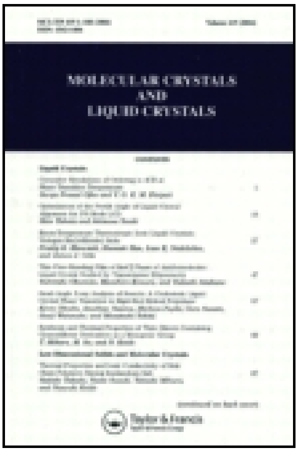

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Liquid Crystal Alignment on LB Films of Phthalocyanine Derivatives

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Liquid Crystal Alignment on LB Films of Phthalocyanine Derivatives

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It has been found that contrast ratio of nematic liquid crystal (LC) on phthalocyanine (Pc) derivative Langmuir-Blodgett (LB) film cell has a correlation with dichroic ratio of the LB film. These results show that this homogeneous alignment force is originated from orientation of rod-like aggregates of the Pc derivative. On the other hand, the LC alignment changes from uniform homogeneous alignment to uniform homeotropic alignment through non-uniform tilted alignment, with the increase of the number of side chain carbon atoms of the Pc derivative. Such alignment change has been also observed with the increase of concentration ratio of a long side chain Pc in a mixed Pc LB film. These show that homeotropic alignment force originates from the ordered long side chain. Therefore, LC alignment is determined by Pc orientation and side chain length, and the feasibility of the tilted LC alignment is shown.

Keywords: alignment layer, dichroism, Langmuir-Blodgett films

1. INTRODUCTION

Liquid crystal alignment method is very important in recent LC display technology. Rubbing treatment is commonly used for LC alignment in device production processes. However, we still don't completely understand the LC alignment mechanism, in spite of extensive investigations using various alignment layers.[1–3]

A Langmuir-Blodgett film is a monomolecular film, and it enables us to control the characteristics of the film in molecular order; for example, we can easily change the surface energy or the surface structure by using LB films. Therefore using LB films as an alignment layer is useful for studying the interaction between LC molecules and substrate surfaces. The LC alignment on polyimide (PI) LB film has been studied extensively.[4] In particular, ferroelectric liquid crystal alignment on PI LB films has been intensively studied.[5,6]

We used the phthalocyanine-derived LB film as an alignment layer, since the Pc LB films show a larger dichroic ratio than that of PI LB films,[7] and their molecular structures are easily changed. In this paper we will report on the effects of the following factors on LC alignment behavior, that is, the effects of the number of the LB film layers, rubbing treatment and the Pc derivative side chain length. We will also report on how to control the pre-tilt angle of a LC by mixing the Pc LB films of different chain lengths.

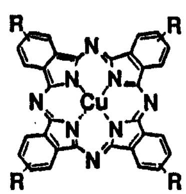
2. EXPERIMENTAL

2.1 Phthalocyanine-Derived LB Films

We synthesized four kinds of Pc derivatives.[8] They are a tetrakis (butyloxycarbonyl) phthalocyaninato Copper (II) complex (PcC4), a tetrakis (hextyloxycarbonyl) phthalocyaninato Copper (II) complex (PcC6), a tetrakis (decanyloxycarbonyl) phthalocyaninato Copper (II) complex (PcC10) and a tetrakis (tetradecanyloxy-carbonyl) phthalocyaninato Copper (II) complex (PcC14). These molecular structures are shown in Figure 1. The Pc derivatives were dissolved in a 1:1 chloroform and tetrahydrofuran solvent. The concentration for each sample solution was 25 mM. The dipping speed was 0.1 mm/s. The suitable surface pressure for the deposition, which was determined from each isotherm, was between the 22 and 30 mN/m region. The dichroic ratio, which is defined as the ratio of absorbance of two polarized lights—one is polarized perpendicular to the dipping direction and the other is parallel to the dipping direction—was measured with a Shimadzu UV365 spectrophotometer.

2.2 LC Cell

LC cells were made by sandwiching the LC between two glass plates on which Pc LB films were deposited. For every cell, dipping directions are opposite to each other. Rubbing treatment was performed using rayon cloth. We checked the texture of nematic LCs (E7, MBBA) with a microscope under crossed polarizers. We measured the contrast ratio of an LC cell in which guest-host LC (ZLI-3237) was injected. The contrast ratio was defined as the maximum transmittance of light



$$\mathrm{R:}\ -\overset{\displaystyle O}{\overset{\|}{C}}-O-C_nH_{2n+1}$$

Pc C4 : n = 4

Pc C6 : n = 6

Pc C10 : n = 10

Pc C14 : n = 14

FIGURE 1 Chemical structures of phthalocyanine.

divided by the minimum transmittance of light during one rotation of the LC cell under one polarizer. The pre-tilt angle had been measured using crystal rotation method. The cell gap was 40 μm for pre-tilt angle measurement, and was 5 μm for other measurements.

3. RESULTS AND DISCUSSION

3.1 LC Alignment Behavior Dependence on Number of Layers

The dichroic ratios of 1 to 9 layer PcC4 LB films are shown in Figure 2. The dichroic ratio increases as the number of layers increase, reaches a maximum value of 4.5 at 7 layers and decreases over 9 layers.

The nematic LC cells were made with glass plates on which 5 layers of PcC4 LB films were deposited. The nematic LCs showed uniform and homogeneous alignment. It has been found that the LC molecules align along the dipping direction of the PcC4 LB film. Though Pc molecules are disk-like in structure, they make rod-like aggregates and are deposited perpendicular to the substrate. The LC molecules align along these deposited aggregates.

The contrast ratios are also shown in Figure 2. In a one-layer LC cell, the LC didn't align uniformly so the contrast ratio couldn't be measured. The contrast ratio depends on the number of layers like the dichroic ratio, and it reaches a maximum at 5–7 layers. Thus the contrast ratio of the LC cell has a strong correlation with the dichroic ratio of the LB film. On the other hand, the contrast ratio is large when LC alignment is uniform. Therefore, LC alignment uniformity depends strongly on the dichroic ratio of the LB film.

3.2 LC Alignment on Rubbed LB Film

Rubbing treatment reduced the dichroic ratio of the PcC4 5 layer LB film to approximately 1, a value which didn't depend on the relation between rubbing

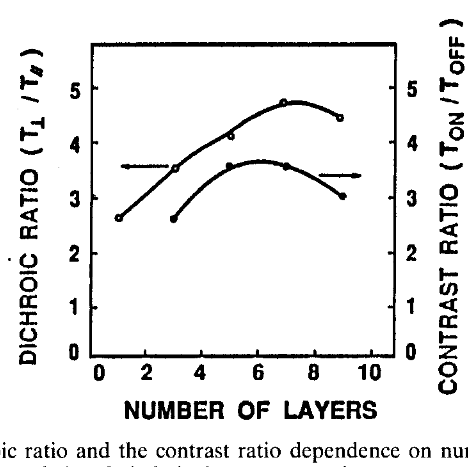


FIGURE 2 The dichroic ratio and the contrast ratio dependence on number of PcC4 layers. Open circle is the dichroic ratio and closed circle is the contrast ratio.

direction and dipping direction. In the LC cell where rubbed LB films were used, the LCs alignment was disordered. The contrast ratio was 2.5 and 3.5 with and without rubbing treatment, respectively. The dichroic ratio and the contrast ratio for PcC4 before and after rubbing treatment are shown in Table I. From Table I, we may say that rubbing treatment has a bad influence on the Pc aggregate orientation, and, hence, LCs don't align uniformly. Though the dichroic ratio of the LB film becomes about 1 after rubbing treatment, the contrast ratio doesn't become so small. The reason may be that rubbing treatment damages the Pc aggregates orientation, but on the other hand it makes small grooves at the same time. LC may align along these grooves and therefore LC alignment isn't disordered completely.

3.3 Influence of Molecular Structure of Pc Derivatives

Dichroic ratios of 5-layer Pc derivatives, which differ in side chain length, are plotted against the number of side chain carbon atoms in Figure 3. The dichroic ratio shows maximum for PcC6 and decreases as the alkyl chain length increases. This suggests that a long alkyl chain has an undesirable effect on the orientation of the Pc aggregate.

Textures of nematic LCs are checked for the four kinds of 5-layer Pc LB films. They showed uniform and homogeneous alignment on the PcC4 LB film as we have already mentioned in the previous section. And they showed uniform and homeotropic alignment on the PcC10 and PcC14 LB films. The pre-tilt angle on

TABLE I

The dichroic ratio and the contrast ratio on 5 layer PcC4 LB film before and after rubbing treatment

	Dichroic ratio	Contrast ratio
Before rubbing	4.1	3.5
After rubbing	1.1	2.5

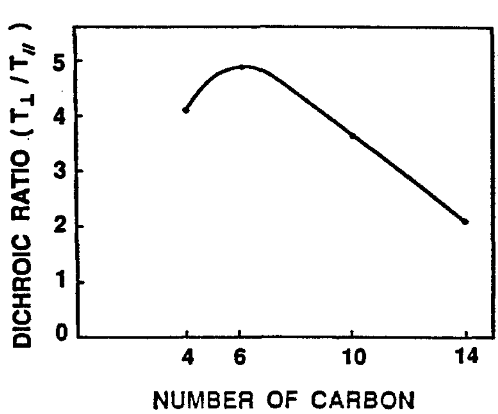


FIGURE 3 The dichroic ratio dependence on number of carbon.

TABLE II

LC alignment on four kinds of Pc LB films

Pc derivative	LC alignment
PcC4	Homogeneous
PcC6	Tilted alignmen (not uniform)
PcC10	Homeotropic
PcC14	Homeotropic

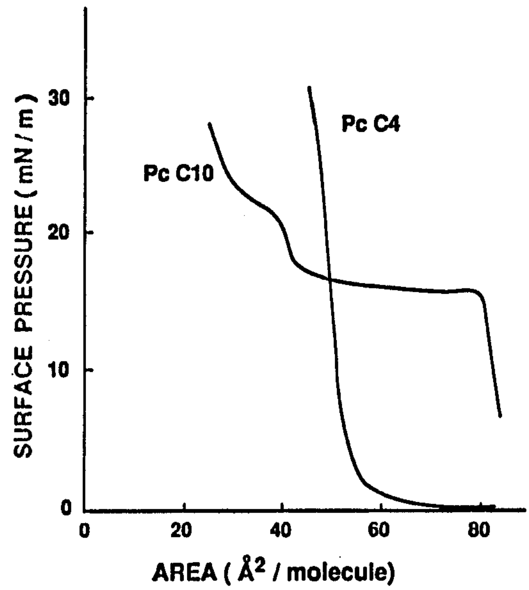


FIGURE 4 Isotherms of PcC4 and PcC10.

the PcC4 LB film is less than 1 degree, and on the PcC10 and PcC14 LB films, they are more than 89 degrees. On the PcC6 LB film, LCs didn't show uniform alignment and, therefore, we couldn't measure the exact pre-tilt angle. However, from the texture check, it is certain that LCs align tilted against the substrate plane.

The Pc aggregate orientation can be derived from the isotherms. The isotherms of PcC4 and PcC10 are shown in Figure 4. The limiting area per molecule is about 52 Å^2 for both Pc derivatives. The Pc chromophores of the PcC4 are deposited perpendicular to the substrate. Since the limiting area per molecule is the same for both Pc derivatives, the chromophores of the PcC10 should be deposited perpendicular to the substrate. On the PcC4 LB film, whose alkyl side chains are relatively short, LCs align along the rod-like Pc aggregates, and, hence, LCs align homogeneously. On the other hand, the PcC10 LB film has long alkyl side chains which may align perpendicular to the substrate. On this LB film the LCs align, not along the Pc aggregates but along the long alkyl chain, and hence, LCs align homeotropically; in the case of the PcC14 LB film, it is the same. Thus homogeneous or homeotropic alignment can be controlled by the length of side alkyl chains of Pc derivatives.

3.4 LC Alignment on Mixed PcLB Film

The isotherms of PcC4 and PcC10 mixed monolayers with various mixing ratios are shown in Figure 5. The isotherm changes gradually from that of PcC4 to that of PcC10 as the PcC10 concentration increases. Nematic LCs showed uniform and homogeneous alignment when the PcC10 content is less than 20% and showed homeotropic alignment when it is over 35%. In the region where the PcC10 content is between 20% and 35%, they don't align uniformly and have a large pre-tilt angle. The pre-tilt angles of E7 on mixed LB films are shown in Figure 6. The pre-tilt angle is 3 degrees for 20% and it is 89 degrees for 35%. Between the 20% and 35% range, pre-tilt angles can't be determined because of poor uniformity. Using the mixture of the two kinds of Pc derivative LB films, the pre-tilt angle of LC may be controlled.

4. CONCLUSIONS

It has been found that nematic LC alignment shows uniform homogeneous alignment on the Pc derivative LB film, and that the contrast ratio of the LC cell has a correlation with the dichroic ratio of the LB film. These results show that this homogeneous alignment force is originated from orientation of the rod-like aggregates of the Pc derivative. On the other hand, the LC alignment changes from uniform homogeneous alignment to uniform homeotropic alignment through non-uniform tilted alignment, with the increase in the number of alkyl side chain carbon

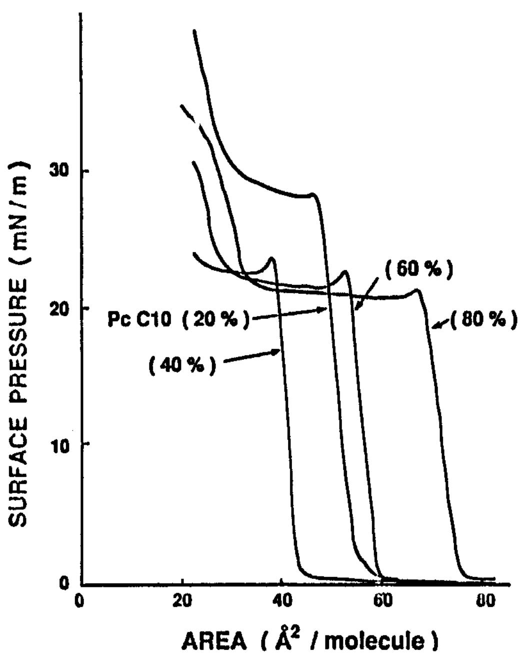


FIGURE 5 Isotherms of the mixed Pc LB film.

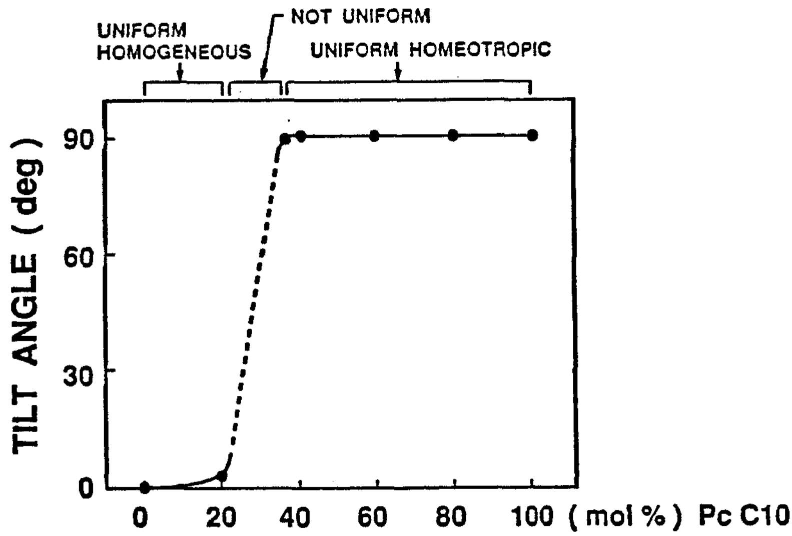


FIGURE 6 Tilt angle of E7 on the mixed Pc LB film.

atoms of the Pc derivative. The pre-tilt angle continuously changes from 0 to 90 degrees according to the increase in the concentration ratio of the long side chain Pc in the mixed Pc LB film. These show that homeotropic alignment force originates from the ordered long side chain. Therefore, LC alignment is determined by the Pc aggregate orientation and the side chain length. The feasibility of the pre-tilt angle control is also shown.

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