

## Different Molecular Structures at Polymer/Silane Interfaces Detected by SFG

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Buried polymer/silane interfacial molecular structures were examined using sum frequency generation (SFG) vibrational spectroscopy. The silanes under investigation included *n*-octadecyltrichlorosilane (OTCS), *n*-octadecyltrimethoxysilane (OTMS), and (3-aminopropyl)trimethoxysilane (ATMS). Poly(methyl methacrylate) (PMMA) and polystyrene (PS) were among the polymers studied, and to avoid spectral confusion, deuterated polymers (d-PMMA and d-PS) were also employed. When OTCS or OTMS contacted a polymer surface, a stable and ordered interface immediately formed. It was found that the silane molecules could adopt different conformations at the interface, depending on the surface structure of the polymer. Such interfacial structures revealed evidence of interfacial molecular interactions at polymer/silane interfaces. Conversely, ATMS molecules tended to become disordered while interacting with the polymer surface, accompanied by the loss of polymer surface order. Through our SFG studies, we demonstrated that by varying the chemistries of both the silane and polymer molecules, the polymer/silane interfacial structures could be altered at the molecular level. Our observations of these different polymer/silane interfaces should further the understanding of the relationships between molecular interfacial structures and properties, such as adhesion.

### Introduction

Gaining an understanding of the molecular structures of interfaces that include polymer materials is widely desired because such structures control the interfacial properties that play crucial roles in many important applications.<sup>1–5</sup> For example, the interfaces between polymer implants and biological molecules, such as proteins, determine the biocompatibility of such devices. Consequently, improved control of these interfaces can increase human life expectancy.<sup>3</sup> The interfaces between anti-biofouling polymer coatings on ships and marine organisms dictate the performance of these materials. Characterization of the molecular structures of such interfaces can help to design environmentally benign polymer coatings with better anti-fouling properties, saving energy to operate marine vessels.<sup>4</sup> The use of polymer-based adhesives is of major importance in a variety of modern microelectronic and photonic applications.<sup>5</sup> Understanding the molecular structures of these adhesives at interfaces is essential because interfacial structures dictate the physical performance of these interfaces. Thus it is necessary to understand interfacial structures to design interfaces with improved properties.<sup>1,2,6–14</sup> The molecular-level understanding of surfaces/interfaces involving polymers has been a challenge, as polymer surface structures and buried interfaces that include polymers are usually very complicated and difficult to examine in situ. In this paper, we use sum frequency generation (SFG) vibrational spectroscopy to investigate several buried polymer/silane interfaces. Here, we demonstrate that the silane molecules can adopt very different conformations while contacting different polymer surfaces. Such interfacial structures provide more insight into the understanding of the interactions between the functional groups of the silane molecules and the polymer surface groups.

As a second-order nonlinear optical laser technique, SFG can selectively collect vibrational spectra of surface/interface molecules, with submonolayer sensitivity,<sup>15–34</sup> from which the molecular structures of surfaces and interfaces can be deduced. Recently this technique has been applied to interfaces that include polymer materials, allowing the interfacial structures to be elucidated.<sup>23–31</sup> In our SFG studies of polymer/water,<sup>23,25</sup> polymer/protein,<sup>26</sup> and polymer/polymer interfaces,<sup>27,28</sup> we have found that the molecular structures, such as the orientation and orientation distribution of different chemical groups, are not the same at the different interfaces.

Here, several interfaces between polymer materials and liquid silanes are investigated using SFG. Silane molecules are easily tailored with different chemical groups and can therefore serve as ideal models to demonstrate different interfacial structures and interactions. Also, many silanes are widely used industrially in applications such as adhesion promotion, corrosion prevention, or wear reduction,<sup>10</sup> and therefore the understanding of polymer/silane interfacial structures is of great importance both experimentally and practically. The polymers under study included poly(methyl methacrylate) (PMMA) and polystyrene (PS), and to avoid spectral confusion, deuterated polymers (d-PMMA and d-PS) were employed in some of the experiments. Through these studies we provide an experimental method to illustrate how polymer surface groups dictate the structure of and interaction with silane molecules at polymer/silane interfaces. Continued successful investigations of these interfacial structures and molecular interactions can help to predict, design, and improve the structures and properties of interfaces involving polymer materials.

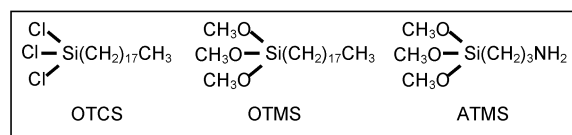
### Experimental Section

PMMA ( $M_w$  350 000) and PS ( $M_w$  393 400; PDI 1.16) were purchased from Scientific Polymer Inc., and the deuterated polymers, d-PMMA ( $M_w$  219 000; PDI 1.04) and d-PS ( $M_w$

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**Figure 1.** Molecular structures of the silanes used in this study.

207 500; PDI 1.25) were obtained from Polymer Source Inc. All polymers were used as received. Fused silica substrates (1 in. diameter,  $\frac{1}{8}$  in. thickness) were supplied by ESCO Products Inc. Thin polymer films were prepared by spin coating 2 wt % polymer/toluene solutions onto the silica substrates at 2000 rpm using a spin coater from Specialty Coating Systems. All spin-cast samples were oven dried at 80 °C for 24 h prior to analysis. The silanes [*n*-octadecyltrichlorosilane (OTCS), *n*-octadecyltrimethoxysilane (OTMS), and (3-aminopropyl)-trimethoxysilane (ATMS)] depicted in Figure 1, were purchased from Gelest Inc. These molecules were envisioned to be composed of three distinct segments: a headgroup ( $\text{Si}(\text{OCH}_3)_3$  or  $\text{SiCl}_3$ ), a  $\text{CH}_2$  "backbone", and an end group ( $\text{CH}_3$  or  $\text{NH}_2$ ).

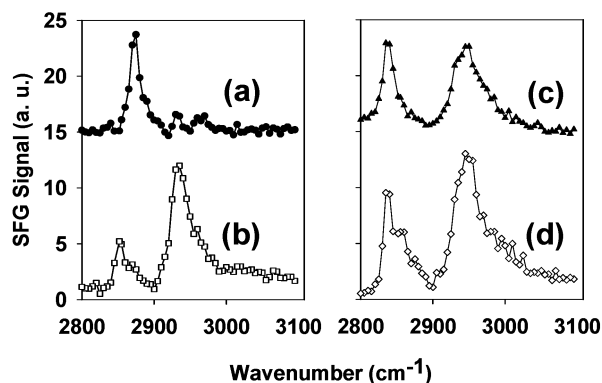
Details of our SFG setup have been reported in our previous publications,<sup>22,23,25–28</sup> and are briefly discussed here. The visible and tunable IR input laser beams were overlapped spatially and temporally on the sample at incident angles of 60° and 54°, respectively, with diameters of about 500  $\mu\text{m}$ . The pulse energies of the visible and the IR beams were  $\sim 200$  and  $\sim 100$   $\mu\text{J}$ , respectively. For the interfaces examined in this research, SFG spectra were collected with the two input laser beams traveling through the fused silica substrate and overlapping on the polymer/silane interface. Our previous research concerned with polymer interfaces demonstrated that the SFG signals were dominated by the polymer/liquid interface, with almost no contributions from the polymer/substrate interface or the polymer bulk.<sup>22,23,28</sup> All SFG spectra were collected using the ssp (s-polarized sum frequency output, s-polarized visible input, and p-polarized IR input) polarization combination and normalized by the intensities of the input IR and visible beams.

## Results and Discussion

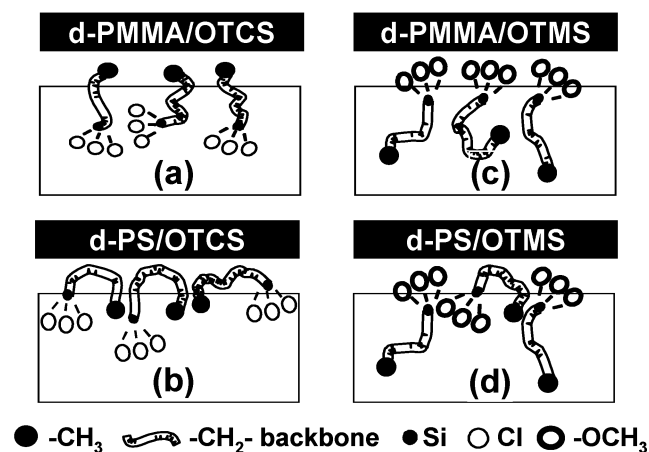
SFG spectra were collected from several polymer/silane interfaces and from our experiments we found that the different silane molecules adopted distinct conformations at each interface, and for some interfaces, the SFG spectra varied with time. In the following discussion we first compare the SFG spectra collected from these polymer/silane interfaces, at a stable state, from which the structures of the interfacial silane molecules and any molecular interactions at the interfaces can be deduced. In such a stable state the interfacial SFG spectra do not change appreciably with time. Then we discuss the time dependence of the observed interfacial structures.

### Silane Structures at Different Polymer/Silane Interfaces.

The SFG spectrum collected from the d-PMMA/OTCS interface (Figure 2a) is dominated by the symmetric stretch of the end methyl group of OTCS at 2870  $\text{cm}^{-1}$ .<sup>17</sup> Two very weak features at 2930 and 2960  $\text{cm}^{-1}$  are attributed to Fermi resonance and the asymmetric stretching of the methyl groups, respectively. This spectrum indicates that the silane methyl end groups are ordered at the interface, and that they are most likely oriented toward the polymer surface. If the methyl groups were to be oriented away from the polymer surface, it is highly likely that their contributions to the SFG signal would be nulled by those from the bulk methyl groups. Nevertheless, the absolute orientation of the interfacial methyl groups can be deduced by a phase measurement.<sup>35</sup> Figure 3a presents a schematic of the



**Figure 2.** SFG spectra collected from the polymer/silane interfaces: (a) d-PMMA/OTCS; (b) d-PS/OTCS; (c) d-PMMA/OTMS; (d) d-PS/OTMS.



**Figure 3.** Schematic representations of different silane molecules oriented at the polymer/silane interfaces. The molecular segments (headgroup, backbone, and end group) of the silane molecules are represented as described by the legend. The boxes represent the bulk silane liquid. The SFG signals detected are primarily contributed from the molecular segments at the polymer/silane interfaces, i.e., from those segments between the polymer substrate and the bulk.

configuration of OTCS molecules at the d-PMMA/OTCS interface. The SFG spectrum collected from the d-PS/OTCS interface (Figure 2b) is very different from that from the d-PMMA/OTCS interface. The two major peaks at 2850 and 2930  $\text{cm}^{-1}$  are characteristic of the silane methylene symmetric and asymmetric stretches, respectively,<sup>17</sup> indicating that the interface is dominated by the OTCS "backbone"  $\text{CH}_2$  groups. As illustrated in Figure 3b, these methylene groups most likely segregate to the d-PS/OTCS interface.

A previous study revealed that the PMMA surface was dominated by ester methyl groups.<sup>22</sup> Using hydrogenated polymer, we confirmed that the interfacial structure of PMMA at the PMMA/OTCS interface was also dominated by the polymer ester methyl groups, as discussed in the following section. SFG studies on the PS surface concluded that phenyl groups segregated to the polymer surface and were oriented toward the surface normal.<sup>24,33</sup> The above studies, which conclude that silane molecules exhibit distinct structures upon contacting different polymer surfaces, suggests that interactions between the chemical groups of the silane molecules and the surface-dominating groups of the polymer dictate these interfacial structures. When the OTCS molecules contact the d-PMMA surface, the ordered methyl group alignment suggests that the methyl groups may have favorable interactions with the d-PMMA surface. The ordered methylene group alignment

at the d-PS/OTCS interface, however, suggests that the methylene groups have favorable interactions with the d-PS surface.

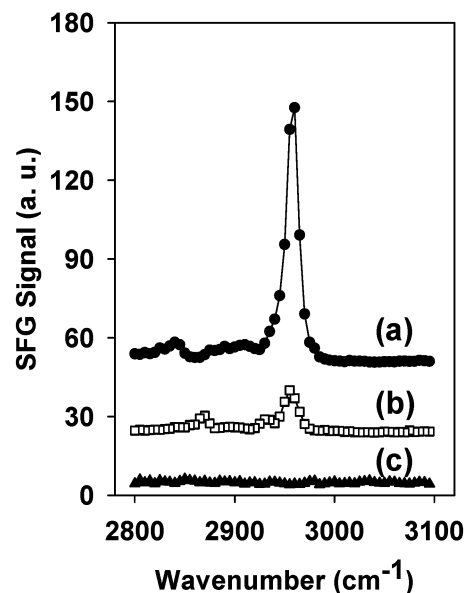
We also investigated the interfaces between d-PMMA or d-PS and another silane, OTMS. Both the OTMS and OTCS molecules are composed of the same methyl end group and CH<sub>2</sub> "backbone" but differ in their headgroups, as the -SiCl<sub>3</sub> head on OTCS is replaced by -Si(OCH<sub>3</sub>)<sub>3</sub> on OTMS. The SFG spectrum collected from the d-PMMA/OTMS interface (Figure 2c) exhibits two strong peaks at 2840 and 2945 cm<sup>-1</sup> assigned to the symmetric and asymmetric C-H stretch of the OCH<sub>3</sub> moiety,<sup>34</sup> respectively. This spectrum is evidentiary of the OCH<sub>3</sub> silane headgroups at the interface rather than of the CH<sub>3</sub> end groups, as at the d-PMMA/OTCS interface. The interpreted interfacial structure, as illustrated in the schematic (Figure 3c), proposes that the methoxy headgroups of the OTMS molecules interact more favorably with the d-PMMA surface than do either the methyl end groups or the methylene groups. As no SFG signal from the methyl end groups is detected from d-PMMA/OTMS interface, these moieties likely orient themselves away from the interface and are buried into the bulk and thus their contribution to the signal is canceled by the methyl end groups of the bulk silane molecules. The SFG spectrum collected from the d-PS/OTMS interface (Figure 2d) is very similar to that from the d-PMMA/OTMS interface, indicating that the silane OCH<sub>3</sub> headgroups segregate to the interface. However, the presence of an additional peak at 2850 cm<sup>-1</sup>, attributed to the OTMS methylene stretch, is evidentiary of the methylene groups also being oriented at the d-PS/OTMS interface, as depicted in the schematic (Figure 3d).

When the d-PMMA/OTCS and d-PMMA/OTMS interfaces are compared, it is concluded that the interfacial structures of the silanes can be varied at different interfaces. Although the silane methyl end groups are ordered at the d-PMMA/OTCS interface, they are not detected at the d-PMMA/OTMS interface. At the latter interface, methoxy groups are ordered and oriented toward the polymer surface, indicative of the more favorable interaction between the silane methoxy headgroups and the PMMA surface than the methyl end groups.

In addition to the polymer/OTCS and polymer/OTMS interfaces, we have also studied the interfacial structures of the silane ATMS, an effective adhesion promoter, upon contacting the two polymers (d-PS and d-PMMA). Different from OTCS and OTMS, ATMS has a shorter methylene "backbone" and is composed of an NH<sub>2</sub> end group. The amino-functional group can strongly interact with many polymers via physical interactions,<sup>36,37</sup> which may be correlated to the wide industrial use of ATMS as a silane adhesion promoter for polymer materials. No SFG C-H stretching signals are detected from either the d-PMMA/ATMS or the d-PS/ATMS interfaces. Compared with OTCS and OTMS, ATMS is less hydrophobic due to the presence of the amine headgroups. Therefore, the interactions between ATMS and the polymer should be very different from those between OTCS or OTMS and the polymer. We propose that the absence of an SFG signal is due to good compatibility or strong interactions between the ATMS molecules and the polymer surfaces, causing the silane molecules to become disordered at the interface.

#### Polymer Structures at Different Polymer/Silane Interfaces.

The studies above elucidated that the silane interfacial structures were dependent upon the composition of both the silane and the polymer surface. Similarly, the interfacial structures of the polymers changed differently while contacting the various silanes. The polymer surface structures were found to be dictated by the interactions of the polymer surface-dominating chemical



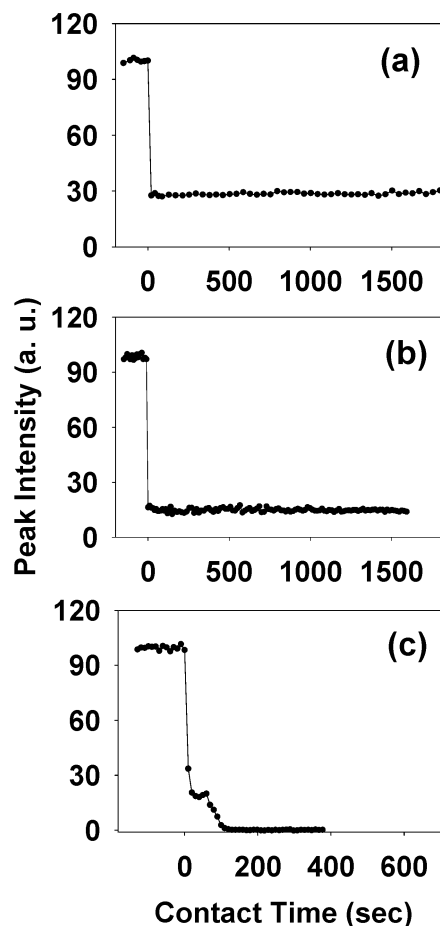
**Figure 4.** SFG spectra of PMMA at the (a) PMMA/air, (b) PMMA/OTCS, and (c) PMMA/ATMS interfaces.

groups with the individual segments of the contacting silane molecules, as was verified using hydrogenated polymers.

The spectrum collected from the PMMA/OTCS interface (Figure 4b) is dominated by an intense peak, not present at the d-PMMA/OTCS interface (Figure 2a), at 2955 cm<sup>-1</sup>,<sup>22</sup> which is characteristic of the symmetric stretch of the ester methyl group of PMMA. The presence of this peak indicates that the PMMA surface is still ordered to some degree upon contacting the OTCS molecules. However, the signal intensity of the PMMA peak is much weaker than that at the PMMA/air interface (Figure 4a), primarily due to the smaller Fresnel coefficient,<sup>23</sup> although a decrease in the PMMA surface order due to interactions with OTCS molecules would also reduce its intensity. The features attributed to the polymer in the SFG spectrum collected from the PMMA/OTMS interface are similar to those in the spectrum from the PMMA/OTCS interface; however no SFG signal is detected at the PMMA/ATMS (Figure 4c) interface. The absence of the SFG signal, a phenomenon that was also encountered at the d-PMMA/ATMS interface, is indicative of the complete loss of order of the chemical groups at the polymer/ATMS interface.

**Time-Dependence of Interfacial Structures.** By monitoring the time-dependent SFG spectra of the polymer/ATMS interface, we have found that when ATMS and a polymer initially contact, the polymer surfaces still possess some order. As the silane molecules begin to strongly interact with the polymer, they start to lose order at the interface and thus the SFG signal disappears.

For the SFG spectra collected from the PMMA/silane interfaces the peak at 2955 cm<sup>-1</sup> can serve as an indicator of the surface order changes of the PMMA film as a function of time. To elucidate the order-disorder change at the PMMA/ATMS interface in more detail and to provide a comparison with other PMMA/silane interfaces, we have monitored the time-dependent intensity changes of the PMMA dominating peak (Figure 5). As each SFG spectrum may take up to 2 min to collect, the intensity change with time is best obtained by monitoring the signal with the IR frequency fixed. In these experiments the SFG intensity has been normalized by the background collected from a blank substrate. Parts a and b of Figure 5 illustrate that at both the PMMA/OTCS and PMMA/OTMS interfaces, the peak intensity decreases drastically after

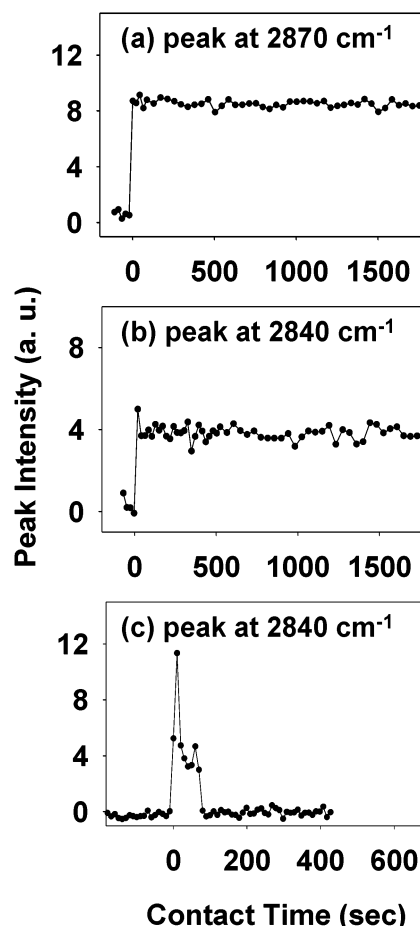


**Figure 5.** Comparison of the time-dependent signal intensity changes of the peak at  $2955\text{ cm}^{-1}$  when the PMMA surface interacts with three different silanes: (a) OTCS; (b) OTMS; (c) ATMS.

the silanes contact the polymer surface and remains constant, indicating that a stable interface forms immediately. The detailed interfacial structures have been analyzed in the previous section (Figure 4b). However, as illustrated in Figure 5c, when ATMS contacts the polymer surface initially, the degree of order of the PMMA surface remains constant for a short time period. The peak then begins to decay to zero with contact time, indicative of the complete loss of interfacial order.

In addition to studying the SFG signal originating from the polymer surface, the time-dependent signal intensity changes for the characteristic peaks of the silanes at  $2840$  or  $2870\text{ cm}^{-1}$  are monitored for the different d-PMMA/silane interfaces (Figure 6) to elucidate the molecular order changes of the silane molecules as they interact with the polymer film. As expected, because d-PMMA does not contain C–H groups, no C–H SFG signals are observed from the d-PMMA/air interface prior to contacting the silanes. We define time zero as the time when d-PMMA is brought into initial contact with the silane. As the polymer is allowed to contact the liquid silane, the C–H signals from the silane molecules are detected. Parts a and b of Figure 6 illustrate that at both the d-PMMA/OTCS and d-PMMA/OTMS interfaces, the characteristic peak intensities for silane molecules increase dramatically after the silanes contact the polymer surface and remain constant, indicating that a stable and ordered silane structure is immediately established. The detailed interfacial structures have been discussed above (Figure 2a,c).

The order–disorder change of the silane interfacial molecular structures has also been detected when ATMS molecules contact

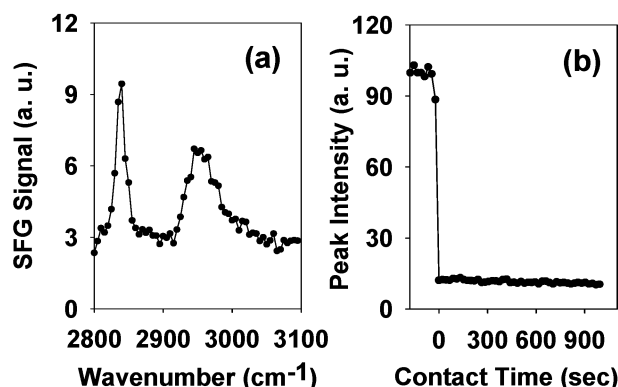


**Figure 6.** Comparison of the time-dependent signal intensity changes of the characteristic peaks for different d-PMMA/silane interfaces: (a) OTCS; (b) OTMS; (c) ATMS.

the d-PMMA surface. Upon initial contact with the d-PMMA surface the silane molecules are found to be relatively ordered, as confirmed by the presence of the peak at  $2840\text{ cm}^{-1}$  (Figure 6c), characteristic of the silane  $\text{OCH}_3$  headgroups. However, the peak intensity begins to decrease to zero with the contact time, indicative of the loss of the interfacial order. The time scale of this process is the same as that encountered at the PMMA/silane interfaces (Figure 5c).

**Interfacial Structures and Interfacial Chemistry.** Through our above experiments we have demonstrated that when a silane molecule contacts a polymer surface, the resultant interfacial structure can be observed using SFG. Such structures depend on the chemical nature of both the silane molecules and the polymer surfaces. For the polymer/OTCS or OTMS interfaces, the interfacial structures are stable and do not change with time, and at the different interfaces, different silane functional groups can dominate the interface. For example, silane methyl end groups dominate the d-PMMA/OTCS interface whereas silane methoxy headgroups are found at the d-PMMA/OTMS interface, evidentiary of the different molecular interactions between the chemical groups on the silane molecules and the polymer surfaces. At the PMMA/ATMS or PS/ATMS interfaces, we observe that the interfacial order of both the silane molecules and the polymer surface disappears shortly after contact. We believe that the loss of the SFG signal is observed because the amino end groups, as well as other groups in the silane, interact with the d-PMMA or d-PS surfaces strongly, resulting in the disordering of the interfaces.





**Figure 7.** (a) SFG spectra collected from d-PMMA/BTMS interface. (b) Time-dependent signal intensity change of the peak at  $2955\text{ cm}^{-1}$  when the PMMA surface contacts BTMS.

As the ATMS methylene “backbone” is much shorter than that of either OTCS or OTMS, there is a concern that the order–disorder change of the PMMA/ATMS interface may be solely attributed to the smaller size of ATMS, as opposed to the presence of amino groups. Another silane, *n*-butyltrimethoxysilane (BTMS), has been employed to demonstrate that the order–disorder change is facilitated by the presence of amino groups, not due to the smaller size of the molecule. Figure 7 presents the SFG spectrum collected from the d-PMMA/BTMS interface and the time dependence of the peak intensity at  $2955\text{ cm}^{-1}$ , both of which illustrate that the behavior of the PMMA/BTMS interface is very similar to that of the PMMA/OTMS interface. A stable interface is immediately formed when BTMS contacts the PMMA surface and both the BTMS and PMMA structures are ordered somewhat at the interface. As at the PMMA/OTMS interface, the methoxy headgroups on BTMS also segregate to the interface with the methyl groups buried into the liquid bulk. The PMMA/OTMS and PMMA/BTMS interfacial structures demonstrate that compared with methoxy moieties, methyl groups do not preferably interact with the PMMA surface, and therefore the methoxy headgroups tend to segregate and orient themselves at the interface. However, substituting amino groups for the methyl end groups changes the interfacial features drastically as the interface becomes disordered when ATMS contacts the PMMA surface. We have confirmed that the order–disorder change is induced by the diffusion of ATMS into the polymer, which also suggests that the stable polymer/OTCS or OTMS interfaces are undiffused interfaces. The detailed mechanisms and in depth molecular level interpretations of the diffusion process are under current investigation and results will be disclosed in a forthcoming paper. However, amino-functional silanes do not lose order at all polymer surfaces. We have observed ordered interfaces between ATMS and nylon 6,6 or poly(ethylene terephthalate) (PET), whose surfaces are dominated by methylene and carbonyl moieties. Details of this study will be published in the future.

We have demonstrated that different interfacial molecular conformations of silane molecules at various polymer/silane interfaces can be detected using SFG. From such structures, we can elucidate interactions between interfacial functional groups, thus providing a deeper understanding of the polymer/silane interface. Theoretical calculations and simulations may provide more details about these interfacial interactions and structures with the SFG results serving as experimental evidence for these theoretical studies. Our previous SFG studies on buried interfaces involving polymers also indicate that molecular interfacial structures can be used to interpret interactions at interfaces.<sup>25</sup> For the poly(*n*-butyl methacrylate) (PBMA)/water

interface, the end methyl groups of the ester side chains on the PBMA surface alter their orientation to accommodate the strong interactions between the polymer surface and the water molecules.<sup>25</sup> Different interfacial structures of poly(ethylene glycol) and poly(propylene glycol) at various interfaces imply distinct molecular interfacial interactions.<sup>28</sup> Furthermore, our SFG studies on polymer/protein interfaces reveal different interactions between proteins and various surface-dominating groups of polymer materials.<sup>26</sup> Similarly, the structures of interfaces between polymers and solid materials, such as the PBMA/PS interface,<sup>27</sup> should also facilitate the interpretation of the interactions between methyl and phenyl groups. From the structures of the interfaces between various silanes and PMMA or PS, as probed by SFG in this research, we demonstrate how ester methyl groups and phenyl groups on the two polymer surfaces interact with silane molecules differently. As previous SFG studies reveal that many polymer surfaces are dominated by one or only a few chemical groups,<sup>20,22,24,34</sup> we can therefore acquire information regarding the interactions at interfaces by studying interfacial structures involving polymer materials.

## Conclusion

By applying SFG vibrational spectroscopy to examine the molecular structures of several polymer/silane interfaces, we have discovered that the silane molecules can adopt different conformations while contacting different polymer surfaces. Some silane molecules form a stable and ordered interface, while in contact with a polymer surface, with specific groups ordered and orientated at the interface. However, other silane molecules adopt a disordered conformation at the interface. The structure changes observed upon the formation of these interfaces can be monitored using SFG. Through our SFG studies, we demonstrated that by varying the chemistries of both the silane and polymer molecules, the polymer/silane interfacial structures could be altered at the molecular level. Our observations of these different polymer/silane interfaces should further the understanding of polymer/silane interactions and can serve as experimental evidence for interfacial molecular interactions and interfacial structures deduced by theoretical calculations and simulations.

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