

Nonlinear Optical Spectroscopic Studies of Polyimide Surfaces and LC Adsorbates

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Sum-frequency vibrational spectroscopy (SFVS) and second-harmonic generation (SHG) were used to probe the structures of rubbed surfaces of polyimide (PI) with and without side chains and the alignment of liquid crystal (LC) monolayers adsorbed on them. The SFVS spectra show clearly the presence of rubbing-induced anisotropy indicating the induced alignment of the PI backbones at the surface, but they hardly exhibit any rubbing-induced anisotropy. The results lead to the conclusion that while the PI backbones are aligned by rubbing, the orientation of alkyl side chains are hardly affected because they are projecting out normally from the surface with a broad orientational distribution. The SHG measurement indicates that the LC monolayers adsorbed on the polymer are more or less aligned along the rubbing direction. The order parameter of the LC monolayer on the rubbed PI with alkyl side chains is smaller than that on the PI without alkyl side chains.

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Polymer surfaces and interfaces play an important role in many applications. Mechanical rubbing of polymer-coated substrates is commonly used to homogeneously align liquid crystal (LC) films in the LC display industry.¹ It is believed that rubbing aligns the surface polymer chains, which in turn align the LC monolayer adsorbed on the polymer surface.² For better understanding of the alignment mechanism, it is important to characterize polymer surfaces and adsorbed LC monolayers on the surfaces at the molecular level.

We note that many analytical techniques have been employed to study polymer surfaces. Ellipsometry,³ optical retardation⁴ and infrared (IR) spectroscopy^{5,6} have all been used to evaluate structural anisotropy induced by rubbing in a surface layer of several tens of nm. Atomic force microscopy⁷ can reveal an image of a rubbed polymer surface, but the resolution is often not sufficient to resolve the surface molecular structure. Near-edge X-ray absorption fine structure spectroscopy⁸⁻¹¹ can probe a surface layer of 1 nm thick and has been most successful in providing surface structure of polymers. Sum-frequency vibrational spectroscopy (SFVS) is another viable technique for probing surface structures of materials, and has recently been applied successfully to rubbed polymer surfaces.¹²

Infrared-visible SFVS and second-harmonic generation (SHG) have been demonstrated to be effective tools to probe polymer surfaces and LC monolayers.^{13,14} 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.¹⁵

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,¹² 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 then 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.

Probing Techniques

The theory of SFVS and SHG for surface studies have been described elsewhere.¹³⁻¹⁷ 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

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

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 \tilde{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

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

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

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.

Experimental

The PIs used in our experiment were poly- n -alkyl-ptromellitic imide ($[-N-(CO)_2-\phi-(CO)_2-N-(CH_2)_6-]_n$) (P6), and poly-oxydiphenylene-pyromellitic imide ($[-(CO)_2-\phi-(CO)_2-N-\phi-O-\phi-N-]_n$) (PMDA-ODA). For the PI with alkyl side chains, we used (for example, $[-(CO)_2-\phi-(CO)_2-N-\phi-O-\phi-C(C_5H_{11}(CH_2)_k-CH_3)-\phi-O-\phi-N-]_n$, $k=0$: C₁ PI, $k=6$: C₇ PI). The polyimide samples with a layer thickness of ~ 20 nm were prepared by spin-coating. To obtain uniform layers, the polyamic acid solution was filtered with membrane filters. It was then dropped on a substrate to be spin-coated at 3500 rpm for 60 second. For the imidization reaction, the samples were baked at 250°C for 20 minutes. Rubbing to align the polyimide surface structure to the saturation level was carried out by a rubbing machine with a velvet cloth. Monolayers of 4'- n -alkyl-4-cyanobiphenyl (nCB, $n=5$ or 8) were deposited on the polyimide-coated substrates by evaporation at 70°C and monitoring SHG signals *in situ*. The SHG output from the surface appeared saturated when the 5CB deposition reached a monolayer.

The experimental setup for SFVS has been described elsewhere.¹⁸ Briefly, a pulsed Nd:YAG laser system was used to generate a visible beam at 532 nm and a tunable IR beam in the 3–6.2 μ m range, both having a 15 ps pulsewidth and a 20 Hz repetition rate. The two beams coming in from the air side overlapped at the sample surface, and the SFG output was detected in the reflection direction.

Results

We first consider the orientation of PI backbones on the rubbed PI surface. We have measured SFVS spectra of rubbed PI in the CO stretch vibrational region. Shown in Fig. 1 are the representative spectra of the CO stretch modes from a rubbed P6 PI 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 assigned to the antisymmetric and symmetric stretch modes of coupled CO groups on the imide ring, respectively.¹⁹ The spectra show explicitly the existence of rubbing-induced anisotropy in the surface structure of P6. Inspection of the spectra obtained with different polarization combinations shows that they originate from the two CO groups protruding out of the surface on the same side of the backbone. We observe the following results: 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, and hence the PI backbones, are aligned more or 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

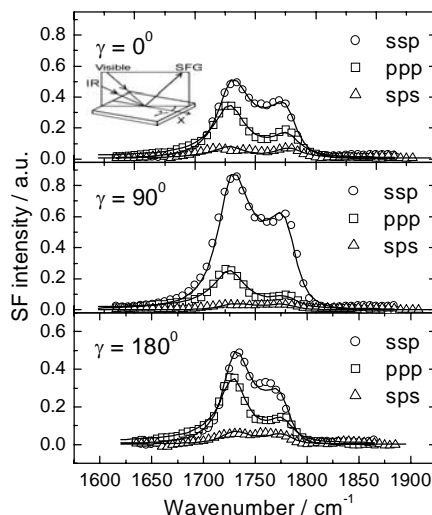


Fig. 1 SFVS spectra of a rubbed PI (P6) film in CO stretch region. Solid lines are fits to the experimental data following Eq. (5).

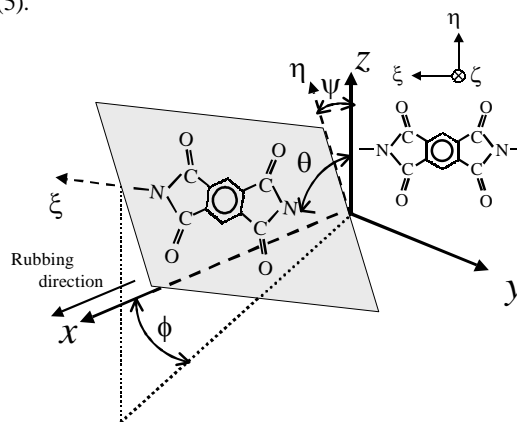


Fig. 2 Definition of laboratory (x,y,z) and molecular (ξ,η,ζ) coordinates of imide group. x is along rubbing direction and z the surface normal. The imide ring lies in the shadowed ξ - η plane.

a slight upward tilt of the backbones along the rubbing direction at the surface. These results provide direct evidence of an induced alignment of the PI backbones at the surface by rubbing. Similar results have also been obtained from a rubbed PMDA-ODA.²⁰

For the more quantitative analysis, we deduced the values of $A_q(\gamma)$ by fitting the measured SFVS spectra. The fitting was made simply by the fact that the peak intensities, peak positions and widths in the spectra do not change with sample orientational angle. From the results with the different polarization combinations, we could then deduce the nonvanishing elements of $(A_q)_{ijk}$. Knowing $(A_q)_{ijk}$ and using Eq.(6), we could determine an approximate orientational distribution function. The detailed analysis is described in Ref.[21]. We obtained, by assuming a Gaussian functional form, the following

$$f(\Omega) = C \exp \left[-\frac{(\theta - \theta_0)^2}{2\sigma_\theta^2} - \frac{(\phi - \phi_0)^2}{2\sigma_\phi^2} - \frac{(\psi - \psi_0)^2}{2\sigma_\psi^2} \right], \quad (7)$$

with $\theta_0=88^\circ \pm 1^\circ$, $\sigma_\theta=9^\circ \pm 2^\circ$, $\phi_0=0$, $\sigma_\phi=39^\circ \pm 5^\circ$, and $\psi_0=65^\circ \pm 25^\circ$ with σ_ψ varying from $\sim 12^\circ$ at $\psi_0=40^\circ$ to $\sim 76^\circ$ at $\psi_0=90^\circ$.

To see how mechanical rubbing affects the alkyl side chains of PI at the surface, we measured SFG spectra of C₁ and C₇ PI thin films before and after rubbing²² as shown in Fig. 3.

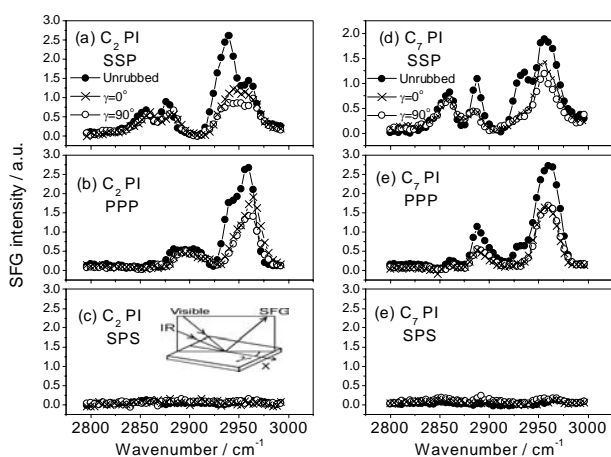


Fig. 3 SFVS spectra for C_1 [(a)-(c)] and C_7 [(d)-(f)] PIs before and after rubbing, with SSP [(a), (d)], PPP [(b), (e)], and SPS [(c), (f)] polarization combinations. Solid circles, open circles and crosses refer to data taken from unrubbed surfaces and rubbed surfaces with incident plane perpendicular and parallel to the rubbing direction, respectively.

The spectra were taken with and without rubbing, and the rubbed films were measured so that the incoming beams were parallel and perpendicular to the rubbing direction with the polarization combinations of SSP, PPP and SPS, respectively. Comparing the spectra between rubbed and unrubbed films, the intensity of the CH_3 symmetric stretch (r^+) and Fermi resonance (r^+_{FR}) modes of the rubbed films is decreased, and the intensity of CH_2 antisymmetric stretch (d^-) is also reduced in comparison to the unrubbed PI film especially in the case of C_7 PI. If the side chains are reoriented towards the rubbing direction, an anisotropy in the SFVS spectra would be expected. This was not obvious in Fig. 5. In the SPS spectra, the spectral features are hardly detectable. The results suggest that the alkyl side chains on PIs are not appreciably reoriented by rubbing, although SFG measurement on the imide cores these PIs do indicate alignment of the PI backbones by rubbing. 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. Alignment of the backbones can hardly affect the orientational distribution of the side chains.

Shown in Fig. 4 are the SFVS spectra (SSP) of a C_7 polyimide film with and without an LC monolayer on it. 5CB molecules were deuterated to avoid confusion of spectra in the CH range. The significantly reduced CH_2 peaks in the spectrum with the adsorbed LC monolayer indicates a significant reduction of gauche defects in the C_7 alkyl side chain. In the literature, the ratio of the peak strength of the CH_2 symmetric stretch (d^+) mode to that of the r^+ mode ($G=A_{d^+}/A_{r^+}$) in the SSP spectrum is often used as a measure to describe the relative conformational order of alkyl chains. From Fig. 4 (a) and (b), we obtain for the unrubbed C_7 polyimide surface without and with the 5CB monolayer, $G=0.76$ and 0.39 , respectively. The difference of these ratios would be considerably larger were it not for the fact that the cyclohexane links always contribute appreciably to the observed CH_2 peaks. The observed spectra allow us to conclude that the gauche defects of the alkyl side chains of a polyimide are greatly reduced upon adsorption of an LC monolayer. For the rubbed C_7 polyimide surface, the observed SFG spectra yield $G=1.17$ and 0.55 , without and with a 5CB monolayer.

To compare LC alignment on rubbed PI with and without alkyl side chains, we have probed the alignment of an adsorbed 5CB LC monolayer on rubbed P6, PMDA-ODA and C_7 using SHG with different polarization combinations.^{23,24} Here, we

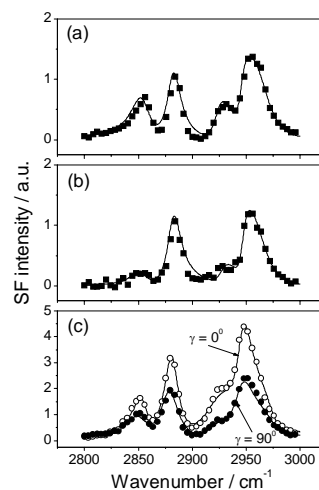


Fig. 4 SFVS spectra for an unrubbed C_7 PI film (a) without and (b) with a deuterated 5CB monolayer, and (c) SFVS spectra of a deuterated 5CB monolayer on a rubbed C_7 PI.

present the LC alignment on rubbed PMDA-ODA and C_7 PI. Fig. 5 shows the plot of SHG from LC monolayers deposited on the rubbed PMDA-ODA and C_7 PI as a function of γ for four different polarization combinations. The LC alignment on the rubbed P6 has also been reported in Ref. [23]. As seen in Fig. 5, the SHG signal exhibits an anisotropy with mirror symmetry about the rubbing direction. The LC monolayer is found to align well along the rubbing direction on the PI surfaces of both with and without alkyl side chains, because of its anisotropic interaction with the aligned PI backbones.

Discussion

The analysis of the CO stretch of the imide ring indicates that mechanical rubbing can effectively induce an alignment of the surface PI backbones along the rubbing direction with a slight upward tilt. The imide cores, however, are inclined towards the surface with a rather broad distribution. It is well known that rubbing can align polymer backbones at the surface. This has been found to be true for a number of polymers. What has been observed here in addition is that the alkyl side chains are not aligned by rubbing, which is not always the case.²⁵

An adsorbed LC monolayer, however, can align alkyl side chains of PI as explained in Fig. 4. Presumably this is because the LC monolayer is first aligned by the rubbed PI surface and then its interaction with the long 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.^{26,27}

In terms of how alkyl side chains affect the orientation of LC monolayers, we first compare the polar angle that can be deduced from fitting the SHG data with an assumed orientational distribution function. The detailed analytical process is described in Ref. [24]. The polar angle of the LC monolayer on the rubbed PMDA-ODA is 79° , while that on the rubbed C_7 PI is 73° . This suggests that alkyl side chains would give a higher pretilt angle. We can also discuss their order parameters. From the orientational distributions deduced from the SHG measurements, we can calculate the orientational order parameters for the LC monolayers on the rubbed PMDA-ODA and C_7 . The tensorial order parameter is defined in the usual way,

$$Q_{ij} = \frac{1}{N} \sum_{k=1}^N \frac{(3l_i^k l_j^k - \delta_{ij})}{2} = \left\langle \frac{1}{2} (3l_i l_j - \delta_{ij}) \right\rangle, \quad (8)$$

where l_i and l_j are components of a unit vector defining the longitudinal axis of a molecule and δ_{ij} is the unit matrix. Following the calculation described in Ref. [24], we find for an

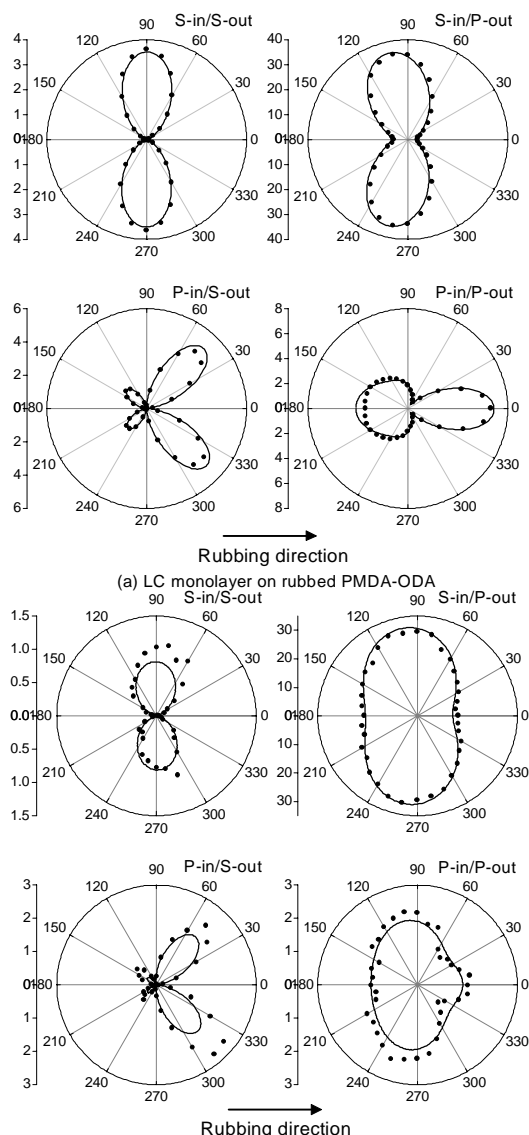


Fig. 5 Polar plots of SHG intensity from rubbed LC monolayer adsorbed on rubbed (a) PMDA-ODA and (b) C_7 PI. The solid curves are theoretical fit.

LC monolayer on the rubbed PMDA-ODA surface, the order parameter $S=0.52$, and for the LC monolayer on the rubbed C_7 PI, $S=0.30$. This indicates that the alignment of the LC monolayer is reduced by the alkyl side chains of PI.

Conclusion

We have used SFVS 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.

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