A Novel Green Template for the Synthesis of Mesoporous Silica

Yeping Xu,[b] Shangjie Xu,[b] Thomas Emmler,[b] Frank Roelofs,[a] Christoph Boettcher,[b] Rainer Haag,[b] and Gerd Buntkowsky*[a]

Abstract: Mesoporous pure silicas and functionalized silica with a narrow pore size distribution centered at 3.8 nm were prepared by a novel template, amphiphilic dendritic polyglycerol. The resulting silica materials were characterized by electron microscopy; nitrogen adsorption; ^{1}H, ^{13}C, and ^{29}Si solid-state cross-polarization magic-angle spinning NMR spectroscopy. It was shown that the template could be completely removed from the pure and functionalized silica in an environmentally friendly way by means of a simple water extraction procedure. Furthermore, it was shown that these materials could be easily functionalized, for example, by employing aminopropyl groups. Thus, a new environmentally friendly pathway to this fascinating class of silica material has been opened.

Keywords: green chemistry · mesoporous silica · polyglycerols · solid-state NMR spectroscopy · sustainable chemistry

Introduction

Following the seminal discovery by Beck et al. in 1992,[1,2] the development and synthesis of mesoporous silica materials is one of the hot topics in materials science.[3–7] The main reason for this interest is that these mesoporous materials have great potential applications in catalysis, separation technology, basic science, and many other fields. Most of these materials are prepared by hydrothermal processes from solutions of surfactants, which include ionic, nonionic, and neutral surfactants,[1,2,8–10] such as cetyltrimethylammonium bromide and Pluronic F127 copolymers. Usually, these kinds of surfactants can form liquid-crystalline phases with special structures at high concentrations, for example, the formation of hexagonal micelles during synthesis, or they can interact with the silicon precursor to form mesostructured silica.[1,8]

Recently, alternative pathways for the synthesis of these materials have been developed, in which some nonsurfactant templates, for example, dibenzoyl-L-tartaric acid, sugar, or dendrimers were employed for the synthesis of mesoporous silica.[11–15] However, to date these alternative templates have problems. In the case of nonsurfactant templates, the reactions only proceed very slowly and it usually takes 15 to 20 days to synthesize the silica and another 2 to 3 days to remove the templates.[11] When dendrimers,[12–15] such as DAB (diaminobutane) or PAMAM (polyamidoamine), are employed, problems with their poor solubility in water and their toxicity arise, which necessitates the removal of these templates by calcinations or by extraction with organic solvents. In the latter, typically more than 100 mL of organic solvent are necessary for 1 g of silica[10,16,17] and this solvent extraction process sometimes takes several days.[11,18]

Of particular interest are functionalized silica materials with their specially designed surface properties. They are useful in many applications, such as separation, catalysis, and drug delivery. If the functional organic group is applied before or during synthesis of the silica, the template can only be removed by solvent extraction because the functional groups would be burnt during calcination. Furthermore, because of the existence of organic groups on the pore surface, the removal of the template by extraction is usually effective, but not complete.[19–21]

Herein, a novel, fast, and environmentally benign synthetic pathway for the synthesis of pure and functionalized mesoporous silica is proposed. This pathway employs hyperbranched polyglycerol (PG) with average molecular weights of 5000 and 6000 g mol^{-1} as templating agents.[22–24] This low-

[a] Dr. F. Roelofs, Prof. Dr. G. Buntkowsky
Institut für Physikalische Chemie
Friedrich-Schiller-Universität Jena
Helmholtzweg 4, 07743 Jena (Germany)
Fax: (+49)3641-948-302
E-mail: gerd.buntkowsky@uni-jena.de

[b] Y. Xu, S. Xu, Dr. T. Emmler, Dr. C. Boettcher, Prof. Dr. R. Haag
Institut für Chemie und Biochemie
Freie Universität Berlin, Takustrasse 3
14195 Berlin (Germany)

cost template is innocuous, biocompatible, and works without requiring organic solvents. Our templating mechanism is based on the size of hyperbranched PGs revealed from small-angle neutron scattering (SANS) measurements. They have shown that single-particle PG dendrimers have generation-dependent, well-defined diameters that can be adjusted from 2 to 5 nm, which corresponds to molecular weights of 2000 to 10000 gmol^{-1}.[25] The expected template size of PG with an average molecular weight of 6000 gmol^{-1} is around 4 nm based on SANS measurements. As a template, hyperbranched PG differs greatly from the surfactants described above.

Owing to its almost spherical structure it cannot form micelles or large-scale clusters. As a result of the good water solubility of PG, the template can be removed by water extraction without the need for organic solvents.

Results and Discussion

Herein, pure and functionalized silica were prepared in a fast and novel reaction pathway without the need for a hydrothermal process by employing hyperbranched PGs as a template (see Table 1 to compare samples described herein). In both cases the silica materials obtained have a mesoporous structure with highly specific inner surface areas.

Table 1. Properties of the porous silica samples.

Sample[a]	PG M_W [kDa]	Surface area[b] [m^{2}g^{-1}]	Pore volume[b] [mLg^{-1}]	Pore diameter[c] [nm]
DMS-5k-W[d]	5	583.6	0.47	3.82
DMS-6k-W[d]	6	623.5	0.51	3.86
DMS-amino[d]	6	422	0.27	3.32
DMS-6k-C[e]	6	749.5	0.67	3.85

[a] DMS=dendrimer-templated molecular sieve, 5k and 6k indicate the size of the PG templates used, W= water-extracted sample, C=calcinated sample, and DMS-amino indicates silica functionalized with aminopropyl groups. [b] Calculation by using BET methods. [c] Calculated by using BJH methods. [d] Template removed by water extraction. [e] Template removed by calcination at 300°C.

In the case of pure silica, the material is characterized by a narrow pore diameter distribution centered at 3.8 nm, as calculated by using the Barret–Joyner–Halenda (BJH) method from the desorption branch.[26] In the case of silica functionalized with aminopropyl groups, the pore size distribution of the material is also narrowed at 3.32 nm, but with a lower specific area. In both cases the template in the synthesized silica was removed below the detection limit by the water extraction.

The first question we wanted to answer with the solid-state NMR spectroscopy experiments was to what extend the template was removed from the silicas. Figure 1a, compares the ^{1}H spin-echo NMR spectra of the samples before and after water extraction. In the ^{1}H NMR spectra, the proton signal at $\delta=3.5$ ppm is shifted to 2.0 ppm with a shoulder peak at around 3.3 ppm after water removal. This spectrum shows that no characteristic signal for the methylene groups of PG at $\delta=3.2$ ppm was observed and that the only proton signals were from the OH groups of adsorbed water and hydroxyl groups on the silica surface. They are in fast exchange with each other and only give a single line at the average shift value, similar to results for other silica materials.[27–29] The ^{29}Si cross-polarization magic-angle spinning (CPMAS) spectrum (Figure 1b) of the sample of DMS-amino proves the success of cocondensation of the functional group into silica by the appearance of the T_2 and T_3 signals at $\delta-62$ and -68 ppm, respectively.[19] The removal of the template below the detection limit is corroborated by the ^{13}C CPMAS NMR spectra in Figure 2, which compares the ^{13}C CPMAS spectra of as-synthesized DMS-6k-W, water-extracted DMS-6k-W, and water-extracted DMS-amino. Note that no carbon signal is detected even after 10240 scans of the DMS-6k-W and DMS-amino samples.

According to the NMR spectroscopy measurements, it can be concluded that the hyperbranched PG template molecules can be completely removed from pure and functionalized silica by a solvent extraction process with water. This is an indication that the hydrogen bond between water and the hydroxyl groups on the periphery of PG are stronger than those between the template and the silica surface.

The Brunauer–Emmett–Teller (BET)[30] surface areas and pore volumes were measured on the calcinated and solvent extracted samples by measuring the N$_2$ adsorption–desorption isotherms. The BET surface area data and pore diameter calculated from the desorption
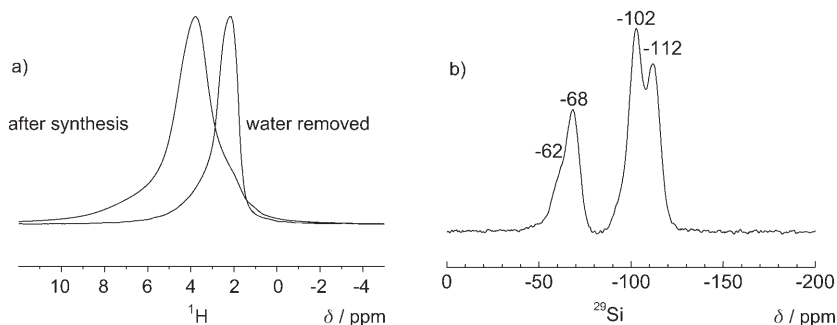

Figure 1. a) ^{1}H CPMAS (7 tesla) NMR spectra of the silica samples. The left-hand line was measured on a sample obtained synthetically. The right-hand line was obtained on a sample from the same batch after water removal. Note the shift in the main intensity towards high field, which indicates the removal of water. b) ^{29}Si CPMAS (7 tesla) NMR spectrum of the DMS-amino sample.
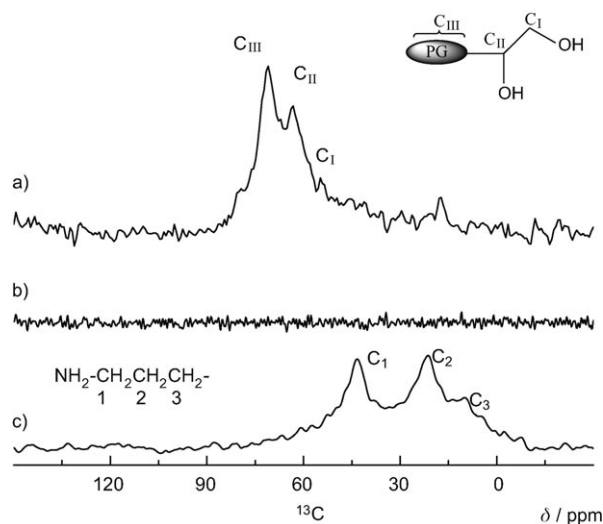
Figure 2. ^{13}C CPMAS (7 tesla) NMR spectra (10240 scans each) of a) as-synthesized DMS-6k-W, b) DMS-6k-W after water extraction, and c) the functionalized sample (DMS-amino) after water extraction. Note the suppression of all ^{13}C-resonances beyond the detection limit.

branch of the N$_2$ isotherm are shown in Table 1. All samples in which the template is removed by water extraction have surface areas of approximately 600 m^{2}g. They exhibit a slight increase in total pore volume with increasing molecular weight of the dendrimer. As the BJH pore diameters only slightly change with the molecular weight of the dendritic polymer, it can be concluded that the latter aggregate during silica gelation. Moreover, the smaller molecular weight polymers aggregate more and the aggregates of the polymers with the same mass concentrations stop at similar sizes. The calcinated sample (DMS-6k-C) has a larger BET surface area than the water-extracted sample (DMS-6k-W), which may be owing to condensation of hydroxyl groups on the surface and/or small changes to the pore framework.

Figure 3a shows the N$_2$ isotherms as a function of the relative pressures (P/P_0). All pure silica samples have type IV isotherms (notation according to IUPAC conventions[20]), and type-H$_2$ hysteresis loops. For the water-extracted samples (DMS-5k-W and DMS-6k-W), the sharp steps in the de-

sorption branches occur between 0.4 and 0.5 in the relative pressure interval, which indicates a homogeneous pore size distribution. The desorption branch of the calcinated sample (DMS-6k-C) indicates a broader distribution of pore diameters, which is caused by the calcinations step. This is confirmed by the evaluation of the BJH pore size distribution (see Figure 3b). Furthermore, the observed initial linear region in the α_s plot indicates the absence of any detectable micropore filling at low relative pressures.[31] The calculated pore size distributions are plotted in Figure 3b. The calculations by BJH methods reveal a very homogeneous pore size distribution, in which the pore diameters of all of the samples are close to the value of 3.8 nm obtained for pure silica. Moreover, with increasing the molecular weight of the template, the distribution of the pores becomes narrower. In particular there are (almost) no micropores with diameters below 3.0 nm detectable in these samples (by using the α_s plot method).

The nitrogen adsorption shows also that there is almost no difference in the pore sizes of DMS-5k-W and DMS-6k-W. This result is attributed to the globular structure of the hyperbranched PG templates, in which the addition of an extra molecular layer through back-folding into inner void regions does not significantly increase the size of the template.

The pore size distribution of the calcinated sample (DMS-6k-C) is also narrowly centered at 3.8 nm. This implies that the pore walls were not damaged when the surface hydroxyl groups condensed during calcinations at 600°C.

Further insight into the stability of the material was obtained by comparing the width of the pore size distribution of the calcinated sample (DMS-6k-C) with the non-calcinated samples (DMS-5k-W and DMS-6k-W). If the framework of DMS-6k-C was unstable then it would shrink during calcination, which would result in a smaller pore volume and specific surface area.[32] Figure 3 shows that the opposite behavior occurs. The calcinated sample exhibits a substantial amount of pores with a larger diameter than the non-calcinated samples. This increase in the average pore diameter shows the good thermal stability of the DMS samples.

The extracted DMS-amino sample has an average pore diameter of 3.32 nm (curve not shown) and a type I iso-
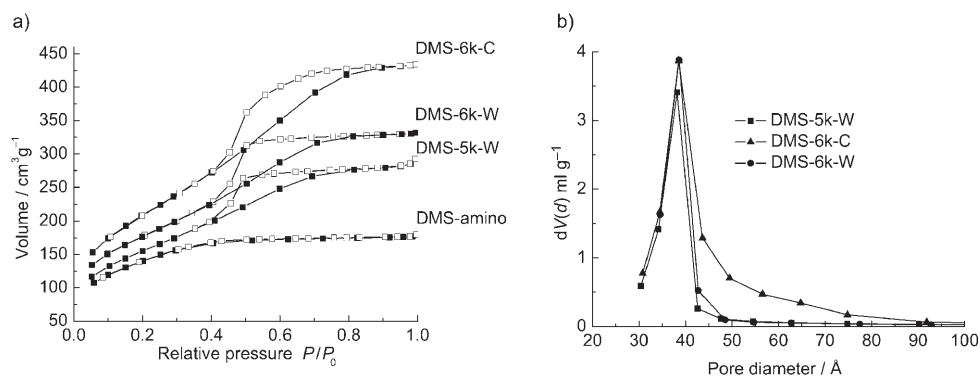

Figure 3. a) N$_2$ isotherms of the samples. b) The pore size distributions calculated by the BJH method.

therm,[30] which indicates an interaction, in this case it is most likely to be hydrogen bonding of the amino group with the template during self-organization of the precursors in the sol–gel step. With this interaction, the template has a different structure than that without functional groups.

Typical transmission electron microscopy (TEM) images are shown in Figure 4. In the TEM images of the samples of DMS-6k-W and DMS-6k-C, the size of pores and particles
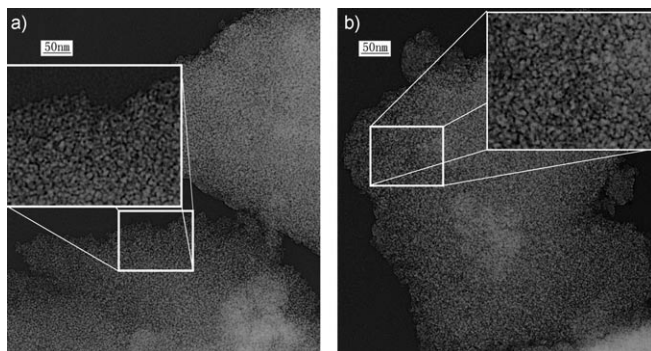

Figure 4. TEM images of water-extracted silica (a) and calcinated silica (b). Scale bars are 50 nm.

are almost all homogeneous. The cylindrically shaped channels with regular diameters are clearly visible in the images. This proves that templating with the hyperbranched polymeric templates indeed plays a crucial role in assembly of the silica. This implies that hydrogen bonds of the PG template to the silicon precursors in sol, gel, and/or ageing procedures organizes the mesoporous phase, which is stabilized after template extraction. The shape of particles and channels in the TEM images are similar to those obtained by the non-surfactant templating route[11] and the nonionic polyethylene oxide surfactant pathway.[10] The TEM result for the calcinated sample shows almost the same particle and pore shapes as the water-extracted silica.

The similarities between the TEM pictures of water-extracted and calcinated samples corroborate the results from the N_2 isotherm measurements that silica templated by dendritic PG has a good thermal stability during calcination. Thus, PG can be used as a very good, well-ordered, mesoporous-structured templating agent.

Conclusion

In conclusion, pure mesoporous silica materials with large surface areas, pore volumes, and narrow pore size distributions have been synthesized by a sol–gel reaction of tetraethylorthosilicate (TEOS) by using hyperbranched PG as a non-surfactant template in a fast and environmentally friendly pathway. The resulting silica materials were characterized by electron microscopy; nitrogen adsorption; and ^{1}H, ^{13}C, and ^{29}Si solid-state CPMAS NMR spectroscopies. The templates can be completely removed by water extrac-

tion, instead of using typical organic solvent extraction procedures, from pure and amino-functionalized silica. The pore diameters of the pure silica samples are always narrowly centered at 3.8 nm at this template concentration.

The mechanism of formation of the mesostructure is not yet clear. However, compared to the TEM of mesoporous silica in reference [10], it can be seen that the structure of mesoporous silica prepared by using PG as a template is quite similar to the structure of the silica templated by nonionic polyethylene oxide surfactant micelles. This implies that hyperbranched PG used in this process has a role similar to the polymer micelle. Furthermore, DMS-6k-W has pore channels that are longer than the diameter of the PG particles. This can imply that hyperbranched PG molecules may aggregate to form short-range micelle-like rods in the absence of hydrophobic groups around which silicate species are organized during the synthesis to obtain well-ordered mesostructures by hydrogen-bonding interactions between the high-density hydroxyl groups of the PG surface and the silicates during the sol–gel process. As PG is an amphiphilic substance with good solubility in water and polar organic solvents, it has a high potential to be used as an environmentally friendly template for the synthesis of well-defined mesoporous silica materials with or without functional groups to avoid incomplete template removal,[19–21,33] or to avoid extraction by using large amounts of organic solvent, and thus, meets the requirements of green chemistry.

Experimental Section

In a typical synthesis in this work, the mesoporous silica was obtained by an HCl-catalyzed sol–gel process of hydrolysis of TEOS in a solution of PG followed by the removal of the dendritic templates through water extraction. The entire procedure consisted of the following steps: First, the dendritic templates were added to an aqueous solution that contained H_2O and HCl (36.5% w/w) in molar ratios of PG/H_2O/TEOS/HCl 10^{-4}:0.5:0.02:0.08 with stirring at room temperature in a plastic bottle. Second, after stirring for 30 min, TEOS (4 g) was added to the solution and stirred for another 30 min at room temperature. Third, the entire system was heated overnight at 60°C with stirring in the closed plastic bottle. Finally, the product was filtered and washed with distilled water (3×), followed by solvent extraction with distilled water (3×500 mL). The final step normally took 6 h. The product was a fine white powder. DMS-amino was synthesized by cocondensation of TEOS and 3-aminopropyl-triethoxysilane (10 mol%) with PG (6 kDa) as the template followed by the water-extraction method mentioned above to remove the template. For comparison, one of the samples (DMS-6k-C) was calcinated at 600°C to remove the template. To prove that the dendritic templates had been removed, ^{1}H (300.1 MHz), ^{13}C (75.5 MHz), and ^{29}Si (59.6 MHz) solid-state CPMAS NMR spectra were measured by using a laboratory-built 300 MHz solid-state NMR spectrometer. To suppress the proton background signal of the probe a spin-echo sequence was employed for the ^{1}H CPMAS NMR spectroscopy measurements. Water adsorbed inside the silica was removed by drying on a vacuum line at 110°C. The N_2 adsorption–desorption isotherms were recorded by using the automatic volumetric sorption analyzer Autosorb-1 (Quantachrome) at 77 K (liquid nitrogen cooled). SAXS data for DMS-6k-W had a single peak at $2\theta \approx 1$ similar to that previously reported.[12]

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