

# Surface characterization and quantitative study of poly(4-vinyl phenol) and poly(4-vinyl pyridine) blends by XPS and ToF-SIMS

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## Abstract

Hydrogen bonding between poly(vinyl phenol) (PVPh) and poly(4-vinyl pyridine) (PVPy) was studied by time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), and contact angle measurements. Systematic studies were performed on various blends of PVPh and PVPy in different solvents, including ethanol and *N,N*-dimethylformamide (DMF). Both X-ray photoelectron spectroscopy and contact angle results showed no surface segregation of any component for the blends and complexes of PVPy and a low molecular weight PVPh. Excess of PVPh was found at the surface of the blends when a high molecular weight PVPh was used. However, after annealing at 90°C in a vacuum oven for five days, the surface and bulk compositions are the same. These findings reveal that the surface of blends of high molecular weight polymers may not be in the thermodynamic equilibrium state. The peak intensity of the characteristic pyridyl ions of the blends, especially the PVPh/PVPy complexes, such as the peak at  $m/z = 106$ , was greatly enhanced by the hydrogen bonding. The quantitative relationship between the ion intensity and the surface composition was studied. A linear relationship was established between the intensity ratio of some of the characteristic ions and the surface concentration determined by XPS. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Surface characterization; Hydrogen bonding; Polymer blends

## 1. Introduction

The surface behaviors of a two-phase polymer mixture are very sensitive to the chemical structure of the polymer components, the interaction between the two polymers, and the processing conditions. For polymer blends prepared by solution mixing, interactions exist between the two polymers and between the polymers and the solvent. These interactions can have a significant effect on the complex formation in the solvent. Hydrogen bonding is one of the typical interactions that causes the formation of intermolecular complexes. Recently, the intermolecular hydrogen-bonding interaction between the two components of the polymer blends prepared by solution mixing has been studied [1–6]. If the intermolecular hydrogen bonding between a proton-donating polymer and a proton-accepting polymer is strong enough, an insoluble complex is formed, resulting in a significant reduction of chain mobility. Hence,

the glass transition temperature of the complexes is higher than that of the individual components.

The intermolecular hydrogen bonding between the hydroxyl group of poly(vinyl phenol) (PVPh) and the pyridyl group of poly(4-vinyl pyridine) (PVPy) was studied by XPS [3]. The results show there are no differences in the interaction between the complexes and blends, and PVPh is enriched on the sample surface. It is well known that XPS is a very effective technique in the determination of the surface chemical composition of polymer blends [7–9]. However, XPS has limitations in the detection of crosslinking and branching at polymer surfaces as well as detailed molecular structure of the polymer components. As a complementary technique to XPS, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is inherently more sensitive to chemical structures of polymer surfaces and more surface-sensitive than XPS. One of the main limitations of SIMS is its ability to perform quantitative analysis. Recently, SIMS data have been used in quantitative studies of polymers [10–18]. There are many factors that hinder SIMS quantification, such as the relative sensitivity factor of the ions and the matrix effects [5]. It is generally believed that

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the positive ions are more structurally specific and more suitable to be used in quantitative analysis. Contact angle measurement is also a very common surface analysis technique because it is sensitive to the chemical composition of the outmost molecular layer and usually used in combination with XPS and SIMS [7]. In this study, the effects of the hydrogen bonding and solvent on the surface properties of the polymer blends and complexes of PVPh and PVPy were studied by ToF-SIMS, XPS and static contact angle analysis. The relationship between the surface composition and the intensity of the positive and negative ions was investigated.

## 2. Experimental

### 2.1. Sample preparation

A high molecular weight ( $\overline{M}_w \sim 300$  kg/mol) PVPh was synthesized by bulk polymerizing 4-acetoxystyrene at 60°C using AIBN as initiator, followed by hydrolysis with hydrazine hydrate in 1,4-dioxane. The hydrolysis was complete, as evidenced from the results of FTIR and  $^1\text{H}$  NMR. The molecular weight and polydispersity index of the PVPh were determined by size exclusion chromatography. The final product was purified by precipitation from tetrahydrofuran (THF) to *n*-hexane three times. PVPy and a low molecular weight ( $\overline{M}_w \sim 30$  kg/mol) PVPh were obtained from Polysciences Inc. (Warrington, PA). The weight-average molecule weight of PVPy was 150–200 kg mol $^{-1}$ . The low molecular weight PVPh was used as received and PVPy was purified by precipitation from ethanol into hexane. A TA 2910 differential scanning calorimeter (DSC) was used to measure the glass transition temperatures ( $T_g$ ). The sample was heated from room temperature to 250°C at a heating rate of 20°C/min and the  $T_g$  was taken as the midpoint at the inflection in the second heating cycle. The glass transition temperatures of PVPy and the low molecular weight PVPh were measured to be 151.0 and 153.6°C, respectively.

Two solvents, *N,N*-dimethylformamide (DMF) and ethanol were used. When DMF was used, a polymer blend solution was obtained and no precipitation was observed. A polymer complex precipitated when ethanol was used as solvent.

PVPh and PVPy were dissolved in DMF at a concentration of 10 g l $^{-1}$  separately. Polymer blend solutions were obtained by mixing and stirring the selected amounts of the two polymer solutions for 2 h. Any excess of either PVPh or PVPy was extant in the solution. Polymer films of the blends for surface analysis were prepared by placing a drop of the DMF polymer blend solution on a silicon wafer and having dried in a vacuum oven at room temperature for a week. Samples for the DSC study were obtained by drying the solution at 90°C in an oven for a week and in a vacuum oven at 90°C for a week.

PVPh and PVPy were dissolved in ethanol at a concentration of 10 g l $^{-1}$  separately. Polymer complexes were obtained by mixing and stirring the selected amounts of the two polymer solutions and stirring for 2 h. The solutions containing the precipitated complexes were centrifuged five times and then the complexes were kept in ethanol at about 0.2 g ml $^{-1}$ . The complex samples for XPS and ToF-SIMS studies were prepared by placing a drop of the complex-containing ethanol solution onto a silicon wafer and having dried in a vacuum oven at room temperature for a week. The bulk composition of the complexes was measured by using the Heraeus CHN-O-Rapid elemental analyzer. Samples for elemental analysis and DSC study were prepared by drying at 50°C in an oven for a week and in a vacuum oven at room temperature for three days.

### 2.2. Surface characterization

The surface chemical composition of the PVPh/PVPy complexes and blends were analyzed by XPS. XPS measurements were performed on a PHI 5600 multi-technique spectrometer equipped with an AlK $\alpha$  X-ray source. The take-off angle (the angle between the sample surface and the axis of the analyzer) for all samples was 45°. The binding energies of N 1s and O 1s core levels were obtained by assigning the CH $_x$  neutral carbon peak to 285.0 eV.

SIMS characterization of the PVPh/PVPy samples were performed using a Physical Electronics PHI 7200 ToF-SIMS. The high-mass resolution spectra were acquired in both positive and negative ion modes by using an 8 kV Cs $^+$  ion source. The examined area was 200  $\mu\text{m} \times 200 \mu\text{m}$  for each sample and the total ion acquisition dose for each area was  $< 4 \times 10^{11}$  ions cm $^{-2}$  for both the positive and negative ion spectra. The charge problem was solved by introducing 0–70 eV low-energy flood electrons which were pulsed out of phase of the primary ion beam.

The surface properties of PVPh/PVPy blends were also studied by a Krüss G10 contact angle measuring system. The contact angle measurements were performed when a drop of high-purity water was deposited on the film surface of the polymer blend.

## 3. Results and discussions

### 3.1. Low molecular weight PVPh and PVPy blends and complexes

#### 3.1.1. XPS and elemental analysis

To prepare the PVPh/PVPy blends and complexes, solutions containing 0.2, 0.4, 0.5, 0.6, and 0.8 mol fraction of PVPh were used. The bulk composition of the polymer films prepared using the polymer blend solutions was assumed to be identical to that of the feed composition. The bulk composition of the complexes was determined by elemental analysis, and the carbon concentration of PVPy was used as the standard.

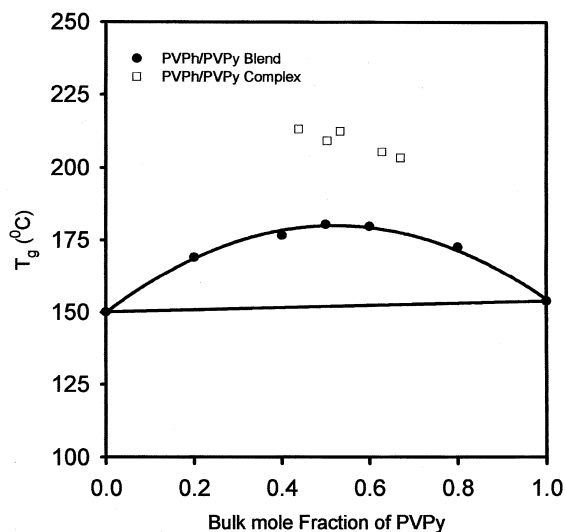


Fig. 1. Plots of  $T_g$  vs. bulk mole fraction of PVPy for the blends and complexes of PVPy and a low molecular weight PVPh.

Fig. 1 shows the determined  $T_g$  of the blends and the complexes of PVPy and a low molecular weight PVPh (30 kg/mol) determined by DSC. Only one  $T_g$  was detected for all the blends and complexes. Hence, we can conclude that PVPh and PVPy are miscible in all compositions. The  $T_g$  of the blends prepared by using DMF as solvent is higher than that of the individual components, indicating that a strong interaction was developed between PVPh and PVPy during the evaporation of DMF. These results are consistent with those of previous studies [5,19]. The  $T_g$  of the complexes precipitated from the ethanol solution is even higher than those of the blends. The difference in the  $T_g$  between the blends and the complexes clearly shows the effects of solvent in the preparation of the mixtures.

Both the O1s and N1s peaks for the blends and complexes contain two component peaks and the binding energy of these two component peaks determined by curve fitting. The results are summarized in Tables 1–4. For the blends (cf. Tables 1 and 2), the binding energy difference of the two O1s component peaks is approximately 0.6–0.8 eV and the binding energy difference of the two N1s component peaks

varies from 0.5 to 0.7 eV. For the complexes, the binding energy difference of the two O1s component peaks is approximately 0.7–1.0 eV and the binding energy difference of the two N1s component peaks varies from 0.5 to 0.9 eV. These results may indicate that stronger hydrogen bonding is formed in the complexes due to the use of a weaker solvent.

The surface composition of the samples was determined by using the N/C peak area ratios and the bulk composition of the complexes was determined by elemental analysis. The results of the elemental analysis show that the complexes contain 0.45–0.65 mol% of PVPy, which is consistent with the results of previous studies [5,19]. Fig. 2 shows the relationship between the surface and bulk compositions. Because DMF was used as solvent, the strong interaction between the polymers and the solvent does not allow the formation of a complex and precipitation from the solution. In this case, the composition of the blend should be very close to that of the feed, thus the feed composition is assumed to be the same as the bulk for the PVPh/PVPy blends. Fig. 2 shows that there is no surface segregation for both the blends and complexes. To obtain additional confirmation for the XPS results, contact angle measurements were performed on the polymer blend film surfaces. As shown in Fig. 3, the static contact angles of PVPh, PVPy, and their blends are very similar. Therefore, it is reasonable to assume that the surface tension of PVPh and PVPy is also very similar, resulting in no segregation of any component at the surface.

### 3.1.2. ToF-SIMS results

Positive ion spectra of PVPh and PVPy and the structure of the major characteristic ions are shown in Fig. 4(a) and (b), respectively. It is clearly seen that the most intense peak for PVPy is at  $m/z = 106$ , which was as observed in a previous study [20]. The other characteristic peaks of PVPy are at  $m/z = 79$  and 120. The PVPh spectrum shows that the most intense peak is at  $m/z = 107$ , contradicting the result of an early study [20] which indicated that the dominant peak for PVPh is at  $m/z = 43$ . The other characteristic peak for PVPh is at  $m/z = 115$  and 121. In the PVPh

Table 1  
O1s core level of the PVPh/PVPy blends

	PVPy (mole fraction)	O 1s (eV)	FWHM	Two peaks	FWHM	$\Delta$ BE (eV)
PVPh	0	533.33	1.60	–	–	–
B1	0.816	532.95	1.89	532.78 533.40	1.69 1.62	0.62
B2	0.578	533.0	1.83	532.66 533.40	1.50 1.60	0.74
B3	0.425	533.03	2.01	532.51 533.38	1.60 1.60	0.87
B4	0.352	533.17	1.91	532.66 533.43	1.60 1.60	0.77
B5	0.154	533.15	1.86	532.46 533.29	1.60 1.60	0.83

Table 2  
N1s core level of the PVPh/PVPy blends

Sample	PVPy (mole fraction)	N 1s (eV)	FWHM	Two peaks	FWHM	$\Delta$ BE (eV)
PVPy	1	399.42	1.35	–	–	–
B1	0.816	399.66	1.42	399.57 400.10	1.35 1.34	0.53
B2	0.578	399.71	1.38	399.51 400.06	1.25 1.30	0.55
B3	0.425	399.66	1.54	399.35 400.00	1.30 1.30	0.65
B4	0.352	399.84	1.52	399.37 400.06	1.31 1.20	0.69
B5	0.154	399.86	1.46	399.35 400.01	1.35 1.40	0.66

positive spectrum, some lower mass peaks, in the range of  $m/z = 40$ – $60$ , usually contain two separated component peaks. One corresponds to the  $C_xH_y$  structure and other represents an oxygen-containing fragment. For example, the peak at  $m/z = 55$  can be resolved into two component peaks which correspond to  $C_3H_3O^+$  (55.033) and  $C_4H_7^+$  (55.044) as shown in Fig. 4(a). In the PVPy spectrum, the peak at  $m/z = 55$  consists only of one peak corresponding to the  $C_4H_7^+$  ion. Therefore, the peaks representing the oxygen-containing fragments can be considered as the characteristic peaks of PVPh in quantitative analysis. The peaks at  $m/z = 73$  and 147 are due to contamination by polydimethylsiloxane.

The typical negative ion spectra of PVPh and PVPy are shown in Fig. 5(a) and (b), respectively. These two spectra are quite different. The major negative peaks of PVPh are at  $m/z = 16(O^-)$  and  $17(OH^-)$ . The peak at  $m/z = 119$  ( $C_8H_7O^-$ ) also has a relatively high intensity. More negative characteristic peaks of PVPh are found at  $m/z = 41$  ( $C_2HO^-$ ), 93 ( $C_6H_5O^-$ ), 117 ( $C_8H_5O^-$ ) and 133 ( $C_9H_9O^-$ ), but their peak intensity is lower. Although these peaks are also present in the PVPy spectrum, the peaks of PVPh are much more intense in the PVPh spectrum than those in the PVPy spectrum (Fig. 5(b)). This figure shows the most intense negative peak of PVPy at  $m/z = 26$  ( $CN^-$ ). The other important negative characteristic peaks of PVPy are

at  $m/z = 27$  ( $CHN^-$ ), 39 ( $C_2HN^-$ ), 50 ( $C_3N^-$ ), 92 ( $C_6H_6N^-$ ), 104 ( $C_7H_6N^-$ ), 116 ( $C_8H_6N^-$ ), and 132 ( $C_9H_{10}N^-$ ). These characteristic peaks in the PVPy spectrum are much more intense than those in the PVPh spectrum (Fig. 5(a)). Therefore, the characteristic peaks of PVPh and PVPy can be used in quantitative analysis of the surface composition of the PVPh/PVPy blends and complexes. The probable structure of some of these negative ions is given in Table 5.

The SIMS spectra of the blends and complexes show features that are significantly different from those found in the SIMS spectra of the pure components. Fig. 6 shows the intensity of the peaks at  $m/z = 106$  and 107 for the blends. The dominant peaks for pure PVPh and PVPy are respectively at  $m/z = 107$  and 106. For the blends with the mole ratio of PVPy/PVPh approximately equals one, the intensity of the peak at  $m/z = 106$  is greatly enhanced (cf. Fig. 6(d) and (e)). Only in the blend with the mole ratio of PVPy/PVPh = 0.18, the intensities of the peaks at  $m/z = 106$  and 107 are similar (cf. Fig. 6(g)) because a much larger amount of PVPh is at the surface. This enhancement of the intensity of the peak at  $m/z = 106$  is observed for all PVPh/PVPy complexes. The spectra of the complexes are very similar to each other and similar to that of the blend with a mole ratio of PVPy/PVPh = 1, as shown in Fig. 6(d), because PVPh and PVPy are present in approximately

Table 3  
O1s core level of the PVPh/PVPy complexes

Sample	PVPy (mole fraction)	O 1s (eV)	FWHM	Two peaks	FWHM	$\Delta$ BE (eV)
PVPh	0	533.33	1.60	–	–	–
C1	0.752	533.05	1.81	532.92 533.63	1.72 1.60	0.71
C2	0.631	533.02	2.00	532.74 533.54	1.75 1.60	0.80
C3	0.486	533.0	1.98	532.66 533.45	1.68 1.60	0.80
C4	0.444	533.01	1.95	532.60 533.48	1.50 1.60	0.88
C5	0.400	533.05	2.20	532.37 533.40	1.75 1.60	1.03

Table 4  
N1s core level of the PVPh/PVPy complexes

Sample	PVPy (mole fraction)	N 1s (eV)	FWHM	Two peaks	FWHM	$\Delta$ BE (eV)
PVPy	1	399.42	1.35	–	–	–
C1	0.752	399.75	1.38	399.44 399.90	1.13 1.35	0.46
C2	0.631	399.67	1.59	399.45 400.10	1.36 1.35	0.65
C3	0.486	399.69	1.54	399.42 400.05	1.35 1.35	0.63
C4	0.444	399.66	1.62	399.46 400.12	1.35 1.35	0.66
C5	0.400	399.66	1.87	399.26 400.17	1.35 1.35	0.91

equal concentration at the surface of the complexes. The increase in the intensity of the peak at  $m/z = 106$  is not caused by the surface segregation of PVPy as confirmed by the results of XPS and contact angle measurements. Therefore, the enhancement of the peak at  $m/z = 106$  can only be explained by the formation of hydrogen bonds between the pyridyl and hydroxyl groups [3]. The hydrogen bonds will enhance the formation of the ions with  $m/z = 106$  as shown below.

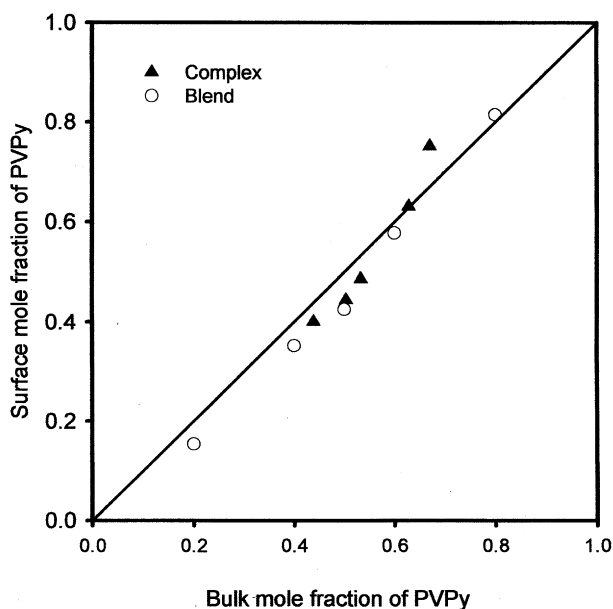
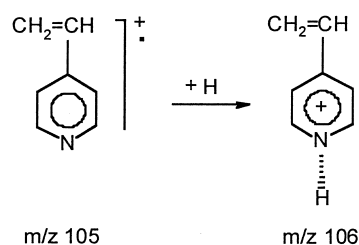


Fig. 2. Surface mole fraction of PVPy vs. bulk mole fraction of PVPy for the blends and complexes of PVPy and a low molecular weight PVPh.

It would be of interest to study the intensity ratios,  $I_{\text{exp}}(m_2/m_1)$ , of the ion pairs that are affected by the formation of hydrogen bonding

$$I_{\text{exp}}(m_2/m_1) = \frac{I_{m_2}}{I_{m_1}} \quad (1)$$

where  $I_{m_1}$  and  $I_{m_2}$  are the intensity of the peaks at  $m/z = m_1$  and  $m/z = m_2 = m_1 + 1$ , respectively. If the hydrogen bonding does not affect the intensity of these peaks and the matrix effects are absent, then the intensity of these peaks in a blend or complex can be calculated by the following equation:

$$I_{\text{cal}}(m_2/m_1) = \frac{x \frac{I_{m_2}^{\text{Py}}}{I_{\text{total}}^{\text{Py}}} + (1-x) \frac{I_{m_2}^{\text{Ph}}}{I_{\text{total}}^{\text{Ph}}}}{x \frac{I_{m_1}^{\text{Py}}}{I_{\text{total}}^{\text{Py}}} + (1-x) \frac{I_{m_1}^{\text{Ph}}}{I_{\text{total}}^{\text{Ph}}}} \quad (2)$$

where  $I_{\text{cal}}(m_2/m_1)$  is the calculated intensity ratio for peaks at  $m/z = m_1$  and  $m/z = m_2$ ;  $I_{m_1}^{\text{Py}}$  and  $I_{m_2}^{\text{Py}}$  are the intensity of the peaks at  $m/z = m_1$  and  $m_2$ , respectively for PVPy;  $I_{m_1}^{\text{Ph}}$  and  $I_{m_2}^{\text{Ph}}$  are the intensity of the peaks at  $m/z = m_1$  and  $m_2$ , respectively for PVPh;  $I_{\text{total}}^{\text{Py}}$  and  $I_{\text{total}}^{\text{Ph}}$  are the total ion intensity of PVPy and PVPh, respectively; and  $x$  is the surface molar concentration of PVPy in the blend or in the complex determined by XPS. The ratio of the experimental intensity ratio to the calculated intensity ratio is defined by the following equation:

$$R(m_2/m_1) = \frac{I_{\text{exp}}(m_2/m_1)}{I_{\text{cal}}(m_2/m_1)} \quad (3)$$

If there is no enhancement of the ion intensity as a result of the hydrogen bonding, then the values of  $R(m_2/m_1)$  should be approximately one (Eq. (3)). However, if strong hydrogen bonding is formed, the intensities of the ions such as  $\text{C}_5\text{H}_6\text{N}^+$  and  $\text{C}_7\text{H}_8\text{N}^+$  are expected to be much enhanced, then the values of  $R(m_2/m_1)$  would be larger than one. The ratio of the experimental ion intensity to the calculated ion intensity of the ion pairs  $m_2 = 80/m_1 = 79$  and  $m_2 = 106/m_1 = 105$  is shown in Table 6. In all cases,  $R(m_2/m_1) > 1$ , indicating that the enhancement of the  $I_{m_2}$  peak intensity is due to the formation of hydrogen bonds.

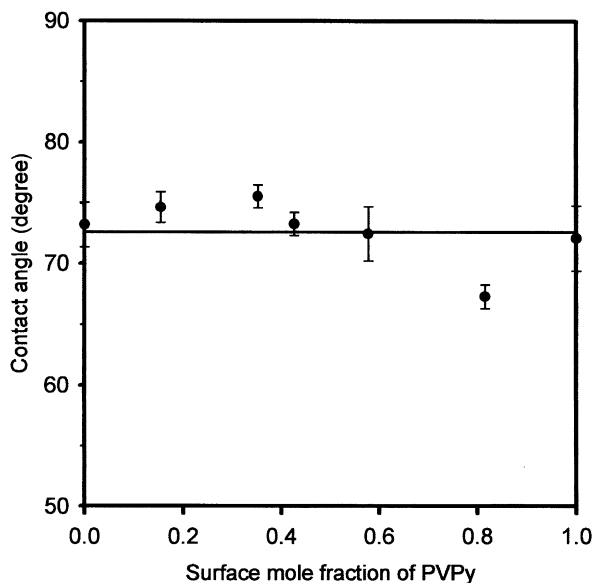


Fig. 3. Contact angle vs. surface mole fraction of PVPy for the blends and complexes of PVPy and a low molecular weight PVPh.

### 3.1.3. Quantitative study by ToF-SIMS

Fig. 7 shows the normalized intensity of several characteristic peaks of PVPh ( $m/z = 121$  and  $55.033$ ) and PVPy ( $m/z = 79$ ,  $80$ ,  $92$ , and  $93$ ) as a function of the surface mole fraction of PVPy. The normalized intensity of a peak is obtained by normalizing the intensity of a peak with respect to the total positive ion intensity. In the normalization procedure, the system effects, such as the effects of the output voltage, primary beam current and sample position, are neglected. The normalized intensity of the peaks at  $m/z = 79$ ,  $80$  and  $93$  shows a nonlinear relationship with the surface composition determined by XPS. However, a linear relationship between the normalized intensity and surface composition is shown for the peaks at  $m/z = 92$  and  $55.033$  ( $C_3H_3O^+$ ). It should be noted that the intensity of the peaks at  $m/z = 80$  and  $93$  is enhanced by the formation of hydrogen bonding.

Fig. 8 shows the plots of the relative intensities of the characteristic positive ion peaks of PVPy as a function of the surface mole fraction of PVPy. The relative intensity is

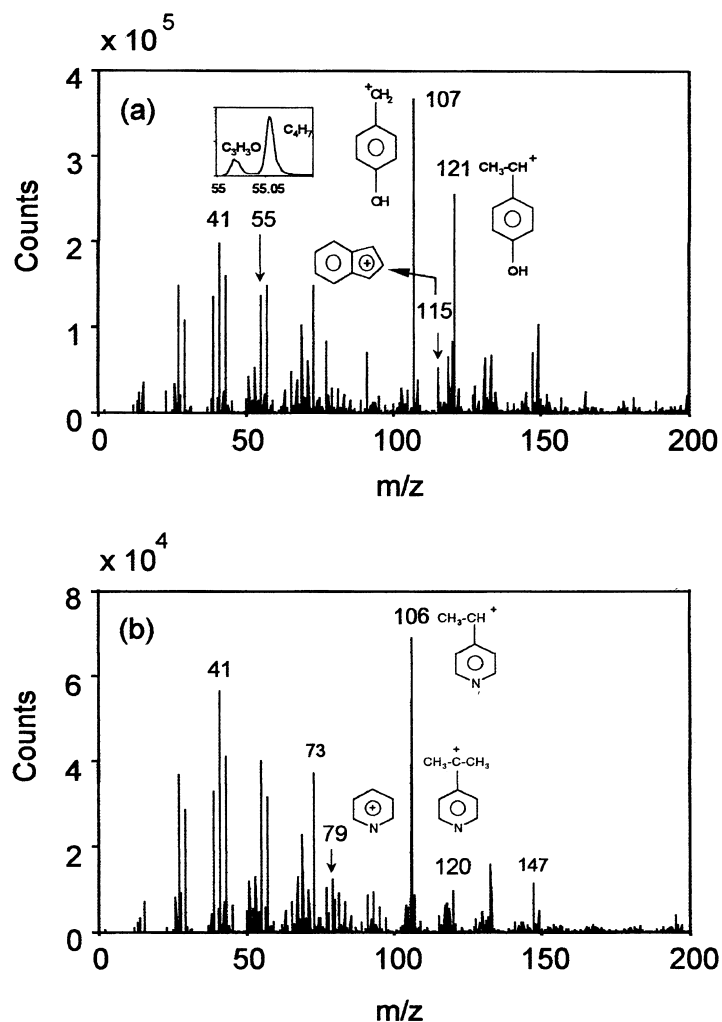


Fig. 4. Positive SIMS spectra for: (a) PVPh; and (b) PVPy.

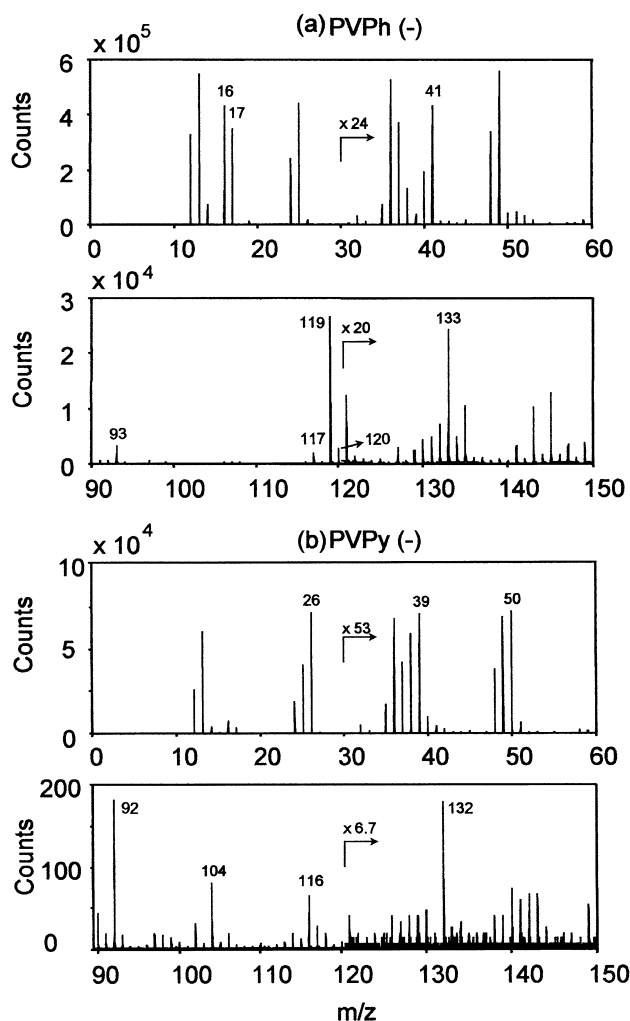


Fig. 5. Negative SIMS spectra for: (a) PVPh; and (b) PVPy.

defined by

$$R_{\text{PVPy}}(m_i) = \frac{I_{\text{PVPy}}(m_i)}{I_{\text{PVPy}}(m_i) + I_{\text{PVPh}}(m_j)} \quad (4)$$

where  $I_{\text{PVPy}}(m_i)$  and  $I_{\text{PVPh}}(m_j)$  are the intensity of a characteristic peak of PVPy and PVPh at  $m/z = m_i$  and  $m_j$ , respectively.  $I_{\text{PVPy}}(m_i = 79, 80, 92, \text{ and } 93)$  and  $I_{\text{PVPh}}(m_j = 121)$  are chosen.  $R_{\text{PVPy}}(m_i = 79, 80, \text{ and } 93)$  shows a linear rela-

tionship with the surface mole fraction of PVPy of the blends. Fig. 9 shows the plots of the relative intensities of the characteristic negative ion peaks of PVPy as a function of the surface mole fraction of PVPy.  $I_{\text{PVPy}}(m_i = 26, 39 \text{ and } 50)$  and  $I_{\text{PVPh}}(m_j = 16 \text{ and } 41)$  are chosen. The plots of  $R_{\text{PVPy}}(m_i = 26, 39, \text{ and } 50)$  as a function of the surface mole fraction of PVPy of the blends and complexes show linear relationships. These results indicate that SIMS data can provide useful quantitative information.

### 3.2. High molecular weight PVPh and PVPy

To determine the effects of the molecular weight on the surface chemical composition of the blends and complexes, a high molecular weight PVPh (300 kg/mol) was used. The XPS results show that PVPy is the excess component at the surface of the polymer blends, as indicated in Fig. 10. However, no surface excess of PVPy is detected after the samples had been annealed at 90°C in a vacuum oven for five days. This finding suggests that the surface of the blends of PVPy and the high molecular weight PVPh is not in the thermodynamic equilibrium state because of the increase in viscosity as the molecular weight of PVPh increases. After annealing at a high temperature, the surface reaches the final equilibrium-state, showing no segregation of any component at the surface. It is important to point out that the annealing temperature of 90°C is below the  $T_g$  of the blends. However, the work of Kajiyama et al. [21] indicated that surface  $T_g$  is much lower than the bulk  $T_g$ . For example, the surface  $T_g$  of the polystyrene component of the poly(styrene-*block*-methyl methacrylate) diblock copolymer film determined at the depth range less than 2.7 nm was measured to be about 60°C lower than the bulk  $T_g$ . Hence, we believe that the annealing temperature 90°C is sufficient for the surface to reach the thermodynamic equilibrium state. We tried to avoid the use of very high temperature to minimize surface oxidation. To ensure that the surface of the blends to be studied is in the thermodynamic equilibrium-state, annealing at high temperatures may be necessary, especially when high molecular weight polymers are used.

Table 5

Probable structure for the negative characteristic ions of PVPh and PVPy

PVPh					PVPy				
$m/z$	93 ( $\text{C}_6\text{H}_5\text{O}^-$ )	117 ( $\text{C}_8\text{H}_5\text{O}^-$ )	119 ( $\text{C}_8\text{H}_7\text{O}^-$ )	133 ( $\text{C}_9\text{H}_9\text{O}^-$ )	$m/z$	92 ( $\text{C}_6\text{H}_6\text{N}^-$ )	104 ( $\text{C}_7\text{H}_6\text{N}^-$ )	116 ( $\text{C}_8\text{H}_6\text{N}^-$ )	132 ( $\text{C}_9\text{H}_{10}\text{N}^-$ )

Table 6  
Values of  $R(106/105)$  and  $R(80/79)$

Sample number	Surface mole fraction of PVPy	$R(106/105)$ blend	$R(80/79)$ blend
B1	0.816	1.60	1.31
B2	0.578	1.87	1.47
B3	0.425	2.65	1.89
B4	0.352	2.21	1.84
B5	0.154	2.53	1.85
Sample number	Surface mole fraction of PVPy	$R(106/105)$ complex	$R(80/79)$ complex
C1	0.752	1.69	1.39
C2	0.631	1.69	1.38
C3	0.486	3.83	1.73
C4	0.444	2.83	1.60
C5	0.400	4.14	1.87

#### 4. Conclusions

The hydrogen-bonding interaction between proton-donating polymer PVPh and the proton-accepting polymer PVPy was studied by using ToF-SIMS and XPS. The surface composition of the blends and complexes of PVPy and the low molecular PVPh was very similar as that of the bulk. For the blends of PVPy and the high molecular weight

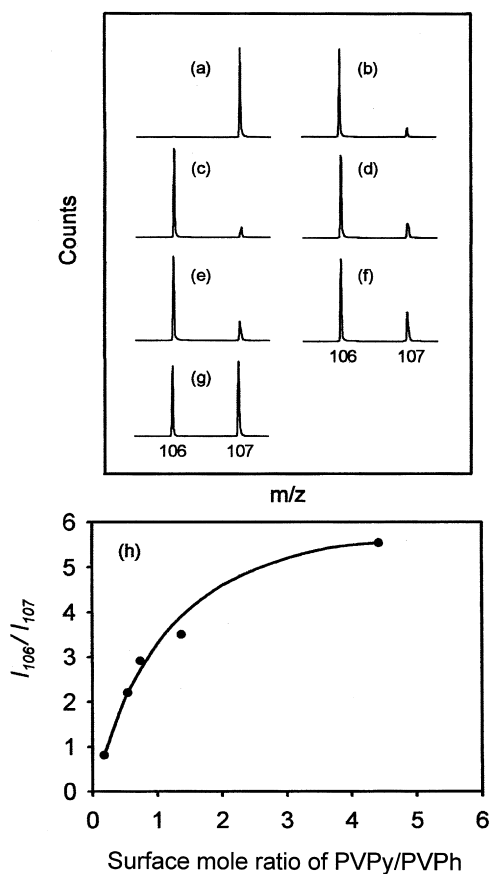


Fig. 6. Positive SIMS spectra showing the intensity of the peak at  $m/z = 107$  and 107. (a) PVPh, (b) PVPy, (c) PVPy/PVPh = 4.4, (d) PVPy/PVPh = 1.4, (e) PVPy/PVPh = 0.71, (f) PVPy/PVPh = 0.56, (g) PVPy/PVPh = 0.18, and (h)  $I_{106}/I_{107}$  vs. surface mole ratio of PVPy/PVPh.

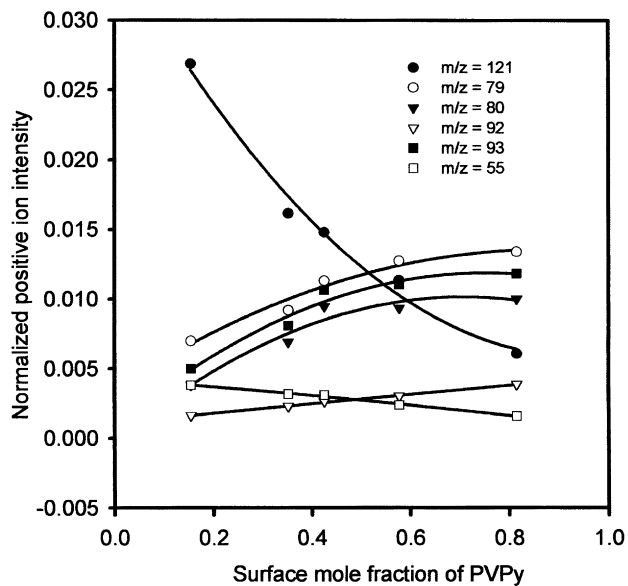


Fig. 7. Normalized positive ion intensity vs. surface mole fraction of PVPy.

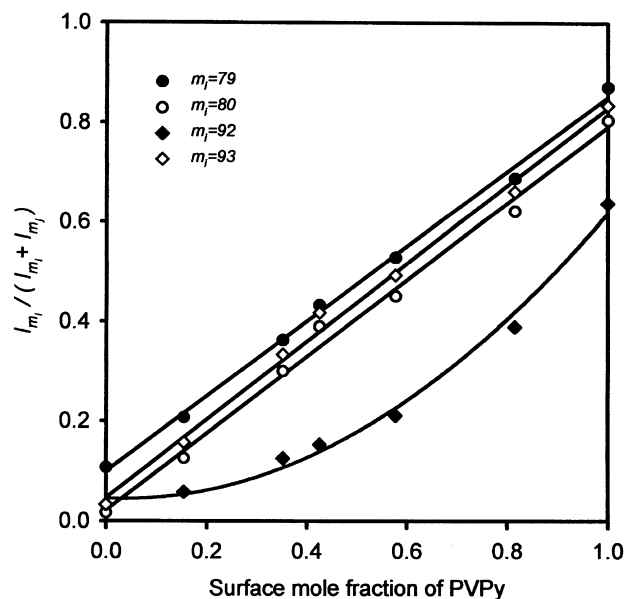


Fig. 8. Intensity ratio of positive ions vs. surface mole fraction of PVPy.



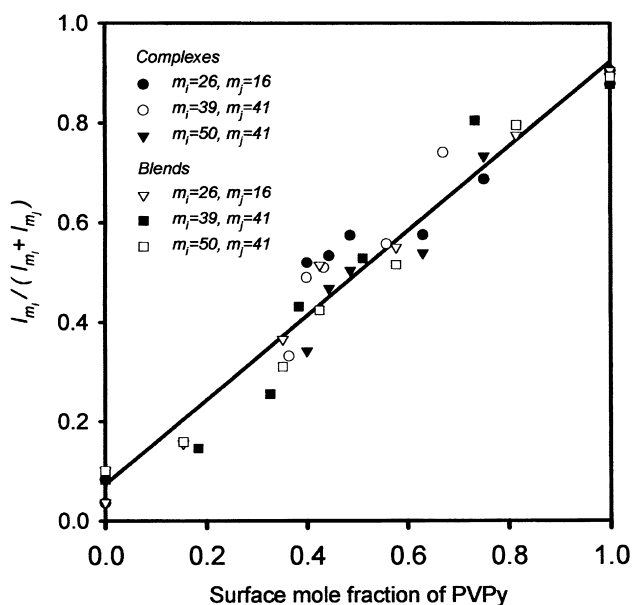


Fig. 9. Intensity ratio of negative ions vs. surface mole fraction of PVPy.

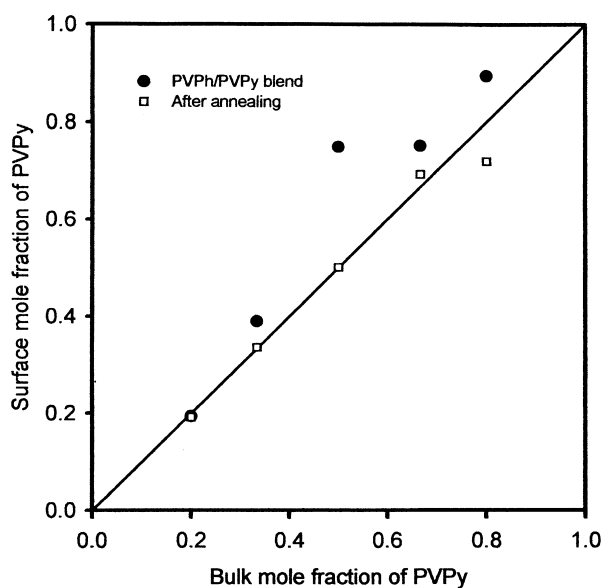


Fig. 10. Surface mole fraction of PVPy vs. bulk mole fraction of PVPy for the blends of PVPy and a high molecular weight PVPh.

PVPh, the surface of the prepared samples showed an excess of PVPy because the surface had not reached the thermodynamic equilibrium-state. After annealing at 90°C for five days, no surface segregation of any component was

observed. These results reveal that the surface of the polymer blends containing high molecular weight components may not be in its thermodynamic equilibrium-state. Good linear relationships have been found between some positive and negative characteristic ion peaks and the surface concentration of the blends and complexes. These findings show that SIMS data can provide useful quantitative information.

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