Liquid crystals for AMLCD and TFT-PDLCD applications

V. F. Petrov[a]

[a] LCD Team 1, Special Division, Semiconductor Business, Samsung Electronics Co., LTD., Suwon, Korea

PLEASE SCROLL DOWN FOR ARTICLE

Liquid crystals for AMLCD and TFT–PDLCD applications

by V. F. PETROV

LCD Team 1, Special Division, Semiconductor Business, Samsung Electronics Co., LTD. San 24 Nongseo-Lee, Kiheung-Eup, Yongin-Gun, Kyungki-Do, Suwon P.O. Box 37, 449-900, Korea

This paper presents a review of the work on the molecular design of liquid crystals for active matrix displays (AMLCDs), thin-film-transistor–polymer dispersed liquid crystal displays (TFT–PDLCDs) and examines in some detail the relationships between liquid crystalline molecular structures and their physico-chemical properties.

1. Introduction

The rapid development of flat panel technology in the last decade has attracted attention throughout the electronic industry. Particularly, liquid crystal displays (LCDs) have greatly expanded in size and complexity, resulting in the availability of completely new kinds of electronic devices. Among all flat panel displays, active matrix LCDs driven by thin film transistors have the best performance and have been developed to become equal to or better than that of the most used device now, cathode ray tubes [1].

It has been shown that AMLCDs require liquid crystals with low viscosity (for reducing the response times [2]); with dielectric anisotropy $\Delta\varepsilon \geqslant 0$, and with the suitable elastic constants (for decreasing threshold voltage of the twist-effect [2] and consequent driver voltage); and also with adjustable optical properties (for the operation in the 1st transmission minimum for optimum viewing angle [2, 3]).

AMLCDs can only contain liquid crystals which possess a very high degree of chemical and photostability with extremely low residual ionic impurities [2, 4]. Therefore, liquid crystals (LCs) suitable for active matrix displays must be purified to such an extent that specific resistivities $\rho > 10^{13}\,\Omega\,\text{cm}$ result [2]. Moreover, ρ should not decrease during the lifetime of the AMLCD owing to ionic contamination of the liquid crystal material from AMLCD substrate surfaces.

Polymer dispersed liquid crystals (PDLCs) have been extensively studied during last decade owing to their suitability to electro-optical applications [5–7]. It has been shown that the droplets of nematic liquid crystals can be embedded in a polymer film [8, 9]. These polymer dispersed liquid crystals can be switched between a translucent 'off' state and a transparent 'on' state due to

mismatching or matching of the refractive indices. Recently, it has been reported about the development of the thin-film-transistor–polymer dispersed liquid crystal displays (TFT–PDLCDs) possessing the brightness, fast response, large area, and grey scale capability [10, 11]. The requirements to liquid crystals for the TFT–PDLCDs are the same as for the AMLCDs excluding the optical properties: since the efficiency of light scattering in the PDLCD depends on the degree of mismatching between the refractive index n_e of the liquid crystal material and the refractive index n_p of the polymer and therefore on the birefringence of the liquid crystal material, the optical anisotropy Δn of liquid crystals should be as much as possible [5–7].

The purpose of this paper is to review the current trends in the molecular design of liquid crystals required for the AMLCDs and TFT–PDLCDs, and the correlations between LC molecular structures and their physico-chemical properties, and thus provide satisfactory selection of the best components of liquid crystal materials for the AMLCDs and TFT–PDLCDs.

2. Molecular design of liquid crystals

Since the material properties of liquid crystals are the result of their molecular properties amplified by the long range molecular interactions, the correct and application specific design of liquid crystalline molecules is very important. It has been shown that liquid crystals for the AMLCDs normally consist of two to four 1,4-disubstituted six-membered rings, linking units and terminal alkyl (alkenyl) and halogenated chains (F, CF_3, OCF_3, $OCHF_2$, OCF_2Cl, etc; see tables 1, 2, 4, 5, 7, 8) [4, 12–39 42–46, 49, 50, 55]. The optimization of their physico-chemical properties can be made by systematically varying many of their structural elements (for example, by lateral mono

Table 1. Mesomorphic, dielectric, optical and viscous properties of liquid crystals:

$$C_5H_{11}\!-\!\langle\ \rangle\!-\!\langle\ \rangle\!-\!(\langle\ \rangle)_n\text{-}Z$$
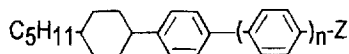
Compound	Z	n	Phase behaviour/°C	$T_{cl}^{extr}/°C$	$\Delta\varepsilon$	Δn	$v/\text{mm}^2\,\text{s}^{-1}$	Reference
1-1	F	0	Cr 34 I		3·2	0·050	3	[13]
1-2	CF₃	0	Cr 21 I	−60	10·9	0·040	9	[14]
1-3	OCF₃	0	Cr 14 I	−40	7·1	0·046	4	[14]
1-4	OCHF₂	0	Cr 1 N (−17) I	−20	7·6	0·058	7	[14]
1-5	SCHF₂	0	Cr 7 I	−60†	7·2†	0·055†	14†	[18]
1-6	COCF₃	0	Cr 7 N (−24) I	−30†	15·5†	0·078†	15†	[18]
1-7	COCHF₂	0	Cr 39 I	−20†	11·1†	0·076†	21†	[18]
1-8	COCF₂C₃H₇	0	Cr 20 S_B 33 N 53·9 I	20†	5·7†	0·096†	17†	[18]
1-9	CH=CF₂	0	Cr 9·2 N 60·2 I					[19]
1-10	OCF₂CH=CH₂	0	Cr 29 S_B (9) N (20·3) I			0·066†		[21]
1-11	C≡C–Cl	0	Cr 66 N 70 I		6·7	0·21	13	[15]
1-12	OCF₃	1	Cr 43 S 128 N 147 I		7·7‡	0·152‡	17‡	[25]
			Cr 43 S 128 N 147 I		9·0	0·140	29	[17]
			Cr 43 S_B 128 N 147·4 I	100	8·9	0·140	16	[14]
1-13	OCHF₂	1	Cr 69·5 S 119·6 N 167·5 I	137	9·7	0·154	28	[16]
			Cr 67 S 120 N 162 I		7·4‡	0·155‡	24‡	[25]
			Cr 67 S_B 120 N 161·8 I	120	9·3	0·155	29	[14]
1-14	SCHF₂	1	Cr 56·2 S 94·7 N 114 I	105	11·4	0·174		[16]
1-15	SCF₃	1	Cr 60 S_B 78 N 105·2 I	70†	9·4†	0·149†	39†	[18]
1-16	CH=CF₂	1	Cr 56·7 S 184 N 232 I					[19]
1-17	CF₃	1	Cr 123 N 124·2 I	90	12·9	0·159	32	[14]

The clearing temperature T_{cl}^{extr}, dielectric anisotropy $\Delta\varepsilon$, optical anisotropy Δn and kinematic viscosity v of the liquid crystals are extrapolated from the 10 % w/w solution in ZLI-1132 at 20°C.

‡ Extrapolated values from the 10 % w/w solution in ZLI-4792 at 20°C.

† Extrapolated values from the 10 % w/w solution in the host liquid crystal materials at 20°C.

or multihalogen substitution; see tables 4–5, 7–8) [4, 13–17, 24–26, 28–39, 50, 55].

There are some most common approaches to the molecular design of liquid crystals for the TFT–PDLCDs: the introduction into molecular structure of liquid crystals with halogen endgroups (halogenated liquid crystals) the acetylene linking groups (see tables 1, 3, 5) [4, 15, 16, 41, 47, 54–60]; lateral mono or multihalogen substitution of the terphenyls with halogen endgroups (see table 6) [17, 40, 51–58]; the combination of these approaches [59]; lateral mono or multifluoro substitution of the 4-chloro-4′-[2-(4-trans-alkylcyclohexyl)ethyl]bi-phenyls (see table 5) [52–55]; the use of lateral unsubstituted and lateral mono or multifluoro substituted four-ring halogenated LCs (see table 7) [53, 55].

3. Mesomorphic behaviour

According to the generalized Van der Waals theory of nematics the nematic–isotropic transition (T_{N-I}) is due to the combination of the dispersion forces and an anisotropic excluded volume [61]. Combination of these ideas with the monomer–dimer equilibrium could provide the explanation of T_{N-I} values for some polar liquid crystals. The degree of overlap of two monomers when forming a dimer depends on the extension of the permanent dipole moment

(related to the amount of conjugation), and on the possibilities of the creation of induced dipole moments in the most polarizable parts of the molecule. Often, but not necessarily, these two effects combine [62].

The investigation of the liquid crystalline CN-derivatives by X-ray diffraction has revealed not only existence of a layer structure in the smectic phase of these compounds but also periodic density fluctuations in the nematic phase having a period $d > L$, and in some cases the simultaneous existence of two fluctuation layer structures with incommensurate periods d_1 and d_2, where $d_1 < L$ and $L < d_2 < 2L$, L-molecular length [63–66]. The dielectric [67, 68] and X-ray measurements have revealed that for liquid crystalline cyano derivatives the balance in the monomer–dimer system of $2M \Leftrightarrow D$ is biased towards dimers determining the liquid crystalline properties [65, 69]. Recent X-ray investigations have demonstrated that for liquid crystalline OCF₃-derivatives as well as for dialkyl weak polar compounds only the monomer layer structure with the period d_1 was found [66, 70], while the OCF₃ molecular group, as distinct from the alkyl group, has a fairly longitudinal dipole moment ($\mu = 2.36$ D [71]). This leads to the possible suggestion that the liquid crystalline properties of halogenated liquid crystals are determined by their monomers. This model can be used in

Table 2. Mesomorphic, dielectric, optical and viscous properties of liquid crystals:

Compound	R	Z	n	Phase behaviour/°C	T_{cl}^{extr}/°C	$\Delta\varepsilon$	Δn	v/mm^{2}s^{-1}	Reference
2-1	C$_5$H$_{11}$	CH=CF$_2$	0	Cr − 1.5 S 49.2 N 62.1 I					[19]
2-2	C$_5$H$_{11}$	(CH$_2$)$_2$CH=CF$_2$	0	Cr − 22.8 S 85.7 I					[19]
2-3	C$_5$H$_{11}$	OCHF$_2$	0		0†	2.3†	0.04†		[22]
2-4	C$_5$H$_{11}$	F	1	Cr 68 S 75 N 157 I					[20]
2-5	CH$_3$CH=CH(CH$_2$)$_2$	F	1	Cr 83 N 175 I		1.65‡			[23]
2-6	CH$_2$=CH(CH$_2$)$_3$	F	1	Cr 66 N 130 I		1.19‡			[23]
2-7	CH$_3$(CH$_2$)$_2$CH=CH	F	1	Cr 80 S (73) N 177 I					[20]
2-8	CH$_3$O(CH$_2$)$_3$	F	1	Cr 75 S 89 N 159 I		1.59‡			[23]
2-9	CH$_3$OCH$_2$CH=CH	F	1	Cr 83 S (≤25) N 170 I					[20]
2-10	C$_3$H$_7$	OCF$_3$	1	Cr 38 S 69 N 154 I		6.5§	0.109§	17§	[24]
			1	Cr 38 S$_B$ 69 N 153.7 I	110†	9.2†	0.088†	16†	[14]
2-11	C$_3$H$_7$	Cl	1	Cr 70 S 79 N 193 I		6.0§	0.125§	24§	[24]
2-12	C$_3$H$_7$	OCHF$_2$	1	Cr 51 S 69.2 N 172.2 I	155†	8.3†	0.114†	23†	[16]
			1	Cr 52 S 69 N 174 I		5.9§	0.119§	22§	[25]
			1	Cr 52 S$_B$ 69 N 173.6 I	140†	10.5†	0.119†	22†	[14]
2-13	C$_3$H$_7$	SCF$_3$	1	Cr 51 N 109.5 I	80¶	8.6¶	0.100¶	29¶	[18]
2-14	C$_3$H$_7$	COCF$_2$CH$_3$	1	Cr 92 N 197.1 I	150¶	7.1¶	0.146¶	56¶	[18]
2-15	C$_3$H$_7$	COCF$_2$C$_3$H$_7$	1	Cr 73 S$_B$ 152 N 199 I	150¶	7.4¶	0.142¶	49¶	[18]
2-16	C$_3$H$_7$	OCF$_2$Cl	1	Cr 82 N 133 I		7.5†	0.100†		[26]
2-17	C$_3$H$_7$	CF$_3$	1	Cr 133 I	100†	13.2†	0.102†	26†	[14]
2-18	C$_3$H$_7$	CH=CF$_2$	1	Cr 51 S 88.6 N 233 I					[19]
2-19	CH$_3$CHFCH$_2$	F	1	Cr 86 N 152 I					[27]

†§ Extrapolated values from the 10 % w/w solution in ZLI-1132 and ZLI-4792, respectively, measured at 20°C.
¶ Extrapolated values from the 10 % w/w solution in the host liquid crystal material at 20°C.
‡ $T = T_{N-1} - 10$°C.

the interpretation of the mesomorphic behaviour of halogenated liquid crystals having lower values of the melting and the clearing temperatures than respective cyano derivatives [12, 16].

3.1. *Effect of terminal group*

This effect is clearly shown by comparing phase transition temperatures for liquid crystals presented in tables 1–8. The *trans*-4-alkyl-(4′-halogen substituted phenyl)cyclohexanes often exhibit low melting points, but are not mesomorphic in general excepting compounds **1-8** and **1-9**, see table 1. The introduction of a second 1,4-phenylene group into compounds **1-1–1-10** to produce the three-ring 4-halogen substituted-4′-(trans-4-alkylcyclohexyl)biphenyls leads to the formation of broad nematic phases at elevated temperatures, see tables 1 and 5. The melting points are increased substantially comparing only compounds with the same substitutents (see tables 1 and 5). As follows from tables 1, 5 and [21], the clearing points for liquid crystals of general formula:
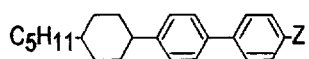
grow as follows: SCF$_3$ < SCHF$_2$ < CF$_3$ < OCF$_3$ < F < OCHF$_2$ < OCH$_2$CH=CF$_2$ < CH = CF$_2$. As follows

from tables 2 and 4, the clearing points for liquid crystals of general formula:
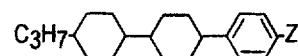
grow depending on the type of the terminal substitutent as follows: CF$_3$ < SCF$_3$ < OCF$_2$Cl < OCF$_3$ < F < OCHF$_2$ < Cl < COCF$_2$CH$_3$ < COCF$_2$C$_3$H$_7$ < CH=CF$_2$. It has been demonstrated that the existence of the carbon–carbon double bond and its position in the structure of alkenyl chain strongly affect the mesomorphic behaviour of halogenated liquid crystals (compounds **2-4–2-7**, compounds **7** and **9**, tables 2 and 8; see also [4, 56, 59]). The introduction of an oxygen atom into alkyl and into alkenyl chains slightly changes the clearing points in both cases and sufficiently reduces smectic thermostability in the last one (compounds **2-4** and **2-8**, **2-7** and **2-9**, table 2; see also [56, 59]).

The data collated in tables 2 and 4 reveal that the introduction of the fluorine atom into alkyl chain of the 1-[*trans*-4-(*trans*-4-alkylcyclohexyl)cyclohexyl]-4-halogen substituted benzenes slightly lowers the melting and clearing points (compounds **2-19** and **4-1**). Double fluoro substition of the alkyl chain decreases the clearing point and increases the melting point [27]. It has been found that the introduction of the chlorovinyl into LC molecular

Table 3. Mesomorphic, dielectric, optical and viscous properties of liquid crystals:
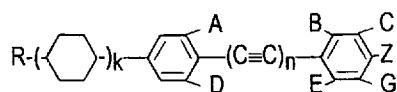
| Compound	R	Z	A	B	C	D	E	G	k	n	Phase behaviour/°C	T_{cl}^{extr}/°C	Δε	Δn	v/mm²s⁻¹	Reference
3-1	C₅H₁₁	F	H	H	H	H	H	H	0	1	Cr 65 I					[58]
3-2	C₅H₁₁	F	H	H	F	H	H	H	0	1	Cr 53 I					[58]
3-3	C₅H₁₁	F	F	H	H	H	H	H	0	1	Cr 17 I	−20‡		0·2†	10†	[54]
3-4	C₄H₉	F	H	H	H	H	H	H	0	1	Cr 56·7 I		5§	0·18§		[56]
3-5	C₄H₉O	F	H	H	H	H	H	H	0	1	Cr 73·5 I					[56]
3-6	C₄H₉	F	H	H	H	H	H	H	0	2	Cr 85·4 N 87·7 I		5·2§	0·309§		[56]
3-7	C₅H₁₁	Cl	H	H	H	H	H	H	0	1	Cr 69 I	37¶		0·24¶	17¶	[48]
3-8	C₅H₁₁	OCF₃	H	H	H	H	H	H	0	1	Cr 48 S 49 I		10||	0·19||	5||	[55]
3-9	C₅H₁₁	OCHF₂	H	H	H	H	H	H	0	1	Cr 28·1 S 37·8 I	28||	8·8||	0·18|		[16]
3-10	C₃H₇	F	H	H	H	H	H	H	1	1	Cr 90 N 189 I					[57]
3-11	C₃H₇	F	H	H	F	H	H	H	1	1	Cr 89 N 148 I					[58]
3-12	C₃H₇	F	F	H	F	F	H	H	1	1	Cr 71 N 123 I		6·6††			[4]
3-13	C₃H₇	F	F	H	F	F	H	F	1	1	Cr 88·8 N 92·9 I					[59]
3-14	C₃H₇	F	F	H	H	F	H	H	1	1	Cr 73·6 N 148·6 I		3·6††			[59]
3-15	C₃H₇	Cl	F	H	H	F	H	H	1	1	Cr 100·4 N 188·9 I					[59]
3-16	C₃H₇	Cl	F	H	F	F	H	H	1	1	Cr 90 N 158·9 I		5·8††			[59]
3-17	Cl-CH=CH	C₃H₇	H	F	H	H	F	H	1	1	Cr 91·7 N 266·7 I					[60]

§ ||Extrapolated values from the 10% w/w solution in ZLI-1132 measured at 22 and 20°C, respectively.
† ‡Extrapolated values from the 10% w/w solution in ZLI-4792 and ZLI-3086, respectively, measured at 20°C.
¶Extrapolated values from the 10% w/w solution in the host liquid crystal material at 20°C.
†† $T = T_{N-I} - 10$°C.

Table 4. Mesomorphic, dielectric, optical, viscous properties of liquid crystals.
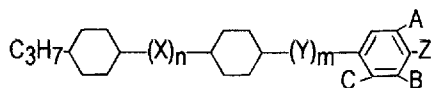
Compound	Z	A	B	C	X	n	Y	m	Phase behaviour/°C	Δε	Δn	v/mm²s⁻¹	Reference
4-1	F	H	H	H		0		0	Cr 90 N 158 I	4·0†	0·097†	16†	[24]
									Cr 90 N 158 I	7·3‡	0·089‡	16‡	[13]
4-2	F	H	H	H	CH₂	2		0	Cr 64·3 N 130·2 I				[34]
4-3	F	H	H	H	CH₂	4		0	Cr 63·6 N 102·3 I				[35]
4-4	F	H	H	H		0	CH₂	2	Cr 48 S 84 N 137 I	6‡	0·1‡	18‡	[17]
4-5	F	H	H	H		0	CH₂	4	Cr 56 S_B 87 N 116 I				[29]
4-6	F	H	H	H		0	CH=CHC₂H₄	1	Cr 33 S_B 74 N 135 I				[29]
4-7	F	H	H	H		0	CH=CHCH₂O	1	Cr 75 N 127 I				[29]
4-8	F	H	H	H		0	(CH₂)₃O	1	Cr 78 N 124 I				[29]
4-9	F	F	H	H		0		0	Cr 46 N 124 I	5·5†	0·089†	21†	[24]
4-10	F	F	H	H	CH₂	2		0	Cr 33·3 N 104·3 I			18¶	[36]
4-11	F	F	H	H		0	CH₂	2	Cr 18·4 S 49·7 N 118 I				[28]
4-12	F	F	F	H		0		0	Cr 64·7 N 93·7 I	8·3||	0·073||	25||	[30]
4-13	Z'	F	F	H		0		0	Cr 82 N 165·5 I	2·07¶			[37]
4-14	H	F	F	H		0		0	Cr 60 N 87·6 I	3·3¶			[37]
4-15	F	F	F	H	CH₂	2		0	Cr 50·7 N 83·4 I	7·8||	0·069||	28·6||	[30]
4-16	F	F	F	H		0	CH₂	2	Cr 41·8 N 98·3 I	7·3|	0·074||	31·6||	[30]
4-17	F	F	F	F		0		0	Cr 64 N 93 I				[39]

Z' = O(CH₂)₂F. †Extrapolated values from the 10% w/w solution in ZLI-4792 at 20°C.
‡Extrapolated values from the 10% w/w solution in ZLI-1132 at 20°C.
||Extrapolated values from the 20% w/w solution in the mixture of 3,4-difluoroderivatives at 20°C (Δε, v) and at 25°C (Δn).
¶Extrapolated values from the 10% w/w solution in the host liquid crystal materials at 20°C.

Table 5. Mesomorphic, dielectric, optical and viscous properties of liquid crystals:

$$C_5H_{11}-\langle\quad\rangle-(X)_n-\langle\overset{A}{\underset{C}{\quad}}\rangle-(Y)_m-\langle\overset{B}{\underset{D}{\quad}}\rangle Z$$
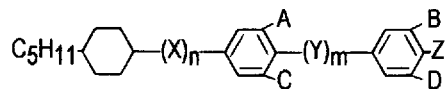
Compound	Z	A	B	C	D	X	n	Y	m	Phase behaviour/°C	T_{cl}^{extr}/°C	$\Delta\varepsilon$	Δn	$v/mm^2 s^{-1}$	Reference
5-1	F	H	H	H	H		0		0	Cr 102 N 153 I		4·9†	0·159†	27†	[25]
5-2	F	H	F	H	H		0		0	Cr 55 N 105 I		6·5†	0·148†	21†	[25]
										Cr 55 N 105 I		10‡	0·13‡	30‡	[17]
5-3	F	H	F	H	F		0		0	Cr 30·4 N 58 I		11·3§	0·134§	32·1§	[30]
5-4	F	F	H	F	H		0		0	Cr 103 I	64†	9·2†	0·123†	46†	[32]
5-5	F	F	F	H	F		0		0	Cr 63 I	37†	13·8†	0·114†	28†	[33]
5-6	F	F	H	F	F		0		0	Cr 72 I	34†	12·4†	0·108†	36†	[32]
5-7	F	F	F	F	F		0		0	Cr 114 I	2†	17·8†	0·09†	38†	[33]
5-8	F	H	F	H	H	CH₂	2		0	Cr 74·8 N 95·9 I					[28]
5-9	F	H	F	H	F	CH₂	2		0	Cr 40·2 N 65·2 I		10·8§	0·124§	18·6§	[30]
5-10	F	H	H	H	H		0	CH₂	2	Cr 57 N 79 I					[38]
5-11	F	H	H	H	H		0	C≡C	1	Cr 94 N 192 I			0·23¶	24¶	[47]
5-12	F	H	H	H	F		0	C≡C	1	Cr 72·5 N 155·4 I					[41]
5-13	F	F	H	H	H		0	C≡C	1	Cr 78 N 163 I			0·23†	33†	[54]
5-14‖	Cl	F	H	H	H	CH₂	2		0	Cr 72·1 N 120 I		5·3†	0·180†	25†	[52]
5-15‖	Cl	H	F	H	H	CH₂	2		0	Cr 64·7 N 120·6 I		5·6†	0·180†		[52]
5-16‖	Cl	H	F	H	F	CH₂	2		0	Cr 61·2 N 87·3 I		12·2†	0·166†		[52]
5-17‖	Cl	F	F	H	H	CH₂	2		0	Cr 55 N 96·6 I		9·0†	0·168†		[52]
5-18‖	Cl	F	F	H	F	CH₂	2		0	Cr 47·2 N 72 I		13·4†	0·151†		[52]
5-19‖	Cl	F	H	H	H	CH₂	2	C≡C	1	Cr 80 N 159 I			0·27†	24†	[54]

† ‡ Extrapolated values from the 10 % w/w solution in ZLI-4792 and ZLI-1132, respectively, measured at 20°C.
§ Extrapolated from the 20% w/w solution in the mixture of 3,4-difluoroderivatives at 20°C ($\Delta\varepsilon$, v) and 25°C (Δn).
¶ Extrapolated values from the 10 % w/w solution in the host liquid crystal material.
‖ n-Propyl homologue.

structure strongly increases its nematic thermostability (compound 3-17, table 3; see also [72]).

3.2. Effect of rigid core's structure

The effect of the replacement of the 1,4-phenylene group by the 1,4-cyclohexylene group in the *trans*-4-alkyl-(4'-halogen substituted phenyl)cyclohexanes to produce the *trans*-4-alkyl-(*trans*-4'-halogen substituted cyclohexyl)cyclohexanes and increasing the length of the terminal halogenated substitutents results in the appearance of the smectic phase (compounds 1-9 and 2-1, 2-2; see also [44,73]), while the substitution of the *trans*-1,4-cyclohexylene group by the 1,4-bicyclo[2.2.2]-octylene group in the *trans*-4-alkyl-(*trans*-4'-difloromethoxyphenyl)cyclohexanes to produce compound 16 (see tables 1, 8 and [14,16]) causes the formation of broad nematic phase.

As can be seen from tables 1, 2, 4 and 5, 1-[*trans*-4-(*trans*-4-alkylcyclohexyl)cyclohexyl]-4-halogen substituted benzenes usually show higher clearing points and broader nematic ranges compared to the respective 4-halogen substituted-4'-(*trans*-4-alkylcyclohexyl)biphenyls.

Comparing the phase transition temperatures of the compounds 7-1–7-4 and 4-1, tables 7 and 4, it can be seen that the replacement of the *trans*-1,4-cyclohexylene group by the 1,4-cyclohexenylene group results in decreasing the melting and clearing points, see also [35,74].

Tables 2, 4 and 7 show that the replacement of the *trans*-1,4-cyclohexylene group by the 6,2-spiro [3.3] heptane group in the 1-[*trans*-4-(*trans*-4-alkylcyclohexyl)cyclohexyl]-4-halogen substituted benzenes leads to decreasing the clearing points (compounds 7-7 and 2-12; 7-8 and 2-10; 7-9) and 4-12), while the replacement of the 1,3-cyclobutylene group by the 6,2-spiro[3.3]heptane group in the compound 7-6 to produce compound 7-5 increases the nematic thermostability.

The effect of the introduction of the *trans*-1,3-dioxane-2,5-diyl, pyridin-2,5-diyl and pyrimidin-2,5-diyl groups into molecular structure of halogenated liquid crystals on their mesomorphic properties was clearly shown in [4, 12, 14, 16, 26, 50, 59]. However, the difficulties in achieving high holding voltage ratio when pyridin-2,5-diyl and pyrimidin-2,5-diyl groups are included in the LC structures do not allow their application as the components of liquid crystal materials for AMLCDs and TFT–PDLCDs [52].

Among all known halogenated liquid crystals, the four-ring compounds usually show the highest nematic

Table 6. Mesomorphic, dielectric, optical and viscous properties of liquid crystals:
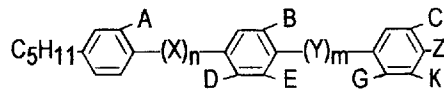
Compound	A	B	C	D	E	G	K	Z	X	n	Y	m	Phase behaviour/°C	Δn†	Δε†	v†/mm²s⁻¹	Reference
6-1	H	H	H	F	H	F	H	Cl		0		0	Cr 68 N 105·5 I	0·24	3		[51]
6-2	H	H	H	F	H	H	H	Cl		0		0	Cr 96·3 S 134·2 N 157·6 I	0·27	5		[51]
6-3	H	H	H	H	H	F	H	Cl		0		0	Cr 64·8 S 94 Sₐ 151 N 158·8 I	0·27	6		[51]
6-4	F	F	H	H	H	H	H	Cl		0		0	Cr 60·3 N 111·7 I	0·25	12		[51]
6-5	F	F	F	H	H	H	H	Cl		0		0	Cr 66 N 76·6 I	0·22	14		[51]
6-6	H	H	H	F	H	H	F	Cl		0		0	Cr 54 Sₐ 101·7 N 112·9 I	0·25	6		[51]
6-7	H	F	F	H	H	H	H	F		0		0	Cr 67 Sₐ 73 N 87·7 I		11·5‡		[40]
6-8	F	H	H	H	H	H	H	F		0	CH₂	2	Cr 35 N 53 I	0·17§	10§	23§	[17]
													Cr 33 N 53 I	0·149‡	3·6‡	21‡	[53]
6-9	F	H	H	H	H	H	H	Cl		2	CH₂	2	Cr 53 N 83 I	0·199‡	4·3‡	30‡	[53]
6-10	F	H	H	H	H	H	H	Cl	CH₂	2		0	Cr 77 N 94 I	0·210	9·5		[52]
													Cr 76·8 N 93·8 I	0·210	9·0		[51]
6-11¶	H	F	F	H	F	H	H	Cl		0	C≡C	1	Cr 92·3 N 142·7 I				[59]
6-12¶	H	F	F	H	F	H	H	F		0	C≡C	1	Cr 90 I				[59]

† Extrapolated values from the 10 % w/w solution in ZLI-4792 at 20°C.
§ Extrapolated values from the 10 % w/w solution in ZLI-1132 at 20°C.
‡ Extrapolated values from the 10 % w/w solution in the host liquid crystal materials at 20°C.
¶ n-Propyl homologue.

thermostabilities (see table 7 and also [74, 75]) comparing only compounds with the same substituents.

As can be seen from tables 1, 3, 4–6 and [4, 14–17, 28–31, 33–35, 38, 41, 47–48, 51–60, 75–76, 79], the effect of the introduction of the different linking groups into molecular structure of liquid crystals is most marked in the case of the three and four-ring compounds; thus, the position and the order of the acetylene and ethylene linking groups in the rigid core of halogenated liquid crystals have the considerable opposite effect on the mesomorphic behaviour of these LCs. So far ethylene linking group increasing the molecular flexibility which in turn leads to effective broadening the molecule and reduction in the effect of intermolecular attractive forces always decreases the melting and clearing points of LCs; while the acetylene linking group increasing the conjugation length of π-electrons and, therefore, enhancing molecular polarizability increases the nematic thermostability.

Table 4 presents a set of mesogens with the different four-unit-linking groups (compounds 4-3, 4-5–4-8). In this case, the nature of the linking group affects the mesomorphic behaviour of these LCs; that is, the smectic phase is disappeared by the presence of an oxygen atom in the linking group (compounds 4-5 and 4-8; 4-6 and 4-7).

As follows from tables 1–8 and [77], the lateral mono and multihalogen substitutions have a considerable effect

on the mesomorphic behaviour of the liquid crystals resulting in reducing the smectic and nematic thermostabilities due to the lateral halogen substitutent broadening the molecule and reducing intermolecular interactions.

Interestingly, the introduction of the fourth fluorine atom in the lateral position of the 1-[trans-4-(trans-4-alkylcyclohexyl)cyclohexyl]-3,4,5-trifluorobenzenes does not affect their mesomorphic behaviour (compounds 4-12 and 4-17, table 4).
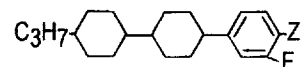
The data presented in tables 1–8 and in [14, 17, 21, 25, 30, 37, 38, 43, 53, 54, 59, 78–81] reveal that the clearing points for liquid crystals of the following general formulas:
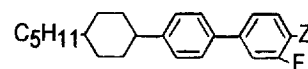
grow as follows: F < OCHF₂ < Cl
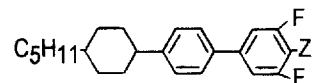
grow as follows: F < OCHF₂ < OCH₂CF₃ < OCF₂CF₂H
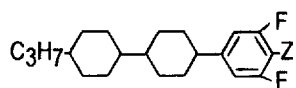

grow as follows: F < OCHF₂ < Cl

Table 7. Mesomorphic, dielectric, optical and viscous properties of some liquid crystals.

Compound	Structure, $R = n - C_3H_7$	Phase behaviour/°C	T_{cl}^{extr}/°C	$\Delta\varepsilon$	Δn	v/mm^{2}s^{-1}	Reference
7-1	R–◯–◯–◯–F	Cr 45 N 91 I					[43]
7-2	R–◯–◯–◯–F	Cr 59 N 150 I					[42]
7-3	R–◯–◯–◯–F	Cr 76 N 95 I					[43]
7-4	R–◯–◯–◯–F	Cr 56 N 97 I					[43]
7-5	R–◯–◯–◇◇–CF$_2$	Cr 58 S$_B$ 151 N 157·4 I	148·4†	3·7†	0·082†	17†	[46]
7-6	R–◯–◯–◇–CF$_2$	Cr 54 S$_B$ 91 N 103·8 I					[45]
7-7	R–◯–◇◇–◯–OCHF$_2$	Cr 31 S$_B$ 80 N 113 I	109·3†	5·5†	0·1†	13†	[46]
7-8	R–◯–◇◇–◯–OCF$_3$	Cr 67 N 95·2 I	84·6†	5·4†	0·096†	9†	[46]
7-9	R–◯–◇◇–◯(F,F,F)	Cr 46 N 61·4 I	36·4†	7·8†	0·069†	13†	[46]
7-10	R–◯–◯–C$_2$H$_4$–◯–◯(F)–Cl	Cr 100 N 208 I		5·4‡	0·225‡	66‡	[53]
7-11	R–◯–◯(F)–◯–C$_2$H$_4$–◯–F	Cr 77 N 211 I		10§	0·22§	50§	[55]
7-12	R–◯–◯(F)–◯–C$_2$H$_4$–◯(F,F)	Cr 56 N 189 I					[55]
7-13	R–◯–◯–C$_2$H$_4$–◯–◯(F,F)	Cr 79·2 N 216·0 I					[31]
7-14	R–◯–◯(F,F)–C$_2$H$_4$–◯(F,F)–◯(F,F)	Cr 113 I	90†	23·4†			[33]

† Extrapolated values from the 10 % w/w solution in ZLI-4792 at 20°C.
‡ Extrapolated from the 10 % w/w solution in the host liquid crystal material at 20°C.
§ Extrapolated values from the 10 % w/w solution in ZLI-1132 at 20°C.

C$_3$H$_7$–◯–◯–◯(F,F)–Z
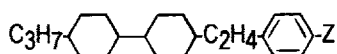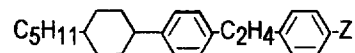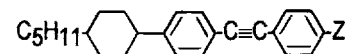
grow as follows:
H < F < OCHF$_2$<OCH$_2$CF$_3$<O(CH$_2$)$_2$F < CH$_2$CH=CF$_2$

C$_3$H$_7$–◯–◯–C$_2$H$_4$–◯–Z

grow as follows: CF$_3$ < OCF$_3$ < F < OCHF$_2$ < Cl

C$_5$H$_{11}$–◯–◯–C$_2$H$_4$–◯–Z

grow as follows: CF$_3$ < OCF$_3$ < F < OCHF$_2$ < Cl

C$_5$H$_{11}$–◯–◯–C≡C–◯–Z

grow as follows: OCF$_3$ < F < OCHF$_2$

Table 8.   Dielectric and visco-elastic properties of some liquid crystals.

Compound	Structure	$T_{N-I}/°C$	$\varepsilon_\parallel$	$\varepsilon_\perp$	$\Delta\varepsilon$	Δn	$\gamma_1/K_1/$ msμm^{-2}	$v/$mm^{2}s^{-1}	τ†	Reference
1	C_5H_{11}—◯—⬡—⬡—$OCHF_2$	167·5	6·8	3·3	3·5				0·88	[16]
2	C_5H_{11}—◯—⬡—⬡—$SCHF_2$	114	7·4	3·6	3·8				0·95	[16]
3	C_3H_7—◯—◯—⬡—$OCHF_2$	172·2	5·0	2·8	2·2				0·85	[16]
4	C_3H_7—◯—◯—⬡—$OCHF_2$	167·7	6·9	3·3	3·6				0·85	[16]
5	C_3H_7—◯—◯—⬡—F	158			3·6				0·85	[30]
6	C_3H_7—◯—◯—⬡(F)—F	135·5			1·2				0·85	[49]
7	C_3H_7—◯—◯—⬡—F, F	124			4·0				0·85	[30]
8	C_3H_7—◯—◯—⬡—F, F, F	93·7			4·3				0·85	[30]
9	CH_3-CH=CH—◯—◯—⬡—F, F	159			3·22‡					[50]
10	CH_3-CH=CH—◯—⬡—⬡—F, F	134			4·04‡					[4]
11	CH_3-CH=CH—◯—◯—⬡—Cl, F	197			2·91‡					[4]
12	CH_3-CH=CH—◯—◯—C_2H_4—⬡—F, F	137			2·73‡					[4]
13	CH_3-CH=CH—◯(O,O)—◯—⬡—Cl, F	144			10‡					[4]
14	C_5H_{11}—◯—◯—C_2H_4—⬡—Cl	161·3	5·0	2·4	2·6		2·2		0·85	[15]
15	C_5H_{11}—◯—◯—C_2H_4—⬡—Cl, F	142·5	7·3	3·2	4·1		3·6		0·85	[15]
16	C_7H_{15}—◯—⬡—$OCHF_2$	31·6			3·8§	0·063§		14§		[16]

† $\tau = T/T_{N-I}$; T/K; T_{N-I}/K.
‡ $T = T_{N-I} - 10°C$.
§ $T = 20°C$.

C_3H_7—◯—C_2H_4—⬡(F)—◯—Z
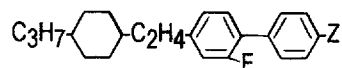
grow as follows: $CF_3 < F < OCF_3 < Cl$

C_3H_7—◯—⬡(F)—C≡C—⬡(F)—Z
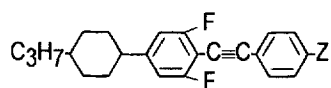
grow as follows: $F < OCF_3 < OCHF_2 < Cl$

C_3H_7—◯—⬡(F,F)—C≡C—⬡(F,F)—Z
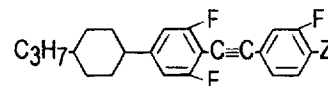
grow as follows: $F < OCHF_2 < Cl$

These examples show that the introduction of the linking groups or/and lateral substitutents into molecular structure of LCs not always leads to the same dependence of the clearing points on the type of the terminal substituent compared to the corresponding laterally unsubstituted compounds without linking groups (§ 3.1).

4. Static dielectric properties

From the dielectric theory of nematic liquid crystals the dielectric anisotropy $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$, where $\varepsilon_\parallel$ and $\varepsilon_\perp$ are, respectively, dielectric constants, that are parallel and perpendicular to the nematic director **n**, is given by equation (1) [82]:

$$\Delta\varepsilon = NhF/\varepsilon_0[\Delta\alpha - F\mu^2/kT(1 - 3\cos^2\beta)]S, \qquad (1)$$

where $h = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$, $\Delta\alpha = (\alpha_\parallel - \alpha_\perp)$, F is the cavity reaction field, μ is the permanent molecular dipole moment, β is the angle between μ and the molecular long axis, N is the number of molecules per unit volume, $\Delta\alpha$ is the anisotropy of induced molecular polarization.

From equation (1) follows the dependence of $\Delta\varepsilon$ on the order parameter S which is given in equation (2):

$$S = 1/2\langle 3\cos^2\Theta - 1\rangle \qquad (2)$$

The temperature dependence $\Delta\varepsilon$ (T) of polar liquid crystals basically varies with S/T. This leads to an increase of $|\Delta\varepsilon|$ with decreasing temperature. Therefore, meaningful comparisons of the dielectric, optical and elastic properties of liquid crystals with different nematic–isotropic transitions T_{N-I} can only be made at a constant reduced temperature T/T_{N-I} [2].

Tables 2–3 and 8 present the results of the direct measurements of the dielectric properties for some liquid crystals. As can be seen from these tables, the replacement of the *trans*-1,4-cyclohexylene group by the 1,4-cyclohexenylene or by the 1,4-phenylene or by the *trans*-1,3-dioxane-2,5-diyl groups in the LC rigid core results in increasing the $\Delta\varepsilon$ (compounds **3** and **4**, **9** and **10**; **11** and **13**, table 8) due to the overall molecular polarizability having been increased.

An odd–even effect in the dielectric properties of the alkenyls (compounds **2-5** and **2-6**, table 2) can be explained in terms of the chain order parameter which is almost twice as large in odd alkenyl double bond positions as the chain order of terminal double bonds at even sites [83].

The introduction of the fluorine atoms into the lateral positions of the liquid crystals has a considerable effect on their dielectric anisotropy (compounds **3-10**, **3-12**, **3-14**; and **6**, **7**, **8**; **14** and **15**, tables 3 and 8). This can be rationalized in terms of the contribution of the individual flourine dipole moments to the overall molecular dipole moment relative to the director.

The introduction of the ethylene linking group into molecular structure of liquid crystals lowers the dielectric anisotropy (compounds **9** and **12**, table 8) due to reducing the molecular polarizability caused by disruption of the overall conjugation.

Tables 1–7 present the dielectric anisotropy data for halogenated liquid crystals with the different clearing

temperatures extrapolated from the solution in the host liquid crystals materials. According to [2], these extrapolations do not have meaningful values. However, for non-mesomorphic and smectic liquid crystals used as the components of liquid crystal materials, these estimations is only one way of rough definition of their dielectric (optical and elastic) properties.

Unfortunately, the difference in values of the dielectric anisotropy received for some compounds by extrapolation from the solution in the different host liquid crystal materials (compounds **1-12**, **1-13**, **2-10**, **2-12**, **4-1**, **5-2**, **6-8**, tables 1, 2, 4–6) prevents accurate comparison of their properties. These differences can be explained in terms of changing the character of intermolecular interactions in the liquid crystal mixtures leading to the deviations from the ideal or additive behaviour of the dielectric properties [69, 84–85].

Tables 2, 3 and 8 and the data presented in [12, 16] show that for definite chemical structure of LCs, its dielectric anisotropy $\Delta\varepsilon$, approximately decreases in the same sequence as values of dipole moments for terminal groups [71]: CN, CF_3, $OCHF_2$, OCF_3, Cl, F diminish: 4·05, 2·56, 2·46, 2·36, 1·58, 1·47, respectively.

5. Optical properties

From the phenomenological relation between the refractive index and the electric polarization follows equation (3) [86, 87]:

$$(n^{*2} - 1)/(n^{*2} + 2) = N\alpha^*/3\varepsilon_0, \qquad (3)$$

where the mean polarizability $\alpha^* = (\alpha_\parallel + 2\alpha_\perp)/3$; the mean refractive index $n^{*2} = (n_e^2 + 2n_0^2)/3$; n_0 is the ordinary and n_e is the extraordinary refractive indices. From equation (3) and §4, it follows that the aromatic compounds and LCs with the acetylene linking groups which have large induced polarizability of their highly conjugated π-electron system exhibit the optical anisotropy $\Delta n = n_e - n_0$ that is much larger than the Δn of non-aromatic compounds and liquid crystals without acetylene linking groups ([88] and tables 1–8). It has been shown that halogenated liquid crystals exhibit lower values of the optical anisotropy compared with the respective cyano derivatives [16, 89], see also tables 1–8. This can be explained in terms of reducing the effective conjugation length of π-electron system resulting in shorter resonance wavelength of UV absorption spectrum for halogenated LCs than for respective cyano derivatives [90].

The difference in values of the optical anisotropy received for some compounds by extrapolation from the solution in the different host liquid crystal materials (compounds **1-12**, **2-10**, **2-12**, **4-1**, **5-2**, **6-8**; tables 1–2, 4–6) can be explained as in the case of the dielectric properties [69, 84, 85].

6. Visco-elastic properties

Since the twisted nematic effect [91] is today predominantly used in active matrix displays, these displays require nematic liquid crystals of positive dielectric anisotropy, discussed in the § 4 and this strongly affects the threshold voltage (V_{90}) of TN–AMLCDs [2]:

$$V_{90} \propto \pi[\kappa/\varepsilon_0 \Delta\varepsilon]^{1/2}, \tag{4}$$

where κ is the elastic expression, $\kappa = [K_1 + (K_3 - 2K_2)/4]$. It is clear from equation (4) that $\Delta\varepsilon$ should be as high, κ be as low as possible, respectively for receiving a low threshold voltage.

For better performance of AMLCDs the response times (switch on, t_{on} and switch off, t_{off} times) should be as short as possible. It has been shown that t_{on} and t_{off} could be approximated by the equations (5) and (6), respectively [92]:

$$t_{on} \propto \eta d^2/(\Delta\varepsilon E - \kappa\pi^2), \tag{5}$$

$$t_{off} \propto \eta d^2/\kappa\pi^2, \tag{6}$$

where η corresponds to the rotational viscosity γ_1 [93], E is the applied electric field, and d is the AMLCDs cell gap. It has been shown that the response time t_{on} and the relaxation time t_{off} of the PDLC film can be defined by [5]:

$$t_{on} = (1/\gamma_1)(\varepsilon_0 \Delta\varepsilon E^2 - K(l^2 - 1)/a^2), \tag{7}$$

$$t_{off} = \gamma_1 a^2/K(l^2 - 1), \tag{8}$$

where a and l are the major axis and the aspect ratio of ellipsoidal droplets, K is an effective elastic constant, E is the applied electric field, and γ_1 is the rotational viscosity of the liquid crystals.

From equations (5)–(8) follows the strong relationship between the response times of the AMLCDs and PDLCDs and visco-elastic properties of liquid crystals. Table 8 presents the visco-elastic properties of some halogenated liquid crystals received from the direct measurements, see also [94]. Tables 1–7 present the values of the kinematic viscosity ν for liquid crystals received by extrapolation from the solution in the different host liquid crystal materials. The difference in values of the kinematic viscosity received for some compounds (compounds 1-12, 1-13, 2-10, 2-12, 5-2, 6-8; tables 1, 2, 5 and 6) can be explained as in the case of the dielectric properties.

From tables 1–8 and [15,88,94], it follows that the viscosity is minimized in the liquid crystalline structures with minimal polarity and polarizability, with short terminal groups and lacking lateral substituents.

As can be seen from [12,16,88] and tables 1–8, halogenated LCs show lower values of the viscosity compared to the respective cyano derivatives. These results can be explained, as discussed earlier, in terms of predominant influence of halogenated LC monomers on their viscous properties.

7. Stability studies of halogenated liquid crystals

One of the most important parameters characterizing liquid crystals for AMLCDs is the RC-time constant of the material within the display [95]. This is due to the fact that the liquid crystal element acts in active matrix addressing as a capacitive load to the non-linear element, which is charged during the addressing cycle. Since the voltage across the liquid crystal element must not fall appreciably before it is refreshed during the next addressing cycle, the RC-time value of the liquid crystal should be considerably larger than the frame time of the display. In order to ensure that the voltage drop is, for example, less than 5 per cent for a frame time of 20 ms, the RC-time has to be larger than 200 ms over the whole operating temperature range [96,97]. The RC-time constant of the liquid crystal

$$\tau_{RC} = \varepsilon_0 \varepsilon_r \rho_{LCD} \tag{9}$$

is determined by the resistivity ρ_{LCD} of the liquid crystal within the LCD [97], requiring values of more than $10^{13}\,\Omega\,cm$ [2]. It has been found that RC-time values are mainly determined by the two factors: the specific resistivity of the liquid crystal material in bulk, and the type of polyimide used as the orientation layer [97]. The relation between bulk resistivity values ρ and RC-times for the given set of compounds is close to a linear function [13,97], and it has been established that increasing the mean dielectric constant of the liquid crystal, ε^* leads to a decreasing the RC-times [13,97] and to decreasing the bulk resistivity [13].

The property directly correlated to the performance of AMLCDs is the ratio of the actual voltages at the individual pixel directly after one addressing pulse and directly before the next addressing pulse. The holding ratio can be determined by simultaneous monitoring of the RMS values of the driving voltage applied to the TFT and the actual voltage at the electrodes of the picture element [13,98,99]. It has been shown that large holding ratios in AMLCDs not only require highly resistive liquid crystal materials stable against exposure to elevated temperatures [13] and UV irradiation [97], they also increase with increasing TFT driving voltage [4].

It has been shown that cyano derivatives can be degradated by heat and light [100] and they do not have sufficient stability to be used in AMLCD and TFT–PDLC [13]. This can be explained by measuring a hydrophobic parameter:

$$\Phi = \log P_x - \log P_h, \tag{10}$$

where P_x is the partition coefficient of substituted benzene derivative, P_h is the corresponding coefficient of benzene, the parent compound, in the system octanol/water. It has been reported that the compounds with a negative hydrophobic parameter Φ [14] are easier soluble in water than in octanol and exhibit a stronger solvation potency for

impurities ions than those with a positive hydrophobic parameter: Under this aspect the halogen endgroups having positive Φ values are better than the cyano group for AMLCD and PDLCD applications [14].

8. Development of liquid crystal materials for AMLCDs and TFT–PDLCDs

In the LCDs at least ten different liquid crystalline material parameters have to be optimized to achieve optimal display performance. Since the single liquid crystal shows at best one or two distinguished properties, mixtures consisting of up to twenty and more components have to be developed for a given application. The principles of the development of liquid crystal materials (LCMs) are briefly discussed in [101], particularly helpful is the review [69], some practical examples of LCMs for active matrix displays and TFT–PDLCD applications are presented in [102, 103].

9. Conclusions

As may be appreciated from the review of the subject presented in this paper, by using modern molecular design principles, it is possible to receive halogenated liquid crystals that are of real use in the liquid crystal materials for active matrix displays and TFT–PDLCD applications attracting the main interest and being in intense development.

References

[1] WU, I.-W., 1994, *J. SID*, **2**, 1.

[2] SCHADT, M., 1992, *Displays*, **13**, 11.

[3] BERREMAN, D. W., 1974, *J. opt. Soc. Am.*, **63**, 1374.

[4] SCHADT, M., 1993, *Liq. Crystals*, **14**, 73.

[5] DOANE, J. W., GOLEMME, A., WEST, J. L., WHITEHEAD, J. B., and WU, B.-G., 1988, *Molec. Crystals liq. Crystals*, **165**, 511.

[6] DOANE, J. W., 1990, *Liquid Crystals-Applications and Uses*, Vol. 1, edited by B. Bahadur, (World Scientific Publishing), p. 361.

[7] KITZEROW, H-S., 1994, *Liq. Crystals*, **16**, 1.

[8] FERGASON, J. L., 1984, US Patent No 4435047.

[9] DOANE, J. W., VAZ, N., WU, B.-G., and ZUMER, S., 1986, *Appl. Phys. Lett*, **48**, 269.

[10] YANIV, Z., DOANE, J. W., WEST, J. L., and TAMURA-LIS, W., 1989, *Japan Display '89 (Proceedings)* (The Society for Information Display and The Institute of Television Engineers of Japan), p. 572.

[11] YOSHIDA, H., NAKAMURA, K., TSUDA, H., OHASHI, M., TOMITA, I., and OKABE, M., 1993, *Eurodisplay '93 (Proceedings)* (The Society for Information Display and The Institute of Television Engineers of Japan), p. 121, Le Club Visu.

[12] PAVLUCHENKO, A. I., FIALKOV, YU, A., SHELYAZHENKO, S. V., YAGUPOLSKI, L. I., SMIRNOVA, N. I., PETROV, V. F., and GREBYONKIN, M. F., 1991, *Rus. J. phys. Chem.*, **65**, 1190.

[13] PLACH, H. J., RIEGER, B., WEBER, G., OYAMA, T., and SCHEUBLE, B. S., 1989, *Proceeding of the 3rd Merck Japan Liquid Crystal Seminar, July 18–19*, Tokyo-Osaka.

[14] BARTMANN, E., DORSCH, D., FINKENZELLER, U., KURMEIER, H. A., and POETSCH, E., 1990, *19 Freiburger Arbeitstagung Flussigkristalle*, Vortrag 8.

[15] WU, S. T., COATES, D., and BARTMANN, E., 1991, *Liq. Crystals*, **10**, 635.

[16] PAVLUCHENKO, A. I., SMIRNOVA, N. I., PETROV, V. F., FIALKOV, Y. A., SHELYAZHENKO, S. V., and YAGUPOLSKI, L. M., 1991, *Molec. Crystals liq. Crystals*, **209**, 225.

[17] RIEGER, B., JACOB, T., NUMATA, H., and SCHEUBLE, B. S., 1990, *The 4th Merck Japan Liquid Crystal Seminar, Proceedings, June 19–20*, Tokyo-Osaka (E. Merck, Industrial Chemicals Division, Merck, Japan Ltd), p. 4.

[18] BARTMANN, E., DORSCH, D., and FINKENZELLER, U., 1991, *Molec. Crystals liq. Crystals*, **204**, 77.

[19] USHIODA, M., USHIDA, M., and SUZUKI, T., 1988, Eur. Pat. Appl. EP 0325796.

[20] KELLY, S. M., GERMANN, A., BUCHECKER, R., and SCHADT, M., 1994, *Liq. Crystals*, **16**, 67.

[21] BARTMANN, E., PLACH, H., BREMER, M., and PAULUTH, D., 1994, Ger. Offen. DE 4223501.

[22] TORGOVA, S. I., KARAMYSHEVA, L. A., GEYVANDOV, R. KH., and PETROV, V. F., 1991, *Summer European Liquid Crystal Conference, Abstracts*, 19–25 August, Vilnius University, Lithuania, A-16, Vilnus University.

[23] TAKATSU, H., TAKEUCHI, K., SASAKI, M., OHNISHI, H., and SCHADT, M., 1991, *Molec. Crystals. liq. Crystals*, **206**, 159.

[24] PLACH, H. J., BARTMANN, E., POETSCH, E., NAEMURA, S., and RIEGER, B., 1992, *SID Digest*, 13.

[25] KOBAYASHI, K., SAWADA, A., PLACH, H. J., BARTMANN, E., POETCH, E., and RIEGER, A., 1992, *The Proceedings of the 3rd Merck Korea Liquid Crystal Seminar*, 16 June, Seoul (Merck Korea Ltd, Merck Liquid Crystal '92).

[26] PAVLUCHENKO, A. I., SMIRNOVA, N. I., PETROV, V. F., FIALKOV, Y. A., SHELYAZHENKO, S. V., SCHADT, M., and BUCHECKER, R., 1995, *Molec. Crystals liq. Crystals*, **265**, 41; BUCHECKER, R., FIALKOV, Y. A., PAVLUCHENKO, A. I., PETROV, V. F., SCHADT, M., SHELYAZHENKO, S. V., and SMIRNOVA, N. I., 1994, UK Patent Application GB 2270913.

[27] OGAWA, S., TAKEHARA, S., TAKEUCHI, K., and TAKATSU, H., 1993, *Proceedings of the 19 Japanese Liquid Crystal Conference*, University of Tokyo, p. 224.

[28] GOTO, Y., OGAWA, T., SAWADA, S., and SUGIMORI, S., 1991, *Molec. Crystals liq. Crystals*, **209**, 1.

[29] KELLY, S. M., 1991, *Molec. Crystals liq. Crystals*, **204**, 27.

[30] TARAO, R., SAITO, H., SAWADA, S., and GOTO, Y., 1994, *SID Digest*, 233.

[31] DEMUS, D., GOTO, Y., SAWADA, S., NAKAGAWA, E., SAITO, H., and TARAO, R., 1995, *Molec. Crystals liq. Crystals*, **260**, 1.

[32] PLACH, H. J., REIFFENRATH, V., and WEBER, G., 1992, *Proc. SPIE*, **1815**, 256.

[33] BARTMANN, E., FINKENZELLER, U., POETSCH, E., REIFFENRATH, V., and TARUMI, K., 1993, *22 Freiburger Arbeitstagung Flussigkristalle*, Vortrag 8.

[34] GUNJIMA, T., and RYUTARO, T., 1983, Eur Pat. Appl. EP 0102047.

[35] MATSUI, S., GOTO, Y., and ONJI, Y., 1993, Eur Pat. Appl. EP 0568040.

[36] GOTO, Y., and OGAWA, T., 1988, Eur. Pat. Appl. EP 0280902.

[37] REIFFENRATH, V., PLACH, H., PAULUTH, D., HITTICH, R., POETSCH, E., GEELHAAR, T., WEBER, G., and BARTMANN, E., 1994, Ger Offen. DE 4222371.

740 V. F. Petrov

[38] KELLY, S. M., and SCHAD, H., 1985, *Helv. Chim. Acta*, **68**, 1444.

[39] REIFFENRATH, V., HITTICH, R., and PLACH, H., 1992, Ger. Offen. DE 4111765.

[40] POETSCH, E., REIFFENRATH, V., HITTICH, R., and RIEGER, B., 1991, Ger. Offen. DE 4107120.

[41] GOTO, Y., and OGAWA, T., 1988, Eur. Pat. Appl. EP 0295602.

[42] SUGIMORI, S., KOJIMA, T., and TSUJI, M., 1983, US Patent No 4405488.

[43] TANAKA, Y., TAKATSU, H., TAKEUCHI, K., and TAMURA, Y., 1988, Eur. Pat. Appl. EP 0310067.

[44] MIYAZAWA, K., and GOTO, Y., 1995, *Molec. Crystals liq. Crystals*, **260**, 277.

[45] FINKENZELLER, U., POETSCH, E., and TARUMI, K., 1992, *14th International Liquid Crystal Conference, Abstracts*, 21–26 June, Pisa, Italy, A-P94.

[46] BINDER, W., KRAUSE, J., POETSCH, E., and TARUMI, K., 1994, *15th International Liquid Crystal Conference Abstracts*, 3–8 July, Budapest, Hungary (Gordon and Breach Science Publishers), p. 124.

[47] TAKATSU, H., SASAKI, M., TONEKA, T., and SATO, H., 1985, UK Pat. App. GB 2155465.

[48] COATES, D., GREENFIELD, S., and GOULDING, M., 1990, UK Pat. Appl. GB 2240544.

[49] NISHI, T., MATSUBARA, A., OKADA, H., ONNAGAWA, H., SUGIMORI, S., and MIYASHITA, K., 1995, *Jap. J. appl. Phys.*, **34**, 236.

[50] SCHADT, M., BUCHECKER, R., and VILLIGER, A., 1990, *Liq. Crystals*, **7**, 519.

[51] GOULDING, M. J., GREENFIELD, S., COATES, D., and CLEMITSON, R., 1993, *Liq. Crystals*, **14**, 1397.

[52] COATES, D., GREENFIELD, S., GOULDING, M., BROWN, E., and NOLAN, P., 1993, *Proc. SPIE*, **1911**, 2.

[53] GRAY, G. W., 1991, *5th Liquid Crystal Seminar organized by Merck Japan, Proceedings*, 17–19 July, Tokyo/Osaka, Japan (Merck Japan Ltd), p. 6.

[54] GREENFIELD, S., COATES, D., BROWN, E., and HITTICH, R., 1993, *Liq. Crystals*, **13**, 301.

[55] REIFFENRATH, V., FINKENZELLER, U., POETSCH, E., RIEGER, B., and COATES, D., 1990, *Proc. SPIE*, **1257**, 84.

[56] WU, S.-T., and HSU, C.-S. 1993, *Proc. SPIE*, **1911**, 39.

[57] TAKATSU, H., SASAKI, M., TANAKA, T., and SATO, H., 1988, US Patent No 4726910.

[58] KOTANI, K., OTSUKA, T., FUJITA, Y., and ONISHI, H., 1993, Jpn. Kokai Tokkyo Koho JP 05-59364.

[59] BUCHECKER, R., MARCK, G., and SCHADT, M., 1995, *Molec. Crystals liq. Crystals*, **260**, 93.

[60] SEILS, F., and SCHADT, M., 1995, *Molec. Crystals liq. Crystals*, **260**, 127.

[61] DE JEU, W. H., 1992, *Phase Transitions in Liquid Crystals*, edited by S. Martellucci and A. N. Chester (Plenum Press), Chaps. 1–3.

[62] DE JEU, W. H., 1983, *Phil. Trans. R. Soc. A*, **309**, 217.

[63] PETROV, V. F., GREBYONKIN, M. F., and OSTROVSKII, B. I., 1988, *Soviet Phys. Crystallogr.*, **33**, 708.

[64] OSTROVSKII, B. I., PAVLUCHENKO, A. I., PETROV, V. F., and SAIDACHMETOV, M. A., 1989, *Liq. Crystals*, **5**, 513.

[65] GREBYONKIN, M. F., PETROV, V. F., and OSTROVSKII, B. I., 1990, *Liq. Crystals*, **7**, 367.

[66] PETROV, V. F., IVANOV, S. A., GREBYONKIN, M. F., and PAVLUCHENKO, A. I., 1990, *Rus. J. phys. Chem.*, **64**, 421.

[67] SCHAD, HP., and OSMAN, M. A., 1981, *J. chem. Phys.*, **75**, 880.

[68] PETROV, V. F., 1994, *15th International Liquid Crystal Conference, Abstracts*, 3–8 July, Budapest, Hungary (Gordon and Breach Science Publishers), p. 694.

[69] PETROV, V. F., 1995, *Proc. SPIE*, **2408**, 84.

[70] LOBKO, T. A., OSTROVSKII, B. I., PAVLUCHENKO, A. I., and SULIANOV, S. N., 1993, *Liq. Crystals*, **15**, 361.

[71] MINKIN, V. I., OSIPOV, O. A., and ZHDANOV, Y. A., 1970, *Dipole Moments in Organic Chemistry* (Plenum Press).

[72] SEILS, F., and SCHADT, M., 1992, *21 Freiburger Arbeitstagung Flussigkristalle*, Vortrag 6.

[73] BARTMANN, E., and FINKENZELLER, U., 1994, Ger. Offen. DE 43080208.

[74] SUGIMORI, S., and KOJIMA, T., 1984, US Patent No 4472293.

[75] POETSCH, E., MEYER, V., BARTMANN, E., HITTICH, R., RIEGER, B., REIFFENRATH, V., COATES, D., and GREENFIELD, S., 1991, Ger Offen. DE 4101543.

[76] HITTICH, R., KRAUSE, J., POETSCH, E., and PLACH, H., 1991, Ger. Offen. DE 4110094.

[77] PAULUTH, D., KURMEIER, H.-A., and PLACH, H., 1993, Ger. Offen. DE 42119819.

[78] POETSCH, E., HITTICH, R., BARTMANN, E., and PLACH, H., 1992, Ger. Offen. DE 4142519.

[79] COATES, D., SAGE, I. C., GREENFIELD, S., SMITH, G., and BAXTER, D., 1990, PCT WO 90/15113.

[80] COATES, D., GREENFIELD, S., SAGE, I. C., RIEGER, B., FINKENZELLER, U., KOJIMA, A., and KOBAYASHI, K., *The 4th Merck Japan Liquid Crystal Seminar, Proceedings*, 19–20 June, Tokyo-Osaka, p. 91.

[81] LIANG, J. C., and CHEN, L., 1989, *Molec. Crystals liq. Crystals*, **167**, 253.

[82] MAIER, W., and MEIER, G., 1961, *Z. Naturforsch. (a)*, **16**, 262.

[83] FRECH, C. B., FUNG, B. M., and SCHADT, M., 1989, *Proc. SPIE*, **1080**, 215.

[84] OSMAN, M. A., SCHAD, HP., 1983, *J. chem. Phys.*, **78**, 906.

[85] SCHAD, HP., and OSMAN, M. A., 1983, *J. chem. Phys.*, **79**, 5710.

[86] DE JEU, W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (Gordon and Breach).

[87] DE JEU, W. H., GERRITSMA, C. J., VAN ZANTEN, P., and GOOSENS, W. A., 1972, *Phys. Lett. A*, **39**, 355.

[88] PAVLUCHENKO, A. I., SMIRNOVA, N. I., PETROV, V. F., GREBYONKIN, M. F., and TITOV, V. V., 1991, *Molec. Crystals liq. Crystals*, **209**, 155.

[89] PETROV, V. F., PAVLUCHENKO, A. I., GREBYONKIN, M. F., and SMIRNOVA, N. I., 1991, *Rus. J. phys. Chem.*, **65**, 1188.

[90] KHOO, I. C., and WU, S.-T., 1993, *Optics and Nonlinear Optics of Liquid Crystals* (World Scientific), Chap. 1.7.

[91] SCHADT, M., and HELFRICH, W., 1970, *Appl. Phys. Lett.*, **18**, 882.

[92] JAKEMAN, E., and RAYNES, P., 1972, *Phys. Lett. A*, **39**, 69.

[93] GERBER, P., and SCHADT, M., 1980, *Z. Naturforsch (a)*, **35**, 1036.

[94] WU S.-T., HSU, C.-S., CHEN, Y.-N., and WANG, S.-R., 1992, *Appl. Phys. Lett.*, **61**, 2275.

[95] BARON, Y., LIEN, A., CANELLA, V., McGILL, J., and YANIV, Y., 1986, *Japan Display '86, Proceedings*, 30 September–2 October, Tokyo (The Society for Information Display and The Institute of Television Engineers of Japan), p. 68.

[96] GREDELLE, T. L., 1988, *SID Digest*, p. 208.

[97] RIEGER, B., BOHM, E., and WEBER, G., 1989, *18 Freiburger Arbeitstagung Flussigkristalle*, Vortrag 16.

[98] TOGASHI, S., SEKIGUCHI, K., TANABE, H., YAMAMOTO, E., SORIMACHI, K., KAJIMA, E., WATANABE, H., and SHIMUSU, H., 1984, *Eurodisplay '84, Proceedings of the Fourth SID Display Research Conference*, 18–20 September, Paris, p. 141.

[99] OKUBU, T., NAKAGIRI, T., OSADA, T., SUGATA, M., KITAHARA, N., and HATANAKA, K., 1982, *SID Digest*, 40.

[100] YAMAGISHI, F. G., MILLER, L. J., SMYTHE, D. S., and MARGERUM, J. D., 1978, *Liquid Crystals and Ordered Fluids* (Plenum Press), Vol. 3, p. 475.

[101] COATES, D., 1990, *Liquid Crystals; Applications and Uses*, Vol. 1, edited by B. Bahadur (World Scientific Press), p. 128.

[102] SASAKI, K., OKADA, M., KOHZAKI, S., FUNADA, F., RIEGER, B., NUMATA, H., HITTICH, R., PLACH, H., GEELHAAR, T., POETSCH, E., and REIFFENRATH, V., 1994, US Patent No 5330679.

[103] NOLAN, P., and COATES, D., 1993, Eur. Pat. Appl. EP 0564869.