

9-17-2020

Behavior of Poly electrolyte Gels in Concentrated Solutions of Highly Soluble Salts

Jessica L. Sargent

Xunkai Chen

Mitchell C. Brezina

Sebastian Aldwin

John A. Howarter

See next page for additional authors

Follow this and additional works at: <https://docs.lib.purdue.edu/msepubs>

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries.
Please contact epubs@purdue.edu for additional information.

Authors

Jessica L. Sargent, Xunkai Chen, Mitchell C. Brezina, Sebastian Aldwin, John A. Howarter, and Kendra Erk

Behavior of Polyelectrolyte Gels in Concentrated Solutions of Highly Soluble Salts

Jessica L. Sargent,¹ Xunkai Chen,^{1,2} Mitchell C. Brezina,¹ Sebastian Aldwin,¹ John A. Howarter^{1,3} Kendra A. Erk¹

1. School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907

2. Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California 94720

3. Environmental and Ecological Engineering, Purdue University, West Lafayette, Indiana 47907

ABSTRACT

Ionic hydrogels are an abundant class of materials with applications ranging from drug delivery devices to high performance concrete to baby diapers. A more thorough understanding of interactions between polyelectrolyte networks and ionic solutes is critical as these materials are further tailored for performance applications in highly targeted ionic environments. In this work, we seek to develop structure-property relationships between polyelectrolyte gels and environments containing high concentrations of multivalent ions. Specifically, this work seeks to elucidate the causes behind differences in hydrogel response to divalent ions of main group metals versus transition metals. PANa-co-PAM hydrogels containing low and high fractions of ionic groups are investigated in solutions of DI water, NaCl, CaCl₂, and CuSO₄ at concentrations ranging from 5 to 100 mM in order to understand 1) the transient or permanent nature of crosslinks produced in these networks by divalent counter-ions, 2) the role of polymer ionic content in these interactions, and 3) how these interactions scale with salt concentration. Gravimetric swelling and mechanical compression testing are employed to characterize water and salt-swollen hydrogels in order to develop guiding principles to control and manipulate material properties through polymer-counter-ion interactions. The work presented here confirms the formation of permanent crosslinks by transition metal ions, offers explanation for the behavioral discrepancy observed between ionic hydrogels and main group versus transition metal ions, and illustrates how such hydrogel properties scale with counter-ion concentration.

INTRODUCTION

Ionic hydrogels are an important class of stimuli-responsive superabsorbent polymers with a rapidly growing breadth of applications [1-5]. These lightly crosslinked networks can contain fractions of or be composed entirely of polyelectrolytes, which imparts the networks with the ability to respond to changes in pH and ionic composition of their environments. These responses include conformational changes in the polymer chains, which leads to changes in permeability, chemical selectivity, and mechanical properties. As such, a thorough understanding of the relationships between hydrogel composition and environmental responses is critical to further advancement of these materials.

The swelling of ionic hydrogels is dominated by osmotic pressure gradients [6], as illustrated in Figure 1. However, there are several complex and interconnected phenomena beyond osmotic pressure that contribute to the performance of these polymer networks, including hydrogen-bonding, electrostatic, and dipole interactions [7]. Several researchers have attempted to decouple and elucidate these interactions, predominately through computational modeling [8-11]. Despite the excellent advances made by such studies, many relationships between hydrogel composition and the physical consequences of these various interactions remain unclear [12].

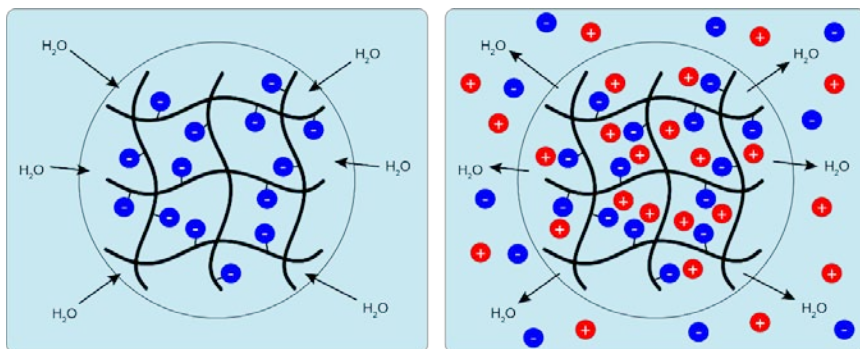


Figure 1. Osmotic pressure-driven swelling. In pure water (left), water diffuses into the hydrogel network to balance the chemical potential gradient produced by the polymer's fixed charges. In saline environments (right), counter-ions diffuse into the network to neutralize the polymer's fixed charges, and water diffuses out as necessary to balance chemical potential.

The current study is focused on the response of ionic hydrogels to multivalent ions of different character. In particular, it has been observed that anionic polymer interactions with transition [13] and post-transition [4] metal cations contribute to the mechanical strength of a hydrogel, while interactions with main group metals possessing the same charge valency do not [13]. This difference suggests that transition and post-transition metal ions form “permanent” ionic crosslinks, while main group metal ions form only transient crosslinks.

Herein we report current results of a work in progress. This work investigates the underlying cause for these differing crosslink strengths and seeks to establish quantitative relationships between hydrogel ionic fraction and changes in swelling and mechanical properties induced by these counter-ions. This work employs the copolymer system of poly(sodium acrylate-co-acrylamide) (PANa-co-PAM), which is a widely utilized hydrogel system [4,14-19] that allows for facile control over the ionic fraction of the gel. By varying the ionic fraction, the underlying cause of these interactions can be better

understood and relationships can be elucidated between gel composition and changes in properties induced by multivalent counter-ions.

EXPERIMENT

Materials and methods

All chemicals were used as received from Sigma-Aldrich unless otherwise noted. MEHQ inhibitor was removed from anhydrous acrylic acid prior to polymer synthesis by passage through a prepacked inhibitor remover column. Deionized (DI) water was purified to 18.0-18.2 M Ω resistance using a Barnstead NANOpure Infinity Water Purification System (Thermo Fisher Scientific). Stock solutions of N,N'-methylenebisacrylamide (MBAM), sodium persulfate (Na₂S₂O₈), and sodium metabisulfite (Na₂S₂O₅) were prepared using DI water for hydrogel synthesis. Elastic modulus measurements were performed using a TA-XTplusC Texture Analyser (Stable Micro Systems). Electrical conductivity was measured using a Hanna Combo pH/EC tester.

Hydrogel synthesis

Hydrogel synthesis was adapted from a previous methodology [4,18]. The amounts of reagents used for each hydrogel composition are reported in Table I. Hydrogels were synthesized in 50 mL polypropylene centrifuge tubes (Fisher Scientific) at room temperature and then placed in a 60°C oven overnight. DI water, acrylic acid (AA), and 10 M sodium hydroxide (NaOH) solution were added to the tube first and stirred for 10 minutes to thermally equilibrate. Acrylamide (AM) and crosslinking agent MBAM were added to the tube and stirred for another 10 minutes. Initiators, Na₂S₂O₈ and Na₂S₂O₅, were added simultaneously. Reaction was allowed to stir for 15 seconds, shaken vigorously for 30 seconds, and allowed to settle for 10 minutes before placing in the oven.

Table I. Amount of reagents used for synthesis of each polymer concentration. Stock solutions of MBAM (15 mg/mL), Na₂S₂O₈ (60 mg/mL), and Na₂S₂O₅ (60 mg/mL) were used.

Polymer Composition	AA	AM	DI water	10M NaOH	MBAM solution	Na ₂ S ₂ O ₈ solution	Na ₂ S ₂ O ₅ solution
17% PANa, 83% PAM	1.5 mL	7.5 g	18.6 mL	2.4 mL	12 mL	1.5 mL	1.5 mL
83% PANa, 17% PAM	7.5 mL	1.5 g	9 mL	12 mL	12 mL	1.5 mL	1.5 mL

Centrifuge tubes were cut open to remove hydrogels. Hydrogels were broken into pieces and submerged in DI water to remove any unreacted small molecules. Rinse water was changed daily for 5 days. Hydrogels were then sliced into flat pieces of 1-2 cm thickness for mechanical testing, air-dried, and placed under vacuum at room temperature overnight. Hydrogels were synthesized containing 2 wt% crosslinker and either 17 or 83 wt% sodium acrylate.

Hydrogel characterization

Gravimetric swelling

Dry hydrogel pieces were ground to a fine powder as in previous studies [18]. Gravimetric swell tests were conducted using the “tea bag” method [20] to determine

equilibrium swelling ratios and provide a qualitative comparison of swelling kinetics in various aqueous environments. The tea bag was submerged in solution until saturated, removed from solution, shaken for 10 seconds, and weighed. Ground polymer was added to the tea bag and the bag was placed back in solution. The bag was removed, shaken, and weighed at set time intervals from 0.5 to 240 minutes. The swelling ratio (Q) was calculated using Equation (1), where m_1 is the mass of dry polymer, m_2 is the mass of the wet teabag, and m_3 is the mass of teabag and swollen polymer.

$$Q = (m_3 - m_2 - m_1) / m_1 \quad (1)$$

Swelling measurements were performed on both hydrogel compositions described previously in order to compare responses of gels with low and high fractions of ionic functionalities. Swell tests were conducted using DI water and 10 mM solutions of NaCl, CaCl₂, and CuSO₄ in DI water. Experiments were conducted using ~150 mg of polymer per tea bag, with each tea bag immersed in 300 mL of the given solution. The experimental results are presented in Figure 2.

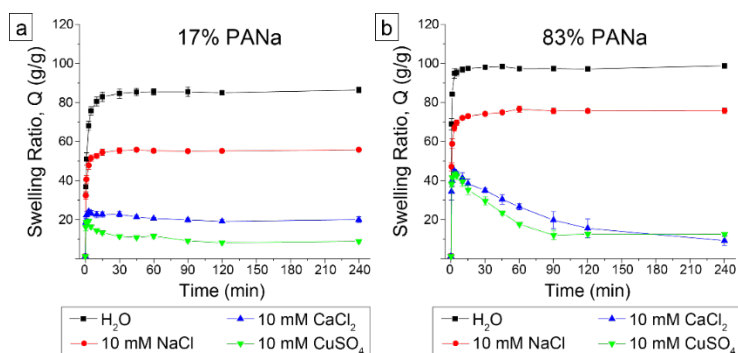


Figure 2. Swelling behavior of 17% PANa, 83% PAM hydrogels (a) and 83% PANa, 17% PAM hydrogels (b) in DI water and 10 mM salt solutions.

Hysteretic swelling experiments were also conducted in order to investigate the reversibility of changes in swelling performance induced by exposure to counter-ions in saline solution. These experiments were conducted using the same mass of polymer and volume of solution as described previously. However, after exposure to saline solutions (Figure 3b), hydrogels in these experiments were collected and dried under vacuum at room temperature. These salt-containing hydrogels were next immersed in DI water to remove all free salt ions. Each polymer was filtered and placed in clean rinse water every 4 hours until electrical conductivity (EC) of the rinse water was $\leq 5 \mu\text{S}/\text{cm}$. This conductivity threshold, which is used for Type IV Reagent Water [21], was selected as a low EC value which would indicate that all ions which were removable under neutral pH had been eliminated from the hydrogel. Rinsed hydrogels were then dried under vacuum at room temperature. Finally, these hydrogels were re-swollen in DI water (Figure 3c).

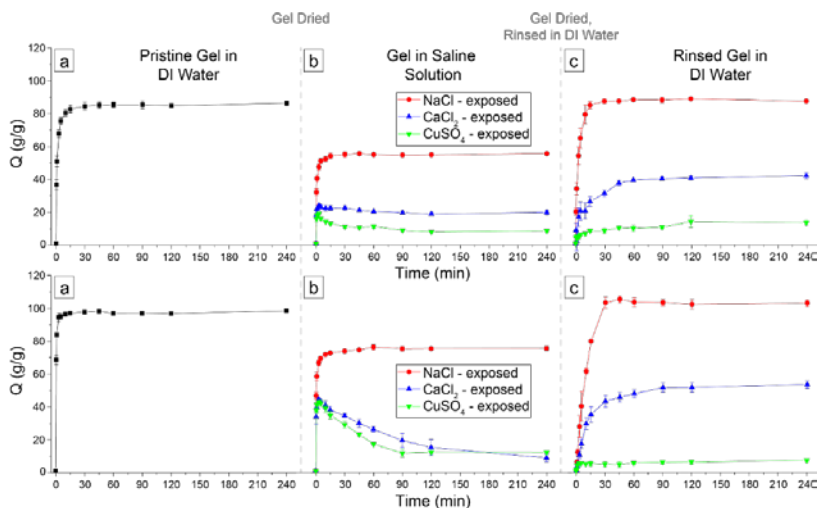


Figure 3. Swelling hysteresis experiments. Hydrogels were swollen in DI water (a), dried, swollen in saline solution (b), rinsed, dried, and swollen again in DI water (c). Top row images are of 17% ANa hydrogels and bottom row images are of 83% ANa hydrogels.

Mechanical analysis

Dried flat slices of hydrogel were swollen to a set swelling ratio of $Q=5$ for all experiments. A swelling ratio below the equilibrium Q of CuSO_4 -swollen samples was chosen in order to compare all compositions and solutions at the same polymer volume fraction ($\phi=1/Q$). Solution was added slowly to each sample until the desired Q was obtained in order to mitigate risks of sample cracking due to rapid and uneven swelling. Separate samples were prepared containing DI water, 5 mM, 50 mM, and 100 mM solutions of each salt.

The elastic modulus (E) of each sample was measured via compression using a 2 mm diameter flat punch on a hydrogel sample of 5-20 mm thickness. The maximum compression force was set to 50 mN, and the approach and return rates were set to 0.01 mm/sec in order to ensure that measurements remained in the elastic regime of the materials and there were no velocity-dependent contributions to the elastic modulus [22]. The elastic modulus was determined from the linear section of each stress-strain curve in order to avoid contributions from an uneven sample surface at low strain. Reported E values are averages obtained from 3-6 measurements collected on each sample type. Figure 4 presents elastic modulus values for both hydrogel compositions in DI water and low concentrations of each salt. 5 mM was chosen as a saline concentration closer to that of biological fluids [23]. Figure 5 presents elastic modulus as a function of salt concentration for 17% ANa (Figure 5a) and 83% ANa (Figure 5b) hydrogels, with concentrations approaching that of many high salinity environments [24,25].

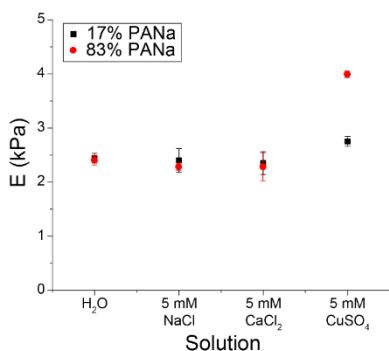


Figure 4. Mechanical responses between the two hydrogel compositions were compared as a function of metal cation at low salt concentrations.

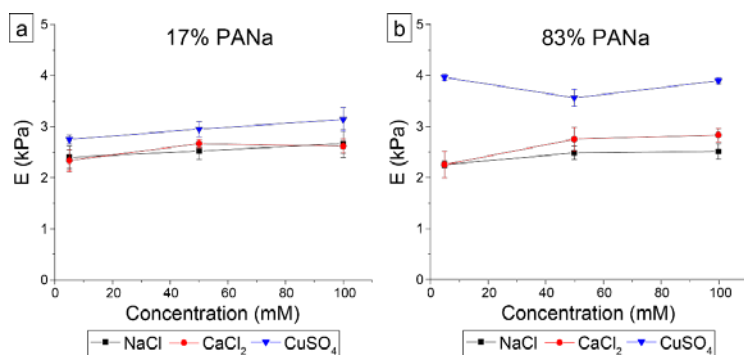


Figure 5. Elastic modulus as a function of salt concentration. 17% ANa (a) and 83% ANa (b) hydrogels were examined in 5 mM, 50 mM, and 100 mM solutions of NaCl, CaCl₂, and CuSO₄.

Optical observations

Differences in counter-ion absorption were also observable through visual inspection, particularly for copper salts. The concentration of Cu²⁺ can be recognized as higher in 83% PANa gels (Figure 6b) than in 17% PANa gels (Figure 6a) by the intensity of blue coloration. This blue is due to copper hydrates present in the hydrogel. Furthermore, in large pieces of 83% PANa hydrogels, an impermeable copper-crosslinked shell was observed (Figure 6c).

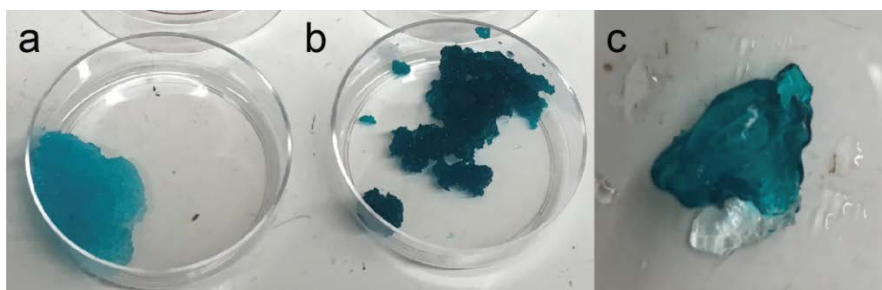


Figure 6. PANa hydrogels after swelling in 10 mM CuSO₄. The lighter color in the 17% PANa gel (a) and darker color in the 83% PANa gel (b) indicate a higher concentration of copper hydrates present in the 83% PANa gel. Larger pieces of 83% PANa gel (c) formed a measurable copper-crosslinked shell which, when cut into, revealed an un-crosslinked center to the hydrogel.

RESULTS AND DISCUSSION

Hydrogel swelling response depends upon both hydrogel and solvent composition. The overall trends observed in the time-response curves in Figure 2 are as expected from previous observations [4,18,19]: 1) increasing ion valency decreases hydrogel swelling capacity, and 2) increasing ionic fraction in the hydrogel increases the impact of counter-ion-induced deswelling. However, it is the difference in swelling behavior between hydrogels in calcium salts and in copper salts that is of interest to this investigation.

The time-dependent deswelling observed in all samples (*i.e.*, high and low PANa hydrogels in solutions of both divalent salts) has been observed and explained in previous works [13,18]. It has also been observed in previous studies that divalent transition metals cause the collapse of ionic networks at lower concentrations than alkaline earth metals [13]. However, the cause of this phenomenon remains poorly understood.

Clues to understanding this phenomenon can be taken from previous studies. In previous PANa-co-PAM work, similar observations were made concerning aluminum, which is a post-transition metal of similar character to copper. Krafcik, et al. [18] observed that swelling plateaued at a higher Q for Al³⁺ than for Ca²⁺, while Zhu, et al. [4] observed the formation of a solid shell similar to that observed in Figure 6c. Horkay, et al. [13] observed in pure PANa hydrogels that transition and post-transition metals increase the elastic modulus, while multivalent main group metals do not.

In order to understand how observations in pure PANa and with post-transition metal salts translated to the current system, mechanical analysis of the PANa-co-PAM gels was required. Elastic modulus measurements of both hydrogel compositions remained similar in DI water and low concentration of NaCl and CaCl₂. (Figure 5) In low concentrations of CuSO₄, the elastic modulus of 17% PANa gels increased slightly, while that of 83% PANa gels increased drastically. (Figure 5) These results indicate that PAM does not play a role in counter-ion-induced changes in mechanical properties, as the trends observed in PANa-co-PAM reflect those observed in pure PANa [13]. These data also show that Cu²⁺ contributes more strongly to the elastic modulus in high PANa gels. Such behavior can be understood within the context of metal ion characteristics. Calcium, an alkaline earth (main group) metal, is only weakly electronegative. It is capable of ionic attraction between itself and the anionic polymer functionalities, but it is unable to form covalent bonds. In turn, these ionic crosslinks, or ion bridges, formed by calcium are only transient in nature, as illustrated in Figure 7. Transition metals (*e.g.*, copper) and post-transition metals (*e.g.*, aluminum), on the other hand, are strongly electronegative and capable of forming coordinate covalent bonds as observed in ceramic matrices [26]. This ability in turn allows transition and post-transition metals to form permanent, covalent-strength bonds with the anionic polymer functionalities. Only by the formation of permanent bonds can an ion bridge be formed that contributes to the mechanical strength of the polymer network.

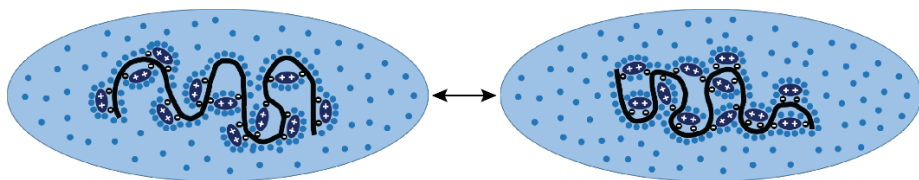


Figure 7. Illustration of fluctuation of transient crosslinks as occurs with multivalent main group metal ions.

This study also investigates how these interactions scale with increasing salt concentration. One must recall that electrostatic repulsion contributes to hydrogel swelling, and counter-ion-screening of those repulsions changes the conformation of the polymer chains. At 5 mM, the ionic strength of the saline solutions is lower than the ionic strength of either hydrogel, which is 9.8 mM for 17% PANa and 42 mM for 83% PANa. However, many saline environments, such as seawater or concrete pore solution, can have ionic strengths well into the millimolar range, significantly above the ionic strength of the hydrogels [24,25].

In Figure 6a, it can be observed that for 17% PANa gels, the elastic modulus remains relatively constant through all concentrations of each salt, with the modulus in CuSO_4 remaining higher than in NaCl or CaCl_2 . This is believed to be because even at 5 mM, a majority – or all, in the case of divalent cations - of the anionic sites in the polymer should be occupied, and increasing counter-ion concentration does not significantly increase the amount of charges being screened from electrostatic repulsion. Conversely, in 83% PANa gels (Figure 6b) we observe that the modulus in NaCl and CaCl_2 increases between 5 mM and 50 mM. In this case, there were still unscreened charges along the polymer chain in 5 mM salt solutions, and so additional screening by higher cation concentrations induced further changes in chain conformation and therefore elastic modulus.

An unexpected result appears in Figure 6b for 83% PANa hydrogels in CuSO_4 solution. Here, the elastic modulus remains high and relatively constant for all concentrations. This data is contrary to the idea of changes in chain conformation as the ionic strength of the gel is surpassed. However, this behavior can be explained in light of the copper-crosslinked shell formation observed as in Figure 7c. Quantification of this shell's thickness and variation with respect to hydrogel composition remains to be investigated. However, it is clear from visual observations that the shell formation is more significant in high PANa gels. Once this shell forms, minimal amounts of water or solute can permeate, and the outer shell of the hydrogel takes on properties different from the center of the hydrogel. In such a case, compression experiments at low forces are measuring the elastic modulus of this shell and not the un-crosslinked gel beneath it. Since this shell forms in 83% PANa gels even at low concentrations, it can be determined that copper ions fully crosslink the outer layer of the hydrogel, after which there is no further conformational change in the polymer chains, even with higher solution concentrations. This is supported by the consistent elastic modulus measured at all CuSO_4 concentrations.

Finally, initial hysteresis experiments also support the permanence of transition metal-induced crosslinks. It will be noted in Figure 3 that there is some level of permanent network constriction even with CaCl_2 . This restriction can be attributed to entrapment of Ca^{2+} ions within the network, which subsequently decreases the osmotic pressure gradient that drives swelling. In the case of CuSO_4 , however, the cleaned, re-swollen hydrogels never surpass the equilibrium Q obtained during swelling in salt solution. This swelling behavior provides additional support that a crosslinked shell is formed along the exterior

of the hydrogel particles, and water is able to permeate only into the free volume within the outer layers of that shell.

CONCLUSIONS

In this work we have investigated PANa-co-PAM hydrogels containing a low and a high ionic fraction and their swelling and mechanical performance in saline solutions. We have confirmed the formation of permanent crosslinks between ionic polymer moieties and transition metal counter-ions and the transience of crosslinks formed by main group metal counter-ions. We have further elucidated the reason for this behavioral discrepancy between metal ions and how this discrepancy scales in high salinity environments. This work will be continued in order to investigate a more comprehensive range of hydrogel ionic fractions and establish quantitative scaling relationships between ionic fraction and hydrogel performance properties in solutions of multivalent cations.

ACKNOWLEDGEMENTS

We would like to thank Professor Chelsea Davis and Naomi Deneke for advisement and training in conducting mechanical testing. We gratefully acknowledge financial support for this work by the National Science Foundation (CMMI 1454360).

References:

- [1] N. A. Peppas, P. Bures, W. Leobandung and H. Ichikawa, *Eur. J. Pharm. Biopharm.* **50**, 27-46 (2000).
- [2] S. Nayak and L. A. Lyan, *Angew. Chem. Int. Ed.* **44**, 7686-7708 (2005).
- [3] B. Rytchinski, *ACS Nano* **5** (9), 6791-6818 (2011).
- [4] Q. Zhu, C. W. Barney and K. A. Erk, *Mater. Struct.* **48**, 2261-2276 (2015).
- [5] H. Cui, Q. Zhao, Y. Wang and X. Du, *Chem. - Asian J.* **14**, 2369-2387 (2019).
- [6] J. Ricka and T. Tanaka, *Macromolecules* **17**, 2916-2921 (1984).
- [7] M. Muthukumar, *Macromolecules* **50** (24), 9528-9560 (2017).
- [8] S. K. De, N. R. Aluru, B. Johnson, W. C. Crone, D. J. Beebe and J. Moore, *J. Microelectromech. Syst.* **11** (5), 544-555 (2002).
- [9] H. Li, T. Y. Ng, Y. K. Yew and K. Y. Lam, *Biomacromolecules* **6**, 109-120 (2005).
- [10] C. E. Sing, J. W. Zwanikken and M. O. de la Cruz, *Macromolecules* **46**, 5053-5065 (2013).
- [11] A. Chremos and J. F. Douglas, *Gels* **4** (20) (2018).
- [12] F. Horkay and J. F. Douglas, in *Gels and Other Soft Amorphous Solids*, edited by F. Horkay, J. F. Douglas and E. Del Gado (Am. Chem. Soc. Symp. Proc. **1296**, Washington, D.C., 2018) pp. 1-13.
- [13] F. Horkay, I. Tasaki and P. J. Basser, *Biomacromolecules* **2**, 195-199 (2001).
- [14] R. A. Gemeinhart, J. Chen, H. Park and K. Park, *J. Biomater. Sci., Polym. Ed.* **11** (12), 1371-1380 (2000).
- [15] S. K. Bajpai and S. Johnson, *React. Funct. Polym.* **62**, 271-283 (2005).
- [16] T. K. Mudiyansele and D. C. Neckers, *Soft Matter* **4**, 768-774 (2008).
- [17] W. A. Laftah, S. Hashim and A. N. Ibrahim, *Polym.-Plast. Technol. Eng.* **50** (14), 1475-1486 (2011).
- [18] M. J. Krafcik and K. A. Erk, *Mater. Struct.* **49**, 4765-4778 (2016).
- [19] M. J. Krafcik, N. D. Macke and K. A. Erk, *Gels* **3** (46) (2017).
- [20] C. R. Davis, S. L. Kelly and K. A. Erk, *J. Appl. Polym. Sci.* **135** (14) (2017).
- [21] ASTM Standard D1193, 1951 (2018), "Standard Specification for Reagent Water," ASTM International, West Conshohocken, PA, 2018, DOI: 10.1520/D1193-06R18, www.astm.org.
- [22] K. R. Shull, *Mater. Sci. Eng., R* **36**, 1-45 (2002).
- [23] F. Horkay, I. Tasaki and P. J. Basser, *Biomacromolecules* **1**, 84-90 (2000).
- [24] F. J. Millero, R. Feistel, D. G. Wright and T. J. McDougall, *Deep Sea Res., Part I* **55**, 50-72 (2008).
- [25] A. Vollpracht, B. Lothenbach, R. Snellings and J. Haufe, *Mater. Struct.* **49**, 3341-3367 (2016).
- [26] C. B. Aakeroy and A. M. Beatty, in *Comprehensive Coordination Chemistry II: From Biology to Nanotechnology*, edited by J. A. McCleverty and T. J. Meyer (Elsevier, Amsterdam, 2003).