Control of liquid crystal pretilt angles by chemical derivatization reaction of polyvinyl alcohol films

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A chemical derivatization technique was used to control the pretilt angle of a liquid crystal. A polyvinyl alcohol (PVA) alignment layer, which gives a very low pretilt angle when in contact with the liquid crystal (LC), was reacted with trifluoroacetic anhydride (TFAA) in the gas phase to change polar –OH groups to –OCOCF$_3$ groups. By introduction of the –OCOCF$_3$ groups in to the PVA, we obtained homeotropic alignment of the E7 LC molecules. The homeotropic alignment of E7 LC molecules in contact with the derivatized PVA alignment layer was confirmed by FTIR and microscopy with crossed polarizers. The change of liquid crystal molecules from homogeneous to homeotropic alignment may be caused by the decrease in surface tension of the PVA alignment layer, due to substitution of the polar –OH groups by –OCOCF$_3$ groups in the gas phase derivatization reaction.

1. Introduction

The surface alignment of liquid crystal (LC) molecules is very important in liquid crystal displays; alignment control in LC devices is traditionally produced using mechanically rubbed polymer films, such as polyimide (PI) [1, 2] and PVA films [2–4]. To reduce the occurrence of reverse tilt disclinations appearing in twisted nematic (TN) displays, the use of tilt angles from 2° to 7° is necessary [1]. In super-twisted nematic (STN) displays, tilt angles of 5–10° are required to suppress the formation of undesired textures and structures which destroy the electro-optical properties of the display [1].

To generate a high LC pretilt angle on rubbed PI surfaces, a PI containing the trifluoromethyl group [5] or long alkyl-branched PI alignment layers have been widely used [6, 7]. The same orientation change, depending on the surface functional groups, was observed for 8CB (4′-*n*-octyl-4-cyanobiphenyl) LC on derivatized self-assembled monolayer surfaces [8]. Surfaces coated by *ω*-functionalized –CF$_3$ groups promoted homeotropic anchoring of the 8CB, and –OH groups promoted planar anchoring.

It is widely known that rubbed PVA alignment films produce uniform homogeneous alignment and very

small pretilt angles for most LCs in contact with the layer [9]. Also, trifluoroacetic anhydride (TFAA) can be used to replace the hydroxyl groups of the PVA surface with the trifluoroacetate moiety, yielding trifluoroacetic acid as a by-product [10, 11], as shown in figure 1. The boiling point of trifluoroacetic acid is 72.4°C, therefore it can be easily removed from the derivatized polymer by heating. To investigate the effect on LC pretilt angle of –CF$_3$ group incorporation in the PVA alignment layer, we derivatized the alignment layer with TFAA. We found homeotropic LC alignment on the layer containing –CF$_3$ groups, and homogeneous alignment on the layer having –OH groups.

2. Experimental

2.1. *Materials*

PVA (98–99% hydrolysed, MW 31 000–50 000) and TFAA (b.p. = 39.5–40°C) were purchased from Aldrich.
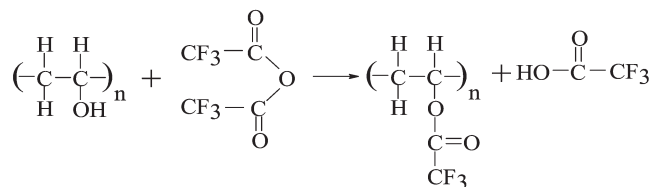

Figure 1. Chemical derivatization of –OH groups to –OCOCF$_3$ groups.

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PVA was dissolved in deionized water with heating to give an approximately 3% solution, which was filtered through a 0.22-μm Nylon filter. For IR spectra observation, the PVA solution was spin-coated onto CaF$_2$ rectangles. Spin conditions were typically 3000 rpm for 30 s, and before spin coating, the CaF$_2$ rectangles were rinsed using isopropyl alcohol, then dried thoroughly at 120°C. After spin coating, the PVA-coated CaF$_2$ rectangles were heated for 10 min at 60°C, then at 150°C for 1 h to remove residual H$_2$O. After heating, the rectangles were taken from the oven, and cooled to room temperature in a desiccator. To convert the –OH functional groups of PVA to –OCOCF$_3$, a PVA-coated rectangle was stood vertically in a jar, and about 3 ml of TFAA introduced. After closing the jar, it was left for 1 h at room temperature to accomplish the gas phase derivatization reaction. After the reaction, the rectangle was placed in an oven at 80°C for 1 h to remove unreacted TFAA and the trifluoroacetic acid by-product.

2.2. Analytical instrumentation

For the study of functional groups and LC molecular orientation in LC cells, a Magna 550 FTIR (Nicolet) instrument was used to record transmission FTIR spectra. The CaF$_2$ spectrum or ITO glass spectrum was subtracted from the collected FTIR spectra, to obtain the sample spectrum. A single diamond IR polarizer from Harrick Co. was used for this study. To reduce the noise level, more than 300 scans were obtained at 4 cm^{-1} resolutions.

2.3. Preparation of liquid crystal cells

Four cells were made, to investigate LC alignment in contact with PVA (rubbed and unrubbed) and derivatized PVA (rubbed and unrubbed) alignment layers. Eight rectangular pieces of ITO-coated glass were cleaned with methanol, and PVA aqueous solution was spin-coated onto the ITO glass using the same method as for CaF$_2$ rectangles. The PVA-coated ITO glass substrates were dried as before. After drying for 1 h, from the eight PVA-coated ITO substrates, two were hand rubbed five times each with velvet cloth, two were derivatized with TFAA, and two were derivatized with TFAA after rubbing. A mixture of UV-curable adhesive and 4.0-μm glass fibre spacers was applied to the four corners of the PVA-coated substrates. Rubbed cells were assembled with anti-parallel orientation. After assembly, the cells were filled with nematic liquid crystal E7 (Cr–N = −10°C and N–I = 60°C, Merck, UK) by capillary action in the isotropic state at 85°C; E7 is a eutectic liquid crystal mixture of 51% 5CB, 25% 7CB, 16% 8OCB, and 8% 5CT [12]. After

filling with E7, the four edges of the cell were completely sealed with 5 Minute Epoxy (Devcon). After the epoxy was cured, the cells were heated to 85°C for 30 min and cooled to room temperature over 2 h to give good alignment of E7.

3. Results and discussion

3.1. Derivatization reaction

To confirm the conversion of –OH groups of the PVA to –OCOCF$_3$ groups by TFAA derivatization, the FTIR spectra of the PVA before and after TFAA treatment were obtained. The results are shown in figures 2 (a) and 2 (b), respectively. The FTIR spectrum before TFAA treatment shows very strong peaks at 3348 and 1144 cm^{-1}, which are caused by the –OH groups of PVA (see table 1) [13]. After TFAA treatment the –OH peaks disappeared completely and new peaks arising from the C=O stretching vibration of –OCOCF$_3$ groups appeared at 1787 cm^{-1}. The peaks at 2940 and 2909 cm^{-1} that can be seen clearly in figure 2 (a), became very small in figure 2 (b). These changes were caused by the change in molar extinction coefficients of the C–H and C=O of TFAA-derivatized PVA. A typical molar extinction coefficients of the –OH group peak at 3348 cm^{-1} is $60 \pm 10 \, 1 \, mol^{-1} \, cm^{-1}$; that of the C=O of the –OCOCF$_3$ group peak at 1787 cm^{-1} is $420 \pm 40 \, 1 \, mol^{-1} \, cm^{-1}$ [14]. The two peaks caused by the asymmetric and the symmetric stretching of –CH$_2$ groups at 2940 and 2909 cm^{-1} must have lower molar extinction coefficients than that of –OH stretching (at 3348 cm^{-1}) as shown in figure 2 (a). Therefore, after normalizing the two spectra using the strongest peak— 3348 cm^{-1} peak in figure 2 (a) and 1160 cm^{-1} peak in figure 2 (b)—the two –CH$_2$ stretching peaks at 2940 and 2909 cm^{-1} became relatively very small in figure 2 (b) compared with those in figure 2 (a).
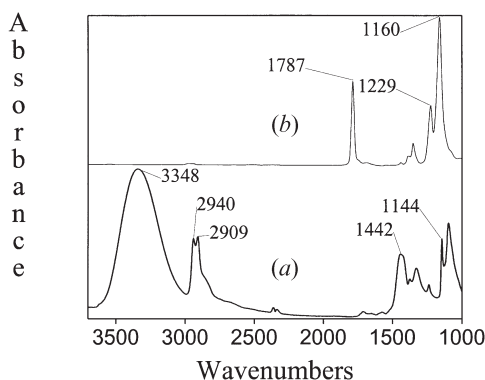

Figure 2. The FTIR spectra of PVA: (a) before derivatization; (b) after TFAA derivatization.

Table 1. Peak assignment for PVA.

Peak/cm^{-1}	Assignment[a]
3348	ν(OH)
2940	ν_a(CH$_2$)
2909	ν_s(CH$_2$)
1713	Residual CH$_3$CO
1442	δ(CH$_2$)
1376	δ(CH)
1328	δ(OH)$+\gamma_w$(CH)
1237	γ_w(CH)
1144	H-bonded OH in crystalline regions
1096	(C–O) unbonded, amorphous

[a]ν_s = symmetric stretching vibration; ν_a = asymmetric stretching vibration; γ_w = wagging vibration; δ = bending vibration.

3.2. Alignment of the LC molecules
3.2.1. Texture of the LC

To investigate the effect of the PVA alignment layer on LC texture, four LC cells with different treatment methods were prepared as described before: (a) untreated PVA, (b) rubbed PVA, (c) PVA derivatized with TFAA without rubbing, (d) PVA derivatized with TFAA after rubbing. After filling with E7 liquid crystal, the cells were observed under the microscope using crossed polarizers; photomicrographs are shown in figure 3. Figure 3(a) shows a schlieren texture, due to imperfect homogeneous alignment of the E7 LC [15], observed in the LC cell prepared using the PVA layer with no treatment. In contrast, the cell with rubbed PVA layer shows perfect alignment of the E7, as shown in figure 3(b). The difference between these two cells is the presence of scratch lines along the rubbing direction for the rubbed PVA layer, which are not present in the unrubbed PVA. With the crossed polarizing microscope, we also confirmed that the alignment directions of the LC molecules were either parallel or perpendicular to the rubbing direction, for the LC cell made with rubbed PVA.

Photomicrographs of LC cells with TFAA-treated PVA layers appear black under the crossed polarizing microscope due to homeotropic alignment of the LC molecules, as shown in figures 3(c) and 3(d). Homeotropic alignment of the LC was confirmed by the birefrigence seen on pressing the cell under the microscope. Figure 3(c) (TFAA-treated PVA without rubbing) shows a few surface inversion lines and many bright defect points; figure 3(d) (TFAA-treated PVA after rubbing) also shows many bright defect points. These bright defect points may be caused by the imperfect homeotropic alignment of LC molecules due to imperfect flatness of the PVA surface after TFAA treatment. A further study using atomic force microscopy will be published later.

3.2.2. FTIR measurement

To investigate the E7 alignment direction, polarized FTIR spectra were obtained for the ITO glass cell with rubbed PVA alignment layers. These are shown in figure 4; the peak assignments are shown in table 2 [12]. The direction of the transition dipoles of $-C\equiv N$ stretching in E7 is parallel to the molecular long axis
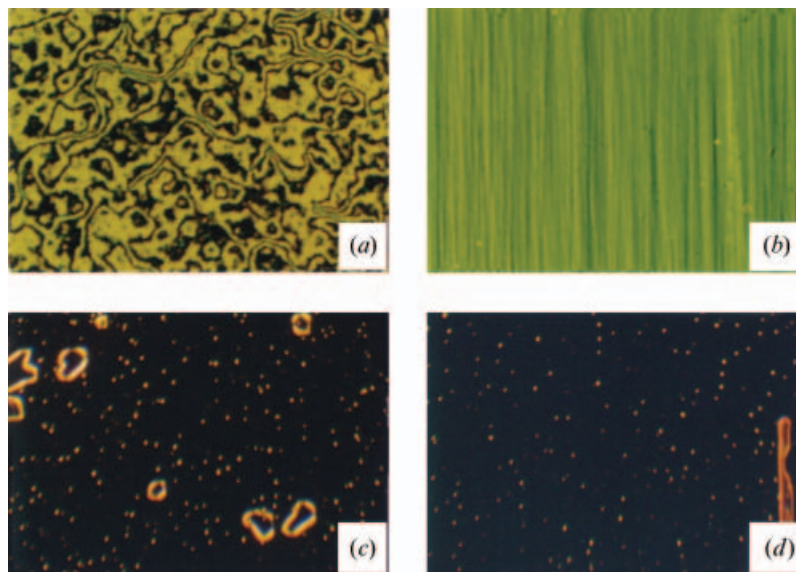

Figure 3. Photomicrographs ($\times$110) of ITO glass LC cells with different alignment layers: (a) PVA with no treatment; (b) rubbed PVA($\updownarrow$ rubbing direction); (c) TFAA-treated PVA with no rubbing; (d) PVA treated with TFAA after rubbing ($\updownarrow$ rubbing direction).

Table 2. Peak assignments for E7 nematic liquid crystal mixture.

Peak/cm^{-1}	Assignment
3027	C–H aromatic stretching
2957	Asymmetric stretching mode of CH$_3$
2929	Asymmetric stretching mode of CH$_2$
2872	Symmetric stretching mode of CH$_3$
2857	Symmetric stretching mode of CH$_2$
2227	Stretching mode of C≡N

of the LC molecules [16]. Also, the symmetric and asymmetric stretching modes of –CH$_3$ have components that are parallel, while the symmetric and asymmetric stretching modes of –CH$_2$ are perpendicular, to the molecular long axis of the LC molecules [17]. Therefore, IR dichroism may be used to study the orientation of the LC molecules in contact with the alignment layer.

Figure 4(a) shows the FTIR spectrum with polarization parallel to the rubbing direction. In this case the –C≡N stretching peak is larger than those of the –CH$_2$ stretching modes. In contrast, figure 4(b) shows strong symmetric and asymmetric stretching mode –CH$_2$ peaks at 2929 and 2857 cm^{-1}, as well as a weak –C≡N stretching peak at 2227 cm^{-1}, in comparison with the other –CH$_3$ stretching mode peaks. These demonstrate that the alignment direction of the E7 molecules is parallel to the rubbing direction. Figure 4(c) shows the difference spectrum obtained by subtracting spectrum (b) from spectrum (a). This clearly shows positive dichroic differences at the 2872 and 2227 cm^{-1} peaks, confirming the preferential alignment of LC molecules along the rubbing direction.

Figure 5 shows the FTIR spectra of LC cells with unrubbed PVA alignment layers. Figure 5(a) gives the

Figure 5. FTIR spectra of ITO glass LC cells with unrubbed PVA alignment layers: (a) with polarization parallel to the horizontal direction of the LC cell; (b) with polarization parallel to the vertical direction of the LC cell; (c) difference obtained by subtracting (b) from (a).

FTIR spectrum with polarization parallel to the horizontal direction of the LC cell. On comparing figures 5(a) and 4(a), we found that the relative peak intensity at 2227 cm^{-1} is weaker, and those at 2929 and 2857 cm^{-1} are stronger in 5(a) than in 4(a). However, on comparing the perpendicular cases, figures 5(b) and 4(b), the reverse trends are observed. Also, the difference spectrum in figure 5(c), shows almost no dichroic difference. These results strongly support the random orientation of the LC molecules when they are in contact with unrubbed PVA layers.

Figure 6 shows the FTIR spectra of the LC cell with TFAA-treated PVA alignment layer after rubbing; two distinct characteristics appear. First, both figures 6(a) and 6(b) show strong –CH$_2$ and –CH$_3$ stretching mode peaks at 2957, 2929, 2872 and 2857 cm^{-1}, and weak –C≡N stretching mode peaks at 2227 cm^{-1}. Second, the difference spectrum of figure 6(c) shows
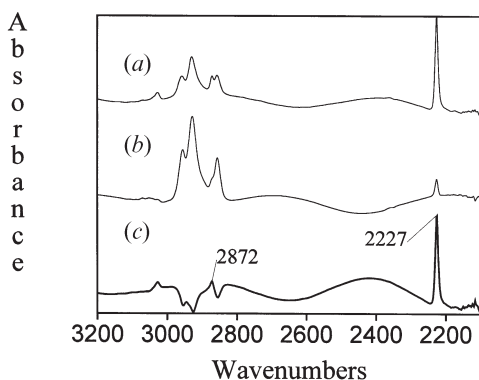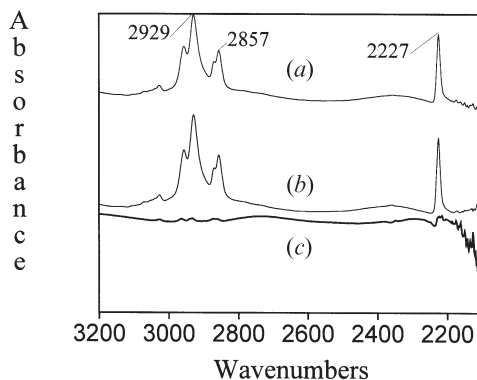

Figure 4. FTIR spectra of ITO glass cells with rubbed PVA alignment layers: (a) with polarization parallel to the rubbing direction; (b) with polarization perpendicular to the rubbing direction; (c) difference obtained by subtracting (b) from (a).
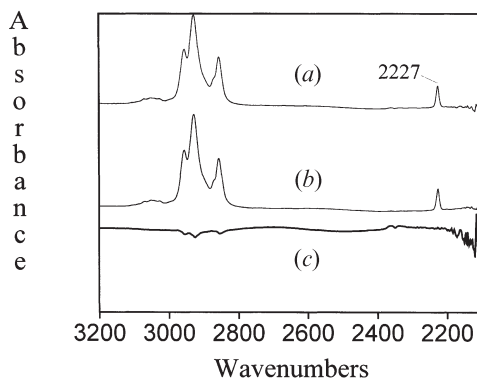

Figure 6. FTIR spectra of ITO glass LC cell with PVA alignment layer with TFAA treatment after rubbing: (a) with polarization parallel to the rubbing direction; (b) with polarization perpendicular to the rubbing direction; (c) difference obtained by subtracting (b) from (a).

very little dichroic difference even though this difference spectrum was expanded considerably as shown in the noise peak at $2116 \, \text{cm}^{-1}$, supporting the absence of preferential alignment orientation of LC molecules.

It is known that LC molecules on a rubbed PVA alignment layer have a very small pretilt angle. The unpolarized FTIR spectrum of the LC cell with rubbed PVA layer is an average of figures 4 (*a*) and 4 (*b*); this spectrum, which is not shown, is almost the same as in figures 5 (*a*) or 5 (*b*). Therefore, comparing the FTIR spectra of figure 6 with the FTIR spectra of the LC cell with unrubbed PVA alignment layer, figure 5 (*a*), will give supporting evidence of the vertical alignment of LC molecules on the TFAA-treated PVA alignment layer.

The peak at $2872 \, \text{cm}^{-1}$ due to $–CH_3$ symmetric stretching vibration is stronger in figure 5 (*a*) than in figures 6 (*a*) and 6 (*b*). Also, the peak intensity at $2227 \, \text{cm}^{-1}$ due to $–C \equiv N$ stretching is stronger in figure 5 (*a*) than in figures 6 (*a*) and 6 (*b*), when it is normalized to the asymmetric stretching of $–CH_2$. The two peaks are weaker in figures 6 (*a*) and 6 (*b*) than in figure 5 (*a*) because the dipole moments are parallel to the LC molecular long axis. Thirdly, the absence of preferential alignment orientation of the LC molecules on the alignment layer is supported by the almost zero dichroic difference, as shown in figure 6 (*c*). If the LC molecules stand vertically on the ITO-coated glass, dipole moment changes perpendicular to the substrate will not be detected by transmission spectroscopy [18]. We thus have confirmation of the vertical orientation of the LC molecules on the TFAA-treated PVA alignment layer, in agreement with the photomicrograph results of figure 3.

Both FTIR and crossed polarizing microscopy strongly support the homeotropic alignment of E7 LC molecules in contact with the derivatized PVA alignment layer. This change of the liquid crystal molecules from homogeneous to homeotropic alignment may be caused by the decrease of the surface tension of the PVA alignment layer due to substitution of the polar $–OH$ groups by $–OCOCF_3$ groups by gas-phase derivatization. The surface tension of PVA is $37 \, \text{dyn} \, \text{cm}^{-1}$, but the surface tension of the $–CF_3$ group, which will be located preferentially at the surface of the derivatized PVA, is $15 \, \text{dyn} \, \text{cm}^{-1}$ [19].

This result may be used for patterning the LC alignment, by controlling the exposure of the PVA alignment layer to TFAA. The areas of PVA exposed to TFAA will produce homeotropic alignment of the LC, and the unexposed area will produce homogeneous LC alignment.

4. Conclusions

We have arrived at the following conclusions:

1. By the derivatization of PVA with TFAA, peak intensities at 3348 and $1144 \, \text{cm}^{-1}$ were almost completely removed due to the disappearance of $–OH$ groups; new strong peaks at 1787, 1229 and $1160 \, \text{cm}^{-1}$ were introduced due to the complete replacement of $–OH$ groups with $–OCOCF_3$ groups.
2. By changing the $–OH$ groups of the PVA alignment layer to $–OCOCF_3$ groups after rubbing, the alignment of liquid crystal molecules in contact with a derivatized PVA layer changed from homogeneous to homeotropic due to a decrease in surface tension.

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