A structural and physical study of sol–gel methacrylate–silica hybrids: intermolecular spacing dictates the mechanical properties‡

Anthony L. B. Maçon,a Samuel J. Page,b Justin J. Chung,a Nadav Amdursky,a Molly M. Stevens,a,c,d Jonathan V. M. Weaver,a,b John V. Hanna*a and Julian R. Jones*b

Sol–gel hybrids are inorganic/organic co-networks with nanoscale interactions between the components leading to unique synergistic mechanical properties, which can be tailored, via a selection of the organic moiety. Methacrylate based polymers present several benefits for class II hybrids (which exhibit formal covalent bonding between the networks) as they introduce great versatility and can be designed with a variety of chemical side-groups, structures and morphologies. In this study, the effect of high cross-linking density polymers on the structure–property relationships of hybrids generated using poly(3-trimethoxysilylpropyl methacrylate) (pTMSPMA) and tetraethyl orthosilicate (TEOS) was investigated. The complexity and fine scale of the co-network interactions requires the development of new analytical methods to understand how network evolution dictates the wide-ranging mechanical properties. Within this work we developed data manipulation techniques of acoustic-AFM and solid state NMR output that provide new approaches to understand the influence of the network structure on the macroscopic elasticity. The concentration of pTMSPMA in the silica sol affected the gelation time, ranging from 2 h for a hybrid made with 75 wt% inorganic with pTMSPMA at 2.5 kDa, to 1 minute for pTMSPMA with molecular weight of 30 kDa without any TEOS. A new mechanism of gelation was proposed based on the different morphologies derived by AC-AFM observations. We established that the volumetric density of bridging oxygen bonds is an important parameter in structure/property relationships in SiO₂ hybrids and developed a method for determining it from solid state NMR data. The variation in the elasticity of pTMSPMA/SiO₂ hybrids originated from pTMSPMA acting as a molecular spacer, thus decreasing the volumetric density of bridging oxygen bonds as the inorganic to organic ratio decreased.

1 Introduction

Sol–gel hybrids are a class of material with inorganic and organic co-networks that are indistinguishable above the nanoscale. In class II hybrids the polymer can covalently bond to the silica network during the sol–gel process.1 This intricate relationship between the organic and inorganic network leads to the synthesis of materials where the physical properties can exceed those of the separate compounds alone or the equivalent conventional composite.2 Establishing the relationship between the structure of silica hybrids and their mechanical properties is challenging as their failure mode can vary from that of a brittle glass to that of an elastomeric polymer.3–5 Therefore it is critical to fully understand the atomic scale and nanostructure before they can be related to the mechanical properties. The organic component of silica based class II hybrids can be classified into three main subcategories: (i) non-polymeric organo-modified silicate precursors, e.g. (3-aminopropyl)triethoxysilane, or (3-glycidoxypropyl)methyltriethoxysilane;6–8 (ii) bridged polymers (polyether, polyester, polysiloxane, etc.), where each end of the polymer can be functionalised with organo-silicate cross linkers;3,9,10 and (iii) polymers containing pending alkoxysilane groups that allow covalent coupling.9,11–13 These pending groups can be a result of functionalisation by organo-silicates molecules or by including monomeric units such as 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) in radical polymerisations.14–16 The latter has the benefit of allowing a
better integration of alkoxysilane precursor as a part of the polymer structure as post-functionalization has been shown to be sensitive to the polymer used and experimental conditions.\textsuperscript{17,18} However, little is known on the influence of the chemistry of methacrylate containing alkoxysilane polymers on the sol–gel process, especially the effect of varying the cross-linking density. Cross-linking density can be controlled by the relative concentration of alkoxysilane radical monomer to the other monomer units within the radical polymerisation. Most of the reports focusing on such materials used free radical polymerisation. Here, the aim was to use TMSPMA based polymers as model polymers for class II hybrid synthesis and to develop analytical methods for characterisation of the submicron structure of the hybrids. The new analysis methods will achieve a better understanding of how the physical properties of class II hybrids are influenced by the presence of high cross-linking density polymers and could be applied to other hybrid systems. Homopolymers of TMSPMA were used as model polymers which gives a cross-linking density of 100\%. Until now, structural studies on hybrids synthesised with polymethacrylate were carried out with polymers having a cross-linking density no greater than 20\%. For instance, Landry and Coltrain showed by small angle X-ray scattering (SAXS) and dynamic mechanical analysis (DMA) that when methyl methacrylate is copolymerised with TMSPMA and added to hydrolysed TEOS, phase separation did not occur and the gelation mechanism was altered, compared to the synthesis of pure inorganic glass.\textsuperscript{19–21} Ravarian et al. reported a significant acceleration in gelation with the addition of similar polymers into the hydrolysed inorganic sol.\textsuperscript{22} Here, the effect of molecular weight ($M_n$) and inorganic to organic ratio, using tetraethyl orthosilicate (TEOS) as an inorganic source, on the sol–gel process were investigated.

2 Results and discussion

2.1 Observations on the synthesis

Poly(3-(trimethoxysilyl)propyl methacrylate) (pTMSPMA) was chosen as a model for the organic source (Fig. 1a). Every repeating unit of the polymer has an alkoxyl-silane moiety, which can potentially covalently bond to a conventional tetrasilicate glass precursor. Hence, pTMSPMA has a potential cross-linking density (the ability of a polymer to interface with the silica matrix) of 100\%. The effect of pTMSPMA molecular weight and its relative concentration to the TEOS were investigated. pTMSPMA was synthesised with $M_n$ ranging from 2.5 to 30 kDa via regulated-free radical polymerisation using thio-glycerol as a chain transfer agent (Table 1 and Fig. 1a)\textsuperscript{16,23}. The hydrodynamic radius of the pTMSPMA increased as the molecular weight increased. However, it was larger than poly(methyl methacrylate) (pMMA) for a given molecular weight, explaining the larger values obtained by GPC calculated against pMMA calibrants.\textsuperscript{24} In addition, due to the high steric hindrance of the alkoxyl-silane moiety, pTMSPMA exhibited a high syndiotacticity as shown by the ratio of the $^1$HN NMR peak area of the tactic ($\delta_{\text{m}} \approx 1.02$ ppm) and syndiotactic ($\delta_{\text{a}} \approx 0.85$ ppm) methyl group on the backbone (Table 1, $^1$HN NMR spectra available in S2, ESI$^\dagger$). This implies that pTMSPMA has a high axial symmetry, where the pending groups have alternating positions along the
chain. No hydrolysis occurred during the polymerisation nor after purification (there was no alteration the integration of Si–OCH₃, δ ≈ 3.58 ppm, relative to the propyl chain, δ ≈ 3.90 ppm). It is important that the polymerisation reaction does not trigger any hydrolysis or condensation of the alkoxysilane moiety of TMSPMA if a true class II inorganic–organic hybrid is to be synthesised as defined by Novak.¹

Crack-free silica class II organic–inorganic hybrids were synthesised using the acid-catalysed sol–gel process, mixing hydrolysed tetrakhooxysilicate (TEOS) and pTMSPMA dissolved in ethanol (Fig. 1b). To focus on the effect of the polymer content and Mₙ, hybrids or pure silica gel were prepared at the same pH (acidic sol–gel process pH ≈ 1) with the same amount of co-solvent. Several studies have shown that these two parameters have an effect on pure silica condensation, intrinsic porosity and in turn the final density.²⁵,²⁶ Hybrids with different silica weight percentage were produced: 29 wt% (hybrids made only from pTMSPMA), 50 wt%, 75 wt% and 100 wt% (pure silica gel), termed I₂₉, I₅₀, I₇₅ and I₁₀₀ respectively. The accuracy of inorganic to organic ratios were confirmed by thermogravimetry (TGA) and found to be within 2.5% of their target, regardless of the composition (see S3, ESI†).

After 1 h of hydrolysis of TEOS, the purified polymer was added to the solution (Fig. 1a). The addition of pTMSPMA had a noticeable effect on the gelation time as shown in Fig. 1c.²⁷ I₁₀₀ gelled within 3 days, which was consistent with literature with an inorganic to organic ratio the gelation time decreased with one minute for I₂₉/₃₀ kDa. The general trend was: (i) at a fixed thermogravimetry (TGA) and found to be within 2.5% of their (pure silica gel), termed I₂₉, I₅₀, I₇₅ and I₁₀₀ respectively.

| Mₙ,Targeted a | Mₙ,GPC b | PDI b | Rₚ (nm) | J₁(J₁)/J₁(J₂) d |
|--------------|----------|--------|--------|-----------------|
| 30 000       | 33 059   | 3.86   | 5.05   | 1.81/1          |
| 15 000       | 20 138   | 3.28   | 3.25   | 1.70/1          |
| 7500         | 11 001   | 2.24   | 2.09   | 1.63/1          |
| 2500         | 3612     | 2.02   | 1.16   | 1.49/1          |

Table 1 Summary of the poly(3-(trimethoxysilyl)propyl methacrylate) (pTMSPMA) characterization synthesised by regulated free radical polymerisation using thioglycerol as a chain transfer agent

A decrease in gelation time has been reported when methacrylate gelled within 3 days, which was consistent with literature with an inorganic to organic ratio the gelation time decreased with one minute for I₂₉/₃₀ kDa. The general trend was: (i) at a fixed thermogravimetry (TGA) and found to be within 2.5% of their (pure silica gel), termed I₂₉, I₅₀, I₇₅ and I₁₀₀ respectively.

The following gelation mechanisms are proposed for pTMSPMA/SiO₂ class II hybrids, depending of the relative concentration of
the polymer to TEOS. Upon the addition of the polymer, TEOS has condensed to formed dimers or cage-like silica particles (≤ 1 Å), which were at least an order of magnitude smaller in diameter than pTMSPMA, 1.16 nm for pTMSPMA at 2.5 kDa (see Table 1).26 Thus, at high concentration (I29 and I50), due to the larger size of the polymer particles, pTMSPMA formed a opened polymeric mesh by self-condensation within which (at I50) the hydrolysed tetrasilicate precursors condensed. The size of the mesh was directly impacted by \( M_n \) of pTMSPMA, as shown in the AC-AFM phase mapping (S5, ESI†). At I75, the concentration of the polymer was not sufficient to form a polymer mesh; therefore, we assume that pTMSPMA catalysed the formation of secondary particles, which are the product of the inter-condensation of silica branched polymer (primary particles) that forms through the reaction limited cluster–cluster aggregation of the hydrolysed tetrasilicate precursor.25,26

2.3 Mechanical properties by depth-sensing indentation

Nanoindentation was used to characterise the mechanical properties of the hybrids. Analysis of nanoindentation data depends on the mode of deformation of the material.35 In other methacrylate based hybrids, Mammeri et al. found that the addition of poly(MMA85-co-TMSPMA3) to the silica matrix led to viscoelasticity.32–34 Therefore, we hypothesised that the conventional Oliver and Pharr method to extract the Young’s modulus, could not be used here, as it assumes deformation to be elastic–plastic.35 Here, the reduced Young’s modulus, hardness and the quadratic viscosity coefficient were extracted from the load-displacement curve using the Viscous-Elastic-Plastic (VEP) model, as formulated by Oyen and Cook.36 In this model, the displacement of an indenter is the sum of a plastic \( h_p \), a elastic \( h_e \) and a viscous \( h_v \) elements placed in series as described by the Maxwell model.37

\[
h = h_v + h_e + h_p
\]

Due to the geometrical profile of the Berkovick indenter, the load-displacement relationship of each element (a spring for the elastic response, a dashpot for the viscous response and a friction block for the plastic response) are expressed quadratically:

\[
\frac{dh}{dt} = \frac{dh_v}{dt} + \frac{dh_e}{dt} + \frac{dh_p}{dt}
\]

\[
\frac{dh}{dt} = \sqrt{\frac{F}{2\gamma_0 \eta_0}} + \frac{1}{\sqrt{F \sqrt{2\gamma_2 E_t}}} + \frac{1}{\sqrt{F \sqrt{2\gamma_1 H}}}
\]
where $F$ is the load applied by the indenter, $E_\text{r}$ the reduced Young’s modulus, $H$ the hardness of the materials, $\tau_{\text{Q}3}$ is the quadratic viscosity, $\tau_1$ and $\tau_2$ are dimensionless geometry constants function of the included angle of the sharp indenter. A schematic representation of the Maxwell model and the expression of the geometrical parameters are given in ESI† (S6).

Fig. 3a shows the experimental and predicted load-displacement curves obtained for the pTMSPMA/SiO$_2$ hybrids. Table 2 summarises the corresponding values extracted from the VEP model from hybrids synthesised with pTMSPMA of $M_n$ of 15 kDa pTMSPMA (full table in T1, ESI†). All samples underwent crack-free deformation under loading as shown by the continuous displacements of the indenter under a constant load rate of 5 mN s$^{-1}$.38,39 As the inorganic–organic ratio increased the displacement at the maximum load decreased from 3.32 $\mu$m (for I29) to 1.68 $\mu$m (for I100) showing an increase in stiffness as the inorganic increased. Likewise, the reduced Young’s modulus and the hardness increased as the organic content increased (Table 2 and Fig. 3b). The mechanical properties measured had a low deviation from their mean values, showing the homogeneity in composition of the hybrid. The displacement of the indenter at the maximum load (dwell of 20 s) increased as the organic content increased, from 77 nm (for I100) to 213 nm (for I29), corresponding to an increase in the viscoelastic response. In addition, the VEP model allowed a quantitative measurement of the viscosity with the extraction of a quadratic viscosity factor, $\tau_{\text{Q}3}$, which decreased as the organic content increased near or above 50 wt%. According to the gelation mechanism proposed earlier, this sudden decrease corresponded to the transition between pTMSPMA being responsible for the gelation of the sol, by the formation of a polymeric mesh (I29 and I50), to acting as a catalyst in the formation of silica secondary particles.26 Interestingly, $\tau_{\text{Q}3}$ was not influenced by the $M_n$ of the polymer. In fact, none of the mechanical quantities extracted from the VEP model were influenced by $M_n$. The scale of the indent was at least one order of magnitude larger than the characteristic size of the polymeric mesh observed by AC-AFM (see Fig. 2), it is therefore likely that a macroscopic average effect on the mechanical properties was observed where pTMSPMA $M_n$ did not have any significant effect.

Mammeri et al. made similar observations on hybrid thin films synthesised with poly(MMA$_{95}$-co-TMSPMA$_5$).32–34 As their inorganic content increased, $E_\text{r}$ increased, ranging from 4.10 to 17.5 GPa. However, at a given inorganic–organic ratio the $E_\text{r}$ reported was greater than the values reported here. The $E_\text{r}$ in the thin films could have been an overestimate due to the empirical method of subtraction of the mechanical influence of the film substrate.46,47 Wei et al. reported lower values of the Young’s modulus to the thin film performing compression strength test on monoliths of similar compositions.42 They also showed that the $M_n$ of the polymer had a minimal effect on the mechanical properties of the hybrids with respect of their experimental conditions.

### Table 2 Reduced Young’s modulus, $E_R$, hardness, $H$, and viscoelastic factor, $\tau_{Q3}$, extracted from nanoindentation data using the Viscous-Elastic-Plastic model at different inorganic to organic ratios. pTMSPMA/SiO$_2$ hybrids synthesised with pTMSPMA $M_n$ of 15 kDa. Mean and standard deviation are given on a basis of 50 measurements. The Young’s modulus, $E$, is related to the reduced Young’s modulus by $E_\text{r} = \frac{E}{1 - \nu^2}$, where $\nu$ is the Poisson’s ratio.

| Hybrid | $E$ (GPa) | $H$ (GPa) | $\tau_{Q3}$ ($10^{12}$ Pa s$^2$) |
|--------|-----------|-----------|-------------------------------|
| I29    | 1.41 ± 0.23 | 0.25 ± 0.03 | 8.57 ± 1.33 |
| 150    | 2.53 ± 0.32 | 0.45 ± 0.03 | 25.19 ± 2.60 |
| 175    | 7.35 ± 0.98 | 1.32 ± 0.05 | 40.89 ± 1.65 |
| 1100   | 15.96 ± 0.73 | 3.40 ± 0.01 | 40.29 ± 1.25 |

### 2.4 Structure–property relationships

Relationship between the structure and the mechanical properties of the pTMSPMA/SiO$_2$ hybrids were investigated using solid state magic-angle spinning nuclear magnetic resonance (MAS-NMR).
29Si MAS-NMR was used to quantify the number of bridging oxygen, \( n \), that a silicon atom can have with other surrounding silica tetrahedra. Thus, two types of bridging oxygen species were detected; from silica network formed through the condensation of pTMSPMA (\( T^n \), centred around \(-60\delta_{T^n}\)) and from the TEOS (\( Q^n \), centred around \(-110\delta_{Q^n}\)). A structural representation of the different species is given in Fig. 4a. Fig. 4b shows the deconvoluted single pulse 29Si MAS NMR spectra of the hybrids synthesised with pTMSPMA at 2.5 kDa at different inorganic to organic ratio.

![Fig. 4](image)

(a) Representation of the different silica species seen in the (b) one pulse 29Si MAS NMR spectra of hybrids synthesised with pTMSPMA at 2.5 kDa at different inorganic to organic ratio.

The proportion of each silica species and the different degree of condensations obtained for the pTMSPMA/SiO2 hybrids are given in Table 3. Despite a decrease in the inorganic content, the chemical shifts of the different Q species remained relatively unchanged within a average deviation of 0.26\( \delta \). Q4 units represent the fully condensed part of the silica network. According to Mauri et al., the chemical shift \( \delta_{Q^n} \) could be linearly correlated to the Si–O–Si bond angle in vitreous silica by the following equation when \( \delta_{Q^n} \) < 120 ppm:

\[
\delta_{Q^n}(\theta) = -93.12 + 8.66 \cos(\theta) - 22.27 \cos(2\theta)
\]

where \( \theta \) is the dihedral angle between two condensed silicon atoms. Thus, according to this equation, the Si–O–Si bond distribution was centred around 147.4° with a variation in mode of 1.2°, typical of a relaxed network, which has not been heat treated. Therefore, this suggests that pTMSPMA had no effect on the silica network formed from TEOS.

From the percentages of T and Q species obtained from deconvoluting the spectra, the average degree of condensation of the silica network was calculated as follows: the partial degree of condensation of the T and Q species, termed \( d_{c,T} \) and \( d_{c,Q} \) as well as the total degree of condensation \( D_{c,total} \) were obtained from the respective area under the curve (A) of each silicate species (\( T^n \) or \( Q^n \)) as shown in eqn (4):

\[
d_{c,X} = \frac{\sum_{n} n \times A_{X^n}}{\sum_{T} A_{T^n}} \times 100; \quad (4)
\]

\[
D_{c,total} = \frac{\sum_{n} n \times A_{T^n} + \sum_{n} n \times A_{Q^n}}{\sum_{n} A_{X^n}} \times 100
\]

where \( X = T \) or \( Q \) for their respective partial degree of condensation and \( X = T \) and \( Q \) for the total degree of condensation. The proportion of each silica species and the different degree of condensations obtained for the pTMSPMA/SiO2 hybrids are given in Table 3. It is noteworthy to mention that each hybrid contained \( Q_2 \), \( Q_3 \) and \( Q_4 \), and \( T_1 \), \( T_2 \) and \( T_3 \), with a distribution of the Q species typical of gel prepared by the acidic route (\( pH < 2 \)).

The total degree of condensation \( D_{c,total} \) increased with the inorganic fraction from 69% for I29 to 87% for I100. I100 did not have a \( D_{c,total} \) of 100% because H+ ions act as network modifiers, leaving Si–OH groups in the silicate structure. For I29, the fast gelation and high tacticity of pTMSPMA is likely to have caused steric hinderance of the condensation. The increase of \( d_{c,T} \) with the molecular suggests that the condensation reaction for I29 is the favoured by the stereochemistry of the polymer with an increase in the \( d_{c,T} \) as the tacticity of pTMSPMA increased. For I50 and I75, we assume that the tetrasilicate precursors co-condensed with the organo-trisilicate precursors of the polymer, causing an increase of \( D_{c,total} \). This hypothesis is reinforced when looking at the partial degree of condensation of the T species, \( d_{c,T} \), which also increased from 69% for I29 to a minimum of 72.8% when pTMSPMA was mixed with hydrolysed TEOS.

Table 3

| Hybrid, \( M_n \) | \( T^n \) | \( T^2 \) | \( T^3 \) | \( Q^2 \) | \( Q^3 \) | \( Q^4 \) | \( d_{c,T} \) (%) | \( d_{c,Q} \) (%) | \( D_{c,total} \) (%) |
|---|---|---|---|---|---|---|---|---|---|
| I100 | 0 | 100 | 32.1 | 57.9 | 0 | 87.0 | 87.0 | 87.0 | 87.0 |
| I29, 30 kDa | 25.1 | 42.9 | 32.0 | 0 | 69.0 | 0 | 69.0 | 69.0 | 69.0 |
| I50, 30 kDa | 5.52 | 11.0 | 14.1 | 5.6 | 27.9 | 35.6 | 76.2 | 85.8 | 82.9 |
| I75, 30 kDa | 1.2 | 4.0 | 2.6 | 6.8 | 35.8 | 49.7 | 72.9 | 86.6 | 85.6 |
| I100, 2.5 kDa | 20.8 | 37.0 | 42.2 | 0 | 73.8 | 0 | 73.8 | 73.8 | 73.8 |
| I50, 2.5 kDa | 8.6 | 12.3 | 15.3 | 7.8 | 24.7 | 31.2 | 72.8 | 84.1 | 80.1 |
| I75, 2.5 kDa | 1.7 | 3.4 | 5.8 | 5.1 | 36.1 | 48.0 | 79.2 | 87.0 | 86.2 |

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Table 4  Skeletal density ($\rho_s$) of the pTMSMPA/SiO$_2$ hybrids and the intermediate results allowing the calculation the volumetric density of bridging oxygen, $\rho_v$Si–O–Si. To calculate $\rho_v$Si–O–Si, first, the molar density (mol cm$^{-3}$) of each silica domain (polymer or tetrasilicate) was extracted using their inherent molar mass and the polymer weight fraction $M_f$ from the skeletal density (N.B. the weight fraction of the polymer is different to the inorganic–organic ratio since it takes into account the contribution of the suboxide from TMSMPA). Then, the volumetric density of Si–O–Si bonds relative to each species was estimated from their partial degree of condensation $d_{c,T}$ and $d_{c,Q}$ and the silica molar densities. Finally, the total volumetric density was given by summation of the above quantities as shown in eqn (5):

$$\rho_v,\text{Si–O–Si} = \rho_s \times M_f \times (\frac{d_{c,T}}{M_w,\text{TMSMPA}} + \frac{1 - M_f}{M_T} \frac{d_{c,Q}}{M_w,\text{SiO}_2})$$

Intermediate results and $\rho_v$Si–O–Si are given in Table 4. Hence, it became clear that the initial concentration of pTMSMPA in the sol had a noticeable effect the final hybrid $\rho_v$Si–O–Si, which varied from $5.2 \times 10^{-3}$ cm$^{-3}$ N$_A^{-1}$ for 129 up to $29 \times 10^{-3}$ cm$^{-3}$ N$_A^{-1}$. This suggests that methacrylate polymers with a high degree of cross-linking, such as pTMSMPA, acts as spacers in the silica matrix, and therefore lowering the density of bridging oxygens as its concentration increases in the hybrid. A linear interdependence was found to exist between $E_r$ and $\rho_v$Si–O–Si as shown in Fig. 5c. The reduced Young’s modulus was also plotted against the different degrees of condensation and the skeletal density $\rho_s$ as shown in Fig. 5a and b, respectively. This decrease in volumetric density of bridging oxygens could therefore explain the decline in the $E_r$ when the inorganic to organic ratio decreased.

3 Conclusion

It is clear from the data presented here that class II silica hybrids are a unique class of material, different to conventional composites. As such, characterisation techniques must be adapted to the intrinsic nature of the relationship between the organic and inorganic phase through the development of new tools or the adaptation of existing methods, such as these developed here. A new gelation mechanism for hybrid sols with polymer of high cross-linking density was proposed based on morphology of the resulting hybrids using acoustic atomic force microscopy. Nanoindentation revealed that the mode of deformation was a function of the inorganic to organic ratio. Thus, hybrids require analytical methods that take into account these changes in properties, such as the VEP model. The volumetric density of Si–O–Si bonds is an important parameter in determining structure–property relationships and can be determined by treatment of solid state NMR data. Variation in the elasticity of the hybrids were a direct consequence of the addition of pTMSMPA, which acts as a bridging oxygen spacer, lowering $\rho_v$Si–O–Si. In this class II hybrids system, control of the mechanical properties can be obtained by varying the inorganic to organic ratio while $M_f$ had no effect. Though a better understanding of the relationship between the organic and
inorganic components, the properties of class II hybrids could fulfill their potential of materials with highly tailorable properties.

4 Experimental

4.1 Polymer and hybrid synthesis

Synthesis of pTMSPMA. 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA) was polymerised by free radical polymerisation, using AIBN as an initiator, in THF, at 60 °C. The average molecular weight of the polymer was controlled by introducing thioglycerol (TG) as a chain transfer agent and varying its concentration relative to the TMSPMA. Thus, the molar ratio \( R_0 = \frac{n_{\text{chain transfer agent}}}{n_{\text{monomer}}} \) varied between 0.8% to 9.9% to give a degree of polymerisation going from 10 to 120 as detailed in Table 5.

The concentration of initiator was kept constant relative to the monomer concentration with a molar ratio \( C_0 = \frac{n_{\text{initiator}}}{n_{\text{monomer}}} = 15\% \). The concentration of monomer was 1 mol L\(^{-1}\). Before any synthesis, the glassware was dried in an oven at 60 °C for a minimum of 2 hours. In a typical synthesis, all reagents were introduced in a round bottom flask by mass with a 0.5 mg accuracy and the flask was sealed with a silicon septa. Then, the polymerisation solution was bubbled with argon for 30 min to reduce the level of oxygen and left under a positive relative pressure by removing the gas inlet last. The polymerisation was carried out by size exclusion chromatography using the sol–gel process with tetraethyl orthosilicate (TEOS) and pTMSPMA as precursors. The polymer was dried from THF by vacuum distillation using Buchi Rotovapor RII (\( T_{\text{bath}} = 60 \degree \mathrm{C}, \text{nominal pressure} = 350 \text{ mbar} \)).

The mass of the polymer was then recorded and pTMSPMA immediately redissolved in ethanol at a molar ratio \( R_{\text{ethanol}} = \frac{n_{\text{ethanol}}}{n_{\text{TMSPMA}}} = 6 \). Meanwhile, in a separate beaker, TEOS was weighed to be further hydrolysed. The mass of TEOS hydrolysed was calculated based on the mass of the polymer \( m_{\text{polymer}} \) and the desired inorganic to organic mass ratio \( I_h \), using the following equation:

\[
I_h = \frac{m_{\text{SiO}_2} + m_{\text{SiO}_1.5}}{m_{\text{SiO}_2} + m_{\text{SiO}_1.5} + m_{\text{Org}}} \\
\]

\[
m_{\text{TEOS}} = \left( \frac{I_h}{1-I_h} \times \frac{m_{\text{polymer}}}{M_{w,\text{TMSPMA}}} \times M_{w,\text{Org}} \right) - \frac{m_{\text{polymer}}}{M_{w,\text{TMSPMA}}} \times \frac{M_{w,\text{SiO}_1.5}}{M_{w,\text{SiO}_2}}
\]

It must be noted that the backbone of the polymer was considered, in this equation, as the organic part of the class II hybrid. Hydrochloric acid and water were added to the beaker relative to the number of alkoxysilane groups taking into account TEOS and pTMSPMA according to the following ratios: \( R_{\text{HCl}} = \frac{n_{\text{HCl}}}{n_{\text{SiO}R}} = 0.01 \) and \( R_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{SiO}R}} = 1 \). However, water from HCl was subtracted to the final amount of distilled water added. The solution was stirred at 1000 rpm for 30 minutes, allowing TEOS to hydrolysed, after which the purified polymer was poured into the beaker. The mixture was allowed to mix for 30 s and casted into PTFE containers and subsequently sealed. After 3 days of ageing, the lids were loosened for the solvent to evaporate. pTMSPMA/SiO\(_2\) monoliths were considered dried when their mass appeared to be stable on the balance.

4.2 Characterisation

\(^1\)H NMR. Spectra were recorded in CDCl\(_3\) using a Bruker AV-400 spectrometer operating at 400 MHz. Spectra were then analysed using MestReNova 7.0 software. Prior integration and chemical shift identification, the baseline was corrected using a built-in Whittaker algorithm and the spectrum calibrated to TMS (tetramethylsilane).

Size exclusion chromatography. Molecular weight characterisation was carried out by size exclusion chromatography using the Viscotek TDA 305 instrument (Malvern instrument, USA) equipped with a Viscotek D6000M and D2500M columns. The TDA module was fitting with a refractive index (RI) detector, a four bridge viscometer (VIS) and a low and right angle laser scattering (LS) detectors. Linear polymethylmethacrylate were equipped with a Viscotek TDA 305 instrument (Malvern instrument, USA) equipped with a Viscotek D6000M and D2500M columns. The TDA module was fitting with a refractive index (RI) detector, a four bridge viscometer (VIS) and a low and right angle laser scattering (LS) detectors. Linear polymethylmethacrylate were applied as a standard for universal calibration. The experimental conditions consisted of dimethylformamide with 0.075% of lithium bromide as a mobile phase flowing at 0.7 mL min\(^{-1}\), 35 °C. A injection volume of 100 µL with a concentration varying between 5 and 10 mg mL\(^{-1}\) were used.

Dynamic light scattering. Dynamic light scattering (DLS) was measured on a Malvern Zetasizer (instrument 2000) instrument with a backscattering detection at 173°, equipped with a He–Ne laser (\( \lambda = 632.8 \) nm).

Thermogravimetry analysis. TGA was performed using a Netzsch sta 449 c in air. The sample was placed in a platinum crucible and heated up to 1000 °C at 10 °C min\(^{-1}\).

Skeletal density. The skeletal density was determined by automated helium displacement pycnometer (Ultrapycnometer 1000, Quantachrome). For each sample, data were acquired.
until 10 consecutive measurements were recorded with a standard deviation inferior to 0.03.

**Acoustic atomic force microscopy.** An AFM 5500 microscope (Keysight technologies, previously Agilent) was used for the AFM study in its acoustic mode. An HQ:NSC15/Al BS tip (μmash) was used for the topography and phase images (tip radius of 8 nm, resonance frequency of 325 kHz, force constant of 40 N m⁻¹). The measurements were performed in ambient atmosphere.

**Solid state NMR.** All 29Si single pulse MAS NMR measurements were performed at 7.0 T using a Varian-Chemagnetics InfinityPlus spectrometer operating at a Larmor frequency of 69.62 MHz. These experiments were performed using a Bruker 7 mm HX probe which enabled a MAS frequency of 5 KHz to be implemented. Flip angle calibration was performed on kaolinite from which a π/2 pulse time of 5.5 μs duration was measured. All measurements were undertaken with a π/2 tip angle along with a recycle delay between excitation pulses of 240 s. All 29Si isotropic measurements were performed in ambient atmosphere. The thermal drift contribution of the indentation system to total shifts were reported against the IUPAC recommended primary reference of Me₄Si (1% in CDCl₃, δ 0.0 ppm), via a kaolinite secondary reference from which the resonance exhibits a known shift of −92.0 ppm. Cross polarised (CP) MAS NMR was also performed to get the chemical shift of each silicon species and used for the deconvolution of the single pulse spectra. The CP spectra are available in ESI†.

**Nanoindentation.** Measurement were performed using a NanoTest Vantage (Micro Materials Ltd, UK) mounted with a Berkovich pyramidal tip. Prior measurement, samples were mounted in epoxy resin with a clearance of at least 5 mm between the bottom of the sample and the bottom of the resin. Load was applied on the sample at a rate of 5 mN s⁻¹ to a maximum load of 50 mN. The tips was unloaded at a rate of 10 mN s⁻¹ after a dwell of 20 s, a rate of 15 mN s⁻¹ down to 5 mN when a final dwell for 60 s was also applied to determine the thermal drift contribution of the indentation system to total placement measured by a capacitive transducer.

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