Liquid Crystal Mixtures Including High Reliability Fluorinated Diluter and RM Monomer for PSVA and PI-less LCDs

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Keywords: Liquid crystal mixture, Difluorinated diluter, 3HFFH3, Reliability, RM-monomer

ABSTRACT

We developed high reliable difluorinated diluters R_1HFFHR_2 (R_1, R_2: alkyl group) for LC compositions. In particular, the difluorinated diluter having two propyl groups (3HFFH3) shows relatively wide nematic temperature range. Therefore, we selected 3HFFH3 as the diluter of LC mixtures for PSVA and PI-less LCDs because those LCD modes need high reliable LC mixtures due to irradiation of high intensity UV light for polymerization of a RM monomer. Regarding the RM-monomer, we have confirmed that the monomer carrying a chalcone unit was the best combination with the 3HFFH3.

1 INTRODUCTION

In recent years, liquid crystal display (LCD) with high response speed and low driving voltage becomes important. One of the useful technologies for this purpose is polymer-sustained vertical-alignment (PSVA) technology [1]. As the PSVA technology has slightly inclined pretilt angle from the vertical-alignment, the response speed and the driving voltage were definitely improved from the conventional VA mode [1]. Furthermore, polyimide (PI)-less VA and/or IPS technologies are focused on well because the PI-less technologies are expected to produce extremely narrow border LCDs [2-4]. In these technologies, a photo-irradiation process is necessary for polymerization of reactive-mesogen (RM)-monomers in the LC layer. The photo-irradiation by ultraviolet (UV) and/or blacklight including UV and visible light for polymerization of the RM-monomer sometimes causes image sticking phenomenon [5]. One of the causes of the image sticking is estimated to come from photo-chemical reaction of a conventional diluter substituted by a vinyl group and the RM-monomer [6,7]. Once the photo-chemical reaction occurred, reliability of the LCD decreases. Hence, in order to avoid the unexpected photo-chemical reaction, we developed new diluters with difluorinated group on a bicyclohexyl unit (difluorinated diluter R_1HFFHR_2 (R_1, R_2: alkyl group)), as shown in Fig.1 [8]. In addition, we have also found the best combination of the difluorinated diluter and the RM-monomer. In the present work, we fabricated PSVA and PI-less IPS cells with using the developed LC mixtures, and evaluated voltage holding ratio (VHR) as a parameter of the image sticking under several conditions [9]. We found that the RM-monomer carrying a chalcone unit combined with the difluorinated diluter showed significantly high VHR.

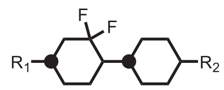

Fig. 1 Chemical structure of the developed difluorinated diluter R_1HFFHR_2.

2 DIFLUORINATED DILUTERS

The difluorinated dilutes R_1HFFHR_2 shown in Fig.1 give low rotational viscosity ($\gamma 1$) and low threshold voltage (V_{th}) for the LCDs. They are also expected to show high level of heat and photo stability because they do not have the photo-reactive functional group such as the vinyl group. In addition, they show high affinity to fluorinated LC compounds with especially negative dielectric anisotropy (Nega-LC). Therefore, one can expect that the difluorinated diluters R_1HFFHR_2 are the alternates of the diluters carrying the vinyl group.

Table 1 Physical properties of the difluorinated diluters**.**

Product Name	R_1	R_2	Phase Transition Temp. [°C]	Decomposition Temp. [°C]
1HFFH3	C1	C3	C -5.3	-
2HFFH2	C2	C2	C 6.2	-
2HFFH3	C2	C3	C 0.1	201
3HFFH1	C3	C1	C -15.5 N -5.5 I	210
3HFFH2	C3	C2	C -29.0 N 2.5 I	206
3HFFH3	C3	C3	C 28.6 N 42.3 I	212
2HFFH5	C2	C5	C -23.3 N 20.0 I	212

Table 1 shows physical properties of R_1HFFHR_2 prepared by our group. Decomposition temperatures of them show more than 200 °C. The difluorinated diluter having two propyl groups 3HFFH3 shows the widest nematic temperature range among the prepared difluorinated diluters.

3 PSVA CELL

3.1 Materials

In this section, we will focus on the PSVA technology. For fabrication of the PSVA cells, we prepared the LC mixtures, which consisted of a host LC (Host LC-1), the diluters, and the RM-monomer. We selected the following two diluters; one is the difluorinated diluter 3HFFH3 (Fig.2(a)), and another one is the diluter carrying the vinyl group 3HHV (Fig.2(b)). In addition, we also selected the following two RM-monomers; one is the RM-monomer carrying the chalcone unit (Fig.3(a)), and another one is the RM-monomer carrying a phenylene unit (Fig.3(b)). By combining each diluter and RM-monomer, we prepared three LC Mixtures I, II, and III, as listed in Table 2. Here, we used the common host LC (Host LC-1).

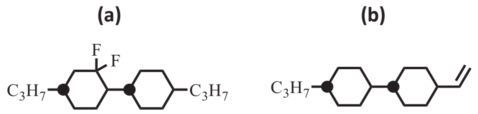

Fig. 2 Chemical structures of the diluters (a) 3HFFH3 and (b) 3HHV.

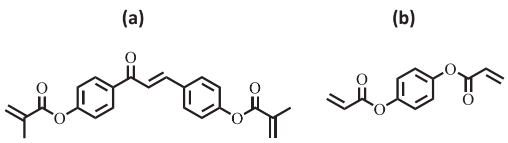

Fig. 3 Chemical structures of the RM-monomers carrying the (a) chalcone unit and the (b) phenylene unit.

Table 2 The LC Mixtures I, II, and III having diluters and RM-monomers for PSVA cells.

LC Mixture	I	II	III	
Diluter	3HFFH3	3HHX	3HFFH3	25.0%
RM-Monomer	Chal-RM	Phe-RM	Phe-RM	0.3wt%
Host	Common Host LC-1			75.0%

3.2 Fabrication of the PSVA Cells

Three kinds of vertically-aligned cells with including the LC Mixtures I, II, and III were firstly fabricated. And then, blacklight was irradiated to each cell while applying 10 V square waveform voltage (60 Hz) for polymerization of the RM-monomers, being obtained the PSVA Cells I, II, and III. The irradiation wavelength from the blacklight was approximately between 300 nm and 390 nm [3]. The reference PSVA cell with the LC mixture being used as the mass production in Sharp was also fabricated in a manner similar to the method described above.

3.3 Evaluation Results of the PSVA Cells

The response speed of the PSVA-LCD was improved by adding the diluter 3HHV [6]. However, image sticking in the LCD had been observed [6,7]. It means that the reliability of the PSVA-LCD with the diluter 3HHV was not enough. The reason for generation of the image sticking was considered that the LC mixtures including the diluter 3HHV had caused lower VHR after irradiation of the blacklight for the polymerization.

Table 3 lists the VHRs of the PSVA Cells I, II, and III before and after irradiation of the blacklight. The VHR was evaluated during an open-circuit period of 16.61 ms after ±5 V application at 70 °C. In the case of the PSVA Cell I, the VHR was maintained high value even after irradiation of the blacklight. In contrast, the PSVA Cell II shows lower VHR after irradiation. We estimate that the result comes from the photo-chemical reaction of the vinyl group of 3HHV with the RM-monomer carrying the phenylene unit. We previously estimated that bifunctional RM-monomers would produce radicals due to the photo-chemical reaction with the vinyl group [3]. Thus, in order to prevent the unexpected photo-chemical reaction, we developed a new LC mixture including 3HFFH3, which does not carry the vinyl group, and the RM-monomer carrying the chalcone unit. As shown in Table 3, the LC Mixture I, which includes the diluter 3HFFH3 and the RM-monomer carrying the chalcone unit, shows significantly high performance with maintaining high VHR after irradiation of the blacklight. Therefore, the result anticipates that the unexpected photochemical-reaction does not occur between 3HFFH3 and the RM-monomer carrying the chalcone unit.

The VHR of the LC Mixture III was also decreased after irradiation of the blacklight. The result anticipates that the conventional RM-monomer leads to decrease the VHR due to irradiation of the blacklight. Since a molecular flexibility of the conventional RM-monomer would be larger than that of the new RM-monomer carrying the chalcone unit, we estimate that a reactivity for the acrylate unit of the conventional RM-monomer would be relatively high, leading to a large decrease in the VHR. The results indicate that the LC Mixture I would be useful for the PSVA technology.

Fig.4 shows the *V*-*T* curve for the PSVA Cell I measured at 25 °C. The V_{th} indicates 2.6 V, and the maximum transmittance reaches at 6.8 V. These voltages are coincident with those of the PSVA cell fabricated with the LC mixture used for mass production. The contrast ratio of the PSVA Cell I determined from the *V*-*T* curve is approximately 3,000:1, as listed in Table 4. This is the same level as that of the mass production PSVA panel. The response times (τ_{on} and τ_{off}) are compared to the mass production PSVA cell. The relative values of τ_{on} and τ_{off} are shown in Table 4. Both τ_{on} and τ_{off} are almost equal to those of the PSVA cell fabricated by the mass production LC mixture. These results indicate that the LC Mixture I would be another candidate for the LC material of the PSVA LCD. We are now developing new LC compositions carrying the 3HFFH3 with faster response speed.

Table 3 VHR before and after irradiation of the blacklight to the PSVA cells.

PSVA Cell (LC Mixture)	VHR(%)	
	Before UV Irradiation	After UV Irradiation
I	99.5	99.4
II	99.5	97.8
III	99.5	98.1

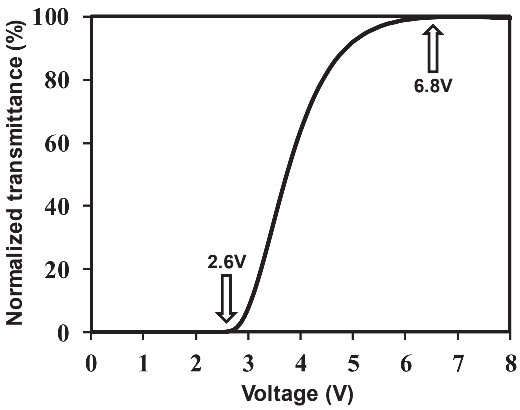

Fig. 4 *V-T* curve of the PSVA Cell I.

Table 4 Contrast ratio and relative response times (τ_{on} and τ_{off}) of the PSVA Cell I.

	Contrast ratio	τ_{on} (%) [relative]	τ_{off} (%) [relative]
LC Mixture I	2,946 : 1	98.3	100.6

*Contrast ratio was determined from the ratio of the highest and lowest transmittance of the *V-T* curve.

**Response times τ_{on} and τ_{off} of the PSVA Cell I were compared to those of the PSVA cell fabricated with using the mass production LC mixture.

Fig. 5(a) and 5(b) indicate the VHRs of the PSVA Cell I as a function of aging time under LED backlight exposure and storage in a 70 °C oven, respectively. The VHRs of the PSVA Cell I were compared to those of the PSVA cell fabricated with the mass production LC mixture. In both tests, the VHRs of the PSVA Cell I were maintained the same level with those of the PSVA cell fabricated with the mass production LC mixture. The result indicates that the reliability of the LC Mixture I would be equal to that of the mass production LC mixture.

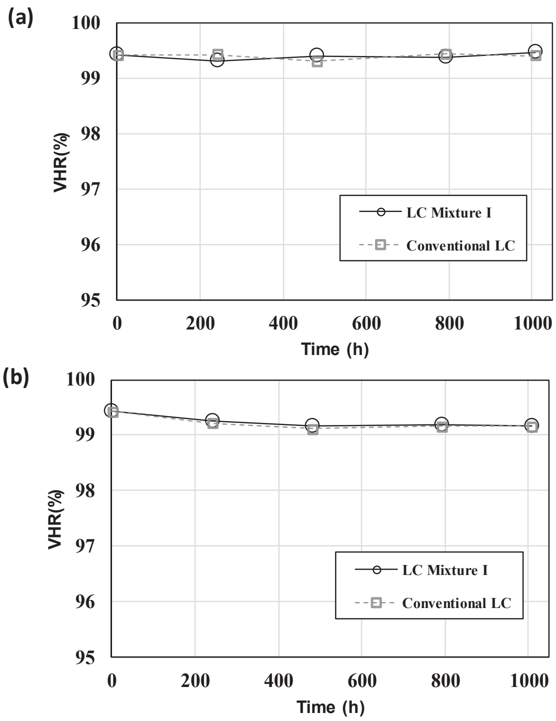

Fig. 5 VHR as a function of aging time for (a) LED backlight exposure and (b) storage in a 70 °C oven.

4 PI-LESS IPS CELL

4.1 Materials

This section focuses on the PI-less IPS technology. For fabrication of the PI-less IPS cell, we prepared the LC mixtures, which consisted of a host LC (Host LC-2), the diluters, and the RM-monomer. We used the same diluters that we used for fabrication of the PSVA cells: difluorinated diluter 3HFFH3 and 3HHV. We used the RM-monomer carrying the chalcone unit because the chalcone unit absorbs polarized UV and induces a uniaxial LC alignment [4,10]. For fabrication of the PI-less IPS cell, the LC Mixtures IV and V were prepared, as listed in Table 5. The common host LC (Host LC-2) was different from the common host LC (Host LC-1) used for fabrication of the PSVA cells.

Table 5 The LC Mixtures IV and V having diluters and the RM-monomer for PI-less IPS cells.

LC Mixture	IV	V	
Diluter	3HFFH3	3HHV	25.0%
RM-Monomer	Chal-RM		1.0wt%
Host	Common Host LC-2		75.0%

4.2 Fabrication of the PI-less IPS Cells

Two non-aligned cells without the PI alignment layers and with the LC Mixtures IV and V were fabricated. And then, the polarized UV was irradiated to each cell from the normal direction for inducing the homogeneous LC alignment (PI-less IPS Cells IV and V). During the irradiation of the polarized UV, the temperature of the cell should be adjusted 90 °C, which was above the nematic-to-isotropic transition temperature (T_{NI}) of the LC mixtures [4,10].

4.3 Evaluation Results of the PI-less IPS Cells

The uniaxial LC alignment was confirmed by polarized optical microscopic observation, which was previously explained in detail [4,10].

Table 6 shows the VHRs of the PI-less IPS Cells IV and V before and after irradiation of the polarized UV above the T_{NI} of the LC mixtures. In the case of the PI-less IPS Cell IV, the VHR did not decrease even after irradiation of the polarized UV. In contrast, the VHR of the PI-less IPS Cell V was definitely decreased after irradiation of the polarized UV. As in the case of the evaluation for the PSVA cell, one can estimate that the result comes from the photo-chemical reaction of 3HHV with the RM-monomer. The photo-chemical reaction would produce radicals, and these radicals would remain in the LC layer of the PI-less IPS cell. Hence, in order to avoid this unexpected photo-chemical reaction, we used the difluorinated diluter 3HFFH3. The result indicates that using the 3HFFH3 is useful instead of using the 3HHV for fabrication of the PI-less IPS cell with high reliability.

Table 6 VHR before and after irradiation of the polarized UV to the PI-less IPS cells.

PI-less IPS Cell (LC Mixture)	VHR(%)	
	Before UV Irradiation	After UV Irradiation
IV	99.3	99.2
V	99.3	98.1

5 CONCLUSIONS

We developed the difluorinated diluters R_1HFFHR_2 to overcome the trade-off relationship between the response speed and the image sticking characteristic, and also developed the RM-monomer carrying the polarized UV absorption unit, chalcone, for inducing the homogeneous LC alignment without forming the conventional PI alignment layer.

Since the diluters R_1HFFHR_2 do not carry the vinyl group, the image sticking is unlikely to occur owing to high VHR. Moreover, the diluters R_1HFFHR_2 carry the difluorinated group on the bicyclohexyl unit, these show high affinity to the fluorinated LC compounds with negative dielectric anisotropy, and also show high photo and thermal stability. With using the diluter 3HFFH3, we succeeded to obtain the PSVA cell with fast response speed and high VHR under the backlight exposure and the storage test in the 70 °C atmosphere.

We further developed the LC mixture including the RM-monomer carrying the chalcone unit. As the chalcone unit absorbs the polarized UV and aligns the LC molecules uniaxially, the homogeneous LC alignment was obtained by irradiation of the polarized UV to the cell without forming the conventional PI alignment layer. In addition, since the LC mixture including the diluter 3HFFH3 and the RM-monomer would not show the photo-chemical reaction, the VHR was maintained high value after irradiation of the polarized UV at high temperature. Thus, we expect that the high reliability PI-less IPS cell can be fabricated with using both the diluter 3HFFH3 and the RM-monomer carrying the chalcone unit.

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