On the Underestimated Impact of Gelation Temperature on Macro- and Mesoporosity in the Preparation of Monolithic Silica

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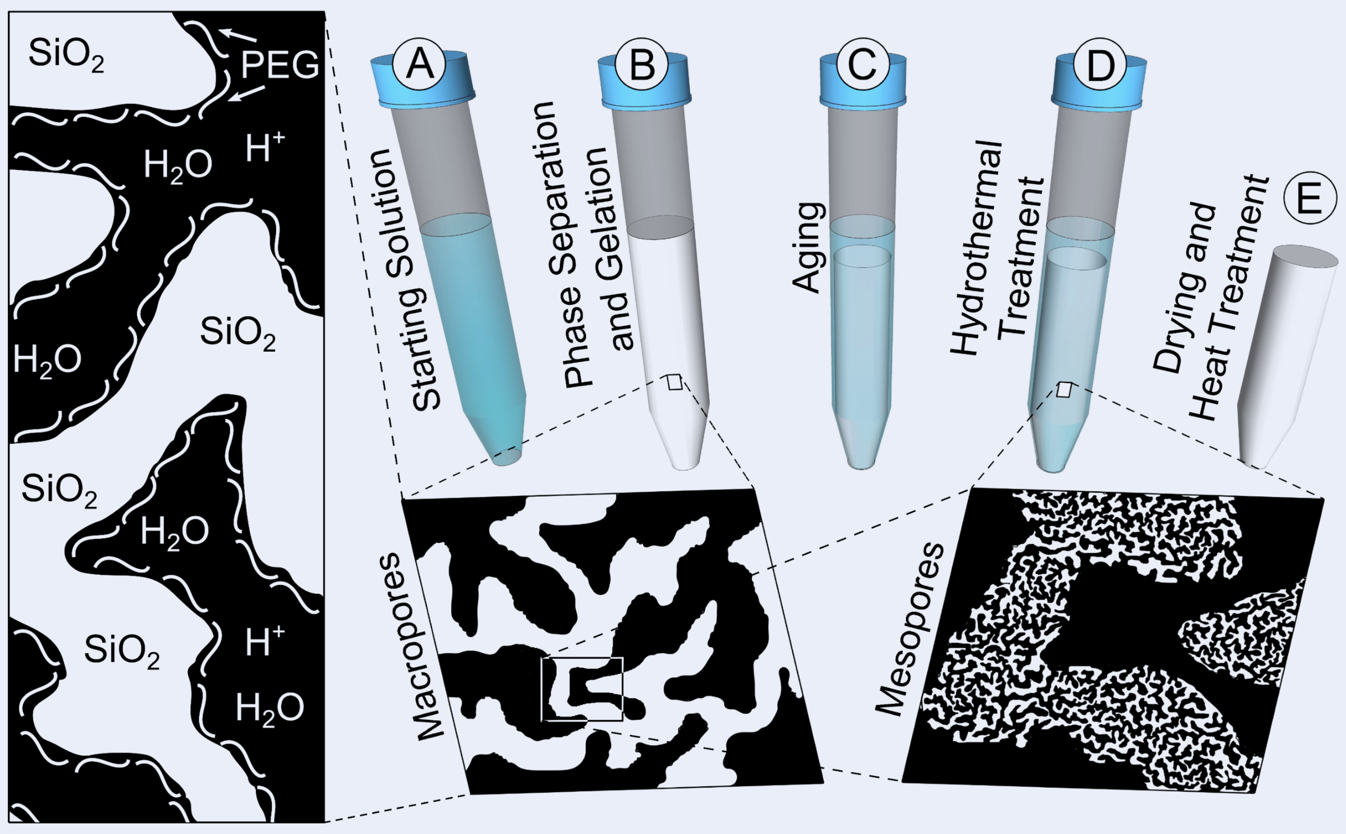
Introduction

- Macro- and mesoporous monolithic silica for electrochemical applications, adsorption, catalysis and separation
- Relationship between preparation protocol and mass transport properties is the origin of an optimized performance
- Reproducibility and homogeneity are essential



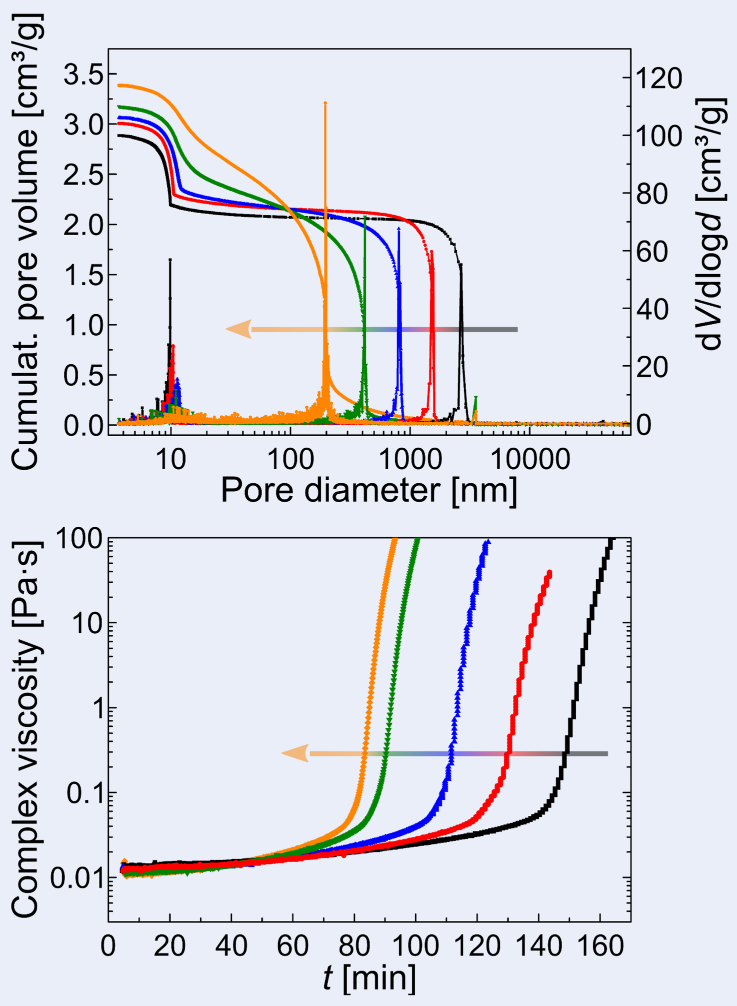
▲ Synthesis

A) Silica precursor, acidic catalyst, organic polymer (PEG) and urea
B) Phase separation induced by spinodal decomposition and frozen in by gelation (formation of macropores)
C) Further condensation leads to shrinkage
D) Decomposition of urea induces dissolution and reprecipitation process (formation of mesopores)
E) Organic moieties are decomposed

Macroporosity

Gelation temperature

22.0°C 25.0°C 28.0°C
23.5°C 26.5°C

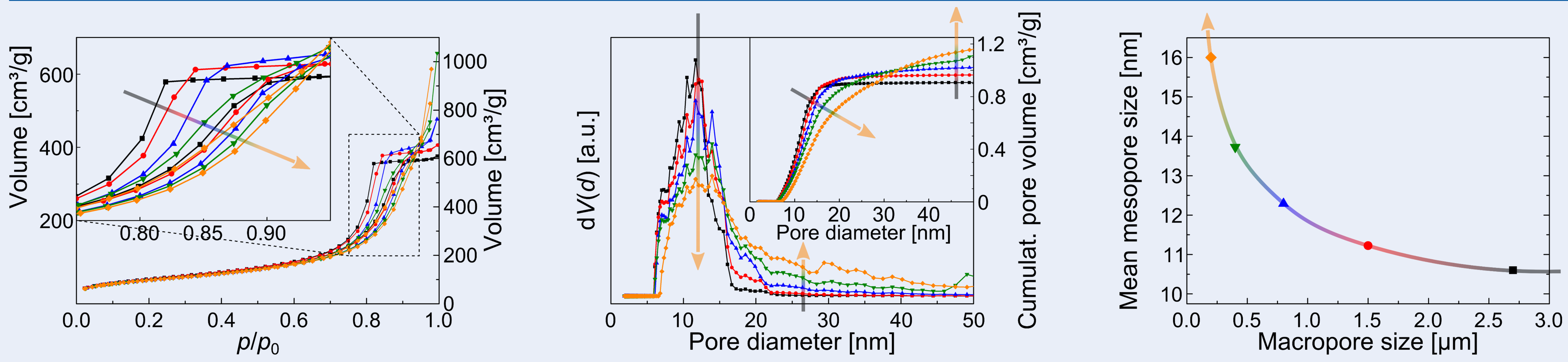


► Mercury intrusion porosimetry
Macropore diameter doubles up by decreasing gelation temperature by 1.5°C

► Rheology
Gelation time is decreased by ~14% by reducing gelation temperature by 1.5°C

Change in macroporosity is predominantly a consequence of the accelerated sol-gel transition → Structure created by phase-separation is frozen in earlier at higher gelation temperatures

Mesoporosity



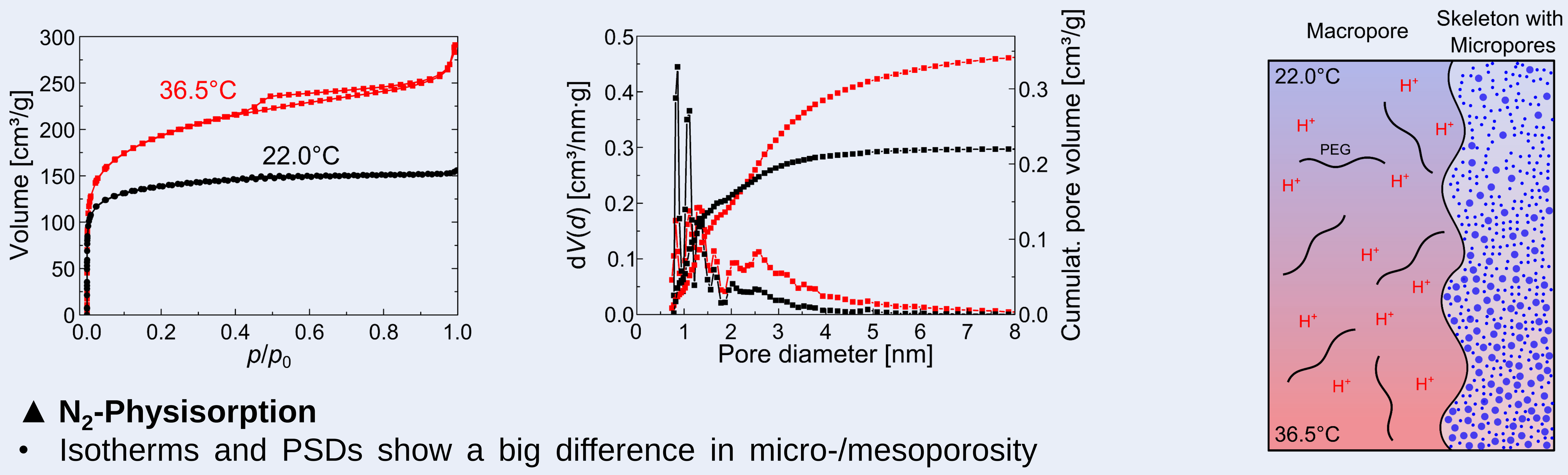
▲ N_2-Physisorption
Isotherms and pore size distributions (PSDs) show an unexpected and systematic change in mesoporosity

unexpected:
mesoporosity is supposed to be generated during hydrothermal treatment (identical for all samples)

systematic:
- mode mesopore size stays constant (12 nm)
- emergence of additional bigger mesopores

▲ Combined porosity data
Mean mesopore size as a function of macropore size

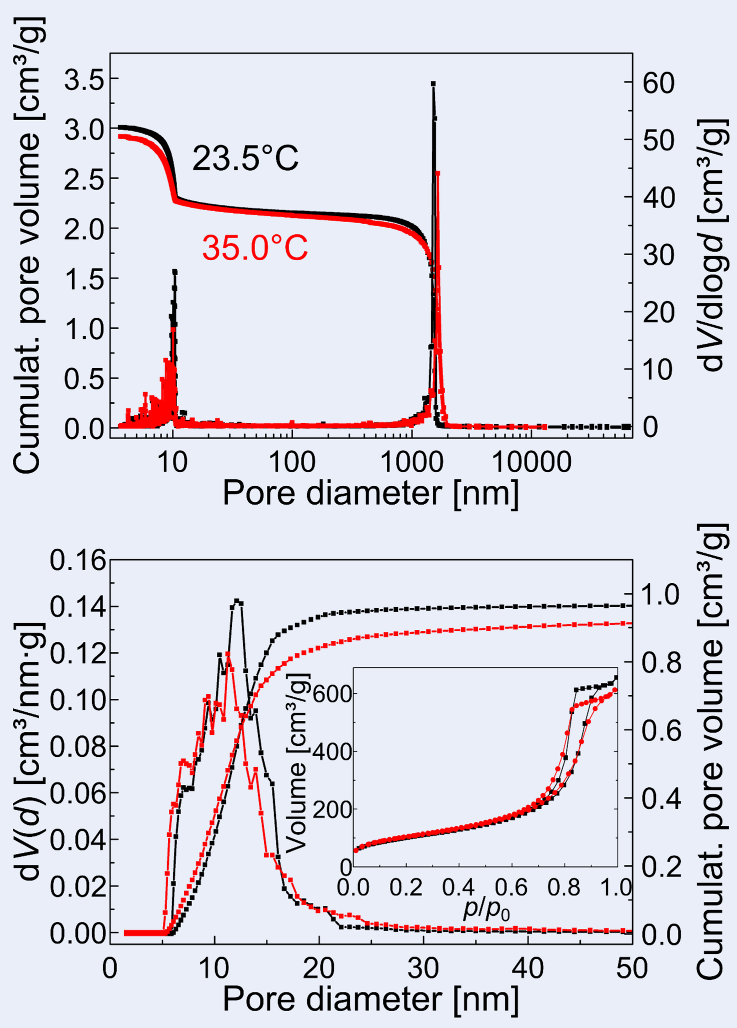
Micro-/mesoporosity prior to hydrothermal treatment



▲ N_2-Physisorption
- Isotherms and PSDs show a big difference in micro-/mesoporosity directly after gelation (temperatures are designated)
- Dissolution and reprecipitation mechanism cannot be neglected at low temperatures and acidic conditions
- Differences at this stage may impact mesopore formation during hydrothermal treatment

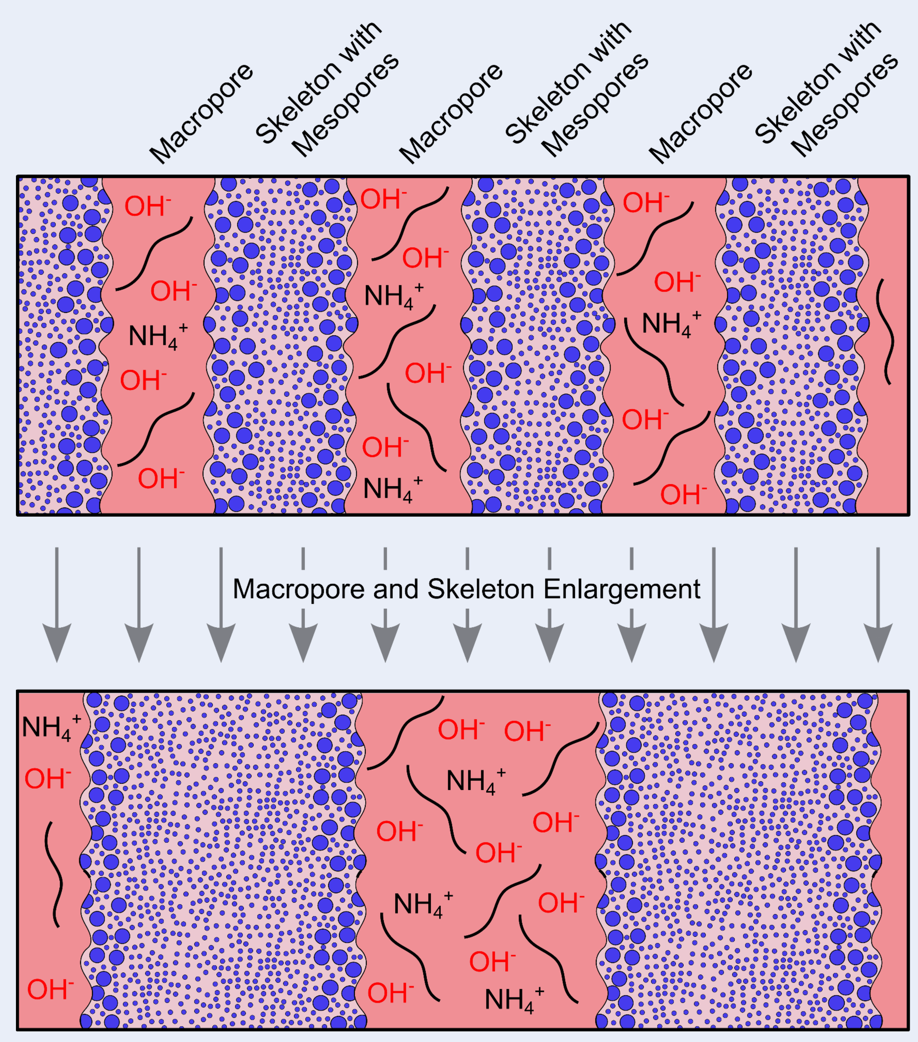
▲ Meso-/microporosity
Scheme illustrating increased micro- and mesopore formation at higher gelation temperature

Mesoporosity as a function of macroporosity



◄ Macro-/mesoporosity
- Samples prepared at different gelation temperatures possess similar mesoporosity when macroporosity is similar (PEG amount adjusted)
- This indicates that mesoporosity is a function of macroporosity

► Postulated mechanism
- Dissolution-reprecipitation is pronounced at interface macropore/skeleton
- Emergence of additional bigger mesopores for smaller macropores /skeletons

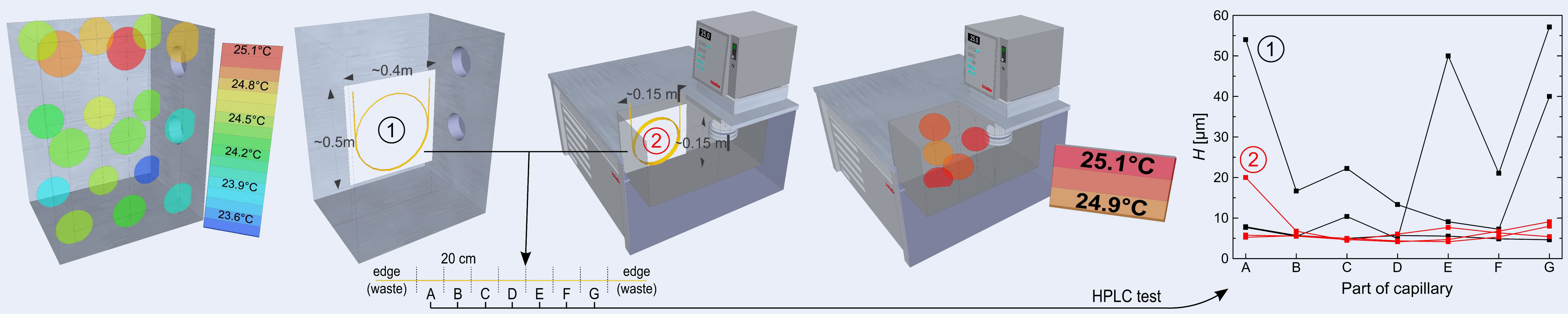


Example of use / Conclusion

▼ Example of use
Impact of quality of gelation temperature control is shown exemplarily for monolithic silica capillary columns in HPLC

- Strong sensitivity of the porosity, especially the macropore size, towards gelation temperature
- Mesoporosity is affected by small differences in gelation temperatures, due to differences in macroporosity

- Synthesis inevitably requires accurate temperature circulators for the preparation of a homogeneous porosity which is essential in high performance flow reactors



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