



Macromolecular Nanotechnology

Synthesis of silsesquioxanes based in (3-methacryloxypropyl)-tri-methoxysilane using methacrylate monomers as reactive solvents

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ABSTRACT

The polycondensation of (3-methacryloxypropyl)-trimethoxysilane in acidic conditions using different methacrylate monomers as reactive solvents resulted in incompletely condensed methacrylate-functionalized silsesquioxanes with a very large fraction of intramolecular cycles. UV-MALDI-TOF-MS analysis demonstrated that the species present after 2 weeks of reaction at 60 °C were: T₆(OH)₂, T₇(OH), T₈(OH)₂, T₉(OH), T₁₀(OH)₂ and T₁₁(OH). Analysis of samples after 30 months of storage at room temperature revealed the presence of T₁₂(OH)₂ and T₁₃(OH) species. The absence of higher molar mass oligomers after prolonged storage periods is attributed to dilution of the reacting medium, which discourages bimolecular reactions that lead to polymer growth. ²⁹Si NMR spectroscopy showed that the conversion in the polycondensation reaction was in the range 0.91–0.96. The methacrylate monomers are not involved in the hydrolysis–condensation reactions with MPTMS and therefore can be polymerized by thermal or photochemical means, thereby cross-linking the preformed nanosized cage-like silsesquioxanes. The formulations containing silsesquioxanes showed a markedly reduced content of extractable monomer after photopolymerization, which makes these resins very attractive for dental filling materials.

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1. Introduction

Silsesquioxanes have been the subject of intensive study in the past, and are becoming important again as a vehicle for the manufacture of novel hybrid organic–inorganic materials [1–3]. In particular, organosilsesquioxanes can be prepared through the hydrolysis and condensation of organotrialkoxysilanes, which undergo a complex series of hydrolysis and self-condensation reactions leading to dimers, trimers, tetramers and ultimately oligomers and polymers designed as silsesquioxanes (SSQO). The generic structure of the organosilsesquioxanes is given by the empirical formula [R–SiO_{1.5}]_n, where the stoichiometric ratio of oxygen to silicon is 1.5 (sesqui) and *n* is the number of *mer* units in the oligomer. R is the organic substituent,

which can contain terminal functional groups capable of specific chemical reactions. The actual structure designated by [R–SiO_{1.5}]_n, can be quite complex and may include polyhedral, ladder, semi-ladder and highly branched forms. The nature of the products formed is determined by the reaction conditions (catalyst, solvent and temperature). The synthetic procedure for the preparation of hybrid organic–inorganic networks from these modified alkoxide, involves two different stages. The hydrolysis and polycondensation reactions of the alkoxy groups lead to the formation of an inorganic oxidic network. This stage is followed by the polymerization reactions of the functional organic groups, R, by thermal or photochemical means, thereby cross-linking the preformed nanosized inorganic species. The basic idea behind the development of organic–inorganic hybrid materials is the combination of inorganic and organic moieties on a molecular scale to achieve a synergetic combination of the properties typical of each of the constituents.

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Methacrylate-based hybrid organic–inorganic materials have recently received a considerable interest for the development of advanced dental composites in order to reduce the volumetric shrinkage during polymerization and improve the wear resistance [4–6]. Unfortunately, in many cases, the synthesis of SSQOs can be very slow, and periods of several months are required before synthetically useful quantities of the final product can be obtained. In addition, the presence of reactive silanol groups in incompletely condensed structures may jeopardize the stability of the SSQO during storage.

The present study was carried out in order to explore the possibility of using reaction conditions that would permit the synthesis of highly condensed oligomers in a convenient reaction time and to assess the stability of the reaction product during storage. Methacrylate-functionalized silsesquioxanes were synthesized by the hydrolysis and condensation of (3-methacryloxypropyl)-trimethoxysilane (MPTMS) using methacrylate monomers as reactive solvents. The methacrylate monomers were selected with regards to their ability to form copolymers with the (methacryloxypropyl) silsesquioxanes. Monomers of different polar character were studied in order to analyze the influence of the chemical nature of the solvent on the rate of polycondensation.

2. Experimental

2.1. Materials and general procedures

Chemical structures of the methacrylate monomers are shown in Scheme 1. The trialkoxysilane 3-(methacryloxy-

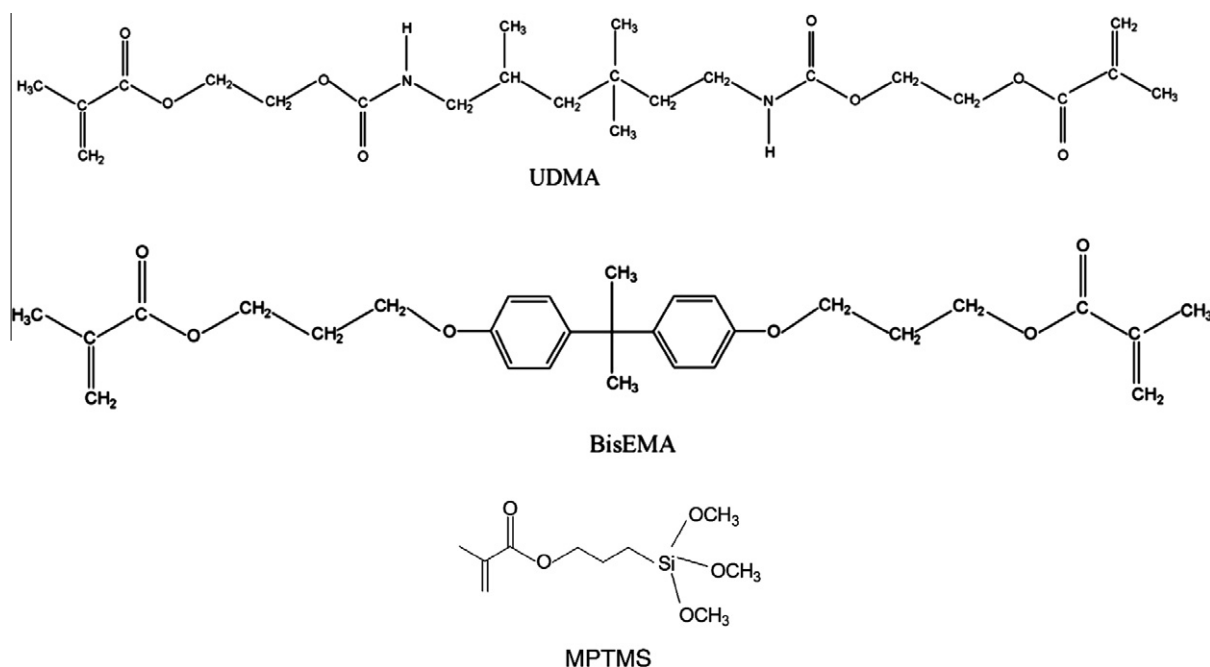
propyl)-trimethoxysilane (MPTMS, Sigma–Aldrich) and formic 98 wt.% (Sigma–Aldrich) were used as received. The methacrylate monomers used as reactive solvents in the hydrolytic condensation of MPTMS were: 2,2-bis[4-(2-methacryloxyethoxy) phenyl]propane (BisEMA) and 1,6-bis(methacryloxy-2-ethoxy-carbonylamino)-2,4,4-trimethylhexane (UDMA). They were supplied by Esstech, Essington, PA. The hydrolytic condensation of MPTMS was performed in a 50:50 weight ratio MPTMS/methacrylate monomers, using HCOOH 98% in a molar ratio HCOOH/Si = 3. The reaction was carried out in open vials immersed in an oil bath at 60 °C. The resins were activated for visible light polymerization by the addition of 1 wt.% camphorquinone (Sigma Aldrich) in combination with equimolar proportion of ethyl-4-dimethyl aminobenzoate (Sigma–Aldrich).

2.2. Characterization

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 10⁴ was added. A refractive index detector (Knauer K-2301) or an UV detector (Knauer S2600) were used. THF was used as a carrier at 1 mL/min.

2.2.1. FTIR

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.



Scheme 1. Structure of the monomers used as reactive solvents in the hydrolytic condensation of MPTMS.

2.2.2. MALDI-TOF-MS

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, *n*Ho). These chemicals were purchased from Sigma–Aldrich. The best results were obtained by using *n*Ho in negative linear ion mode with laser power of 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 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 μ l 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 μ l 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 μ l each) were performed. Method A gave the best results. In all cases, the samples were prepared without salt.

^1H 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 tetramethylsilane. ^{29}Si NMR spectra were recorded with a Bruker AM500 spectrometer operating at 99.359 MHz. Samples were dissolved in deuterated acetone.

2.3. Photopolymerization

The light source employed to cure the resins was a light-emitting diode (LED) unit (Ultralume2, Ultradent, USA) with a wavelength range 410–530 nm and light irradiance of 400 mW/cm². Details of the measurement of conversion by near-infrared spectroscopy (NIR) were reported elsewhere [7]. The conversion profiles were calculated from the decay of the absorption band located at 6165 cm⁻¹. FTIR spectra were acquired with a Genesis II-Mattson FTIR (Madison, WI, USA).

2.4. Leachable residual monomer

The residual monomer content was determined by size exclusion chromatography (SEC). Polymerized specimen disks (diameter 15 mm, height 2 mm) were 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

least-squares line calibration curve constructed from solutions containing different amounts of monomer. All determinations were conducted in triplicate.

3. Results and discussion

3.1. Synthesis of methacrylate-functionalized silsesquioxanes (SSQOs)

The hydrolytic condensation of MPTMS catalyzed by concentrated formic acid was carried out at 60 °C using UDMA or BisEMA methacrylate monomers as reactive solvents, which were selected with regards to their ability to form copolymers with the (methacryloxypropyl) silsesquioxanes. 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 [8]. 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 CH₃ symmetric stretch of the -OCH₃ groups present in MPTMS and the appearance of a band at 1042 and 1120 cm⁻¹ assigned to Si–O–Si.

The development of molar mass distributions during the hydrolysis and condensation of MPTMS was followed by size exclusion chromatography (SEC). This technique is a convenient method to investigate in a qualitative way the influence of reaction parameters on the development of the molar mass distribution during the reaction [9–11]. Figs. 1 and 2 show the SEC chromatograms of the products obtained at different times of the hydrolytic condensation. The retention time of species produced by hydrolysis and polycondensation during the early stages of reaction was in the range of the retention time of the methacrylate monomers. Consequently, the peak of the initial products of reaction overlapped the peak of the monomers. However, after 24 h of heating the chromatograms

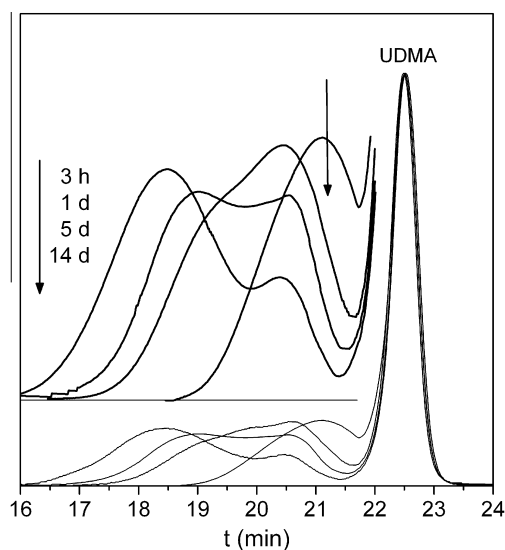


Fig. 1. Evolution of SEC chromatograms during the hydrolytic condensation of MPTMS at 60 °C in UDMA. Three-column set with RI detector.

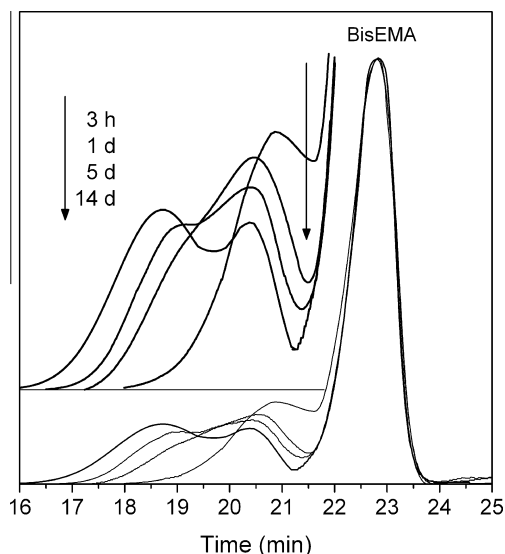


Fig. 2. Evolution of SEC chromatograms during the hydrolytic condensation of MPTMS at 60 °C in BisEMA. Three-column set with RI detector.

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. The SEC chromatograms of the early stages of reaction (not shown here) revealed that the peak of the MPTMS monomer (retention time equal to 25 min) disappeared after about 100 and 180 min of reaction in UDMA and BisEMA, respectively. This trend is explained in terms of the different chemical nature of each solvent. The availability of labile protons (protic versus aprotic solvents) determines whether anions or cations are solvated more strongly. UDMA is a polar protic solvent whereas BisEMA is a polar aprotic solvent. Under acidic conditions, hydrolysis is catalyzed by hydronium ions, which are solvated by BisEMA [12]. Thus, the catalytic activity of the hydronium ions and, consequently, the hydrolysis rate in the presence of BisEMA is reduced. In addition, comparison of SEC chromatograms in Figs. 1 and 2 show that the development of molar mass in the system containing BisEMA was slower than that in the formulation containing UDMA. This is attributed to the preferential solvation of the protonated silanol groups involved in the acid catalyzed condensation reaction by the aprotic BisEMA [12].

The SSQOs 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 or nanostructural phase size. ^1H NMR spectra of the silsesquioxanes obtained after 14 days of reaction at 60 °C in different dimethacrylate monomers showed that the 3-methacryloxypropyl group remained intact. No protons assignable to $\text{Si}-\text{OCH}_3$ (3.5–3.8 ppm), HCOOH (9.60 y 8.05 ppm), CH_3OH (3.42 ppm), HCOOCH_3 (8.02 and 3.7 ppm) or SiOOCH (8.13 ppm) were detected meaning that the hydrolysis was complete and volatiles were eliminated. The absence of a band at 2.04 ppm assigned to $\text{Si}-\text{OH}$ groups that do not exhibit hydrogen bonds to other $\text{Si}-\text{OH}$ groups revealed that $\text{Si}-\text{OH}$ groups were not present in significant concentrations.

3.2. Characterization of products after storage

Figs. 3 and 4 show the SEC chromatograms of the formulations presented in Figs. 1 and 2 after 30 months of storage at room temperature. The slow intermolecular condensation of species after prolonged periods of storage at room temperature resulted in an increase of the high-molar mass peak of SSQOs prepared in BisEMA and gave a third peak in the SSQOs prepared in UDMA. Electrostatic and hydrogen bond interactions, steric effects and mobility of molecules, depend on the solvents used and all may change the reaction rate. Hendricks et al. [13] studied the

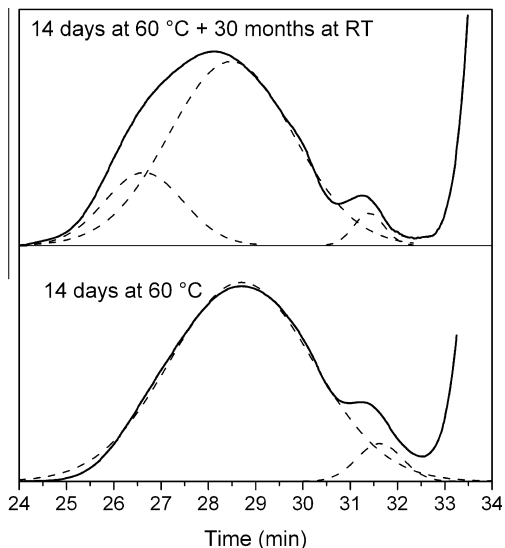


Fig. 3. Comparison of SEC chromatograms of SSQOs prepared in UDMA during 14 days at 60 °C and SSQOs stored 30 months at room temperature (20 ± 2 °C) after the reaction. Four-column set with UV detector.

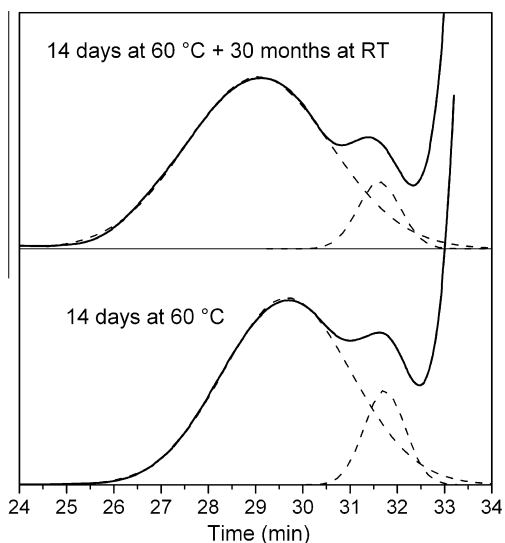
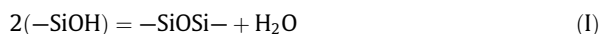


Fig. 4. Comparison of SEC chromatograms of SSQOs prepared in BisEMA during 14 days at 60 °C and SSQOs stored 30 months at room temperature (20 ± 2 °C) after the reaction. Four-column set with UV detector.

effects of solvent structure on the equilibrium distribution of oligomers in silicate solutions. The authors attributed the observed increase in the degree of condensation in the presence of certain solvents to a reduction in the chemical potential of water caused by an increase in the degree of water structuring. Condensation of silanol groups to form siloxane bridge may be represented schematically as:



Considerations of this equilibrium reaction indicate that the extent of condensation will increase if a portion of the water in solution is replaced with an organic solvent. In addition, it is assumed that water exists in two-state equilibrium:



If the introduction of organic solvents shifts the reaction (II) to the right, then the equilibrium for reaction (I) will shift to the right and the extent of condensation will increase. The solvent UDMA forms hydrogen bonds with water and consequently shift the equilibrium of reaction (II) and favors the polycondensation reaction (Fig. 3) compared with formulations containing the aprotic BisEMA solvent (Fig. 4).

Although the polycondensation reaction of the silsesquioxanes prepared in different methacrylate monomers continued slowly during the storage at room temperature, they were stable with respect to gelation. Stability of the polycondensates is of primary importance for practical purposes because a poor shelf-life would restrict their use in certain applications that require storage of the product for several months, as it is the case of dental filling materials.

3.3. Determination of molecular weight by UV-MALDI-TOF-MS

The determination of molecular weights of the products of hydrolysis and condensation of MPMTMS was carried out by UV-MALDI-TOF-MS. This technique has become a very powerful tool for the characterization of molecular weights of silsesquioxanes [9,10,14]. Fig. 5a and b are typical MALDI-TOF-MS spectra of the SSQOs prepared in BisEMA measured in negative ion linear mode using *n*Ho as a matrix. The spectra correspond to SSQOs generated during 14 days at 60 °C and SSQO stored for 30 months at room temperature after the reaction. Table 1 shows the experimental molecular weights and the assignment of the peaks appearing in the mass spectra. From the analysis of results presented in Table 1 it emerges that the SSQOs prepared in the presence of methacrylate solvents at 60 °C consist of incompletely condensed polyhedra with a very large fraction of intramolecular cycles. Species are clearly identified taking into account a consistent shift of about 2 *m/z* unities with respect to the calibration. Incompletely condensed structures containing Si–OH groups, have a general formula $\text{T}_n(\text{OH})_m$. The nominal separation between two consecutive peaks $\text{T}_{n+1}-\text{T}_n$ (*n* an even number) was 170.2 g/mol, which corresponds to the addition of a R–S(OH)₃ group and the loss of two water molecules. Similarly, the nominal separation between two consecutive peaks $\text{T}_{n+1}-\text{T}_n$ (*n* an odd number) was 188.3 g/mol, which corresponds to the addition of a R–S(OH)₃ group and the loss of a water molecule. A good agreement between the experimental molar masses and the predicted values was found (Table 1). It is seen that the product resulting after 14 days of reaction at 60 °C consists of incompletely condensed

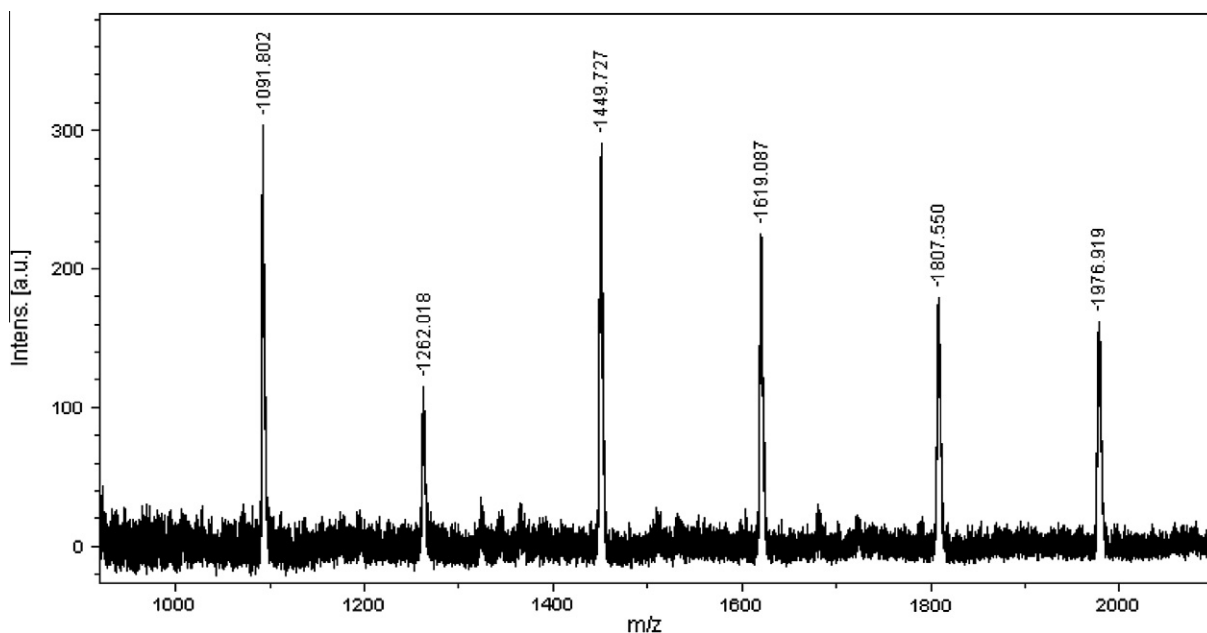


Fig. 5a. UV-MALDI-TOF-MS of the SSQOs prepared during 14 days at 60 °C in BisEMA. Matrix *n*Ho in negative linear ion mode.

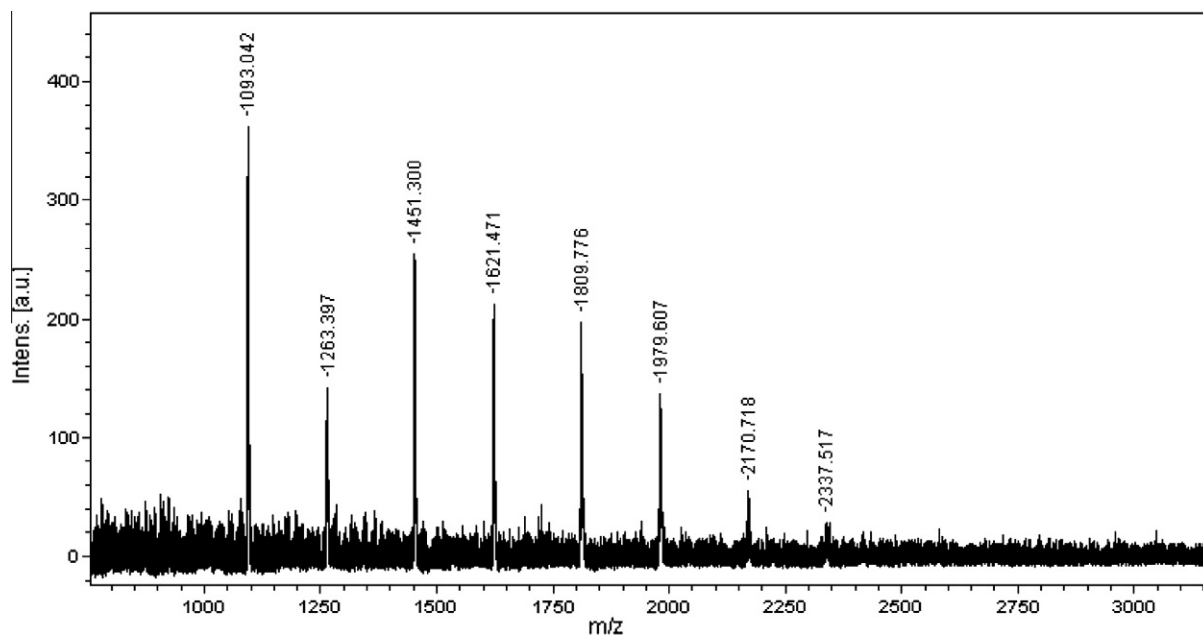


Fig. 5b. UV-MALDI-TOF-MS of the SSQOs prepared during 14 days at 60 °C in BisEMA and stored 30 months at room temperature (20 ± 2 °C) after the reaction. Matrix *n*Ho in negative linear ion mode.

Table 1

Assignment of UV-MALDI-TOF-MS peaks for SSQOs prepared during 14 days at 60 °C in methacrylate monomers. Values with an asterisk correspond to species present after 30 months of storage at room temperature.

(m/z) exp		Assign	m/z calcd.
BisEMA	UDMA		
1093.9	1093.7	T ₆ (OH) ₂	1093.5
1264.3	1264.1	T ₇ (OH)	1263.7
1452.3	1452.5	T ₈ (OH) ₂	1452
1622.4	1622.2	T ₉ (OH)	1622.2
1810.7	1809.8	T ₁₀ (OH) ₂	1810.5
1980.6	1979.8	T ₁₁ (OH)	1980.7
2171.7*	2169.5*	T ₁₂ (OH) ₂ *	2169
2338.5*	2339.9*	T ₁₃ (OH)*	2339.2

cagelike structures having 6–11 Si atoms, irrespective of the kind of methacrylate monomer used as solvent. Samples analyzed after 30 months of storage at room temperature showed the presence of T₁₂(OH) and T₁₃(OH)₂ species. A possible interpretation is that the polycondensation started giving linear polymers T₁(OH)₃, T₂(OH)₄, T₃(OH)₅, T₄(OH)₆, T₅(OH)₇, etc. As soon as the chains were long enough to form stable rings they cyclized to give T₃(OH)₃, T₄(OH)₄, T₅(OH)₅. These structures were identified by capillary electrophoresis-ion-trap mass spectrometry (CE-MS) after 10 min of acid catalyzed hydrolysis of MPT-MS [15]. Intermolecular condensation of the cyclic species formed during the early stages of reaction would then produce the “cagelike” species T₆(OH)₂, T₇(OH), T₈(OH)₂, T₉(OH), T₁₀(OH)₂ and T₁₁(OH). Thus, the reaction of the cyclic species among themselves results in a decrease of the relative area of the low-molar mass peak in the SEC chromatograms (Figs. 1 and 2). Fig. 6 shows possible structures for representative partially condensed polyhedra. The

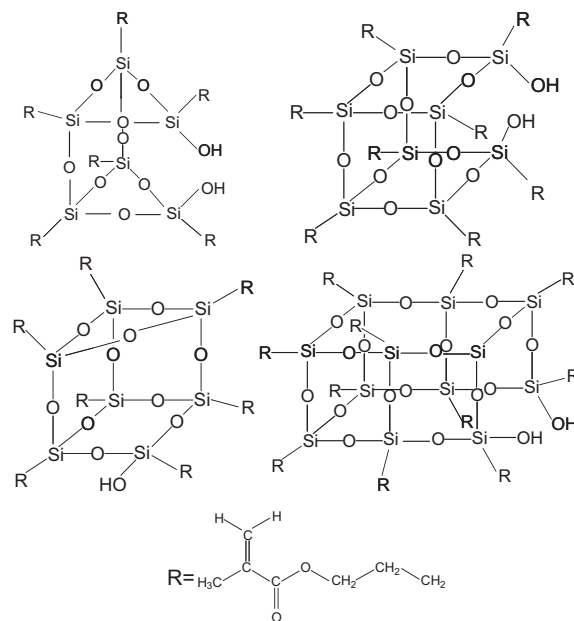


Fig. 6. Possible structures for representative partially condensed polyhedra.

appearance of a third high-molar mass peak in the SEC chromatogram in Fig. 3 is associated to the species T₁₂(OH)₂ and T₁₃(OH), which were generated through the condensation of two T₆(OH)₂, and T₆(OH)₂ with T₇(OH), respectively. The absence of a third peak in the system containing BisEMA (Fig. 4) may be attributed to the fact that the concentration of T₁₂(OH)₂ and T₁₃(OH) species was not high enough to be detected by the SEC equipment.

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 [16]. Pouxviel and Boilot [17] and Yoldas [18] have proposed that during acidic sol–gel polymerization of tetraethoxysilane, dilution of reactants discourages bimolecular reactions that lead to polymer growth and favors cyclization reactions. Generally, preference of cycles formation in a dilute system is typical of a random cyclization due to kinetic reasons as the rate of an intermolecular reaction decreases compared with the rate of an intramolecular one. In the case of the non-random cyclization, however, the reason is solvation stabilization of the condensation products by a diluent [13]. From the analysis of the species present after a prolonged storage period, it emerges that dilution of the reacting medium with polar solvents discourages bimolecular reactions and prevents the generation of high-molar mass oligomers, thereby improving the shelf-life stability of the polycondensates and preventing undesired increases of viscosity.

It is worth noting that the polar BisEMA and UDMA monomers used as diluents have hydrophilic functional groups, e.g., ethylene oxide and urethane groups, respectively. Thus, it is conceivable that MPTMS could also undergo hydrolysis–condensation reactions with the methacrylate monomers. However, UV-MALDI-TOF-MS analysis demonstrated that the methacrylate monomers were not involved in the hydrolysis–condensation reactions with MPTMS and the [3-methacryloxy]propyl group of MPTMS was kept intact during the course of the polycondensation reaction.

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

^{29}Si NMR spectroscopy is particularly effective to analyze the degree of condensation of the reaction product because numerous chemical environments of the ^{29}Si nucleus can be recognized through shifts in resonance lines. Figs. 7 and 8 show ^{29}Si NMR spectra recorded after 14 days of reaction at 60 °C in UDMA and BisEMA, respectively. The lines are very fine and a broad distribution of species is observed. The identification of peaks was based on literature data [19–22]. For trifunctional alkoxy silanes $\text{R}'\text{Si}(\text{OR})_3$, 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 [19]. The multiple lines in the spectra

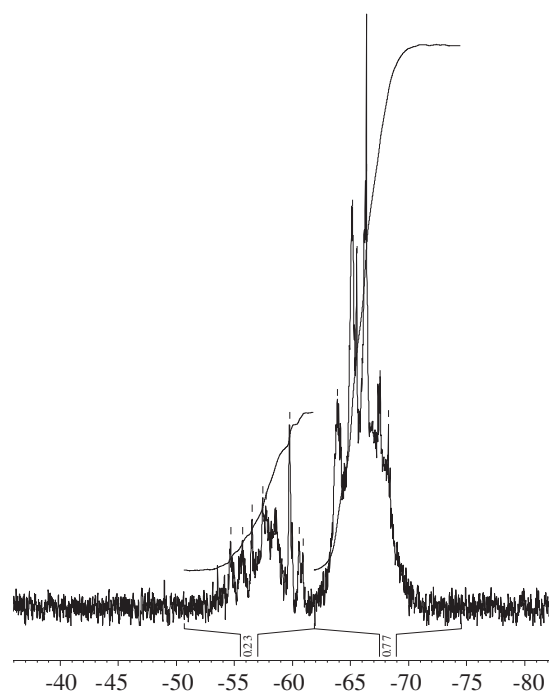


Fig. 7. ^{29}Si NMR spectrum of SSQOs prepared during 14 days at 60 °C in UDMA. (δ : –55.75, –56.56, –57.48, –57.75, –58.61, –59.80, –60.61, –60.96, –63.9, –65.19, –66.40, –67.56 ppm).

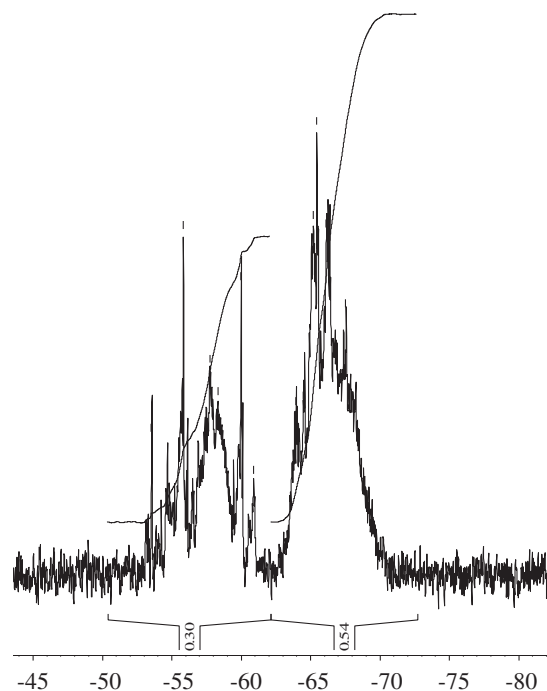


Fig. 8. ^{29}Si NMR spectrum of SSQOs prepared during 14 days at 60 °C in BisEMA. (δ : –55.84, –57.78, –58.34, –60.01, –60.9, –63.97, –64.51, –65.22, –65.45, –66.16, –67.56 ppm).

are attributed to both the presence of diastereoisomers [21,22], and chemical shifts resulting from different degree of strain [20]. Rikowski and Marsmann, prepared

Table 2

Fraction of the T² and T³ structures and conversion in the polycondensation reaction of MPTMS, X, in different methacrylate monomers.

Monomer	T ²	T ³	X
UDMA	0.13	0.87	0.96
BisEMA	0.26	0.74	0.91

deca- and dodeca-silsesquioxane cages by partial rearrangement of octasilsesquioxanes possessing different substituents groups [20]. For the group R:C₂H₅, the ²⁹Si chemical shifts for the octa-, deca- and dodeca-silsesquioxanes reported by the authors were –65.71, –67.56 and –69.79 ppm, respectively. The complexity of the ²⁹Si 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 (T³) 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 (T²). However, as a reasonable approximation the proportion of T³ species present in strained three member rings was calculated from the area of the first peak within the region –54 to –58 ppm. Table 2 shows the proportions of Tⁿ structures as well as the conversion in the polycondensation reaction defined as:

$$X = \sum (n/3) T^n$$

In agreement with SEC results, the conversion in the formulation prepared with BisEMA was lower than that reached in the polar protic UDMA.

3.5. Photopolymerization

Fig. 9 shows the monomer conversion versus irradiation time of SSQ/UDMA and SSQ/BisEMA. The room temperature polymerization of dimethacrylates usually leads to

glassy resins in which only part of the available double bonds are reacted. Before the completion of conversion, the vitrification phenomenon decelerates the reaction to hardly perceptible rate. It was found that the reactivity of the formulations in Fig. 9 was slightly lower than that of the unmodified monomers (vitrification times of UDMA and BisEMA: 40 and 60 s, respectively). This can be attributed to a reduced mobility of the medium caused by the presence of SSQOs. Nevertheless, the polymerization times are satisfactory for clinical practice. 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. Table 3 shows the residual monomer content after polymerization in both unmodified monomers and SSQOs-modified monomers. The markedly reduced amount of leachable monomer in formulations containing SSQOs indicates that the unpolymerized monomer exists mainly as pendant chains instead of free monomer. This is attributed to an increase of sites for polymerization of the BisEMA and UDMA in SSQOs-modified monomers. The markedly reduced amount of extractable monomer makes these resins very attractive for dental filling materials.

It is widely reported that the overall properties of dental restorative composites are improved by embedding filler nanoparticles into methacrylate-based polymers [5]. The size of the nanoparticles greatly affects the nanocomposite properties. However, in order to optimize this effect, the nanoparticles should be well dispersed in the polymer matrix, which is heavily dependent on the chemistry of the polymer–nanoparticle interface. Well dispersed polymer nanocomposites can be prepared by organically modifying the surface of the inorganic nanoparticles. Silane coupling agents are generally selected as the modification agents for colloidal silica particles since the hydroxyl groups on

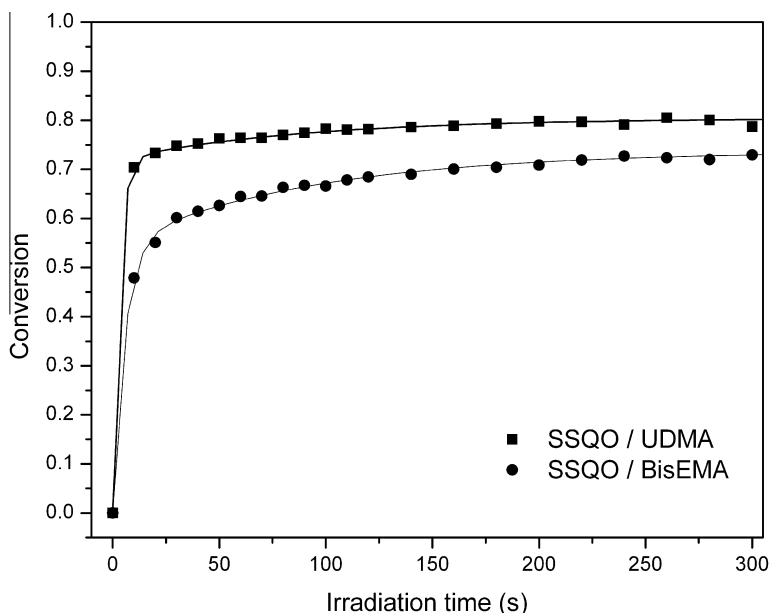


Fig. 9. Monomer conversion versus irradiation time in SSQO modified UDMA and BisEMA monomers.

Table 3

Leachable monomer content expressed as (g of leached monomer/g of polymerized sample) \times 100.

Resin	Residual monomer (%)
BisEMA	3.86
BisEMA-SSQO	1.18
UDMA	0.68
DMA-SSQO	0.15

the surfaces of silica particles can react with siloxane groups of the silane. The attachment of organosilanes molecules to colloidal silica particles prevents the aggregation of the particles and facilitates its dispersion. Results obtained in this research, demonstrated that the hydrolytic condensation of MPTMS in methacrylate monomers generates incompletely condensed SSQOs with a very large fraction of intramolecular cycles. In that way, about 40 wt.% of well dispersed nanosized methacrylate-functionalized polyhedral SSQOs generated in situ are incorporated into methacrylate monomers in a conveniently short period of time. Characterization of the polymerized organic–inorganic materials from the SSQO modified methacrylate monomers synthesized in this study is the purpose of an ongoing research.

4. Conclusions

The hydrolytic condensation of MPTMS at 60 °C using UDMA and BisEMA methacrylate monomers as reactive solvents generates incompletely condensed SSQOs with a very large fraction of intramolecular cycles in a conveniently short period of time (1–2 weeks). In that way, methacrylate monomers are modified with around 40 wt.% of nanosized methacrylate-functionalized polyhedral SSQOs generated in situ by the hydrolysis and polycondensation of MPTMS.

The methacrylate monomers are not involved in the hydrolysis–condensation reactions with MPTMS and therefore can be polymerized by thermal or photochemical means, thereby cross-linking the preformed nanosized cage-like species.

Although the polycondensation of the SSQOs continues during the storage at room temperature, the reaction proceeds at a slow rate. Samples analyzed after 30 months of storage revealed the presence of $T_{12}(\text{OH})_2$ and $T_{13}(\text{OH})$ species, which were generated through the condensation of $T_6(\text{OH})_2$ and $T_7(\text{OH})$ species. The absence of higher molar mass oligomers after a prolonged storage period is attributed to the fact that dilution of the reacting medium with polar solvents discourages bimolecular reactions that lead to polymer growth.

The formulations containing silsesquioxanes showed a markedly reduced content of extractable monomer after photopolymerization, which makes these resins very attractive for dental filling materials.

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