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## Original Research Paper

## A two-step Sol-Gel method to synthesize a ladder polymethylsilsesquioxane nanoparticles

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## ABSTRACT

The ladder polymethylsilsesquioxane (PMSQ) nanoparticles with average diameter size of 15 and 20 nm were synthesized by hydrolysis and condensation of methyltrimethoxysilane (MTMS). An ex situ kinetic study in acidic medium of MTMS hydrolysis was followed by Raman spectroscopy. The PMSQ nanoparticles was studied by infrared spectroscopy, <sup>29</sup>Si and <sup>13</sup>C nuclear magnetic resonance and by X-ray diffraction. The thermal stability was examined by thermogravimetric analysis. PMSQ nanoparticles have a degradation temperature of 390  C under nitrogen and 380  C under oxygen, an excellent specific area (397.21 m<sup>2</sup>/g), a density of 1.42 g/m<sup>3</sup> and hydrophobic surface (apparent contact angle 148     3).

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## 1. Introduction

Siloxane is a functional group in organosilicon chemistry with Silicon-Oxygen-Silicon linkage. The siloxane family includes a large number of compounds placing into two major groups resulting from their structures: cyclic compounds with respect to the aromatic nuclei and large molecular weight compounds, such as silsesquioxanes, which the Si–O bonds form linear chain or three dimensional structures. Used primarily as a coupling agents and coatings [1–3], siloxanes have been a great success as filler in the field of composites specially silsesquioxanes species because of their varied structures. Silsesquioxanes are hybrid materials, organic-inorganic, which possess good thermal stability and excellent mechanical and other interesting properties. All these properties make this material one of the compounds most studied by scientific researchers in recent years, in particular in the field of nanocomposites with organic polymers. The addition of inorganic compounds to the polymer improves the mechanical, thermal, electrical and optical properties of the polymer. In fact, the inorganic Si–O network in silsesquioxanes stabilizes the material and their organic part interacts with the polymeric matrix in order to strengthen it. Silsesquioxanes have shown their potential consistently in the manufacturing of functional materials [4].

Silsesquioxanes are compounds that can be defined by the general chemical formula (RSiO<sub>1.5</sub>)<sub>n</sub>, in which R can be any kind of organic group and H [5,6]. Fig. 1 illustrates the structure of this material as described in the literature [7,8]: compounds in the form of closed cages called polyhedral oligomeric silsesquioxanes (POSS) (Fig. 1A), structures in an open cage (Fig. 1B), a ladder structure in which two chains of Si–O–Si are connected in a regular way by oxane bridges (Fig. 1C), and random structures which do not represent a regular organization (Fig. 1D). This study covered the synthesis and analysis of the properties of the ladder structure of polysilsesquioxane.

Ladder polysilsesquioxanes are obtained by the Sol-Gel method which comprises the hydrolysis and condensation reactions of type R-SiX<sub>3</sub> (X = Cl, OR') precursors. The condensation process must be controlled in order to avoid the formation of an amorphous structure. Under controlled conditions (water concentration, temperature, pH and solvent), a ladder structure of silsesquioxane with a large molecular weight can be obtained. The number of disordered structures in the polysilsesquioxane increases with the increase in its molecular weight. The disordered structure ratio depends strongly on the nature of the substituting on the silicon atom and the operating conditions [9]. The first synthesis of the ladder polysilsesquioxane was obtained by Brown in 1960 [10] but several methods of ladder polysilsesquioxane synthesis have been developed more recently [11–14]. The research effort concentrated on controlling the polymer structure. Most of these methods of

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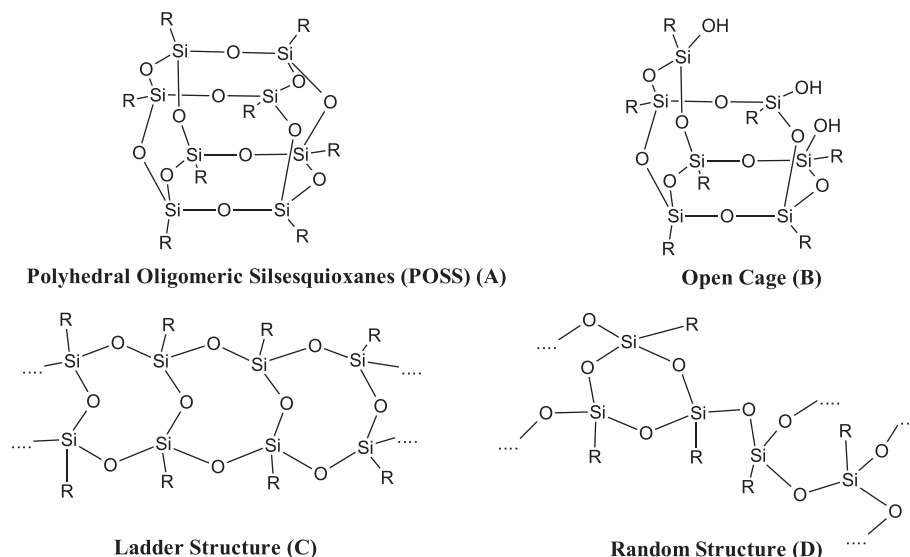


Fig. 1. Chemical structure of silsesquioxanes.

90 synthesis focus on the manufacture of ladder polysilsesquioxanes  
 91 with a large molecular weight because of their broad range of  
 92 applications [15–22] but a few researchers have examined the syn-  
 93 thesis of ladder polysilsesquioxanes of nanometric size. Recently, Li  
 94 et al. [23] have synthesized a microsphere of polymethyl-  
 95 silsesquioxane by the conventional coagulation method. In this  
 96 work, we propose a simple method to synthesize the crystalline  
 97 nanoparticles of ladder polymethylsilsesquioxane (PMSQ) based  
 98 on the Sol-Gel method. The precursor used for this purpose was  
 99 methyltrimethoxysilane (MTMS). For this end, MTMS was hydroly-  
 100 sysis in acid medium which corresponding to the sol and the gel  
 101 was formed after condensation reaction in basic medium. As such,  
 102 the structure of the produced material was identified by several  
 103 spectroscopic methods and the material obtained possesses an  
 104 excellent thermal stability, a nanometric size, and a hydrophobic  
 105 surface.

## 2. Materials and methods

### 2.1. Materials

108 The chemical products used, namely hydrochloric acid, NaOH,  
 109 methanol and 98% methyltrimethoxymethylsilane (MTMS), were  
 110 obtained from the Sigma Aldrich company.

### 2.2. Methods

112 The PMSQ nanoparticles were synthesized by hydrolysis and  
 113 condensation reactions of MTMS. In the experiments, MTMS water  
 114 free 50 g, methanol 38.07 mL, hydrochloric acid 82  $\mu$ L, and deion-  
 115 ised water 19.85 mL were mixed under vigorous stirring for  
 116 24 h at room temperature. Then, using a solution of 1 N NaOH,  
 117 the pH was adjusted to 11 and the mixture was stirred until gel for-  
 118 mation. The gel produced was dried for 4 h at 110  $^{\circ}$ C. The resulting  
 119 powder was washed with deionized water to neutral pH.

120 Raman spectra of the ex-situ kinetic study of the MTMS hydroly-  
 121 sysis were obtained by a SENTERRA Raman spectrometer (Bruker)  
 122 operating in near-infrared mode under the following conditions:  
 123 laser: 785 nm with 100 mW of power, acquisition time: 8 s, lens:  
 124 10 $\times$ , spectral window: 400–3500  $\text{cm}^{-1}$ . A sample was taken sev-  
 125 eral times from the reaction medium during the reaction and then

126 placed in a glass tube for analysis. The infrared spectrum of the  
 127 nanoparticles of the ladder PMSQ was obtained by an infrared  
 128 Fourier transform spectrometer (Perkin Elmer spectrum 100) using  
 129 the attenuated total reflection method (ATR-FTIR) at 2  $\text{cm}^{-1}$  of res-  
 130 olution and 8 scans. ATR accessory equipped with a single reflec-  
 131 tion diamond ATR crystal on Zinc-Selenide (ZnSe) plate was used  
 132 for PMSQ powder analysis.  $^{29}\text{Si}$  and  $^{13}\text{C}$  solid-state spectra were  
 133 recorded on a Bruker Avance 300 MHz (Bruker Biospin Canada,  
 134 Milton, ON) with a 7-mm MAS probe. An echo sequence was used  
 135 to record  $^{29}\text{Si}$  spectra to avoid any background signals. Before any  
 136 measurements, the nanoparticles were dried overnight at 110  $^{\circ}$ C.  
 137 Samples were spun at 5 kHz with a scan number of 2000, a recycle  
 138 delay of 30 s with TPPM decoupling for a total acquisition time of  
 139 16 h typically used to record silicon spectra.  $^{13}\text{C}$  CPMAS experi-  
 140 ments were run with the same probe, with a contact time of  
 141 1 ms and 2000 scans, or a recycle delay of 3 s for a total acquisition  
 142 time of 1.7 h. The crystal structure and morphology of the PMSQ  
 143 nanoparticles were identified respectively by X-ray diffraction  
 144 (XRD) of powders and the transmission electron microscope  
 145 (TEM). XRD powder analysis was performed without prior sample  
 146 preparation with a Siemens D5000 diffractometer (radiation  
 147  $K\alpha = 1.54059$  of Cu). The scans ranged from 2 $^{\circ}$  to 80 $^{\circ}$  in steps of  
 148 0.02 $^{\circ}$ . The PMSQ nanoparticles were dispersed in methanol under  
 149 sonication for 30 min before being analyzed by TEM. The TEM used  
 150 was a JEOL 2100-F MEF field emission gun, operated at 200 kV.  
 151 Thermogravimetric analysis (TGA) was performed with a Mettler  
 152 apparatus TGA/SDTA 851/LF/1600. Aluminum crucibles (100  $\mu$ L)  
 153 without lids were used. The samples were heated from 25  $^{\circ}$ C to  
 154 1000  $^{\circ}$ C at a rate of 10  $^{\circ}$ C/min in an oxygen and nitrogen atmo-  
 155 sphere. Thermal analysis at a constant temperature of PMSQ  
 156 nanoparticles was carried out at 300  $^{\circ}$ C for 1 h under an oxygen  
 157 atmosphere. The specific surface area of the PMSQ nanoparticles  
 158 was computed by the Brunauer–Emmet–Teller (BET) model [24]  
 159 using a Gemini VII series analyzer. The sample was degassed at  
 160 110  $^{\circ}$ C overnight under vacuum. Nitrogen adsorption isotherm  
 161 was measured at liquid  $\text{N}_2$  at 77 K, and  $\text{N}_2$  relative pressure ranging  
 162 from 0.01 to 0.9. The density was measured using a helium pyc-  
 163 nometer. Water contact angle was measured by OCA15 Plus  
 164 Data-Physics equipment at room temperature using the sessile  
 165 drop method. The system included a high resolution camera and  
 166 specific software developed to capture and analyze the contact  
 167 angle on very small and curved surfaces. Ellipse fitting method

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