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Ferroelectric smectic C liquid crystal mixtures: relationship between molecular structure, ferroelectricity and electro-optic response

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The relationship between the physical properties and the molecular structure of a number of smectic C compounds has been investigated. Special emphasis was placed on the study of a new class of laterally substituted smectic C compounds incorporating a *trans*-1,4-disubstituted cyclohexane ring. We have investigated the influence of new chiral dopants on the ferroelectric and physical properties of smectic C mixtures. New chiral smectic C liquid crystal mixtures have been developed. Due to the low response times, low birefringence and excellent chemical and U.V. stability, these mixtures are particularly well suited for electro-optic device applications.

1. Introduction

Since Clark and Lagerwall [1] reported that chiral smectic C (S_C^*) liquid crystals, which are ferroelectric, exhibit bistable switching in the surface stabilized geometry, surface stabilized ferroelectric liquid crystal displays (SSFLCDs) have attracted strong interest for various applications such as fast electro-optic switching elements and high information content panels [2]. The commercial exploitation of these devices depends, among other factors, on the availability of suitable rapidly responding S_C^* mixtures.

The development of optimized S_C^* mixtures requires an understanding of the relationship between the electro-optic display performance, the physical properties of the S_C^* mixture and the molecular structure of the constituent S_C and chiral components. Here we present the results of measurements on a new class of smectic C compounds incorporating a *trans*-1,4-disubstituted cyclohexane ring (see §2) and on novel chiral dopants (see §3). The synthesis and liquid crystal transition temperatures of the S_C compounds have been described recently [3, 4] and the influence of several lateral substituents in various positions on the liquid crystal transition temperatures of these substances has been investigated [5]. Figure 1 shows the molecular structure of the smectic C compounds and the chiral dopants in question. Using some of these compounds fast S_C^* mixtures have been developed. The characteristic data of these mixtures are presented in §4.

2. Smectic C compounds

The speed of the electro-optic response of S_C^* mixtures depends on the viscosity and the spontaneous polarization, P_s . The characteristic time τ_n governing the reorientation of the director \mathbf{n} under the influence of an electric field, \mathbf{E} , is given by [6]

$$\tau_n = \frac{\gamma \sin^2 \Theta}{P_s E}, \quad (1)$$

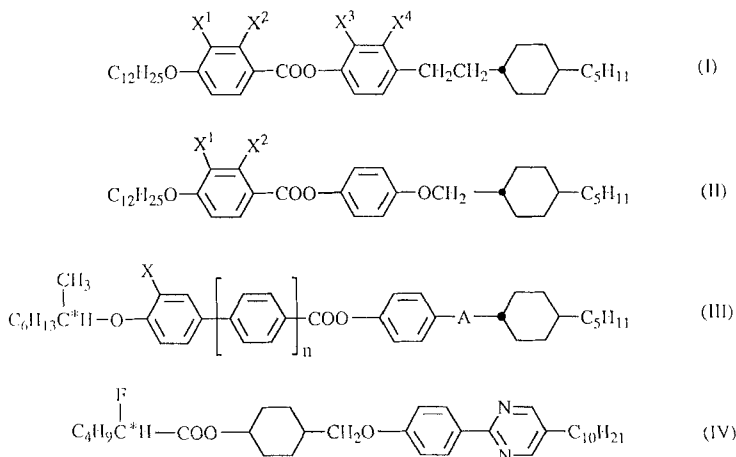


Figure 1. Molecular structures of the smectic C compounds I and II ($X^1 = \text{H, F, Cl, Br}$; $X^{i>1} = \text{H or F}$) and the chiral compounds III ($X = \text{H, F, Cl, Br, CN}$; $n = 0$ or 1 ; $A = \text{CH}_2\text{CH}_2$ or OCH_2) and IV.

where Θ is the tilt angle and the rotational viscosity γ refers to the rotation about an axis perpendicular to \mathbf{n} and P_s [6]. Equation (1) describes the reorientation of the director in the bulk of the sample and disregards the coupling of the director and the spontaneous polarization with the cell boundaries, which can lead to several surface stabilized geometries other than the uniform bookshelf geometry [7]. It should be noted also that the transmission of SSFLCDs depends not only on the director configuration but also on the polarizer orientations, the cell thickness and the refractive index anisotropy. So, *a priori*, we cannot assume that the optic response time τ of SSFLCDs is given by an equation similar to equation (1), i.e. that

$$\tau \approx \frac{\gamma \sin^2 \Theta}{P_s E}. \quad (2)$$

We have verified the validity of equation (2) by measuring the response of $2 \mu\text{m}$ thick SSF-layers exhibiting bistability for a number of long helical pitch ($p > 6 \mu\text{m}$) S_C^* mixtures. The layers were aligned on rubbed polyimide coatings by cooling the mixtures slowly down through the S_A phase. The cells were driven using a square wave voltage ($\pm 10 \text{ V}$, 100 Hz). The transmission was measured using a photomultiplier; τ was taken as the time required for a transmission change from 0 to 50 per cent assuming that the difference between the dark and bright state is 100 per cent. P_s was measured in $10 \mu\text{m}$ thick cells using the triangular wave method [8]. Under appropriate driving conditions this method also yields the parameter $\gamma \sin^2 \Theta$ [6]. Figure 2 shows τ versus $\gamma \sin^2 \Theta / P_s$ for four different mixtures. These mixtures are composed of the same compounds as the commercial mixture FLC 5229 (see §4), although the compositions of the mixtures are different. In figure 2 every mixture is represented by a different symbol. For every mixture the switching time τ has been determined in the interval $10\text{--}40^\circ\text{C}$ at different temperatures and consequently for different values of the parameter $\gamma \sin^2 \Theta / P_s$. The temperature dependence of $\gamma \sin^2 \Theta / P_s$ is due primarily to

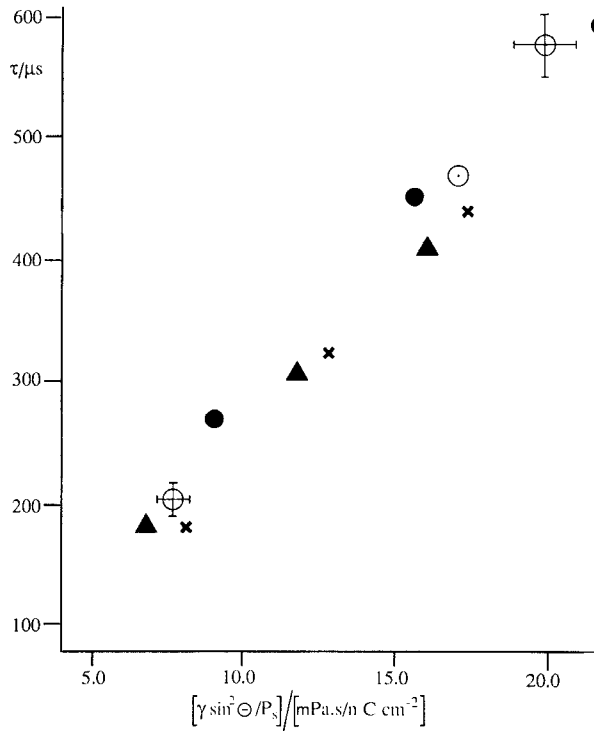


Figure 2. Response time τ , measured in $2 \mu\text{m}$ thick cells, using square wave drive ($\pm 10 \text{ V}$, 100 Hz), versus $\gamma \sin^2 \Theta / P_s$ (γ = rotational viscosity; P_s = spontaneous polarization; Θ = tilt angle). Different symbols refer to different long pitch S_C^* mixtures ($p \gtrsim 6 \mu\text{m}$). The mixtures are composed of the same compounds as the commercial mixture FLC 5229 (see §4), although the compositions of the mixtures are mutually different. The switching time τ has been measured at different temperatures, i.e. for different values of the parameter $\gamma \sin^2 \Theta / P_s$.

the strong temperature dependence of γ . The errors in P_s , $\gamma \sin^2 \Theta$ and $\gamma \sin^2 \Theta / P_s$ are estimated to be not greater than 5, 10 and 5 per cent, respectively. Figure 2 demonstrates convincingly the validity of equation (2). Thus, the bulk parameter $\gamma \sin^2 \Theta / P_s$ is a proper measure of the speed of response of SSFLCDs. It should be noted that equation (1) and consequently equation (2) are only valid within a given voltage range, denoted as the high fields range by Handschy and Clark [9]. In the high-field limit the influence of the surfaces is negligible compared with the strength of the coupling between P_s and E . As a consequence the director reorients practically as if the medium were infinite. At low voltages, well below the voltage used ($\pm 10 \text{ V}$), the influence of the cell surfaces cannot be disregarded and the switching behaviour deviates strongly from the high-field behaviour. At very high voltages, on the other hand, the dielectric coupling, i.e. the coupling between the field and the induced electric dipoles, becomes noticeable. When the dielectric coupling is dominant, the response time increases with increasing field, at least if the dielectric anisotropy, is negative [10].

Compounds I and II (see figure 1) are not chiral. Therefore, the relative differences in $\gamma \sin^2 \Theta$ and P_s for these compounds can only be determined indirectly, i.e. from

Table 1. Viscosity, $\gamma \sin^2 \Theta$, and spontaneous polarization, P_s , at 25°C of an S_C^* basic mixture (phase sequence I-96°C-N*-80°C-S_A-56°C-S_C^{*}) doped with 6 mol % of compounds I.

X^1	X^2	X^3	X^4	$\gamma \sin^2 \Theta / \text{mPa s}$	$P_s / \text{nC cm}^{-2}$	$\gamma \sin^2 \Theta P_s^{-1} / \text{mPa s nC}^{-1} \text{cm}^2$
H	H	H	H	78	7.0	11.1
F	H	H	H	79	7.7	10.3
H	F	H	H	76	6.9	11.0
H	H	F	H	102	7.3	14.0
H	H	H	F	73	7.0	10.4
Cl	H	H	H	90	8.0	11.3
Br	H	H	H	101	8.2	12.3

measurements on an S_C^* basic mixture doped with a given amount of the compound to be investigated. We have used an S_C^* basic mixture with the phase sequence: I-96°C-N*-80°C-S_A-56°C-S_C^{*}. The basic mixture was doped with 6 mol % of I. The results of the measurements are listed in table 1. These show that replacement of a hydrogen by a fluorine atom does not lead to a noticeable change in the viscosity, provided that the fluorine atom is at position 1, 2 or 4. However, a marked increase of the viscosity results if the occurs at position 3. The data collected in table 1 further show that replacement of the fluorine atom (X^1) by a chlorine or bromine atom leads to a strong increase in the viscosity. This increase can be understood merely on the basis of the size of the substituent [5]. Although compounds I are not chiral themselves, the mixtures investigated have different P_s values. The results seem to indicate that P_s increases with increasing viscosity. Such a correlation could in principle be understood by assuming that an increase of the viscosity leads to an enhanced hindrance of rotation along the long molecular axis and consequently to an enhancement of P_s [11]. Finally, it should be noted that the mixtures investigated have approximately the same tilt angle (24–25°).

Table 2 lists $\gamma \sin^2 \Theta$ and P_s of the mixtures containing 6 mol % of compounds II. Comparison of the results in tables 1 and 2 reveals that substitution of the same lateral groups in compounds I and II leads to the same relative viscosity changes. The most striking difference is that the mixtures containing compounds II are significantly more viscous than those containing the corresponding compounds I. The difference is about 20 per cent, which is considerable in view of the low doping concentration. These differences cannot be attributed to differences in the tilt angle which only ranges from 24 to 25°. This increase in viscosity is probably attributable to the presence of the additional oxygen atoms in the bridging group linking the benzene and cyclohexane rings (compounds II) instead of a CH₂ unit (compounds I).

Using a different S_C^* basic mixture (phase sequence: I-87°C-N*-78°C-S_A-53°C-S_C^{*}) measurements on some compounds were repeated. A higher concentration was

Table 2. Viscosity, $\gamma \sin^2 \Theta$, and spontaneous polarization, P_s , at 25°C of an S_C^* basic mixture (phase sequence I-96°C-N*-80°C-S_A-56°C-S_C^{*}) doped with 6 mol % of compounds II. ($X^2 = \text{H}$).

X^1	$\gamma \sin^2 \Theta / \text{mPa s}$	$P_s / \text{nC cm}^{-2}$	$\gamma \sin^2 \Theta P_s^{-1} / \text{mPa s nC}^{-1} \text{cm}^2$
H	97	7.7	12.6
F	93	7.9	11.8
Cl	111	8.5	13.1
Br	130	8.6	15.1

Table 3. Viscosity, $\gamma \sin^2 \Theta$, and spontaneous polarization P_s at 25°C of an S_C^* basic mixture (phase sequence 1-87°C-N*-78°C-S_A-53°C-S_C^{*}) doped with 13 mol % of compounds I ($X^3 = X^4 = H$) or II.

Compound	X^1	X^2	$\gamma \sin^2 \Theta / \text{mPa s}$	$P_s / \text{nC cm}^{-2}$	$\gamma \sin^2 \Theta P_s^{-1} / \text{mPa s nC}^{-1} \text{cm}^2$
I	H	H	56	5.7	9.8
I	H	F	59	5.7	10.4
II	H	H	76	6.5	11.7
II	H	F	73	6.2	11.8
II	F	H	78	6.5	12.0
II	Cl	H	123	7.8	15.8
II	Br	H	143	8.2	17.4

chosen (13 instead 6 mol %). Table 3 lists the results of the measurements. The same tendencies as discussed previously were observed.

3. Chiral materials

The main characteristics of a good chiral dopant would be: a high spontaneous polarization (P_s); a long helical pitch (p) for application in SSFLCDs or a short pitch for application in deformed helix ferroelectric LCDs [12]; high solubility associated with no adverse effects for the S_C^* transition temperatures and a low viscosity. The key characteristic is the spontaneous polarization, because a large value of P_s would allow the use of low concentrations of the chiral dopant(s) with the associated consequence that most properties of the S_C^* mixture would still be determined largely by the non-chiral S_C matrix. However, in the course of our investigations we found that the value of P_s measured depends not only on the concentration of the dopant(s) but also on the non-chiral S_C matrix used. This is illustrated by figure 3, which shows P_s/c , i.e. the value of P_s normalized to the weight fraction $c = 1$, of dopant III ($X = \text{CN}$; $n = 0$) versus the pyrimidine concentration of the non-chiral matrix used, which was composed of compounds I and phenylpyrimidines [13]. Dopant III was dissolved in an amount of 7 wt % ($c = 0.07$) in this matrix. The results in figure 3 indicate that a comparison of different chiral dopants makes sense only if the P_s values have been evaluated using the same non-chiral matrix.

The normalized spontaneous polarization P_s/c and the helical twisting power $1/cP$ of the chiral dopants III (see figure 1) were determined by using a 1:1 mixture of

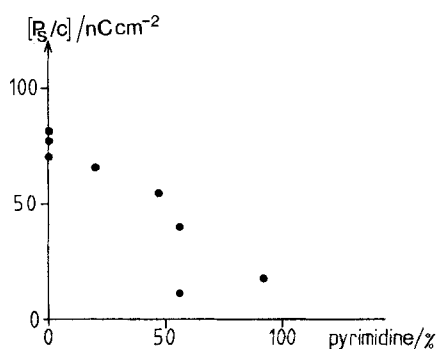


Figure 3. Spontaneous polarization P_s/c of dopant III ($X = \text{CN}$; $n = 0$) versus pyrimidine content of the mixture.

Table 4. Spontaneous polarization P_s/c , normalized to the weight fraction $c = 1$, and helical twisting power $1/cP$ of the S_C^* mixtures obtained by dissolving 7 wt % ($c = 0.07$) of compounds **III** in a 1:1 mixture of compounds **I** and pyrimidine compounds [13]. P_s was determined at $T_{S_C^*S_A} - T = 15^\circ\text{C}$, where $T_{S_C^*S_A}$ is the $S_C^*-S_A$ transition temperature. The quantity μ represents the permanent dipole moment of the X -substituted benzene ring [16].

X	μ/D	n	$P_s c^{-1}/\text{nC cm}^{-2}$	$c^{-1} P^{-1}/\mu\text{m}^{-1}$	$T_{S_C^*S_A}/^\circ\text{C}$
H	0	0	2.4	3.44	63
H	0	1	2.3	—	70
F	-1.47	0	14	—	65
Cl	-1.59	0	15	9.3	63
Cl	-1.59	1	9	6.8	69
CN	-4.05	0	54	9.72	68
CN	-4.05	1	32	6.7	68
Br	-1.57	0	9	—	61
Br	-1.57	1	3.4	6.7	69

compounds **I** and phenylpyrimidines [13]. The results are listed in table 4. The pitch p was determined by measuring the distance between dechiralization lines in 200–400 μm thick S_C^* layers [14]. A doping concentration of 7 wt % was chosen. Table 4 shows some interesting features: (a) the P_s values are approximately proportional to the dipole moment of the ring adjacent to the chiral group; (b) addition of a benzene ring next to the substituted benzene ring leads to a decrease of P_s ; and (c) the helical pitch of the compounds is rather short. So, for application of these dopants in SSFLCD mixtures only relatively low concentrations can be used in order to ensure that the liquid crystal layer thickness $d \ll p$. Higher concentrations of these dopants can only be used in combination with additional chiral compounds having the opposite helical sense of rotation, which leads to a dilation of the pitch without reducing P_s (pitch compensation). A long pitch ($1/cP = 0.75 \mu\text{m}^{-1}$), on the other hand, in combination with a relatively high spontaneous polarization ($P_s/c = 29 \text{nC cm}^{-2}$) has been observed for compound **IV**. Finally, we note that we have found that replacement of the $-\text{CH}_2\text{CH}_2-$ group, linking the benzene and cyclohexane rings, in compounds **III** by an $-\text{OCH}_2-$ group has no influence on the magnitude of P_s . So, modifications in the molecular structure far from the chiral group obviously do not affect the spontaneous polarization.

4. Commercial mixtures

Table 5 lists the physical data for two mixtures (FLC 5229 and FLC 5230) comprising the compounds discussed previously. The response times measured in 2 μm thick cells were determined in two different ways, viz. by applying $\pm 10 \text{V}$ continuous square wave drive (see §2) and by applying 30 V alternating positive and negative pulses. In the latter case the response time, τ_p , was taken to be equal to the minimum pulse width required to achieve full switching between the two bistable states. Table 5 shows that FLC 5229 is very fast, taking into account the relatively low value of P_s . Due to the low value of the birefringence of FLC 5229 optimum contrast is achieved in relatively thick cells ($d \approx 2.0 \mu\text{m}$).

Mixture FLC 5230 contains, in addition to the compounds mentioned previously, novel S_C compounds [15]. The speed of response of the mixture is even faster than that of FLC 5229, despite the broader S_C^* temperature range (see figure 4). Finally, we note

Table 5. Physical properties of mixtures FLC 5229 and FLC 5230. The S_C^* parameters were determined at 20°C. The response times were measured on 2 μm thick cells using ± 10 V continuous square wave (τ) and alternating positive and negative 30 V pulses (τ_p).

	FLC 5229	FLC 5230
Phase transition temperatures/°C	I-85-N*-68-S _A -52-S _C *-5-C	I-93-N*-82-S _A -63-S _C *-10-C
$\tau/\mu\text{s}$	310	250
$\tau_p/\mu\text{s}$	36	26
$P_s/n\text{C cm}^{-2}$	5.8	9.2
$\Theta/^\circ$	22.5	24.0
$\gamma \sin^2 \Theta/\text{MPa s}$	66	76
$\gamma/\text{MPa s}$	450	460
S_C^* pitch/ μm	14.0	8.5
N^* pitch/ μm	≥ 50	≥ 30
Dielectric anisotropy $\Delta\epsilon$	~ -2.0	~ -1.0
Birefringence Δn	0.135	0.130

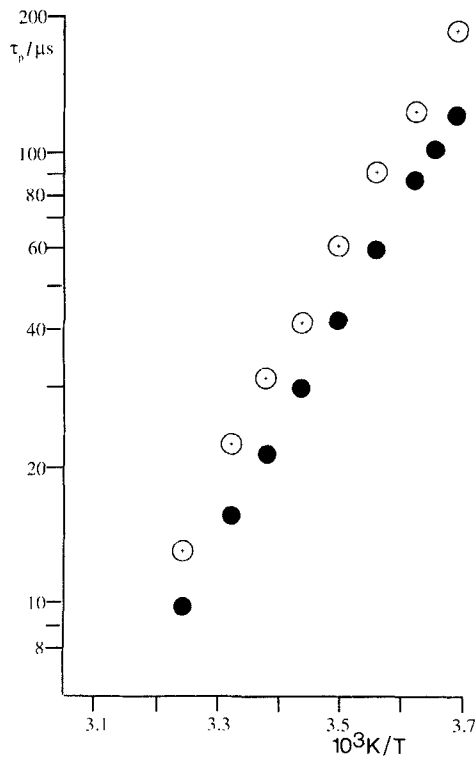


Figure 4. Response time τ_p versus the inverse temperature. τ_p has been measured on 2 μm thick cells using 30 V alternating positive and negative pulses. τ_p was taken to be equal to the minimum pulse width required to achieve full switching between the two bistable states. (○) FLC 5229, (●) FLC 5230.

that mixtures FLC 5229 and FLC 5230 show an excellent chemical, heat and U.V. stability.

5. Conclusions

The viscosity of the laterally substituted compounds **I** and **II** depends strongly on the nature and the position of the substituents. Replacement of a hydrogen by a fluorine atom does not lead to a noticeable change of the viscosity provided that the fluorine atom is at position 1, 2 or 4. A marked increase of the viscosity can be observed if the substitution occurs in position 3. Furthermore, the viscosity increases with increasing size of the substituent. Replacement of a $-\text{CH}_2-$ unit in the linking group between the benzene and cyclohexane rings (compounds **I**) by an oxygen atom (compounds **II**) leads also to a marked increase in viscosity.

The value of the spontaneous polarization of a chiral dopant dissolved in a non-chiral matrix depends strongly on the composition and the nature of this matrix. This implies that a comparison of different chiral dopants is only meaningful if the same non-chiral matrix is used. The spontaneous polarization of chiral compounds **III** is proportional to the dipole moment of the substituted ring adjacent to the chiral group.

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