



Synthesis of a pyrimidine-based new chiral inducer for construction of cholesteric liquid crystal electrolyte solution and its electrochemical polymerization, and stimulated emission like interference



Aohan Wang, Kohsuke Kawabata, Hirotugu Kawashima, Hiromasa Goto*

Faculty of Pure and Applied Sciences, Division of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

ARTICLE INFO

Article history:

Received 25 February 2013

Received in revised form

20 April 2013

Accepted 22 April 2013

Available online 1 May 2013

Keywords:

Chiral inducer
Laser diffraction
Pyrimidine

ABSTRACT

Pyrimidine-based chiral compounds were successfully synthesized via Mitsunobu reaction. The chiral molecules with rigid molecular shape can function as chiral inducers (chiral dopant) to prepare cholesteric liquid crystal (CLC) electrolyte solutions. We carried out electrochemical polymerization in the CLC electrolyte solution thus prepared with the chiral inducer. The polymerization in the CLC afforded chiroptically active polymer films. The synthesis of the pyrimidine-based chiral inducer, electrochemical polymerization, and observation of a surface image of the polymer were carried out. It is noted that the polymer shows laser diffraction in the visible range due to a periodic pattern produced by imprinting of structural chirality of the CLC electrolyte solution. The laser diffraction patterns are multiple circles, implying occurrence of stimulated emission via periodic patterns of the cholesteric order.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Liquid crystals (LCs) have both crystal order and fluidity similar to liquids [1–10]. Nematic LCs have especially low viscosity. They can be used as a reaction solvent [11,12]. In this case, the addition of non-LC compounds to LC materials destroys its liquid crystallinity, resulting in a transformation into isotropic liquid or solid, whereas the addition of a small amount of optically active molecules to non-chiroptically active nematic LC produces cholesteric liquid crystal (CLC) with helical aggregation structure [13,14].

CLC is a twisted nematic phase of liquid crystal in which the director orientation is rotated progressively to form a helical structure [15–17]. The helical aggregation of rod-like molecules in cholesteric LC results in periodicity and the three-dimensional (3D) molecular arrangement produces structural chirality.

The additives to the nematic LC are referred to as chiral inducers (chiral dopants). Chiral inducers require 1) good solubility in nematic LCs, 2) chiral molecular structure for the induction of cholesteric phase, and 3) compatibility with nematic LC to maintain liquid crystallinity after the addition of the inducer into matrix nematic LCs.

To prepare a compound which covers these requirement as chiral inducers, we introduced a chiral moiety into the terminal of a rigid molecule having fluorine atom. A rigid chiral mesogenic

molecule can be expected to function as a chiral inducer because of rigid molecular shape (indicative of good compatibility in nematic LC consisting of rigid molecules), good chiral induction property with the aid of polar fluorine atom directed perpendicular to the molecular axis, and compatibility with nematic LC.

Electrochemical polymerization has been carried out to prepare π -conjugated polymers with electro-activity [18–21]. Electrochemical polymerization in CLC is possible by using indium-tin-oxide (ITO) coated sandwich polymerization method [22,23]. In the present study, the pyrimidine-type chiral compounds are employed as a mesogen for the construction of CLC from nematic LC. Then, electrochemical polymerization in the CLC containing a monomer, electrolyte, and chiral inducer was carried out. The synthesis of the pyrimidine-based chiral inducers, the preparation of CLC electrolyte solution, its electrochemical polymerization, surface observation, and measurements of optical properties are reported in this study.

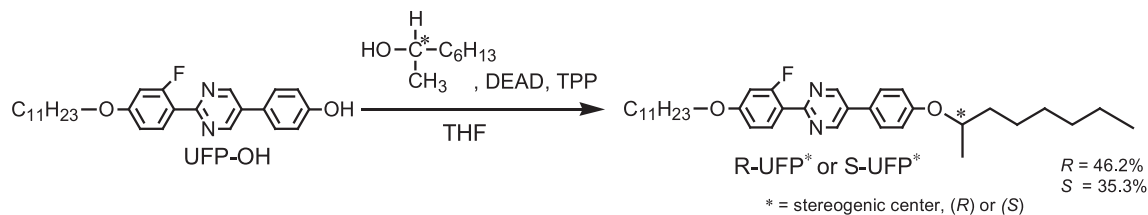
2. Experimental

2.1. Synthesis of chiral inducers

Pyrimidine derivatives having chiral center in its terminal alkyl group, 2-(2-fluoro-4-undecyloxy-phenyl)-5-[4-(1-methyl-heptyloxy)-phenyl]-pyrimidine with *R* or *S* configuration, abbreviated as *R*- or *S*-UFP*, were synthesized (Scheme 1). 4-[2-(2-Fluoro-4-undecyloxy-phenyl)-pyrimidin-5-yl]-phenol (UFP-OH) and (*R*-

* Corresponding author.

E-mail address: gotoh@ims.tsukuba.ac.jp (H. Goto).



Scheme 1. Synthesis of chiral inducers.

or (S)-octanol were coupled using diethyl azodicarboxylate (DEAD) and triphenyl phosphine (TPP) in tetrahydrofuran (THF) solution for 24 h in argon atmosphere at room temperature, according to the Mitsunobu reaction. After the reaction, the solvent was evaporated. The crude product was purified by column chromatography (silica gel, CH_2Cl_2) followed by recrystallization from ethanol to afford the target material as a white solid.

The absolute configuration of the chiral center is inverted during this $\text{S}_{\text{N}}2$ reaction, according to the Mitsunobu inversion. The chemical structure of the inducers was confirmed by ^1H NMR (Fig. 1). The proton at the chiral center showed a sextet signal at around 5 ppm, confirming the chiral fraction was introduced into the mesogen. ^{19}F NMR of S-UPF showed a signal at 113 ppm against tetrafluorotoluene as an internal standard, confirming that this molecule contains a fluorine atom. The UV–vis optical absorption spectroscopy confirmed that the inducers showed λ_{max} at 303 nm due to π – π^* transition of the aromatic rings of the mesogen.

3. Results and discussion

3.1. Liquid crystallinity of the chiral inducers

The chiral inducers show thermotropic liquid crystallinity. Fig. 2 displays dynamic scanning calorimetry (DSC) curves of S-UFP* during heating and cooling process ($10\text{ }^\circ\text{C}/\text{min}$). S-UFP* showed two exothermic peaks corresponding to phase transition from chiral crystal (Cr^*) to cholesteric phase (Ch^*) (Cr^*-Ch^*) and Ch^* to isotropic phase (Iso^*) (Ch^*-Iso^*), while the cooling process displayed three endothermic troughs. These signals correspond to phase transition of Iso^*-Ch^* , $\text{Ch}^*-\text{smectic C}$ (Ch^*-SmC^*), and SmC^*-Cr^* . In the temperature range of the Ch^* phase, typical Grandjean texture of CLC was observed (Fig. 3a). Also, a fingerprint

texture of the CLC was observable depending on the surface contact state to the substrate: rubbing process on the substrate allows appearance of a fingerprint texture. Green colored Schlieren texture typical of the SmC^* phase was observed during the cooling process (Fig. 3b). Both of them are chiral LC phases, indicating that the inducers are chiral and have good compatibility with rigid nematic molecules. Molecular orientation in the Ch^* and SmC^* is shown in Fig. 3c, d. Both chiral LC phases have a helical axis, while the directions of the molecular orientation are different. It should be noted that the Ch^* phase is not layered, while the SmC^* has a layered structure.

3.2. Helical direction of the inducers

Helical direction of the inducers was determined using a miscibility test by observing boundaries between the inducer and cholesteryl oleyl carbonate as a standard CLC material having an anticlockwise helical direction. When both compared compounds have opposite directions, the helicity could be unwound, resulting in a Schlieren texture of the nematic phase. Therefore, the miscibility test between opposite helical directions of the sample and the standard CLC materials showed a nematic phase boundary between the two compounds.

(R)-UFP* (R-configuration at the chiral center) showed no boundary with cholesteryl oleyl carbonate because of the anticlockwise helical direction. On the other hand, (S)-UFP* (S-configuration at the chiral center) showed a boundary against cholesteryl oleyl carbonate because of its clockwise direction. These results indicated that (R)-UFP* is a left-handed helical structure and (S)-UFP* shows right-handed helicity, indicating that the chiral inducers with opposite helical directions were successfully synthesized by the Mitsunobu reaction.

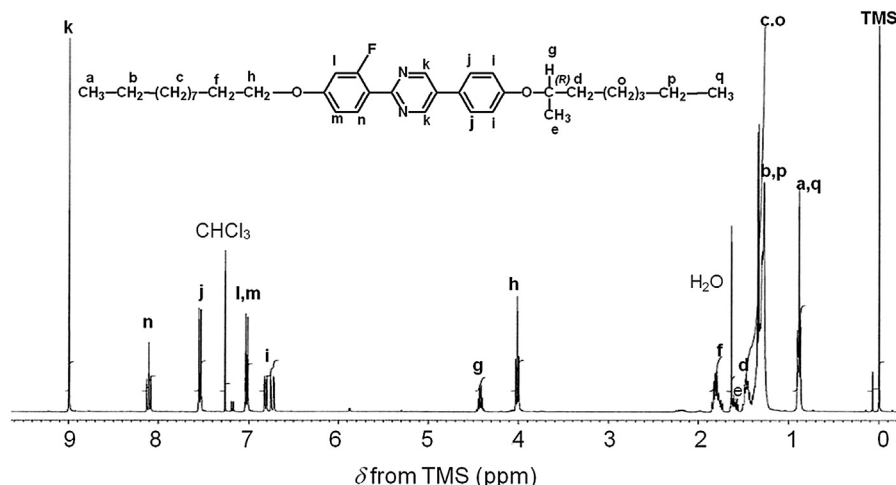


Fig. 1. ^1H NMR analysis result of R-UFP*.

Download English Version:

<https://daneshyari.com/en/article/5182122>

Download Persian Version:

<https://daneshyari.com/article/5182122>

[Daneshyari.com](https://daneshyari.com)