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Interfacial Structure and Melting Temperature of Alcohol and Alkane Molecules in Contact with Polystyrene Films

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Infrared-visible sum-frequency-generation spectroscopy (SFG) is used to investigate the interfacial structure of hexadecanol ($C_{16}H_{33}OH$) and heneicosane ($C_{21}H_{44}$) in contact with polystyrene films (PS) spin coated on a sapphire substrate. The interfacial structure of hexadecanol is very different from heneicosane in contact with PS. In the crystalline state, the hexadecanol molecules are oriented with the C$-$C$-$C axis parallel to the surface plane in contact with PS. For the crystalline heneicosane/PS interface, the SFG spectra are very similar to those observed for molecules oriented with the symmetry axis of the methyl groups parallel to the surface normal. The structure of both hexadecanol (or heneicosane) and the phenyl groups changes sharply at the melting temperature of hexadecanol (or heneicosane). Upon heating the hexadecanol/PS sample above the glass transition temperature (T_g) of PS, the hexadecanol molecules penetrate through the PS film and adsorb on the sapphire substrate. The adsorbed hexadecanol molecules are oriented with the symmetry axis of the methyl groups parallel to the surface normal. The structure of the PS molecules at the sapphire interface is different because the PS phenyl groups are now in contact with the hydrophobic tails of the hexadecanol molecules, rather than the hydrophilic sapphire substrate. The adsorbed hexadecanol molecules do not disorder at the bulk melting temperature of hexadecanol. In comparison, no adsorption of heneicosane molecules next to sapphire interface upon annealing was observed. The differences between the adsorption of hexadecanol and heneicosane can be explained by the preferential interactions between the hydroxyl groups of the alcohol and hydrophilic sapphire substrate.

1. Introduction

Structure of molecules at the liquid/solid interface is important in understanding wetting, adhesion, biocompatibility, nucleation, boundary conditions for fluid flow and permeability of small molecules.[1−5] The traditional vacuum-based techniques that are useful to study solid surfaces cannot be used to study liquids and hidden interfaces. Although X-ray and neutron scattering have been used to study solid/air or liquid/air interfaces,[6] it is only recently that those techniques have been applied in studying liquid/solid interfaces.[7] Recently, several research groups have shown that the surface-sensitive infrared-visible sum-frequency-generation spectroscopy (SFG) is a powerful complementary technique to study polar and nonpolar liquids in contact with various organic and inorganic substrates.[8−17] In the study of polymer surfaces, the focus has been on understanding the changes in the structure of the polymer surface groups in contact with polar and nonpolar liquids.[12,16,17] No information, however, is available on the effects of polymer surfaces on the crystallization of small-molecule liquids. In this paper, we have studied the interfacial structure and transition temperatures of polar (hexadecanol) and nonpolar (heneicosane) liquids in contact with a polystyrene film (PS) spin coated on a sapphire prism. Even though the liquid structure in contact with PS is similar for both these molecules, their orientations upon crystallization are very

different. The orientation of molecules affects the nucleation rates and interfacial energies.

In addition to determining the interfacial structure at the liquid (or crystal)/PS, we have also measured the changes in structure at the hidden PS/sapphire interface in the presence of hexadecanol and heneicosane. After annealing the PS films in the presence of hexadecanol above the glass transition temperature (T_g), we find that the hexadecanol molecules penetrate through the PS film and adsorb on the sapphire substrate. The structure of these adsorbed molecules is very similar to that of bulk hexadecanol in contact with sapphire. This indicates that there is at least a monolayer of hexadecanol molecules adsorbed on the sapphire substrate with its C$-$C$-$C axis perpendicular to the substrate. No such surface segregation was observed for the nonpolar heneicosane. One could attempt to explain these observations as the result of either differences in the solubility of hexadecanol and heneicosane in PS, or a preferential interaction of the OH groups of hexadecanol with the sapphire substrate. However, the solubility argument leads to a prediction of the opposite results than those actually observed because the alcohol molecules are generally less soluble than the linear alkanes in PS.[18] Therefore, we conclude that the interaction of the hydroxyl groups with the hydrophilic sapphire substrate plays an important role in adsorption. These results have important consequences on the stability of polymer coatings in applications for photoresist, barrier coatings in microelectronics, corrosion protection barriers, paints, sensors and adhesion promoters.[19]

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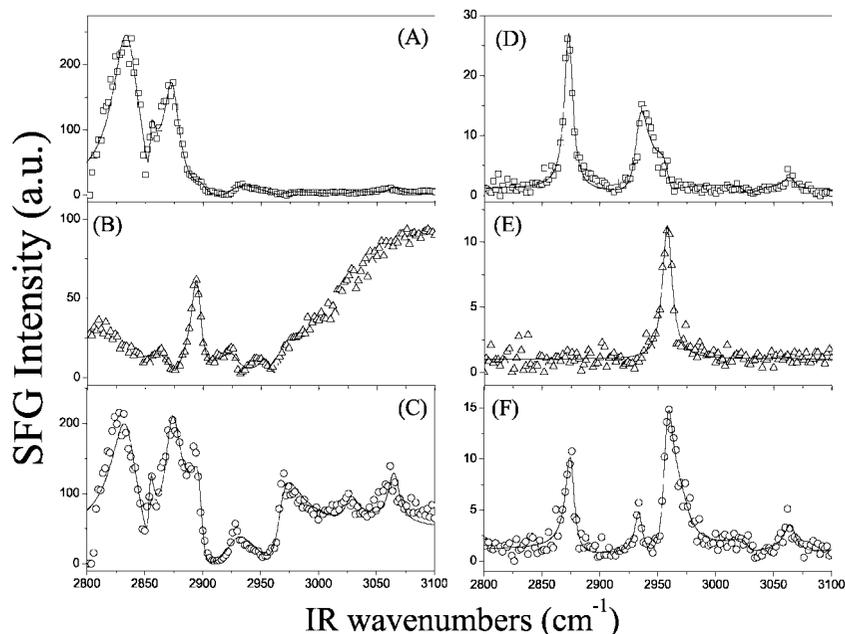
Figure 1. Panels A−C are SSP, SPS, and PPP spectra, respectively, for hexadecanol/PS interface. Panels D−F are SSP, SPS, and PPP spectra, respectively, for heneicosane/PS interface. All these spectra are taken at 25 °C in the crystalline state. The solid lines are fitted using a Lorentzian equation and the parameters obtained from the fits are summarized in Tables 1 and 2. The SPS spectrum in Figure 1b has an additional hydroxyl peak that was not included in the fits.

2. Experimental Section

2.1. Sample Preparation. Polystyrene (PS, M_w = 382 kg/mol, T_g = 100 °C, Aldrich), hexadecanol ($C_{16}H_{33}OH$, purity of 99%, rotator-to-liquid transition temperature (T_m) = 50 °C, crystal-to-rotator transition temperature = 43 °C, Aldrich) and heneicosane ($C_{21}H_{44}$, purity of 98%, T_m = 39 °C, Aldrich) were used as received. A sapphire prism was cleaned in toluene in an ultrasonic bath for 2 h; rinsed with acetone, ethanol, and heptane; dried with N_2; and finally treated with an oxygen plasma for 1−2 min. PS films were spin coated on the sapphire prism at 1500 rpm using 3−5 wt % solution in toluene. PS films were dried in a vacuum oven at 120 °C for 10 h. The thickness of the PS films used with hexadecanol and heneicosane were 300 and 500 nm, respectively, as determined using ellipsometry. For the SFG measurements, a syringe containing hexadecanol or heneicosane was first heated to 60 °C in an oven, and the contents were then injected into the SFG cell that was also preheated to 60 °C. Once the injection was made and it was determined that there were no air bubbles in the SFG cell, the cell was cooled below the freezing temperature at a rate of 1 °C/min to ensure that a uniform layer of the hexadecanol or heneicosane formed in contact with the PS film.

2.2. SFG Measurements. SFG is a second-order nonlinear optical technique that is sensitive to the orientation and concentration of molecules at interfaces. The details of the SFG theory and the SFG spectrometers have been discussed in previous papers.[20,21] SFG involves mixing a visible high intensity laser beam (of frequency ω_{vis}) with a tunable infrared wavelength source (of frequency ω_{IR}). According to the dipole approximation, the generation of SFG photons (at frequency $\omega_{vis} + \omega_{IR}$) is forbidden in the centrosymmetric bulk but is allowed at the interface where the inversion symmetry is broken. The SFG intensity is resonantly enhanced when ω_{IR} overlaps with the resonant frequency of the vibration modes of the surface molecules. The value of the resonance frequency provides the identification of the chemical groups present at the interface. In addition, the SFG intensity of the asymmetric and symmetric vibrations in the SFG spectra collected using different polariza-

tion combinations provides information on the orientation of these chemical groups at the interface.[11,15,22,23] The total internal reflection geometry (TIR) further enhances the SFG intensity by 1−2 orders of magnitude.[9,11] By the proper choice of incident angles in TIR, we can probe the PS/liquid (or crystal) and PS/sapphire interfaces.

For this paper, we used the nanosecond SFG system at ExxonMobil for the SFG measurements. The details of this system are provided elsewhere.[16,24] The visible beam (532 nm) and a tunable IR laser beam are superimposed on the sample and the SFG signals are collected using a photomultiplier tube. For the alcohol/PS interface, we have used an incident angle (visible beam) of 0° for the SFG spectra collected at 60 and 25 °C. For probing the heneicosane/PS interface, we have used an incident angle (visible beam with respect to the face of the sapphire prim) of 8° for measurements at 50 °C and an angle of 0° for measurements at 25 °C. For probing PS/sapphire interface, we have used an incident angle of −10°. The difference between the IR and visible beams was ≤1°. These incident angles are near the critical angles for total internal reflection and were calculated using the Snell's law and the refractive index of the materials at 532 nm.[11,16,22] Additionally, we measured the SFG measurements as a function of incident angle and confirmed that the SFG intensity was maximum at those angles. The position of the maximum intensity also matched with a theoretical model that will be discussed elsewhere.[25] For phase transition measurements we used heating and cooling rates of 1 °C/min.

3. Results and Discussion

3.1. Structure of Hexadecanol and Heneicosane in Contact with PS. Figure 1 shows the SFG spectra in SSP, SPS, and PPP polarization for crystalline hexadecanol (Figure 1A−C) and heneicosane (Figure 1D−F) in contact with PS. Because of the strong crystalline order, the SFG signals in the methyl and methylene modes (2800−3000 cm^{-1}) are much stronger than the phenyl modes (3000−3100 cm^{-1}) of glassy PS. To quantify the peak position and strength we have used a

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TABLE 1: The A_q and Γ_q Values Obtained from Fitting the Data in Figure 1 for Hexadecanol/PS System

		2835 cm^{-1}	2854 cm^{-1}	2873 cm^{-1}	2895 cm^{-1}	2926 cm^{-1}	2955 cm^{-1}	2967 cm^{-1}	3027 cm^{-1}	3065 cm^{-1}
		d^+	d^+	r^+	d_{FR}^+ or d^-	r_{FR}^+	r_b^-	r_a^-	ν_{20b}	ν_2
SSP	A_q	195 ± 24	9 ± 1	76 ± 16	8 ± 10	72 ± 132		41 ± 21	6 ± 12	11 ± 8
	Γ_q	14	2	8	5	15		10	7	6
SPS	A_q			10 ± 2	31 ± 1	16 ± 4	8 ± 3			
	Γ_q			8	5	15	5			

TABLE 2: The A_q and Γ_q Values Obtained from Fitting the Data in Figure 1 for Heneicosane/PS System

		2875 cm^{-1}	2934 cm^{-1}	2958 cm^{-1}	2971 cm^{-1}	3027 cm^{-1}	3065 cm^{-1}
		r^+	r_{FR}^+	r_b^-	r_a^-	ν_{20b}	ν_2
SSP	A_q	18 ± 0.4	17 ± 0.6	7 ± 1.0		14 ± 2.0	4 ± 0.8
	Γ_q	5	5	5		7	6
SPS	A_q			12 ± 0.6			
	Γ_q			5			

Lorentzian equation to fit the data, and the results are shown as solid lines in Figure 1.

$$I(SFG) \propto \left| \chi_{\text{eff, NR}}^{(2)} + \sum_q \frac{A_q e^{i\phi_q}}{\omega_{\text{IR}} - \omega_q - i\Gamma_q} \right|^2 \quad (1)$$

Here A_q, Γ_q, ϕ_q, and ω_q are the strength, damping constant, phase difference, and angular frequency of a single resonant vibration, respectively. $\chi_{\text{eff,NR}}^{(2)}$ is the nonresonant part of the signal. The A_q and ω_q obtained from the fits are summarized in Tables 1 and 2. We have only shown the fit parameters for SSP and SPS polarization because they are more relevant in internal reflection geometry to understand the orientation of the molecules at the interface. Because many independent variables are involved in fitting of the SFG spectra, it is difficult to ascertain if we have converged on the optimum solution. The error bars for some of the peaks are higher, indicating larger uncertainties in fitting those peaks, and the A_q values reported for those peaks should be considered as one set of possible solutions.

We have assigned the peaks at 3027 and 3060−3065 cm^{-1} to the phenyl asymmetric (ν_{20b}) and phenyl symmetric (ν_2) modes, respectively.[26] The peaks at 2850−2855, 2870−2875, 2926−2935, 2955, and 2965−70 cm^{-1} are assigned to methylene symmetric (d^+), methyl symmetric (r^+), methyl Fermi (r_{FR}^+), methyl out-of-plane asymmetric (r_b^-), and methyl in-plane asymmetric modes (r_a^-), respectively.[27] There is an overlap of assignments at 2850 cm^{-1} (symmetric) and 2920 cm^{-1} (asymmetric) from the methylene modes of PS. Because the PS methylene modes have not been observed in the SFG spectra for PS surfaces and interfaces, in this paper we have assigned the peaks at 2850 and 2920 cm^{-1} to methylene groups of alcohol and alkanes.[11,22,28] In the case of hexadecanol, we also observe a strong SFG signal at 2835 cm^{-1} that we have assigned to methylene symmetric mode. This assignment is 10−15 cm^{-1} lower than the assignments for methylene symmetric modes reported in the literature.[27] A lower assignment in poly(vinyl alcohol) has been also reported for CH group bonded to a hydroxyl group.[29] A similar shift is expected for the methylene group bonded to the hydroxyl group in hexadecanol. Because the symmetric methylene band is shifted, we also expect the asymmetric methylene peak to shift to lower wavenumbers (rather than 2910−2915 cm^{-1}). We have assigned the band at 2895 cm^{-1} to asymmetric methylene vibrations. This peak assignment is also in agreement with the expectations of a prominent methylene asymmetric peak in the SPS polarization. Additionally, there is a strong increase in SFG intensity in the

SPS polarization above 3000 cm^{-1} (in Figure 1B) due to the hydroxyl groups. This increase will be discussed later in this paper.

The SFG spectra for hexadecanol and heneicosane crystals in contact with PS are very different from one another, which indicates that the polar alcohol and the nonpolar alkane molecules crystallize with very different orientations. In the case of heneicosane, the SSP spectrum has methyl symmetric (r^+) and methyl Fermi peaks (r_{FR}^+) with very small contribution from methyl asymmetric (r_a^- or r_b^-) and methylene modes.

These spectra are very similar to self-assembled monolayers with terminal methyl groups[16] and alkanes in contact with sapphire substrate.[30,31] The observed strong methyl modes in the heneicosane/PS spectrum could be explained by using a model where the C−C−C axis oriented parallel to the surface.[30,31] However, in this case there is an additional methylene group facing the sapphire surface and it should also contribute to the SFG spectra as was reported for the sapphire/alkane and confined alkane interfaces.[30,31] In contrast to the sapphire/alkane system, the methylene resonance is missing in the heneicosane/ PS spectra, which indicates that the C−C−C axis cannot be parallel to the PS surface.

Strong methyl group signal and vanishingly small methylene signal are also produced when the C−C−C axis is near to the surface normal and only one of the terminal methyl groups contributes to the signal. Therefore, instead of a single chain model we suggest an alternate model based on an ensemble of heneicosane molecules. In this model, we assume that the symmetry is broken only in the vicinity of the PS surface. In that case, the tilt angle for the methyl group can be determined using the ratio of $A_{yzy, r-}/A_{yyz, r-}$. The details of the calculations to determine tilt angles are provided in a previous publications.[16] From the data provided in Table 2 we determine $A_{yzy, r-}/A_{yyz, r-} \approx 1.7$, and the range of acceptable tilt angles for the methyl group is between 0 and 35° with respect to the surface normal. For an all-trans chain, this corresponds to the C−C−C axis oriented at an angle between 0 and 35° with respect to the surface normal.

Our interpretation of the interfacial structure for hexadecanol/ PS interface requires a thorough understandings of the reasons for strong methylene peaks in the SFG spectra. The presence of methylene peaks often has been interpreted as breaking of symmetry due to gauche defects.[10,16] However, it is unlikely that such a large methylene signal originates from defects.[16] Additionally, one has to keep in mind that we cannot increase the defects indefinitely to generate higher methylene signals without affecting the melting temperature (or even destroying crystallinity completely). As discussed later, we have not
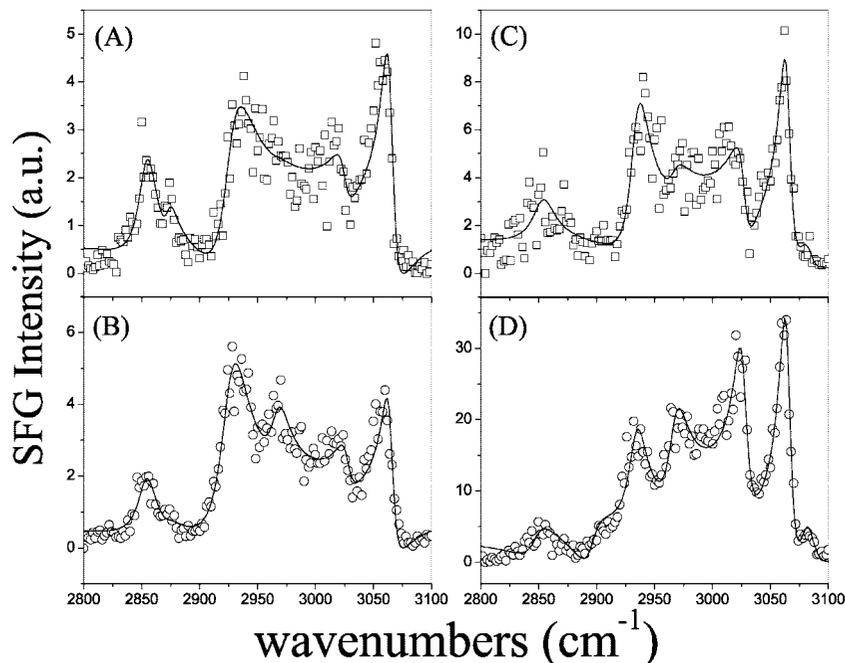
Figure 2. Panels A and B are SSP and PPP spectra, respectively, for hexadecanol/PS interface at 60 °C. Panels C and D are SSP and PPP spectra, respectively, for heneicosane/PS interface at 50 °C. All the spectra in panels A−D are taken when both hexadecanol and heneicosane are in the liquid state. The solid lines are fitted using a Lorentzian equation, and the parameters obtained from the fits are summarized in Tables 3 and 4.

TABLE 3: The A_q and Γ_q Values Obtained from Fitting the Data in Figure 2 for Hexadecanol/PS System at 60 °C

		2854 cm^{-1}	2873 cm^{-1}	2926 cm^{-1}	2967 cm^{-1}	3027 cm^{-1}	3065 cm^{-1}
		d^+	r^+	r^+_{FR}	r^-_a	ν_{20b}	ν_2
SSP	A_q	22 ± 1.0	3 ± 1.0	21 ± 2.0	1 ± 0.8	4 ± 0.2	13 ± 30
	Γ_q	10	8	15	10	7	6
PPP	A_q	19 ± 1.0	1 ± 1.0	26 ± 2.0	5 ± 0.7	3 ± 7	13 ± 48
	Γ_q	10	8	15	10	7	6

TABLE 4: The A_q and Γ_q Values Obtained from Fitting the Data in Figure 2 for Heneicosane/PS System at 50 °C

		2853 cm^{-1}	2895 cm^{-1}	2934 cm^{-1}	2967 cm^{-1}	3027 cm^{-1}	3065 cm^{-1}	3083 cm^{-1}
		d^+	d^+_{FR}	r^+_{FR}	r^-_a	ν_{20b}	ν_2	ν_{20a}
SSP	A_q	8 ± 1.4		38 ± 0.8	4 ± 1.1	7 ± 0.9	16 ± 1.5	12 ± 1.8
	Γ_q	12		10	10	7	6	8
PPP	A_q	13 ± 3.3	20 ± 5.7	21 ± 1.7	17 ± 1.4	20 ± 1.2	32 ± 5.4	20 ± 13.6
	Γ_q	12	11	10	10	7	6	8

observed any differences in melting temperatures between the interface and the bulk, which validates our hypothesis that the large methylene signals cannot be due to defects. We have previously observed strong methylene signals for confined alkane crystal between a poly(dimethylsiloxane) rubber and sapphire substrate.[31] In that work, we showed that for a single all-trans hydrocarbon chain with an odd number of methylene units oriented with C−C−C axis parallel to the surface, the methylene intensity is comparable to that from the methyl ends.[31] We reach a similar conclusion if we consider an ensemble of hexadecanol molecules with the C−C−C axis parallel to the surface where the symmetry is broken for both methyl and methylene groups in contact with the PS substrate. This conclusion is supported by our previous SFG and molecular dynamics simulation results for poly(dimethylsiloxane) (PDMS). We have shown that for an ensemble of PDMS chains next to solid surfaces, the symmetry of the methyl groups facing the surface is broken. In that case, the SFG signals are due to a layer of methyl groups in the immediate vicinity of the surface.[23] Molecular dynamics simulations are in progress to test the validity of the hypothesis that the chemical groups near the PS interface (for both heneicosane and hexadecanol) are primarily responsible for the SFG signals.

In Figure 2 we have plotted the SSP and PPP spectra for liquid hexadecanol and heneicosane in contact with PS. The A_q values obtained from the fits are summarized in Tables 3 and 4. In general, the signal intensity is much weaker in the 2800−3000 cm^{-1} region, which explains why we have observed the SFG intensity of the phenyl modes to be comparable to the SFG intensity of the methyl and methylene modes of alcohol and alkane molecules in the liquid state. The peak at 2926−2934 cm^{-1} is assigned to the methyl Fermi resonance. However, this assignment leads to a Fermi band that is much stronger than the methyl symmetric mode. It is likely that we are including some contribution of the methylene bands in this assignment, and because of the weak SFG signals we have not used additional peaks to fit the liquid spectra. There are some notable differences in the liquid and crystal spectra besides the drop in the SFG intensity upon melting. The methyl symmetric peak in the liquid spectra is weak or absent, indicating weak orientational order. The methylene symmetric peak is at 2850−55 cm^{-1} and not at 2835 cm^{-1} as observed for the crystal structure. A 5 cm^{-1} red shift in the methylene symmetric peak has been observed for bulk alkanes upon transition from liquid to crystal state. As we discussed above, it is also possible that the SFG peak at 2835 cm^{-1} in the crystal state is due to

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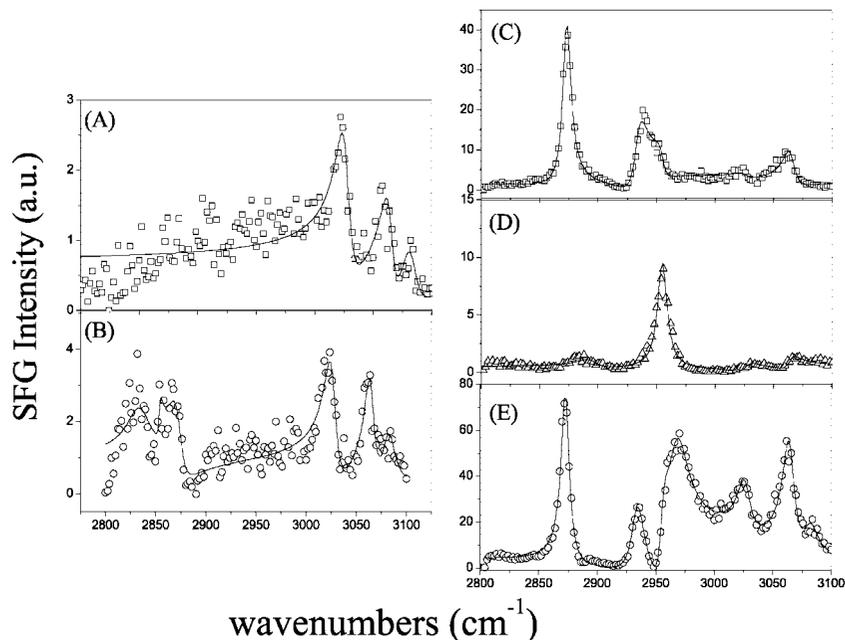
Figure 3. Panels A and B are SSP spectra for PS/sapphire interface in the presence of hexadecanol at 60 and 25 °C, respectively. Panels C−E are SSP, SPS, and PPP spectra, respectively, at the PS/sapphire interface after the sample was heated to 130 °C in the presence of hexadecanol and cooled down to 25 °C. The spectra were collected at 25 °C. The solid lines are fitted using a Lorentzian equation, and the parameters obtained from the fits for panels C−E are summarized in Table 5.

TABLE 5: The A_q and Γ_q Values Obtained from Fitting the Data in Figure 3, Panels C and D, for Hexadecanol/PS System at 25 °C

		2873 cm^{-1}	2895 cm^{-1}	2934 cm^{-1}	2955 cm^{-1}	2967 cm^{-1}	3027 cm^{-1}	3065 cm^{-1}	3083 cm^{-1}
		r^+	d^+_{FR}	r^+_{FR}	r^-_b	r^-_a	ν_{20b}	ν_2	ν_{20a}
SSP	A_q	23 ± 0.3		21 ± 0.9	6 ± 0.6		3 ± 0.9	12 ± 0.8	
	Γ_q	4		7	5		7	6	
SPS	A_q		4 ± 0.7		13 ± 0.2		9 ± 0.9	4 ± 0.6	
	Γ_q		10		5		7	6	

methylene groups bonded to OH groups of hexadecanol, which are much more disordered above T_m. The similarity in the SFG signal for liquid alcohol (or alkane) and PS phenyl groups suggests that the overall orientational order of glassy PS at the interface is similar to that of a liquid. There is a breakdown in the symmetry of the phenyl groups near the vicinity of the interface.[28]

3.2. SFG Results after Annealing Above T_g. Panels A and B in Figure 3 are SFG spectra for PS/sapphire interface in SSP polarization collected at −10° incident angle at 60 and 25 °C, respectively, before annealing the system above T_g. We emphasize that the films were annealed above T_g and done in the presence of the liquids (alkane or alcohol). The PS samples before the SFG measurements were already annealed above T_g before injecting the liquids to remove any anisotropic structure that may be induced due to spin coating. At this incident angle, we are measuring the structure of the molecules at the PS/sapphire interface. The SSP spectrum at 60 °C has predominant phenyl peaks and is identical to the SSP spectrum obtained for PS in contact with sapphire.[11] The asymmetric phenyl modes are stronger than the symmetric phenyl modes. In addition, we observed a peak at 3083 cm^{-1} (assigned to the ν_{20a} mode) as reported before.[11] On cooling to 25 °C, we observe a weak signature in the methyl and methylene region. These signals are much weaker than the SFG intensity observed from the hexadecanol/PS interface. In addition to these observations, the spectral features are similar to those observed for the crystalline hexadecanol/PS interface. Therefore, we cannot conclude that the hexadecanol molecules have diffused to the sapphire interface after annealing the sample at 60 °C.

More dramatic changes at the PS/sapphire interface are observed when we heat the system to 130 °C for 1−2 h and cool it back to 25 °C. We have shown the SFG spectra from the PS/sapphire interface in SSP, SPS, and PPP polarization in panels C−E in Figure 3. The methyl peaks are now much stronger than those observed before heating (or heating to 60 °C). In addition, the phenyl symmetric peak is higher than the asymmetric vibration. There are no methyl groups in PS, and the SFG signal at the PS/sapphire interface has to be due to hexadecanol molecules. This suggests that hexadecanol molecules have diffused through the PS film and formed an interfacial layer between PS and sapphire substrate. The solid lines are fitted using the Lorentzian equation, and the A_q and peak positions are summarized in Table 5. The dominant peaks in the SSP spectrum are methyl symmetric and methyl Fermi bands. The dominant peak in the SPS spectrum is the methyl asymmetric vibration. These spectra are very similar to those of self-assembled monolayers and heneicosane in contact with PS (Figure 1). The ratio of $A_{yzy, r-}/A_{yyz, r-}$ is 2.2 (Table 5) and the methyl group is tilted by ≤33° at the sapphire interface. The structure of adsorbed hexadecanol is very different from the hexadecanol molecules crystallized in contact with PS (Figure 1). The interfacial structure of PS is also different after the adsorption of hexadecanol. The symmetric phenyl modes are more dominant, and this structure is more similar to that of PS in contact with methyl or methylene groups of hexadecanol and heneicosane.

The adsorption of the hexadecanol at the sapphire interface can be explained by the interaction of the hydroxyl groups of the hexadecanol with the hydrophilic sapphire interface. The
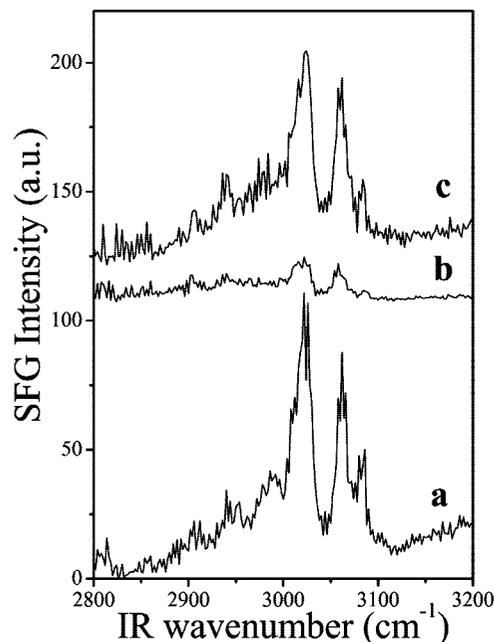
Figure 4. PPP spectra for PS/sapphire interface in the presence of heneicosane at 25 °C (a), 130 °C (b) and after cooling the system down to 25 °C (c).

Figure 5. Panels A−C are SSP, SPS, and PPP spectra, respectively for hexadecanol/PS interface after the system was heated to 130 °C and cooled down back to 25 °C. The solid lines are fitted using a Lorentzian equation.

influence of hydrogen bonding of hydroxyl groups in controlling adsorption of alcohol molecules on graphite substrate has been reported elsewhere.[32] This hypothesis is further supported by annealing nonpolar heneicosane above the T_g of PS. The PPP spectra for the PS/sapphire interface are shown in Figure 4. The PS/sapphire spectrum at 25 °C is similar to that of PS/sapphire without any heneicosane. After heating the system above 130 °C and cooling it back down to 25 °C, we observe no changes in the PPP spectrum. This indicates that heneicosane molecules are not adsorbed onto the PS/sapphire interface because there is no energetic benefit in replacing the PS segments with the alkane molecules at the sapphire interface. Even though the annealing time we have used in these experiments is much longer than those predicted based on the diffusion constants, one could argue that the 2−3 h of exposure time at 130 °C is not enough for diffusion of heneicosane. To eliminate this possibility, we doubled the annealing time at 130 °C. In that case we also did not observe any adsorption of heneicosane at the sapphire interface. These annealing times are sufficient for diffusion even after considering that we have used thicker PS films in the experiments with heneicosane than the experiments with hexadecanol. We believe these differences would be similar for other polar and nonpolar molecules, and these differences have important consequences in understanding adhesion and stability of polymer films in contact with substrate. The sensitivity of SFG to these subtle changes occurring at hidden solid substrates is very unique and demonstrates the importance of SFG technique in studying hidden interfaces.

To show that there are no permanent changes in the integrity of the PS film upon heating above the T_g, we measured the hexadecanol/PS interface at 25 °C after heating the sample above T_g. These results are shown in Figure 5. There are no spectral differences before and after annealing in any of the three polarization combinations we used (SSP, SPS, and PPP) (the SFG spectra before annealing above T_g are shown in Figure 1), which confirms that we did not damage the PS films or alter the structure at the alcohol/PS interface upon heating. The similarity in the SFG spectra before and after annealing above T_g also shows that the local interfacial structure is not affected
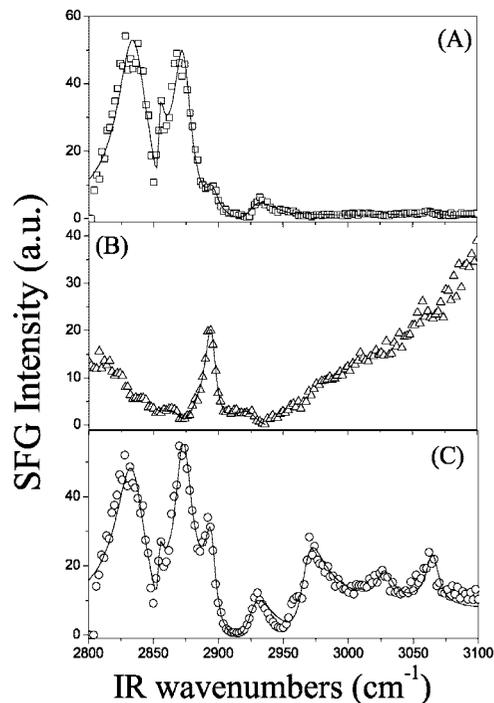
by bulk T_g of PS. We also confirmed the stability of the PS upon annealing at 130 °C for heneicosane/PS system (spectra not shown).

3.3. Melting Temperatures of Hexadecanol and Heneicosane at Interfaces. To measure the melting transition temperature of hexadecanol in contact with PS surface, we collected spectra at various temperatures during the heating run. The spectra were fitted with a Lorentzian equation and the amplitude strengths, A_q, as a function of temperature are plotted in Figure 6. The panels Figures 6A and B show the A_q for the methyl symmetric and phenyl symmetric, respectively, at hexadecanol/PS interface. The bulk melting and rotator transition temperature for hexadecanol are shown as solid and dotted lines, respectively. The drop in A_q between rotator and melting transition suggests disordering of the hexadecanol close to the bulk melting transition temperature. We observe the same trend in the amplitude strength for the phenyl symmetric mode. This trend suggests that the phenyl groups are also responding to the changes in the structure occurring near the melting temperature of hexadecanol, and these changes take place much below the bulk glass transition temperature of PS. We observed the same effects for alkanes in contact with PS.[33] Additionally, we also observed the changes in the PS structure after bringing it in contact with poly(dimethyl siloxane) below the T_g of PS. This observation is consistent with the hypothesis that the local changes in the interfacial structure at the PS interface are independent of bulk T_g of PS.[34]

When we measure the changes in structure of hexadecanol adsorbed at the PS/sapphire interface, we observe no abrupt change in amplitude strength near bulk T_m (Figure 6). The interaction of the hexadecanol molecules must be strong enough to stabilize the orientation order of these adsorbed molecules above T_m. The phenyl symmetric mode also decreases gradually as we heat it above the bulk T_m, unlike the sharp changes in the phenyl structure at the hexadecanol/PS interface, which suggest subtle changes in the interfacial structure. However, it

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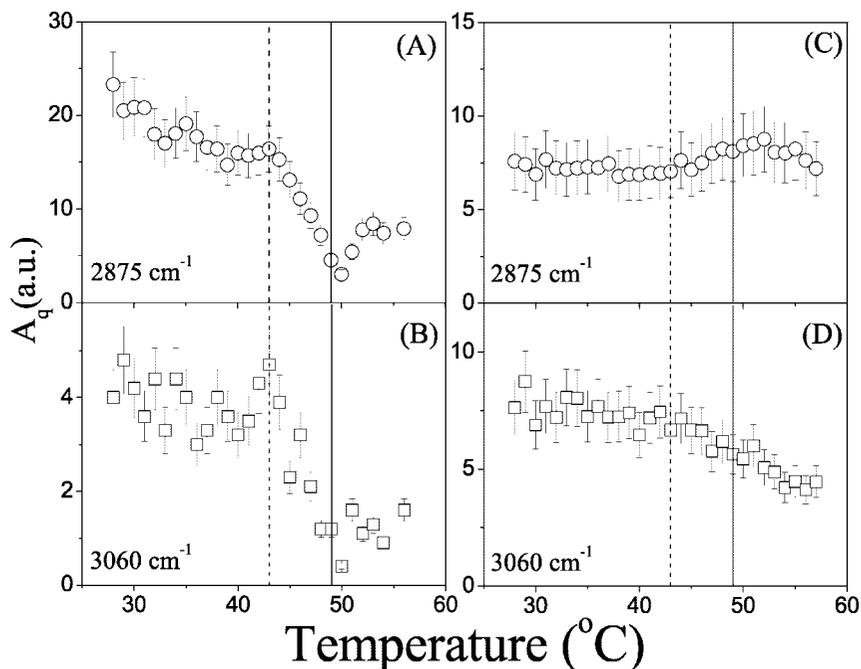
Figure 6. In panels A and B, we have plotted the amplitude strength (A_q) for the methyl symmetric and phenyl symmetric, respectively, as a function of temperature for the hexadecanol/PS interface (collected at 0° incident angle). The solid and dashed lines are the rotator-to-liquid and crystal-to-rotator transition for bulk hexadecanol. In panels C and D the A_q are plotted at −10° incident angle, which corresponds to the critical angle for the PS/sapphire interface.
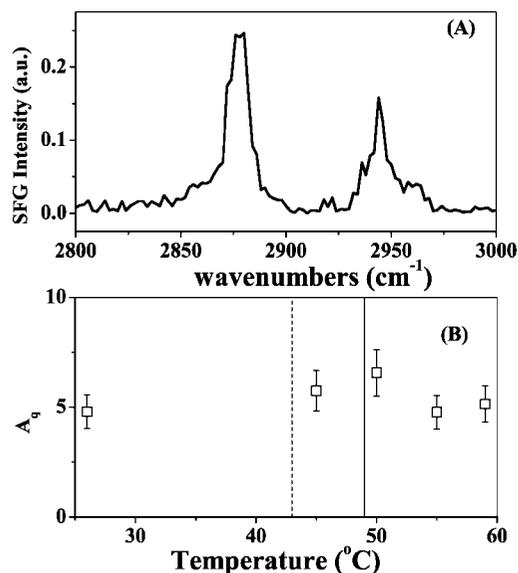
Figure 7. (A) SSP spectrum for hexadecanol/sapphire interface at 25 °C. (B) The data represented as open squares in panel are A_q as a function of temperature for hexadecanol/sapphire interface. The dashed and solid lines are rotator and melting transition temperature for bulk hexadecanol, respectively.

is possible that the T_m for adsorbed hexadecanol is higher than 60 °C. We cannot rule out the possibility that the adsorbed molecules form an ordered noncrystalline structure in contact with sapphire. The experiments to distinguish between these two possibilities are in progress.

As a control, we measured the structure of the bulk hexadecanol crystal in contact with sapphire (without a PS film). The SSP spectrum at 25 °C is shown in Figure 7A. The SSP spectrum is dominated by methyl symmetric and methyl Fermi modes, similar to the adsorbed hexadecanol molecules at the PS/sapphire interface, suggesting that the hexadecanol molecules are aligned perpendicular to the surface plane. The amplitude

strengths as a function of temperature are shown in Figure 7B. The orientational order does not change near the bulk T_m. The similarity in the structure and transition behavior suggest that the adsorbed hexadecanol at the PS/sapphire interface is very similar to the bulk hexadecanol in contact with sapphire. In contrast, we observed no changes in the interfacial melting temperature for alkanes in contact with sapphire and PS.[30,33] The absence of such changes suggests that the interaction of hydroxyl groups is important to stabilize the orientation of hexadecanol at the sapphire interface.

3.4. SFG Spectra in the Hydroxyl Region. Finally, we discuss the SFG results in the hydroxyl region from 3100−3600 cm^{-1}. Figure 8A shows the SSP spectra for hexadecanol/PS interface at various heating and annealing conditions. The bare sapphire surface does not show peaks in the hydroxyl region. For hexadecanol in contact with PS above the bulk T_m at 60 °C, we did not observe any discernible peaks in this region. After cooling the system below T_m we observe a broad OH peak near 3300 cm^{-1} upon crystallization of hexadecanol. The transition temperature where the hydroxyl groups disorders is similar to the transition temperature determined by monitoring the methyl symmetric and phenyl symmetric modes. This similarity also confirms the assignment of the 3300 cm^{-1} peak to the OH groups of hexadecanol. After annealing the system at 130 °C and cooling it back down to 25 °C, we did not observe any major differences in the spectral features.

In comparison, we did not observe any OH bands for PS/sapphire interface even after annealing above 130 °C. This is puzzling because we have already shown that, after annealing, well-ordered hexadecanol molecules have adsorbed onto the sapphire substrate. It is possible that the net orientation of the surface hydroxyl OH and alcohol OH may cancel each other. In the case of hexadecanol/PS interface, the contribution is from only the alcohol OH; thus, we observe a strong SFG signal from the hydroxyl groups at the hexadecanol/PS interface. One could also explain these results based on the orientation of the OH groups. In general, molecules that are oriented with their
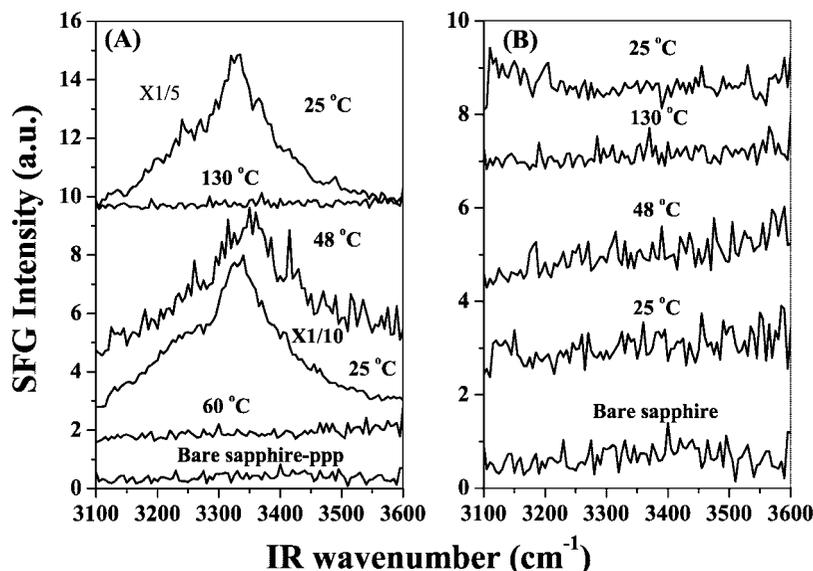
Figure 8. (A) The SSP spectra from 3100−3600 cm^{-1} for hexadecanol/PS interface. As a control, we have also shown the PPP spectra for the sapphire interface. (B) The SSP spectra from 3100−3600 cm^{-1} for PS/sapphire interface in the presence of hexadecanol. The scaling factors correspond to the multiplicative values used to normalize the spectra to help compare the spectral features at different annealing conditions. The spectra are also shifted vertically for clarity.

symmetry axis in the surface plane show weaker SFG signals than those oriented with the symmetry axis perpendicular to the surface plane.

4. Conclusions

We have shown that hexadecanol molecules crystallize in contact with PS with a structure that is very different from the crystallization of a nonpolar heneicosane in contact with PS. In the liquid state, both have a similar interfacial structure in contact with PS. However, upon crystallization, the hexadecanol molecules at the interface are oriented with the C−C−C axis parallel to the PS surface. We suggest that nonpolar heneicosane molecules crystallize with the C−C−C axis perpendicular to the PS surface. When we annealed the samples above the bulk T_g, we observed dramatic differences in the structure at the hidden PS/sapphire interface. The hexadecanol molecules diffused through the PS film, displaced the PS segments, and adsorbed on the sapphire substrate. The adsorbed hexadecanol chains are then oriented perpendicular to the sapphire substrate. The adsorption did not destroy the integrity of the PS film on the sapphire substrate. No such adsorption was observed for heneicosane. The hydroxyl groups of hexadecanol have strong interactions with the hydrophilic sapphire substrate, which has a dramatic influence on the stability of the orientation upon heating above T_m. The ordered structure persisted above the bulk T_m. The structure and stability of orientation of the adsorbed layer was similar to hexadecanol bulk in contact with the sapphire substrate without the presence of PS film. In contrast, the interfacial melting transition temperatures for hexadecanol and heneicosane in contact with PS were very similar to the bulk transition temperatures.

Supporting Information Available: The experimental geometry and the refractive index used to determine the incident angles are provided as Supporting Information. This information is available free of charge via the Internet at http://pubs.acs.org.

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