Electronic Supplementary Information

Polymer network formation mechanism of multifunctional poly(ethylene glycol)s in ionic liquid electrolyte with a lithium salt

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Experimental.

UV-vis spectroscopy. UV spectra for 2 wt% tetra/tetra-PEG (MA/SH ratio = 1:1) and tetra/linear-PEG (MA/SH ratio = 1:0.5, 1:1, and 1:2) gelation systems were recorded using UV-vis spectrophotometer (V-730, Jasco) to investigate gelation kinetics. The two kinds of PEG prepolymers (tetra-PEG-MA and tetra-PEG-SH or linear-PEG-SH) in 0.85 M LiTFSA/IL solutions were mixed and stirred for 600 s, which was then poured to 0.5 cm thick quartz cell at room temperature. The time dependences of the UV spectra were measured at a time interval of 600 s. The absorbance (A) of the unreacted MA terminals within the tetra-PEG-MA was monitored at 300 nm. Using the A (300 nm), the concentration of unreacted MA was plotted as a function of gelation time (t). A (300 nm) at the i-th time point, i, is given as $A_{300,i} = \varepsilon_{300} l[\text{–MA}]_i$, where ε_{300} is the molar absorption coefficient of MA and l is the cell thickness. The concentration of the cross-linking MA–S bond ([MA-S]$_i$) is described by $[\text{MA–S}]_i = [\text{–MA}]_{\text{ini}} - [\text{–MA}]_i$, where $[\text{–MA}]_{\text{ini}}$ is the initial concentration of MA groups. Thus, the following equation is obtained: $[\text{MA–S}]_i = [\text{–MA}]_{\text{ini}} - A_{300,\,i}/\varepsilon_{300}\, l$. As established in our previous studies,[1, 2] the PEG-based gelation (i.e., tetra-PEG-MA + tetra-PEG-SH → tetra-PEG-MA–S-tetra-PEG) proceeds as a following second-order rate equation:

$$\mathrm{d}\frac{[\text{MA–S}]}{\mathrm{d}t}\left(= -\frac{\mathrm{d}[\text{–MA}]}{\mathrm{d}t}\right) = k_{\text{gel}}'[\text{–MA}]_i[\text{–SH}]_{\text{total, i}} \quad (1)$$

where k_{gel}' is an apparent reaction rate constant and $[\text{-SH}]_{\text{total},\,i}$ is the total concentration of the unreacted SH groups at the i-th time point. Based on the rate equation, we performed a least-squares fitting analysis by minimizing the error square sum, $U = \Sigma([\text{MA-S}]_{i,\,\text{exp}} - [\text{MA-S}]_{i,\,\text{calc}})^2$.

Rheological measurements. Rheological measurements were performed using a stress control rheometer (MCR-302, Anton Paar) with cone (CP-25-2; 25 mm in diameter) and plate geometry. The time dependences of the storage (G') and loss (G'') moduli during gelation were monitored to obtain the gelation time (t_{gel}). The two different PEG prepolymers (tetra-PEG-MA and linear-PEG-SH, polymer concentration: 5 wt%) in 0.85 M LiTFSA/IL solutions were mixed at volume ratios of 1:1 and 1:2 (i.e., MA/SH = 1:0.5 and 1:1) for 30 s and set on a thermostatic plate (298 K) to obtain G vs. t profiles (Figure 4). The strain and angular frequency were set at 2% and 6.3 rad s^{-1}, respectively.

The angular frequency dependence measurements were carried out to reveal the network formation process (Figure 5). The frequency range and strain were set at 100–0.1 rad s^{-1} and 2%, respectively. The tetra-PEG-MA and linear-PEG-SH (polymer concentration: 5 wt%,) prepolymers in 0.85 M LiTFSA/IL solutions were mixed at volume ratio of 1:2 (i.e., MA/SH = 1:1) for 30 s and set on a thermostatic plate (298 K). The reaction-time points were set at 300, 6.6 × 10^3, 7.9 × 10^3, 9.3 × 10^3, 1.2 × 10^4, 2.3 × 10^4, 9.4 × 10^4, and 2.3 × 10^5 s, which correspond to p ~ 2.8%, 39%, 44%, 47%, 55%, 69%, 90% and 96%, respectively, according to the p vs. t curve (Figure 3b).

The similar measurements were performed in the tetra/tetra-PEG system with MA/SH = 1:1.

Stretching measurements. Stretching measurements were performed using mechanical testing apparatus (STB-1225S, A&D Company) at a constant velocity of 60 mm min^{-1}. The dumbbell-shaped 5 wt% tetra/tetra-PEG gel (MA/SH ratio = 1:1) and 5 and 10 wt% tetra/linear-PEG gels (MA/SH ratio = 1:1) were prepared at room temperature as a size of a rectangular portion, 2.0×12.0×2.0 mm^3.

Ionic conductivity. The ionic conductivity was measured by AC impedance spectroscopy using a frequency response analyzer (SI-1260, Solartron) in the temperature range from 278 to 338 K (i.e., 5, 15, 25, 35, 45, 55, and 65 °C). The measurements were performed using CR2032 coin-type cells equipped with two parallel stainless-steel (SUS316L) electrodes and Teflon spacer (12 mmϕ) in a thermostatically controlled container.

Reaction efficiency (p)-estimation.

According to the tree-like theory, the relationship between G and p is described as follows. The efficiency of the cross-linking reaction (p) can be estimated from G value by using the equation: $G = cRT(\nu - \mu)$, where R and T are the gas constant and the temperature. $P(F_A^{out})$ is the probability that a chain dose not yield to an infinite network; $P(F_A^{out}) = (1/p–3/4)^{1/2}–1/2$ (tetra/tetra-PEG gel system[3]) and $P(F_A^{out}) = (1/p^2–3/4)^{1/2}–1/2$ (tetra/linear-PEG gel system[4]). $P(X_n)$ is the probability that tetra-arms become n-arm cross-linking points. We can thus estimate $P(X_3)$ and $P(X_4)$ using the following equations; $P(X_3) = {}_4C_3\ P(F_A^{out})[1–P(F_A^{out})]^3$ and $P(X_4) = {}_4C_4[1–P(F_A^{out})]^4$. Here, the concentration of cross-linking points (μ) and elastically effective chains (ν) are given by the following equation: $\mu = c(P(X_3) + P(X_4))$ and $\nu = c(3/2\times P(X_3) + 4/2\times P(X_4))$, where c is the concentration of tetra-arm polymer. As the result, we can obtain the $G–p$ relations for tetra/tetra-PEG and tetra/linear-PEG systems (eqs. 2 and 3, respectively), as follows.

$$G = cRT\left[\left\{\frac{3}{2}-\left(\frac{1}{p}-\frac{3}{4}\right)^{\frac{1}{2}}\right\}^3\left\{\frac{1}{2}+\left(\frac{1}{p}-\frac{3}{4}\right)^{\frac{1}{2}}\right\}\right] \qquad (2)$$

$$G = cRT\left[\left\{\frac{3}{2}-\left(\frac{1}{p^2}-\frac{3}{4}\right)^{\frac{1}{2}}\right\}^3\left\{\frac{1}{2}+\left(\frac{1}{p^2}-\frac{3}{4}\right)^{\frac{1}{2}}\right\}\right] \qquad (3)$$

In this work, we used the experimental G values of 8.3 kPa for the 5 wt% tetra/tetra-PEG gel and 2.4 and 4.8 kPa for the 5 and 10 wt% tetra/linear-PEG gels, respectively. The p value was thus calculated to be 91% for the 5 wt% tetra/tetra-PEG and 93% for both 5 and 10 wt% tetra/linear-PEG systems.

Table S1. The apparent rate constant (k'_{gel}) and molar absorption coefficient at 300 nm (ε_{300}) obtained by the fitting analysis based on a second-order rate equation in tetra/tetra-PEG and tetra/linear-PEG gelation systems. The total polymer content in solutions was fixed at 2 wt% for all the systems.

System	MA/SH ratio	k_{gel}' / M^{-1} s^{-1}	ε_{300} / mol^{-1} dm^2
tetra/tatra-PEG	1:1	0.017	5006
tetra/linear-PEG	1:0.5	0.015	5010
tetra/linear-PEG	1:1	0.017	4988
tetra/linear-PEG	1:2	0.045	4500

Table S2. The fitting parameters obtained from the fitting analysis based on a VFT equation for 10 wt% tetra/tetra-PEG (MA/SH =1:1) gel and 10 wt% tetra/linear-PEG (MA/SH =1:1) gel, together with the corresponding 0.85 M LiTFSA/[C_2mIm][TFSA] solutions with and without 10 wt% linear PEG-chain.

Type	σ_0 /S cm^{-1}	B /K	T_0 /K
tetra/tetra-PEG gel	0.13	315	210
tetra/linear-PEG gel	0.13	321	210
linear PEG-chain in 0.85 M LiTFSA/[C_2mIm][TFSA]	0.13	314	210
0.85 M LiTFSA/[C_2mIm][TFSA]	0.11	331	210

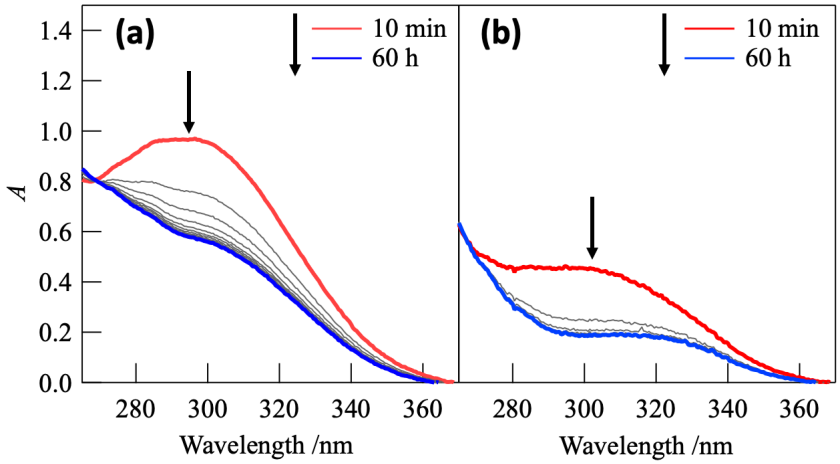

Figure S1. Time-dependent ultraviolet–visible spectra of the (a) tetra-PEG-MA and linear-PEG-SH (MA/SH = 1:0.5) and (b) (MA/SH = 1:2) in a 0.85 M LiTFSA/IL solution. The total polymer content in the solution was fixed at 2 wt% for both systems.

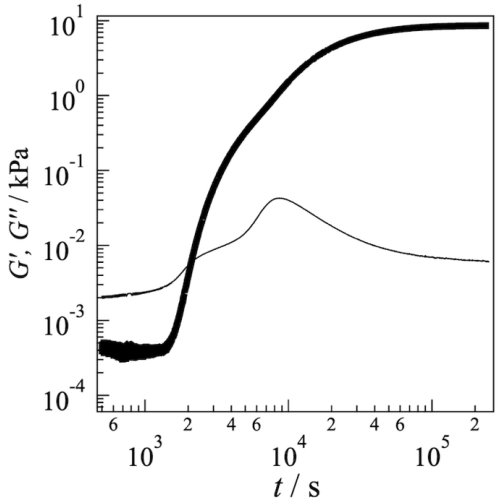

Figure S2. Storage (G', bold line) and loss (G'', thin line) elastic moduli profiles for the 5 wt% tetra/tetra-PEG gelation system with the MA/SH ratio of 1:1.

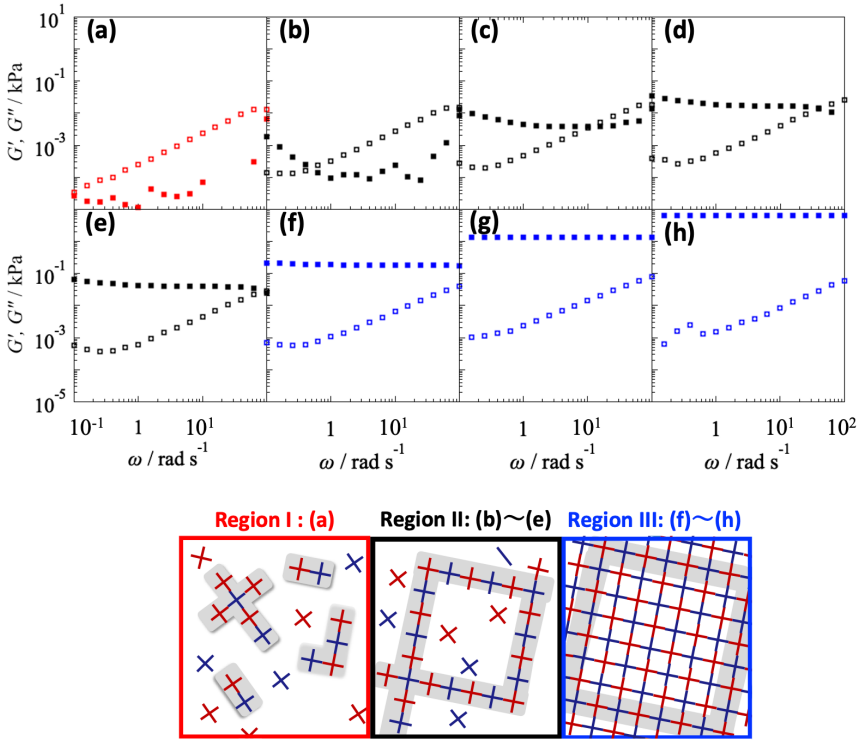

Figure S3. (upper) Storage G' (filled squares) and loss G'' (open squares) moduli as a function of frequency for the 5 wt% tetra/tetra-PEG gelation system (MA/SH = 1:1) at the following reaction times: (a) 340 s, (b) 2.7×10^3 s, (c) 3.6×10^3 s, (d) 4.4×10^3 s, (e) 5.2×10^3 s, (f) 8.3×10^3 s, (g) 3.0×10^4 s, and (h) 3.4×10^5 s. (bottom) Schematic of the suggested gelation mechanism in the three regions of (I) $G' < G''$, (II) $G' = G''$, and (III) $G' > G''$.

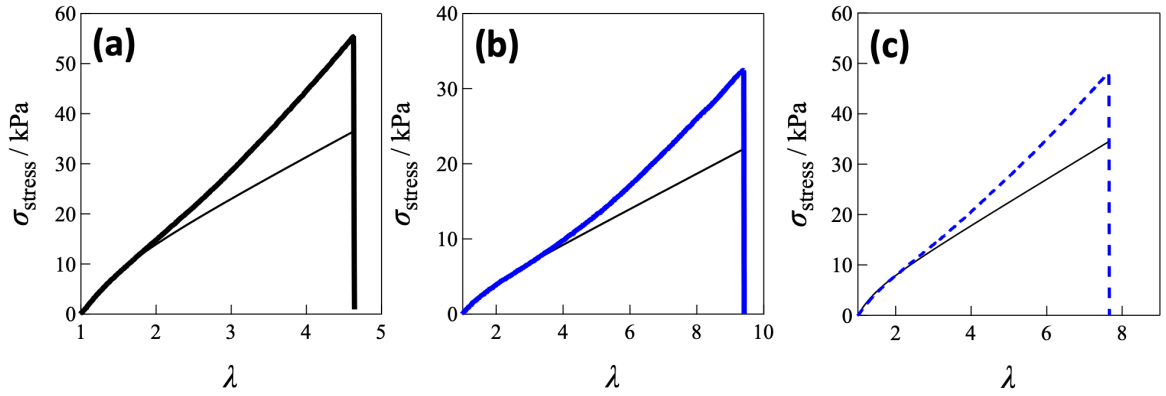

Figure S4. The fitting results (thin black line) using an equation, $\sigma_{stress\_calc} = G(\lambda - \lambda^{-2})$, for the experimental stress-elongation curves of (a) 5 wt% tetra/tetra-PEG ion gel, (b) 5 wt% and (c) 10 wt% tetra/linear-PEG ion gels.

References

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