Environment-Induced Surface Structural Changes of a Polymer: An *in Situ* IR + Visible Sum-Frequency Spectroscopic Study

D. Zhang, R. S. Ward, Y. R. Shen, and G. A. Somorjai

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720; Department of Physics, University of California at Berkeley, Berkeley, California 94720; Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720; and The Polymer Technology Group, Inc., Berkeley, California 94710

The Journal of Physical Chemistry B®

Reprinted from Volume 101, Number 44, Pages 9060–9064
Environment-Induced Surface Structural Changes of a Polymer: An in Situ IR + Visible Sum-Frequency Spectroscopic Study

D. Zhang, R. S. Ward, Y. R. Shen, and G. A. Somorjai

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720; Department of Physics, University of California at Berkeley, Berkeley, California 94720; Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720; and The Polymer Technology Group, Inc., Berkeley, California 94710

Received: June 4, 1997

IR + visible sum-frequency vibrational spectroscopy has been used to monitor structural changes of a polymer surface in response to alteration of environment. The polymer studied is of the polyurethane type, with poly(dimethylsiloxane) (PDMS) grafted on as end groups. Our data reveal that the polymer surface undergoes a significant restructuring when transferred from air to water. With the polymer exposed to air, the surface spectrum shows that the hydrophobic PDMS segments cover most of the surface. When immersed in water, the PDMS component retreats from the surface whereas the initially “buried”, more hydrophilic part of the polymer chain appears at the surface. The surface structural transformation in response to the environmental change from air to water takes about 25 h at 300 K. The structural change is reversible upon dehydration, but takes only 3 h. The results point to the need to characterize the polymer surface in its working environment in order to correctly describe its surface properties. The consistency between the sum-frequency generation (SFG) data and the contact angle measurement in characterizing the hydrophobicity of the polymer surface demonstrates that SFG is a powerful spectroscopic probe to study and provide insight into how polymer surfaces behave at a molecular level.

Introduction

One of the interesting properties of polymers is their dynamic surface behavior.1 Molecular units of a polymer surface can reorient or restructure in response to local chemical environment in order to minimize the interfacial free energy. As a result, the surface composition and structure of a polymer depend strongly on the environment that it is in contact with, air versus water, for instance. The polymer/water interfaces are most important for many applications. We would like to explore how the structure of a polymer surface changes when placed in contact with water, how fast and to what extent this change occurs, and whether the change is reversible. These questions have become increasingly more important as polymer applications to biology and medicine surge,2 because they often involve polymer interfaces in contact with aqueous environments. To answer these questions, it is essential to characterize in situ the surface composition, structure, and mobility of a polymer in air and in water. Information of this type will advance our understanding of polymer surface properties, such as wettability and bioadhesion, which can then guide us to achieve controllable polymer surface modification for various industrial, biological, and medical purposes. Unfortunately, such information is not easily accessible to most conventional surface probes. Experiments in this area were mostly limited to contact angle measurements,3,4 which provided little insight into the behavior of interfaces at the molecular level. More recently, surface composition changes in response to environmental changes were observed5,6 using X-ray photoelectron spectroscopy (XPS), in conjunction with a cryogenic sample handling technique. The drawback of XPS is known to be the requirement of operating in ultrahigh vacuum, making it difficult to study a polymer–water interface in situ. In the past decade, IR + visible sum-frequency generation (SFG) has been developed into a powerful surface spectroscopic tool and successfully applied to a wide variety of surfaces and interfaces.7–10 As a second-order nonlinear optical process, SFG is intrinsically interface-specific because it is electric-dipole-forbidden in a centrosymmetric bulk but necessarily allowed at an interface where the inversion symmetry is broken.11,12 Molecules at an interface can be selectively probed via their resonances in SFG. Observed resonances in the infrared yield the interfacial vibrational spectrum whose polarization dependence allows us to deduce orientational information of different parts of the molecules at the interface.13 As a versatile probe, SFG can be applied to any interface accessible to light and appears ideal for studies of polymer–water interfaces.

In this article, we report our SFG spectroscopic studies of polymer surface structures in response to environmental changes. The polymers chosen in our study are poly(dimethylsiloxane) (PDMS), BioSpan, a polyurethane (SPU) type of polymer, and BioSpan-S, which is BioSpan grafted with PDMS as end groups (PDMS/SPU/PDMS). The molecular structures of these polymers are shown in Figure 1. As seen from its chemical structure, BioSpan-S contains both hydrophobic (PDMS) and hydrophilic (ether and urethane segments of BioSpan) components. In air, the hydrophobic PDMS tails seemed to dominate at the polymer surface. This is consistent with the results obtained by other techniques.14 In contrast, when the polymer was in contact with a highly polar environment such as water, the hydrophilic part of the polymer chain becomes more pronounced at the surface. These changes indicate that in response to water the polymer surface undergoes a restructuring, transforming from a more hydrophobic to a more hydrophilic one to minimize the interfacial energy with the environment. This finding agrees
Figure 1. Molecular structures of PDMS (poly(dimethylsiloxane)), BioSpan, and BioSpan-S.

...well with the result that the contact angle decreases from 94° in air to 79° in water. In addition, reorientations of the functional groups at the polymer surface were manifested by the polarization dependence of the SFG spectrum. Upon dehydation, the polymer surface converted back to the original hydrophobic structure in air. The results illustrate the dynamic nature of the polymer surface and therefore the need to characterize the polymer surface in its working environment in order to properly understand its surface properties.

Experimental Section

The IR + visible SFG surface spectroscopy has been described in detail elsewhere. Brieﬂy, the experiment was performed by overlapping a visible (532 nm, ~20 ps duration pulse) and a tunable infrared (2500–3600 cm⁻¹, ~15 ps duration pulse) beam at an interface, and the reﬂected SF signal was collected by a photomultiplier tube connected to a gated integrator and photon counting system. The liquid cell for the polymer-water interface study was made by sandwiching a thin layer of D₂O between the polymer surface and a calcium fluoride window. The laser pulses were incident from the calcium fluoride side. The contact angle was measured by the sessile drop technique at 300 K using a Rame-Hart contact angle goniometer. The polymers, BioSpan and BioSpan-S, were supplied from The Polymer Technology Group, Inc., of Berkeley, CA. Polymers films (~100 μm thick) were prepared by casting the polymers from their N,N-dimethylacetamide (~1 wt% polymer) solutions onto flat quartz substrates and then dried in air at 65 °C for ~12 h. The PDMS film was made in a similar manner, except that the polymer solution was prepared using a mixture of solvents (tetrahydrofuran and dioxane with 2:1 ratio).

Results and Discussion

Figure 2 shows SFG spectra of PDMS in the C–H stretching region in air at 300 K for two different polarization combinations. In the spectrum with the ssp- (for s-polarized SF output, s-polarized visible input, and p-polarized IR input) polarization combination, there appears a single pronounced peak at 2919 cm⁻¹ that can be assigned to the symmetric stretch of the methyl group. It correlates well with the same vibrational mode found at 2920 cm⁻¹ in the corresponding IR spectrum. With the sps-polarization combination, the SFG spectrum displays, again, a single peak but at 2965 cm⁻¹, which is characteristic of the antisymmetric stretch of the methyl group. The strong polarization dependence of these spectra clearly indicates that the methyl groups have their symmetric axes more or less along the surface normal.

Figure 3 shows the IR spectra of BioSpan and BioSpan-S in the C–H stretching region. The bulk vibrational spectra are very similar for these two polymers. This is probably due to the fact that the PDMS segment only constitutes 6% of the molecular weight of BioSpan-S. The IR peak at 2787 cm⁻¹ can be attributed to the symmetric stretch of CH₂ connected to an oxygen of the carbonate group (COO⁻), while the one at 2852 cm⁻¹ is characteristic of the symmetric stretch of CH₃ connected only to other methylene groups. Assignment of the band at 2941 cm⁻¹ is less deﬁnite. It may arise from the Fermi resonance of the CH₃ symmetric stretch with the overtone of the methylene deformation. Figure 4 shows the SFG surface spectra of BioSpan in air. The three peaks observed in BioSpan IR spectrum also appear in the SFG surface spectra. They can thus be assigned, accordingly, the peaks at 2785 and 2851 cm⁻¹ as the symmetric stretches of CH₂ connected to an oxygen and to carbons only, respectively, and the band at 2945 cm⁻¹ as the Fermi resonance between the CH₃ symmetric stretch with the overtone of the methylene deformation. The stretching resonances of the CH₃ groups at the terminals of the polymer chain were not observed, presumably because of their low surface density and disordered chain conformation. Therefore, the surface spectral features of BioSpan suggest that this polymer surface is dominated by the...
When PDMS is grafted to BioSpan as end groups to form BioSpan-S, although it did not affect the IR spectrum of the latter, it dramatically changes the SFG surface spectra of the latter, indicative of a different surface composition and structure from BioSpan. This is seen explicitly in Figure 5. Three clear peaks are present in both the ssp- and ssp-spectrum of BioSpan-S. They are markedly different from those appearing in its bulk IR spectrum, revealing that its surface and bulk structures and compositions are different. Comparison with the surface spectra of PDMS (Figure 2) and BioSpan (Figure 4) allows us to assign the peaks at 2919 and 2963 cm\(^{-1}\) to the symmetric (r\(^+\)) and antisymmetric (r\(^-\)) stretches of the CH\(_3\) groups of PDMS, respectively, and the one at 2851 cm\(^{-1}\) together with a shoulder at \(\sim 2785\) cm\(^{-1}\) to the symmetric stretch of the CH\(_2\) groups associated with BioSpan. The spectra indicate that PDMS and BioSpan coexist at the surface. The strong intensities of the PDMS methyl resonances at 2919 cm\(^{-1}\) in the ssp-spectrum and at 2965 cm\(^{-1}\) in the ssp-spectrum suggest that the surface is well-populated by PDMS. The polarization dependence exhibiting a stronger r\(^+\) mode in the ssp-spectrum and a stronger r\(^-\) mode in the ssp-spectrum means that the average orientation of these surface CH\(_2\) groups is close to the surface normal. From the ratio of the symmetric stretch intensities in the ssp- and ssp-spectra,\(^{16}\) we estimated that the CH\(_2\) group has an average tilt angle of \(\theta = 35 \pm 5^\circ\) with respect to the surface normal. Compared with BioSpan, the CH\(_3\) peaks of BioSpan-S at 2851 and 2785 cm\(^{-1}\) are weaker, and the Fermi resonance peak of CH\(_2\) is very much suppressed. We assume that, with PDMS grafted onto BioSpan, the chain conformation of BioSpan at the surface remains unchanged. The spectra of BioSpan-S can then be understood if we assert that the surface is largely covered by PDMS. This is energetically more favorable because PDMS is more hydrophobic than BioSpan. With PDMS directly facing air, the CH\(_3\) modes of PDMS are expected to be pronounced while shielding of BioSpan by PDMS at the surface makes the CH\(_2\) modes of BioSpan appreciably weaker. The overall surface
Figure 6. Time evolution of SFG spectra from the BioSpan-S—water interface for the ssp polarization combination.

The structure of BioSpan-S is believed to be more like that of pure PDMS although the average orientation of CH3 is somewhat different. Yet the weak presence of BioSpan at the surface still makes the BioSpan-S surface more polar (or hydrophilic) than pure PDMS. This was confirmed by water contact angle measurements that yielded values of 100°, 94°, and 75° for PDMS, BioSpan-S, and BioSpan, respectively.

When BioSpan-S is in contact with water, a significant change of the polymer surface structure in response to alteration of environment takes place, which is manifested by marked changes in the surface vibrational spectra. Figure 6 displays the time evolution of the ssp-spectra of BioSpan-S in water at 300 K. The key features of the observed spectral changes are weakening of the methyl resonance of PDMS at 2919 cm\(^{-1}\) and strengthening of the 2851 and 2785 cm\(^{-1}\) bands for CH\(_2\) groups of BioSpan. The corresponding ssp-spectra (not shown here) displayed similar behavior. The spectral changes clearly indicate the occurrence of a structural change at the polymer surface. Presumably in air, hydrophobic PDMS tails tend to cover the surface of BioSpan-S in order to shield the more polar BioSpan component and lower the surface tension or free energy. Upon hydration, however, water molecules come to compete with the hydrophobic PDMS surface groups in their interactions with BioSpan. The stronger interaction between water and BioSpan tends to push the PDMS segment away from the polymer surface and reorient them to minimize contact with water. The result is a decrease of the CH\(_3\) peaks of PDMS and an increase of the CH\(_2\) resonances of BioSpan in our SFG spectrum.

The polarization dependence of the SFG spectrum also reflects a surface restructuring process. Figure 7 presents the ssp- and sps-spectra of BioSpan-S in water. Comparing them with the corresponding ones of BioSpan-S in air (Figure 5) shows a clear difference. As discussed earlier, the average tilt of the CH\(_3\) symmetric axis from the surface normal was found to be 35° at the polymer—air interface. The same angle obtained from analysis of the spectra in Figure 7 is 60°. In response to exposure to water, the PDMS segments must have reoriented and reconfigured at the interface, resulting in their CH\(_3\) groups inclined more toward the surface plane on average.

To see how the polymer surface changes in time, in response to alteration of environment from air to water, Figure 8a shows a plot of square root of intensity ratios of the 2919 cm\(^{-1}\) peak versus the 2851 cm\(^{-1}\) peak and the 2785 cm\(^{-1}\) peak versus the 2919 cm\(^{-1}\) peak as functions of hydration time. The former can be used to represent the relative PDMS content at the interface while the latter is related to the relative surface concentration of the oxygen-containing segment of BioSpan. As shown in Figure 8, the former increases while the latter increases with hydration time. Both of them remain relatively constant up to a hydration time of 15 h, change more rapidly around 18 h, and approach final equilibrium after 25 h. The kinetics of the hydration process of BioSpan-S was further confirmed by the water contact angle measurement. Figure 8b shows the compilation of the square root of the intensity ratio of 2919/2851 cm\(^{-1}\) and the contact angle as functions of hydration time, which changed in a similar manner. In air, the water contact angle of BioSpan-S is 94°. Upon hydration, the contact angle decreased slowly at the beginning, and then its decrease accelerated ~15 h of hydration and led to the final angle of 79° for hydrated state. This rather slow changeover is presumably due to the existence of high-energy barriers for hydrating reactions and the necessity of replacing PDMS segments on BioSpan by water at many interacting sites. When water is initially introduced to a surface well covered by PDMS segments, the penetration of water molecules both to reach the interacting sites and to dislodge a PDMS segment by severing its connections with BioSpan at many anchor points is difficult. Thus, the change is slow at the beginning. As the hydration
process progresses, gradual detachment of PDMS segments from BioSpan exposes more of their anchor sites for water molecules to attack. This then speeds up the changeover until the final equilibrium is approached.

Upon dehydoration, recovery of the more hydrophilic surface was observed. It was manifested by regrowth of the 2919 cm⁻¹ band and decrease of the 2785 and 2851 cm⁻¹ resonances, indicating the surface was again mostly covered by PDMS. The reverse process, however, was completed in about 3 h, which is much shorter than the hydration time of ~25 h. The shorter changeover time for dehydoration can be understood knowing that desorption of water molecules is a relatively faster process and would leave the interacting site of BioSpan empty for PDMS segments to readily occupy.

Conclusions

The surface chemical composition and structure different from its bulk and changing with its environment is an ubiquitous phenomenon for polymers. Surface-specific SFG vibrational spectroscopy allows us to study surface structures of polymers and their changes in response to changes of the environment. BioSpan-S containing both hydrophobic and hydrophilic segments was used for the demonstration. It was found that the hydrophobic part (PDMS) of BioSpan-S dominates at the surface in air, while the hydrophilic part (urethane and ether) becomes more appreciable at the surface in water. Transferring the polymer from air to water causes the polymer surface to restructure gradually in time, from more hydrophobic to more hydrophilic, reaching final equilibrium in about 25 h. This increase in surface hydrophilicity observed by SFG agrees well with the contact angle measurement which changed from 94° in air to 79° in water. It is reversible upon dehydoration in a relatively shorter time of ~3 h. Like contact angle measurement, SFG samples the outermost layer of the polymer surface, but as a spectroscopic tool, it has the capability of providing insight into polymer surfaces at a molecular level. Our findings reveal the dynamic nature of the polymer surface which depends strongly on the environment. This is consistent with results obtained by other techniques and points to the need to characterize a polymer surface in its working environment in order to properly describe its surface properties. This work shows that SFG spectroscopy being highly surface-specific is uniquely suited for such studies.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences and Materials Sciences Division of the U.S. Department of Energy.

References and Notes