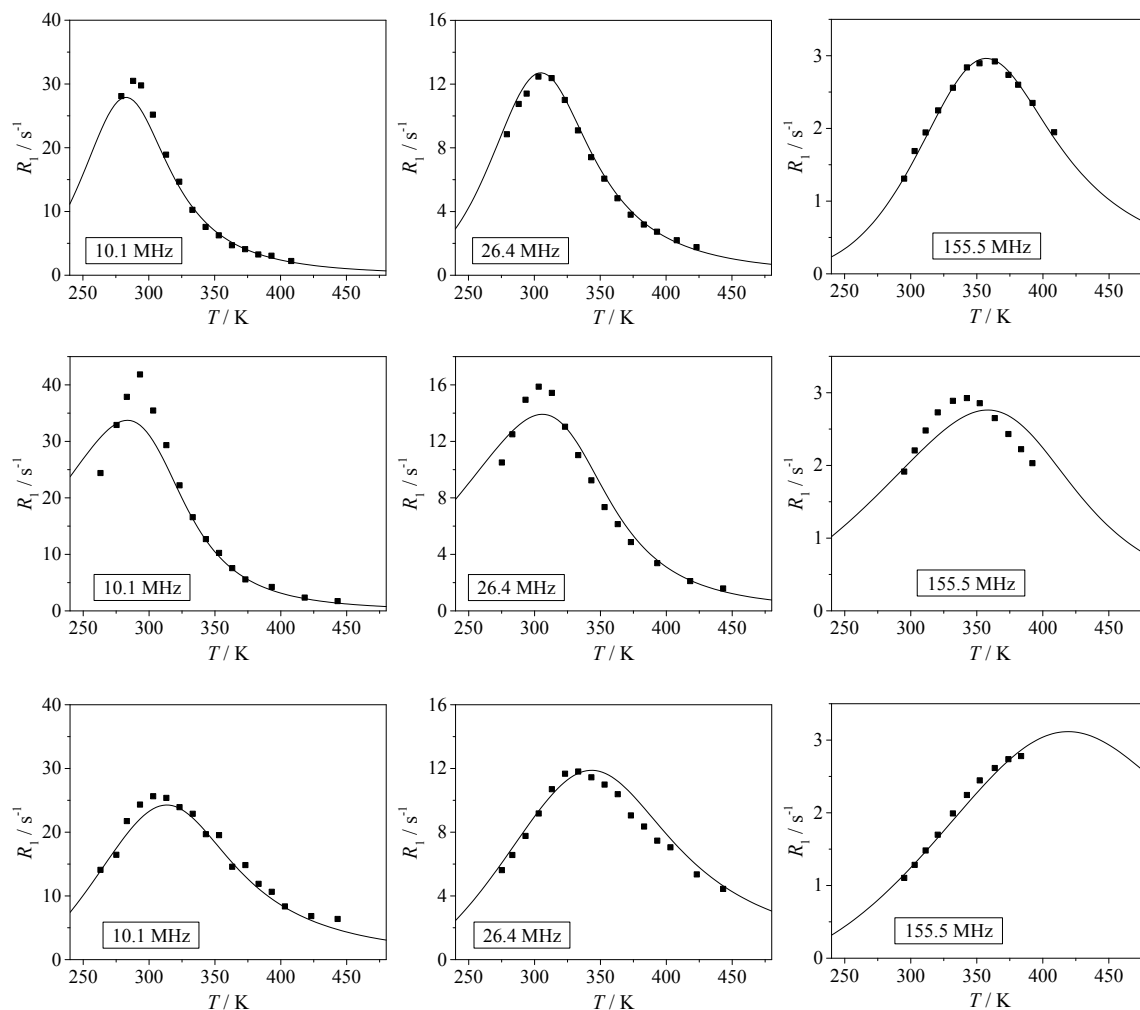


M. Brinkkötter, M. Gouverneur, P. J. Sebastião, F. Vaca Chávez, M. Schönhoff: Spin relaxation studies of Li<sup>+</sup> ion dynamics in polymer gel electrolytes. Phys. Chem. Chem. Phys. **2017**

## Supporting Information

### A: Fit results by the CD model with a temperature dependent prefactor



**Fig. S1.**  $R_1$  data of the samples 20:00:4 Reference (top), 20:20:4 PEO (middle) and 20:20:4 PDADMA (bottom) and global fit for all frequencies with the CD model of the data. A linear temperature dependence of the prefactor  $A$  is used to fit the data.

## **B: Dipolar relaxation**

Spin relaxation is caused by local fluctuations of the magnetic field. For a quadrupolar nucleus like <sup>7</sup>Li, these fluctuations might be induced by quadrupolar or by dipole-dipole interactions. In the investigated electrolyte samples dipolar relaxation might appear between the lithium ion and the fluorine of the fluorinated methyl groups from the TFSI<sup>-</sup>. In literature it was found that the anion is coordinated by the oxygen to the lithium with a distance around 2 Å.<sup>1</sup> Although the fluorine is not directly bound to the cation, it is located next to the oxygen and therefore might interact with the lithium ion. The distance between the fluorine and the lithium has to be longer than the distance between the lithium and the oxygen and therefore at least more than 2 Å.

If the BPP-model is valid and *Arrhenius* behavior is assumed, the prefactor *A* can be calculated from eq. (4) and (7). In the case of dipolar relaxation the prefactor is given by eq. (6) and the distance between two interacting nuclei can be calculated. Using one BPP function and assuming dipolar relaxation to fit the relaxation measurements, prefactor values in the range from 0.5·10<sup>9</sup> s<sup>-2</sup> up to 2.5·10<sup>9</sup> s<sup>-2</sup> can be calculated. The obtained distances are shown in Table S1.

**Table S1. Calculated distances for dipolar relaxation.**

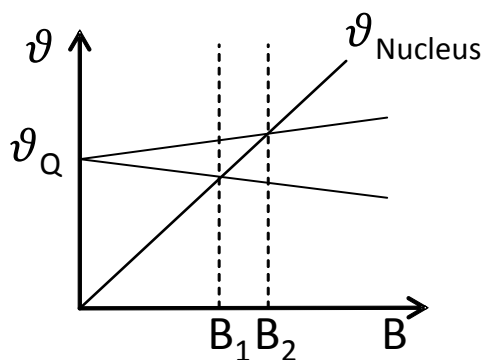
| $A / s^{-2}$        | $r / \text{\AA}$ |
|---------------------|------------------|
| 0.5·10 <sup>9</sup> | 2.3              |
| 1.5·10 <sup>9</sup> | 1.9              |
| 2.5·10 <sup>9</sup> | 1.8              |

These values are not realistic for the lithium fluorine distance indicating that dipolar relaxation is not the dominant factor. Distances of 4 Å or more can be assumed and therefore it can be concluded that the dipolar relaxation is not significantly contributing to the spin relaxation.

### C: Quadrupolar cross relaxation

Besides dipolar and quadrupolar relaxation, cross relaxation might contribute and thus influence the relaxation at the measured frequencies. Cross relaxation can occur if two different nuclei interact with each other and there is an overlap of the energy difference for different states.

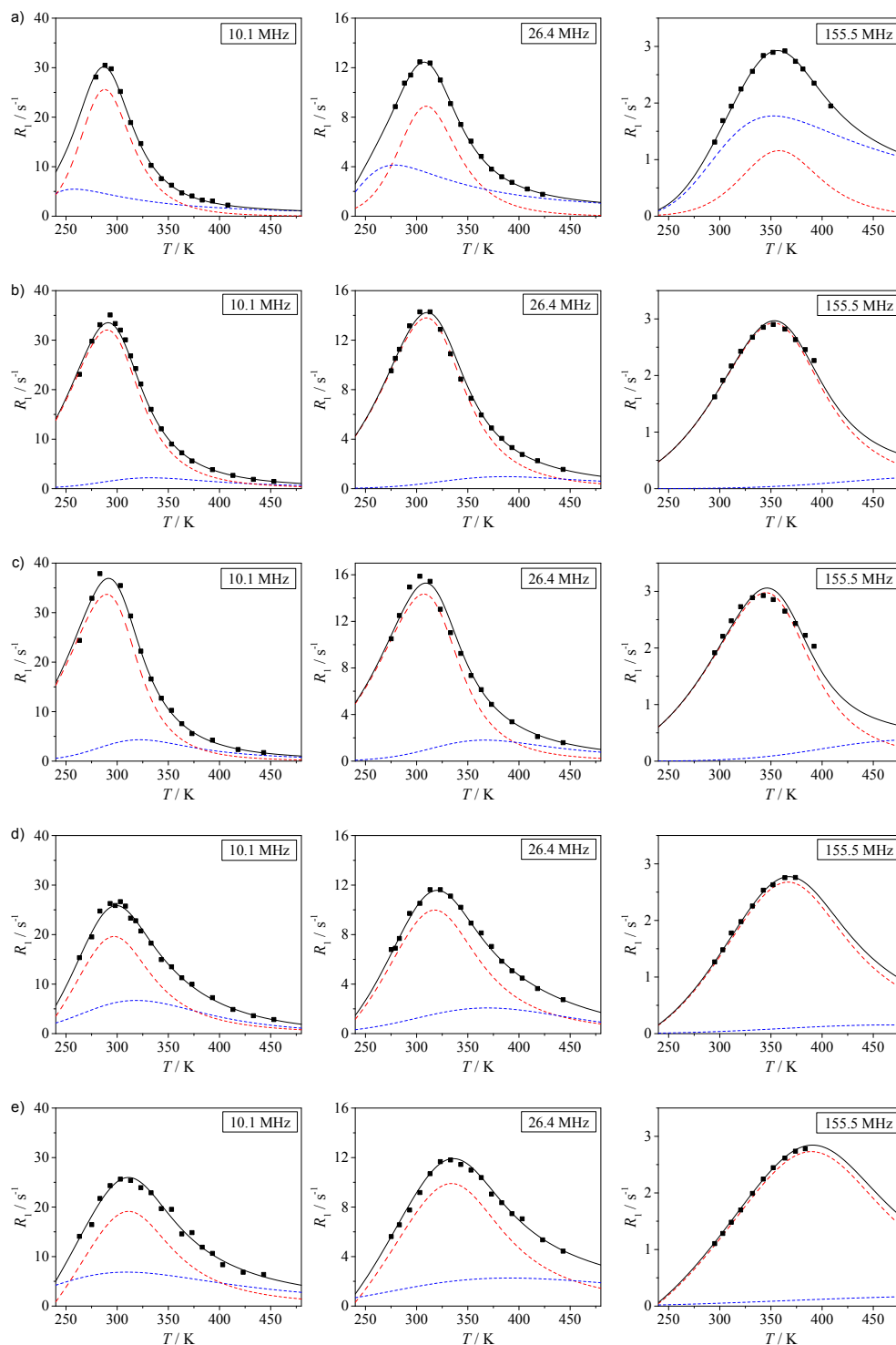
In Fig. 2 an example of cross relaxation for a quadrupolar nucleus is shown. If the resonance frequency ( $\nu = \frac{\omega_0}{2\pi}$ ) of a different nucleus ( $\nu_{Nucleus}$ ) correlates to the energy difference of the quadrupolar splitting of the quadrupolar nucleus ( $\nu_Q$ ), it can interact with this nucleus through the cross relaxation. According to Fig. S2 cross relaxation can then occur if  $B_0 = B_1$  or if  $B_0 = B_2$ .<sup>2</sup>



**Fig. S2. Resonance frequencies of a quadrupolar nucleus.<sup>2</sup>**

In the samples of the present work <sup>7</sup>Li is a quadrupolar nucleus. Therefore it can be assumed that any potential cross relaxation would be caused by the interaction of the quadrupolar nucleus <sup>7</sup>Li with another nucleus, like protons or fluorine. However, since the quadrupolar coupling constant of lithium is in the kHz range, this mechanism is not contributing at the measured frequencies in this work (10.1 MHz - 155.5 MHz for <sup>7</sup>Li).<sup>3</sup>

### D: Fit results by the CD+BPP model each with a temperature dependent prefactor



**Fig. S3.**  $R_1$  data of the samples 20:00:4 Reference (a), 20:10:4 PEO (b), 20:20:4 PEO (c), 20:10:4 PDADMA (d) and 20:20:4 PDADMA (e) and global fit for all frequencies with the CD (red dashed line) + BPP model (blue dashed line) of the data. A linear temperature dependence of the prefactor  $A$  is used to fit the data.

a) Resulting fit parameters of the CD contribution

**Table S2.** Fit parameters  $a$ ,  $b$  and temperature-dependent prefactor  $A_{quad} = a \cdot T + b$ . As examples, values of  $A_{quad}$  at 298 K ( $A_{298}$ ) and at 373 K ( $A_{373}$ ) are shown. The quadrupolar coupling constant  $Q$  is calculated at 298 K and 373 K.

| Sample            | $a / s^{-2}K^{-1}$ | $b / s^{-2}$      | $A_{298} / s^{-2}$ | $Q_{298} / kHz$ | $A_{373} / s^{-2}$ | $Q_{373} / kHz$ |
|-------------------|--------------------|-------------------|--------------------|-----------------|--------------------|-----------------|
| 20:00:4 Reference | $-1.4 \cdot 10^6$  | $7.4 \cdot 10^8$  | $3.2 \cdot 10^8$   | 16              | $2.2 \cdot 10^8$   | 13              |
| 20:10:4 PEO       | $6.2 \cdot 10^6$   | $-8.5 \cdot 10^8$ | $1.0 \cdot 10^9$   | 27              | $1.5 \cdot 10^9$   | 33              |
| 20:20:4 PEO       | $7.8 \cdot 10^6$   | $-1.1 \cdot 10^9$ | $1.3 \cdot 10^9$   | 31              | $1.8 \cdot 10^9$   | 37              |
| 20:10:4 PDADMA    | $1.2 \cdot 10^7$   | $-2.8 \cdot 10^9$ | $8.8 \cdot 10^8$   | 26              | $1.8 \cdot 10^9$   | 37              |
| 20:20:4 PDADMA    | $1.8 \cdot 10^7$   | $-4.4 \cdot 10^9$ | $1.1 \cdot 10^9$   | 29              | $2.5 \cdot 10^9$   | 43              |

**Table S3.** Values of the width parameter  $\epsilon$ , the activation energy  $E_A$  and correlation time  $\tau$ . As examples, values of the correlation time  $\tau_0$  at 298 K ( $\tau_{298}$ ) and at 373 K ( $\tau_{373}$ ) are given.

| Sample            | $\epsilon$ | $\tau_0 / s$         | $E_A / kJ mol^{-1}$ | $\tau_{298} / s$    | $\tau_{373} / s$     |
|-------------------|------------|----------------------|---------------------|---------------------|----------------------|
| 20:00:4 Reference | 1          | $1.6 \cdot 10^{-14}$ | 32                  | $6.2 \cdot 10^{-9}$ | $4.7 \cdot 10^{-10}$ |
| 20:10:4 PEO       | 0.24       | $3.6 \cdot 10^{-15}$ | 38                  | $1.4 \cdot 10^{-8}$ | $6.5 \cdot 10^{-10}$ |
| 20:20:4 PEO       | 0.19       | $8.1 \cdot 10^{-16}$ | 42                  | $1.5 \cdot 10^{-8}$ | $5.2 \cdot 10^{-10}$ |
| 20:10:4 PDADMA    | 0.16       | $2.2 \cdot 10^{-14}$ | 33                  | $1.4 \cdot 10^{-8}$ | $9.4 \cdot 10^{-10}$ |
| 20:20:4 PDADMA    | 0.09       | $6.0 \cdot 10^{-14}$ | 32                  | $2.7 \cdot 10^{-8}$ | $2.0 \cdot 10^{-9}$  |

b) Resulting fit parameters of the BPP contribution

**Table S4.** Fit parameters  $a$ ,  $b$  and temperature-dependent prefactor  $A_{quad} = a \cdot T + b$ . As examples, values of  $A_{quad}$  at 298 K ( $A_{298}$ ) and at 373 K ( $A_{373}$ ) are shown. The quadrupolar coupling constant  $Q$  is calculated at 298 K and 373 K.

| Sample            | $a / s^{-2}K^{-1}$ | $b / s^{-2}$      | $A_{298} / s^{-2}$ | $Q_{298} / kHz$ | $A_{373} / s^{-2}$ | $Q_{373} / kHz$ |
|-------------------|--------------------|-------------------|--------------------|-----------------|--------------------|-----------------|
| 20:00:4 Reference | $1.0 \cdot 10^7$   | $-2.2 \cdot 10^9$ | $8.4 \cdot 10^8$   | 25              | $1.6 \cdot 10^9$   | 35              |
| 20:10:4 PEO       | $3.0 \cdot 10^5$   | $9.9 \cdot 10^9$  | $8.9 \cdot 10^7$   | 8               | $1.1 \cdot 10^8$   | 9               |
| 20:20:4 PEO       | $4.1 \cdot 10^5$   | $6.0 \cdot 10^7$  | $1.8 \cdot 10^8$   | 12              | $2.1 \cdot 10^8$   | 13              |
| 20:10:4 PDADMA    | $-1.0 \cdot 10^6$  | $6.2 \cdot 10^8$  | $3.2 \cdot 10^8$   | 16              | $2.5 \cdot 10^8$   | 14              |
| 20:20:4 PDADMA    | $-4.5 \cdot 10^5$  | $4.5 \cdot 10^8$  | $3.1 \cdot 10^8$   | 15              | $2.8 \cdot 10^8$   | 15              |

**Table S5.** Values of the width parameter  $\epsilon$ , the activation energy  $E_A$  and correlation time  $\tau$ . As examples, values of the correlation time  $\tau_0$  at 298 K ( $\tau_{298}$ ) and at 373 K ( $\tau_{373}$ ) are given.

| Sample            | $\epsilon$ | $\tau_0 / s$         | $E_A / kJ mol^{-1}$ | $\tau_{298} / s$    | $\tau_{373} / s$     |
|-------------------|------------|----------------------|---------------------|---------------------|----------------------|
| 20:00:4 Reference | -          | $1.2 \cdot 10^{-12}$ | 17                  | $1.0 \cdot 10^{-9}$ | $2.6 \cdot 10^{-10}$ |
| 20:10:4 PEO       | -          | $6.5 \cdot 10^{-12}$ | 20                  | $1.9 \cdot 10^{-8}$ | $3.8 \cdot 10^{-9}$  |
| 20:20:4 PEO       | -          | $2.7 \cdot 10^{-12}$ | 22                  | $1.7 \cdot 10^{-8}$ | $2.9 \cdot 10^{-9}$  |
| 20:10:4 PDADMA    | -          | $2.9 \cdot 10^{-11}$ | 16                  | $1.8 \cdot 10^{-8}$ | $5.0 \cdot 10^{-9}$  |
| 20:20:4 PDADMA    | -          | $1.9 \cdot 10^{-10}$ | 10                  | $1.3 \cdot 10^{-8}$ | $5.6 \cdot 10^{-9}$  |

## References

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2. A. Gradišek, P. J. Sebastião, S. N. Fernandes, T. Apih, M. H. Godinho and J. Seliger, *The Journal of Physical Chemistry B*, 2014, **118**, 5600-5607.
3. J. Vega, edited by D. M. Grant and R. K. Harris, in *Encyclopedia of Nuclear Magnetic Resonance*, J. Wiley, Chichester, 1996, pp. 3869-3888.