Development of the high speed response and high clearing temperature LC mixtures for TV Application of IPS-LCD

S.K.You and Y.B.Kim

**Liquid Crystal Research Center, Department of Chemistry,
Division of Natural Sciences, Konkuk University
1, Hwayangdong, Kwangjin-ku, Seoul 143-701, Korea.
Tel: 82-2-450-3417, E-mail: sk5007@hanmail.net**

Abstract

Three ring type LC compounds substituted with isothiocyanato group and fluoro atoms in phenyl ring were synthesized, and blended with KL-series LC mixtures for TV application of TN and IPS-mode. Clearing temperature of new LC mixtures are shown 10~35□ higher than commercial mixtures. And response time was also improved 10~20% faster than conventional LC mixtures.

1. Objectives and Background

The high information content LCD market will have the largest growth rates. New application for LCDs will be in desktop monitors, large size direct view TVs and workstations[1]. Especially in IPS-mode, stronger backlights are used in order to improve panel brightness of LCD TV, most components of the display are permanently heated by the backlight to sometimes more than 60℃. Therefore development of LC mixtures has to be focused on high clearing temperature of 90℃. It is an important to develop higher clearing points LC mixtures without sacrificing the viscosity [2]. Also they require fast response time and wide viewing angle. By using the in-plane switching (IPS) of the liquid crystals which is achieved by the in-plane electric field, the viewing angle characteristics of the electro-optical effects were conformed to be far superior to those of the conventional twisted nematic (TN) mode in which the electric field is applied along the direction perpendicular to the substrates [3]. IPS mode is attractive in the point of wide viewing angle, but switching time must be improved as fast as TN-LCD.

Up to date, in order to be high-speed response time of LCDs, the LC mixtures with a low rotational viscosity were widely used, and the high birefringence for diminishing cell gap is required [4]. They induced the lower clearing point of LC mixtures when the rotational viscosity is low. The low rotational viscosity of LC materials is used to have low elastic constant. Even though rotational viscosity and elastic constant are high, switching time can be improved. In this work,

we introduced that adequate γ_1 / K_{eff} of the new LC mixtures was improved response time. We can show several developed LC mixtures for TN and IPS-mode by utilizing newly LC substance.

2. Experimental and measurement

The chemical structures of products were confirmed by ^1H and ^{13}C NMR spectroscopy (Bruker Avance 400 Spectroscope) and EI mass spectrometer (70eV Hewlett Packard 5972 MSD). The phase transition temperature and liquid crystalline phase were observed with a polarizing microscope (Olympus BH-2) equipped with a heating stage and a controller (Mettler FP82) and Differential Scanning Calorimeter (Perkin-Elmer DSC-7). The dielectric anisotropy $\Delta\varepsilon$ and elastic constants (K_{11} and K_{33}, respectively splay and bend elastic constant) of the homogeneous aligned sample are determined by the capacitive method. The optical birefringence Δn is measured using an Abbe refractrometer at 20℃. The flow viscosity η is obtained by cannon micro viscometer.
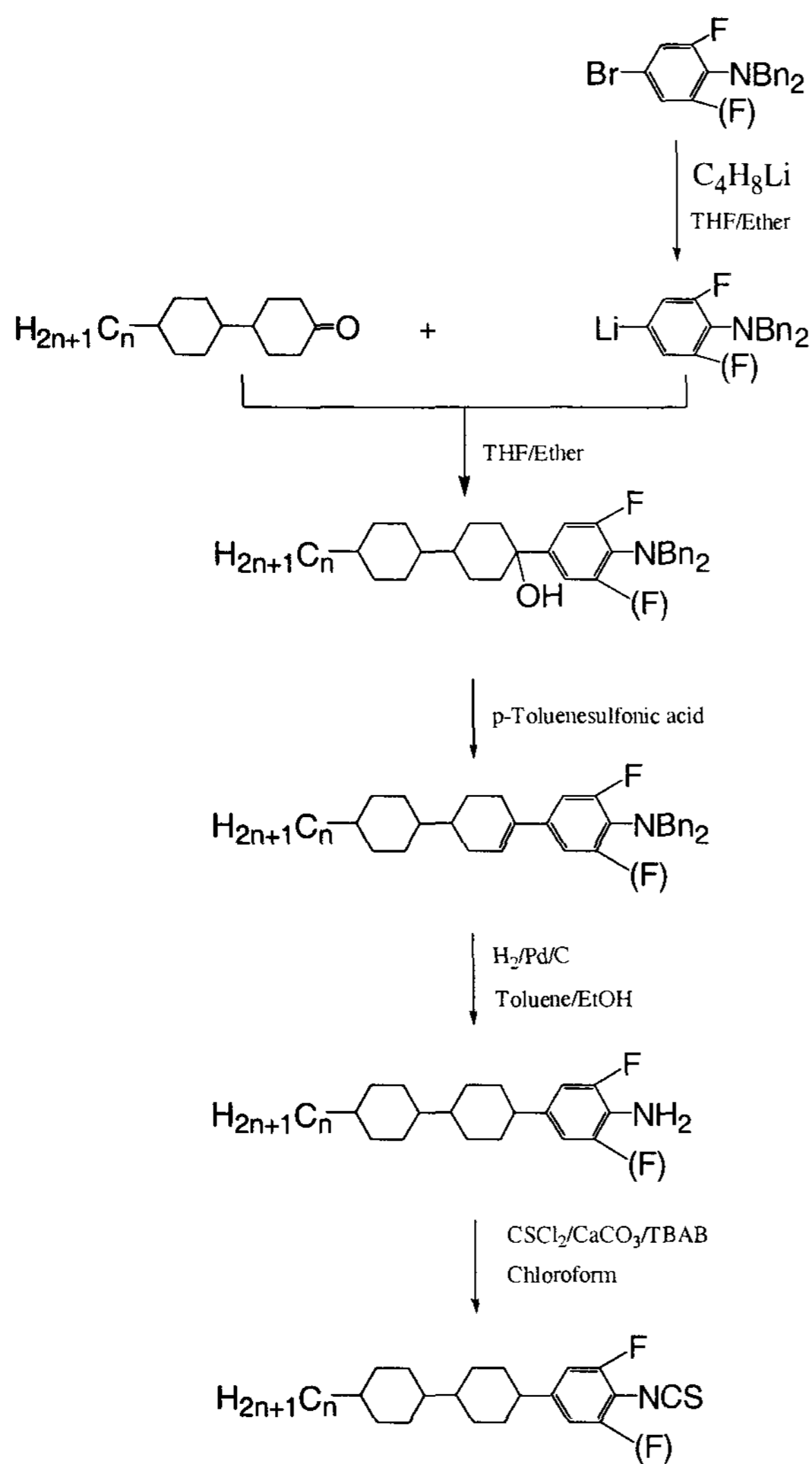
The measurements of electro-optical properties are carried out at a fixed temperature T=293K, taking into account the variation of the physical parameters of the mixture under investigation.

3. Synthesis

The typical synthetic procedure for the preparation of liquid crystalline compounds with fluoro-isothiocyanate group and 2,3,4-trifluoro group in phenyl ring is depicted in Scheme1.[5] All homologues were prepared using the same methods. All compounds were produced by carbon-carbon bond formation from the ketone or aldehyde and the organolithium reagent generated from halogen-metal exchange reaction at 4-bromo-2,(6)-(di)fluoro-N,N-dibenzylaniline or 1-bro-mo-2,3,4-trifluorobenzene These compounds were performed by a dehydration, reduction and iso-thiocyanation.

We synthesized fluoro-isothiocyanted compounds of two types and 2,3,4-trifluoro material is used (see in

Table 1) to realize low γ_1 by keeping the high Δn values.

Br—[ring]—F / —NBn₂ / (F)

↓ C₄H₈Li
THF/Ether

$H_{2n+1}C_n$—[ring]—[ring]=O + Li—[ring]—F / —NBn₂ / (F)

↓ THF/Ether

$H_{2n+1}C_n$—[ring]—[ring](OH)—[ring]—F / —NBn₂ / (F)

↓ p-Toluenesulfonic acid

$H_{2n+1}C_n$—[ring]—[ring]—[ring]—F / —NBn₂ / (F)

↓ H₂/Pd/C
Toluene/EtOH

$H_{2n+1}C_n$—[ring]—[ring]—[ring]—F / —NH₂ / (F)

↓ CSCl₂/CaCO₃/TBAB
Chloroform

$H_{2n+1}C_n$—[ring]—[ring]—[ring]—F / —NCS / (F)

Scheme 1. Synthetic scheme of isothiocyanated and trifluorinated liquid crystal compounds

Table 1.Chemical structures of new liquid crystal substances used for the experiments

Abbreviation	Structure
nCCPFS(F)	$H_{2n+1}C_n$—[ring]—[ring]—[ring]—F/—NCS/(F)
nCCetPFS(F)	$H_{2n+1}C_n$—[ring]—[ring]—CH₂CH₂—[ring]—F/—NCS/(F)
nCCPFFF	$H_{2n+1}C_n$—[ring]—[ring]—[ring]—F,F/—F

* Where n is carbon number of terminal alkyl chain

4. Results and Discussion

In previous paper, we have showed that the fluoro-isothiocyanted compounds with ethylene linkage (nCCetPFS(F)) and direct three ring system (nCCPFS(F)).(see Table 1) These LC compounds had large $\Delta\varepsilon$ value, high T_{NI} points, low viscosity (in comparison to other polar compounds) and large Δn, respectively.[6] And nCCPFFF compound is characterized very low viscosity. These nematic mixtures have excellent properties suitable for TFT-LCD application.

In generally, the conventional LC mixtures have high T_{NI} about 100 °C and switching time about 30~40 ms. As shown in table 2, T_{NI} of developed LC mixtures is 10°C ~ 20°C higher than host mixtures and rotational viscosity is increased. But response time is improved about 15% due to the increment of V_{th}.

In the TN and IPS modes, switching time is expressed by [7]

$$\tau_{on} \propto \frac{\gamma_1 d^2}{\varepsilon_0 \Delta\varepsilon (V^2 - V^2_{th})} = \frac{\gamma_1 d^2}{\pi^2 K_{eff}(V^2/V_{th}^2 - 1)}$$

$$\tau_{off} \propto \frac{\gamma_1 d^2}{\varepsilon_0 \Delta\varepsilon V^2_{th}} = \frac{\gamma_1 d^2}{\pi^2 K_{eff}}$$

τ_{on} is switching-on time and τ_{off} is switching-off time, d presents cell gap, γ_1 is rotational viscosity , V is operating voltage, and K_{eff} is effective elastic constant. V_{th} is expressed by below, where ε_0 represents the dielectric constant in a vacuum.

$$V_{th} = \pi\sqrt{\frac{K_{eff}}{\varepsilon_o \Delta\varepsilon}} \quad \text{(TN, VA, OCB-mode)}$$

$$V_{th} = \left[\frac{\pi \cdot l}{d}\right]\sqrt{\frac{K_{eff}}{\varepsilon_0 \Delta\varepsilon}} \quad \text{(IPS-mode)}$$

l is the distance of each electrode in IPS cell, K_{11}, K_{22}, K_{33} represent elastic constant of splay, twist and bend, respectively. K_{eff} is $K_{11}+(K_{33}-2K_{22})/4$ in TN-mode, K_{22} in IPS mode, and K_{33} in VA, OCB-mode. As the equations can be seen, the switching time has an influence on the rotational viscosity γ_1, driving voltage V, elastic constant K, the value of $\Delta\varepsilon$, V_{th} and so on. The increment of rotational viscosity cause that switching time is slow. Especially, K_{eff} is important factor for threshold voltage, V_{th}. As $\Delta\varepsilon$ value is larger, V_{th} is smaller. If V_{th} is increased, switching-on time is slower and switching-off time is faster. Thus it can be considered that the improvement of response time is induced by increment of elastic constants, K_{eff} and V_{th}.

Table 2. Physical properties of blended LC mixtures

Cell gap	Sample number	Ref. host	T_{NI} ℃	Response time (ms)			V_{th} (TN) V_{max}(IPS)	$\Delta\varepsilon$	Δn	η mm^2s^{-1}	γ
				τ_{on}	τ_{off}	τ_{all}					
TN 4.8 μm	Host 1		84.3	2.3	16.4	18.7	1.24	7.45	0.0803	16.4	101.0
	KL003	Host 1	106.4	3.3	13.9	17.2	1.78	6.36	0.0935	17.6	129.6
	KL004	Host 1	110.8	3.8	13.6	17.4	1.76	6.54	0.0931	20.4	139.5
	KL005	Host 1	103.0	2.8	13.5	16.3	1.59	7.62	0.0932	18.7	156.4
	KL006	Host 1	100.2	2.6	13.3	15.9	1.56	7.18	0.0922	16.8	123.5
	KL007	Host 1	93.7	2.6	13.2	15.8	1.58	7.25	0.0926	16.3	114
	KL008	Host 1	95.0	2.8	13.1	15.9	1.63	6.95	0.0940	14.9	129.3
TN 3.75 μm	Host 2		75.0	1.4	11.4	12.8	1.32	6.10	0.0920	15.2	76
	KL001	Host 2	99.7	1.9	10.3	12.2	1.50	7.39	0.1052	17.2	142
	KL002	Host 2	97.0	1.8	9.6	11.4	1.55	7.04	0.1072	17.6	118
IPS 3.0 μm	Host 3		75.0	7.0	9.0	16.0	9.0	6.23	0.0776	14.5	74.0
	Host 4		84.2	8.2	14.2	22.4	9.0	6.49	0.0800	16.4	94.0
	KLI0001	Host 3	96.0	5.8	10.3	16.4	9.0	8.15	0.0945	17.1	132.1
	KLI0002	Host 4	105.4	5.9	11.3	17.2	9.0	7.31	0.0982	18.6	127.2
	KLI0007	Host 3	104.2	5.6	13.1	18.7	9.0	7.66	0.1008	17.8	117.1
	KLI0008	Host 3	101.7	7.0	12.1	19.1	9.0	7.52	0.1007	18.2	110.9
	KLI0009	Host 3	89.9	8.0	11.9	19.9	9.0	6.97	0.1018	17.1	111.5

As shown in table 2, the rotational viscosity of the new LC mixtures was higher than host1. but fall time was 2~3 ms faster in TN mode 4.8μm cell (Fig.1). Also although $\Delta\varepsilon$ is not increased, switching-on time was slower than host1 (Fig.2) and V_{th} was slightly increased. In 3.75μm cell, though $\Delta\varepsilon$ and rotational viscosity γ_1 were larger than host2, switching-on time was slower and switching–off time was faster due to increased V_{th}. These mean that effective elastic constant, K_{eff} induced the increment of V_{th} thus K_{eff} may be larger than conventional host mixtures. Even though rotational viscosity was larger, K_{eff} was much larger, viscoelastic (γ_1 / K_{eff}) ratio was totally decreased and total response time was improved about 15%.

In IPS mode, the response time of KLI001 is alike host3 but switching time of KLI002 is improved much more than host4. Furthermore, T_{NI} is 10~30℃ higher than reference host and rotational viscosity is also larger. In case of KLI007, KLI008, KLI009, $\Delta\varepsilon$ was much larger but switching time is alike or slower than the reference mixtures. To improve the switching time, lower viscoelastic efficient (γ_1 / K_{eff}) is requested.

Thus it can be considered that rotational viscosity is 40~60 higher than host mixtures but the increment of K_{eff} (K_{22}) is not as large as the increment of rotational viscosity in IPS-mode.
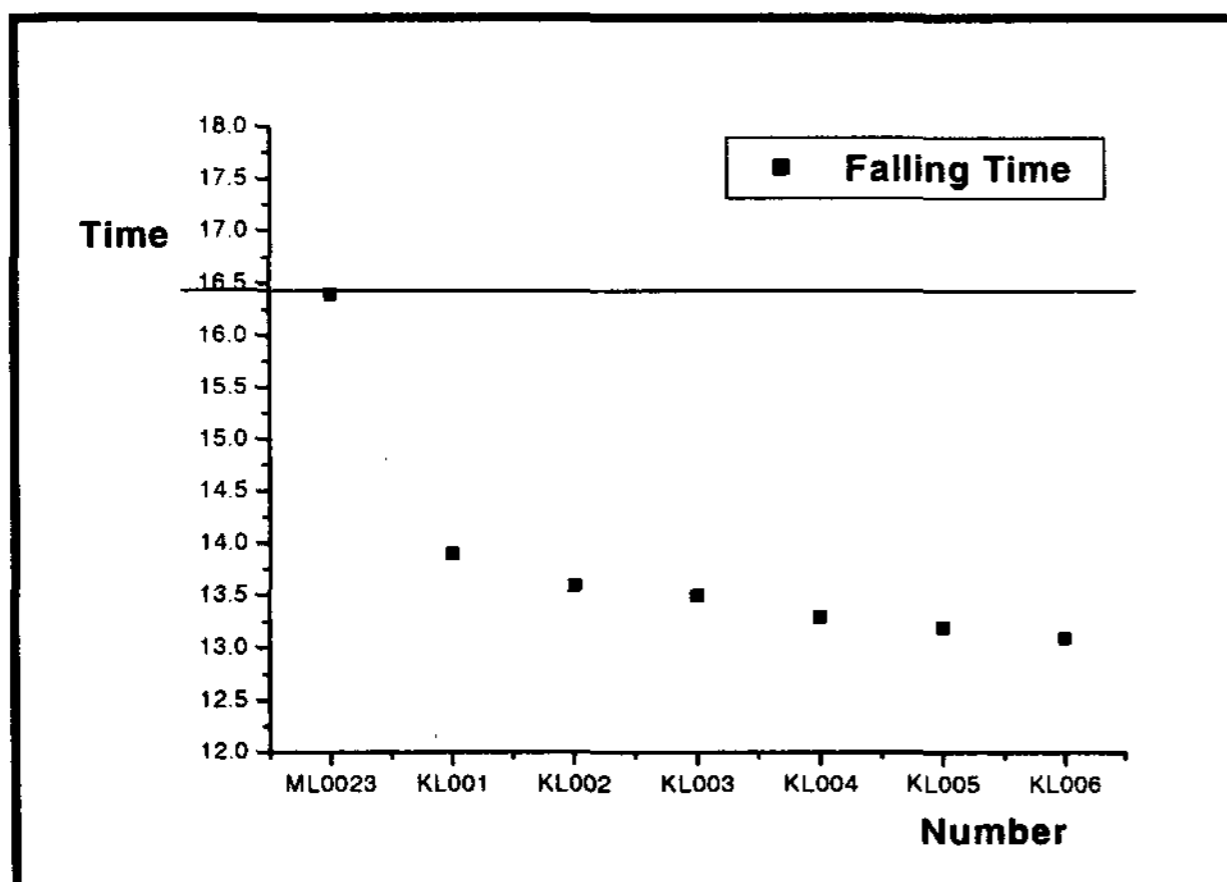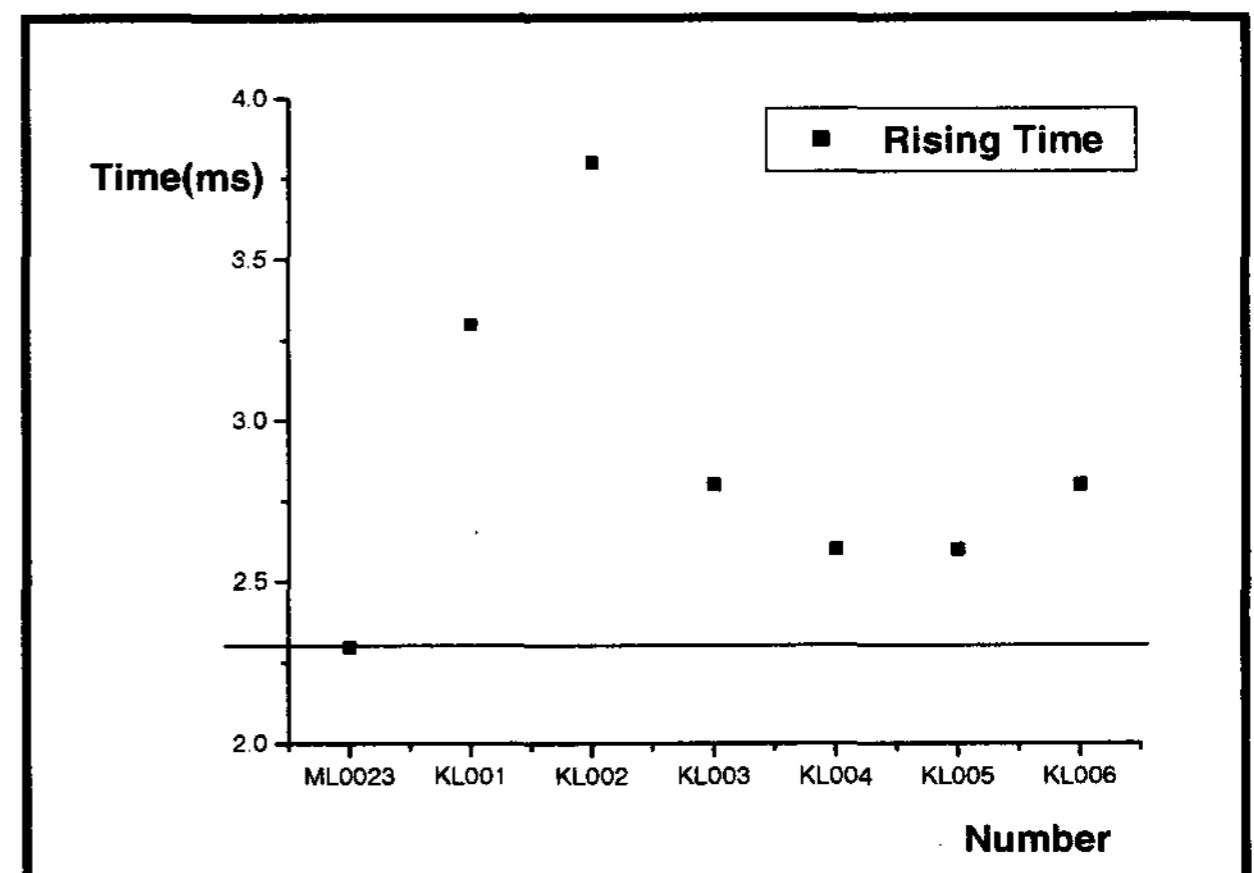

Fig. 1 Falling time of LC mixtures

Fig. 2 Rising time of LC mixtures

5. Conclusion

These mixtures induced a large dielectric anisotropy, birefringence, quick response time and available threshold voltage. These properties were excellent at a mixture including isothiocyanato and difluoro substituted phenylbicyclohexanes among the investigated mixtures.

The development of the IPS-TFT LCDs with its superior picture quality triggered a strong demand for the mode of wide viewing angle and fast response time. In case, materials still require optimization with regard to electro-optic, visco-elastic ratio and mesogenic properties.

6. Acknowledgements

References

[1]   T. Ishinabe, T. Uchida, M. Suzuki, and K. saito, Euro Display '96, p. 119 (1996).

[2]   Y. B. Kim and I. K. Huh, Proceeding of SPIE, 4658, p.67-78 (2002)

[3]   Masahito Oh-E and Kasumi Kondo, Liquid crystals, 4, p.379~390(1997)

[4]   I. K. Huh and Y. B. Kim, Imid 01 digest, (2001),

[5]   I. K. Huh, and Y. B. Kim, Jpn. J. Appl. Physics, 42, p.570-571(2003)

[6]   Y. B. Kim, B. H. Kim. Society of International Display Digest'00 Digest, 2000, 12

[7]   A. Raviol, W. Stille, G. Strobl, J. Chem. Phys., 103, p. 3788 (1995)

[8]   S. Naakajima, Y. Sugiyama, H. Ichinose, H. Numata and S. Naemura, SID '00 Digest, p.242 (2000).

[9]   K.Tarumi, U. Finkenzeller, and B. Schuler, Jpn. J. Appl. Physics, 31, p.2829(1996)

[10] U. Finkenzeller, Kontakte, (2), p.7-14 (Darmstadt, 1988)

[11] D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vill, Handbook of Liquid crystals, 2A, Wiley-VCH Press, weinheim p.199-229(1998).

[12] J. L. Ericksen, Trans.Soc Rheol, 5, p.23(1961)