

Electronic Supplementary Information (ESI)

for

Probing the Effects of Polymers on the Early Stages of Calcium Carbonate Formation by Stoichiometric Co-Titration

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Experimental Procedures

Chemicals

The following chemicals were used as received without further purification: calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, Honeywell, $\geq 99.0\%$), sodium bicarbonate (NaHCO_3 , AppliChem, $\geq 99.0\%$), Sokalan® PA 20 (poly(acrylic acid), PAA, $M \approx 2500 \text{ g mol}^{-1}$, BASF), Sokalan® CP 50 (poly((acrylic acid)-co-(2-acrylamido-2-methyl-1-propanesulfonic acid)), P(AA-co-AMPS), BASF), poly(aspartic acid) (PAsp, $M \approx 5500 \text{ g mol}^{-1}$, BASF), poly(sodium 4-styrenesulfonate) (PSS, Sigma-Aldrich, $M \approx 70000 \text{ g mol}^{-1}$, (poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS, $M \approx 14400 \text{ g mol}^{-1}$, BASF), and poly(vinylphosphoric acid) (PVPA, $M > 70000 \text{ g mol}^{-1}$, Polysciences). All solutions were prepared using water of Milli-Q quality.

Titration experiments

All titration experiments were carried out at room temperature (23°C) with a Titrand system by Metrohm. A beaker equipped with a stirring bar was filled with water (50 mL) or the aqueous polymer solution (10 ppm). CaCl_2 and NaHCO_3 solutions (each 200 mM) were simultaneously added with two dosing units (Metrohm, 800 Dosino) at a rate of 0.04 mL min^{-1} . The pH of the system was kept constant at 8.5 by counter-titration with NaOH solution (100 mM). During titration, the Ca^{2+} potential, pH and transmission of the solution were monitored with an ion-selective electrode (ISE, Metrohm No. 6.0510.100), a flat-membrane pH electrode (Metrohm No. 6.0256.100) and a turbidimetric probe (Optrode, Metrohm No. 8.109.8054). The pH probe was regularly calibrated using buffers from Mettler-Toledo (pH 4.01, 7.00 and 9.21). Calibration of the Ca-ISE was achieved by titrating CaCl_2 solution into water in the absence of co-added NaHCO_3 (i.e. water was co-titrated instead of the bicarbonate solution). After each experiment, all components (vessel, burette tips, and sensors) were thoroughly cleaned with hydrochloric acid (1 M) and then rinsed carefully with water.

Analytical methods

Dynamic light scattering (DLS) measurements on solutions containing CaCO_3 precursors were performed at different times during co-titration using a Zetasizer Nano S instrument from Malvern. For cryo-transmission electron microscopy (cryo-TEM), aliquots of the solutions were drawn from the reaction vessel at predefined times and vitrified as thin film on a TEM support using the Vitrobot™ vitrification robot from FEI. Images were acquired on a TECNAI G2 F20ST microscope from FEI. For ex-situ characterisation, the material precipitated at the end of the co-titration experiments was isolated by vacuum filtration, brief rinsing with water and ethanol, and drying in air. The resulting powders were investigated by means of scanning electron microscopy (SEM, using a Phenom ProX microscope from Thermo-Fisher, operated at 10 kV, after coating the samples with a thin layer of gold), Fourier-transform infrared spectroscopy (FTIR, using a Spectrum Two IR instrument from Perkin-Elmer) and powder X-ray diffraction (PXRD, using a D8 Advance Series II diffractometer from Bruker).

The adsorption of Sokalan® PA 20 and CP 50 on fully developed calcite crystals was studied by means of batch assays based on total organic carbon (TOC) analyses. For this purpose, solutions of the polymers in water were prepared at different concentrations (100, 200, 500 and 1000 ppm) and their organic carbon content was determined using a Shimadzu TOC-L instrument. Then, 20 g polymer solution were mixed with 2 g commercial calcite powder (Omycarb® 2 GU; BET surface area: 3.6 m²/g). The resulting suspension was first brought to a pH of 8.0 by addition of small amounts of 1 M HCl and then stirred overnight to allow for polymer adsorption on the calcium carbonate surfaces to reach equilibrium. Subsequently, the suspension was centrifuged and the supernatant was passed through syringe filters (Millex, PVDF, 450 nm). Finally, the TOC content of the filtrate was measured and compared to the respective value of the original polymer solution. From the difference, the amount of adsorbed polymer can readily be calculated. All values were corrected for TOC contents of the used water and a calcite suspension in the absence of polymer. Rheological studies on CaCO₃ suspensions in the presence and absence of added polymers were performed using an Anton Paar Physica MCR 101 rheometer equipped with a concentric cylinder geometry. The samples were prepared by mixing 70 g calcium carbonate powder (Omycarb® 2 GU) with 30 g of pure water (reference) or an aqueous solution containing 2.33% polymer solution (yielding a polymer/CaCO₃ ratio of 0.01, similar to the adsorption measurements via TOC described above), followed by homogenisation over 72 h using a roller tray. The resulting slurries were then transferred into the rheometer and characterised at shear rates ranging from 0.1 to 100 s⁻¹.

Supplementary Figures

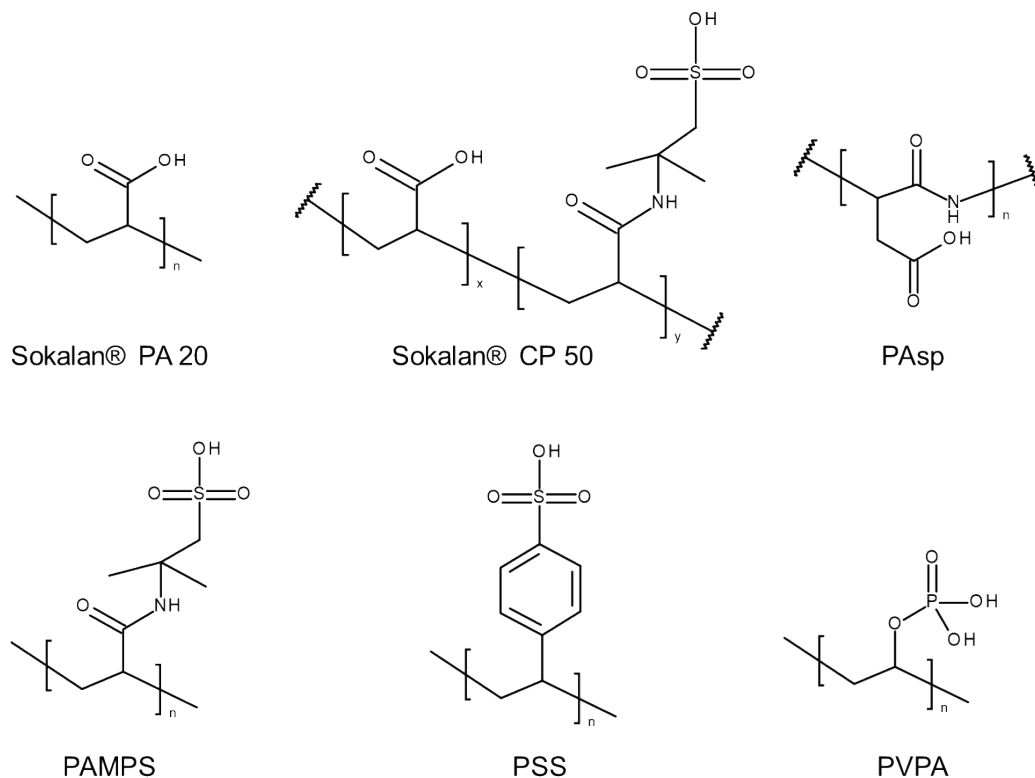


Figure S1: Molecular structures of the polymeric additives used in this work.

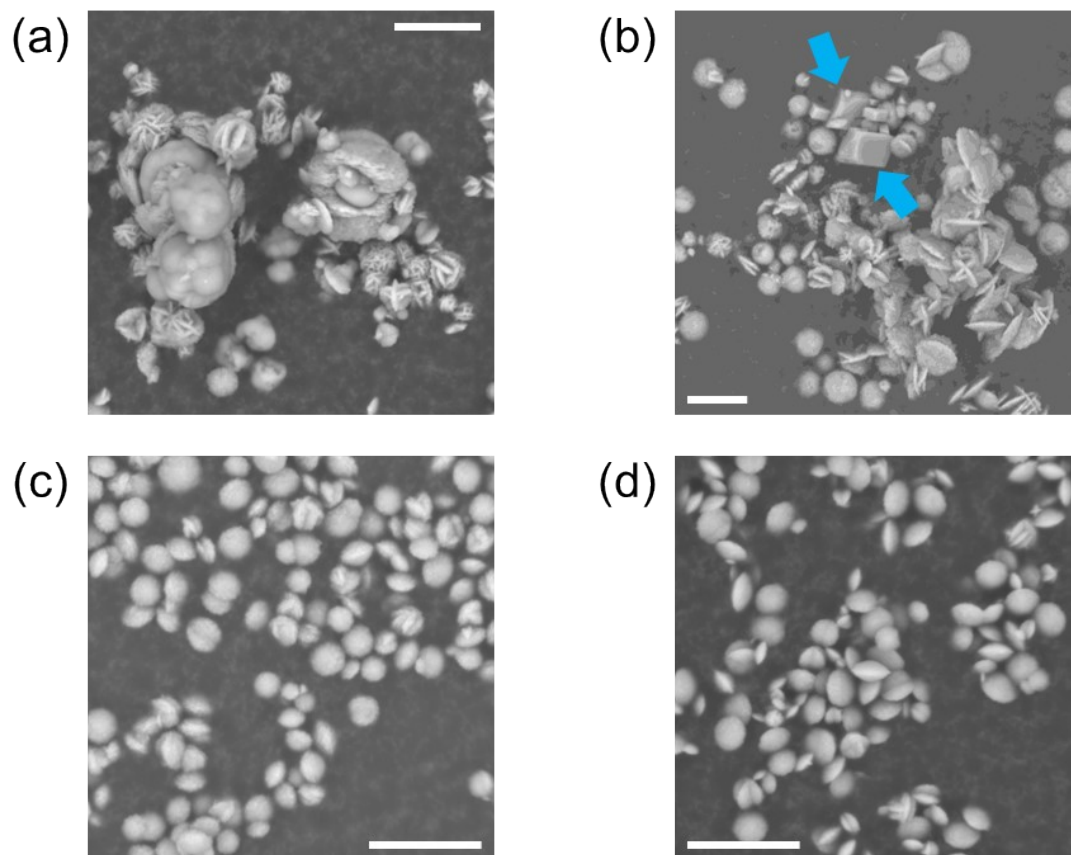


Figure S2: SEM images of crystalline products obtained at the end of titrations were performed in the presence of 10 ppm PAsp (a), PVPA (b), PSS (c) and PAMPS (d). In all cases, vaterite is the main polymorph observed. Blue arrows in (b) indicate rhombohedral calcite crystals. Scale bars are 5 μm .

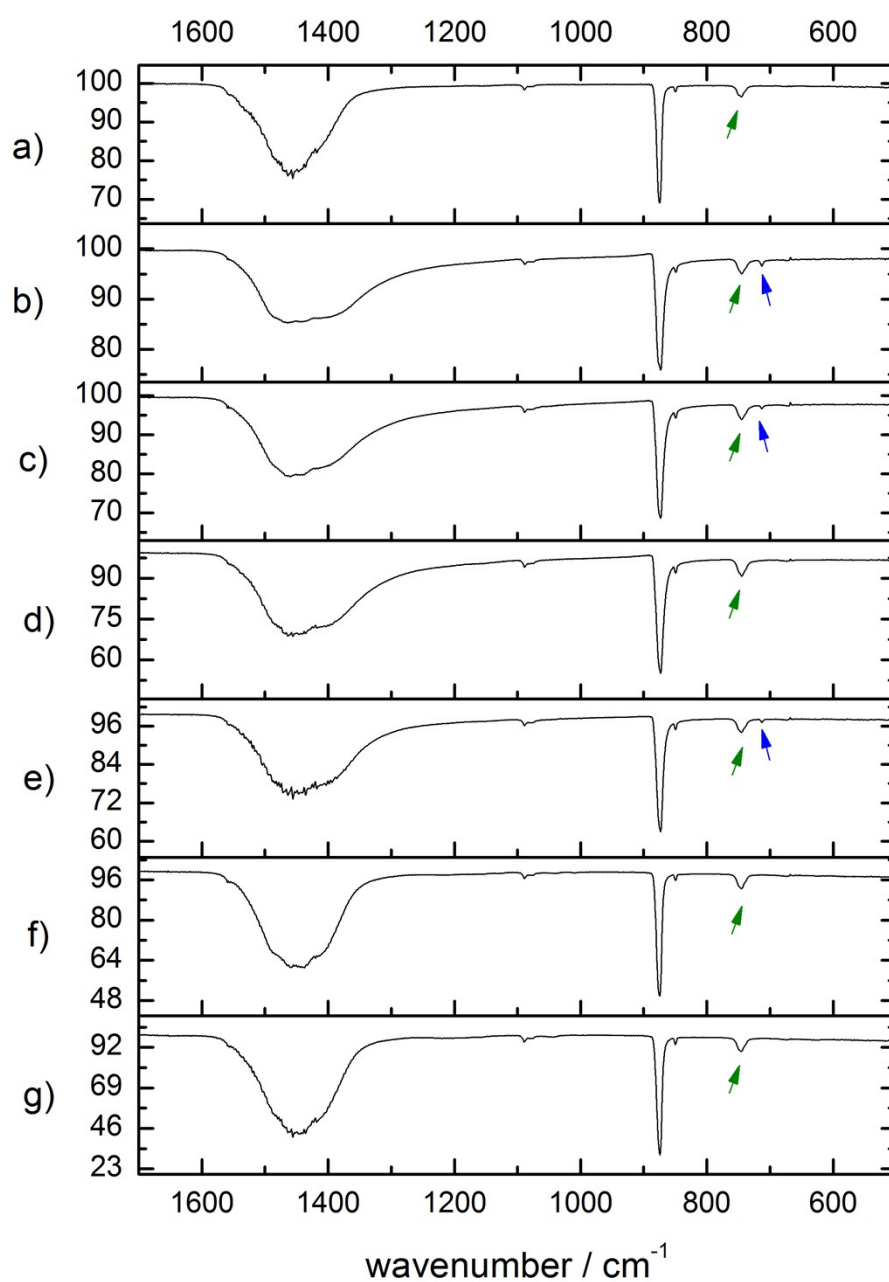


Figure S3: IR spectra of crystalline products obtained at the end of titrations performed without polymer (a) and in the presence of 10 ppm Sokalan® PA 20 (b), Sokalan® CP 50 (c) PAsp (d), PVPA (e), PSS (f) and PAMPS (g). The occurrence of vaterite as main polymorph formed is confirmed by the carbonate deformation vibration at 746 cm^{-1} (green arrows). In the presence of PA 20 (b), CP 50 (c) and PVPA (e), also small amounts of calcite were detected (carbonate deformation vibration at 713 cm^{-1} , blue arrows).

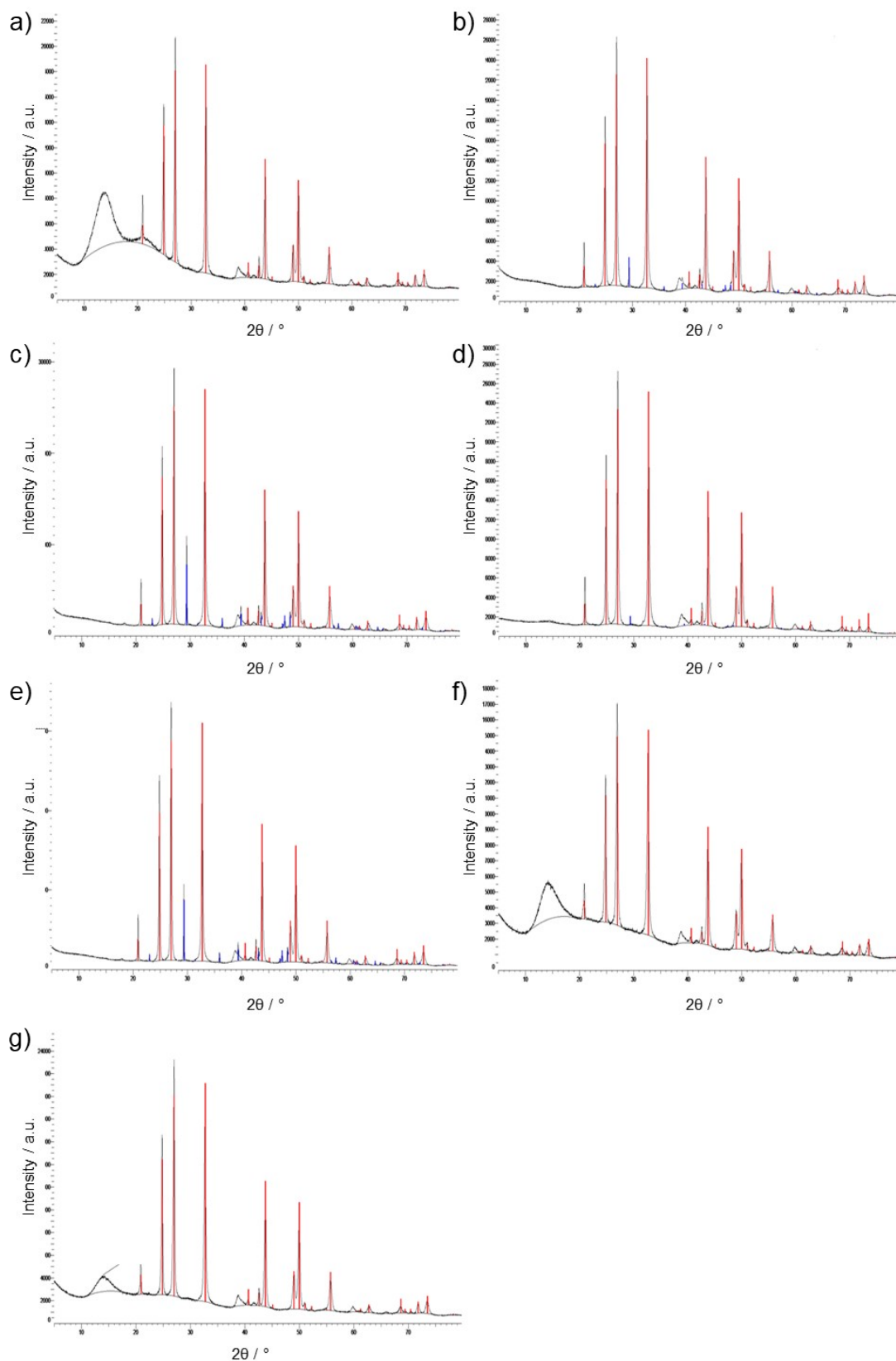


Figure S4: PXRD data of crystalline products obtained at the end of titrations were performed without polymer (a) and in the presence of 10 ppm Sokalan® PA 20 (b), Sokalan® CP 50 (c) PAsp (d), PVPA (e), PSS (f) and PAMPS (g). Reflections marked in red and blue can be assigned to vaterite and calcite, respectively. Note that the broad peak at $2\theta \approx 14^\circ$ observed in some diffractograms originates from polyisobutylene glue used for sample preparation.

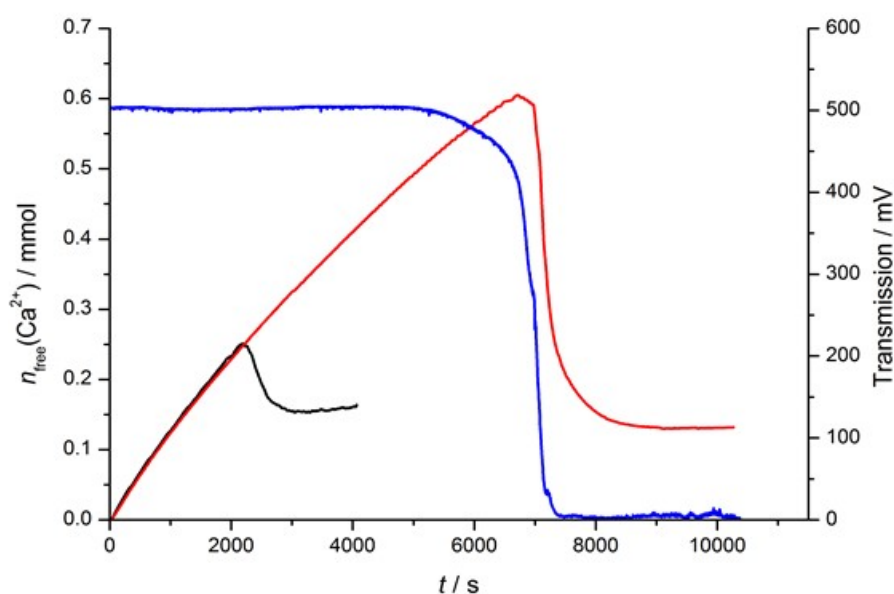


Figure S5: Time-dependent development of the amount of free Ca^{2+} (red) and the optical transmission (blue) during precipitation of calcium carbonate by stoichiometric co-titration in the presence of 10 ppm **PAsp** (initial concentration) at pH 8.5. For comparison, the profile of $n_{\text{free}}(\text{Ca}^{2+})$ measured in the reference experiment without any additive is also shown (black).

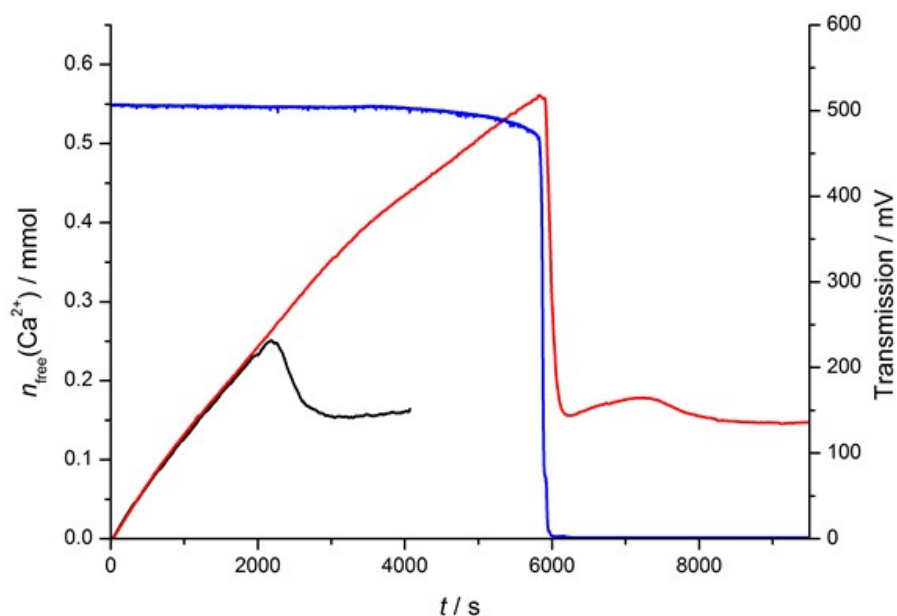


Figure S6: Time-dependent development of the amount of free Ca^{2+} (red) and the optical transmission (blue) during precipitation of calcium carbonate by stoichiometric co-titration in the presence of 10 ppm **PVPA** (initial concentration) at pH 8.5. For comparison, the profile of $n_{\text{free}}(\text{Ca}^{2+})$ measured in the reference experiment without any additive is also shown (black).

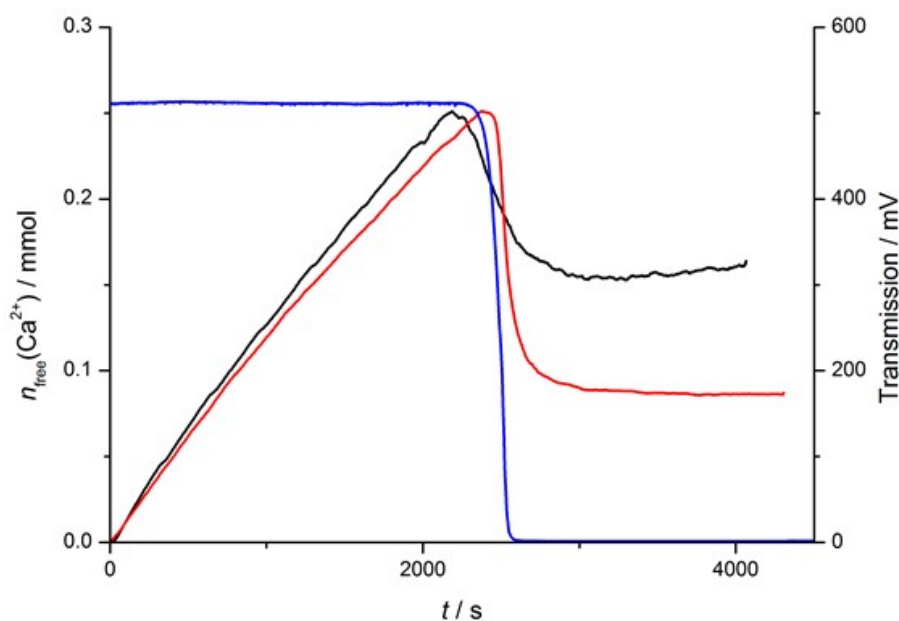


Figure S7: Time-dependent development of the amount of free Ca^{2+} (red) and the optical transmission (blue) during precipitation of calcium carbonate by stoichiometric co-titration in the presence of 10 ppm PSS (initial concentration) at pH 8.5. For comparison, the profile of $n_{\text{free}}(\text{Ca}^{2+})$ measured in the reference experiment without any additive is also shown (black). The observed flattening of $n_{\text{free}}(\text{Ca}^{2+})$ prior to nucleation in the presence of the polymer (as compared to the reference experiment) may indicate that PSS has a certain stabilising effect on associated states, i.e. it seems to shift the equilibrium between free ions and ion pairs and/or PNCs in favour of the latter.

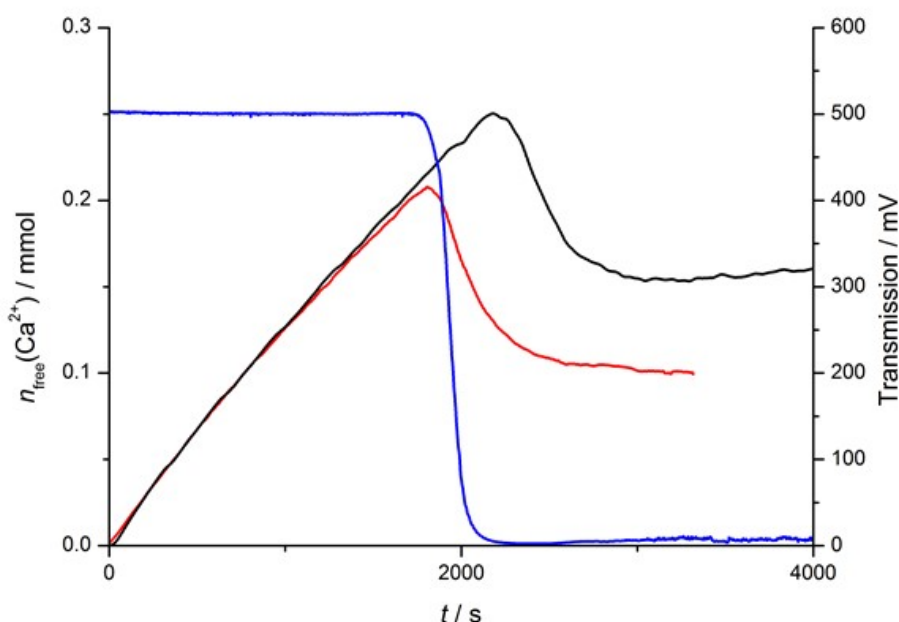


Figure S8: Time-dependent development of the amount of free Ca^{2+} (red) and the optical transmission (blue) during precipitation of calcium carbonate by stoichiometric co-titration in the presence of 10 ppm PAMPS (initial concentration) at pH 8.5. For comparison, the profile of $n_{\text{free}}(\text{Ca}^{2+})$ measured in the reference experiment without any additive is also shown (black).

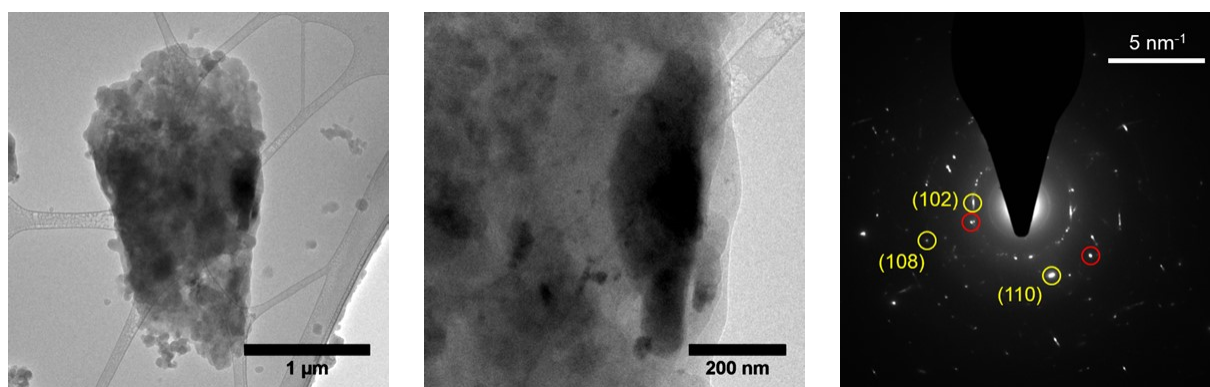


Figure S9: Cryo-TEM micrographs at lower (left) and higher (middle) magnification and selected-area electron diffraction (SAED) pattern (right) acquired from a sample drawn at $t = 8450$ s (cf. Fig. 5 in the main text) during co-titration in the presence of Sokalan® CP 50 (see Fig. 6 in the main text for cryo-TEM images and SAED patterns of samples drawn at earlier times). The structure in the left image suggests that larger crystalline particles have formed through aggregation of smaller subunits (resulting from initial liquid/liquid demixing and later solidification). This aggregation-based growth mechanism is likely impeded by the modified polycarboxylate due to adsorption and enhanced dispersion (cf. Fig. 7 in the main text). The crystalline reflections observed in the SAED pattern can be assigned to calcite (yellow circles) and ice (red circles) formed upon electron irradiation of initially vitrified water.