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### Surface Order Parameter of 4-n-Heptyl-4'-Cyanobiphenyl

H. Mada<sup>a</sup> & S. Kobayashi<sup>a</sup>

<sup>a</sup> Department of Electronic Engineering, Faculty of Technology, Tokyo Univ. of Agriculture and Technology, Koganei, Tokyo, 184, Japan

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# Surface Order Parameter of 4-*n*-Heptyl-4'-Cyanobiphenyl

H. MADA and S. KOBAYASHI

*Department of Electronic Engineering, Faculty of Technology, Tokyo Univ. of Agriculture and Technology, Koganei, Tokyo 184, Japan.*

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We measured the order parameter near the interface between a liquid crystal and the solid substrate treated by several methods. The interfacial order parameter is different according to the surface treatment, and is larger than the bulk order parameter. Moreover, in the temperature above the clearing point, the interfacial order still has a finite value.

## INTRODUCTION

Well aligned single domain liquid crystals are necessary for physical investigation. On the other hand, for display devices, we also need defect free nematic liquid crystal cells. When we evaluate the alignment of liquid crystal molecules, the orientational order parameter is an essential factor, especially for display devices.

In the previous paper,<sup>1</sup> we reported the order parameter in the bulk is different from the order parameter near the interface between liquid crystal and solid substrate. The order parameter near the interface is more convenient for determining the alignment of liquid crystals than the bulk one. This paper describes the temperature dependence of the order parameter near the interface for several treatments of surface alignment.

## EXPERIMENTAL

In order to determine the order parameter, we chose the method of measuring the refractive indices. For measuring the index near the interface, we used the interferometric method.<sup>2</sup>

Paper presented at the Eighth International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

When the light beam of wavelength  $\lambda$  and of intensity  $I_0$  is incident normal to the ordinary liquid crystal cell, the direct transmitted light interferes with multiple reflected light beams. The multi-reflected light intensity is governed by the glass index  $n_0$  and the index of the liquid crystal near the interface  $\bar{n}$ . The ratio of intensity  $I_0$  to  $I$  is thus derived as

$$\frac{I}{I_0} = \frac{8n_0^2 \bar{n}^2}{(n_0^4 + 6n_0^2 \bar{n}^2 - \bar{n}^4) - (n_0^4 - 2n_0^2 \bar{n}^2 + \bar{n}^4) \cos 2\beta},$$

where  $\beta = 2\pi nd/\lambda$ ,  $d$  stands for the liquid crystal layer thickness. The term  $\cos 2\beta$  comes from the interference, thus,  $n$  is the mean value of the refractive index throughout the bulk. Therefore,  $n$  can be measured from the phase of the interferogram, and  $\bar{n}$  from the amplitudes.<sup>1</sup>

The experimental set up is shown in Figure 1. The linearly polarized monochromatic light was incident to the sample cell, and transmitted light was detected by a cooled photomultiplier tube. The amplitude of oscillation by interference is of the order of 5% or so. For expanding the oscillation part, we used the zero level suppressor. The temperature was detected by a chromel-*p* vs constantan thermocouple. We measured from 10°C to 70°C with a heating rate of 0.25°C/min. The liquid crystal used in this experiment was 4-*n*-heptyl-4'-cyanobiphenyl, and the substrates used were Vycor glass. We studied five different samples as shown in Table I. The sample *S* was treated by a 60° oblique evaporation of silicon oxide, and the evaporated layer thickness was about 400 Å. The sample *O* was coated with silane, an inorganic surfactant and treated by rubbing. The samples *C* and *P* are carbon and polyvinylalcohol, respectively. The sample *B* is Vycor glass treated only by rubbing. We measured two or three samples for each treatment.

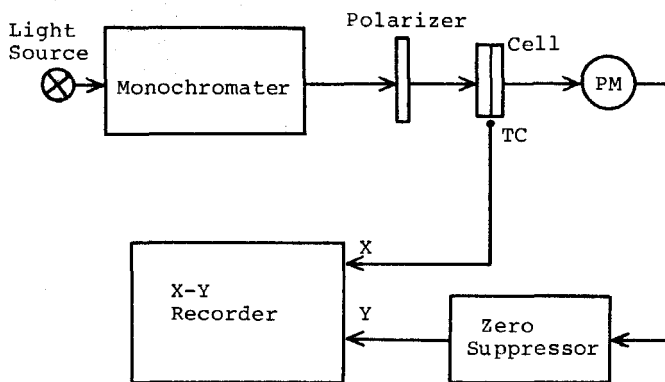


FIGURE 1 Experimental set up for measuring the indices.

TABLE I

Treatment of samples and its Symbols.

| Specimen | Surfactant       | Thickness | Treatment                          |
|----------|------------------|-----------|------------------------------------|
| <i>S</i> | SiO <sub>x</sub> | 400 Å     | 60° oblique evaporation<br>rubbing |
| <i>O</i> | inorganic        | 3000 Å    |                                    |
| <i>C</i> | carbon           | —         |                                    |
| <i>P</i> | PVA              | 4000 Å    |                                    |
| <i>B</i> | —                | —         |                                    |

## RESULTS AND DISCUSSION

The results are shown in Figure 2. The cell thicknesses were 24–25  $\mu\text{m}$ , and the light used to measure the indices was 533 nm. The clearing temperature  $T_c$  of the liquid crystal is 41.9°C. We plotted the bulk order parameter for comparison. The bulk order parameter marked by closed squares has a value of zero above  $T_c$ . However, the surface order parameters for all samples still

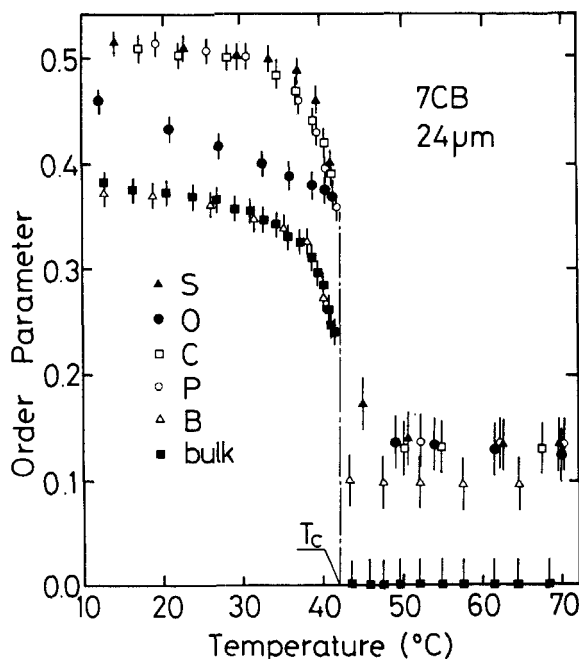


FIGURE 2 Temperature dependence of the order parameters; symbols appeared in the figure are explained in Table I.

remain small, but measurable finite, even above the clearing point. Similar results were also reported by Miyano<sup>3</sup> for MBBA and 5CB. According to his results, the value of the order parameter above the clearing point agrees with our results.

In the nematic phase, the surface order parameters of the samples *S*, *C*, and *P* are almost the same within the experimental error. The vertical bars in the figure indicate accuracy and deviation of data. The sample *B*, open triangles, is smaller than the other samples, and is the same as the bulk order.

The sample *O* behaves differently from the other samples. This phenomenon may be caused by the large tilt angle of the director. For the samples *S*, *C*, *P*, and *B*, the tilt angles range from 0° to 3° measuring from the surface. Namely, the correction in the results is very small and can be neglected. Thus we did not consider the tilt angle in our calculation to determine the order parameter. But the sample *O* has a rather large tilt angle; 10° or so. As we reported previously,<sup>4,5</sup> the tilt angle varies with temperature, so its influence may appear in the behaviour of the order parameter.

On the other hand, the jump of the order parameter at the clearing point is significant to understand the mechanism of surface alignment, as was pointed out by Mada and Kobayashi.<sup>6</sup> The sample *S* (closed triangles) appears to be larger than the other samples near and above  $T_c$ . This fact means the sample *S* has more strong anchoring energy. Detailed discussion, however, can not be done only with these data. We need more precise data, especially around the clearing temperature.

## CONCLUSION

The order parameters near the interface are different according to the surface treatment. So the bulk order may also be different depending on the surface treatment,<sup>7</sup> especially for very thin samples.

The surface problems are very difficult and further development will then be necessary for a more exact explanation of nematic-isotropic phase transitions and to give a better understanding of liquid crystals.

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