# Surface Studies of Polymer Blends by Sum Frequency Vibrational Spectroscopy, Atomic Force Microscopy, and Contact Angle Goniometry

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The surface composition, surface structure, and wetting properties of a polymer blend were studied by a combination of surface-sensitive techniques: IR + visible sum-frequency generation vibrational spectroscopy (SFG), atomic force microscopy (AFM), and contact angle goniometry. The polymer blend studied is composed of Biospan-S (BS) and a phenoxy base polymer (BP). BS is a polyurethane, capped with poly(dimethylsiloxane) (PDMS) end groups, and has a water contact angle of 94°. BP is more hydrophilic with a water contact angle of 74°. The SFG study shows that the more hydrophobic BS component likes to segregate to the blend surface in air and approaches a full surface coverage when the BS bulk concentration is only 1.7 wt %. The surface density of BS decreases with the decrease of its bulk concentration from 1.7 wt % and becomes undetectable at the surface, at a bulk concentration of 0.17 wt %. The surface free energy of the blend varies accordingly, as seen from the contact angle measurements. The AFM study also shows that the blend surface is predominantly occupied by BP for BS bulk concentrations lower than 0.17 wt % and by BS for BS bulk concentrations higher than 1.7 wt %. It reveals a domain pattern in the intermediate region when BS and BP coexist on the surface. The combined information obtained by SFG, AFM, and contact angle goniometry provides a more detailed understanding of interfacial phenomenon of blended macromolecular systems at the molecular level.

## Introduction

Polymer blends are widely used as a means of tailoring the bulk and the surface properties of polymeric materials for various industrial and biomedical applications.[1,2] They are of fundamental importance in relation to interfacial phenomena of macromolecular systems and of technological interest associated with wetting, adhesion, and tribology. A unique feature of these systems is that the surface composition and structure and consequently the surface properties of the material are often different from that of the bulk. This is due to a surface enrichment of the component that will minimize the total surface energy of the system.[3] The challenging problem however is to characterize the surface composition and structure of such polymer blends, so as to obtain the true surface structure− property relationship, and a molecular understanding of the interfacial behavior of such macromolecular mixtures.

Studies of polymer blends have been reported using atomic force microscopy (AFM),[4] attenuated total reflection infrared spectroscopy (ATR-IR),[5] and Raman[6] vibrational spectroscopy. However, they often probe either the surface composition or the surface structure, but not both, and the results are insufficient to provide a complete picture of the polymer surface. Moreover, the optical penetration depth of Raman and ATR/IR is of the

order of one to hundreds of nanometers, so that the spectra are often dominated by contribution from the polymer bulk. In this paper, we report an investigation of a two-component polymer blend using a combination of surface techniques: optical sum-frequency generation (SFG),[7] AFM,[8] and contact angle measurements,[9] all of which have surface sensitivity of ∼1−10 nm. The SFG technique makes use of the wave mixing process that mixes two input waves at frequencies $\omega_{\text{visible}}$ and $\omega_{\text{IR}}$ and generates an output at $\omega_{\text{sum}} = \omega_{\text{visible}} + \omega_{\text{IR}}$. As a second-order nonlinear optical process, SFG is electric dipole forbidden in a centrosymmetric medium but necessarily allowed at an interface where the inversion symmetry is broken. Consequently, it is intrinsically surface specific. Surface vibrational spectra can be obtained through resonant enhancement when $\omega_{\text{IR}}$ scans over surface vibrational resonances, providing information about the composition. On the other two surface probes, AFM is known for its ability to map out the surface structure, and contact angle goniometry is widely used to obtain information about the surface energy. Thus, each probe employed in this study looks at a specific property of the polymer surface. Correlation of these properties can provide a more detailed picture of the polymer surface.

The polymer blend chosen in our study is composed of two thermodynamically compatible components: Biospan-S (BS) and the phenoxy base polymer (BP). The molecular structures of BS and BP are shown in Figure 1. BS is a polyurethane capped with poly(dimethylsiloxane) (PDMS) end groups. As seen from its chemical structure, BS contains both more hydrophobic (PDMS) and more hydrophilic (ether and urethane

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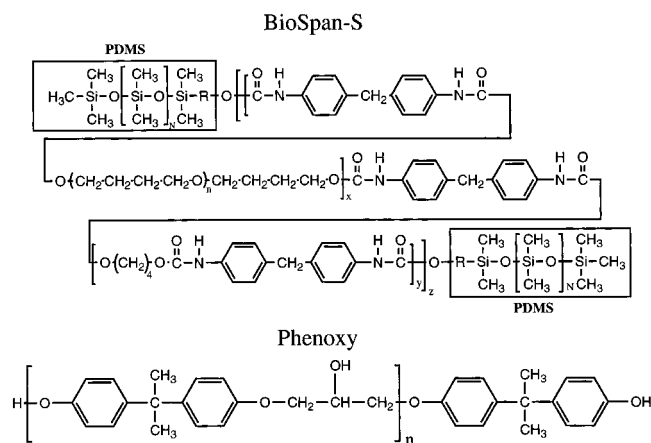**Figure 1.** Molecular structures of BP and BS.



**Figure 2.** SFG spectra of BP and BS in air at 300 K.

segments) components. Such blends of phenoxy with several different block or segmented copolymers can produce extrudable and moldable compounds which soften at a (glass transition) temperature that can be varied via the composition of the blend. The dramatic difference in the stress relaxation rate, above and below the glass transition, gives these blends shape-memory properties. Such blends, with a glass transition between room temperature and the body temperature, e.g., 35 °C, are thus ideal candidates for various biopolymer applications such as intravenous catheter tubings, which will soften after insertion into the veins. Since the surfaces of these blends are in contact with blood after insertion, the surface properties are of great interest in preventing complications related to thrombosis and embolization caused when blood contacts a foreign surface. From a previous study,[10] it was found that the more hydrophobic PDMS tails dominate at the pure BS polymer surface, yielding a water contact angle of 94°. Such a siliconization of surfaces is known to extend blood clotting time and reduce blood platelet adsorption and thrombosis in vivo. However, the other component in the blend, pure BP, is more hydrophilic and has a water contact angle of 74°. We are interested in probing the different surface properties (surface chemical composition, surface structure, and surface free energy) while varying the blending ratio and studying the correlation among them.

From the SFG study, we find that the BS component likes to segregate to the surface and approaches a full BS surface coverage when its bulk concentration is only 1.7 wt %. If the BS concentration is lower than 0.17 wt %, the polymer blend surface is dominated by BP. In the intermediate BS concentration region, 0.17−1.7%, the relative surface content of BP decreases rapidly with the addition of BS. These findings correlate well with the contact angle results, which show that the surface free energy decreases in the same way. They indicate the fact that the surface likes to be enriched by the component of lower surface energy. From the AFM measurements, we find that, below 0.17 wt % BS in BP, the surface morphology of the polymer blend is very similar to that of pure BP, while above 1.7 wt %, it resembles that of pure BS. Between 0.17% and 1.7% there appears to be a separation of BS and BP into domains at the surface. By measuring the spatial variations of friction of the polymer blend, the two components were distinguished on the surface in this concentration regime. The combination of the three techniques thus provides a more complete physical picture of the polymer blend surface at a molecular level. The observed variation of the surface structure with the blend composition shows that it is indeed possible to precisely control the surface properties of a polymer through adjustment of the bulk composition.
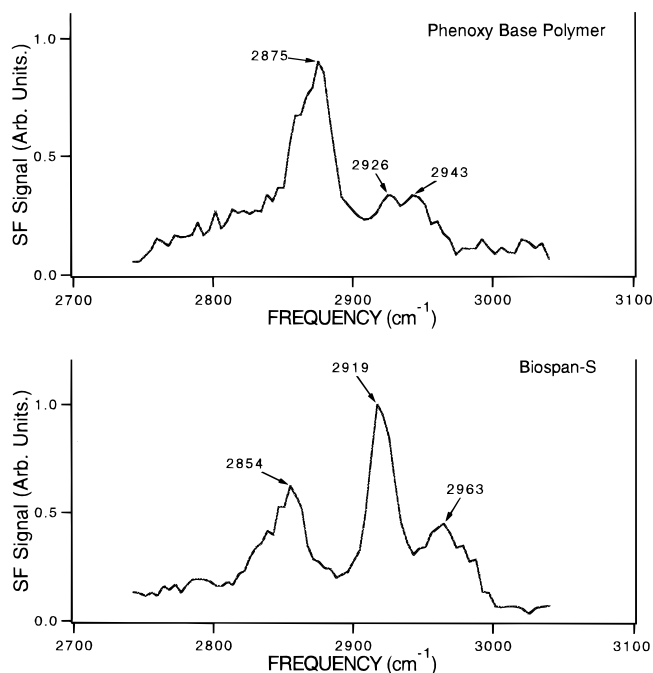
## Experimental Section

**Infrared−Visible SFG Surface Vibrational Spectroscopy**. The SFG technique has been described in detail elsewhere.[12,13] Briefly, the experiment was performed by overlapping a visible and a tunable IR beam on a polymer surface, at incident angles of 45° and 50°, respectively. The visible beam used was the 532 nm output from a Continuum YAG-PY61 laser (generating ~20 ps pulses at 20 Hz). The IR beam, tunable from 2500 to 3600 cm$^{-1}$, was generated from an optical parametric generation/optical parametric amplification (OPG/OPA) system, composed of LiNbO$_3$ crystals pumped by the fundamental output of the YAG laser at 1064 nm. The SF output from the polymer surface in the reflected direction was collected by a gated integrator and photon counting system. The surface vibrational spectra were obtained by tuning the IR beam and measuring the SF signal as a function of the IR frequency. The spatial size (i.e., in the plane of the surface) probed is around 100 $\mu$m in diameter. In this work, we present only results with the polarization combination of ssp (for s-polarized SF output, s-polarized visible input, and p-polarized infrared input).

**Atomic Force Microscopy**. The AFM used for imaging was a commercial Park Scientific M5 instrument. All imaging and friction measurements were done in the contact mode with Park Scientific silicon contact ultralevers of force constant ~0.1 N/m and loads between 10 and 20 nN.

**Contact Angle Goniometry.** A Rame-Hart NRL contact angle goniometer was employed to measure the contact angle of liquids with known surface tension on polymer films, using the sessile drop technique.[14] The liquids used in this study are water (72.8 dyn/cm) and methylene iodide (50.8 dyn/cm). The advancing contact angle was measured directly using the movable protractor scale of the goniometer. The geometric mean method[15] was used to deduce the surface free energy of the polymer films from the contact angles of two different liquids, water and methylene iodide. The spatial size probed (in the plane of the surface) is 1−2 mm in diameter.

**Sample Preparations**. The BS polymer (MW = 65 000) was synthesized by The Polymer Technology Group, Inc., of Berkeley, CA.[16] The homopolymer of BP (MW = 16 000) was

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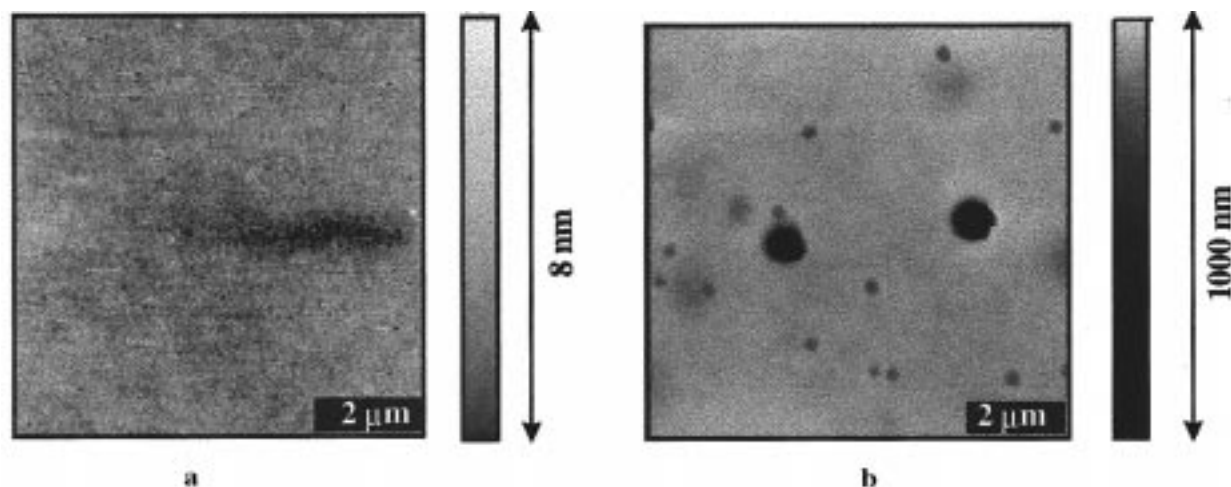*J. Phys. Chem. B, Vol. 102, No. 32, 1998* **6227**



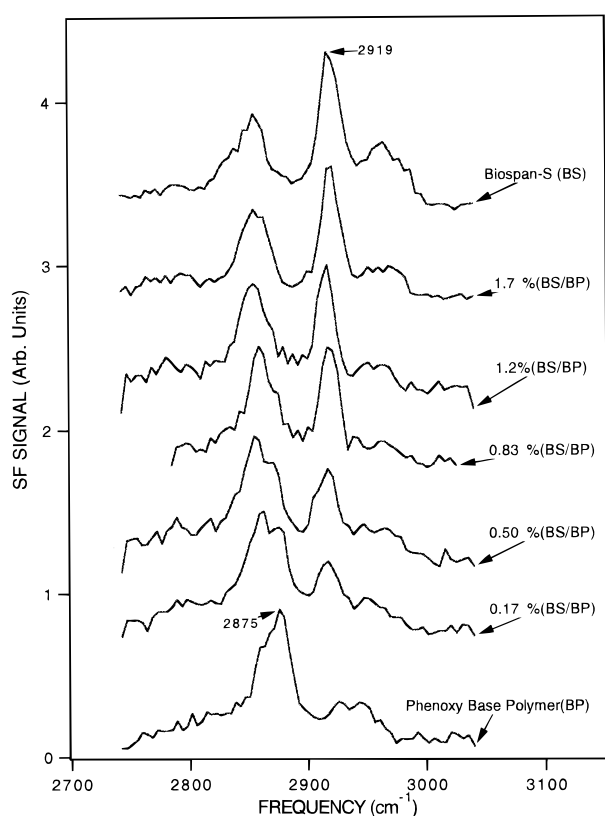**Figure 3.** Topographic AFM images of BP and BS in air at 300 K.



**Figure 4.** SFG spectra of pure BP, pure BS, and BS/BP blends as a function of BS bulk concentration in wt %.

purchased from Union Carbide. The molecular structures of these polymers are shown in Figure 1. Polymer films of different blend composition were prepared by casting the polymer blends from their *N,N*-dimethylacetamide (~1 wt % of the polymer) solutions onto flat quartz substrates. Then the films were dried in air at 65 °C for 24 h. The film thickness was measured by an Alpha-Step 50V surface profiler after it was cooled to room temperature. The thickness of these films was in the range of 100 $\mu$m.

## Results and Discussion

Figure 2 shows SFG spectra of pure BP and pure BS in air at 300 K in the C−H stretching region. In the BP spectrum, a pronounced peak at 2875 cm$^{-1}$ was observed and assigned to the symmetric stretch of the methyl group. The other two weak

features at 2926 and 2943 cm$^{-1}$ are attributed to the antisymmetric stretch and the Fermi resonance band of the CH$_2$ groups, respectively. In the latter analysis, the symmetric stretch of CH$_3$ at 2875 cm$^{-1}$ is taken as the characteristic band for BP. The contact angle of pure BP is 74°, indicating that it is a polymer of high surface energy. The SFG spectrum of BS is very different from that of BP. Three prominent peaks are present. According to a previous study,[10] we can 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 2854 cm$^{-1}$ to the symmetric stretch of the CH$_2$ groups of biospan. The strong PDMS modes in the SFG spectrum suggest that the BS surface is well populated by PDMS, yielding a hydrophobic surface with a water contact angle of 94°.

The AFM images of the morphology of pure BP and BS are shown in Figure 3. The surface of BP is featureless with an rms roughness of ~5 nm. The BS surface contains large holes. These holes range from 100 to 500 nm wide and 20 nm to 1 $\mu$m deep and are observed all over the surface. The reason for the hole formation is not clear but could result from solvent evaporation from the cast film during sample preparation.

The SFG spectrum of BP changed significantly when BS was added to BP. Figure 4 shows the SFG spectra of BS/BP blends of various blending ratios. The key features of the observed spectral changes with increasing BS bulk concentration are the weakening of the prominent methyl resonance of BP at 2875 cm$^{-1}$ and the strengthening of the prominent 2919 cm$^{-1}$ band for the CH$_3$ groups of BS. These changes clearly show an enrichment of the BS component at the polymer blend surfaces. Because BS is more hydrophobic, it tends to segregate at the polymer surface to lower the surface energy. It is so surface active that it completely covers the polymer surface at a bulk concentration as low as 1.7 wt %.

To obtain the surface free energies of polymer blends, we have performed contact angle measurements of water and methylene iodide on the polymer blend surfaces. The following "geometric mean equations"[15] were used to calculate the solid surface tension for each sample from contact angles.

$$(1 + \cos \theta_w)\gamma_w = 2[(\gamma_w{}^d\gamma_s{}^d)^{1/2} + (\gamma_W{}^P\gamma_s{}^P)^{1/2}] \qquad (1)$$

$$(1 + \cos \theta_m)\gamma_m = 2[(\gamma_m{}^d\gamma_s{}^d)^{1/2} + (\gamma_m{}^P\gamma_s{}^P)^{1/2}] \qquad (2)$$

where $\theta_w$ and $\theta_m$ are the contact angles of water and methylene iodide on the sample respectively, $\gamma_w$, $\gamma_m$, and $\gamma_s$ are the surface
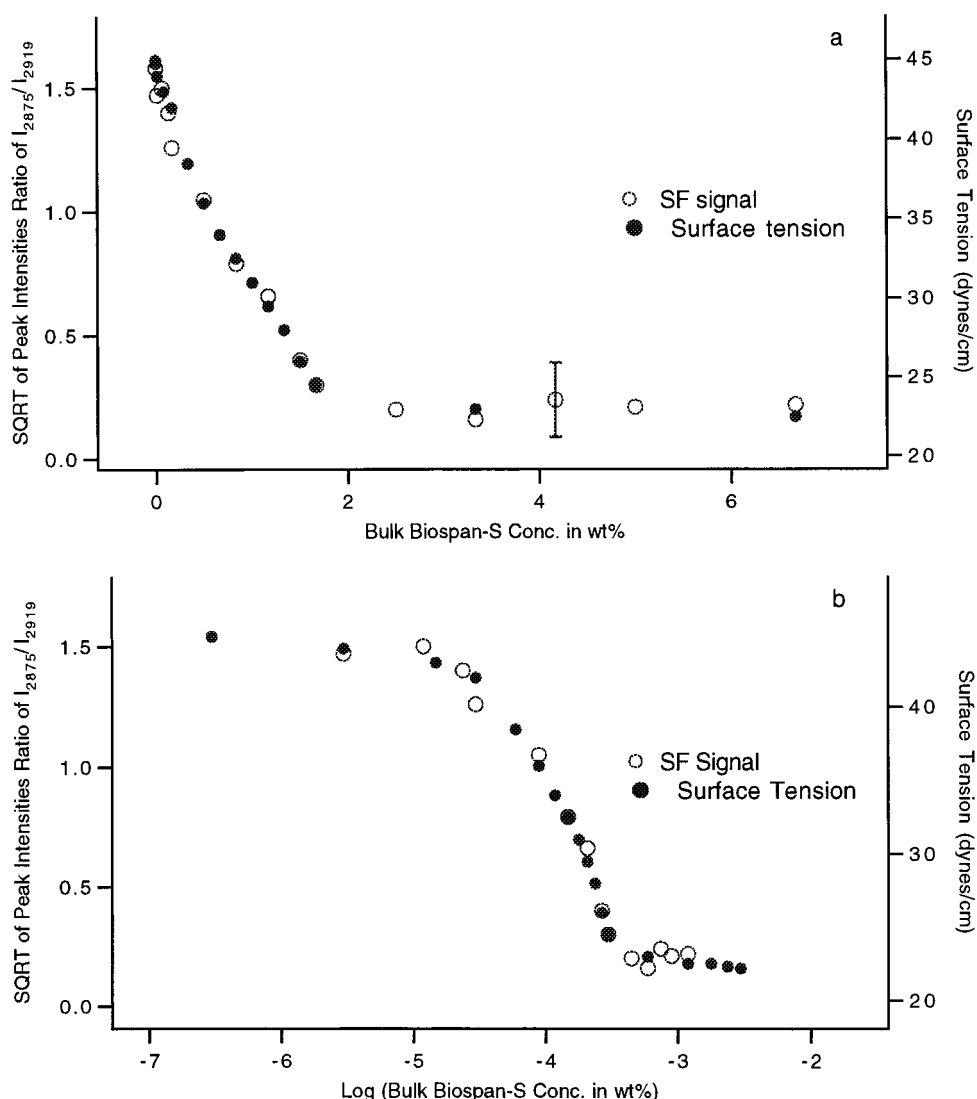
**Figure 5.** (a) Square root of SFG peak intensity ratios and surface tension as functions of BS bulk concentration, with $(I_{2875}/I_{2919})^{1/2}$ in open circles and surface tension in black dots. (b) SF signal, $(I_{2875}/I_{2919})^{1/2}$, and surface tension as functions of $\log(C_{BS})$.

tension of water, methylene iodide, and the sample, respectively, and the superscripts d and p denote the dispersive (nonpolar) and polar components of the surface tensions. By measuring $\theta_w$ and $\theta_m$ and inserting known values[15] for $\gamma_w{}^p$, $\gamma_w{}^d$, $\gamma_m{}^p$, and $\gamma_m{}^d$, the solution of the two equations yields $\gamma_s{}^p$ and $\gamma_s{}^d$. The solid surface tension or surface energy is given by $(\gamma_s{}^d + \gamma_s{}^p)$. Figure 5 presents the results on surface tension and SFG for the polymer blend surfaces as functions of BS bulk concentration. The surface tension of pure BP and BS is 44.9 and 22.2 dyn/cm, respectively. When the BS bulk concentration is lower than 0.17 wt %, the surface tension of the BS/BP blend is very close to that of pure BP, and when the BS concentration is higher than 1.7 wt %, it approaches that of pure BS. In the intermediate region of 0.17−1.7 wt % BS, the surface tension of the blend decreases almost linearly with increasing BS concentration. The SFG data displayed in Figure 5 are the square roots of intensity ratios of the 2875 cm$^{-1}$ peak versus the 2919 cm$^{-1}$ peak. The former is the characteristic peak of BP, and the latter is that of BS. Since the square root of the SFG intensity of a peak is proportional to the number of chromophores at the surface[7] contributing to the peak, the intensity ratio can be used as a measure of the relative surface concentration of the two components assuming that there is no orientational change. Thus, the SFG results presented in Figure 5a can be used to quantify

the relative BP content at the polymer blend surface. As seen in Figure 5, the change of surface tension correlates well with the relative BP surface composition measured by SFG. The result clearly shows the surface enrichment of the low surface energy component (BS) in order to minimize the overall surface free energy of the binary macromolecular system. This interfacial behavior of adsorption of BS at the polymer blend surface is very similar to what has been universally observed for binary liquid mixtures of small organic molecules.[17] However, it should be noted that the changes of the surface tension ($\gamma$) as a function of the concentration ($C$) of the lower surface energy component are different for polymer blends and liquid mixtures. The usual analysis of such a function of a binary liquid mixture uses the Gibbs equation.[11] In a typical $\gamma$−log $C$ plot, the slope of the curve remains essentially unchanged in a given region where the surface tension keeps changing, indicating that the surface concentration of the surface active component reaches a constant maximum value at the liquid surface. However, in our study, as shown in Figure 5b, both the surface composition and the surface tension change simultaneously with the BS bulk concentration in the region of 0.17−1.7 wt %. Then both of them reach the constant value when the BS bulk concentration is 1.7 wt %. This different behavior between the polymer blend and the liquid mixture is
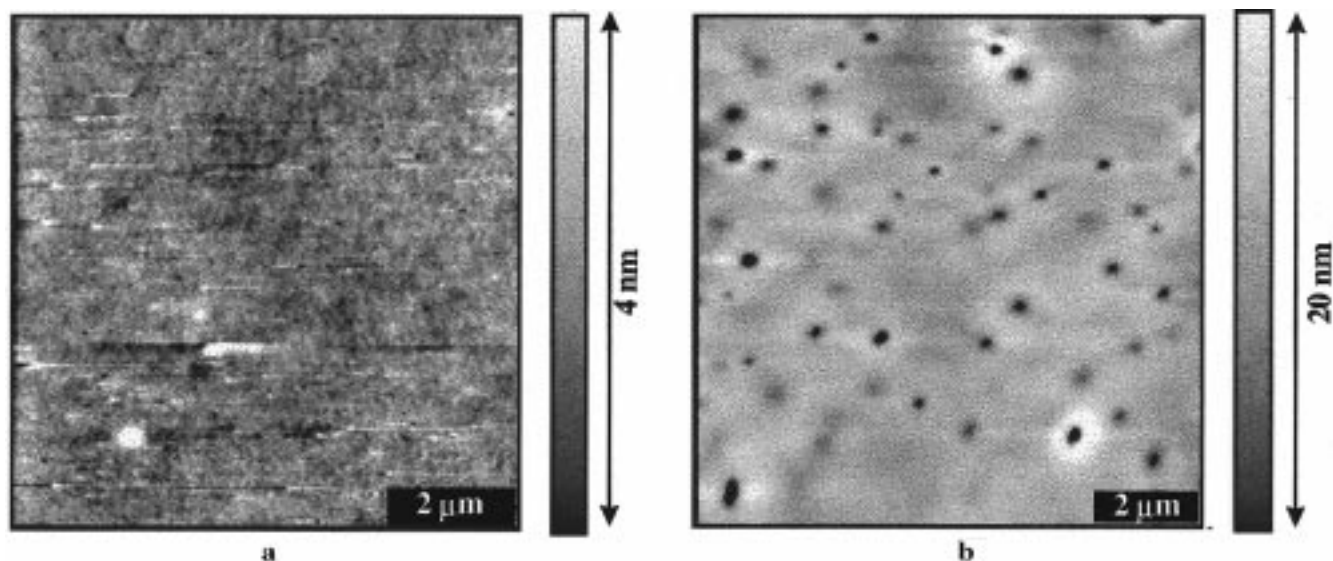
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**Figure 6.** Images of BS/BP blends (a) at low concentrations of BS, below 0.17 wt %, the image appears featureless and resembles that of pure BP and (b) at high concentrations of BS > 1.7 wt %, where the morphology of the surface resembles that of pure BS.

probably due to surface segregation of each of the blend components, as revealed by AFM, thus deviating from the ideal liquid mixture case.

The AFM images for the blend surfaces of different BS bulk concentrations are displayed in Figure 6. For BS concentrations lower than 0.17 wt % (Figure 6a), the surface appears featureless and resembles that of pure BP (Figure 3a). This correlates well with the SFG result which shows that the blend surface consists mainly of BP in this concentration regime. Figure 6b is an image obtained at concentrations higher than 1.7 wt % and
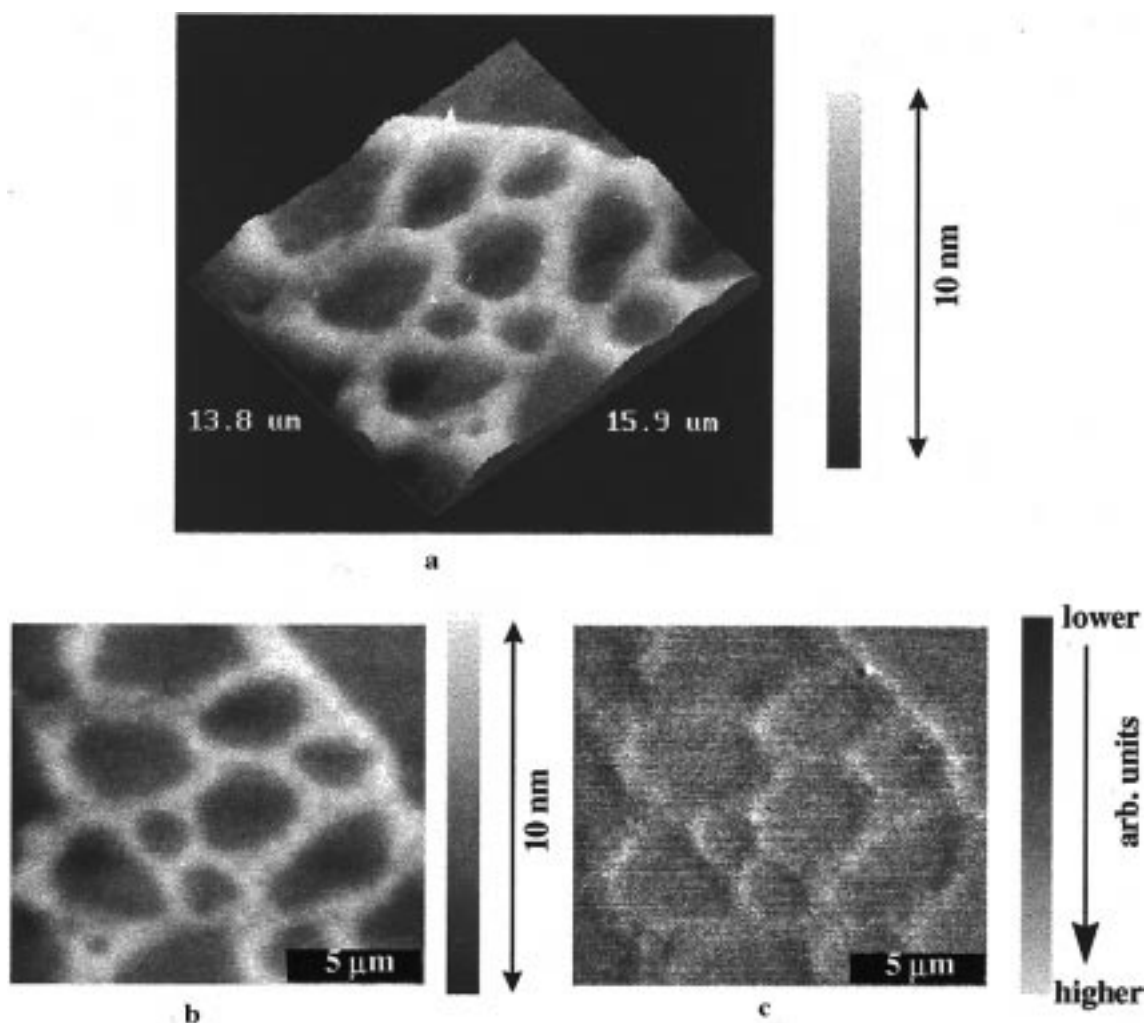


**Figure 7.** AFM image of the segregation at 0.3 wt % BS in BS/BP. (a) is a 3-d view of the surface and (b) is a planar projection. (c) is a friction image (difference of right and left scans) obtained simultaneously with the topographic image in (b).

consists of holes. This is similar to the surface of pure BS (Figure 3b) and is consistent with the presence of BS at the surface of the blend at these concentrations as observed by SFG.

What is perhaps more interesting are the AFM images of blend surfaces for BS bulk concentrations in the range 0.17–1.7 wt %. As shown in Figure 7, they exhibit a domain structure, very similar to the patterns observed in other phase-segregated macromolecular systems.[18] The average height of the ridges is around 4 nm, which is equivalent to stacking of only a few molecules. The pattern appears to be very stable; it remains after a period of 3 months without any discernible change. It is of course interesting to know the composition of the ridges and the base. This we hoped to achieve by measuring the surface friction with the AFM. As references, we first measured and found the friction of pure BP to be higher than that of pure BS by a factor of 2, at a load of 20 nN. The higher friction on BP at these small loads can be explained by the higher surface energy of BP as compared to that of BS. This results in a larger contact area between the AFM tip and the surface,[19] which increases the friction.[20] We then measured the frictional force on the segregated surface (0.17–1.7%) while simultaneously imaging the surfaces at a load of 20 nN using the same tip and the same instrumental setup. The friction image of the blend is shown in Figure 7c. The images plotted are difference friction images, i.e., the difference in the friction signal for right and left scans. This is done to remove any artifacts that might be introduced by topography. As can be seen from the image, the friction on the ridges is higher than that of the base, and we can thus conclude that the ridges are rich in the BP component of the blend.

Previous work[21] has shown that such blends are thermodynamically compatible, in the bulk, over the composition range investigated in this study, whether melt blended or solvent cast. Hence, no bulk phase segregation is expected. We thus attribute these domains to the preferential segregation of the BS component to the surface. In doing so, the BP component gets displaced at the surface and forms the ridges. From the shape of these patterns one can conclude that the segregation is isotropic in the plane of the surface, since the polygons show no preferential orientation. The dramatically different morphologies are responsible for the large changes, at the blend surface, in this concentration regime, as indicated by the SFG and surface tension data.

## Conclusions

We have used a combination of surface-sensitive techniques, IR + visible SFG, AFM, and contact angle goniometry to study the surfaces of the BS/BP blend. As expected, the surface structure of the polymer blend is very different from the bulk.

The BS surface content becomes noticeable at BS bulk concentrations as low as 0.17 wt %. It increases with the BS concentration and reaches a full coverage at 1.7 wt %. Apparently there is a strong tendency for BS to segregate to the surface. When BS and BP coexist on the surface, AFM pictures reveal a pattern of domains. It is clear that by using a combination of techniques we observe a more complete picture of the surface of the polymer blend. Studies of this kind could lead to a more fundamental understanding of interfacial phenomena of polymer blend systems.

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