Supplementary Information (SI) for Materials Advances.

Supporting information

Accelerated aerogel development via Soxhlet extraction and freeze-drying

Figure S1 shows the accelerated solvent exchange process.

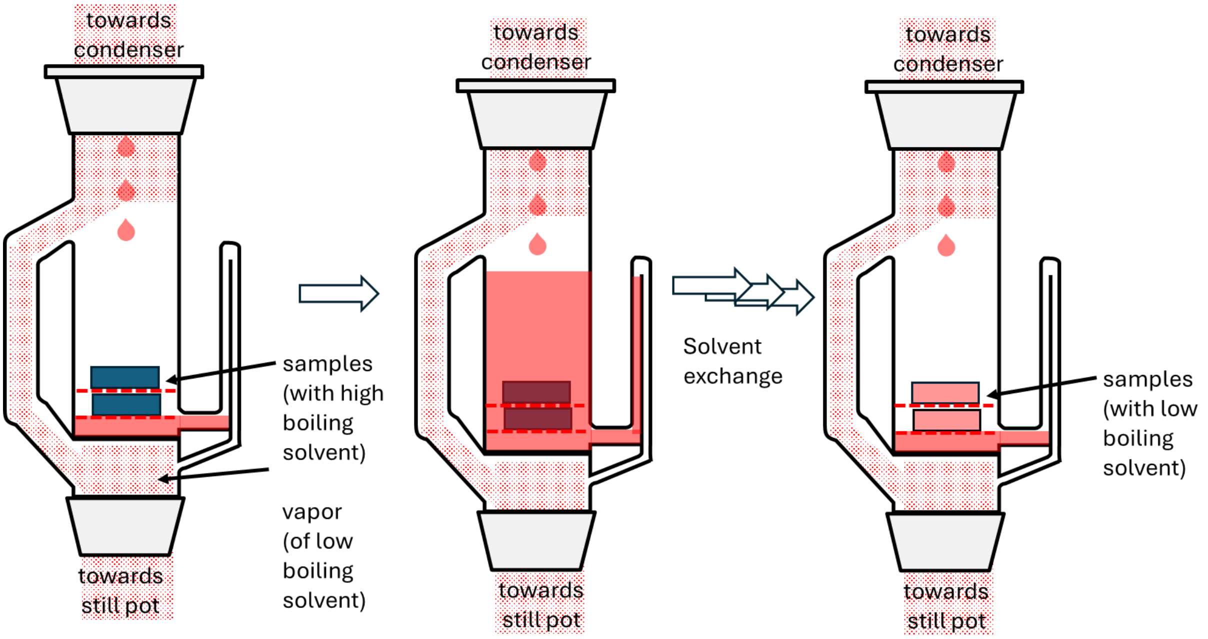

Figure S1: Schematic representation of the accelerated solvent exchange from high boiling to low boiling solvent in gels within a Soxhlet extractor

Syntheses

Figure S2 shows the reaction for the preparation of the MTMS-based aerogel.

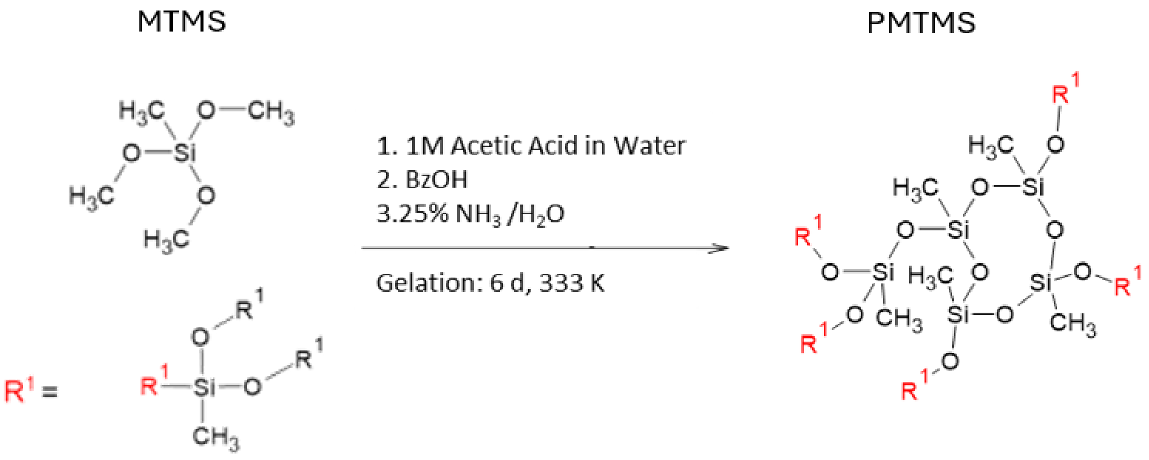

Figure S2: Polycondensation of MTMS to polymethylsiloxane

Solvent combinations for PU-Aerogels

For a straight-forward Soxhlet extraction, the boiling point of solvents for the synthesis should be above 150°C. Therefore suitable solvents/solvent combinations were screened with respect to stability of the gels and the properties of the resulting aerogels, the results are summarized in Table S1.

Table S1: Solvents for PU synthesis

Solvent	**comment**
Cyclohexanone	Soft, unstable gels
2-nonanone or 2-octanone	Soft, unstable gels
Cyclohexanone 50% 2-nonanone or 2-octanone 50%	Stable gels with high mechanical stability and low thermal conductivity in aerogel
Cyclohexanone 40% 2-nonanone 40% propylene carbonate (up to) 20%	Very robust gels, some segregation problems, greater shrinkage, higher thermal conductivity in aerogel
DMSO	High stability, transparent gels (very fine structure), solvent exchange leads to loss of structure

Mixtures of cyclohexanone and 2-octanone are very well suited for synthesis in mixing ratios of 50/50 w% to 40/60 w%. Propylene carbonate provides greater robustness, but also has a number of disadvantages. The synthesis becomes more susceptible to interference, the hydrophilic character can introduce water, and shrinkage during exchange results in higher densities and poorer thermal conductivity. In general, the use of PC was not considered to be effective. DMSO would be an ideal solvent for the synthesis, but it solvates the structures formed so well that the solvent exchange always causes damage and shrinkage to the gel.

SC CO_2-Reactor

Figure S3 shows the setup used for supercritical drying.

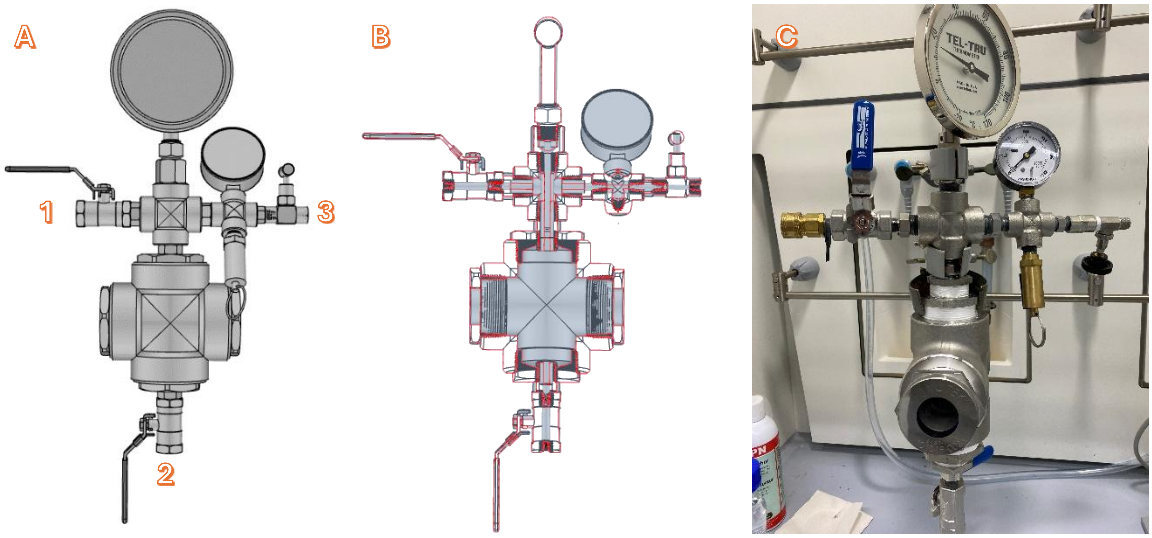

Figure S3: Reactor model (A), cross-section (B) and actual setup (C)

CO_2 is introduced via the ball valve (1) at the top left and discharged via the lower valve (2) after replacement. During replacement, the samples are permanently submerged in liquid gas. In the actual drying step, the reactor was heated via a water bath and the supercritical gas was slowly discharged via the needle valve (3)(left).

Solvent exchange

Solvent exchange rate of 2-nonanone vs propylene carbonate (PC)

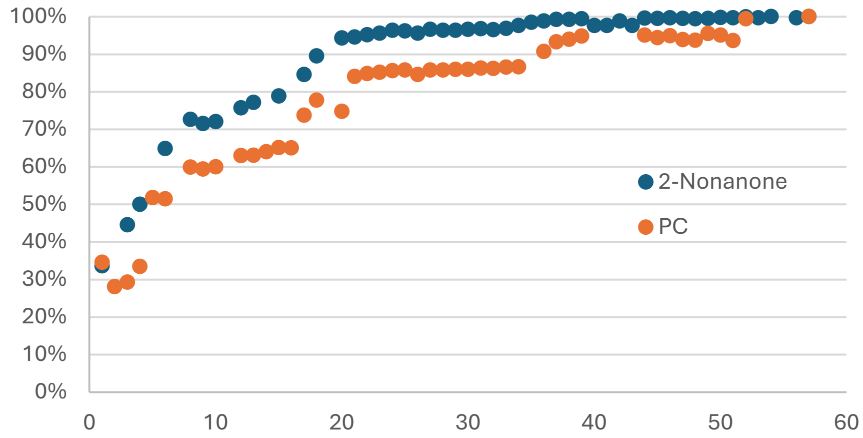

Figure S4: Batch exchange of PU aerogels against t-BuOH; Amount of solvent extracted as a percentage of the total amount applied to the samples taken (see Figure 4 in the main text)

Due to the different solubilities of the components of the solvent mixture in relation to the target solvent, PC is washed out more slowly than 2-nonanone or cyclohexanone. This applies to both batch experiments and Soxhlet extraction.

MTMS Aerogels

DSC and TGA measurements of MTMS Aerogels

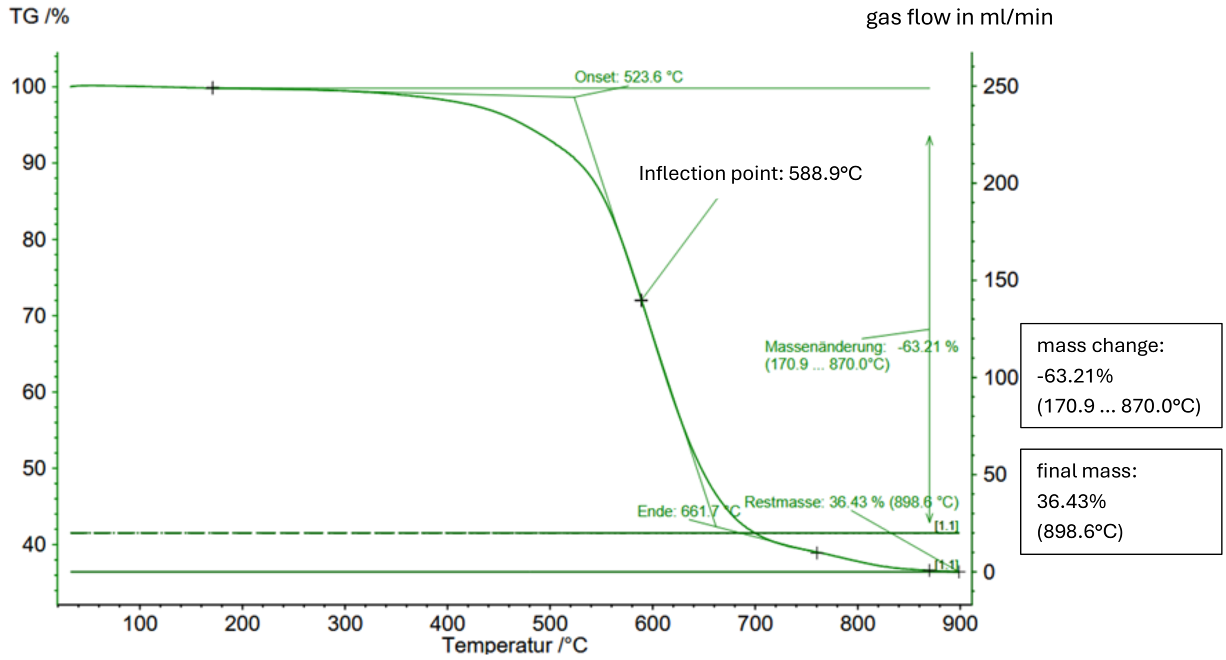

Figure S5: TGA measurement of an MTMS aerogel

Figure S6 shows an example of a DSC measurement of the freezing of t-BuOH in a gel.

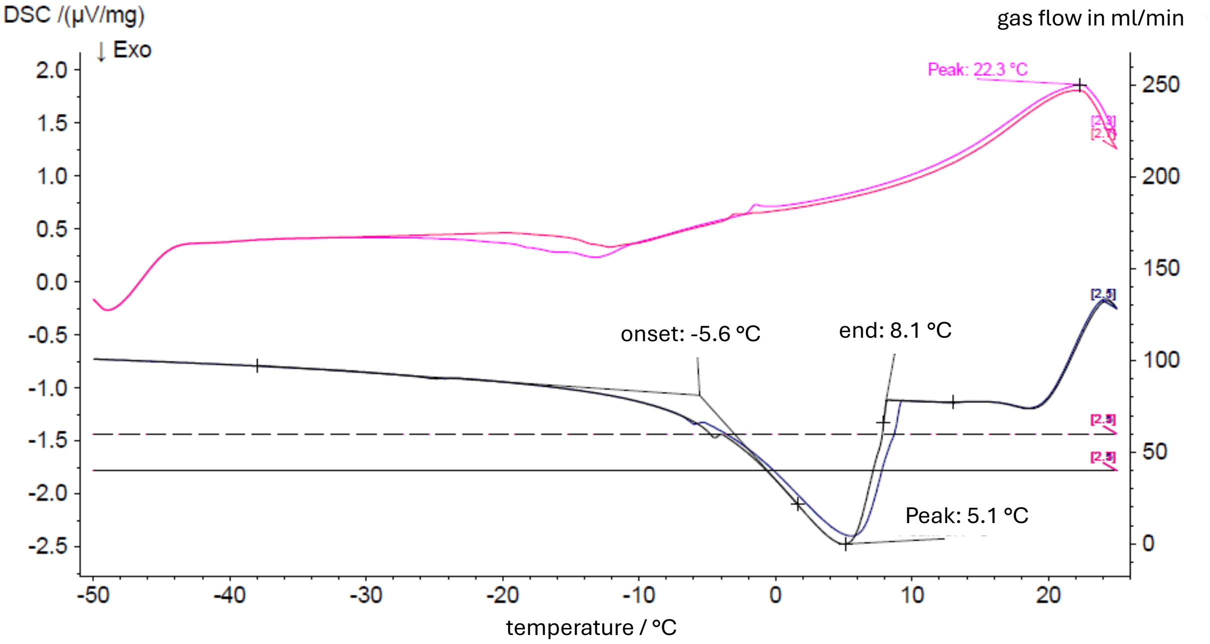

Figure S6: DSC measurement of a t-BuOH-exchanged solvogel

Figure S7 compares the freezing of cyclohexane from the exchange with cyclohexane in two solvogels.

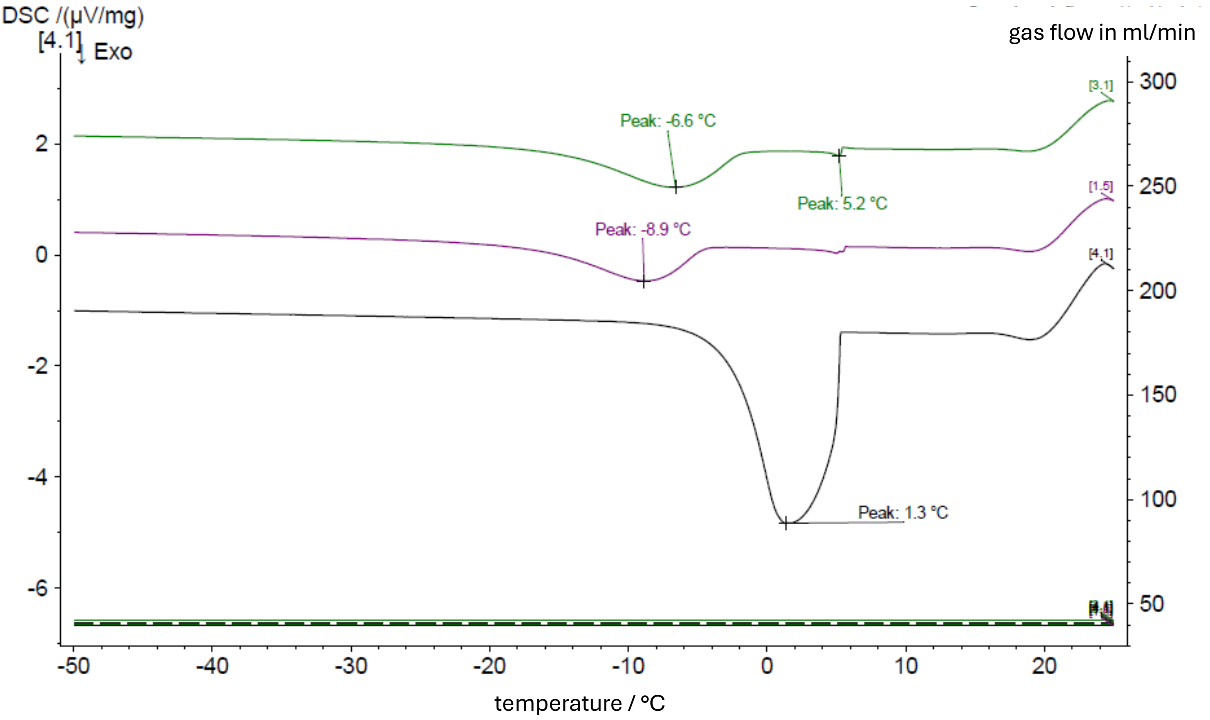

Figure S7: DSC measurement of cyclohexane-containing solvogels (green and purple) with cyclohexane from the overlay (grey)

PU-Aerogels

Images of PU aerogels

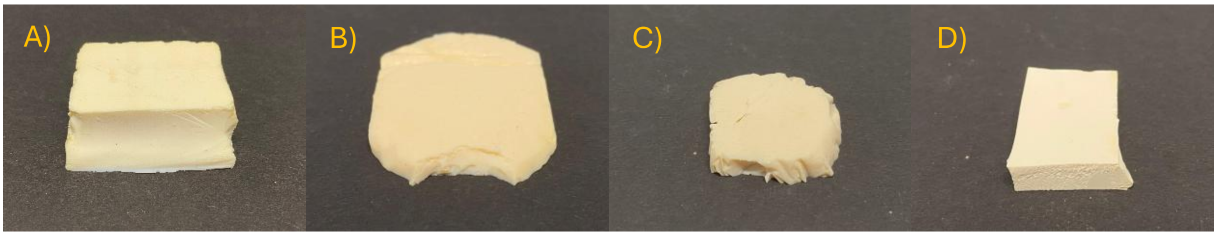

Figure S8: Images of PU aerogels (A = reference material; B = supercritically dried; C = FD from t-BuOH; D = FD from cyclohexane) (Colours may appear different due to lighting conditions – the same background was used for all images)

The reference sample cannot be distinguished from either a supercritically dried sample or a freeze-dried sample from t-BuOH. The colour and structure at the fracture edges are very similar. Samples that have been exchanged for cyclohexane are lighter in colour, in some cases almost white. It is possible that more by-products or oligomeric structures are washed out during this exchange. However, the change in colour does not correlate with an improvement of any other properties in the material.

Figure S9 shows the Shore hardness A of PU aerogels as a function of their density and the drying method used.

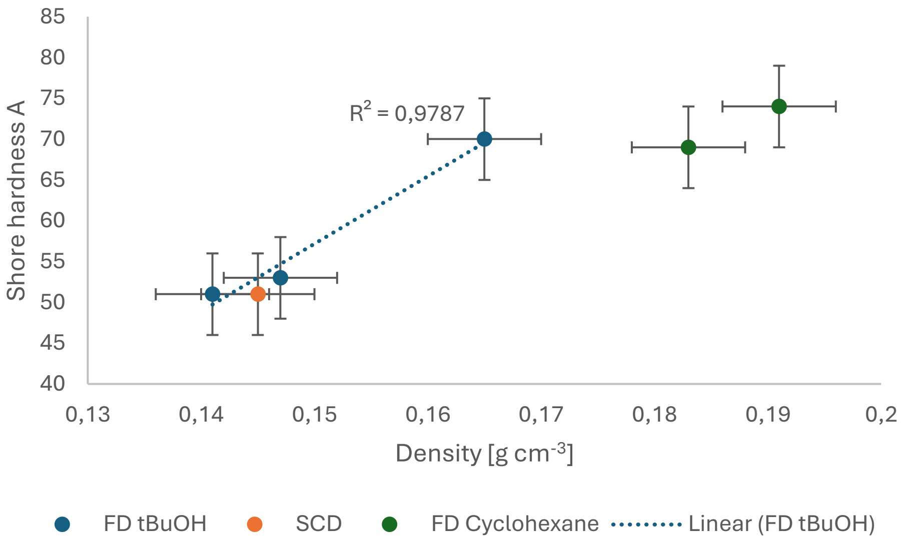

Figure S9: Shore hardness A of PU aerogels plotted against the density of various dried samples

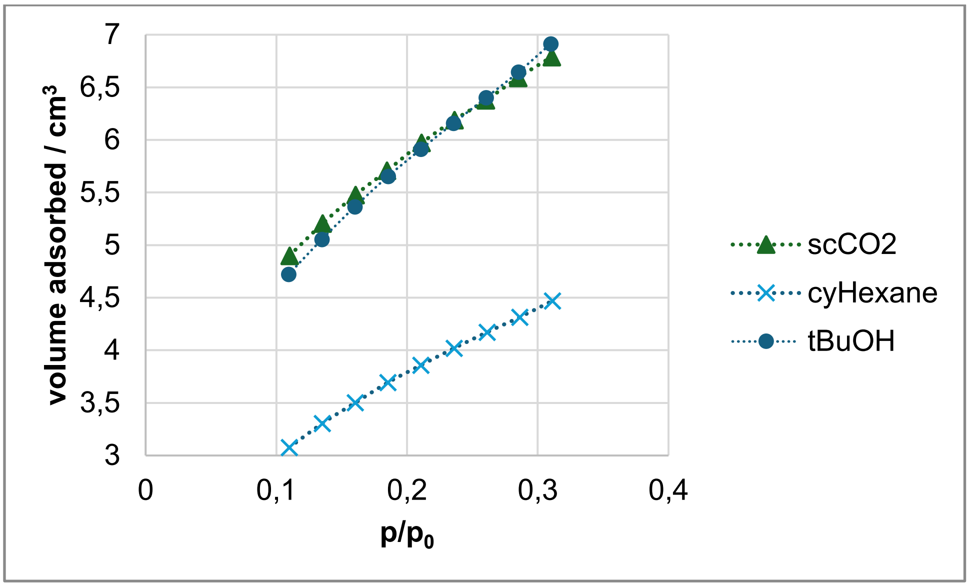

Figure S10: Nitrogen sorption of MTMS aerogel dried in different methods

Estimation and comparison of energy consumption of Soxhlet extraction versus batch extraction with subsequent solvent recovery

Let us assume that a Soxhlet is used to exchange two samples (approx. 13 mL sample volume including gel body - 11 mL solvent per sample) with tBuOH, the dead volume is 94 mL (1 mol), the average chamber temperature is 15 K below the boiling point during the process, and 15 exchange steps are performed. The approximate energy consumption (including processing, cooling not taken into account) is about 800 kJ. Batch exchange (without shaker, with solvent recovery processing, cooling not taken into account) consumes only about 415 kJ for 4 steps, each with 10 times the amount of tBuOH. The Soxhlet can be optimised through thermal insulation and efficient use of space, but it will always perform worse in terms of energy efficiency than batch exchange. The conclusion of this calculation example is that, with about twice the energy requirement, a solvent exchange can be achieved in 8 hours instead of 4 days (+solvent recycling). The batch exchange might be optimized to less than 24 hours per step, but 2 hours per steps is clearly impossible.