Supplementary Information for

Superior Water Anchoring Hydrogel Validated by Colorimetric Sensing

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Experimental Section

***Materials*:** Pluronic F127 (PF-127, 12600 Daltons, 70% w/w PEO) was purchased from Sigma-Aldrich. Acryloyl chloride, triethylamine, 4-(Dimethylamino) cinnamaldehyde (P-DMAC), bisphenol A glycerolate dimethacrylate and 2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) were purchased from Aladdin. Propanediol, glycerinum, methylbenzene, n-hexane and sulfuric acid (H_2SO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd.

***Preparation of the Pluronic F127 dimethacrylate (F127-DA)*:** The double-bond end-capped Pluronic F127 (F127-DA) was synthesized based on the previously reported report.[1, 2] Briefly, hydroxyl-terminated F127 was acylated in an ice bath under nitrogen environment, with toluene as solvent and triethylamine as catalyst. After 24 h reaction, the viscous liquid was precipitated in n-hexane to form the final white product. The resulting product was dried under vacuum at 30 ℃ for 24 h. Specific chemical equation see Scheme S1. The products were analyzed by FT-IR and ^{1}H-NMR, as shown in Fig. S1.

***Preparation of the P-F127-B-hydrogel and its parallel hydrogels (F127-hydrogel; P-F127-hydrogel)*:** A simple one-pot method was followed for the preparation of P-F127-B-hydrogel with alternating hydrophilic and hydrophobic structure. Firstly, propanediol (4.33 mol L^{-1}), glycerinum (1.097 mol L^{-1}), bisphenol A glycerolate dimethacrylate (0.39 mol L^{-1}) and F127-DA (0.0157 mol L^{-1}) were dissolved in deionized water in sequence and continuously stirred in an ice bath until homogeneous. Then, 1 wt% of 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone with respect to deionized water was added as a photoinitiator to copolymerize F127-DA with bisphenol A glycerolate dimethacrylate. Subsequently, the prepared hydrogel precursor was stored in refrigerator away from light for use. The P-F127-B-hydrogel was formed by photocuring of the precursor fluid in a mold with an illumination for 10 minutes at a wavelength of 365 nm in a UV chamber. For the control experiment, another two sets of hydrogels were prepared. The first group, F127-hydrogel, was a group without polyols and rigid small molecules (bisphenol A glycerolate dimethacrylate) based on the preparation of P-F127-B-hydrogel. The second group was P-F127-hydrogel, which was a group without rigid small molecules based on P-F127-B-hydrogel.

Instrumentation and Characterization**:** Field-emission Scanning Electron Microscope (FE-SEM JEOL JSM-7610F Plus, Japan) operating at 4.0–6.0 kV was performed on the freeze-dried hydrogels to characterize the network density, pore distribution of the network matrix. All samples imaged by FE-SEM were freeze-dried for 48 h by Freeze dryer (China, SCIENTZ-10ND) with the lowest freezing temperature of -50 ^{o}C, and sprayed with gold. The Fourier transform infrared (FT-IR) spectra of hydrogels were recorded by the PerkinElmer Frontier FT-IR spectrometer with a Smart Orbit diamond crystal ATR attachment to characterize the hydrogel composition. The dynamic particle diffusion and color diffusion process of reaction products were observed by a video camera (Imavision, MER-2000-5GM/C-P) with a minimum resolution of 1.2 μm × 1.2 μm. The diffusion diameter and the average RGB values of methyl orange (MO) dye particle, and the color diffusion diameter of the reaction product was extracted using the Adobe Photoshop software. The absorbance spectra of the reagent solutions for urea identification before and after detection were measured using a UV-vis spectrophotometer (Hitachi, UV-3900).

Water-retaining ability of the P-F127-B-hydrogel and its parallel hydrogels (F127-hydrogel; P-F127-hydrogel)**：**For dehydration tests, the samples were kept in a chamber with temperature of 24 °C and relative humidity of 44% rh for observation. The mass of hydrogel was recorded by an analytical balance at a certain time, and the water loss formula is as follows:

$$Water\ loss = \frac{(M_0 - M_i)}{(M_0 - M_e)} \times 100\% \tag{1}$$

M_0 (g) represents the mass of synthetic hydrogel before dehydration;

M_i (g) represents the mass of hydrogel after dehydration at time i;

M_e (g) represents the mass of the hydrogel after completely freeze-drying.

The content of the entrapped water in the P-F127-B-hydrogel : To obtain the content of the entrapped waters in the hydrogels, we polymerized a batch of P-F127-B-hydrogels (15 mm in length, 10 mm in width, 3 mm in thickness), and weighed the mass of the fresh hydrogel and the xerogel completely dried at 60 ^{o}C for 24 h.

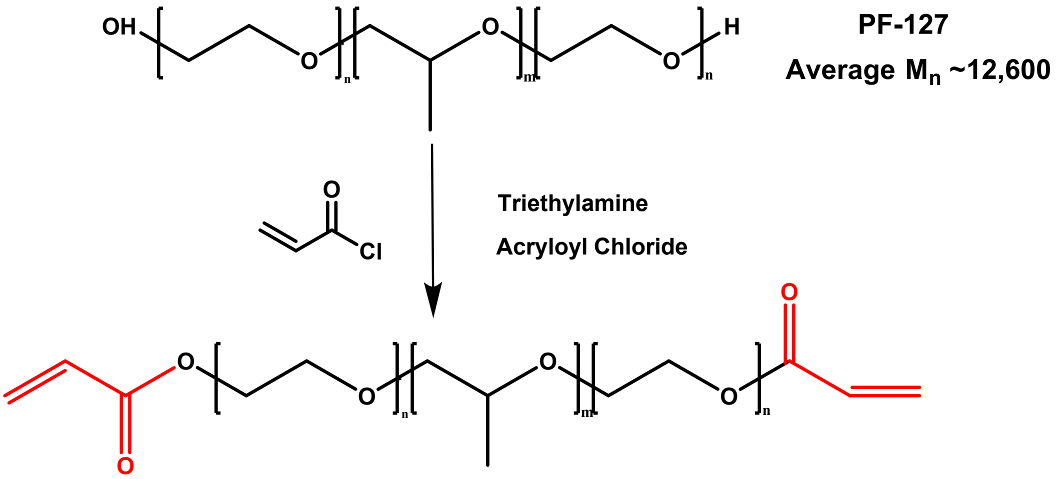
$$The\ content\ of\ the\ entrapped\ water = \left(M_0 - M_x\right)/M_0 \times 100\% \tag{2}$$

M_0 (g) represents the mass of the fresh hydrogel;

M_x (g) represents the mass of the xerogel.

Structural optimization of Bisphenol A glycerolate dimethacrylate : In order to obtain the reasonable conformation, DFT computation was performed by applying the B3LYP[3] hybrid exchange-correlation functional with 6-311+G**[4, 5] basis set to optimize the molecular structure and to calculate the vibrational frequency. This vibrational frequency calculation further confirms that this optimized structure is the local minimum. Calculations were carried out using the Gaussian 09[6] program package.

Supporting Scheme and Figures



Scheme S1. The chemical equation of preparation of the Pluronic F127 dimethacrylate (F127-DA).

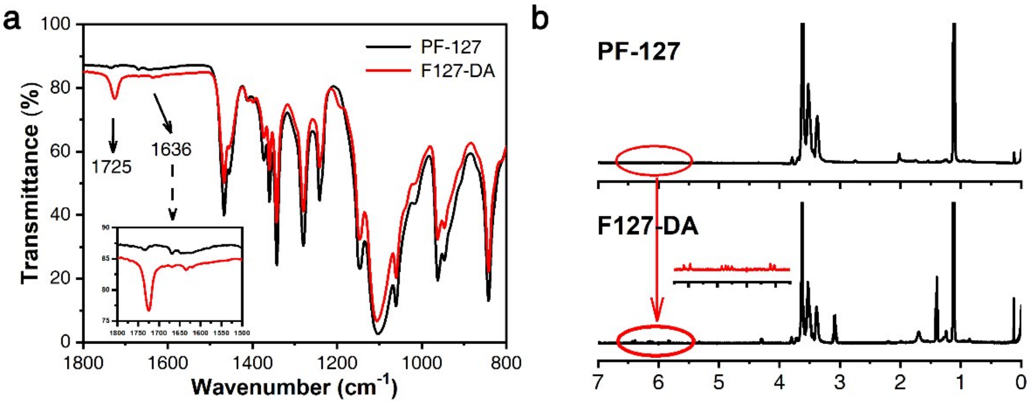


Fig. S1. The structural proof of the Pluronic F127 dimethacrylate (F127-DA). (a) FT-IR and (b) ^{1}H-NMR spectra of PF-127 and F127-DA.

Discussion: The chemical structure of the Pluronic F127 dimethacrylate (F127-DA) and its raw material was analyzed by the Fourier transform infrared (FT-IR) spectra and nuclear magnetic resonance spectroscopy (NMR, $CDCl_3$). As shown in Fig. S1a, in the infrared spectrum of F127-DA (red curve), the peaks at 1725 cm^{-1} and 1636 cm^{-1} represent the stretching vibration of C=O and C=C, respectively, and these peaks did not appear in the raw material F127 (black curve). At the same time, in the ^{1}H-NMR spectra (Fig. S1b), δ5.4-6.5 corresponds to the hydrogen on the double bond, which is the typical signal of acrylation of F127-DA. The results of FT-IR and ^{1}H-NMR prove the successful grafting of the double bond.

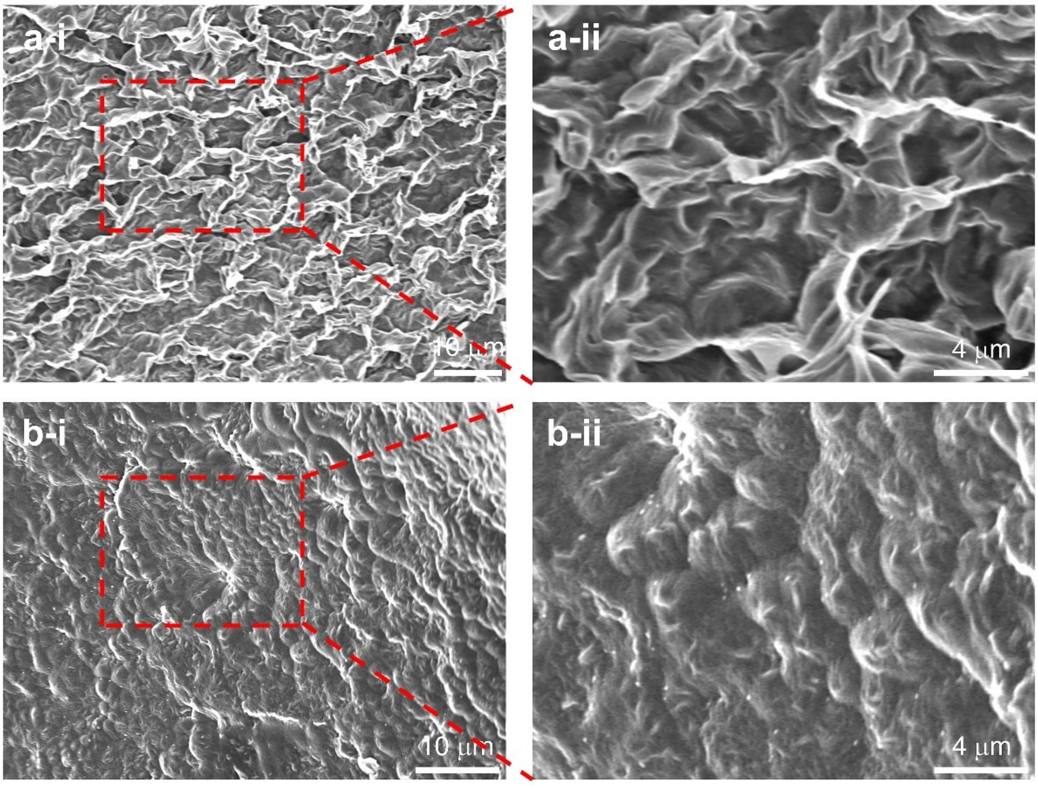


Fig. S2. FE-SEM images of (a) F127-hydrogel, and (b) P-F127-hydrogel.

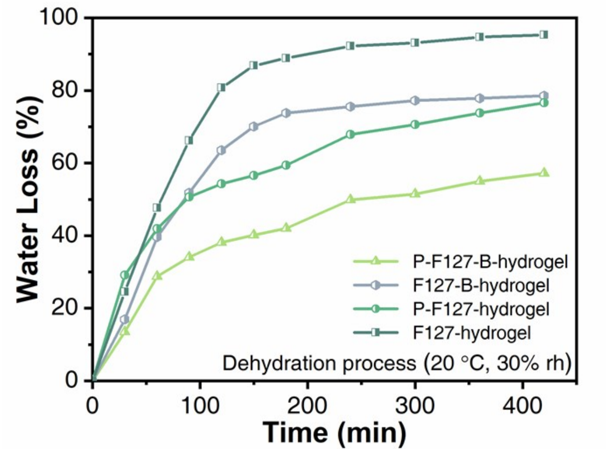


Fig. S3. The water loss curves of hydrogels derived from small rigid molecules, polyol substances, or the synergistic effect of the two.

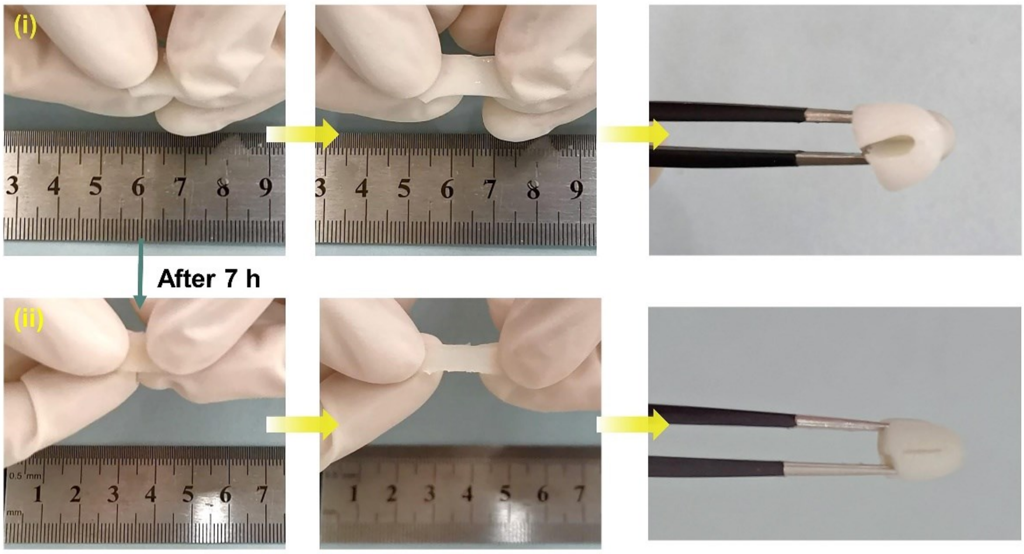


Fig. S4. The tensile and bending tests of the P-F127-B-hydrogel before and after drying for 7 h at room temperature in open environment.

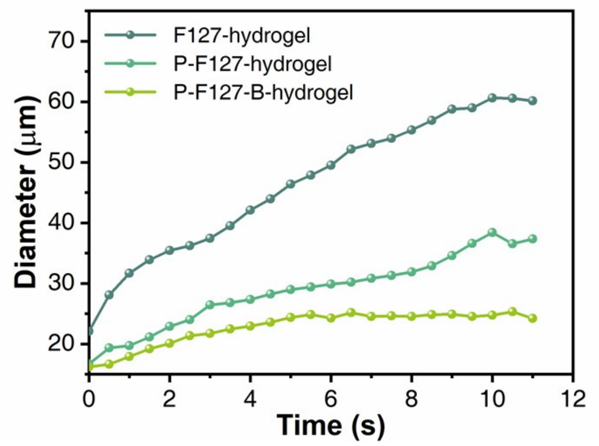


Fig. S5. Curves of diffusion diameter of the MO dye particle with time on the three hydrogels.

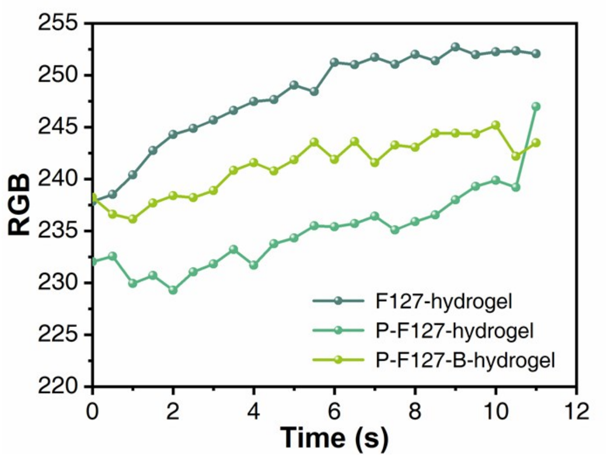


Fig. S6. Time-varying average RGB values of the colored area due to MO dye particle diffusion on the three hydrogels.

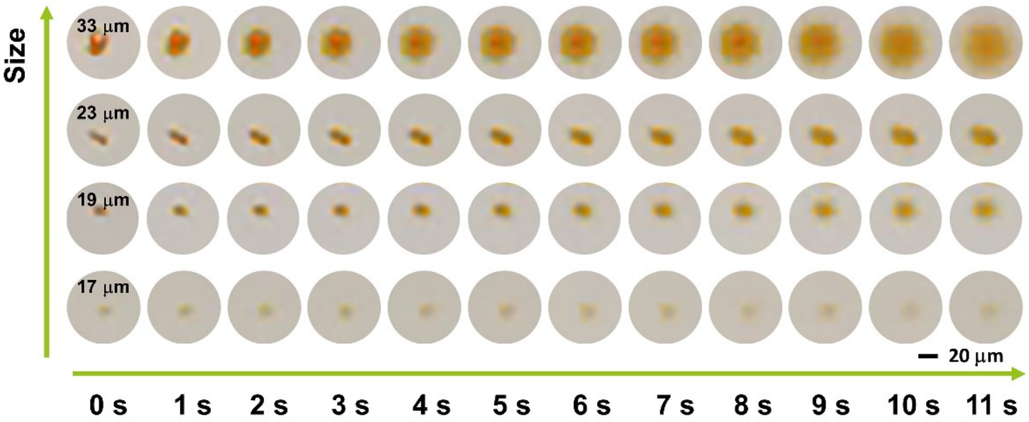


Fig. S7. Comparison chart of diffusion of MO dye particles with different sizes.

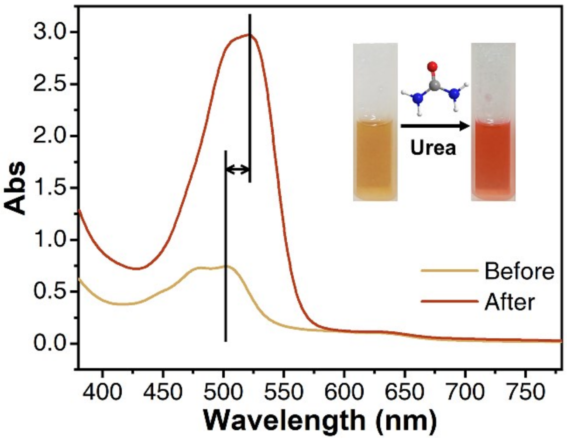


Fig. S8. UV–vis spectra and the corresponding photos of the reagent solutions for urea identification before and after detection.

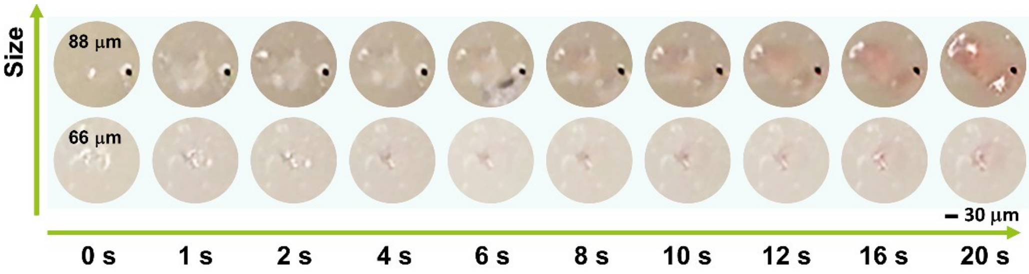


Fig. S9. Real-time detection images for urea microparticulates with different sizes

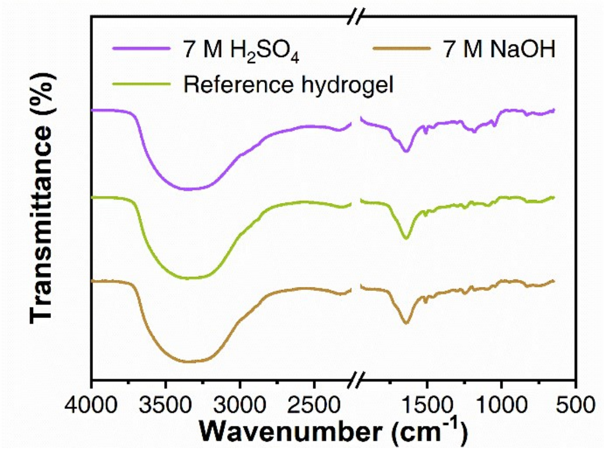


Fig. S10. FT-IR spectra of P-F127-B-hydrogel after soaking with 7 M sulfuric acid and 7 M sodium hydroxide.

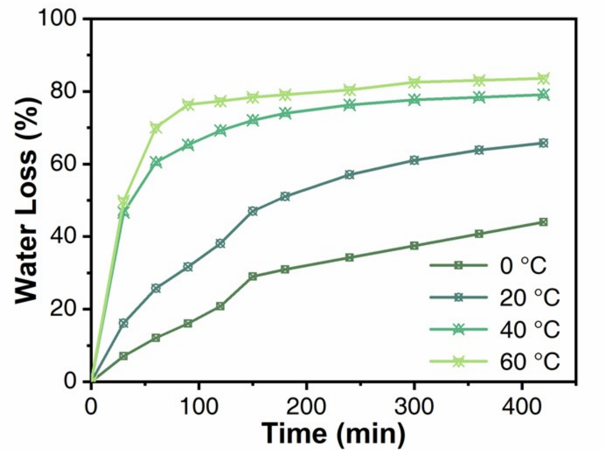


Fig. S11. The water loss curves of the P-F127-B-hydrogel in open environment at different temperatures.

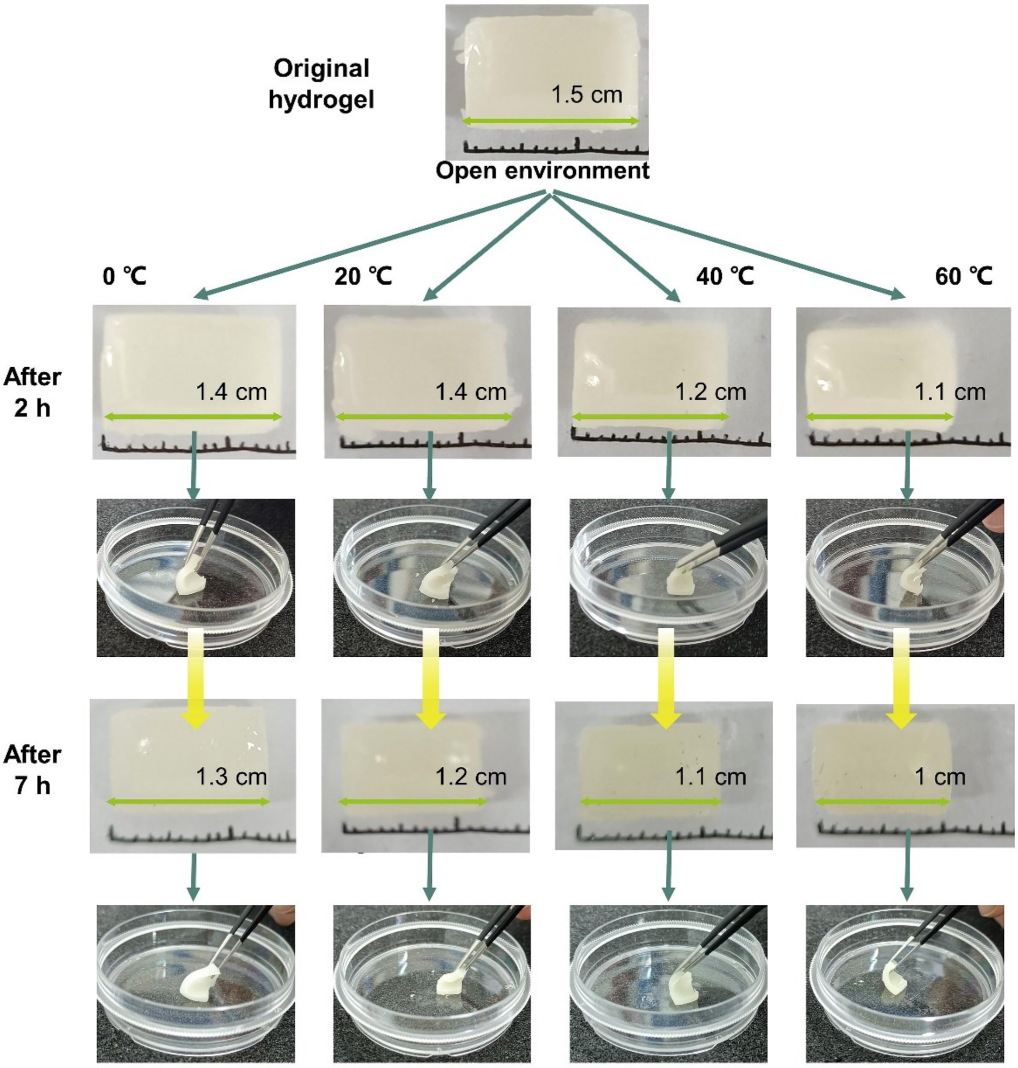


Fig. S12. Digital images of the morphology and mechanical deformation of the P-F127-B-hydrogel in open environment at different temperatures.

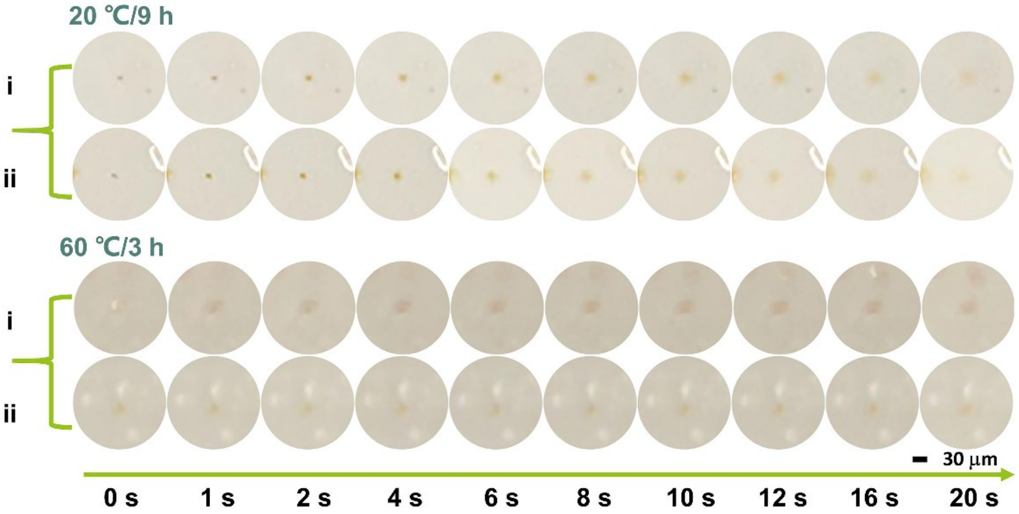


Fig. S13. The dynamic diffusion process of MO dye on the surface of the P-F127-B-hydrogels naturally dried for 9 h at room temperature and dried in oven for 3 h at 60 °C.

References

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