Sum-Frequency Vibrational Spectroscopy Study of Photoirradiated Polymer Surfaces

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ABSTRACT: Sum-frequency vibrational spectroscopy can be used to study photoinduced structural change at polymer surfaces. Results on rubbed and unrubbed surfaces of poly(vinyl cinnamate) (PVCi), a well-known photopolymer, show that polarized UV irradiation dimerizes rather than isomerizes the protruding cinnamoyl side chains at the surfaces and creates significant surface structural anisotropy needed in many applications. Anchoring energy measurements of a nematic liquid crystal film on PVCi irradiated by low UV dosages yield results in good correlation with the observed spectral anisotropy.

Introduction

Polymer surfaces play an essential role in modern science and technology. Their properties are generally governed by their molecular structures. For many applications, one would like to modify surface properties of polymers without affecting the corresponding bulk properties. This is the case, for instance, when polymer surfaces are used as templates for aligning deposited biological molecules or liquid crystal (LC) films.[1] Photoinduced modification of polymer surfaces being the only effective noncontact method has attracted much attention,[1−5] but how they are modified at the molecular level has not been well explored due to the limitation of common surface probes. The case of poly(vinyl cinnamate) (PVCi) is an example.

PVCi and its derivatives form a well-known class of photopolymers.[6] It is known that UV irradiation of PVCi and derivatives induces surface structural anisotropy that can align LC films,[7−10] but there is a long-standing controversy on whether dimerization[6−8] or isomerization[9,10] of the cinnamoyl side chains (sketched in parts a and b of Figure 1, respectively) is the dominant photoreaction. Past efforts to identify their surface structural change induced by UV excitation of the cinnamoyl side chains relied mostly on UV/IR spectroscopy.[4,7−10] The observed suppression of the band at ∼300 nm and growth of the band at shorter wavelength in UV absorption spectra was taken as evidence of the dimerization process that reduces C═C to C−C.[4,8] It was supported by IR spectroscopy showing suppression of the C═C stretch mode at 1637 cm^{-1} and a shift of the C═O stretch mode from 1712 to 1735 cm^{-1}.[7,8] Ichimura et al., on the other hand, observed UV spectral change suggesting that isomerization dominated at low UV doses.[9] LC alignment switchable by successive UV irradiation with different polarizations was also considered as support of the isomerization mechanism.[9,10] These spectroscopic measurements carried out on thin films, however, are not surface-specific as both UV and IR have large penetration depth in PVCi, and the information deduced may not apply to the surface. Olenik et al. used the surface-specific second-harmonic generation technique to probe an irradiated PVCi surface.[11] They could obtain from the measurements the surface density and orientational order parameter of the residual *trans*-cinnamoyl chains, but the method was not sensitive to the converted species.

Recently, surface-specific sum-frequency vibrational spectroscopy (SFVS) has been demonstrated to have the unique capability of producing vibrational spectra directly related to the molecular structure of the polymer surface.[12,13] We describe here how the technique can be employed to probe photoinduced surface modification of unrubbed and rubbed PVCi surfaces by polarized UV irradiation and yield results clearly in favor of the dimerization process. At low UV dosages, the observed photoinduced change of spectral anisotropy of the CH and C═C stretch modes of the *trans*-cinnamoyl side chains correlates well with results of LC anchoring energy measurement, indicating that the undimerized side chains are responsible for LC alignment. When the surface is heavily dimerized, the spectral anisotropy becomes difficult to detect, but the structural anisotropy of the surface can still be recognized by the existence of a weak anchoring energy.

Theoretical Basis

The basic principle of SFVS is described elsewhere.[13] The SF signal generated by inputs at ω_{vis} and ω_{IR} from a surface in the reflected direction is proportional to $|\chi_S^{(2)}(\omega_{\text{SF}} = \omega_{\text{vis}} + \omega_{\text{IR}})|^2$, where $\chi_S^{(2)}$ denotes the surface nonlinear susceptibility and exhibits resonant enhancement as ω_{IR} approaches a surface vibrational mode. Input/output polarization dependence of a resonant peak provides information on the average orientation of the moiety that contributes to the peak. A more detailed description of the basic theory of SFVS and detailed procedures to analyze a spectrum are given in the Supporting Information.

Experimental Section

Our SFVS setup was the same as the one depicted in ref 13. A schematic of the beam geometry is given in Figure 1c. The PVCi material was purchased from Scientific Polymer Products, Inc. Films ∼100 nm thick were prepared by spin-coating followed by thermal annealing. Both rubbed and unrubbed films were used in the study. Rubbing was performed on films using a velvet-wrapped roller.[14] It aligned the main chains and the phenyl rings on the side chains parallel and perpendicular to the rubbing direction, respectively,[14] making the subsequent photoinduced structural change easier to monitor. The UV irradiation source was the fourth-harmonic output at 266 nm from an Nd:YAG laser. It had a pulse width of 25 ns and irradiated the sample with 1 mJ/cm^2 per pulse at 2 Hz.

To measure the azimuthal anchoring energy, we used ∼5−6 μm thick films of nematic 4,4′-pentylcyanobiphenyl (5CB) sandwiched between two PVCi-coated substrates that had been treated by rubbing and/or photoirradiation in the same way. The easy axes of

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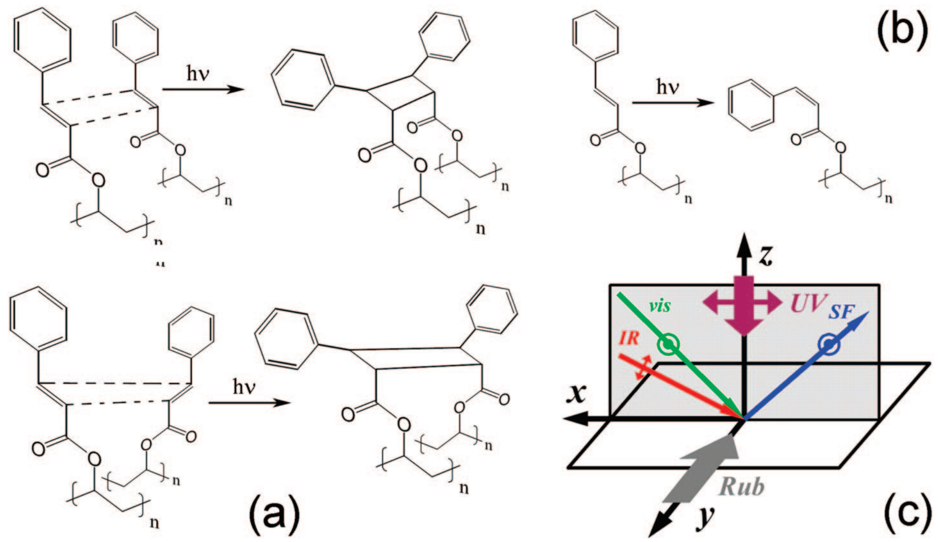

Figure 1. Schematics of (a) molecular structures showing dimerization and (b) isomerization of PVCi side chains; (c) the geometry of beams, rubbing direction and UV polarization, showing the SSP measurement with rubbing along *y* and UV along *x*.

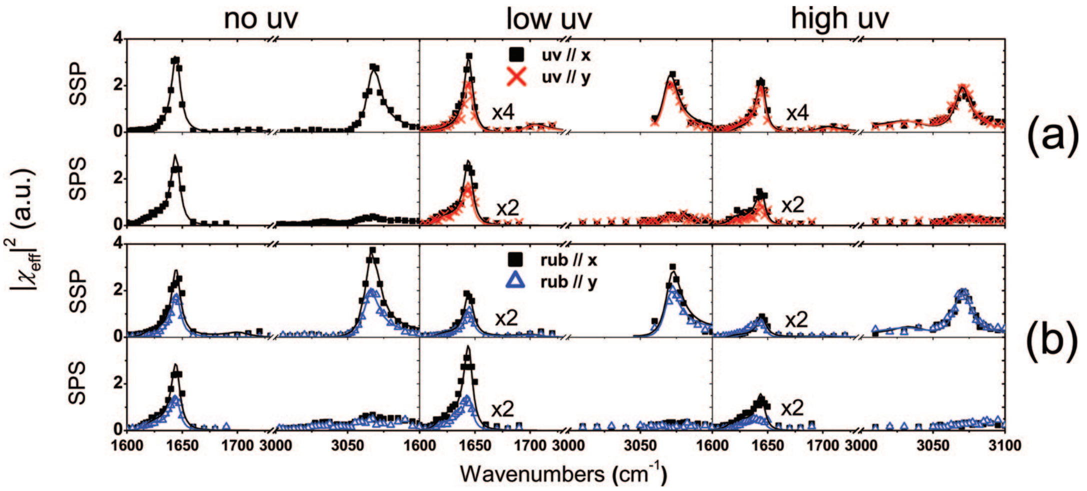

Figure 2. SF vibrational spectra of CH(ν_2) and C═C stretch modes of unrubbed (a) and rubbed (b) PVCi surfaces without UV irradiation (column 1) and at low (column 2) and high (column 3) UV dosages. The beam polarization combinations are SSP and SPS. The directions of rubbing and linear polarization of UV irradiation are along either *x* or *y* as specified. C═C spectra without UV irradiation are magnified by 4 times with respect to C−H for clarity and further magnified after irradiated by UV (specified in each frame). Solid curves are theoretical fits (described in the Supporting Information).

the two substrate surfaces were aligned at an angle $\varphi_1 = 89 \pm 0.2°$, but because of the twist elastic energy of the nematic LC, the twist angle, φ_2, of LC alignment across the cell was less than φ_1.[15,16] Measurement of the polarization rotation of light passing through the LC cell, following the procedure described in ref 16, allowed us to measure φ_2 with an accuracy of ∼0.05°. The anchoring energy *A* was then obtained using the expression[16]

$$A = 2K_{22}/(d \sin \Delta\varphi)$$

where K_{22} is the twist elastic constant, *d* is the cell spacing, and $\Delta\varphi = \varphi_2 - \varphi_1$.

The sample preparation and measurements were all carried out under room temperature and ambient conditions. The possibility of having PVCi surface modified by photoinduced oxidation upon UV irradiation was excluded by observing that PVCi films UV-irradiated in air and in dry N_2 gas have the same LC aligning power.

Results and Discussion

SF Spectra and Surface Molecular Structures. A representative set of SF vibrational spectra of PVCi surfaces in the 1600−1750 and 3000−3100 cm^{-1} range is presented in Figure 2. They were taken with all beams in the *x*−*z* plane, where *z* is along the surface normal (Figure 1c). The SF spectra are specified by the polarization combination SSP (denoting S-, S-, and P-polarized SF output, visible input, and IR input, respectively) or SPS. In the 1600−1750 cm^{-1} range, the C═C stretch mode at ∼1640 cm^{-1} is most prominent in both SSP and SPS, and the C═O stretch appears as a weak broad peak at ∼1710 cm^{-1}.[7] In the 3000−3100 cm^{-1} range, the prominent peak is the ν_2 CH stretch mode of the phenyl ring in SSP at 3070 cm^{-1}.[14] The peak intensity of a mode depends on the beam polarizations through their projections onto the contributing moiety, which allows deduction of average orientation of the moiety, as described in the Supporting Information.

Figure 2a displays a set of spectra from unrubbed PVCi surfaces. Without UV irradiation (Figure 2a, column 1), analysis of the polarization dependence of the CH(ν_2) mode revealed that the phenyl rings have their 2-fold axes along the surface normal with a distribution width of ∼30°. One would then expect from the molecular structure of the cinnamoyl chain that the polar angle of its C═C bond should be centered at 60°, which agrees with the value ∼40°−70° deduced from the polarization dependence of the C=C stretch mode. Linearly polarized UV irradiation excites the C=C bonds and reduces the strengths of both CH(ν_2) and C=C modes. At low dosage it induces an azimuthal anisotropy in the orientations of the moieties with respect to the UV polarization (Figure 2a, column 2). With increasing UV dosage, the anisotropy decreases (Figure 2a, column 3), and eventually the C=C mode vanishes completely, while the CH(ν_2) mode approaches a nonzero value. This is a clear indication that UV-induced dimerization of the cinnamoyl chains is the predominant process at the surface, as it converts the C=C double bonds to single bonds and tilts the phenyl rings toward the surface together with an azimuthal rotation of ~90°,[8] resulting in an appreciable reduction of the intensity of CH(ν_2) in SSP and C=C in both SSP and SPS. If isomerization (Figure 1b) were important,[9,10] the CH(ν_2) and C=C modes would merely have their azimuthal anisotropy altered if *cis*-isomers should be unstable at the surface and rapidly transform back to the *trans*-isomers,[9,10] or the C=C stretch mode should remain but shift to lower frequency if resultant *cis*-isomers were sufficiently stable.[17] Yet neither agrees with our observation. Figure 2b shows similar effects of UV irradiation on rubbed PVCi surfaces. Rubbing initially created anisotropy in the surface structure (Figure 2b, column 1) by aligning the main chains along the rubbing direction as in the case of poly(vinyl alcohol).[18] Analysis of the polarization dependence of the CH(ν_2) mode revealed that the planes of the cinnamoyl side chains are aligned perpendicularly to the rubbing direction.[14] The UV irradiation, both polarized parallel and perpendicular (not shown) to the rubbing direction, reduces the overall intensity of the C=C mode by converting C=C to C−C, and the altered spectral anisotropy reflects the anisotropic distribution of the residual C=C bonds.

SF Spectral Anisotropy. To see more clearly how the CH(ν_2) and C=C modes of PVCi decrease in strength upon UV irradiation, we plot in Figure 3 the peak intensity of the modes in SSP and SPS spectra versus UV dosage for various cases. In all cases, the peak strength decreases rapidly with UV irradiation at sufficiently low UV dosages but levels off after several hundred mJ/cm^2 of UV dosage, toward a finite value for CH(ν_2) and zero for C=C, as expected from full dimerization of the side chains at the surface. The spectral anisotropy seen in Figure 3 at low UV dosages comes mainly from azimuthal distribution of *trans*-cinnamoyl chains not yet dimerized and disappears upon full dimerization. One may expect that since the dimerized cinnamoyl chains are preferentially aligned perpendicularly to the UV polarization, the anisotropic distribution of the phenyl rings should be detectable in the spectra. This is unfortunately not the case because the phenyl ring planes on dimerized chains are tilted away from the surface normal and have an average orientation facing toward the surface, thus yielding little anisotropy in the SSP spectrum (see details in the Supporting Information). Nonetheless, the fully dimerized surface is still structurally anisotropic, as can be verified by LC anchoring energy measurement that will be discussed later.

At low UV dosages, it is possible to see from Figure 3 how the surface structural anisotropy sets in as UV irradiation dimerizes the cinnamoyl chains. Let us focus on the C=C mode, although the discussion can be extended to the CH(ν_2) mode. Remember that $x-z$ is the incident plane for SFVS, and the signal of C=C stretch in both SSP and SPS spectra comes mainly from undimerized cinnamoyl chains inclined toward $y-z$. For unrubbed surfaces (Figure 3, row 1), the spectra show that under linearly polarized UV irradiation the C=C mode appears to have an anisotropic distribution favoring the direction perpendicular to the linear polarization, as expected from the fact that photodimerization through electronic excitation of C=C is stronger if the UV polarization is more along the cinnamoyl chains. For rubbed surfaces, the same is true except that there is an initial anisotropy created by rubbing in favor of cinnamoyl planes perpendicular to rubbing.

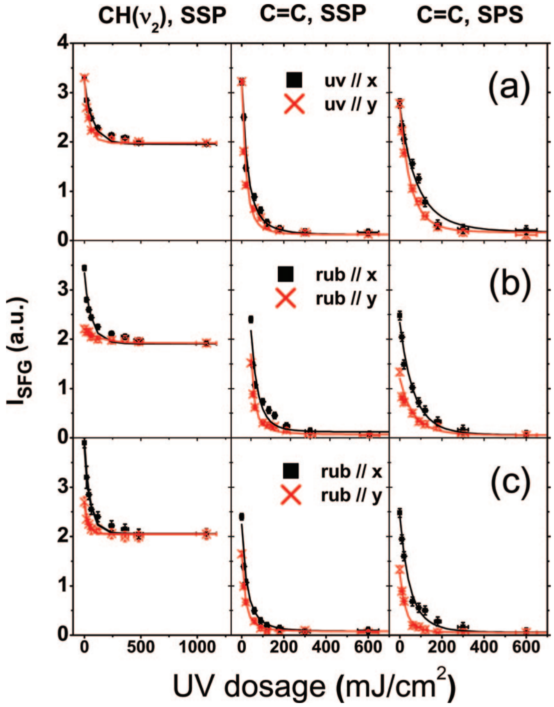

Figure 3. Decay of peak strengths of the CH(ν_2) and C=C modes described in Figure 2 with increasing UV dosage on PVCi surfaces. Frames (a), (b), and (c) refer respectively to unrubbed and rubbed surfaces with UV polarization perpendicular and parallel to rubbing. Input/output polarizations for SFVS and rubbing direction are labeled on each frame or column. Solid curves in column 2 and 3 are fits using eq 2. Solid curves in column 1 are guides for the eye.

We can understand the experimental data in Figure 3 quantitatively assuming the dimerization process dominates upon UV irradiation. We sketch here the approach and leave the details in the Supporting Information. Again we focus on the C=C stretch mode. Upon depletion of the double bonds, the surface number density N of C=C with orientation specified by the polar and azimuthal angles θ and ϕ decreases at a rate

$$\mathrm{d}N(\theta,\phi,t)/\mathrm{d}t = -N(\theta,\phi,t)P(\theta,\phi) \tag{1}$$

with $P(\theta,\phi) = C(\hat{e}_{\mathrm{UV}}\cdot\hat{e}_{\mathrm{D}})^2 I_{\mathrm{UV}}$. Here, I_{UV} is the UV intensity, C a constant, and $\hat{e}_{\mathrm{UV}}$ and $\hat{e}_{\mathrm{D}}$ are respectively the unit vectors along directions of the UV polarization and the transition dipole moment of C=C excitation at 266 nm. Because the π-electron delocalization of the cinnamate group extends from the phenyl ring through C=C to the carboxyl group,[19] $\hat{e}_{\mathrm{D}}$ should be close to the direction of C−C=C−C, which is at 43° from the C=C double bond. We assume the angle between $\hat{e}_{\mathrm{D}}$ and C=C be β and use it as an adjustable parameter in fitting. Fom eq 1 we find $N_0(\theta,\phi,U_{\mathrm{UV}}) = N_0(\theta,\phi)\exp[-C(\hat{e}_{\mathrm{UV}}\cdot\hat{e}_{\mathrm{D}})^2 U_{\mathrm{UV}}]$ with $U_{\mathrm{UV}} = \int_0^t I_{\mathrm{UV}}\mathrm{d}t$ being the UV dosage and $N_0(\theta,\phi) = N_0 f_\phi(\phi)$ the initial surface distribution of C=C bonds. We can then calculate the decay of the SF signal with increasing U_{UV}. For SPS and SSP cases, we have

$$I_{\mathrm{SPS}}(U_{\mathrm{UV}}) \propto \left| \int \cos\theta \sin^2\theta \cos^2\phi (a_{\zeta\zeta\zeta} - a_{\xi\xi\zeta}) N(\theta, \phi, U_{\mathrm{UV}})\, \mathrm{d}\Omega \right|^2$$
$$I_{\mathrm{SSP}}(U_{\mathrm{UV}}) \propto \left| \int \cos\theta\, (\sin^2\theta \cos^2\phi (a_{\zeta\zeta\zeta} - a_{\xi\xi\zeta}) + a_{\xi\xi\zeta}) N(\theta, \phi, U_{\mathrm{UV}}) \mathrm{d}\Omega \right|^2 \tag{2}$$

Here, (ξ, η, ξ) denotes the molecular coordinates of the C=C bond with ζ along the bond, and $a^{(2)}_{\xi\xi\zeta} = a^{(2)}_{\eta\eta\zeta} = ra^{(2)}_{\zeta\zeta\zeta}$ with $r \sim 0.3$[20] are the nonvanishing SF polarizability elements of the C=C bond. In the calculation, we approximate $f_\theta(\theta)$ and $f_\phi(\phi)$ using orientation information deduced from the polarization dependence of SF spectra. We take $f_\theta(\theta)$ as constant for $\theta \sim$ 40°−70° and zero otherwise. For an isotropic surface, we have $f_\phi(\phi) = 1/2\pi$, and for a rubbed surface, we have $f_\phi(\phi) = [1 + d \cos(2(\phi - \gamma_{\mathrm{rub}}))]/2\pi$ with $d \sim 0.3-0.4$. As shown in Figure 3, the decay curves (solid lines) calculated using eq 2 with $\beta \sim$ 30°−40° fit reasonably well with the experimental data in all cases. This is quite satisfactory considering the complexity of the problem, approximation made in the model calculation, and uncertainty of the measurements. We notice that for all cases in Figure 3 it takes no more than 100 mJ/cm^2 to reduce C=C bonds by half (with SF signal drops to ~25% of the initial values). This is much less than that (>225 mJ/cm^2) observed in PVCi bulk films,[7,8] presumably because the protruding cinnamoyl side chains are more orderly arranged than those in the bulk, increasing the probability of dimerization when excited.

LC Anchoring Energy Measurements. LC films deposited on PVCi (or derivatives)-coated substrates can be aligned by surface structural anisotropy of the substrate via directional interaction between LC molecules and surface cinnamoyl chains. Using the method described earlier, we carried out measurements of azimuthal anchoring energies of nematic 5CB on various PVCi surfaces. Figure 4 shows measured anchoring energy versus UV dosage for unrubbed surface and rubbed surfaces with UV polarization parallel and perpendicular to rubbing. The result correlates well with the observed SF spectral anisotropy before saturated dimerization sets in and indicates the existence of azimuthal anisotropy on highly dimerized surfaces.

On the unrubbed isotropic surface (Figure 4a), polarized UV irradiation induces a finite anchoring energy for preferential LC alignment perpendicular to the UV polarization. It first increases rapidly with UV irradiation, showing good correlation with the observed growth of spectral anisotropy of CH(ν_2) and C=C modes depicted in Figure 3a. On the highly dimerized surface, the observed anchoring energy comes mainly from the anisotropic distribution of dimerized side chains, which have a preferred orientation perpendicular to the UV polarization.[8] Since dimerized chains have weaker LC aligning power compared to *trans*-cinnamoyl chains,[8] the LC energy anchoring eventually decreases as the degree of dimerization increases.

On the rubbed PVCi surface, initially, rubbing induces a preferred orientation of cinnamate chains perpendicular to rubbing and yields a finite and relatively strong anchoring energy (defined as positive) for LC alignment, which is rapidly suppressed by UV irradiation polarized perpendicular to rubbing (Figure 4b). This correlates well with the observed reduction in SF spectral anisotropy (Figure 3b) and is clearly due to the preferential dimerization of cinnamate chains initially oriented along the UV polarization. With increasing UV dosage, more side chains are dimerized. Both the dimerized side chains and the remaining undimerized ones have preferred distribution along the rubbing direction. Thus, the preferred LC alignment switches from perpendicular to parallel to rubbing, with the anchoring energy switched from positive to negative (the latter defined for LC alignment parallel to rubbing).

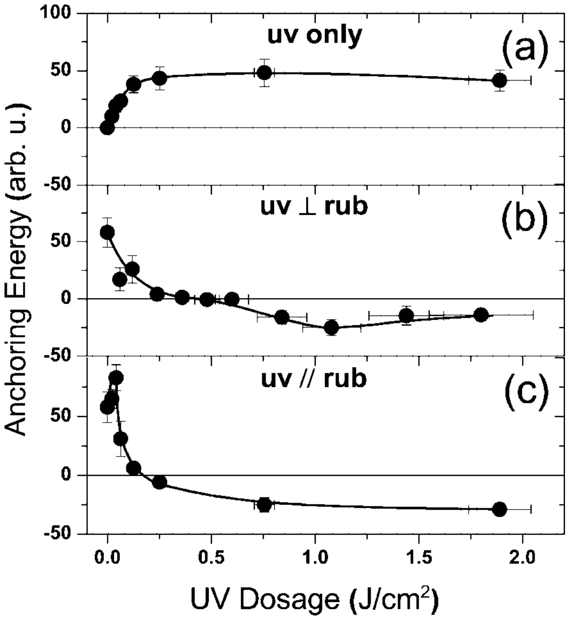

Figure 4. Azimuthal anchoring energy of 5CB on unrubbed and rubbed PVCi surfaces as a function of UV dosage. Solid lines are guides to the eye.

For UV irradiation polarized along rubbing, Figure 4c shows that the anchoring energy for LC alignment perpendicular to rubbing first increases slightly (not observed in SF spectra due to limited sensitivity), as UV irradiation preferentially dimerizes those side chains oriented along rubbing and enhances the overall anisotropy created by rubbing. Further irradiation dimerizes also side chains oriented more perpendicularly to rubbing, leading to the rapid decay of the positive LC anchoring energy. Again, switching of LC alignment to parallel to rubbing (switching of anchoring energy from positive to negative) happens when the surface is highly dimerized, with the surface anisotropy dominated by the orientation distribution of dimerized chains biased toward rubbing. In all cases, the LC alignment on a fully dimerized surface was along the preferred azimuthal orientation of the dimerized chains, which is perpendicular to the UV polarization. We note that the anchoring energy of a fully dimerized surface is significantly weaker than that of a rubbed undimerized surface, indicating that the former has a much weaker LC aligning power than the latter.

With small UV dosage, it was observed that the direction of LC alignment on PVCi (or derivatives)-coated substrates could be repeatedly switched by successive UV irradiations polarized along different directions.[9,10] Such observation is not in contradiction with the dimerization mechanism. Before the PVCi surface is appreciably dimerized, the LC alignment is dominated by the azimuthal orientation distribution of the undimerized *trans*-cinnamoyl, which can be altered by switching the UV polarization. After the surface is fully dimerized, however, switching of LC alignment can no longer occur. This is indeed what we have found in our experiment.

Conclusion

We have carried out a comprehensive study on both the structural change and mechanism of photoreactions occurring at a polymer surface using surface-specific SFVS. We probed the C=C and CH(ν_2) vibrational stretch modes of protruding cinnamoyl side chains on rubbed and unrubbed PVCi surfaces and monitored their changes upon UV irradiation. The results show conclusively that UV irradiation of PVCi dimerizes, rather than isomerizes, the cinnamoyl chains at the surface, reorients their phenyl rings with ring planes tilted toward the surface, and aligns them preferentially perpendicular to the UV polarization. With the help of anchoring energy measurement on 5CB films deposited on PVCi-coated substrates, we are able to correlate the structural anisotropy of the PVCi surface with 5CB alignment. While spectral anisotropy of a fully dimerized surface is difficult to detect, the anisotropy energy measurement can still reveal the existence of structural anisotropy at the surface, although its LC aligning power is relatively weak.

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Supporting Information Available: Analyses of the molecular orientation, spectral anisotropy, and dimerization dynamics. This material is available free of charge via the Internet at http://pubs.acs.org.

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