Electronic Supplementary Information for:

Decoupling Salt- and Polymer-Dependent Dynamics in Polyelectrolyte Complex Coacervates via Salt Addition

Frances J. Morin, Marissa L. Puppo, and Jennifer E. Laaser*

S1 Supplemental Results

S1.1 Thermogravimetric Analysis

Thermogravimetric analysis data for the starting coacervate samples and the samples with added salt are shown in Figures S1 and S2. As noted in the main text, the TGA protocol involved isotherms at 110 °C and 610 °C to eliminate water and salt, respectively; the mass remaining 10 °C above each of these isotherms (e.g. 120 °C and 620 °C) was used to calculate the volume fractions as described in the text. The initial mass loss observed in each trace at 25 °C was due to slow evaporation of water during the 5 min hold before the start of the temperature ramp, as shown in Figure S3. This mass loss was included in the mass fraction of water for each sample.

^{*}Department of Chemistry, University of Pittsburgh, 219 Parkman Ave, Pittsburgh, PA, USA. E-mail: j.laaser@pitt.edu



Figure S1. Thermogravimetric analysis traces for all initial coacervates used in this work and their corresponding supernatant phases. Mass loss below 120 $^{\circ}$ C was attributed to water, mass loss between 120 $^{\circ}$ C and 620 $^{\circ}$ C was attributed to polymer, and mass remaining above 620 $^{\circ}$ C was attributed to inorganic salt.



Figure S2. Thermogravimetric analysis traces for all samples used in this work. Mass loss below 120 °C was attributed to water, mass loss between 120 °C and 620 °C was attributed to polymer, and mass remaining above 620 °C was attributed to inorganic salt. Note that for a small number of samples, balance instabilities made the data at 620 °C unusable; for these samples, the mass in a stable portion of the trace above 620 °C was used to calculate the remaining mass of salt.



Figure S3. Representative time-dependent mass loss trace for the coacervate prepared at 1.6 M KBr with no added salt, showing (a) the full TGA trace, and (b) the first 20 minutes of the measurement run.

S1.2 Rheology

Amplitude sweeps for all samples included in the rheology analysis are shown in Figure S4. Amplitude sweeps were conducted at an angular frequency of 10 rad/s over three decades of strain amplitudes. In the frequency sweeps presented in the manuscript, the strain was ramped from 0.1% at 600 rad/s to 100% at 0.1 rad/s; in the frequency sweeps, the strain at 10 rad/s was approximately 2%. As seen in Figure S4, all samples were in the linear viscoelastic regime at this reference point, and most were linear to strains of 100%. Because the range of strains giving linear response is expected to increase with decreasing frequency¹, we conclude that the frequency sweeps were all conducted in the linear regime.

Superposed frequency sweeps on all samples included in the shift factor analysis are presented in Figure S5. As seen in this figure, the tan δ plots generally superpose well, and a reasonable time-salt superposition is achieved in the range of salt concentrations studied in this work. The most significant deviations from time-salt superposition were observed for samples prepared at 1.6 M initial salt concentrations.

Shift factors as a function of measured ϕ_{salt} are presented in Figure S6 for each starting salt concentration. The shift factors were fit to the functional form

$$a_s = Be^{-A\phi_{salt}^C} \tag{S1}$$

with selected values of C ranging from 0.2 to 1.8. As seen in Figure S6, all values of C yielded equivalent fits to the experimental data; in future work, a wider range of salt concentrations will need to be included to allow extraction of a unique value for this exponent.

Shift factors as a function of ϕ_{pol} are shown in Figures S7 and S8, along with fits to the form $a_s \sim \phi_{pol}^{\beta}$. As noted in the main text, the errors reported for the polymer-dependent scaling factors for [KBr]_{target}=1.9 M and $\phi_{salt} = 0.074$ may be artifically low. For the [KBr]_{target}=1.9 M dataset, fitting data resampled with random errors selected from a normal distribution with standard deviations of 5% in ϕ_{pol} and 10% in the horizontal shift factor (representing reasonable estimates for the

accuracy of our data) suggests that the true error is closer to ± 1 ; for the other [KBr]_{target} datasets, the resampling method returns similar errors to those reported from the covariance method used in the main text. For the $\phi_{salt} = 0.074 \pm 0.0005$ data, only two datapoints fell into this narrow salt range, so the regression fit appeared exact. Applying a similar resampling method as described for [KBr]_{target}=1.9 M yielded a scaling exponent of 5.4 ± 5.8 .

The global fit to all obtained shift factors is shown in Figure S9. In this fit, the shift factors were simultaneously fit to the form

$$a_s = Be^{-Ac_{salt}^C} \phi_{pol}^\beta \tag{S2}$$

As described in the main text, the fit was poorly conditioned on the salt-dependent exponent *C*, and as a result, *C* could not be uniquely determined from this fit, although we find that the value of β was independent of the choice of *C*. When *C* was set equal to 0.5 and *A* was allowed to vary, the fits yielded a prefactor $A = 14.0 \pm 2.5$ and polymer-dependent scaling exponent of $\beta = 5.4 \pm 0.8$. When *A* was instead fixed to its theoretical value,^{2,3}

$$A = \frac{\sqrt{2000N_A}e^3}{2\pi(\epsilon\epsilon_0 k_B T)^{1.5}}$$
(S3)

which comes out to approximately 6.7 when calculated using $\varepsilon = 62$ (appropriate for aqueous KBr at a reference concentration of 1.5 M,^{4,5} in the middle of the range of salt concentrations investigated in this work), the polymer-dependent scaling exponent was found to be $\beta = 6.4 \pm 0.8$. Thus, while there is some ambiguity about the most appropriate value of *A* due to variation in the contributions of the polymer and salt ions to the dielectric constant of the medium,⁶ we find that the polymer-dependent scaling exponent remains high over a relatively large range of possible values of this prefactor, indicating that our conclusions about the magnitude of this scaling exponent are robust.



Figure S4. Amplitude sweeps on all samples characterized in the rheology experiments. Samples prepared at initial salt concentrations of 1.5 and 1.6 M began to show evidence of slip and/or other nonlinearities only above 100% strain; below 100% strain, all samples were in the linear response regime.



Figure S5. Superposed frequency sweeps on all samples included in the shift factor analysis, separated by starting salt concentration. As in the main text, the sample prepared at 1.2 M salt with 0.2 M added KBr was used as the reference trace for all samples.



Figure S6. Horizontal shift factors obtained from superposition of all rheology data as a function of measured ϕ_{salt} , with fits to the functional form described in the text. Each plot contains data from samples prepared from a single starting coacervate, and thus the data in each plot have approximately the same value of ϕ_{pol} .



Figure S7. Horizontal shift factors for samples with the same target salt concentrations, with fits used to extract the polymer-dependent scaling exponent from the data. Note that the circled point (1.5 M + 0.2 M KBr) reflects a potential outlier; when this point is removed from the data set, the fit gives a polymer-dependent scaling exponent of 4.1 ± 1.8 .



Figure S8. Horizontal shift factors for samples with the measured salt concentrations, with fits used to extract the polymer-dependent scaling exponent from the data.



Figure S9. Global fit to all obtained shift factors with C = 0.5 and (a) the prefactor A allowed to vary (fit coefficients: $A = 14.0 \pm 2.5$, $\beta = 5.4 \pm 0.8$), and (b) A = 6.69 (fit coefficient $\beta = 6.4 \pm 0.8$). Note that the circled point (1.5 M + 0.2 M KBr) reflects a potential outlier; when this point is removed from the data set, the fit coefficients are $A = 17.7 \pm 2.3$, $\beta = 4.3 \pm 0.7$ when A is allowed to vary and $\beta = 6.1 \pm 0.9$ when A is fixed.



Figure S10. Vertical shift factors obtained from superposition of all rheology data as a function of (a) volume fraction of salt (ϕ_{salt}) and (b) volume fraction of polymer (ϕ_{pol}). The sample prepared at 1.2 M + 0.2 M KBr was used as the reference trace, and has a vertical shift factor of 1.

S2 Supplemental Analysis

S2.1 Concentration Regimes for Sticky Rouse Model

In the main text, the overlap concentration between stickers for the samples investigated in this work is estimated to be at least 60 wt%. Here, we describe the assumptions used in this analysis.

First, following Schlenoff et al.,⁷ we note that the polyelectrolytes undergo a salt-mediated ion unpairing reaction described by

$$\mathbf{M}_{s}^{+} + \mathbf{A}_{s}^{-} + \operatorname{Pol}^{+} \operatorname{Pol}^{-}_{PEC} \rightleftharpoons \operatorname{Pol}^{+} \mathbf{A}_{PEC}^{-} + \operatorname{Pol}^{-} \mathbf{M}_{PEC}^{+}$$
(S4)

where M^+ and A^- are the salt ions, Pol⁺ and Pol⁻ are the charged sites on the polyelectrolytes, and the subscripts "s" and "PEC" indicate whether the species are present in the solution or complex phases, respectively. The equilibrium constant for this reaction can be written as⁷

$$K_{unpair} = \frac{y^2 [\text{PE}]_{PEC}}{(1-y)[\text{MA}]_s^2}$$
(S5)

where *y* is the fraction of charged sites that are paired with small counterions, $[PE]_{PEC}$ is the concentration of polymer in the complex phase, and $[MA]_s$ is the concentration of salt (here, KBr) in the solution. For PSS/PDADMAC coacervates made with KBr, this equilibrium constant has been found to be $K_{unpair} \approx 0.48$.⁷ Additionally, for PSS/PDADMAC coacervates made with KBr, the salt concentration in both phases is essentially equal,⁷ so the above expression for the equilibrium constant can be rewritten

$$K_{unpair} = \frac{y^2 [\text{PE}]_{PEC}}{(1-y) [\text{MA}]_{PEC}^2}$$
(S6)

where $[MA]_{PEC}$ is the salt concentration in the complex phase.

The concentrations of polyelectrolyte and KBr in the coacervate phase were calculated from the weight fractions obtained by TGA, using the same densities listed in the main text (1 g/cm³ for water, 2.75 g/cm³ for KBr, and 1.27 g/cm³ for the PSS/PDADMA ion paired polymers^{7,8}).

Solving equation S6 for *y* for the samples investigated in this work yielded values between 0.6 and 0.85; since *y* is the fraction of charged sites that are paired with small counterions, the fraction of sites that engage in inter-chain ion pairs and function as sticky sites is then just 1 - y, or between 0.15 and 0.4. Thus, on average, one in every 3-7 charged monomers is expected to function as a "sticky" site in the present samples.

With even one in seven monomers participating in sticky interactions between chains, the average degree of polymerization of the strands between stickers is only 6, corresponding to a molecular weight between stickers of approximately 1000 g/mol (for PDADMAC) to 1200 g/mol (for PSS). Scaling from the reported radii of gyration for large PSS and PDADMAC chains (approximately 20 nm for 200 kg/mol PSS and 350 kg/mol PDADMAC^{9–11}), with the assumption that the high concentration KBr solution acts as a good solvent for these polymers ($R_g \sim M^{0.6}$), the chains between stickers are expected to have a radius of gyration of approximately 1 nm. Finally, assuming each polymer chain pervades a volume of $V = \frac{4}{3}\pi R_g^3$, the overlap concentration ($c^* = 1/V$) is approximately 3 mol/L (monomer basis), corresponding to a weight fraction of approximately 60%. Because the overlap concentration increases with decreasing chain length, this analysis provides a *lower* limit on the overlap concentration for the strands between stickers; the overlap concentration will be even higher for samples in which a larger proportion of the charged monomers are engaged in inter-chain ion pairs.

References

- [1] S. S. Velankar and D. Giles, *Rheology Bulletin*, 2007, 76, 8–20.
- [2] E. Spruijt, M. A. C. Stuart and J. van der Gucht, Macromolecules, 2013, 46, 1633–1641.
- [3] V. M. S. Syed and S. Srivastava, ACS Macro Letters, 2020, 9, 1067–1073.
- [4] J. M. Mollerup and M. P. Breil, AIChE Journal, 2015, 61, 2854–2860.

- [5] R. Fuentes-Azcatl and M. C. Barbosa, *Physica A: Statistical Mechanics and its Applications*, 2018, **491**, 480–489.
- [6] S. Ali and V. Prabhu, Gels, 2018, 4, 11.
- [7] J. B. Schlenoff, M. Yang, Z. A. Digby and Q. Wang, *Macromolecules*, 2019, 52, 9149–9159.
- [8] H. M. Fares, Q. Wang, M. Yang and J. B. Schlenoff, *Macromolecules*, 2018, 52, 610–619.
- [9] G. Marcelo, M. P. Tarazona and E. Saiz, Polymer, 2005, 46, 2584-2594.
- [10] M. Z. Markarian, H. H. Hariri, A. Reisch, V. S. Urban and J. B. Schlenoff, *Macromolecules*, 2011, 45, 1016–1024.
- [11] J. B. Schlenoff, J. Chem. Phys., 2018, 149, 163314.