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Andrei Jitianu
CUNY Lehman College

Sylvian Cadars
Université de Nantes

Fan Zhang
National Institute of Standards and Technology

Gabriela Rodriguez
CUNY Lehman College

Quentin Picard
CUNY Lehman College

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Authors

Andrei Jitianu, Sylvian Cadars, Fan Zhang, Gabriela Rodriguez, Quentin Picard, Mario Aparicio, Jadra Mosa, and Lisa C. Klein

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²⁹Si NMR and SAXS investigation of the hybrid organic–inorganic glasses obtained by consolidation of the melting gels†

Andrei Jitianu,^{a,b} Sylvian Cadars,^{c,d} Fan Zhang,^e Gabriela Rodriguez,^a Quentin Picard,^a Mario Aparicio,^f Jadra Mosa^f and Lisa C. Klein^g

This study is focused on structural characterization of hybrid glasses obtained by consolidation of melting gels. The melting gels were prepared in molar ratios of methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DMEDES) of 75%MTES–25%DMEDES and 65%MTES–35%DMEDES. Following consolidation, the hybrid glasses were characterized using Raman, ²⁹Si and ¹³C Nuclear Magnetic Resonance (NMR) spectroscopies, synchrotron Small Angle X-Ray Scattering (SAXS) and scanning electron microscopy (SEM). Raman spectroscopy revealed the presence of Si–C bonds in the hybrid glasses and 8-membered ring structures in the Si–O–Si network. Qualitative NMR spectroscopy identified the main molecular species, while quantitative NMR data showed that the ratio of trimers (T) to dimers (D) varied between 4.6 and 3.8. Two-dimensional ²⁹Si NMR data were used to identify two distinct types of T³ environments. SAXS data showed that the glasses are homogeneous across the nm to micrometer length scales. The scattering cross section was one thousand times lower than what is expected when phase separation occurs. The SEM images show a uniform surface without defects, in agreement with the SAXS results, which further supports that the hybrid glasses are nonporous.

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1. Introduction

The concept of melting gels was first introduced in 2001 by Matsuda *et al.*¹ They studied the formation of poly(benzylsilsesquioxane) particles, which were then deposited on an ITO substrate by electrophoretic deposition. After heat treatment, continuous and uniform transparent thick coatings were obtained. In reality the process called “melting” is a softening process. Melting gels are hybrid organic inorganic materials in which the presence of the covalent bonds between the organic

components and inorganic network places the melting gels in the Class II of hybrids.² The precursors used for preparation of hybrid melting gels are a mixture between a mono-substituted organo-modified alkoxide such as phenyltriethoxysilane^{3,4} or methyltriethoxysilane⁵ and a di-substituted organo-modified alkoxide such as diphenyldiethoxysilane³ or dimethyldiethoxysilane.⁵ Hybrid melting gels differ from classical hybrids through their properties. The defining property of these hybrid melting gels is that they are solid at room temperature, become fluid at a softening temperature T_1 (~110 °C), return to rigidity at room temperature, and can be re-softened many times. All the hybrid melting gels also present a consolidation temperature which varies with the composition.^{3,5} However, after consolidation at a temperature T_2 ($T_2 > T_1$), the gels no longer soften. The consolidation temperature T_2 corresponds to cross-linking of the silica chains.^{5,6} At the consolidation temperature the melting gels are transformed into hybrid glasses.⁴

The most studied system is the phenyl based melting gel.^{3,6–8} For this system Kakiuchida *et al.*^{6,7} found a correlation between the structure of a melting gel and its viscoelastic properties. Using ²⁹Si MAS NMR and Gel Permeation Chromatography (GPC) they identified the complex nature of the structure of the melting gels. Furthermore, they demonstrated that the softening ability is controlled by the number

^aDepartment of Chemistry, Lehman College, CUNY, Davis Hall, 250 Bedford Park Boulevard West, Bronx, New York 10468, USA.

E-mail: andrei.jitianu@lehman.cuny.edu; Fax: +718-960-8750; Tel: +718-960-6770

^bPh.D. Program in Chemistry and Biochemistry, The Graduate Center of the City University of New York, New York, NY 10016, USA

^cInstitut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP32229, 44322 Nantes Cedex 3, France

^dCEMHTI CNRS UPR3079, Université d'Orléans, France

^eNational Institute of Standards and Technology (NIST) 100 Bureau Drive, Stop 8520, Gaithersburg, MD 20899-8520, USA

^fInstituto de Cerámica y Vidrio, Consejo Superior de Investigaciones Científicas (CSIC), Kelsen 5, 28049 Madrid, Spain

^gDepartment of Materials Science and Engineering, Rutgers University, 607 Taylor Road, Piscataway, New Jersey 08854, USA

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of oxygen bridges and the intramolecular structure, and the viscosity follows a free volume model. Despite a growing number of studies on melting gel properties, there are only a few studies that characterize the hybrid glasses obtained from the melting gel consolidation. Masai *et al.*⁸ prepared melting gels and the corresponding low temperature hybrid glasses from phenyltriethoxysilane and diphenyldiethoxysilane. Using ²⁹Si MAS NMR and FT-IR spectroscopy, they identified the phenomena that take place during the thermal transition from melting gels to hybrid glasses. Using the same system³ and phenyltriethoxysilane along with dimethyldiethoxysilane⁴ we characterized the structure of the hybrid glasses by Raman and FT-IR spectroscopy. The structure and the orientation of the organic groups was found to promote hydrophobicity to the surface of the hybrid glasses.

In our earlier works, hybrid glasses were also obtained using methyl-substituted melting gels.^{5,9–12} Mainly the focus was on preparation^{5,9} using methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DMEDES), on their thermal stability,^{10,11} and on their viscoelastic properties.¹¹ The hybrid glasses obtained from these melting gels were characterized by FT-IR and Raman spectroscopy.^{5,12} These glasses, which are obtained at relatively low temperatures (135–160 °C),⁵ perform well as anticorrosive coatings¹² and as hermetic barriers^{13,14} and also have low dielectric constants.¹⁵ While several applications have been pursued for these hybrid glasses, an understanding of their molecular structure is still incomplete.

NMR spectroscopy is among the most powerful techniques for structural studies of the silica-based sol-gel materials. For the sol-gel method, NMR spectroscopy can be used either in solutions to elucidate the early stages of formation of the molecular species of the inorganic or hybrid materials¹⁶ or on the final material when solid state NMR can be used to elucidate the structure.¹⁷

Historically, “horizontal and vertical polymerization in the silane phase” of MTES and DMEDES was first studied by Sindorf *et al.*¹⁸ in comparison with their chlorosilane partners using ²⁹Si and ¹³C NMR by using cross polarization (CP) and magic angle spinning (MAS). It was found that while the ethoxysilanes and chlorosilanes have similar chemistries in the silylation reactions of silica surfaces, ethoxysilanes are less reactive than their chlorosilane partners. Fyfe *et al.*¹⁹ studied the copolymerization of the tetraethoxysilane (TEOS) and MTES using two dimensional ¹H/²⁹Si NMR correlation, which revealed these two components mixed well in the final gel and no phase separation was induced. Another interesting study on the copolymerization of TEOS along with MTES or ethyltriethoxysilane (ETES) or octyltriethoxysilane (OTES) was carried out by Peeters *et al.*²⁰ Using the CP and single-pulse excitation (SPE) MAS NMR, the effect of the length of the organic tail on the degree of condensation was studied. They observed that CP MAS NMR cannot be used to quantitatively obtain reliable data for the system with a long organic tail due to the large distance between the proton and a part of Q⁴ or T³ silicon atoms. For this reason, SPE MAS-NMR was required in quantitative measurements.²⁰ It was also concluded that the

total number of network bonds decreases with the increasing level of substitution.

The formations of silicon-oxycarbide glasses obtained by cohydrolysis and polycondensation of the TEOS along with DMEDES^{21,22} or triethoxysilane (TES) along with methyl-diethoxysilane (MDES)²³ or TEOS and MTES²⁴ or MTES along with methyltrimethoxysilane (MTMS)²⁵ were investigated by using ²⁹Si, ¹³C and ¹H MAS NMR. ²⁹Si and ¹³C MAS NMR²³ was used for identification of the distribution of the organic groups in the gel phases. In addition, these techniques were used to characterize the evolution between gel and silicon oxycarbide glasses.^{23,24} Moreover, Suyal *et al.*²⁴ showed that the addition of colloidal silica delayed the decomposition of the methyl groups from MTES.

Brus *et al.*,^{26–28} published a series of studies upon co-hydrolysis polycondensation of TEOS with DMEDES or TEOS with MTES using ¹H MAS NMR²⁶ ¹H and ²⁹Si CP/MAS NMR²⁷ and 2D ¹H–²⁹Si heteronuclear experiments. They observed that the dynamic behavior and the nature of the silanol protons in the presence of water are influenced by the amount of methyl groups in the hybrid network.²⁶ In addition, it was observed that the formation of clusters of OH protons with different strength of hydrogen bond is related to the arrangements of the siloxane units in the final network.²⁸ Based on the interatomic distances a cage-like model was proposed for the structure of the final copolymer.²⁷

Small angle X-ray scattering (SAXS), being a premier, non-destructive technique that probes mesoscopic structure inhomogeneities, provides statistically significant characterization of the network structure within hybrid gels and glasses. SAXS is based on the elastic scattering of X-rays at scattering angles very close to the direction of the incident beam. Depending on the detailed instrumental setup, SAXS can access structural information in the reciprocal space from sub-nanometer to tens of nanometers (conventional pinhole setup) and even tens of micrometers (Bonse–Hart type setup).

As a general technique, SAXS has been used to investigate the microstructures of polymeric gels and glasses.^{29,30} In particular, SAXS was deployed to study the static structure and formation kinetics of a broad range of silicon-based materials, ranging from nanocomposites, nanoparticles, and mesoporous silica films.^{31–42} Notably, SAXS was combined with ²⁹Si to reveal the condensation kinetics of hydrolyzed alkoxides where progressive assembly of small organized units were found to be followed by growth of fractal clusters in tetravalent TEOS.³¹ This study illustrated the potency of combined NMR and SAXS characterizations, where detailed local conformations can be derived from NMR and SAXS reveal global morphological characteristics.

This work will focus on the structure characterization of the hybrid organic–inorganic glasses which contain direct bond between silicon and methyl groups, obtained after consolidation of melting gels. The consolidation of the melting gels represent a new pathway to obtain hybrid organic–inorganic glasses. We seek to provide a comprehensive and across-length-scale view of the structures by making use of Raman

spectroscopy, ^{13}C and ^{29}Si NMR spectroscopy along with synchrotron-based SAXS and scanning electron microscopy (SEM).

2. Experimental

2.1. Melting gel/hybrid glasses preparation

The preparation of the melting gels, reported previously,⁵ is briefly discussed below. We used two types of alkoxides, mono-substituted methyltriethoxysilane (MTES) (Sigma-Aldrich, Milwaukee, WI[‡]) and di-substituted one dimethyldiethoxysilane (DMDES) (Sigma-Aldrich, Milwaukee, WI), without further purification. Hydrochloric acid (Fisher Scientific, Atlanta, GA) and ammonia (Sigma-Aldrich, Milwaukee, WI) were used as catalysts while anhydrous ethanol (Sigma-Aldrich, Milwaukee, WI) was used as solvent. Two melting gels presented in Table 1, with compositions of 75% MTES-25% DMDES and 65% MTES-35% DMDES (in mol%) have been investigated in this study. The synthesis was performed in three different steps with predetermined amount of reactants. The molar ratios of MTES:EtOH:H₂O:HCl were 1:4:3:0.01. First, water was mixed with hydrochloric acid and half of the ethanol. Separately, MTES was mixed with the other half of ethanol. Then, the mixture between ethanol and MTES was added dropwise to the water solution under continuous stirring. The container was sealed with Parafilm® while the mixture was continuously stirred at room temperature for three hours. In the second step, the di-substituted alkoxide DMDES was diluted with ethanol in a molar ratio of DMDES:EtOH = 1:4. The DMDES-EtOH mixture was added dropwise to the first mixture. This resulting solution was kept under continuous stirring in the sealed container at room temperature for two additional hours. In the third step, ammonia was added to the mixture, which was stirred for one more hour in the sealed container. The molar ratio of (MTES + DMDES):NH₃=1:0.01. The final solution was continuously stirred for 48 hours at room temperature in an open container until gelation occurred. Ammonium chloride was formed as a byproduct during gelation. To remove this, 10 ml of dry acetone (Spectranal, Sigma-Aldrich) was added to the samples. The ammonium chloride was removed by vacuum filtration. Then the clear solution was stirred until all the acetone evaporated. The obtained gel was treated at 70 °C for 24 hours to remove any remaining acetone and ethanol, followed by another heat treatment at 110 °C for 24 hours to remove of unreacted water. The hybrid glasses were obtained by consolidation of the melting gels on 15 mm × 15 mm mica substrates (Grade V-4 muscovite, SPI Co., West Chester, PA). The consolidation temperatures^{5,10} for each composition are a function of

the molar % between MTES and DMDES and are listed in Table 1. At these temperatures the melting gels are transformed into hybrid glasses within a 17 hour consolidation heat treatment.

For the NMR and BET surface area measurements the hybrid glasses were removed from the mica substrates by thermally shocking the samples. The samples were immersed in the liquid nitrogen (77 K) and then very quickly exposed to the room temperature. Repeating this process a few times allowed hybrid glasses to be detached from the substrates. Subsequently, the removed hybrid glasses underwent cryogenic grinding in liquid nitrogen until fine powders were achieved.

For the SAXS and Raman measurements, the hybrid glasses samples as deposited on the mica supports were used. The thickness and density of the coatings are listed in Table 1.

2.2. Sample characterization

The consolidated hybrid glasses were characterized using Raman, ^{13}C and ^{29}Si NMR spectroscopy, SAXS and SEM.

Raman spectra were recorded using Renishaw® in Via Raman Microscope (Renishaw, Gloucestershire, UK) equipped with 765 nm laser between 4000–200 cm^{−1}. The spectra were acquired under a Leica optical microscope at 20× magnification.

NMR ^{13}C and ^{29}Si quantifications and T_1 measurements were conducted at 7.0 T on a Bruker spectrometer equipped with a 4 mm double resonance probehead. The MAS frequency was set at 12 kHz. T_1 longitudinal relaxation time measurements were conducted with a saturation-recovery approach, using 10 saturation pulses for both ^{13}C and ^{29}Si experiments with a saturation train of 10 pulses spaced by delays decreasing step by step from 50 to 5 ms. Quantitative measurements were collected with an echo-MAS sequence and a short echo duration of two rotor periods. Full magnetization recovery was ensured by recycling delays at least quintupling the longest T_1 measured under the same conditions. The number of scans was adjusted for each recovery delay to optimize the experimental time while maintaining good signal-to-noise. The peak intensities were extracted from sets of peak-profile parameters (positions, widths and Gaussian to Lorentzian ratios), allowing only the amplitudes to vary. These sets of parameters were obtained, for each sample and experimental condition, from a simultaneous fit of multiple spectra, including the echo-MAS spectra with the highest signal to noise and CP-MAS spectra collected with different contact times, which ensures the robustness of the spectral decomposition into individual components. Uncertainty evaluation was performed with a Monte-Carlo approach using an in-house MATLAB program. Random noise within the experimental standard deviation was introduced to the experimental data to produce a large number of datasets, which were subsequently fitted. Statistical analysis was conducted on the fitting parameters to yield the uncertainty of the measured T_1 value.

Two-dimensional $^{29}\text{Si}[^{29}\text{Si}]$ dipolar double quantum (DQ) experiments were conducted on sample 2 using a 9.4 T Bruker spectrometer with a 7 mm double-resonance probe, using symmetry-based⁴³ SR26₁₁ recoupling,⁴⁴ at the MAS frequency of

[‡] Certain commercial equipment, instruments, software or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the Department of Commerce or the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1 The starting compositions of the melting gels, their temperatures of consolidation and the thicknesses and densities of the hybrid glasses obtained by consolidation of the melting gels

Sample	Composition (mol%)		Temperature of consolidation (°C)	Thickness of coatings (mm)	Density (g cm ⁻³)	BET surface area (m ² g ⁻¹)
	MTES	DMDDES				
1	75	25	135	1.284	0.86	0.0255
2	65	35	150	1.252	1.06	0.0141

5.5 kHz and a ²⁹Si nutation frequency of 35.7 kHz (optimized for maximum recoupling efficiency). Heteronuclear ¹H decoupling was achieved using CW decoupling at a ¹H nutation frequency of 60 kHz during the recoupling, and SPINAL64 at 60 kHz during acquisition in both dimensions. The DQ creation and reconversion blocks used 5 recoupling supercycles each, corresponding to 7.1 ms blocks. A two-rotor-period echo was added at the end of the pulse sequence to ensure a flat baseline. The indirect dimension was collected with 48 *t*₁ increments using the States procedure,⁴⁵ with 7424 scans and a recycle delay of 1.5 s (total duration: 6 days). The spectral width in the indirect dimension was 5500 Hz (to ensure synchronization with the rotor rotation). This is too small to observe the full range of the DQ dimension, where cross-peak frequencies correspond to the sum of the individual sites that are coupled (such that the width is typically twice the width of the standard spectrum) and lead to a folding of the peaks. An unfolded spectrum can nevertheless be obtained by a “shearing” transformation that yields a SQ–SQ spectrum, instead of the double-quantum – single-quantum (DQ–SQ) 2D spectrum that is obtained after standard Fourier transformation. This is done by first performing Fourier transform on the direct dimension of the 2D time-domain signal, and then applying a first-order phase correction of the indirect-time domain signal with a coefficient that varies linearly with the frequency in the direct dimension, and finally applying the Fourier transform in the indirect dimension to obtain the sheared SQ–SQ spectrum.^{46,47} All chemical shifts are given relative to (neat) tetramethylsilane (TMS).

The densities of the samples were measured on the ground hybrid glasses using a pycnometer with helium AccuPyc II 1340 (Micromeritics, Norcross, GA).

The BET surface area of the samples was determined by absorption/desorption of nitrogen at 77 K using a Tristar II 3020 BET surface analyzer. Samples were previously outgassed at 110 °C in a nitrogen flow overnight. Surface areas were determined using the Brunauer–Emmet–Teller (BET) method.

SAXS scattering experiments were conducted at the ultra-small angle X-ray scattering (USAXS) instrument at the Advanced Photon Source, Argonne National Laboratory.⁴⁸ This instrument makes use of Bonse–Hart type of crystal optics to access a scattering *q* range that is normally unavailable to a conventional pinhole based small angle scattering camera. Here *q* is the magnitude of the scattering vector, and is defined as $q = 4\pi/\lambda \sin(\theta)$, where λ is the X-ray wavelength and θ is one half of the scattering angle. The USAXS instrument has a *q* resolution of $\approx 1 \times 10^{-4} \text{ \AA}^{-1}$. Coupled with an add-on

Pilatus 100 K detector, the USAXS instrument can access a *q* range from $1 \times 10^{-4} \text{ \AA}^{-1}$ to $1 \text{ \AA}^{-1}$.⁴⁹ Particularly, it is worth noting that the USAXS instrument is primary-calibrated, *i.e.*, the measured intensity is directly related to the differential scattering cross section, a physical property of the material being studied.⁵⁰

1D-collimated USAXS experiments were conducted in fly-scan mode using monochromatic 17.5 keV X-rays ($\lambda = 0.708481 \text{ \AA}$). The beam size was 0.8 mm × 0.8 mm. The X-ray flux density was $\approx 10^{13}$ photon per s per mm². The high X-ray flux ensures that weak scattering signals, commonly expected from a melting gel system, be captured. Total scan time was 120 s. The sample was placed on a standard sample holder. SAXS experiments were conducted twice on some of the samples as a check of damage to the samples caused by the X-ray beam. It was found that in these hybrid glasses, the exposed X-ray dosage does not alter the materials microstructures.

To visually examine the materials microstructures, the surface and the cross-sections of the fractures of the hybrid glasses were evaluated using a HITACHI S-2700 SEM. The SEM was operated at 25 keV acceleration voltage. The SEM was equipped with an AMT digital camera system.

3. Results and discussion

In this study we focused on the two compositions listed in Table 1 for two reasons. First, the melting gel with 75% MTES–25%DMES composition is the gel with the highest content of MTES which retains the melting properties.⁵ On the other hand, the melting gel with 65%MTES–35%DMES composition is the borderline gel between solid and liquid state¹¹ at room temperature. Second, the hybrid organic inorganic glasses obtained using those compositions proved to be the best anticorrosive coatings.¹²

The Raman spectra of the investigated hybrid glass samples are presented in Fig. 1a while the assignments of the peaks are listed in Table 2.

3.1. Raman characterization

Although more than 60% of the studied hybrid glasses contain SiO₂,¹⁰ the characteristic peaks for the presence of the Si–O–Si bonds, identified at 790 cm⁻¹ (assigned to ν_{sym} Si–O–Si) and at 1090 cm⁻¹ (assigned to ν_{asym} Si–O–Si), have very low intensity.^{51,52} On the other hand, the characteristic peaks for the Si–O–Si ring breathing mode, identified at 461 cm⁻¹ (attributed to the 8-member ring structure) and at 202 cm⁻¹ (characteristic

Fig. 1 The Raman spectra of the hybrid glasses. (a) Complete Raman spectra; (b) partial spectra between 600 cm^{-1} and 900 cm^{-1} which illustrate an increasing of Si-C bonds in the hybrid glass with a higher amount of DMEDES (sample 2).

Table 2 The Raman peak assignments of the hybrid glasses obtained by consolidation of the melting gels

Raman Shift/ cm^{-1}	Assignments
2971 (w)	$\nu_{\text{asym}} \text{CH}_3$
2901 (s)	$\nu_{\text{sym}} \text{CH}_3$
2808 (vw)	Overtone
1413 (vs)	$\delta_{\text{asym}} \text{CH}_3(\text{Si}-\text{CH}_3)$
1223 (sh)	$\delta_{\text{sym}} \text{CH}_3(\text{Si}-\text{CH}_3)$
1097 (sh)	$\nu_{\text{asym}} \text{Si}-\text{O}-\text{Si}$
860 (m)	$\delta_{\text{asym}} \text{Si}-\text{O}-\text{C}(\text{alkoxy})$
797 (w)	$\nu_{\text{sym}} \text{Si}-\text{O}-\text{Si}$
743 (w sh)	ρCH_3
704 (m)	$\nu \text{Si}-\text{C}(\text{Si}-\text{CH}_3)$
589 (w)	Si-O-Si ring breathing vibration for 6 member
461 (s)	Si-O-Si ring breathing vibration for 8 member ring
202 (s)	$\sigma \text{Si}-\text{O}-\text{Si}$

The peak intensities are given in parentheses as (s) for strong, (m) for medium, (w) for weak, (vw) for very weak and (sh) shoulder.

$\sigma \text{Si}-\text{O}-\text{Si}$), are high in intensity.^{53–55} These results demonstrate that the main structure of the matrix is formed by an 8-member ring structure. Additionally, we identified a very weak peak at 589 cm^{-1} that is characteristic of a 6-member ring structure,⁵³ which suggests that small amount of this structure is also present. Raman spectroscopy also reveals the presence of Si-C bonds. These was identified at 705 cm^{-1} and was assigned to the $\nu \text{Si}-\text{C}$ at ref. 52 and 55.

Besides the peaks mentioned above, the most intense peaks belong to the methyl groups bonded to the silica backbone. These were identified at 2971 cm^{-1} and 2901 cm^{-1} , which were assigned to $\nu_{\text{asym}} \text{CH}_3$ and $\nu_{\text{sym}} \text{CH}_3$, respectively. In addition, Raman bands placed at 1413 cm^{-1} , 1223 cm^{-1} and 743 cm^{-1} were assigned to $\delta_{\text{asym}} \text{CH}_3$, $\delta_{\text{sym}} \text{CH}_3$ and ρCH_3 , respectively.⁵⁵ The high intensity of the peaks assigned to the organic groups can be credited to the presence of the methyl groups to the surface of the hybrid glasses investigated.^{4,5,12} Moreover, in the Raman spectra of the both samples, we also identified a very weak peak at 864 cm^{-1} which was assigned to the $\delta \text{Si}-\text{O}-\text{C}$. The existence of this band demonstrates that few ethoxy groups from the original alkoxides remain unreacted and are entrapped in the hybrid glasses.

Fig. 1b details the normalized Raman spectra of the two hybrid glasses investigated in this study. It can be observed that the Raman intensity of the band assigned to the $\nu \text{Si}-\text{C}$ is increasing for sample 2, which has a higher amount of DMEDES (35 mol%) than sample 1 (25 mol%). Here, the higher amount of the DMEDES leads to a higher number of Si-C bonds, which is reflected by the higher intensity of the $\nu \text{Si}-\text{C}$ peak in the sample 2.

3.2. NMR peak assignments

^{29}Si NMR measurements are used to distinguish between the different Si environments formed in the hybrid glasses on the basis of the number of attached carbons and the degree of condensation. The notation T^n and D^n are used to designate $\text{CSi}(\text{OSi})_n(\text{OR})_{3-n}$ and $\text{C}_2\text{Si}(\text{OSi})_n(\text{OR})_{2-n}$ units originating from MTMES and DMEDES monomers, respectively, with $\text{R} = \text{H}$ corresponding to silanol groups or $\text{R} = -\text{CH}_2-\text{CH}_3$ corresponding to unreacted $\text{Si}-\text{O}-\text{CH}_2-\text{CH}_3$ functions from the alkoxide. Quantitative ^{29}Si NMR spectra recorded at room temperature for the hybrid glasses samples are shown in Fig. 2a. Assignments of the different signals to D^1 , D^2 , T^2 , and T^3 signals can be made based on literature data.^{56–59} The variations of relative intensities between T^n and D^n sites in the materials of the sample 1 and 2 reflect the different compositions of their synthesis mixtures, with larger proportions of DMEDES in the sample 2 leading to higher relative intensities of the D^n sites.

At room temperature, different conformations of the polymer chains are dynamically averaged on the NMR time-scale (fast exchange regime) since they are frozen. The line-widths in the slow motional regime are typically of the order of 5 ppm (full width at half maximum, FWHM) corresponding to 300 Hz for ^{29}Si at 7.0 T. The characteristic time corresponding to the intermediate exchange regime for a pair of peaks with a

Fig. 2 (a) Quantitative ^{29}Si NMR spectra collected of the hybrid glasses. (b) Quantifications with estimated uncertainties based on ^{29}Si NMR peak areas. Samples 1 and 2 are depicted in blue and red color, respectively.

frequency difference $\Delta\nu$ between 2 sites is given by $1/(\pi\Delta\nu)$.⁶⁰ Thus, in order for chemical shift dispersions on the order of 5 ppm to be dynamically averaged out, it typically requires the chain reorientation dynamics to be significantly faster than 10^{-3} s. The fast motional regime is clearly reached at room temperature. Some chemical shift dispersion nevertheless remains for each type of T^n or D^n environment, which points to chemically distinct local environments. This is particularly clear for D^2 sites, which show two clearly-resolved peaks, but also for the T^2 and T^3 peaks which show more or less pronounced shoulders (more clearly visible on $^{29}\text{Si}[^1\text{H}]$ cross polarization MAS spectra that have better signal to noise, data not shown). The deconvolution of spectra in individual components are shown in ESI (Fig. S1†). These different components may be due to differences in the nature of the neighboring Si sites (D^1 , D^2 , T^2 or T^3) or, for T^2 species, to the nature of the R group of uncondensed O atoms (O–H or unreacted O–CH₂–CH₃ moieties). Attempts to assign these different contributions are discussed further below.

The ^{29}Si NMR spectra of the hybrid glasses, samples 1 and 2, shown in Fig. 2a, are very similar and their assignments are presented in Table 3. This is more clearly reflected in a quantitative analysis of the ^{29}Si NMR data shown in Fig. 2b, which

are based on the spectral decompositions shown in ESI (Fig. S1†).

Another important observation from these quantitative analyses is the discrepancy between the overall populations of D^n and T^n sites and the relative amounts of DMEDES and MTES used for the synthesis. The stars in Fig. 2b indicate the populations expected based on the composition of the synthesis mixtures. They reveal that a significant proportion of the D sites have been lost in the course of the synthesis procedure or during the thermal treatments necessary to remove the solvent (70 °C/24 h), to remove the water (110 °C/24 h) or to consolidate the hybrid glasses (temperature of consolidation is listed in Table 1). This effect is significantly more pronounced in the case of the sample 2, which has the highest DMEDES content (35%) in the synthesis mixture. As shown in Table 4, this different behavior appears to be due to a very subtle difference of D^n and T^n relative proportions, with T^n/D^n ratios varying between 4.6 and 3.8 in hybrid glass samples 1 and 2, respectively, compared to MTES/DMEDES ratios of 3.0 and 1.9 in the synthesis mixtures.

These unexpected results are corroborated by quantitative ^{13}C NMR data, which also shed some light on the nature of uncondensed O atoms. Fig. 3a shows quantitative ^{13}C NMR spectra recorded at room temperature for hybrid glasses 1 (in blue) and 2 (in red). The signatures of $(\text{CH}_3)_2\text{-SiO}_2$ species originating from DMEDES monomers (at –3 ppm) and $\text{CH}_3\text{-SiO}_3$ species originating from MTES monomers (at –1 ppm) are well resolved in all ^{13}C spectra. Changes in relative amplitudes reflect again to some extent the relative ratios of monomers in the synthesis mixtures and confirm the assignments. Two other peaks are detected in the ^{13}C NMR spectra, at 18 and 58 ppm, which may be assigned to $\text{CH}_3\text{-CH}_2\text{-O}$ and $\text{-CH}_2\text{-O-}$ environments (respectively) corresponding to partially unreacted ethoxy groups, $\text{Si-O-CH}_2\text{-CH}_3$ functions carried by D^1 or T^2 Si atoms. Those data are in good agreement with the Raman results which also show the presence of some unreacted ethoxy groups.

Quantitative analyses of ^{13}C NMR data, shown in Fig. 3b and Table 4, confirm the loss of a significant proportion of the DMEDES monomers (or of their products) in the course of the materials synthesis. These data provide very reliable results since solid nature of the hybrid glasses allowed the use of faster MAS spinning rates (typically 12 kHz as compared to 5.5 kHz for gel samples). The ratios between the area of the peak assigned to $\text{CH}_3\text{-SiO}_3$ species (at –3 ppm) and half the area of the peak assigned to $(\text{CH}_3)_2\text{-SiO}_2$ species (at –1 ppm) are 4.8 and 3.7 for gel samples 1 and 2, respectively. These results are

Table 3 The assignments of the ^{29}Si MAS NMR Spectra

Sample	Chemical shift/ppm							
	D^0	D^1	D^2	T_a^2	T_b^2	T_c^2	T_a^3	T_b^3
1	–17.2	–19.0	–21.1	–54.5	–56.8	–59.1	–64.5	–66.4
2	–16.4	–19.0	–21.3	–54.0	–57.0	–59.3	–64.5	–66.3

Table 4 Summary of the quantitative ^{13}C and ^{29}Si NMR analyses

Sample	Synthesis mixture composition			NMR quantifications		
	MTES (%)	DMDDES (%)	MTES/DMDDES	$\sum I(\text{T}^n)/\sum I(\text{D}^n)$	$I(\text{CH}_3\text{-SiO}_3)/\frac{1}{2}I[(\text{CH}_3)_2\text{-SiO}_2]$	$n(\text{O-CH}_2\text{-CH}_3)/(n(\text{D}^1) + n(\text{T}^2))^a$
1	75	25	3.0	4.6	4.8	0.24
2	65	35	1.9	3.8	3.7	0.27

^a Proportion of incompletely condensed Si (D^1 or T^2 sites) forming $\text{Si-O-CH}_2\text{-CH}_3$ rather than Si-OH moieties, calculated from the combination of ^{13}C and ^{29}Si quantitative NMR data (see details in ESI).

Fig. 3 (a) Quantitative ^{13}C NMR spectra for the hybrid glasses after the consolidation treatment (b) quantifications based on ^{13}C NMR peak areas with hybrid glasses prepared using 75%MTES-25%DMDDES and 65%MTES-35%DMDDES depicted in blue and red, respectively. Uncertainties are estimations.

in quantitative agreement with the ratios between the cumulated areas of T^n and D^n ^{29}Si NMR peaks (4.6 and 3.8, respectively), and considerably higher than the MTES/DMDDES ratios of the synthesis mixture (3.0 and 1.9, respectively). As already observed from ^{29}Si NMR data, the loss of DMDDES moieties is more severe in the sample 2 containing the higher amount of these monomers in the synthesis mixture, which tends to even out the contrast of compositions between the two samples.

Quantifications of the areas of the two resonances assigned to the $-\text{O-CH}_2\text{-CH}_3$ groups reveal the nature of the incompletely condensed D^1 and T^2 Si environments detected in ^{29}Si NMR data. Combining both quantitative ^{29}Si and ^{13}C NMR data (see details in ESI†), we find that 24% of non-polymerized Si-O sites are in the form of $\text{Si-O-CH}_2\text{-CH}_3$ groups in the sample of hybrid glass 1 (we note that we cannot tell whether these are supported by D^1 and T^2 sites.) This fraction is as high as 27% for the sample of hybrid glass 2, which has the higher DMDDES content in the synthesis mixture. And yet the amount of D^1 in the sample is too small to explain such a difference by a concentration of unreacted $\text{Si-O-CH}_2\text{-CH}_3$ on

D^1 sites. It seems instead that the more hydrophobic character of the sample of hybrid glass 2 stabilizes these $\text{Si-O-CH}_2\text{-CH}_3$ moieties (both on D^1 and T^2 sites), which may well contribute to their inherent flexibility and hydrophobicity. The amount of uncondensed Si sites (whether in the form of Si-OH or Si-OEt) D^1 and T^2 was used to calculate the probability for a Si-O bond to remain uncondensed. We find that, in both hybrid glasses, this probability is between 11 and 12% for Si-O bonds in T sites as compared to 3 to 5% for D sites. This means that DMDDES precursors tend to condense more easily than MTES.

3.3. The network analysis of the hybrid glasses

One-dimensional ^{29}Si NMR spectra resolve a certain number of local Si environments, or “molecular motifs”⁶¹ characterized by the number of Si-C bonds and the number of Si neighbors connected *via* bridging O atoms as showed in Fig. 2. More extended motifs can however be identified by recording two-dimensional correlation spectra that probe the connectivities between Si atoms, in the hope to better understand in particular the fine structures of the ^{29}Si spectra. Examples of these fine structures are highlighted on the top Fig. 4 by the spectral decomposition of a $^{29}\text{Si}[^1\text{H}]$ CP-MAS NMR spectrum collected for the sample hybrid glass 2, with individual components shown as grey lines. Between 2 to 3 different types of D^2 , T^2 , and T^3 environments are thus distinguished, which are designated thereafter as D_a^2 , D_b^2 , D_c^2 , T_a^2 , T_b^2 , T_c^2 , T_a^3 , and T_b^3 .

The two-dimensional spectra shown in Fig. 4 were collected to try to better understand the origins of these different features. They were obtained with a sequence of radio-frequency pulses designed to reintroduce the homonuclear dipole-dipole couplings between nearby ^{29}Si nuclei to probe their spatial proximities.⁴⁴ This experiment was conducted in conditions specifically optimized to yield intense cross peaks for the short Si-Si distances of *ca.* 3 Å between connected $^{29}\text{Si-O-}^{29}\text{Si}$ pairs and weak or negligible cross peaks for the longer distances associated with non-connected pairs.⁶² The result of such an experiment (after the “shearing” transformation, see details in Experimental section) is a 2D map in which pairs of correlation peaks appear on both parts of the spectrum diagonal at horizontal and vertical ^{29}Si frequencies corresponding to the nuclei that are connected. Because of severe signal to noise limitations in the original 2D spectrum (shown in blue), a symmetrization procedure was applied to gain signal to noise (in principle by the square root of 2) by adding up the regions on

Fig. 4 Dipolar-mediated ^{29}Si – ^{29}Si correlation NMR spectra for the sample hybrid glass 2 65%MTES–35%DMEDES, revealing close proximities between Si atoms characteristic of Si–O–Si framework connectivity. The blue contours correspond to the original spectrum (sheared from SQ–DQ to DQ–DQ representation, see experimental section for details) whereas the red contours correspond to a spectrum obtained by symmetrization with respect to the diagonal (shown as a black dashed line) of the former, to increase signal to noise. Only the upper-left half of this symmetric spectrum is shown to better see the original spectrum underneath. 1D spectra shown in black on top and right side of the 2D spectrum are ^{29}Si [^1H] CP–MAS spectra recorded with identical contact time as the 2D experiment. The 1D model obtained by decomposition of this ^{29}Si [^1H] CP–MAS spectrum in individual contributions (shown as grey lines) is shown in red.

both sides of diagonal. The resulting 2D spectrum is shown in red in Fig. 4, overlaid with the original spectrum. Because of the symmetry of this spectrum with respect to the diagonal, only its upper-left half is shown to better illustrate the original (blue) spectrum underneath (the symmetric representation can sometimes be misleading by making high noise level points look like correlation peaks).

The main features of the correlation spectrum reveal extended molecular motifs centered on Si–O–Si pairs that are depicted schematically in Fig. 4 (using the same color code as in Fig. 2), and which point to different levels of network ramification, with 4-fold-branched T^3 – T^3 pairs, 3-fold-branched T^2 – T^3 and D^2 – T^3 pairs, linear D^2 – T^2 , D^2 – T^2 and D^2 – D^2 pairs. The 2D spectrum shows a higher intensity of D^2 – D^2 correlations as compared to D^2 – T^2 correlations, which barely point out of the noise level after symmetrization (and only at the D_c^2 – T^2 position). The quantitative 1D spectra of all samples show D_a^2 intensities comparable to the D^1 intensities, suggesting that the D_a^2 position (–17 ppm) could be a signature of a D^2 – D^1 end chain.

Semi-quantitative estimations of the conditional probability for each site to be correlated with another may be calculated assuming that (i) Si–Si distances between connected Si–O–Si sites are all identical (resulting in equal efficiencies of the double-quantum excitation during the NMR sequence) and (ii) that signal losses during the sequence are the same for all sites. The results indicate that site T_b^3 environments are primarily connected to T^3 environments (primarily to other T_b^3), with only *ca.* 12% probability to be connected to T^2 sites and *ca.* 11% probability to be connected to D^2 sites. They are hence indicative of strongly reticulated regions. In contrast, T_a^3 environments have higher probabilities to be connected to T^2 sites (17%) and 10% to be connected to D^2 sites. They are nevertheless connected primarily to other T_a^3 sites and to T_b^3 environments (49% and 23%, respectively), indicating that they may well correspond to edges of these strongly interconnected domains.

The quantitative analyzes of 1D ^{29}Si NMR spectra of samples may be re-examined in the light of this difference of reticulation degrees around T_a^3 and T_b^3 Si environments. In both samples the more reticulated T_b^3 sites appear to account for *ca.* 46% of the total amount of T^3 sites, in hybrid glass sample 1, 75%MTES–25%DMEDES and 51% in hybrid glass sample 2, 65%MTES–35%DMEDES.

Other 2D peak intensities are less intense and thereby less reliable, making it difficult to understand the differences between different types of D^2 sites and different types of T^2 sites.

We observe however that D^2 sites in general tend to have a stronger probability to be connected to other D^2 sites rather than to T^2 sites, whereas T^2 sites are connected to other T^2 sites rather than to D^2 sites. Both have comparable (and rather high) probabilities to be connected to T^3 sites.

While NMR provides deep insights regarding the structure at the molecular level, the microstructural morphologies of the sol-gel materials are also known to affect materials properties.⁶³ SAXS, due to its nature of being a nondestructive and statistically significant technique, is applied to probe the possible segregation, separation, and presence of micro/nanopores within the consolidated hybrid glasses. In particular, we made use of the high-brilliance synchrotron X-ray beam to ensure that weak scattering intensities can be captured.

The SAXS profiles of both hybrid glass samples are shown in Fig. 5. It is clear that these profiles bear much resemblance. First, the reduced (slit-smeared) differential scattering cross section $d\sum(q)/Vd\Omega$ is very low in intensity and noisy, which indicates that the scattering contrast that gives rise to the scattering signal is weak. This high degree of noise originates from data reduction, whereas the sample scattering, although weak, is unmistakably evident from the raw scattering data (not shown). Second, a broad scattering feature at q s below $0.01 \text{ \AA}^{-1}$ exists, which indicates certain degree of microphase separation. This scattering feature also does not appear to have a strong dependence on the molar ratio between MTES and DMEDES.

NMR results of these hybrid glass materials strongly indicate that they possess a network structure. To fully account for

Fig. 5 Synchrotron SAXS data and fit using Debye-Bueche model of sample 1 (75%MTES + 25%DMDDES) and sample 2 (65%MTES + 35%DMDDES).

the scattering profiles, we made use of the Debye-Bueche model,⁶⁴ which describes scattering from a randomly distributed two-phase system, a situation very similar to the hybrid glasses. This model assumes that the pair-correlation function $\gamma(r)$ follows a simple exponential decay,

$$\gamma(r) = \exp\left(-\frac{r}{\xi}\right) \quad (1)$$

where r is the interatomic distance, and ξ , the correlation length, is a measure of the average separation distance between the separated phases.

The scattering cross section, following eqn (1), is

$$\frac{d\Sigma(q)}{d\Omega} = \frac{8\pi(\Delta\rho)^2\phi_1\phi_2\xi^3}{[1 + (q\xi)^2]^2} \quad (2)$$

Here, $\Delta\rho$ is the scattering contrast; ϕ_1 and ϕ_2 are the volume fraction of the two phases, respectively.

Fig. 5 shows that despite the high degree of noise, the Debye-Bueche model describes the scattering intensity profiles very well. The correlation lengths were found to be 10.3 ± 0.8 nm for sample 1 and 7.5 ± 0.1 nm for sample 2, respectively. This result indicates that higher MTES-to- DMDDES ratio leads to a larger phase-separation distance. We also note that our observed scattering profiles are similar to those acquired by Hagiwara *et al.*⁶⁵ in a similar hybrid organoalkoxide material prepared using sol-gel synthesis. Instead of characterizing possible phase separation, these authors opted to view the gels as fractal structures, perhaps due to the limited q range of their SAXS camera. In our case, the broad q range of the USAXS instrument leaves little doubt about the bend of scattering curve near $0.01 \text{ \AA}^{-1}$, which prompted our analysis of a phase-separated network structure that is consistent with NMR findings. Such type of separation was also visually confirmed by atomic force microscopy in a study of nanohybrids containing 1,8-bis(triethoxysilyl)octane.⁶⁶

Table 5 Scattering length density and contrast

	Mass density ^a (g cm ⁻³)	Scattering length density (10 ¹⁰ cm ⁻²)	Scattering contrast (10 ²⁰ cm ⁻⁴)
MTES	1.332	11.66	2.31
DMDDES	1.122	10.14	

^a Mass densities of MTES and DMDDES are estimated from a series of mass densities of hybrid glasses containing different molar ratios of MTES and DMDDES.

We also evaluated the degree of phase separation following eqn (2). For this purpose, we calculated the scattering length densities of both MTES and DMDDES, which are tabulated in Table 5. Assuming complete phase separation, the theoretical X-ray scattering contrast between MTES and DMDDES is $2.31 \times 10^{20} \text{ cm}^{-4}$. Empirically, the ratio between the experimental and theoretical scattering contrasts could serve to gauge the phase separation. Here, following the fitting results from Fig. 5, we found that the experimental scattering contrasts for samples 1 and 2 are $8.35 \times 10^{16} \text{ cm}^{-4}$ and $1.97 \times 10^{17} \text{ cm}^{-4}$, respectively. In other words, the experimental contrasts are on the order of 10^{-3} of the theoretical contrast. This result shows that MTES and DMDDES are fairly homogeneously mixed and do not phase separate to form well defined phase structures. In other words, from an electron density point of view, the hybrid glass materials possess a high degree of uniformity across nm to micrometer length scales.

Last but not least, we note that the low scattering intensities also confirm that micro- and nano-pores are completely absent in these hybrid glasses, as the pores have the highest possible X-ray scattering contrast and their presence would have been eminently captured by the scattering methods. From a mechanical property point of view, the lack of pore-related defects is beneficial in improving fracture toughness and reducing fatigue cracks.

3.4. The BET surface area analysis

The N₂ physisorption data are summarized in the Table 1. Both samples demonstrate very low BET surface areas with values on the order of $0.01 \text{ m}^2 \text{ g}^{-1}$, which is in good agreement with SAXS findings, which show a level of porosity below detection limit. Furthermore, these results suggest that samples with higher amount of disubstituted alkoxide have a lower BET surface areas.

3.5. The SEM analysis

The SEM images of the surface fractures and the cross sections of the fractures of both studied hybrid glass samples are presented in Fig. 6. The images of the surface Fig. 6a and b show a smooth surface without defects or glass domains. Because the surfaces are defect-free, and hence featureless, we opted to show SEM results near the fracture, where the defects that emerged during the fracture process are also highlighted. The images of the cross sections of the fracture (Fig. 6c-f) show homogenous structures without formation of any domains or

Fig. 6 The SEM images of the surfaces of (a) 75%MTES-25%DMDES; and (b) 65%MTES-35%DMES hybrid glass samples (c) and (e) show the cross-sections of fracture for the 75%MTES-25%DMDES sample; (d) and (f) show the cross-sections of fracture for the 65%MTES-35%DMES sample.

without any visible phase separation which is in agreement with the previous data. No micro- or macro-pores were detected in the hybrid glasses. These surface-sensitive SEM data are in very good agreement with the SAXS data, which are connected to the bulk microstructure. The cross section of the

fracture of the hybrid glass with composition 65%MTES-35% DMES presented in Fig. 6d and f display a flaky area which shows also a certain orientation of the material. The presence of the flakes can be correlated with the higher concentration of the organic content in this sample. On the other hand, the

images of the cross section of the hybrid glass with composition 75%MTES-25%DMES presented in Fig. 6c and e show a clear fracture with longitudinal lines. This aspect of the fracture can be correlated with higher content of Si–O–Si bonds in sample 1 as it was revealed by the NMR analysis. The highest content of Si–O–Si bonds is increasing the rigidity of the sample which can determine a clearer fracture.

4. Conclusions

The structure and morphology of hybrid glasses prepared with different ratios of MTES and DMDES have been investigated in this study using Raman, one- and two-dimensional ^{29}Si and one dimensional ^{13}C NMR spectroscopy, SAXS and SEM microscopy.

The Raman spectroscopy showed that the structure of the matrix is formed mainly by 8-member ring structures. In addition, the Raman measurements revealed that organic groups are placed at the surface of the hybrid glasses.

The ^{13}C and ^{29}Si NMR spectroscopy offered information about the molecular structures of the hybrid glasses. The main molecular species were quantitatively identified. Quantitative ^{29}Si NMR of the hybrid glasses samples shown characteristic signals to D^1 , D^2 , T^2 , and T^3 . The quantitative measurements identify the final ratio between the mono substituted species $\text{CH}_3\text{--SiO}_3$ and the di-substituted species $(\text{CH}_3)_2\text{--SiO}_2$ which are present in each studied hybrid glass. This points out a loss of DMDES precursors during the synthesis. Our data reveal the presence of unhydrolyzed Si–OEt groups which was also identified in the Raman spectra. These Si–OEt groups, seem to be stabilized when higher amounts of DMDES are present, and may increase the inter-chain mobility by acting as lubricant owing to their inherent flexibility and hydrophobicity, in contrast with Si–OH groups that form hydrogen bonds. This can explain the higher rigidity of sample 1.

Two-dimensional ^{29}Si NMR data show more extended structural motifs within the framework, which seem to reveal that two distinct types of T^3 Si environments (the dominant type of Si sites in both materials) exist, that correspond to Si atoms located in regions with different extents of framework condensation.

The SAXS data revealed that the mono substituted species $(\text{CH}_3\text{--SiO}_3)$ and the di-substituted species $((\text{CH}_3)_2\text{--SiO}_2)$ that are coming from hydrolysis and polycondensation of the MTES and DMDES are homogeneously mixed and do not separate to form a well-defined phase structure. In addition, the SAXS data confirmed the absence of any nano- or micro-pores.

The absence of the pores was confirmed also by the BET and SEM analyses. The SEM images of the fractures confirmed that the sample 1 (75%MTES-25%DMDES) has higher rigidity than sample 2(75%MTES-25%DMDES) which contains a higher amount of DMDES. Based on the NMR data it was concluded that the samples with higher amount of DMDES retain a higher amount of unhydrolyzed Si–OEt groups which can increase the flexibility of the hybrid glass 2.

We have performed a thorough investigation of the structure of hybrid glasses at both a molecular level and a micro-structure level. We envisage that our findings in this study would serve as a bridge to connect the molecular arrangements of the hybrid glasses to their physical characteristics, and potentially impact the synthesis and design of a broader range of hybrid glass materials by consolidation of melting gels with improved physical, mechanical, chemical and electrochemical performances.

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References

- 1 A. Matsuda, T. Sasaki, K. Hasegawa, M. Tatsumisago and T. Minami, Thermal softening behavior and application to transparent thick films of poly(benzylsilsesquioxane) particles prepared by the sol-gel process, *J. Am. Ceram. Soc.*, 2001, **84**, 775–780.
- 2 C. Sanchez, Chemical design of hybrid organic-inorganic materials synthesized via sol-gel, *New J. Chem.*, 1994, **10**, 1007–1040.
- 3 A. Jitianu, G. Amatucci and L. C. Klein, Phenyl-substituted siloxane hybrid gels that soften below 140 °C, *J. Am. Ceram. Soc.*, 2008, **92**, 36–40.
- 4 A. Jitianu, G. Gonzalez and L. C. Klein, Hybrid Sol-Gel Glasses with Glass Transition Temperatures below Room Temperature, *J. Am. Ceram. Soc.*, 2015, **98**, 3673–3679.
- 5 A. Jitianu, J. Doyle, G. Amatucci and L. C. Klein, Methyl modified siloxane melting gels for hydrophobic films, *J. Sol-Gel. Sci. Technol.*, 2010, **53**, 272–279.
- 6 H. Kakiuchida, M. Takahashi, Y. Tokuda, H. Masai, M. Kuniyoshi and T. Yoko, Viscoelastic and Structural properties of the Phenyl-Modified Polysiloxane System with a three-dimensional Structure, *J. Phys. Chem. B*, 2006, **110**, 7321–7327.
- 7 H. Kakiuchida, M. Takahashi, Y. Tokuda, H. Masai, M. Kuniyoshi and T. Yoko, Effects of Organic Groups on Structure and Viscoelastic properties of Organic-inorganic polysiloxane, *J. Phys. Chem. B*, 2007, **111**, 982–988.
- 8 H. Masai, Y. Tokuda and T. Yoko, Gel-melting method for preparation of organically modified siloxane low-melting glasses, *J. Mater. Res.*, 2005, **20**, 1234–1241.
- 9 L. C. Klein and A. Jitianu, Organic-inorganic hybrid melting gels, *J. Sol-Gel Sci. Tehnol.*, 2011, **59**, 424–431.

- 10 A. Jitianu, K. Lammers, G. A. Arbuckle-Keil and L. C. Klein, Thermal analysis of organically modified siloxane melting gels, *J. Therm. Anal. Calorim.*, 2012, **107**, 1039–1045.
- 11 M. Jitianu, A. Jitianu, M. Stamper, D. Aboagye and L. C. Klein, Melting Gel Films for Low Temperature Seals, in *Solution Synthesis of Inorganic Functional Materials – Films, Nanoparticles, and Nanocomposites*, ed. M. Jain, Q. Jia, T. Puig and H. Kozuka, Materials Research Society, Warrendale, PA, 2013, MRS vol. 1547, pp. 81–86.
- 12 M. Aparicio, A. Jitianu, G. Rodriguez, A. Degnah, K. Al-Marzoki, J. Mosa and L. C. Klein, Corrosion Protection of AISI 304 Stainless Steel with Melting Gels Coating, *Electrochim. Acta*, 2016, **202**, 325–332.
- 13 A. Jitianu, J. Doyle, G. Amatucci and L. C. Klein, Methyl-modified melting gels for hermetic barrier coatings, in *Proceedings MS&T 2008 Enabling Surface Coating Systems: Multifunctional Coatings*, Pittsburgh, PA, 2008, pp. 2171–2182.
- 14 A. Jitianu and L. C. Klein, Encapsulating Battery Components with Melting Gels, in *Ceramic Transactions, Advances in Materials Science for Environmental and Energy Technologies III*, ed. T. Ohji, J. Matyas, N. J. Manjooran, G. Pickrell and A. Jitianu, American Ceramic Soc., Westerville, OH, 2014, vol. 250, pp. 279–286.
- 15 L. Gambino, A. Jitianu and L. C. Klein, Dielectric behavior of organically modified siloxane melting gels, *J. Non-Cryst. Solids*, 2012, **358**, 3501–3504.
- 16 A. Jitianu, A. Britchi, C. Deleanu, V. Badescu and M. Zaharescu, Comparative study of the sol-gel processes starting with different substituted Si-alkoxides, *J. Non Cryst. Solids*, 2003, **319**, 263–279.
- 17 M. E. Smith and D. Holand, Atomic Scale Structure of Gel Materials by Solid State NMR, in *Handbook of Sol-Gel Science and Technology, Processing Characterization and Application*, ed. S. Sakka, Characterization of the Sol-Gel materials and products, 2005, vol II, pp. 35–63.
- 18 D. W. Sindorf and G. E. Maciel, Solid-State NMR Studies of Reactions of Silica Surfaces with polyfunctional Chloromethylsilanes and Ethoxymethylsilanes, *J. Am. Chem. Soc.*, 1983, **105**, 3767–3776.
- 19 C. A. Fyfe, Z. Zhang and P. Aroca, An alternative preparation of organofunctionalized silica gels and their characterization by two-dimensional high-resolution solid state heteronuclear NMR correlation spectroscopy, *J. Am. Chem. Soc.*, 1992, **114**, 3252–3255.
- 20 M. P. J. Peeters, W. J. J. Wakelkamp and A. P. M. Kentgens, A ^{29}Si solid-state magic angle spinning nuclear magnetic resonance study of TEOS-based hybrid materials, *J. Non-Cryst. Solids*, 1995, **189**, 77–89.
- 21 L. Bois, J. Maquet, F. Babonneau, H. Mutin and D. Bahloul, Structural Characterization of sol-gel derived oxycarbide glasses. 1 Study of the pyrolysis process, *Chem. Mater.*, 1994, **6**, 796–802.
- 22 L. Bois, J. Maquet, F. Babonneau and D. Bahloul, Structural Characterization of sol-gel derived oxycarbide glasses. 2 Study of the thermal stability of silicon oxycarbide phase, *Chem. Mater.*, 1995, **7**, 975–981.
- 23 G. Trimmel, R. Badheka, F. Babonneau, J. Latournerie, P. Dempsey, D. Bahoul-Houlier, J. Paramentier and G. D. Soraru, Solid-state NMR and TG/MS study of transformation of methyl groups during the pyrolysis of preceramic precursors to SOC glasses, *J. Sol-Gel Sci. Technol.*, 2003, **26**, 279–283.
- 24 N. Suyal, D. Hoebbel, M. Mennig and H. Schmidt, A solid state ^{29}Si and ^{13}C NMR study on synthesis of thin silicon-oxycarbide glass sheets by a sol-gel route, *J. Mater. Chem.*, 1999, **9**, 3061–3067.
- 25 M. Sitarz, C. Czosnek, P. Jelen, M. Odziomek, Z. Olejniczak, M. Kozanecki and J. F. Janik, SiOC glasses produced from silsequioxanes by aerosol-assisted vapor synthesis method, *Spectrochim. Acta, Part A*, 2013, **112**, 440–445.
- 26 J. Brus and M. Skrdlantova, ^1H MAS NMR study of structure of hybrid siloxane-based networks and the interaction with quartz filler, *J. Non-Cryst. Solids*, 2001, **281**, 61–71.
- 27 J. Brus, Solid state NMR study on Phase separation and order of water molecules and silanol groups in polysiloxane networks, *J. Sol-Gel Sci. Technol.*, 2002, **25**, 17–28.
- 28 J. Brus and J. Dybal, Hydrogen Bond Interactions in Organically-Modified Polysiloxane networks studied by 1D and 2d CRAMPS and double-quantum ^1H MAS NMR, *Macromolecules*, 2002, **35**, 10038–10047.
- 29 B. Chu and B. S. Hsiao, Small-angle X-ray scattering of polymers, *Chem. Rev.*, 2001, **101**(6), 1727–1762.
- 30 F. Zhang and J. Ilavsky, Ultra-small-angle X-ray scattering of polymers, *J. Macromol. Sci., Polym. Rev.*, 2010, **50**(1), 59–90.
- 31 F. Devreux, J. P. Boilot, F. Chaput and A. Lecomte, Sol-gel condensation of rapidly silicon alkoxides: A joint ^{29}Si NMR and small-angle x-ray scattering study, *Phys. Rev. A*, 1990, **41**, 6901–6909.
- 32 Y. Xu, L. Zhang, D. Wu, Y. H. Sun, Z. X. Huang, X. D. Jiang, X. F. Wei, Z. H. Li, B. Z. Dong and Z. H. Wu, Durable sol-gel antireflective films with high laser-induced damage thresholds for inertial confinement fusion, *J. Opt. Soc. Am. B*, 2005, **22**, 905–912.
- 33 Z. H. Li, Y. J. Gong, D. Wu, Y. H. Sun, J. Wang, Y. Liu and B. Z. Dong, SAXS analysis of interface in organo modified mesoporous silica, *Surf. Interface Anal.*, 2001, **31**, 897–900.
- 34 A. F. Craievich, Small Angle X-ray scattering by nanostructured materials, in *Handbook of Sol-Gel Science and Technology, Processing Characterization and Application*, ed. S. Sakka, Characterization of the Sol-Gel materials and products, 2005, vol. II, pp. 161–190.
- 35 K. Dahmouche, C. Santilli, E. Lafontaine, P. Judeinstein and A. F. Craievich, Effect of addition of MTES on the structure of Siloxane-PPG nanocomposites, *J. Sol-Gel Sci. Technol.*, 2000, **19**, 429–433.
- 36 K. Dahmouche, C. V. Santilli, S. H. Pulcinelli and A. F. Craievich, Small-angle X-Ray scattering study of sol-gel derived Siloxane-PEG and Siloxane-PPG hybrid materials, *J. Phys. Chem. B*, 1999, **103**, 4937–4942.

- 37 Z. H. Li, Y. J. Gong, M. Pu, D. Wu, Y. H. Sun, B. Z. Dong, Z. H. Wu and H. Zhao, Determination of SiO₂ colloid core size by SAXS, *J. Mater. Sci. Lett.*, 2003, **22**, 33–35.
- 38 G. Porod, in *Small-Angle X-Ray Scattering*, ed. O. Glatter and O. Kratky, Academic Press, London, 1982, ch. 2.
- 39 Y. J. Gong, Z. H. Li and B. Z. Dong, Evaluation of average wall thickness of Oranically modified mesoporous silica, *Chin. Chem. Lett.*, 2005, **16**, 139–142.
- 40 H. Boukari, J. S. Lin and M. T. Harris, Small-angle X-ray scattering study of the formation of colloidal silica particles from alkoxides: primary particles or not?, *J. Colloid Interface Sci.*, 1997, **194**, 311–318.
- 41 H. Boukari, J. S. Lin and M. T. Harris, Probing the Dynamics of the silica nanostructure formation and Growth by SAXS, *Chem. Mater.*, 1997, **9**, 2376–2384.
- 42 H. Boukari, G. G. Loung and M. T. Harris, Polydispersity during the formation and Growth of Stober Silica particles from Small-Angle X-ray Scattering measurements, *J. Colloid Interface Sci.*, 2000, **229**, 129–139.
- 43 M. Carravetta, M. Eden, X. Zhao, A. Brinkmann and M. H. Levitt, Symmetry principles for the design of radio-frequency pulse sequences in the nuclear magnetic resonance of rotating solids, *Chem. Phys. Lett.*, 2000, **321**, 205–215.
- 44 P. E. Kristiansen, M. Carravetta, W. C. Lai and M. H. Levitt, A robust pulse sequence for the determination of small homonuclear dipolar couplings in magic-angle spinning NMR, *Chem. Phys. Lett.*, 2004, **390**, 1–7.
- 45 D. J. States, R. A. Haberkorn and D. J. Ruben, A two-dimensional nuclear overhauser experiment with pure absorption phase in four quadrants, *J. Magn. Reson.*, 1982, **48**, 286–292.
- 46 R. R. Ernst, G. Bodenhausen and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Oxford Science Publications, New York, 1987.
- 47 F. Fayon, G. Le Saout, L. Emsley and D. Massiot, Through-bond phosphorus–phosphorus connectivities in crystalline and disordered phosphates by solid-state NMR, *Chem. Commun.*, 2002, 1702–1703.
- 48 J. Ilavsky, P. R. Jemian, A. J. Allen, F. Zhang, L. E. Levine and G. G. Long, Ultra-small-angle X-ray scattering at the Advanced Photon Source, *J. Appl. Crystallogr.*, 2009, **42**(3), 469–479.
- 49 J. Ilavsky, F. Zhang, A. Allen, L. Levine, P. Jemian and G. Long, Ultra-small-angle X-ray scattering instrument at the advanced photon source: history, recent development, and current status, *Metall. Mater. Trans. A*, 2013, **44**(1), 68–76.
- 50 F. Zhang, J. Ilavsky, G. G. Long, J. P. Quintana, A. J. Allen and P. R. Jemian, Glassy carbon as an absolute intensity calibration standard for small-angle scattering, *Metall. Mater. Trans. A*, 2010, **41**(5), 1151–1158.
- 51 A. Bertoluzza, C. Fagnano, M. A. Morelli, V. Gottardi and M. Guglielmi, Raman and infrared spectra on silica gel evolving towards glass, *J. Non-Cryst. Solids*, 1982, **48**, 117–128.
- 52 B. Riegel, S. Plittersdorf, W. Kiefer, N. Hüsing and U. Schubert, Raman spectroscopic analysis of the sol-gel processing of RSi(OMe)₃/Si(OMe)₄ mixtures, *J. Mol. Struct.*, 1997, **410–411**, 157–160.
- 53 C. Pakjamsai, N. Kobayashi, M. Koyano, S. Sasaki and Y. Kawakami, Characterization of the benzene-insoluble fraction of the hydrolyzate of phenyltrimethoxysilane in the presence of benzyltrimethylammonium hydroxide, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4587–4597.
- 54 Y. S. Li, Vibrational spectroscopic studies on triethoxy (-(trifluoromethyl)-phenyl) silane and its sol-gel coatings, *Spectrochim. Acta, Part A*, 2012, **96**, 868–873.
- 55 A. D. Chomel, P. Dempsey, J. Latournerie, D. Hourlie-Bahloul and U. A. Jayasooriya, Gel to glass transformation of methyltriethoxysilane: a silicone oxycarbide glass precursor investigated using vibrational spectroscopy, *Chem. Mater.*, 2005, **17**, 4468–4473.
- 56 R. H. Glaser and G. L. Wilkes, Bronnimann, Solid-state ²⁹Si NMR of TEOS-based multifunctional sol-gel materials, *J. Non-Cryst. Solids*, 1989, **113**, 73–87.
- 57 Y. Zhang, D. Wu, Y. Sun and S. Peng, Sol-Gel Synthesis of Methyl Modified Optical Silica Coatings and Gels from DDS and TEOS, *J. Sol-Gel Sci. Technol.*, 2005, **33**, 19–24.
- 58 G. Engelhardt, H. Jancke, E. Lippmaa and A. Samoson, Structure investigations of solid organosilicon polymers by high resolution solid state ²⁹Si NMR, *J. Organomet. Chem.*, 1981, **210**, 295–301.
- 59 Y. Xu, R. Liu, D. Wu, Y. Sun, H. Gao, H. Yuan and F. Deng, Ammonia-catalyzed hydrolysis kinetics of mixture of tetraethoxysilane with methyltriethoxysilane by ²⁹Si NMR, *J. Non-Cryst. Solids*, 2005, **351**, 2403–2413.
- 60 R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*, Longman, Harlow, 1986.
- 61 M. Deschamps, F. Fayon, J. Hiet, G. Ferru, M. Derieppe, N. Pellerin and D. Massiot, Spin-counting NMR experiments for the spectral editing of structural motifs in solids, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1298–1303.
- 62 D. H. Brouwer, P. E. Kristiansen, C. A. Fyfe and M. H. Levitt, Symmetry-Based ²⁹Si Dipolar Recoupling Magic Angle Spinning NMR Spectroscopy: A New Method for Investigating Three-Dimensional Structures of Zeolite Frameworks, *J. Am. Chem. Soc.*, 2005, **127**, 542–543.
- 63 C. J. Brinker and G. W. Scherer, *Sol-gel science: the physics and chemistry of sol-gel processing*, Academic Press, 2013.
- 64 P. Debye and A. Bueche, Scattering by an inhomogeneous solid, *J. Appl. Phys.*, 1949, **20**(6), 518–525.
- 65 Y. Hagiwara, A. Shimojima and K. Kuroda, Alkoxysilylated-Derivatives of Double-Four-Ring Silicate as Novel Building Blocks of Silica-Based Materials, *Chem. Mater.*, 2007, **20**(3), 1147–1153.
- 66 T. Nakanishi, T. Norisuye, H. Sato, T. Takemori, Q. Tran-Cong-Miyata, T. Sugimoto and S. Nomura, Studies on microscopic structure of sol-gel derived nanohybrids containing heteropolyacid., *Macromolecules*, 2007, **40**(12), 4165–4172.