

polymer communications

Flow-induced high pretilt alignment of liquid crystalline molecules on polymer surface evaluated by optical second-harmonic generation

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The alignment of liquid crystalline molecules at the interface between liquid crystal and polyimide surface was investigated on the basis of an optical second-harmonic generation method. It was confirmed for the first time that a uniform alignment of liquid crystalline molecules with a pretilt of about 10° was achieved by simply flowing the liquid crystal on the polyimide-coated substrate surface which produced no pretilt by a standard rubbing treatment. Copyright © 1996 Elsevier Science Ltd.

(Keywords: liquid crystal; flow-induced alignment; polymer surface)

Introduction

In the general case of nematic liquid crystals (LCs), the molecules are spontaneously aligned with their long axes parallel to a common direction. The molecular orientational direction is governed by external minor effects because of the fluid-like nature of nematic LCs. In the absence of an external field such as an electric or a magnetic one, the orientational direction of LC molecules is determined by the boundary conditions contacting with them. On properly treated substrate surfaces, for example rubbed polymer-coated substrate, the molecules prefer to be aligned to a specific direction by an anchoring effect¹. The anchoring effect of the substrate surface is practically important in order to control the alignment of the bulk of LC.

The pretilt angle is defined as the angle between the LC director and the plane of the surface. The pretilt angle strongly influences the performance of LC devices based on the super-twisted nematic (STN) mode or the surface-stabilized ferroelectric (SSF) mode^{2,3}. A high pretilt angle can be achieved by oblique evaporation of SiO on the substrate⁴. However, this method is inconvenient for mass production. Though a rubbing technique is a practically useful method to align the LC molecules to a specific in-plane direction, it is difficult to produce a high pretilt. The practical application of a more simple and effective method is anticipated.

In this study, the generation of a high pretilt angle induced by flowing the LC on a polymer-coated substrate surface was studied on the basis of the optical second-harmonic generation (SHG) technique, which is an extremely surface-sensitive analytical tool.

Theory of surface second-harmonic generation

Optical second-harmonic generation (SHG) technique has been exploited as a sensitive analytical tool for studying the molecular orientation on surfaces and

interfaces⁵. Shen and co-workers investigated the molecular orientation at the rubbed polymer–LC interface by the surface SHG method^{6,7}. They found a strong correlation between the rubbing direction on the polymer surface and the resulting direction of LC molecules which contact directly with the polymer surface. Two possible reasons why the rubbed polymer surface gives good alignment of LC molecules have been proposed. One is based on microgrooves (long-range interaction)⁸, and the other is based on the oriented polymer molecules (short-range interaction)^{9–11}. The experimental results on the basis of surface SHG study by Shen and co-workers supported a mechanism whereby the surface alignment of LC molecules was generated via short-range intermolecular interaction⁷.

A second-order non-linear optical effect is forbidden in a medium with inversion symmetry. Since the inversion symmetry is necessarily broken at a surface or an interface, the SHG method is highly surface-specific for a centrosymmetric medium. The signal at the second-harmonic frequency, 2ω is generated by the induced surface non-linear polarization, $P^{(2)}$ described by:

$$P^{(2)}(2\omega) = \chi^{(2)} : E(\omega)E(\omega) \quad (1)$$

where $\chi^{(2)}$ is the surface non-linear susceptibility which is the third-rank tensor reflecting the symmetry of the first monolayer on the surface. The intensity of SHG is given by:

$$I(2\omega) \propto |e_{2\omega} \cdot \chi^{(2)} : e_{\omega} e_{\omega}|^2 I^2(\omega) \quad (2)$$

where $e_{2\omega}$ and e_{ω} denote the output- and the input-polarization vectors at the frequencies of 2ω and ω , respectively; $e_{2\omega}$ and e_{ω} contain products of linear Fresnel factors. Also, $I(\omega)$ is the laser intensity at the frequency of ω . When the molecular hyperpolarizability tensor, $\alpha^{(2)}$ is dominated by a single component, $\alpha^{(2)}_{\xi\xi\xi}$ along the molecular long axis, ξ , $\chi^{(2)}$ takes the form

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given by:

$$\chi_{ijk}^{(2)} = N_s \langle (\hat{i} \cdot \hat{\xi})(\hat{j} \cdot \hat{\xi})(\hat{k} \cdot \hat{\xi}) \rangle \alpha_{\xi\xi\xi}^{(2)} \quad (3)$$

where N_s is the surface density of LC molecules, i, j, k refer to the sample coordinates (x, y, z), and the angle bracket denotes an average over the molecular orientations. For LC molecules with a C_{1v} symmetric alignment, $\chi^{(2)}$ has six types of non-vanishing elements which are functions of the pretilt angle, θ_p and the azimuthal angle, ϕ of LC molecules as defined in Figure 1⁷.

Experimental

Sample preparation. Figure 2 shows the chemical structures and the physical properties of samples used in this study. LC used for our experiment was 4-cyano 4'-pentyl biphenyl (5CB). Polyimide films were prepared by spin-coating (4000 rev min⁻¹) the precursor poly(amic acid) (supplied from Chisso Co.) dissolved in *N*-methylpyrrolidinone onto glass substrates at room temperature. The poly(amic acid) was converted to the polyimide by curing the film under N₂ at 570 K for 2 h. The rubbing treatment was performed at room temperature by pressing the polyimide-coated glass onto a velour cloth under a load of 2 g cm⁻² and then unidirectionally

pulling the cloth over 300 cm at 1 cm s⁻¹. Two types of sandwich cells were fabricated to compare the LC alignments induced by both the rubbing and the flow treatments. In the case of rubbing-induced alignment, a pair of the rubbed substrates was assembled with rubbing directions parallel to each other, and then the cell was filled with 5CB in an isotropic state. In the case of the flow-induced alignment, the polyimide-coated substrates were used without any surface treatment. To induce a unidirectional molecular alignment by hydrodynamic flow, 5CB in a nematic state was spread into a narrow gap between two substrates by capillary action. In order to produce a satisfactory unidirectional flow throughout the cell, the two substrates were combined to form a wedge cell. 5CB in a nematic state was spread from the thinnest (14 μm) to the thickest (50 μm) edge of the cell at 303 K.

Evaluation of LC alignment. The in-plane alignment of 5CB in the cell was evaluated by both polarizing optical microscopy and the dichroic ratio of dichroic dye molecules, D27 doped in 5CB.

Measurement of optical surface SHG. A schematic diagram of the experimental set-up to evaluate $\chi^{(2)}$ is shown in Figure 3. A pulsed Nd:YAG laser of wavelength 1.064 μm was used as an excitation source. The laser beam was s- or p-polarized and was incident to the sample set on a rotating stage. The signs, p and s correspond to the polarizing directions of laser light parallel and perpendicular to the plane of incidence, respectively. The incident angle was 45°. The reflected beam of 1.064 μm wavelength was subsequently blocked and the second-harmonic (SH) output of 532 nm wavelength was selected using a filter. From the reflected SH output, the s- and p-polarized components were selected by an analyser. The intensity of SH output signal was detected by a photomultiplier and recorded with a storage oscilloscope. The geometry of SHG from the interface between polymer surface and liquid crystal is shown in Figure 1.

Results and discussion

It has been empirically known that without any pretreatment, like rubbing, on the substrate surface, a uniform alignment of LC molecules can be produced by

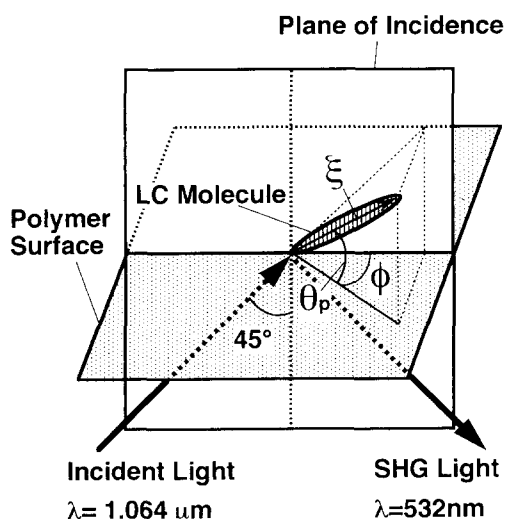


Figure 1 The geometry of SHG from the interface between polymer surface and liquid crystal

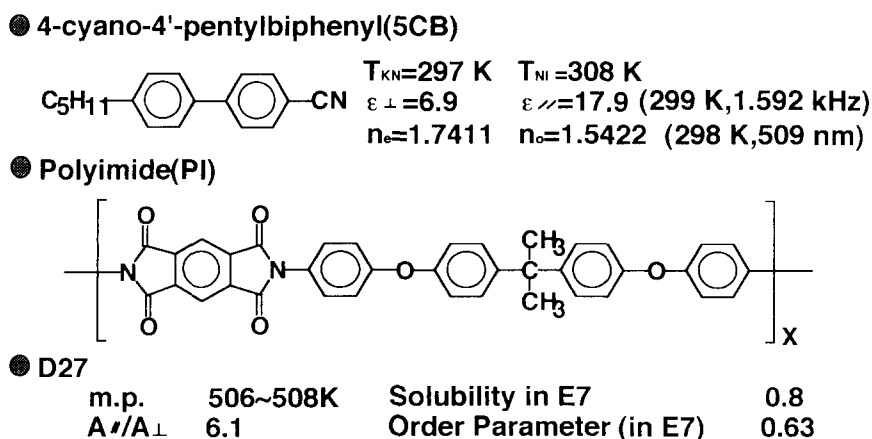


Figure 2 The chemical structures and physical properties of samples used in this study

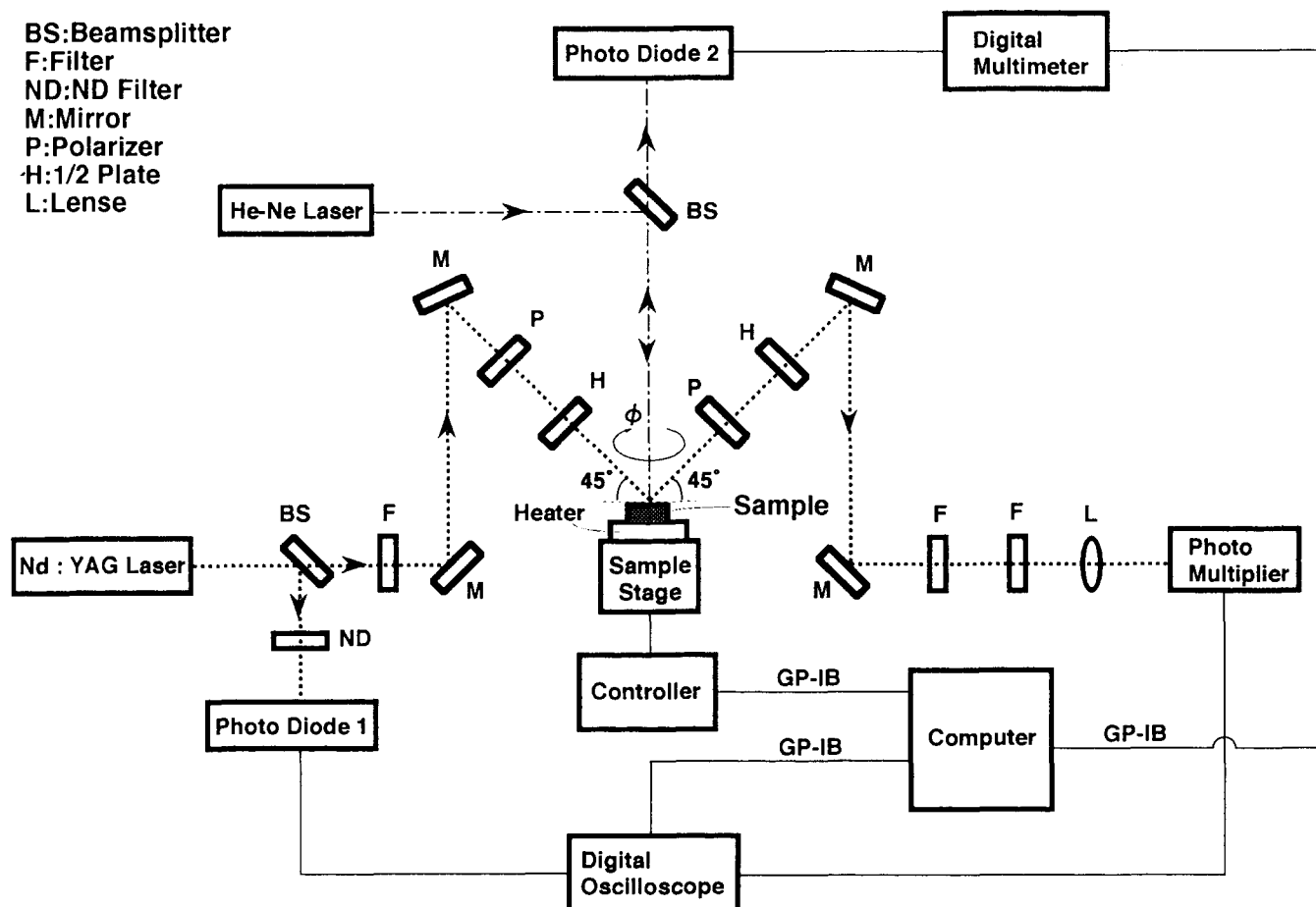


Figure 3 Schematic diagram of the experimental set-up to evaluate $\chi^{(2)}$

a flow of LC materials (flow-induced alignment). In general, the long axes of molecules prefer to align along the flow direction in the case of a steady laminar flow between two parallel plates. This is due to a coupling of the anisotropy of viscosity and the dynamic distortion of LC. The flow-induced alignment of LC molecules remains even after stopping the flow. It is reasonable to consider that the molecules in the first monolayer contacting with the substrate surface are possibly anchored with their direction along the flow direction. However, the physical mechanism of flow-induced alignment of LC molecules is not yet understood. In our study, it was confirmed again by polarizing optical microscopic observation that 5CB was unidirectionally aligned along the flow direction for the flow-induced alignment cell.

It is generally accepted that a highly ordered homogeneous alignment is achieved by the rubbing treatment. However, the order of flow-induced alignment has not been investigated in detail. In order to evaluate the orientational order of the bulk of LC, a dichroic dye molecule, D27 was doped in 5CB. D27 absorbs light at around 600 nm wavelength. This absorption selectively occurs when the light is polarized along the direction of the electric dipole transition moment of D27. D27 is designed to orient it along the director of the 5CB when a small amount of D27 is dissolved in the 5CB. This effect is called the guest-host interaction, in that the dye molecules are the 'guest' molecules being oriented by the

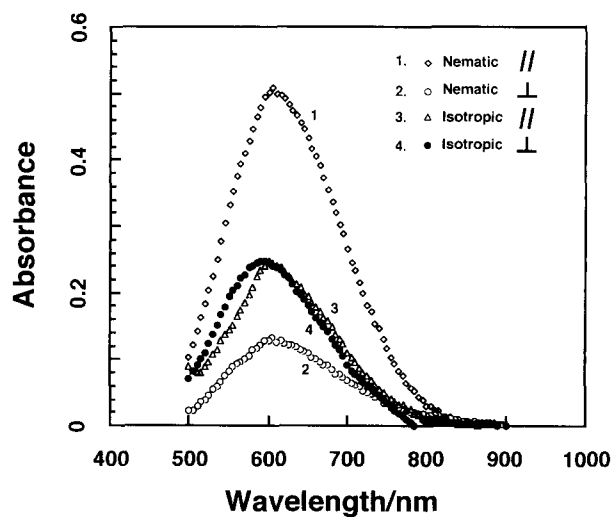


Figure 4 Ultraviolet-visible absorption spectra for the flow-induced LC alignment cell

LC 'host' molecules. The order of the bulk of 5CB can be evaluated by measuring the dichroic ratio of the doped D27. The dichroic ratio, R is defined as:

$$R = \frac{A_{\parallel}}{A_{\perp}} \quad (4)$$

where A_{\parallel} and A_{\perp} are the absorbances of the cell when the polarizing direction of incident light is parallel and

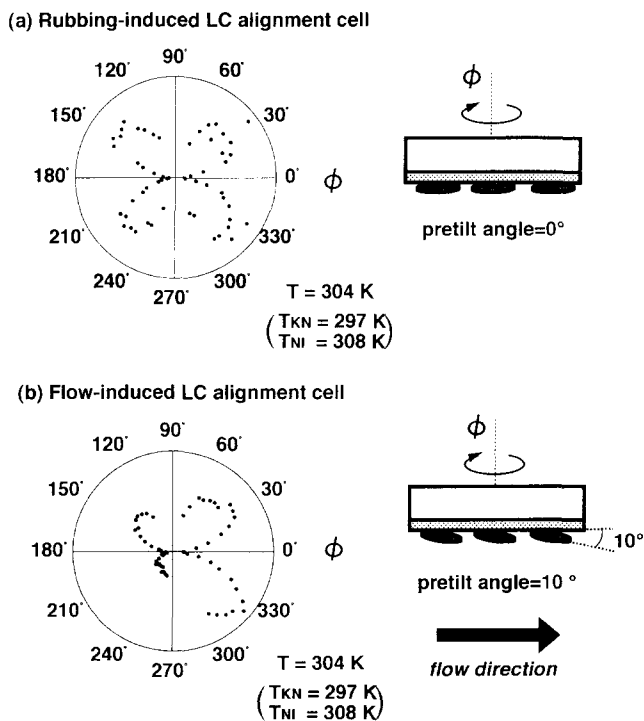


Figure 5 Polar plots of the SHG intensity for s-in-p-out as a function of the rotation angle ϕ around the surface normal for the cell substrate. $\phi = 0^\circ$ corresponds to the flow or the rubbing direction of each cell

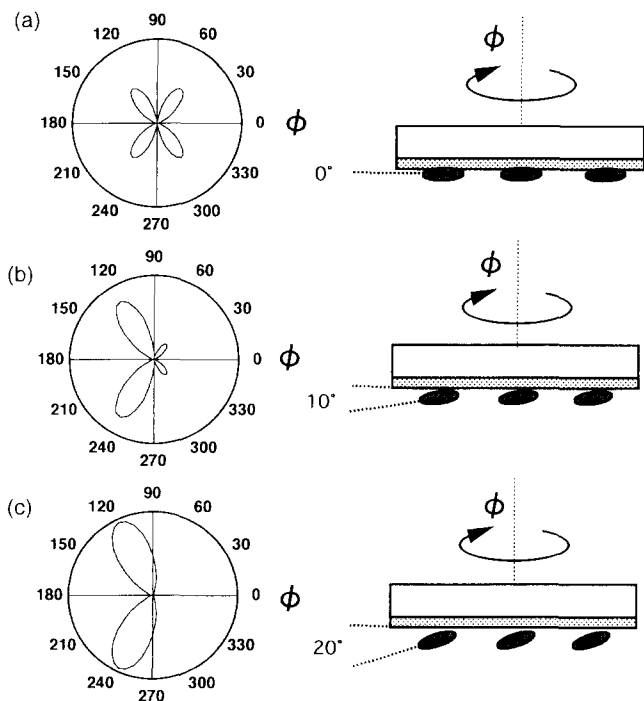


Figure 6 The calculated intensity distribution as a function of ϕ for molecular pretilt of 0° , 10° and 20°

perpendicular to the direction of molecular alignment, respectively. Figure 4 shows the ultraviolet-visible absorption spectra for the flow-induced LC alignment cell. In the case of the flow-induced LC alignment cell in a nematic state, R was 3.96, a magnitude comparable to that for the rubbing-induced LC alignment cell, that is, 3.85. In an isotropic state, the magnitudes of R for both

the cells were nearly unity. Therefore, it can be concluded from the results of dichroic ratio that the order of in-plane alignment for the flow-induced LC alignment cell is comparable to that for the rubbing-induced LC alignment.

The intensity of the SHG signal depends on the direction of the preferred LC molecular alignment with respect to the beams and on the polarization directions of the incident (input) and the reflected (output) lights. Let ϕ be the angle between the plane of incidence and the direction of the long axis of 5CB. The ϕ dependence of $I(2\omega)$ reflects the direction of the preferred alignment of 5CB. There are, furthermore, four different input-output polarization combinations, i.e. s-in-s-out, p-in-s-out, s-in-p-out and p-in-p-out. Large SHG signals from the blank cell without 5CB were observed for the combinations of s-in-s-out, p-in-s-out and p-in-p-out. Since the magnitudes of those signals were not negligible compared with the SHG from the cell with 5CB, it was quite difficult to evaluate experimentally the SHG intensity from the interface between 5CB and the substrate surface. The cause of large SHG from the blank cell is not yet known. However, since the SHG intensity of the s-in-p-out combination was negligible for the blank cell, the SHG intensity from the interface between 5CB and the substrate surface was experimentally obtained for the s-in-p-out combination. Figure 5 shows polar plots of the SHG intensity for s-in-p-out as a function of the rotation angle ϕ around the surface normal for the cell substrate. $\phi = 0^\circ$ corresponds to the flow or the rubbing direction of each cell. The simulation calculations of the SHG intensity were carried out based on equations (3) and (4)^{5,7}. The calculated intensity distributions as a function of ϕ for the case of the molecular pretilt of 0° , 10° and 20° are shown in Figure 6. It is reasonable to conclude from comparison between Figure 5 and Figure 6 that 5CB molecules at the interface align along the rubbing direction with no pretilt in the case of the rubbing-induced alignment cell and also, they align along the flow direction with the pretilt angle of about 10° in the case of the flow-induced alignment cell. The molecular tilt was directed toward the flow direction, as shown in Figure 5. Even after the sample cell was heated up above the nematic-isotropic phase transition temperature of 5CB and then cooled to the original temperature, the original pretilted alignment was reproduced. This suggests that a remarkably stable anchor of 5CB molecules on the polyimide surface is attained by the flow method.

Conclusion

The molecular orientation of the LC at the interface of LC and polyimide surface was evaluated by the surface SHG method. The simple laminar flow of LC on the unpretreated polyimide surface induced a unidirectional uniform alignment with pretilt angle of about 10° toward the flow direction, though the rubbed polyimide surface gave no pretilt.

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