



# Surface quantitative characterization of poly(styrene-*co*-4-vinyl phenol)/poly(styrene-*co*-4-vinyl pyridine) blends with controlled hydrogen bonding interactions

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## Abstract

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*-4-vinyl phenol) (STVPh)/poly(styrene-*co*-4-vinyl pyridine) (STVPy) blends or complexes when the hydroxyl contents in STVPh copolymers were gradually increased. It was found that different mixing thermodynamics such as immiscibility, miscibility and complexation has little effect on the quantitative analysis of surface concentrations in the blends or complexes using ToF-SIMS. In the positive spectra, the normalized intensities or relative peak intensities can both be used to quantitatively analyze the surface vinyl phenol (VPh), styrene and vinyl pyridine (VPy) concentrations when peaks at  $m/z = 119, 120$  are used for VPh, peaks at  $m/z = 103, 105, 115$  for styrene and peaks at  $m/z = 80, 93, 106$  for VPy monomer units. In the negative spectra, the normalized intensities of peaks characteristic of VPh monomer units ( $m/z = 16, 17, 93$ ) seems to be not affected by hydrogen bonding formation and can be used in quantitative analysis.

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## 1. Introduction

Many materials properties (wetting, adhesion, compatibility, catalysis, 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 ppm, respectively) [3–8]. Thus, ToF-SIMS has gained

more and more importance in the surface characterization of materials owing to its unique advantages 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 [2, 9–16], the intensities of some SIMS characteristic peaks unique 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 compositions showed that SIMS can be used as a quantitative technique. However, the selection of SIMS peaks needs to be made carefully and

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there is 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 hopefully be established.

It was known that 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 an immiscible blend could become miscible but also the blends could further form interpolymer complexes, i.e. the two polymers form precipitates (complexes) upon mixing the two constituent polymer solutions in a common solvent [18–20]. It is believed that two different types of polymer chains are randomly mixed in a miscible blend while they are ‘paired’ in the interpolymer complexes [18].

The different mixing thermodynamics in polymer blends described above will have a large effect on the matrix effect, which was always attributed to the ill quantitative results of SIMS. 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 pre-secondary ion was associated, this is called the matrix effect. 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, 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. 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 interactions between functional groups on the different neighboring chains. In interpolymer complexes where unlike chains are interwoven with each other [18], the interpolymer interaction are much stronger and the matrix side-effect should be more deleterious for SIMS quantification.

There have been no reports in the literature about ToF-SIMS surface quantitative analysis on interpolymer complexes. Thus it is interesting to try to use ToF-SIMS as a quantitative tool for surface analysis of polymer blends with increasing mixing thermodynamics. In this contribution, ToF-SIMS was used to quantitatively characterize the surfaces of poly(styrene-*co*-4-vinyl phenol)/poly(styrene-*co*-4-vinyl pyridine) (STVPh/STVPy) blends or complexes where the mixing thermodynamics changes substantially from immiscibility to miscibility and then to complexation by increasing the hydroxyl contents in STVPh.

## 2. Experimental section

### 2.1. Materials

STVPh copolymers were synthesized by bulk copolymerization of styrene and 4-acetoxystyrene at 60 °C using AIBN as initiator, followed by hydrolysis with hydrazine hydrate in 1,4-dioxane, the conversion of hydrolysis was quantitative, as evidenced from FT-IR and <sup>1</sup>H NMR [18]. The molecular weight, polydispersity index and VPh content of STVPh random copolymers was determined by size exclusion chromatography (SEC) and <sup>1</sup>H NMR from the precursor—poly(styrene-*co*-4-acetoxystyrene). The final products were purified by precipitation from THF to *n*-hexane three times. STVPy copolymers were synthesized as previously described [18]. The molecular weight of STVPy was controlled by altering reaction temperature and the amount of initiator (AIBN). The molar content of 4-vinyl pyridine (VPh) was determined from nitrogen measurements. The number-average molecular weight and polydispersity index of STVPy copolymers were determined from SEC. Table 1 lists the physical properties of STVPh and STVPy copolymers. Polystyrene prepared by anionic polymerization was also used in this study.

### 2.2. Sample preparation

STVPh copolymers and STVPy-74 were separately dissolved in THF at a concentration of 15 g/l. A blend solution was prepared by mixing the same amount of each polymer solution under stirring. Depending on the VPh contents in STVPh, the mixed solutions might remain clear or form an interpolymer complex precipitate. For STVPh-0/STVPy-74, STVPh-3/STVPy-74, STVPh-9/STVPy-74, STVPh-16/STVPy-74, the clear solutions were spin-cast at 3800 rpm onto silicon wafers. The film thickness was kept at about 200–230 nm using the same concentration of the solution and the same spin rate. When the VPh contents in STVPh reach or are higher than 21 mol%, the blend solution contains interpolymer complex precipitate, the precipitate was separated by centrifugation, washed with THF three times, and then kept in THF. The chemical compositions of complex precipitates were determined from nitrogen

Table 1  
The characteristic data of STVPh and STVPy samples used in this study

Sample code	VPh or VPy contents (mol%)	$M_n/10^3$	$M_w/M_n$	$T_g$ (°C)
STVPh-0	0	116.2	1.03	101.2
STVPh-3	2.86	89.5	1.60	105.9
STVPh-9	9.02	101.8	1.52	113.4
STVPh-16	16.13	116.7	1.50	120.7
STVPh-21	21.30	115.0	1.55	125.3
STVPh-48	48.4	144.0	1.52	139.9
STVPh-76	75.5	202.5	1.67	163.4
STVPy-74	74.4	108.5	1.68	145.9

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 over night.

### 2.3. Surface characterization

The surface properties of a series of STVPh/STVPy blends or complexes were studied by XPS, ToF-SIMS. The surface chemical composition and the binding energy were obtained from XPS. The XPS spectra were obtained with a PHI 5600 multi-technique system equipped with a monochromatic Al  $K_{\alpha}$  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  $45^{\circ}$ , corresponding to a sampling depth of approximately 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  $200 \mu\text{m} \times 200 \mu\text{m}$ , and the total ion dose for each spectrum acquisition was  $<4 \times 10^{12}$  ions/cm<sup>2</sup>. 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 STVPh/STVPy blends or complexes were acquired in negative modes using a  $^{69}\text{Ga}^{+}$  beam at 25 kV.

## 3. Results and discussion

The glass transition temperatures of STVPh/STVPy blends or complexes with different VPh contents in STVPh are shown in Table 2. STVPh-0/STVPy-74, STVPh-3/STVPy-74 blends are immiscible showing two distinct  $T_g$ 's. STVPh-9/STVPy-74 blends are miscible which shows only one  $T_g$ . When VPh contents in STVPh reach or being higher than 21 mol%, STVPh and STVPy-74 form interpolymer complexes which certainly shows one  $T_g$ . The  $T_g$  values of interpolymer complexes are much higher than calculated  $T_g$  from Fox equation. The higher the VPh

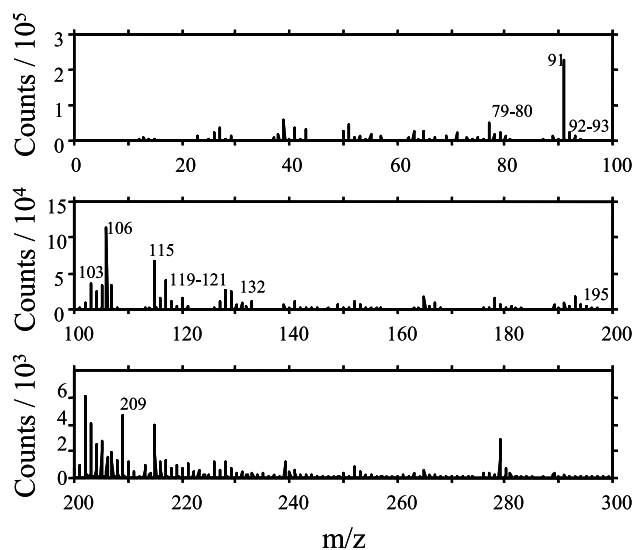


Fig. 1. Positive ToF-SIMS spectra of STVPh-21/STVPy-74 complexes in the range of  $m/z = 0$ –300.

contents, the larger the differences between the measured and calculated  $T_g$  indicating that in the STVPh/STVPy complexes, the mobility of individual chains is greatly reduced as a result of increasing hydrogen bonding interactions between STVPh and STVPy [18,23].

The surface chemical composition of the blends or interpolymer complexes was calculated from the N/C peak area ratio in the XPS spectrum and the results are also shown in Table 2. When the hydroxyl contents in STVPh increased from 3 to 76 mol%, STVPh/STVPy blends or complexes have undergone an immiscibility–miscibility-complexation transition; there is a first increase of surface STVPh excess; when the hydroxyl contents in STVPh reach or are higher than 21 mol%, the surface and bulk composition are very close. This indicates that interpolymer complexation can almost eliminate surface enrichment of polymer blends due to chain segment pairing between STVPh and STVPy chain segments in the interpolymer complexes [23].

### 3.1. ToF-SIMS surface quantification

Fig. 1 shows a typical positive ToF-SIMS spectrum of

Table 2  
Characteristic data of STVPh/STVPy blends or complexes

Sample code	Bulk composition (STVPh, mol%)	$T_g$ (°C)	Surface concentration (STVPh, mol%)	Surface excess of STVPh (mol%)
STVPh-0/STVPy-74	50.18	102.0/145.8	77.51	27.33
STVPh-3/STVPy-74	50.07	112.4/145.7	84.96	34.89
STVPh-9/STVPy-74	49.84	134.2	91.46	41.62
STVPh-16/STVPy-74	49.57	140.6	94.22	44.65
STVPh-21/STVPy-74	58.71	150.5	62.47	3.76
STVPh-48/STVPy-74	62.43	159.7	64.16	1.73
STVPh-76/STVPy-74	60.20	173.9	61.21	1.01

STVPh-21/STVPy complexes. The SIMS spectra of STVPh [24] and STVPy [25] have previously been reported. Peaks at  $m/z = 119, 120, 121$  characteristic of VPh monomer units and peaks at  $m/z = 80, 93, 106, 132, 195$  characteristic of VPy can distinguish them from styrene units, the characteristic peaks of which is at  $m/z = 27, 39, 51, 77, 91, 103, 105, 115, 128, 141, 152, 165, 178$  and  $193$ . In the negative ion SIMS spectrum of STVPh-21/STVPy-74 complexes shown in Fig. 2, VPh and VPy monomer units can distinguish them from styrene units by the presence of peaks at  $m/z = 16$  ( $O^-$ ),  $17$  ( $OH^-$ ),  $93, 117, 119$  and peaks at  $m/z = 50$  ( $C_3N^-$ ), respectively. Some of the possible structures of the positive and negative ions are shown in Table 3.

The surface chemical composition of the polymer blends or complexes was obtained from XPS (see Table 2). The ToF-SIMS data were analyzed with the objective to test whether these data can be used in quantitative surface 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 monomer units in STVPh or STVPy can be used. The normalized intensity is the intensity of a peak normalized by the total intensity.

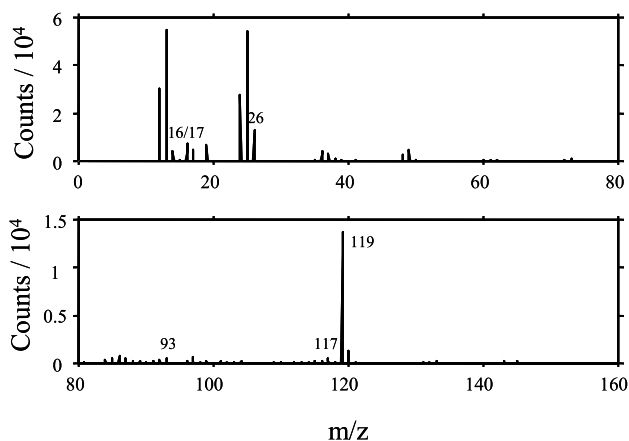


Fig. 2. Negative ToF-SIMS spectra of STVPh-21/STVPy-74 complexes in the range of  $m/z = 0-160$ .

### 3.2. Positive spectrum

Li et al. [25] have previously reported that the absolute intensities of positive secondary ions characteristic of STVPy at  $m/z = 80, 93, 106$  in STVPh/STVPy blends are enhanced due to hydrogen bonding formation. We have first checked whether the normalized intensities of these peaks characteristic of VPy units can be used in quantitative surface analysis. Fig. 3 shows the variation of normalized

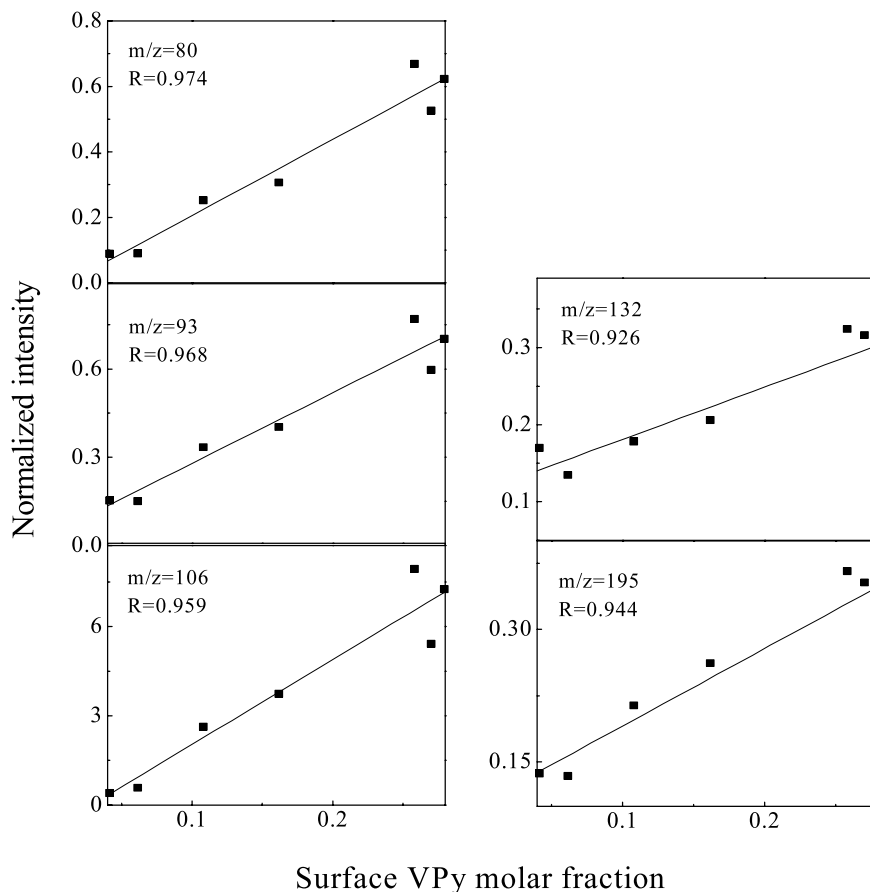
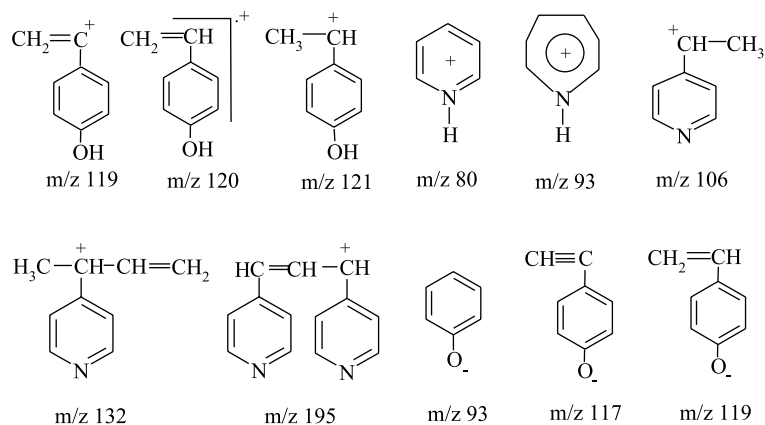


Fig. 3. Normalized intensities of peaks at  $m/z = 80, 93, 106, 132, 195$  as a function of surface VPy molar fraction.

Table 3

Proposed secondary ion structures for the some of characteristic peaks in the positive and negative ion SIMS spectra of STVPh/STVPy blends or complexes



intensities of peaks at  $m/z = 80, 93, 106, 132, 195$  as a function of surface VPy concentrations which is calculated from  $[VPy]/([St]_{STVPh} + [St]_{STVPh} + [VPh] + [VPy])$ . It was unexpected that all five curves show fairly good linear fit. This indicates that although hydrogen bonding formation between STVPh and STVPy has certain effect on the

secondary ion yield of peaks characteristic of VPy, they do not influence the use of these peaks in quantitative analysis if normalized intensities were used.

We have also used the relative intensities ( $I_{m1}/(I_{m1} + I_{m2})$ ) of the characteristic peaks that are related to VPy, VPh and St monomer units in the surface quantitative analyses.

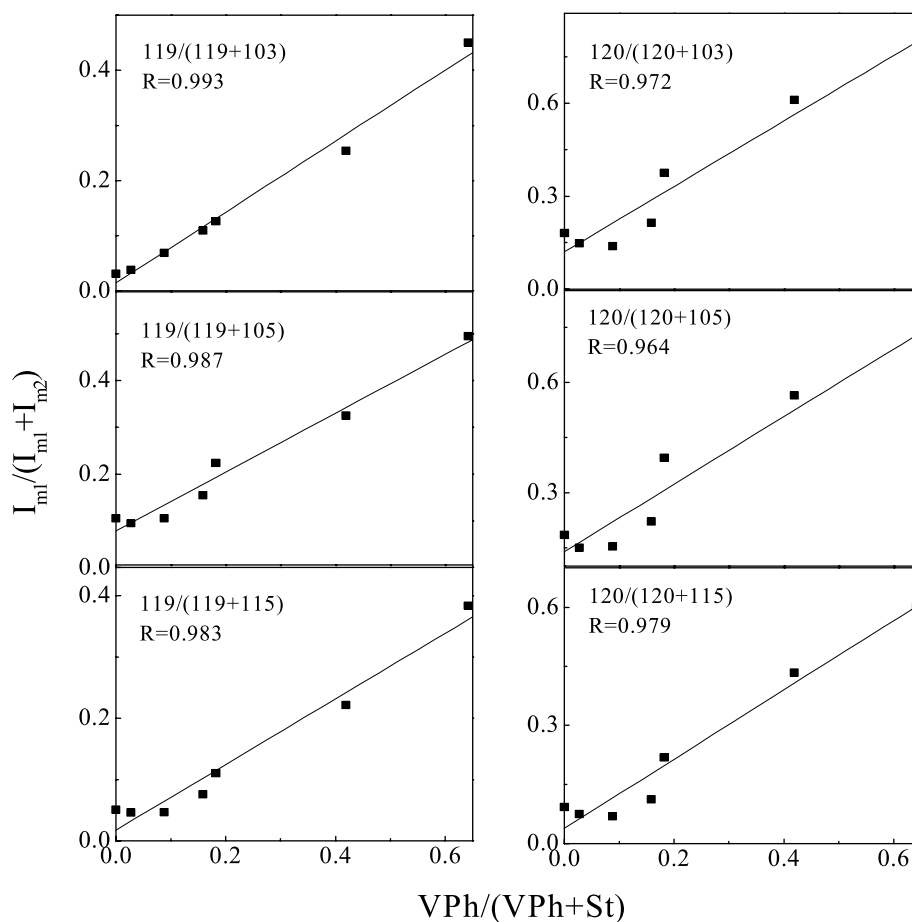


Fig. 4. Intensity ratio of several positive ion peaks: 119/(119 + 103), 119/(119 + 105), 119/(119 + 115), 120/(120 + 103), 120/(120 + 105), 120/(120 + 115) as a function of surface concentration ratio of  $[VPh]/([VPh] + [St]_{STVPh} + [St]_{STVPh})$ .

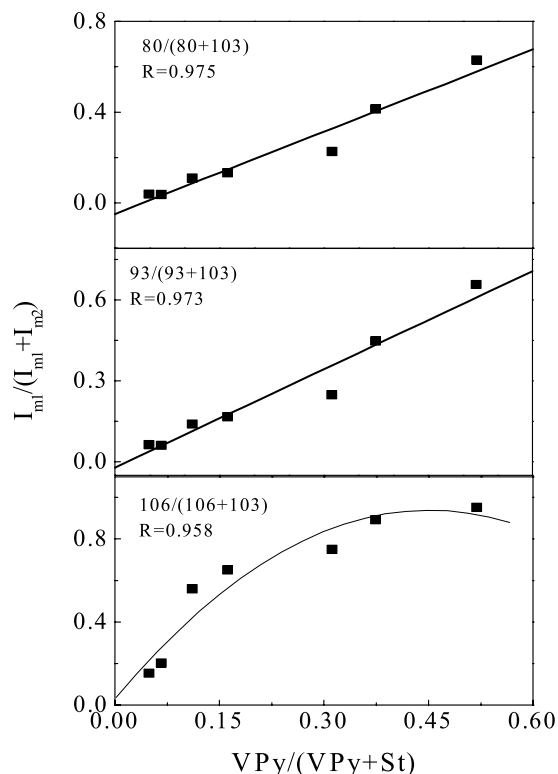


Fig. 5. Relative peak intensities of several ion peaks: 80/(80 + 103), 93/(93 + 103), 106/(106 + 103) as a function of surface concentration ratio of  $[VPy]/([VPy] + [St]_{STVPy} + [St]_{STVPh})$ .

The peaks at  $m/z = 119, 120$  have been used for VPh, the peaks at  $m/z = 80, 93, 106$  used for VPy and peaks at  $m/z = 103, 105$  and  $115$  for styrene monomer units. Fig. 4 shows the variation of relative peak intensities as a function of surface concentration ratio of  $[VPh]/([VPh] + [St]_{STVPy} + [St]_{STVPh})$  when peaks at  $m/z = 119, 120$  are used for VPh and peaks at  $m/z = 103, 105$  and  $115$  are used for St. They all give linear fit with small deviation at low  $[VPh]/([VPh] + [St]_{STVPy} + [St]_{STVPh})$  except for  $119/(119 + 103)$ , with which very good linear fit is obtained.

Fig. 5 shows the variation of relative peak intensities as a function of surface concentration ratio of  $[VPy]/([VPy] + [St]_{STVPy} + [St]_{STVPh})$  when peaks at  $m/z = 80, 93, 106$  are used to represent VPy monomer units and peaks at  $m/z = 103$  are used for styrene units. Good linear fit was obtained when peaks at  $m/z = 80, 93$  were used. But when peaks at  $m/z = 106$  were used for VPy, non-linear fit was obtained, this is possibly due to the contribution of styrene units to the SIMS peak at  $m/z = 106$ .

### 3.3. Negative spectrum

The variation of normalized intensities of peaks at  $m/z = 16, 17, 93, 117$  and  $119$  as a function of surface VPh molar fraction calculated from  $[VPh]/([St]_{STVPy} + [St]_{STVPh} + [VPh] + [VPy])$  are shown in Fig. 6. Peaks

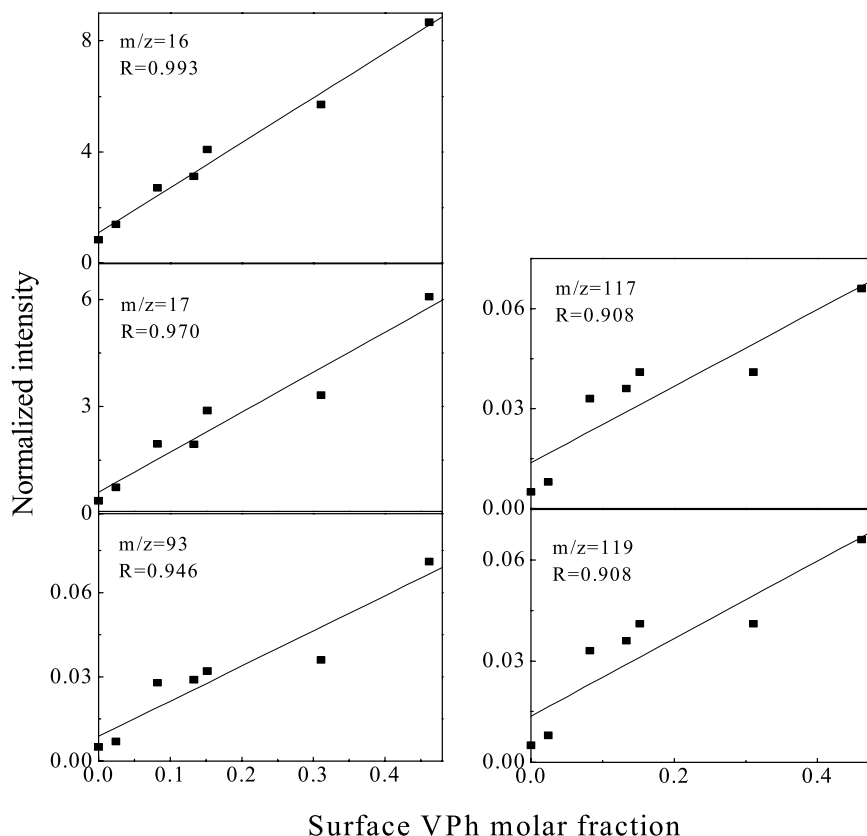


Fig. 6. Normalized intensities of peaks at  $m/z = 16, 17, 93, 117, 119$  as a function of surface VPh molar fraction.

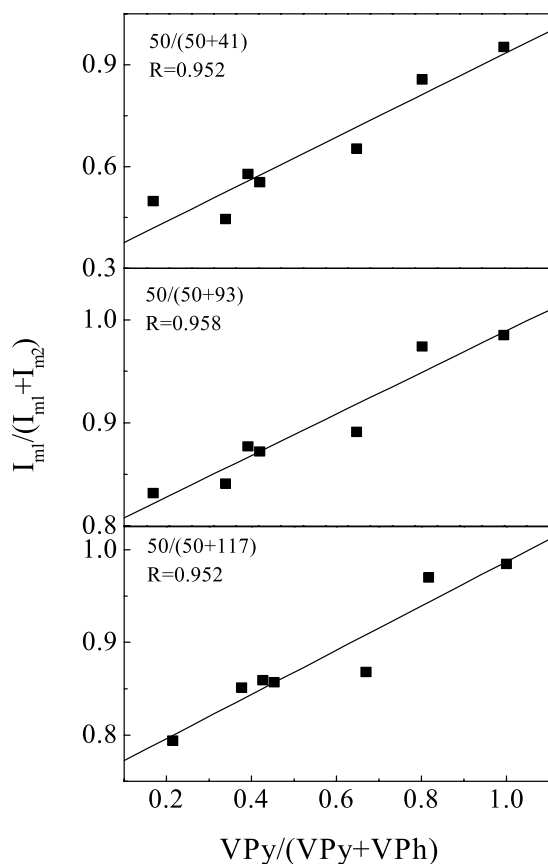


Fig. 7. Relative peak intensities of several ion peaks: 50/(50 + 41), 50/(50 + 93), 50/(50 + 117) as a function of surface concentration ratio of  $[VPy]/([VPy] + [VPh])$ .

at  $m/z = 16, 17$  and  $93$  give very good linear fit while the fit of the normalized intensities of peaks at  $m/z = 117$  and  $119$  is not good although the structures of negative ions associated with peaks at  $m/z = 117$  and  $119$  are directly related to VPh structure. Since the intensities of peaks at  $m/z = 117$  and  $119$  are very low, they are not sensitive to the surface composition and cannot be used in quantitative analysis.

Fig. 7 shows the variation of relative peak intensities as a function of surface concentration ratio of  $[VPy]/([VPy] + [VPh])$  when peaks at  $m/z = 50$  ( $C_3N^-$ ) are used to represent VPy monomer units and peaks at  $m/z = 41$  ( $C_2HO^-$ ),  $93, 117$  are used for VPh units. All three curves show good linear fit.

All of the above results indicate that ToF-SIMS surface quantitative analysis is possible in polymer blends with varying mixing thermodynamics, i.e., immiscibility, miscibility and complexation states, if appropriate peaks are chosen.

#### 4. Conclusions

Different mixing thermodynamics in polymer blends such as immiscibility, miscibility and complexation has less

than expected effect on the ToF-SIMS quantitative analysis of surface compositions in the blends or complexes. In the positive spectra, the normalized intensities or relative peak intensities can both be used to quantitatively analyze the surface vinyl phenol (VPh), styrene and vinyl pyridine (VPy) concentrations when peaks at  $m/z = 119, 120$  are used for VPh, peaks at  $m/z = 103, 105, 115$  for styrene and peaks at  $m/z = 80, 93, 106$  for VPy. In the negative spectrum, the normalized intensities of peaks characteristic of VPh monomer units ( $m/z = 16, 17, 93$ ) can be used in quantitative analysis.

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