

## Supporting Information

### Coordination Effects in Polymer Electrolytes: Fast Li<sup>+</sup> Transport by Weak Ion Binding

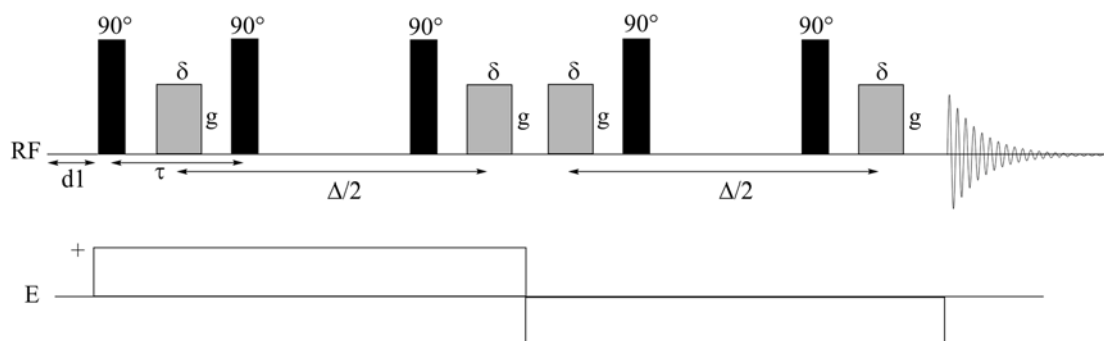
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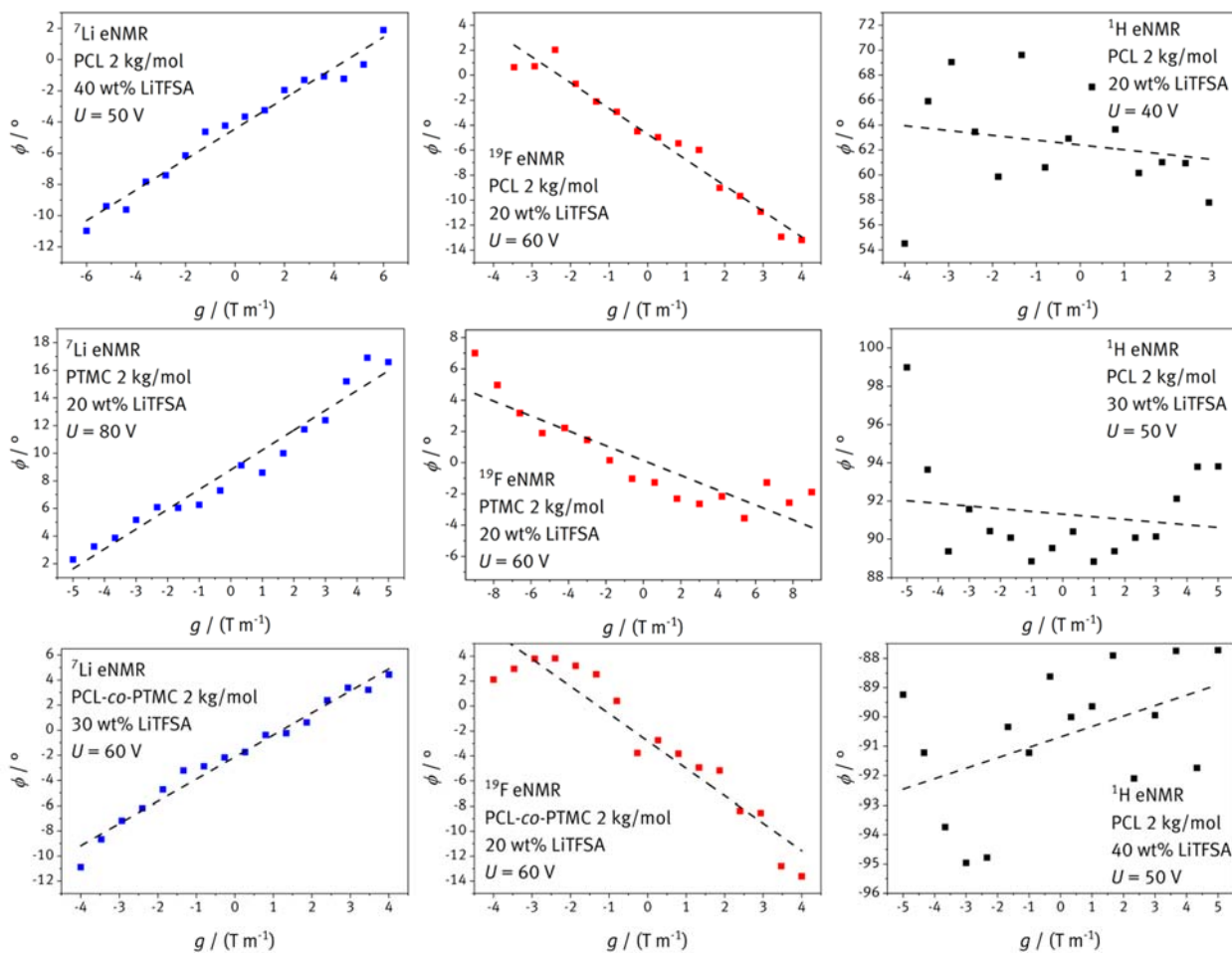
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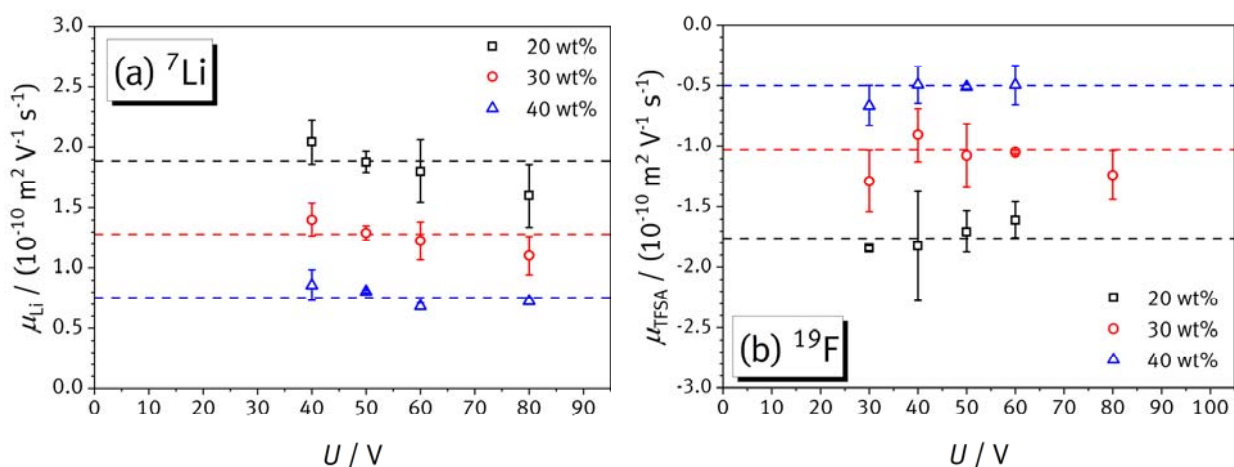
#### 1. Figures



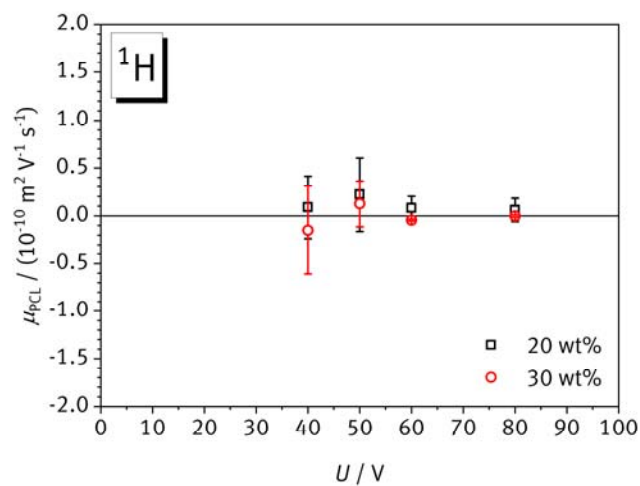
**Figure S1.** Pulse sequence used for the eNMR measurements based on the double-stimulated echo pulse sequence supplemented by electric field reversal.



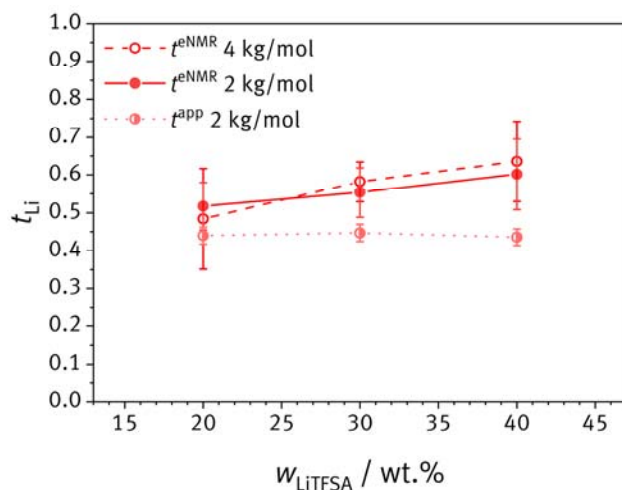
**Figure S2.** Exemplary raw data of single eNMR experiments, giving phase shift data as a function of the gradient strength  $g$ . Dashed lines represent linear fits. Sample and measurement specifications are given in the plots.



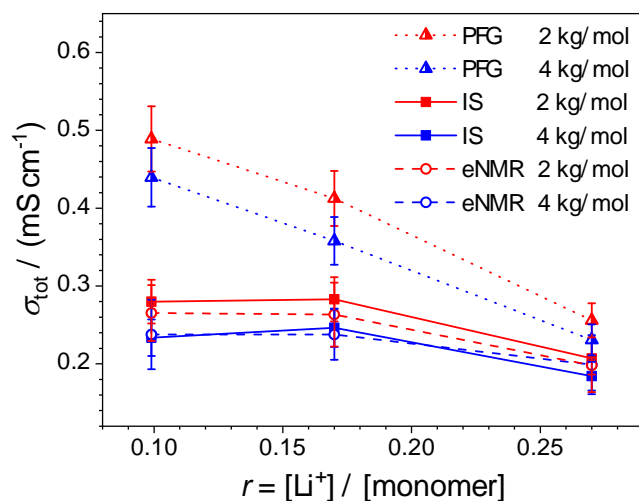
**Figure S3.** Electrophoretic mobilities of (a) lithium and (b) TFSA as a function of the applied voltage for the samples PCL with  $M_n = 2000$  g/mol and 20 wt% (black), 30 wt% (red) and 40 wt% (blue) LiTFSA. The dashed lines represent the average value for each concentration. The error bars result from the statistical error of repeated measurements at the same voltage.



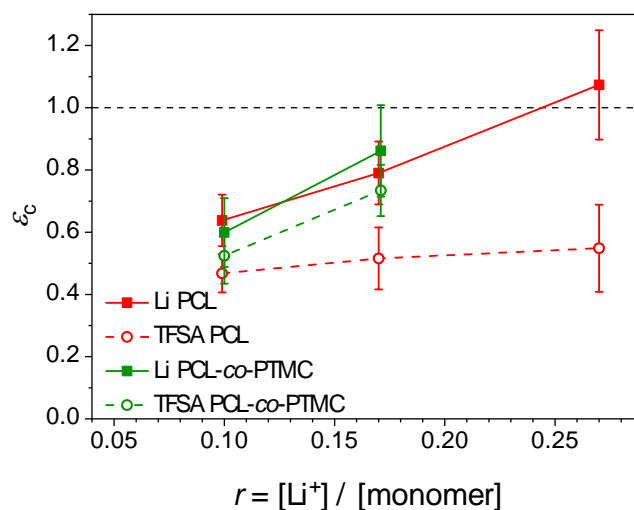
**Figure S4.** Electrophoretic mobilities of PCL determined via  $^1\text{H}$ -eNMR as a function of the applied voltage for the samples with  $M_n = 2000$  g/mol and 20 wt% (black) and 30 wt% (red). The error bars result from the statistical error of repeated measurements.



**Figure S5.** Lithium transference numbers for the samples PCL  $M_n = 2000$  g/mol (solid line, filled symbols) and  $M_n = 4000$  g/mol (dashed line, open symbols) as a function of the salt concentration. For comparison, the apparent lithium transference numbers from PFG-NMR are also depicted for PCL with  $M_n = 2000$  g/mol (dotted line, half-filled symbols). Lines serve as a guide to the eye. Error bars result from error propagation.



**Figure S6.** Total ionic conductivities calculated from eNMR (open circles, dashed lines), PFG-NMR (triangles, dotted lines) and measured by impedance spectroscopy (filled squares, solid lines) for PEO (blue) and PCL (red) with  $M_n = 2000$  g/mol and 4000 g/mol, respectively, as a function of the lithium-to-monomer ratio  $r$ . Lines serve as a guide to the eye. Error bars result from error propagation.



**Figure S7.** Effective charges of Li (filled squares, solid lines) and TFSA (open circles, dashed lines) for PCL (red) and PCL-co-PTMC (green) with  $M_n = 2000$  g/mol as a function of the lithium-to-monomer ratio  $r$ . Lines serve as a guide to the eye. Error bars result from error propagation.

## 2. Tables

**Table S1.** Composition of the investigated samples showing the type of polymer, the lithium-to-monomer ratio  $r$ , the weight percentage of salt  $w_{\text{LiTFSA}}$ , the measured density  $\rho$  and the molar salt concentration  $c_{\text{Li}}$ .

Polymer	$M_n / \left( \frac{\text{g}}{\text{mol}} \right)$	$r = \frac{[\text{Li}]}{[\text{monomer}]}$	$w_{\text{LiTFSA}} / \text{wt}\%$	$\rho / \left( \frac{\text{g}}{\text{cm}^3} \right)$	$c_{\text{Li}} / \left( \frac{\text{mol}}{\text{L}} \right)$
PCL	2000	0.10	20	1.08	0.75
		0.17	30	1.13	1.18
		0.27	40	1.18	1.64
PCL	4000	0.10	20	1.13	0.79
		0.17	30	1.12	1.17
		0.27	40	1.23	1.71
PCL-co-PTMC	2000	0.10	20	1.05	0.73
		0.17	30	1.07	1.12
PTMC	2000	0.10	20	1.14	0.79

**Table S2.** Electrophoretic mobilities determined by eNMR  $\mu^{\text{eNMR}}$  of lithium and TFSA and lithium transference numbers  $t_{\text{Li}}$  for all samples studied in this work. The error of the mobility is the statistical uncertainty resulting from repetitions of the experiment, while the error of the transference number was calculated by error propagation.

Polymer	$M_n / \left( \frac{\text{g}}{\text{mol}} \right)$	$r$	$\mu_{\text{Li}}^{\text{eNMR}} / \left( 10^{-10} \frac{\text{m}^2}{\text{V s}} \right)$	$\mu_{\text{TFSA}}^{\text{eNMR}} / \left( 10^{-10} \frac{\text{m}^2}{\text{V s}} \right)$	$t_{\text{Li}}$
PCL	2000	0.10	$1.9 \pm 0.2$	$-1.8 \pm 0.2$	$0.52 \pm 0.06$
		0.17	$1.3 \pm 0.2$	$-1.0 \pm 0.2$	$0.55 \pm 0.07$
		0.27	$0.8 \pm 0.1$	$-0.5 \pm 0.1$	$0.60 \pm 0.09$
PCL	4000	0.10	$1.5 \pm 0.4$	$-1.6 \pm 0.1$	$0.48 \pm 0.13$
		0.17	$1.2 \pm 0.1$	$-0.9 \pm 0.1$	$0.58 \pm 0.05$
		0.27	$0.8 \pm 0.1$	$-0.4 \pm 0.1$	$0.64 \pm 0.11$
PCL-co-PTMC	2000	0.10	$1.4 \pm 0.3$	$-1.5 \pm 0.2$	$0.49 \pm 0.09$
		0.17	$1.2 \pm 0.2$	$-1.1 \pm 0.1$	$0.52 \pm 0.08$
PTMC	2000	0.10	$0.7 \pm 0.1$	$-0.3 \pm 0.1$	$0.67 \pm 0.10$

**Table S3.** Fitting parameters for the NMR titration experiment according to Equation 6.

Polymer	$a / \text{ppm}$	$b$	$c / \text{ppm}$
PEO	2.78	0.19	0.64
PCL	1.72	0.07	1.12
PCL-co-PTMC	1.29	0.09	1.37
PTMC	0.46	0.17	1.79