

# How Do Liquid Crystal Molecules Align on Treated Surfaces?

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## Abstract

We have studied liquid crystal (LC) molecular alignment on rubbed and photoaligned surfaces. Particular attention was paid to the intermolecular liquid crystalline interaction. We will first show that uniform molecular orientation on a rubbed surface does not mean spatially uniform interaction between the surface and LC molecules. Rather LCs tend to align themselves through LC interaction. The existence of nonuniformity of rubbing was successfully visualized by double surface treatment. The importance of intermolecular LC interaction was also found in the orientation formation process in 5CB evaporated on rubbed and photoaligned surfaces. By simultaneously analyzing polarized UV/VIS absorption and second-harmonic generation (SHG) using the maximum entropy method, we succeeded in obtaining the temporal variation of the orientational distribution functions in the film forming process. The distribution anisotropy and pretilt are found to be generated under the influence of intermolecular LC interaction.

**Keywords :** liquid crystal, alignment, surface treatment, rubbing, photoalignment, orientational distribution function.

## 1. Introduction

Alignment of liquid crystal (LC) molecules on treated surfaces is important and interesting from both viewpoints of fundamental science and device application of LCs. However, there are still many problems to be solved. One of the most important problems is the alignment mechanism. Two models have been proposed: (1) LC molecules tend to align microgrooves induced by rubbing to minimize the elastic distortion energy [1]. (2) Anisotropic intermolecular interaction between oriented polymer surfaces and LC molecules gives good alignment [2,3]. Both mechanisms implicitly involve the importance of intermolecular LC interaction. Namely, if rubbing is not uniform, both mechanisms do not work macroscopically, and uniform

alignment cannot be achieved without the intermolecular interaction between LC molecules. However, the importance of the intermolecular LC interactions has never been seriously considered in LC alignment.

Several techniques have been employed to probe LC alignment on treated surfaces. Among them, second-harmonic generation (SHG) has been widely used because of its surface specificity and easiness [4-7]. However, because of the lack of axial information, unrealistic distribution was obtained. This problem was solved in the simulation process, i.e., modified maximum entropy method [8,9]. It is of course desired that the information of the axial order is supplied by experiments. In the present study, we experimentally solved this problem by including the results of polarized absorption.

In this paper, we cast a light on the importance of the intermolecular interaction through two experimental results, i.e., LC molecular alignment on doubly treated surface and LC molecular alignment process on treated surfaces at the early stage of LC molecular evaporation. In the former work, we succeeded in visualizing the nonuniformity of rubbing [10]. In the latter work, we analyze the data of SHG and polarized absorption simultaneously using the maximum entropy method and determined surface molecular orientational distribution

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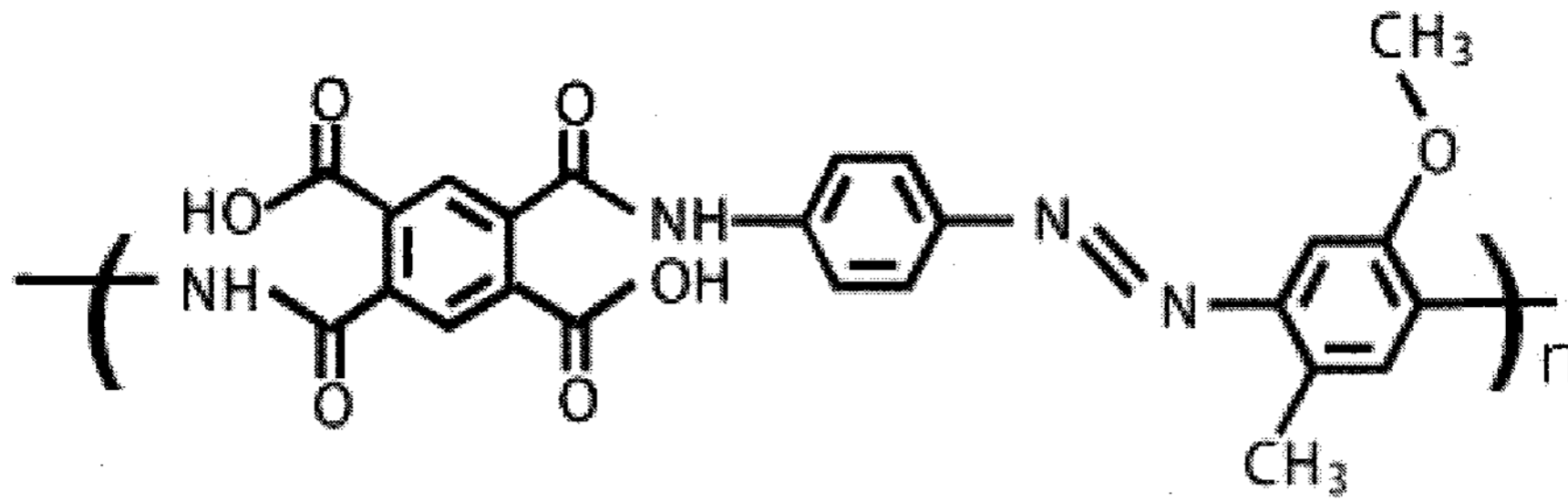


Fig. 1. Chemical structure of polyamic acid used.

functions [11].

## 2. Experiments

As an alignment layer, we used polyamic acid (PAA) with azobenzene groups in the main chain [12,13], as shown in Fig. 1. PAA was dissolved in N-methyl-2-pyrrolidinone with a concentration of 3 wt%. The polymer solution was spin-coated onto a glass plate at 3000 rpm and dried at 70 °C for 30 min. By imidizing this film after photoalignment treatment, the films become very stable against heat and light irradiation [12].

Photoisomerization was performed using a 500 W ultrahigh pressure mercury lamp without passing through optical filters. The substrates were normally illuminated with weakly focused linearly polarized UV (LPUV) light or rubbed. The second surface treatment, if necessary, was made along the direction making 45 ° with respect to the first treatment direction. These treated substrates were used for making sandwich cells or for evaporating 5CB on the substrates. For the evaporation, 5CB was heated on a hot plate at 90 °C and was adsorbed on the treated surface that was located 4 cm above the LC source at room temperature in air. The adsorbed amount of 5CB molecules was controlled by the duration of exposing substrate to vaporized LC atmosphere.

Polarized absorption measurements were conducted at incidence angles of 0° and 45° as a function of sample rotation angle. The absorbance of 5CB at 300 nm was determined by extracting the background absorption due to the PAA film. SHG measurements were conducted using an optical parametric oscillator pumped by the third harmonics of a Nd:YAG laser. SHG wavelength at 300 nm was chosen, because of the resonance enhancement of 5CB signal and the negligible signal

from PAA. *p*-polarized SHG was detected from the transmittance direction by the incidence of *p*-polarized fundamental light at 45 ° incidence as a function of sample rotation angle.

## 3. Results and Discussion

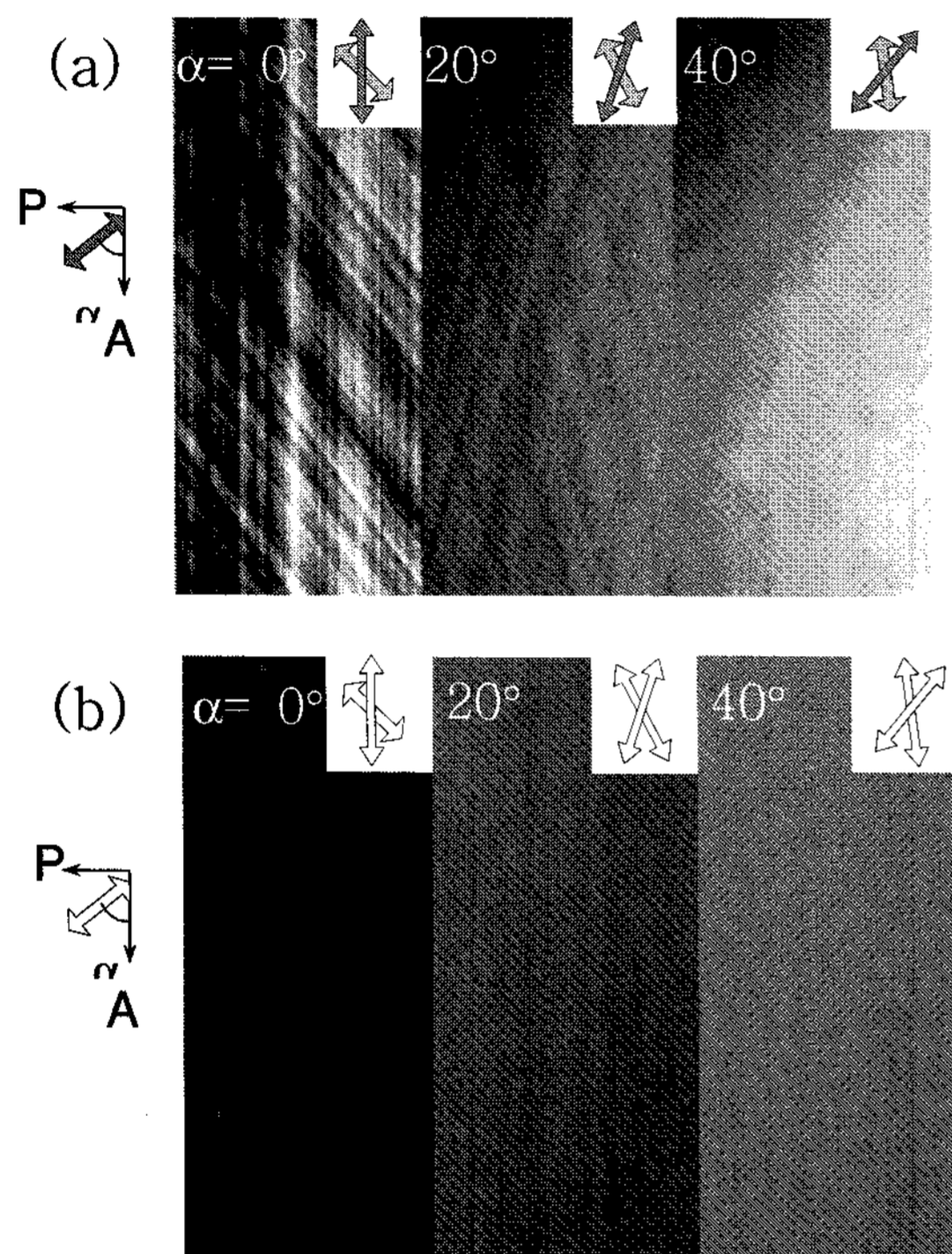
### 3.1 Visualization of rubbing nonuniformity

Since long time ago, we know that rubbing treatment is effective to align LC molecules and obtain homogeneously aligned uniform domains. The present PAA layer can be used as an alignment layer for rubbing. We actually confirmed that a single rubbing gives a good alignment. In this way, the microscope observation tells us that rubbing is apparently made uniformly. However, as a matter of fact, the spin-coated polymer is not flat in molecular scale and rubbing cloth is made of huge fibers compared with LC molecules. This means that rubbing is not necessarily uniform at least in a molecular dimension. Nevertheless, liquid crystal molecules tend to align themselves through intermolecular LC interactions regardless of nonuniform rubbing condition, so that uniform alignment is established. Here we introduce a technique to visualize the nonuniformity of rubbing.

Fig. 2(a) displays photomicrographs of a nematic cell with substrate surfaces doubly rubbed along 45° to each other. We can clearly see scratches by rubbing. In this way, if rubbing is not uniform, LC molecules align under the competition of the rubbing strength of the first and second rubbings. On the other hand, a doubly photoaligned surface gives perfect alignment as shown in Fig. 2(b).

In order to see whether or not the rubbing nonuniformity depends on the rubbing strength, rubbing with a slanted substrate was carried out. Namely, the

substrate was inclined by  $4.4^\circ$  with respect to the surface plane by inserting a  $700\ \mu\text{m}$  spacer at only one side edge below the substrate. If rubbing was made subsequently after photoalignment, rubbing scratches are clearly observed, as shown in Fig. 3. In the figure, it is seen that the dark region shifts with sample rotation. This is a consequence of competition between rubbing with various rubbing strengths and photoalignment.



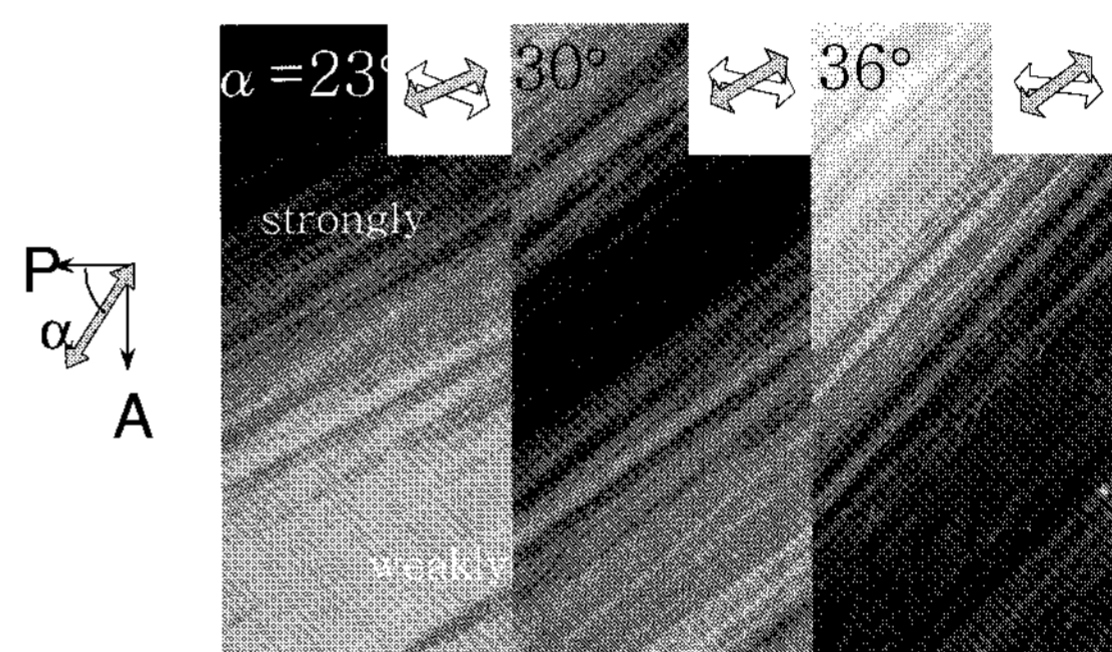
**Fig. 2.** Microphotographs of nematic LC (5CB) cell between crossed polarizers at several sample rotation angles. The substrates were doubly treated, i.e., (a) double rubbing and (b) double photoalignment treatment, the directions of which are mutually  $45^\circ$  apart, as indicated by gray (rubbing) and white (photoalignment) arrows.

In this way, rubbing is inherently not uniform. In case of single uniform rubbing process, liquid crystal molecules automatically align themselves and give no problems. However, when more precise control of surface alignment is necessary, the fact that rubbing is not uniform at all will give us a problem.

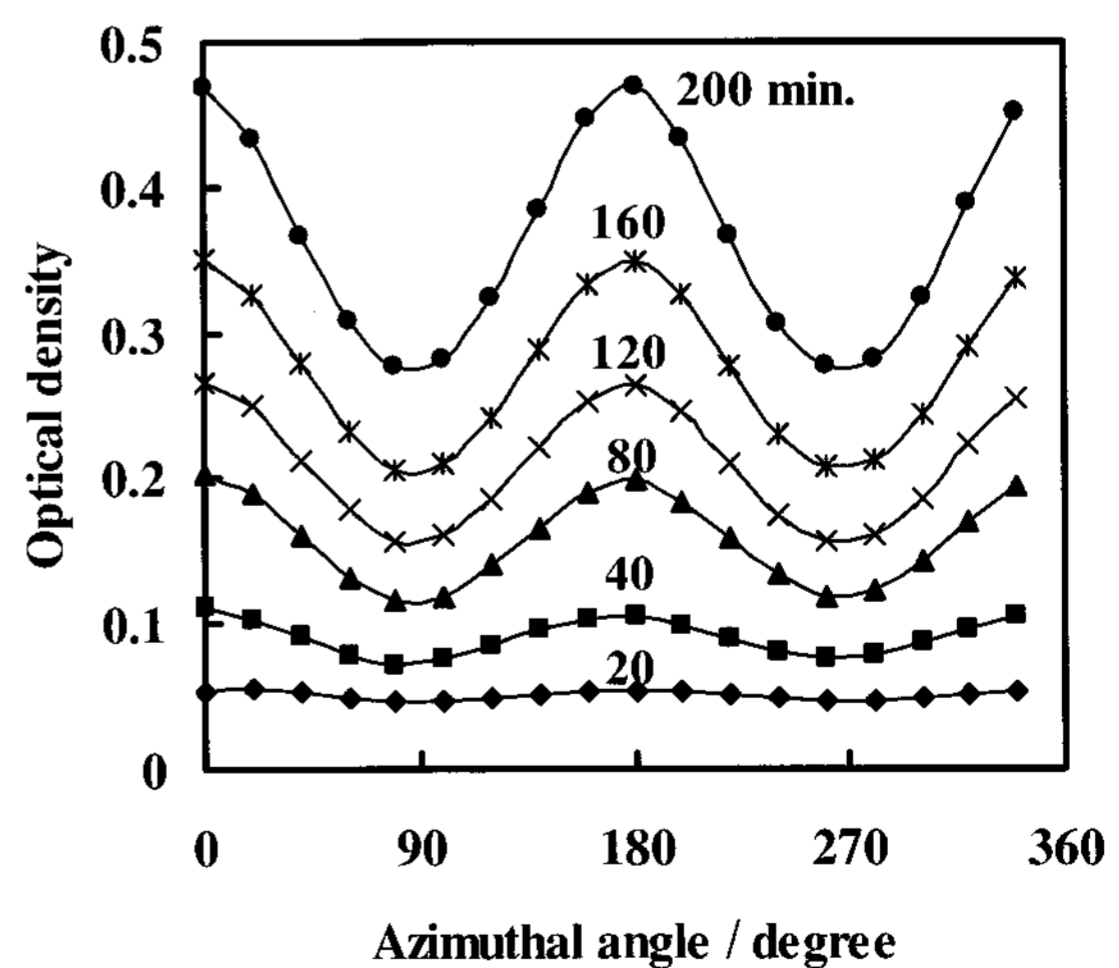
### 3.2 Orientation distribution function of 5CB evaporated on treated surfaces

Fig. 4 shows absorbance of 5CB molecules evaporated on a rubbed surface at  $300\ \text{nm}$  at normal incidence of light as a function of sample rotation angle.

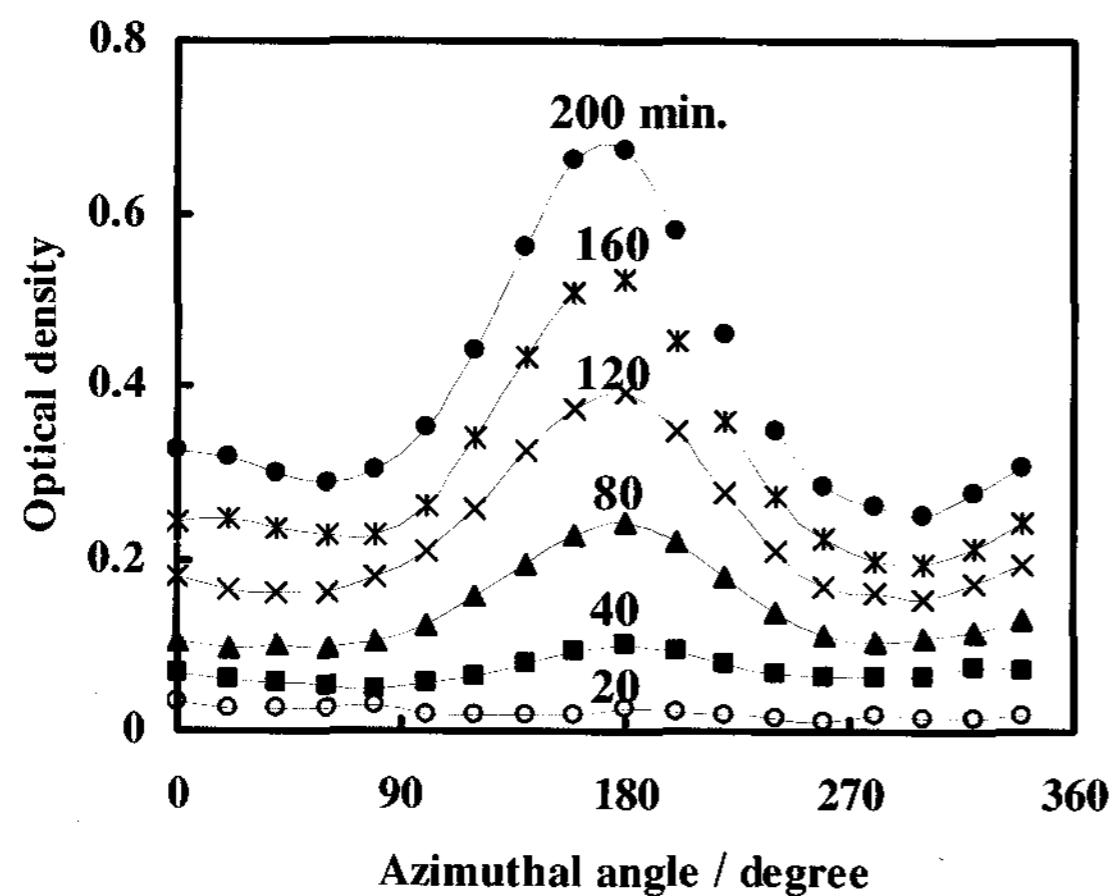
Since the absorbance of alignment layer is properly subtracted from the data, the signal intensity is attributed only to the 5CB molecules. It is clear in Fig. 4 that anisotropy appears along the  $0^\circ$ - $180^\circ$  (rubbing) direction and increases after 80 min. In contrast, anisotropy is quite small at 20 min, when the density of molecules is quite low and the molecules do not cover whole the surface. Polarized absorption measurements were also made in oblique incidence. As shown in Fig. 5, large difference is observed at  $0^\circ$  and  $180^\circ$ , indicating the existence of the pretilt angle.



**Fig. 3.** The microphotographs of nematic LC (5CB) cells with continuous rubbing strengths between crossed polarizers at several sample rotation angles. The substrates were covered with PAA layers slantingly rubbed after photoalignment, the directions of which are mutually  $45^\circ$  apart, as indicated by gray (rubbing) and white (photoalignment) arrows.

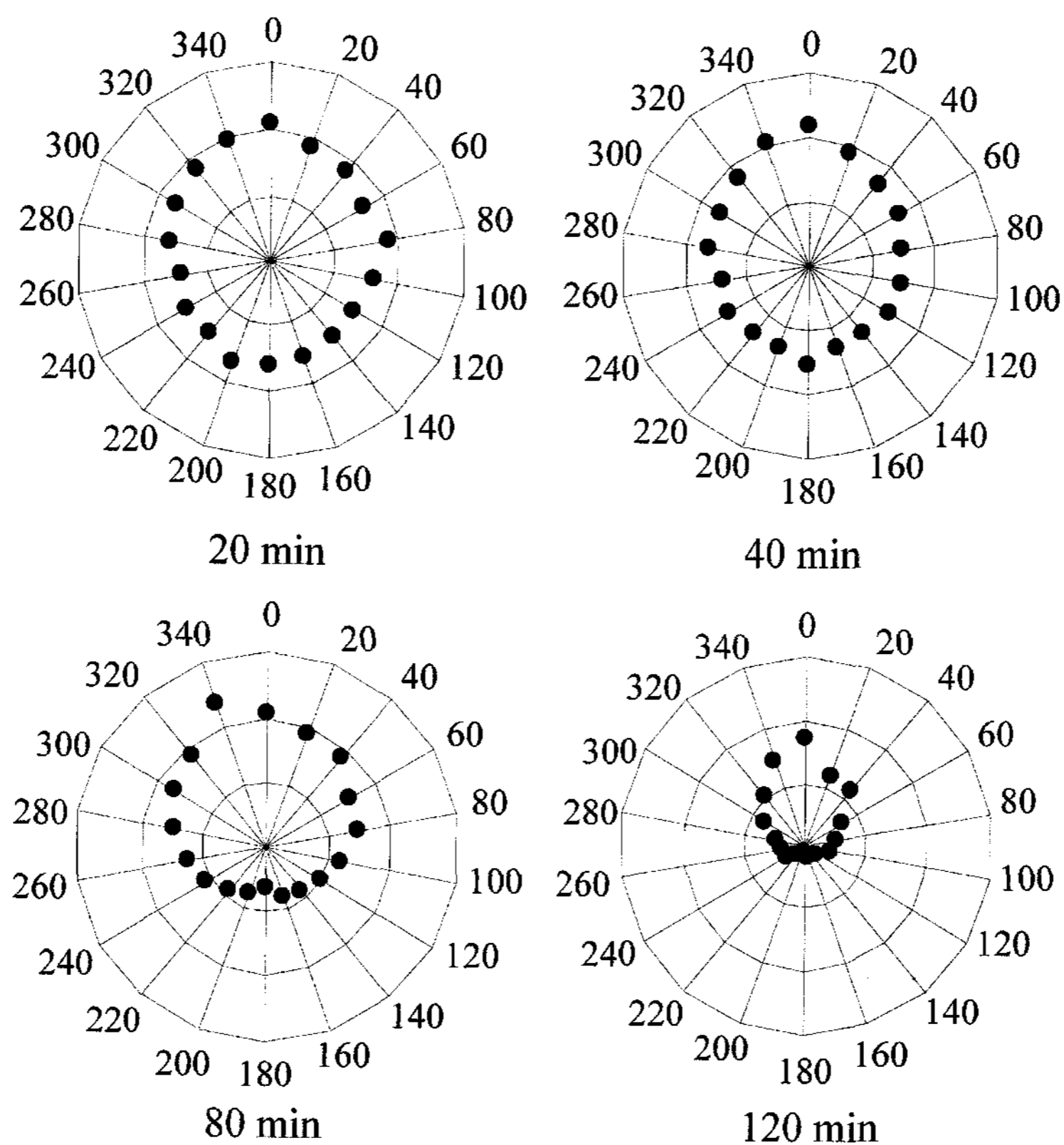


**Fig. 4.** Optical density of 5CB films evaporated for various evaporation times. Plots are for normal incidence at  $300\ \text{nm}$  as a function of sample rotation angle about the surface normal.



**Fig. 5.** Optical density of 5CB films evaporated for various evaporation times. Plots are for oblique incidence ( $45^\circ$ ) at 300 nm as a function of sample rotation angle about the surface normal.

Next, let us show the SHG in-plane anisotropy in Fig. 6, where  $p$ -polarized SHG by the oblique incidence of  $p$ -polarized light is shown as polar plots. As same as in polarized UV/VIS absorption anisotropy, anisotropy increases after about 40-80 min, when molecules cover



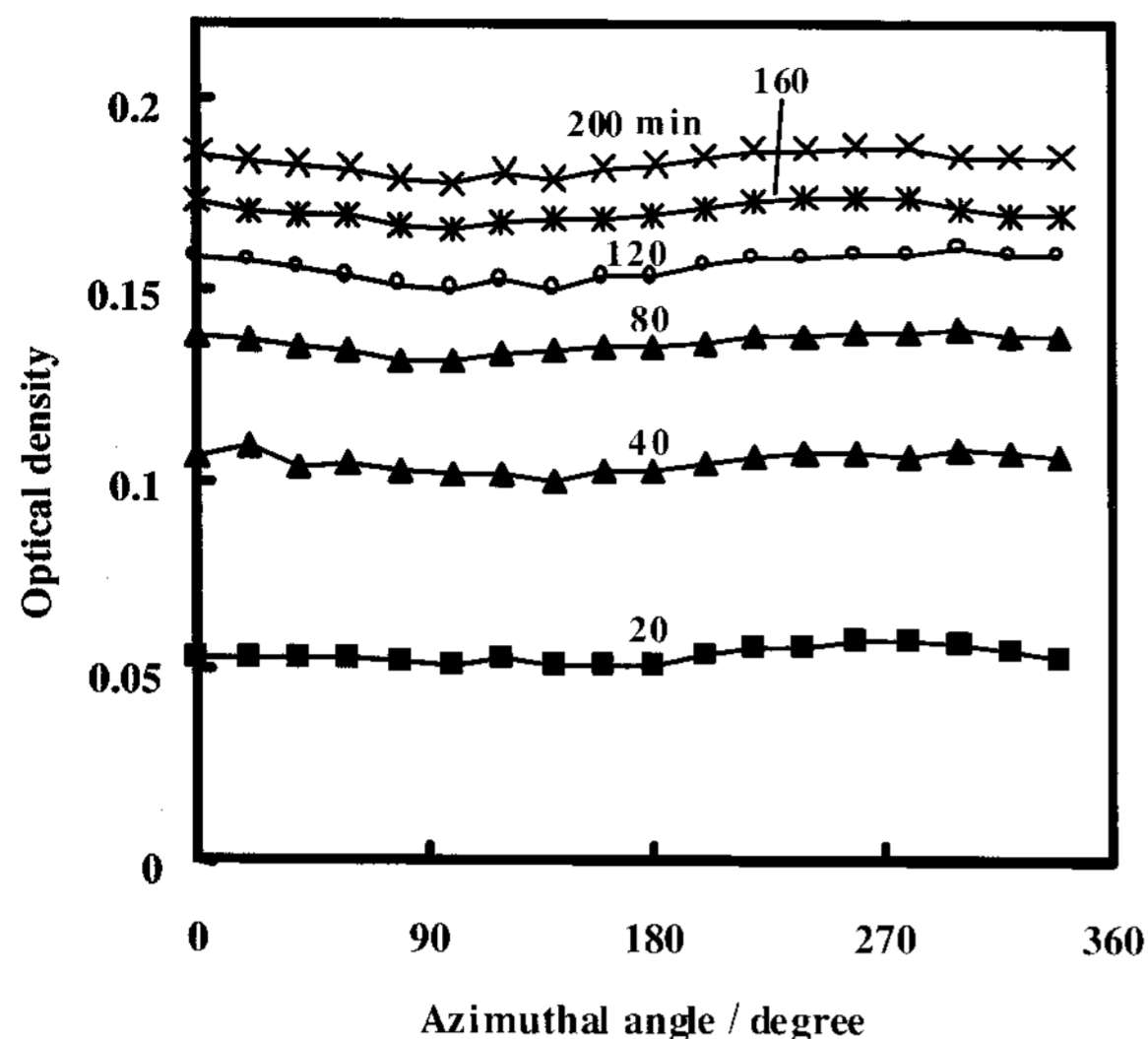
**Fig. 6.** Polar plots of SHG intensity for four films of different amounts of adsorbed 5CB molecules as a function of sample rotation angle about the surface normal.

the whole surface.

In this way, we can imagine the following picture for the alignment process of liquid crystal molecules on the rubbed surface. At the first stage, where molecular density is too low to cover the whole surface, the direct interaction between the surface alignment layer and individual molecules is not so strong to achieve high order of orientation. With increasing the evaporation time and the number density of molecules, the intermolecular liquid crystalline interaction becomes operative and higher anisotropy is brought about.

In order to confirm this consideration, we made the same measurements using 4CB that shows no mesogenic phase. We have only negligible anisotropy even in thick films, as shown in Fig. 7. In this way we can conclude that liquid crystalline interaction plays an important role for the alignment of molecules on treated surfaces.

Finally, let us describe the orientation distribution of 5CB evaporated on treated surfaces. The molecules adsorbed on treated substrates have  $C_{1v}$  symmetry, so that there are six independent  $\chi^{(2)}_{ijk}$  components, each of which is expressed by



**Fig. 7.** Optical density of 4CB films evaporated for various evaporation times. Plots are for normal incidence at 300 nm as a function of sample rotation angle about the surface normal.

$$\chi_{ijk}^{(2)} = N_s \langle (\hat{i} \cdot \hat{\xi})(\hat{j} \cdot \hat{\xi})(\hat{k} \cdot \hat{\xi}) \beta_{\xi\xi\xi} \rangle, \quad (1)$$

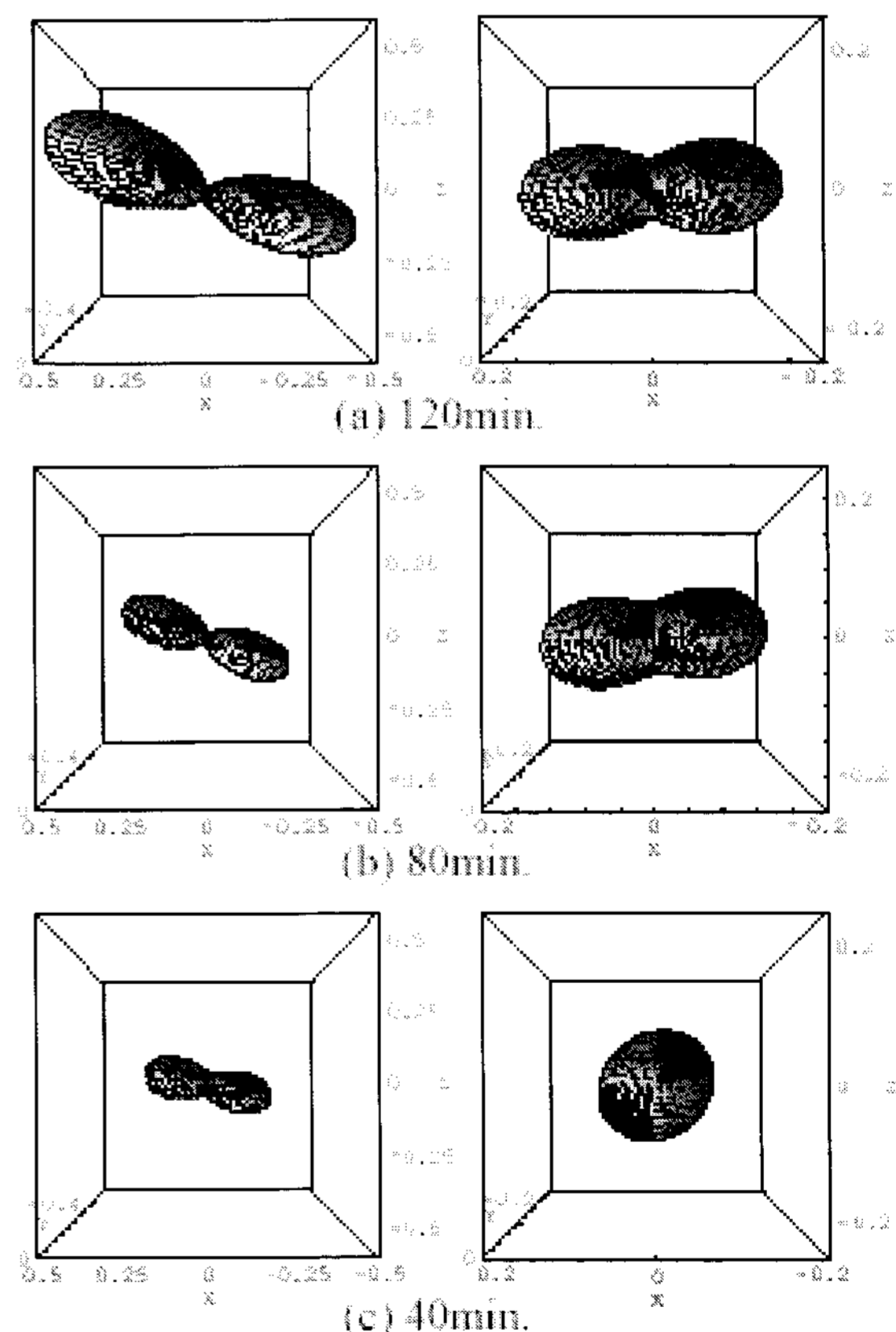
since the 5CB molecule has only one dominant molecular hyperpolarizability tensor element  $\beta_{\xi\xi\xi}$  along the long molecular axis  $\xi$ . Here  $N_s$  is the surface number density of 5CB molecule and  $(i, j, k)$  is the laboratory coordinates. The bracket denotes an average over the orientational distribution, that is given by

$$f(\theta, \phi) = \frac{\exp[\sum \lambda_i f_i]}{\iint \exp[\sum \lambda_i f_i] \sin \theta d\theta d\phi} \quad (2)$$

as functions of polar and azimuthal angles,  $\theta$  and  $\phi$ , using the maximum entropy method.  $f_i$ s are the constraint functions given by the experiments, polarized absorption and SHG, and  $\lambda_i$ s are the Lagrange undetermined multipliers. If nine undetermined multipliers  $\lambda_i$ s are determined once, then one can calculate  $\langle f_i \rangle$ s, and then simulate the experimental results. Therefore, by simultaneously fitting the experimental results of polarized absorption and SHG using  $\lambda_i$ s as fitting parameters, we can determine the distribution function  $f(\theta, \phi)$ .

Fig. 8 shows the orientational distribution functions of 5CB adsorbed on rubbed (left column) and photoaligned (right column) PAA at the stages of 40 min, 80 min and 120 min evaporation times. These

distributions are the side views of the cell surface; the length from the origin to the surface of the profile stands for the number of molecules along this particular direction. Several observations should be made in the orientational distribution functions shown in Fig. 8: (1) The pretilt angle is small at the early stage of evaporation and gradually increases on rubbed surfaces, while average molecular direction is almost flat to the surface during the whole evaporation process on photoaligned surfaces. (2) Anisotropy gradually increases with the evaporation time on both the surfaces. (3) The polar order is not so distinct but the molecular distribution is rather axial even on rubbed surfaces. This means that dimerization of 5CB molecules starts to occur at the early stage of evaporation. (4) 5CB molecules do not form a polar order even along the surface normal direction.



**Fig. 8.** The side views of the orientational distribution functions of 5CB adsorbed on rubbed (left column) and photoaligned (right column) PAA at the stages of 40 min, 80 min and 120 min evaporation times.

All these observations are enough to reconsider the general idea of the evaporation process of 5CB

molecules on treated surfaces. The changes in the anisotropy and the pretilt angle suggest the importance of intermolecular liquid crystalline interaction to form an ordered structure.

#### 4. Conclusions

LC molecular alignment on rubbed, photoaligned and doubly treated surfaces has been studied using a polyamic acid with azo linkages in the main chain. We succeeded in visualizing nonuniformity of rubbing under optical microscope using doubly treated surfaces. Alignment under the influence of single rubbing appears to be uniform, since the intermolecular liquid crystalline interaction forces liquid crystalline molecules align along the rubbing direction, that is uniquely defined regardless of the distribution of the rubbing strength. Under the constraints of doubly treated directions, however, competition between the two treated directions induces spatial variation of the director, resulting in the visualization of rubbing-induced scratches under crossed polarizers.

In order to study the intermolecular interaction of liquid crystal molecules, the orientation of 5CB molecules evaporated on treated surfaces was examined by means of polarized UV/VIS absorption and SHG measurements. Simultaneous analysis of these data using the maximum entropy method successfully gives the

orientational distribution functions. Azimuthal anisotropy and pretilt angle depend on surface number density of 5CB molecules evaporated, implying the importance of the intermolecular liquid crystalline interaction.

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