

Supporting Information for

Melt-Processable Shape-Memory Hydrogels with Self-Healing Ability of High Mechanical Strength

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Experimental

Materials. n-octadecyl acrylate (C18A, Sigma-Aldrich), sodium dodecylsulfate (SDS, Sigma-Aldrich), NaCl (Merck), ammonium persulfate (APS, Sigma-Aldrich), and sodium metabisulfite (SMS, Merck) were used as received. Acrylic acid (AAc, Merck) was freed from its inhibitor by passing through an inhibitor removal column (Sigma-Aldrich). The supramolecular hydrogels were prepared by conducting the micellar copolymerization of AAc and C18A at 55 °C in aqueous 1.5 M NaCl solutions containing 22 w/v% SDS. Because C18A is insoluble in SDS solutions, we added NaCl into the surfactant solution to induce the micellar growth and thus, to solubilize C18A in the grown SDS micelles.¹ C18A content in the comonomer feed was varied between 20 and 50 mol% C18A while the total monomer concentration was fixed at 1.0 M. The polymerization reaction was initiated using a redox initiator system consisting of 0.79 mM APS and 1 mM SMS. The reactions were conducted for 24 h in plastic syringes of 4.8 mm internal diameter as well as between two glass plates (5x5 cm) separated by a 0.5 mm Teflon spacer.

Swelling and gel fraction measurements. Hydrogel samples were immersed first in ethanol for 3 days and then in a large excess of water at 24 °C for 1 month by replacing water every day to extract any

soluble species. SDS concentration in the external solutions (before refreshing) dropped below the detection limit of the methylene blue method² (0.20 mg.L⁻¹) after about 10 d indicating completeness of SDS extraction from gel samples. Note that the pre-immersion of the gel samples in ethanol before contact with water is to prevent their initial swelling in water due to the presence of SDS, which otherwise resulted formation of cracks in the gel samples. The equilibrium swollen gel samples were taken out of water and dried at 55 °C under vacuum to constant mass. The water content of the hydrogels was estimated as $H_2O \% = 1 - m_{dry}/m$, where m and m_{dry} are the swollen and dry masses of the gel sample, respectively. The gel fraction W_g , i.e., the conversion of monomers to the water-insoluble polymer (mass of water-insoluble polymer / initial mass of the monomer) was calculated from the masses of dry, extracted polymer network and from the comonomer feed.

Rheological experiments. The gel samples in the form of sheets were subjected to rheological measurements between the parallel plates of the rheometer (Gemini 150 Rheometer system, Bohlin Instruments) equipped with a Peltier device for temperature control. The upper plate (diameter 40 mm) was set at a distance of 500 to 700 μm , depending on the swelling degree of the hydrogels. During all rheological measurements, a solvent trap was used to minimize evaporation. Further, the outside of the upper plate was covered with a thin layer of low-viscosity silicone oil to prevent evaporation of solvent. A frequency ω of 6.3 rad.s⁻¹ and a deformation amplitude $\gamma_0 = 0.001$ (0.1%) were selected to ensure that the oscillatory deformation is within the linear viscoelastic region. Thermal behavior of the gels was investigated by first keeping the samples at 65 °C for complete melting and then, cooling down to 25 °C, after keeping for 10 min at 25 °C, heating back to 65 °C. The cooling/heating steps were carried out at a fixed rate of 1 °C/min. The changes in the dynamic moduli of gels were monitored during the course of the cycle as a function of temperature. The gel samples were also subjected to frequency-sweep tests at $\gamma_0 = 0.001$ and at both 25 and 65 °C over the frequency range 0.06 to 180 rad.s⁻¹.

DSC measurements. DSC measurements were conducted on a Perkin Elmer Diamond DSC under nitrogen atmosphere. The gel samples sealed in aluminum pans were scanned between 5 and 80 °C with a heating and cooling rate of 5 °C/min. From the DSC curves, enthalpy changes during melting, ΔH_m , were calculated from the peak areas. The degree of crystallinity f_{cry} was estimated by $f_{cry} = \Delta H_m / \Delta H_m^o$, where ΔH_m^o is the melting enthalpy of crystalline C18A units, which was taken as 71.2 kJ.mol⁻¹.^{3,4}

X-ray diffraction. X-ray diffraction patterns of hydrogel samples were collected on a Rigaku SmartLab diffractometer using a Cu-K α source ($\lambda = 0.15418$ nm) operating at 30 kV / 15 mA. The XRD patterns were collected in the 1-35°, 2 θ range with a scan rate of 1°/min.

Mechanical and shape-memory tests. Uniaxial compression measurements were performed at 23 ± 2 °C on a Zwick Roell test machine using a 500 N load cell. Before the test, an initial compressive contact to 0.01 ± 0.002 N was applied to ensure a complete contact between the gel and the plates. Paraffin oil was used as lubricant to reduce friction and adhesion between the plates and the gel surface. The tests were conducted at a constant crosshead speed of 0.3 and 1 mm.min⁻¹ below and above 15% compression, respectively. Load and displacement data were collected during the experiment. Compressive stress was presented by its nominal σ_{nom} and true values σ_{true} , which are the forces per cross-sectional area of the undeformed and deformed gel specimen, respectively. Assuming the gel volume remains constant during deformation, the true stress σ_{true} was calculated as $\sigma_{true} = \lambda \sigma_{nom}$ where λ is the deformation ratio (deformed length / original length). The compressive strain ε_c is defined as the change in the length relative to the initial length of the gel specimen, i.e., $\varepsilon_c = 1 - \lambda$. The strain is also given by the biaxial extension ratio $\lambda_{biax} (= \lambda^{-0.5})$.⁵ The Young's modulus E was calculated from the slope of stress-strain curves between 5 and 15% compressions.

Uniaxial elongation measurements were performed with a Zwick Z2.5 tensile test instrument equipped with a 20 N load cell on hydrogel samples immersed in a temperature controlled water tank, utilizing an Ecoline Star Edition RE306 (Lauda, Königshofen, Germany). The actual temperature of the samples was measured by a Voltcraft multi-thermometer DT-300 positioned near the sample. A preforce of 10 mN was applied before the start of the measurements. The gel samples were stretched at 56 °C and at a strain rate of 10 mm.min⁻¹ up to 1500% strain ε ($= 1 - \lambda$) due to the instrumental limitation. Stress-relaxation tests were carried out by stretching the gel samples at 56 °C and at a strain rate of 10 mm.min⁻¹ up to a maximum strain ε_m of 100 and 200%, waiting at ε_m for 10 s, followed by retraction with a relaxation rate of 0.1 N.min⁻¹ to zero relaxation force which was 20 mN. After waiting for 15 min at zero relaxation force, the test was repeated four times.

The shape memory behavior of the hydrogel with 50 mol% C18A was investigated using cyclic thermomechanical tests.⁶ The gel sample was first stretched at 56 °C to ε_m of 100% at a strain rate of 10 mm.min⁻¹. After a waiting time of 5 min at ε_m to allow relaxation, the loaded sample was cooled to 35 °C while keeping the strain at ε_m . Finally, the sample was unloaded to zero relaxation force, 10 mN, and the strain $\varepsilon_u(n)$ of the sample in the temporary shape was obtained. The recovery behavior was followed by reheating the sample up to 56 °C with a rate of 1 °C.min⁻¹ and then keeping at this temperature. The total time at zero relaxation force was fixed at 50 min. After completion of the recovery process, the permanent elongation of the sample $\varepsilon_p(n)$ was determined. The strain recovery rate $R_r(n)$ and strain fixing rate $R_f(n)$ of the n th cycle were calculated by

$$R_r(n) = \frac{\varepsilon_m - \varepsilon_p(n)}{\varepsilon_m - \varepsilon_p(n-1)} \quad (S1)$$

$$R_f(n) = \frac{\varepsilon_u(n)}{\varepsilon_m} \quad (S2)$$

The shape memory effect was also examined by a bending test as follows: The cylindrical hydrogel samples with a diameter of 4.8 mm and a length about 6 cm is folded at 60 °C and then cooled to 25 °C to keep the deformation. The deformed sample is then stepwise heated from 25 to 70 °C at 1-3 °C steps. The recovering of the permanent shape is recorded in terms of the deformation angle θ_d depending on temperature. The measurements of θ_d were conducted using an image analyzing system consisting of a microscope (XSZ single Zoom microscope), a CDD digital camera (TK 1381 EG) and a PC with the data analyzing system Image-Pro Plus. The recovered angle R_θ to the permanent one was calculated as $R_\theta = \theta_d / 180$.

Self-healing tests. To quantify the healing efficiency, cylindrical gel samples of 5 mm diameter and 6 cm length were cut in the middle, and then the two halves were merged together within a plastic syringe (of the same diameter as the gel sample) at 80 °C by pressing the piston plunger for 24h. Thereafter, uniaxial compression and elongation tests were conducted as described above. The results were compared with those of the virgin gel samples.

References

- (1) Bilici, C.; Okay, O. Shape memory hydrogels via micellar copolymerization of acrylic acid and n-octadecyl acrylate in aqueous media. *Macromolecules* **2013**, 46, 3125-3131.
- (2) ISO 7875-1, 1996. Water quality. Determination of surfactants. Part 1: Determination of anionic surfactants by measurement of the methylene blue index (MBAS). ISO/TC 147.
- (3) Mogri, Z.; Paul, D. R. Gas sorption and transport in side-chain crystalline and molten poly(octadecyl acrylate). *Polymer* **2001**, 42, 2531-2542.

- (4) Bisht, H. S.; Pande, P. P.; Chatterjee, A. K. Docosyl acrylate modified polyacrylic acid: synthesis and crystallinity. *Eur. Polym. J.* **2002**, *38*, 2355-2358.
- (5) Webber, R. E.; Creton, C.; Brown, H. R.; Gong, J. P. Large strain hysteresis and Mullins effect of tough double-network hydrogels. *Macromolecules* 2007, **40**, 2919-2927.
- (6) Sauter, T.; Heuchel, M.; Kratz, K.; Lendlein, A. Quantifying the shape-memory effect of polymers by cyclic thermomechanical tests. *Polym. Rev.* **2013**, *53*, 6-40.