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Electro-optical characteristics for the photoaligned vertical alignment cell using photopolymer surfaces containing chalconyl and cholesterly groups

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A new photoalignment material, copoly(4-methacryloyloxychalcone-cholesteryl methacrylate) (copoly(M4Ch-ChMA)), was synthesized and the electro-optical characteristics for the photoaligned vertically aligned (VA) liquid crystal display (LCD) were studied. Excellent voltage-transmittance characteristics were achieved for the photoaligned VA-LCD with 1 min polarized UV exposure at an oblique direction of 30° on the copoly(M4Ch-ChMA) surfaces. The response time of the VA-LCD was about 39 ms, and increased with increasing UV exposure time. We suggest that the proportion of photodimerized chalcone group increased with increasing UV exposure time, contributing to a higher response time.

1. Introduction

The rubbing process has been widely utilized to align liquid crystal (LC) molecules. Most LC displays (LCDs) with pretilted homogeneous LC alignment are prepared with rubbed polyimide (PI) cell surfaces. They have appropriate characteristics such as high transparency, uniform alignment, and good pretilt angle stability. Surface alignment effects caused by unidirectional rubbing in nematic (N) LCs on various PI layers have been demonstrated [1–3]. However, the rubbing method creates several problems, such as the generation of electrostatic charges and contaminating particles; thus rubbing-free techniques for LC alignment are required in LC technologies [4]. Many investigators have proposed photoalignment methods such as photodimerization [5–8] and photodissociation [9–11]. More recently, we reported the synthesis of the photoalignment material poly(4-methacryloyloxychalcone) (PM4Ch), and the electro-optical (EO) performance of photoaligned TN-LCDs on PM4Ch surfaces [12].

In this study, we report the synthesis of a new photoalignment material copoly(4-methacryloyloxychalcone-cholesteryl methacrylate), copoly(M4Ch-ChMA), for homeotropic LC alignment and the EO performance of the resulting photoaligned vertical liquid (VA) LCD.

2. Experimental

Figure 1 shows the chemical structure of the copoly(M4Ch-ChMA) used. The polymer was synthesized from copolymers poly-4-methacrylchalcone (M4Ch) and cholesteryl methacrylate (ChMA), which are sensitive to UV and have vertical alignment ability. 4-Methacryloyloxychalcone (M4Ch) was first synthesized by esterification of 4-hydroxychalcone and methacryloyl chloride. In a 250 ml round-bottomed flask, 4-hydroxychalcone (4.89 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) were dissolved in 75 ml of 2-butanone and the solution was cooled to $-5 \sim 0^\circ\text{C}$ in an ice bath. Excess methacryloyl

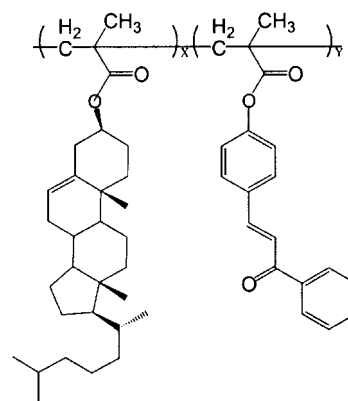


Figure 1. Chemical structure of copoly(M4Ch-ChMA).

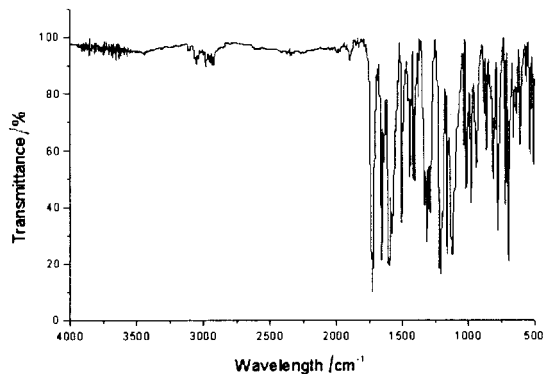
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chloride (2.6 g, 25 mmol) in 25 ml of 2-butanone was added dropwise with stirring, while maintaining the temperature at $-5 \sim 0^\circ\text{C}$. After stirring at room temperature for 4 h, the precipitated ammonium salt was filtered off; the organic layer was washed with 5% aqueous sodium hydroxide and distilled water. The crude product was dried over anhydrous magnesium sulfate, and the 2-butanone evaporated. The product was purified by column chromatography.

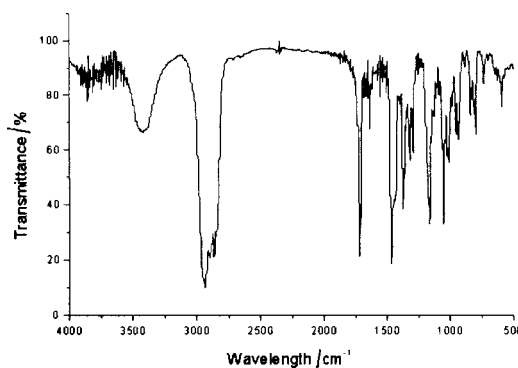
Next, cholesteryl methacrylate (ChMA) was prepared by etherification of cholesterol and methacryloyl chloride. In a 250 ml round-bottomed flask, cholesterol (7.73 g, 20 mmol) and triethylamine (2.02 g, 20 mmol) were dissolved in 75 ml of chloroform and stirred at room temperature. An excess of methacryloyl chloride (2.6 g, 25 mmol) in 25 ml of chloroform was then added dropwise with stirring, while maintaining the temperature. After stirring at room temperature for 24 h, the organic layer was washed repeatedly with 5% aqueous sodium hydroxide and distilled water, dried over anhydrous magnesium sulfate, and the chloroform evaporated off. The product was purified by recrystallization from ethanol. Figure 2 shows the FTIR spectra of M4Ch and ChMA.

Homopolymerization and copolymerization of the monomers M4Ch and ChMA were carried out as a solution polymerization in toluene using 2,2'-azobutyronitrile (2 mol%) as a initiator at 70°C . The required amounts of monomer, initiator and toluene were mixed in a flask flushed with oxygen-free nitrogen for 30 min. After 48 h at 70°C , the polymer was precipitated by addition of excess methanol. The crude polymer was purified by reprecipitation from methanol and dried under vacuum to give pure copoly(M4Ch-ChMA). We ascertained by NMR analysis that the ChMA units in the copoly(M4Ch-ChMA) was about 2%.

The polymers were coated onto indium tin oxide coated glass substrates by spin-coating, and were cured at 150°C for 1 h. The thickness of the polymer layer was 400 \AA . Figure 3 shows the UV exposure system used in this study. The UV source was a 500 W Xe lamp, giving UV light at a wavelength of 365 nm for exposure of the substrates. The UV exposure times were 1, 3, and 7 min. To measure the EO characteristics of the photoaligned VA-LCD, the cell was fabricated with an anti-parallel structure, with polarized UV exposure in the oblique direction of 30° on the copoly(M4Ch-ChMA) surfaces. A rubbing-aligned VA-LCD was assembled at medium rubbing strength (164 mm) for comparison with the photoaligned VA-LCD. The thickness of the LC layer used for the photoaligned VA-LCD was $4.25 \mu\text{m}$, and the cell thickness was $60 \mu\text{m}$ for pretilt angle measurements. The NLC as used with negative-type dielectric



(a) M4Ch



(b) ChMA

Figure 2. The FTIR spectra of M4Ch and ChMA.

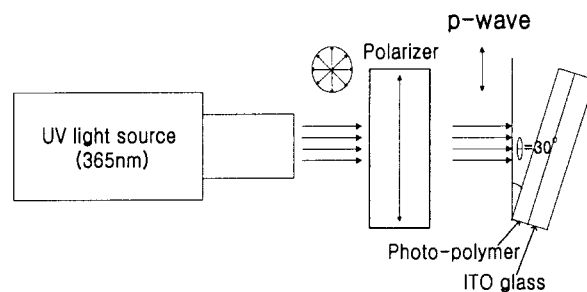


Figure 3. Schematic diagram of UV exposure system.

anisotropy ($\Delta\epsilon = -3.8$). The pretilt angle, voltage-transmittance ($V-T$), and response time measurements for the photoaligned VA-LCD were performed at room temperature.

3. Results and discussion

Figure 4 shows the thermo gravimetric analysis (TGA) characteristics of the synthesized copoly(M4Ch-ChMA); good thermal stability was indicated.

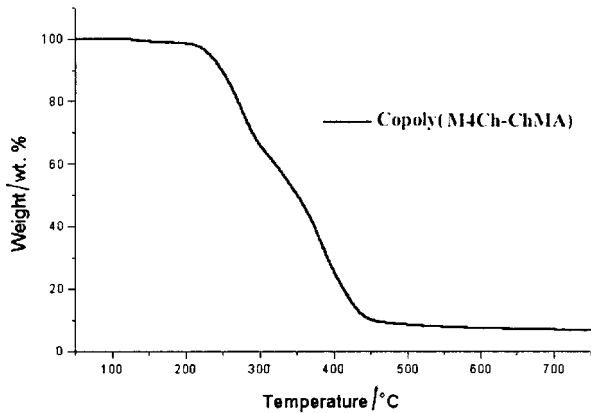


Figure 4. TGA characteristics of copoly(M4Ch-ChMA).

Figure 5 shows the transmittance versus angle of incidence in a NLC with 1 min polarized UV exposure at an oblique direction of 30° on the copolymer surface; the generated NLC pretilt angle was 89.9° . Pretilt angles of 89.8° and 89.7° were obtained with UV exposure of 3 and 7 min, respectively. Therefore, we consider that homeotropic alignment can be achieved by adding 2% of cholesteryl moiety to the chaconyl moiety.

Figures 6(a–c) shows photomicrographs of a vertically aligned negative-type NLC with UV exposure of 1, 3, and 7 min, respectively on the copolymers surface. Monodomain alignment of the NLC was obtained.

Figures 7(a) and 7(b) show photomicrographs of the photoaligned VA-LCD with 1 min polarized UV exposure at 30° on copoly(M4Ch-ChMA) surfaces; monodomain alignment of the NLC was observed. Homeotropic alignments of the NLC on copoly(M4Ch-ChMA) surfaces were achieved.

The V - T curves for the photoaligned VA-LCDs is shown in figure 8. Excellent V - T characteristics for 1 min

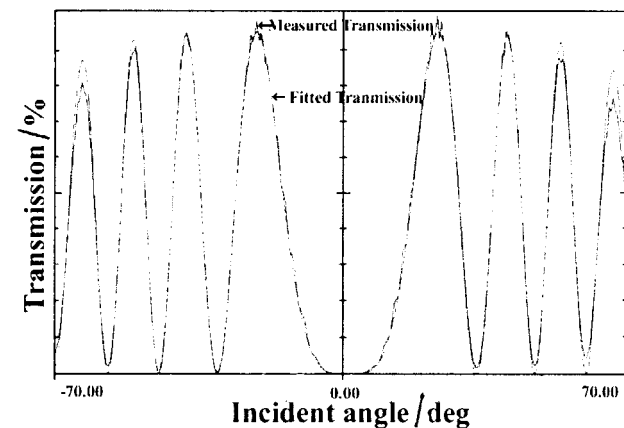
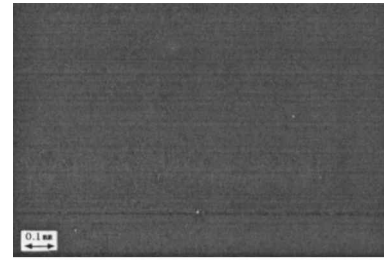
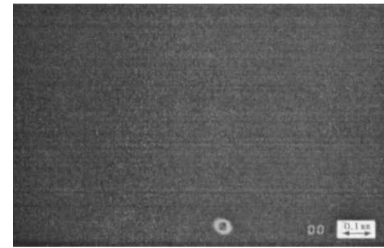


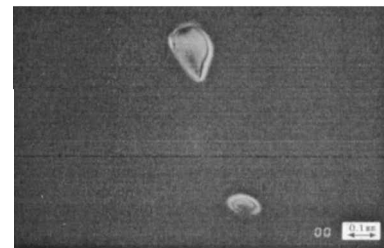
Figure 5. Transmission versus angle of incidence in NLC on the copoly(M4Ch-ChMA) surface.



(a)



(b)



(c)

Figure 6. Photomicrographs of vertically aligned NLC by UV exposure for (a) 1 min, (b) 3 min, and (c) 7 min on the copolymers (in crossed Nicols).

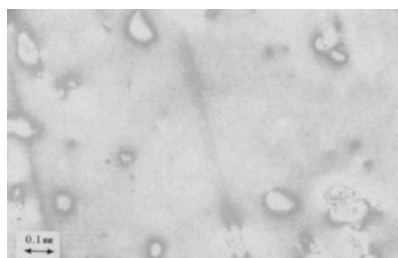
UV exposure time were observed; poor V - T characteristics for 3 and 7 min exposure were measured. The transmittances of the photoaligned VA-LCD thus decreased on increasing the UV exposure time on the copoly(M4Ch-ChMA) surfaces.

Table 1 shows the threshold voltages for various photoaligned VA-LCDs on copoly(M4Ch-ChMA) surfaces and for a rubbing-aligned VA-LCD on a PI surface. The threshold voltages for the photoaligned VA-LCDs with UV exposure for 1–7 min averaged about 2.35 V. The threshold voltage for the photoaligned VA-LCD was almost the same as that of the rubbing-aligned VA-LCD.

Figure 9 shows the response time characteristics for photoaligned VA-LCDs with 1, 3 and 7 min polarized UV exposure at 30° on copoly(M4Ch-ChMA) surfaces.

Table 1. Threshold voltages for various photoaligned VA-LCDs on copoly(M4Ch-ChMA) surfaces, and for a rubbing-aligned VA-LCD on a PI surface.

Orientation film	Threshold voltage/V	
	V_{10}	V_{90}
Copoly(MCh-ChMA) (1 min)	2.34	4.17
Copoly(MCh-ChMA) (3 min)	2.52	4.65
Copoly(MCh-ChMA) (7 min)	2.18	3.66
Rubbing-aligned	2.56	4.39



(a)



(b)

Figure 7. Photomicrographs for the photoaligned VA-LCD with linearly polarized UV exposure at 30° for 1 min on copoly(M4Ch-ChMA) surfaces (crossed Nicols); (a) on-state ($V = 5$ V), (b) off-state.

Good response time characteristics were measured for a UV exposure of 1 min. The transmittances of the photoaligned VA-LCD decreased on increasing the UV exposure time. We conclude that the UV exposure time needed to achieve good V - T curve and response time characteristics is about 1 min, as shown in figures 8 and 9.

Table 2 shows the response times for the three kinds of photoaligned VA-LCDs and for a rubbing-aligned VA-LCD on a PI surface. The response time for the photoaligned VA-LCD with UV exposure of 1 min was 39.3 ms. The response time of the photoaligned VA-LCD was almost the same as that of the rubbing-aligned VA-LCD. However, longer response times were measured for photoaligned VA-LCDs with UV exposures of 3 and 7 min. We consider that the content of photodimerized

Table 2. Response times for the three kinds of photo-aligned VA-LCDs on copoly(M4Ch-ChMA) surfaces, and for a rubbing-aligned VA-LCD on a PI surface.

Orientation	Response time/ms		
	τ_r	τ_d	τ
Copoly(MCh-ChMA) (1 min)	23.1	16.2	39.3
Copoly(MCh-ChMA) (3 min)	50.4	16.1	66.5
Copoly(MCh-ChMA) (7 min)	40.3	18.4	50.7
Rubbing-aligned	18.2	18.5	36.7

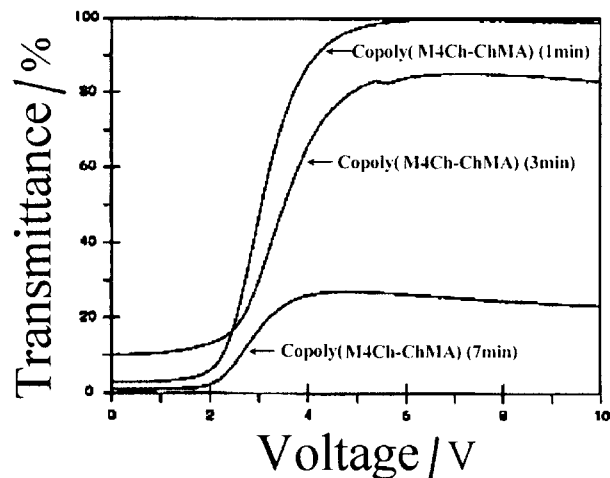


Figure 8. V - T curves for photoaligned VA-LCDs with polarized UV exposure of 1, 3 and 7 min at 30° on copoly(M4Ch-ChMA) surfaces.

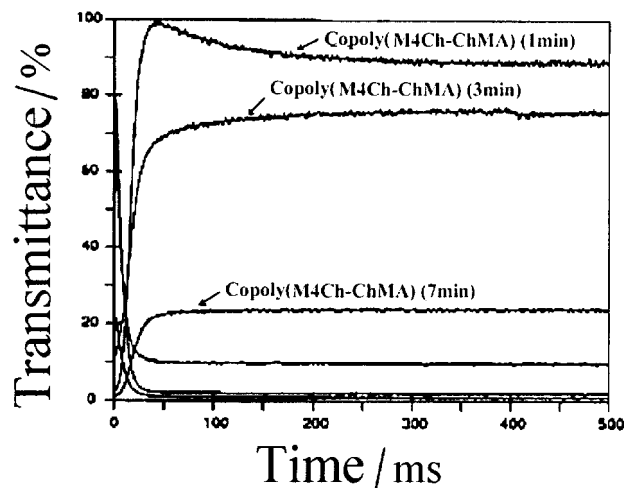


Figure 9. Response time characteristics for photoaligned VA-LCDs with linearly polarized UV exposure at 30° on the copoly(M4Ch-ChMA) surfaces.

chalcone groups increases with increasing UV exposure time, contributing to longer response times for the photoaligned VA-LCD.

4. Conclusion

A new photoalignment material, copoly(M4Ch-ChMA), was synthesized and the EO performances for photoaligned VA-LCDs were studied. Good thermal stability of the synthesized copoly(M4Ch-ChMA) was observed by TGA measurement. Uniform alignment of the NLC was observed for VA-LCDs photoaligned with UV light. Excellent $V-T$ characteristics for a photoaligned VA-LCD with 1 min UV exposure of the copoly(M4Ch-ChMA) surfaces were achieved. The response time of the photoaligned VA-LCD after UV exposure for 1 min was 39.3 ms, almost the same as that of the rubbing-aligned VA-LCD. We suggest that slower response times of the photoaligned VA-LCD are related to the increase of photodimerized chalcone groups on increasing the UV exposure time of the copoly(M4Ch-ChMA) surfaces.

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