

# Improvement of Display Performance for PSVA-LCD Based on Novel RM Monomer with Short Alkyl Spacer

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**SUMMARY** We proposed a novel UV curable reactive mesogen monomer for VA-LCD with Polymer-Sustained (Stabilized) Vertical Alignment (PSVA) which shows a high display performance. The experimental results reveal that the PSVA by the novel-monomer realizes less image sticking and better response time.

**key words:** polymer-sustained (polymer-stabilized), phase separation, reactive mesogen, VA-LCD, PSVA

## 1. Introduction

Liquid crystal (LC)/polymer composite have been studied since 1970s as electro-optical modulators. For example, by polymerization-induced phase separation from a homogeneous mixture comprising LC and a polymer precursor (monomer), which forms polymer phase and, provides a mechanical support of the LC orientation [1], [2]. The characteristics of electro-optical devices are determined by the LC orientation. Doane et al. [3] and Gunjima et al. [4] reported the electro-optical device which shows opaque state at zero fields, in which the directors of LC in droplets comprising LC molecules dispersed in polymer matrix (PDLC) or domains in continuous LC phase combined with continuous polymer phase (LCPC) are randomly oriented so as to be opaque state at zero field. Besides, Yang et al. [5] and Niiyama et al. [6] reported the other types of LC/polymer composites, in which liquid crystal molecules were controlled to be aligned in a prefixed direction at zero field by polymer phase in those composites.

On the other hands, liquid crystal display with a vertical-alignment (VA) has been commonly used for application of flat panel display for TV, a mobile phone and so on. Several approaches such as multi-domain induced by a surface structure (MVA) [7], fringe-field switching (FFS) [8] and patterned vertical alignment (PVA) [9] are adopted to improve its image quality, such as a viewing angle. However, an issue of its slow response time, especially in, rising time, still remains in conventional technologies.

In order to solve these problems, new solution for a pretilt-control of VA-LCD has been proposed by introducing LC/polymer composite in which a small amount of polymer

predetermines its alignment of LC [10], [11]. It is called as Polymer-Sustained (Stabilized) VA (PSVA). In PSVA, the pretilt angle is determined by polymerization of reactive mesogen (RM) monomers in the presence of electric field in a prefixed direction. The favorable pretilt angle induced by PSVA can drastically improved its response time [12]. Severe issues, on the other hand, have been reported in the aspect of image quality in a PSVA-LCD [13]–[15]. One of the issues is an image sticking phenomena induced by remaining RM monomers after polymerization. The UV intensity and total energy of the irradiation for photo-polymerization of RM monomer will be limited because a partial decomposition of LC molecule might lead a decrease of the voltage holding ratio. Surface Controlled Patterned VA (SC-PVA) mode has been proposed to solve this problem, SC-PVA is realized by doping RM monomer to polyimide alignment layer and its polymerization in the presence of electric field [16]. Remaining RM monomers in the alignment layer after polymerization might be eluted to LC even in SC-PVA modes.

In this paper, we proposed a new concept of RM monomers for a Polymer-Sustained VA-LCD application, which leads to less image sticking and improved response times. Furthermore, less UV irradiation energy is required for polymerization of new RM monomers. Design of alkyl spacers between the core mesogen structure and reactive acrylic moiety in RM monomer is important factor for improving its display performance. Recommend RM monomers in paper didn't realize only a stable alignment of liquid crystal molecules, but also an effective reduction in a period of UV irradiation for its polymerization.

## 2. Experimental

### 2.1 Preparation of PSVA-LCD

A cleaned indium tin oxide (ITO) glass substrate is coated with a vertical alignment polyimide layer. The VA cell is assembled by the two coated-glass substrates on which the surface is rubbed in one direction to give a small pretilt of LC molecules. The VA cell with rubbed alignment layer is more favorable to evaluate the polymer-stabilized alignment state in case that, the tilt angle from the normal direction is small, though a cell with slits in electrodes is usually used for an evaluation of PSVA. In this study, the tilt angle is suppressed below  $0.5^\circ$  from the normal direction, and the cell gap is  $2.7\ \mu\text{m}$ .

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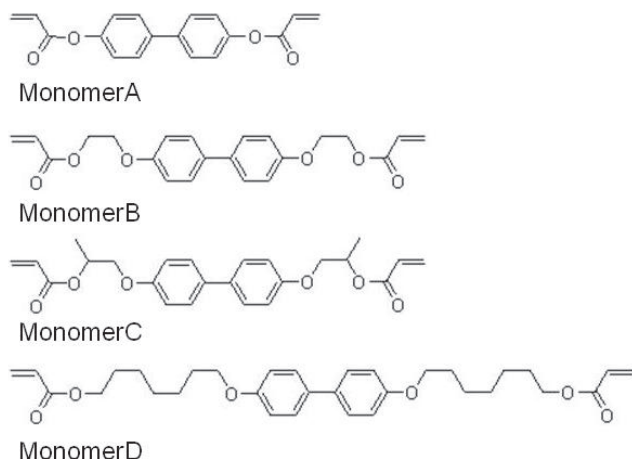
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**Fig. 1** Chemical structure of RM monomers. Monomer B, C: proposed monomers [6] in this paper. Monomer A, D: reference monomers [6], [11].

A nematic LC having a negative dielectric anisotropy ( $\Delta\epsilon = -2.1$  and  $\Delta n = 0.116$ ) is used. The concentration of UV curable RM monomer (Fig. 1) for the total compositions is 0.5 wt%~1.0 wt% and a photo-initiator (Benzoin isopropyl ether) is doped for promoting its photo-polymerization reaction, mass concentration of 1% for the UV curable RM monomer.

After filling the LC composition into a cell in nematic phase, the cell is irradiated by UV light source using (Hg-Xe lamp) to polymerize the monomer under the application of electric field at room temperature. The intensity of UV light was 3 mW/cm<sup>2</sup> (365 nm) and the irradiation time was 10 min. The applied voltage was 3 V, which is slightly larger than the threshold voltage of the LC composition.

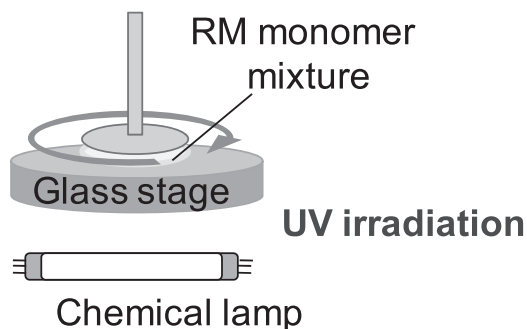
Then the UV curable RM monomers are polymerized in a certain direction so as to produce a favorable pretilt, which is maintained even after removing the voltage. A crystal rotation method was adopted for measuring the pretilt angle.

A He-Ne laser (632.8 nm) was used to characterize the electro-optical properties of the cell, which was sandwiched between a pair of crossed-polarizers as its, rubbing direction is posed 45° to the transmission axis. The dependence of transmittance on applied voltage and both response time of rising and falling for each PSVA-LCD-cell were measured. The response time was defined as the time for 90% of relative change in its transmittance to initial state after a pulse of voltage was applied. The dependence of capacitance on applied voltage was measured by the impedance analyzer to detect a change of LC orientation under the applied field.

Durability for the alignment with a pretilt stabilized by polymerized monomer was evaluated by detecting a changes of optical properties after storage at 80°C with field of 10 volts for 500 hours.

## 2.2 Measurement Method of Curing Speed Rate of RM Monomers

9wt.% of UV curable RM monomer (Fig. 1), 1 wt% of



**Fig. 2** Schematic diagram of the method for measurement of shear modulus ( $G'$ ) for the mixture comprising each RM monomer.

Polytetramethylene glycol diacrylate (A-PTMG-65, Shin-Nakamura Chemical Co., Ltd.) and Benzoin isopropyl ether (TCI) as a photo-initiator which concentration was 1 wt% for UV curable monomer were homogeneously solved in DMF solvent without dissolved monomer after being stirred at 100°C for 1 hour. A change of viscoelastic characteristics for the mixture during photo-polymerization reaction under UV irradiation was observed with 1% of shear strain after setting the mixture on the glass stage of Rheometer (Physica MCR-301, Anton Paar). The gap between the glass stage and its spindle (detector) was controlled to be 0.4 mm in distance. A chemical lamp (FL15BL, NEC Corporation) was used as an UV light source and the intensity was 0.3 mW/cm<sup>2</sup> through the glass stage. The temperature of the mixture comprising RM monomer on the glass stage was controlled to be at 25°C. Figure 2 shows a schematic diagram of the method for measurement of shear modulus ( $G'$ ) for the composition of RM monomer.

## 3. Results and Discussions

### 3.1 Characteristics of PSVA-LCD

Table 1 shows the results of tilt angle of each VA-LCD at zero fields. The tilt angle = 0° is defined as the direction for vertical alignment of LC to a glass substrate. A tilt angle of monomer-free VA-LCD cell was controlled only by the rubbed alignment layers. The tilt angles of PSVA-LCDs are larger than that of monomer-free VA-LCD. The tilt angles depend on the content of RM monomers so as to increase, the induced tilt angles according to the content of RM monomer. It is clearly shown in the Table 1 that an orientation of LC is supported by the polymer phase.

Figure 3 shows the dependence of relative capacitance of VA-LCDs in this study on its applied voltage. The PSVA-LCD by every RM monomer shows a lower  $V_{th}$  than that of monomer-free VA-LCD. Figure 4 shows the voltage-transmittance (V-T) characteristics for VA-LCDs. The PSVA-LCDs by Monomer B and Monomer C show lower  $V_{th}$ s than that of Monomer-free VA-LCD. On the other hand, PSVA-LCD by Monomer A and Monomer D show the same or slight higher  $V_{th}$ s than that of Monomer-free VA-LCD.

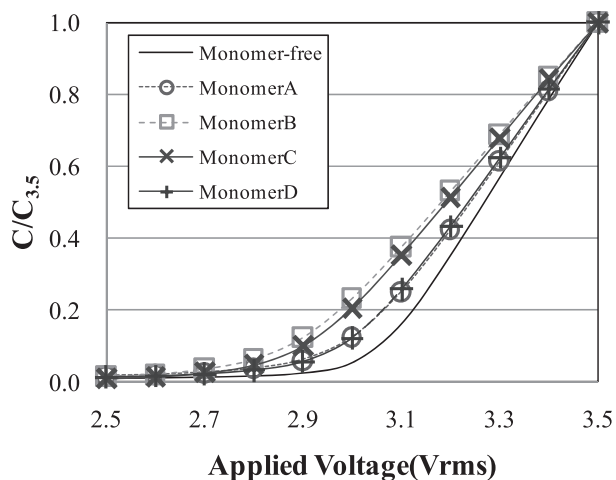
**Table 1** Results of tilt angle of VA-LCDs.

	Tilt angle (°)	Tilt angle (°)
Monomer-free	0.4	-
	monomer content:0.5wt%	monomer content:1.0wt%
Monomer A	0.8	1.6
Monomer B	1.0	2.0
Monomer C	0.8	1.5
Monomer D	0.9	1.2

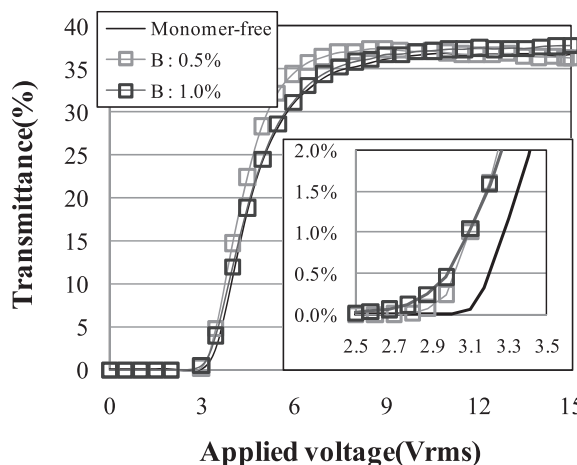
**Table 2** Comparison of response time (msec) for VA-LCDs including PSVA-LCDs by various RM monomers (monomer content: 0.5 wt%) measured at 25°C.

measured at 25 °C.			
	Rise time	Fall time	Total time
Monomer-free	7.62	5.23	12.89
Monomer A	6.23	4.18	10.41
Monomer B	4.85	4.51	9.36
Monomer C	5.64	4.06	9.72
Monomer D	6.37	6.65	13.02

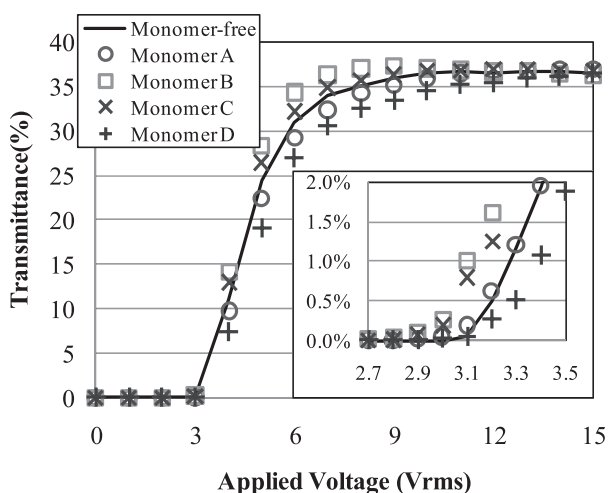
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**Fig. 3** The dependence of relative capacitance for VA-LCDs including PSVA-LCDs by various RM monomers (monomer content: 0.5 wt%) in this study on applied voltage.



**Fig. 5** The dependence of transmittance for PSVA-LCDs by Monomer B (monomer content: 0.5 wt%, 1.0 wt%) and Monomer-free VA-LCD on applied voltage.



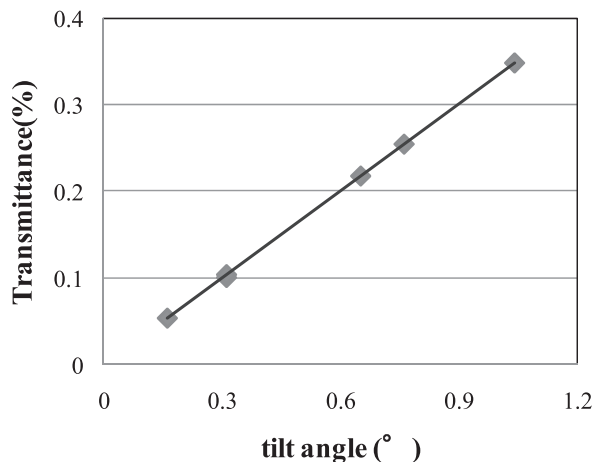
**Fig. 4** The dependence of transmittance for PSVA-LCD by each RM monomer (monomer content: 0.5 wt%) and monomer-free VA-LCD in this study on applied voltage.

Table 2 shows the response time of each VA-LCD measured at 6 V of its driving voltage. The rise response time for PSVA-LCDs are effectively shorter than that of monomer-free VA-LCD in which alignment of LC is sustained by rubbed alignment layer. It is remarkable that those fall re-

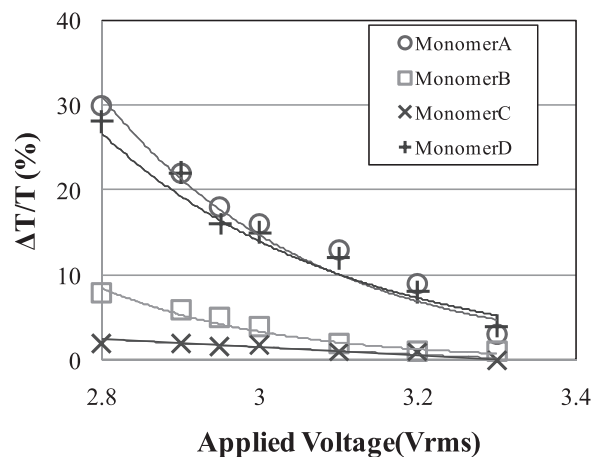
sponse times are also improved in case of PSVA-LCDs by Monomer B and Monomer C. It is supposed that characteristics such as elastic modulus, density and anchoring energy to LC and so on of polymer phase on the substrate affect those electro-optical characteristic and response characteristic of PSVA-LCD. PSVA-LCD by Monomer D shows slower fall response than the other PSVA-LCDs in this study. One of the cause might be that its tilt on the substrate is less stable by the polymer phase which contains LC molecule in a larger amount because of its higher reaction rate in polymerization.

Figure 5 shows the dependence of monomer content on its V-T characteristics for PSVA-LCD by Monomer B. A larger content of Monomer B leads to a lower Vth in a threshold voltage range. Mobility of liquid crystal molecule in PSVA-LCD by larger content of Monomer B might be restricted in a higher voltage range on its V-T characteristics.

Figure 6 shows the dependence of tilt angle on transmittance of several PSVA-LCDs at field off state in careful measurement because transmittance of PSVA-LCD is almost proportional to its tilt angle in small pretilt region. In the aspect of content of RM monomer, a larger amount of monomer leads to a slower fall response and lower contrast ratio because the polymer phase might not affect an alignment of LC only near the alignment layer but also that of LC a little way from the alignment layer [17].



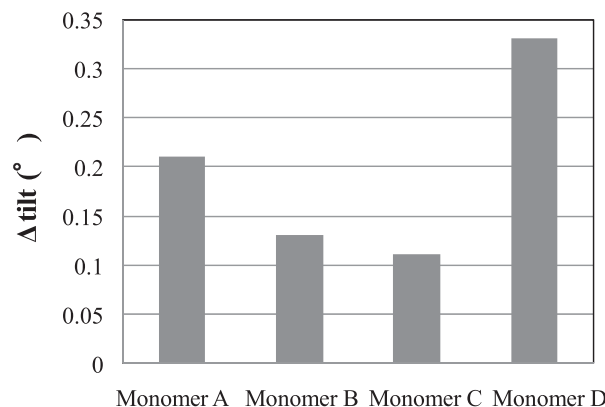
**Fig. 6** The dependence of tilt angle and transmittance of PSVA-LCD at field off state.



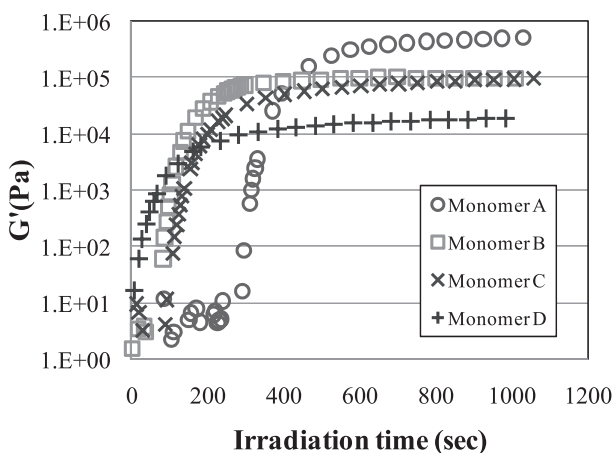
**Fig. 7** Relative changes of transmittance on applied voltage for PSVA-LCDs (monomer content: 0.5 wt%) after storage at 80° with field for 500 hrs.

Figure 7 shows relative changes of transmittance on applied voltage for PSVA-LCDs after storage at 80°C with field of 10 volts for 500 hours. Vertical axis indicates a relative change value to the transmittance value before storage. The PSVA-LCDs by Monomer A and Monomer D show large changes of transmittance value around  $V_{th}$ s. On the other hand, the PSVA-LCDs by Monomer B and Monomer C show little changes of transmittance value around  $V_{th}$ s.

Figure 8 shows the estimated change value of the tilt angle ( $\Delta$ tilt) for PSVA-LCD by each RM monomer according to Fig. 6. It is shown that the  $\Delta$ tilt angles of PSVA-LCDs by Monomer A and Monomer D are larger than that of PSVA-LCDs by Monomer B and Monomer C. These results indicate that the RM monomers which have short length spacers give a better stability to the PSVA-LCDs. The stability of PSVA-LCD depends on various factors, such as a kind of monomer material, its content, an applied voltage level during polymerization, UV energy for polymerization and so on. It is remarkable that PSVA-LCDs by Monomer B and Monomer C show a few image sticking phenomena



**Fig. 8** The estimated value of  $\Delta$ tilt angles for PSVA-LCDs (monomer content: 0.5 wt%) after storage at 80°C with field for 500 hrs.



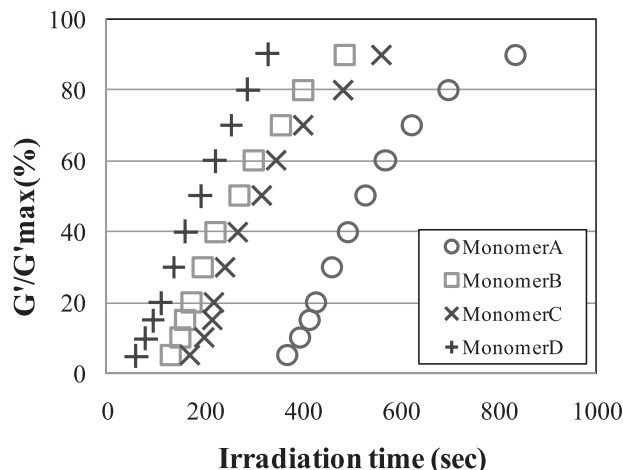
**Fig. 9** Change of shear modulus ( $G'$ ) of the mixture comprising each RM monomer during photo-polymerization by UV light irradiation.

comparing with PSVA-LCDs by Monomer A and Monomer D.

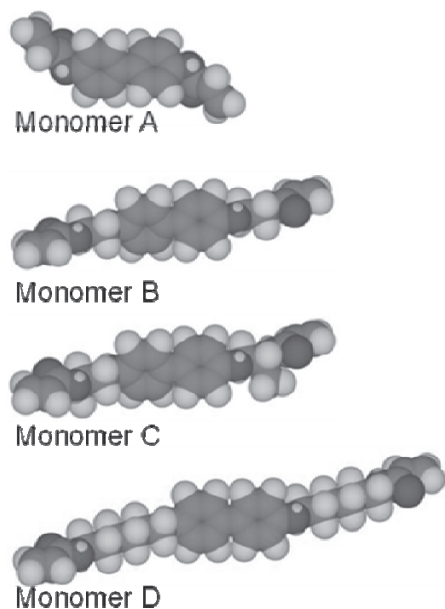
### 3.2 Reactivity of RM Monomer to UV Light and Characterization of the Polymer Phase

Figure 9 shows the shear storage modulus ( $G'$ ) of the mixture comprising each RM monomer in DMF solvent with photo-initiator during photo-polymerization by UV light irradiation.  $G'$  of the mixtures becomes higher and saturated on proceeding in polymerization. The saturated value of  $G'$  for each RM monomer mixture depends on its chemical structure, especially the spacer length of alkyl chain between the core mesogen structure and reactive acrylic moiety. It is suggested in Fig. 9 that a longer alkyl spacer leads to a lower  $G'$  for the mixture in the saturated value.

Relative change of  $G'$  to the saturated value for the mixture comprising each RM monomer during photo-polymerization by UV light irradiation is shown in Fig. 10. It is indicated that the structure of alkyl spacer in RM monomer strongly affects its rate of polymerization. Figure 8 suggests that better flexibility of the reactive acrylic



**Fig. 10** Relative change of shear modulus ( $G'$ ) to the saturated value for the mixture comprising each RM monomer during photo-polymerization by UV light irradiation.



**Fig. 11** Schematic diagram in 3D molecule model of chemical structure for each RM monomer.

moiety leads to faster reaction in polymerization because a longer alkyl chain results in better flexibility of the acrylic moiety. Besides, it is supposed that Monomer C shows a little slower reaction than Monomer B because methyl side chain in Monomer C might restrict the mobility of its methylene spacer.

Figure 11 shows the chemical structure in 3D molecule model for each RM monomer. The chemical structure of Monomer A suggests that molecular conformation of the acrylic moiety of Monomer A is very restricted and the polymer seems to be rigid without flexibility because the acrylic moiety directly bonded to core mesogen structure, which has a very little mobility in reaction of polymerization. A larger amount of UV light irradiation might be required for

the completeness of polymerization for a lower reactivity. A small amount of decomposition for LC in PSVA-LCD by UV energy or a remaining monomer after polymerization might result in less reliability because of its lower resistivity for PSVA-LCD. Furthermore, it is suggested that the change of LC alignment by applied field during storage at high temperature could be easy to stick on the polymer-stabilized alignment layer as shown in Fig. 6 and Fig. 7 because the rigid polymer phase by Monomer A has little flexibility. It is reported that a rigid alignment layer induced a severe image sticking in phase transition of chiral-nematic LCD [18].

On the other hand, the long C6 spacer between the core mesogen structure and reactive acrylic moiety in Monomer D gives a high reaction rate in polymerization and comparatively low shear modulus of the polymer phase. It is supposed that the polymer phase might have less stable orientation of LC on the polymer-stabilized alignment layer because containing LC molecule in a larger amount induced by its high reaction rate in polymerization and its flexibility caused by the long spacer in its chemical structure result in too soft polymer phase by Monomer D.

Suitable length of alkyl spacers both in Monomer B and Monomer C give a better reliability with less image sticking at high temperature with field and an improved reaction rate in polymerization.

#### 4. Conclusion

Dependence of a display performance for PSVA-LCD on the chemical structure of RM monomer from which the polymer phase is made was studied in the aspect of the durability and reaction rate in this paper. Design of alkyl spacer between the core mesogen structure and reactive acrylic moiety in RM monomer is important factor for improvement of the display performance. PSVA-LCD by RM monomer which has a short alkyl chain such as ethylene or propylene shows a stable orientation of LC after storage at high temperature with field and good reaction rate in polymerization.

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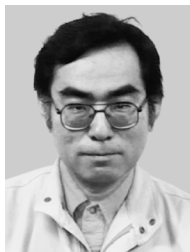
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