Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Rheological Characterization of Liquid-to-Solid Transitions in Bulk Polyelectrolyte Complexes

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Material Characterization

Poly(4-styrenesulfonic acid, sodium salt) (PSS) was purchased as a 15 wt% solution in water (AkzoNobel, VERSA TL130). Poly(diallyldimethylammonium chloride) (PDADMAC) was purchased as a 20 wt% solution in water (average M_w 200,000-350,000 medium molecular weight, Sigma-Aldrich). Both polymers were characterized by gel permeation chromatography (GPC Agilent Technologies, TSKgel 3000). GPC of PDADMAC was performed using a volume ratio 50/50 mixture of 0.5M sodium acetate ($C_2H_3NaO_2$, ACS Grade, Fisher) and 0.5M acetic acid (CH_3COOH, ACS Grade, Fisher) as the mobile phase. PSS was tested using a volume ratio 80/20 mixture of 0.1M sodium nitrate ($NaNO_3$, Sigma-Aldrich) and acetonitrile (C_2H_3N, ACS Grade, Fisher). The PDADMAC sample was prepared in mobile phase at a concentration of 2.1 mg/mL while PSS sample was prepared in mobile phase at 2.2 mg/mL. The flow rate was 1 mg/mL for both samples. Assuming 100% mass recovery, analysis of molecular weight based of multi-angle light scattering (Wyatt Technology, DAWN HELEOS II) determined that PSS has an average M_w~ 354,400 g/mol and PDI (M_w/M_n) of 1.7, while PDADMAC has an average M_w~289,100 g/mol and an apparent PDI of 1.3 (Figure S1).

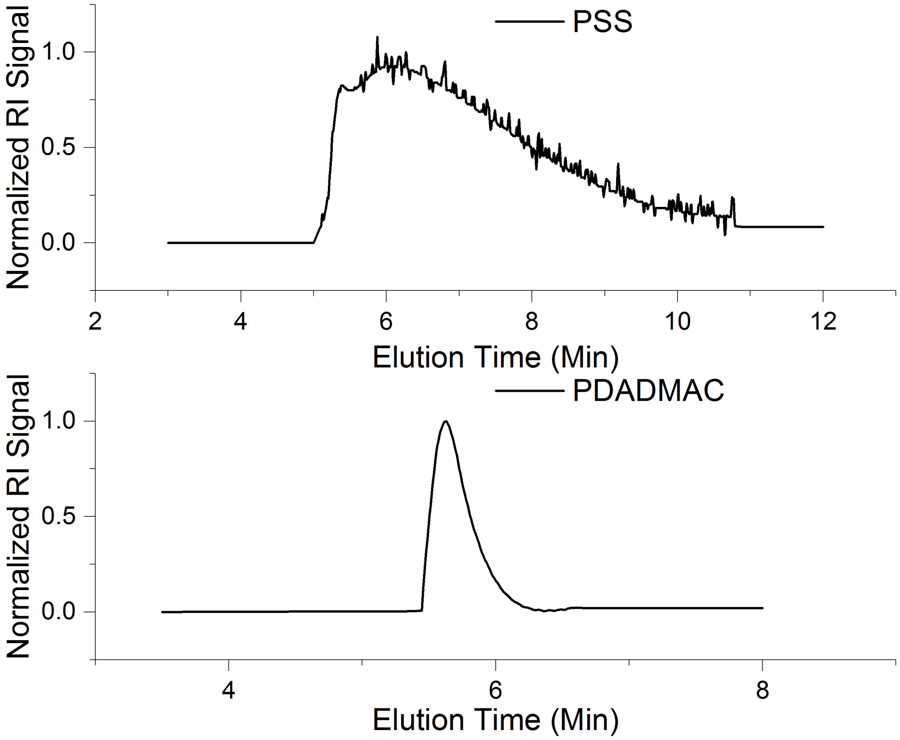

Figure S1. GPC chromatograms of PSS and PDADMAC. The vertical axis is the normalized refractive index (RI) signal and horizontal axis is the elution time.

Sample Preparation

Stock solutions of 0.125M (on a monomer basis) were prepared via dilution with Milli-Q water (resistivity of 18.2 MΩ cm, Millipore, USA) and filtered through a 0.22 μm filter (poly(ethersulfone), Thermo Scientific). A stock solution of 4M potassium bromide (KBr, ACS Grade, Fisher) and a stock solution of 2.5M KBr were similarly prepared. To make coacervates, water, followed by KBr solution, 0.125M PSS and PDADMAC were added into a 50 mL Falcon tube. The sample was vortexed after each addition to ensure that the sample was well mixed. The resulting samples were then centrifuged at 4,000 rpm (Thermo Scientific Legend X1R) for five minutes to facilitate coalescence of the dense phase and stored overnight at room temperature (~25°C) to allow for sample equilibration. The detailed recipe for each sample is given in Table S1.

Table S1. Recipe for the preparation of rheology samples at final salt concentrations from 0.9M to 1.7M. Stock solutions of PSS and PDADMAC were prepared at 0.125M on a monomer basis, while KBr salt solution was prepared at 2.5M and 4.0M (indicated in blue).

Final KBr Concentration (M)	Volume of 0.125M PSS (mL)	Volume of 0.125M PDADMAC (mL)	Volume of KBr (mL)	Volume of Water (mL)
0.9	9.0	9.0	18.0	14.0
1.0	9.0	9.0	20.0	12.0
1.1	9.0	9.0	22.0	10.0
1.2	9.0	9.0	24.0	8.0
1.3	9.0	9.0	26.0	6.0
1.4	9.0	9.0	28.0	4.0
1.5	9.0	9.0	30.0	2.0
1.6	9.0	9.0	32.0	0.0
1.7	9.0	9.0	21.25	10.75

Turbidity Experiments

Turbidity was used to qualitatively measure of the extent of phase separation as a function of charge stoichiometry and salt concentration. Turbidity measurements were made using a microplate reader (Bio Tek Synergy H1). Turbidity was measured at a wavelength of 562 nm and a temperature of 25°C. None of the polymers absorb light at this wavelength. Turbidity is defined as $-\ln(I/I_0)$, with I_0 = incident light intensity and I = intensity of light passed through the sample volume, and is measured in absorption units (a.u.).

Samples were prepared using the same protocol as for rheology samples but at a 200-µL scale and were not centrifuged. After preparation, 50 µL of sample was pipetted in triplicate into a 384-well plate (Fisher) for analysis. Triplicate measurements were made for each well, and all experiments were repeated three times. Error bars on turbidity plots represent the calculated standard deviation of the data. All samples were referenced to Milli-Q water.

The effect of charge stoichiometry was examined at 1.6M KBr to ensure the formation of liquid coacervates. Samples were prepared at mole fractions of PSS (on a monomer basis) ranging from 0.1 to 0.9. The data in Figure S1 show a broad peak in the observed turbidity signal, centered around a mole fraction of 0.5 PSS, or conditions where the number of negative PSS groups equals the number of positively-charged PDADMAC monomers. All subsequent experiments were performed using this ratio of the two polymers.

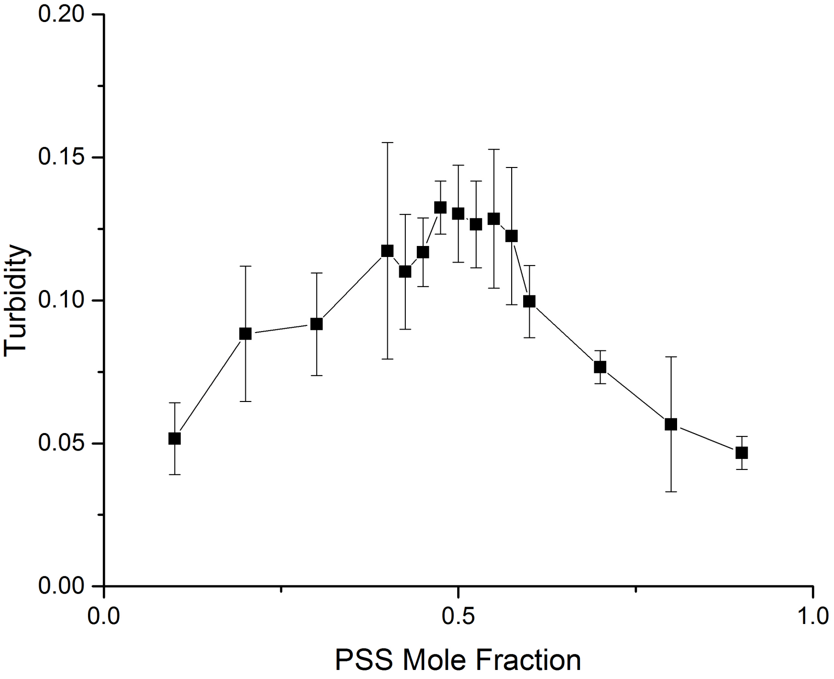

Figure S2. Plot of turbidity as a function of the mole fraction of the polyaion (PSS). All samples were prepared at 0.045M total monomer concentration and 1.6M KBr. Data are the average of three samples measured in triplicate. Error bars are the standard deviation of the three runs.

Experiments investigating the effect of salt concentration were subsequently performed (Figure S2). Visual inspection and optical microscopy (EVOS FL Auto) were used to confirm the presence of solid precipitates, liquid complex coacervates, or the absence of phase separation (Figure 1). We observed precipitation from 0.5M to 0.9M KBr, coacervation from 0.9M to 1.8M, and a single solution phase above 1.9M. These results are similar to those reported previously by Schlenoff and coworkers, who observed precipitation in the range of 0.5M to 1.3M KBr.[1] We anticipate that the differences observed between these two systems are a consequence of the slightly lower molecular weight of the PDADMAC used in our study.

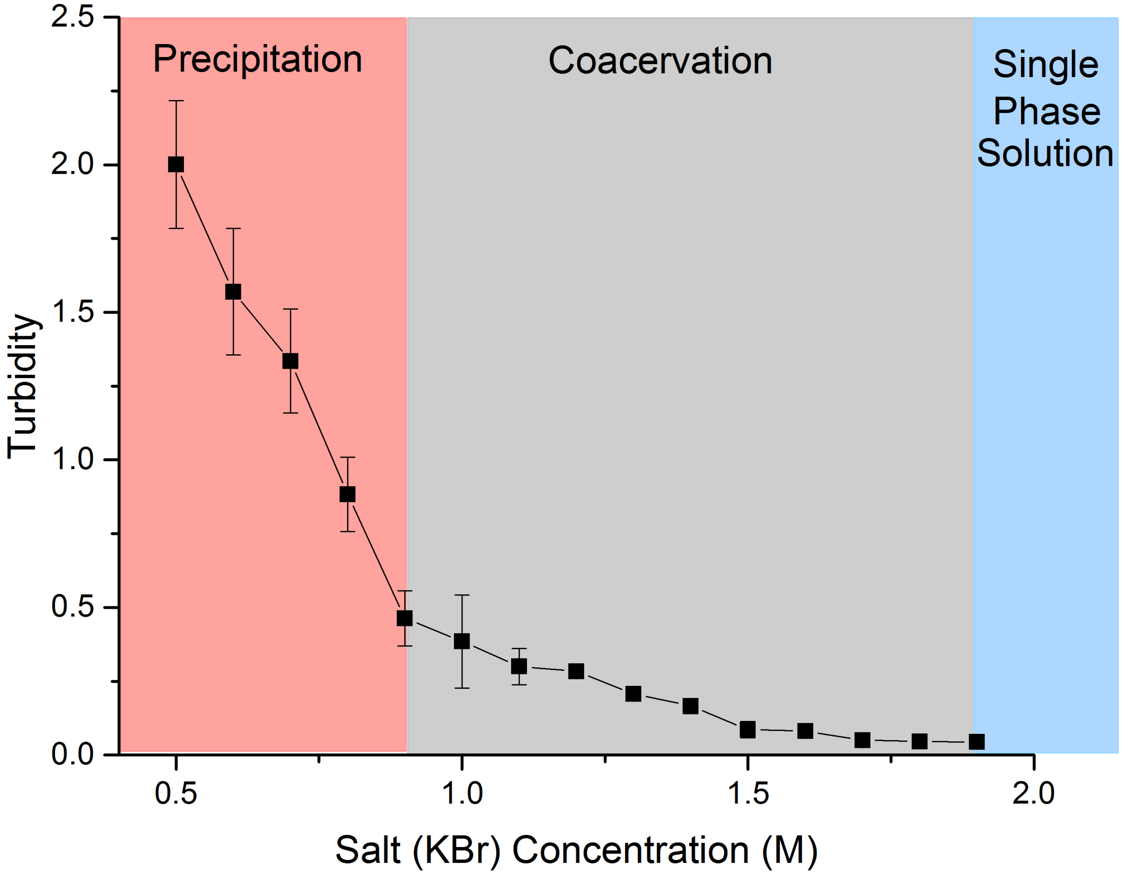

Figure S3. Plot of turbidity as a function of KBr concentration from 0.5M to 1.9M. Precipitation (shown in red area) coacervation (grey) and a uniform single-phase solution (blue) are labeled in the figure. All samples were prepared at 0.045 M total monomer concentration, and 50/50 PSS/PDADMAC. Data are the average of three samples measured in triplicate. Error bars are the standard deviation of the three runs.

Rheometry

Experiments were performed using a Malvern Kinexus Pro stress-controlled instrument, run in strain-controlled oscillatory mode. A 20 mm diameter stainless steel parallel plate fixture with a solvent trap was utilized for all rheological experiments for salt concentrations between 0.5M and 1.5M. For salt concentrations above 1.5M, a 50 mm 2° cone-and-plate fixture was used. In this study the experimental temperature was consistently 25°C. The gap resolution is 0.1 µm. Environmental control on the instrument has a 0.01°C resolution and a range of -40°C to 200°C. The torque range of the rheometer in oscillatory mode is 0.05 µN-m to 200 mN-m with a 0.1 nN-m resolution. The frequency range for the instrument is 6.28 rad/s to 942 rad/s. In this study a frequency range of 1 rad/s to 100 rad/s was used. The strain amplitude used in the measurements was beteween 0.1% and 1%. This strain was confirmed to be in the linear viscoelasticity region for all samples by strain-sweep experiments. All frequency sweep measurements were thus carried out under small amplitude oscillatory shear (SAOS).

For salt concentrations between 0.9M and 1.5M KBr, the 20 mm parallel plate fixture was mounted to the rheometer, allowed to equilibrate at 25°C, and then the gap was zeroed. The gap was then set to 70 mm for loading. The supernatant was poured from the centrifuge tubes and the coacervate was removed from the tubes and transferred to the bottom plate of the rheometer using a stainless steel spatula. Care was taken to prevent bubble formation. The reservoir around the plate was filled with the supernatant removed from the centrifuge tube. This reservoir does not contact the sample but is enclosed with the sample under the solvent trap. The top plate was then lowered to a gap of 0.81 mm and the sample was trimmed using a nylon edge and a razor blade. Once the sample was trimmed, the gap was lowered to 0.80 mm and the solvent trap was put into place. The experimental procedure was identical for samples above 1.5M KBr requiring the cone-and-plate fixture, except the trimming gap was 0.077 mm and the working gap was 0.07 mm. The system was then allowed to equilibrate at 25°C for around 3 minutes before measurements commenced. Two frequency sweeps were run in series and then compared to ensure that drying did not significantly change the material during the experimental time period. The rheological data were analyzed using the IRIS software package (IRIS Development LLC).

Results and Discussion

Frequency sweep analysis shows storage (G') and loss (G'') moduli data vs. frequency (ω) with KBr salt concentration from 0.5M to 1.6M. An increase in the overall magnitude of the storage (G') and loss (G'') moduli appears as the samples became more solid like with decreasing salt (Figures 2a and S3). Confirmation of this solidification can also be seen in a plot of the tangent of the phase angle (δ) ($\tan(\delta) = G''/G'$) (Figure S4). Liquid-like samples show a trend of decreasing values of $\tan(\delta)$ with increasing frequency, which decays to an almost frequency-invariant response at lower salt concentrations, followed by inversion to a more solid-like upward-trend for the lowest salt concentrations (Figures 2b and S4).

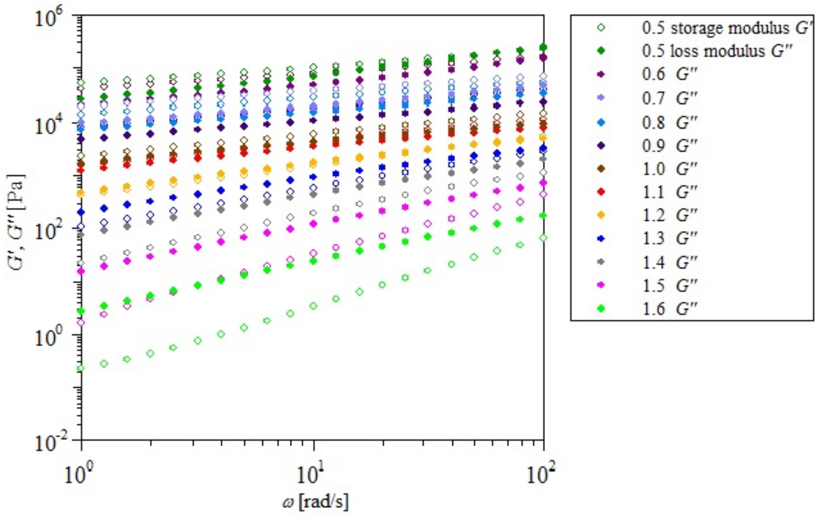

Figure S4. Frequency sweep data for PSS/PDADMAC samples with PSS/PDADAMC mole ratio of 50/50 prepared from 0.5M (dark green) to 1.6M (light green) KBr, shown as the elastic modulus (*G'*) and viscous (*G''*) modulus vs. frequency (*ω*).

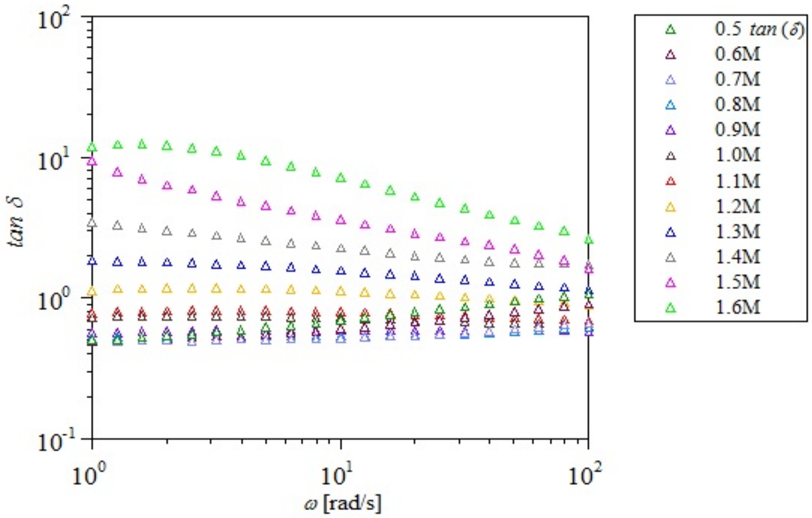

Figure S5. Frequency sweep data for PSS/PDADMAC samples with PSS/PDADAMC mole ratio of 50/50 prepared from 0.5M (dark green) to 1.6M (light green) KBr, shown as the tangent of the phase angle (*δ*) vs. frequency (*ω*).

References:

(1) Wang, Q.; Schlenoff, J. B. *Macromolecules* **2014**, *47* (9), 3108–3116.