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New Diluter Solubilized in Liquid Crystal Compounds for High Stability and Fast Response Speed Liquid Crystal Displays

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Abstract: Diluters play a crucial role for reducing the rotational viscosity of liquid crystal (LC) materials for improving the response property of LC displays (LCDs). However, conventional diluters tend to deteriorate relatively easily under ultraviolet (UV) exposure, due to existence of vinyl groups. Hence, it was difficult to prepare polymer layers in the LC cells by exposing UV for polymerization regarding polymer-sustained vertically-aligned (PS-VA) and polyimide-free (PI-free) technologies. In this study, however, we succeeded to develop a high stable diluter, which shows a symmetrical structure and carries fluorinated groups for stable nematic phase and high affinity with other fluorinated LC compounds. With the use of the symmetrical-structured diluter, we developed the PS-VA and the PI-free in-plane switching cells with a fast response rate and high voltage holding ratio, by combining a reactive monomer including an azobenzene moiety.

Keywords: liquid crystal display; liquid crystal mixture; diluter; stability; polymer-sustained vertically aligned (PS-VA); PI-free

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1. Introduction

Liquid crystal displays (LCDs), which show a high contrast ratio and utilize a fast response speed have become significantly important in our lives. In particular, polymer-sustained vertically-aligned (PS-VA) LC is useful for large sized LCDs [1–3]. The PS-VA LCD shows high contrast ratio, fast response speed, and low driving voltage because LC molecules exhibit a slightly inclined pretilt angle from homeotropic alignment [1,2]. In addition, polyimide (PI)-free VA and in-plane switching (IPS) technologies are also paid much attention because the PI-free LCDs are expected to prepare extremely narrow picture frame LCDs [4–8]. In these techniques, ultraviolet (UV) light is generally exposed to prepare polymer layers by polymerization of reactive monomers in the LC layer. However, the UV exposure process for preparation of the polymer layer from the reactive monomers often induces serious image sticking [2,9]. One of causes for the image sticking is presumed to derive from a photo-chemical reaction between previous diluters carrying a vinyl group and the reactive monomers [10,11]. In the case that the photo-chemical reaction takes place in the LC layer, the image sticking tends to become observable. Hence, it is significantly important to develop new diluters for preventing the unexpected photo-chemical reaction. For this purpose, we developed a novel diluter with including two cyclohexane groups and two saturated alkyl groups (R_1-CyFF-Cy-R_2 (R_1, R_2: saturated alkyl groups)), which is depicted in Figure 1 [12]. We found that the number of saturated alkyl groups of R_1 and R_2 should be same for stable nematic phase. This fact indicates a symmetrical structure of the diluter is suitable for the LC materials. In addition, we prepared the LC mixtures, which are constructed from the LC materials and the reactive monomer, for the PS-VA and PI-free LC cells. In this study, we produced the PS-VA and PI-free IPS LC cells using the LC mixtures including the symmetrical diluter and various reactive monomers, and evaluated voltage holding ratio (VHR). The VHR is generally known as the image sticking parameter [13–16]. We confirmed that the combination of a newly developed diluter, and the reactive monomer carrying an azobenzene moiety exhibited high alignment stability and high VHR.

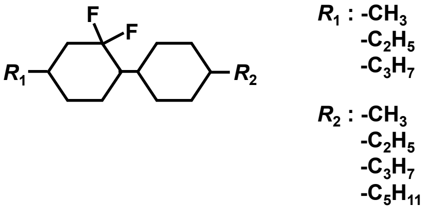
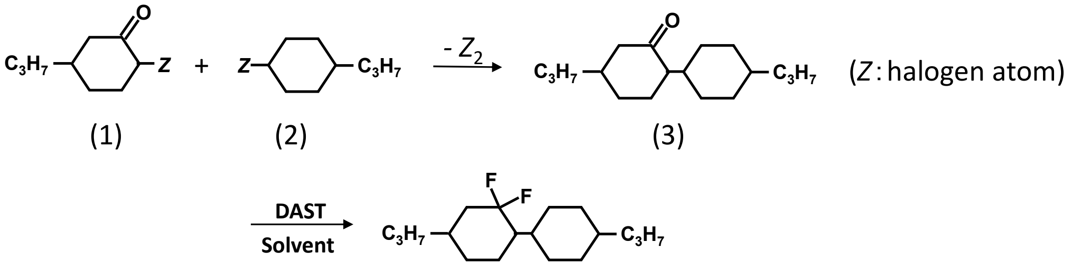


Figure 1. Chemical structure of the diluters R_1-CyFF-Cy-R_2 (R_1 and R_2 are saturated alkyl chains).

2. Experimental

2.1. Preparation of a New Diluter C3-CyFF-CyC3

As one of diluters, C3-CyFF-Cy-C3 is focused here, and we show a preparation procedure in the following Scheme 1. As the first step, a dehalogenation reaction between the compounds (1) and (2) prepared the compound (3). Then, the deoxofluorination reaction was performed by using diethylaminosulfur trifluoride (DAST) shown in the following scheme [12]. The GC-MS chart of the final compound is shown in Figure 2. The peak m/z 286 is observed, which is equal to the molecular weight of C3-CyFF-Cy-C3. Thus, we confirm that the diluter C3-CyFF-Cy-C3 is successfully obtained.



Scheme 1. Synthetic scheme of C3-CyFF-Cy-C3.

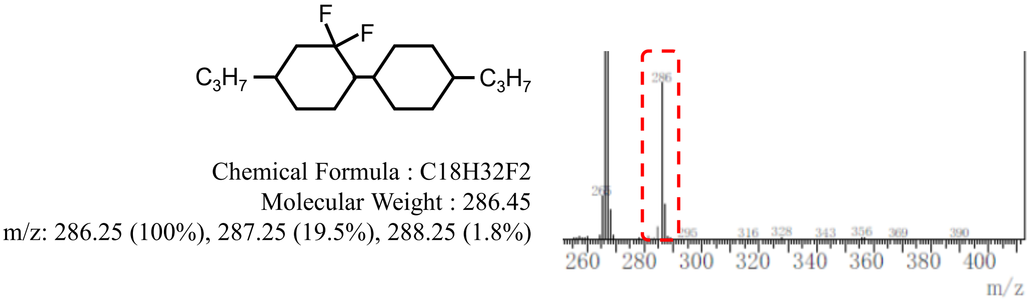


Figure 2. GC-MS chart of C3-CyFF-Cy-C3.

2.2. DSC Evaluation

DSC evaluation of the diluters R_1-CyFF-Cy-R_2 are performed by DSC7000X (Hitachi High Tech Science Corporation, Japan). The weight of samples was in the range of approximately 3.5–4.0 mg. The samples were encapsulated in Al pans, and were heated and cooled in dry nitrogen atmosphere. Measurements were carried out at 10.0 °C/min. The samples were heated from room temperature to 100 °C and cooled back to −50 °C at the same rate, and heated up to 100 °C again. The heat/cool cycles were repeated three times. The transition temperatures for various phase changes were obtained from endothermic peak of enthalpy, and determined from the third running.

2.3. Evaluation of the LC Cells

The LC cells (PS-VA and PI-free IPS cells) were prepared described in the following sections. The evaluation methods of each LC cell are described in the following sections.

The VHR measurements were carried out in a 70 °C controlled bath with a 6254-type VHR meter developed by Toyo Technica. The VHR was evaluated during an open-circuit period of 16.61 ms after ±5 V application.

A voltage-dependent transmittance curve (V-T curve) of the LC cells was measured at 25 °C with a Photal 5200 electro-optical evaluation system manufactured by Otsuka Electronics Corporation.

Response times, turn-on (τ_{on}) and turn-off (τ_{off}) times, are determined as transient times from 10% to 90% and from 90% to 10% of the maximum transmittance, respectively. These were determined by Photal 5200 electro-optical evaluation system.

Polarized optical microscopic (POM) images were observed by an ECLIPSE E600 POL system (Nikon Corp) in 25 °C controlled atmosphere.

3. New Developed Diluters

The newly developed diluters R_1-CyFF-Cy-R_2 illustrated in Figure 1 would be expected low rotational viscosity and low threshold voltage (Vth) because the diluters would show weak interaction with other LC compounds [12]. Most LC compounds have phenyl/phenylene rings, which usually interact with other conjugated LC compounds such as π-π interaction. An affinity with other LC compounds having fluorinated units (generally inducing dielectric anisotropy) increases by introducing di-fluorinated units on one of the cyclohexane groups of the diluters [17]. Moreover, they are also expected to show high level of photo and thermal stability because the diluters do not have the photo-reactive groups such as the vinyl and the phenyl/phenylene groups [12]. Table 1 lists transition temperatures of R_1-CyFF-Cy-R_2. Decomposition temperatures of most diluters show more than 200 °C, anticipating that these diluters are thermally stable. In particular, the diluters C3-CyFF-Cy-C3 and C2-CyFF-Cy-C5 show the decomposition temperature over 210 °C. The nematic temperature range of C3-CyFF-Cy-C3 is between 28.6 °C and 42.3 °C, whereas that of C2-CyFF-Cy-C5 is between −23.3 °C and 20.0 °C. The result indicates that the nematic temperature of C3-CyFF-Cy-C3 is higher than that of C2-CyFF-Cy-C5. One of assumptions of this result is due to high thermal stability for the C3-CyFF-Cy-C3 since the chemical structure is more symmetrical than that of C2-CyFF-Cy-C5. Different carbon number between two side alkyl groups would increase the steric disorder, leading to relatively unstable nematic phase. Figure 3 indicates DSC thermograms of C3-CyFF-Cy-C3 and C2-CyFF-Cy-C5. The peak observed between crystal (C) and nematic (N) phases of C3-CyFF-Cy-C3 is more obvious than that of C2-CyFF-Cy-C5, probably supporting our assumption. Furthermore, C3-CyFF-Cy-C3 would be more suitable for often-used LCDs, because the LCDs are generally used under the temperature range between 15 °C and 45 °C. Hence, we decided to evaluate the more symmetrical-structured diluter C3-CyFF-Cy-C3 for application of the PS-VA and PI-free IPS LC cells.

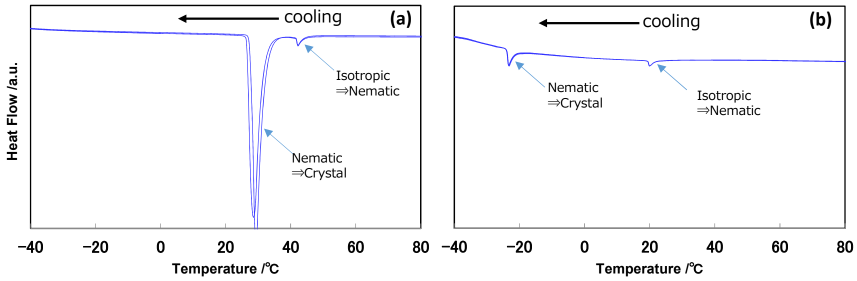
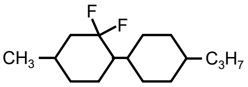
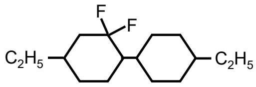
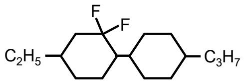
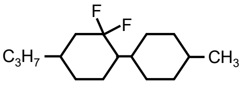
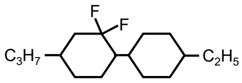
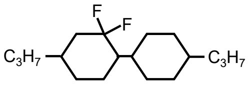
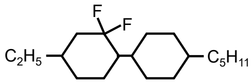


Figure 3. DSC thermograms of (**a**) the C3-CyFF-Cy-C3 and (**b**) the C2-CyFF-Cy-C5.

Table 1. Transition and decomposition temperatures of the diluters R_1-CyFF-Cy-R_2.

Chemical Structure	Product Name	C⇔N Transition Temperature [°C]	N⇔I Transition Temperature [°C]	C⇔I Transition Temperature [°C]	Decomposition Temperature [°C]
	C1-CyFF-Cy-C3	-	-	−5.3	-
	C2-CyFF-Cy-C2	-	-	6.2	-
	C2-CyFF-Cy-C3	-	-	0.1	201
	C3-CyFF-Cy-C1	−15.5	5.5	-	210
	C3-CyFF-Cy-C2	−29.0	2.5	-	206
	C3-CyFF-Cy-C3	28.6	42.3	-	212
	C2-CyFF-Cy-C5	−23.3	20.0	-	212

4. PS-VA Mode

4.1. Materials

In this part, we describe the PS-VA LC cell. For the production of the PS-VA cells, we prepared the LC mixtures, which are consisted of a host LC, the diluter, and the reactive monomer at first. We selected the following two diluters; one is the developed diluter C3-CyFF-Cy-C3 (Figure 4a) in this study, and another is the diluter carrying the vinyl group (C3-HH-V) shown in Figure 4b. In addition, we selected two reactive monomers; one is the reactive monomer carrying the azobenzene moiety (Azo-RM; Figure 5a), and another is the monomer carrying a bi-phenylene moiety (Biph-RM; Figure 5b). The monomer shown in Figure 5b is conventionally used [2]. By combining the host LC, the diluters, and the reactive monomers, three kinds of LC mixtures (LC Mixtures I, II, and III) were prepared, as shown in Table 2.

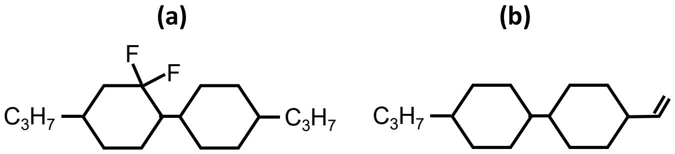


Figure 4. Chemical structures of the diluters (**a**) C3-CyFF-Cy-C3 and (**b**) C3-HH-V.

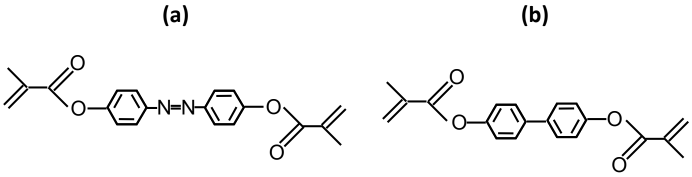
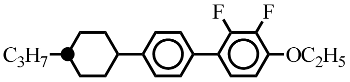
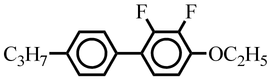
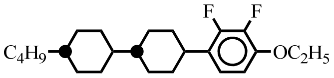
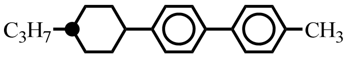
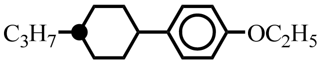


Figure 5. Chemical structures of the reactive monomers including (**a**) azobenzene (Azo-RM) and (**b**) bi-phenylene (Biph-RM) moieties.

Table 2. The LC mixtures I, II, and III including the diluters, host, and reactive monomers for PS-VA LC cells.

	I	II	III	Wt% (LC)	Wt%/LC
Diluter	C3-CyFF-Cy-C3	C30HH-V	C3-CyFF-Cy-C3	25.0	-
RM	Azo-RM	Biph-RM	Biph-RM	-	0.25
Host				20.0	-
				10.0	-
				10.0	-
				20.0	-
				15.0	-

4.2. Preparation of the PS-VA LC Cells

The PS-VA LC cells were prepared as follows. The vertically-aligned PI material was formed on top of ITO substrates, baked at 90 °C for 1 min and 200 °C for 60 min. After baking, photo- and heat-curing sealing material was drawn, and three LC Mixtures, which are shown in Table 2, were each dropped on these substrates. Then, the other substrates, where the same vertically-aligned PI material was formed on them, were laminated on the substrates and heated at 100 °C for 40 min. 10 V square waveform voltage (60 Hz) was applied to each cell, and the black-light (FHF-32BLB developed by Toshiba, in Japan) was exposed to the LC cells at 35 °C for 30 min for preparation of the polymer layers.

4.3. Evaluation of the PS-VA Cell

Response times of PS-VA LC cell were attempted to improve with using the conventional diluter C3-HH-V [10]. However, image sticking has clearly appeared [10,11]. The estimation of the image sticking is the following; the LC mixtures including the C3-HH-V decrease the VHR after exposure of the UV.

Table 3 lists the VHRs of the PS-VA LC cells produced by the LC Mixtures I, II, and III before and after exposure of the black-light. In the LC Mixture I, the VHR was kept high value above 99.2% after exposure of the black-light. In contrast, the VHR decreased significantly for the PS-VA LC cell produced by the LC Mixture II after the black-light exposure. We presume that the result derives from the photo-chemical reaction of the C3-HH-V with the reactive monomer. It was considered that the reactive monomers would generate radicals due to photo-chemical reaction of the monomer with the vinyl group. Hence, for preventing the photo-chemical reaction, we finally designed the symmetrical diluter C3-CyFF-Cy-C3, which does not have the vinyl group and high affinity with the fluorinated LC compounds. As shown in Table 3, the LC Mixture I, which has the diluter C3-CyFF-Cy-C3 and the reactive monomer carrying the azobenzene moiety (Azo-RM), shows high VHR even after the black-light exposure. Therefore, the result indicates that the photo-chemical reaction does not occur between C3-CyFF-Cy-C3 and Azo-RM.

The VHR of the PS-VA LC cell produced by the LC Mixture III, which includes C3-CyFF-Cy-C3 and the conventional-type monomer carrying the biphenylene moiety (Biph-RM), also decreased after the black-light exposure though it was used C3-CyFF-Cy-C3. Since a rate constant of polymerization is relatively slow for the Biph-RM compared with the Azo-RM [18], we presume that unreacted radicals derived from the Biph-RM still exist in the LC layer after the black-light exposure, leading to a significant decrease in the VHR. The results indicate that the LC Mixture I would be the most suitable among the LC Mixtures I, II, and III for the PS-VA LCD.

Table 3. VHRs before and after exposure of the black-light to the PS-VA LC cells.

LC Mixture (PSVA Mode Cell)	VHR (%)	
	Before UV Irradiation	After UV Irradiation
I	99.4	99.2
II	99.3	93.0
III	99.3	97.2

Figure 6 shows the V-T curve of the PS-VA LC cell produced by the LC Mixture I. The threshold voltage Vth indicates about 2.7 V, and the maximum transmittance reaches at 6.4 V. These voltages would be suitable for the real-use. The contrast ratio determined from the ratio of the highest and the lowest transmittance of the V-T curve is over 3000, as listed in Table 4. This is the high level compared with the generally-used LCDs.

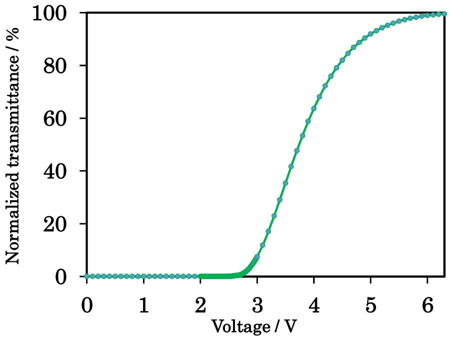


Figure 6. V-T curve for the PS-VA LC cell produced by the LC Mixture I.

Table 4. Contrast ratios and response times of the PS-VA LC cells produced by the LC Mixtures I and II.

	Contrast Ratio	τ_{on} (ms)	τ_{off} (ms)
LC Mixture I	3300:1	9.5	7.3
LC Mixture II	3300:1	9.9	6.7

Response times (τ_{on} and τ_{off}) of the PS-VA LC cell produced by the LC Mixture I were compared with those from the LC Mixture II. Results are also shown in Table 4. Both τ_{on} and τ_{off} are almost equal between the LC Mixtures I and II. The fact supports that the developed diluter C3-CyFF-Cy-C3 would be significantly useful.

Figure 7a,b show the VHRs for the PS-VA LC cells as a function of aging per hour under LED backlight exposure and stored in a 70 °C controlled bath, respectively. Regarding the PS-VA LC cell produced by the LC Mixture I, the VHRs were kept at a high value above 98.0% for 1000 h of the LED backlight exposure and then stored in a 70 °C controlled bath. The result indicates that the photo- and thermal-stability of the LC Mixture I is significantly high. In contrast, the VHRs of PS-VA LC cells produced by both the LC Mixtures II and III decreased under the LED backlight exposure and the storage in 70 °C. The results imply that the photo- and thermal-stability of the LC Mixtures II and III are not enough compared with the LC Mixture I. The VHR of the PS-VA LC cell produced by the LC Mixture II decreased remarkably under the LED backlight exposure. This would be one of the supportive results that the photo-chemical reaction was progressed between the conventional diluter C3-HH-V and the monomer Biph-RM. Thus, we confirm that the combination of the new developed diluter C3-CyFF-Cy-C3 with Azo-RM is significantly useful for the PS-VA LCD, because it shows both fast response speed and high stability.

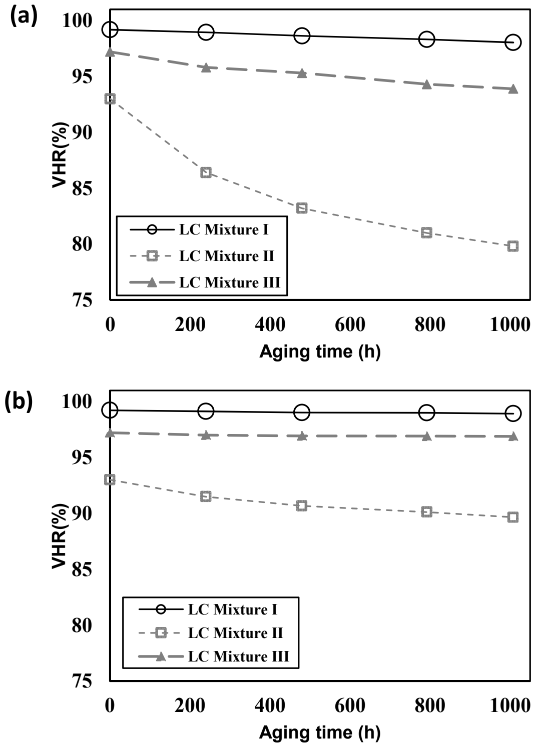


Figure 7. VHR as a function of aging time for PS-VA cells under (**a**) LED backlight exposure, and (**b**) storage in a 70 °C controlled bath.

5. PI-Free IPS Mode

5.1. Materials

In this part, we will describe the PI-free IPS LC cells. For production of the PI-free IPS LC cells, the LC mixtures were firstly prepared. We selected two diluters, C3-CyFF-Cy-C3 and C3-HH-V. The reactive monomer Azo-RM was also selected because the azobenzene unit absorbs polarized UV and induces the uniaxial alignment of the LC [18,19]. For producing the PI-free IPS LC cell, the LC Mixtures IV and V were prepared as shown in Table 5.

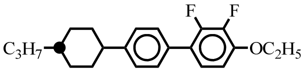
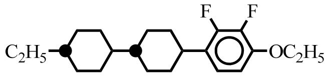
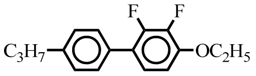
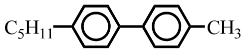
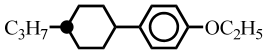
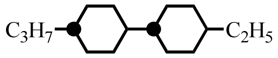
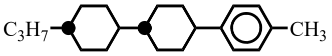
5.2. Preparation of the PI-Free IPS Cell

The PI-free IPS LC cells were produced are follows. A pair of IPS mode substrates were prepared; one side of the substrate has pixel and common electrodes, and the other side does not have any electrode. Photo- and heat-curing type sealing material was drawn, and the LC Mixtures IV and V were each dropped on these substrates. The other substrates were then laminated on the substrates and heated at 100 °C for 40 min. The polarized UV was exposed to the LC cell from the normal direction of the LC cell. The exposure of the polarized UV was conducted above nematic-to-isotropic transition temperature (T_{NI}) [18,19]. The homogeneously aligned LC cells were finally obtained.

5.3. Evaluation of the PI-Free IPS Cell

Homogeneously aligned LC was convinced by POM observation, as shown in Figure 8. Before exposure of the polarized UV, the transmittance at axes of 0° and 45° polarized UV to the crossed polarizers are almost same level, and these are not uniform (Figure 8a). This anticipates that the state of the LC alignment was random. After the polarized UV exposure (1 J/cm^2) at 95 °C (above the T_{NI} of the LC composition), dark state was observed at axis of 0° polarized UV to the crossed polarizer, whereas high and uniform transmittance was observed at axis of 45° polarized UV to the crossed polarizers (Figure 8b). The result indicates that the homogeneously aligned LC was obtained by the polarized UV exposure.

Table 5. The LC mixtures IV and V including the diluters, host, and reactive monomers for PI-free IPS LC cells.

	IV	V	Wt% (LC)	Wt%/LC
Diluter	C3-CyFF-Cy-C3	C3-HH-V	25.0	-
RM	Azo-RM	Azo-RM	-	1.0
Host			25.0	-
			10.0	-
			5.0	-
			13.0	-
			10.0	-
			10.0	-
			2.0	-

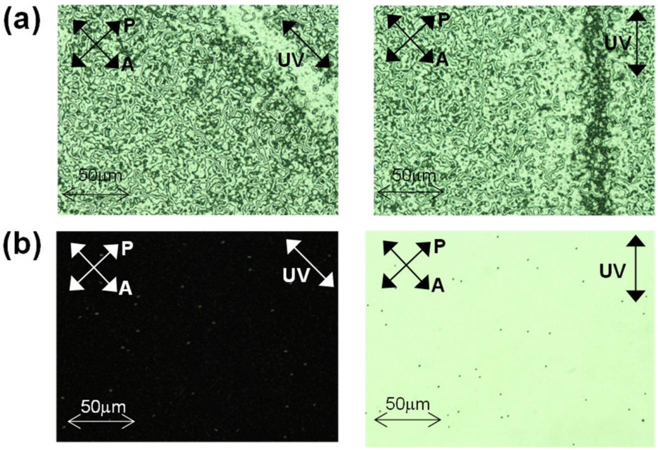


Figure 8. POM images before (**a**) and after (**b**) 1 J/cm^2 polarized UV to the PI-free IPS cells; the angles between crossed polarizers and polarized UV are 0° and 45°.

Table 6 lists the VHR of the PI-free IPS LC cells produced by the LC Mixtures IV and V before and after the polarized UV exposure. Regarding the LC Mixture IV, decrease of the VHR was only slightly after the polarized UV exposure. On the other hand, the VHR of the LC cell produced by the LC Mixture V decreased obviously after exposure of the polarized UV. We presume that the decrease of the VHR is derived from the photo-chemical reaction of the C3-HH-V with Azo-RM. The photo-chemical reaction would induce a generation of radicals, and these radicals would remain in the LC layer of the PI-free IPS LC cell. Therefore, we confirm that using the developed diluter C3-CyFF-Cy-C3 is effective for preventing the photo-chemical reaction with the Azo-RM.

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

LC Mixture (PI-Free IPS Cell)	VHR (%)	
	Before UV Irradiation	After UV Irradiation
IV	99.2	98.8
V	99.0	97.3

Figure 9 plots the VHR of the PI-free IPS LC cell produced by the LC Mixture IV as a function of aging hour under LED backlight exposure, and storage in a 70 °C controlled bath, respectively. The VHRs were kept at a high value during 1000 h for both the LED backlight exposure and the storage in the 70 °C atmosphere. In the case of the storage test at 70 °C, the VHR decreased, but only slightly, and the value was approximately 98.0% at 1000 h storage. We estimate that the thermal stability is enough level for real use of the LCD. In the case of the LED backlight exposure, the VHR showed approximately 97.2% after 1000 h aging, indicating that the slight decrease of the VHR was obtained though it is relatively high value compared with the LC mixtures having the conventional diluters. We presume the reason in the following. Since the concentration of the Azo-RM in the Mixture IV is four times higher than that in the Mixture I (Table 2), unreacted monomer molecules and/or polymerized compounds, which are not incorporated into the polymer layer, would be easily remained in the LC layer of the LC Mixture IV. Hence, the residual monomer or polymerized compounds in the LC layer would induce the slight decrease of the VHR, as shown in this figure. Hence, further improvement of the VHR under the LED backlight exposure and the storage in the 70 °C atmosphere is now under consideration.

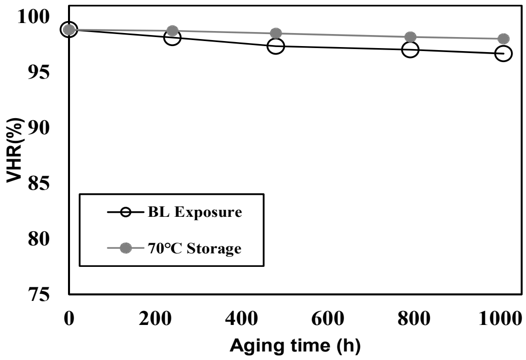


Figure 9. VHR as a function of aging time for the PI-free IPS cells under the LED backlight exposure and the storage in a 70 °C controlled bath.

6. Conclusions

We developed new diluters R_1-CyFF-Cy-R_2 to overcome the tradeoff between the response speed and the image sticking parameter. The newly developed diluters are constructed from two cyclohexane units (Cy) and two side saturated alkyl chains (R_1 and R_2), which are symmetrical in structure. Di-fluorinated groups were introduced into one of the cyclohexane units for increasing the affinity of the other fluorinated LC compounds, which are shown to have negative dielectric anisotropy. The diluters are expected to be significantly stable under the UV because they do not have vinyl groups. In the comparison between two diluters C3-CyFF-Cy-C3 and C2-CyFF-Cy-C5, the temperature showing the nematic phase of C3-CyFF-Cy-C3 is higher than that of C2-CyFF-Cy-C5. This would be due to high thermal stability. We estimate that this is derived from the fact that the chemical structure C3-CyFF-Cy-C3 is more symmetrical than that of C2-CyFF-Cy-C5.

Since the diluter C3-CyFF-Cy-C3 does not have the vinyl groups, the VHRs for both the PS-VA and PI-free IPS LC cells were significantly high after the UV exposure, leading to an extremely small level of image sticking. Moreover, since the diluter C3-CyFF-Cy-C3 carries the di-fluorinated groups on the cyclohexane unit, it shows a high affinity to other fluorinated LC compounds and also shows a fast response speed. We finally succeeded in obtaining the PS-VA LC cell with both the fast response speed and high VHR under both the LED backlight exposure and the storage in the 70 °C controlled bath. We further developed the LC mixture including the Azo-RM for the PI-free IPS LC cell. As the azobenzene moiety absorbs the polarized UV and aligns the LC molecules uniaxially, the homogeneously aligned LC was successfully obtained by the polarized UV exposure to the cell without conventional PI alignment layer. The VHR was kept relatively high after the polarized UV exposure. Therefore, we expect that the high stability PI-free IPS LC cell can be produced by using the diluter C3-CyFF-Cy-C3 and the Azo-RM. As the final conclusion, the combination of the diluter C3-CyFF-Cy-C3 and Azo-RM is significantly useful for the PS-VA and PI-free LCDs.

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