ABSTRACT: Mechanically adaptive materials that soften upon exposure to physiological conditions are useful for biomedical applications, notably as substrates for implantable neural electrodes. So far, device fabrication efforts have largely relied on shaping such devices by laser cutting, but this process makes it difficult to produce complex electrode architectures and leads to ill-defined surface chemistries. Here, we report mechanically adaptive, physiologically responsive polymers that can be photopolymerized and thus patterned via soft lithography and photolithography. The adaptive polymer networks produced exhibit, in optimized compositions, a ca. 500-fold decrease of their storage modulus when exposed to simulated physiological conditions, for example, from 2.5 GPa to 5 MPa. This effect is caused by modest swelling (30% w/w), which in turn leads to plasticization so that the polymer network’s glass transition temperature is reduced from 145 to 25 °C. The polymer networks can further be rendered pH-responsive by the incorporation of methacrylic acid. The dual stimuli-responsive materials thus made show promise as coatings or substrates for drug delivery devices.

INTRODUCTION

Mechanically adaptive polymers, which modify their mechanical properties in response to a specific trigger, constitute a subset of the ever-growing class of stimuli-responsive materials. They include polymers that soften upon exposure to physiological conditions, which are considered useful for biomedical applications, notably as substrates for implantable neural electrodes. Such electrodes are part of artificial brain—machine interfaces, but the mechanical mismatch between the currently tested rigid electrodes and the much softer cortical tissue appears to be one factor that limits their in vivo lifetime. Mechanically adaptive materials have been shown to overcome this problem as they allow the fabrication of devices that are initially rigid and robust and can be readily implanted into the soft tissue and then soften and therefore minimize the mechanical mismatch relative to the tissue.

Indeed, studies have shown that implants based on such materials elicit reduced chronic tissue responses, even if the modulus of the adaptive material in the soft state was still 3 orders of magnitude higher than that of the cortical tissue. Sea cucumber-inspired nanocomposites composed of various polymer matrices and cellulose nanocrystals (CNCs) have previously been shown to soften when placed in living tissue, emulated physiological conditions (artificial cerebrospinal fluid, ACSF, at 37 °C), or simply water. The mechanical contrast displayed by such materials upon swelling depends on the nature of the polymer matrix and the type of cellulose nanocrystals, but typical stiff states are characterized by a storage modulus (E’ ) of 4.0–13.7 GPa in the dry state, whereas the ACSF-swollen materials display E’ values of 5–160 MPa (at 37 °C). The largest water-induced modulus change was demonstrated for materials in which water take-up causes plasticization of the polymer matrix such that the glass transition temperature (Tg) of the material is lowered from above to below the body temperature. In addition, the hydrogen-bonded percolating CNC network that reinforces the polymer matrix in the dry state is weakened or disassembled upon the interaction of the CNCs with water that amplifies the softening. Another approach based on photopolymerizable (meth)acrylate and thiol-ene shape-memory polymers with glass transition temperatures in the range of 40–60 °C has also been investigated.

The thermally- and water-responsive thiol-ene-based shape-memory polymers studied exhibited reduction of their Young’s moduli E from ca. 1–2 GPa to ca. 15–50 MPa upon immersion in a phosphate-buffered saline (PBS) buffer at 37 °C, on account of the temperature increase and minute swelling (ca. 3–6% w/w). Mechanically adaptive neural electrodes were subsequently fabricated by a transfer-by-polymerization process. In a first step, a gold electrode was patterned on a sacrificial layer using electron-beam lithography. The thiol-ene-based resin was then poured between the patterned gold electrode and a glass slide and photopolymerized, using the gold pattern as a mold. After the
removal of the sacrificial layer and addition of a patterned isolating layer on the electrode, the final device was cut from the laminated structure via laser ablation. Laser cutting, which represents a low-cost and well-established technique for microdevice fabrication,23 was also used to process the above nanocomposites. However, the inherent thermal degradation of the substrate and the limitations with respect to feature size and complex three-dimensional (3D) structures may limit its applicability in the context of neural electrode fabrication beyond proof-of-concept studies.3,21,24,25 Thus, the desire to increase the complexity and reduce the size of electrode architectures constitutes a challenge not only from a material perspective but also for the microfabrication process.26–29 Photolithography, another well-established technique for miniaturized device fabrication, does not suffer from the same limitations as laser cutting. Two-dimensional (2D) and, under certain conditions, three-dimensional (3D) features with resolution down to the sub-50 nm scale can be achieved,30–32 thus rendering the technique particularly attractive in the context of bioelectronics and neuroprosthetics.33,34 A mechanically adaptive polymeric system suitable for photolithographic processing would simplify the device fabrication process and thus broaden the scope of potential applications but also require a (significant) revision of the material design.35,36 Thus, as a stepping stone toward photolithographically processable, mechanically adaptive neural electrodes, we herein report the development of a photopolymerizable methacrylate-based polymer substrate that exhibits water-induced softening. While photopolymerizable (meth)acrylates, in particular, based on solution-polymerized 2-hydroxyethyl methacrylate (HEMA), have been widely studied as cross-linked stimuli-responsive hydrogels for biomedical applications,36–41 the water-responsive, mechanically adaptive characteristics of bulk-polymerized HEMA-based networks have remained largely unexplored.42 We show that straightforward tailoring of the response and of the properties of the material is possible by simple compositional changes and that these materials can be patterned using soft- or photolithography, thus making it attractive as substrate for implantable neural electrodes. Other potential applications of such materials include microneedles. Current designs of polymer-based microneedles usually decouple the insertion capacity from the drug delivery function,43 by blending, for example, a stiff polymer with a drug-loaded hydrogel,44 or by incorporating the drug in a stiff, water-soluble polymer.45 The materials studied here would allow the photolithographic fabrication of smart microneedles, which would be stiff enough to penetrate the skin and could then, upon (tunable) swelling, release their cargo in a controlled manner inside the body. The range of applications for which the materials might be useful was further expanded by rendering them pH-responsive through the incorporation of methacrylic acid, which we expected to be mainly protonated or deprotonated in a biologically relevant pH range.46 pH-Responsive hydrogels are of interest for drug delivery applications,46–50 for example, in oral drug delivery systems that experience a pH increase from 1.0 to 6.6 as they travel through the acidic stomach to the intestine or colon where they release their content.51,52

RESULTS AND DISCUSSION

(Co)polymer networks based on 2-hydroxyethyl methacrylate (HEMA) and optionally methacrylic acid (MAA) were prepared via a photoinitiated solvent-free polymerization procedure using ethylene glycol dimethacrylate (EGDMA) as cross-linker (Scheme 1). The composition was systematically varied with the objective to maximize the stiffness in the dry state and minimize the stiffness in the water-swollen state at minimum water uptake. A soft lithography approach was used to produce samples of a shape suitable for mechanical analysis, i.e., rectangular samples that were 12 mm long, 5 mm wide, and ca. 250 μm thick. Thus, in a first series, HEMA was photopolymerized in the presence of 8, 12, or 16 mol % of EGDMA (in the absence of MAA) in a silicone mold to afford p(HEMA-x-co-EGDMA-y). In a second series, HEMA (60–90 mol %) and MAA (10–40 mol %) were co-polymerized in the presence of 8 mol % of EGDMA in a silicone mold to give p(HEMA-x-co-MAA-y-co-EGDMA). The subscripts x, y, and z represent the mol % of each monomer in the feed. The monomer mixtures were polymerized by irradiation with UV light (365 nm, 200 W/m², 150 s), followed by an overnight postexposure bake at 80 °C in an oven. Residual monomers and other extractables were removed by immersion in an ethanol/isopropanol mixture (1:1 v/v). After a final drying step at 80 °C under vacuum, the samples were stored in a dry box to avoid any moisture uptake. The cross-linked p(HEMA) networks were assumed to display mechanical switching as a consequence of plasticization by water, expecting that this effect would cause the glass transition temperature (Tg) to drop from above to below physiological temperature (37 °C).53 The softening is therefore intimately related to the swelling behavior and to the thermomechanical properties, i.e., the Tg of the polymer networks in both the dry and water-swollen state. Thus, dynamic mechanical analysis (DMA) was carried out to characterize the mechanically adaptive polymer networks. In a first step, the thermomechanical properties of the dry

Scheme 1. Synthesis of HEMA and HEMA-co-MAA Networks Using EGDMA as Cross-linker and Irgacure 184 (2% w/w) as Radical Photoinitiator (PI). Irradiation Conditions: 365 nm, 200 W/m², 150 s

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p(HEMA) networks were investigated (Figure 1a and Table 1). We first discuss the storage modulus $E'$ in the glassy state (determined at 25 °C), the $T_g$ and $E'$ in the rubbery regime (determined at 195 °C), as quantities that are relevant for the switching process. The dynamic mechanical analysis traces of dry samples of the p(HEMA) series show storage moduli $E'$ between 2.0 and 2.5 GPa in the glassy regime. Their stiffness is thus somewhat lower than that of the mechanically adaptive nanocomposites reported before,54,55 but similar to that of shape-memory polymer systems considered for cortical implants.56,57 In the rubbery plateau, $E'$ values between 5 and 28 MPa were measured. These values reflect the different cross-link densities of the polymer networks and provide some indication as to the modulus range that might be achievable in the case of plasticization-induced softening. Indeed, Flory and Rehner demonstrated that in the case of a large extent of plasticization, i.e., swelling, will occur on account of plasticization-induced softening.54 Furthermore, the $T_g$, determined from the maximum of the loss tangent curves, was found to slightly increase with the cross-link density from 145 to 159 °C. These rather high $T_g$ values indicate that significant plasticization, i.e., swelling, will be required to reduce the transition to below the body temperature.

To simulate the conditions experienced by implants in vivo, the p(HEMA) networks were swollen in artificial cerebrospinal fluid (ACSF) at the body temperature (37 °C) for 24 h.58,59 The results of kinetic swelling experiments with p(HEMA$_{100-\text{co}-\text{EGDMA}_8}$) (Figure S3) reflect that under these conditions equilibrium swelling has been reached. Figure 1b shows that the swelling is governed by the hydrophilic nature of HEMA on the one hand and the extent of cross-linking on the other. The swelling of the p(HEMA-co-EGDMA) networks in ACSF at 37 °C could be tuned between 32% w/w (8 mol % cross-linker) and 18% w/w (16 mol % cross-linker). Higher or lower swelling values could be achieved by expanding the concentration range of the cross-linker, as reported elsewhere.58,59 As the preparation method of hydrogels is known to influence the structure and properties of the materials,60,61 we emphasize that the materials explored here were prepared via bulk polymerization, in contrast to the vast majority of solution-polymerized HEMA hydrogels previously reported. The mechanical response of p(HEMA-co-EGDMA) networks under simulated physiological conditions was determined by conducting DMA experiments in submersion mode in ACSF, after conditioning the samples in ACSF at 37 °C for 24 h. The experimentally accessible temperature range was 5–75 °C. The submersion DMA traces show glass transitions of 25–53 °C. Gratifyingly, the $E'$ values in the rubbery regime are comparable to those measured for the dry materials well above the $T_g$ (Figure 1a,c and Table 1), supporting the conclusion that the softening is largely due to a shift of the $T_g$ on account of plasticization. At body temperature (37 °C), $E'$ values of 7, 98, and 342 MPa were measured for the p(HEMA) networks with cross-link densities of 8, 12, and 16 mol %, respectively (Figure 1c). The material with the lowest cross-link density, p(HEMA$_{100-\text{co}-\text{EGDMA}_8}$), has the lowest $T_g$ of the series and is in the rubbery regime at 37 °C, in contrast to the copolymers with 12 and 16 mol % of cross-linker, where the glass transition occurs at higher temperatures. To eliminate the possibility that the softening is the result of specific interactions that involve ACSF components, measurements for p(HEMA$_{100-\text{co}-\text{EGDMA}_8}$) were also carried out in water, but
no significant difference was observed (Figure S1). Thus, the data shown in Figure 1 unambiguously link the magnitude of the mechanical contrast to the extent of swelling (i.e., water plasticization), which in turn is controlled by the cross-link density. From the three compositions studied, p(HEMA-co-MAA-co-EGDMA) exhibits the largest mechanical contrast between the dry and the swollen state, while displaying a swelling behavior that is comparable to that of the adaptive CNC nanocomposites previously reported by our group.p,16,17 p(HEMA90-co-EGDMA8) is the only studied material that in the ACSF-swollen state displays a $T_g$ below the body temperature, and thus displays by far the largest mechanical switching (modulus drop of >2 orders of magnitude) capacity at 37 °C (Figure 1c).

The second material series involved copolymerizing HEMA (60–90 mol %), MAA (10–40 mol %), and EGDMA (8 mol %) with the aim of producing polymer networks exhibiting both pH-responsive characteristics and the ability to change their mechanical properties, which would be useful for drug delivery devices. The general shapes of the dynamic mechanical analysis traces of dry samples of the p(HEMA-co-MAA) series mirror those of the MAA-free polymers, revealing a glassy regime with a storage modulus $E'$ of 2.4–2.5 GPa and a rubbery plateau above the $T_g$ (Figure 2a and Table 2). The $T_g$ was found to increase from 150 to 180 °C with increasing MAA content, on account of the higher $T_g$ displayed by p(MAA). The pH-responsive character of the p(HEMA-co-MAA-co-EGDMA) networks was evaluated by immersing the samples at 37 °C in different buffers, having pH values of 3, 5, or 7 and molarity of 40 mM. The extent of swelling was measured, and the mechanical properties of the samples thus conditioned were studied by submersion-mode DMA in the same buffer. As expected, the swelling of the p(HEMA-co-MAA-co-EGDMA) copolymer networks is strongly pH-dependent (Figure 2b and Table 2). At pH 3 and 5, where the MAA is protonated, the swelling ranges from 23 to 28%, independent of the MAA content, and the extent of swelling is dependent (Figure 2b and Table 2). At pH 3 and 5, the deprotonation of the carboxylic acid groups of the MAA units increases the hydrophilicity and consequently the extent of swelling to 58 ± 10% w/w, i.e., the pH change from 3 to 7 triggers a 4-fold increase of the swelling for the materials with 40 and 25 mol % of MAA and a 2-fold increase for that with 10 mol % of MAA.

For the p(HEMA-co-MAA-co-EGDMA) copolymer networks, we also conducted isothermal DMA experiments at 37 °C in submersion mode at pH 3, 5, and 7 (Figure 2c). Prior to measurement, all samples were conditioned by immersion in pH buffers for 24 h. An inspection of the data shows that also in the case of this series, the magnitude of the softening is related to the dry $T_g$ and the extent of swelling. At pH 3 and 5, all samples show comparable swelling (22–28%) but exhibit distinct softening behaviors. While p(HEMA90-co-MAA10-co-EGDMA8) displays $E'$ values of 29 and 23 MPa at pH 3 and 5, respectively, p(HEMA90-co-MAA40-co-EGDMA8) shows an $E'$ value an order of magnitude higher (235 and 177 MPa).

![Figure 2](https://dx.doi.org/10.1021/acsomega.9b04336)

**Figure 2.** (a) Storage modulus of p(HEMA-co-MAA-co-EGDMA) copolymer networks in the dry state, (b) pH dependence of the swelling of p(HEMA-co-MAA-co-EGDMA) copolymer networks, and (c) pH dependence of the storage modulus of swollen p(HEMA-co-MAA-co-EGDMA) copolymer networks in buffers at 37 °C.

**Table 2. Thermomechanical Properties of the Dry p(HEMA-co-MAA-co-EGDMA) Networks with 60–90 mol % of HEMA, 10–40 mol % of MAA, and 8 mol % of Cross-Linker**

| type of sample | property | dry network | pH-buffer-swollen network |
|---------------|----------|-------------|--------------------------|
|               | $T_g$ [°C] | 180 ± 1     | 163 ± 1                  |
|               | $E'$ at 25 °C [GPa] | 2.4 ± 0.1    | 2.5 ± 0.1                |
|               | $E'$ at 195 °C [MPa] | 11 ± 1.5     | 7.7 ± 0.1                |
|               | swelling at pH 3 at 37 °C [% w/w] | 23 ± 0.1     | 23 ± 1.3                 |
|               | swelling at pH 5 at 37 °C [% w/w] | 26 ± 0.3     | 25 ± 0.1                 |
|               | swelling at pH 7 at 37 °C [% w/w] | 102 ± 8      | 93 ± 7                   |
|               | $E'$ at pH 3 at 37 °C [MPa] | 236 ± 13     | 83 ± 14                  |
|               | $E'$ at pH 5 at 37 °C [MPa] | 178 ± 12     | 75 ± 5                   |
|               | $E'$ at pH 7 at 37 °C [MPa] | 11 ± 1       | 8 ± 2                    |

“Swelling data in pH buffer (3, 5, and 7) at 37 °C, and thermomechanical properties of the pH-buffer-swollen samples. All data are based on DMA experiments.”
respectively). At a similar extent of swelling, the drop of $T_g$ is expected to be comparable for the different compositions and the disparities observed are thus attributed to the different $T_g$ values of the dry copolymer networks. Indeed, the dry $T_g$ is 30 °C higher for the composition with 40 mol % of MAA than for the material made with 10 mol % of MAA. The latter is therefore expected to have a swollen $T_g$ below the body temperature, while p(HEMA$_{60}$-co-MAA$_{40}$-co-EGDMA$_8$) remains above. At pH 7, the considerable increase of swelling drops the $T_g$ of all of the compositions well below the body temperature and the $E'$ values measured at this temperature are in the $\sim$1–10 MPa range.

With the ultimate goal of fabricating devices of complex shapes, we explored the feasibility of processing the polymer networks using a photolithographic process (Figure 3a). For this purpose, the liquid resin used to prepare p(HEMA$_{60}$-co-MAA$_{40}$-co-EGDMA$_8$) was placed between two glass substrates, one of which was equipped with a photomask. Spacers were used to control the resin thickness to ca. 100 μm. The resin was cured in a spatially controlled manner by irradiation with non-collimated UV light through the mask. After irradiation, the samples were developed by immersion in isopropanol, which removed the non-cross-linked resin. Initial tests showed significant signs of cross-linking in the unexposed regions, which appear to be related to the high photosensitivity of the resin and the simple setup employed. However, the photosensitivity of the resin to low-intensity stray light could be reduced by the addition of 0.5% w/w of 4-methoxyphenol, a polymerization inhibitor, to the resin formulation, as reported by Pardon et al. Thus, under irradiation conditions similar to those employed for the initial formulation (365 nm, 200 W/m$^2$, 30 s), the inhibitor-containing formulation could be processed into features with a good pattern fidelity in the 100 μm to 10 mm range, namely a difference of about 2.5 μm on a 145 μm feature (Figures 3b, e and S2a, c). Patterns with features that were smaller than 10 μm could only be processed with somewhat limited fidelity. For example, a feature with a width of about 4 μm (Figures 3f and S2d) showed a 20% reduction size compared to the photomask (Figures 3d and S2b). It can be expected that the use of collimated light would further improve the resolution and thus reduce the achievable feature size. Typical intracortical electrodes have feature sizes in the 100–1000 μm range, and the formulation used here should be suitable for the photolithographic patterning of the electrode substrate.

\section*{CONCLUSIONS}

We demonstrated the mechanically adaptive, physiologically responsive character of polymer networks based on cross-linked poly(2-hydroxyethyl methacrylate). The p(HEMA) networks exhibit a modulus drop of more than 2 orders of magnitude when exposed to simulated physiological conditions. The variation of the cross-link density allowed controlling the extent of water absorption, which in turn determined the extent of plasticization and glass transition temperature reduction and thus led to the observed softening. Gratifyingly, it was possible to design compositions exhibiting attractive properties in the context of an application as a substrate for neural electrode, namely a 500-fold modulus decrease, from 2.5 GPa to 5 MPa at a modest swelling of 30% w/w.

The stimuli-responsive behavior could be expanded by the introduction of methacrylic acid as a comonomer that imparted a pH-responsive behavior to the material. The pH response, as well as the extent of swelling and softening, were tuned by adjusting the composition of the copolymer networks. The relatively high swelling of the HEMA-co-MAA platform at neutral pH and the (herein not evaluated) potential delamination issues would preclude the use of such materials in neural electrodes but the development of mechanically adaptive, pH-sensitive coating/substrates for drug delivery devices can be achieved with these copolymers. Importantly, the preparation of polymer networks in desired shapes by soft- or photolithography, which makes them attractive for rapid prototyping of devices, was demonstrated. While the biocompatibility of the new materials is yet to be explored, the results presented here provide a first indication that the platform could be useful as a substrate for mechanically adaptive neural interfaces.

\section*{METHODS}

\textbf{Materials.} 2-Hydroxyethyl methacrylate (HEMA, Sigma-Aldrich, 97%), methacrylic acid (MAA, Sigma-Aldrich, 99%), ethylene glycol dimethacrylate (EGDMA, Sigma-Aldrich, 98%), Irgacure 184 (Ciba), and 4-methoxyphenol (MEHQ, Sigma-Aldrich, 99%) were used without further purification. All solvents used were reaction grade and used without further purification.

\textbf{Dynamic Mechanical Analysis (DMA).} Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 DMA using a multifrequency strain analysis (temperature ramp 0°C–180°C, 3 °C/min, 10 min equilibration time at 0 °C), with an amplitude of 15 μm, and a frequency of 1 Hz. Submersion DMA in artificial
cerebrospinal fluid or deionized water was performed on the same equipment using either a multifrequency strain analysis temperature ramp (5–75 °C, 3°C/min) or isothermal conditions at 37 °C with an amplitude of 15 μm and a frequency of 1 Hz. Before submersion experiments, samples were conditioned by immersion in ACSF at 37 °C for 24 h. All data extracted from DMA experiments are averages and standard deviation from triplicate measurements. DMA curve graphs show representative experiments.

**Optical Microscopy.** Optical microscopy images were acquired with an Olympus BX51 microscope equipped with a DP72 digital camera.

**Artificial Cerebrospinal Fluid (ACSF).** Artificial cerebrospinal fluid was prepared by dissolving sodium chloride (8.66 g), potassium chloride (224 mg), calcium chloride dihydrate (206 mg), magnesium chloride hexahydrate (163 mg), sodium phosphate dibasic heptahydrate (214 mg), and sodium phosphate monobasic monohydrate (27.0 mg) in deionized water (1 L). 63

**pH Buffers.** Citric acid monohydrate (7.19 g) and sodium citrate dihydrate (1.70 g) were dissolved in deionized water (1 L) to afford a buffer solution with pH 3. Acetic acid (778 μL) and sodium acetate (2.13 g) were dissolved in water (1 L) to afford a buffer solution with pH 5. Dibasic potassium phosphate (3.55 g) and monobasic potassium phosphate (2.61 g) were dissolved in deionized water (1 L) to afford a buffer solution with pH 7. All buffers had molarity of 40 mM/L.

**Polymer Network Preparation.** All photopolymerization reactions were performed using a Dr. Hönle LED Cube 100 at a wavelength of 365 nm. 2-Hydroxyethyl methacrylate (HEMA, 60–100 mol %), methacrylic acid (MAA, 0–40% w/w), ethylene glycol dimethacrylate (EGDMA, 8–16 mol %), and Irgacure 184 (2% w/w) were mixed in a brown glass vial. The quantities of each component were calculated to prepare ca. 10 mL of resin. The resin formulation was purged with nitrogen for 5 min prior to polymerization, poured into a silicone mold (12 mm long, 5 mm wide, 0.1 mm high), and irradiated with UV light (200 W/m², 150 s). The superficial nonreacted layer was removed with a tissue before curing the samples overnight in an oven at 80 °C under air. The samples were then immersed in isopropanol/ethanol 1:1 for at least 8 h and subsequently dried overnight in a vacuum oven at 40 ºC.

**Mold-Free Photolithography.** 2-Hydroxyethyl methacrylate (100 mol %, 49.5 mmol, 6.44 g, 6.00 mL), ethylene glycol dimethacrylate (8 mol %, 4.0 mmol, 0.78 g, 0.75 mL), Irgacure 184 (2% w/w, 0.71 mmol, 0.15 g), and (optionally) 4-methoxyphenol (0.5% w/w, 0.29 mmol, 0.04 g) were mixed in a brown glass vial. The resin formulation was purged with nitrogen for 5 min and was then poured onto a glass slide equipped with spacers of a thickness of 100 μm. A chrome-on-glass photomask was placed on top of the assembly. The assembly was then irradiated with UV light (365 nm, 200 W/m², 30 s). The photomask was removed and the non-cross-linked parts were washed away with isopropanol. The patterned resin was again exposed to UV light (365 nm, 200 W/m², 120 s) and cured in an oven (80 °C, overnight).

**Determination of the Extent of Swelling.** A precisely weighed amount (10–15 mg) of a dry polymer sample was immersed in ACSF or in an aqueous buffer (4–5 mL) for 24 h at 37 °C. The sample was wiped dry with a paper tissue and immediately weighed. The extent of swelling was calculated using the following formula:

\[
\text{extent of swelling} = \frac{m_s - m_D}{m_D} 	imes 100
\]

where \(m_s\) is the dry sample mass and \(m_s\) is the swollen sample mass. Values quoted are averages of three samples. Swelling kinetics was measured over 72 h using the procedure described above.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04336.

Submersion DMA of p(HEMA100-co-EGDMA8); optical microscopy pictures of the patterned samples; swelling kinetics of p(HEMA100-co-EGDMA8) in ACSF at 37 °C (PDF)

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**Author Contributions**

C.W. and D.M. developed the original concept for the study and designed the materials and experiments. B.M. and A.G.D. synthesized and characterized the materials and performed the experiments. All authors discussed the results and contributed to the interpretation of the data. B.M. and C.W. wrote the paper. All authors contributed to the editing of the manuscript.

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**Notes**

The authors declare no competing financial interest.

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