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The best chiral compounds for the design of shock-free ferroelectric liquid crystal compositions with a wide temperature range of the chiral smectic C phase have been developed. For these experiments about 70 different 4-ring chiral compounds were synthesized and investigated. The influence of the chiral fragment, the mixing ratio between chiral and non-chiral molecules, and the pretilt angle of the alignment materials on the quality and on the mechanical stability of the orientation were investigated. New optimized ferroelectric liquid crystal compositions for the fabrication of shock-free ferroelectric liquid crystal displays with high contrast ratio are presented.

Keywords Chiral compounds; ferroelectric liquid crystal compositions; shock-free

1. Introduction

A basic requirement for the application of ferroelectric liquid crystals (FLC's) in electro-optical devices is the availability of chemically stable liquid crystal compounds and of materials which exhibit the ferroelectric phase (chiral smectic C) over a substantial temperature range around room temperature. FLC mixtures possessing the chiral smectic C (SmC^*) phase with a useful temperature range can be obtained by admixing chiral dopants into liquid crystal hosts formed by non-chiral material [1].

These FLC's respond much faster to an applied electric field than the nematics. These can be used for the manufacturing of fast-switching and bistable electro-optic devises. Therefore electro-optical effects with sub-microsecond switching speed are achievable using FLC's [2]. One of the main obstacles hindering the display application of FLC's is the fact that FLCD's are still sensitive to mechanical shock.

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The structure of the FLC layers in the cell can be easily destroyed by applying mechanical shock due to unstable molecular anchoring at the surface. The stability of device can be improved due to the existence of the uniform stripe-shaped domain (SSD) structure or due to the special alignment of the smectic layers in the display when an original chevron geometry of the smectic layers has been converted into a quasi-bookshelf geometry under electrical field treatment [3,4]. Nevertheless, the technological realization was not successful.

In our opinion, this problem can be solved through the development of new shock-free FLC compositions. The results presented in this paper allowed us to choose the right chiral compounds and the needed non-chiral molecules for the optimization of compositions able to create shock-free FLCD's with high optical contrast ratio. Our first studies in this area have shown that for such purposes the best choice is stiff and lengthy chiral molecules, so we decided to synthesize and to investigate 4-ring chiral compounds with different chiral fragments, different alkyl chains and different lateral substitutes in various positions [5,6]. The influence of the chiral fragment and the mixing ratio between chiral and non-chiral molecules on the quality and the stability of the orientation was investigated. Determination of physical properties (transition temperatures, phase sequence, spontaneous polarization and tilt angle) allowed to select a new chiral compounds suitable for preparation of FLC compositions. For the comparative experiment with new chiral compounds, we prepared two mixtures out of phenylpyrimidines and biphenylpyrimidines. In order to optimize the mixing ratio of the shock-free FLC compositions the right selection of testing cells is essential for performing the experiments.

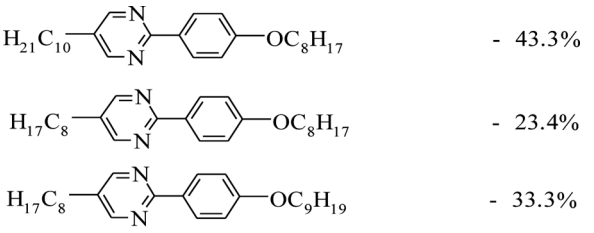
Finally we prepared few eutectic shock-free mixtures with a wide temperature range of the SmC^* phase.

2. Experimental Methods

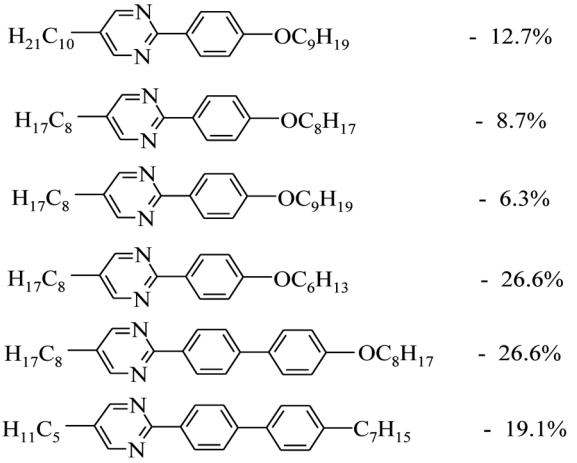
Phase transition temperatures of the single compounds and mixtures were measured using a Linkam hot stage connected with the polarizing microscope (MEIJI ML9400). Solution of the alignment materials were spin coated on a glass substrate with indium-tin oxide (ITO) layer (resistance of about 10–20 Ω/cm^2) at a 3000 rpm and then baked at 200°C for one hour. We used six different alignment materials with different pretilt angles (0–8°), but similar anchoring energy. For our experiments, testing cells with a pretilt angle between 0° and 1° are optimal. Aligning layers were unidirectional rubbed under a velvet-covered cylinder. The thickness of the cells was about 1.5–4 μm and measured in each case interferometrically. Change of a thickness of the cells (geometrical deviation) was also monitored interferometrically. The textures of the cells were observed using a polarizing microscope. The electro-optical properties were measured between crossed polarizers using a He-Ne laser. The light transmittance was detected by a photomultiplier and recorded in a digital oscilloscope. The rise and decay times were defined as the transmittance changes from 10% to 90% and vice versa. During electro-optic measurements, the temperature of the cells was controlled with the accuracy of 0.3°C. Determination of pretilt angle in a liquid crystal cell was based on the measurement of transmittance during cell rotation [7].

3. Results and Discussion

Two non-chiral eutectic mixtures BM-1 and BM-2 with low melting points and with a wide temperature range of the SmC-phase were prepared [6]:



Cr -7°C SmC 57.8°C SmA 67.2°C N 68.1 I



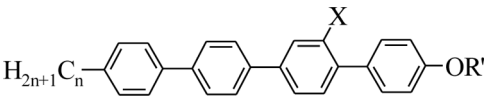
Cr -5°C SmC 89.6°C SmA 93.7°C N 111.1 I

On the other hand, 14 new chiral compounds were considered (Table 1). These compounds are characterized by a low enough melting point and the presence of the SmC*-phase, and therefore provides a good solubility with other classes of compounds allowing adding a big amount of such compounds to the non-chiral matrix.

One can see that the most promising compounds are those with 6–0 carbon atoms in the alkyl chain, further oxygen close to the chiral center, and Cl or CH_3 groups in the third position of benzene ring. Introduction of a COO-group before the chiral center and change of the position of lateral substitutes leads to strong increase of the melting temperature or the absence of the SmC*-phase, and therefore the solubility of these compounds with other classes of liquid crystals degrades. The spontaneous polarization and the tilt angle for the compounds from Table 1 are presented in Table 2.

The chiral compounds are characterized by a wide temperature range of the SmC*-phase, a moderate value of the spontaneous polarization (about 50 nC/cm^2) and a moderate tilt angle (about 30°). All those chiral compounds of Table 1 were combined with the base matrixes BM-1 and BM-2 in order to prove for "shock-free" FLC properties. For these purposes we prepared new mixtures which

Table 1. Phase transition temperatures of compounds (**1**)



LC No.	n	X	R′	Transition temperatures/°C								
				Cr		SmC*		SmA		N		I
a	6	Cl	$CH(CH_3)C_6H_{13}$	•	44	•	85	•		–	158	•
b	6	Cl	$CH(CH_3)C_5H_{11}$	•	50	•	99	•		–	165	•
c	6	Cl	$CH(CH_3)COOCH(CH_3)C_6H_{13}$	•	44	•	85	•		–	158	•
d	6	Cl	$CH(CH_3)COOC_4H_9$	•	43	•	100	•		–	150	•
e	8	Cl	$CH(CH_3)C_5H_{11}$	•	38	•	117	•		–	151	•
f	8	Cl	$CH(CH_3)CH_2OCH_3$	•	61	•	115	•	168	•	172	•
g	8	CH_3	$CH(CH_3)C_6H_{13}$	•	29	•	99	•		–	140	•
h	8	CH_3	$CH(CH_3)C_5H_{11}$	•	40	•	125	•		–	160	•
i	8	Cl	$CH(CH_3)CH_2OC_3H_7$	•	39	•	115	•		–	160	•
k	8	Cl	$CH(CH_3)OOCCH(CH_3)CH_3$	•	43	•	78	•		–	145	•
l	10	CH_3	$CH(CH_3)C_6H_{13}$	•	47	•	119	•		–	145	•
m	10	Cl	$CH(CH_3)C_6H_{13}$	•	39	•	129	•		–	146	•
n	10	Cl	$CH(CH_3)C_5H_{11}$	•	46	•	129	•		–	157	•

consist of 25 wt% of chiral compounds (see Table 3) and measured the main physical properties (see Table 4). 25 wt% were chosen because in previous experiments under combining the base mixture BM-1 with compounds **1e**, **1i**, and **1m** (different chiral fragments, see Table 1) the optimal mixing ratio were found to be between 20%–40%.

In order to determine the optimal pretilt angle we used cells with different alignment materials under varying the pretilt angle (0°, 1°, 2°, 4°, 6°, 8°). The obtained

Table 2. Some physical parameters at 24°C of the compounds in Table 1

Compounds	Saturated value of P_s (nC/cm^2)	Tilt angle (°)
1a	49	32.3
1b	47	31.8
1c	65	30.8
1d	64	35.8
1e	49	32.4
1f	43	29.5
1g	47	28.7
1h	44	28.2
1i	47	28.4
1k	61	29.7
1l	50	29.9
1m	52	33.2
1n	51	33.0

Table 3. Mixing ratio of some FLC-mixtures

Mixtures	Components	Mixtures	Components
LS-1	BM-2 + 1e	LS-10	BM-1 + 1c
LS-2	BM-1 + 1g	LS-11	BM-1 + 1d
LS-3	BM-1 + 1e	LS-12	BM-2 + 1d
LS-4	BM-1 + 1h	LS-13	BM-1 + 1i
LS-5	BM-2 + 1h	LS-14	BM-1 + 1k
LS-6	BM-1 + 1a	LS-15	BM-1 + 1f
LS-7	BM-2 + 1a	LS-16	BM-1 + 1n
LS-8	BM-1 + 1b	LS-17	BM-1 + 1l
LS-9	BM-2 + 1b	LS-18	BM-1 + 1m

results show that for creating "shock-free" FLCD's the use of alignment materials with the lowest possible pretilt angle (about 0°) (see Fig. 1) is necessary. Therefore, for further experiments testing cells with pretilt angle between 0° and 1° were used.

Cells filled with prepared mixtures LS-1, LS-4, LS-5, LS-7, LS-9, LS-10, LS-12, and LS-14–LS-16 show good switching behavior, high contrast ratio (CR = 140:1–180:1) and good orientation quality. After applying strong mechanical pressure the quality of orientation decreased, because of defects which can be connected with the breaking of layers. Only cells with mixtures LS-2, LS-6, LS-15 and LS-18 show no decrease of the quality of orientation after mechanical pressure, and therefore the contrast ratio have the same values (see Table 5). In cells with mixtures LS-3, LS-8, LS-11, and LS-17 some small defects appeared, which disappeared after some time.

Table 4. Physical parameters of some FLC mixtures

Mixtures	SmC* range (°C)	P_s (nC/cm^2)	Tilt angle (°)	t_{on} (ms)	t_{off} (ms)
LS-1	20<–+97.4	12	23.5	0.52	0.57
LS-2	0<–+66.4	13	23.8	0.37	0.49
LS-3	0<–+66.8	15	24.3	0.38	0.48
LS-4	0<–+69.4	11	22.8	0.46	0.52
LS-5	20<–+103.4	11	22.4	0.49	0.53
LS-6	0<–+66.2	15	24.7	0.33	0.44
LS-7	20<–+100.9	14	24.1	0.45	0.50
LS-8	20<–+62.1	13	23.5	0.43	0.49
LS-9	20<–+94.1	12	23.1	0.47	0.52
LS-10	0<–+58.2	19	23.2	0.33	0.29
LS-11	0<–+60.2	17	25.2	0.078	0.13
LS-12	20<–+99.7	17	25.1	0.10	0.15
LS-13	0<–+64.0	9	22	0.4	0.4
LS-14	0<–+55.0	10	22.6	0.29	0.24
LS-15	20<–+64.0	9	21.5	0.42	0.41
LS-16	0<–+65.1	12	23.2	0.49	0.56
LS-17	20<–+63.7	11	23.0	0.50	0.55
LS-18	20<–+65.2	13	23.6	0.53	0.57

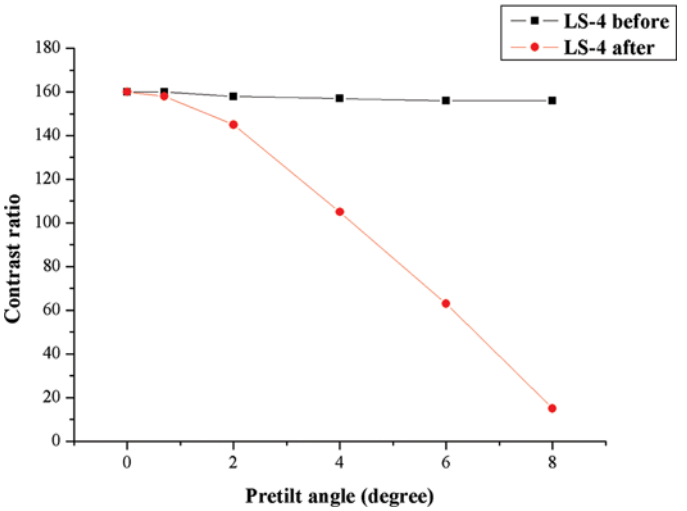


Figure 1. Contrast ratio vs. pretilt angle before and after applying mechanical pressure (geometrical deviation 50%). (Figure appears in color online.)

After analysis of obtained data, one can see the most promising chiral compounds for the preparation of "shock-free" compositions are **1e**, **1g**, **1h**, **1i** and **1m** (see Table 1). Most remarkable the values of spontaneous polarization and tilt angle for such compounds are almost constant over the range of 30°C–85°C (see Figs. 2, 3). Therefore one can create "shock-free" compositions, stable in such wide temperature range.

Table 5. Dependence of the contrast ratio on mechanical pressure

Mixtures	CR (before deformation)	CR (after deformation)
LS-1	140:1	115:1
LS-2	140:1	140:1
LS-3	150:1	90:1
LS-4	165:1	145:1
LS-5	165:1	140:1
LS-6	170:1	170:1
LS-7	170:1	135:1
LS-8	160:1	50:1
LS-9	160:1	150:1
LS-10	150:1	110:1
LS-11	175:1	105:1
LS-12	175:1	150:1
LS-13	145:1	30:1
LS-14	160:1	35:1
LS-15	155:1	155:1
LS-16	140:1	110:1
LS-17	140:1	75:1
LS-18	140:1	140:1

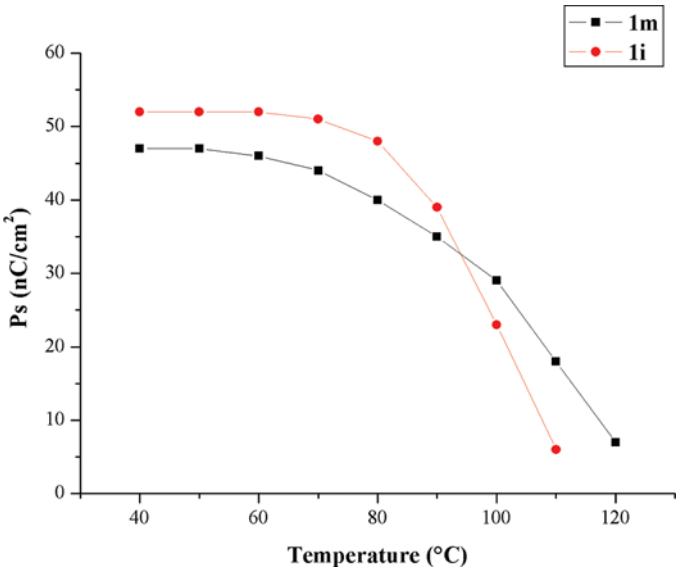


Figure 2. Temperature dependence of the spontaneous polarization of chiral compounds **1m** and **1i**. (Figure appears in color online.)

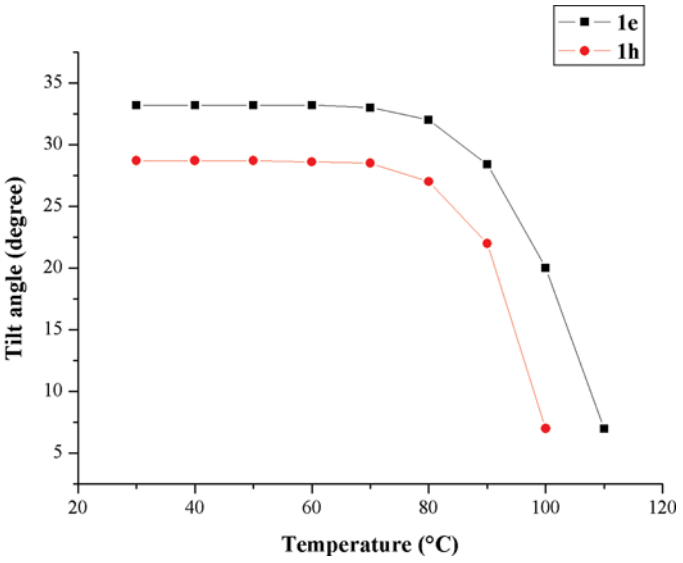


Figure 3. Temperature dependence of tilt angle of chiral compounds **1e** and **1h**. (Figure appears in color online.)

4. Conclusions

Experiments with different 4-ring chiral compounds were done. For the preparation of "shock-free" compositions one should use compounds with 6–10 carbon atoms in the alkyl chain, oxygen close to chiral center, and Cl or CH_3 groups in the benzene

ring. The alkyl chain after the chiral center should have 3–8 carbon atoms, $CH_2OC_nH_{2n+1}$ or $COOC_nH_{2n+1}$ fragment, where $n = 2$–4. The phase sequence does not influence the shock stability of the mixtures.

The use of desired compounds allowed us to design shock-free FLCD's with a high contrast ratio.

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