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Plasma Treatment of Polystyrene Thin Films Affects More Than the Surface

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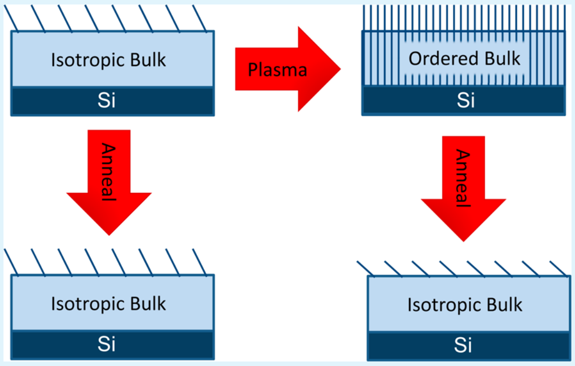
ABSTRACT: Plasma treatment of polymer materials introduces chemical functionalities and modifies the material to make the native hydrophobic surface more hydrophilic. It is generally assumed that this process only affects the surface of the material. We used vibrationally resonant sum-frequency generation spectroscopy to observe changes in the orientation of phenyl groups in polystyrene (PS) thin films on various substrates before and after plasma treatment. VR-SFG selectively probes regions of broken symmetry, such as surfaces, but can also detect the emergence of anisotropy. On dielectric substrates, such as fused silica, the spectroscopic peak corresponding to the symmetric stretching (ν_2) mode of the phenyl rings was undetectable after plasma treatment, showing that surface phenyl rings were altered. This peak also diminished on conducting substrates, but the intensity of another peak corresponding to the same mode in a bulklike environment increased significantly, suggesting that plasma treatment induces partial ordering of the bulk polymer. This ordering is seen on conducting substrates even when the polymer is not directly exposed to the plasma. Annealing reverses these effects on the polystyrene bulk; however, the surface phenyl rings do not return to the orientation observed for untreated films. These results call into question the assumption that the effects of plasma treatment are limited to the free surface and opens up other possibilities for material modification with low-temperature plasmas.



KEYWORDS: *surface modification, molecular orientation, plasma treatment, bulk polymer modification, sum frequency generation, field-responsive polymers*

INTRODUCTION

Exposure to an air- or oxygen-plasma induces a variety of modifications in polymers at a low cost and with minimal environmental impact. These modifications include removal of surface contaminants, polymerization of monomers, cross-linking of polymer chains, etching away thin layers of polymer, functionalizing polymer surfaces, and improved hydrophilicity of the surface.[1] Because of the versatility, economy, and environmental cleanliness of the process, plasma treatment is often preferred over other modification methods and has become a common processing step in a variety of applications.

One assumption that is commonly invoked about plasma treatment of polymers is the idea that only the free surface is modified. In fact, the purported surface-specificity of plasma treatment is often identified as an advantage of the technique. This surface-specificity is of particular importance in cases where the native bulk properties of the polymer play an important role in its ultimate application. However, even if the only aim of the treatment is to alter the surface chemistry, the bulk properties of the polymer can still influence the surface properties. For example, plasma treatment of polydimethylsiloxane induces a difference in the surface and bulk modulus that results in cracking, which causes the cracked surface to be more hydrophobic than surfaces without cracks.[2]

We used vibrationally resonant sum-frequency generation (VR-SFG) spectroscopy[3] to study changes in the orientation of the phenyl rings of polystyrene (PS) in response to plasma treatment. In VR-SFG, two beams from a pulsed laser overlap spatially and temporally at the sample, generating a new beam with a frequency equal to the sum of the two input frequencies. VR-SFG spectra give both compositional and orientational information about the molecules in the sample. Additionally, unlike linear vibrational spectroscopies such as FTIR and Raman that probe all molecules in the sample, VR-SFG signal originates only from locations in the sample that lack inversion symmetry. When the bulk of the material is largely isotropic, this technique can be used to selectively probe molecules at surfaces and interfaces. However, because the molecules probed with VR-SFG are selected by symmetry and not proximity to the free surface, it also has the advantage of detecting signal from other regions of broken symmetry. In other words, when areas of broken symmetry are present in subsurface regions, VR-SFG probes deeper into the material than surface-specific techniques such as XPS or TOF-SIMS.

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Previous VR-SFG studies of plasma-treated PS films used fused silica substrates and reported a loss of signal intensity that they attributed to destruction of phenyl rings on the polymer surface.[4−6] In our more comprehensive study, which included the use of multiple substrates and removal of nonresonant interference, we have seen that this understanding is incomplete. Although some destruction of the phenyl rings certainly occurs on all substrates, we show here that the more dominant change on conducting substrates is a reorientation of the bulk polymer material.

In a study by Poncin-Epaillard et al.,[7] the response of isotactic polypropylene films exposed to microwave plasmas affected the orientation of the polymer bulk, although these polymer films already had some crystalline character prior to plasma exposure. Our study with atactic PS demonstrates that bulk polymer orientation can be affected by plasma treatment even when the polymer initially lacks long-range order. Although the previous study proposed that the changes they observed in the bulk were caused by exposure of the polymer to high levels of vacuum ultraviolet (VUV) radiation present in the treatment chamber, we show that such exposure does not significantly influence the bulk structure of the polymer in our experiments. We additionally show that the effects of plasma treatment depend on the substrate used to support the films, that bulk modification occurs with short treatment times (~1 s), and that the modifications to polymer bulk require 80% less power in the plasma than reported in the previous study. In light of the information presented here, common assumptions about the surface-specificity of the plasma treatment process need to be revised.

EXPERIMENTAL METHODS

Silicon, sapphire, and fused silica substrates were cleaned by immersion in piranha solution (18 M sulfuric acid and 30% hydrogen peroxide, 3:1 by volume) for one hour. (***Note**: Piranha solution is very corrosive, and extreme care must be used when handling.*) The substrates were then rinsed with Millipore-purified water (18 MΩ), then immersed in Millipore-purified water for at least one hour. Immediately prior to coating with polymer, substrates were dried under a stream of nitrogen gas. Stainless steel mirrors (24 gauge, Mirrored Stainless Solutions) were prepared simply by removing the protective plastic backing just prior to spin-coating to avoid the risk of rusting in piranha solution.

Substrates were spin-coated with PS (M_w = 230 000 from Aldrich) solution in toluene (UltimAR from Mallinckrodt Chemicals) with a spin-coater (Model WS650SZ-6NPP/A1/AR1 from Laurell Technologies) to give ~100 nm thick films. For certain samples, poly(methyl methacrylate) (M_w = 120 000 from Aldrich) was spin coated on top of PS from a nitromethane (spectrograde from Fisher Scientific) solution to give ~150 nm thick films. Film thicknesses were determined using spectroscopic ellipsometry (M-2000 from J. A. Woollam Co., Inc.). Solvent-cast PS samples were prepared by dispensing a solution of PS in toluene to cover the surface of the substrate, then allowing the solvent to evaporate for at least 24 h. Two weight percent PS was used to collect the data reported here, but similar results were obtained independent of solution concentration.

Plasma treatment was performed with an 18 W RF plasma from a Harrick Plasma basic plasma cleaner (PDC-32G), consisting of a cylindrical glass tube with the electrode coiled around it. Samples were placed with the coated side facing up near the center of the cylindrical chamber. Plasma was generated in the evacuated chamber (~200 mtorr), bleeding in dry room air as necessary to sustain the plasma. Unless otherwise stated, the plasma was sustained for 1 s to treat each sample. The plasma treatment time of 1 s was chosen to minimize changes in film thickness due to etching and to directly compare our results to the previous VR-SFG study by Zhang et al.[5] The effects of plasma treatment were generally greater with longer treatment times for up to 60 s of exposure, but significant changes in film thickness were also observed. For the solvent-cast sample reported here, a plasma treatment of 10 s was needed in order to obtain a measurable response to the treatment. Measurement of film thickness following 1 s of plasma treatment verifies that the etching of polymer causes a negligible (less than 1 nm) decrease in thickness.

VR-SFG spectroscopy was performed using the setup described in detail elsewhere.[8] The system uses an amplified femtosecond laser (Quantronix, Integra C) that is split into two beams. One beam is spectrally narrowed with two Fabry−Perot etalons for use as the upconverting visible beam centered at 798 nm. The other is used to pump an optical parametric amplifier (Light Conversion via Quantronix, TOPAS-C) to generate broadband infrared light centered at ~3300 nm (~3030 cm^{-1}). All spectra were collected using the *ssp* (*s*-polarized SFG output, *s*-polarized visible input, *p*-polarized IR input) polarization combination. Nonresonant VR-SFG signal was suppressed by delaying the visible pulse relative to the IR pulse by approximately 2 ps.[9] All spectra presented together in a single figure were collected on the same day with the same degree of nonresonant suppression.

Freshly prepared samples were scanned with VR-SFG within 48 h of coating. Freshly plasma-treated samples were scanned immediately after treatment. Annealed samples were stored in a vacuum oven heated to 120 °C for 24 h, then cooled slowly to room temperature over a period of 24 h before being scanned.

RESULTS & DISCUSSION

Effects of Plasma on Bulk Polystyrene. As shown in Figure 1, the VR-SFG spectrum of a 100 nm film of untreated PS contains two readily distinguishable features: a prominent peak at 3069 cm^{-1} assigned to the phenyl ν_2 mode, and a less intense peak at 3027 cm^{-1} assigned to the ν_{20b} mode.[10] Our discussion will also focus on a much smaller peak centered around 3059 cm^{-1}, assigned to the ν_2 mode in a more densely packed environment.[11] Although the ν_2 peak at 3059 cm^{-1} is usually weak in VR-SFG spectra of untreated PS, the IR spectrum of PS shows a strong peak attributed to the ν_2 stretching mode around 3060 cm^{-1} with no peak present at 3069 cm^{-1}. The linear spectroscopic technique is sensitive to the bulk, whereas VR-SFG is more sensitive to the surface, assuming the bulk is completely isotropic. Resonant spectra of untreated PS films are identical on all substrates, as shown previously[8] and again confirmed in this study.

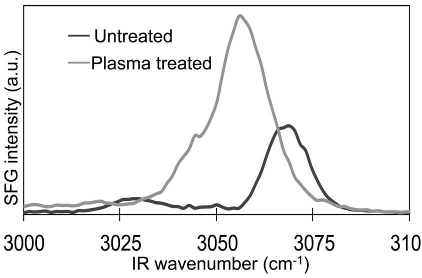

Figure 1. VR-SFG spectra (ssp polarization combination) of untreated and plasma-treated PS. Untreated PS exhibits a strong peak at 3069 cm^{-1} and a weaker peak at 3059 cm^{-1}. After plasma treatment, the 3069 cm^{-1} peak corresponding to surface phenyl rings is no longer detected and the 3059 cm^{-1} peak corresponding to bulklike phenyl rings increases in intensity.

Following plasma treatment of PS on silicon, the peak at 3069 cm^{-1} decreases in intensity, and the peak at 3059 cm^{-1} increases in intensity, as shown in Figure 1. The change in the intensities of the ν_2 peaks corresponds to a change in the type of phenyl rings that contribute to the measured spectrum. Prior to plasma treatment, the signal from the surface phenyl rings dominates, whereas after plasma treatment, the signal from more densely packed, bulk-like phenyl rings dominates. Because randomly oriented phenyl rings cannot produce VR-SFG signal, the observation of phenyl rings in a noninterfacial environment suggests that the bulk of the polymer is no longer completely isotropic.

Not only is a change in the relative intensities of the ν_2 peaks observed following plasma treatment, but this change is also typically accompanied by a significant increase in absolute VR-SFG intensity, also shown in Figure 1. Even samples that normally do not produce any resonant VR-SFG signal, such as the solvent-cast PS shown in Figure 2, exhibit a discernible VR-SFG peak at 3059 cm^{-1} after plasma treatment for 10 s. (For the solvent-case samples, a longer treatment time was necessary to induce a detectable response.) The increase in absolute VR-SFG intensity supports the idea that previously unordered bulk PS becomes ordered to some degree with plasma treatment; the greater abundance of bulk phenyl rings compared to surface groups gives rise to a larger signal. Although this increase in signal strength occurs with many samples, the magnitude of the effect varies from sample to sample. This variability likely originates from factors beyond our control, such as an intensity gradient within the plasma treatment chamber, the exact placement of the sample in the cylindrical sample chamber, slight variations in polymer thickness, and/or slight variations in the time of plasma treatment.

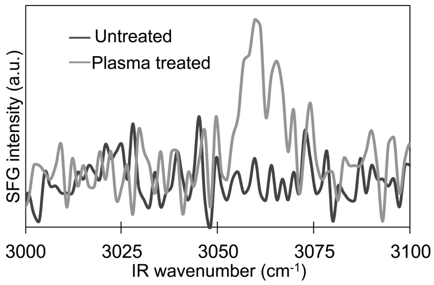

Figure 2. VR-SFG spectra of a PS thin film solvent cast onto polished silicon before and after plasma treatment. Untreated solvent-cast samples give no resonant VR-SFG signal; however, after 10 s of plasma treatment, a weak resonant signal appears around 3059 cm^{-1}.

Our investigation of layered polymers on silicon substrates further confirms that phenyl rings of PS are aligned by plasma treatment. An additional 150 nm of poly(methyl methacrylate) (PMMA) was coated on top of a 100 nm film of PS prior to plasma treatment. The spectra collected before and after plasma treatment are shown in Figure 3. Prior to plasma treatment, the response of PS is too weak to be seen; however, after plasma treatment the peak at 3059 cm^{-1} becomes apparent, and the peak at about 2950 cm^{-1} assigned to the symmetric stretch of the ester methyl group of PMMA,[12] also increases in intensity. Because the thickness change from the plasma exposure is negligible compared to the total thickness of the PMMA film, the observed structural modification of PS in these samples was achieved without direct exposure of PS to the plasma.

Determining Relative Orientations from VR-SFG Data. Use of polarized light in VR-SFG experiments allows orientational information to be extracted from the spectra. Assuming no preferred orientation about the axis of the bond that attaches the phenyl group to the polymer chain, and assuming complete azimuthal symmetry at the surface, the relative amplitudes of the peaks in *ssp* polarized spectra can be related to the average tilt angle of the phenyl rings from the surface normal using the following equation[13−15]

$$R = \left|\frac{A_{B1}}{A_{A1}}\right| = \left|\left(\frac{\beta_{caa,B1}}{\beta_{aac,A1}}\right)\left(\frac{2(\langle\cos 3\theta\rangle - \langle\cos\theta\rangle)}{(7+2r)\langle\cos\theta\rangle + (1-2r)\langle\cos 3\theta\rangle}\right)\right| \quad (1)$$

In the above equation, A_{A1} and A_{B1} represent the amplitudes of the peaks corresponding to modes of A_1 and B_1 symmetry, respectively. For phenyl groups, the peak at 3027 cm^{-1} corresponds to the ν_{20b} mode, which has B_1 symmetry, and the 3069 and 3059 cm^{-1} peaks both correspond to the ν_2 mode, which has A_1 symmetry. $\beta_{aac,A1}$ and $\beta_{caa,B1}$ represent the respective hyperpolarizabilities of the same two modes, and r is the ratio of β_{ccc}/β_{aac} for the ν_2 mode. The r value for the ν_2 mode has been theoretically calculated as 1.13 by Briggman et al.[16] θ is the tilt angle relative to the surface normal, illustrated in the inset to Figure 4. Orientation information can be extracted by comparing the ratio of the intensities of the 3027 cm^{-1} and 3069 cm^{-1} (or 3059 cm^{-1}) peaks, which are the most dominant features in the spectrum.

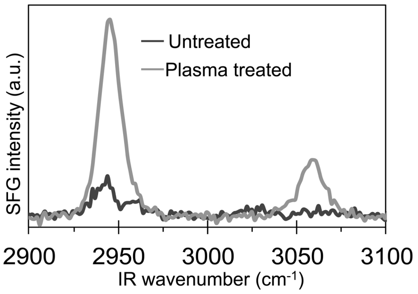

Figure 3. VR-SFG spectra of a sample of PS on silicon with an additional thin film of PMMA spin coated on top of it before and after plasma exposure. The 3059 cm^{-1} peak of PS appears after plasma treatment without exposure to the free surface to plasma species. The 2950 cm^{-1} peak of PMMA not only persists, but also increases in intensity following treatment.

The absolute magnitude of the curve described by eq 1, and shown graphically in Figure 4, depends on the hyperpolarizability ratios of the vibrational modes. Unfortunately,

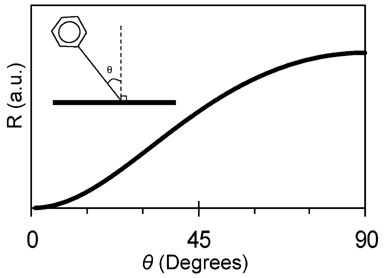

Figure 4. Chart of eq 1 used in the determination of tilt angles (θ, in inset figure) from VR-SFG spectra. The plotted curve represents only the angular portion of the equation and assumes no knowledge of hyperpolarizability values. The hyperpolarizability ratio offsets this curve by a constant value, but the general shape is always the same.

exact values of the hyperpolarizabilities are not available, but qualitative changes can still be determined by observing trends in relative peak amplitudes.[17] In this fashion, the orientation of PS phenyl rings on the different substrates after plasma treatment can be compared relative to the orientation of phenyl rings in untreated PS.

For the spectra of plasma-treated PS on silicon, the intensity of the ν_2 peak increases relative to the intensity of the 3027 cm^{-1} peak. This provides a smaller value for R in eq 1, corresponding to a smaller tilt angle from the surface normal than in untreated PS. Because these spectra are dominated by signal from the bulk, this information reveals that the bulk phenyl rings of PS become more upright with plasma treatment. Any discernible information about the surface, however, is lost.

Although signal intensity often increased after plasma treatment for PS on silicon, the coatings on fused silica substrates suffered significant signal loss following plasma treatment. The disappearance of the ν_2 peak at 3069 cm^{-1} is the most apparent spectral difference between untreated and freshly plasma-treated PS on fused silica, as shown in Figure 5. A weakening or disappearance of this peak has also been observed in previous VR-SFG investigations of plasma-treated PS thin films on fused silica substrates, but with a different interpretation of results than we propose.[4−6] Prior investigators attributed this change to destruction of the phenyl ring by the plasma; however, as seen in our studies, the aromatic peak at 3027 cm^{-1} persists at nearly the same intensity after plasma treatment. The persistence of this peak demonstrates that phenyl rings are still present on the surface with nearly equal concentration but have adopted a different orientation. Interference from the nonresonant SFG signal can often mask this feature;[8] this was likely the case in the earlier studies.

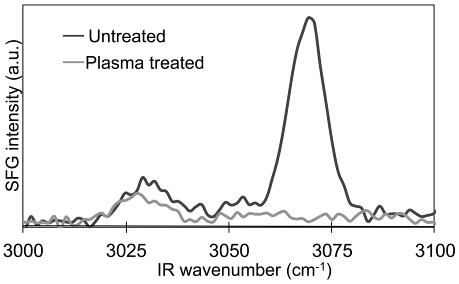

Figure 5. VR-SFG spectra of PS on fused silica before and after plasma treatment. Prior to plasma treatment, the resonant signal detected from PS on fused silica substrate is identical to that obtained from PS on polished silicon. Following plasma treatment of PS on a fused silica substrate, the signal from the ν_2 peak is greatly diminished.

For plasma-treated PS on fused silica, the value of R in eq 1 is very large due to the disappearance of the ν_2 peaks. This change corresponds to a relatively high tilt angle, or phenyl rings that are more parallel to the plane of the surface than before plasma treatment. We do not see the 3059 cm^{-1} peak corresponding to bulk PS in these samples, but this observation alone is not enough to verify that the bulk is not ordered. The bulk may adopt a preferred orientation on fused silica substrates, but if the phenyl rings lie parallel to the surface plane, we would still expect the absence of the 3059 cm^{-1} peak. Although it cannot be distinguished from these spectra alone whether the bulk of PS on fused silica is ordered with a large tilt angle or remains isotropic, the phenyl groups that are observed are nearly lying down. However, further experimental constraints applied to study the connection between substrate properties and plasma effects do suggest that plasma modifications of PS films on fused silica substrates are in fact limited to the free surface, as shown below.

Substrate Dependent Response to Plasma Treatment. Three properties of the substrate potentially cause the different response of PS to plasma treatment: crystallinity, transparency to vacuum ultraviolet (VUV) radiation, and/or conductivity. The crystallinity of the substrate was shown to have no effect; PS films on sapphire substrates behaved similarly to those on fused silica substrates whether the sapphire was a *z*-oriented single crystal or amorphous. As mentioned previously, Poncin-Epaillard et al. proposed that VUV exposure was responsible for the bulk modifications they observed.[7] However, as more recent studies have shown, exposure times on the order of minutes to are required to affect the structure of PS, whereas plasma exposure requires only seconds to cause a change of similar magnitude.[4] We further confirmed that VUV exposure is not responsible for the results obtained on the different substrates by plasma treating PS films on fused silica with an additional fused silica substrate placed on top of the free surface. This prevents direct exposure of the PS to reactive species in the plasma but allows the VUV radiation generated in the plasma to access both the free surface and buried interface. The VR-SFG spectra of the films plasma-treated in this way were identical to those of untreated PS films.

These results not only confirm that penetration of VUV radiation through the transparent substrates is not a significant factor in the orientation of plasma-treated PS, but also suggest that the effects of plasma treatment for PS on fused silica and similar substrates is actually limited to the free surface. One possibility for the large tilt angle of phenyl rings after plasma exposure on insulating substrates is the selective destruction of phenyl rings of a particular orientation. The tilt angle obtained through the analysis of VR-SFG data is the weighted average in the distribution of tilt angles of probed molecules. Phenyl rings with smaller tilt angles that are standing up further from the plane of the surface would be more susceptible to reaction with plasma species, selectively leaving behind phenyl rings with a large tilt angle. Although we offer this simple explanation as a possibility, we acknowledge that the true explanation may be more complex.

After eliminating crystallinity and substrate transparency to VUV radiation, the only link we have been able to establish between substrate properties and the response to plasma treatment is the conductivity of the substrate. As shown in Figure 6, the effects observed for PS on silicon substrates also

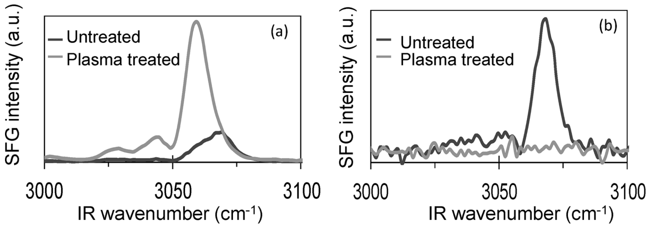

Figure 6. VR-SFG spectra of PS on (a) stainless steel and (b) sapphire. PS on stainless steel substrates showed an increased VR-SFG response and change in the dominant ν_2 peak following plasma treatment, similar to films on silicon substrates. PS films on sapphire substrates behaved similarly to those on fused silica substrates.

occur on other conductive substrates, such as steel (it should be noted that these spectra contain some nonresonant interference). When other insulating substrates, such as sapphire, are used, the effects are similar to those observed on fused silica. We note that 3027 cm^{-1} peak is not clearly discernible in the spectra of PS on sapphire. Its absence could be attributed to insufficient suppression of the nonresonant signal, which can sometimes mask this peak.

Results from previous studies investigating the effects of electric fields on diblock copolymers support the reasoning that the behavior of the different materials is due to conductivity. Thurn-Albrecht et al. showed that when an electric field of sufficient strength is applied to a diblock copolymer of PMMA and PS at elevated temperature, the cylindrical domains reorient parallel to the applied electric field.[18] For that study, the copolymer was rolled between aluminized Kapton sheets, which acted as electrodes; on one side the aluminum directly contacted the copolymer, and on the other side the Kapton contacted the copolymer. Similarly, in the present study, one side of the PS directly contacted a conducting substrate, and the other side was either directly exposed to plasma or separated from the plasma by a thin film of PMMA. Although the results observed in the previous study required elevated temperatures to overcome intermolecular interactions, the environment inside the plasma chamber likely provides the energy necessary to reorient polymer chains at much lower temperatures.

Effects of Annealing on Plasma-Treated Polymer. Previous studies have shown that after a plasma-treated surface is annealed, it recovers some of the properties of the untreated polymer.[1,2,6,19−25] During the annealing process, the polymer is heated above the glass transition temperature, and polymer chains are able to move past each other more freely and into a thermodynamically preferred orientation, if one exists. If no orientation is favored, they assume a random orientation. The extent and nature of the corresponding structural recovery was investigated by comparison of the VR-SFG spectra of plasma-treated PS after annealing to those of untreated samples.

Annealing of untreated PS changes the overall intensity of the VR-SFG signal, but does not change the relative peak intensities in the resonant spectrum.[8] This consistency in the VR-SFG signal indicates that the average orientation of the phenyl groups remains unchanged. A comparison of annealed and unannealed films before plasma treatment confirmed these results. Because annealing has no effect on the orientation of phenyl rings in untreated PS films, any differences observed between plasma-treated films and untreated films after annealing must be due to residual effects of the plasma treatment, not the annealing process itself.

Although annealing does not affect the orientation of phenyl groups of untreated PS, the annealing process has a significant effect on plasma-treated PS. Figure 7 compares spectra of plasma-treated and untreated PS on silicon substrates after annealing. The 3059 cm^{-1} peak that dominates immediately after plasma treatment diminishes with annealing, and the 3069 cm^{-1} peak becomes prominent again, similar to an untreated film; however, the relative intensities of the 3069 and 3027 cm^{-1} peaks do not return to the same ratio as untreated PS. The change of the dominant ν_2 peak from 3059 cm^{-1} back to 3069 cm^{-1} suggests that the phenyl rings in the bulk have again adopted a random orientation and that only surface phenyl groups are detected.[11] Because the substrate is more electron-dense than the polymer, and can therefore minimize interfacial energy independent of PS orientation, the polymer can recover the same orientation in the bulk and at the buried interface as untreated samples.[26] Once the bulk returns to the original isotropic orientation, VR-SFG is no longer sensitive to bulk contributions, and the detected signal must originate from the free surface. The lack of recovery in relative intensities, however, indicates that although the density of detected phenyl rings returns to that of untreated polymer, the orientation of those phenyl rings is not fully restored upon annealing.

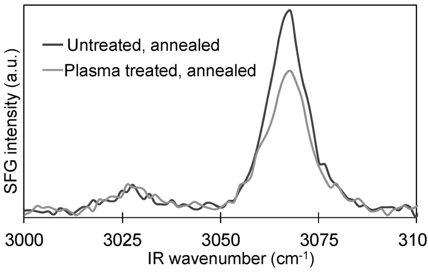

Figure 7. VR-SFG spectra of treated and untreated PS on silicon following annealing for 24 h at 120 °C. The 3069 cm^{-1} peak is restored after annealing, but the ratio between the 3069 and 3027 cm^{-1} peaks for plasma-treated samples differs from that of the untreated samples.

Plasma-treated films on fused silica (and all other substrates studied) recovered in a manner similar to those on polished silicon. As shown in Figure 8, after annealing the 3069 cm^{-1} peak reappeared with signal comparable to that collected from untreated annealed samples on fused silica. Like PS on silicon, the final ratio of amplitudes of the 3027 cm^{-1} and the 3069 cm^{-1} peaks was greater than that of an untreated sample following annealing. In Figures 7 and 8, the ratio of the two peak amplitudes is not identical, but this variability also occurs among PS films on the same substrate. The recovery of intensity by the ν_2 peak after annealing further supports the idea that many surface phenyl groups remain after plasma treatment; if a significant fraction of surface phenyl groups had been chemically altered or destroyed, surface recovery would not be possible.

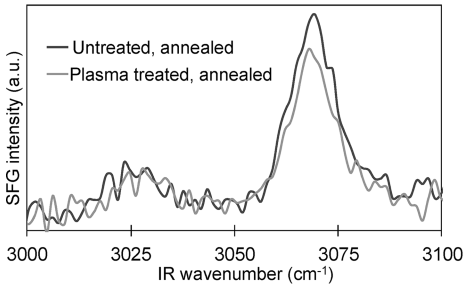

Figure 8. VR-SFG spectra of treated and untreated PS on fused silica following annealing for 24 h at 120 °C.

Although plasma treatment primarily results in the reorientation of phenyl rings, additional chemical functionalities do influence surface reordering. A study by Zhang et al.[4] reported a peak in the C═O region of the VR-SFG spectrum after plasma treatment that is not initially present, and X-ray photoelectron spectroscopy (XPS) also confirmed the addition of oxygenated moieties to the surface. Although we emphasize the modification of PS bulk with plasma treatment, we agree with this prior claim of some chemical modification to the surface. In fact, the failure of the phenyl rings to completely recover the orientation of the untreated polymer following annealing supports this idea. If the only modification to the surface with plasma treatment were the removal or reorientation of phenyl rings on the free surface, we would expect to see the recovery of that original surface with annealing. We see, however, a greater tilt angle of surface phenyl groups on annealed plasma-treated films than on annealed untreated films. Because the structure of the polymer has been chemically altered at the surface, the preferred orientation at equilibrium also changes, which causes the phenyl rings to tilt closer to the surface than they do in untreated films.

There is still more to do to develop a complete sense of the long-term behavior of plasma-treated PS films on conducting substrates. We previously showed that freshly spin-coated PS films resemble annealed films after about 1 week at ambient conditions.[8] When plasma-treated samples were stored at ambient conditions, we still observed the increased intensity of the 3059 cm^{-1} peak for at least 6 weeks. This result indicates that significant alignment of the bulk phenyl rings persists for some time and does not relax without heating. The recovery of the surface seems to depend on whether the samples were stored in an inert environment; the more hydrophilic surface is probably quickly contaminated, which could affect the ability of the remaining phenyl rings at the surface to reorient. These aspects of material aging are still under investigation.

CONCLUSIONS

Plasma treatment is generally thought to only affect the surface of a material, but our work has shown that plasma treatment can induce anisotropy in polystyrene thin films. The ordering of the bulk during plasma treatment can be selectively controlled by choice of substrate. On conducting substrates, previously isotropic phenyl rings in the bulk of the polymer organize and adopt an orientation more parallel to the surface normal. Plasma treatment of PS on insulating substrates, however, does not result in significant change to the bulk structure but results in surface phenyl rings that are mostly lying down. In addition to altering the orientation of phenyl rings on the surface and, for some cases, in the bulk, the plasma treatment also results in a chemically altered surface. This chemical change has been reported previously and is evident in the addition of a small CO signal to the VR-SFG spectra[4] and the inability of plasma-treated PS to recover an untreated orientation after annealing. Although the density of phenyl rings on the annealed surface approaches that of the untreated surface, the tilt angle of the rings is typically greater than what is observed on the untreated PS surface. Work to investigate the effects of plasma treatment on other polymers is ongoing.

Our results have shown that the effect of plasma treatment of polymers is not always limited to the free surface; therefore, plasma treatment is not necessarily a surface-specific treatment. The knowledge that it is possible to modify more than just a free surface with exposure to plasma provides new possibilities regarding the practical aspects of plasma treatment of polymers. The effect of plasma treatment on the bulk of the material must now be considered in applications where it is desirable to selectively modify the surface. Conversely, if an application requires an ordering of the bulk only, plasma treatment with surface protection may be a possible route to accomplish this goal.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Liston, E. M.; Martinu, L.; Wertheimer, M. R. In *Plasma Surface Modification of Polymers: Relevance to Adhesion*; Strobel, M., Lyons, C., Mittal, K. L., Eds.; VSP BV: Netherlands, 1994; 3−39.

(2) Fritz, J. L.; Owen, M. J. *J. Adhes.* **1995**, *54*, 33−45.

(3) Zhu, X. D.; Suhr, H.; Shen, Y. R. *Phys. Rev. B* **1987**, *35*, 3047−3050.

(4) Zhang, D.; Dougal, S. M.; Yeganeh, M. S. *Langmuir* **2000**, *16*, 4528−4532.

(5) Zhang, C.; Wang, J.; Khmaladze, A.; Liu, Y.; Ding, B.; Jasensky, J.; Chen, Z. *Opt. Lett.* **2011**, *36*, 2272−2274.

(6) Li, J.; Oh, K.; Yu, H. *Chin. J. Polym. Sci.* **2005**, *23*, 187−196.

(7) Poncin-Epaillard, F.; Brosse, J. C.; Falher, T. *Macromolecules* **1997**, *30*, 4415−4420.

(8) Curtis, A. D.; Reynolds, S. B.; Calchera, A. R.; Patterson, J. E. *J. Phys. Chem. Lett.* **2010**, *1*, 2435−2439.

(9) Lagutchev, A.; Hambir, S. A.; Dlott, D. D. *J. Phys. Chem. Lett.* **2007**, *111*, 1345−13647.

(10) Varsányi, G.; Szöke, S. *Vibrational Spectra of Benzene Derivatives*; Academic Press: New York, 1969.

(11) Curtis , A. D. ; Calchera , A. C. ; Asplund, M. C.; Patterson , J. E. *J. Phys. Chem. C.* Submitted for publication.

(12) Miyamae, T.; Nozoye, H. *Surf. Sci.* **2003**, *532*, 1045−1050.

(13) Gautam, K. S.; Schwab, A. D.; Dhino, W. A.; Zhang, D.; Dougal, S. M.; Yeganeh, M. S. *Phys. Rev. Lett.* **2000**, *85*, 3854−3857.

(14) Hirose, C.; Akamatsu, N.; Domen, K. *Appl. Spectrosc.* **1992**, *46*, 1051−1072.

(15) Duffy, D. C.; Davies, P. B.; Bain, C. D. *J. Phys. Chem.* **1995**, *99*, 15241−15246.

(16) Briggman, K. A.; Stephenson, J. C.; Wallace, W. E.; Richter, L. J. *J. Phys. Chem. B* **2001**, *105*, 2785−2791.

(17) Curtis, A. D.; Burt, S. R.; Calchera, A. R.; Patterson, J. E. *J. Phys. Chem. C* **2011**, *115*, 11550−11559.

(18) Thurn-Albrecht, T.; DeRouchey, J.; Russell, T. P.; Jaeger, H. M. *Macromolecules* **2000**, *33*, 3250−3253.

(19) Garbassi, F.; Morra, M.; Occhiello, E. *Polymer Surfaces: From Physics to Technology*; Wiley: New York, 1998.

(20) Fridman, A. *Plasma Chemistry*; Cambridge University Press: New York, 2008.

(21) Murakami, T.; Kuroda, S.; Osawa, Z. *J. Colloid Interface Sci.* **1998**, *202*, 37−44.

(22) Morra, M.; Occhiello, E.; Garbassi, F. *J. Colloid Interface Sci.* **1989**, *132*, 504−508.

(23) Occhiello, E.; Morra, M.; Morini, G.; Garbassi, F.; Humphrey, P. *J. Appl. Polym. Sci.* **1991**, *42*, 551−559.

(24) Occhiello, E.; Morra, M.; Garbassi, F.; Johnson, D.; Humphrey, P. *Appl. Surf. Sci.* **1991**, *47*, 235−242.

(25) Pennings, J. F. M.; Bosman, B. *Colloid Polym. Sci.* **1979**, *257*, 720−724.

(26) Dowben, P. A.; Xu, B.; Choi, J.; Monkawa, E. In *Characterization and Spectroscopy of Thin Films*; Nalwa, H. S., Ed.; Academic Press: San Diego, 2002; Vol. *2*, p 98.