Soft Matter

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Journal:	*Soft Matter*
Manuscript ID	SM-ART-06-2019-001101.R1
Article Type:	Paper
Date Submitted by the Author:	15-Aug-2019
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ARTICLE

Enhanced elasticity in poly(acrylic acid) gels via synthesis in the presence of high concentrations of select salts

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Poly(acrylic acid) (PAA) gels synthesized via free-radical polymerization of acrylic acid, N,N'-methylenebisacrylamide and high molarities of salts in water exhibit properties markedly different from PAA gels synthesized without salt, even when the latter are incubated in high-molarity salt solutions after gelation. Particularly noteworthy is unusual mechanical behaviour that includes substantially increased elongation, increased modulus, and rapid recovery after strain. The greatest enhancement in viscoelastic behaviour is evident in 2M LiCl and $ZnCl_2$ samples, with LiCl samples having a modulus of 39 kPa and reaching an extension ratio of 10 and a fracture stress of 135 kPa, and $ZnCl_2$ samples having a modulus of 43 kPa and reaching an extension ratio of 8.5 and a fracture stress of 175 kPa. This enhanced elasticity is thought to be brought about by a combination of coiled but only weakly-entangled PAA chains with phase-separated regions of salt acting as a plasticizer and modulating intermolecular interactions among AA units.

Introduction

Polyelectrolytes, in general, are a fascinating topic of study given the vast number of complimentary and competing factors governing the structure and behaviour of these materials. For example, the swelling behaviour of weak polyelectrolyte hydrogels is strongly influenced by pH and ionic strength of the swelling solution, and is dependent on crosslink density and number of ionic groups. Real gels are inhomogeneous, possessing defects on a number of different size scales, including intramolecular cycles, multiple crosslinks with variable molecular weights between crosslinks, and microphase-separated regions.[1,2] Overall, such materials are incredibly complex, and specific behaviours of different systems still warrant interest and investigation. Fortunately, the Flory-Rehner theory enables the elucidation of key system properties based on equilibrium swelling, repeat unit characteritics[3,4] and crosslink density that can frequently explain physical property data.

Poly(acrylic acid) (PAA) is an anionic polyelectrolyte that is familiar to almost all consumers, as it is commonly used in products that benefit from lightly-crosslinked PAA's super-absorbency in the acrylate salt form, such as diapers, feminine care products, and water-retention coatings.[5,6] Additionally, blends of PAA and other polymers have seen use in applications such as sensors, building materials, and soft robotics.[7-9] The acrylic acid repeat unit is a weak acid with a pK_a of about 4.7[5] and the anionic polyelectrolyte form is obtained by either incorporation of base during synthesis or post-synthesis neutralization.

One particularly impactful use of crosslinked, anionic PAA is as a model nerve and muscle analog, given its ease of preparation and cation exchange behavior.[10] This aspect of PAA has long been of interest to those seeking to study ion exchange in model biological systems, and many groups have observed the behaviour of PAA gels incubated in solutions of biologically relevant ions, such as Ca^{2+} and Na^+.[8,10] In particular, ion exchange of neutralized (e.g., Na^+ form) PAA in the presence of calcium has been studied extensively.[11] These studies tend to focus on the incubation of PAA materials in salt solutions and the resultant complexes formed between the charged COO^- groups and the cations in solution, which yield a dimensional change in the material, generally a pronounced shrinkage upon replacement of monovalent cations with divalent cations such as Ca^{2+}.[12] These studies have found that calcium ion bridging does not have a pronounced effect on the elastic modulus of the material, indicating a lack of permanent crosslinks in PAA gels incubated in high-salt solutions. [13]

There has also been exhaustive study of the behaviour of un-ionized PAA gels, as well as extensive study of the interaction of PAA gels with salt solutions post-synthesis.[2,5] However, relatively little attention has been paid to the properties of un-ionized PAA gels with salts added during synthesis, with only a handful studies investigating gels synthesized with additives besides bases to produce a substantially un-ionized form of the polymer.[9]

Toward that end, this investigation sought to explore PAA gel synthesis in the presence of selected high salt loadings, and led to the discovery of interesting and unexpected mechanical properties. Adding high concentrations of chloride salts of lithium, sodium, and zinc yielded interesting properties, with the lithium chloride and zinc chloride samples developing increasing elasticity as the concertation added during synthesis was increased. These samples exhibited extension ratios of up to 12, which is unusual for simple un-ionized poly(acrylic acid) systems. This behaviour is exciting from both a fundamental and applied perspective. From a fundamental point of view, it is speculated that the reason for this increase in elasticity is due to a drastic decrease in polymer-solvent interaction, leading to a compact-coil structure with little entanglement. Support of this hypothesis would be a positive addition to the larger body of knowledge surrounding polyelectrolyte structure-property relationships. From an applied perspective, this study describes straightforward, one-pot synthesis of a highly elastic, inorganic salt-loaded material. There is potential for this material to be useful in a variety of applications, including soft robotics, electronics, and

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sensing devices. The phase of this investigation described herein is an initial exploration into the unique properties exhibited by these materials, and introduces a possible theoretical explanation for this behaviour.

Experimental Section

Polyacrylic acid synthesis

Poly(acrylic acid) gels were synthesized via a formulation adapted from Tasaki et al.[8] but without added base to retain PAA in its acid form, a necessary condition to realize the unusual properties to be discussed shortly. 3 M acrylic acid (AAc), 5 mM N,N'-methylenebisacrylamide ('bis'), and 3 mM potassium persulfate (KPS) (Sigma) were added to distilled, deionized water. In the case of the salt-loaded gels, 5 M aqueous solutions of salt were added in order to bring the samples to the desired molarity, specifically 0.5 M, 1.0 M, 1.5 M, or 2.0 M. The salts used were lithium chloride, sodium chloride, and zinc chloride (Fisher). Samples remained at a pH of about 2 regardless of salt loading level. As no base was employed during or after synthesis to neutralize acrylic acid (AA) units, the gels are believed to be mostly un-ionized.

Samples were mixed vigorously on a vortex mixer for 90 seconds and degassed for 60 seconds. The solutions were then poured into polypropylene microcentrifuge tubes or glass petri plates and incubated in an oven at 80°C for 60 minutes. In general, 1 mL samples were prepared in microcentrifuge tubes, and 15 mL samples were prepared in glass plates.

Upon cooling, the crosslinked samples were cut and stored in excess mineral oil to prevent drying and maintain their "as-synthesized" state prior to mechanical testing. Samples were removed from the mineral oil prior to any testing, and were tested within 36 hours of synthesis. Samples intended for swelling studies were not stored in mineral oil, and were instead tested shortly after polymerization was complete. Swelling studies in water discussed below were employed to characterize the networks produced, but it should be emphasized that swelling irreversibly removes salt and the interesting mechanical properties to be discussed cannot be re-established by simply soaking salt-extracted gels in high-molarity salts.

A set of samples with 0.5 mM bis, rather than 5 mM, was also produced using the method described above. This formulation was intended for the analysis of a system with reduced covalent crosslink density.

Mechanical, Solubility, and Equilibrium Swelling studies

Samples containing no salt, and 0.5 to 2.0 M of NaCl, LiCl, or $ZnCl_2$, were fabricated for mechanical testing and swelling studies in water. Mechanical testing was performed using a Zwick and Roell Universal Testing Apparatus with a 100 N load cell at a constant strain rate of 0.3. Swelling studies were conducted by incubating samples in distilled, deionized water. Samples were cut into 4 mm discs and dried prior to incubation. The water was changed and samples were weighed every 24 hours until the samples reached sustained, stable weights. Swollen samples of salt-free PAA and 2 M salt-loaded PAA were then tested using a TA Q800 Dynamic Mechanical Analyzer configured for compression testing to collect post-swell mechanical data. Swelling was calculated using the following equation:

$$Percent\ swelling\ (\%) = \left(\frac{M_{eq} - M_0}{M_0}\right) \times 100\%$$

where M_{eq} is the weight of the gel after reaching equilibrium after incubation in water and M_0 is the weight of the dried gel. Gel fraction was assessed by drying the gels a final time and comparing that to the initial dried weight pre-swelling. The equation follows, where M_d is the mass of the dried sample after swelling in water.

$$Gel\ fraction\ \% = \left(\frac{M_0}{M_d}\right) \times 100\%$$ [14,15]

Since many of the interesting properties of the samples are exhibited immediately after synthesis with no further preparation, the study focused on assessing properties of the as-synthesized materials, rather than of swollen materials. Okay et al. offer a method for utilizing the properties of as-synthesized gels, rather than fully swollen gels to calculate critical properties such as molecular weight between crosslinks and crosslink density.[16] This method allows for a first pass at characterization of the system. First, normalized volume of the equilibrium swollen hydrogels is given by

$$V_r = \left(\frac{D}{D_0}\right)^3$$

where D and D_0 represent the diameter of the hydrogel after swelling to equilibrium and immediately after synthesis, respectively. In addition to percent equilibrium swelling shown above, it is important to define equilibrium volume swelling ratio, q_v, as

$$q_v = \frac{V_r}{v_2^0}$$

In this equation, v_2^0 is the volume fraction of uncrosslinked polymer after synthesis. Since comparison of dried gels and gels that have been swollen and washed extensively and dried again show that the gel found that the gel conversion is near 100%, this can be calculated from the initial molar concentration of monomer, C_0 and V_r, the average molar volume of the polymer repeat unit, using the relation

$$v_2^0 = 10^{-3} C_0 \overline{V_r}$$

With this in mind, the elastic modulus (G) of a system swollen to equilibrium can be used to determine network crosslink density via

$$G = A\frac{\rho}{\overline{M}_C}RT(v_2^0)^{2/3}(v_2)^{1/3}$$

where ρ is the polymer density, v_2 is the volume fraction of crosslinked polymer in equilibrium swollen gel, and R and T are gas constant and temperature. In this system $v_2^0 = v_2$, so the modulus of the as-synthesized material can be written as

$$G_0 = A\frac{\rho}{\overline{M}_C}RT v_2^0$$

The constant A equals one for an affine network, and (1-2/ ϕ) for a phantom network. The crosslink density of a system can then be found via

$$\rho_c = \frac{1}{\overline{M}_C \bar{v}}$$

where $\overline{v}$ is polymer specific volume, or the inverse of polymer density.[16,17]

X-Ray Absorption Studies

To understand the arrangement and interaction of the salts in these gels, as well as the behaviour of the chains as salt concentration changed and as the materials underwent tension, x-ray absorption fine structure (XAFS) studies were conducted at the Advanced Photon Source (APS) at Argonne National Laboratory.

For these studies, PAA was loaded with rubidium chloride or zinc chloride (Sigma) at a 2 M loading level. The equipment and source we used for XAFS at APS disallowed for the analysis of lithium and sodium. For this reason, rubidium chloride was used as a monovalent comparison for the sodium salt.

3 M PAA samples that had been loaded with salt were tested in their as-synthesized condition. The change in the metals as the PAA materials underwent strain was of primary interest. To explore this change, samples were tested at fixed strains of 0, 100, or 500%. Samples were strained wet (as-synthesized) and sealed in kapton tape.

This study utilized the same crosslinker and initiator concentration as the other samples discussed in this study (5 mM bis and 3 mM KPS), but, in the case of zinc-loaded samples, both 3 M and 6 M acrylic acid concentrations were analysed. In addition to this, samples made with 3 M acrylic acid in 50% glycerol/50% water were also analysed. Samples were tested at beamlines 10-BM-B and 12-BM-B.

Results

Sample Appearance and Swelling Behavior

After synthesis, samples removed from the molds left behind no residual water or material, and samples were roughly the same mass before and after polymerization. Samples made with no salt or NaCl remained mostly clear, regardless of loading level. Samples made with LiCl and $ZnCl_2$ possessed increasing opacity as the amount of salt increased from 0.5 M to 2.0 M. An image of the as-synthesized, dried, and fully swollen gels is shown in **Figure 1.**

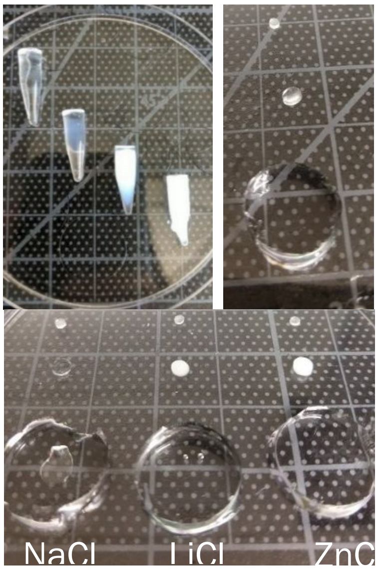

Figure 1. Lithium-loaded PAA gels immediately after synthesis displaying uniform initial size and increasing opacity with increasing salt concentration from top to bottom (left). PAA gels synthesized without salt showing, from top to bottom, fully dried samples, as-synthesized samples, and fully swollen samples (middle). Salt-loaded PAA gels showing the same (right). The squares on the mat below the samples are 1 cm x 1 cm.

Furthermore, upon exhaustive soaking in distilled water to extract salt and understand water retention, increased equilibrium swelling was exhibited by the samples synthesized with salt. Equilibrium swelling results are summarized in the chart in **Figure 2**.

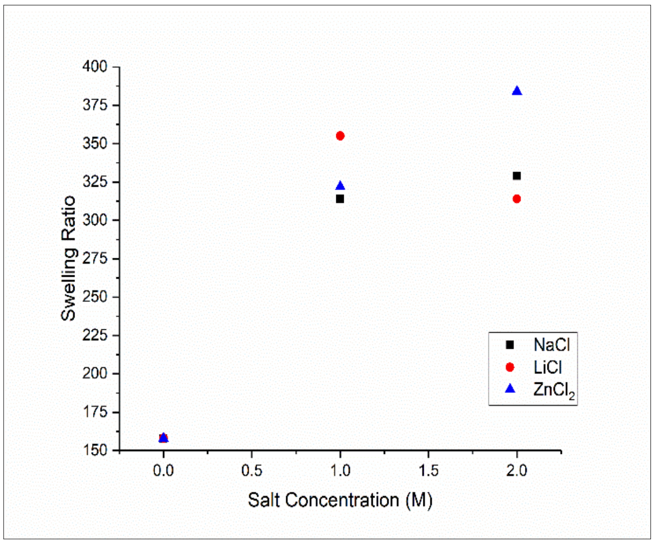

Figure 2. Equilibrium swelling ratio vs. salt concentration. $ZnCl_2$ samples exhibited the greatest amount of swelling overall. In general, the 2 M samples exhibited significantly increased swelling as compared to the samples with no salt.

Mechanical Testing

A plot of the elastic modulus of the different gels vs. salt concentration is shown in **Figure 3**.

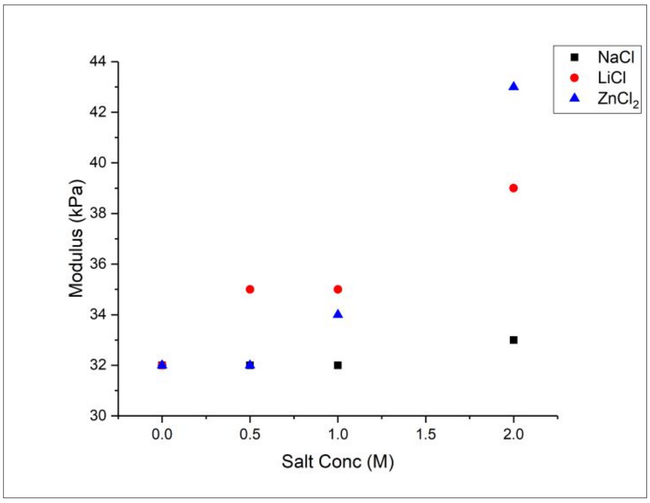

Figure 3. Modulus vs. salt concentration for salt-loaded PAA samples. The highest modulus was exhibited by the 2 M $ZnCl_2$ samples, with samples with loading levels 1 M or lower maintaining similar moduli to those of samples synthesized without salt.

In general, at loading levels of 1.0 M or less, the samples possessed moduli reasonably similar to that of samples with no salt loading during synthesis. NaCl samples also had moduli similar to that of the unsalted samples, between 32 and 33 kPa. The 2 M LiCl and 2 M $ZnCl_2$ samples possessed moduli of 39 kPa and 43 kPa, respectively. Stress-strain curves giving a general overview of the mechanical properties of the samples are shown in **Figure 4**.

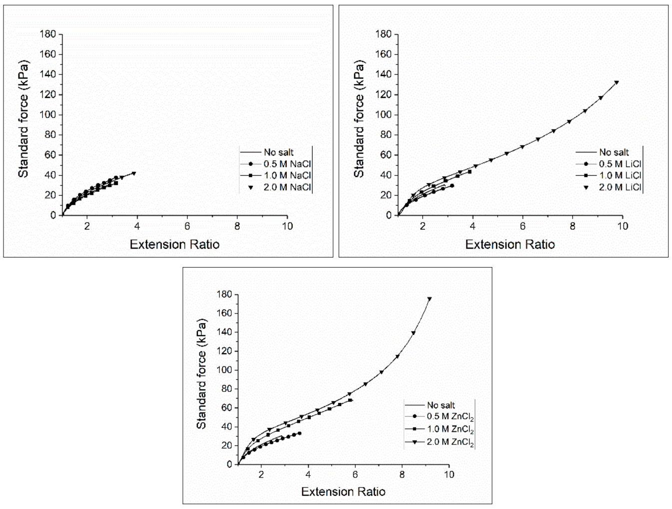

Figure 4. Stress-strain curves of PAA loaded with sodium chloride (top left), lithium chloride (top right), and zinc chloride (bottom) at different salt loading levels of no salt (line), 0.5 M (circles), 1.0 M (squares) and 2.0 M (triangles).

PAA gels with no salt exhibited a typical extension ratio of 2.8, a modulus of 30 kPa, and a fracture stress of 30 kPa. Samples loaded with NaCl showed similar results, with the highest extension ratio being about 4, exhibited by samples at the 2 M loading level. The LiCl-loaded samples, on the other hand, showed a maximum extension ratio of 10 in the 2 M loading level. The $ZnCl_2$ loaded samples exhibited similar behaviour, with an extension ratio of 8.5 in samples at the 2 M loading level. A particularly interesting feature of the stress-strain curves of the 2 M LiCl and 2 M $ZnCl_2$ samples is their remarkable adherence to the shape of stress-strain curves predicted by classical rubber elasticity. Both materials exhibited a sharp increase in stress at low initial strain, followed by a significant extension associated with chain uncoiling, and culminating with rapidly increasing stress as chains partially align and approach rupture. This behaviour is not evident at the lower salt loading levels, nor is it evident in NaCl-loaded samples. The NaCl-containing samples were similar in behaviour to the samples without salt, with a modulus of 32-33 kPa, extension ratio of about 4, and a fracture stress of 42 kPa. Given this, it is clear that the high loadings of lithium or zinc salts are critical to the enhanced properties evident in the rubber-like gels. Hysteresis testing showed roughly 98% recovery in the non-salt loaded PAA samples, and nearly 99% recovery in the 2 M NaCl-loaded gels after 5 cycles. The 2 M LiCl and 2 M $ZnCl_2$-loaded gels showed 94% and 96% recovery, as shown by **Figure 5.**

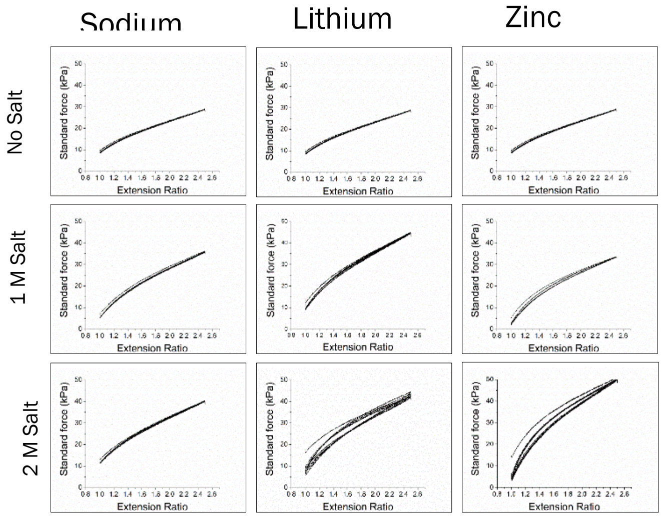

Figure 5. Hysteresis testing of salt-loaded PAA samples. More significantly decreased recovery in evident in the 2 M LiCl and $ZnCl_2$ samples than in the NaCl samples.

Using the moduli above, the calculated molecular weight between crosslinks was calculated using equation 7. These are summarized in **Table 1** below:

Table 1. A summary of the molecular weight between crosslinks (M_c) for the samples at various loading levels of different salts. M_c is expressed in kDa.

Salt Type	No Salt	0.5 M	1.0 M	2.0 M
NaCl	2.1 ± 0.2	2.1 ± 0.2	2.0 ± 0.1	2.0 ± 0.2
LiCl	2.1 ± 0.2	1.9 ± 0.3	1.9 ± 0.1	1.7 ± 0.2
$ZnCl_2$	2.1 ± 0.2	2.2 ± 0.3	2.0 ± 0.3	1.6 ± 0.4

Zinc chloride samples at the 2 M loading level exhibited the lowest $\overline{M_c}$, at roughly 1.6 kDa. As expected, given the data above, the sodium chloride samples and samples with salt loadings 1 M or less maintained a M_c roughly similar to that of the samples synthesized with no salt. Overall, all of the samples maintained a roughly similar $\overline{M_c}$, particularly when accounting for error, meaning that the addition of salt did not necessarily result in wildly different molecular weights across the different salt types and loading levels. The modulus of 2 M Li and Na samples at equilibrium swelling was 1.5 kPa for both samples, and the salt-free samples possessed a modulus of 1.7 kPa. This is reasonable given the similarity in molecular weight between crosslinks displayed across each of the sample types. The 2 M $ZnCl_2$-loaded samples displayed a slightly lower modulus of 1.1 kPa, which tracks with the zinc sample's significant increase in equilibrium swelling as compared to the other salt types.

To further explore the influence of salt on PAA gel mechanical properties, the contribution of covalent crosslinking was assessed by reducing the amount of crosslinker present during synthesis by a factor of 10 and loading with 2 M $ZnCl_2$. This is shown in **Figure 6**.

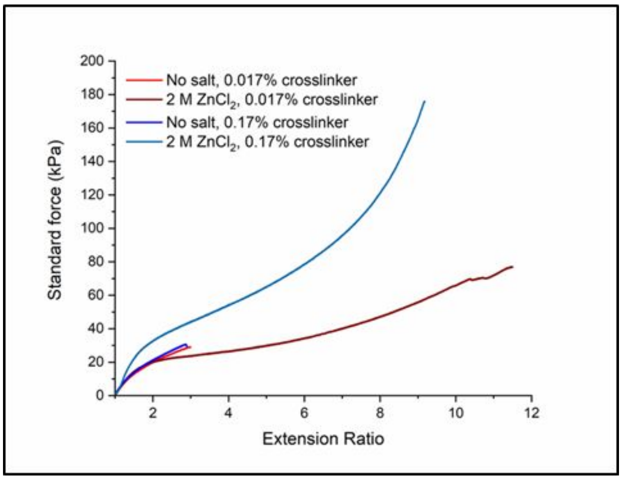

Figure 6. Stress strain curves of PAA synthesized with 0.017% (reds) or 0.17% (blues) N,N'-methylenebisacrylamide either with no salt or 2 M $ZnCl_2$.

Both the 0.5 mM bis and 5 mM bis $ZnCl_2$ gels showed a similar stress-strain curve shape. The 0.5 mM bis gels did not exhibit a sharp increase in stress prior to failure. Instead, such samples had a long period of extension and then reached failure at an extension ratio of roughly 12. The reduced number of covalent crosslinks still yields a network that is capable of higher extension, but possesses a decreased ultimate tensile stress, as there should be fewer covalent crosslinks to break in the high strain regime. This stands in contrast to the gels prepared without salt. Neither no-salt sample reached extensions comparable to those loaded with zinc chloride. Given this result, it is evident that the addition of high amounts of $ZnCl_2$ during synthesis has a measurable effect on the mechanical behaviour of the material. This merits further study, specifically an assessment of the molecular weight between crosslinks of the low-crosslinker samples and overall crosslink density of the system. The purpose of the information presented here is as a confirmation that the high extensibility of the systems is preserved even with a modification of the crosslinker amount, and that the samples still exhibit rubberlike behaviour. Due to difficulty in sample handling, the intricacies of this system will be a focus of future study.

X-ray Absorption Studies

Following mechanical characterization, we sought to develop a deeper understanding of the behaviour of the metal ions in our systems so to uncover their influence on the unique mechanical properties reported above. For this, we utilized extended X-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES), which allows for the investigation of local metal ion structure via synchrotron radiation. Our initial experiments attempted to probe changes in the coordination environment of zinc ion as the sample was strained. For this, 2 M $ZnCl_2$ loaded samples in their as-synthesized state were examined at 0, 100, and 500% strain and compared against aqueous zinc chloride. **Figure 7** compares EXAFS and XANES spectra.

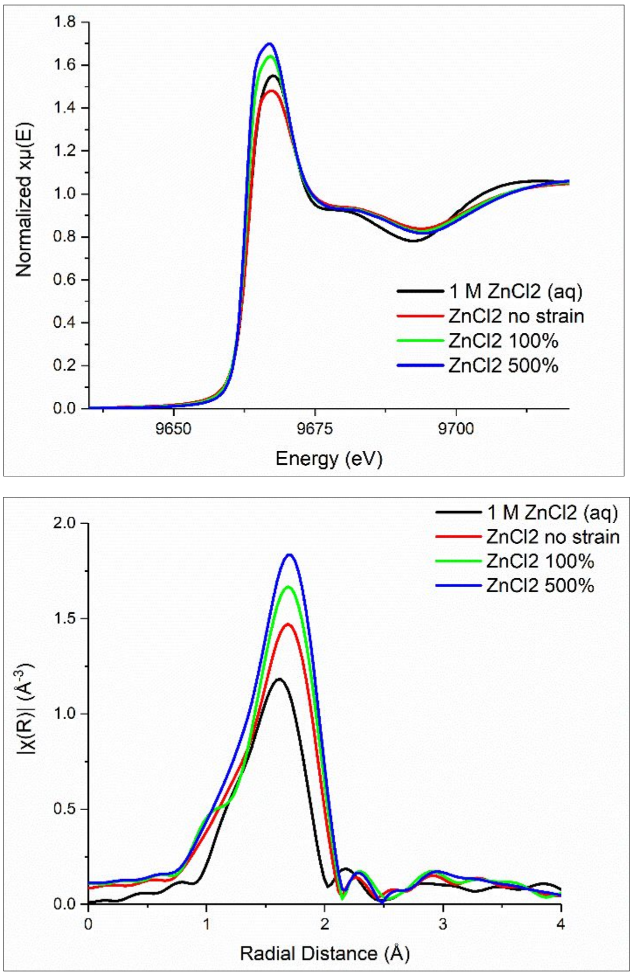

Figure 7. XANES of $ZnCl_2$-oaded PAA samples at increasing strain. The magnitude of the peak steadily increases with increasing strain (left). The EXAFS spectra (right) show a steady increase at roughly 1.9 Å, indicating a steady increase in Zn coordination with strain.

The Zn^{2+} k-edge data EXAFS analysis shows a primary peak at roughly 1.9 Å. This peak shows an increase in intensity as the material is strained. This likely represents an increased zinc ion-polymer interaction. We postulate that as the chains strain, the C=O and C-OH groups are able to coordinate more effectively to the positively charged zinc ion, with a concomitant decrease in zinc ion-water interactions. This is supported by the XANES spectrum. As strain increases, the energy at the XANES edge decreases, indicating a zinc ion that is less shielded and therefore requires less energy to affect a core electron. This is in contrast with the 6 M PAA samples and the 50/50 water/glycerol samples (**Figures 8** and **9**), which were also synthesized with 2M $ZnCl_2$ and strained from 0-500%.

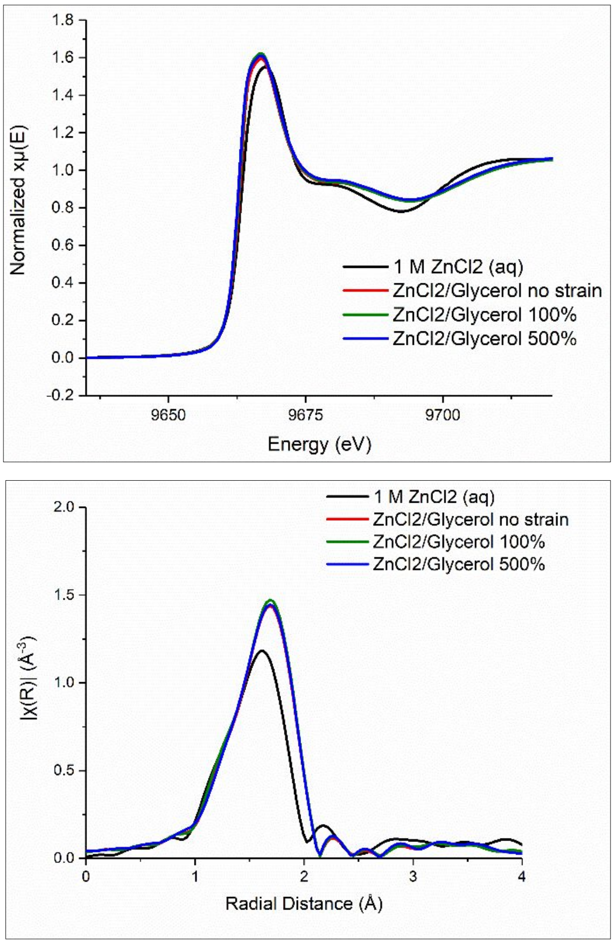

Figure 8. (Top) XANES of 2 M $ZnCl_2$-loaded PAA in 50:50 Water:Glycerol showing little change in white line location and intensity. (Bottom) EXAFS of the same samples showing a pronounced difference between the 1 M aqueous $ZnCl_2$ and the Zn-loaded samples.

For the 50:50 water:glycerol samples, there is little difference between the different strain levels, indicating a lack of any increased Zn ion-polymer interaction perhaps due to a greater similarity between a glycerol/water environment and PAA.

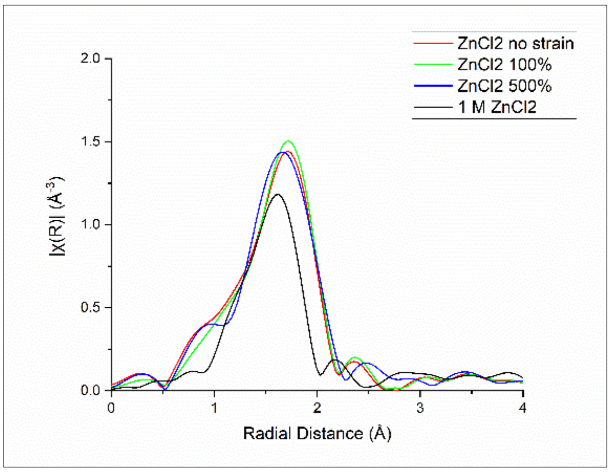

Figure 9. EXAFS of 2 M $ZnCl_2$-loaded PAA samples made with 6 M AAc rather than 3 M AAc. Once again, there is less apparent change upon strain as compared to the 3 M PAA samples discussed above.

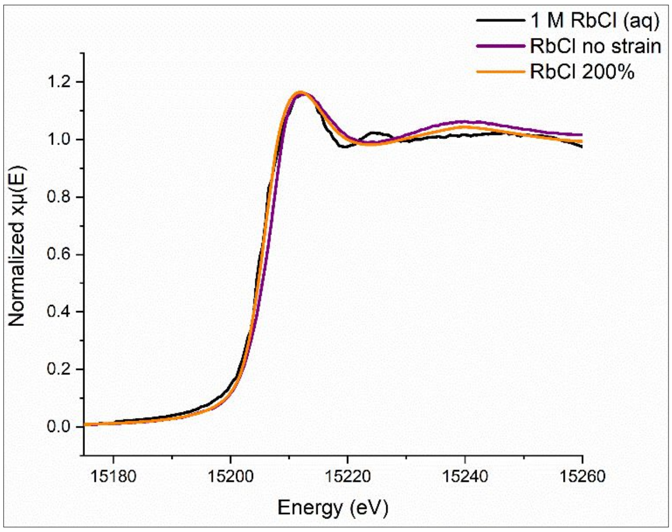

Figure 10. XANES comparing aqueous RbCl, unstrained 2 M RbCl-PAA, and 2 M RbCl-PAA at 200% strain. The white line intensity across all samples is roughly similar.

Figure 10 shows the XANES spectra of RbCl-loaded PAA gels under strain. Since RbCl gels act like NaCl gels, they cannot be strained nearly as much as the $ZnCl_2$ gels.

Rb k-edge data did not show nearly as much change between the strained sample and the unstrained sample, nor did edge data for any of the PAA gels differ significantly from aqueous RbCl. Thus, there is much less change in the coordination environment upon strain in these samples.

Modelling of the Zn K-edge data supports this emerging picture of changes in metal organization as the material is strained. For the standard $ZnCl_2$-loaded samples, the Zn-O coordination number (CN) of the unstrained sample is similar to that of aqueous $ZnCl_2$, and increases as the sample is strained to 500%. Such an increase in coordination number is not evident, however, in the 2 M $ZnCl_2$-loaded samples containing glycerol. In both water and water/glycerol systems, the nearest-neighbour distance (NND) does not change significantly as the samples are strained, nor does the mean-squared variation in path length (σ^2). These results are summarized below in **Table 2**.

Table 2. CN, NND, and σ2 obtained from modeling the Zn K-edge.

Sample	Zn-O CN	Zn-O NND (Å)	Zn-O σ^2
1 M $ZnCl_2$	4.62 ± 0.23	2.088 ± 0.008	0.005 ± 0.001
Standard 0	4.46 ± 0.28	2.10 ± 0.01	0.005 ± 0.001
Standard 100	4.84 ± 0.32	2.11 ± 0.02	0.005 ± 0.002
Standard 500	5.36 ± 0.33	2.11 ± 0.02	0.005 ± 0.002
Gly 0	4.71 ± 0.30	2.11 ± 0.02	0.005 ± 0.002
Gly 100	4.87 ± 0.31	2.11 ± 0.02	0.005 ± 0.002
Gly 500	4.77 ± 0.30	2.11 ± 0.02	0.005 ± 0.003

Discussion

Typically, PAA is synthesized via free-radical polymerization of AA, and the kinetics of these polymerizations are rather well-studied.[18] Events such as cyclization, a phenomenon in which the propagating active center of the growing polymer chain reacts intramolecularly, have been studied empirically and modified kinetic models have been developed.[19,20] In general, structural inhomogeneities are not uncommon in uncontrolled free-radical polymerizations such as those used herein to produce PAA gels.[21] Such inhomogeneities in gels tend to be on the scale of 10-1000 nm, with some gels possessing heterogeneous microphase-separated regions, imparting additional structural complexity. These regions occur in systems where the gelation threshold and the spinodal phase-transition critical point are reached simultaneously.[22]

In most rubbers, the genesis of the long regions of extension is facilitated by physical entanglements of long polymer chains. Given that the divalent $ZnCl_2$-loaded PAA gels exhibit rubberlike behaviour, a simple explanation might be that there is multivalent ionic "crosslinking" occurring, with zinc complexing with two polymer chains, yielding a stable pseudo-crosslink. This explanation does not stand, however, when presented with lithium chloride-loaded samples, which exhibit similar behaviour as the $ZnCl_2$ samples, although Li^+ is monovalent. Furthermore, this system is synthesized at very low pH, limiting the ionization of the carboxylic acid groups, and thus limiting this type of ionic interaction. Finally, previous studies have found that divalent cations, and Zn^{2+} in particular, do not necessarily undergo 2:1 coordination with poly(acrylic acid).[23]

The XAFS data indicate a very interesting event in the 2 M $ZnCl_2$-loaded PAA samples under strain. There is a pronounced difference in the coordination behaviour of the Zn upon stretching. This is not surprising in the sense that mechanical strain will have a profound effect on chain conformation, which then changes the charge distribution and the effective charge, which can induce a change in general ion environment around the polymer. What is interesting is that this effect is not seen in RbCl-loaded samples, nor is it present when the amount of water in the system is reduced in the case of samples made with 6 M AA or 50:50 glycerol. The availability of water to solvate the ions and interact with the polymer is clearly an important facet of this system. For the $ZnCl_2$ system, the solvent availability (which could then be extended a step further to consider solvent quality) is profoundly important, and likely contributes strongly to the interesting behaviour we have been investigating.

The behaviour of our systems likely results from a complex interplay involving hydration, coordination, and solvation. Water clearly plays an important role, and it is important to again emphasize that the samples that exhibit a uniquely large elongation all possess fairly large hydrated ionic radii. In light of this, we offer a hypothesis that considers multiple phenomena that may contribute to the properties of these materials.

First, during synthesis, the unionized (acidic) nature of the pre-polymer strongly impacts mixing. The growing polymer associates with itself rather than the solvent, which is comprised of AA and water, with progressively diminishing AA concentration, leading to collections of highly coiled regions of polymer. Simultaneously, the salt weakly associates with the polymer chains within these coils, screening the dipolar and hydrogen bonding interactions of the AA groups along a chain with one another, further allowing for heightened coiling.

Next, given that lithium chloride- and zinc chloride-loaded gels exhibit high elongation but sodium chloride-loaded samples do not, it is reasonable to correlate this behaviour not to valence, but rather to hydrated ion radius and the effect of individual ions on the water network that surrounds both the ions and the polymer. Lithium in particular has a large hydrated radius as compared to other monovalent ions (Na^+, K^+, Rb^+), and that of Zn^{2+} is even larger.[24]

Along with this, the system is already at low pH and the chains are substantially unionized. Some salt should participate in coordination with carboxylic acid groups, but there is a huge excess of salt in the system. The metal ions not participating in interaction with the polymer are free to exist as at least partially solvated ions, which draws significant amounts of water away from PAA chains. Thus, not only are the chains likely collapsed in response to high ionic concentration, but salt hydration causes a further decrease in solvent quality, which in turn can further facilitate the development of highly collapsed chains.

This emerging picture is not untrodden territory for macromolecular systems. Oftentimes, the Hofmeister series is invoked as an explanation of macromolecule solubility and structural stability. This theory classifies a series of salts by their structure-making or structure-breaking character, or their ability to "salt out" or "salt in" proteins in solution. The ability for the ions to structure water molecules beyond their first solvation shells, or, the ability for an ion with a large hydrated radius to syphon water away from the protein surface, leads to this "salting out" behavior.[25] In this case, protein-water interaction becomes less favourable, and the proteins collapse and crash out of solution.[26] This on its own seems to reinforce the idea that the large hydrated radii of zinc and lithium is a reasonable enough explanation for the formation of tightly coiled chains which exhibit increased elongation of the PAA material.

We therefore propose that the PAA chains exists as collapsed globules surrounded by some amount of water (dependent on excess cation's affinity for water) and are loosely associated with a limited number of cations. The collapsed chains are surrounded by a large excess of solvated salt that does not directly participate in the polymer interaction. **Figure 11** is a schematic representing these ideas. Overall, the high-salt polymer exists as an abundance of chains that are highly coiled and surrounded by a solvated ion rich region, perhaps developing a structural arrangement not dissimilar to those proposed for highly elastic biopolymers such as resilin and elastin.[27]

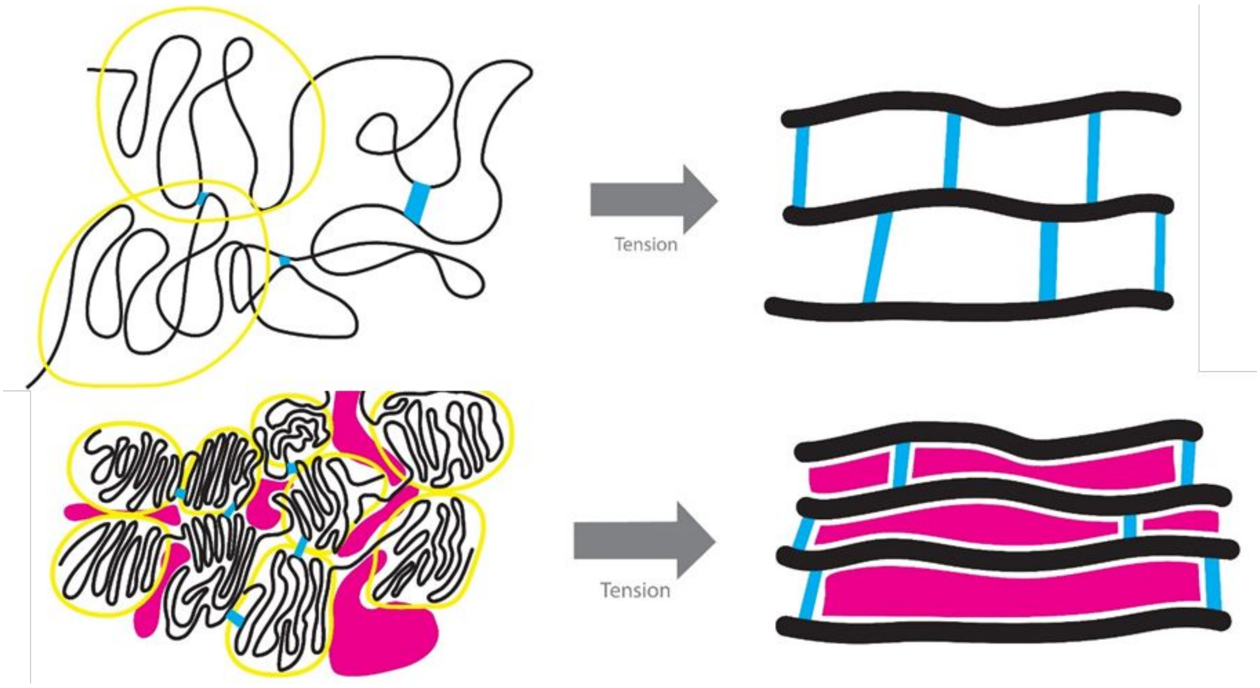

Figure 11. Illustration of PAA gel synthesized without salt with unscreened side groups and more polymer-solvent interaction, resulting in an chain behaving as an expanded coil(top) and PAA gels synthesized with high concentrations of salt, which forces more polymer-polymer interaction, leading to highly coiled regions, as well as to the formation of phase-separated regions of salt that act withdraw large quantities of water from the chain, reducing solvent quality and further facilitating collapse. Figure based on schemes presented by Weis-Fogh, Obukhov, and Daniel.[27, 29, 30]

Conclusions

Poly(acrylic acid) gels, while generally brittle and inelastic, can be made mechanically robust and highly elastic by the addition of salt during synthesis. In order to achieve extension ratios of 9 or higher, it is necessary to add salts in a rage of concentration above 1.5 M. This behaviour is not exhibited in PAA gels incubated in equivalent molarity solutions of salt post-synthesis. We believe that high salt imparts poor solvent conditions and high degrees of screening during synthesis, forcing the polymer into collapsed structures. Ions with large hydrated radii sequester water, further inducing poor solvent conditions around the polymer. The similarity of this system to the basic concept of the Hofmeister series is unsurprising, but may give clues to the genesis of protein folding and add another tool in the understanding of complex biological systems.

Of particular interest is the ability to tune extensibility for applications in, for example, soft robotics or artificial tissue. However, as shown by the post-wash mechanical data, these materials are reliant on a specific, unstable environment to maintain enhanced mechanical properties. Water content has a significant effect on the system, so, in order to find applications, we must first determine a way to preserve the system's stability. Initial attempts have been made to seal the polymers into a flexible outer material to create a barrier to water or salt loss. These solutions do not allow us to take advantage of the high extensibility of the material, but show some preliminary promise in applications such as actuators and strain gauges. Much of the future work on this system will be on applying the lessons about synthesis and metal organization learned here to develop other, more stable systems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was funded in part through a subcontract from Connecticut Analytical Corp. via a contract from the Defense Advanced Research Projects Agency (DARPA) and in part by the NSF Partnerships for International Research and Education (PIRE) program (NSF-1743475). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National

Laboratory under Contract No. DE-AC02-06CH11357. Graphics were drawn by Kelli Valverde, and her efforts are greatly appreciated.

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