Nanoparticle-doped polyimide for controlling the pretilt angle of liquid crystals devices

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Abstract: The pretilt angles of liquid crystal molecules can be controlled by using conventional polyimide (PI) alignment material doped with different concentrations of Polyhedral Oligomeric Silsequioxanes (POSS) nanoparticles, which have been observed to spontaneously induce vertical alignment. The addition of POSS in the homogenous PI changes the surface energy of the alignment layer and generates a variable pretilt angle. Experimental results demonstrate that the pretilt angle θ_p is a function of the POSS concentration, and can be tuned continuously over the range of $0° < \theta_p < 90°$. The polar anchoring energy of POSS/PI alignment layer is almost constant regardless of the POSS concentration. This technique is very simple and is compatible with methods familiar in the current LCD industry.

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1. Introduction

The pretilt angle of a conventional liquid crystal (LC) device is either near zero degrees or 90 degrees for the homogeneous and homeotropic alignments, respectively. The technique of producing homogeneous and homeotropic surface alignment is mature in the LC display (LCD) industry. However, many LCDs, such as the no-bias optically-compensated bend (OCB) LCD and the bi-stable bend-splay (BBS) LCD, require high pretilt angles in the range of 45° - 60° [1,2]. The OCB LCD has attracted much attention in recent years by reason of its fast response and inherent wide view angle property [3]. The memory effect of a bistable LCD is very highly suitable for electronic-paper applications due to the low power consumption. There are many methods have been developed to control the pretilt angle of LC with a wide range, such as: SiOx oblique evaporation [4,5], polymer-stabilized alignment [6], nanostructured surfaces [7–9], hybrid mixture of two materials [10–12], and chemical synthesis [13,14]. However, the reliability, the mass production capability and ease of material synthesis for those developed techniques are questionable. For example, a high vacuum system is required for oblique evaporation of SiOx. Hence, the throughput of production is low, and the display size will be limited.

Recently, we have reported a new method, nanoparticle-induced vertical alignment (NIVA), to align LC vertically by adding polyhedral oligomeric silsesquioxane (POSS) nanoparticles with POSS molecules of diameters of the order of a few nanometers to the liquid crystal [15,16]. In practice, the NIVA phenomenon results from the adsorption of the nanoparticles on the inner surfaces of the ITO glass substrates. The aptitude of vertical alignment induced by POSS nanoparticles was found to be significantly influenced by the doped POSS concentrations [15,16]. The NIVA technique was applied to generate variable liquid crystal pretilt angles based on doping different concentrations of POSS nanoparticles in the planar-aligned LC layer. The competition between the nanoparticle-induced vertical alignment domains and the horizontally aligned polyimide (PI) will result in the LC molecules realigning themselves to achieve a variable pretilt angle near the alignment surface [17]. However, it is not easy to reach a uniform distribution of POSS nanoparticles in the LC layer and to avoid POSS aggregation in the LC layer, therefore some scattering is produced around the POSS clusters and these reduce the contrast of LCDs. In this work, we propose and demonstrate a novel method that the pretilt angle of liquid crystal molecules can be continuously controlled by using conventional homogeneous PI alignment material doped with different concentrations of POSS nanoparticles. The addition of POSS in the homogenous PI lowers the surface energy of the alignment layer and generates the variable pretilt angle θ_p in a range of $0°<\theta_p<90°$. This method utilizes the conventional PI alignment materials, the manufacture processes and facilities, therefore it can readily be adopted by the current LCD industry.

2. Experimental

The mixture of the POSS/homogeneous alignment PI solution was prepared at different POSS weight ratios from 0.01% to 0.18% by using an ultrasonic processor (S4000, Misonix) to

obtain a good dispersion. Propyl-hepta-isobutyl substituted POSS (aminoethyl-aminopropylisobutyl-POSS, Aldrich) which have been observed to spontaneously induce vertical alignment (NIVA) and which was used as the nanoparticle. The POSS/PI mixture was then spin-coated on the ITO glass substrates to obtain a thin alignment film. Afterward, a prebaking at 100°C for 10 minutes and post baking at 200°C for 1 hour, were applied to cure the POSS-doped PI mixture to form the alignment layer. Then the surface of the alignment layer was subjected to rubbing treatment using a nylon cloth in such a way that the alignment layer was rubbed once in each direction. The surface energy of the alignment layer was determined by measuring the contact angle of distilled water (DIW) on the films according to the Girifalco-Good-Fowkes-Young model [18]. To determine the pretilt angle of LC molecules on POSS/PI alignment layers, the antiparallel LC test cells were fabricated with a cell gap of 6.75μm and the capillary filled with LC molecules (E7, $\Delta\varepsilon = 14.1$, $\varepsilon_\perp = 5.2$; Merck). The electro-optical properties of the LC cells were evaluated by means of the polarizing optical microscope (POM), phase retardation-voltage (PV) and transmittance-voltage (TV) measurements, respectively. The pretilt angles of LC cells were measured by the modified crystal rotation method [19]. The voltage-dependent optical transmission of the LC cell, placed between crossed polarizers, was measured using a 633-nm He-Ne laser, and the applied voltage was a 1-kHz square wave. The polar anchoring energy (PAE) of the POSS/PI alignment layers was measured by using the high electric field method [20].

3. Results and discussion

The results of the contact angle of DIW drop on the PI/POSS alignment layer with different POSS wt% doped in PI are shown in Fig. 1. The contact angle increases with the POSS wt% doped in PI; that is the surface energy decreases with the POSS concentration as shown in Fig. 1. It indicates that the addition of the POSS nanoparticles in the PI mediates and lowers the surface tension of the alignment layer.
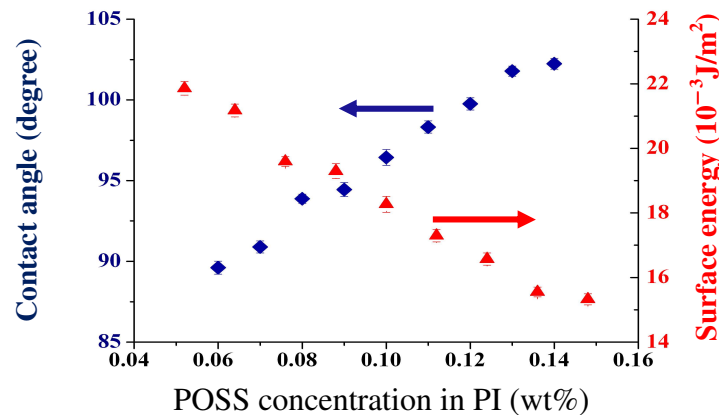

Fig. 1. Contact angle of distilled water drop on POSS/PI alignment layer and surface energy of POSS/PI alignment layer as a function of POSS concentration in PI.

The photographs of antiparallel LC cells with different POSS wt% doped in PI film observed by the POM are shown in Fig. 2. Each color represents a different pretilt angle corresponding to a different phase retardation. From the uniform color images of different LC cells, we can conclude that this novel method of POSS/PI alignment layer provides a simple way to reach a uniform and controllable pretilt angle in each LC cell. By using our previous method of doping POSS into LC bulk, ~1.2 wt% POSS in LC is required to reach the maximum pretilt angle due to only part of POSS absorbed on the PI surface [17]. In this work, only ~0.16 wt% POSS are added into the PI to reach the maximum pretilt angle. Therefore,

the proposed method in this work shows better uniformity of POSS distribution and less POSS aggregation than our previous work.
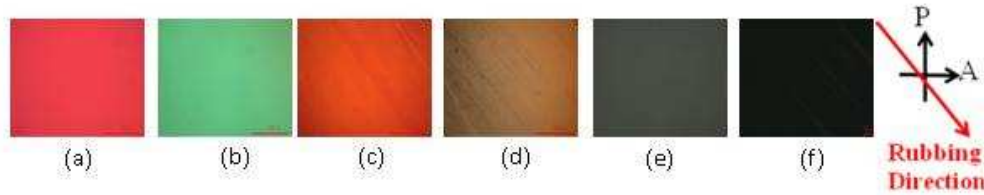

Fig. 2. Photographs of antiparallel LC cells observed by POM with various POSS concentration doped in PI: (a) 0.05%, (b) 0.08%, (c) 0.10%, (d) 0.11%, (e) 0.12%, and (f) 0.14%.

The pretilt angles of the LC cells with different POSS wt% doped in PI film are shown in Fig. 3. The pretilt angle is observed to increase with increasing the POSS concentration doped in PI material, and a wide range of pretilt angles, $0° < \theta_p < 90°$, can be generated by varying the doped POSS concentration from 0 to 0.16 wt %. The pretilt angle of the LC molecules on the rubbed alignment layer was mainly determined by the anchoring factors, steric effect, and electronic interaction [21]. The dependence of an increase of pretilt angle with a decrease of the surface energy of alignment layer was reported [21–23]. The addition of the POSS nanoparticles in the PI mediates and lowers the surface energy of the alignment layer as shown in Fig. 2. Consequently, both the lower surface energy, and the higher POSS wt% doped in PI, correspond to a higher pretilt angle as shown in Fig. 3.
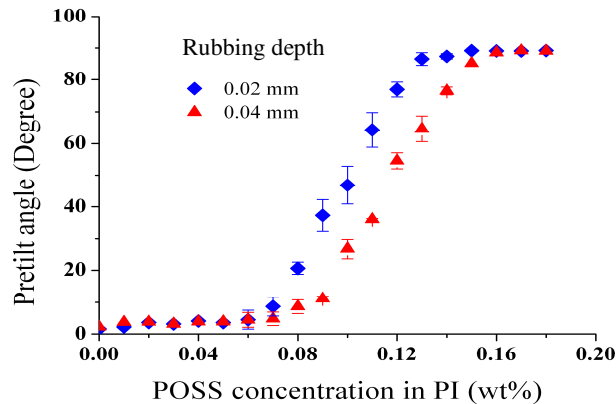

Fig. 3. Dependence of pretilt angle on POSS concentration in PI for two different rubbing depth.

The dependence of rubbing depth on pretilt angle is also illustrated in Fig. 3. A stronger rubbing depth produces a lower pretilt angle. The increase of rubbing depth can enhance the polarity of the POSS/PI alignment surfaces due to the anisotropic alignment of the polymer chain to the rubbing direction [22]. The influence of surface polarity of alignment layer on pretilt angle has been investigated [21–23]. It showed that an alignment layer with more polar surfaces gives the lower pretilt angle due to the increased attractive strength between LC molecules and molecules of the alignment surface.

The voltage-dependent optical phase retardation of antiparallel LC cells with different POSS wt% doped in PI was measured by common path heterodyne interferometry [24] as shown in Fig. 4. In the voltage-off state, the LC molecules are mainly aligned by alignment layers with a pretilt angle θ_p, meaning that the maximum phase retardation φ_{max} of the LC cell

is reached and equal to $\Gamma_{max} = \dfrac{2\pi}{\lambda}(n_e^{eff} - n_o) \cdot d$. Here $n_e^{eff} = \dfrac{n_e \cdot n_o}{\sqrt{n_e^2 \sin^2\theta_p + n_o^2 \cos^2\theta_p}}$, where n_e

and n_o are the extraordinary and ordinary refractive indices of the LC material, respectively. The maximum phase retardation below the threshold voltage decreases with the POSS wt% doped in PI, indicating that the liquid crystal pretilt angle increases from ~0° to ~90° as the concentration of POSS doped in PI increases. These results are consistent with the results of Fig. 3.
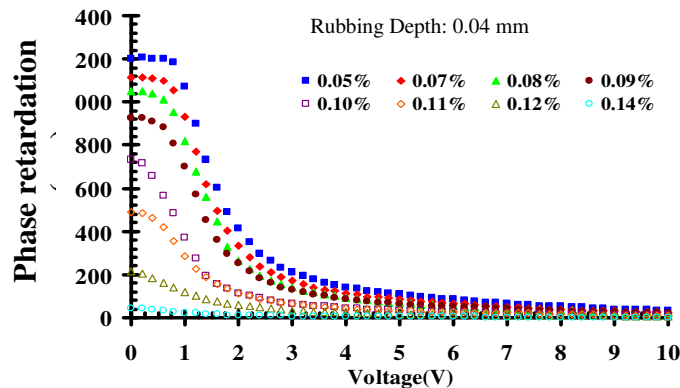

Fig. 4. Voltage dependent phase retardation curves of antiparallel LC cells with different POSS concentration doped in PI.

Dependence of the PAE of the alignment layer on POSS concentration doped in PI is shown in Fig. 5. The PAE does not depend on the rubbing depth in this work, so the Fig. 5 only illustrates the average value of PAE of two rubbing depths (0.02mm and 0.04 mm). The PAE is almost constant around 2.4×10^{-4} J/m^2 regardless of the POSS concentration doped in PI. From the literatures, the anchoring energy can vary with pretilt angle [25] or maintain at an approximately constant value regardless of pretilt angle [7]. The alignment mechanism of LC on PI is complex and still not well understood. Two models, elastic deformations of the LC configuration due to alignment surface topologies and anisotropic molecular interaction between LCs and alignment layer, are mainly adopted to explain the alignment properties. The anchoring of the POSS/PI alignment layer investigated in this work may fall into the alignment region dominant by surface topology. Therefore, the anchoring energy is not changed with the surface energy. The constant PAE of POSS/PI alignment layer for each pretilt angle makes this novel method good for many LCDs application requiring a tunable pretilt angle and moderate PAE.

To verify the technique of pretilt angle control proposed in this work, one traditional OCB LCD without POSS dopant in PI (θ_p~2°) and one proposed OCB LCD with 0.1 wt% POSS dopant in PI (θ_p~48°) were fabricated for comparison. The voltage dependent transmission properties of each OCB LCD were measured as shown in Fig. 6, by applying forward voltage (0V to 10 V) and backward voltage (10V to 0 V) where there was no bias voltage applied on the OCB LCDs and the data were recorded for one second at the first second after the voltage was applied. Due to the energy barrier between the splay and bend state of a traditional OCB LCD, some transient time (warm-up time) is required to switch a traditional OCB LC cell between those two states, and that is the reason that the forward voltage dependent transmission curve does not overlap with the backward voltage one as shown in Fig. 6. The proposed OCB LC cell with a high pretilt angle could overcome the energy barrier and show a better electro-optical property than the traditional one.
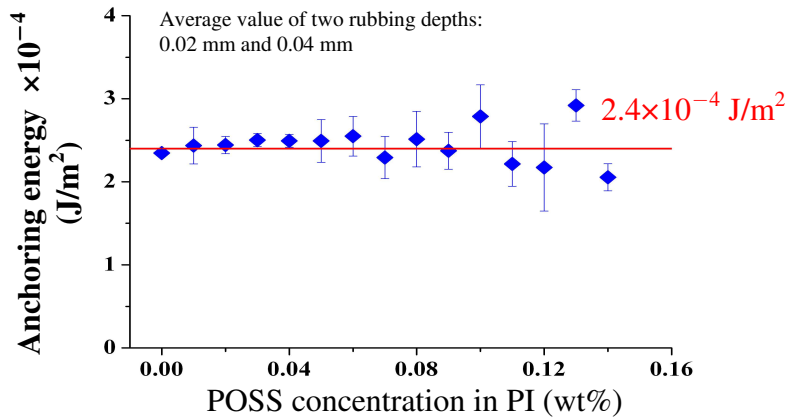
Fig. 5. Polar anchoring energy (PAE) as a function of POSS concentration doped in PI.
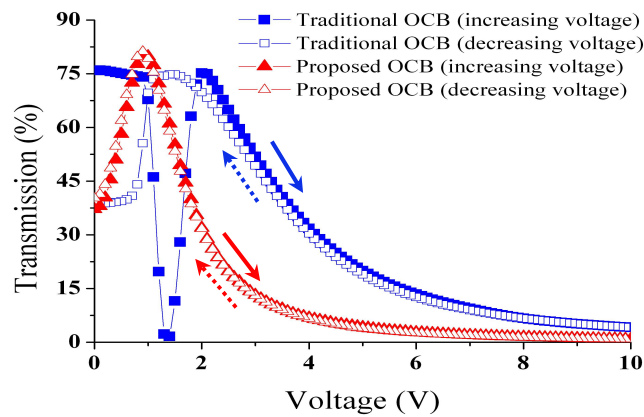

Fig. 6. Voltage dependent transmission curves of traditional and proposed OCB LC cells by applying forward (0 V to 10 V) and backward (10 V to 0V) voltages.

4. Conclusion

Based on the experimental results, the pretilt angle of the LC molecules can be continuously controlled over a range of $0° < \theta_p < 90°$ by adjusting the POSS concentration doped in a homogenous PI layer. The addition of POSS in the PI changes the surface energy of the alignment layer and generates the variable pretilt angle. The anchoring energy of POSS/PI alignment layer keeps a constant value for each pretilt angle regardless of the POSS concentration doped in PI. The proposed method of making the pretilt angle tunable in this work is very simple and is compatible with methods familiar in the current LCD industry.

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