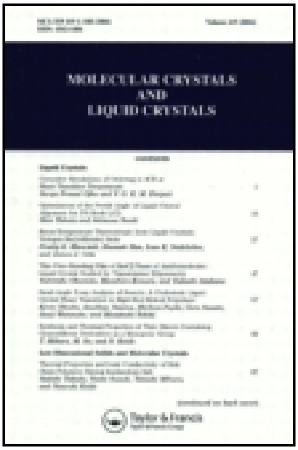

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Synthesis of Vertically Aligned Helical Polyacetylene Films in Homeotropic Chiral Nematic Liquid Crystals

Guangzhe Piao [a] [b] , Toshihiro Otaka [a] , Tetsuya Sato [a] , Kazuo Akagi [a] [b] & Mutsumasa Kyotani [b] [c]

[a] Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, 305-8573, Japan

[b] Center for Tsukuba Advanced Research Alliance (TARA), University of Tsukuba, Tsukuba, Ibaraki, 305-8577, Japan

[c] National Instituted of Materials and Chemical Research, Tsukuba, Ibaraki, 305-0046, Japan

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Synthesis of Vertically Aligned Helical Polyacetylene Films in Homeotropic Chiral Nematic Liquid Crystals

GUANGZHE PIAO [ab], TOSHIHIRO OTAKA[a], TETSUYA SATO[a], KAZUO AKAGI[ab] and MUTSUMASA KYOTANI[bc]

[a]*Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305–8573, Japan,* [b]*Center for Tsukuba Advanced Research Alliance (TARA), University of Tsukuba, Tsukuba, Ibaraki 305–8577, Japan and* [c]*National Instituted of Materials and Chemical Research, Tsukuba, Ibaraki 305–0046, Japan*

Vertically aligned helical polyacetylene thin films were synthesized by adding a chiral dopant into homeotropic nematic LC solvent to induce chiral nematic phase with homeotropic orientation. A scanning electron microscope (SEM) measurements showed that twisted polyacetylene fibrils are grown along the direction of film thickness, giving vertically aligned helical fibrillar morphology.

Keywords: helical polyacetylene; vertical alignment; homeotropic orientation; nematic liquid crystal; chiral nematic liquid crystal

INTRODUCTION

We previously developed liquid crystal (LC) polymerization method for highly oriented polyacetylene (PA) films by using nematic LC as a polymerization solvent for soluble Ziegler-Natta catalyst [1-5]. Recently, we synthesized helical PA under chiral nematic (N*) LC reaction field. The N* LC was prepared by adding an asymmetric center-including phenylcyclohexyl (PCH) derivative, (*R*)- or (*S*)- 4-(*trans*-4 -*n*- propylcyclohexyl) -2-octyloxybenzene [(*R*)- or (*S*)-PCH308*] and an axially chiral binaphthol derivative, (*R*)- or (*S*)-1, 1' -bi-naphthyl-2,2'- bis [*p*-(*trans*-4-*n*-pentylcyclohexyl) phenoxy-1-hexyl] ether [(*R*)- or (*S*)-PCH506-binol], as a chiral dopant, into an equi-weighted mixture of two nematic LCs, 4-(*trans*-4-*n*-propylcyclohexyl) -ethoxybenzene (PCH302) and 4-(*trans*-4-*n*-propylcyclohexyl) - buthoxybenzene (PCH304) [6-7]. Moreover, we found that chiroptical titanium complexes induce the N* phase when dissolved in nematic LCs and they are catalytically active for synthesizing helical PA [8]. Observed fibril orientation of the PA films was mostly parallel to the film plane because of homogeneous orientation of the N* LCs. If the N* LC makes a homeotropic orientation, a vertically aligned helical PA film can be synthesized. Very recently, we found that an addition of newly synthesized LCs with two PCH mesogenic cores, 1,6-bis-[(4-*trans*-4-*n*-propylcyclohexyl) phenoxy] hexane [$(PCH30)_2 6$], 1,6-bis- [(4-*trans*-4-*n*-pentylcyclohexyl) phenoxy]hexane [$(PCH50)_2 6$] or 1,8-bis-[(4-*trans*-4-*n*- pentylcyclohexyl)phenoxy]octane [$(PCH50)_2 8$] into nematic LC, 4-(*trans*-4-*n*-pentylcyclohexyl) hexyloxy-benzene (PCH506), induced the homeotropic orientation. Subsequently, a chiral dopant was added into the homeotropic nematic LC to prepare homeotropic N* phase.

In this paper, we report the morphology and circular dichroism (CD) spectrum of the helical PA film synthesized in the homeotropic N* LC.

SEM measurements show that twisted PA fibrils are grown along the direction of film thickness, giving vertically aligned helical fibrillar morphology. The CD spectrum of the PA film shows positive or negative Cotton effect in the region of $\pi \rightarrow \pi^*$ transition of PA chain, indicating that the PA chain itself is also helically screwed.

EXPERIMENTAL

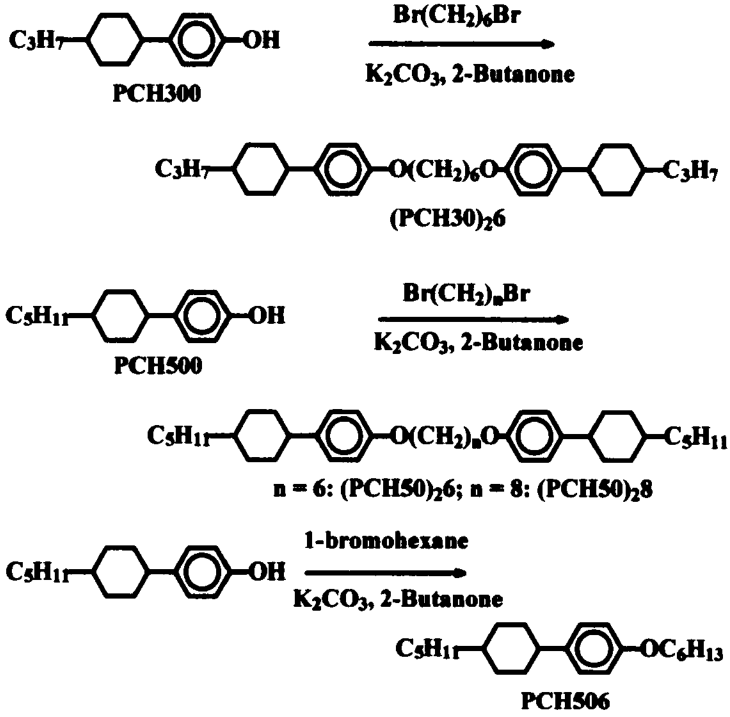
General

NMR spectra were recorded on a JEOL EX-270 spectrometer in $CDCl_3$. Circular dichroism spectra were recorded with a Jasco J-720 spectrophotometer. Thermal transition characteristics were determined with a Perkin-Elmer differential scanning calorimeter (DSC 7) at a rate of 10 ℃ min $^{-1}$ under argon atmosphere. The phase changes were also observed by a polarizing optical microscopy constructed with an Olympus SZH-PT system with a Linkam TM-600 hot-stage and controller. SEM micrographs were taken on a TOPCOM Model DS-720 scanning electron microscope.

$(PCH30)_2 6$, $(PCH50)_2 6$, $(PCH50)_2 8$ and PCH506 were synthesized by the Williamson etherification reaction shown in Scheme 1. (*R*)- and (*S*)-PCH506-binol were synthesized through the Williamson etherification reaction of (*R*)- and (*S*)- Binol with PCH derivatives [6], respectively. (*R*)- and (*S*)- PCH308* were synthesized by Mitsunobu reaction of (*S*)- and (*R*)-2-octanol with PCH300, respectively [7].

Synthesis of LCs

$(PCH30)_2 6$. To a solution of PCH300 (5.0 g, 22.4 mmol) and 1, 6 dibromohexane (3.0g, 12.3 mmol) in 2-butanone (100 ml) was added



Scheme 1

K_2CO_3 (6.4g, 45.7 mmol). The resulting reaction mixture was refluxed under argon for 24 h. After it was cooled to room temperature, the mixture was filtrated. The crude residue obtained after removal of the solvent was extracted with ether. The extract was dried with anhydrous $MgSO_4$. After evaporation of the solvent, the product was purified on a silica gel column (hexane: EtOAc=1: 4). A white solid was obtained in a yield of 75.7 % (4.4g). ^1H NMR (270 MHz $CDCl_3$): δ 7.13 (d, 4H, J = 8.6 Hz), 6.85 (d, 4H, J = 8.6 Hz), 3.97 (t, 4H, J = 6.4 Hz), 2.44 (m, 2H), 1.87~0.87 (m, 40H), ^{13}C NMR (67.8 MHz $CDCl_3$): δ 157.2, 140.0, 127.6, 114.2, 67.8, 43.7, 37.3, 37.3, 34.6, 33.8, 33.4, 32.2, 29.3, 26.7, 25.9, 22.7, 14.1. Elemental analysis: Calc. for $C_{36}H_{54}O_2$: C 83.34, H 10.49, O 6.17; Found C 83.20, H 10.32.

(PCH50)$_2$6 and (PCH50)$_2$8 were synthesized by the same procedure as that of (PCH30)$_2$6 by the Williamson etherification reaction of PCH500 with 1,6-dibromohexane and 1,8-dibromooctane, respectively. (PCH50)$_2$6: ^{1}H NMR (270 MHz $CDCl_3$): δ 7.11 (d, 4H, J = 8.6 Hz), 6.82 (d, 4H. J = 8.6 Hz), 3.93 (t, 4H, J = 6.4 Hz), 2.43 (m, 2H), 1.87 ~ 0.87(m, 48H). ^{13}C NMR (67.8 MHz $CDCl_3$): δ 157.2, 140.0, 127.6, 114.7, 67.8, 43.7, 37.4, 37.3, 34.6, 33.7, 32.2, 29.3, 26.7, 25.9, 22.7, 14.1. Elemental analysis: Calc. for $C_{40}H_{62}O_2$: C 83.56, H 10.87, O 5.57; Found C 83.13, H 10.69.

(PCH50)$_2$8: ^{1}H NMR (500 MHz $CDCl_3$): δ 7.10 (d, 4H. J = 8.6Hz), 6.81 (d, 4H J = 8.6 Hz) 3.92 (t, 4H, J = 6.50 Hz), 2.40 (m, 2H), 1.87 ~ 0.87 (m, 52H); ^{13}C NMR (125 MHz CDCl3): δ 157.1, 140.0, 127.6, 114.7, 67.6, 43.7, 37.4, 37.3, 34.6, 33.7, 33.4, 32.2, 30.2, 29.1, 26.7, 25.1, 22.7, 14.1. Elemental analysis: Calc. for $C_{42}H_{66}O_2$: C 83.66, H 11.03, O 5.31; Found: C 83.50, H 11.06.

PCH506 was synthesized by the same procedure as that of (PCH50)$_2$6 by using 1- bromohexane. ^{1}H NMR (270 MHz $CDCl_3$): δ 7.10 (d, 2H, J = 8.6 Hz). 6.81 (d, 2H. J = 8.6 Hz), 3.92 (t, 2H, J = 6.4 Hz), 2.40 (m, 1H), 1.87 ~ 0.87 (m, 31H); ^{13}C NMR (67.8 MHz $CDCl_3$): δ 157.2, 140.0, 127.6, 114.7, 68.0, 60.7, 43.8, 37.4, 34.6, 33.7, 33.4, 32.3, 31.6, 30.9, 29.4, 26.7, 25.8, 22.7, 14.1. Elemental analysis: Calc. for $C_{23}H_{38}O_2$: C 83.57, H 11.59, O 4.84; Found: C 83.69, H 11.59.

Preparation of N* LCs

PCH506 showed a Schlieren texture characteristic of nematic phase in heating process, and a nematic phase followed by a fan-shaped texture assignable to smectic A phase in cooling process. Both (PCH50)$_2$6 and (PCH50)$_2$8 showed two unidentified smectic phases and a nematic

Table I Phase transitions of the LCs

Compound	Phase transition temperature (℃)
PCH506	C 38 N 45 I
	I 44 N 35 S_A 15 C
(PCH30)$_2$6	C 130 N 147 I
	I 140 N 74 I
(PCH50)$_2$6	C 106 S_1 118 S_2 131 N 142 I
	I 141 N 130 S_2 115 S_1 85 C
(PCH50)$_2$8	C 106 S_1 118 S_2 131 N 142 I
	I 141 N 130 S_2 115 S_1 85 C

C: crystalline solid, I: isotropic liquid, N: nematic phase, S_A: smectic A phase, S_1 and S_2: unidentified smectic phases.

phase, and (PCH30)$_2$6 showed a nematic phase in both heating and cooling processes, respectively. Phase transitions of the LCs were characterized by polarizing optical microscope and DSC. Phase transition temperatures obtained by DSC are summarized in Table I. Since the temperature ranges of the LC phases were not suitable for safe acetylene polymerization, the mixed system was prepared by adding 5 weight-% of (PCH30)$_2$6, (PCH50)$_2$6 or (PCH50)$_2$8 to PCH506. The mixture of LCs showed nematic phase in heating process and nematic and smectic phases in cooling process. The temperature range of the nematic phase of the mixture was slightly widened compared with that of PCH506 (Table II).

TABLE II Phase transitions of the mixtures of LCs

	Mixture of LCs	Phase transition temperature (℃)
I	PCH506 + (PCH30)$_2$6	C 39 N 78 I
		I 53 N 27 S_1 21 C
II	PCH506 + (PCH50)$_2$6	C 37 N 55 I
		I 54 N 31 S_1 20 C
III	PCH506 + (PCH50)$_2$8	C 36 S_1 38 N 51 I
		I 50 N 35 S_1 -3 C

See the footnote of Table I.

Next, the N* LC was prepared by adding 5 weight % of (*R*)- or (*S*)-PCH506-binol and (*R*)- or (*S*)- PCH308*, as chiral dopants, into the mixtures of I [PCH506 + $(PCH30)_2 6$], II [PCH506 + $(PCH50)_2 6$] and III [PCH506 + $(PCH50)_2 8$]. The N* phase was confirmed by characteristic finger-printed texture. Temperature ranges of the N* phase were 36 ~ 46 ℃ and 32 ~ 44 ℃ in heating and cooling process, respectively.

Polymerization of acetylene

The N* LCs were used as solvents for Ziegler-Natta catalyst consisting of $Ti(O\text{-}n\text{-}Bu)_4$ and Et_3Al. Typical concentration of the catalyst was 50 mmol / l of $Ti(O\text{-}n\text{-}Bu)_4$ and the ratio of Et_3Al to $Ti(O\text{-}n\text{-}Bu)_4$ was 4.0. The catalyst solution was aged for 30 min at room temperature and was moved using a syringe into a flat-bottom container inside Schlenk flask [4]. The polymerization was carried out by introducing acetylene gas onto the catalyst solution. Polymerization temperature was kept 35 ~ 40 ℃ to maintain the N* phase. The initial acetylene pressure was 20 ~ 60 Torr and the polymerization time was 2 ~ 10 min. The PA film formed was washed with purified toluene several times, and with methanol solution containing 1N hydrochloric acid and THF. Then the film was vacuum-dried on a Teflon film. Thickness of the films thus synthesized was in the range of 3 to 6 μm with both surfaces of dull silver shine.

RESULTS AND DISCUSSION

Homeotropic Orientation of the Liquid Crystals

Fig. 1 shows polarizing optical micrographs of the catalyst-containing LC mixture of II (a) and the catalyst-containing LC mixture of II added with the (*R*)- PCH308* (b) at 40 ℃ in cooling process. The dark domain indicates the homeotropic orientation. The N* phase was maintained between 28 ~ 43 ℃ in cooling process, even after the addition of the catalyst into the LC mixtures of I, II, and III including chiral dopants, such as (*R*)- or (*S*)-PCH506-binol and (*R*)- or (*S*)-PCH308*.

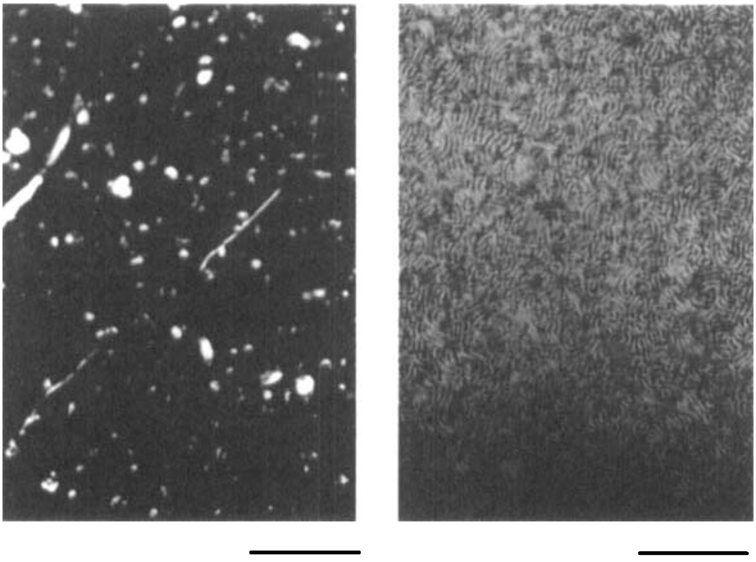
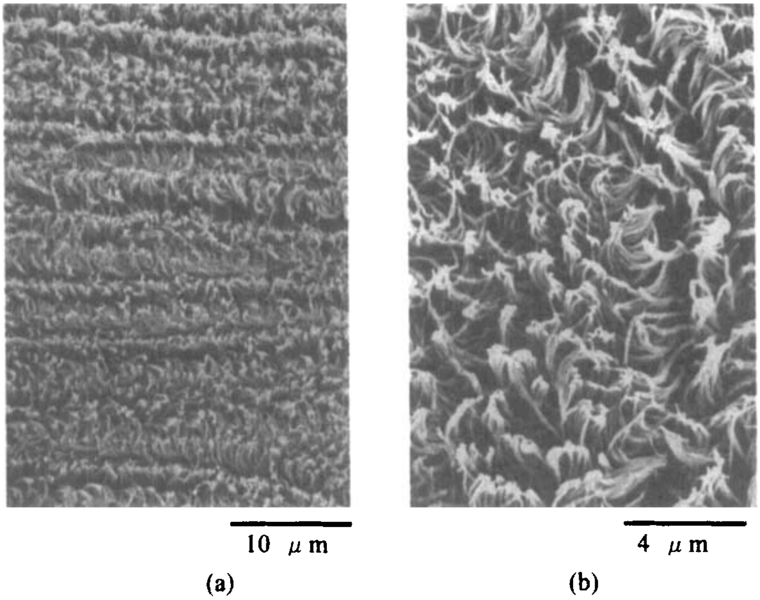


FIGURE 1 Polarizing optical micrographs of the catalyst-containing LC mixture of II (a) and the catalyst-containing LC mixture of II added with the (*R*)- PCH308* (b) at 40 ℃ in cooling process.
See Color Plate IV at the back of this issue.

Characterization of Helical PA Films

Fig. 2 shows SEM micrographs of PA film synthesized under a N* LC solvent, PCH506 + $(PCH30)_2 6$ + (*S*)-PCH506-binol. In a micrograph taken at lower magnification (Fig 2 (a)) one can see a helical morphology originating from a domain texture of the chiral LC phase.

Fig. 2 (b) shows twisted fibrils that are grown in vertical direction through the film thickness. This observation suggests that the homeotropic orientation of the LC mixture of I, [PCH506 and $(PCH30)_2 6$], is maintained even after addition of the chiral dopant and the catalyst. The same morphology was also observed in a film synthesized under the other homeotropic N* LCs [9].



(a) (b)

FIGURE 2 SEM images of helical PA synthesized under N* LC solvent, PCH506 + $(PCH30)_2 6$ + (*S*)-PCH506-binol at 40℃.
See Color Plate V at the back of this issue.

It is found that the bundles of PA fibrils synthesized under N* LCs including by (*R*)- and (*S*)-PCH506-binol are screwed with left-handed and right-handed manners, respectively. As shown in Fig. 3, the (*R*)- and (*S*)- PA films exhibited positive and negative Cotton effects, respectively, in the region from 550 to 800 nm corresponding to $\pi \rightarrow \pi^*$ transition of PA chain. The result indicates that PA chain itself is also helically screwed.

The electrical conductivity of the film synthesized under N* LC solvents of PCH506 + $(PCH30)_2 6$ + (*R*)-PCH506-binol was 290 Scm^{-1} at room temperature after iodine doping. Since the measurement was carried out by the usual four-probe method, namely, four platinum wires were attached on the surface of the film using carbon paste, the direction of the electrical current might be perpendicular to the conjugated chains. In contrast, the conductivity of the helical PA film with parallel (homogeneous) orientation to the substrate was 1.5 ~ 1.8×10^3 Scm^{-1} after iodine doping.

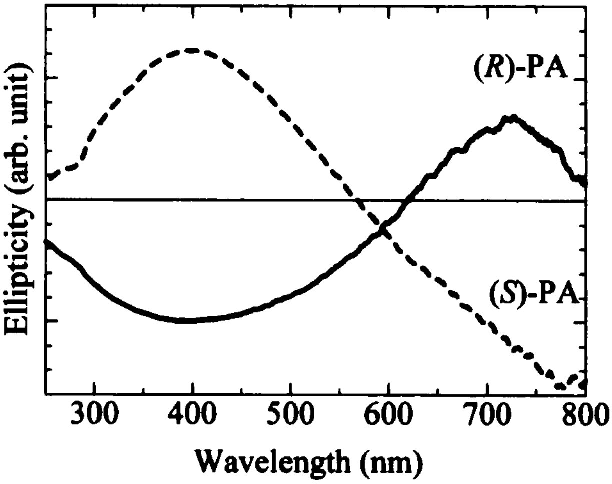


FIGURE 3 CD spectra of helical PA films. (*R*)- and (*S*)- PA indicate polyacetylenes synthesized under N* LC solvents of PCH506 + $(PCH30)_2 6$ + (*R*)-PCH506-binol and PCH506 + $(PCH30)_2 6$ + (*S*)-PCH506-binol, respectively.

CONCLUSIONS

We have constructed a novel vertical N* LC reaction field for synthesis of vertically aligned helical PA film. The vertical N* LC was prepared by adding chiral dopant, (*R*)- or (*S*)-PCH506-binol and (*R*)- or (*S*)-PCH308* into the homeotropic nematic LCs consisting of PCH506 + $(PCH30)_2 6$, PCH506 + $(PCH50)_2 6$, and PCH506 + $(PCH50)_2 8$. It is expected that the present polymerization method using the homeotropic LC might be applicable for synthesis of other kinds of π-conjugated polymers with vertically aligned morphology.

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