9130 *Macromolecules* **2002,** *35,* 9130−9135

Sum Frequency Generation Vibrational Spectroscopy Studies on Molecular Conformation of Liquid Polymers Poly(ethylene glycol) and Poly(propylene glycol) at Different Interfaces

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Received April 19, 2002

ABSTRACT: The conformation of poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) molecules at various interfaces has been investigated by sum frequency generation (SFG) vibrational spectroscopy. The interfaces studied include interfaces between pure liquid PEG (or PPG) or aqueous PEG (or PPG) solutions and air, fused silica, or solid polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA). Depending on the hydrophobicity of the solid contacting media, the liquid polymers show different conformations at different interfaces, which can be correlated to molecular interactions at these interfaces. The favorable interaction between hydrophobic media and the hydrophobic segments, methylene or methyl groups, of polyethers causes an ordered conformation with these groups standing up at the interface. The unfavorable interaction between hydrophilic media and hydrophobic segments of the polyethers induces interfacial methylene or methyl groups to have a random structure or to lie down at the interfaces, indicated by the weakening or even absence of SFG signals. For comparison, interfaces between aqueous PEG or PPG solutions and air, PS, PMMA, and fused silica have also been investigated. The weak SFG signals of PEG at the PEG solution/air interface indicates that PEG molecules do not have very ordered structures at the interface, due to their strong affinities with water molecules. The absence of SFG signals of PEG at all PEG solution/solid interfaces indicates that PEG molecules do not segregate to these interfaces. PPG is more surface or interface active, and it tends to be strongly adsorbed to all interfaces. At different solid/PPG solution interfaces, adsorbed PPG molecules show conformations different from those at different solid/PPG liquid polymer interfaces. This study provides a direct in-situ observation that polyethers can have different conformations at different interfaces.

Introduction

Studies on liquid polyethers such as poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG), especially their copolymer PEG−PPG−PEG, known as pluronics, have been of great scientific and technological interest for decades due to their broad applications in surface chemistry, colloid chemistry, and biological science.[1−4] Different responses of PEG and PPG blocks in pluronics to various chemical environments or temperatures control their behavior in micelle formation, emulsification, drug stabilization, or drug delivery. These different responses are caused by their different structures. Therefore, structures such as conformations of different blocks of the pluronics determine the applications of these copolymers.

The bulk conformation of PEG and PPG in different media or at different temperatures has been widely studied.[5−14] Both PEG and PPG have the same backbone structure of $-(O-C-C)_n-$. Quantum mechanical calculations[5] indicate that the conformation of $-O-C-C-O-$ segments can be divided into two general states. One is a polar conformation with lower internal energy, and the other is a nonpolar conformation with higher internal energy. Depending on the environment or temperature, one of these conformations may be statistically dominating while the other one is unfavorable. For example, a helical structure has long been observed for PEG molecules in water solution, liquid state, or other polar organic solvents such as chloroform.[7,8] This structure has gauche (g) $-C-C-$ bonds and trans (t) $-O-C-$ bonds and bridged hydrogen bonding between water molecules and oxygen atoms of polyethers. This conformation, normally called the polar conformation, has lower internal energy, as confirmed by more studies recently.[5,9−12] The nonpolar conformation for PEG becomes favorable in the gas phase or in nonpolar organic solvents. The molecular simulation shows that the polar helical PEG structure collapses and transforms to a random coil-like conformation in the benzene solution. In the gas phase, it was also found that the conformation of PEG molecules shows a contrasting result with that in water.[13] For PPG molecules, the conformational change from nonpolar to polar was detected during the dissolution process in water.[14] In summary, the PEG or PPG molecules can have different conformations in different physical states (e.g., gas or liquid) or in different chemical environments (e.g., polar or nonpolar solvents).

Recently, studies on these polyethers and their copolymers at interfaces have attracted more attention because most of their applications are governed by their different interfacial behaviors.[15−18] Unlike bulk media discussed above, the environment changes dramatically at the interface or surface. It is believed that interfacial molecules will have different structures or conformations. Therefore, elucidation of their structures and their interactions with the contacting media is of great importance to better understand their behaviors in different applications. However, because of the lack of

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10.1021/ma020614j CCC: $22.00

appropriate interface sensitive characterization techniques, little information is obtained on the molecular-level structures of PEG and PPG at different interfaces, including liquid/air and liquid/solid interfaces. Recently, as a powerful surface/interface-specific spectroscopic tool with submonolayer sensitivity, sum frequency generation (SFG) vibrational spectroscopy has contributed important molecular level structural information for surface and interface studies.[19−24] SFG has been successfully applied to study conformations of small molecules at different solid/liquid,[25,26] liquid/air,[27,28] and liquid/liquid[29] interfaces. SFG spectra are generated by molecules without inversion symmetry under the electric-dipole approximation. Unlike the bulk, the inversion symmetry of molecules at interfaces studied in this paper is broken because one side of these polymer molecules contacts the liquid bulk or solution, while the other side contacts air or an impenetrable solid surface. The absence of inversion symmetry allows SFG spectra to be collected from these interfaces. SFG intensities of different vibrational modes are correlated with interfacial density, orientation of functional groups, and degree of interfacial molecular order. Generally, a highly ordered system can generate stronger SFG signals than a less ordered system with similar average orientation. From SFG spectra collected using different polarization combinations of input and output laser beams, orientation information on surface/interface functional groups can be deduced. From the SFG intensity of symmetric and asymmetric stretches in an SFG spectrum, orientation information can also be deduced. Therefore, conformational information on polymer molecules at interfaces can be deduced from SFG spectra.

In this paper, we study the conformation of PEG and PPG molecules at various interfaces by using SFG. The interfaces that will be discussed include interfaces between pure liquid PEG (or PPG) or aqueous PEG (or PPG) solutions and air, fused silica, or solid polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA). To avoid spectral confusion between PEG or PPG and solid hydrogenated polymers, deuterated PS (d-PS) and deuterated PMMA (d-PMMA) are used. From the orientation information on functional groups at different interfaces, conformation of interfacial PEG and PPG molecules can be inferred. The liquid polymers show different conformations, depending on the hydrophobicity of the solid contacting media. At the same time, results from polymer solution studies at different interfaces show differences in interfacial activity of PEG and PPG. Either PEG molecules have a disordered structure at the solution/air interface or they do not segregate to solid/solution interfaces because of the strong interaction with water. PPG molecules segregate to all interfaces, and their interfacial structures at different interfaces depend on the contacting media.

Experimental Section

PEG (M_n 400) and PPG (M_n 425) were purchased from Aldrich, and PS (M_w 393 400, PDI 1.16) was purchased from Scientific Polymer Products, Inc. The d-PS (M_w 207 500, PDI 1.25) and d-PMMA (M_w 219 000, PDI 1.04) polymers were from Polymer Source Inc., and fused silica (1 in. diameter, $^1/_8$ in. thickness) substrates were ordered from ESCO Products Inc. All polymers were used as received. Polymer films were prepared by spin-coating 2 wt % solutions of polymer in toluene onto fused silica. The samples were spun at 2000 rpm for 30 s using a spin-coater purchased from Specialty Coating System. All spin-cast samples were oven dried at 80 °C for 24 h before analysis. The aqueous solutions of the liquid polymers were prepared by dissolving 0.5 g of polymer into 100 g of deionized water.

Details of SFG theory have been reported.[19,20] 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 vibrational resonances of molecules, SFG is resonantly enhanced, thus producing a vibrational spectrum characteristic of the material. The intensity of the SFG spectra is related to the average orientation and orientation distribution of functional groups inside the optical field. As a second-order nonlinear optical process, SFG spectral intensity will be zero in a medium with inversion symmetry under the electric dipole approximation. SFG spectra can be detected from the material where the inversion symmetry is broken. Most bulk materials have inversion symmetry; thus, they do not generate SFG signals. The inversion symmetry of molecules at a surface or interface is broken; thus, these molecules will generate SFG signals. Both experimental results and theoretical calculations indicate that SFG is a submonolayer surface/interface sensitive technique. In our experiments, sum frequency spectra were collected by overlapping a visible and a tunable IR beam on an interface. The visible beam had a wavelength of 532 nm and was generated by frequency-doubling the fundamental output pulses of 20 ps pulse width from an EKSPLA Nd:YAG laser. The IR beam, tunable from 1000 to 4300 cm^{-1}, was generated from an EKSPLA optical parametric generation/amplification and difference frequency system based on LBO and $AgGaS_2$ crystals. Both beams were overlapped spatially and temporally on the sample at incident angles of 60° and 54°, respectively. The diameters of both beams on the sample (including the solid/liquid interface and the liquid/air interface) were about 0.5 mm. The pulse energies of the visible and the IR beams were $\sim$200 and $\sim$100 μJ, respectively. The sum frequency (SF) signal from the interface was collected by a photomultiplier tube. A separate photomultiplier was used to collect the bulk SFG signal from a ZnSe plate as a reference channel. Two photodiodes monitored the input visible beam and IR beam powers by collecting the back-reflections of these two beams from the focus lenses. SFG spectra from the sample's surface or interface can be normalized by the reference signal from ZnSe or by the power of the input laser beams. We found that the SFG spectra normalized by these two methods were the same. Therefore, we arbitrarily chose to use the measured power of the two input laser beams to normalize all the SFG spectra in this paper.

For the solid/liquid interface, the SFG spectra were collected with two input laser beams traveling through the fused silica substrate and overlapping on the solid/liquid interfaces. Using a thickness dependence experiment, our early research[30] has demonstrated that SFG signals were dominated by polymer/liquid interfaces, with almost no polymer/substrate interface or polymer bulk contributions. For the liquid/air interface, SFG spectra were directly collected with two input laser beams overlapping on the liquid/air interface.

Results and Discussion

Conformation of PEG and PPG at the Liquid/Air Interface. To provide a standard for later solid/PEG or PPG liquid polymer interface studies, SFG spectra were first collected from PEG and PPG liquid/air interfaces as shown in Figures 1 and 2. For a clear comparison, ssp spectra in these two figures and later figures as well were offset along the *y*-axis. In both figures, SFG spectra collected by using different polarization combinations of input and output beams including ssp (s-polarized signal beam, s-polarized visible beam, and p-polarized IR beam) and ppp were displayed. Vibrational spectra of bulk polyether materials have been widely studied for decades.[31−34] SFG spectra of PEG with different end groups collected from polymer/

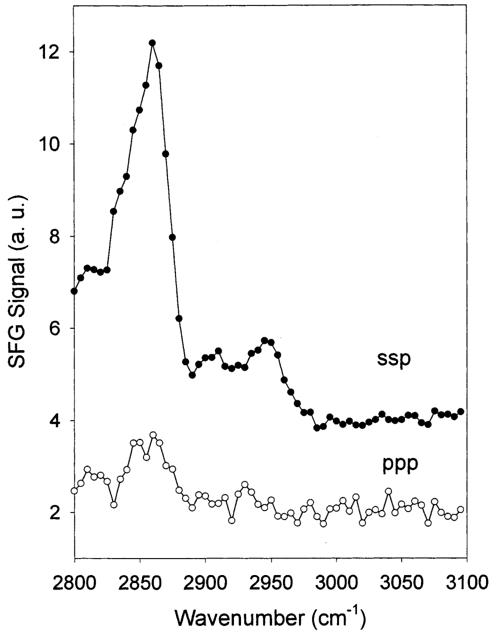

Figure 1. SFG (ssp and ppp) spectra of the PEG/air interface.

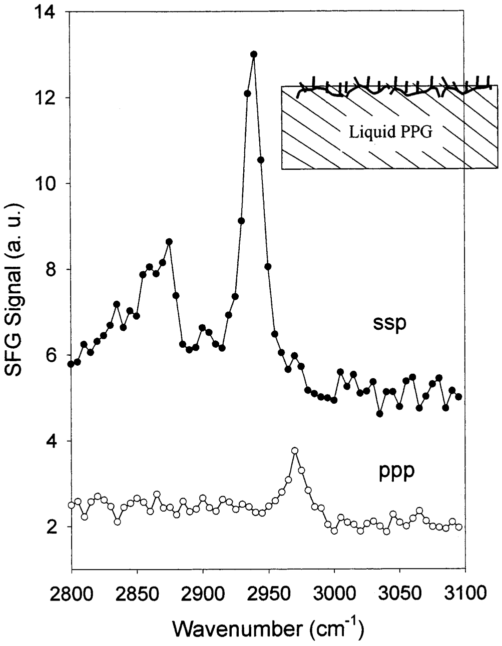

Figure 2. SFG (ssp and ppp) spectra of the PPG/air interface.

air interfaces have also been published.[35] According to the literature, the symmetric and asymmetric C−H stretching peaks of normal methylene groups are typically at 2850 and 2920 cm^{-1}, respectively. Differently, the symmetric C−H stretching peak of CH_2 groups in PEG is at 2860 cm^{-1}, due to the influence of the oxygen atom connected to the this group.[32] Figure 1 shows that the ssp SFG spectrum of PEG is dominated by the symmetric stretch at 2860 cm^{-1}. There are two weak peaks around 2910 and 2945 cm^{-1}, assigned as the asymmetric stretch of the CH_2 group and the Fermi resonance, respectively. The ppp spectrum of PEG/air interface is dominated by the peak around 2860 cm^{-1}. For the ssp SFG spectrum collected from the PPG/air interface, as shown in Figure 2, one peak at 2935 cm^{-1} dominates the spectrum. This peak is assigned to the symmetric stretch of the side chain $-CH_3$ group.[31] The asymmetric stretch of the $-CH_3$ group at 2970 cm^{-1} appears as the shoulder of the 2935 cm^{-1} peak in the ssp spectrum and dominates the ppp spectrum. The dominating SFG signals of methyl groups show that the surface of PPG liquid is covered mostly by methyl groups in air. The inset of Figure 2 is a schematic representation of the structure of the liquid PPG polymer/air interface.

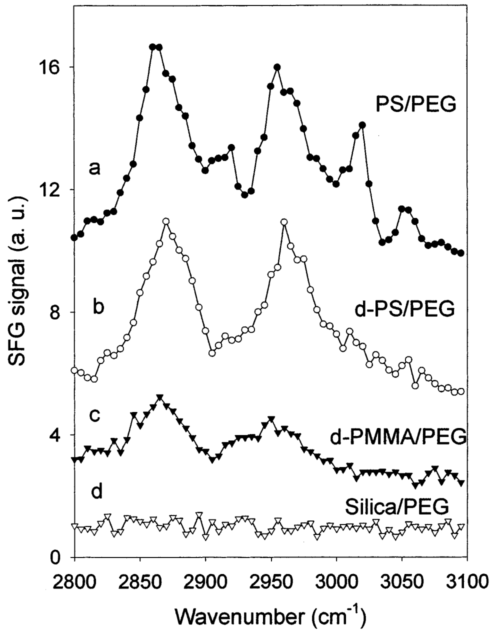

Figure 3. SFG spectra (ssp) collected from different solid/PEG interfaces indicate that PEG molecules can have different conformations at these interfaces.

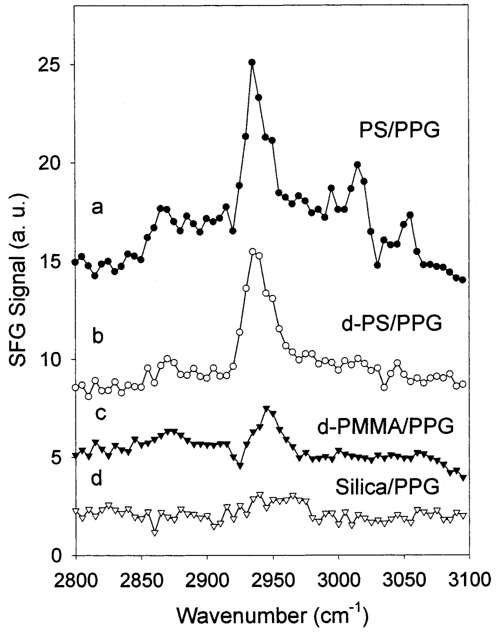

Figure 4. SFG spectra (ssp) collected from different solid/PPG interfaces indicate that PPG molecules can have different conformations at these interfaces.

Conformation of PEG and PPG at Different Solid/Liquid Polymer Interfaces. SFG spectra (ssp) were collected from interfaces between PEG or PPG liquid and several solid materials, including fused silica, PS, d-PS, and d-PMMA (Figures 3 and 4, ssp). In SFG spectra collected from PS/PEG (Figure 3a) and PS/PPG (Figure 4a) interfaces, there are signals that occur above 3000 cm^{-1}, due to aromatic C−H stretches of phenyl groups on PS. The analysis of phenyl group structures at various interfaces will not be the focus of this current paper; thus, we will only mention this briefly. The SFG spectrum collected from the PS/air interface[36] shows a strong symmetric aromatic C−H stretch at 3060 cm^{-1}, demonstrating that PS surface in air is dominated by phenyl groups, and these phenyl groups tend to stand up on the surface. While for the PS/PPG and PS/PEG interfaces, the asymmetric aromatic C−H stretching modes at 3020 and 3055 cm^{-1} dominate the spectra, indicating that the phenyl groups tend to tilt more toward the surface.[36,37]

Comparing SFG spectra collected from interfaces between polyethers and three different solid media d-PS, d-PMMA, and fused silica (Figures 3b−d and 4b−d), we found that the intensity of the dominating peak (symmetric C−H stretch for both PEG and PPG) decreases from the d-PS interface to the d-PMMA interface and drops to zero for the fused silica/liquid polymer interface. For the symmetric stretches of CH_2 group on PEG or methyl group on PPG, the stronger SFG intensity indicates that these functional groups tend to align along the interface normal with an ordered structure (or narrower orientation distribution). Therefore, at the d-PS/polyether interfaces, strong SFG signals show that polyethers should have ordered structures, with CH_2 (for PEG) or CH_3 groups (for PPG) oriented along the interface normal. At the fused silica/polyether interface, no SFG signal can be detected, showing that both polyethers have random structures or the methylene and methyl groups are lying down at the interface. Structures of polyethers at the d-PMMA/polymer interface are between these two extremes, evidenced by SFG spectra with intermediate intensities.

The hydrophobicities of these solid contacting media are quite different. The d-PS surface is the most hydrophobic, while fused silica is the least hydrophobic. From the hydrophobic to the hydrophilic media, the interactions between the media and polyether molecules are apparently different. For hydrophobic d-PS, the interactions between the surface groups from the solid polymer and CH_2 groups on PEG or methyl groups on PPG molecules are favorable to form ordered structures, orientating the CH_2 or CH_3 groups along the surface normal. However, unfavorable interactions between hydrophilic fused silica and CH_2 or CH_3 groups cause a randomized conformation of PPG or PEG molecules or force the CH_2 or CH_3 groups to lie down. The hydrophobicity of d-PMMA is between d-PS and fused silica; thus, polyethers have intermediate conformations compared to those contacting d-PS and fused silica. SFG studies of solid/polyether interfaces clearly demonstrate that polyethers can have different conformations while contacting different solid materials.

Interfacial Activity and Conformation of PEG and PPG at Solution/Air Interfaces. SFG spectra (ssp) collected from PEG solution/air and PPG solution/air interfaces are shown in Figure 5. Comparing the SFG spectrum collected from the PEG solution/air interface (Figure 5a) with that from the pure PEG/air interface (Figure 1), we can see that the ssp SFG signal in the C−H stretching region at the PEG solution/air interface is very weak. SFG signals collected from the PEG solution/air interface using other polarization combinations of input and output beams of our SFG system such as sps and ppp are hardly detected. The spectral difference for liquid PEG/air and PEG solution/air interfaces indicates that PEG molecules have very different conformations at these two interfaces. We believe that this is due to the strong interaction between PEG molecules and water molecules. The adsorption of PEG or PEO (high molecular weight) at the solution/air interface has been widely reported in the literature.[38−40] Both theoretical calculation and experimental results indicate that the adsorbed polymer layer at the solution/air interface is divided into two major regions. One part of the layer lies on top of the water (polymer−air region), and the other part is immersed into the water (polymer−water region). The neutron reflection studies have shown that the adsorbed polymer layers were found to be essentially completely immersed in the water.[40] We believe that PEG molecules at the solution/air interface do not have a very ordered structure; thus, the SFG spectral intensity is quite weak. On the other hand, comparing the SFG spectrum collected from the PPG solution/air interface (Figure 5b) with that from the PPG liquid polymer/air interface (Figure 2), they are quite similar. At the solution/air interface, the strong methyl symmetric stretching peak can still be detected, showing that PPG likes to segregate to the solution/air interface and shows an ordered structure. The intensity of this peak is even stronger than that collected from the pure PPG/air interface, possibly because of the difference in Fresnel coefficients of the interfaces.[21] We believe that the different behaviors of PEG and PPG at the solution/air interface are due to their different surface activities.

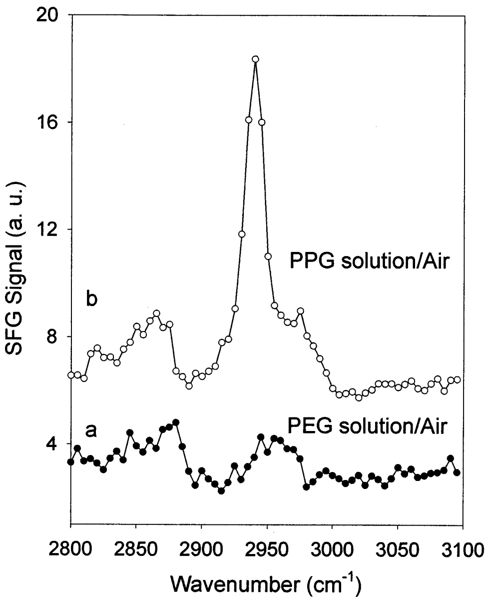

Figure 5. SFG spectra (ssp) collected from the PEG and PPG aqueous solution/air interfaces.

The surface activities of PEG and PPG have been studied by a variety of techniques such as surface tension measurement,[41,42] light scattering,[43] and neutron reflectivity.[40] Surface tension measurements indicate that PPG molecules are more surface active than PEG molecules in water. The surface tension of PPG is 31.1 dyn/cm, while that of PEG is 42.9 dyn/cm.[44] Through the simulation of the experimental results by using the mean-field lattice model, it was found that the interaction parameter χ_{EG-air} is larger than χ_{PG-air}, while $\chi_{EG-water}$ is smaller than $\chi_{PG-water}$.[39] These results are reasonable because the interaction between hydrophilic PEG molecules and water molecules should be

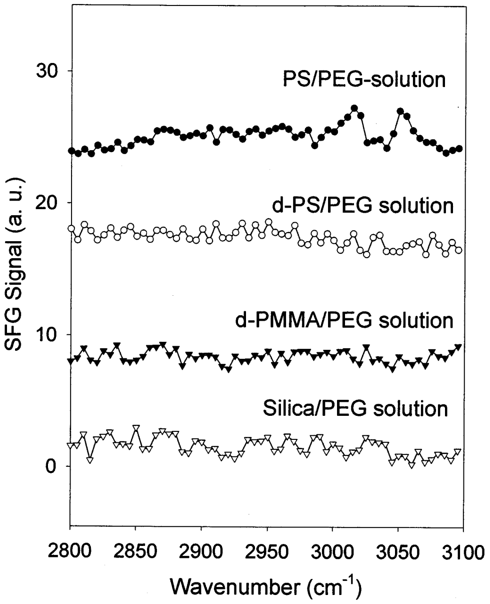

Figure 6. SFG spectra (ssp) collected from different solid/PEG aqueous solution interfaces. No PEG signal was detected.

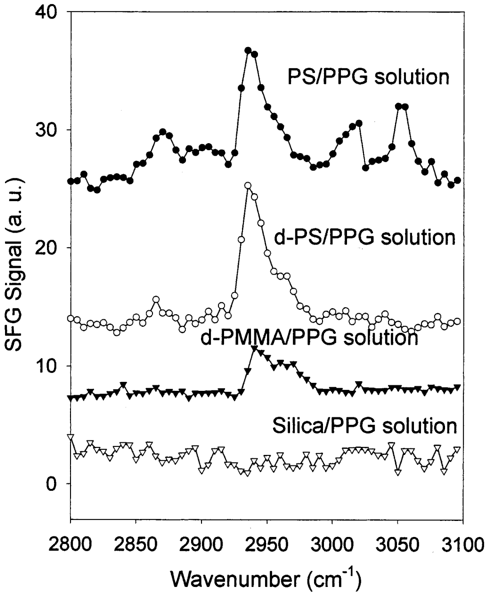

Figure 7. SFG spectra (ssp) collected from different solid/PPG aqueous solution interfaces indicate that PPG molecules can have different conformations at these interfaces.

more favorable than that between more hydrophobic PPG molecules and water molecules. By contrast, the more hydrophobic PPG molecules have more favorable interaction with air; thus, they like to segregate to the solution/air interface. Our SFG results as discussed above show direct evidence that the more surface active PPG tends to come to the surface and shows an ordered structure. On the other hand, the hydrophilic PEG molecules at the solution/air interface do not have an ordered structure.

Interfacial Activity and Conformation of PEG and PPG at Solid/Solution Interfaces. PEG, PPG, and their copolymers are mostly used in aqueous solutions. In this paper, we have also investigated the interfacial response of PEG and PPG in aqueous solution to different contacting media. Similar to the solid/pure liquid polymer interfaces mentioned above, SFG spectra (ssp) were collected from the solid/polymer solution interfaces (Figures 6 and 7). No SFG signals corresponding to PEG molecules were detected for any solid/PEG solution interfaces. For the PS/PEG solution interface, only two weak aromatic C−H stretching peaks of phenyl groups on PS were observed by SFG. The absence of SFG signals indicates that either PEG molecules do not segregate to various interfaces, or all PEG molecules in the interfacial region have random structures, or all functional groups at the interface are lying down. As discussed earlier, because of strong hydrogen bonding between PEG and water, PEG tends to interact with the water phase and is surrounded by water molecules. We believe this is the origin of the absence of SFG signals. More detailed discussions will be presented later.

SFG signals of PPG collected from PS (or d-PS)/PPG solution interfaces are very similar to those of PS (or d-PS)/pure PPG liquid interfaces. Again, the small difference in spectral intensity is due to the Fresnel coefficient effect. These results show that the PS (or d-PS)/PPG solution interface is covered by a layer of PPG molecules, with ordered methyl groups standing up along the interface normal. We have discussed the surface activity of PPG and PEG earlier. PPG is more surface or interface active due to the low surface free energy of the side chain methyl groups. As with the various solid/PPG liquid interfaces, SFG spectra collected from different solid/solution interfaces are also different. Compared to those at the d-PS/PPG solution interface, the molecules at the d-PMMA/PPG solution interface are less ordered, which is indicated by the weaker SFG intensity of the symmetric C−H stretch of the methyl groups. At the fused silica/PPG solution interface, no SFG signal is detected, indicating that a random structure is formed at this interface. In general, similar to the solid/PPG liquid interface, SFG studies also reveal that PPG can have different conformations at different solid/PPG solution interfaces.

Comparing the fused silica/PEG solution and fused silica/PPG solution interfaces, we see that both interfaces generate no SFG signals. As discussed earlier, we believe that PEG molecules do not segregate to the silica surface due to their favorable interaction with water molecules.Unlike PEG molecules, PPG molecules are more hydrophobic, and it is believed that adsorption behavior of PPG at the silica/solution interface is different from that of PEG molecules. The different adsorption behavior of PPG and PEG at the fused silica/solution interface has been confirmed by collecting an SFG spectrum from the fused silica surface after contacting it with the polyether solution and then removing it from the solution and exposing it to air (Figure 8). Figure 8 shows clearly that no strong SFG signals of PEG can be detected from the fused silica after removing it from PEG solution, indicating that there is almost no PEG segregation at the fused silica/PEG solution interface. On the contrary, strong SFG signals of PEG can be detected from fused silica after spin coating a thin layer of PEG on it (not shown). We have also collected SFG spectra from the solid substrate PS after removing it from PEG solution. The spectrum is similar to that of PS in air, before contacting the PEG solution. Again, this proves that PEG molecules do not segregate to solid/solution interfaces. Strong PPG SFG signals were collected from the fused silica surface after removing it from the PPG solution, showing that PPG molecules are strongly adsorbed to the fused silica surface.

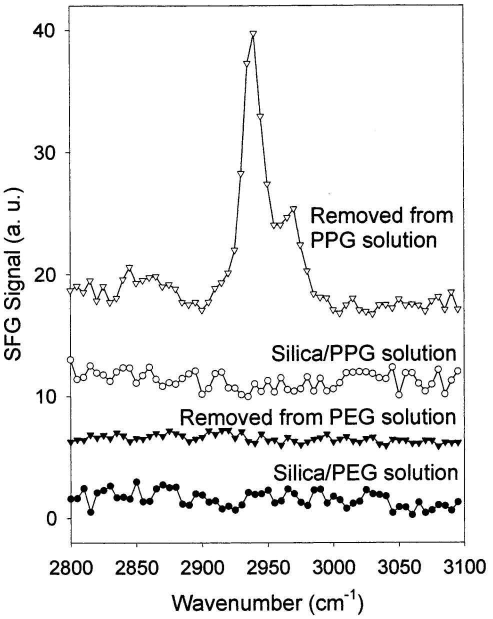

Figure 8. SFG spectra (ssp) collected from the fused silica after removing it from the PEG solution or the PPG solution.

Conclusions

Conformation of liquid polyethers PEG and PPG at different solid/liquid and liquid/air interfaces has been observed by SFG. It was found that PEG and PPG have different conformations while contacting different media, such as air, fused silica, PMMA, and PS. Both PEG and PPG show strong signals upon contacting hydrophobic media such as air and PS and much weaker signals or even an absence of signals while contacting hydrophilic media such as PMMA and fused silica. Different conformations of polyethers at different interfaces are correlated to molecular interactions at these interfaces. The favorable interaction between hydrophobic media and hydrophobic segments, CH_2 or CH_3 groups, of polyethers causes an ordered conformation with these groups standing up at the interface. The unfavorable interaction between hydrophilic media and hydrophobic segments of the polyethers causes a random conformation or forces CH_2 or CH_3 groups to lie down at the interface.

For comparison, interfaces between aqueous PEG (or PPG) solution and air, PS, PMMA, and fused silica are investigated. Because of the strong affinity with water molecules, PEG molecules show a relatively disordered structure at the solution/air interface and do not segregate to the solid/solution interfaces. PPG is more surface or interface active and segregates to all interfaces. At different solid/solution interfaces, PPG molecules have very different conformations. Similar to solid/PPG pure polymer interfaces, PPG molecules at the d-PS/solution interface are more ordered, with methyl groups oriented more toward the surface normal, than those at the d-PMMA/solution interface, which is indicated by the stronger SFG intensity. At the fused silica/solution interface, no SFG signal is detected, due to a different conformation.

This study provides a direct in-situ observation that PEG and PPG can have different conformations at different interfaces. Further investigation of the conformation of different PEG and PPG blocks in pluronics at different interfaces will be presented in a following paper.

Acknowledgment. This work was supported by the Petroleum Research Fund (37547-G7) and the start-up fund from the University of Michigan.

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MA020614J