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**Supporting information for article:**

**Wetting of alginate aerogels, from mesoporous solids to hydrogels:  
a small-angle scattering analysis**

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## **Supporting Information**

### **Wetting of alginate aerogels, from mesoporous solids to hydrogels: a small-angle scattering analysis**

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#### **Chemicals and preparation of Ca-alginate aerogel (CaAG) beads**

Sodium alginate was purchased from Sigma life science (catalogue no. 71238). Ethanol (99.8) and CaCl<sub>2</sub> were purchased from H. Möller GmbH (Germany) and Th. Geyer GmbH & Co. KG, Lohmar, Germany, respectively, and used without any further purification. Double deionized and ultrafiltered water ( $\rho = 18.2 \text{ M}\Omega \text{ cm}$ ) prepared by a MilliQ (Millipore) equipment was used for all experiments. Carbon dioxide with a purity of >99.9% was supplied by AGA Gas GmbH (Hamburg, Germany).

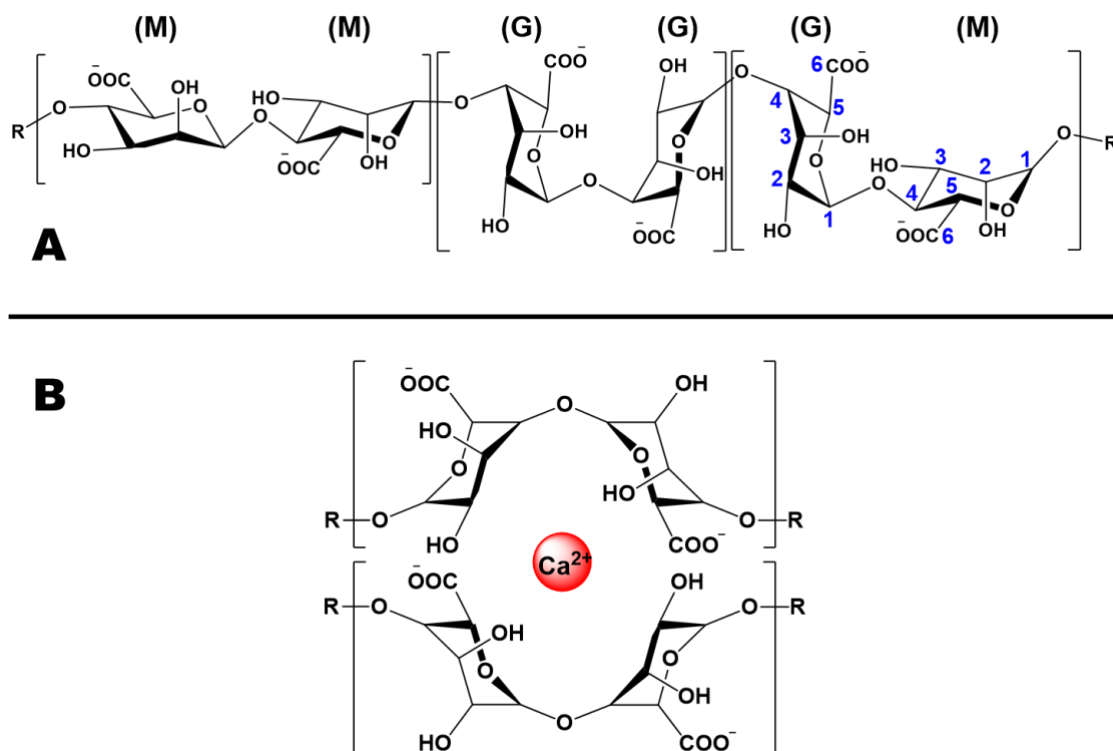
Spherical Ca-alginate aerogel (CaAG) beads of ca. 0.2 mm were synthesized using the jet cutting method as described previously.<sup>1-2</sup> Briefly, 1 w/w% aqueous solution of Na-alginate was dropped into CaCl<sub>2</sub> solution (20 g/L) using a commercial JetCutter (Type S from geniaLab GmbH, Braunschweig, Germany). The gelation bath was moderately stirred in order to ensure the formation of spherical beads and to prevent their aggregation.

After gelation, the gel beads were subjected to multiple step solvent exchange. The Ca-alginate beads were placed for 24 h into 30, 60 and 90 w/w% ethanol-water mixtures and then two times into anhydrous ethanol. Hydrogel-to-solution volume ratio was at least 5. After the last step, the ethanol content in the soaking liquid was checked by measuring its density with a density meter (DMA 4500, Anton Paar Company, Austria). The drying procedure was initiated only when the ethanol content reached min. 98.5 w/w% in order to ensure single phase conditions during subsequent supercritical drying.

The gel beads were dried by extraction of ethanol with a continuous flow of supercritical CO<sub>2</sub> in a high-pressure autoclave. Briefly, filter paper bags containing the samples were placed into a high-pressure autoclave (250 mL) and covered with a few milliliters of ethanol in order to prevent premature solvent evaporation. The autoclave was sealed and preheated to 313 – 323 K. Preheated carbon dioxide was supplied into the autoclave until the desired working pressure (12 MPa) was achieved. Then, the outlet valve was adjusted to achieve carbon dioxide flow rate through the autoclave of ca. 25 g min<sup>-1</sup>. The outgoing flow was directed into a separator to split the fluid into ethanol and gaseous CO<sub>2</sub>. The drying lasted for 3 h; then, the autoclave was slowly depressurized (0.5 MPa min<sup>-1</sup>) and the dry as-prepared CaAG beads were collected. The aerogel samples were kept in a desiccator under freshly dried silica gel.

### **Magic angle spinning (MAS) NMR spectroscopy**

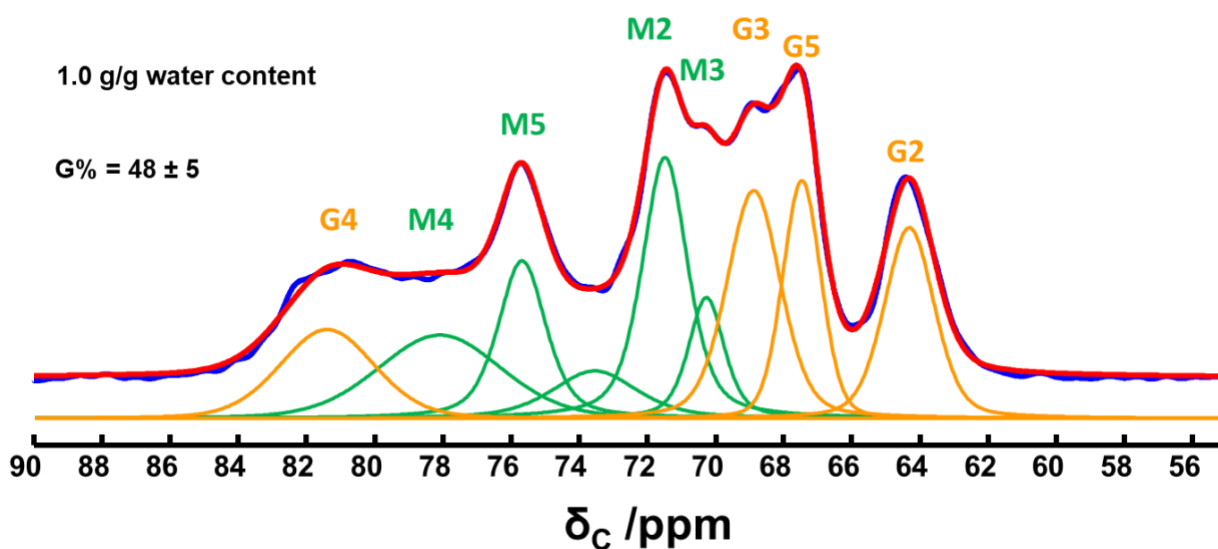
Magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy is able to effectively explore the structural evolution of polysaccharide aerogels upon hydration by following the <sup>13</sup>C and <sup>1</sup>H MAS NMR chemical shifts and linewidths. This technique provides information on the chemical composition of the backbone of the aerogel, the primary to quaternary structures of the macromolecular chains, the state of hydrogen bonding in the solid network, and the state and the localization of water in the hydrated sample.<sup>3-7</sup> Importantly, the hydration of linear chain polysaccharides may cause alterations in the conformations of the chains or even the separation of chains that were originally bound together in the dry state of the material, that is well-expressed in the MAS NMR spectra.<sup>8</sup>



**Figure S1.** General molecular structure of alginate macromolecules (A), and the structure of the “eggbox” junction zone of the  $\text{Ca}^{2+}$  crosslinked alginate chains (B). M =  $\beta$ -D-mannuronate unit, G =  $\alpha$ -L-guluronate unit.

**Table S1.**  $^{13}\text{C}$  CPMAS NMR chemical shifts of the Ca-alginate aerogel assigned according to the spectrum of the hydrated aerogel of 1.0 g/g water content. The nomenclature of the carbon atoms of Ca-alginate is given in **Fig. S1**. M =  $\beta$ -D-mannuronate unit, G =  $\alpha$ -L-guluronate unit.

Carbons	$^{13}\text{C}$ chemical shifts (ppm)
G1, M1	101; 99
G2, M2	65; 71
G3, M3	68; 71
G4, M4	81; 76
G5, M5	68; 76
G6, M6	175.5; 175.5



**Figure S2.** The deconvolution of the  $^{13}\text{C}$  CPMAS NMR spectrum of the Ca-alginate of 1.0 g/g water content. Based on the deconvolution, the percentage of the G units in the alginate chain is  $48 \pm 5$  %. The nomenclature of the carbon atoms of Ca-alginate is given in **Fig. S1**. M =  $\beta$ -D-mannuronate unit, G =  $\alpha$ -L-guluronate unit.

**Table S1.** Preparation conditions and structural parameters of the investigated as-prepared Ca-alginate aerogels.

<b>PROPERTY</b>	<b>VALUE</b>
<b>source alginate solution</b>	1.10 (w/v)%
<b>gelling CaCl<sub>2</sub> solution</b>	180 mM
<b>formulation</b>	jet cutting
<b>bead size</b>	ca. 200 $\mu\text{m}$
<b>final solvent</b>	ethanol
<b>steps of solvent exchange</b>	4 steps (30-60-90-100% EtOH)
<b>drying</b>	scCO <sub>2</sub> (45 °C, 120 bar) flow of 25 g/min for 3 h
<b>apparent surface area</b> (N <sub>2</sub> -sorption / BET)	544 m <sup>2</sup> /g
<b>mean pore diameter</b> (N <sub>2</sub> -sorption / BJH)	42 nm
<b>total pore volume</b> (N <sub>2</sub> -sorption / BJH)	7.5 cm <sup>3</sup> /g
<b>skeletal density</b>	ca. 2.0 g/cm <sup>3</sup>
<b>envelope density</b>	ca. 0.82 g/cm <sup>3</sup>

## References for the Supporting Information

- (1) Ganesan, K.; Budtova, T.; Ratke, L.; Gurikov, P.; Baudron, V.; Preibisch, I.; Niemeyer, P.; Smirnova, I.; Milow, B. Review on the Production of Polysaccharide Aerogel Particles. *Materials* **2018**, *11* (11), 2144, DOI: 10.3390/ma11112144.
- (2) Preibisch, I.; Niemeyer, P.; Yusufoglu, Y.; Gurikov, P.; Milow, B.; Smirnova, I. Polysaccharide-Based Aerogel Bead Production via Jet Cutting Method. *Materials* **2018**, *11* (8), 1287, DOI: 10.3390/ma11081287.
- (3) Mollica, G.; Ziarelli, F.; Lack, S.; Brunel, F.; Viel, S. Characterization of insoluble calcium alginates by solid-state NMR. *Carbohydr. Polym.* **2012**, *87* (1), 383-391, DOI: 10.1016/j.carbpol.2011.07.066.
- (4) Paul, G.; Bisio, C.; Braschi, I.; Cossi, M.; Gatti, G.; Gianotti, E.; Marchese, L. Combined solid-state NMR, FT-IR and computational studies on layered and porous materials. *Chemical Society Reviews* **2018**, *47* (15), 5684-5739, DOI: 10.1039/C7CS00358G.
- (5) Salomonsen, T.; Jensen, H. M.; Larsen, F. H.; Steuernagel, S.; Engelsen, S. B. Alginate monomer composition studied by solution- and solid-state NMR – A comparative chemometric study. *Food Hydrocoll.* **2009**, *23* (6), 1579-1586, DOI: 10.1016/j.foodhyd.2008.11.009.
- (6) Sperger, D. M.; Fu, S.; Block, L. H.; Munson, E. J. Analysis of composition, molecular weight, and water content variations in sodium alginate using solid-state NMR spectroscopy. *J. Pharm. Sci.* **2011**, *100* (8), 3441-3452, DOI: 10.1002/jps.22559.
- (7) Maleki, H.; Montes, S.; Hayati-Roodbari, N.; Putz, F.; Huesing, N. Compressible, Thermally Insulating, and Fire Retardant Aerogels through Self-Assembling Silk Fibroin Biopolymers Inside a Silica Structure-An Approach towards 3D Printing of Aerogels. *ACS Appl. Mater. Interfaces* **2018**, *10* (26), 22718-22730, DOI: 10.1021/acsami.8b05856.