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Characterization of light-cured dimethacrylate resins modified with silsesquioxanes

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Abstract Methacrylate-functionalized silsesquioxanes (SSQO) were synthesized by the hydrolytic condensation of 3-(methacryloxypropyl) trimethoxysilane (MPTMS) using dimethacrylate monomers as reactive solvent. Resins containing about 40 wt% SSQO displayed a modest increase in viscosity compared with the unmodified methacrylate monomer. This is attributed to a dilution of the reacting medium, which discourages bimolecular reactions that lead to the generation of high-molar mass oligomers and, consequently, prevents undesired increases of viscosity. Substitution of monomer with SSQO reduced the volumetric shrinkage during photopolymerization. The amount of leachable monomer detected in formulations containing SSQO was markedly reduced. This indicates that the unreacted monomer exists mainly as pendant chains instead of free leachable monomer. The presence of different proportions of SSQO in the methacrylate monomer resulted in no apparent change in the flexural modulus and in a modest decrease in the compressive yield stress of the polymerized materials. From results presented in this research, it emerges that methacrylate monomers modified with SSQO are attractive for applications that require reduced volumetric shrinkage and long storage periods, such as light-cured dental restorative composites.

Introduction

Light-cured dental composites have been available for over four decades. In general, they have shown relatively satisfactory clinical results. However, one major limitation of composite resins is their relatively high volumetric shrinkage during polymerization [1, 2]. This shrinkage contributes to the development of contraction stresses that often lead to bond failure and recurrent caries. In addition, the polymerization of dental resins in the absence of external heating leads to glassy resins in which only part of the available monomer is reacted. If undesired high levels of leachable residual monomer are present, the biocompatibility of the dental composite can be compromised. Therefore, the main efforts to improve the performance of composites for dental fillings center on reducing the volumetric shrinkage and the leachable monomer content without sacrificing other useful properties. Recently, the development of dental restorative composites has focused on the use of organic–inorganic hybrid nanocomposite materials [3–13].

Nanocomposite materials based on polyhedral oligomeric silsesquioxanes (POSS) are receiving increasing attention because of the unique features derived from their hybrid nanometer-scale architecture. As illustrated in Scheme 1, POSS molecules are cage-like organic–inorganic structures, described by the general chemical structure $(RSiO_{3/2})_n$, which consist of a Si–O–Si inorganic cage surrounded by an organic substituent (represented by R). The inorganic cage may be a fully condensed closed or open structure. The diameter of these structures ranges from 1 to 3 nm, depending on the number of silicon atoms in the central cage and the peripheral substitution groups surrounding this core. The POSS unit can be viewed as a nanoparticle for both its size and filler function or a well-defined macromonomer for its ability to undergo polymerization. The presence of

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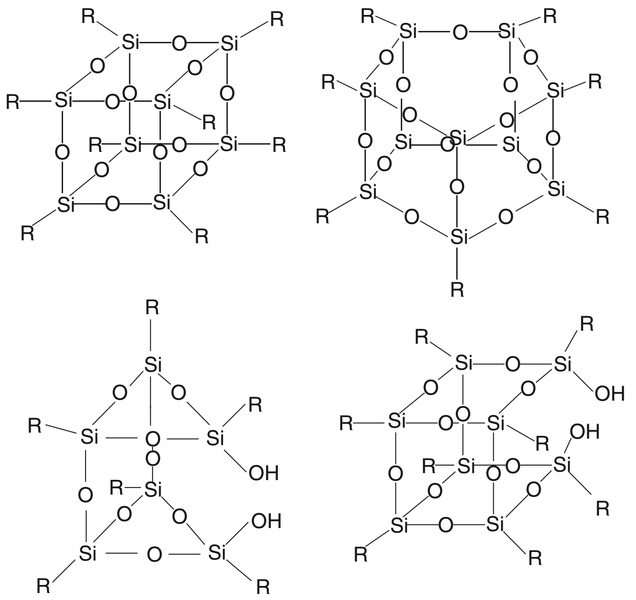


Scheme 1 Typical POSS structures of open cage and closed cages

peripheral reactive organic substituent as illustrated in Scheme 1 allows subsequent polymerization reactions to cross-link the individual inorganic condensates and embedding them into an organic matrix. POSS were successfully used with the main polymer groups such as epoxy resins [14] and poly(methyl methacrylate) [15, 16] showing improved mechanical properties as well as reduced flammability. Particularly interesting is the application of silsesquioxanes to improve thermal and fire resistance of polymers, thanks to their ceramisation upon heating [17].

The purpose of the present study was the synthesis and characterization of methacrylate-functionalized silsesquioxanes (SSQO), which were incorporated to methacrylate monomers commonly used in dental restorative resins. The SSQO were characterized by size exclusion chromatography (SEC), Fourier-transform infrared spectra (FTIR), matrix-assisted ultraviolet laser desorption ionization time of flight mass spectra (UV-MALDI-TOF MS), and ^{29}Si NMR spectroscopy. The methacrylate monomers modified with SSQO were photopolymerized, and the performance of the resulting nanocomposites was assessed by measuring the volumetric shrinkage during polymerization, the leachable monomer content, the flexural modulus, and the compressive yield strength.

Experimental

Materials

The resins were formulated from blends of {2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane} (bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) at mass fractions 70:30 bis-GMA/TEGDMA (Bis-TEG). bis-GMA (Esstech, Essington, PA, USA) and TEGDMA (Aldrich) were used as received. The trialcoxysilane 3-(methacryloxypropyl) trimethoxysilane (MPTMS, Sigma-Aldrich), formic acid 98 wt% (Sigma-Aldrich), and tetrahydrofuran solvent (THF, Sigma-Aldrich) were used as received. The structure of the monomers and MPTMS are depicted in Scheme 2. The resins were activated for visible light by the addition of 1 wt% camphorquinone (Sigma-Aldrich) in combination with equimolar proportions of ethyl-4-dimethyl aminobenzoate (Sigma-Aldrich).

Synthesis and characterization of SSQO

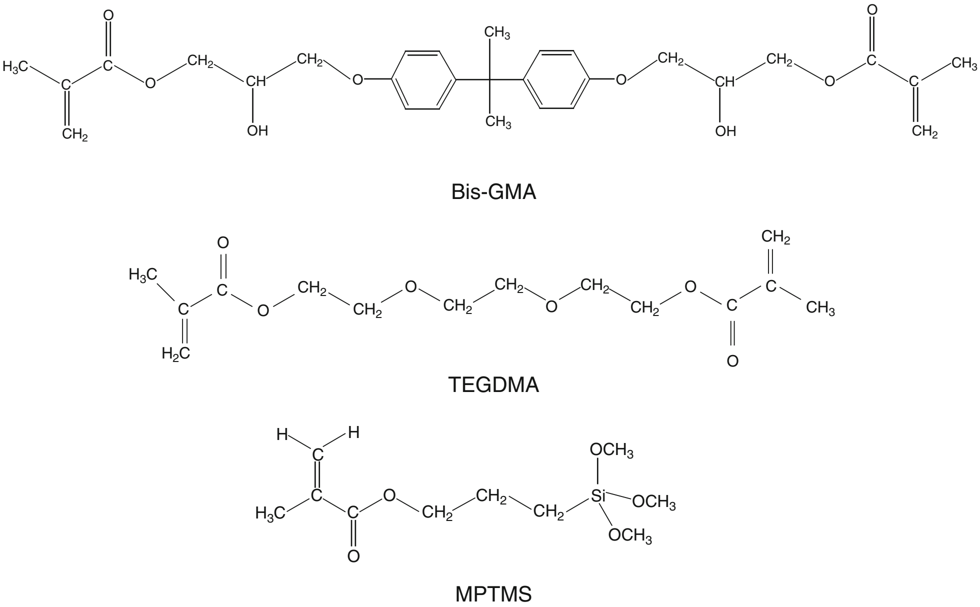
The hydrolytic condensation of MPTMS silane was performed using the following methods: (a) in bulk at room temperature (20 ± 2 °C) and (b) in a 50:50 weight ratio MPTMS/BisTEG at 60 °C. In both methods, formic acid (HCOOH) 98% in a molar ratio HCOOH/Si = 3 was used. In method B, the reaction was carried out in open vials immersed in an oil bath at 60 °C.

Size exclusion chromatography (SEC) was performed with a Knauer K-501 device using a set of three Phenogel columns: 50, 100, and M2. For high-molar mass oligomers, a fourth column Waters styragel 10^4 was added. A refractive index detector (Knauer K-2301) or an UV detector (Knauer S2600) was used. THF was used as a carrier at 1 mL/min. Polystyrene standards were employed for molecular weight calibration.

Fourier-transform infrared spectra (FTIR) were obtained using a Genesis II-Mattson device in the transmission mode. Samples were cast from a solution on NaCl windows.

Matrix-assisted ultraviolet laser desorption ionization time of flight mass spectra (UV-MALDI-TOF MS) were obtained using an Ultraflex II TOF/TOF Bruker Daltonics GmbH (Leipzig, Germany), equipped with a pulsed Nd-Yag laser ($\lambda = 355$ nm). TOF analyzer was used at 25 kV, and ions were obtained by irradiation just above the threshold laser power. Samples were measured in both positive and negative ion modes. Usually 100 spectra were accumulated. Several chemicals were tested as matrices: 2,5-dihydroxybenzoic acid (DHBA), α-cyano-4-hydroxycinnamic acid (CHCA), and 9H-pyrido[3,4-b]indole (nor-harmane, nHo). These chemicals were purchased from Sigma-Aldrich. The best results were obtained using nHo in negative linear ion mode with laser power in the 38–42% range. Several proteins [des-Arg1-Bradikinin, Angiotensin I, Glu1-Fibrinopeptide B, ACTH (1-17) clip, ACTH (18-39) clip and ACTH (7-38) clip (Sigma)] dissolved in aqueous 0.1% TFA (Merk) were used for calibration purposes with CHCA as matrix. The matrices (2 mg/mL) were dissolved in

Scheme 2 Structure of the monomers and silane used in the synthesis of SSQO



acetonitrile (Aldrich, HPLC grade):water (1:1 v/v), and the analyte solutions were prepared in THF (4 mg/mL). Two methods of sample preparation were used. In method A (sandwich), 0.5 μL of the matrix solution was placed on the probe, and the solvent was evaporated at room temperature. This solid deposit was covered with 0.5 μL of the analyte solution, and the solvent was removed. This was followed by two additional coatings with the matrix solution. In method B, matrix and analyte solutions were mixed in different volumetric ratios, and two coatings (0.5 μL each) were performed. Method A gave the best results. In all cases, the samples were prepared without salt.

^{1}H NMR spectra were recorded with a Bruker AC200 spectrometer operating at 200.133 MHz. Samples were dissolved in deuterated chloroform. Chemical shifts are reported as δ units (ppm) relative to tetramethylsilasane. ^{29}Si NMR spectra were recorded with a Bruker AM500 spectrometer operating at 99.359 MHz. Samples were dissolved in deuterated acetone.

The viscosity of the resins was measured at 30 °C using an Anton Paar rheometer (model Physica MCR-301) provided with a CTD 600 thermo chamber. A parallel-plate configuration (diameter $D = 25$ mm, gap $H \approx 1$ mm) was used in oscillatory mode at a frequency range of 0.1–100 s^{-1}. All the tests were performed using small strains to ensure the linearity of the dynamic response. All runs were repeated using different samples.

Degree of conversion, volumetric shrinkage, and leachable residual monomer

The light source employed to cure the resins was a light-emitting diode (LED) unit (Ultralume2, Ultradent, USA) with its emittance centered at 470 nm and light irradiance 400 mW/cm^2. FTIR spectra were acquired with a Genesis II Mattson FTIR (Madison, WI, USA). The near-infrared spectroscopy (NIR) spectra were acquired over the range 4500–7000 cm^{-1} from 16 co-added scans at 2 cm^{-1} resolution. Unfilled resins were sandwiched between two glass plates separated by a 2-mm rectangular rubber spacer, which were tightly attached to the sample holder using small clamps. With the assembly positioned vertically, the light source was placed in contact with the glass surface. The specimens were irradiated at regular time intervals equal to 10 s. Spectra were collected immediately after each exposure interval. The background spectra were collected through an empty mold assembly fitted with only one glass slide to avoid internal reflectance patterns. The conversion profiles were calculated from the decay of the absorption band located at 6165 cm^{-1} [18, 19]. Three replicates of each of the resins were used in the measurement of conversion.

A noncontact, Fizeau-type interferometric method for monitoring the shrinkage development during photopolymerization was employed. Details of the technique were reported elsewhere [2]. The technique enables quantitative measurements providing data for the continuous shrinkage evolution during photopolymerization. The light source employed in the conversion measurements (Ultralume2, Ultradent) can only be operated for short (ca. 20 s) periods. Conversely, the light source employed in shrinkage studies was assembled from an LED (OTLH-0090-BU, Optotech Inc.), which functions in a continuous fashion. The emittance of this LED was centered at 470 nm and its irradiance was 12.8 mW/cm^2. It is worth noting that high-intensity LEDs units consist of arrays of multiple LEDs and are not prepared to operate continuously during prolonged times (around 300 s). Conversely, the simple geometry of sources assembled from a single LED can be operated in a continuous fashion and their intensity can be easily and accurately set by varying the electrical voltage through the semiconductor. Unfortunately, the described benefits are accompanied with a lower irradiance compared with high intensity LEDs. The main effect is that the timescales will be reduced.

The residual monomer content was determined by SEC. Specimen disks (diameter 15 mm, thickness 3 mm) were irradiated for 60 s on each side at 400 mW/cm^2 (LED Ultralume2) and were immediately immersed in THF at room temperature. After 4 days, samples of THF solvent were analyzed by SEC. The mass of leachable residual monomer was calculated from the area of the peak and a calibration curve constructed from solutions containing different amounts of monomer. All determinations were conducted in triplicate.

Mechanical characterization

Flexural and compressive tests were carried out at room temperature (20 ± 2 °C) in an Instron testing machine (Model 4467) at a crosshead displacement rate of 2 mm/min. The flexural modulus, E, was measured in three-point bending using sample dimensions recommended by the ISO 4049: 2000(E): (25 ± 2) mm × (2 ± 0.1) mm × (2 ± 0.1) mm. A minimum of five specimens were prepared for each system by photo curing the specimens at 400 mW/cm^2 for 1 min on each side. Prior to mechanical testing, the specimens were stored at room temperature for about 24 h. Multifunctional methacrylates are brittle in nature. Like other brittle materials, they are weak in tension but quite strong in compression and capable of yielding under uniaxial compression. Therefore, the yield strength was determined in compression. Samples for compression testing were made by injecting the resins into polypropylene cylindrical disposable molds of 6 mm internal diameter. Samples were irradiated at 400 mW/cm^2 for 1 min on each side. The shrinkage during polymerization facilitated the removal of the specimens from the polypropylene mold. Prior to mechanical testing, the specimens were stored at room temperature for about 24 h. Cylindrical specimens having a length/diameter ratio of 1.5 were deformed between metallic plates lubricated with molybdenum disulfide. The deformation was calculated directly from the cross-head speed. True stress–deformation curves were obtained by dividing the load by the cross-sectional area. The compressive yield strength, σ_y, was determined at the maximum load. The results of E and σ_y are the average of five and four measurements, respectively.

Results and discussion

Synthesis of SSQO

Tetrafunctional alkoxysilanes form densely crosslinked silica structures SiO_2, whereas trifunctional alkoxysilanes polymerize to branched polysilsesquioxanes of the general formula $[RSiO_{3/2}]_n$. Polymerization of MPTMS consists in hydrolysis and condensation of methoxysilane groups and results in the formation of silsesquioxane structures $RSiO_{3/2}$.

$$nR - Si - (OCH_3)_3 + 1.5nH_2O \rightarrow \left[RSiO_{3/2}\right]_n + 3nCH_3OH \quad (1)$$

where R is a methacrylate group. The formic acid serves the multiple roles of solvent, water source, and catalyst for both hydrolysis and condensation reactions. The initial presence of water is not required because it is generated during the reaction [20].

The hydrolytic condensation of MPTMS in bulk at 50, 60, and 70 °C resulted in gels after around 4–10 days of reaction; therefore, the synthesis of SSQO in bulk was performed at room temperature (20 ± 2 °C). Although this method prevented the gelation of the systems, the development of oligomeric species was very slow. SEC chromatograms showed that the MPTMS monomer disappeared after 10 days of reaction. This is in agreement with a previous research by Piana et al. [21], who found that in the presence of 1-methylimidazol, methacrylic acid, or (dimethylamino)ethanol, the MPTMS monomer disappeared after 7, 13, or 21 days, respectively. In order to increase the reaction rate and avoid the gelation of the reacting system, the hydrolytic condensation of MPTMS was carried out at 60 °C using BisTEG resin as reactive solvent. FTIR of samples taken during the course of the reaction confirmed the decrease of the intensity of the band at 2841 cm^{-1} assigned to the CH_3 symmetric stretch of the $-OCH_3$ groups present in MPTMS and the appearance of a band at 1042 and 1120 cm^{-1} assigned to Si–O–Si.

The progress of the hydrolysis and condensation of MPTMS was also followed by SEC. This technique is a convenient method to monitor in a qualitative way the development of the molar mass during the reaction [12, 21]. Figure 1 shows the SEC chromatograms at different times of the hydrolytic condensation. The peaks of species produced by hydrolysis and polycondensation during the early stages of reaction overlapped the peaks of the methacrylate monomers. However, after 24 h of heating the chromatograms displayed a bimodal distribution of molar masses, therefore, the progress of the reaction could be assessed from the change in the relative area of each peak. Figure 2 shows the SEC chromatogram of a formulation reacted during 14 days at 60 °C and a formulation

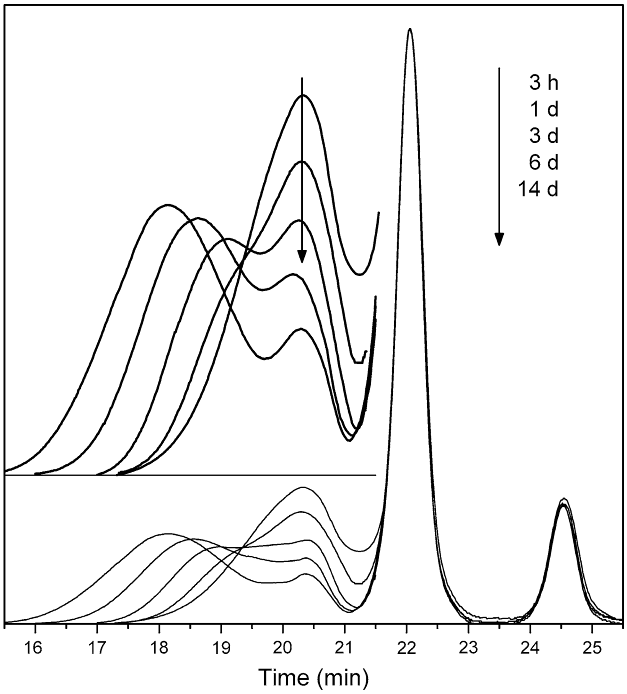


Fig. 1 Evolution of SEC chromatograms during the hydrolytic condensation of MPTMS at 60 °C in BisTEG. Three-column set with RI detector

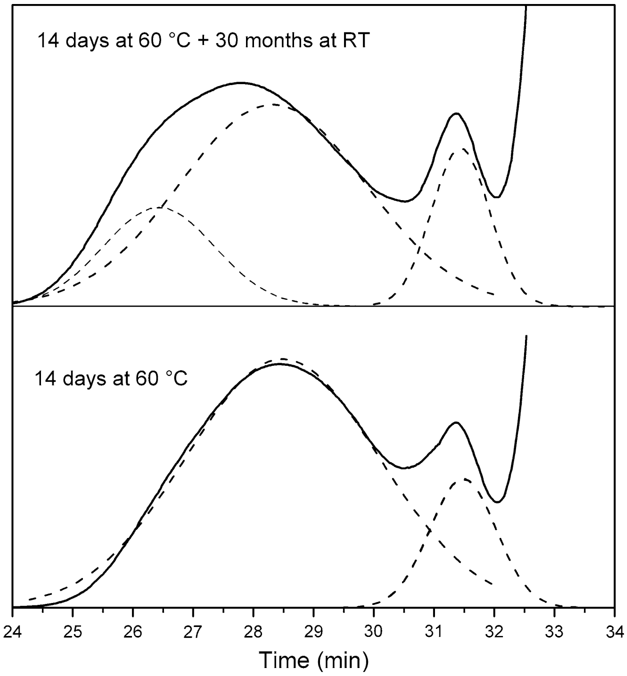


Fig. 2 SEC chromatograms of SSQO prepared in BisTEG during 14 days at 60 °C and SSQO stored 30 months at room temperature after the reaction. Four-column set with UV detector

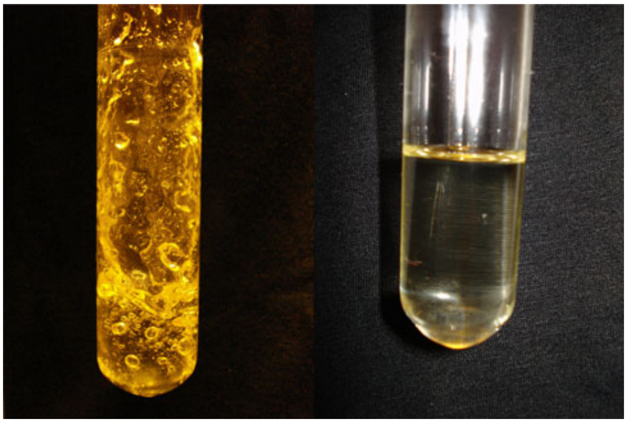


Fig. 3 Gelled sample of SSQO prepared in bulk and liquid mixture of SSQO prepared using BisTEG as solvent

stored during 30 months at room temperature after the reaction. The slow intermolecular condensation of species after prolonged periods of storage at room temperature resulted in a third peak in the SEC chromatogram. Although the polycondensation reaction continued slowly during the storage at room temperature, the SSQO were stable with respect to gelation. Stability of the polycondensates is of primary importance in applications that require storage of the product for several months, as it is the case of dental restorative materials. The SSQO were soluble in the methacrylate monomers, and no precipitated was observed during the reaction. The high transparency of the polycondensates is a further hint to their submicrometer size (Fig. 3).

UV-MALDI-TOF MS analysis

The determination of molecular weights of the products of hydrolysis and condensation of MPTMS was carried out by UV-MALDI-TOF MS. This technique has become a very powerful tool for the characterization of molecular weights of silsesquioxanes [22–24]. Figure 4 is a typical UV-MALDI-TOF spectrum of the SSQO generated in BisTEG during 14 days at 60 °C and stored for 30 months at room temperature. Species are clearly identified taking into account a consistent shift of about $2\Delta m/z$ unities with respect to the calibration. The typical distance between peaks $\Delta m/z = 170.2$ corresponds to the addition of an R–S–$(OH)_3$ group and the loss of two water molecules. Similarly, the separation between two consecutive peaks $\Delta m/z = 188.3$ corresponds to the addition of an R–S$(OH)_3$ group and the loss of a water molecule. Table 1 shows the experimental molecular weights and the assignment of the peaks appearing in the mass spectra. Values obtained for the SSQO prepared in bulk at room temperature are shown for comparison. A good agreement between the experimental molar masses and the predicted values was found. Figure 5 shows possible structures for representative partially condensed polyhedra. It is seen that the product

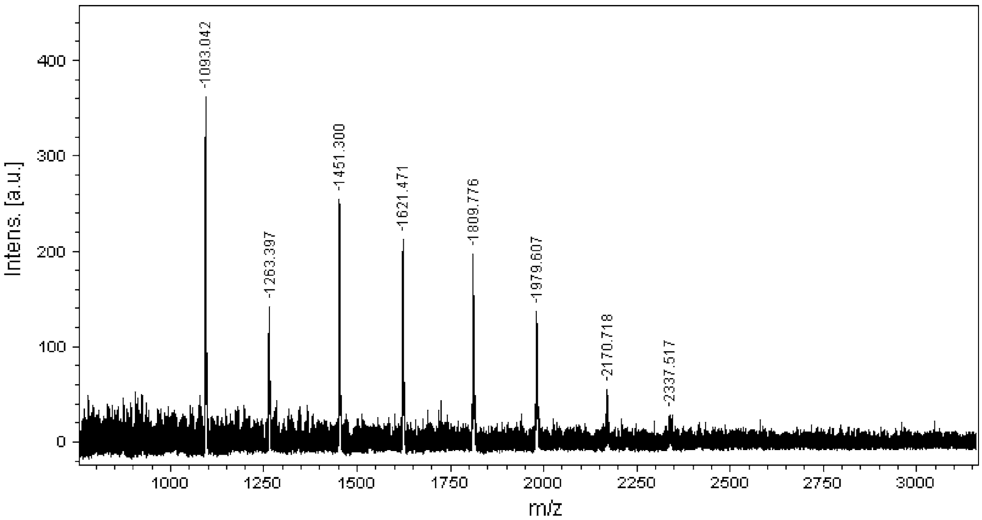


Fig. 4 UV-MALDI-TOF MS of the SSQO prepared during 14 days at 60 °C in BisTEG. Matrix nHo in negative linear ion mode

Table 1 Assignment of UV-MALDI-TOF MS peaks for SSQOs prepared during 14 days at 60 °C in BisTEG monomer and SSQOs prepared in bulk with concentrated formic at room temperature

BisTEG (*m*/*z*) exp	SSQO (*m*/*z*) exp	Assignment	*m*/*z* Calcd
1093.9	1093.6	$T_6(OH)_2$	1093.5
1264.1	1263.8	$T_7(OH)$	1263.7
1452.7	1452.2	$T_8(OH)_2$	1452
1622.6	1622.2	$T_9(OH)$	1622.2
1810.9	1810.4	$T_{10}(OH)_2$	1810.5
1980.6	1979.8	$T_{11}(OH)$	1980.7
2169.8*	2168.5*	$T_{12}(OH)_2$*	2169
2340.3*	2338.7*	$T_{13}(OH)$*	2339.2

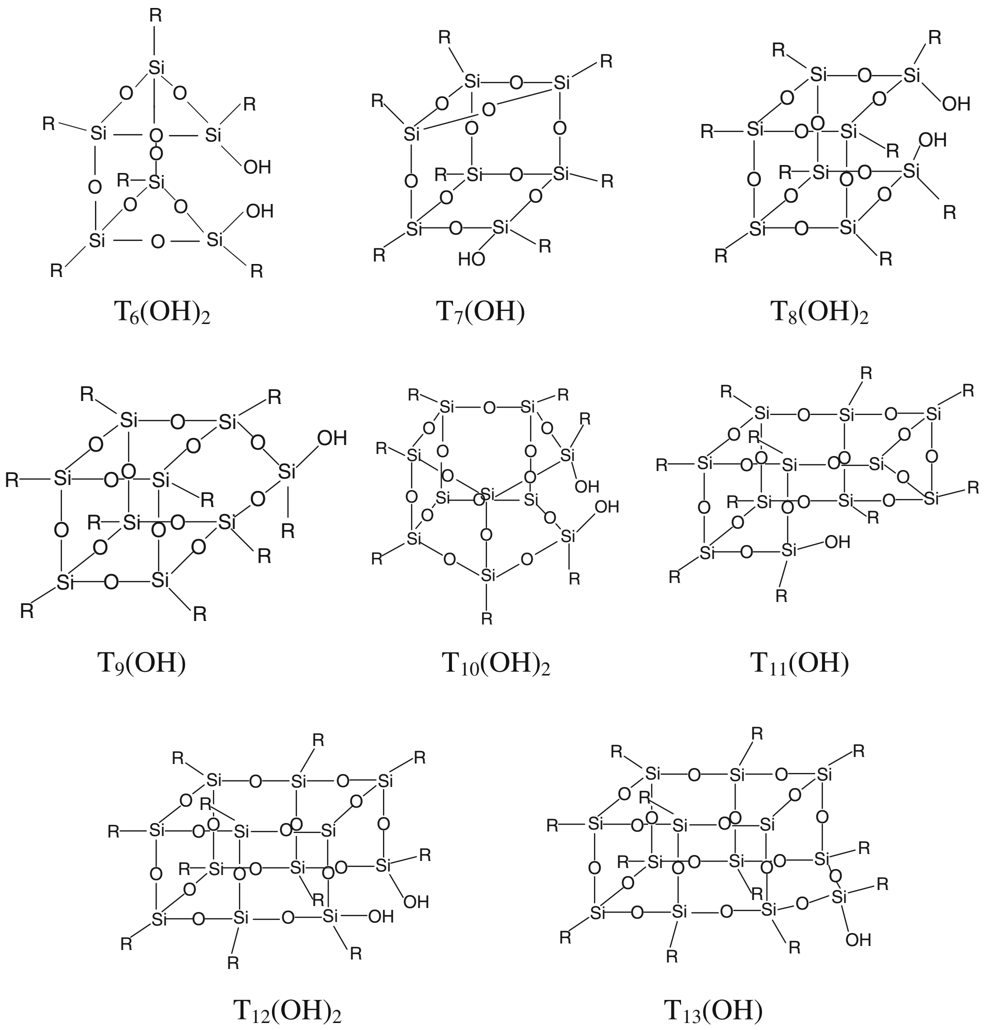
Values with an asterisk correspond to species present after 30 months of storage at room temperature

resulting after 14 days of reaction at 60 °C consists of incompletely condensed polyhedra having 6–11 Si atoms with a very large fraction of intramolecular cycles. Samples analyzed after 30 months of storage at room temperature showed the presence of $T_{12}(OH)$ and $T_{13}(OH)_2$ species, which are associated to the appearance of a third high-molar mass peak in the SEC chromatogram in Fig. 2. These species were generated through the condensation of two $T_6(OH)_2$ and $T_6(OH)_2$ with $T_7(OH)$.

Ideally, trifunctional monomers such as MPTMS would be expected to polymerize to highly crosslinked networks analogous to silica gels. However, in many silsesquioxane polymerization processes, cyclization reactions play an important role giving rise to soluble species. From results presented in Table 1, it emerges that dilution of reactants with BisTEG monomer discourages bimolecular reactions that lead to polymer growth and favors cyclization reactions. Assuming that condensation reaction in Eq. 1 is complete, then a mixture 50:50 weight ratio MPTMS/BisTEG results in around 40 wt% SSQO in BisTEG resin. In that way, a relatively high proportion of well-dispersed nano-sized methacrylate-functionalized polyhedral SSQO generated in situ is incorporated into methacrylate monomers. Moreover, the analysis of the species present after a prolonged storage period reveals that dilution of the reacting medium prevents the generation of high-molar mass oligomers, thereby improving the shelf-life stability of the polycondensates. Under the synthesis conditions used in the present study, the BisTEG monomer was not involved in the hydrolysis–condensation reactions with MPTMS and therefore it can be copolymerized by thermal or photochemical means, thereby cross-linking the pre-formed nano-sized cage-like species.

Determination of conversion in the polycondensation reaction by ^{29}Si NMR

Figure 6 shows ^{29}Si NMR spectra recorded after 14 days of reaction at 60 °C in BisTEG. The lines are very fine and a broad distribution of species is observed. The identification of peaks was based on literature data [25]. For trifunctional alkoxysilanes $R'Si(OR)_3$, the ^{29}Si chemical shifts range extends from −35 ppm to about −70 ppm, and in this range, four groups of lines corresponding to different environments of silicon atoms are distinguished. Signals of monomer (T_0) and end groups of chains (T_1), which are located in the region 48 to −51 ppm, are not present in the final product. The peak in the region −54 to −61 ppm is assigned to Si atoms bonded to three other Si atoms through Si–O–Si bonds present in strained triangular cycles (−54 to −58 ppm) (T_3 structures) and to Si atoms bonded to two other Si atoms through an Si–O–Si bond and to an OH group (T_2 structures) (−58 to −61 ppm). The peak in the range −64 to −68 ppm is assigned to Si atoms joined to three other Si atoms through Si–O–Si bonds (T_3 structures), in unstrained structures [25]. The multiple lines in



$T_6(OH)_2$ $T_7(OH)$ $T_8(OH)_2$

$T_9(OH)$ $T_{10}(OH)_2$ $T_{11}(OH)$

$T_{12}(OH)_2$ $T_{13}(OH)$

Fig. 5 Possible structures for representative partially condensed polyhedra

the spectra are attributed to both the presence of diastereoisomers, and chemical shifts resulting from different degree of strain. The complexity of the ^{29}Si NMR spectra, which is attributed to the variety of species present in the final product (Table 1), makes difficult the unambiguous peak assignment and then quantitative interpretations. The strained three member structure (T_3) is expected to resonate in the region near the signal of the Si atoms bonded to two other Si atoms and to an OH group (T_2). However, as a reasonable approximation, the proportion of T_3 species present in strained three member rings was calculated from the area of the first peak within the region −54 to −58 ppm. The conversion in the polycondensation reaction, X, is given by:

$$X = \sum (n/3)T_n.$$

From the spectrum presented in Fig. 6, the fraction of T_2 and T_3 structures and conversion in the polycondensation reaction of MPTMS were 0.16, 0.84, and 0.95, respectively.

Viscosity measurements

The rheological characterization of the SSQO prepared in bulk, the BisTEG monomer modified with around 40 wt% SSQO, and the unmodified BisTEG monomer are summarized in Fig. 7. Measurements were carried out in samples stored at room temperature for 30 months. It is seen that all resins behave as Newtonian liquids; i.e., the viscosity remains constant during the duration of the test. The relatively modest increase in viscosity in resins containing 40 wt% SSQO is attributed to the absence of high-molar mass oligomers. Dilution of the reacting medium during the hydrolysis and condensation of MPTMS discourages bimolecular reactions that lead to the generation of high-molar mass oligomers and, consequently, prevents undesired increases of viscosity.

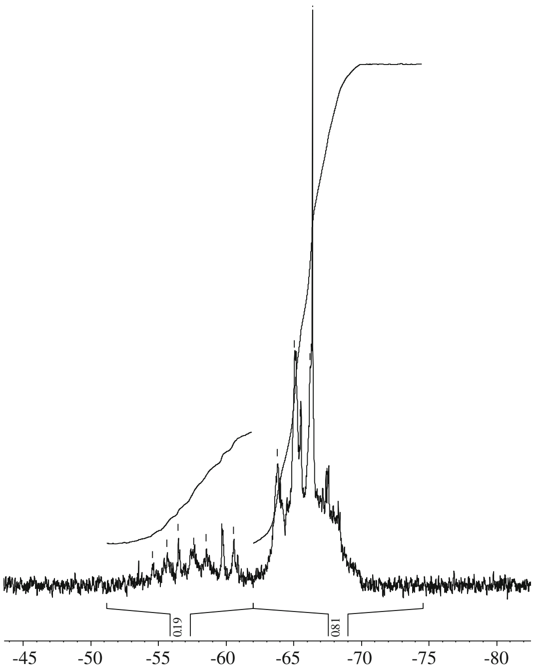


Fig. 6 ^{29}Si NMR spectrum of SSQO prepared during 14 days at 60 °C in BisTEG. The fraction of T_2 and T_3 structures and conversion in the polycondensation reaction of MPTMS were 0.16, 0.84, and 0.95, respectively

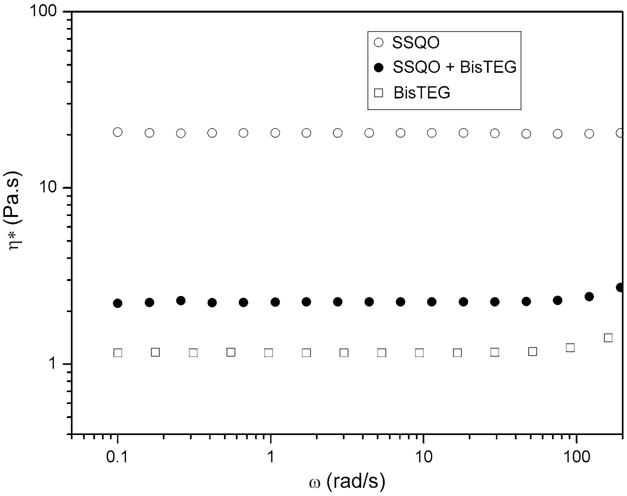


Fig. 7 Viscosity of BisTEG monomer, SSQO-modified BisTEG monomer, and SSQO prepared in the absence of methacrylate monomers

Degree of conversion, volumetric shrinkage, and leachable monomer content

Figure 8 shows the conversion of methacrylate groups versus irradiation time in BisTEG monomer modified with around 40 wt% SSQO and in unmodified BisTEG monomer. The conversion in SSQO prepared in bulk is also shown for comparison. The polymerization of dimethacrylate monomers in the absence of external heating leads to glassy resins in which only part of the available double bonds are reacted [19]. Before the completion of conversion, the vitrification phenomenon decelerates the reaction to hardly perceptible rate. Results presented in Fig. 8 show that the substitution of BisTEG with SSQO affected both the methacrylate double bond conversion and the photopolymerization rate. The higher the POSS monomer content, the lower was the double bond conversion, and the slower the photopolymerization rate. A similar trend was reported by Moszner et al. in studies related to crosslinking alkoxysilane methacrylates prepared by the sol–gel method [8, 9]. Similarly, Fong et al. [12], who studied dental restorative composites containing polyhedral SSQO, found that an increase in the proportion of silsesquioxanes was accompanied with a lower methacrylate conversion. This trend is probably connected with lower reactivity of methacrylate groups in organic–inorganic hybrid monomers compared to mixtures of conventional dimethacrylates, steric hindrance and reduced mobility of the reacting medium caused by the presence of SSQO. The slower polymerization rate of methacrylate groups in organic–inorganic hybrid monomers compared to mixtures of conventional dimethacrylates has been compensated by Moszner et al. [9] by the addition of a highly reactive UV photoinitiator.

Figure 9 shows the shrinkage over time during photopolymerization of BisTEG monomer modified with around 40 wt% SSQO, unmodified BisTEG monomer, and SSQO prepared in bulk. The reduced shrinkage in formulations containing SSQO is consistent with the reduced degree of conversion presented in Fig. 6 [2]. The irradiance of the light source employed in the conversion measurements is 400 mW/cm^2 while that used in shrinkage studies is 12.8 mW/cm^2. Thus, the timescales in the conversion studies will be reduced compared with that in the shrinkage experiments. However, this observation does not change the conclusions drawn from the results. In agreement with trends presented in Fig. 9, reduced volumetric shrinkage has been observed in experimental resins based on branched macromonomers [3], methacrylate modified triethoxysilanes polycondensates [7], and experimental formulations of methacrylate monomers containing polyhedral oligmeric silsesquioxane [11].

It is worth noting that clinically, there are concerns raised if photocurable dental composite materials are under-cured. If undesired high levels of leachable residual monomer are present after the polymerization, the biocompatibility of the dental composite can be compromised. The amount of residual, unreacted monomer in a resin composite restoration has been implicated in causing increased potential for cytotoxicity [26]. Table 2 shows the residual monomer content after polymerization in both unmodified BisTEG resin and SSQO-modified resins. The

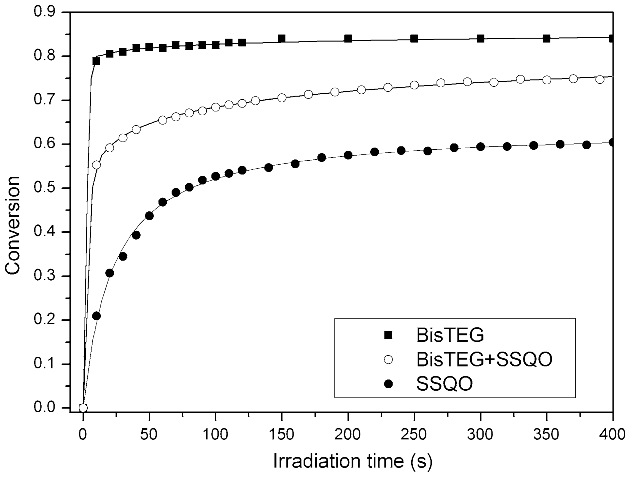


Fig. 8 Monomer conversion versus irradiation time in unmodified BisTEG monomer, BisTEG monomer containing 20 wt% SSQO and SSQO prepared in the absence of methacrylate monomers

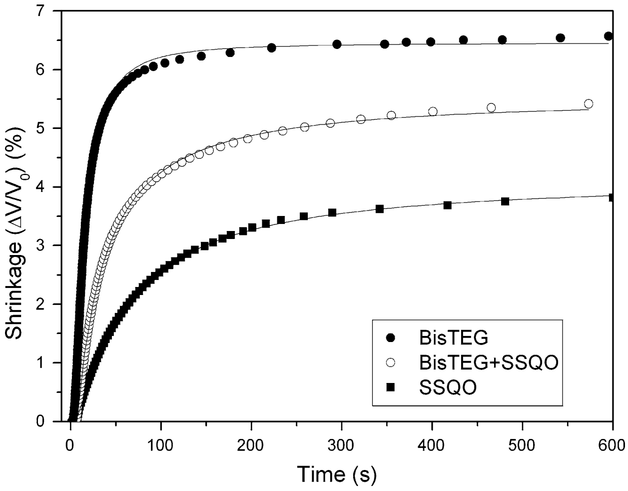


Fig. 9 Shrinkage versus irradiation time in unmodified BisTEG monomer, BisTEG monomer containing 20 wt% SSQO and SSQO prepared in the absence of methacrylate monomers

Table 2 Leachable monomer content expressed as (g of leached monomer/g of polymerized sample) × 100

Resin	Monomer	Residual monomer (%)
BisTEG	BisGMA	3.01 (±0.03)
	TEGDMA	1.15 (±0.02)
BisTEG-SSQO	BisGMA	0.64 (±0.05)
	TEGDMA	0.34 (±0.03)

markedly reduced amount of leachable monomer in formulations containing SSQO indicates that the unreacted monomer exists mainly as pendant double bonds instead of free leachable monomer. This observation is in agreement with results reported by Moszner et al. on crosslinking alkoxysilane methacrylates prepared by the sol–gel method [6, 7]. The authors investigated copolymer networks consisting from triethoxysilanes polycondensates with functional methacrylate groups and organic multimethacrylate monomers. The photocured networks contained high concentration of non-reacted double bonds, while the amount of migrating monomer into toluene was negligible indicating that the non-reacted double bonds were present as pendant double bonds.

Table 3 Flexural modulus (*E*) and compressive yield strength (σ_y) of BisTEG monomer modified with different proportions of methacrylate-functionalized SSQOs

wt% SSQO	*E* (GPa)	σ_y (MPa)
0	3.1 (±0.05)	110 (±0.8)
5	2.9 (±0.1)	83 (±2)
10	3.1 (±0.08)	86 (±3)
20	2.9 (±0.12)	89 (±2)

Mechanical characterization

The condensation reaction led to highly brittle inorganic networks with poor mechanical properties. Materials prepared from SSQO synthesized in bulk were so brittle that samples for mechanical testing broken during preparation. The additional formation of the organic networks by methacrylate polymerization led to increased toughness of the materials. Table 3 summarizes the flexural modulus (*E*) and compressive yield strength (σ_y) of materials prepared from BisTEG modified with different proportions of methacrylate-functionalized SSQO. The selected mechanical properties of the hybrid networks were dominated by the contribution of the organic network. The presence of SSQO produced no apparent change in the flexural modulus. Conversely, the addition of SSQO resulted in a significant decrease in the compressive yield stress.

In comparison to Culbertson's work [11] and Fong's work [10], the present study further suggested that different methods of incorporation of SSQO (either through direct mixing or through incorporation of SSQO generated in situ into methacrylate monomers) had similar effects on the selected mechanical properties of the nanocomposites, as long as the SSQO are well dispersed in the composite resin. Concerning the flexural and compressive strength values, it is worth noting that when a strength testing of brittle materials is performed, the sample size has a large influence on the measured value [27, 28]. This means that a minimum number of specimens should be tested to obtain a proper estimation. As a compromise between minimizing both the dispersion of the evaluation method and the experimental effort, the use of a minimum number of 20 specimens has been suggested [27, 28]. Flexural strength values were not reported here because the values averaged from five sample specimens resulted in an important data scatter and did not describe properly the statistical distribution of flexural strength.

Conclusion

Methacrylate-functionalized silsesquioxanes were synthesized by the hydrolytic condensation of MPTMS using methacrylate monomers as reactive solvent. In that way, about 40 wt% of nano-sized polyhedral SSQO could be incorporated without evidence of precipitated.

Resins containing 40 wt% SSQO displayed a modest increase in viscosity compared with the unmodified BisTEG monomer. This is attributed to a dilution of the reacting medium, which discourages bimolecular reactions that lead to the generation of high-molar mass oligomers and, consequently, prevents undesired increases of viscosity.

Substitution of BisTEG with SSQO resulted in a substantial decrease in the volumetric shrinkage during photopolymerization.

The amount of leachable monomer detected in formulations containing SSQO was markedly reduced, which indicates that the unreacted monomer exists mainly as pendant chains instead of free leachable monomer.

The addition of different proportions of SSQO to the BisTEG monomer resulted in no apparent change in the flexural modulus and a decrease in the compressive yield stress of the polymerized materials.

The decrease in both volumetric shrinkage and free leachable monomer content in SSQO-modified methacrylate monomers makes these resins attractive for the manufacture of dental composites.

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