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Stretchable Self-Healing Polymeric Networks with Recyclability and Dual Responsiveness

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ABSTRACT

Intelligent polymers with tough networks are of considerable significance for the development of highly proficient polymer science and technology. In this work, polymeric elastomers with integrated stretchable and self-healable characteristics were designed by cross-linking hyperbranched polymers with flexible segments. The hyperbranched polymer with multiple terminal groups provided various cross-linking points, so that mechanically robust networks could be achieved. Driven by the reversibility of imine and disulfide bonds employed, the elastomers exhibited good self-healing property and the healing efficiency reached up to 99% under ambient environments. Furthermore, the dynamic reversibility of the polymers was investigated at molecular level. The imine and disulfide bonds were incorporated into the networks to construct soluble and recyclable hyperbranched polymer with pH and redox responsiveness via A_2+B_3 approach and Schiff base polymerization. The polymers containing imine bonds could complete the polymerization–depolymerization transition and undergo reversible cycles for several times through changing pH. Moreover, in the presence of disulfide bonds, the polymers were provided with redox cleavage property triggered by dithiothreitol. This study may provide new opportunities for the design and application of intelligent polymers with tough networks through regulating topological structures.

KEYWORDS: reversible covalent bonds, hyperbranched polymers, stretchable, recyclable, self-healing

INTRODUCTION

Dynamic covalent bonds (DCB),¹⁻³ which can be dissociated and regenerated with changed environmental factors including temperature, pressure or pH, has received dramatic interest. This adaptability offers great potential for developing functional materials through the utilization of DCB.⁴⁻⁵ Thermally activated alkoxyamine bond,⁶⁻⁷ pH-sensitive imine,⁸⁻¹⁰ acylhydrazone bond,¹¹⁻¹³ redox and visible light-induced diselenide bond,¹⁴ thermally reversible Diels–Alder reaction,¹⁵⁻¹⁶ and multi-responsive disulfide bond triggered under pH, light, and redox conditions¹⁷⁻¹⁹ can all be used as reversible covalent bonds.²⁰ If the DCB is employed to construct polymeric networks, the resulting dynamic networks or dynamic polymers can be endowed with fascinating smart properties. It is well known that the main objective of the emphasis on traditional polymer design is to enhance thermal, mechanical, electrical, optical, magnetic, or chemical properties and prevent the cleavage of bonds in case the performance deteriorates. Once the chemical bonds are broken, they may lose the practical value because the irreversible bonds are not repairable. Unlike traditional polymers; however, the dynamic networks or dynamic polymers with reversible characteristics can reorganize or optimize the networks on exposure to stimulus and be adaptable to environmental change through the cleavage and recombination of the reversible covalent bonds.^{4,21} Therefore, the self-healable and recyclable polymers containing DCB are attractive because they can be regenerated with functionalities recovered and extend usage lifetime, and reduce environmental burden.²¹⁻²⁴

As one of the dynamic bonds, imine bond (C=N) is easily formed from an amine and an aldehyde under weakly acidic environments.²⁵⁻²⁶ The imine bonds generated from aromatic

amine and aromatic aldehyde are more stable than their aliphatic counterparts. However, the generation of a lot of benzene in polymeric architecture leads to the rigid backbone, which may render the polyazomethine²⁷⁻²⁸ poorly soluble, thus limiting its applications in many fields. On the other hand, the rigid structure can be used to regulate the mechanical properties of polymers associated with moderate soft segments. Besides, disulfide bond is also attractive due to its merits in facile operation, easily available raw materials, and multiple stimuli-responsiveness.

Nowadays, various topological structures such as linear,²⁹ cross-linked,³⁰ dendritic,³¹ hyperbranched,³² star-shaped,³³ brush-shaped,³⁴ and polyrotaxane networks³⁵ are widely applied to constructing polymeric networks. Notably, hyperbranched polymers show a great deal of special features, such as low intrinsic viscosity, low inter-chain entanglements, excellent solubility, and the existence of multi-functional groups.³⁶⁻³⁸ Therefore, if hyperbranched architecture is incorporated into polyazomethine, a type of soluble polyazomethine with good performance could be achieved. Moreover, taking advantage of hyperbranched structure with large number of terminal groups, robust cross-linking networks can be easily constructed. The investigation opens up new avenues for designing dynamic polymers and networks with ideal structures for applications in self-healing materials, molecular logical gate,³⁹⁻⁴⁰ programmable polymers,⁴¹⁻⁴² and recyclable and sustainable materials.⁴³

In this work, the reversible imine and disulfide bonds were combined to prepare the

hyperbranched polymer with intelligent dynamic response characteristics, and the stretchable self-healing polymeric networks were designed benefiting from the special features of hyperbranched architecture. Herein, the dynamic hyperbranched polyazomethine (hb-PAM) with terminal aldehyde groups and good solubility was synthesized via A_2+B_3 approach. At the molecular level, the dynamic reversibility of hb-PAM was systematically investigated. For the pH-sensitivity of imine bond, hb-PAM could realize polymerization–depolymerization transition for several times. Meanwhile, hb-PAM containing disulfide bond was endowed with redox cleavage property. Besides, hb-PAM could be further cross-linked with soft segments to achieve stretchable and tough self-healing polyazomethine (SH-PAM). SH-PAM exhibited good elasticity and self-recovery capability. Moreover, the mechanical performances of SH-PAM elastomers were tunable, to obtain polymeric networks with high strength or stretchability. Remarkably, SH-PAM elastomers were demonstrated to present excellent self-healing property and dual responsiveness.

EXPERIMENTAL SECTION

2.1. Materials

Trimethylolethane (TME, 98.0%), *p*-toluenesulfochloride (TsCl, 99.0%) and 4,4'-dithiodianiline (98.0%) were purchased from TCI (Shanghai) Development Co., Ltd. 4-Hydroxybenzaldehyde (99.0%), potassium carbonate (99%), dithiothreitol (DTT, 99%) and poly(propylene glycol)bis(2-aminopropyl ether) 2000 (PEA 2000) were provided by Aladdin Shanghai Co. All reagents were used as received without further purification.

2.2. Synthesis of hyperbranched polyazomethine

1, 1, 1-Tris[(4-formylphenoxy)methyl]ethane (FPME) was synthesized as previously reported method⁹ with a little improvement (see the details in Supporting Information). FPME (0.290 g, 0.6 mmol) was completely dissolved in *N,N*-dimethylformamide (DMF, 10 mL), followed by adding glacial acetic acid (AcOH, 60 μ L, 0.3% v/v) as an acid catalyst. Then 4, 4'-dithiodianiline (0.152 g, 0.6 mmol) dissolved in anhydrous DMF (10 mL) was added dropwise to the solution for over 1 h. The mixture was further reacted at 25 °C under nitrogen atmosphere for 26 h. After DMF was evaporated, the mixture was redissolved in tetrahydrofuran (THF, 5 mL) and subsequently added dropwise into methanol (60 mL) with stirring. The formed precipitate was collected and dried in vacuum at 35 °C. Eventually, the yellow powders of hyperbranched polyazomethine (hb-PAM) were obtained (0.388 g, 92.3%).

2.3. Reversibility of imine bonds

The hb-PAM was dissolved in DMF, followed by adding hydrochloric acid (HCl, 1% v/v) to the solution to cleave hb-PAM. After a certain time, HCl was saturated with equivalent amount of triethylamine (NEt₃), which resulted in the formation of the salts of HCl and NEt₃. Then the de-monomers were extracted with dichloromethane. Subsequently, the solvent was evaporated. To regenerate hyperbranched polyazomethine hb-PAM^C, the purified de-monomers were dissolved in DMF, to which AcOH (0.3% v/v) was added. The reaction conditions of hb-PAM^C were same as that of hb-PAM. After the reaction, a part of hb-PAM^C and residual monomers were extracted with dichloromethane, from which the AcOH and

DMF were removed with water. The remaining solution was used for the next step. In the same way, imine linkage was constantly broken and reformed, and correspondingly hyperbranched polyazomethines hb-PAM₂^c to hb-PAM₄^c were obtained.

2.4. Reduction degradation of hyperbranched polyazomethine

The hb-PAM (5 mg) and DTT (15 mg) were dissolved in THF (1 mL, in flask) with stirring under nitrogen atmosphere at room temperature to start the disulfide degradation in polymer.

2.5. Preparation of self-healing polyazomethine

Typically, FPME was dissolved in anhydrous DMF, which was followed by the addition of AcOH (0.3% v/v). Then 4, 4'-dithiodianiline dissolved in DMF was added dropwise over 1 h. The mixture was further reacted at 25 °C under nitrogen atmosphere for 26 h. Subsequently, PEA dissolved in DMF was added to the solution. After the mixture was further reacted for 12 h, the solution was cast into a Teflon mold. Finally, the resulting polymer was put into an oven at 40, 50, and 60 °C for 3 days. Two kinds of self-healing polyazomethine (SH-PAM-1 and SH-PAM-2) were prepared according to the above methods. The molar ratios of FPME, 4, 4'-dithiodianiline, and PEA were 2:2:1 and 2:1:2 for SH-PAM-1 and SH-PAM-2, respectively.

2.6. Characterizations

Nuclear magnetic resonance (NMR) analyses were performed on a Bruker Avance 400 spectrometer (Bruker Biospin, Switzerland). The deuterated dimethyl sulfoxide (DMSO-*d*₆) and deuterated chloroform (CDCl₃) were used as solvents. Fourier transform infrared (FTIR)

spectroscopy analyses were recorded on an FTIR spectrophotometer (Perkin-Elmer, USA). The ultraviolet–visible spectra (UV–vis) were performed using a Shimadzu UV2550 UV–vis spectrophotometer (Shimadzu UV2550, Japan). Molecular weight and molecular weight distribution were measured on size exclusion chromatography (SEC) with multi-angle laser light scattering systems (MALLS, DAWN EOS, Wyatt, USA) quipped with a Waters 515 pump, an autosampler and two MZ gel columns (103 Å and 104 Å). The flow rate was 0.5 mL min⁻¹ in THF (HPLC grade) at 25 °C. The refractive index increments of polymers in THF were measured at 25 °C on a differential refractometer (OptilabrEX, Wyatt, USA). The mechanical tensile tests (dumb-bell shaped specimens, 12 mm × 2 mm × 0.8 mm) were performed using an Instron E1000 all-electric dynamic test instrument with a stretching speed of 20 mm min⁻¹ according to ISO37-4 standard.

RESULTS AND DISCUSSION

3.1. Synthesis of hyperbranched polyazomethine

The synthesis process of hb-PAM is exhibited in **Figure 1**. It could be obtained via Schiff base polymerization between amino groups of 4,4'-dithiodianiline (A₂) and aldehyde groups of FPME (B₃). Commonly, gelation easily occurs in A₂+B₃ system; however, it is important to control the reaction conditions. Herein, the rate of reaction was controlled by slowly adding A₂ monomer to B₃ monomer in dilute solution, as well as a catalytic amount of acid. Moreover, the molar ratio of the reactive monomers was adjusted to 1:1. By taking these factors into account, a type of hyperbranched polymer based on imine bond (hb-PAM) with excellent solubility was successfully synthesized.

The structure of hb-PAM was identified by FTIR and ^1H NMR spectroscopy. As shown in **Figure 2**, compared to the monomers, a new peak appears at 1624 cm^{-1} for hb-PAM, attributed to the generation of imine bond ($\text{CH}=\text{N}$). Moreover, the two broad peaks in the range of $3300\text{--}3700\text{ cm}^{-1}$ resulted from amine groups almost disappear and a peak at 1680 cm^{-1} assigned to carbonyl ($\text{C}=\text{O}$) becomes weaker, indicating the successful synthesis of hb-PAM with terminal aldehyde groups (CHO). **Figure 3a** exhibits ^1H NMR spectra of hb-PAM, where the appearance of the peak at 8.37 ppm further validates the formation of imine bond. Furthermore, weak peak at 6.70 ppm ascribed to the protons of benzene near the amine reveals the presence of a little unreacted amine groups resulting from steric hindrance. The proton peak of the end aldehyde groups is also observed at 9.91 ppm . In addition, the $M_{w,\text{SEC}}$ of hb-PAM is $19,600\text{ g mol}^{-1}$ and the PDI is 1.53 (**Table 1**). The increased molecular weight evidently demonstrated the polycondensation. The MALLS is an effective technique for determining the absolute molar mass, thus the combination of SEC with MALLS analysis could avoid the mismatch between hyperbranched architecture and linear polystyrene calibration in normal SEC technology.

3.2. Reversibility of imine bonds

The formation of imine bond could be accelerated by adding a tiny amount of acid. At low pH; however, the imine linkage was cleaved.¹⁰ Therefore the polymer containing imine bond could be decomposed into monomers under the acidic conditions, and the de-monomers could polymerize again to generate polymer via regulating the reaction conditions as shown

in **Figure 1**. The pH responsive cleavage of hb-PAM was investigated first. When the apparent pH was adjusted to 4–5 by adding HCl (1% v/v) to the solution of hb-PAM, the decomposition of imine bonds occurred. Moreover, the polymer degraded into monomers over time. The de-monomers were extracted with dichloromethane and washed with water in order to remove residual HCl and some other impurities, in order to avoid any adverse effect on the subsequent reaction. The cleavage of hb-PAM was examined by ^1H NMR spectroscopy and SEC-MALLS. **Figure 3b** presents ^1H NMR spectra of purified de-monomers in d_6 -DMSO. Compared to the spectra of hb-PAM, the proton peak of imine at 8.52 ppm becomes much weaker, the proton peak at 9.86 ppm corresponding to the terminal aldehyde groups is relatively strong, and the proton peak of amine groups at 5.50 ppm appears. The residual proton peak of imine resulted from high reactivity between amine and aldehyde groups, as well as the reversibility of the reaction. **Figure 4** shows the SEC trace of the de-monomers, revealing that the time of appearance of peak was much later than that of hb-PAM, and the distinct bimodal distribution could be observed, indicating the presence of two monomers and some oligomers. The dependence of cleavage of the imine bond on time was further investigated in THF and the pH value of the solution was adjusted to about 5 by adding AcOH. The reproduced UV–visible absorption spectral curves of hb-PAM measured in various time intervals were obtained as depicted in **Figure 3c**. Clearly, intensity of the absorption band at around 338 nm, corresponding to conjugated imine, decreases with time. After 9 h, the system reached equilibrium. These results demonstrated imine bond could be cleaved when the pH below 5.0.

Then the de-monomers regenerating hyperbranched polyazomethine and the transition process of polymer and de-monomers were explored. The de-monomers were still highly active to polymerize, forming hb-PAM₁^C under the mild reaction conditions same as that of hb-PAM. Herein, the transition process of polymer and de-monomers was repeated for four circles in one system, and the corresponding polymers (hb-PAM₂^C, hb-PAM₃^C, hb-PAM₄^C) were obtained. Each time the polymer was depolymerized, the results were monitored by ¹H NMR spectroscopy. As shown in **Figure 3b**, the ¹H NMR spectra of de-monomers (M₁₋₄^D) are almost the same, and all peaks at 8.52 ppm assigned to the imine proton CH=N become weak, indicating that the depolymerization to monomers was successfully triggered at low pH. **Figure 3a** presents that the ¹H NMR spectra of hb-PAM and hb-PAM_{2,4}^C remain almost the same, and the characteristic signals of proton on CH=N bond (8.37 ppm) grow stronger. Moreover, in the SEC traces, the peaks of hb-PAM and hb-PAM_{2,4}^C appear almost at the same time at about 12 min (elution time) as shown in **Figure S4** in Supporting Information. The similarity of the traces might be coincidental and more variation would be expected if these experiments were repeated. The corresponding molecular weights of the cyclic hb-PAMs are summarized in **Table 1**. **Figure 3d** depicts relatively small change in weight average molecular weight with cyclic times for hb-PAM and hb-PAM_{2,4}^C. After the dissociation of hb-PAM, the de-monomers still have the ability to polymerize to regenerate the hyperbranched polymer with high molecular weight close to that of the original polymer hb-PAM. The results indicate that the polymers based on imine bond had the characteristic of dynamic reversibility, which was controllable, and the polymer–monomer transition was able to undergo repeated cycles through regulating pH.

3.3. The intramolecular cyclization of hb-PAM and hb-PAM_{2,4}^C

Intramolecular cyclization occurs during the synthesis process of hyperbranched polymers via A₂+B₃ polycondensation. For the obtained hyperbranched polymers with A or B terminal groups, the r parameter can be defined to determine the degree of intramolecular cyclization.⁴⁴ In our previous work,⁴⁵⁻⁴⁶ the quantitative relationship between cyclic structures and structural units for hyperbranched polymers was derived as:

$$N_C = \begin{cases} N_{A_0} - N_{B_0} - N_{B_1} - N_{B_2} + N \\ 2 \times N_{B_0} + N_{B_1} - N_{A_0} - N_{A_1} + N \end{cases} \quad (1)$$

where N , N_C , N_{A_0} , N_{A_1} , N_{B_0} , N_{B_1} , and N_{B_2} represents the number of total macromolecules, cyclic structures, A₀, A₁, B₀, B₁ and B₂ units, respectively. Noteworthy, A₀ and A₁ units refer to the structural units containing 0 and 1 A group, and B₀, B₁, and B₂ units refer to the structural units containing 0, 1, and 2 B groups (**Figure 5**). Equation (1) after the transformation is represented as the following equation:

$$N_{A_1} + N_{B_1} + 2N_{B_2} = N_{B_0} + N_{B_1} + N_{B_2} + 2N - 2N_C \quad (2)$$

($N_{A_1} + N_{B_1} + 2N_{B_2}$) is total number of terminal groups and ($N_{B_0} + N_{B_1} + N_{B_2}$) means total number of B units. In Equ. 2, it can be found that the quantitative relationship between the end groups and B units closely correlated with the intramolecular cyclization. As a consequence, a parameter r is defined as the number proportion of total terminal groups to B units:

$$r = \frac{N_{A_1} + N_{B_1} + 2N_{B_2}}{N_{B_0} + N_{B_1} + N_{B_2}} = 1 + 2 \frac{N - N_C}{N_{B_0} + N_{B_1} + N_{B_2}} \quad (3)$$

Here, the r value is inversely proportional to degree of intramolecular cyclization. Through the integration of proton peak area in ¹H NMR spectra, the r value can be calculated. **Table 1**

summarizes that the r values of dynamic hyperbranched polymers hb-PAM and hb-PAM_{2.4}^C were all above 1.5, indicating that the intramolecular cyclization of the polymers was low. The r value of hb-PAM was lower than that of hb-PAM_{2.4}^C. This was attributed to the fact that hb-PAM_{2.4}^C specimens were not purified, and they contained unreacted monomers leading to decreasing value of intramolecular cyclization. Moreover, the r values of hb-PAM_{2.4}^C did not change much, illustrating that the topological structure of the polymers remained nearly the same after repeatedly experiencing the reversible polymer–monomer transitions.

3.4. Reductive degradation of hyperbranched polyazomethine

The DTT was utilized to trigger the degradation of the hb-PAM. The disulfide bonds have the characteristic of redox responsibility; therefore, the hb-PAM containing disulfide bonds could be dissociated by reductant. The cleavage of the polymer was monitored by SEC-MALLS. **Figure 4** exhibits that the degradation behavior could be observed in the SEC trace. Compared to the peak of hb-PAM in the range from 12 to 20 min, a new peak of the degradation product appeared at 24 min, indicating that the hb-PAM was reduced by DTT.

3.5. Mechanical performance of the cross-linked polyazomethine

In polymerization system, the higher the functionality of the reactants, the more likely gelation occurs. The hyperbranched polymers (hb-PAM) have abundant functional end groups. Therefore, they are exceptionally useful in curing systems, compared to low-functionality monomers. The hb-PAM was further cross-linked with PEA through Schiff base reaction to achieve self-healing polyazomethine (SH-PAM), as shown in **Figure 6**. The

hb-PAM with amounts of aldehyde terminal groups facilitated the formation of three-dimensional cross-linked networks. Moreover, PEA 2000 served as a soft and hydrophobic segment, thus we could obtain a stretchable polymeric network. On the one hand, soft macromolecular chains contribute to enhance the flexibility and deformability. On the other hand, incorporating hydrophobic PEA segments into the cross-linked networks is to avoid hydrolysis of imine bond.

The mechanical performances of cross-linked polymers were greatly influenced by the ratio of monomers. Two kinds of SH-PAM (SH-PAM-1 and SH-PAM-2) were designed and prepared through adjusting the content of 4, 4'-dithiodianiline and PEA, in which the total molar ratio of amino and aldehyde was maintained at 1:1. The typical stress-strain behaviors for SH-PAM-1 and SH-PAM-2 are shown in **Figure 7a**. SH-PAM-1 presented maximum stress of 3.8 MPa and Young's modulus of 2.4 MPa, which were about 10 times higher than that of SH-PAM-2. While the SH-PAM-2 exhibited excellent stretchability with fracture strain of 510% (**Figure 7b**). The above results were for the reason that there were more rigid benzene and conjugated structure, as well as cross-linking points in SH-PAM-1. It is acknowledged that the molar ratio of A_2 to B_3 monomers controlled at 1:1 is more prone to obtain hyperbranched macromolecules with higher molecular weight,⁴⁷ indicating a larger number of terminal groups per polymeric chain. Additionally, in our previous work, an elastomer based on imine bond cross-linked through PEA and FPME was reported, with a peak stress of 0.79 MPa and fracture strain of 215%.⁹ Obviously, SH-PAM-1 exhibited more robust mechanical property.

SH-PAM-1 was selected for further investigation. The cross-linked networks exhibited good elasticity and self-recovery capability. As shown in **Figure 7c**, loading-unloading cycle tests were performed with stretching to a strain of 50%. During the consecutive loading-unloading process, it showed obvious hysteresis, resulting from the energy dissipation. Subsequently, in cycle 2, the energy dissipation (within the loop of a cycle) was decreased, which could be ascribed to the enhancement of elastic deformation. After relaxing for 30 min, the sample was allowed to stretching again. It was found that the curve almost overlapped with that of cycle 1, indicating the sample fully recovered with the mechanical performance restored to its original state. This phenomenon might be assigned to the synthetic action of imine and disulfide bonds with dynamic characteristics through bond breakage and reformation.

3.6. Self-healing performance of the cross-linked polyazomethine

Driven by the reversibility of imine and disulfide bonds, the as-prepared SH-PAM elastomers were endowed with excellent self-healing property. A piece of SH-PAM film specimen was cut from the middle, and one of them was dyed in red color. Then they were brought into full contact. After healing, the sample could be subjected to be bent and twisted (**Figure 7d**). Then, the quantitative analysis of self-healing characteristic was conducted by the uniaxial tensile tests at 25 °C (**Figure 7e, f**). The healing efficiency is deduced from the ratio of the fracture strain of the healed sample to that of the original sample. The calculations proved that the time-dependent healing efficiency of SH-PAM-1 was about 91% after healing for 48 h. Remarkably, the healing efficiency of SH-PAM-2 reached to 99% after 12 h. The

difference of healing efficiency between SH-PAM-1 and SH-PAM-2 was due to the flexibility of networks. SH-PAM-2 was softer than SH-PAM-1, leading to the molecular chains moving more easily. The ideal self-healing property results from the mobility of soft segments and synthetic effects of imine and disulfide bonds. The soft segments in the polymer networks facilitate the intimate contact between the broken surfaces. Therefore, the imine bonds could be reformed by the active aldehyde and amino groups generated at the scratched surfaces. Meanwhile, with the exchange and metathesis of imine, the system is in dynamic equilibrium.²⁵ For the reversibility of the reaction, there might be unreacted terminal groups which could also form imine bond, contributing to self-healing process. Moreover, the aromatic disulfide undergoes inconstant exchange at room temperature,¹⁸ leading to the healing of the cracked SH-PAM elastomers.

3.7. Dual responsiveness of self-healing polyazomethine

At the molecular levels, the pH and redox responsiveness of imine and disulfide bonds were investigated through the soluble hb-PAM. Therefore, undoubtedly, the cross-linked SH-PAM elastomers were provided with dual responsiveness. **Figure 8** depicts that the soaking of SH-PAM-1 in the solution of AcOH, led to their complete dissociation. The solid state was transformed to liquid solution due to the cleavage of imine linkages and dissociation of cross-linked networks at low pH (**Figure 8a, b**). Interestingly, the cross-linked polymer could be prepared after adjusting pH and evaporating solvent at 80 °C (**Figure 8c**). Similarly, when DTT was added onto the surface of SH-PAM-1, the bulk polymer was completely decomposed. After exposure to air environments and volatilization of solvent, the film could

be reformed due to the redox feature of disulfide bonds. Therefore, dual responsiveness of SH-PAM-1 could conveniently be achieved by common operations of dissociation and evaporation based on cleavage and polymerization of imine or disulfide bonds.

CONCLUSIONS

Stretchable and self-healable elastomers with dual pH and redox responsibility were successfully synthesized, which were cross-linked through recyclable hyperbranched polymers based on reversible covalent bonds. The soluble hb-PAM exhibited the transitional behaviors between polymers and de-monomers. The polymer containing imine bonds could be decomposed into monomers at low pH, and the de-monomers could polymerize again to generate the hyperbranched polymer via regulating the reaction conditions. Moreover, this process could be repeated for several times. The topological structures of the regenerated hb-PAM nearly remained the same after undergoing the reversible polymer–monomer transitions. Moreover, the hb-PAM was provided with redox cleavage ability triggered by DTT. Benefiting from the hb-PAM with multiple terminal groups, furthermore, the hb-PAM could be cross-linked with PEA through Schiff base reaction to achieve tough networks. Furthermore, the SH-PAM elastomers demonstrated excellent self-healing performance of with a healing efficiency as high as 99% under ambient environment. Moreover, the SH-PAM elastomers exhibited remarkable dual responsiveness. The dynamic polymers might have promising applications in smart structures, programmable polymers, and soft electronics fields.

ASSOCIATED CONTENT

Supporting Information

¹H NMR of monomers and SEC traces of polymers. The Supporting Information is available free of charge on the ACS publications website.

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Notes

The authors declare no competing financial interest.

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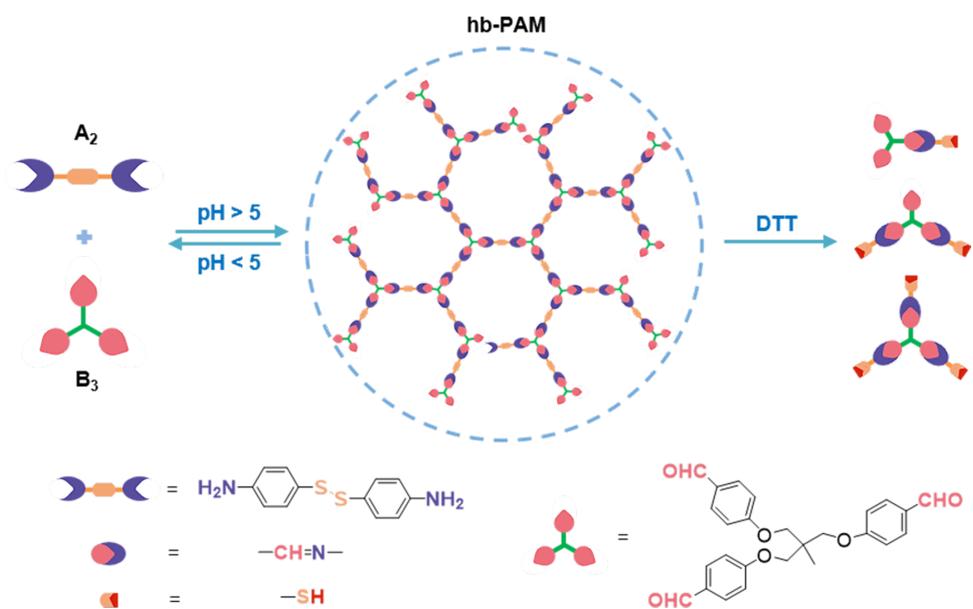


Figure 1. Schematic illustration of synthesis of hyperbranched polymer (hb-PAM) based on imine and disulfide bonds, with reversible pH and redox responsiveness.

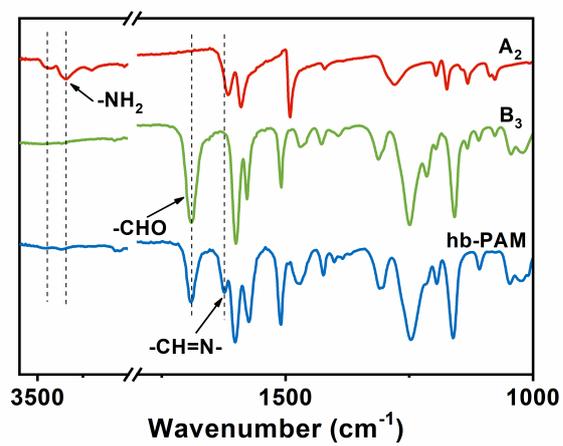


Figure 2. FTIR spectra of A₂ monomer (4, 4'-dithiodianiline), B₃ monomer (1, 1, 1-tris[(4-formylphenoxy)methyl]ethane) and hyperbranched polyazomethine (hb-PAM) between 3600–1000 cm⁻¹.

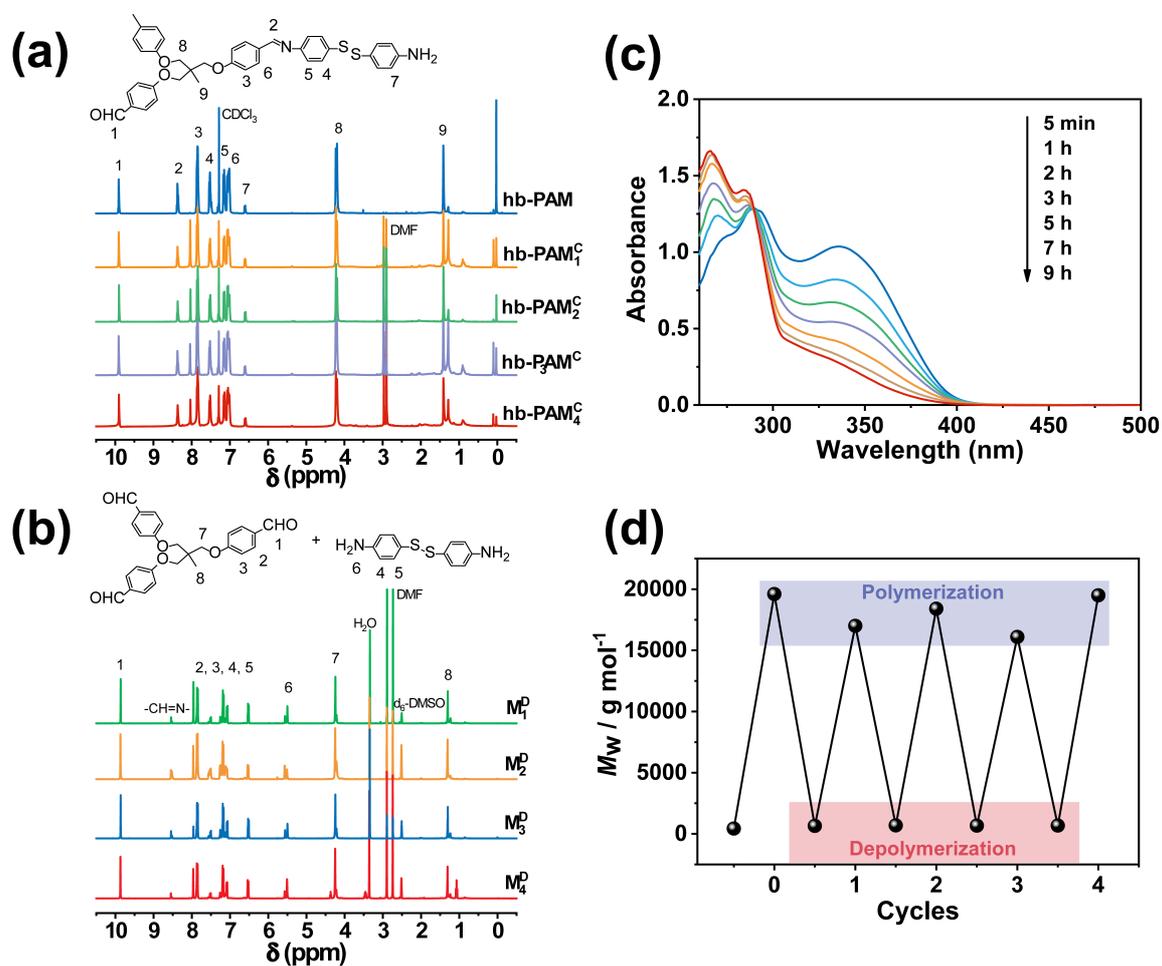


Figure 3. (a) ^1H NMR spectra of hyperbranched polyazomethines in CDCl_3 , (b) ^1H NMR spectra of de-monomers in d_6 -DMSO, (c) UV-visible absorption spectra of hb-PAM obtained at various time intervals at pH = 5, (d) Change in average molecular weight of hyperbranched polyazomethines for four cycles of depolymerization–repolymerization.

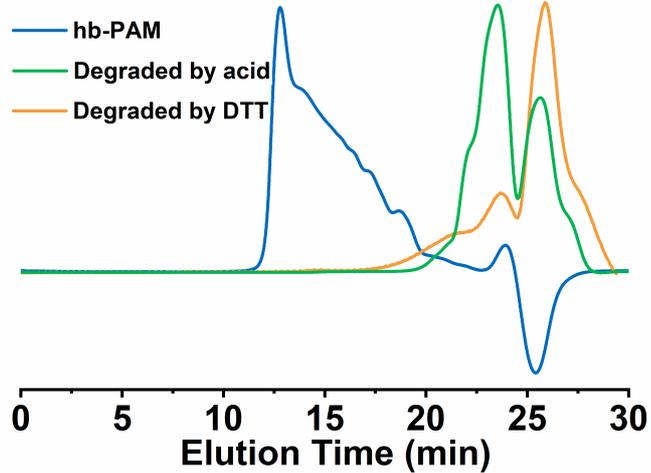


Figure 4. SEC trace of the hb-PAM and hb-PAM degraded by acid and DTT with a flow rate of 0.5 mL min^{-1} in THF.

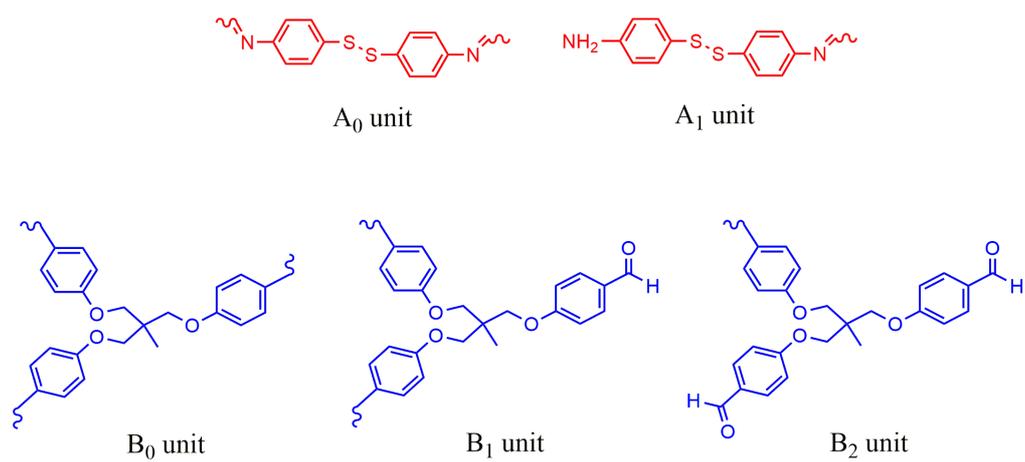


Figure 5. Division of topological units of the A₂ monomer, B₃ monomer and hyperbranched polymer.

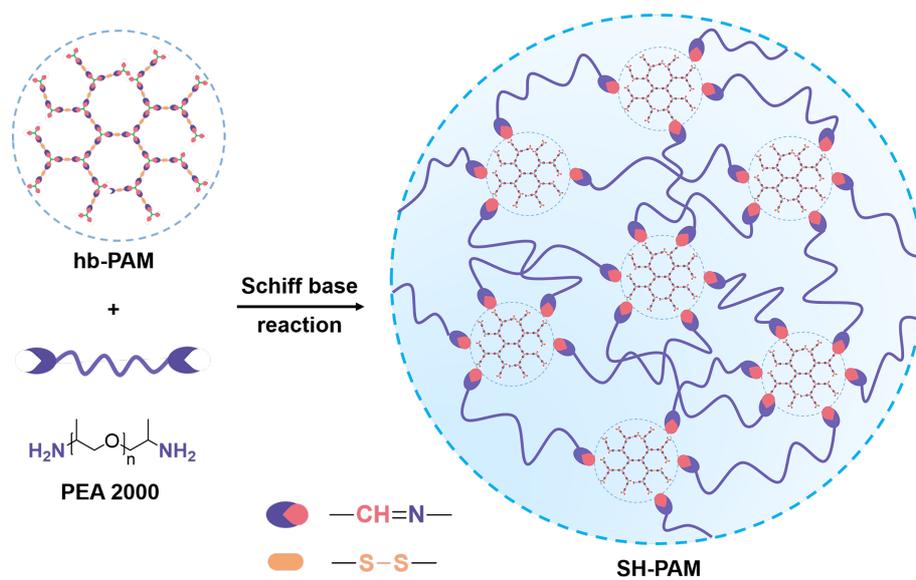


Figure 6. Schematic illustration of fabrication of self-healing polyazomethine (SH-PAM)

elastomer cross-linked through Schiff base reaction.

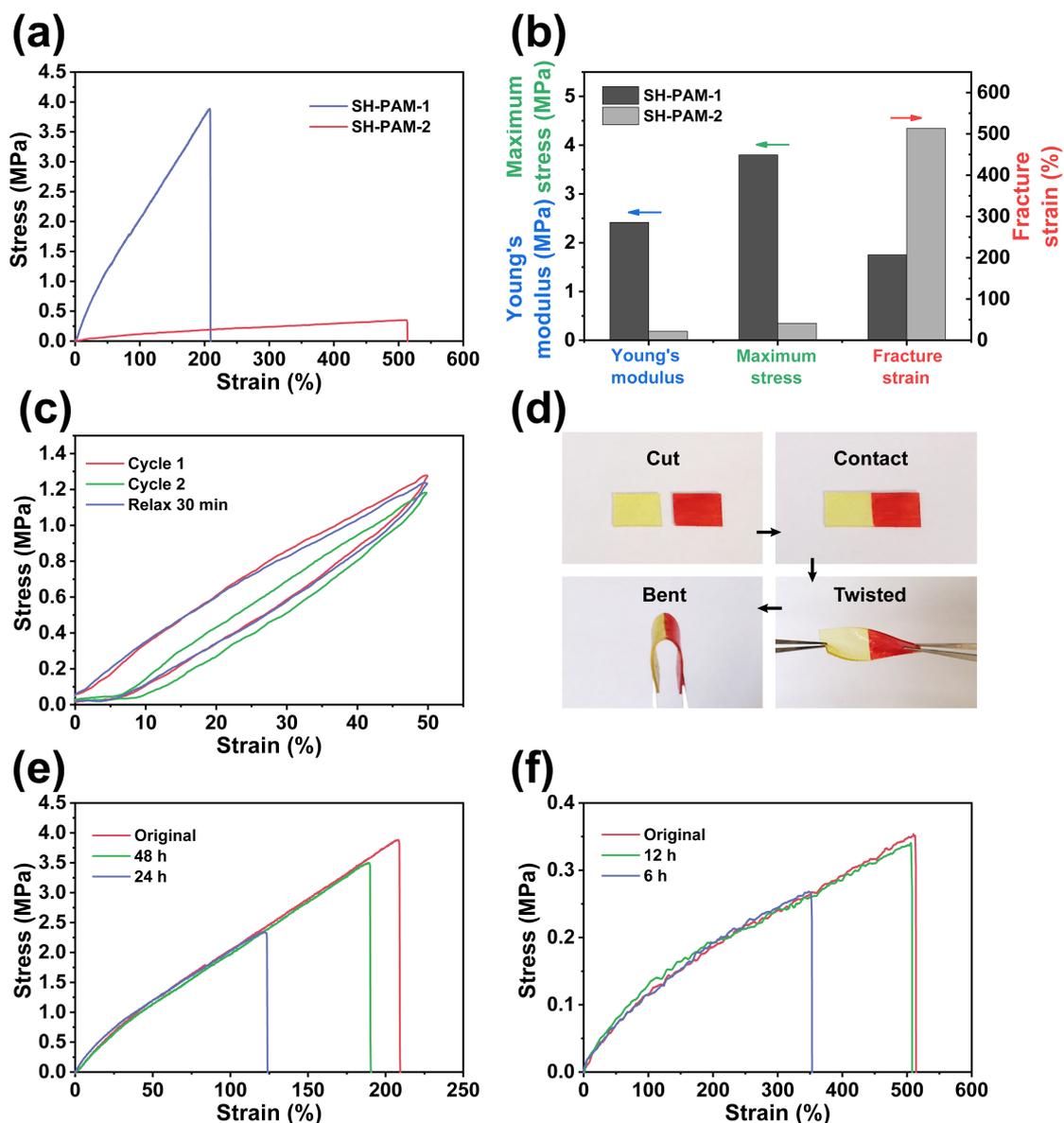


Figure 7. (a) Stress–strain curves of SH-PAM elastomers. (b) Young’s modulus, maximum stress, and fracture strain of SH-PAM elastomers. (c) Recovery and cyclic loading–unloading curves of SH-PAM-1 to a strain of 50%. (d) Optical images showing self-healing behavior of SH-PAM-2. (e) Stress–strain curves of the original and self-healed elastomers at various healing times for (e) SH-PAM-1 and (f) SH-PAM-2. The tensile rates in (a), (c), (e), and (f) were 20 mm min^{-1} .

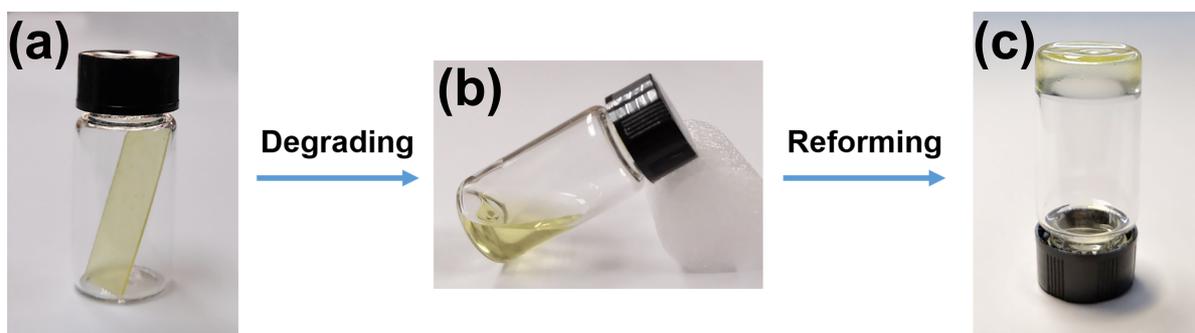


Figure 8. Optical photographs showing the responsiveness of SH-PAM-1: (a) the original, (b) soaking in the solution of AcOH or DTT, and (c) after evaporation of solvent.

Table 1. Characterization results of A₂+B₃ type hyperbranched polyazomethines

Sample	<i>M_w</i> (g mol ⁻¹)	<i>M_n</i> (g mol ⁻¹)	PDI ^a	r ^b
PAM	19,600	13,300	1.47	1.53
PAM ₁ ^c	17,000	12,100	1.40	1.92
PAM ₂ ^c	18,400	12,200	1.51	1.92
PAM ₃ ^c	16,100	11,800	1.37	1.74
PAM ₄ ^c	19,500	12,900	1.51	1.83

^aPDI = M_w/M_n , ^br value was calculated as the integral ratio of characteristic protons on –CHO at 9.90–9.94 ppm and benzene near the amino group at 6.55–6.63 ppm to that of characteristic protons on –CH₂– at 4.11–4.26 ppm. Polymer notation: C = cyclic, the numbers 1–4 indicate the cyclic times.

ToC Figure

