Secondary Ion Mass Spectrometry of Poly(styrene-*co*-isoprene) Diblock Copolymers: Improved Surface Sensitivity Using the High-Mass Region

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ABSTRACT: Thin film preparations of symmetric poly(styrene-*co*-isoprene) (PS−PI) diblock copolymers on silver were examined by TOF-SIMS. This diblock system is known to segregate, forming a PI block layer at the surface. A direct comparison between the low- and high-mass regions of TOF-SIMS spectra is presented. In the low-mass region, characteristic PI ions indicate that the surface is primarily composed of PI; however, a detectable amount of PS is also present at the surface. Thick polymer films were found not to have measurable quantities of PS at the surface. This indicates that surface segregation of thin film preparations on silver is not as extensive as in thick films or that a matrix effect exists due to the silver foil. In contrast, the high-mass region of TOF-SIMS spectra indicates that the surfaces of PS−PI diblocks are composed entirely of PI. In the high-mass region, large PI fragment ions form a repeat spectral pattern, providing unambiguous identification of the PI chain**.** Absence of PS fragment ions in the high-mass region suggests that the escape depth for high-mass ions is less than for low-mass ions. The estimated escape depth of high-mass ions is ≤5 Å. This is a 2-fold improvement in surface sensitivity over low-mass ions, which have a reported information depth of approximately 10 Å. It is probable that high-mass ions are formed in less-energetic regions of the collision cascade further from the center of impact and closer to the surface. Various molecular weight (MW) PS−PI diblocks were examined, and it was observed that the relative intensity of the $R_n - \Delta$ and R_n clusters is sensitive to the molecular weight of the PI block. PI homopolymers, similar in MW to the diblock copolymers, yield high-mass spectra nearly identical to PS−PI diblocks, supporting the conclusion that the surface of the diblocks is composed only of PI.

1. Introduction

Block copolymers can be used to engineer special surfaces for a variety of purposes, for example, stabilizing colloidal dispersions by coating particle surfaces.[1] In the field of microelectronics, thin-film resists are made from block copolymers,[2] and biocompatible surfaces can be created using block copolymers or polymer blends.[3] Recently, researchers have demonstrated that ultrathin diblock copolymer films can be used as templates for nanolithography.[4,5] In many of these applications, advantage is taken of the fact that one block segregates to the free surface.[6] Therefore, an understanding of the surface composition is important to fully take advantage of block copolymer surface properties.

Secondary ion mass spectrometry (SIMS) in the static mode has been used to characterize copolymer surfaces. In the case of random copolymers, SIMS provides bulk composition information because surface segregation does not occur for most systems. Quantitative and semiquantitative analysis is possible by measuring the relative peak intensities of secondary ions (SI) unique to each monomer type.[7−12] Even in the absence of characteristic peaks unique to each monomer, it is still possible to perform quantitative analysis, as long as the peaks are carefully chosen. Weng et al.[13] demonstrated this approach for styrene−butadiene random copolymers; however, the method is not as sensitive to composition as copolymer systems with SI peaks unique for each monomer.

SIMS can also be used to examine surface enrichment of block and segmented copolymer surfaces.[14−18] To date, the majority of SIMS studies have only utilized the low-mass region (<500 *m*/*z*). However, time-of-flight mass analyzers (TOF-SIMS) offer a large mass range, in addition to high sensitivity and high mass resolution. Secondary ions in the mass range 500−4000 Da, and in certain instances higher, are observed.[19] This region of TOF-SIMS spectra is rich with information about the polymer surface composition.[20] Clear, unambiguous repeat patterns separated by the mass of the monomer(s) are observed. The TOF-SIMS high-mass region has been applied to characterize a wide variety of polymer types.[21−25]

Only a few examples utilizing the high mass-region (>500 *m*/*z*) of TOF-SIMS spectra to study block and segmented copolymer surfaces have been published. Briggs et al.[18] suggested that information about the molecular weight of poly(ethylene glycol) side chain blocks of a polyurethane can be obtained from high-mass spectra. Zhuang et al.[17] used the high-mass region to determine the distribution of poly(dimethylsiloxane) segment lengths at the surface of segmented urethane copolymers. High-mass TOF-SIMS has also been applied to characterize polyester polyurethanes.[26] However, it is still not clear how useful the high-mass (>500 *m*/*z*) fragment ions are for studying surface segregation (enrichment) in block copolymer surfaces.

The purpose of the present study is to further examine the utility of the high-mass region of TOF-SIMS spectra for characterizing block copolymer thin films. An important question to consider is how the ion yields of polymer fragments derived from homopolymers relate to block copolymer fragment ion yields. Does the homopolymer ion yield play an important role, or does surface

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enrichment play the more important role in determining what fragment ions appear in the high-mass region of diblock spectra?

In the present study, a series of varying molecular weight symmetric poly(styrene-*co*-isoprene) (PS−PI) diblock copolymers are examined. The PS−PI system has been studied previously by other techniques and is known to undergo surface segregation, the lower surface tension PI block residing at the surface.[27] Nicholas et al.[16] utilized the low-mass region of TOF-SIMS spectra to study the surface of PS−PI diblocks of varying composition. Low-mass secondary ions were used to determine that PI enrichment occurs for samples containing only 10% PI. In the present study, monolayer-like films were prepared on silver substrates to enable large silver cationized fragment ions to be detected by TOF-SIMS. The spectra of the block copolymers are compared with the constituent homopolymer spectra to evaluate the influence of surface composition on the formation of high-mass fragment ions. Information derived from the high-mass and low-mass regions is also compared.

2. Experimental Section

2.1. Instrumentation. A TOF-SIMS III from Ion-Tof GmbH, Münster, Germany, was used for these studies. Primary argon ions are generated in a conventional electron-impact gas source. The primary ions (Ar^+) are accelerated to 10 keV and directed through a 90° beam pulsing unit which produces short ion packets and also mass filters the beam. The ion pulses are further compressed to less than 1 ns width using an axial buncher. The Ar^+ ions are focused on the target using an Einzel lens, and the beam diameter varies between 10 and 50 μm. X,Y deflection plates allow beam rastering.

Secondary ions are accelerated to 3 keV into a 2 m flight tube. The flight tube is connected to an Einzel lens and a reflectron, which improve mass resolution. Post-acceleration to 10 keV is used to improve detection sensitivity. Ion detection is achieved using a channel plate/scintillator/photomultiplier combination. Spectra are accumulated in the single ion counting mode with a maximum of 256 stops per pulse, a time resolution of 1.25 ns per channel, and a time range of 320 μs. Detailed descriptions of the instrument can be found in the literature.[28,29]

In the present experiments the primary ion source was operated at a pulsing frequency of 3 kHz, producing an average primary ion current of 0.6−0.8 pA. The primary ion beam was rastered over a 200 × 200 μm area. Each spectrum was acquired for 500 s, resulting in a total ion dose of approximately 6.3×10^{12} ions/cm^2. Mass resolution was 3500 at $m/z = 500$. Charge compensation was necessary for thick film analysis and was accomplished using a pulsed electron flood gun emitting low-energy electrons at 10 eV.

2.2. Sample Preparation and Data Analysis. The symmetric diblock poly(styrene-*co*-isoprene) (PS−PI) copolymers were a generous gift from Dr. Jimmy Mays of the University of Alabama, Birmingham. The diblocks were made by anionic polymerization. Styrene was polymerized in benzene at 20 °C using *sec*-butyllithium as the initiator. High-vacuum purification procedures and all-glass reactors with break-seals were used. Following complete polymerization of the styrene (48 h), isoprene was added to the reactor, and the color immediately changed from orange to light yellow. After 24 h the diblocks were terminated by addition of rigorously degassed methanol. The polymer was precipitated into a large volume of methanol containing the generic antioxidant BHT and vacuum-dried. The copolymers were characterized by a combination of SEC and NMR. The following PS−PI diblocks were examined in the present study: $M_w = 10\,000$, 50 wt % PS; $M_w = 20\,000$, 50 wt % PS; $M_w = 54\,000$, 69 wt % PS; $M_w = 90\,000$, 43 wt % PS.

Polyisoprene (PI) and polystyrene (PS) homopolymers were obtained from commercial sources. The PS ($M_w = 22\,000$) was purchased from Scientific Polymer Products, Inc., Ontario, NY, and the PI ($M_w = 3000$, $M_w/M_n = 1.08$) was purchased from Polysciences, Inc., Warrington, PA. The remaining PI samples were purchased from Polymer Source, Inc., Dorval, Quebec, Canada, and included the following: $M_w = 17\,700$, $M_w/M_n = 1.04$; $M_w = 34\,500$, $M_w/M_n = 1.04$; $M_w = 86\,700$, $M_w/M_n = 1.03$; and $M_w = 144\,800$, $M_w/M_n = 1.03$.

All solvents used for preparation of TOF-SIMS samples were HPLC grade, Fisher Scientific, Pittsburgh, PA. Samples were prepared in toluene at concentrations ranging from 2 to 4 mg/mL. The 1.0 cm diameter silver foil substrates were cleaned by acid etching in 20 vol % aqueous nitric acid and washed by sonication in water three times followed by three times in methanol. Thin film samples, approximately “monolayer” thickness, were prepared by depositing 2 μL of the polymer solution (2−4 mg/mL) onto the silver substrate which was held at an angle of 45°, allowing excess solution to run off the target, followed by air-drying.

Thick polymer films, approximately 1−5 μm thick, were prepared by dissolving the polymer samples in toluene at 15 mg/mL. A 10 μL aliquot of the solution was deposited onto silicon substrates (≈1.0 cm^2). The silicon substrates were previously cleaned by washing several times in toluene, then acetone, and finally water.

Smooth silver-coated mica substrates were prepared by sputter deposition. Freshly cleaved mica substrates (2 × 1 cm) were placed in a Pelco model 3 sputter coater, Redding, CA (vacuum = 0.1 Torr; current = 25−30 mA; sputter time = 100 s; Ar gas). To prepare the polymer films, 5 μL of polymer solution (4 mg/mL in toluene) was deposited onto the substrate. The substrate was held at an angle of roughly 45°, and the lower edge of the substrate was placed in contact with absorbent tissue to absorb the excess solution.

Linear least-squares regression analysis (LLSRA) was performed using in-house generated software (GOOGLY) by Andrew Proctor.

3. Results and Discussion

3.1. Low-Mass Region. The high-mass region of SIMS spectra is generally underutilized for the characterization of macromolecules. Reasons for this are twofold. First, only TOF-SIMS instruments can detect large fragment ions; quadrupole and magnetic-sector instruments have inadequate mass range and sensitivity. Second, only certain sample preparation methods will yield high-mass fragment ions. A common, and generally effective, sample preparation method is to create (spin-coat, solution deposition) a “monolayer” polymer film on a silver foil.[30] During the SIMS sputtering process, large neutral polymer fragments are desorbed and cationized by Ag^+. Thick films generally do not yield high-mass ions, although there are exceptions.[17,31] In the present work PS−PI diblocks are examined for surface segregation.

It is important to compare the low-mass and high-mass regions of TOF-SIMS spectra. Figure 1 shows low-mass range spectra for PS−PI diblocks obtained from thin films on etched silver for the mass range 25−200 Da. Spectra from PS and PI homopolymers are included for comparison. These so-called “fingerprint” spectra contain peak intensity patterns which are dependent on polymer type.[32,33] The two homopolymers, PS and PI, each have characteristic peaks which are significantly more intense in only one of the two homopolymer spectra. Table 1 provides a list of peaks which are characteristic of PS and PI. The relative intensities (relative to base peak) are included for the PS−PI diblocks and the PS and PI homopolymers. Structures for many of these ions have been reported elsewhere

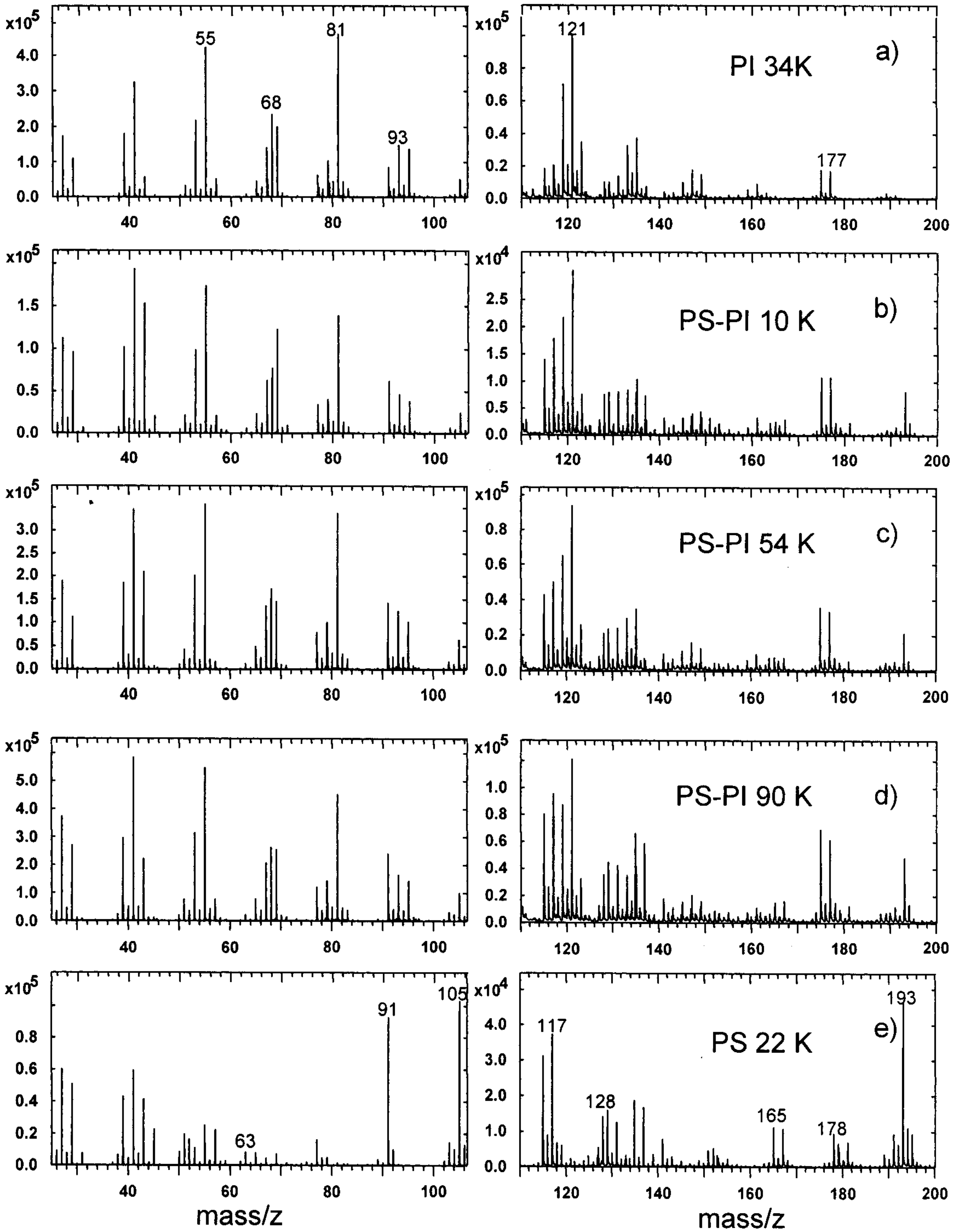

Figure 1. TOF-SIMS spectra obtained from thin films on etched silver. Polyisoprene homopolymer: M_w = 34 500 (a). Poly(isoprene-*co*-styrene) diblock copolymers: M_w = 10 000 (b), M_w = 54 000 (c), and M_w = 90 000 (d). Polystyrene homopolymer: M_w = 22 000 (e). The mass range 106−110 Da is omitted because of intense $^{107}Ag^+$ and $^{109}Ag^+$ peaks.

for PS[34] and PI.[32,33] Peaks in the PI homopolymer spectrum at 175/177 Da are due to the silver cationized PI monomer.

Using the characteristic PS and PI peaks, information about the surface composition of the PS−PI diblock films can be obtained. Characteristic PI peaks at 68, 69, 81, 93, 119, and 121 Da all have significantly higher relative intensities in the PS−PI diblock spectra than in the pure PS homopolymer. In addition to listing the relative intensities for the individual PS and PI peaks, Table 1 gives summed ion intensities of the characteristic PS and PI peaks for each polymer sample. Figure 2 shows a graph of the summed ion intensities for the PS−PI diblocks and the PI homopolymer. Data are presented for spectra obtained from both thin polymer films on etched silver and from thick films. Compare the summed intensities for the diblocks with the summed intensities for the PI homopolymer in Figure 2. It is clear that the PI intensities from the diblocks do not vary significantly from those for the PI homopolymer whether measured on silver (◆) or for the thick polymer films (△). The solid lines show linear least-squares fits for the two data sets; the slopes of these two lines are not significantly different from zero at the 95% confidence level. Because

Table 1. Relative Intensities of Characteristic Polyisoprene and Polystyrene Ion Peaks; Relative Standard Deviations of the Values Are in the Range 9−14

m/z	PI 34K	PS-PI 10K	PS-PI 20K	PS-PI 54K	PS-PI 90K	PS 22K
A. Thin Films on Etched Silver: Polyisoprene Peaks						
41	62.0	100.0	82.0	86.0	99.4	36.2
68	38.3	34.8	34.9	35.1	41.3	0.6
69	40.3	57.7	51.5	51.8	49.3	5
81	100	82	100	100	98.7	1.7
93	35.7	35.7	41.8	39.9	38	1.1
119	9.9	10.4	12.6	11.7	14.4	3.1
121	17.7	13.9	17.4	16.5	16.6	1
totals	303.9	334.5	340.2	341.0	357.7	48.7
B. Thin Films on Etched Silver: Polystyrene Peaks						
63	1.8	3.3	4.6	4.4	4	5.6
91	21.5	48.8	68.7	68.8	52.1	86.1
103	2	4	7.7	8.1	6.8	11.2
105	13.8	20.4	27.0	26.8	22.4	100.0
115	2.7	6.1	12.3	11.4	9.9	17.5
117	3.3	8.1	16.4	15.3	10.3	17.9
128	1.5	2.7	4.8	4.7	4.4	6.4
152	0.3	0.6	1.6	1.5	1.2	2.6
165	0.4	1.1	3.5	3.5	3	7.6
167	0.2	1.2	3.7	3.6	2.6	5.4
178	0.4	1.1	4	4.1	3.2	8.5
193	0.1	3.8	11.5	11.1	8	27.2
totals	48.0	101.2	165.8	163.3	127.9	296.0
C. Thick Polymer Films: Polyisoprene Peaks						
41	100.0	100.0	100.0	100.0	100.0	7.0
68	48.6	39.2	36	39.8	38.1	0.6
69	34.4	62.9	45.1	32.8	32	0.3
81	77.8	78.5	70.5	67.3	72.9	0.8
93	32.4	28.3	26.7	27.3	27	0.9
119	9.9	7.6	7.6	7.8	7.9	1.7
121	7.2	8.8	8.6	7.1	7.9	0
totals	310.3	325.3	294.5	282.1	285.8	11.3
D. Thick Polymer Films: Polystyrene Peaks						
63	4.1	3.2	3.3	3.5	3.2	17.1
91	34.8	31.1	29	28.6	27	100
103	3.3	3.1	2.8	2.5	2.8	18.8
105	17.4	14.6	13.4	13.9	13.3	64.4
115	4.8	4.3	3.9	4.2	4.1	36.1
117	3.9	3.9	3	3.1	2.5	17.1
128	2.5	2.3	1.7	2.2	2.1	18
193	0.0	0.2	0.0	0.0	0.0	13.2
totals	70.8	62.7	57.1	58.0	55.0	271.5

the characteristic PI peak intensity sums are similar for the diblocks and the PI homopolymer, it can be concluded that the surfaces of the diblocks are enriched with PI whether for thin films on silver or for thick polymer films.

However, there is evidence for PS at the surface as well for thin polymer films on silver. In Figure 1, characteristic PS peaks at 91, 115, and 117 are more intense in the PS−PI diblock spectra than in the PI homopolymer spectrum. The summed intensities for the characteristic PS peaks listed in Table 1 for thin films on silver are generally larger in the PS−PI spectra by a factor of 2.1−3.5 than for these peaks in the PI homopolymer spectra (see Table 1B). The graph of summed ion intensities for PS in Figure 2 for polymer spectra obtained from thin films on silver (□) shows a significant increase in intensity for all of the diblock spectra. The line fitting these points is a third-order polynomial function and does not necessarily have any physical significance, although it does indicate that the PS intensity in the higher molecular weight diblocks is greater than in the 10K diblock. Also, increases are readily apparent for all of the individual PS peaks summarized in Table 1. Therefore, the conclusion is that, for thin polymer films on etched silver, the surfaces are largely composed of PI but that significant amounts of PS are present as well. This makes such films ideal for comparing the low-mass and high-mass regions of TOF-SIMS for studying surface segregation.

Other authors have found that the surfaces of symmetric PS−PI diblocks are completely composed of PI. Using transmission electron microscopy (TEM) of cross-sectioned films, Hasegawa and Hashimoto[27] found that a 540 000 mol wt symmetric PS−PI diblock had a single layer of PI block at the surface. Their samples were prepared by slow solvent evaporation techniques over several days, thus promoting surface enrichment of the PI block. In the present case, the polymers are lower in molecular weight and were prepared by fast solvent evaporation. Therefore, surface enrichment by the PI block may not be as extensive. Nicholas et al.[16] used low-mass TOF-SIMS to characterize thick PS−PI diblock films spin-coated onto silicon. The molecular weights were similar to the samples tested in the present study. These authors found that samples containing 50% or greater bulk PI content had very little PS at the surface. Even a sample with 75% bulk PS content was significantly enriched with PI at the surface. On the basis of these reports, it was assumed that a surface layer of PI should exist for the PS−PI diblocks examined in the present study. The presence of characteristic PS peaks in the spectra of thin PS−PI diblock films on silver

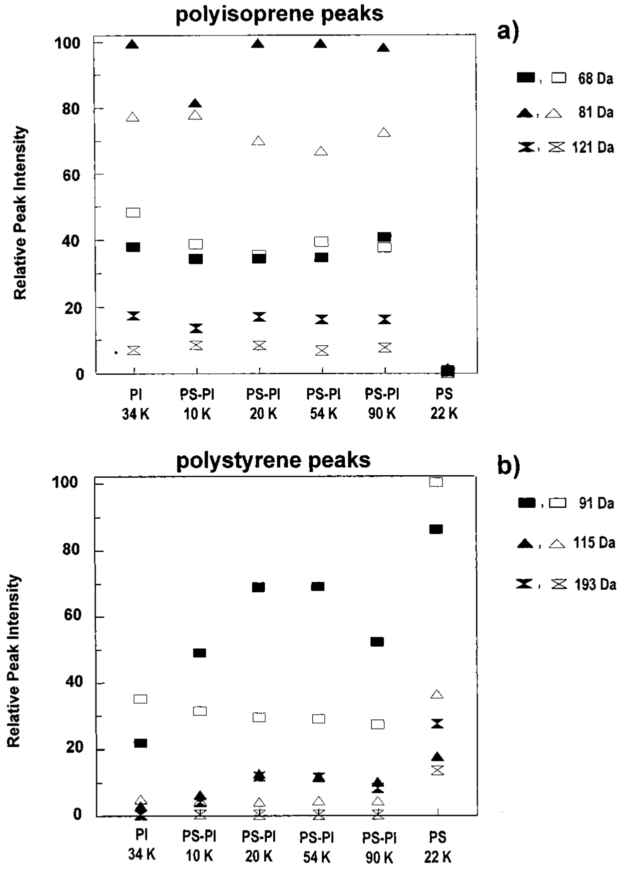

Figure 2. Summed ion intensities for the low mass range: (◆) PI on silver; (△) PI from thick films; (□) PS on silver; (×) PS from thick films. See Table 1 for data.

shown in Figure 1 suggests that there are some differences between sample preparations (thin films on silver vs thick films). Therefore, thick diblock films were prepared and analyzed by TOF-SIMS for comparison.

Figure 3 shows low-mass spectra for thick films of the PS−PI diblock copolymers over the mass range 25−200 Da. The relative intensities of characteristic PS and PI low-mass ion peaks are listed in Table 1 for thick films of PS, PI, and the PS−PI diblocks. Comparing the spectra in Figures 1 and 3 and the data in Table 1, it can be seen that the relative intensities of the characteristic PS peaks are all much lower in the thick film PS−PI spectra than in the thin film PS−PI spectra. For example, the PS peaks at 91, 115, 128, and 193 Da are either less prominent or absent in the thick film PS−PI diblock spectra. Also, the PS ion intensity totals are much lower in the spectra obtained from thick films. It can be seen in Figure 2 that the summed ion intensities (×) of the PS peaks for the PS−PI diblocks are not much different from the summed intensities of the same peaks for the PI homopolymer. The least-squares line in Figure 2 has a slight negative slope with increasing molecular weight. Given that there is no significant difference in characteristic peak intensities between the PI homopolymer and the PS−PI diblocks, one can conclude that only PI occupies the surfaces of the thick film copolymer samples.

The results of comparing thin films on silver with thick films show that there are some differences between sample preparations. The data suggest an apparent increase in PS content for thin films on silver compared with the thick films. It is expected that as the film thickness decreases, the substrate will have a greater influence on the spectrum. Delcorte et al.[35] found that for "monolayer" film thickness the yield of low-mass ions is greater compared with thicker films on silver. Another study comparing the molecular secondary ion yields of adenine ($[M + H]^+$, $[M + CH_3]^+$) with sputtered neutral yields showed that the effect is the same for both secondary molecular ions and secondary molecular neutrals, suggesting that the sputtering process is influenced by film thickness and the type of substrate (Au, Ag, Cu, Ni, and Si were compared), not the ionization process.[36] However, for low-mass fragment ions there is evidence that the effect is ion-dependent.[35] In Table 1, the relative intensity of the PS peak at 193 Da is greater for the thin PS homopolymer film on silver than from the thick PS homopolymer film. The converse is true for the 115 and 91 Da peaks. Also, the base peak changes from 105 to 91 Da for the PS thin film on silver and the PS thick film, respectively. Differences in peak intensities between the thin films on silver and thick films also occur for the PI homopolymer, as seen in Table 1. For the PI homopolymer, the base peak is 81 Da for the thin film on silver sample and 41 Da for the thick film sample. These changes in relative peak intensity suggest that the apparent increase in PS surface content for thin films on silver may in part be due to a matrix effect caused by the silver foil. Substrate roughness could also be a factor contributing to the observed spectral difference between the thin and thick films. The etched silver foil substrates used to prepare the thin films are rough, and the resulting polymer film is not uniform in thickness.[30] Etched silver substrates are preferred over smooth substrates due to improvement in secondary ion yields for silver cationized high-mass fragment ions. To determine whether roughness of the etched silver substrate influences the low-mass spectra, smooth silver substrates were also used. The smooth silver substrates were prepared by vacuum sputtering silver onto mica. The resulting spectra (data not shown)[37] were essentially identical to spectra obtained from etched Ag substrates. This indicates that substrate roughness is not a factor contributing to the observed spectral differences between thin films on silver and thick films.

By comparing thick and thin films, it was found that differences between the two sample preparation methods exist. Some PS is present at the surface of the thin films, which is not the case for the thick films. However, the low-mass ion data indicate that the surface of the PS−PI diblocks is enriched with PI and that the thin film polymer surface approximates a thick film surface. This conclusion is important for validating the use of thin films on silver to evaluate diblock surfaces using high-mass TOF-SIMS.

3.2. High-Mass Region. Figure 4 shows a portion of the high-mass TOF-SIMS spectra obtained from thin films on etched silver over the mass range 800−1200 Da for two PI homopolymers (M_w = 3000 and M_w = 34 500), a PS−PI diblock (M_w = 20 000), and a PS homopolymer (M_w = 22 000). The two PI homopolymer spectra both show repeat patterns spaced by 68 Da, characteristic of the isoprene monomer unit. The PS homopolymer spectrum contains a repeat pattern spaced by 104 Da, characteristic of the PS monomer unit. Details about the high-mass fragmentation patterns for PI[38] and PS[39] have been presented elsewhere. It was found that large neutral polymer fragments are formed, by cleavage of the polymer backbone, which are then

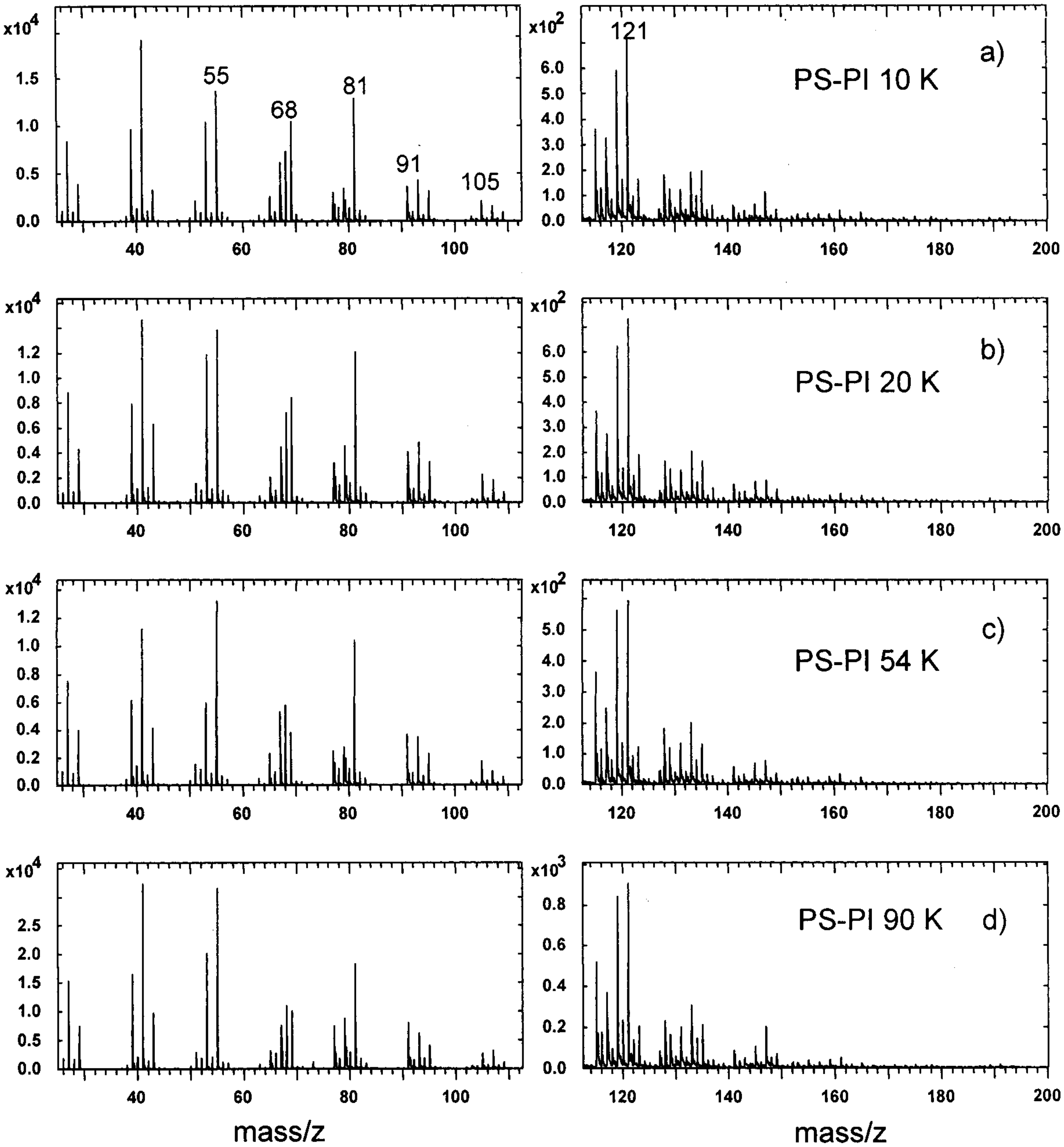

Figure 3. TOF-SIMS spectra obtained from thick films. Poly(styrene-*co*-isoprene) diblock copolymers: M_w = 10 000 (a), M_w = 20 000 (b), M_w = 54 000 (c), and M_w = 90 000 (d).

cationized by silver.[20] Examination of the 20K PS−PI diblock spectrum reveals that only a repeat pattern for PI is present. There is no indication of PS fragment ions in the spectrum. Figure 5 shows the high-mass spectra for the other PS−PI diblocks studied. Consistent with the 20K diblock, these spectra show only PI fragmentation patterns. PS fragment ions are not present in any of the PS−PI diblock spectra.

There are differences between the PI-containing polymers, both homopolymers and diblocks. As the molecular weight increases, the absolute signal intensity tends to decrease, typical of TOF-SIMS spectra of polymers.[21] Another difference between the spectra is the change in the relative intensities of the peak clusters with molecular weight. As indicated in Figures 4 and 5 by asterisks (*) and open circles (○), the relative intensities of the two most prominent clusters in each pattern change with molecular weight. This is observed for both the PI homopolymers and the PS−PI diblocks. Xu et al.[38] found the same behavior for a series of PI homopolymers of varying molecular weight.

Absolute high-mass fragment ion intensity measurements were made for the two homopolymers, PS (22 K) and PI (17 K), to determine which of the two homopolymers has greater ion yield. The methodology for these measurements has been validated independently in our laboratory.[40] The PS (22 K) and PI (17 K) homopolymer samples were selected for comparison because of similar molecular weights. Absolute ion intensity values were obtained by using three spectra for both homopolymers, collected under identical instrumental conditions. In each spectrum the intensity of the most intense cluster within each repeat pattern was determined by integrating the cluster area. The process was performed for eight repeat patterns, from $n = 7$ to $n = 14$, and then averaged. The average intensity observed for PS was 13 376 counts and for PI 1521 counts, making the relative ion yield of PS 8.8 times that of PI. The relative

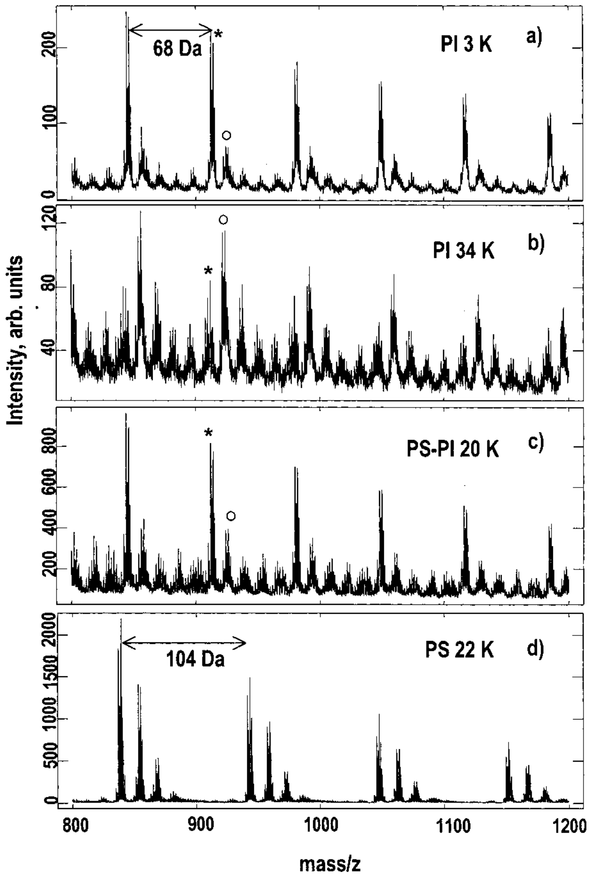

Figure 4. High-mass TOF-SIMS spectra. Polyisoprene homopolymers: $M_w = 3000$ (a) and $M_w = 34\ 500$ (b). Poly(styrene-*co*-isoprene) diblock with $M_w = 20\ 000$ (c). Polystyrene homopolymer with $M_w = 22\ 000$ (d).

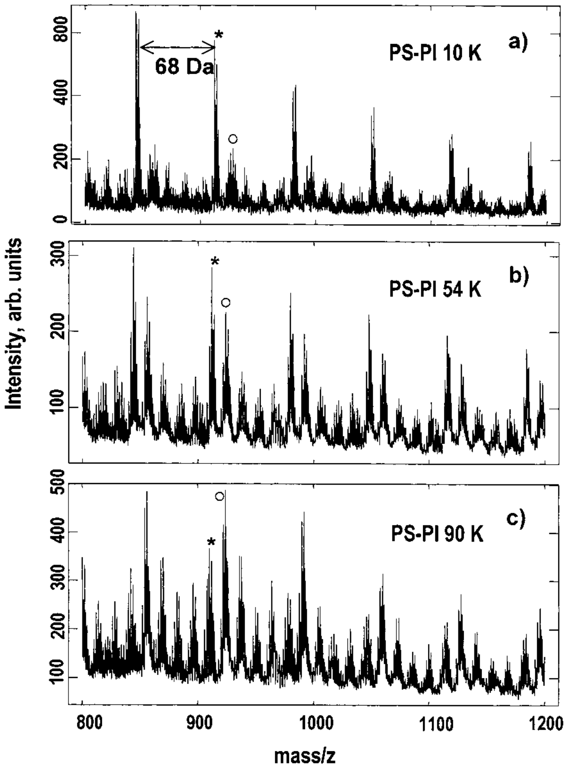

Figure 5. High-mass TOF-SIMS spectra. Poly(styrene-*co*-isoprene) diblocks: $M_w = 10\ 000$ (a), $M_w = 54\ 000$ (b), and $M_w = 90\ 000$ (c).

standard deviations in intensities were 13% and 22%, respectively. Since the high-mass ion yield of PS is 8.8 times greater than PI, if PS were present at the diblock surface, then high-mass PS ions definitely should appear in the diblock spectra.

The presence of only PI fragments in the high-mass spectra of PS–PI diblocks indicates that the surface is comprised only of PI blocks. PI has lower surface tension than PS (PI: 30–32 dyn/cm, PS: 32–36 dyn/cm),[41] as discussed above, and tends to occupy the surface region of PS–PI diblocks. The low-mass spectra, however, indicate that the surface contains some PS, as indicated by the presence of characteristic low-mass PS peaks. This contradiction between the low-mass and high-mass regions suggests that there is a difference in the surface sensitivity for the two spectral regions.

During the SIMS sputtering process, high impact energy (10 keV Ar^+primary ions) is converted to lower energy through a collision cascade.[42] A single primary ion can sputter material over a region on the order of 50 Å diameter.[20,43] Though the formation of organic ions in the static SIMS process is still poorly understood, it is reasonable to expect that larger fragment ions will originate from less energetic regions within the action area. In contrast, low-mass organic ions will originate from more energetic regions closer to the center of primary ion impact. In a model detailed by Benninghoven,[44] energy transfer decreases radially from the primary ion track. Delcorte et al.[35] measured kinetic energy distributions (KED) of secondary ions produced from organic films and found that a saturated ion has a narrower KED than an analogous unsaturated ion. It was suggested that unsaturated ions are formed closer to the center of primary ion impact. Larger, more saturated ions are formed at greater distances from the center of impact. This explanation can be extended to explain the difference in escape depth (information depth) between high-mass ions and low-mass ions generated by fragmentation of polymers. Since energy transfer decreases radially from the center of impact, it is reasonable to assume that the amount of material sputtered from the surface decreases with distance from the point of impact. High-mass ions formed in less energetic regions farther from the impact point would necessarily originate closer to the surface, making the escape depth of large ions shallower than that of small ions. This can explain the absence of PS fragment ions in the high-mass region but the presence of PS ions in the low-mass region.

Low-mass ions have an estimated information depth of approximately 10 Å.[45–47] An estimate of the information depth for high-mass ions can be made by assuming similar behavior for the PS–PI diblocks studied here and the reported surface behavior of a PS–PI diblock studied by TEM.[27] Inspection of the published micrographs indicates that the thickness of the surface PI layer is approximately 250 Å. The authors indicate that the surface PI layer is one PI block chain thick, which corresponds to an average of 3700 PI monomer units for the copolymer studied. The thickness of the PI surface layer for the 10 K PS–PI in the present study corresponds to 74 PI monomer units. Therefore, using 3700 PI units/250 Å as a conversion factor, an information depth of ≤5 Å is estimated for high-mass ions. This is greater than a 2-fold improvement over low-mass ions.

At present, the conclusion that high-mass ions have a superior information depth relative to low-mass ions

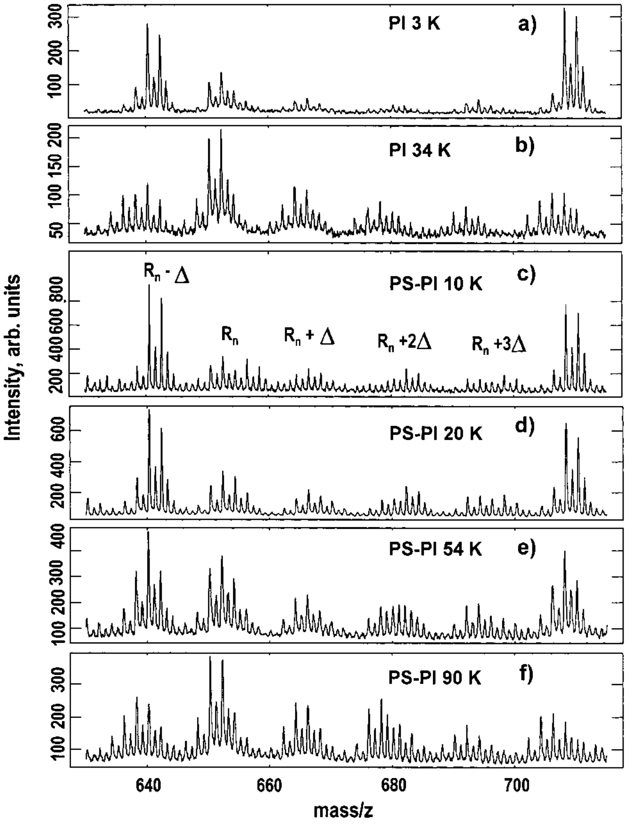

Figure 6. High-mass TOF-SIMS spectra. Polyisoprenes: $M_w = 3000$ (a) and $M_w = 34\,500$ (b). Poly(styrene-*co*-isoprene) diblock copolymers: $M_w = 10\,000$ (c), $M_w = 20\,000$ (d), $M_w = 54\,000$ (e), and $M_w = 90\,000$ (f).

is somewhat speculative. Other reasons for the observed differences between the low- and high-mass regions must be considered. The influence of the silver substrate on the high-mass region cannot be entirely dismissed. As mentioned in the previous section, evidence of a slight matrix effect was found by comparing thin films on silver with thick films. Additionally, lateral segregation must be considered. If PI forms domains that are thinner than the PS domains, then PI could be preferentially cationized by silver during sputtering. This would require a very significant difference in thickness to compensate for the higher ion yield for PS.

3.3. Repeat Pattern. Figure 6 shows an expanded portion of the high-mass region (630−710 Da) for the PS−PI diblock copolymers and the 3K and 34.5K PI homopolymers. Each repeat pattern consists of five groups of peaks corresponding to the number of carbon atoms in the isoprene repeat unit. Each group of peaks will be referred to as a *cluster*. Within each pattern there appears a cluster corresponding to an integral number of monomer units, indicated by R_n. The spacing between adjacent clusters will be represented by the symbol "Δ". The value of Δ is not constant but varies from 12 to 16 Da due to differing degrees of unsaturation within the different clusters. In Figure 6 the five clusters are referred to as $R_n - \Delta$, R_n, $R_n + \Delta$, $R_n + 2\Delta$, and $R_n + 3\Delta$, as indicated in spectrum c. Each cluster contains several isotopic peaks from ^{12}C, ^{13}C, ^{107}Ag, and ^{109}Ag in addition to fragment species with varying degrees of unsaturation. Details about the fragmentation pathways leading to formation of PI clusters have previously been reported.[38]

Referring to Figure 6, there is a clear trend in the relative intensities of the $R_n - \Delta$ and R_n clusters. As the molecular weight of the PS−PI copolymer is increased, and consequentially the molecular weight of the PI block, the intensity of the R_n cluster increases relative to the $R_n - \Delta$ cluster intensity. A similar effect was found for PI homopolymers of varying molecular weight.[38] Figure 7 illustrates the change in relative intensity of the $R_n - \Delta$ and R_n clusters as a function of PI chain length for the PS−PI diblock copolymers and PI homopolymers. The relative cluster intensities were obtained by averaging over eight repeat patterns in each spectrum, from $n = 7$ to $n = 14$. As the PI chain length increases from approximately 25 to 500 monomer units, the intensity of the R_n cluster increases relative to the $R_n - \Delta$ cluster. Above 500 monomer units, the relative intensity remains constant. An increase in the standard deviation for longer PI chain lengths, as indicated by the error bars, is due to a decrease in spectral signal-to-noise for higher molecular weight samples. It can be seen from Figure 7 that the PS−PI diblocks behave similarly to the homopolymers, suggesting that the PS block has little influence on the PI sputter/cationization process for large ions. The large PI fragment ions appear to be originating from a pure PI layer at the surface of the diblock films. The change in the $R_n / R_n - \Delta$ intensity ratio with molecular weight means that it is possible to obtain information about the size of the PI chain for lengths ranging up to approximately 500 monomer units.

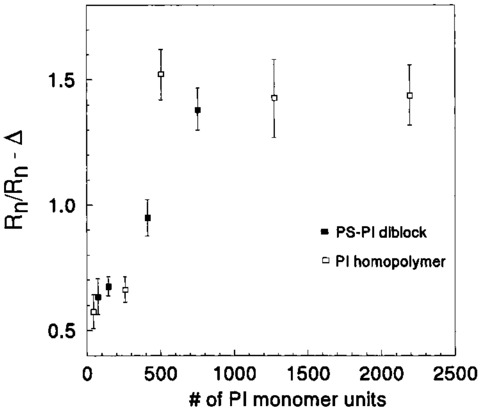

Figure 7. Relative intensities of the R_n and $R_n - \Delta$ clusters vs PI chain length for polyisoprene homopolymers and poly(styrene-*co*-isoprene) diblock copolymers.

Presently, it is not clear why the intensity of the $R_n - \Delta$ cluster changes with molecular weight. Xu et al.[38] described possible fragmentation pathways leading to formation of the clusters found in PI homopolymer spectra. However, the authors did not explain the relative intensities of the clusters. In many cases where relative peak intensities change with molecular weight, the behavior is due to involvement of end groups.[48] Fragment ions containing an end group are more intense for lower molecular weight samples. As the molecular weight increases, the concentration of end groups decreases, resulting in a decrease in signal intensity for ions containing the end group. Thus far, attempts to rationalize the formation of ions containing the end group (the end group is H for the PI blocks) which contribute to the $R_n - \Delta$ cluster have been unsuccessful. It remains uncertain why the intensity of this cluster changes with molecular weight. Nonetheless, the $R_n - \Delta$ cluster intensity can be used to estimate the molecular weight of the PI block up to 34 000 g/mol.

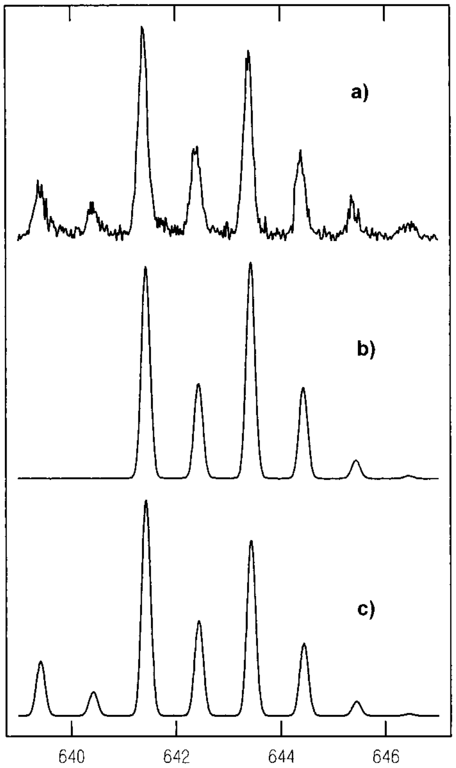

Figure 8. Detailed cluster structure of the $R_n - \Delta$ ($n = 8$) fragment for the poly(styrene-*co*-isoprene) diblock with M_w = 10 000 (a). Theoretical spectrum for the single $C_{39}H_{66}Ag^+$ species (b). Theoretical cluster spectrum based on results of LLSRA (c).

3.4. Cluster Structure. As mentioned above, each cluster consists of a convolution of isotopes: ^{12}C, ^{13}C, ^{107}Ag, ^{109}Ag, and species with varying degrees of unsaturation. Xu et al.[38] have described the detailed structure of the R_n clusters obtained from PI homopolymers, but a detailed examination of the $R_n - \Delta$ cluster was not reported. Figure 8a shows the expanded $R_8 - \Delta$ cluster from the 10K PS−PI diblock spectrum. The mass of the cluster corresponds to a species having the empirical formula $C_{39}H_{66}Ag^+$. A theoretical spectrum corresponding to this ion formula is shown in Figure 8b. Comparison of experimental and theoretical spectra indicates that more than one species is present in the experimental spectrum. In TOF-SIMS polymer spectra it is typical to observe clusters containing several species differing in their degree of unsaturation.[39] Therefore, by considering species with different degrees of unsaturation, a more complete fit of the experimental spectrum is possible. Linear least-squares regression[21,38] was used to determine the number of species contributing to the experimentally observed cluster. Theoretical spectra were generated for single species: $C_{39}H_{66}Ag^+$, $C_{39}H_{64}Ag^+$, and $C_{39}H_{62}Ag^+$, corresponding to zero, one, and two additional degrees of unsaturation. Increasing numbers of species were included in the curve fit of the experimental cluster. The resulting theoretical spectrum which minimized the residual consists of 75.7% $C_{39}H_{66}Ag^+$, 21.5% $C_{39}H_{64}Ag^+$, and 2.8% $C_{39}H_{62}Ag^+$ and is shown in Figure 8c. By referring to Figure 6, it is realized that the $R_n - \Delta$ cluster structure changes with the PI chain molecular weight. This indicates that the number of species contributing to the cluster, and the relative contributions of the species, is dependent upon molecular weight of the PI block.

4. Conclusions

TOF-SIMS was used to examine the surfaces of symmetric poly(styrene-*co*-isoprene) (PS−PI) diblock copolymers films on silver. The low-mass and high-mass spectral regions were compared. High-mass spectra contain only large silver cationized polyisoprene (PI) fragment ion peaks; no polystyrene (PS) fragment ions are observed. Absolute high-mass ion intensity measurements performed on PS and PI homopolymers show that PS has an 8.8-fold higher ion yield than PI. Since PS has higher ion yield than PI, the presence of only PI fragment ions in the PS−PI diblock spectra is strong evidence that the PI block forms a surface layer. In the low-mass region, the relative intensities of characteristic PS and PI peaks indicate that the surface is enriched with PI, but a detectable amount of PS is also present. This contradiction between the low- and high-mass spectral regions can be interpreted as evidence of the greater surface sensitivity of high-mass ions; it was possible to estimate the ion escape depth at 5 ≤ Å. The high-mass region of the diblock spectra contain repeat peak patterns characteristic of PI. It was found that the relative intensity of the two most prominent clusters is sensitive to the molecular weight of the PI block. The results of this investigation demonstrate that valuable information about the surface composition of diblock copolymers systems is provided by the high-mass region of TOF-SIMS spectra.

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