Electronic supporting information

A thermo-responsive hydrogel for body temperature-induced spontaneous information decryption and self-encryption

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1 Experiment parts

1.1 Materials

N-isopropyl acrylamide (NIPAM, purity 98%) and 2-hydroxy-2-methylpropiophenone (Darocur 1173, purity 95%) were purchased from Tokyo Chemical Industry Co. Ltd. *N,N'*-methylenebisacrylamide (MBA, purity 99.7%), hydroxypropyl cellulose (HPC, Mw = 10 kDa) and dimethyl sulfoxide (DMSO, purity 98%) were purchased from the Shanghai Aladdin Biochemical Technology Co. Ltd. The NIPAM was recrystallized by a mixture of hexane and acetone before use, and other chemicals were used as received. Pure water (18.2 MΩ·cm, 25 ºC, Milli-Q system) was used throughout the experiments.

1.2 Preparation of hydrogels

With MBA as the crosslinker, NIPAM as the monomer, darocur 1173 as the photoinitiator, HPC as the porogen and DMSO-water mixed solution as the solvent, hydrogels were prepared by UV polymerization. The molar ratio of NIPAM to MBA is fixed at 18:1. Taking 3.6 M hydrogel as an example, 2.0369 g (18.0 mmol) of NIPAM, 0.1542 g (1.0 mmol) of MBA, and 0.1079 g of HPC (1.5 wt%) were weighed and added to 5 mL of DMSO-water mixture with the DMSO mole fraction of 0.55 and 25 µL of Darocur 1173, which were vigorously stirred. The precursor solution was injected into a gap formed by a PTFE spacer sandwiched between two quartz plates and irradiated with UV light (365 nm and 20 W) 60 s to provide satisfactory integrity and mechanical strength of hydrogel. The polymerization temperature of the precursor solution was in situ measured by a thermocouple, and it gradually increased from room temperature to ~ 34 ºC in 15 s and stabilized at 40 ºC in the last 30 s. The polymerization temperature is elevated to a high level due to the exothermic reaction of chain growth

polymerization and UV radiation. The hydrogel was removed from the mould and immersed in a large amount of pure water for 24 h, changing the water and stirring for several times to remove the DMSO, HPC and unreacted small molecules. A series of different hydrogels were prepared by adjusting three important factors, monomer concentration (1.8 M, 2.7 M and 3.6 M), HPC concentration (0.0 wt%, 1.0 wt%, 1.5 wt% and 2.0 wt%) and DMSO molar fractions (0.45, 0.50, 0.55, 0.60 and 1.0).

1.3 Microstructure and chemical composition characterization

The microstructure of hydrogel was observed by scanning electron microscope (SEM, Phenom Pro 6, Phenom). The hydrogel that swelled to equilibrium at 25 ℃ was rapidly frozen with liquid nitrogen; the hydrogel swollen to equilibrium at 35 ℃ was rapidly transferred to pure water of 25 ℃ for a certain period of time and then quickly placed in liquid nitrogen to freeze the hydrogel. The sample could be obtained after drying with a freeze dryer (FD-1A-50, Beijing BoYiKang) for 12 hours, and then was gold sprayed for 120 s and observed using a 10 kV accelerating voltage.

The chemical composition of hydrogels was characterized by potassium bromide (KBr) compression method using a Fourier transform infrared spectrometer (FT-IR, iS 50, Thermo Fisher Scientific). To obtain the sample, 0.1 g of KBr and 0.005 g of freeze-dried hydrogel were weighed and ground until well mixed, and then the tablets were pressed and dried under infrared light. As reference, HPC polymer is also measured in the same way.

The chemical compositions of pure solvent DMSO and the hydrogel after being washed were characterized by Laser microscopic Raman spectroscopy (DXR, Thermo Fisher Scientific) at the laser wavelength of 455 nm. During the measurement, the solvent DMSO is encapsulated

in a glass capillary and fixed on a slide, while the hydrogel wiped off the surface water is placed on slides, which are subjected to be tested after focusing using the microscope of the Laser microscopic Raman spectroscopy.

1.4 NIPAM monomer conversion

The conversion of NIPAM monomer, defined as the ratio of the mass of NIPAM in the hydrogel to the feed amount of NIPAM, is quantitively calculated by Equation (1).

$$Conversion = \frac{m_d - m_{MBA}}{m_{NIPAM}} \times 100\% \tag{1}$$

where m_d is the mass of freezing-dried hydrogel (g), m_{MBA} and m_{NIPAM} are the feeding amount (g) of MBA and NIPAM, respectively. Due to the molar ratio of monomer NIPAM to crosslinker MBA fixed at 18:1 in the preparation of the hydrogel, it is assumed that the MBA is completely reacted.

1.5 Equilibrium water content and mechanical properties of hydrogels

After the hydrogel had fully swollen in pure water at 25 ºC for 1 h, it was quickly removed from the water and the surface water was carefully wiped off, and the mass of the hydrogel was measured in its wet state (m_{eq}). After weighing, the hydrogels were frozen in a refrigerator at -20 ºC for 12 h and frozen dried for 12 h to remove the water. The hydrogels were then weighed again after drying (m_d). Three samples of each hydrogel were measured and averaged. The equilibrium water content (*EWC*) was defined as the mass ration of water contained in the hydrogel to the dry hydrogel, and calculated by Equation (2).

$$EWC = \frac{m_{eq} - m_d}{m_{eq}} \times 100\% \tag{2}$$

Using the same formula as in Section 1.2, hydrogels with a height of about 10 mm and a

diameter of about 10 mm after swelling at 25 ℃ were prepared with plastic tubes. Subsequently, their compressive mechanical properties were tested using a universal testing machine (EZ-LX, Shimadzu). Before the experiment, the height (H_0) and base radius (r_0) of the hydrogel were measured. The hydrogel was compressed on the test platform using a 100 N sensor and a compression rate of 100 mm/min. Data was recorded throughout the compression process until the hydrogel broke and was substituted into Equation (3) and Equation (4) to calculate the strain (ε) and stress (σ) of the hydrogel during compression.

$$\varepsilon = \frac{H_0 - H}{H_0} \tag{3}$$

$$\sigma = \frac{P \times H}{\pi \times r_0^2 \times H_0} \tag{4}$$

where H and P were the height of the hydrogel (m) and the pressure exerted on it (N) during compression, respectively.

1.6 Thermo-responsive property characterization of hydrogels

Equilibrium thermo-responsive property: the hydrogel was immersed in pure water with temperature stabilized by a cryostat bath for 30 min, and its optical pictures were taken with a camera (Nikon-Z50, Nikon) at a temperature range of 25 ℃ to 35 ℃. The diameter of the hydrogel at 25 ℃ (d_{25}) and at T ℃ (d_T) were measured using the software Digimizer and the equilibrium relative diameter (ERD) was calculated using Equation (5).

$$ERD = \frac{d_T}{d_{25}} \tag{5}$$

Dynamic thermo-responsive property: the hydrogel was fully swollen in pure water at 25 ℃, and it was then quickly transferred to pure water at 35 ℃ for 10 min, followed by quickly transfer to pure water at 25 ℃ for another 80 min. The camera photographed the change in

diameter of the bottom surface of the hydrogel throughout the process. The initial diameter (d_0) and the diameter at the moment t (d_t) of the hydrogel were measured and the relative diameter (RD) was calculated using Equation (6).

$$RD = \frac{d_t}{d_0} \tag{6}$$

The size of the hydrogels used in the above experiments was 15 mm × 1 mm (diameter × height). Three samples of each hydrogel were tested and averaged. The repeatability of the performance of the hydrogel was characterized by testing the transmittance after cooling for 0.5 min and RD of the hydrogel during the consecutive five heating-cooling cycles.

1.7 Transparency characterization of hydrogels

The hydrogels, which had been swollen to equilibrium in pure water at 25 ºC, were cut into sizes of 40 mm × 9 mm × 1 mm (length × width × thickness) to test transmittance changes during the deswelling (heating process) and swelling (cooling process) experiments. To test the changes in transmittance of the hydrogels during the heating process, the hydrogel was swelling in pure water at 25 ºC until equilibrium (~ 30 min), then it was quickly placed in a cuvette containing pure water of 35 ºC, and its transmittance at the wavelength of 600 nm was recorded by a UV-visible spectrophotometer (UV-2700i, Shimadzu). The hydrogel was first required to reach equilibrium at 35 ºC (~ 10 min) before transferring it to pure water of 25 ºC, to obtain the transmittance change during the cooling process.

1.8 Transmitted intensity ratio

The transmitted light intensity as a result of scattering in the transparent matrix embedded spherical particles can be described in Equation (7).[1] The higher the transmitted intensity ratio I/I_0, the weaker the light scattering, and the higher transparency the hydrogel. Similarly, the

pores inside the hydrogel can be considered as particles embedded in the matrix, and relationship between the transmitted light intensity and the pore size of hydrogel can be also analyzed by Equation (7).

$$Transmitted\ intensity\ ratio = \frac{I}{I_0} \sim \exp\left[\frac{-3xV_w d^3}{32\lambda^4}\left(\frac{n_w}{n_h}-1\right)\right] \tag{7}$$

where I is the intensity of transmitted light, I_0 is the initial intensity of light, x is the optical path-length, V_w is the volume fraction of the particle or pore, n_w and n_h are the refractive indexes of the water and the hydrogel matrix, d is the pore diameter in the hydrogel, and λ is the wavelength of the light.

The transmitted intensity ratio (I/I_0) is proportional to an exponential function with a natural constant (e = 2.718281828) as the base while its power is related to d^3 and (n_w/n_h - 1). When the ratio n_w/n_h does not equal to 1, the I/I_0 value is significantly affected by pore size, which x, V_w and λ can be considered as constants. The refractive indexes of water (n_w) and PNIPAM hydrogel (n_h) are 1.33 and 1.50,[2] respectively.

1.9 Application in information encryption

To obtain the information encryption device, a quick response (QR) code was covered with the $X_{0.55}$ hydrogel and then sealed between the coverslip and the slide with AB adhesive. The device was touched with two fingers for 2 min to shrink the hydrogel, then the device was placed in air at 25 ºC and the whole cooling process was recorded with a camera.
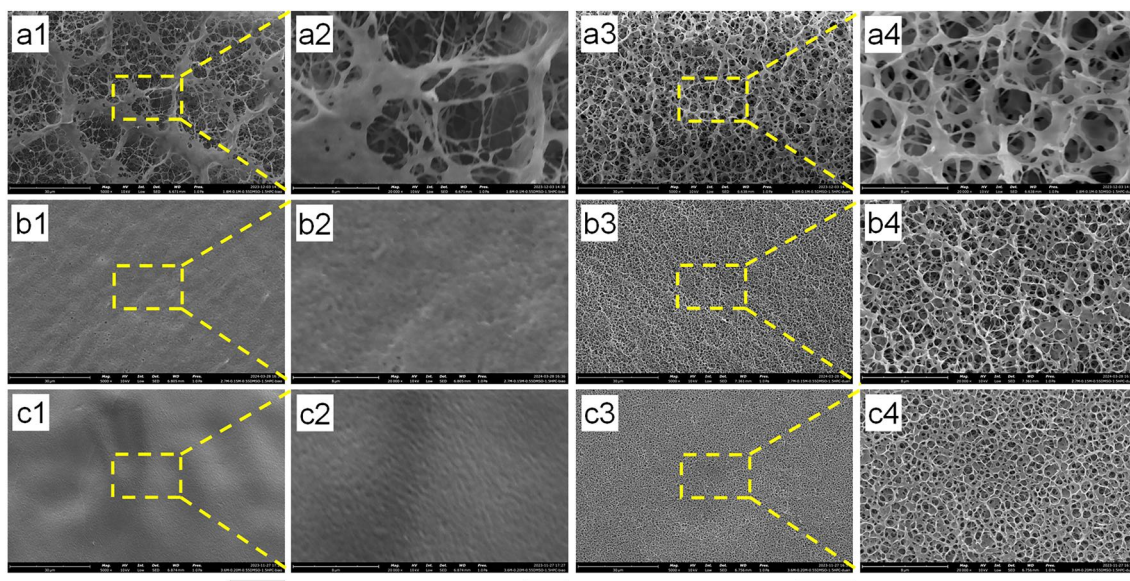
2 Figures

Fig. S1 Surface (a1-c1, a2-c2) and cross-sectional (a3-c3, a4-c4) SEM images of hydrogels prepared with different NIPAM concentrations, with HPC concentration (1.5 wt%) and DMSO molar fraction in the mixed solvent (0.55). The scale bars are 20 μm (a1-c1, a3-c3) and 4 μm (a2-c2, a4-c4), respectively. (a) 1.8 M, (b) 2.7 M, (c) 3.6 M
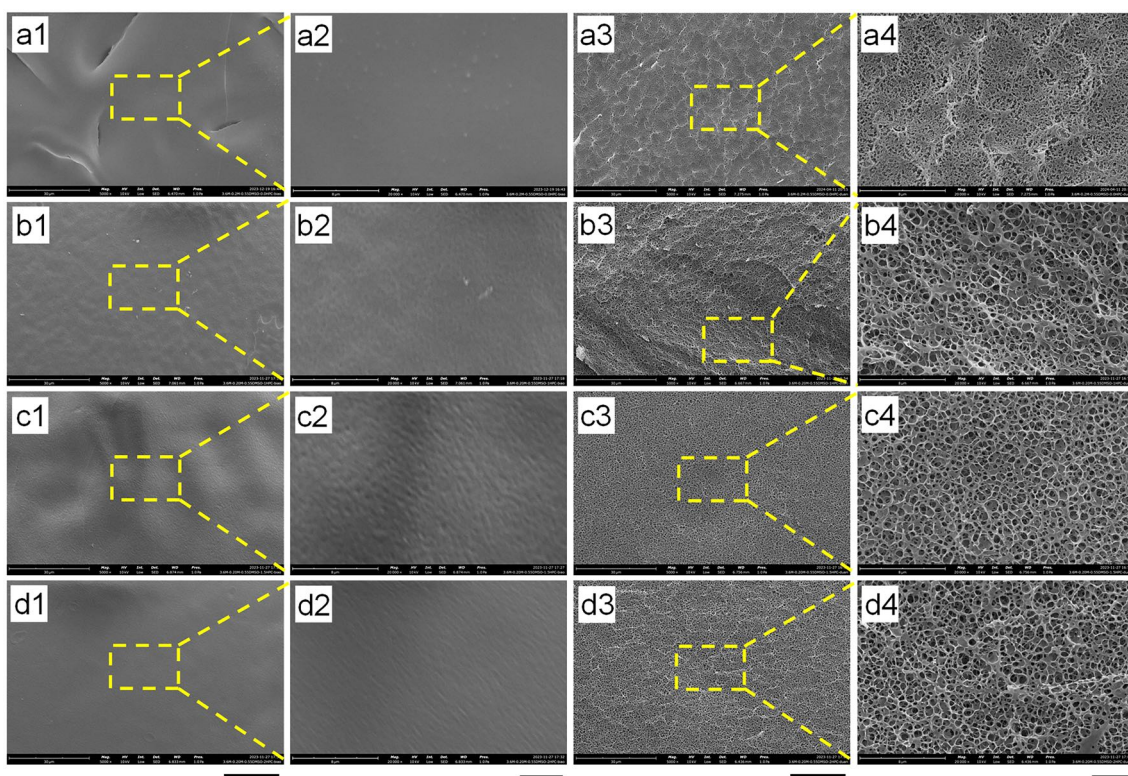
Fig. S2 Dynamic thermo-responsive properties and transparency changes of hydrogels prepared with different monomer concentrations during the heating (25 ℃ to 35 ℃) and rapid quenching (35 ℃ to 25 ℃) processes. (a) Optical pictures, (b) Transmittance and (c) Relative Diameter (*RD*). The scale bar is 1 cm.
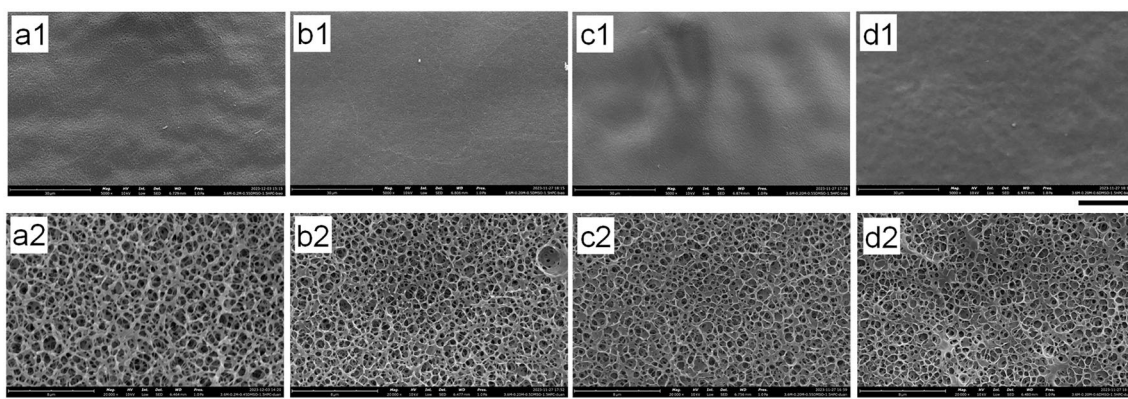
Fig. S3 Surface (a1-d1, a2-d2) and cross-sectional (a3-d3, a4-d4) SEM images of hydrogels prepared with different HPC concentrations while the constant NIPAM concentrations (3.6 M) and DMSO molar fraction in the mixed solvent (0.55). The scale bars are 20 μm (a1-d1, a3-d3) and 4 μm (a2-d2, a4-d4), respectively. (a) 0.0 wt%, (b) 1.0 wt%, (c) 1.5 wt%, (d) 2.0 wt%
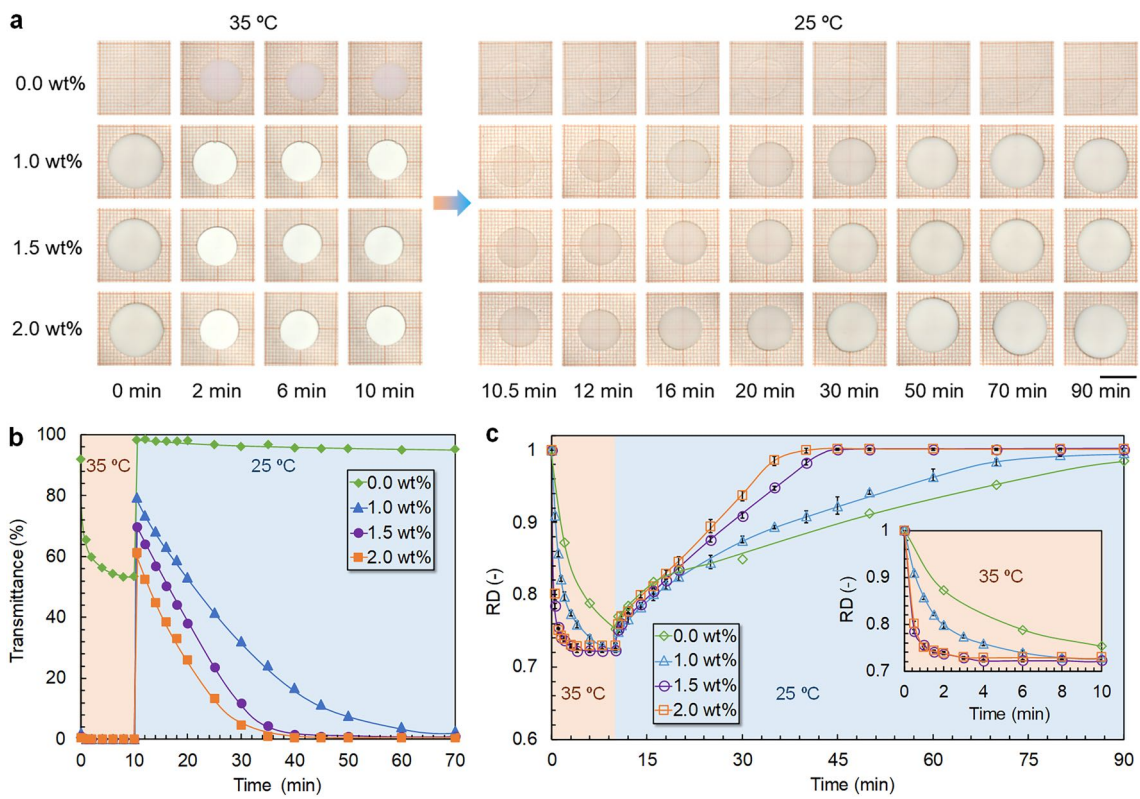
Fig. S4 Dynamic thermo-responsive properties and transparency changes of hydrogels prepared with different HPC amounts during the heating (25 ºC to 35 ºC) and rapid quenching (35 ºC to 25 ºC) processes. (a) Optical pictures, (b) Transmittance and (c) Relative diameter. The scale bar is 1 cm.

Fig. S5 Surface (a1-d1) and cross-sectional (a2-d2) SEM images of hydrogels prepared with different DMSO molar fractions, which sufficiently equilibrated in water at 25 ℃ before measurement (t = 0 min). The scale bars are 20 μm (a1-d1) and 4 μm (a2-d2), respectively. (a) 0.45, (b) 0.50, (c) 0.55, (d) 0.60.
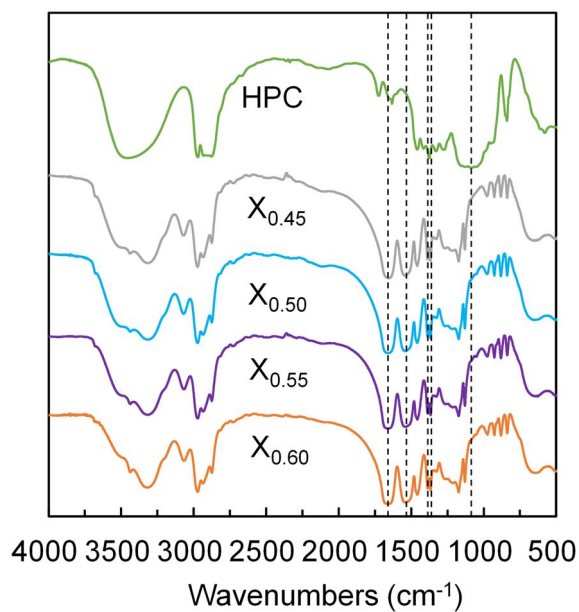
Fig. S6 FT-IR spectra of HPC polymer and hydrogels prepared with different DMSO molar fractions.
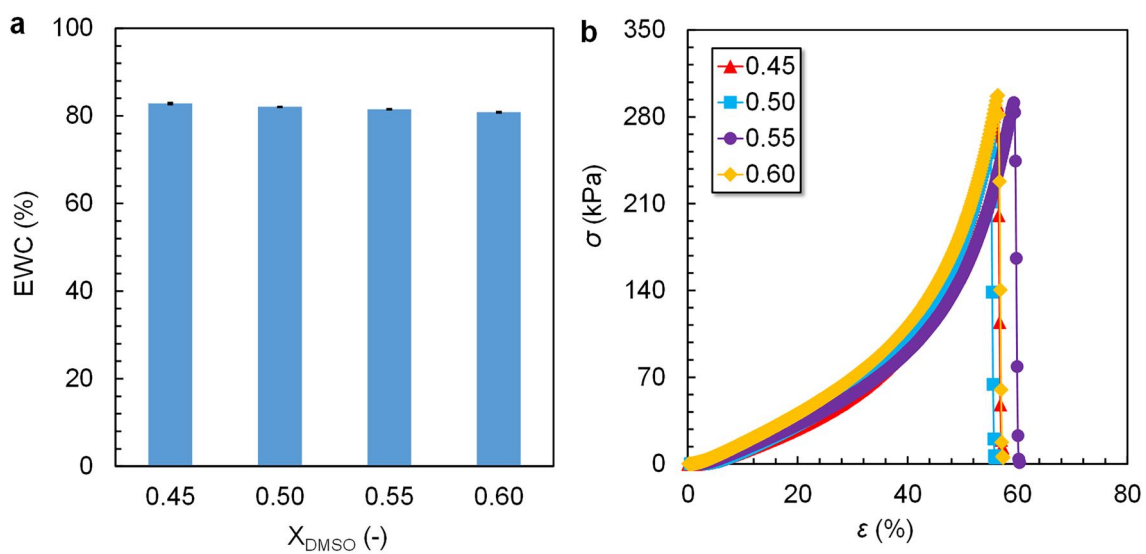
Fig. S7 Equilibrium water contents (*EWC*) (a) and compressive stress-strain curves (b) of

hydrogels prepared with different DMSO molar fractions.
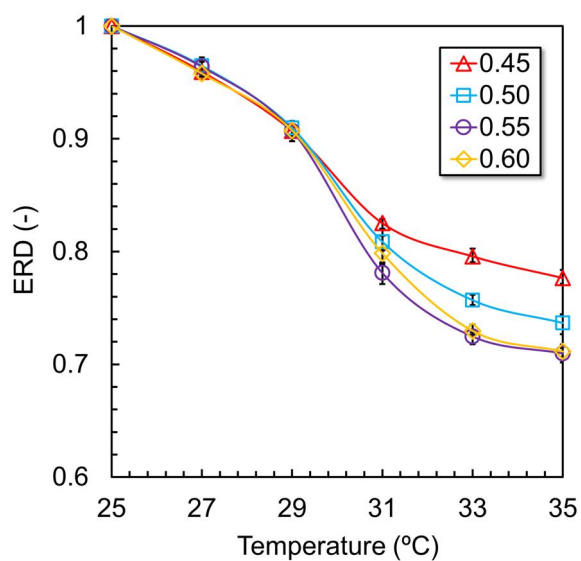
Fig. S8 Equilibrium relative diameter (*ERD*) of hydrogels prepared with different DMSO molar
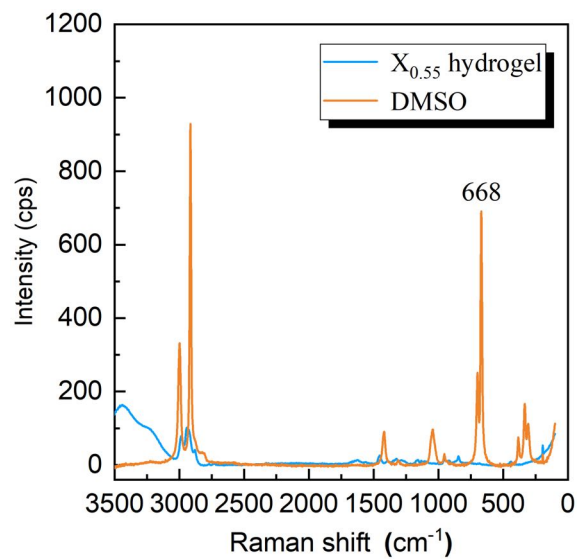
fractions.

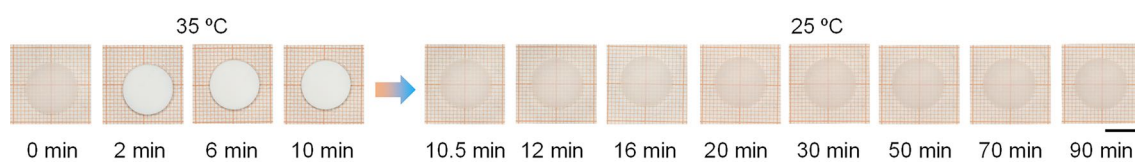Fig. S9 Raman spectra of DMSO and $X_{0.55}$ hydrogel.

Fig. S10 Optical pictures of hydrogels prepared with 1.5 wt% HPC during the heating (25 ºC to 35 ºC) and rapid quenching (35 ºC to 25 ºC) process. The molar fraction of DMSO is 1.0. The scale bar is 1 cm.
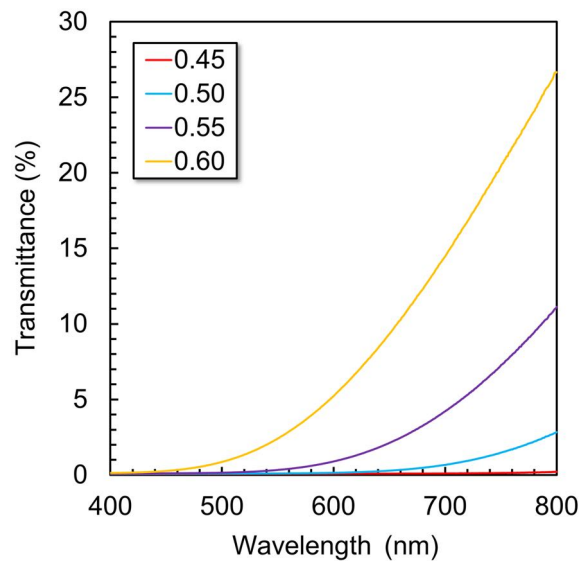
Fig. S11 Transmittance changes of hydrogels prepared with different DMSO molar fractions at

25 ℃.

References

1. A. Seeboth, R. Ruhmann and O. Muehling, *Materials*, 2010, 3, 5143-5168.

2. X.-Q. Wang, S. Yang, C.-F. Wang, L. Chen and S. Chen, *Macromol. Rapid Commun.*, 2016, 37, 759-768.