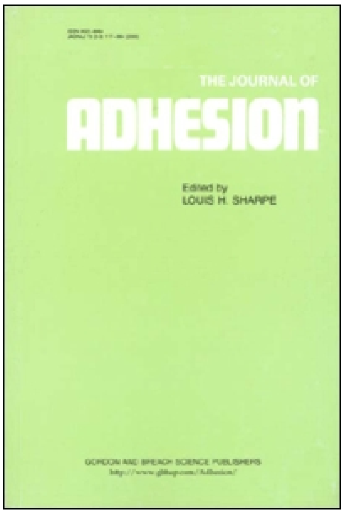

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Polymer-Silane Interactions Probed by Sum Frequency Generation Vibrational Spectroscopy

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Polymer-Silane Interactions Probed by Sum Frequency Generation Vibrational Spectroscopy

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Gaining an understanding of the molecular mechanisms of adhesion to polymeric materials is crucial for the design of better adhesives and adhesion promoters. Silane coupling agents are widely used as polymer-polymer adhesion promoters. However, a molecular level understanding of how silanes enhance adhesion between solid polymeric surfaces is largely unknown. Here we exploit the extreme surface sensitivity of sum frequency generation (SFG) vibrational spectroscopy to probe various interactions at buried interfaces between polymers and silanes in situ. It has been elucidated that silanes can adopt various conformations at the interfaces with different polymers depending on the chemical groups that comprise the silane and the surface-presenting groups on the polymer. Some silanes have been found to diffuse into certain polymers, and SFG has been used to monitor the moving polymer/silane interface and deduce the diffusion coefficient. Hydrogen bonding between polymer surface carbonyl groups and silane amino groups has

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also been detected. Finally we demonstrate that SFG can probe the buried interface between a polymer and a cured silicone elastomer, and the segregation of silane adhesion promoting molecules to the polymer/elastomer interface can be detected.

Keywords: Polymer adhesion; Adhesion promoter; Silane coupling agent; Interface; Interfacial interaction; Diffusion; Sum frequency generation vibrational spectroscopy

INTRODUCTION

Silicone adhesives that cure by hydrosilylation are used in many industrial applications because they exhibit adhesion to a wide rage of surfaces while offering rapid non-volatile cure, unique rheological properties, and excellent thermal stability and flexibility over a wide range of temperatures [1–3]. However, because these addition curing silicone elastomers by themselves cannot adhere well to most glassy or semi-crystalline polymeric surfaces, they must be formulated with adhesion promoting additives for bonding to untreated plastic substrates [4]. Silane coupling agents are among the most commonly used adhesion promoters, especially for silicone elastomers. Many organosilane-based adhesion promoters have been developed to enhance adhesion to metals, inorganic substrates, and some polymers [5–7].

The interface between an adhesive and an adherend is where the first contact between the two materials is made and thus it is at that interface where an adhesive bond must originate. To design better adhesives and adhesion promoters for polymers we must have an understanding of the molecular mechanisms that contribute to the formation of the bond at the adhesive/substrate interface. For example, there exist a number of mechanisms at various length scales that may contribute to wetting and adhesion including the segregation of adhesion promoters to the interface, the ordering and alignment of different interface-presenting functional groups, the formation of interfacial hydrogen and chemical bonds, and the diffusion of molecules across the interface [8–12]. For strongly adhering rigid polymer/elastomer interfaces it is likely that some type of covalent bonding is operative, perhaps in concert with inter-diffusion of a particular species. It is unknown whether the absence of significant adhesion to certain polymers is due to simple unreactivity or to the lack of a pre-requisite physical condition, such as the failure of the functional groups at the interface to establish the necessary concentration, order, or orientation for such reactions to occur.

Polymer interfaces have been extensively studied in the last few decades by a number of methods [13–19]. Unfortunately, conventional surface analytical techniques cannot simultaneously provide, in situ, the detailed molecular structures and sufficient surface sensitivity to define the governing molecular mechanisms of adhesion to organic surfaces. For example, although X-ray photoelectron spectroscopy (XPS) is regarded as among the most sensitive surface techniques, the contribution from a siloxane background of a silicone elastomer will detract from the signal intensity of small molecule additives even when they are enriched at the interface. Further, XPS requires high vacuum and is primarily an elemental technique. Both attenuated total reflection Fourier transform infrared (ATR-FTIR) and Raman spectroscopies have been successfully applied to adhesion studies of interfaces comprising of polymers and silane materials [17–19]. However, both techniques lack intrinsic surface or interface sensitivity. For example, ATR-FTIR spectra are often dominated by bulk contributions, as the penetration depth of the infrared light limits the surface sensitivity of the technique to the micrometer scale rather than the nanometer scale. Additionally, a significant limitation for most conventional surface analytical methods in adhesion studies is the inability to study a buried interface in situ. By definition, well-adhered surfaces cannot be readily separated, making it difficult to expose such buried interfaces for analysis.

Recently, sum frequency generation (SFG) vibrational spectroscopy has emerged as a valuable technique to study polymer surfaces and interfaces at the molecular level [20–36]. As disclosed below, the selection rules for SFG render this technique inherently surface and interface sensitive. A laser technique, any interface accessible by light can be probed, making SFG an ideal tool to elucidate, at the molecular level, the prevailing mechanisms of adhesion to polymers. Here, we present a brief overview of the SFG experiment and provide examples from our research of how this technique is being used to probe polymer/silane, and more recently, polymer/silicone elastomer interfaces. Through these studies we are beginning to develop a molecular-level picture of silane-promoted adhesion in addition curing elastomers.

SFG Technique

As schematically depicted in Figure 1a, SFG is a process by which two input laser beams at frequencies ω_1 and ω_2 spatially and temporally overlap in a medium generating an output beam at the sum frequency $\omega_3 = \omega_1 + \omega_2$. For SFG vibrational spectroscopy, conventionally ω_1 is in the visible region of the spectrum and ω_2 is a tunable infrared (IR) beam. As ω_2 is scanned over the vibrational resonances of the molecules in the probed material, the SFG signal becomes resonantly

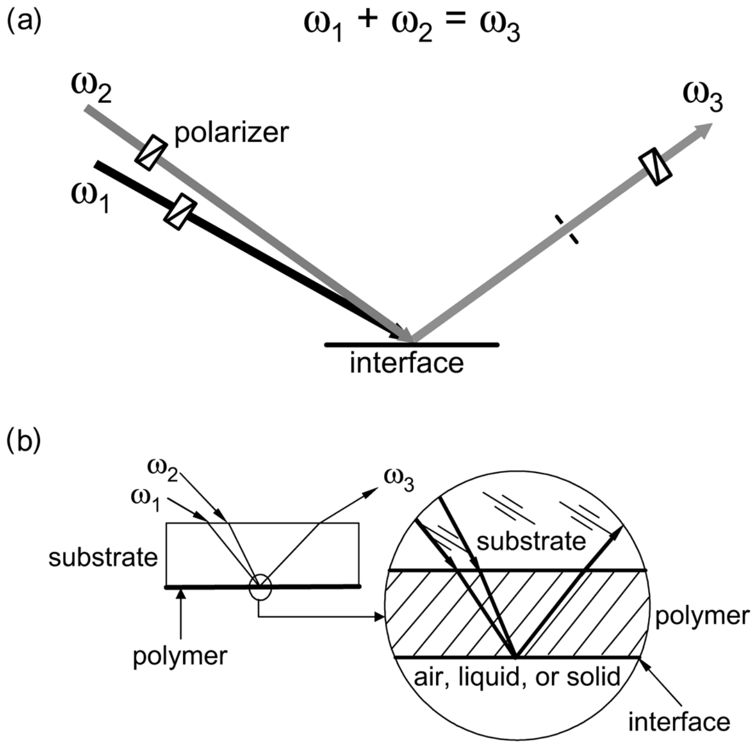

FIGURE 1 (a) The SFG process. (b) Sample geometry adopted in these studies.

enhanced, generating a vibrational spectrum characteristic of the sample, much like an IR or Raman spectrum. Only those vibrational modes that are both IR and Raman active will be SFG-active. The intensity of the SFG signal, is described by

$$I(\omega_{sum}) \propto \left|\chi^{(2)}\right|^2 = \left|\chi_{nr} + \sum_q \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q}\right|^2, \tag{1}$$

and is proportional to the square of the second-order nonlinear susceptibility of the material, $\chi^{(2)}$, where ${\chi_{nr}}^{(2)}$ is the nonresonant contribution to the signal, and the terms A_q, ω_q, and Γ_q represent the oscillator strength, frequency, and damping constant of mode q, respectively [37].

SFG is a second-order nonlinear optical process and under the electric-dipole approximation the selection rules for SFG indicate that an SFG signal is not generated in a medium with inversion symmetry. Most bulk materials such as polymers possess a center of inversion and thus do not exhibit SFG signals. However, at surfaces and interfaces where the inversion symmetry is broken an SFG signal is observed. Therefore, SFG signals arise from vibrational modes that are associated with those molecules or chemical groups that are both present at the interface and exhibit a net orientational order there. Both experimental evidence and calculations have deemed SFG as a submonolayer surface-sensitive technique. The orientation and orientational distribution of surface/interfacial functional groups can be deduced by collecting the SFG spectra using different polarization combinations of the input and output beams [37–39]. A more detailed discussion on SFG theory is presented in the literature [37–42].

EXPERIMENTAL

Materials

The polymers used in the examples provided below included poly (methyl methacrylate) (PMMA; M_w 350,000) and polystyrene (PS; M_w 393,400; PDI 1.16), which were purchased from Scientific Polymer Inc., and poly(ethylene terephthalate) (PET; M_v ca. 18,000), which was acquired from Sigma-Aldrich, Inc. Fully deuterated polymers, d-PMMA (M_w 219,000; PDI 1.04) and d-PS (M_w 207,500; PDI 1.25), and PET with deuterated ethylene glycol subunits (d_4-PET; M_v72,000) were obtained from Polymer Source, Inc. The silanes *n*-octadecyltrichlorosilane (OTCS), *n*-octadecyltrimethoxysilane (OTMS), (3-aminopropyl)-trimethoxysilane (ATMS), *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AATMS), and *n*-butyltrimethoxysilane (BTMS) were purchased from Gelest, Inc. Dow Corning Corp. provided (3-glycidoxypropyl)-trimethoxysilane (γ-GPS) and the Sylgard® 184 Silicone Elastomer Kit. The structures of these polymers and silanes are depicted in Figure 2.

Polymer films were prepared by spin coating 1–2 wt % solutions of the polymer in an appropriate solvent onto fused silica (for spectra collected in the C–H stretching region) or CaF_2 (for spectra collected in the carbonyl stretching region) substrates. The samples were either placed in an 80°C oven or under vacuum for at least 18 h prior to analysis to ensure adequate removal of the solvent. The cured silicone elastomer was prepared by following the manufacturer's instructions and mixing the base and curing agent in a 9:1 ratio and applying it to a spin coated polymer film. The elastomer was allowed to cure for 1 h in a 150°C oven.

SFG Experiment

In the following examples the SFG spectra were collected by overlapping a visible laser beam at a fixed frequency of 18800 cm^{-1} (532 nm)

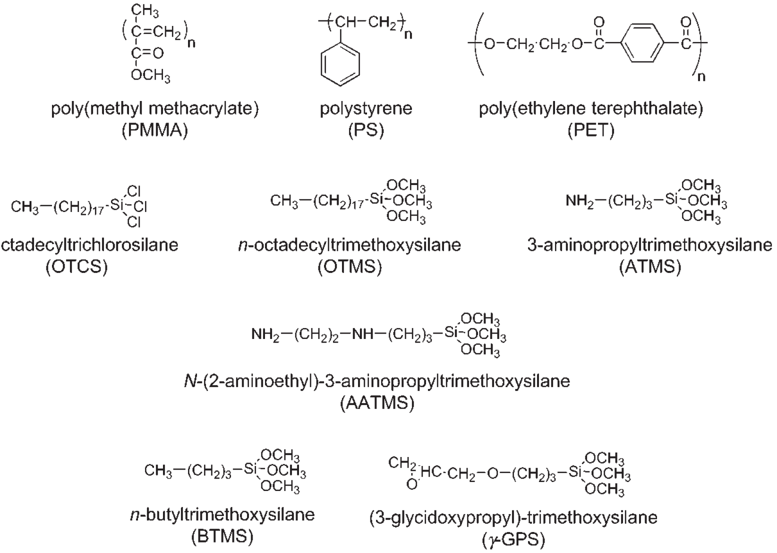

FIGURE 2 Chemical structures of the polymers and silanes studied in the examples.

and an IR beam, which was tunable from 1100 to 4000 cm^{-1}, temporally and spatially on the polymer interface at incident angles of 60° and 54°, respectively. The diameters of both beams on the sample were about 500 μm. The resultant SFG signals from the interface were directed into a monochromator, detected by a photomultiplier tube, and processed with a gated integrator. The input visible and IR beam powers were monitored by collecting their back reflections onto two photodiodes and the SFG spectra from the samples were normalized by the powers of the two input beams. All SFG spectra discussed in these examples were collected in the ssp (s-polarized SFG output, s-polarized visible input, p-polarized IR input) polarization configuration.

The systems investigated in these examples included polymer/air, polymer/liquid silane, and polymer/cured silicone elastomer interfaces. For these interfaces the SFG spectra were collected with the two input beams traveling through the fused silica (or CaF_2) substrate and overlapping at the interface of interest (Figure 1b). Previous research in our group demonstrated that SFG spectra from polymer/air, polymer/liquid, and polymer/solid interfaces were dominated by the interface under investigation with almost no contribution from the polymer/(fused silica or CaF_2) substrate interface or from the polymer bulk [30–32].

EXAMPLES

Molecular Structures at Polymer/Silane Interfaces

Our initial research was focused on developing an understanding of how polymer surface structures could dictate the interfacial conformations of contacting molecules [34]. We chose to examine the structures of silanes at polymer interfaces not only because these molecules are commonly used as adhesion promoters but because they are widely available and can be tailored with a number of different functional groups. The silane molecules were envisioned to be comprised of three distinct groups: a silane headgroup, a methylene "backbone," and an endgroup. For example, OTCS has a $SiCl_3$ headgroup, a backbone consisting of 17 methylene groups, and a methyl endgroup. OTMS is identical to OTCS except for its headgroup, which is comprised of the methoxy functionality ($Si(OCH_3)_3$). The amino group (NH_2) terminates the shorter methylene backbone of ATMS. The first experiments involved contacting these silanes with the polymers PMMA and PS. The deuterated polymers, d-PMMA and d-PS, were substituted at times to avoid confusion between the C–H stretching vibrational modes arising from the polymer and those from the interfacial silane molecules. Previous studies revealed that the PMMA surface in air is dominated by the ester methyl groups [30] while phenyl groups are present on the PS surface [25, 26].

Depicted in Figure 3 are the SFG spectra collected from the various polymer/silane interfaces. The SFG spectrum from the d-PMMA/

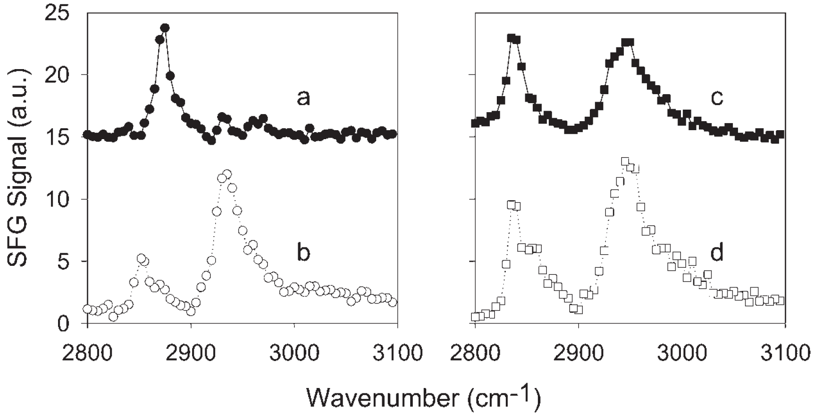

FIGURE 3 SFG spectra collected from the (a) d-PMMA/OTCS, (b) d-PS/OTCS, (c) d-PMMA/OTMS, and (d) d-PS/OTMS interfaces. (Reprinted with permission from Chen, C. Y., Loch, C. L., Wang, J., and Chen, Z., *J. Phys. Chem. B* **107**, 10440–10445 (2003). Copyright (2003) American Chemical Society.)

OTCS (Figure 3a) interface was dominated by the peak at 2870 cm^{-1}, which is characteristic of the symmetric C–H stretching of the methyl endgroup of OTCS [34]. This spectrum revealed that these groups were ordered at this interface and that the silane molecules likely adopted a configuration such that the methyl groups were directed towards the polymer surface, as illustrated in Figure 4a. A much different SFG spectrum was acquired from the d-PS/OTCS interface (Figure 3b). The two peaks at 2850 and 2930 cm^{-1} were from the symmetric and asymmetric C–H stretching of the silane methylene groups, respectively [34], as the OTCS backbone segregated to the polymer/silane interface (Figure 4b). The SFG spectra collected from these interfaces where OTCS was allowed to contact different polymers suggest that the interactions between the chemical groups of

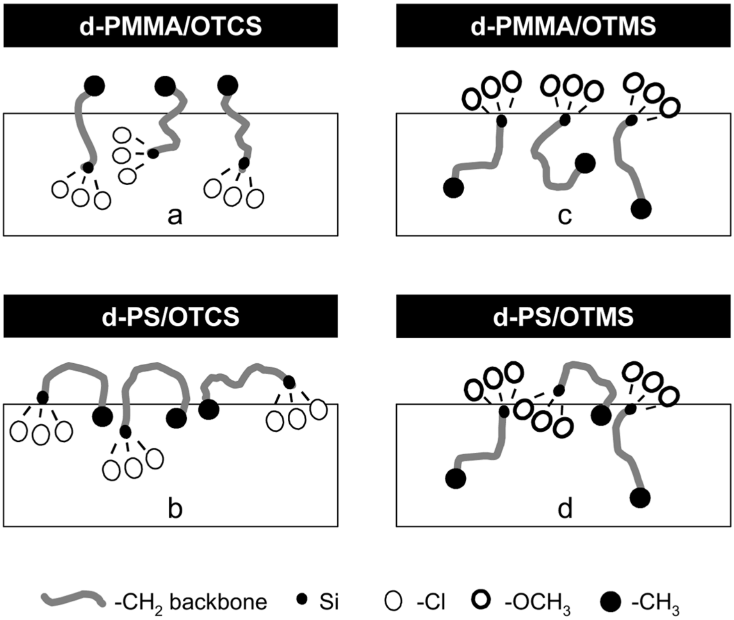

FIGURE 4 Schematic representations of the (a) d-PMMA/OTCS, (b) d-PS/OTCS, (c) d-PMMA/OTMS, and (d) d-PS/OTMS interfaces as interpreted from the SFG spectra. The different molecular segments of the silane molecules are described by the legend and the boxes are representative of the bulk silane liquid. The SFG signals primarily originate from those segments of the silane molecules between the polymer surface and the bulk silane. (Reprinted with permission from Chen, C. Y., Loch, C. L., Wang, J., and Chen, Z., *J. Phys. Chem. B* **107,** 10440–10445 (2003). Copyright (2003) American Chemical Society.)

the silane and the surface-presenting groups of the polymers induce the silane molecules to adopt the most favorable interfacial configurations. For example, the surface dominating ester methyl groups of PMMA have the most favorable interactions with the methyl groups of OTCS, while the phenyl groups on the PS surface interact with the silane methylene groups.

Also depicted in Figure 3 are the SFG spectra collected from the d-PMMA/OTMS (Figure 3c) and d-PS/OTMS (Figure 3d) interfaces. The peaks centered at 2840 and 2945 $\mathrm{cm^{-1}}$ were present in both spectra and were assigned to the symmetric and asymmetric C–H stretching of the silane methoxy headgroup, respectively [17]. At the d-PMMA/OTMS interface the silane methoxy headgroups were ordered (Figure 4c) as opposed to the methyl endgroups, as was observed at the d-PMMA/OTCS interface (Figure 4a). This implies that the OTMS methoxy groups have a more favorable interaction with the d-PMMA ester methyl groups than do the methyl groups. The methoxy groups of OTMS were also ordered at the d-PS surface; however, there is the appearance of a shoulder at 2850 $\mathrm{cm^{-1}}$ in the SFG spectrum from the interface with d-PS, which can be attributed again to the methylene backbone (Figure 4d).

These initial studies illustrate that the conformations of silane molecules at polymer/silane interfaces are dictated by both the functional groups present on the polymer surface and the chemical groups that comprise the silane. In such situations where the neat liquid silane has very high mobility in the bulk, groups on the silane that have the most favorable interactions with the polymer surface groups should segregate to the interface and adopt an ordered structure there. Similarly, the surface structure of the interfacial polymer can also change upon contacting different silanes. Presented in Figure 5 are the SFG spectra collected from hydrogenated PMMA/silane interfaces. The SFG spectrum from the PMMA/air interface (Figure 5a) was dominated by the peak at 2955 $\mathrm{cm^{-1}}$ which is characteristic of the C–H stretching of the side chain ester methyl groups [30]. When the polymer contacted OTCS (Figure 5b) this peak was still present indicating that the ester methyl groups on the PMMA surface were still ordered. It was noted that the intensity of the feature at 2955 $\mathrm{cm^{-1}}$ was weaker in the SFG spectrum collected from the PMMA/OTCS interface than at the polymer/air interface. This decrease in the SFG signal intensity may be primarily due to the difference in the refractive indices of air and the silane [28], although a loss in the surface order of the ester methyl groups on the PMMA surface while in contact with OTCS would also reduce the peak intensity. Similar results were also obtained from the PMMA/OTMS interface. Interestingly, no SFG

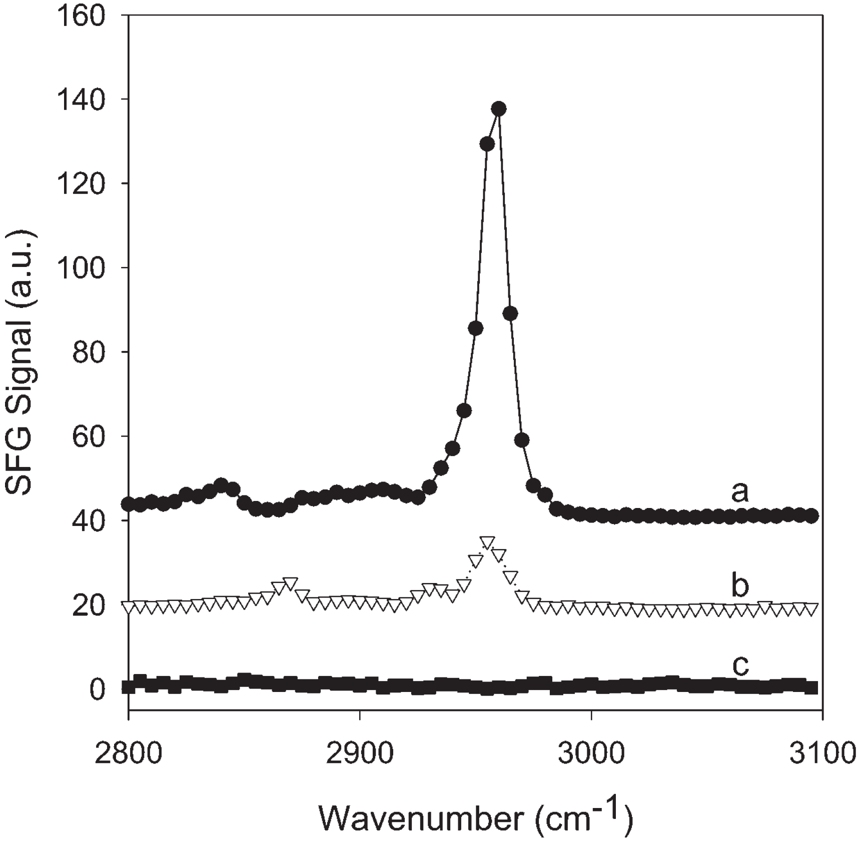

FIGURE 5 SFG spectra collected from the interfaces between hydrogenated PMMA and (a) air, (b) OTCS, and (c) ATMS. (Reprinted with permission from Chen, C. Y., Loch, C. L., Wang, J., and Chen, Z., *J. Phys. Chem. B* **107**, 10440–10445 (2003). Copyright (2003) American Chemical Society.)

signals were detected at the PMMA/ATMS interface (Figure 5c) (or d-PMMA/ATMS interface), which is indicative of the polymer surface ester methyl groups being disordered. This phenomenon is further examined in the following example.

Diffusion of Silanes into a Polymer

In the previous example it was concluded that silane molecules can adopt various conformations at different polymer surfaces and that the polymer surface structure may also change upon contacting silanes. In particular, disordering of the ester methyl groups on the

PMMA surface occurred at the interface with ATMS. To provide further insight SFG spectra were collected from the d-PMMA/ATMS and similarly the d-PMMA/AATMS interfaces as a function of the time elapsed after the polymer was brought into contact with the liquid silanes (Figure 6). The SFG spectrum from the d-PMMA/air interface was first obtained to ascertain that no discernible C–H stretching signals could be detected from the deuterated polymer [35]. SFG spectra were then acquired in the C–H stretching region from the polymer/silane interfaces upon initial contact of d-PMMA with ATMS (Figure 6a) and AATMS (Figure 6b). A peak at 2840 cm^{-1} was resolvable in the SFG spectrum from the interface with ATMS while peaks at 2840 and 2945 cm^{-1} were observed in the spectrum from the interface with AATMS. These spectral features were consistent with those associated with the C–H stretching of the silane methoxy headgroup [17]. SFG spectra were continuously collected from these interfaces; however the peaks disappeared with time, a phenomenon that was not observed at the interfaces between d-PMMA or d-PS and OTMS or OTCS. Of particular interest was the observation that the SFG spectra disappeared faster from the d-PMMA/ATMS interface than from the d-PMMA/AATMS interface. The initial presence of the peaks attributed to the silane methoxy headgroup in the SFG spectra indicate that the silane molecules were at first ordered. The disappearance of the SFG signals however leads to the conclusion that the molecules become disordered with time.

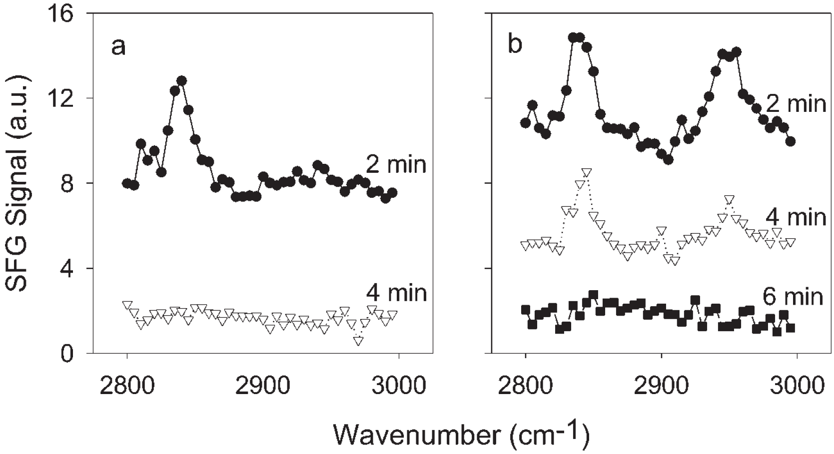

FIGURE 6 SFG spectra collected from the interfaces between d-PMMA and (a) ATMS and (b) AATMS as a function of time. (Adapted from Chen *et al*. [35].)

Thus we refer to this appearance and disappearance of the SFG signals as an interfacial order-disorder transition.

It takes at least 2 minutes to acquire an SFG spectrum such as those shown in Figure 6, and thus it is not practical to follow the dynamics of the interfacial order-disorder transitions observed by continuously collecting spectra with time. To provide more details into the kinetics at the d-PMMA/AATMS interface, the IR frequency was instead fixed at the silane characteristic peak frequencies of 2840 or 2945 cm^{-1} and the SFG peak intensities were monitored as a function of time (Figure 7). We chose to study the kinetics with AATMS because the interfacial order-disorder transition at the polymer/AATMS interface appeared to be slower than at the polymer/ATMS interface and thus more information on the dynamics of this transition could be elucidated. Before the silane was allowed to contact the d-PMMA film the SFG input IR and visible beams were overlapped on the polymer surface and there were negligible SFG signals at 2840 and 2945 cm^{-1} as there were no silane molecules present at the interface. However, once

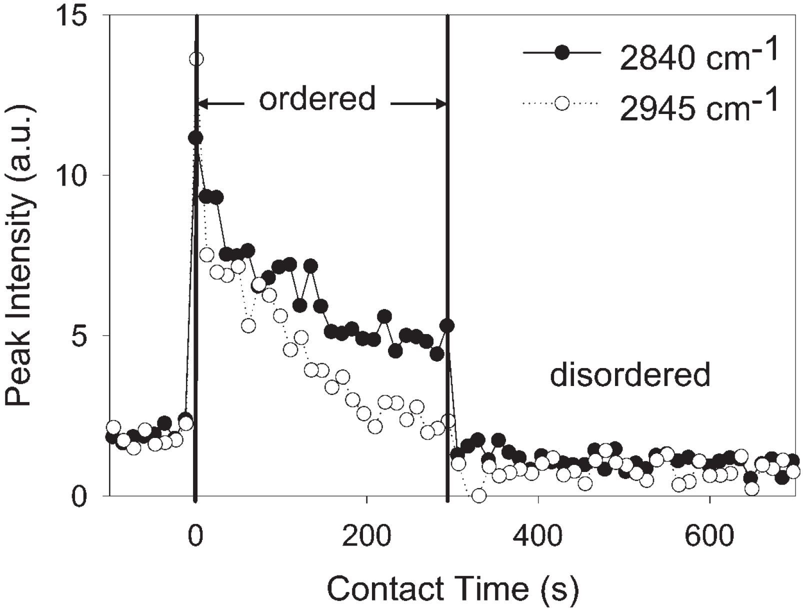

FIGURE 7 SFG signal inensities at 2840 and 2945 cm^{-1} monitored as a function of time from the d-PMMA/AATMS interface. (Reprinted with permission from Chen, C. Y., Wang, J., Loch, C. L., Ahn, D., and Chen, Z, *J. Am. Chem. Soc.* **126**, 1174–1179 (2004). Copyright (2004) American Chemical Society.)

the liquid silane was brought into contact with d-PMMA (contact time = 0 sec) the peaks at 2840 and 2945 cm^{-1} immediately emerged indicating both the presence and ordering of the methoxy headgroups of AATMS at the interface. The peak intensities were continuously observed for about 330 seconds before dropping to zero. From this it is determined that the silanes were ordered at the interface for some time before becoming disordered.

There are a number of scenarios that can explain the interfacial order-disorder transition at the polymer/amino-silane interfaces. For example, the silane molecules may gradually dissolve the polymer film, destroying the stable interface, and resulting in the loss of the SFG signal at the d-PMMA/AATMS interface. This possibility was excluded by observing that AATMS did not appear to dissolve d-PMMA beads and by performing a simple FTIR experiment [35]. An FTIR spectrum was collected from a d-PMMA film in the C-D stretching region. Upon contacting the film with AATMS for 30 min and subsequently removing the silane with water, the FTIR spectrum remained the same indicating no dissolution of the polymer occurred. For comparison, when a d-PMMA film was allowed to contact a solvent such as toluene, the FTIR spectrum completely disappeared in the C-D region. Two other mechanisms that would lead to the dynamical changes in the SFG spectra collected from the d-PMMA/AATMS interface include a simple randomization of both the polymer and silane functional groups or a process associated with the diffusion of the silane molecules through the polymer film.

To determine whether the AATMS molecules diffuse into the d-PMMA film an SFG experiment was designed. A PS/d-PMMA bilayer film was constructed by first spin coating a PS film onto a fused silica substrate. A d-PMMA film was spin coated on top of the PS film by using acetic acid as a selective solvent [35]. An SFG spectrum was collected from the bilayer film in air (Figure 8a). As there should be no SFG signals in the C−H stretching region arising from the d-PMMA layer, the only peaks in the spectrum must originate from the PS layer. Specifically, these peaks are characteristic of the C−H stretching of the PS phenyl groups. An SFG spectrum was also collected from the bilayer when the d-PMMA surface contacted water (Figure 8b). The SFG signals from the PS phenyl groups were still discernable and stable with time ascertaining that the signals arose from the buried PS surface and that the interface was still ordered in water. When the bilayer initially contacted AATMS (Figure 8c), the silane characteristic peaks at 2840 and 2945 cm^{-1} emerged and the SFG signals from the PS layer were still detected. SFG spectra were continuously collected and after 20 minutes (Figure 8d) the peaks were no longer

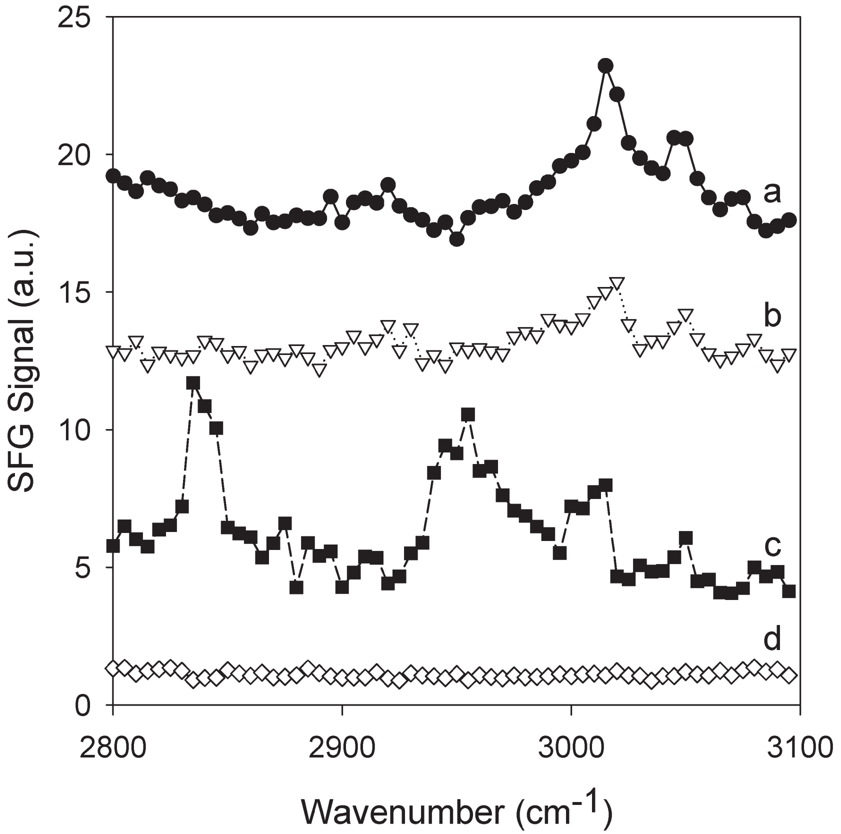

FIGURE 8 SFG spectra collected from the interfaces between a PS/d-PMMA bilayer and (a) air, (b) water, (c) AATMS after 5 minutes, and (d) AATMS after 20 minutes. (Reprinted with permission from Chen, C. Y., Wang, J., Loch, C. L., Ahn, D., and Chen, Z, *J. Am. Chem. Soc*. **126**, 1174–1179 (2004). Copyright (2004) American Chemical Society.)

resolvable. These spectra suggest that the AATMS molecules were initially ordered at the d-PMMA surface, while the buried PS layer remained unperturbed. The silane then diffused through the d-PMMA film and reached the interface between the two polymer layers. It was noted however that the SFG signals from AATMS were detected for 20 minutes before disappearing suggesting that the silane molecules retained some order while traversing through the d-PMMA film. Diffusion of the silane through d-PMMA must have occurred otherwise the interfacial PS structure should not have been interrupted.

The total disappearance of the SFG peaks attributed to the silane at both the d-PMMA/AATMS and PS/d-PMMA bilayer/AATMS interfaces is believed to occur once the silane diffuses through the polymer and reaches the fused silica substrate. To confirm this, SFG spectra were collected from the fused silica/AATMS interface and no resolvable signals were detected [35]. In the case of the PS/d-PMMA bilayer experiment, it is noted that the loss of the SFG signals from the silane and PS occurred at almost the same time, suggesting that AATMS may also be diffusing into PS, although at a much faster rate than with d-PMMA. The time-dependent SFG signals at 2840 and 2945 cm^{-1} were monitored from the d-PS/AATMS interface and were indeed lost after only about 25 seconds of contact [35].

To provide further evidence of diffusion, d-PMMA films of various thicknesses were prepared and placed into contact with AATMS and the SFG signal intensities at 2840 and 2945 cm^{-1} were continuously monitored with time (Figure 9a). It was observed that as the thickness of the d-PMMA film increased, so did the amount of time that elapsed before the SFG signals disappeared. This not only proved that AATMS diffused into d-PMMA but also that the silane molecules were ordered

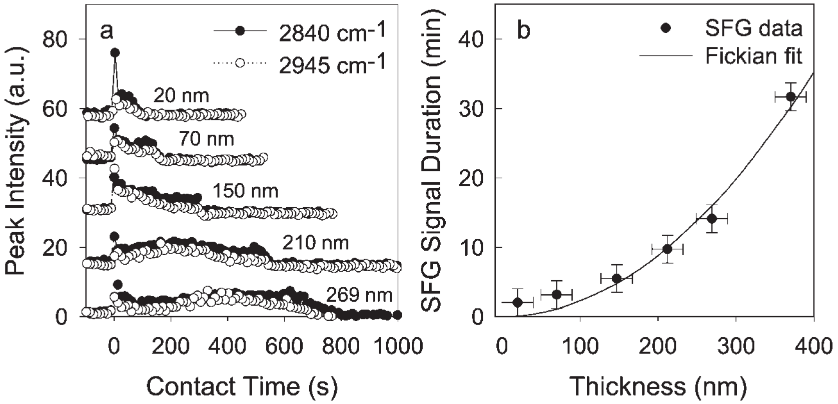

FIGURE 9 (a) Time-dependent SFG signal intensities at 2840 and 2945 cm^{-1} as AATMS molecules diffuse into d-PMMA films. Polymer film thickness is indicated next to its respective plot. (b) Determination of diffusion kinetics using the Fickian model. Deviation in the d-PMMA film thickness is indicated by the horizontal error bars and the deviation in the time duration measured with films of similar thickness is represented by the vertical error bars. (Reprinted with permission from Chen, C. Y., Wang, J., Loch, C. L., Ahn, D., and Chen, Z, *J. Am. Chem. Soc.* **126**, 1174–1179 (2004). Copyright (2004) American Chemical Society.)

during the diffusion process and only when the molecules reached the fused silica substrate did they become disordered resulting in the loss of the SFG signals. As shown in Figure 9b, the diffusion time as the AATMS molecules traversed through the polymer film, or SFG signal duration, was plotted versus the thickness of the d-PMMA film. The resultant curve was fitted to the Fickian diffusion model in which the diffusion distance (L, the thickness of the film) was related to the diffusion time (t, the time duration of which the SFG signal can be detected) by the formula, $L^2 = 2Dt$, where D is the diffusion coefficient. From this, the diffusion coefficient of AATMS in d-PMMA was deduced to be $(3.80 \pm 0.39) \times 10^{-13}\,\mathrm{cm}^2/\mathrm{s}$. Similarly, ATMS was also found to diffuse into d-PMMA, although at a faster rate, which may be attributed to the smaller size of the ATMS molecule [34, 35]. Although ATR-FTIR and other techniques have been developed into powerful tools to measure the diffusion kinetics of molecules into polymers, more structural information can be obtained using SFG. Also, the diffusion coefficient of AATMS into d-PMMA, as deduced by SFG, is several orders of magnitude less than those of other small molecules detected using ATR-FTIR. Using ATR-FTIR to study compounds with such a slow diffusion rate as was investigated here would be impossible because it would take years for such molecules to diffuse through a film with a thickness of 100 μm [43–48].

Hydrogen Bonding at a Polymer/Silane Interface

In the previous example, it was demonstrated that amino-functional trialkoxy silanes such as ATMS and AATMS diffuse into a PMMA (or d-PMMA) film. However, ATMS does not diffuse into all polymers as shown in the present example where a stable interface is formed between the silane molecules and PET. An SFG spectrum was collected from the PET surface in air in the carbonyl stretching region (1600–$1800\,\mathrm{cm}^{-1}$) and it was dominated by the peak at $1725\,\mathrm{cm}^{-1}$ (Figure 10a). The peak is characteristic of the PET ester carbonyls [49, 50] and the presence of this feature in the SFG spectrum indicates that these groups are both present and ordered on the polymer surface.

The silanes studied herein should not exhibit any SFG signals in the carbonyl stretching region of the spectrum and therefore will not interfere with the ester carbonyl signal from PET. Carbonyl groups can interact both chemically and physically, and this can be observed at the PET/silane interfaces by using SFG and monitoring the peak intensity and position. In fact, in Figure 10b it is evident that the peak at $1725\,\mathrm{cm}^{-1}$ shifted to $1715\,\mathrm{cm}^{-1}$ in the SFG spectrum collected from the PET/ATMS interface. It is noted that the amino endgroup of

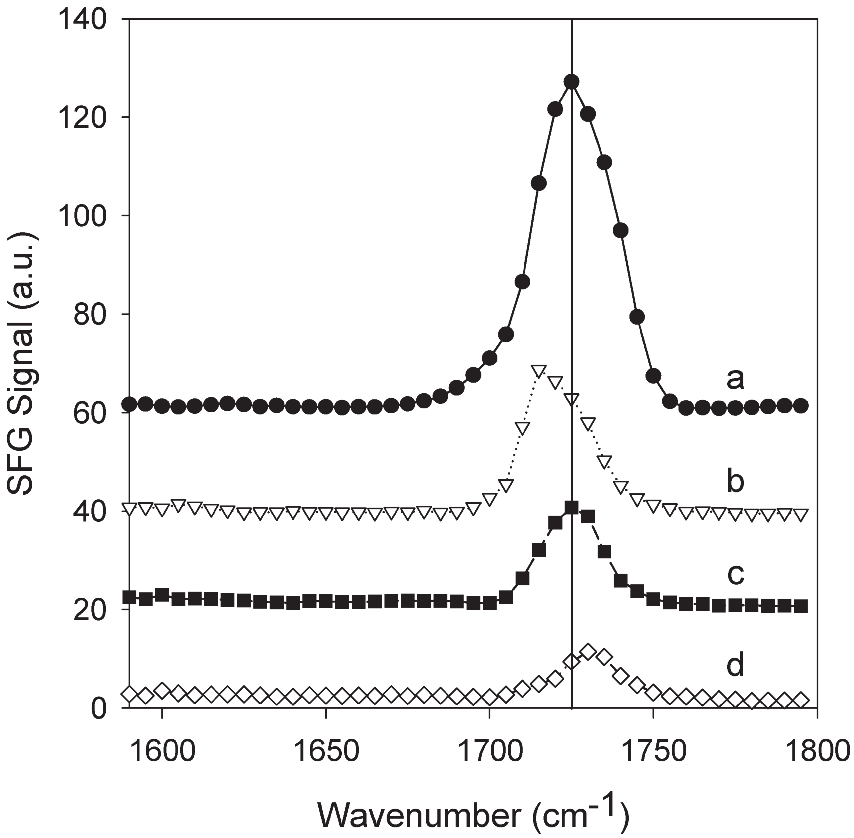

FIGURE 10 SFG spectra collected in the carbonyl stretching region from the PET surface in contact with (a) air, (b) ATMS, (c) γ-GPS, and (d) BTMS. The vertical line at 1725 cm^{-1} is provided to guide the eye. (Reprinted with permission from Loch, C. L., Ahn, D., Chen, C. Y., Wang, J., and Chen, Z., *Langmuir* **20,** 5467–5473 (2004). Copyright (2004) American Chemical Society.)

ATMS can form a hydrogen bond with the ester carbonyl group of PET and a 10 cm^{-1} red shift of a carbonyl stretching peak is typical for hydrogen bonded polymers [51]. Therefore, we attributed this shift to the formation of interfacial hydrogen bonds between PET and ATMS. It was observed that the ester carbonyl peak did decrease in intensity when the polymer contacted the liquid silane. A decrease in the SFG signal by a factor of 3–4 is typical due to the differences in the refractive indices of air and the silane [37]. The adjusted intensity of the ester carbonyl peak in the SFG spectrum collected from the

PET/ATMS interface would therefore be slightly higher. This increase in intensity may have resulted from either a change in orientation or a change in the orientational order of the carbonyl groups on the PET surface induced by their interaction with the silane amino endgroups.

SFG spectra were also collected from the PET/γ-GPS and PET/BTMS interfaces (Figures 10c and 10d) to confirm that the shifting of the PET ester carbonyl peak to a lower energy was due to interfacial hydrogen bonding. Unlike ATMS, whose amino endgroup serves as a hydrogen bond donor, there are no functional groups on either γ-GPS or BTMS that are capable of forming hydrogen bonds with PET. In the SFG spectrum from the PET/γ-GPS interface (Figure 10c), the ester carbonyl peak remained at 1725 cm^{-1}, as was expected in the absence of hydrogen bonding. The SFG spectrum was also acquired from the PET/BTMS interface (Figure 10d). The peak was found to be shifted to a slighter higher frequency, which we attribute to a change in the local environment of the ester carbonyl moieties when PET contacted BTMS [36].

From the SFG spectra acquired from the different PET/silane interfaces in the carbonyl stretching region it was concluded that interfacial hydrogen bonds form between the amino endgroups of the ATMS molecules and the ester carbonyl groups on the polymer surface. To gain more insight into the conformation of the silane molecules at this interface, SFG spectra were collected from the interface between d$_4$-PET (to avoid spectral confusion) and ATMS in the C–H stretching region (Figure 11b). An SFG spectrum was also obtained from the d$_4$-PET surface in air (Figure 11a) to illustrate that the only signals arose from the C–H stretching of the hydrogenated phenyl rings. The peak at 2835 cm^{-1}, which is characteristic of the silane methoxy headgroup [17] dominated the SFG spectrum from the d$_4$-PET/ATMS interface implying that these groups were present and ordered at the interface. If in fact the amino endgroups of ATMS were participating in the formation of hydrogen bonds with the PET surface, as evidenced by the SFG spectrum collected in the carbonyl stretching region, then these groups must be directed towards the polymer surface at the interface. Although the methoxy headgroups of the silane molecules were ordered at the interface, it is not obvious from the SFG spectrum obtained in the C–H stretching region whether the headgroups were directed towards or away from the polymer surface. It was hypothesized that the configuration in which the amino endgroups were directed towards the polymer/silane interface while the methoxy headgroups were directed towards the silane bulk would be the most favorable conformation for the ATMS molecules to adopt, however further supporting evidence was needed.

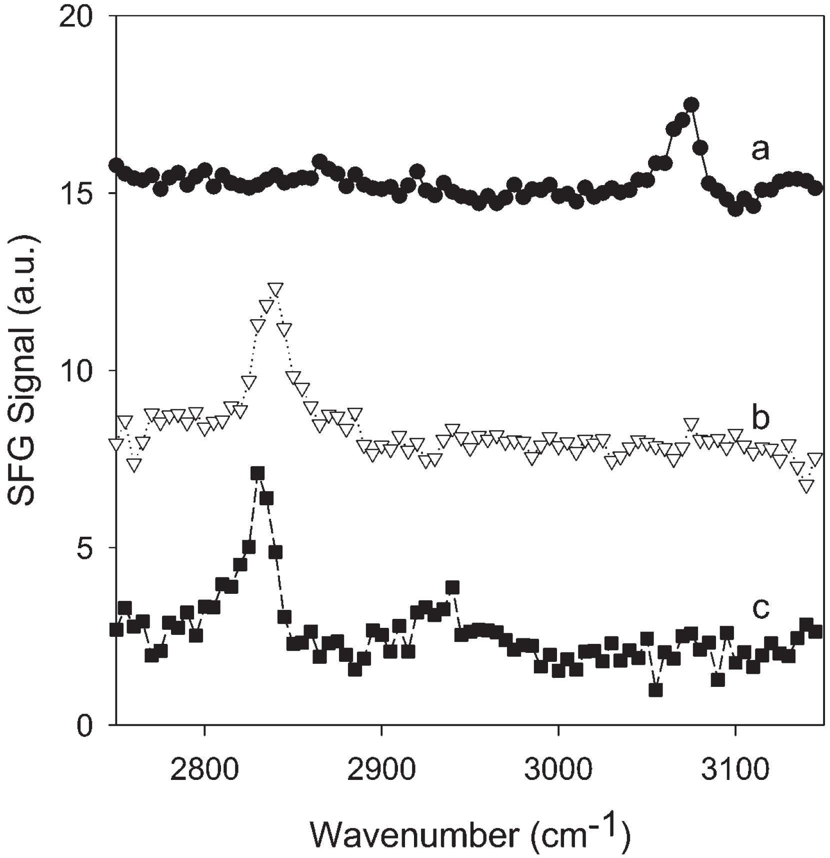

FIGURE 11 SFG spectra collected from the d_4-PET surface in contact with (a) air, (b) ATMS, and (c) BTMS in the C–H stretching region. (Reprinted with permission from Loch, C. L., Ahn, D., Chen, C. Y., Wang, J., and Chen, Z., *Langmuir* **20**, 5467–5473 (2004). Copyright (2004) American Chemical Society.)

For comparison, an SFG spectrum was also collected from the d_4-PET/BTMS interface in the C–H stretching region (Figure 11c). The peak attributed to the methoxy headgroup at 2835 cm^{-1} [17] was the only dominating feature. It is noted however that no SFG C–H stretching signals attributed to the methyl endgroup were observed indicating that the methyl groups were not very ordered at the interface and therefore were not likely directed towards the polymer surface. From this spectrum it was concluded that the ordered methoxy headgroups of BTMS were more likely to be oriented towards the polymer at the interface. A small peak at 2930 cm^{-1}, attributed to the C–H stretching of the methylene groups of BTMS [34] was also observed in the SFG spectrum collected from the d_4-PET/BTMS interface as the backbone of the silane may also have been ordered at the interface.

One advantage of the SFG technique is that it can measure the absolute orientation of functional groups at interfaces. In this specific case we are interested in determining which functional groups of the interfacial silane molecules are oriented toward the polymer surface and which are oriented toward the bulk silane. Such a measurement can be done by analyzing SFG signals resulting from the interference between the SFG vibrational peaks arising from these silane functional groups and a nonresonant background. Here, using this method, we want to confirm our previous analysis that at the PET/BTMS interface the silane methoxy headgroups of BTMS are oriented toward the PET surface while at the PET/ATMS interface these groups are oriented toward the silane bulk with the amino endgroups then directed toward the PET surface so that hydrogen bonds can be formed. To conduct such an experiment we spin coated PET onto a fused silica substrate with a TiO_2 interlayer [36].

From Equation 1, there is a nonresonant contribution (χ_{nr}) to the SFG signal intensity. This frequency-independent nonresonant background was negligible in the SFG spectra collected from the interfaces with PET (or d_4-PET) prepared on a bare fused silica substrate. However, a TiO_2 interlayer can generate a nonresonant SFG signal that can interfere with the resonant SFG signals emerging from the PET/air or PET/silane interfaces. This interference can thus provide information regarding the relative phases of the interfacial functional groups from which the absolute orientation (“up” or “down”) of these groups can be deduced. Since we believe that the methoxy headgroups of ATMS and BTMS should adopt different absolute orientations at the PET/silane interfaces, the peaks arising from these interfaces should have different interferences with the TiO_2 nonresonant background. Illustrated in Figure 12 are the SFG spectra obtained from the PET surface when the polymer was spin coated onto a bare fused silica substrate (Figure 12a) and when a substrate with a TiO_2 interlayer was used (Figure 12b). Both spectra were dominated by the peak at 2960 cm^{-1} which is attributed to the C−H stretching of the methylene groups of PET [49, 50] and the peak arising from the C−H stretching of the phenyl groups was also present. The influence of the nonresonant background provided by the TiO_2 was apparent by the differences in the peak shapes in the two spectra.

The peak attributed to the silane methoxy headgroup at 2835 cm^{-1} was detected in the SFG spectra collected from the PET/ATMS and

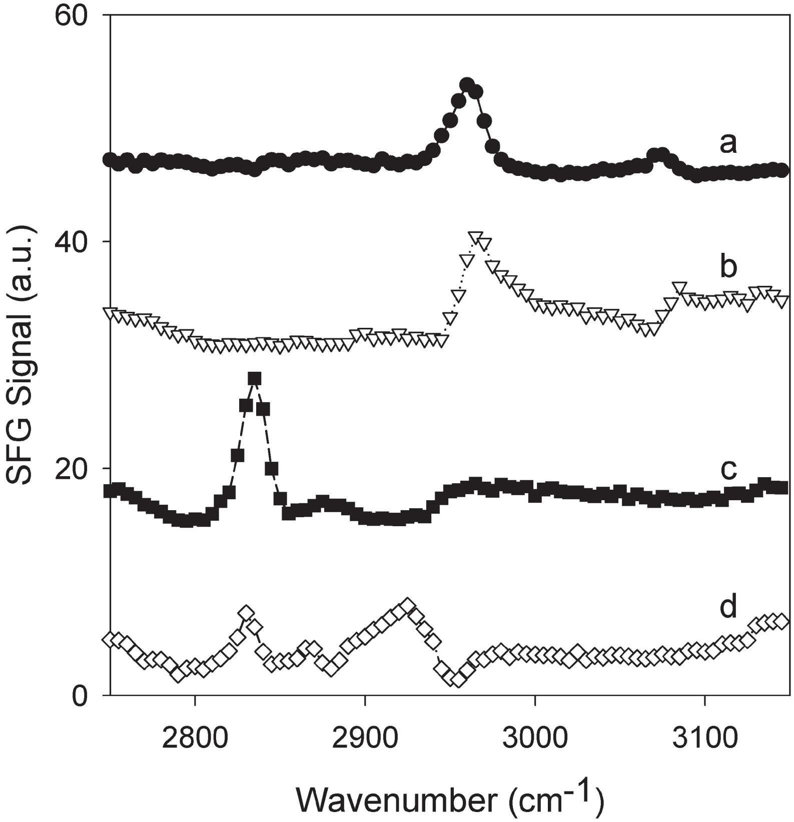

FIGURE 12 SFG spectra collected from the (a) PET surface in air when the polymer is spin coated onto a bare fused silica substrate and the PET surface in contact with (b) air, (c) ATMS, and (d) BTMS when PET is spin coated onto a TiO_2 film. (Adapted from Loch et al. [36].)

PET/BTMS interfaces when the TiO_2 interlayer was present (Figures 12c and 12d); however its intensity was greater at the interface with ATMS. Furthermore, the intensity of this feature appeared to be enhanced by the TiO_2 interlayer as it was weaker when d_4-PET (or PET [36]) was prepared on a bare fused silica substrate (Figure 11b). The difference in the intensity of the peaks from the silane methoxy headgroups in the SFG spectra collected from the PET/ATMS and PET/BTMS interfaces in the presence of the TiO_2 indicated that the resonant signals arising from these groups at the two interfaces interfered differently with the nonresonant signal originating from the TiO_2 interlayer. This was likely a consequence of the silane methoxy

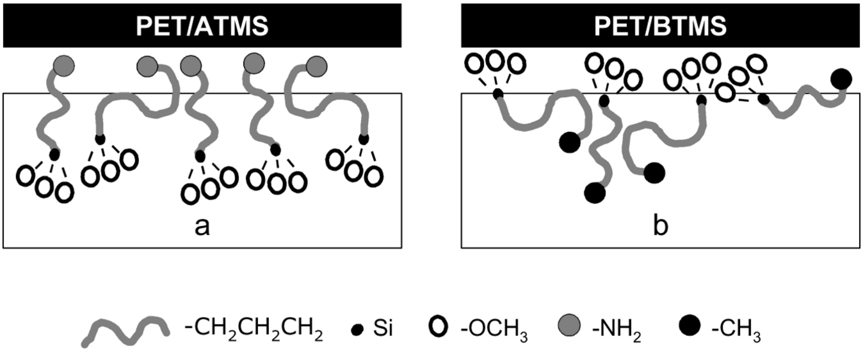

FIGURE 13 Schematic representations of the (a) PET/ATMS and (b) PET/BTMS interfaces as interpreted from the SFG spectra. The different molecular segments of the silane molecules are described by the legend and the boxes are representative of the bulk silane liquid. The SFG signals primarily originate from those segments of the silane molecules between the polymer surface and the bulk silane. (Reprinted with permission from Loch, C. L., Ahn, D., Chen, C. Y., Wang, J., and Chen, Z., *Langmuir* **20**, 5467–5473 (2004). Copyright (2004) American Chemical Society.)

headgroups of ATMS and BTMS having different net orientations with respect to the polymer surface.

By these analyses of the SFG spectra acquired from the polymer/silane interfaces we can speculate as to the conformation of the ATMS and BTMS molecules at the interfaces with PET (or d_4-PET). Interfacial hydrogen bonding between the surface ester carbonyl groups of PET and the amino endgroups of ATMS induces the silane molecules at the interface to adopt a conformation such that these endgroups are oriented toward the polymer surface while the methoxy headgroups are oriented towards the silane bulk. The headgroups still possess a net orientational order at the interface and thus the peak attributed to the methoxy groups is present in the SFG spectra. There are no moieties on BTMS capable of forming hydrogen bonds with PET and the methoxy headgroups preferentially orient toward the interface while the methyl endgroups are directed towards the silane bulk and have little order. The proposed structures of the ATMS and BTMS molecules at the interfaces with PET are depicted in Figure 13.

Probing Polymer/Cured Elastomer Interfaces

The ability to examine the interfaces between polymers and silanes in situ using SFG, as was described in the previous three examples, provided important insights into how silane molecules can adopt different conformations at these interfaces, diffuse into a polymer, and interact with a polymer surface via hydrogen bonding. However, in order to gain a more complete understanding of how silanes may act as adhesion promoters for polymer materials it would be beneficial to probe the interfaces between polymers and an adhesive that contains an adhesion promoter. Here we provide some preliminary results of our SFG studies on buried polymer/cured silicone elastomer interfaces with and without the addition of a silane adhesion promoter.

A two-part addition-curing silicone elastomer was applied to a spin coated polymer film such as PET and allowed to cure completely. The uncured material contained either no adhesion promoter or about 1–2 wt% of γ-GPS, which was mixed in with the two parts of the elastomer. This epoxy-functional silane was chosen because it is commonly employed in commercial adhesive products used with plastics [6, 7]. Using the experimental geometry employed in the previous three examples we were able to collect SFG spectra from the polymer/cured cured elastomer interfaces.

Figure 14a depicts the SFG spectrum collected from the PET/cured elastomer interface when no silane is added to the elastomer. The peak at 2960 cm^{-1} dominated the spectrum and was attributed to the C$-$H stretching of the PET methylene groups [49, 50]. This assignment was confirmed as no SFG signals originated from the d_4-PET/cured elastomer interface. It was noted that three distinct interfaces are present when the silicone elastomer is cured onto the spin coated polymer film: the substrate/polymer interface, the polymer/cured elastomer interface, and the cured elastomer/air interface. It has already been shown that the SFG signals arising from the substrate/polymer interfaces are negligible [30–32]. Furthermore, no SFG signals should be detected from the cured elastomer/air interface. The cured elastomer is much thicker than the spin coated polymer film and using our experimental geometry the input IR beam would be absorbed by the thick elastomer and therefore no SFG signals could be generated from the interface with air. This was confirmed by contacting several polymer/cured elastomer samples with water and observing that there were no changes in the SFG spectra and hence any signals must have originated from the polymer/elastomer interface.

The SFG spectrum acquired from the PET/cured elastomer interface in which γ-GPS was incorporated into the elastomer (Figure 14b) again contained the peak from the PET surface methylene groups at 2960 cm^{-1}; however an additional feature was detected at 2840 cm^{-1}, which is characteristic of the silane methoxy headgroups [52]. This SFG spectrum suggested that the silane molecules in the uncured

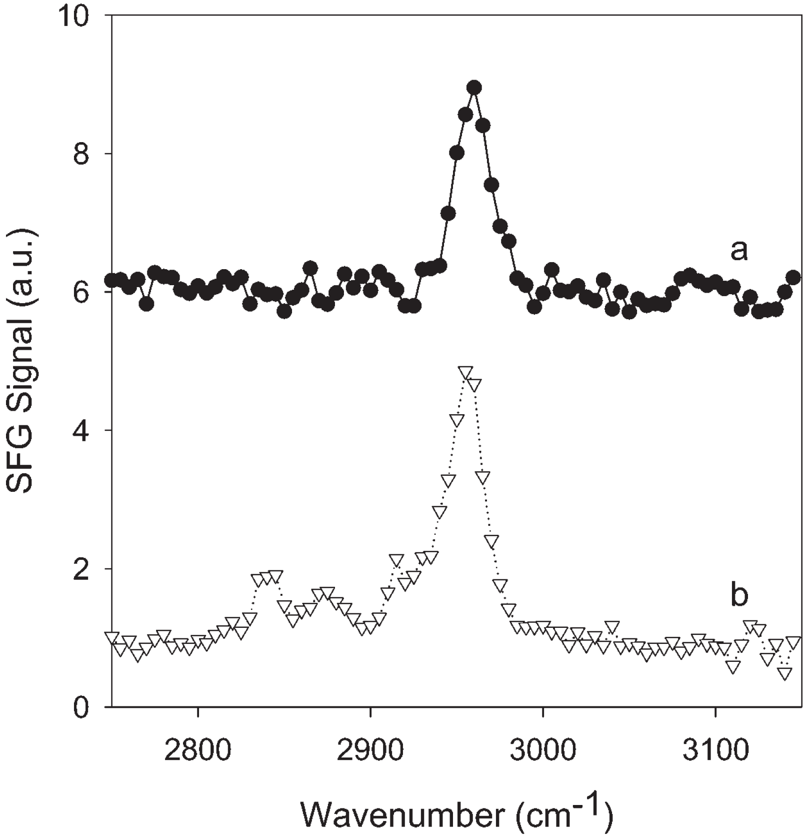

FIGURE 14 SFG spectra collected from PET/cured silicone elastomer interfaces when (a) no adhesion promoter is added to the elastomer and (b) γ-GPS is added to the uncured elastomer (1–2 wt %).

silicone elastomer must have segregated to the PET surface and that the methoxy headgroups were ordered there. It is obvious that adhesion promoting molecules must segregate to the adherend/adhesive interface in order to facilitate the formation of an adhesive bond. The ability of the SFG technique to be able to detect the interfacial segregation of adhesion promoting molecules to this interface is therefore the first step in elucidating the molecular mechanisms of adhesion. We hope that in the future the interfacial orientation of these molecules will be deduced and the formation of chemical bonds or other interactions such as hydrogen bonding will be detected by performing more SFG experiments in situ. Not only will other polymer/adhesive interfaces be probed using SFG but parameters such as cure time and temperature and adhesion promoter concentration will be systematically examined to provide a more complete picture of adhesion at the molecular level.

SUMMARY

Gaining a better understanding of the molecular mechanisms that contribute to an adhesive bond at a polymer surface would lead to the development of adhesives and adhesion promoters that would perform better for these materials. Many of the conventional analytical techniques used to study adhesion at interfaces either do not provide the necessary surface or interface sensitivity or cannot yield molecular level information. Alternatively, SFG vibrational spectroscopy, which is a nonlinear optical laser technique, can probe buried interfaces in situ providing information regarding the segregation, ordering, and orientation of chemical groups at these interfaces.

The examples described above demonstrate our SFG studies of buried polymer/silane interfaces. We first illustrated how silane molecules can adopt different conformations at the d-PMMA and d-PS surfaces. The chemical groups that comprise the silane also had an effect on their interfacial conformations. However, some silanes did not form stable interfaces with polymers, as was the case with d-PMMA and AATMS (or ATMS), and rather diffused through the polymer film. SFG could provide quantitative information, such as the diffusion coefficient. In addition, hydrogen bonding between the amino groups of ATMS and the ester carbonyl moieties of PET were detected. More recently SFG was used to probe the interfaces between polymers and cured silicone elastomers and γ-GPS was found to segregate to the PET/cured elastomer interface.

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