

Self-healing and shape-memory in mechanically robust hydrogels



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Hydrogels, 3D networks of hydrophilic polymers, are fascinating materials with a wide range of applications due to their unique properties such as softness, hydrophilicity, viscoelasticity, biocompatibility, and the capacity to store large amount of water (Figure 1a).[1,2] They are commonly used in various fields, including biomedical and tissue engineering, sensors, artificial organs, and actuators.[3,4] The history of gel science can be traced back to significant contributions made by various scientists. In 1960, Otto Wichterle, a Czech chemist and inventor, made a groundbreaking discovery in the field of biomedical hydrogels by developing the first soft contact lenses using a hydrogel material.[5] This breakthrough not only improved the comfort and safety of contact lenses but also opened up new possibilities for the use of hydrogels in various biomedical applications. In 1978, Toshio Tanaka, a Japanese chemist, made significant contributions to the development of smart hydrogels.[6] He discovered a unique phenomenon in certain hydrogels known as the “volume phase transition.” This phenomenon involves a dramatic change in the hydrogel’s volume in response to external stimuli, such as changes in temperature, pH, or ionic strength. This discovery paved the way for the design and fabrication of stimuli-responsive hydrogels, also known as smart hydrogels, which have the ability to change their properties and shape in response to specific environmental cues. Smart hydrogels have since found applications in drug delivery systems, tissue engineering, sensors, and other fields where controlled responses to external stimuli are desirable.

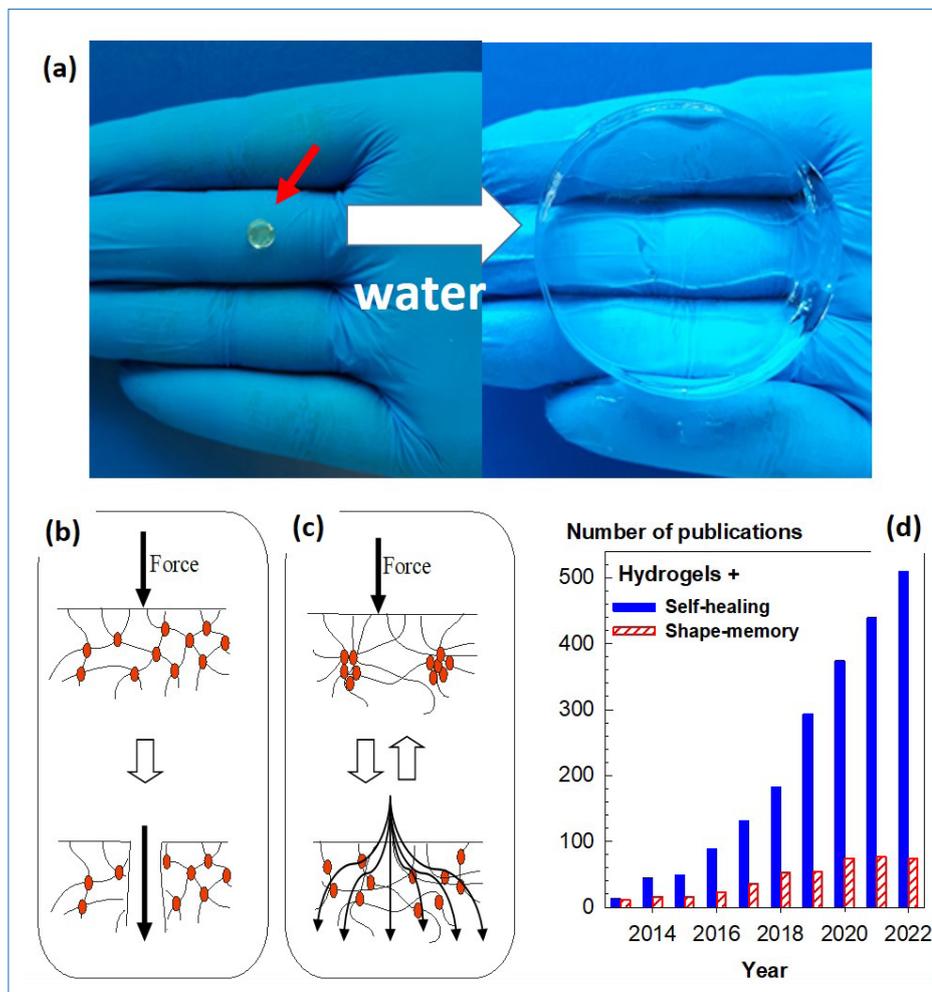


Figure 1. (a) Images of a physical PAMPS hydrogel before and after swelling in water. From [2] with permission from the American Chemical Society. (b, c) Scheme illustrating crack of a covalently cross-linked hydrogel due to the localization of the fracture energy (b), and dissipation of the fracture energy in a hydrogel formed by reversible intermolecular bonds (c). Reprinted with permission from ref. [8]. Copyright 2009 Elsevier Ltd. (d): The number of papers with keywords “hydrogels + self-healing”, and “hydrogels + shape-memory” according to the WoS portal on July 29, 2023.

All these classical hydrogels mentioned above have been prepared by free-radical cross-linking copolymerization or chemical cross-linking of hydrophilic polymers, and hence they often exhibit brittle behavior limiting their potential for load-bearing applications.^[7] The primary reason for their mechanical weakness is the absence of an efficient energy dissipation mechanism within the covalently cross-linked network. When a force is applied to these hydrogels, the lack of an effective energy dissipation mechanism leads to the localization of the fracture energy at the point of force application. As a result, cracks propagate rapidly, leading to failure at relatively low strains (Figure 1b).^[8] This behavior significantly restricts their utility in applications where mechanical robustness and toughness are required.

To address this limitation, researchers in the past 20 years have directed their efforts

towards creating hydrogels with improved mechanical properties via the introduction of physical bonds in addition to the covalent cross-links.^[9] Physical bonds in hydrogels are reversible, meaning they can break and reform under certain conditions without permanently damaging the network structure (Figure 1c). These bonds provide an effective energy dissipation mechanism, allowing the hydrogels to withstand and absorb larger amounts of strain without undergoing catastrophic failure. The second-generation hydrogels with enhanced mechanical performance were also prepared by generating energy dissipation in chemically cross-linked networks, especially in the form of double-network (DN) hydrogels exhibiting mechanical properties comparable to load-bearing tissues like tendons, cartilage, and ligaments (Figure 2).^[10,11] DN hydrogels are composed of brittle and ductile network components. At a low strain, the brittle network component starts breaking and forming many cracks by dissipating energy while the ductile network prevents the complete disintegration of the hydrogel. DN hydrogels exhibiting remarkable mechanical parameters are suitable for a wide range of engineering and biomedical applications, such as biomedical devices, soft robotics, and wearable electronics, where flexibility and toughness are essential.

The challenge in recent years is to design hydrogels with self-healing and shape-memory functions.^[12-16] Self-healing is the ability of a material to repair its own damage autonomously or upon exposure to external stimuli, such as heat, solvents, light, etc. In synthetic polymers, the incorporation of self-healing

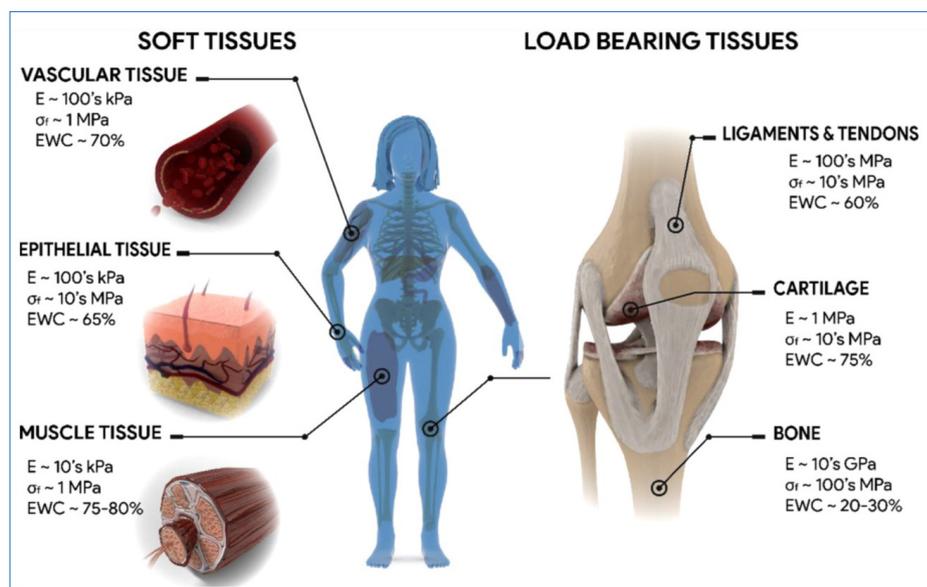


Figure 2. Young's modulus (E), fracture strength (σ), and equilibrium water content (EWC) values of biological tissues. From [11] with permission from the American Chemical Society.

capabilities is crucial to extend their lifetimes and reduce the accumulation of waste polymers, including harmful microplastics, in the environment. Additionally, self-healing is of paramount importance for hydrogels used as scaffolds in tissue engineering, biomaterials, and drug delivery systems. Drawing inspiration from natural processes like blood clotting and bone repair, various strategies have been developed to introduce self-healing properties in polymers and hydrogels.^[12-14,17-19] Shape-memory is another fascinating feature of materials that allows them to remember one or more shapes under specific stimuli. Shape-memory hydrogels have garnered significant interest due to their versatile applications as actuators, sensors, and implants in minimally invasive surgeries.^[15,16,20] These hydrogels can be programmed to change their shape in response to external triggers, making them highly useful in various biomedical and engineering fields.

The interest in self-healing and shape-memory hydrogels has been growing steadily in the past decade, as evidenced by the increasing number of publications (Figure 1d). This surge in research activities indicates the significance and potential of these materials in various scientific and technological applications. This review presents an overview of the latest developments in this area, with a primary focus on achievements made in the past decade, aiming to contribute to the ongoing advancement of these innovative materials.

Hydrogen-bonded self-healing hydrogels

By replacing the chemical cross-links in hydrogel 3D networks with physical ones of finite lifetimes, researchers have achieved self-healing capabilities in mechanically strong hydrogels while avoiding the need for complicated synthetic methods. One approach to creating self-healing hydrogels involves utilizing vinyl monomers that carry multiple amide groups capable of forming strong H-bonds. For instance, N-acryloyl glycinamide (NAGA), with its dual amide H-bonds, leads to the formation of a hydrogel with impressive mechanical properties, such as a tensile strength in the range of MPa and an elongation ratio at break of 1400% (Figure 3a, b).^[21] The multiple H-bonding domains in NAGA hydrogels contribute to their mechanical strength and stability in water. These hydrogels can efficiently self-heal with a healing efficiency of 80% by inducing heating at 90 °C, which causes the dissociation of H-bonds.^[21] After cooling back to room temperature, the H-bonds reform to bridge the damaged surfaces. Incorporating specific functional groups, such as diaminotriazine (DAT) or ureidopyrimidinone (UPy), into the hydrogel

network leads to the formation of H-bonded dimers or higher-order aggregates, resulting in mechanically strong hydrogels with self-healing properties (Figure 3c, d).^[22-25] For instance, UPy-containing hydrogels with 80 wt % water exhibit a tensile strength of 1 MPa and efficient self-healing abilities due to the formation of UPy-UPy dimers with quadruple H-bonds.^[24]

The introduction of hydrophobic groups in H-bonded hydrogels enhances the H-bond strength and improves their mechanical properties. For example, the mechanical

strength of 1-vinylimidazole / acrylic acid (AAc) copolymer hydrogels significantly increases when AAc units are replaced with methacrylic acid (MAAc) units due to the presence of methyl motifs.^[26,27] Another strategy involves copolymerizing vinyl monomers with H-bond acceptor and donor sites in aqueous solutions, leading to self-healing hydrogels with good mechanical properties. For instance, copolymerizing MAAc and N,N-dimethylacrylamide (DMAA), which have strong H-bond donor carboxylic and H-bond acceptor carbonyl groups, respectively, results in self-healing H-bonded

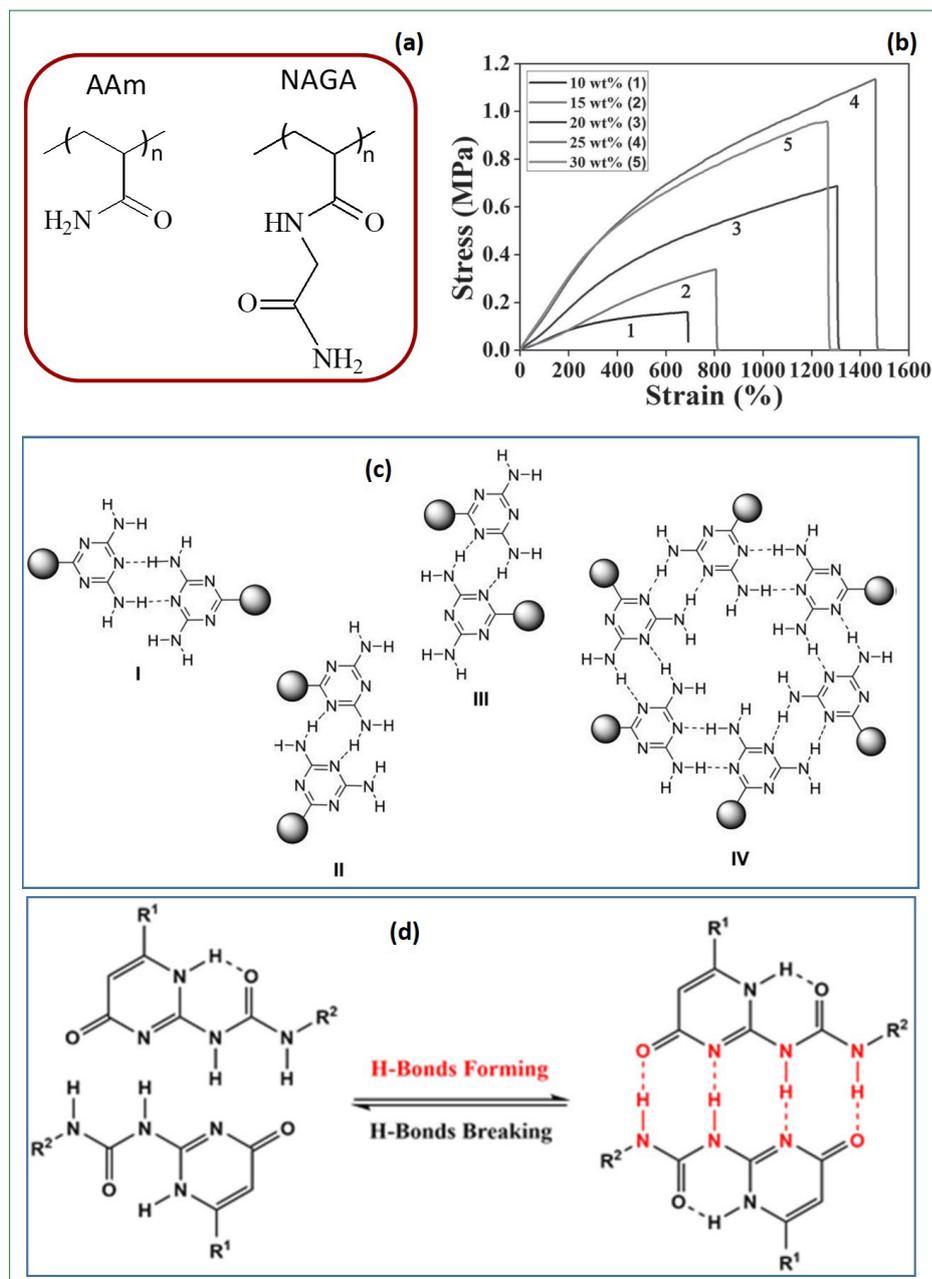


Figure 3. (a) Chemical structure of acrylamide (AAM) and N-acryloyl glycinamide (NAGA) segments. (b) Stress–strain curves of NAGA hydrogels at various NAGA concentrations as indicated. From [21] with permission from Wiley. (c) Chemical structure of diaminotriazine (DAT) groups. From [22] with permission from the Royal Society of Chemistry. (d) Ureidopyrimidinone (UPy) groups and their self-healing mechanism.^[25]

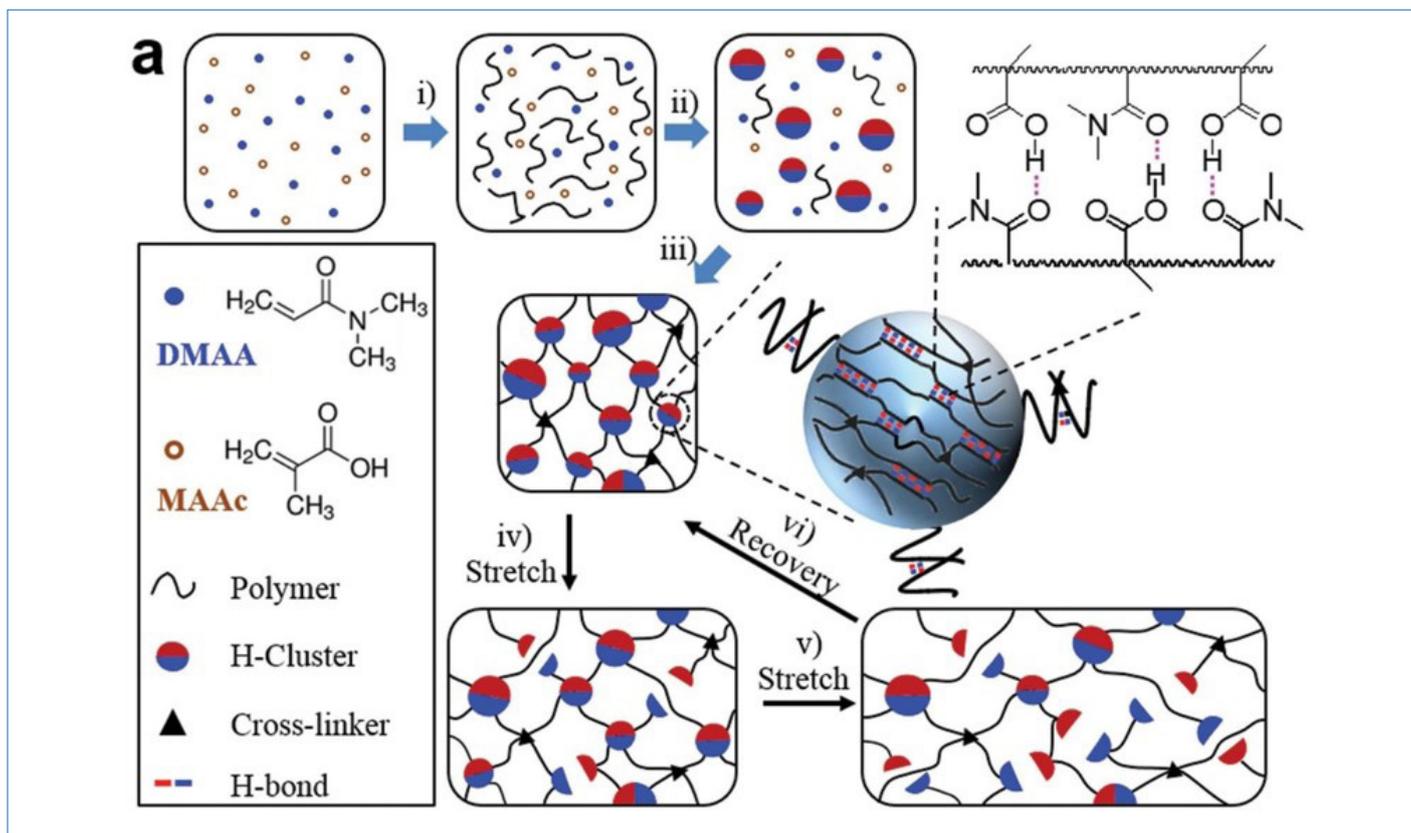


Figure 4. Cartoon illustrating formation of MAAc/DMAA hydrogels. Formation of oligomeric radicals (i), their phase separation due to multiple H-bonds to form polymer-rich clusters with trapped radicals (ii), and formation of a hydrogel containing clusters embedded into a polymer poor phase (iii). Stretching the hydrogel leads to fragmentation of weak (iv) and strong clusters (v) followed by complete recovery after unloading (vi). From [28] with permission from Wiley.

hydrogels with a Young's modulus of 28 MPa and an elongation at break of 800% (Figure 4).^[28] Overall, the incorporation of non-covalent interactions, such as H-bonding and hydrophobic interactions, offers a promising approach for creating self-healing hydrogels with improved mechanical properties and stability in water. These materials have the potential for various applications in fields like tissue engineering, drug delivery, and soft robotics.

The cooperativity of H-bonds plays a crucial role in determining both the mechanical and self-healing properties of H-bonded hydrogels.^[29] To illustrate this effect, two hydrogels with identical composition can be compared: (i) Hydrogel prepared by free-radical copolymerization of acrylamide (AAm) and N-vinylpyrrolidone (VP) in an aqueous solution. (ii) Hydrogel prepared by free-radical polymerization of AAm alone in an aqueous solution containing preexisting poly(N-vinylpyrrolidone) (PVP). In both cases, H-bonding interactions occur between the amide groups of AAm and the pyrrolidone groups of VP or PVP, respectively. The hydrogel formed using the in situ formed PVP (Case 1) has a lower tensile strength compared to the hydrogel formed using preexisting PVP (Case 2).^[29] This difference

in tensile strengths suggests that the in situ formed PVP generates weaker H-bonds with the PAAm chains compared to the pre-existing PVP. The concept of the "proximity effect" in H-bonding interactions becomes evident in this example. Thus, when H-bonds form between two polymer chains, they restrict the conformational freedom of the chains, which in turn facilitates the formation of subsequent H-bonds. This effect becomes more pronounced with increasing the number of segments in a polymer molecule, leading to enhanced cooperativity of the H-bonding network and, consequently, improved mechanical properties.

Another example involves hydrogels based on 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), which are desirable for preparing superabsorbent materials. When AMPS is polymerized using UV radiation without the addition of a chemical cross-linker, the resulting hydrogels are water-insoluble. These hydrogels have a high swelling ratio of approximately 1000 g/g, indicating their ability to absorb a significant amount of water (Figure 1a).^[2] In contrast, PAMPS hydrogels prepared using thermal polymerization at 80 °C under similar conditions are soluble in water. Young's modulus of the hydrogels formed by thermal

polymerization is approximately three times lower compared to those formed by UV polymerization. The reason behind this difference lies in the molecular weight of the primary chains in the hydrogels formed by UV polymerization, which is much larger than in those formed by thermal polymerization. This indicates that the proximity effect in H-bonded hydrogels contributes to the formation of a more extended and interconnected H-bonding network, resulting in hydrogels with higher mechanical strength and improved properties. The combination of N, N-dimethylacrylamide (DMAA) as a strong H-bond acceptor and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) in hydrogels results in physical hydrogels with remarkable properties, e.g., a high stretchability (1000%), excellent mechanical strength, and complete self-healing efficiency.^[2] These hydrogels can absorb a large quantity of water without dissolving, reaching a swelling ratio of approximately 1700 g/g. The increase in DMAA amount in the gel network significantly enhances the effective cross-link density, indicating that H-bonds formed between AMPS and DMAA act as stronger cross-links, further strengthening the hydrogel's structure.

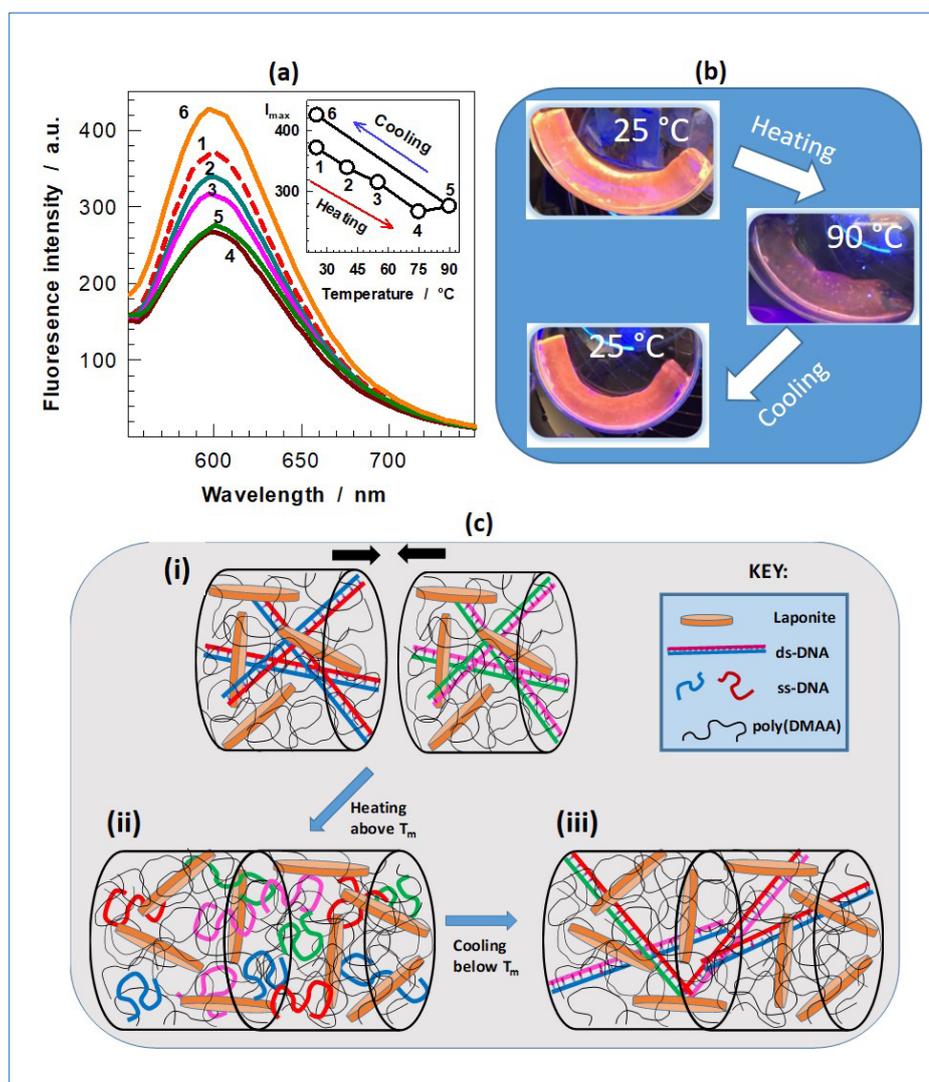


Figure 5. (a): EtBr fluorescence spectra in a DNA/clay hydrogel at 25 (1), 40 (2), 55 (3), 75 (4), and 90 °C (5), and after cooling back to 25 °C (6). The inset shows EtBr emission intensity plotted against the temperature. (b): Images of a DNA/clay hydrogel swollen in 10 mM EtBr solution. They were taken under UV light at 25 and 90 °C, and after cooling back to 25 °C. (c): Cartoon showing cut surfaces of DNA/clay hydrogels (i), and after bringing them together at above (ii), and below T_m of ds-DNA (iii). From [31] with permission from the American Chemical Society.

DNA hydrogels, on the other hand, are chemically or physically cross-linked networks of DNA strands that exhibit unique characteristics.^[30] Self-healable double-stranded (ds) DNA/clay nanocomposite hydrogels have been recently developed using DMAA polymerization via a free-radical mechanism in an aqueous solution of ds-DNA (2000 base pairs) and Laponite nanoparticles.^[31] These DNA/clay hydrogels are highly stretchable (1500%) and demonstrate thermally induced denaturation and renaturation behavior of ds-DNA. Ethidium bromide (EtBr) is used to monitor the conformational transition of ds-DNA in the gel network. EtBr intercalates between DNA base pairs, resulting in a significant increase in fluorescence intensity compared

to single-stranded (ss) DNA. The fluorescence intensity of EtBr decreases as the temperature increases up to 90 °C, reflecting the conformational transition from double-stranded to single-stranded DNA within the gel network (Figure 5a).^[31] However, upon cooling back to 25 °C, the EtBr intensity in the gel increases and rises above its initial value, indicating the reformation of double-stranded DNA.

The optical photographs of DNA/clay hydrogels under UV light visualize this conformational transition between ds-DNA and ss-DNA (Figure 5b).^[31] The initial yellow-orange color of the gel specimen under UV light weakens at 90 °C due to the decrease in fluorescence intensity. However, the initial

color is recovered upon cooling to 25 °C, indicating that ds-DNA molecules retain their characteristic features within the hydrogel network. DNA/clay hydrogels also exhibit complete healing efficiency when heated at 90 °C for 30 minutes. During heating, the H-bonds holding the double strands together weaken and break, forming flexible ss-DNA strands within the hydrogel network. Upon cooling, the released single strands at the cut region combine to form ds-DNA bridges, facilitating the healing of the hydrogels (Figure 5c). These findings demonstrate the fascinating behavior of DNA-based hydrogels and their potential for various applications, including self-healing materials. The ability to control conformational transitions of DNA within the hydrogel network opens up new opportunities for designing smart and responsive materials.

Hydrophobically modified self-healing hydrogels.

Hydrophobically modified self-healing hydrogels developed in our research group contain both hydrophilic and hydrophobic regions, and have been prepared using a micellar polymerization technique.^[13,14,32,33] This technique involves copolymerization of water-soluble and water-insoluble monomers in the presence of surfactant micelles in an aqueous solution. The process starts by solubilizing a hydrophobic monomer within the micelles, and then it is copolymerized with a hydrophilic monomer through a free-radical mechanism. The resulting polymers have a blocky structure, which significantly enhances their associative properties. One advantage of this approach is that instead of using a traditional chemical cross-linker to create permanent chemical bonds within the hydrogel, a hydrophobic monomer is incorporated into the hydrophilic polymer chains. These hydrophobic associations act as reversible cross-links within the hydrogel network. This reversible cross-linking is essential for the unique properties of the hydrogel. However, incorporating larger hydrophobes with side chain lengths greater than 12 carbon atoms presented a challenge because they are insoluble in micellar solutions due to their size exceeding that of the micelles. To overcome this limitation, worm-like micelles (WLMs) with a high solubilization power for hydrophobes were used during micellar polymerization (Figure 6a).^[34] WLMs were formed by adding salts to aqueous solutions of ionic surfactants such as sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB), weakening electrostatic interactions and causing the micelles to grow, which facilitated the solubilization of larger hydrophobes. Interestingly, solubilization of the monomers in WLMs resulted in a conformational transition from worm-like to spherical micelles, as demonstrated

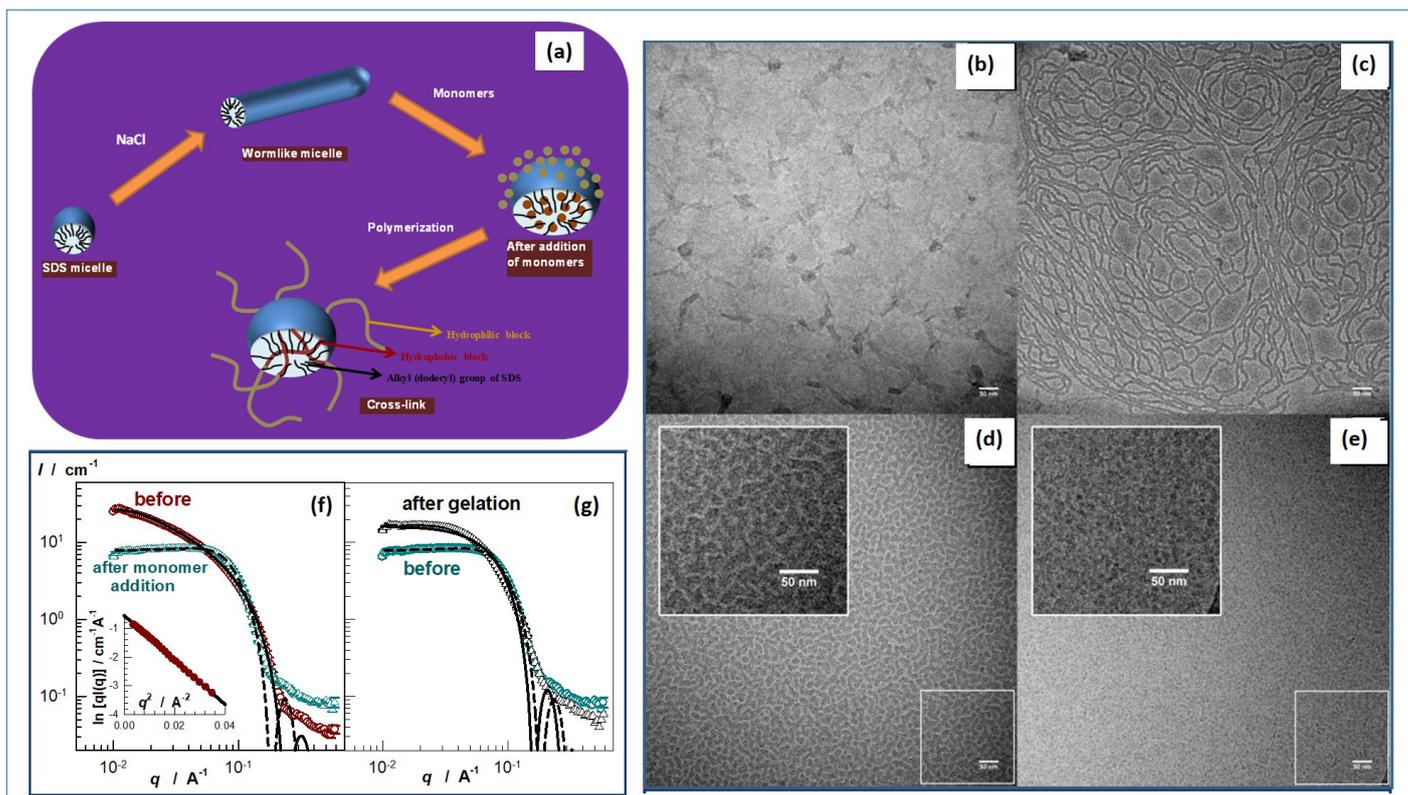


Figure 6. (a): Cartoon showing formation of self-healing micellar hydrogels in aqueous SDS–NaCl solutions via hydrophobic interactions. (b–e): Cryo-EM micrographs of surfactant solutions. Scale bars = 50 nm. (b, c) 243 mM SDS solution before (b) and after addition of NaCl (c). (d, e) 243 mM SDS + 1 M NaCl solution after addition of n-hexadecane (d), and the monomers AAm + C18M (e). (f) SANS profiles for SDS–NaCl solution before and after monomer addition. The solid and dashed curves are best fits to a form factor of wormlike micelles and spheres, respectively. (g) SANS profiles for SDS–NaCl solution containing the monomers before and after gelation. The curves are best fits to a form factor of spheres with a radius of 2.4 nm (before gelation) and 2.8 nm (after gelation). From [34] with permission from the American Chemical Society.

by cryo-EM micrographs and SANS measurements (Figure 6b–g). Several hundred nm long wormlike SDS micelles with a cross-sectional radius of 1.60 nm formed after salt addition disappear upon addition of the monomers, and a system consisting of monodisperse spheres with a radius of 2.4 nm appears.^[34] Copolymerization of the solubilized large hydrophobes such as n-octadecyl acrylate having a side chain length of 18 carbon atoms with hydrophilic monomers in surfactant solutions results in highly stretchable hydrogels with complete self-healing behavior.

High-strength self-healing hydrogels were recently fabricated by trapping the surfactant alkyl chains electrostatically in a supramolecular polymer network formed via hydrophobic interactions.^[35] Such physical networks were generated from hydrophobically modified poly(acrylic acid) (PAAc) with oppositely charged cetyltrimethylammonium (CTA) counterions via hydrophobic and electrostatic interactions (Figure 7a–c). They were prepared at various CTAB / AAC molar ratios (b_o) and total monomer concentrations (C_o). The mixed micelles acting as reversible cross-links are formed by the

aggregates of polymer-bound surfactant alkyl cations and the hydrophobic blocks of the hydrophilic polymer. These physical cross-links remain stable in water due to the electrostatic interactions between surfactant counterions and polymer backbone.^[35] The hydrogels exhibit a high tensile strength (0.7–1.7 MPa) and stretchability (800–900%), and self-healing ability. The photographs in Figure 7d, e show healing of a ruptured PAAc hydrogel sample in equilibrium with water. The joint reformed between cut surfaces withstands large external stresses as the original gel sample before its fracture. The hydrogels' self-healing ability was also quantified by conducting cut-and-heal tests at 35 °C for various times using a CTAB – NaBr mixture as the healing agent. In Figures 8f–h, stress–strain curves of the virgin and healed gel samples in equilibrium with water are shown for various healing times. The fracture stress of healed gels increases with increasing healing time or with decreasing PAAc concentration (C_o) of the hydrogels. For instance, after a healing time of 30 min, almost complete healing was achieved in the hydrogels formed at $C_o = 20\%$ (Figure 7g), while increasing C_o to 30% decreases the healing efficiency to 50%. After a healing

time of 60 min, the hydrogel sample formed at $C_o = 30\%$ and $b_o = 1/6$ sustains 1.5 ± 0.2 MPa stresses and ruptures at a stretch of 7 ± 1 (Figure 6h).^[35] To our knowledge, this fracture stress is the highest value reported so far in the literature.

The self-healing process of micellar hydrogels was studied in our group by time-dependent monitoring of the cut surfaces using scanning force microscopy (Figure 8A).^[34] It was observed that the healing process occurs in two steps, namely fast and slow steps. The first step involves formation of hydrophobic associations between nearby hydrophobes at the damaged surface, which transforms the trenches and protrusions created by cutting the gel into circular shapes. The second slower step requires diffusion of hydrophobes along the gel surface, which takes longer. This step involves the healing of the damaged regions farther away from each other. The mechanism proposed for the self-healing involves the behavior of surfactant molecules and polymer chains at the air-gel interface (Figure 8B).^[34] The hydrophilic parts of the surfactant molecules and polymer chains are oriented toward the bulk gel phase containing water,

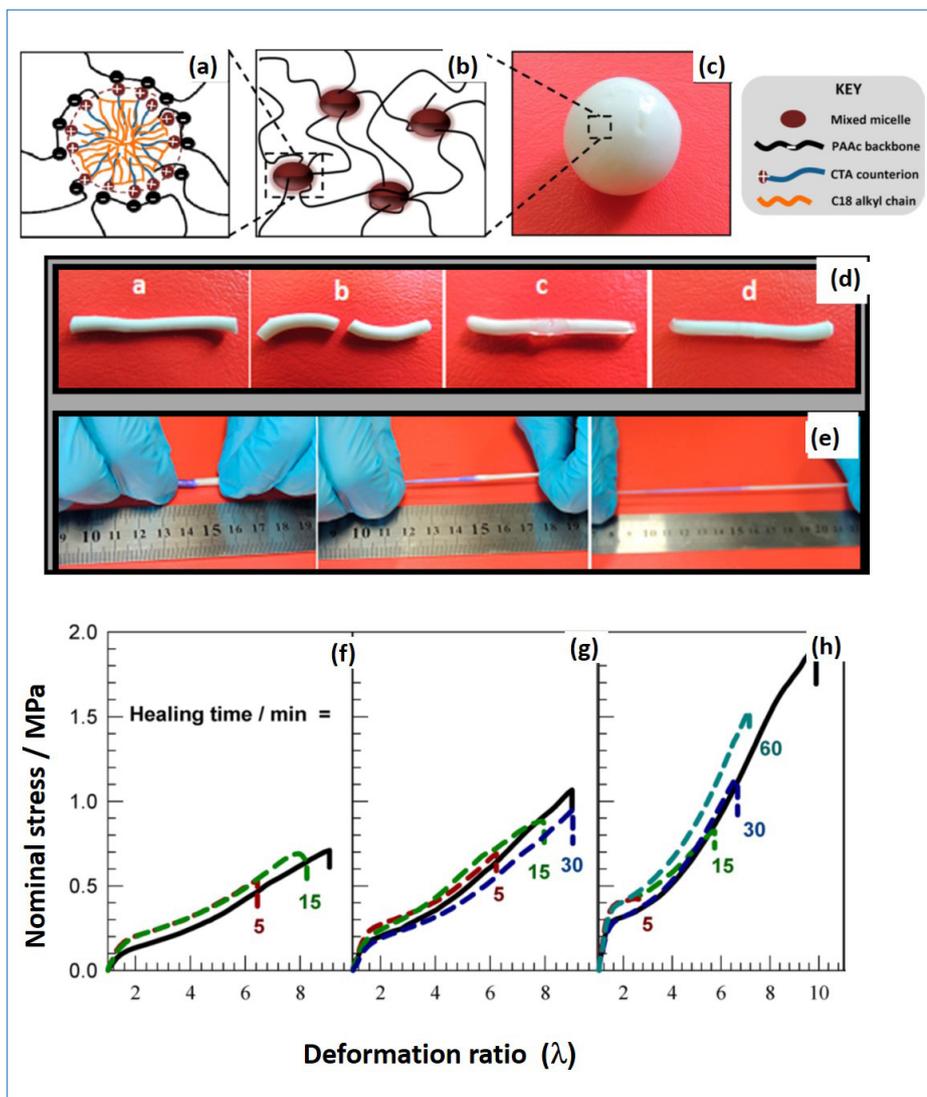


Figure 7 (a, b): Cartoon presenting the micellar cross-links in self-healing PAAc hydrogels. (c): Image of a spherical PAAc hydrogel sample in equilibrium with water. $C_0 = 20\%$. $\beta_0 = 1/8$. (d): Healing of swollen PAAc hydrogel samples formed at $C_0 = 30\%$ and $\beta_0 = 1/6$. Healing agent: CTAB (10%) – NaBr (0.25 M) solution at pH = 1. Photographs before (a) and after cutting of the sample into two pieces (b). After the treatment of cut surfaces with the surfactant solution and pressing them together (c), they merge into a single piece (d). (e): Photographs during stretching of a hydrogel sample self-healed via heating and surfactant treatment. One of the virgin samples forming the healed gel is colored with crystal violet for clarity. (f-h): Stress-strain curves of virgin (solid curves) and healed PAAc hydrogels samples in swollen state. (dashed curves). (f): $C_0 = 15\%$. $\beta_0 = 1/8$. (g): $C_0 = 20\%$. $\beta_0 = 1/8$. (h): $C_0 = 30\%$. $\beta_0 = 1/6$. From [35] with permission from the American Chemical Society.

while the hydrophobic parts are oriented away from the gel toward the cut surface. XRD results suggest that the mixed micelles act as mobile cross-links in the hydrogel and form a layered structure similar to molecules in molecular liquids. The micelles exhibit fast mobility within the layers but slower mobility between the layers. Because increasing humidity and temperature facilitate both intra- and interlayer mobilities of the micelles, the healing process occurs more effectively at higher humidity and temperature. Indeed,

when a gel sample is subjected to increased humidity (87% RH) and temperature (35 °C), the holes and islands formed by cutting the gel has shifted laterally, indicating gel dynamics. The holes and islands also decrease in depth and height, respectively, showing the healing process. After a sufficient time of resting the gel sample under elevated temperature and humidity, all the holes consume the islands, and the gel sample heals completely.

Self-healing and/or shape-memory hydrogels

Shape-memory hydrogels are a type of hydrogel that can undergo a reversible change in shape in response to external stimuli, such as temperature. These hydrogels typically consist of a 3D network structure formed by both permanent and temporary cross-links. The permanent shape of the hydrogel is determined by chemical cross-links, while the temporary shape is fixed by glassy or crystalline domains, which act as the switching segments. Figure 9A shows a typical example of shape-memory behavior in a hydrogel containing both chemical cross-links and crystalline domains with a melting temperature (T_m) of 48 ± 2 °C.^[36] The hydrogel's permanent shape is a rod. When heated above T_m , it becomes soft and can be easily deformed into a spiral shape. This temporary shape is fixed by cooling the specimen below T_m , during which the crystalline domains reform and lock the deformed chain conformation. By heating the sample above T_m again, it returns to its initial rod shape within 20 seconds. The chemically cross-linked network structure of the hydrogel determines the permanent rod shape, while the crystalline domains serve as the switching segments to fix the temporary spiral shape.^[36] The thermo-responsive shape-memory behavior is based on the covalently cross-linked network structure restoring its random coil conformation when the temperature is elevated above the T_m of the crystalline domains.

The hydrogels prepared by complex formation between hydrophobically modified PAAc and CTA counterions discussed in the previous section also exhibit shape-memory behavior due to significant variations in their moduli with temperature.^[35] Figure 9B demonstrates shape-memory behavior of a hydrophobically modified PAAc hydrogel sample containing CTA counterions. The permanent shape of the sample is ITU, the abbreviated name of our university (a). After heating to 70 °C, the gel become soft and could easily be deformed into a temporary shape (b). This temporary shape is fixed by cooling the sample to 25 °C. After immersing the gel sample in a water bath at 70 °C (c → e), it returns back to its initial shape within 10 s. All hydrogel samples exhibit 100% shape-recovery ratios at 70 °C, as determined by the bending tests.^[35]

A simple and versatile strategy to prepare self-healing and shape-memory hydrogels is bulk photopolymerization of hydrophilic and hydrophobic monomers, resulting in hydrogels containing hydrophobic associations and crystalline domains.^[37,38] These hydrogels were prepared by bulk

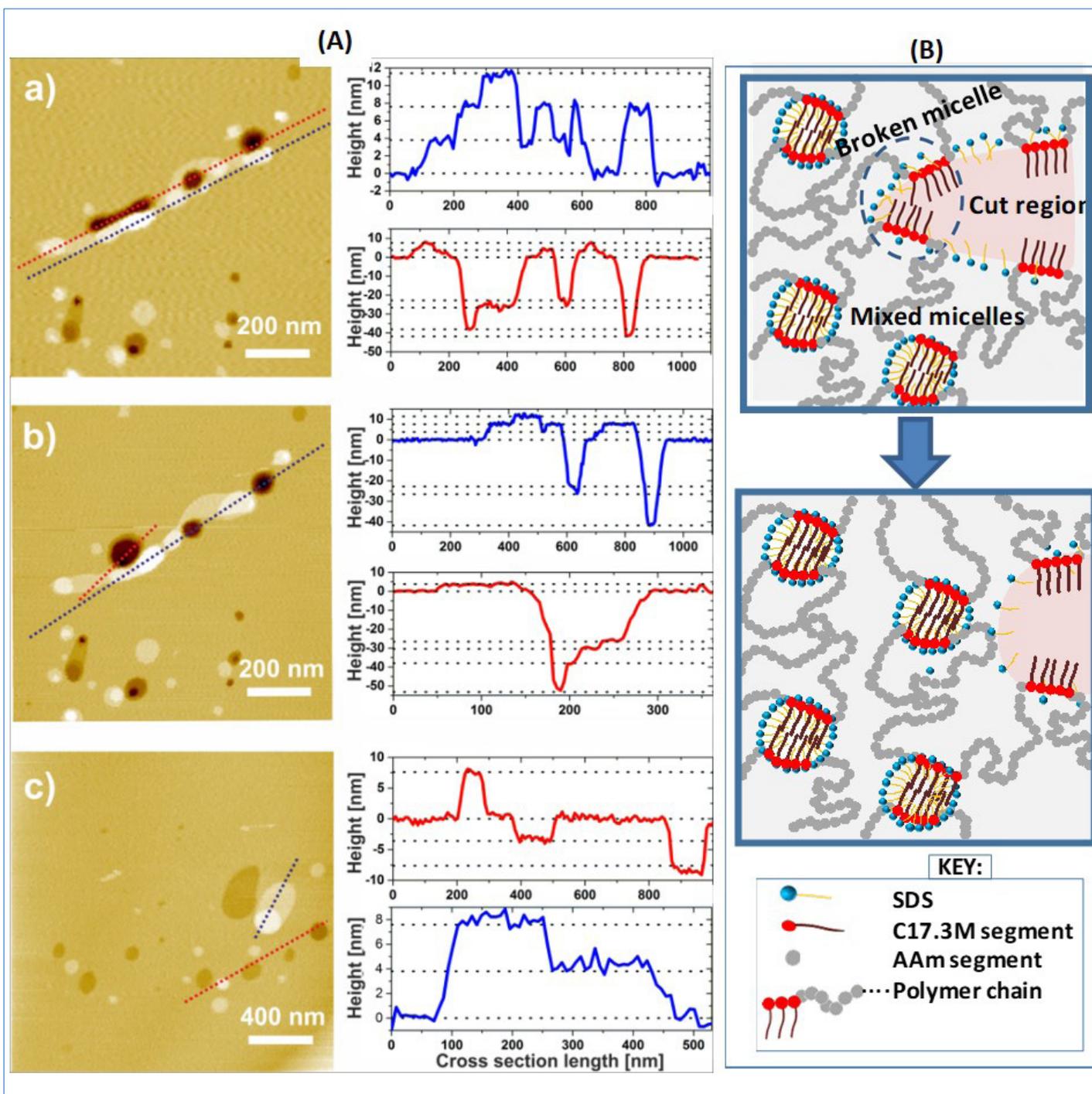


Figure 8. (A): Topography images of gel surface just after cutting the surface (a), after a few tens of seconds (b); and after 75 min (c). The colored dotted lines across the images indicate the cross sections on the right side of the images in the respective colors. The color scale of the images is 50 nm from black to white. (B): Cartoon showing self-healing mechanism of hydrophobically modified hydrogels containing surfactant micelles. From [34] with permission from the American Chemical Society.

copolymerization of the hydrophilic monomers DMAA or AAc with the hydrophobic monomers stearyl methacrylate (C17.3M) and C18A. The melting temperature T_m and the degree of crystallinity of the hydrogels are between 36–56 °C and 3–33%, and they increase with increasing hydrophobic monomer content, or by replacing C17.3M units with C18A ones. The hydrogels exhibit significant reversible changes in storage modulus G' modulus depending on temperature due to the melting and recrystallization of

alkyl crystals providing effective self-healing and shape-memory functions (Figure 10A). Figure 10B presenting the stress-strain curves of virgin (solid curves) and healed hydrogel samples after cutting (dashed curves) reveals a complete healing at 80 °C after a healing time of 24 h.^[37] The hydrogels also exhibit an excellent shape recovery at or above 52 °C, with a shape-recovery ratio R of 100% (Figure 10C). This behavior is attributed to the reversible nature of the hydrophobic associations and the formation

of crystalline domains that allow the hydrogel to switch between its temporary and permanent shapes in response to changes in temperature.

Conclusions

The second-generation hydrogels developed in the past 20 years exhibit extraordinary mechanical properties comparable to load-bearing tissues like tendons, cartilage, and ligaments. They have a wide range of engineering, biomedical, and load-bearing

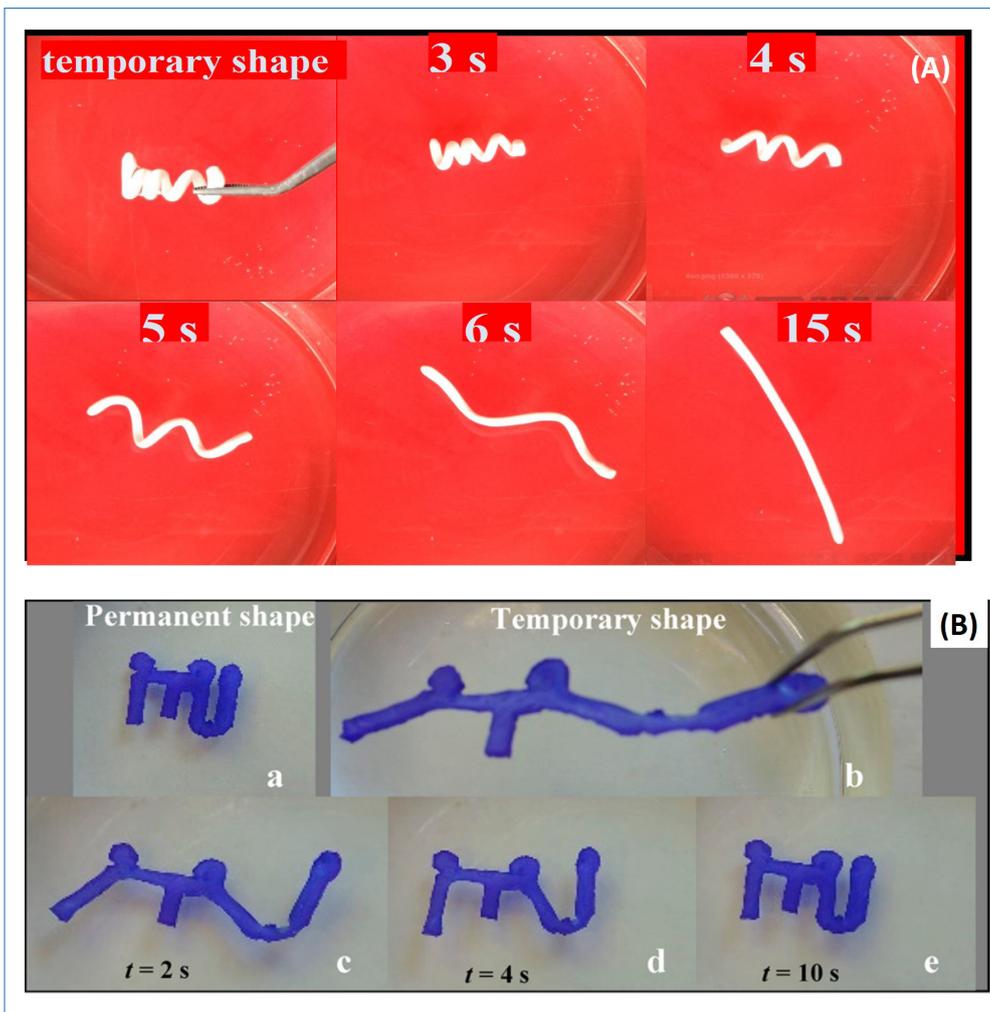


Figure 9(A): Images demonstrating the transition from the temporary spiral shape to the permanent rod shape for a PAAc hydrogel with 50 % C18A. From [36] with permission from the American Chemical Society. (B): Images of permanent (a) and temporary shapes (b) of a hydrogel sample at $v_{WH20} = 12\%$ and the transition from the temporary shape to the permanent shape (b \rightarrow e). The recovery takes 10 s after immersing the gel sample in a water bath at 70°C. $C_0 = 20\%$. $\beta_0 = 1/8$. From [35] with permission from the American Chemical Society.

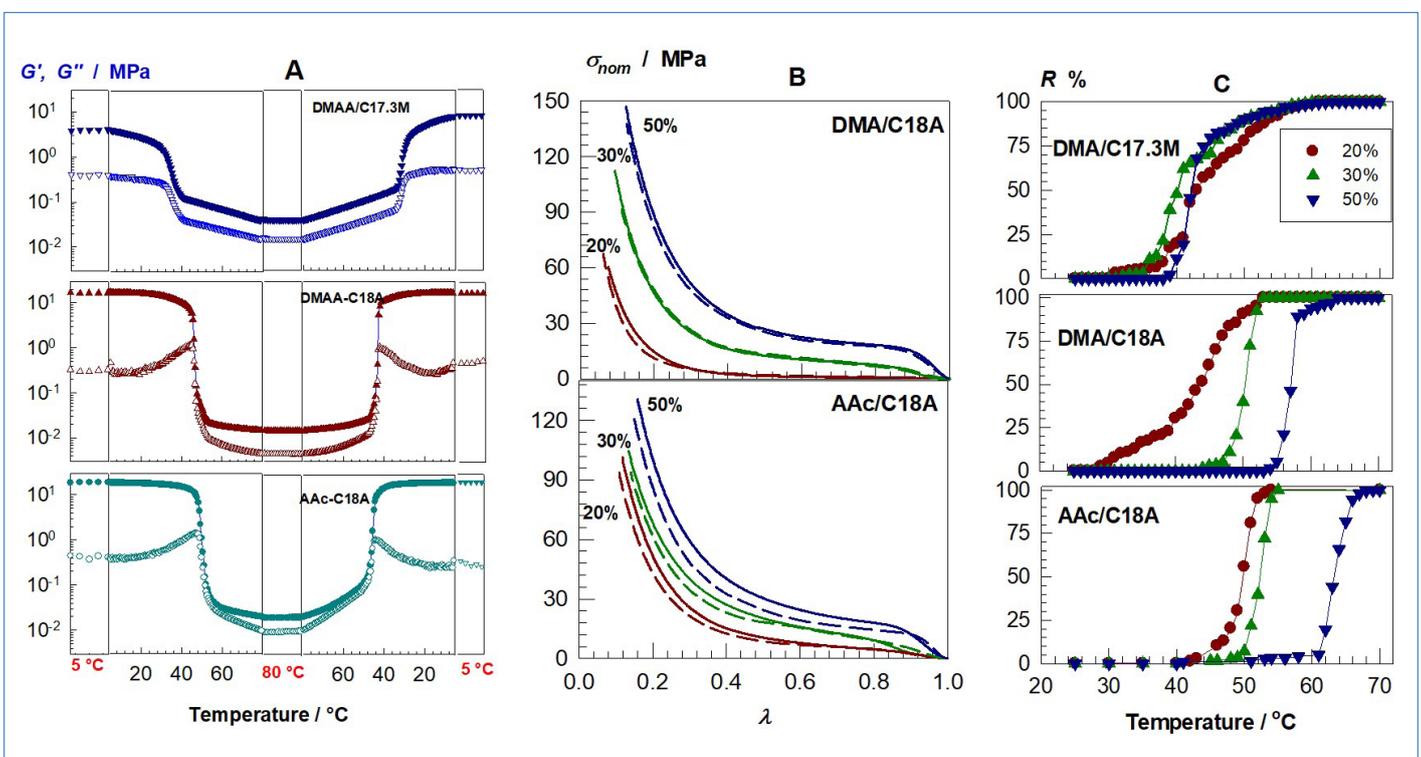


Figure 10. (A): G' (filled symbols), and G'' (open symbols) of DMAA/C17.M, DMAA/C18A, and AAc/C18A hydrogels with 50 mol % hydrophobe during their heating - cooling cycles between 80 and 5 °C. $\omega = 6.28$ rad/s. $\gamma_0 = 0.1\%$. (B; C) Stress-strain curves of virgin and healed hydrogel samples, solid and dashed curves, respectively (B), and the temperature-dependent shape-recovery ratios R (C). Hydrophobe contents are indicated. From [37] with permission from Elsevier.

applications. Another challenge in the gel science is to generate self-healing and shape-memory functions in mechanically strong hydrogels to extend their application areas. The focus on self-healing hydrogels formed via non-covalent interactions, such as H-bonding and hydrophobic interactions, has shown promising results in creating mechanically strong and stable hydrogels with self-healing behavior. Multiple H-bonding interactions between polymer chains have been utilized to produce mechanically strong hydrogels with self-healing ability. Monomers like NAGA,

DAT, and UPy, which can form multiple H-bonds, have been used to achieve this property. Another approach involves the copolymerization of vinyl monomers with H-bond acceptor and donor sites, which also leads to the formation of self-healing hydrogels. Hydrophobically modified hydrogels, prepared through micellar copolymerization of hydrophilic and hydrophobic monomers, have shown increased mechanical strength with higher hydrophobe content and longer side alkyl chains. The physical network structure of these hydrogels, based on hydrophobic associations and

crystalline domains, enables self-healing and shape-memory functions. The combination of self-healing and shape-memory capabilities in hydrogels opens up exciting possibilities for various applications, including in biomedical devices, sensors, actuators, and other fields where flexibility, responsiveness to stimuli, and mechanical strength are desirable features. These recent advancements in self-healing and shape-memory hydrogels pave the way for the development of innovative and functional soft materials with broad potential in diverse industries.

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