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Highly Porous Silica Monoliths from Ethyl (*L*)-Lactate Modified Silanes[#]

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Summary. A new type of silica precursor was synthesized by (trans)alkoxylation of alkoxy- and chlorosilanes with ethyl (*L*)-lactate. This novel ethyl lactate modified silane was hydrolyzed and condensed in the presence of a non-ionic surfactant – poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (P123) – to give monolithic silica gels. The wet gels were dried using two different drying techniques resulting in crack-free monoliths: a) supercritical drying with CO_2 to yield a porous inorganic material and b) surface silylation with trimethylchlorosilane to yield an inorganic–organic nanocomposite material. The obtained porous gels were characterized by different techniques including thermal analysis, nitrogen sorption, and electron microscopy (TEM, SEM).

Keywords. Sol–Gel chemistry; Silicon compounds; Gels; Template synthesis; Aerogels.

Introduction

Highly porous silica gels, also called aerogels, are extraordinary materials prepared by sol–gel processing – typically of alkoxysilanes – combined with advanced drying techniques. This class of materials shows a unique combination of properties due to the high porosity (even up to 99%), high specific surface area, and very low bulk density (in the range of $0.004-0.500\,g\cdot cm^{-3}$) [1, 2].

In 1998, first attempts have been made to organise the statistical distribution of pores and network forming particles within the aerogel structure into periodic arrangements relying on cooperative self-organisation processes of ionic surfactants in the presence of hydrolysable and condensable inorganic species [3]. The same cooperative self-organisation processes, but in the presence of non-ionic block copolymers as structure-directing agents, have been

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[#] Dedicated to Prof. *U. Schubert* on occasion of his 60th birthday used previously to prepare silica powders with a high degree of mesoscopic order [4].

Monolithic silica-based gels exhibiting a highly porous structure with a hierarchical organization of the pores and well-defined surface properties are of interest, *e.g.* for chromatographic applications. *Nakanishi et al.* have shown for a variety of systems that silica monoliths with a co-continuous macroporous morphology can be prepared relying on phase separation phenomena, *e.g.* by the presence of a polar solvent such as formamide or by spinodal decomposition during sol–gel transition induced by the presence of an organic polymer [5, 6]. *Lindén* and *Nakanishi* extended this approach to materials with weakly organized mesopores by applying a combination of macroscopic (PEO) polymer-controlled phase separation and mesoscopic phase separation induced by an ionic or non-ionic surfactant as structure-directing agent in the nanometer regime [7, 8]. In our group we could show recently that highly porous, hierarchically organized silica monoliths can be prepared by phase separation processes, which are induced by the siliceous precursor itself in the presence of a block copolymer surfactant reagent. Glycol-modified silanes such as tetrakis(2-hydroxyethoxy)silanes (*EGMS*) release ethylene glycol upon hydrolysis and condensation and allow for the preparation of hierarchically structured silica monoliths with periodically arranged mesopores comprising a macroporous cellular network structure [9–12].

Only a few publications cover the synthesis of highly porous silica materials from non-conventional precursors. Typically tetraalkoxysilanes such as the methoxy- or ethoxyderivatives, chlorosilanes, or water glass are used. The aim of this work was first, to synthesize a novel silicon-based precursor molecule (in our case the ethyl (*L*)-lactate modified silane) comprising an optically active leaving group upon hydrolysis and second to apply it in the synthesis of highly porous silica monoliths. The application of this silane in sol–gel processes closes the gap between the commercially available tetraalkoxysilanes such as the ethoxy- or methoxyderivatives and the tailor-made glycol-modified derivatives, which are increasingly applied recently for the incorporation of biomolecules into sol–gel derived materials, with respect to polarity and functionality. One of the major questions to be answered is the influence of the released ethyl lactate on the structural features of the resulting silica gel. Therefore, experiments were performed that allow to deliberately tailor the pore structure of the silica materials *via* a structure-directing agent – a block copolymer surfactant (P123) – which was added to the silica sol. Whereas sol–gel processing of tetraethoxysilanes in the presence of P123 results in particulate mesoporous gels, hydrolysis and condensation reactions of glycol-modified silanes result in distinct periodically arranged mesoporosity in a cellular macroporous scaffold.

To retain the structural features from the wet gel to the dried one, the inorganic–organic nanocomposite wet gels were converted into highly porous silica monoliths by either supercritical extraction with carbon dioxide – resulting in a pure silica monolith, or by silylation with trimethylchlorosilane – resulting in an inorganic–organic hybrid monolith with methyl-groups covering the silica surface (the surfactant is completely extracted from the wet gel by this process).

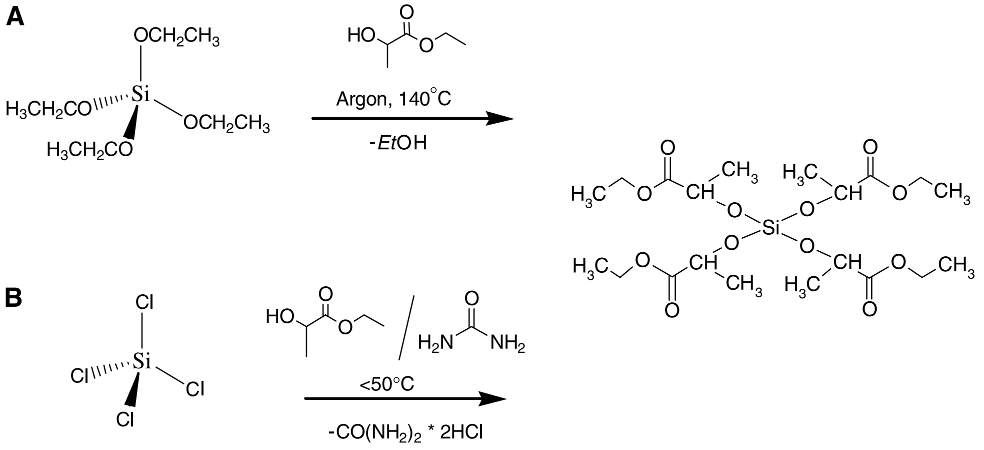
Results and Discussions

The different lactate modified silanes were prepared by direct reaction of tetraethyl orthosilicate or tetrachlorosilane with ethyl (*L*)-lactate (Scheme 1). For the trans-alkoxylation reaction with tetraethyl orthosilicate the reaction conditions – especially the high reaction temperatures of 140°C – are obviously too harsh, since side reactions such as condensation and formation of siloxane bonds were observed in the ^{29}Si(H) HMBC NMR spectra by the presence of mono-, di-, and trimers of the substituted silane. In addition, ^{13}C NMR studies as well as GC/MS analyses indicated the presence of residual ethanol in the product.

^{29}Si(H) HMBC NMR investigations of the precursor synthesized *via* reaction path B showed a single peak at −88.24 ppm corresponding to a single silicon species – in this case the monomeric ethyl lactate modified silane – as schematically presented in Scheme 1. This species was isolated and no residual ethanol was observed in the ^{13}C NMR spectra.

In addition to NMR investigations, the precursor was analyzed by thermal analysis (Fig. 1). For sol–gel processing the amount of silicon in the precursor is essential for the final network density of the SiO_2-gel. Significant differences can be seen between the silanes obtained from route A and B. Precursors prepared by reaction path B with tetrachlorosilane at low reaction temperatures start to decompose in the temperature range of about 180 – 380°C. Here a ceramic yield of about 12% is obtained which matches exactly the theoretically expected value for the ethyl lactate substituted silane.

Pathway A was performed with tetraethoxysilanes at the higher temperatures of 140°C, resulting in a product mixture which consists of species with a higher degree of condensation (from NMR data). In addition, the solvents (ethanol and ethyl lactate) could not be removed completely. These results are supported by the TGA data, which show a more complex decomposition in at least four steps, thus indicating the presence of solvent species. The ceramic yield is extremely low with about 4%, again indicating the high amount of organic species (ethanol/ethyl lactate) compared to silicon – probably due to a partial removal of tetraethoxysilane during the reaction. Figure 1 shows the TGA results of the two precursors A1 and B.



Scheme 1

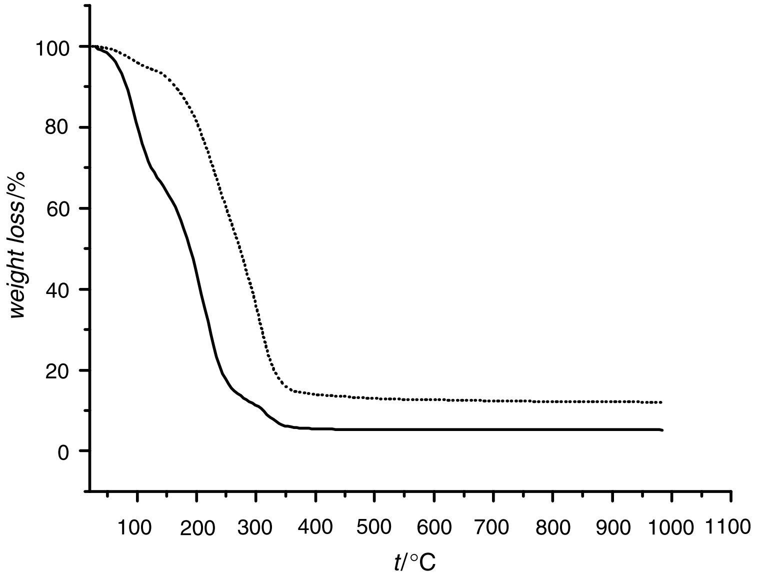


Fig. 1. TGA traces of the two different precursors A1 (solid line) and B (dashed line)

In contrast to the commercially available tetraethoxysilane, the ethyl lactate modified precursor molecule is miscible with water, *i.e.* in acidic conditions. It can be processed *via* hydrolysis and condensation reactions to form silica gels without an additional homogenizing solvent. This is advantageous especially for gelation processes, in which other species such as liquid crystalline phases of surfactants are added, which are very often not compatible with ethanol or methanol [12].

Figure 2 and Table 1 give the gelation times for precursors A1 and B at different *pH*. In comparison to tetraethoxysilane the gelation times are very short [13]. For all investigated samples two trends can be seen: a) the gelation time is

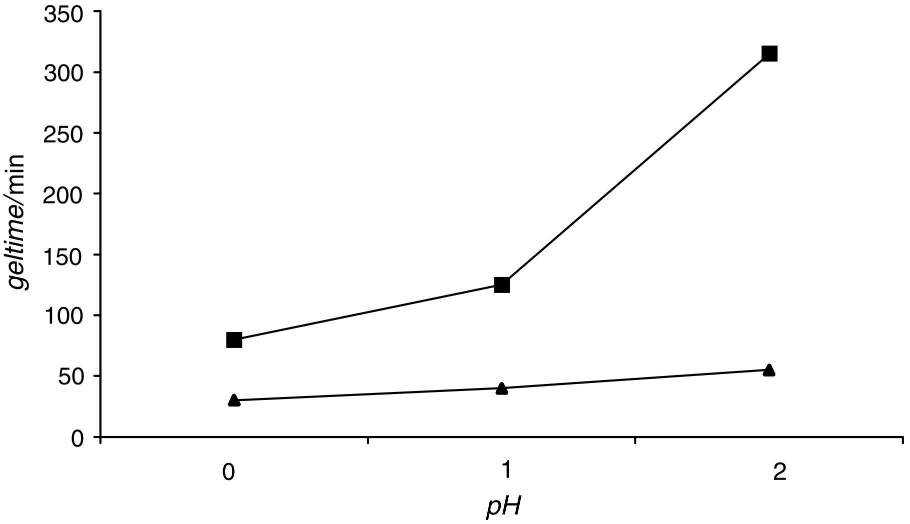


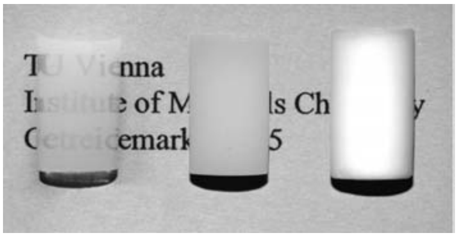
Fig. 2. Gelation times of the ethyl (*L*)-lactate modified silanes from reaction A (A/3.2 – squares) and B (B/7.4 – triangles) at different *pH*

Table 1. Starting mixtures, bulk densities, gelation times, *BET* surface areas, pore volumes, and pore diameters obtained from the maxima in the *BJH* pore size distribution of the prepared aerogels

Samples Type of the precursor// SiO_2/wt%//HCl/*M*	Density/g cm^{-3}	t_{gel}/min	$S_{BET}/m^2\,g^{-1}$	$V_t/cm^3\,g^{-1}$	D_{BJH_max}/nm
A1/2.7/10^{-2}	0.11	315	996.5	5.4	33.2
A1/3.2/10^{-2}	0.12	315	1020.4	5.0	18.5
A1/3.2/1	0.1	125	966.1	4.5	33.2
A1/2.7/1	0.08	280	1109.5	5.1	17.7
A1/3.2/2	0.1	80	908.5	4.5	17.2
A1/3.8/1	0.13	80	901.2	4.4	18.9
A1/3.8/2	0.13	75	835.4	3.9	18.6
A2/2.7/10^{-2}	0.16	420	918.0	4.6	15.2
A2/3.2/10^{-2}	0.18	400	748.8	3.4	22.8
A2/2.7/1	0.14	115	919.1	4.8	12.2
A2/3.2/1	0.17	105	908.8	4.4	12.9
A2/3.2/2	0.17	70	891.3	4.2	12.9
B/7.4/10^{-2}	0.13	55	916.4	4.2	15.2
B/8.8/10^{-2}	0.15	50	790.1	3.0	23.8
B/7.4/1	0.13	40	870.3	4.0	13.5
B/8.8/1	0.15	35	688.6	2.0	15.5
B/7.4/2	0.13	30	823.9	4.8	13.3
B/8.8/2	0.17	30	729.2	2.4	18.7

dependent on the concentration of the silica precursor in a way that the higher the silica content the faster gelation occurs (gel times for B are significantly lower than for A) and b) the lower the *pH* of the solution the faster the condensation reactions proceed – this trend is more pronounced for the precursor A. Similar results have been obtained in a previous work for the gelation times of glycol-modified silanes, *e.g.* ethylene glycol, propylene glycol, or even glycerol modified ones [12].

The gelation time is a direct indication for the rate of the condensation reaction and thus the silica network formation. The results here can be interpreted based on the charges present in the silica-based solution. The isoelectric point of silica lies around $pH = 2.5$. Below this *pH*, the silanol groups are protonated and positively charged, therefore condensation is facilitated and obviously accelerated.



A1/2.7/10^{-2} (transparent)
A1/3.2/1 (opaque)
A1/3.8/2 (white)

Fig. 3. Representative photographs of silica gels obtained from ethyl (*L*)-lactate modified silanes; from left to right: A1/2.7/10^{-2} (transparent), A1/3.2/1 (opaque), A1/3.8/2 (white)

For all materials discussed in the following, crack-free, monolithic gel rods with diameters of 10 – 11 mm and lengths of 18 – 20 mm were obtained after supercritical drying with carbon dioxide as well as after surface silylation (Fig. 3).

For both drying procedures, the surfactant is quantitatively extracted from the nanocomposite gel during the different washing and/or surface treatment procedures [11]. The density of the dry silica gel monoliths was measured by determination of the volume and the weight of the samples and found in most cases to be very low with values in the range of 0.08 – 0.18 g cm^{-3}. Interestingly, the appearance of the highly porous silica gels varies depending on the synthesis conditions: from transparent to opaque and white monoliths. The bulk densities (Table 1) correspond very well to the low silica content in the starting mixtures and also support that complete extraction of the surfactant occurred in both drying procedures. The low densities also indicate that shrinkage upon drying is negligible. All data given in Table 1 are from gels dried supercritically. Similar values with respect to density, surface area, and other structural characteristics are obtained for the materials dried with trimethylchlorosilane.

TGA analyses (Fig. 4) of the final dried gels show a weight loss of about 12 – 15% in the temperature range of 30 – 450°C. The first weight loss corresponds to the loss of solvent, *e.g.* water *etc.*, which can be (physically) adsorbed in the material. The difference in weight loss for the two sets of samples can be explained by the different hydrophobic character. Gels that have been silylated should be rather hydrophobic and therefore, adsorb less water. The weight loss starting at 170°C can be attributed to the loss of organic groups covalently linked to the silica network structure. For supercritically dried samples these organic groups correspond to methoxy moieties that cover the inner surface due to the solvent exchange processes from water to methanol prior to supercritical extraction. In the case of silylated samples methyl groups from the trimethylsilyl-group are decomposed.

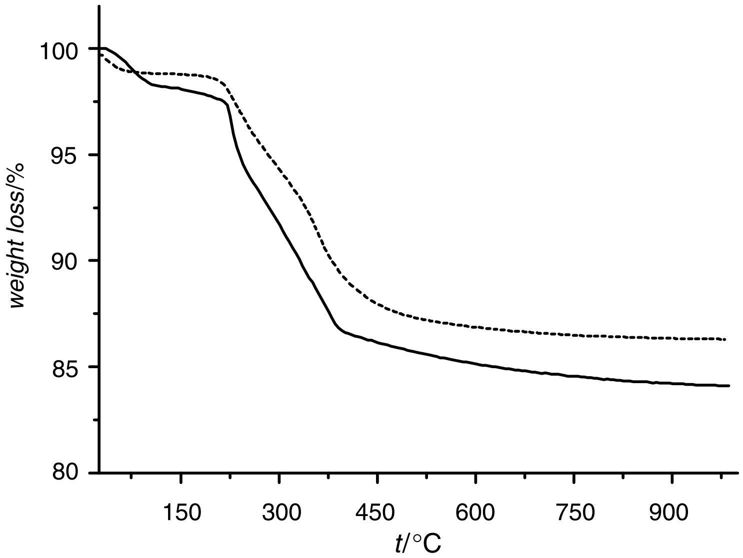


Fig. 4. TGA plot of samples B/8.8/1 supercritically dried (scf, solid line) and A/2.8/1 dried by surface silylation (sil, dashed line)

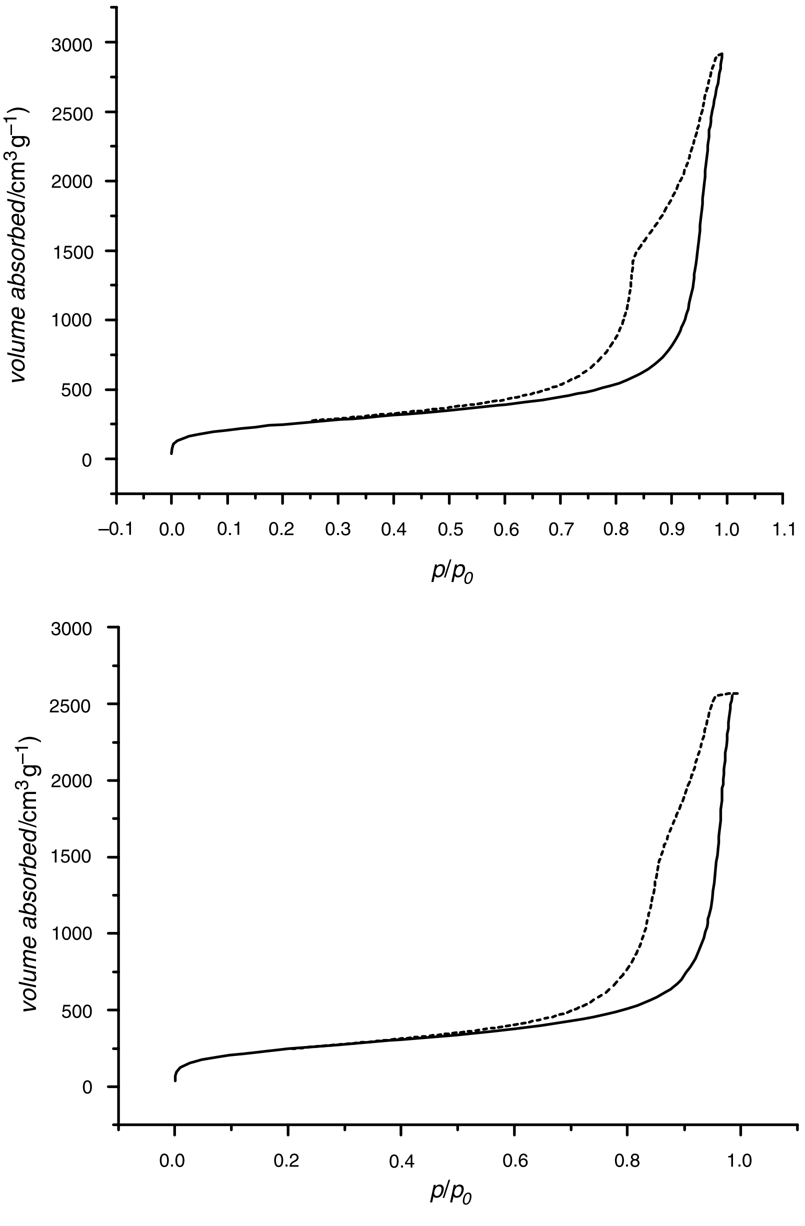


Fig. 5. The representative nitrogen sorption isotherms for samples A/3.2/2 (top) and B/7.4/1 (bottom)

Structural characterization of the dried silica gels samples was performed by N_2-sorption. Figure 5 shows representative nitrogen sorption isotherms. According to the IUPAC classification type IV isotherms can be observed for all obtained samples. The hysteresis corresponds to the type H2, which indicates the presence of mesopores (between 2 – 50 nm; filling and emptying by capillary condensation). All silica monoliths exhibit high specific surface areas (S_{BET}), evaluated using the *BET* (*Brunauer-Emmett-Teller*) method and high total pore volumes (V_t) in the range of 2.0 – 5.4 $cm^3\,g^{-1}$. The *BJH* (*Barrett-Joyner-Halenda*) pore size distributions evaluated from the desorption branches of the isotherms exhibit maxima in the range of 12.2 – 33.2 nm (Table 1).

The *BET* surface areas for the samples prepared from reaction path A are significantly higher than for the ones prepared from precursor B. This result corresponds well to the obtained bulk densities of the material and indicates smaller particles for gels prepared from precursor A. In general, the surface area is higher for the aerogels containing smaller amounts of SiO_2 and varies from 1020 – 835 $m^2 g^{-1}$ for gels prepared from A in comparison to 916 – 688 $m^2 g^{-1}$ from B. The effect of the acid concentration is not as pronounced, but for monoliths from B, a higher concentration of hydrochloric acid seems to result in lower *BET* surface areas.

The morphology and microstructure of the samples can be seen on SEM and TEM images (Fig. 6). For aerogels prepared from compositions containing a lower amount of "Si"-species in the starting mixture (1.65 wt%), macroporosity with interconnected open pores in the range of 300 – 900 nm can be observed. Less cellular structures composed more of particles can be observed for the samples obtained from the compositions containing 3.2 wt% and 7.4 wt% of silica in the starting mixture (Fig. 6, middle and bottom). The corresponding TEM images of

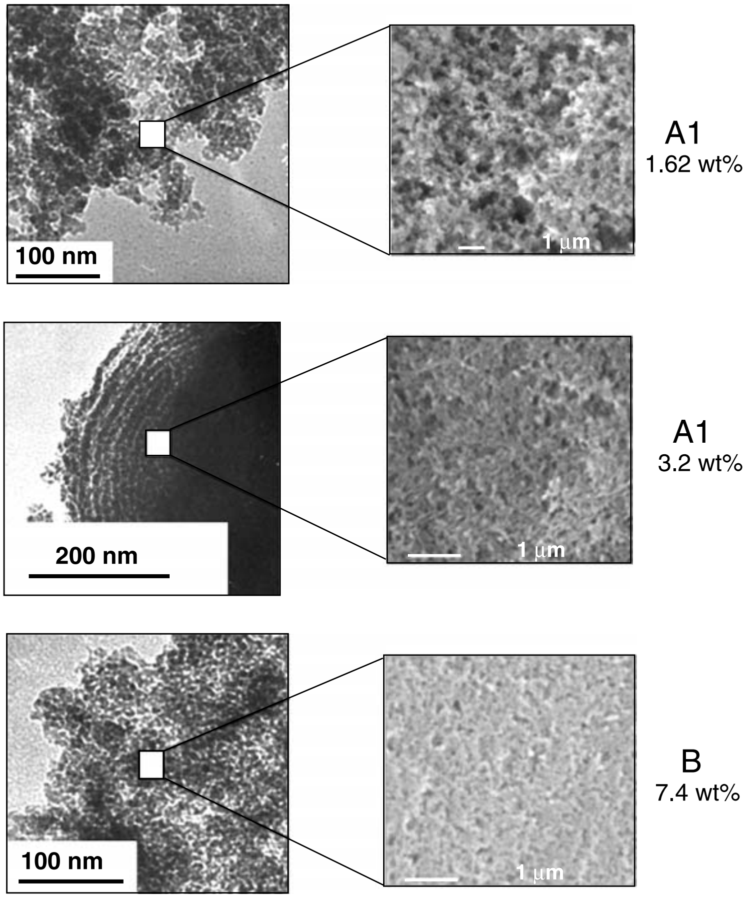


Fig. 6. Representative SEM and the corresponding TEM images for samples A1/1.64/1, A1/3.2/2, and B/7.4/2

the monoliths show wormhole like arrangements of particles. It can clearly be seen that the block copolymer template molecule acts as macroscopic phase separation agent, thus allowing for the formation of materials with macro- and mesopores, but only for A/3.2/2 a weak organisation of the structure is observable. This can be correlated to the very sensitive hydrophobic/philic balance of the starting mixture, which is influenced by the release of the ethyl lactate during hydrolysis and condensation. For ethylene glycol modified silanes a very hydrophilic alcohol is released during hydrolysis, supporting phase separation on the meso- and the macroscopic scale. For ethoxysilanes, the ethanol does not really interfere with the network forming processes and does also not allow for cooperative self-organisation on the mesoscale. Ethyl lactate seems to play an intermediate role – allowing for macroscopic phase separation, but not for mesoscale ordering.

In conclusion, highly porous silica monoliths are prepared by the use of a novel type of precursor, which was synthesized *via* the reaction of ethyl (*L*)-lactate with tetraethoxysilane and tetrachlorosilane. Simple transalkoxylation reaction of tetraethoxysilanes with the ethyl lactate at high temperatures resulted in the formation of condensed species, whereas reaction of tetrachlorosilane with ethyl lactate in the presence of urea allowed for the formation of the pure ethyl lactate modified silane. This novel precursor molecule (from both synthesis procedures) was applied in the sol–gel processing to form highly porous silica aerogels *via* supercritical drying or silylation reaction with trimethylchlorosilanes. For all gels, crackfree monoliths with very low densities combined with high specific surface areas and large total pore volumes with bimodal pore sizes were obtained. The surface polarity can be controlled by the type of drying process – resulting in more hydrophilic surfaces after supercritical extraction and hydrophobic ones from silylation. The application of the ethyl (*L*)-lactate silane offers some distinct advantages over the conventionally applied tetraethoxy- or methoxysilanes due to its miscibility with water and the rather low gelation times. Further investigations concerning the influence of the stereochemistry of the released alcohol on network formation are under way.

Experimental

Synthesis of the Precursor

A) Ethyl (*L*)-lactate (95%, Acros and 97%, Acros) was reacted with tetraethoxysilane (98%, Fluka – purified by vacuum distillation) in a flask equipped with a *Vigreux* column and a *Liebig* condenser for continuous removal of ethanol. The reaction was performed in an Ar atmosphere at 140°C. Residual ethanol was distilled from the viscous, transparent precursor under vacuum. The resulting material was characterized by ^{1}H NMR, ^{29}Si NMR, and thermal analysis. The precursor from 95% ethyl (*L*)-lactate is denoted as A1, the one from 97% ethyl (*L*)-lactate corresponds to precursor A2.

^{29}Si(H) HMBC NMR (300.13 MHz, $CDCl_3$): $\delta = 1.2$ ($CH_2C\mathit{H}_3$), 1.4 ($CHC\mathit{H}_3$), 4.1 ($C\mathit{H}_2CH_3$), 4.65 ($C\mathit{H}$–O) ppm. All signals show a splitting, which corresponds to the formation of condensed species such as dimers, trimers, *etc*. Several signals for the silicon nuclei are observed in the ^{29}Si NMR, again due to the presence of higher condensed species. The spectra for A1 and A2 seem to be identical exhibiting the same set of signals. Thermal analysis of the precursors showed a ceramic yield of A1 5.2% and A2 4.4% (theoretical value: 12.04%).

B) Ethyl (*L*)-lactate (97%, Acros) was reacted with tetrachlorosilane (purified by vacuum distillation) in the presence of urea (99%, Aldrich). In a three-necked flask, $SiCl_4$ was added dropwise to the mixture of ethyl (*L*)-lactate and urea. The reaction temperature was kept below 50°C. The organic phase comprising the ethyl (*L*)-lactate modified silane as a transparent and viscous liquid was separated from the HCl–urea adduct phase in a separation funnel. The resulting material was characterized by ^{1}H NMR, ^{29}Si NMR, and thermal analysis.

^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.2$ (CH_2CH_3), 1.4 ($CHCH_3$), 4.1 (CH_2CH_3), 4.65 (CH–O) ppm; ^{29}Si NMR (59.62 MHz, $CDCl_3$): $\delta = -88.24$ ppm. The ceramic yield of the material obtained from thermal analysis was 12.1% (theoretical value: 12.04%).

Preparation of Wet Nanocomposite Gels

The gel monoliths were prepared from the ethyl (*L*)-lactate modified silane by sol–gel processing in the presence of a non-ionic surfactant, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (P123, $EO_{20}PO_{70}EO_{20}$/BASF) as the structure directing agent.

P123 was homogenised in different aqueous HCl solutions ($10^{-2}\,M$, $1\,M$, and $2\,M$) in a constant ratio of triblock copolymer to water (30 wt% of polymer in H_2O). Gels were prepared by addition of the homogenized water/surfactant mixture to the modified silane (40 – 80 wt% with respect to the H_2O/surfactant mixture).

Gelation occurred after a certain time (depending on the acid concentration and the amount of silicon in the mixture) and the wet gel samples were aged for 7 d at 45°C. The obtained gels were denoted as follows: type of the precursor (A or B)/SiO_2 amount (mass fraction of SiO_2 in the starting composition, wt%)/molar concentration of HCl (see Table 1).

Drying Techniques

Either supercritical drying or surface silylation was performed for drying:

a) *Supercritical drying*: prior to the drying process, the H_2O/ethyl (*L*)-lactate pore fluid in the wet gel bodies were exchanged to methanol to ensure miscibility with liquid carbon dioxide. Supercritical drying itself was performed by putting the wet gel samples into a steel autoclave, closing it, increasing the temperature and thus simultaneously the pressure until the critical values of carbon dioxide are reached ($T_c = 31$°C, $p_c = 73.7$ atm). After that, the fluid is slowly released from the vessel and monolithic dried gels were obtained [14].

b) *Surface silylation*: Treatment with trimethylchlorosilane (*tmcs*) was performed by immersing the whole gel body in a *tmcs*/petroleum ether (1/10 *w*/*w*) solution for 10 h. After washing with petroleum ether (3×) and ethanol (5×), the wet gel bodies were dried by slowly heating the sample from room temperature to 150°C within 6 d [11]. By this procedure, the surfactant is extracted completely from the gel.

Characterization

The bulk densities of the aerogels were calculated from the mass and the volume of the silica monoliths. N_2 sorption analysis was carried out using an adsorption porosimeter Micromeritics ASAP 2010/2020. Samples were outgassed for 8 h in the degas unit of the adsorption apparatus at 150°C. SEM images were recorded with a FEGSEM JEOL 6330 fitted with a secondary electron detector at an accelerating voltage of 10 kV. TEM images were taken on a JEOL 100 CX (W filament operating at 100 kV in the bright field mode). Thermogravimetric analyses were carried out using a Netzsch TG 209C at synthetic air conditions with the heating rate 5 K/min. ^{1}H, ^{29}Si, and ^{13}C NMR measurements of the liquid precursors were performed on a Bruker DRX Avance 300 spectrometer at 300.13 MHz, 59.62 MHz and 75.46 MHz.

Acknowledgements

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