Room temperature chiral smectic C liquid crystal bearing para-phenylchclohexyl mesogenic core

Doo Hun Kim and Munju Goh
Department of Chemical Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029, Republic of Korea
E-mail: mgoh@konkuk.ac.kr
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Abstract

Novel calamitic chiral liquid crystal (LC) was synthesized by introducing chiral butanol moiety into the para-phenylcyclohexyl mesogenic core. We confirmed the liquid crystallinity of chiral LC using DSC, POM and XRD measurements. The chiral LC shows a stable enantiomeric LC phase both cooling and heating procedure. It was found that the chiral LC exhibits a stable LC phase at room temperature. In addition, the chiral LC was assigned as chiral smectic C (Sc*) phase with a tilted angle of 22.7°.

1. Introduction

The creation of chiral phase due to the chirality of liquid crystals (LCs) is a most interesting research field in LC and industrial applications [1]. So far, many types of chiral LCs, such as chiral nematic [2] chiral smectic C (Sc*) [3], blue phase [4] and twisted grain boundary (TGB) phase [5] are reported. The thermochromic behaviour of cholesteric LC and the twisted nematic LC display are due to the chiral phase of the LC. In addition, ferro-, ferri-, antiferro- and piezo-electric behaviour and nonlinear optical properties are derived from chiral LCs. In particular, Sc* is expected to be a ferroelectric material that has a large spontaneous polarization and quick response to an electric field. Since the ferroelectric material can be used as a memory device by using residual polarization remaining after the external electric field is turned off, Sc* is also expected to be an organic memory device capable of fast switching [6].

For obtaining the ferroelectric Sc*, it is prerequisite that the spontaneous polarization should be generated by assembling of dipole moments on the LC molecules. When designing ferroelectric Sc*, It must have a large dipole moment perpendicular to the longitudinal direction of LC molecule and be optically active. Fluorine atoms are often used for designing ferroelectric Sc* because they can provide a large dipole moment to the LC molecules [7–9]. In addition, most typical methods for giving optical activity to the LC molecules is to introduce chiral molecule through covalent bond to achiral LC molecule. It should be mentioned that even if Sc* is obtained, it is difficult to be used in actual device when the LC temperature range is high. Indeed, many Sc* are obtained above 100 °C, but there is an increasing need for a way to easily obtain Sc* at lower temperatures.

In this study, for obtaining a novel Sc* with low temperature LC, 4-bromo-2,3-difluorophenol, which substituted with fluorine at 2, 3 position of benzene ring, was cross-coupled to phenylcyclohexyl (PCH) based mesogen core to obtain large dipole moment. Then, optically active (S)-butan-2-ol was introduced for the chirality on LC molecule. The synthesized LC molecule showed a stable enantiotropic LC phase. In particular, on the cooling process it showed a stable Sc* phase at room temperature.

2. Experimental

All synthesis were performed under nitrogen atmosphere. Toluene and tetrahydrofuran (THF) were distilled prior to use. Suzuki coupling and Mitsunobu etherification were used to obtain the chiral LC molecule (3). The chemical compounds, (S)-butan-2-ol was purchased from Tokyo Chemical Company (TCI). The mesogenic
compound 1-bromo-4-(4-pentylcyclohexyl)benzene was purchased from Kanto Chemical Ltd. Synthetic routes for the chiral LC are shown in scheme 1. Proton (1H) NMR spectra were measured in CDCl₃ using a Varian 600 MHz NMR spectrometer. Figure 1 shows the 1H-NMR spectrum of the chiral LC. Typical pair of doublets only seen with a para-disubstituted benzene were observed at 7.3 and 7.4 ppm. Another pair of doublets were seen derived from 2,3-difluor substituted benzene at 6.8 and 7.1 ppm. Peak derived from hydrogen attached to the chiral carbon center next the oxygen of the ether group was observed at 4.4 ppm. Multiple peaks were observed at 2.5 ppm from one hydrogen substituted on carbon of phenyl substituted cyclohexane.

2.1. 4,4,5,5-tetramethyl-2-(4-(4-pentylcyclohexyl)phenyl)-1,3,2-dioxaborolane
To a mixture of 1-bromo-4-(4-pentylcyclohexyl)benzene (2 g, 6.46 mmol) in anhydrous THF (35 ml) at −75 °C was added 2.58 ml n-butyllithium (2.5 M in hexane). The mixture was stirred at −75 °C for 1 h. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.4 g, 7.75 mmol) was added dropwise to the solution. The resulting mixture was allowed to warm up to room temperature and the reaction proceeded for 24 h. To terminate the reaction, water was added to the mixture and extracted with chloroform. The organic layer was washed with brine and the residual moisture was dried over Na₂SO₄. The solvent was removed in vacuo after filtration. The organic layer was submitted to chromatography on silica using CHCl₃/n-hexane = 1/1 as an eluting agent to give a white powder 1 (1.7 g, 74%). ¹H NMR (600 MHz, CDCl₃, Me₄Si): 7.74 (d, 2 H), 7.23 (d, 2 H), 2.47 (t, 1 H), 1.86 (t, 4 H), 1.48 (m, 2 H), 1.32 (s, 12 H), 1.31–1.21 (m, 9 H), 1.02 (t, 2 H), 0.89 (t, 3 H).

2.2. (R)-1-bromo-4-(sec-butoxy)-2,3-difluorobenzene
The solution of 4-bromo-2,3-difluorophenol (3 g, 14.35 mmol), (S)-butan-2-ol (1.58 ml, 17.22 mmol), and triphenylphosphine (TPP) (4.89 g, 18.65 mmol) in anhydrous THF (35 ml) were added dropwise to an diethyl
azodicarboxylate (DEAD) (9.79 ml, 21.53 mmol) at 0 °C. It was allowed to reach room temperature 24 h and extracted with CHCl₃. The organic layer was washed with brine and the residual moisture was dried over Na₂SO₄. The solvent was removed in vacuo after filtration. The organic layer was submitted to chromatography on silica using CHCl₃/n-hexane = 1/1 as an eluting agent to give a white powder, 2 (2.73 g, 72%). ¹H-NMR (600 MHZ, CDCl₃, Me₄Si): 7.18 (t, 1 H), 6.67 (t, 1 H), 4.29 (m, 1 H), 1.77 (m, 1 H), 1.66 (m, 1 H), 1.32 (d, 3 H), 0.99 (t, 3 H).

2.3. (R)-1-bromo-4-(sec-butoxy)-2,3-difluorobenzene
To a solution of 1 (1 g, 2.81 mmol) and 2 (0.82 g, 3.09 mmol) in THF (20 ml) was added tetrakis (triphenylphosphine)palladium(0) (0.34 g, 0.295 mmol). After fully dissolved in THF solvent, degassed 2 M aqueous K₂CO₃ solution (10 ml) was added, and aliquot 336 was added 3–4 drops. The reaction mixture was stirred at 70 °C for 24 h in the dark. After the quenching the reaction, the product was extracted from the organic layer by adding CHCl₃, and washed with D.I. water and brine. The residual moisture of the organic layer was dried over anhydrous Na₂SO₄, and the solvent was removed by rotary vacuum evaporator. The residue was purified by column chromatography to give a white powder 0.97 g (84%). ¹H-NMR (600 MHZ, CDCl₃, Me₄Si): 7.42 (d, 2 H), 7.28 (d, 2 H), 7.06 (t, 1 H), 6.78 (t, 1 H), 4.33 (m, 1 H), 2.50 (t, 1 H), 1.87 (m, 4 H), 1.81 (m, 1 H), 1.49 (m, 2 H), 1.35–1.23 (m, 12 H), 1.07 (t, 3 H)1.01 (t, 3 H), 0.89 (t, 3 H).

3. Results and discussion
The mesomorphic properties of the chiral LC were investigated with DSC, POM, and XRD. The phase transition temperature of chiral LC was K → 62 °C (42.62 J g⁻¹) → Sc⁺ → 77 °C (3.05 J g⁻¹) → Sx → 83 °C (0.53 J g⁻¹) → I and I → 82 °C (0.77 J g⁻¹) → Sx → 75 °C (4.32 J g⁻¹) → Sc⁺ → 12 °C (34.92 J g⁻¹) → K for the heating and cooling processes, respectively (figure 2). Here, I, Sx, Sc⁺ and K stand for the isotropic phases, smectic x, chiral smectic C and crystal respectively, and the enthalpy changes associated with the phase transitions are given in parenthesis. The phase behaviours of the LC transitions in chiral LC was enantiotropic nature.

POM photographs of chiral LC showed typical fan-shape textures characteristic of smectic phases at 75 °C of the heating and cooling procedure, respectively (figures 3(a) and (c)). Very interestingly, striated fan-shape was observed near the clearing point where droplets began to form (figure 3(b)). This shows that chirality is transferred to the liquid crystal under the influence of chiral butane connected to mesogenic core, resulting in the formation of chiral smectic phase. Interestingly, the blue phase was observed during the cooling process at 83 °C, but only in very narrow temperature range, and not during the heating process (figure 4).

XRD measurement of chiral LC was measured during the cooling process (figure 4(a)). At 68 °C, a broad diffraction peak was appeared in the large angle region (2θ = 18.6°), corresponding to the LC intermolecular distance of 4.7 Å. A sharp diffraction peak in the small angle region (2θ = 3.65°) corresponds to an interlayer distance of d = 24.17 Å. Theoretical molecular length (l) of chiral LC molecule was evaluated as 26.2 Å using density functional theory (DFT) at the B3LYP/6-31 G(d) level basis set in Gaussian09. It follows that the d/l ratio of 0.92 implies the
The tilted structure, yielding the $S_c$ phase [10]. The tilt angle ($\alpha$) defined between the layer normal ($z$) and the director of LC molecules ($n$) was calculated to be 22.7$^\circ$ from the equation $\alpha = \cos^{-1}(d/l)$. Therefore, from the striated fan shape morphology of figure 3(b) and the result of $S_c$ phase with tilted structure as seen from XRD (figure 5(a)), the chiral LC could be assigned as chiral smectic C ($S_c^*$) phase. The schematic representation of the $S_c^*$ phases chiral LC is shown in figure 5(b).
4. Conclusion

We synthesized novel calamitic chiral liquid crystal (LC) by introducing chiral butanol moiety using Mitsunobu reaction into the para-phenylcyclohexyl mesogenic core. The liquid crystallinity of chiral LC molecule was evaluated with DSC, POM and XRD measurements. The chiral LC showed an enantiomeric LC that showed a stable LC phase during both cooling and heating procedure. In particular, it was found that the chiral LC exhibits a stable LC phase even at room temperature on the cooling process. In addition, the POM and XRD results showed that the chiral LC was a chiral smectic C (Sc*) phase with a tilted angle of 22.7°.

In the future, this stable Sc* at room temperature is expected to be applied to ferroelectric liquid crystal materials that react quickly to an electric fields and organic non-volatile memory devices by utilizing residual polarization of ferroelectric liquid crystals.

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ORCID iDs

Doo Hun Kim  https://orcid.org/0000-0003-3275-0060
Munju Goh  https://orcid.org/0000-0002-6061-8625

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