Supporting Information

Quadruple Shape-Memory Organohydrogels with Adjustable Trigger Temperatures

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Text S1. Microstructure of OHG components before and after polymerization

We have previously examined the Amide I region of the FTIR spectra of the aqueous SF solution before and after the addition of ethanol and of the emulsion system before and after polymerization.[S1] Before polymerization, all samples show a sharp peak at 1640 cm^{-1} corresponding to the random coil conformation. After polymerization, the peak at 1640 cm^{-1} shifts to 1620 cm^{-1}, indicating a conformational transition in SF from the random coil to the β-sheet structure.[S1] The XRD pattern of SF before gelation shows a broad peak at 21°, corresponding to a random coil conformation.[S1] After gelation, the SF hydrogel component of OHG exhibits an intense peak at 20.6° and two weak peaks at 8.6 and 24.5°, corresponding to β-sheet crystal spacings of 4.3, 10, and 3.7 Å, respectively. Moreover, the XRD peaks of PDMAA at 10.5° and 22.8° overlap with the characteristic peak of SF at about 20°, which is due to the β sheet structure.[S2] Therefore, the peaks of PDMAA and SF cannot be distinguished based on XRD curves. In addition, the dispersed PC18A component of OHG shows a crystalline peak at 21.3°, corresponding to a Bragg d-spacing of 4.2 Å, which is typical of the paraffin-like hexagonal lattices formed by the packing of octadecyl (C18) side chains.[S1] The same peak also appears in the spectrum of OHG, indicating that the C18A droplets in the emulsion system have polymerized and formed crystalline domains. Besides this peak, second-order diffraction peaks appear at 25.3, 23.5, and 19.6°, which we attribute to the crystalline β-sheet structure.

Text S2. The relationship between σ_{nom} and σ_{true}

The compressive stress was represented by its nominal σ_{nom} and true values σ_{true}, which are the forces per cross-sectional area of the original and the deformed gel specimens, respectively. Thus, σ_{nom} and σ_{true} are given by

$$\rho_{nom} = \frac{l}{A_o} \quad \text{(S1)}$$

$$\rho_{true} = \frac{l}{A} \quad \text{(S2)}$$

where l is the sample length under force, A_o and A are the cross-sectional area of the original and the deformed gel specimens, respectively. Assuming isotropic deformation during compression, i.e., assuming that the gel volume remains constant during deformation, one obtains,

$$A_o\, l_o = A\, l \quad \text{(S3)}$$

$$\frac{A_o}{A} = \frac{l}{l_o} = \lambda \quad \text{(S4)}$$

where l_o is the initial length of the sample, and λ is the deformation ratio. From equations S1-S4, the relationship between σ_{nom} and σ_{true} is as follows:[S3]

$$\rho_{true} = \rho_{nom}\, \lambda \quad \text{(S5)}$$

Moreover, the change in the sample length ε (= $\Delta l/l_o$) relates to λ by $\varepsilon = \lambda - 1$.

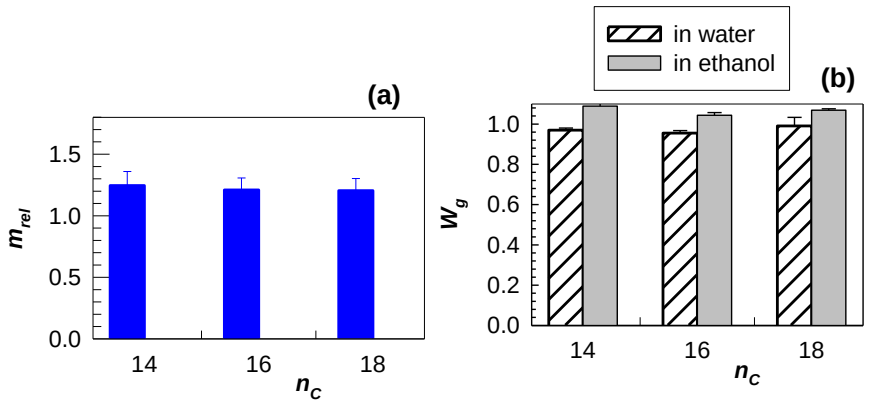

Figure S1. (a) Relative weight swelling ratio m_{rel} of OHGs plotted against n_C. (b) Gel fraction Wg of OHGs in water and in ethanol plotted against n_C.

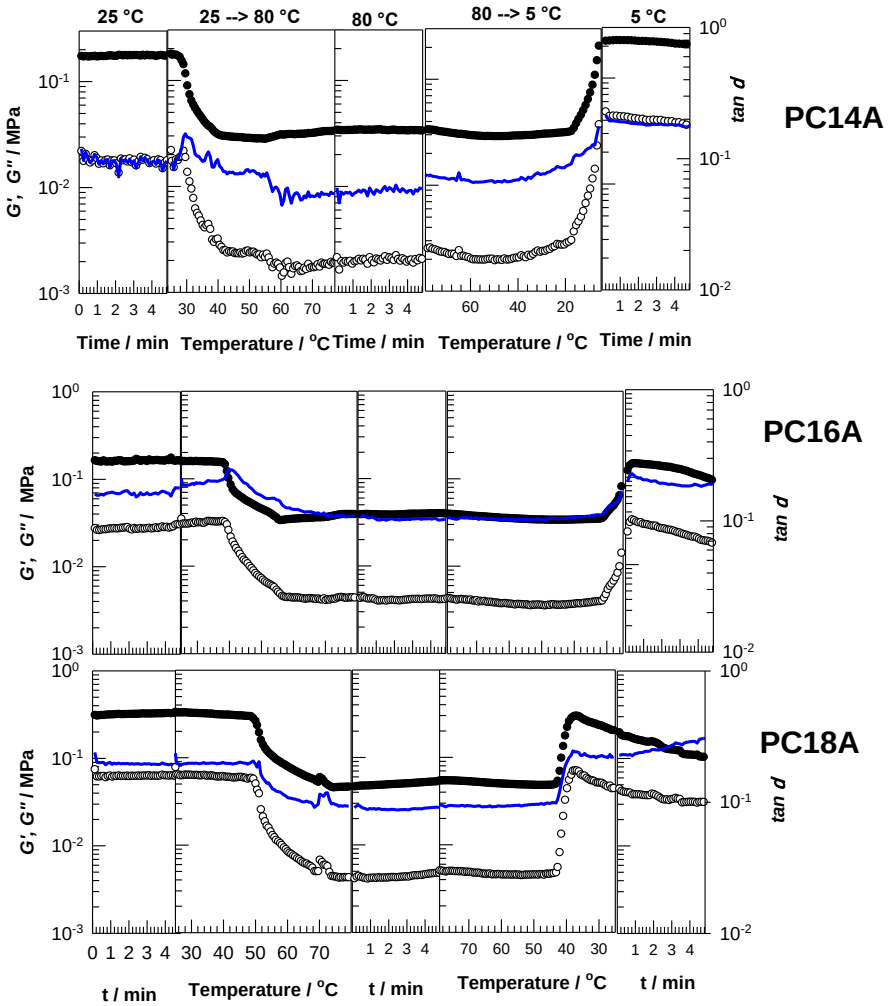

Figure S2. Storage modulus *G'* (filled symbols), loss modulus *G''* (open symbols), and loss factor *tan δ* (lines) of OHGs containing PC14A, PC16A, and PC18A micro-inclusions subjected to a thermal cycle between 25 and 65 °C. γ_0 = 0.1%. ω = 6.28 rad·s^{-1}.

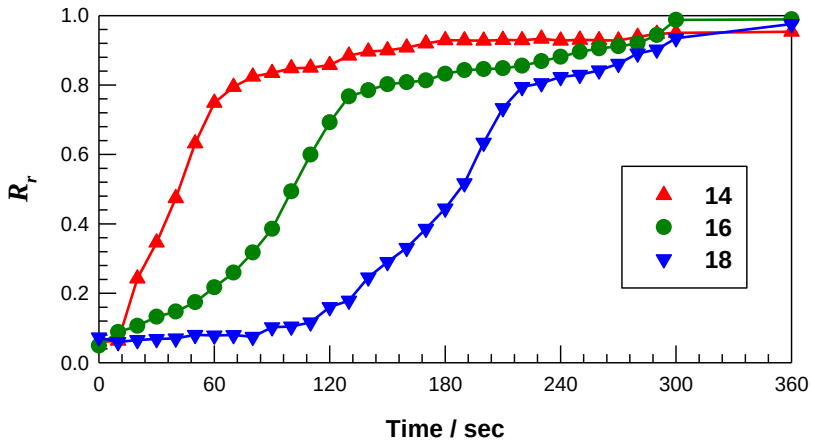

Figure S3. Time-dependent shape-recovery ratio R_r of OHG's with various n_C as indicated. Temperature = 65 °C

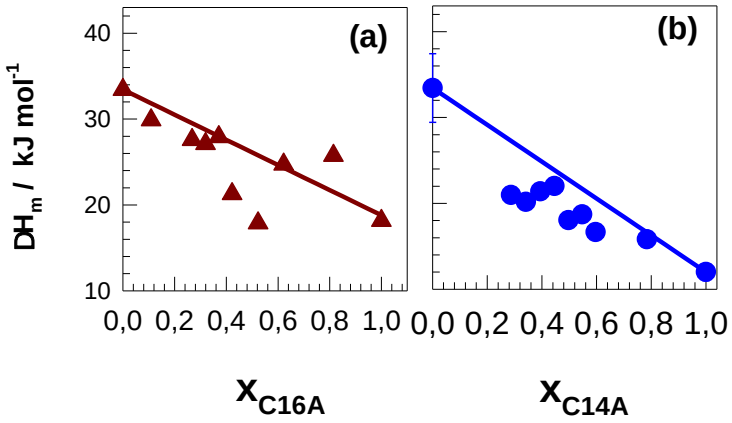

Figure S4. Composition dependence of the melting enthalpies ΔH_m of P(C18A-co-C16A) (a) and P(C18A-co-C14A) copolymers (b). The solid lines are predicted values using the equation $\Delta H_m = \sum \Delta H_{m,i}\, x_i$, where $\Delta H_{m,i}$ and x_i are melting enthalpy and the mole fraction of component i in the copolymer, respectively.

References

(S1) Oral, C. B.; Yetiskin, B.; Cil, C.; Kok, F. N.; Okay, O. Silk Fibroin-Based Shape-Memory Organohydrogels with Semicrystalline Microinclusions. *ACS Appl. Bio Mater*. **2023**, 6, 1594−1603.

(S2) Oral, C. B.; Yetiskin, B.; Okay, O. Stretchable silk fibroin hydrogels. *Int. J. Bio. Macromol.* **2020**, 161, 1371-1380.

(S3) Argun, A.; Can, V.; Altun, U.; Okay, O. Non-ionic Double and Triple Network Hydrogels of High Mechanical Strength. *Macromolecules* **2014**, 47, 6430-6440.