

Direct Formation of Aerogels by Sol–Gel Polymerizations of Alkoxysilanes in Supercritical Carbon Dioxide

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Sol–gel processing has proven to be an important method for producing amorphous, porous silica^{1–3} and polysilsesquioxane gels.⁴ Commercial applications of monolithic sol–gels have been limited, despite the advantages of mild reaction and processing conditions, due to shrinkage (and often cracking) of gels during drying. While a variety of processing techniques have been developed to minimize shrinkage and prevent cracking, one of the most successful is to avoid the capillary forces associated with air-drying altogether by drying the gel at a temperature and pressure above the critical point of the solvent.^{5,6} The resulting *aerogels* retain more of the original volume of the wet gel and are potentially useful insulating materials due to their low density, high surface area, and low thermal conductivity. However, the high temperature and pressures required for supercritical drying of gels in alcohols increase the costs and hazards associated with preparing a dry gel. Exchanging the original solvent in the gel for supercritical carbon dioxide (SCCD) permits drying at lower pressures and temperatures,⁷ but the required additional extraction step makes this technique (Figure 1) less attractive. We have simplified the preparation of aerogels by eliminating the organic (alcohol) solvent altogether by using SCCD as the sol–gel polymerization solvent. In this report, we describe the first sol–gel polymerizations of tetraalkoxysilanes and 1,4-bis(triethoxysilyl)benzene (BESP) in SCCD to give silica aerogels (Figure 2) and 1,4-phenylene-bridged polysilsesquioxane aerogels, respectively.

Recently, there has been considerable progress using SCCD as a solvent for free radical^{8–10} and Lewis acid-catalyzed^{11–13} polymerizations of vinyl monomers, and

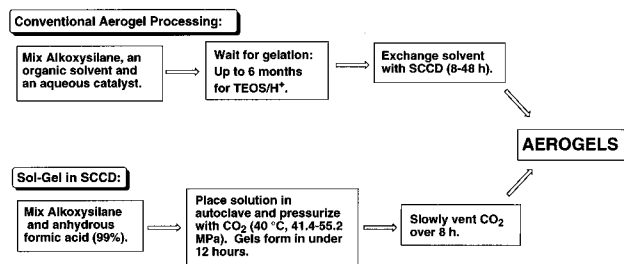


Figure 1. Schematic for preparation of aerogels. Conventional method (top) involves polymerization of a tetraalkoxysilane in alcohol to give a gel, exchange of SCCD for alcohol in gel and, finally, supercritical drying to give an aerogel. Direct polymerization in SCCD using formic acid (bottom) allows direct supercritical drying to aerogels without a solvent exchange.



Figure 2. Photograph of a monolithic silica aerogel (1 cm × 3.2 cm) prepared by polymerizing tetramethoxysilane (TMOS) in supercritical carbon dioxide (SCCD).

ring-opening polymerizations.^{14,15} This research is driven by the need to reduce VOCs and hazardous organic solvent waste in the polymer industry. This process has been extended to include condensation polymers such as polyesters^{16,17} and polysiloxanes. Because SCCD is a relatively nonpolar medium, sol–gel polymerizations in SCCD using standard formulations are not possible due to the large quantities of water necessary for the hydrolysis and condensation of the alkoxysilane monomers. Complete hydrolysis and condensation of tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) to silica requires a minimum of 2 equiv of H₂O or 7.2% (vol/vol) at 2 M monomer concentration. A minimum of 3 equiv of H₂O is needed to form gels from BESP, but because hydrocarbon-bridged triethoxysilanes form gels at lower monomer concentrations (0.4–0.8 M) than do tetraalkoxysilanes, this translates to only 2.2–4.4% H₂O (vol/vol). Alcohols are needed as sol–gel solvents primarily to permit mixing of water and the nonpolar

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Table 1. Surface Areas (Five Point BET) and Mean Pore Diameters (BJH) for Silica and Phenylene-Bridged Polysilsesquioxane Aerogels Prepared by (A) Sol–Gel Polymerization with Formic Acid Directly in SCCD, (B) Sol–Gel Polymerization with Formic Acid in Ethanol, Followed by SCCD Extraction and (C) Sol–Gel Polymerization in Formic Acid, Followed by SCCD Extraction^a

monomer	equiv of formic acid	(A) surface area (m ² g ⁻¹)	(A) mean pore diam (Å)	(B) surface area (m ² g ⁻¹)	(B) mean pore diam (Å)	(C) surface area (m ² g ⁻¹)	(C) mean pore diam (Å)
TMOS (1.9 M)	4	308	31	481	121	739	83
TMOS (1.9 M)	3	261	92	197	121		
TMOS (2.3 M)	6	268	35	533	107		
TEOS (2.2 M)	6	no gel	no gel	no gel	no gel		
BESP (0.4 M)	6	471	55	no gel	no gel	434	23
BESP (0.8 M)	6	586	24	18	51		

^a Data were obtained from 40-point nitrogen sorption isotherms obtained with a quantachrome autosorb-6 porosimeter on ground samples that were degassed at 100 °C.

alkoxysilane monomers to give homogeneous solutions. Thus, sol–gel polymerizations in nonpolar solvents such as benzene or cyclohexane would be possible only through formation of microemulsions or by generating the water as needed from a relatively hydrophobic precursor.

In light of recent successes in forming polyacrylates from emulsion polymerizations in SCCD,^{8,18–20} our initial attempts were directed toward formation of stable microemulsions of water, catalyst, and alkoxysilane in SCCD. We have successfully used this approach to prepare silica and silsesquioxane gels in nonpolar hydrocarbon solvents such as toluene.²¹ However, we were not able to identify conditions that would permit dispersion of sufficient water into SCCD to give homogeneous, monolithic gels. For example, introduction of a phase-transfer catalyst (NR₄OH·xH₂O, R = Me, butyl) to a solution of the tetraalkoxysilane or BESP, or their precondensed oligomers, and a surfactant (1–3%) in SCCD gave only low yields (<10%) of silica or bridged polysilsesquioxanes in the form of precipitates. The surface areas of these materials were low. For example, a phenylene-bridged polysilsesquioxane gel was obtained with a surface area of 21 m² g⁻¹.

It was possible to avoid the problems associated with the poor miscibility of water in SCCD and substantially reduce gelation times for TMOS by applying the “water-free” sol–gel polymerization technique recently reported by Sharp et al.^{22,23} Alkoxysilanes were shown to react with anhydrous formic acid to give silanols that can condense to afford the siloxane bonds necessary for creating a network polymer that will form a gel. The alcohol generated by the reaction is converted to the formate ester which could be recovered for recycling. SCCD and formic acid are completely miscible at the temperatures and pressures used in these experiments. TMOS or BESP mixed with formic acid (99%) readily dissolved in SCCD to give clear colorless solutions that gelled in less than 12 h. Although TEOS also formed homogeneous solutions (2 M) with SCCD and formic acid (2–4 equiv), no gels were obtained in the 12 h experiments.

In a typical experiment (Table 1), formic acid (2–4 equiv) was mixed with TMOS or TEOS. The resulting

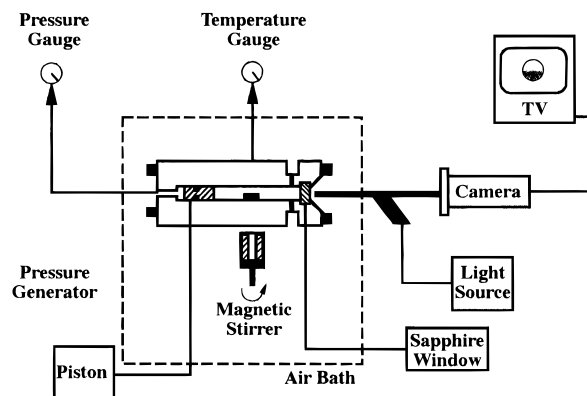
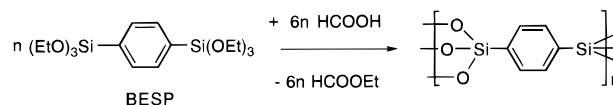
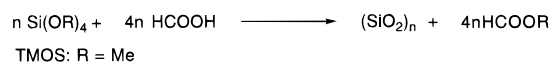


Figure 3. Schematic showing the autoclave used to prepare aerogels while permitting observation of the illuminated cell through a sapphire window. The autoclave was built by Walter J. Krug at John Hopkins University from Nitronic steel (5.7 cm o.d. × 1.59 cm i.d., 22 cm³ working volume, fitted with a 1.9 cm o.d. × 1.3 cm thick sapphire window).²⁵



solution of monomer and formic acid was quickly placed into an autoclave (Figure 3) that was charged with SCCD (35–40 °C, 41.4 MPa; 10 mL final volume) with stirring until a homogeneous clear, slightly amber solution was observed through the sapphire observation port (Figure 4a). Because the concentrations of silica gel precursors were necessarily high in order to form gels, the amount of formic acid required for the stoichiometric condensation was sufficiently large (23–36 wt % for TMOS; 13–19 wt % for BESP) for it to be considered as a cosolvent with SCCD. Gelation, which could be readily detected when the stir bar inside the autoclave was immobilized and the entire volume of the pressure vessel was filled with a translucent gel, occurred in under 12 h for TMOS (Figure 4b). After the TMOS-derived silica gels were aged for 12–18 h, the pressure was slowly released over 8–18 h to afford opaque white silica aerogels in nearly quantitative yield. Similarly, translucent, phenylene-bridged polysilsesquioxane gels were prepared by mixing BESP (0.2–0.8 M) with anhydrous formic acid (4–6 equiv) and dissolving the solution in SCCD. For comparison, TMOS, TEOS, and BESP were also polymerized with identical quantities of formic acid while substituting methanol or ethanol at ambient pressure and temperature for

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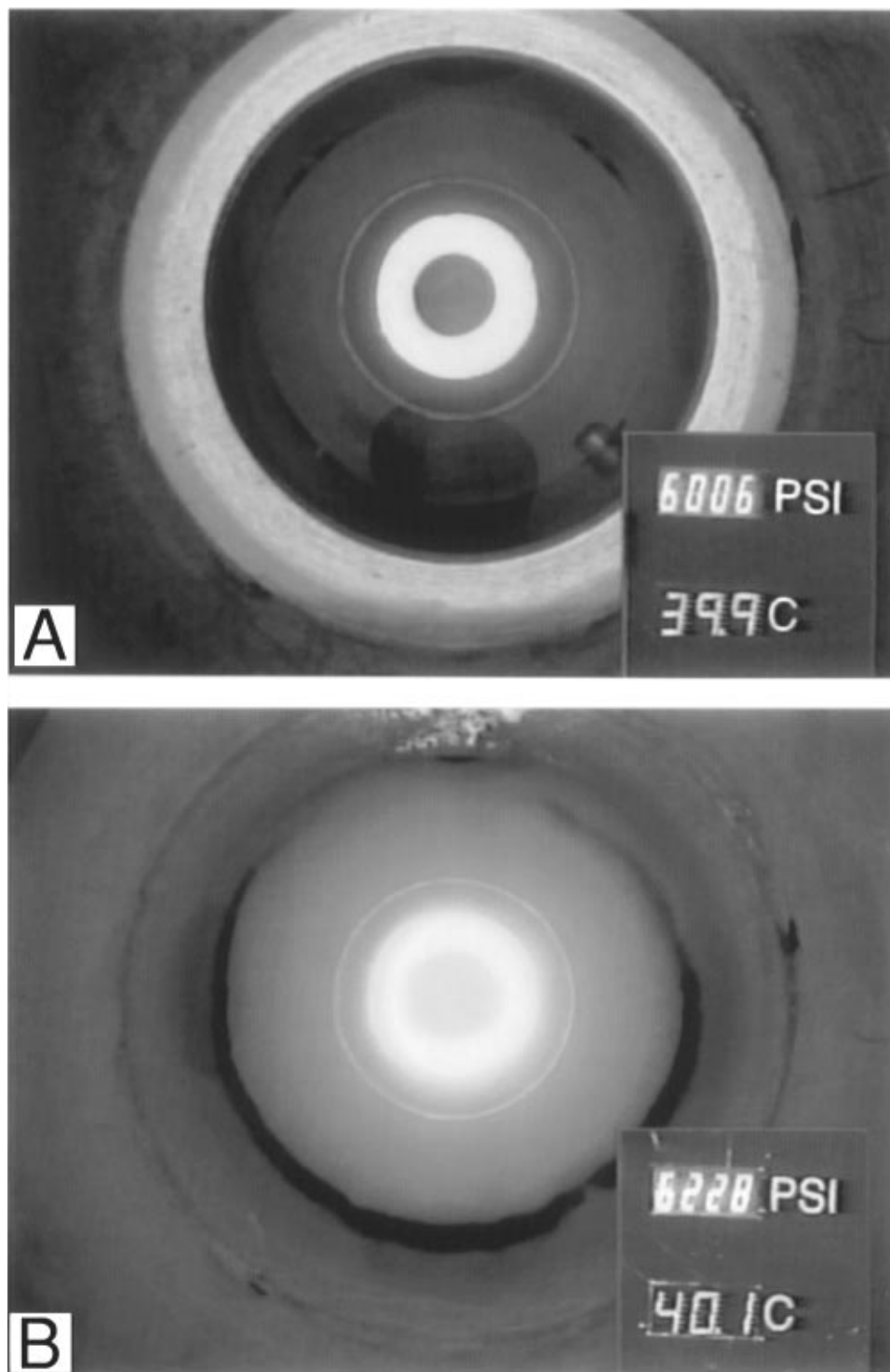


Figure 4. (a) Photograph of the interior of the autoclave showing a homogeneous solution of polymerizing TMOS, formic acid and SCCD before gelation. The light ring is the reflection from the light source; the gray cylinder on the floor of the chamber is a magnetic stir bar. (b) Photograph taken after gelation had occurred showing opaque white monolith that has shrunk from the walls of the chamber.

SCCD as the polymerization solvent. Because both polymerizations in SCCD and ethanol involve premixing the monomers with formic acid, we also prepared gels from solutions of just TMOS or BESP and formic acid with no additional polymerization solvent. Under these conditions, gels took at least 1 h to form. Both the gels prepared in alcohols and the gels prepared with formic acid alone were extracted with SCCD to give aerogels by the conventional supercritical process (Figure 2).

Unlike experiments using surfactants to form microemulsions in SCCD which led to precipitates, the formic

acid-alkoxysilane polymerizations (of TMOS and BESP) in SCCD formed gels that, to the eye, appeared identical with gels prepared through conventional sol-gel techniques. The failure of TEOS to form a gel is consistent with the lower reactivity of the monomer; aqueous acid-catalyzed sol-gel polymerizations of TEOS can require months for gels to form. The gels prepared in SCCD exhibited some signs of cracking while still in the autoclave, particularly between the gel and the walls of the vessel, due to syneresis. In addition, some shrinkage, and in some cases cracking, was observed

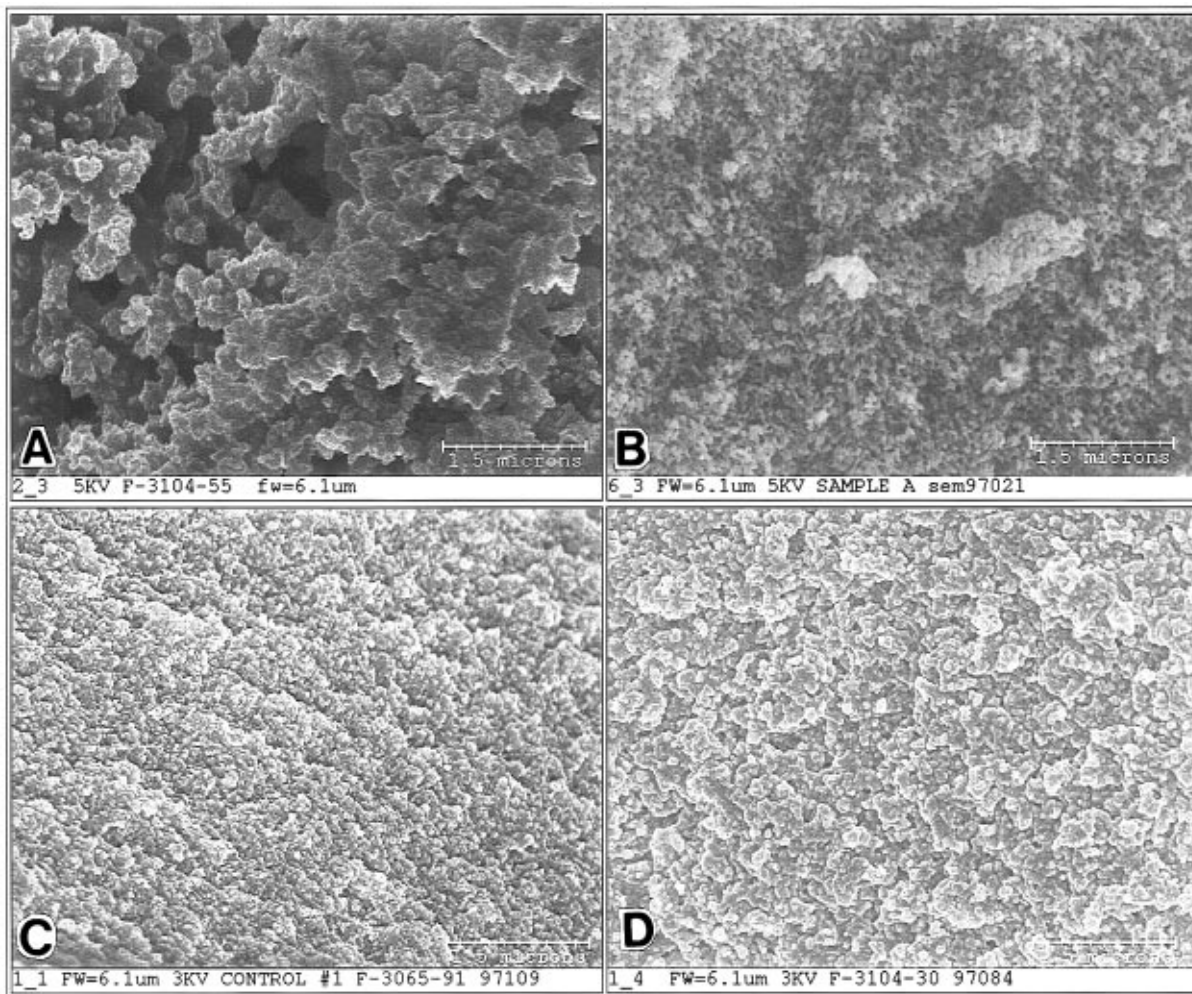


Figure 5. SEM images of (a) a silica aerogel prepared by polymerization of TMOS with formic acid in SCCD, (b) a silica aerogel prepared by the conventional polymerization of TMOS with formic acid in methanol, followed by extraction with SCCD, (c) a silica aerogel prepared only from TMOS and formic acid followed with SCCD extraction and drying, and (d) a phenylene-bridged polysilsesquioxane aerogel prepared by the polymerization of 1,4-bis(triethoxysilyl)benzene with formic acid in SCCD. Aerogels were ground into a powder. Conductive silver paint was used to adhere the sample particles to a sample mount. The particles were then coated with chrome using a high-resolution ion beam coater. Two minutes of chrome (approximately 150 Å) was typically applied as the sample was tilted and rotated under the chrome plasma. If the samples still charged too much to image, another coating was applied. The samples were imaged using a high-resolution Hitachi S4500 field emitter gun scanning electron microscope. Low accelerating voltages, 1–2 kV, were used to minimize charging problems. PGT Imix imaging software was used to acquire the images.

during drying. Similar shrinkage has been often observed for aerogels prepared from BEBP in organic solvents even with SCCD extraction and may reflect formation of a very compliant polymeric gel. Bulk densities for silica and phenylene-bridged polysilsesquioxane aerogel monoliths were between 0.28 and 0.31 g cm⁻³.

The aerogels were, with the exception of a transparent aerogel prepared from BEBP, opaque due to light scattering from the aggregate structure of the materials. Closer inspection using scanning electron microscopy revealed the silica aerogels to be highly porous structures composed of interconnected particles. The silica gels prepared in SCCD consistently exhibited larger particle diameters (100–2000 nm; Figure 5a) and more macroporosity than those aerogels prepared by SCCD extraction of gels formed in ethanol (20–40 nm; Figure 5b). Similar, mesoporous structure (20–40 nm) in the silica aerogel (Figure 5c) prepared in formic acid followed by SCCD extraction demonstrates that using SCCD as a polymerization solvent contributed to the

pore structure of the gel. One possible explanation of the microstructural differences between the aerogels is that the SCCD is a “better” solvent than ethanol for the growing silica polymers that form the particles.

Scanning electron micrographs of phenylene-bridged polysilsesquioxane aerogels prepared in both SCCD (Figure 5d) and methanol revealed no macroporosity analogous to that observed in the silica aerogels. Transmission electron micrographs revealed the gel structure to be that of a tightly packed aggregate of particles between 40 and 80 Å in diameter, independent of the concentration of BEBP used in the sol–gel polymerization. Both SEM and TEM micrographs are remarkably similar to those obtained with phenylene-bridged polysilsesquioxane aerogels prepared by aqueous acid-catalyzed sol–gel polymerization of BEBP followed by SCCD extraction. Integration of the resonances in the solid state ²⁹Si CP MAS NMR spectrum of the phenylene-bridged polysilsesquioxane aerogel polymerized in SCCD revealed that the extent of condensation to siloxane bonds (70%) was comparable

to gels prepared under acidic conditions in alcohol. These similarities suggest that SCCD is as suitable a solvent for forming these hybrid organic-inorganic gels as ethanol.

Surface analyses of nearly all of the aerogels using nitrogen sorption porosimetry revealed type IV isotherms consistent with mesoporous materials (mean pore diameters between 20 and 500 Å). Surface areas of the silica aerogels prepared in SCCD (260–308 m² g⁻¹) were equal to or slightly lower than those measured for the corresponding aerogels prepared in ethanol or formic acid (200–500 m² g⁻¹). The most interesting result was that the pores detected by nitrogen sorption in the silica aerogels prepared in SCCD were less than 100 Å in diameter and appear to lie *within* the aggregate particles. The macroporous structures in the SCCD silica gels evident in the electron micrograph (Figure 5a) are too large (>500 Å) to be observed by nitrogen sorption analysis. Thus, the SCCD-silica aerogels possess two different populations of pores: mesopores based on the architecture of the individual particles, and macropores that are the interstitial voids between the particles that make up the gel.

In contrast, the pore size distribution found in the aerogels (100–121 Å) prepared in methanol corresponds only with the smaller, interstitial mesopores observed in the SEM micrographs of the aggregate-like structures. Surface areas of the BESP aerogels prepared in SCCD were also lower (471–586 m² g⁻¹) than those of aerogels obtained by aqueous (HCl or NaOH-catalyzed) sol-gel polymerizations in organic solvents (1000–1600 m² g⁻¹).²⁴ As would be expected with the fine grained structure observed in the SEM micrographs, the mean pore diameters of these materials were smaller (24–50 Å) than in the silica aerogels prepared in SCCD. The

discovery that phenylene-bridged aerogels prepared in ethanol exhibited very low surface areas indicates that there were significant differences in the interactions between SCCD and ethanol with the growing polymers.

Our results show for the first time that sol-gel polymerizations can be conducted directly in supercritical carbon dioxide as the polymerization solvent by using formic acid as the condensation reagent. SCCD appears to be an excellent solvent for preparing highly porous architectures with both meso- and macroporous structure. In fact, SCCD appears to be a better solvent than ethanol for preparing phenylene-bridged polysilsesquioxane aerogels from BESP. In addition, the process can be successfully used to generate monolithic aerogels in a single step from their monomeric precursors. We believe that this technique will greatly simplify the preparation of aerogels and open a new frontier for sol-gel processing using SCCD or other nonpolar organic solvents coupled with nonaqueous chemistry.

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