Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Lackner, A. M. , Wong, S. M. , Lim, K-C. , Margerum, J. D. and Neubert, M. E.(1989) 'Properties of new ferroelectric materials', Liquid Crystals, 5: 4, 1259 — 1267

To link to this Article: DOI: 10.1080/02678298908026432

URL: http://dx.doi.org/10.1080/02678298908026432

LIQUID CRYSTALS, 1989, VOL. 5, NO. 4, 1259–1267

Properties of new ferroelectric materials

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A homologous series of chiral 4-(3-methylpentyl)benzenethio-4′-*n*-alkoxybenzoates has been studied. These thioesters display a ferroelectric, chiral smectic C phase in addition to cholesteric and smectic A phases. A comparison is made between the thioester series and a phenylbenzoate, having the same molecular end group. The effect of the different central linkage on the transition temperature, and on the physical and ferroelectric liquid crystal (FLC) properties has been investigated. Several mixtures, containing these thioester components, were calculated and formulated to obtain room temperature chiral smectic C phases. Spontaneous polarization P_s values and electro-optical response times are correlated with chemical structures. Although these thioesters have very low P_s values, they are useful components for FLC mixtures because of their convenient chiral smectic C temperature ranges and their low viscosities.

1. Introduction

Ferroelectric liquid crystals (FLCs) are potentially attractive for devices, because they permit direct interaction of the liquid crystal with an electric field in both the turn-on and turn-off directions by reversing the polarity of the field. The switching times can be much faster than in nematic electro-optic effects, partly because of the field interaction with the directional polarization of bistable FLCs. The basic ferroelectric liquid-crystal properties, discovered by Meyer [1], demonstrated that a tilted smectic phase formed from chiral mesogenic molecules possesses an electric dipole, which is perpendicular to the molecular tilt direction, and parallel to the smectic layer plane. Clark first demonstrated [2, 3] surface-stabilized ferroelectric liquid-crystal devices of 1–2 μm thickness with microsecond responses at elevated temperatures. In recent years numerous components and room-temperature mixtures have been synthesized [4, 5] for fast electro-optic applications. In the present work we report studies of the formulation and characterization of new room-temperature FLC mixtures containing thioester components. This work was initiated to evaluate the use of alkyl, alkoxy thioesters as FLC components, which we expected to have a good chiral smectic C range and a lower viscosity than the dialkoxy phenyl benzoate structures being used. The transitional properties of the single components and their eutectic mixtures were evaluated, together with the measurements of their electro-optic properties.

2. Experimental

We have studied a homologous series of optically active branched-chain thioesters. The synthetic procedure for this 4-(3-methylpentyl)benzenethio-4′-*n*-alkoxybenzoate series was described by Neubert *et al.* [6]. To formulate various room-temperature eutectic mixtures, we have synthesized ester components, such as the dioctyloxyphenyl benzoate (80-08) and (+)-2-methylbutyl 4-(4-*n*-octyloxyphenyl)benzoate (BE08), a known FLC component [4]. For the BE08, we used a standard synthetic procedure [7], namely hydrolysis of the octyloxycyanobiphenyl (BDH-M24) starting material, followed by the reaction of the octyloxyphenylbenzoic acid with the optically active 2-methylbutanol. Two new esters (E010 and E0101) were synthesized with terminal substituents containing carbonyl groups [8], and their chemical structures are shown in table 1. Commercially available phenylbenzoate (W82) and lactic ether (W7 and W37) FLC materials [9] were also used for mixture preparations. The transition temperature and heat of fusion ΔH measurements were done on a Mettler Differential Scanning Calorimeter TA2000B System (scanning at 3°C min^{-1}); the smectic phases were identified on a Zeiss polarizing microscope equipped with a Mettler FP5 hot stage (heating rate at 2 or 3°C min^{-1}). The pitch of the FLC components was recorded by optical microscopy, and the twist direction by contact studies with known materials. Dielectric anisotropy was measured in the S_A phase, near the S_C^* transition temperature, using a 7 kG magnetic field [10]. For the measurement of the electro-optic properties, transmission mode test cells were fabricated from indium–tin oxide (ITO) coated optical flats, with 2·5 μm thick SiO_x spacers, or 5·0 μm Mylar spacers. The FLC alignment was obtained by directional rubbing of the spin-coated polyimide layer on the conductive ITO layer.

The experimental apparatus for the simultaneous measurement of the ferroelectric and optical responses is shown in figure 1. P1 and P2 are a pair of cross-polarizers, C is a parallel-aligned thin FLC cell with one of its stable optic axes parallel to the optic axes of one of the polarizers. The intensity of the light transmitted through P1 and P2 was measured with a photodiode. Low-frequency square-wave signals from the signal generator were amplified and applied serially across the FLC cell and a load resistance R_L. The displacement current, due to the charge stored in the capacitance of the cell, and the spontaneous polarization of the FLC were measured as the voltage drop across the load resistance. The signals from the photodiode and the load resistance were stored in a Tektronix storage oscilloscope and analysed with an IBM-AT computer. A square-wave driving voltage of ±70 V was used across an

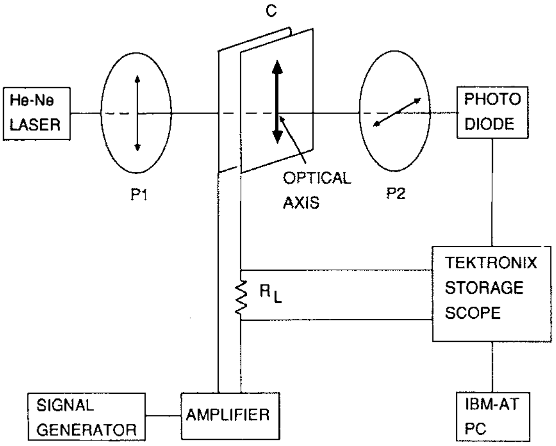
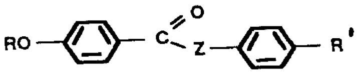


Figure 1. Optical set-up used for the spontaneous-polarization measurements.

Table 1. Physical properties of new ferroelectric liquid-crystal components



Code	R	Z	R′	P_s/nC cm^{-2} at 21°C	Pitch/μm	Twist	Δε	$T_{S_C^*C}$/°C	$T_{CS_C^*}$/°C	$T_{S_C^*S_A}$/°C	T_{S_ACh}/°C	T_{ChI}/°C	ΔH/kJ mol^{-1}
S07	C_7H_{15}	S	$(CH_2)_2\underset{CH_3}{\overset{*}{C}}HC_2H_5$	< 1	~4	L	+	(19·1)	42·5	50·8	52·0	63·3	27·4
S08	C_8H_{17}	S	$(CH_2)_2\underset{CH_3}{\overset{*}{C}}HC_2H_5$	< 1	~4	L	+	(6·0)	38·3	59·0	65·3	68·4	30·6
S09	C_9H_{19}	S	$(CH_2)_2\underset{CH_3}{\overset{*}{C}}HC_2H_5$	< 1	~4	L	+	(22·9)	50·4	65·0	67·6	68·2	25·8
S010	$C_{10}H_{21}$	S	$(CH_2)_2\underset{CH_3}{\overset{*}{C}}HC_2H_5$	< 1	3·9	L	+	(2·2)	39·0	68·6	—	71·4	26·9
E010	$C_{10}H_{21}$	O	$COO\underset{CH_3}{\overset{*}{C}}HC_6H_{13}$	> 12				(22·3)				28·7	24·5
E0101	$C_{10}H_{21}$	O	$CH_2COO\underset{CH_3}{\overset{*}{C}}HC_6H_{13}$	< 0·1				(17·2)				34·2	42·7

approximately 5 μm thick surface-stabilized FLC sample cell. Response-function data were corrected for the *RC* time constant of the sample cell, the displacement current due to the capacitance, and the conductivity of the liquid crystal. For temperature-dependence measurements, the sample cells were heated in an oven with temperature stability of ±0.1°C.

3. Results and discussion

3.1. *Thermal properties*

Optically active thioesters were considered here for ferroelectric liquid-crystal studies because of indications that they would have more smectic phases and wider temperature ranges than the corresponding phenylbenzoates. Dialkoxy thiophenylbenzoates have been reported [11, 12], but the branched chain alkyl–alkoxy thioesters promised to have lower viscosity and therefore a faster response time. For alignment of the FLCs and device fabrication, the following four-phase sequence is considered important [13]: chiral smectic C (S_C^*), smectic A (S_A), cholesteric (Ch of N*) and isotropic (I). Most of the 4-(3-methylpentyl)benzenethio-4′-*n*-alkoxybenzoate homologues showed all of these phases, with the S_C^* phases not far above room temperature. The transition temperatures for the 7–10 carbon chain thioesters are in good agreement with prior measurements [6] and are listed as the first four components in table 1. The freezing points (C) of the chiral thioesters were observed while cooling the samples. The heat of fusion data were calculated by integrating the crystalline-to-S_C^* transition peak. All four branched-chain thioesters have a left-handed twist direction with a small pitch of about 4 μm. These components all have positive dielectric anisotropy ($\Delta\varepsilon$). Measurement of a binary mixture of S07 + S010 gave $\Delta\varepsilon = 0{\cdot}2$ in the nematic phase at 65°C and $\Delta\varepsilon = 0{\cdot}1$ in the smectic C* phase (25–55°C). The last two components listed in table 1 are optically active 2-octanol phenylbenzoate derivatives, which have no apparent liquid-crystalline phases, but which are useful as dopants. The (+)-2-methylbutyl 4-(4-*n*-octyloxyphenyl)benzoate (BE08), used in a table 2 mixture, showed both S_A and S_C^* phases on cooling, with a chiral smectic C range of 37–44°C, in good agreement with Goodby [4].

With these newly synthesized FLC components and some commercially obtained components, we calculated room-temperature eutectic mixtures, using a revised version of the computer program in [14], based on the Schroeder–van Laar equation, previously set up for calculation of nematic mixtures. The S_C^*–S_A and S_A–N* transition temperatures were calculated as the arithmetic averages of the components' phase transition temperatures multiplied by their mole fraction used in the FLC mixture. The calculated transition temperatures for smectic mixtures were all in good agreement with experimental data. We have formulated wide-temperature-range chiral smectic C mixtures, with accurately predicted transition temperatures for their smectic A and nematic phases. Four typical mixtures, listed in table 2, showed good agreement between experimental and calculated phase-transition values. These mixtures represent examples of a binary thioester mixture (FLC-1), the combination of thioesters with phenylbenzoates (FLC-7, -14), and the combination of thioester with a lactic ether phenylbenzoate (FLC-26). We found that the spontaneous polarization is very low for the thioester components and their mixture. However, they are favourable as FLC hosts because of their good smectic temperature ranges and their ease of mixing with other ester structured components. A binary thioester mixture had a 25–58°C S_C^* range, while mixing three chiral thioesters and a non-chiral phenylbenzoate with an S_C phase extended the FLC phase to a 3–60°C range. The close

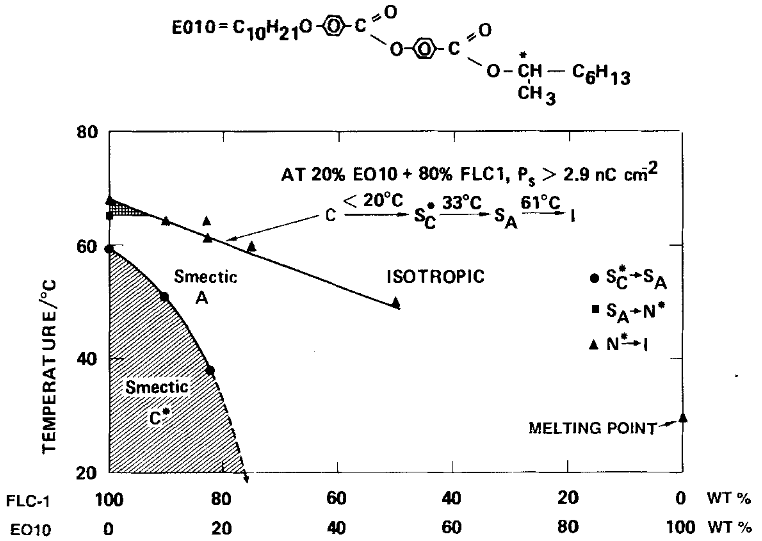


Figure 2. Phase diagram of chiral 4-(4′-*n*-decyloxybenzoyloxy)-1-methylheptylbenzoate crystal component (E010) and FLC-1 thioester mixture, where FLC-1 is 47 per cent S07 and 53 per cent S010.

Table 2. Eutectic FLC mixtures: calculated versus measured properties

Mixture	HRL-FLC-1		HRL-FLC-7		HRL-FLC-14		HRL-FLC-26	
Components								
thioesters	S07, S010		S07, S08, S010		S07, S08, S010		S07, S010	
phenylbenzoates	—		80-08		BE08		W37	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
Melting point/°C	22·1	25·0	9·4	3·4	7.3	< 22	12·7	< 22
Transition temperature/°C								
$S_C^* \to S_A$	60·3	58·6	60·8	60·0	57·4	53·3	48·2	48·5
$S_A \to N^*$	62·3	65·2	63·9	65·8				
$S_A, N^* \to I$	67·6	67·3	69·6	69·1	67·6	66·5	59·8	61·0
P_s/nC cm^{-2} at 21°C	< 1				~2	0·4	~5	1·0

agreement of measured versus calculated transition temperatures for FLC-14 and FLC-26 indicated favourable mixing of optically active thioesters, esters and lactic ether phenylbenzoates.

The binary thioester mixture FLC-1 was used as a host for studies of the optically active 2-octanol derivatives, which have a large molecular dipole but lack any liquid-crystalline properties. This was the inverse of a prior report [15] in which an achiral thioester component was mixed with a chiral 2-octanol derivative (Merck S811) to form an S_C^* phase. We determined a phase diagram with mixtures containing up to 25 per cent of E010 in FLC-1, shown in figure 2, where the transition temperatures and smectic-phase identification were obtained with the microscope hot stage. This showed a very narrow cholesteric range (only with less than 5 per cent E010), but a wide smectic A phase, and a room temperature chiral smectic C phase up to

25 per cent E010 concentrations. We select the mixture with 20 per cent E010 and 80 per cent FLC-1 for more detailed testing, it had an S_C^* range extending from below 20 to 33°C.

3.2. *Electro-optic properties*

The switching time of ferroelectric liquid crystals is nominally related to P_s by:

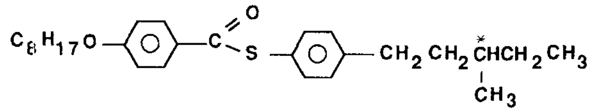
$$\tau \approx \eta/P_s E,$$

where P_s is the spontaneous polarization, E is the applied field strength and η is the viscosity. The switching time can be decreased by increasing the value of P_s. However, except for the sign of P_s with respect to helicity [15], the prediction of the magnitude of the resultant P_s for a mixture of liquid crystals is not straightforward. We have investigated the result of mixing two different classes of FLC materials. Our results for mixing a lactic ether (W7) with a phenylbenzoate (W82), or with a thioester such as S08 showed that P_s, given in table 3, is less than the arithmetic average of the components, even though all three components have the same sign, $+P_s$. The W7 component did not improve the P_s value, as expected, but the mixtures did form binary eutectics, as shown by good agreement of the experimental and predicted transition temperatures.

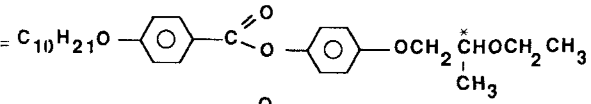
Table 3. Comparison of chiral thioester and ester properties in binary mixtures with W7 lactic ether phenylbenzoate

Mixture† 1 : 1	$T_{S_C^*S_A}$/°C	T_{S_AI}/°C	P_s‡/nC cm^{-2}	Response time‡/ms
S08/W7	43·7	55·0	3·3	0·35
W82/W7	49·0	60·8	4·5	0·51

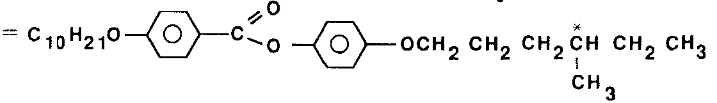
†S08 =



W7 =



W82 =



‡Measured at 21°C, with ±70 V, 15 Hz signal, electrode 3·1 cm^2, cell spacing 5 μm.

The temperature dependence of P_s for the samples of W82/W7 and S08/W7 are shown in figures 3 and 4. The linear scale plots (see figure 3) show that P_s vanishes above T_c, as expected. The log–log plot of P_s versus $T - T_c$ (see figure 4) shows that P_s decreases according to $P_s \sim (T - T_c)^{0 \cdot 5}$; the exponent of 0·5 is slightly higher than most published values [16]. Both samples have similar temperature dependences, as shown in figures 3 and 4. The square-wave-driven (±70 V, 15 Hz) optical response times at 21°C of the samples W82/W7 and S08/W7 are 0·51 and 0·35 ms respectively. The faster response time observed with the S08/W7 mixture (despite its smaller P_s value) clearly indicates that this S08 alkyl alkoxy thioester component has a lower

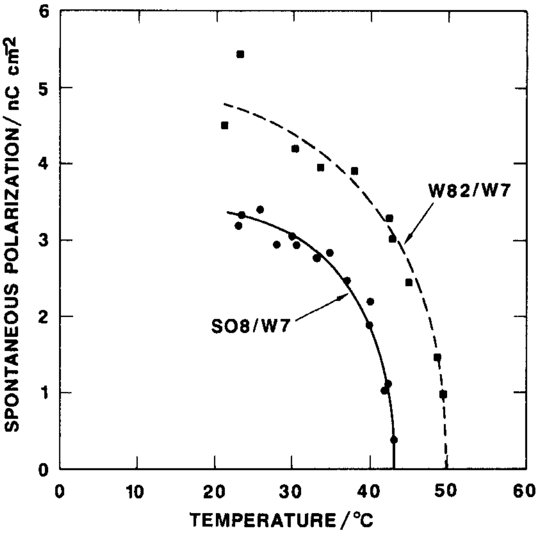


Figure 3. Temperature effect on the spontaneous polarization of S08/W7 and W82/W7 FLC mixtures.

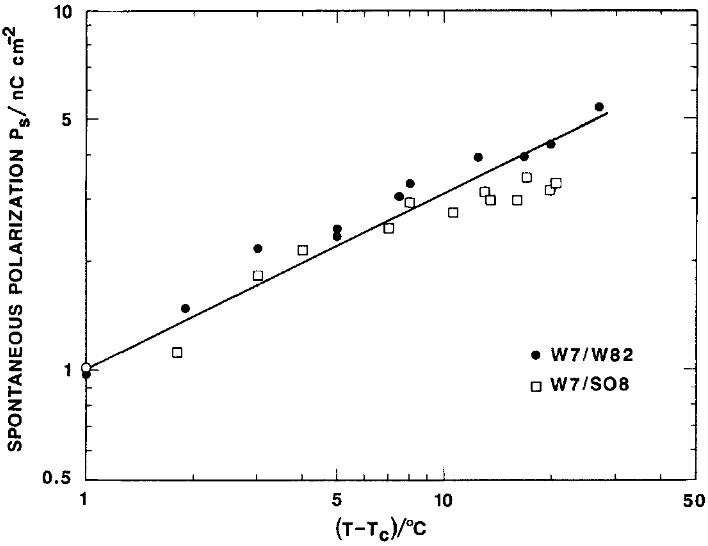


Figure 4. Spontaneous polarization versus reduced temperature in S08/W7 and W82/W7 FLC mixtures.

room temperature viscosity than the W82 dialkoxy phenylbenzoate. As shown in table 3, the S08/W7 mixture has a S_C^*–S_A transition temperature that is about 5°C lower than for the W82/W7 mixture; this would contribute to the lower viscosity of the former mixture. However, this effect is compensated for by the smaller P_s value and is probably small compared with the chemical structure differences.

The optically active 2-octanol phenylbenzoate derivative E010 was expected to have a high P_s, because of its conjugated structure and strong electric dipole (see table 1). We studied the effect of inserting a $-CH_2$ spacing group into this structure, thereby reducing the conjugation and moving the chiral centre further away from the core in the E0101 component. These solids did not show liquid-crystalline phases and so we evaluated their electro-optic properties in a thioester host, 80 per cent FLC-1/20 per cent E010 and 80 per cent FLC-1/20 per cent E0101 (in weight per cent). The chiral group in E010 is more rigidly connected to the centre core than in E0101, where the optically active carbon was further separated by a methylene group. E010 and E0101 are not FLCs; however, because of the expected strengthening of the conjugation in E010; it should have a larger mixture-induced P_s compared with that of E0101. This is indeed the case; the measured P_s for FLC-1/E010 was more than $2{\cdot}9\,nC\,cm^{-2}$ and for FLC-1/E0101, $P_s < 0{\cdot}01\,nC\,cm^{-2}$ at 21°C. From the measured spontaneous-polarization values, we extrapolated $P_s > 12$ and $< 0{\cdot}1\,nC\,cm^{-2}$ for the E010 and the E0101 single components respectively. We are not able to align the FLC-1/E010 for surface stabilization. From visual microscopic observation, it appeared to have an extremely short pitch, which may account for the difficulty in alignment. Because of the poor alignment of the sample, the actual P_s could be higher than the measured value of $2{\cdot}9\,nC\,cm^{-2}$. For the FLC-1/E0101, it had reasonably good alignment, and the measured value for P_s of $0.01\,nC\,cm^{-2}$ is near the limit of our instrumental resolution. In both cases, because of the low P_s of the host FLC, FLC-1, we did not expect the 20 per cent doped mixtures to have high P_s values.

A more interesting aspect of the thioester mixtures is in some of their resultant response times. The response time of FLC-1/E0101 is 0·155 ms (at 21°C with ±70 V, 15 Hz square-wave signal across a 5 μm thick cell), which is quite fast considering that the P_s of the mixture is nearly zero ($< 0{\cdot}01\,nC\,cm^{-2}$). This result is potentially important, as it implies that the viscosity of thioester-type mixture is low. Although the thioester itself may have a very low P_s, it could be used as a component in mixtures of FLCs to improve the switching speed of the resultant FLC materials.

We are indebted to Willis H. Smith, Jr., for his assistance with the ferroelectric liquid-crystal alignment and D.S.C. studies.

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