Sum Frequency Generation Vibrational Spectroscopy Studies on "Buried" Polymer/Polymer Interfaces

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ABSTRACT: Sum frequency generation (SFG) vibrational spectroscopy has been successfully applied to study "buried" poly(*n*-butyl methacrylate) (PBMA)/polystyrene (PS) or deuterated PS (d-PS) interfaces in situ. Orientation information on ester side chain methyl groups of PBMA at these interfaces has been deduced from the SFG spectra and compared to those of PBMA/air and PBMA/water interfaces. Our results indicate that the ester side chain methyl groups have different orientation at different interfaces. These methyl groups tend to stand up on the PBMA surface in air and tend to lie down on the surface upon contacting water. At the PBMA/PS (d-PS) interface, the orientation of ester side chain methyl groups is between the two extremes of the PBMA/air and PBMA/water interfaces. To further prove that the orientation change of methyl groups at the PBMA/PS interface is due to the interaction effect with PS, the "buried" interface between PBMA and a thin layer of polymer with phenyl groups on water has also been investigated.

Introduction

Understanding polymer/polymer interface structures is crucial to evaluate miscibility and bulk properties of polymer blends and adhesion of polymer/polymer interfaces.[1,2] Most polymer pairs are immiscible, and thus the mixtures separate into distinct phases. Properties of phase-separated polymer systems are governed to a large extent by interfacial characteristics between unmixed phases; therefore, their control is very important to tailor basic properties of such polymer systems. Knowledge of adhesion of polymer/polymer interfaces can be applied to many important industrial applications including coatings, lithography, microelectronic devices, and liquid crystal displays. Different from most distinct solid/liquid and liquid/liquid interfaces, polymer/polymer interfaces are typically broader due to the diffusion of the polymer chains at these interfaces. The interfacial width between polymer materials is strongly determined by the features of the polymer pairs. For example, the equilibrium interface width between two immiscible polymers is typically in the range of 2−15 nm, depending on the compatibility of different components.[3] Different experimental techniques,[4−15] especially neutron reflectivity,[11,12] forward recoil spectrometry,[7,13] and asymmetric double cantilever beam testing,[9,13] provide understanding of these interfaces; however, they cannot reveal molecular level details of the interfacial structures. Theoretical calculations[16−19] have been applied to study polymer/polymer interfaces. It is believed that conformation of molecules or orientation of functional groups at interfaces between polymers are directly correlated to properties of polymer/polymer interfaces. Unfortunately, molecular conformation or orientation information has never been observed experimentally at polymer/polymer interfaces due to the lack of appropriate tools to study the "buried" interfaces at the molecular level.

Recently, sum frequency generation (SFG) vibrational spectroscopy has been developed into a powerful tool to study surfaces and interfaces[20−26] in situ at the molecular level with submonolayer sensitivity. The first investigation of polymer structures at the buried solid/solid interface is to study the orientation of phenyl groups of PS molecules at the sapphire/PS interfaces.[27] However, the study of the buried polymer/polymer interface by SFG has not been reported yet.

In this paper, using the poly(*n*-butyl methacrylate) (PBMA)/polystyrene (PS) or deuterated PS (d-PS) interface as an example, we explored the possibility of investigating molecular conformations at the buried polymer/polymer interface. We demonstrate that SFG can provide molecular level structural information such as functional group orientation at the "buried" polymer/polymer interface. Orientation information on ester side chain methyl groups of PBMA at the polymer/polymer interfaces has been deduced and compared to the polymer/air and polymer/water interfaces. We believe that this is the first time that vibrational spectra of interfaces between polymer materials have ever been observed. For comparison, the interface between PBMA and a layer of PS-*graft*-poly(ethylene oxide) (PS-*g*-PEO) on water has also been examined to elucidate interactions between PBMA and PS phenyl groups.

Experimental Section

PBMA and atactic PS were purchased from Scientific Polymer Inc., with molecular weights of 180 000 and 339 500, respectively. PS-*g*-PEO and d-PS samples were purchased from Polymer Source Inc. The molecular weight of d-PS is 207 500. Molecular weights of PS-*g*-PEO are 8700 for PS backbone and 10 000 for 20 PEO side chains. Fused silica substrate (1 in. diameter, $^1/_8$ in. thick) was ordered from ESCO Products Inc. A thin film of PS (or d-PS) with the thickness around 80 nm was made by spin-coating its 2 wt % toluene solution on the silica substrate and oven-dried at 120 °C for 5 h. A thick PBMA film with the thickness around 200 μm was solvent cast directly on top of the PS film and oven-dried again at 120 °C for 12 h. Acetic acid, which selectively dissolves PBMA and not PS, was used to make the PBMA solution for solvent casting.

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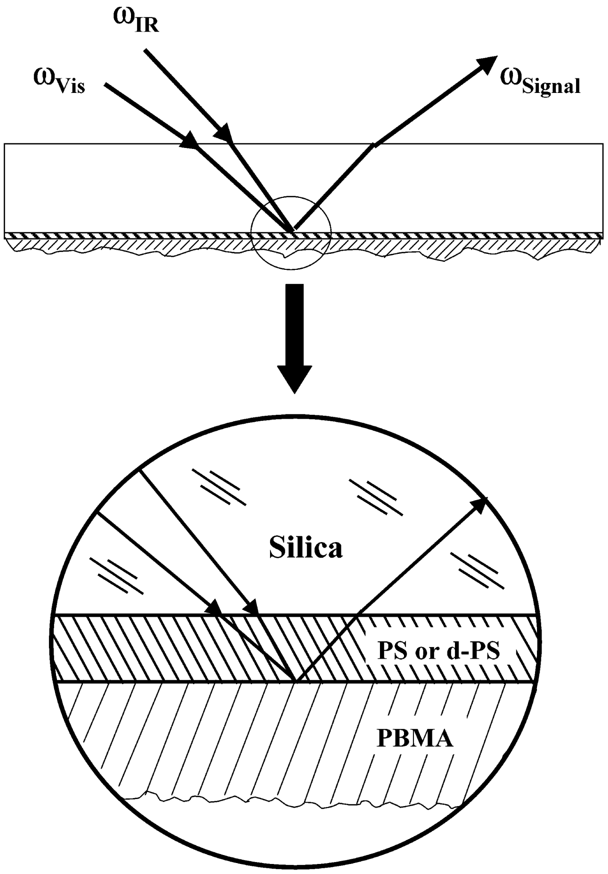

Figure 1. SFG experimental geometry.

The SFG spectra shown in this paper were collected by a customer designed EKSPLA SFG spectrometer, which was described in detail elsewhere.[28,29] Briefly, the visible input beam at 0.532 μm was generated by frequency doubling a part of the fundamental output from an EKSPLA Nd:YAG laser. The IR beam tunable between 2.5 and 10 μm (with a line width < 6 cm^{-1}) is obtained from an optical parametric generation/amplification/difference frequency generation (OPG/OPA/DFG) system based on LBO and $AgGaS_2$ crystals, which were pumped by the third harmonic and the fundamental output of the laser. Both beams had a pulse width of $\sim$20 ps, a repetition rate of 20 Hz, and a typical beam diameter of $\sim$0.5 mm at the sample surface or interface. The incident angles of the visible beam and the IR beam were 60° and 54°, and their energies at the sample surface were $\sim$250 and $\sim$70 μJ, respectively.

Results and Discussion

The SFG spectra were collected with two input laser beams traveling through the substrate and the thin PS (or d-PS) film to the PS/PBMA interface (Figure 1). We have ensured that the spectra we collected came from the polymer/polymer interface, not from the PS/substrate or PBMA/air interfaces. We attempted to collect SFG spectra from a thick solvent cast PS film on fused silica substrate, using the experimental geometry mentioned above. For the thick film, the input IR beam was absorbed by the film and could not penetrate to the polymer/air interface; thus, no SFG signal could be generated from the PS/air interface. If any SFG signals were detected, they would have been contributed by the PS/substrate interface. Here, no SFG signal could be detected from this thick PS film on fused silica, demonstrating clearly that no SFG signal was generated from the PS/fused silica interface (Figure 2). Details of similar experiments showing that no SFG signal generated from the polymer/fused silica interface using our experimental geometry can be found in our previous publications.[28,29]

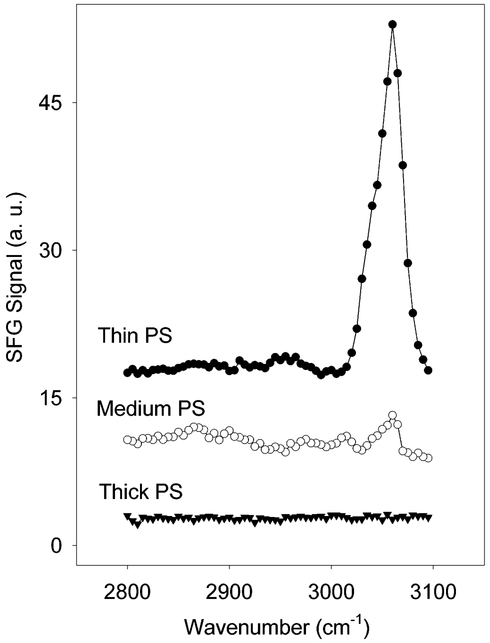

Figure 2. SFG spectra of PS with different thickness using the experimental geometry shown in Figure 1.

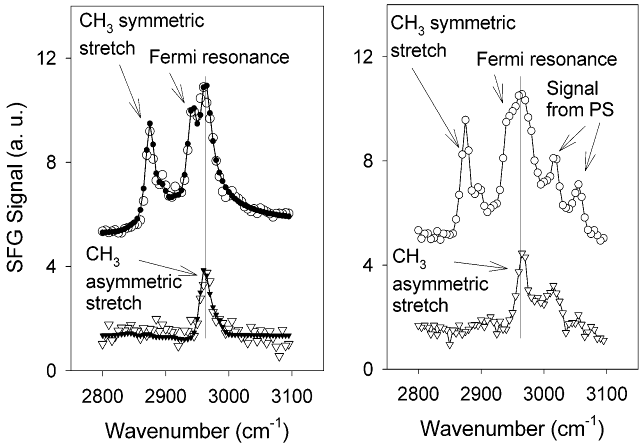

Figure 3. SFG spectra collected from polymer/polymer interfaces. (left) PBMA/d-PS: fitted spectra are shown by black symbols and lines. (right) PBMA/PS: upper spectra, ssp; bottom spectra, sps.

SFG spectra collected from the polymer film of PBMA/PS (or d-PS) on fused silica are displayed in Figure 3. As mentioned, the SFG signal could not come from the interface between PS and fused silica. Since the PBMA film is very thick, we believe that no IR beam could penetrate it to reach the PBMA/air interface to generate an SFG spectrum of this interface. We confirmed this by contacting the sample with water to replace the PBMA/air interface with a PBMA/water interface, while keeping the PBMA/PS (or d-PS) interface unchanged. Our previous research shows that when the thin PBMA polymer film contacted water, the spectra changed, and thus SFG signals of polymer/water interface were detected.[29] Unlike the thin PBMA film, no change was detected after the PBMA/PS (or d-PS) sample contacted water (Figure 4). On the basis of the above analysis, we proved that the SFG spectra shown in Figure 3 came

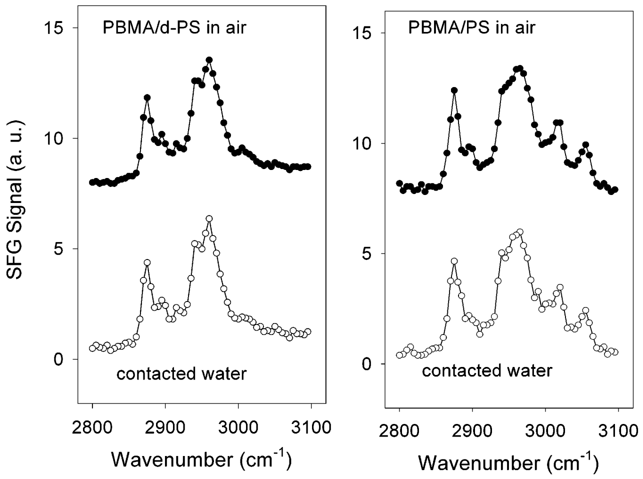

Figure 4. Identical SFG spectra collected from PBMA/PS (or d-PS) when the sample was exposed to air and in contact with water.

from the PBMA/PS (or d-PS) interfaces rather than the PS/fused silica or the PBMA/air interface. We collected very similar spectra from a PS/PBMA sample made by a different method. This sample was made by covering a thin spin-coated PBMA film with a thick solvent cast PS film that was peeled off from its original substrate in water. SFG spectra were collected after the sample was annealed. Therefore, we have successfully demonstrated that SFG can provide vibrational spectra of the "buried" polymer/polymer interfaces.

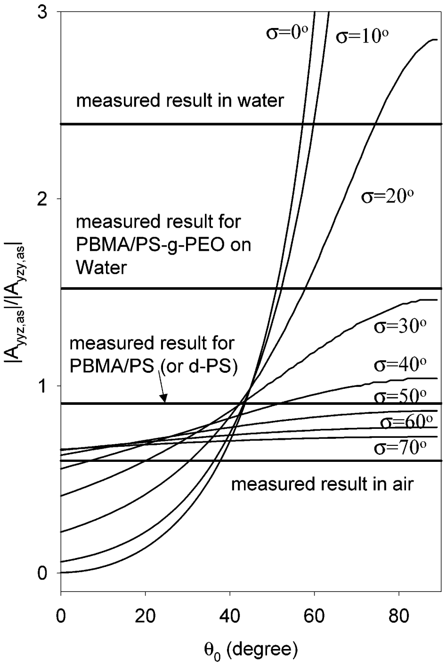

Figure 5. Calculated values related to intensity ratio between asymmetric stretches of ester side chain methyl groups of PBMA in the ssp and sps spectra vs their orientation and orientation distribution. Measured results are also shown.

Table 1. Fitting Results of SFG Spectra (ssp and sps) Collected from the PBMA/d-PS Interface

wave-number (cm^{-1})	$\lvert(A^{(2)}_{yyz}/\Gamma)\rvert^2$	$\lvert(A^{(2)}_{yzy}/\Gamma)\rvert^2$	assignment
2850			CH_2 (s)
2876	4.74		(ester side chain) CH_3 (s)
2893	1.21		
2914	0.49		
2932	0.49		(alpha) CH_3 (s)
2941	2.78		Fermi resonance
2959	2.78	3.51	(ester side chain) CH_3 (as)
2990			(alpha) CH_3 (as)

Orientation information on surface/interface functional groups can be deduced by SFG spectra collected using different polarization combinations of input and output beams in the SFG setup.[27,30] Figure 3 shows the SFG spectra of the PBMA/PS (d-PS) interface collected by the ssp (s-polarized sum frequency signal, s-polarized visible input beam, and p-polarized infrared input beam) and sps polarization combinations. The ssp spectrum of the PBMA/PS interface shows signals from both PBMA and PS. Detailed peak assignments of PBMA and PS spectra have been published.[26,27,31] Signals from PBMA are due to the symmetric and asymmetric stretches of ester side chain methyl groups at 2875 and 2960 cm^{-1}, respectively, and Fermi resonance at 2940 cm^{-1}.[31] Signals from PS are due to the aromatic stretches of phenyl groups, whose wavenumbers are higher than 3000 cm^{-1}. The sps spectrum of the PBMA/PS interface indicates the asymmetric stretch of the ester side chain methyl groups of PBMA and the aromatic C$-$H stretches of PS phenyl groups. The spectral features of the PBMA/d-PS interface below 3000 cm^{-1} are identical to those of the PBMA/PS interface, confirming that these signals are due to PBMA. The aromatic C$-$H stretches disappear because of the deuteration of the PS. The different aromatic C$-$H stretching signals of PS at the PS/air interface shown in Figure 2 and at the PBMA/PS interface shown in Figure 3 indicate that phenyl groups at these two interfaces have different orientations. At the PS/air interface, the SFG spectrum is dominated by the peak at 3060 cm^{-1}, showing that phenyl groups tend to stand up on this surface.[26,27] At the PBMA/PS interface, peaks at 3015 and 3055 cm^{-1} dominate the surface, indicating that phenyl groups tend to lie down. In this paper, we will focus on the study of orientation information on ester side chain methyl groups of PBMA at the "buried" polymer/polymer interface, not the detailed orientation of phenyl groups. Before analyzing these spectra in more detail, we first review orientation information on ester side chain methyl groups on the PBMA surface in air and in water. The ester side chain methyl groups dominate both the PBMA/air and the PBMA/water interfaces but have very different average orientation and orientation distribution.[31] Our previous results indicate that the average orientation of ester side chain methyl groups on the PBMA surface is more toward the surface normal in air than in water.[31]

As with the PBMA/air and PBMA/water interface,[31] the orientation information on ester side chain methyl groups at the "buried" PBMA/PS (or d-PS) interface can be deduced from the intensity ratio of the asymmetric methyl stretching peak in the ssp and sps spectra after fitting these SFG spectra. The fitted ssp and sps SFG spectra for the PBMA/d-PS interface are shown in Figure 3 as black dots and lines. The fitting data are displayed in Table 1. We treat side chain methyl groups as having C_{3v} symmetry. The calculated values of $|A^{(2)}_{yyz,as}|/|A^{(2)}_{yzy,as}|$ (the ratio between two second-order nonlinear susceptibility components of the asymmetric methyl stretch at 2960 cm^{-1} in the lab fixed frame) vs the orientation angle (θ_0) and angle distribution (σ) are shown in Figure 5. The orientation distribution was assumed to be a Gaussian function $f(\theta) = C\ \exp[-(\theta -$

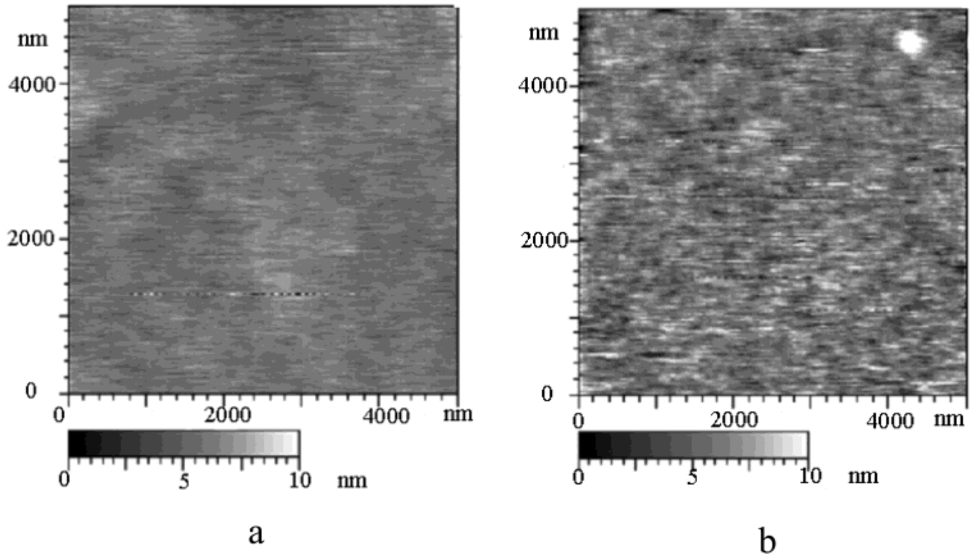

Figure 6. AFM topographic images of (a) PS/air interface and (b) PS/PBMA interface after dissolving PBMA by acetic acid.

$\theta_0)^2/2\sigma^2$]. From Table 1, we know that the measured result of $|A^{(2)}_{yyz,\mathrm{as}}|/|A^{(2)}_{yzy,\mathrm{as}}|$ for ester side chain methyl groups at the PBMA/d-PS interface is about ∼0.9, which is shown in Figure 5. The measured $|A^{(2)}_{yyz,\mathrm{as}}|/|A^{(2)}_{yzy,\mathrm{as}}|$ of ester side chain methyl groups at the PBMA/PS interface is similar. In addition, for comparison, measured results for PBMA/air and PBMA/water interfaces are also depicted in this figure. Details of deducing the range of possible orientation and orientation distribution of surface methyl groups can be found in refs 28 and 31. Figure 5 clearly shows that the range of possible orientation of ester side chain methyl groups at the PBMA/PS (or d-PS) interface is between the two extremes of the PBMA/air and PBMA/water interfaces. On the PBMA surface in air, the ester side chain methyl groups have greater freedom, and they tend to extend into the air, leading to a small average orientation angle vs the surface normal. Upon contacting water, the strong repulsion between the methyl groups and water molecules directs the methyl groups toward the surface, resulting in a larger average orientation angle. At the PBMA/PS (d-PS) interface, the ester side chain methyl groups interacted with phenyl groups, but the repulsion must be weaker compared to the situation in water. Therefore, the orientation of ester side chain methyl groups is between the two extremes of the PBMA/air and PBMA/water interfaces. The repulsion force between side chain methyl groups and phenyl groups also directs phenyl groups away from the interface normal compared to the PS/air interface, shown by different aromatic C−H signals in Figures 3 and 2.

Because PBMA and PS are immiscible, we believe that the PBMA/PS interface is still distinct. To exclude the possible effect of roughness on the deduction of ester side chain methyl group orientation at the PBMA/PS interface, we imaged the interface by using AFM (Figure 6) after dissolving the PBMA film by acetic acid and exposed the interface to air. AFM images show that the interface is still optically flat, with the magnitude of topographic features of ∼4 nm, not very different from that of the surface in air (∼2 nm). This is in the reasonable range for an interfacial width of two immiscible polymers and is compatible with neutron reflectometry studies of the d-PS/PBMA interface.[3,32] Since topographic features (magnitude ∼ 4 nm) were measured over a very large area (5000 nm by 5000 nm), the "local" roughness of the interface should be very small. On the basis of the surface area/roughness ratio and early reports,[33,34] we believe that this interfacial roughness will not affect the deduction of the orientation of surface/interface functional groups.

To further confirm our results about the effect of phenyl groups on the orientation of ester side chain methyl groups at the "buried" polymer/polymer interface, we have also studied the interface between PBMA and a thin layer of polymer with phenyl groups on water by SFG. Clearly, this interface will be as flat as the PBMA surface in air or in water. It is impossible for PS itself to disperse on the water surface due to its hydrophobicity. An amphiphilic block or graft copolymer can form a monolayer polymer-brush-type structure at the water/air interface under controlled conditions, e.g., under controlled concentration, temperature, or surface pressure. Normally, hydrophobic groups of the monolayer point out to the air, and hydrophilic parts protrude into the water solution.[35] We thus spread a drop of PS-*g*-PEO THF solution on water. The THF solvent will gradually evaporate or diffuse into the bulk water, leaving a thin layer of polymer on top of the water. Then we collected SFG spectra from the liquid/air interface as a function of time. The time-dependent SFG spectra indicate that a thin layer of PS spread on the water gradually as the PEO segments interacted favorably with water (Figure 7). After about 10 min, the structure of PS layer on water is stable. A PBMA film was brought to contact the PS-*g*-PEO layer on water, and SFG spectra from the solid/liquid interface were collected using the experimental geometry published earlier.[29] Again, orientation information on ester side chain methyl groups of PBMA at this interface can be deduced from the SFG spectra collected (Figure 8). The value of $|A^{(2)}_{yyz,\mathrm{as}}|/|A^{(2)}_{yzy,\mathrm{as}}|$ has been obtained and is also shown in Figure 5. This value is between the results of the PBMA/PS (or d-PS) and PBMA/water interfaces. At the interface of PBMA/PS-*g*-PEO on water, there might be some water molecules in the PS-*g*-PEO layer that can interact with PBMA polymers; thus, the result is between the PBMA/PS (or d-PS) and PBMA/water interfaces. We believe that the disappearance of the aromatic C−H stretches of PS phenyl groups at this interface is due

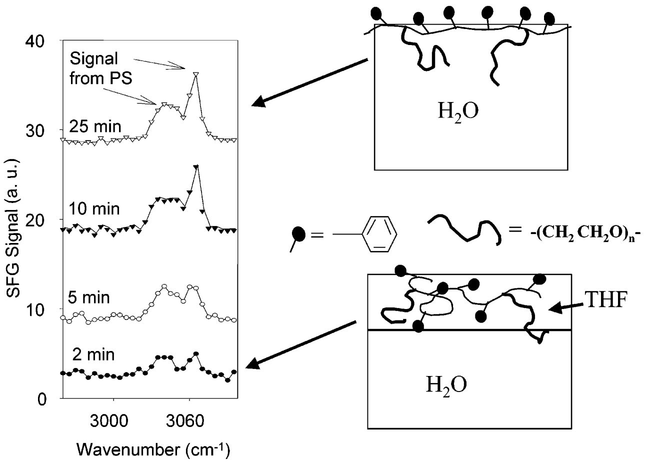

Figure 7. Time-dependent SFG spectra collected after PS-*g*-PEO THF solution spread on water.

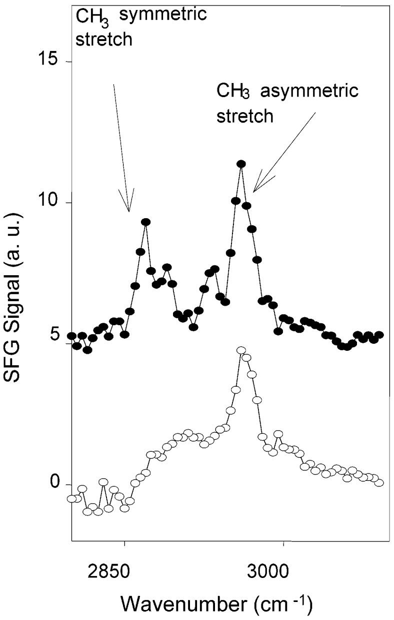

Figure 8. SFG spectra of the interface between PBMA and PS-*g*-PEO on water: upper spectrum, ssp; bottom spectrum, sps.

to the fact that the phenyl groups become totally disordered. This experiment provides evidence to show the effect of phenyl groups on the orientation of the ester methyl groups at the PBMA surface. The correlation of ester side chain methyl group orientation at different interfaces and interactions between methyl groups and other groups such as water molecules and phenyl groups are under investigation. Quantitative relationships between adhesion of polymer materials and functional group orientation at polymer interfaces will be elucidated in the future.

Summary and Conclusions

In conclusion, we demonstrate that SFG can detect molecular structural information on the buried polymer/polymer interfaces, presenting new possibilities to investigate polymer/polymer interfaces in situ. The ester side chain methyl groups tend to stand up on the PBMA surface in air. Upon contacting water, they tend to lie down on the surface. At the PBMA/PS (d-PS) interface, the orientation of ester side chain methyl groups is between the two extremes of the PBMA/air and PBMA/water interfaces. SFG studies on polymer/polymer interfaces may provide detailed understanding of polymer interfacial behavior at the molecular level and better control and design of these interfaces.

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