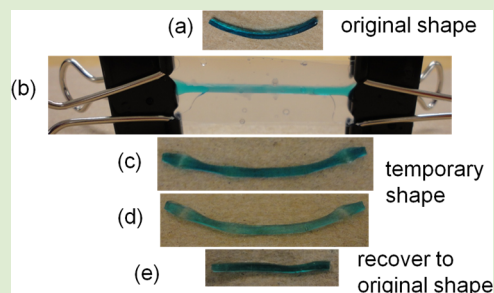


Mechanically Tough, Thermally Activated Shape Memory Hydrogels

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ABSTRACT: The shape memory behavior of a series of strong, tough hybrid hydrogels prepared by covalently cross-linking quad-polymers of *N,N*-dimethylacrylamide (DMA), 2-(*N*-ethylperfluoro-octanesulfonamido) ethyl methacrylate (FOSM), hydroxyethyl acrylate, and 2-cinnamoyloxyethyl acrylate was investigated. The hybrid hydrogels, which had physical and covalent cross-links, contained ~60–70% water, were relatively soft and elastic, and exhibited high mechanical strength, extensibility, and fracture toughness. The temporary network was derived from glassy nanodomains due to microphase separation of the FOSM species. The switching temperature for shape memory was the glass transition temperature of the nanodomains. Some creep relaxation occurred in the fixed shape due to viscoelastic effects of the nanodomain cross-links, but shape fixing efficiencies of 84–88% were achieved for the fixed shape after 24 h at 10 °C. Shape recovery to the permanent shape was achieved by reheating the hydrogel to 65 °C and was essentially quantitative.



Shape memory polymers (SMPs) are stimuli-responsive materials that can be deformed and fixed into a temporary shape and have the ability to recover the original, permanent shape upon exposure to an external stimulus, such as temperature, light, moisture, or electric field.^{1,2} SMPs have many biomedical or sensory applications, such as smart medical devices, implants for minimally invasive surgery, or heat-shrinkable tubing and films. Most of the research on SMPs has been confined to neat polymers in their dry state. Relatively little work has considered shape memory hydrogels, which are soft and predominantly water, similar to biological tissues.^{3,4} Early work on shape memory hydrogels concerned chemically cross-linked poly(vinyl alcohol),^{5,6} which can be stretched to 200% in boiling water and quenched in a poor solvent to “pin” a temporary shape. The programmed shape can be recovered by reimmersing the gel in boiling water.⁵ More recently, shape memory behavior was observed in a hydrogel containing a collagen end block which could self-assemble into triple helical nodes to fix a temporary shape. That hydrogel, however, was very soft, with a modulus only in a range of 10²–10⁴ Pa, and weak, which limited its application.⁷

Hydrogels are usually weak and brittle, and very few strong, robust hydrogels that exhibit shape memory behavior have been reported.^{8,9} Osada and co-workers^{8,10–12} reported a shape memory hydrogel composed of a covalently cross-linked copolymer of acrylic acid and a hydrophobic long alkyl side group, e.g., *n*-stearyl acrylate (SA), wherein the reversible cross-links were due to microphase separation of crystalline alkyl groups. The shape memory effect was based on a reversible order–disorder transition of the hydrophobic domains where Young’s modulus decreased by about 3 orders of magnitude, from 10² MPa at 25 °C (hard plastic) to 10^{−1} MPa at 50 °C (soft gel). More recently, Han et al.⁹ demonstrated an ion-triggered shape memory effect in a high-strength hydrogel made from a chemically cross-linked copolymer of acrylonitrile

with 2-methacryloyloxyethyl phosphorylcholine. Shape memory was achieved by association and dissociation of dipole–dipole interactions of the cyano groups in response to the presence or absence of zinc ions.

A common feature of the robust shape memory hydrogels described above is that they behave as hard plastics when they are in the temporary state, which defeats one of the important features of a hydrogel, i.e., softness (relatively low modulus). In this paper, we describe a tough hydrogel, containing physical and covalent cross-links, which exhibits thermally activated shape memory behavior. The hydrogels were synthesized from quad-polymers of *N,N*-dimethylacrylamide (DMA), 2-(*N*-ethylperfluoro-octanesulfonamido) ethyl methacrylate (FOSM), hydroxyethyl acrylate, and 2-cinnamoyloxyethyl acrylate (Scheme 1).¹³

The microstructure of the hybrid hydrogels was composed of glassy hydrophobic nanodomains that behave as multifunctional physical cross-links. The glass transition temperature of the glassy nanodomains was the switching temperature between the temporary and permanent shapes. The temporary shape was fixed by the physical cross-links formed from the nanodomains, and the permanent shape was set by covalently photo-cross-linking of the cinnamate groups in the quad-polymer. The hybrid hydrogels are denoted as F_{*x*}–C_{*y*}, where *x* and *y* indicate the mol % of FOSM and cinnamate, respectively, rounded to an integer value, and the properties of the hydrogels are listed in Table 1.

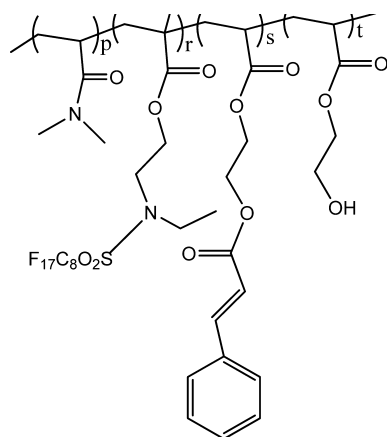
Previous work on physical hydrogels prepared from copolymers of *N,N*-dimethylacrylamide (DMA) and 2-(*N*-ethylperfluoro-octane sulfonamido) ethyl acrylate (FOASA) showed that the hydrophobic associations of the FOASA groups

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Scheme 1. Structure of Fx–Cy



produced ~6 nm diameter core–shell nanodomains that were composed of a 4–5 nm FOSA core surrounded by a water-depleted shell of DMA.¹⁴ The water-poor shell of the DMA is presumably composed of the chain segments attached to the FOSA repeat units, such that the nanodomains are multifunctional cross-links. Those hydrogels exhibited temperature- and frequency-dependent viscoelastic behavior and a solid–liquid transition above the glass transition of the nanodomains, ~45 °C.¹⁵

The Fx–Cy hybrid hydrogels discussed in this paper used FOSM¹³ for the hydrophobic monomer, which is the methacrylate analogue of FOSA. It was assumed that the difference between the methacrylate (FOSM) and the acrylate (FOSA) had no effect on the microstructure that was produced by the presence of the fluorocarbon groups, which was the same in both monomers. The hybrid hydrogels contained ~60–70% water and had relatively high mechanical strength and extensibility at room temperature (see Table 1).

The low and high deformation mechanical response of these hybrid hydrogels were described in detail in another paper.¹³ The tensile modulus and strength increased with increasing cross-link density (physical + covalent), and the elongation to break for each hydrogel was greater than 500%. In general, the tensile moduli of the three samples used in this work were 60–180 kPa; the ultimate tensile stress was 270–540 kPa; and the elongation to break values were 500–580% (see Table 1). The fracture toughness for the three hydrogels measured by single-edge notch fracture experiments was 119–188 J·m⁻², which is much higher than the ~0.1–1 J·m⁻² exhibited by conventional chemically cross-linked hydrogels.¹⁶ The dynamic properties of the Fx–Cy hydrogels were temperature and frequency dependent, and the dynamic shear modulus decreased with increasing temperature due to the softening of the physical network. Above the T_g of FOSM nanodomains, ~45 °C, $\tan \delta$ reached values of 0.5–0.6 at low frequency.

Table 1. Characteristics of the Fx–Cy Hydrogels

polymer ID	composition ^a (see Scheme 1)				water absorbed (wt %)	ν_e^b (mol·m ⁻³)	E^c (kPa)	σ_u^c (kPa)	ϵ_u^c (%)
	p	r	s	t					
F5–C6	0.870	0.055	0.060	0.015	73 ± 1	256	64 ± 2	270 ± 20	514 ± 74
F10–C3	0.854	0.099	0.031	0.016	67 ± 2	536	108 ± 5	470 ± 50	575 ± 11
F10–C6	0.808	0.096	0.064	0.034	57 ± 1	631	184 ± 18	540 ± 30	503 ± 46

^aMole fraction. ^bCross-link density calculated from G' @ 100 rad·s⁻¹. ^cTensile properties at room temperature (~23 °C): E = Young's modulus; σ_u = ultimate stress; ϵ_u = elongation to break.

The Fx–Cy hydrogels exhibited thermal activated shape memory behavior with a switching temperature, T_c , that corresponded to the T_g of the FOSM nanodomains. The covalent, chemical network provided a permanent shape. Above T_c the hydrogel was deformable, and a fixed temporary shape was achieved by cooling the sample under stress to below T_c . The hydrogel reverted to its permanent shape when reheated to above the T_c . Figure 1 shows the shape fixing and shape

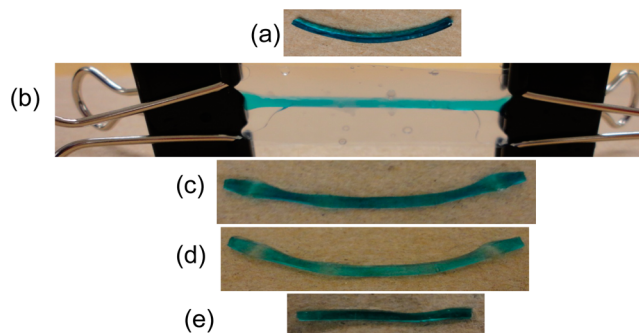


Figure 1. Shape memory behavior of the F10–C6 hydrogel (dye to blue for clarity): (a) the original shape of the gel (length = 26.3 mm, width = 1.7 mm, thickness = 1.1 mm); (b) gel heated in 65 °C water and stretched to 45.2 mm; (c) the shape of the gel immediately after cooling to 10 °C (temporary shape) and removing the stress upon; (d) after 24 h soaking in 10 °C water—the length of gel decreased to 43.0 mm; (e) after reheating gel in 65 °C water without any external stress (recovery back to permanent shape)—the length of sample recovered to 26.0 mm.

recovery process of the F10–C6 hydrogel. The sample was dyed to improve the visual clarity. The original shape of F10–C6 was a rectangular film with a 26.3 mm length, a 1.7 mm width, and a 1.1 mm thickness (Figure 1(a)). It was heated to 65 °C and stretched to 45.2 mm (72% strain) (Figure 1(b)), and that temporary shape was fixed by cooling to 10 °C under stress. The length of the sample recovered only a negligible amount when the stress was removed (Figure 1(c)); however, the length continued to change with time, and after 24 h without load at 10 °C the length of the hydrogel recovered to 43.0 mm (~63% strain) (Figure 1(d)). When the sample was reheated to 65 °C, the length recovered to 26.0 mm, which was within experimental error of the original length (Figure 1(e)).

The shape fixing efficiency denotes the ability of the sample to hold its temporary shape and was calculated from eq 1.¹⁷

$$F(t) = \frac{l(t) - l_0}{l_s - l_0} \times 100\% \quad (1)$$

where l_0 is the original length; l_s is the stretched length; and $l(t)$ is the time-dependent length of the hydrogel after removal of the load. The fixing efficiencies of the three hybrid hydrogel

samples are given as a function of time in Table 2, and it is clear that considerable recovery of the temporary shape occurred in

Table 2. Shape Fixing Efficiency and Shape Recovery Parameters of Fx–Cy Hydrogels

sample	$F(t)/\%$			$R(t)/\%$
	1 h	7 h	24 h	
F5–C6	80 ± 3.7	74 ± 2.1	68 ± 2.9	99 ± 1.2
F10–C3	96 ± 1.6	91 ± 1.9	84 ± 5.4	102 ± 4.8
F10–C3 (cycle 2)	98 ± 0.3	94 ± 0.8	90 ± 0.8	101 ± 3.1
F10–C6	97 ± 1.2	92 ± 3.1	88 ± 4.5	103 ± 1.2

these hydrogels when they were held in the temporary shape without load. The stretching strain for the experiments ranged from 60 to 95%.

The shape recovery efficiency, R , is defined by eq 2¹⁷

$$R = \frac{l_s - l_r}{l_s - l_0} \times 100\% \quad (2)$$

where l_r is the length of sample after recovery and l_0 and l_s have the same definition as for eq 1. After aging the Fx–Cy hydrogels for 24 h at 10 °C, the hydrogels were reheated to 65 °C without any external stress, and the original permanent shape was completely recovered (see Table 2). Despite the time dependence of the fixing efficiency, the recovery efficiency for all the samples was ~100%. The values of $R > 100\%$ were within experimental error of 100%, but at this point, we cannot rule out the possibility of some permanent creep of the sample due to imperfections of the covalent cross-linked network. The covalent network should be responsible for maintaining the original shape in the completely relaxed hydrogel.

For each of the hybrid hydrogels, the temporary shape exhibited considerable relaxation, and the shape fixing efficiency decreased with time (see Table 2). That recovery is most likely due to the inability of the FOSM nanodomains to support the residual stress in the network strands, even though they were in the glassy state. As a result, some creep relaxation occurred in the chains connected to the nanodomains.¹³ The relaxation behavior was much more evident in the sample with only 5 mol % FOSM, F5–C6. After 24 h, the temporary shape efficiency for F5–C6 was only 68%, while it was 84–88% for the two samples that contained 10 mol % FOSM. Comparison of the two hybrid samples with 10 mol % FOSM and varying cinnamate concentration indicates that changing the covalent cross-linking concentration had a negligible effect on the shape fixing efficiency. Those results indicate that the concentration of the glassy FOSM nanodomains is the critical factor for achieving a robust temporary shape.

The reason for the time-dependent behavior of the temporary shape is the physical nature of the nanodomain cross-links. The glassy nanodomains are viscoelastic, so that at sufficiently high stress and long time (low frequency) the FOSM groups in the domains can move. The residual stress that remains in the network chains when the sample is fixed in a temporary shape is sufficient at long enough times to pull FOSM groups out of the domains and hopping of those groups from one domain to another, which is responsible for the creep recovery of the sample length. However, the relaxation of the temporary network does not affect the permanent shape of the hydrogel, which is controlled by the covalent network skeleton. That is demonstrated by the recovery efficiencies shown in

Table 2 and the reproducibility of the fixing efficiency and its time dependence for a second shape memory test of F10–C3, the results of which were similar to those from the first test (see Table 2).

The relaxation behavior of the temporary shape increased with temperature, which is consistent with the viscoelastic nature of the nanodomain cross-links and the explanation given in the previous paragraph. While $F(24 \text{ h}) \sim 84\text{--}88\%$ for the F10–Cy hydrogels at 10 °C, it decreased to ~60% when the temperature was 23 °C. The reason is that as the temperature becomes closer to the T_g of the FOSM nanodomain the relaxation time of the nanodomain cross-links decreases, and under the internal stress of the network chains, the nanodomains appear softer. That result promotes more frequent interdomain hopping of FOSM groups. It also suggests that better shape fixing efficiency may be achieved by increasing the concentration of FOSM—i.e., increasing the cross-link density of the temporary network. An alternative approach to improving shape fixing would be to increase the T_g of the nanodomains.

Figure 2 shows the relaxation behavior over a period of 10 days for the temporary shape fixing effectiveness at ~10 °C for

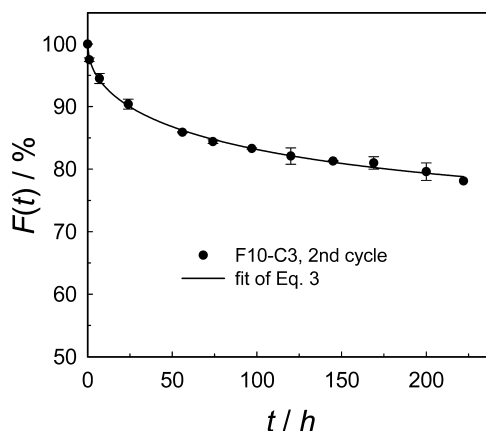


Figure 2. Shape fixing efficiency at ~10 °C as a function of time for F10–C3 for the 2nd shape fixing and recovery test cycle. The datum points represent the average of three separate experiments using strains of 75–95%, and the error bars are the standard deviation.

F10–C3 hydrogel in the second shape fixing and recovery test cycle. After the removal of stress upon fixing the temporary shape, a relatively fast relaxation of the strain occurred within the first 24 h, and that was followed by a slow relaxation. A stretched exponential equation¹⁸ was used to fit the strain fixing data in Figure 2

$$F(t) = F_{eq} + ce^{-(t/\tau)^\beta} \quad (3)$$

where $F_{eq} = F(\infty)$ is the equilibrium value for the fixing efficiency; $c = F(0) - F(\infty)$; τ is a characteristic relaxation time; and β is a constant that is a function of the distribution of relaxation times ($0 < \beta < 1$). The fit of eq 3 for the F10–C3 hybrid hydrogel is shown by the solid line in Figure 2, and the fitting parameters are listed in Table 3.

For the F10–C3 hydrogel, the $F(t)$ relaxes to an equilibrium value of ~71%, and the relaxation time τ for the relaxation process is ~129 h. The relaxation of temporary shape arises from the relaxation of the stress in the network chains by FOSM hopping as was discussed above. The permanent shape

Table 3. Fitting Parameters for Equation 3 Calculated from the Data in Figure 2

sample	$F(0)/\%$	$F_{eq}/\%$	τ/h	β	$(r^2)^a$
F10-C3	99.9	71.2	129	0.52	0.998

^aCoefficient of determination for the regression of the experimental data with eq 3

recovered completely for this sample and for the other hybrid hydrogels.

In conclusion, a thermally actuated shape memory effect has been demonstrated for a strong, tough hybrid hydrogel. The weakness in the shape memory behavior is a time-dependent relaxation of the temporary shape, which is due to insufficient strength of the hydrophobic interactions in the nanodomains to prevent the temporary network from creeping. That problem may be rectified by increasing the FOSM concentration to increase the volume fraction of hydrophobic nanodomains, but that approach will also increase the cross-link density of the physical network and hence the modulus, as well as lower the water absorption. Despite this shortcoming, these hydrogels exhibit >70% retention of the temporary shape and, if the use period of the temporary shape is relatively short (e.g., one day), that retention increases to >80%. The recovery of the permanent shape appears to be quantitative. The advantage of these tough shape memory hydrogels compared to others that have been described in the literature is that these hybrid hydrogels are tough and also soft in both permanent and temporary shape.

EXPERIMENTAL METHODS

The hydrogels used in this study were prepared by photo-cross-linking of Fx-Cy quad-polymers in solution. The details of the synthesis and characterization of Fx-Cy quad-polymers were reported elsewhere.¹³ The preparation of hydrogels was as follows. Polymer solutions (15 wt %) were prepared in isopropanol with a photoinitiator (Irgacure 2959) concentration of 0.5 wt %. The solution was then transferred to a reaction dish, degassed, and radiated with a UV lamp with a 365 nm wavelength for 40 min. The gels were washed with isopropanol and soaked in isopropanol for 1 day to remove any noncovalent cross-linked polymer and then soaked in deionized water for at least 7 days with frequent water change. The replacement of the isopropanol with water allowed the hydrophobic associations to occur and develop the second, physical network in addition to the covalent network. The shape fixing experiment was as follows. A hydrogel strip with a width of 1.7–4.0 mm, thickness of 1.1–1.7 mm, and length of 18–30 mm was immersed into 65 °C water for 1 h without any load, then stretched to 60–95% strain, and then equilibrated in the 65 °C water for 1 h under load at constant strain. The temporary shape was then fixed by quenching the sample to 8–10 °C and equilibrating overnight while still under stress at 8–10 °C. The stress was then removed. The sample was stored at 8–10 °C without load, and its length was measured after aging for various times. The shape recovery experiment involved reheating the sample in water to 65 °C after the shape fixing experiment and measuring the length after 1 h.

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Notes

The authors declare no competing financial interest.

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