

Demonstrating the Feasibility of Monitoring the Molecular-Level Structures of Moving Polymer/Silane Interfaces during Silane Diffusion Using SFG

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Abstract: In this paper, the feasibility of monitoring molecular structures at a moving polymer/liquid interface by sum frequency generation (SFG) vibrational spectroscopy has been demonstrated. *N*-(2-Aminoethyl)-3-aminopropyltrimethoxysilane (AATM, $\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$) has been brought into contact with a deuterated poly(methyl methacrylate) (*d*-PMMA) film, and the interfacial silane structure has been monitored using SFG. Upon initial contact, the SFG spectra can be detected, but as time progresses, the spectral intensity changes and finally disappears. Additional experiments indicate that these silane molecules can diffuse into the polymer film and the detected SFG signals are actually from the moving polymer/silane interface. Our results show that the molecular order of the polymer/silane interface exists during the entire diffusion process and is lost when the silane molecules traverse through the thickness of the *d*-PMMA film. The loss of the SFG signal is due to the formation of a new disordered substrate/silane interface, which contributes no detectable SFG signal. The kinetics of the diffusion of the silane into the polymer have been deduced from the time-dependent SFG signals detected from the AATM molecules as they diffuse through polymer films of different thickness.

Introduction

The diffusion of small molecules through polymer materials plays a crucial role in many applications such as polymer coatings, membrane separation, polymer solvation, and adhesion.¹ For decades, many techniques have been extensively used to investigate diffusion processes such as the gravimetric method, mass spectrometry, and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR).^{1–6} However, the molecular-level structure of the polymer/penetrant interface during diffusion has never been investigated. In addition, monitoring the kinetics of slow diffusion using the above-mentioned techniques is time-consuming. This paper introduces the application of sum frequency generation (SFG) vibrational spectroscopy to study the interfacial molecular structures as a silane, *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AATM, $\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$), diffuses into

a deuterated poly(methyl methacrylate) (*d*-PMMA) film. Compared to typical small molecules, the diffusion of AATM into a polymer film is quite slow. We demonstrate that SFG can not only detect the interfacial structures of liquid molecules at the diffusing interface but also quantitatively measure the diffusion kinetics of such slow processes.

The diffusion of silane molecules into polymers is an important problem to investigate.^{4–6} Many silane coupling agents are applied to the surfaces of metals, glasses, or minerals to promote better adhesion with polymeric materials. Therefore, the interacting mechanism between silane and polymer materials has been of wide interest for decades.^{4–8} Plueddemann⁷ has reviewed several of such mechanisms including the development of chemical bonds, compatibility, and the formation of interpenetrating networks (IPNs). The development of chemical bonds at the interface successfully explains the effectiveness of active coupling agents for thermosetting resins; however, it cannot simply account for the enhancement of adhesion by silanes for thermoplastic polymer materials because most of these polymers have no chemically reactive groups on the surface. Compatibility and the formation of IPNs play very important roles in the enhancement of thermoplastic polymer/silane interfacial adhesion. A detailed understanding of the nature and extent of polymer/silane interpenetration or the diffusion of silane molecules into the polymer is therefore

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necessary for the design of efficient silane adhesion promoters for most thermoplastic polymer materials.

As a second-order nonlinear optical laser technique, SFG selectively collects the vibrational spectra of surface/interface species, with submonolayer sensitivity,^{9–29} from which the molecular structures of these surfaces/interfaces can be deduced. SFG has been successfully applied to study interfacial structures and molecular conformations at different liquid/liquid,^{16,17} solid/liquid,^{13,18–23} and solid/solid interfaces.^{24–26} Recently, we applied SFG to study silane conformations at buried polymer/silane interfaces.²⁷ Our research shows 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. SFG spectra collected from such interfaces are stable with time. However, the intensity of SFG spectra collected from other polymer/silane interfaces can change with the contact time and finally decay to zero. In this paper, using the *d*-PMMA/AATM interface as an example, we demonstrate that such spectral changes are due to the diffusion of silane molecules into the polymer.

Experimental Section

Materials. Deuterated PMMA (*d*-PMMA, M_w 219 000, PDI 1.04) was purchased from Polymer Source, Inc., and atactic polystyrene (PS, M_w 339 500, PDI 1.16) was obtained from Scientific Polymer Inc. The liquid silane material (AATM) was from Gelest, Inc., and fused silica (1 in. diameter, 1/8 in. thickness) substrates were facilitated by ESCO Products Inc.

Sample Preparation. Polymer films were prepared by spin-coating polymer/toluene solutions onto fused silica substrates at 2000 rpm for 30 s using a spin coater purchased from Specialty Coating Systems. The PS/*d*-PMMA bilayer film was prepared by spin-coating a *d*-PMMA/acetic acid solution (as a selective solvent, acetic acid will not dissolve PS) on top of a thin PS film, which was also prepared by spin-coating onto a fused silica substrate. All samples were dried in an 80 °C oven

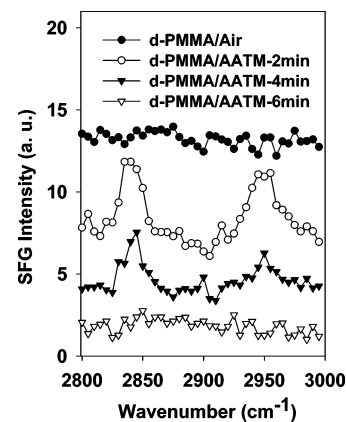


Figure 1. SFG spectra (ssp) collected from the *d*-PMMA/AATM interface as a function of time. The thickness of the *d*-PMMA film is 150 nm.

for 24 h prior to analysis. Film thickness was varied using polymer solutions with different concentrations for spin-coating and measured by a Dektak profilometer.

Sum Frequency Generation (SFG). SFG is a process in which two input beams at frequencies ω_1 and ω_2 mix in a medium and generate an output beam at the sum frequency $\omega = \omega_1 + \omega_2$. Usually ω_1 is in the visible range and ω_2 is a tunable infrared beam. If ω_2 is scanned over the vibrational resonances of molecules, SFG will become resonantly enhanced, thus producing a vibrational spectrum characteristic of the material. Research indicates that SFG is a submonolayer surface/interface-sensitive technique.^{9–29} Our SFG setup and the experimental geometry employed to investigate polymer/liquid interfaces have been reported in our previous publications.^{18–20,22–23} Generally, SFG spectra were collected with the two input laser beams traveling through the fused silica substrate and overlapping at the polymer/silane interface. In our setup, the visible and IR input laser beams were overlapped spatially and temporally on the sample at incident angles of 60° and 54°, respectively. Our previous research has demonstrated that SFG signals were dominated by the polymer/liquid interface, with almost no contributions from the polymer/substrate interface or polymer bulk.^{15,19} The diameters of both beams on the sample were about 500 μm , and the pulse energies of the visible and the IR beams were ~ 200 and ~ 100 μJ , respectively. SFG spectra were collected using the ssp (s-polarized SFG output, s-polarized visible input, and p-polarized IR input) polarization combination.

Results and Discussion

Time-Dependent Silane Structural Changes at the *d*-PMMA/Silane Interface. The SFG spectra collected from the *d*-PMMA/AATM interface, as a function of the time elapsed after the *d*-PMMA film was brought into contact with AATM, are presented in Figure 1. The SFG spectrum from the *d*-PMMA/air interface is also shown to illustrate that no discernible C–H signals were detected from the deuterated polymer. When the silane initially contacted the polymer film, an SFG spectrum in the C–H stretching region was detected from AATM at the interface. The presence of the peaks in the spectra at 2840 and 2945 cm^{-1} , attributed to the symmetric and asymmetric C–H stretches of the silane methoxy groups,²⁷ respectively, demonstrates that these moieties tended to possess a specific average conformation or alignment at the *d*-PMMA/AATM interface. From hereon we will refer to such structures as being ordered. This structural order was lost after 6 min, as the SFG signals disappeared.

It is not practical to follow the detailed kinetics of these order–disorder changes by collecting the SFG spectra, such as

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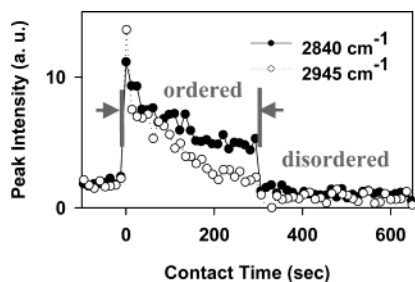


Figure 2. Time-dependent SFG signal intensities at the two characteristic peaks of the silane, 2840 and 2945 cm^{-1} , collected after AATM was brought into contact with *d*-PMMA. The thickness of the *d*-PMMA film is 150 nm.

those presented in Figure 1, as a function of time, as it takes about 2 min to collect such a spectrum while the observed changes occur on a similar time scale. Here, we monitored the SFG spectral peak intensities as a function of time with the IR frequency fixed at the silane characteristic peak frequency of 2840 or 2945 cm^{-1} (Figure 2). Such intensity values were normalized by the background signal collected from a blank substrate. Before AATM contacted the *d*-PMMA film surface, the SFG beams were focused on the *d*-PMMA surface. As illustrated in Figure 2, because there were no silane molecules on the polymer surface, the silane characteristic peaks at 2840 and 2945 cm^{-1} were not detected, and therefore the SFG signal intensities at both wavenumbers were zero before the AATM molecules contacted the *d*-PMMA surface. When the liquid AATM was brought into contact with the polymer surface, the silane characteristic peaks at 2840 and 2945 cm^{-1} immediately emerged, demonstrating that the AATM molecules were at least somewhat ordered at the interface upon contacting the *d*-PMMA film. The fact that these peaks are continuously observed for 330 s after the initial contact indicates that the ordered silane structures existed for a period of time. After this, the SFG intensities of both peaks decreased to zero, suggesting that the interface became disordered, as illustrated in Figure 2. In the next section, we demonstrate that this order–disorder structural change is due to the diffusion of AATM into the *d*-PMMA film.

Evidence of the Diffusion of AATM into *d*-PMMA. The following experiments demonstrate that the order–disorder transition observed above is accompanied by a process associated with the silane diffusing through the polymer film and reaching the fused silica substrate. The ordered silane structures, as detected by SFG, originate from the moving polymer/silane interface during the diffusion, whereas the final disordered structures are detected from the substrate/silane interface once the silane molecules traverse through the entire polymer film. Before the elucidation of such a diffusion process, we first discuss other possible reasons for the SFG spectra at the *d*-PMMA/AATM interface to disappear.

One possibility of the SFG signal loss from the *d*-PMMA/AATM interface as a function of time is that AATM gradually dissolves *d*-PMMA and finally destroys the stable interface. We excluded such a possibility by the following experiments. First, no apparent solvation occurred after *d*-PMMA beads were placed in liquid AATM for 72 h. In addition, after the *d*-PMMA film contacted AATM, deionized water was used to wash off the silane and the FTIR spectrum in the C–D stretching region was obtained. The FTIR spectrum collected from the *d*-PMMA film with a thickness of 300 nm, after contacting AATM for 30 min and being washed by water, is exactly the same as that

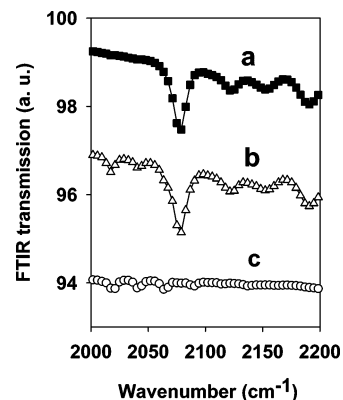


Figure 3. FTIR spectra collected from the *d*-PMMA film before and after contacting AATM and toluene. The thickness of the *d*-PMMA film is 300 nm. (a) *d*-PMMA film in air, (b) *d*-PMMA film after contacting AATM for 30 min and being washed by water, (c) *d*-PMMA film after being washed by toluene.

from the *d*-PMMA film before contacting AATM (Figure 3a and b). This experiment suggests that the *d*-PMMA film was still present after contacting the liquid silane for 30 min and therefore was not dissolved by AATM. Our later SFG experiment has demonstrated that when the silane contacts a *d*-PMMA film with a thickness of 300 nm, the SFG signals disappeared after around 25 min. Therefore, the 30-min period for the FTIR experiment was long enough to confirm whether the disappearance of the SFG signals was due to the dissolution of the film by the silane. Conversely, when the film was brought into contact with a good solvent, such as toluene, it was dissolved immediately as evidenced by the disappearance of the FTIR C–D stretching peaks from the deuterated polymer (Figure 3c).

In addition to solvation of the *d*-PMMA film, two other possibilities for the gradual loss of the SFG signals from the *d*-PMMA/AATM interface exist. Such loss of the SFG signals may be attributed to either a simple surface randomization or a process associated with diffusion. If the order–disorder transition is due to a diffusion process, then the SFG signals may be generated from the diffusing silane molecules, as the polymer/silane interface moves during the diffusion.

A simple SFG experiment was designed to confirm that AATM molecules diffuse into the *d*-PMMA film. A thin polystyrene (PS) film was spin-cast onto a fused silica substrate. Using acetic acid as a selective solvent, a layer of *d*-PMMA was then spin-coated on the top of the PS film, thereby constructing a PS/*d*-PMMA bilayer film. An SFG spectrum was collected from this PS/*d*-PMMA film in air, and peaks corresponding to the C–H stretching modes of the phenyl groups of PS at the buried interface were detected (Figure 4a). Because *d*-PMMA does not contribute any C–H signals to the spectrum, the detected SFG signals in the C–H region are only from the buried PS layer. For comparison, SFG spectra were collected from the buried PS/*d*-PMMA interface after the film was brought into contact with water and AATM. When the *d*-PMMA surface of the bilayer film contacted water, the signals arising from the phenyl moieties were still discernible and stable, indicating that the PS/*d*-PMMA interface was still ordered (Figure 4b). The peak intensities in the SFG spectrum collected in water were weaker than those in air due to the change in the Fresnel coefficient at the PS/*d*-PMMA interface as the thin *d*-PMMA layer contacted different environments.^{18–19,22–23} On the other

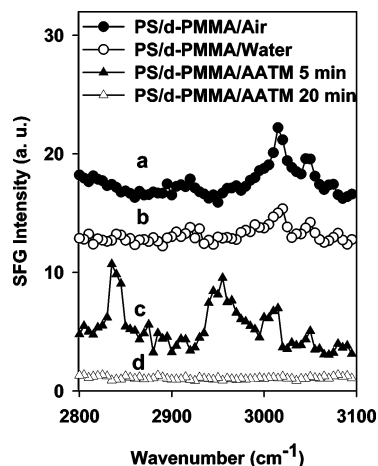


Figure 4. SFG spectra (ssp) collected from the PS/*d*-PMMA bilayer film in contact with (a) air, (b) water, (c) AATM for 5 min, and (d) AATM for 20 min. Both spectra a and b are stable and do not change with time; therefore, they are not labeled with the contact time. The film thickness of the PS and *d*-PMMA layers are 60 and 300 nm, respectively.

hand, when the PS/*d*-PMMA film was brought into contact with AATM, the SFG signals from the buried PS surface were continuously detected for a period of time and then disappeared (Figure 4c and d). The final disappearance of the buried PS signals after 20 min of contact suggests that the AATM molecules traversed through the *d*-PMMA film and reached the buried PS. Otherwise, the buried PS structure should not have been interrupted. Figure 4c shows one representative spectrum collected from the bilayer film during silane diffusion into the *d*-PMMA layer and before reaching the PS layer. According to Figure 4c, the silane characteristic peaks at 2840 and 2945 cm^{-1} were detected at the same time the buried PS signals were detected. These spectral features in Figure 4c were continuously observed for 20 min before the silane reached the buried interface, which confirms that the AATM molecules have some molecular order during the diffusion process. In Figure 4, the thickness of the *d*-PMMA in this bilayer film was 300 nm. Figure 4d demonstrates that it took 20 min for AATM to traverse through the *d*-PMMA layer and reach the buried interface. We found that as the thickness of the *d*-PMMA layer increased, so did the amount of time elapsed between the initial contact of the film with AATM and the complete loss of the signal from the buried PS layer. These results indicated that the amount of time it took the silane molecules to reach the buried PS/*d*-PMMA interface was dependent on the thickness of the *d*-PMMA layer through which the molecules must diffuse through.

We noticed that the disappearance of the PS signal at 3015 cm^{-1} and the AATM signal at 2840 cm^{-1} occurred almost at the same time, suggesting that AATM also diffuses into PS and the diffusion in PS is much faster than in PMMA (or *d*-PMMA). We confirmed this hypothesis by monitoring the SFG spectral changes after AATM was brought into contact with a deuterated PS (*d*-PS) film that has the same thickness as the PS layer in the bilayer film (Figure 5). After the initial contact, SFG signals of AATM at 2840 and 2945 cm^{-1} were detected. However, such SFG signals disappeared after about 25 s. This experiment demonstrates that the AATM molecules also have some molecular order during their diffusion into the *d*-PS film, but the diffusion process is much faster than with *d*-PMMA. The

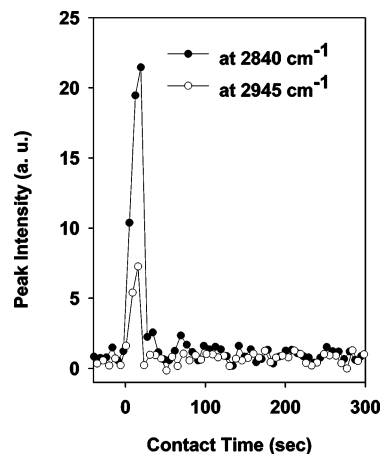


Figure 5. Time-dependent SFG signal intensities at 2840 and 2945 cm^{-1} as AATM molecules diffuse into a *d*-PS film with a thickness of 60 nm.

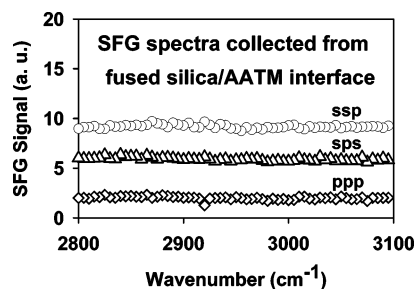


Figure 6. SFG spectra collected from the fused silica/AATM interface by using different polarization combinations. No signal is detected, indicating a disordered silane conformation at the interface.

evidence of the fast diffusion of the silane into PS also elucidates why the AATM signals at 2840 and 2945 cm^{-1} disappear at almost the same time as the PS signals.

Our PS/*d*-PMMA bilayer experiment indicates that the AATM molecules diffused into the *d*-PMMA film, reached the buried PS/*d*-PMMA interface, and continued to quickly diffuse through the PS layer to the fused silica substrate. As previously mentioned, during the silane diffusion through the polymer film, the SFG spectra represent the silane structures at the moving polymer/silane interface. The polymer/silane interface is replaced by the fused silica substrate/silane interface when the silane molecules reach the substrate and become disordered, as evidenced by the loss of the SFG signals. We directly contacted AATM with a fused silica substrate, and the SFG spectra (ssp, sps, and ppp) were collected from the fused silica substrate/silane interface, as presented in Figure 6. Compared with a polymer surface, the fused silica substrate surface is more hydrophilic; therefore, the unfavorable interaction between the hydrophilic substrate and the hydrophobic silane methoxy groups may cause these groups to become disordered at the interface. This is similar to our previous discovery that most liquid molecules such as PEG and PPG tend to have a disordered structure upon contacting a hydrophilic surface.^{22,23} This experiment clearly demonstrated that the disappearance of the SFG signals after the *d*-PMMA film contacts AATM is due to the AATM molecules diffusing into the polymer and finally reaching the fused silica substrate. During the diffusion process, SFG signals can be collected from the silanes, indicating that the liquid molecules show a relatively ordered structure during diffusion into the *d*-PMMA film. We believe that the SFG

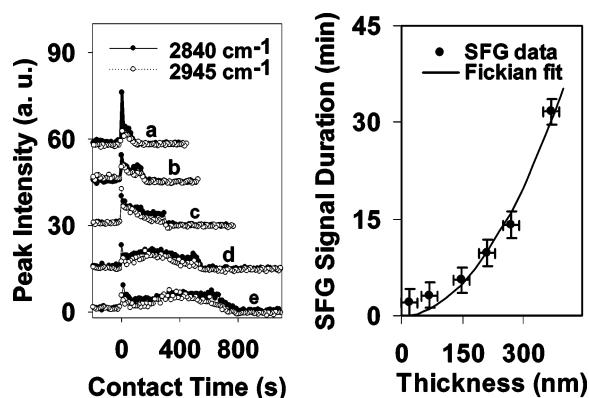


Figure 7. (Left) Time-dependent SFG signal intensities at 2840 and 2945 cm^{-1} as AATM molecules diffuse into *d*-PMMA films of different thickness: (a) 20, (b) 70, (c) 150, (d) 210, and (e) 269 nm. (Right) Diffusion kinetics fitted by the Fickian model. The horizontal error bars show the deviation in the thickness of films made by the same preparation method. The vertical error bars show the deviation in the time duration measured with the similar films.

signals arise from the moving *d*-PMMA/AATM interface, not the bulk AATM molecules in the *d*-PMMA or the original polymer/silane interface. Otherwise, the SFG signal would not disappear after the moving interface reached the fused silica surface. The ordered structure of the liquid during diffusion seems counterintuitive. Possibly, it is due to a finite diffusion rate for all silane molecules, and therefore, there is a wave front of the AATM molecules in the *d*-PMMA. We believe this phenomenon is also affected by the interfacial polymer/silane interactions. Due to the specific interactions between the different chemical groups on AATM and the *d*-PMMA surface, molecules at such a wave front keep some order in the diffusion process. More details of such molecular interpretations may be developed by a simulation, which can be performed in the future.

Diffusion Coefficient Deduced by the Structural Kinetics. By comparing the interfacial order–disorder transition process for several *d*-PMMA films with different thickness after contacting AATM, we further confirmed that this structural change process was accompanied by the diffusion of AATM through the polymer film, and the diffusion coefficient was then deduced based on the time dependence of the silane structural changes. Five thin films of *d*-PMMA, varying in thickness, were prepared by spin coating *d*-PMMA/toluene solutions of different concentrations. Similar to the previous experiment, SFG signals were collected from the *d*-PMMA/AATM interfaces with the frequency of the infrared input beam fixed at the characteristic silane peak positions of 2840 and 2945 cm^{-1} . For all of these *d*-PMMA/AATM interfaces, the SFG signal intensities at these two frequencies changed as a function of the time elapsed after the *d*-PMMA film was placed into contact with AATM and finally decayed to zero (Figure 7, left). Figure 7 (left) indicates that for *d*-PMMA films of different thickness, the times required for the SFG signal to disappear are not the same, due to the different times required for the silane molecules to diffuse through such films and reach the fused silica substrate. Again, the presence of the AATM characteristic peaks during the diffusion process suggests that as the AATM molecules diffuse through the polymer film, the interfacial molecules still possess some molecular order. Only when the silane molecules reach the substrate do they become completely disordered, resulting in no SFG signal. In the right panel of Figure 7, we plotted the

duration of the SFG signal detected from AATM after the liquid contacted the *d*-PMMA film versus the film thickness. Such durations can be deduced from the curves shown in the left panel of Figure 7. We plotted Figure 7 (right) by using six data points, including the five data points from Figure 7 (left). The time dependence of the SFG intensity for the sixth data point is not shown in Figure 7 (left). Since such a time duration represents the diffusion time as the AATM molecules traverse through the polymer film, we should be able to quantitatively deduce the diffusion coefficient by the diffusion time and the film thickness. According to the Fickian model, the diffusion distance (L , the thickness of the film) is 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. Using the above formula to fit the curve in the right panel of Figure 7, the diffusion coefficient of AATM in *d*-PMMA is deduced to be $(3.80 \pm 0.39) \times 10^{-13} \text{ cm}^2/\text{s}$. It is noted that for the two very thin films, the diffusion time measured by our SFG experiment is slightly offset from the fitted diffusion curve. There are several possible reasons. For ultrathin films, the interaction between the polymer and the substrate may need to be considered, and such an interaction may affect the film structure. Also, very thin films may have a different density from thick films, which will affect the diffusion rate of liquid molecules.

As AATM diffused through the *d*-PMMA film, the SFG signal intensities of the silane peaks changed slightly (Figure 7, left). Such signal intensity changes may have been a result of interferences between the silane molecules in the moving interface as the interface gradually broadened during the diffusion process. Further analyses of these data are under current investigation.

Among many other techniques, ATR-FTIR has been developed into a powerful tool to measure the diffusion kinetics of molecules into polymers.^{2–6} Here we want to emphasize that more structural information can be obtained using SFG. As monitored by the time-dependent SFG spectra, the moving interface between AATM and *d*-PMMA during diffusion was still structurally ordered, but this order was lost as the silane molecules reached the substrate. Such structural information cannot be obtained using ATR-FTIR. In addition, the diffusion coefficient of the silane AATM into *d*-PMMA, deduced by SFG, is several orders of magnitude less than those of other small molecules such as O_2 , CO_2 , or ethanol,¹ which suggests that AATM diffuses much more slowly. On the basis of the micrometer-level resolution of FTIR-ATR, it is very time-consuming to study the kinetics of such a slow diffusion process.^{4–6} Therefore, SFG can provide a more efficient way to obtain or compare slow diffusion kinetics between polymers and large penetrants such as silanes, surfactants, plasticizers, and antioxidants.

Conclusion

For the first time, SFG has been applied to examine the moving interface as silane molecules diffuse into a polymer film. We detected that the molecular order of the polymer/silane interface exists during the whole diffusion process and is lost when the silane molecules reach the substrate. It is therefore feasible to detect molecular structures of these moving interfaces by collecting the SFG signals as a function of time, at various

IR frequencies, and then constructing the time-dependent SFG spectra. The diffusion kinetics of the silane into the polymer can also be deduced from these SFG studies. This research provides a novel method of investigating the ordering and structural information of the moving interface during the diffusion process. By comparing the interfacial structures and the diffusion kinetics between the polymer film and different penetrants, more detailed information about polymer/penetrant interactions can be obtained. Furthermore, SFG studies on polymer/penetrant interfaces may provide important perspectives

for the design of many extensively used materials such as silane adhesion promoters, polymer membranes for separations, and polymer films that serve as barriers.

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