Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Hiromi Kimura-suda, Tatsuo Wada, Su-An Choi, Yadong Zhang & Hiroyuki Sasabe (1999): Molecular Orientation of Polar Self-Assembled Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 327:1, 91-94

To link to this article: http://dx.doi.org/10.1080/10587259908026787

Mol. Cryst. Liq. Cryst., 1999, Vol. 327, pp. 91-94
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Molecular Orientation of Polar Self-Assembled Films

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(Received August 26, 1998; In final form September 15, 1998)

Molecular orientation of polar self-assembled films of carbazole main-chain polymers having a chromophore in a side-chain were investigated by a second-harmonic generation (SHG) phase measurement. In our SHG phase measurement, poly(methyl methacrylate) thin film doped with p-nitroaniline (PNA/PMMA) was used as a standard sample and an oscillator, because the directional sense of PNA was able to be controlled by the polarity of an electric field. The interference pattern between the two poled PNA/PMMA films was shifted by π depending on the polarity of the films. The interference pattern between the poled PNA/PMMA film and the self-assembled film indicated that the directional sense of the net dipole moment of the self-assembled film was the same as the direction of shear stress.

Keywords: carbazole polymers; phase measurement; interference; SHG; self-assembled film

INTRODUCTION

Organic noncentrosymmetric materials have been developed as nonlinear optical (NLO) materials due to their potential application for optoelectric device. Second order NLO materials are investigated for optical modulator and frequency doubler. Polar orientation, their stability and

ease preparation are important issues for the application of NLO materials. The second order NLO responses result from the orientation of chromophore and their susceptibility in polymers. While an electric poling is generally used to align chromophore in polymers, the control of orientation in polymers through the self-assembly of side-groups attached to flexible backbones has attracted much attention[1]. In our previous work[2], we have succeeded in making self-assembled thin films of carbazole main- and side-chain polymers[3], as shown in Figure 1. The alignment was achieved during film preparation process, such as thermal treatment and flow casting without an electric filed[2].

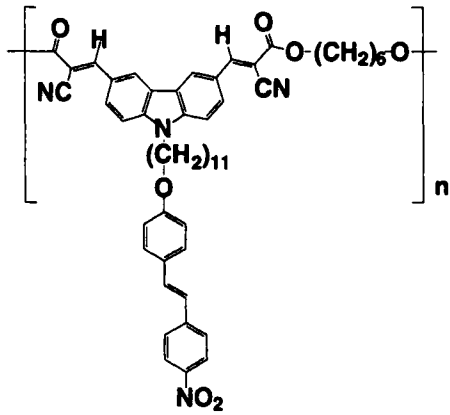

FIGURE 1 Molecular structure of carbazole main- and side-chain polymer.

It was found by the conventional second-harmonic generation (SHG) measurement that the self-assembled thin film had an in-plane polar anisotropy[2]. In this paper, we confirmed the directional sense of the net dipole moment in the carbazole self-assembled thin film by a SHG phase measurement[4-6].

EXPERIMENTAL

The interference of SHG signals were generated in a sample and an oscillator. The light source was a Q-switched Nd:YAG laser of p-polarization, and p-polarized second-harmonic signal was detected. The interference patterns were modulated by rotating the glass plate inserted between the sample and the oscillator and they depended on the polarity of the sample and the oscillator[5,6]. In our experiment, poly(methyl methacrylate) thin films doped with p-nitroaniline (PNA/PMMA) were used as a standard sample and an oscillator because the directional sense of PNA could be controlled by the polarity of an electric poling. The interference pattern between the two PNA/PMMA films was shifted by π depending on the polarity of the films[6]. The result indicated that the directional sense of the net dipole moment of the film is able to be determined by the comparison with that of poled PNA/PMMA film.

RESULTS AND DISCUSSION

The interference pattern in the self-assembled thin film was obtained by the SHG phase measurement, as shown in Figure 2.

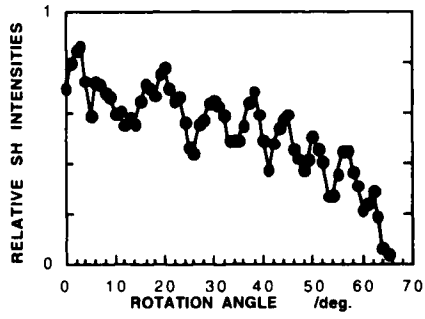

FIGURE 2 Interference pattern in the self-assembled thin film.

The interference pattern was sifted by π when the film was inversed. It was confirmed from the result that the thin film had an in-plane polar anisotropy, and the directional sense of the net dipole moment of the film was parallel to the direction of shear stress.

CONCLUSION

Chromophores in the thin film of the carbazole main- and side-chain polymer prepared by thermal treatment were aligned parallel to the substrate. The directional sense of the net dipole moment was the same as the direction of shear stress.

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