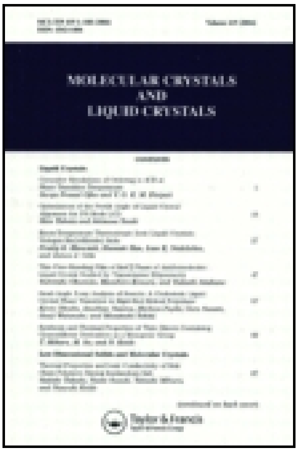

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Synthesis and Mesomorphic Properties of Ferroelectric Liquid Crystals Bearing 2-Phenyl-1,3,4-Thiadiazole Rings

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Sixteen homologs of chiral 2-phenyl-1,3,4-thiadiazoles were synthesized and their mesomorphic properties were evaluated with a DSC and a polarizing microscope. All compounds studied possessed an alkyl or alkoxy side chain at the *p,p'* position of the 2-phenyl-1,3,4-thiadiazole core and an optically active carbon atom at one of the terminal chains. We found that compounds in these series show a strong tendency to generate chiral smectic C (Sc*) phases. We also measured some compounds for their spontaneous polarizations (Ps) and switching times (τ) and found that the switching times were relatively fast, though the spontaneous polarizations were very small.

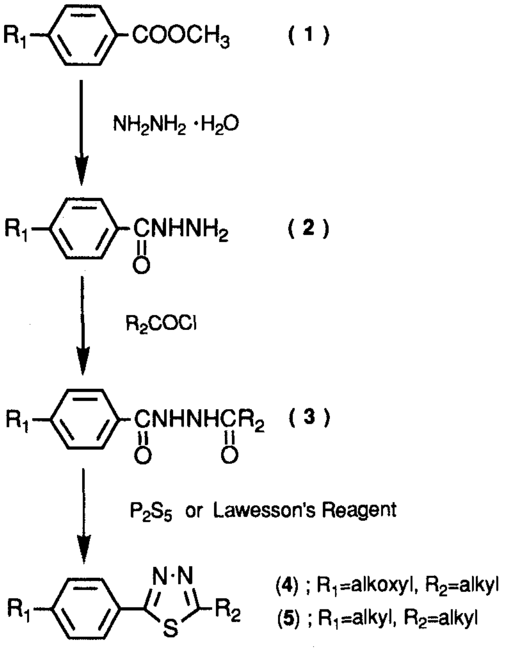
Keywords: ferroelectric liquid crystal, phase transition, thiadiazole

INTRODUCTION

Since the discovery of ferroelectricity in the chiral smectic C (Sc*) phase by R. Meyer in 1975[1] and the proposal of electro-optical devices using ferroelectric liquid crystals by Clark and Lagerwall in 1980,[2] extensive studies have been done on ferroelectric liquid crystal materials and their applications. As pointed out by Goodby, ferroelectric liquid crystals require at least two aromatic rings in the core and two terminal chains at the end of the core, one of which contains at least one chiral group.[3] In order to obtain new ferroelectric liquid crystal materials with broad Sc* range and also to study the relationship between the molecular structure and the mesomorphic and electro-optical properties of ferroelectric liquid crystals, we have synthesized chiral compounds having heterocycles in the core and investigated their mesomorphic and electro-optical properties.[4] In this paper, we describe the synthesis and the mesomorphic and electro-optical properties of chiral compounds bearing 2-phenyl-1,3,4-thiadiazole rings.

SYNTHESIS

The compounds studied were prepared as outlined in Scheme I. The methyl ester of 4-substituted benzoic acid (**1**) was converted to acylhydrazide (**2**) with hydrazine



SCHEME I Synthetic route of 2-phenyl-1,3,4-thiadiazole

hydrate, followed by acylation with corresponding acid chloride to afford diacylhydrazide (**3**). Construction of the 1,3,4-thiadiazole ring was achieved by treatment with phosphorous pentasulfide or Lawesson's reagent in 35–70% yield. The starting materials, **1**, were commercially available or obtained by etherification of methyl 4-hydroxybenzoate with corresponding alkyl tosylate. The final products were purified by column chromatography on silica-gel using hexane and ether as the eluent, followed by recrystallization from ethanol.

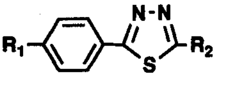
RESULTS AND DISCUSSION

Melting and transition temperatures were measured with a polarizing microscope equipped with a heating stage and a differential scanning calorimeter (DSC). Identity of the mesophases was confirmed by examining the texture of a thin sample sandwiched between glass slides.[5] The phase transition temperatures of homologous series of **4** and **5** are given in Table I and Table II, respectively. The phase transition diagrams for these compounds are shown in Figure 1.

Most members of 2-phenyl-1,3,4-thiadiazole derivatives investigated exhibited the chiral smectic C (Sc*) phase and the nematic phase was not observed in any homologs. Compounds of **4** series exhibited a high propensity to show the Sc* phase and had I-Sc*-C mosomorphogy, excepting **4i** and **4j**, which have a monotropic unidentified smectic phase below the Sc* phase. On the other hand, compounds of **5** series showed the monotropic Sc* phases which can be readily supercooled at room temperature. For example, compound **5e** exhibited the monotropic

TABLE I

Phase transition temperatures of homologous series **4**



Compound	R_1-	-R_2	Phase transition temp.$^{a)}$				
			Cr	Sx	Sc*	SA	Iso
4a		-C_8H_{17}	• 57.0				•
4b		-C_7H_{15}	• 65.5		• 67.4		•
4c		-C_8H_{17}	• 59.0		• 66.6		•
4d		-C_9H_{19}	• 58.5		• 69.0		•
4e		-$C_{10}H_{21}$	• 58.0		• 68.8		•
4f		-C_8H_{17}	• 47.5		• 63.6		•
4g		-C_7H_{15}	• 70.0		• 75.0		•
4h		-C_8H_{17}	• 61.8		• 75.4		•
4i		-C_9H_{19}	• 59.0	(•57.0)	• 78.3		•
4j		-$C_{10}H_{21}$	• 55.0	(•54.4)	• 77.5		•

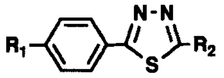
a) Cr: crystalline solid, Sx: unidentified smectic phase, Sc*: chiral smectic C phase, SA: smectic A phase, Iso: isotropic liquid phase. ( ) indicates a monotropic phase transition.

Sc* phase from 27.4°C to 11.9°C. Comparing the homologous series of **4** with **5**, lacking the oxygen in compounds **5** series, it is noticed that the oxygen exerts a stability effect on the smectic phase, resulting in reducing the stability of the smectic phase. Compounds of **5** series which have no dipole moments at the side chains, exhibited the smectic phase. This must imply that the dipole moment in a vertical direction to the molecular axis of the thiadiazole ring contributed to generate the smectic phase. Moreover, the bent structure of the 1,3,4-thiadiazole ring also seems to contribute to the formation of the smectic layers. The reason for this is now under investigation. The Sc* thermal stabilities of compounds of **4** series were not affected so much by the length of the terminal alkyl chain which was attached to the thiadiazole ring (R_2), however melting points decreased with increasing the length of the alkyl chain. As a result, the Sc* ranges increased with increasing the length of the terminal alkyl chain which was attached to the thiadiazole ring (R_2). Compound **4j** showed the broadest Sc* range, about 23°. From the above results, it is clear that thiadiazole ring strongly promotes the occurrence of the chiral smectic C phase and seems to suppress the appearance of other smectic phases and the nematic phase.

For compounds **4h** and **5e**, the spontaneous polarizations (Ps) and optical response times (τ) were measured on 2 μm thick cells at a temperature 10°C below

TABLE II

Phase transition temperatures of homologous series **5**



Compound	R_1-	-R_2	Phase transition temp.[a)]				
			Cr	Sx	Sc*	SA	Iso
5a	C_8H_{17}-		· 19.0				·
5b	C_9H_{19}-		· 23.6				·
5c	C_6H_{13}-		· 39.5			(·24.0)	·
5d	C_7H_{15}-		· 42.6		(·27.5)	(·34.0)	·
5e	C_8H_{17}-		· 28.6	(·11.9)	(· 27.4)	·33.5	·
5f	C_9H_{19}-		· 34.2	(·22.5)	(·32.5)	·39.0	·

a) Cr: crystalline solid, Sx: unidentified smectic phase, Sc*: chiral smectic C phase, SA: smectic A phase, Iso: isotropic liquid phase. ( ) indicates a monotropic phase transition.

the upper limit of the Sc* phase. The results are shown in Table III. Spontaneous polarization was obtained by the triangular wave method (±10 V, 200 Hz).[6] Optical response time was obtained by applying a rectangular wave (±10 V, 200 Hz) and was defined as the time difference between voltage reversal and a 90% change in optical transmission. The Ps values were very small, in agreement with the general rule that if the dipole is remote from the chiral center, the Ps values will be small.[7] Optical response times, however were relatively fast. This is probably due to the effect of the small rotational viscosity of the 2-phenyl thiadiazole ring.

EXPERIMENTAL

IR, ^1H NMR and mass spectra were recorded on a Shimadzu IR-408, Varian EM-360 and Hitachi M-80, respectively, under standard conditions. The final products were purified by column chromatography on silica-gel followed by recrystallization from ethanol. The phase transition temperatures were determined using a Rigaku Denki DSC-8230 apparatus and texture observations were made using a Nikon XTP-II polarizing microscope in conjunction with a Mettler FP-82 hot stage and FP-80 control unit. The preparation of compound **4h** as a representative is given below.

Methyl (S)-4-(6-methyloctyloxy)benzoate (2: R_1 = (S)-6-methyloctyloxy)

To an ice-cooled suspension of 60% sodium hydride (0.44 g, 11.0 mmol) in dry DMF (5 ml) was added a solution of methyl 4-hydroxybenzoate (1.50 g, 9.9 mmol)

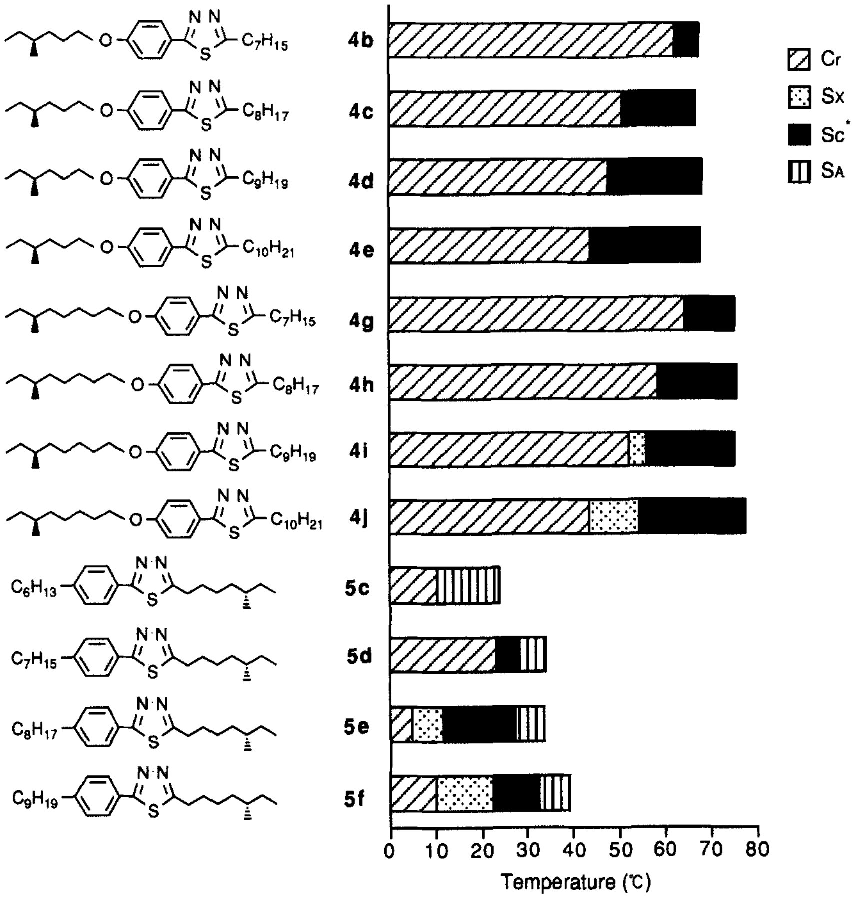


FIGURE 1 Phase transition diagrams of homologous series **4** and **5**

TABLE III

Spontaneous polarizations (Ps) and optical response times (τ) of compounds **4h** and **5e**[a]

Compound	Ps (nC/cm^2)	τ (μsec)
4h	<0.1	400
5e	<0.1	500

a) Ps and τ were measured on 2 μm thick cells at a temperature 10℃ below the upper limit of the Sc* phase.

in dry DMF (10 ml). After stirring for 30 min, (*S*)-6-methyloctyl *p*-toluenesulfonate (3.3 g, 11.1 mmol) was added dropwise and the mixture was stirred for 1 hour at room temperature and then heated at 50°C for 1 hour. After cooling, the reaction mixture was poured into cold water and extracted several times with ether. The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was purified by column chromatography on silica-gel with hexane-ether as eluent to yield methyl (*S*)-4-(6-methyloctyloxy)benzoate (2.50 g, 91.1%).

IR (Neat) 3010, 2950, 1730, 1560, 1505 cm^{-1}; NMR ($CDCl_3$) δ = 0.75–1.07 (6H, m), 1.05–2.00 (11H, m), 3.90 (3H, s), 4.04 (2H, t, *J* = 7 Hz), 6.96 (2H, d, *J* = 9 Hz), 8.04 (2H, d, *J* = 9 Hz); Mass: m/z 278 (m^+)

(*S*)-4-(6-methyloctyloxy)benzoic hydrazide (3: R_1 = (*S*)-6-methyloctyloxy)

A mixture of (*S*)-methyl-4-(6-methyloctyloxy)benzoate (2.3 g, 8.26 mmol), hydrazine hydrate (3.0 g, 59.3 mmol) and 3.0 ml of ethanol was stirred at 100°C for 3 hours. After cooling to room temperature, the resulting precipitate was collected and washed several times with water to afford (*S*)-4-(6-methyloctyloxy)benzoic hydrazide (2.10 g, 91.3%).

IR (Nujol) 3250, 2950, 1650, 1600, 1590 cm^{-1}; NMR ($CDCl_3$) δ = 0.60–1.00 (6H, m), 1.05–2.10 (11H, m), 4.00 (2H, t, *J* = 7 Hz), 4.60–5.50 (2H, br), 6.95 (2H, d, *J* = 9 Hz), 7.50–7.95 (3H, m); Mass: m/z 278 (m^+)

(*S*)-2-{4-(6-methyloctyloxy)phenyl}-5-*n*-octyl 1,3,4-thiadiazole (4h)

To an ice-cooled solution of (*S*)-4-(6-methyloctyloxy)benzoic hydrazide (1.0 g, 3.60 mmol) in pyridine (10 ml) was added nonanoyl chloride (0.67 g, 3.80 mmol) for 30 min. and the mixture was stirred for 1 hour at room temperature and then heated at 80°C for 1 hour. After cooling to room temperature, phosphorous pentasulfide (1.60 g, 7.20 mmol) was added in several portions and refluxed for 15 hours. The reaction mixture was poured into cold water and extracted with ether. The combined ethereal layers were washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was purified by column chromatography on silica-gel with hexane-ether as eluent followed by recrystallization from ethanol to yield **4h** (0.70 g, 46.8%).

IR (Nujol) 1600, 1570, 1510 cm^{-1}; NMR ($CDCl_3$) δ = 0.70–1.05 (9H, m), 1.05–2.10 (23H, m), 3.13 (2H, t, *J* = 7 Hz), 4.03 (2H, t, *J* = 7 Hz), 7.00 (2H, d, *J* = 9 Hz), 7.90 (2H, d, *J* = 9 Hz); Mass: m/z 416 (m^+); Found: C, 72.31; H, 9.59; N, 6.69; S, 7.70%. Calcd for $C_{25}H_{40}N_2OS$: C, 72.06; H, 9.67; N, 6.72; S, 7.69%.

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