# 러빙처리된 폴리이미드막 LB막에 있어서 네마틱액정의 결합강도의 홀수짝수 효과

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# Odd-Even Effects of the Anchoring Strength for Nematic Liquid Crystal on Rubbed Polyimide LB Surfaces

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### ABSTRACT

The odd-even effect of the alkyl chain length of rubbed polyimide Langmuir-Blodgett (LB) surfaces extrapolation length of 5CB has been successfully evaluated for the first time by measuring polar anchoring strength. The extrapolation length of 5CB for rubbed PI-LB surfaces with even-numbers is small compared with odd-numbers for alkyl chain lengths of greater than 7 carbons. The extrapolation length of 5CB on rubbed PI-LB surfaces with odd-numbers increases gradually as the temperature increases but tends to diverge near the clearing temperature (Tc=35.3°C). The extrapolation length diverges because of rapidly decreasing surface order near T<sub>c</sub>. We suggest that the polar anchoring strength on rubbed PI-LB surfaces with even-number is strong because of relatively high surface ordering caused by more crystalline surfaces. Finally, we conclude that the odd-even effects of the polar anchoring strength in NLCs are strongly related to the character of the polymer and observed clearly for long alkyl chain lengths.

#### 1. Introduction

Uniform alignment of liquid crystals (LCs) on substrate surfaces is very important in LC science and technology. Interfacial properties between the LCs and the alignment surfaces are key to understanding the alignment mechanism of LCs. Rubbed polyimide (PI) surfaces have been widely used to align LC molecules, but the detailed mechanism of LC alignment is not yet fully understood. Most recently, odd-even effects of the alkyl chain length on pretilt angles of LC on rubbed PI surfaces has been reported by H.Yokokura et al.<sup>10</sup> High pretilt angles were observed on rubbed PI surfaces with an even-number of carbons in the alkyl chain. The odd-even effect in pretilt angles and orientational order

of LCs on rubbed polyimide surfaces was measured by D.Johannsmann et al. using surface optical second harmonic generation (SHG) and birefringence measurements.<sup>2)</sup> They demonstrated that PI surfaces with even-numbers of carbon in the alkyl side chain are smoother and capable of inducing higher surface order in an 8CB surface layer. PI-Langmuir-Blodgett (LB) surfaces have been demonstrated for LC alignment.3-61 The anchoring strength (energy) between the LCs and the alignment layers on treated substrate surfaces has been demonstrated and discussed by many investigators. 6,77 We recently reported the polar (out-of-plane tilt) anchoring strength of 5CB on various PI-LB surfaces.<sup>5,6)</sup> We also reported the first measurement of the temperature dependence of the polar anchoring strength of weakly rubbed PI surfaces in 5CB.89 In this paper, we report for the first time the odd-even effects of the anchoring strength in NLC on alignment layers.

Specifically, we report the odd-even effects of the polar anchoring strength in NLC, 4-n-pentyl-4-cyanobiphenyl (5CB), on rubbed PI-LB films with alkylene 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 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 of 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 (Y<sub>0</sub>-15-N, Yoshikawa Chemical Industries Co. Ltd.). The definition of the rubbing strength, RS, was given in previous papers.<sup>4,6,9)</sup>

The LC was assembled in sandwich-type cells with antiparallel-rubbed surface. All LC layers were  $60\pm0.5\mu\text{m}$ . We used the high electric-field technique<sup>71</sup> to measure the polar anchoring strength. 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

Figure 1. Used polymer molecular structure

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 de is determined by using the relationship between the measured values of the electric capacitance and the optical retardation:

$$\frac{R}{R_0} = \frac{I_0}{CV} - \frac{2d_e}{d}$$
, when V >> 6V<sub>th</sub> (1)

where Io 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 following relation:

$$A = \frac{K}{d_e} \tag{2}$$

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  $K_1$ ,  $K_2$ , and  $\theta_0$  stand for the elastic constant of the splay and bend deformation, and the pretilt angle, respectively. We used measured elastic constants in this work.

#### 3. Results and Discussion

Figure 2 (a), (b), and (c) shows the temperature dependence of the extrapolation length of 5CB on rubbed PI-LB surfaces with alkylene chain lengths for medium

rubbing. The extrapolation length of 5CB for rubbed PI-LB surfaces with even-numbers is relatively small compared with odd-number alkyl chain lengths above 7. The anchoring strength of 5CB on rubbed PI-LB surfaces with even-numbers is strong compared with odd-number of carbons.

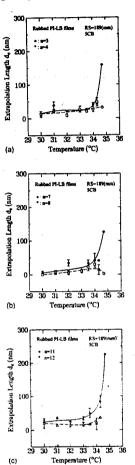


Figure 2. Temperature dependence of the extrapolation length of 5CB on rubbed PI-LB surfaces with alkylene chain lengths for medium rubbing. (a) n=3 and 4; (b) n=7 and 8; (c) n=11 and 12.

In this work, we determined that the polar anchoring energy of 5CB at 30°C on rubbed PI-LB surfaces for medium rubbing is about 510-4 J/m², which indicates weak anchoring compared with rubbed PI surfaces. 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-numbers is strong because of relatively high surface ordering caused by more crystalline surfaces. The odd-even effect on polar anchoring strength is clear for long alkyl chain lengths. The extrapolation length of

5CB on rubbed PI-LB surfaces with odd-numbers increases gradually toward the clearing temperature and tends to diverges near the clearing temperature. A similar behavior near the clearing temperature has previously observed for 5CB on obliquely evaporated SiO films for both polar and azimuthal anchoring strength. We also previously observed the effect for 5CB on weakly rubbed PI surfcaes. We predict that the extrapolation length of 5CB on rubbed PI-LB surfaces with odd-numbers diverges because of rapidly decreasing surface ordering near the clearing temperature. In Fig. 2 (a), (b), and (c), the extrapolation length of 5CB for rubbed PI-LB surfaces with numbers of 7 and 8 alkyl chain lengths is small compared with numbers of 3, 4, 11 and 12 alkyl chain lengths. It is considered that the polar anchoring strength of 5CB for rubbed PI-LB surfaces with numbers of 7 and 8 alkyl chain lengths is stabilized compared with numbers of 3, 4, 11, and 12 alkyl chain lengths.

### 4. Conclusions

In conclusions, we suggest that the polar anchoring strength of 5CB on rubbed PI-LB surfaces with even numbers is strong compared with odd numbers because of relatively high surface ordering caused by more crystalline surfaces. We also demonstrate that the odd-even effect of the polar anchoring strength is clear for long alkyl chain lengths.

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