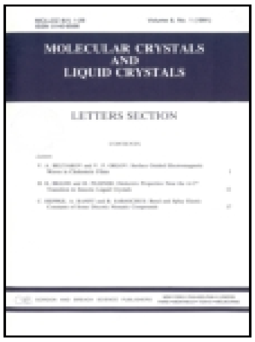

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Liquid Crystal Alignment Behavior on Rubbed Films of Cellulose Acetate

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ABSTRACT
The liquid crystal (LC) alignment behaviors of LC cells fabricated with cellulose acetate films were investigated. These polymer films exhibited good optical transparency in the visible light region (400–700 nm). For example, transmittance value (92%) of the cellulose acetate film onto glass substrate at 550 nm is better that (89%) of the polyimide (PI) film, the most commonly used LC alignment layers. These LC cells fabricated with the rubbed cellulose acetate films showed the homogeneous planar LC alignment with parallel direction with respect to the rubbing direction. The electro-optical characteristics of the LC cells made from the cellulose acetate films such as response time were as good as those fabricated from rubbed PI films.

KEYWORDS
Alignment; cellulose acetate; liquid crystal; rubbing

1. Introduction

Polyimide (PI) has been principally studied as a polymeric liquid crystal (LC) alignment material [1]. Mechanical rubbing of PI surfaces, commonly extensively used in LC display (LCD) industry, can produce planar LC alignment layers where the LCs are aligned parallel with respect to the rubbing direction on these surfaces [2], by combination of two factors, geometric restrictions between microscale/nanoscale grooves on the PI surfaces and LC molecules and physicochemical interaction at the interface between oriented PI chains on the alignment layer surfaces and LC molecules [3]. This planar LC alignment on PI film has superior thermal stability as well as a high azimuthal anchoring energy (>10–5 J/m2). Hard baking processes using high temperature, usually over 200°C, are commonly widely used to produce PI alignment layers, while the baking temperature is too high for manufacturing flexible plastic devices [4–7]. In addition, generally, PIs have intrisically yellowish coloration problem related to the extent of diimide fragment conjugation [8].

Cellulose is one of the most plentiful natural polymer on earth and polysaccharide consisting of a linear chain of several hundred to many thousands of α-linked D-glucose units [9]. These cellulose-based polymers have been studied for food, textile, biomedical, and energy applications due to their fascinating characteristics such as hydrophilicity, biocompatibility, biodegradability, and chemically modifiable characteristics [10–13]. Due to an extended

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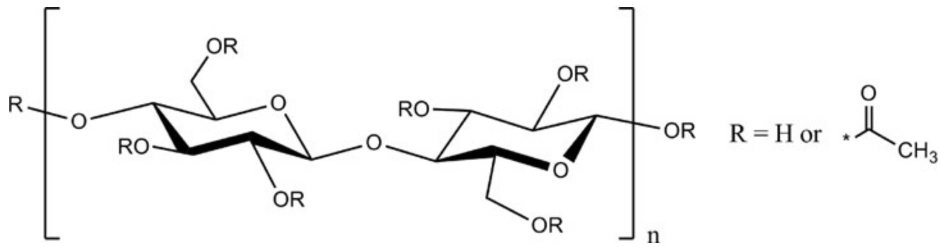

Figure 1. Chemical structure of cellulose acetate.

hydrogen-bond network, pure cellulose cannot be processed like conventional thermoplastic polymers without chemical modification reaction. For example, the processabillity of the cellulose-based polymers has been enhanced by chemical modification reaction such as acetylation attached to the pure cellulose having nonsoluble characteristic in general solvent system [14].

In this article, the LC alignment behavior of the LC cells produced using the cellulose acetate films, one of the thermoplastic cellulose ester, as an alignment layers was studied. Homogeneous planar LC alignment layers were produced from the LC cell fabricated with cellulose acetate film through a rubbing process. The optical transparency of the cellulose acetate film is better than that of the widely used PI as a LC alignment layer. The electro-optical (E–O) characteristics of the LC cells fabricated with the polymer films are also included.

2. Experimental

2.1. *Film preparation and LC cell assembly*

Cellulose acetate (Sigma-Aldrich) as shown in Fig. 1 was used. The cellulose acetate was fully dissolved in acetone (Sigma-Aldrich) at room temperature with mechanical stirring for 1 hr, resulting in the transparent cellulose acetate solution (1 wt.%) in acetone. These solutions were filtered through a polytetrafluoroethylene membrane with a pore size of 0.45 µm. Thin films of the cellulose acetate were prepared by spin-coating (4000 rpm, 60 sec) them onto 20 mm × 20 mm indium tin oxide (ITO) coated glass substrates, followed by the drying at 80°C for 1 hr. Polyimide (PI, Nissan Chemical SE-7492 K) alignment agents were spin coated (3000 rpm, 40 sec) 20 mm × 20 mm ITO coated glass substrates. The PI films were prebaked at 80°C for 15 min and then were fully baked at 220°C for 45 min. These polymer films were rubbed using a rubbing machine (RU-AS01, SHINDO Eng.); number of rubbing and rubbing depth were 2 and 0.5 mm, respectively. Twisted nematic (TN) and antiparallel LC cells were fabricated using the rubbed polymer films onto the ITO coated glass slides. The TN and antiparallel LC cells were made by assembling the films together orthogonally and antiparallel with respect to the rubbing direction for the rubbed polymer films using spacers with a thickness of 4.75 µm, respectively. The fabricated LC cells were filled with a nematic LC, 4-*n*-pentyl-4′-cyanobiphenyl (5CB, $ne = 1.7360$, $no = 1.5442$, and $\varepsilon = 14.5$, where ne, no, and ε represent extraordinary refractive indexes, ordinary refractive indexes, and dielectric anisotropy, respectively), in the isotropic state in order to avoid creating flow alignment by capillary action. The manufactured LC cells were sealed with epoxy.

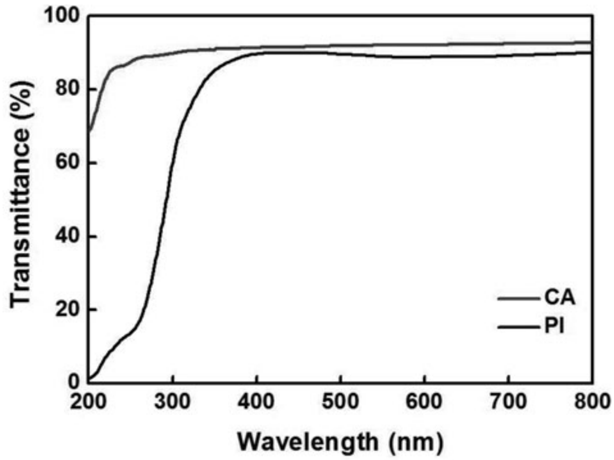

Figure 2. UV-Vis transmittance spectra of cellulose acetate and PI alignment layers onto quartz substrates.

2.2. *Instrumentation*

The optical transmittance of the polymer films was obtained using UV-Vis spectroscopy (Perkin Elmer Lamda 20 spectrometer). For the UV-Vis spectroscopy of polymer, the polymer films were prepared by spin-coating cellulose acetate in acetone onto ITO coated glass substrates at 4000 rpm for 60 sec. The LC alignment direction of the antiparallel LC cells made from polymer films was investigated by measuring the angular dependence of the absorbance of a nitrile (C=N) group in 5CB as a function of the rotation angle of the polarizer using polarized Fourier transform infrared (FTIR) spectroscopy measurement. The pretilt angle of the antiparallel LC cell was measured by the crystal rotation method. The cell gap was measured before filling the LCs using a spectrophotometer (Ocean optics Inc., S 2000). The polarized optical microscopy (POM) images of the LC cells were observed using an optical microscopy (Nikon, ECLIPSE E600 POL) equipped with a polarizer and digital camera (Nikon, COOLPIX995). The response time and voltage-transmittance (V-T) were measured from the LC cells using the same method as that reported by others [15, 16]. The threshold voltage (*V*th) and driving voltage (*V*on) in the V-T curve are defined as the voltages at which the transmittance was decreased to 90% and 10% of the initial transmittance value, respectively. The rising (*T*r) and falling (*T*f) response times for the white-to-black and black-to-white changes, respectively, are defined as the time to transition from 10% to 90% transmittance and vice versa [15, 16].

3. Results and discussion

Quantitative analysis of transparency of cellulose acetate films was evaluated using UV-Vis spectra to investigate the possibility for the surface coating applications (Fig. 2). The transmittance value of the coated cellulose acetate film onto glass substrate is about 92% at 550 nm. This value is higher than that (89%) of the widely used PI film having intrisical yellowish coloration problem related to the diimide fragment conjugation as a LC alignment layer [8], which is similar with that of bare glass substrate. Conclusively, the optical transparency of the cellulose acetate film in the visible light region is good enough to be used as optical materials for display devices.

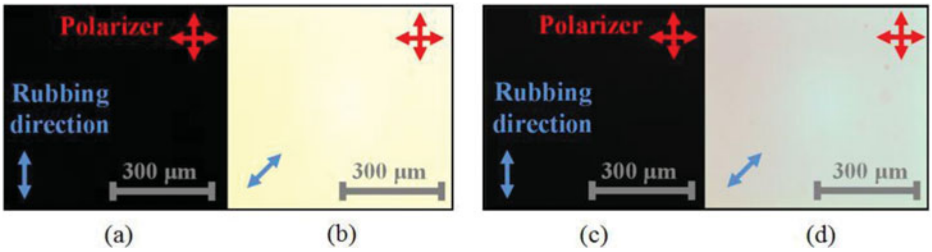

Figure 3. POM images of the LC cells made from rubbed cellulose acetate ((a) dark and (b) bright) and PI ((c) dark and (d) bright) films.

The LC alignment behavior of the LC cells fabricated with the rubbed cellulose acetate and PI films was investigated using POM and polarized FTIR spectroscopy, respectively. A nematic pure LC (5CB) with a positive dielectric anisotropy was used to make the antiparallel LC cells for our studies. 5CB molecules have been commonly used in order to determine the LC aligning ability and alignment direction [2]. At first, random planar LC alignment was observed for the LC cells made from the unrubbed cellulose acetate films. The POM images of the LC cells made from rubbed cellulose acetate Fig. 3(a) dark and Fig. 3(b) bright) and PI Fig. 3(c) dark and Fig. 3(d) bright) films clearly show homogeneous planar LC alignment behavior (Fig. 3). We found that the aligning ability of the LC cells made from the rubbed cellulose acetate films exhibited similar LC alignment behavior compared with the LC cells fabricated with rubbed PI films by POM image as well as LC cell image by naked eyes under crossed polarizers. The good uniformity of the planar LC alignment behavior of the LC cells fabricated with rubbed cellulose acetate and PI films was observed over the whole area, respectively. The homogeneous planar LC alignment was maintained for at least more than 12 months since we first made the LC cells from the rubbed cellulose acetate films.

Angular dependence of the IR source transmittance through antiparallel LC cells made from rubbed polymer films was also observed by polarized FTIR spectroscopy in order to investigate LC alignment direction accurately. Before the rubbing process, any good polar diagrams showing good orientation of LCs on the cellulose acetate film could not be measured due to the random planar LC alignment. After the rubbing process, the antiparallel LC cells made from rubbed cellulose acetate films showed maximum intensities along the 0° ↔ 180° direction by monitoring the polar diagrams of the intensity of the nitrile (C=N) stretching band of the 5CB in the LC cells as a function of rotation angle of polarizer, indicating that the LC molecules on cellulose acetate films are oriented parallel with respect to the rubbing direction Fig. 4(b), as in the case of the LC cell made from rubbed PI film as shown in Fig. 4(d), which is similar with previous reports by others [1–3].

The V-T and response time values were measured in order to investigate the driving property of the LC cell having the same cell gap of about 4.75 μm using the same conditions. In this study, a nematic pure LC with a positive dielectric anisotropy, 5CB, which is a suitable switching behavior in TN mode, was used. A stable V-T curve was observed for the TN LC cell fabricated with the rubbed cellulose acetate and PI film (Fig. 5). The V-T curves were almost identical for the two alignment films when 10 V was applied to each cell. The response time characteristics of the LC cells made from rubbed cellulose acetate and PI films are shown in Fig. 6. The *V*th, *V*50, and response time of the rubbed cellulose acetate film were 1.13 V, 1.51 V, and 16.40 ms, respectively, which are close to those of rubbed PI in the LCD industry, 1.13 V, 1.20 V, and 17.34 ms, respectively (Table 1). In particular, the response time (about 16.40 ms) of the LC cell made from the rubbed cellulose acetate film is faster than that (about

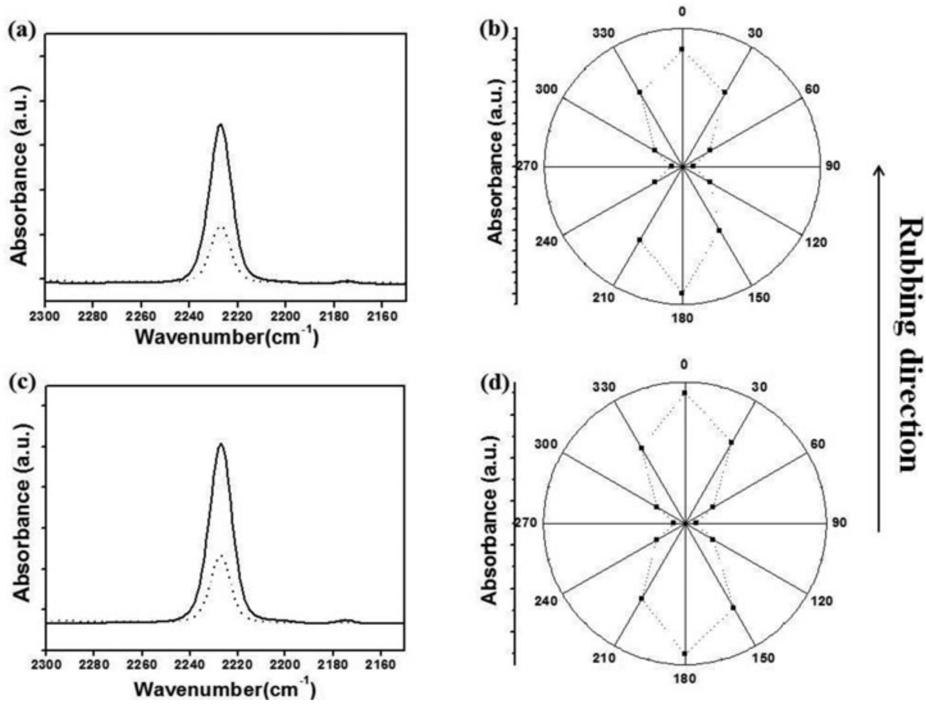

Figure 4. FTIR spectroscopy dichroic spectra of the LC cells made from rubbed (a) cellulose acetate and (c) PI films. Solid and dotted lines indicate the results obtained from the IR source parallel and perpendicular, respectively, with respect to the rubbing direction. Polar diagram of specific vibrational IR peaks of nitrile (C=N) of 5CB in the LC cells fabricated with rubbed (b) cellulose acetate and (d) PI films measured as a function of rotation angle of polarizer.

17.34 ms) of the LC cell made from the rubbed PI film. We measured the pretilt angles of the LC cells made from rubbed cellulose acetate and PI films to investigate the effect of the pretilt angle on the response time. The pretilt angles about 7.7o and 6.3o of the LC cells made from rubbed cellulose acetate and PI films were observed, respectively. The response time of the cellulose acetate cell is faster than the rubbed PI cell, possibly due to the pretilt angle effects of

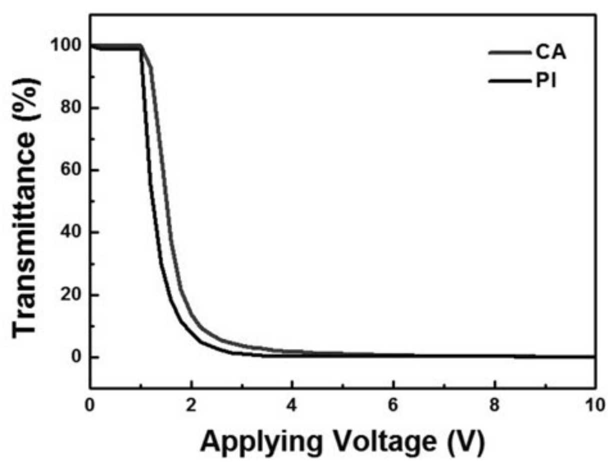

Figure 5. V-T curves of the LC cells fabricated with rubbed cellulose acetate and PI films.

Table 1. V-T and response time value of the LC cells made from polymer films.

	Voltage-transmittance (V-T)(V)			Response time(ms)		
Polymer	*Vth*	*V50*	*Von*	*Tr*	*Tf*	*Tt*
Cellulose Acetate (CA)	1.13	1.51	8.80	1.51	14.89	16.40
PI	1.13	1.20	8.20	1.54	15.80	17.34

the alignment layer surfaces [3]. The E-O performance of the LC cell made from the rubbed cellulose acetate film was as good as or even better than that made from the rubbed PI film, which suggests that the rubbed cellulose acetate system can be used for practical LCD applications. Therefore, we believe that these cellulose derivatives films can be good candidates as an alignment layer for advanced LCD applications including flexible ones.

4. Conclusions

The LC cell prepared using the cellulose acetate film having good optical transparency as the alignment layer showed the homogeneous and planar LC alignment behavior. The superior optical transparency of the cellulose acetate films compared with PI film was observed in the visible light region. Good E-O properties were observed for the LC cells made from the cellulose acetate film. For example, *V*th, *V*50, and response time of the rubbed cellulose acetate film were 1.13 V, 1.51 V, and 16.40 ms, respectively, which are close to those of rubbed PI film, 1.13 V, 1.20 V, and 17.34 ms, respectively, indicating that these LC cells can be used for practical LCD applications, because they also have a low processing temperature and low

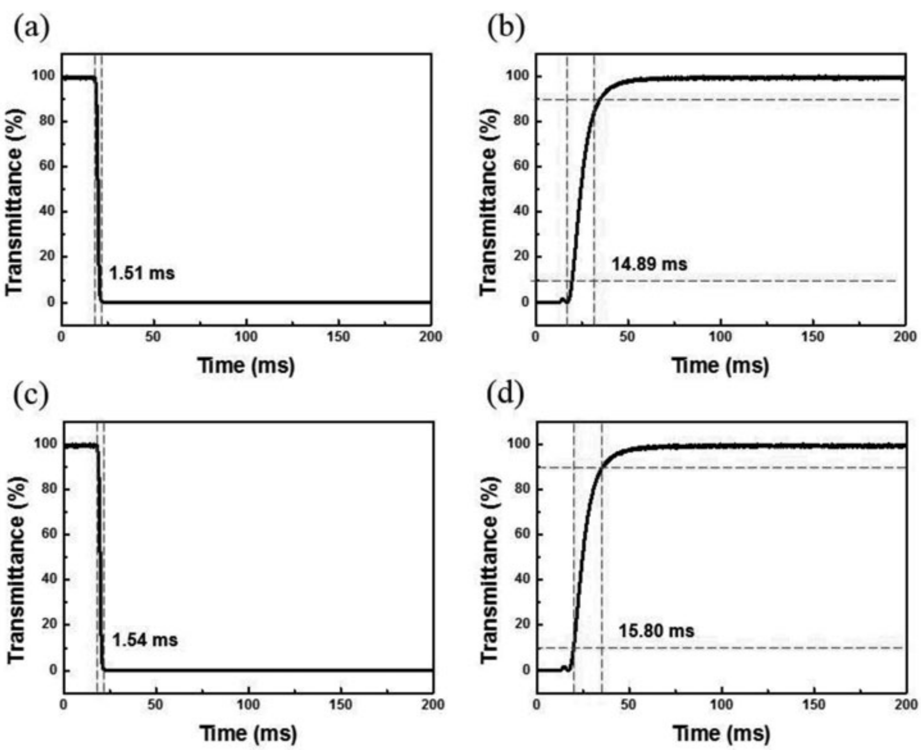

Figure 6. Response time for TN LC cells made from rubbed cellulose acetate ((a) rising and (b) falling time) and PI ((c) rising and (d) falling time) films.

cost. These results provide the fundamental information required for the design of polymer alignment layers for advanced LC devices using planarly aligned LCs.

Acknowledgment

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