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End-Functionalized Polymers. 2. Quantification of Functionalization by Time-of-Flight Secondary Ion Mass Spectrometry

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ABSTRACT: The applicability of time-of-flight secondary ion mass spectrometry (TOF-SIMS) for quantification of functionalization is demonstrated using five 1.0×10^3 g/mol polystyrene samples which were synthesized by living anionic polymerization. The polymerizations were functionally terminated to various extents (0, 25, 50, 75, and 100%) by using sequential termination techniques with chlorodimethylphenylsilane and methanol. Two distinct molecular weight distributions of intact oligomer signals are resolved in the TOF-SIMS spectra resulting from the functionalized and unfunctionalized (protonated) oligomer species in each sample. Through direct comparison of the signal intensities of the two types of oligomers, the extent of functionalization is determined at each degree of polymerization and agrees well with expected values. The results are substantiated using physical mixtures of dimethylphenylsilyl (100% functionalized) and proton (0% functionalized) terminated polymers. The relative oligomer intensities for the physical mixture of polymers corresponds well to the ratio in which they were initially combined. Sputter yield, extent of fragmentation, and ionization and detection probabilities are determined to be very similar for the proton- and dimethylphenylsilyl-functionalized oligomers. Thus, quantification of endgroups can be achieved without standards calibration. Analysis by gel permeation chromatography (GPC) shows a systematic shift to higher $\langle M_n \rangle$ values as the extent of functionalization of the polystyrene samples is increased from 0 to 100%. $\langle M_n \rangle$ values calculated from TOF-SIMS analysis for the oligomers agree well with GPC results. The $\langle M_n \rangle$ values for the functionalized and unfunctionalized components in each sample can also be determined by TOF-SIMS and are distinct for each oligomer type.

Introduction

The endgroups of polymer chains often play a significant role in determining the processing and performance capabilities of a polymer. Termination of polymer chains with functional species can allow copolymerization of the product with other monomers to form block, segmented, or graft copolymers. Polymer endgroups can also influence the orientation (e.g., surface segregation) of polymer chains and ultimately define their technological applicability. Thus, quantitative characterization of the functionalization of polymer chain ends is crucial in relating structure to desired properties.

Traditional methods of endgroup characterization allow only indirect quantification of the extent of functionalization. Nuclear magnetic resonance (NMR), ultraviolet–visible (UV–vis), and infrared (IR) spectroscopies, elemental analysis techniques, and titration methods can distinguish the presence of specific chemical species in the endgroup. If the molecular weight of the polymer is known, the percent of chains terminated can be approximated by ratioing the endgroup signal to the repeating unit signal.

Herein, we employ time-of-flight secondary ion mass spectrometry (TOF-SIMS) for polymer characterization, including direct quantification of functionalization. SIMS is a microanalytical technique based on the energetic ion beam bombardment of solid samples resulting in vaporization and ionization of surface species. Through TOF analysis, quasi-simultaneous detection of the secondary ions, a high transmission, and a theoretically unlimited mass range can be obtained. The capability of TOF-SIMS for molecular weight determination and structural and chemical characterization of polymers has been demonstrated elsewhere.[1–3] The technique allows identification of mass-resolved polymer chains, including intact oligomers within a molecular weight distribution. As a result, signals for functionalized and unfunctionalized chains arise at distinct masses.

To demonstrate the utility of TOF-SIMS for endgroup quantification, five samples of functionalized polystyrene were synthesized having 0, 25, 50, 75, and 100% of the chains terminated with the dimethylphenylsilyl endgroup. The other portions of the chains in each sample were terminated with a proton. The extent of functionalization was determined from the relative intensities of the signals at each degree of polymerization.

Secondary ion intensities may be influenced by sputter yield, extent of fragmentation, and detection and ionization probabilities of an oligomer. To account for these differences when comparing oligomers with two distinct endgroups, the termination reactions of varying degrees of success have also been modeled using physical mixtures. The combination of 100 and 0% functionalized polystyrene in appropriate proportions yields samples analogous to the 75, 50, and 25% functionalized samples obtained by synthetic means. The results from the physical mixtures can be used to normalize results from the synthetic materials to compensate for any signal anomalies inherent in the TOF-SIMS technique. Quantification by TOF-SIMS also is compared to the results from more conventional methods of analysis.

Experimental Section

Reagents. Cyclohexane (Phillips Petroleum) was stirred over concentrated sulfuric acid for ca. 2 weeks, decanted, and distilled under argon from sodium metal. Tetrahydrofuran (Fisher, Certified Grade) was distilled under argon from the purple

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sodium/benzophenone ketyl. Styrene (Fisher, Certified Grade) was vacuum distilled from dibutylmagnesium (FMC Lithium Division) following three freeze–thaw cycles. Methanol (Baxter, S/P) was deoxygenated with argon. Chlorodimethylphenylsilane (Aldrich) was used as received. The initiator, *sec*-butyllithium (FMC Lithium Division), was used as received, and the molar concentration was determined by the Gilman double-titration method.[4] The anionic polymerization was conducted in an oven-dried, flamed, one-neck, 1000-mL, round-bottomed flask equipped with a magnetic stir bar and rubber septum under a 6–8 psig argon atmosphere.

Synthesis of Polystyrene–$Si(CH_3)_2C_6H_5$. The "parent" polystyrene was synthesized with a target number-average molar mass, $\langle M_n \rangle$, of 1K g/mol. The synthesis of the 1K g/mol sample was conducted as follows. The flask was charged with 55.0 mL (50.0 g) of styrene in 500 mL of dry cyclohexane. The polymerization was initiated by the addition of 31.5 mL of a 1.59 M solution of *sec*-butyllithium in cyclohexane. The resulting orange-red solution was allowed to stir in a cool water bath in order to dissipate the heat of the resulting polymerization exotherm. After 2 h, ca. 10 mL of dry tetrahydrofuran was added to the solution. Four one-neck, 500-mL, round-bottomed flasks were prepared in the same manner as described above and additionally rinsed with 2 mL of *sec*-butyllithium in order to neutralize any protic impurities. The living polystyryl carbanion solution was transferred to the respective flasks via cannula. The termination volumes of methanol and chlorodimethylphenylsilane were calculated based on the mass of polystyryl carbanion (calculated from solution w/w concentration) in each flask. The polymerization was terminated to the desired percentage with the addition of the calculated amount of methanol followed by 10 min of stirring. The calculated amount of chlorodimethylphenylsilane was then added to each flask to terminate the remaining polystyryl carbanion. Methanol was added to the parent polymer solution for the 0% Si sample. The solutions were allowed to stir for ca. 1 h. During this time, the solutions which had been terminated with the chlorosilane became cloudy due to the precipitation of lithium chloride. The polymers were isolated by simple rotary evaporation, redissolved in dichloromethane, and washed with water. The dichloromethane solution was then rotary evaporated to dryness. All of the polymers were dried under reduced pressure at 40 °C for 12 h.

Instrumentation and Methods. A Waters 150-CV gel permeation chromatograph with Ultrastyragel columns of 100-, 500-, 10^3-, 10^4-, and 10^5-Å porosities in tetrahydrofuran was used with polystyrene standards (Showa Denko) for the determination of molar mass and molar mass distribution.

The time-of-flight secondary ion mass spectrometry (TOF-SIMS) spectra were acquired using the TOF-II reflectron instrument developed and located at the University of Münster.[5] Typical instrumental conditions during TOF-II spectrum acquisition were 1.2-pA primary Ar^+ current, 200-s acquisition times, 0.25-mm^2 analysis area, and 10-keV postacceleration. Thus, analysis conditions were maintained within the static regime, with primary ion doses being of approximately 1×10^{12} ions/cm^2. Samples were prepared by depositing 1 μL of polymer solution in chloroform (1 mg/mL) on about 80 mm^2 of an etched silver substrate (monolayer preparation). Typically, silver atoms sputtered from the substrate surface are abducted by oligomers and fragments and aid in cationization and stabilization, thereby enhancing the sensitivity of the technique for these ions. The polymer solutions of the physical mixtures were prepared by combining appropriate portions of the polymers prior to dissolving in chloroform. For example, to model the 75% synthetically functionalized polymer, 3.00 mg of functionalized polystyrene was combined with 1.00 mg of protonated polystyrene and the mixture was dissolved in 4.00 mL of chloroform. Three samples of each of the synthetic and physical mixtures were prepared and analyzed.

Results and Discussion

To model successful and unsuccessful functionalization reactions, five samples of polystyrene were synthesized having 0, 25, 50, 75, and 100% of the chains functionalized with the dimethylphenylsilyl endgroup. Styrene was polymerized in a living manner to a molar mass of 1.0×10^3 g/mol, forming the "parent" polymer solution. The living polymer solution was divided into five separate flasks. The sample in each flask was then stoichiometrically terminated with chlorodimethylphenylsilane and methanol to give the various extents of functionalization (Figure 1).

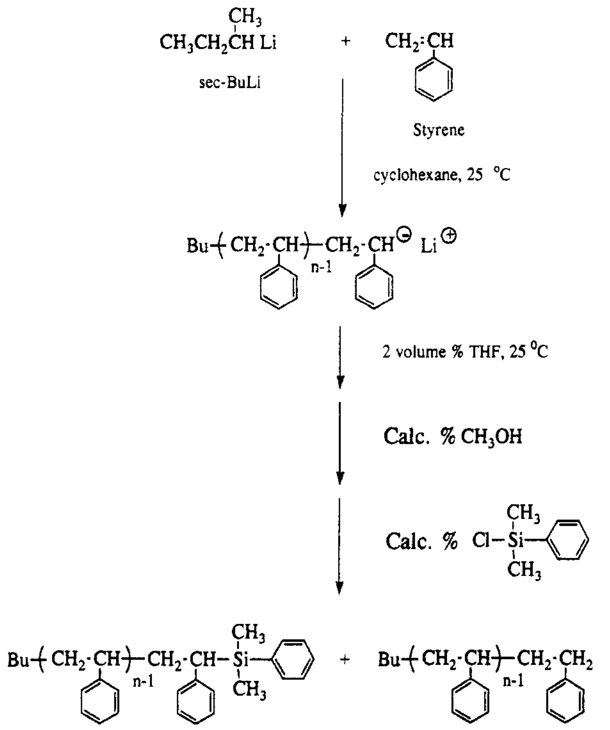

Figure 1. Synthesis scheme for styrene polymerization and stoichiometric functionalization with dimethylphenylsilyl and proton endgroups.

The TOF-SIMS spectra of the five samples of polystyrene are shown in Figure 2. The most intense series of signals (in the mass range 600–2100 Da) in each spectrum results from the desorption of silver-cationized intact oligomer chains with a specific degree of polymerization (n). The ions detected in this series have mass values corresponding to the mass of the *sec*-butyl initiator, n repeating units, the appropriate endgroup, and a silver atom (which aids in the ionization process), indicating that the desorption of oligomers occurred without fragmentation. The mass separation between consecutive oligomers with the same endgroup is equal to the molar mass of the polystyrene repeating unit (104 Da).

In the top spectrum, a single distribution of signals can be seen for the dimethylphenylsilyl functionalized oligomers. The signal intensities in the bottom spectrum, for the proton-terminated oligomers, mirrors that of the top spectrum since both samples originated from the same parent polystyrene. The masses at which the proton-terminated oligomers arise, however, are distinct from those of the functionalized oligomers due to the difference in molar mass of the two endgroups (134 Da). The spectra of the samples without complete functionalization (75, 50, and 25%) contain a combination of the two distributions, one for each type of endgroup.

The high resolution of TOF-SIMS is illustrated by the presence of several isotopic peaks within each signal, for an oligomer at a specific degree of polymerization (Figure 3). Each set of peaks corresponds to the intact polymer chain, with endgroups, and results from a convolution of isotopic contributions from C, Ag, and H. For example, predominant contributors to the five main peaks in Figure

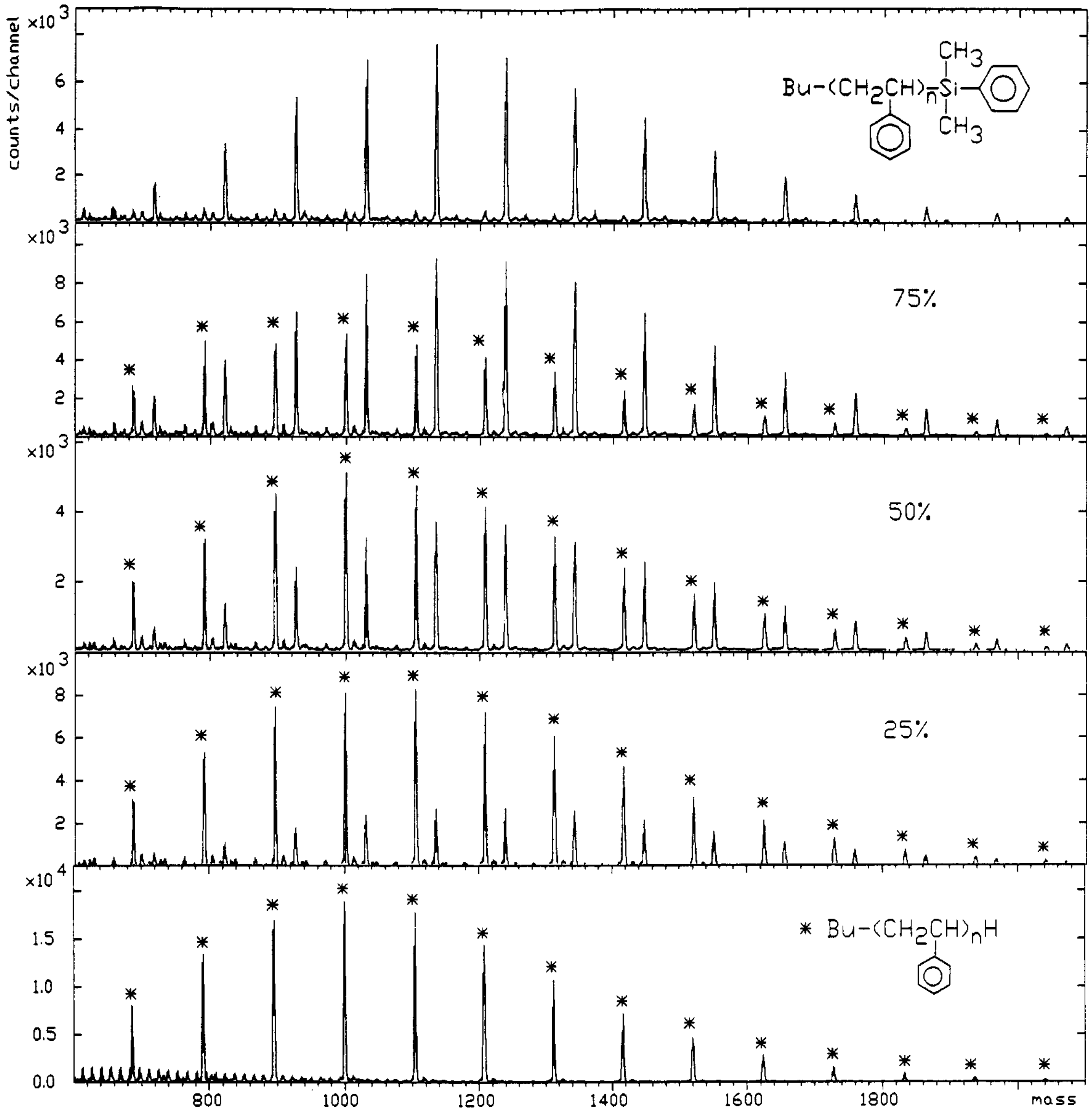

Figure 2. TOF-SIMS spectra of five samples of polystyrene functionalized with a dimethylphenylsilyl endgroup to varying extents: 100, 75, 50, 25, and 0%. Peaks labelled with * represent nonfunctionalized (protonated) intact oligomers.

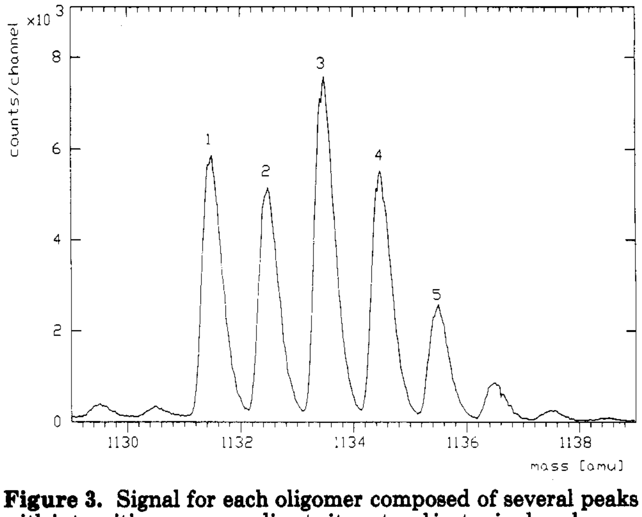

Figure 3. Signal for each oligomer composed of several peaks with intensities corresponding to its natural isotopic abundances.

3 are as follows: A polymer chain with one ^{107}Ag isotope is represented by peak 1, while a polymer with a ^{109}Ag isotope gives rise to peak 3. Contributions from the polymer chain with two ^{13}C isotopes and one ^{107}Ag are also incorporated in peak 3. Peak 2 corresponds to the polymer with one ^{13}C isotope and one ^{107}Ag isotope. Peak 4 corresponds to the polymer with one ^{13}C isotope in the polymer and one ^{109}Ag isotope. Finally, peak 5 corresponds to two ^{13}C isotopes in the polymer and one ^{109}Ag isotope.

Through direct comparison of the relative signal intensities (inclusive of all isotopes) of the functionalized and protonated oligomers, the extent of functionalization can be determined at each degree of polymerization. To quantify percent functionalization, the area of the functionalized oligomer signal, with n repeating units, is ratioed to the sum of intensities for the two oligomer types where both have n repeating units. Figure 4 shows the results for the three synthetic samples functionalized 75, 50, and 25%. The extent of functionalization determined by TOF-SIMS is nearly constant for oligomers having 4–17 repeating units: 0.67 ± 0.03 for the sample synthesized to be 75% functionalized, 0.44 ± 0.02 for the 50% sample, and 0.28 ± 0.04 for the 25% sample. The calculated extent of functionalization for oligomers having four repeating units deviates from the values for the oligomers having a greater number of repeating units. A higher ion yield for these small molecules could cause the peak intensity to be enhanced relative to the other oligomers. In addition, a study of the reproducibility of the distribution of oligomer intensities has demonstrated that the shortest discernible oligomer (n = 4) also has the greatest relative standard

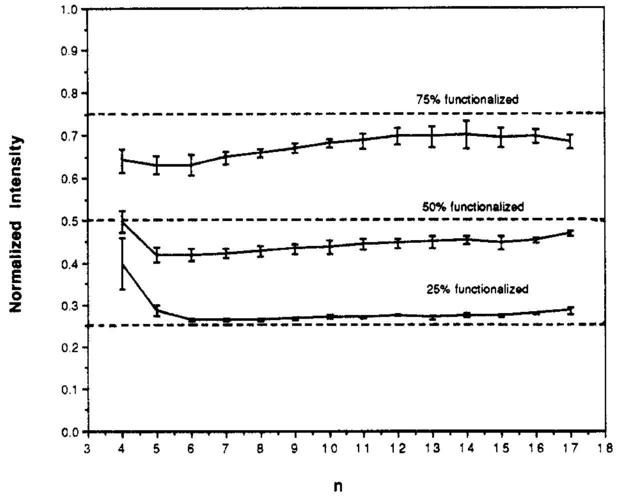

Figure 4. Synthetic model: plot of the intensity of functionalized oligomers as a function of the degree of polymerization.

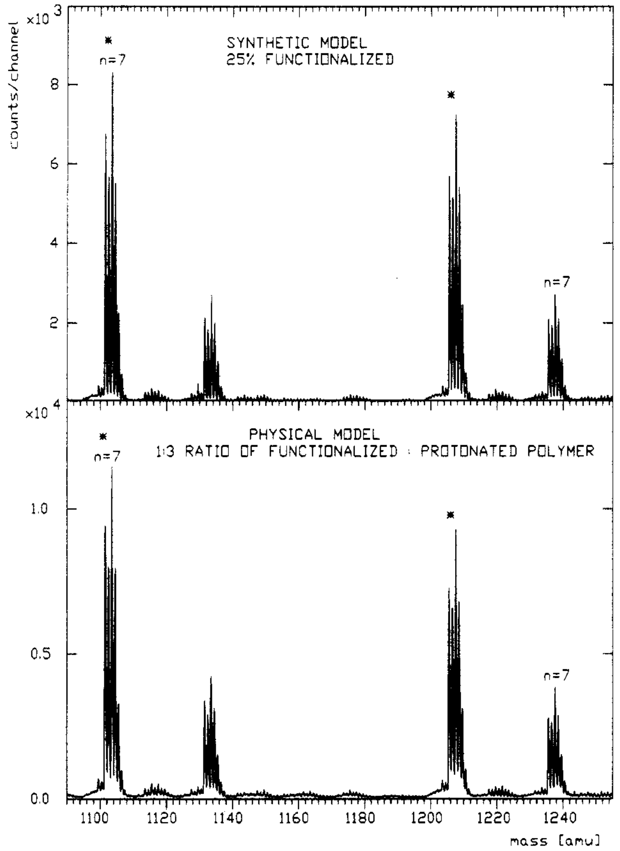

Figure 5. Selected region of oligomer distributions demonstrating that TOF-SIMS data of a physical combination of two polymers (right) are very similar to the results obtained from a synthetic matrix (left). Quantification of functionalization is possible from the relative signal intensities at each degree of polymerization (here $n = 7$).

deviation (15%) compared to all other oligomers having equal or greater signal intensity (3% rsd, for $n = 5$–14). Although no interferences were directly evident, contributions from fragments and other molecules could cause the variance in signal intensities and are more likely at these lower masses.

The determination of the extent of functionalization was substantiated using physical mixtures of dimethylphenylsilyl (100% functionalized) and proton (0% functionalized) terminated polymers. Figure 5 demonstrates the success of the physical combination of two polymers (1:3 ratio) in mimicking a matrix that had been created synthetically (25% functionalized). A selected high-mass region (1090–1230 Da) of the TOF-SIMS spectra illustrates signals for oligomers with $n = 7$, one representing proton-terminated chains (*) and the other dimethylphenylsilyl-terminated chains. With GPC, the physical mixture of two polymers also appears to be identical to the partially functionalized product (Figure 6). Both samples give M_n values of 1060.

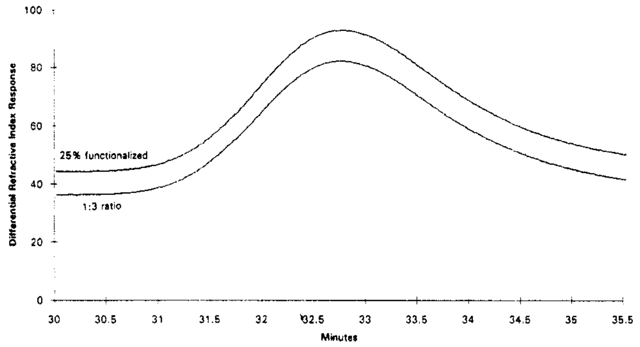

Figure 6. Gel permeation chromatograms curves showing identical molecular weight distributions for the physical and synthetic matrices.

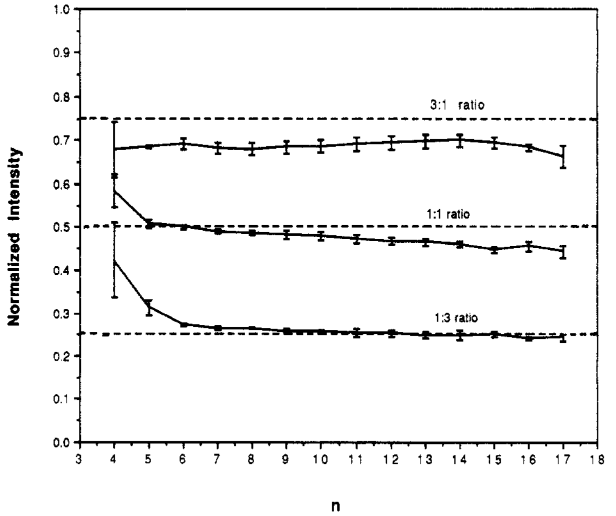

Figure 7. Physical model: plot of the intensity of functionalized oligomers as a function of the degree of polymerization.

Table 1. Average Value of Functionalized Oligomer Intensity as Determined by TOF-SIMS

	physical			synthetic	
	for all n	for n = 5–14		for all n	for n = 5–14
3:1 mix	0.69 ± 0.02	0.69 ± 0.01	75% func	0.67 ± 0.03	0.67 ± 0.03
1:1 mix	0.48 ± 0.04	0.48 ± 0.02	50% func	0.44 ± 0.02	0.44 ± 0.02
1:3 mix	0.27 ± 0.05	0.26 ± 0.02	25% func	0.28 ± 0.04	0.27 ± 0.01

Additional physical mixtures of 1:1 and 3:1 ratios were used to mimic the 50 and 75% synthetically functionalized samples. The peak intensities at each degree of polymerization in the TOF-SIMS spectra of the physical mixtures were compared in an analogous manner as the synthetic samples. The resulting plot of functionalized oligomer intensity vs degree of polymerization (Figure 7) is quite similar to the plot for the synthetic samples: virtually constant value as a function of n, with largest deviation in value at $n = 4$. The average intensity values for all degrees of polymerization as well as for $n = 5$–14 (where rsd $< 3\%$) are listed in Table 1 for both synthetic and physical models. The expected values for the physical mixtures are 0.75, 0.50, and 0.25 which reflect the 3:1, 1:1, and 1:3 combinations of functionalized:unfunctionalized polystyrene, respectively. The TOF-SIMS calculated

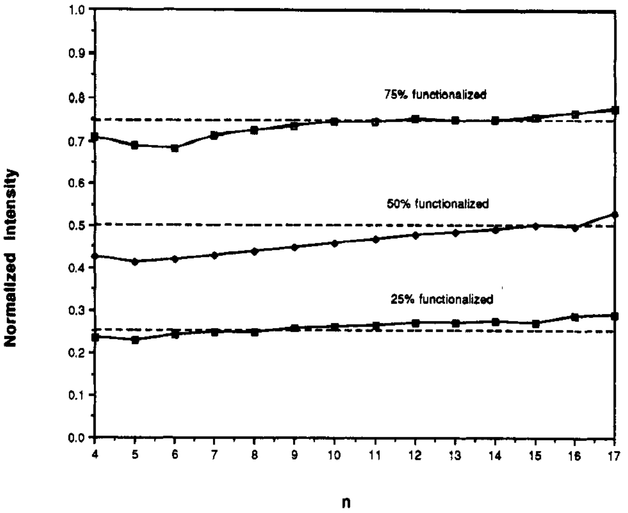

Figure 8. Calibrated signal intensities of functionalized oligomers for the synthetic samples plotted as a function of the degree of functionalization.

values correspond fairly well to the expected values (0.69 ± 0.02 for the 3:1 mixture, 0.48 ± 0.04 for the 1:1, and 0.27 ± 0.05 for the 1:3). These results suggest that for our models, oligomer signal intensity is not substantially influenced by endgroup type. In other words, the combination of sputter yield and ionization and detection probabilities are very similar for the *dimethylphenylsilyl- and proton-terminated oligomers*. Thus, the extent of functionalization can be directly quantified from the ratio of oligomer intensities in the synthetic materials, without the use of calibration standards. Further comparisons with other endgroups are currently being investigated to establish the general applicability of this method for the determination of percent functionalization.

Note in the 3:1 physical mixture the average intensity value (0.69 ± 0.02) is lower than the value that corresponds to the ratio in which they were originally combined (0.75). For the other two physical mixtures, the ratioed value falls within the deviation of the calculated intensity (see Table 1). This trend is similar with the synthetic samples. The composition of the 3:1 mixture and 75% functionalized samples is more enriched in oligomers containing the dimethylphenylsilyl endgroups compared to the other physical mixtures. Perhaps the functionalized oligomers are less likely to desorb from a sample as the quantity of dimethylphenylsilyl endgroups increases in the matrix. This would result in the ratio of functionalized to unfunctionalized oligomers being less than the actual composition of the mixture. To compensate for signal anomalies inherent in the TOF-SIMS technique, the results from the physical mixtures were used to calibrate the results from the synthetic materials. Consequently, the calibrated functionalized oligomer intensity for the synthetic materials is nearly uniform across all *n* (see Figure 8), and the average values agree well with expected values: 0.73 ± 0.03, 0.46 ± 0.04, 0.26 ± 0.02. The largest deviation from expected values occurs when *n* is small and could result from the lower precision in relative signal intensity for the shorter oligomers.

The samples of variably functionalized polystyrene also can be compared through the calculation of their molar mass. Figure 9 shows GPC plots of the synthetic model demonstrating a systematic shift of the molecular weight distributions to higher molar mass values with increasing extent of functionalization. Molecular weight determinations can also be made from the TOF-SIMS spectra by taking into account the intensity of the oligomer signals and the mass at which they arise:

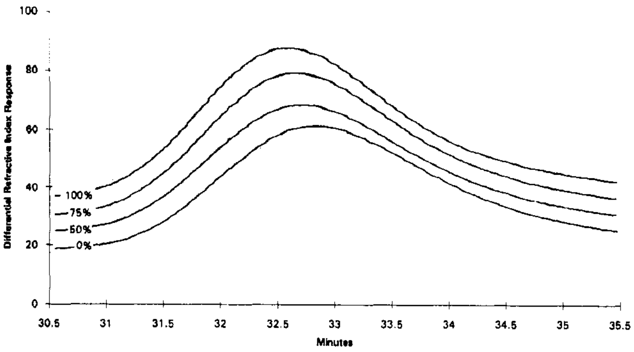

Figure 9. Gel permeation chromatograms showing a systematic shift of the polystyrene samples to higher molecular weights as the extent of functionalization is increased from 0 to 100%.

Table 2. $\langle M_n \rangle$ Values of Variably Functionalized Polystyrene and Corresponding Physical Mixtures as Determined by TOF-SIMS and GPC

		M_n			
	sample	expected	GPC (av ± std)	TOF (av ± std)	TOF (best)
synthetic	100 % func	1135	1140 ± 10	1123 ± 15	1136
	75 % func	1101	1110 ± 10	1124 ± 21	1105
	50 % func	1067	1080 ± 10	1063 ± 33	1062
	25 % func	1034	1060 ± 10	1062 ± 33	1031
	0 % func	1000	1030 ± 10	1036 ± 22	1011
physical	3:1 mix	1101	1110 ± 10	1072 ± 14	1087
	1:1 mix	1067	1080 ± 10	1099 ± 13	1089
	1:3 mix	1034	1060 ± 10	1019 ± 2.0	1021

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \qquad M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \qquad \text{MWD} = \frac{M_w}{M_n}$$

where N_i is the integral number of counts for the molecular ion containing *i* repeating units and M_i is the molecular weight of the oligomer with *i* repeating units. The molar mass and molecular weight distribution values determined from these methods are listed in Table 2. The increasing $\langle M_n \rangle$ values determined by GPC with increasing extent of functionalization reflect the systematic shift in MWD curves. This demonstrates the optimal working conditions of our GPC instrumentation, where polymers having approximately a 34 difference in molecular weight are discernible due to the precision of the $\langle M_n \rangle$ having a relative standard deviation of 1%. From TOF-SIMS, the calculated $\langle M_n \rangle$ values are higher for the most highly functionalized polymers than the minimally functionalized polymers. However, the progressive shifts of 34 in the $\langle M_n \rangle$ value is not distinguishable in the variably functionalized samples due to a relative standard deviation of up to 4% in the TOF-SIMS calculation of $\langle M_n \rangle$. Results for the physical mixtures are similar: the shift in $\langle M_n \rangle$ increases as the functionalized component of the sample increases and can be seen in the tabulated GPC $\langle M_n \rangle$ values.

TOF-SIMS is advantageous in that the high mass resolution of the technique allows for the calculation of $\langle M_n \rangle$ values, in a mixed endgroup sample, for oligomer distributions with each endgroup type. The $\langle M_n \rangle$ values for the functionalized and unfunctionalized component of each sample are listed in Table 3. The $\langle M_n \rangle$ value of the functionalized component of all the samples is expected to be constant since all samples were obtained from the same polymerization. The TOF-SIMS calculated $\langle M_n \rangle$ values vary by 70 Da for each component due to the inherent relative standard deviation. Within each sample,

Table 3. ⟨M_n⟩ Values Determined by TOF-SIMS for the Functionalized and Unfunctionalized Component of Each Sample

		M_n	
	sample	PS-EG (av ± std)	PS-H (av ± std)
synthetic	100% func	1123 ± 15	
	75% func	1178 ± 14	1023 ± 30
	50% func	1143 ± 31	1007 ± 33
	25% func	1156 ± 28	1032 ± 36
	0% func		1036 ± 22
physical	3:1 mix	1116 ± 14	983 ± 15
	1:1 mix	1159 ± 14	1050 ± 13
	1:3 mix	1152 ± 47	996 ± 1.7
GPC values		1140 ± 10	1060 ± 10
expected M_n		1135	1000

however, the functionalized and unfunctionalized components can be distinguished by ⟨M_n⟩ values as their difference is determined experimentally by TOF-SIMS to be greater than 100 Da in all examples.

^{1}H NMR methods were also considered to determine the extent by which the macromolecules were functionalized. However, the ⟨M_n⟩ and extent of functionalization could not be determined due to the overlap of the methylene proton signals of the polystyrene backbone and the *sec*-butyl initiator and the poor integration due to the limited resolution of the peaks. Also, the aromatic protons of the silyl endgroup overlap with the signal which corresponds to the phenyl groups in the styrene repeating unit.

Conclusions

TOF-SIMS is shown to be a powerful tool for the characterization of endgroup functionalization and determination of molar mass, using a model polystyrene system. In a mixed endgroup system, where the polymer has not been fully functionalized, two distinct molecular weight distributions of intact oligomer signals can be resolved from the TOF-SIMS spectra: from the functionalized and unfunctionalized (protonated) oligomer species. Through direct comparisons of signal intensities of the two types of oligomers, the extent of functionalization can be determined at each degree of polymerization.

When comparing oligomers with two distinct endgroups, secondary ion intensities may be influenced by differences in sputter yield, extent of fragmentation, and detection and ionization probabilities. Here, the results from physical mixtures of 100 and 0% functionalized polymers were used to evaluate any signal anomalies inherent in the TOF-SIMS technique. For quantification of functionalization in general polymer systems, however, fully functionalized polymers may not be available to create physical mixtures. In this case, the use of a protonated aliquot of the polymer as an internal standard in the sample for TOF-SIMS analysis should allow evaluation of relative secondary ion intensities for intact functionalized and unfunctionalized oligomers. The ⟨M_n⟩ values for the functionalized and unfunctionalized components in each low molecular weight polymer sample can be determined by TOF-SIMS and are distinct for each oligomer type.

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