Supplementary Information

Structure and Rheology of Polyelectrolyte Complex Coacervates

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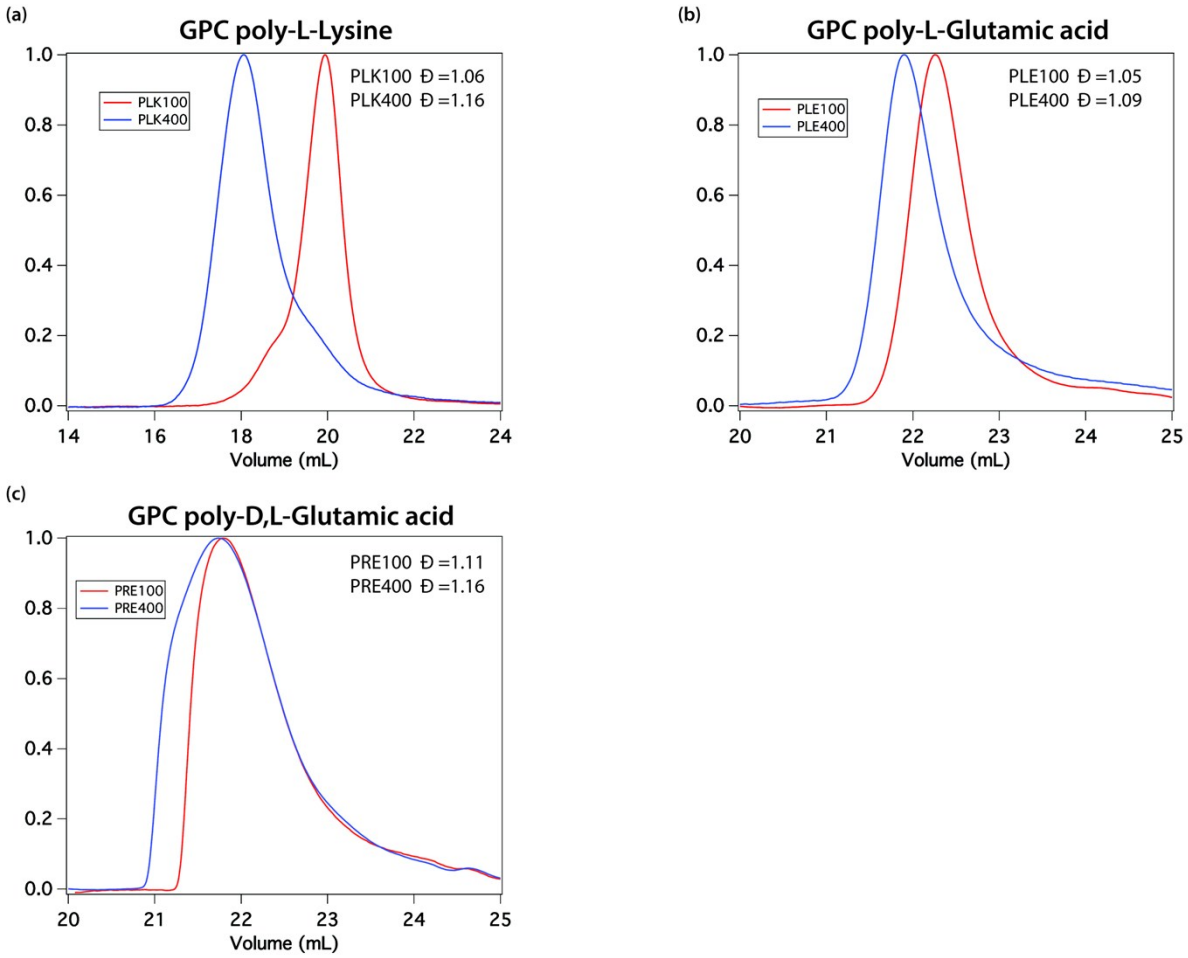

Figure S1. Dispersity of each polymer was assessed via gel-permeation chromatography using three 7.8 x 300 mm columns (Waters Ultrahydrogel 120, 250, 500) in series with a flow rate of 1 mL/min over 40 minutes at room temperature. Refractive index data was collected using an Optilab T-rEX detector (Wyatt Technology) and dispersity was calculated against a ReadyCal 200 – 1.2x10^6 D PEG/PEO analytical standard (Fluka). (a) The poly(L-lysine) 100- and 400-mer were run with a mobile phase consisting of .1% TFA/40% Acetonitrile and measured dispersity of 1.06 and 1.16 respectively, (b) the poly(L-glutamic acid) 100- and 400-mer with .1 M $NaNO_3$ and measured dispersity of 1.05 and 1.09 respectively and (c) the poly(D,L-glutamic acid) 100- and 400-mer with .1 M $NaNO_3$ and measured dispersity of 1.11 and 1.16 respectively. These dispersity values are comparable to the values provided by the manufacturer Alamanda™ Polymers.

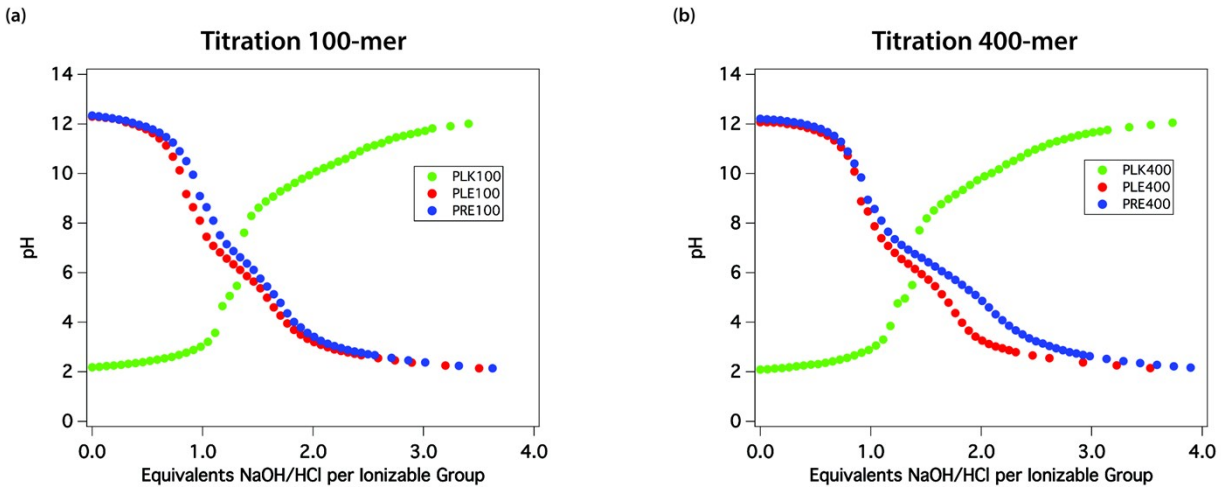

Figure S2. Titration curves of poly(L-lysine) (green circles), poly(L-glutamic acid) (red circles) and poly(D,L-glutamic acid) (blue circles). The charge state of each polymer was studied by titrating 4 μL increments of .5 M NaOH or HCl to 1 mg/mL polymer solutions (total volume 5 mL). The pH was equilibrated (1-2 minutes) and then recorded. The pH was then plotted against molar equivalents of NaOH/HCl per ionizable group. The crossover point denotes the pH value where the polymers are equally charged. (a) 100-mer (b) 400-mer. It must be noted that the titration of poly(lysine) and poly(glutamic acid) should result in three inflection points due to the strongly acidic carboxyl end group (pKa 1 ~2), the less acid ammonium end group (pKa ~ 9) and the side chain pKa (4.3 and 10.5 for PRE and PLK, respectively). The titrations were conducted at pH values above the first pKa so two only two inflection points were observed in all the cases.

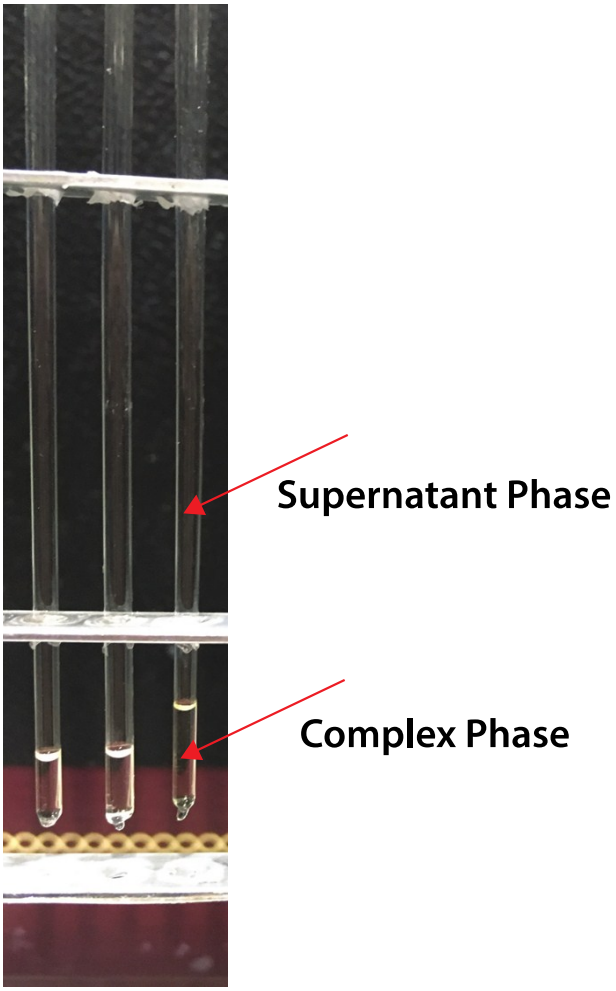

Figure S3. Image showing experimental set-up for small angle X-ray scattering experiments. Initially, polyelectrolyte complexes are formed in 1.5 mL tubes by mixing the anionic and cationic polymers at the desired concentration. The complexes are then transferred to 2 mm quartz thin-walled capillaries and centrifuged at 5000xg for 10 minutes resulting in two coexisting phases: the complex phase and the supernatant phase.

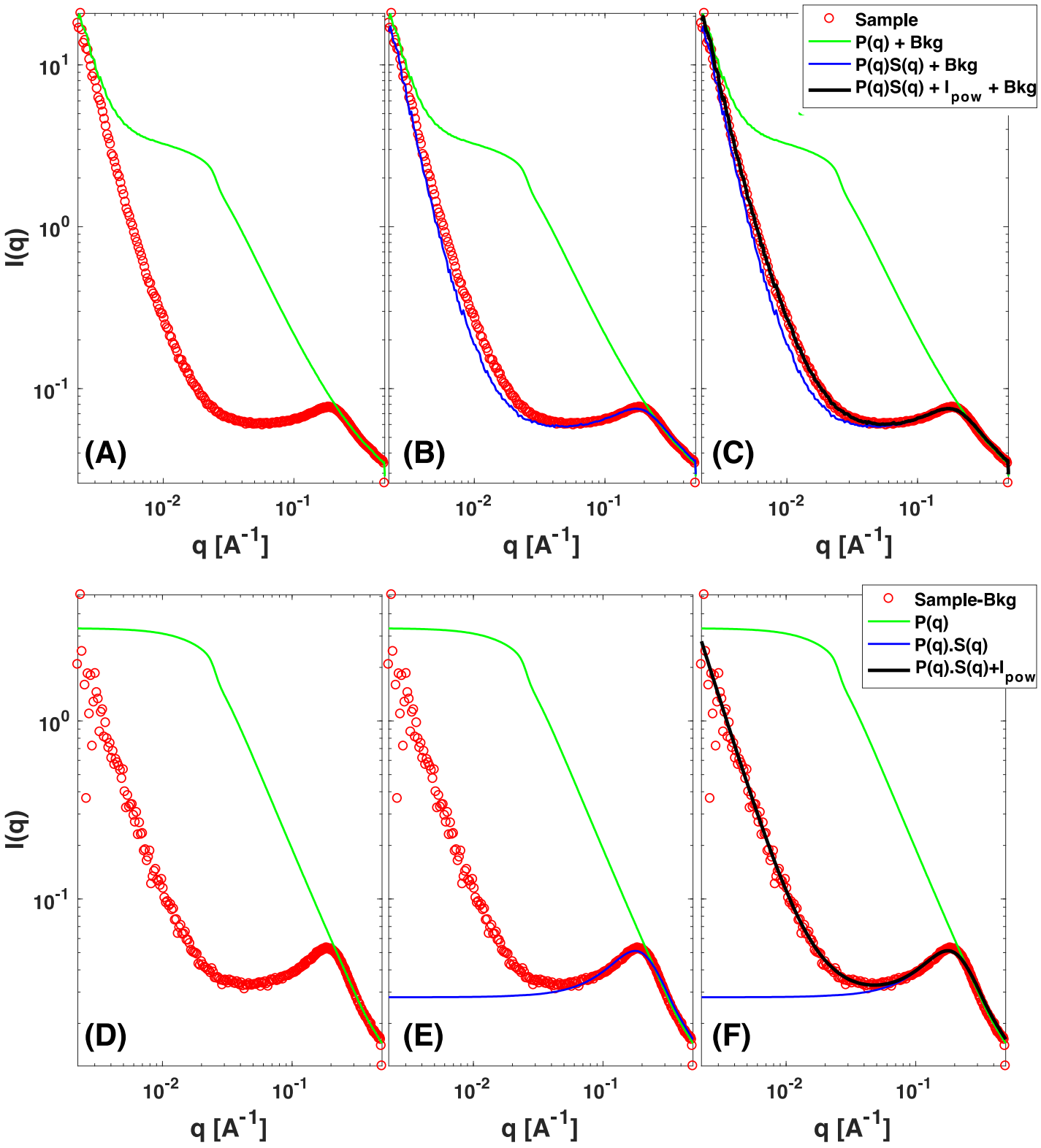

Figure S4. Piecewise fitting of the scattering data. (A-C) SAXS intensity $I(q)$ along with the corresponding fits: (A) $P(q)+$ background scattering, (B) $P(q)S(q)+$ background scattering, and (C) $P(q)S(q)+I_{pow}+$ background scattering. The final fit is shown in (C). (D-F) show the corresponding fits to the scattering data after subtracting the background scattering intensity.

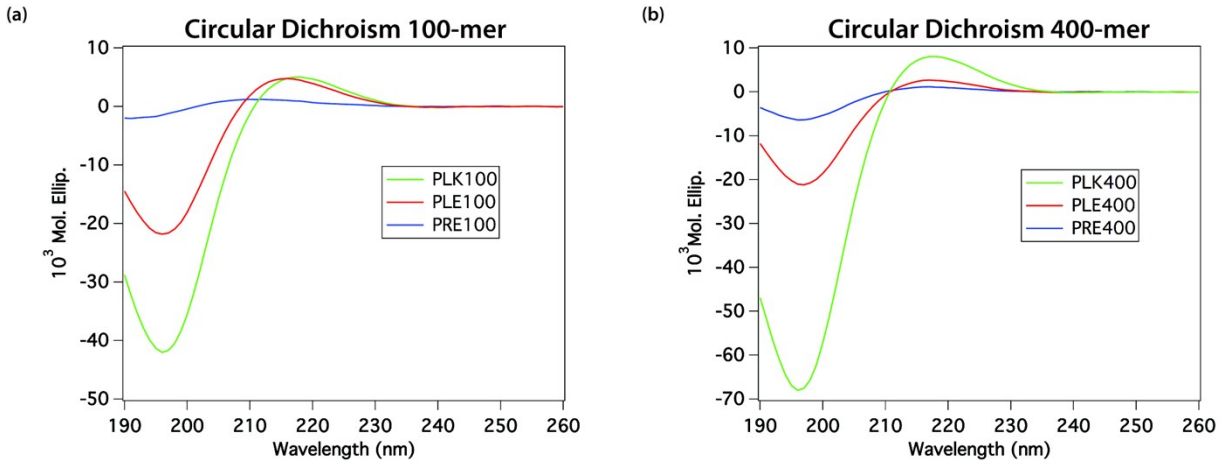

Figure S5. Circular dichroism spectroscopy was used to investigate the secondary structure of individual polymers in solution (poly(L-lysine) (green), poly(L-glutamic acid) (red) and poly(D,L-glutamic acid) (blue)). Polymer solutions were prepared in ddH2O at 1 mM charge concentration and subsequently loaded into 1 mm pathlength Spectrosil quartz cells. Samples were equilibrated at 25 °C and scanned from 260-190 nm (5X) with a .1 nm data pitch and 50 nm/min scanning speed using a Jasco J-815 Circular Dichroism Spectrometer. The 5 scans were then averaged and units converted from mdeg to molecular ellipticity via the charge concentration of each polymer (1 mM). The negative peak at 195 nm indicates that the homochiral L polymers are in a random coil configuration. As expected, poly(D,L-glutamic acid) exhibits very little signal due to the racemic nature of the polymer. (a) 100-mer[1] (b) 400-mer.

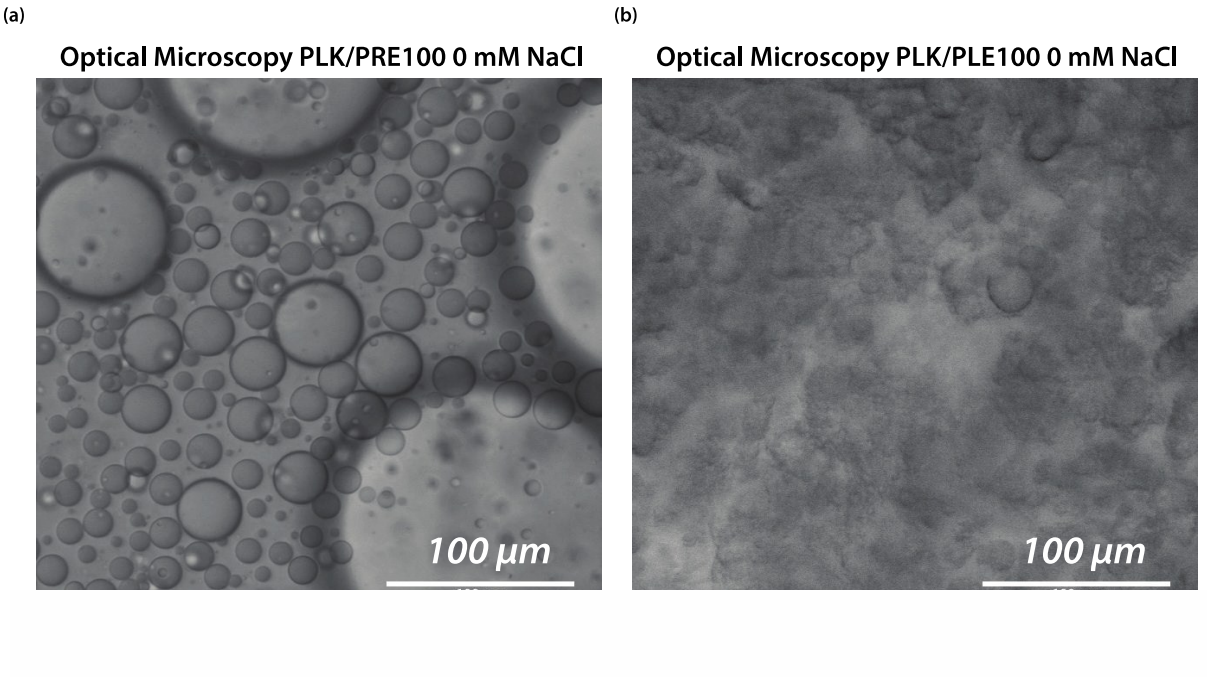

Figure S6. Phase and morphology of polyelectrolyte complexes (PECs) were analyzed by phase contrast optical microscopy using a Leica DMI-6000B inverted microscope with white light illumination and 20X magnification. Directly after mixing, 100 uL aliquots of complexes in solution were loaded into an ultra-low attachment 96 well plate (Costar, Corning) and imaged. (a) 2 wt% poly(L-lysine) and poly(D,L-glutamic acid) phase separate and form liquid droplets (0 mM NaCl, pH 7) (b) 2 wt% poly(L-lysine) and poly(L-glutamic acid) phase separate and form glassy solid-like structures (0 mM NaCl, pH 7).[1]

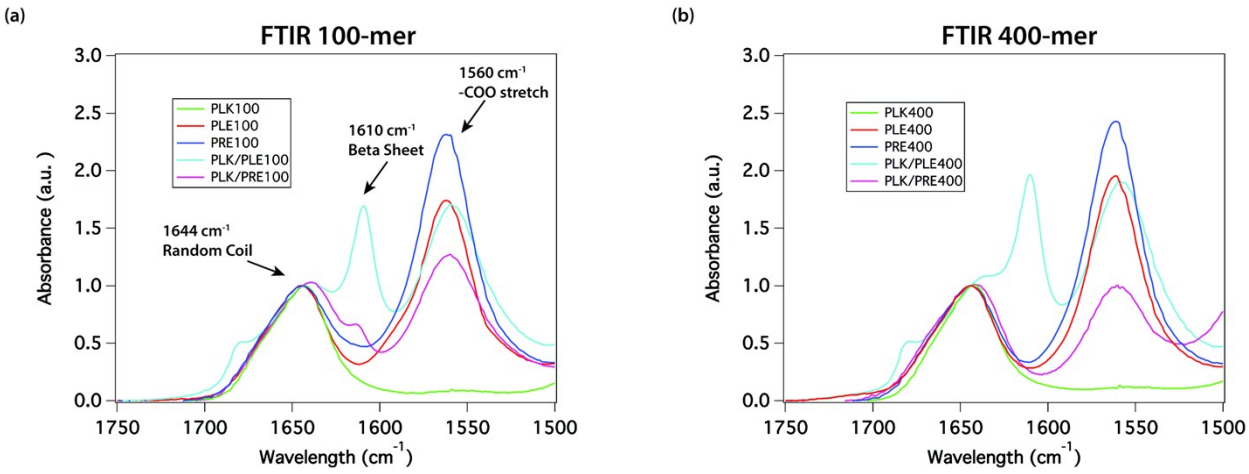

Figure S7. Fourier-transform infrared (FTIR) spectroscopy was used to confirm the secondary structure of individual polymers, as well as determine if secondary structure arises in the polyelectrolyte complex (PEC) state. Individual polymer solutions were prepared in D_2O at 20wt% and complexes were prepared at 20 mM charge-matched conditions (centrifuged at 17,000 rpm for 15 minutes prior to loading). Samples were directly loaded onto a ZnSe plate and measured using attenuated total reflectance (ATR) geometry. Each sample was scanned using a PerkinElmer® Frontier™ FT-IR Spectrometer from 4000 – 500 cm^{-1} (36X) with a scanning speed of .2 cm/s and signal averaged using a resolution of 2 cm^{-1} at room temperature. D2O background subtraction was deemed satisfactory by a flat baseline at 1750 cm^{-1} and signals were normalized by the amide I peak (1644 cm^{-1}) for further analysis. Individual polymers in solution exhibit a strong amide I bands at 1644 cm^{-1} denoting random coil polymer conformation for both the L- and D,L-polymers. Complexes formed using poly(D,L-glutamic acid) form glassy solid-like structures. FTIR-spectra of these solids show a peak at 1610 cm-1 denoting formation of beta-sheet hydrogen bonded structures. Complexes formed with poly(L-glutamic acid) form liquid coacervates and show random-coil configurations at 1644 cm^{-1} (a) 100-mer[1] (b) 400-mer.

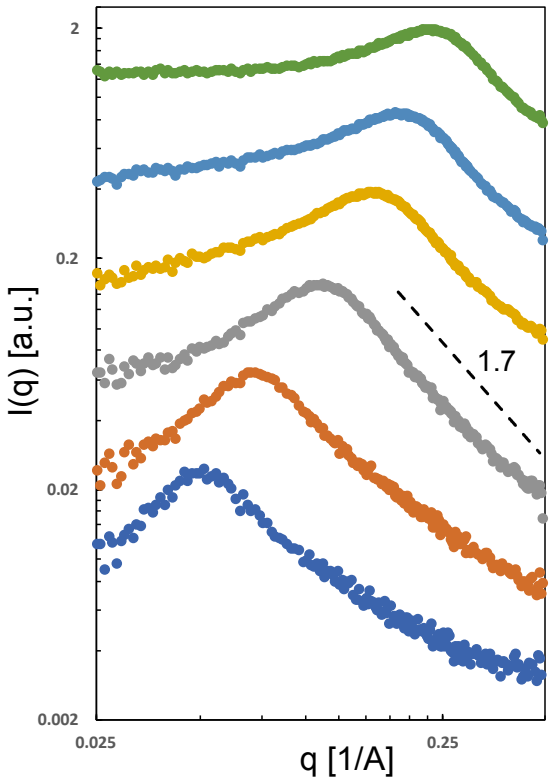

Figure S8. Background subtracted scattering intensity $I(q)$ as a function of wave vector q obtained from SAXS experiments on semidilute polyelectrolyte solutions of PLK_{400} at varying polymer concentrations with no added salt. The polymer concentrations are 1, 2, 5, 10, 15 and 20 wt%, increasing from bottom to top. The black dashed line denotes a $I(q) \sim q^{-1.7}$ power law. The curves are shifted vertically for clarity.

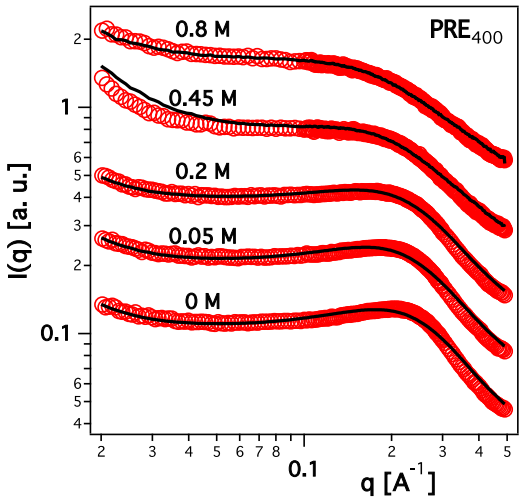

Figure S9. Scattering intensity $I(q)$ as a function of wave vector q obtained from SAXS experiments on 20 wt% semidilute polyelectrolyte solutions of PRE_{400} for varying added salt concentrations. The black lines denote the fit from the models described in the text. The curves are shifted vertically for clarity.

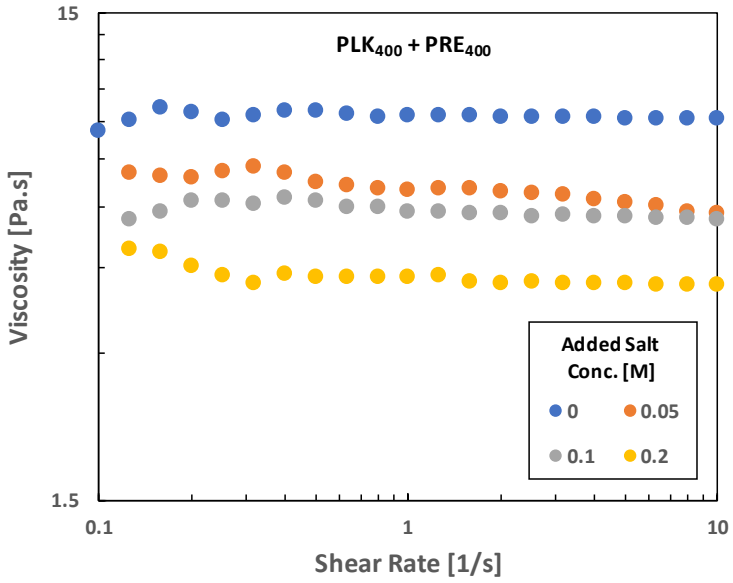

Figure S10. Viscosity as a function of shear rate obtained from steady shear experiments on PLK_{400} + PRE_{400} coacervates with varying added salt concentrations.

Section 1. Shift factor analysis using models for dynamics of associating polymers

The coacervate volume fraction as a function of added salt concentration can be approximately described by the following relation[2]

$\phi_p \cong 0.32 - 0.15c_S$

At the same time, the salt concentration in the solution can be adjusted to account for the counterions that accompany the polypeptides.

Therefore, following Spruijt et al.,[3] the shift factors can be expressed as

$$a_T = \frac{1}{\omega_0} N^{\alpha} \phi_p^{\beta} \exp\left[-a(T)(c+c_S)^{0.5} + b(T)\right] \cong K(0.32 - 0.15c_S)\exp\left[-a(T)(c+c_S)^{0.5}\right];\ K = \frac{1}{\omega_0} N^{\alpha} \exp\left[b(T)\right];\beta \sim 1$$

The corresponding fits to the data are shown in Figure S9. It is clear from the figure that our experimental data cannot be described by a $a_T \sim \exp\left[-a(c+c_S)^{0.5}\right]$ dependence, and rather exhibits a $a_T \sim \exp\left[-k(c+c_S)\right]$ dependence.

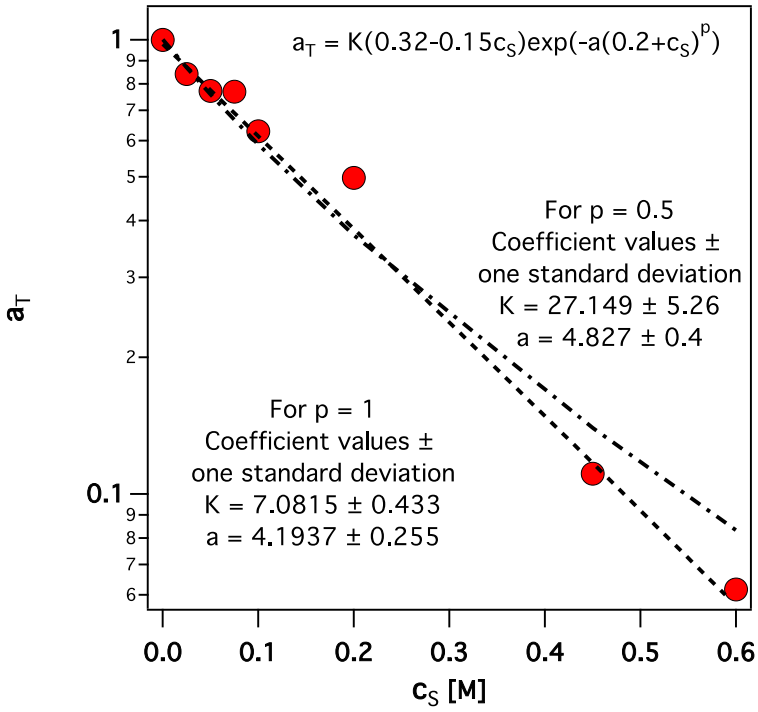

Figure S11. Shift factors as a function of added salt concentration. The dashed and the dashed-dot lines indicate the best fits to the data according to $a_T = K(0.32 - 0.15c_S)\exp\left[-a(T)(0.2+c_S)^p\right]$, with $p = 1$ and 0.5, respectively. The values of the coefficients corresponding to each of the fits are also shown in the Figure.

References

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2 L. Li, S. Srivastava, M. Andreev, A. B. Marciel, J. J. de Pablo and M. V. Tirrell, *In prep.*

3 E. Spruijt, J. Sprakel, M. Lemmers, M. A. Cohen Stuart and J. van der Gucht, *Phys. Rev. Lett.*, 2010, **105**, 208301.