Supporting Information

Control of Dynamics in Polyelectrolyte Complexes by Temperature and Salt

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Figure S1. SEC chromatograms of PMA-Na and PMAPTAC samples in 0.3 M NaNO₃ mobile phase.
Figure S2. Linear viscoelasticity taken before a series of measurements at different temperatures and after, showing no change in sample response. ($n_{av} = 662$ sample in 0.1 M NaCl at 25 °C)
Figure S3. $^1$H solution NMR spectra of PMA-Na/PMAPTAC 2097B coacervate dissolved in 1.0 M KBr in D$_2$O. H$_2$O is at 4.75 ppm. Integrals of peaks corresponding to PMAPTAC only (Area A) and PMAPTAC+PMA-Na (Area B) are shown. Theoretical area ratio is 13:12 for a 1.00:1.00 stoichiometric ratio of MAPTAC:MA-Na.
Figure S4. LVE of PMA/PMAPTA PEC in pure water. Note the crossover point at high frequencies apparent for the entangled samples ($n_{av} = 763$ and 662). Reference temperature = 25 °C.
Figure S5. Photograph of PMA/PMAPTA PEC (coacervate), sample \( n_{av} = 2097 \) B, in 0.3 M NaCl at room temperature.

Figure S6. \( G' \) and \( G'' \) (upper panels) and complex viscosity (lower panels) for some of the PECs in 0.10 M KBr and 0.10 M NaCl illustrating the greater degree
of "doping" for KBr. 0.30 M KBr leads to the lowest G', G" and η values. G': filled points, G'": open points. Data were collected at 25 °C.

Figure S7. TTS a and b shift factors for PECs in 0.03 M, 0.1 M and 0.3 M NaCl at various temperatures. Reference temperature = 25 °C.
Figure S8. TTS of PECs in 0.03 M, 0.1 M, 0.3 M NaCl presented with upwards translation of $G'$ (filled circles) and $G''$ (open circles) by the amount indicated. Reference temperature = 25 °C.
**Figure S9.** Example of the use of the minimum in tanδ to obtain $G_0$. ($n_{av} = 2097B$ sample in 0.03 M NaCl, reference temperature = 25 °C.

**Figure S10.** $G'$ as a function of $\omega a_T$ in 0.03 M (left) 0.10 M (center), and 0.3 M (right) NaCl, reference temperature = 25 °C.
**Figure S11.** Extrapolations of $n_{av} = 2097$B PEC viscosities to estimate zero shear viscosity. Data from Figure 5.

**Table S1.** Zero shear viscosities $\eta_0$ (including $n_{av} = 2097$B)

<table>
<thead>
<tr>
<th>[NaCl]</th>
<th>0.03 M</th>
<th>0.10 M</th>
<th>0.30 M</th>
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<tr>
<td></td>
<td>$\eta_0$ (Pa s)</td>
<td>$\eta_0$ (Pa s)</td>
<td>$\eta_0$ (Pa s)</td>
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<tr>
<td>$n_{av} = 213$</td>
<td>470</td>
<td>112</td>
<td>1.5</td>
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<tr>
<td>$n_{av} = 343$</td>
<td>1070</td>
<td>270</td>
<td>5.8</td>
</tr>
<tr>
<td>$n_{av} = 662$</td>
<td>10600 (7500)$^b$</td>
<td>1700 (1200)</td>
<td>49 (20)</td>
</tr>
<tr>
<td>$n_{av} = 763$</td>
<td>13500 (8500)</td>
<td>2940 (2300)</td>
<td>103 (50)</td>
</tr>
<tr>
<td>$n_{av} = 2097$B</td>
<td>~400000$^a$ (280000)</td>
<td>~100000$^a$ (740000)</td>
<td>~2000$^a$ (800)</td>
</tr>
</tbody>
</table>

$^a$estimated from the curve fitting in Figure S11.

$^b$quantities in parentheses are zero shear viscosities calculated from $\eta_0 \approx G_0 \tau_{rep}$ using values in Tables 4 and 5. Calculated viscosities are about 30-50% lower than measured.
Example calculation for estimating $d^{-3}$, the chain density for PECs

In 0.03 M NaCl the volume fraction of polymer = 0.298. In 1.0 m$^3$ there is 0.3 m$^3$ polymer or 330 kg. For an average monomer molecular weight of 135 g mol$^{-1}$ this is $2.44 \times 10^3$ moles or $1.47 \times 10^{27}$ monomers m$^{-3}$ or $1.14 \times 10^9$ monomers per m or $8.8 \times 10^{-10}$ m between monomers on average. i.e. $d = 0.88 \times 10^{-9}$ m.

Figure S12. Volume fraction of polymer as a function of [NaCl]. The point at 0.6 M is obtained from the equation $y = q[MA]$ where $q = 1.71$ and $y = 1$ (i.e. polymer is completely dissociated and the volume fraction $\rightarrow 0$).
Figure S13. Temperature dependence from Figure S7, \( n_{av} = 2097 \) sample, replotted to obtain activation energies according to the Arrhenius relationship. Reference temperature = 25 °C.
Figure S14. Plot of $1/\tau_{b,e}$ versus $(1-y)y^2$. Using $y = q[MA]$ where $q = 1.71$, $\tau_{b,y}$ values from Table 5, Equation 19 $\frac{1}{\tau_{b,y}} = \frac{1}{\tau_{b,i}} + \frac{1}{\tau_{b,e}}$, and $\tau_{b,i} = 1.4 \times 10^{-4}$ from Table 5.

Figure S15. Doping level $y$ versus [NaCl] using the data of Table 3. The slope (1.71) is $q$, the where $y = q[NaCl]$. 
Table S2. TTSS shift factors.

<table>
<thead>
<tr>
<th>n_{av}</th>
<th>2097B</th>
<th>763</th>
<th>662</th>
<th>343</th>
<th>213</th>
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<tbody>
<tr>
<td></td>
<td>a_s</td>
<td>b_s</td>
<td>a_s</td>
<td>b_s</td>
<td>a_s</td>
</tr>
<tr>
<td>Water</td>
<td>1.62</td>
<td>0.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>0.03M</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>0.1M</td>
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<td>0.3M</td>
<td>0.00453</td>
<td>1.04</td>
<td>0.0116</td>
<td>1.28</td>
<td>0.00593</td>
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</table>

**Figure S16.** Rheological behavior of 31 wt% solutions of individual PMA-Na_{2081B} and PMAPTAC_{2112B} in 1.0 M NaCl: G' (filled symbols), G" (open symbols) and complex viscosity are all much lower than for the corresponding PEC, also shown for comparison. Reference temperature = 25 °C.
Figure S17. $\tau_{b,y}$ as a function of doping level, $y$, for PMA/PMAPTA PEC with $n_{av} = 763$. 