



# Hydrogen Bond-Reinforced Double-Network Hydrogels with Ultrahigh Elastic Modulus and Shape Memory Property

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Received 13 February 2018; accepted 11 April 2018; published online 00 Month 2018

DOI: 10.1002/polb.24620

**ABSTRACT:** Development of tough hydrogels has greatly expanded their applications as load-bearing materials. However, the elastic modulus of tough hydrogels is usually lower than 1 MPa. It remains a challenge to design tough hydrogels with high modulus. We report here a series of tough double-network (DN) hydrogels with ultrahigh elastic modulus (up to 200 MPa) by forming robust hydrogen bonds between the first poly(acrylic acid) network and the second poly(*N*-isopropyl acrylamide) network. The dense cooperative hydrogen bonds greatly reduce the segmental mobility and thus improve the rigidity of gel matrix. Owing to the dynamic nature of hydrogen bonds, the modulus of

hydrogels is strongly influenced by temperature and pH, affording the gels shape memory property. The strategy by forming robust noncovalent bonds between interpenetrating networks should be applicable to other systems for designing tough and versatile hydrogels with diverse promising applications. © 2018 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2018**, 00, 000–000

**KEYWORDS:** high modulus; hydrogels; hydrogen bonds; interpenetrating networks; shape memory; tough hydrogels; toughness

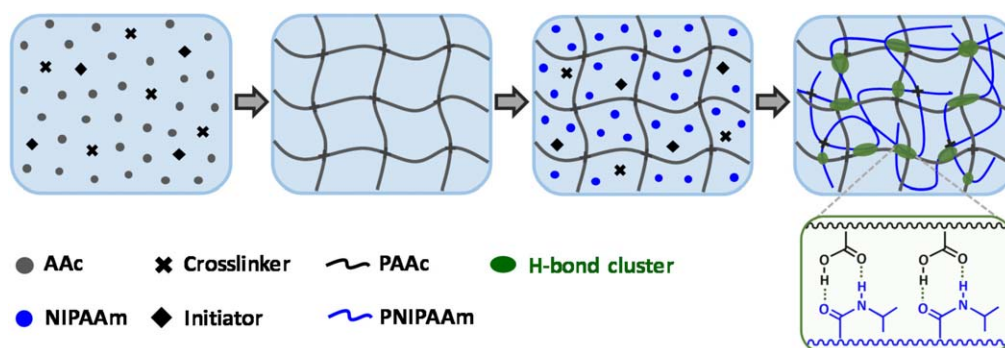
**INTRODUCTION** Designing hydrogels with robust mechanical properties has both scientific significances and practical values due to their promising applications as load-bearing biomaterials, soft actuators, flexible electronics, and so forth.<sup>1</sup> In recent years, various tough hydrogels have been developed by designing the network structure and incorporating an energy-dissipating mechanism.<sup>2–6</sup> Among these achievements, double-network (DN) hydrogels developed by Gong et al. have superior combined mechanical properties in terms of strength, extensibility, and toughness.<sup>4</sup> DN gels were prepared by two-step polymerization to sequentially form a highly crosslinked brittle network and a loosely crosslinked flexible network. Under loading, the first network was “sacrificially” fragmented into small clusters to dissipate large amount of energy, whereas the second network held these clusters together to maintain the integrity of gel. The intensively studied poly(2-acrylamido-2-methylpropanesulfonic acid)/polyacrylamide (PAMPS/PAAm) DN gels showed excellent mechanical performances, with tensile breaking stress  $\sigma_b$  of 1–10 MPa, breaking strain  $\varepsilon_b$  of 1000–2000%, and tearing fracture energy  $G$  of 1–6 kJ/m<sup>2</sup>, which are comparable to tough soft

biotissues such as cartilages and tendons.<sup>4</sup> However, the elastic modulus  $E$  of these DN gels was only 0.1–1 MPa, much lower than that of native cartilages and skins (20–100 MPa).<sup>7</sup> To expand the applications of hydrogels as structural biomaterials, it is really desired to improve the modulus of tough hydrogels. For example, using tough hydrogels with low elastic modulus as artificial cartilages may result in mechanical mismatch and thus undesirable displacement under loading. Although scientists have prepared tough gels with modulus up to tens of MPa, it remains a big challenge to develop tough hydrogels with high elastic modulus over 100 MPa.<sup>8,9</sup>

We report here tough DN hydrogels of poly(acrylic acid)/poly(*N*-isopropyl acrylamide) (PAAc/PNIPAm) with ultrahigh elastic modulus. Owing to the formation of robust hydrogen bonds between the two networks, the DN gels showed remarkable mechanical properties, with  $\sigma_b$ ,  $\varepsilon_b$ , and  $E$  being 2–4.6 MPa, 98–275%, and 11–226 MPa, respectively. Evident yielding was observed in these stiff and tough gels during the tensile loading at room temperature, which was absent

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**FIGURE 1** Schematic for the synthesis of PAAc/PNIPAm DN hydrogels by two-step polymerization. Robust hydrogen bonds formed between the two networks. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

in the parent single network gels. The mechanical properties of DN gels were significantly influenced by the temperature and pH due to the dynamic nature of hydrogen bonds. The stiff DN hydrogels became soft and ductile at high temperature. As a consequence, temperature-mediated shape memory behavior was observed in these tough DN gels. The combination of high modulus, high strength, and shape memory ability makes these hydrogels promising in load-bearing applications in artificial organs, biomedical devices, and so forth.

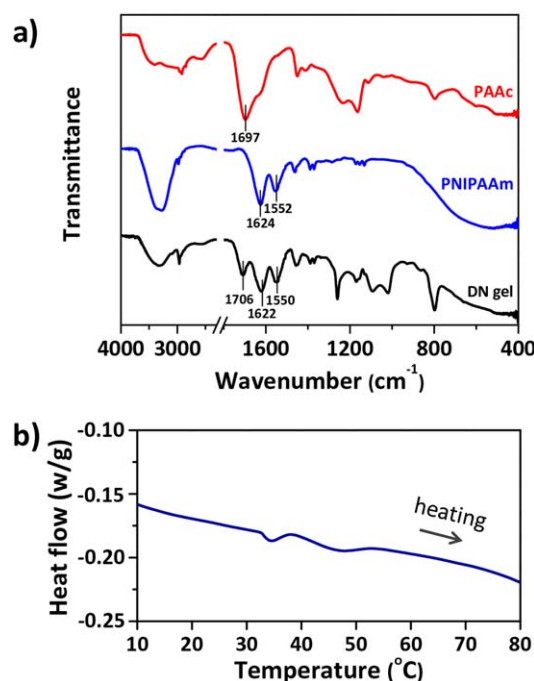
## RESULTS AND DISCUSSION

The hydrogels were prepared by the conventional procedure, as shown in Figure 1.<sup>4</sup> Single network hydrogel of PAAc was synthesized by photopolymerization of an aqueous solution containing AAc, chemical crosslinker, and photoinitiator. The as-prepared PAAc gel was swelled in another precursor solution containing NIPAm, chemical crosslinker, and photoinitiator. The equilibrated hydrogel was sandwiched by two glass substrates and then irradiated under UV light to trigger the second polymerization and form an interpenetrating DN hydrogel. The resultant gel was swelled in a large amount of water to remove the residual and reach the equilibrium state. In this work, the concentration of AAc was 1.5 M, and the concentration of NIPAm was varied from 1 to 2 M. The molar ratio of monomer, crosslinker, and initiator was kept constant (see details in the Experimental section). The samples are coded as DN-1.5- $C_n$ , in which  $C_n$  is the concentration of NIPAm in M. We should note that reverse sequence with PNIPAm as the first network will produce DN gel with poor mechanical properties, because the PNIPAm gel became turbid in concentrated AAc precursor solution that hampered the photopolymerization.

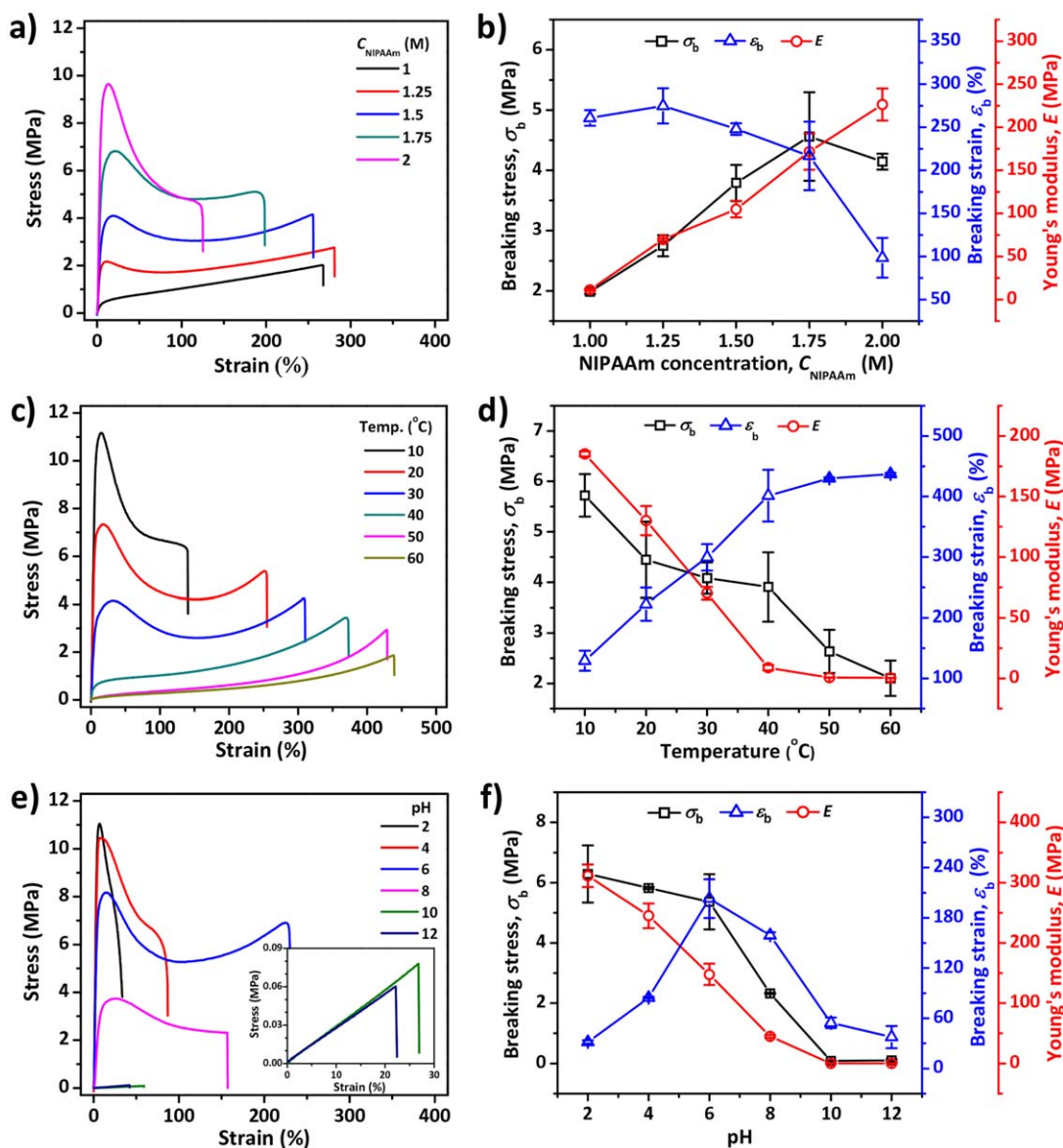
The DN gels with water content of 44–72 wt % (Supporting Information Fig. S1) were turbid at room temperature, indicating the formation of micron-sized aggregates driven by hydrogen bonding between the two networks, as confirmed by Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) measurements. As shown in Figure 2(a), the peak at  $1697\text{ cm}^{-1}$  in the spectrum of PAAc hydrogel was assigned to the stretching vibration of carbonyl group. In the spectrum of PNIPAm hydrogel, the peaks at 1624 and  $1552\text{ cm}^{-1}$  corresponded to amide I (C=O) and amide II

(NH), respectively. In contrast, the peak of carbonyl group of PAAc in DN gel was red shifted to  $1706\text{ cm}^{-1}$ , indicating the hydrogen bonding between the carboxylic group of PAAc and amide group of PNIPAm.<sup>10</sup> In the DSC thermogram of DN gel, endotherm peaks appeared at 32–37 and 42–52 °C, corresponding to the phase transition of PNIPAm segments and the destruction of hydrogen bonds, respectively [Fig. 2(b)].<sup>11</sup> The latter peak was very wide, suggesting a wide distribution of bonding strength, probably due to the existence of cooperative hydrogen-bond clusters with different size.<sup>12</sup>

As shown in Figure 3(a,b), the hydrogen bond-reinforced DN hydrogels possessed excellent mechanical properties, with  $\sigma_b$  of 2–4.6 MPa,  $\epsilon_b$  98–275%, and  $E$  of 11–226 MPa. In general,  $\sigma_b$  and  $E$  increased, whereas  $\epsilon_b$  decreased with the increase in  $C_n$  from 1 to 2 M, due to the formation of more compact hydrogen



**FIGURE 2** (a) FTIR spectra of the PAAc and PNIPAm single network hydrogels, and the PAAc/PNIPAm DN hydrogel. (b) DSC thermogram of the DN hydrogel. Heating rate: 5 °C/min. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



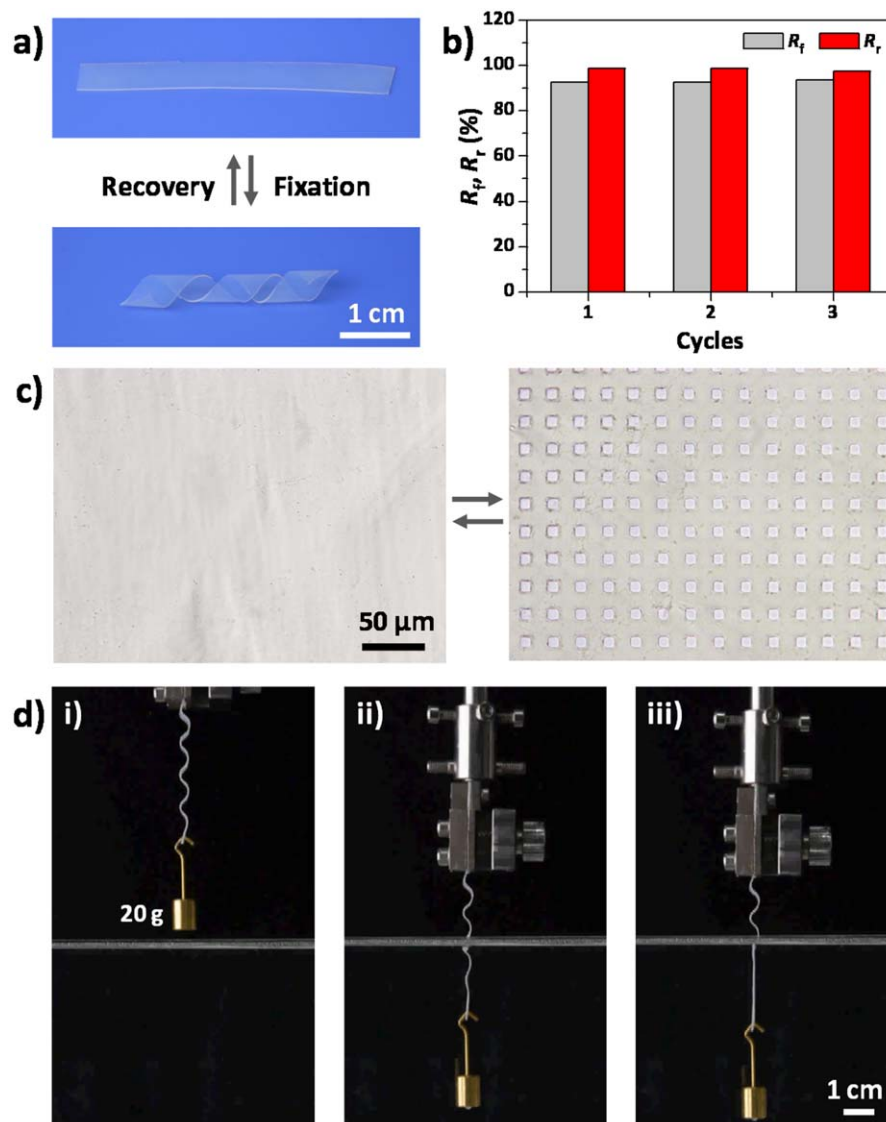
**FIGURE 3** (a, b) Tensile stress–strain curves (a) of the DN hydrogels prepared with different concentration of NIPAAm,  $C_n$ , and corresponding mechanical parameters (b). (c–f) Tensile stress–strain curves (c, e) of the DN hydrogel ( $C_n = 1.75$  M) and corresponding mechanical parameters (d, f) at different temperatures (c, d) and different pH values (e, f). [Color figure can be viewed at wileyonlinelibrary.com]

bonding and thus the increase in crosslinking density. More evident yielding was observed in the gels prepared with higher  $C_n$ . Such typical yielding and dramatic softening were usually observed in glassy polymers. The high-modulus DN gels should also be in a glassy state. The cooperative hydrogen bonds between the interpenetrating networks should greatly reduce the segmental mobility and thus result in high elastic modulus and the typical mechanical behaviors.<sup>12</sup>

Due to the dynamic nature of hydrogen bonds, the mechanical properties of DN gels were significantly influenced by temperature and pH.<sup>13</sup> With the increase in test temperature,  $T$ , from 10 to 60 °C, the gels became soft and stretchable;  $\sigma_b$  and  $E$  decreased from 5.7 and 185 MPa to 2.1 and 0.4 MPa,

respectively, whereas  $\varepsilon_b$  increased from 130% to 440% [Fig. 3(c,d)]. Yielding was absent when  $T$  was above 50 °C and hydrogen bonds were destroyed. We should note that the gel only achieved a temperature equilibrium during the test rather than the swelling equilibrium after incubated the sample in water bath with controlled temperature for 3 min. There was no evident volume change of the gel after being incubated at 60 °C for a short time, yet the diameter of gel increased by 27% after 1.5 h (Supporting Information Fig. S2). The swollen gel at high temperature cannot return to its original state after being cooled to room temperature.

The temperature-dependent elastic modulus of the DN gel [with constant water content, Fig. 3(c)] clearly indicated that



**FIGURE 4** (a, b) Shape memory behavior of the DN-1.5-1.75 gel (a) and shape fixity ratio  $R_f$  and recovery ratio  $R_r$  (b). The gel was reversible deformed in 60 °C water bath and fixed in 20 °C water bath. (c) Shape memory behavior of the DN gel at micron scale by using a stamp to create micron-sized patterns. (d) Snapshots to show the stiff and tough hydrogel with shape memorized wave structure that softened and recovered to flat shape after being swelled in 60 °C water bath. The thickness and width of the DN gel are 1 and 7 mm, respectively. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

the high modulus was mainly originated from the dense cooperative hydrogen bonds between the two networks. The lifetime and strength of hydrogen bonds decreased at elevated temperature, resulting in decrease in the elastic modulus of the gel. Relatively low water led to high density of hydrogen bonds, which might be another prerequisite for the high modulus of hydrogels.<sup>13</sup> The low water of DN gel should be also related to the formation of hydrogen bonds. At room temperature, both PAAc and PNIPAm single network gels were highly swollen due to the hydrophilic gel matrix. In the DN gels the hydrophilic carboxylic and amide groups were involved in the formation of hydrogen bonds, yet the hydrophobic motifs were remained, leading to increase in hydrophobicity of the gel matrix and thus decrease in water

content. Enhancing the interaction between the interpenetrating networks should be an effective strategy to design tough hydrogels with high modulus.<sup>14</sup>

It is well known the ionization degree of the carboxylic group of PAAc network depends on pH,<sup>15</sup> which will affect the strength and stability of the hydrogen bonds between PAAc and PNIPAm networks. The DN gel became more rigid and fragile in acidic condition than in neutral condition [Fig. 3(e)]. As pH decreased from 6 to 2,  $\sigma_b$  and  $E$  of the equilibrated gel increased from 5.3 and 148 MPa to 6.3 and 311 MPa, respectively, whereas  $\varepsilon_b$  decreased from 203% to 32% [Fig. 3(f)]. In contrast, the gel was weakened as pH increased from 6 to 12. Especially at pH = 10 and 12, the gel

was highly swollen (Supporting Information Fig. S3) and mechanically weak, due to the ionization of carboxylic group and the destruction of hydrogen bond.<sup>15</sup>

Based on the aforementioned temperature-mediated variation of mechanical properties, the DN gel showed shape memory behavior.<sup>16</sup> As shown in Figure 4(a), a rigid, slender gel strip was softened and deformed into a helix structure in hot water (60 °C) and fixed after transferring it to cold water (20 °C) for 3 min and then removing the external force. The gel readily recovered to the original flat shape after being placed in hot water. The fixity ratio,  $R_f$ , and recovery ratio,  $R_r$ , of this DN gel were further quantitatively characterized by cyclic shape fixation and recovery.  $R_f$  and  $R_r$  were as high as 93% and 99%, respectively [Fig. 4(b)]. The DN gel also showed shape memory behavior at micron scale because of the high compliance of the gel at high temperature.<sup>17</sup> Well-defined patterns were created on the surface by pressing a stamp against the DN gel in hot water and then fixed in cold water [Fig. 4(c)]. The patterns were erased and the gel recovered to original flat state when placed in hot water again. Due to the ultrahigh elastic modulus, the shape memorized gel stripe can bear 20 g weight at room temperature. However, it became softened readily and recovered to the original shape after being immersed in 60 °C water bath [Fig. 4(d)]. Such shape memory property should expand the applications of these stiff and tough hydrogels such as to construct biomedical devices.

## CONCLUSIONS

In conclusion, we have developed tough PAAc/PNIPAm DN hydrogels with ultrahigh elastic modulus by forming dense cooperative hydrogen bonds between the two networks. The DN gels with water content of 44–72 wt % showed remarkable mechanical performances with  $\sigma_b$  of 2–4.6 MPa,  $\varepsilon_b$  of 98–275%, and  $E$  of 11–226 MPa. In terms of modulus, these DN gels had filled in the gap, to some extent, of mechanical properties between the synthetic tough hydrogels and native soft tissues. The mechanical properties of gels also strongly depended on the temperature and pH due to the dynamic nature of hydrogen bonds. Therefore, these DN gels showed temperature-mediated shape memory property. Such tough hydrogels with high elastic modulus and shape memory ability should be an ideal structural material to design load-bearing artificial organs and biomedical devices.

## EXPERIMENTAL

### Materials

Acrylic acid (AAc) was purchased from Aladdin Industrial Corporation. *N*-Isopropyl acrylamide (NIPAm) was purchased from Tokyo Chemical Industry Development Co., Ltd. *N,N*-Methylenebisacrylamide (MBAA) and 2,2'-azobis(2-methylpropionamide)dihydrochloride (V-50) were used as received from Sigma-Aldrich. Millipore deionized water was used in all the experiments.

## Synthesis of Double Networks Hydrogel

The DN hydrogels were prepared by the conventional procedure, as schemed in Figure 1.<sup>4</sup> The precursor aqueous solution containing 1.5 M AAc, 2 mol % MBAA, and 1 mol % V-50 (relative to the monomer) was injected in a reaction cell consisting of a pair of glass substrates separated with 1 mm silicone spacer, which was irradiated under UV light (365 nm, 5 mW/cm<sup>2</sup>) for 2 min. The resultant PAAc hydrogel was swelled in another precursor solution containing NIPAm, MBAA, and V-50, in which the concentration of NIPAm,  $C_n$ , varied from 1 to 2 M, yet the concentration of MBAA and V-50 were kept constant (2 and 1 mol %, respectively). The equilibrated PAAc hydrogel was sandwiched by two glass substrates and then irradiated under UV light for 2 min to form an interpenetrating DN hydrogel. The resultant DN gel was swelled in a large amount of water to remove the residual and reach the equilibrium state.

## Characterizations

FTIR spectroscopy was performed to the PAAc and PNIPAm single network hydrogels, as well as the PAAc/PNIPAm DN hydrogel, at room temperature by using a Nicolet iS10 FTIR spectrometer (Thermo Scientific, USA). The mass ratio between the first PAAc network and the second PNIPAm network was measured by elemental analysis, and the results were presented in Supporting Information Table S1. The spectra were obtained with 32 scans and a resolution of 2 cm<sup>-1</sup> in the range of 4000–400 cm<sup>-1</sup>. Thermal behaviour of the equilibrated DN hydrogel was measured by using differential scanning calorimeter (DSC, Q100, TA Instrument, USA). The sample with mass of ~10 mg was sealed in an aluminium DSC pan and scanned under a nitrogen atmosphere from 10 to 80 °C with a heating rate of 5 °C/min. The water content of equilibrated hydrogels,  $q$ , was calculated by  $q = (w_s - w_d)/w_s$ , in which  $w_s$  and  $w_d$  are the mass of gels in the swollen and dried states, respectively. Mechanical properties of the DN hydrogels were measured by using a commercial tensile tester (Instron 3343 Tester). The plate hydrogel was cut into dumbbell shape with initial gauge length of 12 mm and width of 2 mm. The tensile stress-strain curves were recorded, and the elastic modulus was calculated from the initial slope of the curve with a strain below 8%. The tensile tests at different temperatures were performed to the samples in a water bath.

## ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (51773179), Scientific Research Foundation for the Returned Overseas Chinese Scholars (J20141135), and Thousand Young Talents Program of China.

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