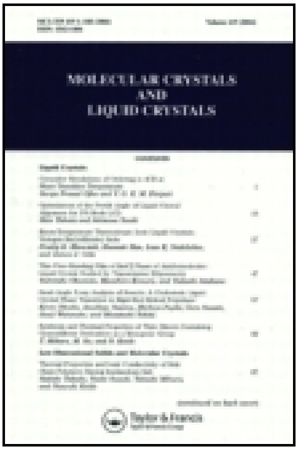

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Helical Polyacetylene Synthesized under Asymmetric Reaction Field Constructed with Chiral Nematic Liquid Crystals

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Helical Polyacetylene Synthesized under Asymmetric Reaction Field Constructed with Chiral Nematic Liquid Crystals

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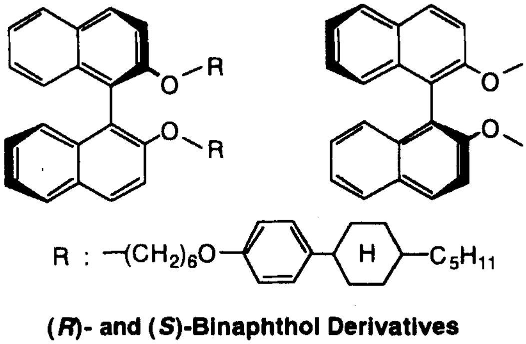
Helical polyacetylene was synthesized under asymmetric reaction field constructed with chiral nematic liquid crystal (LC). The chiral nematic LC was prepared by adding a chiral phenylcyclohexyl (PCH) derivative, (*R*)- or (*S*)-PCH308*, as a dopant, into an equi-weighted mixture of two kinds of nematic LCs. Acetylene polymerization was carried out with $Ti(O\text{-}n\text{-}Bu)_4 - Et_3Al$ catalyst dissolved in the chiral nematic LC. It is found from SEM measurements that the polyacetylene films is composed of helical fibrils that are bundles of polyene chains. CD spectrum of the polyacetylene film showed positive or negative Cotton effect, depending on the helicity of the chiral nematic LC.

Keywords: helical polyacetylene; chiral dopant; chiral nematic solvent; morphology; circular dichroism; electrical conductivity

INTRODUCTION

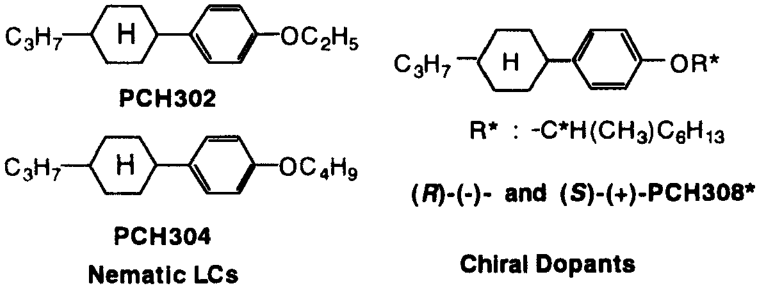
It has been generally accepted so far that polyacetylene has a planar structure consisting of linear conjugated chains, which is irrespective of *cis* and *trans* isomeric forms [1]. If the polyacetylene might be helical, it could exhibit peculiar physicochemical properties by virtue of screw structure. Very recently, we synthesized helical polyacetylene under the chiral nematic liquid crystal (N* LC) [2]. The N* LC was prepared by adding the axially chiral (*R*)- or (S)-2,2'-binaphthol derivative, as a chiral dopant, into a mixture of two kinds of nematic

LCs. It was found that the screw direction of helical polyacetylene was strictly determined by that of the N* LC.



SCHEME 1

The present study is aimed to elucidate that the N* LC available for synthesis of helical polyacetylene can also be prepared with other kind of chiral dopant, except the axially chiral binaphthol derivatives (Scheme 1). Here we subjected asymmetric center including phenylcyclohexyl derivatives, designated as (*R*)- and (*S*)-PCH308* (Scheme 2). Through characterizations of catalyst dissolved in N* LC solvent and polyacetylene films, the feasibility of the PCH308* as the chiral dopants was examined.

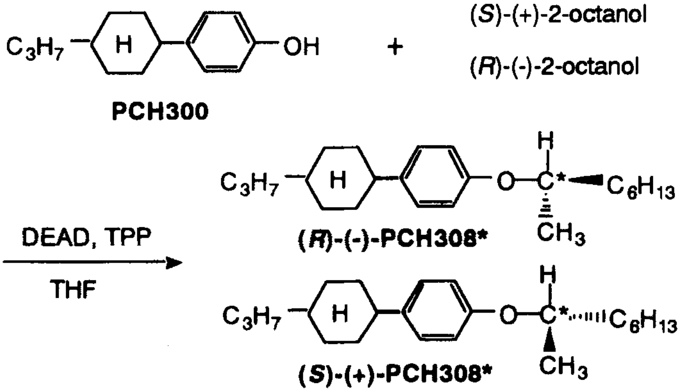


SCHEME 2

RESULTS AND DISCUSSION

Synthesis of chiral dopants

Coupling reaction between *p*-(*trans*-4-propylcyclohexyl)phenol (PCH300) and (*S*)-(+)-2-octanol or (*R*)-(-)-2-octanol was carried out according to Mitsunobu reaction with diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP), producing a chiral phenylcyclohexyl derivative, (*R*)-(-)-, or (*S*)-(+)-2-(4-(*trans*-4-*n*-propylcyclohexyl)phenoxy)octane. (Yields : 29.3 and 28.4 %). For simplicity, they are abbreviated as (*R*)-PCH308* and (*S*)-PCH308*, respectively. Note that this kind of coupling reaction is of S_N2 type, the steric configuration is inversed, as shown in Scheme 3.



SCHEME 3

Fig. 1 shows CD spectra of (*R*)- and (*S*)-PCH308*, where negative and positive Cotton effects are observed, respectively. Specific rotatory powers, $[\alpha]_D$, for (*R*)- and (*S*)-PCH308* were respectively -9.2° and +9.2° (c = 1, THF). It should be noted that although the absolute values of the specific rotatory powers are substantially smaller than those of chiral binaphthol derivatives ($[\alpha]_D$= +24.0°), the chiral PCH308* derivatives were confirmed to be feasible for the chiral dopant to the nematic LC, as will be shown below.

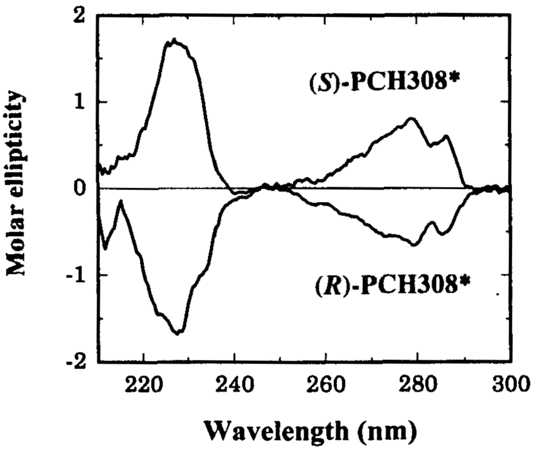


FIGURE 1 CD spectra of (*R*)- and (*S*)-PCH308* in cyclohexane.

Next, the chiral nematic LC was prepared by adding the 5 weight% of the (*R*)- or (*S*)-PCH308* into the equi-weighted mixture of nematic LCs, PCH302 and PCH304 [3-6]. To elucidate the screw direction of the N* LC, the miscibility test was carried out using cholesteryl chloride that is a representative cholesteric (N*) LC with right handed screw direction. The mixture of the (*R*)-N* LC and cholesteryl chloride showed no change in optical texture, keeping a chiral nematic phase. In contrast, the mixture of the (*S*)-N* LC and cholesteryl chloride lost the striae characteristic of a chiral nematic phase in the optical microscope, yielding instead a feature corresponding to an ordinary nematic phase. The results demonstrate that the screw directions of the (*R*)- and (*S*)-N* LCs are the same as and opposite to that of cholesteryl chloride, respectively. Namely, the (*R*)- and (*S*)-N* LCs are screwed clockwise and counterclockwise, respectively.

Preparation of catalyst and acetylene polymerization

The (*R*)- and (*S*)-N* LCs were used as solvents for Ziegler-Natta catalyst consisting of $Ti(O\text{-}n\text{-}Bu)_4$ and Et_3Al. The concentration of $Ti(O\text{-}n\text{-}Bu)_4$ was 20 mmol/l, and the mole ratio of the cocatalyst to catalyst, $[Et_3Al]$ / $[Ti(O\text{-}n\text{-}Bu)_4]$, was 4.0.

Fig. 2 shows polarizing optical micrographs of (*R*)- and (*S*)- N* LC systems including Ti(O-*n*-Bu)$_4$ - Et$_3$Al catalyst. In both cases were observed striated Schlieren textures characteristic of chiral nematic phases. The catalyst solution was aged for 0.5 hour at room temperature and was moved using a syringe into the flat-bottom container inside Schlenk flask [5,6].

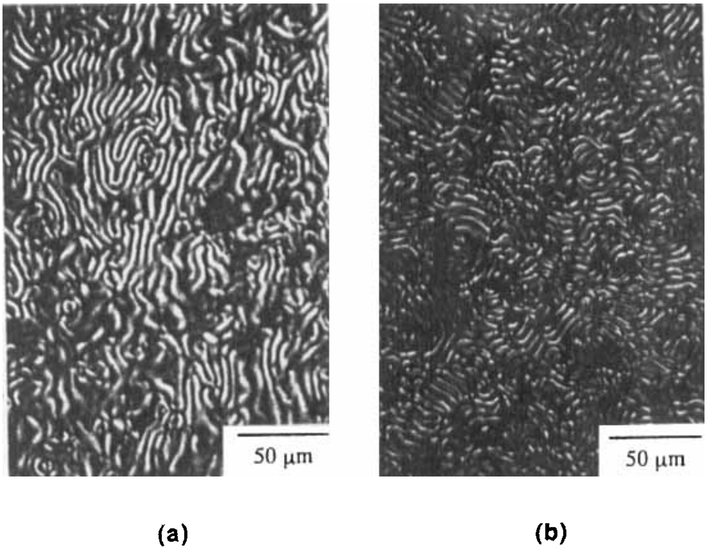


FIGURE 2 Polarizing optical micrographs of (*R*)-(**a**) and (*S*)-(**b**) N* LC systems including Ti(O-*n*-Bu)$_4$ - Et$_3$Al catalyst.

The polymerization was carried out by introducing acetylene gas onto the catalyst solution. The polymerization temperature was kept 18 °C to maintain the chiral nematic phase. The initial acetylene pressure was 130 Torr, and the polymerization time was 5 to 8 minutes. After the polymerization, the polyacetylene film was carefully stripped off from the container and washed with toluene and subsequently with 1N HCl - methanol mixture under argon gas. The film was dried through vacuum pumping on a Teflon sheet and stored in a freezer at -20 °C.

Characterization of helical polyacetylene

Fig. 3 shows scanning electron micrographs of polyacetylene films. It is found that the bundles of polyacetylene fibrils synthesized under the (*R*)- and (*S*)-N* LCs are screwed clockwise and counterclockwise, respectively. Besides, the screw directions of the bundles of the fibrils coincide with those of the N* LCs used as polymerization solvents. The locally aligned fibril morphology is due to spontaneous orientation within the LC domain.

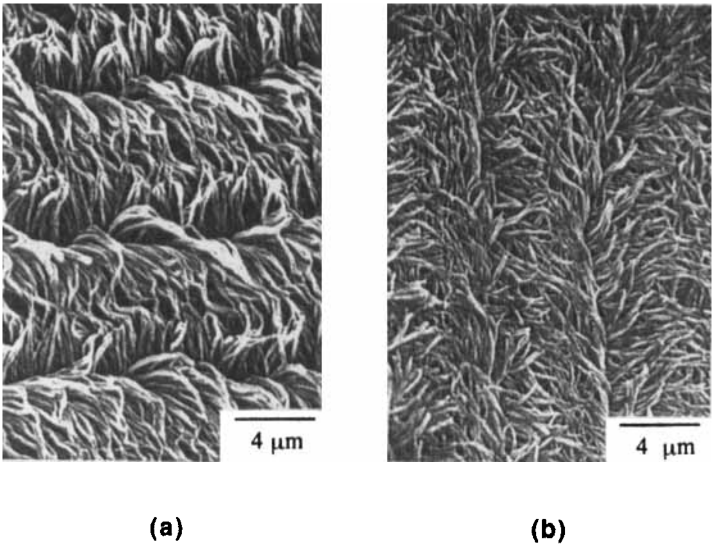


FIGURE 3 Scanning electron micrographs photographs of polyacetylenes films synthesized under (*R*)- (**a**) and (*S*)- (**b**) N* LCs, respectively.

As seen in Fig. 4, the (*R*) and (*S*)-polyacetylene films showed negative and positive Cotton effects, respectively, in the region from 400 to 800 nm corresponding to $\pi \rightarrow \pi^*$ transition of polyacetylene chain. This indicates that the polyacetylene chain itself is also helically screwed. The right handed direction of the (*R*)-polyacetylene is determined by the (*R*)-N* LC; Similarly, the left handed direction of the (*S*)-polyacetylene by the (*S*)-N* LC.

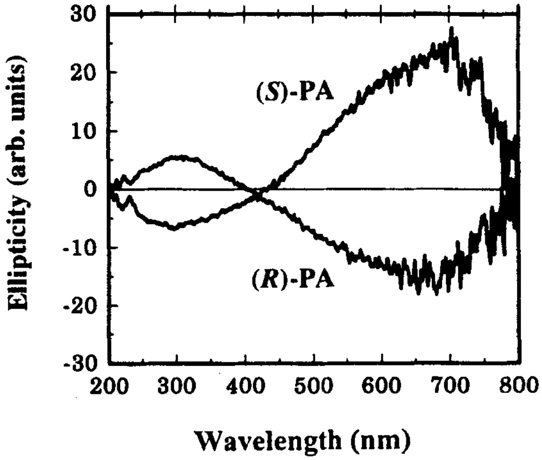


FIGURE 4 CD spectra of helical polyacetylene films. (*R*)-PA and (*S*)-PA indicate polyacetylenes synthesized under (*R*)- and (*S*)- N* LCs, respectively.

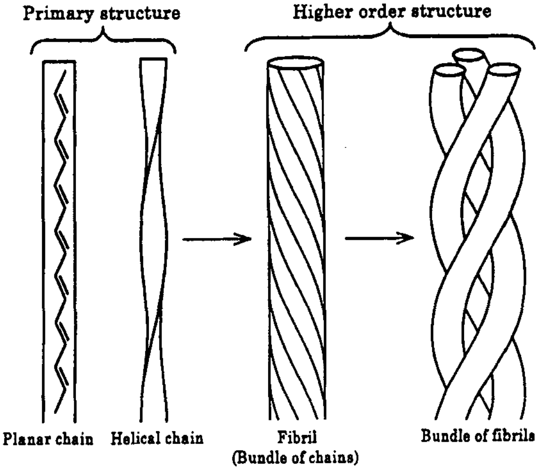


FIGURE 5 Primary and higher order structures of helical polyacetylene.

In Fig. 5 is schematically described the hierarchy of primary and higher order structures of the helical polyacetylene. The helical polyacetylene chains are bundled through van der Waals interaction, forming the helical fibrils which have the same screw directions as those of the polyacetylene chains.

Lastly it is worth noting that the present polyacetylene film showed high electrical conductivities of 1.5 ~ 4.0 × 10^3 S/cm after iodine doping. The high conductivity and the helical structure may allow us to expect that the present polyacetylene could be available for molecular solenoid, in which an induced magnetic field is generated by virtue of solenoidal current in molecular level. As an another application, the helical polyacetylene is anticipated to be a second-order nonlinear optical material, as well as a third-order nonlinear one [7].

CONCLUSION

Helical polyacetylenes were synthesized under asymmetric and anisotropic reaction field constructed with the chiral nematic LC. It is expected that the present polymerization method using the chiral nematic LC might be applicable even for synthesis of other kinds of helical π-conjugated polymers without chiral substituents.

Acknowledgements

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