Silsesquioxane functionalized with methacrylate and amine groups as a crosslinker/co-initiator for the synthesis of hydrogels by visible-light photopolymerization

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ABSTRACT

A silsesquioxane bearing methacrylate and amine groups was synthesized by reacting half of the NH groups of *N*-[3-(trimethoxysilyl)-propyl]ethylene diamine with glycidyl methacrylate, followed by the hydrolytic condensation of methoxysilane groups. This led to a water-soluble silsesquioxane functionalized with methacrylate and amine groups (SFMA) that was characterized by UV-MALDI TOF MS. A formulation containing safranine-O as sensitizer and SFMA as co-initiator (electron donor)/crosslinker was used for the visible-light photopolymerization of water solutions of 2-hydroxyethylmethacrylate (HEMA) and acrylamide (AAm). Without SFMA addition no reaction was observed while in the presence of 0.8 wt% SFMA with respect to monomers, crosslinked polymers (hydrogels) were obtained. Swelling of the resulting hydrogels in a broad pH range was investigated.

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1. Introduction

Water-soluble photoinitiator systems for the visible-light photopolymerization of (meth)acrylic monomers have gained increasing interest in recent years [1–4]. The most commonly employed photoinitiators are those whose radicals are formed in a bimolecular process comprising an excited state of a dye and a co-initiator that behaves as electron donor (typically an aliphatic amine like triethanolamine [4]). Although the activated co-initiator (a radical) is incorporated to ends of polymer chains, the fraction that is not activated during the photopolymerization remains in the sol fraction of the final material. A possible way to avoid this problem is to use polymeric or polymerizable photoinitiators [5–7]. A novel photoinduced simultaneous polymerization and crosslinking of monovinyl monomers containing pendant hydroxyl groups has been recently reported based on the use of specially designed benzodioxinones [8]. These molecules have the ability to generate initiating species as well as crosslinking agents for a photoinduced polymer network formation.

For a photopolymerization carried out in water, a suitable co-initiator/crosslinker should have electron donor groups (e.g.,

aliphatic amines) for the generation of free radicals using a convenient sensitizer, two or more C=C groups (e.g., methacrylate groups) to perform as a crosslinker, and hydrophilic groups to provide water solubility. We will show that this can be achieved employing the chemistry of silsesquioxanes. These oligomers may be obtained by the hydrolytic condensation of organotrialkoxysilanes, RSi(OAlk)$_3$, performed in the presence of water and an acid or base as catalyst [9]. A convenient selection and chemical modification of the organic group may be used to introduce the necessary amine and methacrylate groups. The hydrolysis of alkoxy groups to SiOH groups provides water solubility and their partial condensation generates oligomers with increased methacrylate functionality. Silsesquioxanes exhibit a double distribution of molar masses; every species is characterized by the number of elemental units incorporated to its structure (monomer, dimer, trimer, etc.), and by the fraction of intramolecular cycles formed by Si–O–Si bonds. The double distribution of molar masses can be determined employing MALDI TOF mass spectrometry [10–21].

The chemistry of silsesquioxanes has been previously employed for the synthesis of multifunctional methacrylates [22,23]. Michael addition of acryloxyalkyl methacrylates with aminopropyltriethoxysilane led to organotrialkoxysilanes bearing 2 or more methacrylate groups and 1 tertiary amine in the structure. The hydrolytic condensation of these monomers produced methacrylate-functionalized silsesquioxanes that exhibit low viscosities

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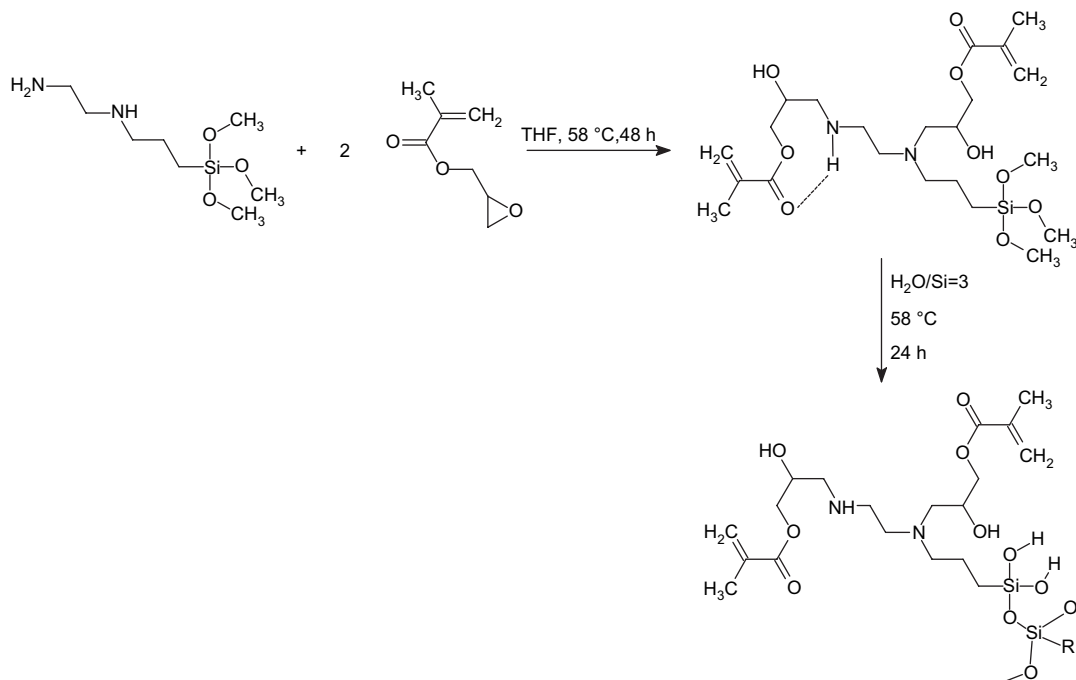
Scheme 1. Steps in the synthesis of the functionalized silsesquioxane for the particular case of a product incorporating 2 mol GMA.

and were suitable for dental applications. However, these products are not soluble in water and there was no report on their behavior as co-initiators in the photopolymerization reaction.

In this study, the functionalized silsesquioxane was synthesized in two steps starting from a commercial organotrialkoxysilane with amine functionalities in the organic moiety (Scheme 1). In the first step, amine groups were partially reacted with glycidyl methacrylate by a typical epoxy–amine addition reaction. In a second step, the hydrolysis of alkoxy groups and the partial condensation of the resulting SiOH groups led to the functionalized silsesquioxane. Due to the small conversion in the condensation reaction, the resulting silsesquioxane was soluble in water and could be used as a suitable co-initiator/crosslinker for the visible-light photopolymerization of methacrylic monomers. The dye selected as sensitizer was safranine-O (Saf) that has been extensively studied in combination with aliphatic amines both in aqueous solutions [2,4,24] and in organic solvents [25]. In these studies it was shown that under the action of visible light amino radicals were generated that acted as initiators of vinyl polymerizations.

Results will be discussed in the following order. First the synthesis and characterization (UV-MALDI TOF MS) of the water-soluble silsesquioxane functionalized with methacrylate and amine groups (SFMA) will be reported. Then, it will be shown that a combination of Saf/SFMA initiates the visible-light photopolymerization of an aqueous solution of 2-hydroxyethylmethacrylate (HEMA). Finally, the synthesis of hydrogels from aqueous solutions of HEMA and acrylamide (AAm) by visible-light photopolymerization in the presence of Saf/SFMA will be described. The effective incorporation of SFMA as crosslinking units of the hydrogel will be assessed by dynamic mechanical characterization and by determining the swelling behavior in a broad pH range.

2. Experimental

2.1. Synthesis of the trialkoxysilane functionalized with methacrylate and amine groups

The trialkoxysilane functionalized with methacrylate and amine groups was synthesized by reacting *N*-[3-(trimethoxysilyl)-propyl]ethylene diamine (Fluka, 97% purity) with glycidyl methacrylate (GMA, Aldrich, 97% purity), employing a molar ratio GMA/silane = 1.5. The reaction was carried out in a closed vessel using a 50% THF solution at 58 °C for 48 h under a nitrogen atmosphere. THF was previously refluxed in KOH and distilled over 4 Å molecular sieves.

2.2. Synthesis of the silsesquioxane functionalized with methacrylate and amine groups (SFMA)

The functionalized silsesquioxane (SFMA) was synthesized adding water (previously purified through a Millipore Milli-Q system) to the reaction product obtained in Section 2.1, in a molar ratio [H$_2$O]/Si = 3. The vessel was opened and the reaction was carried out at 58 °C for 24 h allowing continuous evaporation of volatiles (the hydrolytic condensation was catalyzed by the residual amine groups of the starting silane). The product was stored for 2 weeks at room temperature to allow complete evaporation of the organic solvent.

2.3. Visible-light photopolymerization

Aqueous solutions of 2-hydroxyethylmethacrylate (HEMA, Aldrich, 0.5 g/ml) containing safranine-O (Saf, Merck, recrystallized twice from methanol, absorbance at 460 nm is equal to 0.3 in a 1-cm path cell) as sensitizer and SFMA (0.1275 g/ml) as co-initiator were photopolymerized using a LED unit Ultralume 2 as light source (wavelength range 410–490 nm, Ultradent, USA). Blanks were performed eliminating either Saf or SFMA from the formulation. Samples were irradiated for fixed times and the conversion of C=C unsaturations was determined by infrared spectra (FTIR) in the near-infrared range.

2.4. Synthesis of hydrogels by visible-light photopolymerization

Hydrogels were synthesized from aqueous solutions containing HEMA (0.5 g/ml) acrylamide (AAm, Aldrich, 0.0543 g/ml), Saf (absorbance = 0.3 at 575 nm in a 1-cm path cell) and SFMA

$(4.3 \times 10^{-3}$ g/ml). A Rayonet model RPR-100 merry-go-round photochemical reactor supplied with 8 RPR-5750A lamps was used. In a typical experiment every tube was filled with 2 ml of the solution and irradiation was carried out for 2 h. Tubes were broken and cylindrical hydrogels were cut as disks and immersed in purified water to remove soluble materials. Water was replaced every 24 h and the treatment continued for 1 week. After this period hydrogels were dried at room temperature for 72 h.

2.5. Characterization techniques

Size exclusion chromatography (SEC) was performed with a Knauer K-501 device using a set of Phenomenex 5 μ-columns: 50 A, 100 A and M2, and a refractive index detector (Knauer K-2301). THF was used as a carrier at 1 ml/min.

Fourier-transform infrared spectra (FTIR) were obtained using a Genesis II-Mattson device in the transmission mode. SFMA samples and hydrogels were analyzed in the mid-infrared range; the first ones were cast from solutions on NaCl windows, the second ones were freeze-dried (24 h in a Virtis Benchtop SLC device) and then pressed with KBr. The consumption of C=C groups during photopolymerization was determined by following the decay of the 6165 cm^{-1} absorption band as described by Stansbury and Dickens [26]. Glass cells were employed for this purpose.

Matrix-assisted ultraviolet laser desorption-ionization time-of-flight mass spectra (UV-MALDI TOF MS) of SFMA were obtained using: (i) Applied Biosystems Voyager DE-STR and (ii) Shimadzu Kratos, Kompact MALDI 4 (Pulsed Extraction), both equipped with a pulsed nitrogen laser ($\lambda = 337$ nm; pulse width = 3 ns), tuneable time delay capability and PSD device. TOF analyzers were used at 20 kV and ions were obtained by irradiation just above the threshold laser power. Samples were measured in the linear mode, in both positive and negative ion modes. Usually 50 spectra were accumulated. Several chemicals were tested as matrices including β-carbolines: 9H-pyrido[3,4-b]indole (norharmane), and classical matrices: 2,5-dihydroxybenzoic acid (gentisic acid, GA), 3,5-dimethoxy-4-hydroxycinnamic acid (SA), 1,8-dihydroxy-9(10H)anthracenone (dithranol), and 2-(4-hydroxyphenylazo)benzoic acid (HABA). These chemicals were purchased from Sigma, Aldrich, Acros Organics (Japan) and Wako Pure Chemical Ind. (Japan). The best results were obtained by using GA in positive ion mode. Several proteins (Sigma) dissolved in aqueous 0.1% TFA (Merck) or in water (Milli Q grade), and dextran 5000 were used for calibration purposes. The matrix was dissolved in acetonitrile (Aldrich, HPLC grade):water (3:2 v/v). Two methods of sample preparation were used. In method A (sandwich), 0.5 μl of the matrix solution was placed on the sample probe tip and the solvent was removed by blowing air at room temperature. Then, 0.5 μl of the analyte solution in water (Milli Q grade) was placed 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.

Dynamic mechanical spectra of dried hydrogels were obtained with a Perkin–Elmer DMA-7 system. Disks of the hydrogels of 7.5 mm diameter and 1.78 mm thickness were cut into two halves across the diameter. A half disk was placed in the DMA device supported by two points separated by a 5 mm span. The specimen was heated to 190 °C at 10 °C/min to eliminate volatiles and cooled to room temperature. The DMA test was performed at 1 Hz, with a heating rate of 10 °C/min, and employing a static force of 477 mN and a dynamic force of 318 mN. Due to the non-standard geometry employed, absolute values of moduli had no physical meaning. Only the glass transition and the presence of a rubbery modulus, characteristic of a crosslinked polymer, were searched in this test.

Disks of dried hydrogels were weighed and immersed in commercial buffer solutions with pHs ranging from 2 to 13. Swollen samples were removed from the solutions at different times, blotted with filter paper and weighed. The swelling degree (S_w) was defined as the ratio between the mass of absorbed water over the mass of dry polymer. Determinations were carried out until S_w reached a constant value. Drying of the swollen gels was performed in air at room temperature.

3. Results and discussion

3.1. Trialkoxysilane functionalized with methacrylate and amine groups

The synthesis of the trialkoxysilane functionalized with methacrylate and amine groups was performed by reacting 1 mol of N-[3-(trimethoxysilyl)-propyl]ethylene diamine with 1.5 mol of glycidyl methacrylate (GMA). The first step, shown in Scheme 1, illustrates the formation of the particular product that incorporates 2 mol GMA. The starting trialkoxysilane has a primary amine and a secondary amine in its structure. The 3 mol of amine hydrogens (NH) might in principle be reacted with 3 mol of epoxy groups as proved when employing phenyl glycidyl ether (PGE) [15,27,28]. However, it was not possible to achieve 100% conversion of NH groups when employing 3 mol of GMA. Scheme 1 shows the possible formation of intramolecular H bonds between C=O and N–H groups in the reaction product containing 2 mol of GMA, leading to a relatively stable 8-member intramolecular cycle. This could explain the decrease in reactivity of the residual amine groups that does not allow an easy reaction of a third GMA molecule. The use of 1.5 mol GMA per mol of N-[3-(trimethoxysilyl)-propyl]ethylene diamine allowed a complete conversion of epoxy groups.

The evolution of the reaction for the formulation with a molar ratio GMA/silane = 1.5 was followed by SEC and FTIR. Fig. 1 shows SEC chromatograms of the initial solution and the reaction product (dashed line) obtained after 30 h at 58 °C. After this time, GMA was completely consumed as revealed by the disappearance of its characteristic peak in SEC chromatograms and the appearance of two peaks assigned to the reaction product containing 1 mol and 2 mol GMA. The starting silane did not show any signal in the SEC chromatogram; the peak of an internal standard: (3-trifluoromethyl)aniline, is also shown.

FTIR spectra of the initial solution and the reaction product obtained after 48 h at 58 °C are shown, respectively, in Fig. 2A and B.
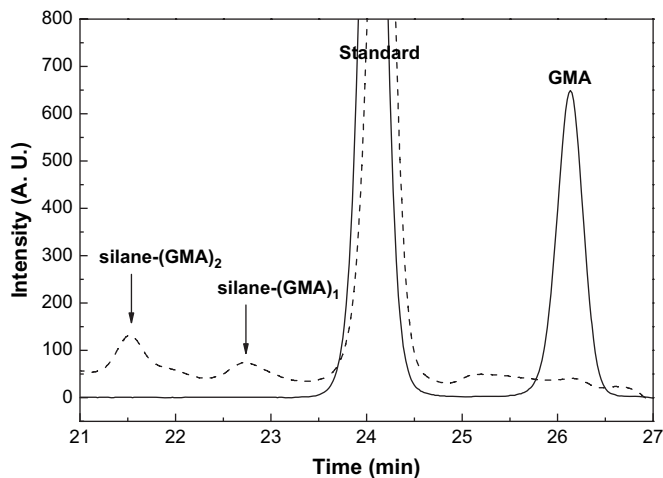

Fig. 1. SEC chromatogram of the initial solution (1.5 mol GMA per mole of silane) and the reaction product (dashed line) obtained after 30 h at 58 °C. The two peaks are assigned to the silane reacting with 1 mol and 2 mol GMA.
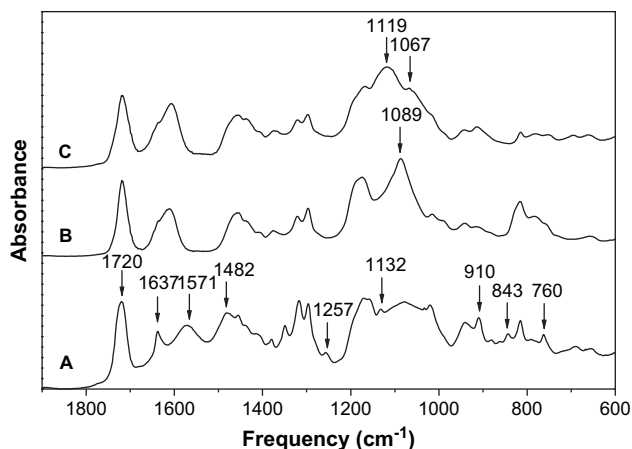
Fig. 2. FTIR spectra of a formulation containing 1.5 mol GMA per mole of silane; (A) as prepared, (B) after the first step of the synthesis (48 h at 58 °C), (C) after the second step of the synthesis ([H_2O]/Si = 3; 24 h at 58 °C + 2 weeks at RT).

Table 1
Assignment of main peaks present in UV-MALDI TOF mass spectrum

Exp. mass (Da)	Theor. mass (Da)	Species
397.2	398.0	Monomer + 2 GMA–MA (+H^+)
465.2	465.6	Monomer + 2 GMA (+H^+)
609.3	609.8	Dimer + 2 GMA–H_2O (+H^+)
627.3	627.8	Dimer + 2 GMA (+H^+)
683.4	683.9	Dimer + 3 GMA–H_2O–MA (+H^+)
701.4	701.9	Dimer + 3 GMA–MA (+H^+)
769.4	770.0	Dimer + 3 GMA (+H^+)
775.5	776.0	Dimer + 4 GMA–2 MA (+H^+)
843.5	844.1	Dimer + 4 GMA–MA (+H^+)
911.5	912.2	Dimer + 4 GMA (+H^+)
1005.7	1006.3	Trimer + 4 GMA–MA (+H^+)
1073.7	1074.4	Trimer + 4 GMA (+H^+)
1147.7	1148.5	Trimer + 5 GMA–MA (+H^+)
1166.8	1168.6	Tetramer + 4 GMA–MA (+H^+)
1235.8	1236.7	Tetramer + 4 GMA (+H^+)

The spectra show the disappearance of characteristic bands of the epoxy ring at 1482 cm^{-1}, 1257 cm^{-1}, 1132 cm^{-1}, 910 cm^{-1} and 843 cm^{-1} (residual contributions as for the band at 910 cm^{-1} are produced by overlapping with other bands). The disappearance of the NH$_2$ in-plane bending mode (scissoring motion) at 1571 cm^{-1} and the out-of-plane NH$_2$ bend at 760 cm^{-1} [29] indicates the complete reaction of primary amine groups. The presence of strong bands at 1720 cm^{-1} (carbonyl ester) and 1637 cm^{-1} (C=C group) confirms the functionalization of the silane with methacrylate groups.

3.2. Silsesquioxane functionalized with methacrylate and amine groups (SFMA)

The silsesquioxane was obtained by the hydrolytic condensation of the functionalized silane using a molar ratio [H_2O]/Si = 3, as shown by the second step in Scheme 1. The reaction is illustrated by the generation of 2 SiOH groups by the hydrolysis of SiOCH$_3$ groups and 1 Si–O–Si bond produced by condensation. This leads to a distribution of oligomers that constitute the final silsesquioxane.

A primary evidence of the hydrolytic condensation was obtained by the FTIR spectrum of the final product (Fig. 2C). It shows the disappearance of the band at 1089 cm^{-1} characteristic of SiOCH$_3$ groups and its replacement by two bands at 1067 cm^{-1} and 1119 cm^{-1} assigned to Si–O–Si bonds.

UV-MALDI TOF MS is possibly the best experimental technique to characterize a functional silsesquioxane as the one synthesized in this study. By determining the masses of species present in the reaction product one can obtain the following information: (a) distribution of oligomers and fraction of intramolecular cycles, (b) GMA units reacted with NH groups, (c) presence of secondary reactions (the hydrolysis of ester groups can be characterized by the loss of methacrylic acid units; intermolecular transesterification reactions between ester groups and secondary alcohols can be assessed by the gain and loss of methacrylic acid units). Table 1 shows the assignment of main peaks of the reaction product found in the UV-MALDI TOF mass spectrum.

Main species could be assigned to monomers, dimers, trimers and tetramers ionized with protons (some larger *n*-mers were also present but in very small amounts). All of them were completely hydrolyzed species confirming the fact that no residual Si–OCH$_3$ groups remained in the product (an expected result taking into account that the silsesquioxane was dissolved in water to obtain the mass spectrum). Trimers and tetramers were linear species with only 1 Si–O–Si bond between constitutive units (this is the case

illustrated in Scheme 1). A fraction of dimers showed the loss of 1 water molecule that can only arise through the formation of an intramolecular cycle involving 1 SiOH group and 1 COH group closing the loop through a Si–O–C bond. We have previously shown the possibility of forming this type of intramolecular cycles for another family of silsesquioxanes [19]. GMA units were present in every one of the species. Residual monomers contained 2 GMA units. A monomer with 3 GMA units was not expected as previously explained. However, as the average number of GMA moles per mole of monomer was 1.5, monomers with 1 GMA unit could have appeared in the mass spectrum. The fact that they did not appear enabled us to infer that their reactivity towards condensation was higher than that of monomers with 2 GMA units. This is confirmed by the fact that tetramers present in highest proportions contain 4 GMA units (the average number would have been 6). Some of the species loosed a methacrylic acid residue (MA) but there were no species where a gain of an MA residue was observed. This can be explained by a partial hydrolysis of ester groups when dissolving the silsesquioxane in water, a fact that was confirmed by following the evolution of the pH of an aqueous solution of the silsesquioxane with time. The dissolution occurred at a slow rate during 24 h increasing the pH to about 8.6. Then, a slow hydrolysis of ester groups liberated methacrylic acid producing a decrease of pH tending towards an asymptotic value of pH close to 8. In photopolymerization reactions aqueous solutions of SFMA were used after 48 h of the beginning of dissolution.

3.3. SFMA as co-initiator of photopolymerization

The visible-light photopolymerization of HEMA was performed in the presence of Saf as sensitizer and SFMA as co-initiator. Fig. 3 shows the evolution of the conversion of C=C groups determined by the decay of the near-infrared band at 6165 cm^{-1}. Two other runs were carried out for formulations where either Saf or SFMA was not added. In these cases no reaction was observed, as expected. These tests showed that SFMA behaved as a co-initiator in the visible-light photopolymerization.

The mechanism of generation of radicals using Saf as initiator and an amine as co-initiator has been described in the literature [2,4,24,25] and is represented in Scheme 2. In the proposed mechanism, the active amino radicals are produced by an electron transfer reaction between the deprotonated excited state of the dye and the amine. This reaction leads to the formation of semi-reduced safranine in the form of a radical anion and the radical cation of the amine. The latter undergoes a second fast proton transfer leading to an active radical that initiates the polymerization [30].
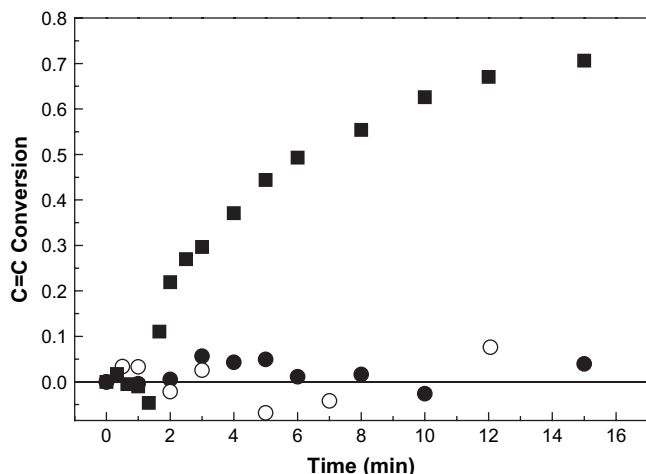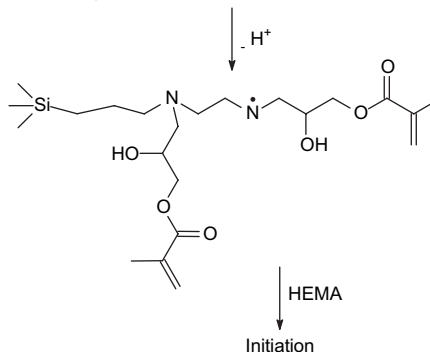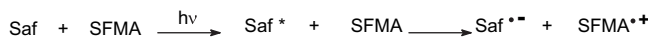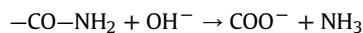
Fig. 3. Conversion of C=C groups determined by the decay of the near-infrared band at 6165 cm^{-1} during the photopolymerization of an aqueous solution of HEMA in the presence of Saf as sensitizer and SFMA as co-initiator (■); runs for formulations where either Saf (○) or the co-initiator (●) was not added did not show any reaction.

3.4. Synthesis and characterization of hydrogels

Hydrogels were synthesized from formulations containing HEMA and AAm in the presence of Saf/SFMA. Hydrogels based on HEMA are widely used for biomedical and pharmaceutical applications [8]. AAm was added as a co-monomer to generate a pH-responsive hydrogel as will be discussed in what follows.

Dynamic mechanical characterization of the hydrogel previously dried by heating to 190 °C to remove volatiles is shown in Fig. 4. The glass–rubber transition takes place over a broad temperature range, from about 90 °C to about 170 °C, giving a qualitative indication of a corresponding broad distribution of crosslink density. But the point we want to emphasize is the existence of a rubbery modulus that is characteristic of a crosslinked polymer. The participation of SFMA as a crosslinker of the polymer network is effectively proved by DMA characterization.

The materials could be reversibly swollen in buffer solutions of pH varying from 2 to 13, a phenomenon that is characteristic of crosslinked hydrogels. The water uptake as a function of time is shown in Fig. 5. In the pH range comprised between 2 and 11 the equilibrium was reached in a few hours attaining S_w values in the range of 0.8–1. Increasing the pH to 12 and 13 led to slower swelling kinetics and much higher values of the swelling degree. This behavior is explained by the hydrolysis of amide groups at these high pH values:

$$-CO-NH_2 + OH^- \rightarrow COO^- + NH_3$$
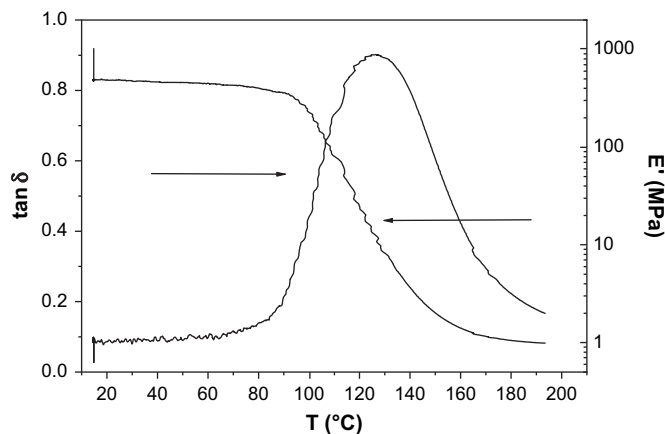

Fig. 4. Storage modulus (E') and loss factor (tan δ) as a function of temperature, for the hydrogel previously heated to 190 °C to remove volatiles.
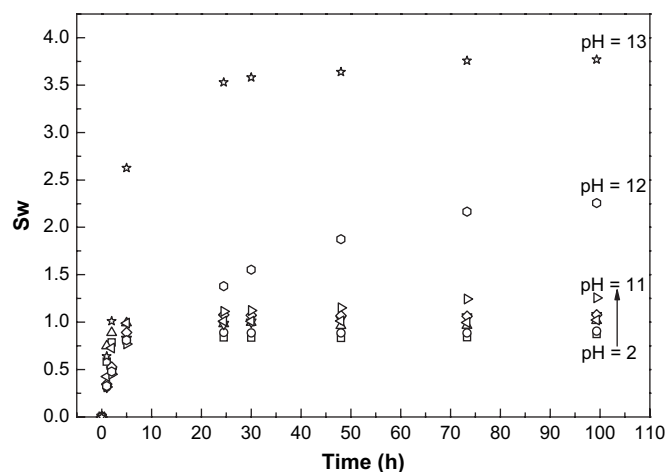

Fig. 5. Water uptake as a function of time for crosslinked HEMA/AAm hydrogels immersed in buffer solutions of different pH values.

The repulsion among negative charges of carboxylate anions fixed in the network structure produced a significant increase in the swelling degree at pH = 13.

FTIR spectra of freeze-dried hydrogels swollen at different pH values confirmed the hydrolysis of amide groups (Fig. 6). Increasing the pH to 13 produced the appearance of the characteristic carboxylate band at 1570 cm^{-1} assigned to the asymmetric CO_2 stretch [29]. The appearance of the less intense band corresponding to the symmetric CO_2 stretch at 1410 cm^{-1} [29] is also observed for the hydrogel swollen at pH = 13.
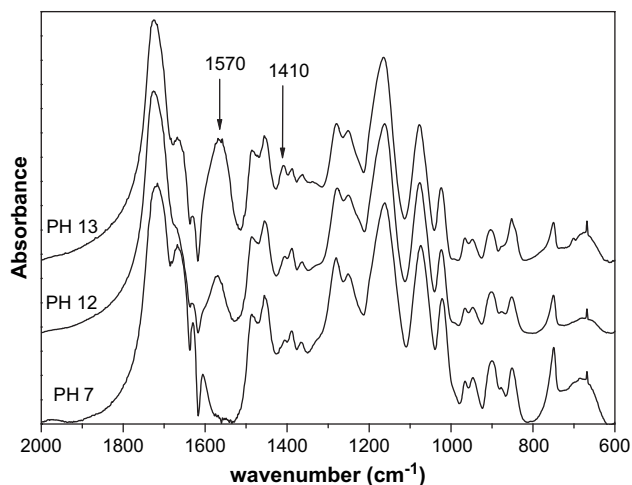

Scheme 2. Steps of the photoinitiation process.

Fig. 6. FTIR spectra of freeze-dried hydrogels swollen at different pH values.
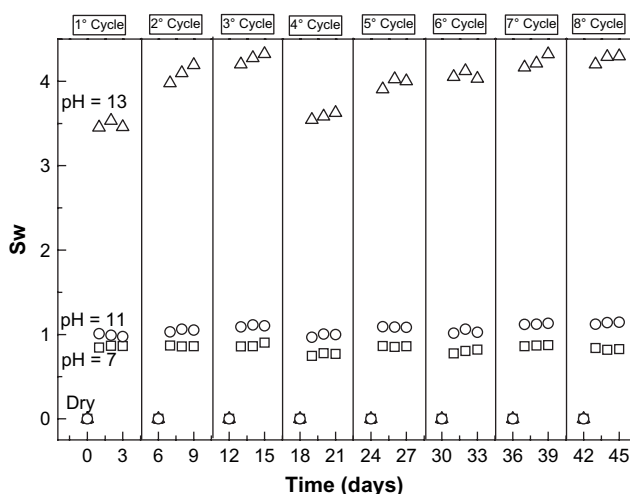
Fig. 7. Cycles of swelling (pH = 7, 11 and 13) followed by drying in air.

incorporated 2 or more GMA units to the structure and could therefore be used as crosslinkers in a free radical polymerization. When SFMA was dissolved in water, a small fraction of ester groups was hydrolyzed liberating methacrylic acid.

SFMA could be used as a co-initiator in the visible-light photo-polymerization of aqueous solutions of HEMA and AAm, in the presence of Saf as sensitizer. Resulting hydrogels exhibited a rubbery modulus and a reversible swelling behavior indicating that SFMA was effectively incorporated as crosslinking junctions in the polymer network.

Sequences of 8 swelling/drying cycles performed during 45 days are shown in Fig. 7. The swelling was performed at pH = 7, 11 or 13 and drying was carried out in air at room temperature. The behavior was completely reversible within experimental error. Hydrogels recuperated the initial weight when dried in air and could be repeatedly swollen to the same value of S_w at the corresponding pH. In particular, the first swelling cycle at pH = 13 led to the irreversible hydrolysis of most of the amide groups since subsequent cycles did not modify significantly the maximum swelling degree.

4. Conclusions

A silsesquioxane functionalized with methacrylate and amine groups (SFMA) was synthesized by reacting half of the NH groups of *N*-[3-(trimethoxysilyl)-propyl]ethylene diamine with glycidyl methacrylate (GMA), followed by hydrolysis and condensation adding water in a molar ratio [H$_2$O]/Si = 3. UV-MALDI TOF MS showed that SFMA was a mixture of the residual hydrolyzed monomer up to linear trimers and tetramers. Each of these species

References

[1] Encinas MV, Lissi EA. In: Salomone JC, editor. Polymeric materials encyclopedia, vol. 7. Boca Raton: CRC; 1996. p. 5205.
[2] Encinas MV, Rufs AM, Neumann MG, Previtali CM. Polymer 1996;37:1395.
[3] Erddalane A, Fouassier JP, Morlet-Savary F, Takimoto Y. J Polym Sci Part A Polym Chem 1996;34:633.
[4] Gómez ML, Avila V, Montejano HA, Previtali CM. Polymer 2003;44:2875.
[5] Decker C. Macromol Rapid Commun 2002;23:1067.
[6] Valderas C, Bertolotti S, Previtali CM, Encinas MV. J Polym Sci Part A Polym Chem 2002;40:2888.
[7] Corrales T, Catalina F, Peinado C, Allen NS. J Photochem Photobiol A Chem 2003;159:103.
[8] Tasdelen MA, Kumbaraci V, Talinli N, Yagci Y. Macromolecules 2007;40:4406.
[9] Baney RH, Itoh M, Sakakibara A, Suzuki T. Chem Rev 1995;95:1409.
[10] Wallace WE, Guttman CM, Antonucci JM. J Am Soc Mass Spectrom 1999; 10:224.
[11] Wallace WE, Guttman CM, Antonucci JM. Polymer 2000;41:2219.
[12] Eisenberg PE, Erra-Balsells R, Ishikawa Y, Lucas JC, Mauri AN, Nonami H, et al. Macromolecules 2000;33:1940.
[13] Kim HJ, Lee JK, Park SJ, Ro HW, Yoo DY, Yoon DY. Anal Chem 2000;72:5673.
[14] Tecklenburg RE, Wallace WE, Chen H. Rapid Commun Mass Spectrom 2001; 15:2176.
[15] Fasce DP, Williams RJJ, Erra-Balsells R, Ishikawa Y, Nonami H. Macromolecules 2001;34:3534.
[16] Williams RJJ, Erra-Balsells R, Ishikawa Y, Nonami H, Mauri AN, Riccardi CC. Macromol Chem Phys 2001;202:2425.
[17] Lee JK, Kim HJ, Kim JB, Park ES, Park SJ, Yoo DY, et al. J Am Chem Soc 2001;123: 12121.
[18] Eisenberg P, Erra-Balsells R, Ishikawa W, Lucas JC, Nonami H, Williams RJJ. Macromolecules 2002;35:1160.
[19] dell'Erba IE, Fasce DP, Williams RJJ, Erra-Balsells R, Fukuyama Y, Nonami H. J Organomet Chem 2003;686:42.
[20] Hu H, Zhang X, You H, Liu Y, Zhang H, Sun D. J Mater Sci 2004;39:1331.
[21] Klapdhor S, Moszner N, Kickelbick G, Krüger RP. Monatsh Chem 2006;137:667.
[22] Müh E, Marquardt J, Klee JE, Frey H, Mülhaupt R. Macromolecules 2001;34: 5778.
[23] Moszner N, Völkel T, Cramer von Clausbruch S, Geiter E, Batliner N, Rheinberger V. Macromol Mater Eng 2002;287:339.
[24] Gómez ML, Previtali CM, Montejano HA. Polymer 2007;48:2355.
[25] Previtali CM, Bertolotti SG, Neumann MG, Pastre IA, Rufs AM, Encinas MV. Macromolecules 1994;27:7454.
[26] Stansbury J, Dickens S. Dent Mater 2001;17:71.
[27] Fasce DP, Williams RJJ, Méchin F, Pascault JP, Llauro MF, Pétiaud R. Macromolecules 1999;32:4757.
[28] Fasce DP, dell'Erba IE, Williams RJJ. Polymer 2005;46:6649.
[29] Smith B. Infrared spectral interpretation: a systematic approach. Boca Raton: CRC; 1999.
[30] Hassoon S, Neckers DC. J Phys Chem 1995;99:9416.