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Polyhedral Oligomeric Silsesquioxane-Supported Ionic Liquid for Designing Nanostructured Hybrid Organic-Inorganic Networks

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Keywords: Ionic Liquid, Polyhedral Oligomeric Silsesquioxane (POSS), Nanostructured Network, Epoxy, Hybrid Organic-Inorganic Materials.

ABSTRACT: In this work, two polyhedral oligomeric silsesquioxane-supported imidazolium ionic liquid have been successfully synthesized and used as organic-inorganic hybrid nano-objects in order to design nanostructured epoxy-amine networks. In fact, two partially condensed POSS have been covalently grafted with an ionic liquid-functionalized silane. The thermal properties of the ionic liquid (IL)-modified POSS have highlighted a significant enhancement of the thermal stability (400 vs 300 °C). Then, these hybrid organic-inorganic nano-objects (5 wt. %) have been incorporated into a conventional epoxy prepolymer (diglycidyl ether of bisphenol A) which was copolymerized with the isophorone diamine in order to prepare nanostructured networks. Thus, an excellent dispersion of the IL-functionalized POSS was obtained in the thermosetting networks, characterized by the formation of spherical or ellipsoidal inorganic-rich nanoparticles with nanoscale sizes (10 to 80 nm).

1. Introduction

In materials science, the ability to create and design new polymer-based materials with unprecedented improvements in their final properties is an extremely important challenge. Nanoscale materials often exhibit physical and chemical properties that are dramatically different from their neat counterparts. During last two decades, polymer nanocomposites were designed from the introduction of nanofillers (*e.g.*, nanoparticles, nanoplatelets, nanotubes) in order to improve for example coatings, reinforced polymers, barrier films. The design of functional nanomaterials requires the control of the diffusion and structuration at different scales, *i.e.* from the individual nanoscale objects, to micrometer scale [1, 2]. As consequence, tailoring structures and morphologies at various length scales is the key feature to display advanced functionalities [3].

Polyhedral oligomeric silsesquioxanes (POSS) are known as nanobuilding blocks for constructing such functional nanomaterials [4, 5]. They could be considered as organic-inorganic hybrid nano-objects according to their cage structure having different geometries and symmetries (about 1 to 3 nm in size) [6]. As a general feature, the mo-

lecular structure of these compounds consists of silicon atoms bonded to one and-a-half oxygen (“sesqui-”) and hydrocarbon (“-ane”) moieties, such as alkyl, aryl, or any of their derivatives (herein denoted as R), leading to an O/I hybrid nano-objects with a chemical composition $(\text{RSiO}_{1.5})_n$ bond units, where n is equal to 6, 8, 10, and 12. These substituents may be simple alkyl groups or functionalized organic ligands. The most common POSS are cubic with a general formula $\text{R}_8\text{Si}_8\text{O}_{12}$ [7]. Besides fully condensed polyhedral silsesquioxanes, open-corner POSS compounds, structurally related to cubic systems where a Si vertex is removed leaving incompletely condensed silanol groups (with general formula $\text{R}_7\text{Si}_7\text{O}_9(\text{OH})_3$) offer the possibility to be corner-capped in order to design specific functionalities via the reaction with organosilane and hetero-element precursors. In particular, partially condensed POSS can react with a large variety of trialkoxy or trichloro-silanes (RSiY_3 , $\text{Y} = \text{OEt}$, OMe , Cl , etc.), leading to fully condensed POSS (T_8 -POSS) [8-10].

Nowadays, ionic liquids (ILs) offer a new route for designing polymer-based materials. Their unique characteristics, *i.e.* high thermal stability, low saturation vapor pressure, low flammability, dispersant capabilities, and high ionic

conductivity make them very attractive [11, 12]. As a consequence, not only their molecular features but also their morphologies that they could form have a great potential to display advanced functions that are very different from those of conventional small organic molecules. ILs based-POSS have attracted much attention as platforms for developing and designing multifunctional polymer nanomaterials. Incorporated directly in the polymer, bulk ILs can generate nanostructures from a nano-phase separation phenomena [13-15]. These ionic salts are also ideal candidates for tailoring the surface properties of fillers and tuning the physico-chemical and mechanical properties of polymer composites [16]. ILs can also participate in the polymerization process as they can initiate the opening of epoxy groups and lead to the formation of cross-linked polymers [17]. The incorporation of IL-based POSS in a variety of polymers brings to significant modifications of their physical properties, such as the enhancement of thermal and mechanical stability, toughness improvement, and modifications in optical properties, dielectric constant, and solubility [18-20]. Such hybrid O/I nanomaterials could be used as a high-performance electrolyte, due to their unique internal nano structures which can enhance the ion transport capability [21]. Monofunctional imidazolium-based POSS, which can self-assemble into lamellar nano structures, is also used as an organic modifier for clays [22]. Dapeng *et al.* outlined that by using of imidazolium-based POSS, solid electrolytes for lithium ion batteries could be developed with high ionic conductivity and broad electrochemical windows [23]. Orel *et al.* also reported that POSS-imidazolium/iodide ILs could be successfully used as electrolytes for fuel cells [24].

The aim of this work is the molecular design of nanostructured epoxy-amine networks by using IL-grafted POSS as organic-inorganic nano-building blocks. To the best of our knowledge, there has been no precedent report on nanostructured thermosets polymers obtained by using IL-grafted POSS. In the present work, we reported in the first part the synthesis and characterization of two imidazolium ionic liquid-based POSS, hereafter named IL-g-POSS^{IB} and IL-g-POSS^{Ph} starting from two types of partially condensed POSS named POSS^{IB}-triol and POSS^{Ph}-triol. The molecular structure of the resulting IL-g-POSS was determined using ¹H, ¹³C, ²⁹Si NMR, and MALDI-TOF mass spectrometry, and its thermal properties (by DSC, and TGA). In the second part of this work, the preparation of epoxy nanomaterials based on POSS-triols and IL-g-POSSs is described. The morphology and thermal properties of hybrid O/I nanomaterials are comparatively investigated on

the basis of transmission electron microscopy (TEM), and differential scanning calorimetry (DSC).

2. Experimental

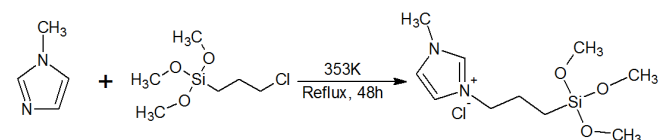
2.1. Synthesis of the silylated imidazolium ionic liquid (Si-g-Im-Cl)

According to the literature [25, 26], the silylated imidazolium ionic liquid denoted Si-g-Im-Cl was synthesized in one step from 1-methylimidazole and 3-chloropropyltrimethoxysilane. Under a positive argon atmosphere, 1 equiv. of 1-methylimidazole (2.05 g; 25 mmol) and 1 equiv. of 3-chloropropyltrimethoxysilane (5.12 g; 25 mmol) were added in a 100 mL flask. The mixture was allowed to react at 80 °C for 48 h. A viscous oil was obtained. Then, the product was filtered and washed repeatedly with dried diethyl ether (5 x 10 mL) in order to remove unreacted species. The solvent was removed under vacuum and the final product was dried at 60 °C during 24 h. In this case, silylated imidazolium IL was obtained with an excellent yield (96 %) and its purity was confirmed by ¹H- and ¹³C-NMR (the assignment of resonance peaks are reported below):

¹H NMR (400 MHz, CDCl₃, 25 °C, ppm): 10.69 (1H, s, -NCHN-), 7.6 and 7.40 (2H, -NCHCHN-), 4.33 (2H, t, -CH₂N-), 4.14 (3H, s, -NCH₃), 3.51 (9H, s, -OCH₃), 2.02 (2H, m, -SiCH₂CH₂CH₂N-), 0.64 (2H, t, -SiCH₂-).

¹³C NMR (100 MHz, CDCl₃, 25 °C, ppm): 6.01 - 7.34 (SiCH₂), 24.19 (SiCH₂CH₂), 36.59 (CH₂N), 50.74 (OCH₃), 51.75(NCH₃), 122.03; 123.89 (=CN), 137.8 (N-C=N).

In addition, the formation of the following molecule was confirmed the MALDI-TOF mass spectrometry (see Figure S1 of ESI). The general procedure for the synthesis of the IL silane is detailed in scheme 1:



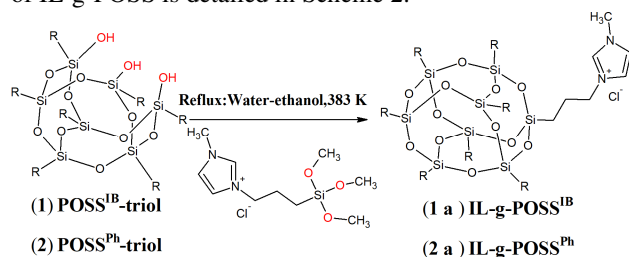
Scheme 1. Reaction scheme for the synthesis of 1-(3-trimethoxysilylpropyl)-3-methyl-imidazolium chloride (Si-g-Im-Cl).

2.2. Synthesis of IL-g-POSS

Under dry argon atmosphere, the imidazolium ionic liquid modified POSS (IL-g-POSS) was synthesized by corner-capping reaction between POSS-triol and Si-g-Im-Cl IL in two steps. First, in a 500 mL flask, 1 equiv. of Si-g-Im-Cl (0.71 g, 2.53 mmol) in water/ethanol (20 / 80, v:v) was added drop wise to 1 equiv. of POSS-triol (2 g, 2.53 mmol) in water/ethanol under vigorous stirring at 40 °C for 6 h. Then, the mixture was heated to 110 °C and stirred overnight. The product was filtered and washed repeatedly with ethanol (2 x 30 mL) in order to remove unreacted

reagents. The solvent was removed under vacuum and the final product was dried at 80 °C for 48 h. In both cases, independently on the POSS nature (1 vs 2), a white powder was obtained with very satisfactory yields, 93 % for IL-g-POSS^{IB} (1a) and 89 % for IL-g-POSS^{Ph} (2a).

The follow up of the different reaction steps, the purity, and the chemical composition of the final product were investigated by ²⁹Si, ¹H and ¹³C-NMR (Figures S4, S5 and S6 of ESI) as well as by MALDI-TOF (Figure S7 of ESI) mass spectroscopy. The general procedure for the synthesis of IL-g-POSS is detailed in Scheme 2.



Scheme 2. Synthesis of imidazolium ionic liquid-modified polyoligomeric silesquioxane (IL-g-POSS).

2.3. Epoxy network preparation

To prepare epoxy-amine networks, epoxy prepolymer (DGEBA) and isophoronediamine (IPD) used as commoners were mixed under mechanical stirring with a stoichiometric ratio amino hydrogen-to-epoxy equal to one. 5 wt. % of IL-g-POSS, either IL-g-POSS^{IB} or IL-g-POSS^{Ph}, were considered for POSS-modified epoxy networks. First, IPD and IL-g-POSS were premixed before adding to the epoxy prepolymer. Then, the mixture was degassed and poured into molds. Finally, epoxy networks without and with IL-g-POSS were cured for 2 h at 140 °C and post-cured 8 h at 190 °C [27-29].

3. Results and Discussion

²⁹Si NMR is a powerful technique to determine the molecular structure and to evidence the functionalization of POSS by the silylated IL from corner-capping reaction. Thus, ²⁹Si NMR spectra of unmodified- and modified-POSS denoted POSS^{IB}-triol, POSS^{Ph}-triol, IL-g-POSS^{IB}, and IL-g-POSS^{Ph} are shown in Figure 1.

In the case of unmodified heptaphenyl- and heptaisobutyl-POSS, denoted as POSS^{IB}-triol and POSS^{Ph}-triol, respectively, similar signals have been highlighted in the ²⁹Si NMR spectra. In fact, two main resonances are evidenced at -69 ppm and at -77 ppm for POSS^{Ph}-triol while POSS^{IB}-triol displays also two signals at -60 ppm and at -69 ppm. The first peak with an abundance of 43 % for POSS^{Ph}-triol (calculated by the peak integration from -62 to -72 ppm) and with an abundance of 42 % for POSS^{IB}-triol (calculated by the peak integration from -55 to -63 ppm) corresponds to Si atoms from silanol groups. The second peak with an abundance of 57 % (calculated by the peak integration

from -74 to -84 ppm) for POSS^{Ph}-triol and with an abundance of 58 % (calculated by the peak integration from -65 to -74 ppm) for POSS^{IB}-triol is assigned to Si atoms of the POSS cage (Si-O-Si). These results are in agreement with the literature [30]. Maven Ye *et al* [30], reported the same assignments for POSS^{IB}-triol with two distinct signals at -59 and -69 ppm, for the POSS^{Ph}-triol, two Si resonance peaks at -69 and -78 ppm.

After the reaction with ionic liquid-functionalized silane (Si-g-Im-Cl), the resonances at -69 ppm and -60 ppm, attributed to the silanol species from the partially condensed POSS, significantly decrease in intensity (from 43 % to 22 % for IL-g-POSS^{Ph} and from 42 % to 8 % for IL-g-POSS^{IB}). The quantification of the two types of Si atoms for the POSS-triol and IL-g-POSS obtained by ²⁹Si-NMR are summarized in Table S2 of ESI.

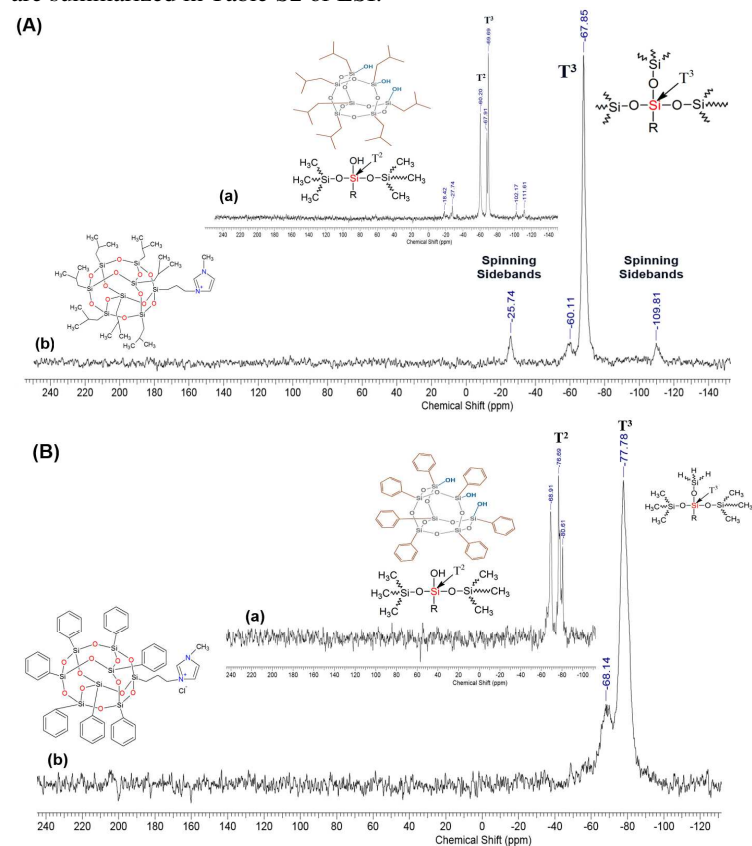


Figure 1. (A): ²⁹Si NMR spectra of POSS^{IB}-triol (a) and IL-g-POSS^{IB} (b); (B): ²⁹Si NMR spectra of POSS^{Ph}-triol (a) and IL-g-POSS^{Ph} (b).

In addition, after corner-capping reaction, the dialkylation of imidazole is preserved. FT-IR (Figures S2, S3 of ESI) and NMR spectroscopy (¹H and ¹³C) (Figures S4, S5 and S6 of ESI) demonstrate the two structure obtained and that the imidazolium ring remains unchanged after grafting of Si-g-Im-Cl IL.

In order to confirm the chemical structure of IL-g-POSS obtained, MALDI-TOF mass spectrometry was used and the different spectra are presented in Figure S7 (see ESI).

For the two types of POSS, two expected peaks are clearly identified on the positive MALDI-TOF mass spectra. For the two IL-g-POSS, the first peaks detected at m/z 939.2 and m/z 1079.2 were assigned to the cationic species $[R_7T_7(\text{Si-g-Im})]^+$. This value is in agreement with the mass of a monomeric structure in which the Si-g-Im^+ ion is completely bound to the Si-O- units of the POSS cage. Then, another peaks were observed on the spectrum at m/z 957.5 for IL-g-POSS^{IB} and m/z 1097.2 for IL-g-POSS^{Ph} corresponding to POSS-triol bound to the IL with two free Si-OH groups (open cage) as described in Figure 2. No evidence of dimeric or multimeric species, was detected for IL-g-POSS prepared in this work.

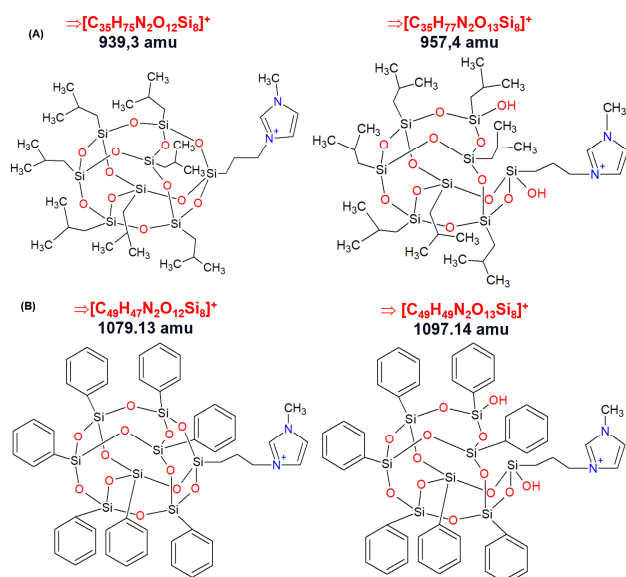


Figure 2. Chemical formula of IL-g-POSS obtained by corner-capping reaction from POSS^{IB}-triol with Si-g-Im-Cl (A) and POSS^{Ph}-triol with Si-g-Im-Cl (B).

The DSC traces of POSS-triols and IL-g-POSSs are given in Figures 3 and S8 of ESI, respectively. For both types, the DSC thermograms of IL-g-POSS compounds indicate a similar thermal behavior as well as a broad crystallization. For IL-g-POSS^{IB}, a glass transition temperature (T_g) of 23 °C, a crystallization region at 89 °C followed by two smaller melting endotherms at 127 and 167 °C, are observed. In the case of IL-g-POSS^{Ph}, a T_g at 14 °C, a crystallization exotherm at 67 °C and two melting endotherms at 134 and 168 °C, are observed. The two melting points are due to the presence of the two types of crystalline phases of the IL-g-POSS (Figure 2). In the opposite, the POSS-triols compounds display higher melting temperatures at 200 °C for POSS^{IB}-triol and at 217, 230 °C for the POSS^{Ph}-triol. In the literature, Tanaka *et al.* have obtained the same behavior for synthesized imidazolium-type ionic liquid-grafted POSS [6]. This author attributed the decrease of the melting temperature to the presence of large globular POSS entities reducing the packing density and isolating the distal ion pairs. These results demonstrate that the addition of ionic liquid on the POSS cores affects the mobility of

chains and the free volume leading to the presence of a glass transition temperature as well as to the formation of regular structures in the liquid phase. In fact, the hydrophobic effects among the ion pair moieties of the IL-g-POSS molecules leads to the formation of well-aligned and high-dimensional structures.

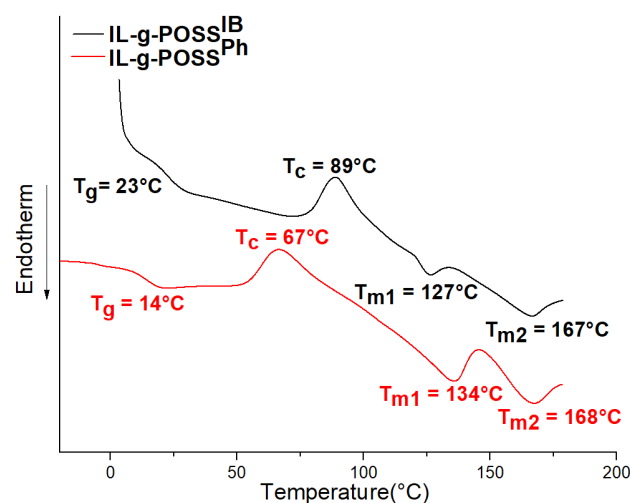


Figure 3. DSC traces for IL-g-POSS: IL-g-POSS^{IB} and IL-g-POSS^{Ph}.

Thermogravimetric analysis (TGA) were carried out to highlight the impact of ILs on the thermal behavior of the modified POSS. Figure 4 shows the evolution of the weight loss as a function of the temperature. The initial decomposition temperature, which can be also defined as the temperature corresponding to a mass loss of 5 wt. % ($T_{d5\%}$), the temperature at the first maximum loss rate (T_{dmax1}), the temperature at the second maximum mass loss rate (T_{dmax2}), and the residue yield at 800 °C are reported in Table S3 (see ESI).

In all cases, an excellent thermal stability was shown for unmodified and IL-modified POSS with a thermal degradation starting at temperatures higher than 200 °C. The presence of the imidazolium IL in the POSS-triol plays a key role on the thermal stability of IL-g-POSS^{IB} and IL-g-POSS^{Ph}. Indeed, a significant increase (100 K) of the decomposition temperatures ($T_{d5\%}$ and T_{dmax}) could be evidenced. These results confirm the stabilizing effect obtained by closing the silica core of the POSS-triols using IL. In both cases, TGA traces of the two IL-g-POSS display a two-step degradation process corresponding to water loss resulting from the hydroxyl crosslinking and the breakage of the POSS structure [30]. Based on the literature, the first decomposition step corresponds to the degradation of the alkyl chain of the imidazolium and to the water loss between 250 and 400 °C. The second degradation that takes place from 450 to 650 °C corresponds to the decomposition of alkyl chain contained in the POSS core [31-33]. Moreover, the residue yield (73 %) for IL-g-POSS^{Ph} is higher than one of the IL-g-POSS^{IB} (12 %) due to the decomposition of substituted oligomeric silsesquioxane which depends strongly on the nature of grafted organ-

ic groups. In general, POSS with small aliphatic side chains sublime during heating in absence of oxygen and have relatively low residue yield. Larger aliphatic and aromatic substituents prevent sublimation, and polymerization of POSS cage may occur, that attributed to the entrapment of carbon in the structure, resulting in a larger amount of residue [33, 34]. A similar effect was observed by Jifang *et al.* who obtained increases of 100 to 200 K compared to their unmodified POSS [11]. Those results indicate that the connection of ILs onto POSS-triol allow to prepare closed structures. These structures may increase the stability of the system by limiting the thermal motion of the remote alkyl chains [35]. In summary, the supported ionic liquid-polyhedral oligomeric silsesquioxane (IL-g-POSS) are thermally stable and can be used for the design of new advanced nanostructured epoxy-amine networks requiring high processing temperatures and open also new perspectives in the development of polymer materials with improved fire resistance.

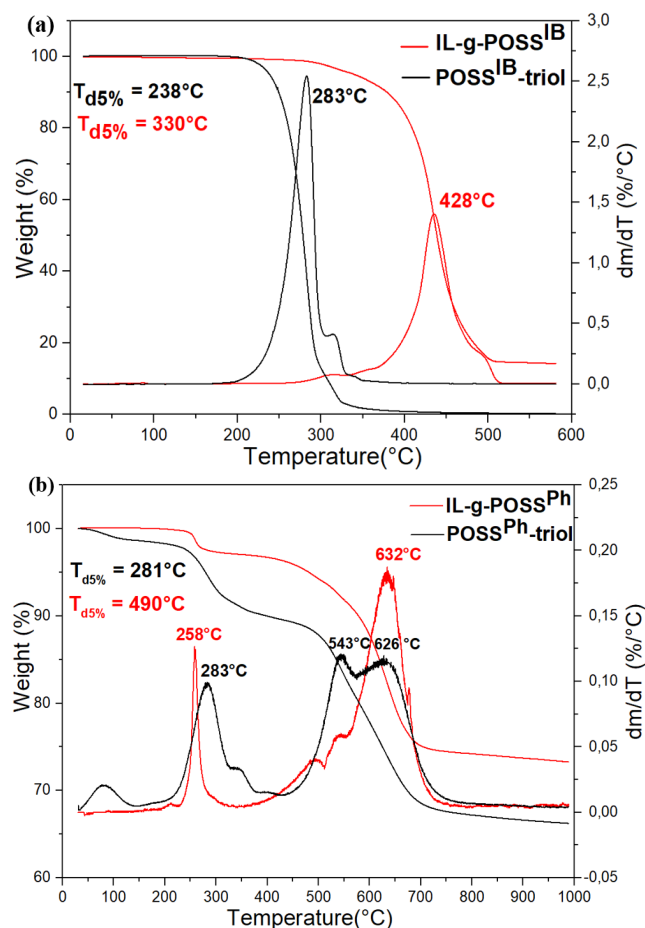


Figure 4. TGA traces for: (a) IL-g-POSS^{IB} with POSS^{IB}-triol and (b) IL-g-POSS^{Ph} with POSS^{Ph}-triol.

Transmission electronic microscopy was used to highlight the influence of the grafting of imidazolium IL on the dispersion of the POSS nanoclusters into epoxy network.

The morphologies obtained for untreated and IL-grafted POSS-based epoxy-amine networks (cured) are displayed in Figures 5 and S9 of ESI. In addition, size distribution analysis using Image J Software is reported in Figure 6.

In all cases, TEM micrographs confirmed a homogeneous distribution of the unmodified POSS clusters in the epoxy matrix whatever the nature of the ligands (isobutyl or phenyl). Nevertheless, the hybrid networks based on POSS-triol display a morphology characterized by a spherical or ellipsoidal shape uniformly dispersed in the continuous epoxy matrix with a diameter from 100 to 900 nm for POSS^{IB}-triol and from 30 to 250 nm for POSS^{Ph}-triol. For the epoxy networks containing 5 wt. % of IL-g-POSS, the TEM images show that the phase separation between epoxy network and POSS occurred at the nanoscale, a spherical dispersed phase is based on small assemblies of POSS-POSS interaction with an average diameter from 10 to 80 nm for IL-g-POSS^{IB} and from 20 to 50 nm for IL-g-POSS^{Ph}. The imidazolium IL grafted on POSS leads to a better distribution of POSS nanoclusters into the epoxy matrix and acts as an interfacial agent confirming the results reported in the literature for similar systems based on nanofillers designed by ionic liquids [36-38]. Recently, similar results were obtained by Donato *et al.* who used ionic liquid-grafted silica (IL-silica) precursors with different anions [39, 40]. Uniform and well-dispersed silica aggregate with the size of about 30 nm were formed when less than 6.8 wt. % of each IL-silica precursor were introduced into the epoxy-amine network.

Glass transition behavior. The thermal behavior of the epoxy hybrids nanomaterials containing POSS was investigated by DSC in order to determine the glass transition temperatures of all the systems. The DSC thermograms of the resulting epoxy networks are presented in Figure 7. The presence of a single glass transition temperature is attributed to the epoxy matrices since the T_g of POSS-rich phases cannot be detected due to the high rigidity of POSS monomers.

For neat epoxy-amine network, one glass transition temperature of 164 °C was obtained corresponding to the T_g values reported in the literature. Then, the incorporation of POSS-triols denoted POSS^{IB}-triol and POSS^{Ph}-triol displayed lower T_g compared to the neat epoxy-amine network. In the opposite, the epoxy materials containing IL-g-POSS maintain a glass transition temperature close to the neat epoxy network. According to the literature, two competitive factors can affect the glass transition temperatures. First, the restriction effect of POSS cages on polymer chain motions will enhance glass transition temperature through local chain reinforcement. Secondly, the inclusion of the bulky POSS cages could give rise to the increase in free volume of the system due to voluminous POSS molecule, leading to a decrease of the T_g . Depending on the nature of the interactions between POSS cages and polymer matrices (*e.g.*, functionalities of POSS, types of polymer matrices, and organic groups in POSS vertexes, etc.). POSS thus acts as nanofiller or as a plasticizer. The POSS-containing

nanocomposites can display increased [41-43] or decreased [44, 45] T_g [46] in comparison with the neat polymers. The behavior of glass transition of the epoxy nanomaterials based on POSS-triols and IL-g-POSSs could be the comprehensive embodiment of the above two factors. These

results imply that the presence of the IL ligand on the POSS cage with different ligands compensates the plasticizing effect of the POSS cages keeping the glass transition of the neat system.

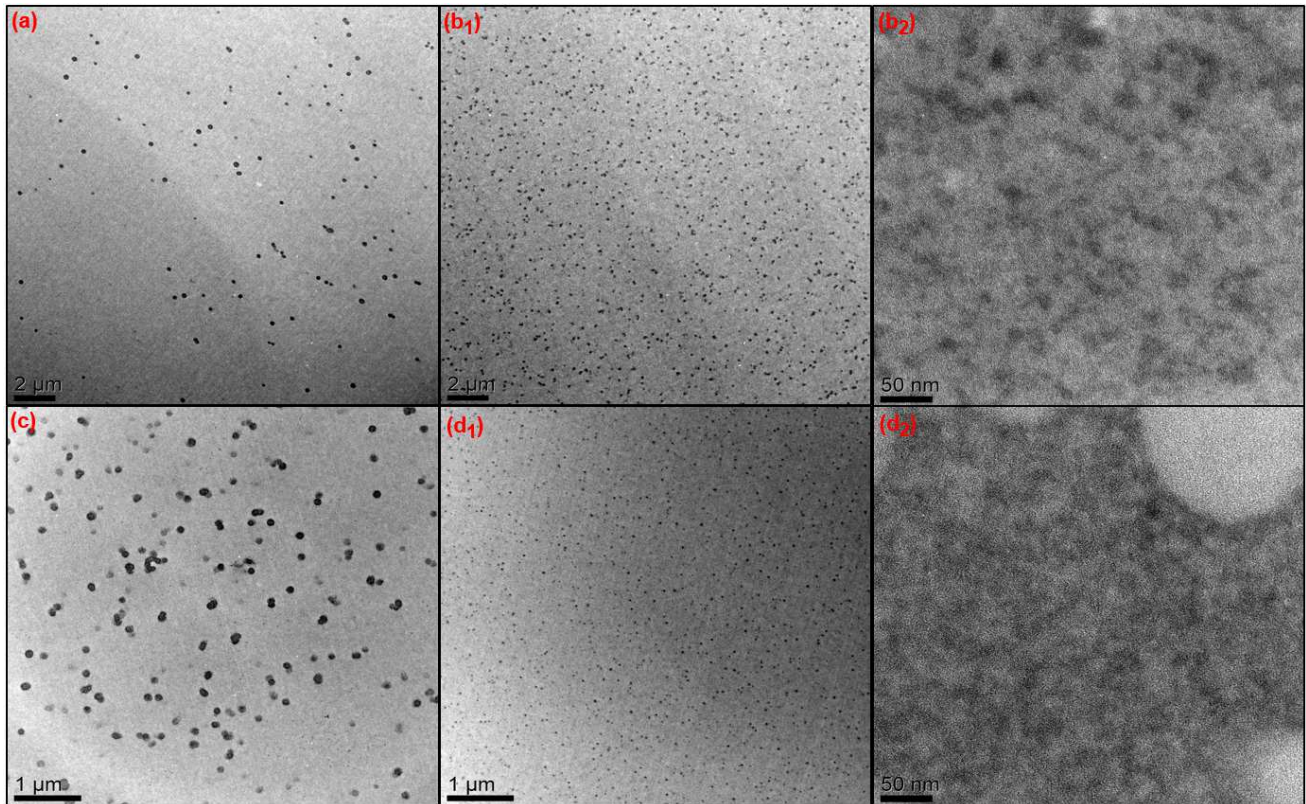


Figure 5. TEM image of the epoxy amine networks with: (a) POSS^{IB}-triol and (b): IL-g-POSS^{IB} at different magnification (b₁; b₂), (c) POSS^{Ph}-triol and (d): IL-g-POSS^{Ph} at different magnification (d₁; d₂).

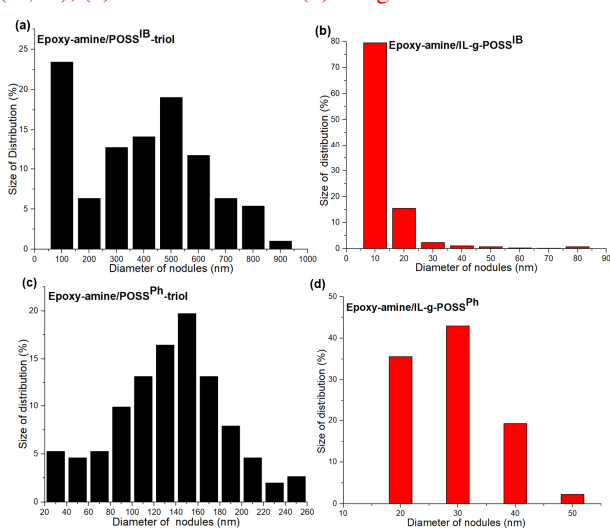


Figure 6. Size distribution of POSS-rich dispersed phase in the epoxy matrix (a) POSS^{IB}-triol, (b) IL-g-POSS^{IB}, (c) POSS^{Ph}-triol and (d) IL-g-POSS^{Ph}.

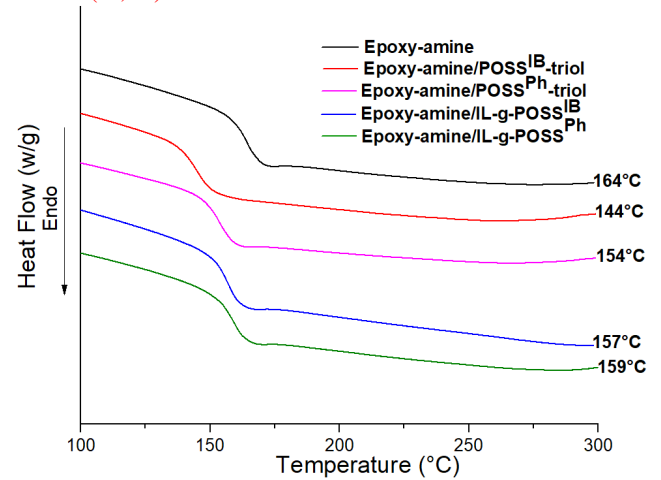


Figure 7. DSC curves of the epoxy-amine network and epoxy hybrids O/I nanomaterials containing POSS^{IB}-triol, IL-g-POSS^{IB}, POSS^{Ph}-triol and IL-g-POSS^{Ph}.

4. Conclusions

In this study, two new imidazolium ionic liquid-supported polyhedral oligomeric silsesquioxanes, denoted IL-g-POSS^{IB} and IL-g-POSS^{Ph}, were successfully prepared. Their chemical structures were confirmed from investigation by ²⁹Si NMR and MALDI-TOF mass spectrometry. Their thermal properties were also studied by TGA and DSC, highlighting an excellent thermal stability (up to 400 °C) of these new compounds. Then, 5 wt. % of IL-g-POSS were incorporated into epoxy-amine networks leading to the formation of homogeneous nanostructured networks. In conclusion, these promising results open up new perspectives in the development of nanostructured organic-inorganic epoxy-amine networks and highlight the role of ionic liquid as an interfacial agent for such new organic-inorganic hybrid nanomaterials. Future works are in progress to show the impact of this POSS nanostructuration on the functionalities of these nanomaterials.

ASSOCIATED CONTENT

Experimental details; supporting figures and tables regarding the Si-g-Im-Cl IL, IL-g-POSS synthesis and characterization; the TEM images of the epoxy matrix (epoxy-amine) are given in the ESI.

AUTHOR INFORMATION

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REFERENCES

- [1] P. Liu, A.L. Cottrill, D. Kozawa, V.B. Koman, D. Parviz, A.T. Liu, J. Yang, T.Q. Tran, M.H. Wong, S. Wang, Emerging trends in 2D nanotechnology that are redefining our understanding of “Nanocomposites”, *Nano Today* (2018).
- [2] B. Reddy, *Advances in diverse industrial applications of nanocomposites*, 2011.
- [3] L. Peponi, D. Puglia, L. Torre, L. Valentini, J.M. Kenny, Processing of nanostructured polymers and advanced polymeric based nanocomposites, *Mater. Sci. Eng., R.* 85 (2014) 1-46.
- [4] R.M. Laine, Nanobuilding blocks based on the [OSiO 1.5] x (x= 6, 8, 10) octasilsesquioxanes, *J. Mater. Chem.* 15 (2005) 3725-3744.
- [5] L. Matějka, P. Murias, J. Pleštil, Effect of POSS on thermomechanical properties of epoxy-POSS nanocomposites, *Eur. Polym. J.* 48 (2012) 260-274.
- [6] K. Tanaka, F. Ishiguro, Y. Chujo, POSS ionic liquid, *J. Am. Chem. Soc.* 132 (2010) 17649-17651.
- [7] D.B. Cordes, P.D. Lickiss, F. Rataboul, Recent developments in the chemistry of cubic polyhedral oligosilsesquioxanes, *Chem. Rev.* 110 (2010) 2081-2173.
- [8] K.M. Kim, Y. Chujo, Liquid-crystalline organic-inorganic hybrid polymers with functionalized silsesquioxanes, *J. Polym. Sci., Part A: Polym. Chem.* 39 (2001) 4035-4043.
- [9] C.M. Leu, Y.T. Chang, K.H. Wei, Synthesis and dielectric properties of polyimide-tethered polyhedral oligomeric silsesquioxane (POSS) nanocomposites via POSS-diamine, *Macromolecules* 36 (2003) 9122-9127.
- [10] P.P. Pescarmona, A.F. Masters, J.C. van der Waal, T. Maschmeyer, Osmium silsesquioxane as model compound and homogeneous catalyst for the dihydroxylation of alkenes, *J. Mol. Catal. A: Chem.* 220 (2004) 37-42.
- [11] J. Fu, Q. Lu, D. Shang, L. Chen, Y. Jiang, Y. Xu, J. Yin, X. Dong, W. Deng, S. Yuan, A novel room temperature POSS ionic liquid-based solid polymer electrolyte, *J. Mater. Sci.* 53 (2018) 8420-8435.
- [12] G. Yang, H. Oh, C. Chanthad, Q. Wang, Dumbbell-Shaped Octasilsesquioxanes Functionalized with Ionic Liquids as Hybrid Electrolytes for Lithium Metal Batteries, *Chem. Mater.* 29 (2017) 9275-9283.
- [13] L.C. Lins, S. Livi, M. Maréchal, J. Duchet-Rumeau, J.F. Gérard, Structural dependence of cations and anions to building the polar phase of PVDF, *Eur. Polym. J.* 107 (2018) 236-248.
- [14] S. Livi, J. Duchet-Rumeau, J.F. Gérard, Nanostructuration of ionic liquids in fluorinated matrix: influence on the mechanical properties, *Polymer* 52 (2011) 1523-1531.
- [15] J. Yang, S. Pruvost, S. Livi, J. Duchet-Rumeau, Understanding of versatile and tunable nanostructuration of ionic liquids on fluorinated copolymer, *Macromolecules* 48 (2015) 4581-4590.
- [16] J. Gu, X. Yang, Z. Lv, N. Li, C. Liang, Q. Zhang, Functionalized graphite nanoplatelets/epoxy resin nanocomposites with high thermal conductivity, *Int. J. Heat Mass Transf.* 92 (2016) 15-22.
- [17] S. Livi, A.A. Silva, Y. Thimont, T.K.L. Nguyen, B.G. Soares, J.F. Gérard, J. Duchet-Rumeau, Nanostructured thermosets from ionic liquid building block-epoxy prepolymer mixtures, *Rsc Adv.* 4 (2014) 28099-28106.
- [18] H. Ghanbari, B.G. Cousins, A.M. Seifalian, A nanocage for nanomedicine: polyhedral oligomeric silsesquioxane (POSS), *Macromol. Rapid Commun.* 32 (2011) 1032-1046.
- [19] A. Ullah, S. Ullah, G.S. Khan, S.M. Shah, Z. Hussain, S. Muhammad, M. Siddiq, H. Hussain, Water soluble polyhedral oligomeric silsesquioxane based amphiphilic hybrid polymers: Synthesis, self-assembly, and applications, *Eur. Polym. J.* 75 (2016) 67-92.
- [20] W. Zhang, G. Camino, R. Yang, Polymer/polyhedral oligomeric silsesquioxane (POSS) nanocomposites: An overview of fire retardance, *Prog. Polym. Sci.* 67 (2017) 77-125.
- [21] V. Jovanovski, B. Orel, R. Ješe, A. Šurca Vuk, G. Mali, S.B. Hoc̃eṽar, J. Grdadolnik, E. Stathatos, P. Lianos, Novel polysilsesquioxane- I/I₃⁺ ionic electrolyte for dye-sensitized photoelectrochemical cells, *J. Phys. Chem. B* 109 (2005) 14387-14395.
- [22] D.M. Fox, P.H. Maupin, R.H. Harris, J.W. Gilman, D.V. Eldred, D. Katsoulis, P.C. Trulove, H.C. De Long, Use of a polyhedral oligomeric silsesquioxane (POSS)-

- imidazolium cation as an organic modifier for montmorillonite, *Langmuir* 23 (2007) 7707-7714.
- [23] D. Shang, J. Fu, Q. Lu, L. Chen, J. Yin, X. Dong, Y. Xu, R. Jia, S. Yuan, Y. Chen, A novel polyhedral oligomeric silsesquioxane based ionic liquids (POSS-ILs) polymer electrolytes for lithium ion batteries, *Solid State Ion.* 319 (2018) 247-255.
- [24] M. Čolović, I. Jerman, M. Gaberšček, B. Orel, POSS based ionic liquid as an electrolyte for hybrid electrochromic devices, *Sol. Energy Mater. Sol. Cells* 95 (2011) 3472-3481.
- [25] J. Davarpanah, P. Rezaee, S. Elahi, Synthesis and characterization of a porous acidic catalyst functionalized with an imidazole ionic liquid, and its use for synthesis of phthalazinedione and phthalazinetrione heterocyclic compounds, *Res. Chem. Intermed.* 41 (2015) 9903-9915.
- [26] D. Deb, S. Bhattacharya, Influence of Ionic-Liquid-Tethered Al_2O_3 Nanoparticle on the Nonisothermal Cold Crystallization in Ionic-Liquid-Based Nanofluids, *J. Phys. Chem. C* 121 (2017) 6962-6976.
- [27] F.G. Garcia, B.G. Soares, V.J. Pita, R. Sánchez, J. Rieumont, Mechanical properties of epoxy networks based on DGEBA and aliphatic amines, *J. Appl. Polym. Sci.* 106 (2007) 2047-2055.
- [28] E. Mounif, V. Bellenger, P. Mazabraud, F. Nony, A. Tcharkhtchi, Chemorheological study of DGEBA/IPD system for reactive rotational molding (RRM), *J. Appl. Polym. Sci.* 116 (2010) 969-976.
- [29] Y.g. Won, J. Galy, J.F. Gérard, J.P. Pascault, V. Bellenger, J. Verdu, Internal antiplasticization in copolymer and terpolymer networks based on diepoxides, diamines and monoamines, *Polymer* 31 (1990) 1787-1792.
- [30] M. Ye, Y. Wu, W. Zhang, R. Yang, Synthesis of incompletely caged silsesquioxane (T_7 -POSS) compounds via a versatile three-step approach, *Res. Chem. Intermed.* 44 (2018) 4277-4294.
- [31] P.A. Ledin, I.M. Tkachenko, W. Xu, I. Choi, V.V. Shevchenko, V.V. Tsukruk, Star-shaped molecules with polyhedral oligomeric silsesquioxane core and azobenzene dye arms, *Langmuir* 30 (2014) 8856-8865.
- [32] A. Fina, D. Tabuani, F. Carniato, A. Frache, E. Boccaleri, G. Camino, Polyhedral oligomeric silsesquioxanes (POSS) thermal degradation, *Thermochimica. Acta* 440 (2006) 36-42.
- [33] M. Le Bras, C.A. Wilkie, S. Bourbigot, General Considerations on the Use of Fillers and Nanocomposites. An Introduction to the Use of Fillers and Nanocomposites in Fire Retardancy, in: *Fire Retardancy of Polymers*, 2005, pp. 1-14.
- [34] I. Blanco, L. Abate, F. Bottino, P. Bottino, M. Chiacchio, Thermal degradation of differently substituted cyclopentyl polyhedral oligomeric silsesquioxane (CP-POSS) nanoparticles, *J. Therm. Anal. Calorim.* 107 (2011) 1083-1091.
- [35] K. Tanaka, F. Ishiguro, J.H. Jeon, T. Hiraoka, Y. Chujo, POSS ionic liquid crystals, *NPG Asia Materials* 7 (2015) e174.
- [36] Y.E. Liu, C.E. He, R.G. Peng, W. Tang, Y.K. Yang, Ionic Liquid Assisted Dispersion of Reduced Graphene Oxide in Epoxy Composites with Improved Mechanical Properties, in: *Advanced Materials Research*, vol 738, Trans Tech Publ, 2013, pp. 56-60.
- [37] E.C.L. Pereira, B.G. Soares, Conducting epoxy networks modified with non-covalently functionalized multi-walled carbon nanotube with imidazolium-based ionic liquid, *J. Appl. Polym. Sci.* 38 (2016) 43976.
- [38] C. Zhang, X. Mi, J. Tian, J. Zhang, T. Xu, Supported Ionic Liquid Silica as Curing Agent for Epoxy Composites with Improved Mechanical and Thermal Properties, *Polymers* 9 (2017) 478.
- [39] M. Perchacz, R.K. Donato, L. Seixas, A. Zhigunov, R. Konefał, M. Serkis-Rodzeń, H. Beneš, Ionic Liquid-Silica Precursors via Solvent-Free Sol-Gel Process and Their Application in Epoxy-Amine Network: A Theoretical/Experimental Study, *ACS Appl. Mater. Interfaces* 9 (2017) 16474-16487.
- [40] R.K. Donato, L. Matějka, H.S. Schrekker, J. Pleštil, A. Jigounov, J. Brus, M. Šlouf, The multifunctional role of ionic liquids in the formation of epoxy-silica nanocomposites, *J. Mater. Chem.* 21 (2011) 13801-13810.
- [41] H. Xu, S.W. Kuo, J.S. Lee, F.C. Chang, Preparations, thermal properties, and T_g increase mechanism of inorganic/organic hybrid polymers based on polyhedral oligomeric silsesquioxanes, *Macromolecules* 35 (2002) 8788-8793.
- [42] Y. Ni, S. Zheng, Epoxy resin containing octamaleimidophenyl polyhedral oligomeric silsesquioxane, *Macromol. Chem. Phys.* 206 (2005) 2075-2083.
- [43] Y. Deng, J. Bernard, P. Alcouffe, J. Galy, L. Dai, J.F. Gérard, Nanostructured hybrid polymer networks from in situ self-assembly of RAFT-synthesized POSS-based block copolymers, *J. Polym. Sci. Part A: Polym. Chem.* 49 (2011) 4343-4352.
- [44] I.A. Zucchi, M.J. Galante, R.J. Williams, E. Franchini, J. Galy, J.F. Gérard, Monofunctional epoxy-POSS dispersed in epoxy-amine networks: Effect of a prereaction on the morphology and crystallinity of POSS domains, *Macromolecules* 40 (2007) 1274-1282.
- [45] M.J. Abad, L. Barral, D.P. Fasce, R.J. Williams, Epoxy networks containing large mass fractions of a monofunctional polyhedral oligomeric silsesquioxane (POSS), *Macromolecules* 36 (2003) 3128-3135.
- [46] G.Z. Li, L. Wang, H. Toghiani, T.L. Daulton, K. Koyama, C.U. Pittman, Viscoelastic and mechanical properties of epoxy/multifunctional polyhedral oligomeric silsesquioxane nanocomposites and epoxy/ladderlike polyphenylsilsesquioxane blends, *Macromolecules* 34 (2001) 8686-8693.

Polyhedral Oligomeric Silsesquioxane-Supported Ionic Liquid for Designing Nanostructured Hybrid Organic-Inorganic Networks

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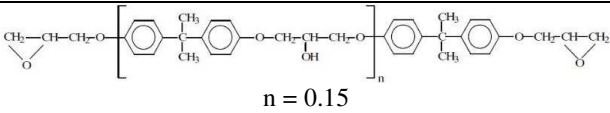
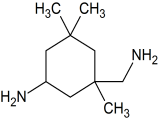
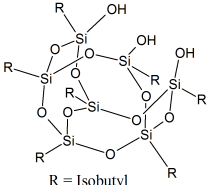
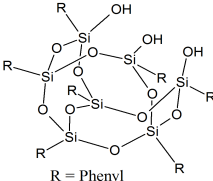
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1. Materials and Characterization Methods

1.1 Materials

All reagents for the synthesis of IL-functionalized silanes, *i.e.* 1-methylimidazole (99 %), 3- chloropropyltrimethoxysilane (97 %), the different solvents (diethyl ether, ethanol, chloroform) and the amine comonomer, *i.e.* the isophoronediamine (IPD), were purchased from Sigma Aldrich and were used as received, *i.e.* without further purification. Epoxy prepolymer based on diglycidyl ether of bisphenol A (DGEBA) EPON 828 from Hexion was used as received. The two type of POSS, *i.e.* bearing isobutyl or phenyl ligands, were provided from Hybrid Plastics, Inc. All the chemical formula of components used are summarized in Table S1.

Table S1. Chemical formula of components used to design nanostructured epoxy-amine networks.

Name	Chemical formula	Characteristics
Diglycidyl ether of bisphenol A (DGEBA)	 $n = 0.15$	377 g.mol ⁻¹ , EEW : (185-192 g/eq) ^a , T _g = -14 °C ^b , T _d = 330 °C ^d
Isophoronediamine (IPD)		170.3 g.mol ⁻¹
Heptaisobutyl-trisilanol POSS (POSS ^{IB} -triol)	 R = Isobutyl	791.42 g.mol ⁻¹ , T _m = 200 °C ^c , T _d = 283 °C ^d
Heptaphenyl-trisilanol POSS (POSS ^{Ph} -triol)	 R = Phenyl	931.34 g.mol ⁻¹ , T _{m1} = 217 °C ^c , T _{m2} = 230 °C ^c , T _d = 617 °C ^d

^a EEW : epoxy equivalent weight, ^b T_g: Glass transition, ^c T_m: Melting temperature, ^d T_d: Degradation temperature determined at the maximum of the first derivative of the weight loss as temperature.

1.2 Characterization methods

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet Magna 550 spectrometer at room temperature (25 °C) with Golden Gate (ATR). The spectra were collected in 32 scans with a spectral resolution of 4 cm⁻¹ from 4000 to 525 cm⁻¹.

Single pulse ²⁹Si solid-state NMR measurements were performed using a JEOL 600 MHz NMR spectrometer operating at 14.1 T (119.2 MHz for ²⁹Si) equipped with 3.2 mm rotors and for a rotation of 5 kHz. The relaxation delay was 60 s for POSS^{IB}-triol and POSS^{Ph}-triol and 90 s for IL-g-POSS^{IB}, IL-g-POSS^{Ph}.

¹H- and ¹³C-NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer. Samples were dissolved in an appropriate deuterated solvent (CDCl₃) at 25 °C. The chemical shifts (δ) are expressed in ppm relative to internal tetramethylsilane for ¹H and ¹³C nuclei, and coupling constants are indicated in Hz. Abbreviations for signal coupling are as follows: s=singlet; d=doublet; dd=doublet of doublets; t=triplet; q=quartet; quin=quintet; m=multiplet; br=broad signal.

MALDI-TOF mass spectra were acquired using a Voyager-DE STR (Absciex, USA) and were obtained using a nitrogen laser emitting at 337 nm with 3 ns pulses. The instrument operated in the linear or reflectron modes. Ions were accelerated under a final potential of 20 kV. The positive ions were detected in all cases. Mass spectra are the sum of 300 shots and an external mass calibration of mass analyzer was used (mixture of peptides from SequazymeTM standards kit, Absciex, Life

Sciences Holdings France SAS, France). The matrix used for all analyses is dithranol purchased from Sigma Aldrich used without further purification. The solid matrix and samples were dissolved at 10 mg.mL⁻¹ in chloroform. A volume of 9 μL matrix solution was then mixed with 1 μL of sample solution. An aliquot of 0.5 μL of resulting solution was spotted onto the MALDI sample plate and air-dried at room temperature.

Differential scanning calorimetry (DSC) analysis was performed on a Q10 DSC calorimeter from TA instrument in a dynamic mode at 10 C.min⁻¹ from 0 °C to 250 °C for the hybrid O/I nano-objects and from -70 °C to 300 °C for the hybrids O/I networks. The equipment was regularly calibrated using Indium standard. About 5 - 7 mg of samples were sealed in hermetic aluminum pans and heated under nitrogen atmosphere.

Thermogravimetric analyses (TGA) was achieved using a Q500 TGA from TA Instrument Inc. with a platinum pan. The samples (about 10 - 20 mg) were heated from ambient temperature up to 900 °C under 50 mL.min⁻¹ nitrogen flow at a heating rate of 20 C.min⁻¹.

Transmission electron microscopy (TEM) was performed at the Technical Center of Micro-structures (University of Lyon) using a Phillips CM 120 microscope operating at 80 kV to characterize the dispersion of the inorganic-rich components in the resulting epoxy networks. 60 nm-thick ultrathin sections of samples were obtained using an ultramicrotome equipped with a diamond knife and then set on copper grids for observation.

2. Results and Discussion

2.1. Characterization of the silylated imidazolium ionic liquid (Si-g-Im-Cl)

The MALDI-TOF mass spectrum of the Si-g-Im-Cl IL (Figure S1) confirmed the expected cationic species of the IL: Calcd for (C₁₀H₂₁N₂O₃Si⁺) [M⁺, 100 %] 245.1; found 245.1, and reveals that the chemical environment around IL atoms is the same, which confirms the very pure IL has been obtained.

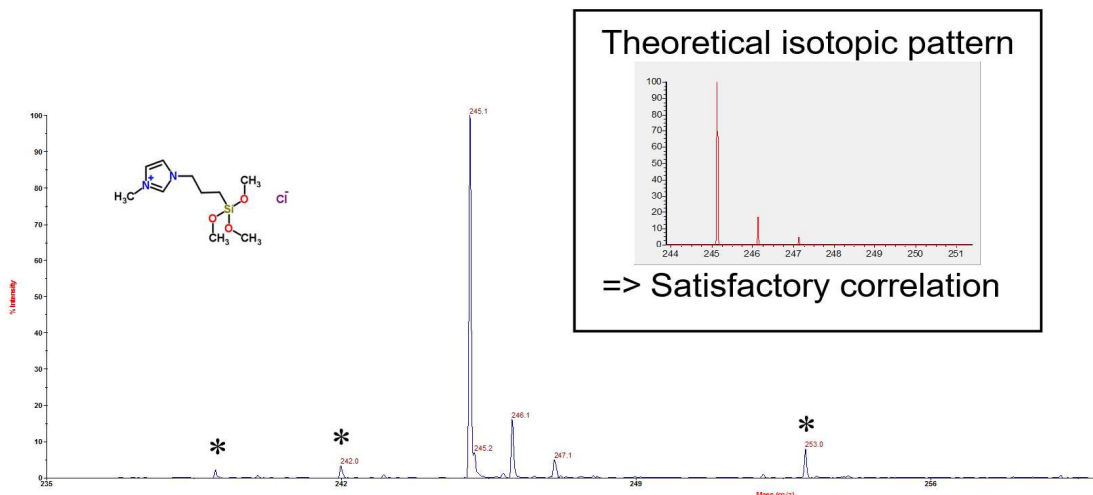


Figure S1. Mass spectrum of 1-(3-trimethoxysilylpropyl)-3-methyl imidazolium Chloride (Si-g-Im-Cl).

2.2. Characterization of IL-g-POSS

The occurrence of the corner-capping reaction of the open cage POSS was monitored by FT-IR spectroscopy. The IR spectrum of the IL-g-POSS (1a, 2a) samples, was compared to the vibrational profile of the reactant POSS-triols (1, 2) (Fig. S2 and S3). The compounds after and before the reaction show very similar IR features in the region of the stretching and bending modes of the ligands (isobutyl or phenyl) chains and the ν_{as} (Si-O-Si) of the cage framework (1500-1100 cm⁻¹). This is proof that the POSS cage structure was essentially preserved from the chemical point of view during the corner-capping reaction. The most important differences between the two samples fall in the 3500-3000 cm⁻¹ and 1000-500 cm⁻¹ IR ranges. In particular, the vibrational profile of samples 1 or 2 before the reaction shows two absorptions at 888 cm⁻¹ and 3250 cm⁻¹, relative to the stretching modes of Si-OH and O-H groups [1], respectively, that are almost completely absent in 1a or 2a after the reaction, where the cage is completely condensed [2]. The presence of additional bands, i.e. at, 1570, 928 cm⁻¹ (imidazolium ring mode) and the corresponding C-H stretching ring modes at 3140 and 3054 cm⁻¹ signaled the presence of the imidazolium ring [3]. IR data have been supported by NMR spectroscopy applied to ¹H, ¹³C and ²⁹Si nuclei NMR.

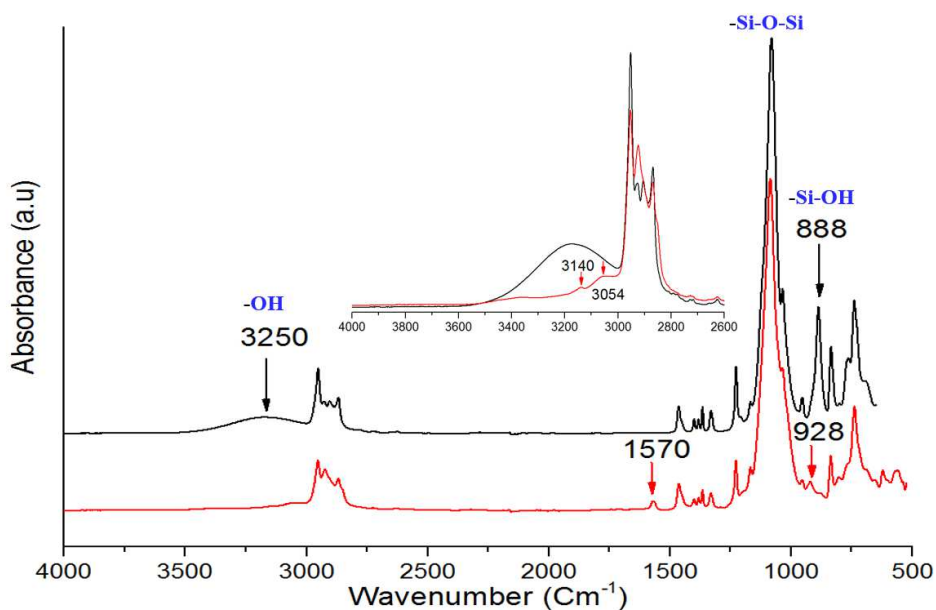


Figure S2. IR spectra of POSS^{IB}-triol (up curve) and IL-g-POSS^{IB} (Down curve).

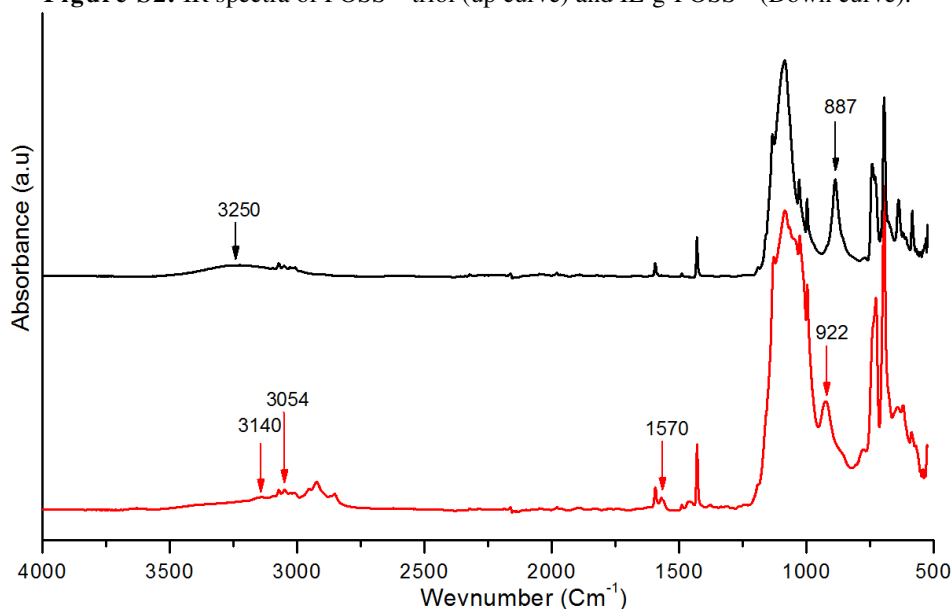


Figure S3. IR spectra of POSS^{Ph}-triol (up curve) and IL-g-POSS^{Ph} (Down curve).

¹H spectrum (**Figure S7**) of the IL-g-POSS^{IB} provided the important information that dialkylation of imidazole had been conserved. This was inferred from the existence of seven new signals attributed: i) to the imidazolium ring protons at $\delta = 10.85, 7.52, 7.35$ ppm; ii) to the double alkylation protons at $\delta = 4.14$ ppm corresponding to the N-CH₃ and iii) the chemical shifts at $\delta = 4.33, 2.01, 0.95$ ppm to the silicopropyl Si-(CH₂)₃ chain. The disappearance of methoxy proton signal at around 3.51 ppm of the IL proves the completion of hydrosilylation reaction. The significant suppression of -OH proton signals at 7.14 ppm indicates the successful coupling of Si-g-Im-Cl to the POSS^{IB}-triol and confirms the results obtained by ²⁹Si-NMR.

The ¹³C-NMR spectrum of product IL-g-POSS^{IB}, dissolved in CDCl₃ (**Figure S5**) shows the resonance peaks at 25.59, 23.72 - 24.06, and 22.34 ppm, ascribed to -CH₃, -CH₂, and -CH carbon of the isobutyl groups bound to the siliceous framework [4]. Additional seven major peaks centered at 8.86, 22.92, 36.61 ppm correspond to the Si-(CH₂)₃ silicopropyl chain, 51.85 ppm to N-CH₃ and the others at 120.86, 123.52, 138.42 ppm to the imidazole ring with total disappearance of methoxy carbon peaks at 50.74 ppm of the IL, evidence of complete reaction.

On the ^{13}C -NMR spectrum of IL-g-POSS^{Ph}, dissolved in DMSO (**Figure S6**), peaks of the phenyl carbons groups appear at 133.79, 131.22, 128.22, and six major additional peaks centered at 23.90, 36.22 ppm correspond to the $\text{Si}(\text{CH}_2)_3$ silicopropyl chain, 51.1 ppm to $\text{N}-\text{CH}_3$ and the others at 124.02, 137.23 ppm to the imidazole ring with total disappearance of methoxy carbon peaks at 50.74 ppm of the IL, evidence of complete reaction.

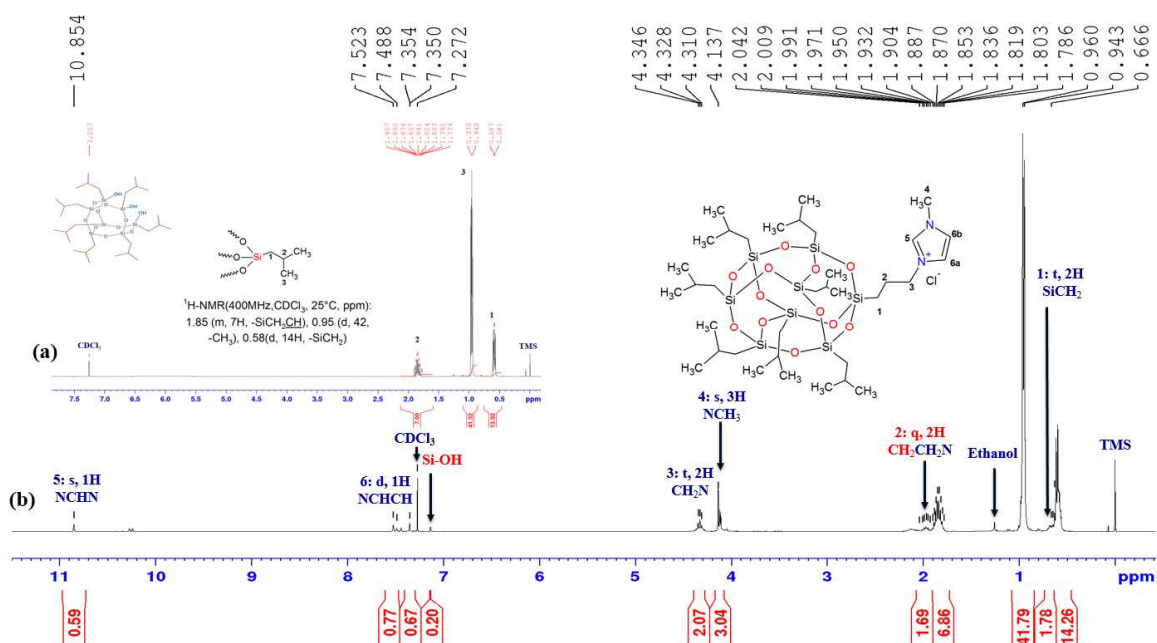


Figure S4. ^1H NMR spectra of POSS^{IB}-triol (a) and IL-g-POSS^{IB} (b).

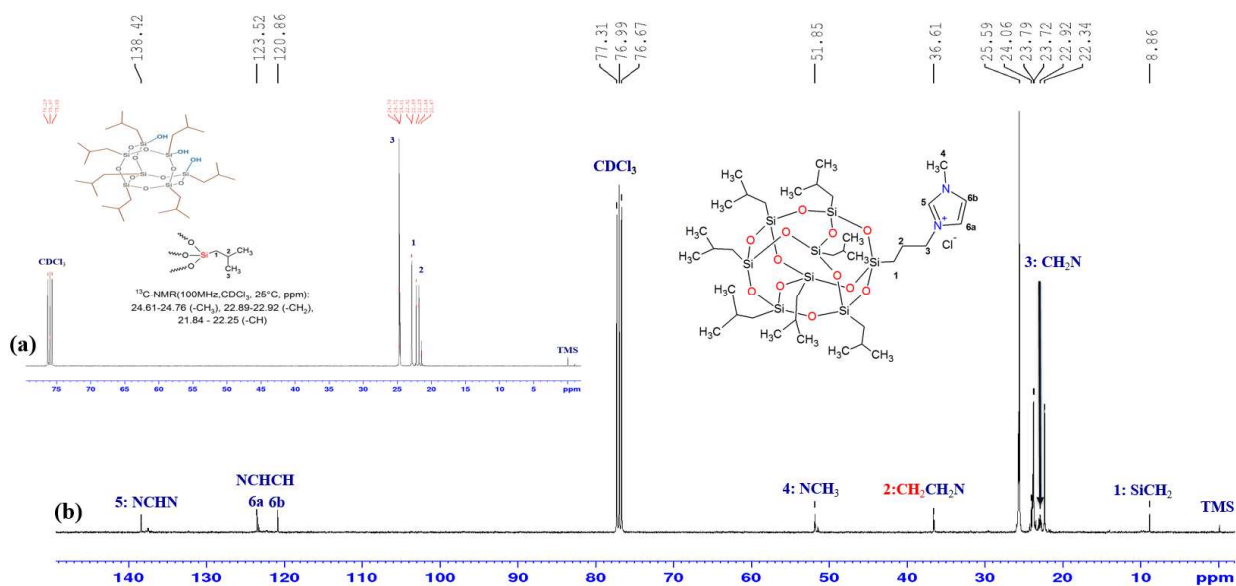


Figure S5. ^{13}C NMR spectra of POSS^{IB}-triol (a) and IL-g-POSS^{IB} (b).

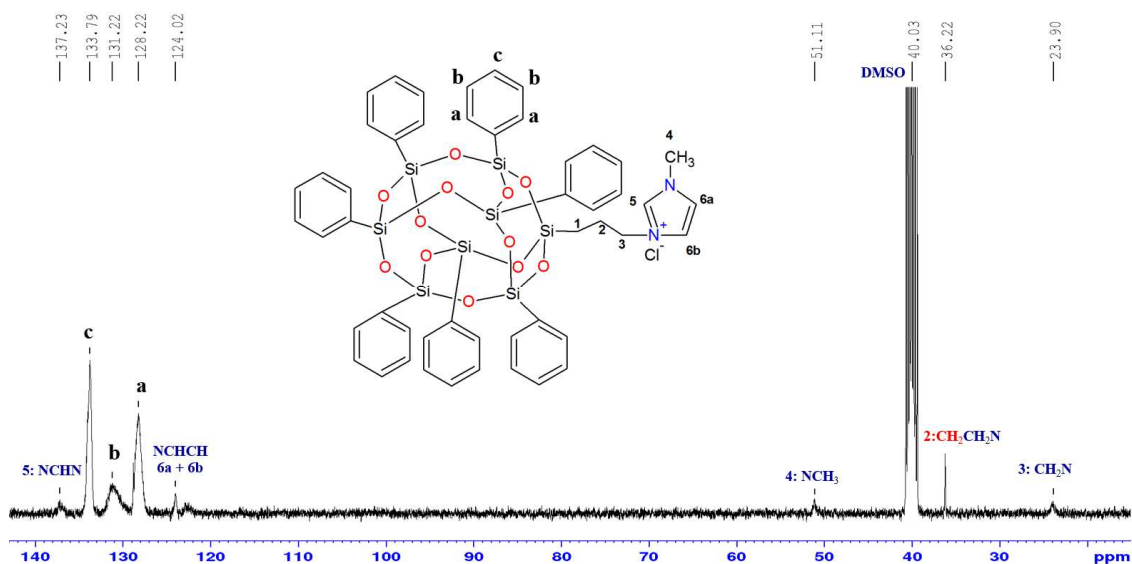


Figure S6. ^{13}C NMR spectrum of IL-g-POSS^{Ph}.

Table S2. Contents of the two types of Si atoms in the POSS cage.

Compound	Si-OH band (%) ^a	Si-R band (%) ^a
POSS ^{Ph} -triol	43	57
IL-g-POSS ^{Ph}	22	78
POSS ^{IB} -triol	42	58
IL-g-POSS ^{IB}	8	92

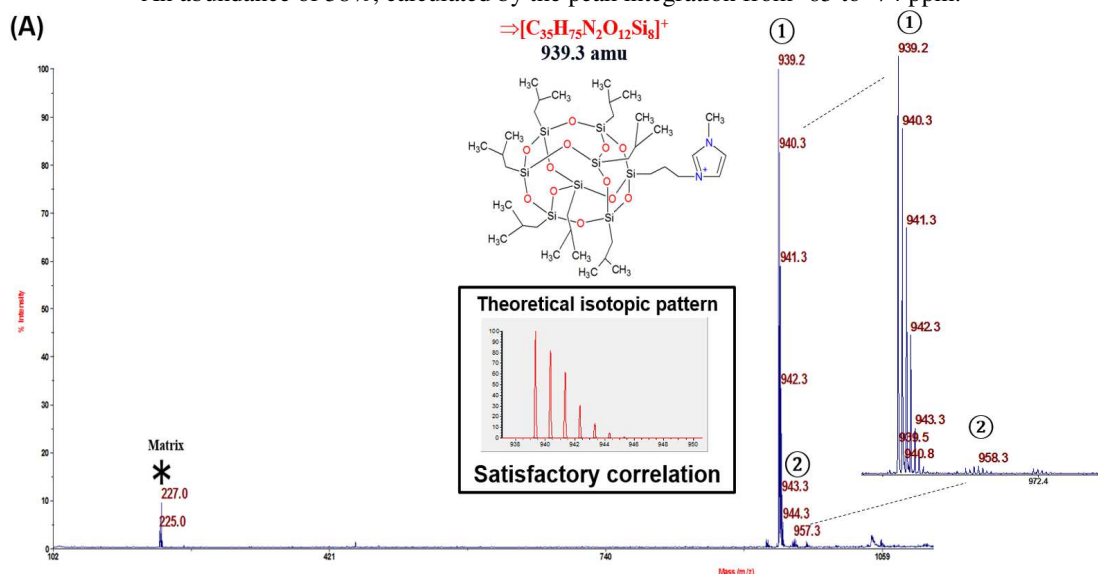
^a Calculated from ^{29}Si from ^{29}Si NMR results:

An abundance of 43%, calculated by the peak integration from -62 to -72 ppm;

An abundance of 57%, calculated by the peak integration from -74 to -84 ppm;

An abundance of 42%, calculated by the peak integration from -55 to -63 ppm;

An abundance of 58%, calculated by the peak integration from -65 to -74 ppm.



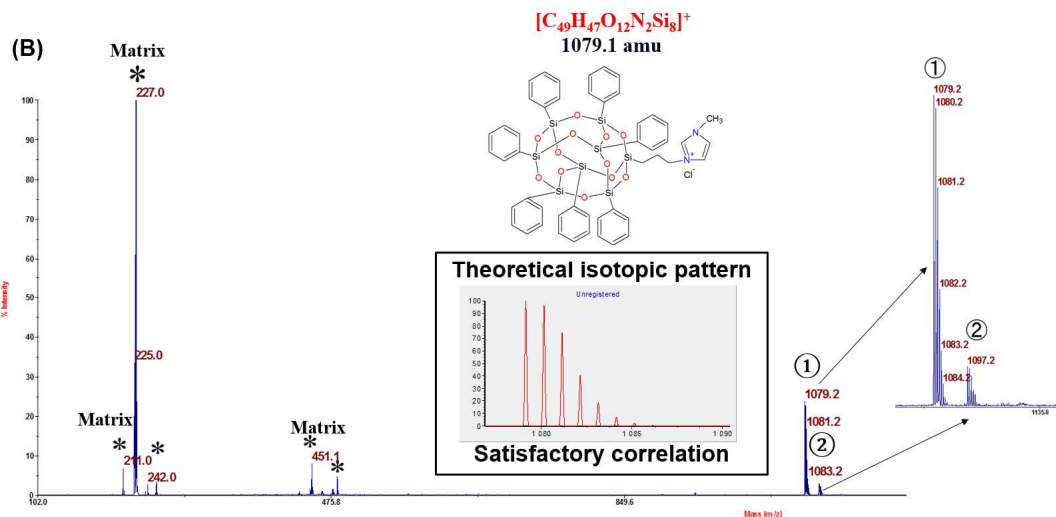


Figure S7. Positive MALDI-TOF mass spectra of IL-g-POSS^{IB} (A) and IL-g-POSS^{Ph} (B) (Dithranol matrix).

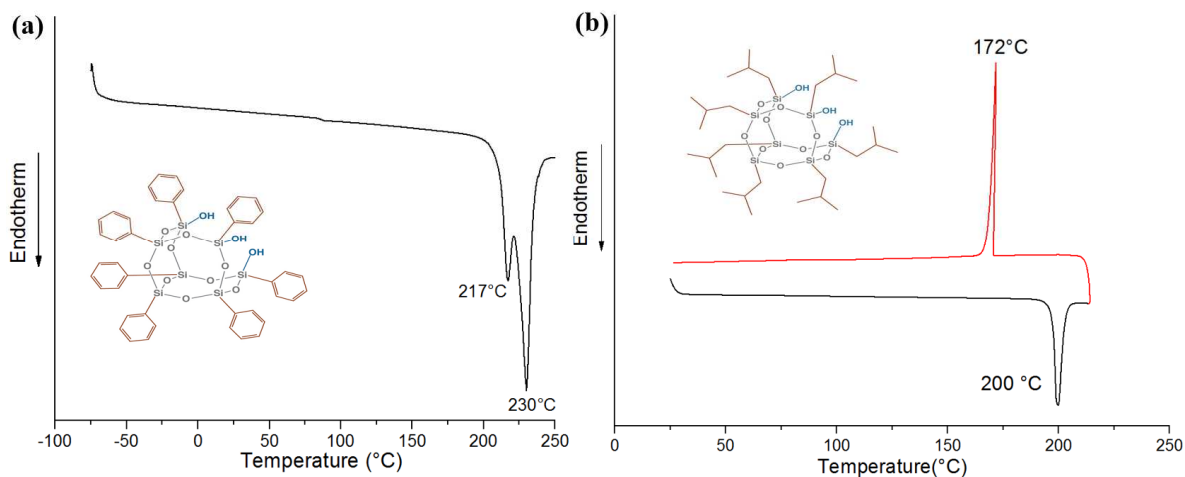


Figure S8. DSC traces for POSS-triols: (a) POSS^{Ph}-triol and (b) POSS^{IB}-triol.

Table S3. TGA data of POSS^{IB}-triol, POSS^{Ph}-triol, IL-g-POSS^{IB} and IL-g-POSS^{Ph}.

Sample	T _{d5%} (°C) ^a	T _{dmax1} (°C) ^b	T _{dmax2} (°C) ^c	Residue (%) ^d
POSS ^{IB} -triol	238	-	283	0.25
POSS ^{Ph} -triol	281	543	626	66
IL-g-POSS ^{IB}	330	-	428	12
IL-g-POSS ^{Ph}	490	-	632	73

^a T_{d5%}: Degradation temperature determined at a mass loss of 5 wt. %, ^b T_{dmax1}: Degradation temperature determined at the first maximum of from the first derivative of the weight loss as temperature, ^c T_{dmax2}: Degradation temperature determined at the second maximum of the first derivative of the weight loss as temperature, ^d the residue yield at 800 °C.

Hybrid Organic-Inorganic Networks

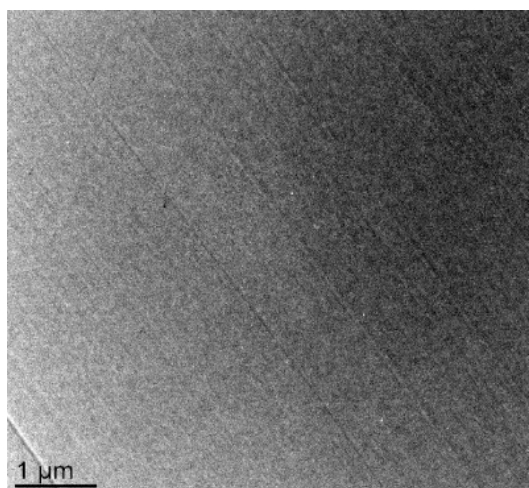
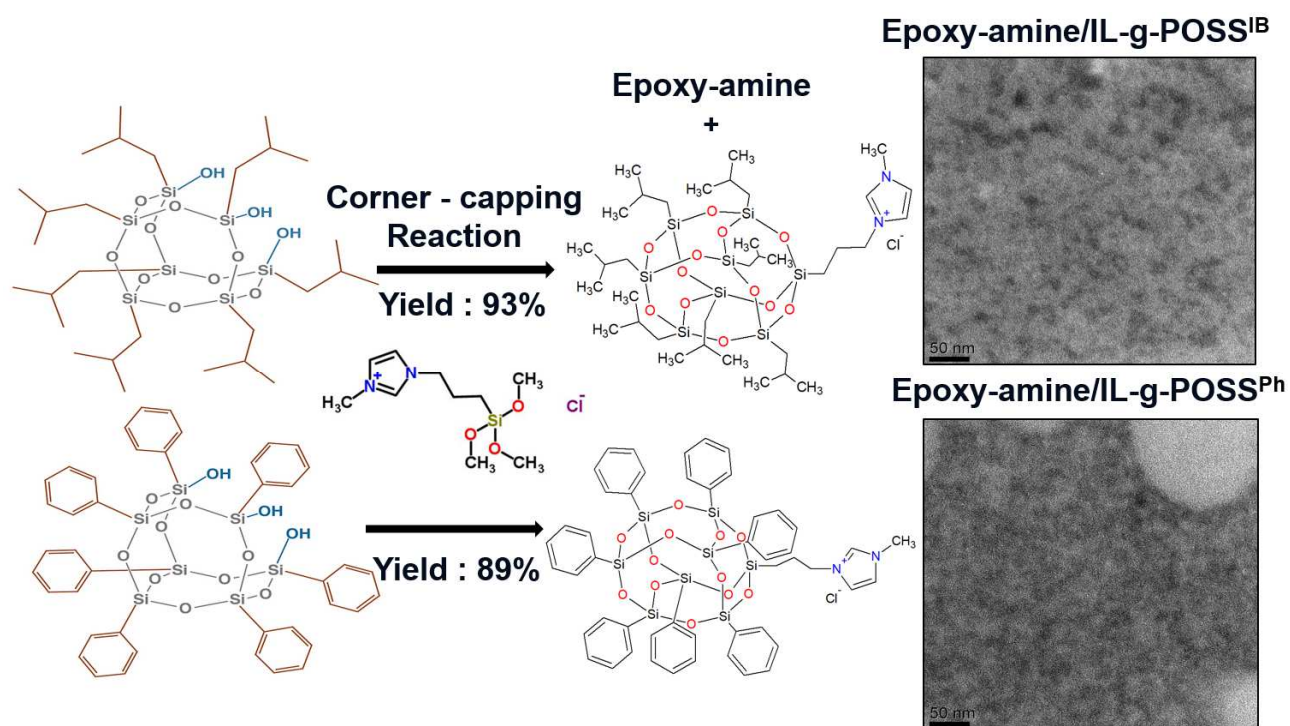


Figure S9. TEM image of the epoxy matrix (epoxy-amine).

REFERENCES

- [1] I. Jerman, M. Koželj, B. Orel, The effect of polyhedral oligomeric silsesquioxane dispersant and low surface energy additives on spectrally selective paint coatings with self-cleaning properties, *Sol. Energy Mater. Sol. Cells* 94 (2010) 232-245.
- [2] I. Jerman, V. Jovanovski, A.Š. Vuk, S.B. Hočevar, M. Gaberšček, A. Jesih, B. Orel, Ionic conductivity, infrared and Raman spectroscopic studies of 1-methyl-3-propylimidazolium iodide ionic liquid with added iodine, *Electrochim. Acta* 53 (2008) 2281-2288.
- [3] N. Brun, P. Hesemann, G. Laurent, C. Sanchez, M. Birot, H. Deleuze, R. Backov, Macrocellular Pd@ ionic liquid@ organo-Si (HIPE) heterogeneous catalysts and their use for Heck coupling reactions, *New J. Chem.* 37 (2013) 157-168.
- [4] M. Ye, Y. Wu, W. Zhang, R. Yang, Synthesis of incompletely caged silsesquioxane (T₇-POSS) compounds via a versatile three-step approach, *Res. Chem. Intermed.* 1-18.

Graphical Abstract



The molecular design of nanostructured epoxy-amine networks by using IL-grafted POSS as inorganic-organic nano-building blocks