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## NONLINEAR OPTICAL SPECTROSCOPIC STUDIES OF POLYMER SURFACES FOR LIQUID CRYSTAL ALIGNMENT: PHOTO-IRRADIATED POLYIMIDE AND RUBBED POLYSTYRENE SURFACES

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*Surface specific sum-frequency vibrational spectroscopy (SFVS) and second-harmonic generation (SHG) were used to study the structures of polymer surfaces modified by linearly polarized UV irradiation or mechanical rubbing. The spectroscopic results show that the surface anisotropy of a polyimide surface resulting from bond breaking by linearly polarized UV irradiation is extremely small compared to a rubbed surface. On a rubbed polystyrene surface, the phenyl sidegroups are well aligned by rubbing in the direction perpendicular to rubbing but tilt from the surface normal with a broad distribution.*

**Keywords:** interface; liquid crystal; nonlinear optics; polyimide; sum-frequency generation; surface; vibrational spectroscopy

### INTRODUCTION

Polymers are commonly used to align liquid crystal (LC) films for LC devices. A presently prevailed technique is mechanical rubbing of a polymer surface, [1] but much attention has recently been attracted by photo-induced alignment techniques as alternative methods [2–4]. For better understanding of the alignment mechanism, it is important to characterize such polymer surfaces and LC monolayers on them at the molecular level in a proper way.

Infrared-visible sum-frequency vibrational spectroscopy (SFVS) and second-harmonic generation (SHG) are effective probes for surface

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characterizations [5,6]. Being surface-specific, they allow quantitative determination of molecular orientation and alignment at a polymer surface. Applications of the techniques to rubbed surfaces of polyvinyl alcohol (PVA) [7] and polyimide (PI) [8] have provided us a physical picture that the surface polymer main chains are well aligned along the rubbing direction, and so are the LC molecules adsorbed on them.

We here present the spectroscopic results regarding two kinds of polymer surfaces that align LC molecules: (1) a linearly polarized UV irradiated PI (poly[4,4'-oxydiphenylenepyromellitimide]),  $[(\text{CO})_2\text{-}\phi\text{-(CO)}_2\text{-N-}\phi\text{-O-}\phi\text{-N-}]_n$ : PMDA-ODA) surface, and (2) a rubbed polystyrene  $[(\text{-CH}_2\text{-CH(C}_6\text{H}_5)\text{-}]_n$ : PS) surface. The purpose is to know how linearly polarized UV irradiation modifies a PI surface and how different it is from a rubbed one. Rubbing of a polystyrene surface is known to induce an LC film alignment perpendicular to the rubbing direction [1,9]. One would then expect that if rubbing aligns the polymer chains along the rubbing direction, the phenyl sidegroups protruding out of the surface must have an orientation perpendicular to the rubbing.

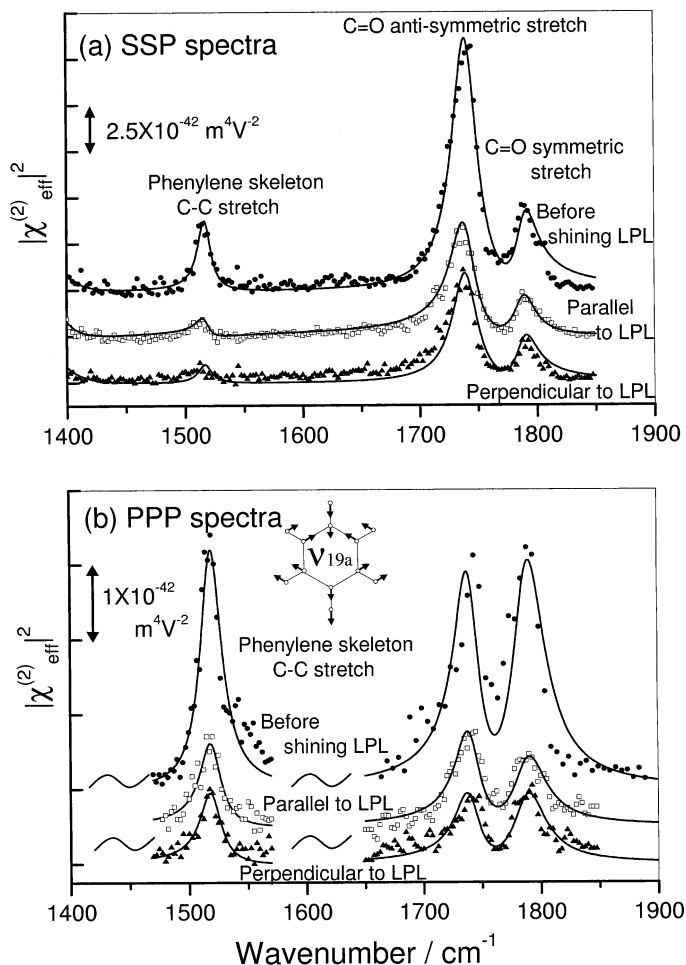
## EXPERIMENT AND THEORY

The experimental setup and the theoretical background for SFVS and SHG have been described elsewhere [10]. The PMDA-ODA and isotactic PS films with a layer thickness of  $\sim 25$  nm and  $\sim 400$  nm were prepared by spin-coating, respectively. To obtain uniform layers, the PMDA-ODA polyamic acid solution in 1-methyl-2-pyrrolidone and the PS solution in toluene (Scientific Polymer Products, Inc.) were filtered by membrane filters. Each solution was then dropped on a substrate to be spin-coated at 3500 rpm for 60 second. The PMDA-ODA PI and PS samples were baked at  $250^\circ\text{C}$  for 20 min. and  $170^\circ\text{C}$  for 60 min., respectively. Rubbing was carried out by a rubbing machine with a velvet cloth. A 248 nm KrF-excimer laser beam, linearly polarized and homogenized, was used to irradiate the spin-coated PI film.

## RESULTS AND DISCUSSION

### I. Photo-Irradiated PDMA-ODA Surface

Shown in Figure 1 are the representative SFG spectra of PMDA-ODA before and after UV irradiation (with the incidence plane parallel and perpendicular to the polarization of UV irradiation in the latter case). The input/output polarization combinations were (a) SSP (denoting s-, s-, and p-polarization for SF output, visible input, and IR input, respectively)



**FIGURE 1** SFVS with (a) SSP and (b) PPP polarization combinations for a PMDA-ODA thin film before and after the linearly polarized UV laser irradiation.

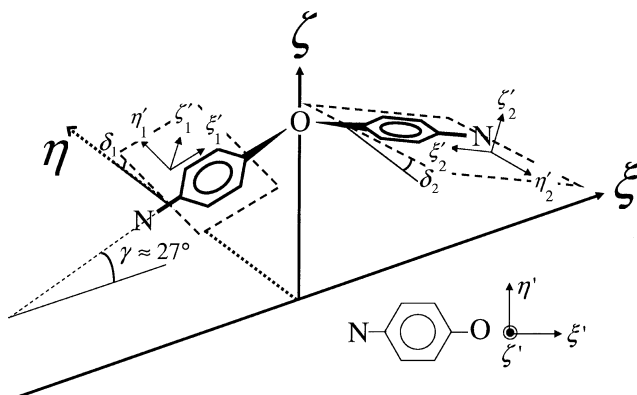
and (b) PPP. In SPS, the spectral features were too weak to be detected. The sample measured was irradiated with a total dosage of  $30 \text{ J/cm}^2$  obtained from 4000 laser pulses with  $7.5 \text{ mJ/cm}^2$  per pulse. Such irradiated PMDA-ODA samples used as substrates for an LC display cell were able to yield a good homogeneous LC bulk alignment perpendicular to the UV polarization. Referring to the IR and Raman spectra of PMDA-ODA, we can assign the spectral peaks: C=O symmetric stretch at  $\sim 1785 \text{ cm}^{-1}$ , C=O antisymmetric stretch at  $\sim 1740 \text{ cm}^{-1}$ , and phenylene skeleton C-C stretch at  $\sim 1515 \text{ cm}^{-1}$  [11]. The spectra show that in both SSP and PPP

cases, the peak intensities of both phenylene skeleton C-C stretch and CO stretch modes were significantly reduced by UV irradiation and the anisotropy seen in the spectra after irradiation is extremely weak. These features indicate that UV irradiation provides a rather severe fragmentation of the PI backbones at the surface.

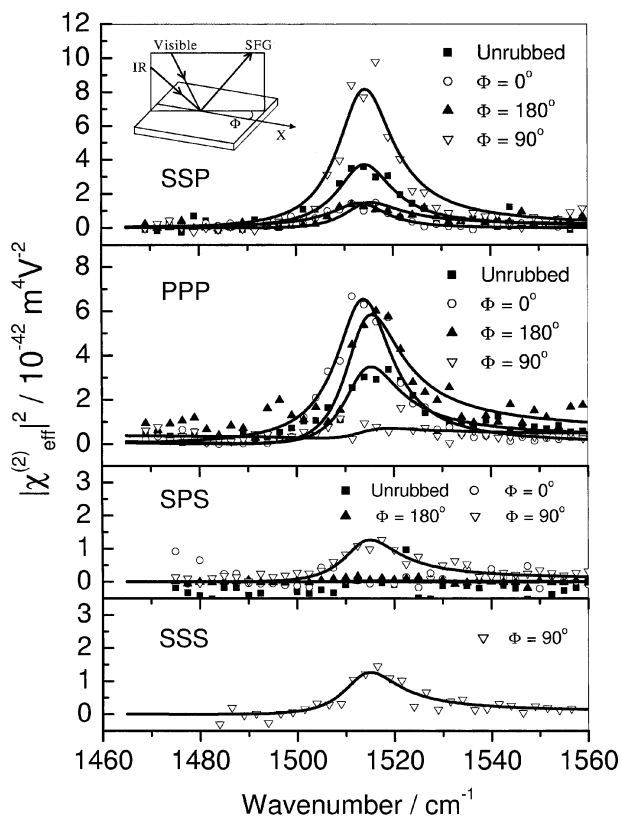
In order to deduce the rates of bond breaking of PI backbones at the surface, we use a mechanically rubbed PI surface that has main chains aligned, focusing on phenylene skeleton C-C stretch at  $\sim 1515\text{ cm}^{-1}$ . Let  $f(\mathbf{\Omega}, t) = N(\mathbf{\Omega}, t)/N_0$  be the orientational distribution of the molecular units at time  $t$  with orientation specified by  $\mathbf{\Omega}(\theta, \phi, \psi, \delta)$  and  $N_0 = \int N(\mathbf{\Omega}, t) d\mathbf{\Omega}$  being the total surface density of molecular units. Then its decay with time is expressed by  $f(\mathbf{\Omega}, t) = f(\mathbf{\Omega}, 0) \exp[-\kappa(\hat{e} \cdot \mathbf{\Omega}) \cdot t]$ .  $\hat{e}$  is the unit polarization vector of the UV irradiation and  $\kappa$  is the rate of bond breaking of phenylene ring, which, we assume, is proportional to the rate of UV excitation (See Figure 2) [12,13].

$$\kappa = \alpha \left[ (\hat{e} \cdot \hat{\xi}'_1)^2 + (\hat{e} \cdot \hat{\xi}'_2)^2 \right] + \beta \left[ (\hat{e} \cdot \hat{\eta}'_1)^2 + (\hat{e} \cdot \hat{\eta}'_2)^2 \right] \quad (1)$$

Figure 3 shows the SFG spectra of the phenylene skeleton stretch mode of PMDA-ODA before and after rubbing. The spectra taken with the incident plane parallel and anti-parallel to the rubbing direction are significantly weaker than the one taken with the incident plane perpendicular to the rubbing direction. The result indicates that after rubbing, the phenylene rings of PMDA-ODA are preferentially oriented along the rubbing direction. It also suggests that the phenylene rings must, on average, incline at an angle with the surface plane. (If the rings lied flat in the surface plane,

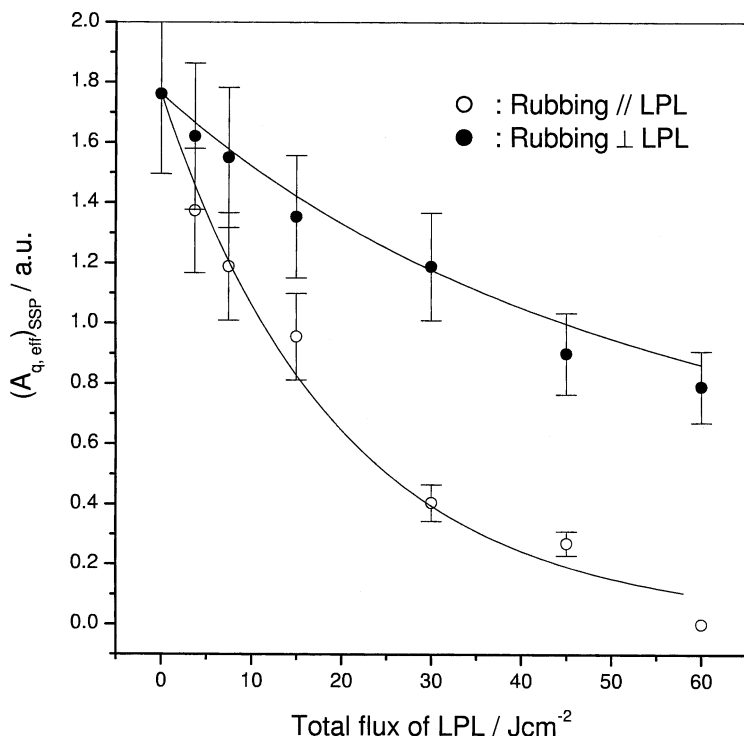


**FIGURE 2** Geometry of a PMDA-ODA molecular unit.



**FIGURE 3** SFVS for a PMDA-ODA thin film before and after rubbing.

the phenylene modes would not be excited by the SSP polarization combination). The spectra also show a weak forward-backward asymmetry along the rubbing direction. A quantitative analysis of the spectral data allows us to deduce an approximate orientational distribution function  $f(\Omega, 0)$  for the PI backbones lying on the rubbed surface. Knowing  $f(\Omega, 0)$  and some quantity  $Q(t) = \int Q(\Omega) f(\Omega, t) dt$  that exhibits the photo-induced effect, we can deduce the coefficients  $\alpha$  and  $\beta$ . The detailed analysis is described in Ref. [14]. The quantity  $Q(t)$  is the mode amplitude  $A_{q,eff}(\Phi = 90^\circ, SSP)$  for the phenylene stretch mode presented in Figure 4. From the decay of  $A_{q,eff}(\Phi = 90^\circ, SSP)$ , we find  $\alpha = (3.0 \pm 0.3) \times 10^{-2} J^{-1} \cdot cm^2$ ,  $\beta = (2.6 \pm 0.2) \times 10^{-2} J^{-1} \cdot cm^2$  [14]. These values also describe the experimental data of unrubbed PI surface. The ratio  $\alpha/\beta = 1.15$  is approximately the same as that obtained by IR spectroscopy ( $\alpha/\beta = 1.23$ ) [15].



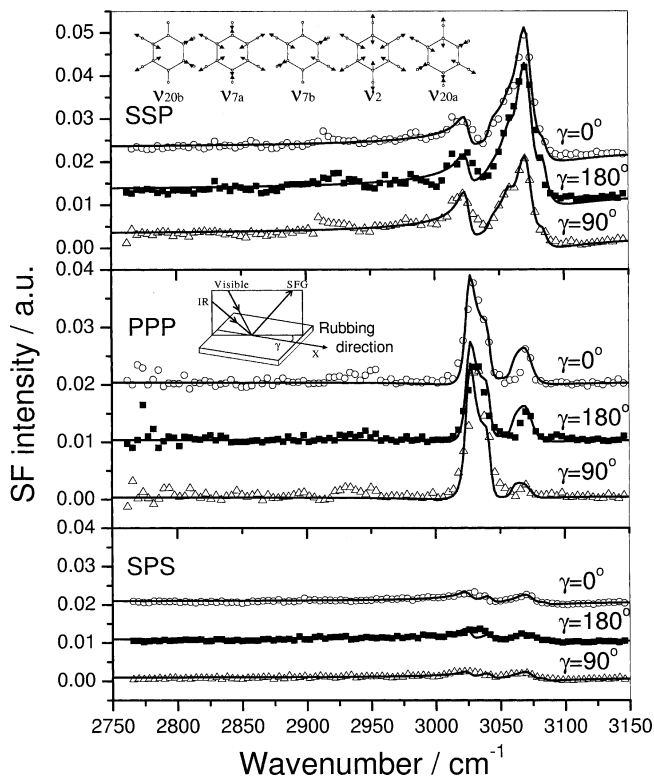
**FIGURE 4** Decays of the peak amplitude of the phenylene stretch mode for a rubbed PMDA-ODA film as functions of UV dosage.

## II. Rubbed Polystyrene Surface

Figure 5 presents the SFVS spectra in the C-H stretch region of a rubbed PS/air interface taken at three different angles ( $\gamma = 0^\circ, 90^\circ$ , and  $180^\circ$ ) between the incidence plane and the rubbing direction with three input/output polarization combinations: SSP, PPP, and SPS. The spectra exhibit five aromatic C-H vibrational stretches associated with the phenyl sidegroups. They appear at 3024, 3036, 3057, 3069 and 3084  $\text{cm}^{-1}$  which can be assigned to the  $\nu_{20b}$ ,  $\nu_{7a}$ ,  $\nu_{7b}$ ,  $\nu_2$ , and  $\nu_{20a}$  vibrational modes, respectively [16]. SFVS on PS films has recently been reported by several groups.[17,18]. In all investigations, it was concluded that the observed SF signal is dominated by contribution from the PS/air interface. Therefore in our case, we can consider SF signals in Figure 5 as coming mainly from the phenyl sidegroups projecting out of the PS surface.

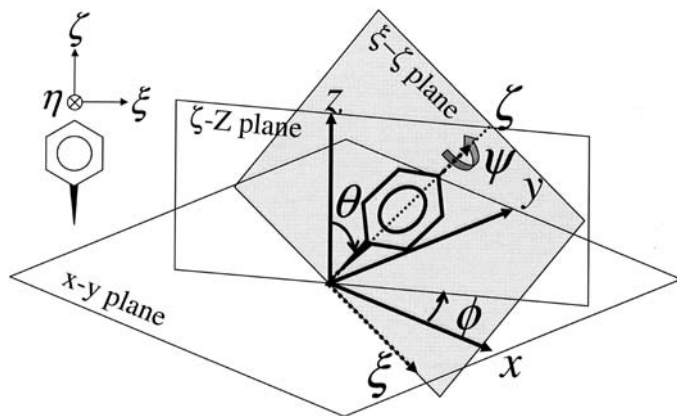
We now focus on the symmetric stretch  $\nu_2$  at 3069  $\text{cm}^{-1}$  of the phenyl group as it is most prominent in the spectra. This mode can be strongly





**FIGURE 5** SFVS spectra with (a) SSP, (b) PPP and (c) SPS polarization combinations for a rubbed isotactic PS film.

excited by IR field along  $\zeta$  in the molecular coordinates described in Figure 6 and by Raman excitation with a symmetric polarizability tensor component in the  $\xi$ - $\zeta$  plane. Thus, the nonlinear polarizability for SFVS in resonance with this mode is dominated by components  $\alpha_{\zeta\zeta\zeta}^{(2)}$  and  $\alpha_{\xi\xi\zeta}^{(2)}$ . Then, from the SFVS spectra, we can readily obtain a qualitative picture for the rubbing-induced alignment of the phenyl sidegroups. First, the SSP spectra at  $\gamma = 0^\circ$  and  $180^\circ$  are significantly stronger than the one at  $\gamma = 90^\circ$ , indicating that the phenyl sidegroups are more or less along the direction perpendicular to the rubbing direction. Second, hardly detectable forward-backward asymmetry in the spectra suggests that the phenyl groups do not have an appreciable tilt toward the rubbing direction, or the polymer backbones lie nearly flat on the surface. The observed azimuthal anisotropy is relatively small compared to the cases of rubbed PVA and PI. This is partly because we rubbed PS only gently to avoid possible removal of the PS film from the substrate. The degree of



**FIGURE 6** Geometric relations between the molecular coordinates and the lab coordinates. The rubbing direction is defined along x axis.

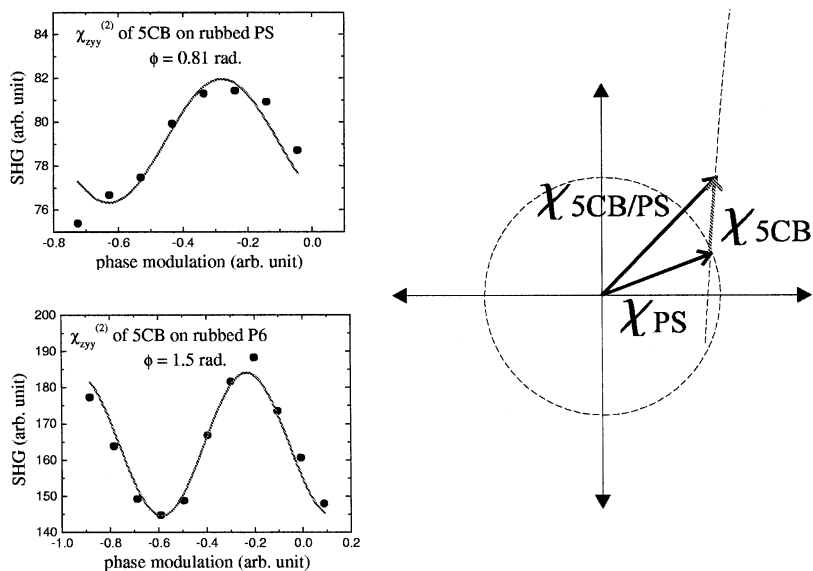
anisotropy in the spectra is a measure of how broad a distribution the chain orientation has around its mean.

More quantitatively, we can deduce the orientational distribution function of the phenyl sidegroup by a Gaussian form using the same analysis described in Ref. [7,8].

$$f(\Omega) = C \exp \left[ -\frac{(\theta - \theta_0)^2}{2\sigma_\theta^2} - \frac{(\phi - \phi_0)^2}{2\sigma_\phi^2} - \frac{(\psi - \psi_0)^2}{2\sigma_\psi^2} \right] \quad (2)$$

We have found  $\alpha_{\xi\xi\xi}^{(2)}/\alpha_{\xi\xi\xi}^{(2)} = 1.68 \pm 0.15$ ,  $\phi_0 = 90^\circ$ ,  $\sigma_\phi = 49 \pm 5^\circ$ ,  $\psi_0 = 90^\circ$ ,  $\sigma_\psi = 68 \pm 9^\circ$  and  $\theta_0$  in the range from  $72 \pm 6^\circ$  to  $83 \pm 7^\circ$  with  $\sigma_\theta$  varying from  $\sim 3^\circ$  at  $\theta_0 = 72^\circ$  to  $\sim 17^\circ$  at  $\theta_0 = 83^\circ$  [19].

Knowing the orientation of phenylene sidegroups at the surface, we also studied the orientation of 4'-n-pentyl-4-cyanobiphenyl (5CB) adsorbed on PS using SHG. During the evaporation, the *in-situ* measurement showed that SHG increased monotonously and then leveled off [20]. The saturated signal from the 5CB layer was rather weak, less than one tenth of that from a 5CB monolayer on PI. The ratio of  $\chi^{(2)}$  of PS to  $\chi^{(2)}$  of 5CB on PS was around 1:1.4. This indicates that polar adsorption of 5CB on the nonpolar PS surface is probably poor, leading to only a partial coverage of the surface by polar-oriented 5CB molecules. That the surface was actually partly covered by 5CB molecules with their CN terminals toward the surface was found from an SHG phase measurement [21]. As shown in Figure 7, interference of the SH signals from 5CB on rubbed PS and on n-hexyl pyromellitic polyimide (P6) with that from a quartz plate yielded the phase  $\phi$



**FIGURE 7** Experimental data and line fits for SHG phase measurements of 5CB monolayers on rubbed PS and P6, respectively.  $\chi_{PS}^{(2)}$ ,  $\chi_{5CB}^{(2)}$  and  $\chi_{PS/5CB}^{(2)}$  are the susceptibilities of the PS surface, the 5CB monolayer, and the 5CB monolayer on rubbed PS, respectively.

of  $\chi^{(2)}$  for the two cases. SHG from 5CB on P6 is dominated by contribution from 5CB that adsorb with the CN terminal facing P6 [22–23]. Therefore  $\chi_{5CB}^{(2)} \sim \chi_{5CB/P6}^{(2)}$ . The vector diagram of  $\chi^{(2)}$  in Figure 7 shows that the polar-oriented 5CB molecules on PS must also have their CN terminals facing PS; an opposite orientation of 5CB would change the sign of  $\chi_{5CB}^{(2)}$  and would lead to an SHG signal from 5CB/PS that decreases with increase of 5CB coverage, contrary to the observation.

We have found equal SHG signals (in reflection) from homogeneous 5CB films sandwiched between rubbed PS substrates and between rubbed PVA substrates, despite the significant difference of SHG from evaporated 5CB layers on PS and PVA. This indicates that with the presence of the bulk 5CB film, the 5CB molecules at the PS surface are forced to assume the polar orientation with CN facing the surface as in the case of 5CB on PVA [7]. Presumably when 5CB molecules are forced to be next to the phenyl rings, they would prefer to have the biphenyl cores interact with the phenyl rings, and hence the CN terminals toward the surface. We have also found, from a 5CB film sandwiched between rubbed PS surfaces, a stronger SHG with the input polarization perpendicular to the rubbing direction than parallel to the rubbing direction, indicating that 5CB molecules in the film were

aligned perpendicular to the rubbing direction. This was also verified by linear optical measurement.

## CONCLUSION

We have used SFG vibrational spectroscopy to probe UV photo-induced bond breaking and anisotropy on PMDA-ODA. We observe bond breaking of the PI backbones taking place in the part of the phenylene rings and imide core. By analyzing the experimental results from a rubbed surface before and after the photo-induced bond breaking, we are able to deduce information about the surface orientations of the PI backbones and the photo-dissociation rates for UV irradiation polarized parallel and perpendicular to the PI backbones.

We have also shown that mechanical rubbing aligns phenyl sidegroups of PS perpendicular to the rubbing direction. The phenyl planes incline towards the surface with a rather broad distribution. The aligned phenyl sidegroups at the PS surface can interact with nearby 5CB molecules and force them to polar-orient with the CN terminals facing the surface. The orientation and alignment of the 5CB surface monolayer can then induce a homogeneous alignment of the 5CB bulk film through molecular correlation.

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