Tuning the properties of hydrogels made from poly(acrylic acid) and calcium salts

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Hydrogels consisting of poly(acrylic acid) (PAA) and calcium ions are a promising class of materials with shapeable, stretchable and self-healing behaviour originating from the reversible and dynamic nature of the electrostatic and hydrogen bonds in the structure. In the dry state, such materials – referred to as “mineral plastics” – can be transparent, hard and flame-resistant, while addition of water will result in rehydration and complete recovery of the initial gel-like state. These desirable characteristics strongly depend on the molar mass of the used type of PAA and the experimental conditions at which the hydrogels are prepared. In this work, we show how the macroscopic properties of the materials can be adjusted by controlling the initial concentration of dissolved PAA and/or its molecular weight, and how rheological measurements can be used to monitor the resulting physical properties. Furthermore, we have employed isothermal titration calorimetry (ITC) to investigate thermodynamic aspects of the hydrogel formation to gain a better understanding of the underlying mechanism(s). Our results reveal that, and explain why, PAA molar masses between 50 and 100 kDa are particularly suitable for the formation of hydrogels with optimized properties, thus establishing a rational basis for targeted design of such materials with tailor-made characteristics.

Introduction

In recent years, a growing demand for smarter and more sustainable materials has led to a shift in research away from passive structures towards more dynamic systems that can adapt their structure and properties to external stimuli.\textsuperscript{1–5} These materials are able to perform mechanical work or heal themselves through reversible chemical bonds.\textsuperscript{1,6–11} One of the most prominent material classes showing this behavior are hydrogels, i.e. three-dimensional swollen polymeric networks that are insoluble, but interpenetrated by water.\textsuperscript{6,11–18} Due to interesting features such as sensitivity to the environment and mechanical properties similar to both fluids and solids, hydrogels have made their way into numerous applications in the pharmaceutical and biomedical sectors as well as other industries.\textsuperscript{3,4,11–13,16,19–21}

Various hydrogels with different compositions have been reported in the literature, for example alginate chains cross-linked by multivalent cations or block-co-polymers.\textsuperscript{22–24} In a recent publication, we presented a new type of hydrogel – a so-called “mineral plastic hydrogel” – which consists of poly(acrylic acid) chains cross-linked by Ca\textsuperscript{2+} ions and CaCO\textsubscript{3} nanoparticles.\textsuperscript{25} The synthesis of this material is exceptionally simple and just requires two aqueous solutions (typically CaCl\textsubscript{2}(aq) and Na\textsubscript{2}CO\textsubscript{3} + PAA (aq)) to be mixed under ambient conditions. The resulting hydrogel was found to be self-healing, stretchable and shapeable, and could be molded into hard, transparent and non-flammable films. In addition, the gel can be reversibly de- and rehydrated by removal and addition of water respectively.\textsuperscript{25} In the gel state, “mineral plastic hydrogels” also proved to be strong adhesives – another advantageous property in view of potential applications such as wet gluing.\textsuperscript{26}

However, almost all of the observations described above were made for PAA with a fixed molecular weight (MW) of ca. 100 kDa variations (except for the adhesive properties, which were determined for a PAA with MW = 250 000 g mol\textsuperscript{-1}), and it was not assessed whether variations of MW or other experimental parameters could expand the spectrum of attractive material properties accessible via this straightforward approach.\textsuperscript{25} However, it is known that transparent films prepared with a low-MW poly(acrylic acid) (2000 g mol\textsuperscript{-1}) could not reversibly be transformed to the gel anymore after dehydration.\textsuperscript{24}
More recent studies showed that hydrogels with very similar properties can also be obtained in the absence of any carbonates, i.e. when Na₂CO₃ is replaced by a carbonate-free base like NaOH. These findings led to the conclusion that, in this gel, the poly(acrylic acid) chains are cross-linked solely by Ca²⁺ ions. Earlier work had already demonstrated that the amount of Ca²⁺ bound by poly(acrylic acid) can be successfully determined via potentiometric titration using calcium ion-selective electrodes (Ca²⁺-ISEs). Moreover, isothermal titration calorimetry proved to be a valuable tool to investigate the ion binding behavior of different polymers. For PAA, binding of Ca²⁺ ions was indeed found to be endothermic with decreasing enthalpy for growing PAA molecular weight. The driving force for ion complexation thus is of entropic nature, namely the release of ordered water molecules from the hydration shell of Ca²⁺ ions and the poly(acrylic acid) chains, as also observed during ion association in dilute CaCO₃ solutions.

Herein we present a systematic study of the properties of hydrogels formed upon interactions of poly(acrylic acid) chains and Ca²⁺ ions at different solution conditions and for PAA types with average molecular weights ranging from 5 to 450 kDa. The obtained hydrogels were characterized by rheological measurements, ion-selective potentiometric titration and isothermal titration calorimetry. The combined results give detailed insights into the formation mechanism of the hydrogels and their variability in terms of property profiles.

**Experimental**

Different grades of poly(acrylic acid) were obtained from Sigma-Aldrich (\(M_w \sim 100\,000\, \text{g}\,\text{mol}^{-1}\), 35 wt% in H₂O, and \(M_w \sim 450\,000\, \text{g}\,\text{mol}^{-1}\)) and BASF SE (\(M_w \sim 2500\, \text{g}\,\text{mol}^{-1}\) with PDI = 5.8, \(M_w \sim 5000\, \text{g}\,\text{mol}^{-1}\) with PDI = 2.7, \(M_w \sim 15\,000\, \text{g}\,\text{mol}^{-1}\) with PDI = 4.0, \(M_w \sim 50\,000\, \text{g}\,\text{mol}^{-1}\) with PDI = 5.4, \(M_w \sim 100\,000\, \text{g}\,\text{mol}^{-1}\) with PDI = 6.6, \(M_w \sim 250\,000\, \text{g}\,\text{mol}^{-1}\) with PDI = 7.2). CaCl₂ (>95%) was purchased from Fisher Scientific. The poly(acrylic acid) sodium salt standards with molecular weights of 50\,000 \text{g} \text{mol}^{-1} (PDI = 1.8), 100\,000 \text{g} \text{mol}^{-1} (PDI = 1.74) and 200\,000 \text{g} \text{mol}^{-1} (PDI = 1.6) were obtained from Agilent. The acrylic acid/maleic acid copolymers (50\,000 and 70\,000 \text{g} \text{mol}^{-1}) were provided by BASF SE. All chemicals were diluted and the glassware was cleaned with water of MilliQ quality (18.2 MΩ cm). The pH values were adjusted with hydrochloric acid (Merck, 0.1 M and 1 M) and sodium hydroxide (Merck, 0.1 M and 1 M).

The hydrogels were synthesized by slow addition of an aqueous CaCl₂ solution into an equally concentrated aqueous PAA solution with a preset pH value (adjusted by HCl/NaOH) under vigorous stirring at room temperature (note that all syntheses were conducted in the presence of added carbonate species, although some carbonate may have entered the systems from atmospheric CO₂, especially at higher pH). The pH of the solution changed during the synthesis due to the addition of CaCl₂. The turbidity of the solution increased with the addition of CaCl₂ and vanished after the addition had been completed and the solution had been stirred for another 20 minutes. The PAA solution needs to be oversaturated with CaCl₂ for a successful gel formation. The supernatant was removed and the remaining hydrogel was washed three times with MilliQ water. The solution concentration, (0.1 M, 0.5 M, 1 M; always equal for PAA and CaCl₂), the pH value (7, 10) as well as the molecular weight of the PAA (5300 \text{g} \text{mol}^{-1}, 7920 \text{g} \text{mol}^{-1}, 14\,700 \text{g} \text{mol}^{-1}, 49\,200 \text{g} \text{mol}^{-1}, 101\,000 \text{g} \text{mol}^{-1}, 450\,000 \text{g} \text{mol}^{-1}) were varied systematically.

Scanning electron microscopy (SEM) images were obtained using a Zeiss Gemini 500 equipped with an Oxford Ultim Max 100 EDX detector.

The rheology measurements were performed on a Thermo Scientific HAAKE MARS modular advanced rheometer using parallel-plate geometry at 25 °C in oscillation mode with a fixed strain at 0.2%. One plate was static while the other one oscillated and thus exerted a force on the gel sample. The angular frequencies were varied from 0.01 to 10 Hz. The surface of the hydrogel was dried using a filter paper prior to the measurement. The first and last data points were left out for better evaluation of the data.

GPC measurements of the initial PAA solutions and the supernatant after gel formation were performed using a hydroxylated polymethacrylate column coupled with refractive index (RI) and UV detectors (at 260 nm). The analyses were performed at 35 °C using a 0.01 M phosphate buffer as mobilephase at a flow rate of 0.8 \text{mL} \text{min}^{-1}. The injection volume was 100 \text{µL}. The concentration of the neat PAA solution was 10 mg \text{mL}^{-1}. The instrument was calibrated using Na-PAA standards prior to the measurement.

For the Ca²⁺ selective potentiometric titration a typical set-up from Metrohm was used consisting of a titrator (titrand 905 or 836) and two dosing units (dosino 800) with anti-diffusion tips allowing exact dosing up to 0.2 µL. A Faraday cage is installed for all our titration set-ups to ensure a stable system voltage. The system was controlled over the standard titration software tiamo 2.3. During the experiment the pH value was monitored with a flat membrane electrode (Metrohm, 6.0256.100), while the amount of free Ca²⁺ was measured with an ion selective electrode (Metrohm, polymer membrane electrode Ca, 6.0508.110). The pH electrode was frequently calibrated with standardized buffer solutions from Mettler-Toledo. For measurement, 15 mL of PAA solution with different concentrations were placed in a titration vessel and after adjustment of the pH, 10 mL equally concentrated CaCl₂ solution was added at a rate of 0.1 mL min⁻¹. The pH value was held constant during the titration by automated counter titration with NaOH. In order to be able to quantify the complexation of Ca²⁺ ions by the different polymers, a calibration experiment was conducted by adding CaCl₂ solution in water under the same conditions.

For the determination of particle sizes during the titration, DLS measurements were performed with a Zetasizer Nano from Malvern. Data was evaluated with the corresponding Zetasizer Nano software v3.30. The ζ-potential measurements were performed with the same instrument of the supernatant after the titration experiments.
ITC measurements were carried out on a Micorcal iTC200 system from Malvern. The data was analyzed using the programs NITPIC (The University of Texas Southwestern Medical Centre) and ITCgy (sedphat) and plotted with GUSSI (The University of Texas Southwestern Medical Centre) and Origin 2018. The experiments were carried out for each polymer in triplicates. The pH values were adjusted prior to the measurements and 27% in respect to the molar amount of PAA of a buffer solution (potassium dihydrogen phosphate/di-sodium hydrogen phosphate) was added. The PAA solution (with adjusted pH and added buffer) was placed in the reaction vessel and CaCl₂ solution was added (as 1 μL injections with a spacing between the injections of 150 s) under stirring (1000 rpm). The measurements were performed at 25 °C with a reference power of 6 μcal s⁻¹. A reference measurement of CaCl₂ into acrylic acid at the required conditions was subtracted from the measurement data prior to further evaluation. The thermodynamic parameters \( \Delta H, \Delta S, \Delta G \) and the stoichiometry of Ca²⁺ binding to the carboxylic acid groups were calculated from the fitted data points with a model of simple hetero association as shown in Fig. S1 (ESI†).

**Results and discussion**

The properties of the synthesized hydrogels differed significantly depending on the synthesis conditions. An overview of all tested conditions and the resulting gel properties are visualized in Fig. 1.

Lower molecular-weight PAAs tend to form less viscous gels that are stickier towards external surfaces, which allows fast self-healing but limits shapeability. For PAA types with MWs of 47 200 and 101 000 g mol⁻¹, shapeable, stretchable and self-healing hydrogels were obtained (much like what was reported for “mineral plastic hydrogels” in previous work), whereas gels prepared with higher molecular weights are less stretchable and lose their self-healing properties completely (Fig. 1).

Additionally to the macroscopic properties, the morphology of the hydrogels was investigated via SEM measurements (Fig. S2–S9, ESI†).

These trends in the macroscopic appearance of the hydrogels can be quantified via frequency dependent rheological characterization, giving access to the storage \( G' \) and loss modulus \( G'' \) of the materials. The relative magnitude values of the two moduli indicate if the gels display a more liquid-like \( (G' < G'') \) or solid-like \( (G' > G'') \) behavior. Fig. 2 shows the storage and loss moduli for the Ca²⁺/PAA hydrogels synthesized at pH 7 using the following molecular weights and concentrations of PAA and Ca²⁺ solution: (a) 7920 g mol⁻¹, 0.5 M, (b) 47 200 g mol⁻¹, 0.5 M, (c) 101 000 g mol⁻¹, 1 M, and (d) 450 000 g mol⁻¹, 0.1 M. The insets show pictures of the gels to visualize their macroscopic appearance.

The rheology results agree well with properties observed visually for the different hydrogels. Less viscous gels obtained with lower molecular weights of PAA show predominantly liquid-like behavior (Fig. 2a and b) while the rheological data of the hydrogel formed with 450 kDa confirms a predominantly solid-like character for this kind of material (Fig. 2d). The hydrogel based on PAA with an intermediate molecular weight of about 100 kDa shows similar real and imaginary parts of the complex shear modulus (Fig. 2c) as expected for a “good” hydrogel. Indeed this gel displays the “best” (i.e. most desirable) macroscopic properties, it can easily be shaped into a fixed form that still maintains the ability to stretch and self-heal.

To gain further information on the composition of the obtained hydrogels, the supernatant solutions remaining after completed gel formation were investigated using gel permeation chromatography (GPC) and compared to the data collected from the same polymer solutions prior to reaction with calcium chloride. The results (summarized in Fig. 3) reveal that for all
tested conditions the higher molecular weight fractions of the original MW distribution are preferentially incorporated into the hydrogels. Indeed, within the detection limits of GPC only polymers with short chain lengths (ranging roughly from 500 to 10 000 g mol\(^{-1}\)) remain in the supernatant after complexation with calcium ions. Moreover, the fraction of longer polymer chains remaining in the liquid phase after hydrogel formation is lower at higher pH (cf. Table 1), suggesting stronger association with calcium ions for PAA chains with higher charge densities (note that the ionic strength increases only about 50 m\(\text{mol L}^{-1}\) at pH 10 compared to the conditions at pH 7, while the degree of PAA protonation decreases from 0.4% at pH 7 to 0.0004% at pH 10).

Interestingly, the molecular weight distributions and polydispersities of the polymers in the supernatant after gel formation (Fig. 3b and c) do not show significant differences between the distinct PAA types despite their different initial molecular weights. Generally, shorter polymer chains are expected to form less cross-links in a hydrogel than PAAs with higher MW, resulting in a viscous and non-shapeable gel body. This notion is in line with the fact that PAAs with lower MW yield overall less hydrogel (cf. Table 1), due to the relatively low amounts of longer chains available in the original MW distribution. The higher fraction of longer chains in the distribution of high MW PAAs allows more cross-links to be formed in the presence of calcium ions, yielding more hydrogel-like materials with more viscous and increasingly stiff networks. To confirm these assumptions the average MW between cross-links was calculated using the Flory–Rehner equation (ESI\(\dagger\)). The calculated molecular weights indicate a higher cross-link density with increasing MW of the PAA. The type with the lowest molecular weight (5300 g mol\(^{-1}\)) forms one cross-link about every fifth monomer unit, yielding a cross-linking density of about 20%. In turn, the PAA with a MW of 101 kDa is able to form a cross-link every 1.3rd monomer unit, which corresponds to a cross-link density of about 75%.

The degree of calcium complexation by the different PAA grades can be monitored via potentiometric titration. Fig. 4a shows the amount of Ca\(^{2+}\) ions bound per carboxylate group in the polymer at pH 7, determined from titration experiments that were performed as described in detail elsewhere. The results indicate that PAAs with higher molecular weights bind larger relative fractions of Ca\(^{2+}\) ions per COOH group. For low molar masses (up to 15 kDa), about 0.2–0.3 Ca\(^{2+}\) are bound per COO\(^{-}\) in line with literature, while the Ca\(^{2+}\)/COO\(^{-}\) ratio increases up to 0.5 for the high MW grade (450 Da), which

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**Table 1** Results from GPC measurements of PAA solutions before and after hydrogel formation as well as yields of the gel synthesis

<table>
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<tr>
<th>PAA</th>
<th>(M_n) [g mol(^{-1})]</th>
<th>(M_w) [g mol(^{-1})]</th>
<th>PDI</th>
<th>(M_n) supernatant</th>
<th>(M_w) supernatant</th>
<th>PDI supernatant</th>
<th>Polymer concentration supernatant [mg mL(^{-1})]</th>
<th>Amount of gel [mg]</th>
<th>Average MW between cross-links [g mol(^{-1})]</th>
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<td>188/1700</td>
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<td>1120/1030</td>
<td>0.72/0.76</td>
<td>532/368</td>
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<tr>
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<td>5.8</td>
<td>1880/1700</td>
<td>4.0</td>
<td>1900/1770</td>
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<td>1290/1140</td>
<td>0.72/0.76</td>
<td>978/996</td>
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<td>3650</td>
<td>4.0</td>
<td>2190/1770</td>
<td>5.4</td>
<td>1260/992</td>
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<td>0.72/0.76</td>
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<tr>
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<td>15300</td>
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<td>95/96</td>
<td>0.72/0.76</td>
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**Fig. 3** GPC data of the used polymers (a) in 0.1 M solutions prior to gel formation (before CaCl\(_2\) addition), and in the supernatant after hydrogel formation at pH (b) 7 and (c) 10.

**Fig. 4** Results of potentiometric titration experiments (20 mM solutions, pH 7) on the binding of calcium ions by PAA grades of different molecular weight. (a) Calculated amount of Ca\(^{2+}\) bound per carboxylate group in PAA chains of different length as indicated. (b) Sizes of colloidal species determined from DLS measurements at different time points during the titration. The corresponding potentiometric titration measurements and autocorrelation functions of are shown in Fig. S10 and S11 in the ESI\(\dagger\).
corresponds to stoichiometric binding. Such high degrees of calcium association with PAA have so far only been observed by analyses based on atomic absorption or emission spectroscopy.39,40

For individual polymers (i.e. no crosslinking) stoichiometric binding is statistically and thermodynamically improbable because each pair of neighboring COO groups would have to bind one Ca2+ ion. Therefore, the found ratio of 0.5 indicates that some of the bound Ca2+ can be trapped in nanogel precursor structures (possibly together with Cl− for charge neutrality when high-MW PAA grades are used). This may be promoted by aggregation processes occurring when cross-linking sets in, while the coils simultaneously are still collapsing.41

DLS measurements performed on samples drawn at different points during the titration experiment show the formation of large colloidal entities (i.e. nanogels), initially about 100 nm in diameter, irrespective of the polymer molecular weight (Fig. 4b). Over time, the scattering species grow to bigger sizes for the lower molecular weights (5–15 kDa), while slower growth occurs for the higher molecular weights (50–450 kDa). The smallest particles are observed for the 47 kDa PAA. This counter-intuitive behavior might be caused by stronger intermolecular interactions for shorter, stiffer chains and an overall lower amount of cross-links. Due to the intermolecular nature of the cross-linking the species are probably solvent filled and therefore bigger. More pronounced cross-linking, i.e. dominant intramolecular interactions as expected for longer chains, will in turn result in more compact networks and therefore smaller nanogels entities.41

Another factor might be the surface charge of the nanogel colloids. The higher the charge, the stronger the repulsion and thus the smaller the ultimate size. At low MW, moderate amounts of Ca2+ are bound, which catalyzes crosslinking. At high MW, the large amount of bound Ca2+ reverses the charge and may lead to repulsions and hence smaller structures. However, ζ-potential measurements did not show a trend so that this point remains speculative (Fig. S12, ESI†).

Finally, we have performed ITC measurements to investigate the thermodynamics of hydrogel formation and, based thereon, obtain deeper insights into the underlying mechanism and parameters governing the Ca2+/PAA binding process. The results for 5 mM PAA solutions with an AA/Ca2+ ratio of 4:3 at pH 7 are summarized in Fig. 5. There are three different models to describe the association of Ca2+ to the AA units in the system. A hetero association model where one Ca2+ ion binds to one AA unit, a model of two symmetric sites of the Ca2+ ion or a model of two unsymmetrical sites of the Ca2+ ion. The first two models fit the ITC data sufficiently and give similar results for the thermodynamic parameters (ln(K) = 10.1 for the hetero association and ln(K) = 11.2 for the symmetric sites model). The discussed data in the following section is fitted with the hetero association model. Fitting the raw data (heats of injection: see Fig. S13, ESI†) yields four parameters characterizing the association between calcium ions and PAA polyelectrolyte chains: the enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) of the reaction, as well as the corresponding stoichiometry (Ca2+ bound per carboxylate unit). For all investigated PAA molecular weights, the process of calcium association (and hydrogel formation) is clearly endothermic (ΔH > 0), with absolute values for the change in enthalpy being in good agreement with results from previous studies.33,42 This endothermic Ca2+ association can mainly be attributed to the loss of Ca2+/H2O as well as COO−/H2O interactions upon Ca2+ coordination to COO−, which over-compensates the enthalpy gain upon binding of Ca2+ to COO−.

Indeed, there seems to be a maximum in ΔH at a molecular weight of about 50 kDa, while for longer PAA chains the enthalpy change decreases again. The increase of ΔH from the low-(5–15 kDa) to medium-MW (50 kDa) PAA grades can be explained by the increasing amount of bound Ca2+ per carboxylate unit (cf. Fig. 5a and d). The decrease in ΔH at still higher molecular weight might be caused by a change of the type of binding or a different kind of formed species – for example a shift from a regime dominated by intermolecular interactions to one where intramolecular interactions prevail (or vice versa). Another potential reason is that the hydration sphere around calcium-bearing carboxylate units changes (i.e. its balance with the uncomplexed state becomes less unfavorable) for longer chains and/or higher degrees of calcium association. The change in entropy upon Ca2+/PAA association shows very similar trends as the enthalpy, with a clear maximum in ΔH at a molecular weight of about 50 kDa. In these systems the entropy balance is mainly influenced by two factors: (i) the release of hydration water upon ion binding,33 which increases the net entropy and (ii) the structural constraints imposed on the polymer chains due to complexation of and cross-linking by calcium ions, which will obviously lead to a loss in conformational entropy. Both contributions should become more pronounced as the molecular weight of the used PAA is increased. According to our ITC measurements, these two opposing factors result in ΔH and ΔS maxima centered around 50 000 g mol⁻¹. Furthermore, the Gibbs free energy (ΔG) shows a minimum at the same molecular weight, i.e. the greatest driving force for Ca2+/PAA association and hydrogel formation is observed at a molecular weight.
of 50 kDa. This trend of intermediate molecular weights showing strongest binding propensity is commensurate with the differences seen in the macroscopic properties of the hydrogels and their rheological behavior. Although there is no perfect coincidence, the minimum in Gibbs free energy parallels with the macroscopic ability of the formed hydrogel to shape, stretch and self-heal. The correlation between the minimum in ΔG (and corresponding to maxima in ΔH and ΔS) and to the macroscopic optimum in terms of rheological gel properties can be rationalized as followed: the high-molecular weight PAA shows strong Ca2+ cross-linking and thus suffers from a considerable loss in conformational entropy (“solid-like behavior”); on the other hand, the lower PAA molar masses gain only little entropy by the release of hydration water and form less cross-links (“liquid-like behavior”). Therefore, it is reasonable that the balance between these two states, where the thermodynamic driving force for gel formation is highest, corresponds to the optimum gel properties as discussed Fig. 2. Additionally, the amount of adsorbed Ca2+ could also be determined from the ITC experiments. The results (Fig. 5d) show similar trends between the different molecular weights as the titration experiments (Fig. 4a). However, the amount of bound Ca2+ is by far lower than that from the titration experiments (Fig. 4). This is likely a result of the Ca2+ addition speed, which was magnitudes lower in the ITC measurements (0.38 μL min⁻¹) than for the titration experiments (100 μL min⁻¹), this effect was already observed in other systems.39

It is worth noting that for all different applied characterization techniques (potentiometric titration, ITC and rheology), there were no systematic differences in the results when the concentrations of PAA and CaCl₂ were varied (at the same Ca2+/COO⁻ ratio) over a range of 2–20 mM in case of the titration and ITC experiments and 0.1–1 M for the rheology measurements. Therefore, the observed gel formation processes appear to be independent of concentration, at least within the investigated range. Indeed at higher concentrations (10 and 20 mM PAA) the ITC data collected for the higher molecular weights show a kink in the curve of the heat of injection (Fig. S14, ESI†). However, this is probably related to the onset of precipitation as reported for similar systems.42

However, a variation of the pH value seems to influence the process significantly as seen in the macroscopic hydrogels and the results from the potentiometric titration (Fig. S15, ESI†). Titration experiments were carried out at an initial pH value of 10. The curves at pH 10 follow a similar trend as the ones at pH 7. The pH value seems to have a bigger impact on smaller chain lengths as the curves for 7920 g mol⁻¹ differ more from each other. Therefore the differences in the macroscopic gels at the two pH values probably result from additional effects like the ionic strength or in-diffused atmospheric CO₂ in the solution at different pH values.43 Because the difference of the ionic strength between the two pH values is not significant the higher Ca2+ adsorption for higher chain lengths might result from higher amounts of enclosed Ca2+ and formation of calcium carbonate with the in-diffused CO₂ from the air. In a further set of experiments, we have studied the influence of PAA polydispersity on the gel formation process by using as three PAA standards with narrow distributions an different nominal MW (50 000, 100 000 and 200 000 g mol⁻¹). Gels could be obtained with all three polymers (at 0.1 M PAA), and their properties followed the same MW-dependent trends as the more polydisperse materials used otherwise in this study. The best “mineral plastic” hydrogel regarding transparency, stretchability, plasticity and self-healing was obtained for the molecular weight of 100 000 g mol⁻¹. Possibly, the longer chains in the distribution of the more polydisperse PAA grade 47 200 g mol⁻¹ accounts for the “good” properties of the corresponding hydrogels, making it comparable to the material obtained with the 100 kDa standard. This assumption could be verified by GPC measurements (Fig. S16, ESI†), which showed that the fraction of chain lengths above 100 000 g mol⁻¹ is lower for the analytical standard compared to the polydisperse commercial grade with an average molecular weight of about 50 000 g mol⁻¹. Again, this suggests that for successful gel formation a certain amount of long PAA chains seems to be crucial. These longer chains become incorporated into the hydrogel and probably account for the solid-like properties of the resulting viscoelastic material. In turn, the shorter chains are important for the stretching and self-healing properties (i.e. the liquid-like features), and may act as plasticizers. ITC measurements on the calcium complexation by PAA standards give similar results (Fig. S17 and S18, ESI†) as the more polydisperse ones, but the actual values (heats of injection) are slightly lower in case of the standards. This decrease might be due to a smaller amount of long chains in the solution of the analytical standard. Another interesting observation is that the amount of Ca2+ bound per COO⁻ group is lower for the PAA standard with 200 000 g mol⁻¹ compared to the shorter chain lengths, which means that the highest molecular weight binds less Ca2+. This supports the assumption that the higher molecular weights of the polydisperse commercial PAA grades rather enclose Ca2+ ions than actually binding the detected amounts on a stoichiometric basis. Because only three PAA standards were measured there were no significant trends of the thermodynamic parameters with respect to the molecular weight observed.

Finally, we have also succeeded in transferring the concept of calcium/polyelectrolyte hydrogel formation to another polymer. Indeed, similar hydrogels were obtained for copolymers of acrylic acid and maleic acid with two different molecular weights (50 000 and 70 000 g mol⁻¹) upon addition of CaCl₂ (Fig. 6). The hydrogels showed the same properties regarding

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**Fig. 6** Hydrogels obtained by calcium complexation of acrylic acid and maleic acid copolymers at a pH value of 6 with a molecular weights of 70 000 g mol⁻¹ (left) and 50 000 g mol⁻¹ (right).
plasticity, stretchability and self-healing as the original “mineral plastic” with PAA. In contrast to the synthesis with poly(acrylic acid) at pH 7, the pH value for a successful hydrogel formation with the copolymers had to be lowered to 6. This observation can be explained by the higher carboxylic acid group density in the copolymer due to the additional carboxylic acid groups in maleic acid. The density of carboxylate group seems to have the same influence on hydrogel formation as higher pH values or higher molecular weights. This is probably caused by the higher acidity of the copolymer compared to PAA, resulting from the lower $pK_a$ value of maleic acid ($pK_a = 1.9$).

**Conclusions**

In this work, we have characterized the physico-chemical properties of so-called “mineral plastic hydrogels” and linked them to the macroscopic rheological behavior of these remarkable materials.\(^{25}\) The properties of the synthesized PAA/Ca\(^{2+}\) gels can be adjusted by varying the molecular weight of the used PAA, the pH value, the polydispersity and the kind of used (co)polymer. These properties can easily be monitored via rheology measurements, which revealed that for the PAA grades with average molecular weights of 50 000 and 100 000 g mol\(^{-1}\), the liquid (\(G'\)) and solid (\(G''\)) character are in the same order of magnitude. By means of isothermal calorimetry experiments, the thermodynamics of the process could be elucidated, showing a maximum thermodynamic driving force \(\Delta G\) for hydrogel formation at an average molecular weight of about 50 000 g mol\(^{-1}\) (at the chosen pH value of 7). This behavior proved to be widely independent of the concentrations of the reagents, but varied as a function of polymer polydispersity. The stretchable, shapeable and self-healable properties of the hydrogel result from the unique co-existence of solid- and fluid-like domains, which becomes manifest in nearly equal storage and loss moduli in the rheology measurements. To obtain this kind of gel, the average molecular weight of the PAA has to be between 50 000 and 100 000 g mol\(^{-1}\), with a solution concentration of about 0.1 M and a pH value of 7. Additionally, the polydispersity of the poly(acrylic acid) should not be too low because the range of different chain lengths is crucial for the properties of the resulting hydrogel, with the longer chains forming the hydrogel network and shorter ones acting as plasticiser. Properties different from those optimized here can likely be realized by adjusted synthesis parameters.

**Author contributions**

LMF synthesized the samples and performed the measurements except rheology and GPC. HC designed the study, VB and MK selected and characterized the polymers, analyzed the data and interpreted the results. STS performed the rheology experiments. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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**Conflicts of interest**

There are no conflicts to declare.

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