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Influence of the washing process on the aligning capability of a nematic liquid crystal on polymer surfaces

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The influence of washing processes on the liquid crystal (LC) aligning capability on rubbed polyimide (PI) surfaces containing the CONH moiety were investigated. The induced optical retardation from a non-washing process on a rubbed PI surface is larger than when the washing processes are included. The pretilt angles in 4-*n*-pentyl-4'-cyanobiphenyl (5CB) were decreased by the washing process. The polar anchoring energy of 5CB was decreased by the washing processes on a weakly rubbed PI surface. The surface order parameter S_s of 5CB strongly depends on the rubbing strength and washing materials. Consequently, the LC aligning capability may be strongly attributed to the polymer characteristics and the washing processes.

1. Introduction

Twisted nematic (TN) liquid crystal display (LCD) devices are widely utilized for information displays. Pretilt angle is significant in preventing the creation of reverse tilt disclinations in a TN-LCD [1]. The generation of pretilt angle in a nematic liquid crystal (NLC) on various alignment layers by unidirectional rubbing has been demonstrated and discussed by many investigators [2–9]. Rubbed polyimide (PI) surfaces have been widely used to align LC molecules. PIs are widely employed in orientation films since they have appropriate characteristics such as high transparency, uniform LC alignment, high charge retention and good thermal stability.

TN-LCDs have been fabricated using mechanical rubbing to align the LCs, but this generates dusts and electrostatic charges. The thin film transistor (TFT)-LCD and super (S) TN-LCD are damaged by the induced electrostatic charge produced during rubbing. Previously, Matsuda *et al.* reported on the induced electrostatic charges and pretilt angles of NLC on various rubbed PI surfaces as a function of rubbing strength [10]. In the practical fabrication of LCDs, a washing process is used to remove the dust and electrostatic charges caused by surface rubbing.

The anchoring energy between the LCs and the alignment layers on treated substrate surfaces has been demonstrated and discussed by many investigators [11–19]. In a previous paper, we reported the first measurement of the temperature dependence of the polar (out-of-plane tilt) anchoring energy of weakly rubbed PI

surfaces in 4-*n*-pentyl-4'-cyanobiphenyl (5CB) [17]. We also reported the temperature dependence of the polar anchoring energy of 5CB on various PI-Langmuir–Blodgett (LB) surfaces [20, 21]. Most recently, we reported the effect of washing on the anchoring energy of 5CB on rubbed PI surfaces with a side chain [22].

In this paper, we report the influence of washing processes on pretilt angle generation, polar anchoring energy, and surface order parameter in the NLC, 5CB, on rubbed PI surfaces containing a CONH moiety.

2. Experimental

The molecular structure of the polymer material used is shown in figure 1. The PI films were coated onto indium tin oxide (ITO) coated glass substrates by spincoating, and were imidized at 250°C for 1 h. The PI layer thickness was about 500 Å. The PI films were rubbed using a machine equipped with a nylon roller (Y_o -15-N, Yoshikawa Chemical Industries Co., Ltd.); the definition of the rubbing strength *RS* has been given in previous papers [4, 5]. The rubbed PI surfaces were washed after rubbing. Using the following washing materials: isopropylalcohol (IPA), pure water, and freon.



Figure 1. Chemical structure of the polymer.

The characteristics of the washing materials are amphiphilic, hydrophilic, and hydrophobic, respectively. We used the wet method for 20 min for the washing process.

LC cells were assembled with the substrates antiparallel to the rubbing direction. The LC layer thickness was set to $60.0 \pm 0.5 \,\mu\text{m}$. To measure pretilt angles, we used the crystal rotation method for values up to 10° and the magneto-capacitive null method for values above 10° [23]. The measurement of pretilt angle was carried out at room temperature (22°C). We also measured the induced optical retardation. Anchoring strength was measured using 'high electric-field techniques' [11, 13]. Optical retardation *R* and electrical capacitance *C* were measured as a function of applied voltage *V* in order to determine the polar anchoring strength.

The optical retardation measurement system consists of a polarizer, an acousto-optic modulator, and an analyser. The output signal is detected by a photo-diode. The electrical capacitance of the LC cell was obtained by measuring the out-of-phase component of the current produced by changing the voltage applied to the cell. The extrapolation length d_e was determined by using the relationship between the measured values of the electric capacitance and the optical retardation [11, 13]:

$$\frac{R}{R_0} = \frac{I_0}{CV} - \frac{2d_e}{d}, \quad \text{when } V \gg 6V_{\text{th}}$$
(1)

where I_0 is a proportionality constant depending on the LC materials; V and d stand for the applied voltage and LC film thickness, respectively.

The polar anchoring energy A was obtained from the following relation:

$$A = K/d_{\rm e} \tag{2}$$

where K is the effective elastic constant which is given by $K = K_1 \cos^2 \theta_0 + K_3 \sin^2 \theta_0$, where K_1 , K_3 , and θ_0 stand for the elastic contants of the splay and bend deformations, and the pretilt angle, respectively. We used the measured elastic constants in this work. The surface order parameter S_s was obtained by measuring the residual optical retardation induced on the PI surface above the nematic-isotropic transition temperature T_c [24].

3. Results and discussion

Figure 2 shows the induced optical retardation on a rubbed PI surface with CONH moiety for non-washing and washing processes as a function of RS. The induced optical retardation for the non-washing process increases with increasing RS; this is attributed to the rubbing process giving rise to an enhanced orientation of polymer chains, thereby creating a more anisotropic environment for the LC alignment. The induced optical retardation on rubbed PI surfaces was decreased by the washing



Figure 2. Induced optical retardation as a function of *RS*, for non-washing and washing processes on a rubbed PI surface with CONH moiety.

processes, a behaviour similar to that observed in previous work [22]. The induced optical retardation decreased due to the removal of dust by the washing process.

Figure 3 shows the generation of pretilt angles in 5CB for non-washing and washing processes on a rubbed PI surface with CONH moiety as a function of *RS*. The pretilt angles obtained for non-washing and washing processes on the rubbed PI surfaces increase with increasing *RS*, and then saturate. The pretilt angles were decreased by the washing processes at high *RS*. It is considered that the generated 5CB pretilt angles strongly depend on the washing process.

Figure 4 shows the extrapolation length d_e of 5CB for non-washing and washing processes on weakly rubbed PI surfaces with CONH moiety. The extrapolation length decreases with increasing RS. For all washing processes d_e is larger than for the non-washing process. The effect of washing on the 5CB extrapolation length is clearly observed at low RS.

The dependence of the polar anchoring energy on rubbing strength in 5CB for non-washing and washing processes on a weakly rubbed PI surface with CONH moiety is shown in figure 5. It is approximately 3×10^{-4} J m⁻² at RS = 57 mm for the non-washing process; it then increases with increasing RS. The anchoring



Figure 3. Pretilt angle of 5CB as a function of *RS*, for nonwashing and washing processes on a rubbed PI surface with CONH moiety.



Figure 4. Extrapolation length d_e of 5CB as a function of *RS*, for non-washing processes on rubbed PI surface with CONH moiety.



Figure 5. Polar anchoring energy of 5CB as a function of *RS*, for non-washing processes on a rubbed PI surface with CONH moiety.

energy of 5CB on the rubbed PI surface is strongly attributed to the surface ordering due to the increase of LC aligning capability [20, 25]. Figure 5 also shows that the polar anchoring energy of 5CB is decreased by the washing process. We recently reported the effect of washing on the polar anchoring energy of 5CB on a rubbed PI surface with side chain [22]: in that case it was increased by the washing process. From these results, we consider that the washing effects on LC aligning capability strongly depend on the characteristics of the polymer.

Figures 6(a) and 6(b) show the residual optical retardation of 5CB for non-washing and washing processes on a rubbed PI surface above the clearing temperature. The retardation of 5CB for all the washing processes if smaller than for the non-washing process when RS = 114 mm, as shown in figure 6(a). However, the retardation of 5CB after washing with water or freon is larger than that for the non-washing process, see figure 6(b).

The surface order parameter S_s of 5CB for nonwashing and washing processes on a rubbed PI surface with CONH moiety, as a function of *RS*, is shown in figure 7. For the non-washing process S_s increases with increasing *RS* and then decreases above *RS* = 114 mm. A variable behaviour of S_s in 5CB was observed; it



Figure 6. Residual optical retardation in 5CB for nonwashing and washing processes on rubbed PI surfaces with CONH moiety, above the clearing temperature. (a) RS = 114 mm, (b) RS = 406 mm.

strongly depends on the rubbing condition and washing materials. Consequently, we suggest that the pretilt angle, anchoring strength, and surface order parameter are strongly affected by the washing conditions.

4. Conclusion

The influences of the washing process on the LC aligning capability for the NLC, 5CB, on a rubbed PI surface with CONH moiety has been successfully investi-



Figure 7. Surface order parameter S_s of 5CB as a function of RS, for non-washing and washing processes on a rubbed PI surface with CONH moiety.

gated. The induced optical retardation for the nonwashing process is larger than for the washing process. Pretilt angles in 5CB are decreased by washing processes. The polar anchoring energy of 5CB is decreased by washing processes on weakly rubbed PI surfaces. The surface order parameter S_s in 5CB depends on the rubbing condition and washing materials. We suggest that the LC aligning capability is attributable to the washing process and the nature of the PI materials.

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