# **Electronic Supplementary Information**

Defect-free network formation and swelling behavior in ionic liquid-based electrolytes of tetraarm polymers synthesized using a Michael addition reaction

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### **Preparation of TetraPEG Ion Gel Electrolytes.**

5 wt% TetraPEG-MA and TetraPEG-SH prepolymers dissolved in aqueous solutions at pH = 3.2 (disodium hydrogen phosphate / citric acid) were mixed and was in capillary for 24 h at room temperature, resulting in a free standing 5 wt% TetraPEG hydrogel. The obtained hydrogel was immersed in water for 24 h to eliminate the influence of buffer components and in Tetrahydrofuran (THF) for 24 h. The gel swollen in THF was dried in a vacuum at 70 °C for 24 h to completely remove water from the support polymer. The dried gel was re-swollen in the ionic liquid-based electrolytes to measure the swelling behavior.

## Data Analysis in Gelation Kinetics.

In the current UV measurements, the absorbance (300 nm) at *i*-th time point is described as

$$A_{300,i} = \varepsilon_{300} l[-\mathrm{MA}]_i \qquad (1)$$

where  $\varepsilon_{300}$  is the molar absorption coefficient of unreacted MA at 300 nm and *l* is the cell thickness (= 1 cm). Therefore, [-MA]<sub>*i*</sub> is given by

$$[-MA]_i = A_{300, i} / \varepsilon_{300} l$$
 (2)

As mentioned in the Experimental section, the reaction rate of  $[-MA]_i$  obeys the following rate equation;  $-d[-MA]/dt = k_{gel}[-S^-]_i[-MA]_i$ . Here we note that aqueous solutions of TetraPEG-SH show an acid-base equilibrium: TetraPEG-SH  $\leq$  TetraPEG-S<sup>-</sup> + H<sup>+</sup>. The equilibrium constant ( $K_a$ ) is defined as  $K_a = [-S^-][H^+]/[-SH]$ . In this analysis, we assumed that the terminal SH groups are not reactive species in the gelation system, only the deprotonated S<sup>-</sup> groups, because the observed gelation rate strongly depended on solution pH (see, Figure 2). Finally, the rate equation is represented as follows,

$$-d[-MA]/dt = k_{gel} f[-SH]_{total, i} [-MA]_i$$
(3), and then

where *f* is the fraction of deprotonated thiol to total thiol groups:  $f = [-S^-]_i/[-SH]_{total, i} = K_a/(K_a+[H^+])$  and  $[-SH]_{total, i}$  is the total concentration of unreacted thiol groups at a given time point, *i*:  $[-SH]_{total, i} = [-S^-]_i + [-SH]_i$ . Here, the unreacted MA at reaction time, *i* is given by  $[-MA]_i = [-MA]_{i-1} - |-d[-MA]|$  (4), and thus we can obtain the following equation using eq. 3 and 4,

 $[-MA]_i = [-MA]_{i-1} - k_{gel} f[SH]_{total, i} [-MA]_{i-1} dt$ 

$$= [-MA]_{i-1} - k_{gel}(K_a/(K_a+[H^+])[SH]_{total, i}[-MA]_{i-1}dt$$
 (5)

Based on this equation, we performed least-square fitting analysis; minimizing the error square sum,  $U = \sum ([-MA]_{i, exp} - [-MA]_{i, calc})^2$ . And then the optimized fitting parameters;  $\varepsilon_{300}$ ,  $k_{gel}$  and  $K_a$ were obtained. The  $[-MA]_{i, exp}$  (= $A_{300, i}/\varepsilon_{300}l$ , eq. 2) and  $[-MA]_{i, calc}$  correspond to the experimental plots (open black marks) and the solid red line in Figure 2, respectively.

## p vs. t Plots.

The network connectivity *p* is defined as p (%) = [MA-S]/[-MA]<sub>ini</sub>×100 and the [MA-S] (i.e., concentration of the linking point) is equal to the concentration of the reacted [-MA]; i.e., [MA-S]<sub>i</sub> =  $\sum_i d$ [-MA]<sub>i</sub>. In this work, we determined the rate constant,  $k_{gel}$  value based on the gelation rate equation: -d[-MA]/ $dt = k_{gel}(K_a/(K_a+[H^+])[SH]_{total}[-MA])$  (as described above). On the basis of this equation, we can thus calculate the *p* at a given reaction-time point *i*, if we know the parameters of (1)  $k_{gel}$ , (2)  $K_a$ , (3) solution pH, and (4) initial polymer concentration. That is,

 $p_i = [MA-S]_i / [-MA]_{ini} \times 100$ 

 $=\sum_{i}d[-MA]_{i}/[-MA]_{ini}\times 100$ 

= { $k_{gel}(K_a/(K_a+[H^+])[SH]_{total, i}[-MA]_i)$ }/[-MA]<sub>ini</sub>×100.

Using above equation, we obtained *p* vs. *t* plot as shown in Figure 3.

### Estimation of Vini Based on Theory of Tree-like Structures.<sup>[1]</sup>

According to the tree-like theory, the probability that one of four-arms in TetraPEG prepolymer leads out to a finite chain,  $P(F_{out})$  is related to the network connectivity (reaction efficiency), *p*, as follows,

$$P(F^{\text{out}}) = (1/p - 3/4)^{1/2} - 1/2$$

Based on  $P(F^{\text{out}})$ , the probability that a given tetra-arm polymer is a connection degree of *n*,  $P(X_n)$ , can be calculated using the following equation;

## $P(X_n) = {}_4C_n P(F^{\text{out}})^{(4-n)} [1 - P(F^{\text{out}})]^n$

Here, note that only when n is equal to or higher than 3, the connections are "cross-links". The concentration of elastically effective chains, v, is given by the following equation:

 $v = c[3/2 \times P(X_3) + 2P(X_4)]$ 

where *c*,  $P(X_3)$  and  $P(X_4)$  is the concentration of the tetra-arm polymer, the effective cross-link probabilities of degree 3 and of degree 4, respectively. The  $P(X_3)$  and  $P(X_4)$  are calculated by  $P(X_n) = {}_4C_nP(F^{\text{out}}){}^{(4-n)}[1-P(F^{\text{out}})]^n$ ; thus,  $P(X_3) = {}_4C_3P(F^{\text{out}})[1-P(F^{\text{out}})]^3$  and  $P(X_4) = [1-P(F^{\text{out}})]^4$ , respectively. In this work, we used "p = 98%" (corresponding to the TetraPEG hydrogel after gelation reaction was completed), and we thus estimated the v value to be  $5.0 \times 10^{-6}$  mol cm<sup>-3</sup>.

Reference: [1] Y. Akagi, T. Matsunaga, M. Shibayama, U. Chung and T. Sakai, *Macromolecules*, 2010, **43**, 488-493.

**Table S1.** The rate constant ( $k_{gel}$ ), equilibrium constant for acid-base reaction of thiol groups (p $K_a$ ), and molar absorption coefficient at 300 nm ( $\varepsilon_{300}$ ) obtained by the fitting analysis for the 3.5 wt% TetraPEG solution with various pH (upper) and the TetraPEG solutions at constant pH (=2.5) with various polymer concentration (bottom).

solution pH	$k_{\rm gel}/{\rm dm^3mol^{-1}s^{-1}}$	$pK_a / \text{mol dm}^{-3}$	$\varepsilon_{300}$ / dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup>
2.5	1.1×10 <sup>6</sup>	10.5	472
3.2	$0.9 \times 10^{6}$	10.6	480
4.0	1.1×10 <sup>6</sup>	10.5	487
polymer concentration / wt %	$k_{\rm gel}/\rm dm^3mol^{-1}s^{-1}$	$pK_a/mol dm^{-3}$	$\varepsilon_{300}$ / dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup>
3.5	1.1×10 <sup>6</sup>	10.5	472
5.0	$1.4 \times 10^{6}$	10.5	508
6.0	$1.5 \times 10^{6}$	10.6	493



**Figure S1.** Time dependence of UV spectra observed for 3.5 wt% TetraPEG aqueous solutions at (a) pH = 3.2 and (b) pH = 4.0.



**Figure S2.** Time dependence of swelling ratio, Q for 0 M (neat IL) and 0.5 M LiTFSA/[C<sub>2</sub>mIm][TFSA] electrolyte solutions observed from the volume change measurement.