Supporting Information:

Average MW between cross-links:

Flory-Rehner equation:

$$-ln(1-\varphi_P)+\varphi_P+\chi_{P,S}\varphi^2=\frac{V_S}{\tilde{\nu}M_c}\left(1-\frac{2M_c}{M}\left(\varphi^{\frac{1}{3}}-\frac{\varphi}{2}\right)\right) \quad (1)$$

The volume fraction of the polymer in the swollen network φ_P was determined from the degree of swelling (SI) and the density of PAA (1.35 g/mol), $\chi_{P,S}=0.41$ is the Flory-Huggins-interaction parameter of polymer and solvent (Safronov 2015), V_S is the molar volume of the solvent and $\tilde{\nu}$ and M are the specific volume and the molecular weight of the used polymer. The Degree of swelling was calculated by dividing the weight of the wet hydrogel by the weight of the dried one. It was determined twice for each synthesis condition. The gels were air dried for 48 h and swelled again in MilliQ water for 24 h.

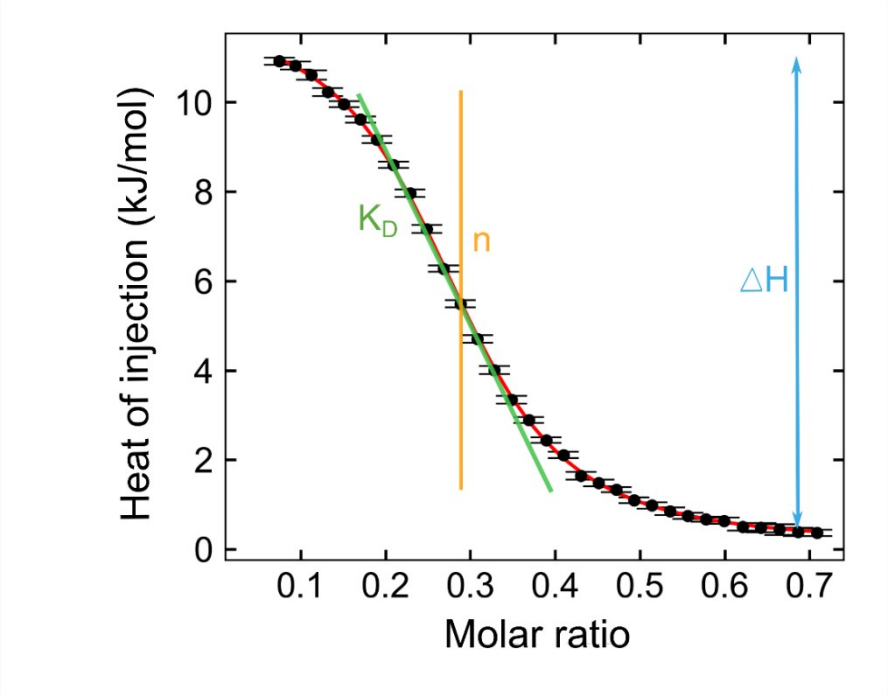

Figure S 1: Evaluation of the thermodynamic parameters from the ITC data with ΔH as the offset, n as the turning point and K_D as the slope at the turning point. The data was fitted with a model of simple hetero association (A + B ⟷ AB).

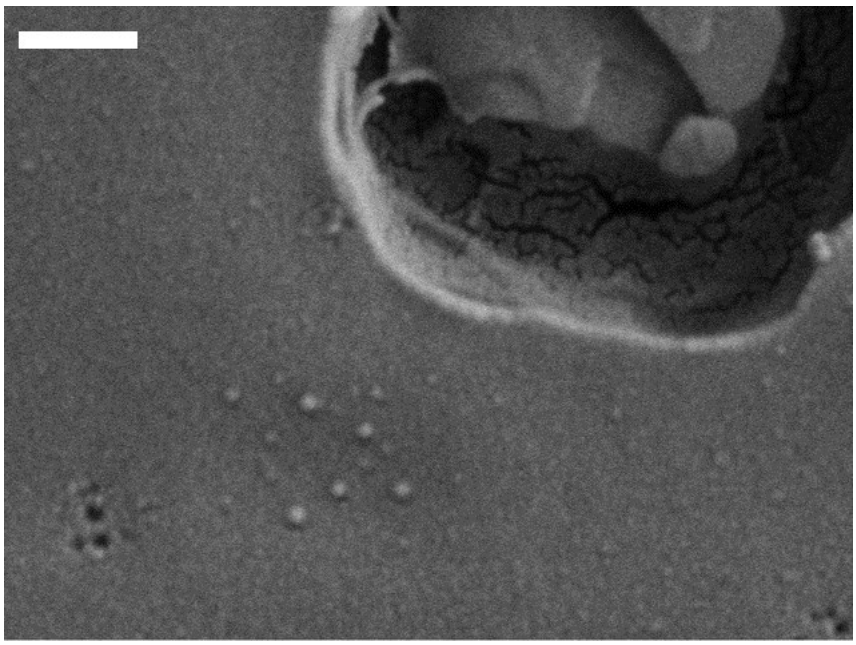

Figure S 2: SEM image of the dried hydrogel from a 0.1M PAA solution (M_w =5300 g/mol) at pH 7. Scale bar 200 nm.

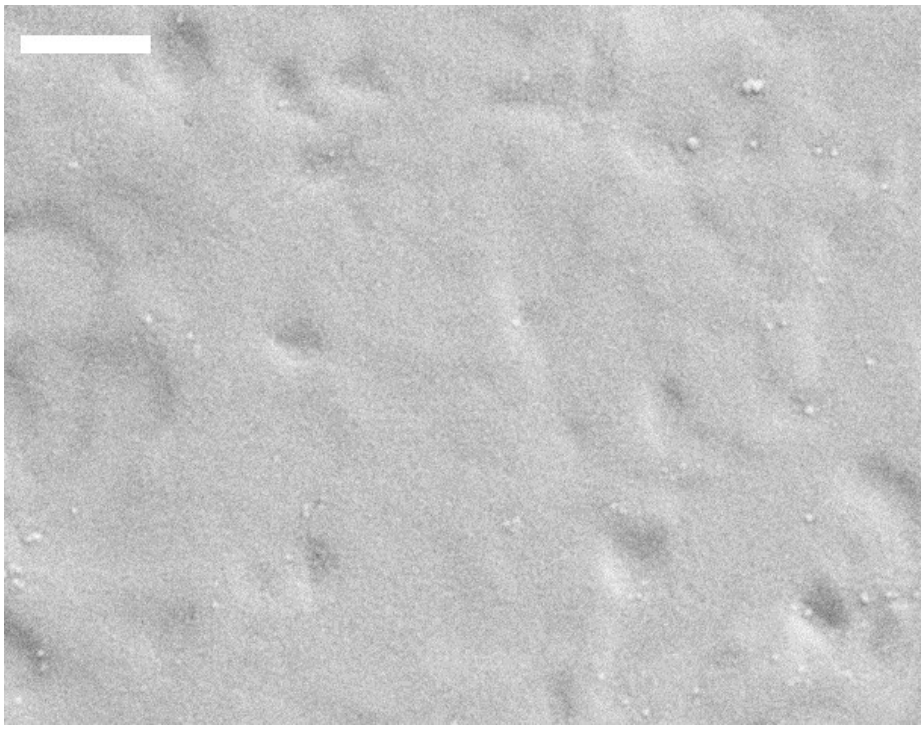

Figure S 3: SEM image of the dried hydrogel from a 0.1M PAA solution (Mw =14700 g/mol) at pH 7. Scale bar 200 nm.

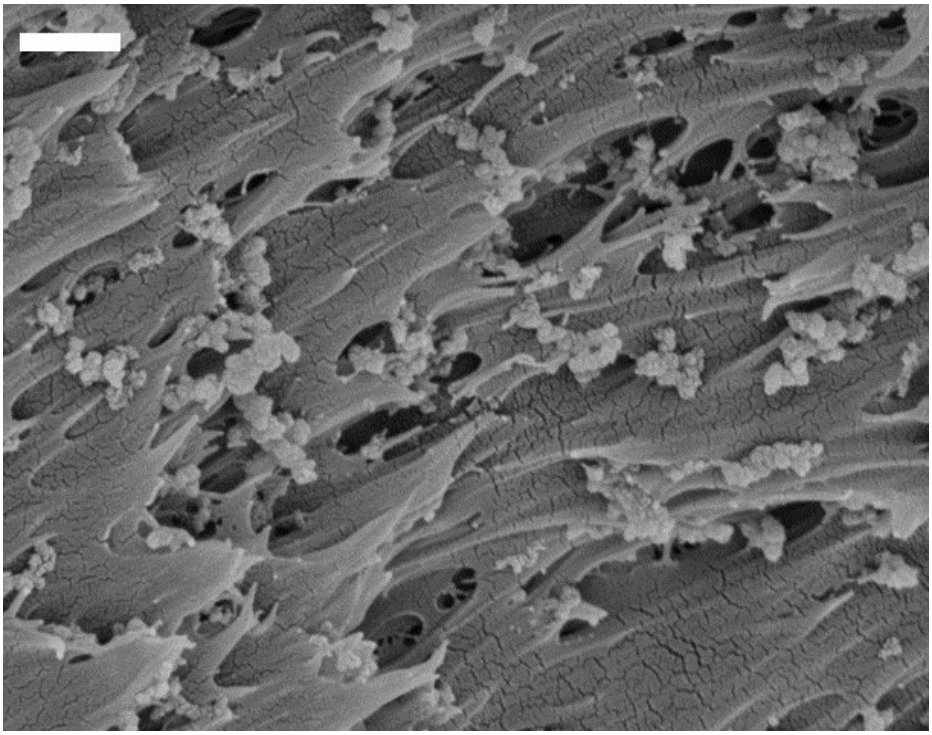

Figure S 4: SEM image of the dried hydrogel from a 0.1M PAA solution (Mw =49200 g/mol) at pH 7. Scale bar 400 nm.

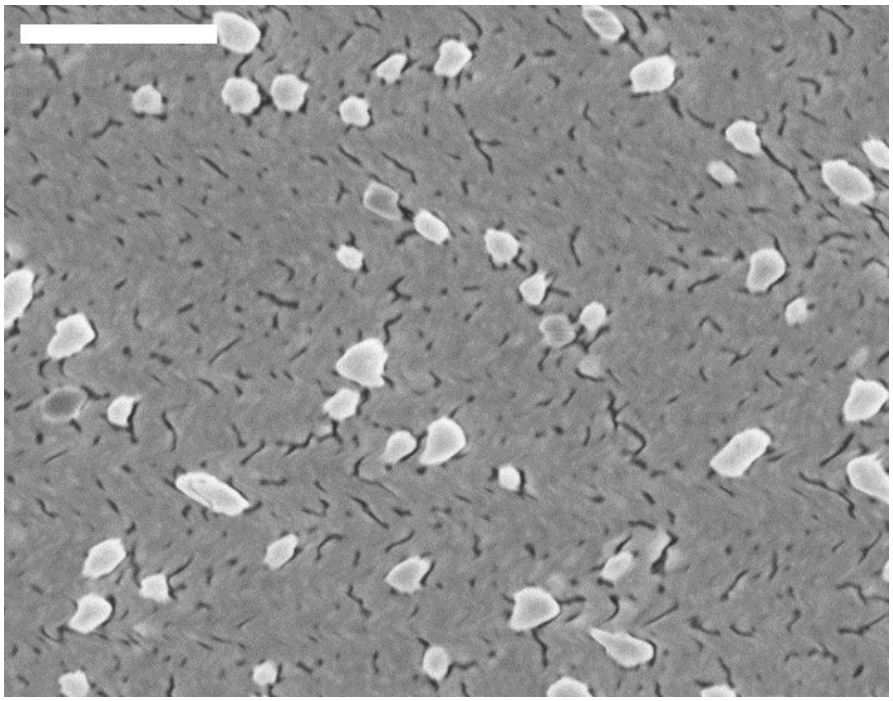

Figure S 5: SEM image of the dried hydrogel from a 0.1M PAA solution (Mw =101000 g/mol) at pH 7. Scale bar 400 nm.

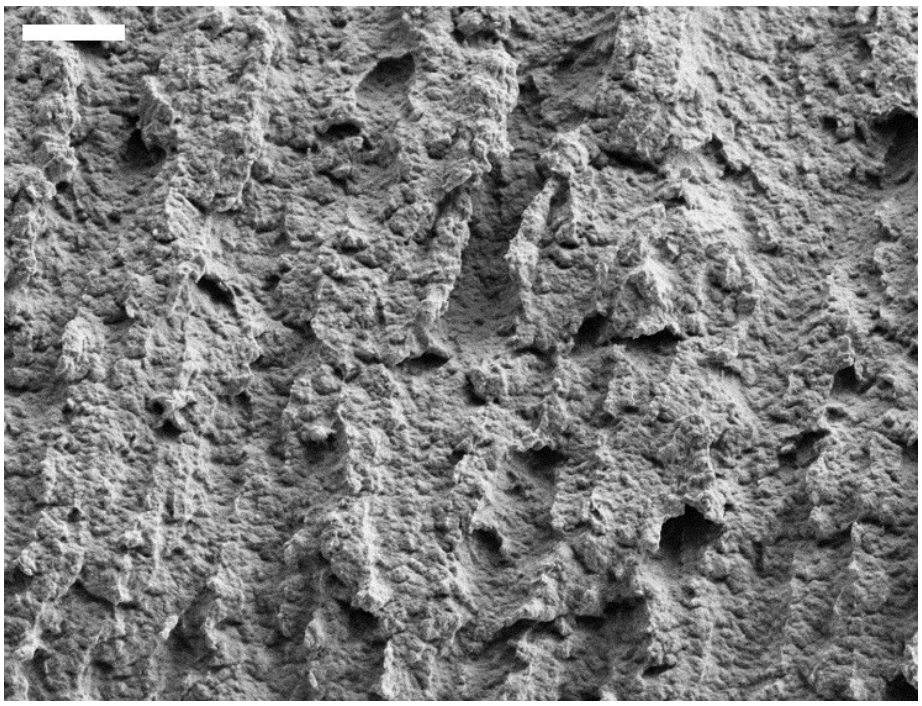

Figure S 6: SEM image of the dried hydrogel from a 0.1M PAA solution (Mw =5300 g/mol) at pH 10. Scale bar 2µm.

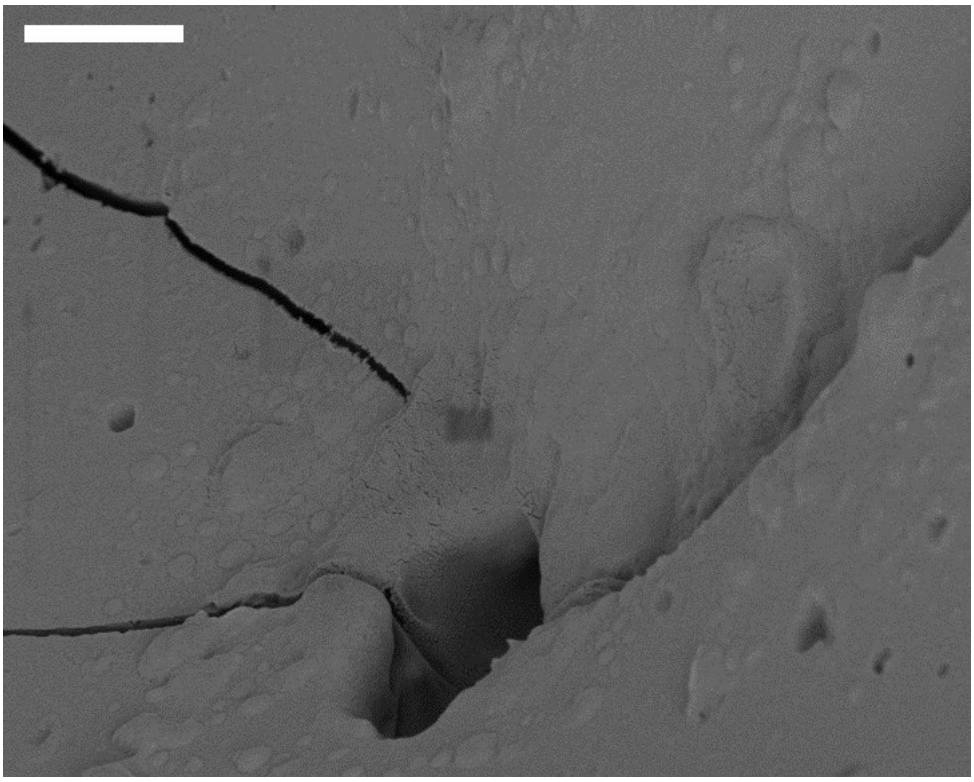

Figure S 7: SEM image of the dried hydrogel from a 0.1M PAA solution (Mw =7920 g/mol) at pH 10. Scale bar 2µm.

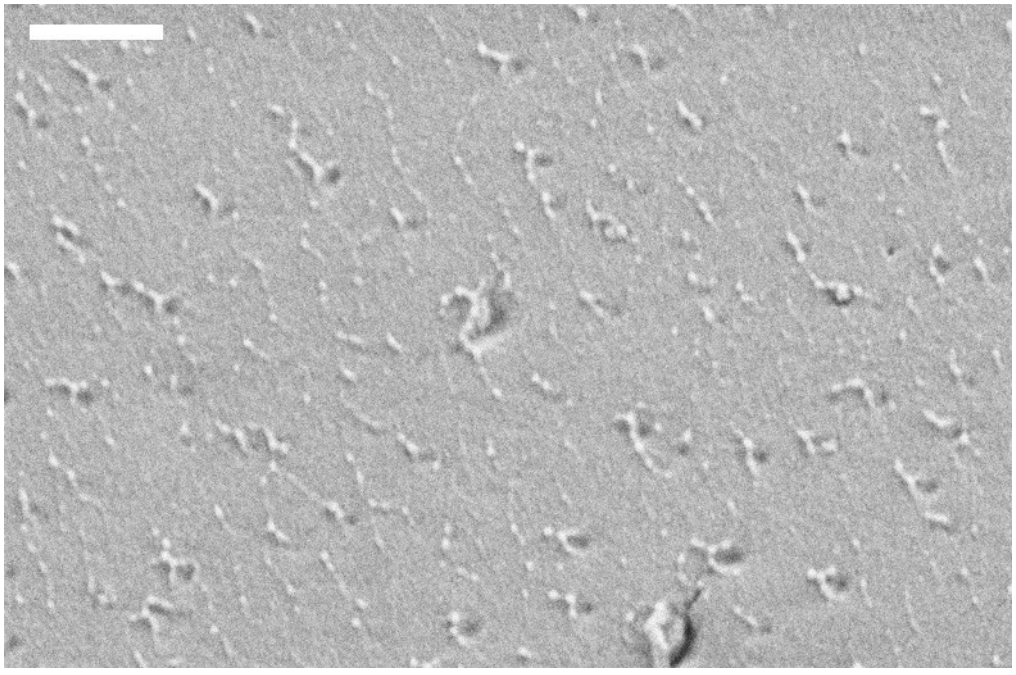

Figure S 8: SEM image of the dried hydrogel from a 0.1M PAA solution (Mw =47200 g/mol) at pH 10. Scale bar 400 nm.

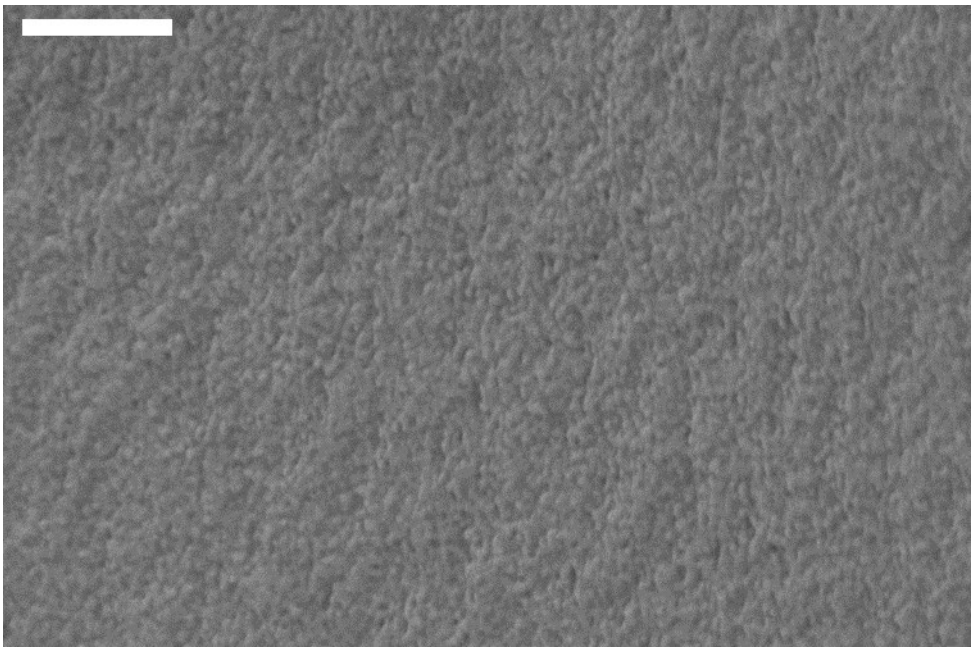

Figure S 9: SEM image of the dried hydrogel from a 0.1M PAA solution (Mw =101000 g/mol) at pH 10. Scale bar 400 nm.

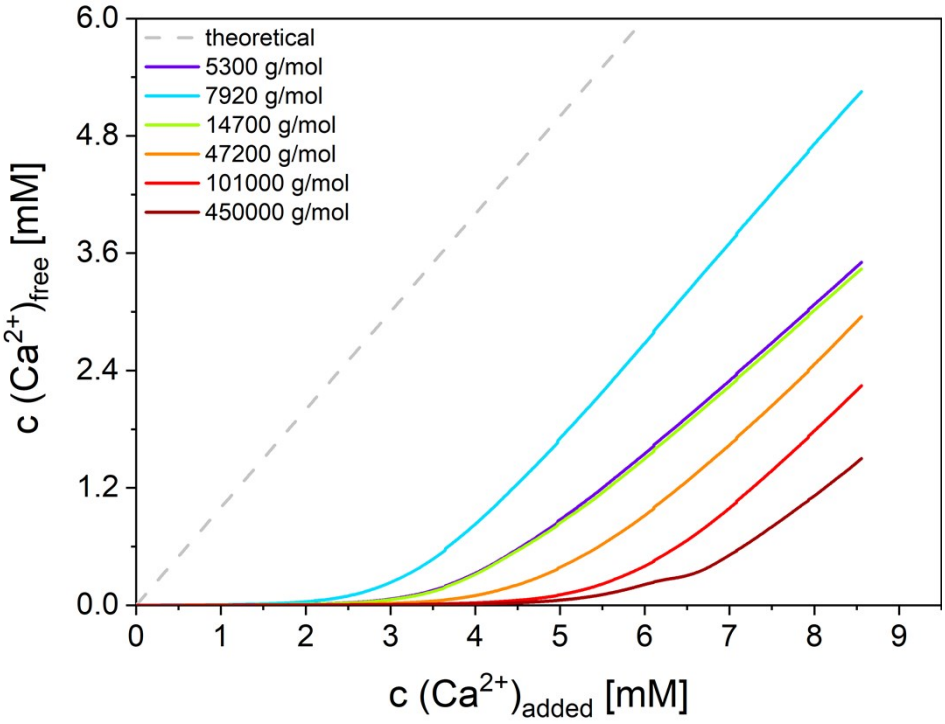

Figure S 10: Free and added Ca^{2+} from the titration data for an initial PAA concentration of 20 mM and pH value of 7 for 6 molecular weights.

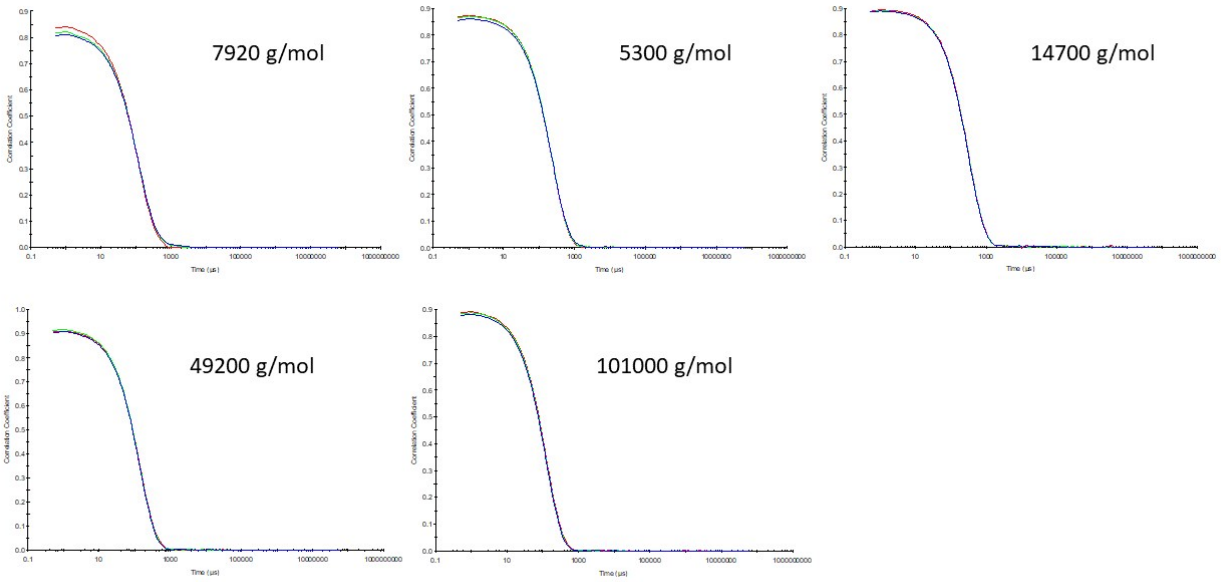

Figure S 11: Autocorrelation functions of the DLS measurements at different time points during the titration.

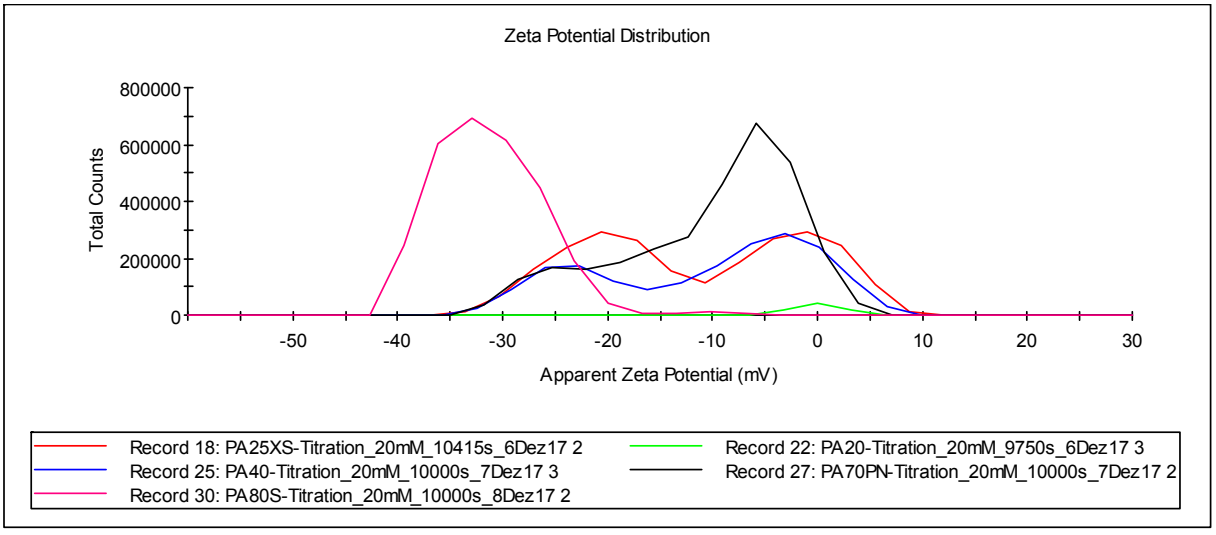

Figure S 12: Zeta-Potential measurement of the titration solution after the titration finished.

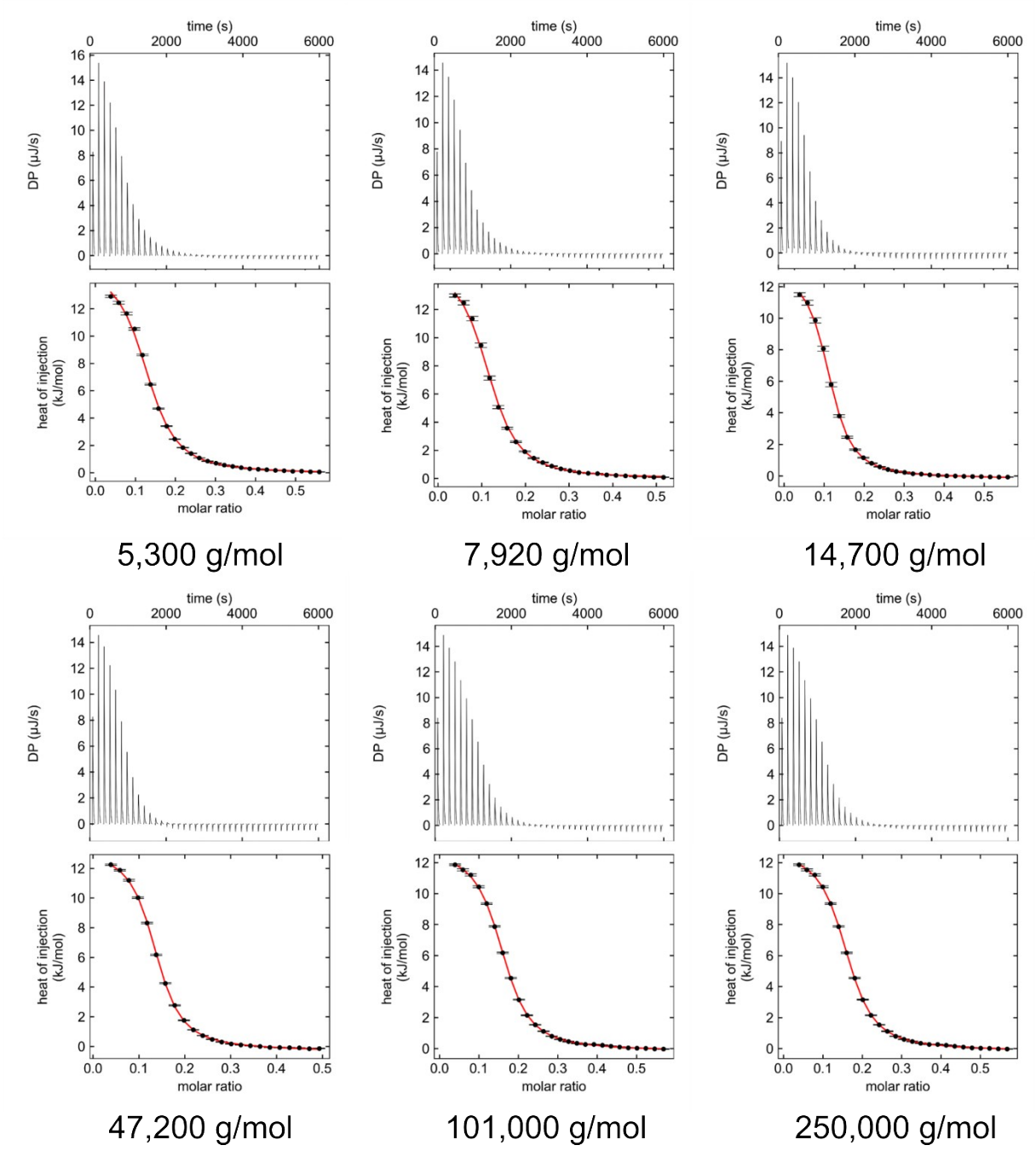

Figure S 13: Raw data and integrated, fitted heat of injection from the ITC measurement with a 5 mM PAA and a molar PAA:$CaCl_2$ ratio of 4:3 at pH 7.

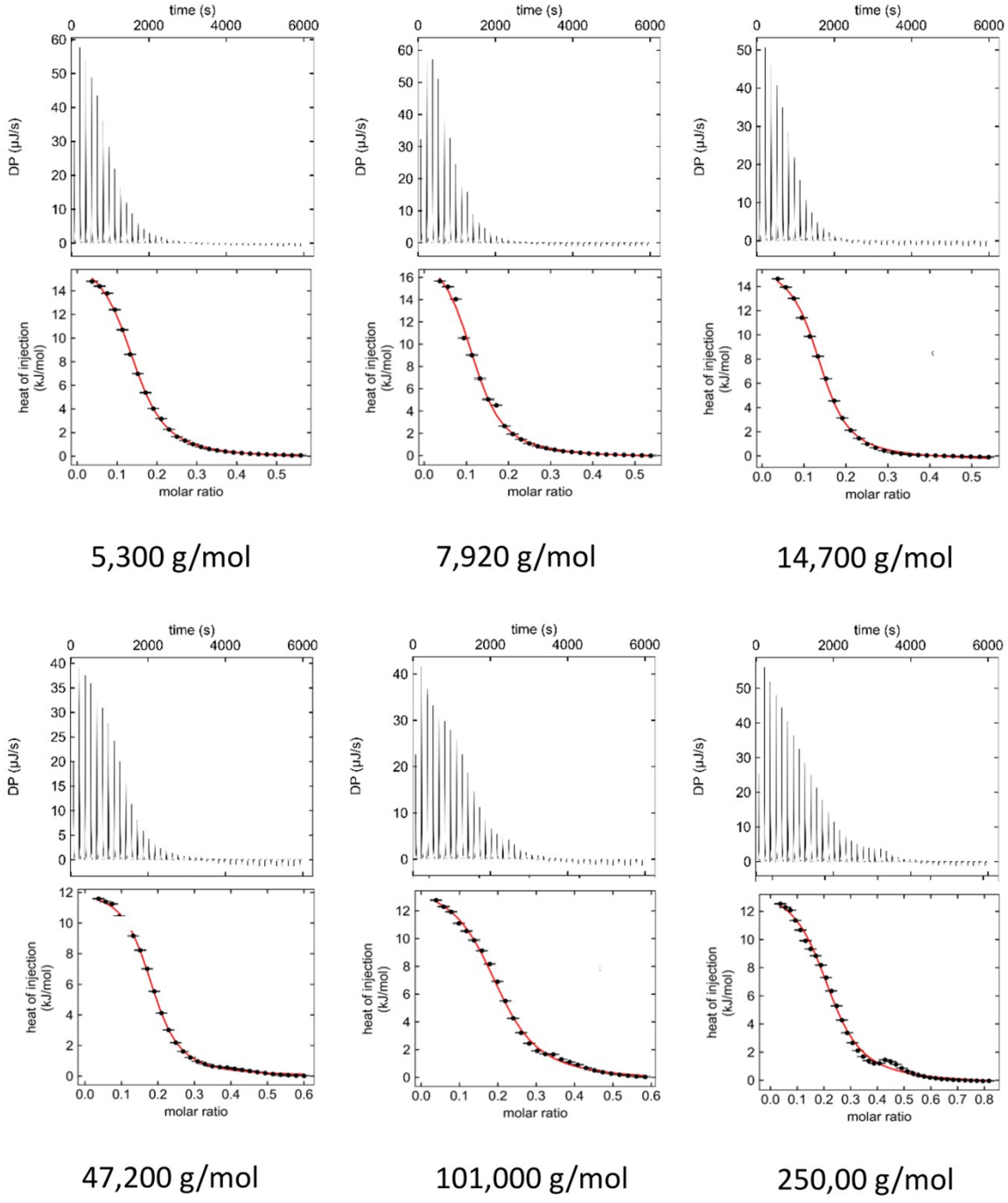

Figure S 14: Raw data and integrated, fitted heat of injection from the ITC measurement with a 10 mM PAA and a molar PAA:CaCl2 ratio of 4:3 at pH 7.

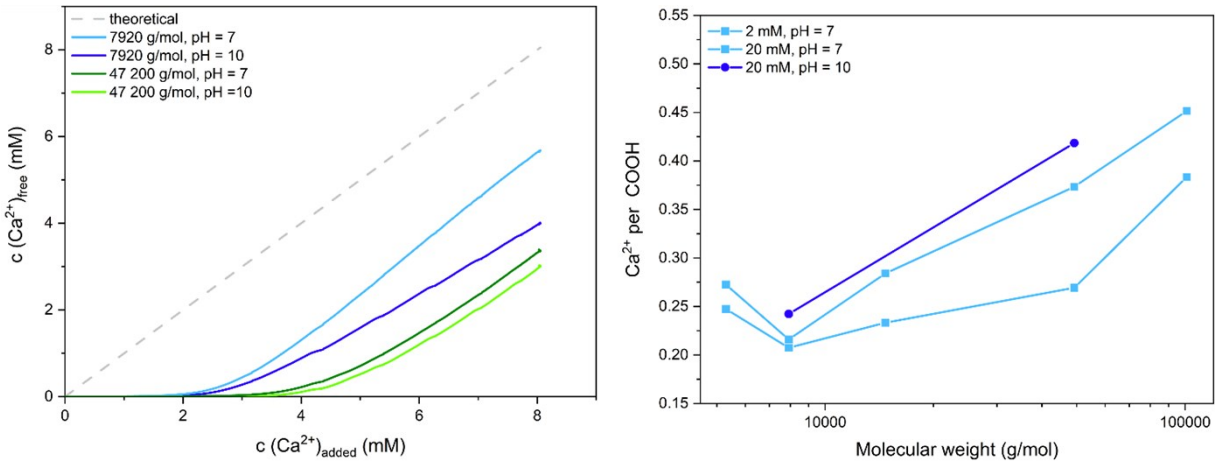

Figure S 15: Free and added Ca^{2+} from the titration data for an initial PAA concentration of 20 mM and pH values of 7 and 10 for two molecular weights(left). Calculated amount of adsorbed Ca^{2+} from the titration experiments with 20 mM and 2 mM solutions at pH 7 and 10 (right).

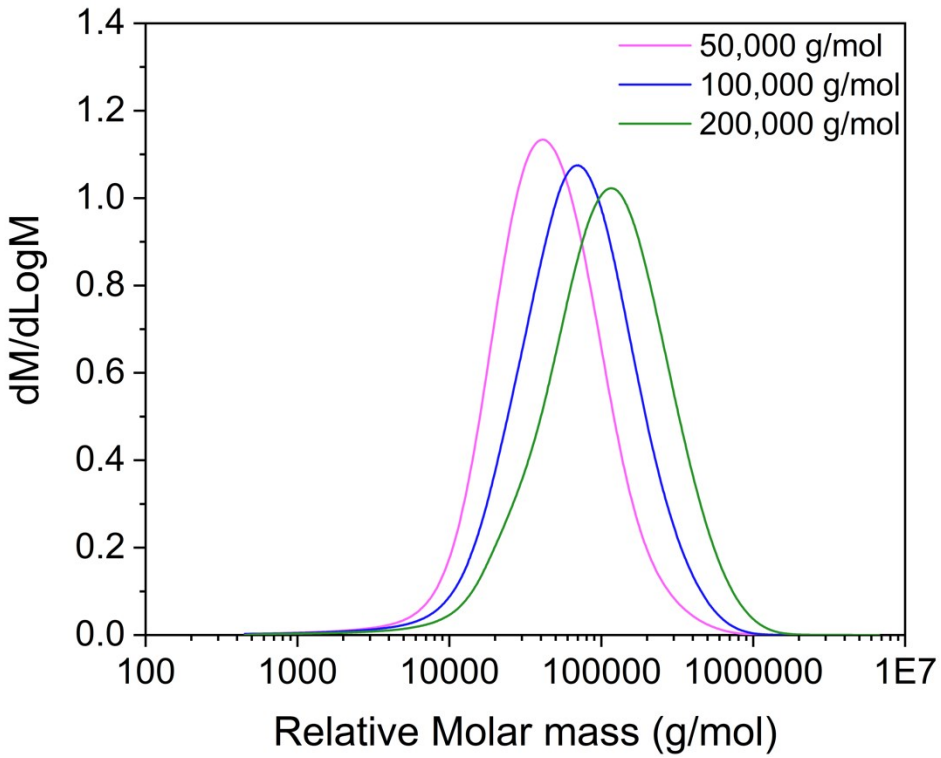

Figure S 16: GPC data of the used polymer standards with three different molecular weights.

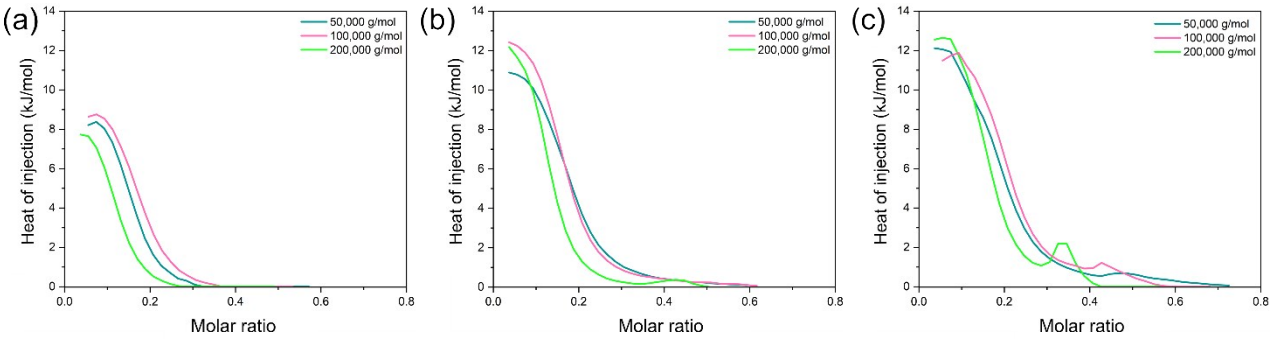

Figure S 17: Raw data and integrated, fitted heat of injection from the ITC measurement with a 2 mM PAA solution (a), a 5 mM PAA solution (b) and a 10 mM PAA solution (c) from PAA standards of three different molecular weights and a molar PAA:$CaCl_2$ ratio of 4:3 and pH 7.

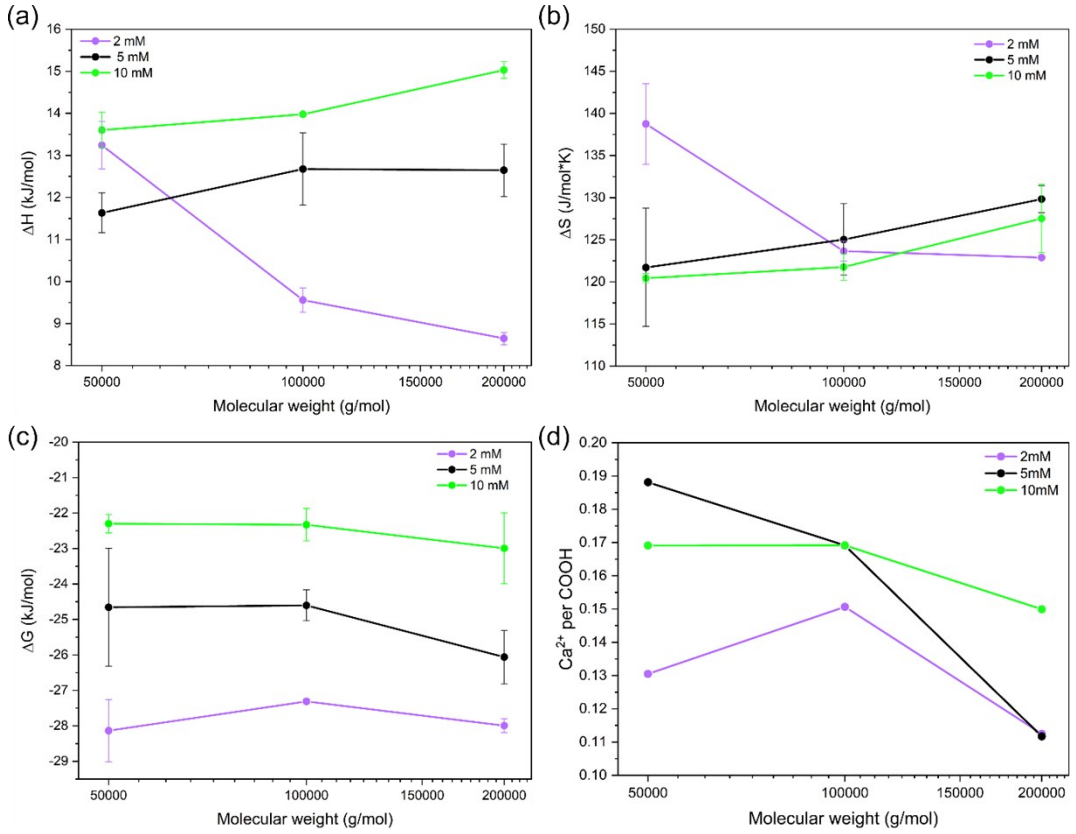

Figure S 18: Calculated thermodynamic parameters, change in enthalpy (a), change in entropy (b), change in Gibbs free energy (c) and Ca^{2+} intake (d) from PAA standards of three different molecular weights and a molar PAA:$CaCl_2$ ratio of 4:3 and pH 7.