

Supporting Information for

Linear Viscoelasticity and Swelling of Polyelectrolyte Complex Coacervates

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Supernatant Viscosity

Viscosity titration was used to study the soluble complexes at different polycation/polyanion fractions to determine the positive charge fraction X of the coacervate. Solutions of PDADMA-Cl (4wt%) and IBMA-Na (5wt% for all molecular weights) were mixed and a VWR Vortex Analog Mixer was used ensure proper mixing. Polyelectrolyte complex samples with different charge fractions were prepared using each of the polyelectrolytes as titrants. A Contraves Low Shear 30 Viscometer was used to measure the viscosities of 2.5 mL of the supernatant in a concentric cylinder geometry. Temperature was controlled at 25 °C using a circulating water bath.

Viscosity of soluble complexes depends on their concentration in solution, where higher concentrations have higher viscosities. Figure S1 shows the specific viscosity values of the supernatant obtained at different positive charge fractions, using either polyion as the titrant.

The general trend among the different molecular weights reveals a minimum around the 0.5 charge fraction, which is the region that corresponds to the formation of neutral coacervates. Measurements of pure IBMA-Na ($X = 0$) show that higher molecular weight polyanions have higher viscosities. These results are expected because higher molecular weight polyelectrolyte has lower overlap concentration.

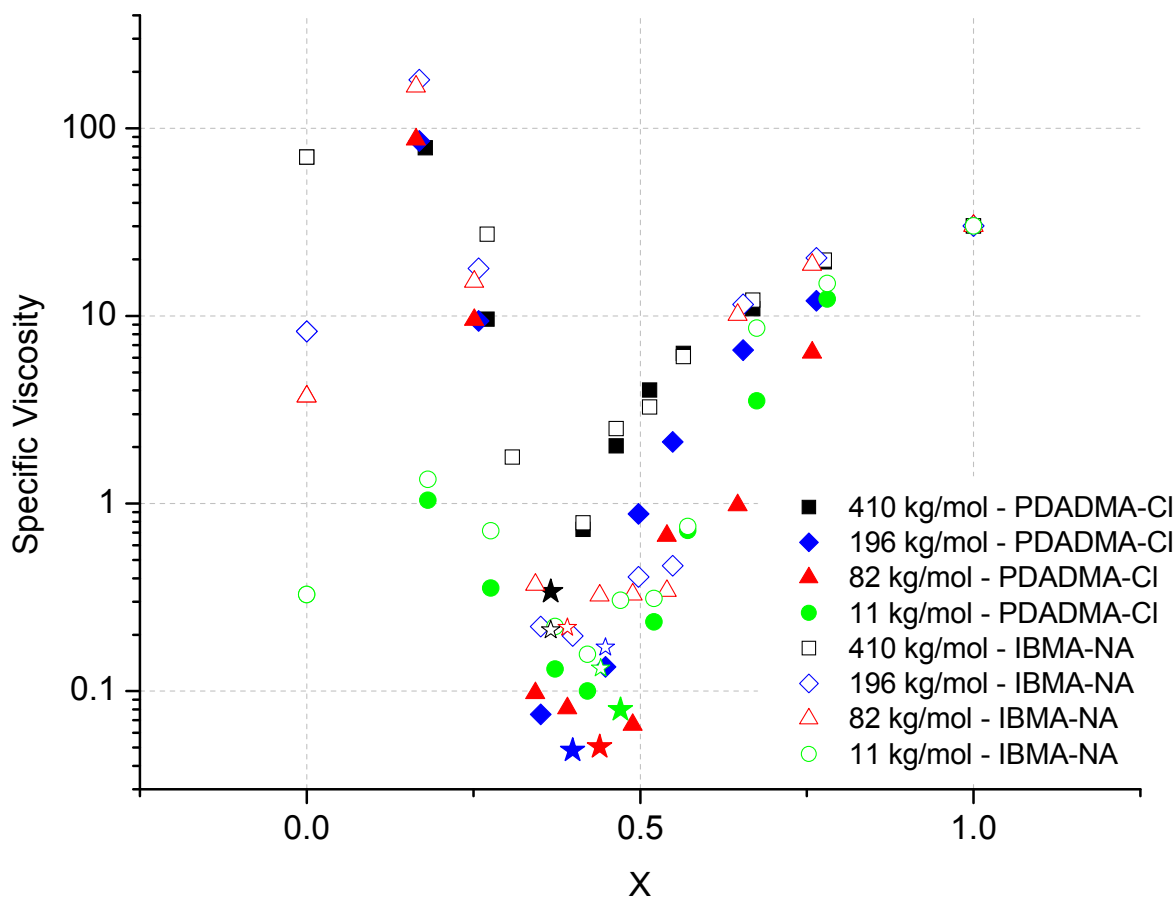


Figure S1. Specific viscosity of nonstoichiometric soluble polyelectrolyte complexes (4-5 wt% polymer, some of which is in the coacervate phase on not contributing to the measured viscosity) at different overall positive charge fraction X. Using PDADMA-Cl (filled symbols) and IBMA-NA (empty symbols) as titrants. Each ★ symbol indicates the minimum specific viscosity of each titration (giving a measure of the positive charge fraction X of the coacervate).

Initially, the system starts forming net-anionic soluble complexes with some degree of bridging after mixing the first drops of PDADMA-Cl, as a consequence the viscosity first increases. The charge fraction region between pure polyanion solution and neutral coacervate (at $X \approx 0.2$), shows the highest viscosity value due to the fact that the concentration of soluble complexes in this range is very high. After this peak, further addition forms roughly charge-neutral coacervates that settle as sediment lowering the concentration remaining in the supernatant phase. The viscosity keeps decreasing until everything drops out of solution and becomes free of any soluble complexes ($\eta_{sp} \approx 0.1$ meaning $\eta \approx 1$ mPa·s). This implies

that the positive charge fraction X of the coacervate can be estimated from the specific viscosity as it approaches zero. Charge fractions corresponding to minimum specific viscosity are shown in Table 1.

Figure S1 also shows that coacervates return to being non-stoichiometric soluble complexes if additional polyelectrolyte solution is titrated in. The increase in viscosity indicates that newly added polyelectrolytes get reincorporated into the complex to give it a net charge causing partial redissolution. Interestingly, the viscosities measured after the minimum specific viscosity are similar to the viscosities measured before the minimum specific viscosity with the opposite titrant. This concludes that the viscosity of the supernatant is just a function of charge fraction X and molecular weight, regardless of which polyelectrolyte is being titrated, indicating a reversibility that is consistent with the coacervate exhibiting LVE response and swelling that does not depend on the details of mixing.

Supernatant ζ -potential

In order to verify the coacervate X values obtained through viscosity measurements, ζ -potential titrations were also performed. The charge fraction of a net-neutral coacervate was determined at the zero volt potential point. The charge fractions retrieved using both techniques are similar as shown in Table 1. Due to the subtle region in the vicinity of the positive charge fraction of the coacervate, where most of the polyelectrolytes have left the supernatant and are in the coacervate, obtaining very precise charge fractions is a challenging task. Figure S2 summarizes the ζ -potential measurements in the supernatant.

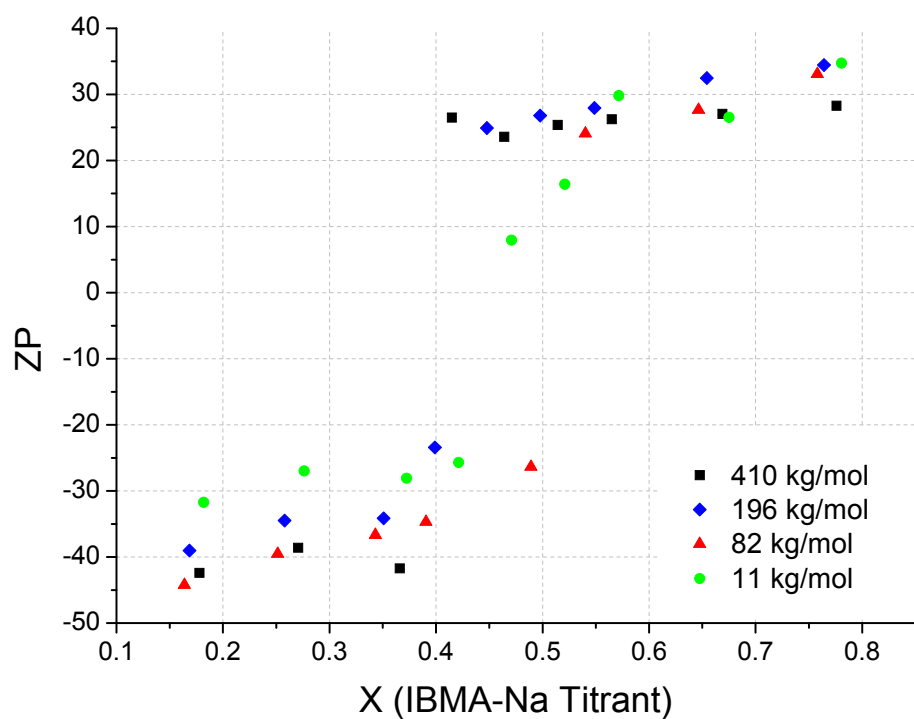
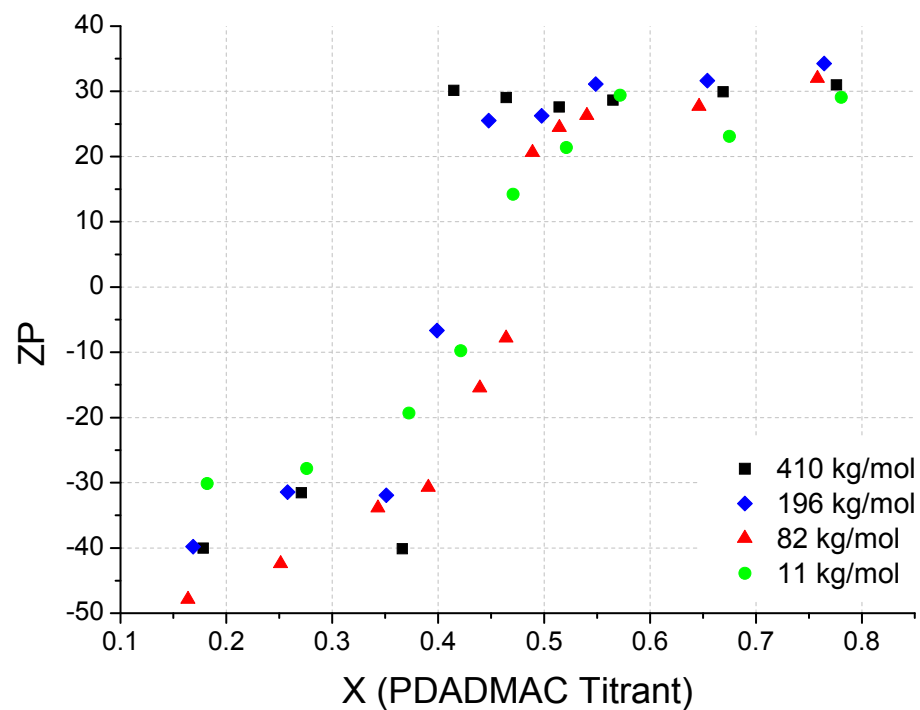


Figure S2. ζ -potential measurements in the supernatant for polycation being titrated into polyanion (upper plot) and for polyanion being titrated into polycation (lower plot). The abrupt jump from negative to positive ζ -potential indicates the point where the soluble complexes in the supernatant are on average charge balanced.

Coacervate Dielectric Permittivity

The frequency dependence of dielectric permittivity was measured using a Novocontrol Concept 40 broadband dielectric spectrometer at 25 °C for the four coacervates with no added salt. While full interpretation of the data shown in Figure S3 is beyond the scope of this paper, it is clear that the two coacervates made using the two highest molecular weight polyanions are considerably more polarizable than those made from low molecular weight polyanions, giving support for the idea that while the coacervates made from low molecular weight polyanions are quite close to charge-balanced, the higher molecular weight polyanions lead to coacervates with a net charge and mobile counterions.

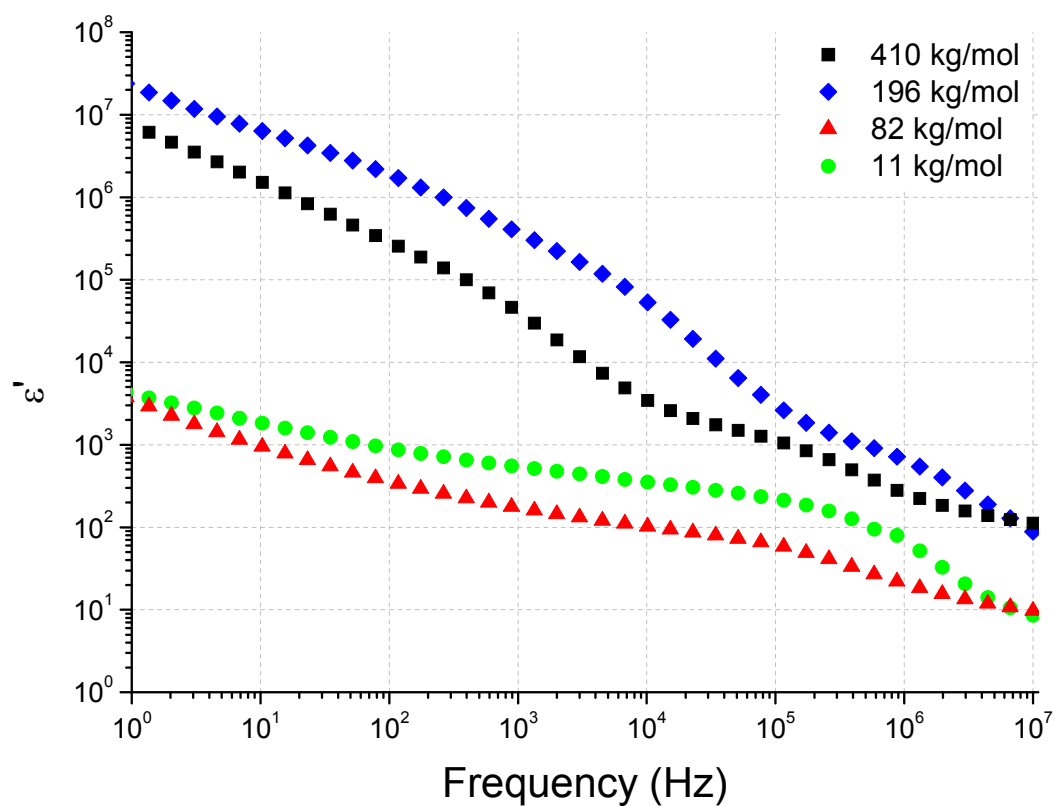


Figure S3. Frequency dependence of dielectric permittivity at 25 °C for the four coacervates with no added salt (equilibrated with deionized water). The average cation fraction $X = 0.45$ for the coacervate made using IBMA-Na with 11 kg/mol (green), $X = 0.46$ for the coacervate made using IBMA-Na with 82 kg/mol (red) and these two are far less polarizable than the coacervates made with the two higher molecular weight polyanions: IBMA-Na with 196 kg/mol (blue) has $X = 0.42$ and IBMA-Na with 410 kg/mol (black) has $X = 0.39$ (see Table 1).

Coacervate Time-Salt Master Curves

While G' and G'' master curves of all four coacervates are shown in Figure 7 of the paper, the corresponding master curves for the loss tangent $\tan(\delta) = G''/G'$ are shown below in Figure S4 to better assess the quality of the superposition.

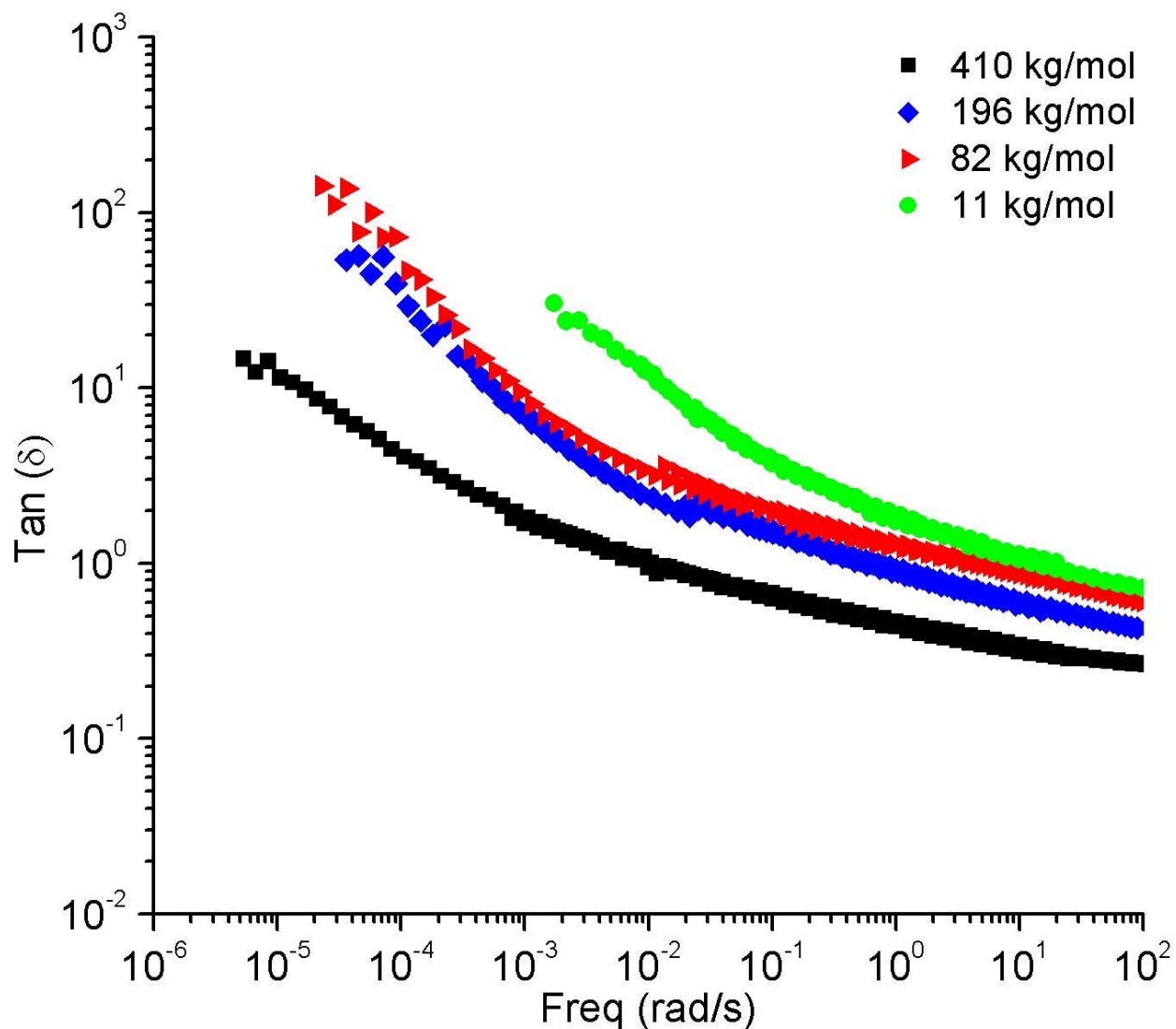


Figure S4. Frequency dependence of loss tangent for the time-salt superposition master curves of the four coacervates presented in Figure 7, at 23°C. IBMA-Na 410kg/mol (■), 196 kg/mol (◆), 82 kg/mol (▲), and 11 kg/mol (●).