



Title	Thermoresponsive Lamellar Hydrogels with Tunable Turbidity, Structural Color, and Anisotropic Swelling
Author(s)	Han, Yang; Guo, Yunzhou; Nakajima, Tasuku et al.
Citation	ACS Applied Materials & Interfaces, 15(49), 57687-57698 https://doi.org/10.1021/acsami.3c14334
Issue Date	2023-11-29
Doc URL	https://hdl.handle.net/2115/93636
Rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in ACS applied materials & interfaces, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://pubs.acs.org/articlesonrequest/AOR-R5UBAEZNT6DB8HAT4VUW .
Type	journal article
File Information	SI-PDGIPAAm-PNIPAM-rev.pdf



Supporting Information

Thermo-responsive lamellar hydrogels with tunable turbidity, structural color, and anisotropic swelling

Yang Han^a, Yunzhou Guo^{ab}, Tasuku Nakajima^{*,cd}, and Jian Ping Gong^{*,cd}

^a Graduate School of Life Science, Hokkaido University, Sapporo 001-0021, Japan;

^b ZJU-Hangzhou Global Scientific and Technological Innovation Center, Zhejiang University, Hangzhou 311215, China;

^c Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo 001-0021, Japan;

^d Faculty of Advanced Life Science, Hokkaido University, Sapporo 001-0021, Japan

Corresponding author

E-mail: *gong@sci.hokudai.ac.jp; *tasuku@sci.hokudai.ac.jp

1. The investigation of the lower critical solubility temperature (LCST) of PDGI/PAAm-PNIPAM hydrogels with different NIPAM concentrations through differential scanning calorimetry (DSC).

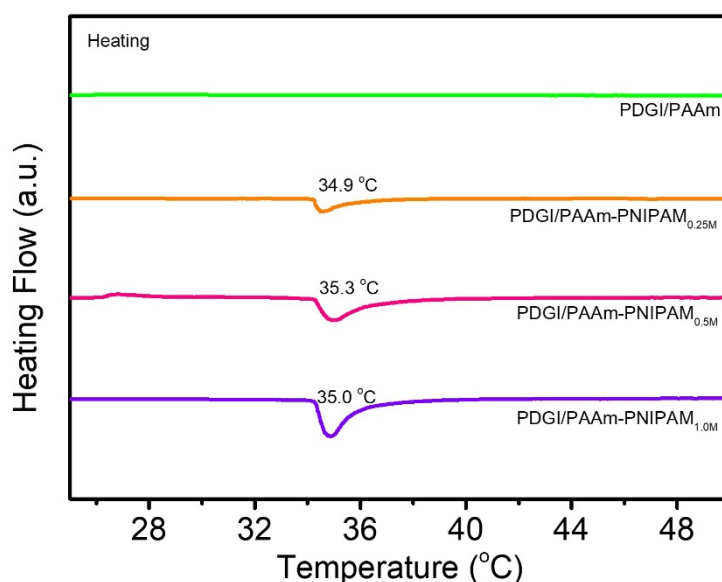


Figure S1. DSC thermograms of the PDGI/PAAm and PDGI/PAAm-PNIPAM gels with different NIPAM concentrations.

The lower critical solubility temperature (LCST) of the PDGI/PAAm-PNIPAM gels with different NIPAM concentrations were determined through differential scanning calorimetry (DSC). As shown in Figure S1, the PDGI/PAAm gel showed no endothermic peak, suggesting no LCST in this temperature range. The PDGI/PAAm-PNIPAM_{0.25M}, PDGI/PAAm-PNIPAM_{0.5M}, and PDGI/PAAm-PNIPAM_{1.0M} exhibited the endothermic peak around 34.9 °C, 35.3 °C, and 35.0 °C, respectively. These peaks correspond to the LCST of PNIPAM. These results indicate that the incorporation of PNIPAM networks into PAAm soft layers gives the PDGI/PAAm-PNIPAM hydrogels the temperature-responsive property of PNIPAM.

2. The turbidity of PDGI/PAAm-PNIPAM_{0.5M} gel in water at different temperatures

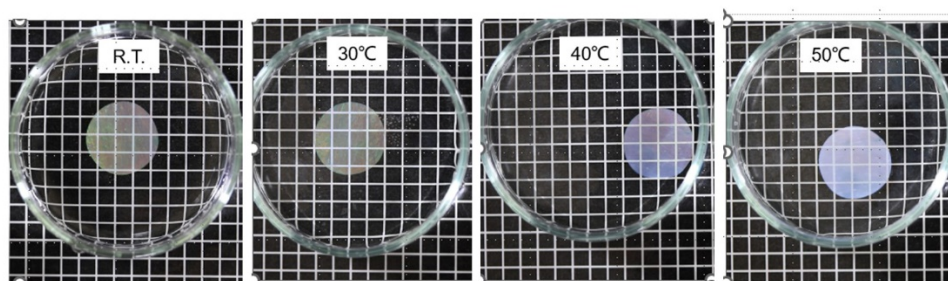


Figure S2. Photographs of PDGI/PAAm-PNIPAM_{0.5M} in pure water at different temperatures. Background lattices are 5 × 5 mm.

As shown in Figure S2, at room temperature and $Temp = 30\text{ }^{\circ}\text{C}$, the PDGI/PAAm-PNIPAM_{0.5M} gel shows no turbidity and exhibits structural color. At $Temp = 40$ and $50\text{ }^{\circ}\text{C}$, the gel turns turbid immediately once immersed in hot water. The hydrogel exhibits lower turbidity in $40\text{ }^{\circ}\text{C}$ hot water compared to $50\text{ }^{\circ}\text{C}$ hot water. It indicates that the turbidity of PDGI/PAAm-PNIPAM hydrogel is determined by the heating temperature.

3. Effect of temperature on the transmittance of PDGI/PAAm-PNIPAM_{0.5M} gel

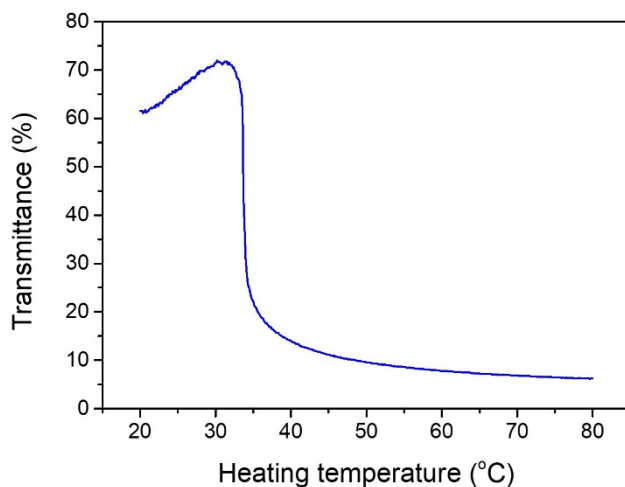


Figure S3. The transmittance of the PDGI/PAAm-PNIPAM_{0.5M} gel at 400 nm during heating at a heating rate of 1.0 °C/min. The gel was initially equilibrated in water at 20 °C for 1 h before measurement and then heated from 20 to 80 °C.

The effect of temperature on the transmittance of the PDGI/PAAm-PNIPAM_{0.5M} gel is shown in Figure S3. The original gel ($Temp = 20\text{ }^{\circ}\text{C}$) exhibited high transmittance at 400 nm. By increasing $Temp$, the transmittance of the gel dropped dramatically when the temperature reached to $\sim 33\text{ }^{\circ}\text{C}$ and then reached a plateau. This corresponds to the LCST-type thermo-responsive behavior of the gels. The gels undergo phase separation when the temperature is above the LCST due to entropy-driven dehydration and collapse upon heating (Figure S2).^[1,2]

4. Effect of heating time on the transmittance of the PDGI/PAAm-PNIPAM_{0.5M} gel

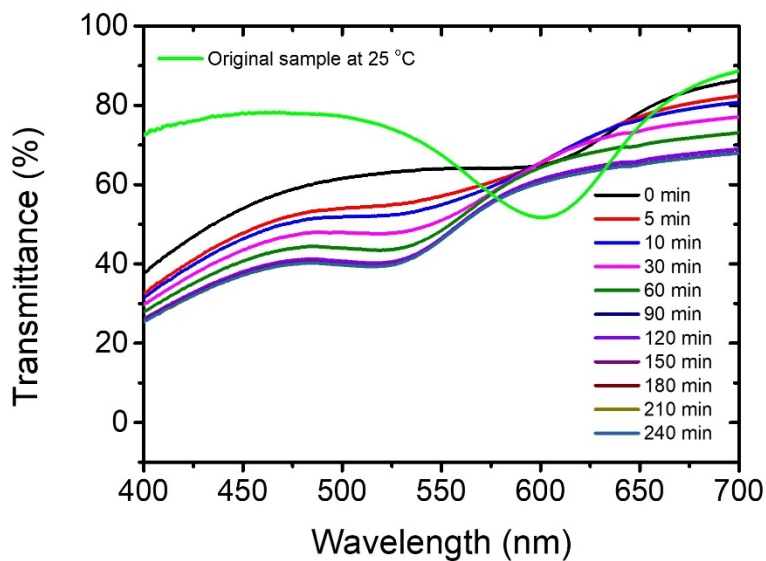


Figure S4. The transmittance of PDGI/PAAm-PNIPAM_{0.5M} gels during the heating process at 50 °C.

As shown in Figure S4, the transmittance of the PDGI/PAAm-PNIPAM_{0.5M} gel during the heating process at 50 °C in the range of 400–700 nm was measured to quantify the characteristics of the turbidity. The transmittance of the gel barely changed with increasing heating time at 50 °C ($Temp > LCST$), which is associated with LCST-type gels where the turbidity is determined by the heating temperature independent of the heating time.^[1-3]

5. Reflection spectra of the PDGI/PAAm-PNIPAM_{0.5M} gel during the heating and cooling process

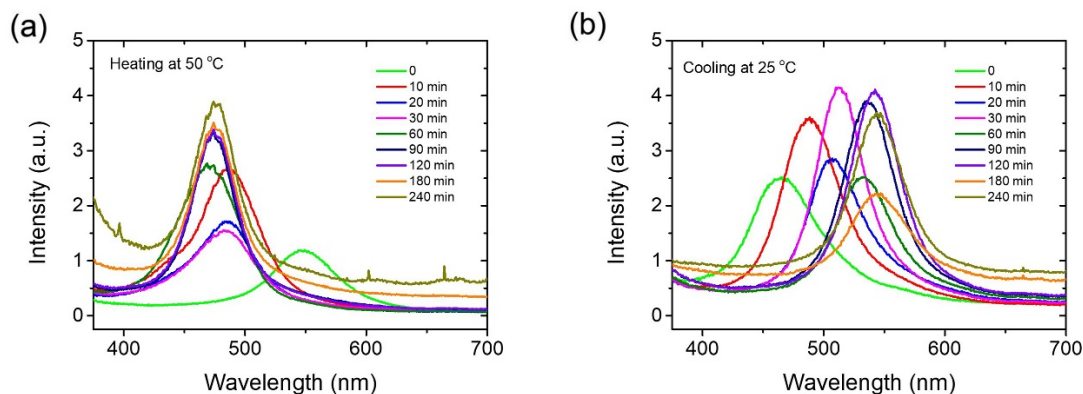


Figure S5. (a) Reflection spectra of the PDGI/PAAm-PNIPAM_{0.5M} gel heated at 50 °C for varied t_1 and then quenched in a cold water bath ($Temp = 25\text{ }^{\circ}\text{C}$). The spectra were obtained immediately after the quenching. (b) Those of the gel heated at $Temp = 50\text{ }^{\circ}\text{C}$ for more than 2 h and then cooled in a cold water bath ($Temp = 25\text{ }^{\circ}\text{C}$) for varied t_2 . The reflection spectra were obtained by keeping the incident at 60° and reflection angles at 45° .

The reflection spectra of the PDGI/PAAm-PNIPAM_{0.5M} gel at different heating and cooling times are shown in Figure S5. During the heating process at 50 °C, the gel deswells gradually and exhibits a large blue shift in λ_{max} with increasing heating time t_1 . The notable blue shift in λ_{max} , which is in accordance with the decrease in the d -value, is attributed to the deswelling of the PAAm-PNIPAM layers in the direction perpendicular to the layers owing to the hydrophobic interactions of PNIPAM networks at $Temp > LCST$.^[4] The gel reaches the new equilibrium after 2 h heating at 50 °C. The gel was then immersed in the cold water at 25 °C for t_2 . During this cooling process at 25 °C, the gel gradually absorbed water and recovered the original state and reflection peak after 2 h. The notable red-shift in λ_{max} can be observed, which is in accordance with the increase in the d -value, is attributed to the reswelling of the PAAm-PNIPAM

networks in the direction perpendicular to the layers owing to the hydrophilicity of the PNIPAM networks at $Temp < LCST$.

6. The turbid/transparent transition and isotropic de-swelling/re-swelling behavior of the PAAm-PNIPAM_{0.5M} gel around LCST.

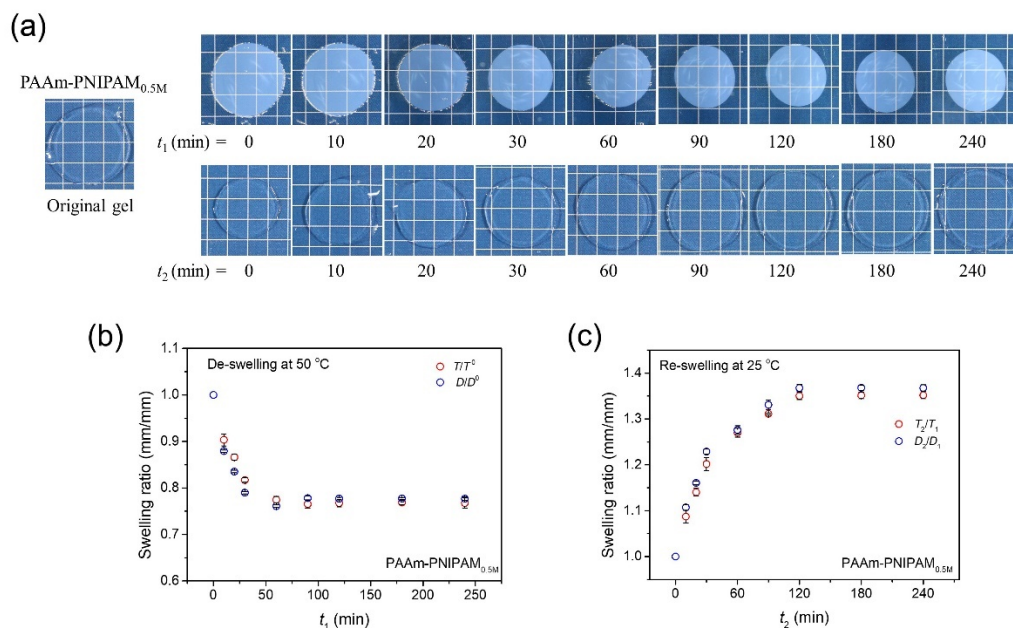


Figure S6. Deswelling/reswelling behaviors of the PAAm-PNIPAM_{0.5M} gel during the heating and cooling process. (a) Optical images of the original PAAm-PNIPAM_{0.5M} gel at 25 °C in pure water during the heating process at 50 °C at the desired time, t_1 and cooling process at the desired time, t_2 at 25 °C in pure water; (b) deswelling and (c) reswelling ratios of the PAAm-PNIPAM_{0.5M} gels in water as a function of time during heating and cooling process. Background lattices in (a) are 5×5 mm.

The visual change and deswelling/reswelling behaviors of the PAAm-PNIPAM_{0.5M} hydrogels (diameter ≈ 20 mm, thickness ~ 1.0 mm) during the heating and cooling process around LCST are shown in Figure S6. The original PAAm-PNIPAM_{0.5M} gel at the 25 °C water bath was transparent (Figure S6a, left). The gel turned to turbid instantly when immersed into the 50 °C hot water bath owing to the hydrophobic association of

the PNIPAM chains in the gel, and the turbidity of the gel did not decay with time during heating (Figure S6a, upper-right). After a 4 h heating process, the heated (deswollen) gel was cooled to 25 °C for the desired time, t_2 (Figure S6a, lower-right). The turbidity disappears immediately and the gel becomes transparent because the PNIPAM chains return to hydrophilic.

The PAAm-PNIPAM_{0.5M} gel showed isotropic deswelling/reswelling behaviors during the heating and cooling process around LCST, as shown in Figure S6b and Figure S6c. The diameter of the gel decreased during the heating process before reaching equilibrium. As can be seen in Figure S6b, the deswelling ratio of the PAAm-PNIPAM_{0.5M} gel in the thickness direction (T_1/T_0) and the diameter direction (D_1/D_0) decreased together to ~ 0.78 with increasing heating time. In addition, the gel fully recovers to the original size ($T_2/T_1 \approx D_2/D_1 \approx 1.35$) after the cooling process. This indicates that the PAAm-PNIPAM gel shows reversible and isotropic deswelling/reswelling behaviors,

7. Appearance of the PDGI/PAAm and PDGI/PAAm-PNIPAM gels with different NIPAM concentrations at different states during the heating and cooling process around LCST.

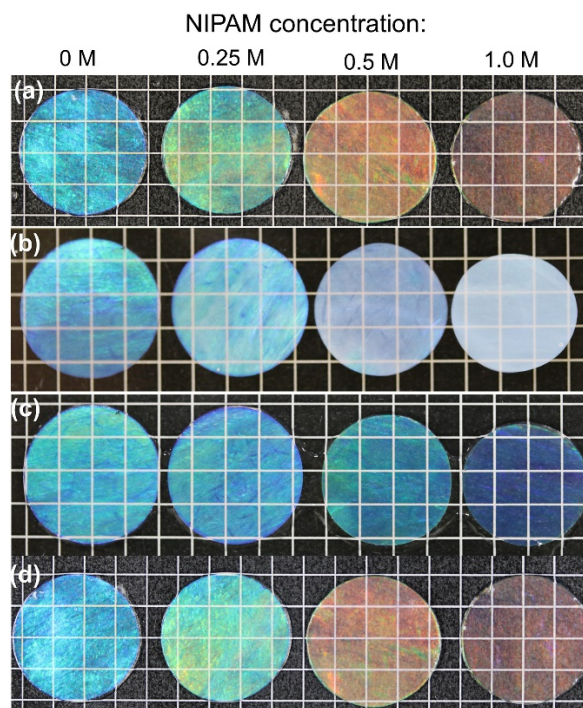


Figure S7. Optical images of the PDGI/PAAm, PDGI/PAAm-PNIPAM_{0.25M}, PDGI/PAAm-PNIPAM_{0.5M} and PDGI/PAAm-PNIPAM_{1.0M} gels at different state during the heating process at 50 °C and cooling process at 25 °C in pure water: (a) original state 25 °C, (b) after reaching new equilibrated state at 50 °C, (c) quenched state at 25 °C after reaching de-swollen equilibrium, and (d) recovery state at 25 °C. The corresponding color of the turbid gel after reaching a new equilibrium during the heating process was captured immediately after quenching the gel in a cold water bath ($Temp = 25\text{ }^{\circ}\text{C}$). Background lattices are $5 \times 5\text{ mm}$.

Figure S7 shows the effect of the NIPAM concentration on the appearance of the PDGI/PAAm-PNIPAM gels at each step. At room temperature in pure water (Figure S7(a)), the PDGI/PAAm-PNIPAM gels ($D \sim 20\text{ mm}$) exhibited distinctive red-shift in color with increasing incorporated NIPAM concentration. At equilibrium in 50 °C hot water (Figure S7(b)), the PDGI/PAAm-PNIPAM_{0.25M} gel showed slight turbidity, while PDGI/PAAm-PNIPAM_{1.0M} gel showed high turbidity. After quenching the gels at this

state, the gel color shows a large blue shift with increasing NIPAM concentration (Figure S7(c)). After reaching re-equilibrium in 25°C cold water, all the gel recovered the original color as shown in Figure S7(d).

8. Gel color shift of PDGI/PAAm and PDGI/PAAm-PNIPAM with different NIPAM concentrations during the deswelling and reswelling process.

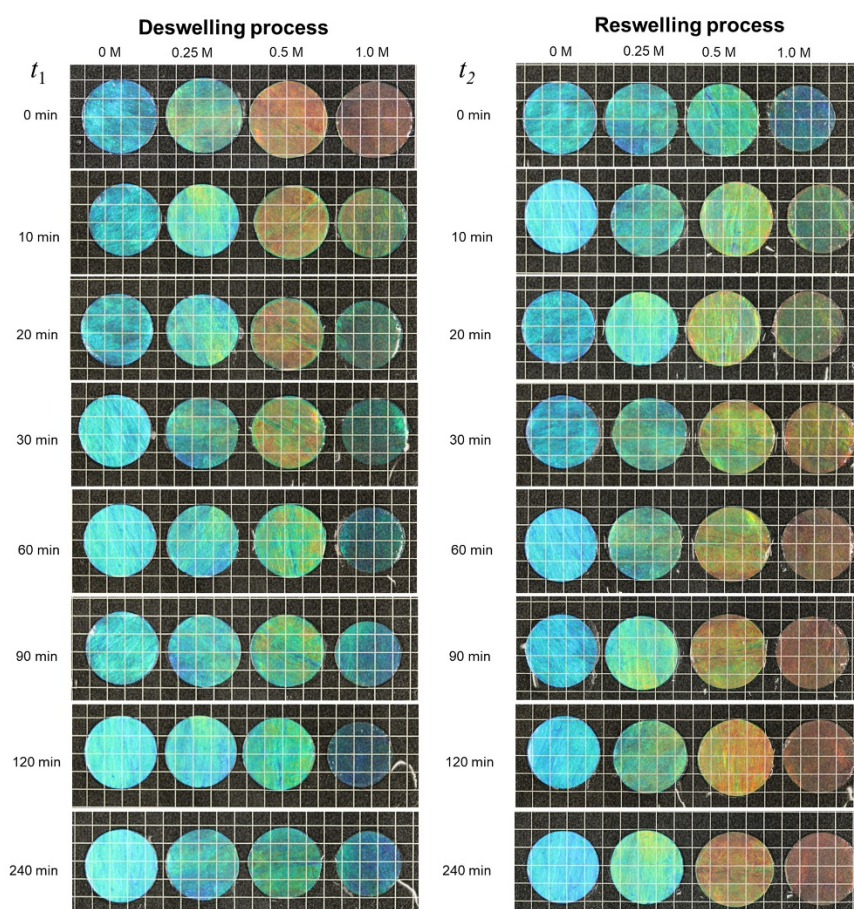


Figure S8. Optical images of the PDGI/PAAm, PDGI/PAAm-PNIPAM_{0.25M}, PDGI/PAAm-PNIPAM_{0.5M}, and PDGI/PAAm-PNIPAM_{1.0M} gels during the deswelling process at 50 °C for t_1 and reswelling process at 25 °C for t_2 . The corresponding color of the gel during the deswelling process was captured immediately after quenching the gel in a cold water bath ($Temp = 25\text{ }^{\circ}\text{C}$). Background lattices: $5 \times 5\text{ mm}$.

As shown in Figure S8, during the deswelling process in a 50 °C hot water bath, the PDGI/PAAm-PNIPAM gels with different NIPAM concentrations showed a clear blue shift in color with increasing heating time, t_1 . During the reswelling process in a 25 °C cold water bath, the PDGI/PAAm-PNIPAM gels with different NIPAM concentrations show a red shift in color with increasing cooling time, t_2 . Particularly, high NIPAM concentration gel shows a larger shift in color.

9. Reflection spectra of PDGI/PAAm, PDGI/PAAm-PNIPAM_{0.25M}, and PDGI/PAAm-PNIPAM_{1.0M} hydrogels at different times during the heating and cooling process.

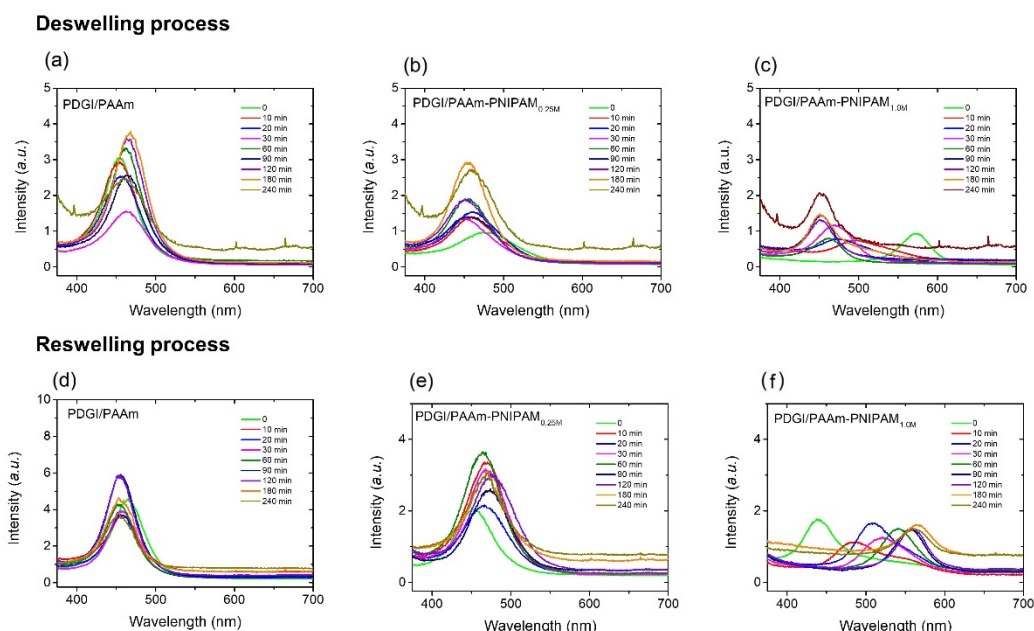


Figure S9. Reflection spectra of (a,d) PDGI/PAAm, (b,e) PDGI/PAAm-PNIPAM_{0.25M}, and (c,f) PDGI/PAAm-PNIPAM_{1.0M} gel in water during the heating process at 50 °C (a-c) and cooling process at 25 °C (d-f). The corresponding reflection spectra of the gel at different heating time was captured after quenching the gel in a cold bath ($Temp = 25\text{ }^{\circ}\text{C}$). The reflection spectra were obtained by keeping the incident at 60° and reflection angles at 45°.

The reflection spectra of the PDGI/PAAm, PDGI/PAAm-PNIPAM_{0.25M}, and PDGI/PAAm-PNIPAM_{1.0M} gels at different heating times are shown in Figure S9.

10. Reversibility in color and interplanar distance of the PDGI/PAAm-PNIPAM_{0.5M} gel

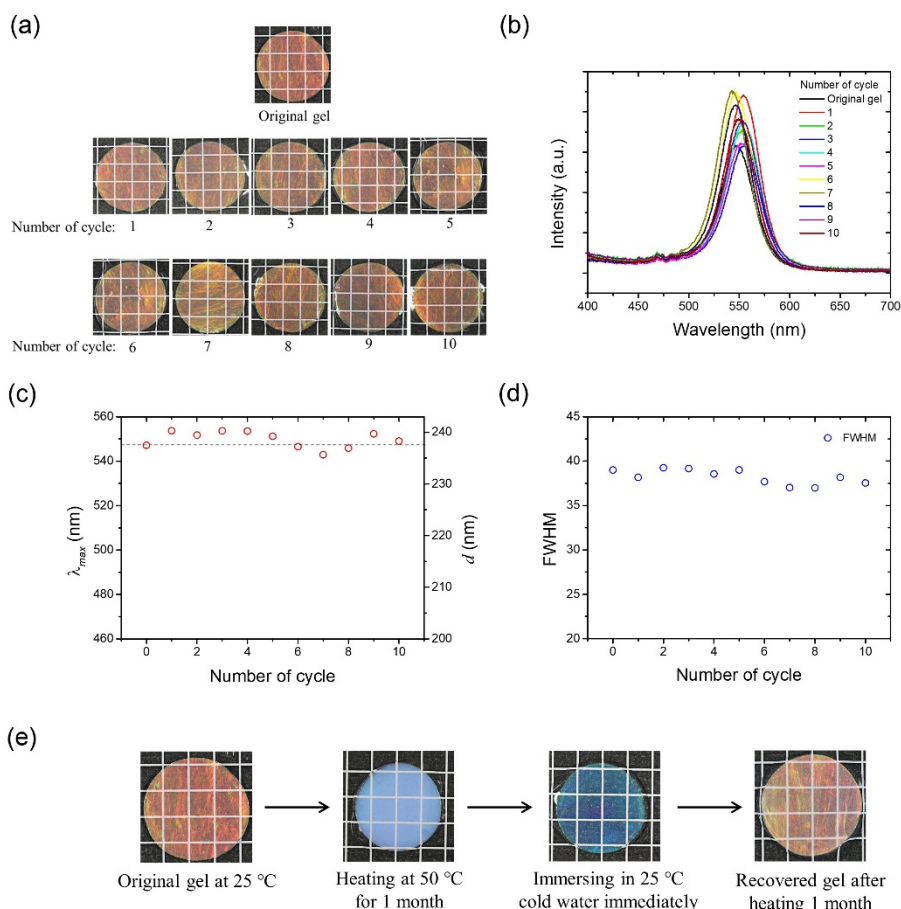


Figure S10. (a) Photographs and (b) reflection spectra of the PDGI/PAAm-PNIPAM_{0.5M} gel after experiencing several heating-cooling cycles. The heating-cooling cycle consists of heating at 50 °C hot water bath for 4 h and cooling at 25 °C cold water bath for 4 h. (c) Peak wavelength, λ_{max} , of the reflection spectrum and the corresponding interplanar distance, d , as a function of number of cycles; (d) The full width at half maximum (FWHM) of the reflection spectra of the gel as a function of number of cycles; (e) photographs of the PDGI/PAAm-PNIPAM_{0.5M} gel after heating in 50 °C hot water bath for 1 month. Background lattices in (a): 5×5 mm. The reflection spectrum was obtained by keeping the incident at 60° and reflection angles at 45°.

The heating-cooling cycle (heating at 50 °C hot water bath for 4 h and then cooling at 25 °C cold water bath for 4 h) of the PDGI/PAAm-PNIPAM_{0.5M} gel was repeated 10 times to check the reversibility. As shown in Figure S10a, the red structural color of the gel barely changed after 10 heating-cooling cycles. The reflection spectra of the gel of each recovery are shown in Figure S10b. The gel showed no clear shift in peak

wavelength, λ_{max} , in accordance with no shift in color (Figure S10c, left axis). It indicates that no clear change in interlayer distance, d , of the gel after 10 cycles (Figure S10c, right axis). The full width at half maximum (FWHM) of the reflection spectra of the gel during each heating and cooling process was not changed (Figure S10d). These results indicate that the gel possesses excellent stability and reversibility against the heating-cooling cycles. As shown in Figure S10e, the original PDGI/PAAm-PNIPAM_{0.5M} gel, which was initially red at 25 °C cold water bath, turned turbid when heated at 50 °C hot water bath. Remarkably, it maintained its turbidity during a one-month immersion in the hot water bath. Once quenching the gel in a 25 °C cold water bath, the turbidity disappeared, and the gel turned blue. After cooling for 4 hours in a 25 °C cold water bath, the blue gel gradually regained its original red color.

11. Reversibility in thickness and diameter of the PDGI/PAAm-PNIPAM_{0.5M} gel during 10 heating-cooling cycles.

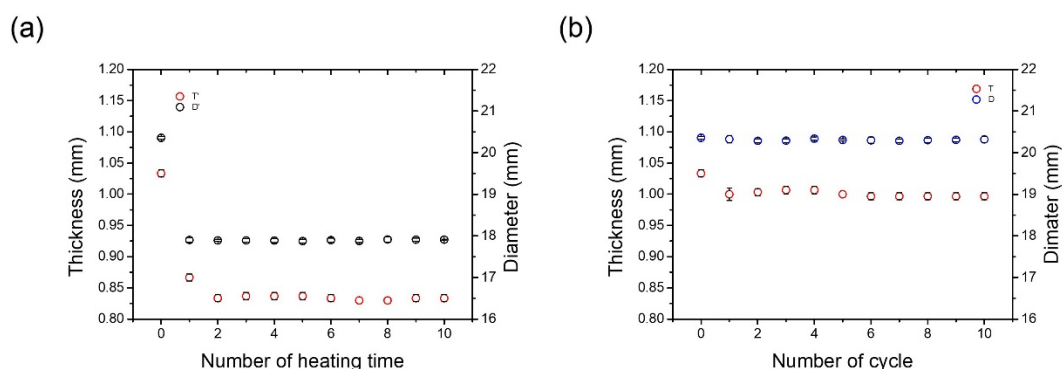


Figure S11. (a) Thickness (left axis) and diameter (right axis) of the PDGI/PAAm-PNIPAM_{0.5M} gel in water after heating at 50 °C hot water bath for 4 h as a function of heating times (after each heating process, the gel was put back to 25 °C cold water bath for 4 h to recover); and (b) thickness (left axis) and diameter (right axis) of PDGI/PAAm-PNIPAM_{0.5M} gel in 25 °C water during heating at 50 °C hot water bath for 4 h and cooling at 25 °C cold water bath for 4 h as a function of the number of heating-cooling cycles.

The thickness and diameter after each heating and cooling process of the PDGI/PAAm-PNIPAM_{0.5M} gel were measured and shown in Figure S11. Except for the first heating process, the thickness and diameter of the gel after each heating process were at the same minimum value, indicating that the number of heating processes does not affect deswelling (Figure S11a). The diameter and thickness of the gel almost recovered their original value after each cooling process (Figure S11b). It indicated that PDGI/PAAm-PNIPAM gel exhibits highly thermos-reversible properties.

12. Structural color/turbid transition of the PDGI/PAAm-PNIPAM gel pattern embedded in the PDGI/PAAm gel.

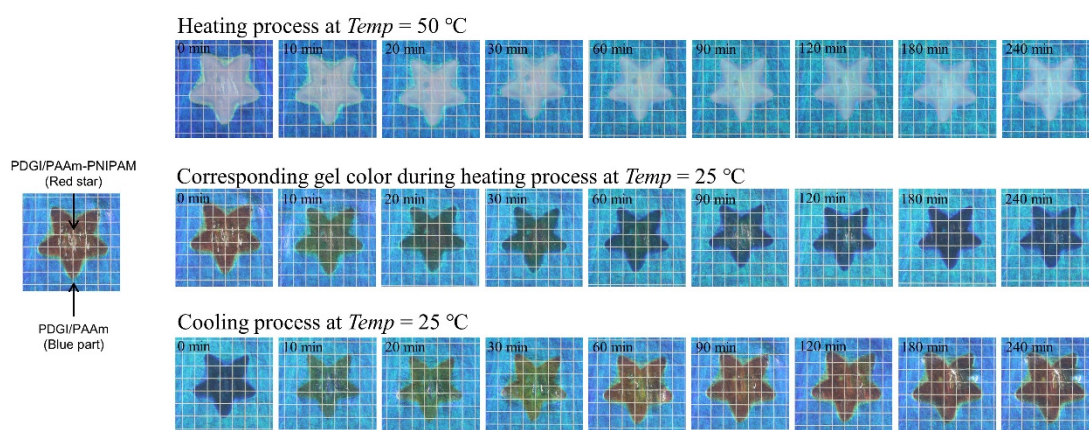


Figure S12. The structural color/turbid change of the PDGI/PAAm-PNIPAM gel pattern in the PDGI/PAAm gel upon heating and cooling processes. Background lattices: $5 \times 5\text{ mm}$.

As shown in Figure S12, the original PDGI/PAAm-PNIPAM gel pattern in PDGI/PAAm gel is red color at $Temp = 25\text{ }^{\circ}\text{C}$. To investigate the structural color/turbid transition of the pattern, the original gel was immersed in $50\text{ }^{\circ}\text{C}$ hot water for 4 h. The original patterned gel showed a short-term turbid phenomenon once immersed in $50\text{ }^{\circ}\text{C}$

hot water and the turbidity did not decay during heating (Figure S12, upper). By quenching the gel into cold water, the turbidity disappeared immediately and the bright structural color of the pattern appeared again (Figure S12, middle). When the heated pattern gel was quenched in 25 °C cold water for a long time, the dark-blue star gradually absorbed water and recovered the original red color (long-term, Figure S12, lower).

13. The dry-swelling test, UV exposure, and the pH responsiveness of the PDGI/PAAm-PNIPAM_{0.5M} hydrogel.

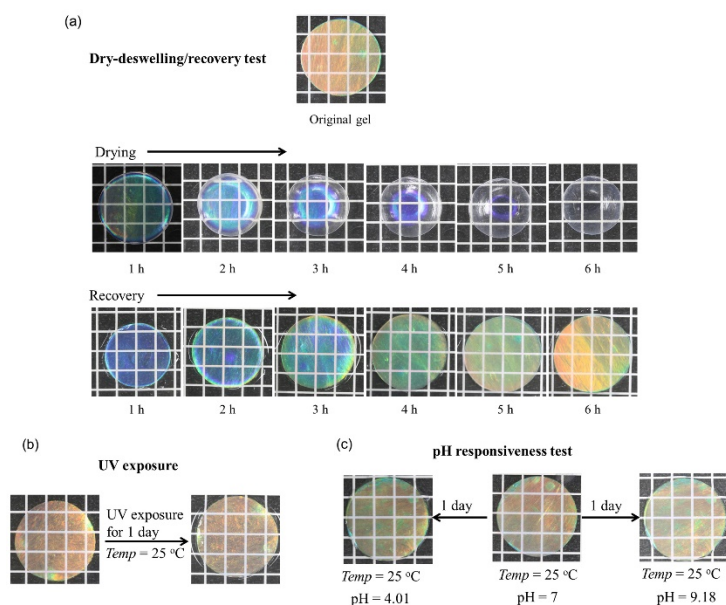


Figure S13. The structural color of the PDGI/PAAm-PNIPAM_{0.5M} gel (a) during drying in air and recovery in water at 25 °C, (b) during UV exposure for 2 days, (c) at different pH for 1 day. The gel during UV exposure was irradiated at 365 nm UV with an intensity of 3.9 mW/cm² for 1 day in the glovebox.

As shown in Figure S13a, during the drying process in air, the gel gradually released water, resulting in a noticeable blue shift in its color. After 6 h drying, the gel

transformed into a transparent state. Immersing the dried gel back to water at 25 °C, the gel gradually absorbed water and recovered its original color. The gel shows no responsiveness to UV exposure (Figure S13b) or pH (Figure S13c).

Reference

- [1] F. Doberenz, K. Zeng, C. Willems, K. Zhang, T. Groth. Thermoresponsive Polymers and their Biomedical Application in Tissue Engineering - A Review. *J. Mater. Chem. B* **2020**, 8, 607-628.
- [2] Y. Ding, X. Zhang, B. Xua, W. Li. LCST and UCST-type Thermoresponsive Behavior in Dendronized Gelatins. *Polym. Chem.*, **2022**, 13, 2813-2821.
- [3] C. Yu, K. Cui, H. Guo, Y. N. Ye, X. Li, J. P. Gong. Structure Frustration Enables Thermal History-Dependent Responsive Behavior in Self-Healing Hydrogels. *Macromolecules* **2021**, 54, 9927-9936.
- [4] Y. F. Yue, M. A. Haque, T. Kurokawa, T. Nakajima, J. P. Gong. Lamellar Hydrogels with High Toughness and Ternary Tunable Photonic Stop-Band. *Adv. Mater.* **2013**, 25, 3106-3110.