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Washing effects on the anchoring energy and surface order parameter on rubbed polymer surfaces containing the trifluoromethyl moiety

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The washing effects on liquid crystal (LC) alignment capability in a NLC, 4-*n*-pentyl-4'-cyanobiphenyl (5CB), on a rubbed polyimide (PI) surface containing the trifluoromethyl moiety were studied. The extrapolation length d_e of 5CB on the rubbed PI surface decreases with the rubbing strength RS . Also, the large extrapolation length d_e of 5CB for washing with IPA was measured at $RS=114$ mm. The polar anchoring energy of 5CB on the rubbed PI surface was decreased by the washing process; it increased with the rubbing strength RS on the PI surface. The surface order parameter S_s of 5CB for all the washing processes is smaller than for the non-washing process. Consequently, the polar anchoring energy and surface order parameter S_s in 5CB are largely attributed to washing effects.

1. Introduction

Liquid crystal displays (LCDs) are widely used for information display devices. The pretilt angle prevents the creation of reverse tilt disclinations in a LCD [1]. Pretilt angle generation in a nematic liquid crystal (NLC) on various alignment layers by unidirectional rubbing has been discussed by many investigators [2–9]. Rubbed polymer surfaces have been widely used to align LC molecules; and LCDs have been fabricated using mechanical rubbing to align the LCs, but this generates dusts and electrostatic charges. The thin film transistor LCD is damaged by induced electrostatic charges produced during rubbing. Previously, Matsuda *et al.* reported the induced electrostatic charges and pretilt angle generation of a 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 after the PI surfaces are rubbed.

The anchoring strength (energy) between the LCs and the alignment layers on treated substrate surfaces has been discussed by many investigators [11–19]. In a

previous study, we reported the first measurement of the temperature dependence of the polar (out-of-plane tilt) anchoring strength of 5CB on weakly rubbed PI surfaces [17]. We also reported the temperature dependence of the polar anchoring strength of 5CB on various PI-LB surfaces [20, 21]. In this paper, we report the polar anchoring strength and the surface order parameter S_s in a NLC, 5CB, resulting from the washing process on rubbed PI surfaces containing the trifluoromethyl moiety.

2. Experimental

The molecular structure of the polymer (from Nissan Chemical Industries Co.) used is shown in figure 1. The PI films were coated on indium tin oxide (ITO) coated glass substrates by spin-coating, and were imidized at 250°C for 1 h. The thickness of the PI layers was about 500 Å. The PI films were rubbed using a machine

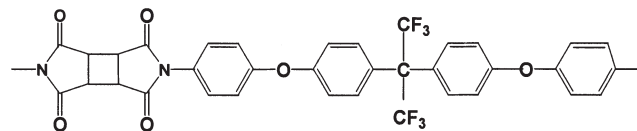
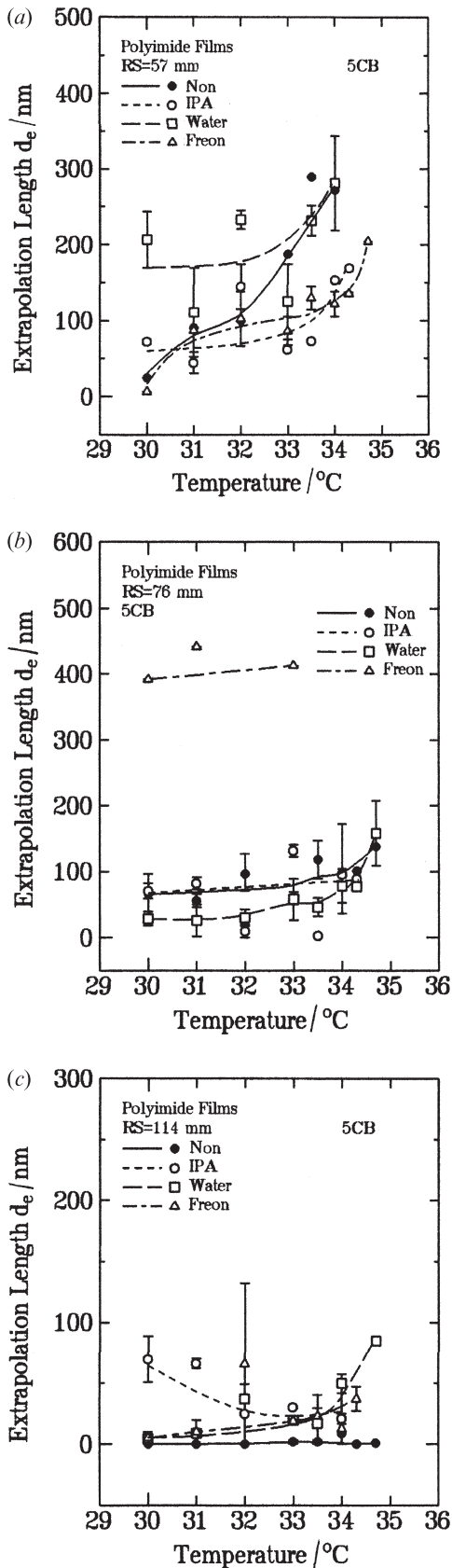


Figure 1. Chemical structure of the polymer.

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equipped with a nylon roller (Y_o-15-N, Yoshikawa Chemical Industries Co.); the definition of the rubbing strength RS has been given in previous papers [4, 5]. The rubbed PI surfaces were washed using the following washing materials: isopropyl alcohol (IPA), pure water and freon. The characteristics of the washing materials are amphiphilic, hydrophilic and hydrophobic, respectively; we used the wet method for 20 min for the washing process, with immersion of the plates. LC cells were assembled antiparallel to the rubbing direction.

Anchoring strength was measured using 'high electric field' techniques [13–15]. We measured the optical retardation R and the electric capacitance C 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 photodiode. The electrical capacitance of the LC cell is 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 is determined using the relationship between the measured values of the electrical capacitance and the optical retardation [13–15]:

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

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

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

$$A = K/d_e \quad (2)$$

where K is the effective elastic constant given by $K = K_1 \cos^2 \theta_0 + K_3 \sin^2 \theta_0$; K_1 , K_3 , and θ_0 are the elastic constants 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 [22].

3. Results and discussion

Figure 2 shows the temperature dependence of the extrapolation length d_e of 5CB for non-washing and washing processes on a rubbed PI surface containing

Figure 2. Temperature dependence of the extrapolation length d_e of 5CB for non-washing and washing processes on rubbed PI surfaces containing the trifluoromethyl moiety: (a) $RS=57$ mm, (b) $RS=76$ mm, (c) $RS=114$ mm.

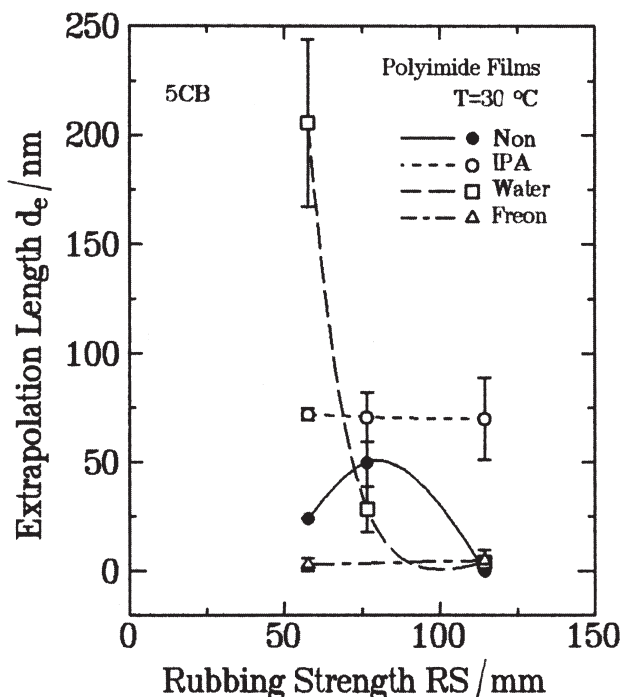


Figure 3. Extrapolation length d_e of 5CB for non-washing and washing processes on the rubbed PI surface containing the trifluoromethyl moiety as a function of rubbing strength RS .

the trifluoromethyl moiety. The extrapolation length d_e increases with increasing temperature, which is considered to be due to the decrease of surface ordering [15–20].

The extrapolation length d_e of 5CB for non-washing and washing processes, as a function of rubbing strength RS , is indicated in figure 3. For the non-washing process on the rubbed PI surface at $RS=114$ mm, d_e was measured as about zero, indicating a large anchoring strength. For all the washing processes on the rubbed PI surface d_e is larger than for the non-washing process, indicating a weak anchoring strength.

Figure 4 shows the temperature dependence of the polar anchoring energy of 5CB for non-washing and washing process on the rubbed PI surface containing the trifluoromethyl moiety. The polar anchoring energy of 5CB for both non-washing and washing processes increases with temperature; for the non-washing process it is approximately $1 \times 10^{-3} \text{ J m}^{-2}$ at 30°C , as shown in figure 4(c) for $RS=114$ mm. In this case the

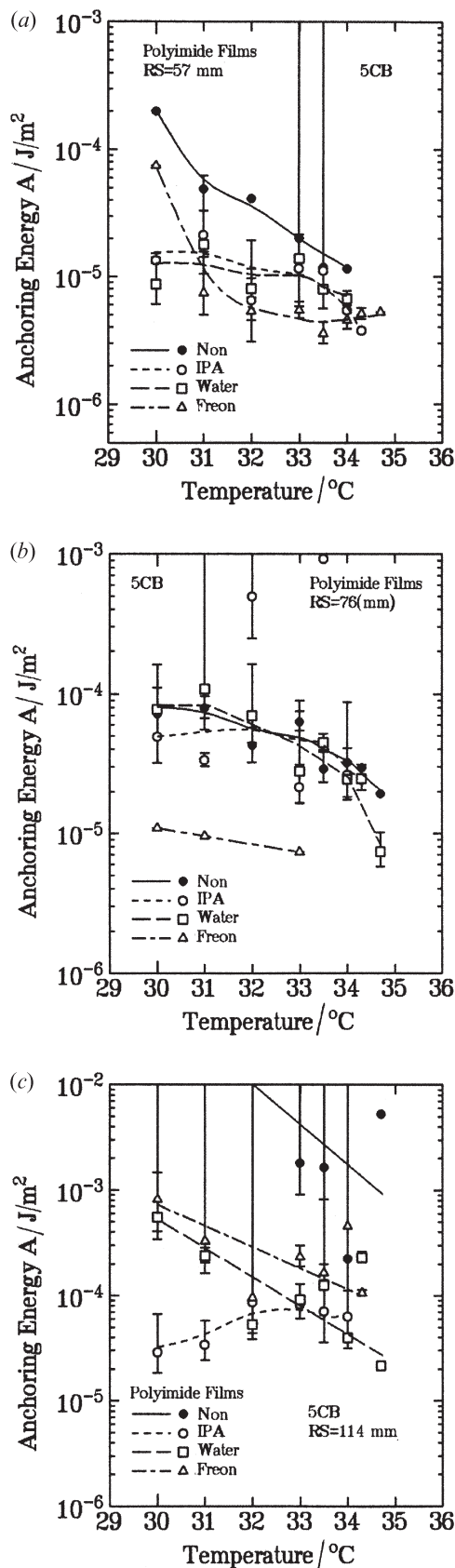


Figure 4. Temperature dependence of the polar anchoring energy of 5CB for non-washing and washing processes on rubbed PI surfaces containing the trifluoromethyl moiety: (a) $RS=57$ mm, (b) $RS=76$ mm, (c) $RS=114$ mm.

polar anchoring energy of 5CB for the non-washing process is larger than for all the washing processes at all temperatures.

Figure 5 shows the polar anchoring energy of 5CB for non-washing and washing processes as a function of rubbing strength RS . For the non-washing process it is approximately $2 \times 10^{-4} \text{ J m}^{-2}$ at $RS=57 \text{ mm}$, and then increases with increasing RS . The polar anchoring energy of 5CB on a rubbed PI surface is strongly attributed to the surface ordering due to the increase of LC aligning capability [20–23]; it is decreased by the washing process, whose effects are clearly observed. In a previous study by contrast, the polar anchoring energy of 5CB on a weakly rubbed PI surface with alkyl side chains was increased by the washing process [24].

Figures 6(a) and 6(b) show the residual optical retardation of 5CB for the non-washing and washing processes on rubbed PI surfaces containing the trifluoromethyl moiety above the clearing temperature (the wavelength of the light is 632.8 nm). The surface ordering of 5CB for all the washing processes is smaller than for the non-washing processes.

The surface order parameter S_s of 5CB for non-washing and washing processes as a function of rubbing strength RS is indicated in figure 7, at 30°C . For the non-washing process S_s increases with the rubbing strength and saturates above $RS=100 \text{ mm}$; this behaviour is similar to that seen with the washing processes.

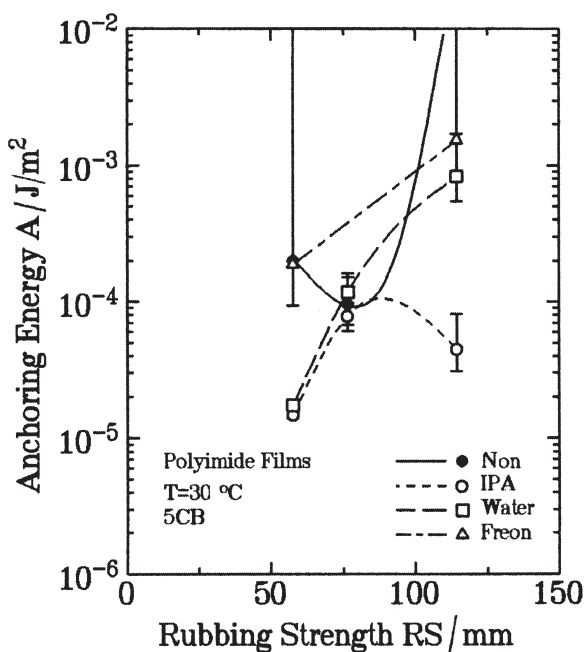


Figure 5. Polar anchoring energy of 5CB for non-washing and washing processes on rubbed PI surfaces containing the trifluoromethyl moiety, as a function of rubbing strength RS .

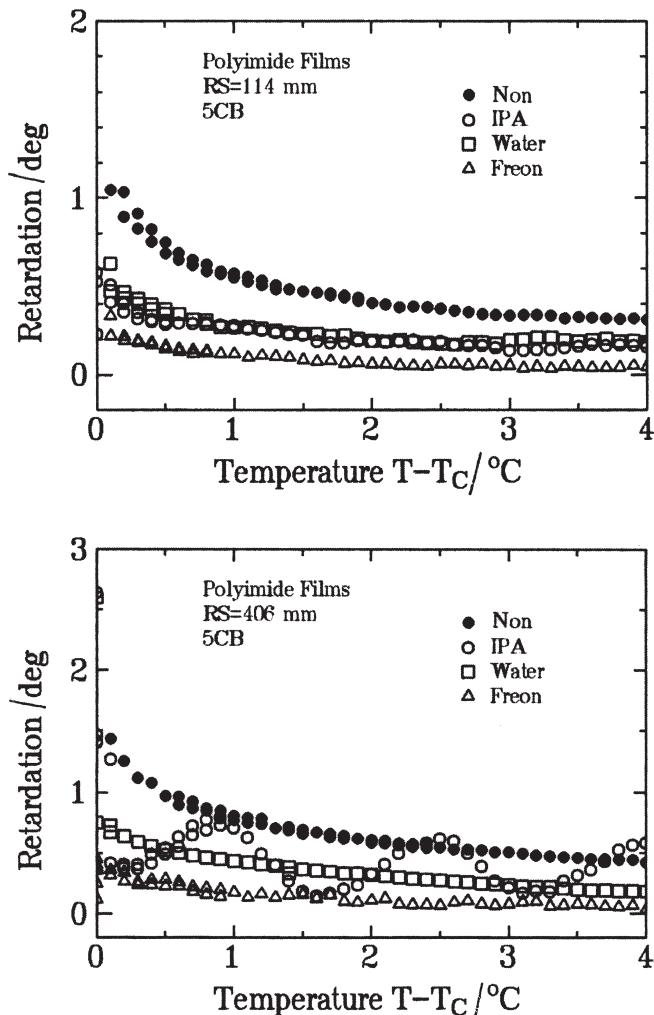


Figure 6. Residual optical retardation in 5CB for the non-washing and washing processes on rubbed PI surfaces containing the trifluoromethyl moiety, above the clearing temperature: (a) $RS=114 \text{ mm}$, (b) $RS=406 \text{ mm}$.

The surface order parameter S_s of 5CB for all the washing processes is smaller than for the non-washing process.

Figure 8 shows the pretilt angle of 5CB on a PI surface with the trifluoromethyl moiety, as a function of surface tension. The pretilt angle for the washing process is larger than for the non-washing process; the washing effects are clearly observed. Also, the 5CB pretilt angle decreases with increase in surface tension. The 5CB pretilt angles may therefore be attributed to van der Waals (VDW) dispersion interactions between the LC molecules and the polymer surface, which has a low surface energy. The rubbing treatment is considered to generate an obliquely inclined force at the PI surfaces. Before rubbing, the PI chains in side view and overview show a zig zag conformation; in the axial view they show a circular conformation [8, 25]. After the

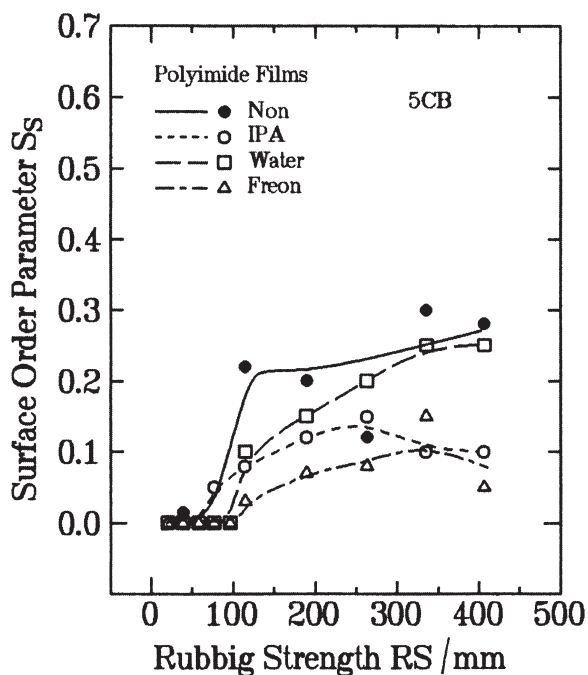


Figure 7. Surface order parameter S_s of 5CB for the non-washing and washing processes on rubbed PI surfaces containing the trifluoromethyl moiety, as a function of rubbing strength RS .

rubbing treatment, an expansion of the PI chains is seen in the side view, along with an inclination of the zig-zag. The generation of microscopic asymmetric triangles may be the origin of the pretilt angle.

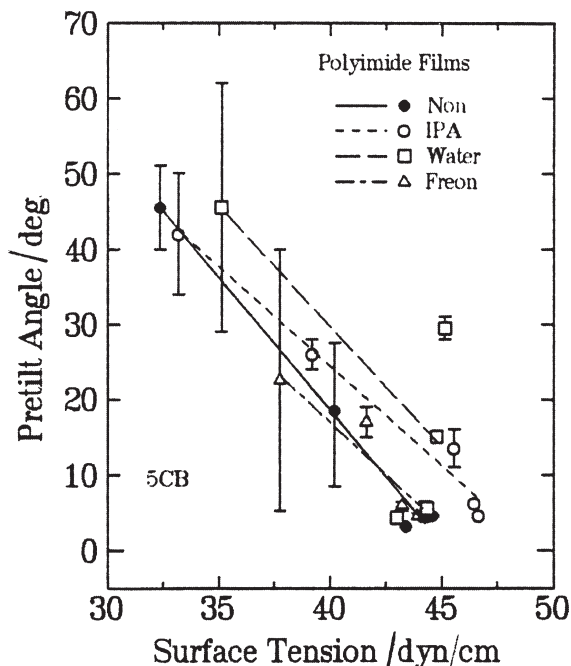


Figure 8. Pretilt angle of 5CB on the PI surface with the trifluoromethyl moiety, as a function of surface tension.

Therefore, the pretilt angle may be caused by the combination of VDW dispersion and steric interaction between the LC molecules and the polymer surface containing trifluoromethyl moieties.

Consequently, we suggest that the polar anchoring energy and surface order parameter S_s in 5CB are destabilized by the washing processes; LC aligning capability is thus largely attributable to washing effects.

4. Conclusion

In summary, the LC aligning capability in 5CB resulting from the washing process on a rubbed PI surface containing the trifluoromethyl moiety was studied. The extrapolation length d_e of 5CB on the rubbed PI surface decreases with the rubbing strength. A large extrapolation length d_e of 5CB for the IPA washing process was measured at $RS=114$ mm. The polar anchoring energy of 5CB on rubbed PI surfaces is decreased by the washing process; it is increased with increasing rubbing strength. The surface order parameter S_s of 5CB for all the washing processes is smaller than for the non-washing process. Consequently, the polar anchoring energy and surface order parameter S_s in 5CB are largely attributable to washing effects.

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