

Rapid Shape Memory and pH-modulated Spontaneous Actuation of Dopamine Containing Hydrogels*

Jie-xin Liao^a, Jia-he Huang^a, Tao Wang^{a**}, Wei-xiang Sun^a and Zhen Tong^{a, b**}

^a Research Institute of Materials Science, South China University of Technology, Guangzhou 510640, China

^b State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

Abstract The dopamine containing hydrogels with rapid responsive shape memory capability were synthesized by a one-pot method. The temporary shape of hydrogel was fixed within 20 s in NaOH solution by the tris-complex crosslinking of metal-ligand complex between Fe³⁺ ions and catechol groups, while the permanent shape was recovered completely in HCl solution within 60 s upon the change from tris-complex to mono-complex. The hydrogel showed unique spontaneous actuation behavior. It could curl spontaneously without further external force deformation when immersed in NaOH solution again after the first shape recovery in HCl solution. This might be attributed to the competitive result of swelling and additional tris-complex crosslinking formation when immersed in NaOH solution. In addition, the hydrogels also had proper modulus, elongation ratio and tensile strength. Such hydrogel provides a new candidate material for designing soft actuators and robots modulated with spontaneous actuating.

Keywords Shape memory hydrogel; Spontaneous actuation; Dopamine; pH-modulated; Metal-ligand cross-link

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-017-1991-9>.

INTRODUCTION

Shape memory hydrogels are a sort of stimulus-responsive soft materials, which can be fixed at temporary shapes under appropriate conditions and recover to the permanent shape upon corresponding stimulus^[1–4]. The permanent shape of shape memory hydrogels is determined by the invariable crosslinking network, while the temporary shape is fixed by forming a new reversible crosslinked network, and the shape recovery to the permanent shape is realized as the new crosslinking disappears^[5]. The shape memory capability along with the soft matter features makes the shape memory hydrogels an ideal candidate in tissue engineering, soft actuator, and so on^[6–12].

Various reversible crosslinked structures have been developed to build shape memory hydrogels, such as hydrogen bonding, host-guest inclusion, dynamic chemical bonding, metal-ligand complexation^[13–23] *etc.* The hydrogels with metal-ligand complex supramolecular crosslinking have attracted numerous attention due to the facile regulation in crosslinking and hydrogel strength. For example, the shape memory hydrogel based on Ca²⁺

* This work was financially supported by the National Natural Science Foundation of China (Nos. 51573060 and 21427805) and the Pearl River S&T Nova Program of Guangzhou (No. 201710010146).

** Corresponding authors: Tao Wang (王涛), E-mail: fetwang@scut.edu.cn

Zhen Tong (童真), E-mail: mcztong@scut.edu.cn

Invited paper for special issue of “Hydrogel”

Received April 26, 2017; Revised May 30, 2017; Accepted June 6, 2017

doi: 10.1007/s10118-017-1991-9

and alginate^[22], Zn²⁺ and imidazole^[24], and pH regulated Fe³⁺-poly(acrylic acid) showed multiple shape memory behaviors^[18, 25]. In addition, redox induced Fe³⁺-poly(acrylic acid) shape memory hydrogel^[26], chemical and electrochemical manipulated copper-crosslinked hydrogels^[27] have also been reported. However, for most of the hydrogels with metal-ligand complex crosslinking structures, it often takes tens of minutes, even several hours to complete the shape memory process, which limits their application in soft actuators. Usually, the temporary shape of a shape memory hydrogel is formed by external force deformation. For the hydrogels with excellent repeatable shape memory capacity, the temporary shape of each step must be fixed by reversible binding interactions^[13]. This also restricts the design of actuators from shape memory hydrogels with continuous actuation.

As reported, the mussel-inspired dopamine (DOPA) forms strong complex with Fe³⁺ ions. The coordination state between the catechol group of DOPA and Fe³⁺ of mono-, bis-, and tris-complex, is controlled by pH^[28–32] with the mono-complex at pH < 5.6, bis-complex at 5.6 < pH < 9.1, and tris-complex at pH > 9.1. At the same time, the color of hydrogel changes from green to blue and to red for the mono-, bis-, and tris-complex, respectively^[28]. The versatile catechol-Fe³⁺ metal-ligand interaction has been adopted in design of self-healing hydrogels and actuators^[33–37]. Lee *et al.* prepared the hydrogel actuators based on reversible DOPA-metal ion coordination, nevertheless which spent tens of minutes in completing the bending action^[36, 37].

Herein, we report the synthesis of hydrogels containing chemically crosslinked dopamine methacrylamide (DMA) by the copolymerization of DMA and *N,N*-dimethylacrylamide (DMAA). Rapid shape fixing and recovery were realized within 1 min. The present DMA hydrogel showed a novel spontaneous actuation induced by pH change. The modulus of the hydrogels was manipulated reversibly through pH responsive Fe³⁺-catechol complex, which provides a new modulating method for the soft actuators and robots.

EXPERIMENTAL

Materials

Monomer *N,N*-dimethylacrylamide (DMAA, 99%, J&K), dopamine hydrochloride (DOPA, 99%, Strem Chemicals Co., Ltd.), methacrylic anhydride (MAA, 94%, J&K), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure-2959, 98%, Sigma-Aldrich) and *N,N'*-methylenebisacrylamide (BIS, 99%, Alfa Aesar) were used as received. Pure water was produced by deionization and filtration using a Millipore purification apparatus (resistivity 18.2 MΩ·cm) and bubbled with N₂ for 3 h to remove O₂ prior to use. All other chemicals were analytical grade. DMA was synthesized according to the method reported in the literature^[38] and described in supporting information (SI).

Synthesis of Hydrogels

The hydrogels were prepared as follows: DMAA and BIS were dissolved in distilled water. DMA and initiator Irgacure-2959 were dissolved in dimethyl sulfoxide (DMSO) and then added into the above aqueous solution. The volume ratio of H₂O to DMSO was 4:1 at low DMA content (0.2 and 0.5 mol/L) and 3:2 at high DMA content (0.8 mol/L) due to poor water solubility of DMA. The molar ratio of total monomers to initiator was 100:0.297. The solution was subsequently degassed with N₂ for 10 min to remove O₂. After that, the solution was injected into a laboratory-made mold of 100 mm × 100 mm × 1 mm, which consisted of two glass sheets with a rubber spacer. The polymerization was initiated by UV irradiation (365 nm) at room temperature for 3 h. The distance between UV lamp and glass sheets was 40 mm. The DMA hydrogels were referred to as D_xDMA_m, where *x* and *m* represented the molar concentrations of DMAA and DMA in the polymerization solution, respectively. Such contents of DMAA and DMA were 2–6 mol/L and 0.2–0.8 mol/L, respectively, while the BIS concentration was kept at 0.4 mmol/L.

Shape Memory Observation

The shape memory behavior of D_xDMA_m hydrogels was observed in the following way. A hydrogel strip of 30 mm × 3 mm × 1 mm was immersed in 0.01 mol/L FeCl₃ solution for 30 s and then curled into a tight spiral

followed by immersing in a NaOH solution of pH about 11.5 for 20 s to fix the temporary shape. The shape recovery of the hydrogel in temporary shape was carried out in a HCl solution of pH about 1.5. To evaluate the shape-fixing ability quantitatively, we defined the shape-fixing percentage P_f as $P_f = \theta_m/\theta_0 \times 100\%$, where θ_0 was the curled angle and θ_m was the remained angle after fixing in NaOH solution and stabilizing in air at room temperature for 1 min. The curling angle $\theta = 360^\circ$ meant that the sample was curled for one round. The shape recovery was expressed by the recovered angle θ when immersed in HCl solution. For this work, the time required for $\theta = 270^\circ$ was estimated.

The swelling ratio R_s of the hydrogels during immersion in a specified solution was monitored, which was calculated from $(m_i - m_0)/m_0 \times 100\%$, where m_i was the weight after immersion and m_0 was the initial weight of the as-prepared hydrogel sample. Each datum was obtained by the average from three samples.

Characterization

The viscoelastic behaviors of the as-prepared gels and the gels after immersed in different solutions were observed by a stress-controlled rheometer AR-G2 (TA) with a parallel plate fixture of diameter of 25 mm. Silicone oil was laid on the edge of the fixture plates to prevent water evaporation. The frequency sweep was performed over the range of 0.1–100 rad/s at a fixed strain of $\gamma = 0.1\%$ and room temperature.

Tensile test was carried out by a Shimadzu AG-X plus 50 N system at room temperature and the crosshead speed of 50 mm/min on the as-prepared gels and the gels after immersion in specified solutions with 4 mm width $\times$ 30 mm length $\times$ 1 mm thickness. The tensile strain was taken as the length change related to the original length and the tensile stress was evaluated on the cross section of the original sample.

The Fe^{3+} concentration in the DMA hydrogel after different treatments was indirectly measured with a Hitachi Z2000 atomic absorption spectrometer. The D₄DMA_{0.8} gel was treated in 0.01 mol/L FeCl_3 solution for 30 s, followed by immersed in NaOH solution (pH $\sim$ 11.5) for 20 s, and then 0.15 g of the treated hydrogel sample was immersed in 10 mL HCl for a certain time. The Fe^{3+} content in the 10 mL HCl solution was determined to estimate its content in the gel after immersed in the 0.01 mol/L FeCl_3 solution.

RESULTS AND DISCUSSION

Shape Memory and Spontaneous Actuation

The shape memory of the D₄DMA_{0.8} hydrogel is realized in aqueous media of different pH. For easy observation, photos of the sample were taken after each immersing treatment. As shown in Fig. 1, the as-prepared colorless hydrogel becomes jade-green after immersed in 0.01 mol/L FeCl_3 solution (pH $\sim$ 2.2) for 30 s (Figs. 1a and 1b), indicating the formation of mono-complex of Fe^{3+} ions and catechol groups^[28]. Then, the hydrogel turns to reddish after treated in NaOH solution of pH $\sim$ 11.5 for another 20 s to fix the temporary curled shape (Fig. 1c). This color change indicates the formation of tris-complex crosslinking of metal-ligand coordination, and the increased crosslinking fixes the temporary shape. The shape recovery is rapidly completed within 60 s by immersing in HCl solution of pH $\sim$ 1.5 (Figs. 1d–1f). At the same time, the color of the gel gradually changes to yellow green, revealing recovery of the mono-complex from the tris-complex (Fig. 1f). Eventually, the hydrogel recovers to its permanent shape driven by the entropic elasticity of the original chemical crosslinking network. The gel color in Fig. 1(f) is lighter than that in Fig. 1(b), implying loss of some Fe^{3+} during immersion in HCl. By further immersing the recovered gel in the FeCl_3 solution for 30 s (Fig. 1g), the color becomes jade-green again same as in Fig. 1(b). The hydrogel can be fixed to the temporal curled shape in NaOH for 60 s and recovered in HCl for the second time, showing a good repeatability of the metal-ligand crosslinking. But, the repeat time is limited and the shape fixing capability decreases due to swelling of the gel as shown in Fig. S2 (in SI).

The swelling behavior of D₄DMA_{0.8} hydrogel during the shape memory process was investigated. The acid-base dissociation equilibrium constants for the first ($\text{p}K_{a1}$) and second ($\text{p}K_{a2}$) catecholic hydroxyl groups of dopamine are about 9.05 and 11.98, respectively^[39], so that the DMA hydrogel may swell at high pH, and cannot

swell at pH lower than pK_a . Figure 2 depicts the swelling ratio of $D_4DMA_{0.8}$ hydrogel in three solutions successively. Fast swelling in $FeCl_3$ solution was observed during the first 10 s due to the solvent exchange between DMSO and water, followed by slow swelling during 20–30 s. As the sample was transferred into NaOH solution, the swelling became fast again as the result of hydroxyl group dissociation. On the other hand, the swelling in HCl was not distinct. At the same time, the strength of the hydrogel gradually weakened during the immersion due to swelling, leading to limited repeat times of the shape memory process.

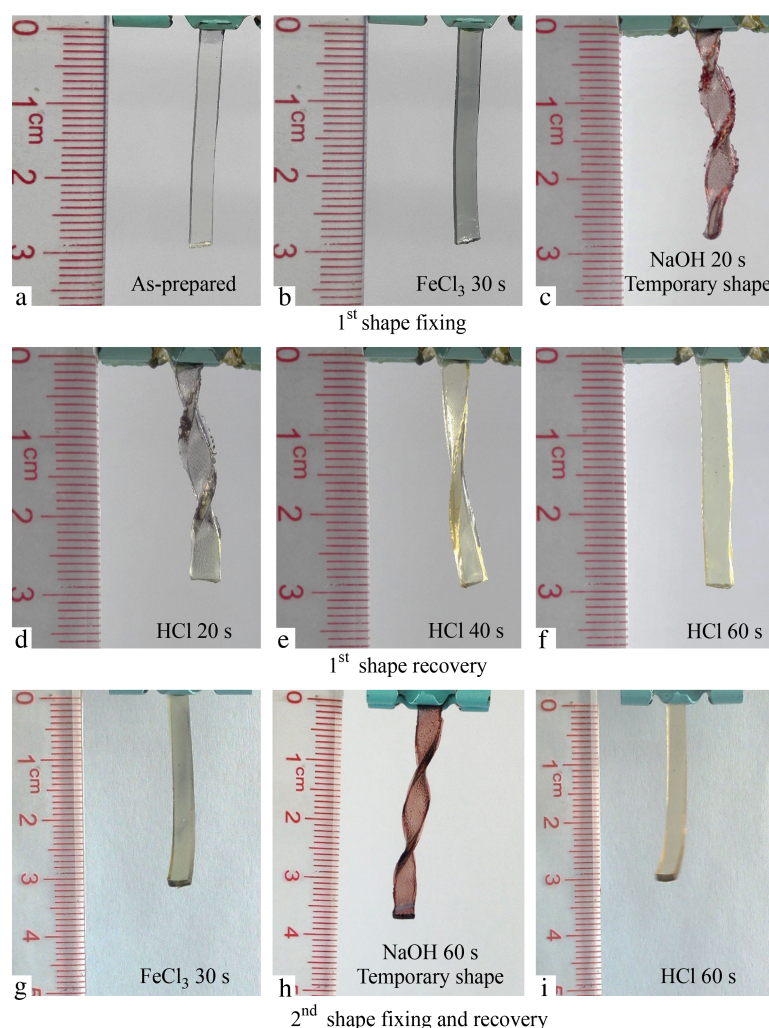


Fig. 1 The states of $D_4DMA_{0.8}$ hydrogel: (a) as-prepared, (b) Fe^{3+} loaded, (c) fixed temporary shape in NaOH for 30 s, (d–f) recovered in HCl for different time; (g–i) the second shape fixing and recovery process (The online version is colorful.)

The shape memory of the hydrogel is based on the strength of permanent network and temporary network, which depends on the hydrogel composition. Thus, the DMA content dependence of the shape fixing and recovery was detected. Figure 3(a) displays the shape fixing percentage P_f as a function of hydrogel composition, which decreases from over 70% to only about 15% when DMAA is increased from 2 mol/L to 6 mol/L. This is owing to the fact that the chemically crosslinked permanent network becomes stronger at higher DMAA content, resulting in the shape fixing harder. On the contrary, P_f increases greatly from about 20% at 0.2 mol/L of DMA to 100% at 0.8 mol/L of DMA, confirming that the temporary crosslinking is formed by the DMA- Fe^{3+} complex.

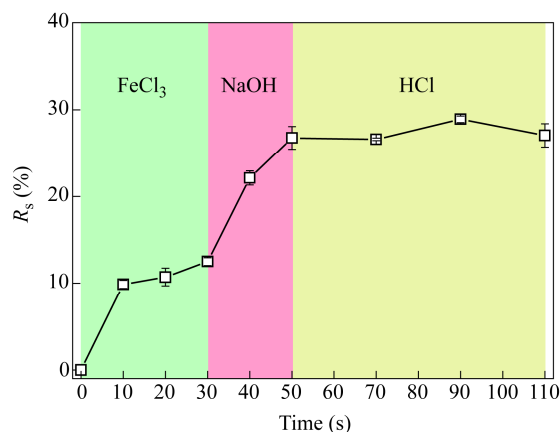


Fig. 2 The swelling ratio R_s of the D₄DMA_{0.8} hydrogel during continuous immersion in 0.01 mol/L FeCl₃ for 30 s, in NaOH solution (pH ~11.5) for 20 s and in HCl solution (pH ~1.5) for 60 s

The shape recovery rate was evaluated by the time required for the DMA hydrogel to restore to 270° in this work, which is presented in Fig. 3(b). The shape recovery of the D₆DMA_{0.5} and D₄DMA_{0.2} hydrogels was not detectable due to their poor shape-fixing capability. The effect of the monomer content on the shape recovery rate is not as obvious as that on the shape fixing shown in Fig. 3(a). The recovery time becomes shorter at higher DMAA content due to the increase in elasticity of the permanent network. On the contrary, it takes slightly longer time at higher DMA content for more tris-complex crosslinking of the permanent network that must be dissociated in HCl. Besides, other metal ions such as Zn²⁺, Cu²⁺, Al³⁺ and Zr⁴⁺, can also be used to accomplish the shape memory capability of the present DMA hydrogels through the metal-ligand complex structure instead of Fe³⁺ as displayed in Fig. S3 (in SI).

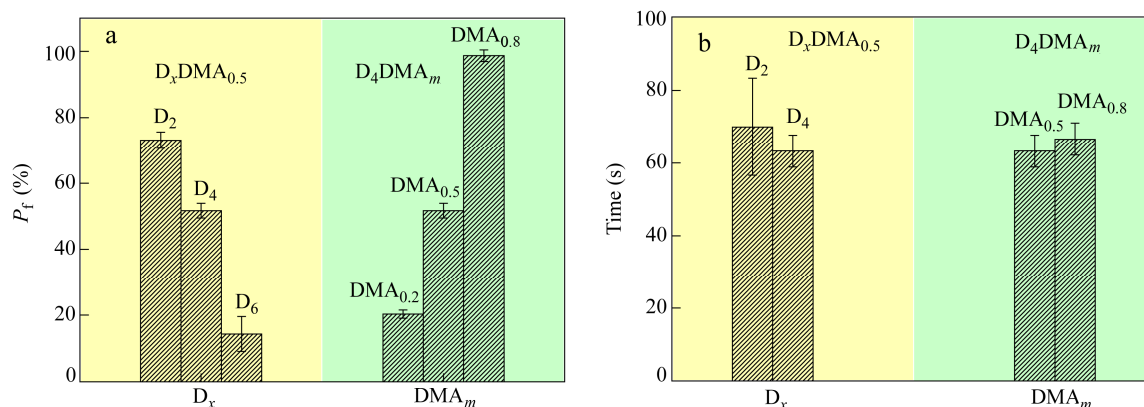


Fig. 3 (a) Shape-fixing percentage P_f of D_xDMA_m hydrogels with different DMAA and DMA contents; (b) Recovering time required for the D_xDMA_m hydrogels with different DMAA and DMA contents to restore to 270°

The most exciting behavior of this DMA hydrogel is the spontaneous actuation induced by pH change as illustrated in Fig. 4. Generally, the temporary shape of a hydrogel is formed by external force deformation and fixed by certain reversible interactions. However, the DMA hydrogel can curl spontaneously when it is immersed in NaOH again after the first shape recovery in HCl. Figure 4(a) shows the recovered state of the DMA hydrogel in HCl with a little residue deformation from the temporary shape. When it is immersed in NaOH again for about 2 min, the hydrogel curls to a spiral shape without any external force (Fig. 4b). The permanent shape of straight strip is recovered when immersed in HCl again for 30 s (Fig. 4c). This spontaneous curling-recovery actuation

can be successively demonstrated four times as displayed in Fig. 4, indicating the excellent repeatability of this straight-spiral transition.

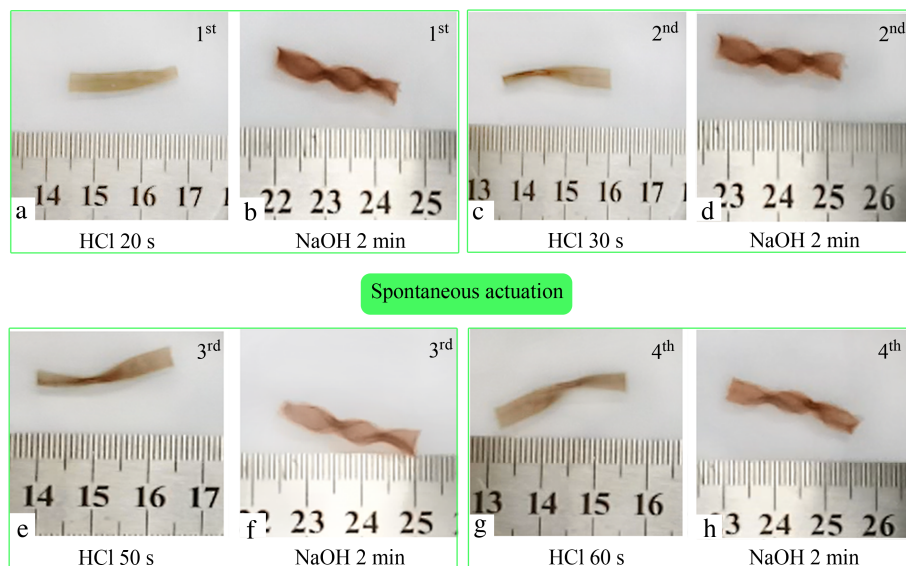


Fig. 4 Four times successful self-actuation of the D₄DMA_{0.8} hydrogel based on spontaneous straight-spiral transition: (a, b) the 1st, (c, d) the 2nd, (e, f) the 3rd and (g, h) the 4th self-actuation (The online version is colorful.)

We speculate that such a spontaneous actuation is due to the synergistic effect of the swelling and metal-ligand crosslinking in NaOH solution. As shown in Fig. 2, the DMA hydrogel swells in NaOH solution, while the color of hydrogel in NaOH becomes red (Fig. 4b), indicating the formation of tris-complex crosslinking of metal-ligand. Therefore, most of mono- and bis-DMA-Fe³⁺ metal-ligand complexes change to the tris-complex in the alkaline medium, and the excessive ferric ions are released within the hydrogel as freely movable counterions, which causes two competitive results of increasing crosslinking density and increasing swelling osmotic pressure. At the same time, the edges of the hydrogel usually swell first due to the solvent diffusion, and extended edges cause the hydrogel curling. This curled shape is fixed by newly formed tris-complex crosslinking. If the curled hydrogel is continuously immersed in NaOH for a longer time (such as 20 min), the temporary curling shape disappears due to the decrease in crosslinking density by larger swelling (Fig. S4, in SI). This unique spontaneous actuation of the DMA hydrogel induced by pH change provides a novel modulating mode for designing new soft actuators.

Crosslinking Structure and Mechanical Properties

Based on the above phenomena, we schematically illustrate the evolution of the crosslinking structure of DMA hydrogel with medium pH in Fig. 5. The P(DMAA-co-DMA) chains of as-prepared hydrogel are chemically crosslinked with BIS (Fig. 5a). Mono-complex of Fe³⁺ ions and catechol groups is formed during Fe³⁺ loading process in FeCl₃ solution (Fig. 5b), and tris-complex is formed after being treated in NaOH (Fig. 5c), which recovers to the mono-complex with the loss of some Fe³⁺ upon immersing in HCl (Fig. 5d). The formation of metal-ligand complex can be repeated with the supplement of Fe³⁺ (Fig. 5d to Fig. 5b). The evolution of hydrogel crosslinking structure has been verified through ferric ion content in the hydrogel and the crosslinking density.

Figure 6 presents the ferric ions released in HCl solution from the DMA hydrogel after treating with FeCl₃ and NaOH solutions, which reflects the change in ferric ion content in the hydrogel during the recovery process.

This means that when the DMA hydrogel is immersed in HCl solution, the hydroxyl groups become neutral, and the excessive ferric counterions will diffuse out of the hydrogel to maintain the electric neutrality of the hydrogel. As a result, the metal-ligand tris-complex changes to the mono-complex in the DMA hydrogel, and the curled shape recovers the permanent strip shape due to the decrease of the metal-ligand crosslinking.

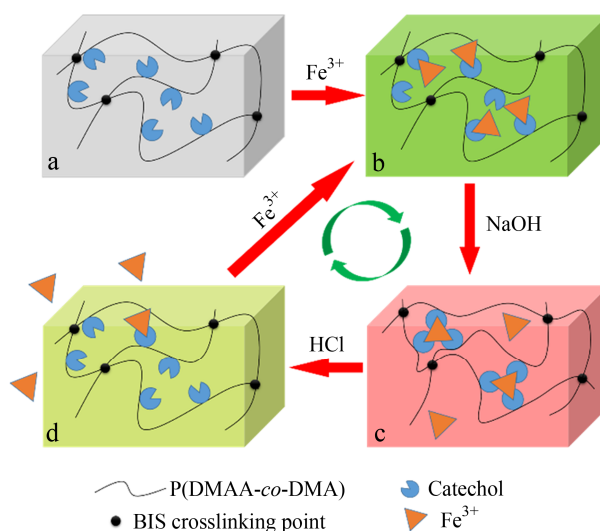


Fig. 5 The reversible DMA-Fe³⁺ complex crosslinking structure evolution of DMA hydrogels in the solutions with different pHs: (a) as-prepared hydrogel, (b) Fe³⁺-loaded hydrogel, (c) NaOH-treated hydrogel, (d) HCl-treated hydrogel

The storage modulus G' of the D₄DMA_{0.8} hydrogel after specified treatments is plotted in Fig. 7. G' plateau relates to the crosslinking density, and is almost unchanged after immersing in the Fe³⁺ solution. Fe³⁺ ions and catechol groups mainly form the mono-complex, which contributes little to the crosslinking density^[33]. G' increases evidently after the treatment in NaOH solution, indicating an increase in crosslinking density by forming the tris-complex between Fe³⁺ ions and catechol groups. G' decreases quickly when the hydrogel is immersed in HCl solution, representing the dissociation of the tris-complex.

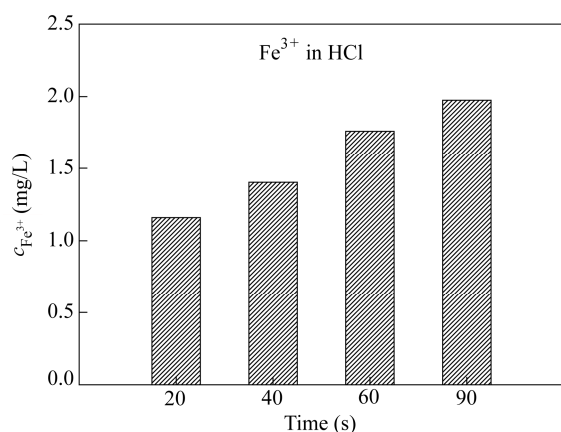


Fig. 6 Fe³⁺ concentration ($c_{\text{Fe}^{3+}}$) in HCl solution released from the D₄DMA_{0.8} hydrogel after FeCl₃ and NaOH treatments as a function of immersion time

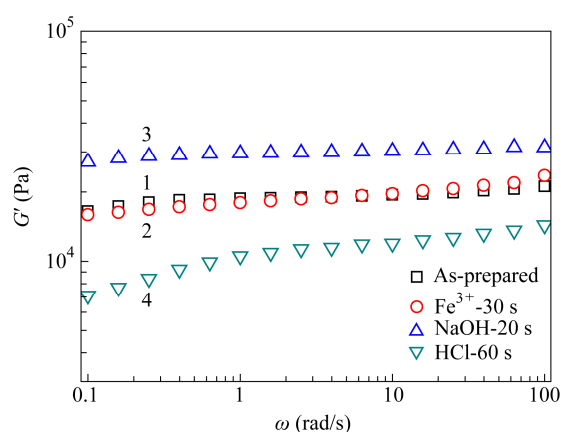


Fig. 7 The relationship between storage modulus G' of the D₄DMA_{0.8} hydrogel and the angular frequency ω . The sequence of treatments is FeCl₃ solution, NaOH solution and HCl solution, and the hydrogel is designated by the last treatment.

The above-mentioned pH-modulated crosslinking structure of the DMA hydrogel is also manifested in the mechanical properties. Figure 8 summarizes the tensile stress-strain curves of the DMA hydrogel after specified treatments. The strength and breaking strain of the as-prepared $D_4DMA_{0.8}$ hydrogel are about 95 kPa and 70%, respectively. The strength shows a little change while the breaking strain increases to about 300% after immersing in $FeCl_3$ solution caused by swelling during the immersion (Fig. 2). After the treatment in NaOH solution, the breaking strain decreases to about 80%, but the slope of the curve increases, indicating the increase of crosslinking density due to the formation of tris-complex. When immersed in HCl for 60 s, the strength quickly drops to 40 kPa with the breaking strain reaching over 450%, indicating the decrease of the crosslinking density owing to the disappearance of tris-complex.

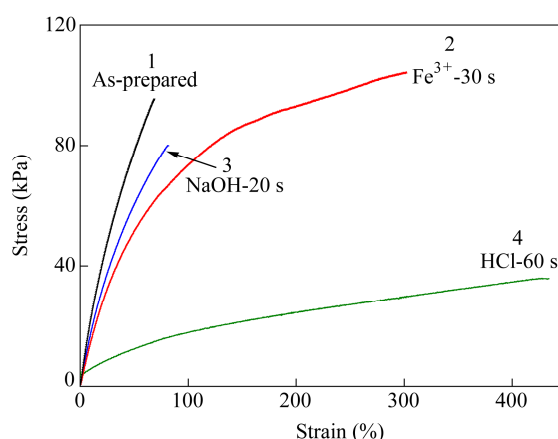


Fig. 8 Tensile stress-strain curves of the $D_4DMA_{0.8}$ hydrogel after specified immersing treatments. The sequence of treatments is $FeCl_3$ solution, NaOH solution and HCl solution, and the hydrogel is designated by the last treatment.

Figure 9 shows the tensile stress-strain curves of the DMA hydrogels with different compositions. With increase of DMAA content, the breaking strain decreases with increasing strength due to the increase of polymer concentration in the hydrogel, resulting in a stronger network. The strength (~ 100 kPa) and strain at break ($\sim 100\%$) have almost no change with the variation in DMA content from 0.2 mol/L to 0.8 mol/L, for the variation of DMA content is too narrow.

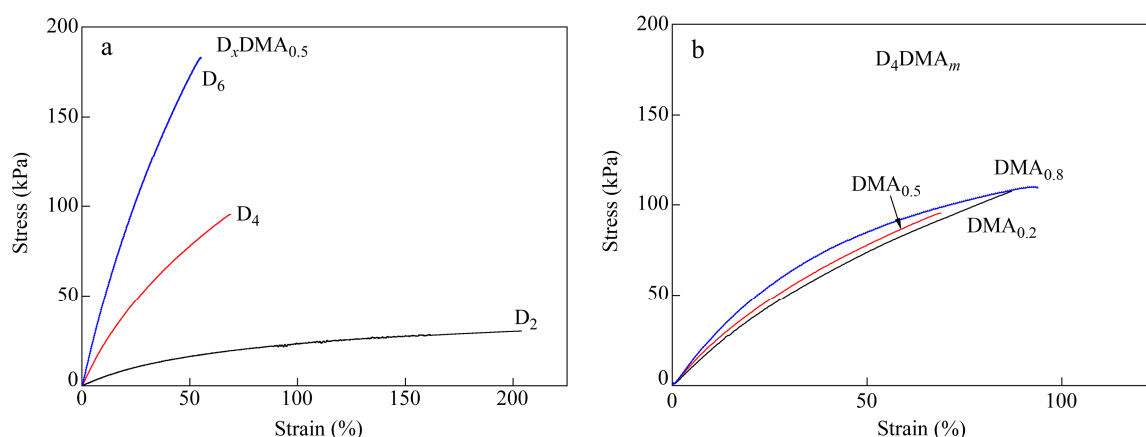


Fig. 9 Tensile stress-strain curves of the D_xDMA_m hydrogels with indicated (a) DMAA and (b) DMA contents

CONCLUSIONS

The dopamine containing hydrogels with rapid responsive shape memory capability were synthesized. The temporary shape was fixed in NaOH solution through the formation of tris-complex metal-ligand crosslinking between ferric ions and catechol groups, and the permanent shape was completely recovered within 60 s when immersed in HCl solution due to the change from tris-complex to mono-complex. The DMA hydrogel showed interesting spontaneous actuation phenomenon. The hydrogel could curl spontaneously without further external force deformation in NaOH solution after the first shape recovery in HCl solution. This might be attributed to the synergistic effect of swelling and additional tris-complex crosslinking formation when immersed in NaOH solution. This finding provides a new hydrogel for designing soft actuators and robots modulated with spontaneous actuation.

REFERENCES

- 1 Zhao, Q., Qi, H.J. and Xie, T., *Prog. Polym. Sci.*, 2015, 49-50(1): 79
- 2 Hager, M.D., Bode, S., Weber, C. and Schubert, U.S., *Prog. Polym. Sci.*, 2015, 49-50(1): 3
- 3 Osada, Y. and Matsuda, A., *Nature*, 1995, 376(6537): 219
- 4 Lu, W., Le, X., Zhang, J., Huang, Y. and Chen, T., *Chem. Soc. Rev.*, 2017, 46(5): 1284
- 5 Behl, M., Razzaq, M.Y. and Lendlein, A., *Adv. Mater.*, 2010, 22(31): 3388
- 6 Chaterji, S., Kwon, I.K. and Park, K., *Prog. Polym. Sci.*, 2007, 32(8-9): 1083
- 7 Ren, Z., Zhang, Y., Li, Y., Xu, B. and Liu, W., *J. Mater. Chem. B*, 2015, 3(30): 6347
- 8 Lu, X., Chan, C.Y., Lee, K.I., Ng, P.F., Fei, B., Xin, J.H. and Fu, J., *J. Mater. Chem. B*, 2014, 2(43): 7631
- 9 Nan, W., Wang, W., Gao, H. and Liu, W., *Soft Matter*, 2013, 9(1): 132
- 10 Han, Y., Bai, T. and Liu, W., *Sci. Rep.*, 2014, 4(1): 5815
- 11 Annabi, N., Tamayol, A., Uquillas, J.A., Akbari, M., Bertassoni, L.E., Cha, C., Camci-Unal, G., Dokmeci, M.R., Peppas, N.A. and Khademhosseini, A., *Adv. Mater.*, 2014, 26(1): 85
- 12 Ionov, L., *Mater. Today*, 2014, 17(10): 494
- 13 Huang, J., Zhao, L., Wang, T., Sun, W. and Tong, Z., *ACS Appl. Mater. Interfaces*, 2016, 8(19): 12384
- 14 Qi, X., Yao, X., Deng, S., Zhou, T. and Fu, Q., *J. Mater. Chem. A*, 2014, 2(7): 2240
- 15 Yasin, A., Zhou, W., Yang, H., Li, H., Chen, Y. and Zhang, X., *Macromol. Rapid Commun.*, 2015, 36(9): 845
- 16 Meng, H., Zheng, J., Wen, X., Cai, Z., Zhang, J. and Chen, T., *Macromol. Rapid Commun.*, 2015, 36(6): 533
- 17 Miyamae, K., Nakahata, M., Takashima, Y. and Harada, A., *Angew. Chem. Int. Ed.*, 2015, 54(31): 8984
- 18 Le, X., Lu, W., Xiao, H., Wang, L., Ma, C., Zhang, J., Huang, Y. and Chen, T., *ACS Appl. Mater. Interfaces*, 2017, 9(10): 9038
- 19 Wei, M., Zhan, M., Yu, D., Xie, H., He, M., Yang, K. and Wang, Y., *ACS Appl. Mater. Interfaces*, 2015, 7(4): 2585
- 20 Chen, Y., Peng, L., Liu, T., Wang, Y., Shi, S. and Wang, H., *ACS Appl. Mater. Interfaces*, 2016, 8(40): 27199
- 21 Li, Z., Lu, W., Ngai, T., Le, X., Zheng, J., Zhao, N., Huang, Y., Wen, X., Zhang, J. and Chen, T., *Polym. Chem.*, 2016, 7(34): 5343
- 22 Le, X., Lu, W., Zheng, J., Tong, D., Zhao, N., Ma, C., Xiao, H., Zhang, J., Huang, Y. and Chen, T., *Chem. Sci.*, 2016, 7(11): 6715
- 23 Xiao, H., Lu, W., Le, X., Ma, C., Li, Z., Zheng, J., Zhang, J., Huang, Y. and Chen, T., *Chem. Commun.*, 2016, 52(90): 13292
- 24 Xu, B., Li, Y., Gao, F., Zhai, X., Sun, M., Lu, W., Cao, Z. and Liu, W., *ACS Appl. Mater. Interfaces*, 2015, 7(30): 16865
- 25 Zhao, L., Huang, J., Wang, T., Sun, W. and Tong, Z., *Macromol. Mater. Eng.*, 2017, 302(2): 1600359
- 26 Geng, Y., Lin, X.Y., Pan, P., Shan, G., Bao, Y., Song, Y., Wu, Z.L. and Zheng, Q., *Polymer*, 2016, 100: 60

- 27 Harris, R.D., Auletta, J.T., Motlagh, S.A.M., Lawless, M.J., Perri, N.M., Saxena, S., Weiland, L.M., Waldeck, D.H., Clark, W.W. and Meyer, T.Y., *ACS Macro Lett.*, 2013, 2(12): 1095
- 28 Yang, J., Cohen Stuart, M.A. and Kamperman, M., *Chem. Soc. Rev.*, 2014, 43(24): 8271
- 29 Taylor, S.W. and Waite, J.H., *Inorg. Chem.*, 1994, 33(25): 5819
- 30 Liu, Y., Ai, K. and Lu, L., *Chem. Rev.*, 2014, 114(9): 5057
- 31 Sedó, J., Saiz-Poseu, J., Busqué, F. and Ruiz-Molina, D., *Adv. Mater.*, 2013, 25(5): 653
- 32 Dong, M., Liu, S., Tan, L., Cen, L. and Fu, G., *Chinese J. Polym. Sci.*, 2016, 34(5): 637
- 33 Krogsgaard, M., Behrens, M.A., Pedersen, J.S. and Birkedal, H., *Biomacromolecules*, 2013, 14(2): 297
- 34 Hou, S. and Ma, P.X., *Chem. Mater.*, 2015, 27(22): 7627
- 35 Holten-Andersen, N., Harrington, M.J., Birkedal, H., Lee, B.P., Messersmith, P.B., Lee, K.Y.C. and Waite, J.H., *P. Natl. Acad. Sci. USA*, 2011, 108(7): 2651
- 36 Lee, B.P. and Konst, S., *Adv. Mater.*, 2014, 26(21): 3415
- 37 Lee, B.P., Narkar, A. and Wilharm, R., *Sens. Actuators B*, 2016, 227(1): 248
- 38 Glass, P., Chung, H., Washburn, N.R. and Sitti, M., *Langmuir*, 2009, 25(12): 6607
- 39 Malisova, B., Tosatti, S., Textor, M., Gademann, K. and Zürcher, S., *Langmuir*, 2010, 26(6): 4018