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Liquid Crystal Alignment Capability on Polyimide Langmuir-Blodgett Surfaces with Alkyl Chain Lengths

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The liquid crystal (LC) alignment capability in 4-n-pentyl-4'-cyanobiphenyl (5CB) on polyimide (PI) Langmuir-Blodgett (LB) surface with alkyl chain lengths was investigated. The pretilt angle of 5CB increased by unidirectional rubbing treatment on PI-LB surface. The induced optical retardation on PI-LB surface increased by the rubbing. The extrapolation length d_e of 5CB for rubbed PI-LB surfaces with even-number is small, compared with odd-number near the clearing temperature T_c . The extrapolation length d_e of 5CB with odd-number increases gradually as the temperature increases but it tends to diverge near the T_c . Therefore the polar anchoring strength with even-number is strong because of relatively high surface ordering caused by more crystalline surfaces. The anchoring energy of 5CB with alkyl chain length of 7 carbons is approximately 1×10^{-3} (J/m²); it indicates the strong anchoring strength. In consequence, we suggest that the LC align capability in NLC on PI-LB surface is strongly related to the characteristics of the polymer.

Keywords: Nematic liquid crystal; polyimide LB; rubbing strength; extrapolation length d_e ; anchoring strength; surface ordering

1. INTRODUCTION

Liquid crystal displays (LCDs) are widely used in the fields such as the electronic game, notebook computer, and color television. Uniform alignment of LCs on substrate surfaces is an important matter from a scientific viewpoint as well as a technological viewpoint.¹ Interfacial properties between the LCs and the alignment surfaces are a key to understand the alignment mechanism of LCs.^{1,2} Rubbed polyimide (PI) surfaces have been widely used to align LC molecules.

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The odd-even effects of the alkyl chain length on pretilt angles of LC on rubbed PI surfaces have been reported by H.Yokokura et al.³ High pretilt angles were observed on rubbed PI surfaces with an even-number of carbons in the chain alkyl.³ The odd-even effects in pretilt angles and orientational order of LCs on rubbed PI surfaces were measured by D.Johannsmann et al. by using surface optical second harmonic generation (SHG) and birefringence measurements.⁴ Recently, LC alignment on PI-LB surfaces has been demonstrated by many investigators.⁵⁻¹¹ The anchoring strength (energy) between the LCs and the polymer surface on treated substrate surfaces has been demonstrated and discussed by many investigators.^{2,12-19} In the previous work, we reported the first measurement of the temperature dependence of the polar (out-of-plane tilt) anchoring strength of weakly rubbed PI surfaces in 5CB.¹⁷ The polar anchoring strength of 5CB on various PI-LB surfaces was also reported by authors.^{7,8,11,20} Recently, we have reported the odd-even effects of polar anchoring strength in 5CB on rubbed PI-LB surface with alkyl chain length are successfully demonstrated.²⁰ In this work, we report the LC alignment capability in NLC, 5CB, on PI-LB surfaces with alkyl chain lengths.

2. EXPERIMENTAL

The PI-LB films were obtained by the chemical imidization of LB films of the precursor polyamic acid alkylamine salts. The precursor polyamic acids were prepared from the reaction of 2,3,5-tricarboxycyclopentyl acetic dianhydride (TCAAH), 2,2-bis[4-(4-aminophenoxy) phenyl] propane BAPP), and alkylamine C=3,4,7,8,11, and 12) in N-methylpyrrolidone at 60 °C. The polyamic acid and alkylamine acids were obtained by adding a molar equivalent of N,N-dimethylhexadecylamine relative to the carboxyl group in the polyamic acid.

The PI films were obtained by chemical imidization of the corresponding polyamic acid alkylamine salts using pyridine and acetic anhydride as catalysts. The chemical structure of PI is shown in Fig. 1. The PI-LB films were rubbed using a machine equipped with a nylon roller Yo-15-N, Yoshikawa Chemical Industries Co., Ltd.). The definition of the rubbing strength (RS) was given in previous papers.^{6,8,21} LC cells were assembled with the antiparallel to rubbing direction. The LC layer thickness was set at 60.0 ± 0.5 μm . Pretilt angles were measured by the crystal rotation method and all the measurements were done at room temperature (22°C). Also, we measured the induced optical retardation on PI-LB surface with alkyl chain lengths. Next, we measured the anchoring strength by using "high electric-field techniques".^{1,12,13} 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. Figure 2 shows the meas-

uring system of polar anchoring strength. The optical retardation measurement system consists of a polarizer, an acousto-optic modulator (PEM), and an analyzer. The output signal is detected by a photodiode. The electric 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 by using the relationship between the measured values of the electric capacitance C and the optical retardation R :^{1,12,13}

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

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

The polar anchoring energy A is obtained from the following relation:^{1,12,13}

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

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 constants of the splay and bend deformations, and the pretilt angle, respectively. We used measured elastic constants in this work. The surface ordering was measured by measuring the residual optical retardation induced on the polymer surface above the clearing temperature T_c .²²

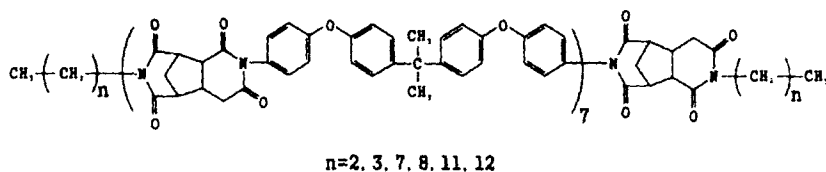


FIGURE 1 Chemical structure of the polymer

3. RESULTS AND DISCUSSION

Figure 3 shows the dependence of the alkyl chain length of the pretilt angle in 5CB on PI-LB surface. The pretilt angles on the PI-LB surfaces remain almost vanishing without rubbing, but they increase with the rubbing process ($RS=189\text{mm}$). The large pretilt angle in 5CB on rubbed PI-LB surface is attributed due to increasing the azimuthal surface ordering by the rubbing. Previously, D.Johannsmann et al. have reported that the high pretilt angle in 8CB on PI surfaces with even-number of carbon in the alkyl side chain is generated by the

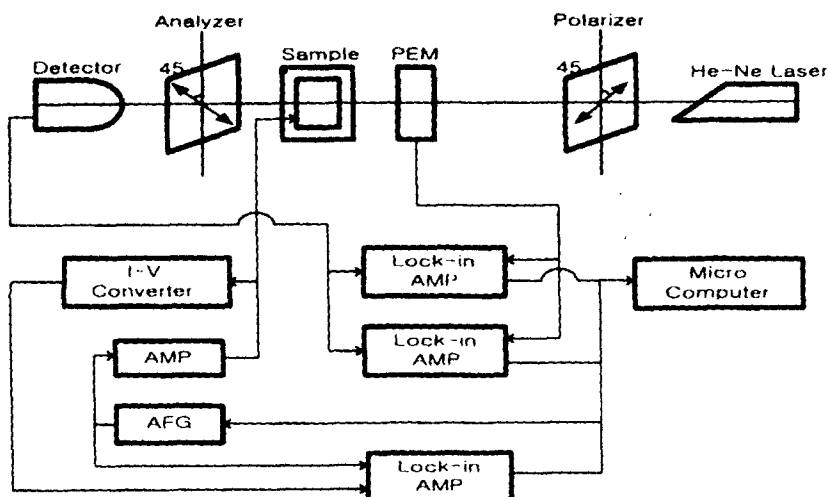


FIGURE 2 Measuring system of polar anchoring strength

higher surface ordering.⁴ Also, the similar effects have been reported by author group in a previous paper.¹¹

The induced optical retardation on PI-LB surface as a function of alkyl chain lengths for medium RS ($RS=189\text{mm}$) is shown in Fig. 4. The induced optical retardation on PI-LB surface for all alkyl chain lengths is almost 0; it is increased by the rubbing process. It is considered that the rubbing treatment gives rise to an enhanced orientation of polymer chains, thereby creating a more anisotropic environment for the LC alignment.

Figure 5 shows the plots of R/R_0 vs $1/CV$ observed at two different temperatures, 30°C and 34.3°C , on PI-LB surface. The intersect of the extrapolated line with the Y-axis gives the extrapolation length d_e , indicating that the anchoring strength weakens with temperature.

Figure 6 (a), (b), and (c) show the temperature-dependence of the extrapolation length d_e of 5CB on rubbed PI-LB surfaces with alkyl chain lengths for medium rubbing ($RS=189\text{mm}$). The extrapolation length d_e of 5CB for rubbed PI-LB surfaces with even-number is relatively small compared with odd-number above the alkyl chain length of 7 carbons. Therefore, the anchoring strength of 5CB on rubbed PI-LB surfaces with even-number is strong compared with odd-number of carbons. Also, the extrapolation length d_e of 5CB on rubbed PI-LB surfaces with odd-number increases gradually toward the clearing temperature and tends

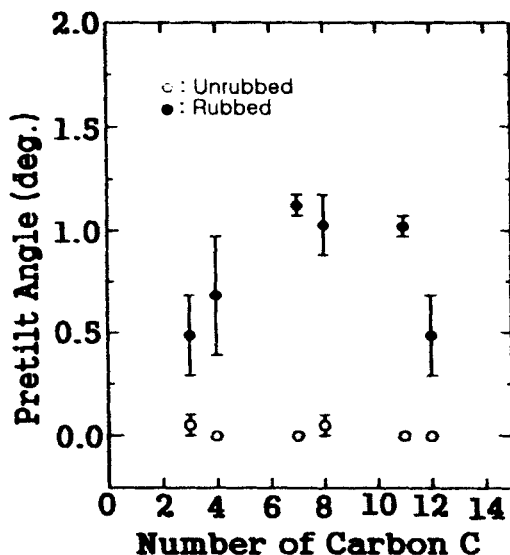


FIGURE 3 Pretilt angle in 5CB on PI-LB surface as a function of carbon number

to diverge near the clearing temperature. A similar behavior near the clearing temperature T_c has previously observed for 5CB on obliquely evaporated SiO surfaces for both polar¹⁵ and azimuthal¹³ anchoring strength. We also previously observed the effect for 5CB on weakly rubbed PI surfaces.¹⁷ We predict that the extrapolation length d_e of 5CB on rubbed PI-LB surfaces with odd-number diverges because of rapidly decreasing surface ordering near the clearing temperature T_c .^{11,13,15,17}

Figure 7 (a), (b), and (c) show the polar anchoring energy of 5CB on rubbed PI-LB surface as a function of temperature. It is shown that the polar anchoring energy of 5CB for rubbed PI-LB surface with even-number is large compared with odd-number. Also, the polar anchoring energy of 5CB at 30°C on rubbed PI-LB surfaces for numbers of 3, 4, 1, and 12 alkyl chain length is approximately 3×10^{-4} (J/m²), which indicates weak anchoring strength. The obtained polar anchoring energy of 5CB is about 1×10^{-3} (J/m²) on rubbed PI-LB surfaces with number of 7 and 8 alkyl chain lengths. It is considered that the polar anchoring energy of 5CB for rubbed PI-LB surface with numbers of 7 and 8 alkyl chain lengths is stabilized compared with numbers of 3, 4, 11, and 12 alkyl chain lengths. Also, we have reported that the polar anchoring energy of 5CB is $> 1 \times 10^{-3}$ (J/m²) on weakly rubbed PI surfaces in previous work.¹⁷ Consequently,

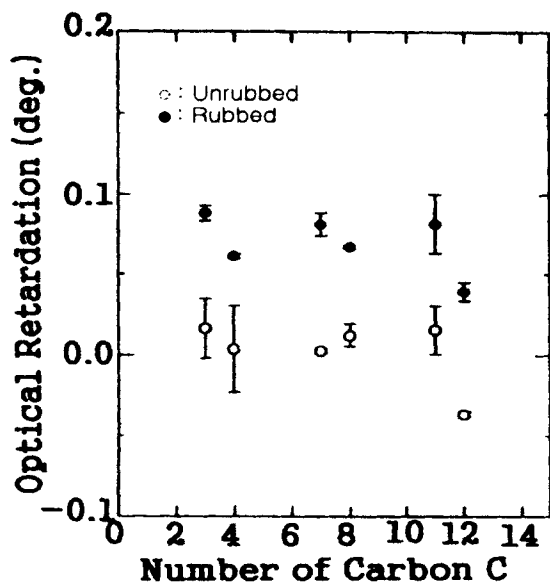


FIGURE 4 Induced optical retardation on PI-LB surface as a function of alkyl chain lengths for medium rubbing (RS=189mm)

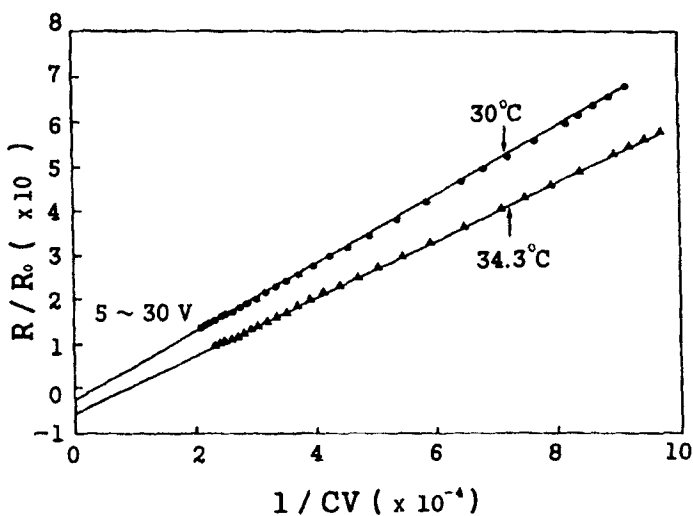
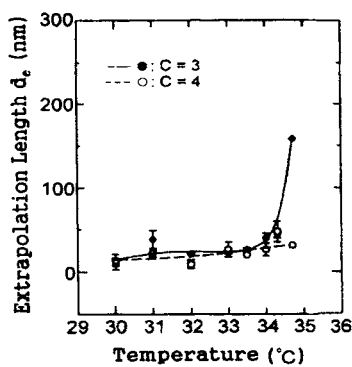
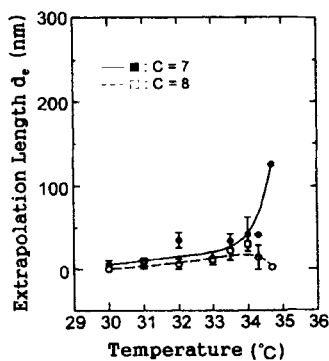


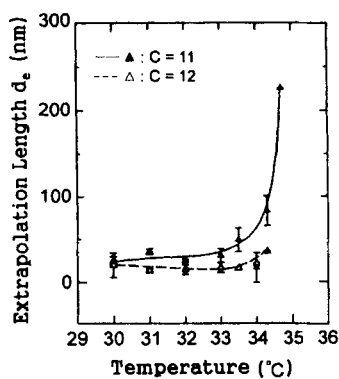
FIGURE 5 Plots of R/R_0 vs $1/CV$ observed at two different temperatures of 30°C and 34.3°C on PI-LB surface



(a)



(b)



(c)

FIGURE 6 Temperature dependence of the extrapolation length d_e in 5CB on rubbed PI-LB surfaces with alkyl chain lengths for medium rubbing ($RS=189\text{mm}$)

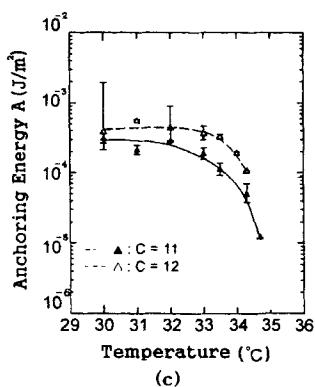
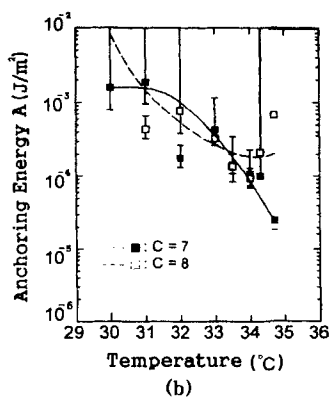
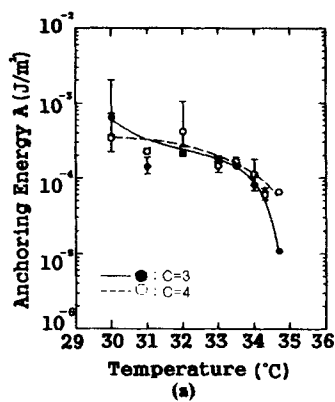


FIGURE 7 Temperature dependence of the polar anchoring energy in 5CB on rubbed PI-LB surface for medium rubbing ($RS=189\text{mm}$) with alkyl chain lengths

the anchoring energy of 5CB on rubbed PI-LB surface with alkyl chain lengths is low compared with rubbed PI surface. Also, we postulate that the alignment of LCs is related to surface ordering and crystallinity of the orientation film. From these results, we suggest that the polar anchoring strength of 5CB for rubbed PI-LB surfaces with even-number is strong because of relatively high surface ordering caused by more crystalline surfaces. The odd-even effects on polar anchoring strength is clear for long alkyl chain lengths.

Figure 8 shows the residual optical retardation on rubbed PI-LB surface with numbers of number of alkyl chain length of 7 carbons and rubbed PI surface above the clearing temperature T_c . The induced optical retardation for unrubbed PI-LB surface is almost 0, which increases with the rubbing process above the clearing temperature T_c . It is considered that the surface ordering is increased by the rubbing process. The surface ordering of 5CB on rubbed PI-LB surface is low when compared with the rubbed PI surface; it is attributed to the polar anchoring strength.

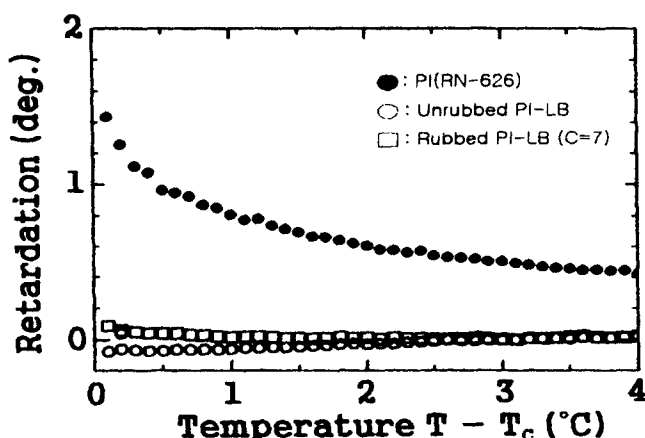


FIGURE 8 Residual optical retardation on rubbed PI-LB surface with number of alkyl chain length of 7 carbons and rubbed PI surface above the clearing temperature T_c

4. CONCLUSION

In conclusion, LC aligning capability in NLC, 5CB, on PI-LB surfaces has been evaluated by measuring the pretilt angle, the induced optical retardation, and the extrapolation length d_e of 5CB. The generated pretilt angle of the 5CB increased by the rubbing. Also, the induced optical retardation on PI-LB surface increased

by the rubbing. The extrapolation length d_e of 5CB for rubbed PI-LB surfaces with even-number is small for alkyl chain lengths of more than the numbers of 7 carbons compared with odd-number. The polar anchoring strength on rubbed PI-LB surfaces with even-number is strong because of relatively high ordering and more crystalline surfaces. The anchoring energy of 5CB with alkyl chain length of 7 carbons is approximately 1×10^{-3} (J/m²); it indicates the strong anchoring strength. Finally, we conclude that the odd-even effects on the polar anchoring strength in NLC are strongly related to the characteristics of the polymer.

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