Supplementary Information (SI) for Soft Matter.

Electronic Supplementary information for

Divalent Cation Effects in the Glass Transition of Poly (diallyl dimethylammonium)-Poly (styrene sulfonate) Complexes

Tamunoemi Braide,[1] Suvesh Manoj Lalwani,[1] Chikaodinaka I. Eneh,[1] Jodie L. Lutkenhaus[1,2]

1. Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843, United States
2. Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77840, USA

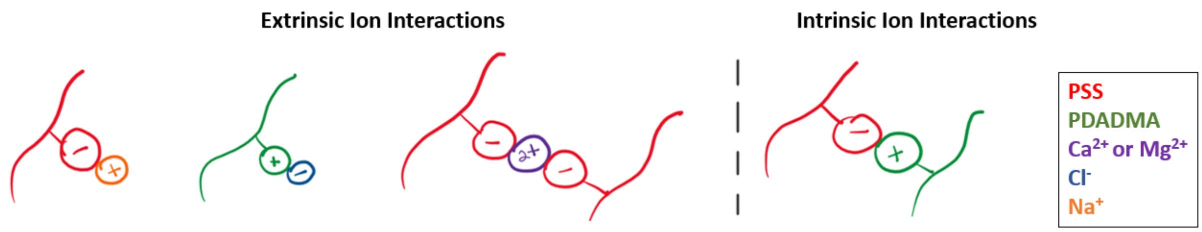

Figure S1. Types of interactions occurring within the PDADMA-PSS complex in the presence of NaCl, $CaCl_2$, and $MgCl_2$. In our system containing PDADMA and PSS in the presence of NaCl, $CaCl_2$, and $MgCl_2$, two distinct ion interactions are possible: extrinsic and intrinsic. Under these broad types, **Figure S1** shows the four types of ion-ion interactions that can occur.

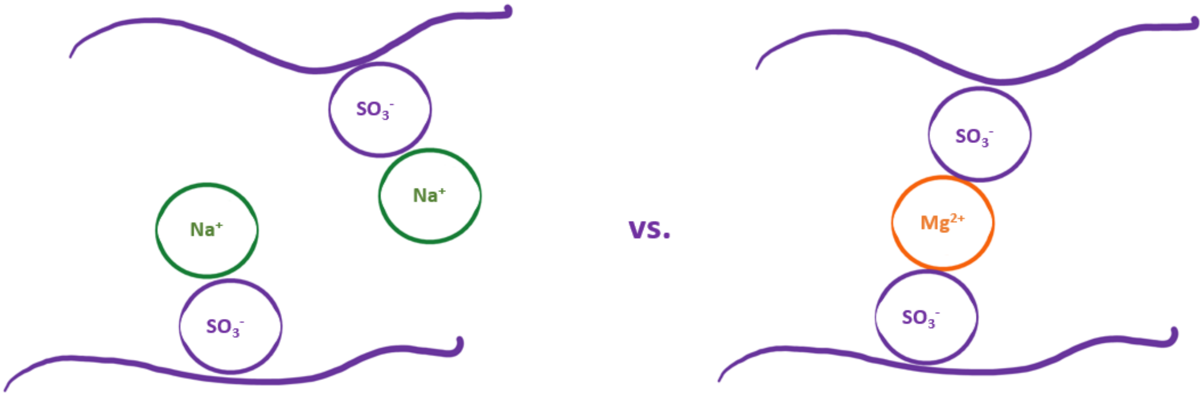

Figure S2. Schematic of monovalent and divalent counterion interaction with PSS chains, illustrating the formation of crosslinks in a complex when divalent cations (Ca^{2+} or Mg^{2}) are introduced to PDADMA/PSS polyelectrolyte assemblies. This results in a molecule with a denser structure, reduced water permeability, and increased salt retention and stability. [1]

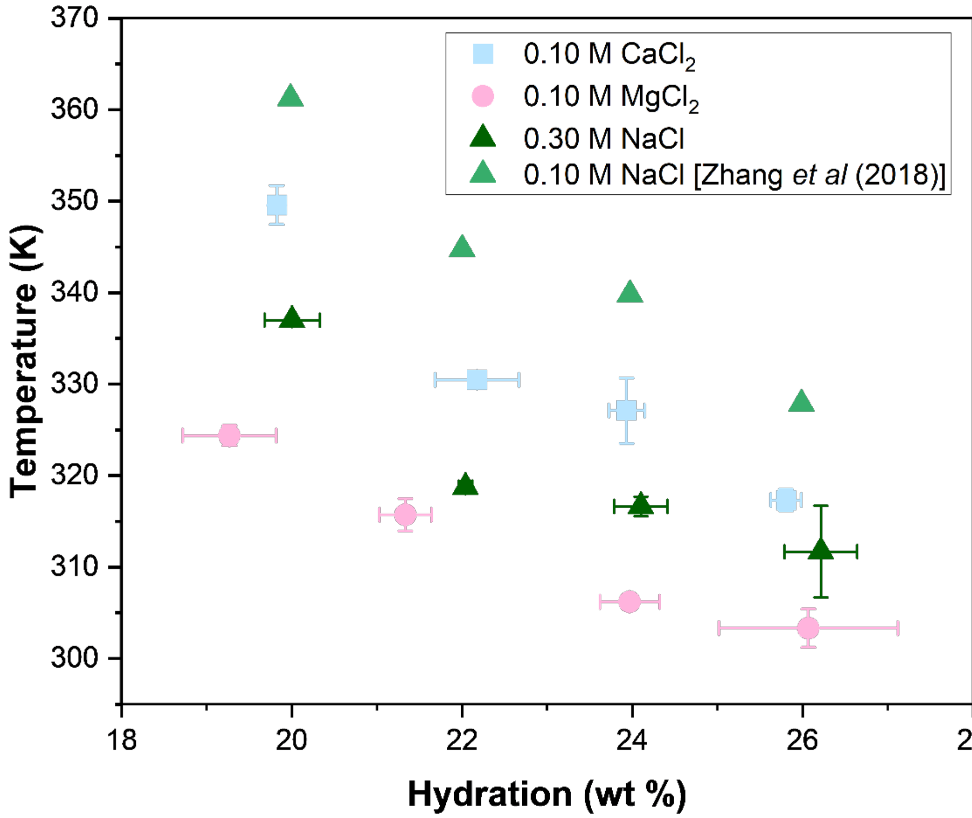

Figure S3. Glass transition temperatures of PDADMA-PSS PECs prepared from NaCl, $CaCl_2$, or $MgCl_2$ solutions. The isolated PECs were rehydrated with a solution matching that of its assembly and examined using MDSC. 0.10 M NaCl reproduced with permissions from [2] "Molecular Origin of the Glass Transition in Polyelectrolyte Assemblies." By Zhang, Y.; Batys, P.; O'Neal, J. T.; Li, F.; Sammalkorpi, M.; Lutkenhaus, J. L. 2018. *ACS Central Science*, *4* (5), 638-644. Copyright (2018) American Chemical Society.

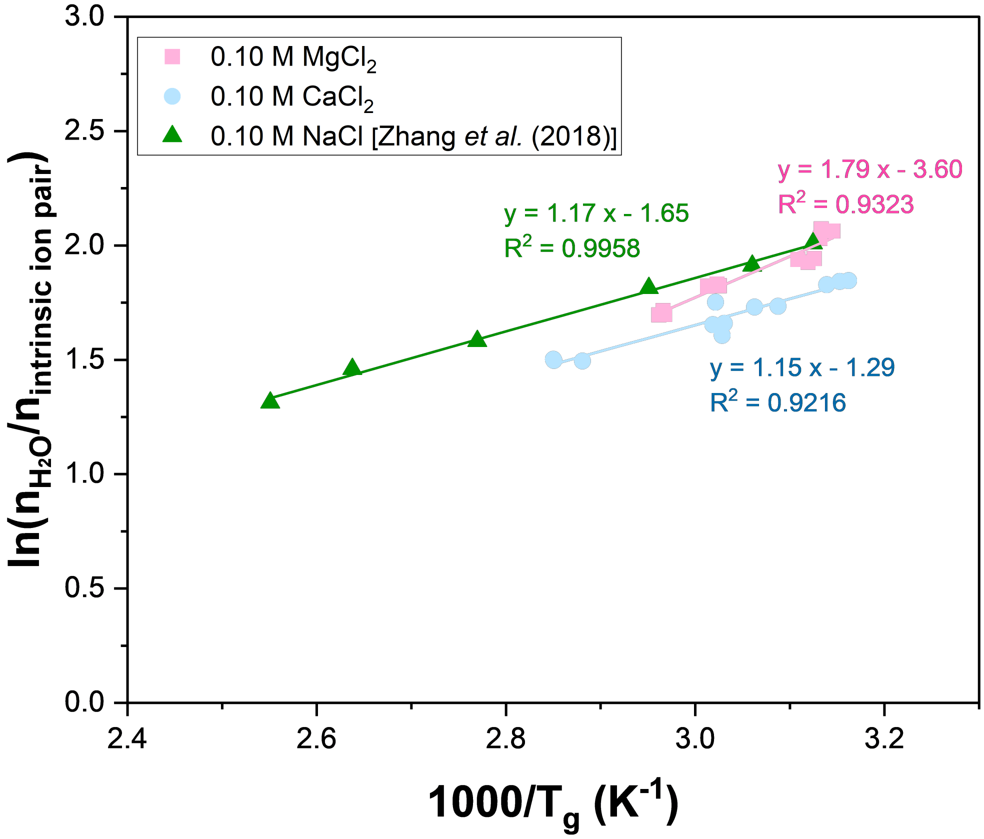

Figure S4. $ln\left({}^{n_{H_2O}}/_{n_{intrinsic\ ion\ pair}}\right)$ vs $\frac{1000}{T_g}$ for PDADMA-PSS PEC systems made from 0.10 M $MgCl_2$, 0.10 M $CaCl_2$, and 0.10 M NaCl solutions. The data for PDADMA-PSS PECs at 0.10 M NaCl were reproduced with permission from [2] "Molecular Origin of the Glass Transition in Polyelectrolyte Assemblies." By Zhang, Y.; Batys, P.; O'Neal, J. T.; Li, F.; Sammalkorpi, M.; Lutkenhaus, J. L. 2018. *ACS Central Science*, *4* (5), 638-644. Copyright (2018) American Chemical Society. The lines are linear first of the data to Equation 1. Each data point represents a single experiments.

Table S1. Summary of compositional analysis from NAA for $CaCl_2$-PECs

	Na (wt%)	S (wt%)	Cl (wt%)	Ca (wt%)	N (wt%)
0.03 M	1.83E-02 ± 5.00E-04	9.05E+00 ± 6.0E-02	1.12E+01 ± 7.00E-02	3.96E-02 ± 5.00E-04	1.67E+01 ± 7.62E-02
0.10 M	2.41E-02 ± 6.77E-03	1.02E+01 ± 2.28E+00	2.14E+00 ± 4.59E-02	2.07E-01 ± 5.13E-02	1.04E+01 ± 2.00E+00
0.15 M	3.76E-02 ± 1.10E-02	9.91E+00 ± 2.74E+00	2.30E+00 ± 5.58E-02	1.53E+00 ± 2.15E-01	9.36E+00 ± 2.40E+00
0.20 M	3.23E-02 ± 1.30E-02	7.98E+00 ± 3.26E+00	2.91E+00 ± 7.67E-02	1.60E+00 ± 2.70E-01	8.11E+00 ± 2.86E+00

Table S2. Summary of compositional analysis from NAA for $MgCl_2$-PECs

	Na (wt%)	S (wt%)	Cl (wt%)	Mg (wt%)	N (wt%)
0.03 M	1.94E-02 ± 6.00E-04	9.46E+00 ± 6.00E-02	1.04E+01 ± 9.00E-02	3.52E-02 ± 5.00E-04	1.64E+01 ± 8.84E-02
0.10 M	2.22E-02 ± 7.60E-04	8.73E+00 ± 6.98E-02	1.38E+01 ± 6.00E-01	2.30E-01 ± 2.74E-03	1.82E+01 ± 4.78E-01
0.15 M	3.05E-02 ± 9.40E-04	8.37E+00 ± 6.70E-02	1.75E+01 ± 8.00E-01	3.93E-01 ± 4.66E-03	2.07E+01 ± 6.35E-01
0.20 M	2.92E-02 ± 9.73E-03	8.23E+00 ± 2.71E+00	2.54E+00 ± 6.92E-02	7.98E-01 ± 9.92E-02	8.25E+00 ± 2.37E+00

Table S3. NMR integration comparing monovalent and divalent salt in PDADMA-PSS PECs

	Ratio of PSS:PDADMA in complex	**PSS mol%**
0.30 M NaCl - PEC	0.85 ± 0.03	46 ± 1
0.10 M NaCl – PEC (from ref. [2])	0.84± 0.09	46 ± 3
0.03 M $CaCl_2$ - PEC	0.88 ± 0.03	47 ± 1
0.10 M $CaCl_2$ - PEC	0.88 ± 0.04	48 ± 1
0.15 M $CaCl_2$ - PEC	0.88 ± 0.04	47 ± 1
0.20 M $CaCl_2$ - PEC	0.93 ± 0.02	48 ± 0.5
0.03 M $MgCl_2$ - PEC	0.92 ± 0.02	48 ± 1
0.10 M $MgCl_2$ - PEC	0.87 ± 0.04	48 ± 0.1
0.15 M $MgCl_2$ - PEC	0.86 ± 0.03	46 ± 1
0.20 M $MgCl_2$ - PEC	0.91 ± 0.01	48 ± 0.2

Table S4. Ion properties of sodium, calcium, and magnesium ion

	Na^{+}	Ca^{2+}	Mg^{2+}
Jones Dole B Coefficient[3]	0.085	0.298	0.385
Hydrated radius (pm)[4]	358	412	428
Bare ion radius (pm)[3]	102	100	72
Hydration number[3]	3.5	7.2	10

Table S5. Doping levels, composition, and the enthalpy associated with PECs prepared from different salts and concentrations.[a]

Salt–concentration	y^{+}	y^{-}	**PSS: PDADMA ratio**	**Enthalpy (kJ/mol)**
$CaCl_2$-0.03 M	0.500 ± 0.004	0.0020 ± 0.0001	0.88 ± 0.03	9.6 ± 0.7
$CaCl_2$-0.10 M	0.20 ± 0.03	0.008 ± 0.003	0.88 ± 0.04	9.5 ± 2.0
$CaCl_2$-0.15 M	0.20 ± 0.05	0.060 ± 0.020	0.88 ± 0.04	11.7 ± 2.2
$CaCl_2$-0.20 M	0.3 ± 0.1	0.080 ± 0.040	0.93 ± 0.02	9.6 ± 1.5
$MgCl_2$-0.03 M	0.500 ± 0.005	0.0020 ± 0.0001	0.92 ± 0.02	9.4 ± 1.3
$MgCl_2$-0.10 M	0.60 ± 0.03	0.0200 ± 0.0003	0.87 ± 0.04	14.9 ± 2.8
$MgCl_2$-0.15 M	0.70 ± 0.04	0.0300 ± 0.0005	0.86 ± 0.03	10.3 ± 2.1
$MgCl_2$-0.20 M	0.20 ± 0.07	0.060 ± 0.020	0.91 ± 0.01	12.5 ± 2.0

[a]The error in y^{+} and y^{-} represents the standard deviation of a minimum of three experiments. The error in the enthalpy represents the 95% confidence interval from linear fits (see **Figure 6**).

References

(1) Reurink, D. M.; Willott, J. D.; Roesink, H. D. W.; de Vos, W. M. Role of Polycation and Cross-Linking in Polyelectrolyte Multilayer Membranes. *ACS Applied Polymer Materials* **2020**, *2* (11), 5278-5289. DOI: 10.1021/acsapm.0c00992.

(2) Zhang, Y.; Batys, P.; O'Neal, J. T.; Li, F.; Sammalkorpi, M.; Lutkenhaus, J. L. Molecular Origin of the Glass Transition in Polyelectrolyte Assemblies. *ACS Central Science* **2018**, *4* (5), 638-644. DOI: 10.1021/acscentsci.8b00137.

(3) Marcus, Y. *Ion Properties*; CRC Press, 1997.

(4) Volkov, A. G.; Paula, S.; Deamer, D. W. Two mechanisms of permeation of small neutral molecules and hydrated ions across phospholipid bilayers. *Bioelectrochemistry and Bioenergetics* **1997**, *42* (2), 153-160. DOI: https://doi.org/10.1016/S0302-4598(96)05097-0.