The Novel Liquid Crystal Materials for AM-LCDs

T. Yamaguchi, S. Kibe, S. Matsui, H. Yamamoto
Specialty Chemicals Research Center, Chisso Petrochemical Corporation
5-1 Goikaigan, Ichihara, Chiba 290-8551, JAPAN,
Phone: +81-436-23-5615, E-mail: t.yamagu@chisso.co.jp

Abstract

We have developed the novel liquid crystal materials with a difluoromethyleneoxy (CF2O) moiety as a linkage group in order to satisfy the diversified various requirements for AM-LCDs. These novel CF2O LC materials have excellent physical properties that are high dielectric anisotropy, low viscosity and wide nematic temperature ranges. Physical properties measurement results that mixtures containing CF2O LC materials have suitable for characteristics for AM-LCDs. The CF2O LC materials are excellent compound for quick response and low driving voltage application.

1. Introduction

In spite of experiencing 2 times the bottom of the crystal cycles in past, LCD business has extremely expanded. Needless to say that such expansion has been supported by the progress of LCD performance. Before the establishment of "LCD business" meant mainly Notebook PC application, the progress of LCD performance made LCD business expanded for various LCD applications, PC Monitor, LCD-TV, and Mobile communication tools.

Although these requirements for LCD performance depend on each LCD application, it has been improved gradually for suitable each LCD performance. In particular in the field of Monitor application, characteristics of viewing angle and response that had been disadvantage of TN-LCD were dramatically improved by appearance of a compensation film[1], low viscosity LC materials[2] and technical approach from LC cell configuration. In addition, by appearance of these several modes, IPS mode[3], VA mode[4], OCB mode[5] and ASV mode[6], in present situation, it's not a dream that LCD would replace CRT application. In fact, market of LCD-TV has gradually been expanding. Further, regarding to Mobile tool application, it's required lower power consumption and high image quality. To satisfy these requirements, reflective and transflective mode[7], high transmittance color filter[8], and also optimized cell configuration were applied. Quick response is also required for a next generation cellular phone with TV and movie image function. In the field of LCD for the Notebook PC that has been more important field since before, the trying to reduce lower driving voltage has been done to achieve low power consumption, low cost, and thin module assembly. Furthermore, also LCD manufacturing process has gradually progressed to response to scale large production line and One Drop Filling (O.D.F) process[9].

As mentioned above, LCD has extremely evolved from both LCD performance and LCD manufacturing. Along with these progresses, the requirements for LC material become various and shall be specialized for each application. Under suck a circumstance, we designed the novel LC material's having a difluoromethyleneoxy (CF2O) moiety as a novel linkage group and succeeded in the development of LC material that is able to adapt to these various demands. This paper presents physical properties of these LC materials and the effect for each application.

2. Requirement to Liquid Crystal Material

Physical properties required for LC materials depend on driving mode of LCDs. Furthermore, even by the same driving modes, it depends on various factor such as, cell gap, peripheral materials (PI etc) and operation voltage. To satisfy these various requirements for physical properties of LC material, LC mixture usually consist of 10-20 kinds of LC materials. In particular, for AM-LCDs, fluorinated LC materials are mainly applied because they have high chemical stability toward heat, light and pollution from peripheral materials. Thus many fluorinated LC materials have been developed[10]. At present of AM-LCDs, low driving voltage and quick response are required to achieve low cost and, low power consumption, and high image quality of moving picture. Namely high dielectric anisotropy and high reliability for Notebook PC, low viscosity for PC Monitor and LCD-TV are focused. And at recent a few years, cell gap is gradually getting thinner to 3.5-4.0 μm for quick response. Thus comparatively high optical anisotropy LC materials are required in proportion to the change of cell gap[11]. On the other hand, LC materials with low birefringence and wide nematic range are required for reflective / transflecitive LCD owing to cell configuration. Further, high dielectric anisotropy, high birefringence and low viscosity are suitable for OCB mode. As above mentioned, requirements for

LC materials are quite various and specialized.

3. Physical Properties of Novel Liquid Crystal Materials

Table 1 shows physical properties of novel LC materials with a difuluoromethyleneoxy (CF2O) moiety as a linkage group to satisfy above various and specialized requirements. The characteristics of these novel LC materials are high dielectric anisotropy, low viscosity, and wide nematic temperature range compared with corresponded LC materials without the CF2O moiety. In particular, these CF2O LC materials have an excellent balance between dielectric anisotropy and viscosity. Generally the viscosity of LC materials increases along with dielectric anisotropy, however these CF2O LC materials can restrain increase of viscosity even at the case to get higher dielectric anisotropy. These data are obtained from nematic mixtures containing 20% of fluorinated materials listed in table 1 and 80% of a base mixture FB-01 (Fluorinated LC mixture Tni 112.8℃, $\Delta\varepsilon_{(25℃)}$ 4.8, $\Delta n_{(25℃)}$ 0.079, $\eta_{(20℃)}$ 25.6 mPa·s , $\gamma_{1(25℃)}$ [12] 174.4mPa·s).

Table 1 Structures of LC compounds

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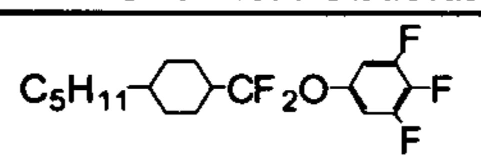
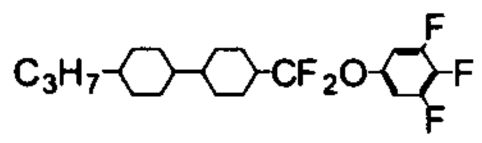
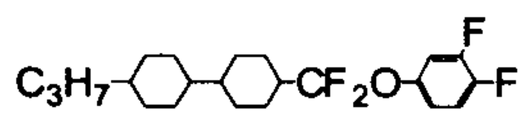
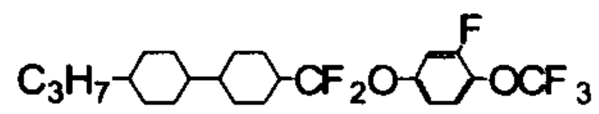
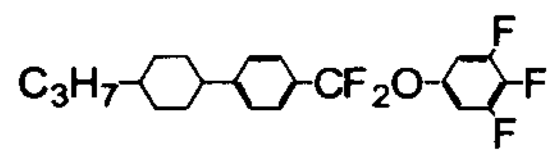
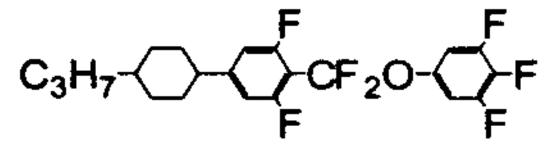
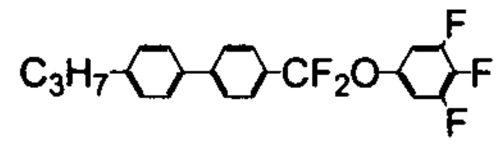
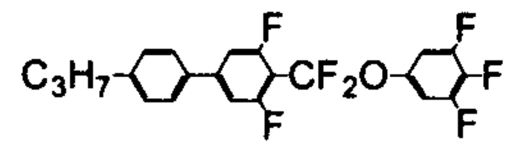
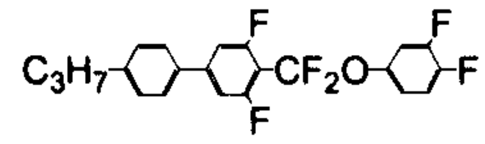
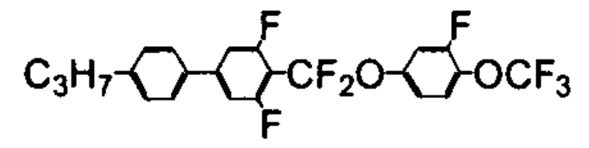
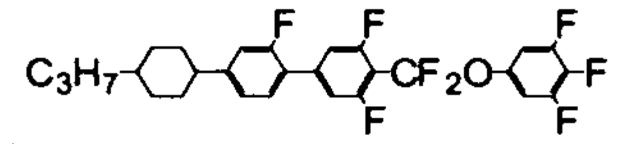
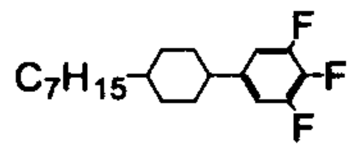
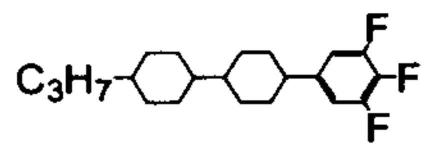
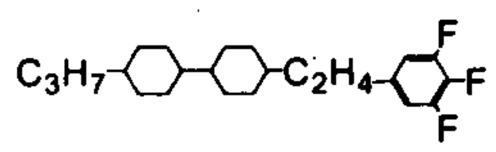
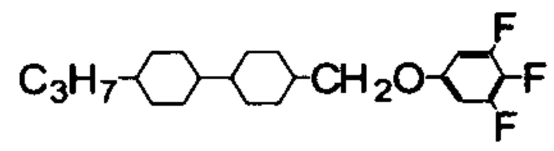
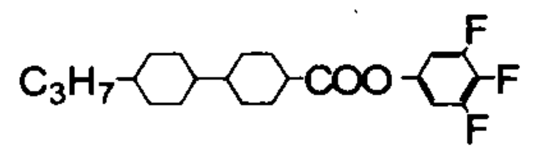
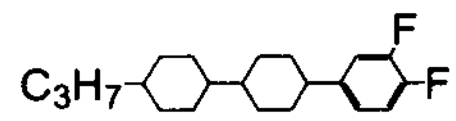
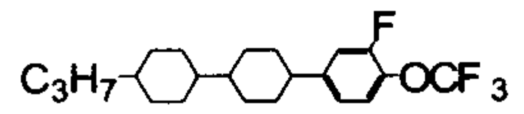
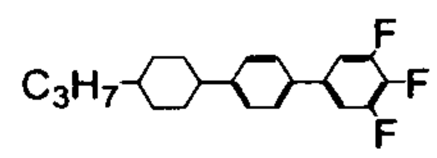
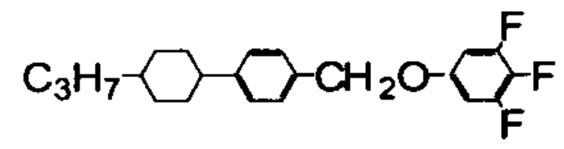
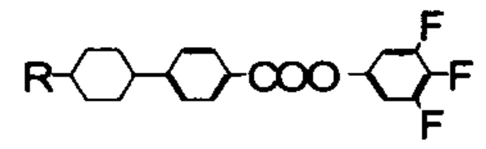
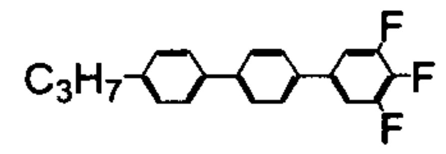
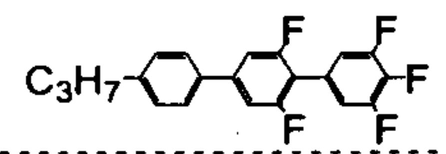
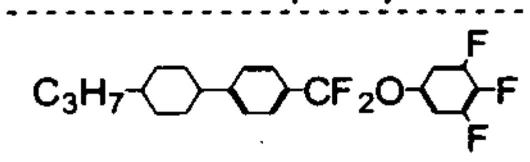
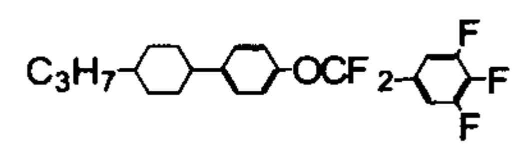
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	
13	
14	
15	
16	
17	
18	
19	
20	
21(R=2,3,5 ; 6:8:6)	
22	
23	
24	
25	

3.1 Mesophase

In the case of phenylcyclohexylcyclohexane structure, the introduction of CF2O moiety as a linkage group decreased the melting point by 21.8℃ and increased the clearing point by 11.8℃ in comparison with compound **2** and **13**. On the other hand, at the case of biphenylcyclohexane and terphenyl structure, melting point became a bit higher in comparison of compound **5, 7, 19** and **22**. However the introduction with lateral fluorine atom to their phenyl moiety made melting point lower as like compound **6** and **8**.

Table 2 Physical properties of LC compounds

No.	Mesophase	$\Delta\varepsilon$	Δn	γ_1 [12]
1	C-0.6I1	7.8	0.035	-
2	C42.9N105.5I	9.8	0.070	184.8
3	C35.6N129.0I	6.3	0.070	212.3
4	C32.0N136.5I	8.3	0.080	242.8

5	C67.3I	13.8	0.080	71.3
6	C39.9I	15.5	0.074	87.2
7	C79.1I	16.0	0.147	54.2
8	C47.0I	22.3	0.125	63.3
9	C40.9I	16.8	0.135	77.8
10	C38.7I	19.3	0.135	108.8
11	C83.1N129.5I	25.3	0.129	446.0
12	C25.6I	6.2	0.034	-
13	C64.7N93.7I	8.3	0.073	174.3
14	C41.8N98.3I	7.3	0.074	225.1
15	C83.7(N78.7)I	6.3	0.079	327.8
16	C56.8N117.5I	11.2	0.074	237.9
17	C44.2N1118.0I	5.3	0.084	214.9
18	C35.7N128.8I	6.8	0.080	248.8
19	C40.7(N33.2)I	11.3	0.135	143.3
20	C40.1I	7.3	0.094	211.1
21	-	23.2	0.119	314.9
22	C70.0S119.1I	12.0	0.227	193.5
23	C108.3I	22.0	0.161	275.5
24*	C70.5I	15.0*	0.077*	-
25*	C58.1I	6.3*	0.082*	-

<Δε ,Δn at 25℃, γ_1[12] at 20℃>

* Data are extrapolated from ZLI-1132 (Cyano LC mixture Tni 72.4℃ $\Delta\varepsilon_{25℃}$ 11.0 $\Delta n_{25℃}$ 0.119 $\eta_{20℃}$ 27.0mPa·s)

3.2 Dielectric Anisotropy (Δε) and Elastic Constant (K_{11},K_{22},K_{33}, K)

In TN mode, Vth is expressed by the next equation[13].

$$V_{th}=\pi (K/\varepsilon_0 \Delta\varepsilon)^{1/2} \quad (1)$$

$$K=K_{11}+(K_{33}-2K_{22})/4 \quad (2)$$

Wherein ε_0 represents the dielectric constant in a vacuum and K_{11}, K_{22} and K_{33} represent elastic constants of splay, twist and bend respectively.

The introduction of CF2O moiety induced an increase of dielectric anisotropy by around 20% in comparison with compound **2, 5, 7, 13, 19** and **22** in table 1. Furthermore by the introduction of lateral fluorine atom induced a great increase of dielectric anisotropy in compound **5, 6, 7** and **8**. These phenomena are easily understood by increase of dipole moment. We have already reported an effect of a linkage group and the number of fluorine atom[10], since the dipole moment of CF2O moiety combines with the group of dipole moment of the fluorinated obtained moiety, thus large dipole moment was produced. Ester compounds show a bit higher dielectric anisotropy in comparison with compound **2** and **16**. Also these data were supported by the calculation of dipole moment[14].

Table 3 Calculation result of dipole moment by MOPAC Ver.6 AM-1[14]

No.	μ (Debye)	β (Deg.)
With CF_2O moiety		
2	4.9003	9.6
6	7.1665	4.9
8	7.6633	4.0
Without CF_2O moiety		
No.	μ (Debye)	β (Deg.)
13	3.7818	7.3
16	5.169	14.9
19	4.1592	3.3
21(R=3)	6.1219	11.0

When the direction of the CF2O moiety is reversed, the dielectric anisotropy is decreased like as compounds **24** and **25**. Figure **1** shows the temperature dependency of Δε in base mixtures (20%) fluorinated comprised compounds. From table 1 and figure **1**, compound **8, 9** and **10** were very effective to reduce Vth on Δε parameter.

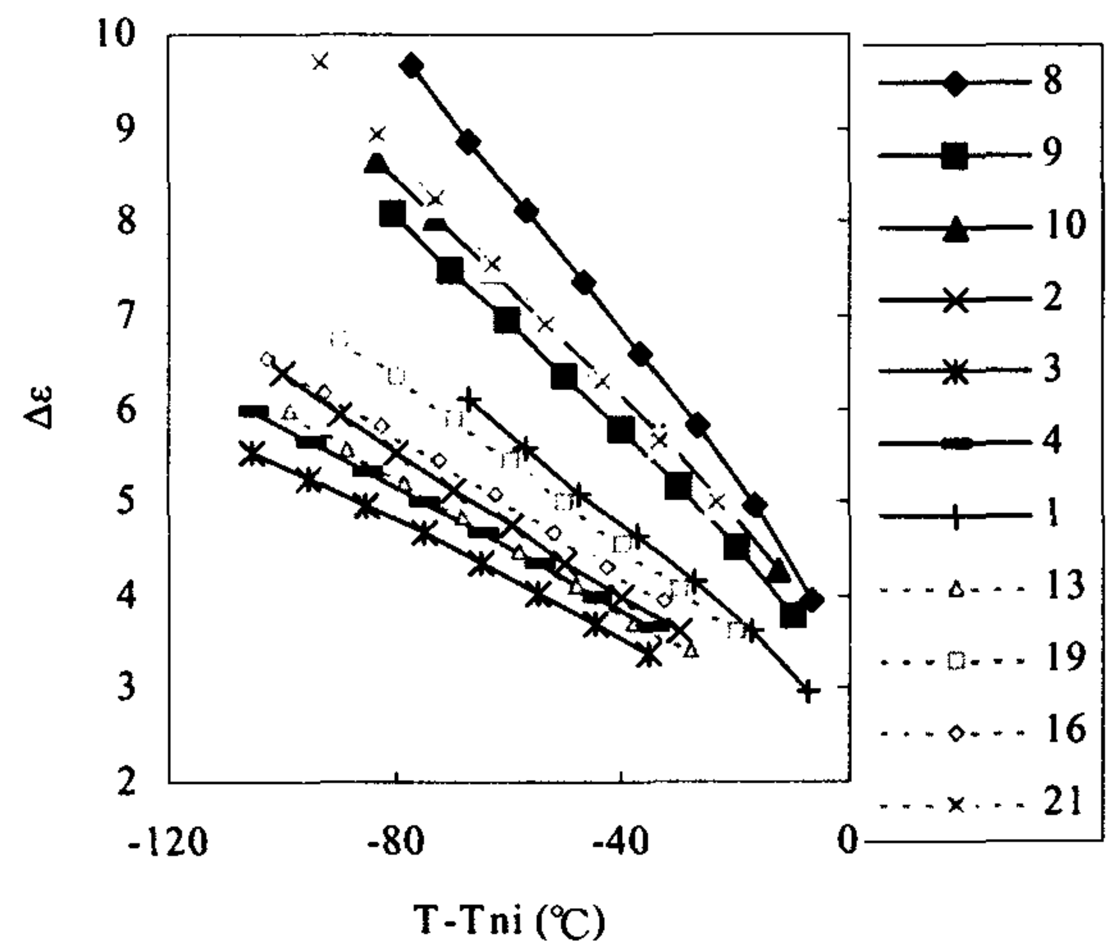


Figure 1 Temperature dependence of Δε in FB-01(20%)

Elastic constant is also important for operation voltage of AM-LCDs. Figure 2 shows the temperature dependence of elastic constant (K; $K_{11}+(K_{33}-2K_{22})/4$). The remarkable difference was not observed in the case of phenylcyclohexylcyclohexane containing structure. But precisely, compound **2** that contains the CF2O moiety was lower than **13** in K. Namely CF2O moiety showed the effect to reduce K value as same as compound **16** with ester moiety, are expected effective for reducing Vth.

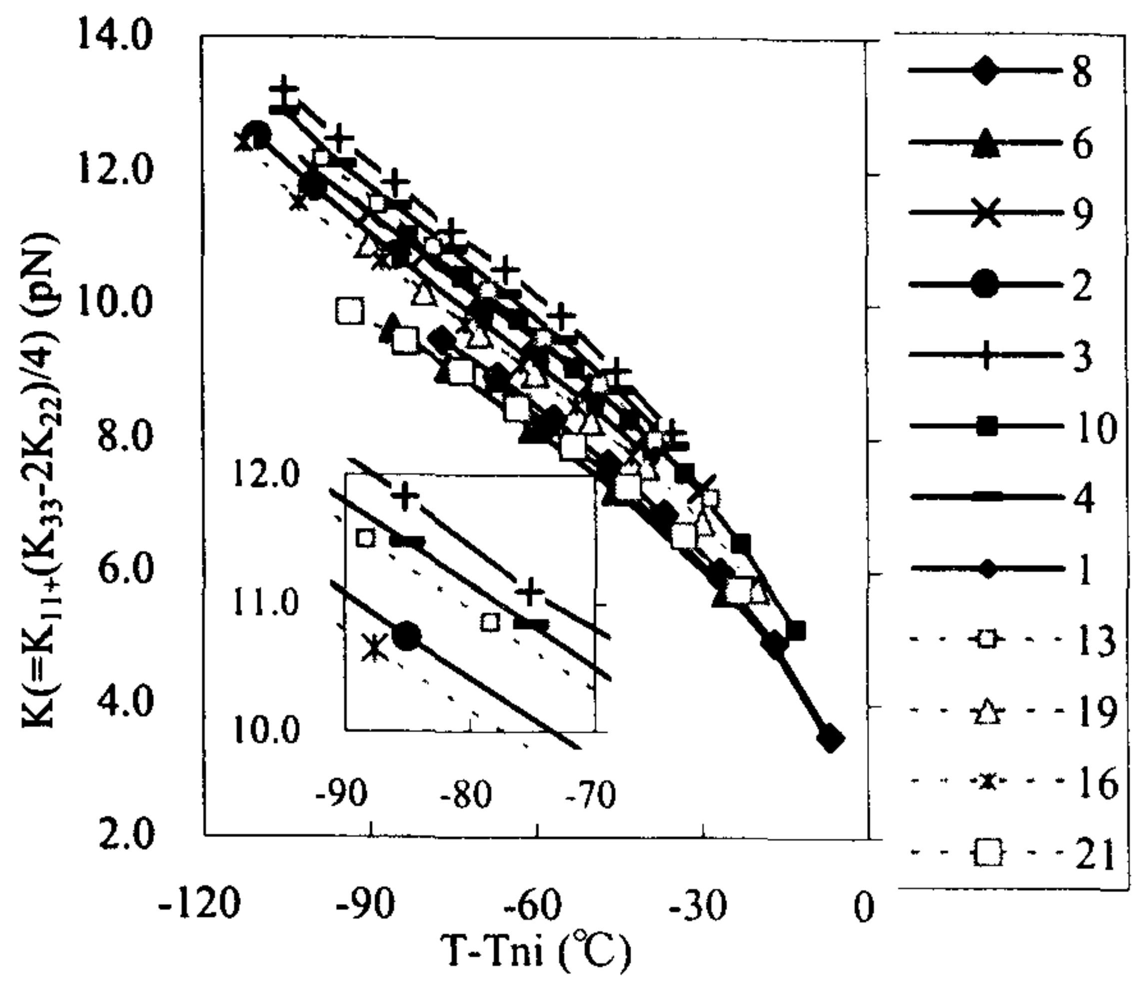


Figure 2 Temperature dependence of elastic constant (K)

3.2 Optical Anisotropy (Δn)

For AM-LCD applications, to optimize various optical cell configurations, LC materials independently have diverse value of optical anisotropy should be prepared. As listed in table 1, these CF2O LC materials have optical anisotropy from around 0.03 to 0.14. Precisely optical anisotropy was slightly diminished by the introduction of CF2O moiety at figure 3.

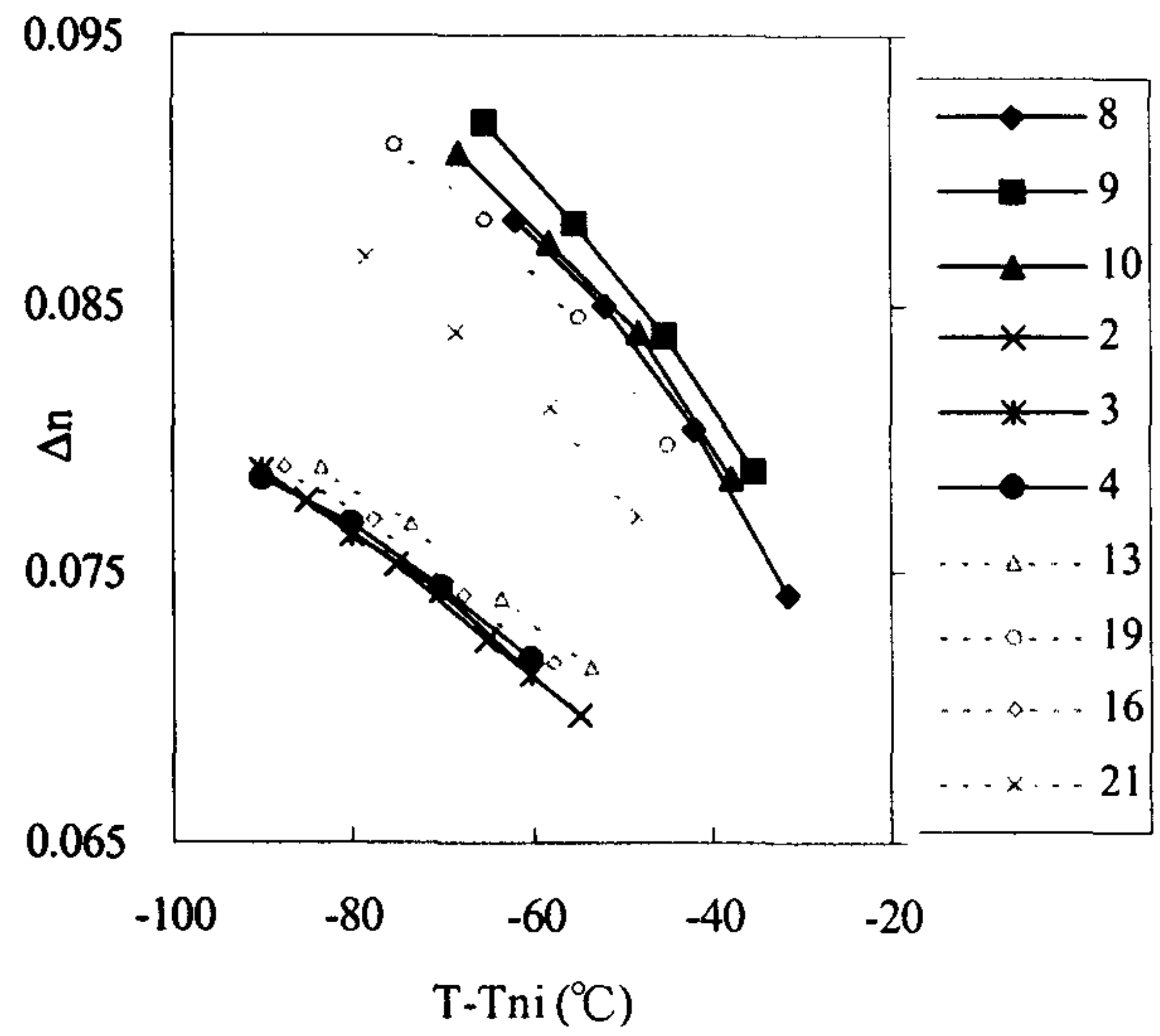


Figure 3 Temperature dependence of Δn in FB-01 (20%)

The order was non-linkage (compound **13**), then ester (compound **16**), and finally CF2O LC materials (compound **2**). This means that by the introduction of CF2O moiety, order parameters and polarizability anisotropy (Δα) would become lower, as expected by the next equation[15].

$$n_{\parallel}^2 - n_{\perp}^2 = \Delta\varepsilon \propto \Delta\alpha \cdot S \quad (3)$$

3.3 Rotational Viscosity (γ_1)

It's well known that rotational viscosity is strongly related to response time for all LCD modes[16]. It' s quite important to reduce rotational viscosity for quick response.

In phenylcyclohexylcyclohexane structure at Figure 4, the introduction of CF2O moiety enables to restrain an increase of rotational viscosity compared with the introduction of other linkage groups as compound **2, 14, 15** and **16**. Figure 5 shows the relationship between dielectric anisotropy and rotational viscosity. Generally rotational viscosity of conventional LC materials tends to increase in proportion to dielectric anisotropy without exception. But these compound **5, 6, 7, 8, 9** and **10** have lower rotational viscosity even with high dielectric anisotropy. This means that the CF2O moiety is an excellent linkage group to contribute low rational viscosity. The reason was not cleared in this time, however we are considering a molecular interaction of mesogenic core structure, an energy balance of electrical and steric factor.

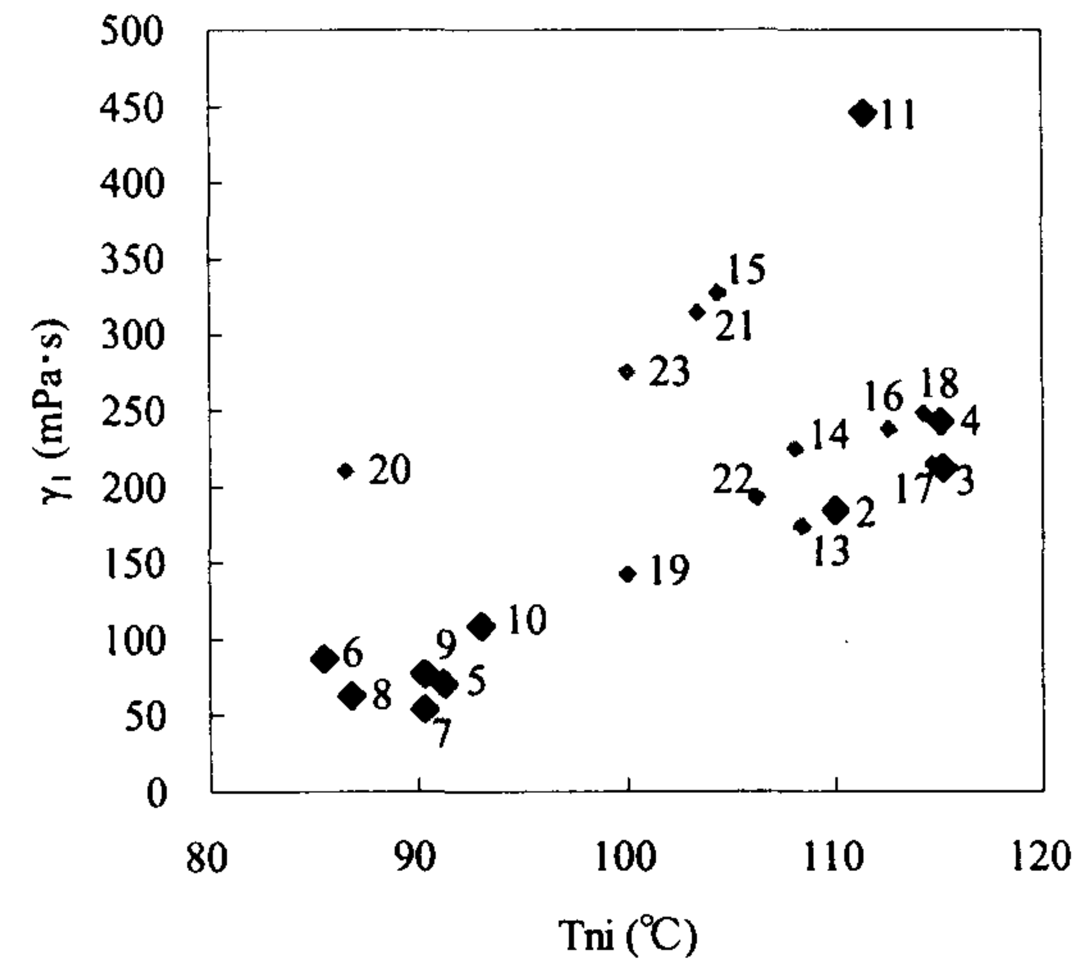


Figure 4 Relationship between Tni in FB-01(20%) and γ_1 extrapolated from FB-01

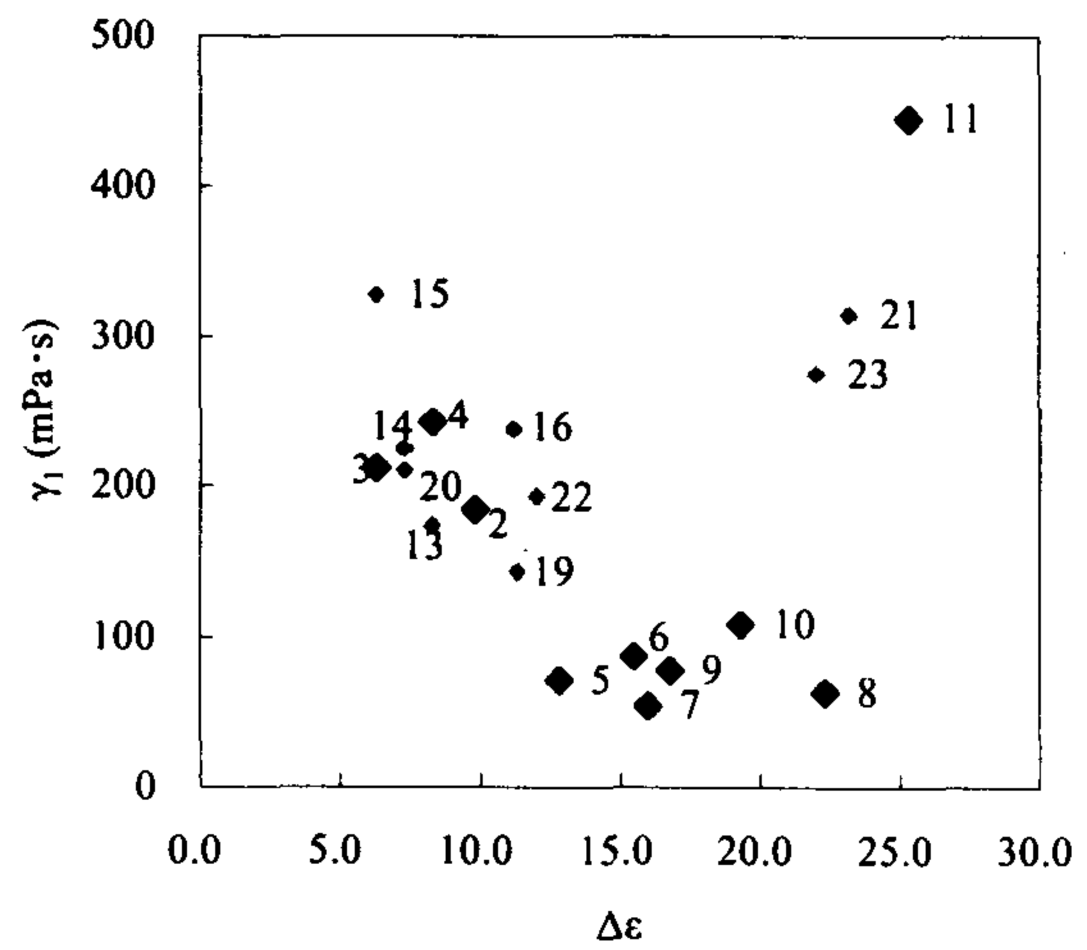


Figure 5 Relationship between Δ ε and γ1 extrapolated from FB-01

3.4 Voltage Holding Ratio (VHR)

Voltage holding ratio (VHR) is one of the important parameter for the reliability of AM-LCDs. Figure 6 shows VHR of these CF2O LC materials. The introduction of CF2O moiety hardly gave any poor influence as observed. Thus, any kind of CF2O LC materials will be accepted for AM-LCDs, considering the comparison of conventional LC materials.

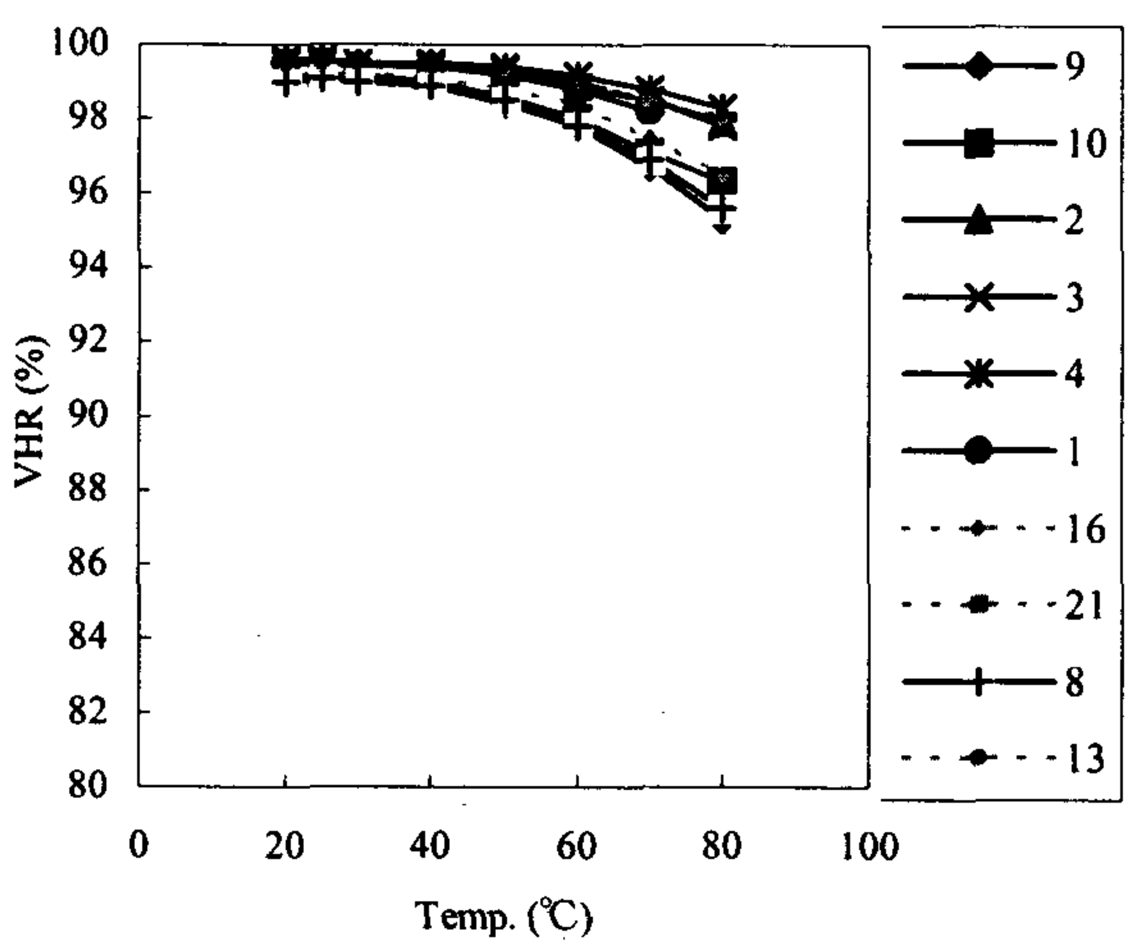


Figure 6 Temperature dependence of VHR in FB-01 (20%)

4. Application to Liquid Crystal Mixture

For many kind of applications, the display properties like viewing angle, response time and power consumption have to be evolved continuously. In order to achieve these aims, properties of LC mixture have to be optimized for various LCD technologies. Following sections show our examined result by applying these CF2O LC materials for several LCD modes and applications.

4.1 Low Voltage drive application

Low cost and long operation life are required for Notebook PC. Low voltage driving (3.3V, 2.5V) of LCD is one of the solutions to meet these requirements. High dielectric LC mixtures are effect to reduce operation voltage from equation 1, thus compound **5, 6, 7, 8, 9** and **10** are valuable to get high dielectric anisotropy of LC mixture. Figure 7 shows the relationship between $1/(\Delta\varepsilon)^{1/2}$ and flow viscosity (η) as response time in LC mixtures. LC mixtures with CF2O LC material enabled to reduce flow viscosity around 20-30% and 30 % at 3.3V and 2.5V condition respectively, compared with LC mixture without CF2O LC materials. Generally there is the trade off relation between dielectric anisotropy and viscosity. Nevertheless these CF2O LC mixtures enabled to overcome this trade off relation at low voltage drive field.

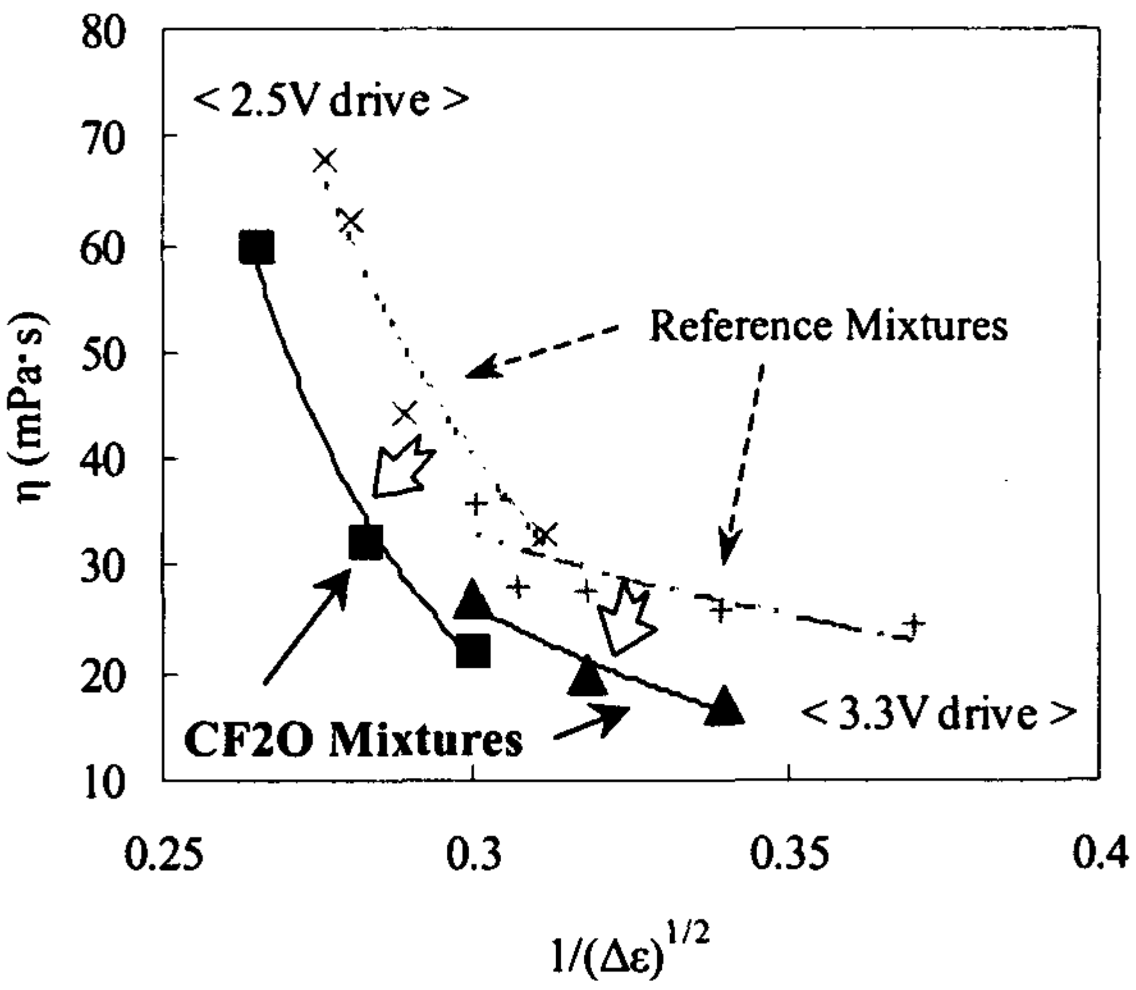


Figure 7 Relationship between $1/(\Delta\varepsilon)^{1/2}$ and η of LC mixtures

4.2 Quick Response application

For all of LCD modes, TN, IPS, VA and OCB, quick response is essential for moving picture. As stated above, CF2O LC materials are excellent to reduce viscosity of LC mixture. Basically response time is closely related for its viscosity at all LCD modes, thus it's expected that the novel materials will contribute for these quick response application. In these several LCD modes, various optical anisotropy values are required to meet each suitable cell configuration. Therefore, it's important to optimize a combination of several LC material derivatives, which means phenylcyclohexylcyclohexane (compound **2**, **3** and **4**), biphenycyclohexane(compound **5** and **6**) and terphenyl (compound **7**, **8**, **9** and **10**) structure. At certain LC specification, roughly the improvement rate of response time was estimated by 10% at 5V TN mode, by 30% at IPS mode, and by 20% at OCB mode compared with conventional LC mixtures.

4.3 Mobile Communication Tool

Reflective and transflective TFT LCDs are applied to mobile communication tools because of low power consumption and high image quality. Usually retardation values are adjusted by using the Gooch-Tarry condition[11] in order to optimize the contrast ratio. However in reflective and trasflective mode, retardation values are nearly half of transmissive mode because of twist angle and other cell layout configuration[17]. From such a reason, low birefringence LC mixtures are required. Among many CF2O LC materials, phenylcyclohexane (compound **1**) and phenylcyclohexylcyclohexane (compound **2**, **3** and **4**) derivatives are suitable because of low birefringence. The combination of these CF2O LC materials and conventional materials enable to achieve high dielectric anisotropy and high clearing point with high reliability.

4.4 Developed LC mixtures

Table 4 shows some examples of LC mixture using CF2O LC materials for several applications. Although the efficiency by using CF2O LC materials depends on target specifications of LC mixture, dielectric anisotropy, optical anisotropy, threshold voltage and so on. To satisfy various requirements, furthermore it's necessary to examine an optimization of CF2O LC materials in various LC specifications.

Table 4 Physical properties of CF2O LC mixtures

Mixture	Low Vop	FR MNT	IPS	OCB	Mobile
Tni (℃)	80.4	80.1	73.5	100.3	89.7
η(mPa·s)	20.2	15.6	18.9	37.56	24.7
γ1(mPa·s)	103.1	66.7	87.1	156.8	148.2
Δn	0.090	0.091	0.092	0.156	0.069
Δε	9.3	5.3	10.1	8.4	7.8
ρ(Ω·cm)	$> 10^{14}$	$> 10^{14}$	$> 10^{14}$	$> 10^{14}$	$> 10^{14}$

* FR means Fast Response

5. Conclusion

By the introduction of CF2O moiety as novel linkage group into LC molecules, several advantages compared with conventional LC materials were obtained, which were high dielectric anisotropy, low viscosity, wider namatic temperature range and so on. These novel LC materials were all chemically stable, its reliability would be accepted for AM-LCDs. Moreover LC mixtures by using these materials exhibited excellent physical properties, particularly low voltage driving and quick response.

6. Acknowledgments

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