PREPARATION AND FERROELECTRIC PROPERTIES OF NEW CHIRAL LIQUID CRYSTALLINE ORGANIC RADICAL COMPOUNDS

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Abstract – We have synthesized new chiral liquid crystalline (LC) organic radical compounds 2 and 3, which are the derivatives of the previously reported compounds 1 containing a chiral cyclic nitroxide unit and an ester group in the mesogen core, and their ferroelectric properties have been studied. The enantiomerically enriched (2S,5S)-2 and (2S,5S)-3 showed an SmC* phase for which their ferroelectric properties such as spontaneous polarization ($P_s$) and tilt angle ($\theta$) were compared with those of (2S,5S)-1.

INTRODUCTION

Recently, we have shown that a 2,2,5,5-tetrasubstituted pyrrolidin-1-yloxy (PROXYL) structure is stable enough for repeated heating and cooling cycles below 150°C in the air and thereby this radical unit can serve as the excellent source of the magnetic spin ($S = 1/2$) and spontaneous polarization ($P_s$) for elaborating paramagnetic as well as ferroelectric all-organic liquid crystals (LCs), which can combine the optical and electric properties of conventional ferroelectric LCs (FLCs) with the magnetic properties of paramagnetic compounds. 1-9 For example, it is quite interesting to know whether magneto-electric effects can be observed in the FLC state of paramagnetic materials. The magneto-electric effects are well known to arise from the intra- and intermolecular interactions between magnetic and electric dipole moments and to be observed in ferroelectric rare earth metal manganite crystals such as YMnO$_3$, TbMnO$_3$, and...
HoMnO$_3$ with magnetic order at low temperatures.$^{10-12}$ Experimentally, the effects can be detected as the influence of a magnetic (electric) field on the polarization (magnetization) of a material and *vice versa.$^{13-15}$

In this context, we successfully obtained the prototypic all-organic chiral LC radical compounds 1 which have a PROXYL group with a large electric dipole moments (3 Debye) in the mesogen core as well as a polar ester group (1.8 Debye) used very often for the preparation of conventional FLCs.$^{16}$ Indeed, (2S,5S)-1 (n=11–15) showing an SmC* phase exhibited ferroelectricity in a thin sandwich cell (4 μm thickness); the highest $P_s$ value of 24 nC cm$^{-2}$ was recorded for (2S,5S)-1 (n=13).$^{23}$

In order to improve the $P_s$ value which should become a crucial factor for observing magneto-electric effects in the paramagnetic FLCs, we have designed compounds (2S,5S)-2 and (2S,5S)-3 with an additional benzene ring on either 2 or 5 position of the PROXYL ring, compared to (2S,5S)-1 (Chart 1). This structural modification is expected to result in the strong intra-layer interactions in the SmC* phase and hence to increase the overall $P_s$ value.$^{17}$ Here we report the synthesis, LC characterization and ferroelectric properties of (2S,5S)-2 and (2S,5S)-3.

Chart 1. PROXYL type of LC compounds (2S,5S)-1–3 showing an SmC* phase.

Scheme 1. Preparation of (2S,5S)-2 and (2S,5S)-3.
RESULTS AND DISCUSSION

Synthesis of (2S,5S)-2 and (2S,5S)-3. (2S,5S)-2 and (2S,5S)-3 were synthesized with high stereoselectivity by repeating the addition of an appropriate Grignard reagent to nitrones [4 (ca. 90% ee) and 5] and the subsequent oxidation twice, followed by benzylation of the phenolic hydroxy group after desilylation, similarly to the synthesis of (2S,5S)-1 (Scheme 1).\(^ {1-3,18-23}\)

Characterization of LC phases. The phase transition behavior of (2S,5S)-2 and (2S,5S)-3 was characterized by DSC, POM, and XRD analyses, which were measured below 160°C because these compounds instantly decompose in the isotropic phase above 160°C (Table 1, Figure 1 and 2).

Table 1. Phase transition temperatures of (2S,5S)-2 and (2S,5S)-3 on the first heating run.

<table>
<thead>
<tr>
<th>(2S,5S)-2 or 3</th>
<th>ee (%)</th>
<th>Transition temperature (°C) and ΔH (in parentheses, kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>2a (n=12)</td>
<td>89.3</td>
<td>105.9 (30.6)</td>
</tr>
<tr>
<td>2b (n=13)</td>
<td>91.0</td>
<td>105.5 (33.2)</td>
</tr>
<tr>
<td>2c (n=14)</td>
<td>90.9</td>
<td>106.5 (36.9)</td>
</tr>
<tr>
<td>2d (n=15)</td>
<td>90.8</td>
<td>106.2 (38.1)</td>
</tr>
<tr>
<td>3a (n=13)</td>
<td>91.2</td>
<td>105.6 (22.8)</td>
</tr>
<tr>
<td>3b (n=14)</td>
<td>89.0</td>
<td>107.2 (37.3)</td>
</tr>
</tbody>
</table>

\(^ a\) Two peaks were overlapped.

Figure 1. LC behavior of (a) (2S,5S)-2 and (b) (2S,5S)-3. Transition temperatures determined by DSC analysis at a scanning rate of 5°C min\(^{-1}\) upon the first heating and cooling processes. Heating was turned down at 160°C for the subsequent cooling run.
As expected, (2S,5S)-2 and (2S,5S)-3 showed stable LC phases over wide temperature ranges and at higher temperatures than (2S,5S)-1 due most likely to the stronger inter-layer interactions. Similarly to the case of (2S,5S)-1, (2S,5S)-2 with C12 to C15 chains and (2S,5S)-3 with C13 and C14 chains exhibited SmC* and N* phases, with respective broken fan-shaped and oily-streak textures observed on the cooling run (Table 1, Figure 1 and 2). Variable temperature XRD analysis verified the existence of the SmC* and N* phases (Figure 3).

Figure 2. Polarized optical micrographs showing (a) oily-streaks texture (N*) under random conditions at 158°C and (b) broken fan-shaped texture (SmC*) in a thin sandwich cell (4 mm) under homogeneous planar boundary conditions at 130°C for (2S,5S)-2b, and (c) oily-streaks texture (N*) under random conditions at 160°C and (d) broken fan-shaped texture (SmC*) in a thin sandwich cell (4 µm) under homogeneous planar boundary conditions at 150°C for (2S,5S)-3b.

Figure 3. XRD patterns of (a) (2S,5S)-2a at 120 (SmC*) and 150°C (N*) and (b) (2S,5S)-3a at 145 (SmC*) and 158°C (N*).
Ferroelectric properties. The magnitude of $P_s$ and the optical and calculated tilt angles [$\theta$ and $\cos^{-1}(d/l)$] of (2S,5S)-2 and (2S,5S)-3 are summarized in Figures 4 and 5 and Table 2. On the cooling run from the N*-to-SmC* transition temperature, the $P_s$ values rapidly increased (Figure 4). On the whole, the $P_s$ values of (2S,5S)-2 were larger than those of the corresponding (2S,5S)-1 and (2S,5S)-3; (2S,5S)-2d showed the highest $P_s$($-10^\circ$) value of 32 nC cm$^{-2}$ (Figure 4a and Table 2). Such high $P_s$ values observed for (2S,5S)-2 can be interpreted in terms of the increased intra-layer interactions. The tilt angles of (2S,5S)-2 and (2S,5S)-3 were too large to measure the optical response time (Figure 5 and Table 2); only a bright-dark-bright or dark-bright-dark texture change was observed upon switching the polarity of the applied electric field.

Figure 4. Temperature dependence of the $P_s$ value in the SmC* phases of (a) (2S,5S)-2 and (b) (2S,5S)-3.

Figure 5. Temperature-dependence of the tilt angle ($\theta$) of (a) (2S,5S)-2 and (b) (2S,5S)-3 measured by hot-stage POM.

Moreover, in contrast to the case of (2S,5S)-1, we observed the relaxation of the ferroelectric state of (2S,5S)-2a and (2S,5S)-2b in the same type of FLC cell, i.e., POM texture change by turning off the
electric fields (Figure 6). At the same time, the textures in the two field-free states of (2S,5S)-2a or (2S,5S)-2b considerably differed from each other, suggesting the short-pitch SmC* nature and the incomplete formation of a helical superstructure in the FLC cell used (Figures 6b and d).

![Figure 6](image)

Figure 6. Ferroelectric switching modes of (2S,5S)-2b in a sandwich cell (4 μm) at 130°C under homogeneous planar boundary conditions between crossed polarizers. Applied DC voltage dependence of texture change in the same area at 110°C: Electric field sweeping in the order of (a) +12 V, (b) 0 V, (c) –12 V, and (d) 0V.

Table 2. Ferroelectric properties measured in the SmC* phases of (2S,5S)-2 and (2S,5S)-3, layer distances, calculated molecular length, and geometrical tilt angles.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$P_s(-10^5)^{a,b}$ [nC cm$^{-2}$]</th>
<th>$\theta(-10^5)^{b,c}$ [deg]</th>
<th>$d^d$ [Å]</th>
<th>$l^e$ [Å]</th>
<th>$\cos^{-1}(d/l)^f$ [deg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a (n=12)</td>
<td>28 (119°C)</td>
<td>41</td>
<td>41.2 (120°C)</td>
<td>50.6</td>
<td>35</td>
</tr>
<tr>
<td>2b (n=13)</td>
<td>21 (137°C)</td>
<td>38</td>
<td>40.3 (120°C)</td>
<td>53.1</td>
<td>41</td>
</tr>
<tr>
<td>2c (n=14)</td>
<td>27 (143°C)</td>
<td>36</td>
<td>41.5 (120°C)</td>
<td>54.8</td>
<td>41</td>
</tr>
<tr>
<td>2d (n=15)</td>
<td>32 (142°C)</td>
<td>36</td>
<td>43.7 (130°C)</td>
<td>57.4</td>
<td>40</td>
</tr>
<tr>
<td>3a (n=13)</td>
<td>12 (141°C)</td>
<td>34</td>
<td>40.9 (145°C)</td>
<td>55.4</td>
<td>42</td>
</tr>
<tr>
<td>3b (n=14)</td>
<td>23 (146°C)</td>
<td>36</td>
<td>42.6 (145°C)</td>
<td>57.7</td>
<td>42</td>
</tr>
</tbody>
</table>

$^a$Spontaneous polarization. $^b$Measured at a temperature 10°C below the phase transition from the N* phase to the SmC* phase during the cooling process. $^c$Tilt angle measured by hot-stage POM. $^d$Layer distance from XRD data. $^e$Molecular length determined by a PM3 semiempirical calculation (PC Spartan’02). $^f$Calculated geometrical tilt angle from $d$ and $l$ values.

In summary, we could obtain new chiral organic radical compounds with strong inter-layer interactions which showed FLC properties at high temperatures and over wide temperature ranges. Above all, (2S,5S)-2d showed the highest $P_s(-10^5)$ value of 32 nC cm$^{-2}$, which was larger than that (24 nC cm$^{-2}$) of (2S,5S)-1 (n=13) previously reported.23
EXPERIMENTAL

General. Transition temperatures refer to the peak top of each transition curve by DSC analysis, which was performed at a scanning rate of 5 °C min⁻¹. Enantiomeric excess (ee) were determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralpak AD, 0.46 x 25 cm), a mixture of hexane and 2-PrOH (9:1) as the mobile phase at a flow rate of 1.0 mL min⁻¹, and a UV-vis spectrometer (254 nm) as the detector. Ps was measured by the triangular wave method at a frequency of 20 Hz in a thin sandwich cell (EHC Co., Japan; thickness of 4 µm) coated with ITO electrodes and covered with antiparallel-rubbed polyimide films in an electric field of 10 V peak to peak. Tilt angles were measured by polarized optical microscopy (POM). Their g values and hyperfine coupling constants (aN) were determined by electron paramagnetic resonance (EPR) spectroscopy in THF at 25 ºC. The variable temperature X-ray diffraction (XRD) patterns were recorded at a continuous scanning rate of 2° 2θ min⁻¹ at a heating and cooling rate of 4 °C min⁻¹ using CuKα radiation (40 kV, 20 mA), with the intensity of the diffracted X-rays being collected at intervals of 0.02° 2θ.

General synthetic procedure for (2S,5S)-2 and (2S,5S)-3. Enantiomerically enriched nitrone (R)-4 (ca. 90% ee) was prepared according to the published procedure. The nitrone (R)-4 (0.452 g, 4.0 mmol) was reacted with the first Grignard reagent (8.0 mmol) in THF (5 mL) at ~78 ºC. The reaction temperature was slowly raised to 25 ºC. After being stirred overnight, the reaction mixture was poured into saturated aqueous NH₄Cl solution (50 mL), followed by extraction with CH₂Cl₂ (2 x 50 mL) and concentration in vacuo. The residue was dissolved in MeOH (20 mL) and oxidized by treatment with Cu(OAc)₂·H₂O(0.13 g), conc. NH₃ solution (1.1 mL), and O₂ bubbling until dark blue color developed in solution. The solution was evaporated in vacuo, and the residue extracted by CHCl₃ (50 mL). The organic phase was washed with saturated aqueous NaHCO₃ solution (50 mL), dried over MgSO₄, and concentrated in vacuo to give the crude nitrone (S)-5. The crude (S)-5 was reacted with the second Grignard reagent (8.0 mmol) and the resulting crude addition product was oxidized by the same procedure. The crude (2S,5S)-6 was roughly purified by column chromatography on silica gel (hexane:CH₂Cl₂:Et₂O 6/4/0~6/3/1) to remove mainly the less polar impurities. Then to this crude (2S,5S)-6 dissolved in THF (20 mL) was added a THF solution of Bu₄NF (1 M solution, 1.0 mL) at 0 ºC. After being stirred at 0 ºC for 20 min, the reaction mixture was poured into saturated aqueous NH₄Cl solution (30 mL), followed by extraction with CH₂Cl₂ (2 x 50 mL), drying over MgSO₄, and concentration in vacuo. The crude product was purified by column chromatography on silica gel (hexane:CH₂Cl₂:Et₂O 6/3/1~5/3/2) to give the pure desilylated product of (2S,5S)-6 as yellow solid in ca. 10% yield from (R)-4.
To a mixture of the desilylated product (0.3 mmol) and Et3N (0.9 mL) in THF (10 mL) was added an appropriate p-alkoxybenzoyl chloride (0.9 mmol) in THF (3 mL) at 0°C. The reaction mixture was slowly warmed to 25 °C and stirred for 40 h. Then the mixture was poured into a saturated aqueous NaHCO3 solution (20 mL) and the aqueous mixture was extracted with Et2O (2 x 50 mL). The combined organic phase was dried over MgSO4 and evaporated in vacuo. Column chromatography on silica gel (hexane:CH2Cl2:Et2O 8/2/0~7/2/1) of the residue gave pure (2S,5S)-2 or (2S,5S)-3 as yellow solid in 70-80% yield from (2S,5S)-6.

(2S,5S)-2a: [α]D24 −71.49 (89.3% ee, c 1.001, THF). EPR (THF): g = 2.0057, aN = 1.33 mT. IR (KBr): 2923, 2850, 1734, 1607, 1507, 1395, 1254, 1164, 1071, 813, 764. Anal. Calcd for C55H77NO5: C, 79.47; H, 9.22; N, 1.69. Found: C, 79.39; H, 9.44; N, 1.70.

(2S,5S)-2b: [α]D25 −72.91 (91.0% ee, c 0.982, THF). EPR (THF): g = 2.0060, aN = 1.34 mT. IR (KBr): 2849, 1735, 1604, 1507, 1395, 1250, 1164, 1078, 820, 765. Anal. Calcd for C57H81NO5: C, 79.68; H, 9.38; N, 1.63. Found: C, 79.69; H, 9.41; N, 1.60.

(2S,5S)-2c: [α]D25 −70.40 (90.9% ee, c 0.991, THF). EPR (THF): g = 2.0058, aN = 1.33 mT. IR (KBr): 2915, 1731, 1607, 1498, 1371, 1254, 1201, 1165, 1077, 819, 764. Anal. Calcd for C59H85NO5: C, 79.86; H, 9.54; N, 1.58. Found: C, 79.90; H, 9.60; N, 1.55.


(2S,5S)-3b: [α]D25 −67.84 (89.0% ee, c 1.003, THF). EPR (THF): g = 2.0056, aN = 1.32 mT. IR (KBr): 2921, 2851, 1730, 1605, 1510, 1372, 1255, 1206, 1169, 1079, 876, 767. Anal. Calcd for C59H85NO5: C, 79.86; H, 9.54; N, 1.58. Found: C, 79.76; H, 9.53; N, 1.63.

REFERENCES AND NOTES


