

# Hyperbranched Azopolymer with Quadruple Responsibility

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## Electronic Supplementary Information

**Abstract** Simply constructing multiple responsive polymers with obvious shape and dimension variations on their assemblies upon different stimuli is still rarely reported. In this study, we report a hyperbranched polymer named HPAzoBAHB-*star*-PEG<sub>9</sub> with quadruple-response to light, temperature, pH and oxidation stimuli. The polymer contains azobenzene chromophore, sulfide, amide and amine groups in its hydrophobic hyperbranched core, and the core is capped with hydrophilic polyethylene glycol (PEG<sub>9</sub>) arms. HPAzoBAHB-*star*-PEG<sub>9</sub> could assemble into unusual leaf-like lamellar micelles at 25 °C under the guidance of orderly arranged *H*-aggregate of azobenzene moieties. These leaf-like lamellar micelles can transform into vesicles upon UV irradiation and lower temperature, or convert to smaller spherical micelles in acidic or oxidative environments, respectively, with the destroy of ordered azobenzene arrangements. This quadruple-responsive hyperbranched polymer is suitable to construct multiple stimuli-responsive micro/nanostructures, or accurate delivery and release following subtle stimuli sequences.

**Keywords** Hyperbranched; Azopolymer; Multiple responsibility; Self-assembly

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## INTRODUCTION

Smart polymers, also known as stimuli-responsive polymers, are sensitive to a variety of stimuli such as pH,<sup>[1]</sup> temperature,<sup>[2,3]</sup> light<sup>[4]</sup> and oxidizing agents.<sup>[5]</sup> In general, the majority of smart polymers are synthesized by coupling functional moieties to the side-chain or main-chain of linear polymers. For example, photo-responsiveness could be accomplished by introducing azobenzene (reversible *trans-cis* isomerization), *o*-nitrobenzyl (photo cleavage of block junction) and coumarin etc.<sup>[4,6,7]</sup> into polymer architectures. Poly(*N*-isopropylacrylamide) (PNIPAM, features lower critical solution temperature (LCST)) and poly(phosphonate) (PPE, features upper critical solution temperature (UCST)) segments endow block copolymers with temperature sensitivity.<sup>[6]</sup> Besides, hydrazine, oxime, acetal and ketal linker enable the polymers pH sensitivity,<sup>[1,8]</sup> and the existence of disulfide bond, thiol and sulfides make the polymers oxidation sensitive.<sup>[7,8]</sup> Taking the advantage of the unique responsiveness, such smart polymers have been found

various biological and medical applications such as controlled drug delivery,<sup>[9–11]</sup> artificial muscles and tissue engineering,<sup>[12]</sup> as well as chemo- and biosensors.<sup>[13–17]</sup>

In recent years, hyperbranched polymers have received increasing interest because their highly branched architecture provides massive internal cavities and modifiable terminal groups that are beneficial to various applications.<sup>[18–20]</sup> Consequently, many hyperbranched polymers are designed stimuli-responsive to stimulating factors as smart carriers.<sup>[21–23]</sup> On one hand, responsive groups could be introduced directly in hyperbranched architecture. For example, Yan *et al.* designed abundant amide and amine groups in hyperbranched poly(methylene bisacrylamide aminoethyl piperazine) (HPMA) to form thermo-responsive physical gels in organic solvents.<sup>[24]</sup> Ding *et al.* developed AB<sub>2</sub> monomer 4-undecyloxyloxycarbonyl-4'-[bis(2-ethyl acrylate) amino] azobenzene to prepare hyperbranched azopolymer with photo-sensitivity through acyclic diene metathesis polymerization.<sup>[18]</sup> On the other hand, hyperbranched polymers could be further modified by conjugating various stimuli-responsive groups onto their terminal groups. Multiple-responsive hyperbranched polymers could be obtained simply by combining the two strategies. For instance, Zhang *et al.* modified hyperbranched polyethylenimine with isobutyramide terminal groups (HPEI-IBAm), and prepared a series of supramolecular complexes by mixing HPEI-IBAm with 4-(phenylazo) benzoic acid (PABA) in

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different ratios. The resulted supramolecular complexes exhibited temperature-, pH-, and photo-responsive properties.<sup>[25]</sup> However, facile preparation of multi-responsive hyperbranched polymers is still rarely reported at present. Very recently, we reported the synthesis of a triple responsive hyperbranched azopolymer through simple  $A_2+B'_2$  type Michael addition, but it could only self-assemble into large compound micelles (LCMs), and merely showed thermal, pH value and photo responsiveness with the shape and dimension changes of LCMs.<sup>[26]</sup>

In this study, we adopt four stimuli-sensitive moieties, including azobenzene chromophore, sulphide, amide and amine, once in all into a hyperbranched architecture through Michael addition to obtain a light, temperature, pH and oxidation responsive hyperbranched polymer named HPAzoBAHB-*star*-PEG<sub>9</sub> (see Scheme S1 in the electronic supplementary information, ESI). The  $A_2+B'_2$  type Michael addition occurred between *N,N'*-(diazene-1,2-diylbis(1,4-phenylene)) diacrylamide (Azo-BA) and 2-aminoethanethiol, and the obtained amino-terminated hyperbranched PAzoBAHB was then capped with poly(ethylene glycol) methyl ether acrylate (mPEG<sub>9</sub>-AA) to prepare HPAzoBAHB-*star*-PEG<sub>9</sub>. Herein, the hydrophobic core is composed of amino moieties, azobenzene, amides and thioether with pH, photo, thermal and redox responsiveness, respectively, and the oligo PEG arms are hydrophilic (see Scheme 1). This hyperbranched polymer could self-assemble into unusual leaf-like lamellar micelles because of the ordered alignment of azobenzene chromophores. Upon UV-light irradiation, the leaf-like micelles curled gradually to form vesicles and the temperature decreased to 10 °C. Moreover, the leaf-like micelles turned smaller and lost their shape while the solution got acidic, and then broke down into much smaller spherical micelles after oxidized by H<sub>2</sub>O<sub>2</sub>. This facilely prepared quadruple-sensible hyperbranched polymer are expected to be applied in subtle multi-step controlled release processes, or constructing stimuli-responsive micro/nanostructures.

## EXPERIMENTAL

### Materials

4,4'-Azodianiline (98%, Adamas), acryloyl chloride (98%,

Adamas), triethylamine (TEA) (99.5%, Aldrich), 2-aminoethanethiol (99%, J&K chemical), monomethyl poly(ethylene glycol) acrylate (mPEG<sub>9</sub>-AA,  $M_n=480$ , Aldrich), hydrogen peroxide (31%, Adamas) and isobutyryl chloride (98%, Aladdin) were used as received. All the solvents, including tetrahydrofuran (THF), *N,N'*-dimethylformamide (DMF), acetone and diethyl ether, were analytic reagents from Titan Regent Co. Ltd., and used without further purification. Deionized water was obtained from a Millipore water purification system. The dialysis bags (Membracel, 3500 Dalton cut off) was provided by Serva Electrophoresis GmbH.

### Synthesis of HPAzoBAHB-*star*-PEG<sub>9</sub>

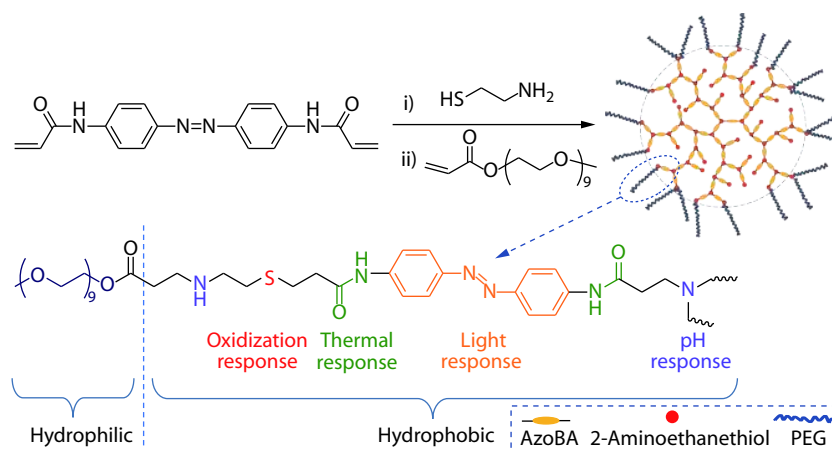
As shown in Scheme S1 (in ESI), AzoBA was synthesized according to previously reported strategy<sup>[19]</sup> and characterized by <sup>1</sup>H-NMR. Next, 2-aminoethanethiol (240 mg, 3.12 mmol) in 4 mL of anhydrous DMF was stepwise added into 6 mL of AzoBA (1.0 g, 3.12 mmol) anhydrous DMF solution under vigorous stirring and kept at 30 °C for 48 h, 40 °C for the next 12 h. 5 mL of the solution was precipitated and washed with acetone before dried under vacuum to obtain HPAzoBAHB for characterization. The rest solution was added with mPEG<sub>9</sub>-AA (170 μL, 0.39 mmol) and vigorously stirred for another 24 h at 40 °C before being precipitated in diethyl ether. The sediment was washed with diethyl ether for three times and then vacuum dried to obtain HPAzoBAHB-*star*-PEG<sub>9</sub>.

### Self-assembly of HPAzoBAHB-*star*-PEG<sub>9</sub>

HPAzoBAHB-*star*-PEG<sub>9</sub> was first dissolved in DMF with an initial concentration of 1 mg·mL<sup>-1</sup>. The same volume of deionized water was added into the solution at the rate of 1 mL·h<sup>-1</sup> under slow stirring. Then, excess water was poured into the mixture to quench the morphology. The aggregate solution was obtained by dialysis against deionized water after 72 h. The obtained solutions were left for at least 72 h before characterization.

### Study of Light, Temperature, pH and Oxidation Responsibility

To study the isomerization of HPAzoBAHB-*star*-PEG<sub>9</sub>, its DMF solution and the micelle solution were irradiated by 365 nm (for *trans*-*cis*) and 450 nm (for *cis*-*trans*) light from Uvata UP114 LED lamp with the intensity of 129 mW·cm<sup>-2</sup>. For the temperature sensitivity studies, the micelle solutions were kept at a certain temperature (10–25 °C) for at least 24 h before the



**Scheme 1** HPAzoBAHB-*star*-PEG<sub>9</sub> and its responsive units.

measurements. To investigate the pH sensitivity, 3.6 mL of HCl aqueous solutions with different pH values were added into 0.4 mL of aggregate solutions, respectively. The final pH value was tuned at 6.0, 4.0, 3.0 and 2.5, respectively. Then the solutions were stirred for at least 24 h at 25 °C before the measurements. To explore the oxidation-responsive behavior, H<sub>2</sub>O<sub>2</sub> (0.5 mL, 31%) was added into 2.0 mL of aggregate solutions, respectively, and the solutions were stirred for at least 12 h at 25 °C before the measurements.

### Characterization

<sup>1</sup>H-NMR and quantitative <sup>13</sup>C-NMR spectra were recorded using a MERCURY plus 400 spectrometer (Varian, Inc., USA) at 30 °C in DMSO-d<sub>6</sub>. Tetramethyl silane (TMS) was adopted as the internal standard for the <sup>1</sup>H-NMR studies. The quantitative <sup>13</sup>C-NMR spectra were measured *via* inverse-gated broadband decoupling. The molecular weight and molecular weight distribution were investigated using gel permeation chromatography (GPC) on a PerkinElmer Series 200 system equipped with RI 2414 detector at 50 °C, and DMF was used as the eluent with the flow rate of 1.0 mL·min<sup>-1</sup>. Isobutyryl chloride-capped HPAzoBAHB was used in the GPC investigation to avoid the absorbance of HPAzoBAHB onto the chromatographic column.<sup>[26]</sup> The morphology of the aggregates was observed using transmission electron microscopy (TEM, JEM-1400), operating at an accelerating voltage of 100 kV. Atomic force microscopy (AFM) measurements were performed using a XE-100 system (Park Systems) in air and a Bio Resolve (Bruker) in fluid using the non-contact mode at the setting temperature. Dynamic light scattering (DLS) measurements were performed as previously reported.<sup>[1]</sup>

## RESULTS AND DISCUSSION

All the 18 types of carbon in HPAzoBAHB have been assigned in detail and labeled accordingly in the quantitative <sup>13</sup>C nuclear magnetic resonance (NMR) spectrum (Fig. S1a in ESI).<sup>[24,26]</sup> The carbon signals of C12, C13 and C14 indicate that branched structure was formed successfully. As shown in Fig. S1(a) (in ESI), there are five possible structural units in HPAzoBAHB, including two linear units, two terminal units and one dendritic unit. Generally, degree of branching (DB) can be calculated according to the following equation:<sup>[24]</sup>

$$DB = \frac{\sum D + \sum T}{\sum D + \sum T + \sum L} = \frac{D + T1 + T2}{D + T1 + T2 + L1 + L2} \quad (1)$$

where D, T1, T2, L1 and L2 represent the fractions of dendritic units (D), terminal units (T1 and T2), and linear units (L1 and L2), respectively. The characteristic carbon content of each unit was integrated and labeled in Fig. S1(a) (in ESI), and thus the DB value of HPAzoBAHB was calculated as 0.60.

Fig. S1(b) (in ESI) shows the <sup>1</sup>H-NMR spectra of HPAzoBAHB and HPAzoBAHB-*star*-PEG<sub>9</sub>. <sup>1</sup>H-NMR (HPAzoBAHB, DMSO-d<sub>6</sub>, δ, ppm) 10.50–10.38 (–CONH–), 7.82 (–C<sub>6</sub>H<sub>4</sub>), 3.25 (CH<sub>2</sub>N–), 2.85–2.80 (–COCH<sub>2</sub>CH<sub>2</sub>S–), 2.76 (–COCH<sub>2</sub>CH<sub>2</sub>N–), 2.60 (–CH<sub>2</sub>S–). Comparing with the spectrum of HPAzoBAHB, the emergence of signals at 3.49 ppm (–CH<sub>2</sub>CH<sub>2</sub>O–) in the <sup>1</sup>H-NMR spectrum of HPAzoBAHB-*star*-PEG<sub>9</sub> indicates that the PEG<sub>9</sub> units have been successfully grafted onto HPAzoBAHB. The molecular weight of HPAzoBAHB (capped with isobutyryl chloride) is 9.1×10<sup>3</sup> g·mol<sup>-1</sup> with a polydispersity index (PDI) of 1.55 and that of HPAzoBAHB-*star*-PEG<sub>9</sub> is 1.5×10<sup>4</sup> g·mol<sup>-1</sup> with a PDI of 1.72 (see Fig. S2 and Table S1 in ESI). Therefore, almost 13 PEG<sub>9</sub> arms were grafted onto each HPAzoBAHB core on average.

The TEM observation shows HPAzoBAHB-*star*-PEG<sub>9</sub> preferentially formed leaf-like lamellar micelles with an average length of 340 nm and width of 120 nm (Fig. 1a) at 25 °C. As shown in AFM image (Fig. 1b), the leaf-like lamellar micelles are as thin as *ca.* 6.5 nm. The thickness of the lamellas is strictly the same value, only if they piled up and therefore doubled the thickness (Fig. 1b, curves 1 and 2). The formation of the unusual anisotropic leaf-like lamellar micelle might be driven by order alignment of the azobenzene groups through π-π stacking,<sup>[27–32]</sup> and also appropriate volume fraction of the hydrophilic arms (Fig. 1c).<sup>[33,34]</sup>

The photo-isomerization behavior of HPAzoBAHB-*star*-PEG<sub>9</sub> was investigated by UV-Visible (UV-Vis) spectroscopy and TEM observation. Upon UV irradiation, the *trans*-*cis* isomerization occurred rapidly in HPAzoBAHB-*star*-PEG<sub>9</sub> DMF solution and resulted a remarkable absorbance decline at 378 nm (π-π\* conjugation) and a slight intensity increase at 447 nm (n-π\* conjugation) in the UV-Vis spectra (Fig. 2a). After the isomerization and irradiated by 450 nm light, the *cis*-structured azobenzene was converted into *trans*- and the absorption curve was recovered within 15 s (Fig. S3a in ESI). In contrast, the leaf-like micelles showed an adsorption at 352 nm (Fig. 2b).

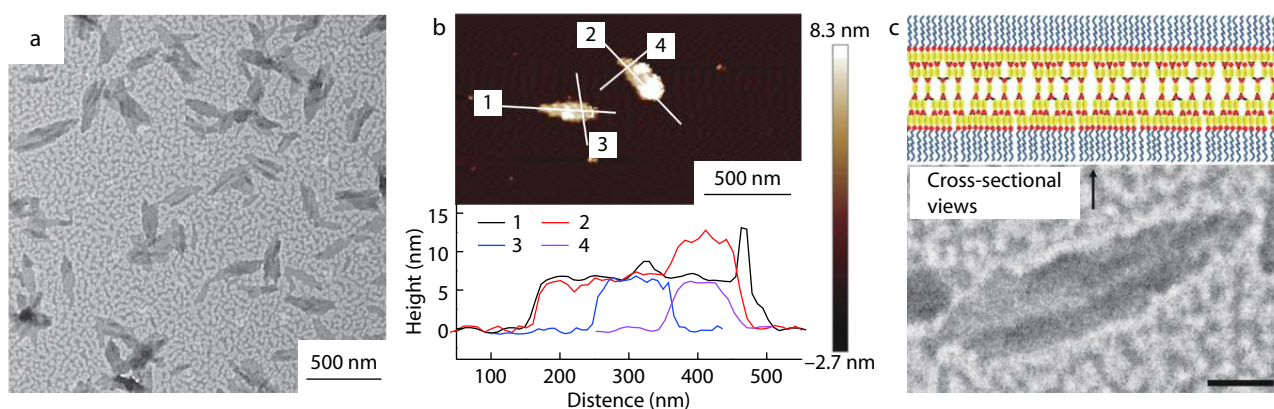


**Fig. 1** (a) TEM image of HPAzoBAHB-*star*-PEG<sub>9</sub> aggregates at 25 °C and (b) the corresponding AFM figure with height profiles; (c) A single leaf-like micelle and the schematic illustrating of the unique anisotropic morphology. The scale bar of the inset in (c) is 100 nm.

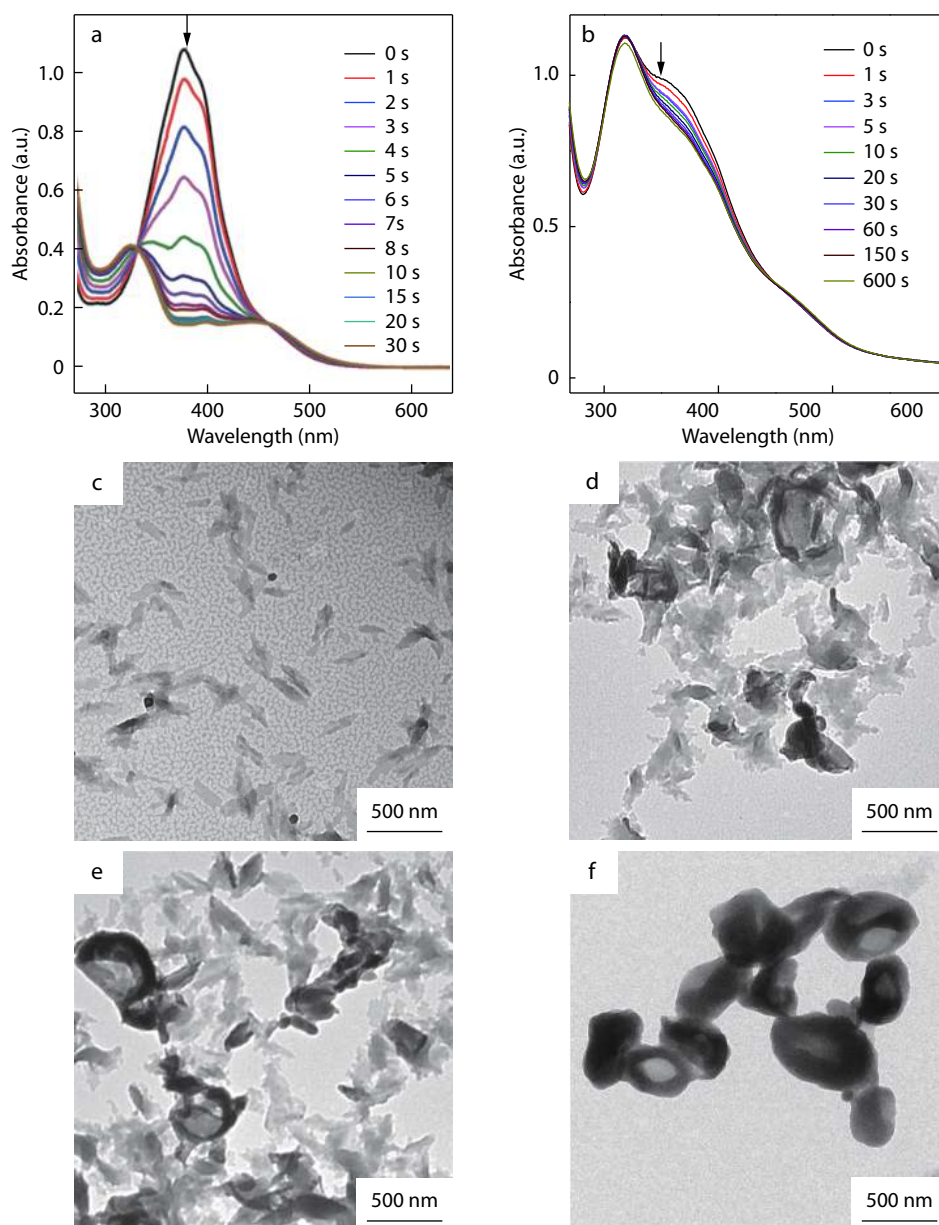


**Fig. 2** UV-Vis spectra of (a) HPAzoBAHB-star-PEG<sub>9</sub> in DMF and (b) HPAzoBAHB-star-PEG<sub>9</sub> aggregates in aqueous solution; TEM images of initial HPAzoBAHB-star-PEG<sub>9</sub> aggregates (c) and upon irradiation with 365 nm light in water for (d) 15 min, (e) 30 min, and (f) 2 h.

The *ca.* 26 nm blue-shift indicates azobenzene were *H*-aggregated in this lamellar assembly, together with appropriate hydrophobic/hydrophilic volume fractions to stabilize the leaf-like morphology.<sup>[35–37]</sup> The absorption at 352 nm showed a slight decline even after UV irradiation for 600 s because the aggregation and arrangement of azo moieties along with light scattering of the assembly hindered the isomerization. TEM observation uncovered that the leaf-like micelles could transform to vesicles (*ca.* 200–500 nm in diameter) upon constant UV light irradiation (Figs. 2c–2f). Herein, only few leaf-like micelles turned into vesicles after 15 min (Fig. 2d), which matches the result of UV-Vis spectra tracking. The amount of vesicles increased with irradiation (Fig. 2e), and finally almost all the lamellar micelles were converted to vesicles with the

diameter of *ca.* 200–500 nm (Fig. 2f). Reasonably, the *trans-cis* isomerization of azobenzene caused the morphological change.<sup>[38–45]</sup> The *cis*-structured azo moieties featured less hydrophobicity, and also destroyed the original ordered arrangement of *H*-aggregate.<sup>[46]</sup> Therefore, HPAzoBAHB-star-PEG<sub>9</sub> self-assembled into vesicles finally (see Scheme S2 in ESI).

As shown in Fig. 3(a), HPAzoBAHB-star-PEG<sub>9</sub> preferentially formed leaf-like lamellar micelles at 25 °C. As the temperature decreased to 15 °C, some of the lamellar micelles transformed into vesicles (Fig. 3b). The leaf-like micelles almost converted to vesicles (300–700 nm in diameter) while the temperature further went down to 10 °C (Fig. 3c). The DLS investigation also recorded the aggregates' size expansion with temperature decrease (Fig. 3d). The wide size distribution at

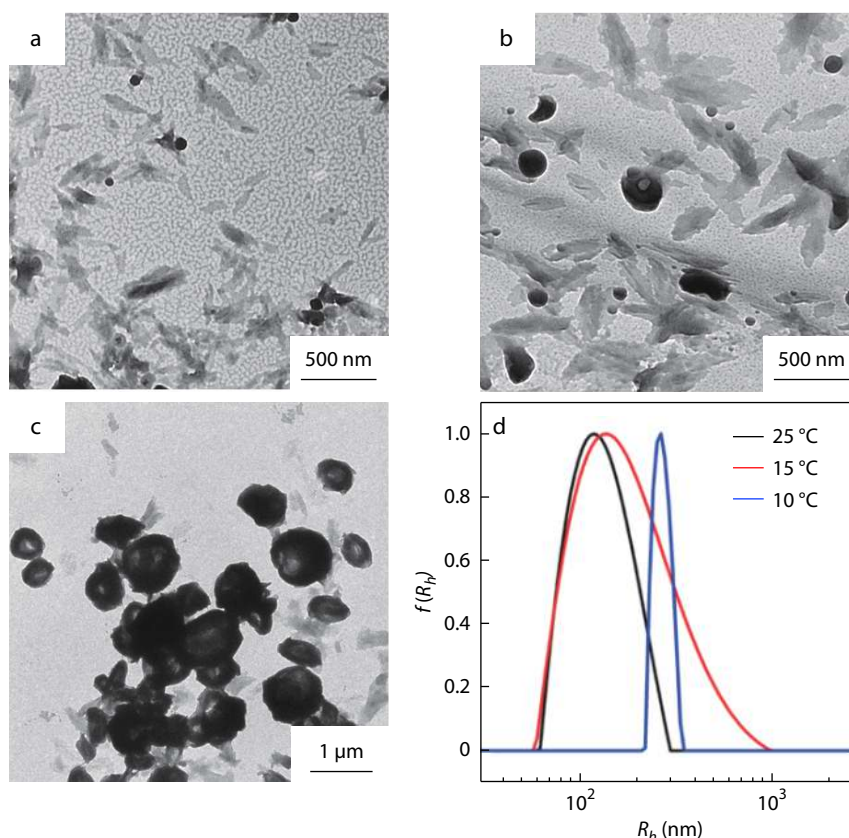


**Fig. 3** TEM images of HPAzoBAHB-*star*-PEG<sub>9</sub> aggregates at (a) 25 °C, (b) 15 °C and (c) 10 °C; (d) Typical hydrodynamic radius distribution of HPAzoBAHB-*star*-PEG<sub>9</sub> aggregates at 25 °C, 15 °C, and 10 °C.

15 °C is attributed to the co-existence of lamellas and vesicles.

The thermal responsiveness of HPAzoBAHB-*star*-PEG<sub>9</sub> derives from abundant acrylamides in its hyperbranched core. As same as most of congeneric polymers, the hydrogen bonds between acrylamides and water enhance the solubility of corresponding sections under lower temperature, and therefore the LCST-depended hydrophilic sections tend to diffuse into the external hydrophilic layers.<sup>[6]</sup> Consequently, the hydrophilic force destroyed the original ordered arrangement of *H*-aggregate, and made the hyperbranched core less hydrophilic to promote the formation of vesicles. As shown in Figs. 4(a), 4(b) and 4(c), the leaf-like lamellar micelles get smaller size and unable to keep their original shape while the pH value decrease. The  $D_h$  to pH value curve of HPAzoBAHB-*star*-PEG<sub>9</sub> aggregates solution (Fig. 4d) also illustrated obvious size reduction that from *ca.* 340 nm (at pH=7.0) to *ca.* 230 nm (at pH=2.5) with the increasing acidity. Herein, HPAzoBAHB-*star*-PEG<sub>9</sub> shows pH-responsiveness because of abundant protonatable amines in its hyperbranched core. The protonated amines turned hydrophilic and strived strongly to combine with water, resulting in the disintegration of leaf-like lamellar micelles and the formation of smaller micelles composed of hydrophobic azobenzene part and hydrophilic PEG/protonated amines part.

Except photo-, thermo- and pH-sensitivity, HPAzoBAHB-*star*-PEG<sub>9</sub> also features oxidation responsiveness. In this study, the original leaf-like lamellar micelles (Fig. 5a) reassembled into much smaller spherical micelles with *ca.* 10 nm

in diameter (Fig. 5b) after treated with hydrogen peroxide because the hydrophobic sulfide moieties in HPAzoBAHB-*star*-PEG<sub>9</sub> were oxidized to hydrophilic sulphone or sulfoxide by H<sub>2</sub>O<sub>2</sub>.<sup>[5,47]</sup> As same as other stimuli-responsiveness of HPAzoBAHB-*star*-PEG<sub>9</sub>, the morphology transformation comes with the destruction of well-arranged azobenzene moieties, in which thermo-, pH- and oxidization stimuli destroy the *H*-aggregate through improving the hydrophilicity of the hyperbranched core, and photo stimuli exert the effect on azobenzene directly.

The quadruple responsiveness makes HPAzoBAHB-*star*-PEG<sub>9</sub> promising for concise delivery and release through subtle stimuli sequences. Herein, we studied the sequential responsive behavior of HPAzoBAHB-*star*-PEG<sub>9</sub> by adopting a simple two-step stimuli strategy. The HPAzoBAHB-*star*-PEG<sub>9</sub> aggregates solution (2 mL) was irradiated with 365 nm UV light for 2 h firstly, and then added with H<sub>2</sub>O<sub>2</sub> (0.5 mL, 31%) and stirred over night at 25 °C in darkness. The TEM observation shows that the original leaf-like lamellar micelles (Fig. 6a) turn into vesicles after UV irradiation (Fig. 6b) as discussed above. However, the vesicles were destroyed into many small pieces with dozens of nanometers in dimension after the oxidation, which differed from the leaf-like lamellar micelles' oxidation (Fig. 5b). The difference could be attributed to that the azobenzene in the hydrophobic part of leaf-like lamellar micelles is *trans*-structured, whereas the vesicles contain the *cis*-styled isomers. Therefore, the oxidation resulted small micelles and pieces, respectively.

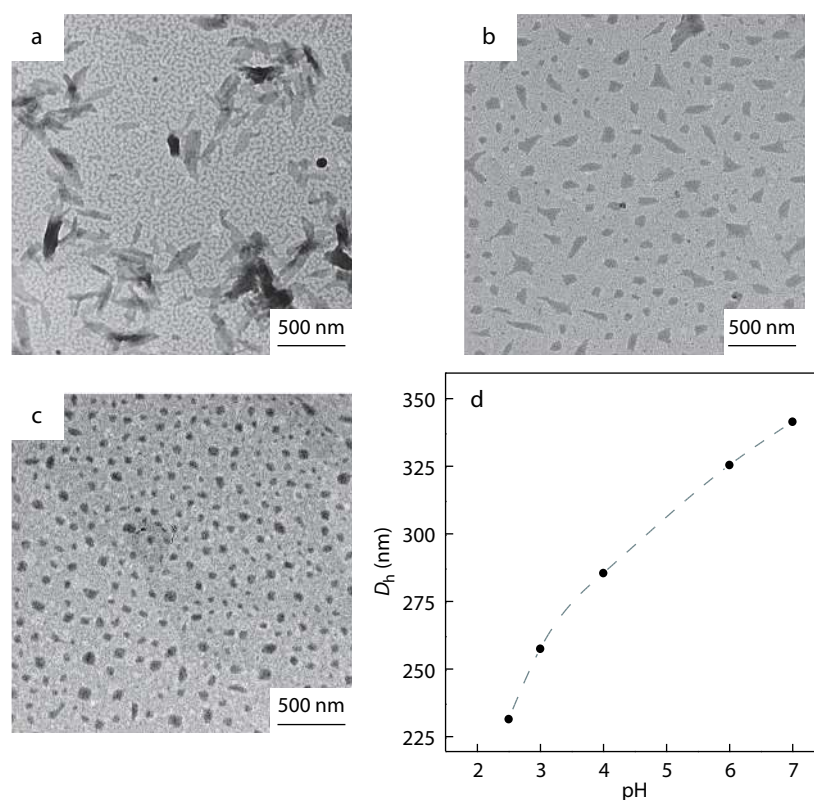


**Fig. 4** TEM images of aggregates at (a) pH=7.0, (b) pH=4.0 and (c) pH=2.5; (d) The plots of  $D_h$  values of HPAzoBAHB-*star*-PEG<sub>9</sub> aggregates solutions at different pH values.

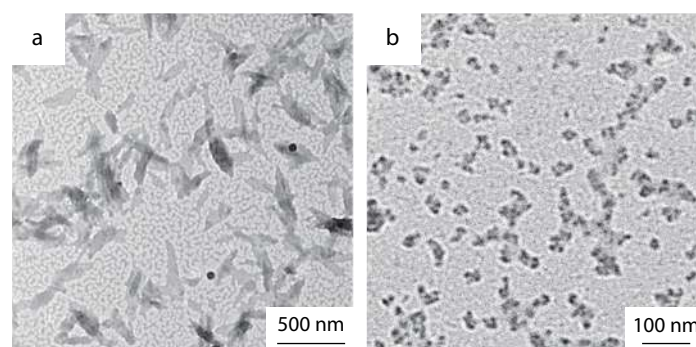


**Fig. 5** TEM images of HPAzoBAHB-*star*-PEG<sub>9</sub> aggregates (a) before and (b) after adding  $H_2O_2$ .

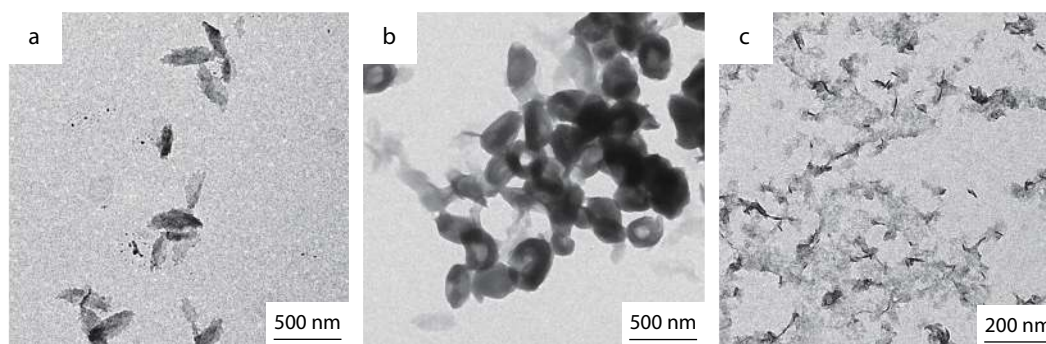


**Fig. 6** TEM images of HPAzoBAHB-*star*-PEG<sub>9</sub> aggregates (a) before UV irradiation and (b) UV irradiation for 2 h, (c) TEM image of HPAzoBAHB-*star*-PEG<sub>9</sub> aggregates after irradiation upon 365 nm light for 2 h and followed by adding  $H_2O_2$ .

## CONCLUSIONS

In summary, we adopted a simple strategy to prepare quadruple responsive hyperbranched polymer HPazo-BAHB-*star*-PEG<sub>9</sub> with temperature, light, pH and oxidation sensitivities. HPazoBAHB-*star*-PEG<sub>9</sub> assembles into unusual leaf-like lamellar micelles in 25 °C because of the order alignment of azobenzene moieties. The lamellar micelles could be transformed into vesicles upon UV irradiation and lower temperature, or converted to smaller spherical micelles in acidic or oxidative environments, respectively. All these responsive processes are derived from the destroy of ordered azobenzene arrangements. This novel quadruple-responsive hyperbranched polymer is promising to construct micro/nanostructures responsive to multiple stimuli, or executing accurate delivery and release following subtle stimuli sequences.

## Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-021-2576-1>.

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