Specific Interaction between Poly(styrene-*co*-4-vinylphenol) and Poly(styrene-*co*-4-vinylpyridine) Studied by X-ray Photoelectron Spectroscopy and Time-of-Flight Secondary Ion Mass Spectrometry

Lin Li and Chi-Ming Chan*

Department of Chemical Engineering, Advanced Engineering Materials Facility,
Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong

Lu-Tao Weng

Materials Characterization and Preparation Facility,
Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong

Mao-Liang Xiang and Ming Jiang

Institute of Macromolecule Science and Laboratory of Molecular Engineering of Polymers,
Fudan University, Shanghai 200433, People's Republic of China

Received December 29, 1997; Revised Manuscript Received August 12, 1998

ABSTRACT: The specific interaction of hydrogen bonding between poly(styrene-*co*-4-vinylphenol) (STVPh) and poly(styrene-*co*-4-vinylpyridine) (STVPy) was investigated by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The density of the hydrogen bond was adjusted by varying the 4-vinylphenol (VPh) content in the STVPh copolymers. Immiscible blends were formed when the VPh content was low, and an interpolymeric complex was formed when the VPh content was above a certain value. In addition, an interpolymer complex was formed between poly(4-vinylphenol) (PVPh) and STVPy-72 (containing 72 mol % of Py). For the complexes, XPS results revealed that the intermolecular hydrogen bonds between the hydroxyl and pyridyl units can induce a shift of 0.6−0.7 eV and 0.4−0.5 eV in the N 1s and O 1s binding energies, respectively. Such large shifts in the binding energy may imply that the nitrogen is partially protonated. The XPS results also showed that STVPy-72 was enriched on the surface of immiscible blends of STVPy-72 and STVPh-*y* (where *y* is the mol % of VPh, $y = 1$, 9, and 22). However, surface segregations of STVPh-50 and PVPh were detected respectively for the complex between STVPh-50 and STVPy-72 and the complex between PVPh and STVPy-72. The intensity ratios of the ions for the complexes that were affected by the formation of hydrogen bonding, such as $C_5H_6N^+/C_5H_5N^+$ and $C_6H_7N^+/C_6H_6N^+$, were larger than those in the STVPy-72 copolymer. The intensity ratios of these ions for immiscible blends of STVPh and STVPy-72 and for the STVPy-72 copolymer were almost the same. The results indicate that hydrogen bonding plays an important role in the distribution of the peak intensities of the ions that are affected by the formation of hydrogen bonding in a SIMS process.

Introduction

It is known that the differences between the surface and the bulk compositions of a miscible polymer blend are caused by the surface segregation of one of the blend components, resulting in the reduction in surface free energy of the system. Specific interactions are of great importance in determining the miscibility of polymer blends,[1,2] though they may have only very small effects on limiting the surface segregation of the low surface energy polymer component.[3,4] In recent years, considerable progress has been made in the recognition of the importance of specific interactions in the phase behavior of polymer blends. One of the most important intermolecular interactions is the hydrogen bonding between a proton donor and a proton acceptor. Poly(styrene-*co*-4-vinylphenol) (STVPh) and poly(styrene-*co*-4-vinylpyridine) (STVPy) form miscible blends at certain hydroxyl and pyridyl contents[5−8] because of the formation of strong hydrogen bonding between the hydroxyl and pyridyl groups. Jiang et al.[6] reported that interpolymer complexes between STVPh and STVPy are formed in nonaqueous solutions as the concentrations of the hydroxyl and pyridyl groups reach certain levels. The size distribution of the complex aggregates is relatively narrow and the size of the aggregates is usually 1 order of magnitude larger than that of individual polymer coils.

X-ray photoelectron spectroscopy (XPS) has been used in the investigation of the electronic structure, the surface chemical composition, and other properties of polymer blends and copolymers.[9−11] The binding energy of a core level electron depends on its chemical environment within the molecule. The influence of specific interactions on the surface chemical composition and structure of polymer blends can be determined by measuring the changes in the binding energies of atoms that are involved in the specific interactions. Only a few studies[3,4,12−15] have been made to investigate the effects of specific interactions, such as hydrogen bonding, on the surface composition and structure of polymer

---

* To whom all correspondence should be addressed.

10.1021/ma9718659 CCC: $15.00

blends. Salaneck et al.[12] reported that the binding energies of C 1s and N 1s increase on going from the undoped to the doped pyrrole. Their results indicated a positive charge transfer from the host polymer to the dopant anion. Since no splitting was observed in either the C 1s or N 1s peaks, it can be concluded that the charge was taken uniformly from the pyrrole units associated with each BF_4^- anion. They also reported[13] that the N 1s peak, found in base emeraldine, splits into two components in the protonated form. The relative intensity of the higher binding energy component was found to be proportional to the concentration of the protonation N 1s core electrons of the sample. Shifts in the binding energy in polymer blends with strong specific interactions have been observed by Goh et al.[3] and Zhou et al.[14,15] The XPS study of Goh et al.[3] on the ionic interactions between sulfonated polystyrene and poly(styrene-*co*-4-vinylpyridine) indicates that the binding energy of the N 1s core level of the pyridinium ions (protonated pyridine), formed by the ionic interactions, is about 2.5 eV higher than that of the pyridine. The strong interaction between poly(vinylphosphonic acid) and poly(4-vinylpyridine) or poly(2-vinylpyridine) causes a shift of 2.1 eV in the binding energy of the N 1s electrons.[14] In a recent study, Zhou et al.[15] have applied XPS to study the specific interaction between poly(*p*-vinylphenol) and poly(4-vinylpyridine) or poly(2-vinylpyridine). Shifts in the binding energy of 1.0 and 1.2 eV for N 1s and O 1s core level electrons were observed. Their results indicated that the lower surface energy component still segregates on the surface of the polymer complex, although the specific interaction between the polymer components is very strong.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been applied to characterize the surface of polymers, copolymers, and polymer blends. It has a much higher surface sensitivity than XPS and can provide detailed information on the surface molecular structure, including polymer tacticity,[16] sequence distribution,[17,18] end groups,[19] and the amounts of branching and cross-linking.[20] The development of a time-of-flight analyzer has made chemical imaging of a polymer surface with submicron resolution possible. The demand for structure and morphology information on polymer and polymer blend surfaces has stimulated research in the area of surface analysis by ToF-SIMS.[21,22] In addition, the effects of chemical interactions of the components on ion formation in SIMS are of fundamental interest. Li et al.[23,24] studied the effects of the proton transfer on ion formation in SIMS. Their results indicate that ion formation can be strongly influenced by chemical interactions of the components at the surface. In this work, ToF-SIMS imaging was used to study the effects of the density of the hydrogen bond on the surface morphology and miscibility of polymer blends and also the influence of hydrogen bonding on the formation of positive and negative fragments in a SIMS process.

Experiment

Materials. A series of STVPh and STVPy copolymers was synthesized as previously described.[25] The molar contents of 4-vinylphenol (VPh) in STVPh copolymers were calculated from the ^{1}H NMR measurements, and the molar content of 4-vinylpyridine (VPy) in the STVPy copolymer was determined from nitrogen measurements. The number-average molecular weight ($\bar{M}_n$) and polydispersity index of those copolymers were determined by size-exclusion chromatography with polystyrene standards. Poly(4-vinylphenol) (PVPh) was purchased from Polyscience, Inc. (Warrington, PA), and used as received. Table 1 shows the physical properties of STVPh and STVPy copolymers.

Table 1. Characterizations of STVPh and STVPy Copolymers

polymer[a]	$\bar{M}_n \times 10^{-3}$ (g·mol^{-1})	$\bar{M}_w/\bar{M}_n$	T_g (°C)[b]
STVPh-1	103	1.48	112.2
STVPh-9	132	2.17	119.6
STVPh-22	130	2.44	121.5
STVPh-50	135	1.92	151.7
PVPh	22		151.3
STVPy-72	19.8	1.58	146.8

[a] The number following STVPh and STVPy represents the molar content of VPh and VPy in STVPh and STVPy copolymers, respectively. [b] The typical error in the measurements of T_g is ±0.5 °C.

Sample Preparation. STVPh and STVPy copolymers were separately dissolved in tetrahydrofuran (THF) at a concentration of 1.5 g L^{-1}. A blend solution was prepared by mixing the same amounts of each polymer solution under stirring. Depending on the amounts of VPh in STVPh, the mixed solutions might remain clear or form an interpolymer complex precipitate. The clear solutions were spin-cast onto silicon wafers. The film thickness was controlled by using the same concentration of the solution and the same spin rate. For the solution containing an interpolymer complex precipitate, the precipitate was separated by centrifugation, washed with THF three times, and then kept in THF. 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.

Surface Characterization. The surface morphology and structure of the STVPh/STVPy blends were studied by XPS and ToF-SIMS. ToF-SIMS measurements were carried out on a Physical Electronics PHI 7200 ToF-SIMS spectrometer. The surface chemical images of STVPh/STVPy blends were acquired in both positive and negative modes using a $^{69}Ga^+$ beam at 25 kV. To obtain high-resolution spatial images, an ion pulse width of about 50 ns was used. The total ion dose for each image acquisition was lower than 4×10^{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 of STVPh/STVPy samples were obtained by using an 8 kV Cs^+ ion source. The scanned area was 200 μm × 200 μm, and the total ion dose for each spectrum acquisition was $<10^{12}$ ions/cm^2.

The surface chemical composition of the STVPh/STVPy samples was calculated using the XPS data. The XPS spectra were obtained with a PHI 5600 multitechnique 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 emission angle (the angle between the surface normal and the axis of the analyzer) of the photoelectron was 45°. For different sampling depth measurements, the emission angle varied from 65 to 15, corresponding to a sampling depth of approximately 28−64 Å (the attenuation length is assumed to be 22 Å).

Table 2. Bulk and Surface Compositions and Glass Transition Temperatures of Mixtures of STVPy with Various STVPh Copolymers

sample	bulk weight ratio	T_g (°C)[a] T_{g1}	T_{g2}	surface STVPy-72[b] (wt %)
STVPh-1/STVPy-72	50:50	114.2	146.2	90.1
STVPh-9/STVPy-72	50:50	124.2	145.3	87.8
STVPh-22/STVPy-72	50:50	128.3	146.6	68.7
STVPh-50/STVPy-72	50:50	171.0		39.8
PVPh/STVPy-72	50:50	198.5		38.4

[a] The typical error in the measurements of T_g is ±0.5 °C. [b] The STVPy-72 surface compositions were calculated from N/C peak area ratios by using STVPy-72 as the standard.

Results and Discussion

DSC and XPS. The physical properties of the copolymers used in this study are summarized in Table 1. The effects of the density of the hydrogen bond on the bulk miscibility and surface composition of STVPh/STVPy blends were studied by DSC and XPS, and the results are summarized in Table 2. DSC results show a single T_g for the precipitated polymer complexes: STVPh-50/STVPy-72 and PVPh/STVPy-72. The measured T_gs, as shown in Table 2, are significantly higher than those measured for each individual component of the complexes, as shown in Table 1, indicating that the mobility of individual chains in the precipitated polymer complexes[5,8] is significantly reduced as a result of the strong hydrogen bonding between the phenol and pyridyl units. As shown in Table 2, the presence of two T_gs for blends of STVPh-1/STVPy-72, STVPh-9/STVPy-72, and STVPh-22/STVPy-72 indicates that STVPy-72 is immiscible with STVPh-1, STVPh-9, and STVPh-22. These results suggest that compatibility of STVPh and STVPy blends can only be achieved when the density of the hydrogen bond and the ratio of the phenol units to the pyridyl units are above certain values.

The surface chemical compositions of the blends were calculated from the N/C peak area ratios by using STVPy-72 as the standard. Comparing the surface and bulk concentrations of STVPy-72, as shown in Table 2, it can be concluded that STVPy-72 is enriched on the surface of the immiscible blends.

The C 1s spectra of STVPh-50 and STVPy-72 are shown in Figure 1. In the spectra shown in Figure 1, curve fitting shows that the C−O and C−N components for STVPh-50 and STVPy-72 are at 286.6 and 286.0 eV, respectively. The C 1s and N 1s spectra of STVPh-9, STVPy-72, and the STVPh-9/STVPy-72 blend are shown in Figure 2a,b. The C 1s and N 1s peaks of the STVPh-9/STVPy-72 blend are almost the same as those of STVPy-72, in both the full width at half-maximum (fwhm) and binding energy. This is reasonable because the surface of the STVPh-9/STVPy-72 blend consists of 87.8 wt % of STVPy-72. The molar ratio of the phenol to the pyridyl units is less than 0.02. Therefore, even if all phenol units form hydrogen bonding with the pyridyl units, the amount of the protonated nitrogen of the pyridyl units will be small and difficult to detect by XPS. The amounts of oxygen in the STVPh-1/STVPy-72 and STVPh-9/STVPy-72 blends are too low to be precisely studied.

The results of the XPS analyses of STVPh-22, STVPh-50, PVPh, STVPy-72, and several blends of STVPh and STVPy-72 are shown in Table 3. The O 1s binding energy of the STVPh-1/STVPy-72 and STVPh-9/STVPy-72 blends cannot be precisely measured because the surface STVPh concentrations are too small. The N 1s binding energy of these blends is the same as that of STVPy-72, because of the low density of the hydrogen bond. These results agree with the DSC results, as shown in Table 2. For the STVPh-22/STVPy-72 blend, a decrease of 0.6 eV in the O 1s binding energy and an increase of 0.5 eV in the N 1s binding energy are observed. The large shifts in the O 1s and N 1s binding energies suggest the formation of strong hydrogen bonds or that the nitrogen is partially protonated. However, two T_gs are still observed in the DSC scan of this blend. The XPS and DSC results reveal that hydrogen bonding exists between the phenol and pyridyl units and these two copolymers are still not fully miscible, probably because of the low density of the hydrogen bond in the blend.

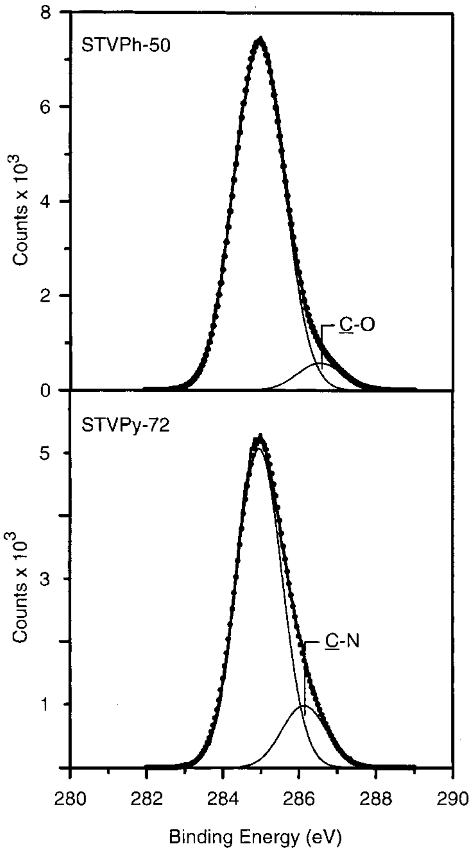


Figure 1. High-resolution C 1s spectra for STVPh-50 and STVPy-72.

The spectra of C 1s, O 1s, and N 1s peaks of STVPh-50, STVPy-72, and the STVPh-50/STVPy-72 polymer complex are shown in Figures 3a−c. The fwhm and binding energy of the C 1s peak for the STVPh-50/STVPy-72 complex are similar to those of the C 1s peaks for the STVPh-50 and STVPy-72 copolymers. The O 1s peak of the polymer complex is 0.4−0.5 eV lower than that of STVPh-50, and the N 1s peak of the polymer complex is 0.6−0.7 eV higher than that of STVPy-72. These shifts in the binding energies are caused by the formation of the hydrogen bonds between the hydroxyl and pyridyl groups. Since there is no observable change in the fwhm of the N 1s peak of the complex and the ratio of the surface phenol units to the pyridyl unit is about 1, it can be concluded that almost all of the pyridyl units interact with the phenol units, forming interpolymer hydrogen bonds in the STVPh-50/STVPy-72 interpolymer complex. These foregoing results suggest that the binding energy shifts of N 1s and O 1s can only be

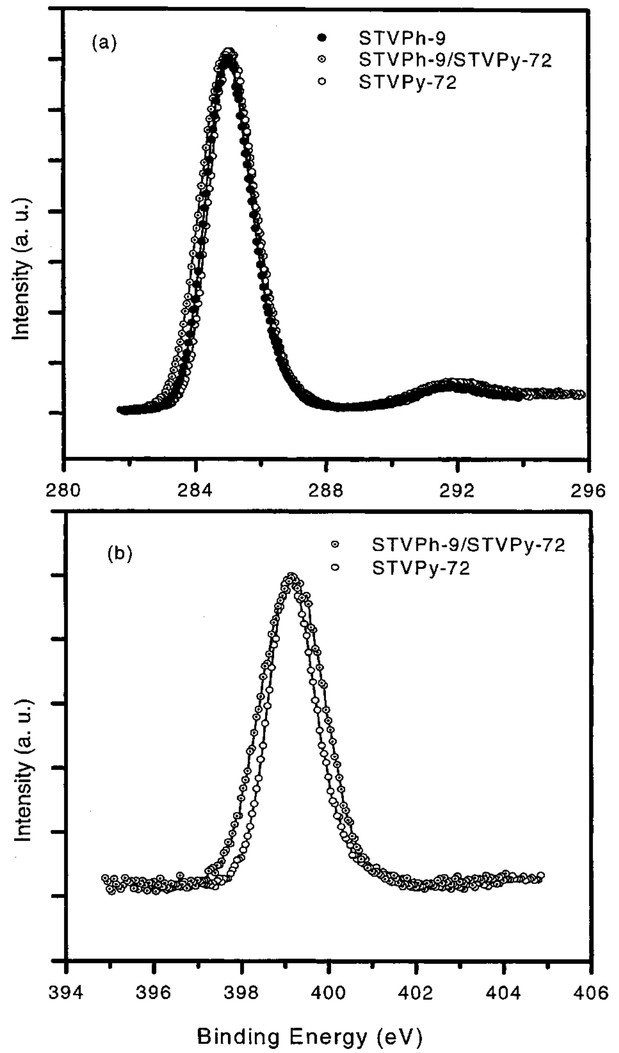
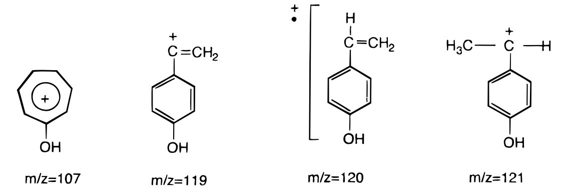


Figure 2. High-resolution XPS spectra of STVPh-9, STVPy-72, and the STVPh-9/STVPy-72 blend: (a) C 1s and (b) N 1s.

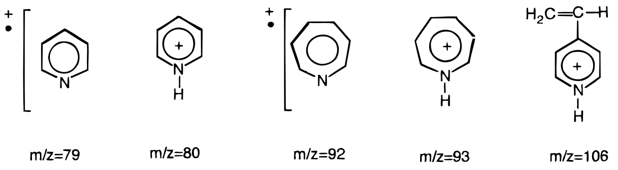
detected when the density of the hydrogen bond on the surface reaches a certain value.

The surface compositions of the immiscible blends and interpolymer complexes are shown in Tables 2 and 3. The surface of the immiscible polymer blends—STVPh-1/STVPy-72, STVPh-9/STVPy-72, and STVPh-22/STVPy-72—is enriched by STVPy-72 (the surface mole ratio of [VPh]/[VPy] is much lower than 1). However, the surface mole ratio of [VPh]/[VPy] is close to or higher than 1 in the polymer complexes—STVPh-50/STVPy-72 and PVPh/STVPy-72. It is interesting to note that, for the STVPh-50/STVPy-72 complex, the surface mole ratio of [VPh]/[VPy] is very close to 1 although the bulk ratio of [VPh]/[VPy] is only 0.66. The strong hydrogen bonding between the pyridyl and hydroxyl units is possibly the driving force for the segregation of STVPh-50 to the surface. For the PVPh/STVPy-72 complex, the surface mole ratio of [VPh]/[VPy] at the surface is much higher than that in the bulk, as shown in Table 3. The mole ratio of [VPh]/[VPy] at the surface is 1.97, which is much higher than the bulk value of 1.23. This result indicates that more PVPh molecules are drawn to the surface after the formation of the complex. When all pyridyl units are used in the formation of hydrogen bonds with the hydroxyl groups, there is still a large amount of free hydroxyl groups at the surface. The formation of intermolecular hydrogen bonds among the PVPh molecules can further introduce the segregation of PVPh molecules at the surfaces of the complex. Two different types of oxygen are observed at the surface of the complex. The presence of these two types of oxygen with binding energies measured at 533.3 and 533.7 eV is attributed to the oxygen involved in the formation of hydrogen bonding between the hydroxyl groups and the formation of hydrogen bonding between the hydroxyl and pyridyl groups, respectively. These results suggest that strong hydrogen bonding can promote the segregation of a component in a polymer complex to facilitate the formation of hydrogen bonds at the surface. Segregation of PVPh in the complexes of PVPh and poly(4-vinylpyridine) or poly(2-vinylpyridine) has been observed and was attributed to the lower surface energy of PVPh.[14] However, based on our results, it is not clear if the segregation is a result of PVPh being the lower surface component. In addition, the surface energies of PVPh and PVPy have not been measured experimentally. Further work is needed to provide a better understanding of the factors that control the surface chemical compositions of polymer complexes.

ToF-SIMS Spectra. Typical positive ToF-SIMS surface spectra (mass range 90—120) obtained from STVPh-9, STVPh-22, STVPh-50, PVPh, and STVPy-72 are shown in Figure 4. STVPy-72 is distinguished from STVPh copolymers and PVPh by the presence of a large peak at *m/z* 106, the largest peak in the STVPy-72 spectrum, and by the presence of characteristic peaks at *m/z* 79, 80, 92, and 93. The largest peak in the STVPh-50 and PVPh spectra is at *m/z* 107, and the largest peak in STVPh-1, STVPh-9, and STVPh-22 spectra is at *m/z* 91, with characteristic peaks at *m/z* 119, 120, and 121. Some probable structures, as suggested by Chilkoti et al.,[26,27] for the oxygen-containing ions in the ToF-SIMS spectra of the STVPh copolymers are shown as follows:



Some possible structures for the nitrogen-containing ions of the STVPy copolymer are also shown as follows:



Parts a and b of Figure 5, which are the partial SIMS spectra for STVPh-50, STVPy-72, and the STVPh-50/STVPy-72 complex, show the intensity of the ions—$C_5H_5N^+$, $C_5H_6N^+$, $C_6H_6N^+$, and $C_6H_7N^+$—that are influenced by the formation of interpolymer complexes. These ions are related to the fragments containing atoms that are involved in the formation of hydrogen bonds. The formation of hydrogen bonding between the phenol and pyridyl units will enhance the formation of ions, such as *m/z* 80 ($C_5H_6N^+$) and *m/z* 93 ($C_6H_7N^+$) and may affect the intensity of ions such as *m/z* 79 ($C_5H_5N^+$) and *m/z* 92 ($C_6H_6N^+$). Therefore, it would be interesting

Table 3. Binding Energies of C 1s, O 1s, and N 1s Core Level Electrons Determined by XPS

sample[a]	[VPh]/[VPy] bulk mol ratio	[VPh]/[VPy] surface mol ratio	C 1s		O 1s[b]		N 1s	
			fwhm	eV[c]	fwhm	eV[c]	fwhm	eV[c]
STVPh-22			1.5	285.0	1.9	533.8		
STVPh-50			1.5	285.0	1.9	533.7		
PVPh			1.3	285.0	1.7	533.6		
STVPy-72			1.5	285.0			1.4	399.1
STVPh-1/STVPy-72	0.014	0.002	1.5	285.0			1.4	399.2
STVPh-9/STVPy-72	0.126	0.018	1.5	285.0			1.7	399.1
STVPh-22/STVPy-72	0.302	0.137	1.5	285.0	1.7	533.2	1.5	399.6
STVPh-50/STVPy-72	0.659	0.999	1.4	285.0	1.8	533.2	1.4	399.7
PVPh/STVPy-72	1.23	1.97	1.5	285.0	1.9	533.3(0.6)	1.5	399.6
					1.9	533.7(0.4)		

[a] The compositions of the blend samples are 50/50 weight ratio. [b] The amount of oxygen in STVPh-1, STVPh-9, and their blends with STVPy-72 is too low to be precisely determined by XPS. [c] The typcial error in the measurements of binding energy is ±0.1 eV.

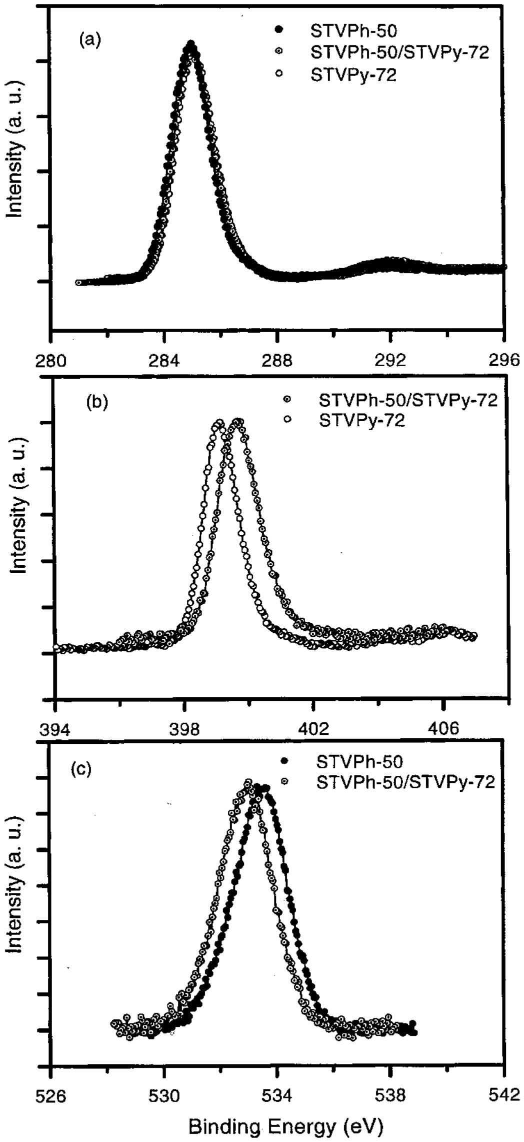
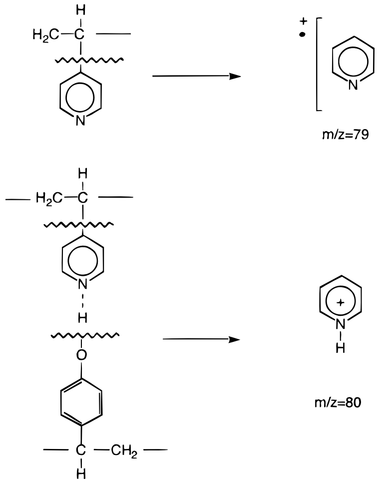


Figure 3. High-resolution XPS spectra of STVPh-50, STVPy-72 and the STVPh-50/STVPy-72 polymer complex: (a) C 1s, (b) N 1s, and (c) O 1s.

to study the intensity ratios, $I_{\mathrm{exp}}(m_2/m_1)$, of the ion pairs that are affected by the formation of hydrogen bonding:

$$I_{\mathrm{exp}}(m_2/m_1) = I_{m_2}/I_{m_1} \tag{1}$$

where I_{m_1} and I_{m_2} are the intensities of the peaks at $m/z = m_1$ and $m/z = m_2 = m_1 + 1$, respectively. The formation of strong hydrogen bonds can change the intensity distribution of the ions at $m/z = m_1$ and $m/z = m_2$. For example, the formation of the ions at m/z 79 and 80 can follow the following scheme:



If the hydrogen bonding does not affect the intensity distribution of these peaks and the matrix effects are absent, then the intensity distribution of these peaks in a blend or complex can be calculated by the equation

$$I_{\mathrm{cal}}(m_2/m_1) = \frac{x\dfrac{I^{\mathrm{Py}}_{m2}}{I^{\mathrm{Py}}_{\mathrm{total}}} + (1-x)\dfrac{I^{\mathrm{Ph}}_{m2}}{I^{\mathrm{Ph}}_{\mathrm{total}}}}{x\,\dfrac{I^{\mathrm{Py}}_{m1}}{I^{\mathrm{Py}}_{\mathrm{total}}} + (1-x)\dfrac{I^{\mathrm{Ph}}_{m1}}{I^{\mathrm{Py}}_{\mathrm{total}}}} \tag{2}$$

where $I_{\mathrm{cal}}(m_2/m_1)$ is the calculated intensity ratio for peaks at $m/z = m_1$ and $m/z = m_2$; I^{Py}_{m1} and I^{Py}_{m2} are the intensities of the peaks at $m/z = m_1$ and m_2, respectively, for STVPy-72; I^{Ph}_{m1} and I^{Ph}_{m2} are the intensities of the peaks at $m/z = m_1$ and m_2, respectively, for STVPh or PVPh; $I^{\mathrm{Py}}_{\mathrm{total}}$ and $I^{\mathrm{Ph}}_{\mathrm{total}}$ are the total ion intensities of STVPy-72 and STVPh or PVPh, respectively; and x is the surface molar concentration of STVPy-72 in the blend or in the polymer complex determined by XPS measurements. The intensity ratios for STVPh-9/STVPy-72, STVPh-22/STVy-72, STVPh-50/STVPy-72, and PVPh/STVPy-72 were calculated using the surface molar concentrations of STVPy-72 determined by using the XPS data obtained at an emission angle of 45° (sampling depth = 47 Å, assuming an attenuation length of 22 Å). The ratio of the experimental intensity ratio to the calculated intensity ratio is defined by the following

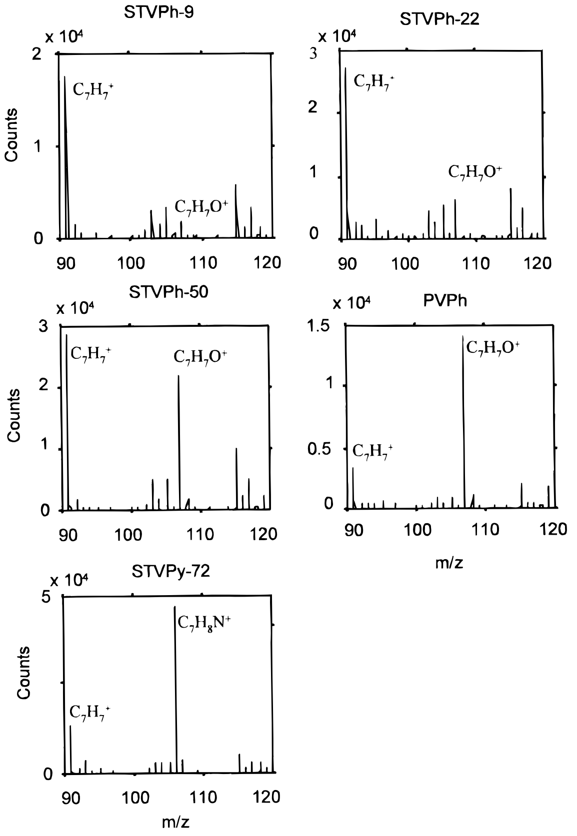


Figure 4. ToF-SIMS positive spectra from the surface of STVPh-9, STVPh-22, STVPh-50, PVPh, and STVPy-72.

equation:

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

Table 4 is a summary showing the values of $R(m_2/m_1)$ for the copolymer STVPy-72, blends and complexes. 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 1. However, if strong hydrogen bonding is formed, the intensities of the ions such as $C_5H_6N^+$ and $C_6H_7N^+$ are expected to be much enhanced, and then the values of $R(m_1/m_2)$ would be larger than 1. Three intensity ratios—*R*(80/79), *R*(93/92), and *R*(106/105)—are chosen. From Table 4, it is noted that the values of $R(m_2/m_1)$ for the STVPh-9/STVPy-72 blend are very close to 1. Since the surface of the STVPh-9/STVPy-72 blend is enriched by STVPy-72 and the density of the hydrogen bond on the surface is small, the values of $R(m_2/m_1)$ are expected to be very similar to those for the STVPy-72 copolymer. In the STVPh-22/STVPy-72 blend, the density of the hydrogen bond increases; hence, the values of *R*(80/79), *R*(93/92), and *R*(106/105) increase to 1.44, 1.15, and 1.17, respectively.

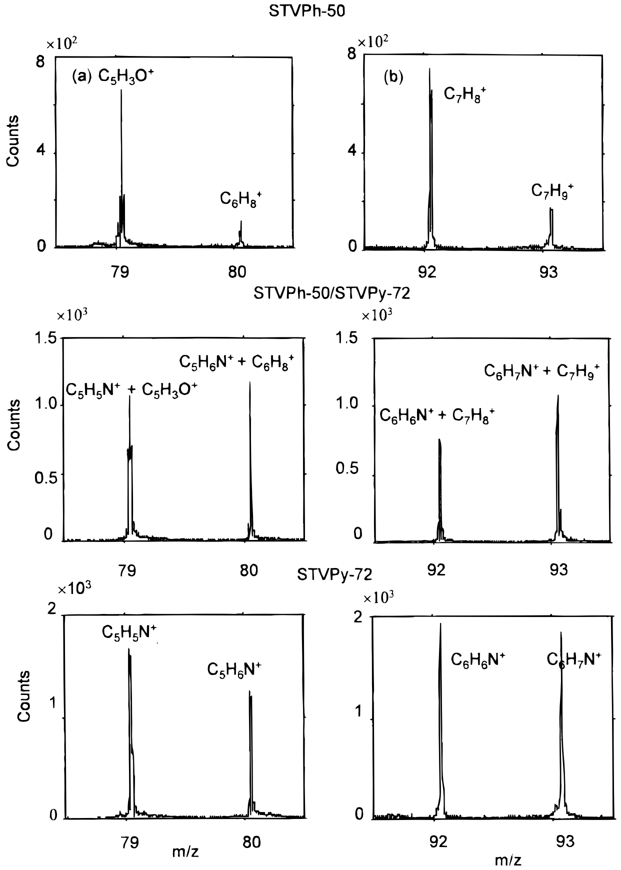


Figure 5. ToF-SIMS positive spectra of STVPh-50, STVPy-72, and the STVPh-50/STVPy-72 complex: (a) mass range 78−81 and (b) mass range 91−94.

Table 4. Values of *R*(80/79), *R*(93/92), and *R*(106/105), Determined by ToF-SIMS

sample[a]	sampling depth, Å	*R*(80/79)	*R*(93/92)	*R*(106/105)
STVPy-72	47	1.00	1.00	1.00
STVPh-9/STVPy-72	47	1.10 ± 0.04	0.96 ± 0.06	0.79 ± 0.10
STVPh-22/STVPy-72	28	1.31 ± 0.04	1.10 ± 0.05	1.07 ± 0.03
	47	1.44 ± 0.04	1.15 ± 0.05	1.17 ± 0.03
	64	1.46 ± 0.04	1.15 ± 0.05	1.20 ± 0.03
STVPh-50/STVPy-72	47	1.53 ± 0.06	2.03 ± 0.10	1.85 ± 0.05
PVPh/STVPy-72	47	1.87 ± 0.10	2.36 ± 0.11	2.34 ± 0.04

[a] The composition of the blends is 50/50 by weight.

The values of *R*(80/79), *R*(93/92), and *R*(106/105) for the STVPh-50/STVPy-72 and PVPh/STVPy-72 polymer complexes are much higher than 1 even though the STVPy-72 surface concentrations for the complexes are low (the surface concentrations of STVPy-72 are 39.8 and 38.4 wt %, for the STVPh-50/STVPy-72 and PVPh/STVPy complexes, respectively). These results show clearly that an increase in the density of the hydrogen bond between the phenol units and pyridyl units increases the values of $R(m_2/m_1)$. This result suggests that these ratios may be used to monitor the surface hydrogen-bonding formation. The increase in the values of $R(m_2/m_1)$ is attributed to the intensity enhancement of the protonated fragments such as $C_5H_6N^+$, $C_6H_7N^+$, and $C_7H_8N^+$ relative to the reference fragments—$C_5H_5N^+$, $C_6H_6N^+$, and $C_7H_7N^+$—because of the proton transfer as a result of the formation of hydrogen bonding. It is important to point out the fact that SIMS data (sampling depth 5−10 Å) are more surface-sensitive than XPS data. Hence, it is important to repeat the calculations with XPS data obtained at various sampling depths. Table 4 shows that the values of *R*(80/79), *R*(93/92), and *R*(106/105) for the STVPh-22/STVPy-72 complex calculated using the XPS data at various sampling depths are quite similar. Hence, we can conclude that surface chemical compositions of these samples are relatively uniform in the top 50 Å.

ToF-SIMS Chemical Imaging. Figure 6a presents the total ions, $O^- + OH^-$ and CN^- images obtained on the polymer surface of an immiscible blend of STVPh-

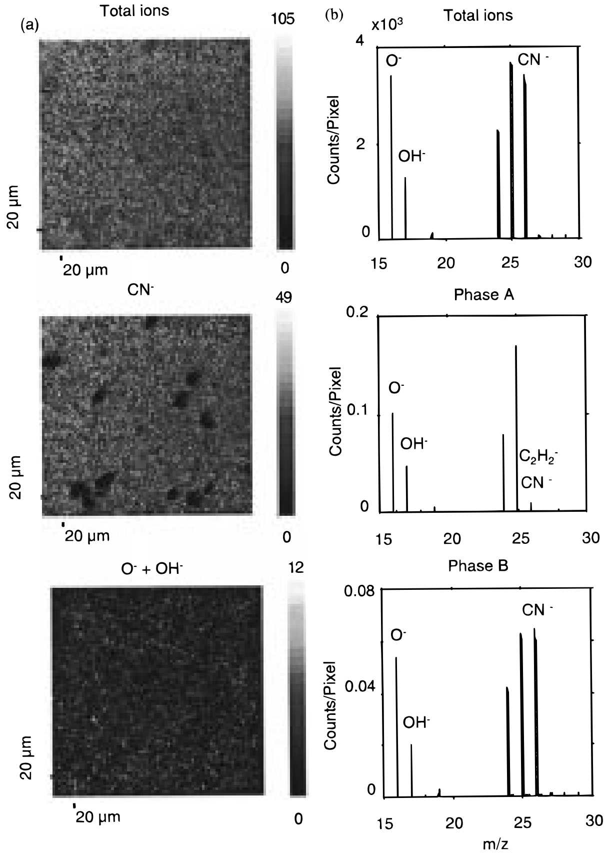


Figure 6. (a) Negative ion images for the STVPh-22/STVPy-72 blend. (b) Negative ToF-SIMS spectra reconstructed retrospectively from phases A and B.

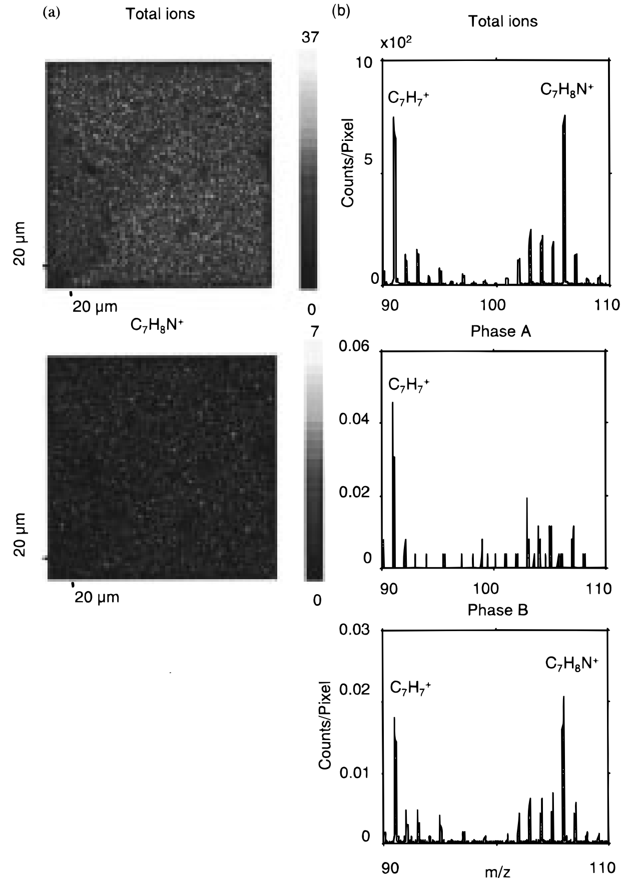


Figure 7. (a) Positive ion images for the STVPh-22/STVPy-72 blend (b) Positive ToF-SIMS spectra reconstructed retrospectively from phases A and B.

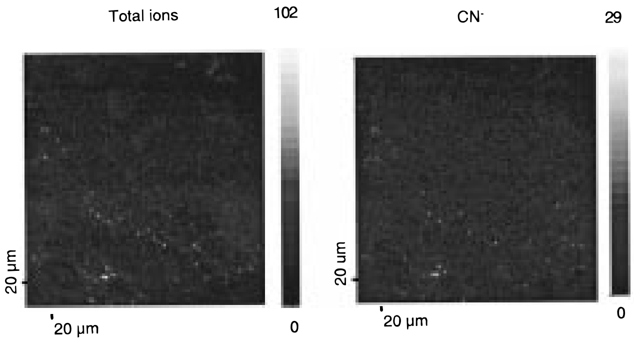


Figure 8. Negative ion images for the PVPh/STVPy-72 interpolymer complex.

22/STVPy-72. The O^- + OH^- and CN^- images represent STVPh-22 and STVPy-72, respectively. The O^- + OH^- and CN^- images are very complementary. The total ions image is significantly affected by the surface topography. For the immiscible blend of STVPh-22/STVPy-72, there are two phases that can be observed from O^- + OH^- and CN^- images: phase A consists of STVPh-22 particles, and phase B is a mixture of STVPh-22/STVPy-72. Figure 6b shows the spectra obtained, retrospectively, from the A and B phases. The spectrum for phase A is very close to that of the STVPh-22 copolymer. The CN^- intensity is almost zero in this phase. The spectrum for phase B shows that the intensities of O^-, OH^-, and CN^- are comparable, indicating that phase B contains comparable amounts of STVPh-22 and STVPy-72. These results clearly show that phase separation occurs on the surface of the STVPh-22/STVPy-72 blend. The positive total ions and $C_7H_8N^+$ ion (*m/z* 106) images of the surface of the STVPh-22/STVPy-72 blend are shown in Figure 7a. The spectra for the A and B phases are given in Figure 7b. In the spectrum for phase A, the most intense peak is $C_7H_7^+$ and the peak of $C_7H_8N^+$, which is the most intense peak in the spectrum for STVPy-72, is absent. In the spectrum for phase B, the peaks for $C_7H_7^+$ and $C_7H_8N^+$ are of comparable intensity, suggesting that both STVPh-22 and STVPy-72 are present. These results are in good agreement with the negative ion images shown in Figure 6. The DSC measurements indicate that there are two distinct T_gs for the STVPh-22/STVPy-72 blend, and the XPS results suggest that STVPh-72 is enriched on the surface of this blend, as shown in Table 2. Therefore, it is reasonable to observe two phases on the surface of the STVPh-22/STVPy-72 blend in the ToF-SIMS images.

Figure 8 shows the total ions and CN^- images of the surface of the PVPh/STVPy-72 polymer complex. It can be observed from the CN^- image that STVPy-72 is uniformly distributed on the surface of the PVPh/STVPy-72 polymer complex, although the surface is enriched by PVPh, as the XPS results suggested.

Conclusion

The STVPy-72 copolymer is shown to form a polymer complex with STVPh copolymers when the concentration of the hydrogen bond between the phenol and the pyridyl units reaches a threshold value. The strong hydrogen-bonding or partial protonation can induce a 0.6−0.7 eV shift in the N 1s binding energy for the pyridyl units and a 0.4−0.5 eV shift in the O 1s binding energy for the phenol units in the immiscible blend of STVPh-22/STVPy-72 and the STVPh-50/STVPy-72 and PVPh/STVPy-72 polymer complexes. No shifts of O 1s and N 1s binding energies were observed for the immiscible polymer blends (STVPh-1/STVPy-72 and STVPh-9/STVPy-72) because the density of the hydrogen bond on the surface is too low.

The strong interaction between the phenol and pyridyl units can increase the values for $I_{\exp}(m_2/m_1)$, which are the ratios of the peak intensities for the ions that are affected by the formation of hydrogen bonding. The values of $I_{\exp}(m_2/m_1)$ for the immiscible blend of STVPh-9/STVPy-72 are almost the same as those of STVPy-72 because STVPy-72 is enriched on the surface of the blends.

ToF-SIMS imaging has been successfully applied for the characterization of the surface of the STVPh/STVPy and PVPh/STVPy blends. It has been shown that STVPh-22 and STVPy-72 are immiscible and that two phases are present on the surface: STVPh-22 particles form a discrete phase and a mixture of STVPh-22/STVPy-72 forms a continuous matrix. For the PVPh/STVPy-72 polymer complex, the ToF-SIMS surface chemical imaging clearly indicates that PVPh and STVPy-72 are present as a single phase at the surface, although one of the blend components, PVPh, is segregated on the surface.

Acknowledgment. This work was supported by the Hong Kong Government Research Grant Council under Grant HKUST6123/97P. Part of the XPS experiment was performed by Mr. Nick Ho in the Materials Characterization and Preparation Facility of HKUST.

References and Notes

(1) Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* **1988**, *21*, 66.
(2) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 954.
(3) Goh, S. H.; Lee, S. Y.; Dai, J.; Tan, K. L. *Polymer* **1996**, *37*, 5305.
(4) Li, L.; Chan, C.-M.; Weng, L. T. *Polymer* **1998**, *39*, 2355.
(5) de Meftahi, M. V.; Frechet, J. M. J. *Polymer* **1988**, *29*, 477.
(6) Xiang, M.; Jiang, M.; Zhang, Y.; Wu, C.; Feng, L. *Macromolecules* **1997**, *30*, 2313.
(7) Jiang, M.; Qin, X.; Qin, W.; Fei, L. *Macromolecules* **1995**, *28*, 730.
(8) Dai, J.; Goh, S. H.; Lee, S. Y.; Siow, K. S. *Polym. J.* **1994**, *26*, 905.
(9) Chan, C. M. *Polymer Surface Modification and Characterization*; Hanser: New York, 1994.
(10) Briggs, D.; Fletcher, I. W.; Reichlmaier, S.; Agulo-Sanchez, J. L.; Short, R. D. *Surf. Interface Anal.* **1996**, *24*, 419.
(11) Chen, X.; Gardella, J. A., Jr.; Ho, T.; Wynne, K. J. *Macromolecules* **1995**, *28*, 1635.
(12) Salaneck, W. R.; Erlandsson, R.; Prisza, J.; Lundstrom, I.; Inganas, O. *Synth. Met.* **1983**, *5*, 125.
(13) Salaneck, W. R.; Lundstrom, I.; Hjertberg, T.; Duke, C. B.; Conwell, E.; Paton, A.; Mac-Diarmid, A. G.; Somasiri, N. L. D.; Huang, W. S.; Richter, A. F. *Synth. Met.* **1987**, *18*, 291.
(14) Zhou, X.; Goh, S. H.; Lee, S. Y.; Tan, K. L. *Appl. Surf. Sci.* **1997**, *119*, *60*.
(15) Zhou, X.; Goh, S. H.; Lee, S. Y.; Tan, K. L. *Polymer* **1997**, *38*, *5333*.
(16) Vanden Eynde, X.; Weng, L. T.; Bertrand, P. *Surf. Interface Anal.* **1997**, *25*, 41.
(17) Galuska, A. A. *Surf. Interface Anal.* **1997**, *25*, 1.
(18) Zhuang, H.-Z.; Gardella, J. A., Jr.; Hercules, D. M. *Macromolecules* **1997**, *30*, 1153.
(19) Affrossman, S.; Bertrand, P.; Hartshorne, M.; Kiff, T.; Leonard, D.; Pethrick, R. A.; Richards, R. W. *Macromolecules* **1996**, *29*, 5432.
(20) Lianos, L.; Quet, C.; Duc, T. M. *Surf. Interface Anal.* **1994**, *21*, 14.
(21) Reichlmaier, S.; Bryan, S. R.; Briggs, D. *J. Vac. Sci. Technol. A* **1995**, *13*, 1217.
(22) Weng, L.-T.; Smith, T. L.; Feng, J.; Chan, C.-M. *Macromolecules* **1998**, *31*, 928.
(23) Li, J. X.; Gardella, J. A., Jr. *Anal. Chem.* **1994**, *66*, 1032.
(24) Li, J. X.; Gardella, J. A., Jr.; McKeown, P. J. *Appl. Surf. Sci.* **1995**, *90*, 205.
(25) Xiang, M.; Jiang, M.; Feng, L. *Macromol. Rapid Commun.* **1995**, *16*, 477.
(26) Leggett, G. J.; Chilkoti, A.; Castner, D. G.; Ratner, B. D.; Vickerman, J. C. *Int. J. Mass Spectrom. Ion Processes* **1991**, *108*, 29.
(27) Chilkoti, A.; Castner, D. G.; Ratner, B. D.; Briggs, D. *J. Vac. Sci. Technol. A* **1990**, *8*, 2274.

MA9718659