Silica/methacrylate class II hybrid: telomerisation vs. RAFT polymerisation†

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Inorganic–organic co-networks prepared by a sol–gel method are a promising class of materials due to their unique physical and biological properties, especially when covalent bonds are formed between the networks. The polymer structure and composition can have a drastic effect on the synthesis and properties. Here, we compared reversible addition fragmentation chain-transfer (RAFT) with telomerisation (TL), for the synthesis of the polymer, to investigate whether refining the polydispersity of polymethacrylate could lead to better and more tailorable properties. 3-(Methoxysilyl)propyl methacrylate was used as a model and successfully synthesised by RAFT and TL using 2-cyano-2-propyl benzodithioate and thioglycerol as chain transfer agents, respectively. The polydispersity of the polymer had a significant effect on the sol–gel process with an increase in gelation time as the polydispersity decreased. Direct correlation was made between the gelation time and $M_z$, suggesting that the gelation of hybrids followed the percolation model. However, regarding the properties, it is a tie. No statistical difference in silica release and mechanical properties of the resulting hybrids was observed, regardless of the polydispersity of the polymer.

1. Introduction

Silica class II hybrids are glassy materials that consist of covalent co-networks of silica and organic polymers with covalent bonds between the networks. They can be synthesised via a sol–gel process through the addition of an alkoxysilane-functionalised polymer into a sol that contains hydrolysed sol–gel precursors, such as tetraethyl orthosilicate (TEOS), allowing their co-condensation and co-existence at a molecular level. Mechanical properties, optical properties, chemical durability and degradability can be tuned as a function of synthesis parameters and by a careful selection of the organic matrix. Among the possible candidates, methacrylate polymers present multiple advantages, compared to other polymers, as their structure, molecular weight and functional pending groups can be selected and controlled independently. In addition, using monomers such as 3-(methoxysilyl)propyl methacrylate (TMSPMA), sol–gel precursors can be easily built in the polymer structure during its polymerisation. Due to their high tailorability, silica class II hybrids made with methacrylate polymers have gained considerable interest in the field of biomaterials, especially as potential bone implant materials. Most reports describing the synthesis of silica class II hybrids intended for this application used polymers synthesised from free radical polymerisation, despite multiple reports on the synthesis of similar polymers using controlled radical polymerisation techniques such as reversible addition–fragmentation chain-transfer polymerisation (RAFT), atom-transfer radical-polymerisation (ATRP) or nitroxide mediated radical polymerisation (NMP). Using advanced polymerisation techniques could potentially add another degree of tailorability for the silica class II hybrids as polymers can be designed with structures that cannot be obtained with free radical polymerisation. For instance, Chung et al. reported an increase in the modulus of toughness using star poly(methyl methacrylate-co-TMSPMA) as compared to its linear equivalent at 70 wt% of polymer using TEOS as an inorganic precursor.

Despite the progress recently made in the use of well-defined polymers in silica class II hybrids, no direct comparison between linear polymers made by free radical polymerisation and controlled polymerisation, at similar average molecular weights, has been reported in the literature. Polymers synthesised by free radical polymerisation inherently give larger molecular weight distribution as compared to controlled
radical polymerisation techniques. Our hypothesis is that lowering the polydispersity could significantly affect the sol-gel process and refine the resulting hybrid properties. In addition, if hybrids are developed as regenerative tissue substrates, non-degradable polymers such as polymethacrylate must be designed with a hydrodynamic radius falling below the excretion limit of the kidney, a criterion which could be fulfilled using a controlled radical polymerisation technique. Homopolymers of poly(TMSPMA) were synthesised here using two different polymerisation techniques, yielding polymers of similar average molecular weight but different polydispersities. The effect of the monomer purity on the polymerisation processes was investigated. Moreover, the effect on the sol-gel process, the mechanical properties and the chemical durability were evaluated.

2. Experimental section

2.1. Materials

All reagents were purchased from Sigma-Aldrich UK and used without further purification unless stated. 3-(Methoxysilyl)propyl methacrylate (TMSPMA), which did not contain any inhibitor, was purified by distillation under reduced pressure to remove hydrolysed monomers. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallised in cold methanol before use. Tetrahydrofuran (THF) and toluene were dried using 3 Å molecular sieves prior to any polymer synthesis.

2.2. Polymerisation and kinetics protocols

Prior to any synthesis, glassware was washed in an alkaline bath overnight, then rinsed with tap water and dried into an acid bath for 2 h and subsequently dried at 120 °C for 2 h.

2.2.1. Telomerisation. In a 50 mL round bottom flask containing a magnetic stirrer, TMSPMA (6209 mg, 25 mmol), AIBN (61 mg, 0.37 mmol) and thioglycerol (TG) (269 mg, 2.49 mmol) were weighed. THF was then added to the flask to achieve a monomeric concentration of 1 mol L\(^{-1}\). The flask was then sealed using a septum and oxygen was removed by bubbling argon for 20 minutes. The reaction was started by placing the flask at 60 °C in preheated oil for 48 h at 500 rpm. The polymers were then precipitated in cold hexane 3 times to remove the unreacted monomers, chain transfer agent, and initiator.

2.2.2. Reversible addition–fragmentation chain-transfer polymerisation. In a 50 mL round bottom flask containing a magnetic stirrer, TMSPMA (9313 g, 37.5 mmol), AIBN (20.5 mg, 0.13 mmol) and 2-cyano-2-propyl benzodithioate (55.3 mg, 0.25 mmol) were weighed. Toluene was then added to the flask to achieve a monomeric concentration of 1.5 mol L\(^{-1}\). The flask was then sealed using a septum and oxygen was removed by bubbling argon for 20 minutes. The reaction was started by placing the flask at 70 °C in preheated oil for a maximum of 8 h at 500 rpm. The polymer was then precipitated in cold hexane 3 times to remove the unreacted monomers, chain transfer agent and initiator.

2.2.3. Polymerisation kinetics. The kinetic studies were performed by taking aliquots of approximately 1 mL at given time points: 0.5, 1, 1.5, 2, 4, 8, 24 and 48 h for the TL and from 1 to 8 h, every hour for the RAFT polymerisation. They were taken under a flow of argon using a purged syringe and subsequently quenched in liquid nitrogen. The monomer conversion was calculated by comparing the integral values given by the protons of the unreacted vinyl from the monomer, H\(_{cis}\) at δ 5.45 and H\(_{trans}\) at δ 6.02, to the singlet of 1,3,5-trioxane, H\(_{trioxane}\) at δ 5.07, which was used as an internal reference. The concentration of thioglycerol (TL) was determined by iodometric titration using starch as an indicator. Starch was mixed with an aliquot at a 1:1 volume ratio in which iodine was added by 250 μL (0.002 mol L\(^{-1}\)) up to a change in colour from transparent to a deep blue, indicating the formation of an iodine–starch complex. The concentration of TG is finally recovered using the following equation:

\[
[RSH]_f^e = \frac{V_{ep}[I_2]_0}{V_{aliquot+starch.0}}
\]

where \(V_{ep}\) is the volume of iodine solution added to reach the end point, \([I_2]_0\) is the concentration of the iodine solution and \(V_{aliquot+starch.0}\) is the volume after mixing an aliquot with the starch before adding iodine.

2.2.4. Polymer characterisation

\(^1H\) NMR. \(^1H\) 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 to 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 of the polymer synthesised by telomerisation 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 fitted with a refractive index (RI) detector, a four bridge viscometer (VIS) and low and right angle laser scattering (LS) detectors. Linear polymethacrylate was applied as a standard for universal calibration. Dimethylformamide with 0.075% of lithium bromide was used as a mobile phase flowing at 0.7 mL min\(^{-1}\), 35 °C. The polymers synthesised by RAFT were characterised using an Agilent, SECURITY GPC system, with a Polymer Standard Service (PSS) SDV analytical linear M column (SDA0830005LIM), running in THF at 1 mL min\(^{-1}\). A single detection unit, consisting of an Agilent 1260 RID detector was used to measure the refractive index signal.

2.3. Polymer selection

Poly(TMSPMA) was synthesised targeting 6 and 12 kg mol\(^{-1}\), by stopping the polymerisation at 1 and 2 h for RAFT polymerisation, respectively, and using \(R_0 = 0.04\) and \(R_0 = 0.02\), respectively, for TL. The molecular weight characterisation of the purified polymers is summarised in Table 1 and values were close to the values targeted. All polymers were purified
3 times by precipitation in n-hexane before being re-dispersed in ethanol and subsequently used for the sol–gel synthesis.

2.4. Hybrid synthesis

tpTMSPMA/SiO₂ hybrids were synthesised using the sol–gel process with tetraethyl orthosilicate (TEOS) and tpTMSPMA as precursors using acidic catalysis at room temperature. The mass of TEOS hydrolysed was calculated based on the mass of the polymer (m\text{polymer}) and the intended inorganic to organic mass ratio (Iₘ), using eqn (2):

\[
Iₘ = \frac{m_{\text{SiO}_2} + m_{\text{SiO}_1}}{m_{\text{SiO}_2} + m_{\text{SiO}_1} + m_{\text{Org}}} 
\]

\[
m_{\text{TEOS}} = \left( \frac{Iₘ \times m_{\text{polymer}}}{M_w,\text{TPMSPA}} \times M_w,\text{Org} - \frac{m_{\text{polymer}}}{M_w,\text{TPMSPA} \times M_w,\text{SiO}_2} \right) \times \frac{M_w,\text{TEOS}}{M_w,\text{SiO}_2} \tag{2} \]

The backbone of the polymer was considered a part of the organic component of the class II hybrid. Hydrochloric acid (HCl) and water were added relative to the number of alkoxysilane groups in TEOS and tpTMSPMA according to the following ratios: R\text{HCl} = n_{\text{HCl}}/n_{\text{SiOR}} = 0.01 and R\text{H}_2\text{O} = n_{\text{H}_2\text{O}}/n_{\text{SiOR}} = 1. Water from HCl was subtracted according to the final amount of distilled water added. The solution was stirred at 1000 rpm, for 30 min, allowing TEOS to be hydrolysed, after which the purified polymer was added into the beaker. The mixture was allowed to mix for 30 s and cast into poly(tetrafluoroethylene) (PTFE) moulds and subsequently sealed. After 3 d of ageing, the lids were loosened for the solvent to evaporate. tpTMSPMA/SiO₂ hybrid monoliths were considered to be dried when their mass stabilised. The gelation point was measured by tilting the aging sol at 45° every 5 minutes until the meniscus no longer remained horizontal. The relative concentration of TEOS to the polymer (Iₘ) was varied to produce hybrids with inorganic to organic weight ratios of 29% (cross-linked polymer chains), 50%, 75% and 100%, termed I₂₉, I₅₀, I₇₅ and I₁₀₀, respectively.

2.5. Hybrid characterisation

2.5.1. Dissolution test. tpTMSPMA/SiO₂ hybrids were immersed in 5 mM Tris-HCl buffered water using a ratio of 75 mg glass to 50 mL of media in an airtight polyethylene container. Dissolution vessels were placed in an incubating orbital shaker held at 37 °C, agitated at 120 rpm. The pH (7.4) and temperature of the media were verified before use. The samples were incubated for 4 h, 8 h, 24 h and 72 h (n = 3). At the end of each time period, the samples were removed from the incubator and the solids were collected by filtration (filter paper with a particle retention of 5–13 μm). The powder was immediately washed with DI water and subsequently with acetone to terminate any reaction. The filtered solution was collected to determine the ion concentrations using an inductively coupled plasma (ICP) analysis; the pH of the solution was also measured. The same protocol was applied to the media alone as a control. Elemental concentrations in solution were measured with a Thermo Scientific ICAP 6300 Duo inductively coupled plasma-optical emission spectrometer (ICP-OES) with an auto sampler. Sample solutions were prepared by diluting the samples by a factor of 10 with analytical grade 2 M HNO₃. Silicon standard solutions were prepared at 0, 2, 5, 20 and 40 μg mL⁻¹ for the calibration. Silicon was measured in the axial direction of the plasma flame.

2.5.2. Mechanical test. Measurements were performed using a NanoTest Vantage (Micro Materials Ltd, UK) mounted with a Berkovich pyramidal tip. Prior to 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. The load was applied on the sample at a rate of 5 mN s⁻¹ to a maximum load of 50 mN. The tips were unloaded at a rate of 10 mN s⁻¹ after a dwell of 20 s and at 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 displacement measured by a capacitive transducer.

3. Results and discussion

3.1. Varying the polydispersity of poly(TMSPMA)

Two radical chain transfer polymerisation techniques were used here (Fig. 1), both allowing the synthesis of polyacrylate with predefined molecular weights, yet with different span distributions. Wide molecular weight distributions (1.5 < Đ < 2.0) were obtained by telomerisation (TL) whereas reversible addition fragmentation chain transfer polymerisation (RAFT)
was used to produce polymers with narrow molecular weight distribution \((D < 1.2)\). A kinetic approach was selected for both polymerisation techniques, in order to stop the reaction at the desired molecular weight for RAFT and confirm the effectiveness of the chain transfer agent for TL. The molecular weights targeted for the hybrid synthesis (section 3.2) were 6 and 12 kg mol\(^{-1}\) with respect to the synthesis criteria of implant for tissue regeneration.\(^{12,26}\)

### 3.1.1. Dithiobenzoate mediated RAFT polymerisation.

Polymers with low molecular weight distribution can be obtained with RAFT polymerisation due to the reversible deactivation of the propagating radicals, extending their lifespan to the extent of the polymerisation time.\(^{29,30}\) The protocol used here was adapted from the work of Mellon et al. who reported the successful polymerisation of TMSPMA using 2-cyano-2-propyl benzodithioate (CPBD) as a chain transfer agent (CTA).\(^{14}\) Thus, kinetic experiments were performed using a constant TMSPMA : CTA : initiator ratio of 150 : 1 : 0.5, CPBD as a CTA and AIBN as an initiator at 70 °C under argon. At first, and against the recommendations provided by Mellon et al., TMSPMA was used as-received without any purification (e.g. vacuum distillation) to keep the synthesis as simple as possible. Fig. 2 shows that a pseudo-first-order kinetic was obtained with an apparent rate of propagation \(k_{\text{app,ND}} = 6.45 \times 10^{-5}\) s\(^{-1}\), reaching 82% of conversion at 8 h. Size exclusion chromatography revealed that the average molecular weight increased linearly with conversion, a characteristic of successful RAFT polymerisation (Fig. 2b). However, the polydispersity index greatly increased with conversion above 60%, reaching \(D = 1.61\) at 80% conversion, due to the formation of a distinctive shoulder peak at lower elution time as shown in Fig. 2c, broadening the molecular weight distribution. This was unexpected as original reports on the polymerisation of TMSPMA did not observe such an effect. A high molecular weight usually originates from undesired and inevitable termination reactions when reaching high conversion.\(^{15,31,32}\) However, the occurrence of these reactions can be significantly reduced by decreasing the radical flux, which could be achieved by reducing the initiator concentration or reducing the reaction temperature with respect to the initiator used.\(^{33}\) Kinetics were performed at 60 and 80 °C to test this hypothesis and resulted in a systematic increase in polydispersity occurring above 40% conversion regardless of the temperature (Fig. S1†). It was therefore likely that the increase in polydispersity originated from a lack of purity of the monomer.\(^{1}H\) NMR of the crude TMSPMA, comparing the integral value of SiO-CH\(_3\) at 3.57 \(\delta\) and the chemical shift given by methanol at 3.47 \(\delta\), revealed that the monomer was hydrolysed by 2%, which is within the manufacturer’s description (Fig. S2†). Khan et al.\(^{34}\) demonstrated that CaH\(_2\) favourably reacts with silanol moieties (reaction enthalpy \(-1787\) kJ mol\(^{-1}\)), isolating the hydrolysed TMSPMA as follows:

\[
\text{CaH}_2 + 2R\text{-Si-OH} \rightarrow R\text{-Si-O-Ca-O-Si-R} + 2\text{H}_2(g). \quad (3)
\]

The kinetic experiments were repeated with the purified monomer, yielding similar apparent propagation rates, \(k_{\text{app,ND}}\)
= 5.14 × 10⁻⁵ s⁻¹ and similar increase of degree of polymerisation as a function of conversion as shown in Fig. 2a and b, indicating no change in the polymerisation kinetics. However, the purification of the monomer positively resolved the increase in molecular weight distribution at high conversion with a polydispersity of D = 1.09 at 73% conversion. Thus, we concluded that the shoulder peaks seen in Fig. 2c with the non-distilled monomer came from the branching of individual polymeric chains through the condensation of the silicate residues originating from the hydrolysed monomers as the viscosity increased. From this point onward, all polymerisations described in this report were performed using the purified monomer.

3.1.2. Telomerisation. In TL, thiols (R-SH) are used as chain transfer agents where their labile protons can irreversibly terminate a growing polymeric chain while initiating another chain from the thiolyl (R-S) formed. If the rate of transfer of a radical to thiol is equal to the rate of propagation of the polymeric radical (i.e. monomer addition), the degree of polymerisation of the polymeric chain is equal to the initial chain transfer agent (CTA) to the monomer (M) molar ratio, RCTA, as follows:

\[
\text{DP}_n = C_T \frac{[M]_0}{[\text{CTA}]_0} \quad \text{where } C_T = \frac{1}{k_0}
\]

where \( C_T \) is the ratio of the propagating rate over the transfer rate and termed chain transfer constant. This can be achieved through a careful selection of the polymerisation parameters with regard to the polarity of the chain transfer agent. Here, thioglycerol and THF were selected as the chain transfer agent and solvent, respectively, as this combination provided a good control over the molecular weight of methyl methacrylate. In order to determine whether the same degree of control could be obtained with TMSPMA, the chain transfer constant \( C_T \) of the system was determined using O’Brien’s law:

\[
\ln \left( \frac{[\text{RSH}]_t}{[\text{RSH}]_0} \right) = C_T \ln \left( \frac{[M]_t}{[M]_0} \right)
\]

varying \( R_{\text{CTA}} \), the monomer to thioglycerol molar ratio, from 0.008 to 0.0994 targeting molecular weight between 2.6 and 30 kg mol⁻¹ as shown in Table 1. The stationary condition and invariance of the propagation rate as a function of the concentration of the chain transfer agent were first checked (see the ESI† for details). Then, the logarithm of the normalised concentration of the chain transfer agent was plotted against the normalised monomeric concentration, as a function of \( R_{\text{CTA}} \) as shown in Fig. 3a. The average \( C_T \) was extracted from the slopes, giving a value of 0.72 ± 0.03 with \( R^2 \geq 0.95 \). Individual values are available in Table 1. The values obtained for \( C_T \) fell in the region allowing a good regulation of the molecular weight with a mono-modal distribution. However, with the polymerisation using the least amount of the chain transfer agent, \( R_{\text{CTA}} = 0.008 \), and after two hours, the concentration of thioglycerol was too low to allow for a complete solubilisation of starch. Thus, the end point was solely observed by the presence of iodine, introducing a substantial human error, which in turn did not guarantee that the polymerisation followed 1st order kinetics. Pardal et al. reported the telomerisation of TMSPMA using acetonitrile as a solvent at 70 °C and thioethylene glycol as a chain transfer agent. A good regulation was obtained with TMSPMA \( (C_T < 1) \) from a kinetic analysis; however, it was not validated by SEC analysis. Fig. 3b shows the chromatographs obtained from the size exclusion after 48 h of polymerisation and purification. Regardless of the molecular weight targeted, all distributions were mono-modal, which corroborated the observations made previously. The measured average molecular weights were in good agreement with their kinetically re-evalu-
ated estimations (see Table 1). The polydispersity index ($D$), characterising the span of a polymeric distribution, increased with the molecular weight. For the smallest molecular weight with $R_{CTA} = 0.1$ and $R_{CTA} = 0.03$, $D = 2.02$ and 2.24, respectively, which is typical of conventional free radical polymerisation when termination occurs solely by disproportionation, or radical transfer. However, for $R_{CTA} = 0.016$ and $R_{CTA} = 0.008$, $D$ exceeded 3. This could be explained by the concentration of the chain transfer agent verging on or dropping below that of the initiator. At these concentrations of CTA, slightly more polymeric chains could be initiated than CTA present. Thus, radical transfer was not the exclusive chain-stopping reaction and conventional termination was competitively taking place, broadening the molecular weight distribution.

3.2. Silica class II hybrid synthesis: effect on the gelation time

Silica class II hybrids were prepared using the same experimental conditions described previously. The relative concentration of TEOS to the polymer ($I_h$) was varied to produce hybrids with inorganic to organic weight ratios of 29% (cross-linked polymer chains), 50%, 75% and 100%, termed $I_{29h}$, $I_{50h}$, $I_{75h}$ and $I_{100h}$, respectively. Once the polymer was mixed with the acidic TEOS, fast hydrolysis of the pending alkoxy silane groups occurred, subsequently followed by the co-condensation of free-silicate moieties, forming a glass network with silicon bridging oxygen (Si–O–Si). The formation of these bridges led to the gelation of the precursor solution as shown in Fig. 4. The time that the sols took to reach the gel point, or gelation time, decreased as the inorganic to organic ratio decreased, regardless of the molecular weight or polymerisation method used (Fig. 5a). In addition, at a fixed inorganic to organic weight ratio, as molecular weight increased, the gelation time decreased, regardless of the polymerisation method used. These observations are in agreement with our previous report. However, the polymerisation method used had two noticeable effects on the gelation time: (i) regardless of the composition targeted, the sols containing poly(TMSPMA) synthesised by RAFT were slower to gel than those containing the polymers synthesised by TL. (ii) The relative increase in the gelation time with an increase in molecular weight, at a given $I_h$, was more significant for the polymers synthesised by TL than by RAFT. These two observations highlight the influence of the polydispersity of the polymer onto the gelation and also suggest that the gelation mechanism needs to be refined accordingly; we previously hypothesised that when using high cross-linking density polymers, the gelation was induced by the co-condensation of alkoxy silane moieties from the polymer forming a macroscopic mesh in which TEOS condenses. The data collected here show that the higher fraction of the molecular weight distribution had a preponderant effect in the formation of the polymeric mesh. Thus, the gelation time was plotted as a function of the higher average molecular weights $M_z$, third moment of the molecular distributions, which is...
more sensitive to the high molecular weight polymers as shown in Fig. 5b. At a fixed $I_0$, the gelation time decreased linearly ($R^2 > 0.97$) as $M_z$ increased, regardless of the polymerisation method used, demonstrating that the gelation of the sols was solely due to the cross-linking of poly(TMSPMA) and reinforcing the observations made previously.$^3$ Based on these observations, it is likely that the gelation of class II hybrids, synthesised with high cross-linking density polymers, follows the bond percolation theory, where adjacent polymers are co-cross-linked randomly along their chains, forming 3-dimen-
sional lattices, which upon reaching a critical size induce macroscopic gelation.$^{41}$ Hence, poly(TMSPMA) acted as large preformed clusters, where the higher fraction of its molecular weight distribution caused gelation, at an earlier stage, with the polymer synthesised with TL compared to RAFT due to higher polydispersity.$^{42}$ Understanding how the mechanism of gelation of these materials worked is important as physical properties of hybrid systems (alkane bridges) can be correlated and predicted using the bond percolation theory.$^6$ However, the data presented here are not sufficient to make such a connection, but suggests its existence.

3.3. Polydispersity/property relationship

Now that the influence of the polydispersity of poly(TMSPMA) on the sol–gel process has been established, the properties of the resulting hybrids were investigated by nanoindentation and immersion of the hybrid in a buffered solution.

3.3.1. Chemical durability in buffered media. In order to study the chemical durability of the hybrids as a function of the polydispersity of poly(TMSPMA), immersion in 5 mM TRIS solution buffered at pH 7.35 over a period of 3 days was conducted (Fig. 6). The silica release profile obtained for $I_{100}$, pure silica glass, was plotted as a control. For the hybrid with an inorganic to organic ratio of 75%, the silicon concentration profiles were statistically equivalent to $I_{100}$, with a steady increase of the level of silicon reaching $39.1 \pm 3.9 \text{ mg} \text{m}^{-1}$. At $I_{50}$, the concentration of silicon did also increase over the 3 d of incubation, however, at a reduced level compared to $I_{100}$ reaching at 3 d, $22.3 \pm 1.1 \text{ mg} \text{m}^{-1}$ and $12.8 \pm 1.43 \text{ mg} \text{m}^{-1}$ for well-defined poly(TMSPMA) at 12 kDa and 6 kDa, respectively. Silica release from hybrids made with $M_n$ of 12 kDa was slightly higher than for $M_n$ of 6 kDa for $I_5$. The values obtained at 3 d from the hybrids synthesised with poly(TMSPMA) obtained by TL were statistically equivalent to these obtained with well-defined polymers. At $I_{50}$, only $\approx 1.5 \text{ mg} \text{m}^{-1}$ of silica was released in solution, a value close to the 1 \text{ mg} \text{m}^{-1} detection limit of the ICP-OES used here. The release of silica from class II hybrid synthesised originates from the hydrolysis of condensed orthosilicate.$^4$ According to the mechanism of gelation from high cross-linking density polymers, the orthosilicate species are present within the polymer mesh formed upon intra-condensation of the polymer chains.$^{3,4}$ Even though the kinetics of gelation varied with the polydispersity, the release of silica from the two sets of hybrids described here did not, suggesting that the spatial characteristic and interconnection of the polymer meshes in which TEOS condensed was principally defined by the average molecular weight which is similar for both polymerisation techniques.

3.3.2. Mechanical properties. As reported previously, poly(TMSPMA)/SiO₂ class II hybrids exhibit a viscoelastic response under mechanical stress. Thus, appropriate tools need to be used to carefully extract their characteristic values.

As a result, the mechanical properties were characterised by nanoindentation, which allows for an indirect measure of reduced Young’s modulus ($E_r$), hardness ($H$) and quadratic viscosity ($\alpha_{Q} I_{Q}$).$^{44-46}$ These values were extracted by fitting the experimental data using the Visco-Elastic-Plastic (VEP) model proposed by Oyen et al.$^{47-49}$ It relies on a Maxwell modelisation of the mechanical deformation, where the response under the tip of an indenter can be represented as the sum of a purely viscous damper ($h_v$), a purely elastic spring ($h_p$) and an elementary friction block ($h_f$), where:

$$\frac{dh}{dt} = \frac{dh_v}{dt} + \frac{dh_e}{dt} + \frac{h_p}{dt}$$

$$\frac{dh}{dt} = \sqrt{\frac{E}{\alpha_{Q} I_{Q}}} + \frac{1}{\sqrt{E} dt 2\sqrt{\alpha_{Q} I_{Q}}} + \frac{1}{\sqrt{E} dt 2\sqrt{\alpha_{Q} I_{Q}} H}$$

Fig. 7a shows the experimental and the fitted load-displacement curves obtained from hybrid synthesis with well-defined poly(TMSPMA) of $M_n$ 12 kDa as a function of the inorganic to organic weight ratio. $I_{100}$ (pure silica gel) was plotted as a
control. All samples at a fixed inorganic/organic weight ratio and poly(TMSPMA) molecular weight gave similar hysteresis and hence are not represented in this manuscript. Table 2 summarises the values extracted from the VEP model for the same samples. All hybrids underwent a crack-free deformation under the load of the indenter, regardless of the synthesis method used and the molecular weight. The polydispersity of the polymer did not have any significant effect on the general behaviour of the samples, under the load of the indenter, which can be seen in Fig. 7b, where no statistical difference could be seen in $E_t$ at fixed $I_h$ and molecular weight. The reduced Young’s modulus was found to increase solely as the inorganic to organic weight ratio increased, the inorganic to organic weight ratio as shown in Fig. 7b with $E_r \approx 1, 3$ and $7.5$ GPa at $I_{29}$, $I_{50}$ and $I_{75}$, respectively.

4. Conclusions

Poly(TMSPMA) was successfully synthesised by RAFT and TL, yielding polymers of similar average molecular weight but different polydispersities. We demonstrate that the polydispersity of polymers with high cross-linking density has a significant effect on the sol–gel process, with a gelation driven by the higher fraction of the molecular distribution while the mechanical and chemical durability properties were not affected. These findings could be of a great interest for applications where a longer gelation time is required as it increases the processability of the sol, which could be beneficial when synthesising a 3D template, or a scaffold, using electrospinning or 3D printing.

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