Supporting Information

Interfacial Polarization and Electroresponsive Electrorheological Effect of Anionic and Cationic Poly(ionic liquid)s

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**Figure S1.** The $^1$H NMR spectra of P(STFSI)[N2222] showing the good accordance of integration values of the styrene backbone and the N2222$^+$ counter cation.
**Figure S2.** Gel Permeation Chromatogram and molecular weight distribution of

(a) P[STFSI][N2222] and (b) P[VBTEA][TFSI].
Figure S3. FT-IR spectra of P[STFSI][N2222] and P[VBTSA][TFSI].
Figure S4. WAXS spectra of P[STFSI][N2222] and P[VBTEA][TFSI].
Figure S5. TGA curves of $\text{P}[\text{STFSI}][\text{N2222}]$ and $\text{P}[\text{VBTEA}][\text{TFSI}]$ in nitrogen.
Figure S6. SEM images of P[STFSI][N2222] (a) and P[VBEA][TFSI] (b) particles.
Figure S7. Shear viscosity as a function of shear rate for ER suspensions of P[STFSI][N2222] (solid symbols) and P[VBTEA][TFSI] (open symbols) at zero electric field (T = 23°C, φ = 20 vol %).
Figure S8. Frequency dependence of real part ($\varepsilon'$) and imaginary part ($\varepsilon''$) of permittivity of silicone oil ($T = 23^\circ\text{C}$).
Table S1. Dielectric parameters of ER suspensions of P[STFSI][N2222] and P[VBTEA][TFSI] at room temperature (φ = 20 vol%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>ε'₀</th>
<th>ε'∞</th>
<th>Δε'</th>
<th>λ(s)</th>
<th>σ(S/m)</th>
<th>A</th>
<th>m</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>P[STFSI][N2222]</td>
<td>7.20</td>
<td>3.30</td>
<td>3.90</td>
<td>1.50×10⁻²</td>
<td>1.06×10⁻¹</td>
<td>3.50×10⁻¹</td>
<td>2.00</td>
<td>0.63</td>
</tr>
<tr>
<td>P[VBTEA][TFSI]</td>
<td>7.40</td>
<td>3.20</td>
<td>4.20</td>
<td>2.65×10⁻³</td>
<td>3.81×10⁻¹</td>
<td>8.05×10⁻³</td>
<td>2.60</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Dielectric spectra analysis: The dielectric data was analyzed by the dielectric relaxation function below containing a Cole-Cole’s term, a DC conductivity term, and an electrode polarization (EP) term,¹,²

\[
\varepsilon^*(\omega) = \varepsilon' + i\varepsilon'' = \varepsilon'_\infty + \frac{\Delta\varepsilon'}{1+(i\omega\lambda)^\alpha} + i \frac{\sigma}{\varepsilon_0\omega} + A\omega^{-m}
\]  

(1)

where, \(\Delta\varepsilon' = \varepsilon'_0 - \varepsilon'_\infty\) is the dielectric intensity (\(\varepsilon'_0\) and \(\varepsilon'_\infty\) are the limit values of \(\varepsilon'\) below and above the relaxation frequencies, respectively), \(\omega\) is the angular frequency, \(\lambda = 1/\omega_{\text{max}}\) is the relaxation time (\(\omega_{\text{max}}\) is the local angle frequency corresponding to the peak of \(\varepsilon''\)), \(\alpha (0<\alpha<1)\) is the Cole-Cole parameter characterizing the broadness of the relaxation time, \(\sigma\) is the DC conductivity, and \(m\) is related to the slope of EP’s high frequency tail, \(A\) is related to the amplitude of EP. The solutions of \(\varepsilon'\) and \(\varepsilon''\) are expressed as flows,

\[
\varepsilon' = \varepsilon'_\infty + \Delta\varepsilon'[\left(1 + 2(\omega\lambda)^\alpha \cos\left(\frac{\pi m}{2}\right) + (\omega\lambda)^2\alpha\right]^{\frac{1}{2}} \cos\left[\tan^{-1}\left(\frac{\sin\frac{\pi m}{2}}{(\omega\lambda)^\alpha + \cos\frac{\pi m}{2}}\right)\right] + A\omega^{-m}
\]  

(2)

\[
\varepsilon'' = \frac{\sigma}{\varepsilon_0\omega} + \Delta\varepsilon'[\left(1 + 2(\omega\lambda)^\alpha \cos\left(\frac{\pi m}{2}\right) + (\omega\lambda)^2\alpha\right]^{\frac{1}{2}} \sin\left[\tan^{-1}\left(\frac{\sin\frac{\pi m}{2}}{(\omega\lambda)^\alpha + \cos\frac{\pi m}{2}}\right)\right]
\]  

(3)

The fitting protocol as follows: First, we took seven sets of \((\omega, \varepsilon', \varepsilon'')\) values from the measuring points and introduced into the Eq. 2 and Eq. 3, respectively. Then, using Matlab to calculate the fitting parameters \((\varepsilon'_\infty, \Delta\varepsilon', \lambda, \sigma, \alpha, A, \text{and} m)\). Finally, slightly adjusting the fitting parameters makes fitting curves are coincide with the measured dielectric data.
Table S2. Information about mobile ions in P[STFSI][N2222] and P[VBTEA][TFSI]

<table>
<thead>
<tr>
<th>Sample</th>
<th>mobile ion</th>
<th>$r_i$ (nm)</th>
<th>$^b M$ (g/mol)</th>
<th>$^c \rho$ (g/cm³)</th>
<th>$^d A_{free}/A_{total}$</th>
<th>$^e n$ (nm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P[STFSI][N2222]</td>
<td>N2222⁺</td>
<td>0.339</td>
<td>444.16</td>
<td>1.39</td>
<td>0.32</td>
<td>0.612</td>
</tr>
<tr>
<td>P[VBTEA][TFSI]</td>
<td>TFSI⁻</td>
<td>0.327</td>
<td>498.50</td>
<td>1.41</td>
<td>1.00</td>
<td>1.703</td>
</tr>
</tbody>
</table>

*a. $r_i$ mobile ion radius taken from Ref. 3.*

*b. $M$ the monomer molecular weight.*

*c. $\rho$ measured densities of the samples at room temperature.*

*d. $A_{free}/A_{total}$ the proportions of dissociated mobile ions.*

*e. $n$ the effective number density of mobile ions.*
Figure S9. RESP charge distribution of P[STFSI][N2222](top) and P[VBTEA][TFSI](bottom) obtained with Multiwfn program. There are some unimportant atomic charges left unmarked.

Figure S10. The calculated ion pair interaction energies of P[VBTEA][TFSI] and P[STFSI][N2222].

DFT calculations: Gaussian program was employed for density functional theory (DFT) calculations. Geometry optimization was performed at M06-2X/6-311+G(d,p)//M06-2X/6-31+G(d) level. Restrained electrostatic potential (RESP) atomic charges were obtained with Multiwfn program. The integral equation formalism polarizable continuum model (IEFPCM)
was used to account for the influence of dielectric constant.\textsuperscript{11}

**Figure S11.** Temperature-modulated dielectric spectra of ER suspensions of P[STFSI][N2222] (a, b) and P[VBTEA][TFSI] (c, d). The lines represent the best fit of data by Eq. 1 ($\varphi = 20$ vol %).
References


(2) Kremer, F.; Schonhals, A.; Luck, W. Broadband Dielectric Spectroscopy; Springer-Verlag, 2002.


