



RESEARCH ARTICLE

Characteristic Fragmentation of Polysiloxane Monolayer Films by Bombardment with Monatomic and Polyatomic Primary Ions in TOF-SIMS

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Abstract

This study reports the characteristic fragmentation patterns from two polysiloxane polymers that form ordered overlayer on silver substrates. Results are compared for the bombardment of various monatomic and polyatomic projectiles of Cs^+ , C_{60}^+ (10 keV), Bi_1^+ , and Bi_3^+ (25 keV) in the high mass range time-of-flight secondary ion mass spectrometry (TOF-SIMS) spectra. Results are reported from sub-monolayer (solution cast) coverages of poly(dimethylsiloxane)s with the number average molecular weights (M_n) of 2200 and 6140 Da, respectively, and Langmuir-Blodgett monolayers of poly(methylphenylsiloxane) with molecular weights (MW) from 600 and 1000 Da. For each film, Bi projectiles resulted in the emission of positive silver cluster ions from the substrate under the polymer overlayer and peaks corresponding to silver cluster ions with larger mass were observed by impact of polyatomic 25 keV Bi_3^+ projectiles. In addition, depending on the change of energy of Bi_3^+ , a different pattern of fragments was observed. With Cs^+ and C_{60}^+ impact, however, the emission of silver cluster ions was not detected. In the case of C_{60}^+ impact for PDMS-6140, peaks corresponding to silver-cationized intact oligomers were not observed. In this paper, these results are explained by the possible bombardment mechanism for each projectile, based on its mass, energy, and split trajectories of the component atoms under the polyatomic impact.

Key words: TOF-SIMS, Polymer fragmentation, Cluster primary ion sources, Silicone polymers

Introduction

The use of polyatomic ion sources in time-of-flight secondary ion mass spectrometry (TOF-SIMS) has recently been developed, promising the enhancement of molecular ion yields and therefore an increase in instrument sensitivity [1–3]. Compared with monatomic projectiles of comparable mass and energy, polyatomic projectiles lead to significant enhancement in the secondary ion formation efficiencies as well as increased secondary ion yield [1–9]. The magnitude of this yield enhancement by polyatomic projectiles is strongly influenced by the mass, energy, and the number of component atoms in the clusters [3]. The

mechanism of ion formation under cluster ion bombardment has yet to be completely explained. Theoretical and experimental studies, however, have shown the increased yield results from an overlap of low energy impact cascades of individual atomic components of cluster ions [10–14].

Various model systems constructed from overlayers of inorganic and organic films on surfaces have also been studied to determine the degree of desorption of molecular ions [3]. For example, under impact of polyatomic primary ions, the increase in secondary ion yield for organic multilayers on silver substrates was more pronounced than that for monolayer coverage [15, 16].

These previous experimental studies for particular projectile-sample combinations have mainly focused on the secondary ion yield, disappearance cross-section, and ion

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formation efficiency of the fragments observed in the low mass range of TOF-SIMS spectra. However, because the high mass range of TOF-SIMS spectra can provide information for the monomeric unit sequence [17], molecular weight distribution [18], end group identification [19], and tertiary conformation [20, 21] of polymers in TOF-SIMS studies, high mass ranges obtained with different primary projectiles should be also compared.

In our previous work, Wells et al. reported the characterization of molecular weight distributions of poly(dimethylsiloxane) with polyatomic primary ions [22]. The results demonstrated that monatomic primary ions induced higher peak intensity with less fragmentation, especially in the determination of molecular weight distribution. This was attributed to the increased momentum transfer in a shallower surface region, creating interactions of the cluster primary ions with the top overlayer and more extensive bond breaking and fragmentation. This effect competed with the emission of intact oligomers necessary for molecular weight determination.

In order to understand the different bombardment mechanism between monatomic and polyatomic projectiles, in the present work we investigate the effect of various monatomic and polyatomic projectiles' bombardment on the fragmentation pattern of (sub)monolayer polymer samples in the high mass range of the TOF-SIMS spectrum. The polysiloxanes were deposited as a (sub)monolayer on silver substrates and the monatomic and polyatomic projectiles of Cs^+ , Bi_1^+ , Bi_3^+ , and C_{60}^+ were utilized for this study. In addition, the difference of fragmentation pattern of the (sub) monolayer polysiloxanes on silver substrates by Bi projectiles with different energy was also investigated.

Experimental

Materials

Poly(dimethylsiloxane)s (PDMS)s with M_n of 2200 and 6140 were purchased from Polymer Source Inc. (Dorval, Quebec, Canada). PDMS-2200 and PDMS-6140 have polydispersity indices (PDI) of 1.09 and 1.07, respectively. Poly(methylphenylsiloxane) (PMPHS) with MW from 600 to 1000 was purchased from Gelest Inc. (Morrisville, PA, USA). Both PDMSs were terminated by sec-butyl and trimethylsiloxy groups; the end groups of PMPHS were not defined by the manufacturer. For the preparation of sub-monolayer films, the silver foil was purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA) and the silver mirror used for manufacturing the Langmuir-Blodgett (LB) monolayer film was prepared following a reference method [21].

Sample Preparation

The PDMSs were dissolved in reagent grade toluene (Fisher Scientific, Suwanee, GA) with a concentration of 1 mg/mL. For the solution casting method, 2 μL of PDMS solution

was deposited on each silver foil in sub-monolayer coverage. The silver foil was cleaned by ultrasonication in both hexane and toluene for 20 min each, and then etched in 10% nitric acid for 10 min. The PMPHS in monolayer film was prepared by using LB technique. For the LB film preparation, PMPHS was dissolved in reagent grade pentane (Sigma Aldrich, Saint Louis, MO) with the concentration of 1 mg/mL. In prior to the LB film preparation, the silver mirror was cleaned with KOH/isopropanol solution and washed with ultrapure water.

Langmuir-Blodgett Film Transfer

A computer-controlled KSV film balance was operated for LB film preparation. By using a cold trap, the temperature was decreased to 13°C, at which the magnitude of the surface pressure was high enough for the PMPHS monolayer to be transferred onto the silver mirror. The surface pressure was measured with the accuracy of 0.1 mN/m. The purified water from a Millipore Mega-Pure system, MP-6A, was used as subphase liquid. 30 μL of PMPHS was spread onto the water subphase and then 3 min were required for the formation of a monolayer on the subphase through evaporation of pentane. The PMPHS monolayer was compressed at a constant rate of 5 cm^2/min up to the surface pressure of 2.0 mN/m before its collapse. At that surface pressure, then PMPHS monolayer was transferred onto the silver mirror with a dipping speed of 2 mm/min upward.

TOF-SIMS

The TOF-SIMS used in this study was an ION TOF Model 5.100 (ION TOF GmbH, Muenster, Germany) equipped with a Bi_n^+ liquid metal ion source, and a dual source column containing Cs^+ and C_{60}^+ sources. For all primary ions, total ion flux dosage during data acquisition was between 1.5×10^{12} and 5.0×10^{12} ions/ cm^2 , which is the accepted value within the static limit. The analyzer is of the reflection type; reflector voltage of 19 eV and post-acceleration voltage of 10 keV were applied for all spectra acquisitions. The pressure of the main chamber was kept between 5×10^{-8} and 5×10^{-9} mbar. ION SPEC software from ION TOF GmbH (Muenster, Germany) was used for the data analysis.

Results and Discussion

The low mass range of the TOF-SIMS spectrum for PDMS deposited on silver substrate has been reported previously [19]. In our work, the dominant peaks corresponding to Si^+ , CH_3Si^+ , $\text{C}_3\text{H}_9\text{Si}^+$, and $\text{C}_5\text{H}_{15}\text{OSi}_2^+$ were also observed at 28, 43, 73, and 147 m/z , respectively, and the spectra of PDMS-2200 and PDMS-6140 were similar in this range. However, the C_{60}^+ ion source yielded higher intensities of PDMS low mass fragment peaks compared to other sources and it was discussed in our previous work [22].

Figure 1 shows the TOF-SIMS spectrum with the mass range between 400 and 1000 Da for PDMS-2200 under

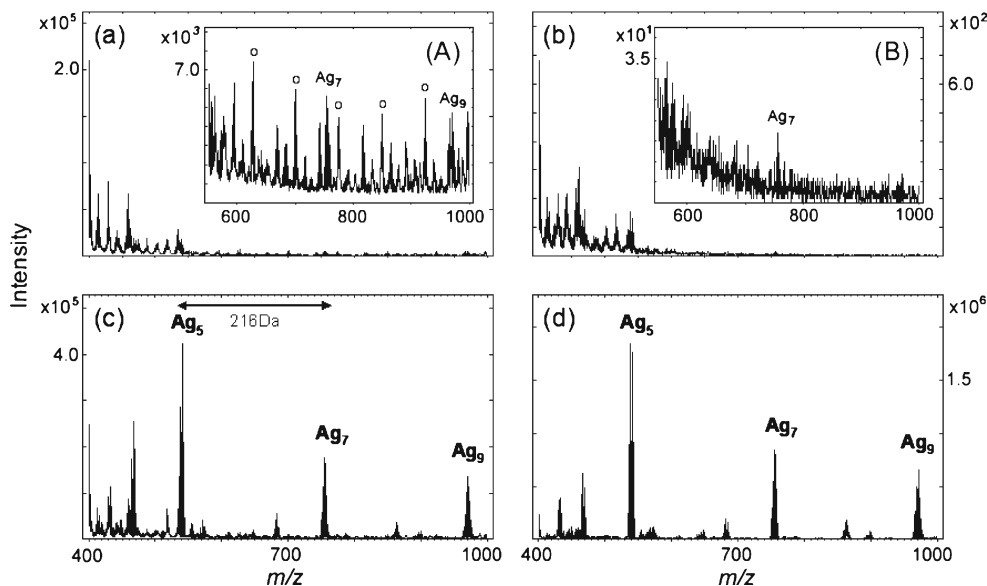


Figure 1. The mass range between 400 and 1000 Da for PDMS-2200 under bombardment of Cs⁺ (10 keV) **(a)**, C₆₀⁺ (10 keV) **(b)**, Bi₁⁺ (25 keV) **(c)**, and Bi₃⁺ (25 keV) **(d)**. The inserted spectra in **(a)** and **(b)** are the detailed PDMS-2200 spectra between 550 and 1000 Da by Cs⁺ (10 keV) **(a)** and C₆₀⁺ (10 keV) **(b)**

bombardment by 10 keV Cs⁺ and C₆₀⁺, and 25 keV Bi₁⁺ and Bi₃⁺. Compared with Cs⁺ and C₆₀⁺, intense fragments corresponding to silver cluster ions with odd composition number were observed by Bi₁⁺ and Bi₃⁺. The ejection of these silver cluster ions detected under the Bi₁⁺ and Bi₃⁺ bombardment can be explained by the difference of atomic mass between the bismuth projectile and the substrate. The bismuth atom cannot be easily deflected by the silver atoms in the solid substrate due to its significantly heavier mass than that of the silver. Thus, the bismuth atoms propagate

downward passing through the polymer overlayer and then transfer their energy to a considerably deep area for the silver atoms to be emitted into vacuum. Consequently, the ejection of the silver cluster ions from the substrate under the polymer overlayer in the (sub)monolayer was detected in TOF-SIMS spectra under all conditions of bismuth ion bombardment. Figure 1a and b show the detailed PDMS-2200 spectra between 550 and 1000 Da by Cs⁺ and C₆₀⁺. With the Cs⁺ projectile, the fragments corresponding to cyclic oligomers cationized by silver (o) as well as silver

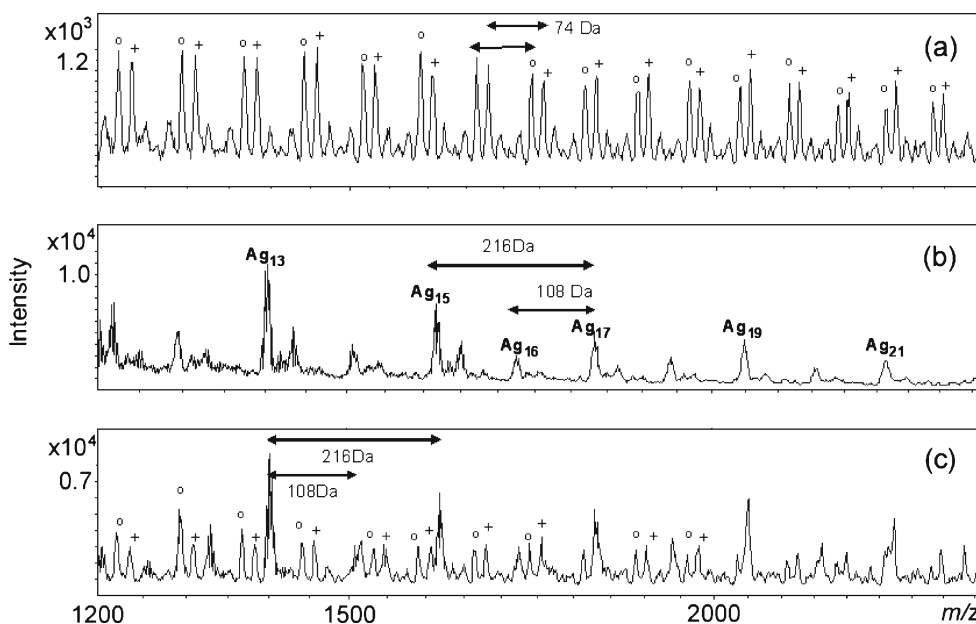


Figure 2. The mass range between 1200 and 2500 Da for PDMS-6140 under Cs⁺ (10 keV) **(a)**, Bi₃⁺ and Bi₃⁺⁺ (25 keV) **(b)**, and Bi₁⁺ (25 keV) **(c)** impact

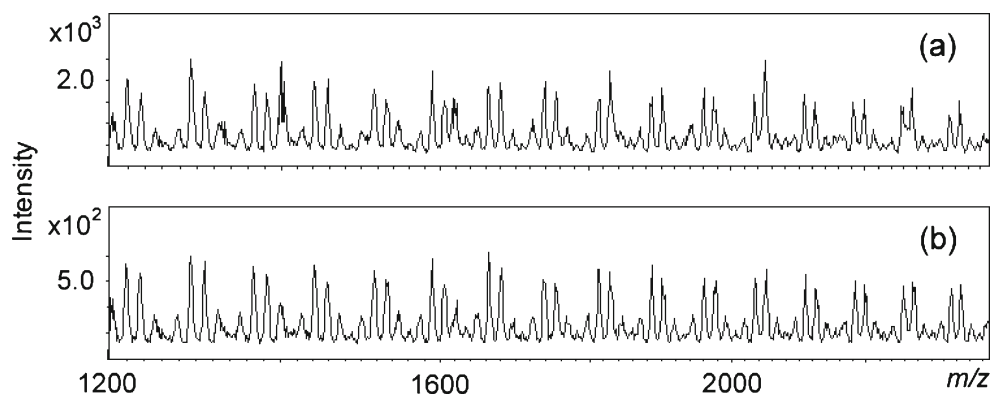


Figure 3. The mass range between 1200 and 2500 Da for PDMS-6140 under bombardment by Bi_1^+ (a) and Bi_3^+ (b) (15 keV)

clusters were observed but only the Ag_7 cluster ion with weak intensity was detected by C_{60}^+ impact. Under both of Cs^+ and C_{60}^+ impact, however, the intense silver cluster ions were not detected in the spectrum. In the case of a Cs^+ projectile, penetration into the substrate occurs but desorption of only the intact and fragmented polymer overlayer occurs without extensive desorption of the silver ions from the substrate. This might be because the Cs^+ projectile is not sufficiently large and energetic to eject the silver ions. This result is consistent with that from the molecular dynamics simulation of the Ga^+ bombardment reported previously [11, 12]. In addition, each carbon atom on C_{60}^+ impact cannot be embedded into the silver substrate and interacts strongly with the polymer overlayer because the carbon atoms are easily deflected by silver atoms. As a result, they deposit most of their energy in a shallower and broader volume of the sample so that the most particles are ejected from polymer overlayer.

For the higher molecular weight PDMS-6140, silver cluster ions were also observed in the particular high mass range of the TOF-SIMS spectrum under Bi_1^+ and Bi_3^+ bombardment. Figure 2 shows the results from the mass

range between 1200 and 2500 Da for PDMS-6140 from primary ions of 10 keV Cs^+ , 25 keV Bi_1^+ , and Bi_3^+ . In the spectrum from Cs^+ bombardment, two intense clusters are observed: a pattern of fragments corresponding to cyclic oligomers cationized by silver, $[\text{Rn} + \text{Ag}]^+$ (o) and a series of the silver-cationized linear PDMS oligomers having the end groups of $-\text{H}$ and $-\text{CH}_3$, $[\text{nR} + 16 + \text{Ag}]^+$ (+). Rn and nR refer to a cyclic and a linear fragment containing an integral number (n) of repeating units, respectively. These two ion clusters were also observed under Ar^+ bombardment by Dong et al. [19], who attributed those peaks to the fragments produced by ion-beam bombardment, not to oligomers originally present in the sample. Under Bi_1^+ impact shown in Figure 2, not only were the ion clusters of $[\text{Rn} + \text{Ag}]^+$ and $[\text{nR} + 16 + \text{Ag}]^+$ still observed, but also silver cluster ions with odd number composition from Ag_{13} to Ag_{21} were detected. However, in case of the Bi_3^+ bombardment, only silver cluster ions were observed. The larger atomic mass of the Bi projectile compared with that of Cs^+ induced emission of the large silver cluster ions from the substrate as well as two series of silver cationized fragments from the polymer overlayer. Upon impact of polyatomic Bi, however, the

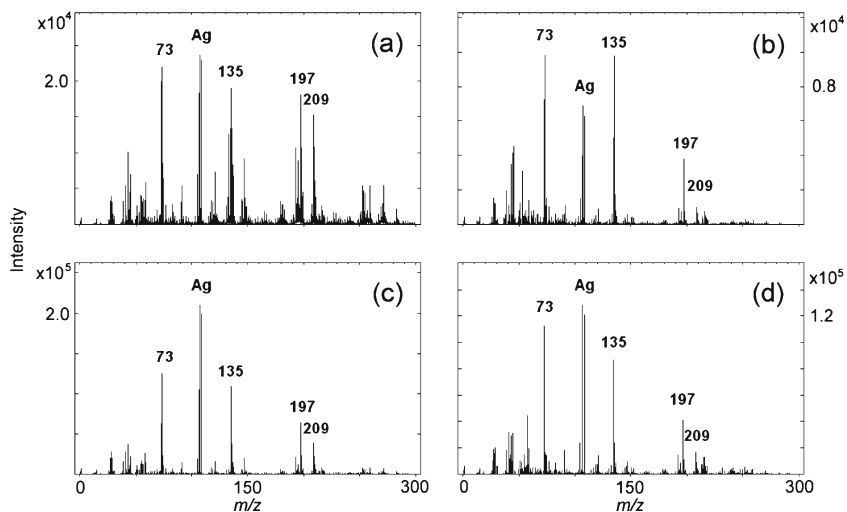


Figure 4. The mass range below 300 Da for PMPHS with MW from 600 and 1000 Da under Cs^+ (10 keV) (a), C_{60}^+ (10 keV) (b), Bi_1^+ (25 keV) (c), and Bi_3^+ (25 keV) (d) impact

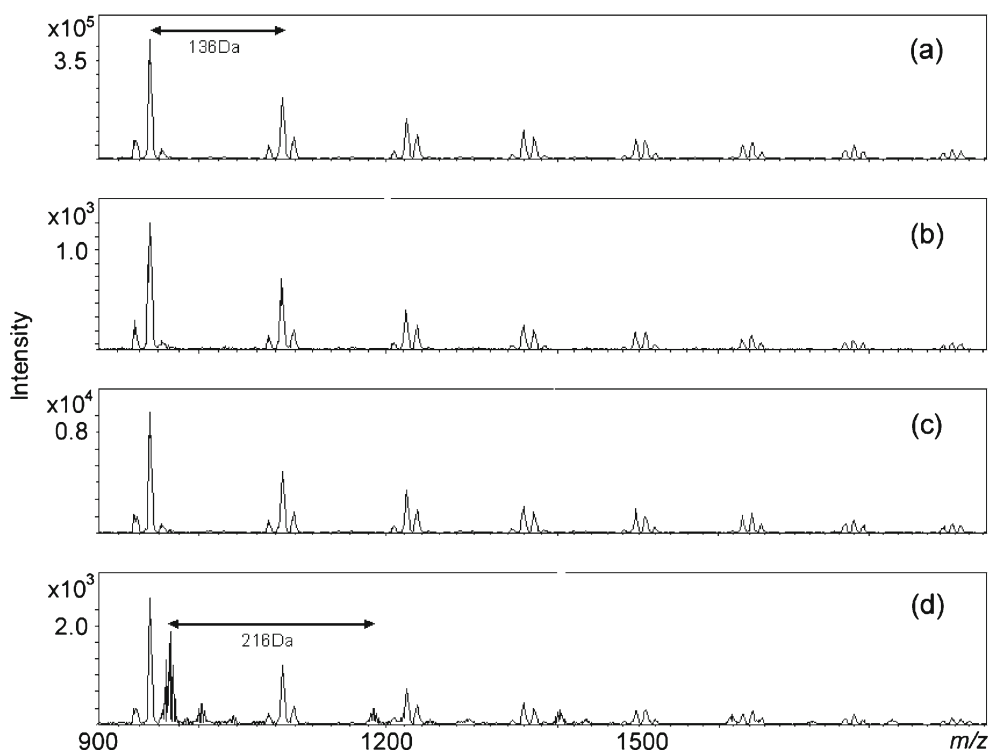


Figure 5. The mass range between 900 and 2000 Da for PMPHS with MW from 600 and 1000 Da under Cs^+ (10 keV) **(a)**, C_{60}^+ (10 keV) **(b)**, Bi_1^+ (25 keV) **(c)**, and Bi_3^+ (25 keV) **(d)** impact

silver-cationized fragments from the polymer overlayer were not detected. This indicates that the main portion of the polyatomic bismuth projectile's momentum was used to emit the silver cluster ions or small fragments, and not to break down the intact polymer overlayer into large size fragments to be emitted into vacuum. This may result from the polyatomic Bi projectile having a deeper sampling depth than monatomic Bi ions, due to the split trajectories of the component atoms [22]. Because triatomic Bi bombardment ejects only silver clusters in this mass range, we can say that it could not provide information related to the high mass ions fragmented from the polymer overlayer on the silver substrate.

Beyond the factors such as ion size and, for primary ions, the trajectories of component atoms that determine the depth of penetration, the effect of Bi primary ion energy on the fragmentation of polymer in the high mass range of the TOF-SIMS spectrum was also investigated in this study. Figure 3 shows the TOF-SIMS spectrum of the medium mass range between 1200 and 2500 Da for PDMS-6140,

bombarded by 15 keV Bi_1^+ and Bi_3^+ projectiles. While the pattern of ion clusters under the impact of 15 keV Bi_1^+ was similar to that with 25 keV Bi_1^+ , two series of ion clusters corresponding to $[\text{Rn}+\text{Ag}]^+$ and $[\text{nR}+16+\text{Ag}]^+$ as well as the silver cluster ions were much less intense than observed with 15 keV Bi_3^+ . Because 25 keV Bi_3^+ induces only silver cluster ions in this mass range, we can conclude, as a result, that depending on the type of projectile, the kinetic energy can be one of the parameters that influences the fragmentation pattern of the polymer.

In the present study, the fragmentation pattern in the TOF-SIMS spectrum of the LB film of poly(methylphenylsiloxane) (PMPHS) is also reported. Figure 4 shows the low mass range below 300 Da for PMPHS with MW from 600 to 1000 Da under each impact of 10 keV Cs^+ and C_{60}^+ , and 25 keV Bi_1^+ and Bi_3^+ . With all projectiles, the intense peaks are observed at 73, 135, 197, and 209 Da, which correspond to $(\text{CH}_3)_3\text{Si}^+$, $[(\text{CH}_3)_2(\text{Ph})\text{Si}]^+$, $[(\text{CH}_3)(\text{Ph})_2\text{Si}]^+$, and $[(\text{CH}_3)_3\text{SiOSi}(\text{Ph})(\text{CH}_3)]^+$, respectively. These peaks were observed for all projectile analyses used in this study and among them

Table 1. Summary of peak intensity ratios of summed high mass peak intensities of PMPHS and PDMS-2200 referenced to the total ion intensities, respectively

	Bombarding species			
	Bi_1^+	Bi_3^+	Cs^+	C_{60}^+
PMPHS	$(1.63 \pm 0.84) \times 10^{-2}$	$(4.34 \pm 3.63) \times 10^{-3}$	$(1.40 \pm 0.53) \times 10^{-2}$	$(1.17 \pm 0.03) \times 10^{-4}$
PDMS-2200	$(1.96 \pm 0.49) \times 10^{-2}$	$(1.21 \pm 0.25) \times 10^{-2}$	$(3.05 \pm 0.54) \times 10^{-2}$	$(1.35 \pm 0.41) \times 10^{-5}$

Bi projectiles yielded higher peak intensities of the low mass fragments. When we compared the peak intensities of characteristic peaks of PMPHS (73 Da and 135 Da) referenced to the intensities of silver substrate peaks (107 Da and 109 Da), however, Figure 4 reveals that C_{60}^+ bombardment induces their higher intensity ratio. This result is in good agreement with our previous work, in which it was discussed that the higher intensity ratios of the low mass PDMS fragments referenced to silver peaks were yielded by C_{60}^+ impact [22].

Figure 5 shows the high mass range between 900 and 2000 Da for PMPHS by 10 keV Cs^+ and C_{60}^+ , and 25 keV Bi_1^+ and Bi_3^+ . The pattern of ion clusters corresponding to the silver cationized intact oligomer was observed for all projectiles. Each of those ion clusters is separated by an interval equal to a monomer unit mass of 136 Da. Under the impact of Bi_3^+ , however, the series of the silver cluster ions as well as the intact PMPHS oligomer cationized by silver was observed. Such ejection of silver cluster ions might be due to a deeper sampling depth resulting from the split trajectories of component atoms under the polyatomic impact. This indicates that the momentum transfer of the Bi polyatomic projectile leads to the ejection of the silver cluster ions even with high mass.

In the PMPHS and PDMS spectra acquired with monatomic and polyatomic projectiles, the differences of intensities of intact oligomer cationized by silver were observed. For the reliable comparison, Table 1 shows a plot of the ratios of summed peak intensities of intact oligomer cationized by silver for PDMS-2200 and PMPHS referenced to total ion intensities with different primary ions, respectively. For both PMPHS and PDMS, C_{60}^+ analysis yielded significantly lower intensities of silver-cationized intact oligomer than the other analysis. Because C_{60}^+ interacts with the polymer overlayer in a shallower volume, it could be giving rise to more small fragments and not lifting the intact polymer chains off the surface. This is evidence of a fundamental difference in the interaction of the C_{60}^+ with the surface. The difference between monatomic and polyatomic bismuth projectiles was also informative; Bi_1^+ analysis induced higher intensity ratios compared to Bi_3^+ . This might be also due to their different sampling depths previously discussed. From this quantitative difference of the intensity ratios, we can say that monatomic primary ion sources yield higher peak intensities of intact polysiloxane oligomers observed in the high mass range of TOF-SIMS spectra. Thus, it can be verified that monatomic ion analysis is more efficient for the study of high mass range polymers on metal substrates in SIMS, supporting our previous study [22].

Conclusion

We have reported the differences of the fragmentation patterns in the high mass range of TOF-SIMS spectra for the

(sub)monolayer film of polysiloxanes under bombardment of Cs^+ , C_{60}^+ (10 keV), Bi_1^+ , and Bi_3^+ (15 and 25 keV). Twenty-five keV Bi projectiles emitted the silver cluster ions from the substrate under the polymer overlayer due to its heavy atomic mass and energetic impact velocity. The emission of silver cluster ions depended on the change of energy and the component atom number of Bi projectile. In the case of Bi_3^+ , the silver cluster ions with much larger mass were detected, and 15 keV Bi_3^+ showed a different fragmentation pattern from that of 25 keV Bi_3^+ . Under impact of Cs^+ and C_{60}^+ , however, silver cluster ions were not detected. Also, bombardment by C_{60}^+ did not lift off the intact oligomer present in the PDMS-6140 polymer overlayer. From these results, the different patterns of fragmentation under the various projectile bombardments could be explained by their possible impact mechanisms. Additionally, monatomic projectiles yielded higher intensities of intact oligomer cationized peaks observed in the high mass range for PMPHS and PDMS. Therefore, we can confirm that there is no benefit to the use of polyatomic projectiles for the study of the characteristic fragmentation observed in high mass range of TOF-SIMS spectra of polymers in (sub)monolayers.

Acknowledgments

The authors acknowledge support in part for this research by the National Science Foundation Chemistry Division, grant CHE0616916. The authors gratefully acknowledge the generous support of Professor Thomas Beebe at the University of Delaware for HKM.

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