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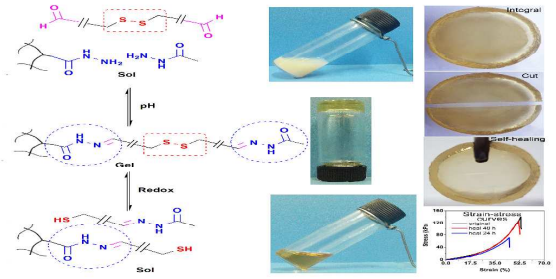

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ARTICLE TYPE

Redox- and pH-responsive polymer gels with reversible sol-gel transitions and self-healing properties

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Covalent dynamic gels based on reversible acylhydrazone and disulfide bonds were prepared by crosslinking of benzhydrazide-containing poly(triazole) (PTB) with a novel disulfide-containing dialdehyde (C2) in DMF at ambient temperature. The PTB was synthesized by the metal- and solvent-free click polymerization of diazide and dialkyne monomers followed by treatment with hydrazine hydrate. The as-fabricated polymer gels exhibited both redox and pH stimuli-responsive behaviours. Analysis of the composition-property relationships of these polymer gels, specifically considering the effects of catalysts, molar ratio of benzhydrazide to aldehyde groups (–NH_2/–CHO), and gelator concentrations on rheological properties, were performed. Additionally, the gel revealed interesting self-healing property through acylhydrazone exchange and/or disulfide exchange reactions. Employing this dynamic character, it is possible to regenerate the used gel, and thus has the potential to perform in a range of dynamic or bioresponsive applications.

1. Introduction

Stimuli-responsive polymer gels have recently been the focus of fundamental and applied researches because they have potential applications in controlled drug delivery devices,[1] sensors,[2] actuators,[3] and biomaterials.[4] Essentially, stimuli-responsive gels can dynamically and reversibly undergo a sol-gel transition in response to changes in their environments, therefore altering their structures and properties. Up to now, two effective strategies, including supramolecular chemistry (noncovalent interactions)[5-7] and dynamic covalent chemistry (dynamic covalent bonds)[8-10] have been developed to fabricate such polymeric networks. Although supramolecular chemistry is a simple way to fabricate stimuli-responsive polymer gels, it is less robust and the resultant gels are usually labile and do not have sufficient mechanical strength, thus may not be suitable for all applications. In contrast, dynamic covalent chemistry relates to chemical reactions carried out reversibly under conditions of equilibrium control.[11,12] These bonds become reversible and reach an equilibrium state once they are exposed to appropriate external stimuli such as pH,[13] light,[14] redox,[15] temperature,[16] biomolecules,[17] and the addition of catalysts.[18] Polymer gels crosslinked with dynamic covalent bonds would provide an energetically favorable, specific, and controlled mechanism for engineering functional dynamic networks. The most significant advantage of such polymer gels is that they are not only flexible in altering their compositions, as in the case of supramolecular polymers with noncovalent interactions, but also stable enough to maintain their structure in the absence of external stimuli, as in the case of conventional covalent polymers.[19] Therefore, dynamic covalent chemistry offers a robust platform to construct stimuli-responsive polymer gels, which integrates the stability of the chemical gels and stimuli-responsibility of the physical gels into a single system.[20]

So far various dynamic covalent chemistries, such as exchange over C=N double bond,[21] disulfide exchange,[22] radical exchange reaction,[23] trans-esterification,[24] Diels–Alder cycloaddition,[25] boronate ester bond,[26,27] and olefin metathesis,[28] have been used to prepare stimuli-responsive polymer gels. Among these, C=N bond in acylhydrazone groups formed by the condensation of hydrazides with carbonyl group exhibit reversibility under mild conditions.[29] Generally, the pH value of the solution significantly affects the reactivity of the C=N bond, which become relatively stable in alkaline solution, while higher acidity will destroy this bond. With such characteristics, the C=N bond can be used as a good stimulus-responsive linker in polymer gels. For example, Deng and his coworkers[20] employed a triple aldehyde derivate to crosslink bisacylhydrazine modified poly(ethylene oxide) in organic solvents, yielding dynamic polymer gels with reversible sol-gel phase transitions and self-healing properties based on the reversible breaking and regenerating of acylhydrazone bonds. However, simply mixing the polymer and crosslinker was useless, only after adding glacial acetic acid, adjusting the apparent pH to 6–7, did gelation finally occur. In a similar way, chitosan based hydrogel was successfully constructed by crosslinking of chitosan with benzaldehyde modified poly(ethylene oxide).[30] The as-formed gel shows its response to changes of the pH value, and gelation still exists after six cycles. The self-healing performance of the hydrogel was also outstanding.

Comparable with the acylhydrazone bond, disulfide exchange[31] is perhaps another promising reaction for dynamic covalent chemistry, which is multi-responsive to pH,[13] light,[32] and redox[33] conditions. Mechanistic studies indicate that thiols can readily oxidize to disulfide bond upon exposure to air. On the other hand, disulfide bond can be cleaved under mild conditions in the presence of reductants such as dithiothreitol (DTT), tris(2-carboxyethyl)phosphine (TCEP), and glutathione (GSH).[34] As a matter of fact, disulfide bond has been successfully used to prepare responsive polymer gels from small molecular gelators[34] or macromolecular gelators.[35] Very recently, multi-responsive polymer gels were fabricated using disulfide bond in conjunction

with acylhydrazone bond, since they have been demonstrated to be compatible with each other and independently operational upon pH changes in a single system. However, so far as we know there is only one report describing the construction of dual-responsive polymer gels based on disulfide and acylhydrazone bonds, in which benzlaldehyde-terminated 3-armed poly(ethylene oxide) was crosslinked with dithiodipropionic acid dihydrazide.[36] As can be seen, only a small percentage of known polymers so far have been used to construct such multi-stimuli responsive polymer gels, thereby placing a restriction on the range of chemophysical properties and potential applications.

In this paper, we report a novel dual-responsive polymer gels based on acylhydrazone and disulfide bonds, in which the benzhydrazide-containing poly(triazole) (PTB) was crosslinked with a novel disulfide-containing dialdehyde in DMF at ambient temperature. The PTB was synthesized by the metal- and solvent-free click polymerization of diazide and dialkyne monomers followed by treatment with hydrazine hydrate.[37] The as-fabricated gels exhibited both redox and pH stimuli-responsive behaviors due to the incorporation of the two dynamic bonds into the same polymer networks (Scheme 1). Additionally, reversible crosslinks allow these networks to restructure dynamically and self-healing after mechanical disruption. Being responsive to multiple stimuli, these polymer gels are expected to be highly advantageous over traditional polymer gels and possess many unique properties that play a significant role in organ repairs, drug-delivery systems, and molecular devices.[38]

2. Experimental

2.1 Materials

Well-defined poly(triazole)s (PTAs) were prepared by the metal- and solvent-free, thermal click polymerization of methyl 3,5-dipropargyloxylbenzoate and methyl 3,5-bis(4-azidobutoxy) benzoate monomers followed by multistep precipitation in different precipitating agents as reported previously by our group[37] (see Supporting Information, SI). The obtained PTAs were further subjected to postfunctionalization and were treated with hydrazine hydrate, yielding benzhydrazide-containing PTAs (PTB) (see SI). The crosslinker, 4,4-[4,4'-dithiobis(1-butoxyl)] diphenylformaldehyde (C2), was prepared according to the literature procedure[39] as shown in Scheme S1. All other reagents were purchased from commercial supplier, which were used as received without further purification.

2.2 Typical procedure for the preparation of gels

By condensation of benzaldehyde groups at the two ends of C2 with benzhydrazide moieties in PTB, a network with acylhydrazone bond as crosslinks is generated. A desired amount of PTB and C2 was dissolved separately in DMF, the appropriate amount of catalyst was added. Gels were formed simply by pipetting the prepared solutions directly into a vial at room temperature. Variable polymer gels prepared by adjusting catalysts (types and contents), molar ratio of benzhydrazide to benzaldehyde moieties (–NH_2/–CHO), and gelator concentrations, were summarized in Table S1.

2.3 Rheological measurements

Dynamic moduli measurements were carried out with a stress-controlled Advance Rheological Expansion System (ARES) equipped with a parallel plate fixture of a diameter of 25 mm diameter at 25 °C. The preliminary dynamic strain sweep was carried out first at angular frequency of 1 rad/s to determine the linear viscoelastic region and then the frequency sweep was performed over the frequency range of 0.01 to 100 rad/s at strain of 1%. And 48 h were taken from mixing the gelator solutions to testing start. Both elastic modulus (G′) and loss modulus (G″) of these polymer gels prepared with different catalysts and contents, –NH_2/–CHO, and gelator concentrations were monitored as a function of frequency to characterize the viscoelastic properties.

2.4 Compression tests

The polymer gel was synthesized in a cylinder that was 10 mm in diameter and 10 mm in height. The compression test was carried out using a mechanical testing apparatus (Instron 5943, Instron Corp.) under uniaxial compression using parallel plate geometry. Test parameters were as follows: load cell 1 kN, crosshead velocity was 1 mm/min. Before loading on to the Instron, the samples were equilibrated at ambient temperature for 48 h. Mechanical compression data were averaged over three samples.

2.5 Self-healing experiments

Polymer gel plates were prepared in a mold with a bottom of 25 mm in diameter. After aged in the mold at room temperature for about 48 h, each of the gel plates was cut by a blade into two halves. Then the two pieces were spliced in the original mold, and the mold was placed in a container at ambient temperature without any other intervention. After 48 h, the gel plate(s) was taken out of the mold and was drawn perpendicularly to the cut lines by tweezers, with picture taken.

3. Results and discussion

3.1 Synthesis of gelators

In order to synthesize polymers containing benzhydrazide groups, benzoate-containing PTAs were produced initially. In this paper, we recount significant milestone in achieving metal-free thermal click polymerization to synthesize polymers. Firstly, a series of well-defined PTAs were prepared by the metal- and solvent-free, thermal click polymerization of methyl 3,5-dipropargyloxyl benzoate and methyl 3,5-bis(4-azidobutoxy)benzoate monomers followed by multistep precipitation in different precipitating agents (Fig. S1) as reported previously by our group.[37] PTA with molecular weight of 32430 g/mol (PDI = 1.22, Fig. S2) was then subjected to postfunctionalization and was treated with hydrazine hydrate under reflux, in which the benzoate groups were easily converted to benzhydrazide moieties,[40] yielding benzhydrazide-containing poly(triazole) (PTB). The functionalization of polymer was confirmed using ^{1}H NMR spectroscopy. As depicted in Fig. S3, a new peak at about δ 9.72 ppm, due to amide protons in the benzhydrazide moiety,[41] was observed, while the peak at δ 3.79 ppm due to methyl protons in the benzoate moiety completely disappeared, confirming that the functionalization reaction was carried out essentially to quantitative conversion.

Next, the crosslinker C2 was synthesized according to the synthetic routes as shown in Scheme S1. Firstly, the 4-hydroxybenzaldehyde reacted with excess 1,4-dibromobutane to introduce bromide groups. Secondly, the halogen group was transformed into thiol group by treatment with freshly prepared sodium hydrosulfide. Crosslinker C2 was finally synthesized by the oxidation of thiol group in air. The crosslinker was well characterized by IR, MS, and NMR spectroscopy (Fig. S4-S9).

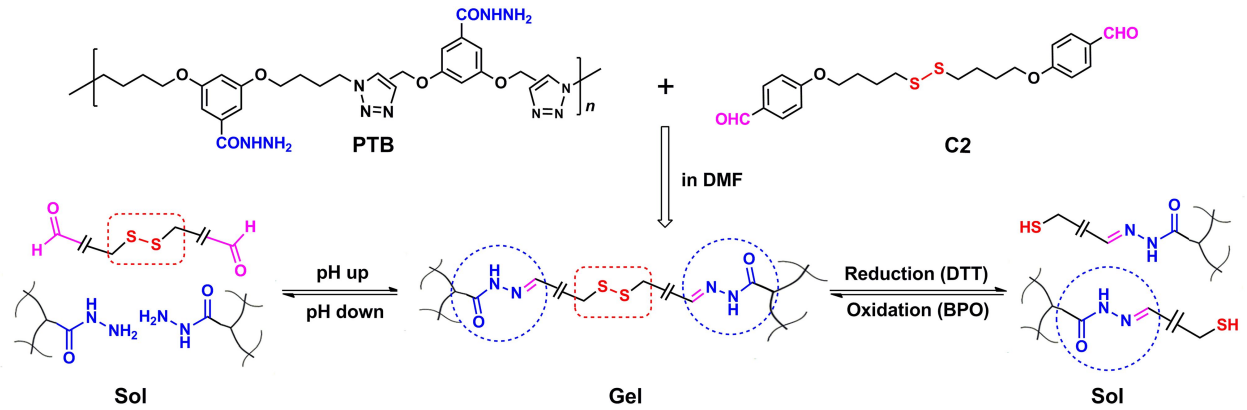
3.2 Preparation of stimuli-responsive polymer gels

As mentioned previously, the primary motivation of this study is to prepare redox- and pH-responsive PTA gels with reversible sol-gel transitions together with self-healing properties. Previous studies have demonstrated that the triazole repeat units of PTAs are structurally similar to the amide bond of native peptide in terms of distance and planarity,[42] and their biocompatibility may allow PTA based gels to find a wide variety of applications in regulate cell culture,[43] bioconjugates,[4] biocontainers,[44] and biocarriers.[45] Considering that acylhydrazone bond formation can be accelerated under mild acidic conditions or by catalytic aniline in neutral conditions, gelation conditions of PTB (M_n = 30560 g/mol, PDI = 1.26, Fig. S2, sic passim) plus C2 in DMF were initially explored with different catalysts, *i.e.*, glacial acetic acid (HOAc) and aniline ($PhNH_2$). Desired amounts of C2/catalyst mixture as well as PTB were separately dissolved in DMF with different catalysts or catalyst contents. As can be seen in Table S1, gel comprising of 15 wt% gelators was formed immediately in the presence of 20 wt% HOAc. However, the gelation time, the interval of time required for the mixed solutions to become a gel, was proved to be dependent on the catalyst contents and related with the used catalysts (Table S1). Decrease the contents of HOAc resulted in the prolongation of gelation time. On the other hand, the gelation time was prolonged to 9 h when the catalyst was changed from HOAc (10 wt%) to $PhNH_2$ (10 wt%) and further prolonged to 17 h without catalyst.

In addition, the gelation time was also proved to be correlated with the $–NH_2$/–CHO molar ratios and gelator concentrations (Table S1). When the gelator concentration and HOAc content were fixed at 15 wt% and 10 wt%, respectively, gels formed quickly within 15 min at room temperature with the $–NH_2$/–CHO ratios ranged from 12.5/1 to 5/1. Similarly, gel formed within 20 min when the gelator concentration was varied from 8 to 20 wt%. However, no gel formed in 10 days when gelator concentration was lower than 5 wt%. These results indicate that the reactivity of benzhydrazide and benzlaldehyde can be tuned by catalyst types as well as catalyst and gelator concentrations.

FTIR analysis provided evidence for the formation of covalent bond between benzhydrazide and benzlaldehyde groups in the gel. Fig. 1 shows the FTIR spectra of C2, PTB, and the dried gel. The characteristic carbonyl infrared absorbances for benzlaldehyde and benzhydrazide groups are observed at 1693 and 1662 cm^{-1}, respectively. For polymer gel, the carbonyl of acylhydrazone group slightly shifts to 1667 cm^{-1}, indicating that benzhydrazide group has reacted with benzlaldehyde group.[29] This result further proves that the gel is a chemical gel. Moreover, the absorbance of benzhydrazide groups (*i.e.*, 1662 cm^{-1}) remains relatively strong in the gel by comparing the FTIR spectra of PTB (spectrum b) and the polymer gel (spectrum c), indicating that certain amount of free benzhydrazide groups are preserved in the gel, which favor further reactions in self-healing.

Scheme 1. Strategy for constructing a dynamic polymer gel with dual responsive sol-gel transitions based on acylhydrazone and disulfide chemistry.



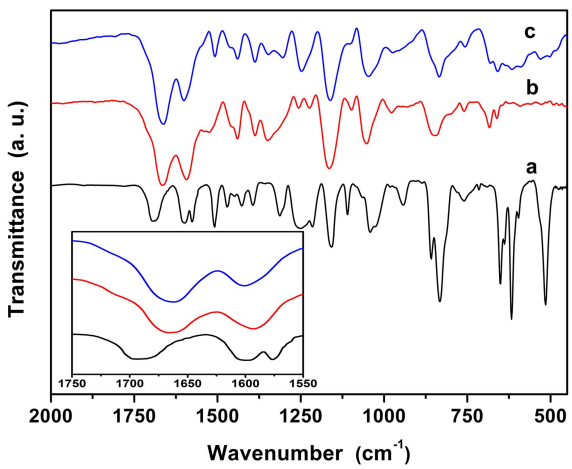


Fig. 1 FTIR spectra of (a) C2, (b) PTB, and (c) polymer gel.

3.3 Rheological characterization and stress-strain behaviors

In an attempt to gain a clearer understanding of the viscoelastic properties of the PTA based gel samples, dynamic rheological

measurements were therefore performed. The effect of catalysts was initially studied. Fig. 2 shows the dynamic frequency sweeps of polymer gels prepared with either 10 wt% of HOAc, 10 wt% of $PhNH_2$, or without catalyst, while the gelator concentration and the $–NH_2$/–CHO molar ratio are kept constant, *i.e.*, 15 wt% and 10/1, respectively. For the three gel samples, G′ exceeded G″ over the entire measured frequency and G′ was independent of angular frequency (Fig. 2a), implying their predominantly solid-like behavior.[46,47] These are the characteristics for a strong polymer gel with covalent crosslinked networks. However, gel prepared with 10 wt% HOAc possessed the largest G′, while gel without catalyst possessed the minimum G′, indicating that HOAc can accelerate the reaction between benzlaldehyde and benzhydrazide, therefore increasing the crosslinking density.

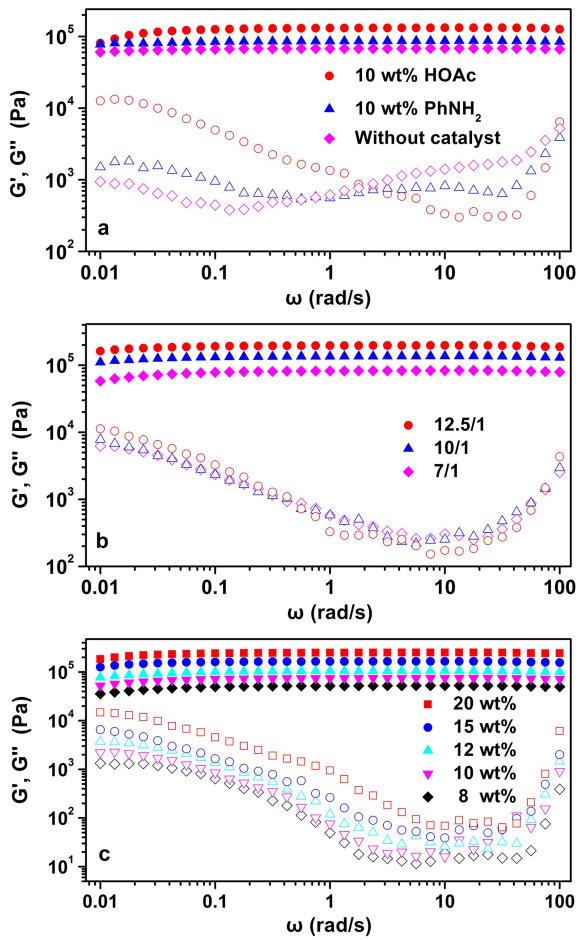


Fig. 2 G' (solid symbol) and G" (open symbol) against frequency (ω) for polymer gels with (a) different catalysts ($–NH_2$/–CHO = 10/1, gelator concn. = 15 wt%); (b) different $–NH_2$/–CHO molar ratios (gelator concn. = 15 wt%, HOAc concn. = 10 wt%); and (c) different gelator concn. ($–NH_2$/–CHO = 10/1, HOAc concn. = 10 wt%).

The viscoelastic properties of the PTA polymer gels can also be affected by the molar ratio of $–NH_2$/–CHO (Fig. 2b). Similarly, G′ is higher than G″ over the entire frequency range for all polymer gels, further indicating that the elastic response of these gels is stronger than the viscous one. Although a stiffer and stronger gel network can be obtained at the $–NH_2$/–CHO molar ratio of 12.5/1, higher G′ is observed with increasing the aldehyde contents due to the increase of crosslinking density in polymer networks. The viscoelastic properties of the polymer gels were further studied by varying gelator concentrations (Fig. 2c). As expected, G′ increased with increasing the gelator concentration due to an increase in crosslink density. Again, G′ was found to exceed G″ over the entire measured frequency and G′ was independent of angular frequency. Similar results were found for polymer gels prepared with different HOAc contents as well as with different PTB molecular weights (Fig. S10-S11).

The effects of gelator concentration on the compressive stress-strain characteristics of the polymer gels are shown in Fig. 3. The corrected true stress and strain were calculated as FH/A_0H_0 and $-\ln(H/H_0)$, where H was the varying sample height, H_0 its original height, A_0 its original cross-section area, and F the applied load.[48,49] Clearly, the compressive stress of the polymer gels increases with the increase of gelator concentrations at the same strain level. This effect is more distinct with the rise of strain ratio. This result is not surprising in view of the increased modulus of polymer gels with increasing gelator concentrations as discussed previously. The compression moduli (E) estimated from the linear region (6–18%) of the stress–strain curves are tabulated in Table S3. As can be seen, the E values increase with increasing of gelator concentrations, which mirrors the trend observed for the dynamic rheology data in Fig. 2c (the G′ values estimated from Fig. 2c are also shown in Table S3). However, exact agreement between the modulus values obtained from dynamic rheology and static compression testing experiments cannot be expected because of the effect of the Poisson ratio and differences in measurement conditions (especially compression speeds) that applied.[50,51]

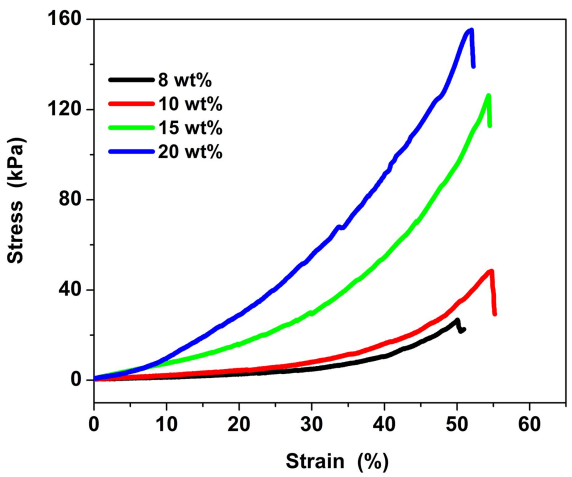


Fig. 3 Stress-strain curves for polymer gels with different gelator concentrations ($–NH_2$/–CHO = 10/1, HOAc concn. = 10 wt%).

3.4 Sol-gel transitions and self-healing properties

Due to the incorporation of acylhydrazone and disulfide dynamic bonds into the same polymer networks, the polymer gels should display reversible sol-gel transitions in response to both pH and redox conditions (Scheme 1). In order to prove the reversible sol-gel phase transition ability of the gel in response to pH change, polymer gel prepared in 0.5 mL of DMF ($–NH_2$/–CHO = 10/1,

gelator concn. = 10 wt%, without catalyst) was aged for 48 h at ambient temperature. After 60 μL of CF_3COOH (TFA) was added on the gel surface, the gel was degelated into a sol in 12 h. And 20 μL of Et_3N (TEA) was needed to transform the sol into gel in 12 days (Fig. 4a). The reversible sol-gel transitions was triggered by reversible breaking and regenerating of acylhydrazone bonds upon pH changes.[52] In the current case, however, it took so long to return to the gel state, indicating that the regeneration of acylhydrazone bonds was very slow due to the poor solubility of polymer in TFA as well as the undissolved salts formed from TFA and TEA. For the same reason, the sol as well as the reformed gel became turbid and the transition process could be run only once.

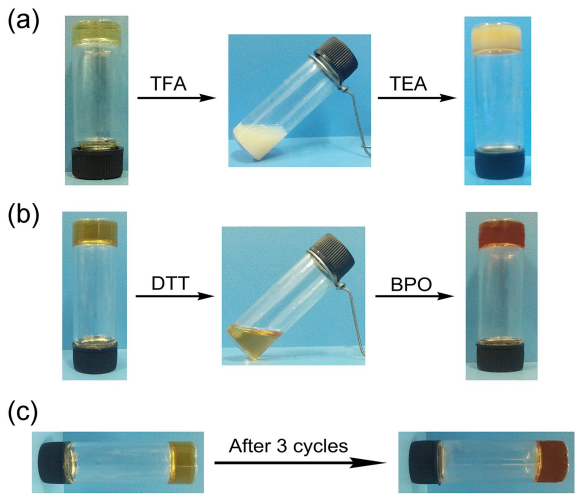


Fig. 4 Sol-gel phase transition of the polymer gels in response to pH (a) and redox (b) triggers, and (c) appearance of the original gel (left) and the gel after three redox cycles (right).

To further prove the redox responsive sol-gel phase transitions of the polymer gels, three gel samples were separately prepared in 0.5 mL of DMF containing either 10 wt% of HOAc, 10 wt% of $PhNH_2$, or without catalyst (Table S1, run 1, 3, and 6) and aged for 48 h. As expected, three transition cycles were repeated with using dithiothreitol (DTT) and benzoyl peroxide (BPO) as the reductant and oxidant, respectively (Fig. 4b, Table S2). For each transition cycle, DTT (30 mg) and BPO (50 mg) were added in sequence. In addition, Et_3N was firstly added to the polymer gels to guarantee alkaline condition for the reduction of disulfide bond, because the disulfide-thiol redox reaction is switched-off under slightly acidic conditions.[53] For the polymer gel prepared with HOAc catalyst, about 50 μL of Et_3N was added and part of it was used to neutralize the HOAc in polymer gel system. During the repeated transition cycles, the polymer gels turn into deep red in color due to the fact that the PTB solution in DMF gradually became brown in air (Fig. 4c, Fig. S12).

In general, dynamic covalent systems have enhanced stability while maintaining the potential for dynamics and self-healing as compared to supramolecular assembly that rely on intermolecular forces. The adaptive self-healing[54-56] properties of these polymer gels, based on the dynamic chemistry of both acylhydrazone and disulfide bonds, were further studied and the results are presented in Fig. 5. Again, three gel samples were separately prepared in 1.5 mL of DMF containing either 10 wt% of HOAc, 10 wt% of $PhNH_2$, or without catalyst (Table S1, run 1, 3, and 6) and aged for 48 h. As shown in Fig. 5, when two pieces of cracked gel plates were put together along the cut line and kept contact f at 40 °C or 48 h in the absence of external intervention, they can merge autonomously into a whole piece of gel. The joint between the two parts in the merged gel was strong enough to be lifted by the tweezers (Fig. 5, 1c-3c). The mechanism of self-healing process should be related with the disulfide–disulfide exchange as well as acylhydrazone–acylhydrazone exchange reactions.[57,58] When the cut surfaces contact each other and within this state, the polymer segments can diffuse and cross the interface of two plates and reactions such as disulfide exchange and acylhydrazone exchange can occur, therefore regenerating acylhydrazone and/or disulfide bonds between the cut edges and eventually healing the gel. Obviously, the chain segments in the network need mobility to allow for the interchange reactions to take place.

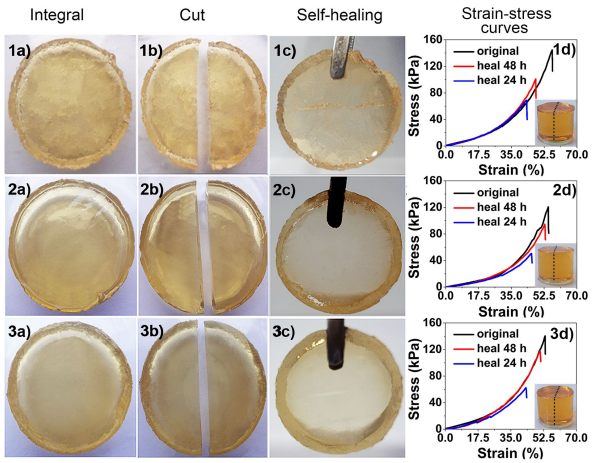


Fig. 5. (a-c) Self-healing properties of polymer gels. (d) Stress-strain curves of the three self-healable polymer gels. 1, 2, and 3 represent polymer gels prepared without catalyst, 10% HOAc, and 10% $PhNH_2$, respectively, $–NH_2/–CHO$ = 10/1, gelator concn. = 15 wt%. Inset of d shows samples for stress-train measurements, black dotted line represents the location of the incision.

In order to prove this self-healing process was repeated and effective, the merged gel was subjected to compressive stress-strain measurements and healing efficiency is defined as the ratio of the stress at break of healed and virgin gels.[59] For the polymer gel prepared without catalyst, the healing efficiency is around 70.6% after 48 h of self-healing (Fig. 5, 1d), due to the fact that both acylhydrazone and disulfide bonds reconstruct slowly in organic solvent under neutral conditions. In addition, the healing efficiency for 48 h is higher than that for 24 h, suggesting that longer self-healing time leads to better healing. Under acidic condition, the acylhydrazone exchange reaction is responsible for self-healing process because disulfide bonds are kinetically locked.[55] In the case of HOAc catalyzed polymer gel, the healing efficiency is around 80.6% after 48 h of self-healing (Fig. 5, 3d). For the $PhNH_2$ catalyzed gel, a maximum healing efficiency of 85% is observed after 48 h of healing since both acylhydrazone exchange and disulfide exchange reactions are responsible for this self-healing process. In the present study, repetitive healing experiments were also conducted. After being cut again along the old cut lines, the healing efficiencies after the second and third

healing process are fully restored.

4. Conclusions

In summary, we have prepared covalent dynamic poly(triazole) gels containing both acylhydrazone and disulfide bonds by crosslinking of benzohydrazide-containing poly(triazole) with disulfide-containing dialdehyde in DMF at ambient temperature. The gelation time is proved to be dependent on the catalyst types and contents and related with the molar ratio of benzohydrazide to aldehyde moieties as well as the gelator concentrations. In addition, the orthogonal dynamic chemistry of the two bonds makes the as-synthesized polymer gels self-healable under a wide range of conditions and the self-healing process is repetitive and effective without an external stimulus. Moreover, the polymer gels also display reversible sol-gel transitions in response to both pH and redox conditions. Being responsive to multiple stimuli, these polymer gels are expected to be highly advantageous over traditional polymer gels and possess many unique properties that play a significant role in organ repairs, drug-delivery systems, and molecular devices.

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Notes and references

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† Supporting Information (SI) available: Synthesis and characterization of PTAs, PTB, and crosslinker C2; The effect of different catalysts, catalyst contents, $-NH_2$/–CHO molar ratio, and gelator concentrations on the gelation time in DMF; The redox responsive sol-gel transitions of polymer gels; G' and G" against frequency for polymer gels with different HOAc contents as well as gels prepared from PTB with different molecular weights. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here.

1. N. Bhattarai, J. Gunn and M. Q. Zhang, *Adv. Drug Deliver. Rev.* 2010, **62**, 83-99.
2. O. Bunkoed, F. Davis, P. Kanatharana, P. Thavarungkul and S. P. Higson, *Anal. Chim. Acta*, 2010, **659**, 251-257.
3. N. Terasawa, N. Ono, Y. Hayakawa, K. Mukai, T. Koga, N. Higashi and K. Asaka, *Sens. Actuators, B*, 2011, **160**, 161-167.
4. E. Ye, P. L. Chee, A. Prasad, X. T. Fang, C. Owh, V. J. J. Yeo and X. J. Loh, *Mater. Today*, 2014, **17**, 194-202.
5. J.-M. Lehn, *Chem. Soc. Rev.*, 2007, **36**, 151-160.
6. J.-M. Lehn, *Prog. Polym. Sci.*, 2005, **30**, 814-831.
7. U. P. Singh, S. Kashyap, H. J. Singh, B. K. Mishra, P. Roy and A. Chakraborty, *J. Mol. Struct.*, 2012, **1014**, 47-56.
8. S. Otto, R. L. Furlan and J. K. Sanders, *Drug Discov. Today*, 2002, **7**, 117-125.
9. S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders and J. F. Stoddart, *Angew. Chem. Int. Ed.*, 2002, **41**, 898-952.
10. T. Yang, R. Ji, X. X. Deng, F. S. Du and Z. C. Li, *Soft matter*, 2014, **10**, 2671-2678.
11. H. Otsuka, K. Aotani, Y. Higaki and A. Takahara, *J. Am. Chem. Soc.*, 2003, **125**, 4064-4065.
12. W. Zhang and J. S. Moore, *J. Am. Chem. Soc.*, 2004, **126**, 12796-12796.
13. I. Asmarandei, G. Fundueanu, M. Cristea, V. Harabagiu and M. Constantin, *J. Polym. Res.*, 2013, **20**, 1-13.
14. Y. Guan, H. B. Zhao, L. X. Yu, S. C. Chen and Y. Z. Wang, *RSC Adv.*, 2014, **4**, 4955-4959.
15. Z. Y. Qiao, R. Zhang, F. S. Du, D. H. Liang and Z. C. Li, *J. Control. Release*, 2011, **152**, 57-66.
16. P. P. Li, L. Huang, Y. J. Lin, L. Shen, Q. Chen and W. Z. Shi, *Nanotechnology*, 2014, **25**, 055603.
17. T. Miyata, T. Uragami and K. Nakamae, *Adv. Drug Deliver. Rev.*, 2002, **54**, 79-98.
18. Z. S. Ge, D. Xie, D. Y. Chen, X. Z. Jiang, Y. F. Zhang, H. W. Liu and S. Y. Liu, *Macromolecules*, 2007, **40**, 3538-3546.
19. R. J. Wojtecki, M. A. Meador and S. J. Rowan, *Nat. Mater.*, 2011, **10**, 14-27.
20. G. H. Deng, C. M. Tang, F. Y. Li, H. F. Jiang and Y. M. Chen, *Macromolecules*, 2010, **43**, 1191-1194.
21. J. A. Nam, A. Al-Nahain, S. Hong, K. D. Lee, H. Lee and S. Y. Park, *Macromol. Biosci.*, 2011, **11**, 1594-1602.
22. B. Gyarmati, Á. Némethy and A. Szilágyi, *RSC Advances*, 2014, **4**, 8764-8771.
23. H. Y. Pan, Y. Y. Zhang, H. T. Pu and Z. H. Chang, *J. Power Sources*, 2014, **263**, 195-202.
24. M. Babazadeh, *J. Appl. Polym. Sci.*, 2007, **104**, 2403-2409.
25. Z. Wei, J. H. Yang, X. J. Du, F. Xu, M. Zrinyi, Y. Osada, F. Li and Y. M. Chen, *Macromol. Rapid Commun.*, 2013, **34**, 1464-1470.
26. J. Xu, D. G. Yang, W. J. Li, Y. Gao, H. B. Chen and H. M. Li, *Polymer*, 2011, **52**, 4268-4276.
27. W. J. Li, M. N. Liu, H. B. Chen, J. Xu, Y. Gao and H. M. Li, *Polym. Adv. Technol.*, 2014, **25**, 233-239.
28. J. S. Kingsbury, S. B. Garber, J. M. Giftos, B. L. Gray, M. M. Okamoto, R. A. Farrer, J. T. Fourkas and A. H. Hoveyda, *Angew. Chem. Int. Ed.*, 2001, **40**, 4251-4256.
29. L. J. Zhu, Y. F. Shi, C. L. Tu, R. B. Wang, Y. Pang, F. Qiu, X. Y. Zhu, D. Y. Yan, L. He, C. Y. Jin and B. S. Zhu, *Langmuir*, 2010, **26**, 8875-8881.
30. E. Lih, J. S. Lee, K. M. Park and K. D. Park, *Acta Biomater.*, 2012, **8**, 3261-3269.
31. R. Bird, T. Freemont and B. R. Saunders, *Soft Matter*, 2012, **8**, 1047-1057.
32. Y. Koyama, T. Yoshii, Y. Kohsaka and T. Takata, *Pure Appl. Chem.*, 2013, **85**, 835-842.
33. H. J. Zhang, L. Peng, Y. Xin, Q. Yan and J. Y. Yuan, *Macromol. Symp.*, Wiley Online Library, 2013, **329**. 66-69.
34. C. H. Ren, Z. J. Song, W. T. Zheng, X. M. Chen, L. Wang, D. L. Kong and Z. M. Yang, *Chem. Commun.*, 2011, **47**, 1619-1621.
35. S. C. Tang, M. J. Glassman, S. L. Li, S. Socrate and B. D. Olsen, *Macromolecules*, 2014, **47**, 791-799.
36. G. H. Deng, F. Y. Li, H. X. Yu, F. L. Liu, C.Y. Liu, W. X Sun, H. F. Jiang and Y. M. Chen, *ACS Macro Lett.*, 2012, **1**, 275-279.
37. F. Y. Deng, B. Xu, Y. Gao, Z. Liu, D. G.Yang and H. M. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 3767-3774.
38. A. P. Zhang, Z. Zhang, F. H. Shi, J. X. Ding, C. S. Xiao, X. L. Zhuang, C. L. He, L. Chen and X. S. Chen, *Soft Matter*, 2013, **9**, 2224-2233.
39. Q. Huang and B. Zheng, *Org. Chem. Int.*, 2012, **2012**, doi:10.1155/2012/208128.
40. J. Amartey, C. Esguerra, B. Al-Otaibi, R. Parhar and I. Al-Jammaz, *Appl. Radiat. Isot.*, 2004, **60**, 839-843.
41. A. Alborzi, S. Zahmatkesh and A. Yazdanpanah, *Polym. Bull.*, 2013, **70**, 3359-3372.
42. M. Ghaemy, S. Qasemi, K. Ghassemi and M. Bazzar, *J. Polym. Res.*, 2013, **20**, 1-15.
43. D. Hazar Apaydın, D. Esra Yıldız, A. Cirpan and L. Toppare, *Sol. Energy Mater. Sol. Cells*, 2013, **113**, 100-105.
44. R. Bagtache, G. Rekhila, K. Abdmeziem and M. Trari, *Mater. Sci. Semicond. Process.*, 2014, **23**, 144-150.

45. M.-K. Song, X. B. Zhu and M. L. Liu, *J. Power Sources*, 2013, **241**, 219-224.
46. J. W. Steed, *Chemical Society Reviews*, 2010, **39**, 3686-3699.
47. Y. Lee, H. J. Chung, S. Yeo, C.-H. Ahn, H. Lee, P. B. Messersmith,and T. G. Park, *Soft Matter*, 2010, **6**, 977-983.
48. I. Arvanitoyannis, E. Psomiadou and A. Nakayama, *Carbohydr. Polym.,* 1996, **31**, 179-192.
49. E. Amici, A. Clark, V. Normand and N. Johnson, *Biomacromolecules*, 2000, **1**, 721-729.
50. T. Lane, J. L. Holloway, A. H. Milani, J. M. Saunders, A. J. Freemont and B. R. Saunders, *Soft Matter*, 2013, **9**, 7934-7941.
51. D. J. Adams, L. M. Mullen, M. Berta, L. Chen and W. J. Frith, *Soft Matter*, 2010, **6,** 1971-1980.
52. J. Y. Li, S. X. Yang, L. Wang, X. B. Wang and L. Liu, *Macromolecules*, 2013, **46**, 6832-6842.
53. Z. Rodriguez-Docampo and S. Otto, *Chem. Commun.*, 2008, 5301-5303.
54. U. Gulyuz and O. Okay, *Soft Matter*, 2013, **9**, 10287-10293.
55. R. P. Wool, *Soft Matter*, 2008, **4**, 400-418.
56. G. Akay, A. Hassan-Raeisi, D. C. Tuncaboylu, N. Orakdogen, S. Abdurrahmanoglu, W. Oppermann and O. Okay, *Soft Matter*, 2013, **9**, 2254-2261.
57. J. A. Yoon, J. Kamada, K. Koynov, J. Mohin, R. Nicolay, Y. Z. Zhang, A. C. Balazs, T. Kowalewski and K. Matyjaszewski, *Macromolecules*, 2012, **45**, 142-149.
58. J. A. Syrett, C. R. Becer, D. M. Haddleton, *Polym. Chem*, 2010, **1**, 978−987.
59. A. M. Peterson, R. E. Jensen and G. R. Palmese, *ACS Appl. Mater. Inter.*, 2010, **2**, 1141-1149.