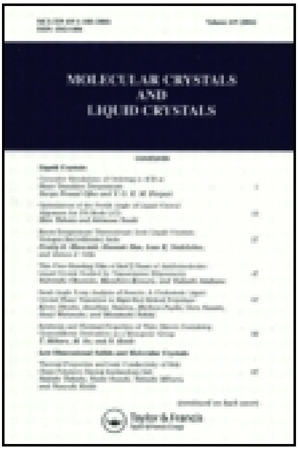

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Vibrational Spectroscopy of Rubbed Polymer Surfaces

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Vibrational Spectroscopy of Rubbed Polymer Surfaces

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Sum-frequency vibrational spectroscopy was used to probe rubbed polymer surfaces. The spectra allowed a quantitative determination of the orientational distribution of the surface polymer chains.

In many modern applications of polymers, the polymer surface or interface plays a most important role. For example, adhesion of a polymer to a metal or semiconductor is vital to electronic devices and systems, and is often governed by the orientation of molecular units at the polymer surface [1]. Bio-compatibility of the surface of a biopolymer determines whether the polymer is suitable as a material for artificial organs [2]. In liquid crystal (LC) industry, rubbed polymer surfaces are generally used to align LC films for LC displays. Rubbing presumably orients and aligns the surface polymer chains which in turn aligns the LC film [3]. A polymer surface with well aligned polymer chains could also serve as a template to grow highly ordered polymeric or organic crystalline films with superb mechanical, electrical, thermal, or optical properties [4]. To study how rubbing affects the polymer surface structure, a number of techniques have been used. Most of them, however, lack the necessary surface sensitivity and yield little information about the surface structure at the molecular level [5]. Recently, infrared-visible sum-frequency vibrational spectroscopy has been demonstrated to be a powerful and effective tool to study polymer surfaces [6, 7]. We have used the technique to probe surface alignment of polymer chains induced by rubbing [8].

As a second-order nonlinear optical process, sum-frequency generation (SFG) is highly surface specific, and is ideal as a surface probe, especially for surfaces of bulk media. For SFG surface vibrational spectroscopy, a

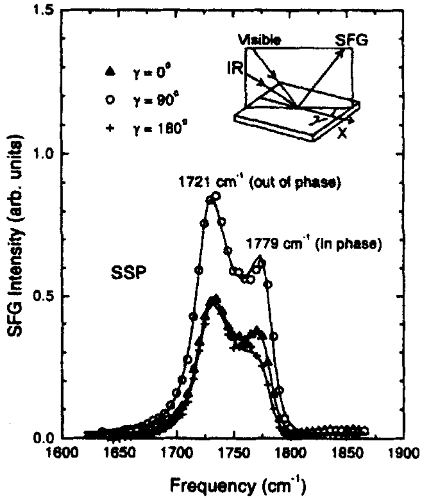

Figure 1: SFG vibrational spectra of a rubbed polyimide surface with the ssp polarization combination for $\gamma = 0°, 90°$, and $180°$. The inset describes the beam/sample geometry. The X axis represents the rubbing direction.

visible input laser pulse at ω_{vis} is arranged to overlap with a tunable infrared input pulse at ω_{ir} at a surface to generate the SF output. When ω_{ir} scans over vibrational resonance, the resonant enhancement of the output naturally yields the surface vibrational spectrum. Details on the theory and experimental arrangement of SFG spectroscopy have been described elsewhere [6]. In our work on polymers, the polymer films were spin-coated on a glass substrate and their surfaces were rubbed by a conventional rubbing machine. The vibrational spectra of the air/polymer interface were measured with different input/output polarization combinations and various sample orientations with respect to the incident plane of the beams. (See inset of Figure 1.)

Figure 1 presents the SFG vibrational spectra in the CO stretch range for a rubbed polyimide ($[\text{-N(CO)}_2\text{C}_6\text{H}_2\text{(CO)}_2\text{N(CH}_2)_6\text{-}]_n$) surface with

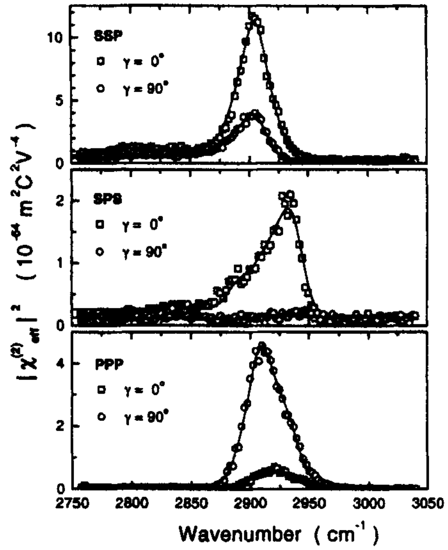

Figure 2: SFG vibrational spectra of a rubbed polyvinyl alcohol surface with various input/output polarization combinations for two sample orientations. The angle γ is defined in Figure 1.

the incidence plane parallel, anti-parallel, and perpendicular to the rubbing direction. The input/output polarization combination used was ssp, denoting s-, s-, and p-polarization for SF output, visible input, and infrared input, respectively. Two peaks appear in the spectra, corresponding to the symmetric and antisymmetric stretch modes of the two coupled CO groups on the imide ring. The spectra for the incidence plane parallel (or anti-parallel) and perpendicular to the rubbing direction are clearly different, showing the azimuthal anisotropy in the surface structure induced by rubbing. (Without rubbing, the spectra are azimuthally isotropic.) The stronger peaks for the $\gamma = 90°$ sample orientation indicate that the polymer chains are preferentially aligned along the rubbing direction with the imide planes inclined more towards the surface normal than parallel to the surface. SFG spectra with other input/output polarization combinations are consistent with this picture.

Figure 2 describes the SFG spectra in the CH stretch range with different input/output polarization combinations and azimuthal orientations for a rubbed polyvinyl alcohol (PVA, $[\text{-CH}_2\text{-CHOH-}]_n$) surface. The CH_2 symmetric and antisymmetric stretch modes, at 2907 and 2940 cm^{-1}, respectively, are most prominent in the spectra. They are much stronger than the bonded OH peak (not shown), indicating that the CH_2 groups on the polymer chains must have projected out of the polymer surface. The spectra in Figure 2 already permit a qualitative description of the orientation of the surface CH_2 groups. Since the CH_2 planes are perpendicular to the polymer chain, the surface chain orientation can also be determined. First, the CH_2 symmetric stretch can be excited only if the IR polarization has a component along the symmetric axis of CH_2. Therefore the weak CH_2 symmetric mode in the sps spectra for both $\gamma = 0^\circ$ and $\gamma = 90^\circ$ (actually true for all γ) is an indication that the CH_2 axis is nearly perpendicular to the surface plane. Then, the CH_2 antisymmetric stretch can be excited only if the IR polarization has a component in the CH_2 plane but perpendicular to the CH_2 symmetric axis. The very weak presence of this mode for $\gamma = 90^\circ$ and very strong presence for $\gamma = 0^\circ$ in all spectra is an indication that the CH_2 plane must be nearly perpendicular, and hence the polymer chain nearly parallel, to the rubbing direction. In the complete experiment, we actually measured the SFG spectra for many different values of γ from 0° to 360° [8]. Quantitative analysis of the spectra allows us to deduce the strengths of the two CH_2 stretch modes as functions of γ. They are related to the nonlinear polarizability components of CH_2 by a coordinate transformation together with an orientational distribution of CH_2. Since the nonlinear polarizability of CH_2 is known from estimate using Raman and infrared data on CH_2, the orientational distribution of CH_2 can be obtained approximately. We assume a Gaussian function for the orientational distribution

$$f(\theta,\phi,\psi) = C\exp\left[-\frac{(\theta-\theta_0)^2}{2\sigma_\theta^2} - \frac{(\phi-\phi_0)^2}{2\sigma_\phi^2} - \frac{(\psi-\psi_0)^2}{2\sigma_\psi^2}\right] \qquad (1)$$

where C is a normalization constant, θ, ϕ and ψ are angles defined in Figure 3, $\phi_0 = \psi_0 = 0^\circ$ (by symmetry), and θ_0, σ_θ, σ_ϕ, σ_ψ are parameters to be determined. From the experimental data, we find

$$\begin{aligned} \theta_0 &= 2.5^\circ \pm 0.7^\circ\ , \\ \sigma_\theta &= 26^\circ \pm 5^\circ\ , \end{aligned}$$

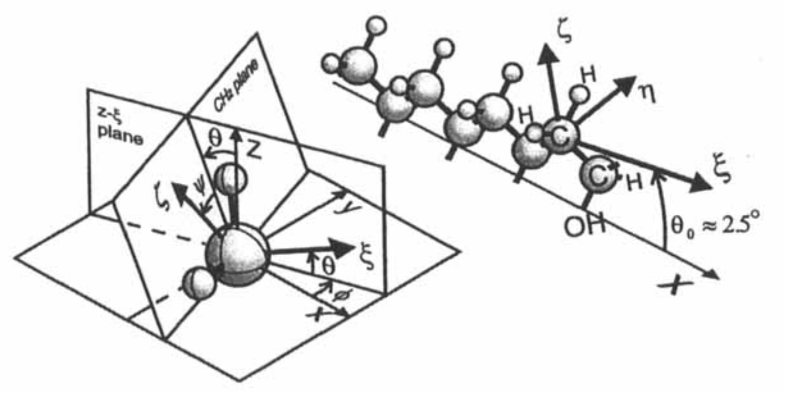

Figure 3: The CH_2 orientation in the lab coordinates and the PVA chain orientation at the polymer surface.

$$\begin{aligned} \sigma_\phi &= 27° \pm 5° , \\ \sigma_\psi &= 35° \pm 5° . \end{aligned}$$

The above result shows how the CH_2 groups orient on the surface. From the CH_2 orientation, we then learn that the surface PVA chains must lie along the rubbing direction with a rather narrow angular spread and an average 2.5° backward tilt (See Figure 3).

Physically, in the rubbing process, the fiber tips of the rubbing cloth must have pulled the surface segments of the polymer chains along the rubbing direction. This causes the surface chain segments to lie preferentially in the rubbing direction. The small backward tilt of the chain orientation indicates that some of the surface chain segments were pulled from region beneath the surface.

The examples presented here demonstrate the power and usefulness of the SFG surface vibrational spectroscopy technique for studies of polymer surfaces and interfaces. Applications of this technique to a large variety of relevant problems in polymer surface science can be anticipated.

Acknowledgments

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