

## Supplementary Information

# Double-network Shape Memory Organohydrogel prepared by one-pot polymerization

*Ya Liu,<sup>a</sup> Li Wang,<sup>a</sup> Hongsheng Lu,<sup>\*a,b</sup> Zhiyu Huang<sup>\*b,c</sup>*

<sup>a</sup>College of Chemistry and Chemical Engineering, Southwest Petroleum University Chengdu 610500, P. R. China

<sup>b</sup>Oil & Gas Field Applied Chemistry Key Laboratory of Sichuan Province Chengdu 610500, P. R. China

<sup>c</sup>School of New Energy and Materials, Southwest Petroleum University Chengdu 610500, P. R. China

**\*Corresponding authors.**

***E-mail addresses:* [hshlu@swpu.edu.cn](mailto:hshlu@swpu.edu.cn) (H. Lu), [zyhuang3019@163.com](mailto:zyhuang3019@163.com) (Z. Huang).**

---

## Table of Contents

### EXPERIMENTAL SECTION

|  |     |
|--|-----|
| Materials  | S-3 |
| Preparation of DN Organohydrogel PVA/PDMA-co-PLMA-HSA (PDLH) | S-3 |
| Mechanical Measurements                                      | S-3 |
| Swelling measurement   | S-3 |
| Shape Memory Behavior  | S-4 |
| Other Characterization                                       | S-4 |

### SUPPORTING FIGURES

|            |   |     |
|------------|---|-----|
| Figure. S1 | Diameter distribution of oil domains in the emulsion analyzed by Image J Software.                                | S-5 |
| Figure. S2 | Rheological measurements of PVA aqueous solution before and after crystallization                                 | S-5 |
| Figure. S3 | Rheological measurements of the organohydrogel, hydrogel and organogel  | S-6 |
| Figure. S4 | SEM image of single network PDMA-LMA organohydrogel.  | S-6 |
| Figure. S5 | The water content of DN hydrogel and DN organohydrogel.   | S-7 |
| Figure. S6 | Stress dependence of $G'$ and $G''$ of 12-HSA organohydrogel (solvent: paraffin liquid, 50 mg mL <sup>-1</sup> ). | S-7 |
| Figure. S7 | X-ray diffraction of organohydrogel, organogel (HSA) and PVA powder.  | S-7 |
| Figure. S8 | DSC curve of paraffin liquid organogel of 12-HSA (20 mg mL <sup>-1</sup> ).                                       | S-8 |
| Figure. S9 | The complex shape memory process for PDLH organohydrogel.   | S-8 |

---

## EXPERIMENTAL SECTION

**Materials.** Poly(vinyl alcohol) powder (PVA,  $M_w \sim 195,000$ ) was obtained from Macklin. *N, N'*-Dimethyl acrylamide (DMA), lauryl methacrylate (LMA), sodium dodecyl sulfate (SDS), and liquid paraffin (LP) were obtained from ChengDu Chron Chemicals Co.,Ltd. Ethyleneglycol dimethacrylate (EGDMA), 3-(trimethoxysilyl)propyl methacrylate (TPMA), 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (I2959), 12-hydroxystearic acid (HSA), 2,2'-diethoxyacetophenone (DEOP), and *Pluronic* F127 were received from Aladdin. These chemical ingredients were not further purified prior to use.

**Preparation of DN Organohydrogel PVA/PDMA-*co*-PLMA-HSA (PDLH).** Firstly, a 5 wt% PVA aqueous solution was prepared at 90 °C with vigorous stirring and then cooled to RT. TPMA was added into the PVA solution (10 mL) as a crosslinker. The aqueous mixture was stirred for 1 h, and then 100  $\mu$ L SDS was added. The oil phase consists of 6.3 g of LMA, 15.8 g of liquid paraffin, 0.04 g of EGDMA, 0.1 g DEOP, and 10 g 12-HSA. Then, this biphasic mixture was mixed at 70 °C and homogenized at a rate of 20000 rpm for 5 min to form an O/W emulsion. Finally, the emulsion was irradiated by UV light (365 nm, 250 W) at 70 °C to form organohydrogel PDLH. Likewise, other organohydrogel samples were prepared by the same procedure.

**Swelling measurement.** The dehydrated hydrogels and organohydrogel ( $\sim 2$  g) were initially soaked in 100 mL of deionized water to attain the swelling equilibrium, and then the swollen gel samples were weighed after removing excess water from their surface using filter paper in each measurement. The water content ( $W$ ) was determined using the following Equation (1),

$$W = \frac{W_s - W_d}{W_d} \times 100\% \quad (1)$$

where  $W_s$  and  $W_d$  represent the weights of the swollen gel and dried gel, respectively.

**Mechanical Measurements.** The tensile stress-strain tests were carried out using a tensile-compressive tester (MTS CWT6104) at an elongation rate of 100 mm per minute in air. The assay was performed on dumbbell-shaped gel specimens standardized to the GB/T 528-2009 4<sup>#</sup> size. Elastic or Young's modulus ( $E$ ) is calculated from the slope of the stress-strain curve at 1-15% elongation. Toughness ( $K$ ) is calculated by integrating the area of the stress-strain curve as Equation (2)

$$K(\varepsilon) = \int_0^{\varepsilon} \sigma d\varepsilon \quad (2)$$

Where  $\sigma$  and  $\varepsilon$  represent stress (MPa) and strain ( $\text{mm mm}^{-1}$ )

---

In the compressive tests, specimens with cylinder shapes ( $\Phi$  8 mm  $\times$  8 mm) were put on a metal plate. The test was performed at a loading velocity of 0.5 mm/min until the gel fractured or the compression deformation was 80%.

**Shape Memory Behavior.** The shape memory behavior of the organohydrogel was performed on a straight strip (80  $\times$  10  $\times$  4 mm). The strip was first curled to a helix shape in hot water. Then the helix shape could be fixed in 30 °C water and finally recover to its permanent shape after being soaked in 80 °C water. Quantitative shape memory characteristic of the DN organohydrogel was determined according to previously reported procedures via U-shaped specimens.<sup>5, 31</sup> The following equations (3) and (4) were used to calculate the shape fixity ratio (Rf) and shape recovery ratio (Rr), respectively.

$$Rf = \frac{\theta_i}{\theta_t} \times 100\% \quad (3)$$

$$Rr = \frac{\theta_f - \theta_i}{\theta_t} \times 100\% \quad (4)$$

where  $\theta_t$  is the deformed angle,  $\theta_i$  is the temporarily maintained angle, and  $\theta_f$  is the final angle.

**Other Characterization.** The crystallinity was characterized by X-ray diffractometer (XRD, X Pert PRO MPD PANalytical B.V), and the data were collected at a range of  $2\theta = 5 - 50^\circ$ . FTIR spectra were measured via WQF520 Ruili IR spectrometer with the range of wavenumbers from 500 - 4200  $\text{cm}^{-1}$ . The morphology of the organohydrogel was characterized using a scanning electron microscopy (SEM ZEISS EV0 MA15). The gel sample for SEM was freeze-dried in a lyophilizer overnight at - 30 °C and then fractured in liquid nitrogen and gold-sputtered on the fracture surface. The differential scanning calorimetry (DSC) using a Mettler Toledo DSC823e under  $\text{N}_2$  atmosphere. The specimens of organogel tested in aluminum pans were scanned at a heating and cooling rate of 5 °C  $\text{min}^{-1}$  between 5 °C and 90 °C. The fluorescence microscope (FM) image was obtained using an Olympus DP80 BX3-RFAA. The oleophilic phase was stained with Perylene Red. Moreover, an FM image of the organohydrogel in a bright field was also characterized under the same conditions. And the diameter

distribution of oil domains can be obtained by manual analysis with diameter-statistics software Image J. The rheological tests were performed on HAAKE MARS III Thermo Fisher Scientific rheometer. The plane-shaped ( $\Phi$  55 mm  $\times$  1 mm) samples were set under a 55 mm diameter parallel plate with a gap of 1 mm. Oscillatory frequency sweeps were carried out in a range of 0.1-100 rad s<sup>-1</sup> at a constant strain ( $\gamma$ ) of 0.5 %. Dynamic mechanical analysis (DMA) was conducted on a TA Instruments Q800 DMA operating in compression mode. The organohydrogel specimens were cut to a dimension of l = 10 mm, w = 5 mm, t = 2 mm, and G' was determined with a fixed strain amplitude = 0.5 % and at an angular frequency of 6.28 rad/s while the temperature was ramped from 0 to 100 °C at a rate of 2 °C/min.

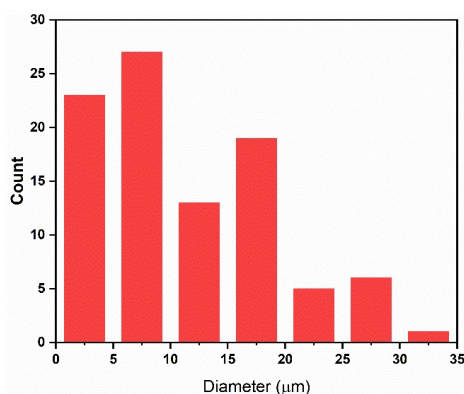


Figure S1. Diameter distribution of oil domains in the emulsion analyzed by Image J Software. The average diameter of oil domains is 11.16  $\mu$ m.

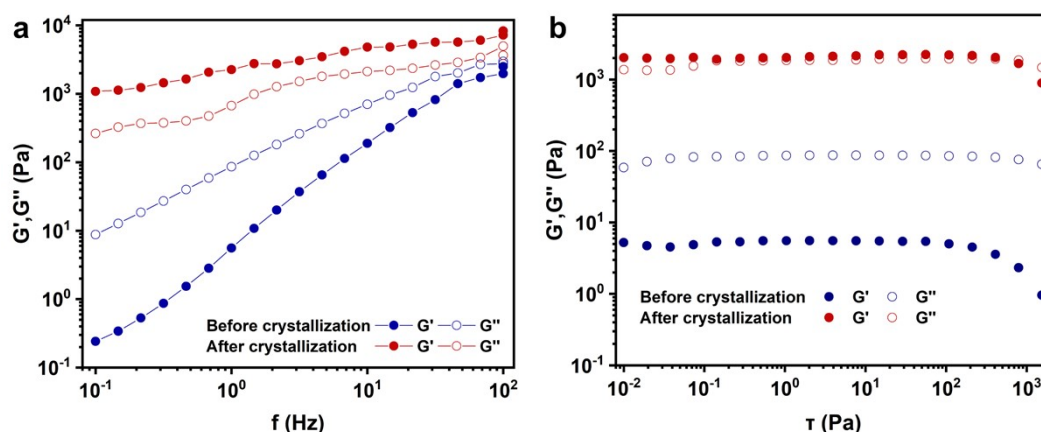


Figure S2. Storage modulus (G') and loss modulus (G'') as a function of frequency (a) and strain ( $\gamma$ ) for PVA solution (5 wt%) before and after crystallization.

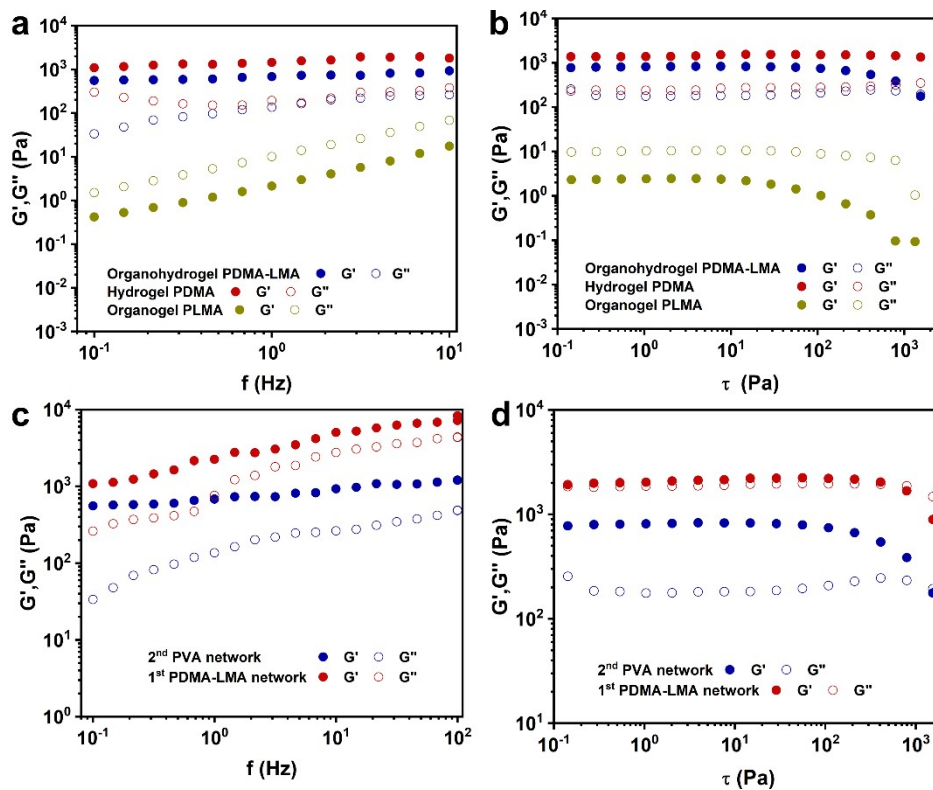


Figure S3. The organohydrogel, hydrogel and organogel were characterized with rheological measurements of  $G'$  and  $G''$  as a function of (a) frequency and (b) strain. The 1<sup>st</sup> and 2<sup>nd</sup> network were characterized with rheological measurements of  $G'$  and  $G''$  as a function of (c) frequency and (d) strain.

It can be seen from Fig. S3 that  $G'$  and  $G''$  of single network organohydrogel PDMA-LMA are both less than DN organohydrogels. In addition, for PDMA-LMA,  $G'$  is always less than  $G''$  in the entire stain range, indicating a deformation-prone property.

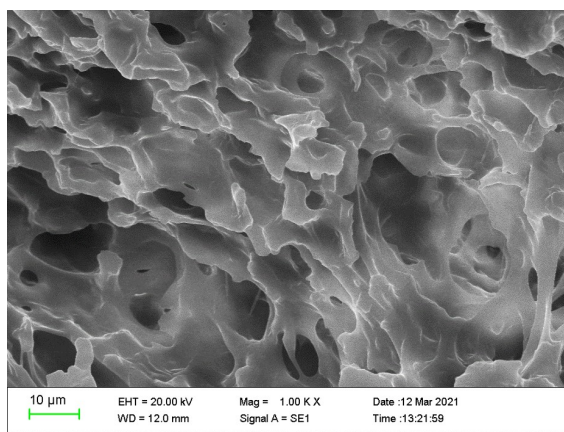


Figure S4. SEM image of single network PDMA-LMA organohydrogel.

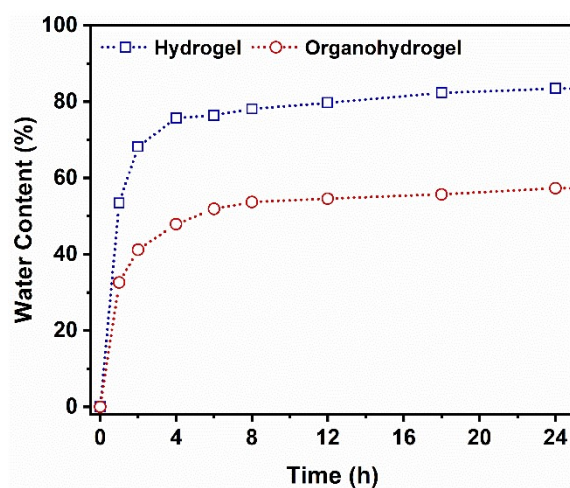


Fig. S5. The water content of DN hydrogel and DN organohydrogel.

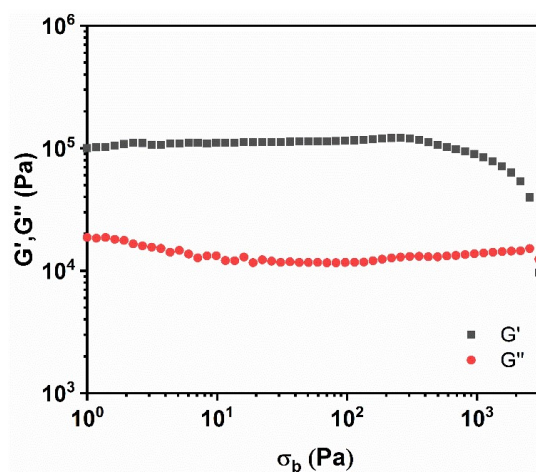


Fig. S6. Stress dependence of G' and G'' of 12-HSA organohydrogel (solvent: paraffin liquid, 50 mg mL<sup>-1</sup>).

The yield stress is above 1000 Pa.

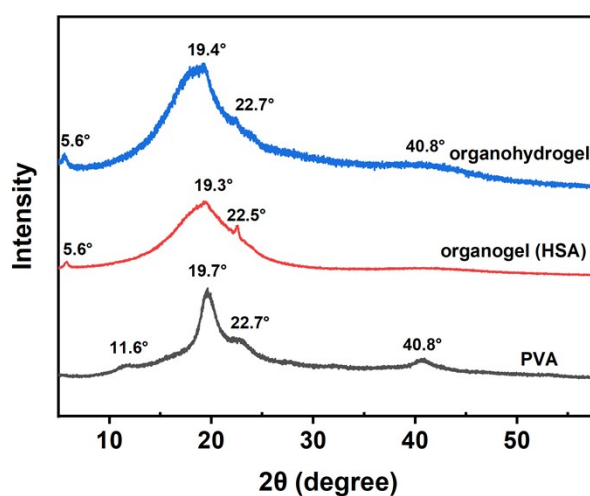


Figure S7. X-ray diffraction of organohydrogel, organogel (HSA) and PVA powder.

Based on XRD analysis for DN organohydrogel, two characteristic peaks at  $5.6^\circ$  and  $40.8^\circ$ , assigned to organogel and PVA, can be observed. Therefore, there are two ordered structures in the organohydrogel network: organogel domains based on self-assembly HSA and crystalline domains of PVA polymer chains.

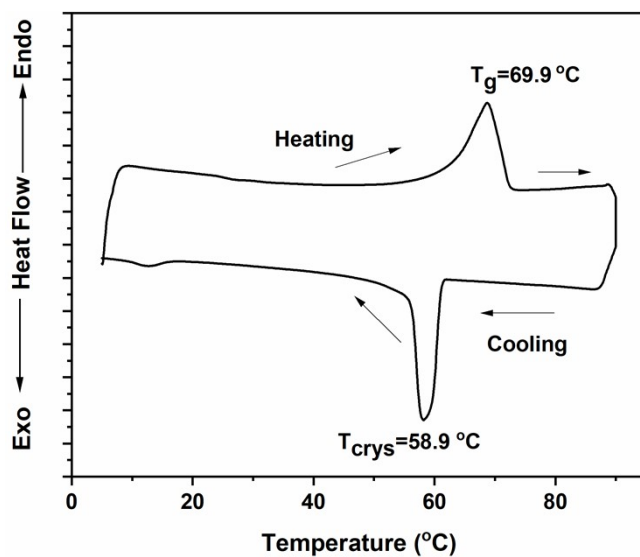


Figure S8. DSC curve of paraffin liquid organogel of 12-HSA ( $20\text{ mg mL}^{-1}$ ).

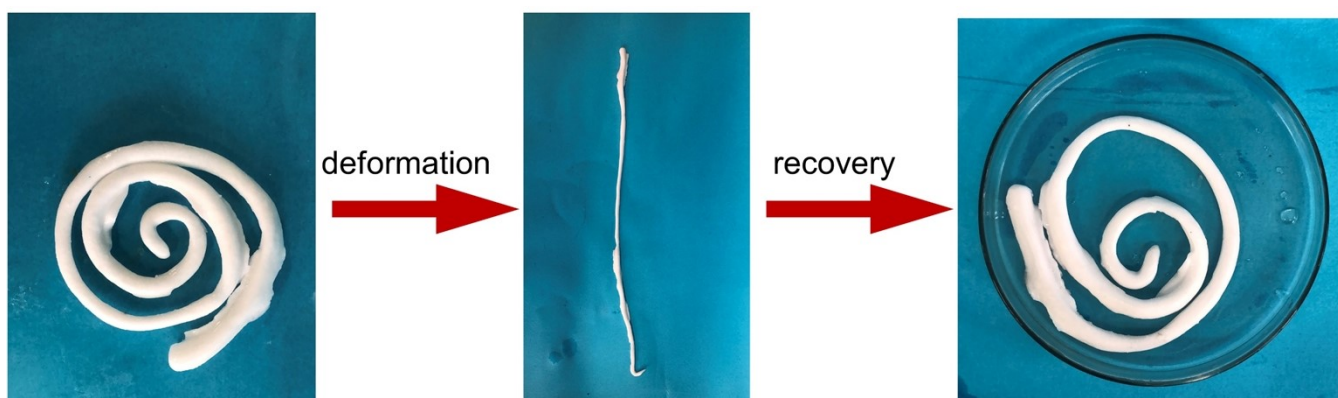


Figure S9. The complex shape memory process for PDLH organohydrogel.