

Orientations of phenyl sidegroups and liquid crystal molecules on a rubbed polystyrene surface

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Surface-specific sum-frequency vibrational spectroscopy and second-harmonic generation have been used to study the structure of a rubbed polystyrene (PS) surface and the orientation of 4'-n-pentyl-4-cyanobiphenyl (5CB) liquid crystal molecules on it. The results show that the phenyl sidegroups are well aligned by rubbing in the direction perpendicular to rubbing but tilt from the surface normal with a broad distribution. Although the PS surface is nonpolar, the 5CB molecules appear to adsorb on PS preferentially with the terminal cyano group facing the PS surface. © 2002 American Institute of Physics. [DOI: 10.1063/1.1435069]

Mechanical rubbing of polymer surfaces is a technique commonly used to align liquid crystal (LC) films for LC devices.¹ Recent studies have found that rubbing aligns the surface polymer chains^{2,3} which in turn align the LC molecules adsorbed on the surface and then molecules throughout the bulk film.⁴ Infrared-visible sum-frequency vibrational spectroscopy (SFVS) and second-harmonic generation (SHG) are effective probes for such studies. 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) and polyimide (PI) have shown that the surface polymer chains are well aligned along the rubbing direction, and so are the LC molecules adsorbed on them.^{3,5} Rubbing of a polystyrene ($[-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-]_n$: PS) surface, however, is known to induce an LC film alignment perpendicular to the rubbing direction.^{6,7} 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. The latter must interact more effectively with the adsorbed LC molecules than the main chains in inducing the LC alignment. To confirm this picture, we have conducted SFVS on rubbed PS and SHG on LC adsorbed on rubbed PS. Here, we report our findings.

The experimental setup and the theoretical background for SFVS and SHG have been described elsewhere.⁸ The samples used were isotactic PS films with layer thickness of ~ 400 nm were prepared by spincoating. To obtain uniform layers, the PS solution in toluene (Scientific Polymer Products, Inc.) was filtered by membrane filters. It was then dropped on a substrate to be spincoated at 3500 rpm for 60 s. The samples prepared were baked at 170 °C for 60 min. Rubbing of a PS surface was carried out by a rubbing machine with a velvet cloth.

Figure 1 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° , and 180°) 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), PPP, and SPS. The spectra exhibit five aromatic C-H vibrational stretches associated with the phenyl sidegroups. They appear at 3024 cm^{-1} , 3036 cm^{-1} , 3057 cm^{-1} , 3069 cm^{-1} , and 3084 cm^{-1} which can be assigned to the ν_{20b} , ν_{7a} , ν_{7b} , ν_2 , and ν_{20a} vibrational modes, respectively.⁹

SFVS on PS films has recently been reported by several groups.^{10,11} In all investigations, it was concluded that the

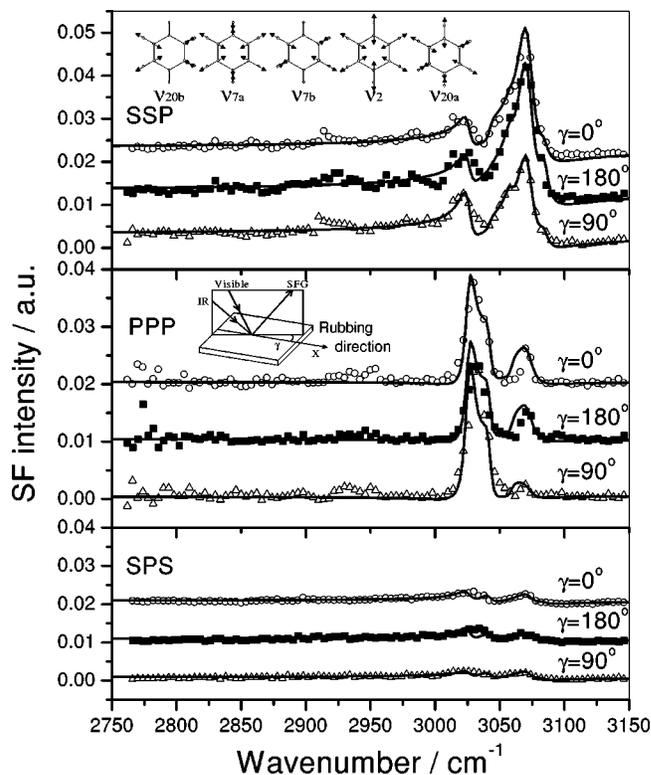


FIG. 1. SFVS spectra with (a) SSP, (b) PPP, and (c) SPS polarization combinations for a rubbed isotactic PS film. The inset of the top graph shows the normal mode vibrations of the aromatic C-H stretch. The angle γ between the incidence plane and the rubbing direction describes the azimuthal orientation of the sample. The spectra are normalized by the SF signal from a z-cut quartz.

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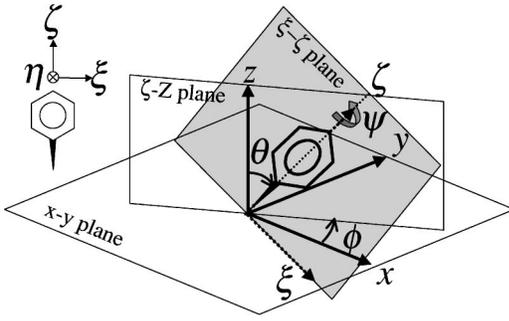


FIG. 2. Geometric relations between the molecular coordinates and the lab coordinates. The rubbing direction is defined along the x axis.

observed SF signal is dominated by contribution from the PS/air interface. Therefore in our case, we can consider SF signals in Fig. 1 as coming mainly from the phenyl sidegroups projecting out of the PS surface.

We now focus on the symmetric stretch ν_2 at 3069 cm^{-1} of the phenyl group as it is most prominent in the spectra. This mode can be strongly excited by the IR field along ζ in the molecular coordinates described in Fig. 2 and by Raman excitation with a symmetric polarizability tensor component in the ξ - ζ plane. Thus, the nonlinear polarizability for SFVS in resonance with this mode is dominated by components $\alpha_{\xi\xi\xi}^{(2)}$ 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 $\gamma = 180^\circ$ 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 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 using the the same analysis described in Ref. 3. We present only a brief sketch of the procedure next. The nonlinear susceptibility $\tilde{\chi}^{(2)}$ responsible for SFVS can be written as

$$\tilde{\chi}^{(2)}(\omega_{\text{ir}}) = \tilde{\chi}_{\text{NR}}^{(2)} + \sum_q \frac{\tilde{A}_q}{(\omega_{\text{ir}} - \omega_q) + i\Gamma_q}, \quad \text{with}$$

$$\tilde{A}_q = N_s \int \tilde{a}_q(\Omega) f(\Omega) d\Omega. \quad (1)$$

Here, $\tilde{\chi}_{\text{NR}}^{(2)}$ denotes the nonresonant contribution, \tilde{a}_q , ω_q , and Γ_q are the strength, resonant frequency, and damping constant of the q th resonant vibrational mode, Ω represents a set of orientational angles (θ , ϕ , and ψ) for a phenyl ring, N_s is the surface density of the phenyl groups, and $f(\Omega)$ is an orientational distribution function of the phenyl groups. The C_{2v} symmetry of a rubbed surface without forward-backward asymmetry allows only five independent nonvanishing elements of the third-rank tensor A_q for each vibra-

TABLE I. Parameters used in the calculation of $(A_q)_{ijk}$, and measured and calculated nonvanishing tensor elements $(A_q)_{ijk}$ for the ν_2 mode of the phenyl stretch. $\epsilon'_{\text{SF}} \approx \epsilon'_{\text{vis}} \approx 1.6$ and $\epsilon'_{\text{IR}} \approx 1.2$.

	ω_{SF}	ω_{vis}	ω_{IR}
Wavelength $\lambda/\mu\text{m}$	0.457	0.532	3.26
Refractive index n (polystyrene)	1.61	1.59	1.56
n (fused quartz)	1.47	1.46	1.41
Beam angle β/deg	46.5	45.0	57.0
Fresnel factor L_{xx}	0.861	0.906	0.982
Fresnel factor L_{yy}	0.598	0.695	0.554
Fresnel factor L_{zz}	$1.139/\epsilon'_{\text{SF}}$	$1.094/\epsilon'_{\text{vis}}$	$1.019/\epsilon'_{\text{IR}}$
	Measured		Calculated
A_{xxz}	3.1 ± 0.2		3.1
A_{yyz}	3.9 ± 0.2		3.9
A_{zzz}	3.3 ± 0.3		3.2
$A_{xzx} = A_{zxx}$	1.2 ± 0.2		1.2
$A_{yzy} = A_{zyy}$	1.9 ± 0.3		2.0

tional mode: $(A_q)_{xxz}$, $(A_q)_{yyz}$, $(A_q)_{zzz}$, $(A_q)_{xzx} = (A_q)_{zxx}$, and $(A_q)_{yzy} = (A_q)_{zyy}$.³ They can be determined, together with the other parameters from fitting of the SFVS spectra obtained with different sample orientations (γ) and input/output polarization combinations (P). For the ν_2 mode of PS, the deduced values of $(A_q)_{ijk}$ and the other parameters are listed in Table I. To find $f(\Omega)$, we know that, for the ν_2 mode, the dominant tensorial elements of \tilde{a}_q in the molecular coordinates are $(a)_{\xi\xi\xi}$ and $(a)_{\xi\xi\zeta}$, which can be transformed into the lab coordinates (i, j, k) as functions of $\Omega = (\theta, \phi, \text{and } \psi)$. Then knowing the values of $(A_q)_{ijk}$ and assuming that $f(\Omega)$ can be approximated by a Gaussian form

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

we can determine $(a)_{\xi\xi\xi}/(a)_{\xi\xi\zeta}$ and all the parameters in Eq. (2). We have found $(a)_{\xi\xi\xi}/(a)_{\xi\xi\zeta} = 1.68 \pm 0.15$, $\phi_0 = 90^\circ$, $\sigma_\phi = 49^\circ \pm 5^\circ$, $\psi_0 = 90^\circ$, $\sigma_\psi = 68^\circ \pm 9^\circ$, and θ_0 in the range from $72^\circ \pm 6^\circ$ to $83^\circ \pm 7^\circ$ with σ_θ varying from $\sim 3^\circ$ at $\theta_0 = 72^\circ$ to $\sim 17^\circ$ at $\theta_0 = 83^\circ$. To show consistency of the result, we used the deduced $f(\Omega)$ to re-evaluate $(A_q)_{ijk}$. The calculated values of $(A_q)_{ijk}$ also listed in Table I are indeed close to those deduced from the measurement.

We also studied the orientation of 4'-*n*-pentyl-4-cyanobiphenyl (5CB) adsorbed on PS using SHG. The LC molecules were deposited on PS by thermal evaporation. During the evaporation, the *in situ* measurement showed that SHG increased monotonously and then leveled off.¹² 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.¹³ As shown in Fig. 3(a), 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 ϕ of $\chi^{(2)}$ for the two cases.

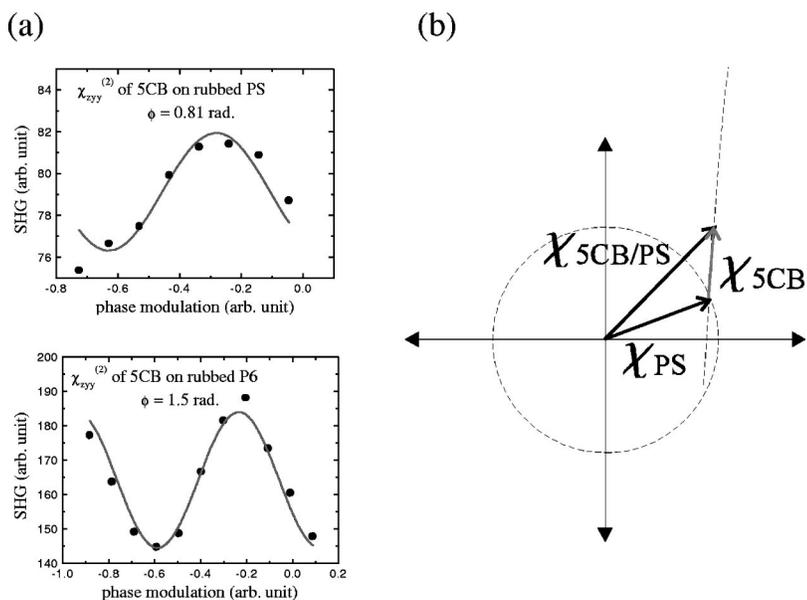


FIG. 3. (a) Experimental data and line fits for SHG phase measurements of 5CB monolayers on rubbed PS and P6, respectively. (b) Schematic phase relationship of $\chi^{(2)}$ for a 5CB monolayer on a PS surface. $\chi_{PS}^{(2)}$, $\chi_{5CB}^{(2)}$ and $\chi_{PS/5CB}^{(2)}$ are the susceptibilities of the PS surface, the 5CB monolayer, and the 5CB monolayer on rubbed PS, respectively.

SHG from 5CB on P6 is dominated by contribution from 5CB that adsorb with the CN terminal facing P6.^{14,15} Therefore, $\chi_{5CB}^{(2)} \sim \chi_{5CB/P6}^{(2)}$. The vector diagram of $\chi^{(2)}$ in Fig. 3(b) 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.

It is interesting to note that we have found equal SHG signals (in reflection) from homogenous 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.³ 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.

In conclusion, we have shown that mechanical rubbing effectively aligns the surface 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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