

Glycol-Modified Silanes: Novel Possibilities for the Synthesis of Hierarchically Organized (Hybrid) Porous Materials

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ABSTRACT

The preparation of porous hierarchical architectures that have structural features spanning from the nanometer to micrometer and even larger dimensions and that exhibit certain functionalities is one of the new challenging frontiers in materials chemistry. The sol-gel process is one of the most promising synthesis routes toward such materials because it not only offers the possibility to incorporate organic functions into the porous host but also offers the possibility to deliberately tailor the pore structure. In this Account, the opportunities given by the application of novel diol-modified silanes are discussed for the synthesis of hierarchically organized inorganic and also inorganic-organic porous monoliths.

1. Introduction

For many applications, chemists in materials science seek to copy the properties of natural materials. That is especially true with respect to structural features of the material, e.g., hierarchical organization of the network from the nanometer up to the micrometer scale (as found in almost all biominerals), and with respect to multifunctionality, e.g., hydrophobicity, catalytic functions, etc. For porous materials, a hierarchical organization of the pore structure is desired for a broad variety of applications, including chromatography and catalysis, because of the multiple benefits that arise from each of the pore-size regimes; e.g., uniform mesopores provide size or shape selectivity and high specific surface areas and macropores facilitate mass transport through the material and to the active sites.

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Doris Brandhuber obtained her diploma degree in 2003 from the Vienna University of Technology. A total of 3 years later, she received her Ph.D. degree from the Vienna University of Technology for her studies on glycol-modified silanes in the synthesis of porous monoliths. In 2006, she joined the Federal Environmental Agency in Vienna.

Nicola Hüsing received her Ph.D. degree in 1997 from the University of Würzburg. In 1998, she was awarded a postdoctoral fellowship with C. J. Brinker on nanostructured thin films. After she returned to Vienna, she finished her habilitation in 2003 and joined the faculty at Ulm University as a full Professor of Inorganic Chemistry in 2004. Her research interests are in the synthesis of sol-gel-based porous materials and mesoscopically organized systems, especially with respect to synthesis-structure-property relations.

Despite the drastic progress in the synthesis of porous inorganic and inorganic-organic hybrid materials with control of pore sizes from angstroms to micrometers, the preparation of materials with simultaneous tailoring of morphology (monoliths, fibers, etc.) and pore structures on different length scales still remains a challenging task. Maximum control of the porous structure of oxidic materials can be obtained by combining different synthetic strategies, such as templating approaches and sol-gel processing. Molecular templating is well-known from the synthesis of the highly organized channel structures of zeolites.¹ In addition to single molecules as templates, also supramolecular arrays of molecules, such as lyotropic phases of amphiphilic surfactants or block copolymers, can be used as structure-directing agents for a deliberate design of pore systems in the mesoscopic regime.^{1–3} Other approaches utilize latex spheres for periodically arranged macropores,^{4,5} microemulsion droplets,⁶ or other macromolecules, such as bacterial threads, to name only a few of the possibilities.⁷

Sol-gel processing, thus, network formation via hydrolysis and condensation reactions of metal alkoxides, very often plays the key role in the synthesis of these porous materials because it provides an exceptional control over the composition and morphology of the final material. Over the last decades, this process has seen major advances, not only with respect to the compositional variety of the inorganic matrix but also with respect to the almost unlimited possibilities given for the incorporation of biological and organic entities into the network, as well as with respect to the different structures (total porosity, pore size and shape, connectivity, etc.) and morphologies formed. In the synthesis of porous (hybrid) silica-based materials, hydrolysis and condensation reactions of alkoxy silanes, such as the commercially available tetramethoxy- or tetraethoxy silanes, represent the “master key” reactions, offering a large variety of parameters, such as the precursor concentration, pH value, temperature, solvent, etc., to deliberately tailor the final network morphology and pore structure (from polymeric to particulate, large or small particles, etc.). However, the sol-gel process with these precursors is limited in its potential, especially when it comes to the incorporation of biomolecules or network formation in the presence of lyotropic liquid crystalline (LC) arrangements, not only because of the *obligatory* presence of the solvent as a compatibilizing agent (typically an alcohol, which is often detrimental to biomolecules, such as enzymes or proteins and LC phases) but also because of the either basic or acidic pH conditions that are necessary for network formation.

Diol- or polyol-modified silanes as substitutes for the typically applied tetramethoxy or ethoxy derivatives seemed to be better candidates, especially with respect to the compatibility of the diol or polyol released upon hydrolysis with LC surfactant phases and biomolecules.

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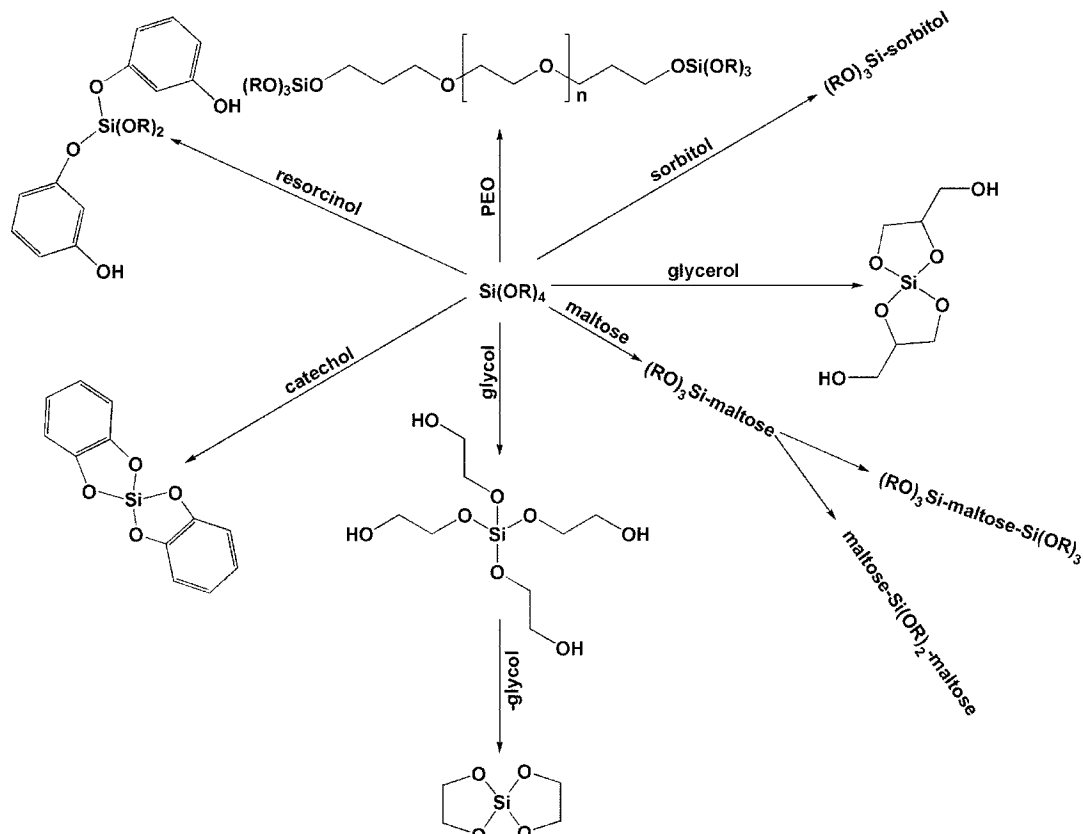


FIGURE 1. Schematic representation of diol- or polyol-modified silanes used in materials syntheses.^{8,10,11,13}

The reaction of silanes with diols/polyols was already reported in the 1950–1960s; however, the hydrolytic instability of these compounds was considered as a big disadvantage for many applications in comparison to other commercially available precursors. Only at the end of the last century, in the 1990s, polyol esters of silicates and siloxanes were identified as ideal precursor candidates in bioencapsulation protocols into silica matrices because of their high water solubility, the autohydrolysis in aqueous media, and the fact that during hydrolysis a nonvolatile and bioprotective alcohol is released, which can also function as drying control chemical additive.⁸ The benefits of diol/polyol-modified silane precursors were also recognized by Hoffmann and Sattler for their compatibility with lyotropic surfactant phases.⁹ Since then, several groups started to use diol/polyol-modified silanes for various applications; e.g., Brook and Brennan described the use of diglycerylsilane as well as sugar- and polysaccharide-derived silanes as precursors for silica monoliths with reduced shrinkage levels during drying and as biocompatible precursors for the entrapment of enzymes into sol-gel-derived silica;¹⁰ Shchipunov et al. applied tetrakis(2-hydroxyethyl)orthosilicate (EGMS) as a water-soluble precursor in sol-gel processes;^{11,12} and our group reported the use of EGMS and its glycerol and 1,2-propanediol derivatives in the synthesis of porous monoliths with hierarchical network architecture.^{13,14} Figure 1 shows some of the diol/polyol precursor molecules that have been applied by the different groups. However, one must

keep in mind that the schematic drawing does not represent truly isolated molecular structures but gives only an indication of the molar composition (silicon to diol/polyol), because in most cases, an equilibrium between bridging and chelating species is present and, in some cases, even hypervalent silicon species are reported.

The focus of this Account lies on the application of diol-modified silanes in the synthesis of inorganic and also inorganic-organic hybrid monoliths that exhibit a hierarchical organization of the pore structure on different levels by sol-gel processing in the presence of a lyotropic LC phase of an amphiphilic molecule. We will concentrate on the novel opportunities given by the modification of silanes with diols.

2. Nonconventional Silanes in the Synthesis of Periodically Organized Monoliths

For many applications, e.g., for membranes, etc., monolithic materials with a periodic organization of the pore structure with attractive properties, such as large surface areas, uniform pore sizes, and tunable periodic structures, are desired. A “true-liquid crystal templating” (TLCT) approach applying a preformed lyotropic LC phase prepared with relatively high surfactant concentrations of typically more than 30% in water presents one of the most promising routes toward such highly ordered mesoporous monoliths. However, one of the major problems related to the synthesis of monoliths is the incompatibility of

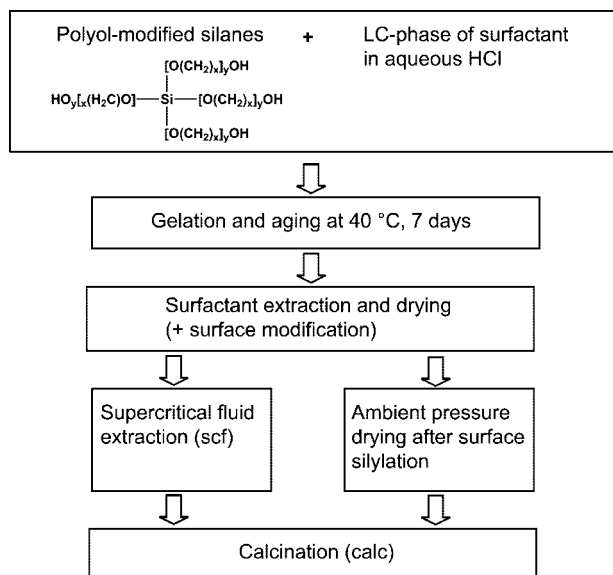


FIGURE 2. General scheme for templating of a preformed lyotropic LC surfactant phase with a diol/polyol-modified silane precursor and the following processing steps.

many lyotropic surfactant phases with alcohols, which are inherently released upon hydrolysis and condensation of alkoxy silanes, such as tetraethoxy- or tetramethoxysilane. Thus, only a limited number of examples of materials with a high degree of mesoscopic order in combination with well-defined macroscopic morphologies (e.g., as monoliths) is known.^{15,16} In these examples, the alcohol was typically continuously removed by rotary evaporation during hydrolysis and condensation reactions.

Alexandridis and coworkers investigated the phase diagrams of a variety of nonionic block copolymer amphiphiles in different alcohols, such as ethanol or various glycols.¹⁷ They could clearly show that the ethanolic system comprises the largest area of an isotropic solution phase, while highly polar glycols resulted in large areas of lyotropic phases, such as hexagonal, bicontinuous cubic, etc. On the basis of these results and the preliminary work by Hoffmann, in which the extraordinary compatibility of the ethylene glycol-modified silane with surfactants was demonstrated, the choice of glycol-modified silanes as optimal candidates in a TLCT synthesis toward mesostructured monoliths is a logical consequence.^{13,14} Figure 2 shows a typical synthesis protocol applied for the formation of such monoliths. Diol- and polyol-modified silanes can easily be prepared by the direct transesterification reaction of tetraethoxysilane with the corresponding diol/polyol at elevated temperatures and upon continuous removal of the released monoalcohol.

First, a preformed lyotropic LC surfactant phase in aqueous HCl is thoroughly mixed with the diol-modified silane. Hydrolysis and condensation reactions start immediately after contact with water, and in comparison to conventional tetramethoxy- or ethoxy- silanes, the gel times are very short. It is a remarkable feature of all glycol-modified silanes that they can be condensed over the whole pH regime, even in neutral conditions with a local minimum in the rate of condensation around the point

of zero charge (PZC) of silica (pH 1.5–3). After gelation, the resulting wet gels are typically aged in the mother liquor for 7 days at 40 °C, followed by either supercritical drying with carbon dioxide or ambient pressure drying via surface silylation reactions. Interestingly, the obtained clear gels turned white after gelation, thus indicating an additional phase separation step on a larger length scale than in the lower nanometer range. Structural investigations of the resulting gels by small-angle X-ray scattering (SAXS), nitrogen sorption, mercury porosimetry, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) confirmed that a hierarchical, low-density network structure is formed, comprising not only periodically organized mesopores with a repeating unit distance of about 11 nm but also a cellular silica backbone with macropores of 500–2000 nm in diameter (Figure 3). The surface areas are very high and vary from 850 to 1000 $\text{m}^2 \text{g}^{-1}$, depending upon the amount and choice of the diol-modified silane in the starting mixture. The structural buildup of the network indicates that at least two competing processes occur simultaneously during network formation: first, the sol-gel transition, thus, the formation of the solid silica network, and, second, phase-separation processes on different levels. On one hand, the desired formation of supramolecular aggregates of amphiphilic surfactant/silica assemblies takes place, resulting in mesoscopic ordering; on the other hand, a macroscopic phase separation into condensed silica/surfactant and water/solvent-rich domains defines the later macroporous structure of the gel. These processes cannot be viewed independently, because the relative rates of phase separation and gel formation define the final gel structure, as can be seen by the strong influence of the pH on the macroscopic morphology (SEM images in Figure 3).

Similar gels without this pronounced degree of mesoscopic ordering were prepared by the groups of Nakanishi and Lindén.^{18–20} These two groups obtained highly porous silica monoliths with a hierarchical organization of the pore structure by applying an organic polymer [mostly poly(ethylene oxide) (PEO)] as an additive to induce macroscopic phase separation. Nakanishi et al. clearly showed that the formation of these biphasic morphologies is induced by the polycondensation reaction of the network-forming silica species and is finally irreversibly frozen by the sol-gel transition. Therefore, all of the parameters that change the relative reaction rates will have a profound influence on the architectural properties of the final gel, including mesoporosity, interconnected macroporosity, degree of macroscopic phase separation, and thus the morphology of the material.^{18,19} To gain more control over the mesopore structure, both groups added cationic or nonionic surfactant molecules and Nakanishi et al. showed that a well-organized mesopore system is accessible by this approach as well.

For diol-modified silanes, the macroscopic phase separation cannot only be influenced by the pH value as seen in the SEM images (Figure 3) but also by the choice of diol used for the modification. While with ethylene glycol as the substituent, mainly cellular networks were obtained,

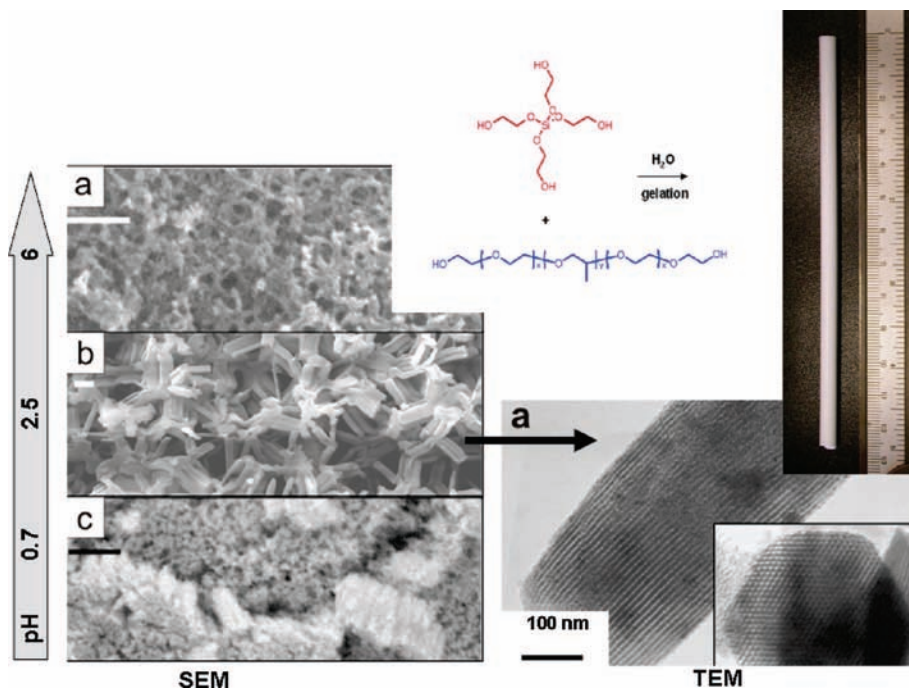


FIGURE 3. SEM images of samples prepared from EGMS in the presence of the block copolymer amphiphile P123 at different HCl concentrations (left) and the corresponding TEM image for the sample prepared at pH 2.5. The scale bar for the SEM images corresponds to 1 μm .

a modification of the tetra-alkoxysilane with the less polar propylene glycol followed by the same general processing route as depicted in Figure 2, now resulting in more particulate appearance of the network-forming units but still exhibiting a multilevel pore system with well-defined mesoscopic ordering.¹⁴ Gels prepared from a glycerol-modified silane did not show any long-range ordering in the mesoscopic range under the given synthesis conditions and exhibit particulate structures typical for silica-based sol-gel systems.

An additional hierarchical level is accessible by simple variation of the templating agent. Applying a block copolymer that still forms lyotropic LC phases but is less miscible in the aqueous silane phase, such as a polyether silicone derivative of the type ABA, with A being a PEO block and B being a poly(dimethylsiloxane) (PDMS) block, an emulsion is formed. Hydrolysis and condensation reactions of EGMS in the presence of such a block copolymer resulted in a gel that exhibited a weakly ordered mesostructure in a cellular macroporous network that again itself is part of a large emulsion templated network (Figure 4). The final material exhibits a rather high surface area with about $1000 \text{ m}^2 \text{ g}^{-1}$ and a monomodal mesopore-size distribution. An interesting feature of the application of silicone-based block copolymers as the structure directing agent is the possibility to tailor the surface polarity of the final gel by selective heat treatment.²⁹ Si nuclear magnetic resonance (NMR) studies have shown that, by calcination at $400 \text{ }^\circ\text{C}$, the pore wall surface is covered with T units (CH_3SiO_3) and thus exhibits partial hydrophobicity in a now inorganic-organic matrix.

3. Hybrid Hierarchically Organized Materials

The structural features of a highly porous oxide material prepared by wet chemical methods, e.g., the sol-gel process, depend not only upon the synthesis parameters, such as the pH, concentration of the precursors, temperature, etc., but also to a great deal upon the drying conditions. The rather compliant wet gel networks with a random distribution of pores are very sensitive to large capillary pressures exerted on the structure during drying, very often resulting in the collapse of the gel body. These so-called xerogels exhibit smaller pores, an increased density compared to the original wet gel, and monolithic structures that are very often destroyed upon drying. To obtain highly porous monoliths, cracking is typically prevented by drying with supercritical fluids (SCFs), e.g., carbon dioxide, to avoid the buildup of a gas/liquid interface; hence, no capillary pressures evolve. However, SCF extraction is expensive and time-consuming and requires relatively high pressures sometimes even combined with high temperatures.

Hybrid Monoliths via Postsynthesis Treatment. One objective of our continuing research was to find alternative routes to supercritical drying to remove the solvent and possibly extract the block-copolymer template but still avoid shrinkage and collapse of the pores. A very promising procedure for drying large silica gels relying on a simple surface modification treatment with trimethylchlorosilane was presented in the mid-1990s as an alternative to supercritical drying.²¹ A similar approach also using organochlorosilanes and organoalkoxysilanes as post-treatment reagents was published recently not for drying but for the extraction of ionic surfactants from self-assembled silica-surfactant powders.^{22,23} As the driving

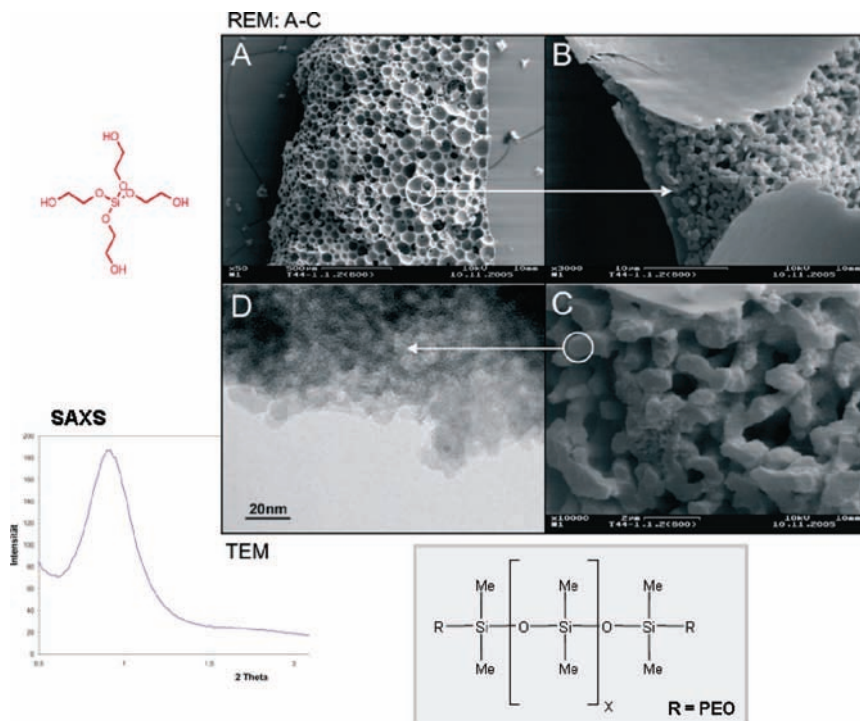


FIGURE 4. PEO–PDMS–PEO block-copolymer templated monoliths exhibiting a multilevel hierarchy. The monoliths are templated from an emulsion, which is easily seen in A, with the closed macropores of about 50–200 μm in diameter. The walls of these closed pores are porous themselves (B), composed of a cellular network structure of strands of about 800 nm in diameter, comprising pores of about the same size (C). In addition, these strands exhibit another level of porosity, and in the SAXS pattern, indications of mesoscopic ordering with a repeating unit distance of about 10 nm can be seen. The corresponding TEM image (D) however, shows a wormhole-like aggregation of the pores.

force for this reaction, the replacement of electrostatic interactions at the inorganic–organic interface by covalent siloxane bonds, that is the formation of Si-O-SiR_3 , was named.

The same approach could also be used for the drying of large hierarchically organized wet silica gels. Upon treatment of the wet gel with trimethylchlorosilane in petroleum ether, a surface silylation process takes place, which completely reverses the surface polarity. The whole gel is turned from a hydrophilic, water-containing system to a nonpolar, hydrophobic one, thus resulting in an almost complete extraction of the nonionic block copolymer (P123) that was used as a structure-directing agent (Figure 5). In addition, drying could now be performed without cracking and with complete structural integrity of the network by simply heating the gels to 150 $^\circ\text{C}$. The surface chemistry of the gels can be deliberately tailored by this approach, resulting in hydrophobic gels after drying. The most intriguing feature of this silylation procedure is that it reduces the number of processing steps and the time necessary for the production of these hierarchically organized monolithic gels drastically.²⁴

Large, low-density silica monoliths with multimodal pore-size distribution are already high-performance materials. However, for many applications, the spectrum of properties needs to be improved by additional functions, e.g., hydrophobic groups, metal-coordinating groups, etc., without deteriorating the existing structural features, such as porosity, periodic ordering, large surface area, etc. Inspired by the successful simultaneous drying, surface

modification, and surfactant extraction of large silica monoliths with a hierarchical network organization by a simple surface silylation reaction of the wet gel structure, we extended this approach to other functional organosilanes.

A variety of organofunctional silanes, such as trimethylchlorosilane, 3-mercaptopropyl-trimethoxysilane, phenyl-trimethoxysilane, 3-[(2,2-dimethyl-1-aza-2-silacyclopent-1-yl)dimethylsilyl]-1-propanamine, a cyclic silazane resulting in aminopropyl-dimethyl-silyl groups on the silica surface, and (methylmethacryloyl)dimethyl-methoxysilane, has been successfully applied in the interfacial modification of the silica surface of these wet gels. Figure 6 shows exemplarily the SEM and TEM images of a methacrylate-modified hierarchically structured silica gel. The delicate gel structure is completely retained during the postsynthesis treatment, and a rather high bonding density of functional groups to the silica surface with 2–4 mmol (g of SiO_2)⁻¹ is achieved.²⁵ This approach can in principle be extended to many more functional groups. Even further reactions at the functional centers now located on the pore wall are possible.

Hybrid Monoliths Prepared from Diol-Modified Organosilanes. An alternative approach toward hybrid inorganic–organic silica-based materials is based on the co-condensation between tetra- and organotrialkoxysilanes, with the latter carrying an organic (functional) group connected via a hydrolytically stable silicon–carbon bond (a large variety of triethoxy- or trimethoxy precursor molecules is already commercially available). Many functional materials, e.g., as coatings, have been prepared by

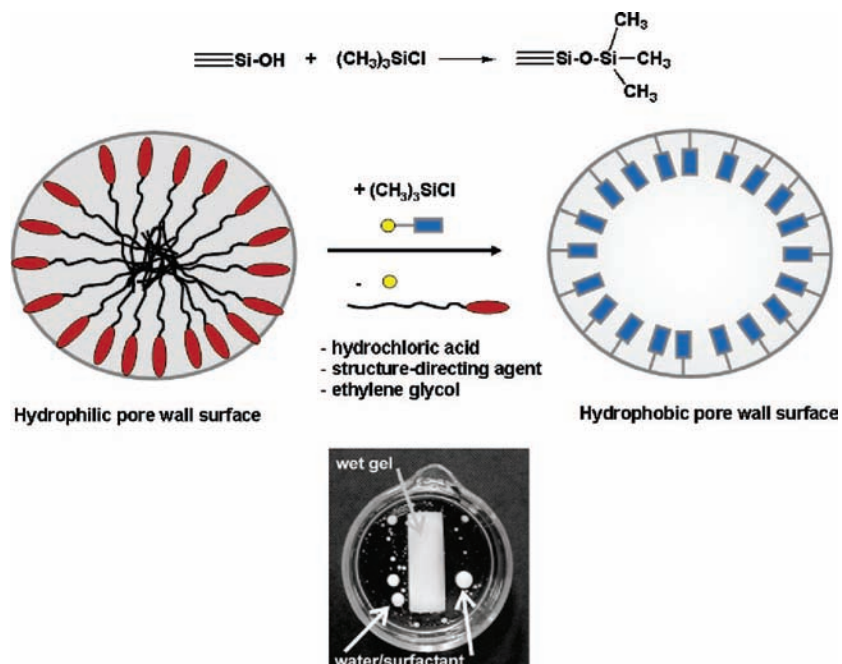


FIGURE 5. Schematic depiction of the silylation of surface silanols with trimethylchlorosilane (top) and the corresponding photograph of the spontaneous expulsion of P123/water/ethylene glycol droplets from a wet gel upon immersion in a petroleum ether (PE)/trimethylchlorosilane mixture (bottom).

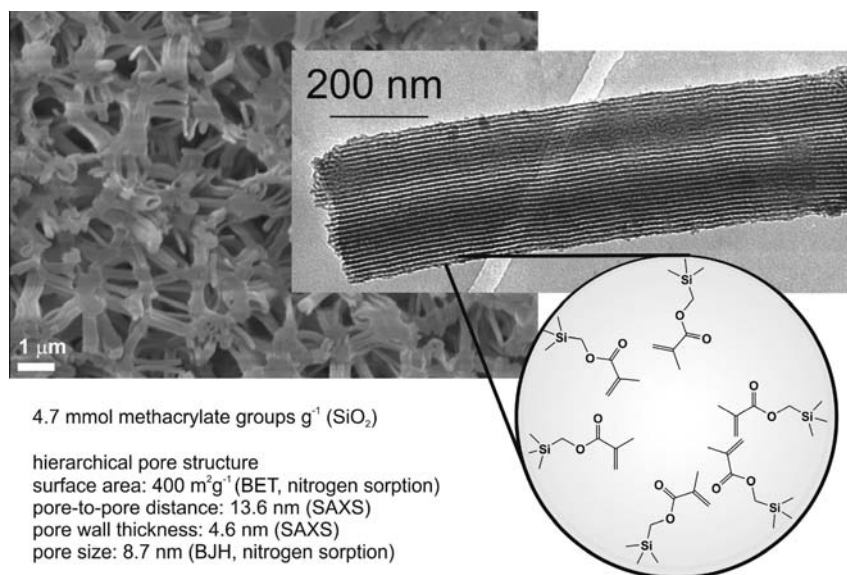


FIGURE 6. Well-ordered methacrylate-modified silica gel prepared from EGMS and treated with (methylmethacryloyl)dimethyl-methoxysilane in the wet gel stage (SEM, TEM, and representative structural data).

just mixing these different silanes; however, one has to keep in mind that the structure of the final material is strongly influenced not only by the ratio of tetra-/trialkoxysilane but also by the nature of the organo (functional) group and the relative reaction rates of the two precursors. This becomes especially important for highly porous materials for which many materials properties are derived by the specific network structure that must not be altered by the organic modification.²⁶

When the glycol-modified silane (e.g., EGMS) is substituted by glycol-modified organo (functional) silanes, such as the phenyl or methyl derivatives, tris(2-hydroxyethoxy)-methylsilane or tris(2-hydroxyethoxy)phenylsilane, organic

groups can be introduced into the silica gel network. One of the main questions here is to what extent does the substitution of tetrafunctional silicon centers (with respect to the degree of condensation) to trifunctional silicon centers alter the network architecture because of changes in the polarity, degree of condensation, different reaction rates, etc. It was shown that the macroscopic gel morphology and periodic ordering of the mesopore structure can be significantly influenced by the choice of the pH, type and degree of substitution with organic functionality, and Si/P123 ratio. For each system, the optimal synthesis parameters have to be fine-tuned to obtain optimal results with respect to long-range periodicity of the mesostructure.²⁷ As a general trend

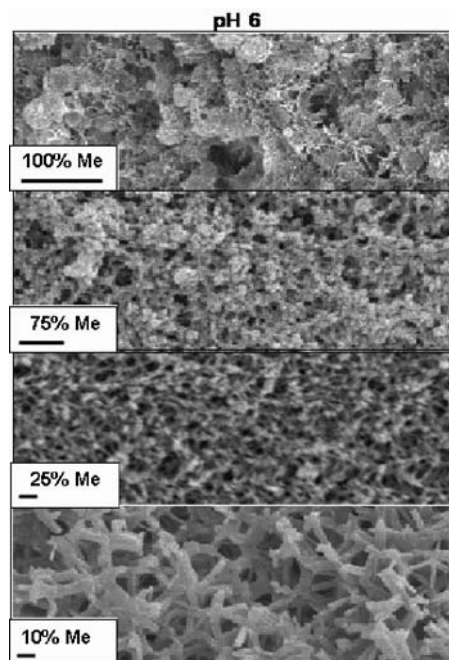


FIGURE 7. SEM images of the methyl silsesquioxane-substituted monoliths (from 10 up to 100 mol % substitution with the methyl-modified silane). Scale bars correspond to 1 μm .

for the preparation of gels of a mixture of EGMS and tris(2-hydroxyethoxy)methylsilane in acidic media, a lower degree of mesoscopic ordering is observed with increasing the amount of organosilane in the starting solution for a given pH value. In addition, the macroscopic morphology is strongly influenced as can be seen in the SEM images in Figure 7. Gels prepared from 100% tris(2-hydroxyethoxy)methylsilane or tris(2-hydroxyethoxy)phenylsilane did not show any mesoscale periodicity under the given set of synthesis parameters. The underlying notion of substituting the alkoxy groups of conventional (organo)alkoxysilane precursors with ethylene glycol can be readily extended to other organic functionalities. This method represents a versatile tool to tailor the chemical functionality of monolithic materials with well-defined, multimodal pore structures, thus increasing their potential of application significantly.

In this case, the structural features of the resulting gels are strongly dependent upon the amount of organically modified silane that was used (varying from 10 to 100 mol %, Figure 7) and upon the pH of the starting solution. The SEM images reveal interconnected (open) macroporosity but various morphologies for the different samples. Both the pH and degree of substitution with methyl-Si groups show a strong influence on the phase-separation process and the resulting morphologies. A cellular network buildup from rod-shaped aggregates of 2–3 μm in length and about 0.5 μm in diameter, very similar to the gels prepared from pure EGMS at pH 2.5, is observed for 10 mol % substitution with the methyl-modified silane prepared at pH 6. The sample with 25 mol % of the methyl-modified silane prepared at pH 6 shows very small, aerogel-like structural features in the nanometer regime; however, macropores are also observed. When the gelling system was carefully fine-tuned, hierarchically structured monoliths with pe-

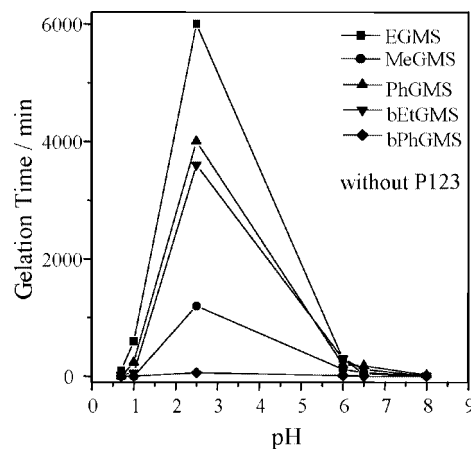


FIGURE 8. Gelation times of the various ethylene glycol-modified (organo)silanes (100%) at different pH without a surfactant.²⁷ [EGMS, tetrakis(2-hydroxyethyl)orthosilicate; MeGMS, tris(2-hydroxyethoxy)methylsilane; PhGMS, tris(2-hydroxyethoxy)phenylsilane; bEtGMS, 1,2-bis[tris-(2-hydroxyethoxy)silyl]ethane; bPhGMS, 1,4-bis[tris-(2-hydroxyethoxy)silyl]benzene].

riodically ordered mesopores were obtained for up to 25 mol % tris(2-hydroxyethoxy)methylsilane.

Only a very few studies report on the formation of highly porous monoliths from pure silsesquioxanes, e.g., methyltrialkoxysilanes.^{28,29} This can probably be led back to the lower degree of cross-linking that is expected when precursors are used with only three potential reaction sites (resulting in long gelation times, Figure 8), as well as the mechanical instability of the resulting gels because of the lower connectivity and phase-separation phenomena of oligomeric or polymeric silsesquioxanes because of the polarity differences within the precursor molecule. As one of the most remarkable features of the modification with diols, it was shown that tris(2-hydroxyethoxy)methylsilane and other organosilanes allow for the formation of gels of very low density composed of 100% methylsilsesquioxane (organosilsesquioxane) over a wide pH range and even in a purely aqueous environment. Again, a minimum in the condensation rate (thus, a maximum in the gel time) is observed around pH 2.5.

Hybrid Monoliths Prepared from Bridged Diol-Modified Organosilanes. Bridged polysilsesquioxanes are a family of hybrid inorganic–organic materials, in which the organic groups are located within the channel walls as bridges between two or more Si centers, thus serving as an integral part of the inorganic network.^{30,31} The most intriguing feature of these materials is the variability of the organic spacer group with respect to the length, rigidity, geometry of substitution, and functionality. Sol-gel polycondensation reactions of these “hybrid” monomers have led to a large variety of different porous hybrid materials exhibiting specific structural properties, such as high surface areas and functionality.

In 1999, the three groups of Stein, Inagaki, and Ozin independently extended the polycondensation reactions of these bridged polysilsesquioxane precursors to a novel class of organic–inorganic nanocomposites with periodically arranged pore systems, the “periodic mesoporous

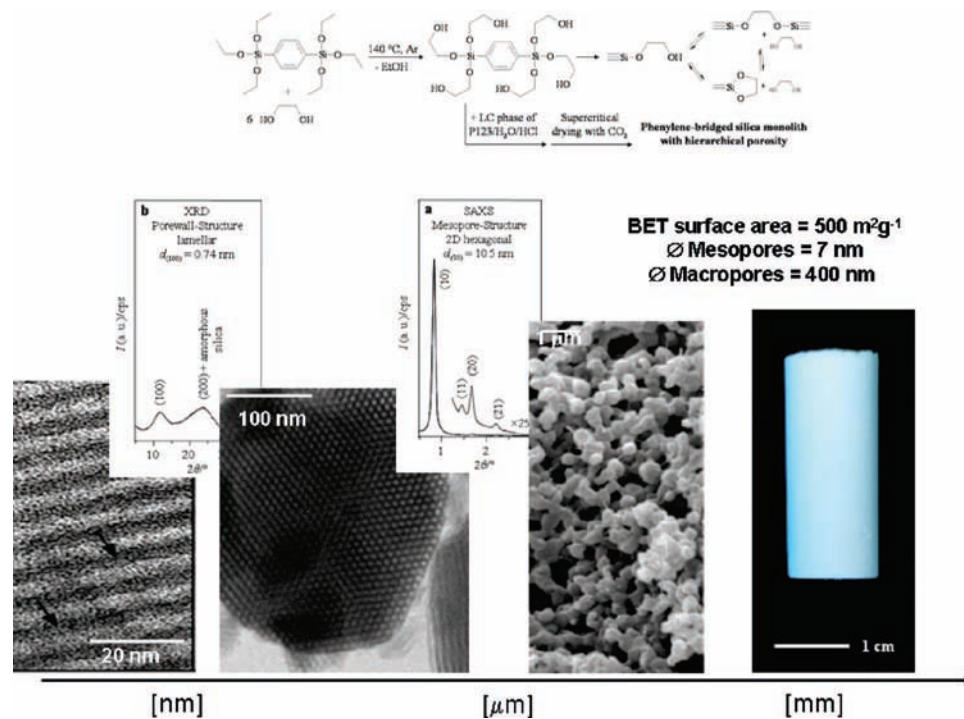


FIGURE 9. Hierarchy on four levels. The monolithic structure (photograph) exhibits an interconnected, uniform macroporous network (SEM image) built from particles of about 200 nm in diameter, with a highly organized hexagonal mesopore system (TEM and SAXS) in addition to molecular-scale periodicity of the phenylene groups in the pore wall [high-resolution (HR) TEM and XRD].

organosilicas” or so-called PMOs.^{32–34} These materials were prepared with a very high degree of periodicity and uniformity of the pores, applying bridged silsesquioxane molecules of the type $(\text{RO})_3\text{Si}-\text{R}'-\text{Si}(\text{OR})_3$ as the sole precursor for network formation in the presence of a structure-directing agent. A multitude of different organic spacers can be incorporated into periodically arranged silica-based materials by this approach. When the synthesis conditions and the organic spacer are carefully chosen, even materials with semicrystalline pore walls can be prepared. Through self-assembly of 1,4-bis(triethoxysilyl)benzene in the presence of a cationic surfactant in basic conditions, a well-organized, mesoporous material was obtained that exhibited molecular-scale periodicity within the pore walls, probably induced by $\pi-\pi$ and hydrophobic interactions of the phenylene moieties.³⁵

However, all synthesis protocols reported thus far describe only the fabrication of PMO powders or films and not the fabrication of monolithic materials, although the ability to mold porous materials into any desired shape and size increases their range of applications significantly. In particular, the synthesis of monolithic materials with hierarchical pore structure is under extensive investigation, because the combination of different pore size regimes within one material leads to multiple benefits arising from each regime. Only recently, the first papers on monolithic organosilica materials with hierarchical architecture were published by us and Nakanishi et al.^{36,37} When a 1,2-bis(triethoxysilyl)ethane was applied in the presence of a nonionic block-copolymer structure-directing agent (P123) in combination with 1,3,5-trimethylbenzene as a swelling agent that enhances the self-organization of the surfactant, a hybrid silsesquioxane monolith with well-defined interconnected

macropores and periodically organized mesopores was obtained by Nakanishi et al.

Again, diol-modified precursors represent another possibility to easily access phase-separated silica monoliths with a hierarchical buildup of highly ordered mesopores and interconnected, uniform macropores. Starting from an ethylene glycol-modified bridged silsesquioxane precursor molecule, 1,4-bis[tris-(2-hydroxyethoxy)silyl]benzene, which was obtained by a simple transesterification reaction of the corresponding ethoxy derivative with ethylene glycol in a molar ratio of 1:6, hydrolysis and condensation were induced by the addition to a preformed lyotropic LC phase of P123 in aqueous hydrochloric acid (as depicted in Figure 2). Large, low-density (0.240 g cm^{-3}) phenylene-bridged silica monoliths were obtained (Figure 9).³⁷ Interestingly, this is the first paper on the stacking of the phenylene units to give semicrystalline pore walls in a mesostructured matrix that was templated by a nonionic amphiphile. The final material now shows four levels of hierarchy.

4. Conclusions and Future Perspectives

The greatest appeal but probably also the major challenge of sol-gel chemistry is the flexibility not only in the design of the final network structure and morphology but also in the choice of the precursors. Already, a simple variation of an alcoholic leaving group from ethanol to ethylene glycol opens completely new opportunities for the later properties and applications of the materials. Diol- and polyol-modified silanes have proven to be very attractive precursor candidates for the synthesis of silica gels, because they cannot only

be processed in purely aqueous conditions without the need of an acid or base catalyst but the diol released upon hydrolysis shows a higher compatibility with many biological species and lyotropic LC phases of surfactants or amphiphilic block copolymers. Thereby, not only access to a large variety of novel biomolecule-doped silica networks is gained but also access to hierarchical organized silica architectures by performing the hydrolysis and condensation reactions in the presence of structure-directing amphiphiles. The few examples presented in this Account give just a few glimpses of the possibilities that are available in a deliberate materials design. For the given systems, the further development of the chemical modification of the pore walls as well as the possibilities of impregnation with functional moieties, such as biological entities, e.g., proteins, living cells, etc., will broaden the potential applications of these hierarchical porous materials. The large variety of functional silanes in combination with the huge amount of different diols/polyols that are available allows for the formation of many different functional hybrid porous architectures. One of the biggest prospects of diol-modified organosilanes lies in the possibility to process them as the sole precursor in the formation of monolithic silsesquioxane gels in reasonable fast gelation times, thereby resulting in 100% substitution with organic moieties.

Modification with diols/polyols is in principle not only limited to siliceous precursors but can also be extended to nonsiliceous materials, e.g., titanium alkoxides, etc., and novel materials with higher levels of complexity, e.g., as hierarchically organized monoliths that will be accessible.

Much room is left for innovative preparation strategies to materials with an even higher level of organization and functionality.

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