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Molecular Structure of Hydrophobic Alkyl Side Chains at Comb Polymer-Air Interface

Keshav S. Gautam and Ali Dhinojwala*

Department of Polymer Science, The University of Akron, Akron, Ohio 44325

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Introduction. Polymers with long side chains (comb polymers) provide unique opportunities to tailor surface properties of polymer films for applications in the areas of adhesion, friction, membrane transport, and biocompatibility.[1−8] In particular, polymers containing long alkyl or fluorinated alkyl side chains have been used to generate hydrophobic surfaces with surface energies that are comparable to those created by well-ordered self-assembled monolayers (SAM).[1−2,9−10] Comb copolymers with alkyl side chains typically show two thermal transitions: one associated with smectic liquid crystalline order where the *d* spacing is proportional to the length of the side groups[1,2] and the other associated with crystallization of the alkyl side chains. The surface energy of alkyl side chain comb polymers decreases with increase in the length of the alkyl side groups until a certain critical chain length, after which it asymptotes to a constant value.[1] These observations are reminiscent of results for SAM's where the length of the alkyl chains, packing, and mobility of the chains control the surface energies.[9,10] Although, considerable work has been done in the past in understanding the molecular ordering of SAM, very little is known about the molecular structure of alkyl chains at the comb polymer−air interface.[11]

In this Communication, we report the first spectroscopic measurement of the molecular structure of octadecyl alkyl side chains at poly(vinyl octadecyl carbamates-*co*-vinyl acetate)-air interface (the polymer will be referred to as octadecyl polymer for simplicity) using the surface sensitive sum-frequency generation (SFG) technique. SFG involves mixing a visible high-intensity laser beam of frequency ω_1, with a tunable infrared wavelength source of frequency ω_2. According to the dipole approximation, generation of a SFG photon at $(\omega_1 + \omega_2)$ is forbidden in the centrosymmetric bulk and is nonzero at interfaces where the inversion symmetry is broken.[12−16] SFG intensities are resonantly enhanced when ω_2 overlaps with the resonant frequency of a molecular vibrational mode that is both infrared and Raman active. The intensity, polarization, and resonance frequency of the SFG signal yield chemical and orientational information on molecules at interfaces.[12−18]

Here, we compare the differences in the surface structure of 65 nm thick octadecyl polymer films prepared by spin-coating to a 7 nm polymer layer prepared by solution dipping on a mica substrate. In both cases, the SFG signals show strong methyl asymmetric and symmetric stretching vibrations indicating ordered methyl terminal groups. For the adsorbed octadecyl films, the SFG signal associated with methylene vibrations is higher indicating increased gauche defects in comparison with the spin-coated thicker films. The irregularity in packing of the alkyl chains for the 7 nm polymer films is also reflected in an unstable and rapidly changing contact angle.

Experimental Section. The polymer, poly(vinyl *N*-octadecyl carbamates-*co*-vinyl acetate) (Figure 1) was kindly provided by 3M Corp. This polymer shows three broad thermal transitions centered at 50, 75, and 93 °C (measured using differential scanning calorimetry at a heating rate of 10 °C/min during the third heating cycle). The 50 °C transition is associated with side chain crystallinity and the other two with smectic layering. Gel permeation chromatography measurements give M_n = 70 000 g/mol and a polydispersity of 3.0 (light scattering detector). The polymer contains 90% octadecyl repeat units as determined by proton NMR. Thin polymer films (7 nm thickness) were prepared by exposing freshly cleaved mica samples to a 0.1 wt % solution of octadecyl polymer in toluene for 15 min followed by drying overnight in a vacuum oven. The samples were also annealed at 60 °C for 3 h before SFG measurements. Thicker films (65 nm) were prepared by spin-coating a 1 wt % solution of octadecyl polymer in toluene on mica substrates. Film thickness was measured using X-ray reflectivity. The spin-coated films were annealed at 110 °C in a vacuum for 3 h before thickness, contact angle, and SFG measurements were performed.

The infrared-visible SFG spectra were measured on a Ti−sapphire laser system with an 800 nm visible output (1 ps pulse width and 1 kHz repetition rates) mixed with a tunable infrared output (2750−3200 cm^{-1}, 1 ps pulse width, 1 kHz repetition rates, and σ (0.85 × fwhm) = 20−22 cm^{-1}). The visible and the infrared beams were overlapped at the sample spatially and temporally with incidence angles of 55 and 60°, respectively. Wavelengths and bandwidths were measured using a 0.5 m spectrometer. The SFG intensity was measured for two polarizations: I_{ppp} (p-polarized signal, p-polarized visible and p-polarized infrared) and I_{ssp} (s-polarized signal, s-polarized visible and p-polarized infrared).

SFG Background. The theory behind SFG as a surface-sensitive spectroscopic technique and the analysis to obtain orientation of methyl and methylene groups has been discussed previously.[12−19] Here we summarize the main points to understand the work reported in this paper. The second-order nonlinear susceptibility can be expressed using a Lorentzian function with a resonance peak at ω_q and width Γ_q corresponding to a resonance mode q.[19]

$$\chi_{\mathrm{tot}}(\omega) \propto |\chi_{\mathrm{eff,NR}} + \sum_q \frac{A_q}{\omega - \omega_q - i\Gamma_q}| \qquad (1)$$

The first term in eq 1, $\chi_{\mathrm{eff,NR}}$, corresponds to the nonresonance contribution that is wavelength-independent and the second term to the resonance contribution. For a monochromatic source, the SFG intensity is proportional to $(\chi_{\mathrm{tot}})^2$. However, for a broad infrared input source, the SFG intensity is determined by a convolution of $(\chi_{\mathrm{tot}})^2$ and the infrared intensity which has a Gaussian distribution in wavenumbers ($\Delta\omega_{IR}$ =

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* To whom correspondence should be addressed.

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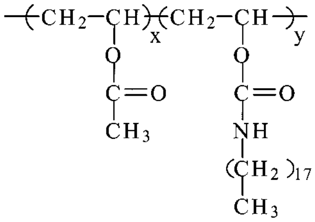

$$-\!(CH_2-\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{|}}{\overset{}{CH}}\!\!\underset{O}{|})_x\!-\!(CH_2-\underset{O-C(=O)-NH-(CH_2)_{17}-CH_3}{CH})_y\!-$$

Figure 1. Chemical structure of poly(vinyl octadecyl carbamate-*co*-vinyl acetate) where *x* and *y* denote the relative mole fractions of the individual units.

$0.85 \times$ fwhm).[20]

$$I_{\mathrm{SFG}}(\omega_{\mathrm{IR}}) \propto \int_{-\infty}^{\infty} \frac{\chi_{\mathrm{tot}}(\omega)^2}{\Delta\omega_{\mathrm{IR}}} \exp\left(-\frac{2(\omega-\omega_{\mathrm{IR}})^2}{(\Delta\omega_{\mathrm{IR}})^2}\right) \mathrm{d}\omega \quad (2)$$

To determine the tilt of the surface molecules, the macroscopic second-order nonlinear susceptibility has to be related to microscopic susceptibilities, β. Here, we discuss only the ratio $R = A_q$(ssp, asymmetric)/A_q(ssp, symmetric) for methyl groups which is independent of the Fresnel coefficients, refractive index, and the incident angles of the input beams.[15]

$$R = \left|\frac{A_{\mathrm{asym,ssp}}}{A_{\mathrm{sym,ssp}}}\right| = \left|\frac{2\beta_{caa}(\langle\cos\theta\rangle - \langle\cos^3\theta\rangle)}{\beta_{ccc}((1+r_{\mathrm{s}})\langle\cos\theta\rangle - (1-r_{\mathrm{s}})\langle\cos^3\theta\rangle)}\right| \quad (3)$$

Here, *a*, *b*, and *c* are molecular axes where the *c* axis is chosen to coincide with the symmetry axis of the methyl group and θ is the angle between the *c* axis and the surface normal, *z* axis. For methyl vibrations, $\beta_{\mathrm{aac}} \cong -\beta_{\mathrm{caa}}$ and $r_{\mathrm{s}} = \beta_{aac}/\beta_{ccc}$. The terms within these braces $\langle\ \rangle$ imply averages of tilt angles. As an example, for a random orientation of methyl groups the $\langle\cos\theta\rangle$ and $\langle\cos^3\theta\rangle$ terms are zero, and there will be no net SFG signal due to resonance contribution. Therefore, unlike infrared spectroscopy, the SFG signals are proportional to the number density as well as the noncentrosymmetric orientation of the molecules. The other two angles (Euler angles) describing the orientation of the methyl groups are assumed to have a random distribution.[15] The values for r_{s} are not agreed upon in the literature and range from 1.6 to 4.2.[16]

Results and Discussion. The SFG spectra for the 7 and 65 nm polymer films at 24 °C in the C−H stretch region are shown in parts A and B of Figure 2, respectively. The SFG signals are reported after normalizing with the infrared intensity. The dominant peaks in the I_{ssp} and I_{ppp} spectra are associated with methyl vibrations indicating well-ordered methyl groups. The Fermi resonance at 2935 cm^{-1} ($\mathrm{r^+_{FR}}$, corresponding to deformation of the HCH modes with the intensity borrowed from the methyl symmetric stretch vibrations) and a symmetric methyl vibration at 2875 cm^{-1} ($\mathrm{r^+}$) contribute to the I_{ssp} spectra. In contrast, the asymmetric methyl peak at 2960 cm^{-1} ($\mathrm{r^-}$) dominates the I_{ppp} spectra. The solid lines correspond to fit using eq 2. The parameters ω_q, A_q, and Γ_q determined from the fits are summarized in Table 1. The methylene asymmetric, symmetric, and Fermi vibrations are denoted by $\mathrm{d^-}$, $\mathrm{d^+}$, and $\mathrm{d^+_{FR}}$, respectively. The ω_q and Γ_q values for methyl and methylene vibrations in Table 1 are in good agreement with those reported in the literature.[16]

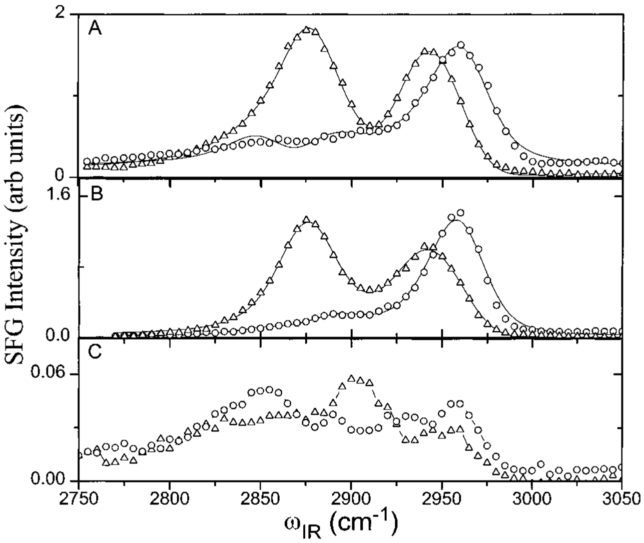

Figure 2. (A) I_{ppp} (circles) and I_{ssp} (triangles) SFG spectra for a 7 nm dip-coated octadecyl polymer on mica at 24 °C. (B) 65 nm spin-coated octadecyl polymer film on mica at 24 °C. (C) spin-coated octadecyl polymer film on mica after a short plasma treatment. Solid lines are fits using eq 2.

Table 1. A_q Values Obtained by Fitting the Results in Figure 2 Using Eqs 1 and 2

			dip-coated films		spin-coated films	
q	ω_q (cm^{-1})	Γ_q (cm^{-1})	A_q (SSP)	A_q (PPP)	A_q (SSP)	A_q (PPP)
$\mathrm{r^-}$	2960	9	−8.4	−15.3	−7.9	−13.6
$\mathrm{r^+_{FR}}$	2935	9	11.2	7.0	9.6	3.2
$\mathrm{r^+}$	2875	10	−16.2	−8.2	−14.4	−5.8
$\mathrm{d^-}$	2920	10	3.9	5.7	3.9	3.1
$\mathrm{d^+_{FR}}$	2900	10	5.8	3.8	−1.2	5.9
$\mathrm{d^+}$	2855	10	−4.9	9.2	1.4	5.1

The $|A_q|$ values for methylene vibrations ($\mathrm{d^-}$, $\mathrm{d^+}$, and $\mathrm{d^+_{FR}}$) are lower than the methyl vibrations ($\mathrm{r^-}$, $\mathrm{r^+}$, and $\mathrm{r^+_{FR}}$) for both the samples. The magnitude of A_q depends on β, the number density, and the orientation of the molecule. Theoretical predictions suggest that the β for a methylene group is higher than a methyl group.[14] For an all-trans alkyl chain, a pair of methylene groups is approximately centrosymmetric, the methylene bands do not normally show up in the SFG spectrum. The appearance of the methylene bands is usually associated with an increase in gauche defects and an additional unpaired methylene unit in the case of octadecyl side chain. Higher $|A_q|$ ($\mathrm{CH_2}$) for the 7 nm films suggests an increase in gauche defects in comparison with the thick spin-coated films. These differences could be due to the polar NH and carbonyl groups strongly adsorbing on a mica substrate and influencing the packing in thinner films. Further temperature measurements are in progress to confirm this hypothesis.

Under the electric dipole approximation, the interfacial layer is often the dominating source for the SFG signal in the reflected direction. Recently, Shen and coworkers have experimentally verified this prediction.[21] For the octadecyl polymer films we find that the SFG intensity is nearly independent of film thickness (measured for 7, 65, and 3000 nm thick films). Furthermore, when the 65 nm films are exposed to a brief plasma treatment (~1 s) the SFG intensity drops by an order of magnitude as shown in Figure 2C. The I_{ssp} spectrum is now dominated by methylene modes in comparison to the spectrum before the plasma treatment (Figure

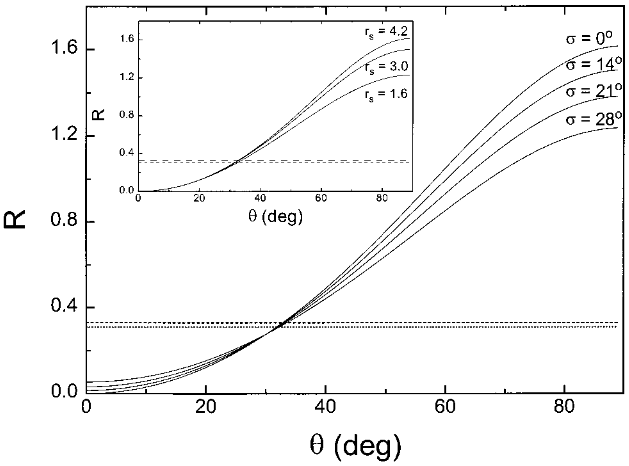

Figure 3. R as a function of tilt angles calculated using eq 3, $r_s = 4.2$, and a Gaussian distribution of tilt angles with $\sigma = 0.85 \times$ fwhm. The short dashed line corresponds to R for dip-coated films and long dashed line, for the spin-coated octadecyl polymer films. The inset corresponds to R as a function of tilt angles for different values of r_s and $\sigma = 0°$.

2B). This further confirms the surface sensitivity of the SFG technique.

To determine the orientation of the methyl terminal groups we plot in Figure 3 the prediction of R, A_q(ssp, asymmetric)/A_q(ssp, symmetric), as a function of tilt angles for the methyl groups (eq 3 and $r_s = 4.2$). Since the symmetric vibration (r^+) loses some of its intensity to the Fermi vibration (r^+_{FR}), we have added the A_q values for r^+ and r^+_{FR} to determine A_q (ssp, symmetric). The values of R for 7 and 65 nm films are shown as a dotted line in Figure 3. The interception of dotted line with the theoretical prediction determines the tilt of the methyl groups. In practice, it is expected that a distribution of tilt angles exists and the predictions assuming Gaussian distribution of tilt angles with $\sigma = 0.85 \times$ fwhm are also shown in Figure 3. The intercepts of the dashed line with the solid lines indicate that tilt angles for the methyl groups are centered near 34° for both the films. For an upright all-trans alkyl chain the methyl groups will have a 37° angle between the c axis and the surface normal. For the octadecyl polymer, the alkyl chains are approximately vertical with respect to the surface normal. Also, changing r_s from 4.2 to 1.6 does not significantly influence the calculations of tilt angles (see insert in Figure 3).

To determine A_{CH_2} and A_{CH_3} we have added the magnitude of A_q for methylene and methyl modes determined from the I_{ssp} spectra (Table 1), respectively. The relative ratios of A_{CH_2}/A_{CH_3} determined from Table 1 are 0.4 and 0.2 for 7 and 65 nm samples, respectively. The increase in methylene contribution for the thin film suggests the presence of higher gauche defects in comparison to the spin-coated films. These SFG results are in good agreement with the water contact angle measurements. The spin-coated samples show a stable water contact angle of 110° indicating well-packed terminal alkyl groups at the surface. In contrast, the water contact angles measured for 7 nm dip-coated films are unstable and change rapidly with time (<10° in 1−4 s), indicating poor packing of the alkyl side chains.

In conclusion, we have for the first time measured the molecular orientation of alkyl side chains at the octadecyl polymer−air interface. Both 7 nm thick dip-coated and 65 nm thick spin-coated surfaces have well-ordered methyl terminal groups. The alkyl chains for the thin layer have higher gauche defects than the thicker spin-coated film. Comparison of surface orientation and wetting on heating above the melting and the smectic-isotropic transition temperatures is the subject of our current work.

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