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COMMUNICATION

POSS as building-blocks for the preparation of polysilsesquioxanes through an innovative synthetic approach

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A novel solvent-free solid-state synthesis was used to prepare a non-crystalline polysilsesquioxane sample, with a peculiar viscous form. The material was synthesized through direct self-condensation of a partially condensed polyhedral oligomeric silsesquioxane (POSS) and its physico-chemical properties, in terms of composition/structure, thermal stability and hydrophobicity, were investigated.

Polyhedral oligomeric silsesquioxanes (POSS) are a class of condensed three dimensional oligomeric organosiliceous compounds. Their molecular structure consists of silicon atoms covalently bonded to one-and-a-half oxygen (“sesqui-”) and hydrocarbon (“-ane”) moieties (herein denoted as R), leading to tetrahedral (RSiO_{1.5}) units.

Besides fully condensed polyhedral oligomeric silsesquioxanes, that are generally identified with the typical cubic R₈Si₈O₁₂ structure,¹⁻⁴ open-corner POSS compounds, bearing in the structure reactive silanol groups (general formula R₇Si₇O₉(OH)₃), seem to be currently more interesting, because of their ability to connect different functionalities (silanes or metal precursors).

Typically, these systems exhibit high chemical versatility, good stability and molecular sizes. Therefore, they have attracted increasing interest in many fields, ranging from catalysis,⁵⁻⁷ to biomedical⁸⁻⁹ and diagnostic uses¹⁰⁻¹¹ and for the preparation of nanocomposite and nanohybrid materials with definite physico-chemical features.¹²⁻¹³

More recently, beside to oligosilsesquioxanes samples, specific attention was also devoted to the preparation of novel polysilsesquioxanes (PSQs),¹⁴⁻²² bearing in the structure co-condensed POSS cages in a tridimensional array. The use of POSS units as precursors may facilitate the preparation of hybrid materials, owing to their ability to act as structural nodes and to react covalently with other organic-inorganic building blocks.

In particular, two different POSS-based PSQs classes have been explored in the literature. The first one consists of hierarchical inorganic-organic hybrid silica-based materials with well-ordered micro- and mesoporous architectures. These solids are in general

synthesized through the acid/base catalyzed condensation of cubic POSS cages in the presence of template agents (surfactants or block-copolymers). Following this approach, robust porous PSQs with high surface area, uniform pore size distribution and hydrothermal stability have been obtained.²³⁻²⁸

The POSS-based PSQs belonging to the second family show typical non-crystalline structure with low molecular weight (dimer or trimer structures).²⁹ Typically, these solids can be prepared in catalyzed aqueous/organic-solvent mixture at high temperature and for long time (several days), starting from closed-cage POSS. To the best of our knowledge, these last systems have been marginally investigated in the literature, despite their interesting physico-chemical properties.

In light of these considerations and taking into account the complexity and often high costs of some synthetic strategies adopted to prepare PSQs materials, an alternative synthetic approach to prepare amorphous PSQs is here proposed. The synthesis here described does not require use of solvents and catalysts (acid or base) and it is very fast (few hours) and economical respect to the traditional methods reported in the literature. Though generally applicable to similar open-cage POSS precursors, in this work the preparation of polysilsesquioxane containing isobutyl groups in the structure (hereafter named PSQ-IsobutylPOSS) is described. The sample was prepared by self-condensation of the open-corner heptaisobutyl-POSS (Fig. S1) and its physico-chemical properties were investigated in detail.

The reaction was carried out in a single step by directly heating at 170 °C in a tubular oven the open-cage heptaisobutyl-POSS under nitrogen flow (100 mL/min) (see experimental section in the supporting information) without solvents addition. Preliminary tests have been also carried out at small-scale level, in order to determine and optimize the experimental parameters (temperature, gas flow and amount of reactant). The synthesis was monitored over the time and the products obtained after 1, 2, 4 and 6 h were submitted to infrared spectroscopy characterization.

FT-IR spectra of the PSQ-IsobutylPOSS samples were compared with the vibrational profile of the partially condensed heptaisobutyl-POSS (Fig. 1). IR spectrum of the commercial heptaisobutyl-POSS

(Fig. 1A, curve a) shows absorptions in the 3000–2700 cm^{-1} and 1500–1200 cm^{-1} ranges, assigned to the stretching and bending modes of the isobutyl moieties, respectively. An intense peak at 1110 cm^{-1} is evident and ascribed to the asymmetric stretching of the Si–O–Si groups ($\nu_{\text{as}}(\text{Si-O-Si})$) of the POSS cage. Beside to the bands typical of the isobutyl groups and of the inorganic cage, additional absorptions clearly appear in the IR spectrum of the partially condensed POSS. In particular, two bands centred at 3250 and 890 cm^{-1} , attributed to the stretching and bending modes of Si–OH moieties, respectively, are evident.^{30–31} The two bands at 3250 and 890 cm^{-1} , typical of partially condensed POSS, gradually decrease in intensity passing from the open-cage POSS to the PSQ-IsobutylPOSS sample prepared in one hour (PSQ-IsobutylPOSS-1h, Fig. 1, b) and the compound synthesized in 4 h (named PSQ-IsobutylPOSS-4h, Fig. 1, d) and almost completely disappear for the sample prepared for long time (PSQ-IsobutylPOSS-6h, Fig. 1, e). This feature can be better evaluated by normalizing the spectra of the products respect to the bending modes of the isobutyl functionalities (*i.e.* the band at 1465 cm^{-1} , assigned to the $-\text{CH}_3$ rocking mode³²), which are not affected by the thermal treatment (Fig. 1B). The intensity ratio of the bands 890/1465 cm^{-1} strongly decreases by increasing the reaction time, following an exponential behaviour (Fig. 1C).

In parallel, a new absorption at 1060 cm^{-1} , assigned in the literature to the asymmetric stretching modes of Si–O–Si bonds in PSQs with a structural ladder-like organization,³³ become more evident in the samples obtained after 4 and 6 h.

Both these features are a proof of the high chemical stability of the inorganic structure, with just a local alteration of the cage symmetry due to the self-condensation of the partially condensed building-block POSS units.

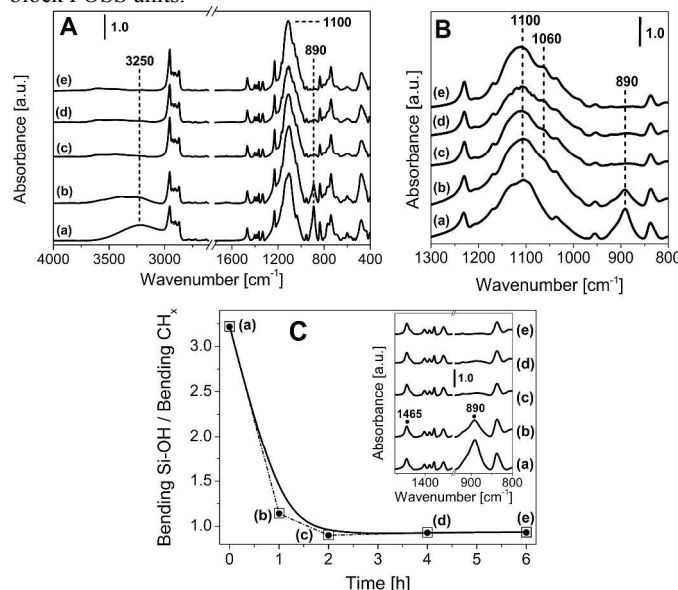


Figure 1. A) FT-IR spectra in KBr matrix of heptaisobutyl-POSS (a), PSQ-IsobutylPOSS-1h (b), PSQ-IsobutylPOSS-2h (c), PSQ-IsobutylPOSS-4h (d) and PSQ-IsobutylPOSS-6h (e). The magnification of the 1300–800 cm^{-1} range is reported in B). The decrease of the intensity of the band at 890 cm^{-1} respect to the bending mode of CH_x groups over the time is shown in C).

It is important to note that the bands typical of the organic functionalities appear unchanged during the thermal treatment. This is a proof that the POSS molecules were essentially preserved by the chemical point of view. The stability of the organic isobutyl groups

was further confirmed by thermogravimetric analysis. PSQ-IsobutylPOSS-6h, submitted to thermal treatment from 50 to 800°C, under argon flow, shows a main weight loss with maximum at 300°C, due to the decomposition of the organic groups (see Fig. S2). All the products have been submitted to X-ray powder diffraction (XRPD) analysis. The diffractograms of the PSQ-IsobutylPOSS samples were compared to the diffraction pattern of the heptaisobutyl-POSS (Fig. 2).

The diffractogram of the reactant POSS (Fig. 2, a) is characterized by well-defined peaks, thus indicating the high crystallinity of the sample. In fact, as indicated in the literature, heptaisobutyl-POSS crystallizes with a monoclinic structure ($P_{21/n}$).³⁴

The XRPD pattern of the PSQ-IsobutylPOSS-1h shows an X-ray profile comparable to that of the partially condensed POSS, with the exception of few modifications of the intensity ratio of some peaks. In agreement with IR data, these results indicate that short reaction times (1h) are not enough to allow a complete self-condensation of the partially condensed POSS. A large fraction of heptaisobutyl-POSS remains entrapped inside the product.

The PSQs prepared prolonging the time deserve further comments. In fact, for these solids, a completely different X-ray profile is observed. The reflections of the open-corner POSS are almost completely eroded and replaced by two broad signals centred at *ca.* 8° and 18° 2 θ . These features are indicative of an irregular structural arrangement occurring during the self-condensation reaction. This is mainly evident for the PSQ-IsobutylPOSS-4h and PSQ-IsobutylPOSS-6h.

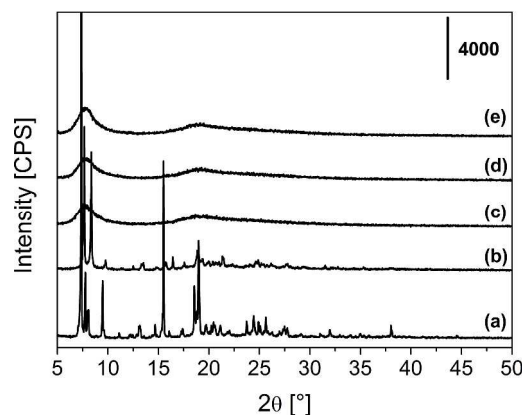


Figure 2. X-ray profiles of the heptaisobutyl-POSS (a), PSQ-IsobutylPOSS-1h (b), PSQ-IsobutylPOSS-2h (c), PSQ-IsobutylPOSS-4h (d) and PSQ-IsobutylPOSS-6h (e).

Further insights on the chemical nature of the PSQ-IsobutylPOSS was obtained through NMR analysis applied to the ^{29}Si nuclei (proton decoupled in CDCl_3 at 25 °C, standard TMS). ^{29}Si -NMR spectrum of the heptaisobutyl-POSS (Fig. 3, curve a) shows three well defined signals at -58.9, -67.4 and -68.7 ppm. The first one is ascribed to the three silicon sites directly bound to the -OH groups, whereas the other two can be assigned to the remaining Si atoms of the POSS cage.³⁵

The same peaks are clearly observed in the ^{29}Si NMR spectrum of the PSQ-IsobutylPOSS-1h sample (Fig. S3). This is in agreement with the IR and X-ray diffraction data. In opposite, PSQ-IsobutylPOSS-6h shows a completely different NMR spectrum (Fig. 3, curve b). The signals typical of the reactant POSS disappear and two more complicated set of peaks are evident. The signals at low ppm (between -65 ppm and -75 ppm) are typical of polycondensed silicon sites in different chemical environment (this can explain the high number of peaks). Whereas, the signals between -55 ppm and -

60 ppm region can be assigned to a fraction of residual Si-OH group (not clearly identified in the IR spectrum), deriving by the self-condensation reaction. The presence of such reactive sites could be in a second step submitted to further functionalization, open the way to the design of other PSQs derived materials.

On the base of XRD and NMR data, we can affirm that PSQ-IsobutylPOSS-6h is characterized by an amorphous and polycondensed structure. Moreover, while the heptaisobutyl-POSS is a white powder, the samples prepared for long times (2-6 h), at the end of the synthesis, appear as transparent gel-like fluids (Fig. S4).

Additional information on the chemical nature of the PSQ-IsobutylPOSS-6h sample was obtained through MALDI-TOF analysis. The mass spectrum of PSQ-IsobutylPOSS-6h shows two main signals centred at 1600 and 2400 m/z, that are consistent with a dimer and trimer structure, respectively. Samples with dimer structure are in larger amount (*ca.* two times) respect to the fragments with trimer structure. The other peaks present in the range 1500-2500 m/z could be related to fragments with variable molecular weight, coming from the fragmentation process of higher condensed multimeric structures, occurred during the analysis (Fig. S5).

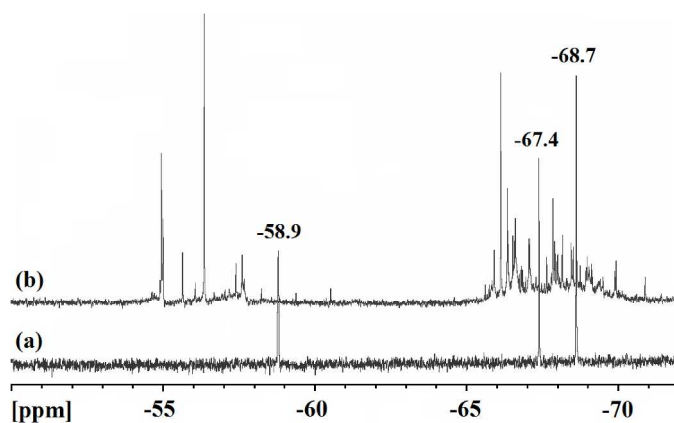


Figure 3. ^{29}Si -NMR spectra of heptaisobutyl-POSS (a) and PSQ-IsobutylPOSS-6h (b) in CDCl_3 .

Finally, the hydrophobic/hydrophilic properties of the PSQ-IsobutylPOSS-6h were also investigated. PSQ-IsobutylPOSS-6h, in form of transparent gel-like film, was deposited by dip-coating on a glass slide (standard size 26x76x1 mm, ISO Norm 8037/1), probably exploiting the hydrogen-bond interaction between the glass surface and the residual Si-OH groups of the PSQ film (Fig. S6). Prior to the coating, the support was washed with ethanol solution.

The wettability test was performed by measuring the contact angle (θ), which is defined as the angle that is formed between a liquid drop (in our case water) and the treated surface. The surface treated with PSQ-IsobutylPOSS-6h shows a contact angle of *ca.* 105° (Fig. 4B), much higher than the untreated glass ($\theta \approx 50^\circ$, (Fig. 4A)) and similar to the values observed for typical hydrophobic polymer as polytetrafluoroethylene (PTFE).³⁶ In fact, surfaces with contact angles greater than 90° are typically considered as hydrophobic.³⁶ The hydrophobic character of the PSQ-IsobutylPOSS-6h film is preserved even after a further soaking treatment in water for 24h (Fig. 4C). A slight decrease of the contact angle of *ca.* 10% is observed after a harsher treatment of the film in acid solution (H_2SO_4 solution - pH = 4) for 1 day (Fig. 4D). Both these tests are a proof of the high stability of the PSQ film.

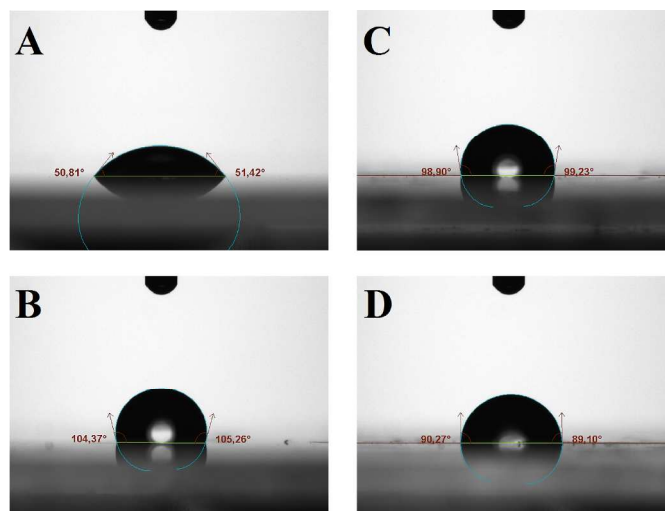


Figure 4. Contact angle measurements of untreated glass support (A), PSQ-IsobutylPOSS-6h film (B) and PSQ-IsobutylPOSS-6h film treated in water (C) and in acid solution (D).

Conclusions

In conclusion, a novel polysilsesquioxane bearing in the structure self-condensed POSS cages arranged in a non-crystalline structure was prepared by adopting a solvent-free solid-state synthesis. This synthetic methodology, that can be generally applied to open-cage POSS precursor systems, allowed to obtain in a very short time and in a simple and “green” way polycondensed materials.

A detailed spectroscopic and structural investigation provided clear information on the nature of the products prepared in this work related to the reaction times explored for the synthesis.

The polysilsesquioxane obtained after 6h showed an amorphous polycondensed structure, bearing residual reactive OH groups and interesting hydrophobic properties when coated as transparent film on a glass surface. This last property renders such material a good candidate for the production of high hydrophobic and protective coatings of interest for numerous technological applications.

The physical nature of the material, that looks like a gel-like fluid with high viscosity, allow an easy handling of it to make coatings without the use of solvents. As well, the obtained fluid proved to be thermally stable up to 240°C (from TGA measurements) and completely free of volatile fractions.

As a general comment, the solid-state “solvent-free” approach here proposed could pave the way for the design of new PSQs with different organic functionalities and tuneable properties.

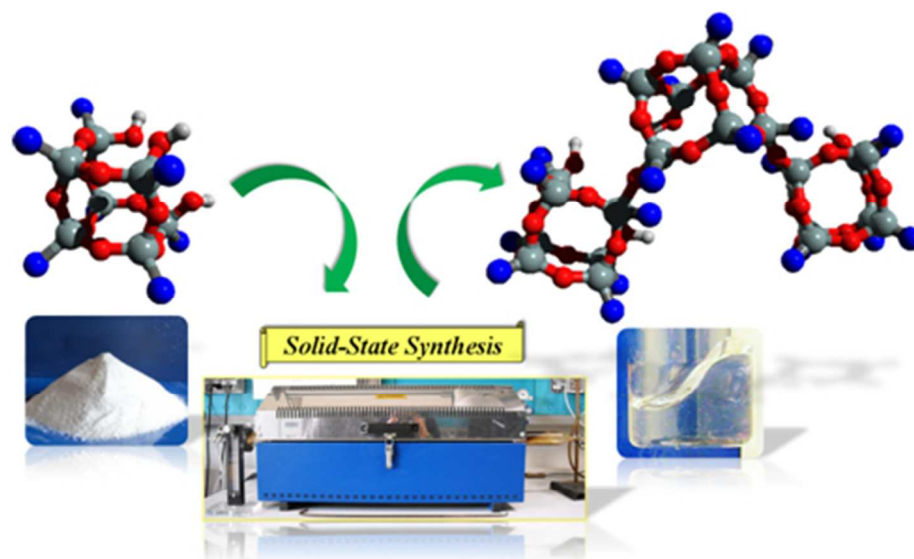
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Notes and references

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