Liquid Crystal Materials and Technologies inside Modern Displays

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Abstract

Computational calculations are now successfully introduced to design liquid crystal molecules for uses in modern active-matrix displays. These material technologies are practically applied to develop novel compounds, enabling formulation of advanced liquid crystal mixtures together with a newly developed mixture purification method. Typical examples of these liquid crystal mixtures are introduced for modern displays in various applications.

1. Introduction

Main application fields of liquid crystal displays (LCDs) are presently TV, PC Monitor, Note-Book PC, Car Navigation, PDA, Mobile Phone, Projector, etc. From a view point of the number of units, significant increases in recent years can be seen in over 15 inch panels for TV and monitor applications and 1.6 to 4 inch panels for PDA and mobile phone applications, and this trend is expected to continue in coming years.

From a technology point of view, all LCD panels for these applications, except some small-size STN panels, are active-matrix (AM) addressed. In this sense, LC materials are required not to contain a large number of mobile ions. The attributes of these ions are reflected on the voltage holding [1] and the residual DC [2] properties of LCD panels, which are also requested to be stable.

The typical electro-optical effect applied to the small-size LCDs is transflective TN mode for which the optical birefringence Δn of LC material is required to be relatively small compared to the transmissive TN mode. Moreover, especially for handy devices, the power consumption is a key issue and the LCD panel is required to be operative at a low voltage. The operation voltage is related mainly to the dielectric anisotropy $\Delta\varepsilon$ of LC materials, which is required to be large in a positive sign for uses in the TN mode.

On the other hand, the display screens of TV and PC monitor are required to be relatively large in size and to be excellent in picture quality in wide viewing cone. Film-compensated TN, IPS, VA and their modified modes are the main players in this category due to their superior image quality. The required Δn values of LC materials differ for each mode

Regarding the picture quality, the switching time of images is one of key issues of TV and multi-media use monitor screens. In this respect, low rotational viscosity γ_1 is strongly required to the LC materials.

With regard to these properties of LC materials, intensive studies have been made on design technologies of LC molecules and LC mixtures. These technologies have also been applied successfully to developing novel LC compounds and formulating advanced LC mixtures suitable for the modern LCDs. In the following sessions, the advanced LC material technologies and typical LC materials developed for uses in modern LCDs will be presented together with their features.

2. Positively large Δε compounds

According to the molecular theory of permittivity, large dielectric anisotropy in a positive sign can be achieved by a strong molecular dipole parallel to the longitudinal molecular axis. This was well confirmed by numerical calculation and measurement of Δε values for variety of LC compounds[3]. Typical examples of sub-structure at a molecular end, exhibiting a large group moment, are trifluoro-substituted benzene ring (Compounds II and III in Table I) and trifluoromethoxy group (I). Fluoro-substitution at ortho positions of a connecting benzene ring (I and III) and 2,6-dioxane sub-structure(II) are also effective to increase the molecular dipole. Carboxy group can be used effectively to connect ring structures and to increase the molecular dipole at a central part of the molecule (I).

Regarding optical birefringence Δn, the anisotropy of electronic polarization is the major player and a conjugated system is typical of highly birefringent substances. An example of this class of substances is Compounds III in Table I . By reducing the number of directly linked benzene rings, the birefringence can be lowered as can be easily seen when comparing Compounds II and III . Computational calculations by using molecular orbital (MO) methods are reported to predict the Δ value of LC substances quite well, too [3].

3. Negatively large Δε compounds

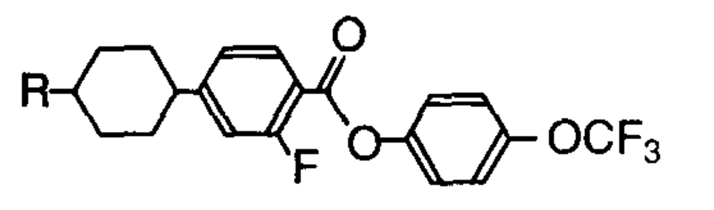
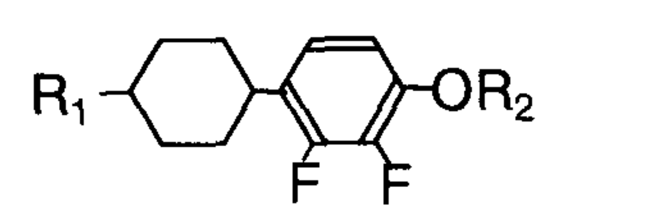
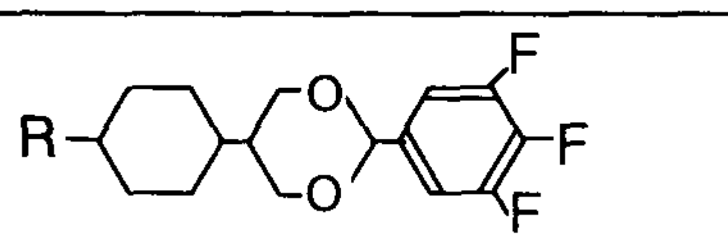
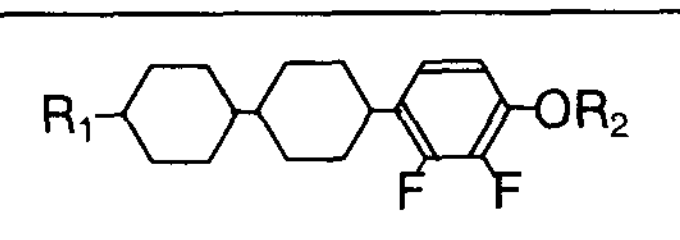
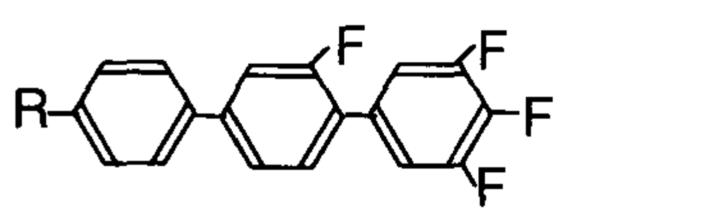
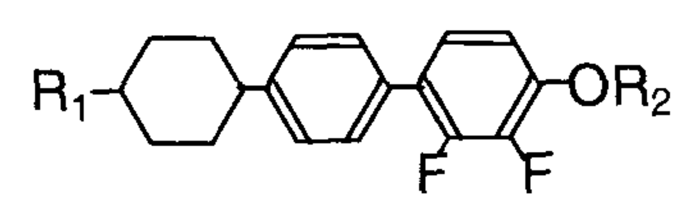
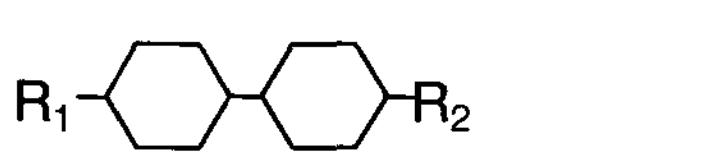
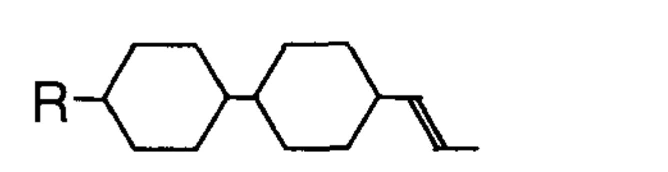
In contrast with positive-Δε substances, a strong molecular dipole perpendicular to the longitudinal molecular axis is required to achieve a large Δε value in a negative sign. This can be obtained typically by a lateral difluoro-substitution of benzene rings as shown in Compounds V ,VI, and VII of Table I . Similar to the case of positive-Δε substances, replacement of a benzene ring by a cyclohexane ring can reduce the Δn value as seen in Compounds VI and VII.

4. Low γ_1 compounds

Even though some molecular theories of rotational viscosity γ_1 [4,5] were experimentally confirmed to explain its temperature dependence quite well [6], they can not be applied effectively to design practical LC molecules to achieve a required low γ_1 value. Computational calculations of γ_1 value of practical LC substances were also reported by using a molecular dynamics method[7], and were successfully applied to explain the dependence of rotational viscosity on molecular structure for limited classes of substances[8]. These studies and accumulated data of γ_1 measurements for tremendous number of LC substances have been effectively used to design LC molecules with a lower γ_1 value. Typical examples of advanced LC substances with regard to the rotational viscosity are Compounds IV and VIII in Table I , featuring introduction of cyclohexane rings at the core part and a double bond at the terminal part of the molecule.

Back flow effects are being studied intensively to understand the contribution of viscous property of LC material to the optical response in LCD panels in a more strict sense.

Table I Examples of advanced liquid crystal compounds and their features

I		large Δε (posi.)	V		large Δε (nega.)
II		large Δε (posi.) low Δn	VI		large Δε (nega.) low Δn
III		large Δε (posi.) high Δn	VII		large Δε (nega.) high Δn
IV		low γ_1	VIII		low γ_1

5. Formulation of LC mixtures featuring less ions contained

Dielectric liquids are generally understood to dissolve ions easily and the density of free ions in a dielectric solution is considered to be reciprocally proportional to the dielectric constant of the liquid. Therefore, LC materials, especially those with a large molecular dipole featuring low operating voltage, are considered to contain mobile ions at a not-negligible density, which can affect the display performance of AM-LCDs unfavorably.

In this sense, LC substances with smaller elastic constant K value are superior to those with larger Δε value for low voltage operative AM-LCDs. Although it is still at a very primitive stage,

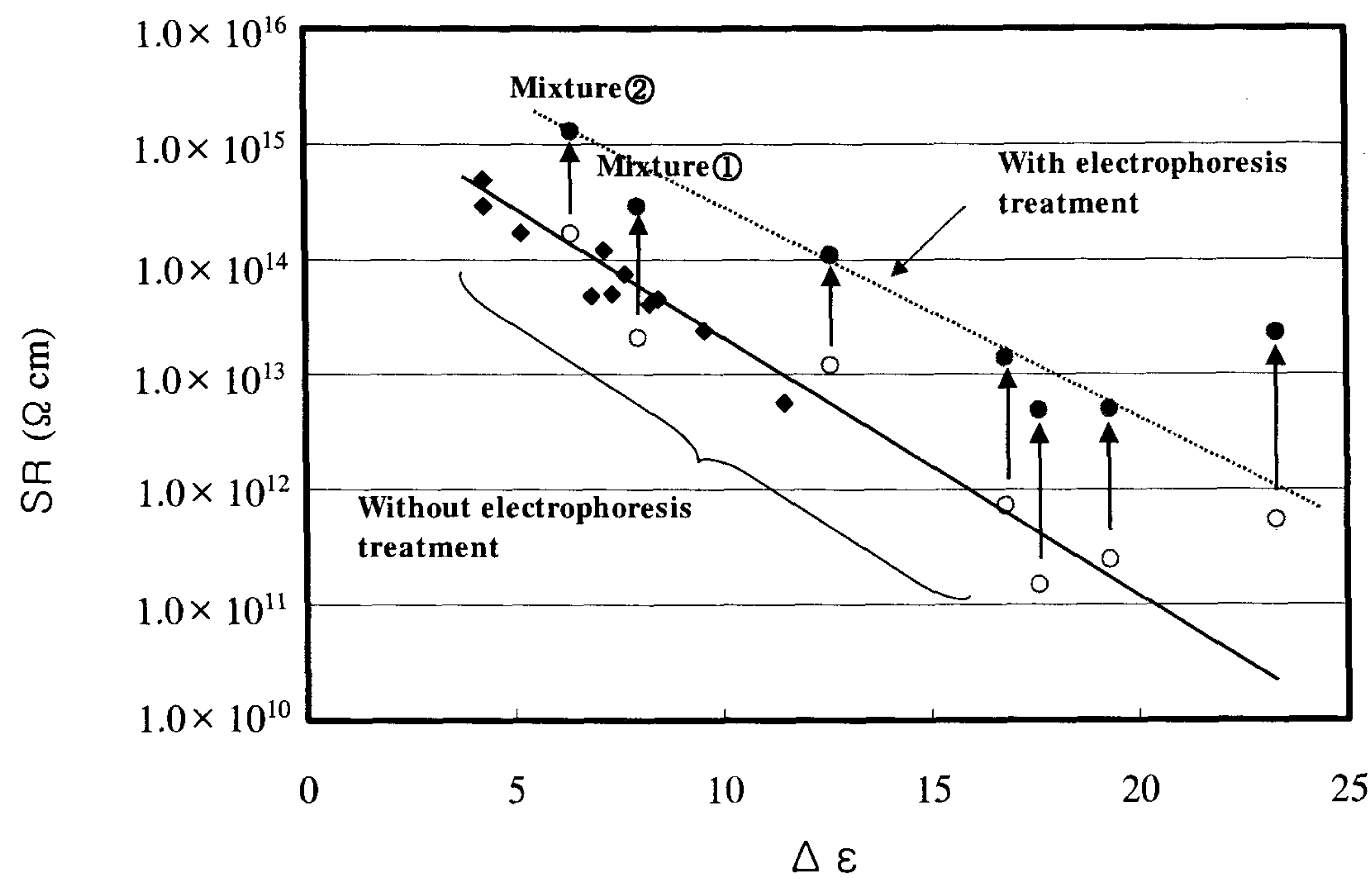


Figure 1 Improvement of specific resistivity (SR) by applying a novel purification method to liquid crystal mixtures in a wide range of dielectric anisotropy (Δε) values

calculation of the K value of practical LC materials are under study by using a molecular dynamics method [9] and informative results have been obtained [10]. It was also experimentally confirmed that direct linked aromatic rings and shorter alkyl chains at the terminal are preferable to achieve a smaller K value. Together with the molecular design concept to achieve a large $\Delta\varepsilon$ value, advanced LC substances with features of large $\Delta\varepsilon$ and small K values have been developed and applied to formulate advanced LC mixtures. The LC mixture EX 2 listed in Table II, with EX 1 as a reference, is a typical example of LC mixtures composed of this class of advanced compounds.

From a viewpoint of macroscopic material properties, the number density of mobile ions is reflected on the electric resistance in concert with their diffusion coefficient and the viscosity of the LC material. For practical purposes, the specific resistivity (SR) is usually used as a measure of the LC material with regard to its applicability to AM-LCDs. A standard value of the SR of LC materials for AM-LCD uses is in the order of 10^{13} $\Omega\cdot$ cm.

Although the SR value is an easy-to-measure and effective parameter, for more precise control of the LC material regarding its quality affecting the display performance, the attributes of contained mobile ions have to be carefully watched in addition to their number density. These are the quantity of electricity and the diffusion coefficient of ions.

Intensive studies have been made on the mobile ions contained in LC materials, providing the typical values of the diffusion coefficient in the order of 10^{-11} – 10^{-12} m^2/s and the number density in the order of 10^{20} m^{-3} at room temperature for crude materials[11,12]. Moreover, these studies provide some idea of the structure of mobile ions contained in typical LC substances.

One of the key technologies to prepare LC materials for AM-LCD uses is to reduce these ions contained. The effective way to reduce the number density of those mobile ions is to apply a newly developed purification method[13] based upon an electrophoretic phenomenon. Figure 1 shows results of SR improvement by applying this novel purification method of LC mixtures. Assuming that the SR value of 10^{13} $\Omega\cdot$ cm is the lower limit , application of this purification method enables to use LC materials with $\Delta\varepsilon$ value of around 18 in AM-LCD panels instead of those around 12, providing high image quality AM LCDs with a very low operation voltage.

Even though this purification method is effective, it cannot be applied to the LC material filled in display panels. Further dissolution of ions can occur during the display panel fabrication process and even after the LC materials are injected into display panels due to their contact with peripheral materials. It is also requested for LC materials, therefore, to be sufficiently resistant to the contamination with ionic impurities.

As ions dissolved into polar LC substance will be energetically stabilized by the interaction between an ion and the dipole of LC molecule, the ion-dipole interaction energy can be a reasonable measure of the resistance power to an increase of free ion density due to contamination of LC materials. A model of ion solvation[14] by polar LC molecules presents a microscopic view of the interaction between a polar LC molecule and an ion. According to the MO calculation based upon the modeling, there exists a local minimum, ΔH, for the interaction of an ion with a polar LC molecule, which corresponds to a solvation potential of LC materials. The calculation of ΔH value of practical LC molecules allows characterization of LC substances with regard to their resistance against contamination with ions. The LC mixture EX 2 is also composed of LC compounds with a favorable ΔH value compared to EX 1 as shown in Table Ⅱ, that contributes to the high SR value and its stability.

Table Ⅱ Concept and properties of highly stable liquid crystal mixtures EX 2

LC Mixture No.	EX1	EX2
Threshold Voltage (Volts)	1.60	1.59
Dielectric Anisotropy	+8.0	+6.4
LC Compound / Heat of Interaction (kcal / mol)		
	A / -10.1	
	B / -6.8	
	C / -6.0	C / -6.0
		G / -5.6
	D / -5.2	D / -5.2
		H / -4.1
	E / -1.4	E / -1.4
	F / -1.1	F / -1.1
Specific Resistivity (Ω·cm)	$2.9 \times 10^{+14}$	$1.3 \times 10^{+15}$

6. Advanced LC mixtures for AM-LCDs

The above mentioned technologies and newly developed compounds were successfully applied to formulate advanced LC mixtures for practical uses in AM-LCDs of various electro-optical modes, such as reflective and transflective TN, transmissive TN, IPS, and VA. TableⅢ shows typical examples of advanced LC mixtures with features of low operation voltage and fast switching These LC mixtures are also designed not to contain a large number of mobile ions and to be stable in panels in various senses, providing excellent picture qualities of modern displays.

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TableⅢ Examples of liquid crystal mixtures and their properties for modern displays

	Reflective/Transflective TN				VA		IPS		TN	
LC Mix. No.	R/T-TN 1	R/T-TN 2	R/T-TN 3	R/T-TN 4	VA 1	VA 2	IPS 1	IPS 2	TN 1	TN 2
Tclp (°C)	90	90	90	90	75	80	81	81	81	81
Δn	0.066	0.066	0.08	0.08	0.082	0.127	0.087	0.114	0.087	0.115
Δε	9.4	7.6	13.7	8.8	-3.7	-3.7	8.3	8.3	10.3	11
Vth (Volts)	1.47	1.6	1.14	1.45	2.06	2.08	1.44	1.44	1.25	1.23
γ_1 (mPa·s)	164	156	203	164	104	151	100	99	129	130

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