Guanidinium can Break and Form Strongly Associating Ion-Complexes

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Supporting Information

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1 Experimental

Materials: Poly(styrene sulfonate) sodium salt (PSS, MW 200K g mol\(^{-1}\)) was purchased from Sigma-Aldrich, poly(4-vinylpyridine) (P4VP, MW 50K g mol\(^{-1}\)) from Scientific Polymers, and poly(allylamine) HCl (PAH, 120-200K g mol\(^{-1}\)) from Alfa Aesar. 1-bromoethane, potassium bromide, guanidinium bromide, and guanidinium thiocyanate were also purchased from Sigma-Aldrich. 1H-Pyrazole-1-carboxamidine hydrochloride was purchased from Chem-Impex International. Deionized water (conductivity \(\approx 5 \mu S/cm\)) was used for making all solutions except when forming coacervates where 18.2 M \(\Omega\) \(*\) cm MilliQ water was used. The pH of water used was observed to be between 5.5-7, as expected from dissolved carbon dioxide, and which is much lower than the pKa of poly(allylamine) at 8.5. Therefore, poly(allylamine) was assumed to be fully ionized.

Quaternization of poly(4-vinylpyridine): In our nomenclature we refer to ethyl substituted P4VP as QVP-C2. QVP-C2 was synthesized by dissolving 10 wt% P4VP in dimethyl sulfoxide before adding a 30% molar excess of bromoethane. The solution was well stirred for 24 hours at 40\(^{\circ}\)C. This solution was used directly to synthesize the complex with poly(styrenesulfonate) and is discussed below.

Guanylation of poly(allylamine): 5-10 wt% PAH was dissolved in water and the pH was adjusted to \(\approx 10\) using sodium hydroxide. Stoichiometric amounts of 1H-Pyrazole-1-carboxamidine hydrochloride was added to the solution and stirred for 4 days at room temperature. Polymer was isolated using dialysis and lyophilization.

Stoichiometric PECs: Once the quaternization reaction was completed (in DMSO), a 1:1 repeat unit molar equivalent of PSS was dissolved in equivalent volume of water separately. This was done by noting the mass was initial P4VP that was quaternized followed by conversion to moles. The two solutions were then simultaneously added to a third beaker of water under stirring. The PECs precipitated out as a white solid that washed with deionized water until the solution conductivity fell to about 50 \(\mu S/cm\). The precipitates were collected via vacuum filtration and then dried. Since pyridines can have poor thermal stability, the PECs were dried at 60\(^{\circ}\)C and in the presence of drierite for 12 hours to obtain the dry PEC. PSS:PAH complexes were made analogously after the guanylation reaction was completed.

Coacervates: Coacervates were formed from the dry PECs by dissolving them in appropriate salt solutions. In all cases, 1 g of dry PEC was dissolved in 10 ml of the salt solution using MilliQ water (18.2 M\(\Omega\) cm). The salt concentrations where coacervation was observed was \(\approx 1.5-1.9\) M KBr for QVP-C2 and \(\approx 3-3.75\) M Guanidinium bromide/thiocyanate for PSS:PAH. The solutions were then well-stirred at room temperature overnight. Once the coacervate phase began to form the solution was annealed at 60\(^{\circ}\)C for 30 min. The
solutions were then allowed to equilibrate between 1 week to 1 month, depending on the sample. Coacervates formed at low salt concentrations required longer equilibration times.

**Quartz Crystal Rheometry:** A custom quartz crystal microbalance (QCM, AWSensors, Valencia, Spain) was used in conjunction with a N2PK impedance analyzer (Thornhill, Canada) for swelling and viscoelastic measurements of spin-coated polyelectrolyte complex films. 1.5 μm polyelectrolyte complex films were directly spin-coated onto 1 inch quartz crystals with Au electrodes (Inficon, East Syracuse, NY) from the polymer-rich coacervate phase. Accurate QCM experiments require highly homogeneous and smooth films. Such high quality films could be obtained by spin-coating coacervates and then annealing them in intermediate ionic strength solutions to smooth the resulting film. Once the coacervate was spin-coated, PSS:QVP-C2 was annealed in 1.0 M KBr solution for 24 hours. PSS:PAH was annealed in 1.25 M GndmSCN for 24 hours. The final film was rinsed with excess deionized water to remove residual salt. The film was then dried over hot drierite to remove all water, and the dry areal mass, \((dp)_{dry}\), was recorded using the QCM. Here, \(d\) is the film thickness and \(\rho\) is the density. The swelling ratio after immersion salt solutions was then computed using Eq. 1.

\[
\text{Swelling\%} = \frac{\text{Weight}_{water+salt}}{\text{Weight}_{polymer}} \times 100 = \frac{dp - (dp)_{dry}}{(dp)_{dry}} \times 100
\]

The QCM provides changes in the resonance frequency \((\Delta f_n)\) and dissipation \((\Delta \Gamma_n)\) of the piezoelectric quartz crystal at the odd nth harmonic of the fundamental frequency (5 MHz for the crystals used in this work). We monitor \(\Delta f_n\) and \(\Delta \Gamma_n\) at n = 3, and 5 by fitting a Lorentzian peak to the conductance and susceptance in the frequency domain. While we prefer to use \(\Delta \Gamma_n\), it is equivalent to the widely used QCM-D instrument that operates in the time domain, with \(\Delta D_n = 2 \Delta \Gamma_n / f_n\), where \(D\) is the dissipation factor and \(f_n\) is the oscillation frequency. The QCM data was analyzed using the open source ECD Analyze code to extract accurate viscoelastic properties. More detailed sample preparation procedures and QCM rheometry were reported previously.\(^1,^2\)

**Interfacial Tension Measurements:** The interfacial tension \((\gamma)\) of the polyelectrolytes used in this work was measured using the pendant drop method. A Kruss DSA100 drop shape analyzer was used. A 12 μL drop of HPLC grade chloroform was formed in an embedding phase of 18.2 MΩ·cm water. The water/chloroform tension was measured for 10 min to verify that \(\gamma\) was ≈32 mN/m (the pristine tension), before polyelectrolyte solutions were injected such that the polymer concentration was 5 mM on a repeat unit basis.

**PSS:PAH-Gu Phase Behavior:** Stock solutions of guanidinium bromide at 2, 2.5, 3, 3.5 and 4 mol/L was prepared. PAH was guanylated at different fractions and using the procedure outlined above and then
dialyzed and lyophilized. PSS was lyophilized from the as received solution from the manufacturer. PSS and PAH-Gu were added to a 3 ml vial in a 1:1 ratio, for a total polymer mass ≈0.1 g. 1 ml of the stock solutions was added to the vial and the complex allowed to equilibrate for 2 months at room temperature. Visual sample characterization was performed for the solid-like complex, clear liquid-liquid phase separated coacervate, and single phase solutions. In cases where a cloudy gel was observed, larger samples where made and their rheological response recorded. A representative rheological profile for this gel is shown in Figure S5.

Rheology: Rheology was performed using an Anton-Paar MCR 302 rheometer with the cone–plate geometry. 50 mm diameter plates with a cone angle of 2° were used to perform frequency sweeps between 0.1 and 300 rads s⁻¹. A 1% strain amplitude was used which was verified to be well within the linear viscoelastic regime using amplitude sweeps. Once the coacervates were loaded, they were allowed to relax for at least 10 min at room temperature. Solvent evaporation was mitigated by placing a small trough of water around the bottom plate of the rheometer and isolating the sample inside a custom chamber. The rheological response of the PSS:PAH coacervate was fitted to the fractional Maxwell liquid model to obtain the relaxation spectrum shown in Figure S4 as reported previously.¹

![Figure S1](image)

Figure S1: (a) Swelling behavior, (b) density-shear modulus, and (c) viscoelastic phase angle of PSS:PAH complex in response to common salts. Halide salts result in an initial swelling response which is not observed for their thiocyanate counterparts. However, thiocyanate salts of sodium and potassium are not as effective as that of guanidinium. The initial swelling response at low concentration of halide anions occur on the order of several hours for a 2 micron film, suggesting an extremely slow relaxation event. Viscoelastic properties were measured at 15 MHz using the quartz crystal microbalance as described in reference 1 and 2. For a basis of comparison, polymer glasses have a shear modulus of ≈ 2 × 10⁹ Pa and a φ ≈ 1° at this frequency, and \( G^* = G' + iG'' \) and \( \phi = \arctan(G''/G') \) as usual.
Figure S2: Dependence of the complex shear modulus-density product of polyelectrolyte complexes on their swelling ratio/water content. Regardless of the salt or polyelectrolytes used, the observed mechanical properties are primarily a function of the water content as seen from the collapse onto a single master curve. Here the swelling ratio is calculated with respect to the completely dry film (Eq. 1), and each complex was swollen from 0-1.0 M of the indicated salt at 0.1 M increments.

Figure S3: Swelling behavior of PSS:QVP-C2 in response to different salts. Bromide salts are the most effective in breaking the complex. While GdnmBr is better than or comparable to KBr at low salt concentrations, its effectiveness in swelling PSS:QVP-C2 is diminished at higher concentrations, suggesting more secondary interactions may be at play in this particular case. Guanidinium is more effective than sodium or potassium when paired with chlorine. Thiocyanate salts are not appropriate to swell PSS:QVP-C2 as they tend to precipitate out QVP-C2.
Figure S4: The relaxation spectrum associated with the rheological response of PSS:PAH in Figure 4 in the main text. Here, a broad distribution of relaxation times is observed. This relaxation spectrum was obtained by fitting the ‘spring-pot’ model reported in reference 1.

Figure S5: Rheological response of a complex of poly(styrenesulfonate) with 15% guanylated poly(allylamine). The typical power-law polymer solution response of coacervates as depicted for PSS:PAH in Figure 4 in the main text is lost when guanidinium is added directly onto the polyelectrolyte. Instead, the rheological response of a colloidal gel is observed, where the storage modulus is nearly independent of frequency at low frequencies (see reference 3). The colloidal gel rheological response supports the hypothesis that insoluble aggregates are forming, which likely also imparts the cloudiness.
Figure S6: The slow swelling response for a PSS:PAH film immersed in 0.1 M KBr from a dry initial $d\rho = 1470 \text{mg/m}^2$. Typically, the PSS:PAH film was observed to swell to 40-50% from an initial swollen state of $\approx 30\%$ in pure water.
Figure S7: Representative NMR spectra for systematic guanylation of poly(allylamine). % Guanylation was calculated using the peaks labeled a and b.

References:

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