

Supporting information

Effect of network homogeneity on mechanical,
thermal and electrochemical properties of solid
polymer electrolytes prepared by homogeneous 4-
arm poly(ethylene glycols)

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Synthesis of macromonomers.

(a) Synthesis of tetra-PEG(NH₂) (10, 20 kDa)

First, tetra-PEG with terminal methanesulfonyl groups (tetra-PEG(Ms)) was synthesized as follows. Tetra-PEG(OH) (10 kDa, 10.0 g, 1.00 mmol) was dissolved in anhydrous dichloromethane (225 mL) under an Ar atmosphere. Triethylamine (0.928 mL, 12.0 mmol) was added to the solution, and the reaction mixture was cooled to 0 °C. Consequently, solution of MsCl (1.39 mL, 10.0 mmol) in dichloromethane (50 mL) was added to the reaction mixture dropwise over 1 h at 0 °C. After addition was complete, the reaction mixture was gradually heated to room temperature, and stirred for 24 h at room temperature. After the reaction, the solution was washed with saturated saline three times. The residual salts were removed by mixing with KYOWAAD (Mg_{0.7}Al_{0.3}O_{1.15}), followed by filtration of KYOWAAD using Celite. After removing the residual salts two times, the moisture was removed by mixing with anhydrous MgSO₄ for 10 min, and the solution was filtered again. The dichloromethane was removed by evaporation, and a white solid was obtained. The resulting polymer was purified by reprecipitation using THF (good solvent) and diethyl ether (poor solvent). After vacuum drying at room temperature, tetra-PEG(Ms) was obtained as a white powder. Complete replacement of the terminals was confirmed from the disappearance of the peak derived from the OH terminal in ¹H NMR spectra (JEOL ECX-400, **Fig. S1**).

Next, tetra-PEG(Ms) (10 kDa, 5.0 g, 0.500 mmol) was dissolved in deionized water (30 mL). The aqueous solution was added to an aqueous ammonia solution (28%, 200 mL, 3.00 mmol) dropwise, and the mixture was stirred for 4 days at room temperature. The reaction mixture was dialyzed against deionized water, and the remaining ammonia was

removed by the repetitive dialysis. After confirming that the pH of the solution is neutral, water was evaporated, and a white solid was obtained. The resulting polymer was purified by reprecipitation using THF (good solvent) and diethyl ether (poor solvent). After vacuum drying at room temperature, tetra-PEG(NH₂) was obtained as a white powder. Complete replacement of the terminals was confirmed from the disappearance of the peak derived from the Ms terminal in ¹H NMR spectra (**Fig. S1**).

For 20 kDa, the same procedure as 10 kDa was used while each reagent was changed according to the molar ratio of reagents to OH terminal in tetra-PEG(OH).

(b) Synthesis of tetra-PEG(Mal) (5, 10, 20, 40 kDa)

Tetra-PEG(OH) (10 kDa, 10.0 g, 1.00 mmol) was dissolved in anhydrous dichloromethane (250 mL) under an Ar atmosphere. DCC (2.47 g, 12.0 mmol), 4-DMAP (48.8 mg, 0.400 mmol), and 6-maleimide hexanoic acid (2.53 g, 12.0 mmol) were added to the solution and stirred for 18 h at room temperature. After the reaction, the solution was washed with saturated saline. The residual salts and remaining water were removed in the same way as the synthesis of tetra-PEG(Ms). The dichloromethane was removed by evaporation, and a pink solid was obtained. The resulting polymer was purified by reprecipitation using dichloromethane (good solvent) and diethyl ether (poor solvent). After vacuum drying at room temperature, tetra-PEG(Mal) was obtained as a pink powder. Complete replacement of the terminals was confirmed from the disappearance of the peak derived from the OH terminal in ¹H NMR spectra (**Fig. S1**).

For 5, 20, and 40 kDa, the same procedure as 10 kDa was used while each reagent was changed according to the molar ratio of reagents to OH terminal in tetra-PEG(OH). The spectra of tetra-PEG macromonomers (tetra-PEG(NH₂), tetra-PEG(Ms), tetra-PEG(OH) and tetra-

PEG(Mal) from top to bottom) are shown in **Fig. S1**. From **Fig. S1(a)**, it was confirmed that the target monomers were successfully synthesized. Also, from **Fig. 1(b)**, the signal of the methylene protons at the end of tetra-PEG(OH) (*), which are marked with pink color, disappears in the spectra of terminal modified tetra-PEGs. Therefore, the terminal modification reaction is considered to have progressed almost 100%.

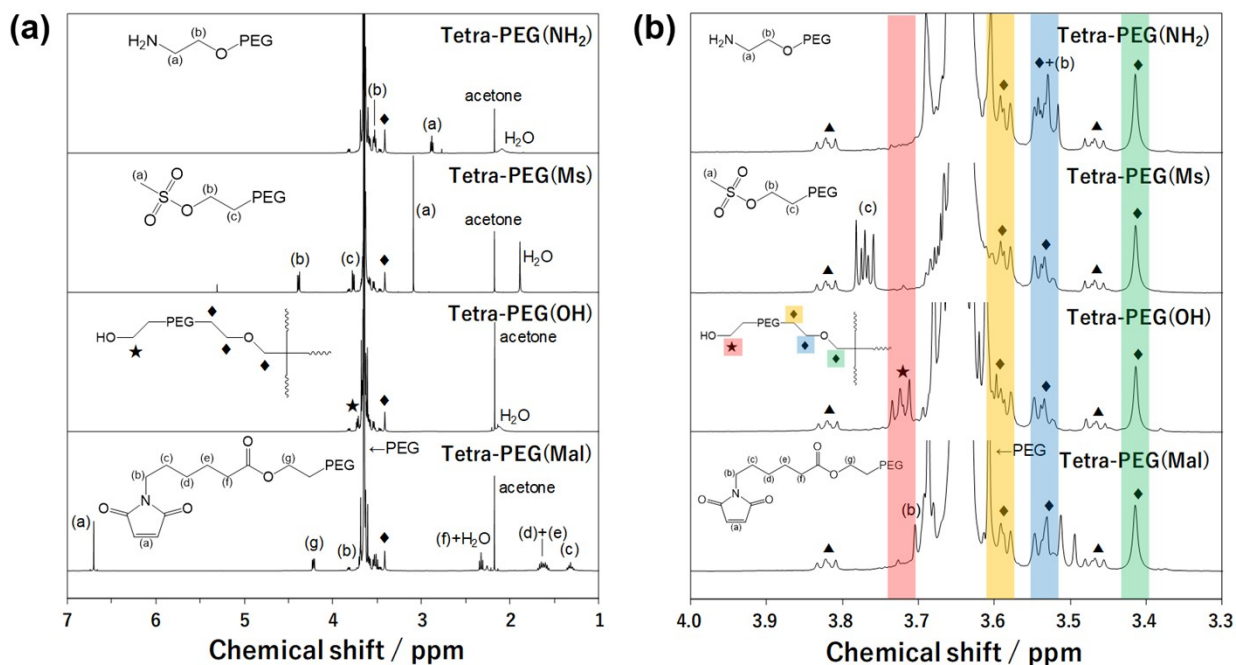


Fig. S1. ^1H NMR spectra of tetra-PEG(Mal), tetra-PEG(OH), tetra-PEG(Ms), and tetra-PEG(NH_2) in CDCl_3 . The peaks indicated by symbols \blacktriangle , \blacklozenge , and \blackstar correspond to the satellite peaks of PEG protons, methylene protons at the center of tetra-PEGs, and methylene protons at the end of tetra-PEG(OH), respectively.

Table. S1 VTF equation parameters for ionic conductivities of tetra-PEG/Li[TFSA] SPEs.

| Sample | $\sigma_0 / \text{S cm}^{-1}$ | $B / 10^2 \text{ K}$ | T_0 / K |
|----------------|-------------------------------|----------------------|------------------|
| 10 : 10 | 0.14 ± 0.02 | 8.2 ± 0.4 | 206 ± 2 |
| 10 : (5 + 20) | 0.23 ± 0.03 | 9.0 ± 0.3 | 203 ± 2 |
| 10 : (5 + 40) | 0.28 ± 0.04 | 9.4 ± 0.3 | 199 ± 2 |
| 20 : 20 | 0.14 ± 0.04 | 6.8 ± 0.6 | 215 ± 4 |
| 20 : (10 + 40) | 0.23 ± 0.02 | 8.2 ± 0.2 | 206 ± 1 |
| 20 : (5 + 40) | 0.21 ± 0.04 | 7.7 ± 0.4 | 208 ± 3 |

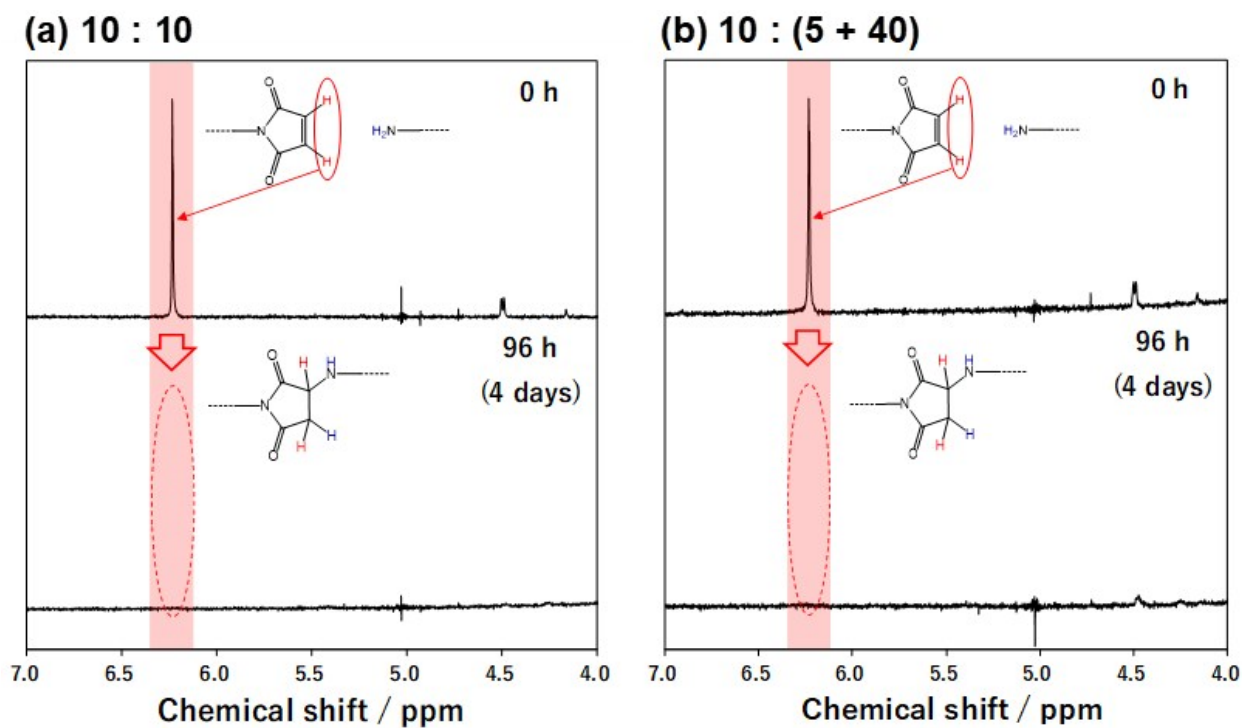


Fig. S2 ^1H NMR spectra of the equimolar mixture of tetra-PEG(NH_2) and tetra-PEG(Mal) for (a) SPE 10 : 10 and, (b) SPE 10 : (5 + 40) in NMP with Li[TFSA] salts ($[\text{Li}]/[\text{O}] = 0.10$) right after mixing (upper) and after 96 h of the reaction at 60 °C (lower).

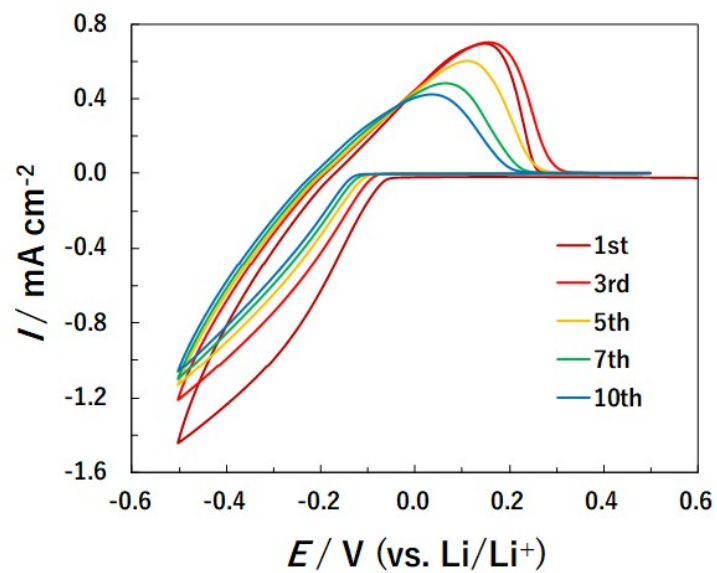


Fig. S3 Cyclic voltammograms for the Li deposition/dissolution in tetra-PEG/Li[TFSA] SPE (10 : 10) at a scan rate of 1.0 mV s^{-1} at $60 \text{ }^\circ\text{C}$.

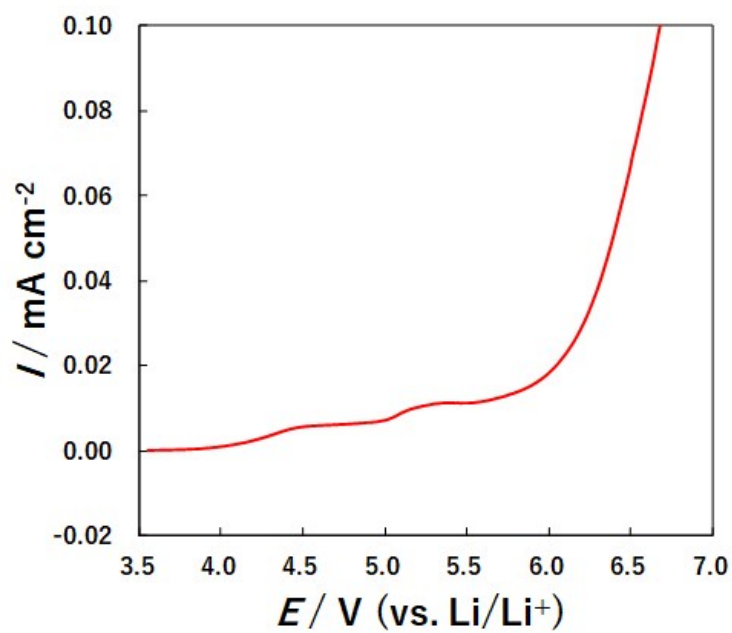


Fig. S4 Linear sweep voltammograms of tetra-PEG/Li[TFSA] SPE (10 : 10) at a scan rate of 1.0 mV s^{-1} at $60 \text{ }^\circ\text{C}$.

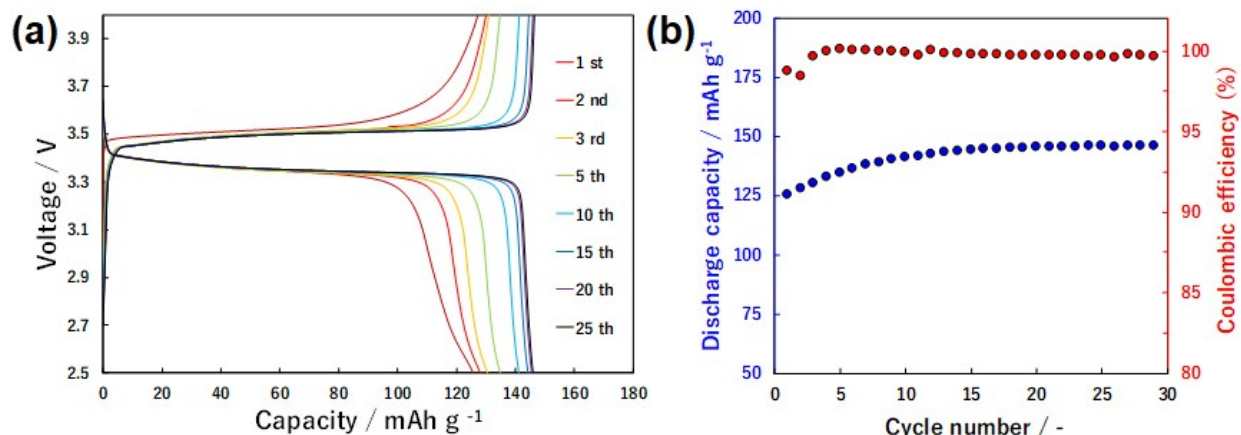


Fig. S5 (a) Charge and discharge curves and (b) cycle performance of [LiFePO₄ | tetra-PEG/Li[TFSA] | Li].

Cathode: LiFePO₄ : AB : PVDF = 80 : 10 : 10, anode: Li, electrolyte: tetra-PEG/Li[TFSA] (SPE 10 : (5+40)) + [Li(G4)][TFSA] 20 μL, current collector: Al, Temperature: 60 °C, LiFePO₄ loading: 2.44 mg cm⁻², rate 0.1 C (39 μA cm⁻²), cut-off voltage: 2.5-4.0 V. [Li(G4)][TFSA] was dropped to reduce the contact resistance between the cathode and the electrolyte.

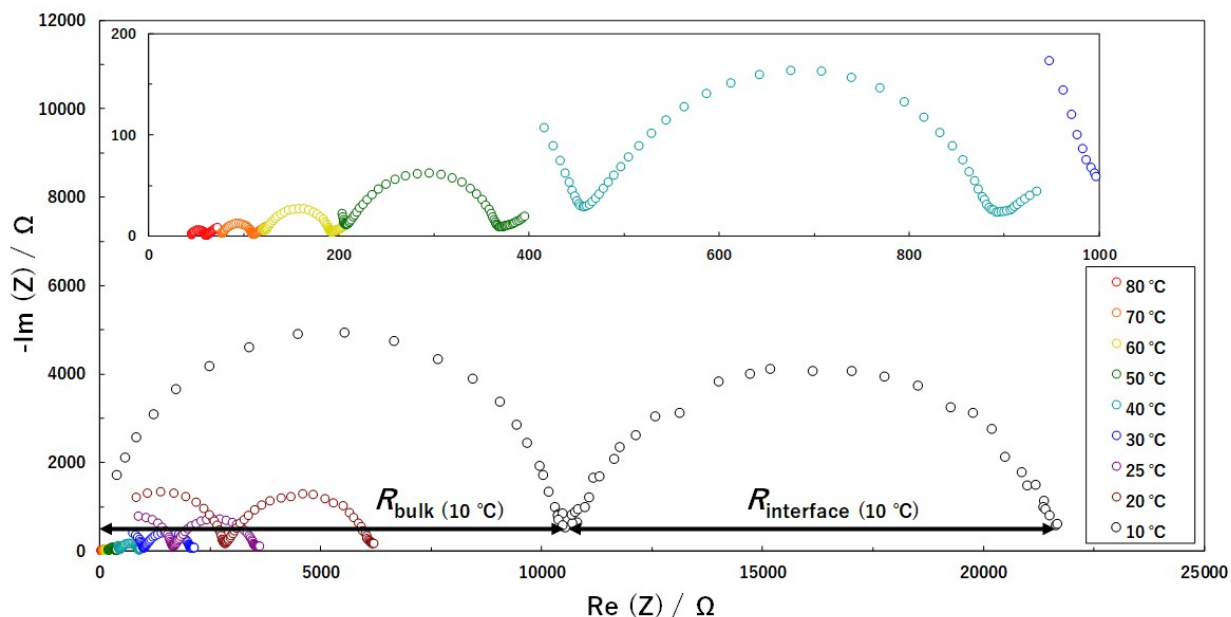


Fig. S6 Nyquist plots for Li symmetric cell using tetra-PEG/Li[TFSA] SPE with homogeneous network (SPE 10 : 10).

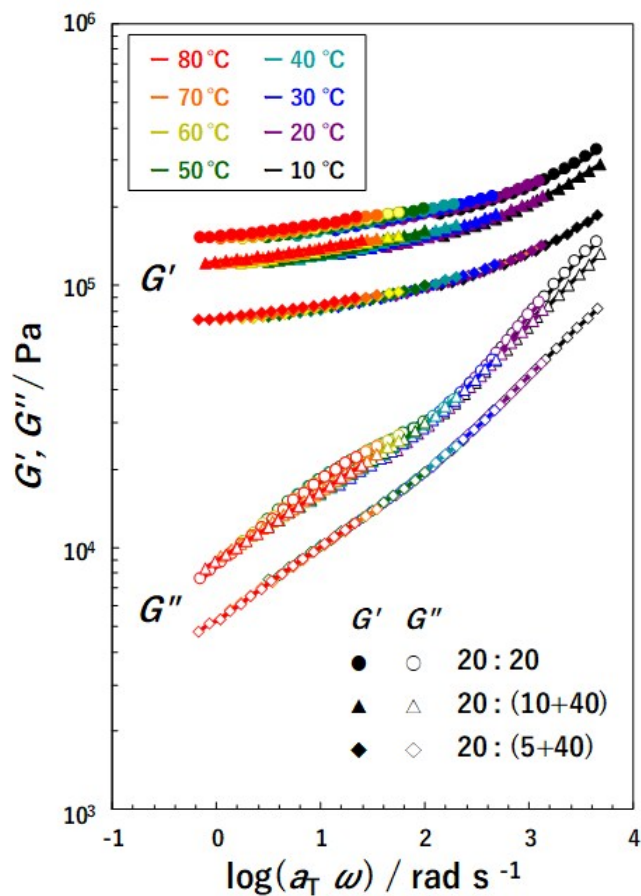


Fig. S7 tTS plots of rheological properties for tetra-PEG/Li[TFSA] (average $M_n = 20$ kDa, $[\text{Li}]/[\text{O}] = 0.10$) with various network inhomogeneities.

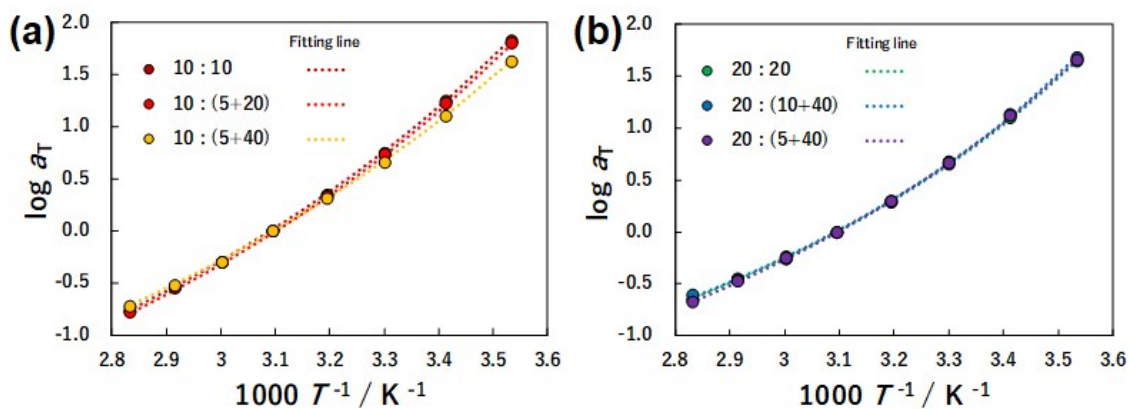


Fig. S8 Arrhenius plots of shift factor, a_T for tetra-PEG/Li[TFSA] SPE with various network inhomogeneities.

Table. S2 VTF equation parameters for shift factor of tetra-PEG/Li[TFSA] SPEs.

| Sample | $a_0 / 10^{-4}$ - | $B_R / 10^2$ K | $T_R /$ K |
|----------------|-------------------|----------------|-----------|
| 10 : 10 | 0.70±0.10 | 126±4 | 192±2 |
| 10 : (5 + 20) | 0.60±0.08 | 129±3 | 190±1 |
| 10 : (5 + 40) | 1.1±0.4 | 124±8 | 187±4 |
| 20 : 20 | 7.7±1.2 | 83±3 | 207±2 |
| 20 : (10 + 40) | 9.4±3.2 | 78±6 | 211±4 |
| 20 : (5 + 40) | 4.1±0.6 | 95±3 | 201±2 |

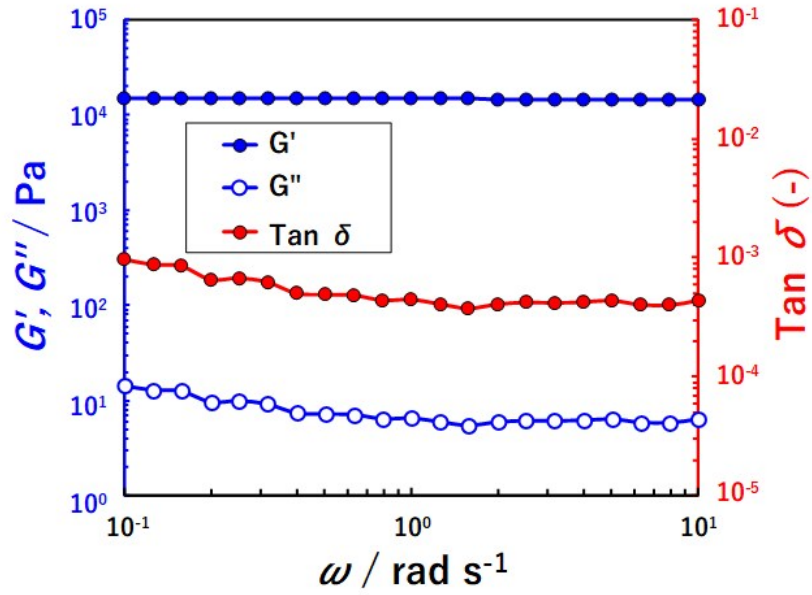


Fig. S9 Frequency sweep of SPE 10:10 organogel before drying at 60 °C.

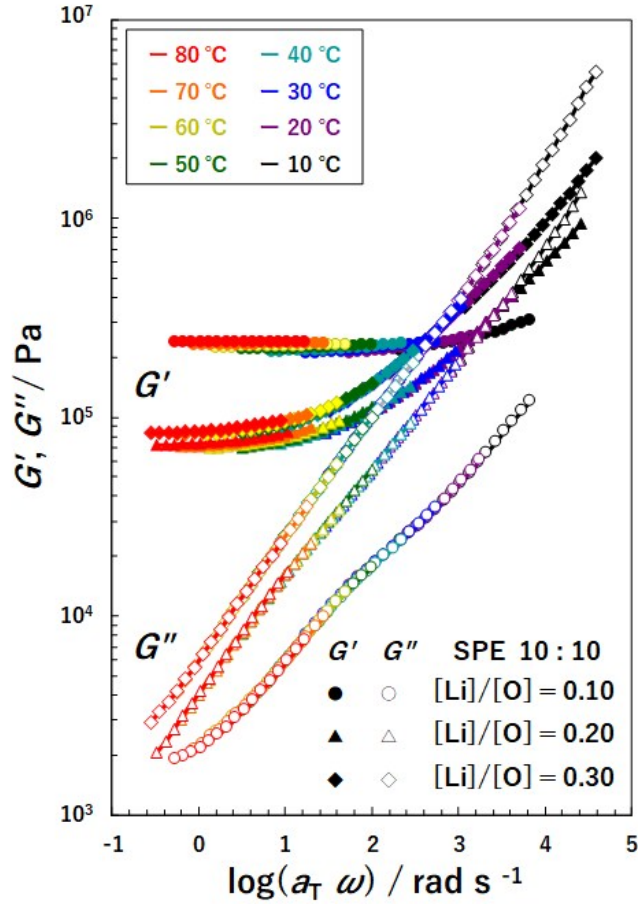


Fig. S10 tTS plots of rheological properties for homogeneous tetra-PEG/Li[TFSA] SPEs (10 : 10, $[\text{Li}]/[\text{O}] = 0.10, 0.20$ and 0.30).

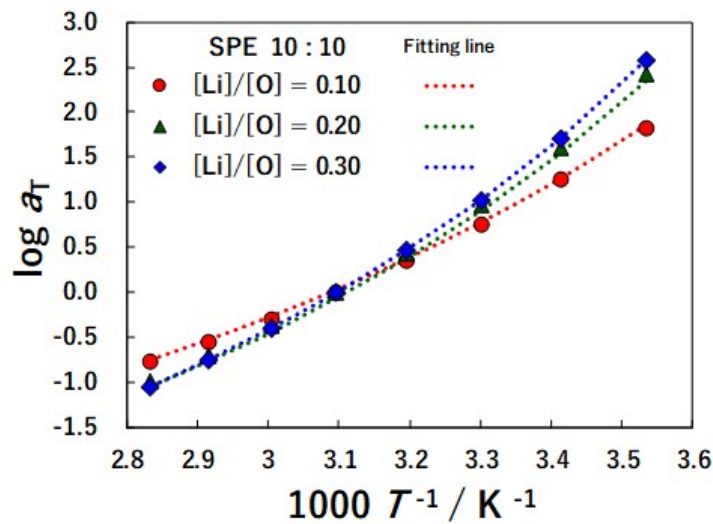


Fig. S11 Arrhenius plots of shift factor, a_T for tetra-PEG/Li[TFSA] SPEs (10 : 10, $[\text{Li}]/[\text{O}] = 0.10, 0.20$ and 0.30) with different salt concentration.

Table. S3 Salt concentration dependence for VTF equation parameters for shift factor of tetra-PEG/Li[TFSA] SPEs.

| [Li]/[O] | $a_0 / 10^{-4}$ | $B_R / 10^2 \text{ K}$ | T_R / K |
|----------|-----------------|------------------------|------------------|
| 0.10 | 0.70 ± 0.10 | 126 ± 4 | 192 ± 2 |
| 0.20 | 0.10 ± 0.01 | 138 ± 2 | 201 ± 1 |
| 0.30 | 0.06 ± 0.01 | 124 ± 8 | 202 ± 2 |