# Characterization of Polysiloxanes with Different Functional Groups by Time-of-Flight Secondary Ion Mass Spectrometry

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Polydimethylsiloxane (PDMS), polyhydromethylsiloxane (PHMS), and polymethylphenylsiloxane (PMPhS) have been studied by TOF-SIMS to investigate effects of functional group changes on polymer fragmentation mechanisms. Cyclic fragments are observed in the low mass range spectra of PDMS and PHMS, but not in the spectrum of PMPhS. Effects of functional group substitution on the fragmentation mechanisms of polysiloxanes are evident in the high mass range spectra (>1000 Da). Peaks of oligomers cationized by silver dominate the high mass range of the spectra of all low molecular weight polysiloxanes. However, fragmentation patterns of these samples are different. Neutral cyclic fragments cationized by silver are identified in the high mass range of the spectra of PDMS and PHMS, but not in the spectrum of PMPhS. The major fragments of PHMS and PMPhS are $[\text{oligomer-14+Ag}]^+$. The PHMS spectrum also shows peaks $[\text{oligomer-28+Ag}]^+$. These distinctive fragmentation patterns can be used to identify the polysiloxanes. (J Am Soc Mass Spectrom 1998, 9, 292–298) © 1998 American Society for Mass Spectrometry

Mass spectrometry is a powerful tool for structural characterization of organic molecules because of its high sensitivity, broad dynamic range, specificity, and selectivity, and has been extensively used in polymer studies since the 1970s. Combinations of different 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 the presence of additives or impurities.

The development of time-of-flight secondary-ion mass spectrometry (TOF-SIMS) has made it possible to investigate polymers in the high mass range by SIMS (up to 10,000 Da) [1]. Although the accessible mass range of TOF-SIMS is lower than that of MALDI, another important mass spectrometric method that has wide application in polymer analysis [2–8], sample preparation for TOF-SIMS is much simpler because no matrix selection is necessary. TOF-SIMS can provide distinctive fragmentation patterns that can be used to distinguish different kinds of polymers.

TOF-SIMS has been used to determine oligomer distributions and to identify end groups and the mass of repeat units [9]. This method has also been used to study the fragmentation mechanisms of various polymers including polystyrenes [10], polyurethanes [11], perfluorinated polyethers [12], polymethacrylates [13], polyacrylates [14], and polybutadienes [15]. Effects of molecular weight [16], terminal group [16], stereoregularity [17], and solvent used for deposition [18] on fragmentation of polymers have been observed.

The functional groups attached to a polymer main chain have profound effects on polymer properties. A functional group may protect the skeleton against chain cleavage reactions and is responsible for most solubility properties of polymers, because it affects their polarity. Steric and polar interactions between functional groups on the same chain or on different chains largely determine the glass transition temperature, crystallinity, and surface properties of the material.

Siloxanes are important industrial materials, used as lubricants, water repellents, and silicone oils. TOF-SIMS has already been used to study the molecular weight distribution [19] and fragmentation mechanism of polydimethylsiloxanes (PDMS) [16]. The dominant fragment peaks observed in the high mass range spectra of trimethylsilyl terminated PDMS were found to be neutral cyclic fragments cationized by silver. Effects of molecular weight and the terminal group on fragmentation of PDMS were also reported [16]. The purpose of the present research is to study polysiloxanes with different functional groups on the polymer main chain to investigate the effect of functional group on the fragmentation of polysiloxanes using TOF-SIMS.

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## Experimental

### *Instrumentation*

The spectra of polysiloxanes were obtained using a time-of-flight secondary-ion mass spectrometer, TOF-SIMS III, designed and manufactured by Ion-Tof GmbH, Münster, Germany. The instrument has been described in detail elsewhere [20]. Targets were bombarded by a 10 keV $Ar^+$ beam with the pulsed primary ion current varying from 0.3 to 0.5 pA. 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 reflection optics were used for focusing the secondary ion beam and for energy compensation, respectively, in a 2-m flight tube. The ions were postaccelerated to 10 keV just ahead of the detector, which was a channelplate–scintillator–photomultiplier combination. A time-to-digital converter was used for data collection.

The summation of $1.5 \times 10^6$ spectra produced Figures 1–5, a process which took 300 s per sample to accomplish. The total primary ion dose during data acquisition was less than $10^{13}$ ions/cm$^2$, which corresponds to static SIMS. The base pressure in the main chamber of the instrument was typically $3 \times 10^{-8}$ Pa and the operating pressure was about $10^{-6}$ Pa with a pressure of $4 \times 10^{-4}$ Pa in the primary ion source.

### *Sample Preparation and Data Analysis*

Polydimethylsiloxane (PDMS) terminated with trimethylsilyl groups was purchased from Gelest Inc. (Tullytown, PA). Polymethylphenylsiloxane (PMPhS) and polyhydromethylsiloxane (PHMS) were purchased from Scientific Polymer Products, Inc. (Ontario, NY). The molecular weights ($M_w$) of the polymer samples used in this research are 2600, 2300, and 2600 Da, respectively. The siloxane samples were dissolved in toluene with concentrations ranging from 0.5 to 1 mg/mL. Sample solution volumes of 1 $\mu$L were deposited onto silver targets with a substrate area of 20 mm$^2$. The silver substrates were first etched in nitric acid (20 vol%) and ultrasonicated in distilled water for about 3 min, then rinsed in distilled water and methanol. Data analysis was completed using in-house generated software, GOOGLY [21].

## Results and Discussion

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 (generally separated by 1 Da) corresponding to a particular ion; *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 linear fragment containing an integral number ($n$) of repeat units. The structures of polydimethylsiloxane (PDMS), polyhydromethylsiloxane (PHMS), and polymethylphenylsiloxane (PMPhS) are shown in Figure 1. The masses of their repeat units are 74, 60, and 136 Da, respectively.

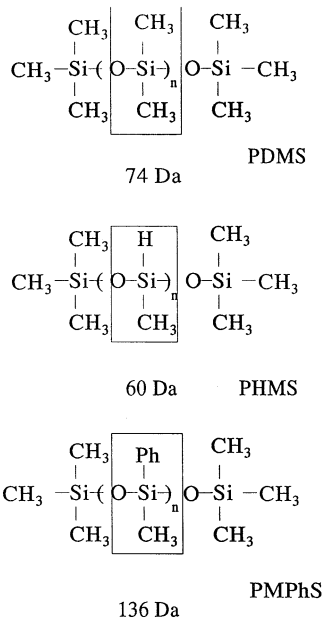



**Figure 1.** Structures of PDMS, PHMS, and PMPhS. The boxes show the structures of repeat units.

### *Low Mass Range Spectra of Polysiloxanes*

Although it is expected that the high mass range spectra (>1000 Da) will provide the most important and distinctive information about polymer structure, useful fragmentation information can also be obtained from the low mass range spectra. The spectra of PDMS, PHMS, and PMPhS below 300 Da are shown in Figure 2. In the low mass range spectrum of PDMS, two series of peaks are observed. One is $[R_n - 15]^+$ (Me = 15) formed by loss of the methyl group from a cyclic fragment, the other is $[nR+73]^+$ ($Me_3Si$ = 73) corresponding to the loss of one methyl group from the linear oligomer. The fragments of PDMS have been previously studied in detail, showing that cyclic fragments are formed in the TOF-SIMS process [16]. The backbone of PDMS is flexible and it is possible for PDMS to form an intermediate with a four-membered ring. During the TOF-SIMS process, two siloxane bonds are broken while two new siloxane bonds are formed, the net energy change is zero. As a result, main chain siloxane bonds are broken (and others formed) instead of the weaker silicon–carbon bond. A cyclic fragment is formed at the same time as the formation of a linear fragment which has the structure of an oligomer but of lower molecular weight.

Two series of peaks are observed in the spectrum of PHMS. One series corresponds to $[nR+73]^+$ and the

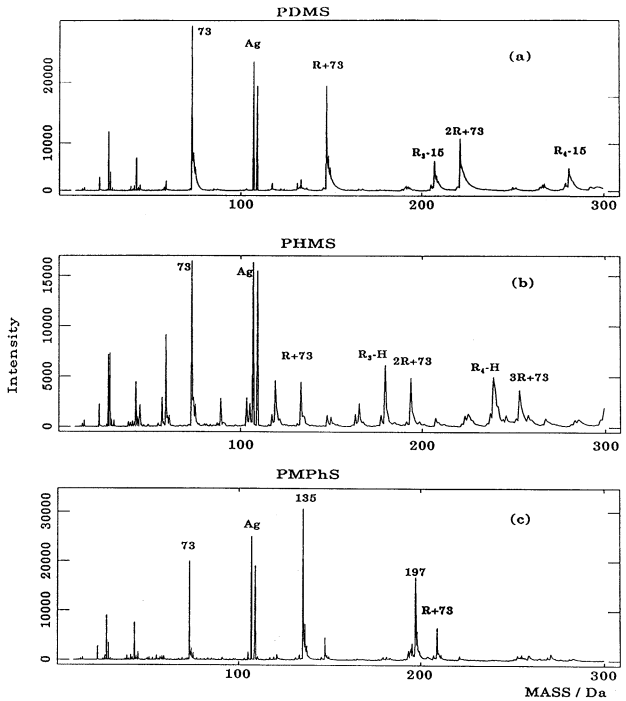



**Figure 2.** Low mass range spectra of polysiloxanes: (**a**) PDMS, (**b**) PHMS, (**c**) PMPhS.

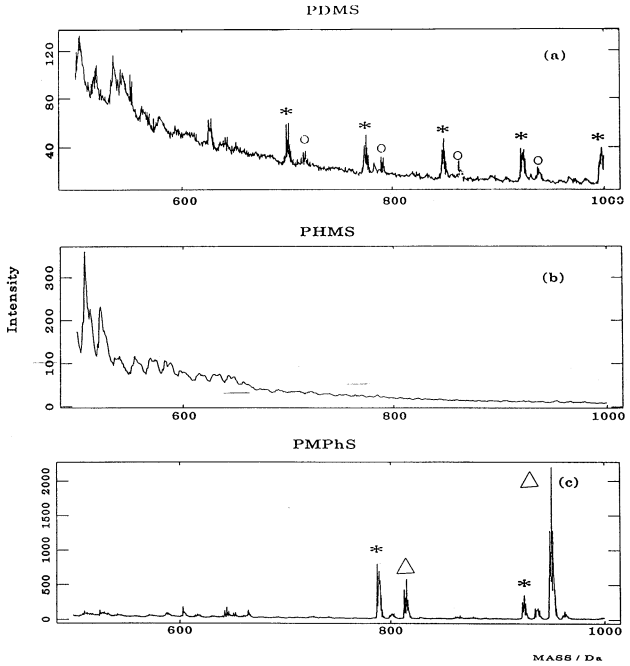



**Figure 3.** Spectra of polysiloxanes in mass range 500–1000 Da: (**a**) PDMS, (**b**) PHMS), (**c**) PMPhS. (asterisk) $[nR+Ag]^+$, (circle) $[nR+16+Ag]^+$, (triangle) $[nR+162+Ag]^+$ ([oligomer+$Ag]^+$).

other corresponds to $[R_n - H]^+$. The $[n\text{R}+73]^+$ cluster has a structure consistent with the oligomer after loss of one terminal group whereas the $[R_n - H]^+$ series is due to loss of H from a cyclic fragment. The cyclic fragments are probably formed by the same mechanism as that of PDMS.

In the spectrum of PMPhS, the dominant peak in this mass range is at 135 Da, which is $[(CH_3)_2SiPh]^+$. The peak at 197 Da is identified as $[Si(Ph)_2CH_3]^+$. These cations result from rearrangement of the phenyl group. The peak at 209 Da corresponds to $[(CH_3)_3Si–OSiPh(CH_3)]^+$ ($[\text{R}+73]^+$); no peaks attributed to cyclic fragments are observed in this mass range. The low mass range spectrum of PMPhS is similar to that obtained by quadrupole SIMS [22]. PMPhS was analyzed after purification by vacuum distillation. The spectrum of purified PMPhS is same as the one shown in Figure 2c. NMR did not show the presence of any impurity. These results indicate that the peaks at 135 and 197 Da are fragments from PMPhS rather than impurity peaks. The peak of the trimethylsilyl group (73 Da) is found in the spectra of all three samples.

The results shown above indicate that the low mass range spectra of PDMS and PHMS are similar, while the fragmentation process of PMPhS is different from those of PHMS and PDMS. Cyclic fragments are observed in the spectra of PDMS and PHMS, but not in the spectrum of PMPhS. Significant rearrangement peaks are observed for PMPhS. A common fragment of siloxanes in the low mass range is $[nR+73]^+$. All three polymers experience a loss of one terminal group.

## *Spectra of Polysiloxanes in the Mass Range 500–1000 Da*

The low mass range spectra of the polysiloxanes are dominated by small fragments with intrinsic positive charge. The major peaks observed in the spectra of polysiloxanes in the mass range 300–500 Da are single peaks that are not parts of series. They may be contributed from impurities that were introduced during sample preparation. Neutral fragments cationized by silver are observed in the mass range above 500 Da. Figure 3 shows the spectra in the mass range 500–1000 Da for PDMS, PHMS, and PMPhS. The spectrum of PDMS contains two series of clusters corresponding to $[R_n+Ag]^+$ (asterisk) and $[nR+16+Ag]^+$ (circle) (the sum of the molecular weights of the two end groups, H and $CH_3$, is 16). Their structures have been characterized previously [16]. Because cyclic oligomers with high molecular weights were not detected in the original polymer sample by NMR, $[R_n+Ag]^+$ must result from silver cationization of a neutral cyclic fragment formed in the SIMS process. The species $[nR+16+Ag]^+$ has a structure that is consistent with silver cationized PDMS terminated by hydrogen and a methyl group. It is a hydrogen transfer product of PDMS formed during the TOF-SIMS process. The mechanism for formation of $[nR+16+Ag]^+$ has been discussed elsewhere [16].

No intense peaks are observed in the spectrum of PHMS in the 500–1000 region, except some impurities that may be introduced through sample preparation. This may result from the high volatility of PHMS so that oligomers with low molecular weight were evaporated

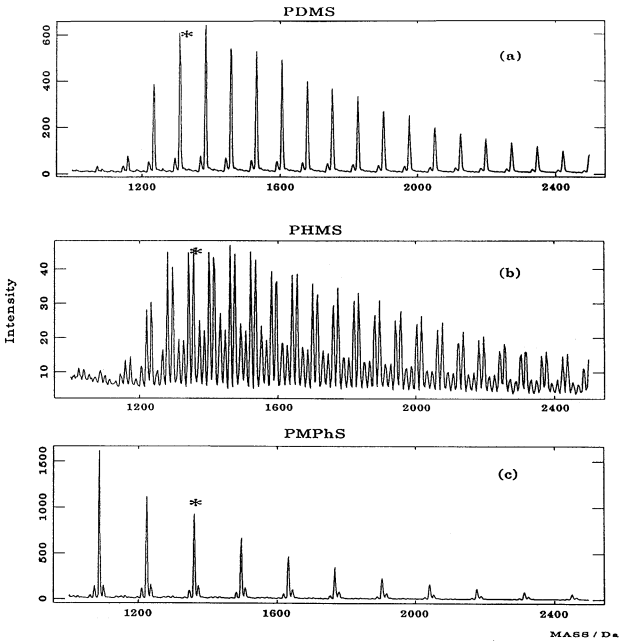



**Figure 4.** Spectra of polysiloxanes in mass range 1000–2500 Da: (**a**) PDMS, (**b**) PHMS, (**c**) PMPhS. (asterisk) one of the peaks of $[\text{oligomer}+\text{Ag}]^+$ series, 14 mer for PDMS, 18 mer for PHMS, 8 mer for PMPhS.

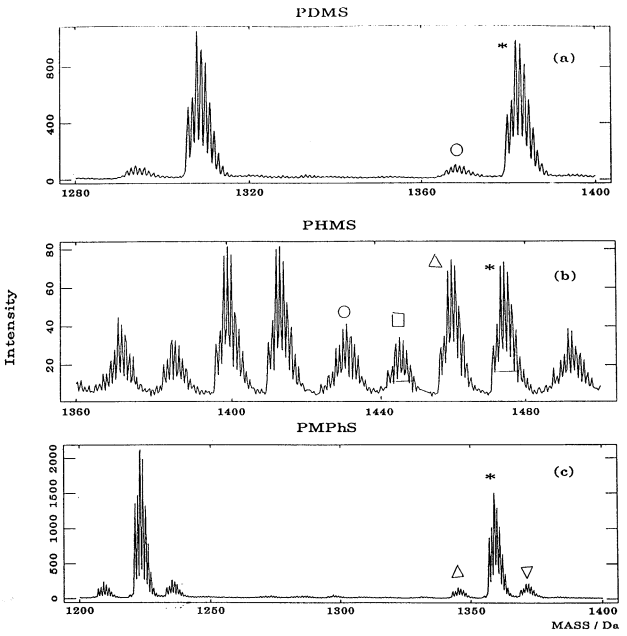


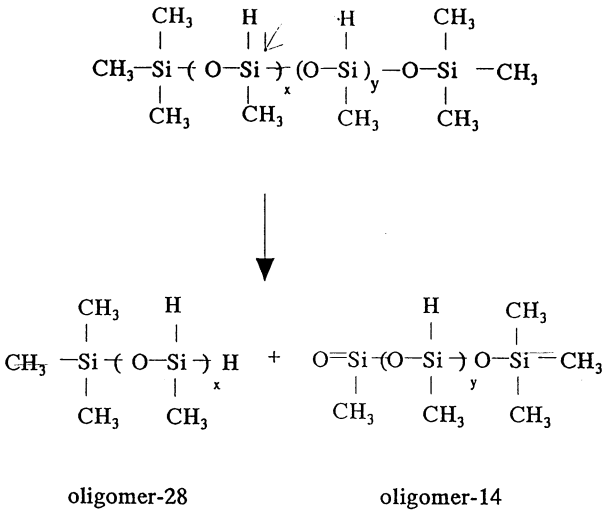

**Figure 5.** Detailed spectra of fragmentation pattern of polysiloxanes (a portion of Figure 4): (**a**) PDMS, (**b**) PHMS, (**c**) PMPhS. (asterisk) $[\text{oligomer}+\text{Ag}]^+$, (circle) $[nR+\text{Ag}]^+$, (square) $[\text{oligomer}-28+\text{Ag}]^+$, (triangle) $[\text{oligomer}-14+\text{Ag}]^+$, (inverted triangle) $[\text{oligomer}-124+\text{Ag}]^+$, number of repeat unit of the highlighted oligomer peaks: 15 for PDMS, 20 for PHMS, 8 for PMPhS.

before analysis. The same phenomenon is seen for PMPhS in the mass range 500–800 Da. Two pairs of clusters are observed in the mass range 800–1000 Da. One pair (asterisk) corresponds to $[R_5+\text{Ag}]^+$ and $[R_6+\text{Ag}]^+$. These two peaks are the only cyclic species observed in the spectrum of PMPhS. Although NMR results could detect no cyclic species in original sample, these two peaks are probably best explained as small cyclic oligomers existing in the original sample cationized by silver. The amount of cyclic species is probably too low to be detected by NMR, which has a detection limit of 2%. These two peaks could result from silver cationized cyclic fragments formed by chain fracture like those observed in the spectra of PDMS. However, it would be difficult to explain why only these two cyclic fragments are formed during the TOF-SIMS process and no other peaks in the $R_n$ series are seen at lower or higher mass. The second pair (triangle) of peaks correspond to $[nR+162+\text{Ag}]^+$ ($\text{Me}_3\text{Si}+\text{OSiMe}_3 = 162$) and are attributed to linear oligomers cationized by silver.

## *High Mass Range Spectra of Polysiloxanes*

A major advantage of TOF-SIMS is that it can provide high mass range spectra, which frequently contain the most important structural information about polymers. The spectra of PDMS, PHMS, and PMPhS in the mass range above 1000 Da are shown in Figure 4. Peaks corresponding to $[\text{oligomer}+\text{Ag}]^+$ (asterisk) are intense in all spectra. Figure 5 shows detailed fragmentation patterns in the mass range 1200–1500 Da. Two types of clusters are identified in the spectrum of PDMS. One is $[R_n+\text{Ag}]^+$ (circle) corresponding to the neutral cyclic fragment cationized by silver, the other is $[nR+88+\text{Ag}]^+$ (asterisk) ($\text{Me}+\text{SiMe}_3 = 88$) (asterisk) corresponding to silver cationized oligomer. The $[nR+88+\text{Ag}]^+$ series may contain contributions from oligomers initially present and linear fragments with the same structure as the oligomers [16]. Linear fragments are formed simultaneously with the formation of cyclic fragments.

Four series of clusters constitute the repeat pattern of PHMS. Similar to the spectrum of PDMS, peaks of silver cationized oligomers (asterisk) are strong in the spectrum of PHMS, but the fragmentation pattern of PHMS is quite different from that of PDMS. An intense series of fragment clusters was observed at $[\text{oligomer}-14+\text{Ag}]^+$ (triangle). This series has the same molecular weight as $[\text{oligomer}+46+\text{Ag}]^+$. Two weaker series of clusters correspond to $[\text{oligomer}-28+\text{Ag}]^+$ (square) and $[R_n+\text{Ag}]^+$ (circle), respectively. The series of $[\text{oligomer}-28+\text{Ag}]^+$ has the same molecular weight as $[\text{oligomer}+32+\text{Ag}]^+$. $[R_n+\text{Ag}]^+$ is attributed to the neutral cyclic fragment cationized by Ag. The $[\text{oligomer}-14+\text{Ag}]^+$ and $[\text{oligomer}-28+\text{Ag}]^+$ series correspond to the silver cationized hydrogen transfer products formed during the SIMS process. The possible mechanism is shown in Scheme I. Hydrogen transfer occurs at the main chain instead of the end group and causes $\beta$-cleavage at the siloxane bond. A comparison of experimental spectra and the spectra predicted from theoretical isotopic distributions of two fragment clusters, $[\text{oligomer}-14+\text{Ag}]^+$ and $[\text{oligomer}-28+\text{Ag}]^+$




**Scheme I.** Proposed mechanism for the formation of cyclic fragment of PDMS.

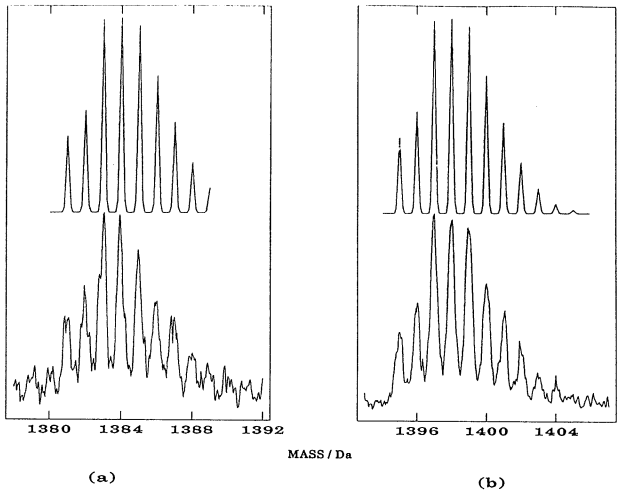



**Figure 6.** Comparison of experimental spectra and spectra predicted by theoretically calculated isotopic distribution of two clusters of PHMS: (**a**) [19*R*+end group − 28+Ag]$^+$, (**b**) [19*R*+end groups − 14+Ag]$^+$.

with 8 repeat unit, is shown in Figure 6a,b, respectively. Good agreement is observed.

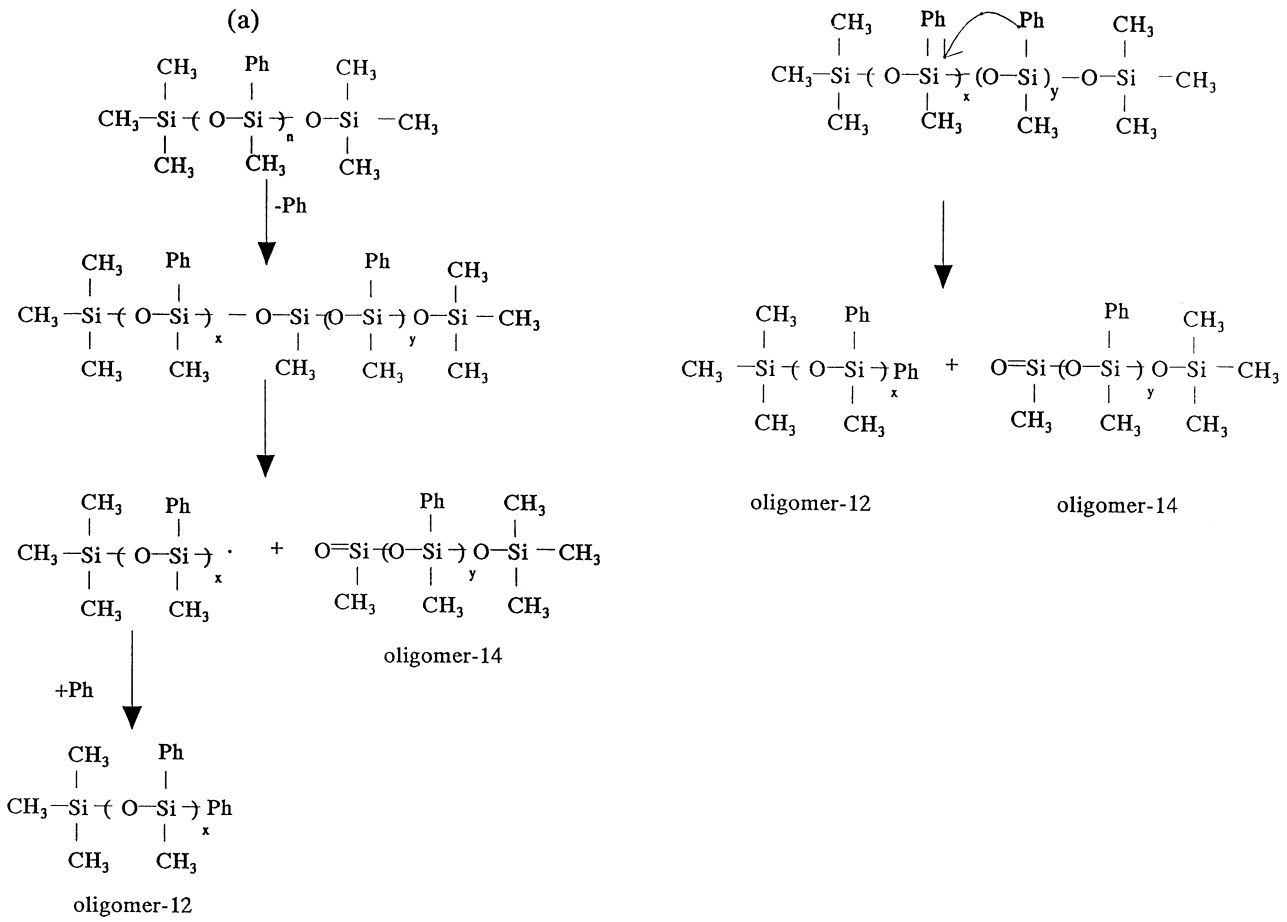
The repeat pattern of PMPhS contains three types of clusters, the most intense being [oligomer+Ag]$^+$ (asterisk). The second series is [oligomer − 14+Ag]$^+$ (triangle), which has the same mass as [oligomer+122+Ag]$^+$. As shown in Scheme II(a), initial loss of a phenyl group can form a silicon radical that causes cleavage of the siloxane bond. As a result, PMPhS terminated by –OSi(CH$_3$)$_3$ and O═Si(CH$_3$)– was obtained. PMPhS terminated by –OSi(CH$_3$)$_3$ and O═Si(CH$_3$)– cationized by Ag corresponds to [oligomer − 14+Ag]$^+$ observed in the spectrum of trimethylsilyl terminated PMPhS. The silicon radical may capture a phenyl group to form another fragment with mass [oligomer − 12]. These two fragments also can result from phenyl group transfer at the main chain as shown in Scheme II(b), which is a similar process to the H-transfer step for PMHS shown in Scheme I. Peaks of the [oligomer − 12+Ag]$^+$ clusters overlap with those of [oligomer − 14+Ag]$^+$ clusters. Figure 7 shows a comparison between the theoretical and experimental isotopic distributions of the [oligomer − 14+Ag]$^+$ cluster having 8 repeat units. The peak at 1343 Da observed in the experimental spectrum is slightly higher than that predicted by theoretical simulation, which indicates the contributions from [oligomer − 12+Ag]$^+$ are small. The intensity of [oligomer − 12+Ag]$^+$ is much lower than that of [oligomer − 14+Ag]$^+$. This observation is consistent with the mechanism shown in Scheme II(a). The capture of a phenyl group is not as easy as the cleavage of the siloxane bond. As a result, formation of the fragment [oligomer − 12] is more difficult than formation of [oligomer − 14]. The result suggests that the mechanism shown in Scheme II(a) is more likely than that shown in Scheme II(b). The third cluster, [oligomer − 124+Ag]$^+$ (inverted triangle) which has the same mass as [oligomer+12+Ag]$^+$, is identified as [oligomer − 2Ph+2CH$_3$+Ag]$^+$. Another possible explanation for [oligomer − 124+Ag]$^+$ is [oligomer − Ph+OSiMe$_3$+Ag]$^+$. The mechanism of formation of this fragment is not clear. The fragmentation of PMPhS and PHMS forms species containing Si═O bonds, which is not stable and can only exist over very short time. However, since it takes 200 $\mu$s to obtain one single TOF-SIMS spectra and much less than 200 $\mu$s for secondary ions to travel from target to detector, it is possible for SIMS to detect those species before they decompose.

The investigation of PDMS, PHMS, and PMPhS has shown that the TOF-SIMS spectra of polysiloxanes with different main-chain functional groups are different. The effect of the functional group on polymer fragmentation will be discussed in the following section.

## *Effects of Functional Group on the Fragmentation of Polysiloxanes*

Comparison of the spectra of PDMS, PHMS, and PMPhS indicates that the nature of the functional group has a significant effect on the fragmentation of polysiloxanes. Cyclic fragments are observed only in the spectra of PDMS and PHMS in both the high and low mass ranges. The spectrum of PMPhS is dominated by linear species. NMR did not show significant impurities or large cyclic oligomers in the original samples, which supports the proposition that strong peaks observed in TOF-SIMS spectra result from fragmentation of polysiloxanes during the SIMS process.

The phenomenon that no cyclic fragments are observed in the spectrum of PMPhS is related to the mechanism of cyclic fragment formation. The mechanism proposed for the formation of cyclic fragments for PDMS involves a four membered cyclic intermediate formed because of the high flexibility of the PDMS main




**Scheme II.** Possible fragmentation mechanisms for PHMS and PMPhS.

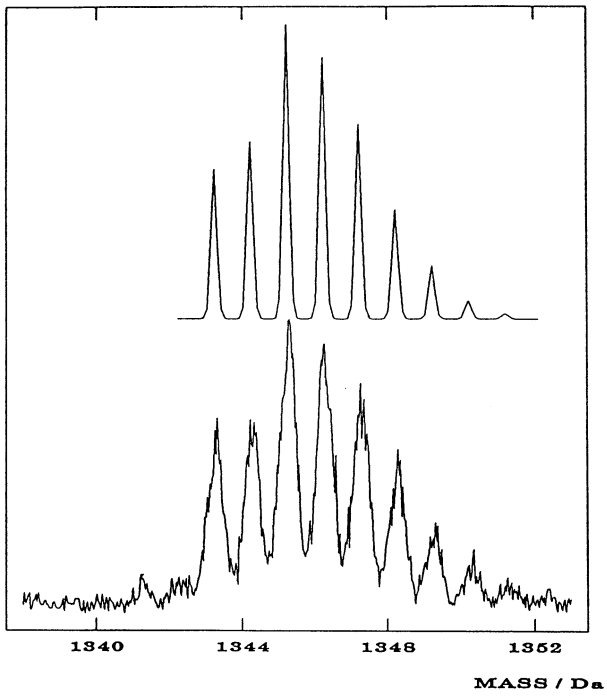



**Figure 7.** Comparison of experimental spectra and spectra predicted by theoretically calculated isotopic distribution of fragmentation cluster of PMPhS: $[8R+\text{end group} - 14+Ag]^+$.

chain [16]. When the functional group on the backbone is changed from methyl to phenyl, the flexibility of the main chain is significantly reduced [23]. The backbone of PMPhS is rigid and it is therefore difficult to form cyclic intermediates. As a result, the loss of a phenyl group and cleavage of the siloxane bond at the main chain become the most likely fragmentation pathways. The loss of a phenyl group instead of a methyl group from PMPhS is consistent with the principle that the largest functional group is most likely to be lost in polymer decomposition [13]. Phenyl transfer is another possible fragmentation mechanism.

If main chain flexibility were the only effect of functional group on the chain fragmentation mechanism, the relative intensity of cyclic fragments of PHMS should be even higher than that of PDMS, because the main chain of PHMS is even more flexible [21]. However, the most intense fragment peaks (their intensities are similar to those of oligomer peaks) observed in the PHMS spectrum are $[\text{oligomer} - 14+Ag]^+$, which are initiated by hydrogen transfer. The possible reason is that the bond strength of Si–H (<299 kJ/mol) is much lower than that of Si–C (451.5 kJ/mol) [24]. As a result, the loss of hydrogen from PHMS is easier than the loss of a methyl or phenyl group from PDMS or PMPhS.

Therefore, hydrogen transfer becomes the dominant fragmentation process of PHMS instead of cyclic fragment formation. This demonstrates that the functional group attached to the main chain can influence the fragmentation pathway through both flexibility of the main chain and the stability of a functional group. Siloxanes with different functional groups can therefore be distinguished by their distinctive fragmentation patterns using TOF-SIMS.

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