

## Liquid Crystal Alignment on Treated Surfaces

*Doo-Han Chung, Tatsutoshi Shioda, Yoshinori Okada, Byoungchoo Park  
and Hideo Takezoe*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku,  
Tokyo, 152-8552, Japan

Phone : +81-3-5734-2436 , E-mail : htakezoe@o.cc.titech.ac.jp

### Abstract

We have studied liquid crystal orientation on rubbed and photoaligned polymer surfaces. The following topics will be presented; (1) visualization of nonuniformity of rubbing, (2) competition between grooves and photoalignment and (3) alignment process of 5CB evaporated on treated surfaces. Through these topics, the importance of the intermolecular liquid crystalline interaction will be emphasized.

### 1. Introduction

Alignment of liquid crystals (LCs) on treated surfaces is very important and interesting from both viewpoints of science and application. However, there are still many unsolved problems. For instance, people still discuss the alignment mechanism of LCs on treated surfaces, effect of grooves and direct intermolecular interaction between polymer and LC molecules. In this paper we focus on this topic using novel ways of observation.

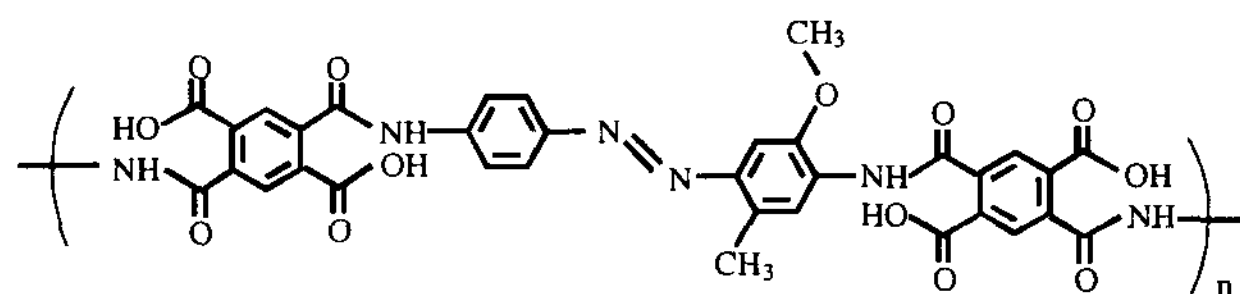
### 2. Experimental

As alignment layers, we mainly used main-chain-substituted polyamic acid (PAA) with azobenzene units shown in Fig. 1 [1,2]. The photoisomerizable PAA was dissolved in N-methyl-2-pyrrolidinone with a concentration of 3wt%. The polymer solution was spin-coated onto a glass plate at 3000 rpm and dried at 70°C for 30 min. If we imidize this film after photoalignment treatment, the films are very stable against heat and light irradiation.

### 3. Results and discussion

#### 3.1 Visualization of rubbing nonuniformity [3]

The PAA layer can be used as an alignment layer for rubbing. When we rub the spin-coated polymer film, fabricate cells and introduce LCs, we will obtain uniformly aligned LC cells. The microscope observation tells us that rubbing is made uniformly.



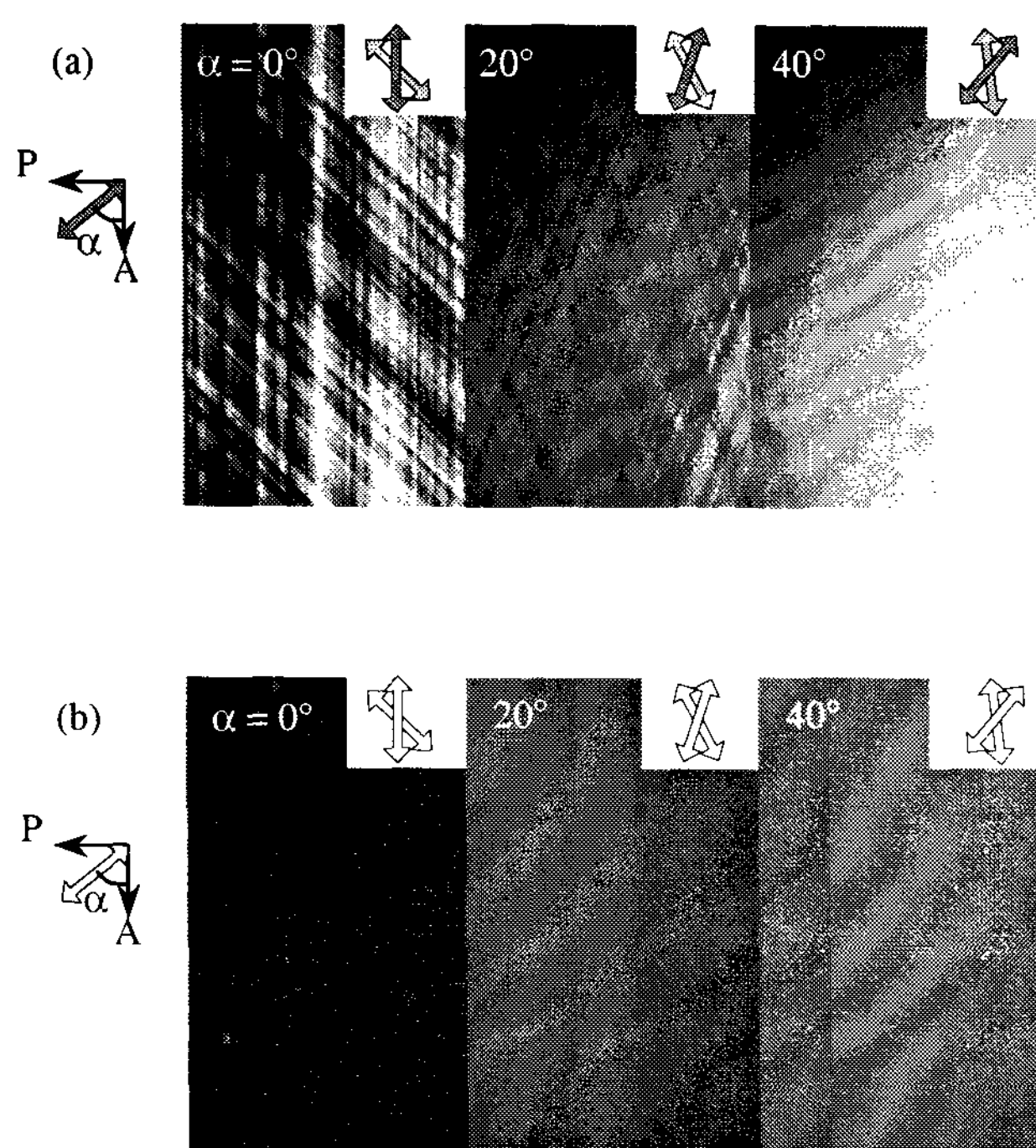
**Figure 1** Chemical structure of the photoalignment layer used.

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 must not be 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.

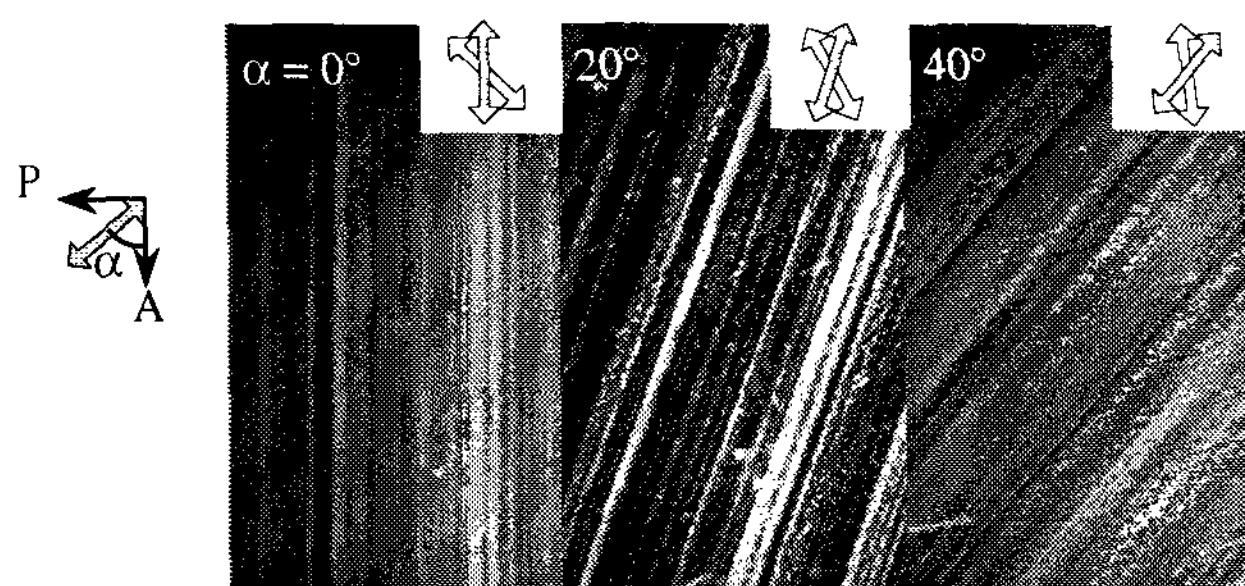
Figure 2(a) displays photomicrographs of a nematic cell with substrate surfaces doubly rubbed along 45° to each other. We can clearly see scratches by rubbing. In this way, if rubbing is not uniform, LC molecules align under the competition of the rubbing strength of the first and second rubbings. On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

To see the rubbing nonuniformity more clearly, we fabricated a cell with doubly treated (rubbed after photoalignment) surfaces. As shown in Fig. 3, rubbing scratches are obvious.

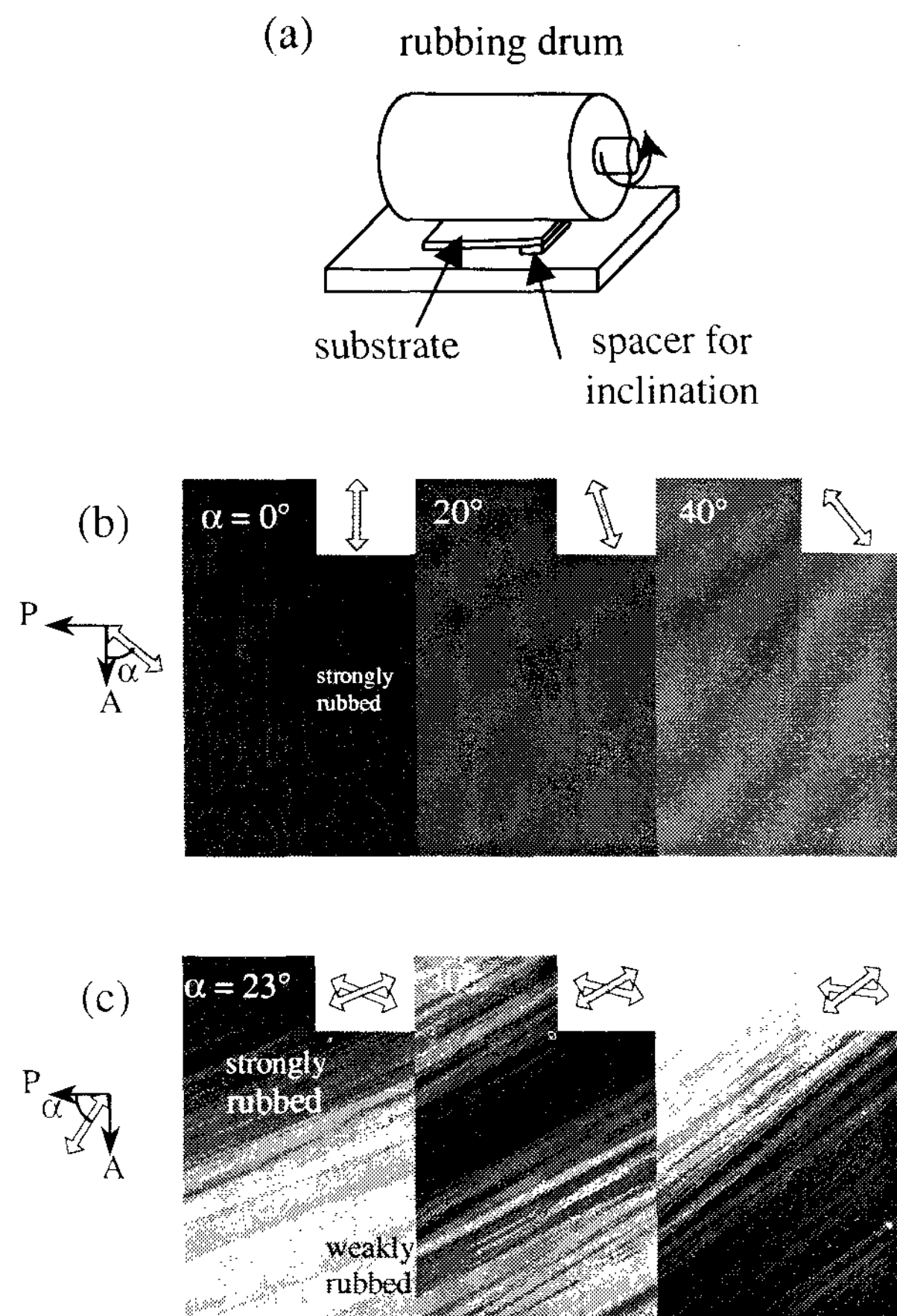
In order to see whether or not the rubbing nonuniformity depends on the rubbing strength, rubbing with a slanted substrate was carried out (see Fig. 4(a)). As shown in Fig. 4(b), single rubbing gives a good uniform alignment. However, if rubbing was made subsequently after photoalignment, rubbing scratches are clearly observed, as shown in Fig. 4(c). 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.



**Figure 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.



**Figure 3** Microphotographs of nematic LC (5CB) cell between crossed polarizers at several sample rotation angles. The substrates were doubly treated, i.e., subsequent rubbing after photoalignment, the directions of which are mutually  $45^\circ$  apart, as indicated by gray and white arrows.



**Figure 4** (a) Illustration of the rubbing geometry used to obtain substrates with continuous rubbing strengths. The microphotographs of nematic LC (5CB) cells with continuous rubbing strengths between crossed polarizers at several sample rotation angles. The substrates were covered with (b) only slantingly rubbed PAA layers and (c) PAA layers slantingly rubbed after photoalignment, 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 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 Competition between grooves and photoalignment [4]

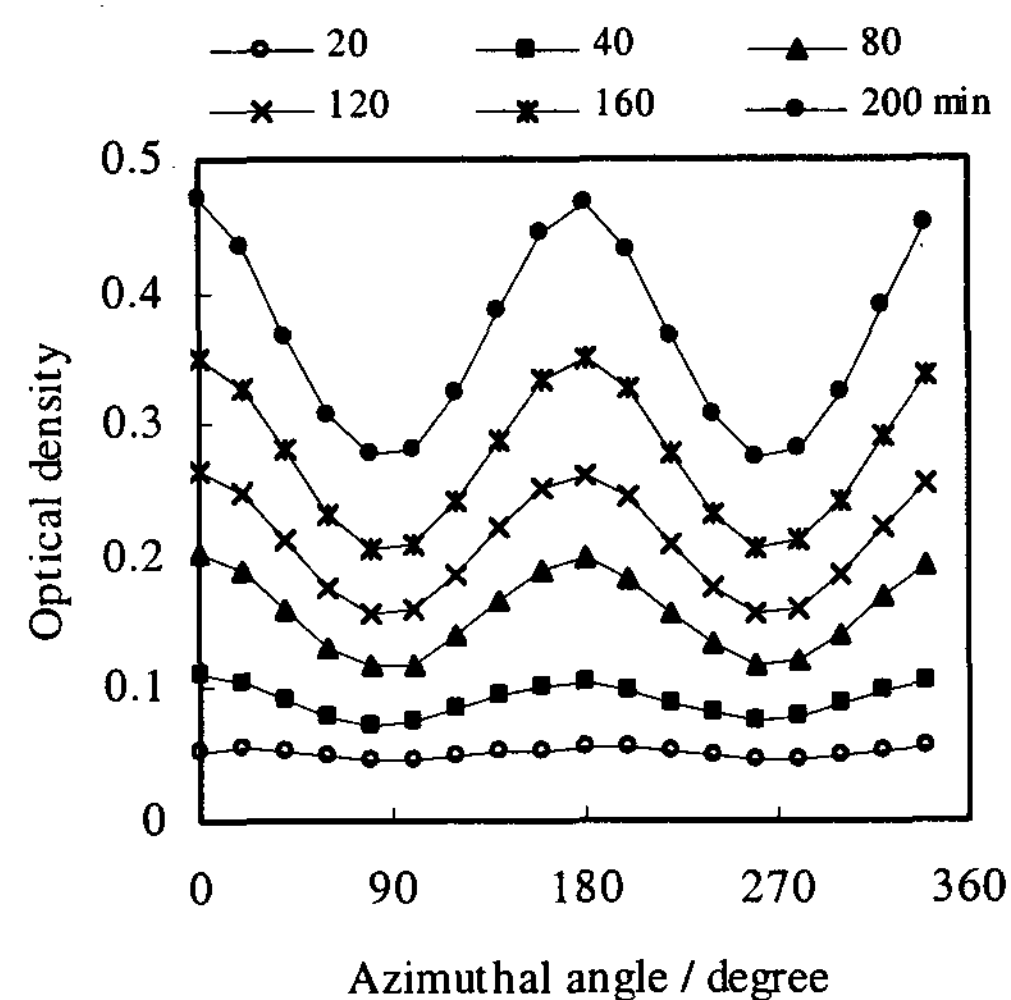
It is known that there are two kinds of alignment force; (1) Due to the existence of grooves by rubbing, molecules tend to align parallel to the grooves to minimize the elastic energy. (2) Direct electrostatic interaction between surface polymer molecule and LC molecules. It is true that either of which is enough to force LC molecules to align. However, it is meaningful to study how both mechanisms contribute the alignment more in particular conditions. We addressed this problem using surface relief grating (SRG) made of a photoalignment layer.

We made SRG with a pitch of 1  $\mu\text{m}$  and the variable depth upto 0.4  $\mu\text{m}$ . Then photoalignment was made along  $45^\circ$  to the groove. When the depth of the groove is less than 200 nm, molecules align along the photoaligned direction. In contrast, molecules change their orientation toward the groove direction with increasing the groove depth and finally perfectly align to the groove when the groove depth is 380 nm. This is interpreted as follows: LC molecules want to align along the photoaligned direction on surface. However, because of LC intermolecular interaction, all the molecules tend to align along the groove direction when the groove depth increases and elastic energy increases.

### 3.3 Alignment process of 5CB evaporated on treated surfaces

As mentioned above, LC molecules align under the influence of surface alignment layer. However, what we can observe is a LC alignment in bulk state. Then, how do LC molecules align at the interface between LC bulk and surface? In order to answer the question, we examined the molecular orientation on treated surfaces. For the purpose, we evaporated 5CB molecules on rubbed and photoaligned surfaces and carried out polarized UV/VIS absorption and second-harmonic generation (SHG) measurements. Using these data we determined the molecular orientation distribution functions.

Figure 5 shows absorbance of 5CB molecules evaporated on a rubbed surface at 300 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 to only the 5CB molecules.



**Figure 5** Optical density of 5CB 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.

It is clear in Fig. 5 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.

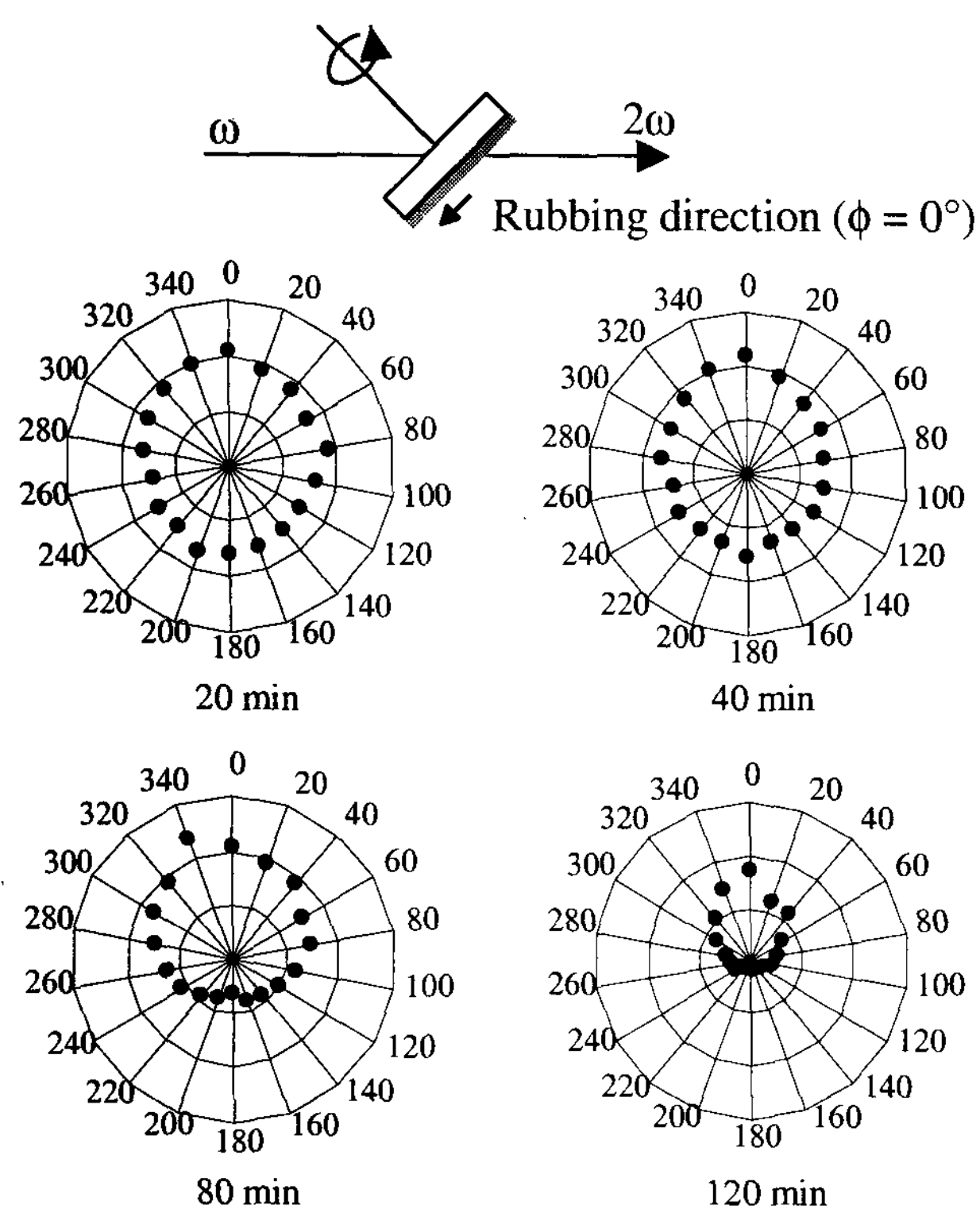
Next, let us show the SHG in-plane anisotropy in Fig. 6, where p-polarized SHG by the oblique incidence of p-polarized light is shown as polar plots. As same as in polarized UV/VIS absorption anisotropy, anisotropy increases after about 40-80 min, when molecules cover the whole surface.

In this way, we can imagine the following picture for the process of alignment 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 cells. In this way we can conclude that



liquid crystalline interaction plays an important role for the alignment of molecules on treated surfaces.



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

Recently, we succeeded in obtaining the orientational distribution function by the simultaneous analysis of polarized absorbance and SHG using the maximum entropy method. The results will be presented in the conference.

#### 4. Conclusion

LC molecular alignment on rubbed, photoaligned and doubly treated surfaces has been studied using mainly a polyimide 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 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.

Under the constraints of the grooves due to a surface relief grating and a photoaligned direction different from the groove direction, the molecular orientation changes with the depth of the groove. Because of the intermolecular liquid crystalline interaction, the distortion energy loss of liquid crystal orientation exceeds the surface interaction between polymer and LC molecules.

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.

#### 5. References

- [1] B. Park, Y. Jung, H.-H. Choi, H.-K. Hwang, Y. Kim, S. Lee, S.-H. Jang, M. Kakimoto and H. Takezoe: *Jpn. J. Appl. Phys.* **37** (1998) 5663.
- [2] B. Park, K.-J. Han, Y. Jung, H.-H. Choi, H.-K. Hwang, S. Lee, S.-H. Jang, and H. Takezoe: *J. Appl. Phys.* **86** (1999) 1854.
- [3] D.-H. Chung, Y. Takanishi, K. Ishikawa, H. Takezoe and B. Park, *Jpn. J. Appl. Phys.* **40** (2001) 1342
- [4] D.-H. Chung, T. Fukuda, Y. Takanishi, K. Ishikawa, H. Matsuda, H. Takezoe and M. M. Osopiv, *J. Appl. Phys.* **92** (2002) 1841.
- [5] T. Shioda, Y. Okada, D.-H. Chung, Y. Takanishi, K. Ishikawa, B. Park and H. Takezoe, *Jpn. J. Appl. Phys.* **41** (2002) L266.