MALDI-TOF-MS Copolymer Analysis: Characterization of a Poly(dimethylsiloxane)-*co*-Poly(hydromethylsiloxane) as a Precursor of a Functionalized Silicone Graft Copolymer

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ABSTRACT: A poly(dimethylsiloxane)-*co*-poly(hydromethysiloxane) (PDMS-*co*-PHMS) polymer has been characterized with respect to chain length distribution, heterogeneity of chemical composition, and sequence distribution using SEC, ^{1}H- and ^{29}Si NMR, and MALDI-TOF-MS. Due to ambiguities in the peak assignment the deconvolution of the mass spectrum into the bivariate copolymer distribution is not possible. Alternatively, the expected mass spectrum is computed from the SEC and NMR data. It is then mapped onto the measured one, and an almost perfect agreement is found within the peak resolved low molar mass range, leaving only a small number of adjustable parameters. As a result it could be shown that a large number of chains contain no functionalizable units at all.

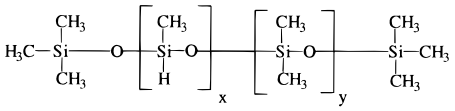
1. Introduction

Functionalized silicone graft copolymers play an important role in technical applications such as foam stabilizers. During the production of polyurethane foams, e.g., they regulate the cell structure and cell size and therefore crucially influence the mechanical properties of the foams. In this paper the precursor of such silicone graft copolymers is characterized, which is a copolymer consisting of dimethylsiloxane and hydromethylsiloxane units (PDMS-*co*-PHMS). The hydromethylsiloxane groups can be grafted with allyl-functionalized polyethers (Chart 1). The properties of the final technical product, the functionalized graft copolymer, do not only depend on average quantities, such as chain length and number of functional substituents, but also on their distribution. Hence, they are expected to be influenced to a large extent by the underlying statistics of the PDMS-*co*-PHMS precursor, whose complete characterization is the goal of the analytical effort described in this paper.

For a copolymer there are different heterogeneity generating mechanisms. As with homopolymers, there is a heterogeneity of the degree of polymerization, corresponding to a distribution of the chain length. Even for a given chain length there is a heterogeneity of the chemical composition. This chemical heterogeneity may either be due to purely statistical fluctuations or be caused by different reactivities of the comonomers during polymerization. In the latter case there may also be a dependence of the average composition on the chain length. Finally, the distribution of the comonomers along the copolymer chain, characterized by the distribution of the sequence lengths, may be quite different. The two extreme cases are marked by a diblock copolymer and an alternating copolymer.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) is a mass spectroscopic technique with huge potential use for polymer characterization due to its ability of gentle desorption and ionization of even high molar mass material up to $M \approx 10^6$ g/mol. Despite being a relatively young technique, a substantial amount of work has already been published concerning its application to homopolymers.[1−6] So far, however, only a little work on the mass spectrometry of copolymers has been reported.[7−13] Due to the high resolution, at least in the low molar mass range, and the precise molar mass assignment to the individual peaks, there is a high information content of the mass spectra, and one might expect that a determination of the copolymer distribution function could be obtained solely from this technique. Indeed, it could be shown that copolymers with unknown composition or end groups can successfully be analyzed[12] and that, under favorable conditions, the bivariate copolymer distribution function can be extracted[13] when high-resolution techniques, such as Fourier transform cyclotron resonance, are employed.

Chart 1



The first aim of the present work is the complete characterization of the PDMS-*co*-PHMS precursor with "conventional" analytical tools such as size exclusion chromatography (SEC), nuclear magnetic resonance (NMR), and fractionation by precipitation. Together with a statistical model the complete bivariate distribution as a function of the degree of polymerization and the chemical composition are obtained.

In the second part of the work MALDI-TOF-MS with a relatively low resolution is employed for the characterization of PDMS-*co*-PHMS. Polydisperse PDMS homopolymers have recently been characterized by combining MALDI-TOF-MS with SEC fractionation, because

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the direct characterization of the broad distribution leads to considerable error in the molar mass averages M_n and M_w.[6,10] In our work we focus on a low molar mass copolymer and test, whether mass spectrometry can reproduce the correct copolymer distribution function, at least within a limited molar mass range.

It turns out that, due to ambiguities—there are different possible combinations for the same molar mass due to the limited resolution of the mass spectrometer employed, a unique peak assignment to one particular degree of polymerization and chemical composition is not possible. As will be shown in this paper, problems for a quantitative deconvolution of the MALDI-TOF-MS spectrum arise from peak overlap, from a sharp loss of sensitivity below 1200 g/mol, from ambiguities in the base line selection, and from a dependence of the relative peak intensities on the experimental conditions. Hence, the copolymer distribution function cannot be derived from the mass spectrum alone without additional a priori information, and the direct interpretation of the mass spectrum as proposed by other authors[12−14] is not feasible due to the above restrictions and the relatively low resolution of the instrument employed in the present work. A quantitative interpretation of the mass spectrum within a limited molar mass range is, however, obtained by computing it from the distribution function, as obtained by SEC and NMR, and mapping this calculated spectrum onto the measured one, leaving only a few adjustable parameters, such as the unknown base line in the mass spectrum or the scale of the intensity axis.

2. Experimental Section

PDMS-*co*-PHMS. The precursor polysiloxane is obtained by reacting a linear poly(hydromethylsiloxane) ("Polymethylsiloxane", Rhone Poulenc) with the appropriate amounts of the cyclic dimethylsiloxane tetramer ("Octamethylcyclotetrasiloxane", Aldrich) in the presence of 50 ppm of concentrated sulfuric acid (8 h, 100 ° C). During this equilibration reaction polymeric siloxanes coexist with oligomeric ones, which can be separated by fractional precipitation in methanol. Due to the low amount of sulfuric acid and self-condensation of the OH-terminated chains, hydrolysis products are not observed in the equilibrated polymer.

Fractionation. For fractionation, PDMS-*co*-PHMS is dissolved in a 20−30-fold volume of THF and brought into a separating funnel. The addition of small amounts of methanol (about 1 vol % with respect to tetrahydrofuran (THF)), which is a nonsolvent for the polymer, causes a high molar mass fraction of the polymer to precipitate, which can be separated from the mixture by filtration. The cycle of methanol addition, precipitation, and filtration is repeated several times, each cycle giving rise to the precipitation of a new polymer fraction with decreasing molar mass.

SEC. Polymers were characterized by SEC in toluene (Riedel-de Häen) using a set of three 10 μm styragel columns with 500, 10^4, and 10^5 Å pore sizes (SDV, Polymer Standards Service, Mainz, Germany) together with differential refractive index detection (ERC 7512). The polymer concentration was 2−4 mg/mL, the injected volume 200 μL, and the flow rate 1 mL/min. Poly(dimethylsiloxane) (PDMS) standards (Polymer Standards Service, Mainz, Germany) were used for calibration.

NMR. ^{1}H NMR spectra were obtained with a Bruker AC 300 and ^{29}Si NMR spectra with a Bruker AMX 500 NMR spectrometer. For the measurements 10 mm o.d. sample tubes with $CDCl_3$ as external lock were used (T_1 = 60 s). Deuteriochloroform (d 99.8%) was obtained from Deutero GmbH; tetramethylsiloxane (TMS), from Cambridge Isotope Laboratories.

MALDI−TOF−MS. The measurements were performed with a Bruker Reflex MALDI-TOF mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm (LSI N_2 laser; 10^6−10^7 W/cm^2, 100 μm diameter spot). The matrix for all experiments was (2-nitrophenyl) octyl ether (Aldrich). Samples were prepared by dissolving the polymer in THF at a concentration of 10^{-4} mol/L. A 10 μL aliquot of this solution was added to 10 μL of a 25 mg/mL matrix solution. A 1 μL aliquot of a solution of potassium trifluoroacetate (Aldrich) in THF (5 mg/mL) as cationization reagent was added to the matrix/analyte solution. The resulting molar matrix/analyte/cation ratio is 766/5/1, assuming M_n = 3235 g/mol for the copolymer. A 1 μL aliquot of the resulting mixture was applied to the multistage target to evaporate the THF and create a thin liquid matrix/analyte film. The ions were accelerated to 33.65 kV and measured in the reflectron mode of the mass spectrometer. In the cases of positive ions only potassium-cationized ions ($M + K^+$) were detected. Polystyrene (M_p = 6000) was used for an external calibration immediately before the measurement. The such determined mass accuracy is approximately 0.05%.

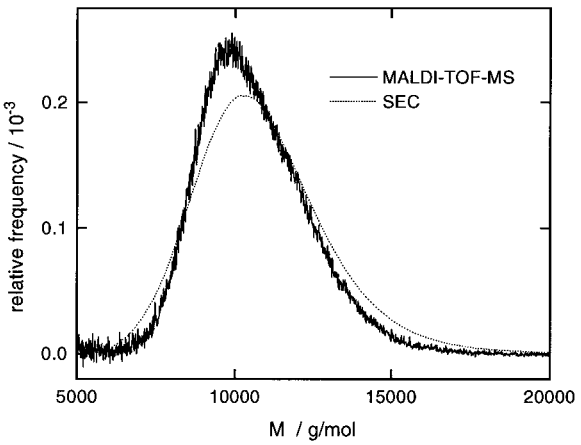

Figure 1. Frequency distribution of a narrow PDMS-*co*-PHMS fraction as measured by MALDI-TOF-MS and SEC.

3. Results and Discussion

Molar Mass Distribution. The original material contained a significant amount of low molar mass contamination originating from the equilibration reaction. It was purified as described in the Experimental Section, and the success of the purification was checked by SEC. All further characterization work was done with the purified sample.

The SEC setup was calibrated with PDMS. Since the hydrodynamic volume of the copolymer may differ from the one of the pure PDMS homopolymer with the same degree of polymerization, it is a priori not clear whether the calibration also holds for PDMS-*co*-PHMS with sufficient accuracy. To verify this assumption, PDMS-*co*-PHMS was fractionated by disconnecting the detector from the SEC columns and collecting samples over intervals of typically 10 s. After reassembling the SEC apparatus, half of every fraction was reinjected and evaluated according to the PDMS calibration. From the other half MALDI-TOF-MS spectra were recorded. SEC fractionation results in narrow molar mass distributions, which can then be analyzed with high accuracy by MALDI-TOF-MS.[10,12,15] The narrow PDMS standards used for calibration were also measured and evaluated by MALDI-TOF-MS as a cross-check. The experimental conditions were the same as the ones for the unfractionated copolymer discussed later.

Figure 1 shows the SEC and the MALDI-TOF-MS molar mass distributions for one of the fractions as an example. To allow a comparison, the original concen-

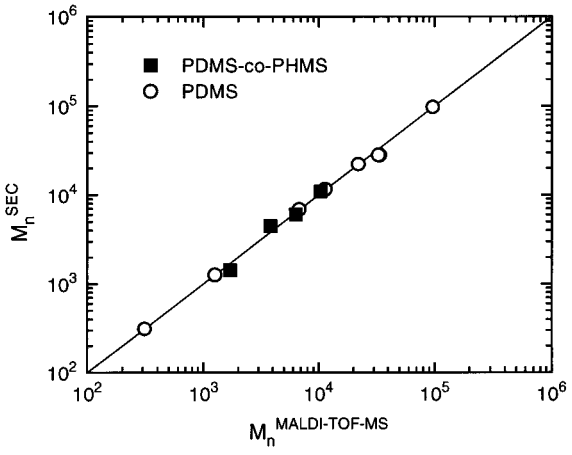

Figure 2. Number average molar mass of fractionated PDMS-*co*-PHMS and PDMS standards as determined by SEC and MALDI-TOF-MS. The PDMS with the lowest M_n has been measured with field ionization MS.

tration proportional SEC signal has been converted to a frequency distribution as measured by mass spectrometry. There is a reasonable agreement both for the peak shapes, with the SEC peaks being somewhat broader, and a good one for M_n: 10 900 g/mol from SEC versus 10 400 g/mol from MALDI-TOF-MS.

The result of the whole procedure is summarized in Figure 2, where the M_n values obtained from both techniques are compared. Two conclusions can be drawn. First, both the copolymer and the homopolymer data fall onto the same line, corresponding to approximately identical hydrodynamic behavior of the homo- and the copolymer. Second, there is good agreement between the number average molar mass M_n as obtained by SEC and MALDI-TOF-MS. Both techniques yield comparable results in the cases of PDMS and PDMS-*co*-PHMS within the molar mass range investigated, and the SEC calibration is valid at least for the low hydromethylsiloxane content of the copolymer of approximately 8% (see below). For this low content the difference between the molar masses of the dimethyl- and hydromethylsiloxane repeat units, 74 and 60 g/mol, respectively, can safely be neglected when molar mass averages are calculated from the SEC data. The error introduced by neglecting the 14 g/mol mass difference for a copolymer chain of average composition with 8% of the dimethylsiloxane units replaced by hydromethylsiloxane is of the order of 2%, which is below the accuracy of the experiment. $M_n = 3200$ g/mol and $M_w = 6500$ g/mol are obtained for the purified copolymer.

No attempt has been made to compare the polydispersities of the individual fractions as measured by SEC and MALDI-TOF-MS, since this would require a careful calibration and characterization of the SEC resolution as a function of retention time. To establish a calibration curve over a broad molar mass range, exact knowledge of the polydispersities of the narrow samples is not necessary. A thorough investigation of PDMS by SEC/MALDI-TOF-MS with a comparison of the polydispersities of the fractions can be found in ref 6.

Composition. PDMS-*co*-PHMS consists of the dimethylsiloxane (d) and the hydromethylsiloxane (h) repeat units and the trimethylsilyl end groups (t). The composition can be analyzed by, e.g., bromine titration[16,17] or ^{1}H NMR.[18] The latter has been chosen in this work. In the ^{1}H NMR spectrum there is a signal from the Si−H protons at $\delta = 4.7$ ppm. The remaining methyl protons are found at $\delta = 0.1$ ppm.

Table 1. Summary of the Sequence Probabilities As Obtained by ^{29}Si NMR

sequence	$p_{sequence}$	sequence	$p_{sequence}$
th	0.074	dhd	0.887
td	0.926	hdh	0.011
hhh		hdd	0.170
hhd	0.113	ddd	0.819

If n_d, n_h, and n_t are the number of d-, h-, and t-units in the sample, then the following equations hold for the ^{1}H NMR intensities I with a suitable but arbitrary normalization:

$$I_{Si-H} = n_h \tag{1}$$

$$I_{Si-CH_3} = 6_{n_d} + 3n_h + 9n_t \tag{2}$$

The third equation for the three unknowns n_d, n_h, and n_t is obtained from the number average degree of polymerization N_n:

$$N_n = \frac{n_d + n_h}{n_t/2} \tag{3}$$

The symbol N is used for the degree of polymerization to avoid confusion with the probability $P_N(n,q)$ introduced in eq 9.

N_n is obtained from the SEC result for M_n:

$$N_n = \frac{M_n - 2M_t}{M_d} = 41 \tag{4}$$

$M_d = 74$ is the molar mass of the d-units and $2M_t = 162$ the one of the two end groups. The correction for the smaller mass of the h-units is again negligible.

The hydromethylsiloxane content was determined for the unfractionated polymer and for 16 different fractions prepared by precipitation fractionation. The molar mass range of the fractions was 1000−7200 g/mol for M_n and 4500−12 600 g/mol for M_w. For both the fractions and the unfractionated polymer $x_h = 0.080 \pm 0.004$ was found without any systematic variation with molar mass. Hence, there is no molar mass dependence of the copolymer composition, except for the end group effect. For the unfractionated polymer $x_t = 0.046$ and $x_d = 0.874$ was found.

Sequence Distribution. ^{29}Si NMR has been employed for the investigation of the sequence distribution.[19−24] The composition analysis from ^{29}Si NMR gives $x_d = 0.882$, $x_h = 0.076$, and $x_t = 0.042$, which is in excellent agreement with the ^{1}H NMR results.

A peak assignment has been possible from literature data and with the help of a model compound containing 41 mol % h-units, with a resolution up to heptads.[25−27] For a statistical description of the sequence distribution we will focus on the six possible triads, three centered around the h- and three around the d-units: hhh, dhh, dhd, ddd, hdd, and hdh. $p_{ijk} = x_{ijk}/x_j$ is the probability of finding a certain triad ijk, normalized to all triads centered around the same unit j. The probability p_{ti} for the diad ti at the chain ends is defined in analogy. The ^{29}Si NMR data for the sequence probabilities are summarized in Table 1. The triad probabilities p_{ijk} are

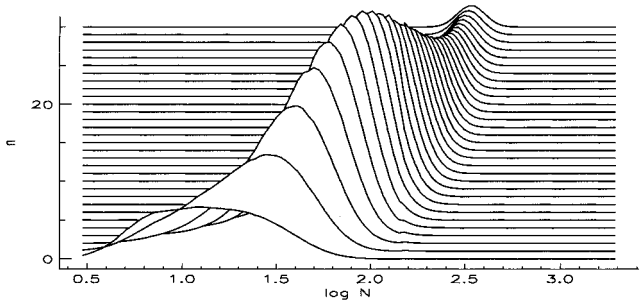

Figure 3. Weight fraction of PDMS-*co*-PHMS as a function of the degree of polymerization N and the hydromethylsiloxane content n.

connected to the run number R:

$$p_{\mathrm{hhh}} = \frac{(x_{\mathrm{h}}^* - R/2)^2}{(x_{\mathrm{h}}^*)^2} \tag{5}$$

$$p_{\mathrm{dhd}} = \frac{R^2}{4(x_{\mathrm{h}}^*)^2} \tag{6}$$

$$p_{\mathrm{hhd}} = \frac{R(x_{\mathrm{h}}^* - R/2)}{(x_{\mathrm{h}}^*)^2} \tag{7}$$

$x_h^* = x_h(x_h + x_d)^{-1} = 0.079$ is the mole fraction of h-units without taking the end groups into account. For a statistical copolymer the run number is[28]

$$R_{\mathrm{stat}} = 2x_{\mathrm{h}}^* x_{\mathrm{d}}^* \tag{8}$$

From eqs 5−7, the corresponding equations, obtained by exchanging h with d, and from eq 8 the persistence ratio $\eta \equiv R_{stat}/R = 1.13 \pm 0.11$ is calculated. $\eta = 0.5$ holds for an alternating copolymer, $\eta = 1$ is for a statistical copolymer, and for $\eta > 1$ there is a blocking tendency. Hence, within the experimental error, the PDMS-*co*-PHMS can approximately be described as a statistical copolymer obeying Bernoulli statistics:

$$P_N(n, q) = q^n(1 - q)^{N-n} \frac{N!}{n!(N - n)!} \tag{9}$$

The binomial distribution $P_N(n,q)$ is the probability of finding a chain with n h-units among all chains with the degree of polymerization N. $q = ({}^{1\mathrm{H}}x_{\mathrm{h}}^* + {}^{29\mathrm{Si}}x_{\mathrm{h}}^*)/2 = 0.082$ is the probability that an arbitrarily selected repeat unit is an h-unit, taken as the average of the ^{1}H and ^{29}Si NMR results.

With knowledge of the molar mass distribution from SEC and the composition and sequence distribution from NMR, the copolymer distribution function $W(N,n)$, which is the weight fraction as a function of the degree of polymerization N and the number of h-units per chain n, is given by

$$W(N, n) = w(N)\, P_N(n, q) = w(N)q^n(1 - q)^{N-n}\frac{N!}{n!(N - n)!} \tag{10}$$

$w(N)$ is the weight fraction of polymer chains with a given degree of polymerization N as obtained by SEC, without counting the end groups. Figure 3 shows the bivariate distribution plotted as a function of log N and n; i.e.

$$W(10^{\log N}, n)\left|\frac{\mathrm{d}\log N}{\mathrm{d}N}\right|^{-1}$$

The curves correspond to the distributions of the copolymer with a fixed number n of h-units. The curve in the foreground with $n = 0$ gives the distribution of the pure PDMS, i.e., the chains that contain no functionalizable units. It is tilted toward low degrees of polymerization N. For longer chains it becomes increasingly unlikely to find chains without h-units. For higher values of N the ridge of the distribution in Figure 3 follows the line $n \approx 0.08\ N$, as defined by the average copolymer composition.

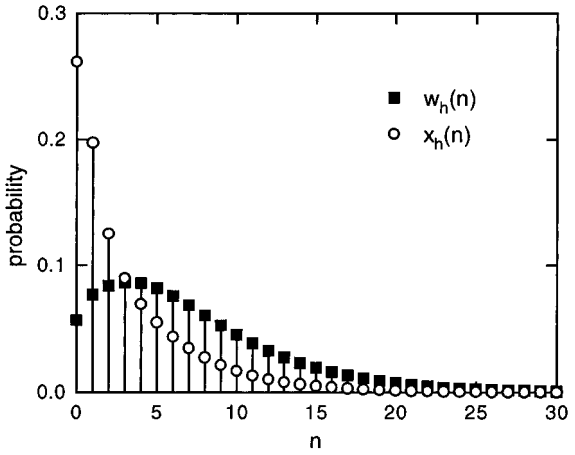

Figure 4. Differential distribution of the weight ($w_{\mathrm{h}}(n)$) and mole ($x_{\mathrm{h}}(n)$) fraction of h-units per chain.

Table 2. Comparison of ^{1}H NMR/SEC and ^{29}Si NMR Results

	SEC/^{1}H NMR	^{29}Si NMR		SEC/^{1}H NMR	^{29}Si NMR
x_{t}	0.046	0.042	N_{w}	86	
x_{h}	0.080	0.076	n_{n}	3.45	3.57
x_{d}	0.874	0.882	n_{w}	7.18	
N_{n}	41	46			

All results accumulated so far from ^{1}H NMR in combination with SEC and from ^{29}Si NMR are summarized in Table 2. n_{n} and n_{w} are the number and weight average of the number of h-units per chain.

An important piece of information for the properties of the final technical product is the distribution of the number of functionalizable h-units per chain, which can readily be answered from eq 10:

$$w_{\mathrm{h}}(n) = \sum_N W(N, n) \tag{11}$$

$$x_{\mathrm{h}}(\mathrm{n}) = \frac{\sum_{\mathrm{N}} N^{-1}W(N, n)}{\sum_{\mathrm{N,n}} N^{-1}W(N, n)} \tag{12}$$

$w_{\mathrm{h}}(n)$ and $x_{\mathrm{h}}(n)$ are the weight and mole fraction of the polymer chains containing n h-units and are plotted in Figure 4. Due to the statistical distribution of the comonomer units, approximately 25% of the chains contain no h-unit at all and, thus, cannot be functionalized.

Mass Spectrometry. As already mentioned in the Introduction, the second aim of this work was the investigation of the suitability of MALDI-TOF-MS for

silicone copolymer analysis in the particular case of PDMS-*co*-PHMS, and the mass spectrum "as measured" is shown in Figure 5.

Despite its overwhelming information content, the deconvolution of the mass spectrum into the bivariate copolymer distribution $W(N,n)$ is not possible, because of ambiguities in the peak assignment. Within the experimental resolution, chains with, e.g., 17 d-units and 5 h-units cannot be distinguished from pure PDMS with $N = 21$, since the mass difference is only 4 g/mol. In the mass range above 1000 g/mol we do not have unit mass resolution, and, thus, the isotope distribution appears as an unresolved envelope. The application of high-resolution MALDI-TOF mass spectrometers equipped with delayed extraction[29−31] or Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometers[32] might extend the mass range with unit mass resolution up to approximately 3000−5000 g/mol, but there is still the limitation of overlapping isotopic distributions. The signal for $N = 16$ consists already of 10 peaks with significant intensity, and an additional peak shape analysis would be necessary to evaluate the contributions to the overlapping signals.

Hence, a different route is followed for a quantitative interpretation of the mass spectra, and the expected MALDI-TOF-MS spectrum is calculated from $W(N,n)$ as obtained by SEC in combination with ^{1}H and ^{29}Si NMR. The measured and the calculated spectra are then matched with only a few adjustable parameters left. The calculated spectrum is obtained as follows.

In MALDI-TOF-MS the number of chains of a particular mass are counted. From eq 10 the mole fraction $X(N,n)$ of chains with degree of polymerization N and the number of h-units n is

$$X(N, n) = \frac{N^{-1}W(N, n)}{\sum_{N,n} N^{-1}W(N, n)} \tag{13}$$

The number of the respective atoms within a particular chain is given by

$$n^{\mathrm{Si}} = N + 2 \tag{14}$$

$$n^{\mathrm{C}} = 2(N - n) + n + 6 \tag{15}$$

$$n^{\mathrm{O}} = N + 1 \tag{16}$$

$$n^{\mathrm{H}} = 6(N - n) + 4n + 18 \tag{17}$$

For a detailed analysis of the spectrum the isotope distribution must be taken into account, and the molar mass of a given chain with a particular isotope distribution is

$$M_{\{\}} = \sum_A n^A M_{\mathrm{A}} \times \mathrm{A} \in \{^{28}\mathrm{Si}, ^{29}\mathrm{Si}, ^{30}\mathrm{Si}, ^{12}\mathrm{C}, ^{13}\mathrm{C}, ^{16}\mathrm{O}, ^{18}\mathrm{O}, ^{1}\mathrm{H}\} \tag{18}$$

For the summation the boundary conditions, $n^{28\mathrm{Si}} + n^{29\mathrm{Si}} + n^{30\mathrm{Si}} = n^{\mathrm{Si}}$, etc., must be fulfilled. M_{A} are the respective isotope masses.

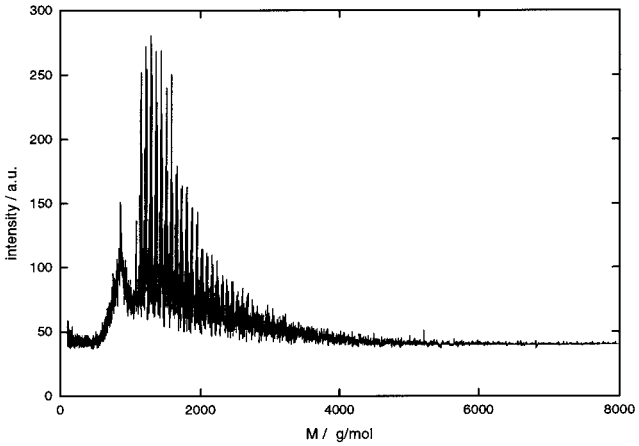

Figure 5. Complete MALDI-TOF-MS spectrum of the PDMS-*co*-PHMS "as measured" without base-line correction.

The relative frequency of finding a chain with a certain isotope distribution, symbolized by the curly braces { }, is

$$X_{\{\}}(N,n) = X(N,n)Q_{n^{\mathrm{Si}}}(n^{^{29}\mathrm{Si}}, q^{^{29}\mathrm{Si}}, n^{^{30}\mathrm{Si}}, q^{^{30}\mathrm{Si}}) \times P_{n^{\mathrm{C}}}(n^{^{13}\mathrm{C}}, q^{^{13}\mathrm{C}})P_{n^{\mathrm{O}}}(n^{^{18}\mathrm{O}}, q^{^{18}\mathrm{O}}) \tag{19}$$

$q^{^{13}\mathrm{C}}$ is the isotopic abundance of ^{13}C, etc.[33] The $P_N(n,q)$ are the binomial distributions according to eq 9, and

$$Q_N(m, q, n, p) = (1 - q - p)^{N-m-n}q^m p^n \frac{N!}{m!n!(N - m - n)!} \tag{20}$$

Now the MALDI-TOF-MS spectrum $S(M)$ can readily be computed:

$$S(M) = \sum_{N,n,\{\}} X_{\{\}}(N,n)\,\delta(M - M_{\{\}}) \tag{21}$$

The summation extends over all possible degrees of polymerization, contents of h-units, and isotope distributions. $\delta(x)$ is Dirac's δ-function.

The spectrum is smeared by the finite resolution of the instrument, in our case $\Delta M/M \approx {}^1/_{350}$, where ΔM is defined as the full width at half-maximum (fwhm) peak width. A Gaussian peak broadening with $\sigma(M) = (M/350)(8 \ln 2)^{-1/2}$ is incorporated by

$$S(M) \rightarrow \int \mathrm{d}M'\; S(M')(2\pi\sigma^2(M'))^{1/2} \exp\left(-\frac{(M - M')^2}{2\sigma^2(M')}\right) \tag{22}$$

yielding the final calculated spectrum, which must be compared with the measured one. While the choice of a Gaussian line shape may not be fully justified, it is sufficient for our purpose, and a detailed line shape analysis is beyond the quality of the measured data.

The result of this procedure is shown in Figure 6, where the peak resolved low molar mass ranges of the measured and the computed mass spectra are superimposed after the proper base-line subtraction and intensity adjustment. The smooth base line and the intensity scale have been defined such that the peak maxima and the valleys of the calculated and the measured spectra coincide in the molar mass range

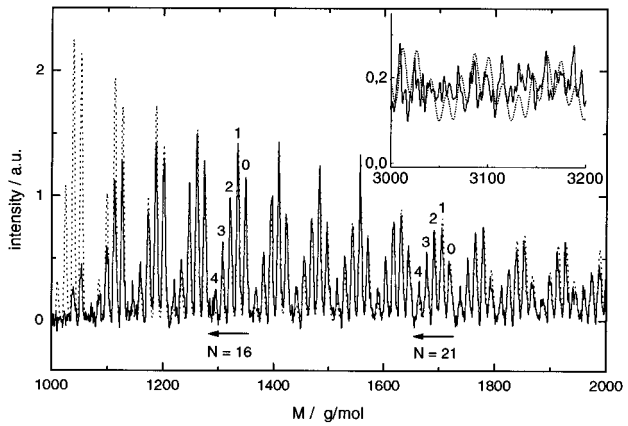

Figure 6. Calculated and measured MALDI-TOF-MS spectra after base-line subtraction and intensity adjustment.

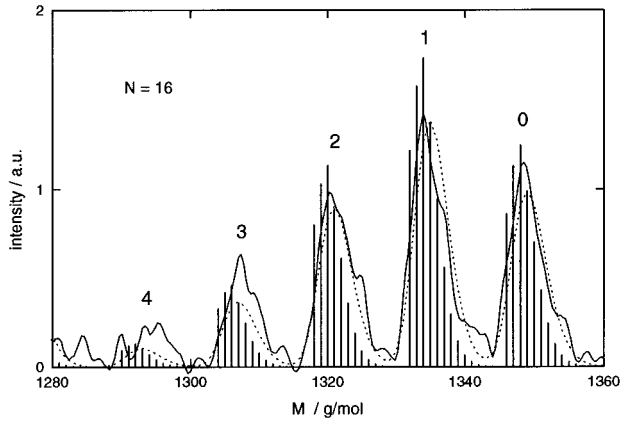

Figure 7. Peak multiplet corresponding to $N = 16$ and different h-unit contents: measured (solid line) and calculated for unit resolution (δ-peaks) and for finite resolution (dotted line).

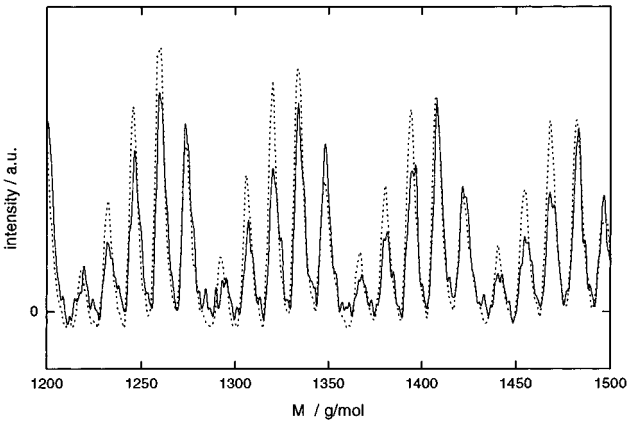

Figure 8. MALDI-TOF-MS spectra as measured with low (solid line, Figure 6) and high (dotted line) laser power.

below $M \approx 2500$ g/mol. Furthermore, the measured spectrum has been shifted by 39 amu to compensate for the K^+ cationization. Above 1200 g/mol the agreement is excellent. Below 1200 g/mol the measured mass spectrum decays rapidly, a finding we tentatively attribute to vacuum loss of the more volatile low molar mass components. At higher molar masses, the resolution decreases and the peak fine structure gradually vanishes in the noise, as can be seen in the insert in Figure 6. When judged with the eye, an almost perfect agreement between the measured and the calculated spectra is achieved, but no attempt has been made to define a numerical goodness parameter.

For a full characterization of the low molar mass fraction below 1200 g/mol supplementary MS methods, such as field ionization (FI), should be applicable.[34] With this technique a fractionation of the sample due to different volatilities can be avoided by a heated gas inlet system, providing a sample gas flow without mass discrimination. Beyond this, FI is a soft ionization technique with negligible fragmentation in the required mass range and has the advantage of being free of background signal, contrary to other soft ionization techniques such as liquid secondary ion mass spectrometry (LSIMS) or MALDI-TOF-MS, which show intense matrix background signals in the low molar mass range.

The spectrum consists of characteristic multiplets, whose members belong to the same degree of polymerization but to different chemical composition. Two such multiplets, corresponding to $N = 16$ and $N = 21$, are labeled in Figure 6. The numbers above the individual peaks indicate the number of h-units n. $n = 0$ stands for the pure PDMS homopolymer. Strictly speaking, the numbers refer to the majority components, since the ($N = 16$, $n = 0$) peak overlaps with the (N=17,n=5) -peak, and so on. While this already discussed ambiguity is negligible at low N, where high values of n are very unlikely, it becomes substantial at high N. It is apparent how the peaks with higher values of n gain relative intensity with increasing chain length. The peak with $n = 0$, on the other hand, decays, reflecting the decreasing probability of finding longer chains without h-units.

Figure 7 shows an enlargement of the multiplet with chain length $N = 16$. The solid line is the measured spectrum. The sharp δ peaks belong to the calculated spectrum and are obtained by taking the isotope distribution into account, however, for unit resolution. The dotted line is obtained by smearing this ideal spectrum with the finite instrument resolution according to eq 22. It is obvious that the isotope distribution is essential for a correct description of the peak shapes.

The coherent picture presented so far is somewhat spoiled by an intensity dependence of the relative peak areas when measured at higher laser powers, leading to an apparent discrepancy between the MALDI-TOF-MS spectrum and the results from conventional analysis. Formally, this discrepancy can be resolved by introducing a composition dependent ionization or desorption probability, which increases linearly with increasing hydromethylsiloxane content. The underlying mechanism is, however, purely speculative.

Figure 8 shows a comparison between the presumably correct measurement from Figure 6 and one taken at high laser power. Both spectra are scaled such that there is an approximate agreement for the peaks with $N = 0$.

Another potential source of error should be mentioned. It stems from the ambiguity in the base-line selection at higher molar masses, where the individual peaks are no longer resolved. Furthermore, the base-line selection at intermediate molar masses around 2000−3000 g/mol strongly depends on the smearing of the peaks due to the finite instrument resolution. This is of particular importance for polymers with a broad molar mass distribution, and it clearly limits the comparability to the molar mass range below say 3000 g/mol in the present work.

Within the low molar mass range the agreement between the different experimental techniques is very

good, except for the vacuum loss below 1200 g/mol, as can especially be seen by the correct intensity ratios within the peak multiplets corresponding to a given chain length but to different chemical compositions. The sharp decay in sensitivity below approximately 1000 g/mol becomes also evident when measuring narrow PDMS standards in this molar mass range. The lowest molar mass in Figure 2, e.g., could not be measured by MALDI-TOF-MS and, hence, has been measured by field ionization MS. The question as to whether the MALDI-TOF-MS sensitivity is constant over a broad molar mass range at high molar masses is more difficult to answer, due to the base-line problems with broad molar mass distributions. To answer this question, experiments with narrow distributions would be necessary, which could, e.g., be obtained from SEC fractionation, as has been demonstrated for PDMS in ref 6.

4. Summary and Conclusion

PDMS-*co*-PHMS as a precursor for a functionalized silicone graft copolymer has been characterized with respect to chain length distribution, chemical heterogeneity, and sequence statistics using conventional analytical tools such as SEC, ^{1}H and ^{29}Si NMR, and fractionation by precipitation. It could be shown that, for the low hydromethylsiloxane content of approximately 8% as determined by NMR, the hydrodynamic behavior of the copolymer is almost identical to that of a PDMS homopolymer, which allows for a PDMS calibration of the SEC to obtain the distribution function for the degree of polymerization. For ^{29}Si NMR a peak assignment up to heptads has been possible. From the triad probabilities the run number is computed, which is almost identical to the one expected for a statistical copolymer. Hence, the sequence distribution is described by Bernoulli statistics, and together with the SEC results the bivariate copolymer distribution $W(N,n)$ is obtained.

It could also be shown that under proper experimental conditions, especially low laser powers, even low-resolution MALDI-TOF-MS provides a suitable tool for the characterization of the PDMS-*co*-PHMS investigated. Despite the huge information content, however, a unique interpretation of the mass spectrum without additional information has not been feasible due to ambiguities in the peak assignment to a particular chemical composition and due to a quantitative interpretation is achieved by computing the expected mass spectrum from the SEC and NMR results and mapping it onto the measured mass spectrum. At least up to a molar mass of 3000 g/mol almost perfect agreement is found. Without additional supporting analytical investigations, however, MALDI-TOF-MS alone may give misleading results, as has been observed for an apparent composition dependence of the desorption and/or ionization probability at high laser powers. Further problems may arise from the base-line subtraction for broad molar mass distributions and from distortions of the molar mass distribution at low molar masses due to vacuum losses.

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