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POSS Induced Enhancement of Mechanical Strength in the RAFT Made Thermo-responsive Hydrogels

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To understand the effect of polyhedral oligomeric silsesquioxane (POSS) moieties on the rheological properties of thermo-responsive hydrogels, poly(ethylene glycol) methyl ether methacrylate (PEGMA) based gels have been synthesized *via* conventional free radical polymerization (FRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization techniques. Two different chain transfer agents (CTA), namely 4-cyano-4-(dodecylsulfanylthiocarbonyl) sulfanylpentanoic acid (CDP) and POSS chain-ended CTA (POSS-CDP) have been employed for the RAFT polymerization of PEGMA in the presence of a di-functional cross-linker, di(ethylene glycol)dimethacrylate (DEGDMA). Swelling, deswelling and reswelling behaviors due to the introduction of POSS moiety have been systematically examined and compared with the CDP based hydrogels at similar compositions. The surface topology and structural porosity of the hydrogel matrix are examined by field emission-scanning electron microscopy (FE-SEM). The mechanical behavior of the swollen hydrogels has been investigated through rheological measurements. Interestingly, we find that the mechanical stability of the hydrogels improved by both cross-linking density and total net fraction of the POSS moieties.

Introduction

Hydrogels, conventionally described as three-dimensional (3D) cross-linked network structures, can absorb and retain water within their network and swell many folds as compared to their initial weight in dry state due to interconnected microscopic channels.¹ Owing to their unique properties such as high water preservation ability, biocompatibility, and softness, a wide variety of applications in drug delivery, agriculture, bio-medical fields, pharmaceuticals, material science implants and hybrid-type organs have been proposed.^{2,3,4} However, most of the covalently cross-linked hydrogels are mechanically fragile and exhibit poor elasticity due to their high water holding capacity into the interior micro channels, as a consequence the large-scale practical application of such kind of materials are tremendously perturbed.^{5,6} Hence, the formation of mechanically stable hydrogels with rapid responsive behavior is still a challenging issue for researchers. Clay nanocomposites, double network structure combined with different hydrophilic monomer, magnetic nanoparticle, organic-inorganic hybrid materials, etc. were incorporated to improve the mechanical toughness as well as to accelerate the response rate towards external stimuli.^{7,8} Among all other hybrid materials, polyhedral

oligomeric silsesquioxanes (POSS) molecule^{9,10} is a promising one and serves as an unique cubic cage like nanoscale building block with novel enhanced properties such as high thermal and mechanical stability, flame retardant, low dielectric constant, etc.¹¹

The POSS moiety has been incorporated in various polymeric systems *via* blending, grafting or cross-linking to improve mechanical strength, thermal stability, oxidation resistance, etc.^{12,13} Incorporation of small amounts of POSS moiety (<5 wt%) into the hydrogel increased the storage modulus 300% compared to the neat hydrogel due to the large surface area of the nanosized mechanically strong POSS particles.⁸ Recently, Xu and co-workers synthesized dual thermo- and pH-responsive *N*-isopropylacrylamide and *N,N*-dimethylaminoethyl methacrylate based hydrogels in the presence of both organic cross-linker *N,N'*-methylenebis(acrylamide) and inorganic cross-linker octavinyl POSS using traditional free radical polymerization (FRP) techniques. Improved mechanical properties and the deswelling rate of gels were reported.⁷ Significant modulation of the mechanical characteristics of the natural gelatin based hydrogels have been reported at different loading of a water soluble octa-ammonium POSS.¹⁴ Kim and Mather synthesized POSS capped poly(ethylene glycol) (PEG) and proposed that these unique material will offer strong alterations in solution rheological behaviour (i.e., associative thickening).¹⁵ POSS-capped PEG telechelics were incorporated into cross-linked poly(*N*-isopropylacrylamide) (PNIPAM) networks, which displayed faster thermo-responsive properties compared to the plain PNIPAM hydrogel.¹⁶ Wang et al. reported stable thermo-responsive hydrogel nanofibres by electrospinning of

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commercial PNIPAM in the presence of epoxide containing POSS molecules. The nanofibres showed excellent hydrogel characteristics with fast swelling and de-swelling responses in response to temperature changes.¹⁷ PNIPAM based hydrogels were also prepared in the presence of a cross-linker and POSS-SH as chain transfer agent by conventional free radical polymerization.¹⁸ Octa(propylglycidyl ether) polyhedral oligomeric silsesquioxane was used as a nano cross-linking agent to prepare the cross-linked PNIPAM hydrogel networks with high POSS content (upto 50 wt%). The authors studied swelling, deswelling and reswelling experiments with the POSS modified PNIPAM hydrogel.¹⁹ In most of the studies either post-polymerization modification or conventional FRP method was used to introduce POSS moiety in the hydrogel matrix, and the effect of POSS moiety on the mechanical properties of hydrogels was not studied.

Therefore, in this contribution we have employed reversible addition-fragmentation chain transfer (RAFT) polymerization technique to develop POSS modified thermoresponsive hydrogels by polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA) in the presence of POSS based chain transfer agent (CTA) and di-functional cross-linker. Lutz's group demonstrated thermoresponsiveness of polymers and hydrogels containing short oligo(ethylene oxide methacrylate).^{20,21} The effect of POSS moiety on the swelling, deswelling and reswelling kinetics was studied with these hydrogels by gravimetric analysis. The mechanical property of the swollen hydrogels was also investigated by rheological measurements. Interestingly, the POSS end functionalized CTA gave rise to gels with much higher storage modulus (G') values than the gels where RAFT CTA without POSS moiety was used.

Experimental Section

Materials

PEGMA (300 g/mol) and di(ethylene glycol)dimethacrylate (DEGDMA, 95%) were purchased from Sigma-Aldrich and purified by passing through a column of basic alumina. Amino isobutyl polyhedral oligomeric silsesquioxane (POSS-NH₂) was purchased from Hybrid Plastics, Mississippi, USA. Anhydrous *N,N'*-dimethylformamide (DMF, Sigma-Aldrich, 99.9%) was used as received. The 2,2'-azobisisobutyronitrile (AIBN, Sigma-Aldrich, 98%) was recrystallized twice from methanol, stored in a refrigerator and used whenever needed. RAFT chain transfer agent (CTA), 4-cyano-4-(dodecylsulfanylthiocarbonyl) sulfanylpentanoic acid (CDP), was synthesized as reported elsewhere.²² POSS-containing RAFT agent (POSS-CDP) was prepared by the coupling reaction of amine terminated POSS with CDP in the presence of dicyclohexylcarbodiimide (DCC, Sigma-Aldrich, 99%) and 1-hydroxybenzotriazole (HOBt, spectrochem, India).²³ The solvents such as hexanes (mixture of isomers), dichloromethane, ethyl acetate and acetone were purified by standard purification methods.²⁴ De-ionized (DI) water was used for purification of cross-linked hydrogels.

General procedure for gel synthesis

Chemically cross-linked RAFT gels were synthesized in the presence of AIBN as radical source, POSS containing CDP as CTA, and DEGDMA as cross-linker in DMF. A typical example of RAFT gel synthesis is as follows: PEGMA (2.00 g, 6.667 mmol), DEGDMA (64.61 mg, 0.267 mmol), POSS-CDP (84.04 mg, 0.067 mmol), AIBN (3.28 mg, 0.019 mmol), and 0.5 mL of anhydrous DMF were taken in a 20 mL septa sealed vial equipped with a magnetic stir bar. Then, the reaction vial was purged with dry nitrogen for 20 min, and placed in a preheated reaction block at 70 °C for 24 h. During the gelation process, stirring was stopped when viscous gel was formed to reduce bubble entrapment in the gel matrix. The reaction was terminated by putting the vial in an ice-water bath and exposure to air. Similar procedure was applied for the synthesis of RAFT gels using CDP as CTA. Also, FRP gels were synthesized in the absence of CTA, but reaction time was 12 h.

Purification of gels

First, the reaction vial was broken carefully to collect the semi-solid gel in a 250 mL beaker. Then, it was dialyzed against DI water (40 h) and acetone (24 h), respectively. In the beaker DI water was changed 6-8 times and acetone was replaced 4-6 times after 2-12 h. Finally, all gels were dried under high vacuum at 40 °C for three days.

Measurement of swelling kinetics

Equilibrium swelling ratio (SR_e) is defined as capability to absorb water in the cavity of the gel matrix with respect to its dry weight until a constant value is reached. To measure the SR_e values by gravimetric analysis, a small piece of hydrogel was taken in a 25 mL beaker and immersed in DI water at 22 °C for 48 h to attain the maximum swelling ratio. Then, the swollen hydrogel was taken out carefully from the beaker, wiped with a blotting paper to remove the surface water and weighed on a dry petridish. The SR_e was calculated from the following equation.²⁵

$$\text{Swelling ratio } (SR_e) = \frac{W_t - W_d}{W_d}$$

Where W_t is the weight of the swollen hydrogel at time t and W_d is the weight of the dry hydrogel.

Measurement of deswelling kinetics

Water retention, corresponds to deswelling ratio, is the ability of a hydrogel matrix to preserve certain amount of water with respect to its swollen state. The deswelling kinetics was carried out gravimetrically below (60 °C) and above (70 °C) the lower critical solution temperature (LCST) of hydrogels. A small piece of swollen hydrogel after achieving the SR_e at 22 °C was transferred to the beakers containing hot water at 60 and 70 °C. Then, the weight of the shrunk hydrogel was taken at different time intervals after wiping off the excess surface water. Water retention is defined by the following equation.²⁶

$$\text{Water retention} = \frac{W_t - W_d}{W_0 - W_d}$$

Where W_t is the weight of the hydrogel at time t and W_0 is the weight of swollen hydrogel below the LCST at equilibrium.

Measurement of reswelling kinetics

A small piece of a swollen hydrogel was put into hot water bath (70 °C) 12 h prior to the experiment. Then, the reswelling kinetics of shrunk hydrogels was measured gravimetrically at 22 °C, after blotting the excess surface water with a moistened tissue paper. The change of the water content during reswelling process was measured at different time interval and the water uptake of the hydrogel was calculated.

Instrumentation

The FT-IR spectrum was measured on KBr pellets using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Thermal studies were carried out using a Mettler Toledo TGA/SDTA 851e instrument at a heating rate of 10 °C min⁻¹ with a sample weight of approximately 4-5 mg under nitrogen atmosphere. The transparency of the swollen hydrogels was measured with U-4100 HITACHI UV-visible spectrometer, with a scan rate of 240 nm/min at a wavelength of 500 nm. Solid state ¹³C CP/MAS NMR was carried out on a Bruker Avance^{III} 500 spectrometer at 298 K using 4 mm MAS probe, and 125 MHz frequency was used for tuning the broad band channel. Pulse length and relaxation time of this experiment was considered 4 μs and 20 s, respectively. The spinning frequency for each sample was coordinated to 8 KHz.

FE-SEM analysis

Surface morphology and interior porous structures of synthesized cross-linked hydrogels were examined by field-emission scanning electron microscope (FE-SEM). A small piece of dried gel sample was immersed in DI water overnight to reach its maximum swelling state. Then, the swelled gel was frozen in liquid nitrogen and freeze dried using a lyophilizer (Orleon instrument) under high vacuum at -50 °C for 32 h. The dry gel sample was coated with a very thin layer of gold-palladium alloy for 1 min under high vacuum and examined by FE-SEM (Carl Zeiss Supra SEM instrument). The same instrument was used for energy-dispersive X-ray (EDX) measurement for analysis of gel composition, where gel sample was coated with carbon for 1 min under high vacuum.

Rheology Study

To understand the mechanical strengths of swollen hydrogels (swollen in DI water overnight), we performed rheological measurements on a AR-G2 rheometer (TA Instrument) using a steel parallel plate geometry with 40 mm diameter at 25 °C. The rheometer is attached to a Peltier circulator thermo cube that helps accurate control of temperature during the experiment. Elastic modulus (G') and loss modulus (G'') of

polymer gels have been recorded in the linear viscoelastic regime at a strain of $\gamma = 2\%$ of angular frequency (0.1–100 rad/s).

Results and discussion

Synthesis and characterization of hydrogels

PEGMA based thermoresponsive “smart” hydrogels were synthesized *via* both FRP and RAFT polymerization techniques by the polymerization of PEGMA in the presence of DEGDMA as a di-functional cross-linker at different [PEGMA]/[DEGDMA] ratios using AIBN as radical source and DMF as solvent at 70 °C (Scheme 1). In our previous report we have demonstrated that CDP acts as effective CTA for RAFT polymerization of PEGMA to give polymers with controlled molecular weight and narrow polydispersity index (PDI).²⁷ Hence, we have prepared PEGMA based hydrogels in presence of CDP and POSS functionalized CDP (POSS-CDP). All RAFT gels were synthesized maintaining the limiting conditions of RAFT gelation process using divinyl cross-linker DEGDMA.²⁸ Total 3 sets of 9 hydrogels were synthesized, and various conditions of gelation reactions are summarized in Table 1. The cross-linked polymer hydrogels were named according to the following rules (Table 1): first letter R or F designates the polymerization mechanism, RAFT or FRP, respectively; letter P after R stands for the use of POSS functionalized CDP moiety; number 25, 35 or 50 stands for the [PEGMA]/[DEGDMA] ratios. For example, the RP25 gel was synthesized by RAFT polymerization technique using POSS-CDP as CTA with [PEGMA]/[DEGDMA] = 25/2.

During the gelation reactions, it has been observed that at the same [PEGMA]/[DEGDMA] ratios the gelation times of FRP gels are reasonably low compared to the RAFT gels. This is because of the high concentration of propagating radicals in the FRP process, as concentration of propagating radicals in case of FRP process is determined by stability between initiation and termination steps.²⁹ On the other hand, when we increased the [PEGMA]/[DEGDMA] ratios from 25 to 50, the gelation time also increased reasonably may be due to the availability of lower number of active sites for cross-linking as concentration of cross-linker density is reduced. We carried out the gelation reactions for 24 h for RAFT gel and 12 h for FRP gel to get maximum conversion and gels were purified by dialysis as reported elsewhere.³⁰ Monomer conversions were calculated gravimetrically by comparing the weight of the purified dry gel with respect to the weight of the monomer feed. The chemical structure of hydrogels was primarily characterized by FT-IR spectroscopy. The strong vibrational stretching frequency at 1735 cm⁻¹ due to the C=O bonds present in the PEGMA and DEGDMA is observed in all three types of gels (Fig. S1 in the supporting information). The broad absorption band centered in the region 2960–3000 cm⁻¹ is ascribed to the aliphatic C–H stretching vibration modes. All three types of gels showed similar spectra and we could not identify POSS moiety in RP gels due to the overlap of POSS characteristic stretching frequencies from Si–O–Si and Si–C bonds respectively at ~1110 and ~750 cm⁻¹. Therefore, incorporation of POSS nanospheres into the hydrogel matrix was confirmed by SEM-EDX measurements (Figure 1 and



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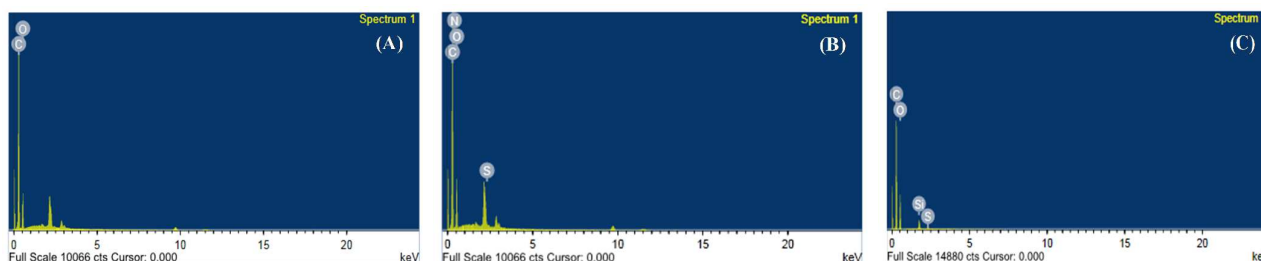
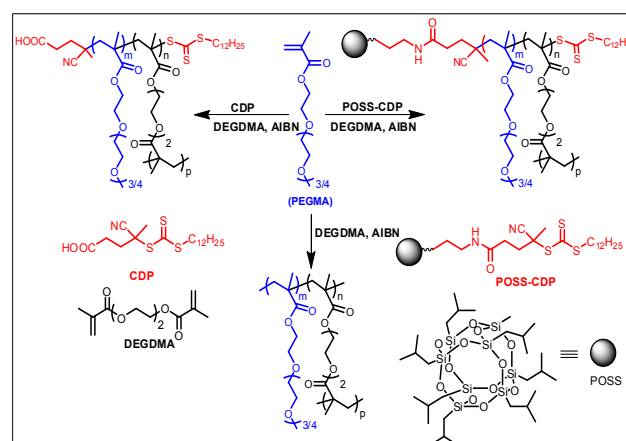


Fig. 1 SEM-EDX spectra of (A) F25, (B) R25, and (C) RP25.

Figure S2). The freeze dried gel material was pasted on carbon tape and coated with carbon powder for 1 min just prior to the analysis. Clear appearance of silicon along with carbon, oxygen and sulphur atoms confirms the successful incorporation of POSS moiety into the RP gel matrix (also see Fig. S2 for RP35 hydrogel). Determination of elemental composition confirmed presence of silicon only in the RP series. As expected, sulphur was present only in RAFT made hydrogels. Solid state ^{13}C CP/MAS NMR was also used for the further confirmation of POSS segment in the hydrogel matrix. Fig. S3 displays strong carbon resonance signals at 75.1–67.3, 59.4 and 45.1 ppm from $-\text{OCH}_2\text{CH}_2\text{O}-$, $-\text{C}(\text{O})\text{OCH}_2-$ and $-\text{OCH}_3$ carbons, respectively. Those signals are present in both R25 and RP25 hydrogels. Two new broad carbon resonance signals appeared in the case of RP25 at 31.5–21.6 ppm regions, due to the isobutyl group attached in each corner of the POSS moiety.

Next, thermal stability of hydrogels were studied by TGA analysis. In general, hydrogels showed two step degradations (Fig. S4). First, side chain ester groups decompose and then residual main chains undergo degradation.³¹ Although RP25 and RP35 showed two steps degradations, RP50 gave single

step decomposition and most probably both side chain and main chain degradations merged here. In the CDP based hydrogels, thermal stability increases marginally with the increasing [monomer]/[cross-linker] ratios. On the other hand,



Scheme 1 Synthesis of thermo responsive hydrogels based on PEGMA via FRP and RAFT techniques in DMF at 70 °C.

Table 1. Synthesis of PEGMA containing thermoresponsive hydrogels in DMF at 70 °C.

Run	Gel composition [PEGMA]/[DEGDMA] /[CDP]/[AIBN]	Gelation time (min)	Conversion (%) ^d	Equilibrium swelling ratio ^e
F25	25:2:-:0.15 ^a	2	99	1.1
F35	35:2:-:0.15 ^a	3	99	2.1
F50	50:2:-:0.15 ^a	5	98	2.4
R25	25:2:0.5:0.15 ^b	35	91	2.0
R35	35:2:0.5:0.15 ^b	40	89	2.9
R50	50:2:0.5:0.15 ^b	42	87	3.5
RP25	25:2:0.5:0.15 ^c	39	90	1.7
RP35	35:2:0.5:0.15 ^c	42	89	2.1
RP50	50:2:0.5:0.15 ^c	42	89	2.5

^a Prepared by FRP method using [PEGMA]/[DEGDMA]/[AIBN]. ^b Synthesized by RAFT technique using [PEGMA]/[DEGDMA]/[CDP]/[AIBN]. ^c Prepared by RAFT method using [PEGMA]/[DEGDMA]/[POSS-CDP]/[AIBN]. ^{d,e} Conversion and equilibrium swelling ratio were measured gravimetrically at room temperature.

thermal stability of RP25 was reasonably higher than the RP50 due to two key factors: firstly, the higher [monomer]/[cross-linker] ratio (enhanced cross-linking density due to subsequent progress of [monomer]/[cross-linker] ratio) and secondly, the net weight fraction of sterically crowded POSS segments which make the gel stiff *via* tighter linkage with the monomer chains.⁷

Thermo responsive behavior of hydrogels

Since, PEGMA based macromolecular structures showed thermo-responsiveness,³² we expect thermoresponsive behavior in the resulting hydrogels. The optical transparency of hydrogels depends upon the structural homogeneity and the gelation mechanism.³³ The clarity and transparency of the FRP gels remained higher in DMF as well as in water whereas the RAFT gel contained the characteristic yellow color in DMF

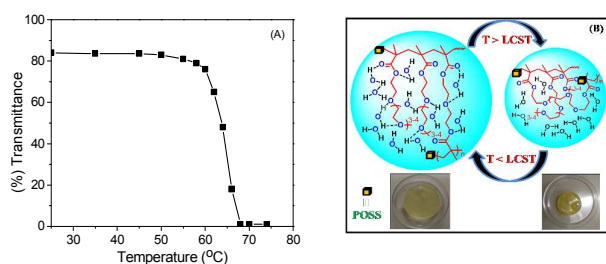


Fig. 2 Plot of percentage transmittance (%T) versus temperature in aqueous medium for RP50 (A) and pictorial representation of temperature induced deswelling-reswelling mechanism of POSS containing thermoresponsive hydrogels (B).

due to trithiocarbonate functional groups present in the CDP moiety.³⁴ Apart from that, the transparency of the gel increases from F25 to F50 as cross-linking density decreases. Similar trend was also followed in the RAFT gels. We have measured % transmittance (%T) at different temperatures for hydrogels by UV-visible spectroscopy. A broad temperature induced phase transition occurred for RP50 (Fig. 2A) and 50% reduction of %T was observed at 64 °C. Since the content of hydrophobic POSS moiety is comparatively low in comparison to highly hydrophilic PEGMA segments, as a result critical temperature induced phase transition remain unchanged compared to the LCST of PPEGMA homopolymer.³⁵ Since transparency of the hydrogel gradually decreases from RP50 to RP25 due to higher cross-linking density; as a consequence we could not measure thermoresponsive behavior of RP25 and RP35. However, F50 and R50 hydrogels showed similar 50% reduction of %T at around 64 °C (data now shown here). Above 64 °C, favorable interactions *via* hydrogen bonding between the side-chain ethylene oxide units in the hydrogel and water molecules are broken and water molecules are expelled from the gel network. Therefore, size of the gel is reduced in response to an elevation of temperature (Fig. 2B). Hence, in the next stage we studied swelling kinetics at room temperature (22 °C), which is well below the critical temperature induced phase transition of these hydrogels.

The comparison of swelling kinetics

First, the SR_e values of synthesized hydrogels of three different sets (FRP, CDP based and POSS-CDP based) have been investigated in DI water at 22 °C. A measured amount of dried hydrogel was soaked in DI water at 22 °C for 48 h to reach equilibrium swelling. Then the swelled gel was taken out from water, wiped with moist tissue paper and weighed. The SR_e values of all hydrogels are represented in the Table 1. It has been observed that the SR_e for the PEGMA containing hydrogels prepared using CDP showed higher value than the FRP and POSS-CDP based hydrogels at various corresponding [PEGMA]/[DEGDMA] ratios under ambient condition. At the same time, the SR_e value increases with the increasing [PEGMA]/[DEGDMA] ratios. Swelling behavior of polymer gels typically depends upon the polarity of solvents, polymeric backbone and pendants, the extent of cross-linking and gelation mechanism.²⁹ RAFT based hydrogels showed higher SR_e owing to their more homogeneous 3D network structure

by reducing the collapsed nanogel domains compared to hydrogel prepared by FRP method.³⁶ In Fig. 3A, it is interesting to note that CDP based RAFT hydrogels showed higher SR_e than POSS-CDP based RAFT hydrogels by generating better hydrophilic water permeable channel. This phenomenon can be illustrated by the fact that highly hydrophobic POSS domains aggregated inside the gel domain in presence of DI water which might occupy some free space in between polymer network. These free spaces would otherwise have been site for hydrophilic interaction between polymeric network and water molecules. These serve as sites for hydrophobic aggregation and additional physical cross-linking

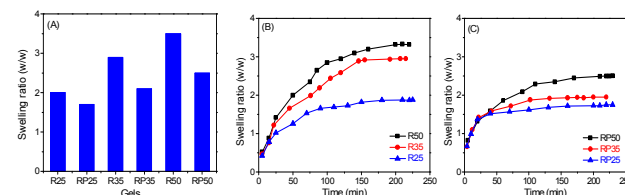


Fig. 3 (A) Comparison of equilibrium swelling ratios for CDP and POSS-CDP based hydrogels. Swelling behavior of (B) CDP and (C) POSS-CDP based hydrogels at 22 °C as a function of time. Error range ($\pm 4\%$) for triplicate experiment.

by restricting penetration of solvent into it. Consequently less than expected amount of water is absorbed by POSS-CDP based gels than the only CDP mediated hydrogels.

The swelling kinetics of hydrogels has been investigated with respect to time at 22 °C as illustrated in Fig. 3. It has been observed that swelling ratio of CDP based gel sharply increased from R25 to R35 to R50 with respect to time (Figure 3B) and gets saturated after a particular time (150, 150 and 190 min for R25, R35 and R50, respectively). A similar trend was also followed by the POSS-CDP gels (Fig. 3C) and FRP gels (Fig. S5). We restricted our study upto [PEGMA]/[DEGDMA]/[POSS-CDP] = 50/2/0.5 ratio because at higher ratios the effect of steric bulk of hydrophobic POSS nanosphere on swelling/deswelling rate diminished, due to the increasing amount of PEGMA segment compared to POSS-CDP.

Comparison of deswelling kinetics

In the next stage, deswelling kinetics study of hydrogels was conducted at two different temperatures (see above thermoresponsive behavior of hydrogels section): 60 °C (below the LCST) and 70 °C (above the LCST). Fig. 4 shows deswelling

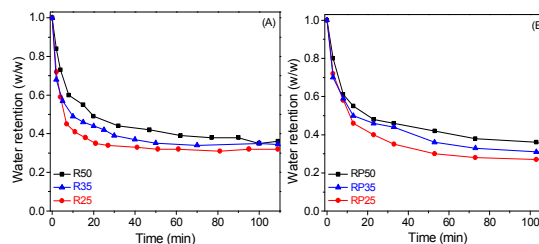


Fig. 4 Comparison of water retention upon deswelling of CDP (A) and POSS-CDP (B) based hydrogels at 60 °C with varying cross-linker densities. Error range ($\pm 4\%$) from triplicate experiments.

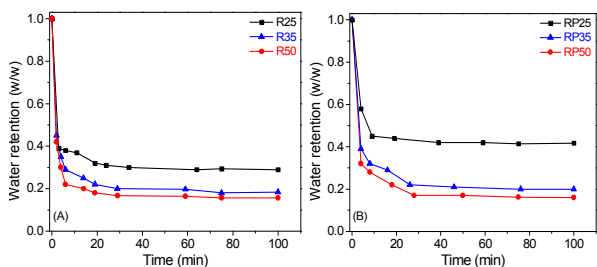


Fig. 5 Comparison of water retention upon deswelling of CDP (A) and POSS-CDP (B) based hydrogels at 70 °C as a function of time. Error range ($\pm 4\%$) from triplicate experiments.

kinetics measured at 60 °C for POSS-CDP and CDP based hydrogels, where at the early stage (0-10min) POSS-CDP based gels dehydrate at a faster rate than the CDP based gels. This happened possibly due to the presence of phase separated hydrophobic POSS microdomains in the POSS-CDP based gels. Initial water expulsion by POSS moiety from polymer matrix leads to randomisation of chains with agglomeration of dehydrated pendant chains into hydrophobic clusters that cause the collapse of macrogel. These agglomerated POSS domains create channels throughout the gel matrix that facilitate expulsion of water. Additionally RP25 expels most water molecules, followed by RP35 and RP50. The same trend is also observed among CDP based gels, where R25 has given out highest amount of water molecules followed by R35 and R50. This observation implies that higher rate of deswelling is associated with increasing cross-linking density of polymer matrix. Densely cross-linked regions tend to lose hydrophilic interaction between polymer chains and water easily.³⁷ Thus, RP25 with highest [cross-linker]/[monomer] and [POSS-CDP]/[monomer] ratio exhibited maximum deswelling while RP50 with lowest [cross-linker]/[monomer] and [POSS-CDP]/[monomer] exhibited lowest deswelling. Accordingly, water retention is highest in RP50 and lowest in RP25 gel networks.

More interestingly, deswelling rate measured for RAFT gels at 70 °C shows reverse trend when compared with the deswelling kinetics at 60 °C (Fig. 5). RP50 deswells the most while RP25 the least and RP35 shows moderate deswelling (Fig. 5B). Similar trend is also observed in Fig. 5A for CDP based hydrogels. This can be explained considering the formation of 'skin layer' and their subsequent rupture at higher temperature (70 °C).³⁷ **Error! Bookmark not defined.** 'Skin layer' is nothing but the crumbled polymer network at the surface on removal of water molecules from hydrogel surface preventing further water removal from the gel matrix. At higher temperature rapid deswelling occurs from the surface of hydrogel, followed by collapse of network at the surface where phase transition occurs rapidly. The tendency towards formation of thick impermeable "skin layer" increased with increasing the cross-linking density. Thus, RP25 and R25, both of which have highest [cross-linker]/[monomer] ratio develop thick layer on the surface which restricts water loss and exhibit maximum water retention. Both RP35 and R35 undergo

moderate deswelling, while RP50 and R50 with least [cross-linker]/[monomer] ratio undergo maximum deswelling. Due to lower content of POSS in RP50 and RP35, the effect of POSS moiety is not pronounced and extent of water loss is almost same for both the pairs RP50, R50 and RP35, R35. However, owing to high content of POSS in RP25, effect of hydrophobic POSS nanodomains become prominent and it adds on to the effect of skin layer preventing further water loss.

Comparison of reswelling kinetics

The reswelling process is one of the key parameter for evaluating the properties of the hydrogel which includes: 1) the diffusion of the water molecules into the 3D gel network structures, 2) the relaxation of hydrated polymer chain during deswelling process, and 3) the expansion of the polymeric network structures *via* interaction with water molecules.³⁸ Figure 6 illustrates the reswelling behavior of RAFT made hydrogels at 25 °C as a function of time. It is interesting to observe that the water uptake vs time profile follows sigmoidal pattern, which indicates that the surface water diffused rapidly into the 3D polymer matrix.^{39,40} In Fig. 6, it has also been clearly observed that gels can reabsorb water after deswelling the hydrogels in hot water at 70 °C for overnight. The observed

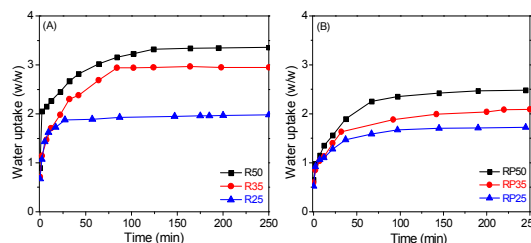


Fig. 6 Reswelling kinetics of the (A) CDP and (B) POSS-CDP based hydrogels as a function of time. Error range ($\pm 4\%$) from triplicate experiments.

lower reswelling ratio as compared to initial value of dried gel can be attributed to the strong hydrophobic interaction among the collapsed and entangled polymer chains; as a result of which reswelling became difficult.⁴¹ The water uptake capacity sharply decreased with increasing the [monomer]/[cross-linker] ratio for both the hydrogel systems. The possible reason can be increased cross-linking density and enhanced heterogeneity in the gel network throughout the deswelling kinetics. During reswelling, R50, R35 and R25 showed SR_e of 3.5, 2.9 and 1.9, respectively, whereas the RP50, RP35 and RP25 showed SR_e values as 2.5, 1.9 and 1.5, respectively. The observed results illustrate clearly that the higher content of POSS segment can affect the reswelling ability of the hydrogel matrix.

Morphology of the hydrogels

The interior morphology and the pore sizes of the hydrogel matrix can be examined by SEM. The structural porosity of the hydrogel matrix depends upon various parameters such as the nature of the monomer, cross-linking density, gelation mechanism, etc.⁴² Fig. 7 clearly demonstrates the porous

interior morphology of the F50, R50 and RP50 hydrogels. The SEM micrograph showed some pores generated after ice (acting as pore templates) diffused out of the freeze dried hydrogel matrix during sample preparation. The size of the pores is not uniform in F50 and it forms highly dense interconnected channels that can happen due to its uncontrolled gelation mechanism which enhance the heterogeneity and structural irregularity into the structure.^{37,43} Whereas, the size of the pores are more uniform in R50 rather than RP50, that may happen due to introduction of sterically bulkier POSS moiety. The highly hydrophobic POSS moiety occupy some space into the gel network which can reduce the interaction between the hydrophilic PEGMA segments with water molecules and enhance the structural heterogeneity due to its self aggregation behaviour and as a result the size of the pores are not well uniform which has direct relation on water holding capacity.

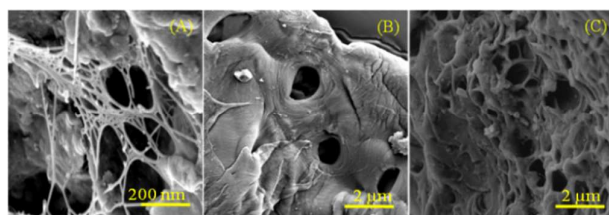


Fig. 7 FE-SEM images of (A) F50, (B) R50 and (C) RP50 hydrogels.

Rheological behavior

The mechanical property of the hydrogels can be triggered either by changing the cross-linking density by varying the [monomer]/[cross-linker] ratio or by introducing the organic/inorganic hybrid materials as a guest molecule. Therefore, mechanical strength of the RAFT made cross-linked swelled hydrogels was studied by the rheological experiments. Fig. 8 illustrates the strain sweep experiment to measure the G' and G'' at room temperature in order to establish the linear viscoelastic regime for both CDP (R25) and POSS-CDP (RP25) based swelled hydrogels. We observed that the R25 gel can bear up to 70 % strain, whereas RP25 can bear only 42 % strain even though both are prepared *via* RAFT polymerization techniques keeping all conditions unchanged except the CTA. The enhancement of G' in RP25 (7900 Pa) in comparison to R25 (6020 Pa) may be attributed to tighter linkage with the polymer chains through sterically crowded POSS segments. But at the same time the heterogeneity of the gel matrix was also improved which disrupt the regular microdomains of the hydrogel. As a consequence the stability with respect to strain decreases in comparison to more homogeneous and regular network structure of R25. Also, higher G' value than the G'' within the linear viscoelastic region indicated that the rheological behaviour in the swelled gel is controlled by an elastic property rather than a viscous property.⁴⁴ Note that the G' values of these hydrogels are much higher than the hydrogel composed of PEG vinyl sulfone cross-linked with PEG-diester-dithiol.⁴⁵

In the next stage, we carried out frequency sweep experiment (Fig. 9) of swelled hydrogels at a fixed strain (2 %), which is

reasonably lower than the deformation limit in both types of RAFT made gels. In all cases G' showed higher value than G'' and was independent of applied frequency (data not shown here); clearly demonstrated the viscoelastic rigid behavior of cross-linked gels. Figure 9A demonstrates that G' value sharply increased from R50 to R25 and exactly similar trend was also followed by POSS containing gels (Fig. 9B). Since, cross-linking density, the key factor for enhancing the mechanical strength, sharply increased from R50 to R25, as a result G' value was increased accordingly. But in Fig. 9B, G' values of POSS modified gels are somewhat higher than only CDP showed higher value than the G'' , which is independent of angular frequency. The G' values of POSS modified swelled gels are higher than the only CDP based gels (Fig. 9A) even at same [monomer]/[cross-linker] ratios. Therefore, these facts clearly demonstrate that the mechanical strength was influenced not only by the higher [monomer]/[cross-linker] ratios but also with associated increasing chain entanglement due to sterically crowded POSS segments.

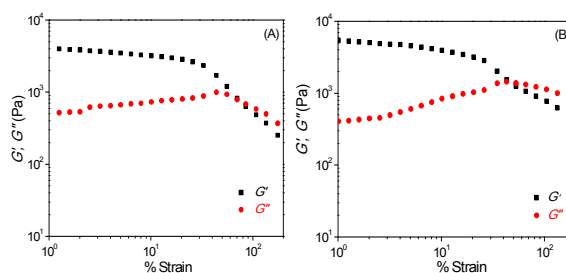


Fig. 8 Storage modulus (G') and loss modulus (G'') versus strain sweep with R25 (A) and RP25 (B) hydrogels.

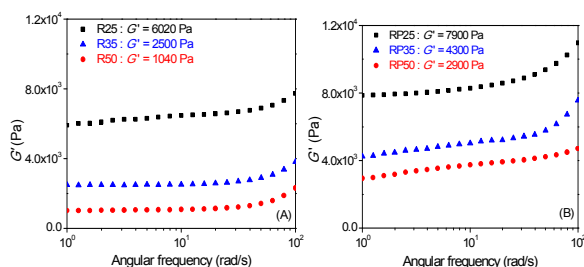


Fig. 9 Storage modulus (G') versus angular frequency (strain: 2%) of CDP based (A) and POSS-end capped CDP hydrogels at different cross-linking ratios (B).

Conclusions

In this study, we have successfully synthesized covalently cross-linked thermoresponsive hydrogels with higher mechanical stability by employing PEGMA as a monomer and POSS-CDP as RAFT agent *via* RAFT polymerization techniques in the presence of DEGDM as cross-linker. During the RAFT polymerization, CDP and POSS-CDP were applied as CTAs for hydrogels preparation and the trends in swelling, deswelling and reswelling behaviors of RAFT hydrogels have been studied in detail. The swelling capability of the hydrogels was significantly perturbed due to the introduction of POSS microdomains through its sterically crowded organic vertex and therefore showed somewhat lower swelling ratio than the only



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CDP based hydrogels for same [monomer]/[cross-linker] ratios. Water retention capacity of hydrogels increased with the increasing content of POSS pendants due to the effect of hydrophobic POSS nanodomains that adds on to the effect of skin layer preventing further water loss. Interestingly, the reswelling ability of the hydrogels was not disturbed by POSS moieties. The POSS moiety reduced the homogeneity and structural porosity of the hydrogels, effectively reflected from its SEM images. Within this viscoelastic range G' always showed higher value than the G'' , which is independent of angular frequency. The G' values of POSS modified swelled gels are higher than the only CDP based gels at same [monomer]/[cross-linker] ratios, indicating mechanical property enhancement by POSS pendants. Therefore, thermoresponsive hydrogels with tunable mechanical stability though chain end functionalization might have potential application in various fields.^{6,46}

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For “Table of contents entry”**POSS Induced Enhancement of Mechanical Strength in the RAFT Made****Thermoresponsive Hydrogels**

Ujjal Haldar, Mridula Nandi, Binoy Maiti and Priyadarsi De*

In this study, covalently cross-linked thermoresponsive hydrogels were prepared with higher mechanical stability by introduction of polyhedral oligomeric silsesquioxane (POSS) moieties.

