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Uniform Alignment of Liquid Crystals Induced by Perfluoropolyether Film Exposed to Linearly Polarized Ultraviolet Light

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*We have succeeded in inducing uniform alignment of liquid crystal (LC) molecules by using end-functionalized-perfluoropolyether (PFPE) (*Fluorocur® *made by Liquidia Technologies) films exposed to linearly polarized ultraviolet light (LPUVL). The average orientation direction of LC molecules was parallel to the polarization direction of LPUVL, which is opposite to most cases of other photo-alignment treatments. In the photo-alignment treatment, use of deep UV light and the existence of oxygen in the atmosphere was found to be important for inducing uniform LC alignment.*

Keywords Liquid crystal; perfluoropolyether; photo-induced alignment

1. Introduction

In today's liquid crystal displays (LCDs), polyimide alignment layers are widely used. Polyimide has several advantages, including simple layer preparation (i.e., liquid precursors of polyimides are available easily deposited as a thin film by spin-coating), high chemical and thermal resistance, and potential for modification of the chemical structure and thus modification of the alignment characteristics [1]. Usually, LC molecules in contact with the polyimide alignment layers are strongly anchored at the surface. Under strong anchoring, bulk LC in a LCD can be quickly returned to the initial state from the state under the applied voltage. However, to manipulate the LC director (the average orientation direction of aligned LC molecules), a high voltage is required.

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On the other hand, weak anchoring of LC molecules at the substrate surface can in principle lead to lower operating voltages and improved steepness of the electro-optic response [2–4]. Recently, J. M. Russell-Tanner et al. reported that Langmuir-Blodgett (LB) films of end-functionalized perfluoropolyether (PFPE) (*Fluorocur*® made by Liquidia Technologies) have a weak surface anchoring energy on the order of $10^{-5}\,\mathrm{J/m^2}$ for bend deformation [5]. The end-functionalized PFPE used in that research is a unique class of fluoropolymers and it is cured by irradiating with ultraviolet (UV) light. Since the precursor is a liquid with no known toxicity, one can easily prepare a film on a substrate. The PFPE polymer film after UV curing has high chemically resistance, gas permeability, and low surface energy [6]. Although the LB technique can control a film thickness in units of a monolayer, it is not very suitable for fabricating LCDs with large area nor for patterning for LC alignment. The patterning capability is effective in realizing high performance LCDs, such as multi-stable LCDs [7]. Various alignment methods to pattern LC alignment have been proposed [7–9]. Among these methods we are focusing on photo-induced alignment of LCs [8, 10–12]. We choose this route to pattening because the photo-alignment treatment can be performed in air under ambient conditions, adapted for large area, and it is easy to control the photo-irradiation conditions such as polarization, incident angle, wavelength, and exposure time. In this study, we have succeeded in inducing a uniform LC alignment by using photo-aligned PFPE films.

2. Experiment

The end-functionalized-PFPE used in this study was *Fluorocur*® obtained from Liquidia Technologies. Figure 1 shows a generic molecular structure of the PFPE oligomer. Quartz substrates covered with Indium-Tin-Oxide (ITO) were used as the substrate. These were treated in an ultrasonic cleaner in ethanol and by a UV ozone cleaner. Then the substrates were modified with 3-(trimethoxysilyl) propyl methacrylate. The PFPE oligomer films were prepared on the substrates by spin-coating. In this study, we used the *Fluorocur*® resin diluted by tetrahydrofuran to 15 wt% in order to control the film thickness. To induce the crosslinking reaction of PFPE oligomers, the films were exposed to unpolarized UV light in a high-purity nitrogen atmosphere. A 500 W deep UV lamp (Ushio Inc. UXM-500SX) was used as the light source and the wavelength was selected with a band-pass filter of transmission wavelength 350–380 nm (Asahi Spectra Co., Ltd.). The wavelength of the light was ~360 nm. The light was directed on the films at normal incidence and the exposure was $40\,\mathrm{J/cm^2}$. After exposure the films were washed in an ultrasonic cleaner in ethanol to remove the uncrosslinked oligomer. The thickness determined with spectroscopic ellipsometry (M-2000U: J. A. Woollam Co. Inc.) was about 100 nm.

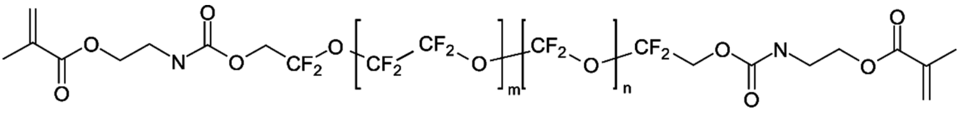


Figure 1. Generic molecular structure of PFPE oligomer.

In the photo-alignment process, the PFPE films were irradiated with linearly polarized UV light (LPUVL) at normal incidence in air. A light source consisted of the deep UV lamp, a band-pass filter, whose center wavelength is 250 nm and full width of half-maximum is 20 nm, and a Glan-Taylor prism polarizer to generate LPUVL.

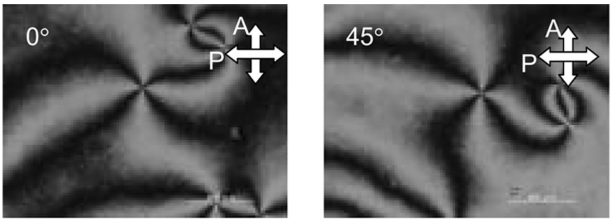
To examine the LC alignment induced by PFPE films, parallel-aligned LC cells were assembled by using the LPUVL-exposed PFPE films as the both cell walls. 25 μm-thick PET films were used for the spacer. The cells were filled with 4-n-pentyl-4′-cyanobiphenyl (5CB) in its isotropic phase by capillary action. The LC alignment was observed by a polarized optical microscope (BX51: Olympus Corporation) at 25°C. To investigate the director orientation of bulk LC generated by the LPUVL-exposed PFPE films, polarized infrared (IR) absorption measurements were performed using a Fourier transform IR (FTIR) spectrometer with a Deuterated L-Alanine Triglycine Sulphate (DLATGS) detector (Vertex 70: Bruker optics). The absorption spectra for both IR light polarized parallel and perpendicular to the polarization direction of LPUVL were measured with a $4\,\mathrm{cm}^{-1}$ resolution at normal incidence.

3. Results and Discussion

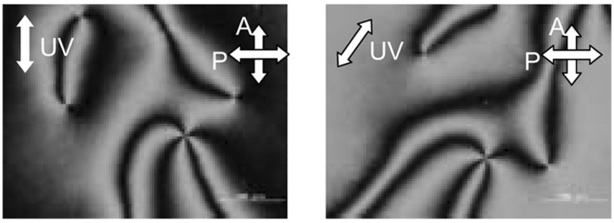
Figure 2 shows birefringent textures observed for the spontaneous alignment of 5CB on the PFPE films exposed to LPUVL at (a) $0\,\mathrm{J/cm^2}$ (before LPUVL irradiation), (b) $2\,\mathrm{J/cm^2}$, and (c) $5\,\mathrm{J/cm^2}$. In Figure 2(a) and (b), schlieren textures were observed, which means a random orientation of the LC director in a plane parallel to the substrate surface—no alignment. On the other hand, the birefringent textures of Figure 2(c) were uniform and the contrast between the extinction and diagonal position was high. This result shows that uniform, in-plane unidirectional (homogenous) alignment was induced by photo-aligned PFPE films. Since the films exposed to LPUVL at $2\,\mathrm{J/cm^2}$ could not induce homogenous alignment, we conclude that exposure to more than $\sim 5\,\mathrm{J/cm^2}$ was required to induce uniform LC alignment. Moreover, we confirmed that the films exposed to LPUVL at more than $20\,\mathrm{J/cm^2}$ could induce uniform LC alignment.

To determine the LC director induced by LPUVL-exposed PFPE films, we measured the polarized IR absorption spectra of the cell of Figure 2(c). Figure 3 shows the polarized IR absorption spectra. Here $A_{//}$ and $A_{\perp}$ are the absorbance for the IR light polarized parallel and perpendicular to the polarization direction of the LPUVL, respectively. The absorption band observed at $2226\,\mathrm{cm}^{-1}$ is assigned to C-N stretching vibration of 5CB molecules [13]. We can see that $A_{//}$ of this band is greater than $A_{\perp}$. Since the polarization direction of this band is parallel to the molecular axis of 5CB [13], this result means that the LC director aligns parallel to the polarization direction of the LPUVL. This alignment direction is opposite to that reported in most cases of photo-induced alignment [12] wherein the director was found to be perpendicular to the polarization direction of the LPUVL.

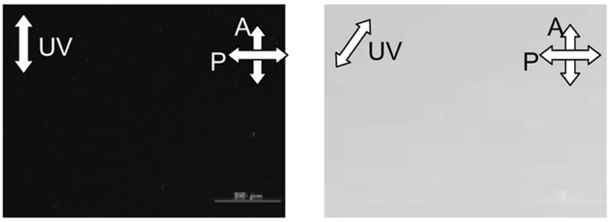
In order to determine suitable photo-alignment conditions, we have investigated the effect of LPUVL-wavelength and the atmosphere environment during LPUVL irradiation on LC alignment. Figure 4 shows the birefringent textures observed for the spontaneous alignment of 5CB on photo-aligned PFPE films prepared under various conditions. In the cell of Figure 4(a), we employ PFPE films exposed to LPUVL with ~360 nm wavelength in air after the crosslinking process. LPUVL with



(a) 0 J/cm²



(b) 2 J/cm²



(c) 5 J/cm²

Figure 2. Birefringent textures observed for alignment of 5CB induced by the unexposed and LPUVL-exposed thin PFPE films. The LPUVL exposures are described in the bottom of the figures. The arrow P and A are the polarization direction of the polarizer and analyzer of the polarized optical microscope. The arrow UV is the polarization direction of linearly polarized UV light. 0° and 45° described in (a) show azimuthal angles of the LC cell.

~360 nm wavelength was produced by passing the light of the deep UV lamp through the bandpass filter (wavelength 350–380 nm) and the Glan-Taylor prism polarizer at normal incidence. The LPUVL-exposure was $200\,\mathrm{J/cm^2}$. This texture was similar to that on PFPE films without photo-alignment treatment (shown in Fig. 2(a)). This result seems to be reasonable. Photocrosslinking induced by irradiation of UV light with ~360 nm wavelength was induced by radicals generated from photo-initiators mixed in the PFPE resin. The radicals are easily inactivated in an atmosphere including oxygen such as air under ambient conditions. Thus, in this case, the radicals generated by LPUVL-irradiation were inactivated instantly and it is expected that the photo-induced formation of crosslinked PFPE did not occur.

The PFPE films used in the cell of Figure 4(b) were exposed to LPUVL with ~360 nm wavelength at $260\,\mathrm{J/cm^2}$ in high-purity nitrogen atmosphere without a UV curing process. In this case, PFPE oligomers are crosslinking during the LPUVL-irradiation. Since the observed texture was also similar to Figures 4(a) and 2(a), we can see that LCs were not aligned by these PFPE films. In this situation, the lifetime of radicals generated by LPUVL irradiation is enough to induce

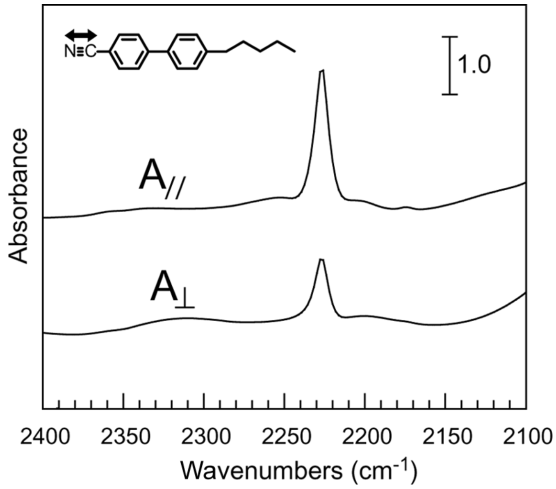
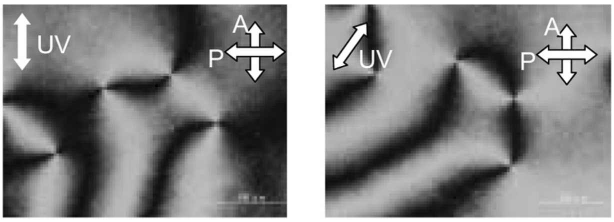


Figure 3. Polarized IR absorption spectra of the LC cell assembled by the LPUVL-exposed PFPE films. $A_{//}$ and $A_{\perp}$ are the absorption spectra for the IR light polarized parallel and perpendicular to the polarization direction of the LPUVL, respectively. The absorption band at 2226 cm^{-1} is assigned to the C-N stretching vibration of 5CB. The arrow shows the polarization direction of the C-N bond.

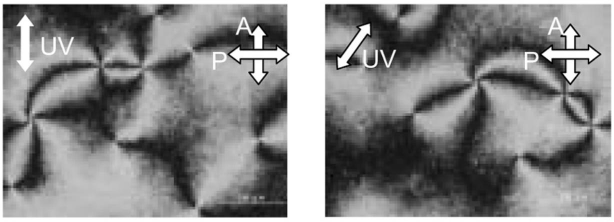
crosslinking reactions. Certainly, the PFPE oligomer films were cured by the LPUVL irradiation. However, radicals could easily move in the precursor film. Therefore, even though the generation of radicals by LPUVL is initially anisotropic, this anisotropy was not reflected in the final anisotropy of the PFPE films and there is no apparent induction of uniform LC alignment.

These two results indicate that the mechanism of photo-induced alignment shown in Figure 2(c) is different from the mechanism of UV curing of PFPE, which is crosslinking induced by radicals from photo-initiators. Irradiation with the deep UV light such as ~250 nm wavelength might induce a photo-reaction in the PFPE oligomer or PFPE polymer directly (without intermediation by the photo-initiator). Thus we can say that use of deep UV light is important for the photo-alignment of PFPE films.

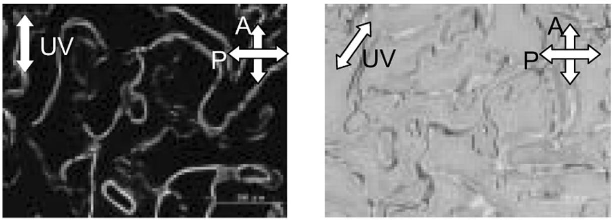
Figure 4(c) shows the birefringent textures of the cell assembled with the PFPE films which were obtained by irradiating the PFPE oligomer films with LPUVL of ~250 nm wavelength at 20 J/cm^2 in a high-purity nitrogen atmosphere. In this case, PFPE oligomers were crosslinked during this process. In this image there are a lot of defects, although LC molecules are generally aligned. We guessed that cause of this bad alignment was radicals induced by irradiation of LPUVL with ~250 nm wavelength. Radicals can be generated not only by light with ~360 nm wavelength but also by light with ~250 nm wavelength. Since the radicals generated by irradiating with deep UV light can also move easily in the film, reaction products induced by the radicals can randomly disturb the LC alignment. On the other hand, in an air atmosphere, the radicals were inactivated instantly, so we believe that such reactions did not occur in the photo-alignment process of the films used in Figure 2(c). Thus we concluded that the existence of oxygen in the atmosphere was important for inducing uniform LC alignment.



(a) λ = ~360 nm, in air



(b) λ = ~360 nm, in N_2



(c) λ = ~250 nm, in N_2

Figure 4. Birefringent textures observed for alignment of 5CB induced by the PFPE films exposed LPUVL as the following conditions: (a) $\lambda = 360\,\text{nm}$, in an air atmosphere, $200\,\text{J/cm}^2$, (b) $\lambda = 360\,\text{nm}$, in a high-purity nitrogen atmosphere, $260\,\text{J/cm}^2$, and (c) $\lambda = 250\,\text{nm}$, in a high-purity nitrogen atmosphere, $5\,\text{J/cm}^2$. The arrow P and A are the polarization direction of the polarizer and analyzer of the polarized optical microscope. The arrow UV shows the polarization direction of the LPUVL.

4. Conclusion

We have succeeded in inducing homogenous LC alignment by using end-functionalized-PFPE (*Fluorocur*®) films exposed to LPUVL. The average orientation direction on the photo-aligned PFPE film was parallel to the polarization direction of LPUVL, which is opposite to most cases of other photo-alignment treatments. Moreover, we have investigated the effect of the wavelength of LPUVL and the atmosphere on the LC alignment. As a result, we have found that irradiation with linearly polarized deep UV light (~250 nm) in an atmosphere containing oxygen was important for inducing uniform LC alignment.

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