Chemical Structures of Liquid Poly(ethylene glycol)s with Different End Groups at Buried Polymer Interfaces

Mark A. Even,[†] Chunyan Chen,[‡] Jie Wang,[†] and Zhan Chen*[,†,‡]

Department of Chemistry and Department of Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109

Received August 6, 2006; Revised Manuscript Received October 3, 2006

ABSTRACT: The interfacial conformational behaviors or structure of liquid poly(ethylene glycol)s (PEGs) with different end groups in contact with solid polymers of different hydrophobicities were investigated by sum frequency generation (SFG) vibrational spectroscopy. The solids at the interface included deuterated poly(methyl methacrylate) (d-PMMA), deuterated polystyrene (d-PS), deuterated polyethylene (d-PE), and a fluorinated polymer AF-2400; the liquids were poly(ethylene glycol) diol (PEGD), poly(ethylene glycol) methyl ether (PEGME), and poly(ethylene glycol) dimethyl ether (PEGDME). For comparison purposes, SFG has also been used to study PEG surfaces in air and in contact with fused silica. Depending on the hydrophobicity of the solid polymer, the hydroxyl O−H and methoxy OCH_3 end groups and ethoxy OCH_2 backbone groups of the liquid PEGs exhibited different interfacial behavior, which can be correlated to molecular interactions at these interfaces. The favorable interaction between the hydrophobic solids and the hydrophobic functional groups of the liquid PEGs causes the OCH_3 end groups, and to some extent the OCH_2 groups of the backbone, to become strongly ordered at the solid polymer/liquid polymer interface. We have shown that the end groups of the liquid PEGs, although comprising a small proportion of the total molecule, actually can dominate the interfacial behavior of the liquid polymer.

Introduction

Because of the widening role of polymers in various applications in chemistry, materials science, medical science, and engineering, the demand for effective methods to elucidate interfacial behavior of solid and liquid polymers can only be expected to increase. Liquid polymers are important for many applications including cleaning, wetting, lubrication, separations, and emulsification. Many physical and chemical properties relevant to these applications depend on the surface or interfacial properties of the liquid polymers.[1−3] It is therefore important to distinguish between the surface or interfacial properties of the liquid polymer from the properties of the bulk. Effective methods must be developed to elucidate the surface/interface structures and properties that govern their behavior. In recent years, extensive research has been devoted to develop powerful analytical techniques to elucidate molecular surface/interface structures, but many of these techniques still have some limitations. For example, some particle scattering techniques may be surface-sensitive and can provide important structural information on surfaces in a vacuum but, because they require high vacuum, they cannot be applied to studies of interfaces involving liquids. Various optical spectroscopic characterization techniques, such as Raman spectroscopy, infrared, and attenuated total reflection infrared spectroscopy, have been applied to polymer surface studies, and excellent results have been obtained,[4−6] but they lack sufficient surface specificity to discern surface structure from bulk structure at the submonolayer level.

Polyethers such as variants of poly(ethylene glycol) (PEG) are an example of a class of materials with important interfacial properties.[7−13] To achieve in-depth understanding of such interfacial properties, it is necessary to examine the interfacial structures in detail because interfacial properties are mediated by interfacial structures. Here, we will apply a nonlinear optical vibrational spectroscopy, sum frequency generation (SFG) vibrational spectroscopy, to study interfacial structures of PEGs with various end groups while they contact a variety of solid polymer materials.

Recently, SFG has been developed into a powerful surface and interface characterization technique that can provide in-situ information about surface and interfacial functional group coverage and orientation at various interfaces.[14−23] It can be used to examine molecular structures of buried interfaces such as solid/liquid interfaces in situ. More details regarding this technique will be shown below. In this study, we will study three liquid PEG polymers including poly(ethylene glycol) diol (PEGD), poly(ethylene glycol) methyl ether (PEGME), and poly(ethylene glycol) dimethyl ether (PEGDME) in contact with several solid polymers, including poly(methyl methacrylate) (PMMA), polystyrene (PS), polyethylene (PE), and a fluorinated polymer (AF-2400). Molecular formulas for PEGD, PEGME, and PEGDME are shown in Table 1. To avoid spectral confusion, deuterated PMMA (d-PMMA), deuterated PS (d-PS), and deuterated PE (d-PE) are used. Previously, SFG has been applied to study surface structures of PEG with different end groups in air,[24] interactions of oligo(ethylene glycol) terminated self-assembled monolayers with different chemical environments,[25,26] PEG/water interfaces,[27] polymers with PEG as side chains,[28] and adsorption behavior of a compound in the presence of PEG.[29] We have also studied interfacial structures of PEG and poly(propylene glycol) (PPG) at various buried interfaces[30] as well as interfacial structures of PEG−PPG copolymers.[31] Here we demonstrate that SFG can provide molecular level information about interactions between the liquid PEG backbone or end groups and various solid polymers at buried solid/liquid interfaces in situ.

Experimental Section

Sample Preparation. PEGD (MW 250), PEGME (MW 350), PEGDME (MW 200), d-PE, toluene (99.8% pure, HPLC grade),

---

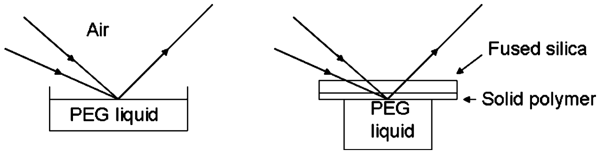
[†] Department of Chemistry.

[‡] Department of Macromolecular Science and Engineering.

* To whom all correspondence should be addressed: e-mail zhanc@umich.edu, Fax 734-647-4865.

10.1021/ma061785h CCC: \$33.50

Scheme 1. Schematic of the Experimental Geometry[a]



[a] Left: SFG spectra can be collected from the PEG surfaces in air; right: SFG spectra can be collected from the solid contacting media/PEG interfaces. For the fused silica/PEG interfaces, there are no polymer films between the fused silica and PEG.

and decalin (98% pure) were purchased from Aldrich; d-PS (MW 207 500) and d-PMMA (MW 219 000) were purchased from Polymer Source, Inc.; AF-2400 (1% solution) and FC-75 (a fluorinated solvent) were ordered from DuPont and 3M, respectively. Fused silica windows (1 in. diameter, $^1/_8$ in. thick) were purchased from ESCO Products, Inc. for use as IR-transparent substrates for the solid polymer films.

Thin films of d-PS and d-PMMA were prepared by spin-casting the respective 2 wt% solutions (in toluene) at 3000 rpm for 30 s onto fused silica substrates which were subsequently oven-dried at 80 °C for 12 h. Thin films of d-PE were spin-cast from a 1 wt% solution in decalin at 2000 rpm and oven-dried at 30 °C for 12 h. Thin AF-2400 films were prepared by spin-casting the AF-2400 solution (diluted to 0.5% by FC-75) at 2500 rpm for 30 s onto fused silica substrates, which were then heated to 350 °C for 30 min. For each run, several drops of the polymer solutions were used in the spin-coating process.

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 $\omega = \omega_1 + \omega_2$.[14−31] As a second-order nonlinear optical process, it is only allowed, under the electric-dipole approximation, in media without inversion symmetry. At surfaces or interfaces where the inversion symmetry of the bulk is broken an SFG signal is generated. Both experimental evidence and calculations show that SFG is submonolayer surface sensitive. For IR−visible SFG, the IR input beam, ω_1, is tunable and thus can produce the vibrational spectra of the surface species. It has been demonstrated that SFG can elucidate molecular structural information on surfaces and interfaces. For example, the development of hydrogen bonds can be detected by peak shifts of certain functional groups,[32,33] while the formation of chemical bonds can be deduced from the appearance of new vibrational modes and disappearance of existing modes in the SFG spectra. The alignment, orientation, orientation distribution, and ordering of surface functional groups can be deduced by examining SFG spectra collected using different polarization combinations of input and output beams and the absolute peak intensities. The interdiffusion of functional groups at the interface can be monitored by the gradual disappearance of the entire SFG spectra, and the kinetics of diffusion can then be measured by following the time-dependent SFG spectral intensity changes of samples of different thickness.[34]

Two SFG systems are available in our lab. Each setup is comprised of four components: a picosecond Nd:YAG laser, a harmonics unit with two KD*P crystals, an optical parametric generation (OPG)/optical parametric amplification (OPA) and difference frequency generation (DFG) system, and a detection system. The visible beam is generated by frequency-doubling the fundamental output pulses, of 20 ps pulse width, from the laser. The IR beam can be tuned from 650 to 4300 cm^{-1} (15.4 to 2.3 μm). The incident angles of the visible and the IR input beams are 60° and 54° vs the surface normal, respectively, and the diameters of both beams at the surface are about 500 μm. In this paper SFG spectra with ssp (s-polarized SFG output, s-polarized visible input, and p-polarized IR input) polarization combination will be collected from the buried solid contacting media/PEG liquid interfaces. SFG spectra will also be collected from the PEG liquid surface in air. A schematic of the sample geometry is shown in Scheme 1. Since the polymers are deuterated or fluorinated, they do not absorb IR in the C−H/O−H stretching frequency range.

Contact Angle Measurement. Water contact angles of the polymer films were measured by a contact angle goniometer from KSV.

Results and Discussion

Previous SFG studies on surface structures of PEGD, PEGME, and PEGDME in air indicate that hydrophobic groups prefer to segregate to the surface because air is a hydrophobic medium.[24] Hydrophobic groups on the surface have favorable interactions with air. Therefore, for the PEGD surface in air, the OCH_2 backbone groups were detected because they are more hydrophobic than the end O−H groups. For the PEGDME surface in air, the end OCH_3 groups dominate because they are more hydrophobic than the OCH_2 backbone groups. The surface structure of PEGME is intermediate to PEGD and PEGDME. In this research we would like to study buried interfaces of these three PEG materials when they are in contact with solid polymers with different hydrophobicities.

As mentioned, d-PMMA, d-PS, d-PE, and AF-2400 are used as solid polymer contacting materials in this research. Contact angle measurements were performed, and the water contact angles of d-PMMA, d-PS, d-PE, and AF2400 were measured to be 71°, 91°, 110°, and 122°, respectively. The hydrophobicity varies for these four polymers, increasing from d-PMMA to d-PS to d-PE and to AF-2400. That is to say, the d-PMMA surface is the least hydrophobic, and AF-2400 is the most hydrophobic.

The three liquid polymers (PEGD, PEGME, PEGDME) were brought into contact with the four different solid polymers. SFG spectra were collected from the buried PEG (liquid)/solid polymer interfaces in situ. As mentioned, all SFG spectra in this experiment were collected by the ssp polarization combination of input and output laser beams. The peak assignments have been discussed in detail in previously published results.[24−31] In this research, we will focus on the symmetric stretch of the OCH_2 backbone groups and the symmetric stretch of the end OCH_3 groups. As mentioned, the solid contacting polymers were either deuterated or fluorinated materials; therefore, they have no SFG-active modes that would cause spectral confusion with the PEG liquids in the C−H or O−H stretching regions. For comparison purposes, we also collected SFG spectra from the surfaces of the three PEG materials in air. In addition, we studied their interfacial structures while in contact with bare fused silica substrates. A clean fused silica surface is very hydrophilic (much more hydrophilic than PMMA), and water can easily spread over the surface. As expected, in our experiments, no SFG signals in the C−H stretching region were detected on the d-PMMA, d-PS, d-PE, AF-2400, or fused silica surfaces, showing that there was no C−H contamination on these contacting media.

Table 1. Molecular Structure of PEGD, PEGME, and PEGDME

end	formula	name	MW	molar ratio $(O)CH_3/(O)CH_2$	 $(O)H/(O)CH_2$
OH	$H(OCH_2CH_2)_nOH$	PEGD	250	0	0.19
OH, OCH_3	$CH_3(OCH_2CH_2)_nOH$	PEGME	350	0.07	0.07
OCH_3	$CH_3(OCH_2CH_2)_nOCH_3$	PEGDME	200	0.29	0

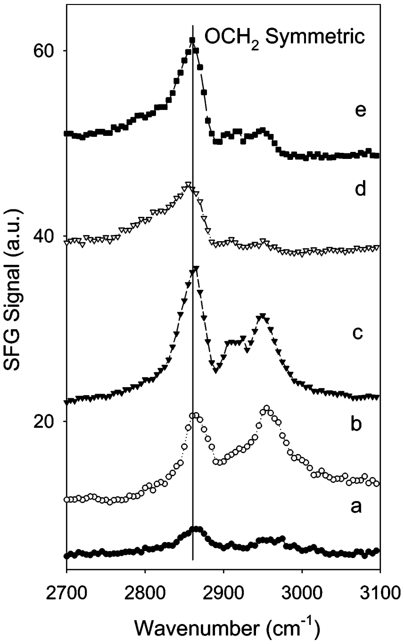


Figure 1. From bottom to top in order of increasing polymer hydrophobicity: SFG spectra of PEGD in contact with (a) d-PMMA, (b) d-PS, (c) d-PE, (d) AF-2400, and (e) air.

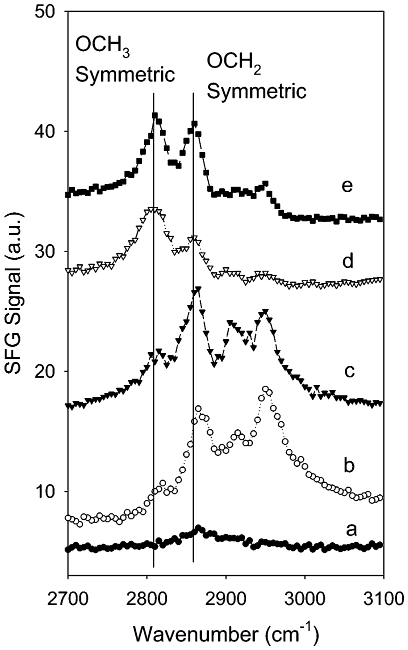


Figure 2. From bottom to top in order of increasing polymer hydrophobicity: SFG spectra of PEGME in contact with (a) d-PMMA, (b) d-PS, (c) d-PE, (d) AF2400, and (e) air.

Results of PEGD. SFG spectra collected from various solid polymer/PEGD interfaces and the PEGD surface in air are shown in Figure 1. The SFG spectrum we collected from the PEGD/air interface is very similar to the published result (Figure 1e).[24] The dominant peak of this spectrum at 2860 cm^{-1} is caused by the OCH$_2$ symmetric stretch of the backbone.[24] No signal is seen for the hydroxyl end groups. (The O−H stretching region is not shown in the spectrum, but there was no detectable SFG signal.) Compared to other polymers with known orientation and signal intensity (e.g., poly(*n*-butyl methacrylate)[22]), the strong SFG symmetric signals show that the PEGD OCH$_2$ groups are quite ordered on the surface, and they more or less orient toward the surface normal. We have shown previously that the CH$_2$ groups in the backbone of a silane molecule can also dominate the PS/silane interface.[35]

When in contact with the solid polymers (Figure 1a−d), the PEGD backbone peaks remain visible, but they change in relative intensity depending on the interfacial interactions between the respective materials. The spectrum of the PEGD/AF-2400 interface (Figure 1d) is dominated by the OCH$_2$ symmetric stretching peak, strongly resembling the spectrum of the PEGD/air interface (Figure 1e). As mentioned, air is a very hydrophobic environment, and AF-2400 is also very hydrophobic, in fact, the most hydrophobic material among the four solid polymers investigated here. Therefore, as with air, the OCH$_2$ groups at the PEGD/AF-2400 interface also orient toward the surface normal.

The SFG spectra collected from the PEGD/d-PE and PEGD/d-PS interfaces are similar to each other (Figure 1b,c), but are somewhat different from those collected from PEGD in air and the PEGD/AF-2400 interface. The OCH$_2$ symmetric signals at 2860 cm^{-1} can still be detected, but the OCH$_2$ Fermi resonance peaks also exhibit very strong intensities, showing that PEG may adopt a different conformation even though the OCH$_2$ groups are still dominate the surface.[36] Strong SFG signals show that at these two interfaces PEGD molecules are still very ordered.

The SFG spectrum collected from the PEGD/d-PMMA interface is much weaker (Figure 1a). We believe that this is due to the fact that the PEGD molecules are more disordered when they are in contact with a less hydrophobic surface. No O−H stretching signals have been detected from the PEGD/PMMA interface because either O−H groups do not segregate to the interface or they are disordered or more or less lie down at the interface.

As we mentioned above, fused silica is more hydrophilic than d-PMMA. We were unable to detect SFG signals from any PEG materials while in contact with fused silica; therefore, SFG spectra collected from all the PEG/fused silica interfaces are not shown in this paper. For the PEGD case, we believe that either the OCH$_2$ functional groups do not segregate to the interface or they must be quite disordered at the interface. No SFG O−H stretching signals were detected because either they are disordered at the interface or they lie down on the surface.

The different SFG spectra of PEGD in contact with different chemical environments indicate that different interfacial structures of PEGD are adopted at various buried interfaces. Generally speaking, on hydrophobic surfaces PEGD is more ordered, and on surfaces with different hydrophobicities, OCH$_2$ orientations can be altered. The different structures of PEGD at various interfaces are due to their different molecular interactions with the different surfaces.

Results of PEGME. SFG spectra collected from various solid polymer/PEGME interfaces and the PEGME surface in air are shown in Figure 2. The SFG spectrum we collected from the PEGME/air interface is also very similar to the previously published result (Figure 2e).[24] The spectrum shows a strong peak at 2815 cm^{-1} corresponding to the symmetric OCH$_3$ stretch of the single methoxy end group of the molecule. As with the PEGD, the same peaks for the Fermi resonance and the OCH$_2$ symmetric stretching peak can still be found, especially the 2860 cm^{-1} OCH$_2$ symmetric stretching peak. Since in PEGME the OCH$_3$ end groups are far less abundant than the OCH$_2$ backbone groups (Table 1), we believe that the OCH$_3$ end groups tend to segregate to the surface more. They must be quite ordered because they generate strong SFG signals; likewise, OCH$_2$ groups are also quite ordered on the PEGME surface in air.

The SFG spectrum collected from the PEGME/AF-2400 interface is not very different from that collected in air (Figure 2d). The relative intensity of the symmetric stretching for OCH_3 end group vs the OCH_2 groups is a little stronger than that of the PEGME/air interface. Perhaps this is due to the fact that more OCH_3 segregates to the PEGME/AF-2400 interface. The AF-2400 surface is more hydrophobic than typical air; thus, the favorable interaction between a more hydrophobic surface and the more hydrophobic OCH_3 end groups is more dominant.

Again, SFG spectra collected from the PEGME/d-PE and PEGME/d-PS interfaces are quite similar to each other but are very different from the PEGME/air and PEGME/AF-2400 interfaces. The d-PE and d-PS surfaces are less hydrophobic than the AF-2400 surface; therefore, they must interact more favorably with the less hydrophobic OCH_2 groups in PEGME. Their SFG spectra have much stronger signals from OCH_2 symmetric stretching (2860 cm^{-1}) than OCH_3 symmetric stretching (2815 cm^{-1}), indicating that OCH_2 is relatively more predominant at the interface. Weaker SFG signals of OCH_3 can be detected, showing that they are still present at the interface.

The SFG spectrum of PEGME/d-PMMA interface shows that only very weak OCH_2 signals can be detected, and signals from OCH_3 end groups are negligible. We believe that this interface is very disordered due to the d-PMMA hydrophilic surface. As mentioned, no SFG signal can be detected from the PEGME/fused silica interface. This is also due to the fact that the fused silica surface is hydrophilic. Very possibly OCH_2 and OCH_3 groups do not segregate to the hydrophilic surfaces. Even if they are present on such surfaces, the unfavorable interactions would induce their disordered orientations. SFG O−H stretching signals were not detected from these two interfaces.

Similar to PEGD, different SFG spectra of PEGME in contact with different chemical environments indicate different interfacial structures of PEGME at various buried interfaces. Because of the favorable molecular interactions, on the very hydrophobic surfaces such as in air or in contact with AF-2400, more hydrophobic OCH_3 end groups are present, resulting in strong OCH_3 signals. The relatively less hydrophobic OCH_2 groups tend to segregate to the surfaces of lower hydrophobicity, such as d-PE or d-PS surfaces. When the surface hydrophobicity is too low, such as with d-PMMA or fused silica, only very weak or even no SFG signals of OCH_2 and OCH_3 can be detected.

Results of PEGDME. SFG spectra collected from various solid polymer/PEGDME interfaces and the PEGDME surface in air are shown in Figure 3. The SFG spectrum we collected from the PEGDME/air interface is again very similar to the previously published result (Figure 3e).[24] This spectrum is dominated by the OCH_3 end-group symmetric stretching peak at 2815 cm^{-1}, with a weak peak for OCH_2 symmetric stretching at 2860 cm^{-1}. This shows that the PEGDME surface is dominated by the methoxy OCH_3 end groups. Compared to PEGME, PEGDME has more OCH_3 end groups, and they can segregate more to the surface in air.

The SFG spectrum of the PEGDME/AF-2400 interface is similar to that of PEGDME in air, with a dominating OCH_3 symmetric stretching peak at 2815 cm^{-1}, showing that the methoxy end groups dominate the interface. As mentioned, AF-2400 is very hydrophobic and should favorably interact with more hydrophobic methoxy OCH_3 groups.

The SFG spectrum of PEGDME at the liquid/d-PE interface is shown in Figure 3c. This spectrum is different from the two SFG spectra collected from the PEGDME/air and PEGDME/AF-2400 interfaces. Both OCH_3 and OCH_2 symmetric stretching peaks can be observed with similar intensity. We believe that both the OCH_3 end groups and the OCH_2 backbone groups of PEGDME can segregate to the d-PE surface with some orientational ordering. As mentioned, air and AF-2400 are very hydrophobic; therefore, they more favorably interact with the more hydrophobic OCH_3 groups, and OCH_3 signals dominate the SFG spectra. The d-PE surface is less hydrophobic, and it can favorably interact with both OCH_3 and OCH_2 groups; thus, SFG signals from both groups can be observed at the interface. Compared to the SFG spectrum collected from the PEGME/d-PE interface (Figure 2c), here the OCH_3 intensity is stronger because more OCH_3 groups are available in PEGDME than PEGME to segregate to the interface.

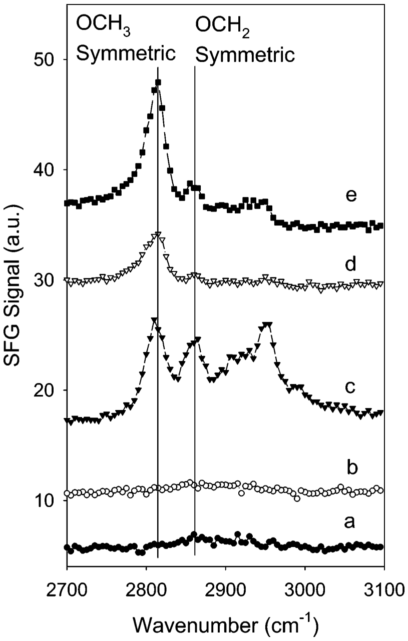


Figure 3. From bottom to top in order of increasing polymer hydrophobicity: SFG spectra of PEGDME in contact with (a) d-PMMA, (b) d-PS, (c) d-PE, (d) AF2400, and (e) air.

For the PEGD and PEGME cases, SFG spectra from the d-PE and d-PS interfaces (Figures 1b,c and 2b,c) are similar because the surface hydrophobicities of d-PE and d-PS are not very different. However, it is different for the PEGDME case. No SFG signal can be detected from the PEGDME/d-PS interface. This is because d-PS can be dissolved by PEGDME. In our experiments we found that PS films are dissolved by PEGDME; therefore, no stable PEGDME/d-PS interface exists after we contact d-PS with PEGDME, and no SFG signal was detected. As with the PEGDME/d-PS interface, no SFG signal was detected from the PEGDME/d-PMMA interface. We also found that the d-PMMA film is dissolved by PEGDME. Also, no SFG signal was detected from the PEGDME/fused silica interface. Unlike the d-PS and d-PMMA cases, the fused silica was not dissolved by PEGDME. The absence of SFG signals must be due to the surface hydrophilicty of fused silica, and there are no favorable interactions at the PEGDME/fused silica interface that can induce ordering of OCH_3 and OCH_2 groups at the interface to generate SFG signals.

Comparison of Various PEG Molecules at Various Interfaces. It has been demonstrated previously that PEG with different end groups can have different surface structures in air.[24] Hydrophobic groups tend to segregate to the surface in air because air is a hydrophobic environment. Therefore, OCH_2 in PEGD and OCH_3 in PEGDME like to segregate to the surface because in PEGD OCH_2 is more hydrophobic than the O−H end groups and in PEGDME OCH_3 end groups are more hydrophobic than the backbone OCH_2 groups. In this research, we have shown that at buried interfaces, as the air case, for the same PEG molecule, functional groups which are more hydrophobic prefer to segregate to the interface while contacting a hydrophobic surface. For example, for hydrophobic AF-2400, OCH_2 in PEGD and OCH_3 in PEGME and PEGDME tend to segregate to the interface because of the favorable interactions. For less hydrophobic contacting media such as d-PE and d-PS, both OCH_3 and OCH_2 groups can segregate to the interface for PEGME and PEGDME. For PEGD, OCH_2 segregates to the interface, but perhaps with a different conformation comparing to those at the PEGD/air and PEGD/AF-2400 interfaces. For more hydrophilic surfaces such as d-PMMA and fused silica, only very weak or even no SFG signals can be detected from the interfaces in the C−H stretching region, showing that both OCH_3 and OCH_2 are quite disordered. At the fused silica/PEGD interface, no O−H stretching SFG signal is generated, showing that at this interface the overall ordering/orientation of O−H groups is not enough to generate detectable SFG signals. This research demonstrates clearly that in contact with different surfaces PEG molecules have different structures because of varied molecular interactions between the PEGs and the contacting surfaces.

If we compare structures of the three different PEG molecules in contact with the same contact medium, we can also observe some general trends. As mentioned above, at the PEG/AF-2400 interfaces, OCH_2 dominates for PEGD because it is more hydrophobic than the O−H end groups. For PEGME, OCH_3 signals can be observed along with those from OCH_2 groups. Although the OCH_3 quantity is much smaller than OCH_2 in PEGME (molar ratio of OCH_3:OCH_2 for a PEGME with a MW of 350 is ∼1:14), the OCH_3 SFG signals are stronger. This is because they are more hydrophobic and tend to segregate to the very hydrophobic AF-2400 surface. For PEGDME, more interfacial OCH_3 groups are detected because more OCH_3 groups are available in PEGDME. A similar trend can be found for the d-PE surface which is not as hydrophobic as air or AF-2400.

Characterization of polymer surfaces solely by hydrophobicity (e.g., very hydrophobic, less hydrophobic, or hydrophilic) is really insufficient. As demonstrated in previous SFG studies, the PMMA surface is dominated by ester methyl groups along with some carbonyl groups,[21] the PS surface is dominated by phenyl groups,[19,23] the PE surface is of course dominated by methylene groups, and AF-2400 must be dominated by CF_2/CF_3 groups. The hydrophobicity differences among the four polymer surfaces are induced by the different surface dominating groups on such surfaces. Therefore, the favorable interactions between such polymer surfaces and PEG molecules at these interfaces are mediated by molecular interactions between the surface dominating groups and different groups in the PEG molecules, resulting in different structures of various PEG molecules at different interfaces. The purpose of the research reported in this article is to qualitatively understand such different interfacial structures at buried interfaces in situ using SFG. More quantitative understanding of such structures and molecular interactions would require some quantitative analysis of SFG spectra presented here along with SFG spectra collected using different polarizations, which will be reported in the future. Computer simulations of interactions between surface dominating groups of polymers and functional groups of PEG molecules should greatly facilitate further understanding of such molecular interactions at buried interfaces.

Conclusion

Although dominance of hydrophobic end groups for these liquid PEG polymers at the air interface has been studied previously,[24] we have demonstrated that different solid contact media of different hydrophobicities can induce varied interfacial conformations of these PEG polymers. SFG can be applied to elucidate molecular structures of buried solid/liquid interfaces, which are difficult to probe using other techniques. As shown in this research, PEGs with different end groups while in contact with different polymer surfaces adopt different structures. Some general trends have been observed relating PEG interfacial structures to polymer surface hydrophobicity.

In this research we use PEG molecules with quite low molecular weights; thus, the samples still have a substantial amount of end groups. Research shows that end groups can be used to modify surface properties of polymers with very high molecular weights. In that case, end groups can influence and even dominate the interfacial behavior of a macromolecular molecule on surfaces or at buried interfaces, out of all proportion to their relative composition in the bulk material. SFG should be a powerful technique to elucidate such end-group behavior at the molecular level in situ.

Acknowledgment. This work is supported by Office of Naval Research (N00014-02-1-0832) and National Science Foundation (CHE-0449469).

References and Notes

(1) Wu, S. H. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.
(2) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook;* Wiley: New York, 1999.
(3) Allara, D. L.; Atre, S. V.; Parikh, A. N. In *Polymer Surfaces and Interfaces II*; Feast, W. J., Munro, H. S., Richards, R. W., Eds.; Wiley: New York, 1992; pp 27−47.
(4) Hill, I. R.; Levin, I. W. *J. Chem. Phys.* **1979**, *70*, 842−851.
(5) Wiesenthal, T.; Baekmark, T. R.; Merkel, R. *Langmuir* **1999**, *15*, 6837−6844.
(6) Guo, C.; Wang, J.; Liu, H. Z.; Chen, J. Y. *Langmuir* **1999**, *15*, 2703−2708.
(7) Harris, J. M. *Poly(ethylene glycol) Chemistry: Biotechnical and Biomedical Applications*; Plenum Press: New York, 1992.
(8) Bailey, Jr., F. E.; Koleske, J. V. *Poly(ethylene oxide)*; Academic Press: New York, 1976.
(9) Begum, R.; Matsuura, H. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3839−3848.
(10) Smith, G. D.; Yoon, D. Y.; Jaffe, R. L.; Colby, R. H.; Krishnamoorti, R.; Fetters, L. J. *Macromolecules* **1996**, *29*, 3462−3469.
(11) Lasic, D. D. In *Poly(ethylene glycol): Chemistry and Biological Applications*; Harris, J. M., Zalipsky, S., Eds.; ACS Symposium Series 680; American Chemical Society: Washington, DC, 1997; pp 31−44.
(12) Harder, P.; Grunze, M.; Dahint, R.; Whitesides, G. M.; Laibinis, P. E. *J. Phys. Chem. B* **1998**, *102*, 426−436.
(13) Li, L.; Chen, S.; Zheng, J.; Ratner, B.; Jiang, S. *J. Phys. Chem. B* **2005**, *109*, 2934−2941.
(14) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984.
(15) Zhuang, X.; Miranda, P. B.; Kim, D.; Shen, Y. R. *Phys. Rev. B* **1999**, *59*, 12632−12640.
(16) Bain, C. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1281−1296.
(17) Eisenthal, K. B. *Chem. Rev.* **1996**, *96*, 1343−1360.
(18) Scatena, L. F.; Brown, M. G.; Richmond, G. L. *Science* **2001**, *292*, 908−912.
(19) Gautam, K. S.; Schwab, A. D.; Dhinojwala, A.; Zhang, D.; Dougai, S. M.; Yeganeh, M. S. *Phys. Rev. Lett.* **2000**, *85*, 3854−3857.
(20) Chen, Z.; Shen, Y. R.; Somorjai, G. A. *Annu. Rev. Phys. Chem.* **2002**, *53*, 437−465.
(21) Wang, J.; Chen, C. Y.; Buck, S. M.; Chen, Z. *J. Phys. Chem. B* **2001**, *105*, 12118−12125.
(22) Wang, J.; Paszti, Z.; Even, M. A.; Chen, Z. *J. Am. Chem. Soc.* **2002**, *124*, 7016−7023.
(23) Briggman, K. A.; Stephenson, J. C.; Wallace, W. E.; Richter, L. J. *J. Phys. Chem. B* **2001**, *105*, 2785−2791.

(24) Chen, Z.; Ward, R.; Tian, Y.; Baldelli, S.; Opdahl, A.; Shen, Y. R.; Somorjai, G. A. *J. Am. Chem. Soc.* **2000**, *122*, 10615−10620.

(25) Zolk, M.; Eisert, F.; Pipper, J.; Herrwerth, S.; Eck, W.; Buck, M.; Grunze, M. *Langmuir* **2000**, *16*, 5849−5852.

(26) Wang, R. Y.; Himmelhaus, M.; Fick, J.; Herrwerth, S.; Eck, W.; Grunze, M. *J. Chem. Phys.* **2005**, *122*, 1647021−1647026.

(27) Dreesen, L.; Humbert, C.; Hollander, P.; Mani, A. A.; Ataka, K.; Thiry, P. A.; Peremans, A. *Chem. Phys. Lett.* **2001**, *333*, 327−331.

(28) McGall, S. J.; Davies, P. B.; Neivandt, D. J. *J. Phys. Chem. B* **2003**, *107*, 4718−4726.

(29) Casford, M. T. L.; Davies, P. B.; Neivandt, D. *Langmuir* **2006**, *22*, 3105−3111.

(30) Chen, C. Y.; Even, M. A.; Wang, J.; Chen, Z *Macromolecules* **2002**, *35*, 8093−8097.

(31) Chen, C. Y.; Even, M. A.; Wang, J.; Chen, Z. *Macromolecules* **2003**, *36*, 4478−4484.

(32) Loch, C. L.; Ahn, D.; Chen, C. Y.; Wang, J.; Chen, Z. *Langmuir* **2004**, *20*, 5467−5473.

(33) Li, G. F.; Shen, Y.; Morita, S.; Nishida, T.; Osawa, M. *J. Am. Chem. Soc.* **2004**, *126*, 12198−12199.

(34) Chen, C. Y.; Wang, J.; Loch, C. L.; Ahn, D.; Chen, Z. *J. Am. Chem. Soc.* **2004**, *126*, 1174−1179.

(35) Chen, C. Y.; Loch, C. L.; Wang, J.; Chen, Z. *J. Phys. Chem. B* **2003**, *107*, 10440−10445.

(36) Fermi resonance signal change may be due to the conformational change of PEG molecules (e.g., OCH_2 groups change their gauch and/or trans conformations), resulting in different coupling between the CH_2 symmetric stretch and overtones of the bending modes.

MA061785H