Supplementary Information for

Mechanism of Temperature-Induced Asymmetric Swelling and Shrinking Kinetics in Self-Healing Hydrogels

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Supplementary Materials & Methods

Materials. The anionic monomer, sodium *p*-styrenesulfonate (NaSS), chemical cross-linker *N,N'*-methylene-bis-acrylamide (MBAA), and ultraviolet (UV) initiator α-ketoglutaric acid (α-keto) were purchased from Wako Pure Chemical Industries, Ltd., Japan. Cationic monomers, methyl chloride quarternized *N,N*-dimethylamino ethylacrylate (DMAEA-Q, 79.2 wt.%), were kindly provided by MT AquaPolymer, Inc., Japan. All chemicals were used as received without further purification. Deionized water was used in all experiments.

Scanning Electron Microscopy (SEM). The microstructures of the gels in the cut cross-sections were measured using SEM. Gels were frozen and fractured using tweezers in liquid nitrogen. Next, the gels were freeze-dried at –80 °C with a freeze-drying machine (Advantage XL-70, VirTis freeze-dryer). Freeze-dried samples were coated with gold using an ion-sputtering device (E-1010, Hitachi, Japan). The SEM measurement was conducted an SEM instrument (JSM-6010LA, JEOL, Japan) with an accelerating voltage of 10 kV.

Water content measurement. The water content of the polyampholyte (PA) gel, C, was measured using an electronic moisture balance (MOC-120H, SHIMADZU Co.). First, the gel was weighed at room temperature. The temperature was then increased to 120 °C to evaporate the water until no weight change occurred. The water content was defined as the ratio of the lost weight to the initial weight of the gel. The polymer volume fraction, ϕ_p, of the PA gel was calculated from the following equation (1):

$$\phi_p^{-1} = 1 + \left(\frac{C}{1-C}\right)\frac{\rho_p}{\rho_w}$$

Where $\rho_p = 1.19$ g/cm^3 and $\rho_w = 0.998$ g/cm^3, are the densities of polymer and water, respectively.

Rheology measurement. The linear rheology tests were performed using an ARES-G2 rheometer (TA Instruments, USA) with a parallel plate geometry. The diameter of upper parallel plate is 25 mm. The lower plate has a U-shape with a diameter of 50 mm (Fig. S5). Disk-like gels with a diameter of 10 mm and thickness from 1.1 to 1.3 mm at 25°C were bonded to the upper and lower plates with a superglue and surrounded with deionized water during testing. Strain sweep test was performed with strain ranging from 0.01% to 100% at 1 Hz at different temperatures from 8 to 88 °C. Frequency sweep test with frequency ranging from 0.1 to 100 Hz was measured at different temperatures from 8 to 88 °C. A strain of 0.3% was used, which locates at the linear viscoelastic region of PA gel (Fig. S6).

Swelling/deswelling kinetics measurement. The swelling/deswelling kinetics measurement was performed using a setup shown in Fig. S9. The kinetics of swelling/deswelling is governed by the smallest dimension of the sample, which is the thickness for the disc-shaped gels. Since the relative size changes in thickness are identical to that in diamter due to the isotropic nature of gels, the diameter change was monitored in this study.

Supplementary Results

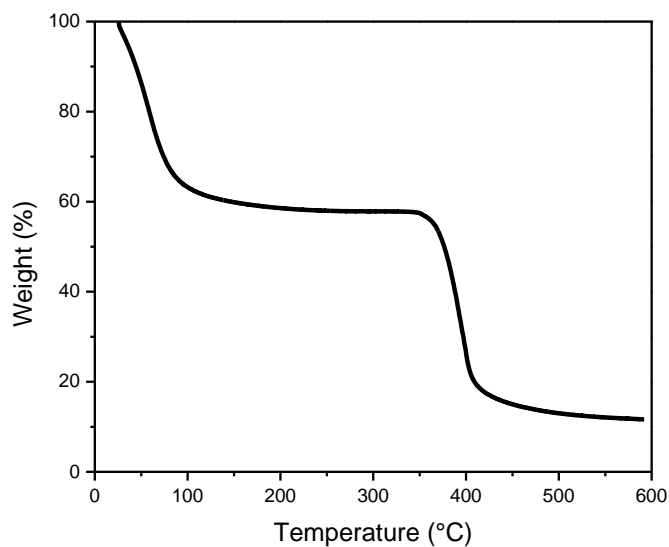### (1) Water content of PA gel with different cross-linker concentrations C_{MBAA}

Fig. S1.
Thermogravimetric analysis (TGA) curve of PA-2.5-0.1 gel. TGA measurement was performed by Pyris 1 TGA (Perkin-Elmer, USA) with a heating rate of 10 °C/min. The weight loss of this gel before 200 °C belongs to water evaporation. The weight loss after 350 °C belongs to the degradation of polymers.
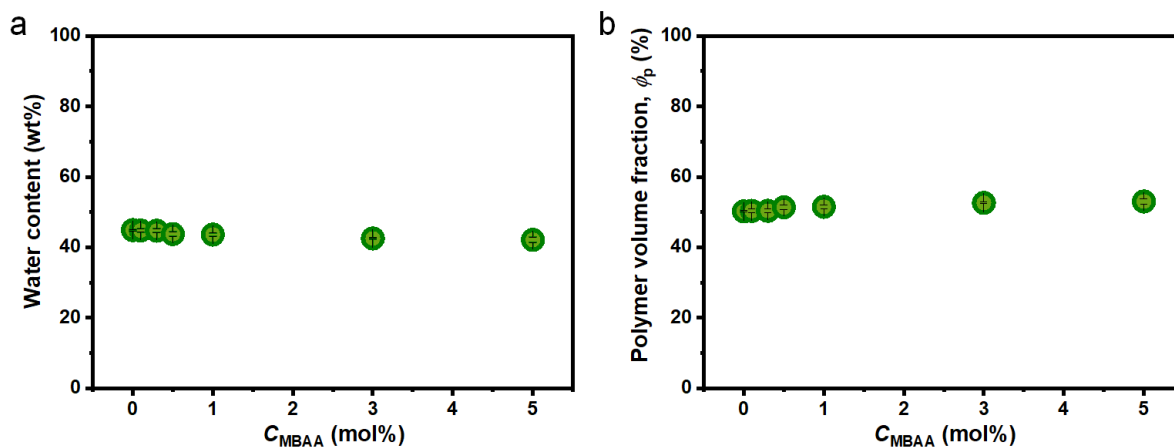

Fig. S2.
Water content of PA gel with different cross-linker concentrations. (a) Water contents and (b) polymer volume fractions of PA gels with different cross-linker concentrations, C_{MBAA}. The PA-2.5-C_{MBAA} set gels were used. The water contents or polymer volume fractions show negligible dependence on C_{MBAA}. Temperature: 25 °C.

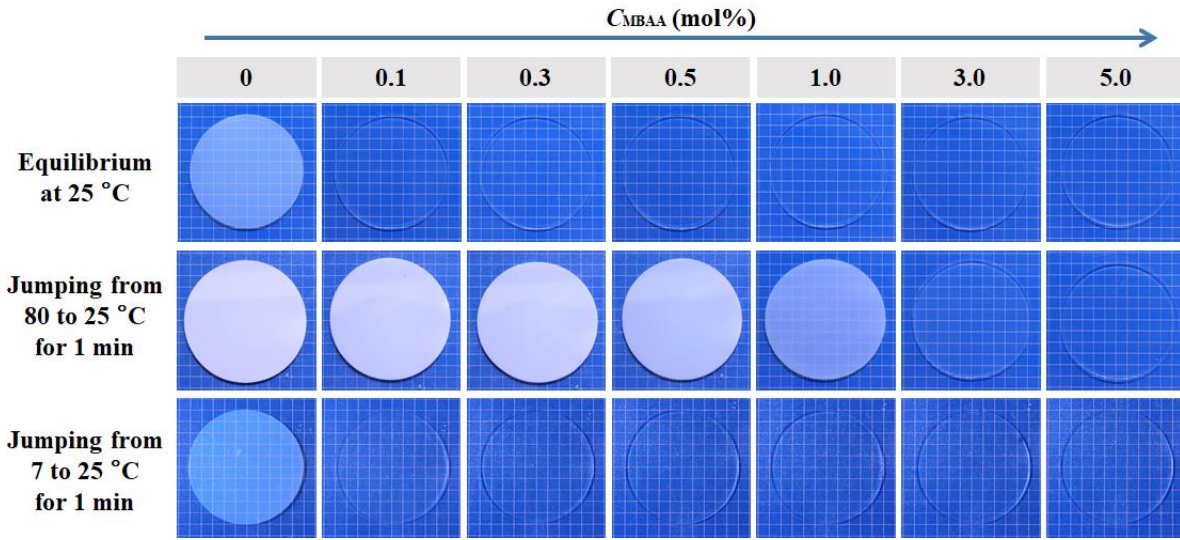## (2) Appearance of gels at cooling and heating

Fig. S3.
Optical appearance of PA gels with different C_{MBAA} ranging from 0 to 5 mol% at cooling and heating. PA gels were initially equilibrated at 25 °C water bath. For the gel without chemical cross-linker ($C_{MBAA} = 0$), the gel is semitransparent, due to the intrinsic phase separation structure. For the gels with $C_{MBAA} \geq 0.1$ mol%, the gels are transparent. These gels were moved to a 7 and an 80 °C water bath for 2 h to reach equilibrium. The water equilibrium gels at both 7 and 80 °C show the same transparency as that equilibrated at 25 °C. After that, these gels were moved to a 25 °C water bath. For the gels being moved from 7 to 25 °C, no obvious change in optical appearance was observed. For the gels being moved from 80 to 25 °C, the gels turned to turbid for $C_{MBAA} \leq$ 1.0 mol%, suggesting the formation of structure frustration. For $C_{MBAA} > 1.0$ mol%, no transparent-to-turbid transition was observed upon cooling, suggesting the suppression of structure frustration by chemical cross-linking. The PA-2.5-C_{MBAA} set gels were used.
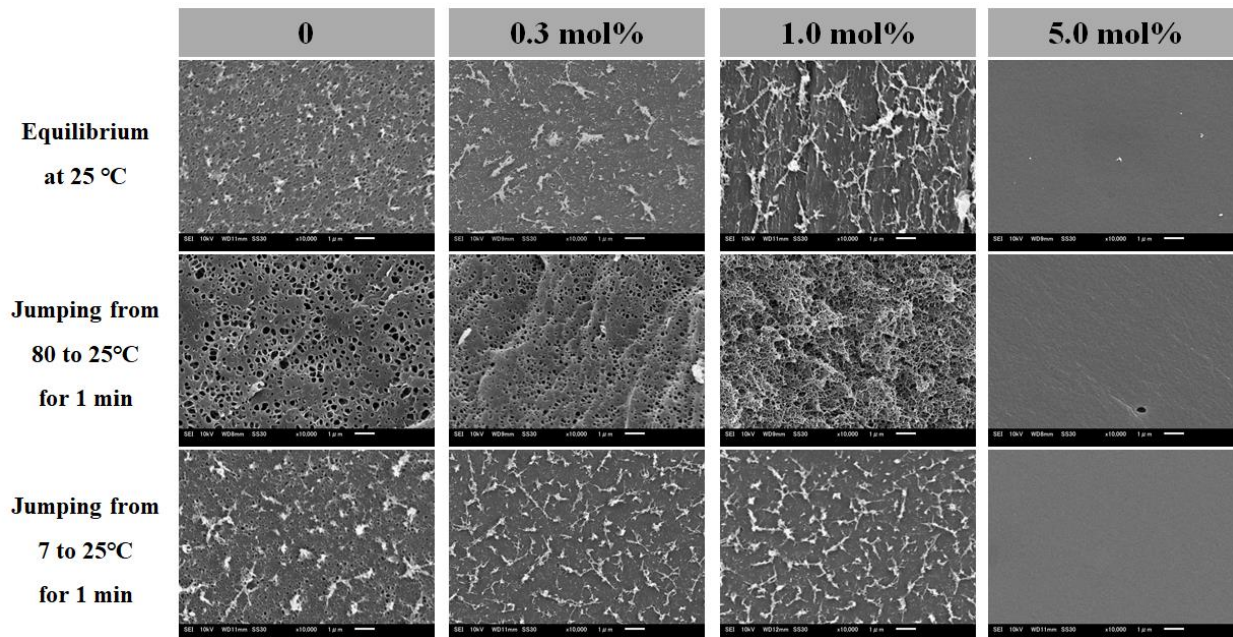
(3) Structure of PA gels with cooling and heating

Fig. S4.
SEM results of PA gels with several selected C_{MBAA} at cooling and heating. The gels have the same monomer concentration and thermal history as described in Fig. S3.
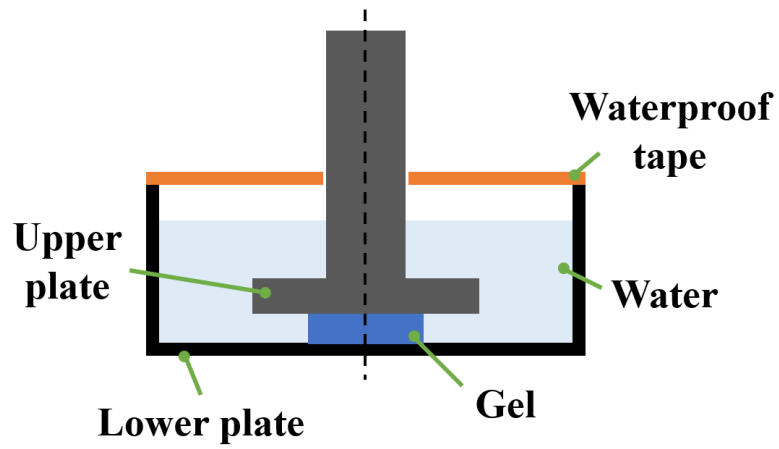
(4) Linear dynamic behavior of PA gels

Fig. S5.
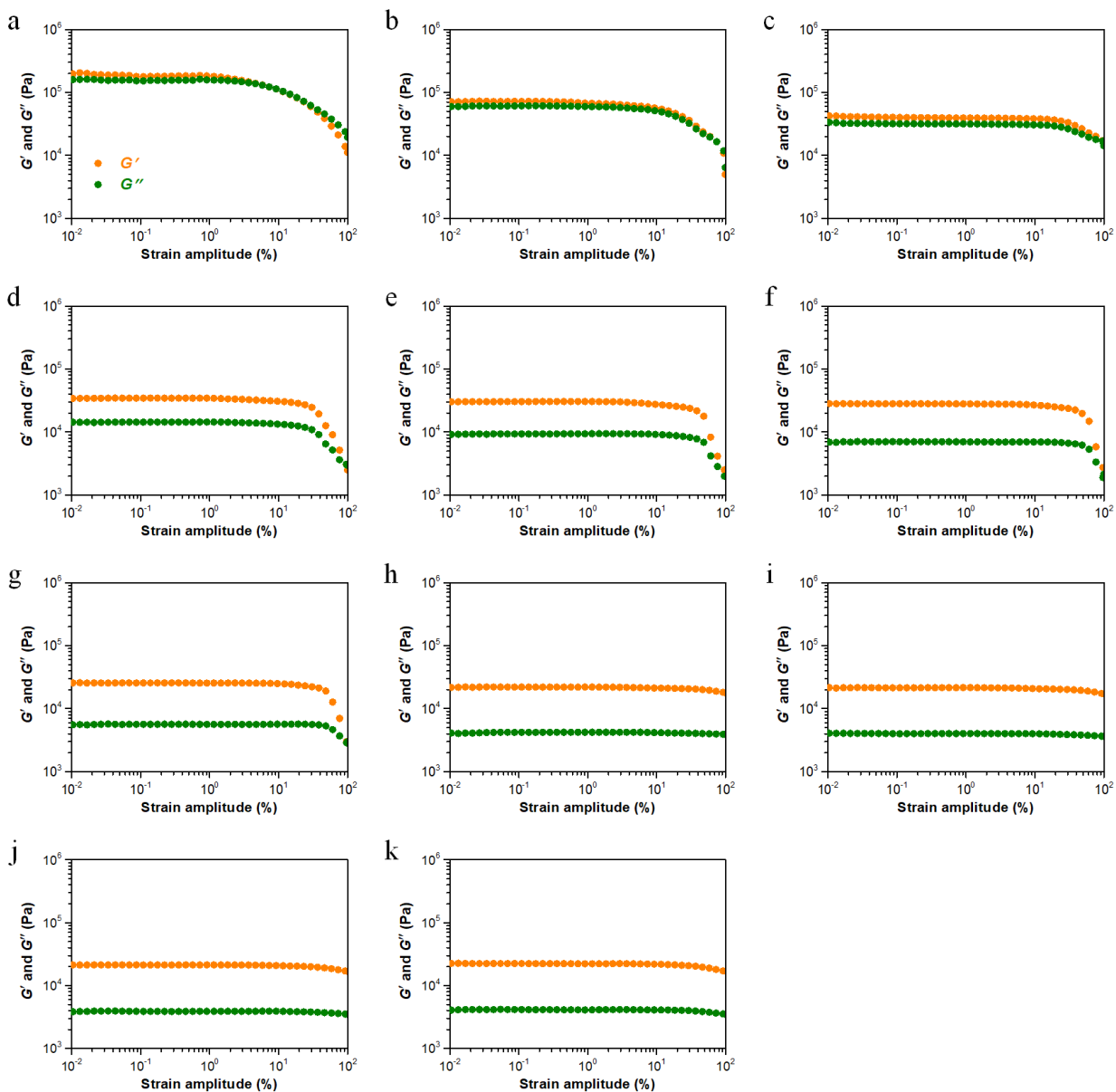**Schematic diagram of rheology test in water environment with a parallel plate geometry.**

Fig. S6
Strain sweep test of a PA-*2.0-0.1* gel at different temperatures from 8 to 88 ˚C. The measurement temperatures are: (a) 8, (b) 16, (c) 24, (d) 32, (e) 40, (f) 48, (g) 56, (h) 64, (i) 72, (j) 80, and (k) 88 ˚C, respectively. The measurement frequency is 1 Hz. The softening at large strain may be due to the softening of the gel or the detachment of sample from the plates.
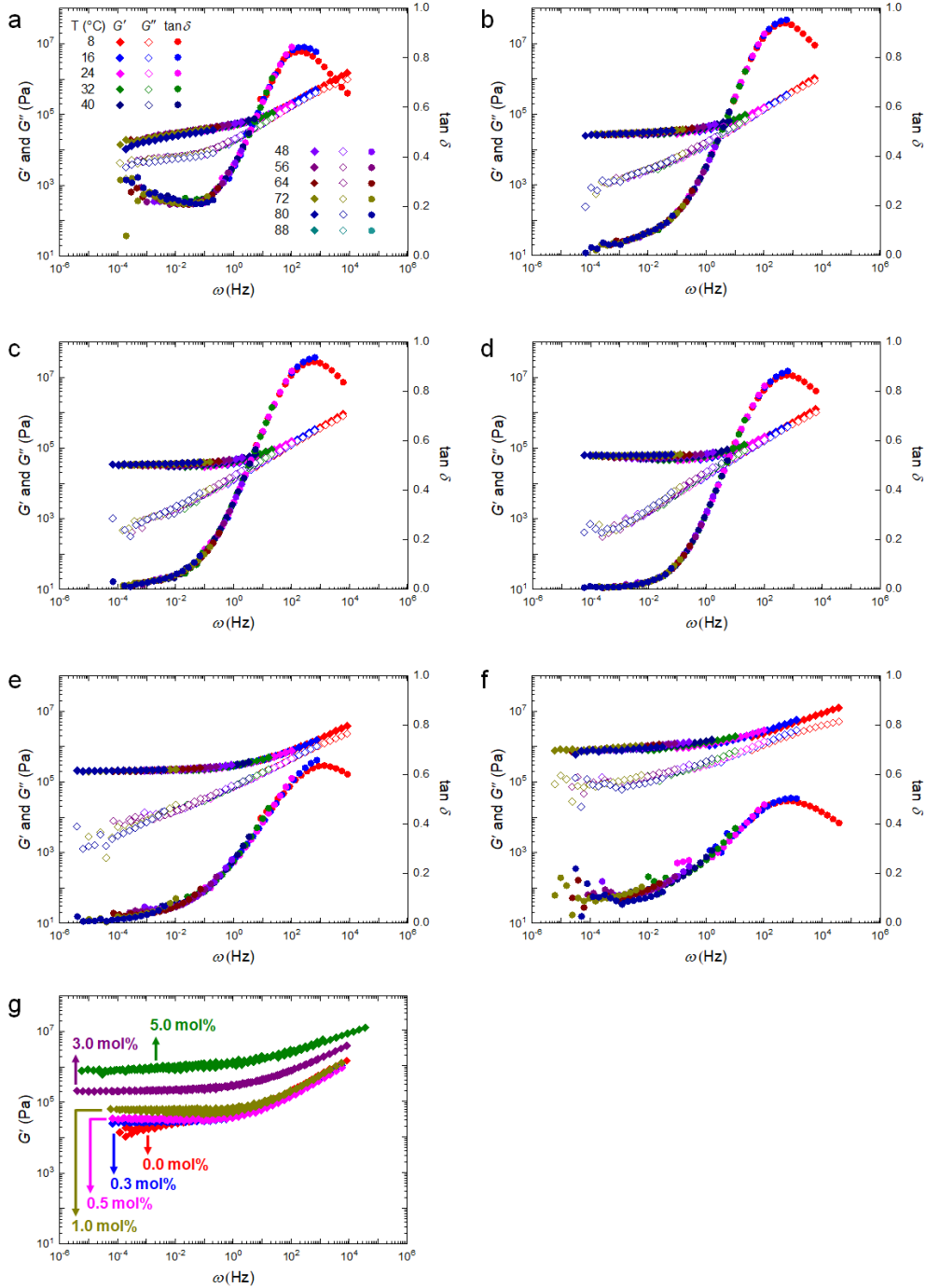
Fig. S7.
Linear dynamic behavior of PA gels with different C_{MBAA}, (a) 0.0, (b) 0.3, (c) 0.5, (d) 1.0, (e) 3.0 (f) 5.0 mol%, and (g) the summary of G'. The PA-*2.5*-C_{MBAA} set gels were used. The master curves of storage modulus G', loss modulus G'', and loss factor tan δ, were constructed from the frequency sweep data at different temperatures following the principle of time−temperature superposition. Reference temperature: 25 °C. The plateau modulus increases with C_{MBAA}, suggesting higher chemcial crosslinkering density at larger C_{MBAA}. The slight difference in frequency range of differerent gels is due to their difference in temperature-dependent shift factor.

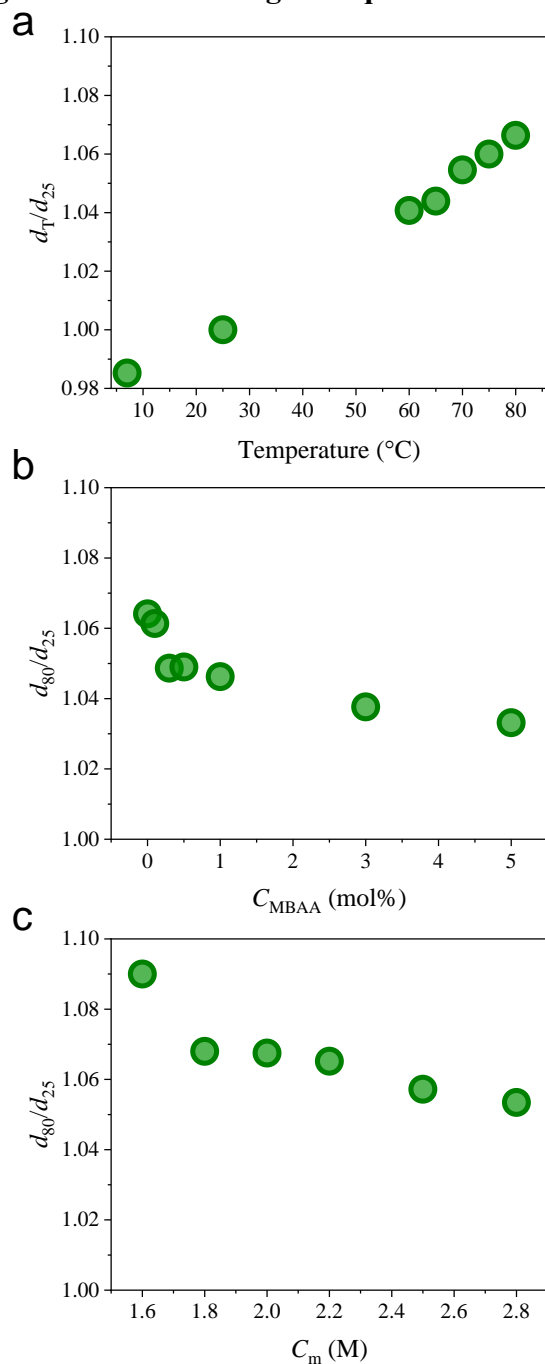**(5) Normalized size change relative to the original equilibrated at 25 °C**

Fig. S8.
Normalized size change of the PA gels relative to the that of the original, equilibrated at 25 °C (d_{25}). (a) Effect of heating temperature. The gels were heated at different temperatures for 2 h to reach equilibrium and obtain the gel size, d_T. The PA-*2.5-0.1* gel was used. (b, c) Effects of cross-linker concentration, C_{MBAA} (b), and monomer concentration, C_m (c). All gels in (b) and (c) were heated to 80 °C for 2 h to reach the swelling equilibrium for obtaining the gel size, d_{80}. The PA-*2.5-C_{MBAA}* and PA-*C_M-0.1* sets of gels were used in (b) and (c), respectively.

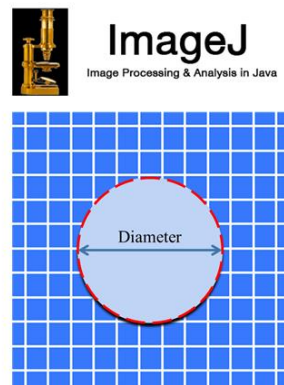**(6) Experimental setup to measure gel size**
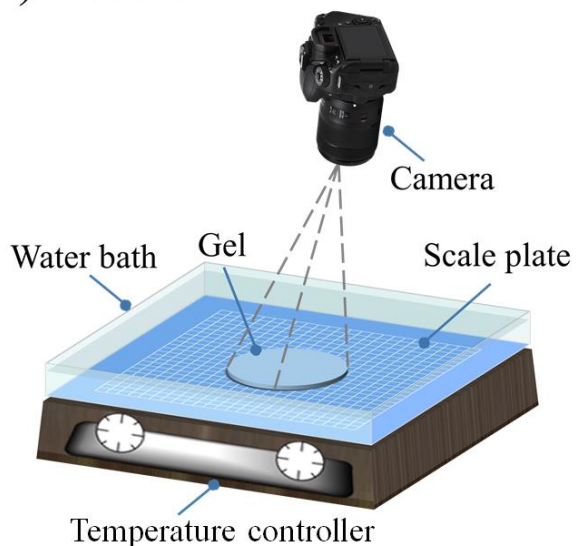
Fig. S9.
Schematic to show the measurement of gel size during swelling or shrinking. (i) A disc-shaped gel of 50 mm in dameter and 1.1~1.3 mm in thickness was put in a water bath with controlled temperature for swelling or shrinking. The diameter change of the gel was tracked by a digital camera. (ii) The diameter of the gel was determined using *ImageJ* software.

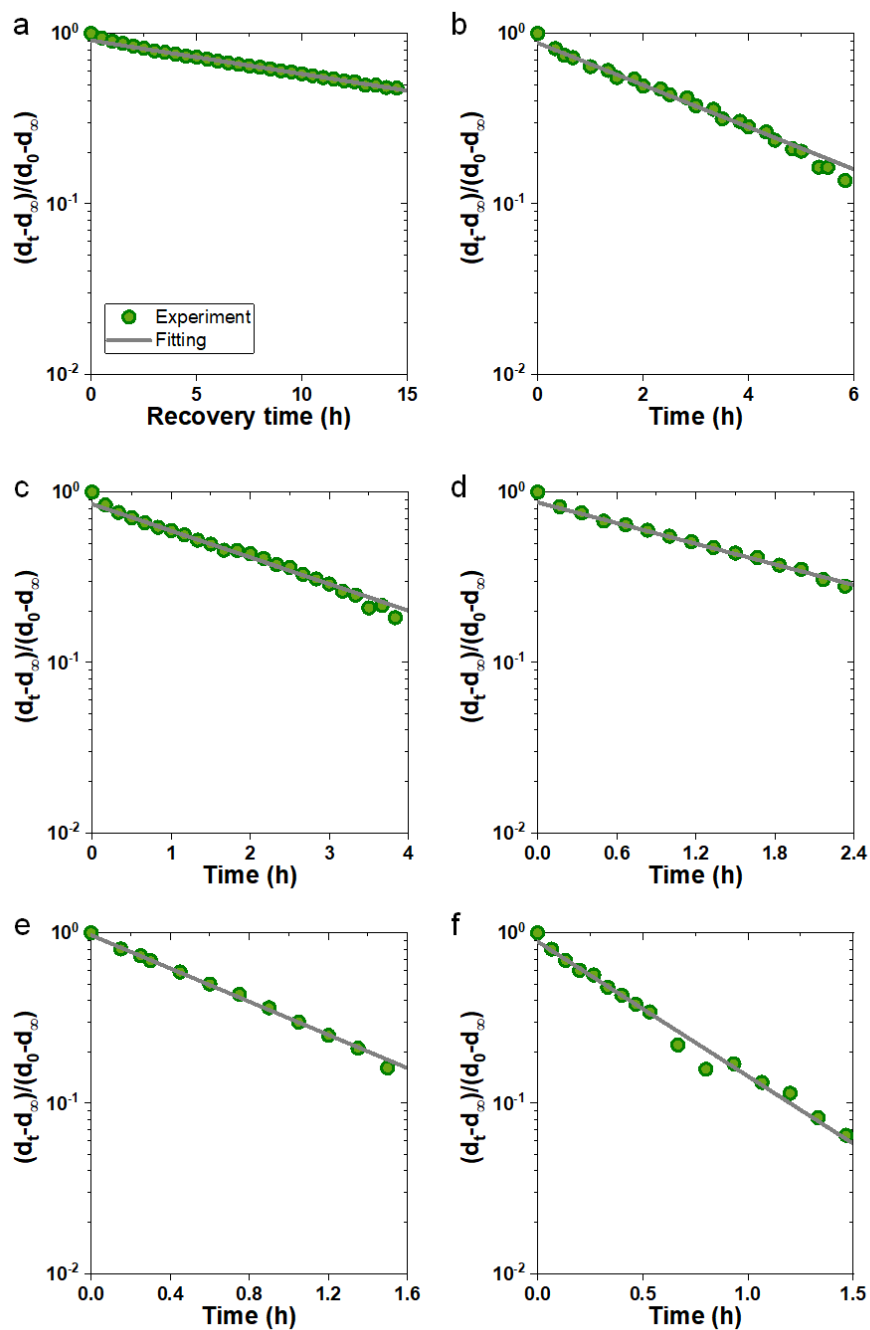**(7) Shrinking kinetics of PA gels with different cross-linker concentrations C_{MBAA}**

Fig. S10.
Shrinking kinetics of gels with different C_{MBAA}, (a) 0.0, (b) 0.3, (c) 0.5, (d) 1.0, (e) 3.0, and (f) 5.0 mol%. The gels were initially equilibrated at 80 °C water bath for 2 h and then moved to a 25 °C water bath for shrinking. The PA-2.5-C_{MBAA} set gels were used. $d_0 = d_{80}$ and $d_\infty = d_{25}$ are shown in Fig. S8.

(8) Swelling kinetics of PA gels with different cross-linker concentrations C_{MBAA}
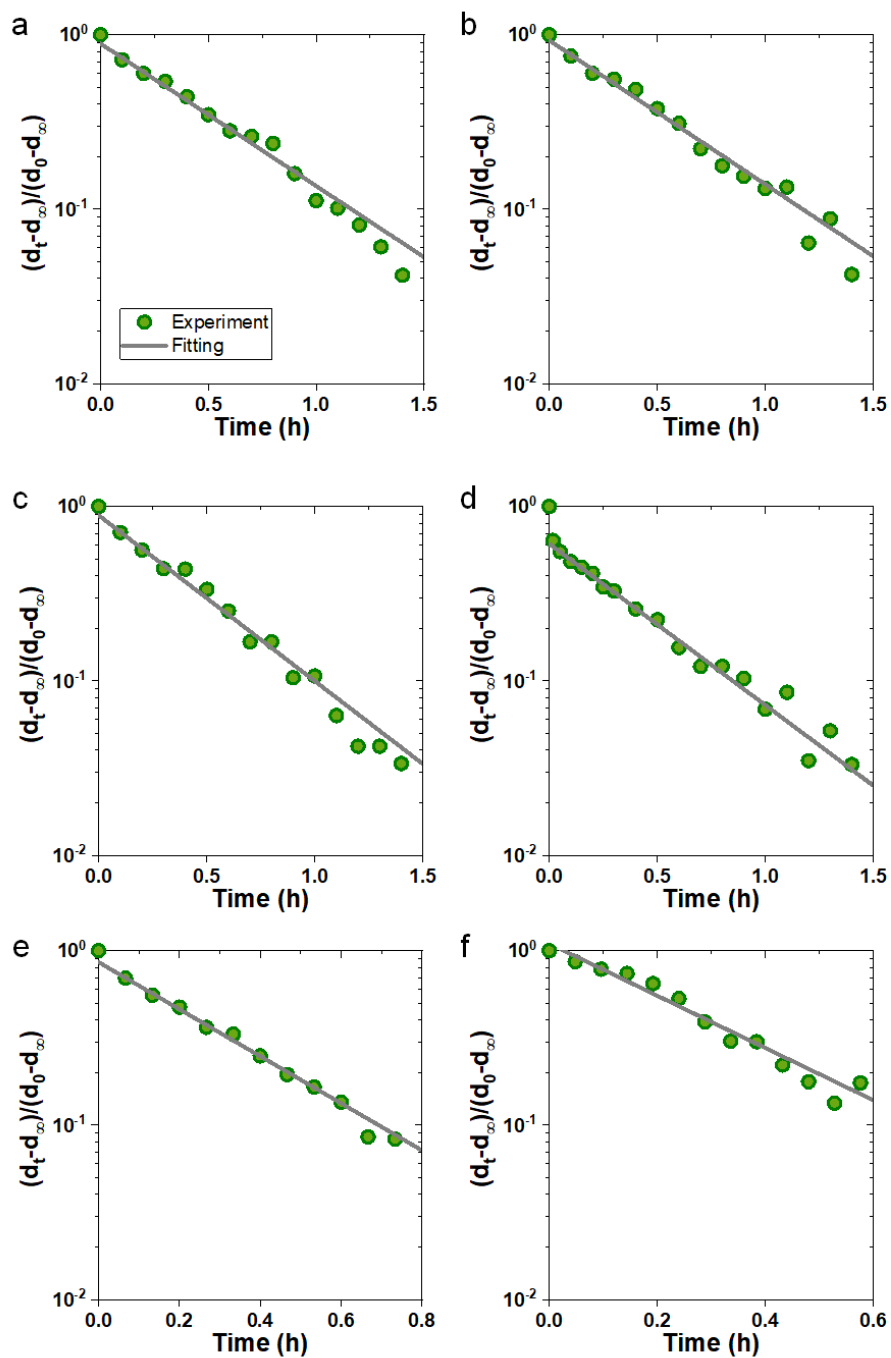

Fig. S11.
Swelling kinetics of gels with different C_{MBAA}, (a) 0.0, (b) 0.3, (c) 0.5, (d) 1.0, (e) 3.0, and (f) 5.0 mol%. The gels were initially equilibrated at 7 °C water bath for 24 h and then moved to a 25 °C water bath for swelling. The PA-2.5-C_{MBAA} set gels were used. $d_0 = d_7$ and $d_\infty = d_{25}$ are shown in Fig. S8.

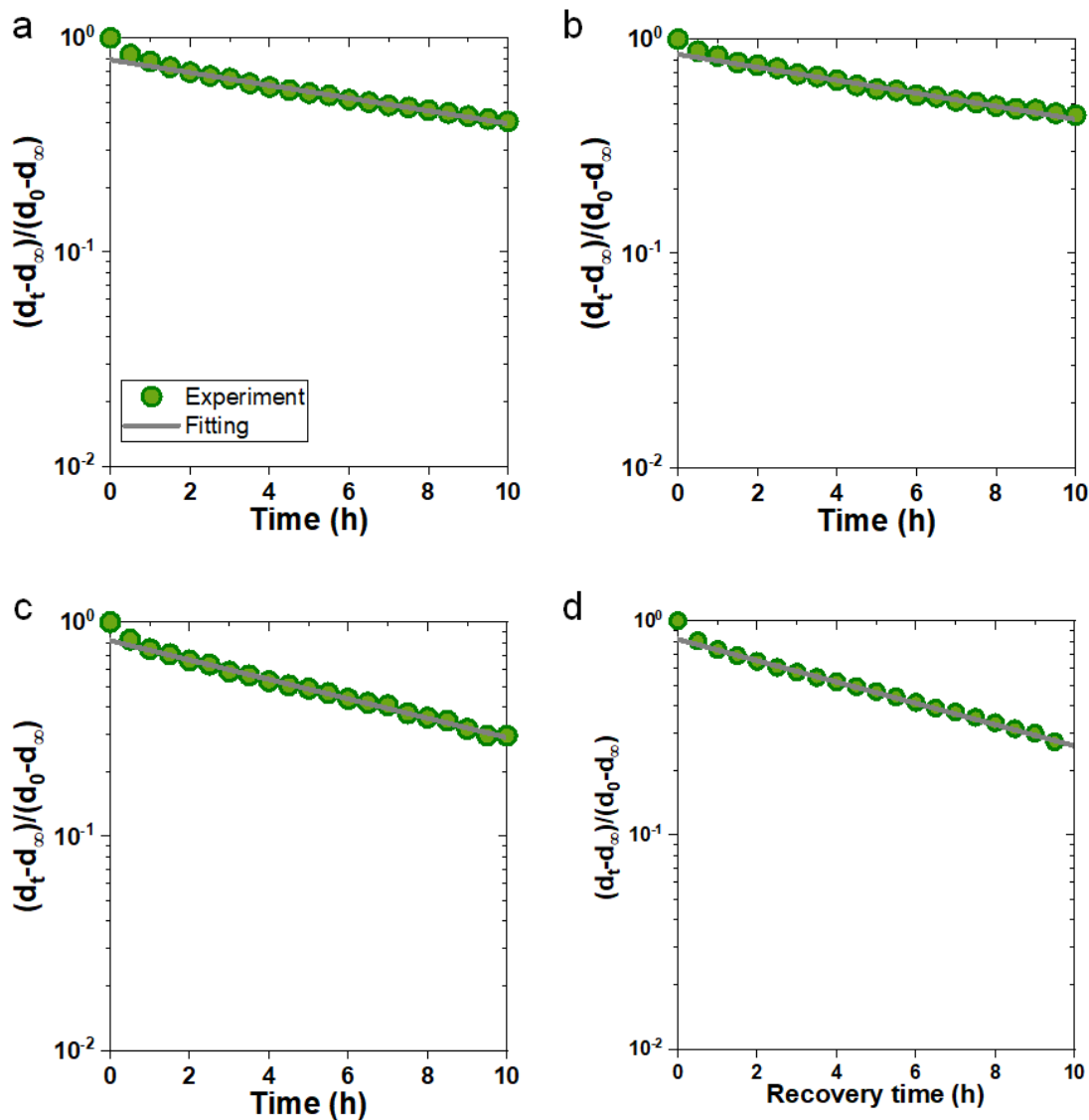## (9) Shrinking kinetics of PA gels with different monomer concentrations C_m

Fig. S12.
Shrinking kinetics of gels with different C_m, (a) 1.8, (b) 2.0, (c) 2.2, and (d) 2.8 M. The gels were initially equilibrated at 80 °C water baths for 2 h to reach swelling equilibrium and then moved to a 25 °C water bath for shrinking. The PA-C_m-0.1 set gels were used. $d_0 = d_{80}$ and $d_\infty = d_{25}$ are shown in Fig. S5.

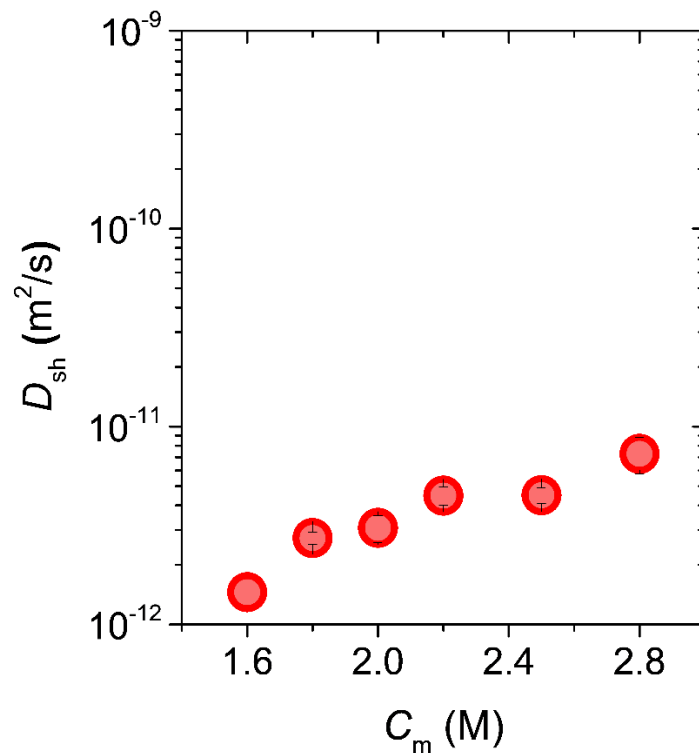**(10) Shrinking cooperative coefficient of PA gels with different monomer concentration C_m**

Fig. S13.
Shrinking cooperative diffusion coefficient of PA gels with different C_m at 25 °C. The gels were initially equilibrated at 80 °C water bath for 2 h to reach swelling equilibrium and then moved to a 25 °C water bath for shrinking. The PA-C_m-*0.1* set gels were used.

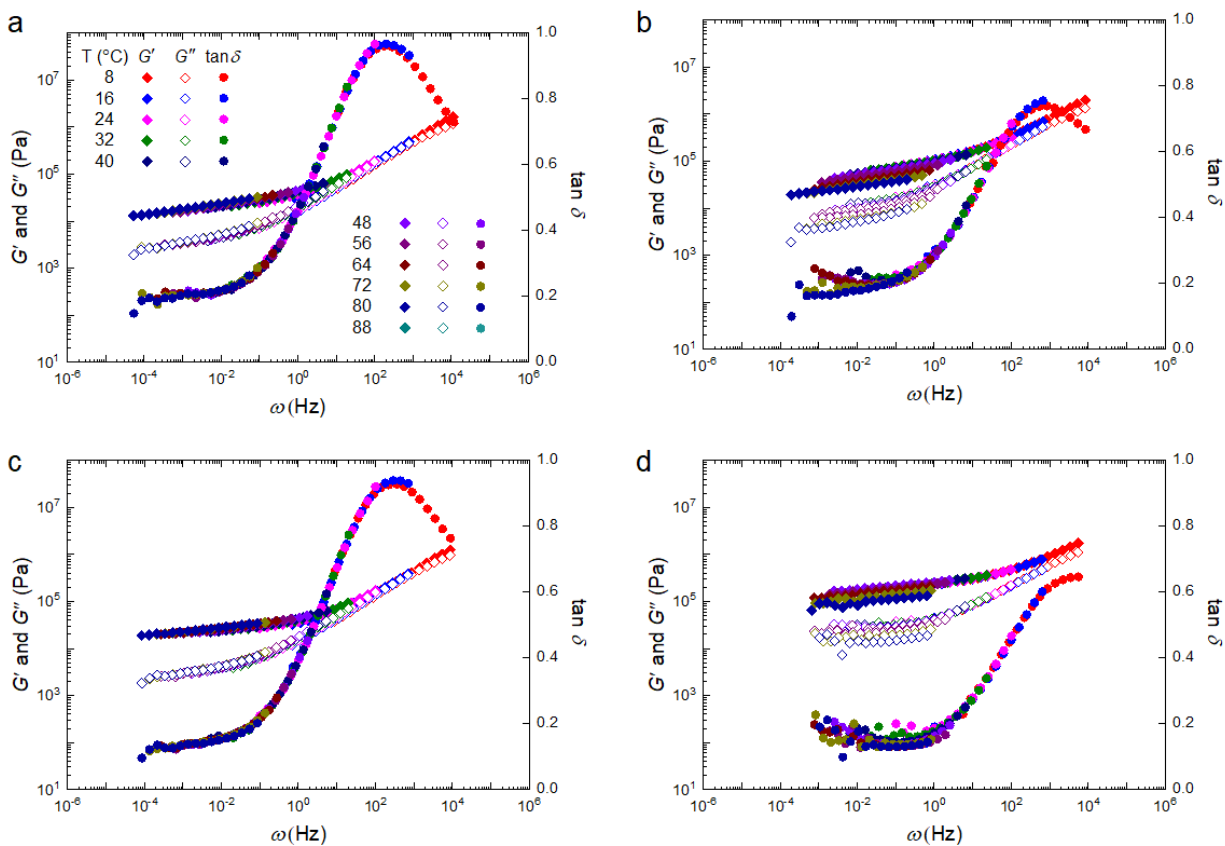**(11) Linear dynamic behavior of PA gels with different monomer concentration C_m**

Fig. S14.
Linear dynamic behavior of PA gels with different C_m, (a) 1.8, (b) 2.0, (c) 2.2, and (d) 2.8 M.
The PA-C_m-0.1 set gels were used. The master curves of storage modulus G', loss modulus G'', and loss factor tan δ, were constructed from the frequency sweep data at different temperatures following the principle of time−temperature superposition. TTS fails at high temperature for some gels, indicating the thermorheologically complex property of this material. Reference temperature: 25 °C.

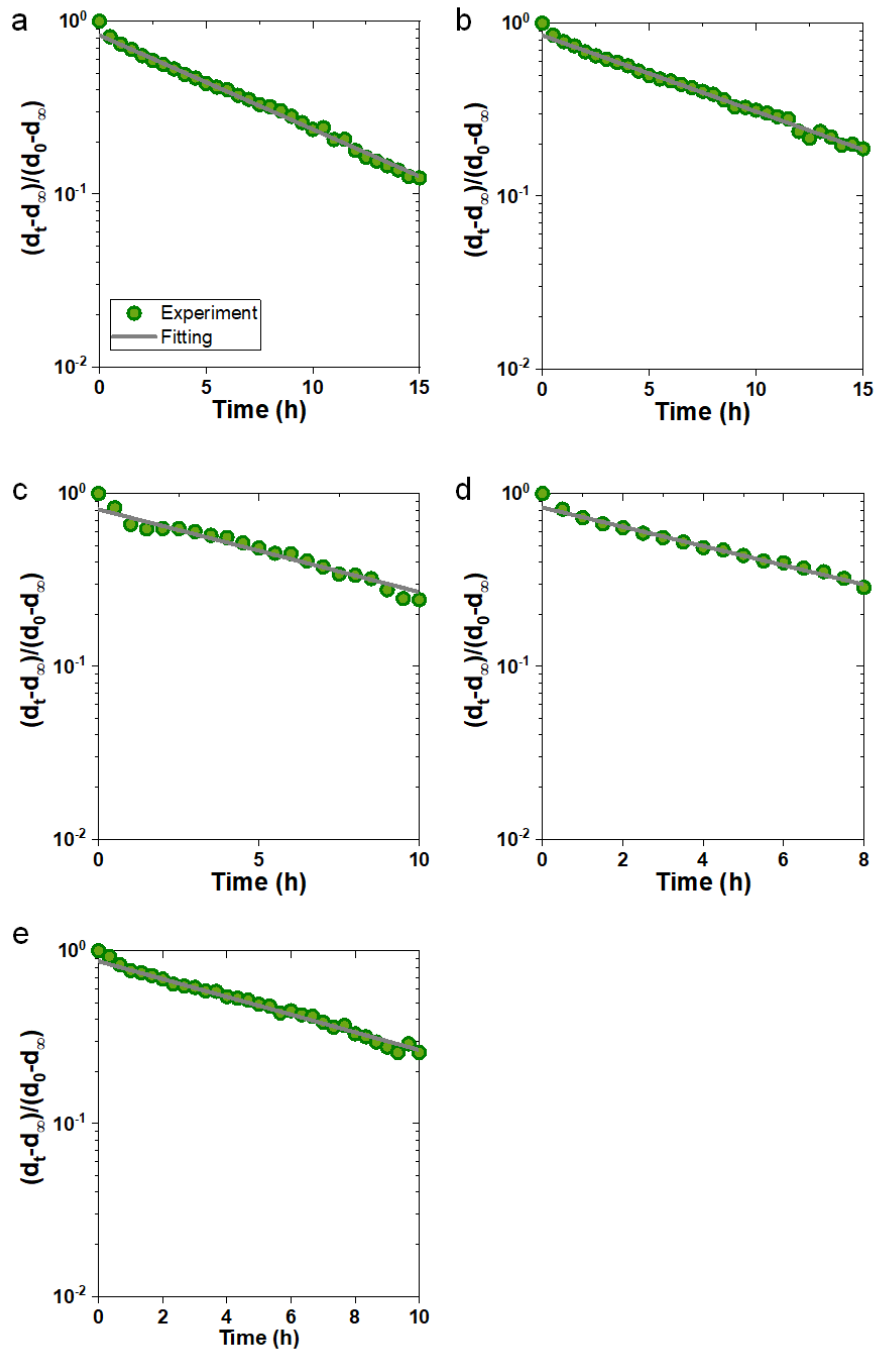**(12) Effect of heating temperature on shrinking kinetics**

Fig. S15.
Effect of heating temperature on shrinking kinetics of PA gels. PA-*2.5-0.1* gels were equilibrated in five hot baths with temperatures of (a) 80, (b) 75, (c) 70, (d) 65, and (e) 60 °C, respectively. They were then moved to the same cold bath with a temperature of 25 °C for shrinking.

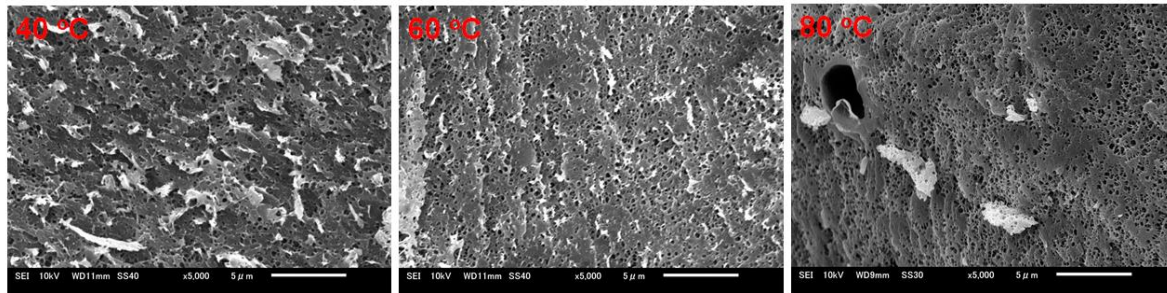**(13) Effect of heating temperature on structure frustration of PA gels**

Fig. S16.
SEM images of PA gels with three heating temperatures (40, 60, and 80 °C). PA gels were heated in water baths with different temperatures for 2 h to reach equilibrium and then moved to a 25 °C water bath for 1 min to measure the SEM. The PA-*2.5-0.1* gel was used.

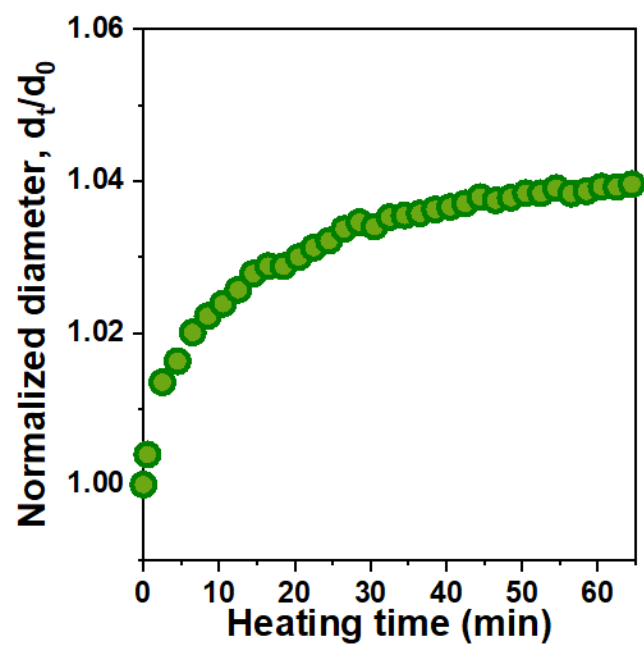**(14) Relative size change of PA gel during swelling**

Fig. S17.
The relative size change of PA gels during swelling at 60 °C. The gel was initially equilibrated in a 25 °C water bath, after which it was moved to a 60 °C water bath for swelling. The PA-*2.5-0.1* gel was used.

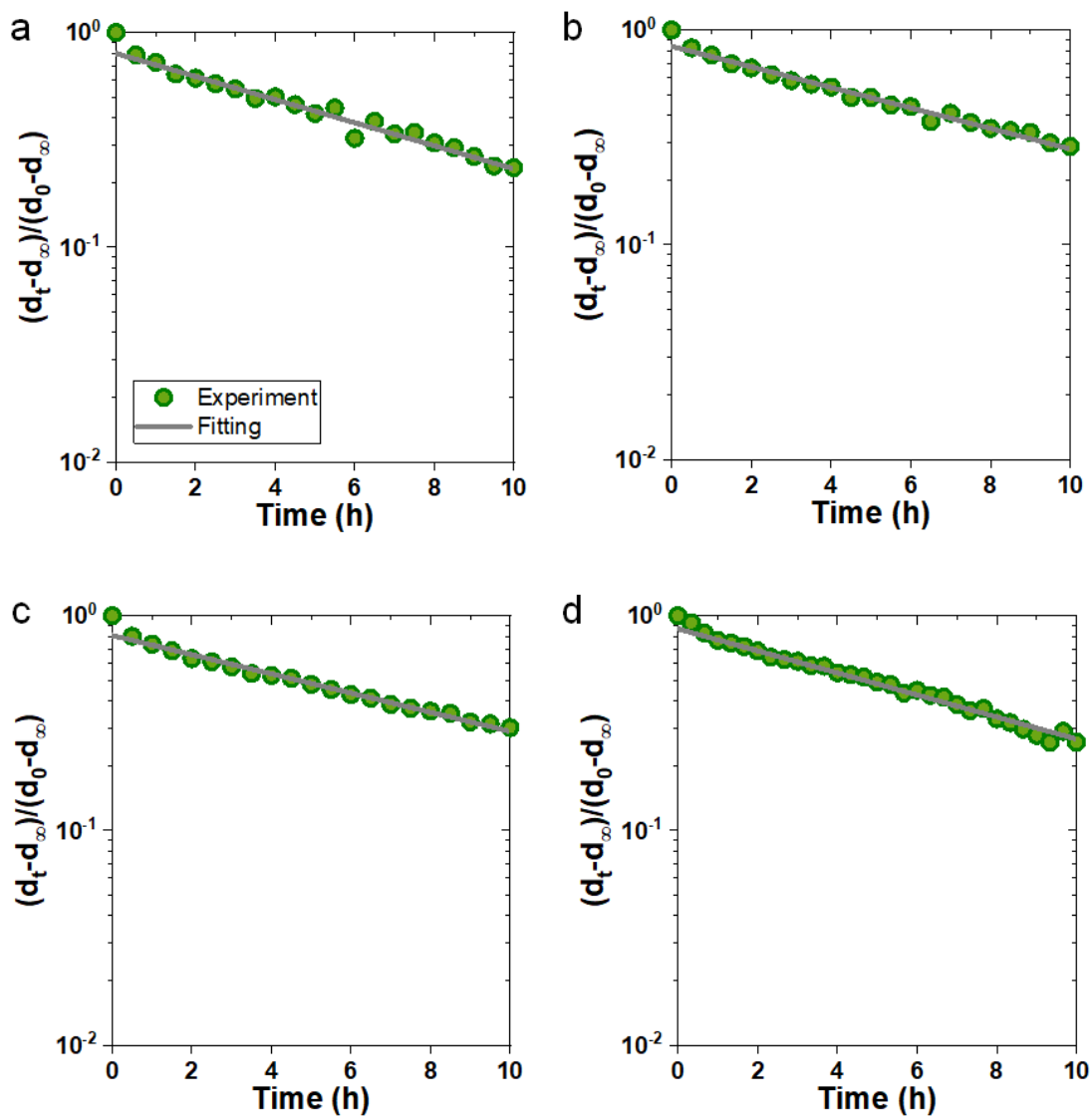**(15) Effect of heating time on shrinking kinetics**

Fig. S18.
Effect of heating time on shrinking kinetics of PA gels. PA-*2.5-0.1* gels were heated in a 60 °C water bath for different heating time, (a) 30 min, (b) 40 min, (c) 1 h, and (d) 2 h. They were then moved to the same cold bath with a temperature of 25 °C for shrinking.

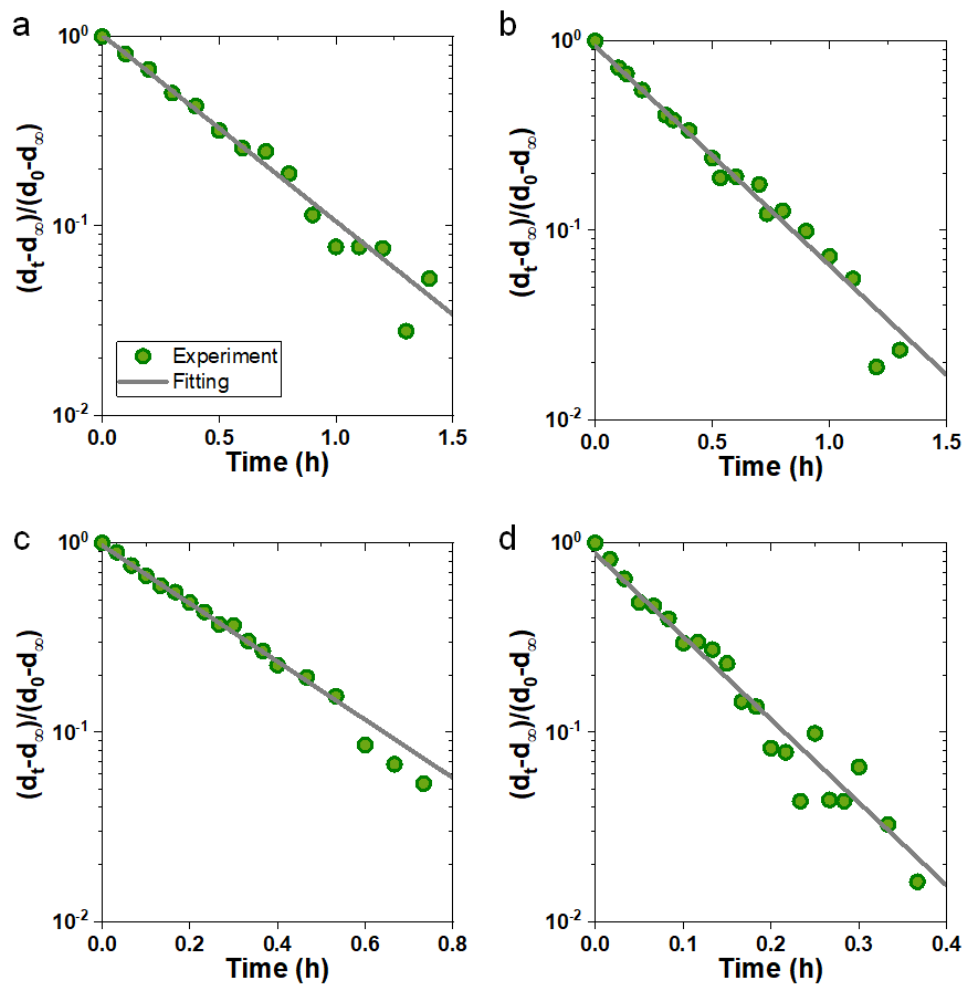**(16) Swelling kinetics at different temperatures**

Fig. S19.
Swelling kinetics of PA-2.5-0.1 gels at different temperatures. Four swelling temperatures were used, (a) 25, (b) 40, (c) 60, and (d) 80 °C. For swelling at 25 °C, the gel was first equilibrated at 7 °C, and then moved to a 25 °C water bath for swelling. For swelling at the other three temperatures, the gels were equilibrated at 25 °C, and then moved to the designated temperature for swelling.
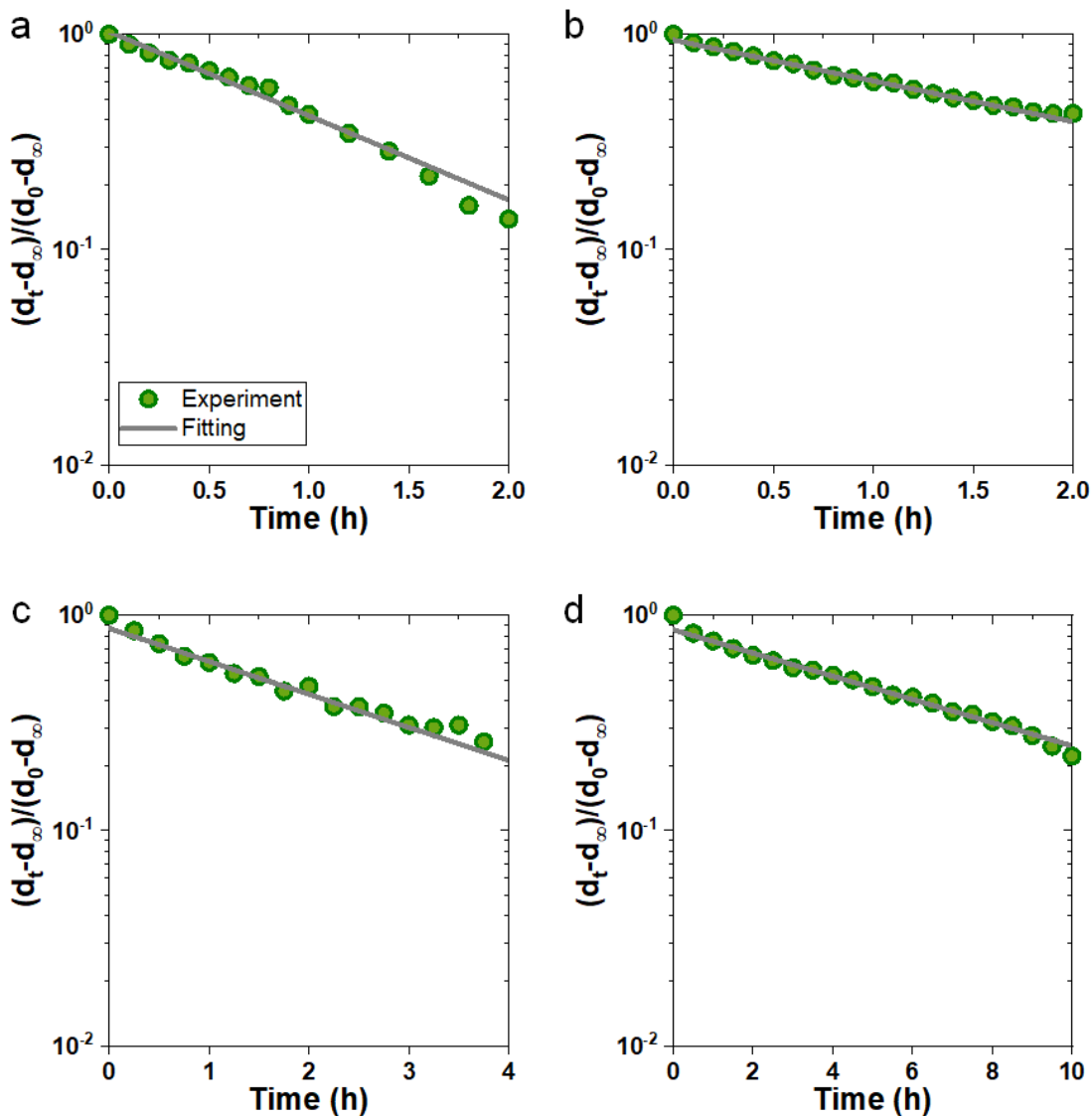
(17) Shrinking kinetics at different temperatures

Fig. S20.
Shrinking kinetics of PA-*2.5-0.1* gels at different temperatures. Four shrinking temperatures were used, (a) 60, (b) 50, (c) 40, and (d) 20 °C. First, the gels were equilibrated at 80 °C, and then moved to the designated temperature for shrinking.

(18) Optical images to show appearance of sample at different time during polymerization
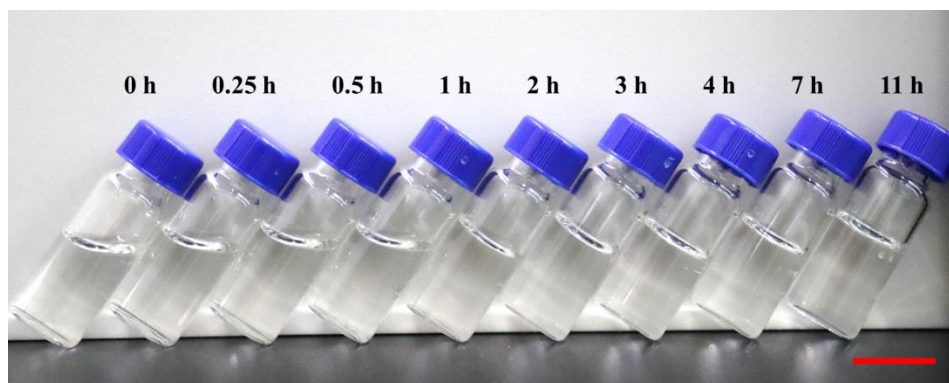

Fig. 21.
Appearance of sample at different time during polymerization. 0 h means the onset of polymerization. Sample: PA-2.5-1.0. Scale bar: 1 cm.

Supplementary References

[1]   T. L. Sun *et al*, Molecular structure of self-healing polyampholyte hydrogels analyzed

from tensile behaviors. *Soft Matter* **11**, 9355–9366 (2015).