

## Supporting Information

### On the underestimated impact of gelation temperature on macro- and mesoporosity in monolithic silica

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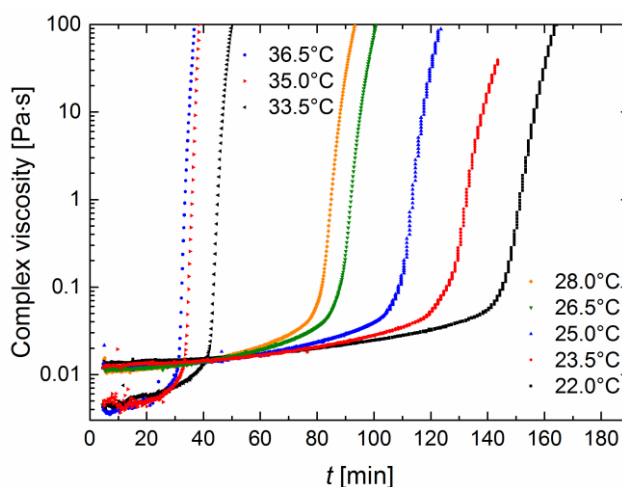
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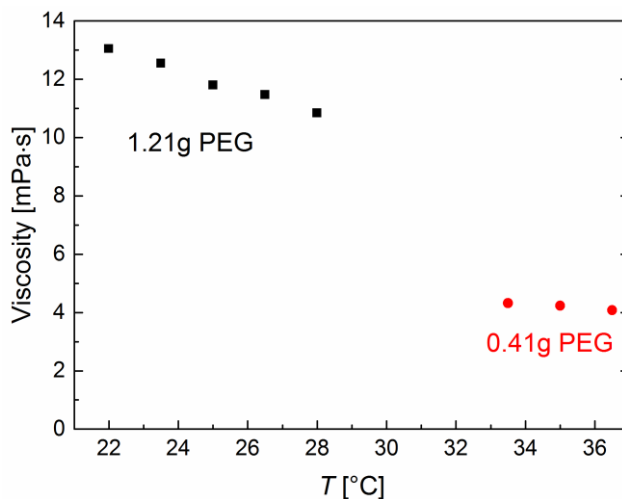
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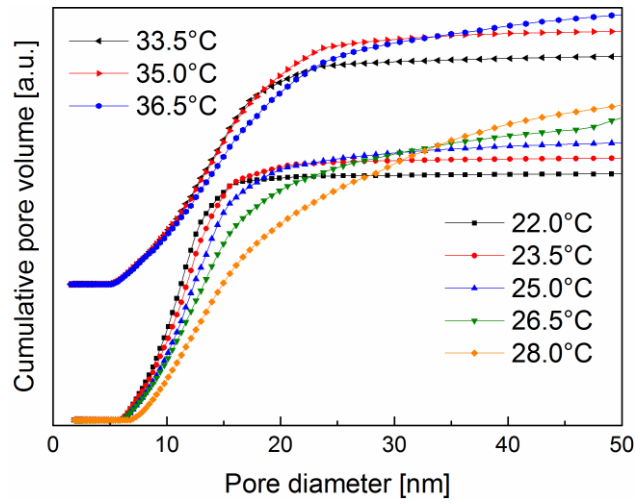
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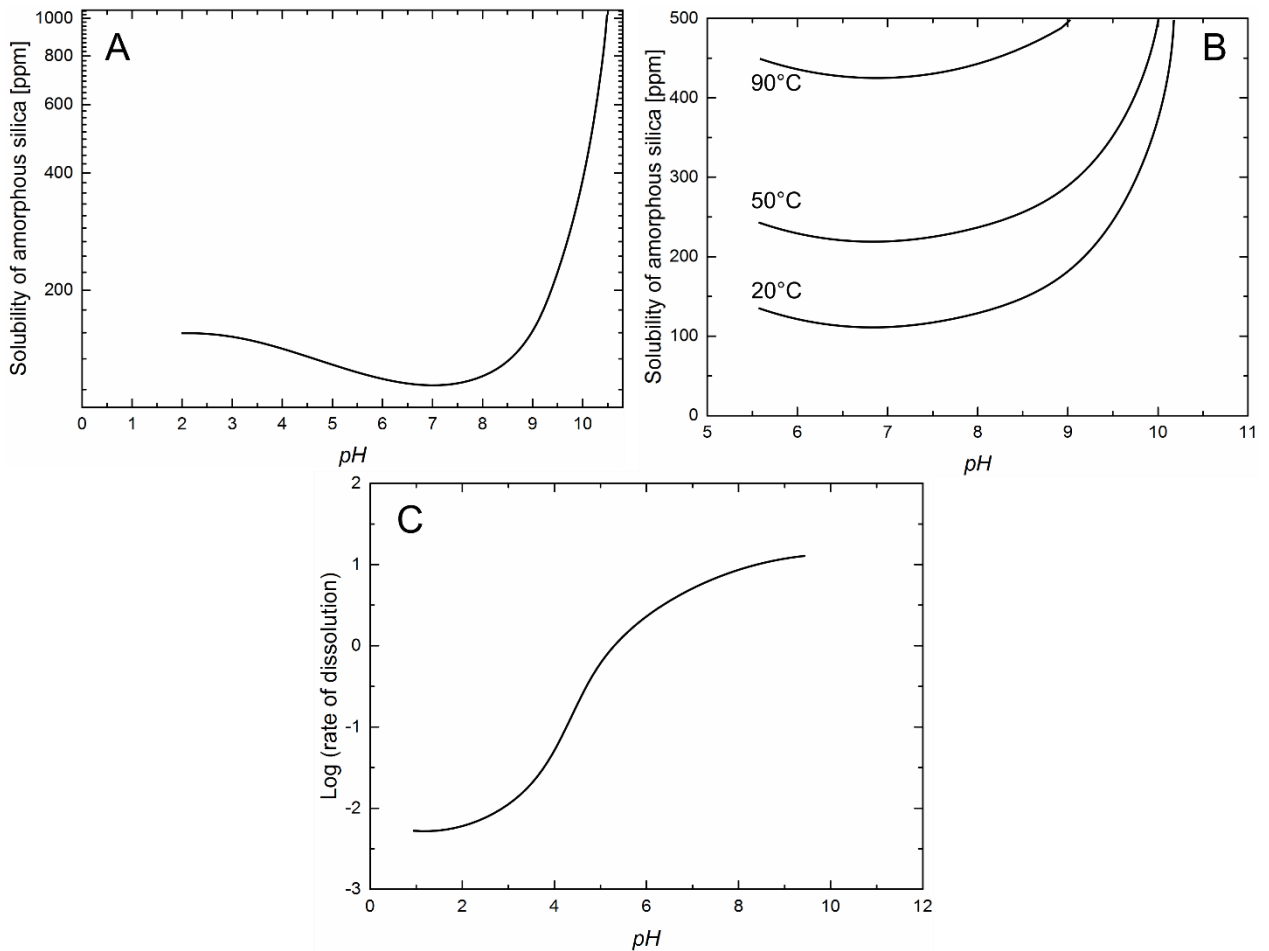
S1: Course of the complex viscosity observed by rheological measurements during the gelation. Data is shown for all samples prepared at slightly different gelation temperatures around 25.0°C and 35.0°C.



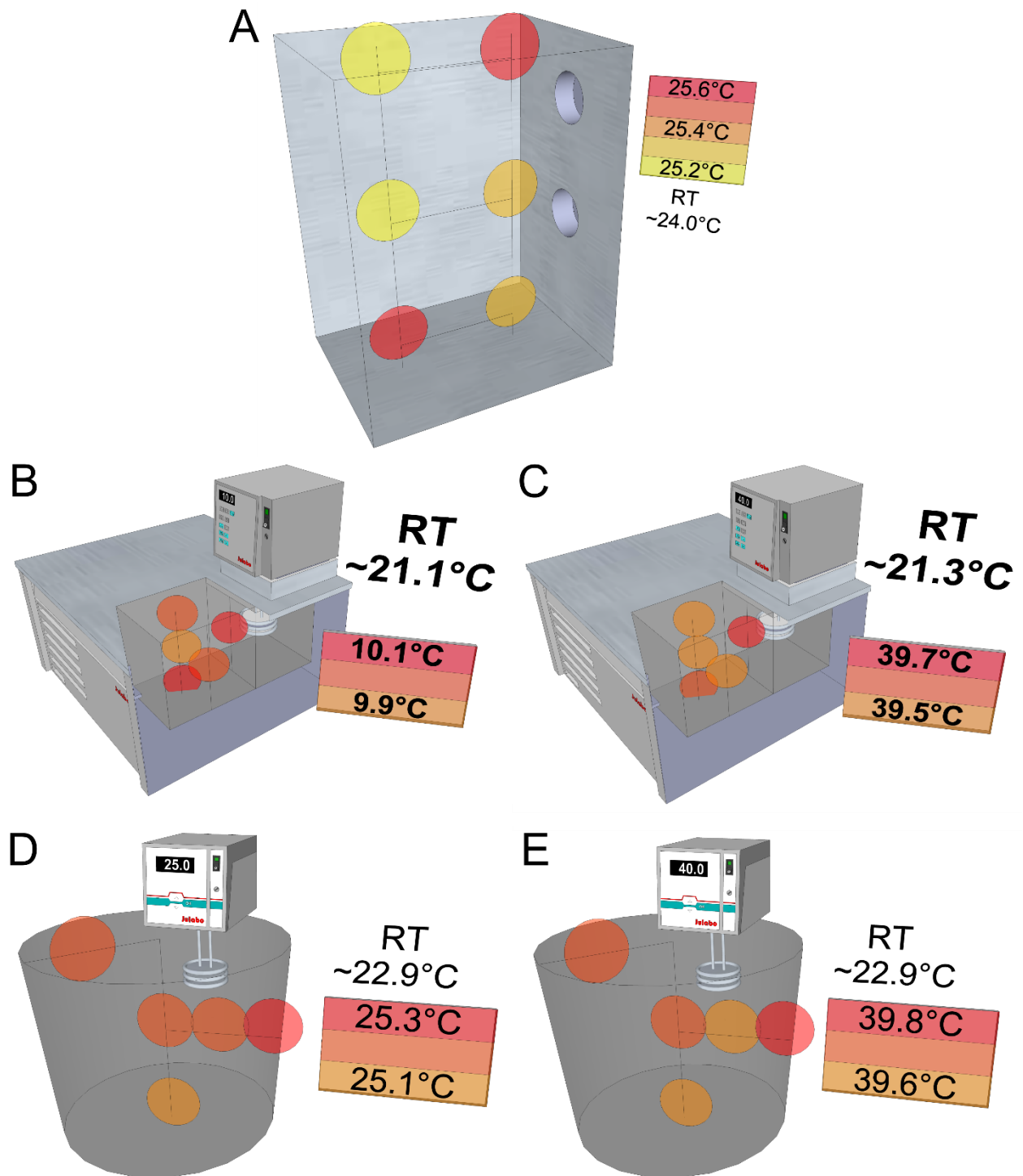
S2: Viscosity at the beginning of the gelation reaction observed by rheological measurements. A small decrease in viscosity can be observed at increasing gelation temperatures. A rather big decrease in viscosity occurs by decreasing the PEG amount in the reaction solution.



S3: Cumulative pore volumes calculated from isotherms shown in Figure 4A using the NLDFT approach on the adsorption branch. Data is shown for all samples prepared at slightly different gelation temperatures around 25.0°C and 35.0°C. Data for temperatures around 35.0°C is shifted on the y-axis to achieve clear arrangement.



S4: (A) Solubility of amorphous silica versus  $pH$ . (B) Solubility of amorphous silica versus  $pH$  at different temperatures. (C) Log rate of dissolution of amorphous silica versus  $pH$ . Figures are adapted from [R. K. Iler, *The Chemistry of Silica, Solubility, Polymerization, Colloid and Surface Properties*, Wiley, New York, 1979].



S5: Temperature profiles measured at several spots for set up temperatures shown in Table 2. Room temperature is indicated as RT. (A) RC1 with a set up temperature at 25.0°C and RT slightly below 25.0°C. (B) RC2 with a set up temperature at 10.0°C and RT at 21.1°C. (C) RC2 with a set up temperature at 40.0°C and RT at 21.3°C. (D) RC3 with a set up temperature at 25.0°C and RT at 22.9°C. (E) RC3 with a set up temperature at 40.0°C and RT at 22.9°C.