

A novel three-cages POSS molecule: synthesis and thermal behaviour

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Abstract

Two novel 4-methyl phenyl (trioxyisobutyl POSS) silane and 4-methyl phenyl (trioxycyclopentyl POSS) silane were synthesized. The nanosystems were characterized by elemental analysis, ¹H NMR and FTIR spectroscopy, in order to verify that the obtained products were those we would prepare. The spectroscopic results were in very good agreement with those expected. The synthesized POSSs were thermally characterized, by the means of thermogravimetric (TGA) and differential scanning calorimetry analyses. TGA was carried out in dynamic heating conditions (25–700 °C), in both flowing nitrogen and static air atmosphere. The temperatures at 5% mass loss ($T_{5\%}$), determined to evaluate their thermal stability, evidenced a better behaviour in inert environment. The obtained $T_{5\%}$ values were much higher for cyclopentyl POSSs and then for isobutyl ones, suggesting a fundamental role of organic group dimensions at the periphery of the synthesized systems, on the thermal properties. The residue at 700 °C, which were also investigated by FTIR spectroscopy, was a further confirmation of the better thermal stability of these novel nanoparticles.

Keywords POSS · Three-cages system · Thermal stability · Nanoparticles · FTIR · Thermogravimetric analysis

Introduction

Among the interesting class of inorganic/organic hybrid materials of silsesquioxanes (random, ladder, caged or partially caged) we found the polyhedral oligomeric silsesquioxanes (POSSs). These nanoparticles consist in a silicon and oxygen cage, externally completed by organic R groups covalently bonded with the silicon atoms. POSSs are well known with the formula (RSiO_{1.5})_n and have 8 as the most common value of *n*, thus presenting a very highly symmetric structure generally indicated in the literature with the symbol T_8 , with a diameter usually falling in the 1.5–3 nm range [1].

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The POSSs history, which although the first published scientific work dates back to 1946 by Scott [2] begins around the 1980s thanks to the essential contribution of Lichtenhan and Schawb [3-5], is a story where the thermal properties have always played a fundamental role. The inorganic-organic nature of POSSs, which allows to obtain hybrid materials different from those achievable by a simple blend at macroscopic level [6, 7], had helped researchers in the target of obtaining high-performance materials not only from the thermal point of view. The inorganic silicate core confers to molecule rigidity, thermal stability and resistance to oxidation [8], whilst the external organic corona affects the solubility of POSS in organic solvents [9] and its compatibility if used as reinforcement agents for polymers [10, 11]. In the light of this background, Bolln et al. [12] studied, by the means of thermogravimetric analysis (TGA), alkyl-substituted POSSs at different chain length of the peripheral organic groups (from C_2 to C_{10}). They found that increasing the alkyl chain length, the initial mass loss onset temperature shifted to higher values. Successively, Mantz et al. [13], by the means of FTIR and mass spectrometry, analysed gases and chars from pyrolysis of POSSs and evidenced their tendency to sublimation on heating in inert atmosphere. They furthermore reported that char analysis, via solid-state ²⁹Si

NMR and X-ray diffraction, indicated a progressive loss of cage structural order and crystalline structure, with increasing thermal treatment temperature. A strong input, to the knowledge of the thermal behaviour of these nanoparticles, was given by the group of Prof. Camino in Turin. They firstly evidenced the different degradation behaviour of octaisobutyl POSSs by passing from inert to oxidative thermogravimetry analysis, by observing evaporation of POSS leading to an almost complete mass loss under nitrogen flowing and obtaining an important residue under oxidative atmosphere [14]. Camino and his collaborators then started a deep insight on POSS thermal properties, in order to be able to tune the final properties of POSS-containing hybrids and nanocomposites. In particular, they evidenced a completely different thermal behaviour between alkyl T₈ POSSs and phenyl T₈ POSSs, due to the organic groups intrinsic stability, which results in a higher thermal stability for these latter compounds [15]. With the aim to study the POSSs compatibility with polymer matrix, and then their capability to undergo nanometric dispersion, our group started a wide research on the synthesis and characterization of new thermally stable POSSs in order to find useful structure-thermal properties relationships. Initially, we focused our attention on the periphery of silicon cage by varying, from time to time, the organic groups bonded to the silicon atoms [8, 16]or by attempting to combine multiple silicon cages with aliphatic or aromatic bridges more or less long [17–20]. As we expected the resistance to the thermal degradation increased by passing from isobutyl to cyclopentyl and phenyl-substituted POSSs and by doubling the number of silicon cages. In this framework, we continue our studies by reporting in this paper the synthesis and the thermal characterization of two novel three-cage POSS molecules (Fig. 1). The purpose was to verify whether this new and, to the best of our knowledge, never seen molecular architecture can lead to a further improvement in thermal stability.

The compounds investigated were the following:

$$\left[(C_4 H_9)_7 Si_8 O_{12} - O \right]_3 - Si - Ar C H_3$$
 (1)

$$\left[(C_{5}H_{9})_{7}Si_{8}O_{12} - O \right]_{3} - Si - ArCH_{3}$$
⁽²⁾

where Ar = $-C_6H_4$ -. We investigated how their resistance to the thermal degradation, evaluated through both temperature at 5% mass loss ($T_{5\%}$) and the residue at 700 °C, changed on modifying the aliphatic groups attached to the silicon cages. In order to compare the founded thermal parameters with those obtained in the past for similar compounds but with single or double silicone cages, the experimental conditions were the same used in the previous works as well as the parameters investigated. The synthesized samples were spectroscopically characterized by Fourier transform IR (FTIR) and ¹H NMR analyses in order to be sure that they corresponded to what was designed to achieve with the synthesis.

Experimental

Materials

Tetrahydrofuran (THF) was distilled over a Na–benzophenone mixture. Trisilanol–isobutyl POSS has been purchased from Hybrid Plastics Co. and used as received. The cyclopentyl–trisilanol (c C_5H_9)₇–Si₇O₉ (OH)₃ were prepared according to the literature methods [21, 22]. *p*-Tolyltrichlorosilane has been purchased from Aldrich Co. and used as received. All the reactions were performed under an atmosphere of dry nitrogen.

Synthesis of POSS nanoparticles

For the synthesis of isobutyl POSS chloride $[(C_4H_9)_7 Si_8O_{12}]$ –Cl a solution of 7.9 g (10.00 mmol) of trisilanol– isobutyl POSS in 100 ml of dry THF at 0–5 °C was added with 1.7 g (10.00 mmol) of SiCl₄ dissolved in 20 ml of THF. The solution was stirred, and 3.03 g (30.00 mmol) of Et₃N in 50 ml of THF was added. After stirring overnight at room temperature, the mixture was filtered to remove Et₃NHCl and the filtrate was evaporated to dryness. The resulting solid was dissolved in THF and dry acetonitrile was added; the fine white precipitated was collected and dried to give 6.90 g (81.0% yield).

¹H NMR: 1.87 (m, 7H), 0.95 (m, 42H), 0.62 (m, 14H). Analysis Calculated for $C_{28}H_{63}ClO_{12}Si_8$: C 39.47, H 7.45. Found: C 39.02, H 7.58.

The same procedure followed for isobutyl POSS chloride was used for the synthesis of cyclopentyl POSS chloride $[(c-C_5H_9)_7Si_8O_{12}]$ -Cl starting from cyclopentyltrisilanol (8.75 g, 10.00 mmol). Yield 78.6%.

¹H NMR: 1.77 (m, 14H), 1.54 (m, 42H), 1.04 (m, 7H). Analysis Calculated for $C_{35}H_{63}ClO_{12}Si_8$: C 44.91, H 6.79. Found: C 44.37, H 6.88.

For the synthesis of isobutyl POSS mono-ol $[(C_4H_9)_7$ Si₈O₁₂]–OH 5.10 g (6.00 mmol) of isobutyl POSS chloride was suspended in a 50 ml mixture 2:1 of THF/H₂O and refluxed for two days. After this time the mixture was rotoevapored to a white solid that was then dried and crystallized from toluene/acetonitrile to give 3.95 g (76.4% yield) of white crystals.

¹H NMR: 1.85 (m, 7H), 0.96 (m, 42H), 0.56 (m, 14H). Analysis Calculated for $C_{28}H_{64}O_{13}Si_8$: C 40.35, H 7.74. Found: C 39.96, H 7.68.

Cyclopentyl POSS mono-ol [(c–C₅H₉)₇Si₈O₁₂]–OH was obtained as described for isobutyl POSS mono-ol starting

Fig. 1 Molecular structure of the novel 4-methyl phenyl (trioxyisobutyl POSS) silane and 4-methyl phenyl (trioxycyclopentyl POSS) silane



from 5.60 g (6.00 mmol) of cyclopentyl POSS chloride to obtain 4.30 g (77.0% yield) of white crystals.

¹H NMR: 1.74 (m, 14H), 1.56 (m, 42H), 0.98 (m, 7H). Analysis Calculated for $C_{35}H_{64}O_{13}Si_8$: C 45.84, H 7.03. Found: C 44.16, H 7.10.

4-Methyl phenyl (trioxyisobutyl POSS) silane [(C_4 - H_9)₇Si₈O₁₂–O]₃–Si–ArCH₃ was synthesized by dissolving, under a dry nitrogen atmosphere, 3.00 g (3.60 mmol) of isobutyl POSS mono-ol in 40 ml of dry THF and then by adding, under stirring, 0,30 g (1.33 mmol) of p-tolyl-trichlorosilane in 10 ml of THF. The clear solution was cooled at 0–5 °C in an ice bath, and 0.41 g (4.00 mmol) of Et₃N was added. The solution was stirred and the temperature was maintained at 0–5 °C for 24 h. After filtration to remove Et₃NHCl, the filtrate was evaporated to dryness and the resulting solid was crystallized from THF/MeCN mixture to give 2.41 g of white crystals (76.9% yield).

¹H NMR: 7.60 (dd, 2H), 7.15 (dd, 2H), 2.38 (s, 3H), 1.81 (m, 21H), 0.94 (m, 126H), 0.59 (m, 42H). Analysis Calculated for $C_{91}H_{196}O_{39}Si_{25}$: C 41.94, H 7.54. Found: C 41.17, H 7.68.

The same procedure just seen for the preparation of 4-methyl phenyl (trioxyisobutyl POSS) silane was used for

the synthesis of 4-methyl phenyl (trioxycyclopentyl POSS) silane $[(C_5H_9)_7Si_8O_{12}-O]_3$ -Si-ArCH₃ starting from 2.75 g (3.00 mmol) of cyclopentyl POSS mono-ol to obtain 1.92 g (66.9% yield) of white crystals.

¹H NMR: 7.63 (dd, 2H), 7.12 (dd, 2H), 2.35 (s, 3H), 1.73 (m, 42H), 1.54 (m, 126H), 0.99 (m, 21H). Analysis Calculated for $C_{112}H_{196}O_{39}Si_{25}$: C 47.06, H 7.54. Found: C 41.17, H 6.87.

Yield, ¹H NMR spectroscopy and elemental analysis

A Varian Unity Inova spectrometer (¹H 500 MHz) was used to record ¹H NMR spectra. Measurements were taken by using CDCl₃ as solvent and TMS as internal standard. The ¹H NMR data found for the various compounds investigated are reported afterwards, together with elemental analysis data and the yields.

FTIR analysis

Fourier transform IR (FTIR) analysis was performed in a PerkinElmer Spectrum 100 spectrometer, at r.t. from 4000 to 650 cm^{-1} with a resolution of 4.0 cm^{-1} . An universal ATR sampling accessory was used for measurements, which were made directly on samples without any preliminary treatment.

DSC analysis

A Shimadzu DSC-60 apparatus was used for the calorimetric characterization. The enthalpy and temperature calibrations of equipment were made according to the procedure suggested by the manufacturer using as standard materials: indium (NIST SRM 2232), tin (NIST SRM 2220) and zinc (NIST SRM 2221a) for temperature; indium (NIST SRM 2232) for heat flow. Samples of about 5.0×10^{-3} g, held in sealed aluminium crucibles, and a heating rate of 10 °C min⁻¹ were used for measurements. Differential scanning calorimetry (DSC) scans were carried out from r.t. to 300 °C under a nitrogen flow of 0.06 L min⁻¹.

Thermogravimetric analysis

The synthesized POSSs were thermally characterized in a Mettler Thermogravimetric Analyzer TGA 1 Star System. Calibration of the furnace was performed according to the procedure reported in the Mettler User's manual of equipment, which is based on the change of magnetic properties of three metal samples (Isatherm, Nickel-allov and Trafoperm 86) at their Curie points (148, 355 and 750 °C, respectively). Samples of about 5 \times 10⁻³ g, put into open alumina crucibles, were degraded from 25 up to 700 °C, at the heating rate of 10 °C min⁻¹, in both flowing nitrogen (0.06 L \times min⁻¹) and static air atmosphere. To correct the error in the mass determination due to the reduction of the buoyancy force on increasing temperature. a blank TG run with an empty pan was preliminarily performed in the same experimental conditions used for samples. This blank curve was subtracted from those of samples, so obtaining corrected degradation TG curves. These data were later used to plot the percentage of undegraded sample, (1 - D)%, as a function of temperature, where $D = (W_0 - W)/W_0$, and W_0 and W were the masses at the starting point and during scanning.

Results and discussion

Elemental analysis and the ¹H NMR spectroscopy of the synthesized samples were firstly performed to verify whether the syntheses had been successful. Results, which are reported in detail in the experimental, were in very good agreement with the expected ones, thus indicating that the obtained products were those we would prepare. In addition, FTIR analysis was carried out on the prepared



Fig. 2 FTIR spectra of 4-methyl phenyl (trioxyisobutyl POSS) silane (1) and 4-methyl phenyl (trioxycyclopentyl POSS) silane (2)



Fig. 3 FTIR spectra of mono-phenyl hepta isobutyl POSS (1) and mono-phenyl hepta cyclopentyl POSS (2)



Fig. 4 DSC curves, at 10 $^\circ C$ min $^{-1},$ under nitrogen flow of samples 1 and 2

compounds and compared with those performed in the past on similar POSSs, always with isobutyl and cyclopentyl periphery. As shown in Fig. 2, the characteristic and different, for isobutyl and cyclopentyl, respectively, bands in the region around 3000 cm⁻¹ and those in the region 1300-1500 cm⁻¹ are the same of those obtained in the past for mono-cage POSSs with the same organic periphery (Fig. 3), thus confirming the presence of different organic

Table 1 Temperatures at 5% mass loss ($T_{5\%}$) and residue % at 700 °C of the synthesized POSSs in flowing nitrogen and in static air atmosphere

POSSs	Air static atmosphere		Nitrogen flow	
	<i>T</i> _{5%} /°C	Residue/%	$T_{5\%}/^{\circ}\mathrm{C}$	Residue/%
1	288.0	37.3	293.8	26.1
2	357.2	49.8	382.0	49.1

groups in the external coronas of the here-synthesized samples.

Samples 1 and 2 were calorimetric characterized by carrying out DSC scans from r.t. to 300 °C in flowing nitrogen. No thermal effect was observed for the compounds before their melting that occurs with decomposition as shown in Fig. 4. From the same figure and in agreement (as we will see) with TGA data (Table 1), it is possible to observe that exothermic decomposition of the isobutyl-substituted three-cage POSS starts about 80 °C before that of the cyclopentyl-substituted one.

Our samples were then degraded, in dynamic heating conditions (r.t.—700 °C), into the TGA equipment in both inert and oxidative environment. The thermogravimetric curves of samples 1 and 2, in flowing nitrogen and static air atmosphere, were reported in Figs. 5 and 6 respectively, where the percentage of un-degraded POSS (1-D%) as a



Fig. 5 TG degradation curves, at 10 $^{\circ}\mathrm{C}\ \mathrm{min}^{-1},$ under nitrogen flow of samples 1 and 2



Fig. 6 TG degradation curves, at 10 °C min⁻¹, in static air atmosphere of samples 1 and 2

function of temperature is plotted. In Table 1, we reported the $T_{5\%}$ values and the amounts of residues at 700 °C, which are the parameters we consider to evaluate the resistance to thermal degradation. In particular, the temperature at 5% mass loss was preferred to the onset temperature because it is not depending on the kinetics of the next-degradation stages and furthermore allows us the comparison with the results obtained in the past for analogues series of POSS molecules. In inert environment, both **1** and **2** samples degraded in two quite well-defined stages, and formed a sizable amount of stable residue up to



Fig. 7 DTG degradation curves, at 10 °C min⁻¹, under nitrogen flow of samples 1

700 °C. The DTG curves of sample 1 in flowing nitrogen is reported as example in Fig. 7. As shown in Fig. 5 and reported in Table 1, cyclopentyl-substituted three-cages POSS present an higher, of about 90 °C, initial decomposition temperature in respect of the isobutyl-substituted sample, thus confirming the trend observed during the calorimetric measurements. The degradation behaviour in static air did not exhibit substantial differences, and also in this oxidative environment, both samples degraded in two stages with the formation of a stable residue at 700 °C that was higher, like in inert atmosphere, for the cyclopentyl POSS. As regards the temperature at 5% mass loss, although maintaining the same difference of about 80 °C recorded in flowing nitrogen, the $T_{5\%}$ values of both compounds are slightly lower in oxidizing environment than in inert one.

The thermal behaviour observed for samples 1 and 2 is in agreement with that observed in the past for similar, from the organic periphery point of view, POSS systems but with a single cage or double cages, thus confirming the hypothesis that when seven more voluminous groups (cyclopentyls) are linked to the silicon atoms of a cage, they form a thermal barrier among various POSSs molecules, which make difficult the heat transfer and increase the $T_{5\%}$ leading to the formation of a higher amount of solid silica residue [16].

Finally, the residues at 700 °C were analysed by FTIR spectroscopy and the obtained spectra (for the sake of shortness only those of the residues obtained in inert atmosphere) are reported in Fig. 8, evidencing only bands attributable to silica in agreement with the literature data regarding POSSs degradation [8, 15].



Fig. 8 FTIR spectra of the residues at 700 °C, under nitrogen flow, of samples 1 and 2

Conclusions

We synthesized, to the best of our knowledge, for the first time a three-cage POSS system. On the basis of the experimental data obtained, the two novel nanosystems obtained, having three isobutyl- and three cyclopentylsubstituted silicon cages, respectively, showed an appreciable resistance to the thermal degradation, as indicated not only by the high temperatures of decomposition, but also by the large quantity of residues at 700 °C. The mass percentage of inorganic fraction of the synthesized nanoparticles is 48% for sample 1 and 50% for sample 2. On considering both the values of the TGA residue at 700 °C and the results of FTIR investigations, we can affirm that no organic fraction is present after degradation. Furthermore, by comparing the percentages of organic fraction with the amount of residue it seems that the presence of cyclopentyl groups at the periphery of the cages acts as shield for the silicon cage and preserves its degradation in respect of the nanoparticles with the isobutylic periphery. The good thermal behaviour, in both inert and oxidative atmospheres, was greater with the presence of more voluminous organic groups (cyclopentyl) at the vertices of the three silicon cages. Calorimetric investigations were in line with our previous studies on these systems and with the literature, showing no thermal effects until the melt with decomposition.

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