

(Supporting Information)
**Rheological Scaling of Ionic Liquid-Based
Polyelectrolytes in Ionic Liquid Solutions: The Effect
of the Ion Diameter of Ionic Liquids**

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S1 Molecular weight measurements

We estimated the weight-average molecular weight M_w of the synthesized PC₄-TFSI from a Debye plot, obtained through static light scattering measurements using a light scattering spectrometer (Zetasizer Nano ZSP, Malvern Panalytical Ltd.). In the Debye plot, the value of M_w is estimated by fitting the experimental data with the following equation:

$$\frac{Kc}{R_\theta} = \frac{1}{M_w P(\theta)} + 2A_2c, \quad (\text{S1})$$

where c , R_θ , $P(\theta)$, and A_2 are the mass concentration of polymers, the excess Rayleigh ratio, the form factor, and the second virial coefficient. Here $K = \frac{4\pi^2 n^2}{N_A \lambda_0^4} \left(\frac{dn}{dc}\right)^2$ is the optical constant, where N_A , n , and $\lambda_0 = 633$ nm are the Avogadro constant, the refractive index of the solution, and the wavelength of incident light. In our experiments, the value of R_θ at a scattering angle of 175° was measured while the mass concentration of PC₄-TFSI was varied from 1 g/L to 8 g/L, dissolved in DMF mixed with 0.5 M of Li-TFSI. The refractive index increment $\frac{dn}{dc} = 0.0263$ mL g⁻¹ was estimated from Fig. S1 obtained by using a refractometer (RA-130, Kyoto Electronics Manufacturing Co., Ltd.). We observed a linear dependence of the measured $\frac{Kc}{R_\theta}$ on c and estimated the weight-average molecular weight of PC₄-TFSI as $M_w = 1.27 \times 10^6$ g mol⁻¹, see Fig. S2. The degree of polymerization N was then estimated as $N = 2944$ since the molar mass of the PC₄-TFSI repeating unit is 431.43 g mol⁻¹.

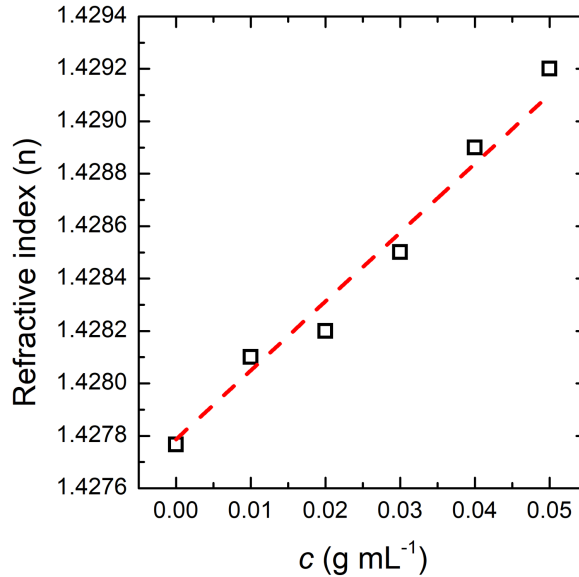


Figure S1: The dependence of the refractive index at room temperature on the mass concentration c of PC₄-TFSI for the mixture of PC₄-TFSI and DMF containing 0.5 mol L⁻¹ of Li-TFSI. The red-dashed line represents the linear fit to the measured refractive index with an estimated slope of $\partial n/\partial c = 0.0263$ mL g⁻¹.

Here, we should note that the estimated M_w of the PC₄-TFSI may have an uncertainty in magnitude due to the following two reasons. First, we measured the values of n using PC₄-TFSI solutions without further pre-treatment, such as an extensive dialysis against

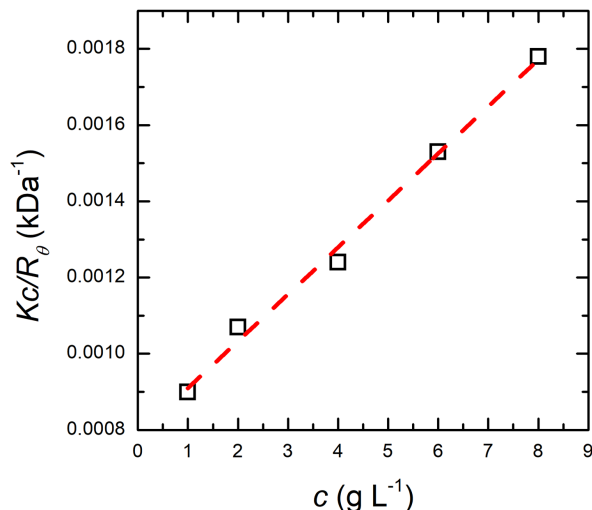


Figure S2: The dependence of $\frac{Kc}{R_\theta}$ on c for the synthesized PC₄-TFSI dissolved in DMF with 0.5 M of Li-TFSI. In the plot, we used $\frac{dn}{dc} = 0.0263 \text{ mL g}^{-1}$ to estimate the value of the optical constant K .

the solvent [1], to match the chemical potential of the added salt between the pure solvent and the polyelectrolyte solution. With this mismatch of the salt chemical potential, Schweins et al. [1] showed that the value of $\frac{dn}{dc}$ became larger than that obtained with the pre-treatment. This is because an unequal distribution of salt ions in polyelectrolyte solutions creates further optical contrast of the dissolved polyelectrolyte chains and thus increases the refractive index. Therefore, the dependence of $\frac{Kc}{R_\theta}$ on c , shown in Fig. S2, may be shifted downward. In this case, the intercept value of the fitted curve in Fig. S2 becomes smaller, i.e., the value of M_w becomes larger, based on eqn (S1). Second, we assumed $P(\theta) = 1$ when estimating the M_w based on eqn (S1). However, this assumption is only valid when the polymer molecular weight is sufficiently small, whereas the value of $P(\theta)$ for high-molecular-weight polymer samples becomes smaller than unity [2]. If this scenario was applicable to our system, the obtained value of M_w from Fig. S2 would become smaller. Nevertheless, since the estimated molecular weight of the PC₄-TFSI is sufficiently large, any potential effects on the polymer dynamics, originated from chain ends, can be neglected.

S2 Supporting figure and table

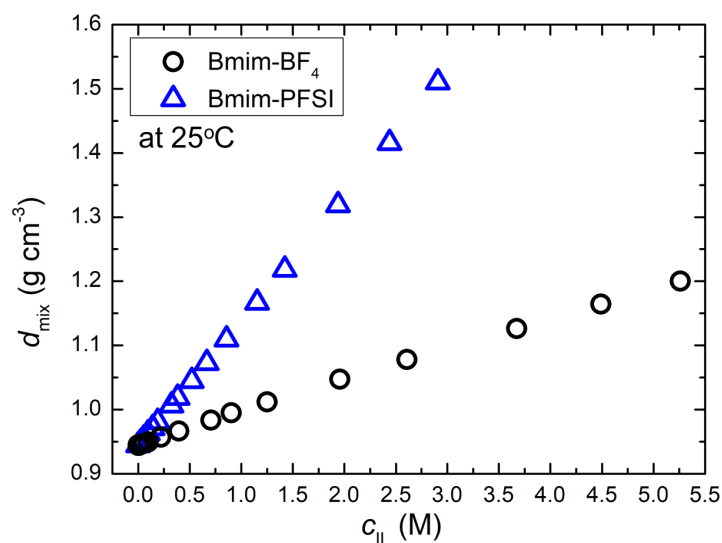


Figure S3: The density d_{mix} at 25° is plotted as a function of the ionic liquid concentration c_{IL} for Bmim-BF₄ (black circles) and Bmim-PFSI (blue triangles) solutions in DMF.

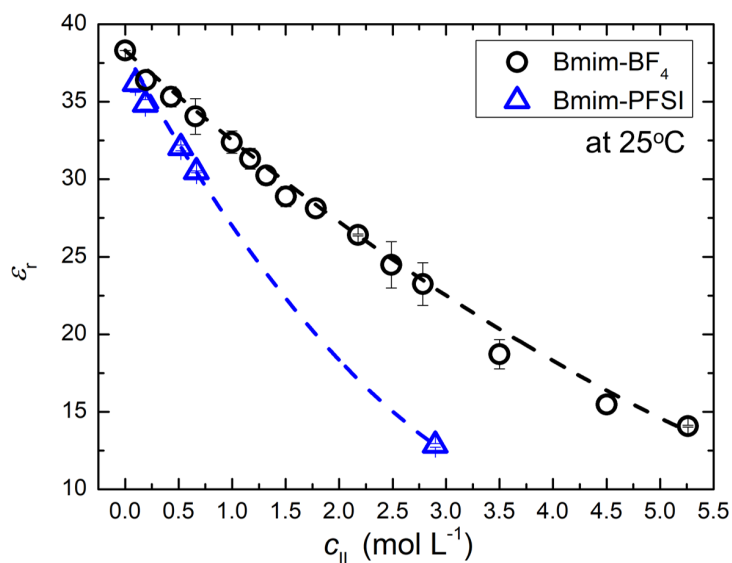


Figure S4: The relative dielectric constant ϵ_r at 25°C is plotted as a function of the ionic liquid concentration c_{IL} for Bmim-BF₄ (black circles) and Bmim-PFSI (blue triangles) solutions in DMF. The dashed lines represent the best curve fit to the measured ϵ_r , obtained using a quadratic function of $\epsilon_r = \epsilon_{DMF} + Ac_{IL} + Bc_{IL}^2$. The corresponding best fitting coefficients are $A = -6.05 \pm 0.06 \text{ mol}^{-1} \text{ L}$ and $B = 0.262 \pm 0.02 \text{ mol}^{-2} \text{ L}^2$ for the mixture of Bmim-BF₄ and DMF, $A = -12.65 \pm 0.26 \text{ mol}^{-1} \text{ L}$ and $B = 1.33 \pm 0.10 \text{ mol}^{-2} \text{ L}^2$ for the mixture of Bmim-PFSI and DMF.

References

- [1] R. Schweins, J. Hollmann, and K. Huber, “Dilute solution behaviour of sodium polyacrylate chains in aqueous nacl solutions,” *Polymer*, vol. 44, no. 23, pp. 7131–7141, 2003.
- [2] M. Rubinstein and R. H. Colby, *Polymer Physics*. Oxford University Press: New York, 2003.