# Supporting Information

# Mechanical Properties of Osmotically Stressed Polyelectrolyte Complexes and Multilayers: Water as a Plasticizer

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**Determining NaCl Activity in PEG Solutions Using VPO**

Vapor pressure osmometry was done on PEG solutions with and without salt. The salt activity was calculated using equations developed by Markarian and Schlenoff.[1] Activity values were plotted against % PEG and were fit to a parabolic function (Figure S1). Data points were fit up to 20% PEG and salt concentration of 0.5 M, since (according to the manufacturer) VPO becomes more error-prone at higher osmotic pressure values.[2] The parabolic equations were used to extrapolate to the higher PEG wt% regime. By plotting activity versus [NaCl] from the extrapolated values (Figure S2), the high salt regime for the high PEG solutions was constructed.

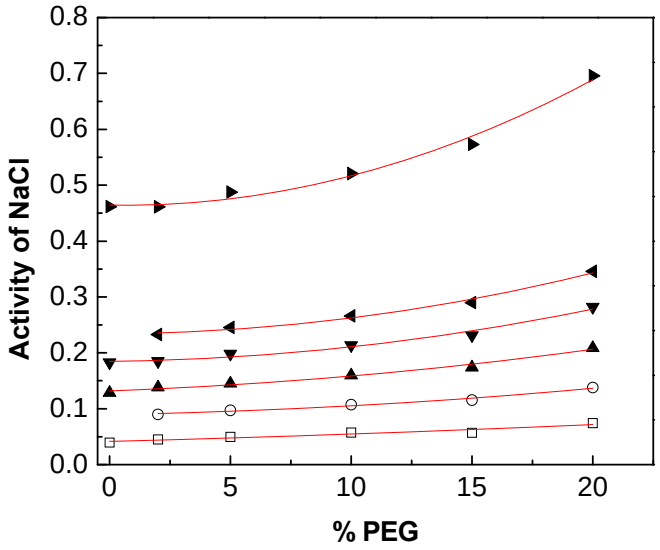



**Figure S1** Activity of NaCl versus PEG 8000 weight percentage in solution for different NaCl concentrations: [NaCl] = 0.05 (□), 0.1 (○), 0.15 (▲), 0.2 (▼), 0.25 (◄), and 0.5 M (►). The lines are fits to quadratic functions.

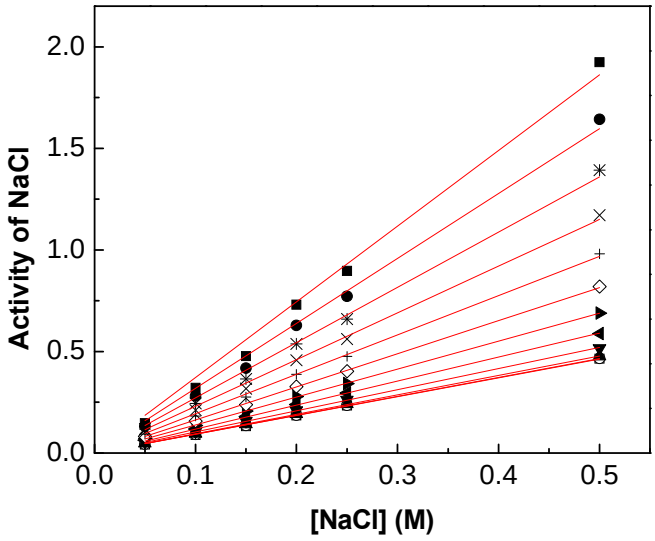



**Figure S2** Extrapolated activity values versus NaCl concentration for all PEG 8000 weight percentages 0% (□), 2% (○), 5% (▲), 10% (▼), 15% (◄), 20% (►), 25% (◊), 30% (+), 35% (×), 40% (□), 45% (●) and 50% (■).

## Calculation of Dry Matrix Thickness ($t_d$) of PEMUs

At ambient conditions (RT = 25 ºC, RH = 30%), the number of water molecules per ion pair in PSS/PDADMA PEMU = 2.4.[3]

Weight ratio of water to dry matrix at ambient conditions $R_a(w/w)$:

$$R_a(w/w) = \frac{m_{H_2O}}{M_d} = \frac{2.4 \times 18}{318.69} = 0.1355 \qquad (1)$$

Where $M_d$ is the dry molar mass of PSS/PDADMA PEMU and is equal to:

$$M_d = 1 \times M_{PSS} + 1 \times M_{PDADMA} + 0.06 \times (M_{PDADMA} + M_{Cl^-}) = 318.69 gmol^{-1} \qquad (2)$$

Where $M_{PSS}$ is 183 g/mol, $M_{PDADMA}$ is 126 g/mol, $M_{Cl^-}$ is 35.45 g/mol, and 0.06 corresponds to ratio of extrinsic PDADMA in PSS/PDADMA PEMUs.[4]

Estimating the density of the PEMU matrix to be 1.2 g/cm$^3$, the weight fraction of water is converted to volume ratio $R_a(v/v)$:

$$R_a(v/v) = \frac{V_{H_2O}}{V_d} = R_a(w/w) \times 1.2 = 0.1626 \quad (3)$$

Volume ratio is equivalent to thickness ratio of water, therefore:

$$t_{H_2O} = 0.1626 \times t_d \quad (4)$$

The thickness of the multilayer at ambient conditions ($t_a$) is the sum of dry matrix thickness and water contribution:

$$t_a = t_d + t_{H_2O} = 1.1626 \times t_d \quad (5)$$

$t_a$ was determined for PEMUs at ambient conditions by AFM, and the above equation was used to determine $t_d$ which was used in calculating water content of PEMUs.

**Fitting Force Curve in AFM**

Indentation and force applied to deflect the cantilever are given by the equations below:

$$\delta = (z - d) \quad (6)$$

$$F_{applied} = Kd = K(z - \delta) \quad (7)$$

where $\delta$ is the indentation of the tip into the material, $z$ is the distance of the tip relative to the material in the $z$-direction, $d$ is the deflection of the tip, and $K$ is the spring constant

of the cantilever. Force curves were analyzed using Hertzian contact mechanics that provide solutions for the indentation of a semifinite substrate with a hard probe. In this work, force curves were analyzed based on punch model represented in Equation 8:

$$F_{punch} = 2E_c R(z-d) \tag{8}$$

Where $E_c$ is the modulus of the material convoluted with the tip parameters and $R$ is the radius of the indenter.

The convoluted modulus, $E_c$, can be related to elastic modulus of the material and the indenter using Equation 9:

$$E_c = \left( \frac{1-\upsilon_1^{\,2}}{E_1} + \frac{1-\upsilon_2^{\,2}}{E_2} \right)^{-1} \tag{9}$$

Where $E_1$ and $\upsilon_1$ are the Young's modulus and Poisson ratio of the indented material respectively, $E_2$ and $\upsilon_2$ are the Young's modulus and Poisson ratio of the silicon indenter that were set to 150 GPa and 0.27 respectively. The value for $\upsilon_1$ was 0.5 since PEMUs are considered to be isotropic elastic materials in the range of loads applied.

Force *vs.* indentation graphs were fit to Equation 8 up to 10 % indentation. The half angle and the radius of the tip were 18° and 10 nm respectively, as provided by the manufacturer.

**PEG is Excluded from CoPECs**

Infra red spectroscopy was done on complexes in salt and PEG to see if PEG goes into the complex during the osmotic dehydration process. Two complex samples one in 0.1 M NaCl and one in PEG 50% with 0.1 M NaCl activity were dried under vacuum, crushed into a fine powder and made into KBr pellets. The complex in PEG was washed for 10

sec in water to get rid of any PEG residue sticking to the sample surface. The spectrum of the complex in PEG matched that of the complex in salt, proving that PEG does not diffuse into the complex while applying osmotic stress.

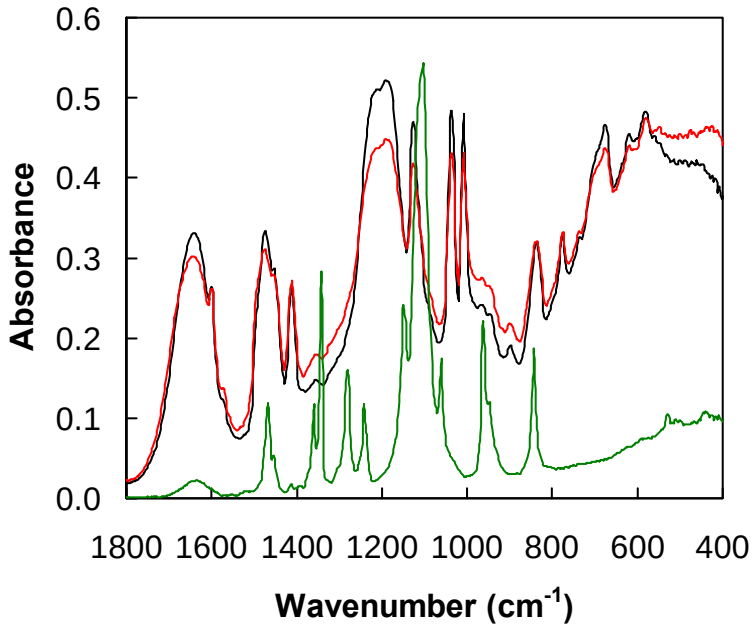



**Figure S3** FTIR spectrum of PSS/PDADMA CoPECs in 0.1 M NaCl (in black) and in PEG 50% with 0.1 M NaCl activity (in red). Spectrum in green is for PEG 8000.

**Osmotic Pressure of PEG 8000**

Osmotic pressure of PEG 8000 without salt was determined by vapor pressure osmometry from osmolality measurements. The osmotic pressure shows a nonlinear increase with PEG concentration (Figure S4). Figure S4 also shows osmotic pressure data determined by Stanley and Strey[5] for PEG 8000 at 20 °C. The slight difference at the higher PEG %wt is probably a result of the difference in temperature in the two studies. Our data was collected at room temperature (23 °C); osmotic pressure was shown to decrease with increase in temperature. [5]

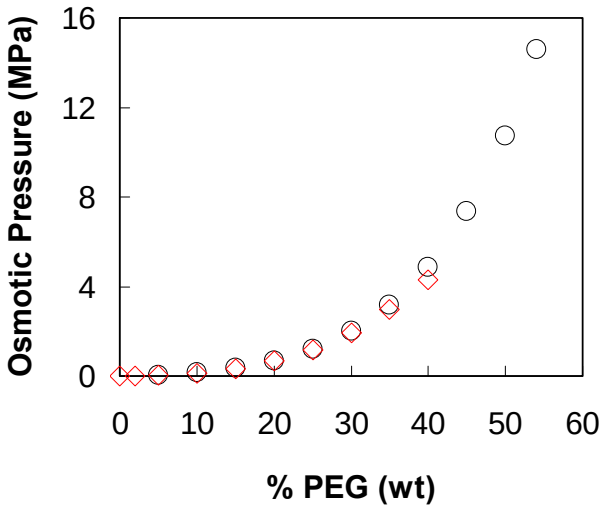



**Figure S4** Osmotic pressure of PEG 8000 at different weight percentages (◊) determined at 23 $^{o}$C by vapor pressure osmometry. (○) is data determined by Stanley and Strey for PEG 8000 at 20 °C.[5]

**Effect of PEG Concentration on Rate of Dehydration**

The rate of dehydration increases with increasing PEG concentration. Figure S5 shows that at 17 hours in PEG, the thickness of the transparent shell increases with increasing PEG wt% in solution, and the samples became completely dehydrated at PEG wt% ≥ 40 at this time. Figure S6 shows decrease in mass of PEC samples as they dehydrate showing that rate of dehydration is faster in the highest PEG concentration solution. The PEC samples had approximately the same weight before treatment in PEG.

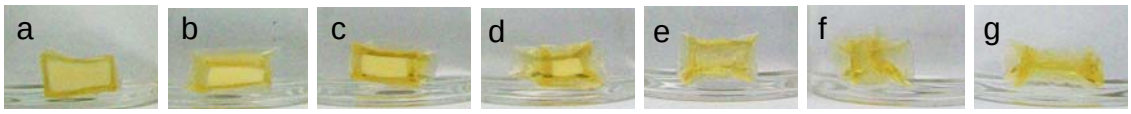



**Figure S5** PSS/PDADMA CoPECs after 17 hrs soaking in PEG (a) 20, (b) 25, (c) 30, (d) 35, (e) 40, (f) 45, and (g) 50%.

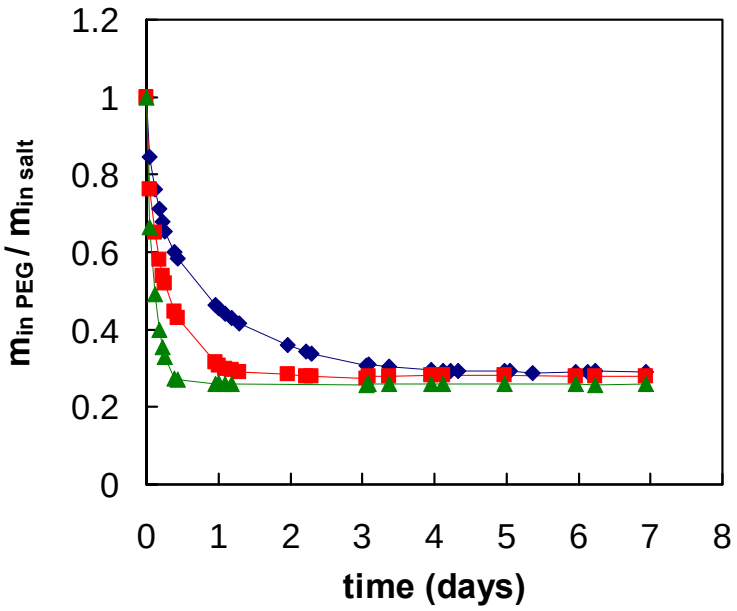



**Figure S6** Ratio of mass of CoPECs in PEG 20% (♦), PEG 30% (■) and PEG 50% (▲) to mass in 0.1 M NaCl versus time of soaking in PEG.

**Rehydration of PEG Dehydrated Sample When Exposed to Salt Solution**

CoPEC samples dehydrated in PEG solutions rehydrated to their initial water content as shown by the increase sample mass (Figure S7) and porosity (Figure S8) after a long time in salt solution.

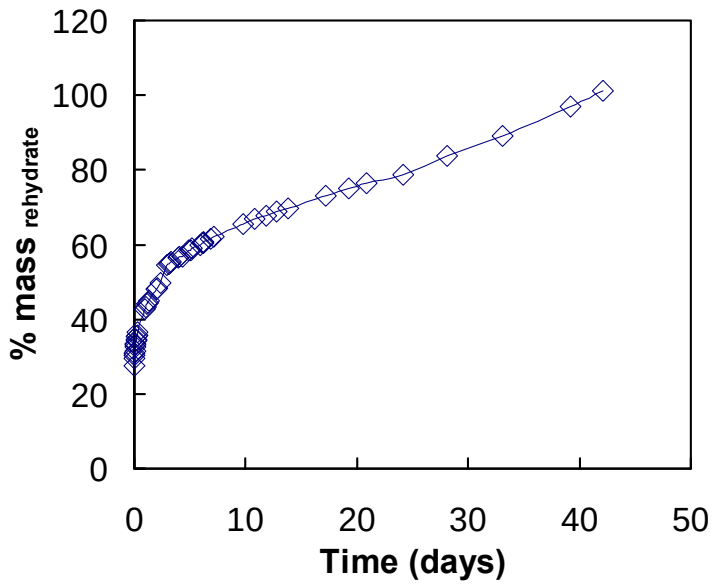



**Figure S7** Percent increase in mass of dehydrated complex sample on soaking in 0.1 M NaCl. The sample was initially equilibrated in 0.1 M NaCl, and then dehydrated in PEG 30% with activity of 0.1 NaCl.

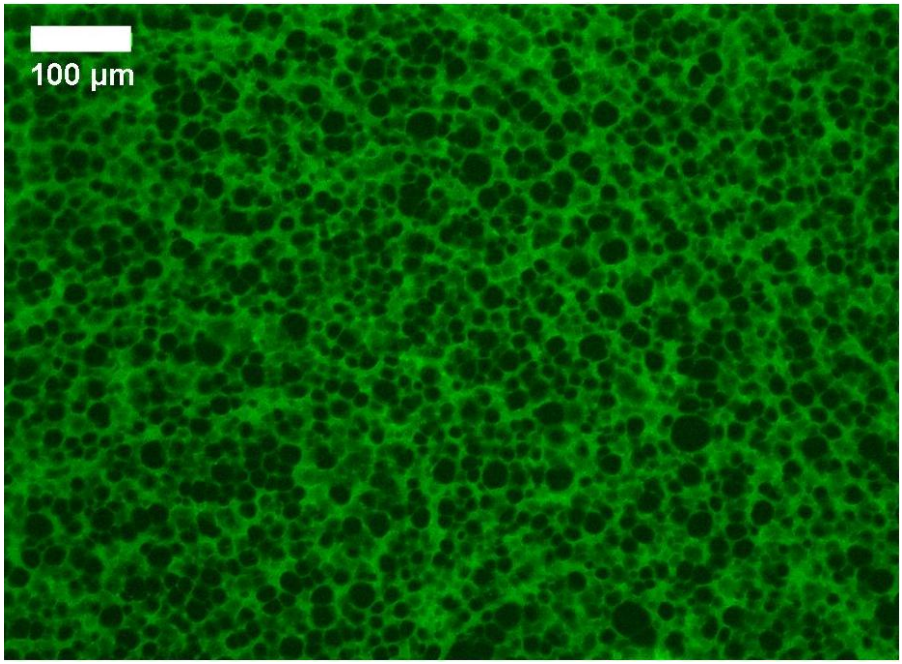
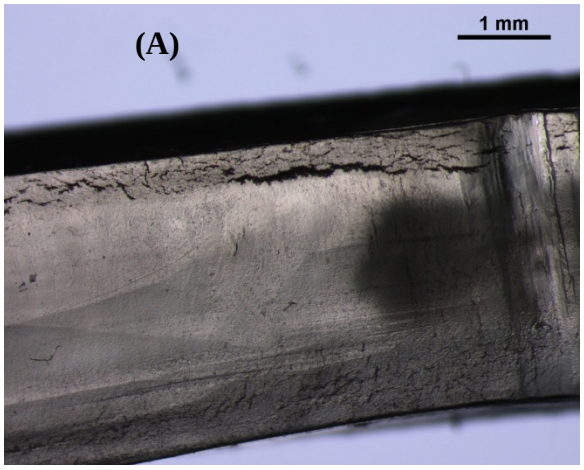


**Figure S8** Epi-fluorescence microscope image of 10 μm-thick rehydrated complex slice in 0.1 M NaCl. The sample was initially swollen in 0.1 M NaCl, and then dehydrated in PEG 25% with salt activity of 0.1 NaCl and allowed to rehydrate for 30 days in 0.1 M NaCl before slicing.

**Crack Formation in PEG-dried CoPECs after Tensile Tests**

Cracks were seen in microscope images of PSS/PDADMA complex sample treated sequentially in increasing PEG weight percentages and tested by tensile testing. Figure S9 shows cracks formed in samples in PEG 45 and 50%.



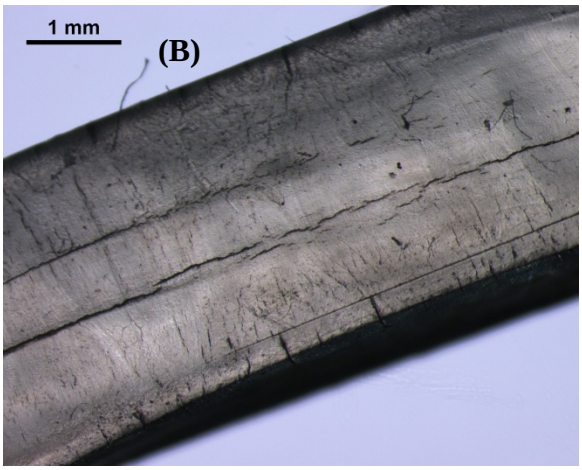



**Figure S9** Image of PSS/PDADMA CoPEC in PEG 45% with NaCl activity equivalent to 0.1 M (A) and PEG 50% with salt activity equivalent to 0.5 M NaCl (B) after uniaxial tensile testing.

**Kinetics of Dehydration of PEMU in PEG 30%**

Change in modulus of PSS/PDADMA multilayers with time in PEG 30% solution was used to determine their rate of dehydration. Figure S10 shows that dehydration of these nanometer thick films is very fast: after only 7 minutes, which is the minimum time needed to set up the AFM instrument for the measurement. After an initial jump the modulus stays constant.

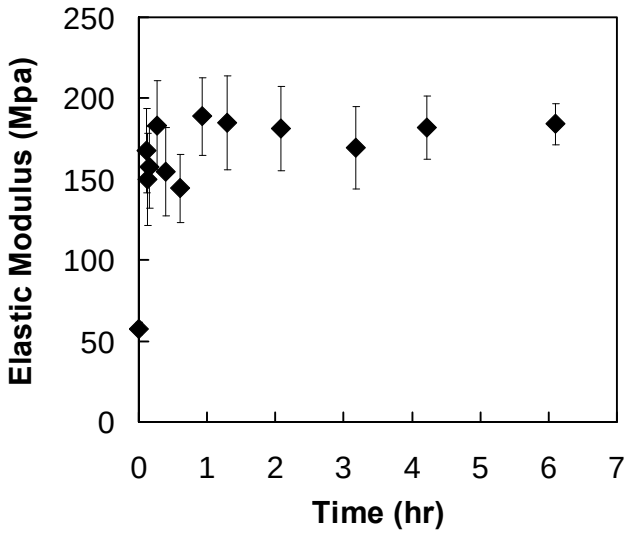



**Figure S10** Kinetics of dehydration of $(PDADMA/PSS)_{30}$ in PEG 30%. The PEMUs were first equilibrated in 10 mM NaCl then PEG 30%, with NaCl activity equivalent to 10 mM, was added. Force curves were collected at tip velocity of 1 μm/sec.

**Calculation of Effective Crosslinking Density in PEMUs at Different PEG wt%:**

The number of water molecules per ion pair is defined by:

$$\#H_2O = \frac{n_{H_2O}}{n_{matrix}} \tag{10}$$

Where $n_{H2O}$ and $n_{matrix}$ are the number of moles of water and polymer matrix in the PEMU.

Given the water content in PEMUs, determined as ratio of thickness from AFM imaging, the number of water molecules was determined:

$$\frac{t_{H_2O}}{t_{matrix}} = \frac{V_{H_2O}}{V_{matrix}} = \frac{m_{H_2O}/\rho_{H_2O}}{m_{matrix}/\rho_{matrix}} = \frac{\left(n_{H_2O} \times M_{H_2O}\right)/\rho_{H_2O}}{\left(n_{matrix} \times M_{matrix}\right)/\rho_{matrix}} \tag{11}$$

*t* is for thickness, *V* is for volume, *m* is for mass, $\rho$ is for density (ca. 1.2 g/cm$^3$ for the matrix and 1 g/cm$^3$ for water), *M* is for molecular weight (ca. 318.69 g/mole for matrix and 18 g/mole for water) and *n* is for number of moles.

Rearranging the equation (11) gives:

$$\#H_2O = \frac{n_{H2O}}{n_{matrix}} = \frac{t_{H2O}}{t_{matrix}} \times \frac{318.69}{18 \times 1.2} \tag{12}$$

To calculate the crosslink density, moles of crosslinks in 1 mole of the PEMU is considered to be equal to 1-y. Ion-pair density (*IP*) is defined as moles of ion pairs ($n_{Ip}$) in unit volume of PEMU ($V_{PEMU}$):

$$IP = \frac{n_{Ip}}{V_{PEMU}} \tag{13}$$

$V_{PEMU}$ is calculated from the total mass of PEMU (mass of water and matrix) and its density (ca. 1.1 g/cm$^3$ for the wet PEMU). Then the equation used to calculate crosslink density at PEG concentration ($x$) becomes:

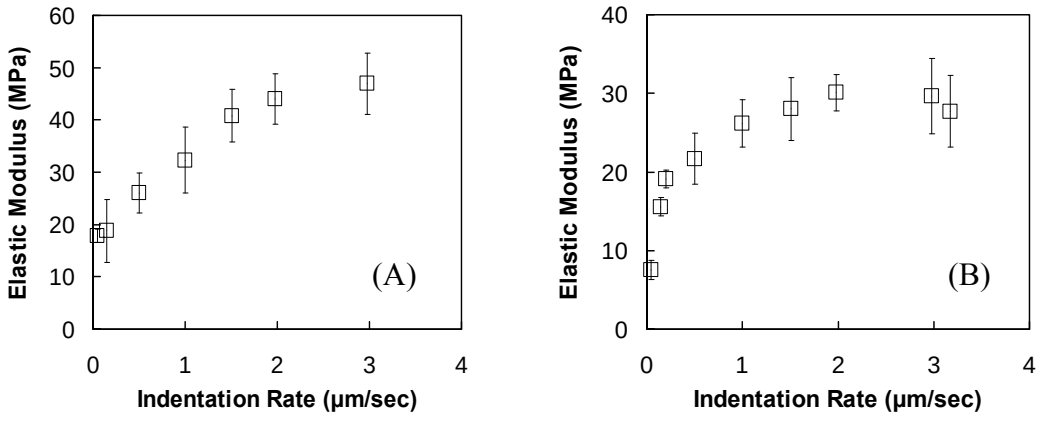
$$IP_{PEG(x)} = \frac{(1-y)\times 1.1}{318.69 + 18\times(\#H_2O)_{PEG(x)}} \qquad (14)$$

Doping level (y) at 10 mM NaCl is assumed to be equal to zero. The effective crosslink density (c') is then calculated assuming 30:70 network to ladder interactions (i.e network fraction $\Omega = 0.3$):

$$c' = \Omega \times IP \qquad (15)$$

**Change in Modulus of PEMUs with Indentation Rate**

Figure S11 shows the change in modulus of PSS/PDADMA PEMUs with indentation rate in different PEG concentrations. As PEG percentage increases in solutions, the modulus shows less change with indentation rate indicating a decrease in damping properties due to loss of water.



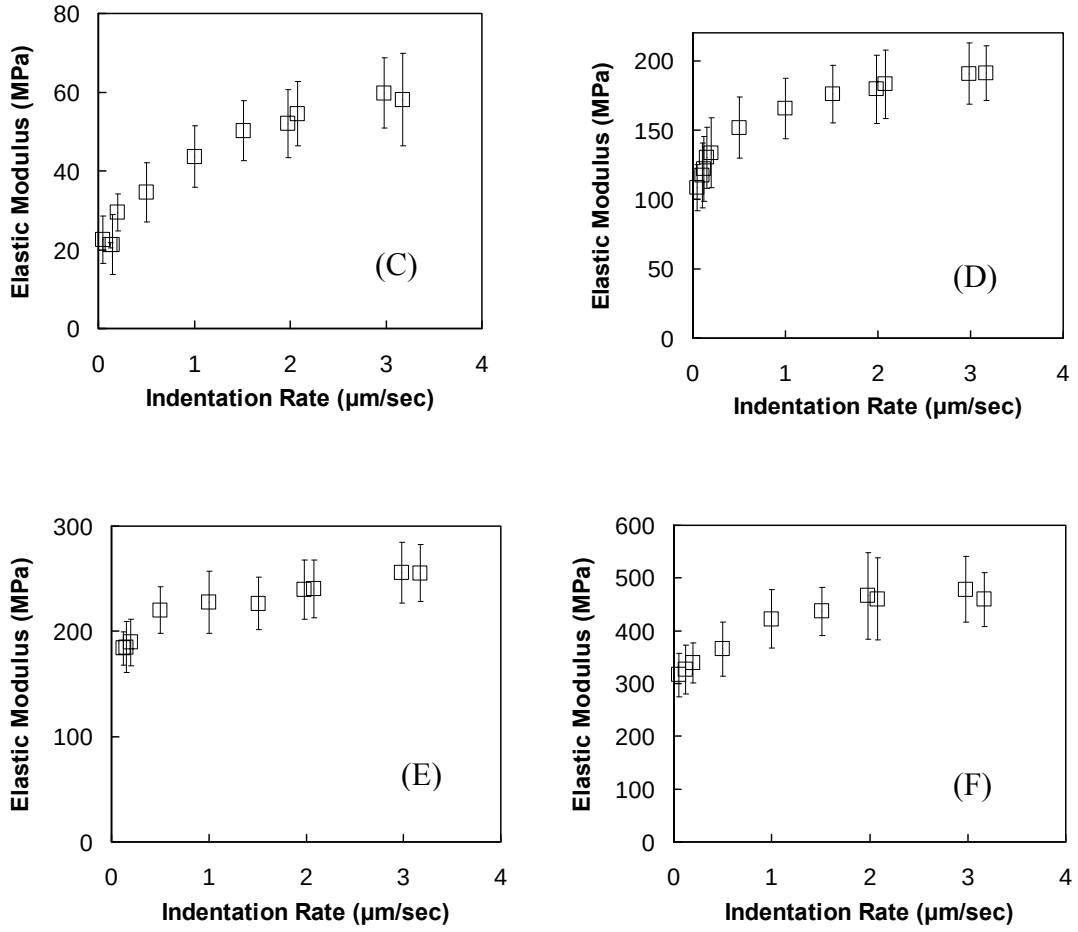



**Figure S11** Change in modulus with increasing indentation rate for $(PDADMA/PSS)_{15}$ PEMUs in PEG (A) 5%, (B) 10%, (C) 15%, (D) 25%, (E) 35% and (F) 45% with salt activity of 10 mM NaCl.

## References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2. http://www.wescor.com/biomedical/osmometer/vapro5600.html.
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4. Schlenoff, J. B.; Rmaile, A. H.; Bucur, C. B. *J. Am. Chem. Soc.* **2008,** *130*, 13589-13597.
5. Stanley, C. B.; Strey, H. H. *Macromolecules* **2003,** *36*, 6888-6893.