

Tough and Multi-responsive Hydrogels Based on Core-Shell Structured Macro-crosslinkers*

Gao-lai Du^a, Yang Cong^b, Long Chen^b, Jing Chen^a and Jun Fu^{a**}

^a Polymers and Composites Division & Cixi Institute of Biomedical Engineering, Ningbo Institution of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

^b School of Chemical Engineering, Ningbo University of Technology, Ningbo 315201, China

Abstract Novel hydrogels based on core-shell structured macro-crosslinkers were synthesized, which exhibited high toughness and multiple responsiveness. Sodium dodecyl sulfate (SDS) micelles mediated by NaCl were used to encapsulate hydrophobic stearyl methacrylate (C18) in the core, and hydrophilic 2-acrylamido-2-methyl-1-propanesulfonic (AMPS) monomers in the corona. Such core-shell micelles were simultaneously copolymerized with acrylamide monomers through free radical polymerization. As a result, hydrogels crosslinked by amphiphilic “poly(C18)-PAMPS” macro-crosslinkers were obtained. These hydrogels showed excellent tensile and compression strength and toughness. Cyclic compression loading-unloading tests demonstrated that the hydrogels were of outstanding fatigue resistance, and showed partial damage of energy dissipation mechanism. The damaged energy dissipation mechanism could be recovered at room temperature and the recovery could be accelerated at elevated temperatures. The hydrogels were sensitive to the change in pH and ion strength, showing reversible swelling/deswelling behaviors.

Keywords Macro-crosslinker; Toughness; Multi-responsive; Hydrophobic association; Hydrogel

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INTRODUCTION

Tough hydrogels with multiple responsiveness have been widely pursued for potential applications in artificial muscles^[1], sensors, soft robotics^[2] or soft actuators^[2, 3] *etc.* The practical applications of conventional responsive hydrogels are limited due to their poor mechanical strength and toughness. In order to improve the mechanical properties of hydrogels, many strategies, including double network^[4, 5], nanocomposite^[6, 7], and polyampholyte^[8, 9] *etc.*, have been developed. Among them, various macro-crosslinkers have been utilized to synthesize hydrogels with not only outstanding mechanical properties, but also multiple responsiveness^[10–12]. Therein, macro-crosslinkers serve as sacrificial units to efficiently dissipate energy^[12]. It is very important that most of the macro-crosslinkers are adaptable with functional monomers, including thermosensitive and ionic monomers, which allows for flexible design and synthesis of tough hydrogels with multiple responsiveness^[3, 13, 14]. Although such hydrogels have excellent mechanical properties, the distribution of macro-crosslinkers in hydrogels is

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** Corresponding author: Jun Fu (付俊), E-mail: fujun@nimte.ac.cn

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unpredictable, which usually results in a heterogeneous network. It has been argued that a homogeneous network may benefit the strength and toughness of the hydrogel. Moreover, despite of triblock copolymer micelles with the typical core-shell structures, less control in the macro-crosslinker structures has yet been demonstrated. It is desired to develop novel macro-crosslinkers, with well-defined core-shell structures and effective energy dissipation for the synthesis of tough and responsive hydrogels.

Various macro-crosslinkers, such as nanoparticles^[3], block copolymers^[9, 15], nanogels^[16] and hydrophobic assemblies^[11, 12], have been used to synthesize hydrogels with high stretchability, self-healing and stimuli responsiveness. In particular, hydrogels crosslinked by core-shell structured F127 micelles showed not only high energy dissipation efficiency^[17] but also multiple responsiveness^[13] due to the non-covalent nature of the physical junction zones. Recently, junction zones of hydrophobes were realized *via* a surfactant assisted technique, where hydrophobic monomers were entrapped into the surfactant micelle cores to provide hydrophobic association after polymerization with hydrophilic monomers^[12].

Inspired by these studies, we further developed a method by using the micelles of ionic surfactants as templates to separately host reactive ionic monomers in the hydrophilic coronae and hydrophobic monomers in the cores. During the polymerization, the monomers entrapped in the micelle coronae and cores are proposed to be covalently bonded together, leading to *in situ* formation of core-shell structured macro-crosslinkers. The surfactant micelles can grow upon the addition of ionic monomers and/or salts, since the mobile electrolytes may screen the electrostatic repulsion of the surfactants^[12, 18]. Such micelle growth may increase the local concentration of hydrophobes within the micelle cores^[11, 12]. Thus, it is convenient to tune the size of the micelle-based macro-crosslinkers, which is critical for the network structures and mechanical properties of the hydrogels.

In this work, sodium dodecyl sulfate (SDS) micelles in aqueous solution were used to encapsulate the hydrophobic stearyl methacrylate (C18) in the cores^[12]. Meanwhile, 2-acrylamido-2-methyl-1-propanesulfonic (AMPS) monomers were dissolved into the SDS solution. With the addition of NaCl, the sphere SDS micelles might be transformed into wormlike SDS-NaCl-NaAMPS micelles^[19], which provided larger cores to encapsulate more hydrophobes (Schemes 1a and 1b). As such, SDS micelles containing AMPS monomers in coronae and C18 in cores were obtained (Scheme 1b). These micelles were mixed with acrylamide (AAM) monomers for free radical polymerization to form hydrogels crosslinked by “poly(C18)-PAMPS” core-shell macro-crosslinkers (Scheme 1c). Different from the macro-crosslinkers reported in the literature^[17, 20], the “poly(C18)-PAMPS” macro-crosslinkers described here were *in situ* formed upon free radical polymerization. The obtained hydrogels show excellent strength and toughness, as well as responsiveness to different pH values and ion strengths.

EXPERIMENTAL

Materials

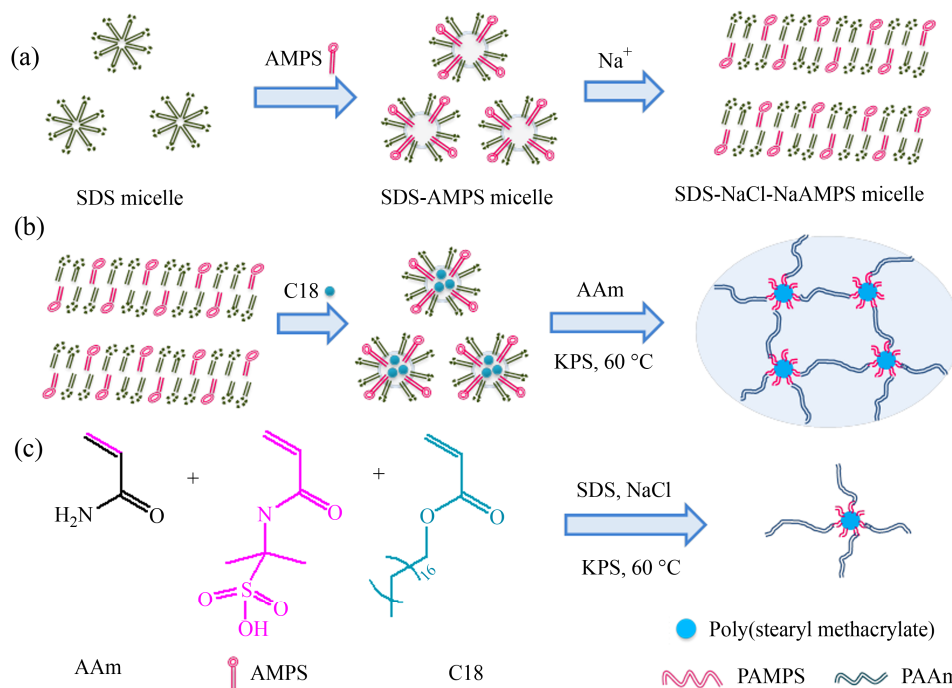
Sodium dodecyl sulfate (SDS, Aladdin), sodium chloride (NaCl, AR, Sinopharm Chemical Reagent Co. Ltd.), stearyl methacrylate (C18, 96%, 0.01% MEHQ, Aladdin), 2-acrylamido-2-methyl-1-propanesulfonic (AMPS, 98%, Aladdin), acrylamide (AAM, AR, 99.0%, Aladdin), potassium persulfate (KPS, AR, 99.5%, Aladdin), and sodium hydroxide (NaOH, AR, Sinopharm Chemical Reagent Co. Ltd.) were used as received.

Experiments

Preparation of C18/SDS-NaCl-NaAMPS micelles

To prepare the SDS-NaCl-NaAMPS micelles, AMPS was dissolved in 0.07 g/mL SDS solution. The AMPS monomers were then neutralized with 8 mol/L NaOH to yield an SDS-NaAMPS solution. Subsequently, 0.5 mol/L sodium chloride was added to SDS-NaAMPS micelle solution and stirred for 2 h at 37 °C to generate SDS-NaCl-NaAMPS micelle solutions (mSol). Into the SDS-NaCl-NaAMPS micelle solution, 0.1 mol/L C18 was added and dissolved with stirring for another 2 h, yielding a homogeneous and transparent C18/SDS-NaCl-NaAMPS micelle solution. Then, AAM and 0.25 mol/L KPS initiator were added to C18/SDS-NaCl-NaAMPS precursor solution. The concentrations of AAM and NaAMPS monomer were kept at 5 mol/L in total. For

comparison, SDS-NaCl and SDS-NaCl-AMPS micelles were prepared as the controls with stoichiometric NaCl and AMPS.



Scheme 1 Schematic illustration to the preparation of (a) novel SDS-NaCl-NaAMPS micelles and (b, c) macro-crosslinked hydrogels

(a) A conversion of AMPS monomer/SDS micelles to wormlike SDS-NaCl-NaAMPS micelles upon addition of high concentration of Na⁺ counterion. (b) Encapsulation of hydrophobic stearyl methacrylate (C18) hydrophobes in the micelle cores. After free radical polymerization, hydrogels are obtained based on the “poly(C18)-PAMPS” core-shell structured macro-crosslinkers. (c) The free radical copolymerization of C18, AMPS and AAm monomers in the system.

Synthesis of hydrogels crosslinked by Poly(C18)-PAMPS core-shell micelles

The C18/SDS-NaCl-NaAMPS micelle precursor solution was injected into a glass mold with a silicone rubber spacer. The assembly was heated at 60 °C for 10 h to generate hydrogels (mGels) via free radical polymerization. The formulations for the mGel synthesis are listed in Table 1.

Table 1 The formulations for the synthesis of hydrogels

Sample	CSDS (g/mL)	CNaCl (mol/L)	CC18 (mol/L)	CAMPS (mol/L)	CAAm (mol/L)	CKPS (mmol/L)
mGel-1	0.07	0.5	0.1	0.16	4.84	25
mGel-2	0.07	0.5	0.1	0.20	4.80	25
mGel-3	0.07	0.5	0.1	0.25	4.75	25
mGel-4	0.07	0.5	0.1	0.31	4.69	25
mGel-5	0.07	0.5	0.1	0.37	4.63	25

Characterizations

Dynamic light scattering measurements

The measurements were performed by using a Zetasizer Nano ZS instrument (Malvern) to determine the micelle sizes of SDS-AMPS, SDS-NaAMPS, SDS-NaCl-NaAMPS (mSol), SDS-NaCl and SDS-NaCl-AMPS solutions at 37 °C. Before the measurements, the solutions were filtrated with a membrane (pore size: 220 nm) and collected into the cuvette. The solutions in the cuvette were heated from room temperature to 37 °C and kept for 4 min before measurement. The data were analyzed by a cumulate method with the Malvern application software.

Transmittance measurements

The transmittance of SDS-NaCl-NaAMPS, SDS-NaCl and SDS-NaAMPS micelle solutions was measured by using a UV-Vis spectrometer (Lambda 950, Perkin-Elmer, US) between 200–700 nm as a function of C18 content in the micelle solutions. The solutions were stirred at 37 °C for 2 h prior to measurement.

Compression tests

The tests were conducted on the cylindrical hydrogel samples (diameter: 9 mm, thickness: 3.5–3.6 mm) by using an Instron 5567 instrument (Boston, MA). The samples were compressed at 10 (%)/min until 98% strain. On the other hand, cyclic loading-unloading compression tests were successively performed on the samples to a series of pre-defined maximum strains. For each loading-unloading cycle, the maximum strain was increased by 15%, from 30% to 90% strain.

Tensile tests

Dumbbell hydrogel samples (width: 4 mm, thickness: 2.0–2.2 mm, gauge length: 20 mm) were uniaxially stretched until fracture by using an Instron 5567 instrument (Instron, Boston, MA) at 100 mm/min. For cyclic tensile tests, the dumbbell hydrogel samples were firstly stretched to 600% strain and immediately unloaded. To study their recovery ability, the hydrogels were treated with a loading-unloading stretching cycle. Then, the tested hydrogels were sealed with silicon oil, coated with PP membrane and stored at 25, 40 and 60 °C. After storage for 0.5, 1.0 and 2.0 h, the hydrogels were tested again with the second stretching cycle.

Responsiveness to pH and ion strength changes

The as-prepared cylindrical hydrogel samples (diameter: 9 mm, thickness: 2.0–2.2 mm) were immersed in buffer solutions. The weights of hydrogels were recorded over immersing time. To study the responsiveness to pH and salt concentration changes, hydrogel samples were immersed in the solutions with pH 3–11 or NaCl concentration ranging from 0.05 mol/L to 0.3 mol/L. On the other hand, the samples were equilibrated in neutral DI water and then shuttled between solutions with different pH values and/or NaCl concentrations. The swelling ratio (SR) was calculated by the equation: $SR = \frac{W_t - W_f}{W_f} \times 100\%$, where W_f and W_t denote the weights of as-prepared hydrogels and swollen hydrogels at time t .

RESULTS AND DISCUSSION

In order to prepare the core-shell C18/SDS/AMPS micelles, it is critical to tune the electrostatic interactions between SDS and AMPS monomers for making stable micelle solutions when incorporating hydrophobic C18 molecules into the cores^[19]. First of all, SDS-AMPS micelles were prepared by dissolving AMPS into the SDS micelle solution, which increased the micelle size. As the AMPS concentration increased from 0.16 mol/L to 0.37 mol/L, the micelle size was increased from (3.6 ± 0.1) nm to (5.6 ± 0.3) nm (Fig. S1, in supporting information, SI) due to the incorporation of AMPS molecules into the SDS coronae, yielding SDS-AMPS micelles. On the other hand, the micelle shape was sensitive to the internal electrostatic repulsion. When the AMPS molecules were neutralized into NaAMPS by NaOH, the SDS-AMPS spherical micelles transformed into wormlike SDS-NaCl-NaAMPS micelles^[12] (Scheme 1a) and the micelle sizes increased (Figs. 1a and 1b).

The SDS-NaCl-NaAMPS micelle size was sensitive to the NaAMPS concentration (c_{NaAMPS}) in solution (Fig. 1). As c_{NaAMPS} increased from 0 mol/L to 0.16, 0.20, 0.25, 0.31 and 0.37 mol/L, the corresponding SDS-NaCl-NaAMPS micelle solutions (mSol-0 to mSol-5) were stable and transparent at 37 °C over months, while it became opaque with c_{NaAMPS} higher than 0.45 mol/L. With increasing c_{NaAMPS} , the micelle size increased from (4.1 ± 0.12) nm (SDS-NaCl) to (11.7 ± 1.2) (mSol-1), (12.9 ± 0.7) (mSol-2), (14.9 ± 0.4) (mSol-3), (16.2 ± 0.6) (mSol-4) and (17.4 ± 0.3) nm (mSol-5), as shown in Fig. 1(b). In order to figure out the contributions of AMPS^- and Na^+ to the size increase, SDS-NaCl micelles free of AMPS^- and SDS-NaAMPS micelles without NaCl were prepared. The SDS-NaCl and SDS-NaAMPS micelles were much smaller than the SDS-NaCl-NaAMPS micelles

(Fig. S2, in SI). These results suggest that AMPS^- and Na^+ play important roles in the increase of micelle size. Such stable and big micelles are favorable for the dissolution of hydrophobic C18 molecules.

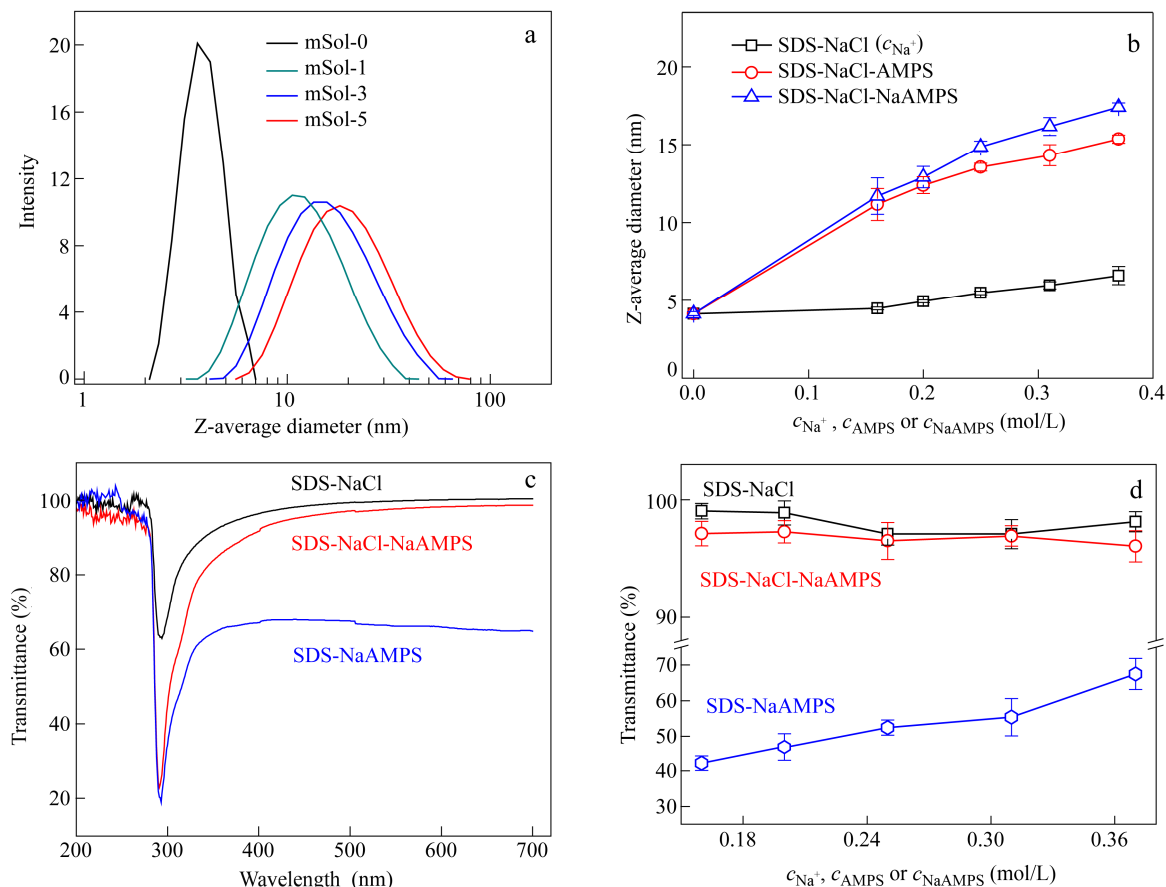


Fig. 1 (a) Dynamic light scattering (DLS) spectra of SDS-NaCl (mSol-0) and SDS-NaCl-NaAMPS (mSol-1, mSol-3 and mSol-5) micelle solutions; (b) The dependence of SDS-NaCl, SDS-NaCl-AMPS and SDS-NaCl-NaAMPS micelle sizes on Na^+ , AMPS or NaAMPS concentrations; (c) Typical UV-Vis spectra of SDS-NaCl, SDS-NaAMPS and SDS-NaCl-NaAMPS micelle solutions and (d) the transmittance of the micelle solutions at 500 nm with the presence of C18

The SDS-NaCl-NaAMPS micelles were used to assist the dissolution of C18 hydrophobes in solutions. With the dissolution of C18, the SDS-NaAMPS micelle solution became opaque, with a transmittance at 500 nm lower than 65%, in sharp contrast to the transparency of the C18/SDS-NaCl-NaAMPS micelle solutions. This is due to the fact that the concentration of Na^+ influenced the transparency of the C18-micelle solutions. When the Na^+ concentration was higher than 0.5 mol/L, the C18/SDS-NaCl-NaAMPS solutions became transparent (Fig. 1c). Such a high transparency may suggest a transformation of wormlike micelles into spheres upon the encapsulation of C18 hydrophobes into the cores (Scheme 1b). Okay *et al.* have systematically investigated the transformation from wormlike micelles to spherical micelles upon the addition of NaCl into the C18/SDS micellar solutions. The increase of Na^+ concentration may reduce the electrostatic repulsion within the NaAMPS/SDS corona, which favors a structure change from wormlike micelles with low curvature to the spherical micelles with high curvature at the core/corona interface^[19].

Thus, SDS-based micelles containing NaAMPS in the coronae and C18 in the cores were obtained. These micelles were used for free radical polymerization with AAm monomers at 60 °C, as initiated by KPS. The AMPS, C18, and AAm were simultaneously initiated within the micelles and polymerized into hydrogels. In order to investigate the effect of micelle structure on the properties of hydrogels, the concentration of C18 in

these systems was kept at 0.1 mol/L. It was likely that C18 and AMPS separately polymerized within the core and corona, while copolymerization might occur at the interface between the hydrophobic core and the hydrophilic corona. Meanwhile, the AAm monomers were copolymerized with AMPS within the micelles and in the solutions. As a result, “poly(C18)-PAMPS” macro-crosslinkers were formed and served as the crosslinkers for PAAm chains (Scheme 1b) that were bonded with the PAMPS chains in the corona. The obtained hydrogels were denoted as mGel- x , where x inherits the code of corresponding mSol micelles, *i.e.*, the concentration of NaAMPS monomers.

The prepared hydrogels crosslinked by “poly(C18)-PAMPS” macro-crosslinkers showed excellent compression toughness. During the compression tests, the mGel samples did not fracture at 98% strain (Fig. 2a). With the increase of NaAMPS concentration in the micelles, the Young’s modulus of mGel hydrogels increased from (115.1 ± 2.3) kPa (mGel-1) to (120.2 ± 2.5) (mGel-2), (125.3 ± 2.3) (mGel-3), (133.3 ± 4.3) (mGel-4), and (140.7 ± 3.5) kPa (mGel-5). The corresponding compression stress at 98% strain ($\sigma_{0.98}$) was increased from (11.8 ± 0.7) MPa to (14.6 ± 1.1) , (16.0 ± 0.8) , (17.9 ± 0.1) , and (20.7 ± 0.4) MPa, respectively. The corresponding energy dissipation during compression to 98% strain, denoted as the area under the stress-strain curves, also increased from (504.5 ± 19.1) kJ/m³ to (582.7 ± 22.1) , (607.8 ± 20.6) , (734.7 ± 70.3) and (839.3 ± 17.5) kJ/m³. The increase in strength and toughness of mGel hydrogels is consistent with the increase in micelle size induced by the incorporation of NaAMPS. The hydrophobic association of poly(C18) within the micelle cores was suggested to account for the energy dissipation upon loading^[13, 19].

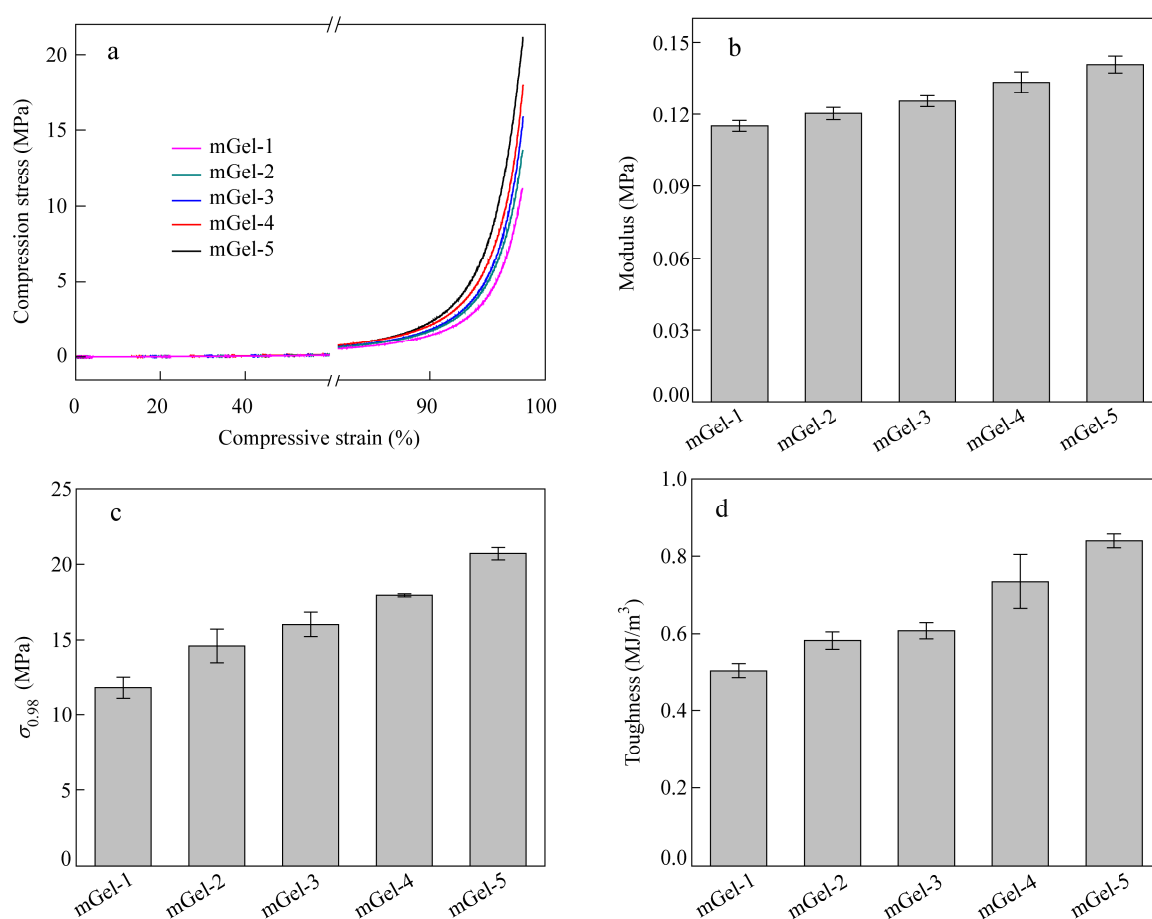


Fig. 2 (a) Representative compression stress-strain curves, (b) Young’s modulus, (c) compression stress at 98% strain ($\sigma_{0.98}$) and (d) compression toughness of mGel hydrogels with different NaAMPS concentrations for the micelles

In order to further investigate the energy dissipation, cyclic compression loading-unloading tests were conducted on the hydrogels. First, the gels were successively compressed to a series of maximum strains and unloaded (Fig. 3a), with the maximum strain increased from 30% to 90% with 15% step. For each cycle, significant hysteresis loop was observed, with the loop area increasing with the strain (Fig. 3a). The loop area indicates the energy dissipation during loading-unloading. Interestingly, for the two successive cycles, the latter loading curve always overlapped with the former one (Fig. 3b). Moreover, cyclic compression loading-unloading tests at 90% strain produced overlapped stress-strain curves for 5 consecutive immediate cycles (Fig. 3c). These results demonstrate that there was no internal structure damage during the compression loadings. The energy dissipation may be originated from the internal friction and deformation of the micelle macro-crosslinkers upon loading. Thus, the hydrogels exhibited a full shape recovery upon unloading.

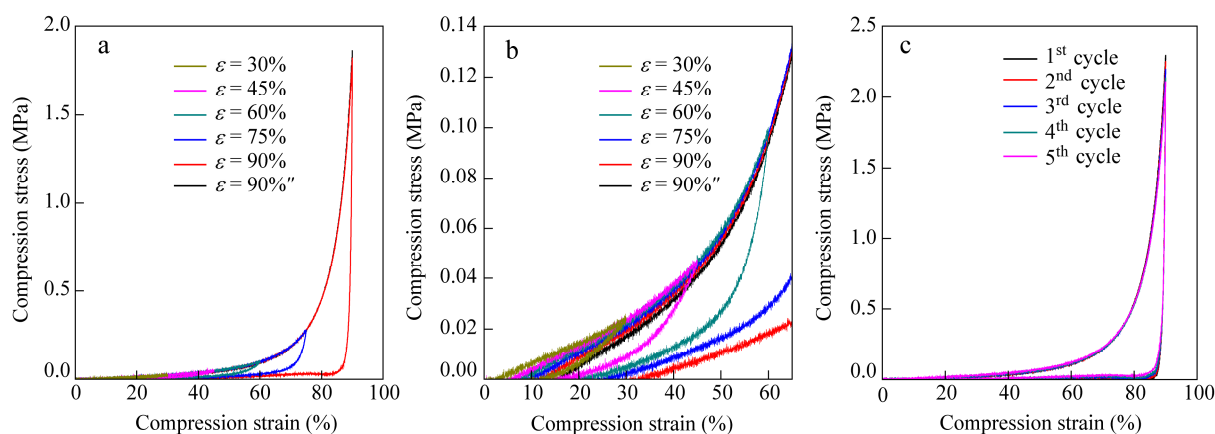


Fig. 3 Representative stress-strain curves of mGel-3 hydrogels experiencing cyclic compression loading-unloading tests (a, b) with incremental strains and (c) at a constant strain of 90%

The poly(C18)-PAMPS micelle-crosslinked hydrogels showed outstanding tensile strength and extensibility. Figure 4(a) displays representative tensile stress-strain curves of the hydrogels with different NaAMPS feeding concentrations. The elongation at break was decreased from $(1670 \pm 70)\%$ (mGel-1) to $(1570 \pm 42)\%$ (mGel-2), $(1500 \pm 39)\%$ (mGel-3), $(1170 \pm 43)\%$ (mGel-4), and $(995 \pm 53)\%$ (mGel-5) as the NaAMPS concentration was increased from 0.16 mol/L (mGel-1) to 0.37 mol/L (mGel-5). The corresponding tensile strength was increased from (153.8 ± 18.8) kPa to (193.3 ± 7.8) , (231.7 ± 10.3) , (289.3 ± 15.9) , and (372.6 ± 29.9) kPa. The fracture energy of these hydrogels was increased from (1.0 ± 0.1) MJ/m³ to (1.3 ± 0.07) , (1.4 ± 0.06) , (1.5 ± 0.08) , and (1.6 ± 0.04) MJ/m³. It is noted that the overall concentrations of NaAMPS and AAm monomer were kept constant at 5 mol/L for these gels. The dependence of tensile properties on the NaAMPS concentration in micelle solution is primarily attributed to the increasing size of SDS-NaCl-NaAMPS micelles (Fig. 1b) and the resulted large sizes of the poly(C18)-PAMPS macro-crosslinkers. Upon tensile tests, the energy dissipation may result from the stretching and pulling of the poly(C18)-PAMPS chains from the cores^[21]. With larger SDS-NaCl-NaAMPS micelles, the hydrophobically associated poly(C18)-PAMPS crosslinkers were larger, which may dissipate more energy upon stretching.

The poly(C18)-PAMPS micelle-crosslinked gels dissipate energy upon cyclic tensile tests. Cyclic tensile loading-unloading tests were conducted on mGel-3. The hydrogel sample was stretched to 600% strain and then immediately unloaded (Fig. 5a). The stretched sample recovered its original length, with a residual strain less than 40%. Representative hysteresis loops were observed during the loading-unloading cycle, which suggested energy dissipation during stretching, probably due to the deformation and partial damage of the macro-crosslinkers (Fig. 5a). Subsequently, the tested hydrogel samples underwent an immediate second tensile cycle (Fig. 5a). The second hysteresis loop was smaller than the first one, with the loop area of about $(50.2 \pm 1.3)\%$ of that for the first loop. During the first stretching, the damage in crosslinking structures did not immediately

recover the original state. However, the third and subsequent loading-unloading loops overlapped with that of the second cycle (Fig. 5a), indicating that few structural damages occurred upon subsequent loadings. Thus, the corresponding energy dissipation reached a plateau value at given strains (Fig. 5b).

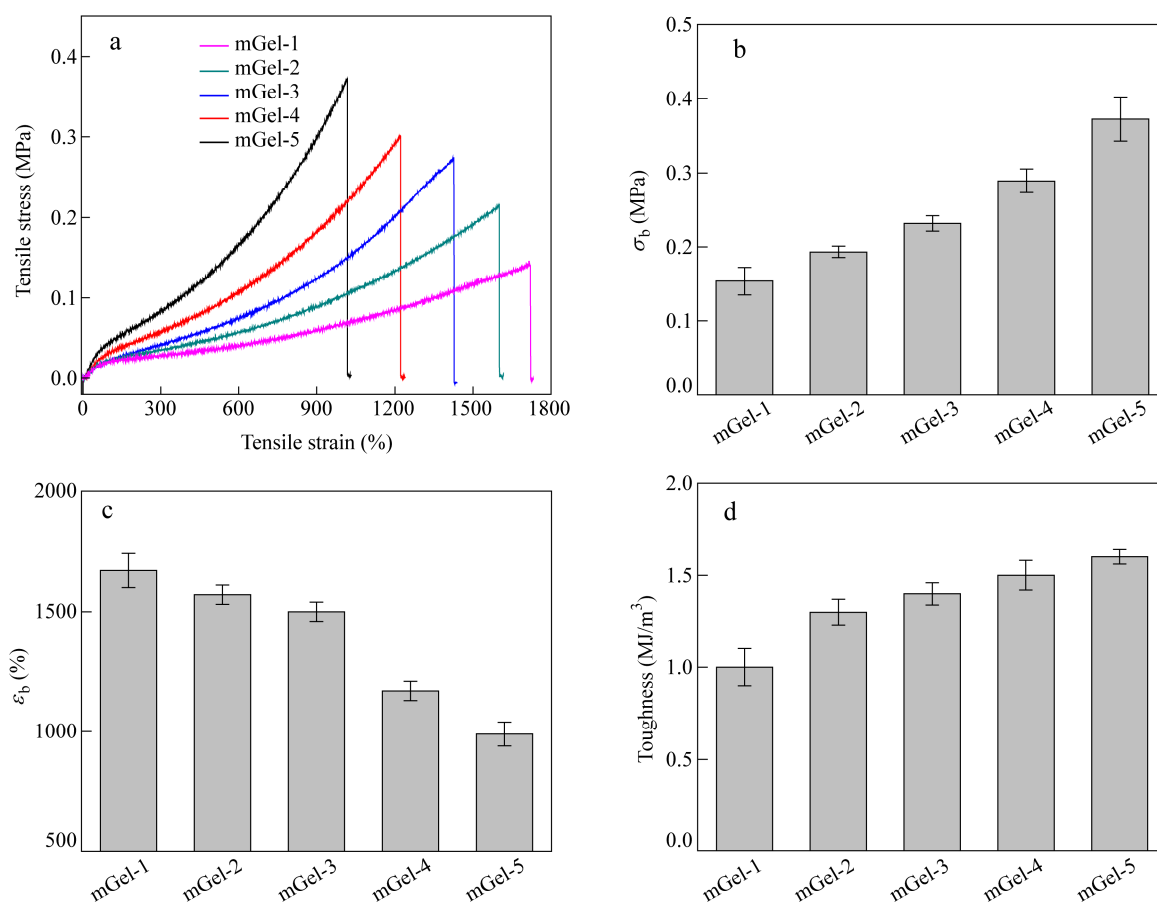


Fig. 4 (a) Representative tensile stress-strain curves, (b) fracture strength (σ_b), (c) elongation at break (ϵ_b) and (d) tensile toughness of hydrogels with different NaAMPS concentrations for the micelle crosslinkers

The energy dissipation mechanism could be recovered for these micelle-crosslinked hydrogels after being treated at elevated temperatures. Hydrogels stretched to 600% were stored at 25 °C for different time and then subject to tensile loading-unloading test. The hysteresis loops for the cycles after recovery at 25 °C for different durations are compared in Fig. 5(c). At 25 °C, the recovery ratio was increased from $(55.9 \pm 2.1)\%$ (0.5 h) to $(71.0 \pm 1.7)\%$ (1.0 h) and $(89.5 \pm 1.7)\%$ (2.0 h). The recovery was accelerated at elevated temperatures. For example, at 40 °C, the recovery ratio was 67.3% in 0.5 h and 90.2% in 1 h (Fig. S3a, in SI). Moreover, the recovery was even faster at 60 °C, showing a recovery ratio as high as $(91.6 \pm 2.7)\%$ in only 0.5 h (Fig. 5d and Fig. S3b in SI). During stretching, the micelle macro-crosslinkers might deform until some chains were pulled out from the hydrophobic cores, which dissipated energy^[22]. For stretching to given strains less than the fracture strain, most of the energy dissipation occurred at the first cycle, including network and macro-crosslinker deformation and partial chain pullout. During subsequent loading to the same strains, the energy dissipation was primarily originated from the network and macro-crosslinker deformation and internal friction. After recovering, some pullout chains might re-assemble into the micelles, or the damaged micelle structures re-adjusted or recovered. The recovery could be accelerated at elevated temperatures. As a result, the energy dissipation mechanism was recovered.

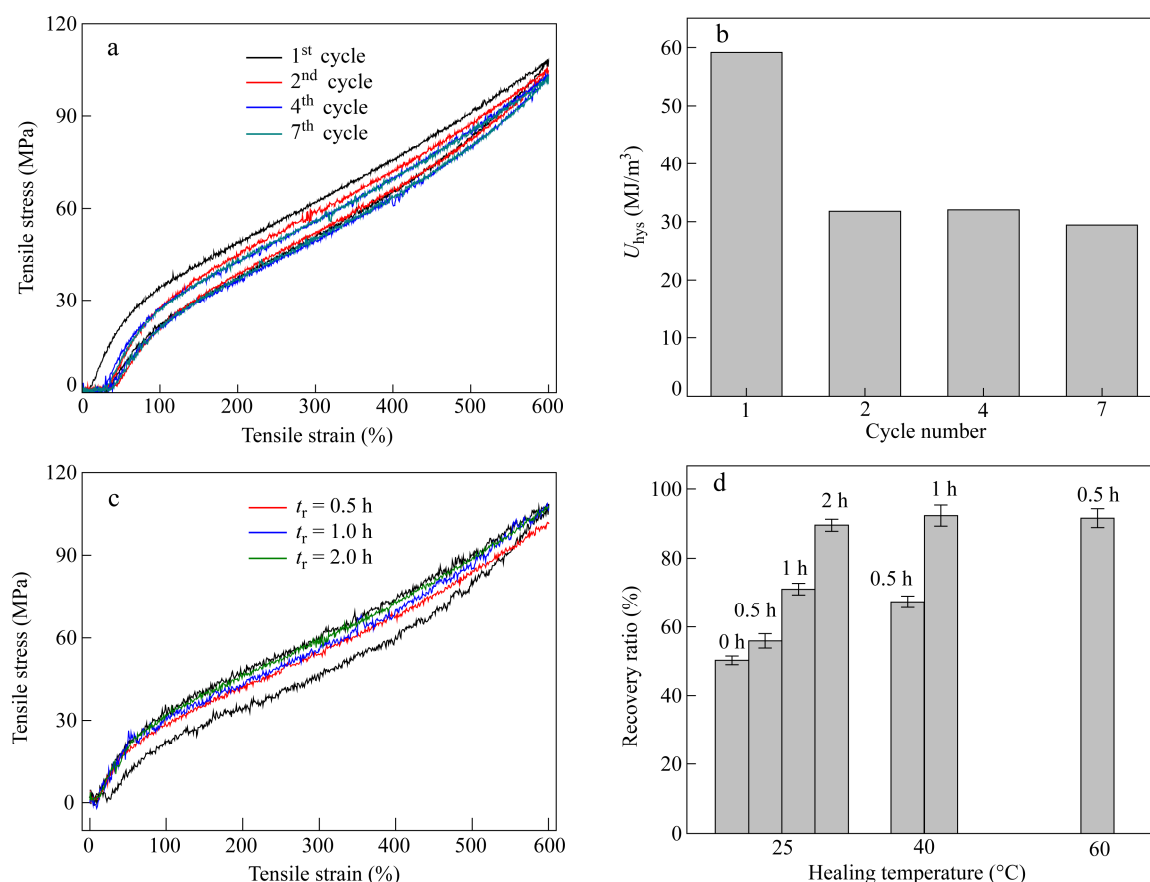


Fig. 5 (a) Cyclic tensile stress-strain curves of mGel hydrogels to 600% strain (Four of ten consecutive loading-unloading curves without waiting between two cycles are shown for clarity); (b) The hysteresis energy (U_{hys} , loop area) as a function of testing cycle number for the mGel-3 hydrogel; (c) Tensile hysteresis loops of tested hydrogels after storing at 25 °C for 0.5, 1.0, and 2.0 h; (d) Recovery ratio of mGel-3 hydrogels after storing at different temperatures over time

The poly(C18)-PAMPS micelle-crosslinked hydrogels are responsive to pH and/or ion strength (I_s) by changing their swelling ratio. For example, the as-synthesized anionic hydrogel (mGel-3) swelled over time in buffer solutions (Figs. 6a and 6b). The swelling ratio and rate depended on the pH and ion strength. The hydrogels exhibited a mild and smooth expansion behavior in all the pH buffer solutions (Fig. 6). As the buffer pH increased from 3 to 5, 7, 9, and 11, the swelling ratio at 650 min, for example, was increased from (9.3 ± 0.2) (pH = 3) to (11.3 ± 0.4) (pH = 11) (Fig. 6a). Note that the AMPS residue has a pK_a of 2. With increasing pH, the electrostatic repulsion between the PAMPS chains became stronger, leading to increasing swelling ratio. On the other hand, as the ion strength was increased from 0.05 to 0.10 and 0.25, the swelling ratio of hydrogels was decreased from (13.3 ± 0.1) ($I_s = 0.05$) to (10.6 ± 0.1) ($I_s = 0.1$) and (7.4 ± 0.2) ($I_s = 0.25$) at 650 min (Fig. 6b), attributed to the reduced electrostatic repulsion between polymer chains within the networks due to the enhanced electrostatic shielding by the salt ions.

The sensitivity of swelling behavior to pH and ion strength is reversible. As the hydrogels were cyclically immersed in solutions with different pH or ion strength, they underwent reversible swelling and deswelling. For example, after equilibrated in the solution with pH = 7 and $I_s = 0.05$ for 24 h, mGel-3 gels deswelled in the solution with $I_s = 0.3$ and pH = 7. The swelling ratio decreased from (18.5 ± 0.2) to (14.8 ± 0.1) within 8 h (Fig. 6c). As the gel samples were transferred into solutions with $I_s = 0.05$ and pH = 7, the swelling ratio increased to about 18.5 (Fig. 6c). As the gels were shuttled between buffer solutions with $I_s = 0.05$ and 0.3, reversible swelling/deswelling

occurred, with almost full recovery of the volume. The hydrogels were stable for a long time during swelling/deswelling in the solutions due to the stable hydrophobic association of poly(C18) chains in the macro-crosslinkers.

These poly(C18)-PAMPS micelle-crosslinked hydrogels showed collective responses to synergistic pH and salt stimuli. The hydrogel with a swelling ratio of 15.3 started to further swell when immersed in solutions with $\text{pH} = 11$ and $I_s = 0.05$. After swelling for 8 h, the gel reached a swelling ratio of 18.5, and then was transferred into solutions with $\text{pH} = 3$ and $I_s = 0.3$. The gel deswelled to 15.6 in 8 h (Fig. 6d) and could not recover the original swelling ratio due to the synergistic effects of pH and ion strength changes. During subsequent swelling/deswelling in these buffer solutions, it was interesting to note that the swelling ratio at 8 h was always larger than the previous one at given pH/ion strength conditions (Fig. 6d). This behavior is attributed to the unrecoverable electrostatic repulsion between the chains. To test this hypothesis, hydrogels were immersed in solutions ($I_s = 0.1$) with oscillatory change of pH values ($\text{pH} = 11$ and $\text{pH} = 3$) (Fig. S4, in SI). At $\text{pH} = 11$, the hydrogel was gradually swelled, while its volume was further increased during subsequent immersion in the solution with $\text{pH} = 3$ (Fig. S4, in SI). Such incremental swelling occurred upon pH changes between 3 and 11. That is, the gels kept swelling during this cyclic process. These results suggest that the unrecoverable electrostatic repulsions between PAMPS chains dominated at the beginning. After long time swelling (e.g., 65 h), the hydrogels reached equilibrium swelling (Fig. S4, in SI).

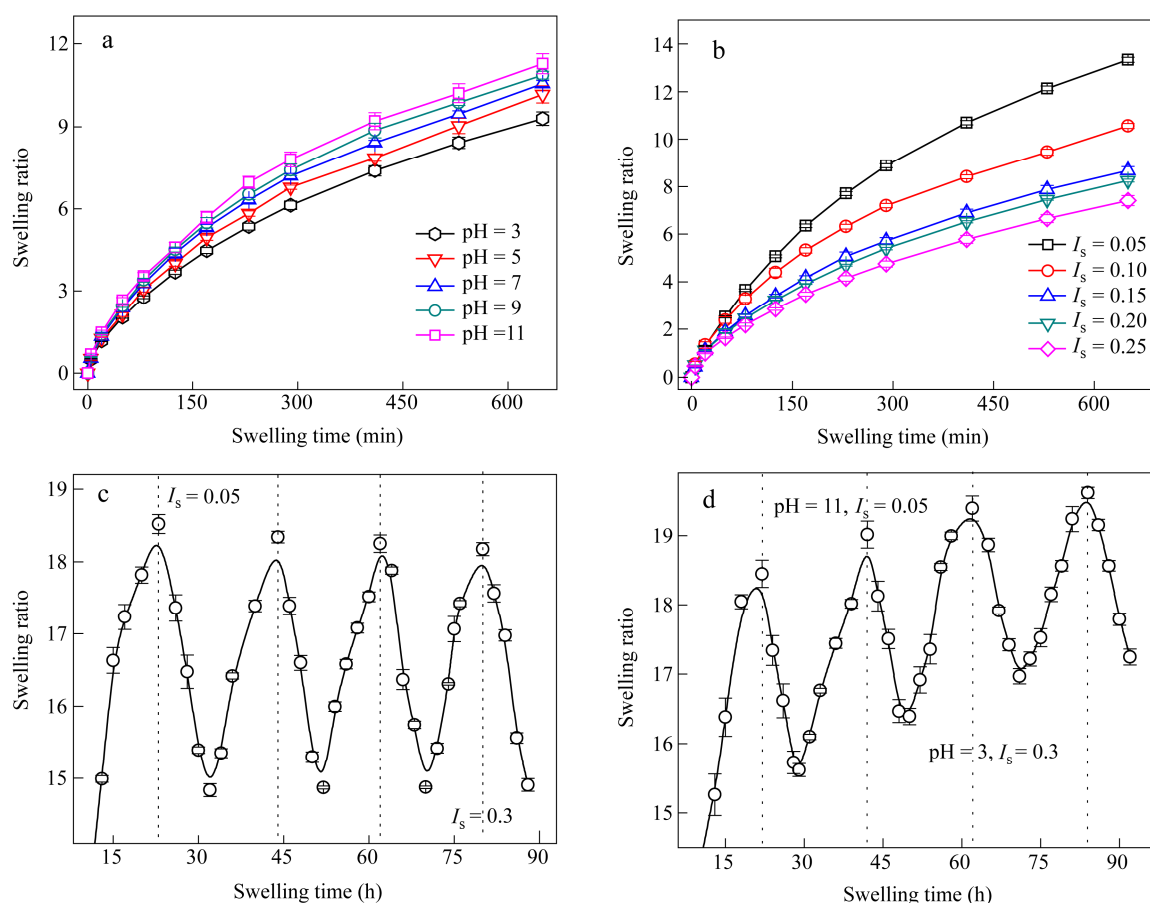


Fig. 6 Swelling curves of the mGel-3 hydrogels in solutions with (a) $\text{pH} = 3, 5, 7, 9$ and 11 or (b) ion strength $I_s = 0.05, 0.1, 0.15, 0.2$ and 0.25 ; Cyclic swelling/deswelling of the mGel-3 gels when shuttled in (c) solutions with $I_s = 0.05$ and 0.3 or (d) solutions with $\text{pH} = 11, I_s = 0.05$, and $\text{pH} = 3, I_s = 0.3$

CONCLUSIONS

Hydrogels based on “poly(C18)-PAMPS” core-shell structured macro-crosslinkers were constructed by using SDS micelles to encapsulate hydrophobic C18 molecules in the cores and hydrophilic AMPS molecules in the coronae. The micelle structures were stabilized and manipulated by using NaCl so that the hydrophobic C18 molecules were efficiently dissolved in the micelles. It is critical that AMPS monomers were first incorporated into the SDS micelles and then 0.5 mol/L NaCl was added to induce a growth of the micelles. The large cores in the SDS-NaCl-NaAMPS micelles efficiently encapsulated C18 hydrophobes. As a result, core-shell micelles consisting of C18 hydrophobes in the cores and AMPS monomer in the coronae were constructed. Such assemblies were used for free radical polymerization with AAm monomers to generate hydrogels with “poly(C18)-PAMPS” macro-crosslinkers, without using any other chemical or physical crosslinkers.

The hydrophobic association of “poly(C18)-PAMPS” micelles provided efficient energy dissipation under loading, leading to the hydrogels with outstanding mechanical properties. The tensile strength and toughness were increased with increasing micelle size. Cyclic loading-unloading tests demonstrated excellent energy dissipation. These poly(C18)-PAMPS crosslinked hydrogels were recoverable at room temperature and the recovery was accelerated at elevated temperatures. The presence of PAMPS polyelectrolyte chains within the networks endowed the hydrogels with reversible responsiveness to pH and ion strength. These tough and responsive hydrogels may find potential applications in soft actuators and artificial muscles, *etc.*

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