

Relative Secondary Ion Yields of Polymers[†]

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A method has been developed to measure the relative secondary ion yields of polymers. Parameters affecting secondary ion yield include primary ion current, detector efficiency, mole concentrations of oligomers, and the extent of oligomer fragmentation. All of these factors are considered in the measurement protocol. Two specific homopolymers were investigated: poly(dimethylsiloxane) and poly(methylphenylsiloxane). The relative secondary ion yields measured for PMPHS/PDMS were in the range of 0.29–0.35, depending on the polymer ratio. Transformation probabilities also were measured for the two polymers, and the PMPHS/PDMS ratio was 0.57. The results of the study indicate that the pendant groups on the siloxane side chain have a significant effect on polymer ion yield and that measurement of relative ion yields for polymer mixtures represents a valid yield comparison.

Introduction

Mass spectrometry has been used extensively to study polymers since the 1970s^{1–7} and provides information about oligomer distributions, average molecular weights, fingerprint patterns for polymer identification, monomeric unit sequences, branching, cross-linking, side-chain substitution, and copolymer structure. Using time-of-flight secondary ion mass spectrometry (TOF-SIMS), it is possible to investigate polymers in the middle mass range (up to 10 000 Da).^{8–15} Although the accessible mass range of TOF-SIMS is lower than that of matrix-assisted laser desorption and ionization mass spectrometry (MALDI/MS), sample preparation for TOF-SIMS is simpler because no matrix selection is necessary.^{16–24} TOF-SIMS provides distinctive fragmentation patterns which can be used to distinguish different kinds of polymers, while MALDI typically provides molecular weight distributions.

The study of copolymers by TOF-SIMS is not always straightforward. For example, the high mass range TOF-SIMS spectra of polycarbonate and poly(dimethylsiloxane) (PDMS) copolymers are dominated by PDMS peaks.²⁵ Similarly, in block copolymers of poly(vinylpyridine) and poly(butyl methacrylate) (PBMA), PBMA fragments dominated the spectrum even though the polymer contained only 10% PBMA.²⁶ There are two possible reasons why one copolymer component should completely dominate the spectra. One is that ion yields of the copolymer components differ drastically; the other is that surface segregation occurs with one component comprising most of the surface layer. Thus, a study of the relative ion yields of copolymer components is important for the interpretation of copolymer spectra. It is also important to know the relative ion yields of different polymers so that relative peak intensities can be correlated with mole ratios.

The ideal way to measure relative secondary ion yields of polymers would be to study single oligomers of different sizes. However, it is not easy to synthesize single oligomers, especially for noncondensation polymers. In the present research, we investigated the parameters which affect measurement of the relative secondary ion yields of a polymer mixture and propose

a method to study relative ion yields from polymer mixtures. The two polymers studied here are poly(dimethylsiloxane) (PDMS) and polymethylphenylsiloxane (PMPHS). Their backbone structures are similar; both contain silicon–oxygen bonds, and the TOF-SIMS spectra of the homopolymers have been investigated.^{27,28}

Experimental Section

Instrumentation. The spectra of polymers were obtained with a time-of-flight secondary ion mass spectrometer, TOF-SIMS III, manufactured by Ion-ToF GmbH, Münster, Germany. The instrumentation has been described in detail elsewhere.²⁹ During analysis, the targets were bombarded by a pulsed 10 keV Ar⁺ beam with current varying from 0.3 to 0.5 pA and a variable spot diameter between 5 and 50 μm ; secondary ions were extracted at 3 keV into a 2-m flight tube. An Einzel lens and reflectron optics were used for focusing the secondary ion beam and for energy compensation. The secondary ions were post-accelerated by 10 keV and were detected by a channelplate–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/cm², which corresponds to static SIMS. The base pressure in 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) (PDMS) terminated with trimethylsilyl groups was purchased from Gelest Inc. (Pittsburgh, PA). Polymethylphenylsiloxane (PMPHS) with the same end groups was purchased from Polyscience Inc. PDMS and PMPHS were dissolved in toluene at various concentrations. Sample solution volumes of 1 μL were deposited onto silver targets with a substrate area of 20 mm². The silver substrate had been etched in nitric acid (20 vol %) and 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 intensi-

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ties were obtained by integrating the peak areas with a linear background correction.

Results and Discussion

Parameters Affecting Relative Secondary Ion Intensities.

The signal for secondary ions from a specific compound on a given substrate is related to the current observed in the detector of the mass spectrometer (I_s), as shown in eq 1. The parameters affecting the measured ion intensity include primary ion current (I_p), number of moles of the compound in the original sample (C), secondary ion yield of the molecule (S), and detection efficiency (η)

$$I_s = I_p S C \eta \quad (1)$$

For two compounds (A and B) in one sample, the relative ion intensities of A and B can be calculated by eq 2

$$I_A/I_B = [I_p^A/I_p^B][C_A\eta_A/C_B\eta_B][S_A/S_B] \quad (2)$$

where I_A and I_B are the currents for compounds A and B measured by the detector, I_p^A and I_p^B are the primary ion currents for A and B, S_A and S_B are the secondary ion yields of A and B, C_A and C_B are concentrations of A and B, and η_A and η_B are the ion collection efficiencies of A and B.

To correlate the relative intensities (I_A/I_B) observed with the relative secondary ion yields (S_A/S_B), it is necessary to know the ratios of the other parameters (I_p^A/I_p^B , $C_A\eta_A/C_B\eta_B$) which affect the relative ion intensities.

Consider the primary ion current used to bombard the target. The primary ion current depends on the argon pressure, the focus of the primary ion beam, and other instrumental conditions. To keep the number of impinging primary ions exactly the same for two polymers ($I_p^A = I_p^B$), the relative intensities should be calculated from a spectrum for a polymer mixture instead of measuring two polymers independently. Under these circumstances, eq 2 can be simplified to

$$I_A/I_B = [C_A\eta_A/C_B\eta_B][S_A/S_B] \quad (3)$$

We assume here that the detection efficiencies of oligomers for two polymers having similar masses are the same. In other words, the detection efficiency is not affected by polymer structure. Therefore, the relative secondary ion yield can be calculated from the relative intensities of two oligomers having similar masses. As a result, eq 3 is simplified to

$$I_{Ai}/I_{Bi} = [C_{Ai}/C_{Bi}][S_{Ai}/S_{Bi}] \quad (4)$$

Because we will measure intensities of single oligomers with i repeat units for polymers A and B, eq 4 is written in terms of the number of repeat units.

The secondary ion yield is defined as the number of secondary ions formed from a sample, divided by the number of primary ions deposited on the target. If the primary ions impinging on the polymer surfaces are the same (which is true for a polymer mixture) and the detection efficiency does vary with polymer structure, the relative secondary ion yields (S_{Ai}/S_{Bi}) will be related only to the relative ion intensities (I_{Ai}/I_{Bi}) and mole ratio of the two polymers (N_{Ai}/N_{Bi}), as shown in eq 5

$$[S_{Ai}/S_{Bi}] = [I_{Ai}/I_{Bi}]/[N_{Ai}/N_{Bi}] \quad (5)$$

Because each polymer has a molecular weight distribution, the number of moles of a polymer is determined by W/M_n , where

W is the weight of polymer deposited on the substrate and M_n is the number average molecular weight of the polymer. Written in terms of individual oligomers, i , $M_n = \sum M_i N_i / \sum N_i$, and $W = \sum M_i N_i$; thus, $W/M_n = \sum M_i N_i / M_n = \sum N_i$, where M_i is the molecular weight of an oligomer with i repeat units and N_i is the number of moles of a single oligomer, i .

The number of moles of an individual oligomer deposited on the substrate can be calculated from the TOF-SIMS spectrum of the pure polymer. The mole fraction of an individual oligomer in a polymer sample can be calculated by $I_i/\sum I_i$, based on the TOF-SIMS spectrum of the pure polymer. Therefore, the number of moles of a given oligomer (N_i) is given by $N_i = [W/M_n] \cdot [I_i/\sum I_i]$. The mole ratio of oligomers with the same number of repeat units (i) for two different polymers (A,B) can be expressed as

$$N_{Ai}/N_{Bi} = [W_A/W_B][M_{nB}/M_{nA}][I_{Ai}/\sum I_{Ai}][\sum I_{Bi}/I_{Bi}] \quad (6)$$

Fragmentation Factors. Investigation of homopolymers by TOF-SIMS shows that almost all polymers fragment during the SIMS process. The extent of fragmentation varies with factors such as polymer structure, molecular weight, and end groups. To accommodate the effect of fragmentation on the ion intensity of a single oligomer, the relative intensity should be calculated based on the intensity of the whole pattern, which includes the intact oligomer and all fragments formed from that oligomer. If only the intact oligomer intensity is used in the calculation, the intensity of an oligomer which tends to fragment will be much lower than that of an oligomer which shows little fragmentation. Assuming that PDMS and PMPhS do not interact with each other during the SIMS process, the extent of fragmentation observed for each homopolymer will be the extent of fragmentation for that polymer in the mixture. Equation 7 can be used to calculate the degree of fragmentation (F) of an oligomer from the TOF-SIMS spectrum of the pure polymer

$$F_i = \sum I_{if}/(I_{io} + \sum I_{if}) \quad (7)$$

$$I_i = (I_{io} + \sum I_{if}) \quad (8)$$

The intensity of an intact oligomer having i repeat units will be I_{io} , and the intensity of a fragment formed from it will be I_{if} . Equation 7 is simply the sum of the fragment ions for the i th oligomer divided by its total intensity. The total intensity for any given oligomer will be given by eq 8. If eq 7 is rearranged and substituted into eq 8, the intensities of the sum of intact oligomers having i repeat units and fragments formed from that oligomer (I_i) can be calculated from the intensities in the spectra of polymer mixtures based on eq 9

$$I_i = I_{io}/1 - F \quad (9)$$

If the sum of the intact oligomer and fragments formed from that oligomer (I_i) is used for calculation of the relative intensities of the two polymers, the effect of fragmentation on the intensities of oligomers with a given number of repeat units can be accounted for.

Investigation of Relative Secondary Ion Yields of PDMS and PMPhS

Interaction between PDMS and PMPhS in Mixtures. To calculate the relative intensities of individual polymers in a mixture, one must make the assumption that the two polymers

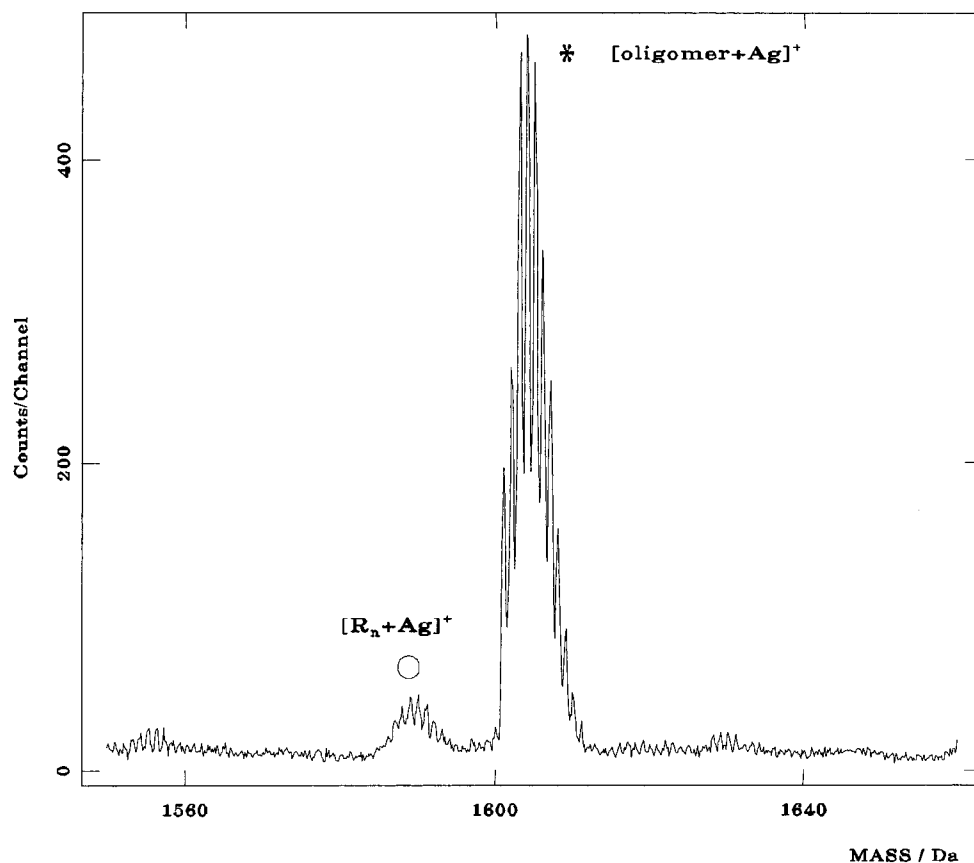


Figure 1. TOF-SIMS spectrum of PDMS in the mass range 1550–1660 Da: (*) [oligomer + Ag]⁺, (○) [oligomer-14 + Ag]⁺.

do not interact with each other during the SIMS measurement. Comparison between the spectra of pure PDMS and pure PMPhS and the spectra of mixtures indicates that this is a valid assumption. Figures 1 and 2 show individual repeat patterns in the TOF-SIMS spectra of PDMS and PMPhS, respectively. Two series of peaks are observed in the spectrum of PDMS, corresponding to a silver cationized oligomer and a silver cationized cyclic fragment (R_n). In the spectrum of PMPhS, three peaks are observed: [oligomer + Ag]⁺, [oligomer-14 + Ag]⁺, and [oligomer-124 + Ag]⁺. The latter two peaks result from chain cleavage following internal phenyl group transfer involving adjacent repeat units.²⁸ Figure 3 shows the spectrum in the same region of a mixture of PDMS and PMPhS, in a weight ratio of 1:5. The two series of peaks for PDMS and the three series for PMPhS are all observed in the spectrum. No other series of peaks is found in the spectrum of the mixture. The intensities of the fragment peaks, relative to those of the oligomer peaks, are the same in the mixture spectra as in the spectra of the pure polymers. These results indicate that PDMS and PMPhS do not interact to modify fragmentation during the SIMS process and do not produce ions which are not observed in the homopolymer spectra.

Another possible interaction between PDMS and PMPhS in mixtures is surface segregation. The surface tensions of PDMS and PMPhS at 20 °C are 20 and 26 dyn/cm, respectively.³⁰ If surface segregation occurs, the surface should be enriched in PDMS, since it has the lower surface tension. It is likely that surface segregation will be more serious at high loadings than at low loadings since it is more likely that PDMS and PMPhS will form mixed phases at high loadings. Therefore, if surface segregation is occurring, the relative intensities of the PMPhS peaks should decrease with increasing loading because the surface should become enriched by PDMS.

Mixtures of PDMS and PMPhS having a weight ratio of 1:2 were deposited on substrates at different total loadings. Figure 4 shows the variation of relative intensities for PMPhS and PDMS as a function of total polymer loading. When the total amounts of polymer on the substrate are in the range of 0.5–2 μg, the $I_{\text{PMPhS}}/I_{\text{PDMS}}$ ratio does not vary significantly. Similar plots were observed for several pairs of peaks in the mass range of 1200–1700 Da. When the total loading was decreased to 0.2 μg, the $I_{\text{PMPhS}}/I_{\text{PDMS}}$ ratio decreased to about $1/3$ the value of that measured for the higher loading samples. When the loading amount was decreased to 0.02 μg, some areas of the target gave spectra only from PDMS, and other areas on the same target gave only spectra from PMPhS. The observation of individual PDMS and PMPhS spectra from different spots on the same target indicates formation of separate islands of PDMS and PMPhS when the loading is very low, islands that are distant from each other. This is consistent with the report that other polymers form separate islands in thin films prepared from solutions containing both polymers.³¹ The observation that the $I_{\text{PMPhS}}/I_{\text{PDMS}}$ ratio increases with increasing loading and becomes constant indicates that surface segregation is not a major effect for mixtures of PDMS and PMPhS, within the loading range measured. Were surface segregation occurring, the PMPhS/PDMS intensity ratio should decrease with increasing loading.

Fragmentation Factors for PDMS and PMPhS. Fragmentation factors were measured for PDMS and PMPhS having different numbers of repeat units. No significant difference in F was observed for PDMS as a function of the number of repeat units, as seen in Figure 5. Although the least-squares line in Figure 5a has a slight positive slope, a slope of zero falls within the 95% confidence limit. For PMPhS, however, fragmentation increases with increasing number of repeat units, as shown in

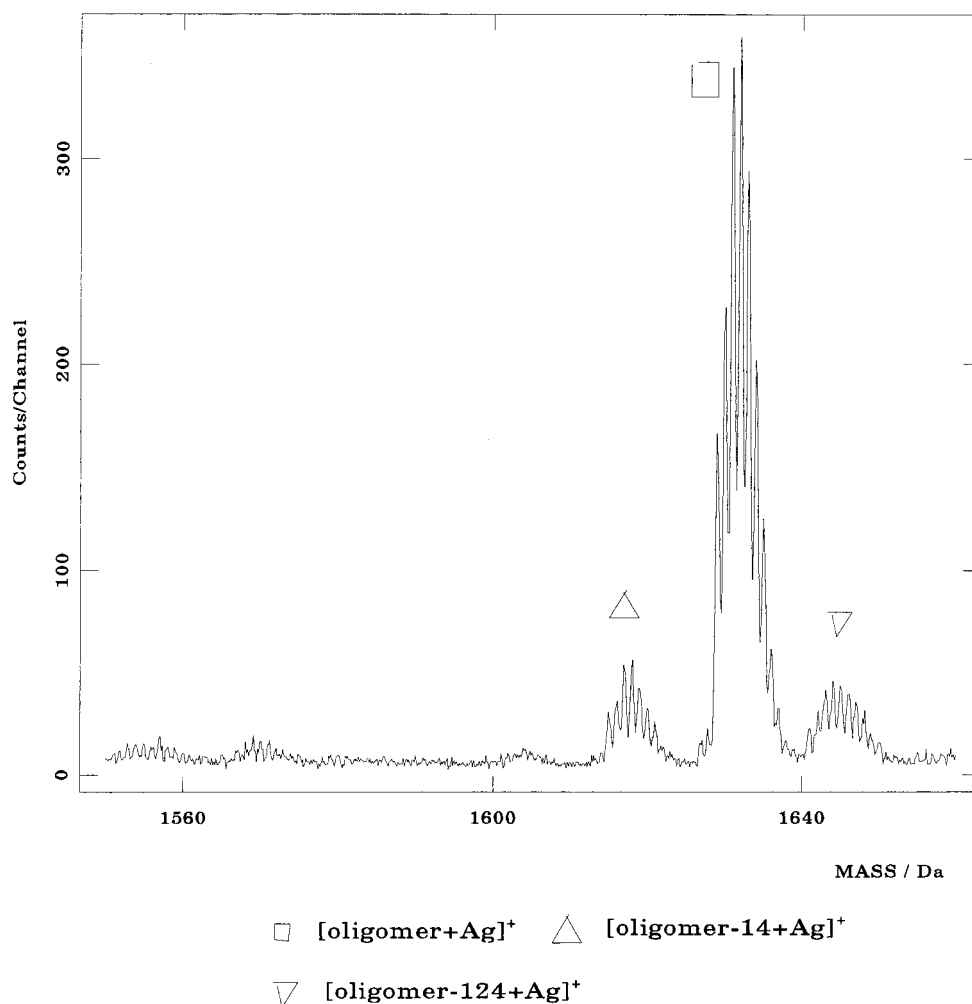


Figure 2. TOF-SIMS spectrum of PMPHS in the mass range 1550–1660 Da: (□) [oligomer + Ag]⁺, (Δ) [oligomer-14 + Ag]⁺ – [oligomer-124 + Ag]⁺.

Figure 5b. The different behavior of F for PDMS and PMPHS is most likely related to structural differences between PDMS and PMPHS, primarily because the main chain of PMPHS is more rigid than that of PDMS. The flexible backbone of PDMS makes it more likely to form a coiled structure, while PMPHS tends to stay as a linear structure.^{27,28} Therefore, the cross-sectional area of a coiled PDMS oligomer will change only slowly with increasing numbers of repeat units. However, the cross-sectional area of a linear PMPHS oligomer will probably increase more than that of PDMS when the number of repeat units increases. The effects of polymer configuration on a metal surface on the sputtering and ionization processes have been discussed previously.³² If the cross-sectional area of the polymer does not vary much compared to the action area of the primary ion, which is most likely the case of PDMS, the extent of fragmentation will change only slowly with increasing molecular weight. On the other hand, fragmentation will increase significantly if the cross-sectional area of the polymer increases compared with the action area. As a result, the fragmentation of PMPHS increases with increasing main chain length, while the fragment factor of PDMS remains essentially constant with increasing number of repeat units.

Investigation of Mole Ratios of PDMS and PMPHS

Another parameter necessary to calculate secondary ion yields is the mole ratio of the two polymers. The mole ratios of

individual oligomers with a given number of repeat units (i) were calculated using eq 6. Two polymer mixtures were investigated in which the ratios of $W_{\text{PDMS}}/W_{\text{PMPHS}}$ were 1:2 and 1:5. The number average molecular weights of PDMS and PMPHS determined by NMR were 1900 and 2100, respectively. Thus, the mole ratios of PDMS to PMPHS in mixtures with 1:2 and 1:5 weight ratios are 0.55 and 0.22, respectively.

Calculation of Relative Secondary Ion Yields

Mixtures of PDMS and PMPHS having different mole ratios were used to measure the relative secondary ion yields of PDMS and PMPHS oligomers. According to eq 5, the relative secondary ion yields can be calculated from relative intensities and the relative mole ratios of individual oligomers with a given number of repeat units (i). This is shown as eq 11. The individual terms in eq 11 are calculated as shown:

$$S_{\text{PDMSi}}/S_{\text{PMPHSi}} = [I_{\text{PDMSi}}/I_{\text{PMPHSi}}]/[N_{\text{PDMSi}}/N_{\text{PMPHSi}}] \quad (11)$$

$$I_{\text{PDMSi}} = I_{\text{PDMSi}}^{\text{oligomer}}/(1 - F_{\text{PDMSi}})$$

$$I_{\text{PMPHSi}} = I_{\text{PMPHSi}}^{\text{oligomer}}/(1 - F_{\text{PMPHSi}}) \quad (11a)$$

$$N_{\text{PDMSi}} = [W_{\text{PDMS}}/M_{\text{nPDMS}}]I_{\text{PDMSi}}^{\circ}/\sum I_{\text{PDMSi}}^{\circ} \quad (11b)$$

$$N_{\text{PMPHSi}} = [W_{\text{PMPHS}}/M_{\text{nPMPHS}}]I_{\text{PMPHSi}}^{\circ}/\sum I_{\text{PMPHSi}}^{\circ} \quad (11c)$$

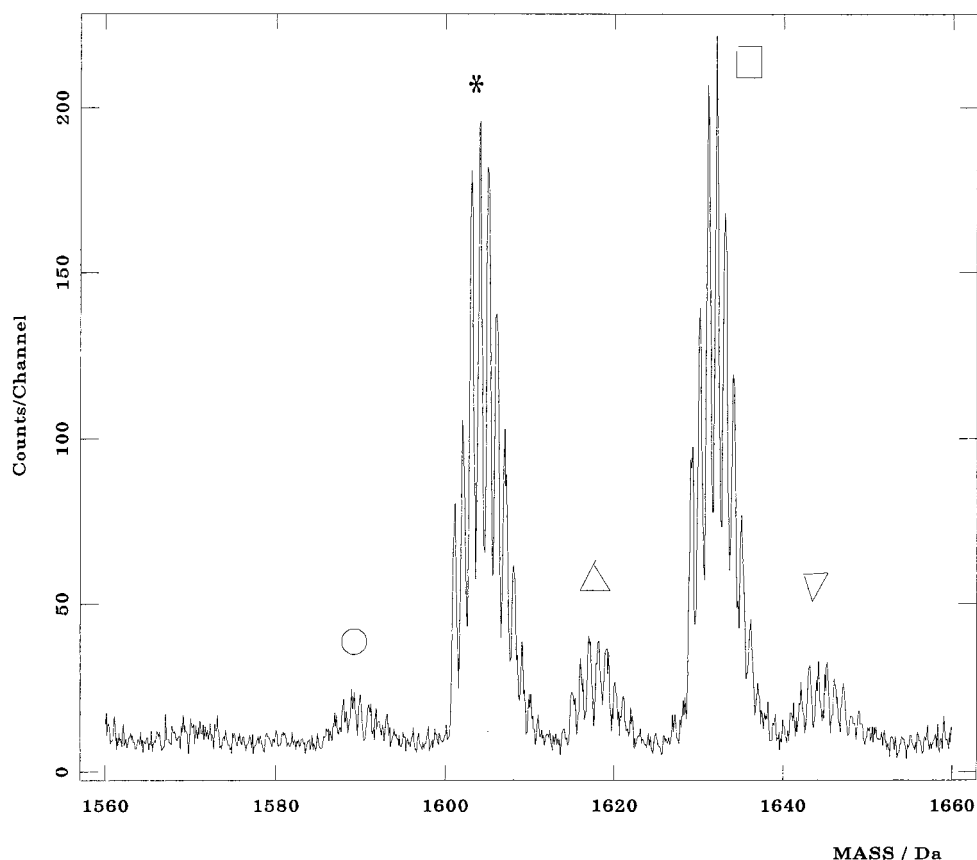


Figure 3. TOF-SIMS spectra of a mixture of PDMS and PMPHS with weight ratio 1:5 in the mass range 1550–1660 Da.

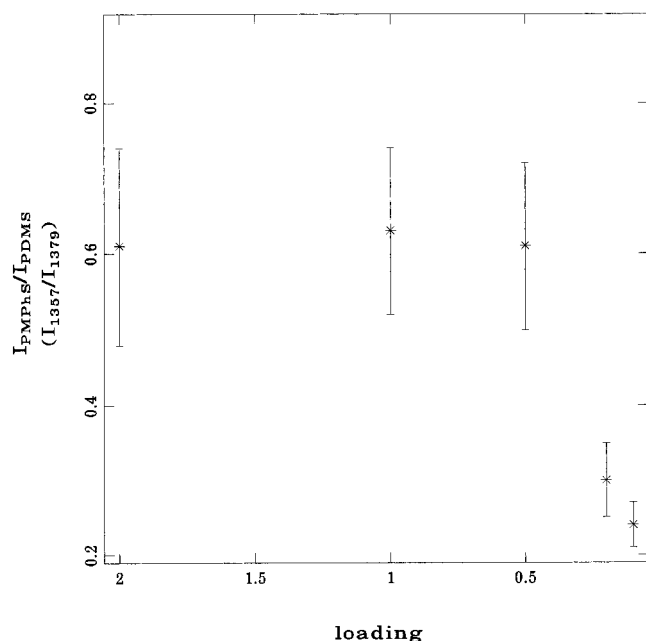


Figure 4. Variations of intensities of PMPHS relative to PDMS with total loading.

in which I_i refers to intensities obtained from the mixture spectra and I_i^0 to intensities obtained from the spectra of homopolymers.

The relative secondary ion yields of three pairs of peaks (1357, 1493, and 1629 Da for PMPHS and 1379, 1453, and 1600 Da for PDMS) were investigated because both PDMS and PMPHS oligomer peaks have high intensities in this mass range.

The numbers of repeat units of PDMS oligomers (16, 17, and 19) are different from those of PMPHS (8, 9, and 10) because the sensitivity of the TOF-SIMS detector is mass dependent; oligomers of PDMS and PMPHS having similar masses should be investigated rather than oligomers having the same number of repeat units. Peak intensities of the oligomers were converted to intensities of the whole fragmentation pattern by eq 9, using fragmentation factors (F) calculated by eq 7 from the spectra of the homopolymers. The number of moles of the individual oligomers in the homopolymer were calculated by eq 6, in which $I_i^0/\sum I_i^0$ was calculated from the homopolymer spectra. The values of F_i and $I_i^0/\sum I_i^0$ are shown in Table 1. The fragmentation factors of PMPHS are around 0.2, twice large as those for PDMS.

Five spectra were examined for each of the two polymer mixtures having weight ratios $W_{\text{PDMS}}/W_{\text{PMPHS}} = 1:2$ and $1:5$. The absolute peak intensities of the individual oligomers of PDMS and PMPHS recorded in these experiments are shown in Table 2. The relative secondary ion yields (RSY) calculated using the data in Tables 1 and 2 are shown in Table 3. The relative secondary ion yields calculated for the three pairs of peaks agree with each other reasonably well, averaging 0.26 for $W_{\text{PDMS}}/W_{\text{PMPHS}} = 1:5$ and 0.35 for $W_{\text{PDMS}}/W_{\text{PMPHS}} = 1:2$. The relative standard deviations were 14% and 15%, respectively. It should be noted that the ratios obtained from the mixtures in which $W_{\text{PDMS}}/W_{\text{PMPHS}} = 1:2$ appear to be higher than those obtained from the mixtures in which $W_{\text{PDMS}}/W_{\text{PMPHS}} = 1:5$. If one examines the results in Table 3 statistically, there is no statistical difference between the 1:2 and 1:5 mixtures for any given subset of single ion peaks (e.g., 1357/1379) at the 95% confidence limit. However, if one compares the 1:2 and 1:5 data sets in their entirety, the difference between them (\bar{x}

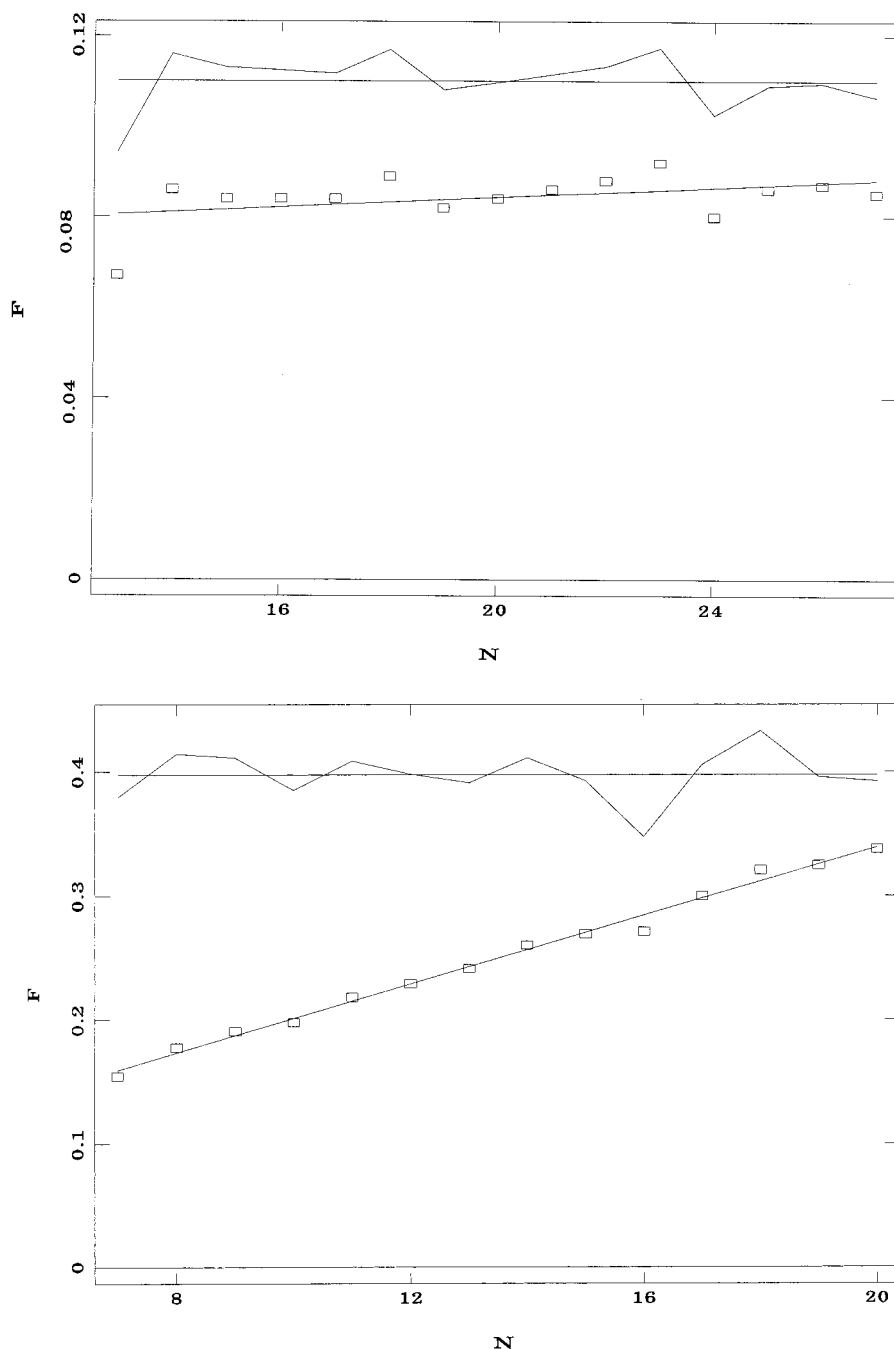


Figure 5. Variations in fragmentation of polymers with repeat unit number: (a) PDMS, (b) PMPHS.

TABLE 1: Fragmentation Factors and Mole Fractions of Specific Oligomers

	PDMS			PMPHS		
	1379	1453	1601	1357	1493	1629
F	0.08	0.08	0.09	0.19	0.20	0.22
$1 - F$	0.92	0.92	0.91	0.81	0.80	0.78
$I_i^0/\sum I_i^0$	0.1	0.09	0.07	0.13	0.10	0.08

= 0.35 and 0.28) is significant at the 95% confidence level due to the larger number of degrees of freedom. Thus, one must conclude that the difference is real, although the reason for this difference is not readily apparent.

Polymer Transformation Probabilities

The transformation probability in SIMS, $P(M-X)$, is defined as the probability that a molecule, M , sputtered from a surface

is emitted as a certain secondary ion species, X .³³ $P(M-X)$ can be calculated from TOF-SIMS spectra on the basis of the following equation:

$$P(M-X) = N_d(X)/N(M)T(X)\eta \quad (12)$$

where $N_d(X)$ is the total number of detectable molecular ions in TOF-SIMS spectra, $N(M)$ is the number of analyte molecules in the analyzed area, $T(X)$ is the transmission of the instrument (assumed to be 0.1), and η is the detection efficiency (assumed to be 1).

The ratio of transformation probabilities of PMPHS and PDMS calculated from the TOF-SIMS spectra of the homopolymers will be compared with the relative secondary ion yields of the same polymers obtained from spectra of mixtures. As discussed above, the number of moles of an individual oligomer with i repeat units can be calculated by $N_i(M) = [W/M_n]$ -

TABLE 2: Intensities of Specific Oligomers Obtained from the Spectra of Mixtures

	$I_{1357}^{\text{oligomer}}$	$I_{1379}^{\text{oligomer}}$	$I_{1493}^{\text{oligomer}}$	$I_{1453}^{\text{oligomer}}$	$I_{1629}^{\text{oligomer}}$	
	$I_{1601}^{\text{oligomer}} W_{\text{PMPHS}}/W_{\text{PDMS}} = 1:2$					
spectrum 1	19945	30000	16155	27660	14039	22722
spectrum 2	74960	96507	58716	89678	44797	71102
spectrum 3	40755	48800	33199	42930	25794	33365
spectrum 4	830	1358	640	1230	520	1064
spectrum 5	1924	2566	1410	2632	1155	2269
	$W_{\text{PMPHS}}/W_{\text{PDMS}} = 1:5$					
spectrum 1	31893	26105	24401	23980	18249	18190
spectrum 2	34618	25084	27156	22342	19755	17883
spectrum 3	81406	61294	64959	57658	52314	47136
spectrum 4	38110	21568	29800	20105	23937	17370
spectrum 5	22480	13032	16787	11768	12181	9874

TABLE 3: Relative Secondary Ion Yields Calculated for the PMPHS:PDMS Mixture^a

	S_{1357}/S_{1379}	S_{1493}/S_{1453}	S_{1629}/S_{1600}
	$W_{\text{PDMS}}/W_{\text{PMPHS}} = 1:2$		
RSY #1	0.32	0.33	0.35
RSY #2	0.38	0.37	0.36
RSY #3	0.40	0.44	0.43
RSY #4	0.30	0.30	0.28
RSY #5	0.36	0.31	0.29
average RSY	0.35 ± 0.04	0.35 ± 0.06	0.34 ± 0.06
RSD	11.8%	16.3%	17.7%
	$W_{\text{PDMS}}/W_{\text{PMPHS}} = 1:5$		
RSY #1	0.24	0.23	0.23
RSY #2	0.27	0.28	0.25
RSY #3	0.26	0.26	0.25
RSY #4	0.34	0.34	0.31
RSY #5	0.33	0.33	0.28
average RSY	0.29 ± 0.04	0.29 ± 0.05	0.26 ± 0.03
RSD	15.4%	16.2%	11.9%

^a Peaks at 1357, 1493, and 1629 are for PMPHS, and those at 1379, 1453, and 1600 are for PDMS.

$[I_i^0/\sum I_i^0]6.02 \times 10^{23}$. Also, $N_{\text{di}}(\text{X}) = N_{\text{d}}^{\text{oligomer}}(\text{X})/(1 - F_i)$, where $N_{\text{di}}(\text{X})$ is the total number of ions formed from oligomers with i repeat units and $N_{\text{d}}^{\text{oligomer}}(\text{X})$ is the total number of detectable intact oligomers with i repeat units. $N_i(\text{M})$ calculated by the above equation is the number of oligomers with i repeat units deposited on the Ag substrate, covering an area of 20 mm². The primary ion beam diameter used for bombardment is approximately 20 μm , so the number of analyte molecules in the analyzed area will be $N(\text{M})_i = [W/M_n][I_i/\sum I_i](6.02 \times 10^{23})/[4\pi r^2/3]/20 \text{ mm}^2$, where r is the radius of the primary ion beam (10 μm).

Six individual spectra of PDMS and PMPHS homopolymers were examined. The loadings of PDMS and PMPHS on the Ag foils were 0.33 μg for PDMS and 0.67 μg for PMPHS, respectively, the same loadings that were used for analysis of the mixtures. The absolute intensities of the specific oligomers measured from the pure polymer spectra are given in Table 4. The variation in absolute intensities is comparable to that reported in Table 2. The large standard deviations of the absolute intensities are due to differences in the substrates used and variations in instrument conditions. This is readily apparent by examining the individual values for a given peak (e.g. 1379).

The transformation probabilities for PMPHS and PDMS calculated for three pairs of peaks (1357/1379; 1493/1453; 1629/1601) are listed in Table 5. Their ratios vary from 0.54 to 0.59. The ratios of transformation probabilities obtained from the homopolymers are comparable to the relative secondary ion yields obtained from the mixtures with the same weight ratios, although the ratios of transformation probabilities are somewhat

TABLE 4: Peak Intensities Obtained from Homopolymer Spectra

	I_{1379}	I_{1453}	I_{1601}
	PDMS 0.33 μg Loading		
spectrum 1	222315	195445	142046
spectrum 2	123967	111866	82427
spectrum 3	182958	163415	119904
spectrum 4	277194	239667	173108
spectrum 5	216121	190786	123083
spectrum 6	144464	125135	90660
average	194503 ± 56020	171052 ± 47670	121871 ± 33660
RSD	29%	28%	27%
	PMPHS 0.67 μg Loading		
spectrum 1	246452	165051	119020
spectrum 2	369638	277009	197966
spectrum 3	118396	86029	53814
spectrum 4	268100	200745	140199
spectrum 5	270060	197111	141319
spectrum 6	118840	86304	61483
average	231914 ± 97586	167708 ± 74992	118969 ± 54297
RSD	42%	45%	45%

TABLE 5: Comparison between $P(\text{M-X})_{\text{PMPHS}}/P(\text{M-x})_{\text{PDMS}}$ and $S_{\text{PMPHS}}/S_{\text{PDMS}}$

	1379	1453	1601
PDMS	1379	1453	1601
$P(\text{M-X})$	9.5×10^{-5}	9.1×10^{-5}	8.7×10^{-5}
PMPHS	1357	1493	1629
$P(\text{M-X})$	5.6×10^{-5}	5.3×10^{-5}	4.7×10^{-5}
PMPHS/PDMS	1357/1379	1493/1453	1629/1601
$P(\text{M})_{\text{PMPHS}}/P(\text{M-X})_{\text{PDMS}}$	0.59 ± 0.3	0.58 ± 0.3	0.54 ± 0.3
$S_{\text{PMPHS}}/S_{\text{PDMS}}$	0.35 ± 0.04	0.35 ± 0.06	0.34 ± 0.06

higher. The high variance in the original data set (Table 4) precludes any meaningful statistical evaluation of the two results; formally a t-test shows that there is no difference between ratios calculated for transformation probabilities and those measured in mixture at the 95% confidence level. Thus, the results show that it is acceptable to use the relative secondary ion yields obtained from mixtures to indicate the behavior of polymers in SIMS.

The results obtained for the relative secondary ion yields of PMPHS and PDMS show that ion yields of PDMS are about 2–3 times those of PMPHS. These differences are most likely due to structural differences between the two polymers since instrument conditions were the same when the relative secondary ion yields were measured for polymer mixtures. It has been shown that pendent groups significantly influence fragmentation²⁸ in siloxane polymers. Calculations using transformation probabilities for the homopolymers of PDMS and PMPHS show results similar to the relative secondary ion yields obtained from the mixture. The ratios of transformation probabilities of PMPHS/PDMS are comparable to their relative secondary ion yields. These results also indicate that the functional groups on the siloxane main chain have effects on ion yields of polymers.

The transformation probabilities of PDMS also can be compared with the value measured for polystyrene (PS),³³ which has a value of 3×10^{-4} . This result helps to interpret the spectra of PS–PDMS block copolymers. It has been found that TOF-SIMS spectra of PS–PDMS block copolymers were dominated by PDMS.³⁴ Since the transformation probability of PS is three times that of PDMS, the domination of PDMS in spectra of PS–PDMS copolymers must be due to surface segregation rather than ion yield differences. This explanation is also consistent with the large difference in surface tensions between PDMS and PS, which are 20 and 40 dyn/cm², respectively.³⁰ PDMS is expected to be enriched on the surface of a PDMS–PS block copolymer, since its surface tension is much lower than that of PS. This shows that the evaluation of relative

secondary ion yields and the transformation probabilities of two polymers are valuable for the investigation of surface segregation in copolymers.

Conclusions

A method to determine the relative secondary ion yields of two polymers by examining polymer mixtures has been developed. The parameters which affect relative secondary ion yields, including primary ion current, detection efficiency, mole number of individual oligomers with a certain chain length, and the extent of fragmentation, have been investigated. Mixtures of PDMS and PMPhS having different weight ratios were examined. The secondary ion yields of PDMS are about 2–3 times those of PMPhS. The relative secondary ion yields obtained from PMPhS/PDMS mixtures and the ratio of transformation probabilities of the two polymers calculated from pure polymer spectra are comparable. The results indicate that the pendent groups on the siloxane main chain have a significant effect on ion yields of the polymers.

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