Supporting Information

Electro-actuated Hydrogel Walkers with Dual Responsive Legs

Daniel Morales, Etienne Palleau, Michael D. Dickey,* Orlin D. Velev*

Charge density analysis. The Peppas-Merill equation[1] was used to estimate the parameters used to calculate the crosslink density of the gel network, N^{-1}, as well as the molecular weight between crosslinks, $\overline{M_c}$, and the number average molecular weight of the polymer chains without crosslinking, $\overline{M_n}$:

$$\frac{1}{\overline{M_c}} = \frac{2}{\overline{M_n}} - \frac{\left(\bar{\upsilon}/V_1\right)\left[ln\left(1-\nu_{2,s}\right)+\nu_{2,s}+\chi\nu_{2,s}^{2}\right]}{\nu_{2,r}\left[\left(\frac{\nu_{2,s}}{\nu_{2,r}}\right)^{1/3}-\frac{1}{2}\left(\frac{\nu_{2,s}}{\nu_{2,r}}\right)\right]} \qquad \text{(S1)}$$

By using the data for the swelling properties of the non-ionic pure polyacrylamide gel composition, $\overline{M_c}$ can be estimated by varying $\overline{M_n}$ and holding the other parameters constant. At a critical molecular weight, the sensitivity of the equation to varying $\overline{M_n}$ becomes negligible and will plateau to a certain value. The molecular weight between crosslinks obtained at this point is valid assuming high conversion of the gel precursor.[2] The high degree of conversion of the acrylamide/sodium acrylate gels was confirmed by NMR experiments to quantify the amount of precursor excluded from the reaction (discussed below). The relationship between the molecular weight between crosslinks and the polymer chain length without crosslinker is plotted in Figure S1. The inset equation and blue line indicate the expected molecular weight if all of the BAAm molecules formed effective crosslinks, where M_r is the molecular weight of the repeat unit (72 g/mol).[3] It is expected for the actual molecular weight of the chains between crosslinks will be higher since the BAAm molecules can be consumed in cyclization reactions, multiple crosslink chains or in the polymer chains themselves.[4] Since both the crosslinker ratio, N^{-1} , and the total monomer concentration were fixed in our experiments, we assumed a constant crosslink density (N^{-1}= 0.005) and molecular weight between crosslinks ($\overline{M_c}$ =10300) for all calculations.

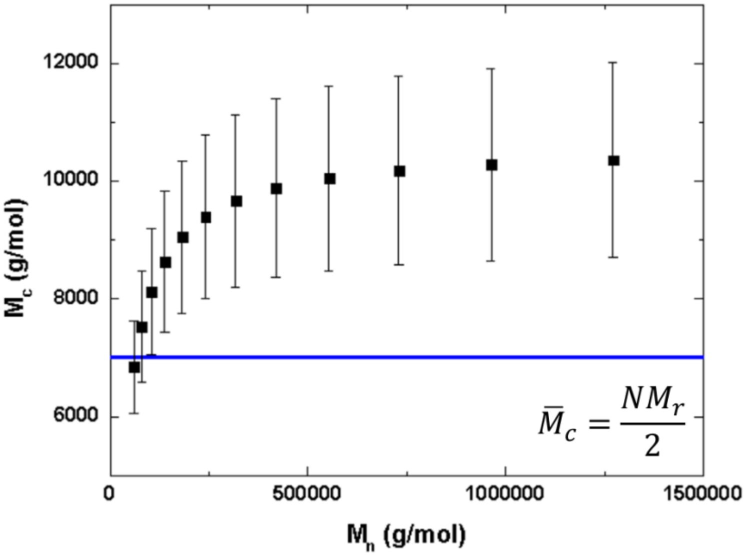

Fig S1. Plot of the molecular weight between crosslinks as a function of the polymer chain molecular weight in the absence of crosslinker. The blue line is the molecular weight between crosslinks if all of the crosslinker molecules formed ideal crosslinks as calculated by the inset equation. The error bars represent the s.d. from five separate pure acrylamide equilibrium swelling values.

The Brannon-Peppas model has been developed as a refinement to the Flory-Rehner theory to take into account polymerization in the presence of solvent. While both models assume that the networks chain lengths have a Gaussian distribution, the Flory-Rehner model assumes the polymer chains were reacted in the solid state. The form of the Brannon-Peppas equation given below describes the equilibrium swelling of an ionic hydrogel in water which has also been polymerized in the presence of water.[5]

$$\frac{\mathrm{V}_1}{\overline{\mathrm{M}}_\mathrm{r}}\left(\frac{\mathrm{K}_\mathrm{a}}{10^{-\mathrm{pH}}+\mathrm{K}_\mathrm{a}}\right)\left(\frac{\nu_{2,\mathrm{s}}}{z_{\bar{\upsilon}}}\right)=\left[\ln\left(1-\nu_{2,s}\right)+\nu_{2,\mathrm{s}}+\chi_1\nu_{2,\mathrm{s}}{}^2\right]$$

$$+\left(\frac{\mathrm{V}_1}{\bar{\upsilon}\overline{\mathrm{M}}_\mathrm{c}}\right)\left(1-\frac{2\overline{\mathrm{M}}_\mathrm{c}}{\overline{\mathrm{M}}_\mathrm{n}}\right)\nu_{2,\mathrm{r}}\left[\left(\frac{\nu_{2,\mathrm{s}}}{\nu_{2,\mathrm{r}}}\right)^{1/3}-\frac{1}{2}\left(\frac{\nu_{2,\mathrm{s}}}{\nu_{2,\mathrm{r}}}\right)\right] \qquad \text{(S2)}$$

The equation was solved numerically in order to calculate the degree of ionization of the sodium acrylate monomer units, which was used to calculate the effective charge density (f):

$$i=\left(\frac{\mathrm{K}_\mathrm{a}}{10^{-\mathrm{pH}}+\mathrm{K}_\mathrm{a}}\right)=\frac{[RCOO^-]}{[RCOOH]+[RCOO^-]} \qquad \text{(S3)}$$

$$f=\frac{i[NaAc]}{[NaAc]+[AAm]} \qquad \text{(S4)}$$

NMR experiments. NMR data were obtained using a 500 MHz Bruker DRX NMR spectrometer. The NMR probe was tuned to ^{1}H frequency - 500.128 MHz. Tetramethylsilane (TMS) was used as internal standard and 128 scans were acquired for each ^{1}H spectrum. NMR spectra were obtained in triplicate from aliquots of water in which the various sodium acrylate gel networks had equilibrated for two weeks directly after polymerization. Water suppression was necessary for all samples analyzed with TMS since the signal-to-noise ratios for the proton peaks were low otherwise. After the appropriate peaks were identified, they were integrated with respect to a known concentration of tetramethylsilane (TMS) doped in the sample (0.1 mM). The integral of the TMS peak was set to 12 protons and used as the reference (0 PPM). Poly (acrylamide-co-sodium-acrylate) peaks, $C_\alpha H$ and $C_\beta H_2$ were identified as (2.35-1.9 PPM) and (1.9-1.2 PPM) respectively. Sodium acrylate peaks CH_2 and acrylamide peaks CH_2 were identified as (5.9-6.14 PPM) and (6.24-6.3 PPM) respectively.

Table 2. Summary of NMR analysis to determine amount of unpolymerized precursor.

Composition	Acrylamide (mM)	Sodium Acrylate (mM)	Polymer Chains (mM)	Total Sol/Gel Fraction (%)
PolyAAm	0.17	n/a	1.63	0.04
10% NaAc	0.36	0.12	1.26	0.04
20% NaAc	0.13	0.13	1.50	0.04
50% NaAc	0.48	0.90	1.20	0.07
70% NaAc	n/a	1.92	2.85	0.08
100% NaAc	n/a	6.60	3.30	0.20

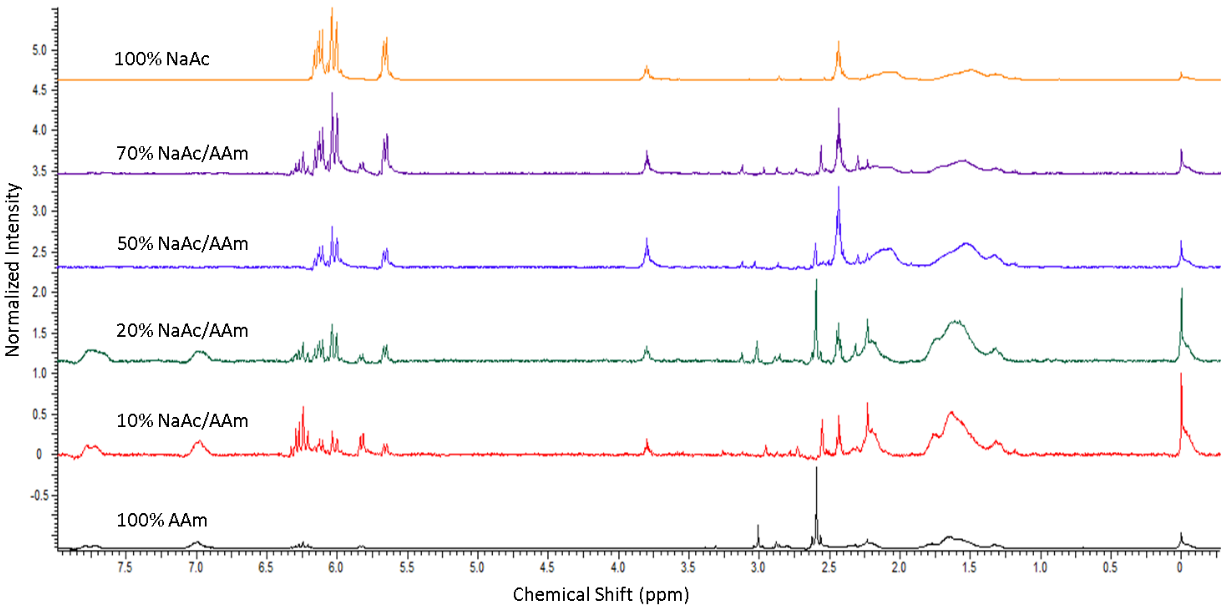

Fig S2. NMR spectra of wash water samples retrieved from equilibrated hydrogels.

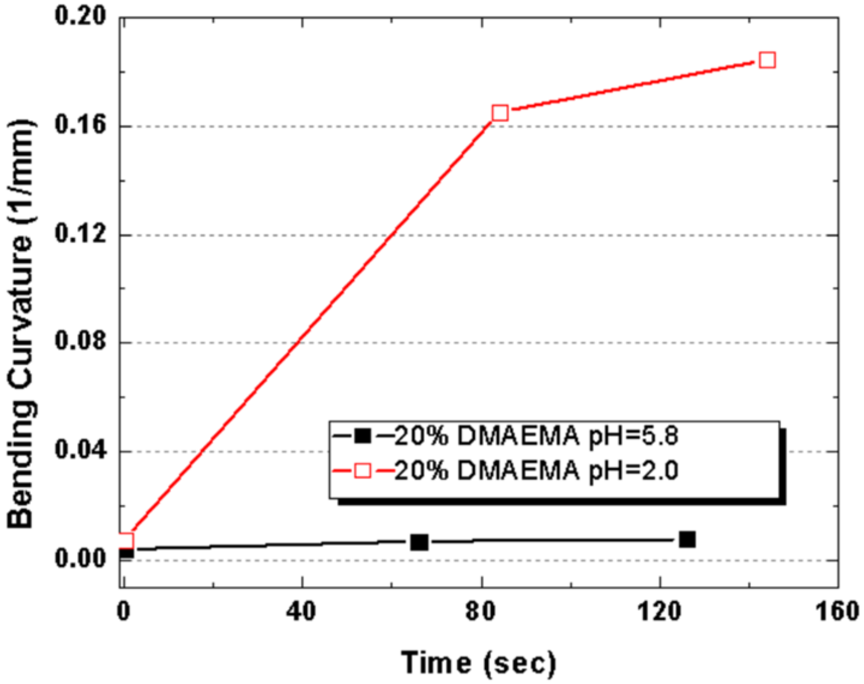

Fig S3. Bending curvature of a 20% DMAEMA hydrogel as a function of time. Bending is effected in acid medium since fixed charges are only present upon protonation of the tertiary amine groups.

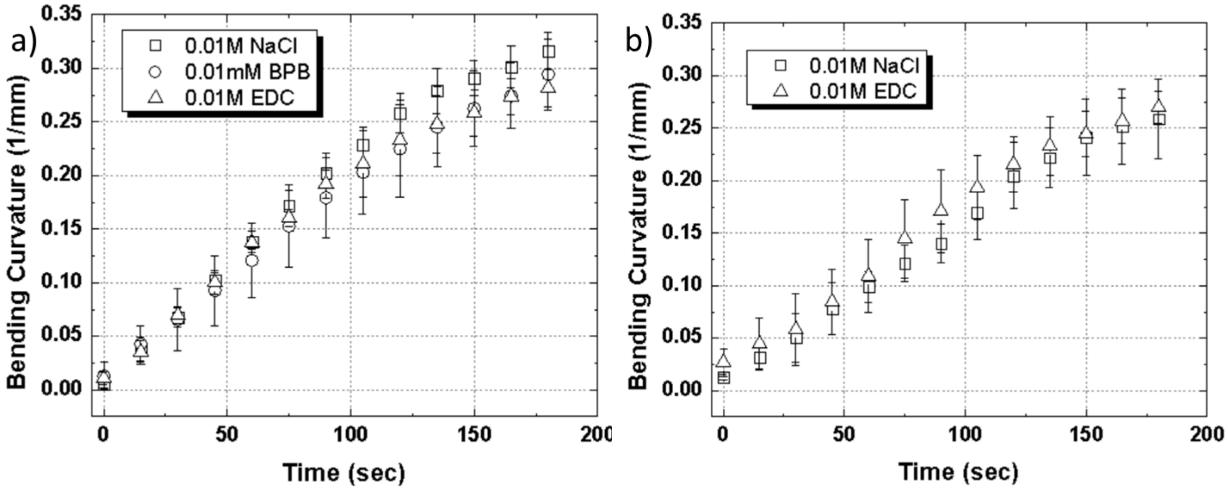

Fig S4. Bending curvature for 20% DMAEMA-Q gels and 20% NaAc gels, respectively, as a function of time. (a) The results indicate that within experimental error, equilibration in EDC and BPB did not affect the bending curvature. This implies that the amine/carboxylic coupling reaction, initiated by EDC, only proceeding to a minimal degree within the gel network. (b) The EDC did not affect the bending degree of the 20% NaAc gel after equilibration.

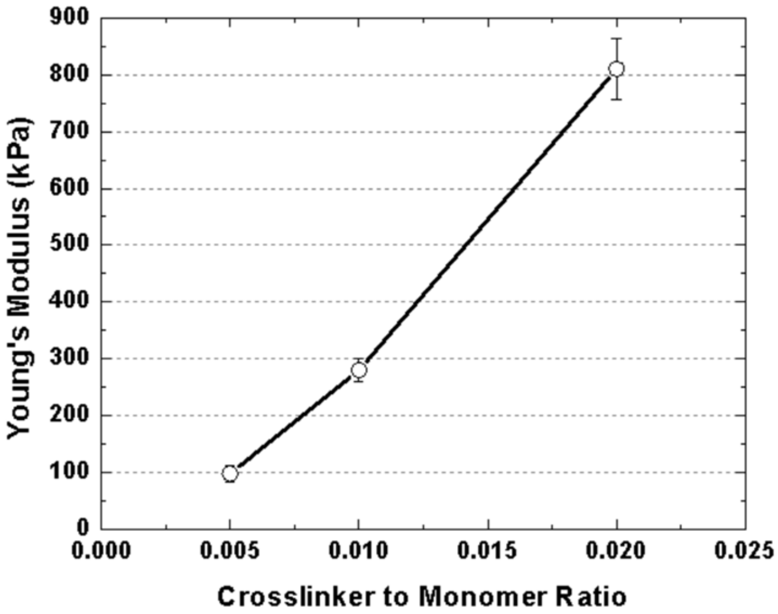

Fig S5. The Young's modulus plotted as a function of crosslinker to monomer ratio for a 20% DMAEMA-Q gel. Increasing the amount of crosslinker within the gel increases the modulus within the range studied.

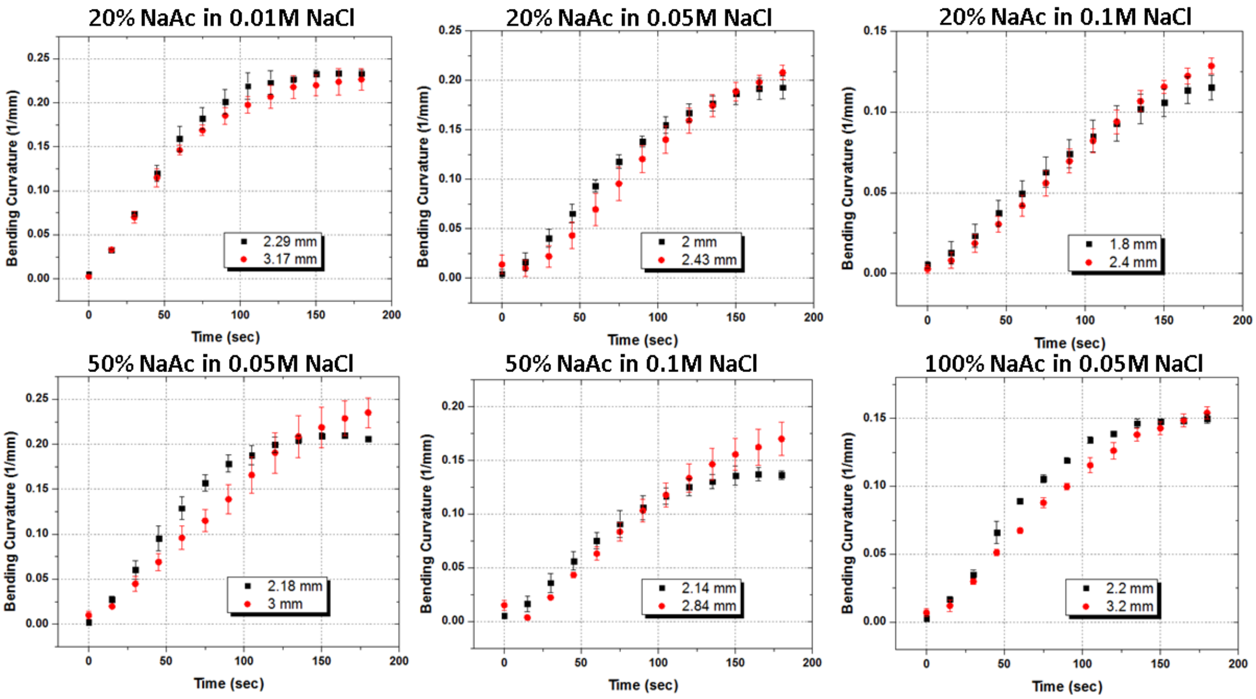

Fig S6. Bending curvature as a function of time for various sodium acrylate gel compositions and external salt concentrations. There is a good agreement between the two gel diameters after normalizing the bending date to 2 mm. This indicates that the bending degree is linearly related to the diameter of the gel cylinder after equilibration.

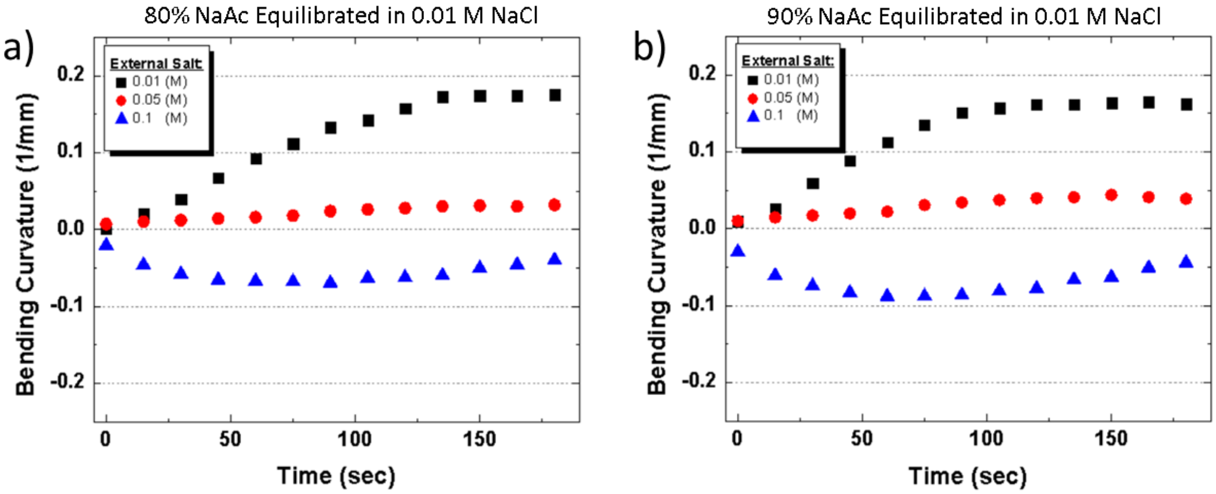

Fig S7. Bending curvature as a function of time for the sodium acrylate gels equilibrated in 0.01 M NaCl. Immediately after placing in 0.05 M NaCl and applying an electric field (5 V/cm), the bending is greatly diminished. The direction of bending temporarily reverses when placed in a salt solution with a concentration much higher than the equilibration solution (0.1 M NaCl).

Movie Legends

Video 1: This video demonstrates our ability to cut gel shapes with a laser writer. Following that, the cationic and anionic gels are bound and unbound by reversing the direction of the electric field.

Video 2: This movie demonstrates the walking motion of a gel walker in 0.01 M NaCl by controlling the direction of the electric field.

Video 3: This video demonstrates the ability to manipulate the motion of multiple gel walkers in solution. It is also possible for the walkers to adhere together if the field direction promotes binding.

References

1. N.A. Peppas, and E. W. Merrill, *J. Polym. Sci. Polym. Chem. Ed.*, 1976, **14,** 441–457.

2. D. A. Carr, and N. A. Peppas, *Macromol. Biosci.*, 2009, **9,** 497–505.

3. N. A. Peppas and A. G. Mikos, in *Hydrogels in Medicine and Pharmacy: Fundamentals*, ed. N. A. Peppas, CRC Press, Boca Raton, vol. 1, ch.1, pp.1-27.

4. N. Orakdogen and O. Okay, *Polym. Bull.*, 2006, **57,** 631–641.

5. L. Brannon-Peppas and N. A. Peppas, *Chem. Eng. Sci.*, 1991, **46,** 715–722.