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CROSSLINKING 3D ASSEMBLIES OF SILICA NANOPARTICLES (AEROGELS) BY SURFACE-INITIATED FREE RADICAL POLYMERIZATION OF STYRENE AND METHYLMETHACRYLATE

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Introduction

Quasi-stable, ultra-low density, three-dimensional assemblies of nanoparticles are referred to as aerogels. Aerogels are open-cell foams derived from supercritical fluid (SCF) drying of wet gels. Their large internal void space is responsible for low dielectric constants, low thermal conductivities and high acoustic impedance. At the same time though those materials are fragile and impractical for high load applications. The fragility problem has been addressed by casting a thin conformal polymer coating over the entire internal porous surface of the nanostructure.[1] That process is referred to as crosslinking. The coating connects chemically skeletal nanoparticles and renders interparticle necks wider. Thus, the internal void space is not compromised significantly, while the flexural strength of a typical monolith is increased by 300× for a nominal increase in density only by a factor of three. A major issue, however, is the fact that current preparation procedures for crosslinked aerogels involve several solvent exchange steps, which are expensive and must be eliminated before crosslinked aerogels become commercially viable. In order to eliminate solvent exchange steps, the reagents for the crosslinking process should be included in the sol, which in turn means that the crosslinking chemistry should be deconvoluted from the gelation chemistry (an ionic process). In this context, there are several chemistries involving nanoparticle surface modification for making core-shell structures. These methods span the entire range from layer-by-layer electrostatic assembly of oppositely charged materials,[2-6] to atom transfer radical polymerization,[7] and direct free radical polymerization of olefins from surface-bound initiators such as peroxides,[8] and AIBN.[9,10] By comparison, free-radical initiators have received the least attention as silica surface modifiers, while all literature examples concern asymmetric peroxide and AIBN derivatives, which are attached on silica only from one side. Such *monodentate* free-radical initiators would not work for our purposes, because upon homolytic cleavage they would produce one surface-bound radical, which is the desirable outcome, but they would also release a second radical in the mesopores. The polymer formed in the solution filling the mesopores will have to be removed, and that introduces more solvent exchange steps. For our purposes, we need *bidentate* free-radical initiators that will attach themselves on silica from both sides. In that regard, we report here the synthesis of AIBN analogue **1**
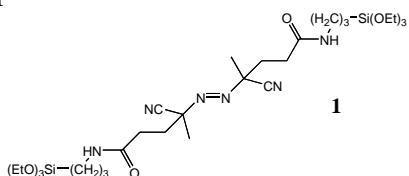

as well as its incorporation into silica, and the surface initiated polymerization of styrene and methylmethacrylate to yield conformal polymer coatings on the mesoporous surfaces of typical base-catalyzed aerogels.

Experimental

Materials. All reagents and solvents were used as received unless otherwise noted. Azobiscyano valeric acid (ABCA), ethylchloroformate, 3-aminopropyl triethoxy silane (APTES), tetramethoxysilane (TMOS), and ammonium hydroxide were purchased from Aldrich Chemical Co. Triethylamine was from Acros Chemicals and was further purified by distillation from calcium hydride. Anhydrous tetrahydrofuran (THF) was made by drying over lithium aluminum hydride. Styrene and methyl methacrylate (MMA) were from Aldrich Chemical Co. and were washed with 5% sodium hydroxide solution to remove the inhibitor, and purified by distillation at reduced pressure.

Synthesis of AIBN-silane 1 (Scheme 1): Azobiscyano valeric acid (ABCA, 1g, 0.00356 mol) was dissolved in 50 ml of anhydrous THF at -50°C in a cooled jacketed three-neck flask under dry and inert conditions (N_2). After 10 min, ethyl chloroformate (0.6822 ml, 0.00712 mol) and triethylamine (0.9918 ml, 0.00712 mol) were added with a syringe through a septum. After 20 min, APTES (1.6795 ml, 0.00712 mol) was added also with a syringe. The reaction temperature was raised to -10 °C. After 24 h, the reaction mixture was allowed to reach room temperature and was filtered under nitrogen. The filtrate was concentrated under reduced pressure, followed by addition of hexane. The precipitate was collected in a dry box under nitrogen and recrystallized from THF/hexane and dried under vacuum to give pure product **1** which was characterized by elemental analysis, ^{13}C and ^1H NMR. Compound **1** was stored as a 0.22 M solution in THF in a freezer to avoid self-condensation.
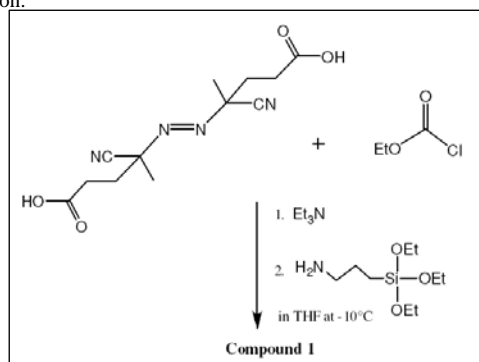
Scheme 1. Synthesis of the bidentate silane derivative of AIBN (compound **1**)

Preparation of crosslinked silica aerogels (Scheme 2): The stock solution of **1** in THF (0.22 M) was allowed to warm to room temperature and an aliquot (10.9 mL, 0.0024 mol) was placed in a round bottom flask and the solvent was removed under reduced pressure. The resulting solid was dissolved by addition of methanol (0.45 mL) and TMOS (3.46 mL, 0.022 mol). This is referred to as Solution A. A second solution (Solution B) was made by mixing 4.5 ml methanol, 1.5 ml distilled water and 40 µL ammonium hydroxide. Solution "B" was added into solution "A" and the mixture was poured into polypropylene molds (Wheaton polypropylene Omni-Vials, Part No. 225402, 1 cm in diameter). All solutions gel in 10-15 min, and newly formed wet gels were aged for 24 h at room temperature. The resulting wet gels were washed with acetone and were either dried with CO_2 taken out supercritically to obtain non-crosslinked silica aerogels, or were crosslinked with polystyrene and PMMA. For crosslinking, wet gels in acetone were further solvent-exchanged (3×, 8h) with toluene. Meanwhile, different concentrations of styrene in toluene were prepared (10 % v/v, 25 % v/v, 50 % v/v and 100 % pure). Several silica wet-gels incorporating **1** were further washed (3×, 8h) with different styrene solutions in toluene. Similar solutions were prepared with MMA, and gels were treated similarly. Gels were heated in the last olefin wash solution at 70°C for 8 h. Subsequently, gels were washed with fresh toluene (3×, 8h) and dried with SCF CO_2.
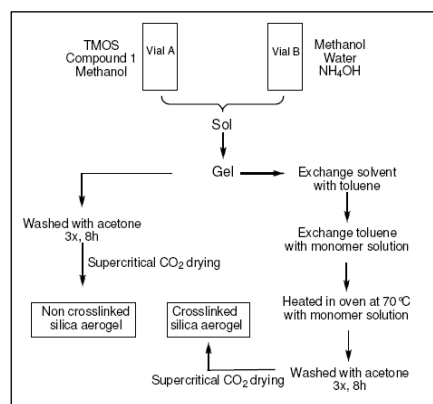
Scheme 2. Preparation of crosslinked silica aerogels

Results and Discussion

Heated with olefins in proper solvents, silica wet-gels decorated with radical initiator sites, act like macro initiators. Thus, thermally generated radicals initiate polymerization from the surface of silica. When radicals at the tips of growing chains meet, they combine and the radical process is terminated resulting in a conformal polymer coating on the silica surface.
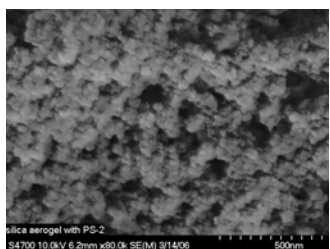

Figure 1. SEM of a silica aerogel crosslinked with polystyrene.

Indeed, despite a significant bulk density increase (from ~0.15 g cm^{-3} to ~0.35 g cm^{-3} upon crosslinking with styrene and up to 0.60 g cm^{-3} upon crosslinking with PMMA), microscopically (by SEM, Fig. 1) we can still distinguish the skeletal silica nanoparticles and the mesoporous space, consistent with a polymer grown conformally to the mesoporous surfaces, as planned. BET surface areas of aerogels crosslinked in pure monomer are in the range of 100-300 m^2 g^{-1} whereas the surface area in the case of crosslinked gels prepared at lower monomer concentrations are closer to those of native silica aerogels (1260 m^2 g^{-1}).

The existence of covalently bound polymer on the surface of silica nanoparticles was confirmed by infrared (IR) spectroscopy. Figure 2 shows the IR spectra of neat PMMA, of a crosslinked silica aerogel with PMMA (silica-PMMA), and of a non-crosslinked native silica aerogel monolith. Silica-PMMA exhibits the features corresponding to neat PMMA as well as those of non-crosslinked, native silica aerogel.
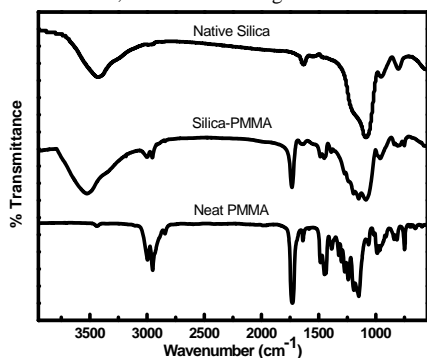
Figure 2. FTIR spectra of non-crosslinked (native) silica aerogel, silica aerogel crosslinked with PMMA and of neat PMMA.
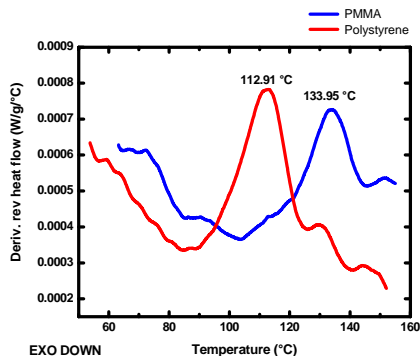
Figure 3. DSC of crosslinked silica aerogel with PMMA and polystyrene.

The shift in the glass transition temperature of surface bound polymer in comparison with neat polymer is in agreement with the literature (Fig. 3). In the case of polystyrene, T_g was shifted from 95 °C to 112.9 °C, whereas in case of PMMA, T_g was shifted from 105 °C to 133.95 °C.

Crosslinked monoliths demonstrate significantly improved mechanical strength over their native counterparts, in agreement with our previous findings.[1] Formal characterization of the mechanical properties is underway.

Conclusions

Surface initiated polymerization of olefins like styrene or MMA give rise to a covalently bound conformal coating on the mesoporous silica surfaces. The strength of those materials is enhanced compared to that of non-crosslinked silica aerogels. In addition to aerogels, the bidentate free radical initiator **1** paves the way for additional applications in the interface of sol-gel and polymer chemistry, with for example the preparation of more effective fillers for composite materials.

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