SUPPORTING INFORMATION

I Polymer synthesis



Figure SI 1 1H-NMR spectrum (300 MHz, D₂O, 25°C) of the poly(acrylic acid co-2-acrylamido-2-propane sulfonate) copolymer C3 (ratio_(AA/AMPS)=80:20, 12.8 kg/mol, PDI:1.22).

The determination of copolymerization parameters has been done according to D. Braun, H. Cherdron, H. Ritter, Polymer Synthesis: Theory and Practice (2001), Springer-Verlag Berlin Heidelberg New York.

II Dynamic light scattering of the Ca-PAA-PAMPS aggregation

Sample preparation

All preparation steps were carried out in a flow box to avoid contamination by dust.

Aggregation of PAA_{80} - $PAMPS_{20}$; $M_w = 6200 \text{ g/mol.}$

Equal volumes of a 20 mM PAA_{80} -PAMPS₂₀ solution (pH=8) and a 50 mM CaCl₂ solution were filtered successively through a Millex-VV filter unit (0.1 µm pore size) into a cylindrical

quarz glass cuvette (Hellma, 20 mm diameter), giving final concentrations of $[PAA_{80}-PAMPS_{20}]=10 \text{ mM}$ and $[CaCl_2]=25 \text{ mM}$.

Aggregation of NaPMAA; $M_w = 1200 \text{ g/mol}$

Na-PMAA (M_W = 1200 g/mol, PDI < 1.2) was purchased from Polymer Standard Service (PSS), GmbH, Mainz, FRG. Since aggregation and precipitation of polyelectrolytes very strongly depends on the polymer mass distribution, Na-PMAA was chosen as a typical polycarboxylate over Na-PAA as it was obtainable at a lower PDI, which was comparable to PAA₈₀-PAMPS₂₀.

2 equivalents of a 3 mM NaPMAA solution and 1 equivalent of a 15 mM CaCl₂ solution were filtered successively through a Millex-VV filter unit (0.1 μ m pore size) into a cylindrical quarz glass cuvette (Hellma, 20 mm diameter), giving final concentrations of [NaPMAA]= 2 mM and [CaCl₂]= 5 mM.

Light scattering setup

DLS experiments were carried out at an ALV-7004 correlator setup, equipped with an ALV/CGS-8FDLS/SLS 5022F goniometer, an ALV 7004 correlator and a QEAPD Avalanche photodiode detector. A He-Ne-laser (λ = 632.8 nm, *P*=200 mW) served as a coherent light source. Incident and scattered beam were polarized vertically with respect to the scattering plane (VV mode). Measurements were carried out at *T*=293 K and at 8 different angles (θ =30, 47, 64, 81, 98, 115, 132, 149°), covering a range of the squared scattering vector q^2 = ($4\pi n \sin(\theta/2)/\lambda_0$)² from 4.7x10⁹ to 6.5x10¹⁰ cm⁻².

Results

In the case of the copolymer, only small aggregates are formed, which lead to weak scattering intensities. Therefore, a calcium dependent study of the aggregation could not be carried out.

A ratio of $[Ca]/[PAA_{80}-PAMPS_{20}] = 2.5$ however yielded correlation functions at 30°, which could be fitted with a biexponential fit to a hydrodynamic radius of 10 nm.



Figure SI 2: Correlation function, acquired at θ = 30°, for the Ca²⁺ mediated aggregation of PAA₈₀-PAMPS₂₀. M_w= 6200 g/mol, [PAA₈₀-PAMPS₂₀]= 10 mM, [CaCl₂]= 25 mM.

On the contrary, NaPMAA formed much larger aggregates at the same [Ca]/[Polymer] ratio. The resulting plot of the diffusion coefficients at different angles is shown in Figure SI 3. Extrapolation to $\theta = q = 0$ gives a z-averaged diffusion coefficient of $\langle D \rangle_z = 2.27 \times 10^{-8} \text{ cm}^2/\text{s}$ and a hydrodynamic radius of $R_H = 95$ nm.



Figure SI 3: Diffusion coefficients of the Ca²⁺-PMAA aggregates measured at different angles. M_w = 1200 g/mol, [NaPMAA]= 2 mM, [CaCl₂]= 5 mM.

III Isothermal titration calorimetry for Ca²⁺ -copolymer complexation



Figure SI 4 Measured heat (normalized by the moles of Ca^{2+} per injection) for **a**) the titration of a 11 mM PAA₂₀-PAMPS₈₀ solution (pH=7.5) with 40 mM CaCl₂ and **b**) the titration of a 16.5 mM PAA₈₀-AMPS₂₀ solution (pH=7.5) with 100 mM CaCl₂, plotted versus the molar ratio of Ca²⁺ and potential carboxylate binding sites, respectively.

	PAA ₂₀ -PAMPS ₈₀	PAA ₈₀ -PAMPS ₂₀	NaPAA ^a
$K_A[M^{-1}]$	3.1×10^3	3.1×10^3	150x10 ³
$\Delta H^{\circ}_{bind.}$ [kJ/mol]	7.2	14.0	17.0
$\Delta S^{\circ}_{bind.}$			
	11.0	13.8	19.0
[R = 8.314 J/(molxK)]			
ΔG° _{bind.} [kJ/mol]	-19.6	-19.6	-29.6
n	0.54	0.36	

Table SI 1 Thermodynamic data and stoichiometry obtained from the ITC measurement.

^{a)} From reference Sinn, C. G., Dimova, R., Antonietti, M. *Macromolecules* **2004**, *37*, 3444–3450.



IV In situ dynamic light scattering monitoring CaCO₃ nucleation and growth

Figure SI 5 Apparent hydrodynamic radius from DLS experiments starting with $[CaCl_2] = [DEC] = 10$ mM and [NaOH] = 8 mM in the absence of any additives. T = 298 K, $\theta = 90^{\circ}$.

V In-situ Atomic Force Microscopy

For the AFM experiments, a different batch of copolymers was used having the same composition and molecular weight as the described copolymers within an experimental error in composition and average molecular weight of 5 %.