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Liquid crystal alignment capabilities on rubbed organic solvent soluble polyimide surfaces with trifluoromethyl moieties

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High pretilt angles, polar anchoring energy (out of plane-tilt), and surface ordering in the nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB) were investigated on rubbed organic solvent soluble polyimide (PI) surfaces with a helical backbone structure and trifluoromethyl moieties. It was found that the pretilt angle of 5CB is about 15° in the wide rubbing region of rubbed soluble PI surfaces with trifluoromethyl moieties attached to the lateral benzene rings. It is suggested that the microscopic surface structure of the polymer contributes to the LC pretilt angle generation at the surface. Also, the polar anchoring energy of 5CB is dependent on the molecular structure of these unidirectionally rubbed soluble PI surfaces. The polar anchoring strength of 5CB on rubbed soluble PI surfaces is as weak with trifluoromethyl moieties attached to the lateral benzene rings weak as when the trifluoromethyl moieties are attached to the polymer backbone. Finally, the polar anchoring energy of 5CB strongly depends on the surface ordering of rubbed soluble PI surfaces.

1. Introduction

Nowadays, thin film transistor (TFT) liquid crystal displays (LCDs) are widely utilized in information displays such as notebook computers, monitors, and television screens, because they have high resolution quality. The uniform alignment of LCs on treated substrate surfaces is very important [1], and interfacial properties between the LC and the alignment surface are a key in understanding the LC alignment mechanism [1, 2]. Unidirectionally rubbed PI surfaces have been widely used in LC alignment, but the detailed mechanism is not yet fully understood.

Pretilt angle, which is a very important alignment characteristic, prevents the creation of reverse tilt disclinations in LCDs. A high pretilt angle is required to prevent stripe domains in super twisted nematic LCDs [3] and for the proper operation of surface-stabilized ferroelectric liquid crystal displays [4]. The generation of nematic liquid crystal (NLC) pretilt angle by a unidirectional rubbing treatment on rubbed PI surfaces has been demonstrated and discussed by many investigators [5–17]. Previously, we reported that the generation of a high pretilt angle in 5CB on rubbed PI surfaces containing trifluoromethyl moieties is caused by fluorine (F) atoms; ESCA measurement was used to determine the surface F/C (carbon) ratio [15]. More, recently we showed the efficacy of polar anchoring energy in achieving high pretilt angles in NLCs on rubbed PI surfaces containing CF_3 moieties [18]. The polar anchoring strength of 5CB with a high pretilt angle is very small, due to a combination of factors: the micro-surface excluded volume effect and the anisotropic dispersion forces between the LCs and the weakly rubbed PI surfaces. The effects of the crystallinity of the PI surfaces and the birefringence of the NLCs on pretilt angle generation for three kinds of rubbed PI surfaces have also been investigated by the author's group [19].

The anchoring energy and the surface ordering that exists between the LC and the surface are very important in understanding the LC alignment. Previously, Yokoyama *et al.* reported the measurement of the polar (out of plane-tilt) anchoring energy of 5CB on obliquely evaporated SiO surfaces [2, 20, 21]. In previous papers, the polar anchoring strength of 5CB on weakly rubbed PI surfaces [22], PI-Langmuir–Blodgett (LB) surfaces [23, 24], and rubbed polystyrene (PS) surfaces has been reported [25]. The polar anchoring strength and the surface

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ordering of three kinds of NLCs on rubbed PI surfaces have also been studied [26]. Recently, we have successfully evaluated the relationship between the polar anchoring energy and the pretilt angle in 5CB on rubbed PI surface with CF_3 moieties [18] and have demonstrated the odd–even effect of the polar anchoring energy of 5CB on unidirectionally rubbed PI-LB surfaces with alkylene chains [27]. It was demonstrated that the polar anchoring strength of 5CB is larger on rubbed PI-LB surfaces with an even number of carbon atoms in the alkylene chain as compared with surfaces with odd numbers of carbon atoms in the chain. The surface ordering of NLCs on alignment layers have previously been demonstrated and discussed [28–30]. By measuring residual optical retardation near the clearing temperature T_c Miyano and Tarczon were able to show the surface order parameters of 5CB in various alignment layers [28, 29]. Recently, we reported the surface order parameters of NLCs on rubbed PI [26] and PI-LB surfaces [31].

In this work, we report the effect of the molecular structure of rubbed soluble PI surfaces with CF_3 moieties on pretilt angle generation, polar anchoring strength, and the surface ordering of 5CB.

2. Experimental

The molecular structures of four kinds of polymers used in this study (Japan Synthetic Rubber Co., Ltd.) are shown in figure 1. Shown here, F1 and F2 are polymers with CF_3 moieties attached to the polymer backbone; F3 and F4 are polymers with CF_3 moieties attached to the lateral benzene rings. The precursors were coated on indium tin oxide (ITO) coated glass substrates by spin-coating, and imidized at 180°C for 1 h. The PI film thickness was 500 Å. The PI films were unidirectionally 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 was derived in previous papers [10, 15, 17], and is given by

$$RS = NM(2\pi rn/v - 1) \tag{1}$$

where N is the number of times the rubbing is repeated (always $N = 1$ in this work), M is the depth of the deformed fibers of the cloth due to the pressed contact (mm), n is the rotational speed of the drum (1000/60 s^{-1}), v is the translation speed of the substrate (7.0 mm s^{-1}), and r is the radius of the drum.

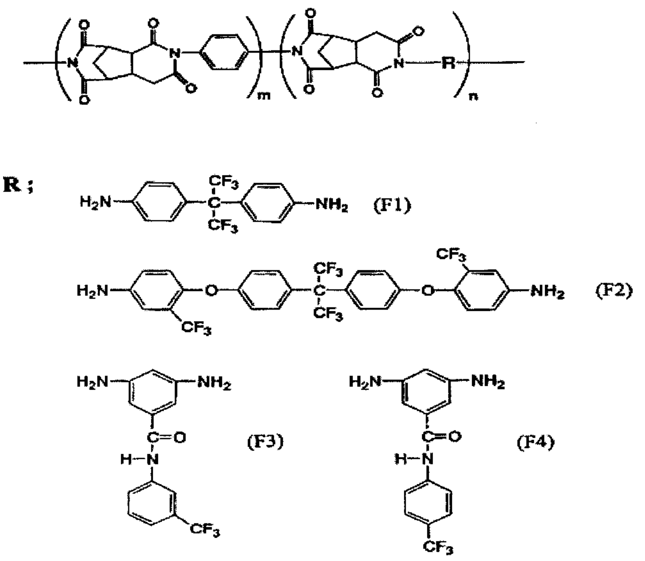

Figure 1. Molecular structures of the polymers used.

Sandwich-type cells with a thickness of $60 \pm 0.5\,\mu m$ were assembled with pairs of substrates having the rubbing direction antiparallel to one other. The pretilt angles of the LCs in the nematic phase were measured by the crystal rotation method [32] at room temperature.

Next, we measured the optical retardation R and the electrical capacitance C as a function of applied voltage V. In order to determine the polar anchoring strength the 'high electric field technique' by Yokoyama *et al.* [2, 20, 21] was used. For optical retardation measurements, a He-Ne laser (632.8 nm) with 2 mW output power was used as the light source and the system consisted of a polarizer, an acousto-optic modulator, and an analyser. The output signal was detected with a photodiode. The electric capacitance of the LC cell was determined by measuring the out-of-phase component of the current produced by changing the applied voltage across the cell. The extrapolation length d_e of 5CB was calculated using the relationship between the measured values of the electric capacitance and the optical retardation [2, 20, 21]:

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

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

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

$$A = K/d_e \tag{3}$$

where K is the effective elastic constant given by $K = K_1 \cos^2\theta_0 + K_3 \cos^2\theta_0$, with K_1, K_3, and θ_0 the elastic constants for the splay and bend deformations, and the pretilt angle, respectively. We used the measured elastic constants in this work.

The surface order parameters were determined by measuring the temperature dependence of the residual optical retardation near the clearing temperature T_c [28, 29].

3. Results and discussion

Figure 2 shows the pretilt angles of 5CB on four kinds of rubbed soluble PI surfaces as a function of *RS*. The pretilt angle of 5CB is small on soluble F1 and F2 PI surfaces. Thus, the pretilt angle of 5CB is small on rubbed soluble PI surfaces with CF_3 moieties attached to the polymer backbone. However, high pretilt angles of 5CB were observed on the soluble F3 PI surface. The pretilt angle peaks at around $RS = 50$ mm and then decreases with *RS* on the rubbed soluble F3 PI surface. For medium values of *RS*, the pretilt angle is about 15° and does not vary much. On the soluble F4 PI surface, we obtained homeotropic alignment at all values of *RS*. This large pretilt angle for 5CB generated on rubbed soluble F3 and F4 PI surfaces is associated with the CF_3 moieties attached to the lateral benzene ring [33].

The induced optical retardation as a function of *RS* for these four kinds of unidirectionally rubbed soluble PI surfaces is shown in figure 3. It increases with *RS* on all four soluble PI surfaces. The increase in optical retardation with *RS* on these PI surfaces is thought to be due to increased orientational ordering and the stretching of polymer chains caused by the mechanical stress of the rubbing process. The induced optical retardation on PI surfaces with CF_3 moieties attached to the lateral benzene rings is less than when the CF_3 moieties are attached to the polymer backbone itself.

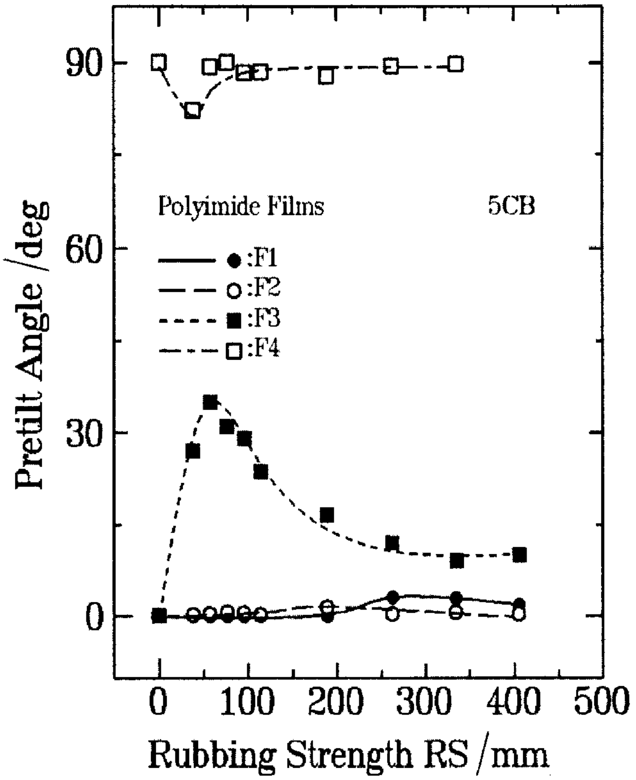

Figure 2. Pretilt angle as a function of *RS* for 5CB on four kinds of rubbed soluble PI surfaces.

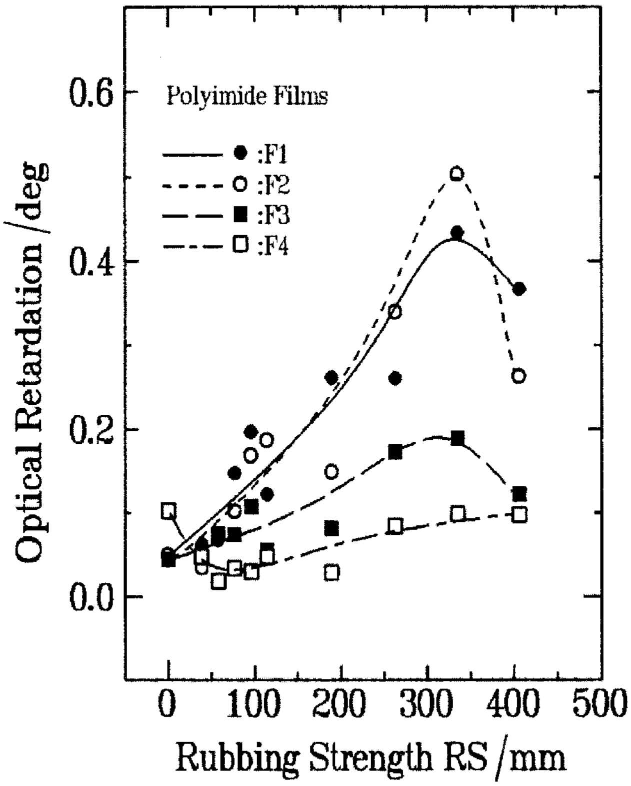

Figure 3. Induced optical retardation as a function of *RS* produced on four kinds of rubbed soluble PI surfaces.

Figure 4 shows the extrapolation length d_e as a function of temperature for 5CB on medium rubbed soluble PI surfaces. It is clear that the extrapolation length d_e of 5CB diverges near the clearing temperature for both the F2 and F3 PI surfaces; this is due to the decrease of surface order near the clearing temperature. A similar behaviour in polar [2, 20, 21] and azimuthal [34] anchoring strengths has been observed previously in 5CB on obliquely evaporated SiO surfaces, and was attributed to reduced orientational order of the LC near the interface [28, 29]. Therefore, it is expected that the polar anchoring strength of 5CB would decrease rapidly due to the decrease of the surface order near the clearing temperature. Also, the extrapolation lengths d_e of 5CB on rubbed F3 PI surfaces is large compared with those on rubbed soluble F1 and F2 PI surfaces near the clearing temperature. This indicates that the polar anchoring strength of 5CB strongly depends on the molecular structure of the polymer. From these results, we consider that the large extrapolation length d_e of 5CB can be attributed to the high pretilt angles on the rubbed soluble F3 PI surface, as seen by comparing figures 2 and 4. Similar effects on the polar anchoring strength and the pretilt angle have been observed in

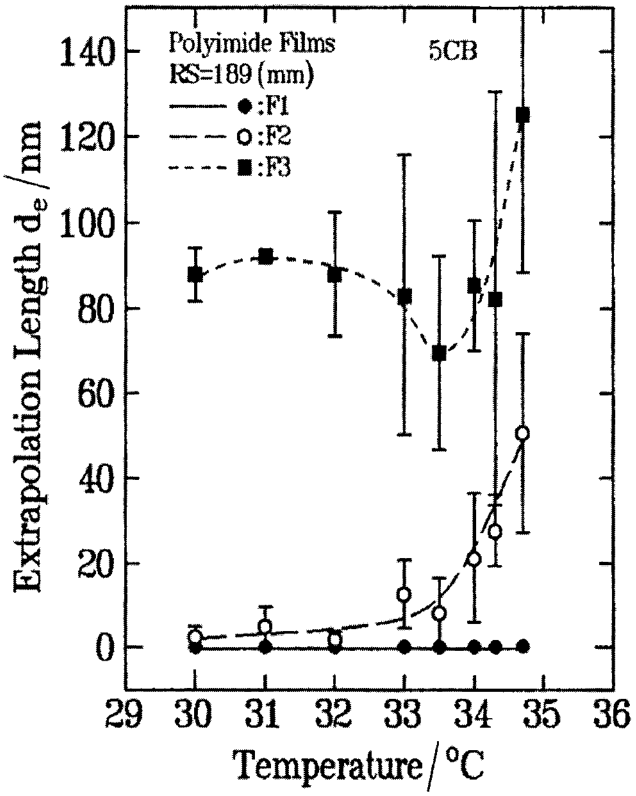

Figure 4. Temperature dependence of extrapolation length d_e of 5CB on rubbed soluble F1, F2, and F3 PI surfaces.

previous work [18]. Figure 5 shows the polar anchoring energy as a function of temperature for 5CB on medium rubbed soluble PI surfaces. For F3 surface its magnitude is approximately 7×10^{-5} J m^{-2} at 30°C, indicating a very weak anchoring strength. However, a large anchoring energy for 5CB was measured on a medium rubbed soluble F1 PI surface.

Figure 6 shows the residual optical retardation as a function of temperature for 5CB on rubbed soluble F3 PI surfaces near the clearing temperature. It is clear that the residual optical retardation increases with *RS*. Figure 7 shows the surface order parameter S_s as a function of *RS* for 5CB on various rubbed soluble PI surfaces. S_s increases with *RS* and then plateaus for the F1 PI surface; on F2 and F3 PI surfaces, very small values for the surface order parameter were observed for all the values of *RS*. It is thought that the anisotropic dispersion force effect on rubbed soluble F1 PI surfaces is larger than on F2 and F3 PI surfaces. By comparison of figures 4 and 7, a good correlation between the polar anchoring strength and the surface order parameter in 5CB can be seen. It is clear that the polar anchoring strength of 5CB strongly depends on the surface ordering of the rubbed PI surface. The polar anchoring strength of 5CB therefore strongly contributes to the anisotropic dispersion force between LC and surface.

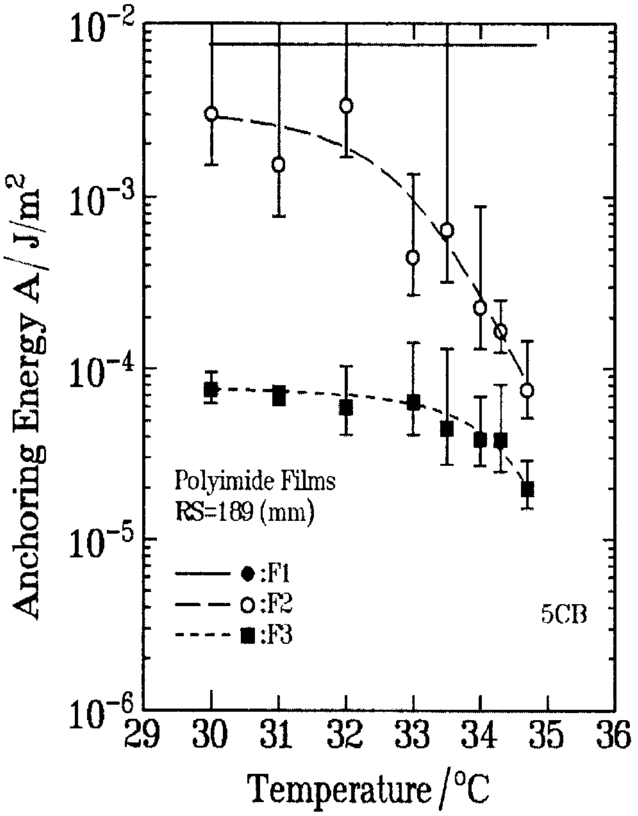

Figure 5. Temperature dependence of anchoring energy of 5CB on three kinds of rubbed soluble PI surfaces.

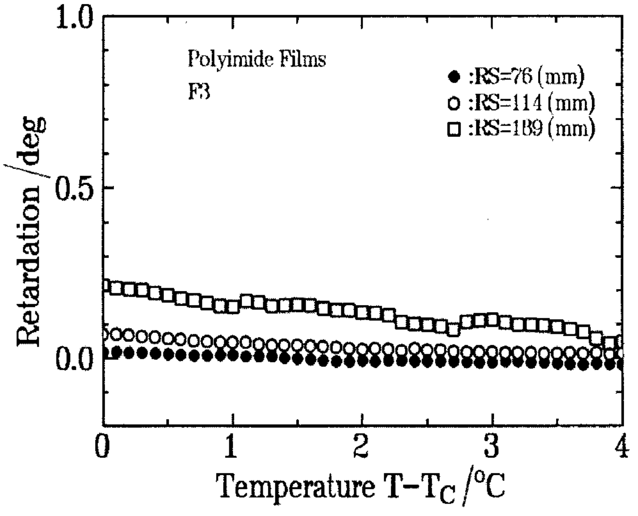

Figure 6. Residual optical retardation of 5CB on rubbed soluble F3 PI surfaces above the clearing temperature.

4. Conclusion

In summary, we have found that the pretilt angles of 5CB on rubbed PI surfaces with CF_3 moieties attached to the lateral benzene rings is larger than those on rubbed PI surfaces with CF_3 moieties attached to the polymer backbone. The observed pretilt angle of 5CB

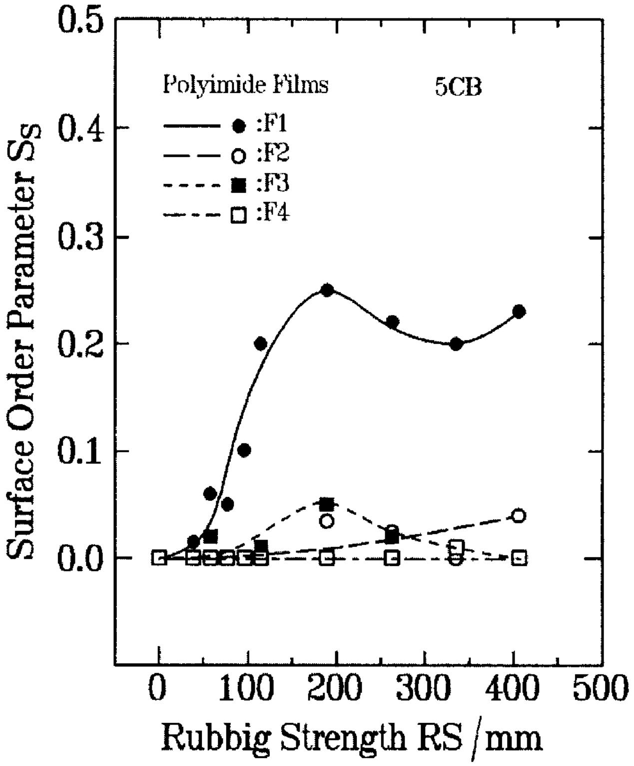

Figure 7. Surface order parameter S_s as a function of *RS* for 5CB on four kinds of soluble PI surfaces.

was about 15° in the wide rubbing region on rubbed PI surfaces with laterally attached CF_3 moieties. The microscopic surface structure of the polymer strongly contributes to this high pretilt angle generation of the LC on the surface. Finally, the effect of the polymer molecular structures of the PI surfaces with CF_3 moieties was successfully investigated by measurement of polar anchoring energy and surface ordering.

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