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Electro-optical characteristics of photo-aligned vertical-alignment cells on photo-crosslinkable copolymer surfaces containing the cholesteryl moiety

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The electro-optical (EO) performances of a photoaligned vertical-alignment liquid crystal display (VA-LCD) on a copoly(4-methacryloyloxychalcone–cholesteryl methacrylate) surface for homeotropic LC alignment were studied. Good thermal stability of the synthesized photo-crosslinkable copolymer was seen during thermogravimetric analysis. A good voltage–transmittance curve and fast response time achieved in the photoaligned VA-LCD with obliquely polarized UV exposure at 30° from the vertical on the photo-crosslinkable copolymer surfaces. The EO characteristics of the photoaligned VA-LCD decreased after long time UV exposure because of dissociation of the ester linkage in the chalcone structure of the photo-crosslinkable polymer.

1. Introduction

Liquid crystal displays (LCDs) are widely used for notebook computers and monitors because they have an excellent image quality. Large size LCD panels such as multidomain vertical-alignment (MVA) mode LCDs [1] have the advantage of saving space and consuming less power. Most LCDs with pretilted homogeneous LC alignment are prepared using a rubbed polyimide (PI) surface. The rubbing process has been widely used to align LC molecules, giving characteristics such as high transparency, uniform alignment, and pretilt angle stability. Surface LC alignment by unidirectional rubbing in nematic LCs on various PI layers has been studied by many investigators [2–7]. However, rubbing creates several problems, such as the generation of electrostatic charges and dust formation [3]. Thus rubbing-free techniques for LC alignment are required. Many investigators have proposed photoalignment methods such as photodimerization [8–14] and photodissociation [15, 16]. More recently, we have reported pretilt angles of a vertically aligned NLC on photo-crosslinkable copolymers containing chalconyl and cholesteryl moieties [14].

In this study, we report the electro-optic (EO) performances of a photoaligned VA-LCD with obliquely polarized UV exposure of a film of copoly(4-methacryloyloxychalcone–cholesteryl methacrylate), hereafter abbreviated to copoly(M4Ch-ChMA).

2. Experimental

Figure 1 shows the chemical structure of the copoly(M4Ch-ChMA) used. The polymer is synthesized from copolymers of 4-methacryl chalcone (M4Ch) and cholesteryl

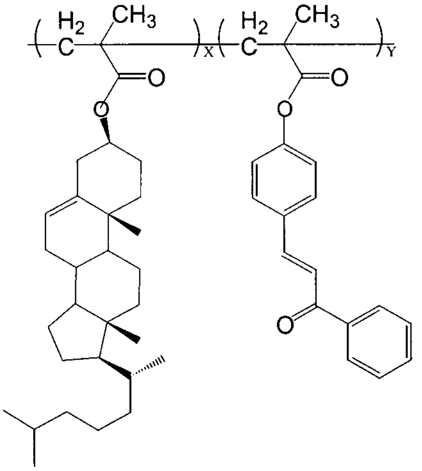

Figure 1. Chemical structure of the photo-crosslinkable copoly(M4Ch-ChMA).

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methacrylate (ChMA), which are sensitive to UV and have vertical alignment ability [13]. Table 1 shows the composition of the copolymers used in this study. The polymers were spin-coated onto indium tin oxide (ITO) coated glass substrates, and were then cured at 150°C for 1 h; the polymer layer thickness was 400 Å. Figure 2 shows the UV exposure system used in this study. The UV source was a 500 W Xe lamp, and substrates were exposed to UV light of wavelength 365 nm. The UV exposure time was 1, 3 or 7 min. To measure the pretilt angle of the NLC, a cell was fabricated with an anti-parallel structure by polarized UV exposure in the oblique direction on the copoly(M4Ch-ChMA) surfaces. The thickness of the LC layer was 60 μm. To measure the EO characteristics of a photoaligned VA-LCD, a cell was fabricated with anti-parallel structure with obliquely polarized UV exposure at 30° on the copoly-(M4Ch-ChMA) surface. The LC layer thickness for the VA-LCD was 4.25 μm. The rubbing-aligned VA-LCD was assembled at medium rubbing strength (164 mm) for comparison with a photo-aligned VA-LCD [2, 3]. A nematic LC was used in negative-type dielectric anisotropy ($\Delta\varepsilon = -3.8$). The NLC was used MJ951294 (Merck). The NLC pretilt angles were measured by the crystal rotation method at room temperature. Voltage–transmittance (*V–T*) and response time measurements of the photo-aligned VA-LCD were performed at room temperature (DMS-501, for autronic-MECHRS GmbH).

3. Results and discussion

The three kinds of copolymer were studied by thermogravimetric analysis (TGA); see figure 3. The TGA results demonstrated satisfactory thermal stabilities for all of the synthesized copolymers.

Table 1. Compositions of the photo-crosslinkable copoly-(M4Ch-ChMA).

Polymer	*X*/%	*Y*/%
Copolymer-1	2	98
Copolymer-2	8	92
Copolymer-3	20	80

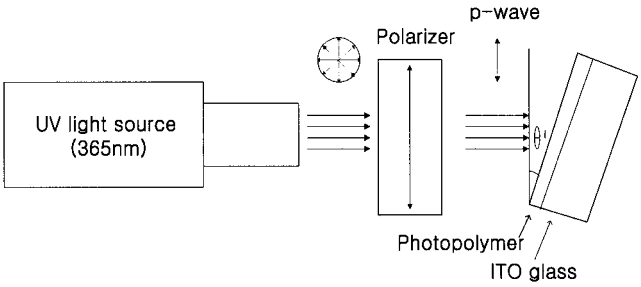

Figure 2. UV exposure system.

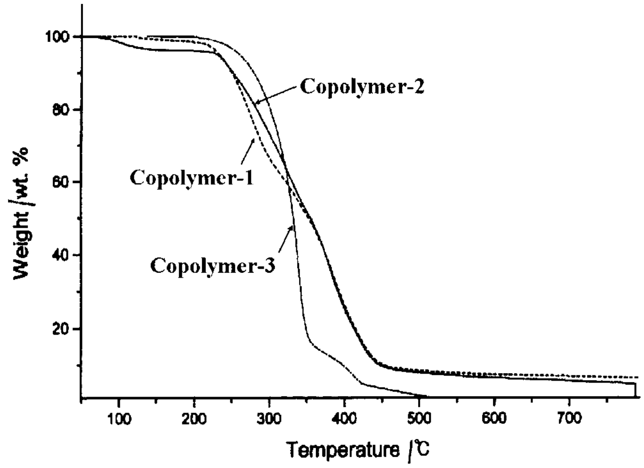

Figure 3. TGA curves for the three photo-crosslinkable copolymers used.

The generated NLC pretilt angle was about 90° for all incident angles on the surfaces of the three copolymers. Figure 4 shows the NLC pretilt angles obtained by linearly polarized UV exposure on the three types of copolymers as a function of exposure time. Pretilt angles of about 90° for all exposure times on the copolymer-1 surface. However, a reduction of about 3°∼9° was observed for UV exposure for 3 min on the copolymer-2 and copolymer-3 surfaces. On the copolymer-3 surface, the NLC pretilt was about 81° for a UV exposure of 3 min.

Figure 5 shows micrographs of a vertically-aligned negative-type NLC with 1 min UV exposure on (*a*) cholesteric only film, and on (*b*) copolymer-1 in homeotropic alignment; also (*c*) of a homogeneously-aligned

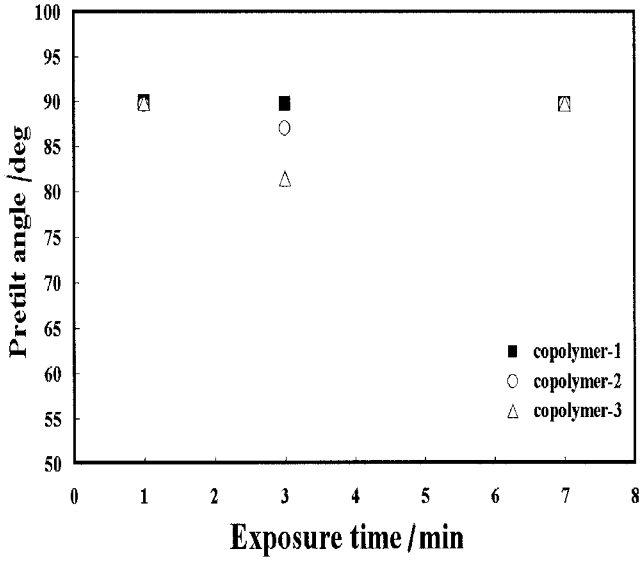

Figure 4. NLC pretilt angles generated by linearly polarized UV exposure at 30° on the three types of copolymer, as a function of exposure time.

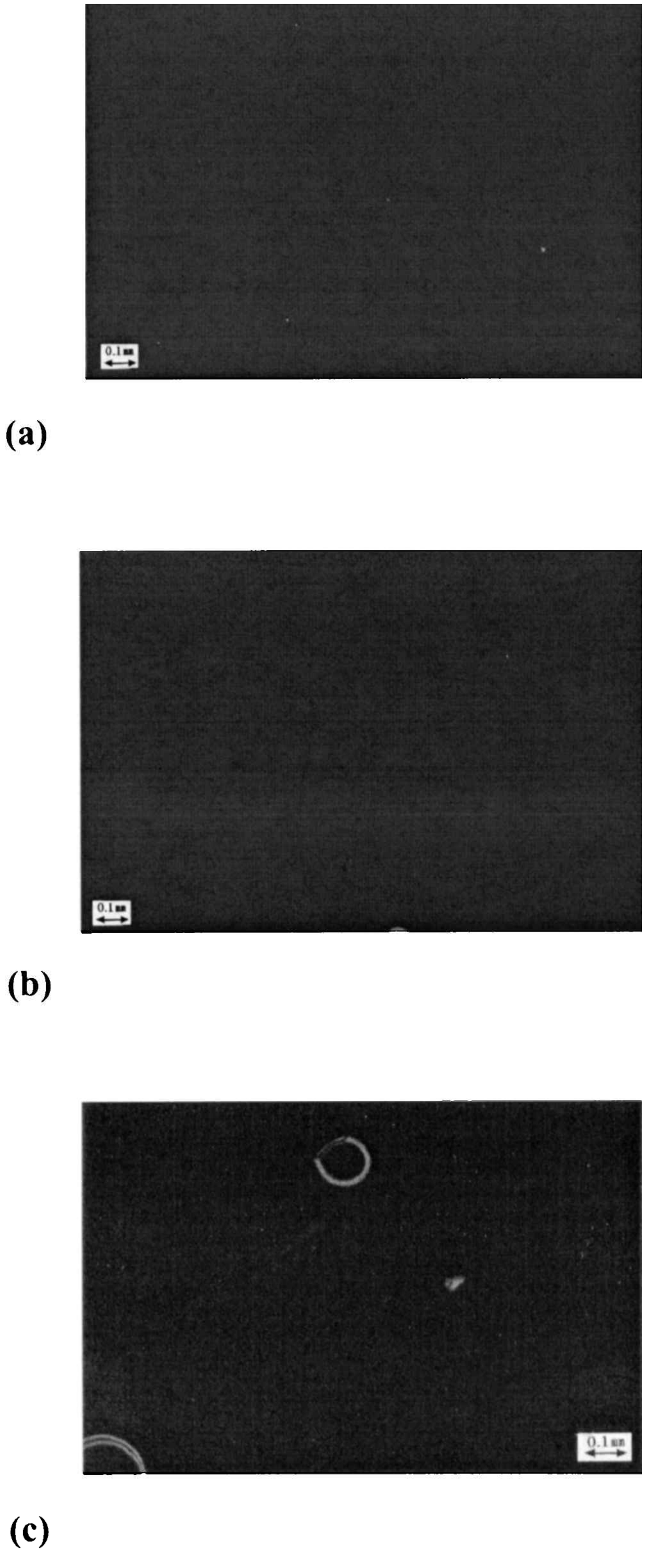

Figure 5. Micrographs of aligned NLC after UV exposure for 1 min on (*a*) cholesteric only (homeotropic alignment), (*b*) copolymer-1 (homeotropic alignment) and (*c*) chalcone only (homogeneous alignment); viewed via crossed Nicols.

positive-type NLC with 1 min UV exposure on chalcone only film. Monodomain alignment of the NLC was obtained.

The *V–T* curve and temporal response of a conventional VA cell, rubbing-aligned on homeotropic PI surfaces, are shown in figure 6. Figure 7 shows the *V–T* and response time characteristics for photoaligned VA-LCD with obliquely polarized UV exposure at 30° on copolymer-1 surfaces. From figure 7 (*a*), it can be seen that good *V–T* characteristics for a UV exposure of 1 min were obtained. Thus the *V–T* characteristics for a photo-aligned VA cell with polarized UV exposure on

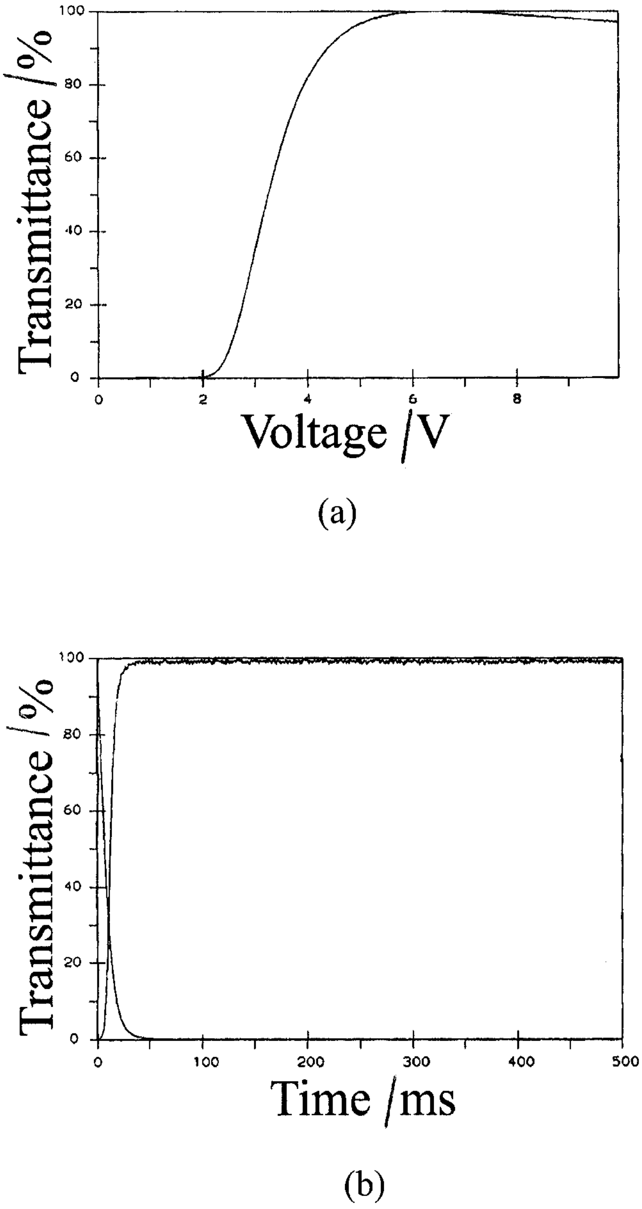

Figure 6. *V–T* curve (*a*) and temporal response (*b*) of a conventional VA-cell, rubbing-aligned on homeotropic PI surfaces.

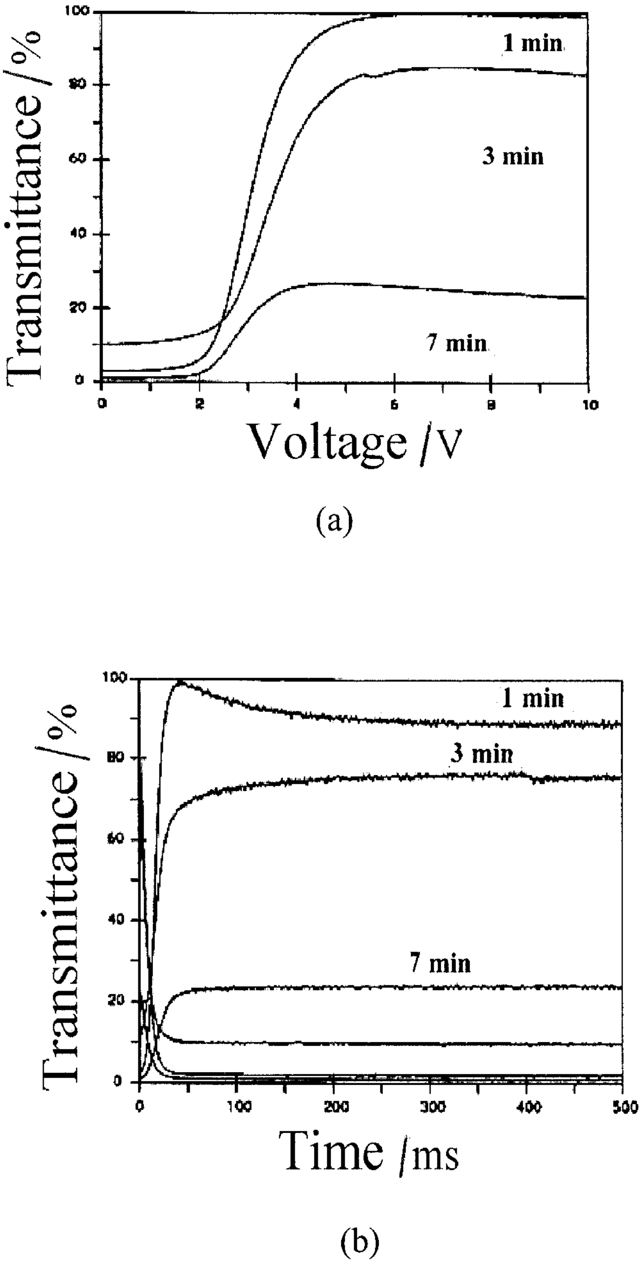

Figure 7. *V–T* and response time characteristics in photo-aligned VA-cells with polarized UV exposure at 30° on photo-crosslinkable copolymer-1 surfaces.

the copolymer surfaces were the same as for a rubbing-aligned VA cell. However, light leakage in the OFF state was seen. Also, the transmittance decreased with increasing UV exposure and reached 20% of the maximum transmission in the cell exposed for 7 min. It is considered that the transmittance in the photoaligned VA-LCD decreased as a result of dissociation of the ester linkage in the cinnamate structure of the photopolymer above 1 min of UV exposure time. Thus increasing UV exposure time decreased the NLC alignment. A good response time for the photoaligned VA-LCD with 1 min UV exposure was measured, as shown in figure 7 (*b*). The response time for the VA-LCD decreases with increasing UV exposure time. It is considered that the EO characteristics deteriorated due to dissociation of the ester linkage in the photo-crosslinkable chalcone structure on the synthesized copolymer containing the chalcone and low cholesteryl moiety (2%) at above 1 min of UV exposure time.

It seems that non-reacted polymer main chain can align toward the UV exposure direction due to photo-reacted chalcone resulting from high UV exposure energy because T_g of the polymer is low. The polymer surface has a high temperature, therefore non-reacted chalcone of the polymer can convert to photo-reacted chalcone. Due to the alignment of chalcone in the UV direction, the LC aligning capabilities increased with the increasing photo-dimerization reaction for short UV exposure times. However, the LC aligning capabilities decreased because of the movement of photodimerized chalcone with increasing UV exposure time. This motion affected the NLC response time, resulting in slower response times with increasing UV exposure time. Therefore, the slow response time of the photoaligned VA-LCD is attributable to LC aligning decrease resulting from the movement of photodimerized chalcone and dissociation of the ester linkage in the photo-crosslinkable chalcone structure of the copolymer-1 for long UV exposure times.

V–T and response time characteristics for photo-aligned VA-LCDs with obliquely polarized UV exposure at 30° on copolymer-2 surfaces are shown in figure 8. Good *V–T* curves for all UV exposure times were observed, as shown in figure 8 (*a*). A good response time with UV exposure of 3 min was measured, as shown in figure 8 (*b*), but a 7 min UV exposure gave low transmittance and poorer response time. The response time for the VA-LCD improved with increasing UV exposure time.

Figure 9 shows the *V–T* and response time characteristics for photoaligned VA-LCDs with UV exposure on copolymer-3 surfaces. As shown in figure 9 (*a*), the best *V–T* curve is observed in the VA-cell with a 3 min UV exposure; furthermore, the fastest response time is observed in the same VA-cell as shown in figure 9 (*b*). However, the lowest transmittance and the longest response time was observed in the VA-cell with a UV exposure of 7 min. This lowest transmittance and the longest response time is attributable to decrease of LC aligning because of the movement of photodimerized chalcone and dissociation of the ester linkage in the photo-crosslinkable chalcone structure of the copolymer after long UV exposure.

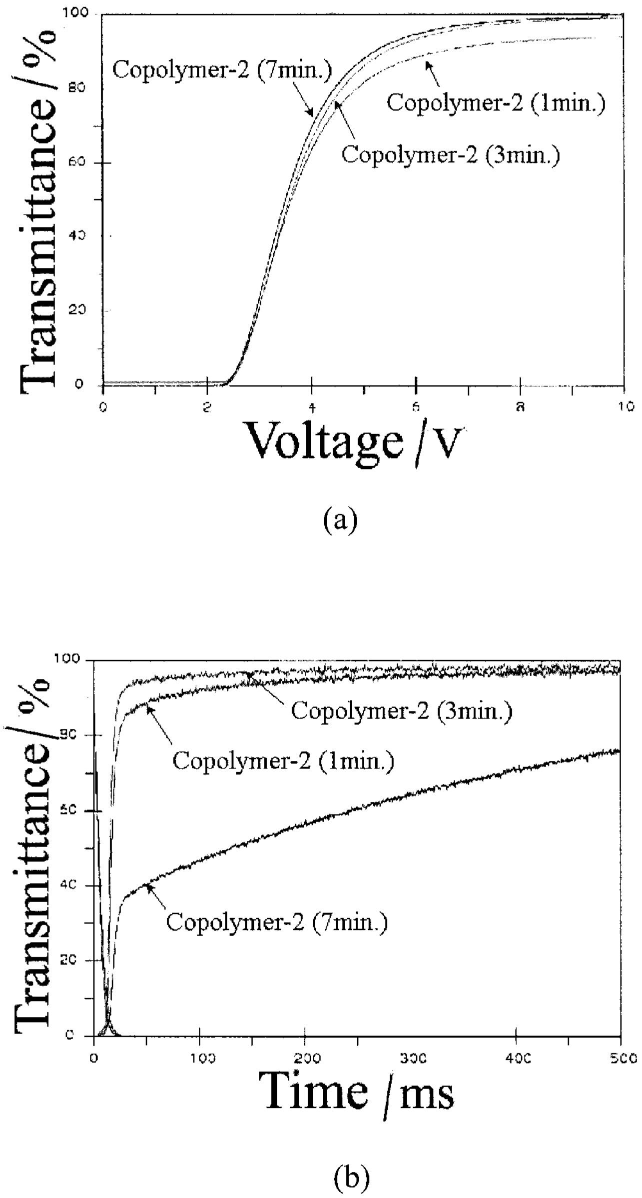

Figure 8. *V–T* (*a*) and response time (*b*) characteristics in photoaligned VA-cells with polarized UV exposure at 30° on photo-crosslinkable copolymer-2 surfaces.

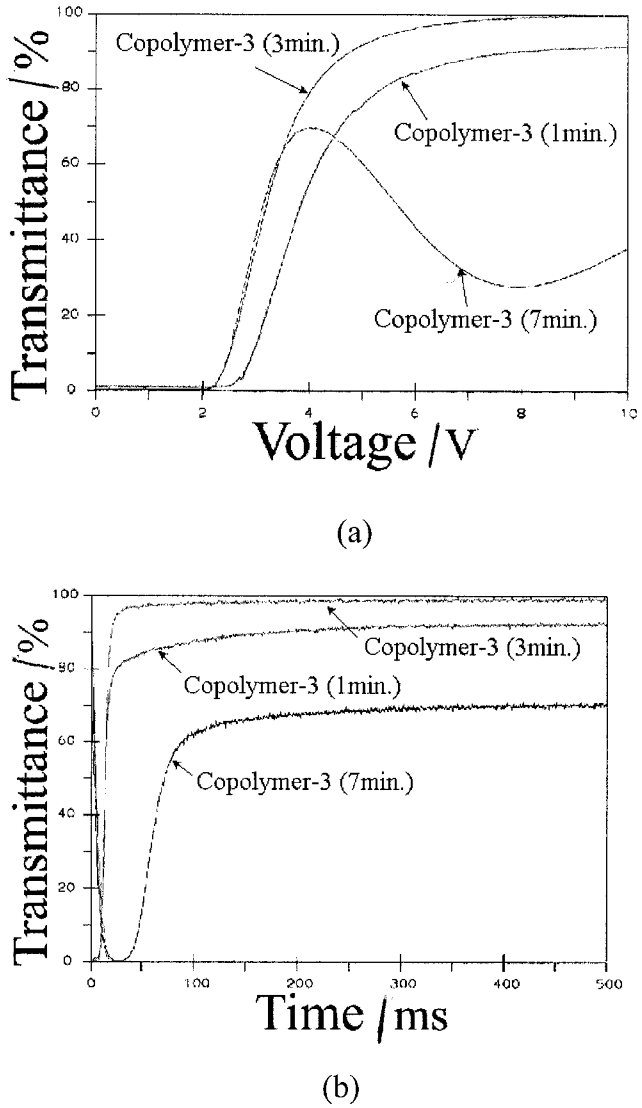

Figure 9. *V–T* (*a*) and response time (*b*) characteristics in photoaligned VA-cells with polarized UV exposure at 30° on photo-crosslinkable copolymer-3 surfaces.

Table 2. Threshold voltages in photoaligned VA-cells on the three kinds of photo-crosslinkable copolymers surface.

	V_{th}		
Alignment film	1 min	3 min	7 min
Copolymer-1	2.34	2.52	2.18
Copolymer-2	2.75	2.76	2.77
Copolymer-3	2.94	2.49	2.45
Rubbing-aligned		2.54	

Threshold voltages for photoaligned VA-LCDs on various copolymer surfaces are shown in table 2. The threshold voltage for UV exposure on copolymer-1 surfaces for 1 min was about 2.34 V. A good threshold voltage of 2.49 V for a 3 min UV exposure on copolymer-3 surfaces was also observed. The threshold voltage for photoaligned VA-LCDs was similar to that for rubbingaligned VA-LCDs.

Table 3 shows the response times (rise time plus fall time) for the three kinds of photoaligned VA-LCDs on copolymer surfaces. The response time for the photoaligned VA-LCD with a 3 min UV exposure on copolymer-3 surfaces was 31.3 ms. Fast response times were also observed for UV exposure on copolymer-1 for 1 min, and on copolymer-2 for 3 min—39.3 and 33.5 ms, respectively. We consider that the LC aligning capabilities

Table 3. Response times in photoaligned VA-cells on the three kinds of photo-crosslinkable copolymer surface: τ_r = rise time, τ_d = decay time.

Alignment film	Time	
	τ_r/ms	τ_d/ms
Copolymer-1 (1 min)	16.2	23.1
(3 min)	16.1	50.4
(7 min)	18.4	40.3
Copolymer-2 (1 min)	10.9	35.2
(3 min)	11.1	22.4
(7 min)	12.7	314.0
Copolymer-3 (1 min)	10.1	34.4
(3 min)	11.8	19.5
(7 min)	14.4	103.3

were increased by the photodimerized chalcone groups on the copolymer-2 and the copolymer-3 surface after 3 min of UV exposure. But for all the copolymers, the longest response time is observed in the VA-cells on substrates exposed for 7 min. Rise time was the same as that for substrates exposed for 1 and 3 min; however a slow response time was particularly seen in the decay time (τ_d). The cholesteryl groups contribute to homeotropic alignment and the photodimerized chalcones contribute to the LC direction on the copolymers. The LC aligning capabilities decreased with increasing UV exposure time because the photodimerized chalcones dissolved into the ester linkage (−COO−) of weak combinations in the photodimerized chalcones caused by high energy density. Also, the glass transition temperature (T_g: 110°C) of the copolymer was low due to the flexible acrylate chains in the backbone structure. Thus azimuthal anchoring energy is weak in the photoaligned VA-cells, and the LC aligning capabilities decreased with long UV exposure times because of fluctuation of the copolymer backbone from heating. Hence, the decrease of LC aligning capabilities caused the decrease in response times.

4. Conclusion

The EO performances of photoaligned VA-LCDs with photo-crosslinkable copolymer surfaces were investigated. *V–T* and response time characteristics in photoaligned VA-cells with polarized UV exposure of the copolymer surfaces were almost the same as for rubbing-aligned VA cells. Also, fast response times were observed for copolymer-1 substrates exposed for 1 min (39.5 ms) and copolymer-2 exposed for 3 min (33.5 ms). But in the case of all the copolymers, the longest response time was observed in VA-cells with substrates exposed for 7 min. This slow response time is attributable to LC aligning decrease caused by the movement of photodimerized chalcone and dissociation of the ester linkage in the photo-crosslinkable chalcone structure of the copolymer after long UV exposure time.

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