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SYNTHESIS AND MESOMORPHIC PROPERTIES OF CHIRAL LIQUID CRYSTALS DERIVED FROM (R)-3-ETHYLMERCAPTO-2-METHYLPROPANOL

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A new optically active (R)-3-ethylmercapto-2-methylpropanol was designed and synthesized by using (D)-2,10-camphorsultam as a chiral auxiliary. Its derivatives with various core structures in the molecules were prepared for investigating mesomorphic properties. Mesophases and the corresponding transition temperatures of the compounds were identified by the polarizing microscopic textures and DSC carlorimetry. Structurally similar compounds were compared to explore the effect of core structures on the formation of mesophases, especially the frustrated phases.

Keywords: chiral liquid crystal; frustrated phase and spontaneous polarization

INTRODUCTION

The development of chiral compounds in chiral liquid crystal system has let to discovery of new phases and their related phase behaviors. Many compounds have been synthesized and investigated, and the structure-property relationship of the chiral molecules on the appearance of mesophases established [1,2]. Among them, chiral moieties that used for the preparation of chiral compounds were generally the commercial available optically active compounds such as 2-alkanols, lactic acid and 2-(6-methoxy-2-naphthyl)propionic acid. Some of the chiral moieties, however, were designed and synthesized for preparing chiral compounds in order to improve and/or explore special properties of the mesophases, such as optically active trifluoroalkanol, fluoroalkanol and α-halohydrin.

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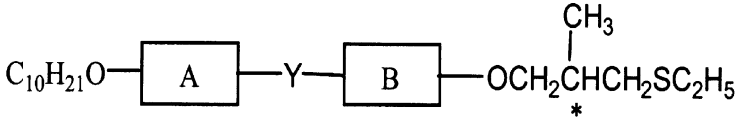
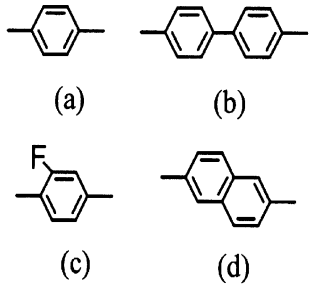


Code	Y	A	B
I	-COO-	a	b
II	-COO-	c	b
III	-COO-	b	a
IV	-COO-	b	d
V	-OCO-	b	a



We had previously designed and synthesized a highly optically pure chiral acid, (R)-3-ethylmercapto-2-methylpionic acid, by using (D)-2, 10-camphorsultam as a chiral auxiliary [3]. The chiral liquid crystals derived from this chiral acid exhibited wide variety of mesomorphic phases, such as antiferroelectric phase [3] and TGB phases [4]. In order to study further, (R)-3-ethylmercapto-2-methylpropanol was synthesized by the reduction of the corresponding chiral acid and used as a chiral building block for the preparation of chiral liquid crystals with various core structures. The corresponding structural formulas of the materials for the study are shown bellow.

EXPERIMENTAL

The purity of the target materials was estimated by thin layer chromatography and further confirmed by elemental analysis using a Perkin-Elmer 2400 spectrometer. The chemical structures of materials were analyzed by proton magnetic resonance spectroscopy using a JEOL Ex400 FT-NMR spectrometer. Mesophases for the materials were identified by observing textures using a Nikon Microphot-FXA optical microscope under crossed polarizers, with a Mettler FP82-HT in connection with FP80 hot stage as a temperature controller. Transition temperatures were determined by a DuPont DSC-910 calorimeter at a scanning rate of 1°C min^{-1}.

Highly optically active chiral alcohol, (R)-3-ethylmercapto-2-methylpropanol, was synthesized by the reduction of (R)-3-ethylmercapto-2-

TABLE 1 The Transition Temperatures T(°C) and Enthalpies $\Delta H(Jg^{-1})$ of the Transitions for Chiral Alcohol Derivatives on Cooling.

Code No.	Iso		BPIII		BPII		N*		TGB_A*		SmA*		TGB_C*		SmC*		SmX*		Cr.	m.p
I	●		–	140.3[a]	●	139.1	●	117.5	●		–		–	114.9	●	77.9	●	64.1	●	89.3
ΔH				–[b]		1.77[c]		–[b]						–[b]		14.0		25.32		68.31
II	●		–	125.0	●	124.0	●		–		–		–	116.0	●		–	69.48	●	79.38
ΔH				–[b]		1.15[d]								2.38				50.71		50.59
III	●		–		–		–		–	155.0	●		–	124.9	●	77.4	●	76.0	●	92.2
ΔH										7.73				–[b]		8.86		42.5		59.0
IV	●	204.6[a]	●	204.5[a]	●	202.9	●	193.1[a]	●	193.0	●		–	192.4	●		–	114.9	●	102.0
ΔH		–[b]		–[b]		1.18[c]		–[b]		1.75[d]				–[b]				34.83		53.72
V	●	139.2[a]	●	139.1[a]	●	138.5	●		–		–	115.1	●	115.0	●		–	97.0	●	101.1
ΔH		–[b]		–[b]		0.67[c]						–[b]		3.23[e]				34.27		37.25

[a] The phase transition temperature was determined by thermal optical microscophy.
[b] The enthaplpy of phase transition was too small to be determined by DSC.
[c] ΔH(Iso-BP-N*).
[d] ΔH(N*-TGB_A*-SmA*).
[e] ΔH(Iso-TGB_C*-SmC*).

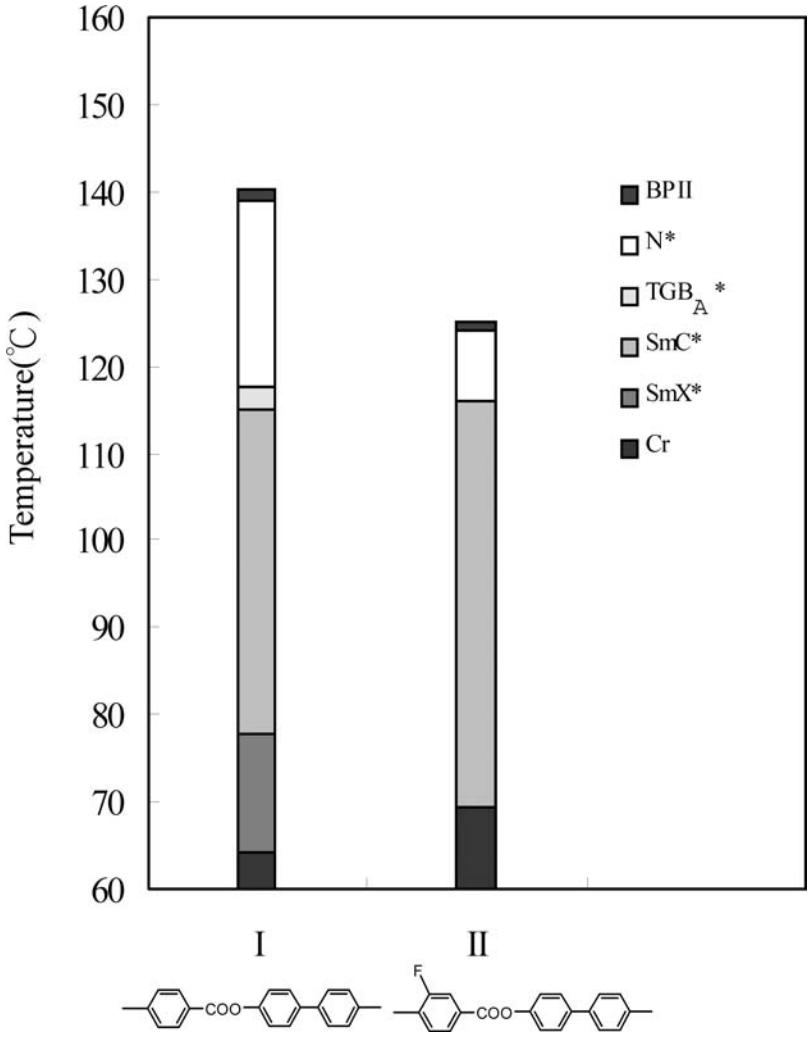


FIGURE 1 Th comparison of mesomorphic phases between compounds I and II.

methylpionic acid, which was prepared by using (D)-2,10-camphorsultam as a chiral auxiliary according to the method described before [3]. Chemical shifts for the chiral alcohol in ^{1}H NMR ($CDCl_3$): δ(PPM) 3.51 (d, 2H, j = 2.11 Hz), 2.36–2.58 (m, 5H), 1.81 (s, 1H, j = 1 Hz) 1.19–1.21 (t, 3H, j = 3.16 Hz), 0.93–0.95 (t, 3H, j = 3.19 Hz). Specific rotation: $[\alpha]_D^{22} = -4.44$ (c 2.22, $CHCl_3$). The synthetic details for the target materials will be described elsewhere.

RESULTS AND DISCUSSION

The mesomorphic phases and their corresponding transition temperatures for chiral materials on the cooling stage are summarized and listed in the Table 1. The mesophases were identified by the microscopic textures. The BPIII phase displayed a blue fog texture, while the BPII phase displayed a iridecent platelet texture. The N* phase showed a paramorphotic

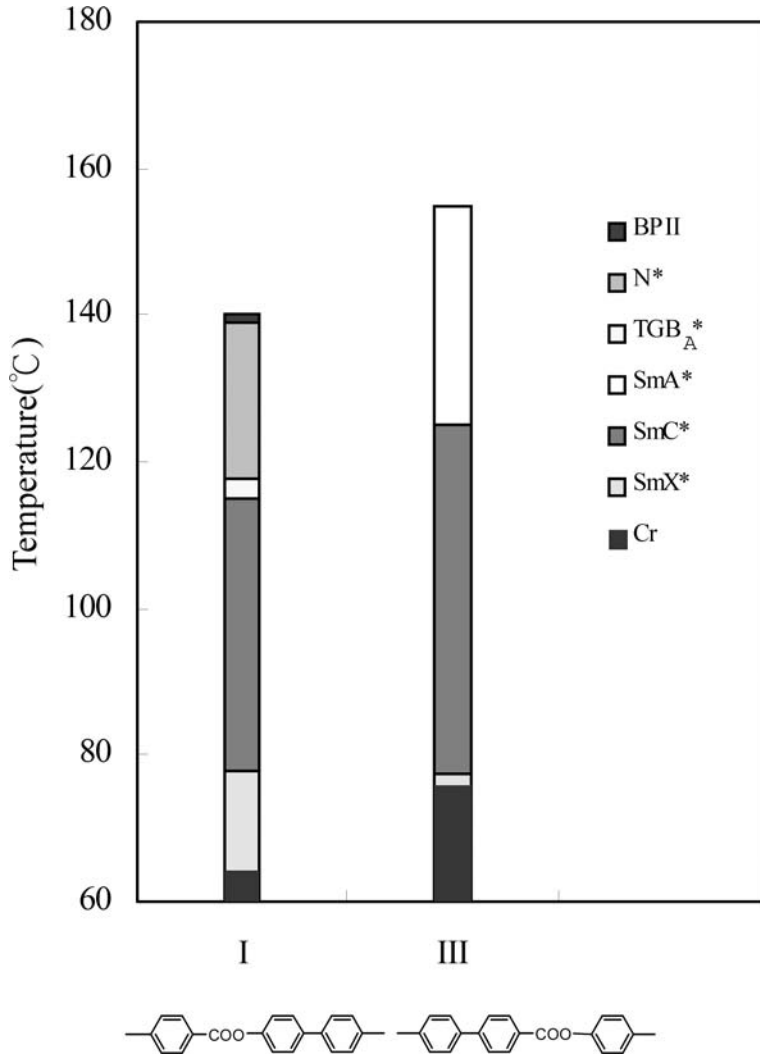


FIGURE 2 The comparison of mesomorphic phases between compounds I and III.

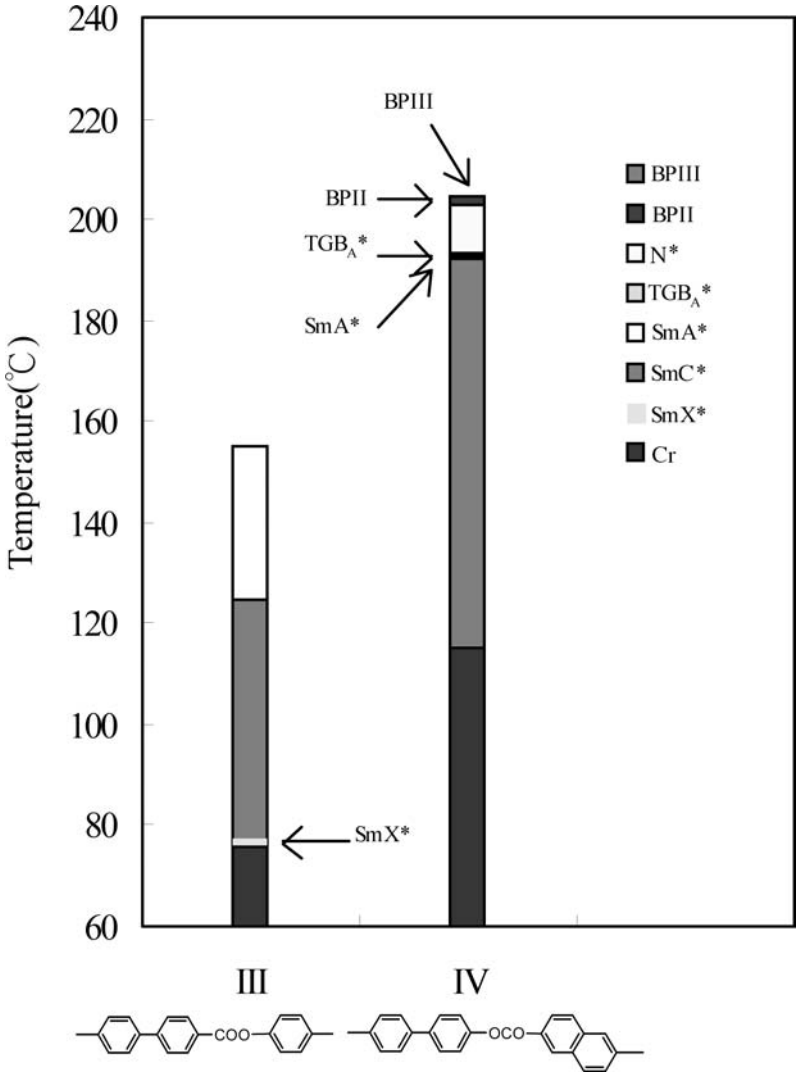


FIGURE 3 The comparison of mesomorphic phases between compounds III and IV.

defective scale-like texture. The TGB_A^* phase was identified by the existence of spiral filament texture [4–6], while the TGB_C^* phase was characterized as a striated spiral filament texture [4,6,7]. The SmC^* phase was confirmed by the formation of striated focal-conic texture.

The results of the mesophases for compound I displayed a phases sequence of BPII-N^*-TGB_A^*-SmC^*-SmX^*. Compounds I and II were com-

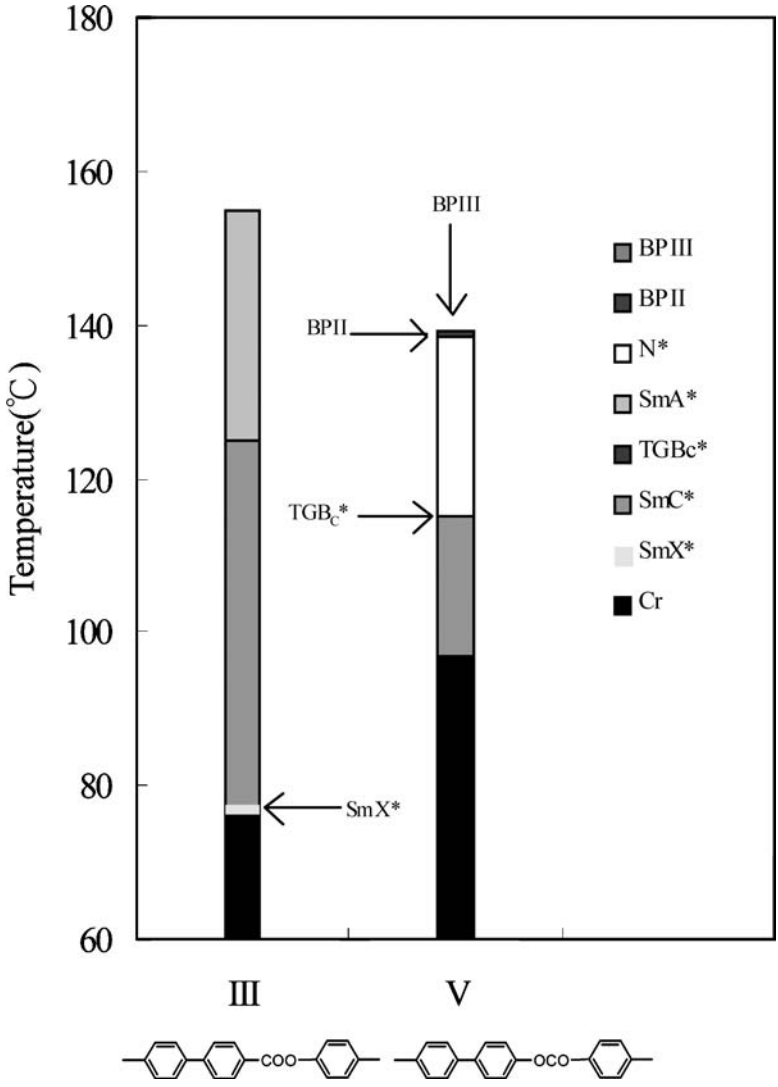


FIGURE 4 The comparison of mesomorphic phases between compounds III and V.

pared, as shown in the Figure 1, to illustrate the effect of fluoro-subtituent at the phenylene (Ph) ring of the core structure of the molecules on the formation of mesophases. It is seen that the fluorinated compound has lower clearing point than its unflourinated one. This phenomenon can be explained that fluoro substituent in phenylene ring could destroy the linearity of the molecular structure and increase the wide of the molecule,

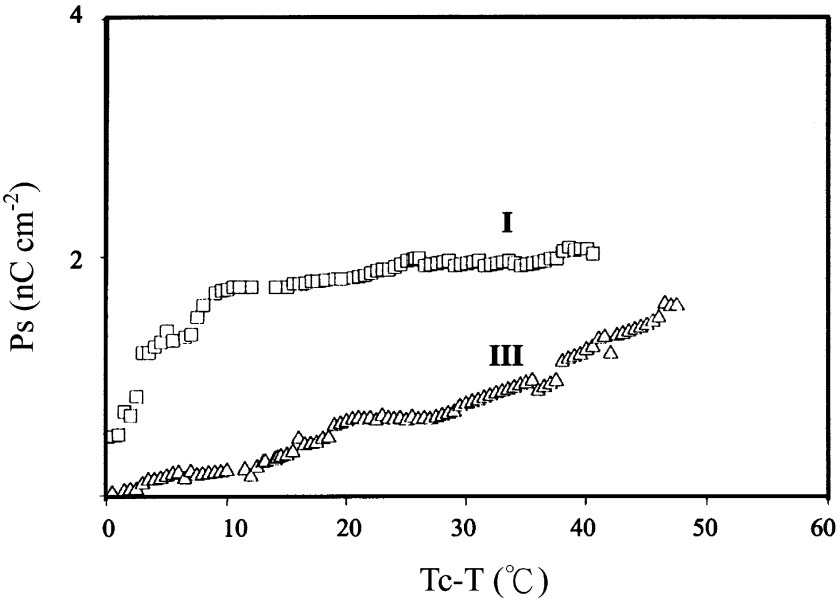


FIGURE 5 The magnitudes of spontaneous polarization determined as function of temperature for compounds I and III.

and consequently it might relax the molecular packing and decrease the thermal stability of mesophases. The introduction of fluoro-substituent also causes a vanishing of TGB_A^* and unidentified higher order SmX* phases.

Compounds I and III were compared, as shown in the Figure 2, to realize the effect of the position of the esters linking group in the core structure of the molecules on the formation of mesophases. It is seen that the replacement of PhCOOPhPh in compound I by PhPhCOOPh as represented in compound III, resulted in a suppressing of frustrated phases, and consequently, changed the phase sequence to SmA*-SmC*-SmX*. This result suggested that compound III has stronger intermolecular interaction. However, as the naphthalene ring (Na) replaced the phenylene ring of compound III to have the core structure of PhPhCOONa as in compound IV, the frustrated phases formed and the phase sequence became BPIII-BPII-N*-TGB_A^*-SmC* as shown in Figure 3. As comparing compound III to compound I, the former has additional BPIII phase but loses of SmX* phase although the clearing point is much higher than the later. It is interesting to find that as PhPhCOOPh in compound III was replaced by PhPhOCOPh as in compound V, the phase sequence became BPIII-BPII-N*-TGB_C^*-SmC* as shown in Figure 4. The =OCO= linkage is favorable of forming frustrated phases as compared to the =COO= linkage in the molecules.

It suggested that the direction of ester linkage in the central core has significant effect on the formation of frustrated phases. All compounds possessed wide temperature range of SmC* phase.

The magnitudes of spontaneous polarization, obtained from compounds I and III as a function of temperature in ferroelectric SmC* phase, were measured at frequency of 200 Hz and amplitude of $2V_{P\text{-}P}$ and are plotted in Figure 5. The maximum Ps values are approximately $2nC\,cm^{-1}$. These small Ps values can be expected since the chiral centre at chiral tail is not directly linked to the core of the molecules.

CONCLUSION

Our results showed that chiral compounds derived from (R)-3-ethylmercapto-2-methylpropanol exhibited wide variety of liquid crystal phases, especially, the frustrated phases. The frustrated phases were significantly affected by the structure of the core in the molecules. All compounds possessed wide temperature range of ferroelectric SmC* phase, but small spontaneous polarization.

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