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Characterization of Poly(dimethylsiloxane)s by Time-of-Flight Secondary Ion Mass Spectrometry

Xia Dong, Andrew Proctor, and David M. Hercules*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37209

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ABSTRACT: A series of poly(dimethylsiloxane)s (PDMS) terminated by trimethylsilyl groups, and having molecular weights from 600 to 20 000, were characterized by time-of-flight secondary ion mass spectrometry. The fragmentation patterns of the PDMS were examined. The predominant fragmentation pathway involves formation of cyclic fragments, probably via an intermediate with a four-membered ring. The relative intensities of the clusters in the PDMS fragmentation patterns were investigated as a function of sample molecular weight. The relative intensities of cyclic fragments increase with increasing polymer molecular weight. Poly(dimethylsiloxane)s containing different end groups were also investigated to determine the effect of the terminal groups on fragmentation. The terminal groups in PDMS were identified by analysis of low mass range spectra. Effects of nitrogen-containing end groups were found on the fragmentation of PDMS. Large fragments with intrinsic positive charge were observed in the spectra of PDMS terminated by (aminopropyl)dimethylsiloxy and (amidopropyl)dimethylsiloxy groups.

Introduction

Mass spectrometry has been proven as a powerful method for the structural characterization of organic molecules due to its high sensitivity, high dynamic range, specificity, and selectivity and has been used extensively to study polymers since the 1970s. Mass spectrometric techniques can provide information about oligomer distributions, average molecular weights, fingerprint patterns for polymer identification, monomeric unit sequences, branching, cross-linking or other side-chain substitution, copolymer structures, and additives or impurities.

Many polymers have been studied by electron impact (EI),[1,2] the most conventional type of mass spectrometry. Chemical ionization (CI)[3] has been used as a softer ion source to avoid the extensive fragmentation caused by EI. Slightly polar and nonpolar polymers have been investigated by desorption chemical ionization (DCI).[4,5] Another important mass spectrometric technique for polymer analysis is pyrolysis mass spectrometry (Py-MS).[6−9] Both direct probe pyrolysis (DP-MS)[8] and pyrolysis gas chromatography mass spectrometry (PyGC-MS)[9] have been widely used to study the thermal degradation of polymers. The development of field desorption (FDMS),[10] electrodynamic (EHDMS),[11] secondary ion (SIMS),[12−15] fast atom bombardment (FABMS),[16] laser desorption (LDMS),[17−19] electrospray,[20] and plasma desorption[21] mass spectrometries have made it possible to analyze polymers without the need for vaporization.

Static SIMS has been used to study polymers for more than a decade. Most early studies done by SIMS were limited to the low mass range (m/z < 500 Da) because of limitations of the quadrupole mass analyzer. Although peaks in the low mass range can be observed by this method, important information such as the oligomer distribution and large neutral fragments cannot be obtained. Often, polymers with similar structures cannot be distinguished on the basis of low mass range spectra alone. The development of time-of-flight secondary ion mass spectrometry (TOF-SIMS) has made it possible to investigate polymers in the high mass range (up to 10 000 Da). TOF-SIMS has been used to determine oligomer distributions and to identify end groups and the mass of repeat units. This method has also been used to study the fragmentation mechanisms of various polymers including poly(styrenes),[22] polyurethanes,[23,24] perfluorinated polyethers,[25] polymethacrylates,[26] Teflon,[27] and poly(butadenes).[28]

Siloxanes are important industrial materials. Because of their special properties such as high chemical and thermal stability and low toxicity, poly(dimethylsiloxane)s (PDMS) have a wide range of commercial applications including rubbers, resins, water repellents, release agents, dielectric fluids, antifoams, polishes, lubricants, and medical and pharmaceutical uses. PDMS has been studied by several mass spectrometric techniques. The EI spectra of several PDMS were obtained as early as the 1970s.[29] DP-MS and Py-GCMS have been used to study the thermal degradation mechanisms of PDMS.[30] All of these studies were limited to the low mass range (m/z below 1000). An earlier study from our group showed that the molecular weight distribution can be obtained from a thick film of PDMS by TOF-SIMS.[27]

The purpose of the present research is to use TOF-SIMS to study the fragmentation of poly(dimethylsiloxane)s. Fragmentation of polymers is important since it can provide information about polymer stability and degradation mechanisms. A series of PDMS terminated by trimethylsilyl groups with different molecular weights have been investigated. First, low mass range spectra and possible fragmentation mechanisms are compared with those obtained from Py-MS. In the high mass range, the cluster structures are analyzed in detail and compared with theoretical structures. Several possible mechanisms for the formation of large neutral fragments are proposed. Effects of the molecular weight and the end group on fragmentation were also investigated.

Experimental Section

Instrumentation. The spectra of poly(dimethylsiloxane)s were obtained with a time-of-flight secondary-ion mass spectrometer, TOF-SIMS III, designed and manufactured by Ion-Tof GmbH, Münster, Germany. The TOF-SIMS has been described in detail elsewhere.[31] Targets were bombarded by a 10 keV Ar^+ pulsed primary ion beam with current varying

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from 0.3 to 0.5 pA. The primary ion has a variable spot diameter between 5 and 50 μm. Secondary ions generated by a primary ion pulse on the target surface were extracted and accelerated to an energy of 3 keV. An Einzel lens and reflectron optics were used for focusing the secondary ion beam and for energy compensation, respectively, in the 2-m flight tube. The ions were postaccelerated to 10 keV just ahead of the detector, which was a channel plate−scintillator−photomultiplier combination. A time-to-digital converter (TDC) was used for data collection.

The total collection time for a spectrum was 300 s. The total primary ion dose during data acquisition was less than 10^{13} ions /cm^2, which corresponds to static SIMS. The base pressure of the main chamber of the instrument was typically 3×10^{-8} Pa and the operating pressure was about 10^{-6} Pa with a pressure of 4×10^{-4} Pa in the primary ion source.

Sample Preparation and Data Analysis. Poly(dimethylsiloxane)s terminated with trimethylsilyl groups were provided by Bayer Inc. (Pittsburgh, PA). Silanol-terminated and (aminopropyl)dimethylsiloxy-terminated PDMS were obtained from Gelest (Tullytown, PA). The PDMS samples were dissolved in toluene with concentrations ranging from 0.5 to 1 mg/mL; higher concentrations were used for lower molecular weight PDMS. Sample solution volumes of 1−7 μL were deposited onto silver targets with a substrate area of 80 mm^2. The silver substrate had been etched in nitric acid (20 vol %), ultrasonicated in distilled water for about 3 min, and then rinsed in distilled water and methanol.

Data analysis was completed using in-house generated software, GOOGLY, written by Andrew Proctor. Peak intensities were obtained by integrating the peak areas for the entire cluster with a linear background correction.

Determination of Molecular Weights by Gel Permeation Chromatography (GPC). The GPC measurements were carried out in THF at 35 °C at a flow rate of 0.35 mL/min maintained by a Perkin-Elmer series 100 pump. The GPC instrument was equipped with two Phenomenex narrow bore GPC columns, a Waters 410 differential refractometer detector, and a Waters 745 data module. Typical sample concentrations were 30 mg/mL. Poly(styrene) standards from Waters were used for calibration. The solutions were filtered before being injected into the column.

Results and Discussion

A. Spectra of Trimethylsilyl-Terminated PDMS. The following terminology will be used to describe TOF-SIMS spectra: *fragment* will refer to a segment cut from a polymer chain; *cluster* will refer to a group of peaks corresponding to ions from a particular fragment; *pattern* will refer to a repeating sequence of clusters; R_n will refer to a cyclic fragment containing an integral number (n) of repeat units and nR will refer to a fragment containing an integral number (n) of repeat units but with a linear structure.

Low Mass Range Spectra. Even though the primary purpose of this study is to investigate polymers in the high mass range, low mass range spectra can also provide useful information. Figure 1 shows the spectrum of PDMS 620 in the mass range from 10 to 500 Da. Extensive fragmentation is observed in this mass range. The spectra of PDMS with different molecular weights are similar in this mass range.

In the mass range below 100 Da, the dominant peak is at 73.06 Da, which corresponds to $(CH_3)_3Si^+$. Peaks at 42.99 Da (CH_3Si^+) and 27.97 Da (Si^+) are also observed. The peak at 59.03 Da corresponds to $C_3H_7O^+$, while the peak at 58.98 Da is due to CH_3SiO^+. Peaks attributed to potassium (39 Da) and sodium (23 Da) were found in the spectra of several samples due to sample contamination.

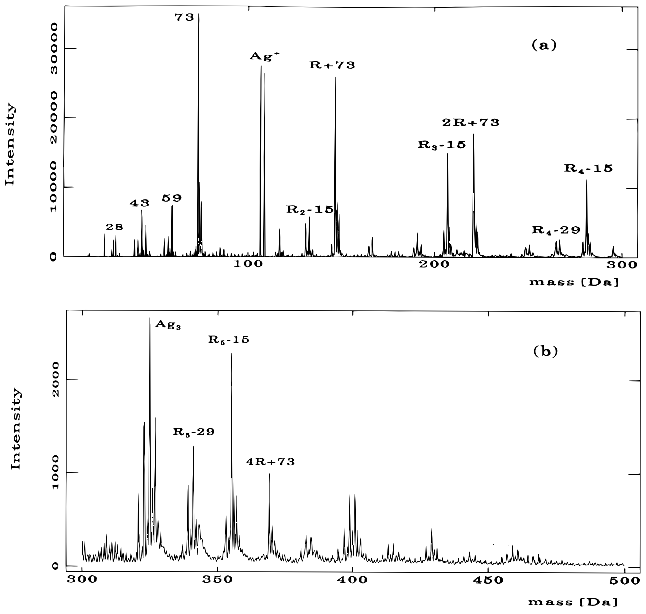


Figure 1. TOF-SIMS spectrum for trimethylsilyl-terminated PDMS (M_n = 620): (a) 10−300 Da; (b) 300−500 Da.

There are three series of peaks in the low mass range spectra: $[nR + 73]^+$ ($(CH_3)_3Si[OSi(CH_3)_2]_n^+$); $[R_n - 15]^+$ ($[Si(CH_3)_2O]_n - CH_3]^+$), formed by the loss of methyl groups from cyclic fragments; and $[R_n - 29]^+$ (bicyclic fragment).[30] Below 250 Da, the $[nR + 73]^+$ series is stronger than the $[R_n - 15]^+$ series, and the $[R_n - 29]^+$ series is fairly weak. The intensities of the $[R_n - 15]^+$ series increase when m/z is greater than 250 Da. The results are consistent with those obtained from Py-MS[30] except that the $[nR + 73]^+$ series is relatively more intense in TOF-SIMS than in Py-MS in the mass range below 250 Da. Silver clusters such as Ag^+, Ag_2^+, and Ag_3^+ are also observed in this region.

It should be noted that the intensity of $[R_2 - 15]^+$ is weak while the peaks of $[R_n - 15]^+$ with $n \geq 3$ are quite strong. This is due to the cyclic structure of this series. For $[R_2 - 15]^+$, the cyclic fragment requires a four-membered ring which is not very stable. When n increases, the ring size and stability both increase.

Mass Range in 500−1000 Da. The spectrum of PDMS 620 in the mass range 500−1000 Da is shown in Figure 2a. Figure 2b shows details of a fragmentation pattern for low molecular weight PDMS (M_n = 620). In this range, three intense clusters are observed, which correspond to $[R_n + Ag]^+$(△), $[nR + 16 + Ag]^+$(○), and $[nR + 14 + 2Ag]^{2+}$ (*). Each cluster within the fragmentation patterns contains several peaks, due to contributions from ^{13}C and the two Ag isotopes. Since silver was used as a sample substrate, Ag cationization was universal for all types of fragments. Even though sodium and potassium were observed in the spectrum, they did not contribute significantly to ion formation.

Cyclic oligomers were not detected in the original polymer sample by NMR. With NMR, one can detect cyclic species at concentrations as low as 2%. If we assume that the ion yield of cyclic species is twice that of linear oligomers and there are 2% cyclic oligomers in original sample, the relative intensity of cyclic species in TOF-SIMS spectrum should be 4%. However, the relative intensities of $[R_n + Ag]^+$ peaks shown in TOF-SIMS spectra are much higher. This indicates that the $[R_n + Ag]^+$ series corresponds to neutral fragments, cationized by silver, produced by ion-beam bombardment. A comparison between the experimental spectrum and the spectrum predicted from the isotopic distribution for $[R_7 + Ag]^+$ is shown in Figure 3a. Good

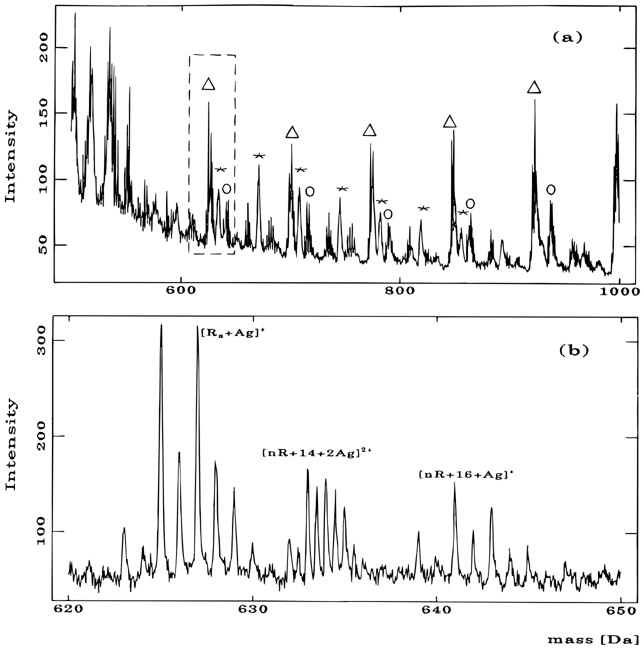


Figure 2. (a) TOF-SIMS spectrum for trimethylsilyl-terminated PDMS ($M_n = 620$) in the mass range 500−1000 Da: (△) $[R_n + Ag]^+$; (*) $[nR + 14 + 2Ag]^{2+}$; (○) $[nR + 16 + Ag]^+$. n: number of repeat units. (b) Details of an individual fragment pattern; the region is shown by dashed lines in (a).

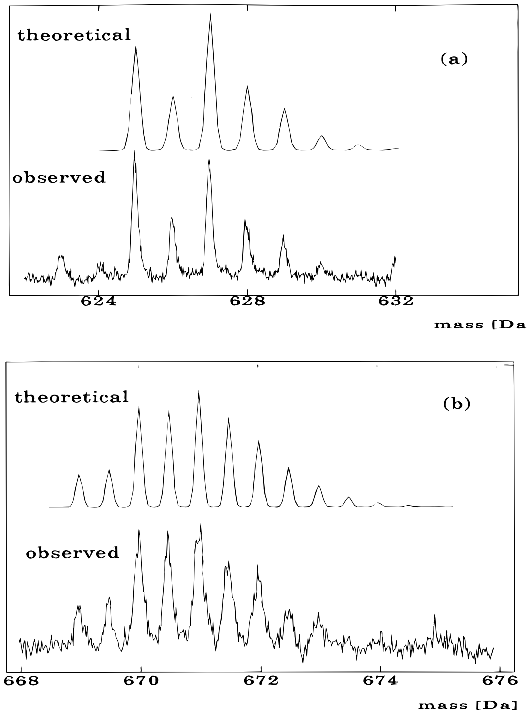


Figure 3. Comparison of theoretical and actual isotopic distributions of fragment peaks of PDMS: (a) $[R_7 + Ag]^+$; (b) $[15R + 14 + 2Ag]^{2+}$.

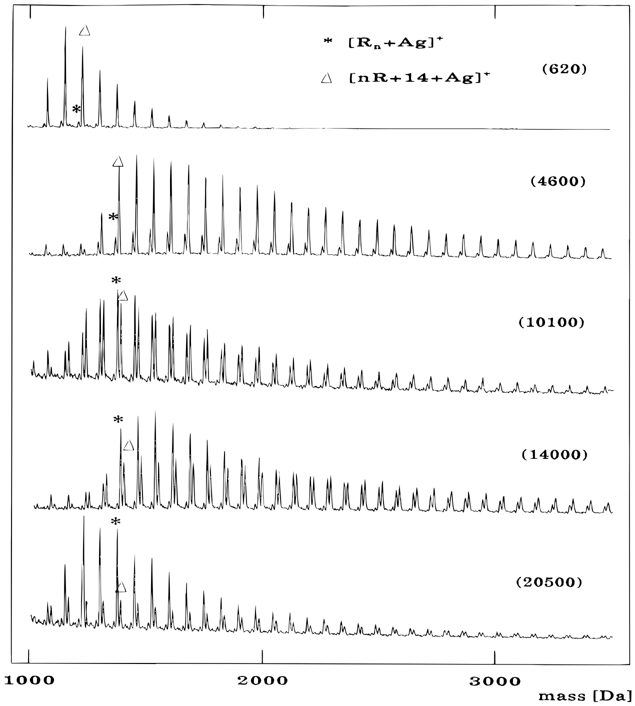


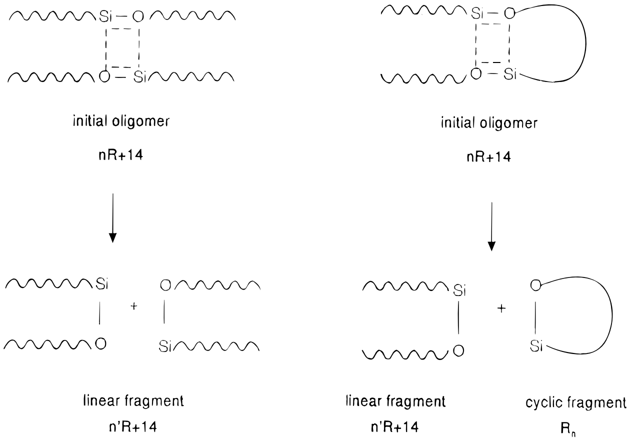
Figure 4. TOF-SIMS spectra for trimethylsilyl-terminated PDMS in the mass range 1000−3500 Da: (△) $[nR + 14 + Ag]^+$; (*) $[R_n + Ag]^+$. The number in parentheses is the number average molecular weight.

agreement is observed except that the peak at 625 Da is a little higher than predicted. The intensities of the $[R_n + Ag]^+$ peaks began to decrease at 1100 Da since the oligomer peaks become the dominant peaks. A possible reason is that the low molecular weight oligomers were pumped away in the vacuum system.

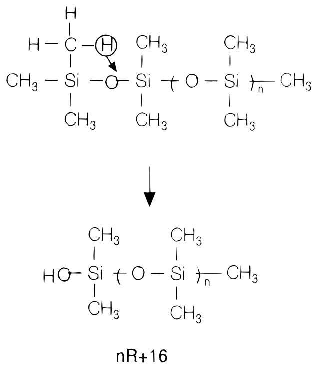
An interesting feature which was observed in the low molecular weight PDMS spectra is the appearance of doubly charged ions in this mass range, shown as (*) in Figure 2a. Doubly charged ions are rarely observed in SIMS spectra of polymers. They are formed by cationization of a linear PDMS oligomer with two silver ions. Figure 3b shows a comparison between the experimental and theoretical spectra for a linear oligomer cationized by two silver ions. Good agreement is seen between the theoretical and observed spectra. The intensity of doubly charged ions decreases quickly with increasing molecular weight of the polymer. No doubly charged ions are observed in the spectra of high molecular weight PDMS. Doubly charged ions would be expected for larger polymers because of the minimization of columbic repulsion. However, the experimental results showed the reverse effect. This is because the formation of cyclic fragments is the dominant process for high molecular weight samples. This will be discussed in section C. As a result, intensities of doubly charged linear species decrease with increasing molecular weight.

Mass Range above 1000 Da. The high mass range ($m/z > 1000$) spectra of five PDMS samples with different molecular weights are shown in Figure 4. The fragmentation pattern in this mass range is different from that in the mass range 600−1000 Da. Two intense clusters are observed: the silver-cationized linear fragment having a formula identical with that of the intact oligomer, $[nR + 14 + Ag]^+$ (△), and a series corresponding to an integral number of repeat units cationized by silver, $[R_n + Ag]^+$ (*). The latter probably has a cyclic structure, as discussed previously. The oligomer of PDMS has an integral number of repeat units plus two end groups, which are $-(CH_3)_3Si$ and $-CH_3$. Since the mass of the repeat unit is 74 Da, the mass of an oligomer corresponds to $[nR + 88]$ which is the same as $[(n + 1)R + 14]$. For low molecular weight samples, the oligomers present in the polymer sample are likely the major species contributing to $[nR + 14 + Ag]^+$. For high molecular weight samples, the peaks at $[nR + 14 + Ag]^+$ must be due mainly to fragments and not to oligomers originally present in the sample. The reason is that the maximum of the “oligomer distribution” shifts toward

Scheme 1. Cyclic Intermediate Mechanism for Fragmentation of PDMS



Scheme 2. Hydrogen Transfer Mechanism for Fragmentation of PDMS



lower mass as the molecular weight of the polymer increases, even though GPC indicates a higher maximum.

B. Fragmentation Mechanisms. Fragmentation mechanisms of many polymers have been studied by TOF-SIMS. The simplest model for polymers having a carbon backbone is chain scission. In this model, the initial bond-breaking events occur at weak points in the polymer chain. However, this model does not readily explain the formation of cyclic fragments in PDMS. The formation of cyclic fragments in PDMS requires that the strong siloxane bond (799.6 kJ/mol) in the main chain be broken in preference to the weak silicon–carbon bond (451.5 kJ/mol) of the pendant group.

A possible mechanism for formation of cyclic fragments is shown in Scheme 1, similar to the thermal degradation mechanism for PDMS.[32] Since the polysiloxane chain has a random coiled structure rather than being linear, it is possible to form an intermediate with a four-membered ring. During the fragmentation process, two siloxane bonds can be broken while two new siloxane bonds are formed simultaneously, requiring no net energy change. Even though the siloxane bond is stronger than the silicon–carbon bond, formation of a four-membered ring intermediate makes it possible to cleave the siloxane bond instead of the weaker silicon–carbon bond during the ion formation process. Four-membered ring intermediates may be formed by either intermolecular or intramolecular mechanisms. Intermolecular interaction will form two linear fragments. Intramolecular interaction can form a linear fragment and a cyclic fragment. In TOF-SIMS experiments, the amount of polymer deposited on the target is very small; therefore, intramolecular interactions should be dominant in chain decomposition.

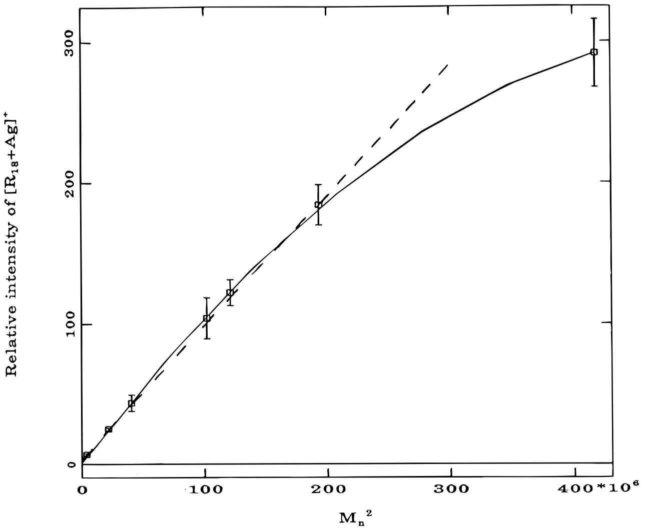


Figure 5. Variation of relative intensity of $[R_{18} + Ag]^+$ as a function of molecular weight. Intensities are normalized to $[18R + 14 + Ag]^+ = 100$.

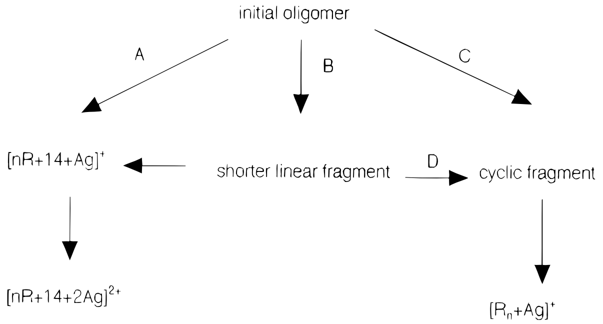
Scheme 2 indicates that H transfer from a methyl group to an oxygen atom can produce a linear PDMS species terminated by hydrogen (H) and methyl groups. This species, cationized by Ag, corresponds to $[nR + 16 + Ag]^+$. Since the intensity of this cluster decreases with increasing molecular weight, H transfer must occur preferentially at the end group rather than in the middle of the chain.

C. Effect of Molecular Weight on Fragmentation. Though TOF-SIMS has been used to determine the molecular weight distributions of many polymers,[33,34] its use is limited for high molecular weight PDMS because fragment ions are the most abundant species in the mass range measured (<3500), rather than oligomers. As a result, molecular weights determined by GPC were used to correlate the observed TOF-SIMS fragmentation patterns with polymer molecular weight. The molecular weight of PDMS 620 was determined by NMR due to the limited resolution of GPC at low masses; all others were determined by GPC.

The effect of polymer molecular weight on fragmentation can be seen in Figure 4. Comparing the spectra of different samples, the intensity of the cyclic fragment ion increases with increasing molecular weight relative to the linear species. The relative intensities of the cyclic fragments of several clusters were calculated for each sample by dividing the peak areas of R_n clusters by the peak areas of $nR + 14$ clusters. The variation of relative intensity of $[R_{18} + Ag]^+$ (normalized to $[18R + 14 + Ag]^+$ equal 100) is shown in Figure 5. A linear relationship between the relative intensity of the cyclic fragment ions and the square of the molecular weight is observed when M_n is in the range 2000–15 000, as indicated by the dashed line. When the molecular weight increases to 20 000, there is a deviation from this linear relationship.

Several competing processes which can occur when PDMS is bombarded by primary ions are summarized in Scheme 3. The initial oligomer may be desorbed as an intact molecule and cationized by silver (process A). It may also decompose to form shorter linear PDMS fragments which can be cationized by one or two Ag^+ ions (process B). This short linear fragment may decompose further to form a cyclic fragment (process

Scheme 3. Competing Processes for PDMS Occurring in TOF-SIMS



D). The cyclic fragment can also be formed from the initial oligomer (process C), either product can combine with one silver cation. Process A is preferred for small polymer molecules which have dimensions approximately the size of the action area of the incident primary ions, or smaller. The primary action area for sputtering polymers is a circle roughly 50 Å in diameter.[35] The length of a PDMS monomer is 3.1 Å. A stretched-out polymer 50 Å in length would contain about 16 repeat units. This plus end groups would correspond to a mass of about 1300 Da. When the molecule is much larger than this action area and is in contact with part of the surface which is not sputtered, the primary action area may underlie only a portion of the polymer chain and fragmentation will occur, causing emission of a segment or segments of the polymer chain. As a result, processes B and C occur preferentially to process A for high molecular weight samples. The spectra will be dominated by fragment peaks instead of initial oligomer peaks. This can explain why the molecular weight distributions measured for all PDMS samples are shifted to lower mass than the GPC results except for PDMS 620. Because cyclic fragments can be formed from both initial oligomers and linear fragments (processes B and C), the relative intensities of cyclic fragments become higher as the polymer molecular weight increases.

D. Effect of End Groups. Poly(dimethylsiloxane)s terminated by silanol, trimethylsilyl, (aminopropyl)dimethylsiloxy, and (amidopropyl)dimethylsiloxy groups were investigated to study the effect of end groups on PDMS fragmentation. The structures of these polymers are shown in Figure 6. Although the polymer is terminated at both ends with the same group, the mass of the ion derived from the terminal group depends on whether fragmentation is caused by cleavage of a Si−O or a Si−C bond. For example, in (aminopropyl)dimethylsiloxy-terminated PDMS, fragmentation of the Si−O bond should yield a $NH_2-(CH_2)_3Si(CH_3)_2$ fragment (116 Da), and Si−C cleavage should yield a $(CH_2)_3NH_2$ fragment (58 Da).

Low Mass Range Spectra. One means of identifying polymer terminal groups is to examine the low mass range (<300 Da) spectra. Figure 7 shows the range from 10 to 300 Da for silanol-, (aminopropyl)dimethylsiloxy (APD)-, and (amidopropyl)dimethylsiloxy (MPD)-terminated PDMS. Number average molecular weights of these PDMS samples were 1200, 2500, and 2500, respectively. Similar to the spectra of trimethylsilyl-terminated PDMS (Figure 1), extensive fragmentation is observed and the major series are $[nR + 73]^+$, $[R_n - 15]^+$, and $[R_n - 29]^+$.

Although the low mass range spectra of PDMS terminated by different end groups are very similar,

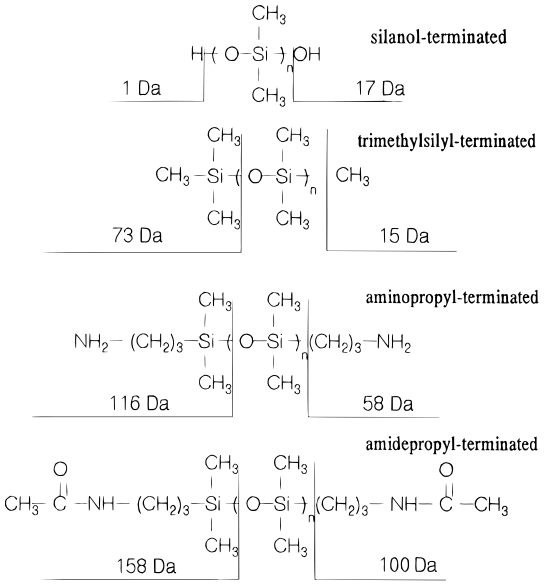


Figure 6. Structures of PDMS terminated with different end groups.

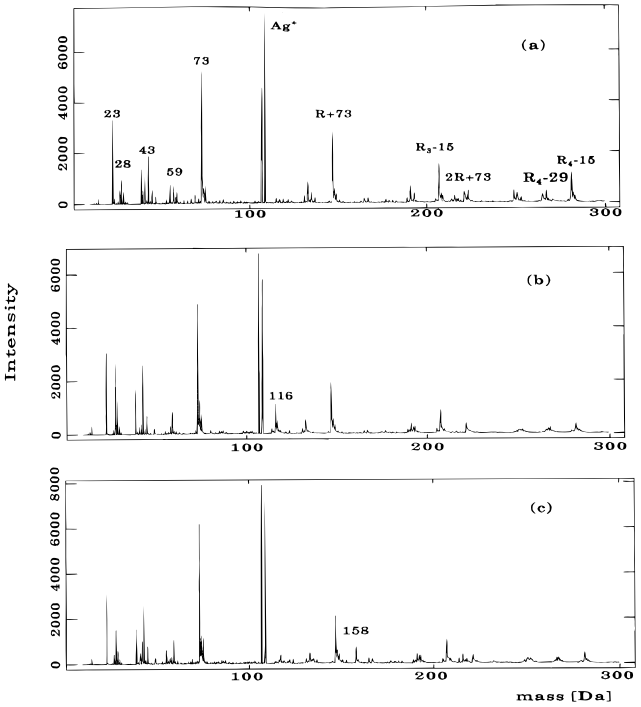


Figure 7. TOF-SIMS spectra in the mass range 10−300 Da for PDMS with different end groups: (a) silanol terminated (M_n = 1200); (b) (aminopropyl)dimethylsiloxy terminated (M_n = 2500); (c) (amidopropyl)dimethylsiloxy terminated (M_n = 2500).

characteristic peaks for (aminopropyl)dimethylsiloxy and (amidopropyl)dimethylsiloxy, 116 and 158 Da, respectively, are observed in the spectra of APD- and MPD-terminated PDMS. However, the spectra of PDMS-APD and PDMS-MPD do not show significant peaks at either 58 ($NH_2(CH_2)_3^+$) or 100 Da ($CH_3CONH(CH_2)_3^+$). This indicates that terminal group cleavage occurs at the siloxane bond with charge transfer to Si. Silicon is more electropositive than oxygen, so the positive charge would more likely reside on silicon than on oxygen when the Si−O bond is broken. The siloxane bond (799.6 kJ/mol) is stronger than the silicon−carbon bond (451.5 kJ/mol), so the Si−C bond should be cleaved more easily. Since silicon is more electropositive than carbon, the

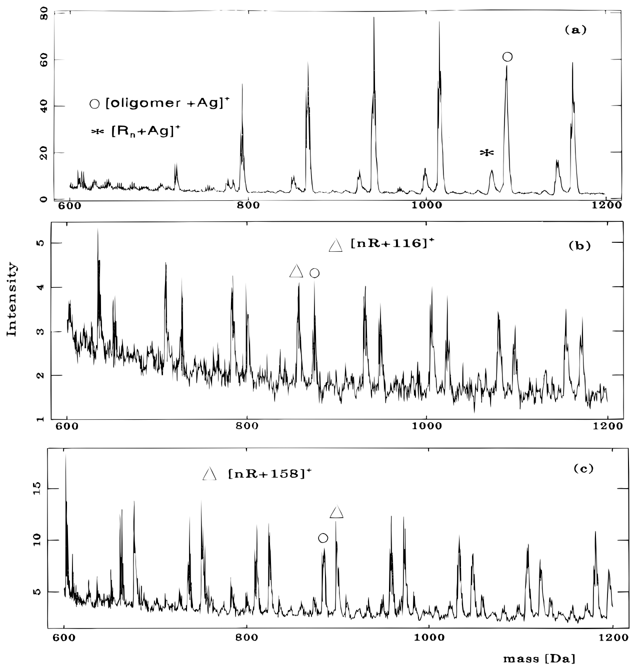


Figure 8. TOF-SIMS spectra in the mass range 600−1200 Da for PDMS with different end groups: (a) silanol terminated ($M_n = 1200$); (b) (aminopropyl)dimethylsiloxy terminated ($M_n = 2500$); (c) (amidopropyl)dimethylsiloxy terminated ($M_n = 2500$); (*) $[R_n + Ag]^+$; (○) $[\text{oligometer} + Ag]^+$; (△) $[\text{oligomer} - \text{one end group}]^+$.

positive charge would also reside on silicon when the Si−C bond is broken, forming fragments like $[nR + 116]^+$ and $[nR + 158]^+$ rather than $[nR + 58]^+$ and $[nR + 100]^+$. These fragments are observed in the higher mass range. The PDMS silanol spectrum does not include a characteristic peak of the hydroxyl group at 17 Da, because the hydroxyl group does not tend to form positive ions.

Mass Range 600−1200 Da. A major difference is observed in the mass range 600−1200 Da for spectra of polymers terminated by different end groups. Spectra of PDMS terminated by silanol, (aminopropyl)dimethylsiloxy, and (amidopropyl)dimethylsiloxy groups are shown in Figure 8. The spectrum of PDMS terminated by a silanol group shows two intense series which correspond to the intact linear oligomer (○) and a cyclic fragment (*), both cationized by Ag^+. No peaks corresponding to $[nR + 16 + Ag]^+$ were observed for the silanol-terminated polymer (Figure 8a) as were observed for the trimethylsilyl-terminated PDMS (Figure 2). The fragmentation patterns observed for PDMS-APD and PDMS-MPD are quite different from those of hydroxyl- or trimethylsilyl-terminated PDMS.

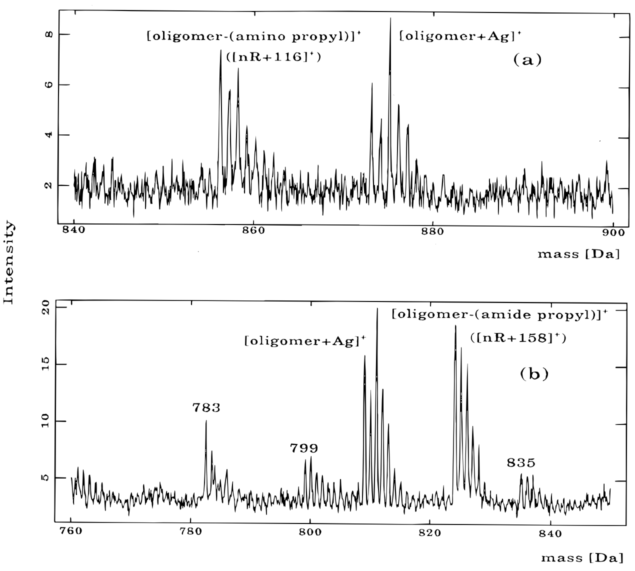


Figure 9. Details of an individual fragmentation pattern of PDMS with different end groups: (a) (aminopropyl)dimethylsiloxy terminated ($M_n = 2500$); (b) (amidopropyl)dimethylsiloxy terminated ($M_n = 2500$).

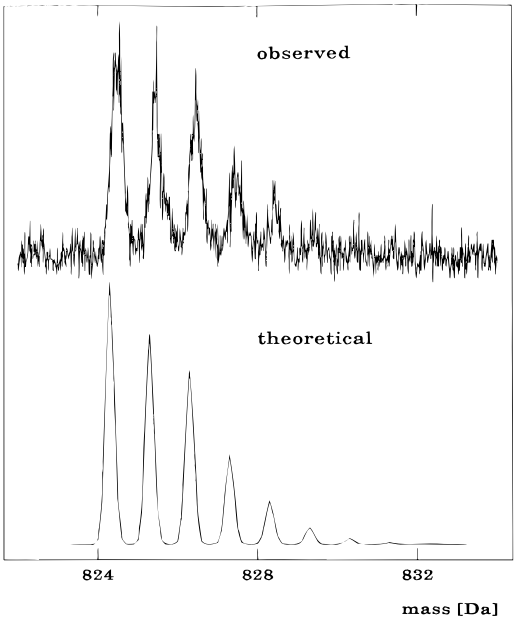


Figure 10. Comparison of theoretical and actual isotopic distributions of fragment peaks $[nR + 158]^+$, for (amidopropyl)dimethylsiloxy terminated PDMS.

Detailed fragmentation patterns for PDMS-APD and PDMS-MPD are shown in Figure 9. There are two intense clusters in the spectrum of PDMS-APD. One corresponds to the intact linear oligomer cationized by silver; the other, to a linear fragment formed by loss of the (aminopropyl) group from the oligomer, *but not cationized by silver* ($[nR + 116]^+$). Similarly, the spectrum of PDMS-MPD contains two intense series, one corresponds to an intact linear oligomer cationized by silver, the other to a linear fragment *with intrinsic charge* formed by loss of the (amidopropyl) group from the oligomer ($[nR + 158]^+$). Figure 10 shows a comparison of the experimental and theoretical spectra of the linear fragment ($[nR + 158]^+$) for PDMS-MPD. Good agreement is observed. In addition to these two strong clusters, other weak clusters are observed at 799 and 835 Da for PDMS-MPD. They correspond to $[R_n - CH_3]^+$ and $[\text{oligomer} - CH_3]^+$, respectively; they are not silver cationized. The cluster at 783 in Figure 9b probably comes from an impurity since it is not part of a series having an interval of 74 Da. Peaks due to the loss of one end group from an oligomer are rarely observed in the high mass range TOF-SIMS spectra of polymers, other than for the perfluorinated polyethers (PFPE).[25] End groups of a polymer can affect its conformation. A PDMS terminated with nitrogen-containing end groups may have a more linear structure on the silver target than silanol- and trimethylsilyl-terminated PDMS, making formation of a cyclic intermediate more difficult. As a result, cleavage of the weak Si−C bond will occur more easily than formation of cyclic fragments. The effect of the end group tends to become smaller with increasing chain length, so cyclic

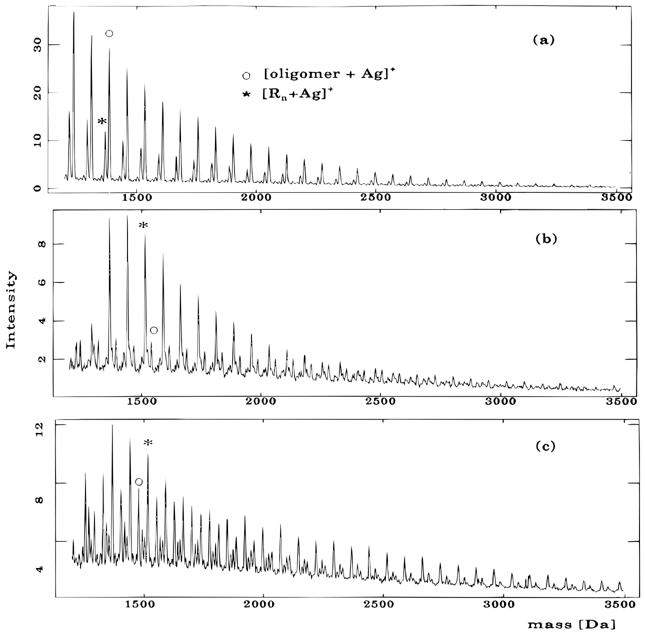


Figure 11. TOF-SIMS spectra in the mass range 1200−3500 Da for PDMS with different end groups: (a) silanol terminated ($M_n = 1200$); (b) (aminopropyl)dimethylsiloxy terminated ($M_n = 2500$); (c) (amidopropyl)dimethylsiloxy terminated ($M_n = 2500$); (○) [oligomer + Ag]$^+$; (*) [R$_n$ + Ag]$^+$.

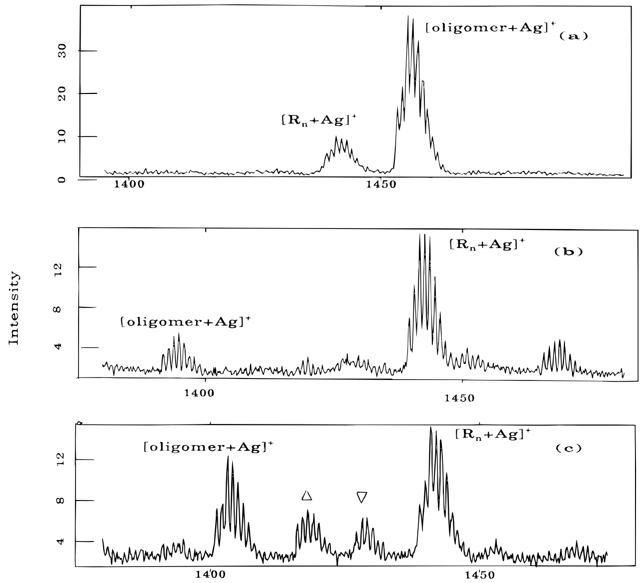


Figure 12. Fragmentation pattern of PDMS with different end groups in the mass range 1400−1500 Da: (a) trimethylsilyl terminated ($M_n = 4600$); (b) (aminopropyl)dimethylsiloxy terminated ($M_n = 2500$); (c) (amidopropyl)dimethylsiloxy terminated ($M_n = 2500$); (△) [nR + 158]$^+$; (▽) [oligomer − CH$_3$]$^+$.

fragments are observed in the mass range above 1200 Da.

Mass Range above 1200 Da. Figure 11 shows the spectra of PDMS terminated by different end groups in the mass range 1200−3500 Da. Similar to trimethylsilyl-terminated PDMS, spectra of PDMS terminated by silanol and (aminopropyl)dimethylsiloxy groups contain two intense clusters which correspond to silver-cationized intact linear oligomers and [R$_n$ + Ag]$^+$. Two additional clusters are observed in the spectrum of PDMS-MPD, as shown in Figure 12. One (△) corresponds to [nR + 158]$^+$, the other cluster (▽) is due to [oligomer − CH$_3$]$^+$.

Extended spectra of APD-, MPD-, and trimethylsilyl-terminated PDMS are shown in Figure 12. The intensity of the cyclic fragment compared to the oligomer peaks in the spectra of PDMS-APD is higher than that observed in the spectra of PDMS with a trimethylsilyl end group, for a similar molecular weight. This indicates that desorption of an intact oligomer is more difficult for APD-terminated PDMS. The limiting factors controlling desorption of intact oligomers are not clear and may be related to the conformation of the polymer chain on the substrate, as suggested earlier. Since there is a lone pair of electrons on nitrogen, and silver tends to from complexes with amines, stronger interaction may occur with the silver target, making desorption of the intact oligomer more difficult.

Conclusions

The fragmentation patterns of a series of trimethylsilyl-terminated poly(dimethylsiloxane)s with different molecular weights were examined by TOF-SIMS. Extensive fragmentation was found in the low mass range spectra of PDMS. The spectra are similar to those obtained by pyrolysis mass spectrometry. In the mass range from 500 to 1000 Da, the spectra are dominated by peaks corresponding to [nR + 16 + Ag]$^+$ and [R$_n$ + Ag]$^+$. For low molecular weight PDMS, doubly charged ions [oligomer + 2Ag]$^{2+}$ are observed in this mass range. In the high mass range (>1000 Da), the spectra are dominated by [nR + 14 + Ag]$^+$, which corresponds to linear fragments having a formula identical with that of an oligomer, and [R$_n$ + Ag]$^+$, which corresponds to a cyclic fragment.

The effect of molecular weight on the fragmentation of PDMS has been studied. The relative intensity of cyclic fragments increases with increasing molecular weight. The formation of cyclic fragments is dominant for high molecular weight samples.

There is an effect of the end group on fragmentation of PDMS. In the spectra of (aminopropyl)dimethylsiloxy- and (amidopropyl)dimethylsiloxy-terminated PDMS, large linear fragments with intrinsic positive charge are observed, which do not appear in the spectra of trimethysilyl- and silanol-terminated PDMS. The relative intensity of the cyclic fragment of (aminopropyl)dimethylsiloxy-terminated PDMS is higher than that of PDMS trimethylsilyl having a similar molecular weight. This may be caused by the strong interaction between the amine group and silver substrate.

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