



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-

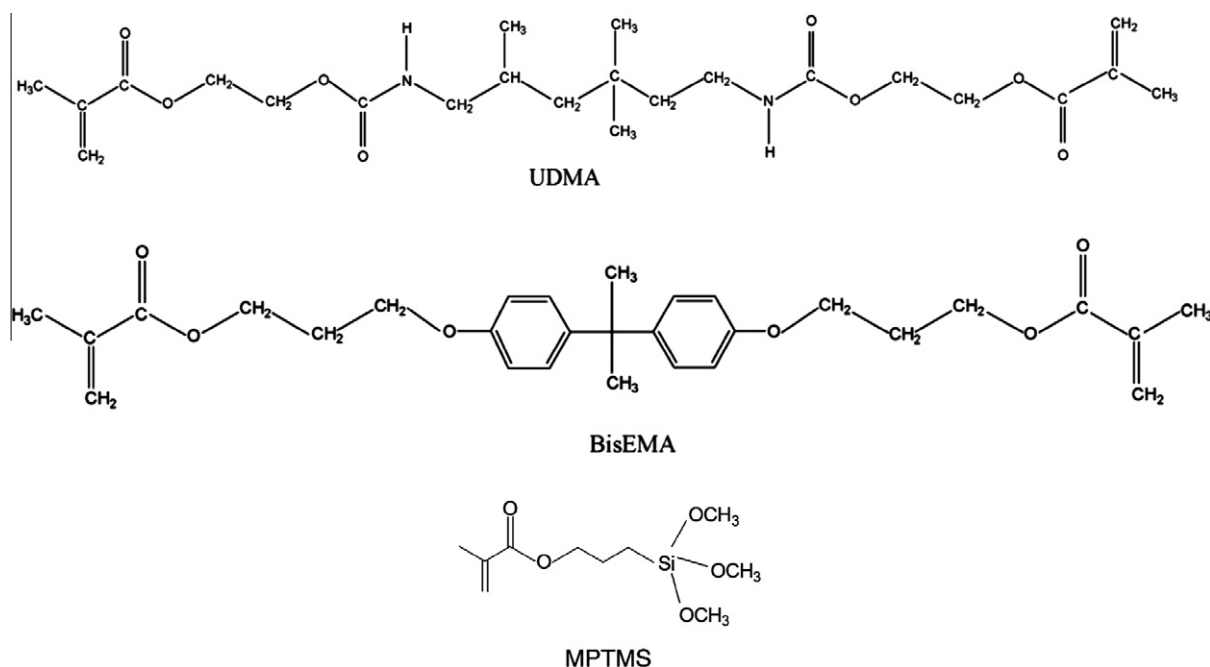
propyl)-trimethoxysilane (MPTMS, Sigma–Aldrich) and formic 98 wt.% (Sigma–Aldrich) were used as received. The methacrylate monomers used as reactive solvents in the hydrolytic condensation of MPTMS were: 2,2-bis[4-(2-methacryloxyethoxy) phenyl]propane (BisEMA) and 1,6-bis(methacryloxy-2-ethoxy-carbonylamino)-2,4,4-trimethylhexane (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.

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