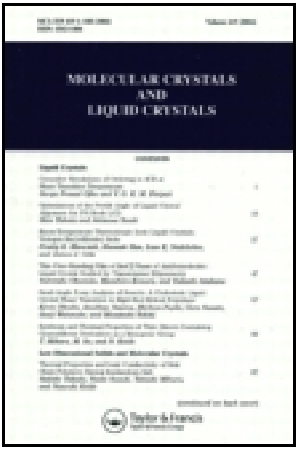

Molecular Crystals and Liquid Crystals

New Liquid Crystalline Materials for Photonic Applications

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NEW LIQUID CRYSTALLINE MATERIALS FOR PHOTONIC APPLICATIONS

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The mesogenic and optical properties of few families of nematic liquid crystals with low, medium and high birefringence as well as high tilted chiral anticlinic (antiferroelectric) smectics recently developed have been shortly characterized and reviewed. They are:

- *alkyl 4-trans-(4-trans-alkylcyclohexyl)cyclohexyl carbonates being liquid crystals with ordinary index n_o lower than silica glass in broad temperature range,*
- *high birefringence two ring 4′-alkyl- and 4′-alkoxy-4′-isothiocyanatotolanes and three ring 4′-(4-alkyl)phenyl-, 4′-(trans-4-alkyl)cyclohexyl- or 4-(4′-trans-alkyl)cyclohexylethyl-4-isothiocyanatotolanes unsubstituted or laterally substituted by fluorine or chlorine atoms,*
- *(S) 1-methylheptyloxyphenyl 4-(perfluoroalkanoyloxyalkoxy)biphenylates and (S) 1-methylheptyloxybiphenylyl-4-yl 4-(perfluoroalkanoyloxyalkoxy)-benzoates having the broad temperature range of antiferroelectric phase.*

The examples of mixtures with low n_o and Δn, high Δn as well as orthoconic antiferroelectric mixtures are given.

Keywords: liquid crystals; nematic mixtures; orthoconic antiferroelectric mixtures; phase transitions; refractive indices; smectic layers; X-ray studies

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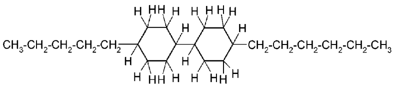
INTRODUCTION

Display and photonic applications of liquid crystalline materials (LCMs) are systematically enhanced but further new ones with other or better physical properties than those commercialized and commonly used now are still needed. Telecommunications applications will be probably the main new consumers of them in the next decades. High or moderate polar nematics with birefringence between 0.08 and 0.2 are the most popular in the display applications and the riches of such materials are actually known and available. Liquid crystals with low birefringence Δn and ordinary index n_o lower than silica glass (1.459) as well as high birefringent materials ($\Delta n > 0.4$) are still very poorly represented. Liquid crystals with ordinary index n_o lower than fused silica enable to keep propagating light inside fiber core and to modified its phase and polarization [1–3]. High birefringent LC enables to design devices with very short response time. They are especially useful for laser beam steering, light modulation in telecommunication line, for reflective and tunable electronic lens [4,5]. LC antiferroelectrics and ferroelectrics are much quicker than nematics. Response times are only dozen μs instead of dozen ms given by nematics. Commonly known ferro- and antiferroelectric LCMs give pure contrast because pretransitional effects are present. This inconveniency may be overcome by using orthoconic antiferroelectric LCMs that ensure huge contrast and large gray scale. Our last results concerning new nematic LCMs with low birefringence and high birefringence and new smectic anticlinic orthoconic LCMs as well as older nematic LCMs with very low viscosity and moderate birefringence will be shortly reviewed.

LOW BIREFRINGENCE LCMs

Compounds with very low ordinary index ($n_o < 1.459$) and low birefringence ($\Delta n \sim 0.05$) should be fully saturated structures. They should contain only carbon atoms in the chain and cycles bonding between themselves by σ bonds and should be substituted only by hydrogen or fluorine atoms, for example such as:



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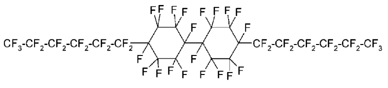


2

The cyclohexane and hexane have refractive indices 1.4262 and 1.3753 at 20°C for $\lambda = 589\,\text{nm}$, respectively [6]. The fluorinated analogues have lower refractive indices 1.296 (15°C) [7] and 1.2498 (25°C) [8], respectively. Therefore we can expect that compound 1 (4,4′-trans-trans-dihexylbicyclohexane) and compound 2 (4,4′-trans-trans-di(perfluorohexyl)perfluorobicyclohexane) should have ordinary refractive index lower than 1.4 and 1.3 respectively.

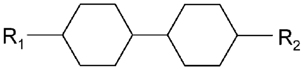
Such fully saturated structures, even when their terminal chains are very short, are not nematics, see Table 1.

They exhibit only high ordered solid like smectic B phase. The presence of an oxygen atom or a carbonyloxy group in molecule is necessary to destroy smectic phases. The nematic phase is observed but only for the members with short terminal chains (see 3c, 3d). Such compounds have small birefringence ($\sim$0.05) and ordinary index $n_o \sim 1.46$ close to silica glass and small positive or negative dielectric anisotropy $\Delta\varepsilon$.

The same is observed in the case of compounds with a bridge between cyclohexane rings. Partially fluorination of the alkyl chains or cyclohexane rings increases the smectic tendency [9], so it is not a tool to achieve the aim.

Compounds, listed in Table 1, enable to formulate multicomponent mixtures with ordinary index n_o lower than 1.46 but only in very short temperature range below the clearing point, see mixture 1110, Figure 1. Mixtures with distinctly lower n_o, for example mixture 1550, Figure 1, have been already obtained. They are composed of alkyl 4-trans,trans-alkylbicyklohexyl carbonates, formula 4, new LC family prepared by us recently [10], see Table 2. Alkyl 4-trans,trans-alkylbicyklohexyl carbonates are nematics for members with short alkyl tails having high clearing points.

TABLE 1 Liquid crystals with small birefringence and refractive indices



3

				Phase transition/°C					
No	R_1	R_2	Cr		SmB		N		Iso
3a	C_3H_7	C_2H_5	*	−10.9	*	66.8	–		*
3b	C_3H_7	C_3H_7	*	64.2	*	81.8	–		*
3c	C_3H_7	OC_2H_5	*	49.0	–		*	49.6	*
3d	$C_3H_7^*$	$COOCH_3$	*	36.1	–		*	62.9	*
3e	C_3H_7	$COOC_2H_5$	*	20.8	*	57.6	–		*
3f	C_3H_7	$COOCH_2CF_3$	*	39.5	*	41.8	–		*
3g	C_3H_7	$COOCH_2CH=CH_2$	*	13.2	*	44.0	–		*
3h	C_5H_{11}	$COOCH_3$	*	40.8	*	56.5	*	77	*

*$\Delta n = 0.059$; $n_o = 1.468$; $\Delta\varepsilon = -0.54$; $\varepsilon_\perp = 3.68$ at 20°C.

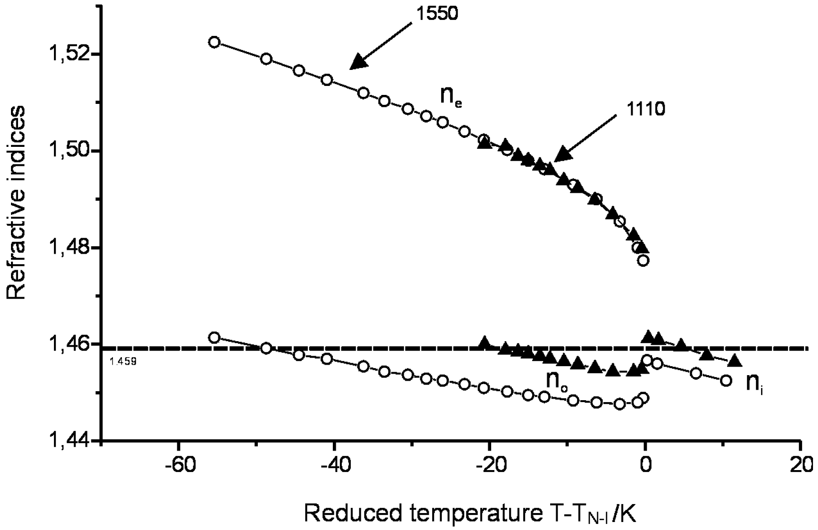


FIGURE 1 Temperature dependence of refractive indices for mixture 1110 (▲) and 1550 (○).

The smectic B phase is also observed for longer tails but with lower thermal stability than in the case of carboxylates, (see compounds 3 h and 4c). The high clearing points probably result from that the molecules are fully symmetric around molecular long axis, see Figure 2.

Ordinary index n_o is the lowest at the temperature 5–10 degree below the transition to the isotropic phase, Figure 3.

Its value is only 1.4430 for propyl methyl derivative and a little higher for compounds with longer chain, see Table 2.

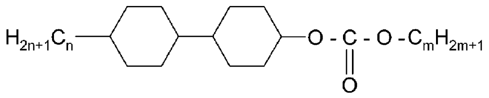
The carbonates have ordinary refractive index in the nematic phase as well as refractive index in the isotropic phase in isotropic phase lower than silica glass in very large temperature range.

The temperature dependence of refractive indices of compounds with low birefringence differs from the temperature dependence of compounds with medium or high birefringence. Their refractive indices are increasing with the decrease of temperature in nematic phase and in isotropic phase, while in the higher polar compounds ordinary index is decreasing or is not changing, see Figure 3.

Alkyl 4-trans,trans-alkylbicyclohexyl carbonates 4 have the lowest ordinary index among nematic compounds prepared until now, see comparison in Table 3.

Their dielectric anisotropy is of a very small negative value, roughly about 0, because dipole moment of carbonate group is near 0, viscosity is

TABLE 2 Phase transition temperatures and refractive indices for compounds 4


4

No	n	m	Cr		SmB		N		Iso	Δn^+	n_o	n_e	n_i	$\Delta\varepsilon$	$\varepsilon_\parallel$	$\varepsilon_\perp$
4a	3	1	*	80.4	–		*	87.9	*	0.0486	1.4431	1.4917	1.4478	−0.07	2.55	2.62
										0.0528	1.4462	1.4990				
4b	3	2	*	59.4	–		*	71.4	*	0.0450	1.4465	1.4915	1.4513	−0.023	2.489	2.512
										0.0504	1.4483	1.4987				
4c	5	1	*	70.5	–		*	95.0	*	0.0460	1.4450	1.4910	1.4487	−0.06	2.53	2.59
										0.0547	1.4476	1.5023				
4d	5	2	*	54.8	*	38.7	*	85.0	*	0.0450	1.4430	1.4880	1.4473	−0.008	2.464	2.472
										0.0503	1.4461	1.4964				
4e	3	3	*	40.0	*	23.6	*	62.3	*	0.0436	1.4504	1.4940	1.4556			
										0.0489	1.4528	1.5017				
4f	5	3	*	38.9	*	63.0	*	80.2	*	0.0432	1.4448	1.4880	1.4492			
										0.0492	1.4468	1.4960				

${}^{*}T–T_{N\text{-}I} = -10$ and -20 upper line and lower line respectively.

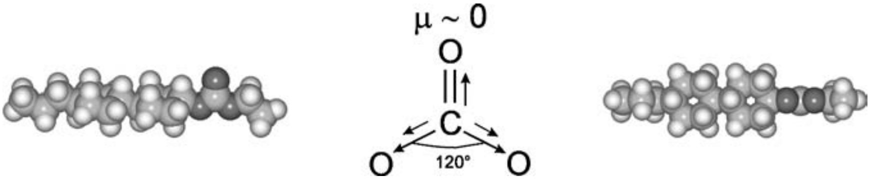


FIGURE 2 Molecule of ethyl 4-trans-(4-trans-propylcyclohexyl)cyclohexyl carbonate.

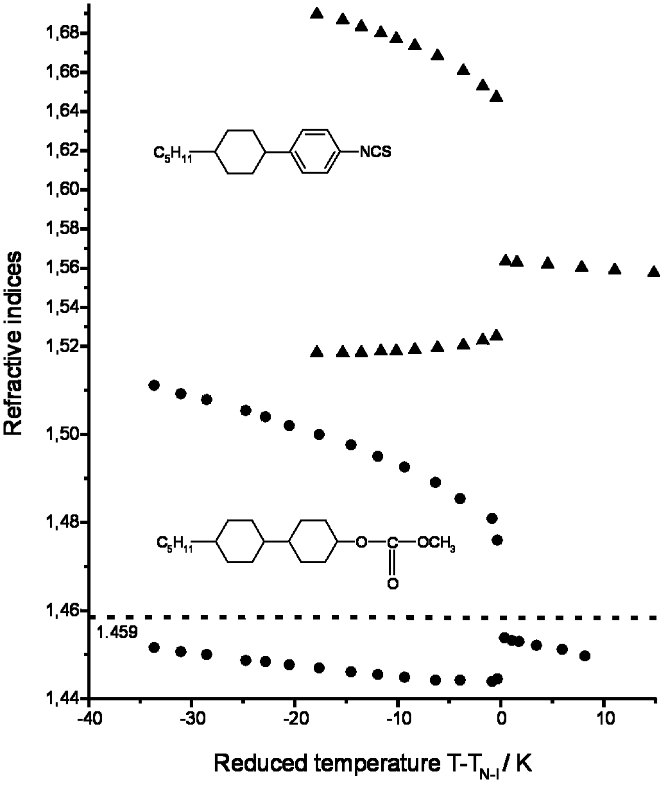
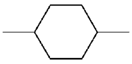


FIGURE 3 Comparison of temperature dependence of refractive dependence for 4-(trans-4-pentylcyclohexyl)isothiocyanatobenzene and methyl 4-trans-(4-trans-pentylcyclohexyl)cyclohexylcarbonate.

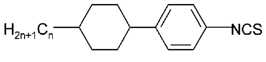
TABLE 3 Comparison of refractive indices in nematic phase and isotropic phase for the bicomponent mixtures of carbonates and similar carboxylates

CH = 	Temp. = $T_{N-I}-T = -10$ or 10			
	n_o	n_e	Δn	n_i
$C_3H_7CHCHCOOCH_3$	1.4559	1.4950	0.0391	1.4552
$C_5H_{11}CHCHCOOCH_3$				
$C_3H_7CHCOOCHC_3H_7$	1.4563	1.4936	0.0373	1.4566
$C_5H_{11}CHCOOCHC_3H_7$				
$C_3H_7CHCHOCOOCH_3$	1.4434	1.4897	0.0463	1.4474
$C_5H_{11}CHCHOCOOCH_3$				

also rather low about 23 mm^{2}s^{-1} at 30°C. They seem to be also excellent components for blending optical properties of different mixtures.

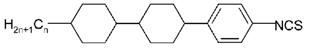
SMALL VISCOSITY POLAR NEMATIC LCMs

Twenty years ago we synthesized 4-(4-trans-alkylcyclohexyl)isothiocyanatobenzenes [11,12] and than their three [13] and four ring analogues [14] (formula 6 and 7).



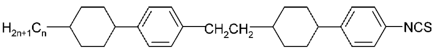
5

n=6 Cr 12.5 N 43 Iso [12]



6

n=3 Cr 76.5 N 246.8 Iso [14]

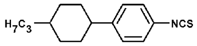
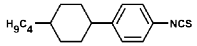
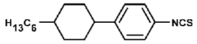
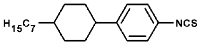
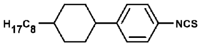


7

n=4 Cr 87.5 N 260 Iso [13]

They have the lowest viscosity and strongest nematic character among the polar compounds.

For example, four component eutectic mixture B has kinematic viscosity at RT 12 mm^{2}sec^{-1} and at −20°C only a little above hundred [13]. The introduction of three ring 4-(trans,trans-4-propylbicyclohexyl)isothiocyanatobenzenes (compound 6) in amount 30 wt.% to mixture A increases clearing point to 93°C. Viscosity changes at RT only by 15% and increases only about twice at −20°C [13].

	Mixture A	Mixture B
	composition, wt. %	
	42.0	38.8
		16.1
	40.0	37.0
		8.1
	18.0	

Although the electrooptical and physicochemical properties of compounds 5, 6 and 7 are excellent and very useful for application they are not commonly use yet, as they should.

Two ring compounds of homologous series 5 (nCHBT) have only nematic phase still with twelve carbon atoms in the alkyl terminal chain, while in analogues series (nPCH) a smectic A_d phase is observed [15]. Hexyl member (6CHBT) has the lowest melting point among single polar liquid crystalline compounds only 12.5°C. The lower melting points are observed for members with even carbon atoms in the terminal chain while the members with odd carbon atoms have lower melting points in cyanocompounds. They are extremely stable to ultraviolet radiation, the same as fluorinated compounds [16], but their thermal stability at higher temperature and holding ratio is not high (0.86) as for other polar compounds. The fluorination of molecule in the benzene ring increases holding ratio up to 0.98 [17].

CHBTs exhibit much higher birefringence than PCHs. Their bends to splay elastic constant ratio as well as elastic expression χ are lower. They have low bulk and rotational viscosity, because their lower tendency to dimerization, see comparison in Table 4:

Such properties are very promising for different photonic and display applications, what we found using them for many years. Excellent mixtures with moderate $\Delta n \sim 0.15 - 0.3$ operating in very broad temperature range for TN effect as well as for STN effect and with very small temperature dependence of their electrooptical parameters and short response times were formulated, see as example mixtures 1280 and 1193A [18], Table 5.

HIGH BIREFRINGENCE NEMATIC LCMs

Structures with short alkyl or alkoxy chains or without them and having few triple bonds, benzene rings and isothiocyanato groups should exhibit very

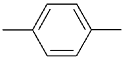
TABLE 4 Physical and electrooptical properties of 4-(trans-4-hexylcyclohexyl)isothiocyanatobenzene (6-CHBT) and 4-(trans-4-pentylcyclohexyl)benzonitrile (5-PCH)

	6-CHBT	5-PCH
1. Dipole moment, $\mu(\times 10^{-30}\,\mathrm{C{\cdot}m})$	3,4	4,7
2. Dielectric constant: $\varepsilon_{\parallel}$	12,0	17,0
$\varepsilon_{\perp}$	4,0	4,8
$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$	8,0	12,2
3. Refractive indeces: n_o	1,52	1,49
n_e	1,67	1,61
$\Delta n = n_e - n_o$	0,15	0,12
4. Bulk viscosity, η(mPa·s)	13,3	21,5
5. Rotational viscosity, γ (mPa·s)	83,0	123,0
6. Elastic constant: k_{11} $(\times 10^{-12}\,\mathrm{N})$	8,57	8,98
k_{22}	3,70	4,73
k_{33}	9,51	18,30
k_{33}/k_{11}	1,11	2,03
$K = k_{11} + \frac{1}{4}(k_{33} - 2k_{22})$	9,1	11,2
7. Visco-elastic ratio, γ/k $(\times 10^{10}\,\mathrm{s{\cdot}m^{-2}})$	0,91	1,14
8. Decay time, t_{off} (ms)	41,0	43,0
9. Threshold, V_{10} (volt)	1,63	1,55

TABLE 5 Physical and electrooptical properties of isothiocyanato mixtures in TN and STN effects

	TN-1280	STN-240°-1193A
Clearing point [°C]	68–76	73
Viscosity at 20°	12.6	18.5
at 0°	33.5	56.6
at −20°	147	
Δn (589 nm. at 20°)	0.1612	0.1287
n_e	1.6698	1.6299
$\Delta\varepsilon$	8.6	
$\varepsilon_{\perp}$	12.3	
V_{10} (10. 0. 20) [V]	2.0	2.08
V_{50} (50. 0. 20) [V]	2.26	
V_{90} (90. 0. 20) [V]	2.66	2.19
$p = V_{50}/V_{10} - 1$ [%]	12.6	
$p = V_{90}/V_{10} - 1$ [%]	32.2	5
N_{max}		420
Temp. dep. (0–40°C) [%/C]	0.33	
Response times: t_{on} 20° [ms]	4.8	112
t_{off} 20° [ms]	36	
t_{on} − 20° [ms]	62	
t_{off} − 20° [ms]	360	

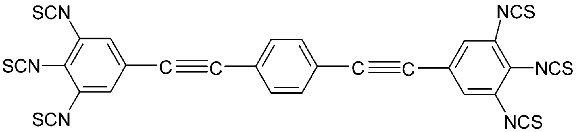
high birefringence. I estimate from contribution of structural units to birefringence:



C≡C NCS

~0,09 ~0,07 ~0,07

that compound 8:

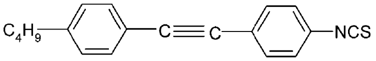


8

should have $\Delta n > 0.80$ at room temperature.

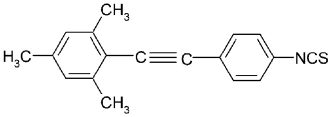
This compound has not been prepared yet, because of serious problem with side reactions. Only isothiocyanatotolanes [19,20] and few diisothiocyanatotolanes are known at this moment.

Examples of prepared compounds are given below:



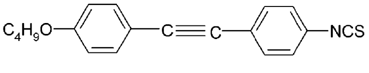
9

Cr 44 SmK 70.5 SmE 86.9 Iso



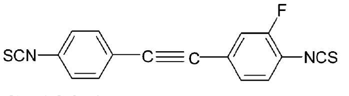
10

Cr 78.4 Iso



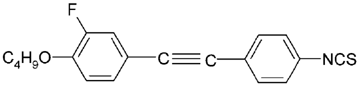
11

Cr 9112.7 (SmE 112.0) N 116 Iso



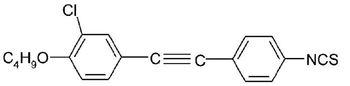
12

Cr 129.1 Iso



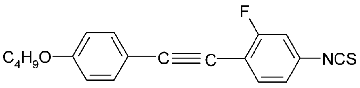
13

Cr 64.2 N 71.6 Iso



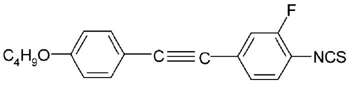
14

Cr 69.8 (N 48.5) Iso



15

Cr 70.3 N 94.4 Iso



16

Cr 96.7 (N 89.9) Iso

Two ring 4′-alkyl-4-isothiocyanatolanes such as compound 9 exhibit only two crystal-like smectic phases: SmK and SmE [19]. Also 4′-alkoxy-4-isothiocyanatolanes are SmE with high thermal stability [19]. The nematic phases are present in some members, but in very short temperature range, see compound 11. The substitution of the benzene ring by fluorine or chlorine atoms or methyl group destroys smectic phases.

Substitution by the fluorine atom gives compounds with the higher isotropic transition temperature than by chlorine or methyl group but simultaneously birefringence diminishes.

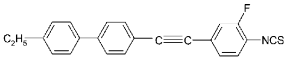
Chemical and photochemical stability of compounds substituted near to the triple bond (orto position) such as compound 15 is lower than compounds substituted further to triple bond (meta position), compounds 13, 14 and 16.

Dielectric anisotropy decreases in order of substitution:

$$16 > 15 > 13$$

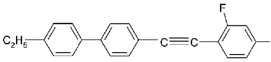
Optical anisotropy extrapolated from 10 wt.% in 6CHBT is about 0.35 and does not change with the fluor position in greater degree.

Three ring compounds – phenyl substituted tolanes should have higher birefringence than two ring tolanes.



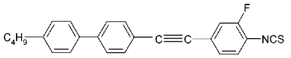
17

Cr 146.2 SmA 148.1 N 254.8 Iso



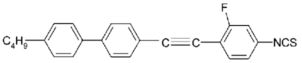
18

Cr 146.5 N 158.2 Iso



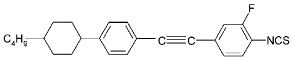
19

Cr 52.3 SmE 85.7 SmB 139.9 SmA 181.3 N 241.5 Iso



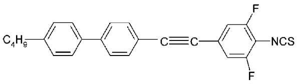
20

Cr 76.0 SmE 88.7 SmB 103.4 SmA 194.6 N 247 Iso



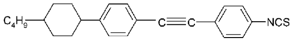
21

Cr 77.1 N 238.9 Iso



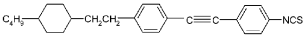
22

Cr 63 SmA 100 N 209 Iso



23

Cr 106.9 SmA 139.9 N 257.4 Iso



24

Cr 102.3 (SmA 99.3) N 207 Iso

Phenyl substituted tolanes with short alkyl tail have very high melting temperatures (compounds 17 and 18). For compounds with longer tails, see butyl derivatives 19 and 20, melting temperature drops drastically, but smectic phases exist in very broad temperature range for mono- and even difluorosubstituted compounds, see compound 22.

Fluorosubstituted alkylcyclohexyltolanes show stronger nematic character, for example, butyl derivative 21 has nematic phase in the range from 77°C to 239°C and exhibits very low melting enthalpy. Designing of further structures with lower smectic tendency is necessary to achieve nematic high birefringent materials.

TABLE 6 Physical properties of isothiocyanatotolanes mixtures.

	1437	1442	1551–2
nematic range	0–152	−5–141	10–65
viscosity$\cdot$ mm^{2}s^{-1}	–	48.5	52
birefringence	0.41	0.37	0,40
k_{33}/k_{11}	1.74	1.82	2.11
$\varepsilon_\perp$	4.8	3.9	4.4
ε	12.1	12.3	12.1
FoM $\left(\frac{k_{11}\cdot\Delta n^2}{\gamma}\right)$	6.5	6.9	7.2
V_{10}	2.13	1.99	1.59
γ_1/k_{11}	24.8	20.0	23.5

Broad range nematic mixtures with Δn between 0.35 and 0.45 is possible to formulate from the isothiocyanatotolanes mentioned above, see for example the mixtures 1437, 1442 and 1551–2.

HIGH TILTED SYNCLINIC AND ANTICLINIC SMECTICS LCMs

Very quickly operating LCMs are chiral smectics having smectic layers in synclinic order (ferroelectrics) or anticlinic order (antiferroelectrics) [21].

For the most hitherto known AFLCMs a small pretransitional effect appears as a slight increase of light transmittance below the threshold. Defects in LC layers orientation are present therefore the light transmission does not fall to zero. These defects are increasing during driving. For this reason high contrast is not possible to obtain for commonly known low tilted AFLCM's but the high contrast is possibly to obtain for new prepared orthoconic AFLCMs, see Figure 4.

Orthoconic AFLCMs have the interlayer conic tilt equal 90°. Electrooptical responses of two mixtures W-193B and W-185 [22] recently formulated in our laboratory are presented in Figure 4. Mixture W-193B has smectic layers tilted at 45° (cone tilt 90°) and does not exhibit the pretransitional effect. The surface defects are not seen, the static contrast is very high 183 and dynamic contrast is equal 70. The mixture W-185 is tilted at 24°. Its contrast is lower: static 34 and dynamic only 16.

The contrast is theoretically infinitely large for orthoconic antiferroelectrics and depends only on quality of polarizes. It results from unusual optical properties of orthoconic antiferroelectric materials [23–25]. They are optically negative uniaxial in the antiferroelectric state and optically positive diaxial in the ferroelectric state. Therefore they behave as isotropic medium in the antiferroelectric state.

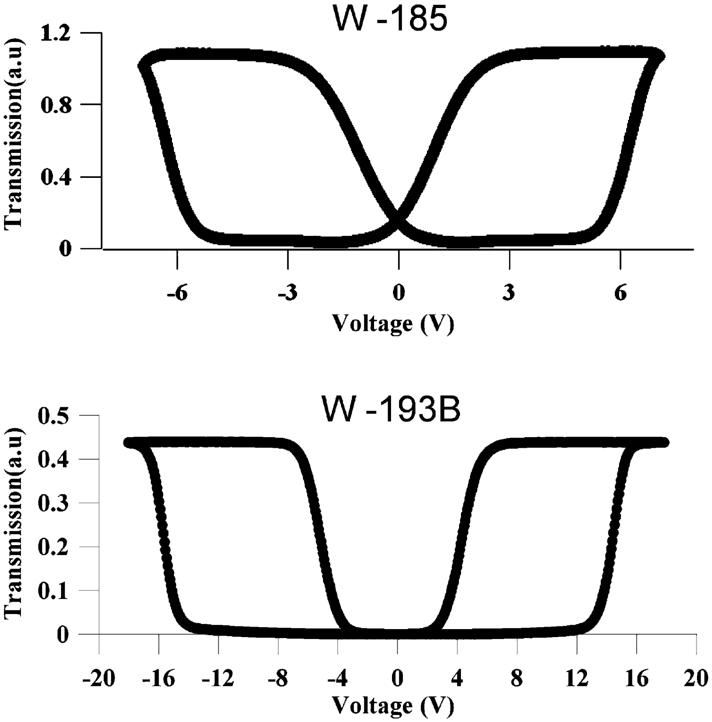


FIGURE 4 The comparison of electrooptical responses of mixtures W-185 and W-193B[22].

Extremely high contrast may be observed during phase transition to the ferroelectric state induced by electric field because defects are not seen on surface [24].

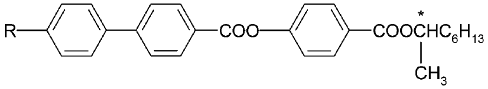
The mixture W-107 was the first our orthoconic antiferroelectric material. Its composition and the properties are given in Table 7.

Actually many types of antiferroelectric orthoconic mixture having a very broad temperature range of antiferroelectric phase, from −20°C to above hundred, see Table 8, have been formulated.

They are not too fast yet. Their response times measured at temperature 35°C is decreasing as the transition SmC_{anti}/SmC is lowering, see Table 9. Actually we are working intensively to improve their dynamic behavior as well as to decrease their threshold voltage.

At the present time the components of all orthoconic antiferroelectric mixtures are chain fluorinated chiral and achiral compounds of common structure:

TABLE 7 Composition and properties of orthoconic mixture W-107


(S) 25

R	composition, wt.%	Properties at 40°C	
$C_3F_7COO(CH_2)_3O-$	20.77	Helical pitch	$p = 320\,nm$
$C_7F_{15}COO(CH_2)_3O-$	32.45	Threshold	$E_{th} = 7.2\,V/\mu m$
$C_3F_7COO(CH_2)_4O-$	40.47	Polarization	$P = 312\,nC/cm^2$
$CF_3CH_2CH_2COO(CH_2)_3O-$	6.31	Tilt	$\theta \approx 45^\circ$

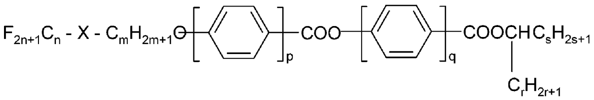
Phase transition: Cr 38 $SmC_A{}^*$ 119 SmC^* 123.1 SmA 133.7 Iso.

TABLE 8 Examples of orthoconic mixtures recently prepared

W-180	Cr –23.0 $SmC^*{}_{Anti}$ 102.7–103 SmC 109.8–110.3 SmA 126.8 Iso
W-182A	Cr <–20 $SmC^*{}_{Anti}$ 88.9–90 SmC 105.4 SmA 110–114 Iso
W-190	Cr <–20 $SmC^*{}_{Anti}$ 89.9–90.7 SmC^* 105.6–106.1 SmA 111.6–114.1 Iso
W-193	Cr <−20 $SmC^*{}_{Anti}$ 83–83.7 SmC^* 95.8–96.1 SmA 100.5–106.3 Iso
W-193A	Cr <−20 $SmC^*{}_{Anti}$ 80.7–81.1 SmC^* 94.6–95 SmA 100.5–104.7 Iso
W-193B	Cr < −20 $SmC^*{}_{Anti}$ 82.3–83.0 SmC^* 98.2–99.2 SmA 105–112.5 Iso
W-193C	Cr <−20 $SmC^*{}_{Anti}$ 72.7–73.2 SmC^* 87.1–91.3 SmA 98–106.7 Iso

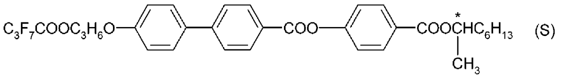
TABLE 9 The response times: t_r – rise time and t_f – fall time for orthoconic mixtures

	W-180	W-182A	W-190	W-193	W-193A	W-193B
SmC_{Anti}/SmC	103	90	90.7	83.7	81.1	83.0
t_r [μs]*	56	44	28	18	25	24
t_f [μs]*	944	667	288	69	344	304


26

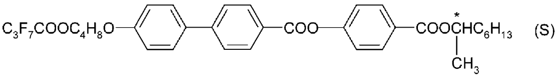
where X = COO or O or single bond, p = 2 or 1 and q = 2 or 1; n = 1–7, m = 3–6, s = 5–8, r = 1–3.

More than hundred new such compounds have been prepared, part of them was described [26,27], the other will be published soon [28,29]. Few more interesting compounds, which have been prepared, recently are given below:



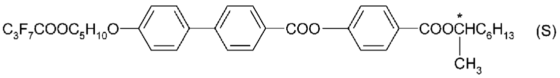
27

ΔH_m=5.56; Cr 83.3 SmC$_{\mathrm{anti.}}$ 121.3 SmC 123.8 SmA 128.9 Iso



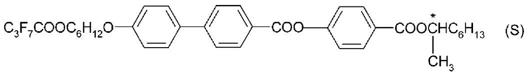
28

ΔH_m=3.28; Cr 67.5 SmC$_{\mathrm{anti.}}$ 120.1 SmC 126.4 Iso



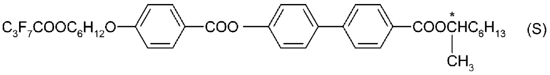
29

ΔH_m=4.70; Cr 65.5 SmC$_{\mathrm{anti.}}$ 121.7 SmC 124.6 SmA 132.7 Iso



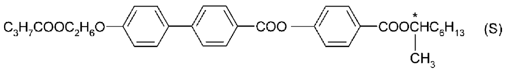
30

ΔH_m=3.77; Cr 29.4 SmC$_{\mathrm{anti.}}$ 111.4 SmC 122.5 SmA 129.3 Iso



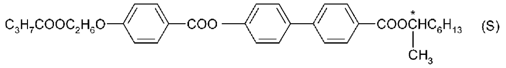
31

ΔH_m=2.87; Cr 18.5 SmC$_{\mathrm{anti.}}$ 98.0 SmC 113.2 SmA 119.6 Iso



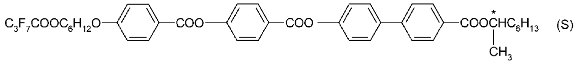
32

ΔH_m=6.6; Cr 61.0 SmC$_{\mathrm{anti.}}$ 87.5 SmC 98.1 SmA 100.5 Iso



33

ΔH_m=12.2; Cr 66 (SmC 75.1) SmA 89 Iso



34

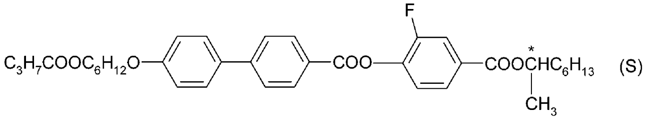
$\Delta H_m=5.7$; Cr 70 SmC_{anti} 137 SmC^* 215.5 SmA 223.3 Iso

The first two compounds 27 and 28 were prepared at first [26]. They are rather still high melting compounds. The increasing of the length of the methylene unit separating the fluorinated part of chain from the aromatic core of molecule involves decreasing of the melting points of the compounds, see compounds 28–31. The single compounds exhibiting the anticlinic antiferroelectric phase in broad temperature range near room temperature were obtained.

The compound 31 with benzene biphenyl sequence in the core of molecule and with perfluoropropyl chain stands out especially in this aspect. Its melting point is only 18.5°C and melting enthalpy is as low as 2.87 kcal/mol. Such fusion data are the lowest among three ring fluorinated esters.

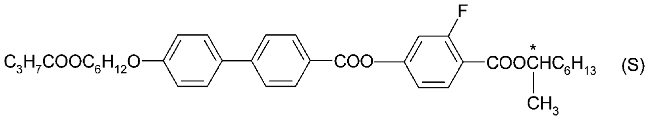
The fully protonated analogues, see compounds 32 and 33 what is surprising, have quite different thermodynamic properties. Their melting points and melting enthalpies are rather high. They have also lower tendency for anticlinic ordering of smectic layers.

The substitution of the molecule core by fluorine atoms is usually a tool for the decrease of melting points of the compounds. In the case of esters with hexamethylene spacer substitution by fluorine atom does not influence much on the phase situation of the compounds, see examples given below:



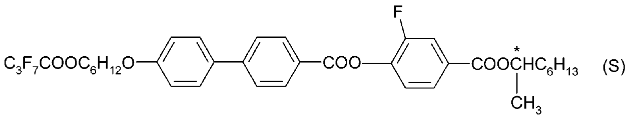
35

$\Delta H_m=10.1$; Cr 49.3 ($SmC_{ant.}$ 34.3) SmC 57.9 SmA 76.4 Iso



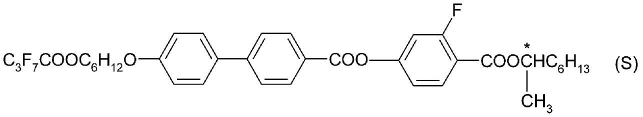
36

$\Delta H_m=5.1$; Cr 58 $SmC_{ant.}$ 86.7 SmC 91.3 SmA 93.5 Iso



37

$\Delta H_m=5.4$; Cr 39.6 $SmC_{ant.}$ 86.6 SmC 98.4 SmA 98.6 Iso



38

ΔH_m=5.0; Cr 30 $SmC_{ant.}$ 95.0 SmC 110.7 SmA 121.3 Iso

Other physical properties such as tilt or electrooptical response may change in profitable way in the results of fluoro substitution. In the case of protonated compounds and also in the case of chain fluorinated compounds with shorter spacer a distinct decrease of melting point is observed after benzene ring substitution by fluorine atoms.

To find relation between structures and the tilt of molecules in smectic C layers interlayer spacing d were measured at different temperatures by small angle diffraction method. The ratio d/d_A at the same distance from SmC/SmA transition was used for the comparison of tilting in different compounds (d_A is a maximum value of d in the orthogonal smectic A phase). The molecules become more tilted in the smectic layers and the smectic layers are shorter when this ratio decreases.

It has found that the tilt in the smectic layers depends on structure and length of terminal chains, the structure of rigid core as well as the phase situation of the compounds.

The ratio d/d_A changes in the following way for the compounds with the some number of atoms (nine) in the terminal chain opposite chiral center but having different structure[30]:

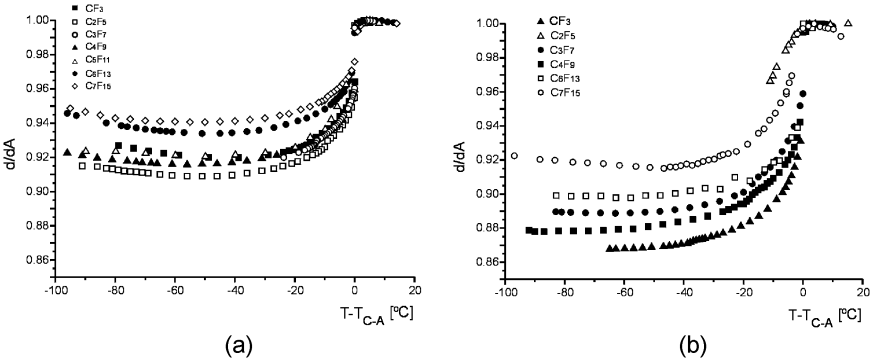
C3F7COOC3H6O < C6F13C2H4O < CF3C2H4COOC3H6O <
CF3CH2OC5H10O < C3H7COOC3H6O

There is an optimal value of terminal chain length to obtain highest tilt, 9–10 atoms in the case of chain fluorinated compounds and 10–11 atoms in the case of chain protonated compounds. The longer methylene spacer the shorter fluorinated unit is necessary to obtain the high tilt.

Perfluorobutanoyloxypropoxy group and perfluorohexylethoxy group ensure the high tilt. Benzoates are higher tilted than biphenylates, substitution by a fluorine atom increases the tilt in some cases. This relation is seen well in Figure 5.

In series with hexamethylene spacer, the lowest values of the ratio d/d_A are observed for members with short fluorinated unit: perfluoromethyl or perfluoroethyl group, while for trimethylene group for perfluoropropyl and perfluorobutyl group [30].

The calculated tilts from the X-ray measurements, in the case of fluorinated compounds, differ distinctly from the tilts measured by optical methods, the latter are usually much bigger [31]. The chain fluorinated



(a) (b)

FIGURE 5 Dependence of layer spacing ratio (d/dA) upon temperature in homologous series of (S) 1-methylheptyloxyphenyl 4-(perfluoroalkanoyloxyalkoxy) biphenylates (a) and (S) 1-methylheptyloxybiphenylyl-4-yl 4-(perfluoroalkanoyloxyalkoxy)benzoates (b).

compounds differ from protonated ones in higher tilts, higher spontaneous polarization (three times), density, but show shorter pitch, lower refractive indices and longer response times [32].

Chiral synclinic smectic C compounds, fluorinated in the terminal chain, have other interesting feature. They are able to induce the antiferroelectric phase, when are mixed with chiral synclinic protonated compounds, see the Figure 6.

We have found many such systems not only among the chiral compounds but also among achiral compounds, although racemization strongly decreases induction ability [33,34].

The induced antiferroelectric phase may show typical threshold tristate electrooptical response as well as V-shaped switching [35].

Threshold switching exists in the region of higher stability of induced antiferroelectric phase and at the side of excess of protonated components while V-shaped switching exists in the region of low stability of the induced antiferroelectric phase and at the side of excess of fluorinated components. Formulation of the antiferroelectric phase by induction enables to use a greater variety of smectic components than in traditional methods.

Orthoconic V-shaped mixtures may be also formulated from the fluorinated compounds [36]. Fluent transition from tristate switching to W-shape switching (simple or reverse) and V-shaped switching may be obtained in the system composed of fluorinated antiferroelectric and fluorinated ferroelectric compounds in some conditions related with frequency range and anchoring strength [36]. Although V-shaped switching is observed also in

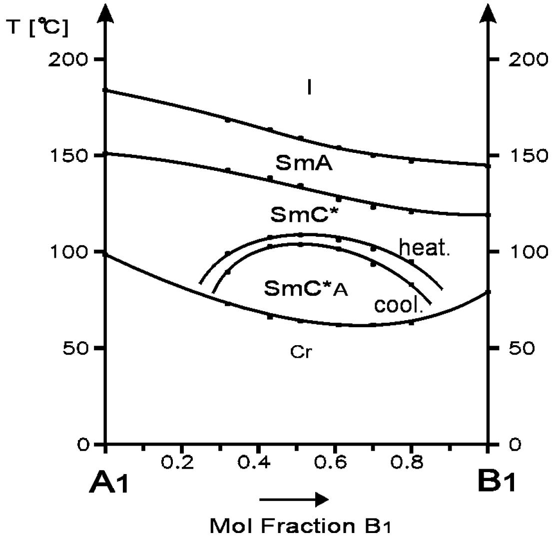


FIGURE 6 Bicomponent systems with induced antiferroelectric phase: A_1–$C_6F_{13}C_2H_4OPhPhCOOPhCOOCOOC^*H(CH_3)C_6H_{13}(S)$ B_1–$C_8H_{17}OPhPhCOOPhCOOCOOC^*H(CH_3)C_7H_{15}(S)$.

concentration and temperature region where the antiferroelectric phase exists, such electrooptical response is rather characteristic for the ferroelectric phase as Chalmers' group postulates [37]. Relaxation time for the transition from the antiferroelectric state to the ferroelectric one is long, therefore the system does not exist in anticlinic order in the dynamic condition of higher frequency.

CONCLUSIONS

- Liquid crystalline mixtures with n_o low as 1.44 and with positive or negative dielectric anisotropy ($\Delta\varepsilon > 0$ or $\Delta\varepsilon < 0$) may be formulated. Further decreasing n_o is possible.
- Mixtures with moderate birefringence, $\Delta n = 0.2$–0.3, and low viscosity at low temperatures are available.
- Mixtures with high birefringence, $\Delta n = 0.4$–0.5 are available, but further efforts are necessary to prepare compounds with better phase situation and higher Δn.
- Orthoconic antiferroelectric mixtures giving high contrast and good gray level are known. They may operate in broad temperature range (−20–100°C), but their performance is not optimal yet.

- Compounds with the broad range of SmC_{anti} phase was prepared, but it is necessary to test carefully their properties and establish relations between chemical structure and electrooptical response on electric field such as it is known for nematic materials.
- Further searching of orthoconic structures is desired.

REFERENCES

[1] Woliński, T. R. & Szymańska, A. (2002). *Mol. Cryst. Liq. Cryst.*, *375*, 723.

[2] Woliński, T. R. & Szymańska, A. (2001). *Meas. Sci. Technol*, *12*, 948.

[3] Woliński, T. R., Szymańska, A., Nasiłowski, T., Nowinowski, E., & Dąbrowski R. (2000). *Mol. Cryst. Liq. Cryst.*, *352*, 361.

[4] Wu, S. T. & Yang, D. K. (2001). *Reflective Liquid Crystal Displays* (Wiley-SID).

[5] McManamon, P.F. *et al.* (1996). *Proc. IEEE 84*, 268.

[6] Poradnik Fizyko-Chemiczny, Wyd. Naukowo-Techniczne, & Warszawa (1997). p. D-116 and D-200.

[7] Tatlow, J. C. & Worthington, R. E. (1952). *J. Chem. Soc.*, *1251*, 1255.

[8] Dresdner, R. D., Reed III, T. M., Tylor, T. E., & Young, J. A. (1960). *J. Org. Chem.*, *25*, 1464.

[9] Kirsch, P., Heckmeier, M., & Tarumi, K. (1999). *Liq. Cryst.*, *26*, 449.

[10] Dąbrowski, R. S., Kędzierski, J., Dziaduszek, J. W., & Stolarz, Z. (12.10.2003). Ciekłokrystaliczne materiały o małym współczynniku załamania promienia zwyczajnego, *Pat. App. filed*.

[11] Dąbrowski, R., Dziaduszek, J., & Szczuciński, T. (1984). *Mol. Cryst. Liq. Cryst. Lett.*, *102*, 155.

[12] Dąbrowski, R., Dziaduszek, J., & Szczuciński, T. (1985). *Mol. Cryst. Liq. Cryst.*, *124*, 241.

[13] Urban, S., Dąbrowski, R., Dziaduszek, J., Janik, J., & Mościcki, J. K. (1999). *Liq. Cryst.*, *26*, 1817.

[14] Dąbrowski, R., Dziaduszek, J., Szczuciński, T., Stolarz, Z., & Czupryński, K. (1989). *Liq. Cryst.*, *5(1)*, 209.

[15] Dąbrowski, R. (1990). *Mol. Cryst. Liq. Cryst.*, *191*, 17.

[16] Szulc, J. & Stolarz, Z. (1995). *Mol. Cryst. Liq. Cryst.*, *263*, 623.

[17] Kim, Y. B. & Kim, B. H. (2000). *SID*, 874.

[18] Stolarz, Z., Dąbrowski, R., Parka, J., Huang, X., & Lapanik, W. (2000). *SPIE 4147*, 41.

[19] Spadło, A, Dziaduszek, J., Drzewiński, W., Dąbrowski, R., Fan, C. Y., & Wu, S. T. (2003). *Liq. Cryst.*, *30(2)*, 191.

[20] Seed, A. J., Toyne, K. J., Goodby, J. W., & Hird, M. (2000). *J. Mater. Chem.*, *10*, 2069.

[21] Lagerwall, S. T. (Ed.). (1999). *Ferroelectric and antiferroelectric liquid crystals*, Willey-VCH: Weinheim.

[22] Measured in prof. J.Oton laboratory, Madrid (Spain).

[23] D'have, K., Dahlgren, A., Rudquist, P., Lagerwall, J. P. F., Anderson, G., Matuszczyk, M., Lagerwall, S. T., Dąbrowski, R., & Drzewiński, W. (2000). *Ferroelectrics*, *244*, 115.

[24] D'have, K., Rudquist, P., Lagerwall, S. T., Pauwels, H., Drzewiński, W., & Dąbrowski, R. (2000). *Applied Physics Letters*, *76*, 3528.

[25] Lagerwall, S., Dahlgren, A., Jagemal, P., Redquist, P., D'have, K., Pauwels, H., Dąbrowski, R., & Drzewiński, W. (2001). *Adv. Funct. Mater.*, *11(2)*, 87.

[26] Drzewiński, W., Dąbrowski, R., Czupryński, K., Przedmojski, J., & Neubert, M. (1998). *Ferroelectrics*, *212*, 281.

[27] Drzewiński, W., Dąbrowski, R., & Czupryński, K. (2002). *Polish J. Chem.*, *76*, 273.

[28] Gąsowska, J., Dąbrowski, R., Drzewiński, W., Filipowicz, M., Przedmojski, J., & Kenig, K. (2003). *Ferroelectics*, (in press).

[29] Gąsowska, J., Dziaduszek, J., Drzewiński, W., Filipowicz, M., Dąbrowski, R., Przedmojski, J., & Kenig, K. (2004). *SPIE*, (in press).

[30] Dąbrowski, R. (2000). *Ferroelectrics*, *243*, 1.

[31] Piecek, W., Raszewski, Z., Perkowski, P., Kędzierski, J., Rutkowski, J., Zieliński, J., Dąbrowski, R., Gąsowska, J. (2003). *Ferroelectics*, (in press).

[32] Raszewski, Z, Kędzierski, J., Rutkowska, J., Picek, W., Perkowski, P, Czupryński, K., Dąbrowski, R., Drzewiński, W., Zieliński, J., & Żmija, J. (2001). *Mol. Cryst. Liq. Cryst.*, 366, 607.

[33] Gauza, S., Czupryński, K., Dąbrowski, K., Kuczyński, W., & Pociecha, D. (2001). *Mol. Cryst. Liq. Cryst.*, *365*, 189.

[34] Gauza, S., Dąbrowski, R., Czupryński, K., Drzewiński, W., & Kenig, K. (2002). *Ferroelectrics*, *276*, 219.

[35] Dąbrowski, R., Otón, J. M., Urruchi, V., Gayo, J. L., Czupryński, K., & Gauza, S. (2002). *Polish J. Chem.*, *76*, 331.

[36] Sinha, A., Haase, W., & Dąbrowski, R. (2003). *Ferroelectrics*, *282*, 229.

[37] Rudquist, P., Lagerwall, J. P. F., Buivydas, M., & Gouda, F. *et al.* (1999). *J. Mater. Chem.*, *9*, 1257.