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Contents

Introduction	3318
Low-Density Organic–Inorganic Hybrids Containing Organic Polymers	3319
Low-Density Hybrids Based on Organopolysiloxanes	3322
Other Relevant Organic–Inorganic Hybrid Porous Materials	3328
Marshmallow-Like Gels	3328
Macroporous Silsesquioxane Monoliths	3331
References	3334

Abstract

Development of aerogel materials has been demanded in terms of increasing mechanical strength and functionalization for extended applications such as thermal superinsulators. Organic–inorganic hybridization is one of the key strategies for these purposes in aerogel science and technology as in other materials demonstrated in the sol-gel field. Herein recent topics in organic–inorganic hybrid aerogels are overviewed. Special emphasis is placed on transparent hybrid aerogels based on organopolysiloxane networks with improved mechanical strength obtained through careful controls over fundamental sol-gel parameters such as pH and additives. Effective organic–inorganic hybridization opens the possibility of cost-effective ambient pressure drying toward xerogels that possess properties comparable with aerogels obtained by supercritical drying.

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Introduction

The term “aerogel” is generally given to highly porous dried gels that have been processed through supercritical drying and contrastively used against the term “xerogel” processed through evaporative drying at ambient conditions (Brinker and Scherer 1990). A typical synthetic process for aerogels includes a liquid-phase synthesis of a wet gel, followed by a careful removal of the solvent from the gel in a supercritical condition. The terminology is, however, somewhat confusing between aerogel and xerogel; that is, highly porous gels obtained through a nonsupercritical drying process such as ambient pressure drying are often called as aerogel.

Aerogels have been gathering a lot of attention for years because of their unique and outstanding physicochemical properties arising from the high porosity (typically >90%) and interconnected nano-sized particles with various chemical compositions (Hüsing and Schubert 1998; Pierre and Pajonk 2002). The most representative property is high thermal insulation ability (i.e., low thermal conductivity, Table 1) due to the intricate pore structure, the length scale of which is shorter than the mean free path of molecules in air and the gaseous thermal conduction is strictly limited. In addition, typical silica aerogels show visible-light transparency, which allows aerogels to be a distinguished class of porous materials among others. Appearance and microstructure of a typical silica aerogel are displayed in Fig. 1. Both transparency and low thermal conductivity are attributed to the fine solid constituents and porous structure in the mesopore size region.

Aerogels are drawing renewed attention from scientists and engineers because excellent thermal insulators are promising for improving the energy efficiency in various thermal processes involved in such as vehicle engines, industrial production plants, oil/gas well pipes, and power plants. Improving thermal insulation in building structures and household devices also gives rise to higher energy efficiency in the civilian sector (Baetens et al. 2011; Koebel et al. 2012). In addition to these environmental purposes, continuous efforts are made to utilize the unique properties of aerogels for extended fields. Transparency for visible light and low refractive index are also important properties when used as optical devices, high-energy particle detectors (Cherenkov counters), and cosmic dust collectors. Because of the unique properties as mentioned above, aerogels will find new distinctive applications which cannot be replaced by any other materials in the world.

Table 1 Values of thermal conductivity in typical thermal insulators^a

	Thermal conductivity/mW m ⁻¹ K ⁻¹
Mineral wool	34–45
Glass wool	31–43
Expanded polystyrene	29–55
Phenolic resin foam	21–25
Polyurethane foam	20–29
Silica aerogel	12–20

^aValues referred to Koebel et al. (2012)

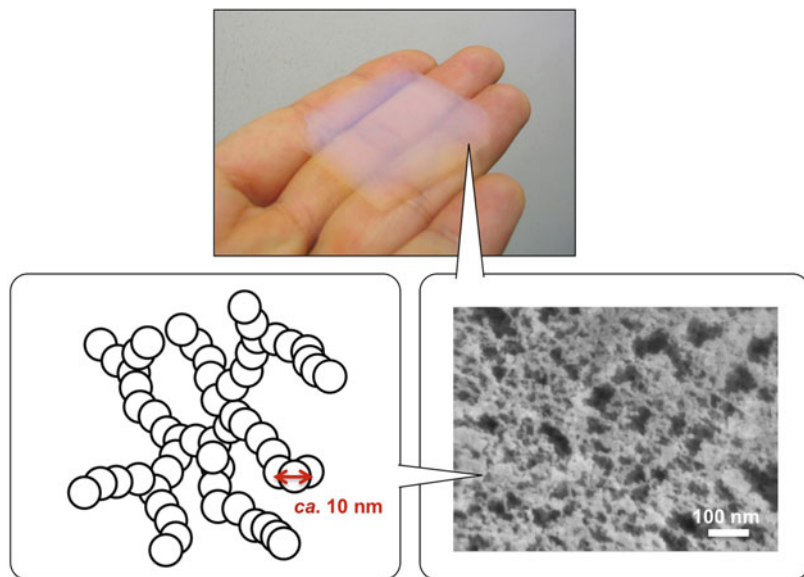


Fig. 1 A typical silica aerogel on hand and the microstructure represented by an electron micrograph and an illustration

The production and handling of aerogels, however, have seriously restricted the practical applications. The supercritical drying process requires a tight-sealed robust autoclave, which limits the available size of aerogels (a $550 \times 550 \text{ mm}^2$ aerogel glazing has been reported in Schultz et al. 2005, which is one of the largest aerogels reported so far). In addition, the friable nature of aerogels discourages the handling and shape-forming abilities, as compared to other competing materials such as polymer foams. Hence, there has been tremendous pursuit of improvements of mechanical properties, which may lead to a development of nonsupercritical drying process and better handling and forming abilities. One of the most important and promising strategies for the mechanical improvements is hybridization with organic moieties that may impart toughness to friable aerogels. In this chapter, improvements of aerogel properties through organic–inorganic hybridization techniques for better applications are focused. Additionally, several examples of derivative materials from hybridization are overviewed.

Low-Density Organic–Inorganic Hybrids Containing Organic Polymers

Organic–inorganic hybrid materials are categorized in class I and II (Sanchez and Ribot 1994; Boury and Corriu 2002), depending on the connectivity between organic and inorganic moieties (Fig. 2); i.e., class II is based on the covalent bonds between organic and inorganic parts whereas class I is not. Among diverse

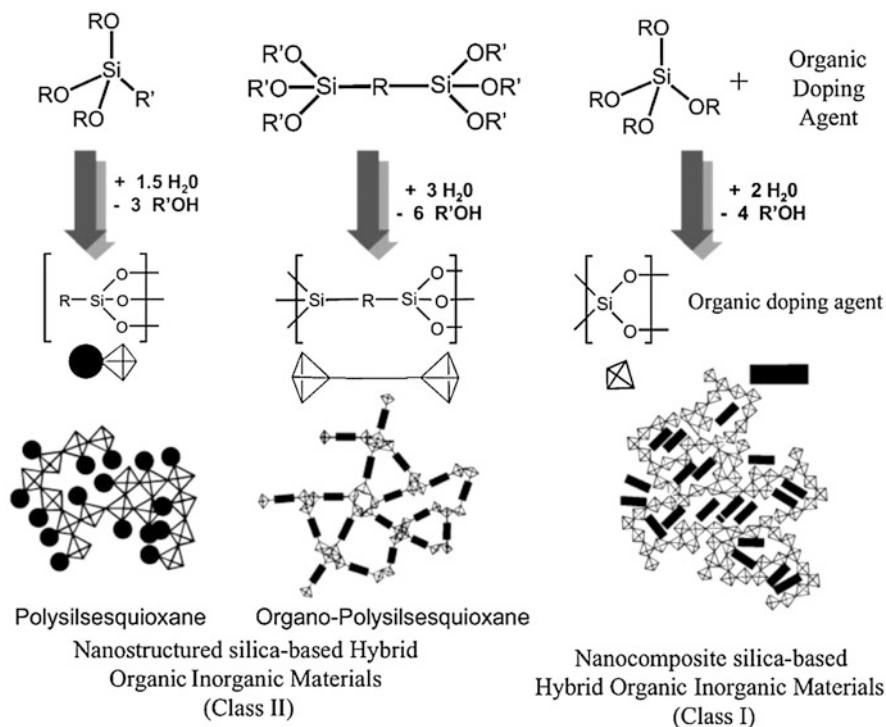


Fig. 2 Several sol-gel ways to organic–inorganic hybrids based on polysiloxane networks (From Boury and Corriu 2002)

kinds of hybrid materials, class II hybrids in general show better physicochemical stability and controllability in microstructures and physical properties. The development of hybrid materials has been encouraged by the progress of sol-gel process and other low-temperature synthetic approaches that do not require high temperature (Sanchez et al. 2011, 2014).

The major purpose to obtain organic–inorganic hybrid materials lies in the exploration of new functional materials through synergetic combinations of organic and inorganic moieties. Class I hybrids can be prepared by mixing two separate organic and inorganic components in a designed sol-gel system, while organo-substituted inorganic precursors or silylated polymers are often employed in the synthesis of class II hybrids. As a pioneering work on low-density class I and II hybrids, Novak et al. introduced the concept of interpenetrating network to aerogels (Novak et al. 1994). Although many linear polymers show leaching from the wet gel during solvent exchange and supercritical drying, poly(2-vinylpyridine) was found to remain in the silica network because of a strong attractive interaction. Co-condensation of silanol-terminated polydimethylsiloxane (PDMS) or poly(methyl methacrylate-co-(3-(trimethoxysilyl)propyl methacrylate)) successfully introduces covalent crosslinks between organic and inorganic

parts. Although moisture resistivity and compressive mechanical properties are improved, maintaining the high transparency is a critical problem in these polymer-incorporated systems. Incorporation of silanol-terminated PDMS into the silica gel network is also reported in Kramer et al. (1996). Although opaque due to phase separation, rubbery elastic *Aeromosils* that show reversible compression-decompression cycles have been synthesized. Similar approaches were taken to prepare hybrid aerogels based on silica-poly(vinylpyrrolidone) (Wei et al. 2008) and silica-syndiotactic polystyrene (sPS) (Wang and Jana 2013). Other than silica, vanadium pentoxide-polypyrrole aerogels were prepared using polypyrrole or pyrrole monomer (in-situ polymerization) to improve electrical conductivity for the use of electrodes (Harreld et al. 1998). Hybrid aerogels based on iron oxide and resorcinol-formaldehyde (RF) resin were prepared using a combination of epoxide-mediated sol-gel (detailed below) toward iron oxyhydroxide and addition-condensation of R and F (Leventis et al. 2009). The obtained hybrid aerogels can be processed through smelting to obtain iron (0) aerogels.

A feasible way to increase mechanical properties by crosslinking (or coating and binding) organic polymers on the pore surface of silica-based aerogels has been developed (Leventis 2007; Leventis and Lu 2011). Crosslinking between diisocyanate and silanol (Leventis et al. 2002; Churu et al. 2015), epoxies and amino-functionalized silica (Meador et al. 2005), styrene and vinyl-functionalized silica (Ilhan et al. 2006), diisocyanates and vanadia (Leventis et al. 2008), acrylonitrile and *N,N'*-azobisisobutyronitrile (AIBN)-modified silica (Leventis et al. 2010), and polynorbornene on norbornene-modified silica (Mohite et al. 2012) have been demonstrated, which in general can be concluded that hybridization by crosslinking through covalent bond on the pore surface significantly improves toughness and robustness, though original high porosity and transparency of silica aerogels are partially sacrificed. Apart from applications as aerogels, these materials are considered to be good for high-energy absorption as in armor.

Hybridization between silica and biopolymers are also studied for the sake of low cost, sustainable resources of polymers. Silica-chitosan composite aerogels were prepared using an acidic solution of chitosan and tetraethoxysilane (TEOS), and decreased shrinkage with increasing chitosan/silica ratio was observed (Ayers and Hunt 2001). More recently, silica-pectin composite aerogels were reported (Zhao et al. 2015). A one-pot sol-gel process followed by hydrophobization with hexamethyldisilazane (HMDS) and supercritical drying yielded opaque monolithic hybrid aerogels with low thermal conductivity ($>14.2 \text{ mW m}^{-1} \text{ K}^{-1}$). Nanofibrous materials are promising for the mechanical improvement as the fibers can support the inorganic networks. Aerogels composed of silica and cellulose nanofibers were demonstrated to show bending flexibility (Cai et al. 2012), though the composite aerogels show increased density of $>0.32 \text{ g cm}^{-3}$. The fibrous structure of bacterial cellulose was used to prepare silica-cellulose composite aerogels, whose microstructure consists of two discrete structures of each component (Sai et al. 2013). It was demonstrated that their good mechanical properties are suitable for repetitive wetting-drying cycles and for removal of oils from a water surface.

Low-Density Hybrids Based on Organopolysiloxanes

Organically modified polysiloxanes (organopolysiloxanes or silicones), developed for long in the silicone science and industry, are one of the most important organic–inorganic hybrid materials, due to their physicochemical stability and extended applications (Brook 2000). Among these, silsesquioxanes (or “T resins”) possess an ideal formulation of $\text{RSiO}_{1.5}$ where R is an organic substituent such as methyl and can be obtained from organically modified silane compounds such as organotrialkoxysilanes (R-Si(OR')_3) and bis(trialkoxysilyl)-modified organometallic compounds termed as bridged alkoxy silanes ($((\text{R}'\text{O})_3\text{Si-R-Si(OR')}_3)$). These organically modified alkoxy silanes are widely available in the market and can be employed as the useful precursors for obtaining desired class II organic–inorganic hybrid materials. Recent interests in the application of silsesquioxanes include low dielectric constant films (Volksen et al. 2010) and composites with organic semiconductors (Kamino and Bender 2013) for electronics, hydrophobic and amphiphobic surfaces (Chu and Seeger 2014), gas/liquid-phase separations (Kanamori and Nakanishi 2011; Castricum et al. 2011), water desalination (Xu et al. 2011; Chua et al. 2013), nanocomposites with polymers for multiple functionalities (Kuo and Chang 2011), cosmetics, and optical materials (Lebeau and Innocenzi 2011) by taking advantages of their high physicochemical, thermal and mechanical stabilities, variable porosity, and tunable affinity with various organic polymers for tailoring composites.

Gelation and controls over the microstructure in silsesquioxanes from organotrialkoxysilanes are indeed difficult because of high cyclization and phase separation tendencies (Loy et al. 2000; Kanamori and Nakanishi 2011), while polyhedral oligomeric silsesquioxanes (POSS) (Baney et al. 1995; Cordes et al. 2010) are extensively studied due to their unique structure and properties. In acid-catalyzed conditions with a low concentration of organotrialkoxysilane, in particular, the formation of cyclic species including POSS rather than crosslinked networks (Fig. 3) would become dominant to result in stable sol or separation of oligomeric oils/polymeric resins (Sugahara et al. 1994; Dong et al. 2003). In addition, since those organosilsesquioxane networks are hydrophobic and leaves a less concentration of remaining silanol group, there is high tendency to form hydrophobic precipitations in an uncontrolled manner (Loy et al. 2000). Because the random network, not cyclic species, is the basis of monolithic gel formation, it is important to promote the random crosslinks through adequate sol-gel design strategies. Careful controls over fundamental sol-gel parameters (pH, solvent, additives, etc.) have been proved to be effective in obtaining monolithic porous silsesquioxane and relevant materials with the length scale of the porous structures from several tens of nanometers (typical aerogels) to microns (macroporous gels) by enhancing the network formation and controlling the phase separation tendency (Kanamori and Nakanishi 2011).

Organically substituted alkoxy silanes ($\text{R}_n\text{Si(OR')}_{4-n}$) are often polymerized with tetraalkoxysilanes such as tetramethoxysilane (TMOS) and TEOS, in order for ensuring the formation of three-dimensional network. In a base-catalyzed

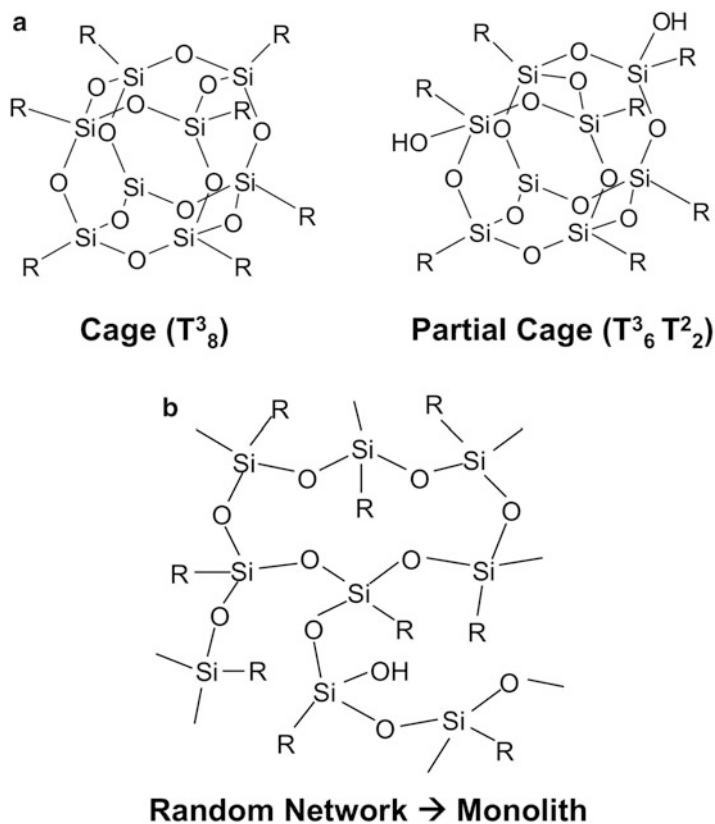


Fig. 3 Some examples of condensates derived from organotrialkoxysilanes. (a) Representative cage species and (b) the random network that may lead to monolithic gels

hydrolysis-polycondensation system of methyltrimethoxysilane (MTMS) and TMOS, it is reported that larger shrinkage occurs with increasing MTMS/TMOS ratio, and no monolithic gel is obtained when MTMS is $>80\%$ (Schwertfeger et al. 1992). While hydrophobicity due to the methyl groups appears and a low concentration of silanol groups is found on the aerogels prepared from $>20\%$ MTMS, visible-light transparency decreases with the increasing MTMS ratio. In other organotrialkoxysilane/tetraalkoxysilane systems, trifunctional alkoxy silanes including substituent groups such as mercaptopropyl, diphenylphosphinoethyl, and chloropropyl give negative effects to aerogels when exceeding 10% (Hüsing and Schubert 1997). Similar results were reported that $>40\%$ MTMS and $>20\%$ 3-methacryloxypropyltrimethoxysilane decrease visible-light transparency, and water contact angle reaches 160° at $>60\%$ MTMS (Martín et al. 2008). Aerogels prepared from MTMS/TMOS mixtures becomes softer with increasing MTMS, but hardness is not changed from nanoindentation results. However, basic substituent groups such as aminopropyl and *N*-(2-aminoethyl)-3-aminopropyl allow the

formation of aerogels with density of 0.07–0.16 g cm⁻³ with an incorporation of as high as 40% (Hüsing et al. 1999). Intermolecular hydrogen bonding between amino groups and silanol groups of Q silicon species may play an important role in the formation of copolymer networks. By contrast, an incorporation of an ethylene-, phenylene-, or hexylene-bridged alkoxy silane in TMOS causes only limited influences in hydrophilicity and elasticity of silica aerogels (Schwertfeger et al. 1994). The bridged alkoxy silane precursors are advantageous in obtaining aerogels as detailed later.

Hydrophobic, flexible aerogels have been prepared from a single precursor MTMS by a two-step acid–base process in methanol followed by supercritical drying (Rao et al. 2006). The polysiloxane network resulted only from MTMS should be termed as polymethylsilsesquioxane (PMSQ) as it has a chemical formulation of CH₃SiO_{1.5} assuming ideal hydrolysis and polycondensation. Aerogels with density from 0.04 to 0.1 g cm⁻³ have been obtained with varied amounts of the solvent methanol, though the aerogels are opaque due to macroscopic phase separation of hydrophobic PMSQ networks in the course of sol-gel transition. The control of phase separation during sol-gel transition is in fact useful in designing macroporous monoliths in some polyorganosilsesquioxane systems as described below. While transparency is lost, these PMSQ aerogels reported by Rao et al. show superhydrophobicity and high absorption of oils (aliphatic and aromatic hydrocarbons and alcohols, Rao et al. (2007)) because of low surface energy of the PMSQ network and roughness in the micrometer scale.

Transparent aerogels with PMSQ networks have been for the first time prepared from MTMS by a two-step acid–base process under the presence of surfactant (Fig. 4a) (Kanamori et al. 2007, 2008, 2009). A one-pot two-step process using urea as the base generator contributes to the preferred formation of three-dimensional random networks over cyclic species with good homogeneity and reproducibility. In addition, appropriate cationic surfactant (such as *n*-hexadecyltrimethylammonium bromide, CTAB, or chloride, CTAC) (Hayase et al. 2012) and nonionic triblock copolymer (such as Pluronic, poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide)) (Kurahashi et al. 2012) are effective to render the hydrophobic MSQ condensates remain miscible in the aqueous sol-gel system. Phase separation of the MSQ condensates/networks is thus suppressed in the aqueous media.

Obtained transparent wet gels can be transformed into aerogels by supercritical drying. It has been found that these aerogels are mechanically strong and flexible against compression (Fig. 5). Xerogel monoliths with aerogel-like properties can be prepared by ambient pressure drying (Fig. 4b), because a drying gel shows a reversible shrinkage-reexpansion (generally termed as spring-back) behavior during evaporative drying (Hayase et al. 2016). Large-area PMSQ xerogel panels can be successfully obtained by optimizing the starting composition and drying process (Fig. 6a). These PMSQ xerogels are confirmed to exhibit thermal conductivity (<0.015 W m⁻¹ K⁻¹ at an ambient condition) comparable with a typical silica aerogel as shown in Fig. 6b. When some remaining issues on the precursor/process costs and mechanical strength against deformations other than compression (such as

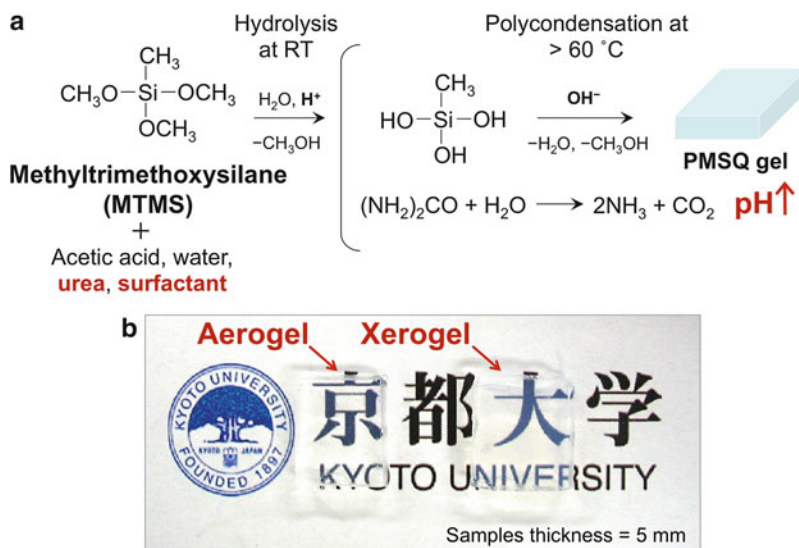


Fig. 4 (a) A two-step acid–base reaction scheme toward transparent PMSQ gels and (b) a typical obtained PMSQ aerogel (supercritical drying) and a xerogel (ambient pressure drying)

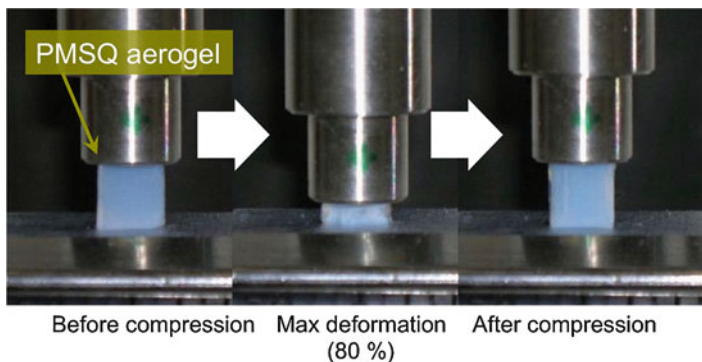


Fig. 5 A reversible shrinkage-reexpansion (spring-back) phenomenon observed in the uniaxial compression-decompression test on a PMSQ aerogel

stretching and shearing) are solved, this material would be a breakthrough for a practical application to thermal superinsulators.

Thermal conductivity of a highly porous material like aerogel predominantly depends on thermal conduction by the gas phase in the pores (Kaganer 1969). The total thermal conductivity drastically changes when the pore size and the mean free path of the gas molecules, which is proportional and inversely proportional to temperature and pressure, respectively, become comparable. Through an extended control of pore size from 50 nm to 3 μm by controlling the phase separation in the

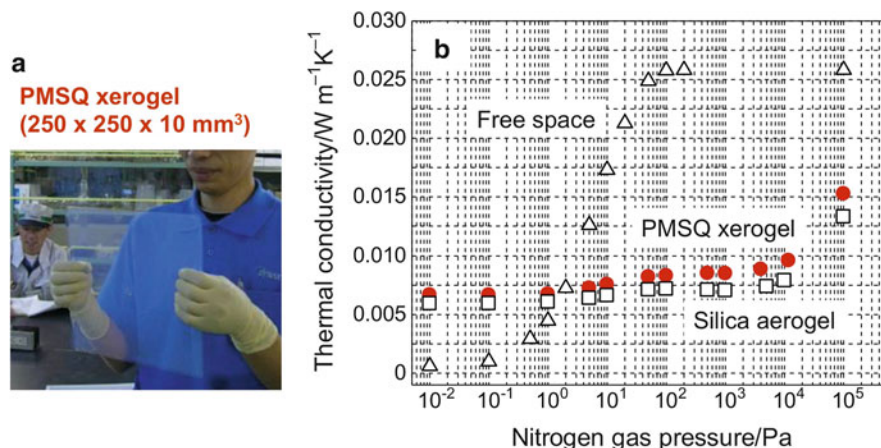
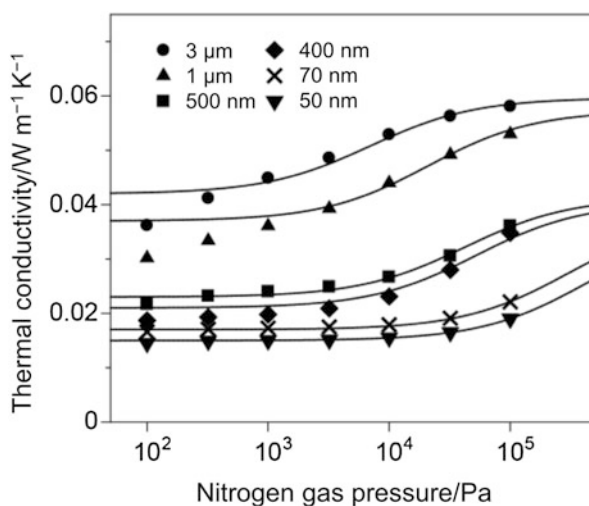


Fig. 6 (a) A large-area PMSQ xerogel panel obtained through ambient pressure drying and (b) dependence of thermal conductivity on nitrogen gas pressure of the PMSQ xerogel and a silica aerogel. The same for the “free space” (without a sample in the measurement chamber) is also shown for comparison

Fig. 7 Dependence of thermal conductivity on nitrogen gas pressure in PMSQ aerogels/xerogels with different pore sizes



PMSQ aerogels/xerogels prepared under the presence of Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆, where EO and PO stand for ethylene oxide and propylene oxide units, respectively) (Kanamori et al. 2011), relationships between pore size, gas pressure, and thermal conductivity have been investigated (Fig. 7; Hayase et al. 2014a). These relationships are confirmed to follow the theoretical treatment proposed by Kaganer, and aerogels with smaller pore sizes show low enough thermal conductivity of 0.015–0.020 W m⁻¹ K⁻¹ at ambient or light vacuum (10⁴ Pa) conditions. Although the xerogels prepared under the presence of F127 show

lower transparency (typically ~30% at 550 nm as compared to 90% in those from CTAB system), these xerogels are mechanically tougher than those from CTAB system.

One strategy for improving mechanical property of the PMSQ system uses cellulose nanofibers (CNFs) extracted from wood to support the whole network structure (Hayase et al. 2014b). It has been confirmed that PMSQ-CNF composite aerogels with improved bending flexibility can be obtained. In addition to the strengthening effect, the PMSQ-CNF composite aerogels reach lower density as compared to the pristine PMSQ aerogels. Although the transparency is deteriorated, these composite materials show preserved thermal insulation ability and would be another candidate for thermal superinsulators.

Another interesting precursor for flexible aerogels is bridged alkoxy silanes ((R'O)₃Si-R-Si(OR')₃, where R is typically alkyl or aryl). The sol-gel research of these precursors was originated by Shea and Loy, and the bridged polysilsesquioxane network ([O_{1.5}Si-R-SiO_{1.5}]_n) with surfactant-templated periodic mesopores is known as periodic mesoporous organosilicas (PMOs, Stein et al. 2000; Hatton et al. 2005; Mizoshita et al. 2011). Bridged polysilsesquioxane aerogels from these precursors have also been a research target because these hexafunctional precursors can form monolithic gels even at low concentrations like 0.1 M (Baugher et al. 1995), which is advantageous in preparing low-density porous solids. Among typical alkoxy silanes bridged with alkyl, aryl, and other groups, one with a relatively long and flexible bridging group, 1,6-bis(trialkoxysilyl)hexane (BTMH), is an attractive candidate to impart flexibility to the polysiloxane-based network. Preparations of hexylene-bridged polysilsesquioxane aerogels with high degree of condensation and low bulk density of <0.1 g cm⁻³ were reported (Loy et al. 1995; Boday et al. 2012), though aerogels both with visible-light transparency and improved flexural strength compared to silica aerogel counterparts have not been reported. A vapor-phase chemical modification of resultant aerogels with polycyanoacrylate effectively increased the flexural strength (Boday et al. 2011), and compressive modulus and strength also improved by chemical modification with hexamethyldisilazane (HMDS) or hexachlorodisilane (Obrey et al. 2011). Other groups demonstrated preparation and mechanical properties of bridged polysilsesquioxane aerogels with larger pore sizes typically in the micrometer range (Wang et al. 2013; Yun et al. 2015; Wang et al. 2015). Bridged precursors containing C-S and C-O bonds in the bridging moiety were prepared by the thiol-ene reaction between 3-mercaptopropyltrimethoxysilane (or 2,2'-(ethylenedioxy)diethanethiol) and vinyltrimethoxysilane (VTMS)/ vinyltriethoxysilane (VTES). The obtained opaque gels are highly flexible and can be used for separation of oil and water by soaking-squeezing cycles with hand.

A more recent study by Kanamori et al. has demonstrated a preparation of transparent hexylene-bridged polysilsesquioxane aerogels from BTMH through a one-step base process in *N,N*-dimethylformamide (DMF) (Aoki et al. 2016; Fig. 8). The solvent DMF works as a compatibilizer in the system to prevent phase separation of BTMH-derived condensates in the course of gelation. Transparent aerogels with bulk density 0.14–0.22 g cm⁻³ have been obtained after supercritical drying.

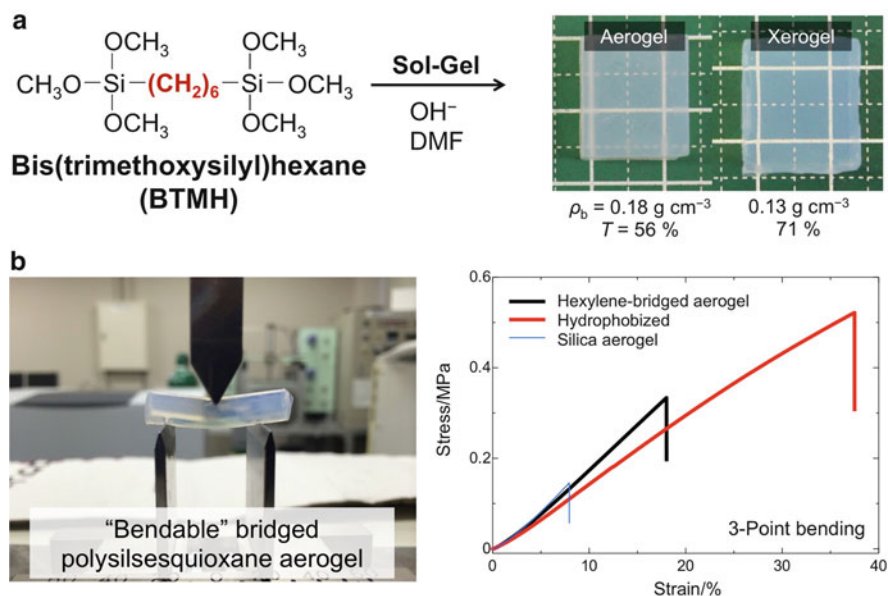


Fig. 8 Transparent hexylene-bridged aerogels and xerogels. (a) A reaction scheme toward the aerogel and xerogel. (b) A photograph showing the bending property of a hydrophobized aerogel, and stress–strain curves of pristine and hydrophobized aerogels (both have density of 0.22 g cm^{-3}). One for a silica aerogel at 0.20 g cm^{-3} is also shown for comparison

Although the resultant aerogels show good flexibility, an insufficient spring-back behavior upon compression has been observed, which is detrimental in ambient pressure drying. Since this can be attributed to the remaining silanol groups on the pore surface, a posttreatment with HMDS has been performed to reduce the silanol groups. Hydrophobic aerogels thus obtained show higher resilience as compared to the untreated, hydrophilic ones. Ambient pressure drying of the HMDS-treated wet gels has been performed, and it is found that xerogels with high transparency (71% at 550 nm through equivalent thickness of 10 mm) and low density (0.13 g cm^{-3}) can be obtained. Since these xerogels exhibit higher bending strength and flexibility as compared to silica with similar density (Fig. 8b), this system would be an interesting candidate for the thermal superinsulators.

Other Relevant Organic–Inorganic Hybrid Porous Materials

Marshmallow-Like Gels

Co-condensation of MTMS with a diorganodialkoxysilane such as dimethyldimethoxysilane (DMDMS) yields bendable, opaque, low-density gels, to which a name of “marshmallow-like gels” is coined (Fig. 9). Starting from a solution similar to that for making transparent PMSQ aerogels/xerogels as described above, an

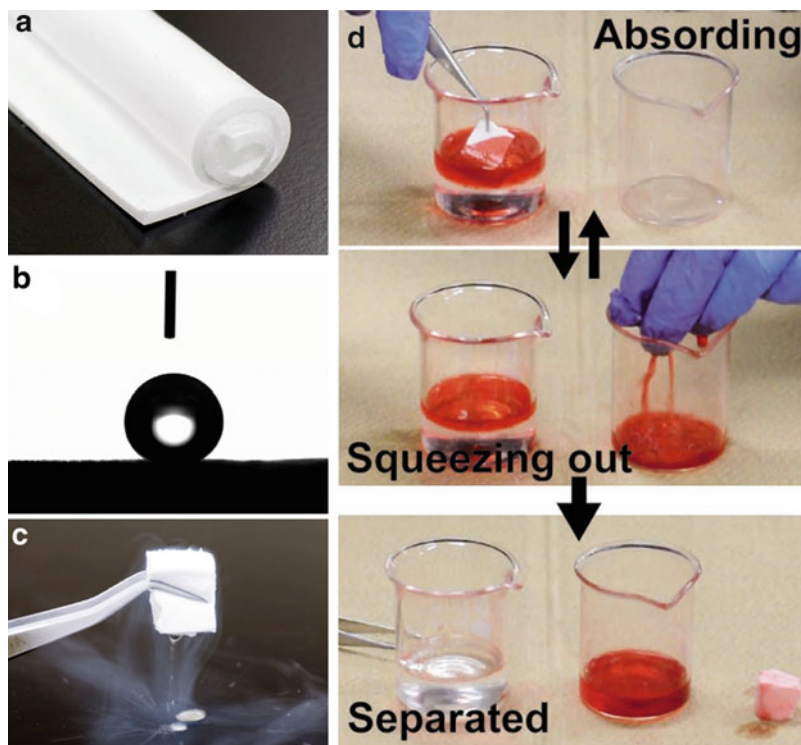


Fig. 9 A marshmallow-like gel prepared from MTMS and DMDMS showing (a) high bending flexibility and (b) superhydrophobicity. (c) The marshmallow-like gel shows flexibility even at liquid nitrogen temperature, demonstrating squeezing out liquid nitrogen. (d) Separating *n*-hexane (colored with *Oil-Red O*) from an *n*-hexane-water two-phase system by hand

introduction of DMDMS with a fixed total amount of alkoxy silanes results in the coarsened pore size toward micrometer range, since hydrophobicity of the polysiloxane network increases with an increasing fraction of DMDMS and phase separation tendency increases (Hayase et al. 2011).

The marshmallow-like gels show bending flexibility (Fig. 9a) and superhydrophobicity with water contact angle $> 150^\circ$ on the surface of the monolith (Fig. 9b), due to the combined effect of hydrophobic nature of the polydimethylsiloxane (PDMS)-like surface and physical roughness by the macropores (Hayase et al. 2013a). A piece of marshmallow-like gel has been used for demonstrating oil–water separation in a two-phase layered system consisting oil (such as *n*-hexane) and water (Fig. 9d). The marshmallow-like gel uptakes only oil and the oil can be squeezed out in a different place by mechanical compression (squeezing), thus leading to efficient oil–water separation. It is worth noting that this behavior can only be seen in materials with high hydrophobicity: a similar material such as kitchen sponge can absorb and squeeze out liquid but cannot selectively absorb a liquid from water. Another unique property includes maintained flexibility even at

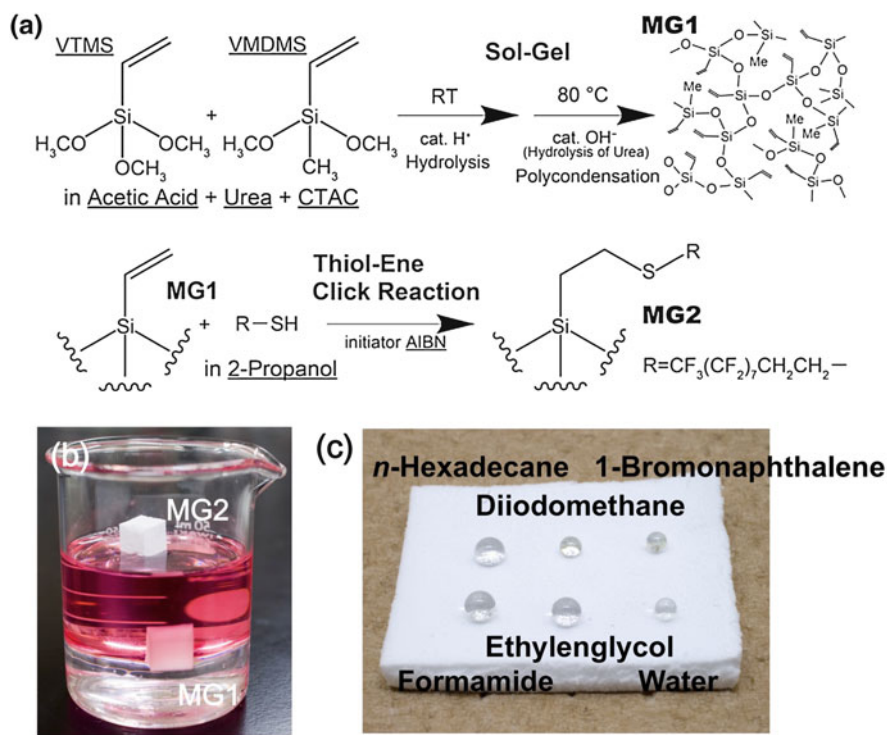


Fig. 10 (a) A synthetic scheme for vinyl-modified marshmallow-like gels (MG1) from VTMS and VMDMS, followed by surface modification by the thiol-ene reaction on the surface to add perfluoroalkyl groups (MG2). (b) MG1 absorbing 1,3,5-trimethylbenzene (colored with Oil-Red O) and floating on the water layer. MG2 does not absorb both liquids. (c) MG2 repelling liquids with a wide range of polarity from water to hydrocarbons

liquid nitrogen temperature (77 K, Fig. 9c). This is presumably due to the low crosslinking density of the polysiloxane network, the thin macropore skeletons, and low density ($\sim 0.1 \text{ g cm}^{-3}$). Some variations of the marshmallow-like gels have been demonstrated by using alkoxy silanes having vinyl, mercaptopropyl, phenyl, and fluorohydrocarbon substituent groups.

A more advanced surface design can be performed when alkoxy silane precursors with reactive groups are employed to prepare the marshmallow-like gel (Hayase et al. 2013b). Figure 10a exhibits an example of co-condensation between VTMS and vinylmethyldimethoxysilane (VMDMS), followed by the thiol-ene reaction on the pore surface. A perfluoroalkylthiol compound is employed to the surface modification in this specific case in order to add oleophobicity, while keeping the flexibility of the marshmallow-like gel. The gel without surface modification (MG1) shows superhydrophobicity and absorbs oil (1,3,5-trimethylbenzene (TMB), colored by Oil-Red O). The modified MG2 does not absorb the oil as well as water below, showing superoleophobicity (Fig. 10b). The hydro- and

oleophobicity are demonstrated on MG2 by repelling liquids with a wide range of polarity (Fig. 10c). These examples of flexible material design would be beneficial for developing multifunctional soft porous materials.

The marshmallow-like gel can also be tailored in a powder form (Tsuchiya et al. 2015). Hydrolysis and polycondensation of tri- and di-alkoxysilanes in an excess amount of water lead to segregation of micrometer-sized marshmallow-like particles in a similar way to dispersion polymerization. The marshmallow-like powders show high dispersion in oil as compared to other polyorganosiloxanes used as a component of cosmetic foundations. In addition to soft, rubbery properties of the marshmallow-like powders evidenced from static and dynamic mechanical measurements, moist touch feelings, and transparent appearance are attractive to cosmetic applications.

Macroporous Silsesquioxane Monoliths

Spinodal decomposition, one of the two-phase separation modes, has been an excellent way to control macroporosity in sol-gel monolithic materials (Nakanishi 1997). The characteristic co-continuous structure with well-defined macropores is imparted to various inorganic oxides and (oxy)hydroxides and organic polymers so far (Nakanishi et al. 2016), and an addition of mesoporosity in the macropore skeletons provide hierarchically macro-mesoporous monoliths, which are effective in applications to separation media (Nakanishi and Tanaka 2007; Guiochon 2007) and continuous flow catalysis (Sachse et al. 2011). Macroporous polysilsesquioxane monoliths as discussed in the previous section have also been developed through careful controls over phase separation in the course of gelation.

The one-step acid or base and two-step acid–base processes yield monolithic gels with a well-defined co-continuous macroporous structure with rather limited ranges of starting composition (Nakanishi et al. 2000; Dong et al. 2005a, b; Dong and Brennan 2006a, b). In fact, the structure of condensates and phase separation behavior strongly depend on the [water]/[alkoxysilane] ratio, solution pH, and kind and amount of solvent. In the one-step acid system, monolithic macroporous materials are obtained only when [water]/[alkoxysilanes] ratio (r) is low (e.g., $r \sim 2.0$) (Nakanishi and Kanamori 2005). In the case where MTMS and VTMS are used as the precursor and formamide (FA) as the solvent, macroporous monolithic gels with co-continuous structure are obtained as a result of sol-gel transition accompanied by phase separation (Itagaki et al. 2003; Kanamori et al. 2004). Enthalpy-driven spinodal decomposition takes place in the course of gelation in water-based solvent, due to the chemical incompatibility between hydrophobic silsesquioxane networks and polar solvent. Polymethylsilsesquioxane gels with well-defined macropores form in a wider range of starting composition as compared to polyvinylsilsesquioxane (PVSQ), because the hydrophobicity by the methyl groups is lower and the controllability of phase separation is higher. The lower steric effect also contributes to the enhanced network formation in PMSQ system. Co-condensation with TMOS extends the compositional region where well-defined

co-continuous structure is obtained as the average polarity of the network becomes higher, which allows higher controllability of the phase separation process.

The PMSQ monoliths thus obtained have been applied as monolithic capillary columns for high-performance liquid chromatography (HPLC) (Kanamori et al. 2004). Moderate retention of polar and nonpolar compounds to the PMSQ surface enables efficient separations both in the normal- and reversed-phase modes in a single column (Kanamori et al. 2006) because of the simultaneous availability of hydrophobic methyl groups and hydrophilic silanol groups. The highest theoretical plate number reaches $N = 100,000 \text{ m}^{-1}$ in the normal-phase mode, though the retention volume is not sufficient because the macropore skeletons have only micropores as evidenced from the type-I isotherm of nitrogen adsorption-desorption, and the micropores are hardly accessible for eluent molecules.

The introduction of mesoporosity is crucial for various applications to increase the contact between guest molecules and the surface. Mesoporosity, in addition to the macroporosity, has been for the first time imparted to PMSQ by employing a different synthetic strategy in sol-gel (Kanamori et al. 2011). A combination of acid-catalyzed hydrolysis and base-catalyzed polycondensation enhances the random network formation, which enables wider controls over pore size and porosity when combined with appropriate surfactant for a better control of phase separation. Figure 11 demonstrates the control of phase separation using a nonionic surfactant Pluronic F127 as aforementioned). The pH swing for the second polycondensation step is conducted by hydrolysis of urea at $>60 \text{ }^\circ\text{C}$. The appearance of the PMSQ gel changes from opaque to transparent with increasing amount of F127. With optimal amounts of F127, a well-defined co-continuous macroporous structure is obtained and the macropore skeletons are found to contain mesopores, thus resulting in hierarchically porous PMSQ monoliths. These mesopores with the size range of 10–20 nm are formed as a result of aggregation of colloidal MSQ condensates in a

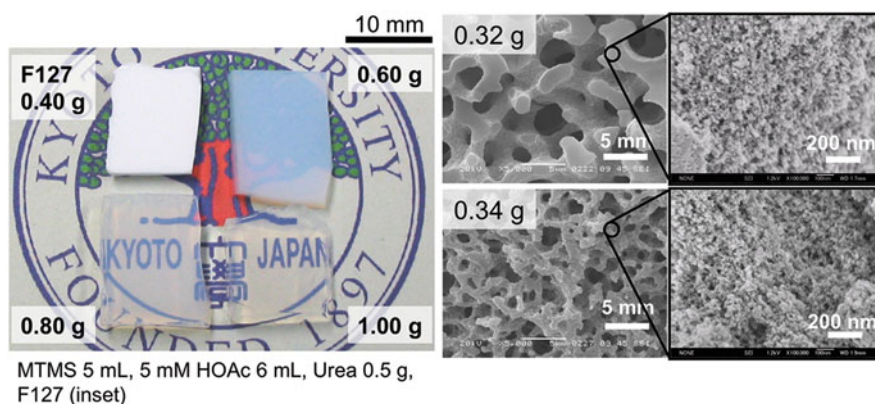


Fig. 11 Appearance of PMSQ monolithic gels prepared with different amounts of Pluronic F127 via the two-step acid–base sol-gel process, and micrographs of the typical co-continuous macroporous structure. Mesopores are also found in the macropore skeletons

higher amount of solvent (mainly water) in the basic condition. These hierarchically porous PMSQ monoliths are demonstrated to be applicable to HPLC separation media in the normal-phase mode (Zhu et al. 2015).

The two-step acid–base process is thus highly promising to design pore structures from the nanometer to micrometer range. Another approach for realizing the two-step acid–base process employs an acid scavenger such as propylene oxide (the epoxide-mediated sol-gel process). This process has been developed by Itoh et al. (1993) and Gash et al. (2001) to obtain gels from ionic precursors such as aluminum chloride and iron nitrate. To a system containing MTMS, methanol, aqueous hydrochloric acid, and ammonium chloride, propylene oxide is added after the hydrolysis of MTMS, which induces an irreversible ring-opening reaction via attacks by proton and chloride ions and the solution pH is swiftly raised. Although the co-continuous macroporous structure has been obtained at a lower temperature (40 °C) in this case, mesoporosity is not introduced without hydrothermal posttreatment at higher temperatures (Guo et al. 2013a, b). Modifications and optimizations of this synthetic system may yield hierarchically porous polysilsesquioxane monoliths with finely controlled mesopores.

Macroporous monoliths of bridged polysilsesquioxane are also developed through sol-gel accompanied by phase separation. Ethylene-bridged polysilsesquioxane monoliths with well-defined macropores have been prepared from 1,2-bis(trimethoxysilyl)ethane in an one-step acid process under the presence of Pluronic P123 (EO₂₀PO₇₀EO₂₀, Nakanishi et al. 2004). An attractive interaction between the condensates and P123 through hydrogen bonding makes the condensates more hydrophobic, which induces phase separation in the course of gelation, and thus well-defined macroporous monoliths are resulted. While the obtained macroporous monoliths possess a small amount of mesopores in the macropore skeletons, an introduction of a swelling agent such as TMB in the starting solution increases mesopores, and a moderate amount of TMB allows a formation of periodic mesopores with a narrow size distribution within the macropore skeletons.

Phenylene- and biphenylene-bridged polysilsesquioxane monoliths with well-defined macropores are also reported following the similar synthetic strategy (Hasegawa et al. 2009, 2010a). Phase separation of condensates derived from 1,4-bis(triethoxysilyl)benzene (BTEB) or 4,4'-bis(triethoxysilyl)-1,1'-biphenyl (BTEBP) is induced under the presence of F127 in a solvent consisting of water and an amide such as DMF. Macroporous monoliths are thus obtained, and hydrothermal treatment in basic media increases the crosslinks and induces Ostwald ripening, which allows a formation of mesopores in the macropore skeletons. During a heat treatment in argon atmosphere of the resultant monoliths, the carbothermal reduction of the silsesquioxane network occurs and SiC and SiC/C composite monoliths have been obtained from monoliths derived using BTEB and BTEBP as the precursor, respectively. Removal of nano-sized silica domains from the SiC/C composites using an aqueous base solution opens micropores in the carbon matrix while maintaining the monolithic form (Hasegawa et al. 2010b, 2012). This would be an alternative approach to obtain “activated” carbon monoliths applicable to electrodes and adsorbents.

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