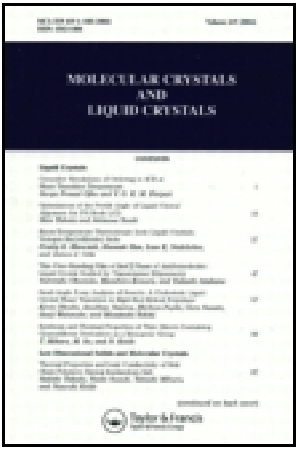

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Nonlinear Optical Studies of Surface Structures of Rubbed Polyimides and Adsorbed Liquid Crystal Monolayers

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Sum-frequency generation (SFG) vibrational spectroscopy and second-harmonic generation (SHG) were used to probe rubbed polyimide (PI) surfaces and liquid crystal (LC) monolayers adsorbed on them. The results show that rubbing preferentially aligns PI backbones along the rubbing direction, but has little effect on the side chain orientation at the surface. However, adsorption of an LC monolayer well aligned by the rubbed PI surface can cause the side chains to tilt towards the rubbing direction.

Keywords: sum-frequency generation; second-harmonic generation; vibrational spectroscopy; polyimide; liquid crystal; surface; interface

INTRODUCTION

Polymers are generally used as alignment layers in liquid crystal (LC) displays. Rubbing of polymer-coated substrates is the commonly adopted technique of the industry to produce homogeneously aligned LC films. For better understanding of the alignment mechanism, it is

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important to be able to characterize polymer surfaces and adsorbed LC monolayers on the surfaces at the molecular level.

Second-harmonic generation (SHG) and infrared-visible sum-frequency generation (SFG) vibrational spectroscopy have been demonstrated to be an effective tool to probe polymer surfaces and LC monolayers[1, 2]. They have 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[3]. In this paper, we report the use of the techniques to study structures of rubbed polyimide (PI) surfaces and LC monolayers adsorbed on them. A similar investigation has been carried out successfully on rubbed polyvinyl alcohol with and without an adsorbed LC monolayer, but PI is the preferred polymeric material in the LC industry. We shall focus on how rubbing aligns the backbones of PI at the surface, and hence the LC monolayer adsorbed on it. For PI with alkyl side chains, it is often believed that rubbing also aligns the side chains at the surface, and then the oriented side chains would affect the orientation and alignment of the adsorbed LC monolayer. Our results, however, show that the reverse is true.

SHG and SFG

The theory and experimental arrangement of SHG and SFG for surface studies have been described elsewhere[1-5]. Briefly, SFG from a medium is generated by the second-order nonlinear polarization $P^{(2)}(\omega_{SF}=\omega_{vis}+\omega_{IR})$ induced in the medium by the incoming fields $E(\omega_{vis})$ and $E(\omega_{IR})$. SHG is a special case with $\omega_{vis}=\omega_{IR}$. We assume here that the bulk contribution to SFG is negligible. The SFG output is given by

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

with $\chi_{eff}^{(2)} = \left[e_{\omega SF} \cdot L(\omega_{SF})\right] \cdot \chi^{(2)} : \left[e_{\omega_{vis}} \cdot L(\omega_{vis})\right]\left[e_{\omega IR} \cdot L(\omega_{IR})\right]$,
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

$$\chi^{(2)}_{ijk} = N_s \sum_{\xi,\eta,\zeta} \left\langle (\hat{i}\cdot\hat{\xi})(\hat{j}\cdot\hat{\eta})(\hat{k}\cdot\hat{\zeta}) \right\rangle \alpha^{(2)}_{\xi\eta\zeta} \quad , \qquad (2)$$

where N_s is the surface density of molecules, i, j, k refer to the lab coordinates (x, y, z), ξ, η, ζ refer to the molecular coordinates and the brackets denote an average over a molecular orientational distribution function. Near resonances, we assume that $\alpha^{(2)}$ can be written as $\vec{\alpha}^{(2)} = \vec{\alpha}_{NR} + \sum_q \vec{a}_q / \left(\omega_{IR} - \omega_q\right) + i\Gamma_q$, where α_{NR} represents the nonresonant contribution, and a_q, ω_q and Γ_q denote the strength, resonant frequency and the damping factor of the qth vibrational mode, respectively. We then have

$$S(\omega_{SF}) \propto \left| \vec{\chi}_{NR} + \sum_q \frac{\vec{A}_{q,eff}}{\left(\omega_{IR} - \omega_q\right) + i\Gamma_q} \right|^2 \quad . \qquad (3)$$

Scanning of ω_{IR} over resonances yields a surface SFG spectrum. Note that $\left(A_q\right)_{ijk}$ and $\left(a_q\right)_{\xi\eta\varsigma}$ are related by the same relation as $\chi^{(2)}_{ijk}$ and $\alpha^{(2)}_{\xi\eta\varsigma}$ in Eq. (2). Analysis of the SFG vibrational spectra with different polarization combinations using Eqs. (1)-(3) allows us to deduce quantitative information about the orientational distribution of the atomic groups associated with the vibrational modes. Here, however, we shall limit ourselves to only a qualitative description and discussion of the results.

RESULTS AND DISCUSSION

Consider first the orientation of backbones on the rubbed PI surface. This can be achieved by studying the CO groups attached to the imide rings. Figure 1 presents the SFG spectra of the CO stretch modes from a rubbed poly-oxydiphenilene-pyromellitic imide surface ($[-(CO)_2-\phi-(CO)_2-N-\phi-O-\phi-N-]_n$) (PMDA/ODA). The two peaks at 1740 and 1788 cm^{-1} are associated with the antisymmetric and symmetric stretch modes of coupled CO groups on the imide ring, respectively. The spectra show explicitly the existence of rubbing-induced anisotropy in the surface structure of PMDA/ODA. Analysis of the results obtained with different

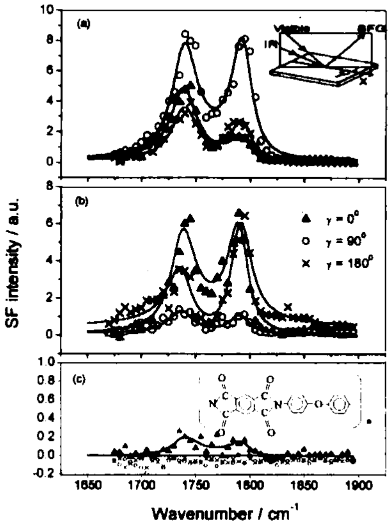


FIGURE 1. SFG spectra for PMDA/ODA PI taken at different angles between the incidence plane and the rubbing direction, with (a) SSP (SF output, visible input, and IR input S-, S-, and P-polarized, respectively), (b) PPP, and (c) SPS polarization combinations.

polarization combinations shows that the spectra originate from the two CO groups projecting out of the surface on the same side of the backbone. We can obtain the following: 1) Because the SPS spectra for all γ angle are relatively weak, the imide core plane must be more or less perpendicular to the surface. 2) The SSP spectrum at γ=90° is significantly stronger than the one at γ=0° or γ=180°, indicating that the imide core, and hence the PI backbones, are more or less along the rubbing direction. 3) There exists a weak forward/backward asymmetry along the rubbing direction. This then yields direct evidence of an induced alignment of the PI backbones at the surface by rubbing. Similar results have also been obtained from a rubbed poly-n-alkyl-pyromellitic imide surface ($[\text{-N-(CO)}_2\text{-}\phi\text{-(CO)}_2\text{-N-(CH}_2)_n\text{-}]$) with n=6 (P6)[6]. We have also probed the alignment of an adsorbed 8CB LC monolayer on rubbed PMDA/ODA using SHG with different polarization combinations[7]. The LC monolayer was found to align well along the rubbing direction on the PMDA/ODA surface, because of its anisotropic interaction with the aligned polymer backbones.

We have also studied the surfaces of PIs with side alkyl chains (for example, $[-(CO)_2-\phi-(CO)_2-N-\phi-O-\phi-C(C_5H_{11}(CH_2)_6CH_3)-\phi-O-\phi-N-]_n$, C_7 PI). The SFG spectra for the CO stretches are similar to those of PMDA/ODA or P6, showing rubbing-induced anisotropy. The CH stretch modes associated with the alkyl side chains, however, exhibit very little induced anisotropy, as seen from the spectra in Fig. 2. The lower spectral intensities in the SSP spectra of the rubbed PIs compared to the unrubbed ones can be understood as the result of a broader orientational distribution of the side chains after rubbing. Analysis of spectra with various polarization combinations indicates that the side chains protrude out from the surface with a broad angular distribution

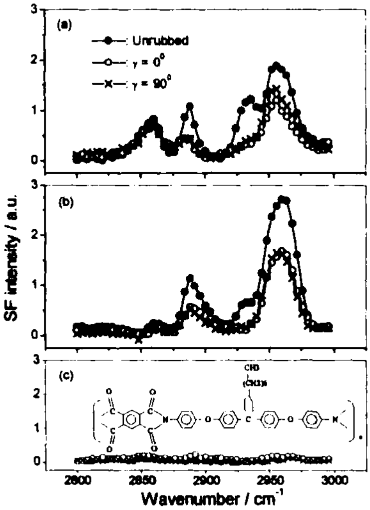


FIGURE 2. SFG spectra for C_7 PI before and after rubbing, with (a) SSP, (b) PPP, and (c) SPS polarization combinations. Solid circles, open circles and crosses refer to data taken from unrubbed and rubbed surfaces with incident plane perpendicular and parallel to the rubbing direction, respectively.

about the surface normal. Alignment of the backbones can hardly affect the orientational distribution of the side chains.

Shown in Fig. 3 are the SFG spectra (SSP) of a C_7 PI film with and without a 5CB LC monolayer on it. 5CB molecules were deuterated to avoid confusion of spectra in the CH range. The significantly reduced CH_2 peak at 2930 cm^{-1} in the spectrum with an LC monolayer indicates a significant reduction of gauche defects in the C_7 side alkyl chain. In addition, as shown in Fig. 3 (c), we observe an appreciable anisotropy in the spectra for the rubbed C_7 PI surface with a 5CB monolayer. This indicates that the 5CB monolayer is aligned by the PI backbones on the rubbed surface, and then its interaction with the alkyl chains of the C_7 PI aligns the alkyl chains at the surface. The reduction of gauche defects in the alkyl chains at a PI surface by adsorption of an LC monolayer is possibly due to an exclusive volume effect[8, 9]. To see LC alignment on rubbed C_7 PI, we have again used SHG. Figure 4 shows the plot of SHG as a function of γ for four different polarization combinations.

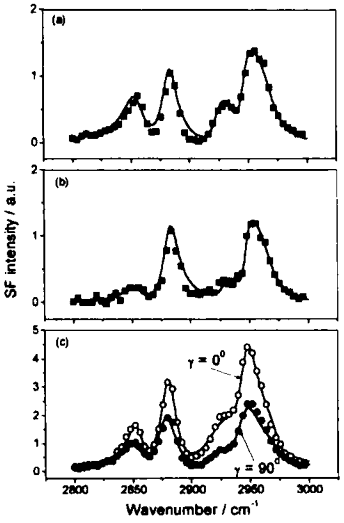
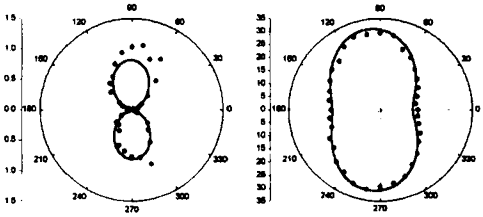
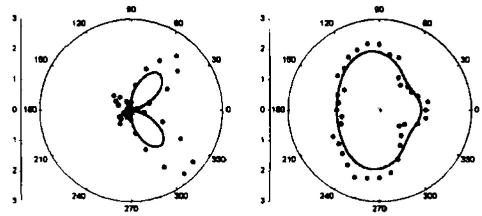


FIGURE 3. SFG spectra for unrubbed C_7 PI (a) without and (b) with a deuterated 5CB monolayer, and (c) SFG spectra of a deuterated 5CB monolayer on a rubbed C_7 PI.

As seen in Fig.4, the SHG signal exhibits an anisotropy with mirror symmetry about the rubbing direction. This shows that the LC molecules are aligned along rubbing direction.



(a) S-in/S-out (b) S-in/P-out



(c) P-in/S-out (d) P-in/P-out

FIGURE 4. Polar plots of SHG from an 5CB monolayer adsorbed on a rubbed C_7 PI. The solid curves are theoretical fit.

CONCLUSION

We have used SFG vibrational spectroscopy and SHG to study surfaces of rubbed PIs with and without side alkyl chains as well as with and without an adsorbed 5CB monolayer. Analysis of the spectra indicates that rubbing causes alignment of PI backbones along the rubbing direction, but does not significantly affect the orientation of the alkyl side chains. The adsorbed LC monolayers are well aligned along the rubbing direction owing to their anisotropic interaction with the PI backbones. The side alkyl chains on the PI have a broad orientational distribution and significant amount of gauche defects. They exhibit little anisotropy induced by rubbing. However, with an LC monolayer adsorbed on the rubbed surface, these alkyl chains become preferentially oriented towards the rubbing axis with appreciably reduced amount of defects. Apparently, the LC monolayer is first aligned by the polymer backbones and then the alkyl chains by the LC monolayer. This is contradictory to the conjecture that rubbing induces alignment of the alkyl chains, which then align the LC monolayer.

Acknowledgments

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