Molecular Orientation at the Interface of Polystyrene/Poly(methyl methacrylate) Blends: Evidence from Sum-Frequency Spectroscopy

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Chemical composition and molecular conformation at the interfacial regions of polymers are often very different from that of the bulk material. A molecular level understanding of polymer interfaces is therefore critical in controlling many important properties such as wettability, adhesion, friction, and biocompatibility.[1] Although much progress has been made in acquiring detailed knowledge about polymer surfaces through the use of surface sensitive techniques, including sum-frequency (SF) spectroscopy, little is known about the conformation of functional groups at the polymer−polymer interface. Most SF studies of polymers have probed polymer structures at air and liquid interfaces.[2] The SF spectra of polystyrene (PS)/poly(butyl methacrylate) blends provide some clues to the orientation of the PS phenyl rings at the blend surface.[3] The SF spectrum of a polymer−polymer interface has only recently been reported.[4]

In this paper, we report the orientation of polymer functional groups at the polymer−polymer interface using SF spectroscopy. In addition, spectra can be used to determine the discontinuous nature of that interface. The highly incompatible PS/poly(methyl methacrylate) (PMMA) blend, whose segregation is reasonably understood, was examined by SF spectroscopy. SF spectroscopy not only has high interfacial selectivity but also possesses in situ capability and is very sensitive to the orientational order of surface functional groups.[5] The laser beams are overlapped at the polymer surface via a total internal reflection geometry.[6] The SF peak of PMMA is the C−H symmetric stretching of the ester methyl group (OCH$_3$) centered at 2960 cm^{-1} (Figure 1A), and the OCH$_3$ groups tend to tilt toward the surface normal.[7] The SF peaks from the PS surface originate from the vibrational modes of the phenyl rings whose C−H stretching frequencies are in the region 3000−3100 cm^{-1} (Figure 1B). The strongest peak occurs at 3064 cm^{-1} and is assigned to the ν_2 vibrational mode. At the PS-air interface, the phenyl rings tend to orient toward the surface normal.[8] The characteristic SF peaks of PMMA and PS appear in two well-separated regions (Figure 1A,B). Therefore, the interference of these two polymer SF bands is minimal, which makes it possible to extract more quantitative information from the SF spectra of the PS/PMMA blends.

To study the molecular orientation at the interface within PS/PMMA blends, we constructed a bilayer structure, PS-on-PMMA, by utilizing the solubility difference of these two polymers in different solvents. The PS-on-PMMA bilayer blends were prepared by spin-coating a layer of PMMA onto the substrate from a 0.25% solution in CHCl$_3$ and then spin-coating a layer of PS onto the dried PMMA layer from a 0.25% solution in cyclohexane, a poor solvent for PMMA. After heating at 80 °C overnight, the PS-on-PMMA blends gave water contact angles of (96 ± 2)°, almost identical to that on a single PS layer prepared in a similar fashion,
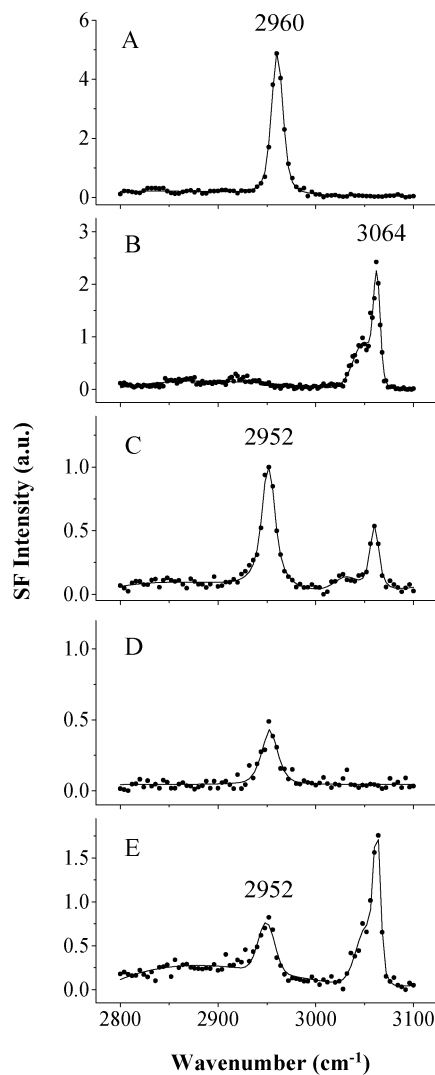

Figure 1. SF spectra of (A) PMMA; (B) PS; (C) PS-on-PMMA bilayer; (D) PS-on-PMMA bilayer at D$_2$O interface; (E) annealed PS/PMMA blend. Spectra were taken under *ssp* polarization. The solid lines are fits to the data using Voight line shapes.

indicating a PS layer was formed on top of the PMMA layer. The SF spectrum under *ssp* polarization of this PS-on-PMMA sample is shown in Figure 1C. SF peaks appear in both PS and PMMA characteristic regions. The peaks in the 3000−3100 cm^{-1} region primarily originated from the PS-air interface. Although the blend surface is almost completely covered by the PS phase, the SF peak in the PMMA region is still noticeable (Figure 1C), suggesting that SF active ester methyl groups exist at the PMMA-PS interface.

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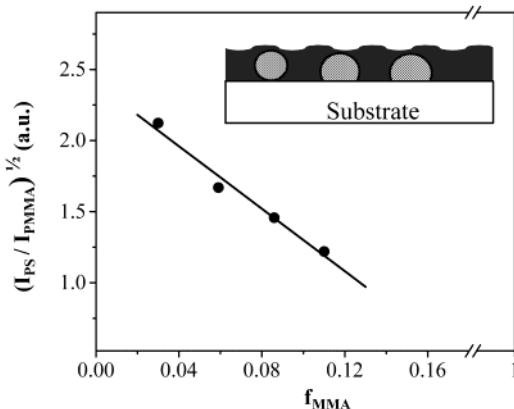
Figure 2. Square root of SF intensity ratio of PS/PMMA blends as a function of bulk mole fraction of MMA units (f_{MMA}). The straight line is a linear fit to the corresponding data.

Note that the SF peak from the buried PMMA-PS interface is red shifted from 2960 to 2952 cm^{-1}, possibly a result of the environmental changes at the interface experienced by the PMMA molecules because the PS molecules provide a more polar environment for PMMA than air. To obtain more evidence confirming that the SF signal is originating from the PMMA-PS interface, we replaced the polymer-air interface by adding a drop of D$_2$O at the PS-on-PMMA sample surface. If the 2952 cm^{-1} peak originates from the polymer-polymer interface rather than polymer-air interface, one would expect that the SF signal is still observable. This is indeed seen in Figure 1D. The PS peaks disappear because they originate from the PS-air interface. The ester methyl peak is still apparent, only the intensity decreases possibly a result of the penetration of D$_2$O into the ultrathin PS phase.

We have also constructed a more closely contacted PMMA-PS interface by utilizing the segregation of these two polymers. This structure will serve to model an interface naturally formed within a polymer blend. First, a 1% CHCl$_3$ solution of PS/PMMA (15:1) was spin-coated onto a clean glass surface and then dried under vacuum at room temperature. Since CHCl$_3$ is a better solvent for PMMA than PS, PS solidifies earlier on the substrate during the spin-coating, leaving an enriched PMMA layer on the surface. However, the blends thus prepared are not in their thermodynamic equilibrium state because PS has lower surface free energy and tends to segregate at the free polymer surface.[9] Annealing the blends at a temperature higher than the glass transition temperature of these two polymers is believed to produce a structure with a PS phase on top, and this is confirmed by our contact angle and XPS measurements. The *ssp* SF spectrum of the annealed PS-on-PMMA sample is shown in Figure 1E, which is quite similar to Figure 1C. Both PMMA and PS peaks appear in the spectrum, and the PMMA peak position is red shifted to 2952 cm^{-1}. Since the blend surface is covered by a PS phase, the observed PMMA peak must come from the PMMA-PS interface. This result is consistent with that observed from the bilayer prepared from sequential spin-coating (Figure 1C). The thickness of this annealed blend was determined by XPS to be roughly 20 nm, and thus it is possible that the PMMA domains may span a large portion of the film depth, reaching to the polymer-glass interface. In this case, the asymmetry between the top and bottom PMMA surface would allow for noncancellation of the nonlinear polarization.

Unlike a randomly oriented system, the oriented ester methyl groups of PMMA can provide more information about the polymer interface because SF intensity is proportional to the square of the surface density of the SF active moieties (N) assuming no change in orientation. Therefore, the SF intensity ratio of the ester methyl and the phenyl ring in Figure 1C and 1E should contain quantitative information about the surface density ratio of PS and PMMA domains. To generate variable interfacial structures, we prepared a series of PS/PMMA blends with various PMMA bulk concentrations by spin-coating from 1% CHCl$_3$ solution and then annealed these samples at 150 °C for 20 h. The bulk PMMA concentration, which is expressed as the mole fraction of the monomer units (f_{MMA}), was varied from 0.03 to 0.11. The SF spectra were taken under *ssp* polarization, and the red-shifted ester methyl peak was observed for all of these blends. The square root of the SF intensity ratio of PS and PMMA, $(I_{PS}/I_{PMMA})^{1/2}$, are calculated, where I_{PS} is the SF intensity of the ν_2 vibrational mode of PS (3064 cm^{-1}) and I_{PMMA} is the SF intensity of the C−H symmetric stretch of the ester methyl groups. Figure 2 shows that the $(I_{PS}/I_{PMMA})^{1/2}$ decreases linearly as a function of f_{MMA}. Since no PS active peaks originate at the PS-PMMA interface (as shown in the D$_2$O experiment), then we can assume that the PS surface density N_{PS} is constant for all four blends. Therefore, the decrease of $(I_{PS}/I_{PMMA})^{1/2}$ must come from the increase of PMMA surface density N_{PMMA} in the blends. This decrease implies that these annealed blends may be modeled as laterally discontinuous PMMA islands embedded in PS matrix as schematically represented in Figure 2. These results show that not only molecular orientation but also the continuous or discontinuous structure of the interfacial contact can be determined by SF spectroscopy.

In summary, we have demonstrated that structure as well as orientation at the polymer−polymer interface can be observed by SF spectroscopy. The ester methyl groups of PMMA are oriented at the interface of the annealed PS/PMMA blends. From these spectra, the interface within a PS/PMMA blend is shown to be laterally discontinuous.

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