Comparative Quantitative Analysis of Surface Anisotropy Induced by Rubbing and Photo-Alignment on Polyimide Films

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ABSTRACT

To elucidate the alignment mechanism of liquid crystals, sum-frequency generation spectroscopy was employed to quantitatively analyze the anisotropy and structure of alignment films. Our findings indicate that rubbing induced anisotropy in both phenylene and methyl groups, while linear polarized UV light exclusively affected phenylene moieties. This demonstrates that the anisotropy of phenylene is the dominant factor governing liquid crystal molecular alignment.

1 Introduction

The electro-optical performance of liquid crystal displays hinges critically on the "pretilt angle," which defines the initial orientation of the liquid crystal molecules. This angle is established by a polymer alignment layer formed on a substrate. Despite its pivotal role, the detailed mechanism behind liquid crystal alignment remains elusive, underscoring the need for molecular-level investigation of alignment film surfaces. In this study, we focused on two primary alignment film fabrication methods: the rubbing method, which involves physical friction, and the photo-alignment method, a non-contact process using linearly polarized ultraviolet (LPUV) light. Using a polyimide with photosensitive cinnamoyl groups in its side chains, the molecular structure of the alignment film surfaces prepared by both methods were analyzed using surface-specific sum-frequency generation (SFG) vibrational spectroscopy. Furthermore, to quantitatively evaluate the in-plane anisotropy of alignment film surfaces, we developed and applied a novel analytical theory based on an orientational distribution function.

Our findings reveal a significant contrast between these two alignment methods. In rubbed alignment films, all constituent polymer parts—the main chain (imide group), side chain (cinnamoyl group), and side-chain terminus (methyl group)—were oriented along the rubbing direction, exhibiting a distinct azimuthal anisotropy. This suggests that the physical friction force mechanically stretches the entire polymer chains, thereby inducing macroscopic alignment. Conversely, photo-alignment films showed substantial orientational anisotropy exclusively in the photoreactive cinnamoyl groups, with negligible anisotropy in the main chain and the side-chain terminus. This striking discrepancy strongly implies that the alignment function in photo-alignment arises from microscopic anisotropy generated by the selective photochemical reaction of these photosensitive sites. While prior research has indicated that the main chain orientation governs the liquid crystal pretilt angle in rubbed films [1], our study experimentally demonstrates that the molecular orientation mechanisms underlying the rubbing and photo-alignment methods are fundamentally distinct.

2 Experiment

2.1 Theory and Experiment

SFG spectroscopy is a surface-specific technique used to probe molecular vibrations at the surfaces or interfaces where the inversion symmetry is broken. SFG light is generated exclusively when the tunable infrared and frequency-fixed visible beams are spatially and temporally overlapped on the sample surfaces, thereby allowing for the acquisition of a vibrational spectrum of the surface molecules to analyze their molecular orientation. In this study, the molecular frame for the phenylene group is defined as shown in **Fig. 1(a)**. Based on this coordinate system, the molecular orientation is described by a polar angle θ, an azimuthal angle ϕ, and a twist angle ψ. These angles relate the molecular frame to the laboratory frame, as defined in **Fig. 1(b)**.

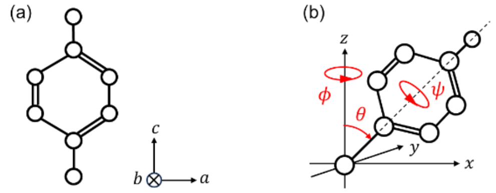

Figure 1. (a) Molecular frame and (b) laboratory frame defined for the phenylene group.

For surfaces exhibiting in-plane anisotropy, the SFG intensity varies with the azimuthal angle, directly reflecting the molecular orientational distribution. We quantitatively determine molecular orientation by measuring the “azimuthal plots” and fitting the data to a theoretical model. A significant challenge with conventional analysis models, however, is their applicability only to isotropically distributed surfaces. To overcome this issue, we developed a novel analysis program based on the theoretical framework of Kim et al. [2], enabling the analysis of molecular orientation in systems with in-plane anisotropy.

The “azimuthal plots” were obtained by first fixing the incident infrared beam wavelength to resonate with a specific vibrational mode of the functional group of interest. The SFG intensity was then recorded at various rotational angles while rotating the sample in-plane about its surface normal. Specifically, as illustrated in **Fig. 2**, we defined the angle between the in-plane symmetry axis of the sample and the plane of incidence as γ. During measurements, the sample stage was rotated from $\gamma = 10°$ to 360° in 10° increments, and the SFG intensity was measured at each angular position. The signal at each data point was obtained by averaging 300 accumulations.

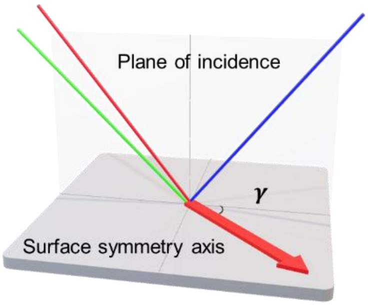

Figure 2. The definition of γ.

2.2 Sample preparation

The samples for the SFG measurements were prepared using the following procedures. A solution of polyamic acid, containing cinnamoyl groups in its side chains and serving as a precursor to polyimide (chemical structure shown in **Fig. 3**), was spin-coated onto a glass substrate. The coated film was subsequently baked at 200 °C for 30 min to induce thermal imidization, yielding a polyimide thin film with a thickness of less than 100 nm.

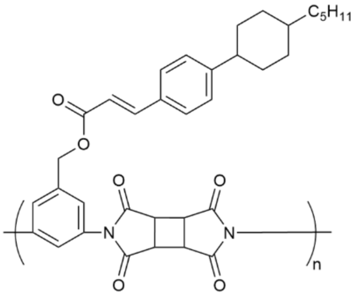

Figure 3. The chemical structure of polyimide used in this study.

Two distinct alignment methods were employed: rubbing and photo-alignment. For the rubbing process, a roller wrapped with rayon cloth was rotated by a stepping motor. The pressing force was controlled by adjusting the Z-stage height. As illustrated in **Fig. 4(a)**, the surface symmetry axis for these samples was aligned with the rubbing direction. For the photo-alignment process, polyimide samples were irradiated with 313-nm LPUV light. The light was directed onto the sample at an incident angle of 40° from the surface normal, with a total exposure dose of 75 mJ cm⁻². For these photo-aligned samples, the surface symmetry axis was defined as the direction of the incident LPUV light (**Fig. 4(b)**).

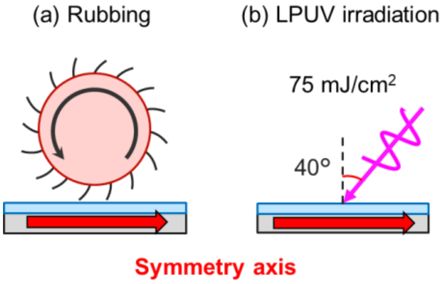

Figure 4. The definition of the surface symmetry axis of (a) rubbing and (b) photo-alignment processes.

3 Results and Discussion

3.1 SFG measurements for rubbed films

Fig. 5 presents the SFG spectra of the rubbed sample, measured at specific azimuthal angles ($\gamma = 0°$, 90°, and 180°). The spectra in **Fig. 5(a)** and **Fig. 5(b)** were acquired using SSP and PPP polarization combinations, respectively. Measurement conditions included a 532 nm incident visible beam with a pulse energy of 300 μJ. The infrared beam energy ranged from 90 to 120 μJ/pulse. Scanned wavenumber regions covered C=C (1550–1800 cm⁻¹) and C-H stretching vibrations (2800–3050 cm⁻¹). Spectra were recorded at 3 cm⁻¹ intervals, with each data point representing an average of 300 accumulations.

As depicted in **Fig. 5**, several characteristic peaks were observed under both SSP and PPP polarization combinations. In the C=C stretching region, peaks at 1610, 1635, and 1725 cm⁻¹ are assigned to the stretching vibrations of the phenylene ring, C=C, and C=O in the cinnamoyl group, respectively. Notably, the intensities of the phenylene ring and C=C stretching vibration peaks exhibited a clear dependence on γ. This result indicates that SFG spectroscopy can sensitively probe the in-plane molecular anisotropy induced by the surface treatment. Similarly, in the C-H stretching region, a peak corresponding to the symmetric stretching vibration of the methyl group was observed at 2880 cm⁻¹. This peak also showed a dependence on γ, particularly evident with the PPP polarization combination. Based on these observations, this study focuses on two specific peaks: the phenylene ring peak at 1610 cm⁻¹, representing the main body of the cinnamoyl group, and the methyl group peak at 2880 cm⁻¹, reflecting the alkyl side-chain terminus. A detailed analysis of the azimuthal plots for these peaks allows for the quantitative evaluation of the orientation angles of each respective moiety.

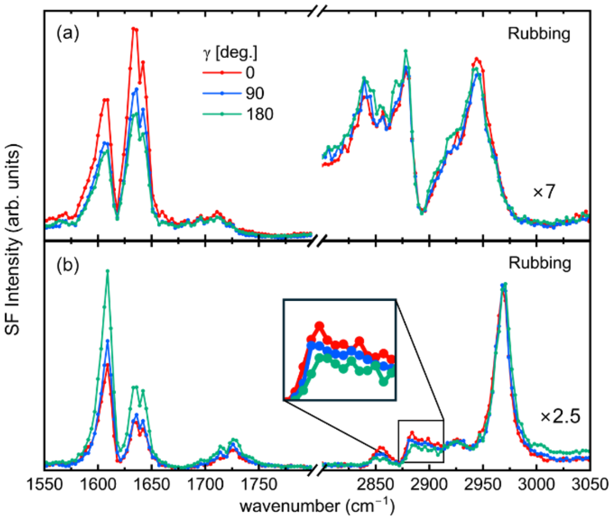

Figure 5. SFG spectra of the rubbed film in the C=C (1550–1800 cm⁻¹) and C-H (2800–3050 cm⁻¹) stretching vibrations regions, measured at different azimuthal angles ($\gamma =$ 0°, 90°, and 180°). The spectra were obtained with (a) SSP and (b) PPP polarization combinations.

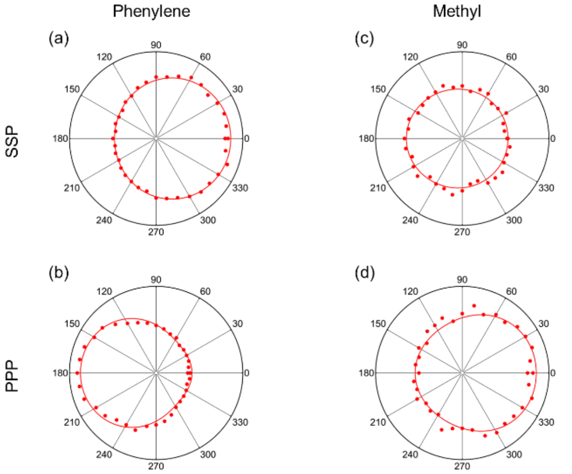

Figure 6. Azimuthal plots for specific vibrational modes of the rubbed film: (a, b) the phenylene stretching; and (c, d) the methyl group symmetric stretching. The plots were measured with SSP (a, c) and PPP (b, d) polarizations.

Following the procedure in **Section 2.1**, we acquired the azimuthal plots for the phenylene ring stretching vibration (1610 cm⁻¹) and the methyl group symmetric stretching vibration (2880 cm⁻¹), as shown in **Fig. 6**. In the figure, the dots represent experimental data, while the solid lines are the simulation curves based on the theoretical model described previously. Each dataset is normalized to its intensity at $\gamma = 180°$. As is evident from **Fig. 6**, the theoretical curves show excellent agreement with the experimental results, thereby providing strong support for the validity of our analysis model. Initially, examining the azimuthal plots corresponding to the phenylene group (**Figs. 6(a)** and **6(b)**), a distinct anisotropy was observed under both SSP and PPP polarization combinations. This finding strongly indicates that the main body of the cinnamoyl group underwent uniaxial alignment induced by the rubbing process. Similarly, the plots obtained for the methyl group at the side-chain terminus (**Figs. 6(c)** and **6(d)**) also display significant anisotropy, which confirms that the entire side chain is oriented with respect to the rubbing direction.

3.2 SFG measurements for photo-alignment films

Fig. 7 displays the SFG spectra of the photo-aligned sample, measured at specific γ (0°, 90°, and 180°). The experimental conditions were identical to those used for the rubbed sample. The overall spectral shape closely resembles that of the rubbed sample shown in **Fig. 5**, with identical peak assignments. However, significant differences were found in the azimuthal dependence of each peak. For the phenylene peak (1610 cm⁻¹), which represents the main body of the cinnamoyl group, clear anisotropy was observed, although its intensity variation was smaller compared to that of the rubbed sample. In contrast, the methyl group peak at the side-chain terminus (2880 cm⁻¹) showed negligible anisotropy.

To gain deeper understanding, the azimuthal plots for the photo-aligned sample were thoroughly investigated and are displayed in **Fig. 8**. These plots were generated from the peak intensities of the phenylene ring stretching vibration and the methyl group symmetric stretching vibration. Upon examining the plots for the phenylene group (**Figs. 8(a)** and **8(b)**), a distinct anisotropy aligned with the γ =0° direction was apparent for both SSP and PPP polarization combinations. This observation strongly suggests that the cinnamoyl group underwent uniaxial alignment due to the LPUV irradiation. It is important to note, however, that the magnitude of this anisotropy is considerably smaller than that observed for the rubbed sample (**Figs. 6(a)** and **6(b)**). Conversely, for the plots of the methyl group at the side-chain terminus (**Figs. 8(c)** and **8(d)**) revealed extremely minimal anisotropy under both polarization combinations. This finding compellingly indicates that the methyl groups at the side-chain termini remain barely aligned by the photo-alignment process, largely retaining a random orientation. From these results, it is clear that the photo-alignment process, unlike the rubbing process which physically aligns the entire side chain, selectively orients only the photo-responsive cinnamoyl groups and has little effect on the orientation of the side-chain termini.

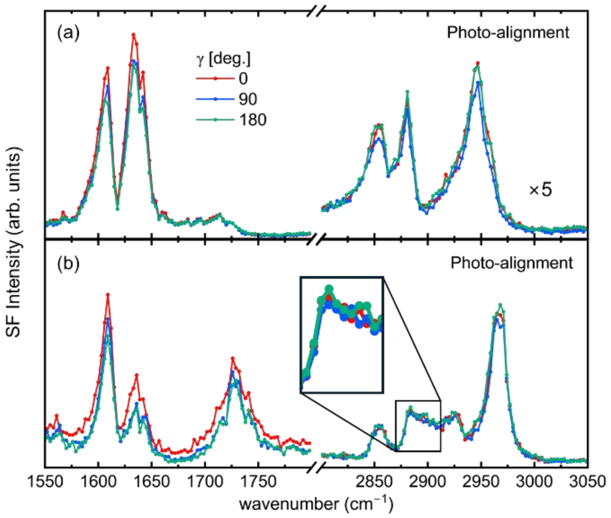

Figure 7. SFG spectra of the photo-alignment film in the C=C (1550–1800 cm^{-1}) and C-H (2800–3050 cm^{-1}) stretching vibrations regions, measured at different azimuthal angles ($\gamma =$ 0°, 90° and 180°). The spectra were obtained with (a) SSP and (b) PPP polarization combinations.

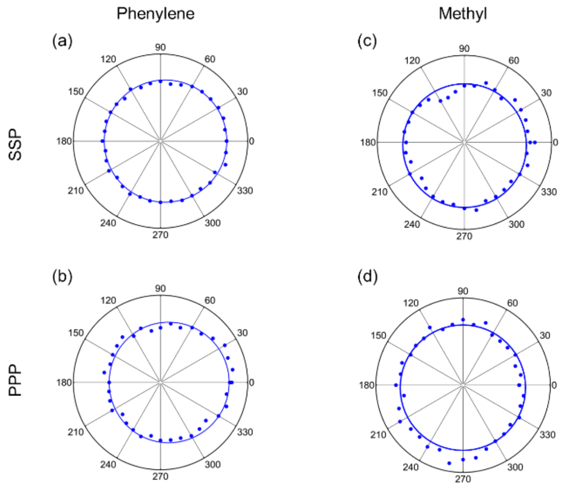

Figure 8. Azimuthal plots for specific vibrational modes of the photo-alignment film: (a, b) the phenylene stretching; and (c, d) the methyl group symmetric stretching. The plots were measured with SSP (a, c) and PPP (b, d) polarizations.

Furthermore, **Fig. 9** illustrates the azimuthal plot for the C-N stretching vibration (1380 cm^{-1}) of the imide ring, a key component of the polymer main chain, as measured with the PPP polarization combination. While a clear uniaxial anisotropy is observed for the rubbed sample (**Fig. 9(a)**), the photo-aligned sample displayed negligible anisotropy, similar to its terminal methyl groups (**Fig. 9(b)**). These results provide compelling evidence that, for photo-alignment film surfaces, the alignment of liquid crystals is exclusively dictated by the anisotropy of the cinnamoyl groups in the side chain, rather than by the orientation of the main chain. This photo-alignment-induced anisotropy mechanism is in clear contrast to a previous study by Sakamoto et al., which reported that for rubbed film surfaces, the pretilt angle originates from the main-chain orientation [1].

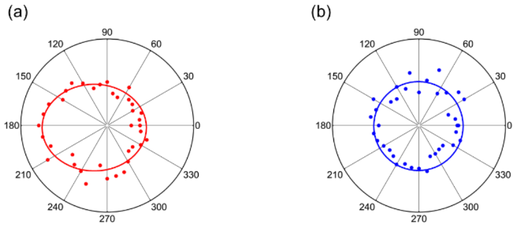

Figure 9. Azimuthal plots of the C-N stretching vibration (1380 cm^{-1}) of the main-chain imide ring. The plots compare the results from (a) the rubbed film and (b) the photo-aligned film. All data were obtained with the PPP polarization combination.

4 Conclusion

This study utilized SFG spectroscopy to investigate the anisotropy of a polyimide film with cinnamoyl side groups, comparing the effects of rubbing and photo-alignment processes. For the rubbed film, the phenylene, methyl group, and imide ring all exhibited clear uniaxial alignment. In contrast, the photo-aligned film showed a significant difference: while the phenylene was uniaxially aligned, the methyl group, as well as the imide ring, remained in a nearly random orientation. This indicates that only the photosensitive functional groups were reoriented. From these results, we have found that the orientation of the photosensitive segment, rather than that of the main chain, determines the alignment of the liquid crystal molecules in this system.

References

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