Supporting Information

Saloplastic Macroporous Polyelectrolyte Complexes: Cartilage Mimics

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Relative Solvent Quality

A turbidimetry experiment was performed on NaPSS and PDADMAC solutions with increasing NaCl content to determine the relative solvent quality at room temperature (22 ºC). The experiment was done using a Cary 100 Bio UV-Visible spectrophotometer; Absorbance values at 500 nm were plotted against [NaCl] (Figure S1)

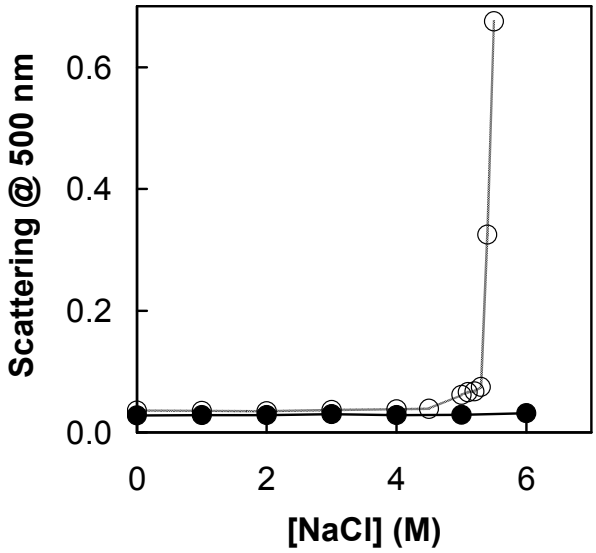


Figure S1. Scattering at 500 nm of NaPSS and PDADMAC solutions in 2.5 M NaCl at room temperature. (○)scattering from PSS; and (●)scattering from PDADMA.

Detection of PSS Release by UV-Vis Absorption

NaPSS released from pores of chopped PSS/PDADMA CoPECS was followed by UV-Vis absorption spectra of the rinsing water over nine days. The rinsing water of complexes prepared with the highest PSS initial concentration showed the highest PSS peak indicating that most of the excess PSS used during preparation was trapped in the pores of the complex and released on chopping.

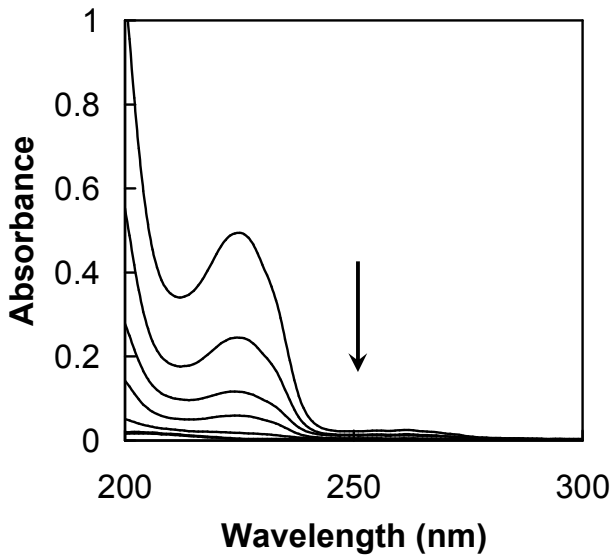


Figure S2. UV-Visible absorption spectra of the washing water of PSS/PDADMA complexes prepared from PSS:PDADMA ratios of 0.6, 0.8, 1, 1.2, 1.4, 1.6, and 1.8 after 2 days of washing. The arrow indicates the decrease of the PSS peak (at 225 nm) in the washing water with decrease of initial PSS concentration used in the sample preparation.

A non-chopped CoPEC was rinsed in water for nine days; the rinsing water was changed every day and a UV-Visible absorption spectrum was collected. The PSS absorbance at 225 nm was compared to the absorbance of a chopped CoPEC (Figure S3). Almost ten times as PSS was released from the latter sample, consistent with closed-shell porosity.

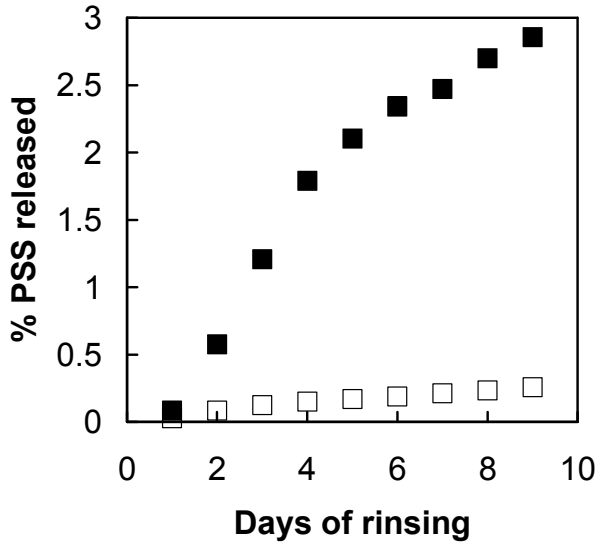


Figure S3. The percentage of PSS released from a PSS/PDADMA CoPEC over a period of 9 days. (■) PSS released from a chopped complex; (□) PSS released from a non-chopped sample.

Detection of Q-PECs by UV-Vis Absorption and Dynamic Light Scattering

Figure S4 shows that ultracentrifugation promotes the precipitation of the quasisoluble complex in the supernatant. The PSS peak, corresponding to the complexed PSS in the supernatant, decreases under the ultracentrifugal fields.

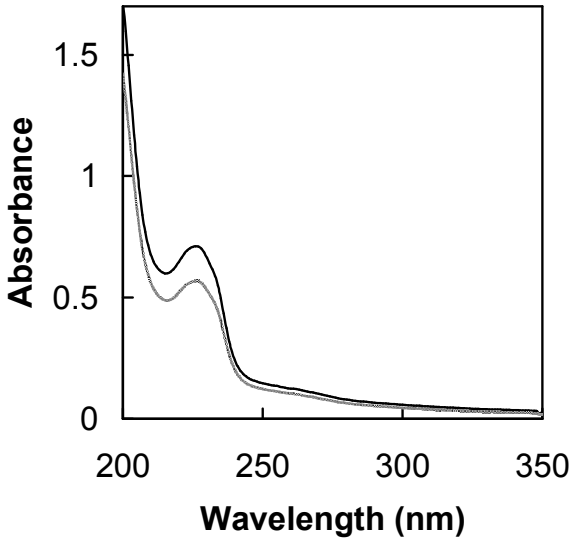


Figure S4: UV-Visible absorption spectra of the supernatant of PSS/PDAMDA complex. The solid line is for the supernatant collected before centrifugation and the dotted line is for the supernatant collected after centrifugation.

Dynamic light scattering of dilute solution of the supernate of PSS/PDADMA shows a correlation function revealing particles of 36.9 nm in hydrodynamic radius (Figure S5).

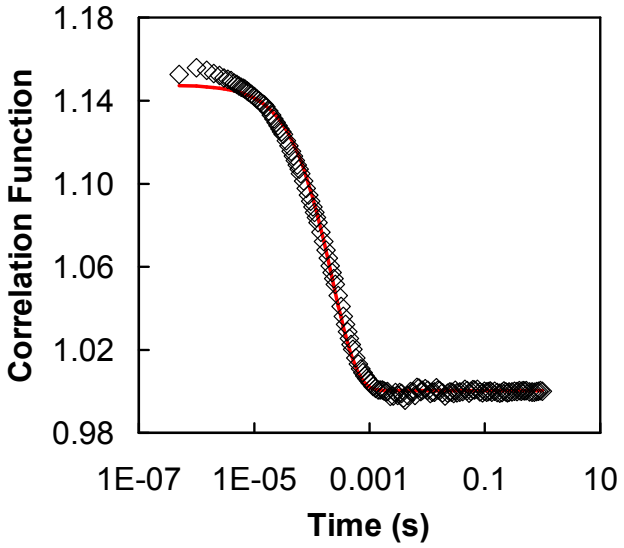


Figure S5. Correlation function of supernate solution of PSS (0.5 M, 2.5 M)/PDADMA (0.5 M, 2.5 M).

Calculation of the PSS Concentration in the Pores

To estimate the concentration of extra PSS in the pores of the complex when immersed in different NaCl concentrations, we used the data determined by Porcel and Schlenoff on the water content of PSS/PDADMA complexes under different saline conditions[1] and the results of the elemental analysis that showed a 14% of excess PSS (by mole fraction). We assume that that all the excess PSS in the complex is present in the pores.

The concentration of PSS in the pores can be determined by this equation:

$$[PSS]_{pore} = \frac{1000 f_{NaPSS}\left(1 - m_{H_2O}\right)}{M_{NaPSS}\left(m_{H_2O} - f_{hydration} m_{matrix}\right)} \quad (1)$$

Where M_{NaPSS} represents the molecular weight of PSS in the sodium form, m_{H_2O} represents the total mass of water in 1 g of wet complex. f_{NaPSS} and $f_{hydration}$ are the weight fractions of PSS in the pores and hydration water respectively that can be estimated by equations (2) and (3):

$$f_{NaPSS} = \frac{0.14 M_{NaPSS}}{M_{matrix} + 0.14 M_{NaPSS}} \quad (2)$$

$$f_{hydration} = \frac{18\left[11.2y + 6.9(1-y)\right]}{M_{matrix}} \quad (3)$$

M_{matrix} is the molecular weight of the complex matrix, which is equal to the molecular weights of the interacting polymers and the doping ions:

$$M_{matrix} = M_{PSS} + M_{PDADMA} + yM_{Na} + yM_{Cl} \quad (4)$$

Where M_{PSS} and M_{PDADMA} represent the molecular weights of the complexed polyelectrolytes; M_{Na} and M_{Cl} represent the molecular weights of the doping ions and y is the doping constant.

m_{matrix} in equation (1) is the mass of complexed polyelectrolytes and doping ions in 1g of complex, which is determined by subtracting the mass of excess PSS and pore salt from the total dry mass of the complex and can be determined using equation (5):

$$m_{matrix} = (1 - m_{H_2O})(1 - f_{NaPSS}) - 0.0584 m_{H_2O} C_{NaCl} \quad (5)$$

The results for PSS/PDADMA complex in different NaCl solutions are shown in Figure S6.

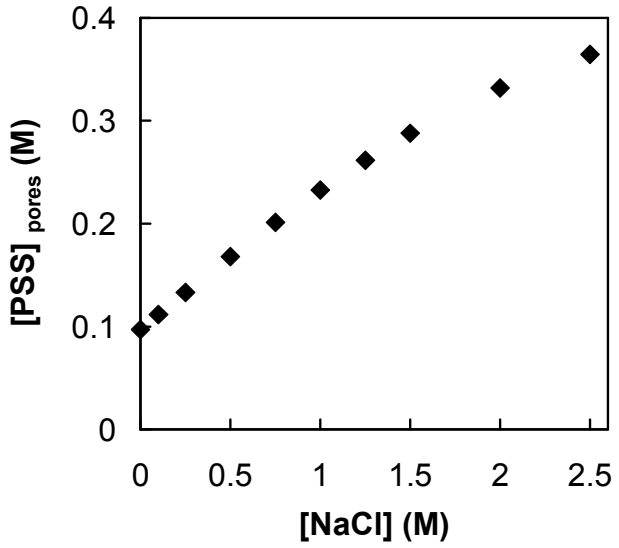


Figure S6. Concentration of PSS in the pores of PSS (0.5 M, 2.5 M)/PDADMA (0.5 M, 2.5 M) when doped in NaCl solutions of different concentrations determined using r_{H_2O} data by Porcel and Schlenoff[1].

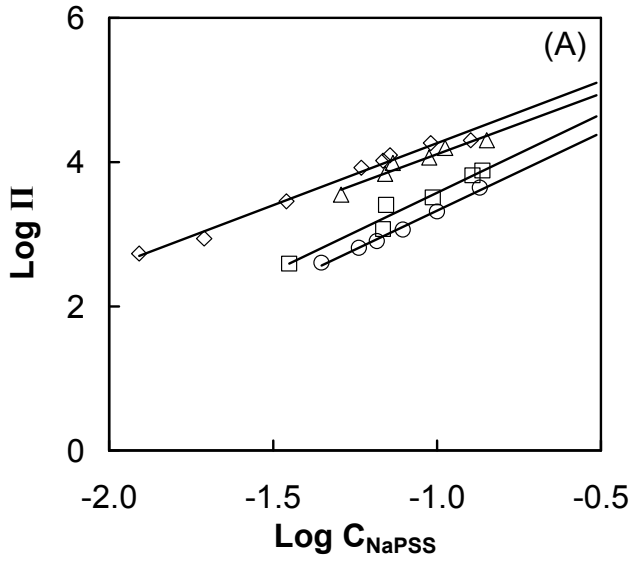
Estimation of the Osmotic Pressure in the Pores of the Complex

Osmotic pressures of PSS under conditions used here were extrapolated from the data of Koene et al.[2] in which osmotic pressure values for PSS (in cm H_2O) at polymer concentration (C_{NaPSS} in g/L) are listed for PSS in four ionic strength media of concentrations C_{salt} = 0.005, 0.01 M, 0.05 M and 0.1 M NaCl. The values determined experimentally by membrane osmometry are presented in the table below in units of Pa and mol/L for osmotic pressure and polymer concentration respectively. Note that the molecular weight dependence of the osmotic pressure is only evident in the dilute concentration regime[3]; we assume, based on Wang and Bloomfield's data[3], that the PSS concentrations in the pores, are in the semidilute regime.

Table S1. Osmotic pressure of NaPSS as a function of concentration at different concentrations of NaCl (M_w of PSS = 650,000 $g.mol^{-1}$)[2]

C_{salt} = 0.005 M		C_{salt} = 0.01 M		C_{salt} = 0.05 M		C_{salt} = 0.1 M	
C_{NaPSS} (M)	Π (Pa)	C_{NaPSS} (M)	Π (Pa)	C_{NaPSS} (M)	Π (Pa)	C_{NaPSS} (M)	Π (Pa)
0.0123	539	0.051	3528	0.0354	392	0.044	401.8
0.0195	872.2	0.0694	6860	0.0684	1176	0.058	646.8
0.0347	2851.8	0.0733	9702	0.0699	2548	0.0655	803.6
0.0587	8388.8	0.0947	11564	0.0971	3234	0.0786	1156.4
0.0684	10486	0.106	15680	0.128	6566	0.1	2058
0.0718	12446	0.142	20090	0.137	7644	0.135	4429.6
0.0956	18326						
0.127	20090						

The data was extrapolated to higher polymer and salt concentrations respectively. Log-log plots of the data in Table S1 were fitted to linear equations and extrapolated to higher PSS concentrations to cover the concentration range in the pores of the doped complex (Figure S7 (A)). For each of the extrapolated PSS concentrations, osmotic pressure values at the four NaCl concentrations (C_{salt}): 0.005, 0.01, 0.05 and 0.1 M were obtained. Log Π vs. Log C_{salt} was plotted for each PSS concentration and extrapolated to higher NaCl concentrations (Figure S7 (B)).



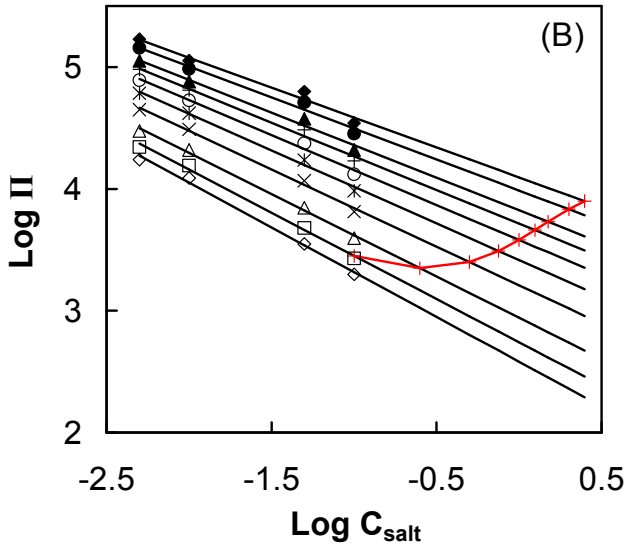


Figure S7. (A) Log-Log plot of the osmotic pressure (in Pa) versus NaPSS concentration C (in M) at the NaCl concentrations: (◊) 0.005 M, (Δ) 0.01 M, (□) 0.05 M, and (○) 0.1 M (data of table SI). The lines show the extrapolation to the high salt concentration regime. (B) Log-log plot of extrapolated osmotic pressure (in Pa) versus NaCl concentration (in M) for different PSS concentrations in NaCl solutions ranging from 0 M to 2.5 M. PSS concentrations are (◊) 0.1 M, (□) 0.12 M, (Δ) 0.14 M, (x) 0.18 M, (x̄) 0.2 M, (○) 0.25 M, (+) 0.28 M, (▲) 0.31 M, (●) 0.35 M, and (♦) 0.39 M (determined from Figure S6). The red plot shows the extrapolated values of the osmotic pressure of PSS at the polymer and salt concentration determined in Figure S6 for the equilibrium swelling state.

Diffusion of extrinsic sites in the complex

The diffusion of extrinsic (doped) sites inside the complex at short times starts from the outer edges forming thin undoped slabs, evident by the change in the optical properties of the complex. These thin complex layers are of higher cross-link density compared to the rest of the complex due to the loss of the extrinsic salt.

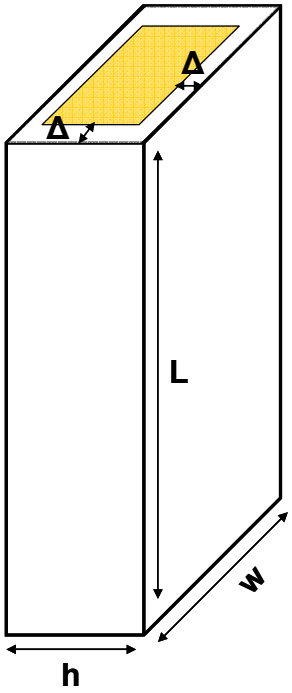


Figure S8. Prismatic sample of PEC for tensile test. L, w and h are the length, width and thickness of the sample and Δ indicates the distance travelled by extrinsic sites at short times.

Assuming the measured modulus at any instant $E(t)$ is a weighted average of the doped and undoped regions:

$$E(t) = f\left(E_{undoped}\right) + \left(1 - f\right)\left(E_{doped}\right) \tag{7}$$

Where f represents the fraction of undoped slab of the complex at time t, E_{doped} is the modulus of the doped complex (at 2.5 M NaCl) and $E_{undoped}$ is the modulus at the equilibrium undoped state in a given salt solution.

To account for the diffusion from all sides of the sample at short times, f is taken as:

$$f = \frac{4\left(\frac{w+h}{w}\right) D_{app}{}^{1/2} t^{1/2}}{\pi^{1/2} h} \tag{8}$$

Where D_{app} represents the diffusion coefficient of the doped sites.

Substituting f in equation (7) gives $E(t)$ as a function of the square root of time:

$$E(t) = \frac{4\left(\frac{w+h}{w}\right) \times \left(E_{undoped} - E_{doped}\right) \times D_{app}^{1/2}}{\pi^{1/2} h} \sqrt{t} + E_{doped}$$

The slope of the linear plot of $E(t)$ versus $\sqrt{t}$ at short times gives the diffusion coefficient of sites in the complex.

References

1. Porcel, C. H.; Schlenoff, J. B. *Biomacromolecules* **2009,** *10*, 2968-2975.
2. Koene, R. S.; Nicolai, T.; Mandel, M. *Macromolecules* **1983,** *16*, 231-236.
3. Wang, L. X.; Bloomfield, V. A. *Macromolecules* **1990,** *23*, 804-809.