

SYNTHESIS OF SILSESQUOXANES DERIVED FROM (3-METHACRYLOXYPROPYL) TRIMETHOXYSilANE BY USING SUPERCRITICAL CO₂ AS A SOLVENT MEDIUM

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The synthesis of silsesquioxanes (SSOs) from (3-Methacryloxypropyl) Trimethoxysilane (γ -MPS) was performed using a “water free” sol-gel polymerization method in a high-pressure carbon dioxide atmosphere. The polycondensation was carried out using 98 wt % formic acid as catalyst (molar ratio HCOOH/Si=3) either at 323 K or 343 K, using a carbon dioxide pressure of 25 MPa for periods of time between 3 to 72 hours followed by thermal treatment of the obtained SSOs at 323 K in open vessels. Supercritical carbon dioxide (SC-CO₂) and formic acid are miscible at the temperatures and pressures used in the experiments. In a conventional process, where no solvent is present, the γ -MPS reacts with formic acid to give sililformates that condense to provide siloxane bonds, required to the formation of a polymeric network. Methanol and methyl formate are produced as secondary products. In a supercritical medium, a similar process is expected to take place. The process at supercritical conditions gave rise to a larger conversion degree of Si-OCH₃ groups at lower reaction times than those obtained with conventional methods. The evolution of the sol-gel reaction was followed by nuclear magnetic resonance of hydrogen and by infrared spectroscopy.

INTRODUCTION

Organic-inorganic hybrids are a class of materials that have attracted a large attention in recent years since they can be designed with specific properties and functionalities. The possibility of combining properties of organic and inorganic components in a unique material on a molecular or nanoscale level allows the development of materials with new properties. These materials have numerous potential applications in many areas such as catalyst, electronics, optics or biomaterials [1,2]. There are many ways in which these materials may be synthesized, however the sol-gel technique starting off trialkoxysilanes is a typical one. The mild reaction conditions of the sol-gel method (“chimie douce”), specially the low reaction temperature, allow to introduce organic groups in inorganic materials. There are essentially two types of hybrid materials obtained by sol-gel: i) organic compounds can be incorporated in the inorganic gel network; and ii) organic and inorganic groups can be linked by stable chemical bonds. The later type of hybrid materials involves precursors that can have non reactive (e.g. methyl, cyclohexyl, phenyl, etc.) or reactive (or polymerizable) organic groups (e.g. vinyl, 3-glycidoxypropyl, etc.).

The hydrolytic condensation of trialkoxysilanes leads to products, generically called poly(silsesquioxanes) or silsesquioxanes (SSOs), that are a class of compounds with the empirical formula $\text{RSiO}_{1.5}$. The term silsesquioxane is also used to indicate partially condensed products $[\text{RSiO}_{1.5-x}(\text{OH})_{2x}]_n$.

Several structural representations of silsesquioxanes with the empirical formula $(\text{RSiO}_{1.5})_n$ are possible (Fig. 1), with the two most common representations being a ladder-type structure (Fig.1 (b)) and a cubic structure (Fig.1(c)) containing eight silicon atoms placed at the vertices of the cube. On the other hand, the partially condensed silsesquioxanes are represented with open structures as is shown in Fig.1 (e).

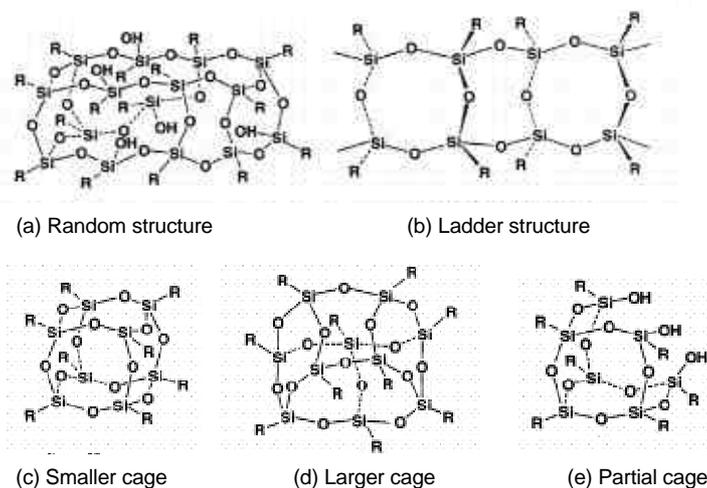


Figure 1. Structural representations of SSOs

The polycondensation of trialkoxysilanes can be carried out using strong carboxylic acids such as trifluoroacetic acid or formic acid in the absence of water. The carboxylic acid can act as a reactant and catalyst. In conventional methods, the polycondensation of trialkoxysilanes is carried out in bulk, without solvent, using catalyst in open vessels placed in an oven, where the continuous evaporation of volatile products takes place [3]. Recently, there has been considerable progress in the use of carbon dioxide in supercritical state (SC-CO_2) as a solvent medium for different types of polymerization reactions [4]. Because SC-CO_2 is a relatively non polar medium, sol-gel polymerization in SC-CO_2 using standard formulations are not possible due to the large quantity of water necessary for the hydrolysis and condensation of the trialkoxysilanes. However, it has been reported that sol-gel reactions can be performed in SC-CO_2 by using formic acid as catalyst [5]. The aim of this study is to analyze the effects of using SC-CO_2 as a solvent medium on the characteristics of synthesized SSOs, by applying the “water-free sol-gel polymerization technique reported by Sharp *et al.* [6]. Results were compared with those obtained by conventional methods.

EXPERIMENTAL

Synthesis of Silsesquioxanes (SSOs)

SSOs were synthesized from (3-methacryloxypropyl) trimethoxysilane (MPMS, Dow Corning Z-6030). Its hydrolytic condensation was performed with concentrated formic acid (Merk, 98 wt %) using a molar ratio of $\text{HCOOH/Si}=3$. The synthesis of SSOs involved a batch-type procedure in a high-pressure atmosphere of CO_2 followed by thermal treatment of the recovered samples added to an open vessel and placed in an air-oven at 323 K. In a typical experiment, the

resulting solution of monomer and formic acid was placed into an autoclave that was charged with liquid CO₂ (6 MPa). Temperature was increased up to 323 K or 343 K. Then, the pressure of the system was raised up to 25 MPa for all experiences. Table 1 shows the experimental conditions used to synthesized the different SSOs. During the time of reaction at supercritical conditions the reaction mixture was continuously stirred at 1000 rpm. The system was then depressurized and homogeneous viscous liquids were obtained. A sample of silsesquioxane was also synthesized in bulk from a mixture of MPMS with concentrated formic acid (HCOOH/Si=3) in an open vessel placed in an air-oven at T= 323 K in order to compare the results with a conventional process.

Sample	T (°C)	Reaction Time
SSO1	50	5 days *
SSO2	50	3 h
SSO3	50	24h
SSO4	50	72h
SSO5	70	24 h
SSO6	70	48 h
SSO7	70	72 h

Table 1. Experimental conditions used for the synthesis of silsesquioxanes.

* Conventional process

Equipment

The equipment consists of a high pressure stainless steel autoclave (Thar Designs, 70 mL of capacity) that has two opposite sapphire windows. The autoclave has a vertically mounted impeller stirrer (DynaMag, 2500rpm) and four resistances for heating. A syringe pump (Thar Design, SP-240) manipulated through a computer was used to compress and deliver the CO₂ into the autoclave. A setup of the apparatus is schematically depicted in Fig. 2.

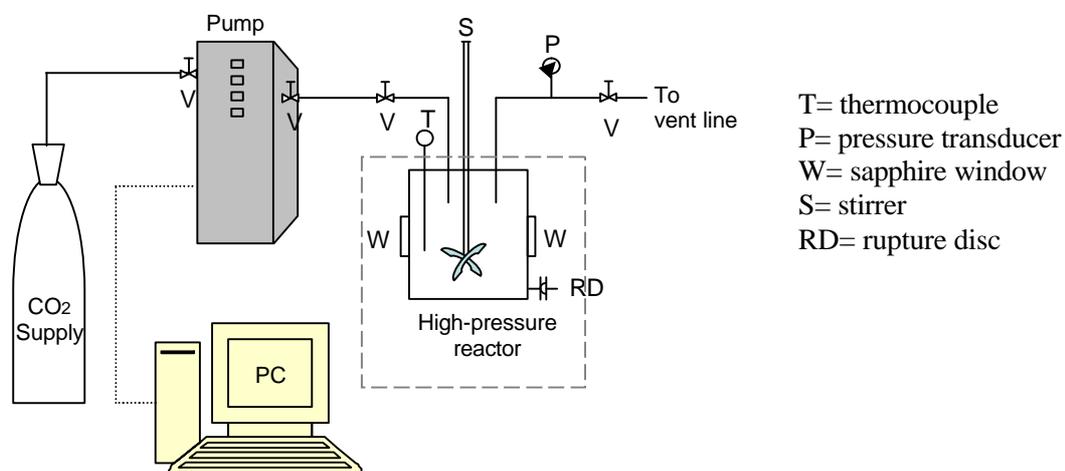


Figure 2. Reactor system for chemical syntheses in SC-CO₂

Characterization

The ¹H NMR spectra were recorded in a Bruker ARX-300 NMR spectrometer, operating at room temperature and 300 MHz, from deuterated chloroform solutions. Chemical shift are reported as δ unit (ppm) relative to tetramethylsilane. Infrared spectra were recorded with an FT-IR (Perkin Elmer, Spectrum One) spectrometer, in the transmission mode, making coating on KBr windows.

RESULTS AND DISCUSSION

Fig.3 shows the ^1H NMR spectra of the viscous liquids obtained immediately after each experience. Peaks assignment is listed in Table 2.

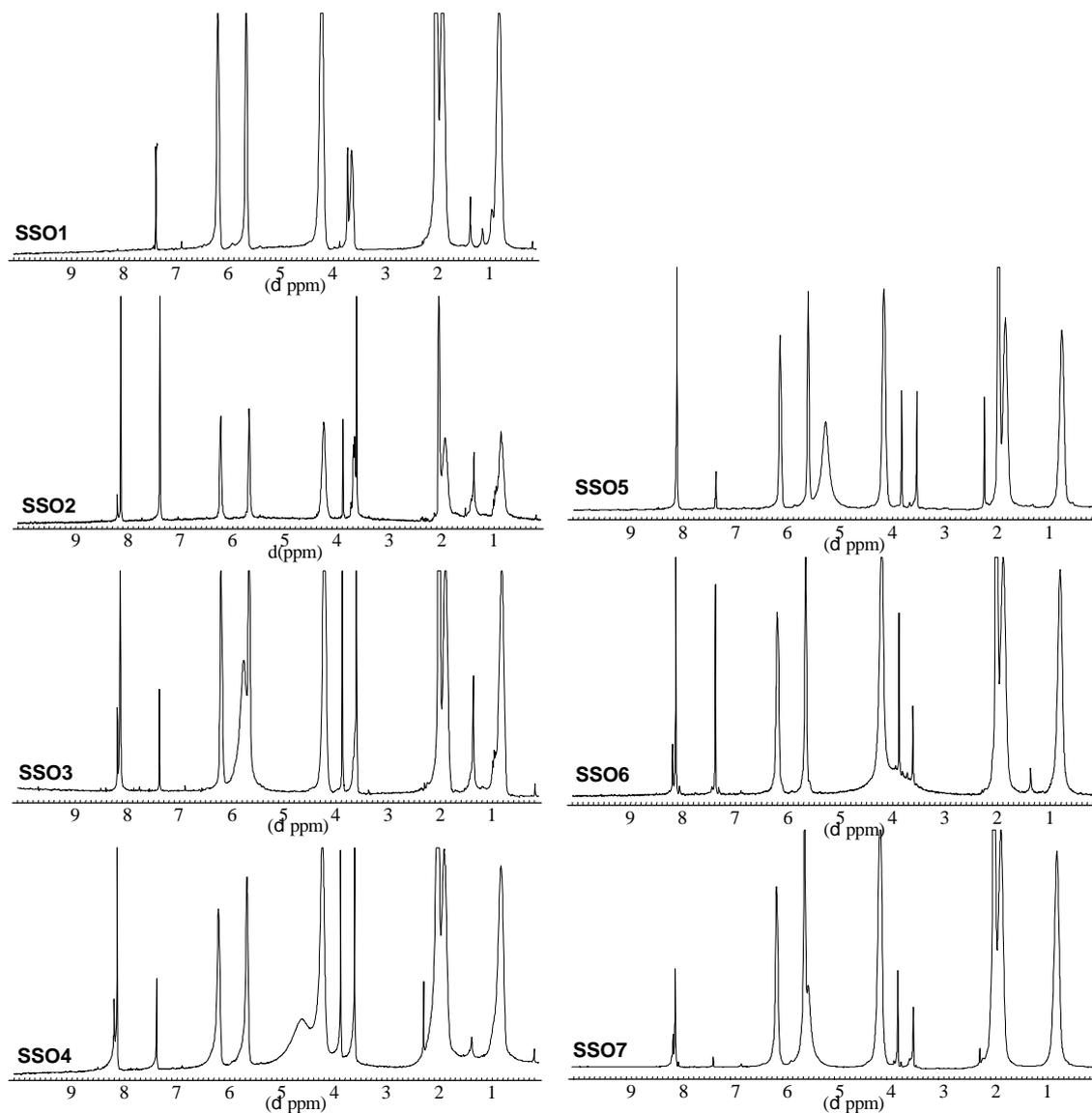
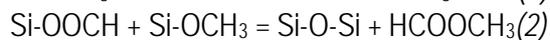


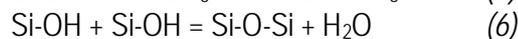
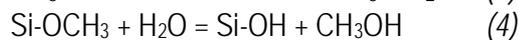
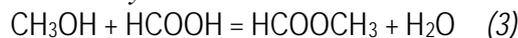
Figure 3. ^1H NMR spectra of the synthesized SSOs.

Alcoxysilanes react with anhydrous formic acid producing silanols that condense to give siloxane bonds required to create a polymeric network that will form a gel. The produced alcohol is converted to a formate ester. For an essential Si-OCH₃ group of MPMS, main and secondary reactions taking place in a conventional method are listed below:

Main reactions:



Secondary reactions:



The amount of residual Si-OCH₃ groups (determined through of the signal at 3.50-3.55 ppm) was used to calculate the degree of conversion of the OCH₃ groups of the MPMS for each sample. The protons of the (3-methacryloxy) propyl residue keep their relative intensities unaltered during the reaction, so that they can be used as internal standards.

d (ppm)	Assigned group	Compound (number of protons)
0.7	CH ₂ (position α to the Si atom)	MPMS (2H)
1.80	CH ₂ (position β to the Si atom)	MPMS (2H)
1.94	CH ₃	MPMS (3H)
3.42	CH ₃ -OH	Methanol (3H)
3.58	OCH ₃	MPMS (9H)
3.70	HCOOCH ₃	Methyl formate (3H)
4.12	CH ₂ (position γ to the Si atom)	MPMS (2H)
5.54 and 6.10	C=CH ₂	MPMS (2H)
8.03	HCOOSi	Sililformate (1H)
8.07	HCOOCH ₃	Methyl formate (1H)

Table 2. Assignment of ¹H NMR signals reported as d unit (ppm) relative to tetramethylsilane.

When the reaction was performed at 323 K, the Si-OCH₃ signal slightly decreased in the ¹H NMR spectra with increasing reaction times. The conversion values of OCH₃ groups for the series SSO2, SSO3, SSO4 were 79, 91 and 95 %, respectively, whereas the SSO1 gave rise to a 93 % of conversion. On the other hand, when the reaction was carried out at 343 K, large values of OCH₃ conversion were obtained. The conversion values of OCH₃ groups were 98, 98 and 99 % for SSO5, SSO6, and SSO7 samples, respectively. A useful effect of the stirring on the conversion degree of OCH₃ groups was also detected in the synthesis of the SSO6 sample.

Formic acid, methanol and methyl formate are miscible with SC-CO₂. ¹H NMR spectrum of the extracted fraction with CO₂ phase after the synthesis of SSO5 showed that some fraction of the residual formic acid was eliminated from the mixture during the depressurization step. It was assumed, that some fraction of produced methanol and methyl formate can be also eliminated with the CO₂ phase during the depressurization process.

The results showed that in the first stage of the reaction the formation of sililformate groups (Si-OOCH) and methanol took place. The later reacted with formic acid to produce methyl formate and water, which favoured the hydrolysis of Si-OCH₃ producing Si-OH groups and more methanol. Hence, the obtained products after the depressurization process have an elevated amount of Si-OH groups and consequently a high reactivity at room temperature. Alternatively, in conventional methods the continuous elimination of volatile compounds helps the condensation reactions to take place rapidly, being the formation of the Si-OOCH groups the limiting rate reaction.

When the SSOs were incubated at 323 K in open vessels all volatile compounds were eliminated and the remaining peaks of the ¹H NMR spectra showed important broadening indicative of a relatively high molecular weigh products. The FT-IR spectra of the SSOs, obtained within 10-20 days after the syntheses, show clearly the disappearance of the band at 2840 cm⁻¹ assigned to OCH₃ groups. The broad band centred at 3482 cm⁻¹ was assigned to the stretching of OH of SiOH groups, indicating that open structures are present in the samples. Also, the bands at about 1120 and 1040 cm⁻¹ assigned to stretching of the groups Si-O-Si are present in the spectra showing that some condensation occurred after thermal treatment of SSOs at 323 K in the open systems. The progressive chemical change during conversion of SSOs, the

loss of OCH₃ groups on hydrolysis to form Si-OH and the condensation of these groups to form Si-O-Si bonds were confirmed by infrared analyses.

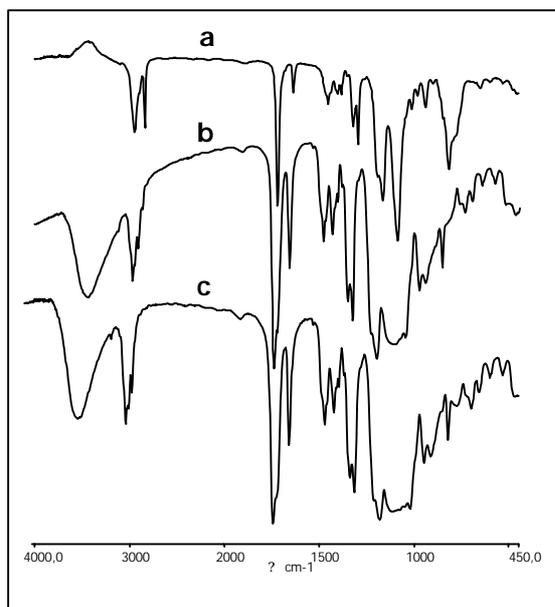


Figure 4. FT-IR spectra of (a) MPMS, (b) SSO3 immediately after the depressurization step and (c) SSO3 after 24 h of storage at room temperature in an open vessel.

CONCLUSIONS

The polycondensation of (3-methacryloxypropyl) trimethoxysilane was performed by using a water-free sol-gel polymerization process, employing formic acid as catalyst and supercritical carbon dioxide as a solvent medium. By using this method, all methacryloxypropyl residues remained intact indicating the non-hydrolysis of ester groups during the synthesis. Similar degree of conversions of OCH₃ groups respect to conventional syntheses at 323 K was achieved at a lower time of reaction. The syntheses carried out at 343 K in SC-CO₂ gave rise to large values of conversion of the OCH₃ groups. However, more effort is required to obtain a more precise control of the condensation reactions in a supercritical medium. The presented preliminary results are part of an ongoing research oriented to investigate the effect of different experimental variables (CO₂ pressure, dilution of the samples, catalyst type, SC-CO₂ extraction of the volatile compounds, etc.) on the polycondensation of trialkoxysilanes.

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