Molecular Structure of Silsesquioxanes Determined by Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

W. E. Wallace, C. M. Guttman, and J. M. Antonucci

Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland, USA

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry was used to deduce the three-dimensional structure of a complex silsesquioxane polymer. Four distinct levels of structure were observed in the mass spectrum. The overall shape of the peak distribution was typical of polymers formed by condensation reactions. The mass separation between major clusters of peaks, each major cluster corresponding to an oligomer with a unique number of repeat units, confirmed that the synthesis proceeded as expected with no side reactions. The mass separation between peaks *within* a major cluster showed that intramolecular reactions during synthesis resulted in the elimination of water. The loss of water was ascribed to the formation of closed loops in the polymer structure. A simple arithmetic algorithm is presented for identifying these peaks. Autocorrelation techniques were used to determine the number and distribution of intramolecular closed loops per oligomer. This knowledge was used to deduce whether a particular oligomer is branched-linear, ladder, polyhedral, or some combination of these. The single-oligomer isotopic distribution was used to determine that cationization was present from both sodium and potassium ions. (J Am Soc Mass Spectrom 1999, 10, 224–230) © 1999 American Society for Mass Spectrometry

olysilsequioxanes [1] have lately begun to receive as much attention as their closely related sibling polysiloxanes. Whereas polysiloxanes have a repeat unit of the form [R₂SiO] with silicon coordinated to two bridging oxygen atoms, polysilsesquioxanes have silicon coordinated with three bridging oxygen atoms in the form of $[RSiO_{3/2}]$. As a result, polysiloxanes are generally linear polymers, whereas polysilsesquioxanes can form a wide variety of complex three-dimensional structures [2]. These are shown in general form in Figure 1. Specifically, the typical branched-linear silsesquioxane may react with itself to form intramolecular topographic closed loops. In the material considered here, two -SiOH groups can react to eliminate water and form a new Si-O-Si bridge. What is generally believed is that these intramolecular closed loops give rise to silsesquioxanes with a ladderlike structure rather than the branched-linear structure. It has also been shown that well-controlled polymerization, usually taking place under very specific reaction conditions, can result in silsesquioxanes that are completely condensed, closed regular polyhedra having no residual -SiOH groups [3-8].

Because the silicon atoms are threefold coordinate

with oxygen, polysilsesquioxanes make useful precursors to fully crosslinked, fourfold-coordinate solid monoliths via the reaction of the lone R group, either by hydrolysis or oxidation to form a final Si-O-Si bridge resulting in nearly pure silica, or by reaction of R groups without elimination, for example by forming R–R or R–X–R bridges, where X is a crosslinking agent. This allows them to be processed at low cost, in solution or as a melt, before being converted to an insoluble, rigid material. Reaction to form an insoluble monolith proceeds most often by the application of heat, but can occur in specific materials by exposure to ultraviolet [9–11] or visible [10] radiation. Application of silsesquioxanes can be found in microelectronics [12, 13], in restorative dental materials [10], and in controlling polymer flammability [14, 15], to name just a few potential uses.

It is widely believed, but remains unproved, that the molecular structure of the polysilsesquioxane plays a critical role in determining the processing properties (such as solubility) as well as the properties of the final solid monolith (such as density). That is, monoliths derived from a polysilsesquioxane with one degree of intramolecular condensation will not have the same properties as ones derived from a polysilsesquioxane with a different degree of intramolecular condensation. This is believed to be true even if the essential chemistry of the two polymers is identical: the same R substitu-

Address reprint requests to Dr. William E. Wallace, Polymers Division, National Institute of Standards and Technology, Building 224, Room B320, Gaithersburg, MD 20899-8541. E-mail: william.wallace@nist.gov



Figure 1. Generalized structures for three-dimensional silsesquioxanes. Shown on the left is a polyhedral-type structure, with a ladder-type structure in the middle, and a branched linear structure on the right. The form of the methacryloxypropyl R group is also given. The essential difference between these structures is the level of –SiOH condensation.

ents, the same molecular weight, etc. A primary reason why this important point remains largely conjecture is the lack of a technique to determine the three-dimensional structure of the polysilsesquioxane polymer. Nuclear magnetic resonance using ²⁹Si has met with some success [16] in understanding the closed polyhedral structures, but may not be as useful for the more complex silsesquioxane structures studied here because data interpretation can be quite difficult. Using highresolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, with the introduction of some new data analysis concepts, the complex structure of silsesquioxanes can now be probed more thoroughly.

We have studied a wide variety of silsesquioxanes but will concentrate here on a methacrylate silsesquioxane made by a facile synthesis technique and intended for restorative dental application. The experiments on this material show a rich phenomenology and illustrate the power of mass spectrometry to elucidate structure in these complex, commercially promising polymers.

Experimental

The polysilsesquioxane was prepared from a commercially available trifunctional silane agent (3-methacryloxypropyltrimethoxysilane) by hydrolysis-condensation methods in a catalyzed aqueous/organic-solvent mixture [10]. The structure of the R group is shown in Figure 1. This is a simple method that is less arduous than forming molecules of a specific three-dimensional structure, and thus more amenable to commercialization; however, it results in a far more complex molecular structure. Infrared spectrometry and ¹H nuclear magnetic resonance spectrometry confirmed the formation of a silsesquioxane polymer from this condensation reaction and further showed that the pendant methacrylate groups remain intact during the formation of the silsesquioxane polymer [10]. This material was developed to form an insoluble monolith by exposure to ultraviolet or visible radiation which leads to crosslinking via the methacrylate groups. This final reaction product is a highly crosslinked network that cannot be studied by MALDI mass spectrometry.

Dithranol or sinapinic acid were each shown to perform satisfactorily as MALDI matrices. The data presented were taken using sinapinic acid. Chloroform was the solvent used with the dithranol matrix, whereas acetone was used with the sinapinic acid. Belu et al. [17] have recommended silver trifluoroacetate as a cationizing agent for methyl siloxane polymers. This was not useful in the ionization of this material with the silver trifluoroacetate having no effect on the quality of the data. Furthermore, no sign of the characteristic silver isotope pattern was seen in the mass spectra. Instead it will be shown that adventitious sodium and potassium were the cationizing agents whether silver salt was added or not. Solution concentrations were typically 45 mg/mL for the matrices and 1.5 mg/mL for the analyte; however, this silsesquioxane produced acceptable spectra over a wide range of analyte to matrix ratios. These solutions were mixed in equal parts and electrosprayed [18] onto the target plate. Electrospraying was done at rates between 3 and 10 μ L/min, from a fine steel capillary with a nominal inner diameter of 0.56 mm held at 5 kV and located about 2 cm from the target plate. The thin electrosprayed films proved to be highly uniform giving good quality spectra at any site on the target.

The mass spectrometry was performed on a Bruker REFLEX II instrument in reflectron mode using delayed extraction [19]. Ions were generated using a 337 nm wavelength nitrogen laser with a pulse duration on the order of 3 ns and an average energy of approximately 5 μ J spread over a spot size of 200 μ m \times 50 μ m. Because the electrosprayed mixture of matrix and analyte produced quite thin films, the laser was constantly rastered over the target to prevent exhaustion of a particular sample spot. Typically, only three to five individual laser firings would exhaust the target area. Thin electrosprayed films were shown to give higher resolution spectra than thicker films at the expense of having to raster the laser beam continually. All data shown are for positive ions: negative ion spectra typically produced only matrix ions and their clusters, e.g., M⁻, 2M⁻, etc. The instrument was periodically calibrated with bovine insulin using the $[M + H]^+$ and $[M + 2H]^{+2}$ peaks.

To check for UV radiation sensitivity of this silsesquioxane, the neat resin was subjected to laser radiation outside the vacuum system. One thousand laser shots of the defocused beam were impinged on a film of neat resin 1 cm \times 1 cm \times 1 mm. The subsequent analysis of this sample by mass spectrometry showed no discernible effects of this radiation treatment. Moreover, changing the laser power during an experiment did not produce new peaks, nor did it change the relative peak



Figure 2. The central portion of the full mass spectrum showing the characteristic shape of a condensation polymer. Estimated standard uncertainty of the peak position from calibration and repeatability is 0.2 u at 3000 u. Estimated standard uncertainty in the overall signal intensity from repeatability studies is 15%.

intensities, only the overall ion current was altered. This consistency was taken to mean that the polymer was not strongly sensitive to the 337 nm UV radiation. Therefore, it is inferred that the peaks in the mass spectrum are indicative of oligomers in the polymer and are not artifacts of the MALDI process.

Results

Figure 2 shows the central portion of a typical mass spectrum for this material. Oligomers were detected from about 1100 u to about 12,000 u, the lower limit being defined by matrix interference and the upper limit by signal to noise ratio. The overall spectrum bears the characteristic shape of a condensation polymer: higher abundances of low molecular weight molecules tapering off gradually in intensity at higher molecular weights. Caution must be exercised in interpreting this aspect of the data: this characteristic shape can also arise purely from detector effects because low mass oligomers that arrive first saturate the detector producing an erroneously low level of the late-arriving highermass oligomers. This effect is especially pronounced in wide polydispersity materials [20]. Low-mass blanking experiments were performed that showed that this curve shape persisted at high mass even when the vast majority of low mass oligomers (and matrix molecules) were prevented, electrostatically, from reaching the detector.

Figure 3 shows the region around two low-mass oligomers. Closer examination shows the spectrum to be made up of clusters of approximately five peaks. The nominal separation between these major clusters, 188.25 u, is equal to the repeat group [RSiO₂H]. That is, two Si–O–Si bridges and one terminal –SiOH group per repeat group, which is broadly indicative of a branched-linear material. The repeat unit spacing of 188.25 u



Figure 3. A two-repeat-unit detail of the full mass spectrum shown in Figure 2. The two major clusters shown have a nominal spacing between them of 188.25 u. The major cluster to the left is for n = 10, whereas that on the right is for n = 11.

indicates that the synthesis proceeded as expected to give a molecular structure of the form shown in Figure 1 with no side reactions. For example, this precise mass spacing strongly suggests that the methacrylate R group was not affected by the hydrolysis-condensation polymerization reaction. Recall that this methacrylate group is intended to react only as a final step to form an insoluble monolith. The nominal spacing of 188.25 u further indicates that the oligomers are singly charged. From its nominal mass, the major group on the left side of Figure 3 corresponds to an oligomer consisting of 10 monomers (n = 10), whereas the major group on the right is the next highest oligomer consisting of 11 monomers (n = 11).

Figure 4 shows the major cluster of peaks corresponding to 10 monomer units. Each peak within this major cluster consists of a set of isotopically resolved individual peaks. These smaller groups will be referred to as minor clusters. The very weak minor cluster on the extreme right is centered at 1923.5 u. This corresponds to 10 monomer units, 1882.5 u plus extra contributions of 18 u for the end groups and 23 u most likely from cationization by adventitious sodium in the sample. To the left of this peak is a more intense minor cluster 18 u lower in mass. This corresponds to a polymer which has a loss of water which can occur when two dangling -SiOH groups in close proximity within a given molecule react intramolecularly to form a Si-O-Si bridge. This polymer must result from an intramolecular reaction because an intermolecular reaction of this type would result in a shift of a multiple of 188.25 u forming a different oligomer, that is, a different major cluster. When such an intramolecular reaction occurs a closed loop forms in the molecule. That is, two silicon atoms go from each having two Si-O-Si bridges and one -SiOH terminal group to being fully coordinated with three Si-O-Si bridges. Moving further to the left in Figure 4 is



Figure 4. A single-repeat-unit detail of the full mass spectrum shown in Figure 2. The distance between peaks in this single major cluster is 18 u indicative of the intramolecular loss of water. These shifts of 18 u are shown at the top along with the number of closed loops *t* per oligomer.

an even higher intensity minor cluster. This peak corresponds to the loss of two water molecules and, therefore, the closure of two loops in the molecule, described here as a t = 2 oligomer. This largest minor cluster is the most probable number of closed loops for this size oligomer. This process continues for two more minor clusters indicating that at the extreme left (at 1833.5 u) some oligomers have as many as five closed loops, or 8 of 10 silicon atoms in the molecule have formed Si-O-Si bridges and what remains are only two -SiOH end groups. There are no detectable peaks at lower mass in this major cluster. Hypothetically there could be a peak at 1815.5 u, as indicated in the figure for six closed loops (t = 6), if the remaining two –SiOH reacted with one another. The absence of a peak above the noise level suggests this is an unlikely occurrence. Thus, this oligomer does not form a fully condensed polyhedral structure but instead retains at least two -SiOH chemically active groups.

Figure 5 shows the central minor cluster of Figure 4. To describe the isotopic shape of this minor cluster we must start with the observation that the nominal mass of potassium is 39 u, or 16 u greater than sodium. This sets up an interference between the potassium adducts and the loss of water from intramolecular reaction leading to a shift of 18 u. A sodium adduct with t closed loops has approximately the same mass as a potassium adduct with t + 1 closed loops. The monoisotopic mass difference in this case is 2 u. The histogram superimposed on the data is for a mixture of the isotopic distribution for this oligomer having a sodium adduct with two closed loops (i.e., loss of two water molecules) or having a potassium adduct with three closed loops (i.e., the loss of three water molecules). Specifically, the distribution shown is for an atomic fraction of 60%



Figure 5. The ideal isotope distribution for the center minor cluster of Figure 4. The isotope distribution is calculated for a atomic fraction of 60% sodium and 40% potassium cationized oligomers.

sodium cationization and 40% potassium cationization. Because the monoisotopic peaks are separated by only 2 u these two distributions overlap. This cationization ratio gives a fairly accurate representation of the observed isotope distribution. No attempts were made to mathematically find a best fit for the cationization ratio because this would involve integrating the separate peaks in Figure 5. Because these peaks do not return to baseline, some sort of fitting function or "de-smearing" algorithm would have to be applied first, which is not an easy task to perform with certainty. Experiments to greatly enhance the sodium adducts by the addition of sodium trifluoroacetate to the solution, as well as experiments to remove the alkali metals with chargeexchange beads followed by intentional sodium salt addition, were not successful. In either case no substantial change was observed in the resulting mass spectrum leading to an inability to isolate the effect of potassium adduction.

Discussion

For the condensation polymer derived from the silsesquioxane monomer considered here, the mass m of the *linear* oligomer having n repeat groups is given in units of u by the equation

$$m = (188.25 n) + p + 18 \tag{1}$$

where *n* is the number of repeat groups (which is equal to the number of silicon atoms per oligomer) whose mass is 188.25 u, *p* is the mass of the cation (either 23 u for sodium or 39 u for potassium), and 18 u is for the two $O_{1/2}H$ endgroups. It is easy to show that either a strictly linear or branched-linear polymer, which does not have one of the branches forming a closed loop with the oligomer itself, follows the above formula for mass.



Figure 6. A plot of the number of intramolecular closed loops, *t*, vs. the number of repeat units in a given oligomer, *n*. The solid circles represent the maximum intensity peak for each oligomer, and points marked with a × give the maximum and minimum number of observed loops. The solid line is a linear regression fit to the solid circles, whereas the dashed line is the expected value $t = \frac{1}{2}n + 1$ (for *n* even) for the fully condensed polyhedral structure. The sample showed an intermediate behavior between a branched linear structure and a fully condensed structure.

This formula would explain a single peak for each oligomer but cannot explain the major clusters that were observed and ascribed to intramolecular ring formation.

This suggests a modified version of eq 1 that includes intramolecular closed loop formation:

$$m = (188.25 n) + p - (18 t) + 18$$
⁽²⁾

where again n is the number of repeat units, p is the mass of the cation, t is equal to the number of closed loops in the molecule, and 18 u in the last term is for the added end groups.

Applying these concepts to the full mass spectrum, Figure 6 gives the number of closed loops t per oligomer with n repeat units, that is, t vs. n. The solid circles give the number of closed loops for the most intense minor cluster of each major cluster. (Recall that a major cluster corresponds to an oligomer with nrepeat units.) The points marked with an *x* are for the least intense peaks observed in each major cluster, that is, the weakest peaks found before the baseline noise overtakes the signal. The regression fit of the solid circles given by the solid line in Figure 6 has a slope of 0.273 with a standard uncertainty of 0.006, an intercept of 0.226 with a standard uncertainty of 0.192, and a correlation coefficient of 0.998. (The "standard uncertainty" is the estimated standard deviation of the fitted parameter.) The first observation is that the ratio of t/nremains roughly constant for all *n* with a value of about This suggests that the molecule is no more or less likely to interact with itself based solely on its size. Stated another way, the molecule may be fractal-like

with its closed-ring topology independent of molecular size [21]. A fully condensed polyhedral structure with an even number of repeat units will follow the equation $t = \frac{1}{2}n + 1$, whereas for an odd number of repeat units the governing equation is $t = \frac{1}{2}(n-1) + 1$. This is shown as a dashed line in Figure 6. On the other hand, a branched linear chain with no closed loops will have t = 0 (by definition), and thus t/n = 0, which is merely the abscissa of the graph. Therefore, in general it appears as if the specific silsesquioxane studied has on the average an assortment of closed loops and linear branches in each molecule. No fully condensed polyhedra were observed except at very low mass (n < 10) because the experimentally observed t/n ratio was on the order of $\frac{1}{4'}$ well below the fully condensed-polyhedron value of $\frac{4}{2}$ (for large *n*).

To further understand the rich detail about this polymer given by the mass spectrum, the autocorrelation function was applied to the data. The general use of correlation functions in mass spectrometry has been reviewed by Owens [22], although not in the context of polymer mass spectrometry. For the typical polymer mass spectrum, with its many periodic peaks, this is a natural mathematical operation to use. The autocorrelation function has a local maximum for each periodic separation of peaks in the original mass spectrum. It is defined as

$$G(L) = \sum_{i} S(m_i) S(m_{i+L})$$
(3)

where $S(m_i)$ is the signal intensity at m_i where m_i takes integer values of mass and L is the lag which was allowed to range from 0 to 1000 u. To obtain the correct autocorrelation function, the original signal, which has data points that are periodic in time, was interpolated with periodic points in mass. This is because the mass spectrum presented in "mass-space" must be interpolated to give evenly spaced points in mass. In time-offlight mass spectrometry the spectrum is derived from the instrument in "time-space" and the original data points are evenly spaced in time. A linear transform converts from time-space to mass-space. Because the density of points varies across the mass spectrum in relation to the peak widths there is a necessary decrease in point density upon interpolation. To overcome this, points at integer values of mass (1 u, 2 u, 3 u, . . .) were used. These are more widely spaced than the original time-space points. This results in a decrease in the data-set length. This also resulted in the loss of isotopic resolution in the autocorrelation function but also enhanced its "smoothing" effect on the data as will be seen. The point density used for interpolation was about one fifth the data point density of the original mass spectrum at low mass but rose to the same density at high mass. The specific effects of these autocorrelation parameters will be addressed in detail in a future publication. The full autocorrelation function for the data shown in Figure 2 with a lag L up to 1000 u is



Figure 7. The full autocorrelation function with a lag, L, from 1 to 1000 u for the mass spectrum shown in Figure 2. The autocorrelation coefficient is plotted vs. L in units of u.

shown in Figure 7. It largely replicates the original mass spectrum without much of the baseline noise. In this way it can be roughly thought of as a kind of "averaging." The peaks at 188.25 u are for correlations of $\Delta n =$ 1, those at 376.5 u are for $\Delta n = 2$, etc. Figure 8 is the low mass region of the autocorrelation function expanded. There are a series of five low mass peaks, marked with asterisks in the figure, starting at 18 u and each 18 u apart. This indicates that the number of closed loop molecules per oligomer should be about five, that is, there should be five peaks in each major cluster. Recall that this was shown in Figure 6 where the difference for each oligomer between the maximum and minimum number of closed loops observed, t, is about five. Likewise, in Figure 8 the number of peaks in the autocorrelation function around mass 188.25 u should



Figure 8. Low-mass-region detail of autocorrelation function shown in Figure 7. The asterisks show the five peaks shifted by 18 u found in each major cluster. The positions marked with an x are the 10 peaks found by correlations between major clusters 188.25 u apart.



Figure 9. Shift of the five-repeat-unit correlation function (dashed line) onto the single-repeat-unit correlation function (solid line) showing the 18 u offset between the maximum peak of each group. See text for details.

be about 10, marked with the symbol x in the figure, that is, correlations of the five peaks of two adjacent major clusters. Finally, because the spacing used in this autocorrelation function is 1 u, the isotopic resolution that should be apparent at 1 u is not seen, instead autocorrelation within the minor peaks is simply smeared out.

Figure 9 shows the autocorrelation function centered at 941.25 u [corresponding to correlations over five repeat unit masses, i.e., 5(188.25 u) = 941.25 u] superimposed over the autocorrelation function at 188.25 u. This was done simply by subtracting 753.0 u [4(188.25 u)] from the autocorrelation function centered at 941.25 u. Notice that the maximum peak for 941.25 u group is 18 u to the left of the maximum peak for the 188.25 u group. This indicates that as four repeat units are added to an oligomer (n = n + 4) one added closed loop is formed per molecule on average (t = t + 1). Once again this can be seen from the slope of the line in Figure 6: for each step of *n* equal to four, *t* is increased by about one. (Strictly, because experimentally t/n =0.273, an increase in n of 4 should yield an increase in *t* of 1.1. This is hinted at in the peak heights of Figure 9.) This provides another view that the molecule is selfaffine in that adding additional repeat groups changes proportionately the number of closed loops. In contrast, a strictly linear polymer undergoing a random walk crosses itself in proportion to the square root of the number of repeat units, i.e., $t \approx \sqrt{n}$. This behavior is clearly not seen in this material.

Conclusions

The three-dimensional structure of a complex silsesquioxane has been studied by MALDI-TOF mass spectrometry. Four distinct levels of molecular structure could be observed from the mass spectrum. The overall shape indicates a condensation polymer. The major cluster repeat distance was found to be 188.25 u as expected from the synthesis chemistry. Each major cluster had about five peaks separated by 18 u indicating the loss of water and the formation of intramolecular closed loops. The isotopic resolution of the minor clusters demonstrated that cationization had occurred by adventitious sodium and potassium in about equal percentages. Autocorrelation on the data indicated that the percentage of closed loops did not vary with oligomer size and that the molecular structure was intermediate between branched linear and simple ladder structure with no evidence that fully condensed structures had been formed in significant amounts.

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