
Time of Flight Secondary Ion Mass Spectrometric Determination of Molecular Weight Distributions of Low Polydispersity Poly(Dimethyl Siloxane) with Polyatomic Primary Ions

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This work reports a comparison of oligomer and fragment ion intensities resulting from primary ion bombardment with several primary ion sources (Bi_n^+ , C_{60}^+ , and Cs^+) at various energies in secondary ion mass spectrometry (SIMS). Although the use of polyatomic primary ions are of great interest due to increased secondary ion efficiency and yield, we demonstrate that monatomic primary ions result in increased oligomer ion yield for polymers prepared as submonolayer films on silver substrates. The enhancement of oligomer secondary ion yield with monatomic ions is evidence that monatomic primary ions have a shallower sampling depth than polyatomic ions, resulting from a collision cascade that is less energetic at the sample surface. The results are also consistent with a lower degree of fragmentation of the resultant secondary ions, which is observed when evaluating the fragmentation data and the spectral data. (J Am Soc Mass Spectrom 2009, 20, 1562–1566) © 2009 American Society for Mass Spectrometry

Technical (synthetic) polymers consist of a mixture of oligomer chains that results in a distribution of molecular weights. This molecular weight distribution (MWD) is a critical factor in determining the mechanical and physico-chemical properties of the polymer [1]. Mass spectrometric methods provide for determination of molecular weight distributions with various advantages over other, indirect measurements, such as light scattering or size based separation methods. Matrix assisted laser desorption ionization (MALDI) mass spectrometry can provide molecular weight distributions of polymers up to 1.5 million Da. However, this can only be used for polymers with narrow polydispersity [2–4]. Electrospray ionization (ESI) mass spectrometry can be utilized to determine molecular weight distributions but this technique suffers from the need to dissolve the polymer in a suitable solvent [2]. Secondary ion mass spectrometry (SIMS), especially with time of flight detection, offers the opportunity to determine MWD, and with the particular advantage of surface sensitivity, yielding MWD information from the surface of a solid polymer matrix [5–7]. If the MWD shows segregation of various oligomer fractions at the surface, different surface properties may result [7–9]. For SIMS, submonolayer deposition from dilute polymer solu-

tions onto silver or silicon substrates provides a model system for determination of MWD for polymers, although limited to those with oligomer weights between 1000 and 10,000 Da [10].

New developments in primary ion sources for SIMS have resulted in wider applicability of the technique [11]. In particular, the bombardment of solids by cluster ion beams (i.e., SF_5 , C_{60} , Au_n , Bi_n) has introduced a new mechanism for the ejection of material in SIMS [11–13]. The application of these sources has been critical to improve depth profiling of soft materials, minimizing subsurface damage to preserve the structure of the polymeric or organic material for accurate depth profiles [11, 12]. Another important aspect of polyatomic primary ion bombardment of organic solids is the enhancement of molecular ion yields, especially at high mass [11, 13]. However, molecular dynamic simulations of polyatomic ion sputtering of small organic molecules on silver substrates predict little enhancement in molecular ion yields [14]. This points to the importance of the substrate (organic versus metallic) in the use of polyatomic versus monatomic primary ion source, elucidated by the work of Schnieders et al. [15], in which a high variability of secondary ion yields from a variety of substrate materials was found. In the case of molecular ion yield enhancement, the thickness of the organic overlayer on the substrate is critical. In work by Schnieders et al. [15], secondary ion yield is shown to peak at approximately one monolayer polymer cover-

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age and falls away as the coverage increases as a result of the changing matrix. Above one monolayer coverage, the primary ion loses more energy in the organic layer below and the organic layer furthermore prevents the efficient ejection of metal atoms from the collision cascade.

Due to the variety of primary ion sources and their different interactions with different substrates, there remains ambiguity as to which primary ion offers optimal performance for acquiring high mass information, such as molecular weight distributions from polymers. A large volume of work exists comparing primary ion source performance [16–19], the effect of different substrates [15, 20], and molecular dynamic simulations, considering both substrate and primary ion type [14, 21–23]. The goal of the present study is to compare the results of MWD and polydispersity index (PDI) determined by TOF-SIMS from a well defined poly(dimethyl siloxane) (PDMS) polymer with narrow molecular weight distribution. Results from different primary ions are compared quantitatively.

Experimental

Two PDMS homopolymers with trimethylsilyl end groups were obtained as synthesized by Polymer Source, Inc. (Dorval, Quebec, Canada) and are designated PDMS-2200 and PDMS-6140, corresponding to their number average molecular weight (M_n). The manufacturer determined M_n , M_w , and PDI values as 6140, 6600, and 1.07, respectively, for the 6140 PDMS, the 2200 PDMS has M_n , M_w , and PDI values of 2200, 2400, and 1.09, respectively, using gel-permeation chromatography (GPC). The polymers were synthesized by ring-opening polymerization using hexamethylcyclotrisiloxane as the monomer, and the anionic syntheses were initiated using butyl lithium, yielding PDIs less than 1.1.

All TOF-SIMS spectra were acquired on a TOF-SIMS 5.100 instrument manufactured by ION TOF GmbH (Muenster, Germany). The instrument is equipped with a Bi_n^+ liquid metal ion source, and a dual source column with Cs^+ and C_{60}^+ sources. Cesium and C_{60} can be operated in both analysis and sputtering modes; in analysis mode both cesium and C_{60} have an acceleration energy of 10 kV with doubly charged ions having twice that amount. The bismuth primary ions can be accelerated with either 15 or 25 kV energy, again with doubly charged species being accelerated to twice that value. The analyzer is of the reflectron type; reflector voltage of 19 V and post-acceleration voltage of 10 kV were applied for all spectra acquisitions. The pressure in the main chamber was maintained between 5×10^{-8} and 5×10^{-9} mbar. All samples received a primary ion dose between 1.5×10^{12} and 5.0×10^{12} ions/cm². Data analysis was performed using ION SPEC software (ver. 4.1) issued by ION TOF GmbH (Muenster, Germany).

All samples were diluted with 99.9% toluene (Fisher Scientific, Pittsburgh, PA, USA) to a concentration of 1 mg/mL. Approximately 2 μ L of the solution was deposited on cleaned, acid etched silver foil (Sigma-Aldrich Inc., St. Louis MO, USA). The silver foil was cleaned by ultrasonication in hexane followed by toluene (ACS certified) for 20 min each. This cleaning was followed by a 10 min etch in 10% nitric acid (bulk-grade).

All spectra were mass calibrated with 10 peaks characteristic of the sample and substrate.

Results and Discussion

Figure 1A and B illustrate the intensities of the oligomer ion ($M + Ag$)⁺ distributions using different primary ions. Since all samples were exposed to a tight range of nearly constant primary ion dosages, the intensity scales can be compared. It is apparent that monatomic primary ion sources consistently provided the highest intensity molecular weight distribution for a given primary ion dose. Results for PDMS-2200 (not shown) were similar to those for PDMS-6140. The only significant difference between the spectra of PDMS 2200 and

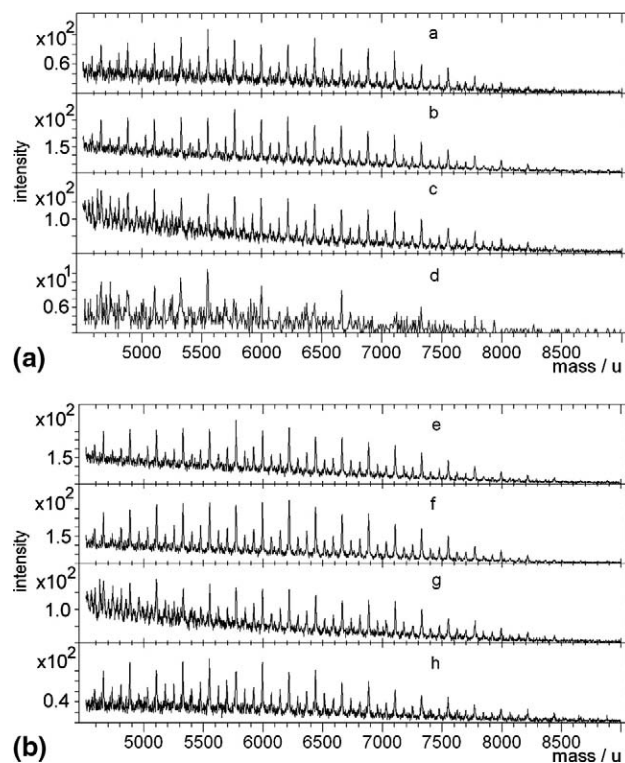


Figure 1. (A) Stacked TOF-SIMS spectra of the oligomer ion distributions obtained from PDMS 6140 using (a) 10 kV Cs^+ , (b) 25 kV Bi^+ , (c) 25 kV Bi_3^+ , and (d) 10 kV C_{60}^+ . All samples received a primary ion dose of 5.0×10^{12} ions/cm². Note different intensity scales. (B) Stacked TOF-SIMS spectra of the oligomer ion distributions obtained from PDMS 6140 using (e) 25 kV Bi^+ , (f) 15 kV Bi^+ , (g) 25 kV Bi_3^+ , and (h) 15 kV Bi_3^+ . Samples received a primary ion dose between 2×10^{12} and 5×10^{12} ions/cm². Note different intensity scales.

those shown of PDMS-6140 is that the oligomer ion distribution was detectable in the spectra of PDMS-2200 obtained by C_{60} . However, these peaks were three orders of magnitude lower intensity than for the other primary ions investigated.

Molecular dynamics simulations performed by Garrison et al. [14, 23] point to mesoscopic and microscopic events that occur during ion impact that may explain the differences observed between monatomic and polyatomic primary ions. A comparison of C_{60} and gallium bombardment of a benzene layer on a silver substrate reveals differing processes of ion interaction with a metal substrate. In particular, when a thin organic layer on a metal substrate (i.e., silver) is bombarded with monatomic primary ions, very little energy is lost by the primary ion as it passes through the organic layer. The small projectile penetrates a considerable distance (several nanometers) into the metal substrate and quickly deposits energy at this final position. The energy then propagates through the dense metal substrate, resulting in ejection of silver, which “lifts off” the intact polymer chains with little degradation [14]. Polyatomic primary ions, on the other hand, break apart when striking the substrate; consequently, each atom carries only a fraction of the initial energy. The polyatomic projectile’s component atoms subsequently penetrate less deeply and deposit their energy much closer to the surface [12]. This higher energy at the surface can result in a higher degree of fragmentation of the organic overlayer. It is also possible that the interaction of the polyatomic primary ion results in something more similar to a jet expansion, which disrupts the surface and undergoes free expansion into the vacuum [19]. This release of pressure may be sufficient to both sweep the organic layer away from the analysis point and/or fragment the oligomer chains.

Furthermore, a study of gold triatomic primary ions compared with C_{60} illustrates the differences between cluster ions from liquid metal ion sources (LMIS) and C_{60} . This work describes how C_{60} breaks apart upon impact and the resulting atoms only penetrate a few nanometers. The gold cluster also breaks apart, however, these atoms penetrate much more deeply, with each atom traveling with similar trajectories. This also results in energy deposition remote from the sample surface [23]. Such simulations indicate that for the intact desorption of material for the oligomer ion distributions, which can be converted to molecular weight distribution, the primary ion’s energy should be deposited more deeply in the substrate. These simulations agree very well with experimental results obtained here, in which monatomic bismuth yielded a higher intensity of oligomeric secondary ion ($M + Ag$)⁺ ion peaks than C_{60} , with Bi_3 having intermediate effectiveness.

Two major differences were observed in the PDMS spectra acquired with monatomic and polyatomic ions. (1) Monatomic ions in general exhibited more intense oligomer ion distributions, which are related (2) to

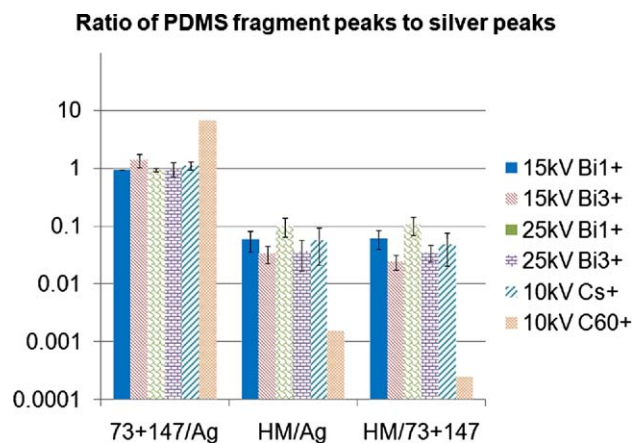


Figure 2. Plot of peak intensity ratios for [Group 1] characteristic peaks of PDMS referenced to the sum of intensities of $^{107}Ag + ^{109}Ag$, [Group 2] summed peak intensities for the entire molecular weight distribution referenced to the sum of intensities of $^{107}Ag + ^{109}Ag$, [Group 3] the molecular weight distribution intensity referenced to the sum of intensities of characteristic fragment ion peaks of PDMS. All data for PDMS-6140, three replicate measurements from each primary ion type.

differences in fragmentation that may result from monatomic versus polyatomic primary ion bombardment. Figure 2 shows quantitative evidence of fragmentation differences resulting from analysis with different primary ions. Group 1 shows the peak intensities of two characteristic fragment peaks for PDMS (73 and 147 Da) divided by the peak intensities of the 107 and 109 Da silver substrate peaks. The data for the ratios are equivalent within one standard deviation for all primary ions except for the ratios from C_{60} bombardment with the ratio near unity, indicating uniform coverage of the sub-monolayer.

Examining Group 1 also reveals that C_{60} analysis yields higher intensity PDMS fragment peaks than the other analyses. Since the uniform coverage of the polymer is confirmed repeatedly with the bismuth and cesium primary ions, it is unlikely that there is a sudden inhomogeneity in the film cast for the C_{60} analysis. This instead indicates a fundamental difference in the interaction of the C_{60} with the organic/inorganic interface. This difference becomes even more apparent when evaluating signal intensities in Groups 2 and 3, which relate the intensity of the molecular weight distribution to the silver substrate and to low mass oligomers. For C_{60} , Group 3 especially shows a much higher intensity of fragment peaks compared to intact oligomer peaks, and this is shown by the much lower intensity ratio (defined with fragment peaks in the denominator). Evaluating Group 3 for differences between monatomic and polyatomic bismuth is also informative; 25 kV Bi_1^+ shows the highest ratio of intact oligomer peaks compared with fragments, 15 kV Bi_1^+ is slightly lower but not significantly different. Bi_3^+ however, is significantly different and shows greater fragmentation.

Fragmentation differences resulting from differing primary ion mass and species have previously been

studied in detail by Gilmore and Seah [16]. Their work resulted in the development of an algorithm to reduce the number of fragment peaks in a SIMS spectrum (G-SIMS) and helps elucidate the characteristic molecular peak. This algorithm requires the acquisition of two mass spectra with different primary ion sources, however, cluster ions are not appropriate for this analysis due to differences in their sputtering mechanism [19, 24]. The current work attempts to elucidate differences of monatomic and polyatomic primary ions for the study of high mass molecular weight distributions.

The present work shows that monatomic primary ions require lower ion doses and offer improved signal to noise (peak intensity) in the mass range of interest for the determination of molecular weight distributions. This is likely due to a different sputtering mechanism that exists between monatomic and polyatomic primary projectiles. Such enhancement is evidence that monatomic primary ions actually have a shallower sampling depth than polyatomic ions, resulting from a collision cascade that is less energetic at the sample surface. The reason for the reduced surface energy is the increased depth of ion penetration into the substrate. Logically, there are several factors that determine the depth of penetration: ion energy, ion size, density of substrate, and for polyatomic ions, the trajectories of component atoms upon interaction with the substrate. It also follows that when considering differing interactions at the substrate surface, there should also be variations in the degree of fragmentation of the resultant secondary ions. This is observed when evaluating the fragmentation data and the spectral data.

The stacked spectra in Figure 1A and B also show the increased peak intensity of the oligomer peaks when using monatomic primary ions. It was determined that lower primary ion doses (8.50×10^{10} ions/cm²) were needed to acquire a MWD that varied significantly from the background when using monatomic primary ions. Monatomic bismuth with both 15 and 25 kV energies require equivalent ion doses and provide similar peak intensities for intact oligomers. This is expected because as the energy decreases the primary ion implantation distance decreases, however, the energy it deposits also decreases. Therefore, one can imagine this in terms of a reflectron, differing initial energies propagating through different distances result in similar collision cascade energy at the surface. A simple ion implantation calculation performed with SRIM [25] shows that 15 kV Bi₁⁺ will travel 37 Å, while 25 kV Bi₁⁺ will travel 48 Å into the substrate. The differences in sampling depth of monatomic compared with polyatomic primary ions are illustrated with the data collected from a sample that consisted of two monolayers of PDMS on a polystyrene (PS) substrate in Figure 3. These data were collected from a sample that consisted of two monolayers of PDMS on a polystyrene (PS) substrate. The monatomic Bi shows a ratio of the PDMS to PS of 1.83, indicating a much higher intensity of the characteristic fragment peak of PDMS. The Bi₃⁺ and Bi₃⁺⁺ have lower

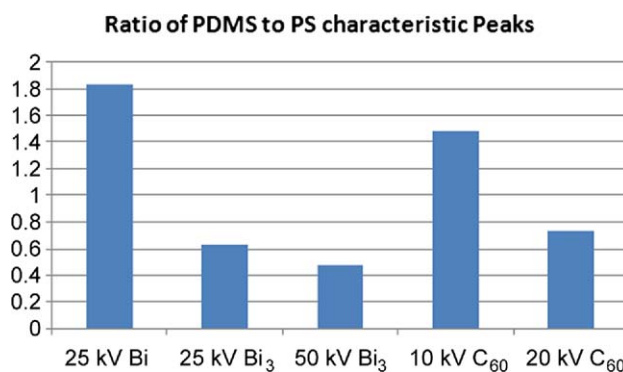


Figure 3. Plot showing the ratio of the intensity of the 73 Da peak to the 91 Da peak characteristic of PDMS and polystyrene (PS) respectively. These data were collected from two monolayers of PDMS cast on a PS substrate.

ratio intensities, 0.64 and 0.48, respectively, indicating enhanced PS signal intensity. The C₆₀⁺ and C₆₀⁺⁺ showed a ratio of 1.49 and 0.74, respectively. These results are of interest because they reinforce the fundamental differences of interaction between C₆₀ and the LMIS. It is expected that as constituent atoms in the cluster increases, the sampling depth would also increase. The results for 10 kV C₆₀, however, shows a ratio that falls between that for monatomic and triatomic bismuth. The simplest explanation is that the energy of the constituent carbon atoms is deposited close to the surface and is insufficient to sputter and/or ionize a more significant volume of the polystyrene substrate. This is in contrast to the results of a submonolayer on silver, where the mass of the carbon atoms is considerably less than that of the silver. These data also illustrate the possibility of ultra-shallow depth profiling within the static regime simply by acquiring multiple spectra utilizing different primary ions.

All primary ions that were evaluated in this work resulted in statistically equivalent molecular weight distributions (MWD) shown in Table 1. TOF-SIMS in general provides a MWD that is lower than that obtained by gel permeation chromatography (GPC) due to lower desorption or ionization yield at higher mass in the SIMS process [26]. A MALDI TOF spectrum (previous work) provides a MWD that is higher than that calculated by GPC and also yields peaks of a broader oligomer range. This is most likely due to less fragmentation resulting from the matrix absorbing a portion of the laser energy, thus resulting in a gentler desorption and ionization process compared with TOF-SIMS. While MALDI TOF provides oligomer chain lengths of $n = 49$ to $n = 130$, TOF-SIMS results have a narrower range ($n = 60$ to $n = 112$). However, the calculated molecular weight distributions determined from the SIMS spectra are not significantly different from each other. Therefore, when evaluating primary ion choices for the measurement of molecular weight distributions, the focus can be placed on signal intensity and frag-

Table 1. Calculated molecular weight distribution from the TOF-SIMS spectra obtained using different primary ions

Primary ion	6140 PDMS standard				2200 PDMS standard		
	Mw	Mn	PDI	Detected chain length	Mw	Mn	PDI
10 kV Cs ⁺	6023 ± 233	5881 ± 210	1.024 ± 0.003	<i>n</i> = 53–111	1909 ± 58	1765 ± 52	1.08 ± 0.002
15 kV Bi ⁺	6183 ± 106	6027 ± 91	1.026 ± 0.003	<i>n</i> = 53–111	2082 ± 97	1888 ± 74	1.10 ± 0.008
25 kV Bi ⁺	6252 ± 53	6078 ± 44	1.029 ± 0.002	<i>n</i> = 53–114	2088 ± 203	1916 ± 138	1.09 ± 0.028
15 kV Bi ₃ ⁺	6308 ± 164	6132 ± 138	1.029 ± 0.004	<i>n</i> = 53–114	2067 ± 19	1883 ± 15	1.10 ± 0.002
25 kV Bi ₃ ⁺	6108 ± 253	5929 ± 232	1.030 ± 0.003	<i>n</i> = 62–111	2127 ± 37	1940 ± 6	1.10 ± 0.018
10 kV C ₆₀ ⁺	*	*	*	*	1998 ± 11	1847 ± 17	1.08 ± 0.004
GPC [^]	6600	6140	1.07	N/A	2400	2200	1.09
MALDI-TOF	7166	6900	1.03	<i>n</i> = 49–130	2980	2535	1.17

*Could not detect. GPC data provided by manufacturer, MALDI-TOF data taken from previous studies [26].

mentation. For these factors, monatomic primary ion analysis is more efficient for the measurement of molecular weight distributions of polymers on metal substrates in SIMS.

Conclusions

Although there is great interest in polyatomic primary ions for the TOF-SIMS analysis of polymers, the present results demonstrate that monatomic primary ions provide higher intensity signals with less fragmentation, especially for determination of MWD data. Obviously, MALDI-TOF provides less fragmentation than TOF-SIMS; however TOF-SIMS can measure oligomer distributions at the sample surface. In particular, C₆₀ analysis of PDMS results in much more fragmentation (Figure 2) than either Bi or Cs. For a given primary ion, different impact energies do not significantly change the ratio of oligomer peaks to characteristic fragment peaks. In other words, 15 and 25 kV Bi₃ are not significantly different from each other, but both provide significantly more fragmentation than 15 and 25 kV Bi. This is clear evidence that cluster primary ion sources interact differently with the target than do monatomic ions. The fragmentation data presented in Figure 2, along with the mechanistic discussion, provide evidence that monatomic primary ions also offer a shallower sampling depth than do polyatomic ions.

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