

**Supplementary Information**

**Block *versus* Random: Effective Molecular Configuration  
of Copolymer Gelators to Obtain High-Performance Gel  
Electrolytes for Functional Electrochemical Devices**

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## S1. Unified model fit

To simultaneously fit both Guinier and Porod regimes and extract the size of styrene agglomerates, the Unified model (see equation below) was applied to the SAXS profile of PEMA-*r*-PS gels.<sup>S1-S4</sup>

$$I(q) = \sum_{i=1}^n (G_i \exp\left(-\frac{q^2 R_{g,i}^2}{3}\right) + B_i \exp\left(-\frac{q^2 R_{g,i-1}^2}{3}\right) \times \left\{ \left[ \operatorname{erf}\left(q R_{g,i} / 6^{1/2}\right) \right]^3 / q \right\}^{D_i}) + \text{Bkg}$$

where  $i$  is the number of structure level,  $R_g$  is the radius of gyration,  $D_i$  is the power-law exponent,  $G$  and  $B$  are the Guinier and exponential pre-factors, respectively, and Bkg is the residual background. Here, we set the maximum structure level as 2 to consider the power-law tail at the low  $q$  region (i.e.,  $q < 0.02 \text{ \AA}^{-1}$ ). At the second structure level ( $i = 2$ ), we assumed that  $R_{g,2}$  would be very large to make the second level of Guinier pre-factor and error function to be 0 and 1, respectively. From the first level ( $i = 1$ ) of the Unified model, the agglomerate styrene size (radius of gyration,  $R_{g,1}$ ) of  $\sim 1.2 \text{ nm}$  and  $D_1$  of  $-2.05$  were extracted. It is noted that  $D_1 \sim -2$  corresponds to the typical mass fractal dimension for polymeric gel systems and implies the network structure of PEMA-*r*-PS-based gels.<sup>S5</sup>

## S2. Percus-Yevick hard sphere model fit

Basically, the typical Unified model, used to fit the SAXS intensity profile for PEMA-*r*-PS gels, only considers form factors from the Guinier and Porod regimes without the correlation scattering effects (i.e., structure factor). In the SAXS intensity profile for PEMA-*b*-PS gels, it clearly presents a correlation scattering peak at  $q \sim 0.025 \text{ \AA}^{-1}$ . To account for the correlation scattering effects arising from multiple scatterers, we need to use a different fitting model including form and structure factor. Therefore, we fit the scattering profile of the gel with disordered PEMA-*r*-PS using the Percus-Yevick hard sphere model,<sup>S6</sup> which is expressed by:

$$I(q) = KS(q)P(q)$$

$K$  is the scattering constant including the number density of the scattering particles,  $S(q)$  is the structure factor derived from the Percus-Yevick hard sphere model, and  $P(q)$  is the spherical form factor. Here,  $P(q)$  and  $S(q)$  can be described as following equations:

$$P(q) = \left[ 3 \frac{\sin(qR) - qR \cos(qR)}{(qR)^3} \right]^2$$

$$S(q) = \frac{1}{1 + 24\nu G(2qR_{HS})/2qR_{HS}}$$

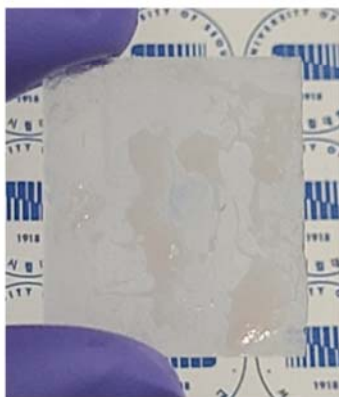
where  $\nu$ ,  $R$  and  $R_{HS}$  correspond to the volume fraction, radius of sphere, and radius of the hard sphere, respectively. Also,  $G(2qR_{HS})$  can be defined as:

$$G = \frac{\alpha}{(2qR_{HS})^2} (\sin(2qR_{HS}) - 2qR_{HS} \cos(2qR_{HS})) + \frac{\beta}{(2qR_{HS})^3} (2(2qR_{HS}) \sin(2qR_{HS}) + (2 - (2qR_{HS})^2) \cos(2qR_{HS}) - 2) + \frac{\gamma}{(2qR_{HS})^5} (-(2qR_{HS})^4 \cos 2qR_{HS} + 4((3(2qR_{HS})^2 - 6) \cos(2qR_{HS}) + ((2qR_{HS})^3 - 6(2qR_{HS})) \sin(2qR_{HS}) + 6))$$

where  $\alpha = \frac{(1+2\nu)^2}{(1-\nu)^4}$ ,  $\beta = -\frac{6\nu(1+\nu/2)^2}{(1+\nu)^4}$ , and  $\gamma = \frac{\nu(1+2\nu)^2}{2(1-\nu)^4}$ .

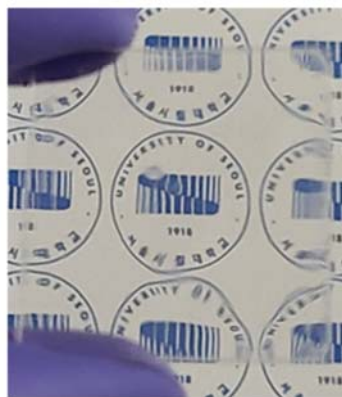
**PEMA-*r*-PS  
(Sty ~53 mol%)  
based gel**

**(a)**

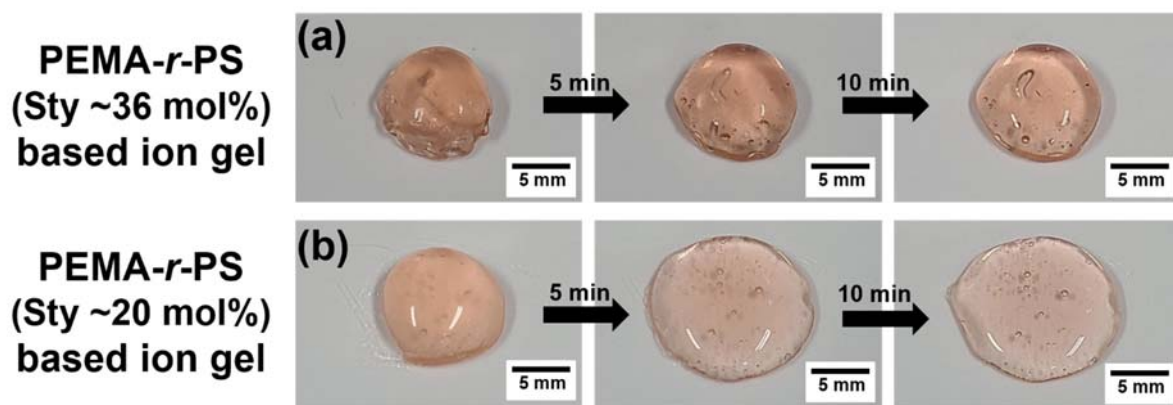


**PEMA-*r*-PS  
(Sty ~36 mol%)  
based gel**

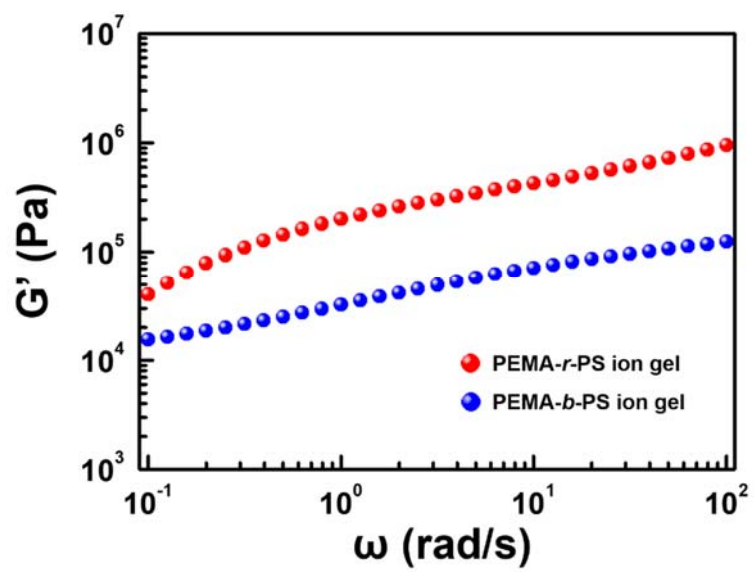
**(b)**



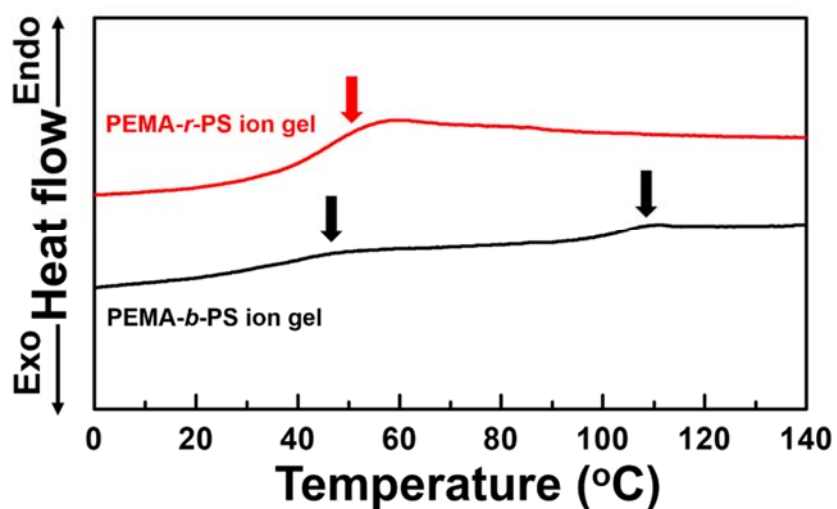
**Fig. S1** Photographs of ion gels based on PEMA-*r*-PSs containing (a) ~53 and (b) ~36 mol% styrene, where 70 wt% [EMI][TFSI] was included in the gels.



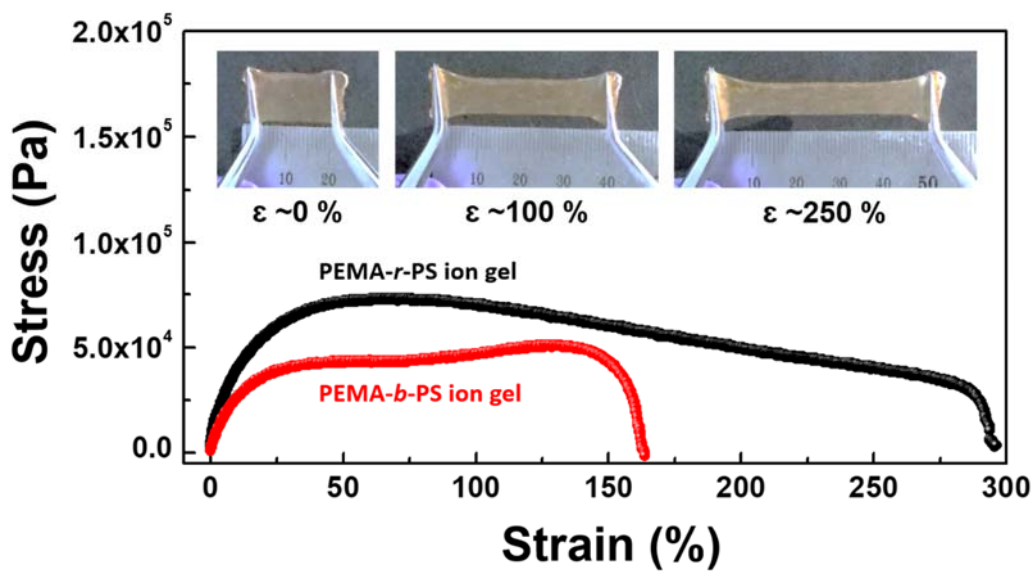
**Fig. S2** Comparison of ion gels based on PEMA-*r*-PSs including (a) ~36 and (b) ~20 mol% of styrene. Both gels are composed of 70 wt% of [EMI][TFSI] and 30 wt% of PEMA-*r*-PS.



**Fig. S3** Isothermal frequency sweeps of dynamic storage moduli ( $G'$ ) for ion gels consisting of 40 wt% copolymer gelator (i.e., PEMA-*r*-PS or PEMA-*b*-PS) and 60 wt% [EMI][TFSI].



**Fig. S4** DSC thermograms of ion gels during second heating at a rate of  $20\text{ }^{\circ}\text{C min}^{-1}$ , in which 80 wt% copolymer gelator (PEMA-*r*-PS or PEMA-*b*-PS) and 20 wt% [EMI][TFSI] were included. The PEMA-*b*-PS gel exhibited two  $T_g$ s of  $\sim 108$  and  $\sim 47.1$   $^{\circ}\text{C}$  arising from the PS agglomerates and the PEMA + [EMI][TFSI] domains, respectively, implying the phase separated structure of the gel.



**Fig. S5** Stress-strain curves of ion gels consisting of 50 wt% copolymer gelator and 50 wt% [EMI][TFSI]. The insets display photographs of the PEMA-*r*-PS based ion gel at various applied strains. The elongation at break for the PEMA-*b*-PS-based gel (~145 %) was distinctly lower than that of the gel containing PEMA-*r*-PS (~280 %).



## References

- [S1] Y. M. Kim, D. G. Seo, H. Oh and H. C. Moon, *J. Mater. Chem. C*, 2019, **7**, 161–169.
- [S2] D. G. Seo, Y. M. Kim, H. Ahn and H. C. Moon, *Nanoscale*, 2019, **11**, 16733–16742.
- [S3] G. Beaucage, *J. Appl. Crystallogr.*, 1995, **28**, 717–728.
- [S4] G. Beaucage, T. A. Ulibarri, E. P. Black and D. W. Schaefer, *ACS Symp. Ser.*, 1995, **585**, 97–111.
- [S5] D. R. Vollet, D. A. Donatti, A. Ibañez Ruiz and F. R. Gatto, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **74**, 024208.
- [S6] D. J. Kinning and E. L. Thomas, *Macromolecules*, 1984, **17**, 1712–1718.