

Molecular orientational surface structures of polymers for liquid crystal alignment

Masahito Oh-e*

¹ Liquid Crystal Nono-system, SORST, Japan Science & Technology Agency,
5-9-9 Tokodai, Tsukuba, Ibaraki-ken, 300-2635 Japan

² Hitachi Displays, Ltd., 3300 Hayano, Mobara, Chiba-ken, 297-8622 Japan
Phone: +81-29-8479818, E-mail: oh-e@nanolc.jst.go.jp

Abstract

Sum-frequency vibrational spectroscopy (SFVS) has been used to study the molecular orientations at the polymer surfaces for liquid crystal alignment. Various molecular orientations appear at the surface depending on various types of surface treatments and polymers.

1. Introduction

Polymer surfaces and interfaces play an important role in liquid crystal display (LCD) devices. Polyimide (PI) films coated on a glass substrate and subsequently rubbed are used to align the liquid crystal (LC) molecules.^{1,2} Rubbing aligns the surface polymer chains, which in turn align the LC monolayer adsorbed on the polymer surface.³ For better understanding of the alignment mechanism, it is important to know molecular orientational structures at polymer surfaces at the molecular level.

Sum-frequency vibrational spectroscopy (SFVS) is a viable technique for probing such surface structures of materials, and has recently been applied successfully to rubbed polymer surfaces.⁴ It has the advantage of being highly surface-specific and sensitive. The surface specificity arises because under the electric-dipole approximation, these processes are forbidden in media with inversion symmetry, but allowed at a surface or interface where such symmetry is broken.⁵

In this paper, we report the summary of a series of research on molecular orientations at the polymer surfaces for LCDs studied by SFVS. Various molecular orientations appear at the polymer surfaces depending on surface treatments and polymers.

2. Theory

The theory of SFVS for surface studies has been described elsewhere.⁶ The output of sum-frequency

generation (SFG) by the input fields of $E(\omega_{vis})$ and $E(\omega_{IR})$ is given by

$$S(\omega_{SF}) \propto |\chi_{eff}^{(2)}|^2 |E(\omega_{vis})E(\omega_{IR})|^2, \quad (1)$$

with

$$\chi_{eff}^{(2)} = \left[\hat{e}_{\omega_{SF}} \cdot \vec{L}(\omega_{SF}) \right] \cdot \vec{\chi}^{(2)} : \left[\hat{e}_{\omega_{vis}} \cdot \vec{L}(\omega_{vis}) \right] \left[\hat{e}_{\omega_{IR}} \cdot \vec{L}(\omega_{IR}) \right], \quad (2)$$

where $L(\Omega)$ is the transmission Fresnel factor at frequency Ω , and e_{Ω} is a unit vector specifying the polarization of the beam at Ω . The nonlinear susceptibility $\chi^{(2)}$ is related to the molecular polarizability by

$$\vec{\chi}^{(2)} = \vec{\chi}^{(2)} + N_s \int \vec{\alpha}^{(2)}(\Omega) f(\Omega) d\Omega, \quad (3)$$

where N_s is the surface density of molecules. Near resonances, we assume that $\alpha^{(2)}$ can be written as

$$\vec{\alpha}^{(2)} = \vec{\alpha}_{NR} + \sum_q \vec{a}_q / \left[(\omega_{IR} - \omega_q) + i\Gamma_q \right], \quad (4)$$

where α_{NR} represents the nonresonant contribution, and \vec{a}_q , ω_q and Γ_q denote the strength, resonant frequency and the damping factor of the q th vibrational mode, respectively. We then have

$$S(\omega_{SF}) \propto \left| \vec{\chi}_{NR} + \sum_q \vec{A}_q / \left[(\omega_{IR} - \omega_q) + i\Gamma_q \right] \right|^2, \quad (5)$$

$$\vec{A}_q = N_s \int \vec{a}_q(\Omega) f(\Omega) d\Omega. \quad (6)$$

Scanning of ω_{IR} over resonances yields a surface SFVS spectrum. Note that A_q and a_q are related by the same relation as $\chi^{(2)}$ and $\alpha^{(2)}$ in Eq. (2). Analysis of the SFG vibrational spectra with different polarization combinations using Eqs. (1)-(6) allows us to deduce quantitative information about the orientational

distribution of the atomic groups associated with the vibrational modes.

3. Experimental

The PI materials used for homogenous LC alignment were poly-n-alkyl-ptromellitic imide ($[-N-(CO)_2-\phi-(CO)_2-CH_2]_n$) (P6), and poly-oxidi-phenylene-pyromellitic imide ($[-(CO)_2-\phi-(CO)_2-N-\phi-O-\phi-N-]_n$) (PMDA-ODA). The PI for homeotropic LC alignment had alkyl side chains ($[-N-(CO)_2-(C_4H_4)-(CO)_2-N-\phi(COO-\phi-(C_6H_{10})-(C_6H_{10})-CH_3)-]_n$). The PI films with a layer thickness of ~ 20 nm were prepared by spin-coating at 3500 rpm for 60 seconds. They were then baked at 250°C for 20 minutes. Rubbing to the PI surface to the saturation level was carried out by a rubbing machine with a velvet cloth. Ionized cluster beam deposition (ICBD) was made using PMDA and ODA. The detailed preparation for ICBD is described in Ref.[7]. A 248 nm KrF-excimer laser was used to irradiate the linearly polarized and homogenized beam to the surface of the spin-coated PMDA-ODA film.

The setup for SFVS has been described elsewhere.⁸ Briefly, a picosecond Nd:YAG laser was used to generate a visible beam at 532 nm and a tunable IR beam around $5.9 \mu\text{m}$, both having a 15 ps pulsewidth and a 20 Hz repetition rate. The two beams coming in from the air side were overlapped at the sample surface, and the SFG output was detected in the reflection direction.

4. Results and Discussion

Figure 1 (a) shows the spectra of the CO stretch modes from a rubbed P6 film taken at three different sample orientational angles between the incidence plane and the rubbing direction with three input/output polarization combinations: SSP (denoting S-polarized SF output, S-polarized visible input, and P-polarized infrared input, respectively), SPS, and PPP. The two peaks at 1729 and 1777 cm^{-1} are associated with the antisymmetric and symmetric stretch modes of coupled CO groups on the imide ring, respectively.⁹ The spectra explicitly show the existence of rubbing-induced anisotropy in the surface structure of P6, which originate from the two CO groups projecting out of the surface on the same side of the backbone. We can obtain the following: 1) The SSP spectrum at $\gamma=90^\circ$ is significantly stronger than the one at $\gamma=0^\circ$ or $\gamma=180^\circ$, indicating that the imide cores, that is, the PI backbones are aligned more or

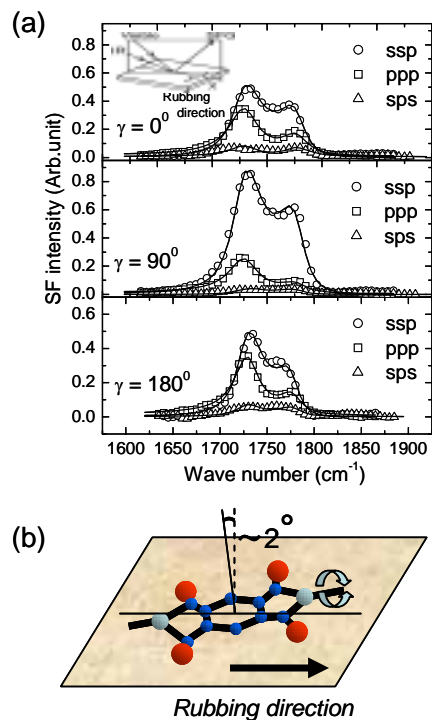


Figure 1 (a) SFVS spectra of a rubbed PI (P6) film in CO stretch region. (b) Molecular orientation of the imide group at the surface.

less along the rubbing direction. 2) The near forward-backward symmetry suggests that PI backbones lie nearly flat on the surface. 3) A very weak forward-backward asymmetry can be observed in the PPP spectra, corresponding to a slight upward tilt of the backbones along the rubbing direction at the surface. Similar results have also been obtained from a rubbed PMDA-ODA.^{10, 11} The more quantitative analysis¹² does indicate that, on a rubbed PI surface, the PI backbones are preferentially aligned along the rubbing direction with the imide core planes being inclined towards the surface with a rather broad distribution as shown in Fig. 1(b).

However, the orientation of the imide core is somewhat different at the surface for homeotropic LC alignment. Figure 2 shows the spectra of a PI film for homeotropic LC alignment. Inspection of the spectra in Fig. 2 gives us qualitative information that are different from the PI that homogeneously aligns LCs. The SSP spectra of the imide ring are weaker than the PPP spectra, indicating that the inclination of the imide ring plane would be close to perpendicular to the surface rather than flat on the surface as is found for the PI for homogeneous LC alignment. The quantitative considerations¹³ also allow us to have a picture that the

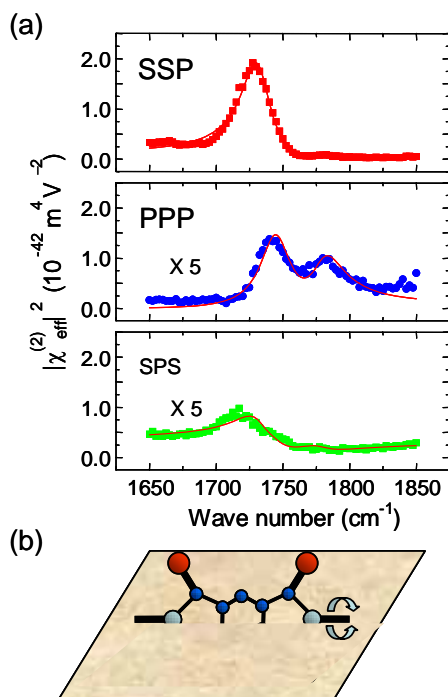


Figure 2 (a) SFVS spectra of a PI homeotropic LC alignment film in CO stretch region. (b) Molecular orientation of the imide group at the surface.

imide ring is close to be perpendicular to the surface rather than flat on it. This orientation would contribute to more dense packing of the molecular units than that flat on the surface. As the imide ring is perpendicular to the surface, the side chain would pack densely at the surface and the distance to nearby side chains would become closer.

The molecular orientation is also different depending on the preparation methods.⁷ In the previous study with spin-coated PI films, the ratio of antisymmetric A_{as} and symmetric A_s peak strengths from the SFVS measurement was 1.4. For ICBD-PI, however, symmetric stretch A_s is 2.5 times stronger compared to A_{as} so the chain conformation is expected to be different from that of the spin-coated PI surface. From the two normal modes in the spectra shown in the inset of Fig. 3, the antisymmetric stretch has a dipole moment directed normal to the backbone, while the symmetric stretch has a dipole moment along the backbone direction. Since our SFVS measurement with a P-polarized infrared input beam probes the dipoles directed along the surface normal, that A_s is much stronger for ICBD-PI indicates that the backbones would be more inclined from the

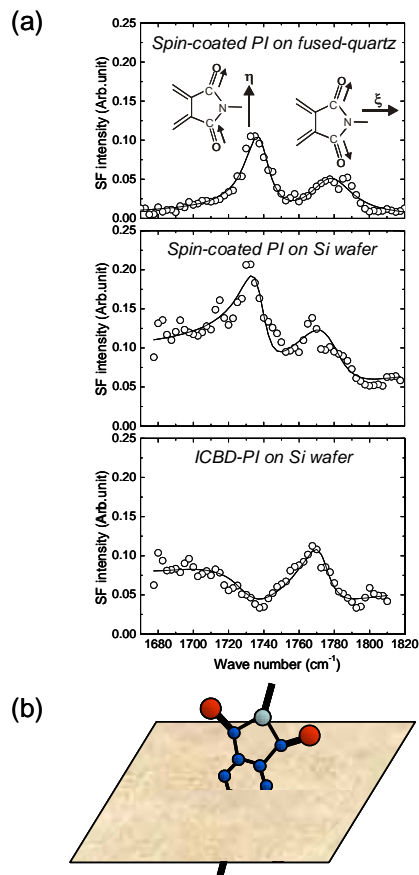


Figure 3 (a) SFVS spectra of a PI films: comparison of an ICBD-PI film with a spin-coated PI film. (b) Molecular orientation of the imide group at the surface.

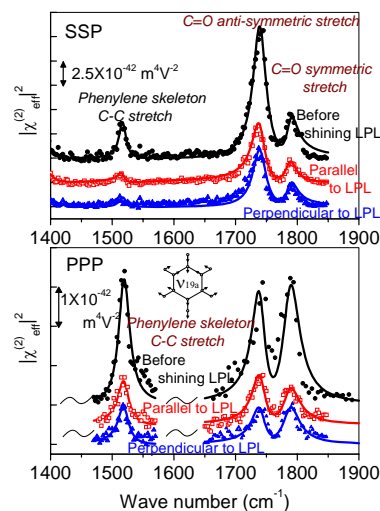


Figure 4 SFVS spectra of a PI film before and after the linearly polarized UV laser irradiation (30 J/cm^2).

surface toward the normal direction. The possible molecular alignment in this case is shown in Fig. 3 (b).

Shown in Fig. 4 are the representative SFG spectra of PMDA-ODA in the range from 1400 to 1850 cm^{-1} before and after linearly polarized light (LPL) irradiation (with the incidence plane parallel and perpendicular to the polarization of UV irradiation in the latter case). The sample measured was irradiated by LPL with a total dosage of 30 J/cm^2 obtained from 4000 laser pulses with 7.5 mJ/cm^2 per pulse. Such irradiated PMDA-ODA samples used as substrates for an LC display cell was able to yield a good homogeneous LC bulk alignment perpendicular to the UV polarization. The spectra in Fig. 4 show that in both SSP and PPP cases, the peak intensities of both phenylene skeleton C-C stretch and C=O stretch modes were significantly reduced by LPL irradiation. The anisotropy seen in the spectra after irradiation is however weak. Both the C=O bonds in the PMDA part and the C-C bonds in the phenylene skeleton of ODA appear to be broken, suggesting a rather severe fragmentation of the PI backbones by UV irradiation.¹⁴

5. Conclusion

We have used SFVS to study various surfaces of polymers for LC alignment. Molecular orientations at the surface can be different for different types of polymers and different treatments for the surface. SFVS is such a powerful and versatile technique that we can analyze various molecular orientations at the surface.

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7. References

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