

## The Novel Texture of a Liquid Crystal induced by Poly- $\gamma$ -benzyl-L-glutamate Chemical Reaction Alignment (CRA) Film

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Poly- $\gamma$ -benzyl-L-glutamate (PBLG) when treated with a silane coupling agent on a glass surface forms a molecular oriented film; a new liquid crystal texture induced by the  $\alpha$ -helical structure of PBLG attached to the substrate surface is observed.

Recently, the anisotropic characteristics of organized molecular films have attracted much attention.<sup>1</sup> However there are only a few reports<sup>2</sup> concerning the functionalization of these films because the orienting forces of organic molecules in the films are not strong enough over a wide temperature range. Previously, we proposed a new method for organizing molecules on a substrate surface by chemical reaction,<sup>3</sup> referred to as chemical reaction alignment (CRA), and showed an application of the CRA method for preparing an oriented poly- $\gamma$ -benzyl-L-glutamate (PBLG) monolayer.<sup>4</sup> PBLG adopts a rigid  $\alpha$ -helical structure and has different functional groups, a carboxy group and an amino group, respectively, at the individual terminal positions of the main chain.<sup>5</sup> These features are suitable for using PBLG as a model polymer in the CRA method. On the other hand, it is well known that the longer molecular axis of PBLG in a Langmuir-Blodgett film is parallel to the substrate (on germanium) and oriented into the substrate dipping direction.<sup>6</sup> In contrast, the tilt angle of the PBLG molecular axis in the CRA film has been estimated to be about 57°. Accordingly, it is expected that the properties of the PBLG-CRA film will be different from those of an LB film. Here, we report a novel texture using the PBLG-CRA film as an orienting interface for a liquid crystal.

The PBLG (*M* 20 000)-CRA film was prepared according to the method described in a previous report.<sup>4</sup> *N*-(2-Aminoethyl)-3-aminopropylmethyltrimethoxysilane and a glass surface were selected as the silane coupling agent and substrate,

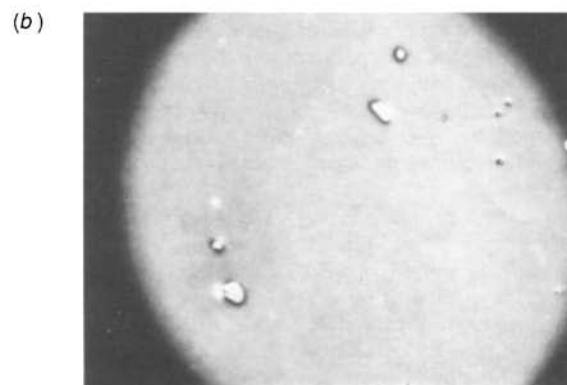
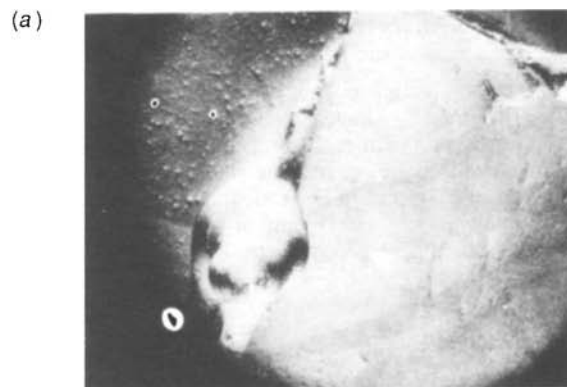
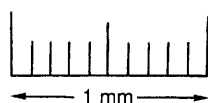
respectively. We used 1-cyano-4-pentylbiphenyl (5CB) as the nematic liquid crystal because of its low clearing point ( $T_c$ ).

A liquid-crystal cell was prepared by the typical method. As the opposite substrate of the PBLG-CRA film, a substrate coated with polyimide (PI) treated by a rubbed technique (to make a parallel-orienting surface) or a substrate treated with octadecyltriethoxysilane (ODES) was used. The cell gap was adjusted with a spacer (5  $\mu\text{m}$ ).

Fig. 1 shows photographs (Olympus BH-2 polarized microscope) of the textures induced by the PBLG-CRA film. Regardless of the opposite substrate, a novel texture of the liquid crystal was observed, which seemed to be influenced by the helical structure of PBLG molecules attached to the glass substrate. We call this spiral texture. Nematic schlieren texture was observed besides the spiral texture, and disclination lines went through the centre of the spiral texture.

The density of the spiral texture was *ca.* 25  $\text{cm}^{-2}$ . This spiral texture was not observed at the  $T_c$  of 5CB (34.7 °C) and could again be seen at the same position below  $T_c$ .<sup>†</sup> We speculate that the spiral texture appears because the director of 5CB in the vicinity of the substrate is affected by the PBLG attached to the substrate.

<sup>†</sup> The rate of the change in temperature was controlled with a Mettler FP 82 hot stage. The rate of increase of the temperature was 0.5 °C  $\text{min}^{-1}$  (up to 34.5 °C), and then 1.0 °C  $\text{min}^{-1}$  (up to 45.0 °C). The rate of decrease of the temperature was 1.0 °C  $\text{min}^{-1}$  (to room temperature).



**Fig. 1** Photographs of the spiral texture using (a) polyimide treated by rubbed technique and (b) octadecyltriethoxysilane as the opposite substrate. The photographs were taken between cross polarisers.

**Fig. 2** Photographs of the texture (a) before raising the cell temperature and (b) after the sequence of raising the cell temperature to 150°C and cooling to room temp.

Interestingly, the spiral texture did not appear using a PBLG cast film and a PBLG LB film<sup>‡</sup> instead of the CRA film. These results strongly suggest that a PBLG orientation not parallel to the substrate is essential for the texture to develop. We, therefore, attempted to elucidate the relationship between the spiral texture and the helical structure of the attached PBLG. The temperature of the liquid-crystal cell was raised gradually above the temperature at which the PBLG structure become a random coil structure (125°C), and then cooled to room temperature. As shown in Fig. 2, once the temperature was raised above 125°C, the spiral texture did not appear again below the clearing point of 5CB.§ This result indicates that the  $\alpha$ -helical structure of PBLG on the substrate is the origin of the spiral texture.

<sup>‡</sup> The LB film of PBLG (Sigma; *M* 116 000) was deposited according to Takenaka's method<sup>6</sup> after treating the glass substrate with 1,1,1,3,3,3-hexamethyldisilazane. The number of withdrawals was 5. The surface pressure was kept at 5.9 dyne cm<sup>-2</sup> (16.8°C). The glass substrate was withdrawn at a fixed rate of 5 mm min<sup>-1</sup>.

§ The rate of change in temperature was controlled with a Mettler FP 82 hot stage. The rate of increase of the temperature was 5°C min<sup>-1</sup> (up to 150°C). The rate of decrease of the temperature was 5°C min<sup>-1</sup> (to room temperature). The photographs of the samples were taken between crossed polarizers.

Since there has been no report concerning the texture induced by a higher order structure of organic molecules attached to the substrate, the PBLG-CRA film is noteworthy as a new type of orienting surface. We are now investigating further applications of the CRA film.

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