Quantitative surface characterization of poly(styrene)/poly(4-vinyl phenol) random and block copolymers by ToF-SIMS and XPS

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A series of spin-cast films of poly(styrene-co-4-vinyl phenol) (STVPh) random copolymers and polystyrene-b-poly(4-vinyl phenol) (PS-b-PVPh), which have the same building units but different chain architecture, were analysed by x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The XPS results show that there was no surface segregation of any component for the STVPh random copolymers. The calibration curves for ToF-SIMS intensity as a function of the VPh content were obtained for the STVPh random copolymers. These calibration curves were used to determine the surface chemical composition of the block copolymers. The ToF-SIMS results agreed well with the angle-dependent XPS results. Time-of-flight SIMS also was shown to be able to distinguish PS-b-PVPh from the STVPh random copolymers by the absence of the peaks corresponding to the St–VPh or St–St–VPh sequence structures. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: ToF-SIMS; XPS; copolymer

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is a well-established surface characterization technique1–3 but in the past 10 years time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used extensively in surface characterization of polymers. The ToF-SIMS technique offers high molecular specificity, extreme surface sensitivity and high mass resolution1–8 but, compared with XPS, it has a significant drawback in that it is not used easily in quantitative analysis. The obstacle to easy quantitative analysis is the fact that the mechanisms from which secondary ions are created and emitted are not well understood.

Nevertheless, quantification by SIMS has become more popular in the past few years. It has been shown that quantitative or semi-quantitative analysis could be done with static SIMS on copolymers,9–20 polymer blends,21–24 etc. In the above systems, the intensities of SIMS characteristic peaks unique to each component were compared with the bulk compositions or with the compositions determined by XPS. The good correlation between these SIMS intensities and copolymer or polymer blend surface compositions showed that static SIMS can be used as a quantitative technique in these cases. However, such conclusions cannot be generalized until more polymer systems are analysed.

To improve the quantification, an established quantitative surface analysis such as XPS could be used to determine independently the surface composition of block and graft copolymers or polymer blends. The correlation between the surface composition and the SIMS intensities then can be established. Unfortunately, XPS also has a few limitations. First, in a blend or copolymer a unique element or functional group has to be present. Second, XPS and SIMS have different sampling depths: SIMS is more surface sensitive than XPS. Hence, the correlation between the surface chemical compositions determined by XPS and the SIMS intensities is not perfect.

In previous studies, ToF-SIMS results were used to characterize quantitatively poly(styrene-co-p-hexafluoro-hydroxyisopropyl-o-methyl styrene) copolymers (poly(St-co-HFMS)).20 For this polymer, the hydroxyl groups of the HFMS segments can form only very weak hydrogen bonds owing to the steric hindrance of neighbouring bulky trifluoromethyl groups. It was found that the intensity ratio of the characteristic peak of each component in the copolymer is related linearly to the copolymer composition. In this work, a copolymer that is structurally similar to poly(St-co-HFMS) but with a stronger hydrogen bonding interaction between the comonomers was studied. We have chosen poly(styrene-co-4-vinyl phenol) (STVPh) random copolymers with a vinyl
phenol content of 0–100 mol.%. In this case, one may suspect that the matrix effect will exert a more adverse effect on the quantification analyses. After the correlation between the surface composition and SIMS intensities is established, surface quantification of block STVPh copolymers will be performed and the results will be compared with the results of XPS.

Ratner et al. reported the results of quadrupole SIMS and XPS characterization of STVPh random copolymers and pure PVPh. It is of interest to compare their results with those obtained by ToF-SIMS. In addition, in the synthesis of STVPh and PS-b-PVPh we used 4-acetoxystyrene as the precursor for 4-vinyl phenol, which can be produced via hydrolysis of 4-acetoxy styrene monomer by hydrazine hydrate in dioxane. This can ensure the complete removal of the acetyl group, with the final products being free from crosslinkings.

EXPERIMENTAL

Sample preparation
Styrene, 4-acetoxystyrene, methacryloyl chloride, ethylene oxide and benzyl bromide were purified and vacuum distilled in the presence of calcium hydride and/or sodium mirror just before use. Copper bromide and 2,2'-dipyridyl were used without further purification. A general scheme for preparing STVPh and PS-b-PVPh is shown in Scheme 1.

The STVPh random copolymers were synthesized by bulk copolymerization of styrene and 4-acetoxystyrene at 60°C using azobisisobutyronitrile (AIBN) as the initiator, followed by hydrolysis with hydrazine hydrate in 1,4-dioxane. The hydrolysis was complete, as evidenced from the results of fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (1H-NMR). The hydrolysis of the 4-acetoxy styrene residues into 4-vinyl phenol was complete, as evidenced from 1H-NMR. The signal due to the –CH3 group of 4-acetoxystyrene (at 2.3 ppm) was absent in the NMR spectrum of STVPh-21, as shown in Fig. 1. The FTIR spectrum obtained after hydrolysis indicates that carbonyl adsorption at 1758 cm⁻¹, which was present in the parent copolymer, disappeared completely. Instead, strong absorption bands were seen at 3531 and 3400 cm⁻¹.

The molecular weight and polydispersity index of the STVPh random copolymers were determined by size exclusion chromatography (SEC). The vinyl phenol (VPh) content of the copolymers was determined by 1H-NMR measurements of the precursor, poly(styrene-co-4-acetoxy styrene). The final products were purified by precipitation from tetrahydrofuran (THF) to n-hexane three times.

The PS-b-PVPh was synthesized by atom-transfer radical polymerization (ATRP) of styrene and 4-acetoxy styrene sequentially. In a typical polymerization, styrene (9.99 g) was combined with benzyl bromide (0.0952 ml, 1 equiv), CuBr (0.1148 g, 1 equiv) and 2,2'-dipyridyl (0.375 g, 3 equiv), with butyl acetate (1 ml) as solvent/plasticizer in a sealable reaction vessel. The heterogeneous solution was degassed, back-filled with nitrogen and placed in a bath at 130°C for 8 h. The brownish solid in the tube was dissolved in THF, precipitated into methanol twice (adding ~2% acetic acid) and then dried at 80°C for 2 days in a vacuum. The molecular weights of polystyrene macroinitiators were determined by SEC using polystyrene as the standard. The number-averaged molecular weight ($\bar{M}_n$) of polystyrene macroinitiators is 12 000 g mol⁻¹ and the polydispersity index is 1.24. The polystyrene macroinitiators (2 g) were combined with CuBr (0.0574 g), 2,2'-dipyridyl (0.1875 g) and

![Scheme 1. Reaction scheme for the preparation of poly(styrene-co-4-vinyl phenol) and polystyrene-b-poly(4-vinyl phenol).](image-url)
Table 1. The molecular weight and polydispersity of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>VPh content (mol.%)</th>
<th>M_n/10^5</th>
<th>M_w/M_n</th>
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<tbody>
<tr>
<td>polystyrene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(anionic polymer)</td>
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<td>1.2</td>
<td>1.0</td>
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<td>STVPh-3</td>
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<td>STVPh-5</td>
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<td>1.4</td>
<td>1.5</td>
</tr>
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<td>48.4</td>
<td>1.4</td>
<td>1.5</td>
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<td>STVPh-57</td>
<td>56.82</td>
<td>2.0</td>
<td>1.4</td>
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<td>2.0</td>
<td>1.66</td>
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<td>STVPh-100</td>
<td>100</td>
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<td>PS-b-PVPh-26</td>
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<td>0.2</td>
<td>1.3</td>
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<td>PS-b-PVPh-41</td>
<td>40.61</td>
<td>0.2</td>
<td>1.3</td>
</tr>
</tbody>
</table>

4-acetoxy styrene (2 ml) in a sealable reaction vessel. The solutions were degassed, back-filled with nitrogen, heated to 130 °C for different times and then quenched in liquid nitrogen. The solids were dissolved in THF and then precipitated out in methanol with a small amount of acetic acid. The polystyrene-b-poly(4-acetoxy styrene) copolymers were characterized by SEC and 1H-NMR and the molecular weight of the poly(4-acetoxy styrene) block was determined by 1H-NMR. The PS-b-PVPh copolymer was produced by hydrolysis of polystyrene-b-poly(4-acetoxy styrene) by hydrazine hydrate in dioxane and then purified by precipitation from THF into n-hexane three times. Then PS-b-PVPh was extracted with cyclohexane and methanol for 12 h to remove the unreacted polystyrene macroinitiator and the PVPh homopolymer, respectively.

All of the characteristic data of STVPh and PS-b-PVPh are listed in Table 1. Samples are denoted by STVPh-X and PS-b-PVPh-X, where X represents the molar content of the VPh monomer unit. The STVPh and PS-b-PVPh copolymers were dissolved in THF and the concentration of the solutions was 1.5% (w/v). The solutions finally were spin-cast onto silicon wafers to prepare uniform polymer films suitable for XPS and ToF-SIMS experiments.

Surface characterization

The XPS spectra were obtained with a PHI 5600 multi-technique system by using a 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 take-off angle θ (the angle between the surface and the axis of the analyser) of the photoelectron was 45°. The sampling depth was calculated to be ~5.5 nm using the equation

\[ d = 3 \lambda \sin \theta \]

where \( \lambda \) is the attenuation length, which is assumed to be 2.6 nm.¹

The ToF-SIMS measurements were carried out on a Physical electronics PHI 7200 ToF-SIMS spectrometer.

RESULTS AND DISCUSSION

Analysis of STVPh random copolymers by XPS

All the STVPh random copolymer films showed the presence of only two elements: carbon and oxygen. No signal from the silicon substrate and other contaminants could be detected, indicating that the copolymers were clean and the film thickness was uniformly more than ~10 nm thick. The XPS C 1s and O 1s spectra of STVPh are similar to those reported previously.² The C 1s spectrum is resolved into four component peaks, representing different chemical environments: the saturated hydrocarbon, aromatic ring carbon, C-OH and π - π* shake-up satellite peaks at 285.0, 284.6, 286.6 and 291.3 eV, respectively. For STVPh with a very low VPh content the C 1s spectrum is similar to that of pure polystyrene.

Figure 2 shows the surface VPh concentration as determined by XPS as a function of the bulk VPh concentration. The results indicate that the surface composition of the pure copolymer films is similar to the bulk composition. Thus, we can develop the correlation between ToF-SIMS intensities and the surface composition of the copolymer. The correlation can be used in the ToF-SIMS surface quantification of PS-b-PVPh.

ToF-SIMS spectra

A typical positive SIMS spectrum of STVPh-76 is shown in Fig. 3. A comparison of Fig. 3 with the spectrum of polystyrene prepared by anionic polymerization indicates the primary ions were generated from a caesium ion source (8 kV). The scanned area was 200 μm × 200 μm and the total ion dose for each spectrum acquisition was <10¹¹ ions cm⁻². Charge compensation was realized by low-energy (0–70 eV) flooding electrons being pulsed out of phase with the primary ion beam. Both positive and negative high-resolution mass spectra were recorded.

Figure 2. The surface VPh concentration versus the bulk VPh concentration for a series of STVPh random copolymers.
Figure 3. Positive ToF-SIMS spectrum of the STVPh-76 copolymer in the range of m/z = 0–400.

Figure 4. Positive ToF-SIMS spectra of the STVPh-76 in an expanded scale for m/z = 29, 42, 43, 53, 55 and 105.

that the characteristic peaks of polystyrene at m/z = 27, 39, 51, 77, 91, 103, 105, 115, 128, 141, 152, 165, 178 and 193 are present also in the STVPh-76 spectrum. The largest peak in STVPh with the VPh content varying from 1 to 57 mol.% is at m/z = 91, whereas that in STVPh with a VPh content of >76 mol.% is at m/z = 107. The STVPh can be distinguished from polystyrene by the presence of a series of oxygen-containing fragments at m/z = 29.00 (CHO⁺), 41.00 (C₂H₂O⁺), 42.01 (C₂H₃O⁺), 43.02 (C₂H₄O⁺), 45.04 (C₃H₅O⁺), 53.00 (C₃H₇O⁺), 55.08 (C₃H₉O⁺), 105.08 (C₇H₉O⁺), 107, 119,
120, 121, 133, 145, 157, 183, 209, 225 and 311. For secondary ions with \( m/z < 107 \), the oxygen-containing peaks are accompanied by large hydrocarbon peaks. However, these oxygen-containing peaks are resolvable from the \( C_3H_y^+ \) hydrocarbon peaks in the high-mass-resolution ToF-SIMS spectra, as shown in Fig. 4. The possible structures of some of the characteristic ions are shown in Scheme 2 and some of these structures were reported by Chilkoti et al.\(^\text{12}\) It should be noted that among these characteristic peaks of STVPh, if we denote the styrene (St) monomer units as A and the VPh monomer units as B, the peak at \( m/z = 193 \) is associated with AA, the peaks at \( m/z = 183 \) and 209 are associated with AB (St–VPh), the peak at \( m/z = 225 \) is associated with BB (VPh–VPh) and the peak at \( m/z = 311 \) is associated with \( A_2B \) (St–St–VPh). The peaks at \( m/z = 381 \) and 451 were observed in the spectra of some copolymer samples. The origin of these peaks is still unclear and could be due to some surface contamination.

Figure 5 shows the negative ion spectrum of STVPh-76. Except for the peaks at \( m/z = 13 \) (CH\(^+\)), 25 (C\(_2\)H\(_3\)\(^+\)), 37 (C\(_3\)H\(_5\)\(^+\)), 49 (C\(_4\)H\(_7\)\(^+\)), 62 (C\(_5\)H\(_9\)\(^+\)) and 73 (C\(_6\)H\(_9\)\(^+\)), which are present also in the negative spectrum of polystyrene, STVPh can be distinguished from polystyrene by the presence of characteristic peaks at \( m/z = 16 \) (O\(^-\)), 17 (OH\(^-\)), 41 (C\(_2\)HO\(^-\)), 52 (C\(_3\)O\(^-\)), 53 (C\(_3\)HO\(^-\)), 89 (C\(_6\)HO\(^-\)), 93, 106, 107, 117, 119, 133, 143, 157, 169, 195, 209, 223 and 237. Some of the possible structures of the negative ions are shown in Scheme 3. The peak at \( m/z = 119 \) has high intensity and is related directly to the VPh monomer units (M – H\(^-\)). Similar to the positive spectra, the peaks at \( m/z = 195 \) and 209 are associated with AB (St–VPh) where the peaks at \( m/z = 223 \) and 237 are associated with BB (VPh–VPh).

**Quantitative analysis of STVPh random copolymers by ToF-SIMS**

**Positive spectrum**

A general feature of this series of STVPh copolymers is that, compared with polystyrene, the intensity of the \( C_3H_y^+ \) clusters (\( m/z < 100 \)) is enhanced, especially in the case of STVPh-100. The intensity of the \( C_3H_y^+ \) ions with a high hydrogen content is enhanced relative to that of the \( C_3H_y^+ \) ions with a low hydrogen content. This is due to the fact that STVPh copolymers with a high hydroxyl content can donate ‘living hydrogen’ or due to the attachment of an oxygen atom to the benzene ring. Owing to the high mass resolution of the ToF-SIMS spectrometer, the enhancement of the \( C_3H_y^+ \) peak intensity can be confirmed and should not be taken as the contribution from \( C_3H_yO^+ \), as reported previously.\(^\text{12}\)

X-ray photoelectron spectroscopy has confirmed that the surface composition of the STVPh random copolymers is similar to the bulk composition, therefore we can develop the correlation between the SIMS intensity of the characteristic peaks and the surface chemical composition of the copolymers. Two methods are used in the quantitative analysis: to look at the peak intensity normalized to the total intensity; and to look at the relative intensity of two peaks unique to the two monomer units in the STVPh copolymers.
Scheme 3. Proposed structures for some of the characteristic negative ions for STVPh random copolymers.

Figure 6. Normalized intensity of the positive ion peaks at m/z = 29.00, 42.01, 43.02 and 53.00 versus the bulk VPh content.

First we will investigate whether the normalized intensities of the characteristic peaks of the STVPh random copolymers are related linearly to the VPh content. Figure 6 shows the normalized intensity of the four oxygen-containing peaks at m/z = 29.00 (CHO\(^+)\), 42.01 (C\(_2\)H\(_2\)O\(^+)\), 43.02 (C\(_2\)H\(_3\)O\(^+)\) and 53.00 (C\(_3\)HO\(^+)\) as a function of the bulk VPh content. The data were fitted to a straight line. It is found that all of the peaks show a very good linear fit (relative intensity \(R > 0.98\)) with the bulk VPh content. Other characteristic peaks at m/z = 41.00 (C\(_2\)H\(_2\)O\(^+)\), 45.04 (C\(_2\)H\(_3\)O\(^+)\), 55.08 (C\(_3\)H\(_2\)O\(^+)\), 145 and 157 give a relatively poorer linear fit because of interference of the large hydrocarbon peaks.

The structure of the peaks at m/z = 107, 119, 120 and 121 is related directly to the VPh monomer in STVPh and their intensities are strong. Figure 7(a) shows the normalized intensity of these four peaks as a function of the bulk VPh content. It can be observed that the linear fits are good when the VPh content is \(< 75\, \text{mol.\%}\) but there is a large deviation from the linear fit when the VPh content is higher. This deviation may be caused by the intensity normalization procedure or matrix effect. In order to check whether the deviation is due to the intensity normalization procedure, the absolute intensities of these peaks are plotted against the bulk VPh content [Fig. 7(b)]. It can be seen that the linear fits are much better than those shown in Fig. 7(a), particularly for the peak at m/z = 119 (deprotonated VPh monomer). These results show that the deviation observed is mainly due to the intensity normalization by the total intensity. As indicated above, the STVPh copolymers with a higher VPh content tend to produce more low-mass C\(_x\)H\(_y\)C peaks (m/z \(< 100\)), which would depress the normalized intensity of the mass peaks at m/z > 100.

Second, we can quantitatively relate the ToF-SIMS relative intensities to the surface composition if appropriate characteristic peaks of the styrene monomer units are chosen. The relative intensity, \(R\), is defined by

\[
R = \frac{I_b}{I_A + I_B}
\]

where \(I_A\) and \(I_B\) are the normalized intensities of the characteristic ions from styrene and VPh monomer units, respectively. The relative intensity \(R\) should reflect the molar composition more precisely than the normalized intensities if the matrix effect increases or decreases \(I_A\) and \(I_B\) to the same extent. Indeed, this turns out to be the case (as shown in Fig. 8) when the peaks at m/z = 103, 105 and 115 are chosen to represent the styrene monomer units and the peaks at m/z = 120 and 121 are chosen to represent the VPh monomer.
Figure 7. (a) Normalized intensity of the positive ion peaks at \( m/z = 107, 119, 120, \) and 121 versus the bulk VPh content. (b) Absolute intensity of the positive ion peaks at \( m/z = 107, 119, 120 \) and 121 versus the bulk VPh content.

Figure 8. Intensity ratio of several positive ion peaks as a function of the bulk VPh content: \( 120/(120 + 115), 121/(121 + 103), 121/(121 + 105) \) and \( 121/(121 + 115) \).

The data were fitted to a straight line. The curves, as shown in Fig. 8, are linearly related to the VPh content up to 100 mol.% VPh. Similar linear fits are found when the peaks at \( m/z = 119 \) and 133 are chosen to represent VPh monomer units. These results show that for this copolymer system, having strong hydrogen bonding interaction, quantitative analysis is possible through the use of the monomer ions: \( m/z = 119–121 \) for VPh and \( m/z = 103–105 \) for styrene. These results also confirm that the peaks at \( m/z = 91 \) and 77 are less characteristic of polystyrene because they may come from several pathways.13,20

It is of interest to note that the fragments associated with AB (St–VPh), in which the peaks at \( m/z = 183 \) and 209 are good examples, show that the normalized intensities have a maximum at the VPh content of \(~50\) mol.%, as shown in Fig. 9. This result is consistent with the fact that the STVPh copolymers have the highest concentration of the AB sequence at the 50 mol.% VPh content. The normalized intensities of the fragments associated with BB (i.e. the peak at \( m/z = 225 \)) were fitted to the square of the VPh concentration. The intensity of the peak at \( m/z = 311 \), which is associated with the AAB (St–St–VPh) fragment, shows a maximum at \(~20\) mol.% VPh content. These results are in agreement with the sequence distribution of the copolymers.

**Negative spectrum**

Figure 10 shows the variation of the normalized intensity of characteristic peaks of STVPh in the negative ToF-SIMS spectrum. The data were fitted to a straight line. The normalized intensity of the characteristic peaks at \( m/z = 41, 93 \) and 117 shows a very good linear fit. The normalized intensity of the peak at \( m/z = 119 \), which is the deprotonated ion \([M -H]^-\) of VPh monomer, gives a non-linear fit. As in the case of positive spectra, we checked the absolute intensities of these peaks and found that the non-linear fits are not due to intensity normalization. This indicates the existence of a matrix effect on the formation and emission of this VPh monomer ion. Similarly, a non-linear fit was found for the negative deprotonated monomer ion of the copolymer poly(St-co-HFMS).20 The hydrogen bonding between the hydroxyl groups in these copolymer systems may affect the secondary ion yield for this type of fragment.

It was found also that when the peak at \( m/z = 13 \) is chosen to represent the total hydrocarbon contribution,
from STVPh random copolymers to determine the surface composition of the PS-b-PVPh copolymers.

Time-of-flight SIMS can distinguish PS-b-PVPh from STVPh random copolymers by the absence of the peaks corresponding to the St–VPh or St–St–VPh sequence structures, such as the peaks at \( m/z = 183, 209 \) and 311. Figure 11 shows the positive ToF-SIMS spectrum of PS-b-PVPh-26 and PS-b-PVPh-41. We can see from the relative intensity ratio of the peaks at \( m/z = 91 \) and 107 and the low intensity of the characteristic peaks of the VPh monomer at \( m/z = 107, 119, 120 \) and 121 that the surfaces of PS-b-PVPh-26 and PS-b-PVPh-41 are similar to that of poly(vinylphenol).

To perform quantitative analysis for the block copolymer surfaces, we choose four calibration curves: plots of \( I_{120}/(I_{120} + I_{115}), I_{121}/(I_{121} + I_{107}), I_{121}/(I_{121} + I_{105}) \) and \( I_{121}/(I_{121} + I_{113}) \) as a function of the bulk VPh content of the STVPh random copolymers. The normalized intensity curves are not used because for random copolymers the St–VPh monomer sequence will contribute significantly to the total intensity, whereas in the block copolymers there is very little such contribution. It is found that the surface concentrations determined by using the four calibration curves agree very well. The averaged values are shown in Table 2, along with the surface compositions calculated from the XPS results determined at different sampling depths (5.5 nm at a take-off angle of 45° and ~2.7 nm at a take-off angle of 20°). The data obtained by SIMS and XPS are not identical owing to the different sampling depths of the two techniques. The XPS values determined at the take-off angle of 20° are closer to the SIMS results.

The PS-b-PVPh-26 and PS-b-PVPh-41 copolymers have the same polystyrene block length but a different polyvinylphenol block length. An increase in the VPh content from 26 to 41 causes a marked increase in the normalized intensity ratio of the peaks at \( m/z = 119 \) and 121, which shows a poor linear fit when its normalized intensity is used, shows little improvement when \( I_{119}/I_{121} \) is used.

When the peaks at \( m/z = 93 \) and 117 are used to represent the VPh monomer unit and the peak at \( m/z = 73 \) is used to represent the styrene monomer unit, the relative intensities \( I_b/(I_b + I_s) \) are linearly proportional to the bulk VPh content. The PS-b-PVPh quantification is similar to that of the random copolymers, and the PS-b-PVPh copolymers should be similar to that of the random copolymers from the point of view of chemical structure and morphology, so we can use the calibration curves derived from STVPh random copolymers to determine the surface composition of the PS-b-PVPh copolymers.

**Figure 10.** Normalized intensity of the negative ion peaks at \( m/z = 41, 93, 117 \) and 119 versus the bulk VPh content.

**Table 2.** Surface compositions (VPh, mol.%) of PS-b-PVPh determined from ToF-SIMS (using four standard curves derived from STVPh random copolymers: A, \( I_{120}/(I_{120} + I_{115}) \); B, \( I_{121}/(I_{121} + I_{107}) \); C, \( I_{121}/(I_{121} + I_{105}) \); D, \( I_{121}/(I_{121} + I_{113}) \)) and XPS

<table>
<thead>
<tr>
<th>Sample</th>
<th>ToF-SIMS (1 nm depth)</th>
<th>Average surface concentration</th>
<th>XPS (ToA: 20°) 2.7 nm depth</th>
<th>XPS (ToA: 45°) 5.5 nm depth</th>
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<td>PS-b-PVPh-26</td>
<td>A 10.0 B 9.5 C 9.7 D 9.9</td>
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<tr>
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<td>A 3.1 B 3.0 C 3.4 D 3.2</td>
<td>3.2</td>
<td>7.8</td>
<td>19.2</td>
</tr>
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</table>

ToA = take-off angle.
41 mol.% increases the surface energy difference between the polystyrene and PVPh blocks, which increases the thermodynamic driving force for the polystyrene blocks to segregate. This leads to a larger surface excess concentration of polystyrene.

CONCLUSIONS

For STVPh random copolymers, the XPS results showed that the surface chemical composition of the STVPh random copolymers is very similar to the bulk composition. The ToF-SIMS spectra of the STVPh random copolymers were analysed and the structures of some of the characteristic ions were presented. The normalized intensity of some of the characteristic peaks of STVPh, such as the peaks at \( m/z = 29.00, 42.01, 43.02 \) and 53.00 in the positive spectrum and at \( m/z = 41, 93 \) and 117 in the negative spectrum, increases linearly with the bulk VPh content. Linear fits also were observed between relative intensity \( I_{VPh}/(I_{VPh} + I_{PS}) \) and the bulk VPh content when the most characteristic peaks were chosen to represent the styrene and VPh monomer units. These characteristic peaks were \( m/z = 119, 120, 121, 133, \) etc. for the VPh unit and 103, 105 and 115 for the styrene unit in the positive spectra, and \( m/z = 93 \) and 117 for the VPh unit and \( m/z = 73 \) for the styrene unit in the negative spectra. The variation of the normalized intensity of some fragments associated with the St–VPh, VPh–VPh or St–St–VPh sequence with the bulk VPh content was found to obey random copolymer statistics. All these data suggest that matrix effects have little influence on the secondary ion yield of the most characteristic ions. Time-of-flight SIMS can distinguish the PS-b-PVPh from the STVPh random copolymers by the absence of peaks corresponding to the St–VPh or St–St–VPh sequence structures. The surface compositions of PS-b-PVPh were obtained from ToF-SIMS analysis using the calibration curves obtained from the STVPh random copolymers.

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