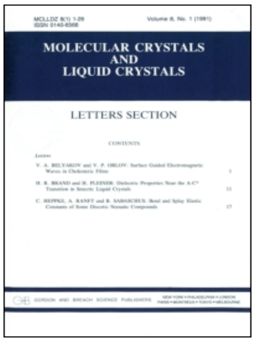
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Vertical alignment of liquid crystals using novel self-assembled molecular layer of alkylated benzoic acid derivatives

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ABSTRACT
The one-step vertical alignment of liquid crystals (LCs) was achieved by forming a novel self-assembled molecular layer of alkylated benzoic acid derivatives on an indium tin oxide substrate through hydrogen bonding. This method utilizes the simple doping of the alignment material into the LCs. The assembled molecular layer promoted the stable homeotropic LC alignment. The electro-optical characteristics of LC devices exhibited stable vertical alignments and fast response times, depending on the number of rigid aromatic rings in the alignment material. Our simplified alignment method allows the fabrication of LC devices without a separate alignment step for fast LC switching.

KEYWORDS
Benzoic acid derivative; liquid crystal alignment; molecular layer; self-assembly

Introduction

Liquid crystal (LC) displays are operated in various LC modes such as in-plane switching (IPS), twisted nematic (TN), and vertical alignment (VA). Among these, the VA mode offers high contrast ratios, wide viewing angles, and fast falling times [1–3]. To realize VA mode, a uniform initial alignment of the LCs is essential; this has typically been achieved through the application of a polyimide layer containing alkyl side chains. This conventional polyimide alignment method has several disadvantages, such as electrical sensitivity reduction by the thick polymeric layer and long processing times. To overcome these deficits, the use of self-assembled layers that use small molecules to align the LCs has been employed. Typically, silane functional groups have been selected for binding with the indium tin oxide (ITO) substrate [4–8]. However, long processing times are required to form the self-assembled layers by this alignment method. There is also the risk of contamination in LC devices, which is caused by impurities from chemical reactions of the silane groups. Except for small molecules, other methods use polymeric materials such as polypropyleneimine dendrimers and polyhedral oligomeric silsesquioxanes (POSS) [9–13]. However, uniform alignment of macromolecules is difficult, giving rise to the possibility of light leakage.

In this study, we propose a novel alignment method using a self-assembled molecular layer of alkylated benzoic acid derivatives. The carboxyl group-containing alignment materials can hydrogen bond to the oxygens of the ITO substrate. The hydrogen-bonded alignment materials orient perpendicularly to the ITO substrate, resulting in the alignment of the LCs. The proposed method utilizing hydrogen bonding is differentiated from other alignment methods

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and offers advantages such as low concentrations and simplified process steps. Furthermore, we investigated the alignment effect according to the number of rigid aromatic rings in the alignment material through electro-optical performance measurements.

Experimental

Undecanoic acid (B0, TCI), 4-*n*-octylbenzoic acid (B1, TCI), and 4-(4-heptylphenyl)benzoic acid (B2, Sigma-Aldrich) were used as the alignment materials. Negative LCs ($\Delta\varepsilon = -3.1$) were mixed with the alignment material with magnetic stirring at 75°C for 20 min. The final concentration of the alignment material was 0.2 wt%. To confirm the vertical alignment of the LCs, LC cells were prepared. ITO substrates without a polyimide layer were used as the top and bottom electrodes, and LC cells with a 5.25 μm cell gap were fabricated using spacers (Sekisui Chemical, SP-205XX). Then, the prepared LC cells were encapsulated using a UV sealant (Sekisui Chemical, SD-25XX) capable of curing under UV 3.0 J cm^{-2} (KJUV, KCHS 04). The LC mixture doped with the alignment material was injected into the LC cell after completion of the UV curing. The prepared LC cell was subjected to an annealing process for 60 min at 100°C. To confirm the vertical alignment of the fabricated LC cell, it was investigated by polarized optical microscopy (POM; Olympus, BX51). Fourier-transform Infrared (FT-IR; Jasco, FT/IR-460 plus) spectroscopy was performed to analyze the hydrogen bonding and photo-polymerization in the LC cell. The electro-optical characteristics were measured with a 632 nm He-Ne laser (JDSU, 1135P), photodetector (EOT, ET-2000), function generator (Agilent, 33210A), and oscilloscope (Tektronix, TBS1062).

Results and discussion

Vertical alignment of the LCs

Figure 1 schematically illustrates the concept behind the vertical alignment of the LC mixture doped with the alignment materials after injecting the LC mixture. The alignment

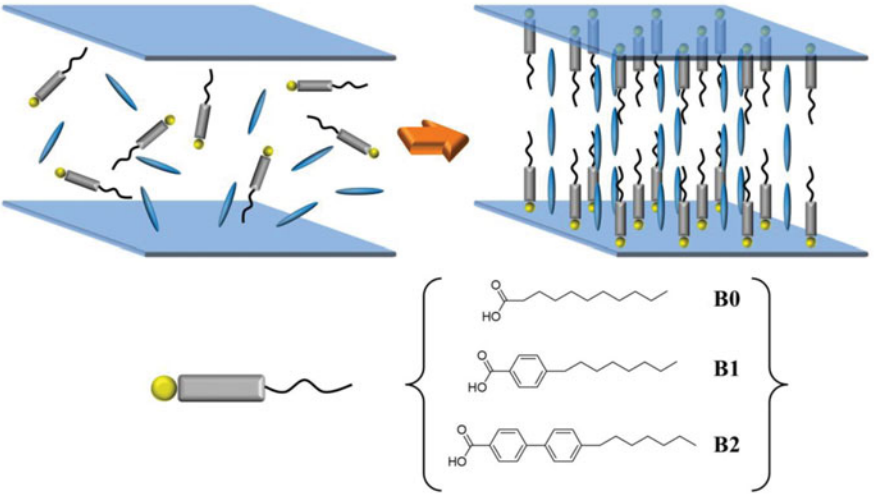

Figure 1. Schematic illustration of vertical alignment of LCs through the formation of self-assembled molecular layers, and structures of the alignment materials.

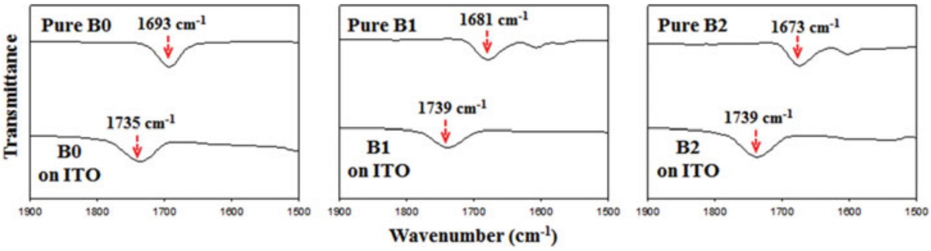

Figure 2. FT-IR spectra of pure alignment materials and the corresponding self-assembled layers on ITO.

materials consist of molecules with carboxylic acid termini, which can form hydrogen bonds with the oxygen atoms in the ITO substrate. Because the hydrogen-bonding alignment materials also have linear dimensions, their alkyl chains and rigid aromatic groups become oriented toward the interior of the LC cell. The oriented alkyl chains and rigid moieties interact with LC molecules, which results in the vertical alignment of the LCs. In order to examine the existence of hydrogen bonds between the alignment materials and ITO surface, FT-IR spectroscopy was performed. Figure 2 shows FT-IR spectra of pure alignment agents and the corresponding self-assembled layers on ITO electrodes. For pure alignment materials, carbonyl peaks appear at around 1680 cm^{-1} due to double hydrogen bonding of carboxylic acid groups. In contrast, the carbonyl peaks of self-assembled layers are displayed at higher wavenumber of about 1740 cm^{-1}, which is ascribed to the formation of single hydrogen bonds between carboxylic acid groups and ITO resulting in an increased stretching vibration of carbonyl groups [14]. Therefore, it is confirmed that the self-assembled layer of alignment materials formed on ITO surface through single hydrogen bonding. To confirm this vertical alignment, POM was performed under cross-polarized light (Fig. 3). Except for some light leakage in the B0 sample, the fabricated LC cells containing B1 or B2 exhibited overall dark areas, which indicates the uniform vertical alignment of the LC molecules. Through POM, the successful vertical alignment of the LCs through the formation of self-assembled molecular layers containing rigid aromatic moieties was confirmed, without notable differences among those samples.

Electro-optical characteristics of fabricated LC cell

To confirm the LCD performance of the fabricated LC cells, their electro-optical characteristics were measured. Voltage-transmittance (*V-T*) curves of the LC cells fabricated by the proposed method were investigated. To obtain fast switching of the LC molecules, the proposed method was applied in conjunction with a polymer-stabilized vertical alignment

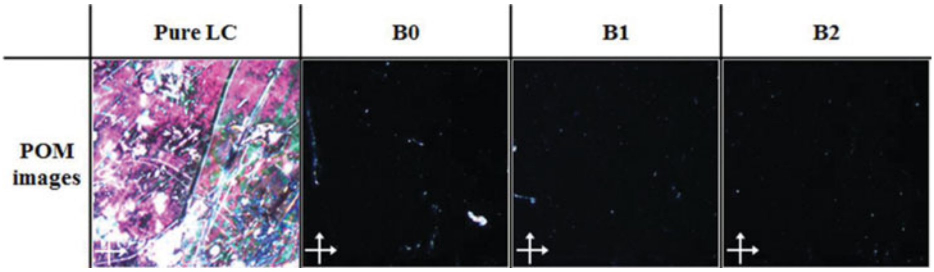

Figure 3. POM images of random and vertical alignments by pure LCs and self-assembled molecular layers.

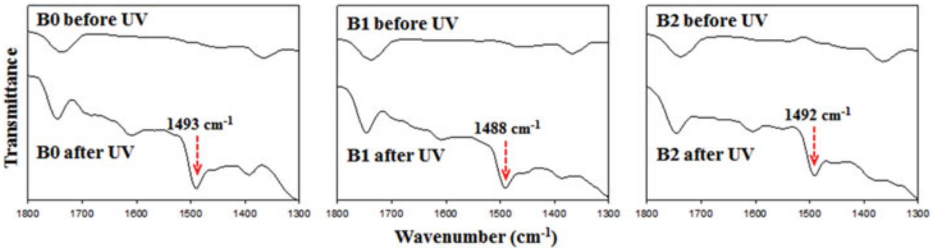

Figure 4. FT-IR spectra of self-assembled layers on ITO before and after UV irradiation.

(PS-VA) technique, which applies a UV-curable reactive monomer (RM) that is used commercially. The RM molecule, which consists of a pair of benzene rings and terminal acrylate moieties, can be polymerized by UV exposure under applied voltage, resulting in the generation of pre-tilt of LC molecules for fast electro-optical switching [15]. To investigate RM polymerization with different alignment materials, we performed FT-IR experiments after UV irradiation (Fig. 4). Contrary to unpolymerized self-assembled layers, a new band at around 1500 cm^{-1} is observed after UV exposure, which originates from aromatic C=C bonds of benzene rings in polymerized RM [16,17]. Since similar absorbances of new bands are obtained for all alignment materials, it is supposed that RM polymerization occurred by a similar amount regardless of alignment materials.

The left panel of Fig. 5 shows the *V-T* curves of the LC cells prepared with B0, B1, and B2 before UV exposure. The shapes of the curves are similar overall, however, the threshold voltages for B0, B1, and B2 are 2.28, 2.33, and 2.37 V, respectively. The threshold voltages increase as the number of rigid aromatic moieties is increased. Since the LC molecules can interact most strongly with the rigid aromatic groups than the alkyl chains, these results suggest that the vertical alignment is more strongly formed as the rigidity increases. The right panel of Fig. 5 presents the *V-T* curves of the fabricated LC cells after UV exposure. In this case, the threshold voltages for B0, B1, and B2 are 1.99, 1.87, and 1.82 V, respectively. Contrary to the previous result, the threshold voltages decrease as the number of rigid aromatic moieties is increased. The PS-VA mode generates a pre-tilt for the fast switching of LC molecules through the UV exposure process under an applied voltage. In the case of the proposed method, the alignment materials containing aromatic groups are more oriented along the LC molecules under the applied voltage because the rigid aromatic moieties interact more strongly with the

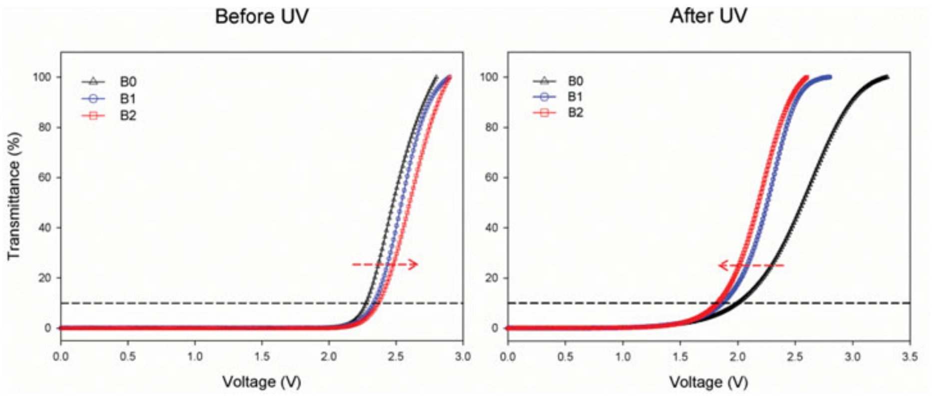

Figure 5. Voltage-transmittance curves of fabricated LC cells using alignment materials before and after UV exposure.

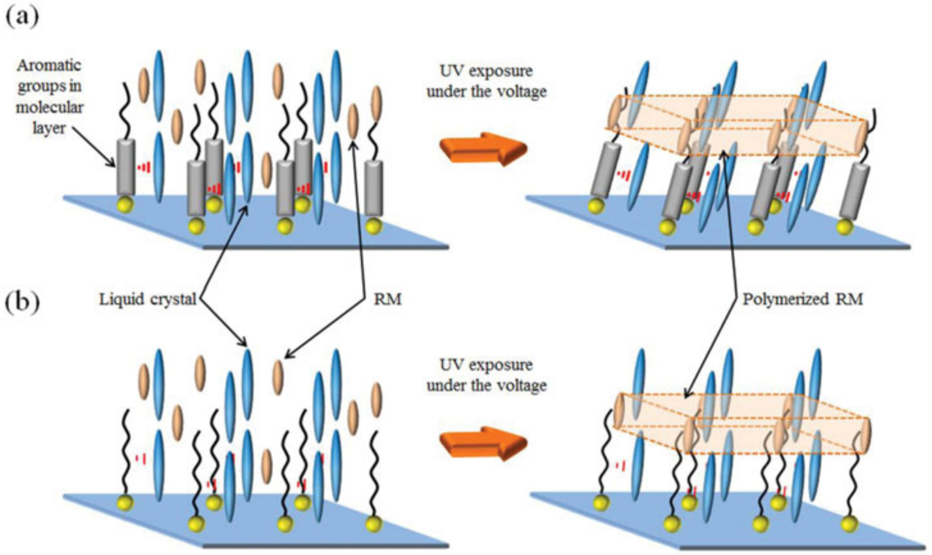

Figure 6. The pre-tilt generation process of LC molecules by the self-assembled molecular layers consisting of alignment materials containing (a) aromatic groups and (b) only alkyl chains.

LC molecules than the alkyl chains, as shown in Fig. 6. While the alignment materials containing rigid aromatic moieties maintain a greater inclination, the RMs are polymerized by UV exposure. Finally, the alignment material containing the rigid aromatic moieties has a larger pre-tilt than that containing the alkyl chains, resulting in the decreased threshold voltage.

To confirm the LC switching according to the number of rigid aromatic rings, response times were investigated. Because the rising time in the VA mode is an important factor that determines the speed of the LC device, the rising times were measured (Fig. 7). In the case of the fabricated LC cell using the alkyl-chain-containing B0, the measured rising time is 369 ms. The slow rising time results from the insufficient generation of pre-tilt caused by the structure of the alignment material without aromatic groups which can strongly interact with the LC molecules. The rising times of the fabricated LC cells using B1 and B2 are much shorter at 62

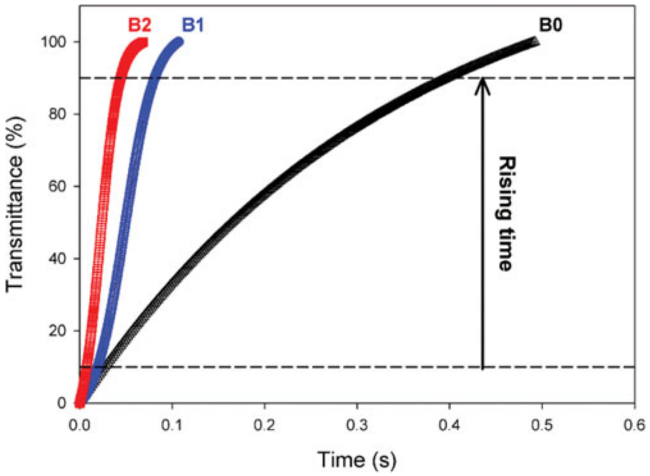

Figure 7. Rising times of the fabricated LC cells according to the number of rigid aromatic moieties.

and 37 ms, respectively. In case of the LC cells fabricated with B1 and B2, sufficient pre-tilt for fast switching is generated because of their strong interactions with LCs.

Conclusions

The uniform vertical alignment of LCs was achieved through the use of alignment materials containing carboxylic acid groups that were capable of hydrogen bonding with the ITO substrate. The alignment materials formed self-assembled molecular layers on the ITO surface without the use of polyimide. The advantages of the proposed method include the thin self-assembled layer, simple alignment procedure, and low concentration. The alignment materials containing rigid aromatic moieties showed faster LC switching than a material with only aliphatic chains, because the rigid aromatic moieties are able to interact more strongly with the LC molecules. Given these results, we expect that the proposed method will be suitable for fast-switching LC devices, especially in the PS-VA mode.

Acknowledgments

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