Detection of Hydrophobic End Groups on Polymer Surfaces by Sum-Frequency Generation Vibrational Spectroscopy

Zhan Chen,[†,‡] Robert Ward,[§] Yuan Tian,[§] Steve Baldelli,[†,‡] Aric Opdahl,[†,‡] Yuen-Ron Shen,[‡,⊥] and Gabor A. Somorjai[†,‡,*]

Contribution from the Department of Chemistry, University of California at Berkeley, Berkeley, California 94720, the Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, The Polymer Technology Group, Inc., Berkeley, California 94710, and the Department of Physics, University of California at Berkeley, Berkeley, California 94720

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Abstract: We report the successful application of SFG to detect segregation of end groups on polymer surfaces. Two groups of polymer samples are studied: one is polyurethane with different surface-modified end groups, the other is poly(ethylene glycol) (PEG) with different end groups. For each group of polymers, both hydrophobic and hydrophilic end groups are chosen. With the surface sensitivity of SFG, we have found that hydrophobic end groups [e.g., methoxy on PEG or poly(dimethylsiloxane) (PDMS) on polyurethane] tend to segregate to the polymer surface in air. However, the hydrophilic end groups (e.g., hydroxyl group on PEG or PEG on polyurethane) remain in the bulk so that the surfaces that are exposed to air are covered by the polymer backbones. Although contact-angle measurements and XPS results can demonstrate that polymer surfaces indeed have been modified by different end groups, only SFG can show the surface structure at the molecular level.

1. Introduction

1A. SFG: a Powerful Technique to Study Polymer Surfaces. Many of the chemical and mechanical properties of polymers, such as wettability, friction, lubricity, wearability, chemical reactivity, biological compatibility, permeability, charge storage capacity, and electrical response, can be correlated with their molecular surface structure and composition.[1,2] To control surface properties by manipulating surface structure, one must have an extensive database of detailed correlations between properties and structures of the polymer surfaces of interest. However, very little work has been reported on such structure−property correlations due to the lack of probe techniques capable of studying polymer surface structure.

Ideally, polymer probe techniques must be sensitive to molecular features such as conformational sequences and hydrogen bonding. Because changes in these features are defined by subtle differences in the energy levels of the structures, highly sensitive valence band or vibrational spectra are needed for characterization. Various spectroscopic techniques, such as reflection infrared spectroscopy, attenuated total reflection infrared spectroscopy, and Raman spectroscopy,[3−5] have been used to characterize polymer surfaces. However, these tools lack surface selectivity, so that the resulting spectra are often obscured by bulk contribution. Contact angle measurement,[6] neutron reflection,[7] and X-ray photoelectron spectroscopy (XPS)[8] are surface sensitive, but they often do not provide structural information, and/or do not allow in-situ measurement.

Recently, IR + visible sum-frequency generation (SFG) vibrational spectroscopy has been developed into a surface-specific spectroscopic tool having monolayer sensitivity and has been successfully applied to various kinds of surfaces and interfaces.[9−11] SFG is a powerful and versatile in situ surface probe, which not only permits identification of surface molecular species but also provides information about orientation of functional groups at the surface. SFG has all of the common advantages of laser techniques, namely, it is nondestructive, highly sensitive, and has good spatial, temporal, and spectral resolution.

In this paper, the successful application of SFG to detect segregation of end groups on polymer surfaces is reported. Two groups of polymer samples are studied: one is polyurethane with different surface modifying end groups, the other is poly(ethylene glycol) (PEG) with different end groups. For each group of polymers, both hydrophobic and hydrophilic end groups were chosen. Using SFG, we found that hydrophobic end groups [e.g., methoxy on PEG or poly(dimethylsiloxane) (PDMS) on polyurethane] tend to partition to the polymer surface in air. However, the hydrophilic end groups (e.g.,

* To whom all correspondence should be addressed. Fax: 510-643-9668. E-mail: somorjai@socrates.berkeley.edu.
† Department of Chemistry, University of California at Berkeley.
‡ Lawrence Berkeley National Laboratory.
§ The Polymer Technology Group, Inc.
⊥ Department of Physics, University of California at Berkeley.

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hydroxyl group on PEG or PEG on polyurethane) remain in the bulk, so that the surfaces are covered by the polymer backbones. Although contact angle measurements and XPS results can demonstrate that polymer surfaces, indeed, have been modified by different end groups, SFG can show the surface structure at the molecular level.

1B. Functionalizing End Groups: an Effective Method to Tailor Polymer Surface Properties. With the surge of polymer applications in the biomedical field, design and synthesis of new materials with biocompatible surfaces have become an important part of academic and industrial research. Polyurethanes have been used for a number of blood-contacting applications due to their favorable tensile and fatigue properties.[12,13] To develop polyurethanes with surfaces that will not activate blood coagulation, a novel method of modifying polymer surface properties without the significant modification of bulk properties has been developed.[14] The method, which is accomplished during synthesis, appends to polymer molecules certain monofunctional surface-active end (SME) groups. A series of polyurethanes (BioSpan) containing a range of chemical structures and/or functional groups are prepared by coupling end groups to the backbone of a polyurethane via a terminal isocyanate group during initial synthesis of the polyurethane. The SME groups occupy the termini of linear polyurethanes and are, therefore, more mobile than the backbone groups. The surface activity of polyurethanes is controlled by careful selection of the surface active groups that are used.

PEG is widely used in several areas of medicine and biological science.[15] Surface modifications with PEG to provide protein and cell rejecting properties is the focus of much research.[16−18] The PEG polymers are widely available with different kinds of end groups, but their surfaces have not been widely studied.

End groups can dramatically affect the polymer surface, so that the surface has a completely different composition from the bulk. The entropically driven end-group attraction to the surface has been studied theoretically.[19−21] Recent experimental investigations by neutron reflection[22] and static second-ion mass spectrometry[23] have shown a slight preference for chain-ends at the surface. Enthalpic attractive, or depletion of, end groups on surfaces has also been widely studied on different polymer surfaces, such as polystyrene, PDMS, and PEG, by different methods, such as surface tension measurements, XPS, and neutron reflection.[24,25] These methods cannot provide molecular level information. The SFG data will show evidence on a molecular level of enthalpic attracted end group segregation on the surface.

2. Experimental Section

2A. SFG Setup. In an SFG experiment, a pulsed visible laser beam (frequency ω_{vis}) is overlapped on a surface with a tunable, pulsed IR laser beam (frequency ω_{ir}) and the light emitted by the nonlinear process at the sum frequency, $\omega_{sum} = \omega_{vis} + \omega_{ir}$, is detected by a photomultiplier. The intensity of the light at ω_{sum} is proportional to the square of the second-order susceptibility, χ^2, of the surface. χ^2 vanishes for a material with inversion symmetry, so that bulk materials usually do not generate sum frequency output. χ^2 is nonzero for a surface (or interface) because surface molecules lack inversion symmetry. A plot of SFG intensities vs the frequency of the IR laser shows the vibrational spectrum of the surface molecules. Orientation of surface molecules has been determined by using different polarization combinations of outgoing and input beams.[26] The SFG experimental setup in this lab has been described in detail.[27]

In this experiment, sum-frequency (SF) spectra were obtained by overlapping a visible and a tunable IR beam on a polymer surface at incident angles of 45° and 50°, respectively. The visible beam at 532 nm was generated by frequency-doubling the fundamental output pulses of 20 ps pulse width from a Continuum Nd:YAG laser. The IR beam, tunable from 2500 to 3600 cm^{-1}, was generated from an optical parametric generation/amplification system based on $LiNbO_3$ crystals. The sum-frequency signal from the polymer surface was collected by a photomultiplier tube and processed using boxcar/averager. The surface vibrational spectra were obtained by measuring the SF signal as a function of the input IR frequency. In this work, only results with the ssp (for s-polarized SF output, s-polarized visible input, and p-polarized infrared input) and sps polarization combination are reported. All spectra were collected at 300 K in air.

2B. Sample Preparation. The biopolymers BioSpan (BN), BioSpan-S (BS), and BioSpan-P (BP) were synthesized by The Polymer Technology Group, Inc., of Berkeley, California.[14] BS (MW = 65 000) is a polyurethane which is based on methylene diisocyanate with mixed diamine chain extenders of ethylenediamine and 1,3-cyclohexanediamine, and polytetramethyleneoxide (PTMO) that are capped with PDMS end groups that exhibit thrombo-resistance properties. BN is the polyurethane backbone of BS. BP is a similar biopolymer with the same BN polyurethane as the backbone but with PEG as end groups. Except for the film-thickness-dependent study, all the BS, BP, and BN polymer films were prepared by casting the polymers from their 2 wt % N, *N*-dimethylacetamide (DMAC) solutions onto flat quartz substrates. BS films with different thickness were prepared by solvent casting BS/DMAC solutions with different concentrations (0.2−5 wt %). Then the films were dried in air at 65 °C for 24 h. The molecular formulas are shown in Figure 1a.

Both high-molecular-weight (M_n = 2000, solid thin films) and low-molecular-weight (200−400, liquid) PEG samples were used in this study (Molecular formulas are shown in Figure 1b). The PEG diol, PEG methyl ether, and PEG dimethyl ether were purchased from Aldrich. The high-molecular-weight PEG films are made by $CHCl_3$ solvent casting on the quartz surface or by melting the sample between two close contacted quartz plates then taking them apart. The SFG spectra were taken at the PEG films/air interfaces and no difference can be detected on the same polymer surfaces prepared by the two methods mentioned above. This shows that PEG film surface structures are independent of these two preparation methods. SFG spectra of low-molecular-weight samples were taken at liquid/air interfaces.

To prove that SFG signals come from the top layer of the solid PEG films, PEG diol (M_n = 2000) films with different thicknesses were prepared by spin-coating PEG diol/$CHCl_3$ solution onto quartz substrates. The film thicknesses were controlled by the solution concentration and the spin speed. To measure the film thickness, a scratch was

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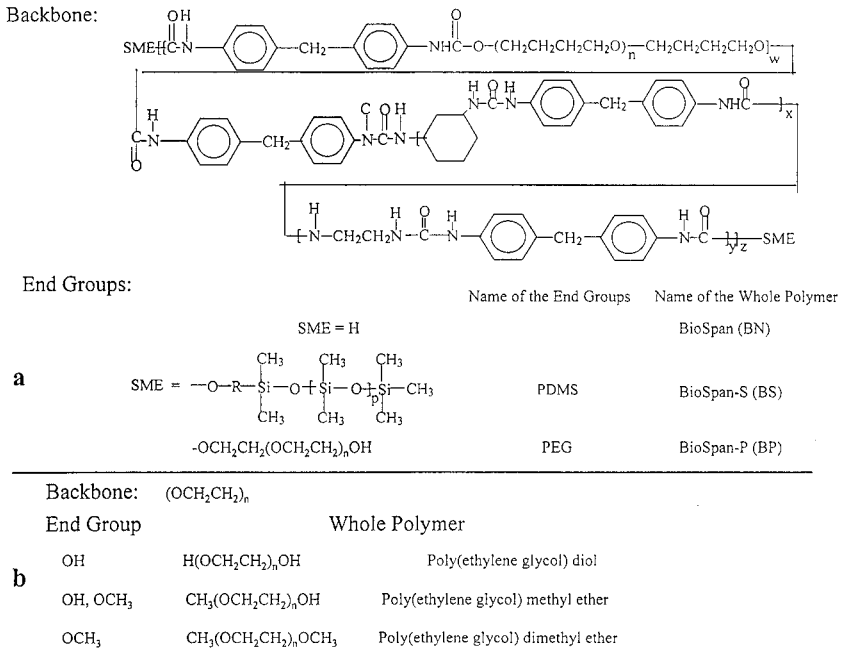

Figure 1. (a) Molecular formulas for BioSpan polymers. (b) Molecular formulas for poly(ethylene glycol).

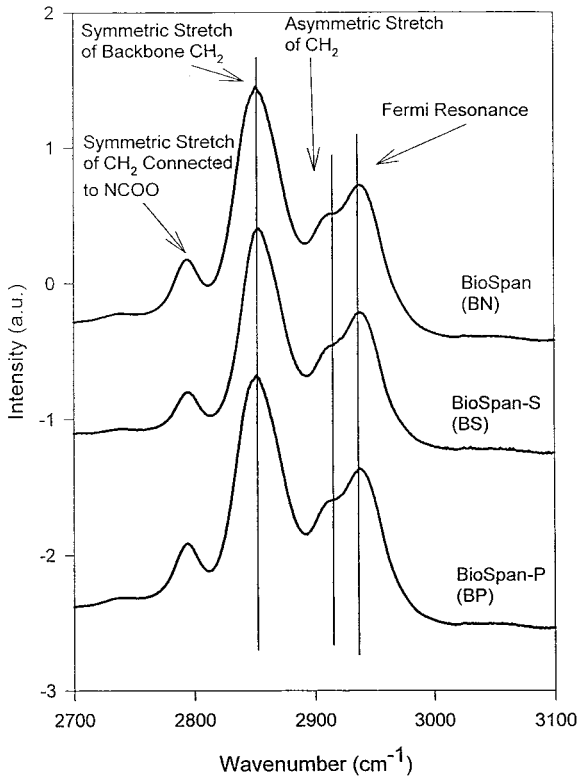

Figure 2. Attenuated total-reflection infrared spectra of different BioSpans.

made in the film. The depth of the scratch was measured using a commercial Park Scientific M5 AFM.

3. Results and Discussions

3A. BioSpan Surfaces. Attenuated total reflection infrared (ATR-IR) spectra of BS, BP, and BN (Figure 2) in the C−H stretching region are essentially identical. The peaks at ∼2850 and ∼2920 cm^{-1} are the symmetric and asymmetric stretches of aliphatic CH_2 groups, respectively. The ∼2940 cm^{-1} peak is Fermi resonance, which comes from the interaction between the symmetric CH_2 stretch and the overtones of CH_2-bending modes.[28] The IR peak at 2787 cm^{-1} can be attributed to the symmetric stretch of CH_2 that is connected to an oxygen atom of the carbamate group (NCOO).[29] The bulk compositions of these three samples are very similar, because the end groups (PDMS and PEG, respectively) of BS and BP are only 3 wt %. The surface sensitivity of 1−5 μm of the ATR-IR technique is not sufficient to detect segregations PDMS or PEG on BS or BP surfaces. The ATR-IR spectra are still dominated by the bulk contributions; thus, all of the three spectra are identical.

Figure 3 shows the SFG spectra of polytetramethyleneoxide (PTMO, the soft segment of the BN backbone), BN (the backbone only), PDMS (the end group of BS), and BS. The spectrum of BN is not very different from PTMO, which indicates that the BN surface is covered by the PTMO soft segments. The BS spectrum is very different from that of BN, which show that the surface structure of BS is very different. The strong ∼2915 cm^{-1} peak in the SFG spectrum of PDMS is from the C−H symmetric stretch of $Si-CH_3$.[30] The BS also has this strong peak, which shows that the hydrophobic PDMS end groups cover the surface of BS. The BS surface is not completely covered by PDMS, because the 2850 cm^{-1} backbone peak is also present. Although there is only 3 wt % PDMS in the BS, it segregates to the BS surface and can be detected by SFG. Different water contact angles of 100°, 94°, and 75° for PDMS (end group of BS), BS, and BN (backbone of BS) surfaces indicate that a small amount (3 wt %) of PDMS end groups can segregate at the BS surface due to their lower surface tension.[27] XPS results also showed surface enrichment of PDMS in BS.[31] Figure 4b shows the sps spectra of BS. The peak at ∼2965 cm^{-1} is the asymmetric C−H stretch of $Si-CH_3$. The peak at ∼2950 cm^{-1} in the ssp SFG spectrum of BS (Figure 4a) is the overlap of Fermi resonance and the C−H asymmetric of $Si-CH_3$. The intensity ratio of the symmetric stretch peak

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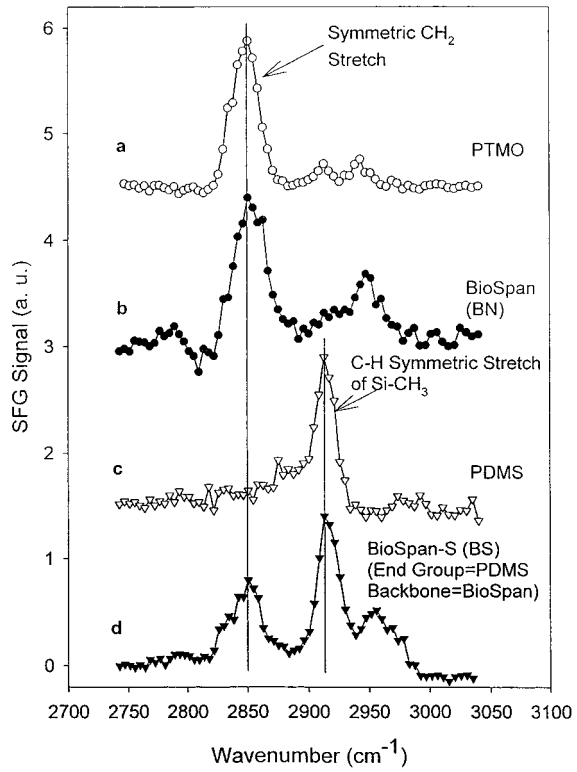

Figure 3. SFG spectra (ssp) of (a) PTMO, (b) BN, (c) PDMS, and (d) BS.

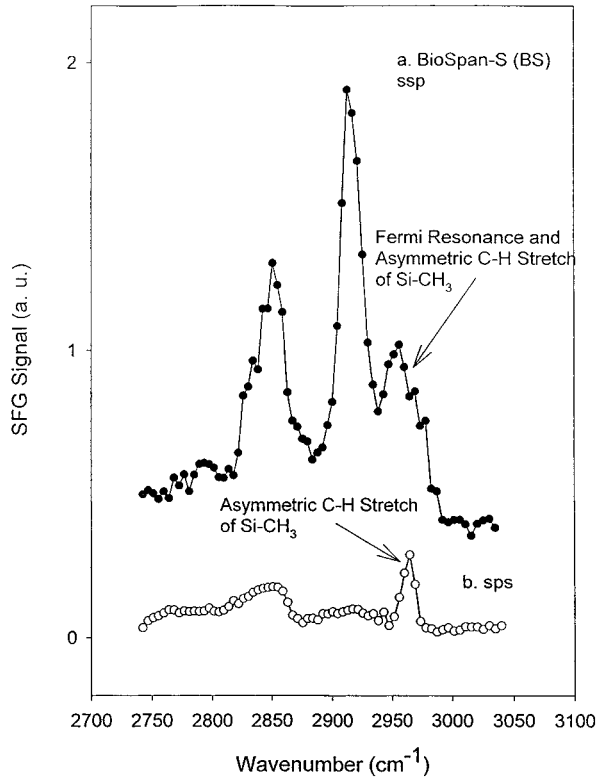

Figure 4. SFG spectra of BS: (a) ssp and (b) sps.

in ssp (s-polarized sum-frequency signal, s-polarized visible input, and p-polarized IR input, Figure 4a) and sps (Figure 4b) spectra showed that the tilt angle between Si−CH_3 and surface normal is 35 ± 5°.[26]

The ssp SFG spectrum of BP (Figure 5c) is similar to that of BN (BP's backbone, Figure 5a), and no hydrophilic PEG end groups (Figure 5b) can be detected on the surface [for details

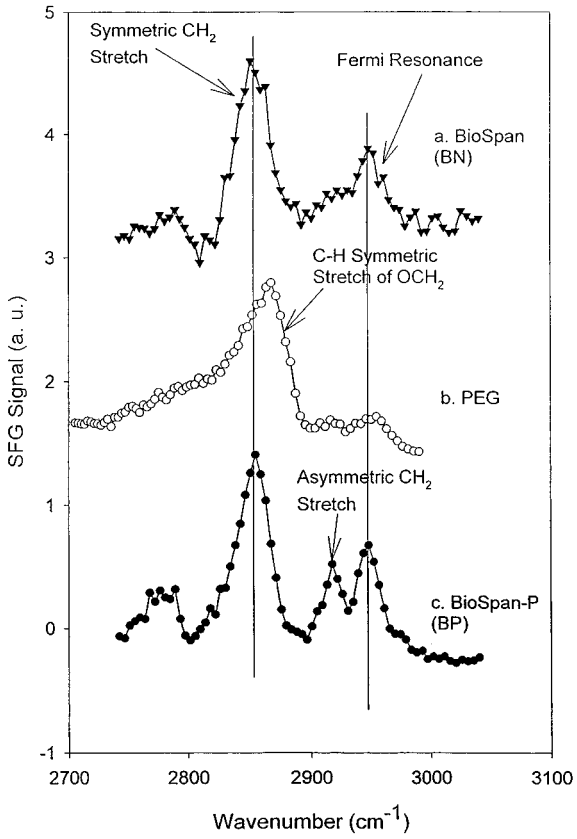

Figure 5. SFG spectra (ssp) of (a) BN, (b) PEG, and (c) BP.

of the PEG spectrum, see the discussion of PEG (below); the C−H stretch of OCH_2 should be around 2865 cm^{-1}, which is not detected on the BP surface here], which shows that the surface is covered by the BN backbone only. The peak at 2920 cm^{-1} in Figure 5c is the asymmetric CH_2 stretch of the backbone, not the C−H stretch of Si−CH_3 (~2915 cm^{-1}). This is suggested by the sps spectrum of BP (Figure 6b). If this peak is from the C−H stretch of Si−CH_3, then in the sps spectrum, the asymmetric C−H stretch peak of Si−CH_3 should appear around 2965 cm^{-1}. This is not the case. No peak around 2965 cm^{-1} can be seen in Figure 6b.

SFG results show that at the molecular level, hydrophobic PDMS can aggregate on the BS surface. But the hydrophilic PEG end groups remain in the BP bulk and the surface is covered by the more hydrophobic backbone.

3B. PEG Surfaces. Figure 7 shows the FTIR transmission spectra of high-molecular-weight PEG samples. All of these spectra are identical and very similar to the published results.[32] The amount of end groups is <3 wt %. These differences of bulk compositions of different PEG samples cannot be detected by their IR spectra.

The different surface tensions (42.9 and 37.1 dyn/cm, respectively)[33] of poly(ethylene glycol) diol and poly(ethylene glycol) dimethyl ether show that hydrophilic hydroxyl and hydrophobic methoxy affect the surface structures. The different surface structures can be detected by SFG at the molecular level.

The SFG spectra of different PEG solid films are markedly different, which shows that the surfaces of PEG polymers with different end groups are distinct. The SFG spectrum of PEG diol in Figure 8a shows the strong C−H symmetric stretch peak

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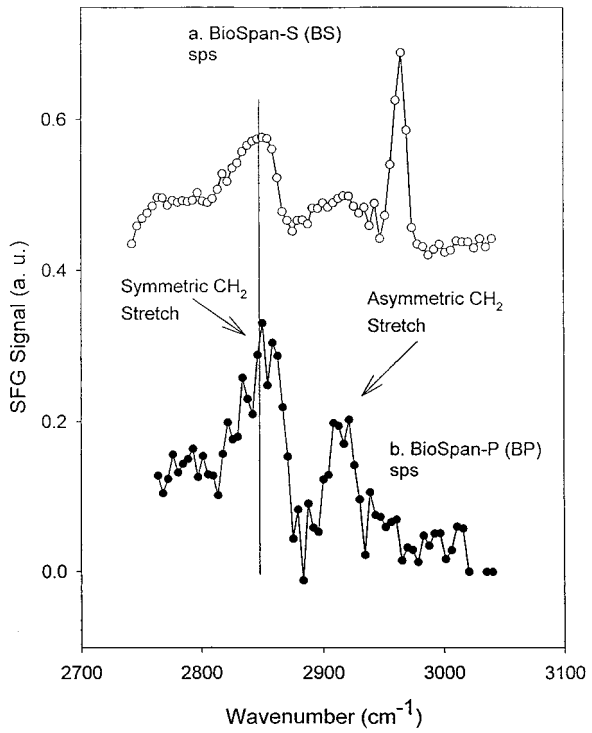

Figure 6. SFG spectra (sps) of (a) BS and (b) BP.

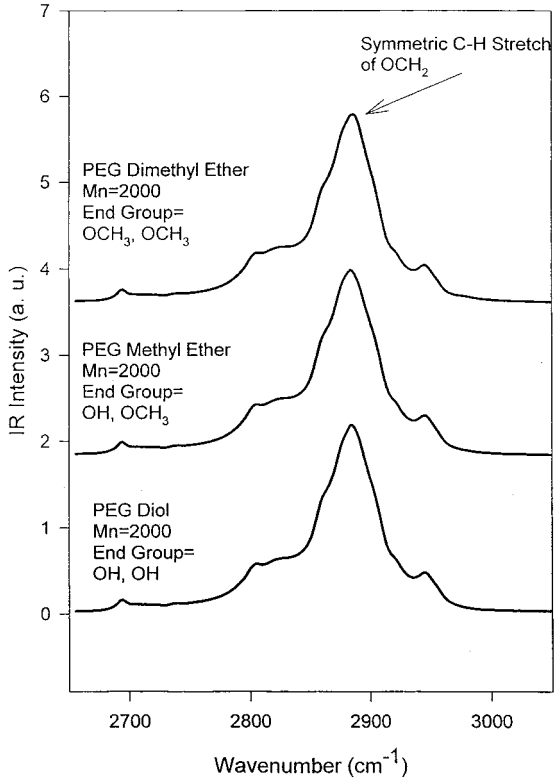

Figure 7. IR spectra of poly(ethylene glycol) (M_n = 2000) with different end groups.

of OCH_2 at 2865 cm^{-1} [32]. No O−H stretch signal can be detected in the frequency range 3000−3800 cm^{-1} (not shown), which indicates that the surface is covered by the backbone. The surface spectrum (Figure 8b) of PEG methyl ether has two strong peaks. The stronger peak at 2820 cm^{-1} is due to the C−H symmetric stretch of the OCH_3 end group, and the peak at 2865 cm^{-1} is due to the backbone. This shows that the hydrophobic methoxy end group covers a fraction of the surface, and the

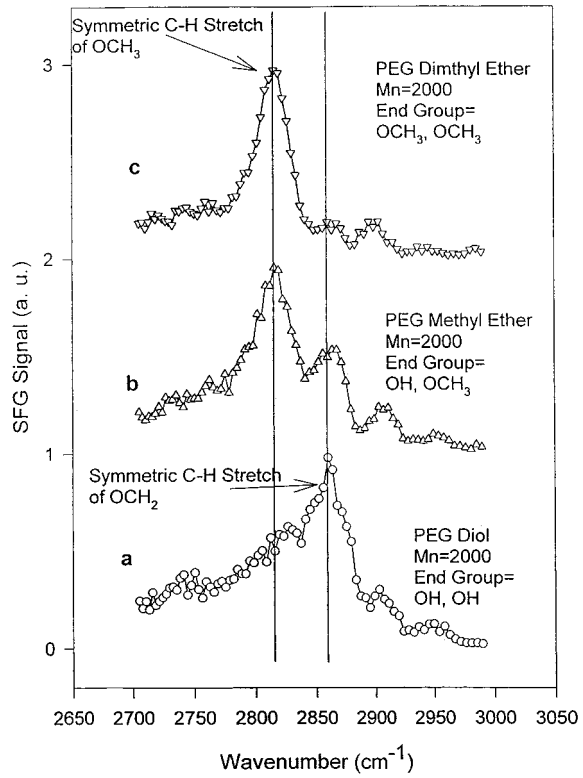

Figure 8. SFG spectra (ssp) of poly(ethylene glycol) (M_n = 2000) with different end groups.

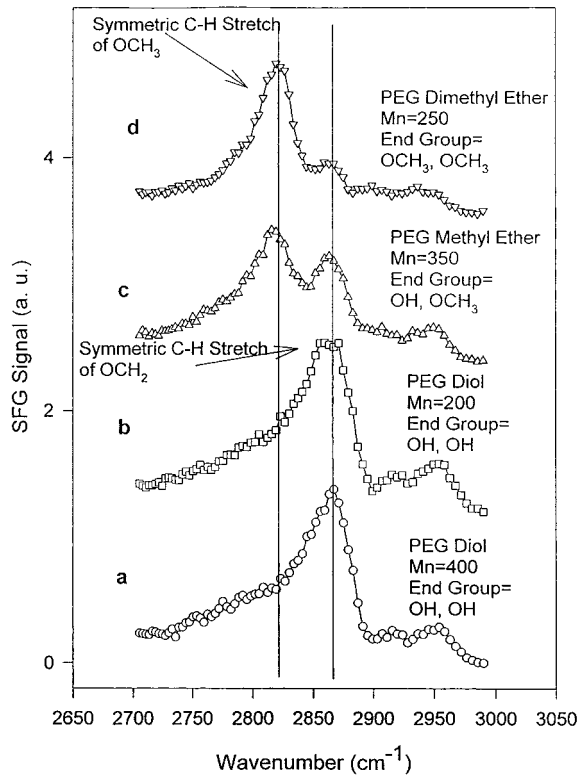

Figure 9. SFG spectra (ssp) of poly(ethylene glycol) (M_n = 200−400) with different end groups.

backbone covers the rest. No hydrophilic hydroxyl end groups can be detected on the surface. The strong peak at 2820 cm^{-1} on the PEG dimethyl ether surface (Figure 8c) shows that the surface coverage of the hydrophobic OCH_3 end group is even higher. The peak at 2865 cm^{-1} due to the backbone is much weaker. As mentioned before, the hydrophobic methoxy end

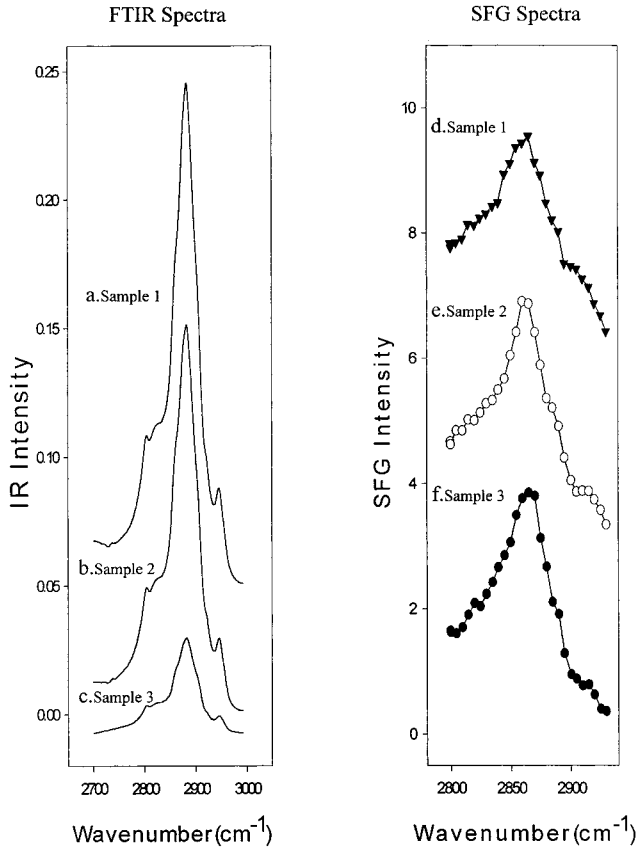

Figure 10. FTIR transmission spectra and SFG Spectra of PEG diol samples with different thicknesses.

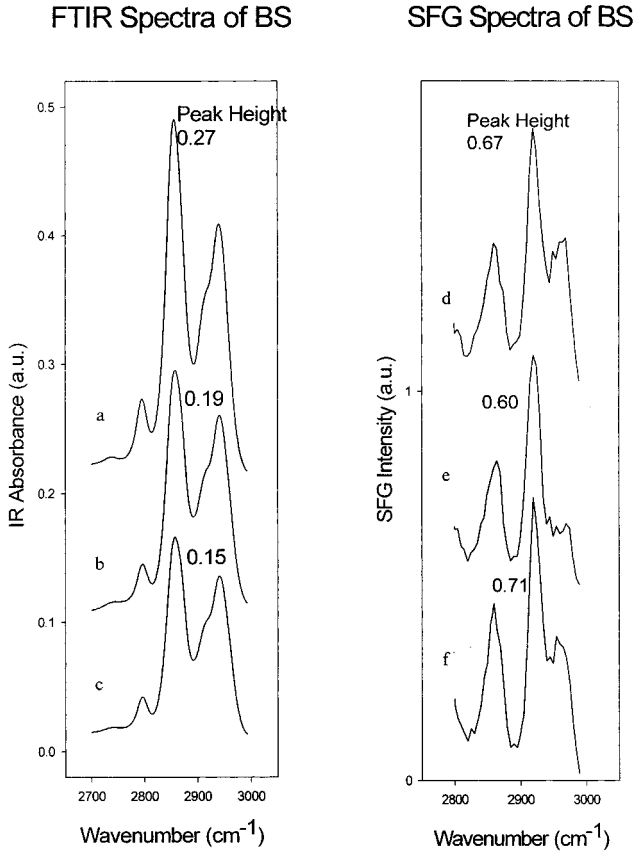

Figure 11. FTIR transmission spectra and SFG Spectra of BS with different thicknesses.

group tends to partition to the surface, due to the lower surface tension.[33]

The SFG spectra of low-molecular-weight PEG with different end groups are also markedly different from each other (Figure 9), but for each sample with the same end group, the spectrum is similar to the high-molecular-weight PEG. Figure 9a,b shows that the PEG diol surfaces are covered by the backbone; no hydrophilic OH groups can be detected by SFG. The surface of PEG methyl ether (Figure 9c) is covered by hydrophobic methoxy end groups and the backbone. Surface coverage of the methoxy end group is even higher on the PEG dimethyl ether surface (Figure 9d). The weight percent of end groups of PEG is smaller in high-molecular-weight samples. By comparing Figure 9c with 8b, and 9d with 8c, one sees that the SFG intensity ratios of the methoxy end groups to the backbone for higher-molecular-weight samples are larger. A possible explanation is that more hydrophobic methoxy end groups segregate to the high-MW PEG surface, despite their smaller bulk concentrations. At room temperature, the high-molecular-weight samples are solid, and the low-molecular-weight samples are liquid. The solid surface is more ordered and lower surface energy hydrophobic end groups segregate more on the surface.

3C. Surface Sensitivity of SFG. The surface specificity of SFG in reflection from a medium with inversion symmetry arises from symmetry breaking at the surface.[9−11] This is also the case for polymers. Defects and microscopic inhomogeneities in a polymer bulk may have local lack of inversion symmetry, but their random distribution preserves the macroscopic inversion symmetry, which then forbids SFG in the bulk. Experimentally, Xing et al. in a recent work[34] showed explicitly that the bulk contribution to SFG in reflection in the C−H stretch range from polymers containing CH_x groups should be negligible.

We have also carried out measurements to show that our SFG study is surface-specific. Figure 10 displays the FTIR transmission spectra and SFG reflection spectra of PEG diol ($M_n = 2000$) films of different thickness (116 ± 8, 535 ± 16, and 730 ± 17 nm). The FTIR peak intensity varies significantly and correlates well with thickness. The SFG spectra, on the other hand, exhibit only a small variation with sample thickness, which presumably is due to the uncontrollable variation of the polymer surface structure. These results clearly indicate that the SFG spectra originate mainly from the air/PEG diol interface. The same conclusion applies to the BS films. As shown in Figure 11, the FTIR spectra for three BS films are very different, but the corresponding SFG spectra are very close. The latter, therefore, must come mainly from the air/BS interface.

4. Conclusions

The small amount of hydrophobic end groups with lower surface tensions tend to segregate to the polymer−air interface and can be detected by SFG at the molecular level. SFG spectra also show that hydrophilic end groups are in the bulk and that the polymer surface is covered by the polymer backbone. SFG studies of polymer films with different thickness show that SFG spectra come from the surface.

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