Combined X-ray Photoelectron Spectroscopy and Time-of-Flight Secondary Ion MS Surface Quantitative Analysis of Polymer Blends with Varying Mixing Thermodynamics

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Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used to quantitatively correlate to the surface chemical composition determined from XPS in poly-(styrene-*co-p*-hexafluorohydroxyisopropyl-α-methyl styrene)/poly(4-vinyl pyridine) (PS(OH)/PVPy) blends or complexes when the *p*-(hexafluoro-2-hydroxyisopropyl)-α-methylstyrene (HFMS) contents in PS(OH) copolymers were gradually increased. It was found that different mixing thermodynamics, such as immiscibility, miscibility, and complexation, have little effect on the quantitative analysis of PS(OH) copolymers in the blends or complexes using TOF-SIMS. In the positive spectra, either the normalized intensities or relative peak intensities can be used to quantitatively analyze the surface HFMS, PS(OH), or PVPy concentration when peaks at $m/z = 257, 271, 285,$ and 373 are used for HFMS, peaks at $m/z = 91, 103, 105, 115$ for styrene, and peaks at $m/z = 132, 195, 209$ for PVPy. In the negative spectra, the normalized intensities of peaks characteristic of PVPy seem to be not affected by hydrogen bonding formation and can be used in quantitative analysis, whereas peaks characteristic of HFMS, such as a peak at $m/z = 283,$ cannot be used in quantitative analysis due to enhancement of its secondary ion yield resulting from hydrogen bond formation.

Many materials properties (adhesion, compatibility, etc.) of polymer blends are directly related to their surface state.[1,2] The surfaces can be characterized by several surface-sensitive techniques, such as X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). The main

differences between these two techniques are the information depth (5 and 1 nm, respectively), their chemical specificity (the chemical shift on atomic core levels for XPS and the detection of molecular fragments coming from functional groups for TOF-SIMS), and the sensitivity (1 at. % and parts per million, respectively).[3–8] Thus, TOF-SIMS has gained more and more importance in the surface characterization of materials owing to its unique advantages, as compared with XPS, due to its high molecular specificity, extreme surface sensitivity, and high-mass resolution. However, difficulty of TOF-SIMS in quantification has been a major obstacle for extending its applications, because the mechanisms of the formation and emission of the secondary ions are not well understood yet.

It has been shown that quantitative analyses can be performed with static SIMS on certain polymer blends, such as polystyrene/poly(vinyl ethyl ether),[9,10] polycarbonate/polystyrene,[11] polycarbonate/poly(methyl methacrylate),[12] polypropylene/poly(ethylene terephthalate),[13] polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide),[14] poly(vinyl chloride)/poly(methyl methacrylate), and poly-(sebacic anhydride)/poly(DL-lactide acid).[4,15–16] In the above systems, the intensities of some SIMS characteristic peaks unique

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to each component can be related to the bulk composition or the surface composition determined by XPS. The strong relationship between SIMS peak intensities and the copolymer or polymer blend composition showed that SIMS can be used as a quantitative technique. However, the selection of SIMS peaks needs to be made carefully, and there are no general guidelines for the selection of SIMS peaks for quantitative analysis. It is, thus, imperative to investigate more polymer systems with controlled structures/compositions and different mixing thermodynamics so that general guidelines may be established.

It is known that for immiscible blends, when two polymers are capable of interacting with each other through specific interactions, such as hydrogen bonding, they are likely to form a miscible blend.[17] By gradually increasing the densities of specific interaction groups, not only could an immiscible blend become miscible but also the blends could further form interpolymer complexes, that is, the two polymers could form precipitates (complexes) upon mixing the two constituent polymer solutions in a common solvent.[18–20] It is believed that the two different types of polymer chains are randomly mixed in a miscible blend while they are "paired" in the interpolymer complexes.[18]

The matrix effect, in which the secondary ion yield for the same secondary ion can vary over several orders of magnitude, depending upon the chemical bonding and type of environment with which the presecondary ion was associated, was always attributed to the undesirable quantitative results of SIMS. The surface of the immiscible blend could be composed entirely of one of the two components;[21,22] therefore, no matrix effect should be observed. Immiscible blends could also have the surface composed of separate domains of each component with an unknown size distribution. If the domain areas are large, as compared to the boundary areas, there may be an insignificant contribution from matrix effects. In miscible blends, lower surface energy species may also be achieved by preferential placement of one component at the surface.[23,24] However, this requires a composition gradient to be maintained between the surface and the bulk, and consequently, the equilibrium surface composition is determined by the minimization of the total system free energy. In miscible polymer blends, matrix effects would be expected to be more important because of the interaction between functional groups on the different neighboring chains. In interpolymer complexes in which unlike chains are interwoven with each other,[18] the interpolymer interactions are much stronger and the matrix side-effect should be more deleterious for SIMS quantification. Thus, it is interesting to try to use TOF-SIMS as a quantitative tool for surface analysis of polymer blends with different thermodynamics. To our knowledge, there is no report in the literature about TOF-SIMS surface quantification of a series of polymer blends covering three different miscibility levels, namely, immiscibility, miscibility, and complexation.

In the previous paper, we used XPS and TOF-SIMS to investigate the surface composition, structure, and morphology of poly(styrene-co-p-hexafluorohydroxyisopropyl-α-methyl styrene)/poly(4-vinyl pyridine) (PS(OH)/PVPy) blends in the process of immiscibility−miscibility−complexation transition when the density of hydrogen bonding was adjusted by varying the hydroxyl content of PS(OH).[25] When the hydroxyl content of PS(OH) increased from 5 to 49 mol %, the blends underwent a miscibility−complexation transition, and there was a gradual increase of PVPy concentration on the surface. The surface excess of PS(OH) decreased dramatically. In the complexes with hydroxyl content in PS(OH) higher than 21 mol %, the surface and bulk composition were very close. It was also found that the absolute intensity of positive secondary ions characteristic of PVPy at $m/z = 80$, 93, 106, and 120 was enhanced due to hydrogen bonding formation. The hydroxyls enhanced the formation of pyridine ring-containing ions which needed to get one proton in the process of ion fragmentation.[25,26]

In this contribution, TOF-SIMS was used to quantitatively characterize the surfaces of PS(OH)/PVPy blends or complexes where the mixing thermodynamics changes substantially by changing the hydroxyl contents.

EXPERIMENTAL SECTION

Materials. p-(Hexafluoro-2-hydroxyisopropyl)-α-methylstyrene (HFMS), copolymers of styrene and HFMS (PS(OH)), and poly-(4-vinyl pyridine) were synthesized as previously reported.[27] PVPy has a molecular weight of 3.52×10^4 determined from intrinsic viscosity in absolute ethanol.[28] X in PS(OH)-X denotes the molar percent of HFMS monomer in PS(OH).

Sample Preparation. PS(OH) copolymers and PVPy were separately dissolved in chloroform(CHCl$_3$) at a concentration of 10 g/L. A blend solution was prepared by mixing the same amount of each polymer solution under stirring. Depending on the HFMS contents in PS(OH), the mixed solutions might remain clear or form an interpolymer complex precipitate. For PS(OH)-1/PVPy, PS(OH)-3/PVPy, and PS(OH)-5/PVPy, the clear solutions were spin-cast at 3800 rpm onto silicon wafers. The film thickness was kept at ∼200 to 230 nm using the same concentration of the solution and the same spin rate. When the HFMS contents reached or were higher than 8 mol %, the blend solutions contained interpolymer complex precipitate, and the precipitate was separated by centrifugation, washed with CHCl$_3$ three times, and then kept in CHCl$_3$. The chemical compositions of complex precipitates were determined from fluorine elemental analysis. The slightly swelled precipitates were pressed onto a silicon wafer to form thin and smooth films. The films were then dried under vacuum at room temperature overnight.

Surface Characterization. The surface properties of a series of PS(OH)/PVPy blends or complexes were studied by XPS and TOF-SIMS. The surface chemical composition was calculated from the N/C ratio determined from XPS data. The XPS spectra were obtained with a PHI 5600 multitechnique system equipped with a

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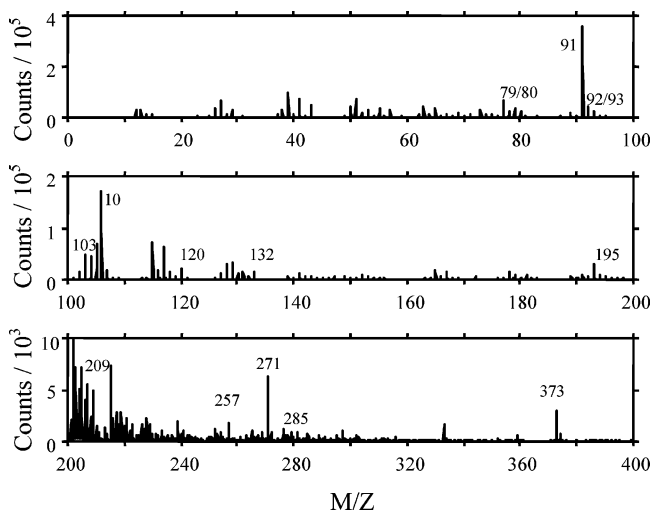(26) Li, L.; Chan, C.-M.; Weng, L.-T.; Xiang, M.; Jiang, M. *Macromolecules* **1998**, *31*, 7248.
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Table 1. Characteristic Data of PS(OH)/PVPy Blend and Complexes Samples

sample code	hydroxyl content in PS(OH) mol %	feed composition (PS(OH), mol %)	bulk composition (PS(OH), mol %)	T_g (°C)	surface PS(OH) concn
PS(OH)-1/PVPy	1	49.8	49.8	104.1/143.2	89.26
PS(OH)-3/PVPy	3.2	48.89	48.89	106.5/132.4	80.82
PS(OH)-5/PVPy	5.1	48.13	48.13	117.8	70.74
PS(OH)-8/PVPy	8.3	46.89	55.15	132.2	70.40
PS(OH)-12/PVPy	12.4	45.4	52.84	149.3	60.81
PS(OH)-21/PVPy	20.6	42.67	49.87	160.4	50.90
PS(OH)-34/PVPy	33.8	38.9	46.81	166.1	44.33
PS(OH)-49/PVPy	49.2	35.29	42.62	176.5	40.47

Figure 1. Positive TOF-SIMS spectra of PS(OH)-20/PVPy complexes in the range of $m/z = 0-400$.

Table 2. Proposed Secondary Ion Structures for the Some of the Characteristic Peaks in the Positive Ion Spectra of PS(OH)/PVPy Blends
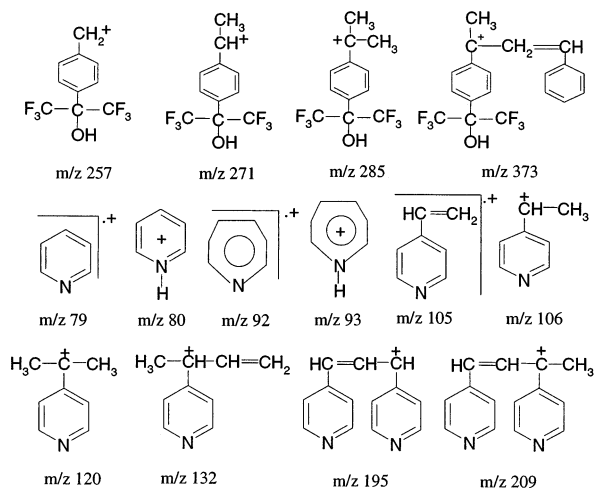

monochromatic Al Kα X-ray source. A pass energy of 23.4 eV was used. All core-level spectra were referenced to the C 1s neutral carbon peak at 285.0 eV. The emission angle (the angle between the surface normal and the axis of the analyzer) of the photoelectron was 45°, corresponding to a sampling depth of ~47 Å.

TOF-SIMS measurements were performed on a Physical Electronics PHI 7200 TOF-SIMS spectrometer. The primary ions were generated from a Cs ion source (8 kV). The scanned area was $200 \times 200 \mu$m, and the total ion dose for each spectrum acquisition was $<4 \times 10^{12}$ ions/cm^2. Charge compensation was realized by low-energy (0−70 eV) flooding electrons being pulsed out-of-phase of the primary ion beam. Both positive and negative high-resolution mass spectra were recorded. The surface chemical images of PS(OH)/PVPy blends were acquired in negative modes using a ^{69}Ga$^+$ beam at 25 kV. At least three positive and negative spectra were taken for each sample.

RESULTS AND DISCUSSION

PS(OH)-1/PVPy, PS(OH)-3/PVPy, and PS(OH)-5/PVPy blend solutions are clear, but mixing the chloroform solutions of PS(OH)-8, 12, 21, 34, and 49 with PVPy led to the formation of gell-like precipitates. The glass transition temperature and surface composition of PS(OH)/PVPy blends or complexes with different hydroxyl contents are shown in Table 1. PS(OH)1/PVPy and PS(OH)-3/PVPy blends are immiscible, showing two distinct T_g's. PS(OH)-5/PVPy is miscible and shows only one T_g. When hydroxyl contents reach or are higher than 8 mol %,

PS(OH) and PVPy form precipitate complexes which shows one T_g.[25]

The surface composition of polymer blends or complexes is obtained from XPS. When the hydroxyl contents in PS(OH) increased from 1 to 49 mol %, PS(OH)/PVPy blends or complexes underwent an immiscibility−miscibility−complexation transition, there was a gradual increase of PVPy concentration on the surface, and the surface excess of PS(OH) decreased dramatically. In the complexes with hydroxyl content in PS(OH) higher than 21 mol %, the surface and bulk composition were very close. This indicates that interpolymer complexation can eliminate surface enrichment of polymer blends due to chain segment pairing between PS(OH) and PVPy in the interpolymer complexes.[25]

TOF-SIMS Spectrum Analysis. Figure 1 shows a typical positive TOF-SIMS spectrum of PS(OH)-21/PVPy complexes. The characteristic peaks of polystyrene, for example, $m/z = 27$, 39, 51, 77, 91, 103, 105, 115, 128, 141, 152, 165, 178, and 193, are also present in the spectrum of the PS(OH) copolymer. Typical TOF-SIMS spectra of PS(OH) have been reported previously.[27] HFMS monomer can be distinguished from styrene monomer by the presence of peaks at $m/z = 257$, 271, 285, and 373, the structures of which are directly associated with HFMS monomer structure and are listed in Table 2. PVPy is distinguished from PS(OH) by the presence of a peak at $m/z = 106$,[26] the largest peak in the PVPy spectrum, and by the presence of characteristic peaks at $m/z = 79$, 80, 92, 93, 106, 120, 132, 195, and 209. Some
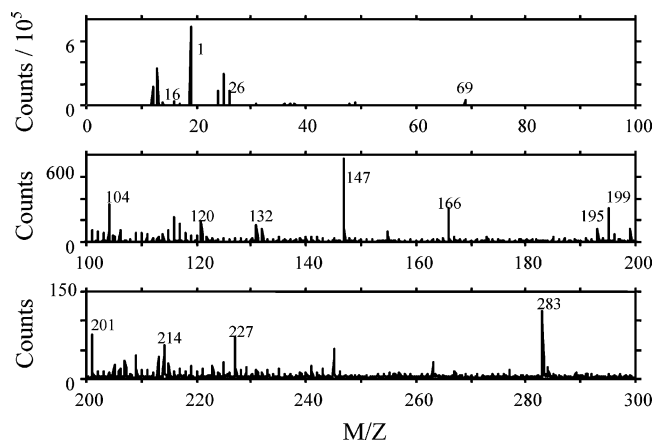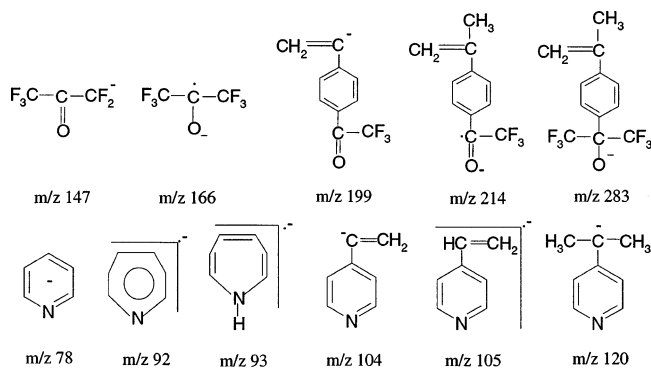
Figure 2. Negative TOF-SIMS spectra of PS(OH)-20/PVPy complexes in the range of $m/z = 0-300$.

Table 3. Proposed Secondary Ion Structures for Some of Characteristic Peaks in the Negative Ion Spectrum of PS(OH)/PVPy Blends

Figure 3. Intensity ratio of several positive ion peaks, 257/(257 + 103), 257/(257 + 105), 257/(257 + 115), 271/(271 + 103), 271/(271 + 105), and 271/(271 + 115), as a function of HFMS content in PS(OH) copolymers.

possible structures for the nitrogen-containing ions of PVPy are shown in Table 2. We have previously reported that the absolute intensity of positive secondary ions characteristic of PVPy at $m/z = 80, 93, 106, 120$ is enhanced due to hydrogen bonding formation. The hydroxyls have enhanced the formation of pyridine ring containing ions, which need to get one proton in the process of ion fragmentation, whereas positive ions at $m/z = 132, 195,$ and 209, also characteristic of PVPy, show little enhancement because their ion structures contain unsaturated double bonds.[25,26]

Figure 2 shows the negative ion spectrum of PS(OH)-21/PVPy complexes. PS(OH) can be distinguished by the presence of peaks at $m/z = 19$ (F$^-$, the largest peak in the spectrum), 31 (CF$^-$), 43 (C$_2$F$^-$), 69 (CF$_3^-$), 93 (C$_3$F$_3^-$), 147, 166, 199, 214, and 283. PVPy can be distinguished from PS(OH) and PVPy by the presence of peaks at $m/z = 78, 92, 93, 104, 105,$ and 120 in the negative ion spectrum. The probable structures of some of these ions are shown in Table 3.

Quantitative Surface Characterization. The surface chemical composition of the polymer blends or complexes was obtained from XPS. The TOF-SIMS data were analyzed with the objective to test whether these data can be used in quantitative analyses. The selection of characteristic peaks is the most crucial step in the quantitative analysis procedure. Both normalized peak intensities and the ratios of the intensities of two
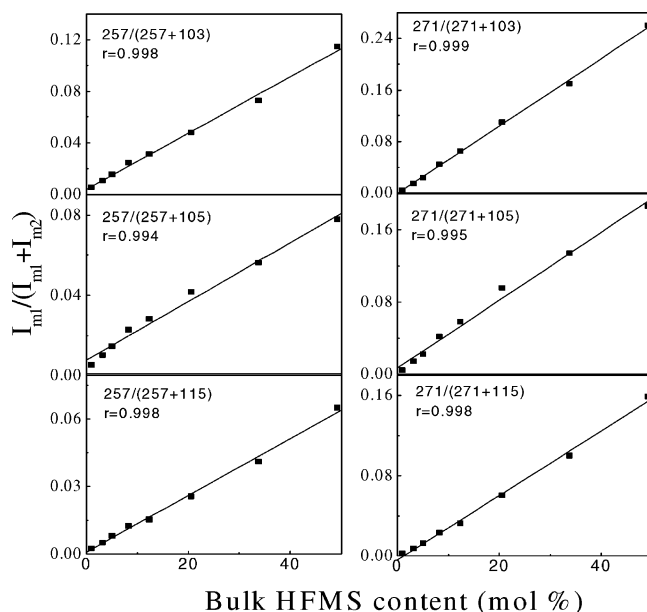
peaks unique to the two monomer units in PS(OH) or PVPy can be used. The normalized intensity is the intensity of a peak normalized by the total intensity. The correlations between TOF-SIMS results and XPS surface compositions are evaluated by the correlation coefficients (r), which are calculated from linear fits.

Positive Ion Spectrum. *Analysis of PS(OH) Copolymers in PS(OH)/PVPy Blends or Complexes.* PVPy contribute little in the positive ion spectrum at $m/z = 91, 103, 105,$ and 115 (characteristic of styrene monomer units) and even less at $m/z = 257, 273, 285,$ and 373 (characteristic peaks of HFMS monomer units), as compared with PS(OH). This has provided a good chance for us to check whether the quantitative SIMS analysis of PS(OH) copolymers could still be kept in the PS(OH)/PVPy blends or complexes, where other polymer chains (PVPy) with different mixing thermodynamics with PS(OH) chains are present. The plots of $I_{m1}^{HFMS}/(I_{m1}^{HFMS} + I_{m2}^{PS})$ as a function of the HFMS content in PS(OH) in a series of PS(OH) blends or complexes are shown in Figures 3 and 4. I_{m1}^{HFMS} and I_{m2}^{PS} are the intensity of a characteristic peak of the HFMS and PS units at $m/z = $ m1 and m2, respectively. The peaks at $m/z = 257, 271, 273$ (plots not shown), and 373 (plots not shown) are used to represent HFMS, and peaks at $m/z = 91, 103, 105,$ and 115 are used for styrene. All the plots show very good linear fits ($r \geq 0.993$). They all can be used in quantitative analyses because $I_{m1}^{HFMS}/(I_{m1}^{HFMS} + I_{m2}^{PS})$ increases linearly with the HFMS content. This phenomenon is in agreement with our previous TOF-SIMS quantitative analysis results in pure PS(OH) copolymers.[27] The peaks at $m/z = 103, 105,$ and 115 can be explained from the same fragmentation sequence of polystyrene. It is surprising that when the peak at $m/z = 91$ was used for PS, the plot still showed a high quality of linear fit, since it was known that the peak at $m/z = 91$ is less characteristic of polystyrene, that is, this peak may come from different pathways or may have undergone rearrangements during
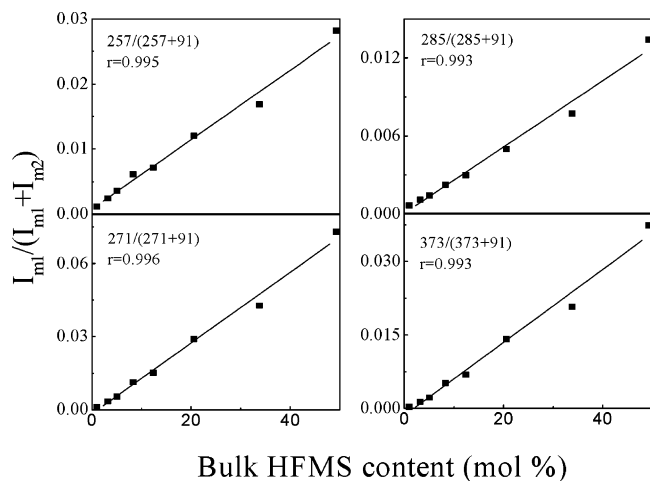
Figure 4. Intensity ratio of several positive ion peaks, 257/(257 + 91), 271/(271 + 91), 285/(285 + 91), and 373/(373 + 91), as a function of HFMS content in PS(OH) copolymers.

ion formation.[29,30] The above result indicates that good TOF-SIMS quantitative analyses of PS(OH) copolymers in PS(OH)/PVPy blends or complexes are still possible, just as in the case of pure PS(OH) copolymers.[27] A further reexamination of the slope of the curve of relative peak intensity ratios versus HFMS molar percent indicates that the slope for PS(OH)/PVPy blends or complexes is much shallower than in the pure PS(OH) case (see Table 4). There may be two reasons for this decrease of slope: one is that PVPy, indeed, has some contributions (although very little) at $m/z = 103$, 105, and 115; another reason is that the secondary ion yield of peaks at $m/z = 257$, 271, 285, and 373, characteristic of PS(OH), is lessened due to hydrogen bond formation, because its interaction with PVPy will possibly retard ion fragmentation.

Normalized Intensities of Peaks Characteristic of PS(OH) and PVPy. One approach to check which factor is the dominating one in the above discussion is to examine the normalized intensity of peaks characteristic of HFMS monomer units in PS(OH). If the latter factor plays an important role, the normalized intensity of peaks at $m/z = 257$, 271, 285, 373 will deviate downward at higher surface HFMS contents because the hydrogen bonding interactions between HFMS monomer units and PVPy are much stronger in PS(OH)/PVPy complexes, and the retarding of secondary ion yield will be more predominant. The normalized intensities of peaks at $m/z = 257$, 271, 285, and 373 were plotted against surface HFMS concentration which is calculated from [HFMS]/([HFMS] + [St] + [VPy]) (Fnot shown). It was unexpected that all four curves would show very good linear fit ($r > 0.994$). This indicates that hydrogen bond formation between PS(OH) and PVPy has very little effect on the secondary in yield of peaks characteristic of HFMS. The hydrogen bonding donor group and these peaks can be well used in quantitative analysis of the surface PS(OH) and HFMS concentrations.

The absolute intensities of positive secondary ions characteristic of PVPy at $m/z = 80$, 93, 106, and 120 have been shown to

be enhanced due to hydrogen bonding formation because the formation of pyridine ring-containing ions need to get one proton in the process of ion fragmentation,[25,26] whereas positive ions at $m/z = 132$, 195, and 209, also characteristic of PVPy, show little enhancement because their ion structures contain unsaturated double bonds. The variation of normalized intensities of peaks at $m/z = 80$, 93, 106, 120, 132, and 195 characteristic of PVPy as a function of surface VPy molar fraction (calculated from [VPy]/([HFMS] + [St] + [VPy])) are shown in Figure 5. Peaks at $m/z = 132$, 195, and 209 (curve of $m/z = 209$ not shown) give good linear fits ($r \geq 0.995$), while the normalized intensities of peaks at $m/z = 80$, 93, 106, and 120 deviate upward from linearity (especially at high VPy molar fractions) as surface VPy molar fractions increase, and they give less linear fits ($r \leq 0.985$). This is in agreement with the variation of the absolute intensities of these peaks, and it further confirms the enhancement of the yield of some pyridine-containing ions due to hydrogen bonding formation.[25,26] It should be noted that all the plots shown in Figure 5 can be used in quantitative analyses because the normalized intensities of peaks at $m/z = 80$, 93, 106, 120, 132, and 195 increase monotonically with VPy molar fraction.

Relative Peak Intensities. We have also used the relative intensities of the characteristic peaks that are related to HFMS, St monomer units in PS(OH) and VPy in PVPy in the surface quantitative analysis. The peaks at $m/z = 257$, 271, 285, and 373 have been identified as good peaks used for quantitative analysis for HFMS monomer units; the peaks at $m/z = 103$, 105, and 115 are used as the characteristic peaks of styrene monomer units. Figure 6 shows the variation of relative peak intensities as a function of surface concentration ratio of [HFMS]/([HFMS] + [VPy]) when peaks at $m/z = 271$ are used for HFMS, whereas peaks at $m/z = 106$, 120, 132, and 195 are used to be characteristic of PVPy. When $m/z = 106$ and 120 are used for PVPy, they give a less linear fit ($r \leq 0.952$), whereas when peaks at $m/z = 132$ and 195 are used for PVPy, a good linear fit is obtained ($r \geq 0.985$). This is because secondary ion yields of peaks at 132 and 195 are almost not affected by the hydrogen bond formation between PS(OH) and PVPy chains. When peaks at $m/z = 257$, 285, and 373 are used for PS(OH) and $m/z = 209$ is used for PVPy, the plots also show very good linear fits.

The relative peak intensities were also plotted against surface concentration ratios of VPy/(VPy + St) when peaks at $m/z = 80$, 93, 106, 120, 132, and 195 were used to represent VPy monomer units and peaks at $m/z = 103$ were used for styrene units. The general trends are the same as the above discussion, and good linear fits were only obtained when peaks at $m/z = 132$ and 195 were used for PVPy.

All of the above results indicate TOF-SIMS quantitative analysis is possible in polymer blends with varying mixing thermodynamics, such as in immiscibility, miscibility, and complexation states, if appropriated peaks are chosen. The specific interactions have, indeed, some effect on the secondary ion yield, especially for the hydrogen bonding acceptor polymers.

Negative Ion Spectrum. In the negative ion spectra, the dominating negative ion species is F⁻, which is a very stable negative ion. Thus, its contribution to the total intensity of the

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Table 4. Comparison of Slopes in the Curve of $I_{M1}/(I_{M1} + I_{M2})$ versus the Bulk HFMS Content in Pure PS(OH) Copolymers[27] and in PS(OH)/PVPy Blends or Complexes

sample code	$271/(271 + 103)$	$271/(271 + 105)$	$271/(271 + 115)$	$373/(373 + 103)$	$373/(373 + 105)$
PS(OH) copolymers[27]	0.007 44	0.005 86	0.005 08	0.005 25	0.003 98
PS(OH)/PVPy blends	0.005 24	0.003 77	0.003 22	0.002 98	0.002 08
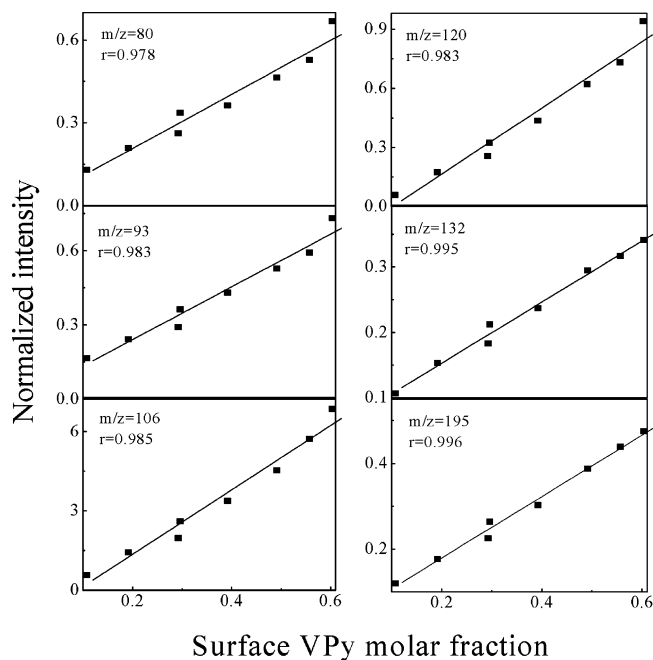
Figure 5. Normalized intensities of peaks at m/z = 80, 93, 106, 120, 132, and 195 as a function of surface PVPy molar fraction.

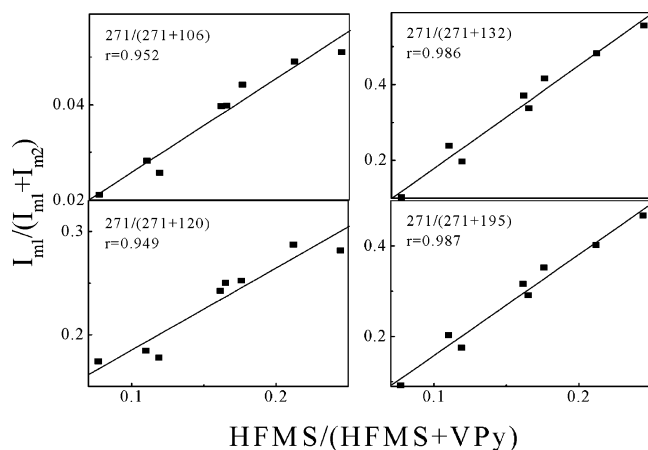**Figure 6.** Intensity ratio of several positive ion peaks, 271/(271 + 106), 271/(271 + 120), 271/(271 + 132), and 271/(271 + 195), as a function of surface concentration ratio [HFMS]/([HFMS] + [VPy]).

Figure 7. Normalized intensities of peaks at m/z = 69, 147, 166, 199, 214, and 283 in the negative ion spectrum as a function of surface HFMS molar fraction.

negative ion peaks is no longer linearly related to surface composition of the sample, leading to errors in calculating the normalized intensities, so the intensity for peaks with m/z <30 was not included in the calculation of the total intensity of the negative ions. Then the normalized intensities based on the corrected total intensities were plotted against the surface HFMS or VPy molar fraction using their characteristic peaks. Figure 7 shows the variation of normalized intensities of peaks at m/z = 69, 147, 166, 199, 214, and 283 as a function of surface HFMS molar fraction. The plots of peak at m/z = 69 and 166 give the
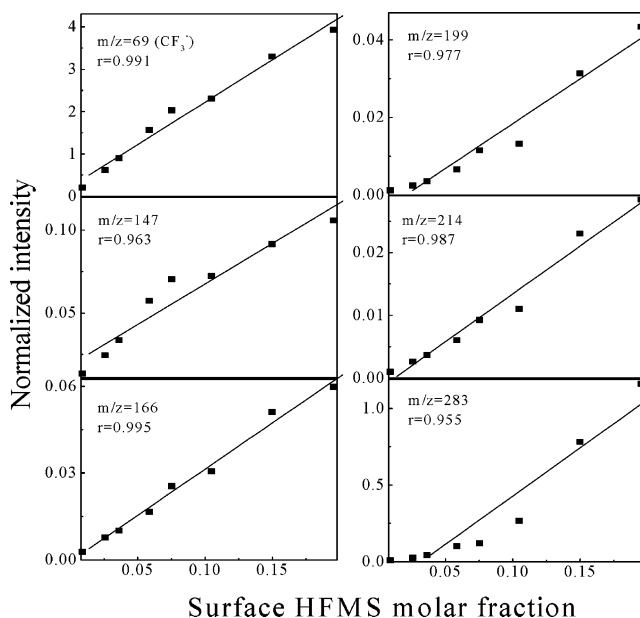
best linear fit ($r > 0.99$), whereas the plot of the peak at m/z = 283 gives the worst linear fit ($r = 0.955$), although its secondary ion structure is directly related to HFMS monomer structure. The plot of peak at m/z = 283 greatly deviates upward from linearity. For normalized intensities of peaks at m/z = 78, 92, 93, 104, and 120 characteristic of PVPy, they all give linear fits ($r > 0.97$) (plots not shown). Contrary to that in the positive ion SIMS spectrum, in the negative SIMS spectra, the secondary ion yields of peaks characteristic of PVPy were almost not affected by the hydrogen bond formation in PS(OH)/PVPy blends or complexes, whereas the secondary ion yields of peaks characteristic of PS(OH), such as peaks at m/z = 283, are enhanced due to hydrogen bond formation. This is reasonable, considering the proton transfer from the hydroxyl to the pyridine groups in the hydrogen bond formation.

CONCLUSIONS

TOF-SIMS and XPS were used to quantitatively analyze the surface chemical composition in PS(OH)/PVPy blends or complexes with different mixing thermodynamics in the immiscibility, miscibility, and complexation region. Good quantitative analysis for PS(OH) species was kept in PS(OH)/PVPy blends or complexes, just as the case in pure PS(OH) copolymers. In the positive ion spectrum, the normalized intensities or relative peak intensities give very good linear correlation with surface component composition when peaks at m/z = 257, 271, 285, and 373 are used for HFMS, peaks at m/z = 91, 103, 105, and 115 are used for St, and peaks at m/z = 132, 195, and 209 are used for PVPy. Peaks at

$m/z = 80$, 93, 106, and 120, characteristic of PVPy, give a less linear correlation due to enhancement of their secondary ion yield resulting from hydrogen bonding interaction. In the negative ion spectrum, the normalized intensities of peaks characteristic of PVPy seem to be not affected by hydrogen bond formation and can be used in quantitative analysis, whereas peaks characteristic of HFMS, such as the peak at $m/z = 283$, cannot be used in quantitative analysis due to enhancement of its secondary ion yield resulting from hydrogen bonding interactions.