Work Group Non-metallic Materials
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Institute of Materials Science and Technology

Hierarchisch strukturiertes Siliziumdioxid und seine mechanischen Eigenschaften

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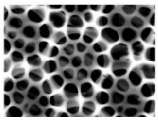
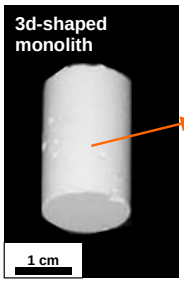
In cooperation with the Institute of Materials Chemistry, TU Vienna, Austria

Sol-gel derived hierarchically structured SiO_2

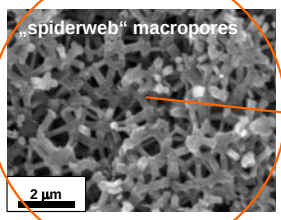


Nature´s strategies: hierarchical buildup, cellular structures, anisotropy, nanocomposites

1st level

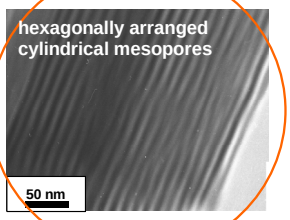


2nd level



SEM

3rd level



TEM

Aims:

- **study the evolution of meso- and macrostructure**
- **test mechanical properties**
- **additional level through macroscopic templating**

Synthesis of the Inorganic Network

sol-gel principle:

Hydrolysis: $\equiv$Si-OR + H_2O $\rightleftharpoons$ $\equiv$Si-OH + ROH

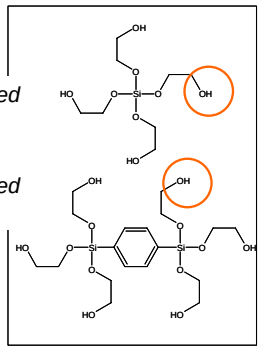
Condensation: $\equiv$Si-OH + HO-Si$\equiv$ $\rightleftharpoons$ $\equiv$Si-O-Si$\equiv$ + H_2O

$\equiv$Si-OH + RO-Si$\equiv$ $\rightleftharpoons$ $\equiv$Si-O-Si$\equiv$ + ROH

Si-precursor

ethylene glycol modified silane

phenylene bridged *ethylene glycol modified* silane



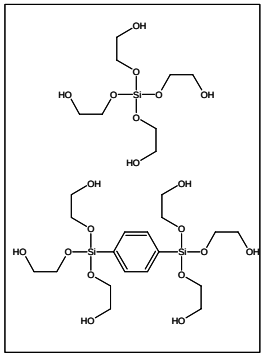
advantage of the modified precursor:

- high water solubility
- no catalyst needed
- high compatibility with lyotropic liquid crystal phases
- easy formation of monolithic material

Brandhuber et al., Chemistry of Materials (2005), 17(16), p. 4262-4271
Brandhuber et al., Small (2006), 2(4), p. 503-506

Supramolecular Self Assembly-Templating

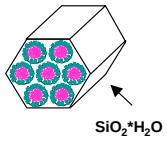
Motivation
Material Synthesis
Structural properties
Mechanical properties
Macroscopic templating
Conclusion



typical experimental procedure:

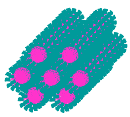
- homogenisation
- gelation at 313 K
- ageing for 1 week at 313 K

→ wet mesostructured gel



Non-ionic block copolymer surfactant

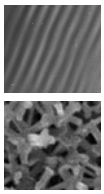
+ HCl →



Pluronic P123, $PEO_{20}PPO_{70}PEO_{20}$

mesopores: liquid crystalline templating

macropores: phase separation (spinodal decomposition)



SAXS

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Material Synthesis
Structural properties
Mechanical properties
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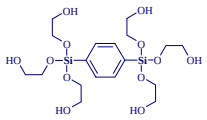
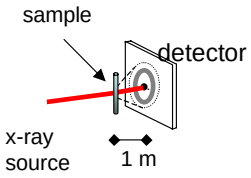
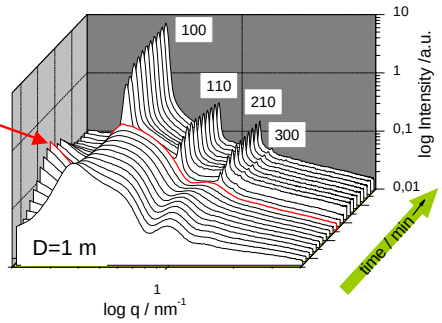
Conclusion

In-situ synchrotron Small Angle X-ray Scattering (ESRF, ID2):





Evolution of the periodic mesostructure during gel-formation



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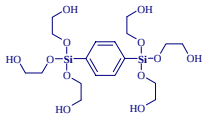

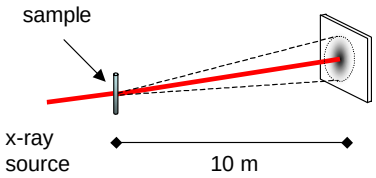

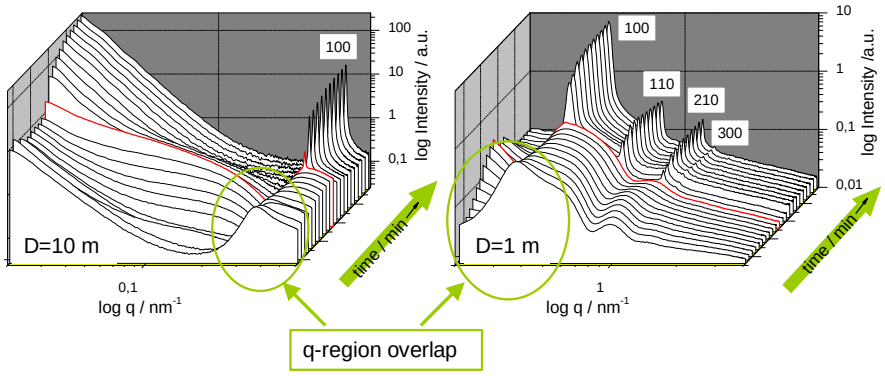

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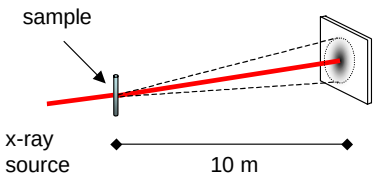
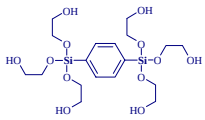
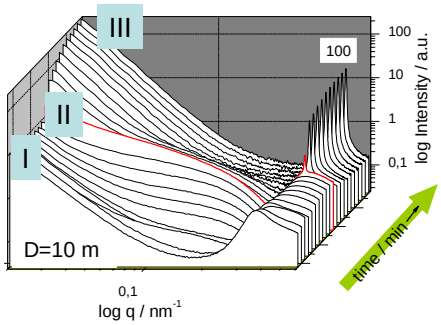




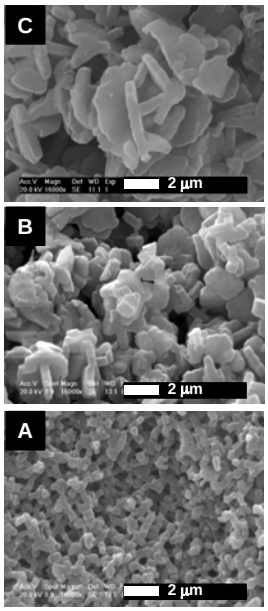


I: growth of silica/surfactant rich agglomerates (> 100 nm)

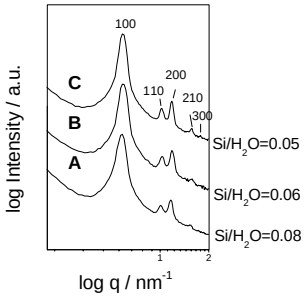
II: formation of spherical particles (R~10 nm)

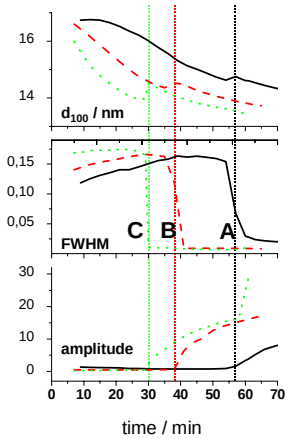
III: formation of periodic mesostructure

Influence of Dilution



SEM





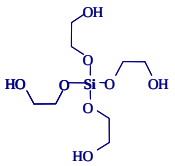
solvent content

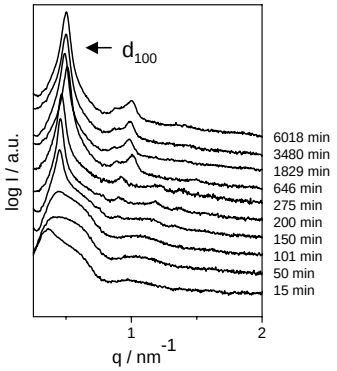
morphology with smaller curverture

time of phase separation and mesostructure formation

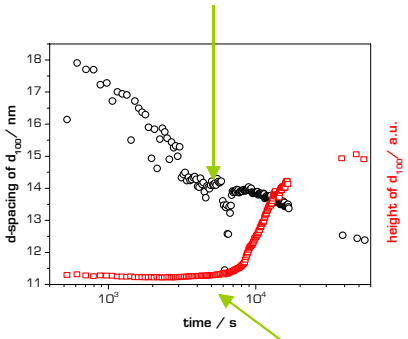
Samples for Mechanical Testing

In-situ synchrotron Small Angle X-ray Scattering (Elettra, SAXS-Beamline):





ordered silica-surfactant phase forms



point of gelation

Fitting of the data

Drying of the Monoliths

Motivation
Material Synthesis
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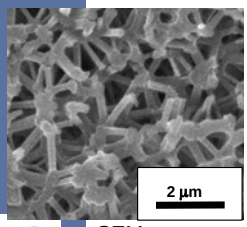
wet monolith (as synthesized) - dry monolith

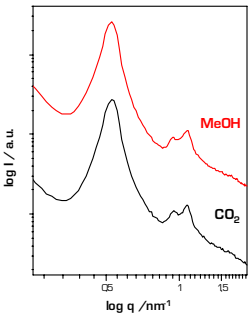
- Problem: capillary forces
- Solution: supercritical drying

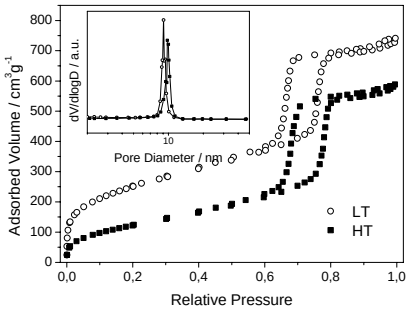
low temperature (LT) with CO_2, high temperature (HT) with MeOH

Supercritical fluid	P_{crit} /bar	T_{crit} /K	shrinkage	d_{100} /nm	S^{BET} m^2/g
CO_2: LT	73.8	304.4	10,4 %	11,64	891
MeOH: HT	80.9	512.8	19,2 %	11,22	462

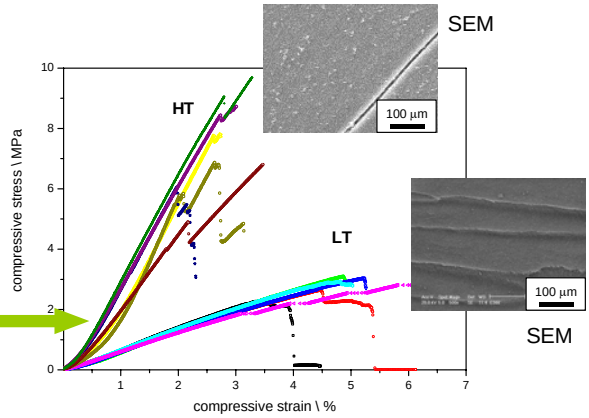


SEM





Mechanical Properties



Young´s Modulus

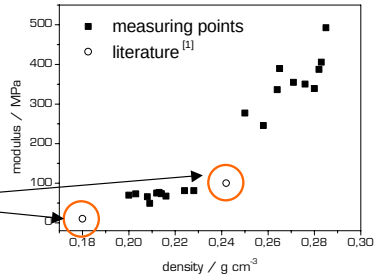
compression test: LT: 72.3 ± 4 MPa

HT: 338.5 ± 52 MPa

Mechanical Properties

correlation between porosity and modulus

values for Si-aerogel (no macropores)



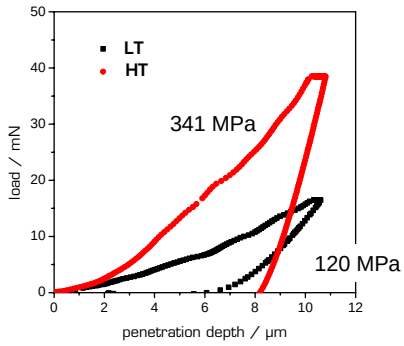
Instrumented indentation testing

LT-samples:

- more easily penetrated
- network relaxes after unloading

HT-samples:

- rigid
- higher degree of irreversible damage



[1] Puchegger et al., Journal of Non-Crystalline Solids (2006), 352, p. 5251-5256

Complex Macroscopic 3D-Shape

Aim:

- macroscopical 3d-shape of the mesostructured SiO_2
  (e.g., high geometric complexity and heavily undercut features)

Why?

- widens the application possibilities of mesostructures materials (e.g., fluidic devices)

How?

- templating by using sacrificial molds

Problem with conventional methods:

- often involve high temperatures to remove the mold (not possible for organically modified gels)
- or are not compatible with the sol-gel process (e.g., water-soluble molds)
- shrinking of the SiO_2-network →cracking before removal of the mold

Mold Processing of Sol-Gel Materials

Motivation
Material Synthesis
Structural properties
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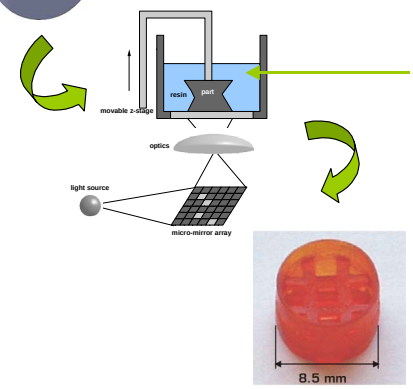
Conclusion

→ **proposed approach:**

Computer aided design

Digital light processing (DLP)



light sensitive resin based on branched dialkylacrylamides and a cleavable crosslinker

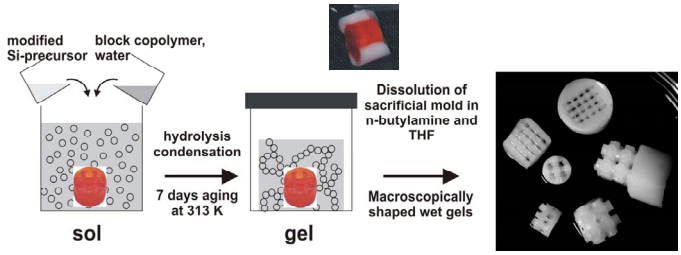
sacrificial organosoluble photopolymer-mold

Inführ et al., RadTech, Conference Proc. (2005), 2, 489-494

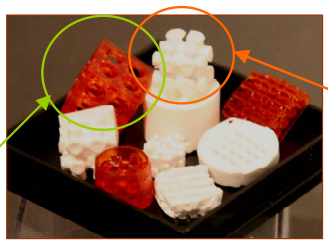
Mold Process

- mesostructured SiO_2: inorganic polymer
- Digital light processing (DLP): sacrificial organosoluble photopolymer-mold

→ additional hierarchical level



Drying with Supercritical MeOH



Corresponding photopolymer part

Hierarchically structured monoliths with 3 structure levels:
nanometer – sub-micron - macrostructure

Summary

- **Synchrotron x-ray scattering with variable camera length** (up to 10m) is a suitable method to study the structure on the nanometer and sub-micrometer scale of hierarchical materials.
- The structure formation can be followed ***in-situ***. The mesostructure and sub-micrometer structure evolution takes place in parallel for a mesostructured silica system based on organically modified EGMS as precursor.
- **Compression tests** and **instrumented indentation measurements** give values for the Young´s modulus that are in accordance with literature and are correlated to the porosity/density of the material.
- By **templating** mesostructured silica with **Rapid Prototyping**-molds made from an organo-soluble resin, an additional 3D structure on the macro-scale can be induced -> 3 levels of structural hierarchy (nano-micro-millimeter).

Thanks

Thanks to R. Liska and R. Inführ (Institute of Applied Synthetic Chemistry, TU Vienna) for developing the organosoluble photopolymers, also special thanks to H. Peterlik and S. Puchegger (Institute of Materials Physics, University of Vienna) for help and fruitful SAXS-discussions and the ICMAB and MATGRAS (Anna Roig, Elena and Raul) in Barcelona for the possibility to dry my samples supercritically.

Special thanks to all who helped me during the synchrotron beamtimes!

Thank you for your attention!