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Non-Volatile, Phase-Transition Smart Gels Visually Indicating *In-Situ* Thermal Status for Sensing Applications

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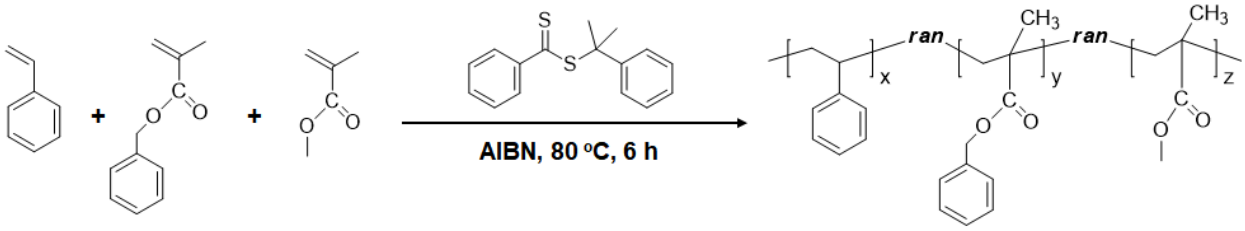
1. Characterizations of P(S-*r*-BzMA-*r*-MMA)s.



Scheme S1. Synthetic route for P(S-*r*-BzMA-*r*-MMA) *via* one-step RAFT polymerization.

A single and sharp size exclusion chromatography (SEC) trace of P(S-*r*-BzMA-*r*-MMA)-I prepared by one-pot RAFT polymerization (see Scheme S1) is shown in Fig. S1a. The number average molecular weight (M_n) and polydispersity index (*Đ*) were determined to be 94,400 and 1.1, respectively. A differential scanning calorimetry (DSC) thermogram of the P(S-*r*-BzMA-*r*-MMA)-I was recorded to verify its perfect randomness (Fig. S1b). The prepared P(S-*r*-BzMA-*r*-MMA)-I showed a single glass transition temperature (T_g) at ~93.7 ^{o}C for the entire experimental temperature range, implying the configuration of P(S-*r*-BzMA-*r*-MMA)-I was not block/tapered but completely random.

The mole fractions of Sty (*x*), BzMA (*y*) and MMA (*z*) were calculated from the ^{1}H NMR spectrum (see Fig. S1c). Because the P(S-*r*-BzMA-*r*-MMA)-I is composed of three monomers (i.e. Sty, BzMA and MMA), equation (S1) is simply obtained:

$$\boldsymbol{x+y+z=1} \qquad \text{(S1)}$$

The three characteristic peaks indicated in Fig. S1c originate from three protons (a) of BzMA + three protons of (b) MMA, two protons (c) of BzMA, and five protons (d) of Sty + five protons (e) of BzMA, respectively. When we consider that the integration area (A_{a+b}), (A_c) and (A_{d+e}) was determined to be 4.82, 1.00 and 6.01, respectively, equations (S2) and (S3) can be derived as

$$\boldsymbol{2y/(3y+3z)=1/4.82} \quad \text{(S2)}$$

$$\boldsymbol{2y/(5x+5y)=1/6.01} \quad \text{(S3)}$$

From these three equations, the mole fractions of each monomer component in P(S-*r*-BzMA-*r*-MMA)-I were calculated to be Sty (x) ~0.30, BzMA (y) ~0.22 and MMA (z) ~0.48.

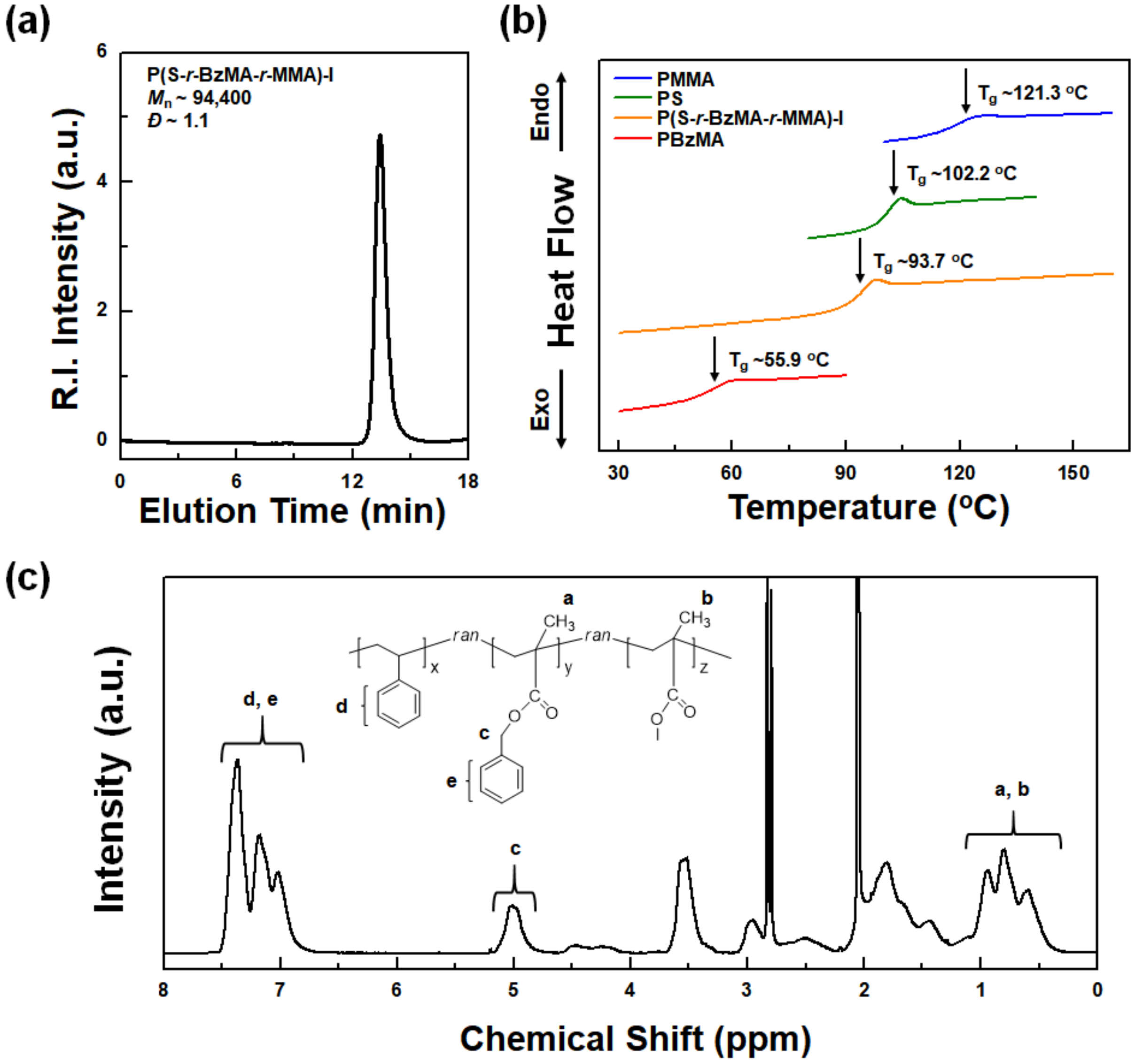


Fig. S1 (a) SEC trace of the thermoresponsive random copolymer, P(S-*r*-BzMA-*r*-MMA)-I. (b) DSC thermograms obtained during the second heating at a rate of 10 ^{o}C/min for synthesized P(S-*r*-BzMA-*r*-MMA)-I, and corresponding homopolymers: PS, PBzMA, and PMMA. (c) ^{1}H NMR spectrum for P(S-*r*-BzMA-*r*-MMA)-I.

We also estimated theoretical composition of the synthesized P(S-*r*-BzMA-*r*-MMA)-I using the Alfrey-Goldfinger equation (equation (S4)) with reactivity ratios (r_{ij}) between binary monomer pairs.[S1]

$$F_1 : F_2 : F_3 = \\ f_1[f_1/(r_{31}r_{21}) + f_2/(r_{21}r_{32}) + f_3/(r_{31}r_{23})][f_1 + f_2/r_{12} + f_3/r_{13}] : \\ f_2[f_1/(r_{12}r_{31}) + f_2/(r_{12}r_{32}) + f_3/(r_{32}r_{13})][f_2 + f_1/r_{21} + f_3/r_{23}] : \\ f_3[f_1/(r_{13}r_{21}) + f_2/(r_{23}r_{12}) + f_3/(r_{13}r_{23})][f_3 + f_1/r_{31} + f_2/r_{32}] \quad \text{(S4)}$$

where F_i, f_i, and r_{ij} correspond to the theoretical mole fraction, feed mole fraction, and the binary copolymerization reactivity ratio of species i and j, respectively. The r_{ij} values used for prediction were provided in Table S1. The calculated composition of P(S-*r*-BzMA-*r*-MMA)-I was determined to be Sty (F_1) ~28%, BzMA (F_2) ~25%, and MMA (F_3) ~47% with the feed mole ratio of Sty:BzMA:MMA ~0.20:0.30:0.50, which agrees with the ^{1}H NMR results (see Table S2).

Other P(S-*r*-BzMA-*r*-MMA)s having different compositions and homopolymers were also prepared by RAFT polymerization. Their SEC traces and NMR spectra are given in Fig. S2 and S3.

Table S1. Binary reactivity ratios for styrene (1), benzyl methacrylate (2) and methyl methacrylate (3).

Reactivity ratio (r_{ij})			
r_{12}[S2]	0.48	r_{21}[S2]	0.42
r_{23}[S3]	0.546	r_{32}[S3]	0.968
r_{13}[S4]	0.48	r_{31}[S4]	0.42

Table S2. Summary of feed ratios and compositions obtained from Alfrey-Goldfinger equation and ^{1}H NMR spectroscopy for random copolymers.

P(S-*r*-BzMA-*r*-MMA)-I		
feed	predicted	^{1}H NMR
f_{Sty}:f_{BzMA}:f_{MMA}	F_{Sty}:F_{BzMA}:F_{MMA}	
0.20:0.30:0.50	0.28:0.25:0.47	0.30:0.22:0.48

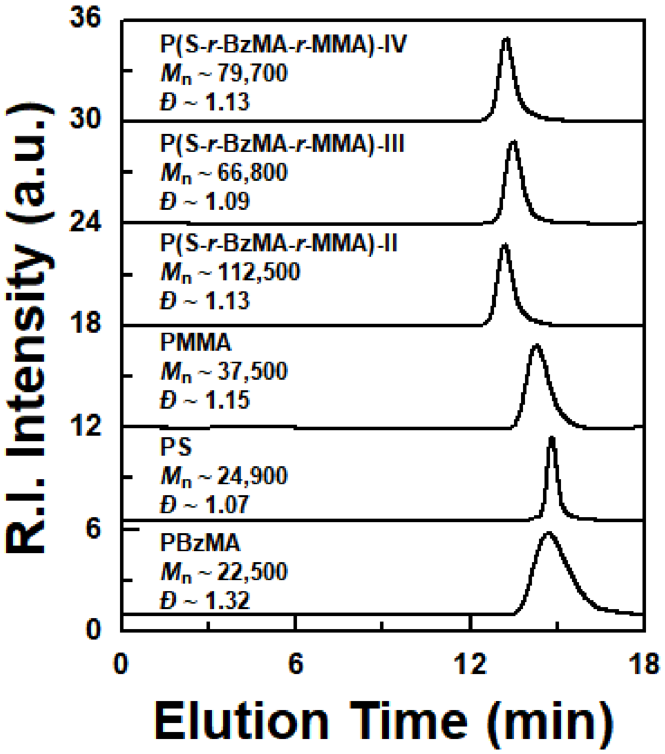


Fig. S2 SEC traces of copolymers and homopolymers prepared in this work.

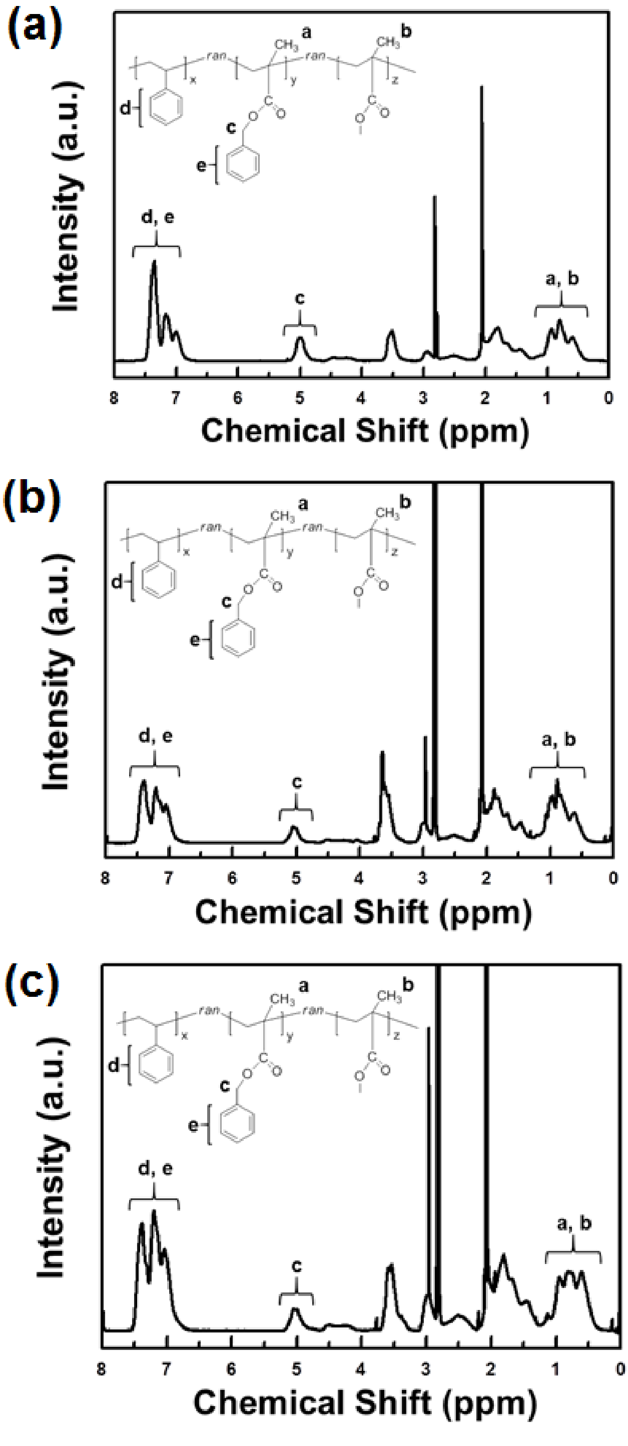


Fig. S3 ^{1}H NMR spectra of (a) P(S-*r*-BzMA-*r*-MMA)-II, (b) P(S-*r*-BzMA-*r*-MMA)-III, and (c) P(S-*r*-BzMA-*r*-MMA)-IV.

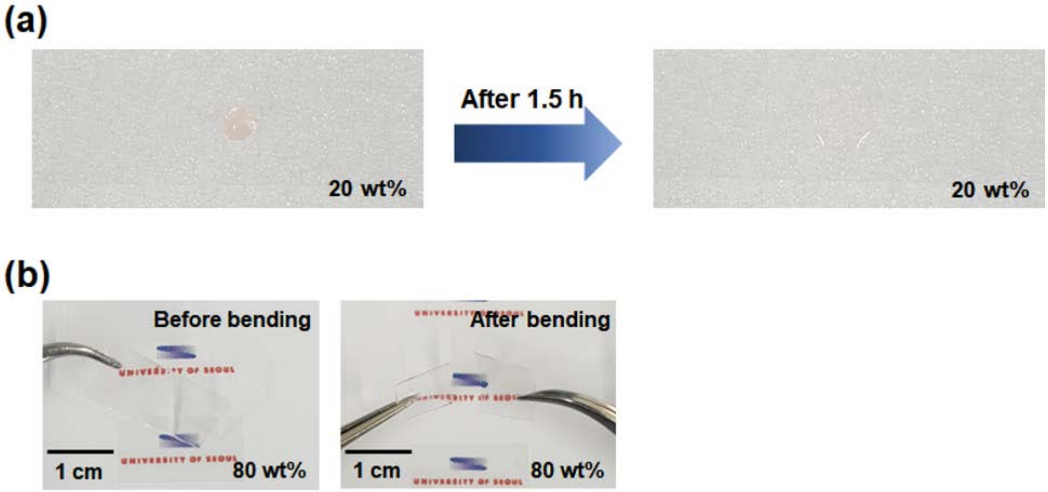


Fig. S4 Photographs of (a) the thermoresponsive gel including 20 wt% of P(S-*r*-BzMA-*r*-MMA)-I: as made (left) and after 1.5 h at ambient conditions (right), and (b) the gel containing 80 wt% P(S-*r*-BzMA-*r*-MMA)-I before and after bending. These photographs indicate that both gels are not suitable as an elastic temperature sensor.

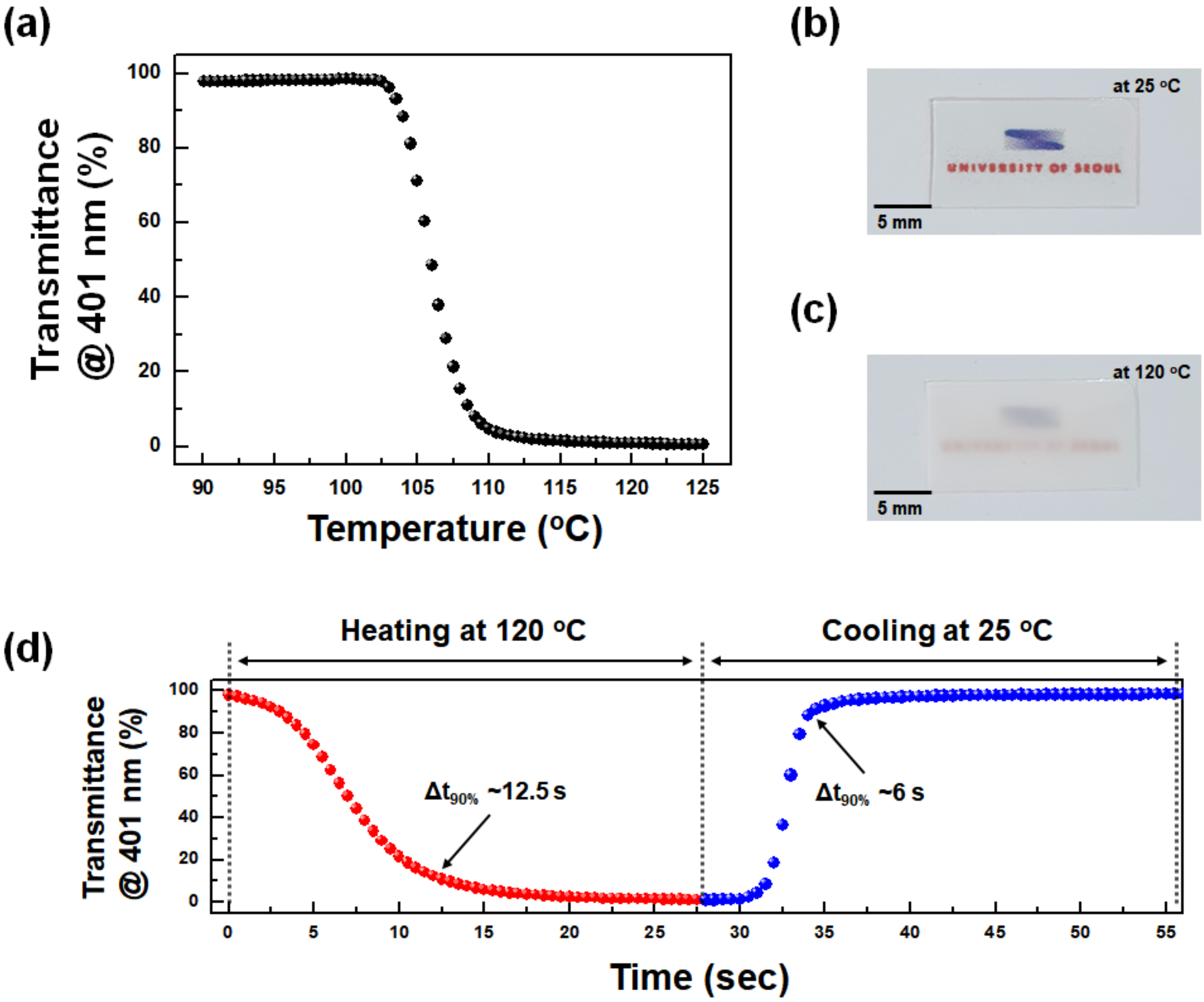


Fig. S5 (a) Change in transmittance at 401 nm for 40 wt% P(S-*r*-BzMA-*r*-MMA)-I and 60 wt% [EMI][TFSI] containing thermoresponsive gels. Photographs of ion gels on a glass substrate of (b) the transparent state and (c) the opaque state. (d) Transient transmittance profiles of the gel upon heating and cooling.

2. Effects of random copolymer and gel compositions on the thermal response.

We comment the effect of random copolymer composition on the thermal response of the gels. The mole fraction of 0.30:0.22:0.48 (Sty:BzMA:MMA) (namely, P(S-*r*-BzMA-*r*-MMA)-I) provided the gel exhibiting reversible thermal response, which will be discussed in detail. Although we slightly increased the portion of BzMA and decreased the amount of MMA (e.g. Sty:BzMA:MMA ~ 0.31:0.28:0.41) (P(S-*r*-BzMA-*r*-MMA)-II), the resulting gels exhibited a large difference in thermoresponsive behaviors. A homogeneous gel was obtained with P(S-*r*-BzMA-*r*-MMA)-II. Although the gel became opaque when heated above the LCST, but leakage of the ionic liquid was observed (Fig. S6). The turbid gel did not completely return to its original transparent state even after cooling. This result is probably attributed to the fact that the whole amount of ionic liquids absorbed in PBzMA and PMMA could not be contained within only the PMMA matrix after PBzMA became insoluble at T > LCST.

In contrast, when the MMA content was increased with decreasing BzMA fraction (P(S-*r*-BzMA-*r*-MMA)-III), the miscibility between copolymers and ionic liquids was improved. As a result, a boundary of homogeneous phase expanded, so that the transition of corresponding system appeared at a higher temperature (~148 ^{o}C) (Fig. S7). If copolymers contained a larger fraction of Sty (P(S-*r*-BzMA-*r*-MMA)-IV), the resultant gel was not homogeneous when blended with 60 wt% of [EMI][TFSI] (Fig. S8a). Although the transparent gel based on P(S-*r*-BzMA-*r*-MMA)-IV can be prepared by decreasing the amount of [EMI][TFSI] (Fig. S8b), the gel exhibited irreversible thermoresponsiveness (Fig. S8c). These results indicate the importance of careful selection of copolymer composition.

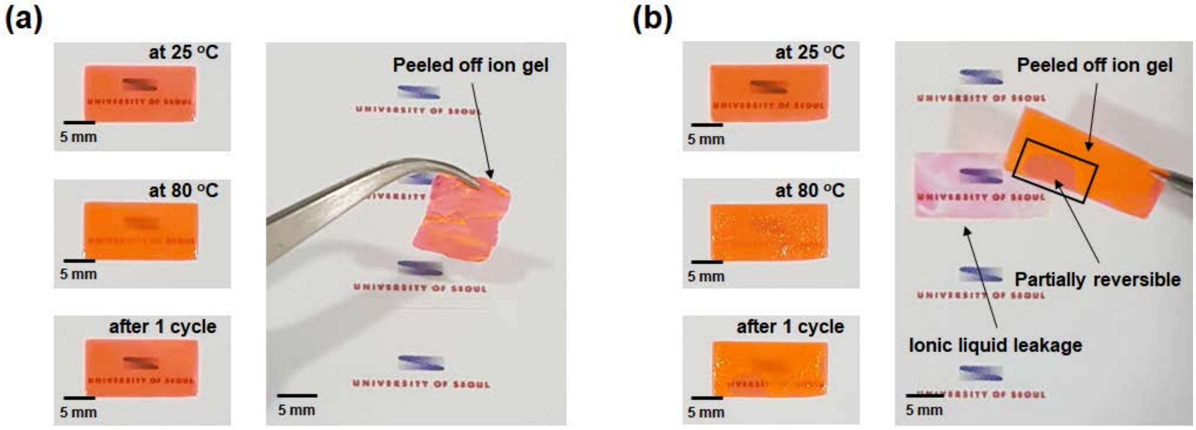


Fig. S6 Photographs of the gels consisting of (a) P(S-*r*-BzMA-*r*-MMA)-I (40 wt%) and mixed ionic liquids containing 5 wt% [EMI][PF$_6$], and (b) 40 wt% P(S-*r*-BzMA-*r*-MMA)-II and 60 wt% [EMI][TFSI] (Rhodamine 6G was used as a dye to show a dramatic contrast of ionic liquid leakage). The irreversible thermal phase separation was only observed on the P(S-*r*-BzMA-*r*-MMA)-II based gel after heating (at 80 ^{o}C) and cooling (at 25 ^{o}C) cycle due to ionic liquid leakage.

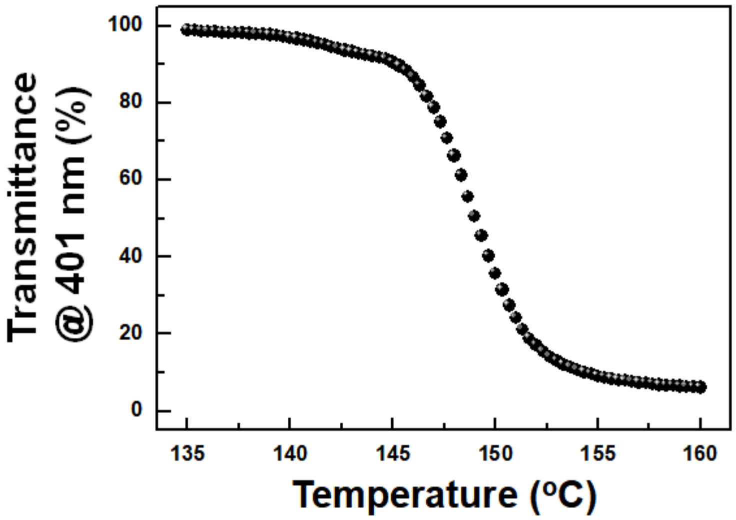
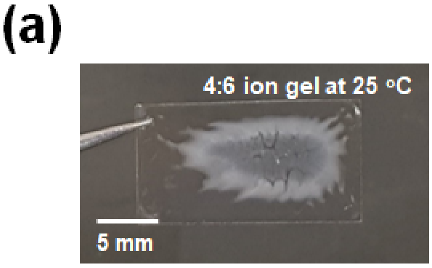
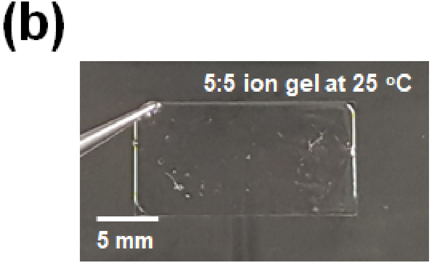


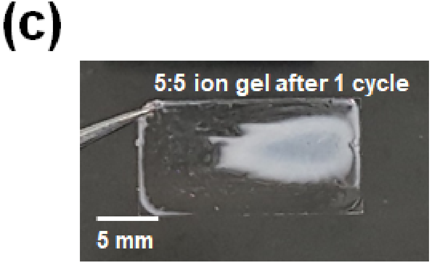
Fig. S7 Temperature dependence of transmittance for the gel composed of 40 wt% P(S-*r*-BzMA-*r*-MMA)-III and 60 wt% of [EMI][TFSI]. The miscibility between copolymers and ionic liquids increased as the MMA content increased, resulting in higher LCST.



Turbid gel at 25 °C



Transparent gel at 25 °C



Irreversible thermoresponsiveness

Fig. S8 Photographs of thermoresponsive gels based on the P(S-*r*-BzMA-*r*-MMA)-IV having a large portion of [EMI][TFSI]-insoluble Sty: (a) Turbid state of the gel containing [EMI][TFSI] of 60 wt%, (b) transparent gel with 50 wt% [EMI][TFSI], and (c) turbid state of the gel including 50 wt% P(S-*r*-BzMA-*r*-MMA)-IV after one heating/cooling cycle, indicating irreversible thermoresponsiveness.

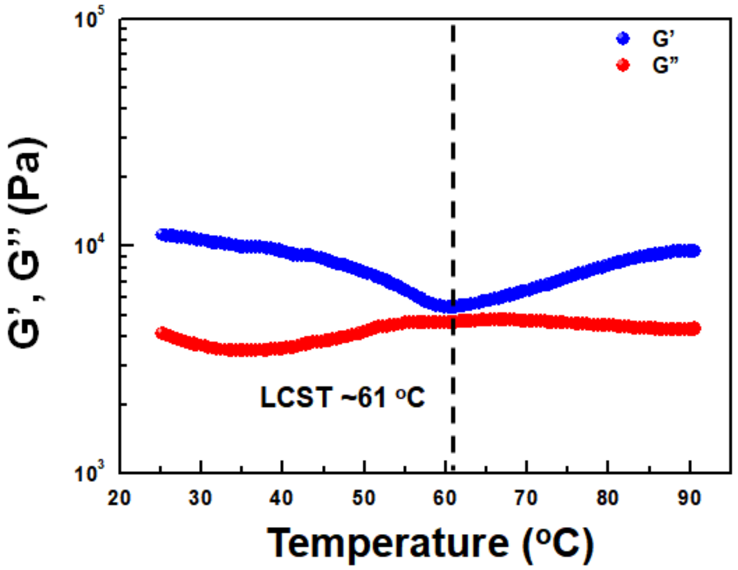


Fig. S9 Dynamic temperature sweeps of G' and G" for the gel containing 5 wt% of [EMI][PF$_6$] at a cooling rate of 1 ^{o}C/min, where the frequency and strain amplitude were fixed at 0.1 Hz and 5%, respectively.

Fig. S10 Unchanged weight of the gel composed of 40 wt% P(S-*r*-BzMA-*r*-MMA)-I and mixed ionic liquids containing 5 wt% [EMI][PF_6] after heating up to ~100 ^{o}C that is obviously higher than its LCST.

References

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