Analysis by Mass Spectrometry of the Hydrolysis/Condensation Reaction of a Trialkoxysilane in Various Dental Monomer Solutions

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ABSTRACT: 3-Methacryloxypropyltrimethoxysilane (MPTMS) was converted to silsesquioxane oligomers by hydrolysis/condensation in three dental monomer solutions. The molecular mass distribution and molecular structures of these oligomers was studied by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. Each dental monomer imparted distinct characteristics on the oligomeric silsesquioxane produced. Ethoxylated bisphenol A dimethacrylate (EBPADMA) produced low-mass oligomer silsesquioxanes that showed complete hydrolysis and a very high degree of intramolecular condensation (i.e., there were no methoxy and few silanol groups remaining on the oligomers). 1,6-Bis(methacryloxy-2-ethoxycarbonylamino) 2,4,4-trimethylhexane also produced fully hydrolyzed oligomeric silsesquioxanes but with twice the average molecular mass as the EBPADMA. Finally, triethylene glycol dimethacrylate produced higher mass oligomeric silsesquioxanes than EBPADMA even though it showed incomplete hydrolysis. The degree of hydrolysis increased with increasing mass, as did the degree of intramolecular condensation. Oligomers with degrees of polymerization below 8 were poorly hydrolyzed and showed little if any intramolecular condensation. Those with degrees of polymerization of 9 or greater were almost completely hydrolyzed with a high level of intramolecular condensation. © 2005 Wiley Periodicals, Inc.* J Appl Polym Sci 99: 1842–1847, 2006

Key words: additives; MALDI; mass spectrometry; resins

INTRODUCTION

The compound 3-methacryloxypropyltrimethoxysilane (MPTMS) is commonly used to surface-modify (silanize) glass fillers for the mechanical reinforcement of dental restoratives and other acrylic-based composites. Surface modification of the glass filler phase can be achieved by the addition of MPTMS directly to, or in solution with, the glass fillers in the presence of moisture. In-solution silanization is followed by removal of the solvent. The byproducts of the hydrolysis/condensation reaction, water and methanol, also need to be removed. To reduce the number of preparation steps in the formation, the dental restorative composite MPTMS can be dissolved directly in the matrix-forming monomer system to bring about in situ silanization of the glass phase. However, it is plausible that the addition of MPTMS to the resin may also promote unwanted interactions involving the monomeric components, especially if they contain dissolved water and/or hydroxylated functionalities. Currently used dental acrylic monomers, even those without hydroxyl functional groups, have nonhydroxyl polar groups in their chemical structures that can serve as sites for moisture absorption. Previous studies using IR spectroscopy have shown that MPTMS and other trialkoxysilanes can form oligomeric silsesquioxanes by a complex sequence of hydrolysis/condensation reactions initiated by the presence of moisture.[1] In this study, we investigated the reaction of MPTMS in three commonly used dental monomers by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS), focusing on the in situ formation of oligomeric silsesquioxanes, which are a byproduct of the silanization reaction.[2–9]
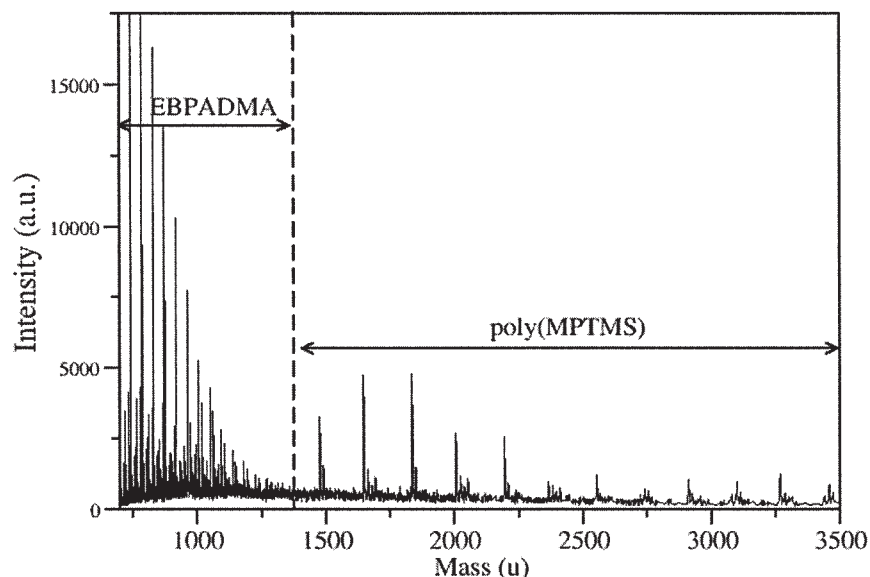
Figure 1 Mass spectrum of 3-MPTMS polymerized by hydrolysis/condensation in EBPADMA. The low-mass region shows EBPADMA monomers with various numbers of ethylene oxide groups with the monomer unit itself and dimers and trimers of the monomer. The higher mass region shows the poly(MPTMS) silsesquioxane.

EXPERIMENTAL

The dental monomers used in this study were obtained from Esstech, Inc. (Essington, PA) They were: ethoxylated bisphenol A dimethacrylate (EBPADMA; lot number 535-32), 1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA or urethane dimethacrylate; lot number PB-2439), and triethylene glycol dimethacrylate (TEGDMA; lot number 550-39). The silane, MPTMS, was obtained from Sigma-Aldrich, Inc. (St. Louis, MO), and was used as received. MPTMS was dissolved in the various monomers at 22°C at a molar ratio of 1.5 : 1 monomer/MPTMS. No effort was made to dry the dental monomers or to carry out the reaction in a dry environment because water is essential for the initiation of the hydrolysis/condensation polymerization reaction. After dissolution, the solutions were heated at 60°C in tarred open vials until no further mass loss was observed, 30 d for EBPADMA and UDMA and 50 d for TEGDMA. The hydrolysis reaction involves cleavage of the $-Si(OCH_3)_3$ bonds, as shown in the following simplified scheme:

$$R-Si(OCH_3)_3 + xH_2O \rightarrow$$
$$R-Si(OH)_x(OCH_3)_{3-x} + xCH_3OH$$
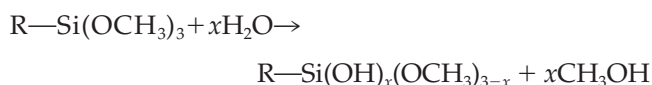
where $x = 1–3$. The silanol-containing products of the hydrolysis reaction condense in to form dimers, trimers, tetramers, and so on. For example, the trifunctional silanol could react in the following way:

$$nR-Si(OH)_3 \rightarrow$$
$$[R-Si(OH)_2-O-Si(OH)_2-R]_n - nH_2O$$
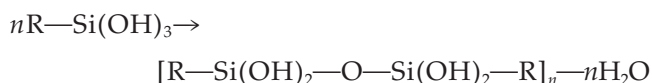
to form the minimally condensed silsesquioxane polymer. Complete condensation, that is, complete removal of all silanol groups, yields a polymer with the repeat unit: $[R-SiO_{3/2}]_n$. Note that attachment to the glass surface (silanization) occurs via the reaction with surface silanol groups and was not studied here.

The mass spectrometry was performed on a Bruker Daltonics (Billerica, MA) REFLEX II instrument in reflectron mode with delayed extraction. Ions were generated with a 337-nm wavelength nitrogen laser with a pulse duration on the order of 3 ns and an average energy of approximately 5 μJ spread over a spot size of 100 × 100 μm. All data shown are for positive ions: negative ion spectra typically produced only matrix ions and their clusters (e.g., M^-, $2M^-$). The instrument was periodically calibrated with bovine insulin with the $[M + H]^+$ and $[M + 2H]^{+2}$ peaks. 2,5-Dihydroxybenzoic acid or 3,5-dimethoxy-4-hydroxycinnamic acid (sinapinic acid; both from Sigma-Aldrich) were used as matrix-assisted laser desorption/ionization (MALDI) matrices. The data presented were taken by the addition of the MALDI matrix directly to the dental monomer solution. Solution concentrations were typically 45 mg/mL for the matrix. These solutions were hand-spotted onto the target plate.

RESULTS AND DISCUSSION

Figure 1 shows the central portion of a typical mass spectrum for MPTMS polymerized in EBPADMA. Silsesquioxane oligomers were detected from 1475 u to above 9000 u, where u is the symbol for the atomic mass unit and is equal to one-twelfth the mass of ^{12}C.
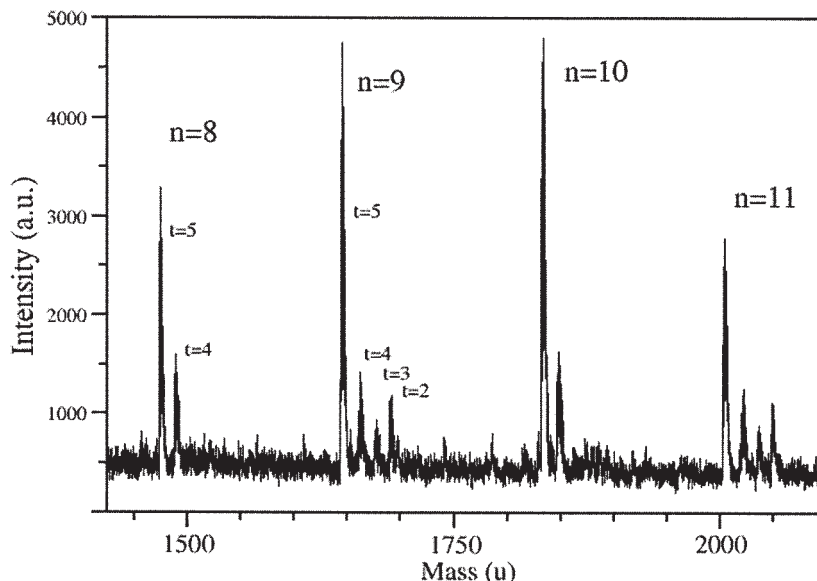
Figure 2 Detail of the spectrum in Figure 1 for oligomers with $n = 8–11$. Selected values for t are also shown.

(Uncertainties in mass from repeatability studies are on the order of ± 0.25 u.) The lowest mass was for a silsesquioxane with a degree of polymerization (n) equal to 8. Below this lower limit were peaks representing oligomers found in the EBPADMA. The EBPADMA itself could have various numbers of ethylene oxide groups. This gave rise to the characteristic 44-u ethylene oxide repeat spacing shown. In addition, the EBPADMA (nominal mass = 496.6 u when three ethylene oxide units are present) also polymerized into dimers and trimers; this gave rise to masses up to about 1350 u. Interestingly, no silsesquioxane oligomers were observed for $n < 8$. The upper limit was determined by the finite signal-to-noise ratio. The overall spectrum bore the characteristic shape of a condensation polymer with higher abundances of low molecular mass molecules tapering off gradually in intensity at higher molecular masses. No evidence for the reaction of the MPTMS with the EBPADMA was observed. For the produced condensation polymer, the number-average molecular weight (M_n) was 2530 g/mol, and the weight-average molecular weight (M_w) was 3000 g/mol. (All of the mass moments reported had an expanded standard uncertainty of ± 200 g/mol).

Figure 2 shows the low-mass silsesquioxane region of the spectrum in Figure 1 and shows the four lowest mass oligomers, $n = 8–11$. It shows the spectrum to be made up of groups of two peaks for even n values and four peaks for odd n values. The nominal mass separation between two major clusters was 188.26 u, which was equal to the isotope-averaged mass of the repeat group [$RSiO_2H$], where R is 3-methacryloxypropyl, that is, two Si—O—Si bridges and one terminal —SiOH group per repeat group, which was broadly

indicative of a branched or linear material. The nominal spacing of 188.26 u further indicated that the oligomers were singly charged; if, for example, they were doubly charged, the mass spacing would be halved. The peaks in each grouping were separated by 18 u. This was indicative of the loss of one molecule of water, which occurs when two dangling —SiOH groups in close proximity within a given molecule react intramolecularly to form a Si—O—Si bridge. The maximum possible mass of an oligomer with n repeat units occurs when every silicon atom has one silanol group in addition to one R group and two bridging oxygen atoms. Two bridging oxygen atoms are the minimum number necessary for the formation of a polymer; that is, conceptually, polymerization requires difunctionality at a minimum. Thus, the repeat unit in this case could be given as [$RSi(O_{1/2})_2OH$]. For an oligomer with n repeat units, the mass of the heaviest oligomer was n times the mass of this difunctional oligomer (plus the mass of the Na^+ ion and the two —OH end groups). This heaviest oligomer was the linear or branched structure. However, the highest intensity peak generally does not occur at the maximum possible mass. Instead, lower mass peaks are more intense. These peaks correspond to the loss of water as a pair of Si—OH groups react. This, in turn, immediately indicates that intramolecular reactions are occurring. If intermolecular reactions were occurring, the value of n would change, and a new, higher mass oligomer would be formed.

In the mass spectrum shown in Figure 2, each loss of 18 u closed a loop in the molecule, which moved it away from a highly branched or linear structure toward a closed polyhedron. In the limit of the loss of all silanol groups, a fully condensed polyhedral structure
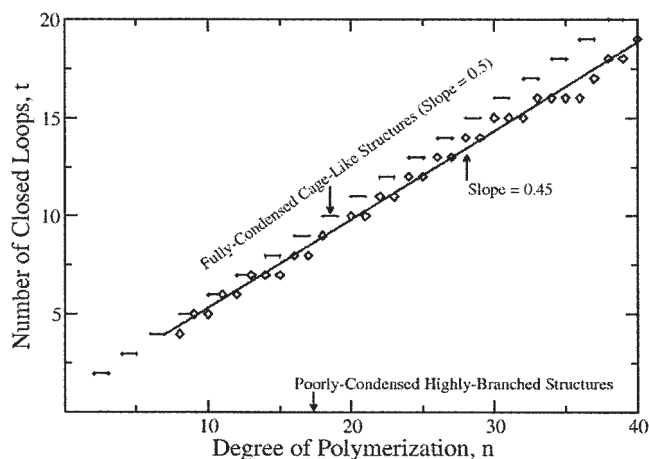
Figure 3 t versus n for the data in Figure 1. The stair-step solid line shows the maximum t possible. The abscissa of the graph is where the points would be in the absence of any intramolecular condensation.

resulted. For example, for $n = 8$, one possible fully condensed structure is a cube with silicon atoms at each corner and Si—O—Si linkages for the cube edges. This involves the loss of four water molecules, which we designate here as a degree of intermolecular condensation (t) of 4. The additional peak in the $n = 8$ cluster occurred at 18 u above the $t = 4$ peak and was for $t = 3$. This corresponded to two —SiOH groups replacing a —Si—O—Si— bridge. For the case of $n = 9$, there had to always be at least one —SiOH end group because 9 is an odd number. As shown in Figure 2, there were four peaks for the $n = 9$ grouping corresponding to one, three, five, and seven —SiOH groups. Molecules with odd n values evidently had greater difficulty forming fully condensed structures.

t for the most intense peak for a given n can be taken as a measure of the degree of intramolecular condensation for a given silsesquioxane. This is shown in Figure 3, where the solid circles show the number of closed loops for the most intense minor cluster of each major cluster. The value of t versus n as a function of n was linear, which indicated that the relative number of closed loops, or t, did not change as the molecular mass increased. This suggests that the local environment was the same with regard to t at any place in the molecule and was independent of the size of the molecule. However, the type of mass spectrometry performed here did not give any information on the specific topology of a given oligomer, only whether or not it existed in detectable quantities. The regression fit of the open diamonds given by the solid line in Figure 3 had a slope of 0.45. The stair-stepped line in Figure 3 had a slope of $\frac{1}{2}$, which was the expected t/n ratio for fully condensed oligomers and followed the equations $t = \frac{1}{2}n + 1$ for even n values and $t = \frac{1}{2}(n - 1) + 1$ for odd n values. Conversely, for a highly branched mol-

ecule showing no condensation, t was equal to 0, which corresponded to the abscissa in Figure 3.

Figure 4 shows the t versus n plot for MPTMS polymerized in a solution of UDMA. The behavior was essentially the same as in EBPADMA with the same t (slope = 0.45). Oligomers were seen from 1828 u ($n = 10$) up to over 10,000 u ($n > 60$). The polymerized MPTMS had a M_n value of 4140 g/mol and a M_w value of 4600 g/mol, which were somewhat higher than those of the silsesquioxane polymerized in EBPADMA.

Figure 5 shows the mass spectrum of polymeric product of MPTMS polymerized in TEGDMA. Oligomers of silsesquioxanes were detected from 675 u ($n = 3$) to above 5000 u ($n > 30$). The polymerized MPTMS had a M_n value of 2310 g/mol and a M_w value of 2640 g/mol. The oligomers at low n values ($n = 3$ and 5) had extremely low degree of hydrolysis (q) values and, therefore, near-zero t values. In the middle mass range ($n = 6$–8), there was a change toward more hydrolysis along with greater intramolecular condensation. At the higher mass range ($n \geq 9$), there was almost complete hydrolysis and a high t.

Figure 6 shows the mass range for $n = 10$. The abundance of peaks arose from two effects. First, this material was not fully hydrolyzed; that is, there were still —SiOCH$_3$ groups present in addition to the —SiOH and —Si—O—Si— groups found in the first two samples. The sample then effectively became a copolymer with three monomers, where each monomer type corresponded to one of these three groups occupying a bond on the silicon atom. (Of the other three positions, two had to be of the Si—O—Si type to form a polymer, and one was the methacryloxypropyl group, —R.) The hydrolysis reaction (Si—O—CH$_3$ → Si—O—H) led to a net loss in oligomer mass of 14 u (i.e., the mass of CH$_2$). We call this value q. The maximum value for q was $n + 2$; this occurred when all
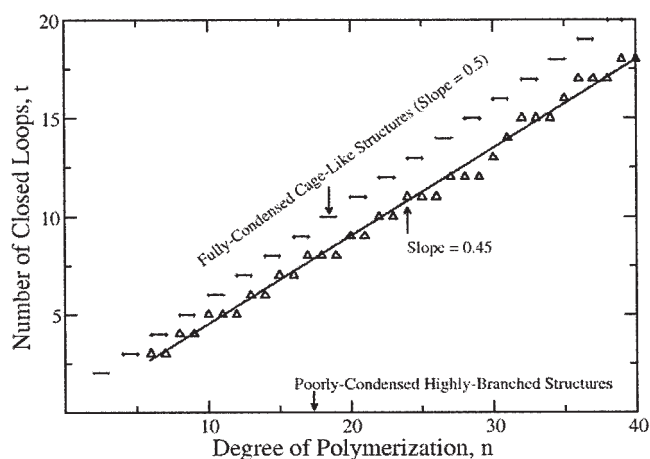

Figure 4 t versus n for MPTMS polymerized by hydrolysis/condensation in UDMA.
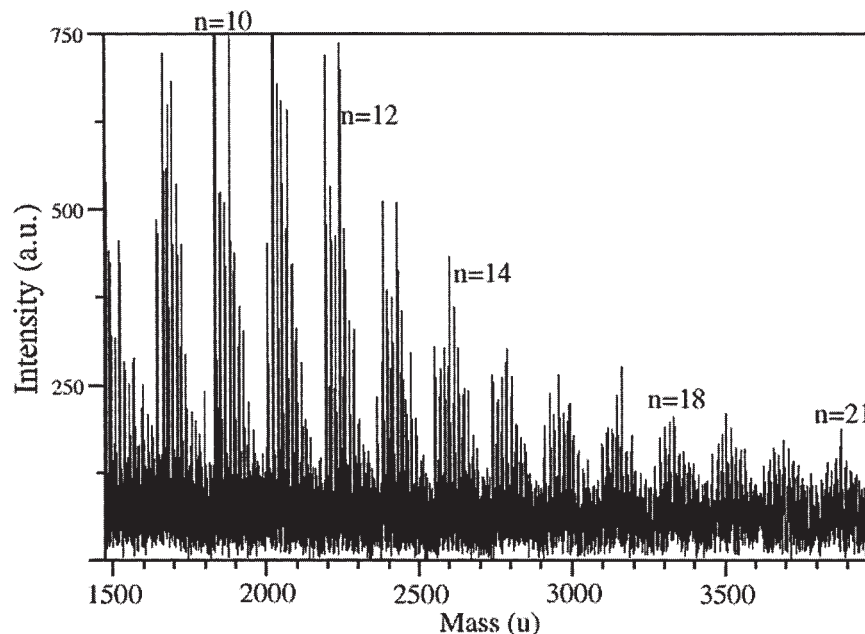
Figure 5 Mass spectrum of MPTMS polymerized by hydrolysis/condensation in TEGDMA with selected n values labeled.

residual methoxy groups had been hydrolyzed. For n = 10, the maximum q was 12. The condensation reaction (Si—O—H + Si—O—H → Si—O—Si + H_2O) led to a loss in oligomer mass of 18 u (i.e., the mass of H_2O). Recall that we call this t. The maximum t was $(n/2)$ + 1. For n = 10, the maximum t was 6. The abundance of peaks also arose from potassium in the preparation from an unknown source. The potassium competed with the sodium, also present, to create silsesquioxane oligomers that were either K^+ or Na^+

cationized. This effectively doubled the number of peaks observed. The mass of sodium was nominally 23 u, and the mass of potassium was nominally 39 u for a difference in cation mass of 16 u. Thus, the abundance of peaks was due to shifts of 14 u for hydrolysis, 16 u for cation species, and 18 u for condensation and to shifts of 1 u for the isotope distribution for each oligomer. For oligomers in this mass range, four or five isotopes peaks were generally visible above the noise. With this many possible combi-
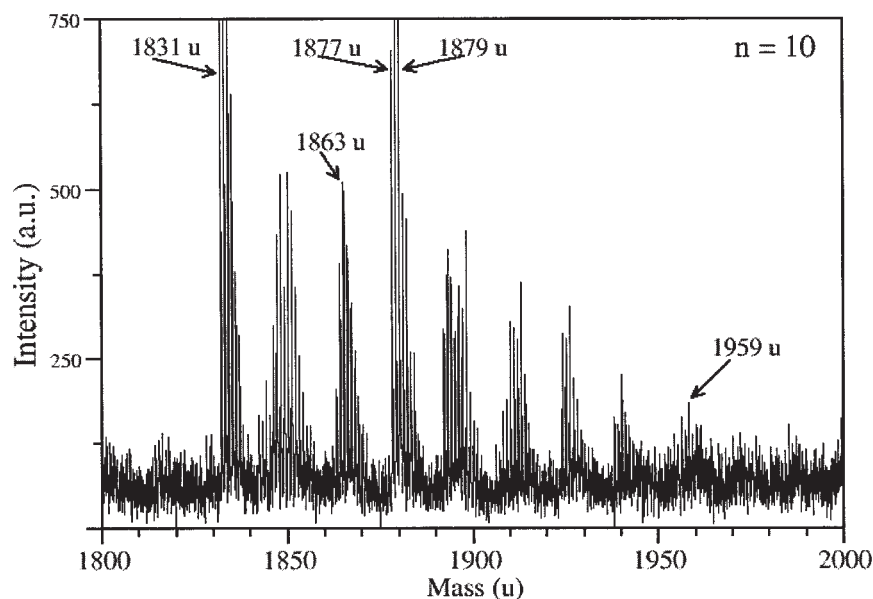

Figure 6 Detail of the spectrum in Figure 5 for oligomers with n = 10. Oligomers with higher q values and high t values are in the left of the graph. Compare this figure to the peak positions listed in Table I.

TABLE I
All Possible Oligomer Masses for MPTMS Polymerized in TEGDMA with $n = 10$ and $q = 6$ or Greater

	$t = 0$	$t = 1$	$t = 2$	$t = 3$	$t = 4$	$t = 5$	$t = 6$
Na^+							
$q = 12$	1921	1903	**1885**	**1867**	<u>**1849**</u>	<u>**1831**</u>	1813
$q = 11$	1935	1917	**1899**	**1881**	<u>**1863**</u>	<u>**1845**</u>	—
$q = 10$	1949	**1931**	**1913**	**1895**	<u>**1877**</u>	1859	—
$q = 9$	1963	**1945**	**1927**	**1909**	**1891**	—	—
$q = 8$	1977	**1959**	**1941**	**1923**	1905	—	—
$q = 7$	1991	1973	1955	1937	—	—	—
$q = 6$	2005	1987	1969	1951	—	—	—
K^+							
$q = 12$	1937	1919	**1901**	**1883**	<u>**1865**</u>	<u>**1847**</u>	1829
$q = 11$	1951	1933	**1915**	**1897**	<u>**1879**</u>	1861	—
$q = 10$	1965	1947	**1929**	**1911**	**1893**	1875	—
$q = 9$	1979	1961	**1943**	**1925**	**1907**	—	—
$q = 8$	1993	1975	**1957**	**1939**	1921	—	—
$q = 7$	2007	1989	1971	1953	—	—	—
$q = 6$	2021	2003	1985	1967	—	—	—

Values in bold indicate that the oligomer was observed in the mass spectrum above the baseline noise. Underlined values indicate particularly intense peaks. Values for sodiated and potassiated peaks are shown. Compare these values to those in Figure 6.

nations, peak overlap severely limited our ability to draw quantitative results from the data.

Table I shows the nominal mass for all of the possible peaks for the spectrum of Figure 6. (The positions marked with a — are oligomers that were not possible.) The numbers in bold indicate the masses that were actually observed. The underlined numbers indicate particularly intense masses. The top half of Table I shows oligomers with a sodium cation, whereas the bottom shows oligomers with a potassium cation. Table I covers a q range of 6–12 because oligomers with a lower q were not observed.

CONCLUSIONS

MPTMS polymerized by hydrolysis/condensation in the solutions of three dental monomers was studied by MALDI-TOF MS. When MPTMS was polymerized in EBPADMA, the oligomeric silsesquioxane had a relatively low average molecular mass but a very high level of intramolecular condensation. When MPTMS was polymerized in UDMA, the average molecular mass was about twice as great, but the same t was found as for the EBPADMA product. Finally, when MPTMS was polymerized in TEGDMA, the average molecular mass was low as was t. In this case, mass

spectrometry revealed that the original MPTMS was not fully hydrolyzed. This lack of complete hydrolysis led to a low molecular mass and a low t. Additionally, it produced a spectrum so complex that quantification was not possible.

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