# Macromolecules

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

Cigdem Bilici,<sup>†</sup> Volkan Can,<sup>‡</sup> Ulrich Nöchel,<sup>§</sup> Marc Behl,<sup>§</sup> Andreas Lendlein,<sup>§</sup> and Oguz Okay<sup>\*,†,‡</sup>

<sup>†</sup>Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

<sup>‡</sup>Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

<sup>§</sup>Institute of Biomaterial Science and Berlin-Brandenburg Center for Regenerative Therapies, Helmholtz-Zentrum Geesthacht, Kantstr. 55, 14513 Teltow, Germany

Supporting Information

**ABSTRACT:** We present here a synthetic strategy for the preparation of melt-processable shape-memory hydrogels with self-healing ability. The supramolecular hydrogel with a water content of 60–80 wt % consists of poly(acrylic acid) chains containing 20–50 mol % crystallizable *n*-octadecyl acrylate (C18A) segments together with surfactant micelles. The key of our approach to render the hydrogel melt-processable is the absence of chemical cross-links and the presence of surfactant micelles. At temperatures above the melting temperature  $T_m$  of the crystalline domains of alkyl side chains, the hydrogel liquefies due to the presence of surfactant micelles effective for solubilizing the hydrophobic C18A segments. At this stage, it can easily be shaped into any desired form by pouring into molds. Cooling below  $T_m$  and removing the surfactant from the gel network results in a hydrogel of any permanent shape with a particularly high compressive strength of 90 MPa and a Young's modulus of 26 MPa. If the hydrogel was damaged on purpose e.g.



by cutting into two pieces, the extraordinary mechanical properties can completely be recovered via temperature-induced healing process. The hydrogel also exhibits a complete shape fixity ratio and a shape recovery ratio of  $97 \pm 2\%$ .

# **INTRODUCTION**

Shape-memory polymers are materials which have the capability to remember one or more shapes under various conditions and therefore have attracted significant interest in industry and academia due to their great potential for applications in sensors, actuators, and implants for minimally invasive surgery.<sup>1–4</sup> Besides the bulk polymers, hydrogels capable of a shape-memory effect have drawn increasing attention in the biomedical field because of their softness, smartness, elasticity, similarity to biological tissues, and excellent permeability for transport of nutrient and metabolites.<sup>5-13</sup> Typically, shape-memory hydrogels consist of a hybrid-cross-linked network structure composed of permanent cross-links (netpoints) and crystalline or glassy, amorphous domains acting as temporary cross-links (switching segments). While the netpoints determine the permanent shape of the hydrogel, the physical cross-links formed by solidification of the switching segments below the melting or glass transition temperatures fix the temporary shape gained by deformation of the gel sample at higher temperatures.<sup>4</sup> Shape-memory hydrogels based on covalently cross-linked poly(acrylic acid) (PAAc) network chain segments containing hydrophobic domains have been prepared in organic media as well as in aqueous micellar solutions.<sup>5,10,14,15</sup> Upon swelling of the hydrogels in water, hydrophilic acrylic acid (AAc) segments provide flexibility to the network chain segments so that hydrophobic units easily align to form crystalline domains with a melting temperature  $T_{\rm m}$  between 30 and 50 °C. The hydrogels exhibited 120–1000-fold increase in modulus by decreasing the temperature from above  $T_{\rm m}$  to a temperature below  $T_{\rm m}$  enabling a shape-fixity ratio ( $R_{\rm f}$ ) as a measure of how good the deformed shape is maintained of >99%.

Shape-memory hydrogels with the ability to self-heal have also been prepared through host-guest interactions, dynamic ester bonds, complexation, and hydrophobic interactions.<sup>16–19</sup> Meng et al. described a supramolecular approach based on dynamic phenylboronic acid-diol ester bonds and complexation of alginate with Ca<sup>2+</sup> ions to produce self-healing hydrogels with a shape-memory effect induced by metal ions.<sup>17</sup> However, the hydrogels are mechanically weak with an elastic modulus below 1 kPa. Zhang et al. prepared lighthealable, chemically cross-linked poly(N,N-dimethylacrylamideco-stearyl methacrylate) hydrogels with a tensile strength of 2.3 MPa possessing shape-memory properties.<sup>15</sup> The chemical cross-links and crystalline domains formed from the hydrophobic segments served as the chemical netpoints and switching segments, respectively. Self-healing PAAc hydrogels withstanding up to 1.7 MPa tensile stresses were recently

Received:July 16, 2016Revised:September 9, 2016Published:September 20, 2016

water (0/)

amustallinity (0/)

	water (70)		$I_{\rm m}$ ( C)		I <sub>crys</sub> (C)		crystallinty (70)	
C18A (mol %)	with SDS	without	with SDS	without	with SDS	without	with SDS	without
20	66	88		51 (0)		46 (0)	0	20 (1)
35	64	70	50 (1)	51 (0)	37 (1)	45 (1)	12 (2)	35 (3)
50	63	64	50 (0)	51 (1)	38 (1)	44 (1)	17 (1)	56 (2)
<sup>a</sup> Standard deviations	are in parenthe	ses while for th	ne water content	s, they are less	than 10%.			
					G', G" / MPa		С	
at Flow Exo	20%	35%		50% a	$ \begin{array}{c} 10^{1} \\ 10^{0} \\ 10^{-1} \\ 10^{-2} \\ 10^{-3} \\ 10^{-4} \\ 10^{-5} \\ 10^{-6} \\ 10^{0} \\ \end{array} $	25 °C	25 °C 65 °C	
ヹ <u></u> 2030		<u> </u>	<b>Ý</b>	40 50 60	10 <sup>-1</sup>	25 °C	A Company and and the factor of the factor o	900
Ze co 40 co co co co 40 co					10 <sup>-3</sup>		65 °C	
Ņ	Without			b	10 <sup>-4</sup> 10 <sup>-5</sup> 10 <sup>-6</sup>	65 °C		щ
Intensity	blank	6 7 8 19	Without Blank	2 23	10 <sup>-1</sup> 10 <sup>-2</sup> 10 <sup>-3</sup> 10 <sup>-4</sup> 10 <sup>-5</sup>	25 °C	25 °C	ш 102
		$2 \theta / ^{\circ}$			10	$\omega/ \text{ rad.s}^{-1}$		

# Table 1. Water Contents, Melting $(T_m)$ and Crystallization Temperatures $(T_{crys})$ , and Degrees of Crystallinity of the Hydrogels<sup>*a*</sup>

 $T (\circ C)$ 

 $T (^{\circ}C)$ 

**Figure 1.** (a) DSC traces of the hydrogels with (solid curves) and without SDS (dashed curves). C18A content of the hydrogels is indicated. (b) XRD pattern of 50% C18A hydrogel without (blue, dashed curves) and with SDS (dark-red, solid curves) in  $1-8^{\circ}$  and  $19-24^{\circ}$  in  $2\theta$  ranges. Scan rate =  $1^{\circ}$  min<sup>-1</sup>. The blank sample was prepared as the hydrogel sample but without C18A addition into the comonomer feed. (c) *G'* (filled symbols) and *G''* (open symbols) of the hydrogels with (left panel) and without SDS (right panel) shown as a function of the frequency  $\omega$ .  $\gamma_0 = 0.001$ . C18A = 50 (top), 35 (middle), and 20% (bottom). Temperature = 25 °C (circles) and 65 °C (triangles). The arrows indicate the changes in the moduli of 50% C18A hydrogel during two successive steps, namely, (i) cooling the gel containing SDS from 65 to 25 °C and (ii) extraction of SDS.

prepared on the basis of complex formation between hydrophobically modified PAAc and cetyltrimethylammonium (CTA) counterions.<sup>18</sup> The hydrogels also exhibited shapememory capability due to the variation of the elastic moduli with temperature. However, the shape fixity ratio of the hydrogels was low due to the noncrystalline state of the hydrophobic segments that cannot support the residual stress in PAAc chains.<sup>18</sup> More recently, it was shown that bulk photopolymerization of hydrophilic and hydrophobic monomers generate self-healing hydrogels with shape-memory effect due to the presence of hydrophobic associations and crystalline domains acting as the netpoints and switching segments, respectively.<sup>19</sup>

Although significant developments have been achieved in the field of shape-memory polymers and hydrogels, many applications demand shape-memory materials that can be melt-processed as thermoplastics. Because cross-linked polymers do not flow, typical methods for the processing of thermoplastic polymers such as injection molding cannot be used for the processing of these materials in a scale relevant for translation into market applications. Hence, ease of processability is an important topic for technological application of shape-memory polymers.<sup>2</sup> In this context a major challenge in

the preparation of shape-memory hydrogels is to combine meltprocessability with a high mechanical strength. Moreover, in terms of sustainability it would be beneficial if the hydrogels provide self-healing ability and could be prepared in a simple synthetic route.

To address this problem, here we present a supramolecular approach for the preparation of melt-processable shapememory hydrogels with self-healing ability. The supramolecular hydrogel with a water content of 60-80 wt % consists of PAAc chains containing 20-50 mol % crystallizable n-octadecyl acrylate (C18A) segments together with surfactant micelles. As compared to previous works,<sup>5,10,14,18,19</sup> the key of our approach is the absence of chemical cross-links and the presence of an extractable surfactant in the hydrogels. At temperatures above  $T_{\rm m}$  of the crystalline domains, the hydrogel liquefies due to the presence of surfactant micelles effective for solubilizing the hydrophobic associations. At this stage, it can easily be processed in any desired shape by pouring into molds. Cooling below  $T_{\rm m}$  and removing the surfactant results in a hydrogel of any permanent shape with a particularly high compressive strength of 90 MPa and a Young's modulus of 26 MPa. If damaged, the extraordinary mechanical properties can completely be recovered via temperature-induced healing. The



**Figure 2.** (a) *G'* (filled symbols) and *G''* (open symbols) of the hydrogels with (triangles) and without SDS (circles) during cooling and heating scans. DSC traces of the hydrogels with and without SDS are also shown by the solid and dashed curves, respectively. C18A = 50 (top), 35 (middle), and 20% (bottom panel).  $\omega = 6.3$  rad s<sup>-1</sup>.  $\gamma_0 = 0.001$ . (b) *G'* and tan  $\delta$  of the hydrogels without (left panel) and with SDS (right panel) at below and above the melting temperature.  $\omega = 6.3$  rad s<sup>-1</sup>.  $\gamma_0 = 0.001$ .

hydrogel also exhibits complete shape recovery due to the hydrophobic blocks of the polymer. As will be seen below, the hydrophobic domains of the hydrogels forming strong associations or crystalline domains above or below  $T_{\rm m}$ , respectively, act both as physical netpoints and switching segments.

## RESULTS AND DISCUSSION

Hydrogels were prepared by micellar copolymerization of the hydrophilic monomer AAc with 20-50 mol % hydrophobic monomer C18A at a total monomer concentration of 1 M by free radical polymerization. The advantage of the micellar polymerization technique over the solution polymerization is the formation of copolymers in a blocky structure because of the local high concentration of hydrophobic monomer in the micelles,<sup>20</sup> facilitating the formation of the aggregates.<sup>21–23</sup> We used an aqueous solution containing NaCl (1.5 M) and sodium dodecyl sulfate (SDS, 22% w/v) as the micellar solution.<sup>10,24</sup> The addition of NaCl into the surfactant solution facilitates the growth of SDS micelles and solubilizes the hydrophobic monomer C18A in this micellar solution.<sup>10,25</sup> In order to obtain supramolecular PAAc hydrogels, there is no chemical cross-linker added during synthesis. The polymerization reaction was initiated using a redox initiator system consisting of ammonium persulfate (0.79 mM) and sodium metabisulfite (1 mM). After a reaction time of 24 h, the conversion of monomers to the water-insoluble polymer was found to be more than 90% (for details, see Supporting Information). The micellar polymerization technique necessarily results in hydrogels containing SDS micelles at a concentration of 22% w/v. To remove the surfactant from the hydrogels, they were first immersed in ethanol for 3 days and then in a large excess of water for 1 month whereby all surfactant molecules could be

removed from the gel network (for details, see Supporting Information). In the following, as-prepared and water-swollen hydrogels will be denoted as those with and without SDS, respectively. Moreover, the hydrogels are denoted as x% C18A in which x is the mole fraction of C18A in the feed. The supramolecular hydrogels with or without SDS contain 64–88 wt % water that increases with decreasing C18A content (Table 1).

DSC traces shown in Figure 1a reveal that except 20% C18A hydrogel with SDS, they all exhibit melting and crystallization peaks. The melting  $(T_m)$  and crystallization temperatures  $(T_{\rm crvs})$  of the physical gels are listed in Table 1 together with the degrees of crystallinity, estimated by assuming that the enthalpy change during melting of crystalline C18A units is 71.2 kJ/mol.<sup>26,27</sup>  $T_{\rm m}$  of the hydrogels is at around 50 °C, regardless of the hydrophobe content or the presence of surfactant micelles, while recrystallization of molten hydrophobic domains occurs at a lower temperature than melting. The degree of the crystallinity increases with increasing C18A content as well as after removal of SDS from the gel network. The latter is related with the formation of mixed micelles composed of SDS and C18A units of the polymer hindering the formation of crystalline domains.<sup>25</sup> Figure 1b shows the X-ray diffraction (XRD) patterns of the hydrogel sample containing 50 mol % C18A with and without SDS. The pattern of the sample without SDS exhibits a sharp peak at 1.4° and a broad, higher angle peak at 21.3° corresponding to Bragg *d*-spacings of 6.3 and 0.42 nm, respectively. The d-spacing of 0.42 nm indicates packing of the side alkyl chains of C18A units in a paraffin-like hexagonal lattice, while the d-spacing of 6.3 nm reveals tail-to-tail alignment of the side chains perpendicularly to the main chains.<sup>S-8,10,28</sup> The hydrogel sample with SDS exhibits several peaks due to the presence of surfactant micelles. To distinguish the surfactant peaks, XRD measurements were



**Figure 3.** Images demonstrating the melt-processability, shape-memory, and self-healing behavior of the hydrogels. (a) Flow behavior of hydrogels containing surfactant at 60 °C. (b) Various permanent shapes after cooling and surfactant extraction, where two gel solutions were colored with dyes. (c) The shape recovery within 15 s from the temporary compressed ring to the permanent ring shape at 60 °C. (d) Photographs of two virgin hydrogel samples after equilibrium swelling in water. One of the gel samples was colored for clarity. Gel samples were brought together in a closed container and fused together by heating to 80 °C for 1 day. After stretching the combined gel samples at 56 °C, the healed gel sustains up to 1500% strain. All images are from hydrogel samples with 50 mol % C18A.

also conducted using control samples obtained by micellar polymerization in the absence of the hydrophobic comonomer C18A. Thus, these samples correspond to a semidilute solution of PAAc and SDS micelles. The XRD pattern of this sample denoted as blank is also shown in Figure 1b. Comparison of the control with the gel sample containing SDS reveals that the gel exhibits a characteristic peak at  $21.6^{\circ}$  (*d*-spacing 0.41 nm) indicating hexagonal packing of the side alkyl chains in the presence of surfactant.

Figure 1c shows the frequency  $(\omega)$  dependencies of the elastic modulus G' (filled symbols) and viscous modulus G" (open symbols) of the hydrogels at 25 and 65 °C, i.e., at below and above  $T_{\rm m}$  of crystalline domains. The data from hydrogels with (left panel) and without SDS (right panel) are shown. At 65 °C, the hydrogels with SDS exhibit a liquid-like response typical for a semidilute polymer solution; i.e., G'' exceeds G'over a wide range of frequencies while there is a crossover point between G' and G'' at a high frequency ( $\geq 160 \text{ rad s}^{-1}$ ). Cooling the hydrogel containing SDS below  $T_{crys}$  forms a weak gel which, after extraction of SDS, exhibits frequencyindependent elastic modulus of 0.2-8 MPa and a loss factor tan  $\delta$  (= G''/G') close to 0.01, as typical for strong gels. Particularly remarkable is the drastic change in the viscoelastic properties of 50% C18A hydrogel during these successive steps, namely (i) cooling the gel containing SDS from 65 to 25 °C and (ii) extraction of SDS. These are illustrated in Figure 1c by the arrows. Starting from a viscoelastic liquid with tan  $\delta$  = 3 at a frequency of 6.3 rad  $s^{-1}$ , one may obtain a hydrogel with an elastic modulus of 8.4 MPa and tan  $\delta$  = 0.02.

The variation of the temperature-dependent moduli of the hydrogels was investigated at a fixed frequency (6.3 rad  $s^{-1}$ ) during the cooling—heating cycles between 65 and 25 °C. Figure 2a shows G' and G" of the hydrogels with and without SDS during cooling and heating scans. DSC traces of the gels with and without SDS are also shown in the figures by the solid and dashed curves, respectively. At a temperature around the melting and crystallization temperatures, the moduli of the hydrogels change reversibly due to the formation and melting of the crystalline domains of the alkyl side chains. In Figure 2b,

G' and the loss factor tan  $\delta$  of the hydrogels without and with SDS at below (25 °C) and above (65 °C)  $T_{\rm m}$  are exhibited. The dashed horizontal lines denote tan  $\delta$  values for sol-to-gel (=1) and weak-to-strong gel (=0.1) transitions. 50% C18A hydrogel without SDS undergoes a reversible 1100-fold change in G'(between 8.4 MPa and 7.5 kPa) below and above  $T_{\rm m}$ . Simultaneously, tan  $\delta$  changes between below and above 0.1, demonstrating reversible weak-to-strong gel transition. Moreover, the hydrogels with SDS undergo reversible sol-gel transitions during thermal cycling; i.e., tan  $\delta$  changes between below and above unity. Hydrogels become solutions at temperatures above 36, 46, and 49 °C for 20, 35, and 50 mol % C18A samples, respectively. On cooling, they recover their gel states at 34, 40, and 48 °C, respectively. Thus, sol-to-gel and weak-to-strong gel transitions can be observed depending on the presence of the surfactant and on the temperature. The results also show easy transformation of a polymer solution into a strong hydrogel possessing a modulus of around 8 MPa.

Figure 3 demonstrates moldability and shape-memory capability of 50% C18A hydrogels. After heating to 60 °C, the hydrogel with SDS is in a liquid state and could be shaped in any desired shape by pouring into molds (Figure 3a,b and Supporting Information movie). After cooling to 25 °C and extracting SDS from the gel, this permanent shape is fixed. When the gel sample is heated above  $T_m$ , the gel becomes soft and could be deformed into any temporary shape, which is fixed afterward by cooling it to 25 °C (Figure 3c). Once the gel sample is heated in a water bath to 60 °C, it recovers its permanent shape within 15 s (Figure 3c).

We propose that the moldability and the shape-memory capability of the hydrogels appear due to the temperature- and surfactant-induced changes in the properties of the physical cross-links, as depicted in Figures 4a–d. For the hydrogel with SDS, mixed micelles consisting of C18A blocks of the polymer and SDS act as the physical cross-links (a).<sup>25</sup> Because of the weakening of hydrophobic interactions in the presence of a surfactant,<sup>24</sup> the hydrogel is weak with an elastic modulus of  $10^{-2}-10^{-1}$  MPa and a loss factor above 0.1 (Figure 1c). Upon heating the hydrogel above  $T_m$ , the hydrophobic domains are

#### Macromolecules



Figure 4. Cartoon showing the physical cross-links of the hydrogels at various stages.

solubilized by the SDS micelles to form a semidilute polymer solution (b). Moreover, removing SDS from the hydrogel drastically changes the viscoelastic properties of the hydrogels due to the increasing extent of hydrophobic interactions (Figure 1c). Hydrophobic groups in the SDS-free hydrogel form stronger associations and larger number of crystalline domains to minimize their exposure to the gel phase; thereby the modulus increases to  $10^{-1}-10^{1}$  MPa and the loss factor decreases below 0.1. Heating above  $T_{\rm m}$  again destroys the crystalline domains while the associations formed act as the physical netpoints in the hydrogels (Figure 4c $\rightarrow$ d). Thus, the hydrophobic associations of C18A blocks of the hydrophilic

polymer chains act as physical netpoints to determine the permanent shape while, below  $T_{\rm m}$ , the same blocks forming side chain alkyl crystals act as molecular switches to fix the temporary shape gained by deformation of the hydrogel sample at a temperature above  $T_{\rm m}$ .

Shape-memory properties of the hydrogels were determined by both bending experiments and uniaxial tensile tests conducted in aqueous environment. Bending test was carried out by first folding the cylindrical hydrogel sample at 60 °C to a deformation angle  $\theta_d$  of 180° and then cooling to 15 °C to fix the deformation (Figure S1). The deformed sample was then stepwise heated from 15 to 70 °C in steps of 1-3 °C whereby the recovering of the permanent shape was recorded in terms of the deformation angle  $\theta_d$  depending on temperature (see Figure S2). Results of bending tests are presented in Figure 5a where the recovered permanent angle  $R_{\theta}$  (= 1 -  $\theta_{\rm d}/180$ ) of the folded hydrogels is shown as a function of the temperature.  $R_{\theta}$ increases to 100% for gels with 35 and 50 mol % C18A over a rather small temperature range, i.e., between 45-59 and 50-61 °C, respectively. Thus, the crystalline domains in these hydrogels are able to fix the temporary folded shape up to a temperature close to their melting temperature  $T_{\rm m}$  (51 °C). In contrast, the  $R_{\theta}$  value of 20% C18A hydrogel steadily increases with temperature, which we attribute to the low crystallinity of this sample, i.e., its lower physical netpoint density (Table 1).

The fixity of the permanent shape solely by hydrophobic associations was explored in stress relaxation experiments. The tests were conducted at 56  $^{\circ}$ C on hydrogel samples with 50 mol % C18A. At this temperature, no more crystalline domains exist, and hence all C18A blocks in the hydrogel involve in



**Figure 5.** (a) Variation of the recoverability  $R_{\theta}$  of the permanent angle of folded hydrogels with temperature as a function of C18 mol % content. (b) Nominal stress  $\sigma_{nom}$  vs strain  $\varepsilon$  curves from stress relaxation tests conducted at 56 °C on hydrogel samples up to a maximum strain of 100% (left) and 200% (right). Five successive loading/unloading cycles conducted on a 50% C18A gel specimen are shown. (c) Results of five successive thermomechanical shape-memory cycles conducted on 50 mol % C18A hydrogel as the dependence of the nominal stress  $\sigma_{nom}$  on the strain  $\varepsilon$ . (d) Strain  $\varepsilon$  (solid curve)/temperature (dashed curve) vs time plots of five successive thermomechanical shape-memory cycles.



**Figure 6.** (a, b) Typical stress-strain curves of the hydrogels under compression as the dependencies of nominal  $\sigma_{nom}$  (a) and true stresses  $\sigma_{true}$  (b) on the compressive strain  $\varepsilon_c$ . Inset to (b) shows the  $\sigma_{true}$  vs  $\lambda_{biax}$  plots. Circles corresponding to the maxima in  $\sigma_{true} - \lambda$  (or,  $\sigma_{true} - \lambda_{biax}$ ) plots are taken as the points of failure in the gel samples. C18A content of the hydrogels is indicated. Solid and dashed (blue) curves are results obtained from virgin and healed hydrogel samples, respectively. (c) Young's modulus *E*, fracture stress  $\sigma_{b}$  and fracture strain  $\varepsilon_{f}$  of the virgin (filled symbols) and healed hydrogels (open symbols) plotted against their hydrophobe (C18A) content. (d) Stress-strain curves of tensile tests conducted at 56 °C on virgin and healed hydrogel samples with 50 mol % C18A.

hydrophobic associations or exist as nonassociated free groups. Stress-relaxation test were performed on a tensile tester Zwick Z2.5 (see Supporting Information) with a tempered water tank at 56 °C in order to determine the elastic recovery of the hydrogel samples at  $T > T_m$ . The specimens were stretched to an elongation  $\varepsilon_{\rm m}$  of 100% or 200% with a deformation rate of 10 mm min<sup>-1</sup> and then held shortly for a time period of 10 s under constant strain. Afterward, the stress was released to a zero force of 10 mN at a rate of 0.1 N min<sup>-1</sup> to enable the sample to recover from the imposed strain. When this zero force condition was maintained for 15 min, the elongation of the sample reached a plateau, and the recovered elongation became stable. This cycle was then repeated four times. The results of five successive stress-relaxation tests are shown in Figure 5b as the dependence of the nominal stress  $\sigma_{\rm nom}$  on the strain  $\varepsilon$ , i.e.,  $\lambda - 1$ , where  $\lambda$  is the elongation ratio. The maximum strain  $\varepsilon_m$  is 100% (left) and 200% (right). In both cases, the first cycle shows the largest mechanical hysteresis and permanent deformation. We attribute this to decoupling of entanglements, disruption of weak associations, and reorientation of polymer chains. However, the following cycles are almost reversible with no additional permanent deformation. The average hysteresis energy  $U_{\rm hys}$  for the second to fifth cycles calculated from the area between the loading and unloading curves is 0.44  $\pm$  0.05 and 0.8  $\pm$  0.1 MJ m<sup>-3</sup> for  $\varepsilon_{\rm m}$  = 100% and 200%, respectively. These are 2 orders of magnitude larger than  $U_{\rm hys}$  of supramolecular hydrogels formed via hydrophobic associations<sup>24,29</sup> and reveal the existence of larger number of associations in the present hydrogels. Moreover, because  $U_{\rm hys}$  is related to the extent of damage in the gel samples, i.e., to the number of bonds broken during the loading/unloading cycle,<sup>24,30</sup> the reversibility of the successive cycles reveals that the damage done to the gel samples is recoverable in nature. Thus, the results indicate temperature-triggered healing ability of the hydrogels. The tests also confirm that the hydrophobic

associations are very effective acting as netpoints determining the permanent shape of the hydrogels.

The hydrogel sample with 50 mol % C18A was also subjected to thermomechanical shape-memory cycles. The gel sample was first stretched at 57 °C to  $\varepsilon_m$  of 100% at a strain rate of 10 mm min<sup>-1</sup>. After a waiting time period of 5 min at  $\varepsilon_m$ to allow relaxation, the loaded sample was cooled to 32 °C while keeping the strain at  $\varepsilon_m$ . 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 57 °C with a rate of 1 °C min<sup>-1</sup> 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 ratio  $R_r(n)$  and strain fixity ratio  $R_f(n)$  of the *n*th cycle were calculated by

$$R_{\rm r}(n) = \frac{\varepsilon_{\rm m} - \varepsilon_{\rm p}(n)}{\varepsilon_{\rm m} - \varepsilon_{\rm p}(n-1)}$$
(1)

$$R_{\rm f}(n) = \frac{\varepsilon_{\rm u}(n)}{\varepsilon_{\rm m}} \tag{2}$$

The results of five shape-memory cycles are shown in Figure 5c as stress  $\sigma_{nom}$  vs strain  $\varepsilon$  plots, while Figure 5d displays corresponding strain/temperature vs time plots. The hydrogel completely preserves its temporary shape after relaxation at 32 °C, which is equivalent to a  $R_f$  of >99%. Moreover, similar to the results of stress-relaxation tests (Figure 5b), the first thermomechanical cycle results in a permanent deformation in the hydrogel and the shape recovery ratio  $R_r(1)$  of this cycle is 76%. However, excellent reproducibility and reversibility of the shape changes were observed in the subsequent cycles (n = 2-5) with an average shape recovery ratio  $R_r(n)$  of 97  $\pm 2\%$ .

Considering the first cycle as the preconditioning cycle, the shape of the hydrogel is almost completely recovered by heating above  $T_m$  of crystalline domains.

The mechanical properties of SDS-free hydrogels after cooling to  $23 \pm 2$  °C were determined by uniaxial compression and tensile measurements. Solid curves in Figures 6a and 6b represent typical stress-strain curves of the hydrogels as the dependencies of the nominal  $\sigma_{nom}$  (a) and true stresses  $\sigma_{true}$  (b) on the compressive strain  $\varepsilon_c$  (= 1 -  $\lambda$ ), respectively. Because uniaxial compression corresponds to biaxial extension,  $\sigma_{\rm true}$  is also plotted against the biaxial extension ratio  $\lambda_{\text{biax}}$  (= $\lambda^{-0.5}$ ) in the inset to Figure 6b. From  $\sigma_{nom}$  vs  $\varepsilon_{c}$  curves, it is seen that the hydrogels sustain compressions up to about 94%, and they rupture under 30-160 MPa nominal stresses. However, the corresponding  $\sigma_{\rm true}$  vs  $\varepsilon_{\rm c}/\lambda_{\rm biax}$  plots pass through maxima below these strains (Figure 6b), indicating that the actual fracture points are below these stress values. This behavior is a result of the formation of microscopic cracks sustaining the stress under large strain.<sup>29,31</sup> Therefore, the fracture nominal stress  $\sigma_{\rm f}$  and strain  $\varepsilon_{\rm f}$  at failure were calculated from the maxima in  $\sigma_{\rm true} - \varepsilon_{\rm c}$ or  $\lambda \sigma_{\rm true} - \lambda_{\rm biax}$  plots, as indicated by the dashed vertical lines and circles in the figures. Filled circles in Figure 6c show Young's modulus E, fracture stress  $\sigma_{tr}$  and fracture strain  $\varepsilon_{f}$  of the hydrogels plotted against the C18A content. All hydrogel samples were capable to sustain up to 85-92% compressive strain. They display particularly high compressive strength (12-90 MPa) and Young's modulus (0.5-26 MPa), which increase with increasing C18A content. Note that the measured Young's modulus is approximately 3 times the frequency independent elastic modulus of the hydrogels (0.2-8 MPa), consistent with an isotropic elastic material of Poisson's ratio close to 0.5.32 The hydrogels were also subjected to tensile testing experiments at 23  $\pm$  2 °C. They exhibited a high Young's modulus (0.1-28 MPa) but a low stretchability (3-40% elongation) and low fracture stress (33-751 kPa) due to the high degree of crystallinity of the hydrogels (Table S1 and Figure S3).

Because of the supramolecular network structure of the present hydrogels, they exhibited self-healing ability when the damaged areas were heated above the melting temperature of the crystalline domains. The large mechanical hysteresis and the reversibility of the loading/unloading cycles shown in Figure 5b already demonstrate the self-healing capability of the hydrogels. This is also illustrated in Figure 3d where photographs of two virgin 50% C18A hydrogel samples after equilibrium swelling in water are shown. After pressing the gel surfaces together in a closed container at 80 °C for 24 h, they merge into a single specimen. The dashed (blue) curves in Figures 6a and 6b show the stress-strain curves of the healed gel samples. A perfect superposition is observed between the stress-strain curves obtained from virgin (solid curves) and healed gel samples. The mechanical data of the healed hydrogels are represented by the open triangles in Figure 6c. The results reveal complete healing efficiency with respect to the compressive modulus, fracture stress, and fracture strain after a healing time period of 24 h at 80 °C. Healing tests were also conducted by uniaxial elongation tests at an elevated temperature. Figure 6d shows tensile test results of virgin and healed hydrogel samples at 56 °C. Note that samples could only be elongated up to 1500% because of the experimental limitation (dimensions of the water tank). A good superposition is observable in tensile stress-strain curves, indicating a complete healing of the gel sample. Indeed, the Young's modulus E of both virgin and healed hydrogels is 12

kPa at 56 °C, indicating complete recovery of the initial microstructure of the physical hydrogel.

The supramolecular approach described here can be extended to create a range of melt-processable hydrogels by varying the hydrophilic and hydrophobic monomers as well as hydrophobically modified polymer-surfactant systems. The key requirement is the presence of surfactant micelles in the physical gels effective for solubilizing the hydrophobic associations at a high temperature. Moreover, the surfactant should not form a complex with the polymer chains such as in oppositely charged surfactant-polymer systems, so that it could be removed from the physical network after determining the permanent shape of the hydrogel. A high mechanical strength and a complete shape-memory effect require hydrophobic segments in hydrophilic polymers able to form strong associations and crystalline domains acting as physical netpoints and molecular switches, respectively. We have to note that the elaborative surfactant removal step from the hydrogels, namely immersion in ethanol for 3 days and then in water for 1 month, is the limitation of the present approach for translation of the materials into marked applications. Further work is in progress to develop an easy surfactant removal process from the hydrogels.

#### CONCLUSIONS

We present a supramolecular approach to the preparation of melt-processable shape-memory hydrogels with self-healing ability. The hydrogels contain 60-80 wt % water and consist of PAAc chains containing 20-50 mol % C18A segments together with SDS micelles. The key of our approach is the absence of covalent cross-links and the presence of surfactant in the hydrogels. Above the melting temperature  $T_{\rm m}$  of the crystalline domains, the hydrogel liquefies due to the presence of surfactant micelles effective for solubilizing the hydrophobic associations. At this stage, it can easily be processed in any desired shape by pouring into molds. Cooling below  $T_{\rm m}$  and removing the surfactant results in a hydrogel of any permanent shape with a compressive strength of 90 MPa and a Young's modulus of 26 MPa. The hydrogel exhibited complete shape recovery due to the hydrophobic blocks of the polymer acting as physical netpoints and switching segments above and below  $T_{\rm m}$ , respectively. If damaged, the extraordinary mechanical properties could be completely recovered via temperatureinduced healing process. The synthetic strategy presented here offers the design of shape-memory hydrogels in various permanent shapes for the production of multifunctional smart hydrogel coatings, thin films, microspheres, tubings, rods, and wires to be used in various applications, including biomedical, packaging, sensors, and actuators.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.6b01539.

Experimental details including synthesis, sample preparation, characterization, and tensile properties of the hydrogels at 23  $^{\circ}$ C (PDF)

The movie showing the flow behavior of hydrogels containing surfactant at 60  $^{\circ}$ C (AVI)

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*(O.O.) E-mail: okayo@itu.edu.tr.

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

Work was supported by Alexander von Humboldt Foundation (Georg-Forster Research Award Program) and the Scientific and Technical Research Council of Turkey (TUBITAK), KBAG 114Z312. O.O. thanks Turkish Academy of Sciences (TUBA) for the partial support.

# **REFERENCES**

(1) Lendlein, A.; Kelch, S. Shape-memory polymers. Angew. Chem., Int. Ed. 2002, 41, 2034–2057.

(2) Liu, C.; Qin, H.; Mather, P. T. Review of progress in shapememory polymers. J. Mater. Chem. 2007, 17, 1543-1558.

(3) Julich-Gruner, K. K.; Löwenberg, C.; Neffe, A. T.; Behl, M.; Lendlein, A. Recent trends in the chemistry of shape-memory polymers. *Macromol. Chem. Phys.* **2013**, *214*, 527–536.

(4) Behl, M.; Razzaq, M. Y.; Lendlein, A. Multifunctional shapememory polymers. *Adv. Mater.* **2010**, *22*, 3388–3410.

(5) Matsuda, A.; Sato, J.; Yasunaga, H.; Osada, Y. Order-disorder transition of a hydrogel containing an n-alkyl acrylate. *Macromolecules* **1994**, *27*, 7695–7698.

(6) Osada, Y.; Matsuda, A. Shape memory in hydrogels. *Nature* 1995, 376, 219.

(7) Tanaka, Y.; Kagami, Y.; Matsuda, A.; Osada, Y. Thermoreversible transition of the tensile modulus of a hydrogel with ordered aggregates. *Macromolecules* **1995**, *28*, 2574–2576.

(8) Uchida, M.; Kurosawa, M.; Osada, Y. Swelling process and orderdisorder transition of hydrogel containing hydrophobic ionizable groups. *Macromolecules* **1995**, *28*, 4583–4586.

(9) Nöchel, U.; Reddy, C. S.; Uttamchand, N. K.; Kratz, K.; Behl, M.; Lendlein, A. Shape-memory properties of hydrogels having a poly(*e*caprolactone) crosslinker and switching segment in an aqueous environment. *Eur. Polym. J.* **2013**, *49*, 2457–2466.

(10) 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.

(11) Balk, M.; Behl, M.; Nöchel, U.; Lendlein, A. Shape-memory hydrogels with switching segments based on  $\text{oligo}(\omega$ -pentadecalactone). *Macromol. Mater. Eng.* **2012**, 297, 1184–1192.

(12) Hao, J.; Weiss, R. A. Mechanically tough, thermally activated shape memory hydrogels. *ACS Macro Lett.* **2013**, *2*, 86–89.

(13) Han, Y.; Bai, T.; Liu, Y.; Zhai, X.; Liu, W. Zinc ion uniquely induced triple shape memory effect of dipole–dipole reinforced ultrahigh strength hydrogels. *Macromol. Rapid Commun.* **2012**, *33*, 225–231.

(14) Lin, X. K.; Chen, L.; Zhao, Y. P.; Dong, Z. Z. Synthesis and characterization of thermoresponsive shape-memory poly(stearyl acrylate-co-acrylamide) hydrogels. *J. Mater. Sci.* **2010**, *45*, 2703–2707.

(15) Zhang, H.; Han, D.; Yan, Q.; Fortin, D.; Xia, H.; Zhao, Y. Lighthealable hard hydrogels through photothermally induced melting– crystallization phase transition. *J. Mater. Chem. A* **2014**, *2*, 13373– 13379.

(16) Miyamae, K.; Nakahata, M.; Takashima, Y.; Harada, A. Self-Healing, expansion-contraction, and shape-memory properties of a preorganized supramolecular hydrogel through host-guest interactions. *Angew. Chem., Int. Ed.* **2015**, *54*, 8984–8987.

(17) Meng, H.; Xiao, P.; Gu, J.; Wen, X.; Xu, J.; Zhao, C.; Zhang, J.; Chen, T. Self-healable macro-/microscopic shape memory hydrogels based on supramolecular interactions. *Chem. Commun.* **2014**, *50*, 12277–12280. (18) Gulyuz, U.; Okay, O. Self-healing poly(acrylic acid) hydrogels with shape memory behavior of high mechanical strength. *Macro-molecules* **2014**, *47*, 6889–6899.

(19) Kurt, B.; Gulyuz, U.; Demir, D. D.; Okay, O. High-strength semi-crystalline hydrogels with self-healing and shape memory functions. *Eur. Polym. J.* **2016**, *81*, 12–23.

(20) Peer, W. J. Polymerization of hydrophobically modified polyacrylamide: Effects of surfactants and comonomers. In *Polymers in Aqueous Media - Performance Through Association*; Glass, J. E., Ed.; Advances in Chemistry; American Chemical Society: 1989; Vol. 223, pp 381–397.

(21) Hill, A.; Candau, F.; Selb, J. Properties of hydrophobically associating polyacrylamides: influence of the method of synthesis. *Macromolecules* **1993**, *26*, 4521–4532.

(22) Candau, F.; Selb, J. Hydrophobically-modified polyacrylamides prepared by micellar polymerization. *Adv. Colloid Interface Sci.* **1999**, 79, 149–172.

(23) Tuncaboylu, D. C.; Argun, A.; Sahin, M.; Sari, M.; Okay, O. Structure optimization of self-healing hydrogels formed via hydrophobic interactions. *Polymer* **2012**, *53*, 5513–5522.

(24) Tuncaboylu, D. C.; Sahin, M.; Argun, A.; Oppermann, W.; Okay, O. Dynamics and large strain behavior of self-healing hydrogels with and without surfactants. *Macromolecules* **2012**, *45*, 1991–2000.

(25) Can, V.; Kochovski, Z.; Reiter, V.; Severin, N.; Siebenbürger, M.; Kent, B.; Just, J.; Rabe, J. P.; Ballauff, M.; Okay, O. Nanostructural evolution and self-healing mechanism of micellar hydrogels. *Macromolecules* **2016**, *49*, 2281–2287.

(26) Mogri, Z.; Paul, D. R. Gas sorption and transport in side-chain crystalline and molten poly(octadecyl acrylate). *Polymer* **2001**, *42*, 2531–2542.

(27) Bisht, H. S.; Pande, P. P.; Chatterjee, A. K. Docosyl acrylate modified polyacrylic acid: synthesis and crystallinity. *Eur. Polym. J.* **2002**, *38*, 2355–2358.

(28) Livshin, S.; Silverstein, M. S. Crystallinity and cross-linking in porous polymers synthesized from long side chain monomers through emulsion templating. *Macromolecules* **2008**, *41*, 3930–3838.

(29) Algi, M. P.; Okay, O. Highly stretchable self-healing poly(N,N-dimethylacrylamide) hydrogels. *Eur. Polym. J.* 2014, *59*, 113–121.

(30) 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.

(31) Argun, A.; Can, V.; Altun, U.; Okay, O. Non-ionic double and triple network hydrogels of high mechanical strength. *Macromolecules* **2014**, *47*, 6430–6440.

(32) Treloar, L. R. G. The Physics of Rubber Elasticity; University Press: Oxford, 1975.