*-rich H-PAs have helical structures, and the screwed directions are controllable by selecting the chiral dopants used for the preparation of the N*-LCs. From comparison with previous results,[5] it was confirmed that the (*R*)- and (*S*)-H-PA have left- and right-handed helical structures, respectively. Of particular interest is the fact that the signs of Cotton effects remained unchanged even after the thermal heating at 150 °C, which corresponded to the thermal isomerization from the *cis* to *trans* form. This indicates that the screw direction of the *cis*-rich H-PA was preserved after the thermal isomerization.

Chemical doping of the H-PAs was carried out by exposing the films to iodine vapor. Electrical conductivities were

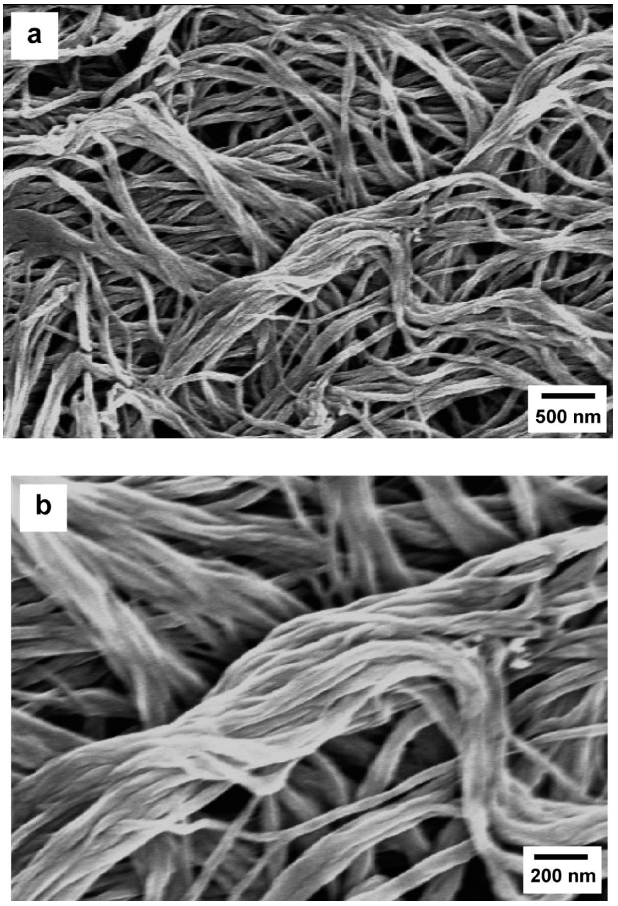
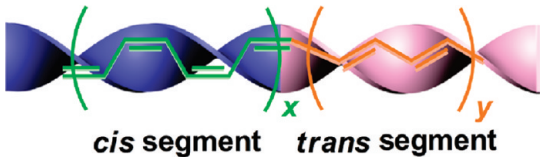



**Figure 2.** *Cis*-rich (*S*)-H-PA (*cis* content: 70%) synthesized in system 2 at −30 °C.

**Table 1. Relationship between Polymerization Temperatures and *Cis* Contents of Helical Polyacetylenes**




| polymerization temperature (°C) | *cis* contents, *x* (%) |
|---|---|
| 23[a] | ~50 |
| −5[a] | 63 |
| −20[b] | 70 |
| −50[c] | 83 |
| −60[c] | 93 |

[a] N*-LC including the equimolar mixture of PCH302 and PCH304 was used as a reaction field.[5] [b] N*-LC of system 2. [c] N*-LC of system 1.

measured with the four-probe method. The maximum value of the conductivity of *cis*-rich (*cis* content: 70%) and *trans*-rich (*trans* content: 90%) H-PA films was $6.5 \times 10^3$ and $1.9 \times 10^3$ S/cm, respectively. The higher conductivity of the *cis*-rich film is similar to the case of typical non-H-PA. The *cis*-rich film was relatively free from cleavage and/or kinks in the polymer chain, leading to a higher mobility of the charge carrier compared with the *trans*-rich film.

In summary, we first synthesized *cis*-rich H-PA in a low-temperature N*-LC reaction field. The N*-LC was prepared by adding chiral dopants into the low-temperature N-LC. The LC temperatures in two kinds of N*-LCs, system 1 and

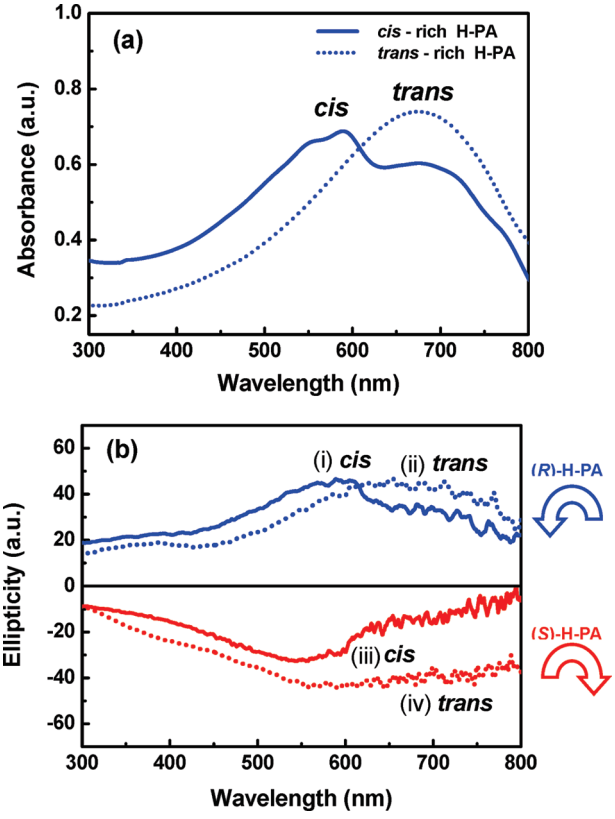



**Figure 3.** UV−vis (a) and CD spectra (b) of (*R*)-H-PAs (i, ii) and (*S*)-H-PA (iii, iv). *Cis* and *trans* forms show $\pi-\pi^*$ transition bands in the region from 400 to 600 nm and from 600 to 800 nm, respectively. (i, iii) *Cis* form; (ii, iv) *trans* form.

2, were −70 to −35 °C and −49 to −11 °C, respectively. It was found that the *cis* content of H-PA could be controlled from 63 to 93% by changing the polymerization temperature from −15 to −65 °C. *Cis*-rich (*R*)- and (*S*)-H-PA films exhibited positive and negative Cotton effects in the region of the $\pi-\pi^*$ transition of the polymer chain, indicating that the *cis*-rich H-PAs have one-handed helical structures. The helical structure formed in *cis*-rich H-PA is preserved in the *trans* form after the thermal isomerization. The present *cis*-rich H-PA should be available for the carbonization precursor of helical graphites with high conductivities.

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**Supporting Information Available:** Experimental details; synthesis of nematic liquid crystals, IR absorption spectrum and electrical conductivity of helical polyacetylene. This material is available free of charge via the Internet at http://pubs.acs.org.

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