

Supporting Information

Table 1. Molecular weight, polydispersities, and initiator efficiency values from the polymers grafted from the surface of the silica gels. The GPC was calibrated with well defined PMMA standards.

Time (h)	Molecular weight (Mw)	Molecular Weight (Mn)	Molecular weight (Mp)	PDI	Initiator Efficiency
6	20390	13122	12941	1.55	21.4
20	43013	34983	51992	1.22	25.3
30	63284	37637	87038	1.68	24.6
40	75246	42895	50645	1.82	33.0
Control ^a 20 h	42570	34327	50645	1.24	30.7

a) Control experiment: PMMA obtained from solution polymerization using non-bound initiators after 20 hours of time: M_w 42570, PD 1.24.

Table 2. Summary of the amount of copper which remained within the silica aerogel composites after SCD.

Sample ID	Density (g/cm^3)	Molecular Weight (Mw)	PPM ($\mu\text{g/g}$) Cu in Aerogel Comp.
PMMA/Silica Aerogel Comp.	0.110	20,390	1334.55
PMMA/Silica Aerogel Comp.	0.171	43,013	1525.81
PMMA/Silica Aerogel Comp.	0.244	63,284	1533.88

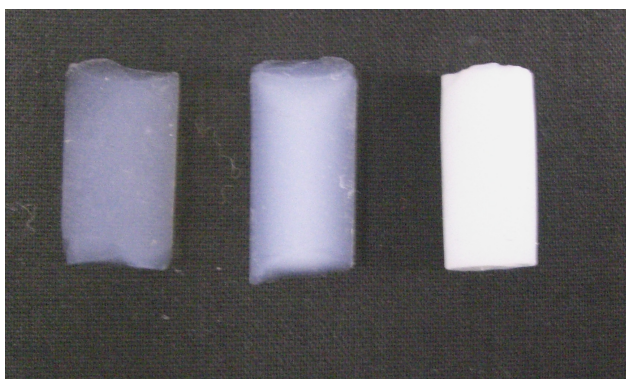


Figure 1. Images of initiator-modified silica aerogel (left), PMMA silica aerogel composite (6 hours) with a density of 0.138 g/cm^3 (center) and PMMA silica aerogel composite (40 hours) with a density of 0.350 g/cm^3 (right).

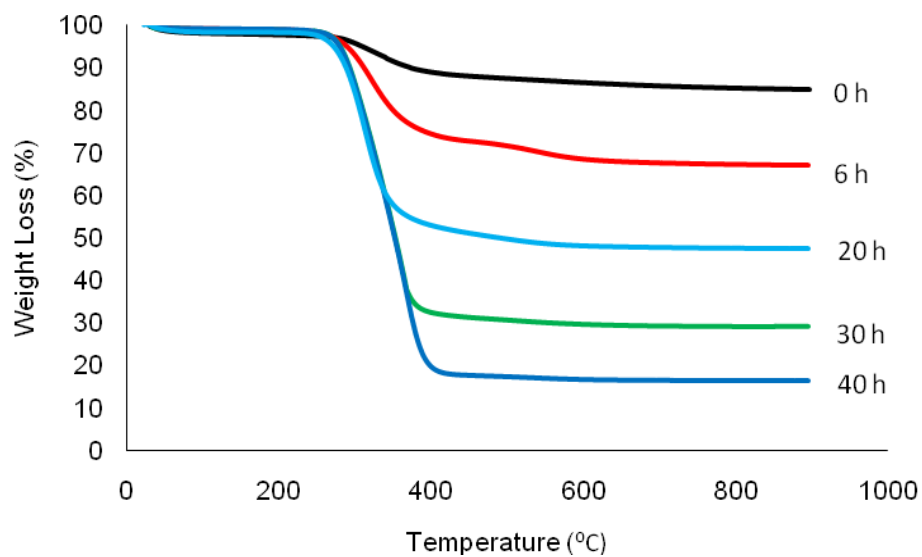


Figure 2. Thermal gravimetric analysis for weight loss determination of silica aerogel composites with polymerization times ranging from 6 h to 40 h.

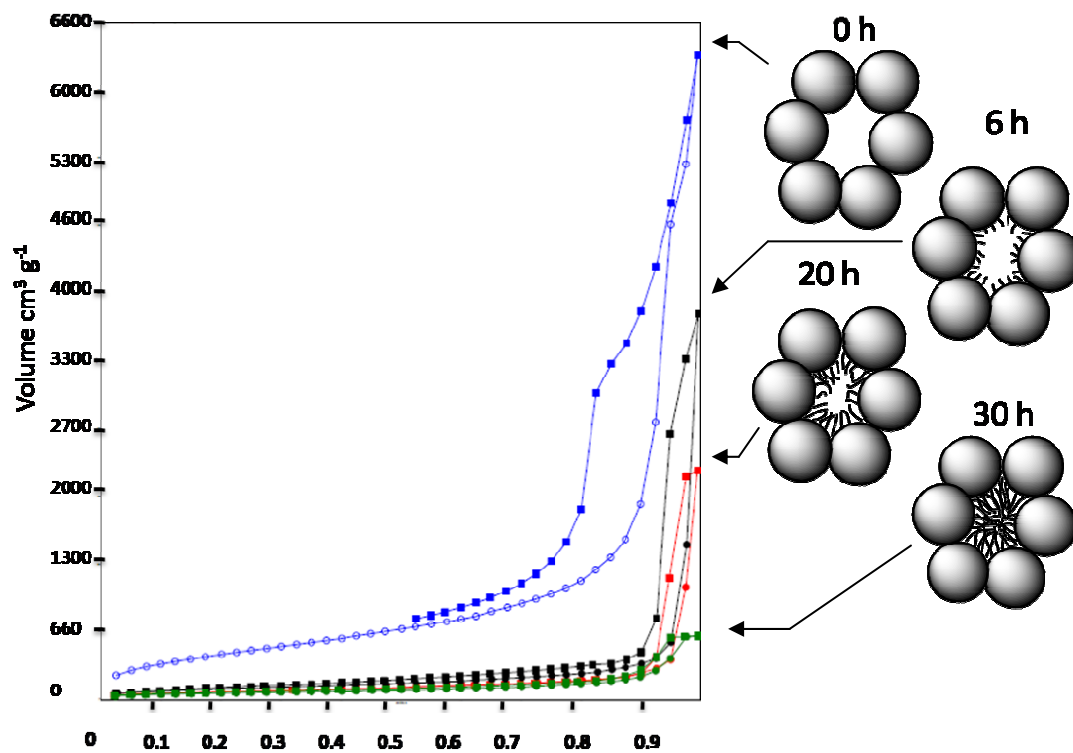


Figure 3. Nitrogen adsorption-desorption isotherms PMMA silica aerogel composites (0 h, blue; 6 h, black; 20 h, red; 30 h, green). The volume of gas adsorbed decreases as the density of the composites increases.

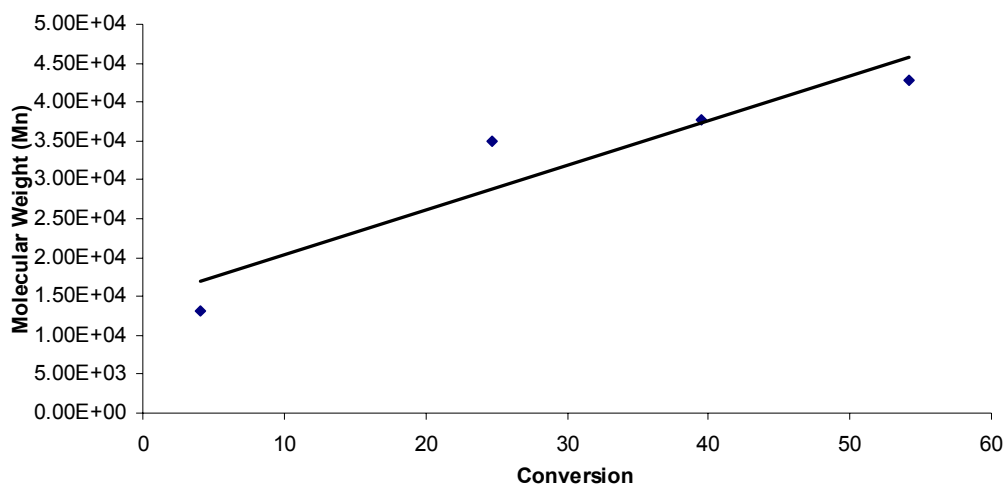


Figure 4. Plot of the molecular weight (M_n) versus the conversion of monomer to polymer.

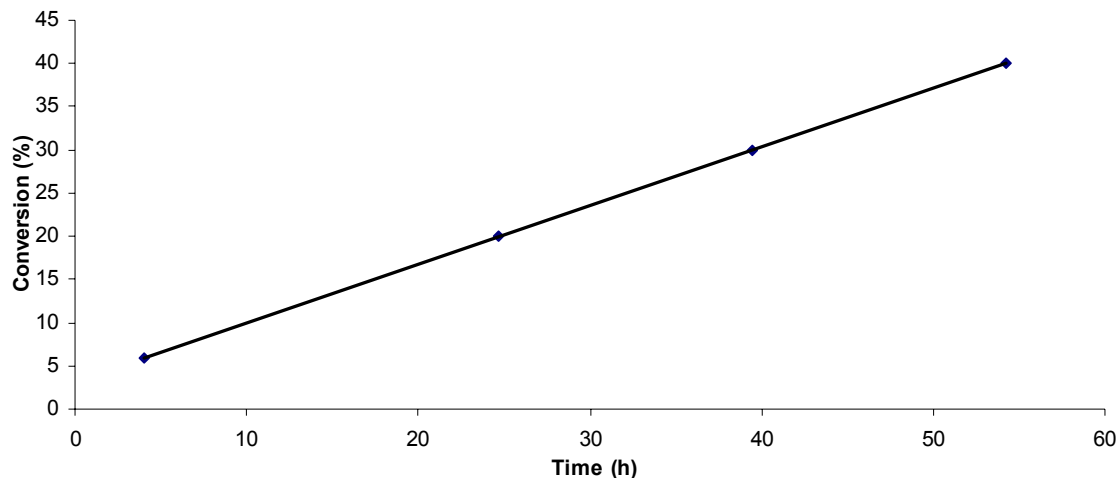


Figure 5. Plot of the monomer conversion (based on Mn) versus the polymerization time.

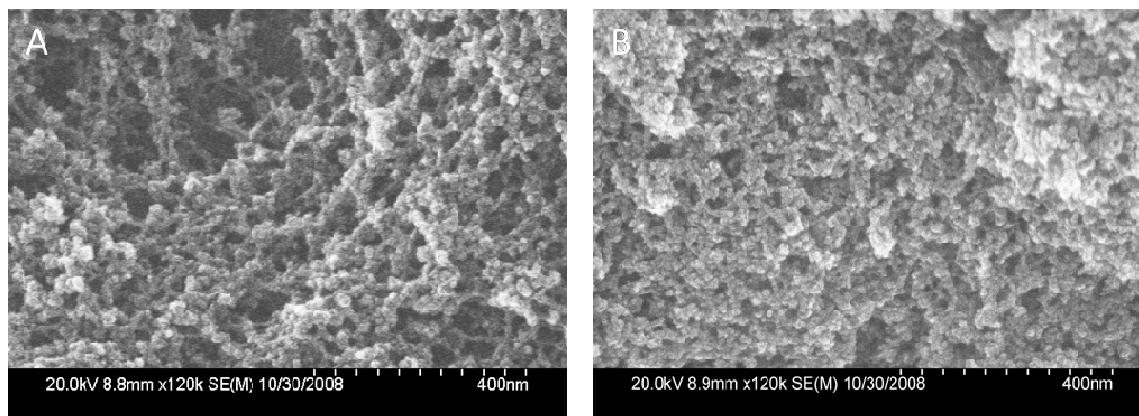


Figure 6. SEM images of A) PMMA silica aerogel composites with a density of 0.117 g/cm^3 show a thickening of aerogels aggregate structure. B) Further thickening can be achieved by extending the polymerization time, resulting in a PMMA silica aerogel composite with a density of 0.220 g/cm^3 .

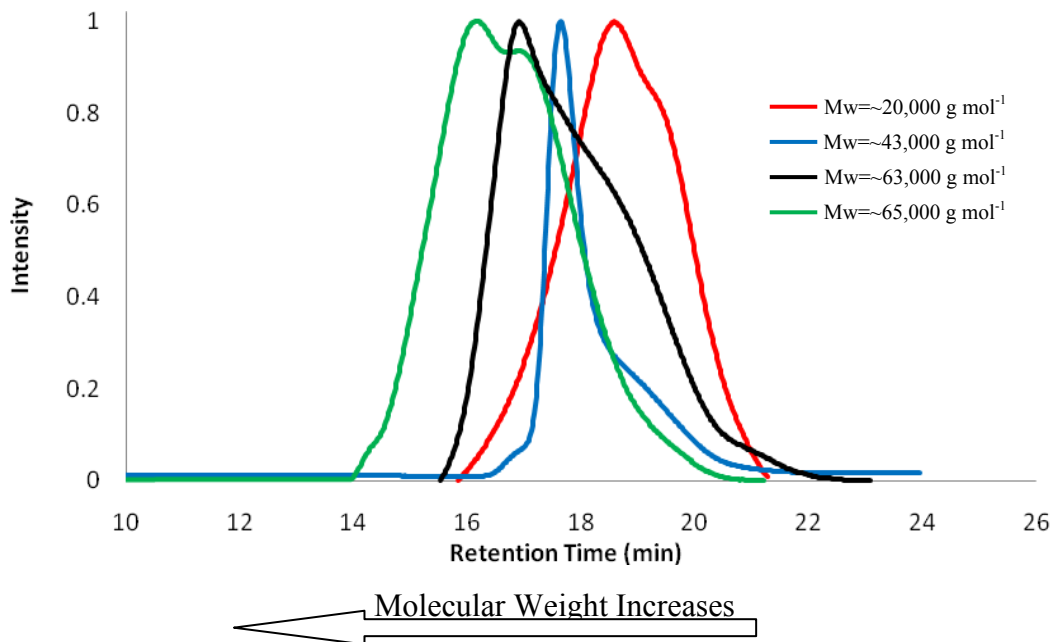


Figure 7. Retention time of PMMA isolated from ATRP-modified silica aerogels after various polymerization times. As retention time increases, molecular weight of the polymer decreases.

Materials:

Tetramethoxysilane (98%), anhydrous methanol (99.5%) toluene (99%), copper (I) bromide, copper (II) bromide, 4,4'-dinonyl-2,2'-dipyridyl (97%), allyl alcohol (98.5%), α -bromoisobutyryl bromide (98%) and aluminum oxide were obtained from Sigma-Aldrich Chemical Company. Methyl methacrylate (99%) was purchased from Polysciences, Inc. and filtered through alumina to remove inhibitors prior to polymerizations. Ammonium hydroxide (1 N) was used as received from VWR.

Platinum-divinyl tetramethyl-disiloxane in xylene (~2 wt% Pt) was purchased from Gelest Inc.

Synthesis of Allyl 2-Bromoisobutyrate [12]:

To a 500 mL three-neck, round bottom flask equipped with a magnetic stir bar, condenser, equalizing addition funnel and a glass stopper THF (100 mL), allyl alcohol (15.78 g, 0.2721 mol) and triethylamine (27.51 g, 0.2713 mol) were added. The round bottom was fitted with a condenser, equalizing addition funnel and a glass stopper. After cooling the solution to 0 °C in an ice bath, α -bromoisobutyryl bromide (50.00 g, 0.2209 mol) in THF (50 mL) was added drop-wise from an addition funnel over a 30 minute period with an immediate formation of a white precipitate. The mixture was stirred overnight which the temperature was slowly warmed to room temperature. The reaction was worked up by the addition of diethyl ether (200 mL) followed by deionized water (200 mL). The aqueous layer was removed and the organic layer was washed with deionized water (2x, 200 mL), followed by wash with saturated sodium bicarbonate (2x, 200 mL) and finally deionized water (100 mL). The ether solution was concentrated *in vacuo*. Product was isolated by distillation (60 °C, 500 mmHg) to obtain allyl 2-bromo-2-methylpropanoate, a colorless oil (40.29 g, 0.1912 mol, yield = 89%). ¹H NMR (500 MHz, CDCl₃) δ 5.85 (m, $J = 9$, 1 H) δ 5.2 (quartet of d, $J = 31$, 2 H), δ 4.6 (dd, $J = 9$, 2 H), δ 1.85 (s, 6 H); ¹³C NMR (125 MHz, CDCl₃) δ 170.93, 131.28, 118.24 66.06, 55.42, 30.57; MS: LRMS (EI); 207.01, 192.96, 148.96, 127.06, 120.94, 109.06, 99.07, 81.07, 70.03, 41.02.

Synthesis of 3-(triethoxysilyl)propyl-2-bromo-2-methylpropanoate:

To allyl 2-bromoisobutyrate (10.00 g, 0.04802 mol) in a 25 mL round bottom flask triethoxysilane (9.520 g, 0.05791 mol), platinum-divinyl tetramethyl-disiloxane (200 μ L) and a stir bar were added. The round bottom flask was fitted with a condenser that was fitted with a drying tube and placed into an oil bath at 80 °C. The solution bubbled for 1 minute upon heating and was left at that temperature for 12 h, at which point it had turned a dark brown color similar to tea. The reaction was worked up by distillation (130 °C, 60 mmHg) to obtain 3-(triethoxysilyl)propyl-2-bromo-2-methylpropanoate (10.56 g, 0.02803 mol, yield = 60%). ^1H NMR (500 MHz, CDCl_3) δ 4.1 (t, $J = 8.5$, 2 H) δ 3.8 (q, $J = 19.5$, 6 H) δ 1.9 (s, 6 H), δ 1.65 (m, $J = 10.5$, 2 H), δ 1.2 (t, $J = 6$, 9 H), δ 0.65 (t, $J = 8.5$, 2 H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.47, 67.87, 58.35, 55.87, 30.75, 22.02 18.23, 6.42; MS: LRMS (EI) 373.12, 371.23, 339.47, 265.42, 221.83, 167.35, 123.52, 69.56, 41.39.

Gels with Surface-Modified ATRP Initiators:

A solution containing tetramethoxysilane (TMOS, 0.5500 g, 3.600 mmol) and 3-(triethoxysilyl)propyl-2-bromo-2-methylpropanoate (0.03560 g, 0.0960 mmol) diluted to 1.8 mL with anhydrous methanol and mixed for one minute with a second solution containing aqueous 1 N ammonium hydroxide (NH_4OH , 0.2590 mL, 0.7200 mmol) which was diluted to 1.8 mL with anhydrous methanol in a poly(propylene) container (4 mL) at room temperature. The final volume was 3.6 mL. Gelation occurred within ~7 minutes. Gels were aged at room temperature for 48 h followed by 48 h at 50 °C. Once removed from the poly(propylene) container, the methanol was slowly exchanged with

toluene over 48 h for ATRP. If processed for silica aerogel formation, gels were dried using the standard procedure for supercritical carbon dioxide drying affording a ATRP initiator-modified silica aerogel (0.255 ± 0.004 g, yield 110%). IR (KBr) 3498, 2961, 2857, 1750, 1625, 1435, 1089, 831, 608 cm^{-1} .

ATRP Polymerizations:

Initiator-modified gels were placed into a Schlenk flask along with toluene (20 mL). The Schlenk vial was sealed and purged with argon for 30 minutes. In a separate vial the monomer was deoxygenated by bubbling argon for 30 minutes. A third vial containing CuBr (0.05700 g, 0.4012 mmol), CuBr₂ (0.004002 g, 0.02012 mmol) and 4,4'-dinonyl-2,2'-dipyridyl (0.3271 g, 8.021 mmol) was evacuated and back-filled with argon (3x, 10 minutes). Then the deoxygenated monomer (0.01871 mol) was transferred into the vial containing the copper catalyst and ligands via syringe. Mixtures were sonicated at room temperature until a homogeneous red solution formed. Then the red solution was transferred into the schlenk flask under argon containing the gel in toluene via syringe. Solutions were allowed to equilibrate for 3 h, after which the Schlenk flask was placed into a thermostated oil bath at 85 °C. The time left in the oil bath depended upon the composite density desired. The density of the polymer composites can be controlled by varying the polymerization times. After a specific reaction time, the composite silica aerogels were removed from the vial and the toluene solution was slowly exchanged for methanol, which is needed for SCCD. Polymer composites were dried using SCCD. (Polymer free ATRP-modified silica aerogel 0.258 ± 0.003 , yield = 109%; 6 h

polymerization composite 0.328 ± 0.003 g; 20 h polymerization 0.728 ± 0.03 g). IR (KBr) 3488, 2963, 2857, 1734, 1608, 1515, 1463, 1412, 1090, 826, 653, 608 cm^{-1} .

Instrumentation:

Molecular weight of the PMMA grafted from the surface of silica aerogel was determined by size exclusion chromatography (SEC) performed in a tetrahydrofuran (THF) mobile phase with a Waters 1515 isocratic pump running three 5-m PLgel columns (Polymer Labs, pore sizes 104, 103, and 102 Å) at a flow rate of 1 mL/min. with a Waters 2414 differential refractometer and a Waters 2487 dual-wavelength UV-vis spectrometer. Molar masses were calculated using the Empower software (Waters), calibrating against lowpolydispersity linear poly(methymethacrylate) standards. The density of the aerogel composites was achieved by weighing the gel and dividing by the volume. The volume was determined by measuring the diameter and length of the gel with a micrometer. Mechanical property measurements were determined using a three-point flexural compression test with an Instron 5540 series single column testing system with a 100 N load cell set with a $0.04 \text{ inch}/\text{min}^{-1}$ crosshead speed. For each data point, 3 samples were prepared. Structural characterization was determined by ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy with a Bruker DRX-500 spectrometer (500 MHz; CDCl_3), and compound purity were accessed using a HP 5988A Gas Chromatograph/Mass Spectroscopy (GC/MS). Samples for SEM were sputter-coated with platinum and microscopy was conducted with a Hitachi S-4800 field-emission microscope. Copper determination was conducted on a Perkin Elmer Atomic Absorption analyzer, using an absorption wavelength of 324.8 nm. Surface area and pore sizes were

determined by nitrogen adsorption porosimetry of one representative sample. Samples were degassed at 30°C for 24 h under vacuum and analyzed with an Autosorb-1 porosimeter (Quantachrome Instruments) at 77 K.