

Elasticity-Gated Thermal Plasticity via Superheating-Mediated Nucleation and Growth in Polymer Networks

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this manuscript the authors reports a systematic study on thermal history-dependent phase separation, representing a significant advancement in the field of viscoelasticity-mediated liquid-liquid phase separation. Focusing on a poly(vinyl acetal)-based system (specifically PVP), the authors disclosed that the soaking environment (including salt type and temperature) would dramatically influence the LCST phase transition temperature and the resulting phase separation morphology (mainly the size of phase domain). This behavior stands in stark contrast to traditional PNIPAM gels, which do not exhibit such pronounced history dependence. The authors successfully combine the Flory-Rehner model with a nucleation and growth mechanism, utilizing multi-scale structural characterization to analyze the mesh size and sub-um level heterogeneity. This approach allows for a semi-quantitative elucidation of the contribution of the shear elastic modulus to the phase separation process. Furthermore, the authors cleverly exploited this so-called "thermal plasticity" to demonstrate an overfreezing time-temperature indicator for vaccine storage, which is a well-conceived application. I think that this work is of high quality and falls into the scope of Nature Communications. I just have several specific suggestions to further strengthen the scientific depth and clarity of the manuscript before publication.

(1) The current study focuses exclusively on poly(vinyl propional) (PVP). To broaden the impact of this work, it is important to address whether similar homologs-such as poly(vinyl butyral) (PVB), which is more widely used in industry-exhibit analogous behaviors. What are the specific structural prerequisites for this phenomenon? I suggest the authors include a discussion or preliminary experimental evidence in the conclusion regarding other similar polymers to inspire future research in this direction.

(2) The acronym "SDTP" was used in the main text without a full definition at its first appearance. Although it is defined in the caption of Figure 1, it should be spelled out in the body text for clarity.

(3) The authors emphasize that PNIPAM gels (whether chemically or physically crosslinked) undergo phase separation during the swelling stage above the phase transition temperature. Are there existing literature precedents that strictly align with this specific observation? Given that PNIPAM is a benchmark LCST system with extensive prior research, adequate citations (other than their own experimental demonstration) are necessary to support this contrast and ensure the accuracy of the comparison in objective level.

(4) In the penultimate paragraph of Section 2.2, the authors state that PVP and PVA have a "similar structure." This expression is somewhat imprecise. If the authors are referring to chain flexibility, the Kuhn segment length is a more appropriate metric. Do the authors have evidence or literature values to demonstrate that PVP and PVA possess similar chain flexibility/stiffness?

(5) In Figure 4D, the authors quantify the relationship between the average pore size and the modulus. It is worth noting that Meng et al. predicted a scaling law of the droplet size versus shear modulus in viscoelastic phase separation (Phys. Rev. Lett., 125, 268001 (2020)). I suggest the authors analyze whether their experimental findings are consistent with this theoretical scaling law, which would provide deeper physical insight into the mechanism.

(6) The manuscript predominantly discusses the Nucleation and Growth (NG) mechanism. However, if the gel were rapidly heated deep into the unstable region (quenching into the spinodal region), would it be possible to observe a bicontinuous pattern characteristic of Spinodal Decomposition (SD) (like Nature Materials, 23, 124-130 (2024))? A brief discussion on this possibility would be beneficial.

(7) The authors demonstrate the reversibility of phase separation over hundreds of cycles (Video S4). However, I am curious about the long-term stability of the phase-separated sample when maintained above the phase transition temperature for an extended period. Theoretically, the solvent in the polymer-rich domains should continue to diffuse out due to concentration gradients (see Soft Matter, 22, 330 (2026)). I recommend that the authors discuss the long-term evolution of the phase-

separated structure and whether macroscopic Oswald ripening occurs over time.

(8) There are several minor issues: Figure 6B, “temperature” should be a typo. Fig. 4A, binodal should be capitalized with the initial “b” for consistency.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

The manuscript presents an innovative investigation into spinodal decomposition-triggered phase transition (SDTP) behavior in PVP-based hydrogel systems, with promising implications for the design of history-responsive materials. While the experimental findings and proposed theoretical framework offer valuable insights, several critical aspects require further clarification and validation to strengthen the scientific rigor and broader applicability of the work. This work demonstrates sufficient innovation to warrant publication in Nature Communications. The following points outline key concerns and suggestions for improvement:

1. The proposed mechanism hinges on the assumption that the increased equilibrium modulus (G_e) at higher storage temperatures (T_s) stems from enhanced entropic elasticity due to reduced water content and higher crosslinking density. However, PVP exhibits relatively high glass transition temperatures (T_g) in the dry state. As water content decreases with increasing T_s , the polymer-rich “tight domains” may approach or even surpass their T_g . If these domains are in a glassy state at T_s , the observed increase in G_e could reflect vitrification rather than rubber-like entropic elasticity. To validate the theoretical framework, the authors should provide direct evidence demonstrating that the network remains in the rubbery state under all experimental conditions.
2. The practical application as a freeze-exposure indicator (Fig. 6) relies on the gel’s ability to reprogram its water content (ϕ_{req}) when exposed to sub-zero temperatures. At such temperatures, the external aqueous medium is likely frozen, and water diffusion through the ice matrix is negligible. It remains unclear how the gel achieves the mass transport necessary to reach a new swelling equilibrium under these conditions.
3. Perform multiple programming-erasing cycles (e.g., >20) on the same gel sample. Monitor the changes in T_c , ΔT , and transmittance after each cycle to verify the material’s reusability and durability.
4. Figure 5D introduces an “elasticity-stabilized supersaturation” region, described as a state where nucleation is kinetically suppressed despite $S > 1$. If elastic constraints merely raise the nucleation barrier, the system should eventually phase separate given sufficient time, since nucleation is a stochastic process. The authors should clarify the expected lifetime of the transparent state in this region and discuss whether the observed behavior represents true thermodynamic stabilization or a kinetic delay.
5. The manuscript claims to establish a “universal design rule” for history-responsive materials. However, the study focuses exclusively on one polymer system—PVP. To substantiate the claim of generality, the authors should demonstrate the SDTP effect in at least one other chemically distinct polymer system. Without such validation, the proposed “universal rule” risks being perceived as a material-specific phenomenon tied to PVP’s solubility parameters.
6. In contrast to the SDTP behavior observed in PVP gels, classical PNIPAM systems exhibit immediate phase separation. This critical difference remains insufficiently analyzed in the manuscript. Based on literature evidence (e.g., *Macromolecules* 2024, 57, 5398), this discrepancy may stem from the extremely narrow temperature gap between the binodal temperature (T_{bn}) and spinodal temperature (T_{sp}) in PNIPAM systems. However, readers may reasonably question: Which intermolecular interactions precisely govern the magnitude of the $T_{\text{bn}}-T_{\text{sp}}$ gap? Furthermore, Can this gap be rationally engineered through molecular design? For instance, how do parameters such as the degree of propanal functionalization and the molecular weight of PVP influence this gap? Addressing these questions would significantly advance the broader applicability of SDTP-based methodologies.

(Remarks on code availability)

Reviewer #3

(Remarks to the Author)

In this manuscript, the authors report a biomimetic material that exhibits trainable thermoresponsiveness. The underlying mechanism is attributed to an elastic-gated nucleation-and-growth process, which is systematically investigated through both qualitative and quantitative analyses under varying temperature and salt conditions. The authors further demonstrate a potential practical application as a low-temperature indicator for monitoring and reporting vaccine over-freezing exposure. Overall, this work presents a forward-looking and potentially impactful advance, and I believe the manuscript would be suitable for publication in Nature Communications.

1. It would be beneficial if the authors could provide a more conclusive discussion of the core mechanism and the associated design principles.
2. Regarding the salt-gated thermal plasticity, it would be important to clarify whether the observed behavior depends solely on the ionic species, or whether it is also influenced by salt concentration.
3. Based on the proposed mechanism, the authors are encouraged to discuss how molecular weight, molecular weight distribution, and grafting ratio may affect the phase diagram and thermoresponsive behavior.
4. The impact of time on the thermally adaptive swelling behavior should be clarified. In particular, do salt-treated samples exhibit consistent T_c values after sufficient equilibration time when measurements are performed?
5. The authors are encouraged to more clearly explain how the training of thermoresponsiveness is manifested experimentally and how it is reflected in the material response.

6. It would be helpful to further clarify the durability, reversibility, and dynamic response of the SDTP-gel under different temperature and salt stimuli. For example, how can a high-T_c state induced by Na₂SO₄ treatment be converted back to a low-T_c state, and is this process reversible and repeatable?

(Remarks on code availability)

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I have no question now and I am pleased to recommend the publication of this manuscript.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

The author has provided detailed responses to the reviewer's questions. The current version can be accepted for publication.

(Remarks on code availability)

Reviewer #3

(Remarks to the Author)

The authors have adequately addressed my concerns, and the current revision is suitable for publication.

(Remarks on code availability)

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Dear Reviewers,

We sincerely thank the reviewers for the review of our manuscript, which helps us to improve the quality of the work. To make it as easy as possible for the Editor and Reviewers to read, we have copied the reviewers' comments below (in *italic*). Our point-by-point response is provided as follows (please see [Our responses](#)). The changes made in the revised manuscript are highlighted in **dark red** in the revised manuscript (please see [Modification to the manuscript](#)).

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Responses to Reviewers' Comments in a Point-to-Point Fashion

Responses to Reviewer #1

General Comment: *In this manuscript the authors reports a systematic study on thermal history-dependent phase separation, representing a significant advancement in the field of viscoelasticity-mediated liquid-liquid phase separation. Focusing on a poly(vinyl acetal)-based system (specifically PVP), the authors disclosed that the soaking environment (including salt type and temperature) would dramatically influence the LCST phase transition temperature and the resulting phase separation morphology (mainly the size of phase domain). This behavior stands in stark contrast to traditional PNIPAM gels, which do not exhibit such pronounced history dependence. The authors successfully combine the Flory-Rehner model with a nucleation and growth mechanism, utilizing multi-scale structural characterization to analyze the mesh size and sub-um level heterogeneity. This approach allows for a semi-quantitative elucidation of the contribution of the shear elastic modulus to the phase separation process. Furthermore, the authors cleverly exploited this so-called "thermal plasticity" to demonstrate an overfreezing time-temperature indicator for vaccine storage, which is a well-conceived application. I think that this work is of high quality and falls into the scope of Nature Communications. I just have several specific suggestions to further strengthen the scientific depth and clarity of the manuscript before publication.*

Our responses: Thanks for these helpful comments and your recognition for this work. Our point-by-point response to your specific comments are listed as follows:

Specific Comment 1: *The current study focuses exclusively on poly(vinyl propional) (PVP). To broaden the impact of this work, it is important to address whether similar homologs-such as poly(vinyl butyral) (PVB), which is more widely used in industry-exhibit analogous behaviors. What are the specific structural prerequisites for this phenomenon? I suggest the authors include a discussion or preliminary experimental evidence in the conclusion regarding other similar polymers to inspire future research in this direction.*

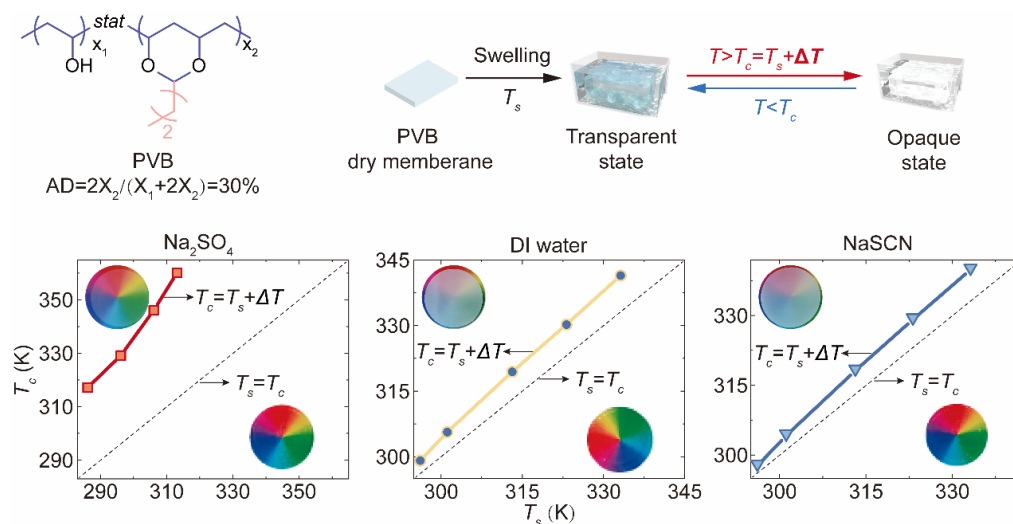
Our response: According to your request, we conducted additional experiments on poly(vinyl butyral) (PVB). The results show that PVB exhibits analogous phase transition behavior: when pre-swollen at different temperatures, its phase transition temperature changes accordingly. This indicates that the phenomenon is not unique to PVP but is likely a general feature of poly(vinyl acetal)-based polymers. We have incorporated this discussion and the corresponding data into the main text (see below).

Modification to the manuscript (Main text, Conclusion section, Page 24): We have extended these design rules to other polyvinyl acetals, such as poly(vinyl butyral) (PVB), as well as to alternative polymer systems beyond polyvinyl acetals (see **Supplementary Note V** and **Supplementary Figures. SVI–SVII**). These systems exhibit analogous thermal plasticity behavior, confirming that the SDTP phenomenon is not unique to PVP but represents a more general design principle across different

polymer chemistries, whereas conventional systems such as PNIPAM exhibit a fixed transition temperature that is insensitive to swelling history.

This raises a key question: what is the physical origin of the thermal plasticity observed here, which is absent in conventional PNIPAM gels? We propose that our system satisfies three synergistic design principles that collectively enable this property. First, and in contrast to the narrow metastable window of typical PNIPAM, our polymer-solvent system must possess a sufficiently wide gap between its binodal and spinodal curves. This thermodynamic stability is essential to prevent phase separation during the history-encoding swelling stage. Second, the network's stiffness must be sensitively tuned by the very conditions (temperature and ionic environment) of that swelling, thereby translating history into a programmable mechanical barrier to phase separation. Third, kinetically, chain relaxation must outpace water diffusion to permit the network to adaptively reorganize during encoding. A complete molecular-level picture will be refined through future studies integrating theoretical modeling and multiscale in situ characterization.

Modification to the manuscript ([ESI, Supplementary Note VI, Page S39](#)):



Supplementary Figure SV-I. Preparation and salt-dependent thermal plasticity behavior of other polyvinyl acetal-based SDTP-Gels (e.g., PVB). A. Schematic of SDTP-gel preparation: PVB powder (with 30% hydroxyl groups in PVA was substituted by butyral) is solution-cast and dried to form a dry sheet, which swells in saline water at temperature T_s to yield a transparent SDTP-gel. The gel undergoes a reversible transparent-to-opaque transition as temperature fluctuates above/below the critical phase transition temperature T_c = T_s + ΔT.

Specific Comment 2: The acronym "SDTP" was used in the main text without a full definition at its first appearance. Although it is defined in the caption of Figure 1, it should be spelled out in the body text for clarity.

Our response: We thank the reviewer for pointing this out. We have revised the text to define "SDTP" upon its first appearance in the main body for clarity (see Modification to the manuscript below).

Modification to the manuscript (Main text, Introduction section, Page 3): ...salt-dependent thermal plasticity (SDTP)...

Specific Comment 3: *The authors emphasize that PNIPAM gels (whether chemically or physically crosslinked) undergo phase separation during the swelling stage above the phase transition temperature. Are there existing literature precedents that strictly align with this specific observation? Given that PNIPAM is a benchmark LCST system with extensive prior research, adequate citations (other than their own experimental demonstration) are necessary to support this contrast and ensure the accuracy of the comparison in objective level.*

Our response: We thank the reviewer for this suggestion. While we are not aware of prior studies that explicitly examine the swelling process of dry PNIPAM films at different temperatures, the phase behavior of PNIPAM/water systems has been well characterized. Afroze et al. (*J. Mol. Struct.*, **2000**, 554, 55) established that PNIPAM/water exhibits a Type II phase diagram, where the binodal curve is largely independent of polymer molecular weight and the swelling curve of the crosslinked network interferes with the liquid–liquid miscibility gap, resulting in a discontinuous volume transition at a fixed temperature determined by the phase diagram. More recently, Wang and Hashimoto (*Macromolecules*, **2024**, 57, 5398) demonstrated that the temperature gap between the binodal and spinodal is extremely narrow (ca. 0.6 °C), meaning that once the temperature exceeds the binodal, the system rapidly becomes unstable and phase separates. These fundamental features explain why PNIPAM gels undergo immediate phase separation when swollen above their intrinsic transition temperature, in contrast to the programmable behavior observed in our SDTP-gels. We have added these citations to the revised manuscript to support the comparison.

Modification to the manuscript (Main text, Thermally Adaptive Swelling section, Page 11): The contrasting behavior can be understood from their respective phase diagrams. In PNIPAM/water, the binodal and spinodal curves are separated by an exceptionally narrow temperature gap (ca. 0.6 °C)²⁹. Consequently, once the temperature exceeds the binodal, phase separation occurs immediately, leaving no room for thermal history programming. In contrast, poly(vinyl acetal)-based systems such as PVP possess a broader metastable region due to the presence of acetal rings and residual hydroxyl groups, which alter the concentration dependence of the polymer–water interaction parameter. This broader window prevents phase separation during swelling, enabling the elastic-gated nucleation mechanism that underlies SDTP behavior.

Specific Comment 4: *In the penultimate paragraph of Section 2.2, the authors state that PVP and PVA have a "similar structure." This expression is somewhat imprecise. If the authors are referring to chain flexibility, the Kuhn segment length is a more appropriate metric. Do the authors have evidence or literature values to demonstrate that PVP and PVA possess similar chain flexibility/stiffness?*

Our response: We thank the reviewer for this insightful suggestion. We agree that chain flexibility is better characterized by the Kuhn segment length. However, to our knowledge, the Kuhn length of poly(vinyl propional) (PVP) has not been reported in the literature. In our calculation of interfacial tension (σ), we needed an estimate of the Kuhn length for PVP.

We approximated it using the reported value for PVA (6.2 Å) based on two considerations. First, PVP is derived from PVA via acetalization and shares the same carbon–carbon backbone. Second, we measured the dry-state glass transition temperatures: PVA exhibits a T_g of approximately 70 °C, while PVP exhibits a T_g of approximately 80 °C. This close agreement suggests comparable segmental mobility in the amorphous state, as T_g directly reflects the cooperative motion of chain segments. Moreover, for flexible polymers with similar backbones, Kuhn lengths typically fall within the same order of magnitude (0.6–1.4 nm; see Page 53, Table 2.1, Rubinstein & Colby, *Polymer Physics*). Thus, using the PVA value as a reasonable estimate for PVP is physically justified. We have revised the text to clarify the basis of this approximation.

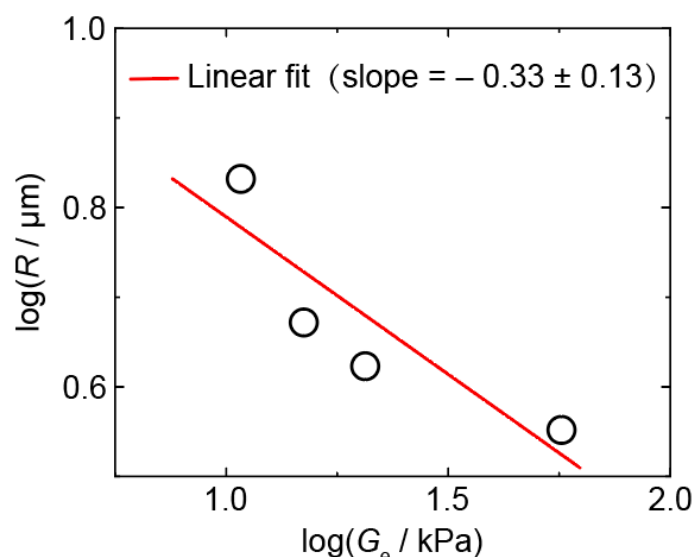
Modification to the manuscript (Main text, Thermally Adaptive Swelling section, Pages 14): Given that PVP is derived from PVA and shares the same carbon–carbon backbone, and considering their comparable glass transition temperatures (75-85°C for PVA⁴⁵; 85 °C for PVP), we approximate $Z \approx 6.2$ Å for PVP based on literature values for PVA⁴⁶. This approximation is reasonable as Kuhn lengths for polymers with similar chain flexibilities typically fall within the same order of magnitude.

Specific Comment 5: *In Figure 4D, the authors quantify the relationship between the average pore size and the modulus. It is worth noting that Meng et al. predicted a scaling law of the droplet size versus shear modulus in viscoelastic phase separation (Phys. Rev. Lett., 125, 268001 (2020)). I suggest the authors analyze whether their experimental findings are consistent with this theoretical scaling law, which would provide deeper physical insight into the mechanism.*

Our response: We thank the reviewer for this valuable suggestion. Following this comment, we further analyzed the scaling relationship between average pore size and shear modulus. The results show that the pore size decreases with increasing modulus, following an approximate power-law relationship with a fitted exponent of approximately -0.33 , which is consistent in order of magnitude with the scaling law $R \propto G^{-1/3}$ proposed by Meng et al. for viscoelastic phase separation. Given the limited number of experimental data points and the structural complexity of the system, we interpret this result as a qualitative agreement in trend rather than a rigorous quantitative validation.

Modification to the manuscript (Main text, Elasticity Constrained Phase Separation section, Page 16): Further analysis reveals that the average pore diameter scales approximately as $R \propto G_e^{-0.33}$ (see **Supplementary Figure. SIV-2**), consistent with the scaling law predicted for viscoelastic phase separation⁴⁸.

Modification to the manuscript (ESI, Supplementary Note IV, Page S34):



Supplementary Figure SIV-2. Double-logarithmic plot of average pore size $\langle R \rangle$ versus equilibrium shear modulus G_e . The dashed line represents the power-law fit with exponent -0.33 . It should be noted that the limited number of data points and the structural complexity of the polymer network preclude a rigorous quantitative validation. Nevertheless, the observed trend provides qualitative support for the elasticity-controlled phase separation mechanism underlying the SDTP behavior.

Specific Comment 6: *The manuscript predominantly discusses the Nucleation and Growth (NG) mechanism. However, if the gel were rapidly heated deep into the unstable region (quenching into the spinodal region), would it be possible to observe a bicontinuous pattern characteristic of Spinodal Decomposition (SD) (like Nature Materials, 23, 124-130 (2024))?* A brief discussion on this possibility would be beneficial.

Our response: We thank the reviewer for this insightful comment. We agree that rapid heating deep into the unstable region (i.e., quenching into the spinodal region) would likely lead to bicontinuous structures characteristic of spinodal decomposition (SD), as elegantly demonstrated in recent work (Nature Materials, 2024, 23, 124–130). In our current study, the phase separation was induced by relatively slow heating or stepwise temperature changes, which favor the nucleation-and-growth (NG) mechanism. Exploring the effect of rapid quenching into the spinodal regime is an intriguing direction that could yield distinct morphologies and further enrich the SDTP behavior. We have added a brief discussion of this possibility in the revised manuscript (see Section 2.3) and note that this will be an interesting focus for future investigation.

Modification to the manuscript (Main text, Elasticity Constrained Phase Separation section, Page 20): In the meanwhile, we note that the NG mechanism dominates under the relatively slow heating conditions employed in this study. However, if the gel were rapidly heated deep into the unstable region (i.e., quenched into the spinodal region), a bicontinuous morphology characteristic of spinodal decomposition would likely emerge, as recently demonstrated in other LCST-type polymer systems⁵⁴. Exploring such rapid quenching conditions could provide additional insights into the elasticity-modulated phase separation dynamics and will be an interesting direction for future research.

Specific Comment 7: *The authors demonstrate the reversibility of phase separation over hundreds of cycles (Video S4). However, I am curious about the long-term stability of the phase-separated sample when maintained above the phase transition temperature for an extended period. Theoretically, the solvent in the polymer-rich domains should continue to diffuse out due to concentration gradients (see Soft Matter, 22, 330 (2026)). I recommend that the authors discuss the long-term evolution of the phase-separated structure and whether macroscopic Oswald ripening occurs over time.*

Our response: We thank the reviewer for the insightful comment. We monitored the transmittance of phase-separated samples at 550 nm for hundreds of hours. Although the chemical potential of water inside the polymer-rich domains is slightly higher than that of the external bulk water, which could theoretically drive continued diffusion, the phase-separated structures remained stationary for tens of hours without any sign of coarsening. We attribute this long-term stability to the elastic constraints of the crosslinked network, which effectively suppress further domain growth. Detailed results (including a discussion and movie) are provided in the revised manuscript.

Modification to the manuscript (Main text, Fabrication and Thermal Plasticity of SDTP-gels section, Page 8): Importantly, in striking contrast to that classical process, the opaque state is stable for hundreds of hours with no observable coarsening (Supplementary Figure. SII-9, Supplementary Movie S5). As shown later, the essential ingredient leading to this unusual stability is the elasticity of the polymer matrix.

Modification to the manuscript (ESI, Supplementary Note VII , Page S40):Supplementary Movie S5. Long-Term Stability of the Opaque State. This video shows the performance of an SDTP-gel after being kept above its phase transition temperature for an extended period. The opaque state remains stable for at least 36 hours with no visible decay or coarsening, confirming the long-term stability of the phase-separated structure.

Specific Comment 8: *There are several minor issues: Figure 6B, “temperature ” should be a typo. Fig. 4A, binodal should be capitalized with the initial “b ” for consistency.*

Our response: We thank the reviewer for carefully reading our manuscript and pointing out these issues. We apologize for these oversights. Following the reviewer’s suggestion, we have corrected “binodal Curve” to “Binodal Curve” in Figure 4A and corrected the typo in Figure 6B.

Responses to Reviewer #2

General Comment: *The manuscript presents an innovative investigation into spinodal decomposition-triggered phase transition (SDTP) behavior in PVP-based hydrogel systems, with promising implications for the design of history-responsive materials. While the experimental findings and proposed theoretical framework offer valuable insights, several critical aspects require further clarification and validation to strengthen the scientific rigor and broader applicability of the work. This work demonstrates sufficient innovation to warrant publication in Nature Communications. The following points outline key concerns and suggestions for improvement:*

Our responses: We sincerely appreciate your positive feedback on our work. According to your comments, more comprehensive experimental studies and detailed analyses have been conducted. Our point-to-point responses to your specific comments are listed as follows.

Specific Comment 1: *The proposed mechanism hinges on the assumption that the increased equilibrium modulus (G_e) at higher storage temperatures (T_s) stems from enhanced entropic elasticity due to reduced water content and higher crosslinking density. However, PVP exhibit relatively high glass transition temperatures (T_g) in the dry state. As water content decreases with increasing T_s , the polymer-rich “tight domains” may approach or even surpass their T_g . If these domains are in a glassy state at T_s , the observed increase in G_e could reflect vitrification rather than rubber-like entropic elasticity. To validate the theoretical framework, the authors should provide direct evidence demonstrating that the network remains in the rubbery state under all experimental conditions.*

Our responses: We thank the reviewer for raising this critical point regarding the possibility of vitrification in polymer-rich domains. To directly validate that the network remains in the rubbery state under all experimental conditions, we performed systematic measurements of the glass transition temperature (T_g) as a function of water content and compared it with our swelling and phase separation conditions.

We prepared PVP films with controlled water contents by equilibrating dry PVP sheets in atmospheres of different relative humidities (see **Supplementary Figure. SIII-7A** in revised ESI). The T_g of each sample was determined from the peak of $\tan \delta$ in temperature-sweep rotational rheometry. As shown in **Supplementary Figure. SIII-7B** in revised ESI, dry PVP exhibits a T_g of approximately 70 °C. Adding only 2.9 wt% water reduces T_g to 60 °C, and 3.85 wt% water further lowers it to 50 °C. This confirms that water is a strong plasticizer for PVP, dramatically lowering the T_g even at low water contents.

We then plotted the swelling equilibrium line (T_s vs. ϕ_{weq}) together with the measured T_g - ϕ_{water} curve for each salt medium (**Supplementary Figure. SIII-7B**). For all swelling conditions (water, Na₂SO₄, NaSCN, across the entire T_s range), the swelling temperature T_s lies well above the corresponding T_g of the gel at that water

content. In combination with the rheological data in **Supplementary Figure. SIII-6**, where the swollen gels exhibit $G' > G''$ and weak frequency dependence, these results directly demonstrate that the swollen SDTP-gel is in the rubbery state before phase separation.

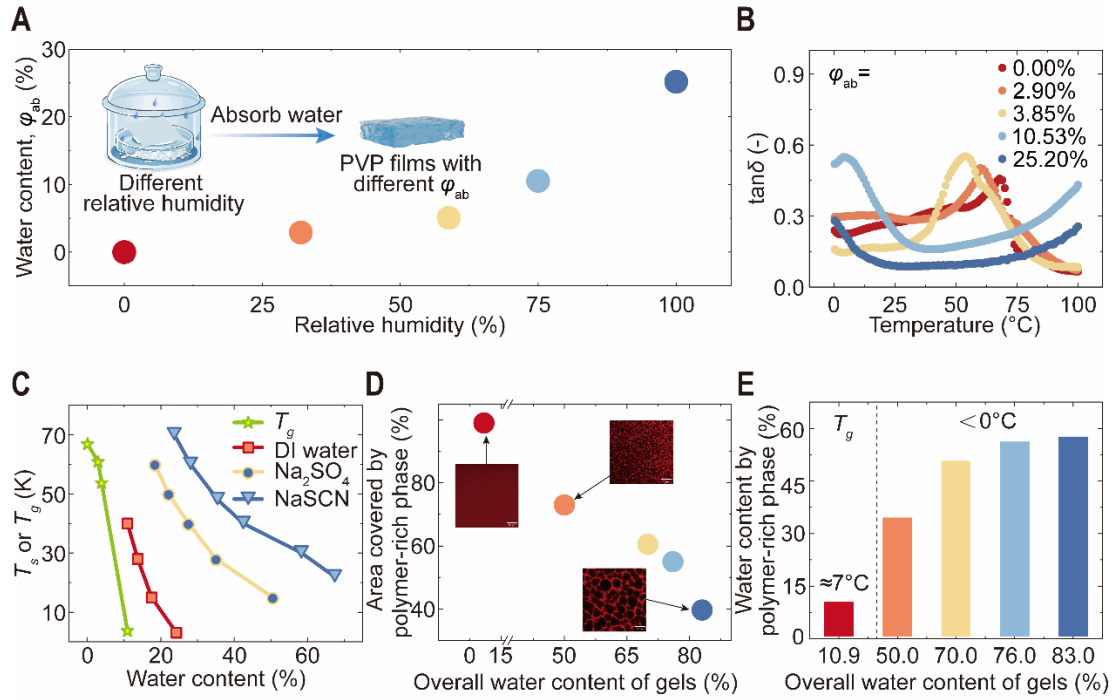
To address the state of the polymer-rich domains that form upon phase separation, we calculated their water content using quantitative image analysis of confocal micrographs (see **Supplementary Figure. SIII-7** in revised ESI). The volume fractions of the water-rich and polymer-rich phases were obtained from 2D area fractions (assuming isotropy), and the water content of the polymer-rich phase ($\phi_{w,rich}$) was derived from mass balance. For the most extreme case, viz, swelling in Na₂SO₄ at 40 °C, which gives the lowest overall water content ($\phi_{weq} \approx 0.11$) – the polymer-rich phase still contains approximately 5–10 wt% water (depending on the exact phase volume ratio). Using the measured T_g – ϕ_{water} relationship, this water content corresponds to a T_g of about 7 °C (or 35 °C even under the most conservative assumption of 50% phase contrast leading to 5 wt% water). Both values are below the experimental temperature (40 °C). Hence, the polymer-rich domains are also in the rubbery state during and after phase separation.

In summary, the combined evidence, including (i) the strong plasticizing effect of water on PVP, (ii) the fact that swelling temperatures T_s always exceed the T_g of the corresponding hydrated gel, and (iii) the calculated T_g of the polymer-rich domains being far below the experimental temperatures, unequivocally demonstrates that the network remains in the rubbery state under all experimental conditions. Therefore, the observed increase in G_e with T_s originates from enhanced entropic elasticity (due to reduced water content and higher effective crosslink density) rather than from vitrification. This validation supports the Flory–Rehner framework used in our manuscript.

We have added the above analysis and figures (**Supplementary Figure. SIII-7**) to the Supporting Information (see Supplementary Note III.) and briefly summarized the conclusion in the main text.

Modification to the manuscript (Main text, Thermally Adaptive Swelling section, Page 13): Furthermore, we confirmed that the network remains rubbery under all experimental conditions by showing that T_g as a function of water content lies well below T_s (**Supplementary Figure. SIII-7**), consistent with the rheological rubbery plateau in **Supplementary Figure. SIII-6**.

Modification to the manuscript (ESI, Supplementary Note III, Page S31):



Supplementary Figure SIII-7. Evaluation of the rubbery state under all experimental conditions. **A.** Schematic illustration showing the control of water content in PVP films by exposure to different relative humidities; and Equilibrium water content of PVP films under different relative humidities; **B.** $\tan \delta$ as a function of temperature for PVP films with different water contents, measured by rotational rheometry. The glass transition temperature (T_g) is taken as the peak of $\tan \delta$; **C.** Swelling equilibrium lines (water content vs. swelling temperature T_s) of SDTP-gels in water, Na_2SO_4 , and NaSCN , overlaid with the T_g -water content relationship derived from (B). In all cases, T_s lies above the corresponding T_g , confirming the rubbery state before phase separation; **D.** Area fraction of the polymer-rich phase calculated from confocal images. Briefly, confocal micrographs of phase-separated SDTP-gels were thresholded to generate binary images, and the area fraction of the polymer-rich phase (red, Nile Red staining) was quantified using ImageJ. At least five independent fields of view were analyzed for each sample, and the area fraction was taken as the volume fraction assuming isotropy; **E.** Water content of the polymer-rich phase ($\phi_{w,\text{rich}}$) calculated from the area fractions in (D) using mass balance, and the corresponding T_g estimated from the T_g -water content calibration in (B). Even for the most dehydrated sample (e.g., Na_2SO_4 , 40°C , overall water content $\approx 10\%$), the polymer-rich phase remains well above its T_g at the experimental temperature, confirming the rubbery state after phase separation.

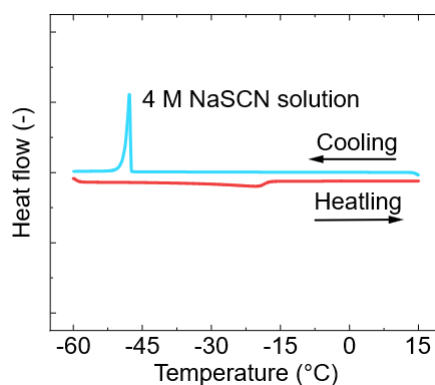
Specific Comment 2: The practical application as a freeze-exposure indicator (Fig. 6) relies on the gel's ability to reprogram its water content (ϕ_{weq}) when exposed to sub-zero temperatures. At such temperatures, the external aqueous medium is likely frozen, and water diffusion through the ice matrix is negligible. It remains unclear how the gel achieves the mass transport necessary to reach a new swelling equilibrium under these conditions.

Our responses: We thank the reviewer for this important question. To verify whether

the external medium freezes under our freeze-exposure conditions, we measured the freezing point of the 4 M NaSCN solution by DSC. The result shows a freezing point of approximately $-40\text{ }^{\circ}\text{C}$, well below the experimental temperature range ($0\text{ }^{\circ}\text{C}$ to $-10\text{ }^{\circ}\text{C}$). Thus, the solution remains liquid, providing liquid channels for water diffusion. This explains how the gel can reprogram its water content during sub-zero exposure. We have discussed this point in revised main text and the DSC data have been added to the ESI.

Modification to the manuscript (Main text, SDPT-gel as Time-temperature Indicator for Freeze-sensitive Vaccines, Page 22): Note that the applied saline (4 M NaSCN) solution does not freeze at the tested subzero temperatures (down to $-10\text{ }^{\circ}\text{C}$; freezing point $\approx -40\text{ }^{\circ}\text{C}$, see **Supplementary Figure. SV-1**), allowing the necessary water transport for reprogramming.

Modification to the manuscript (ESI, Supplementary Note V, Page S38):



Supplementary Figure SV-1. Differential scanning calorimetry (DSC) thermograms of 4 M NaSCN solution. The measurement was performed at a heating and cooling rate of $5\text{ }^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. The cooling curve (blue) shows an exothermic peak corresponding to the freezing event, while the heating curve (red) shows an endothermic peak corresponding to melting. The onset of the melting peak gives a freezing point of approximately $-40\text{ }^{\circ}\text{C}$, confirming that the solution remains liquid at the subzero temperatures used in the freeze-exposure experiments (down to $-10\text{ }^{\circ}\text{C}$).

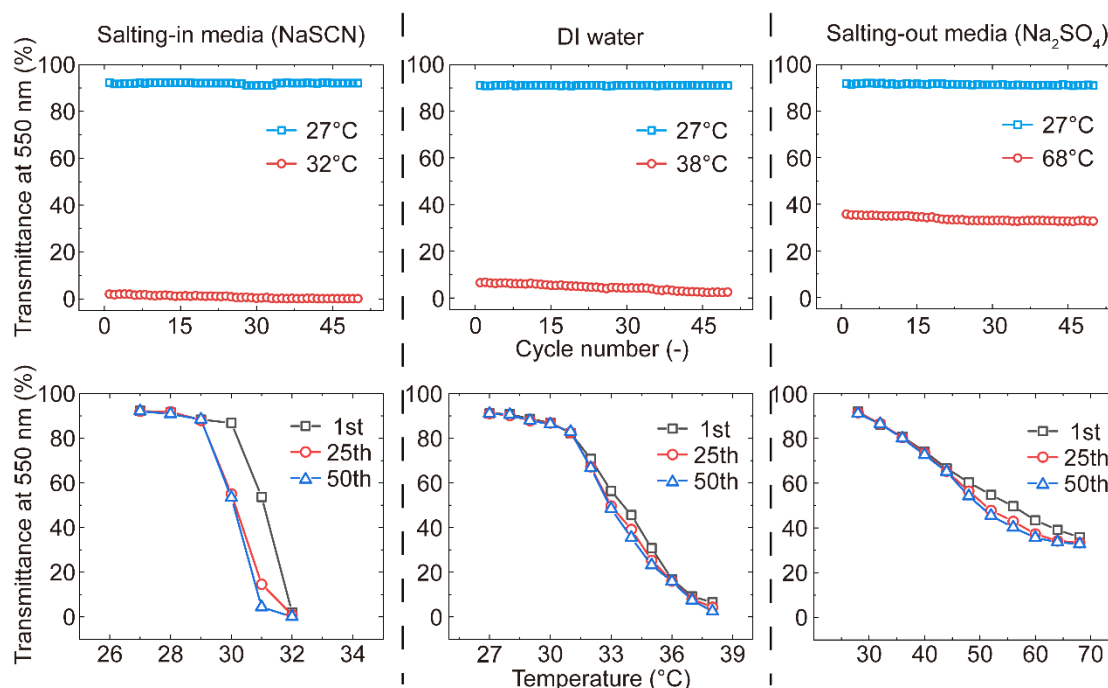
Specific Comment 3: *Perform multiple programming-erasing cycles (e.g., >20) on the same gel sample. Monitor the changes in T_c , ΔT , and transmittance after each cycle to verify the material's reusability and durability.*

Our responses: We thank the reviewer for the suggestion. Following this comment, we analyzed the transmittance changes over 50 programming-erasing cycles. The results show good reversibility with only minor changes in T_c , attributed to microstructural pre-training rather than degradation. This analysis has been added to the main text, and the data are provided in the ESI.

Modification to the manuscript (Main text, Fabrication and Thermal Plasticity of SDTP-gels, Page 8): Importantly, the phase transition behavior remains stable over numerous cycles and extended swelling periods, with negligible change observed

(Supplementary Figure. SII-5B, Supplementary Figure. SII-7).

Modification to the manuscript (ESI, Supplementary Note II, Page S14):



Supplementary Figure SII-7. Transmittance at 550 nm as a function of temperature during repeated programming-erasing cycles. Transmittance curves recorded for the 1st, 25th, and 50th cycles in (left) NaSCN (middle) water, (right) Na₂SO₄ (data shown for the 1st cycle in water as representative). The transmittance at the high-temperature phase-separated state slightly decreases with increasing cycle number, and the transition becomes steeper and shifts slightly to lower temperatures after 25 and 50 cycles, indicating accelerated phase separation due to microstructural pre-training. In contrast, the transmittance in the low-temperature transparent state remains unchanged. These results confirm the excellent reusability and durability of SDTP-gels over multiple cycles.

Specific Comment 4: *Figure 5D introduces an “elasticity-stabilized supersaturation” region, described as a state where nucleation is kinetically suppressed despite $S > 1$. If elastic constraints merely raise the nucleation barrier, the system should eventually phase separate given sufficient time, since nucleation is a stochastic process. The authors should clarify the expected lifetime of the transparent state in this region and discuss whether the observed behavior represents true thermodynamic stabilization or a kinetic delay.*

Our response: We thank the reviewer for this insightful comment. We agree that if elastic constraints merely raise the nucleation barrier, phase separation should eventually occur stochastically. We have estimated the expected lifetime of the transparent state in the “elasticity-stabilized supersaturation” region using classical nucleation theory. The nucleation rate J scales as $\exp(-\Delta G_{NS}/k_B T)$, where ΔG_{NS} is the nucleation barrier. In our network, the elastic contribution increases ΔG_{NS} by a

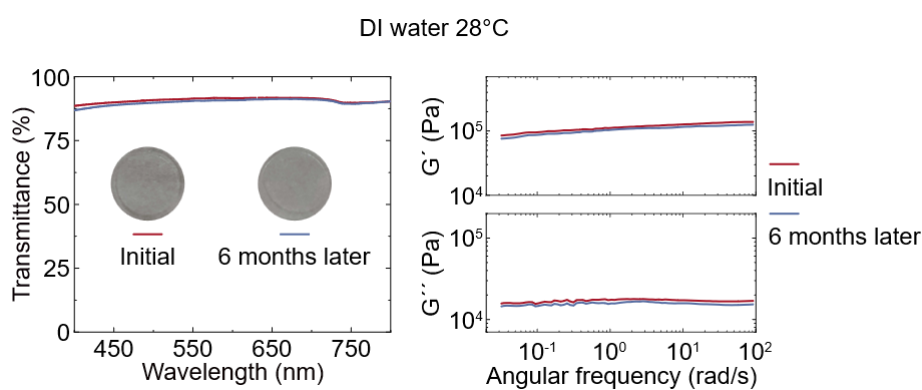
factor of $\sim 10^3$ compared to a system without elasticity (Fig. 5B in main text). Consequently, the nucleation rate is reduced by a factor of $\exp(-10^3)$, and the corresponding induction time ($\tau \sim 1/J$) is increased astronomically. For a typical unconstrained system where τ is on the order of minutes at best, the induction time in our elasticity-stabilized state extends far beyond practical and experimental timescales (e.g., > years).

This estimate aligns with our experimental observation: the as-swollen SDTP-gels show no detectable phase separation for over six months (see **Supplementary Figure. SII-5** in the revised manuscript). Therefore, while thermodynamically metastable, the transparent state is kinetically stabilized to such a degree that it is effectively permanent for all practical applications discussed in this work. We have added this discussion to the revised manuscript (**Sections 2.1 and 2.3**), the ESI.

Modification to the manuscript (Main text, Fabrication and Thermal Plasticity of SDTP-gels, Page 8): This transparent state remains unchanged for over six months (**Supplementary Figure. SII-5A**), demonstrating that kinetic stabilization by the elastic network renders it effectively permanent on all practical experimental timescales.

Modification to the manuscript (Main text, Fabrication and Thermal Plasticity of SDTP-gels, Page 19): Furthermore, the enormous elastic contribution shown in Fig. 5B raises the nucleation barrier ΔG_{NS} by approximately three orders of magnitude compared to an unconstrained system. This reduces the nucleation rate $J \propto \exp[-\Delta G_{NS}/k_B T]$ exponentially, extending the predicted induction time τ ($\sim 1/J$) to values far exceeding practical timescales. This theoretical prediction of extreme kinetic stability is in full agreement with our experimental observation that the transparent state remains unchanged for over six months (**Supplementary Figure. SII-5**).

Modification to the manuscript (ESI, Supplementary Note II, Page S12):



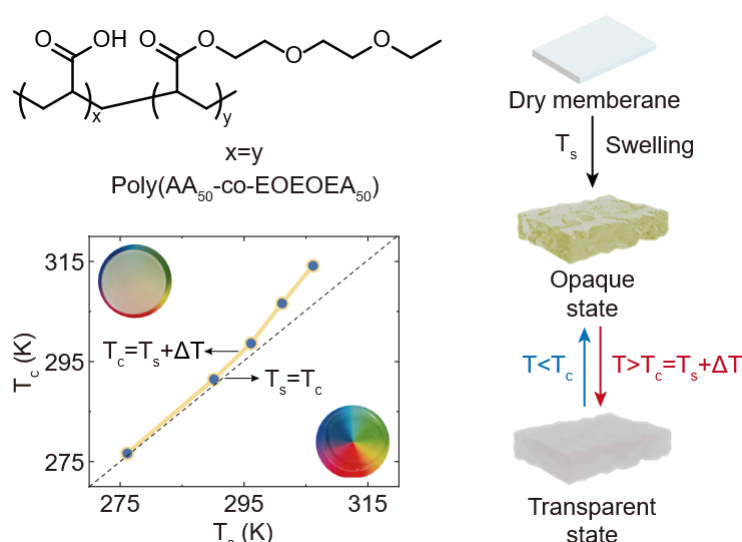
Supplementary Figure SII-5. Long-term kinetic stability of the transparent state. The transmittance at 550 nm (or the visual appearance) of a programmed SDTP-gel in the supersaturated state remains unchanged over a period of six months, indicating exceptional kinetic stability against phase separation.

Specific Comment 5: *The manuscript claims to establish a “universal design rule” for history-responsive materials. However, the study focuses exclusively on one polymer system—PVP. To substantiate the claim of generality, the authors should demonstrate the SDTP effect in at least one other chemically distinct polymer system. Without such*

validation, the proposed “universal rule” risks being perceived as a material-specific phenomenon tied to PVP’s solubility parameters.

Our response: Thanks for this question. As this reviewer required, we showcased one of our recent new findings: a random copolymer (other than polyvinyl acetals), poly(2-(2-ethoxyethoxy)ethyl acrylate-co-acrylic acid), with certain feeding molar ratio of monomers (e.g., 1:1), shows similar thermal plastic effect. We have added this case in our revised manuscript. However, the specific molecular mechanism is still under exploration.

Modification to the manuscript (Main text, Conclusion section, Page 24): We have extended these design rules to other polyvinyl acetals, such as poly(vinyl butyral) (PVB), as well as to alternative polymer systems (e.g., poly(2-(2-ethoxyethoxy)ethyl acrylate-co-acrylic acid)) beyond polyvinyl acetals (see **Supplementary Note V** and **Supplementary Figures. SVI-1–SVI-2, Supplementary Movie S9**). These systems exhibit analogous thermal plasticity behavior, confirming that the SDTP phenomenon is not unique to PVP but represents a more general design principle across different polymer chemistries, whereas conventional systems such as PNIPAM exhibit a fixed transition temperature that is insensitive to swelling history.



Supplementary Figure SVI-2. Thermal plasticity behavior of poly(2-(2-ethoxyethoxy)ethyl acrylate-co-acrylic acid) gel (Supplementary Movie S9).

Modification to the manuscript (Main text, Supplementary Note VII, Supplementary Movie S9): **Supplementary Movie S9. Poly(AA-co-EOEOEA) exhibits tunable phase transition temperatures depending on the swelling temperature.** The turbidity transition is rapid and occurs uniformly across the entire sample, demonstrating a reversible transparent-to-opaque change that records thermal history.

Specific Comment 6: In contrast to the SDTP behavior observed in PVP gels, classical PNIPAM systems exhibit immediate phase separation. This critical difference remains insufficiently analyzed in the manuscript. Based on literature evidence (e.g.,

Macromolecules 2024, 57, 5398), this discrepancy may stem from the extremely narrow temperature gap between the binodal temperature (T_{bn}) and spinodal temperature (T_{sp}) in PNIPAM systems. However, readers may reasonably question: Which intermolecular interactions precisely govern the magnitude of the T_{bn} - T_{sp} gap? Furthermore, Can this gap be rationally engineered through molecular design? For instance, how do parameters such as the degree of propanal functionalization and the molecular weight of PVP influence this gap? Addressing these questions would significantly advance the broader applicability of SDTP-based methodologies.

Our response: We thank the reviewer for raising these insightful questions and suggestions, which are critical for establishing SDTP as a general design strategy. We agree that understanding the molecular origin of the T_{bn} - T_{sp} gap and its dependence on molecular parameters is essential.

In PNIPAM, the extremely narrow T_{bn} - T_{sp} gap arises from the cooperative interplay between hydrogen bonding of the amide groups and hydrophobic interactions of the isopropyl side chains. This strong coupling results in a steep concentration dependence of the interaction parameter $\chi(\phi)$, leading to a metastable region that is both narrow and nearly composition-invariant (Wang and Hashimoto, *Macromolecules*, 2024, 57, 5398). Consequently, once the system exceeds T_{bn} , it rapidly enters the unstable spinodal region and phase separates immediately, leaving no room for thermal history programming.

In contrast, the PVP-based SDTP-gels exhibit a broader metastable region. In this preliminary stage, we attribute this to the distinct molecular structure of poly(vinyl acetal)s: the acetal rings increase chain rigidity, while the residual hydroxyl groups provide additional hydrogen-bonding sites. These features likely moderate the concentration dependence of $\chi(\phi)$, thereby widening the T_{bn} - T_{sp} gap and enabling the elastic-gated nucleation process that underlies SDTP.

Regarding the rational engineering of this gap, our preliminary results suggest that both the degree of acetalization and molecular weight influence the phase behavior. As shown in our response to in Supplementary Note V, increasing the acetalization degree and molecular weight shifts the phase diagram to higher temperatures. However, a systematic mapping of how these parameters quantitatively affect the T_{bn} - T_{sp} gap remains an ongoing effort that will require a combination of theoretical modeling and multiscale structural characterization. We hope such lacking in current state would not delay the publication of this work.

We have added a discussion of these points in the revised manuscript to provide a more comprehensive analysis of the discrepancy between PNIPAM and PVP systems.

Modification to the manuscript (Main text, Thermally Adaptive Swelling section, Page 11):

The contrasting behavior can be understood from their respective phase diagrams. In PNIPAM/water, the binodal and spinodal curves are separated by an exceptionally narrow temperature gap (ca. 0.6 °C)²⁹. Consequently, once the temperature exceeds the binodal, phase separation occurs immediately, leaving no room for thermal history programming. In contrast, poly(vinyl acetal)-based systems such as PVP possess a

broader metastable region due to the presence of acetal rings and residual hydroxyl groups, which alter the concentration dependence of the polymer–water interaction parameter. This broader window prevents phase separation during swelling, enabling the elastic-gated nucleation mechanism that underlies SDTP behavior.

Responses to Reviewer #3

General Comment: *In this manuscript, the authors report a biomimetic material that exhibits trainable thermoresponsiveness. The underlying mechanism is attributed to an elastic-gated nucleation-and-growth process, which is systematically investigated through both qualitative and quantitative analyses under varying temperature and salt conditions. The authors further demonstrate a potential practical application as a low-temperature indicator for monitoring and reporting vaccine over-freezing exposure. Overall, this work presents a forward-looking and potentially impactful advance, and I believe the manuscript would be suitable for publication in Nature Communications.*

Our responses: Thanks for your recognition for this work, and we will continue to strive to do better. Please see our point-by-point response as follows:

Specific Comment 1: *It would be beneficial if the authors could provide a more conclusive discussion of the core mechanism and the associated design principles.*

Our response: We thank the reviewer for this suggestion to strengthen the conclusive discussion of our mechanism. In the revised manuscript, we have significantly expanded the discussion in the Conclusion section (Pages 21-22) to distill the core mechanism and design principles.

The SDTP behavior emerges from two synergistic and essential mechanisms:

- (1) The equilibrium water content of the polymer network is not fixed but adapts to both the temperature and the salt composition of the surrounding solution during swelling. This process allows the gel to autonomously “encode” its thermal and ionic history directly into its thermodynamic state.
- (2) The stiffness (or shear modulus) of the network increases with the temperature at which it was previously swollen, thereby creating a tunable mechanical barrier that opposes phase separation. Upon reheating, this stored history is “read out” as a precisely programmable phase transition temperature. Specifically, the transition occurs at a temperature that equals the original swelling temperature plus a controllable offset, which is determined by the network’s history-dependent stiffness and the degree of supersaturation.

The universal design rules derived from this work are:

- (i) The polymer-solvent combination must possess a wide metastable region to remain stable and avoid premature phase separation during the initial history-writing swelling step.
- (ii) The network’s stiffness must be history-sensitive; that is, it must depend on the specific temperature and solution conditions experienced during swelling. This variable stiffness directly dictates the energy barrier for phase separation, enabling the programmability of the response.

(iii) During swelling, the polymer chains must relax and reorganize faster than water can diffuse into the network. This ensures the network adapts its structure to the encoding conditions.

We believe this clarified framework provides a concrete and practical roadmap for designing the next generation of history-responsive materials. We acknowledge that the field of quantitatively programming material history is still in its early stages. To further elucidate the molecular-level origins of thermal plasticity and to refine these design rules into a predictive theory, future work will necessitate a combination of advanced in-situ experiments, multi-scale simulations, and the systematic exploration of a broader range of polymer chemistries and network architectures.

We have included this core mechanism and the associated design principles in the Conclusion section in the revised manuscript.

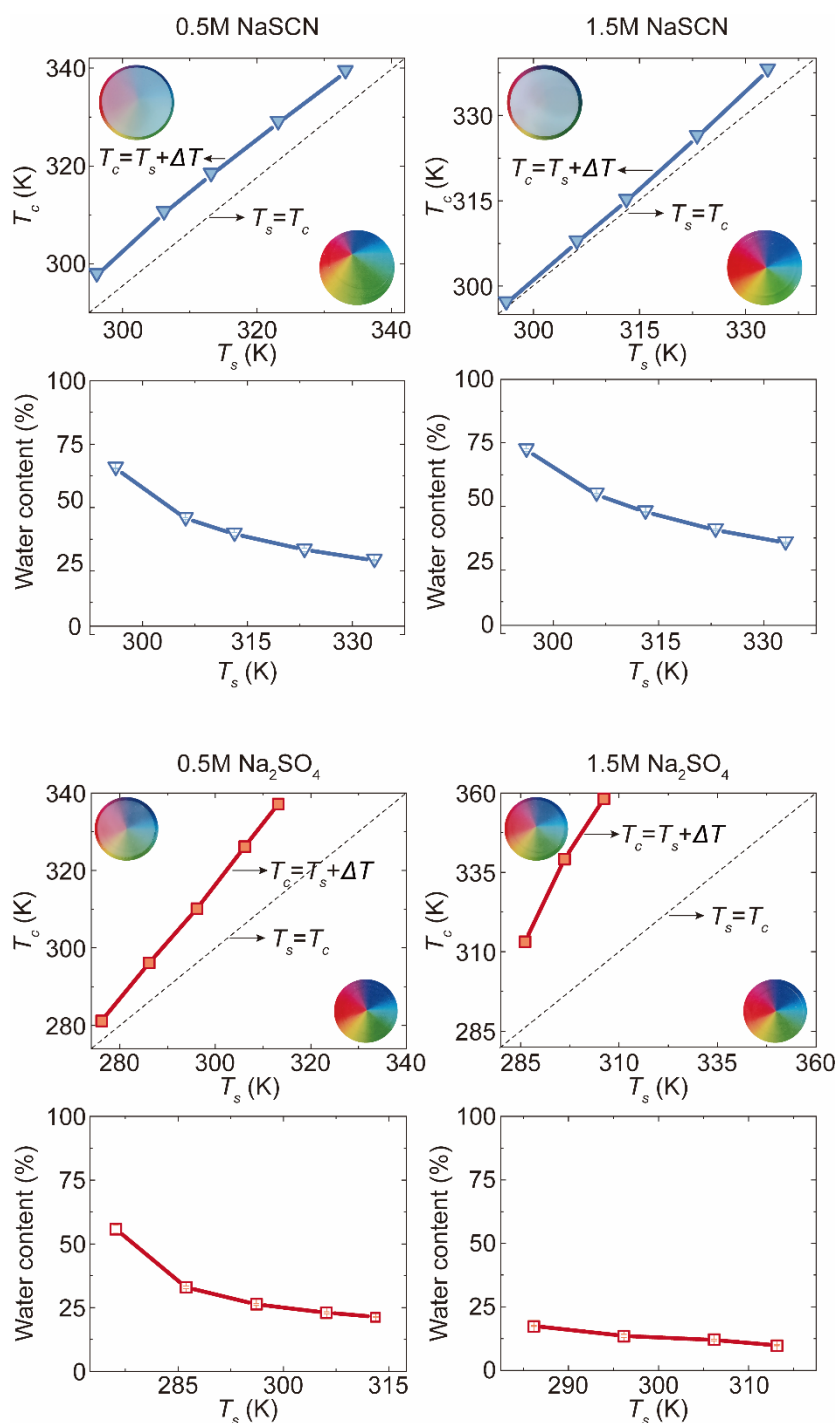
Modification to the manuscript (Main text, Conclusion section, Page 24): This raises a key question: what is the physical origin of the thermal plasticity observed here, which is absent in conventional PNIPAM gels? We propose that our system satisfies three synergistic design principles that collectively enable this property. First, and in contrast to the narrow metastable window of typical PNIPAM, our polymer-solvent system must possess a sufficiently wide gap between its binodal and spinodal curves. This thermodynamic stability is essential to prevent phase separation during the history-encoding swelling stage. Second, the network's stiffness must be sensitively tuned by the very conditions (temperature and ionic environment) of that swelling, thereby translating history into a programmable mechanical barrier to phase separation. Third, kinetically, chain relaxation must outpace water diffusion to permit the network to adaptively reorganize during encoding. A complete molecular-level picture will be refined through future studies integrating theoretical modeling and multiscale in situ characterization.

Specific Comment 2: *Regarding the salt-gated thermal plasticity, it would be important to clarify whether the observed behavior depends solely on the ionic species, or whether it is also influenced by salt concentration.*

Our response: According to your request, we further investigated the effect of salt concentration on the thermal plasticity behavior. In addition to the 1 M NaSCN and 1 M Na₂SO₄ conditions originally reported, we performed experiments at 0.5 M and 1.5 M for both salts. For the NaSCN (salting-in) system, increasing the salt concentration from 0.5 M to 1.5 M leads to higher equilibrium water content and a lower phase transition temperature at the same swelling temperature, indicating an enhanced salting-in effect with increasing concentration. For the Na₂SO₄ (salting-out) system, the opposite trend is observed: higher salt concentration results in lower equilibrium water content and a higher phase transition temperature, demonstrating a stronger salting-out effect. These results show that the ionic species determines the direction of modulation, while the salt concentration controls the magnitude. Thus, the thermally programmable behavior is governed by both the identity and the concentration of the salt, which together tune the equilibrium water content and, consequently, the phase separation conditions. We have added this discussion and the corresponding data (0.5 M and 1.5 M for both salts, measured at multiple swelling temperatures) to the revised manuscript and the ESI.

Modification to the manuscript (Main text, Fabrication and Thermal Plasticity of SDTP-gels section, Page 8): The influence of salt concentration on SDTP behavior was also investigated (**Supplementary Figure. SII-8**). The results confirm that the ionic species determines the direction of modulation, while the concentration controls the magnitude.

Modification to the manuscript (ESI, Supplementary Note II, Page S15):



Supplementary Figure SII-8. Equilibrium water content as a function of swelling temperature (T_s) for SDTP-gels in NaSCN (left) and Na₂SO₄ (right) at

salt concentrations of 0.5 M and 1.5 M. For NaSCN (salting-in), higher salt concentration leads to increased water content, while for Na₂SO₄ (salting-out), higher concentration results in decreased water content. These data demonstrate that the ionic species determines the direction of modulation, whereas the salt concentration controls the magnitude, as reflected in both the swelling degree and the resulting ΔT .

Specific Comment 3: *Based on the proposed mechanism, the authors are encouraged to discuss how molecular weight, molecular weight distribution, and grafting ratio may affect the phase diagram and thermoresponsive behavior.*

Our response: We thank the reviewer for this valuable suggestion. We agree that if the proposed mechanism is general, molecular parameters such as molecular weight, molecular weight distribution, and grafting ratio (acetalization degree) should influence the equilibrium swelling and thermoresponsive behavior by altering network architecture. To address this, we performed a series of comparative experiments.

Specifically, we prepared two sets of samples: (i) varying molecular weight while keeping the grafting ratio constant, and (ii) varying the grafting ratio while keeping molecular weight constant. These samples were equilibrated in water, NaSCN, and Na₂SO₄ at different swelling temperatures, and their equilibrium water content and phase transition temperature were measured.

Regarding molecular weight distribution, we acknowledge that it cannot be independently controlled because our PVP is synthesized from commercial PVA. To probe its effect, we blended PVP samples of different molecular weights and compared the blend with the individual components. The results show that the blend exhibits intermediate responses, with the phase transition temperature and water content varying systematically with the mixing ratio.

Our experimental results show that, under identical swelling conditions, lower molecular weight or lower grafting ratio samples exhibit higher equilibrium water content and lower T_c , while higher molecular weight or higher grafting ratio samples show the opposite trend. These findings are consistent with our proposed mechanism: molecular weight and grafting ratio affect network chain density and elasticity, thereby modulating the swelling equilibrium and phase diagram.

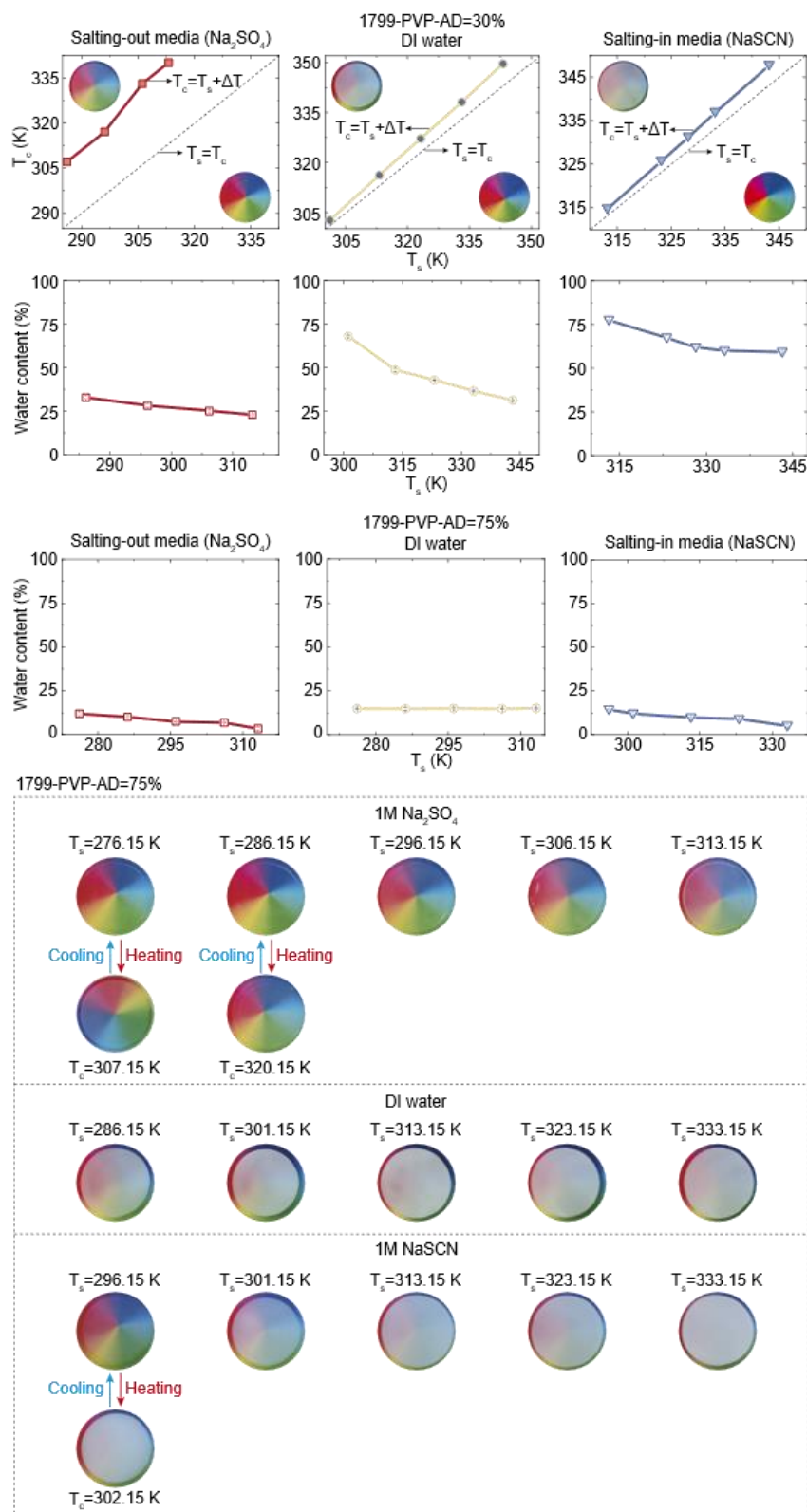
Notably, for the high grafting ratio sample (with the same molecular weight), we observed behavior slightly different from the reference sample. Under certain swelling conditions, this sample became turbid during swelling and failed to form a stable transparent swollen state. We hypothesize that once the acetalization degree exceeds a certain threshold, the thermally adaptive swelling behavior may be compromised. This contrasts with the elasticity-controlled, wide-window thermal adaptability reported for our SDTP-gels. The underlying reasons require further investigation.

We have added the corresponding data and discussion to the ESI and briefly summarized the conclusions in the revised manuscript.

Modification to the manuscript (Main text, Fabrication and Thermal Plasticity of SDTP-gels section, Page 8): The molecular weight and AD also significantly affect the SDTP behavior. As shown in **Supplementary Figures. SII-10–SII11**, lower AD or

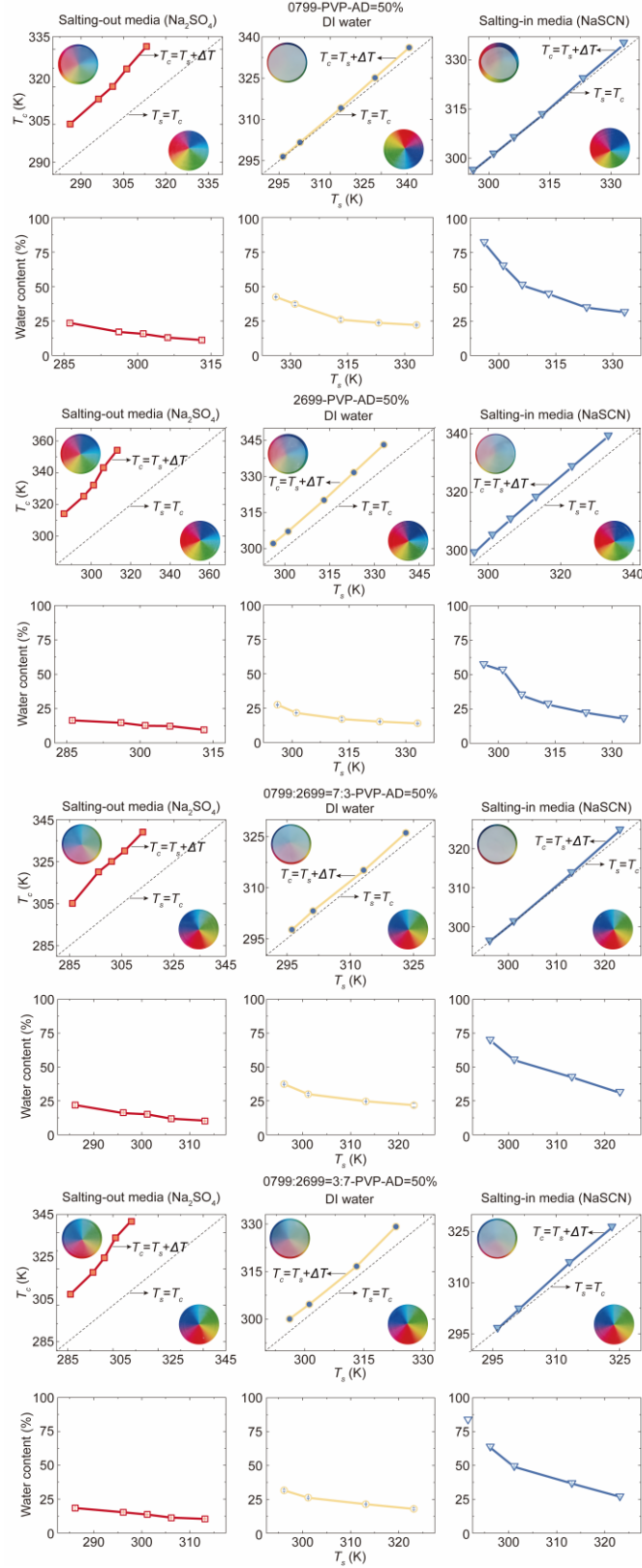
lower molecular weight leads to higher equilibrium water content and a lower T_c . Blending polymers of different molecular weights yields intermediate responses.

Modification to the manuscript (ESI, Supplementary Note II, Pages S17-18):



Supplementary Figure SII-10. Effect of acetalization degree (AD) on SDTP

properties. Equilibrium water content (ϕ_{weq}) and critical transition temperature (T_c) of SDTP-gels with different AD values (low AD vs. 50% AD, the latter corresponding to the reference in Fig. 2 of the main text). Under identical swelling conditions, lower AD leads to higher ϕ_{weq} and lower T_c , indicating that a higher hydroxyl content enhances hydration and reduces the phase transition temperature.



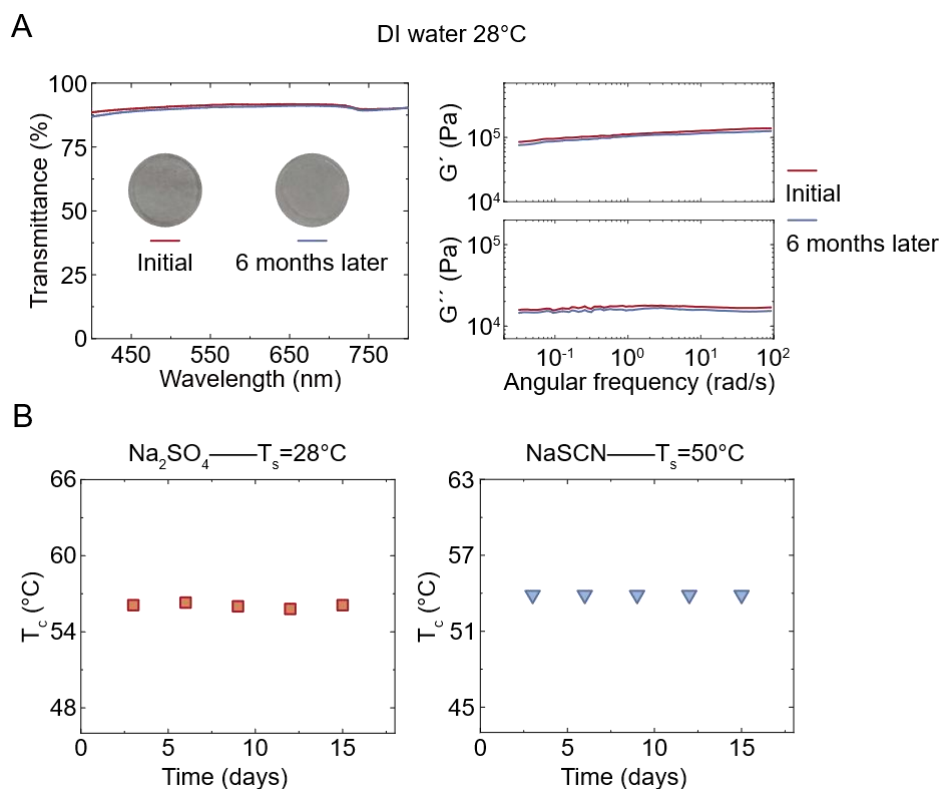
Supplementary Figure SII-11. Effect of molecular weight on SDTP properties. With comparison to the degree of polymerization at 1700 (Fig. 2 in main text), higher molecular weight leading to lower equilibrium water content and higher T_c . The blend of PVP with different molecular weight but identical AD exhibits intermediate responses, with the phase transition temperature and water content varying systematically with the mixing ratio.

Specific Comment 4: *The impact of time on the thermally adaptive swelling behavior should be clarified. In particular, do salt-treated samples exhibit consistent T_c values after sufficient equilibration time when measurements are performed?*

Our response: We thank the reviewer for this question. To verify the stability of T_c over time, we kept salt-treated samples (both Na_2SO_4 and NaSCN) in their respective media at the swelling temperature for more than two weeks and measured T_c at regular intervals. No significant change in T_c was observed, confirming that once the swelling equilibrium is reached, the programmed T_c remains stable over prolonged periods. This point has been clarified in the revised manuscript.

Modification to the manuscript (Main text, Fabrication and Thermal Plasticity of SDTP-gels section, Page 8): Importantly, the phase transition behavior remains stable over numerous cycles and extended swelling periods, with negligible change observed (Supplementary Figure. SII-5B, Supplementary Figure. SII-7).

Modification to the manuscript (ESI, Supplementary Note II, Page S12): Importantly, the phase transition behavior remains stable over numerous cycles and extended swelling periods, with negligible change observed (Supplementary Figure. SII-5B, Supplementary Figure. SII-7).



Supplementary Figure SII-5. Stability of the transparent state and phase transition temperatures upon long-term swelling in water and salt solutions. (A) Transmittance at 550 nm, storage modulus (G'), and loss modulus (G'') of a programmed SDTP-gel during six months of swelling in water at 28 °C. (B) Critical phase transition temperatures (T_c) of SDTP-gels measured after being swollen in 1 M Na₂SO₄ and 1 M NaSCN aqueous solutions for several days.

Specific Comment 5: *The authors are encouraged to more clearly explain how the training of thermoresponsiveness is manifested experimentally and how it is reflected in the material response.*

Our response: Thank you for raising this point. The central experimental observation is that the phase transition temperature of the gel can be precisely programmed through a swelling-based “training” protocol. In practice, this training is performed by equilibrating a dried gel in a specific salt solution (e.g., 1 M Na₂SO₄) at a chosen training temperature. The material’s response directly reflects this training: upon heating, the gel undergoes its phase transition at a new temperature that depends linearly on the training temperature. For example, a gel trained at 20 °C phase-separates at approximately 45 °C, whereas training at 30 °C shifts the transition to about 55 °C. This programmed response is also modulated by the salt identity of the training solution. Importantly, the programmed transition temperature is stable over multiple thermal cycles and can be erased by drying the gel, allowing the material to be reconfigured under a new set of training conditions.

We have more clearly explain how the training of thermoresponsiveness is manifested experimentally and how it is reflected in the material response in the revised manuscript.

Modification to the manuscript (Main text, Fabrication and Thermal Plasticity of SDTP-gels section, Pages 9): The SDTP-gel system replicates three features of biological thermal plasticity: autonomous memory encoding, dynamic threshold adaptation, and non-volatile re-programmability. Experimentally, the “training” is achieved by swelling a dried gel at a defined temperature T_s in a selected salt solution, which sets the equilibrium water content and network elasticity. The material’s thermoresponsive behavior directly reflects this training: upon heating, the gel undergoes its transparency-to-opacity transition at a new critical temperature T_c that scales linearly with T_s . Thermal history is thus autonomously stored, while T_c can be dynamically updated through retraining at a different T_s or in a different salt medium. Crucially, reswelling at reduced T'_s non-destructively resets the thermal memory, enabling sequential adaptation cycles. The thermodynamic basis of these SDTP traits can be further elucidated via analysis of the swollen network phase diagram.

Specific Comment 6: *It would be helpful to further clarify the durability, reversibility, and dynamic response of the SDTP-gel under different temperature and salt stimuli. For example, how can a high- T_c state induced by Na₂SO₄ treatment be converted back to a low- T_c state, and is this process reversible and repeatable?*

Our response: We thank the reviewer for this helpful suggestion. The high T_c state induced by Na₂SO₄ treatment can be converted to a low T_c state by reswelling the gel in water or a salting-in medium such as NaSCN, as shown in Fig. 2CII. This conversion

arises from the change in equilibrium water content and network modulus G_e due to the different Hofmeister effects. Importantly, the process is fully reversible: returning the gel to Na_2SO_4 restores the high T_c state. This reversible conversion can be repeated multiple times without loss of functionality, confirming the durability and versatile reprogrammability of the SDTP-gels. To emphasize this, we have added a reversible arrow in **Fig. 2CII** in the revised manuscript.

Modification to the manuscript (Main text, Fabrication and Thermal Plasticity of SDTP-gels section, Page 9): Notably, the high- T_c state induced by Na_2SO_4 can be reverted to a low- T_c state by subsequent reswelling in water or NaSCN , demonstrating full reversibility.