Supporting Information

Temperature- and Creep-Resistant Diels-Alder Salogels for Shape Stabilization of Salt Hydrate Phase Change Materials

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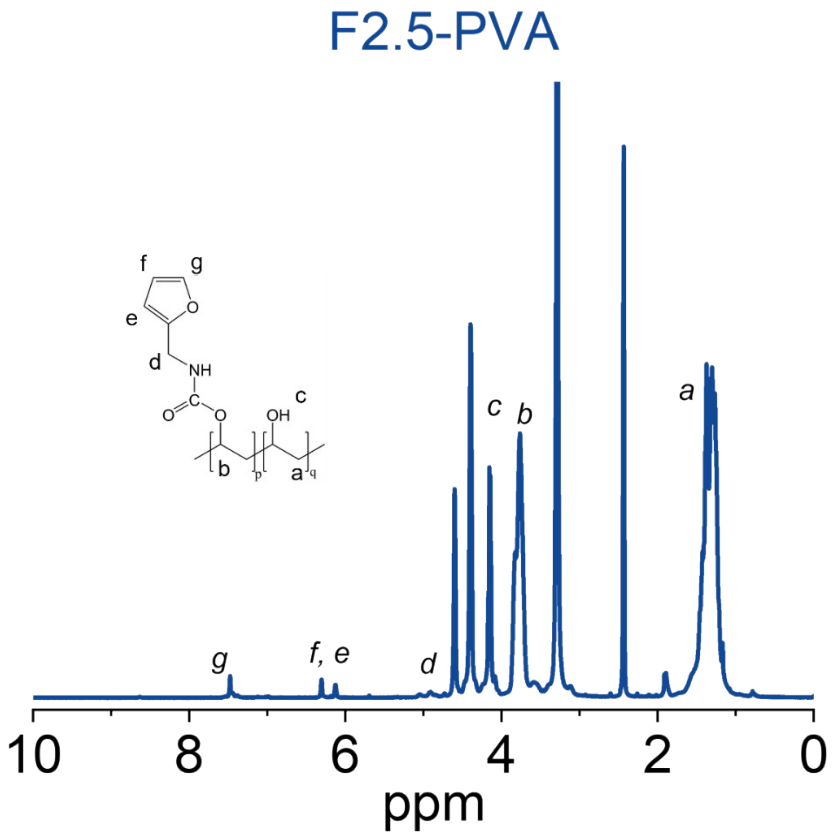

Fig. S1. ^{1}H NMR spectrum of F2.5-PVA.

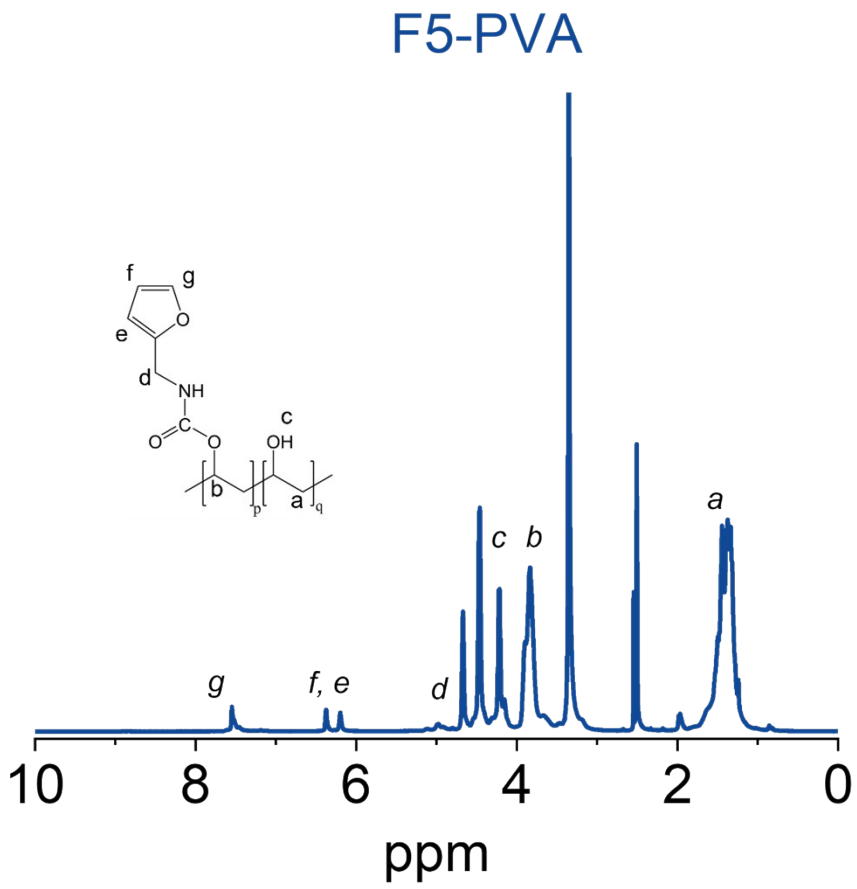

Fig. S2. [1]H NMR spectrum of F5-PVA.

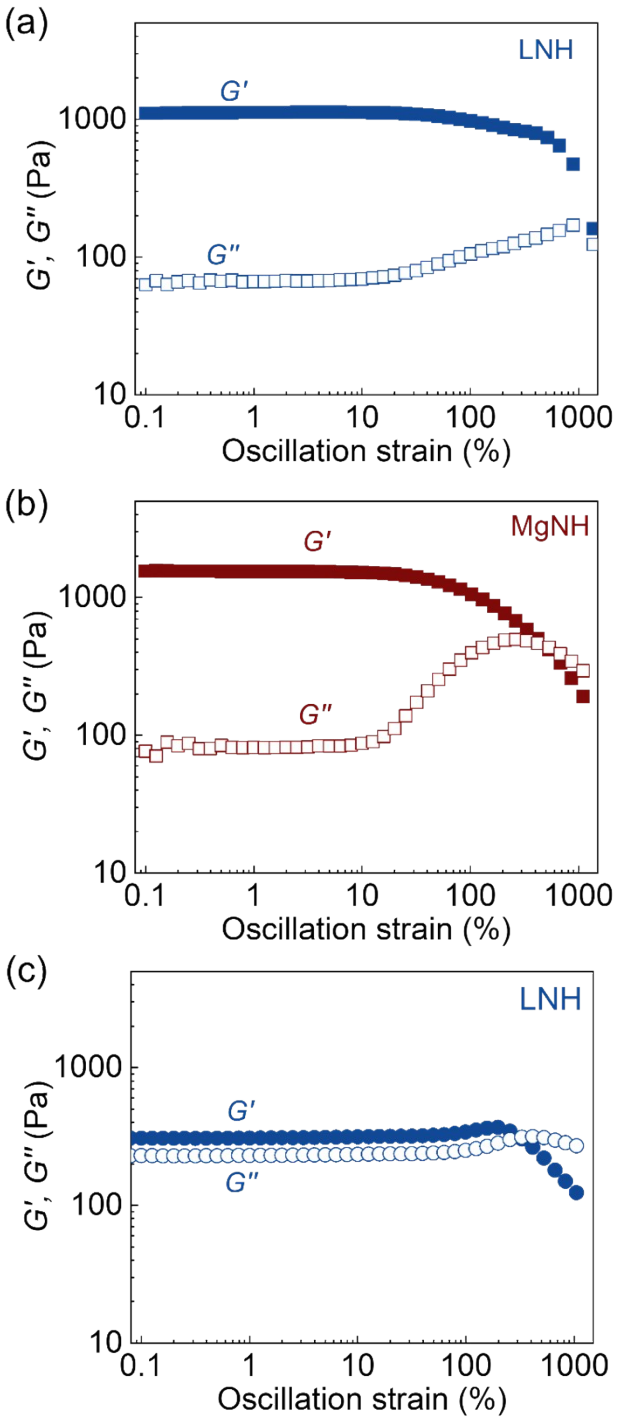

Fig. S3. Oscillatory rheology strain sweep experiments performed at a frequency of 10 rad/s for F10-PVA/BM-PEG salogel in (a) LNH at 25 °C and (b) MgNH at 95 °C, and (c) PVA/borax-10 salogel in LNH at 25 °C. Polymer concentration was 5 wt% for both DA (F-PVA) and boronate ester (PVA) gels. Strain sweep is not shown for PVA/borax-10 salogel in MgNH because the PVA/borax does not exist in the gel state but rather as a sol at 95 °C.

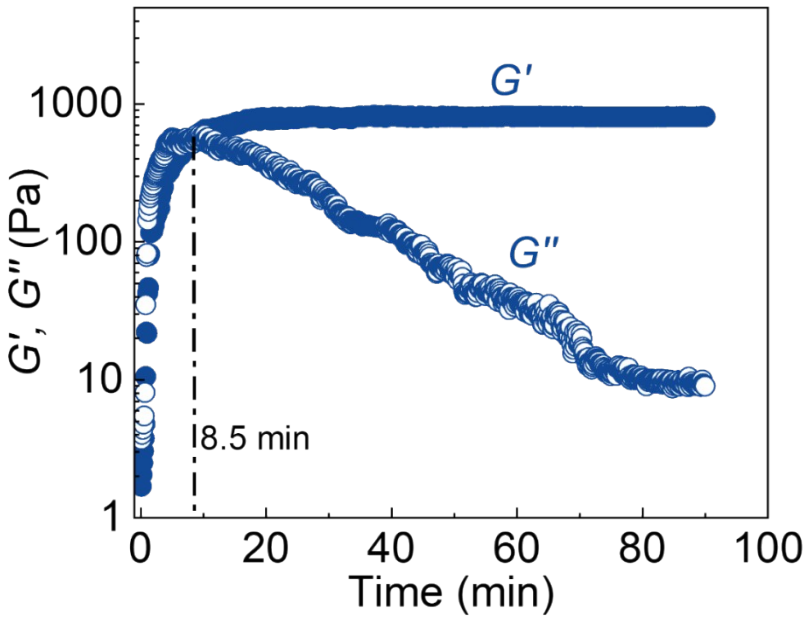

Fig. S4. Oscillatory rheology time sweep experiments at 1% strain and frequency of 10 rad/s showing gelation time from G' and G'' crossover for F10-PVA/BM-PEG salogel at 70 °C in LNH. Polymer (F10-PVA) concentration was 5 wt%.

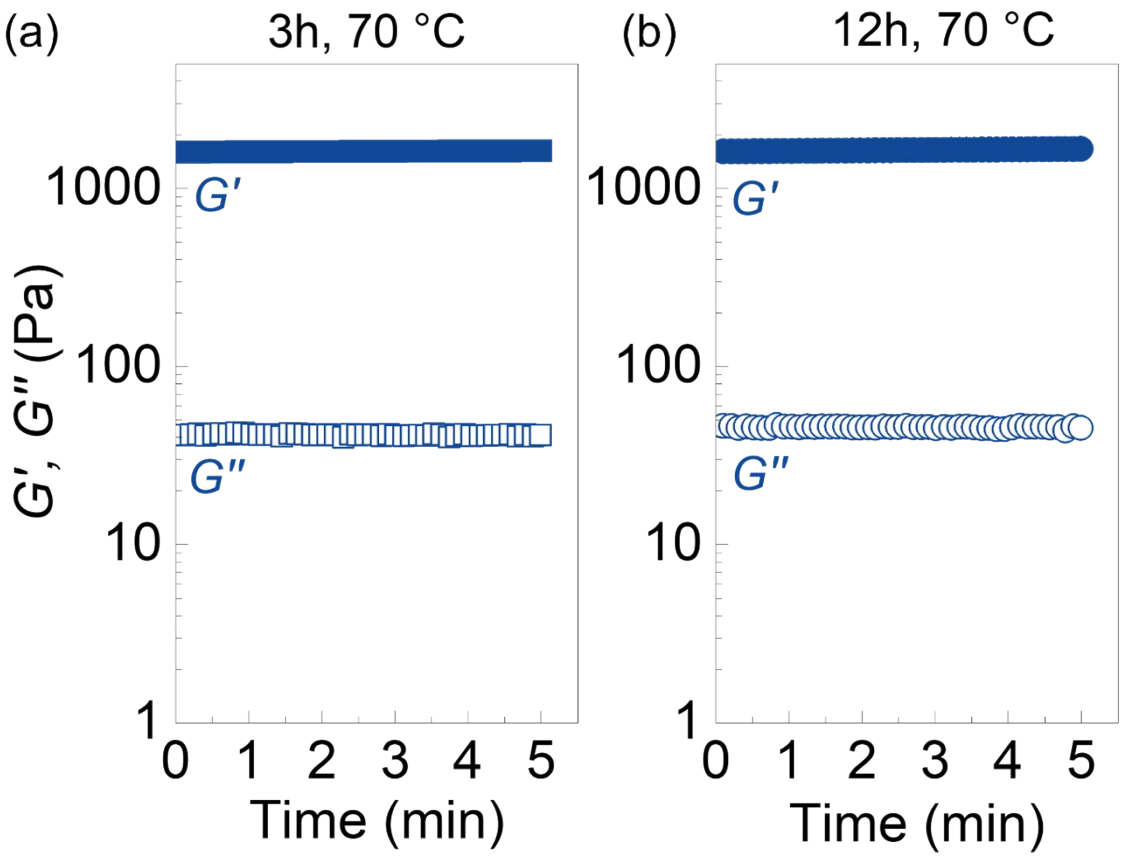

Fig. S5. Oscillatory rheology time sweep experiments at 1% strain and frequency of 10 rad/s to check for completion of DA crosslinking after (a) 3h and (b) 12h exposure of F10-PVA/BM-PEG in LNH to 70 °C. Polymer (F10-PVA) concentration was 5 wt%.

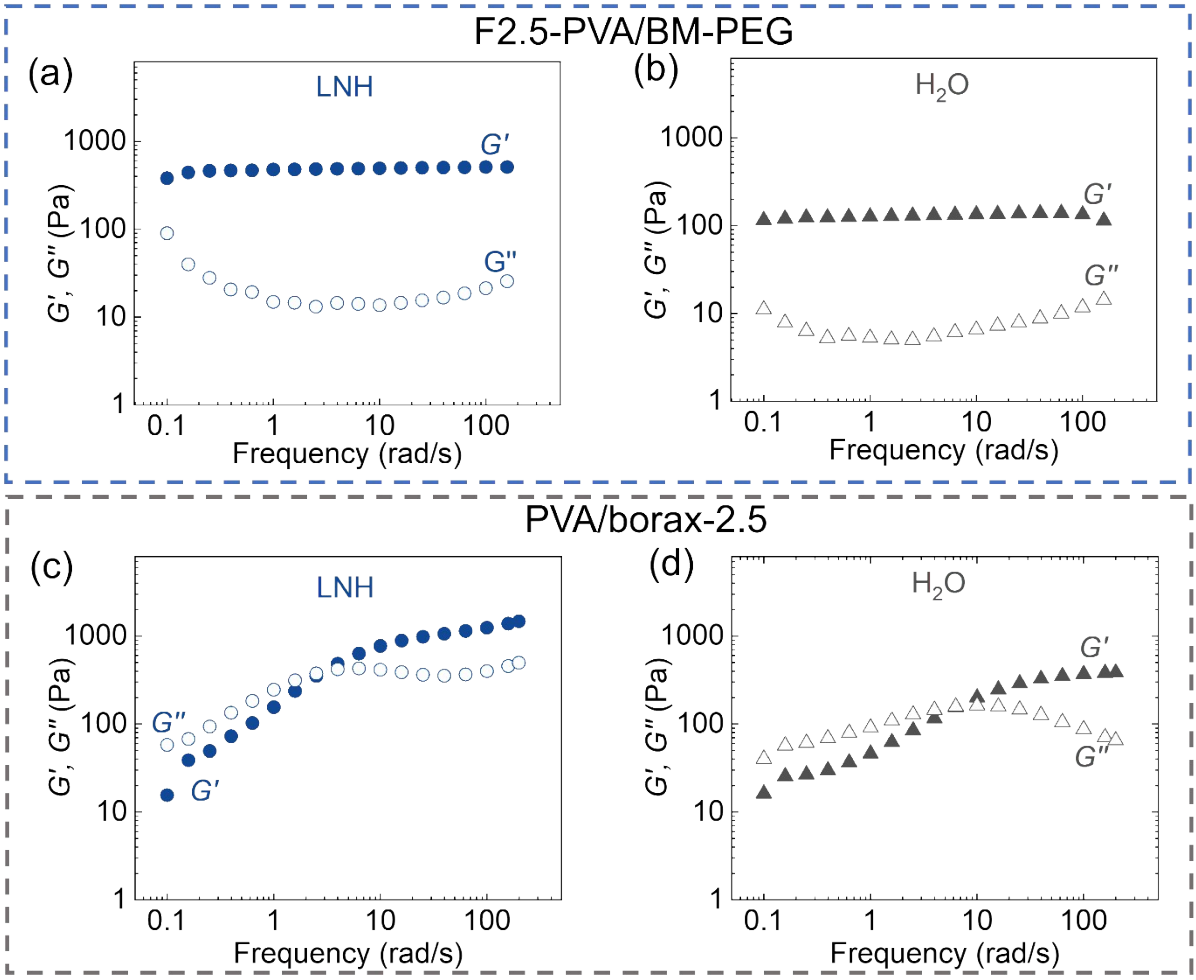

Fig. S6. Frequency sweep oscillatory rheology experiments for DA (a) salogel and (b) hydrogel (F2.5PVA/BM-PEG), and boronate ester (PVA/borax-2.5) (c) salogel and (d) hydrogel. These experiments were performed at 25 °C and 1% strain. Polymer concentration was 5 wt% for both DA (F10-PVA) and boronate ester (PVA) gels.

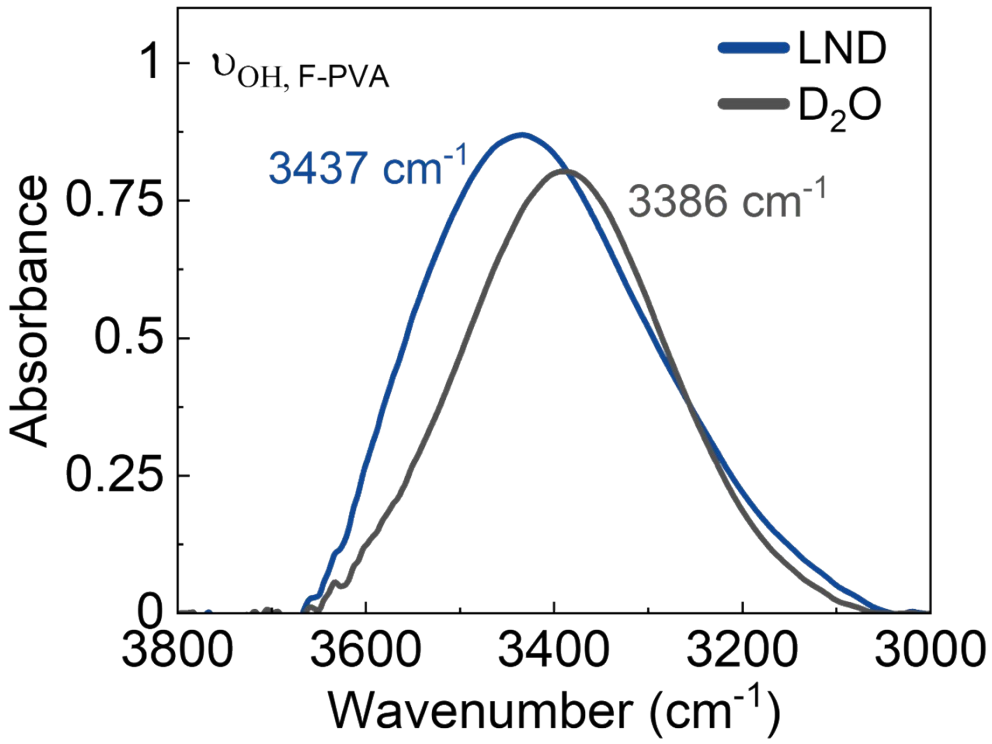

Fig. S7. ATR-FTIR spectrum showing -OH stretch peak from hydroxyl groups in F2.5-PVA in deuterated LNH (LND) and D_2O.

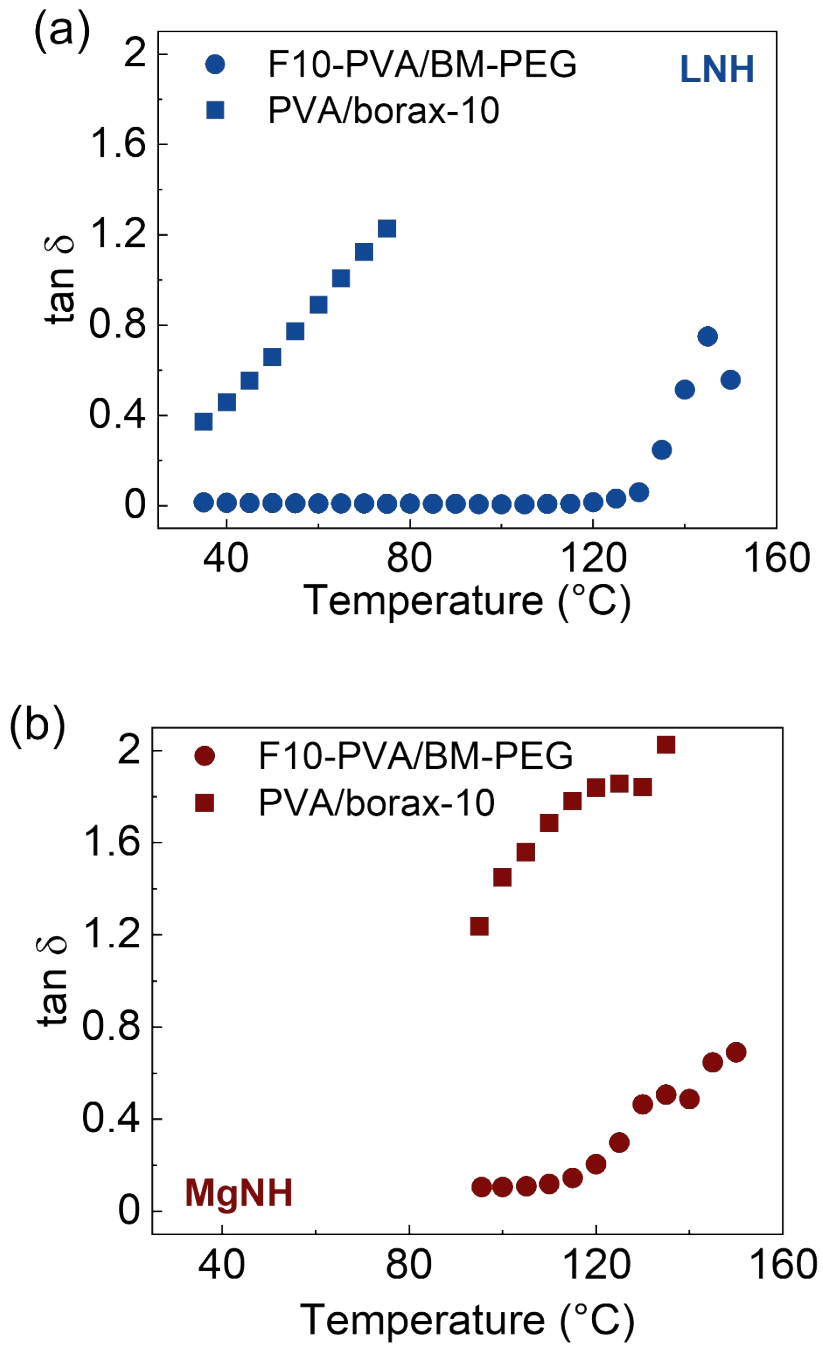

Fig. S8. Tan δ as a function of temperature obtained from temperature sweep rheology experiment for DA and boronate ester salogels with 10 mol% -OH groups consumed by crosslinks in (a) LNH and (b) MgNH. Experiment was performed at a frequency of 10 rad/s and 1% strain. Polymer (PVA and F10-PVA) concentration was 5 wt%.

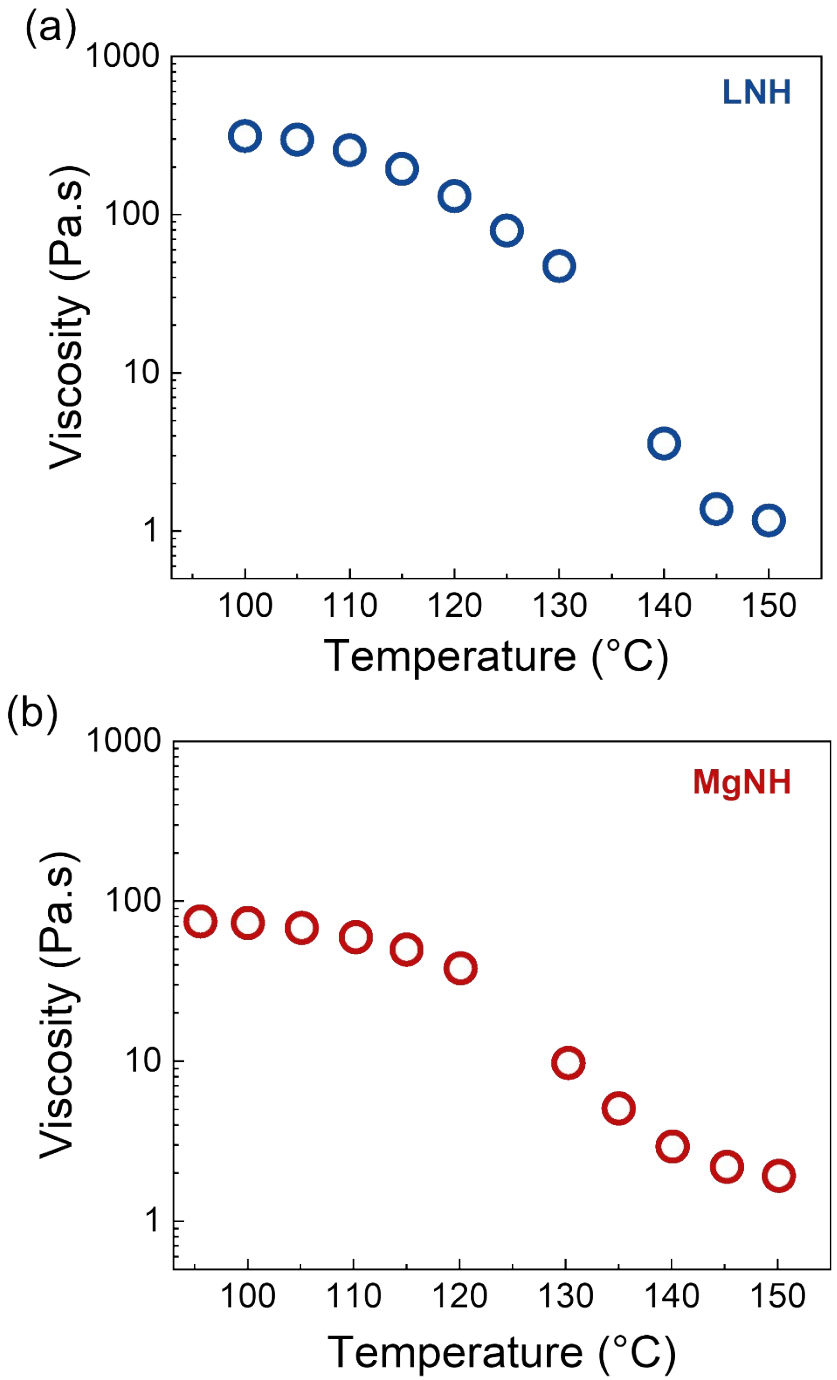

Fig. S9. Viscosity as a function of temperature in the retro-DA reaction region (100-150 °C) obtained from temperature sweep rheology experiment for DA salogels with 10 mol% -OH groups consumed by crosslinks in (a) LNH and (b) MgNH. Experiment was performed at a frequency of 10 rad/s and 1% strain. Polymer (PVA and F10-PVA) concentration was 5 wt%.

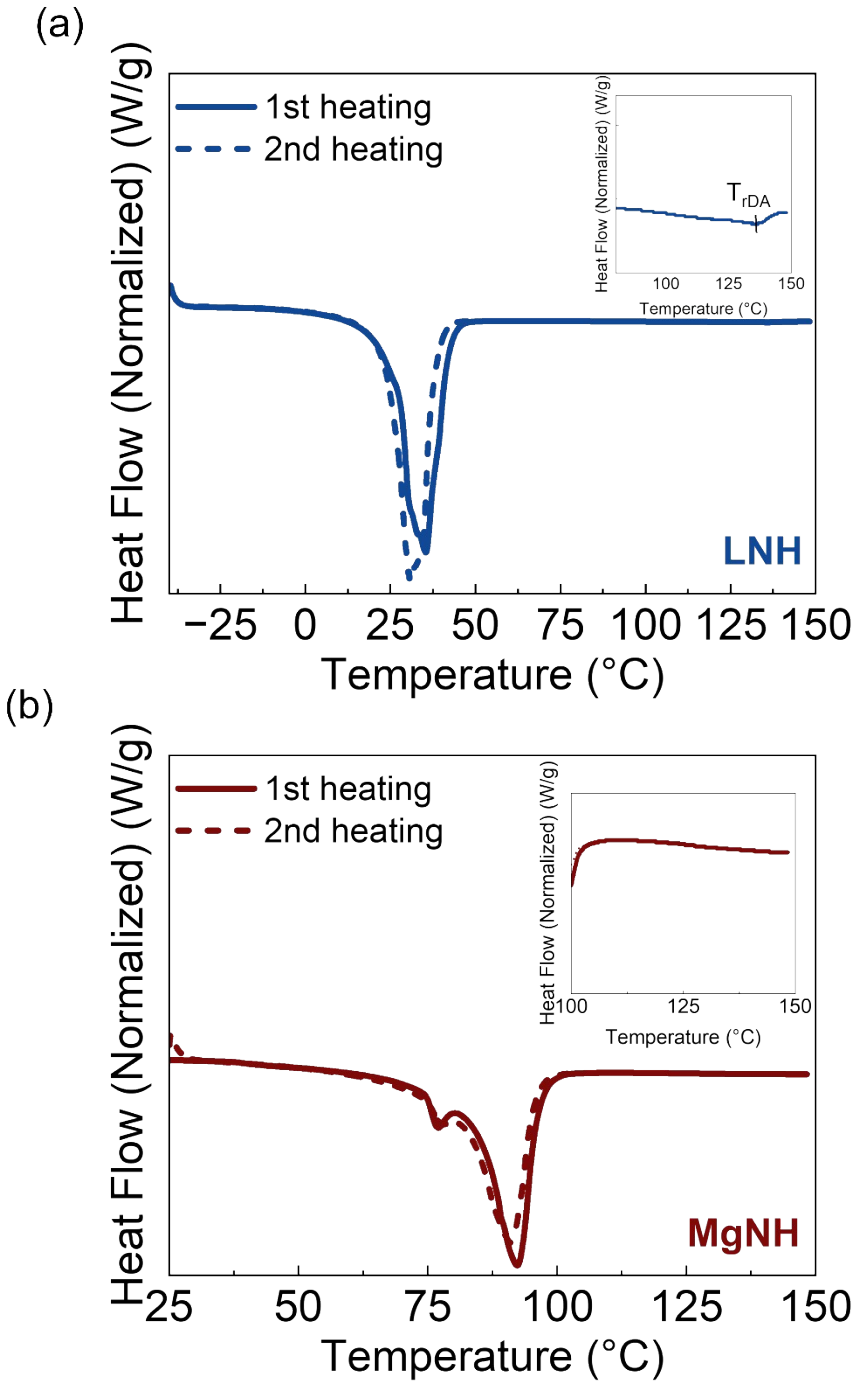

Fig. S10. DSC thermograms of F10-PVA/BM-PEG salogel in (a) LNH and (b) MgNH showing the melting of the salt hydrates during consecutive heating cycles of the DA salogel to 150 °C. Inset showing the retro-DA reaction temperature (T_{rDA}) in LNH in (a) and the retro-DA reaction temperature in MgNH is higher than 150 °C in (b).

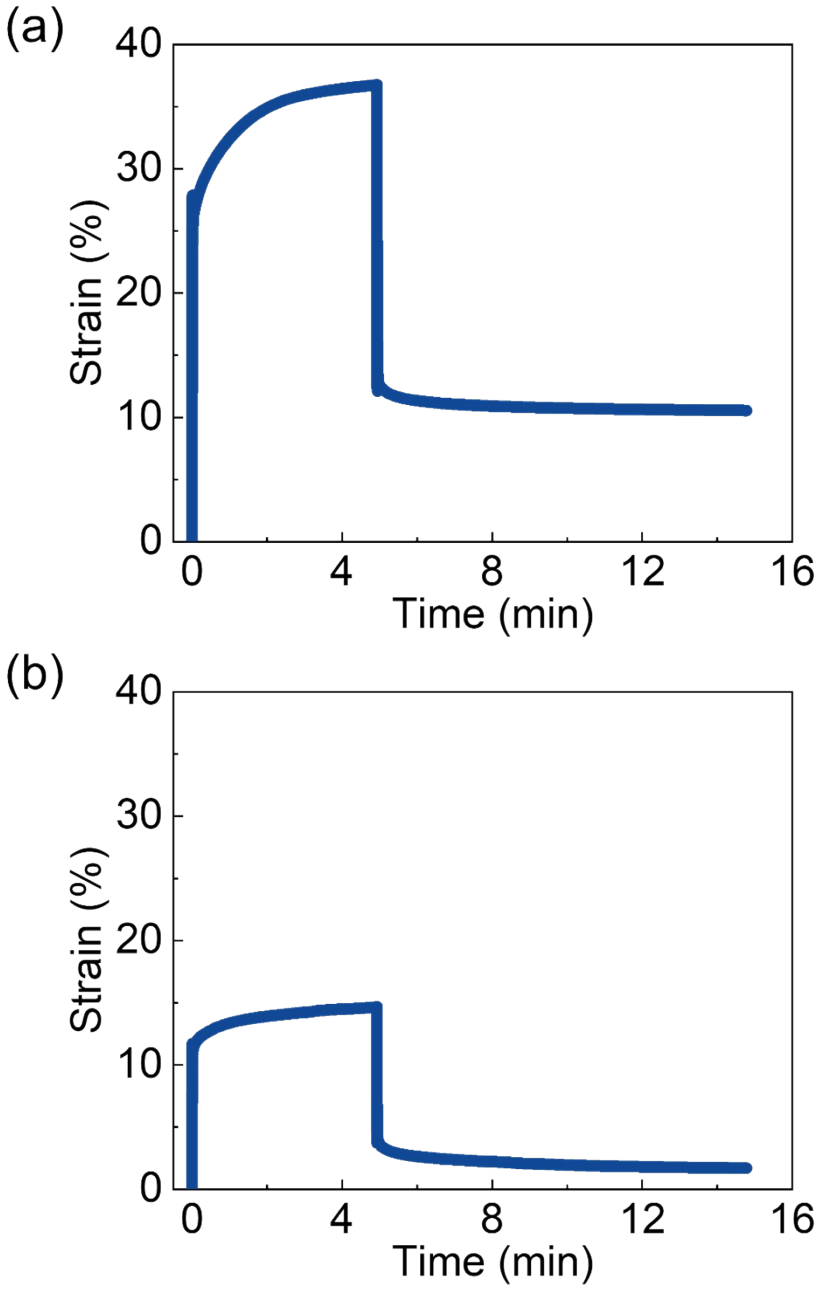

Fig. S11. Creep recovery curves at 25 °C for DA salogels containing (a) F2.5-PVA/BM-PEG and (b) F5-PVA/BM-PEG. Polymer (F10-PVA) concentration was 5 wt%.

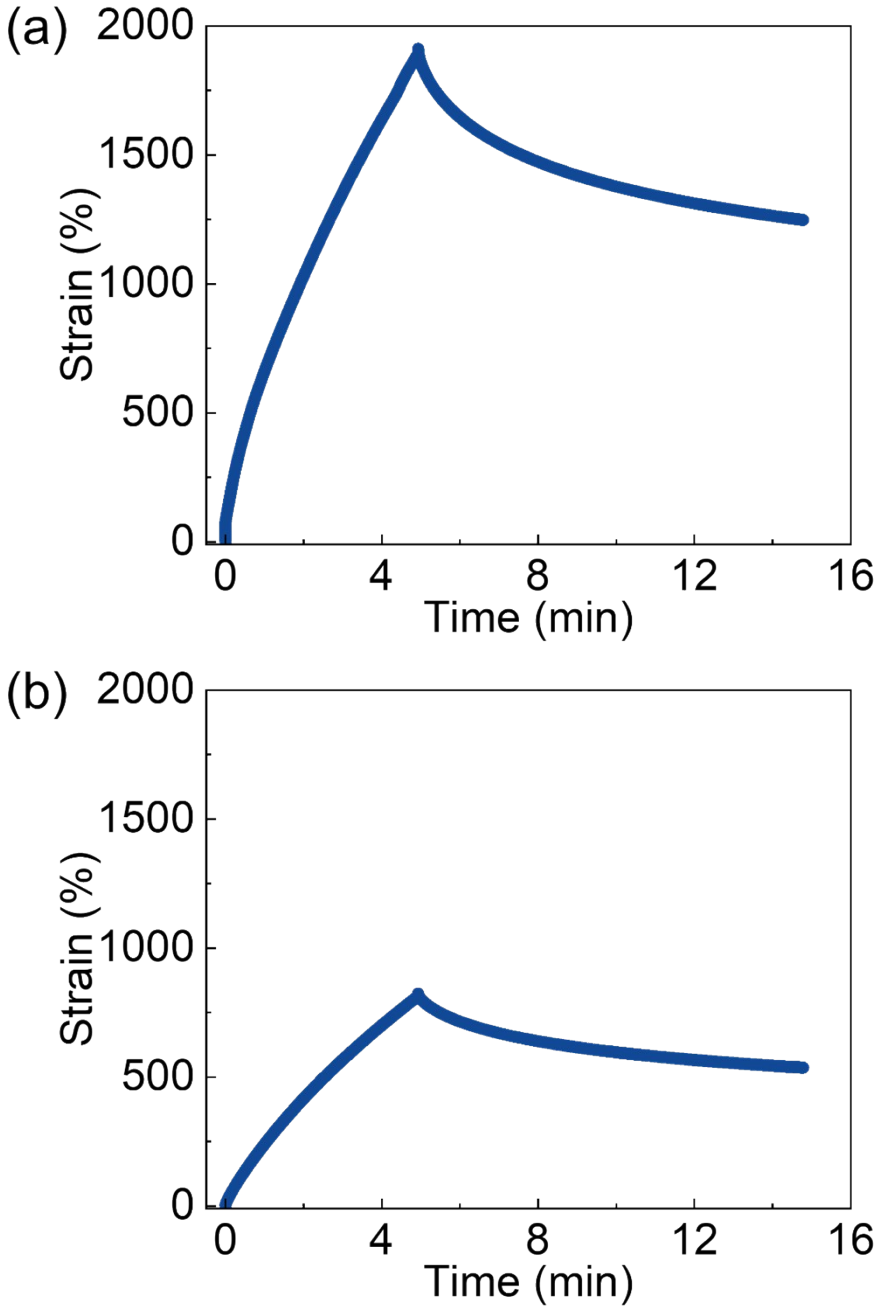

Fig. S12. Creep recovery curves at 25 °C for boronate ester salogels (a) PVA/borax-2.5 and (b) PVA/borax-5. Polymer (PVA) concentration was 5 wt%.

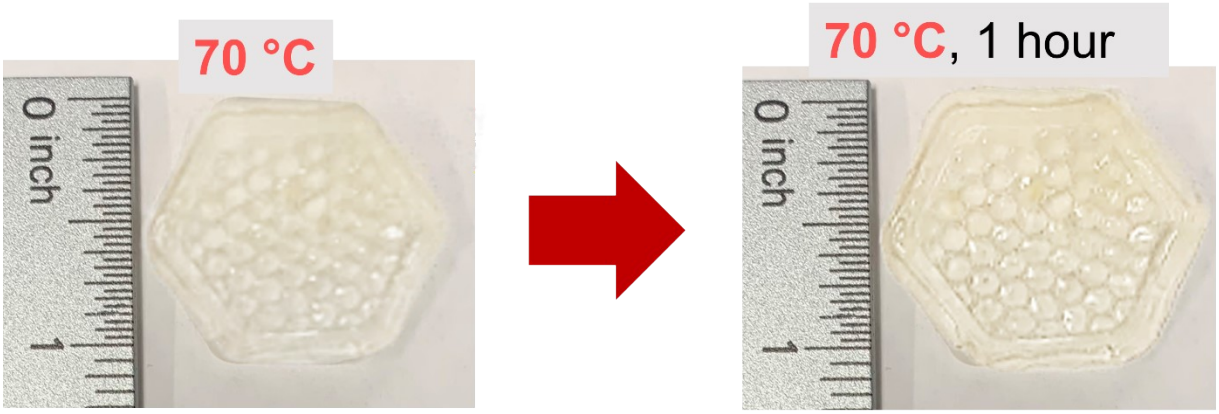

Fig. S13. Optical images of a hexagon-shaped DA salogel (F10-PVA/BM-PEG) showing shape retention and leakage prevention of LNH even after 1 hour at 70 °C. Polymer (F10-PVA) concentration was 5 wt%.

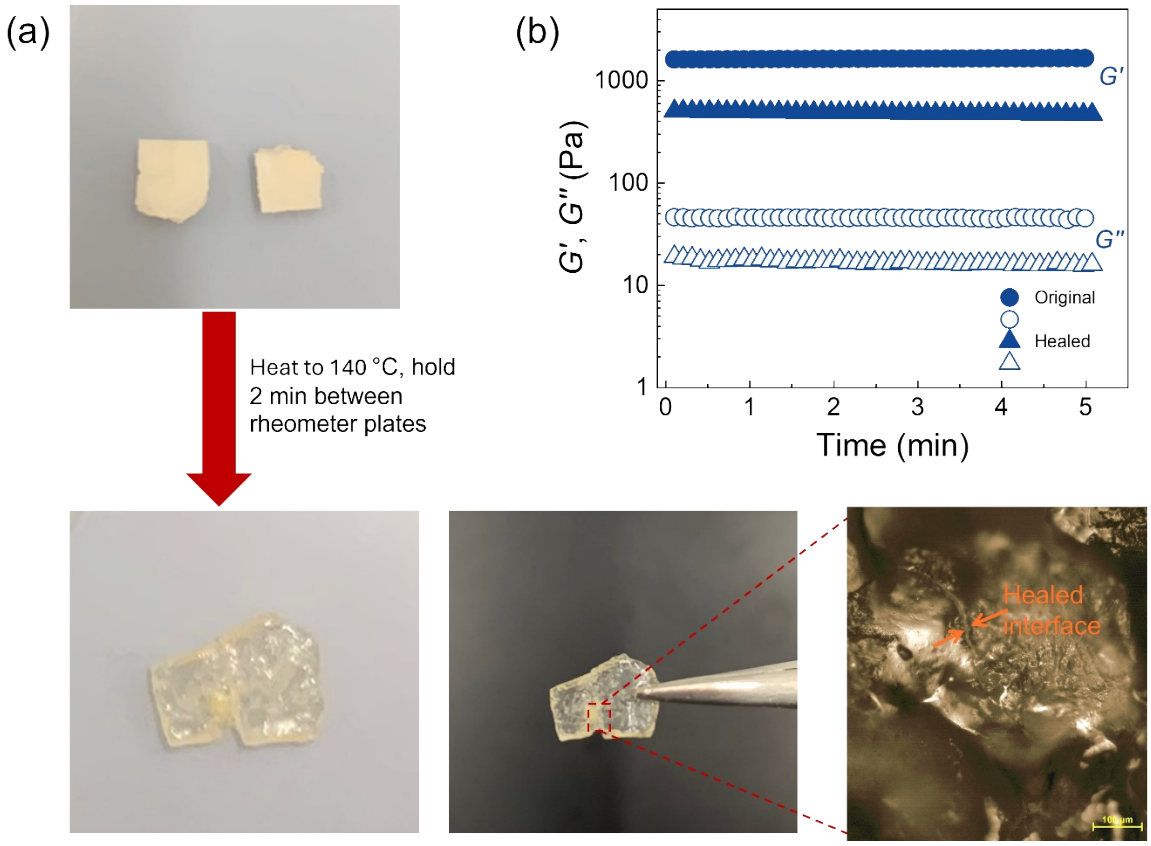

Fig. S14. Experiment showing self-healing capability of two pieces of DA salogel (F10-PVA/BM-PEG) in LNH at polymer concentration of 5 wt%. (a) Top picture shows the two pieces at room temperature, bottom-left picture shows the two pieces right after the samples were removed from the rheometer and the middle picture shows that the healed sample can be handled using tweezers immediately after the experiment. Optical microscope image on the bottom-right showing the healed interface at 10X magnification. Scale bar is 100 microns. All images were taken at room temperature. (b) Oscillatory rheology time sweep experiment at 1% strain and 10 rad/s frequency comparing the moduli of the original and the healed samples.

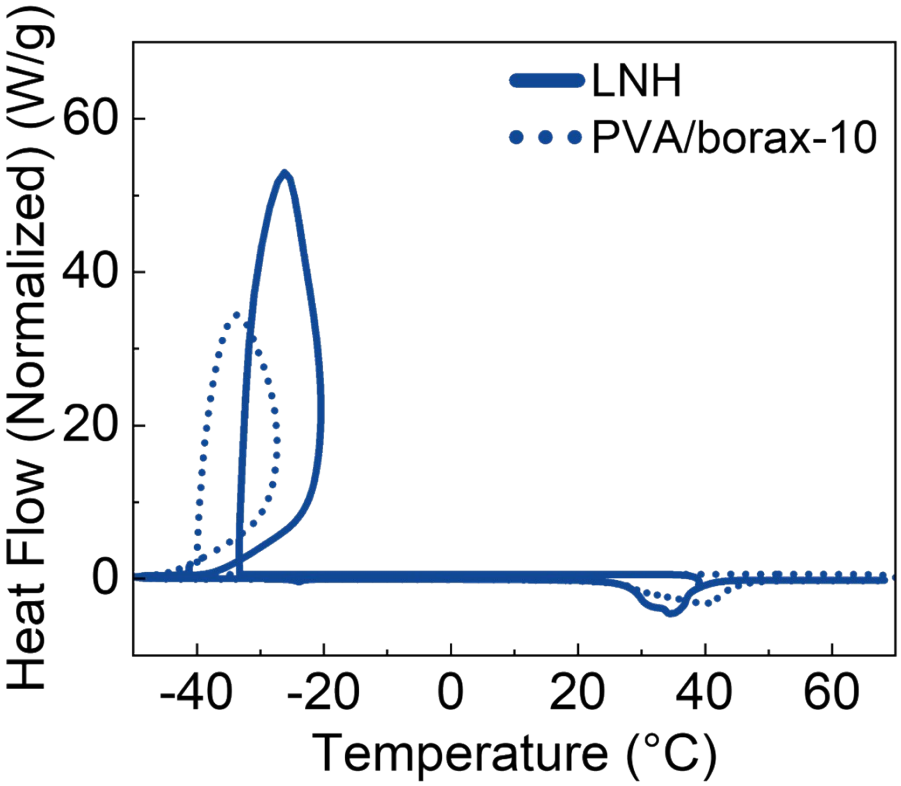

Fig. S15. DSC thermograms showing melting and crystallization transitions in neat LNH and PVA/borax-10 salogel. Polymer (PVA) concentration was 5 wt%.

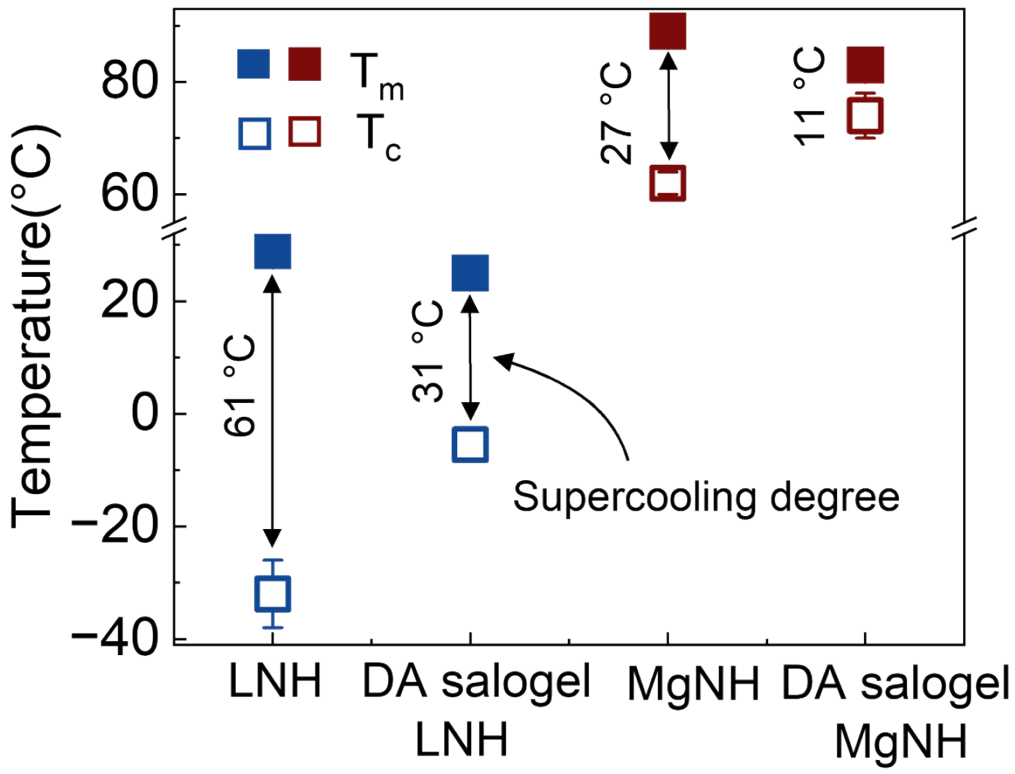

Fig. S16. Comparison of melting (T_m) and crystallization (T_c) temperatures showing reduction in supercooling degree in the DA salogels compared to the neat salt hydrates, LNH and MgNH.

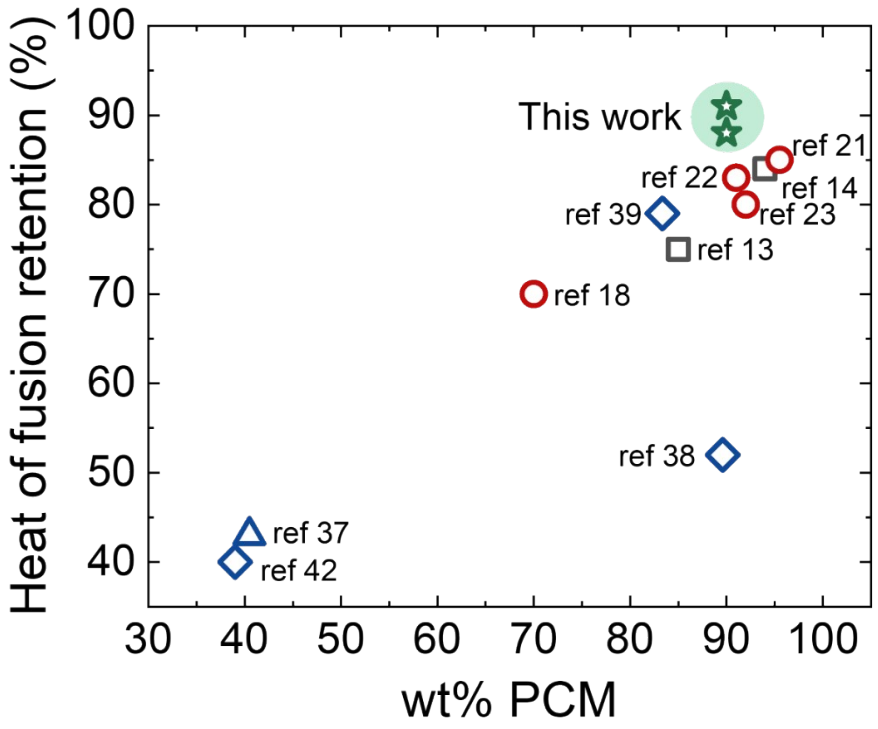

Fig. S17. Comparison of % heat of fusion retention as a function of amount of PCM in the shape stabilizing matrices. Green stars – salogels (F10-PVA/BM-PEG) reported in this work, red circles – MgNH, grey squares – LNH, blue diamonds – DA networks with PEG as PCM, and blue triangle – DA network with beeswax as PCM.

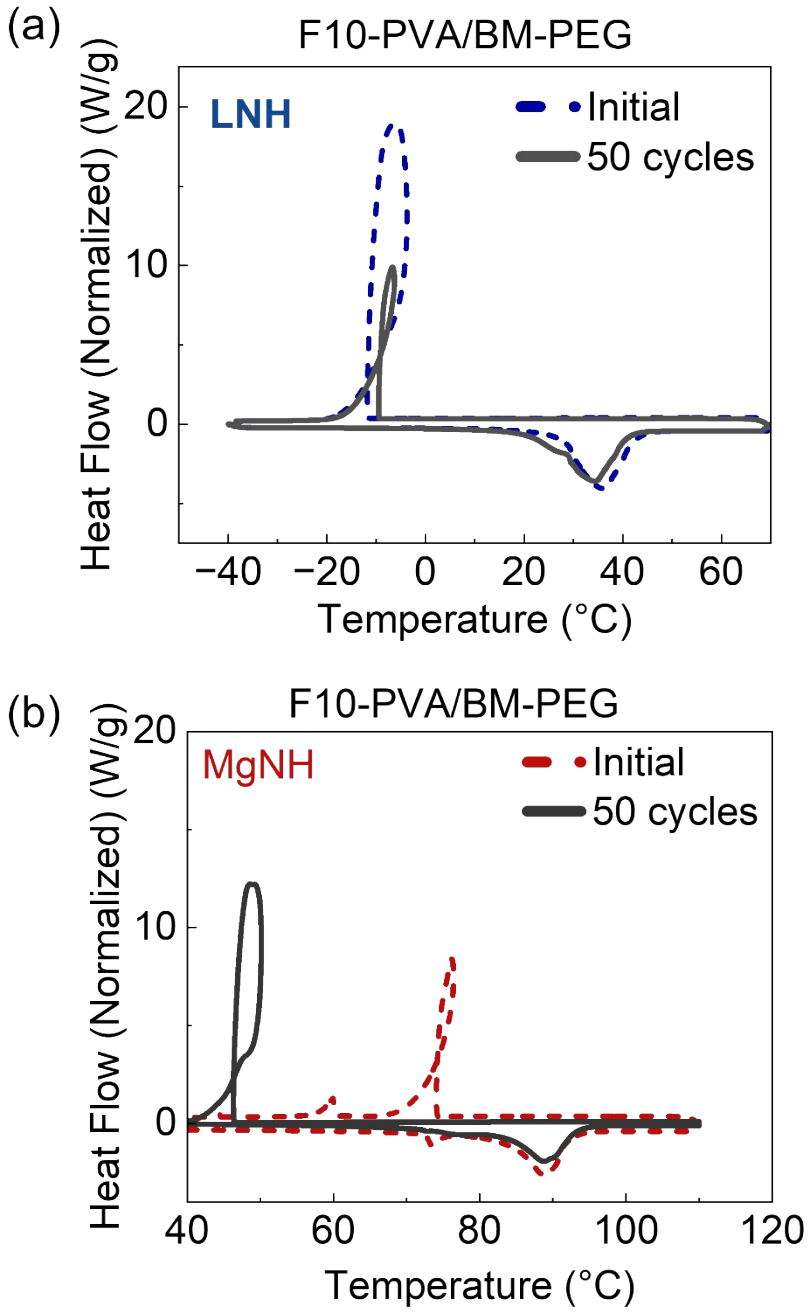

Fig. S18. DSC thermograms before and after 50 melting and crystallization cycles of (a) LNH and (b) MgNH in F10-PVA/BM-PEG salogel. Polymer (F10-PVA) concentration was 5 wt%.

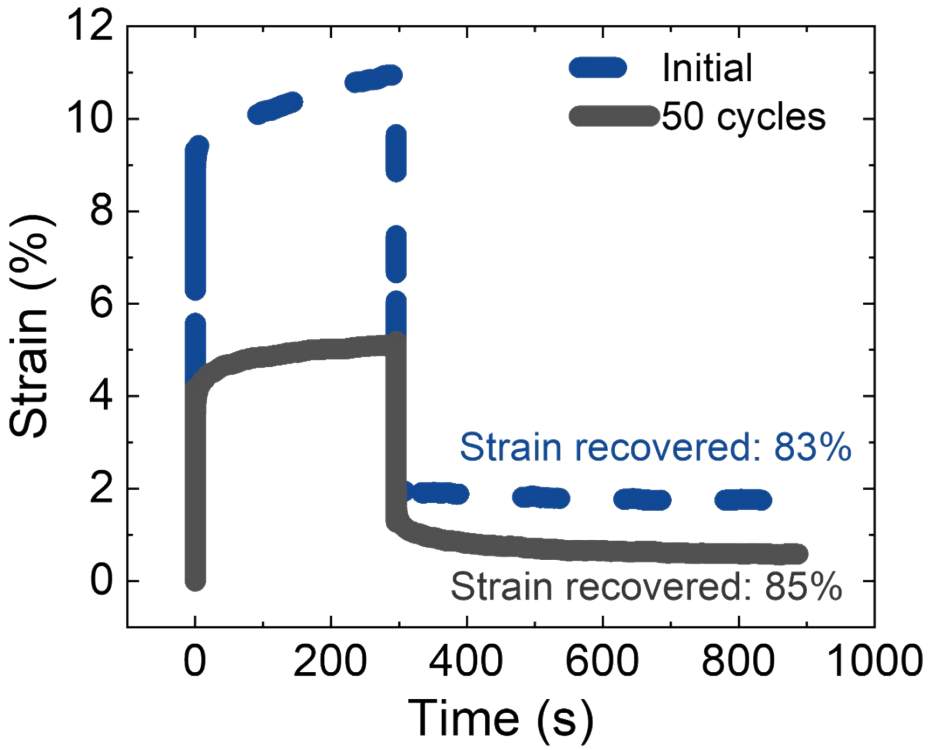

Fig. S19. Creep-recovery curves at 70 °C for DA salogels containing F10-PVA/BM-PEG before and after 50 melting and crystallization cycles. Polymer (F10-PVA) concentration was 5 wt%.

Table S1. Thermal properties obtained from DSC experiments performed with LNH and boronate ester salogel.

Sample	Heat of fusion (J/g)	Melting temperature (°C)	Crystallization temperature (°C)	% heat of fusion retained	Wt% PCM in salogel
LNH	280±4	29±1	-33	- *	N/A
Boronate ester salogel	254±6	26±1	-40	90±1	94.5

* These values were used as reference to calculate the % heat of fusion retention of the salt hydrate in the salogel.

Video S1 (Supplementary Video 1.mp4) shows the DA salogel flame-sealed in an ampoule being heated with a heat gun until the gel turned into a liquid.