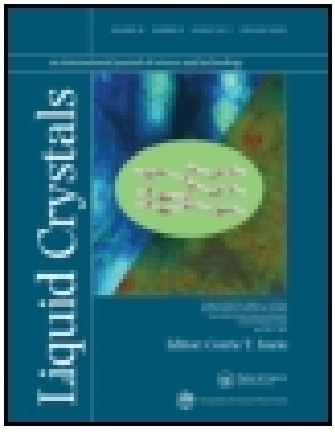

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# Physicochemical properties of long-hydrocarbon-chain-silane-coated indium tin oxide glass for reverse-mode polymer-dispersed liquid crystals

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# Physicochemical properties of long-hydrocarbon-chain-silane-coated indium tin oxide glass for reverse-mode polymer-dispersed liquid crystals

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We prepared silane-coated indium tin oxide (ITO) glass having different surface energies and topologies by using dipping and evaporation methods with the silane solution. The silane-coated ITO glass samples were analysed using contact angles and atomic force microscopy. Liquid crystal (LC) cells with positive and negative dielectric LCs and a mixture of negative dielectric LCs and liquid crystalline monomers were viewed between crossed polarisers. The ITO glass prepared using the dipping method showed a rougher topology and higher surface energy than the ITO glass prepared using the evaporation method. LCs having positive and negative dielectric anisotropy showed vertical alignment on the silane-coated ITO glass samples as viewed between crossed polarisers. However, the mixture of negative dielectric LCs and liquid crystalline monomers showed vertical alignment only for the ITO glass prepared using the evaporation method. The evaporation method was used for fabrication of reverse-mode polymer-dispersed liquid crystals, and the crystals showed well-aligned vertical polymer networks, good reverse operational mode and a double-U-shaped graph around each 40° by the crystal rotation method.

**Keywords:** polymer-dispersed liquid crystals; silane; reverse-mode polymer-dispersed liquid crystals; off-axis haze; surface energy



## 1. Introduction

Polymer-dispersed liquid crystals (PDLCs) are potential electro-optical (EO) devices for future application. There are normal-mode PDLC (N-PDLC) and reverse-mode PDLC (R-PDLC). N-PDLC structure is that positive dielectric anisotropic liquid crystal (P-LCs) droplets and polymer matrix are sandwiched between transparent electrodes. Incident lights are scattered by mismatching of refractive indices of liquid crystals and polymer matrix. Applying electric field between electrodes, N-PDLC becomes transparent state due to matching of refractive indices.[1–4] However, R-PDLC has opposite EO states with N-PDLC.[5] Generally, a mixture of negative dielectric anisotropy liquid crystals (N-LCs) and liquid crystalline monomers (LCMs) is vertically aligned on an electric substrate to fabricate R-PDLC. After polymerisation of the vertically aligned liquid crystals (LCs) and LCMs between two transparent electrodes, the sample becomes transparent. The transparent state can be changed to an opaque state by application of an electric field, which is caused by the mismatching of the refractive indices of the N-LCs and polymerised LCM network.[2] Those PDLCs can be used to control the light intensity, such as in smart windows, refractive-type displays, microlenses, etc.[6–8] Generally, surface treatment of the electrode is required for homeotropic alignment of the LCs.[9–11] Long-hydrocarbon-chain silanes have been being studied as candidates for the vertical alignment of LCs on electric substrates. It is well known that long-hydrocarbon-chain silane makes covalent bonds with hydroxides on the surfaces of inorganic electric substrates, which form a self-assembled monomer (SAM) layer with a lower surface energy than uncoated substrates.[12,13] Furthermore, Khan et al. [13] found that substrates with a lower surface energy than the surface tension of LCs can induce homeotropic alignment of LC molecules. However, Hwang et al. [14] used an amorphous silicon oxide (a-$SiO_x$) layer on indium tin oxide (ITO) glass to induce vertical alignment of the N-LCs. They showed that the surface energy and the vertical alignment of the LCs were unrelated. The mechanism of vertical alignment of LCs on electric substrates cannot be explained only by the relationship between the surface energy and the surface tension of the LCs. The surface energy is also related to the surface roughness and the chemical properties of the substrate surface. [15] Herein, we prepared silane-coated ITO glasses using both dipping and evaporation methods. The physicochemical properties of the silane-coated ITO

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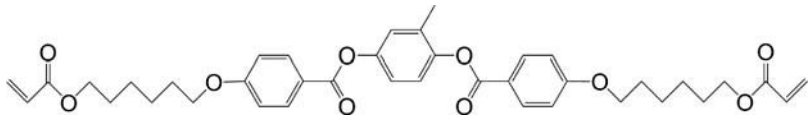

Figure 1. Structure of the liquid crystal monomer molecule.

glass surfaces were investigated with contact angle and atomic force microscopy (AFM), and LC cells having positive- and negative-dielectric anisotropy and LCMs were viewed between cross polarisers. The polymer morphology of the fabricated R-PDLCs with silane-coated ITO glass was observed with scanning electron microscopy (SEM). The EO properties were analysed with a spectrophotometer and the crystal rotation method.

## 2. Experiment and materials

ITO glass substrates (20 × 30 mm) with a root mean square (RMS) roughness of 0.493 nm were washed with Alconox® (5 wt% aqueous). The substrates were sequentially sonicated with acetone (assay ≥99.5%) and isopropyl alcohol (assay ≥99.5%) for 20 min each. The chemicals were purchased from Sigma-Aldrich, Korea. After drying in an oven (90°C), the ITO glass substrates were dipped into a solution of $H_2O_2$ (30 vol%), $NH_4OH$ (30 vol%) and $H_2O$ (40 vol%) for substituting hydroxide function on the ITO surface.[16] After 24 h, the ITO glass substrates were washed with deionised (DI) water. The remaining solution on the ITO glass was removed with $N_2$ gas (UHP grade). For the silane coating on the prepared ITO glass substrates, a solution of 95 vol% of toluene (assay 90%) and 5 vol% of trimethoxy-(octadecyl)silane (assay ≥90%) was prepared.[17,18] For the dipping method, the hydroxide-substituted ITO glass substrates were dipped into the silane solution for 24 h at room temperature. For the evaporation method, for the evaporation method, 2 mL of the silane solution was dropped on the ITO glass, which was heated to evaporate the solvent at 75°C for 1 h on a hotplate. The ITO glass was then rinsed with dried toluene and ethanol sequentially and any residual solution was removed with $N_2$ gas. Finally, the silane-coated ITO glass substrates prepared using the two methods were dried in an oven at 90°C for 1 h.

The physical topologies of the silane-coated ITO glass substrates prepared using the two methods were analysed by AFM (Nanoscope IIIa, Veeco/Digital Instruments, New York, NY, USA). In order to understand the interactions between the LCs and the ITO glass substrates, we prepared glass in which the ITO layer was removed by hydrochloric acid, ITO glass and silane-coated ITO glass prepared by two methods. The contact angles on the glass substrates were measured with the sessile drop method (DSA 100, KRÜSS, Hamburg, Germany) by using DI water and diiodomethane to calculate the surface energy with the Owens–Wendt method.[2] A P-LC (BL001, $\Delta\varepsilon$ = +14, $T_{nI}$ = 65°C, Merck, Germany), N-LC (SLC12V620-220, $\Delta\varepsilon$ = −5.1, $T_{nI}$ = 99.1°C, SLICHEM, China), and mixture of N-LCs and LCMs (1,4-bis-[4-(6-acryloyloxy-hexyloxy) benzoyloxy]-2-methylbenzene, Angene International, Hong Kong) (Figure 1) in a 9:1 weight ratio were used for measuring the contact angles on the glass substrates in order to understand the interactions between the LCs and the silane-coated ITO glass. Furthermore, LC cells with a 20 μm gap were fabricated for each glass substrate and the cells were observed between cross polarisers.

An R-PDLC cell was fabricated with the mixed N-LCs and LCMs in a weight ratio of 9:1. A photoinitiator (2-hydroxy-2-methylpropiophenone, Sigma-Aldrich, Korea) was added at 1 wt% of the LCMs. The mixture was introduced by capillary action in the 20 μm gap between two silane-coated ITO glasses prepared using the evaporation method. After confirmation of vertical alignment of the mixture using crossed polarisers, the prepared cell was cured using 365 nm UV radiation (140 μW/cm$^2$) at room temperature. To observe the polymer network, a cell with a detached upper ITO glass was dipped in methanol for 1 h. After drying in a vacuum box, the cell was observed by using SEM (JSM-5200, JEOL, Korea). The EO properties were analysed by a CM-3500 spectrophotometer (air was used for calibration; MINOLTA, Osaka, Japan) and the crystal rotation method.[2]

## 3. Results and discussion

The dipping method is widely used to coat a silane layer onto inorganic substrates, resulting in a thick non-uniform multilayer. However, the introduction of a base catalyst gives rise to a relatively thin uniform silane SAM layer.[18] Fadeev et al. [19] suggested that silanisation on the substrates depends on the kinetics of the reaction under different conditions. For

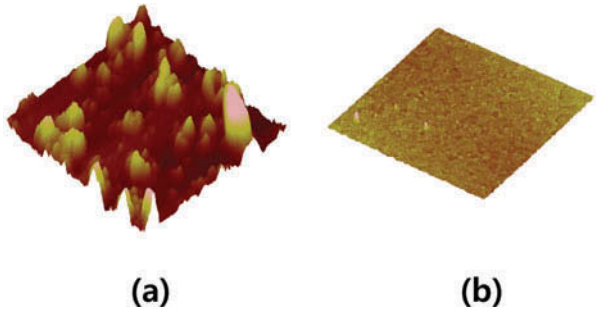


Figure 2. (colour online) AFM images of silane-coated ITO glass prepared with (a) dipping method and (b) evaporation method.

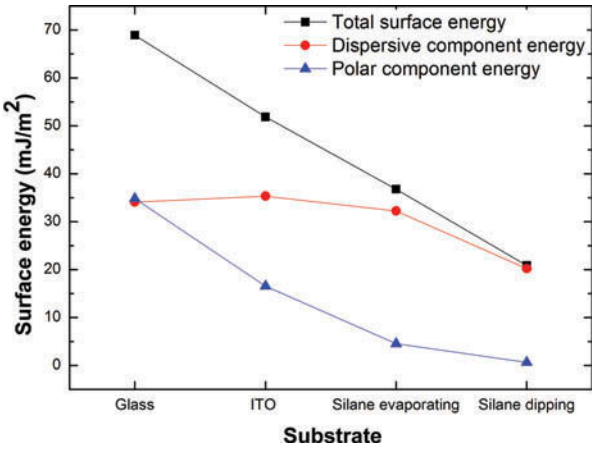


Figure 3. (colour online) Polar, dispersive and total surface energies of glass, ITO glass and silane-coated ITO glass coated by using the dipping and evaporation methods.

example, tri-functional silane would polymerise the self-assembly, covalent attachment and vertical polymerisation layers according to conditions on the inorganic substrates.

The AFM images in Figure 2 show the long-hydrocarbon-chain-silane-coated ITO glass prepared using the dipping and evaporation methods. The dipping method substrate had a rough surface of 9.53 nm RMS and the evaporation-method substrate had a relatively even surface of 0.466 nm RMS. The two silane-coating methods on the ITO glass resulting in different topologies that were caused by different kinetics of reaction. The dipping method resulted in a rough topology that might have slow kinetics at the room temperature between the silane molecules and the ITO glass surface, which would have led to vertical polymerisation consisting of polymeric multi-silane layers.[18,19] Using a catalyst or heating during the polymerisation reaction can increase silanisation reactivity, resulting in a SAM or covalent attachment on the electric substrates, which have even topologies. These different topologies have different effects on the surface energy of the substrate.[20,21] The surface energy change for the glass, ITO glass and silane-coated ITO glass prepared by the two methods was calculated for polar and dispersive components and total energies using the DI water and diiodomethane contact angles by the Owens–Wendt method.

Figure 3 shows the surface energy changes for each substrate. The two silane-coated glass substrates had lower surface energies for the polar and dispersive components and total surface energy than the other samples. Especially, the dipping-method ITO glass, which had the rough topology as shown in Figure 2, showed the lowest energy. Therefore, it is obvious that the different coating processes induce different kinetics of reaction, which in turn affects the roughness and surface energy of the substrates.

The physicochemical properties of electric substrates can influence the LC–LC and LC–substrate interactions, which in turn affect the alignment of LC molecules. Therefore, the changed physicochemical properties of an electric substrate as a result of the effect of silane coating on the surface energy might consequentially affect interactions between the LC molecules because of the changes in LC–substrate interactions. The vertical alignment of LC molecules on the silane-coated electric substrate might depend on the LC–LC and LC–substrate interaction forces (e.g. van der Waals interactions) and also on the induced dielectric (London dispersion) axial direction of the LCs, such as positive and negative dielectric anisotropy.[14] Silane or surfactant molecules having long hydrocarbon chains have been used for vertical alignment on electric substrates whose surfaces become hydrophobic because of alkyl chains,[13,22] forming a hydrophobic screen layer between the LCs and the electric substrate. The interaction force between the LC molecules and the surface-treated electric substrates has been studied in many ways. [14,23] Hwang et al. [14] reported the deposition of a fluorinated diamond-like carbon (FDLC) layer on $SiO_x$ as a screen layer in order to research the interaction forces between LCs and the $SiO_x$ layer. The vertical alignment of LC molecules was maintained on a 30-nm-thick FDLC layer. They proved that the vertical alignment of LC molecules on the FDLC-coated $SiO_x$ was induced by the long-distance interaction forces (London dispersion) between the LC molecules and the $SiO_x$ substrate. To confirm the interaction changes as a result of silane coating, we used the sessile drop method. Figure 4 shows the variations in the contact angles of the LCs on each substrate.[2] The glass, ITO glass and silane-coated ITO glass prepared by the two methods were used for

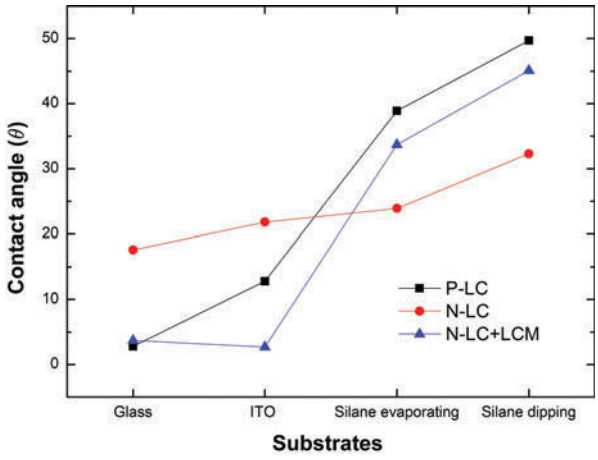


Figure 4. (colour online) Variations of contact angle of the P-LCs, N-LCs and mixture of N-LCs and LCMs on the different substrates.

the substrates and P-LCs, N-LCs and a mixture of N-LCs and LCMs were used for the sessile drops. Interestingly, the N-LCs show a tendency different from that of the P-LCs and the mixture of N-LCs and LCMs.

As shown in Figure 4, the P-LCs and the mixture of N-LCs with LCMs show low contact angles (below 5°) on the glass and ITO glass because the hydroxide functional groups would strongly interact with the LC molecules, whereas the contact angles on the two silane-coated ITO glass substrates were more than 40°. However, the contact angle for the N-LCs tended not to depend on the substrate type. The dielectric properties of LCs on inorganic electric substrates influence the alignment angle of LC molecules.[24] In this study, the P-LCs have a $\Delta\varepsilon$ of +14, which might induce more significant interactions with substrates than the N-LCs ($\Delta\varepsilon$ of −5). In the case of the mixture of N-LCs and LCMs, the LCM molecules have a symmetric structure,[25] which might disturb the electric interaction between LC molecules, thus increasing the interaction force between LC molecules and the substrate. Accordingly, the contact angle of the mixture might be different from that of the N-LCs.

The long-hydrocarbon-chain-silane coating on inorganic substrates usually shows lower polar energies and higher dispersive energies than raw inorganic substrates.[19] In Figure 3, however, both the component energies and contact angles of the LCs decreased as a result of silane coating. The polar component energy of the dipping-method silane-coated ITO glass was almost zero, and the glass had a relatively lower dispersive energy value than the glass prepared using the evaporation method. In Figure 4, the dipping-method substrate has larger angles than the evaporation-method substrate for every LC. These results might be due to the difference physical properties of the substrate surface with nano-size bumps (shown in Figure 2), which can induce super-hydrophobicity. Figure 5 shows LC cells between cross polarisers

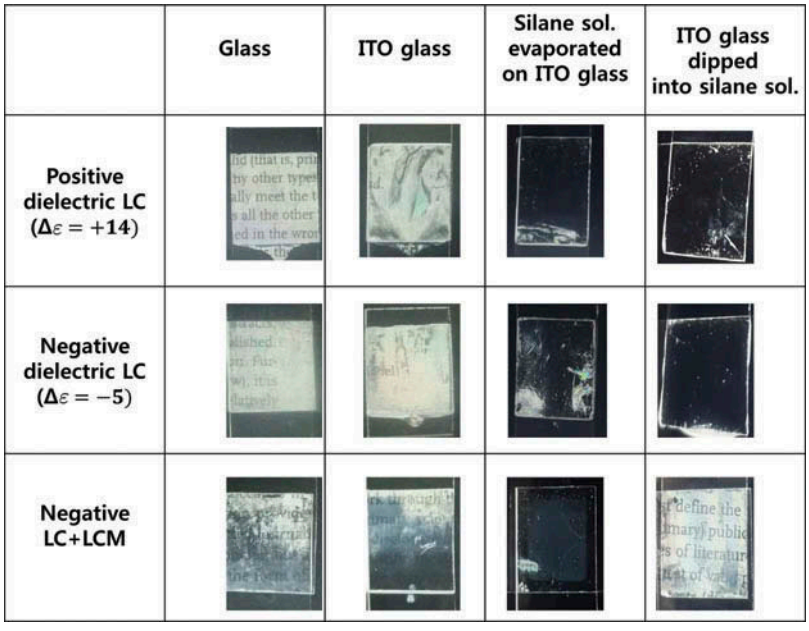


Figure 5. (colour online) LC cells viewed between cross polarisers. The cells were made with glass, ITO glass, and ITO glass coated with silane by using evaporation and dipping methods. The cells were filled with LCs having positive and negative dielectric anisotropy and negative dielectric LCs mixed with 10 wt% LCM.

made with the substrates and LCs in Figure 4. The glass and ITO glass cells show random alignment of LCs due to strong interaction between the LCs and substrates, whereas the silane-coated ITO glass cells show good vertical alignment of the LCs. The dielectric properties of LCs are also an important factor for vertical alignment of the LCs. Many previous studies have reported that large negative dielectric anisotropy makes LCs difficult to align vertically.[24] Our results also show poor vertical alignment in the case of the N-LC cell ($\Delta\varepsilon = -5$), whereas the P-LC cell shows good vertical alignment. Since N-LC molecules have different directions for the large dielectric axis and molecular axis, the vertical alignment of N-LCs is more difficult than that of P-LCs having the same direction of large dielectric axis and molecular axis. Interestingly, the mixture of N-LCs and LCMs shows difference alignments corresponding to the coating method. The evaporation-method cell shows vertical alignment, whereas the dipping-method cell shows random alignment, which might be due to the different physicochemical properties of the silane layer. The dipping-method substrate had a rough surface consisting of multilayers of hydrophobic hydrocarbon silane, as shown in Figure 2. These multilayers could disturb interactions, acting as a screening layer between LCs, LCMs and ITO glass. The evaporation method had a smoother topology that could form a relatively thin hydrophobic layer (Figures 2 and 3), which might have an appropriate screening effect to preserve the long-range interactions that could induce the vertical alignment of LCs and LCMs. Furthermore, the mixed LCMs might make LCs interact appropriately with the silane evaporation layer. As a result, the screening effect as a result of the coating thickness weakens the short-range interaction force, which leads to vertical alignment of the LCs and LCMs.

An R-PDLC sample was fabricated using the evaporation method. Figure 6 shows the SEM image of the polymer network after removing the LCs from the R-PDLC sample. The image shows good vertical alignment of the polymer network on the silane-coated ITO glass, even though shrinking took place on the detached substrate side while drying the solvent. The vertical polymer network maintained its direction after polymerisation of the LCMs due to the vertically aligned N-LCs and LCMs on the hydrophobic and appropriately thick silane layer. Thus, the vertical polymer network in the sample is considered to have maintained well the vertical alignment of the LCs. Consequently, the sample has the ordinary refractive index of the LCs in a direction perpendicular to the electric substrates. Because of the vertical alignment of the LCs and the polymer network,

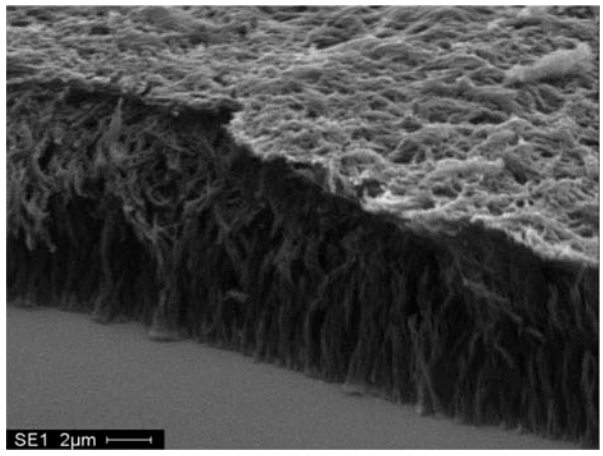


Figure 6. SEM image of polymer networks of R-PDLC.

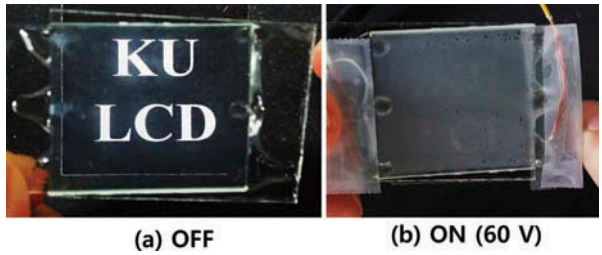


Figure 7. (colour online) Off–on images of R-PDLC sample made with silane evaporation method on ITO glass.

refractive index mismatching does not occur between the LCs and the polymer network.

Figure 7 shows the off and on states of the R-PDLC sample. The sample shows a very transparent off state because the LC molecules in the sample are well aligned perpendicular to the silane-coated ITO glass. Furthermore, for the on state at 60 V, there is strong scattering by the refractive index mismatch between the LCs and the polymer network. The EO properties of the R-PDLC sample were measured by spectrophotometer.

Figure 8 shows the voltage–transmittance ($V$–$T$) curve for the R-PDLC sample with the evaporation-method ITO glass. As shown in the figure, the off state and on (70 V) transmittances are approximately 80% and 15%, respectively. The loss of transmittance is due to the ITO, silane layers and air calibration. The transmittance of R-PDLC at the off state depends on the pre-tilt angle of the LCs. The crystal rotation method was used to confirm the pre-tilt angle of the LCs.

Figure 9 shows the change in the transmitted light intensity of a Ne–He laser according to the angle of the R-PDLC sample, which was controlled to be 5° from side to side. The solid line was curves of ninth-

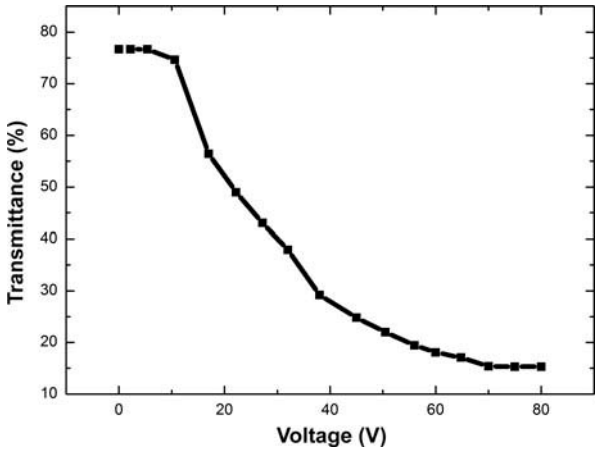


Figure 8. *V–T* curve for R-PDLC with silane-coated ITO glass by evaporation method.

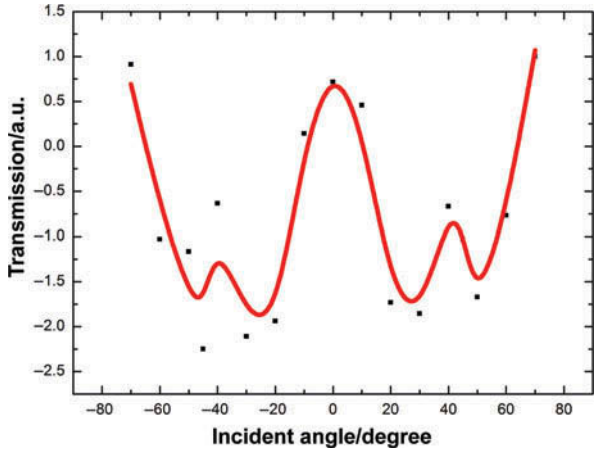


Figure 9. (colour online) Angular dependence of He–Ne laser beam transmission passed through the R-PDLC cell. Solid line is fit to ninth-order polynomials.

order polynomial fits. Previous studies showed that the shape of the R-PDLC graph was sinusoidal like vertical alignment mode LC display.[26] In the current results, the transmitted light intensity again increased at approximately ±40°, which graph was similar to the double-U. Kim et al. [27] have shown a PDLC with transparent state initially that had vertically aligned LC by a polymer alignment layer. They analysed the total scattering cross section of LC droplets depending on angle of samples. The PDLC cell with transparent state initially showed better viewing angle than an N-PDLC. Generally, an N-PDLC has off-axis haze at on state due to refractive indices mismatching between polymer network and liquid crystal.[28–30] Yaroshchuk et al. [30] have reported nanoparticles doped N-PDLC on reducing haze at off-axis. The doped nanoparticle had similar refractive index with $n_e$ of LC, which led to an increase in the refractive index of polymer. The nanoparticle-doped N-PDLC showed low off-axis haze. However, R-PDLCs using LCMs usually have less off-axis haze because they have a thin network or a polymer ball network, which is well known as a haze-free polymer network type.[31] Furthermore, Lee et al. [32] reported a new type of PDLC using dual-frequency LC and LCM which were aligned vertically on the polyimide layer. Their PDLC showed wide viewing angle due to similarity of refractive index of LC and LCM.

The fabricated R-PDLC had 10 wt% polymer, whose networks appeared as thin networks rather than ball type, which is shown in Figure 6. The transmitted light intensity at ±40° depends on the refractive indices of the glass, ITO layer, LC molecules and polymerised LCMs. N-LCs have $n_o$ of 1.49 and $n_e$ of 1.65. The refractive indices of polymerised LCMs have been analysed as approximately $n_o$ of 1.53 and $n_e$ of 1.66.[33] The refractive indices are similar to each other, especially $n_e$, which might result in the double-U-shaped graph at the off-axis seen in Figure 9. However, the relation of refractive indices for N-LCs and the polymer network would be difficult to analyse clearly because of the structural complication of LC domains and the polymer network.

As a result, the hydrocarbon silane coating of an ITO glass by using evaporation induced the vertical alignment of the mixture of N-LCs and LCMs. Silane layer is mechanically more stable due to covalent bond with substrate surface than conventional vertical alignment methods such as using surfactant, nanoparticles and polyimide.[2,9,26] It is easy to apply to a flexible plastic film substrate for roll-to-roll system. An R-PDLC fabrication was also simple and no need other expensive equipment to make vertical alignment of N-LC and LCM.[34] The fabricated R-PDLC displayed good EO properties and low off-axis haze, making it a candidate as a competitor for N-PDLCs.

## 4. Conclusion

The surface of long-hydrocarbon-chain-silane-coated ITO glass using the evaporation method showed hydrophobic properties and even roughness. The silane layer was allowed to interact appropriately with the mixture of N-LCs, LCMs and the ITO substrate in order to induce the homeotropic alignment of the mixture of the N-LCs and LCMs. An R-PDLC fabricated using the evaporation method had a well-aligned vertical polymer network that maintained the homeotropic alignment of N-LCs. The R-PDLC showed good the *V–T* curve and the double-U-shaped

graph which was caused by the low off-axis haze due to the refractive indices of N-LCs and LCMs. The R-PDLC fabricated using the silane evaporation method can be more useful for developing optical devices and smart windows than conventional PDLCs.

## Disclosure statement

No potential conflict of interest was reported by the author(s).

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