Sum-Frequency Generation Spectroscopy of Cinnamate Modified Cellulosic Polymer at the Air–Water Interface

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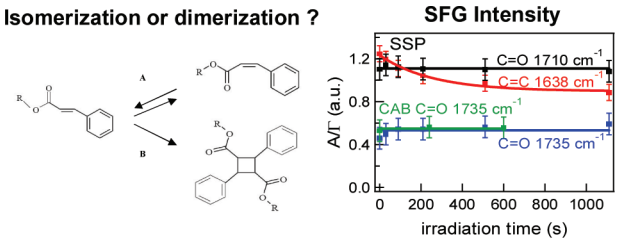
ABSTRACT: Monolayers of a cellulosic polymer bearing cinnamate groups were characterized at the air–water interface by combining isotherm measurements, Brewster angle microscopy, and infrared–visible sum-frequency generation (SFG) spectroscopy. This spectroscopic technique was used to detect the photochemical behavior of the cinnamate groups upon UV photoirradiation of the monolayers. From the disappearance of the C═C mode and the absence of a change in the C═O mode, it could be concluded that isomerization is the dominant photoreaction for a monolayer of this polymer. This conclusion was corroborated by a comparison of the spectra of the monolayer after irradiation with spectra measured for monolayers spread from preirradiated solutions, for which it is known that isomerization is the main process.



1. INTRODUCTION

The photochemical processes involved in thin films of poly(vinyl cinnamate) and its derivatives have extensively been investigated owing to their potential applications in optical memory devices and in liquid crystal display technology.[1,2] Upon UV photoirradiation, cinnamate groups can follow two photochemical pathways: trans–cis isomerization and dimerization (Figure 1). Polymers bearing cinnamate groups can thus be cross-linked through the carbon–carbon double bonds which undergo a (2 + 2) cycloaddition reaction. As a result of the dimerization reaction occurring upon irradiation by linearly polarized UV light, thin films of such polymers have shown their ability to align liquid crystals homogeneously.[2]

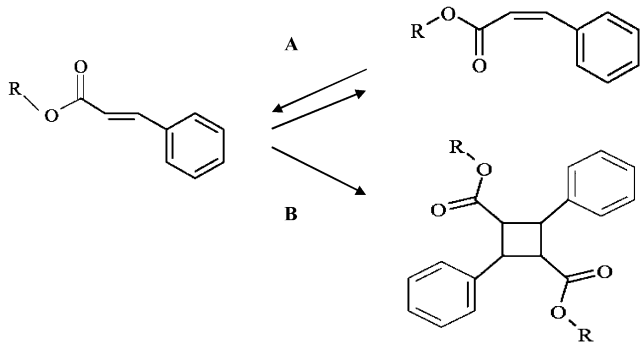


Figure 1. Scheme of the possible pathways upon photoirradiation of cinnamate groups: (A) isomerization and (B) dimerization.

Depending on the chemical structure of the photosensitive molecule, one of the two photochemical reactions, isomerization or dimerization, can occur preferentially.[3] In particular, Ichimura et al.[3] have shown that in spin-coated films of polymethacrylate polymers with cinnamate side chains the predominance of either of the two photoprocesses depends on the regioisomerism of the cinnamate groups. Isomerization takes place more favorably for cinnamate residues at the ortho-position due to steric hindrance, while dimerization is predominant in case of lateral attachment at the para-position. The photochemical behavior of cinnamate derivatives physisorbed as monolayers at the graphite/liquid interface has also been shown to strongly depend on the molecular structure.[4] Indeed, using scanning tunneling microscopy, Abdel-Mottaleb et al. have evidenced that cinnamic acid derivatives symmetrically substituted by two octadecyl chains undergo photodimerization while this reaction does not proceed with an asymmetrically (octadecyl/decyl) substituted molecule. This has been attributed to the difference in self-organization of the compounds at the interface which allows or prevents the reactive centers to approach each other.

The preparation method of the polymer films can also play a significant role in the photochemical behavior upon UV exposure. As an example, Ohtani et al.[5] have shown that the photoreactivity of cinnamate groups in dioctadecyldimethylammonium/cinnamate ions self-assembled films varies accord-

ing to the heat treatment of the films before photoirradiation which leads to different molecular organizations. Also, in a previous work, we have reported that cinnamate groups of modified cellulosic polymers mainly undergo either dimerization in spin-coated films or isomerization in networks synthesized with an exogeneous cross-linker.[6]

Different methods can be used to determine the main photochemical pathway involved upon UV photoirradiation of cinnamate modified molecules. With UV−vis spectroscopy the effect of the UV dosage can be studied. Photoisomerization between the trans and cis forms, both with a distinct absorption spectrum, gives rise to an isosbestic point in UV spectra for different irradiation time. Photodimerization manifests itself by the deviation from the isosbestic points upon prolonged UV irradiation, as evidenced by Ichimura et al. for spin-coated films of polymers bearing cinnamate groups.[3] For monolayers on a solid substrate or at the air−water interface, UV−vis spectroscopy no longer allows to detect the involved photochemical reaction. Infrared−visible sum-frequency generation spectroscopy (SFG), which is inherently specific to surface species, has been shown to be a powerful technique to study monolayers. In such an experiment an infrared and visible beam are overlapped on the sample, and the sum-frequency light is detected. If the infrared beam is resonant with a molecular vibration, the signal is enhanced. In this way SFG allows detecting the orientation and conformational changes at the molecular level.[7,8] Chen et al. have used SFG to characterize UV photoinduced structural changes at the surface of rubbed and unrubbed poly(vinyl cinnamate) spin-coating films.[9] Olenik et al. have reported the study of the photochemical processes in poly(vinyl cinnamate) dip-coated films submitted to linearly polarized UV light by coupling bulk and surface characterizations using respectively UV−vis spectroscopy and second harmonic generation.[10] They concluded that the photoreaction kinetics in the bulk and on a surface are very similar. In addition, the sensitivity of SFG has been shown to allow direct characterization of trans−cis isomerization of azobenzene containing molecules deposited as monolayers at the air−water interface.[11,12]

In this paper, we report on SFG characterization of Langmuir monolayers of a cellulosic polymer modified by cinnamate groups. Both unmodified (CAB) and cinnamate grafted (CABg) acetobutyrate cellulose polymer monolayers have first been characterized by means of isotherm measurements and Brewster angle microscopy observations. Then SFG spectra have been recorded before and after UV photoirradiation in order to study the photochemical processes involved by cinnamate groups at the air−water interface.

2. EXPERIMENTAL SECTION

Materials. Cellulose acetate butyrate (CAB: 6 mol % acetate, 77 mol % butyrate, and 17 mol % hydroxyl; M_n = 20 000 g mol^{-1}) was purchased from Acros. Cinnamate grafted CAB (CABg: 6 mol % acetate, 77 mol % butyrate, 4 mol % hydroxyl, and 13 mol % cinnamate) was synthesized according to a procedure previously described.[6] It thus contains one cinnamate group every 2.5 cellulosic units.

Isotherm Measurements. Isotherm measurements were carried out on a 601BAM Langmuir−Blodgett trough from Nima. The experiments were performed at room temperature (20 °C). An appropriate amount of CAB or CABg chloroform solution (0.3 mg mL^{-1}) was spread onto the water subphase. After 10 min waiting, the monolayers were compressed using a continuous barrier speed of 4 × 10^{-2} nm^2 molecule^{-1} min^{-1}. The isotherms are presented as a function of the mean area per cellulosic repeat unit.

In order to follow the surface pressure evolution at constant molecular area during photoirradiation of the monolayers, a high-pressure Hg lamp (100 W, Lot-Oriel) equipped with a glass filter (λ > 280 nm) was used.

BAM. BAM observations were performed by means of the apparatus developed by Meunier.[13] The air−water interface is illuminated at the Brewster angle (53°) with a collimated laser beam of p polarization, and the reflected beam is received by a microscope. First-order phase transitions can be visualized in this way. Moreover, with an analyzer placed in the path of the reflected light, optical anisotropies due to the tilt of the molecules or to the anisotropy of the unit cell in untilted phases can be detected.[14]

SFG. For the SFG experiments roughly 1 W from a ∼100 fs TiSa laser system (Legend, Coherent Inc.) is frequency converted in an optical parametric generation/amplification (TOPAS, Light Conversion), resulting in tunable infrared pulses with a full width half-maximum bandwidth of around 150 cm^{-1} and a power of ∼3 and 6 μJ at wavelength of 6 and 3.4 μm, respectively. Another part of the laser output was spectrally narrowed to ∼15 cm^{-1} (∼20 μJ) with an etalon to provide the spectral resolution of the experiment. The SFG light was frequency dispersed in a monochromator and detected with an electron-multiplied charge coupled device (EMCCD, Andor Technologies). All SFG spectra were normalized to a reference spectrum taken from z-cut quartz to account for the frequency-dependent IR power. The incident angles of the IR and vis beams were 40° and 35°, respectively, with respect to the surface normal. The experiments were performed in a homemade Teflon-coated trough of 7 × 7 cm^2 or a round Teflon trough with a diameter of 3 cm. The surface pressure was measured with a commercially available tensiometer (Kibron, Finland), and it was controlled by the amount of polymer solution in $CHCl_3$ spread on the water surface. The monolayer was irradiated by a Hg(Ne) calibration lamp (Newport) through a glass plate (λ > 280 nm), resulting in an incident power per area of around 0.1 mW cm^{-2}. To avoid light-induced generation of ozone, which was observed to react with the C═C double bond of the cinnamate moiety, the setup is continuously flushed with nitrogen. For the preirradiation experiments a small glass container with a solution of CAB (or CABg) in chloroform was irradiated with either the high-pressure Hg lamp or the Hg(Ne) calibration lamp with a UV dose of ∼1 mW/mL. Both lamps gave identical results.

To obtain peak amplitudes and frequencies, the SFG spectra were modeled with a Lorentzian line shape model (see e.g. ref 12 and references therein) in which every resonance is described with a Lorentzian with amplitude A_n, frequency ω_n, and line width $2\Gamma_n$. The different Lorentzian peaks are summed up and added to the nonresonant contribution consisting of an amplitude A_0 and a phase φ with respect to the resonant part in the following way:

$$\chi^{(2)}(\omega_{IR}) = \chi^{(2)}_{NR} + \chi^{(2)}_{R}(\omega_{IR}) = A_0 e^{i\varphi} + \sum_n \frac{A_n}{\omega_{IR} - \omega_n + i\Gamma_n}$$

The SFG intensity is subsequently given by

$$I_{SFG}(\omega_{IR}) \propto |\chi^{(2)}(\omega_{IR})|^2 I_{vis} I_{IR}$$

The relative phase of the peaks was checked with the maximum entropy method (MEM). This method allows retrieving phase information from intensity spectra.[15]

Raman and FTIR. The sample for Raman and FTIR measurements consisted of CABg polymer films deposited either on a CaF_2 substrate for Raman experiments or on a KBr pellet for FTIR characterizations. The film was made by dropwise addition of a chloroform solution of the polymer, either nonirradiated or 30 min preirradiated in the same way as described above.

For the Raman experiments, a 100 mW 785-nm laser (CrystaLaser, Reno, NV) is bandpass-filtered, introduced into a modified inverted microscope (Eclipse Ti-U, Nikon) by a 45° ultrasteep dichroic mirror and focused onto the sample with an objective (CFI Plan Achromat 40×, NA 0.65, Nikon). The Raman light is collected in a backscattering geometry by the same objective and is passed through the dichroic mirror and a 785 nm long-pass filter to remove the pump beam. The Raman light is spatially filtered through a 25 μm confocal pinhole, dispersed by a spectrometer, and detected on a deep-depletion CCD (Andor Technologies).

The FTIR spectra were recorded with a Brüker spectrometer (Equinox 55) in the range 1575−1800 cm^{-1} by averaging 10 consecutive scans with a resolution of 2 cm^{-1}.

3. RESULTS AND DISCUSSION

CAB and CABg Monolayers at the Air−Water Interface. The chemical structure of the unmodified CAB and cinnamate grafted CABg polymers is presented in Figure 2.

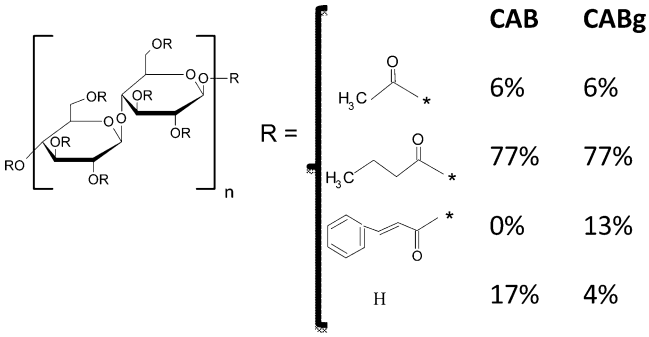


Figure 2. Chemical structure of CAB and CABg.

Figure 3 shows the isotherms measured for CAB and CABg monolayers spread over pure water at room temperature. The molecular area corresponds to the mean area per cellulosic repeat unit. Brewster angle microscopy images for CABg at different stages of the isotherms are also shown in Figure 3. Similar images were obtained for CAB.

The isotherms of the two polymers exhibit similar general features. At zero surface pressure, a coexistence between a gaseous phase (dark) and a liquid phase (bright) is detected by BAM (Figure 3). Then, at molecular areas per repeat unit lower than 75 $Å^2$ for CAB and 87 $Å^2$ for CABg, a first increase in surface pressure is noticed. BAM (result not shown) reveals that the gaseous phase has disappeared and the films appear homogeneous, indicating that the polymer monolayers exhibit a liquid analogous phase. Then for both monolayers, a change in slope is detected above a surface pressure close to 6 mN/m. As visualized by BAM, it is marked by a strong increase in the monolayer rigidity, since film movements are no longer detected. This increase in surface pressure can thus be attributed to the transition from the 2D liquid phase to a condensed state. Moreover, by addition of an analyzer in the path of the reflected light, a slight optical anisotropy is evidenced for a narrow range of analyzer angles (Figure 3b). Regions with different shades of gray are observed with a very low contrast. This slight optical anisotropy probably indicates the organization of the cellulosic units in a lattice, each shade of gray corresponding to a different lattice orientation. This unexpected result indicates that in the condensed state the cellulosic rings display a strong organization at the air−water interface. Then, upon further compression, an inflection is noticed at surface pressures close to 27 mN/m for the CAB monolayer and only 18 mN/m for CABg. The corresponding molecular areas of 32 and 42 $Å^2$, respectively, are too small to be compatible with a single monolayer, as evidenced by BAM (Figure 3). Indeed, three-dimensional bright structures appear. The decrease in the occurring collapse surface pressure for CABg with respect to CAB (18 vs 27 mN/m) probably results from the decrease in polymer hydrophilicity due to cinnamate grafting.

The limiting molecular area corresponding to a monolayer, obtained by extrapolating the slope of the isotherm in the condensed state to zero surface pressure (Figure 3), is significantly increased upon cinnamate grafting, from 48 to 68 $Å^2$ per repeat unit. This indicates that the increase in limiting area is determined in this case by cinnamate side chains interactions. The value of 48 $Å^2$ obtained for the CAB monolayer is lower than the calculated 60 $Å^2$ occupied area of a single anhydroglucose ring.[16] Taking into account that some small hydroxyl functions are replaced by even larger butyrate and acetate groups, this suggests the tilt of the modified glucose ring planes for the CAB polymer with respect to the water surface.[17] Such a behavior was evidenced by Kasai et al. for substituted alkylcellulose ethers having long alkyl side chains.[18] Indeed, for one octadecyl chain per cellulosic repeat unit, the authors deduced from the isotherm a limiting molecular area in the condensed state of 33 $Å^2$. The tilt of the glucose ring planes was then confirmed by thickness measurements of the transferred monolayer using X-ray reflectivity. The same behavior was evidenced for octadecylcellulose ethers having two and three chains per repeat unit. In addition, the limiting molecular area of 48 $Å^2$ measured for the CAB monolayer is noticed to be quite close to the value of 55 $Å^2$ obtained for the monolayer of the cellulose ether bearing two octadecyl chains, in agreement with the two acetate and butyrate groups, in average, per cellulosic unit of the CAB polymer.[18]

Basque et al. reported isotherms of butyl cellulose spread at 25 °C.[19] This polymer has a structure rather similar to the CAB polymer but nevertheless a different molecular weight (M_w = 30 000 g mol^{-1} instead of 20 000 g mol^{-1} for CAB). Surprisingly, its isotherm appears quite different. The pressure starts only to rise at a molecular area of 60 $Å^2$ (75 for CAB). From a molecular area of 60 to 47 $Å^2$, the butyl cellulose monolayer displays a liquid analogous phase. Below 47 $Å^2$ a surface pressure plateau is detected at 15.5 mN/m, which was assigned to the formation of multilayers. These aggregates appear at an area per repeat unit of 47 $Å^2$ very close to the 48 $Å^2$ measured for the CAB monolayers. The differences between the isotherms of CAB and butylcellulose could indicate that the C═O groups of the CAB polymer, which can form hydrogen bonds with the hydroxyl side chains or with the water underneath the polymer, play a significant role in the polymer organization at the air−water interface.

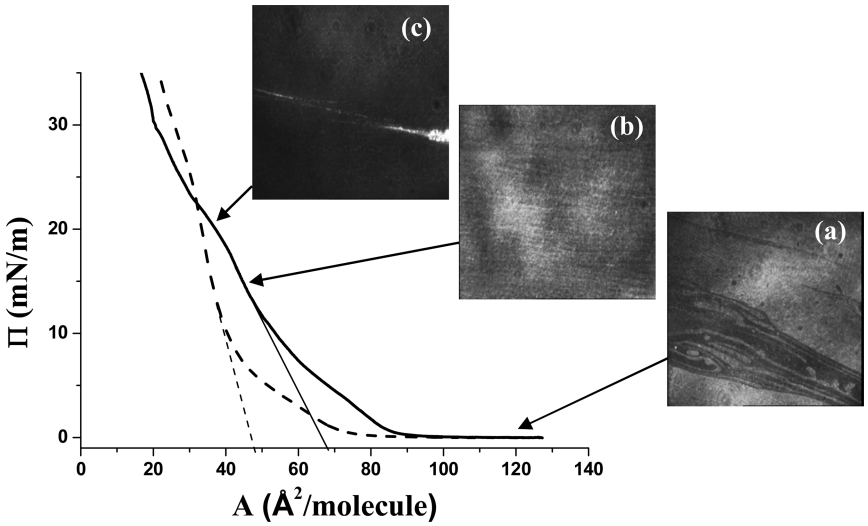


Figure 3. Isotherms of CAB (thick dotted line) and CABg (thick solid line) monolayers over pure water. BAM images (600 μm × 600 μm) recorded at different stages of the CABg isotherm: π = 0 mN/m, A = 120 Å^2 (a), π = 15 mN/m (b), π = 22 mN/m (c). Image (b) was obtained with an analyzer in the path of the reflected light. The extrapolations to zero surface pressure of the slope of the isotherms in the condensed state are indicated as a thin dotted and solid line.

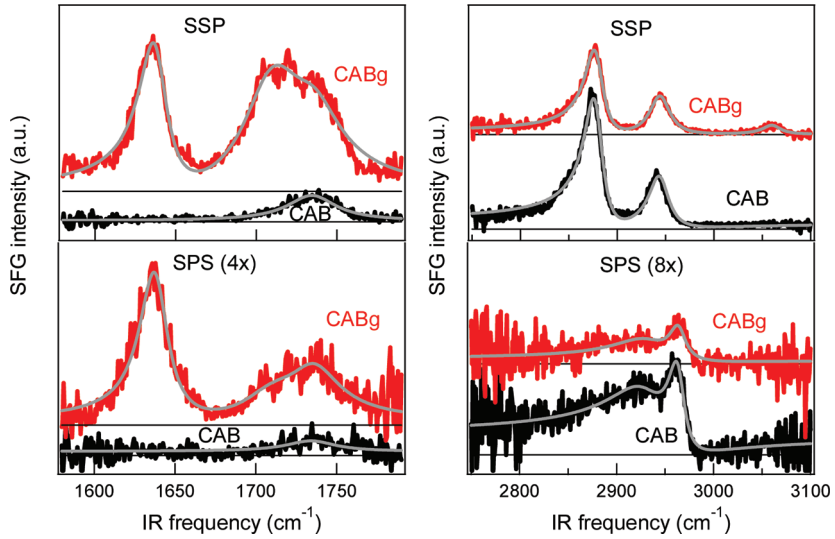


Figure 4. SFG spectra recorded in the range 1550−1800 cm^{-1} (left) and 2750−3100 cm^{-1} (right) for CAB (black) and CABg (red) monolayers at a surface pressure of 10 mN/m, for SSP (up) and SPS (bottom) polarization. The gray lines are fits to a Lorenztian line shape model (see Experimental Section). The data have been offset for clarity, the thin black lines denoting the zero lines. The structure on the 1700−1750 cm^{-1} bands originates from residual water vapor present in the IR beam path.

To obtain information about the interfacial molecular arrangement, SFG spectra were recorded for the CAB and CABg monolayers spread at a surface pressure of 10 mN/m corresponding to the condensed state. Figure 4 shows the spectra obtained in the range 1550−1800 cm^{-1} for two polarization combinations, SSP and SPS, together with fits using the Lorentzian line shape model described in the Experimental Section. The spectra for both CAB and CABg show a broad band around 1735 cm^{-1} that can be attributed to the nonconjugated ester carbonyl group present in the butyrate and acetate groups.[20,21] It cannot be excluded that this band consists of more than one peak, but for simplicity we chose to describe it as one band. For CABg the band is broadened at low frequency (1710 cm^{-1}) due to the conjugated ester carbonyl group in the cinnamate side chain.[20,21] In the CABg spectra, a subsequent band related to the vinylene C═C stretching vibration of the cinnamate moiety is detected at 1638 cm^{-1}.[9,21] The C═C mode for the phenyl ring, expected at ∼1600 cm^{-1},[9,21] is not present in the SFG spectra. Comparing the CABg spectra obtained for the two polarization combinations, it can be observed that with respect to the C═C stretch mode the C═O peak intensity decreases significantly in SPS polarization. As such a polarization corresponds to an infrared beam polarized parallel to the water surface, this means that the C═O groups are, in average, more perpendicular to the surface than the C═C group of the cinnamate.

The SFG spectra of CAB and CABg monolayers spread at 10 mN/m were also recorded in the range 2750−3100 cm^{-1} (Figure 4). The polymers were now spread on D_2O instead of H_2O to avoid interference of the water band (above 3000 cm^{-1}) with the phenyl and/or vinylene CH modes. Both the spectra from CAB and CABg in SSP polarization have peaks at

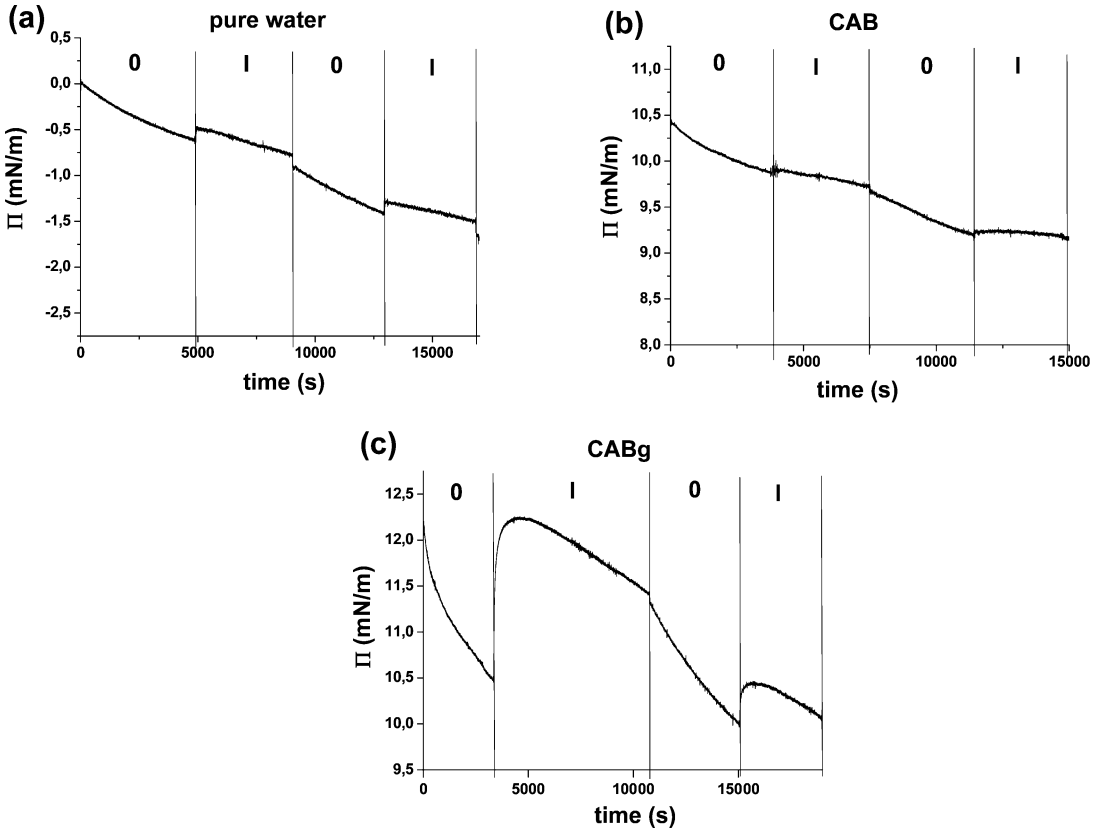


Figure 5. Evolution of the surface pressure at constant area upon two cycles alternating UV photoirradiation (I) and absence of exposure (0) for pure water (a), CAB (b), and CABg (c) monolayers.

2879 and 2945 cm^{-1} which can be assigned to the CH_3 symmetric stretch and CH_3 Fermi resonance of an aliphatic side chain, respectively.[11,22,23] As the butyrate side chain is most dominant in both molecules, we assign these two peaks to the CH_3 group of butyrate. Moreover, due to the proximity of the C═O group, the CH_3 vibration of the acetate side group will be significantly shifted to lower frequency. An additional low-intensity band corresponding to the cinnamate phenyl ring C−H stretching mode is detected at 3061 cm^{-1} in the CABg spectrum.[9] In SPS polarization, the signals are roughly 10 times smaller, and fitting with the Lorentzian line shape model as described in the Experimental Section resolved that the spectra consist of two peaks at 2933 and 2964 cm^{-1}. The former is a typical frequency for a symmetric stretch vibration of a CH_2−O−R feature and as such assigned to the CH_2 group in between the six-ring and the O−R group in our molecule.[24] The mode at 2964 cm^{-1} could originate from the asymmetric CH_3 modes in the butyrate side chain.[11,22,23] Interestingly, the intensity of the SFG spectrum in the CH region for the CAB monolayer is roughly 1.5 times as high as for the CABg monolayer. The fits reveal that the amplitude of the CH_2 and CH_3 modes is on average roughly 1.3 times higher for the CAB molecule, which could indicate that the butyrate side chains are more aligned in the CAB polymer compared to the CABg polymer. Apparently, the cinnamate group could introduce disorder in the butyrate (and maybe acetate) side chains, which may lead to the higher limiting molecular area for CABg as observed in the pressure isotherm (see above). However, the disorder in the side groups seems not to disturb significantly the macroscopic organization of the polymer: BAM images (discussed above) show a strong organization.

Photoirradiation of CAB and CABg Monolayers. Upon irradiation with UV light, cinnamate groups in the CABg polymer can undergo isomerization and/or dimerization. In dilute chloroform solutions, it was recently concluded from UV−vis and ^1H NMR spectroscopies that isomerization is the predominant process.[6] In order to study the effect of this photoirradiation on CABg polymers spread at the air−water interface, the monolayers were submitted to UV exposure. All the SFG measurements were conducted at an initial surface pressure of 10 mN/m.

First, the surface pressure variation induced by UV photoirradiation was measured at constant monolayer area. Figure 5 shows the curves obtained for the CABg monolayer through two cycles of alternating photoirradiation and absence of exposure. For comparison, the same measurements were performed with the CAB monolayer as well as for the bare water surface. Over pure water, one can first notice that the apparent surface pressure decreases continuously as a result of water evaporation during the several hours experiment duration. Then, the UV photoirradiation is marked by a sudden and slight surface pressure rise of 0.13 mN/m. This variation is completely reversed by turning off the lamp. It can be attributed to the heating of the pressure sensor filter paper. The curve recorded for the unmodified CAB monolayer is indistinguishable from the one measured for the bare surface. In contrast, for the CABg monolayer, the first UV photoirradiation leads to a significantly higher surface pressure increase, by as much as 1.80 mN/m. When the lamp is switched off, the pressure drops only by 0.13 mN/m. This small decrease is the same as for the CAB polymer and bare water and caused by cooling of the pressure sensor. However, at the second UV

photoirradiation after 70 min without UV exposure, the surface pressure increases by 0.48 mN/m, more than the 0.13 mN/m expected by heating of the sensor but less than the initial increase. This small increase could be mainly addressed to the photoreaction of molecules that did not react (isomerize or dimerize) during the first UV irradiation. Dimerization is irreversible; thermally induced back-isomerization requires higher temperature.[6] Similar pressure variations as induced by the photoirradiation of the CABg monolayer were previously evidenced for azobenzene-containing molecules upon irradiation and were attributed to the change in molecular area resulting from trans−cis isomerization.[12,11] For cinnamate groups, the photochemical behavior is more complicated since photodimerization reactions could also occur if the distance between cinnamate groups is adequate.

To elucidate the photochemical origin of the observed features, e.g. isomerization or dimerization, SFG spectra were measured upon UV irradiation. The SFG spectra measured for the CAB and CABg monolayers in the SSP and SPS polarization combinations as a function of the UV exposure time in the range 1550−1800 cm^{-1} are presented in Figure 6. The amplitude−width ratio, obtained from a fit with the Lorentzian line shape model (see Experimental Section), for the C═C and C═O vibrations are also plotted versus the irradiation time. As expected for the CAB monolayer (no cinnamate groups present), the intensity of the C═O band at

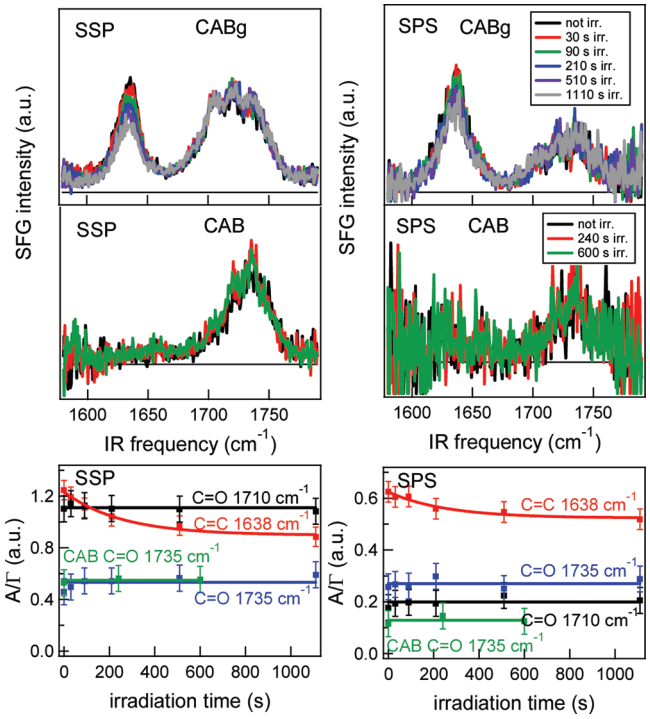


Figure 6. SFG spectra recorded in SSP (left) and SPS (right) polarizations in the range 1550−1800 cm^{-1} for CAB and CABg monolayers spread over pure water at a surface pressure of 10 mN/m as a function of the UV irradiation time. The thin black lines denote zero. The structure on the 1700−1750 cm^{-1} band originates from residual water vapor present in the IR beam path. The bottom panels display the amplitude−width ratio of the different bands obtained by fitting using the Lorentzian line shape model for the CAB (C═O 1735 cm^{-1}, green) and CABg (C═O 1710 cm^{-1}, black; C═O 1735 cm^{-1}, blue; C═C 1638 cm^{-1}, red) monolayers versus the exposure time.

1735 cm^{-1} remains unchanged during irradiation. In case of the cinnamate grafted CABg monolayer, one can notice a gradual intensity decrease of the band assigned to the C═C stretch mode which, however, does not vanish completely. In contrast, no change in both the intensity and frequency of the C═O stretch mode is observed. The decrease of the amplitude width ratio (A/Γ) of the C═C band (which is proportional to the number of C═C bonds all other things (e.g., orientation, polarizability) being equal) after 1110 s of irradiation was found to be 25 ± 5% and 15 ± 5% in SSP and SPS polarizations, respectively: in both polarizations the C═C intensity decreases upon irradiation (lower panel of Figure 6). This indicates that the disappearance of the C═C mode is not dominated by a change of orientation. However, the observation that the decrease is larger in the SSP spectra than in the SPS spectra shows that the C═C groups also change orientation upon irradiation.

Concerning the 2750−3100 cm^{-1} range, Figure 7 shows that the stretching bands of CH_3 and CH_2 in the CAB and CABg

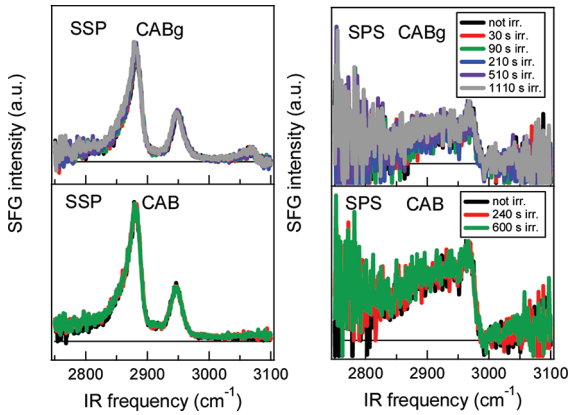


Figure 7. SFG spectra recorded in SSP and SPS polarizations in the range 2700−3100 cm^{-1} for CAB (bottom) and CABg (up) monolayers spread over D_2O at a surface pressure of 10 mN/m, as a function of the UV irradiation time. The thin black lines denote zero.

spectra are not affected by the photoirradiation while the CH stretch mode of the phenyl ring at 3070 cm^{-1} is too weak to follow its shape evolution with time.

Upon photoirradiating with UV light the CABg polymer, only a partly decrease of the C═C vibration is observed in both SSP and SPS polarization. All other detected modes, e.g. C═O and C−H, remain unchanged. Full dimerization should lead to vanishing of the C═C mode at 1638 cm^{-1} as a result of the conversion of the C═C double bonds to single bonds. Indeed, complete disappearance of the 1638 cm^{-1} mode upon UV irradiation has previously been observed by Chen et al.[9] in an SFG study of spin-coated poly(vinyl cinnamate) films and attributed to the UV-induced dimerization of the cinnamate groups. In most studies of polymers containing cinnamate groups, photo-cross-linking is the goal so that each repeat unit of the polymer chain bears a cinnamate moiety. In such cases, the observed decrease of the C═C peak intensity toward zero with increasing UV exposure time could well be attributed to full dimerization of the cinnamate groups.

In contrast, in case of trans−cis photoisomerization of the cinnamate groups, one would expect an intensity decrease of the C═C stretching mode assigned to the trans form at 1638 cm^{-1} and an increase of a new band/shoulder at the slightly

lower frequency of 1631 cm^{-1} based on Raman experiments and calculations.[25,26] It should be emphasized that, to the best of our knowledge, the C═C stretch mode associated with the cis form has never been detected in SFG or FTIR spectra of cinnamate modified molecules.

Besides the C═C mode, the C═O mode could also give useful information about the photoprocess. In FTIR spectra of poly(vinyl cinnamate) thin films upon UV exposure Coleman et al.[20] reported, besides a complete disappearance of the C═C stretching mode, a decrease of the C═O stretching vibration at 1712 cm^{-1} accompanied by the appearance of a new band at 1735 cm^{-1} assigned to a saturated ester carbonyl stretching vibration. These two effects were attributed to the photo-cross-linking of the cinnamate groups. The same observations were made by Chae et al. for spin-coated films of poly(methyl 4-(methacryloyloxy)cinnamate)[21] and by Yamamoto et al. for a cinnamic acid derivative.[27] In case of photodimerization, one should thus detect a shift of the C═O stretching vibration toward higher wavenumber due to the loss of conjugation. In contrast, according to Chakrabarti et al., who reported FTIR and Raman investigations of solid-state photopolymerization of dimethyl ester of α,α'-dicyano-*p*-phenylenediacrylic acid, the frequency shift of the C═O band should be very small in case of photoisomerization.[28] The absence of any change in the C═O band is thus a clear indication that cinnamate groups in the monolayer of the CABg polymer rather isomerized than dimerized.

To confirm this conclusion, we measured SFG spectra from preirradiated CABg, i.e., irradiated before spreading at the surface. From UV−vis and ^{1}H NMR spectroscopies, it could be concluded that photoirradiation of low concentration CABg in chloroform solutions mainly leads to isomerization of the cinnamate groups.[6] We thus compared the SFG spectra measured on CABg monolayers spread at the air−water interface from preirradiated solutions to those obtained after surface photoirradiation (shown in Figures 6 and 7). The spectra measured in the ranges 1550−1800 and 2750−3100 cm^{-1} on the preirradiated CABg monolayers are presented in Figure 8. One can notice that in the same way as for the monolayers irradiated directly at the air−water interface, the strength of the C═C stretching mode decreases with the irradiation time while the C═O and C−H bands do not vary significantly. Surprisingly, although we know from UV−vis and ^{1}H NMR spectroscopy that the cinnamate groups are now (at least partly) in the cis form, the C═C stretching mode assigned to the cis form at the expected frequency of 1631 cm^{-1} is not detected.[26,27] From a comparison of Figures 6−8, it is clear that the spectra resulting from deposition of the preirradiated polymer are rather similar to the spectra obtained after irradiation at the surface: in both cases, an intensity decrease of the C═C mode assigned to the trans form is observed, and the C═O vibration remains unchanged. As trans−cis isomerization has been shown to be the main process in solution, these results corroborate our conclusion drawn above that it is also predominant upon direct photoirradiation of the CABg monolayers at the air−water interface.

Surprisingly, in the SFG spectra after irradiation we only observe a decrease of the C═C band related to the trans form of the molecule and not the expected ingrowth of a peak related to the cis state. Apparently, the cis peak is SFG inactive. As for SFG a vibration has to be active in both FTIR and Raman, the invisibility in SFG means that the band is not active in either FTIR or Raman. To be active in FTIR, a vibration has to

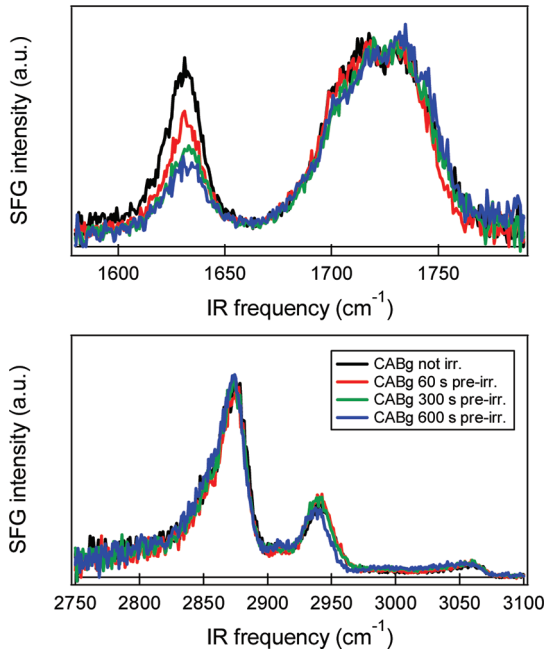


Figure 8. SFG spectra recorded in SSP polarization in the 1550−1800 cm^{-1} (top) and 2750−3100 cm^{-1} (bottom) ranges for CABg monolayers spread over pure water and D_2O, respectively, at a surface pressure of 10 mN/m, from either nonirradiated or three preirradiated CABg chloroform solutions. The preirradiated samples were obtained by irradiating a solution of CABg in chloroform in a small glass container with UV light for 60, 300, and 600 s, respectively, before spreading them on the water subphase. The spectra at different irradiation times are normalized to the C═O band at ∼1730 cm^{-1} (top panel) and ∼2870 cm^{-1} (bottom panel). The thin black lines denote zero.

change the dipole moment of the molecule, while for Raman a change in the polarizability is necessary. To check why the C═C mode for the cis molecule is SFG inactive, we performed both FTIR and Raman spectroscopy measurements on films obtained onto solid substrate from droplets deposition of either nonirradiated or preirradiated CABg chloroform solution. Figure 9 shows the spectra obtained with both techniques in the range 1575−1800 cm^{-1}. In both spectra, the band at 1712 cm^{-1} assigned to the C═O stretching vibration is present. After normalizing to this C═O band between 1700 and 1750 cm^{-1}, two different behaviors are evidenced for the vinylene C═C stretching vibration depending on the spectroscopic technique. The intensity of the C═C mode associated with the trans form decreases relative to the C═O band with increasing UV exposure in both cases. However, in the Raman spectrum a shoulder at lower frequency appears that is not present in the FTIR spectrum for an irradiated sample. This shoulder is located at the expected frequency of the C═C stretching mode assigned to the cis form. Clearly, the C═C mode is absent in our SFG spectra because the band is not active in FTIR. As a result, the intensity decrease of the C═C trans stretching vibration could indicate both dimerization and isomerization, and therefore the C═C mode cannot solely be used to exclude one of the two processes. Moreover, the Raman and FTIR spectra also differ by the observation of a strong Raman band at 1600 cm^{-1} which is due to C═C stretching of the cinnamate aromatic rings[28,29] and also by the ratio between the C═C and C═O vibrations. As the aromatic C═C mode is not IR active, the band is also not observed in our SFG spectra. A more

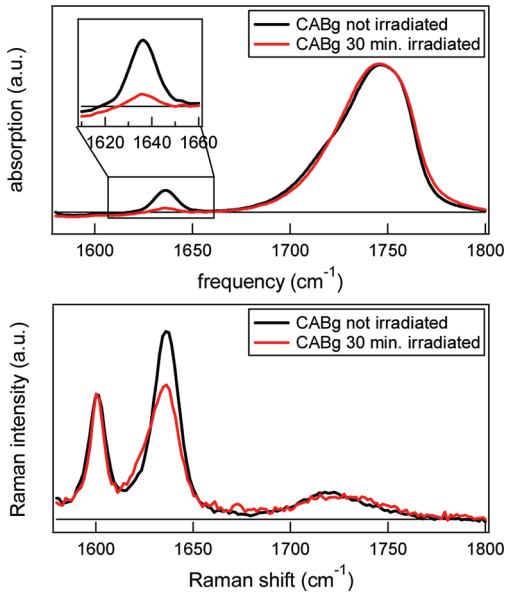


Figure 9. FTIR (top) and Raman (bottom) spectra measured on CABg films obtained onto solid substrate from either nonirradiated or 30 min preirradiated CABg chloroform solutions. Both spectra are normalized to the band between 1700 and 1750 cm^{-1}. The thin black lines denote zero.

detailed look at the spectra shows that there might be a small change upon irradiation in the C═O band as well: the conjugated C═O peak at 1710 cm^{-1} seems to decrease slightly while the nonconjugated peak at 1735 cm^{-1} might get a little broader. From our recent NMR observations in solution, the dimerization reaction is negligible.[6] Nevertheless, considering NMR sensitivity, a few percent dimerization cannot be excluded. Also in the SFG spectra for a preirradiated solution (Figure 8) the slight change in the C═O band might indicate partial dimerization.

The work presented in this paper shows that isomerization is the dominant process after UV irradiation of a monolayer of cinnamate grafted cellulose acetate butyrate polymers on water. Considering the mean density of cinnamate groups close to 1 group every 2.5 cellulosic units, the negligible dimerization is perhaps not so unexpected and indicates that no significant dimerization between the cinnamate groups of neighboring polymer chains occurs. The two-dimensional organization of the polymer at the air−water interface thus prevents the reactive centers to approach each other. This result is similar as the one evidenced by Abdel-Mottaleb et al.[4] for cinnamic acid derivatives asymmetrically substituted by alkyl chains at the graphite/liquid interface. In contrast, as shown in a previous paper,[6] in spin-coated films of CABg, the disorder and 3D packing allow proximity of cinnamate groups leading to photodimerization, in the same way as in poly(vinyl cinnamate) spin-coating or dip-coated films.[9,10] The photochemical process thus depends both on the molecular structure and the film preparation.

4. CONCLUSION

Langmuir monolayers of cinnamate modified (CABg) and unmodified (CAB) cellulose acetate butyrate polymers have been studied by combining isotherms measurements, BAM observations, and SFG characterizations. Above a surface pressure of 6 mN/m, a condensed phase is detected which appears optically anisotropic by BAM, indicating the possible organization of the cellulosic rings at the air−water interface. CAB and CABg monolayers in the condensed state (at ∼10 mN/m) were then submitted to different degrees of UV photoirradiation. The recorded SFG spectra reveal a partial decrease of the C═C vibration of the cinnamate moiety in the CABg polymer in both SSP and SPS polarization combinations. The other detected modes, e.g. C═O and C−H, remain unchanged. The absence of changes in the C═O region and the observed changes in the C═C part of the spectrum can be attributed to trans-to-cis isomerization of the cinnamate group. We show that for the cis state the C═C mode is not infrared active (although Raman active) which explains its absence in SFG spectra.

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Notes

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