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## Light-triggered reversible "one-to-two" morphological transition in a "latent double-amphiphilic" linear-hyperbranched supramolecular block copolymer‡

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This study reports a new category of stimuli-responsive morphological transitions, *i.e.*, from one morphology (e.g., vesicles) to another two different ones (e.g., nanosheets and nanofibers), by investigating the light-responsive self-assembly behaviour of a "latent doubleamphiphilic" linear-hyperbranched supramolecular block copolymer.

Self-assembly of amphiphilic block copolymers in selective solvents has drawn considerable attention for decades. A charming part of it lies in stimuli-responsive self-assemblies.<sup>1</sup> A phenomenon usually involved is the morphological transition of selfassemblies in response to environmental stimuli. Hitherto, the reported morphological transitions can be divided into two categories (Table 1) based on the transition modes. In category I, morphological transitions take a mode from morphology A to unimers in an irreversible or reversible way. This kind of transition is quite common in the self-assembly of double-hydrophilic block copolymers (DHBCs),<sup>2</sup> amphiphilic block copolymers with blocks connected by dynamic covalent bonds such as disulfide bonds,<sup>3</sup> and dynamic non-covalent bonds such as host-guest interactions.<sup>4</sup> As this process involves only one kind of regular morphology A to its disassemblies of unimers, it can be termed as a "one-to-zero" morphological transition. In category II, one type of self-assemblies (type A) will transit into another type (type B) in an irreversible or reversible way, and the intermediates of [A + B]will sometimes appear during this transition (shown as <sup>①</sup>).<sup>5</sup> For example, O'Reilly and co-workers reported a diblock copolymer of poly(methyl acrylate)-b-poly(N-isopropyl acrylamide) (PMA-b-PNIPAM) underwent a fast and reversible transition from micelles (A) to vesicles (B) by raising the temperature. Much

fewer examples took a more complicated mode: from A to B and then to C with or without intermediates during the transition process (shown as 2).<sup>6</sup> The common characteristic in category II is that there is only one new morphology generated in one transition step, which can be summarized as "one-to-one" morphological transition.

To our knowledge, up to now, the reported stimuli-responsive morphological transitions in block polymer self-assembly are limited to "one-to-zero" and "one-to-one" transitions. Another logically reasonable transition from one (A) morphology to the other two (B plus C) or more morphologies, that is, the transition from "one to two or more" (category III in Table 1) has not been disclosed. Herein, we report for the first time on a lightresponsive "A to (B plus C)" reversible morphological transition from a novel amphiphilic linear-hyperbranched supramolecular block copolymer of polyethylene glycol-b-hyperbranched poly(3ethyl-3-oxetanemethanol) (PEG-b-HBPO). Scheme 1 illustrates the overall transition both from molecular and morphological levels. Initially, two amphiphiles of AZO-PEG (azobenzene terminated PEG) and CD-g-HBPO (β-cyclodextrin grafted HBPO) couple together to form the supramolecular block copolymer of PEG-b-HBPO under visible light. PEG-b-HBPO is amphiphilic and selfassembles into vesicles in water. Under UV irradiation, however, PEG-b-HBPO is conversely dissociated into AZO-PEG and CD-g-HBPO, and meanwhile, the vesicles disappear and transit into a mixture of nanofibers from AZO-PEGs and nanosheets from CD-g-HBPOs. This represents a light-responsive "one to two or more" morphological transition. This transition is totally reversible, and the nanofibers and nanosheets can transit

 
 Table 1
 Stimuli-responsive morphological transition modes in the selfassembly of block copolymers in solvents

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**Scheme 1** Schematic illustration of the overall light-responsive transition of the supramolecular block copolymer of PEG-*b*-HBPO.

back into vesicles again under visible light. Since PEG-*b*-HBPO can transform into two amphiphiles under the light stimulus, we define it as a "latent double amphiphilic" supramolecular block copolymer.

Details about the synthesis and characterizations of linear amphiphile AZO-PEG and hyperbranched amphiphile CD-g-HBPO can be found in the ESI.<sup>†</sup> The CD unit grafted on hyperbranched HBPO retains the capability to host the AZO groups (Fig. S5, ESI<sup>†</sup>). Thus, a linear-hyperbranched supramolecular polymer of PEG*b*-HBPO will be obtained through the AZO/CD complexation between AZO-PEG and CD-g-HBPO.

The host-guest complexation of AZO-PEG and CD-g-HBPO (molar ratio of AZO:CD = 1:1) was induced by adding water dropwise into a DMF solution of them. Dynamic light scattering (DLS) measurements showed a unimodal distribution (Fig. 1a) and a continuous increase of hydrodynamic diameter  $(D_h)$  for the aggregates in solution (Fig. 1b) with a volume percentage ratio of water/DMF increasing from 0% to 35%. The change of  $D_{\rm h}$  for the aggregates in Fig. 1b can be divided into two stages.<sup>4a</sup> In the first stage (water/DMF: 0-15%), Dh was increased slightly from 3.1 nm to 5.3 nm. AZO-PEG and CD-g-HBPO are both quite soluble in DMF, and thus the  $D_h$  of 3.1 nm is supposed to represent the size of unimolecular CD-g-HBPOs, which is also supported by the calculation results (ESI<sup> $\dagger$ </sup>). The  $D_h$  of 5.3 nm is equal to the calculated size of the supramolecular polymer of PEG-b-HBPOs (Fig. S7, ESI<sup>+</sup>), which supports the 1:1 host-guest complexation of AZO-PEG and CD-g-HBPO at the water/DMF volume percentage ratio of 15%. In the second stage (water/DMF: 15-35%), a rapid increase of D<sub>h</sub> up to 530 nm was observed, which was attributed to the self-assembly behaviour of the supramolecular PEG-b-HBPOs. Meanwhile the solution turbidity and Tyndall scattering increased gradually, indicating the formation of supramolecular aggregates as well.

The supramolecular aggregates at a water/DMF ratio of 35% (v/v) were dialyzed against water to remove DMF and characterized by size and morphology. The DLS results show that the aggregates have a narrow size distribution with a PDI of 0.013, and the final  $D_{\rm h}$  was kept at around 600 nm (Fig. S8, ESI†).

The scanning electron microscopy (SEM) image (Fig. 2a) suggests the aggregates are spherical particles, and some particles



**Fig. 1** (a) DLS results of AZO-PEG and CD-*g*-HBPO mixed solutions with different water/DMF volume percentage ratios (v/v). (b) Changes in  $D_h$  as a function of water/DMF volume percentage ratios. Insets show the Tyndall scattering of mixed solutions. (c) UV-vis spectra of PEG-*b*-HBPO aqueous solution with different UV irradiation durations ( $\lambda = 365$  nm). Inset shows the magnification of curves at 400–450 nm. (d) Reversible changes of absorbance at  $\lambda = 325$  nm under recycling irradiation of UV and visible light for 24 hours. Insets show photos before and after the vis-UV cycles. (e) DLS plots of PEG-*b*-HBPO aqueous solution with different UV irradiation. (f) The DLS plots of individual AZO-PEG and CD-*g*-HPBO aqueous solution, and their mixtures at different times.

ruptured after freeze-drying under vacuum for a week (insets in Fig. 2a) show their hollow interior, indicating a vesicular structure. The transmission electron microscopy (TEM) image of the samples stained with uranyl acetate clearly shows the particles possess a structure of an inner pool and an outer black thin wall, which further supports that they are unilamellar vesicles (Fig. 2b and ESI<sup>+</sup>). In addition, some intermediates of particles with holes in their membrane, and particles in budding or fusion during the TEM observations further support that the self-assemblies are vesicles (Fig. S9a and b, ESI<sup>†</sup>). The thickness of the vesicle membranes is around 10 nm according to the TEM (Fig. 2b and Fig. S9c, ESI<sup>+</sup>), and atomic force microscopic (AFM) (Fig. S9d, ESI<sup>+</sup>) measurements. Since the molecular size of PEG-b-HBPO is around 5 nm estimated from the DLS result as well as the calculation (Fig. S7, ESI<sup>+</sup>), the vesicles are supposed to possess a bilayer structure. In addition, the vesicles have a core shell structure consisting of hydrophobic HBPO cores and hydrophilic PEG shells according to the <sup>1</sup>H NMR measurements (Fig. S10, ESI<sup>†</sup>). Thus, the packing model of PEG-b-HBPOs in the vesicles can be summarized as shown in Scheme 1.



**Fig. 2** (a) SEM image of the PEG-*b*-HBPO self-assemblies. Insets show the ruptured vesicles after freeze-drying for a week. (b) The TEM image of aggregates stained with uranyl acetate. Inset is a magnified particle. (c) SEM images of aggregates in PEG-*b*-HBPO aqueous solution after UV irradiation for 24 hours. (d) SEM images of the CD-*g*-HPBO nanosheets. (e) TEM images of the CD-*g*-HPBO nanosheets. (f) TEM image of AZO-PEG nanofibers stained with uranyl acetate. Scale bar (a–f) = 5, 1, 1, 0.5, 1, 0.5  $\mu$ m, respectively.

The average size of the vesicles is calculated to be  $630 \pm 90$  nm by randomly measuring 123 particles in the SEM images and  $615 \pm 72$  nm by measuring 88 particles in the TEM images. The sizes calculated from the SEM and TEM images agree well with the DLS data ( $D_{\rm h} \sim 600$  nm). Interestingly, these vesicles in a concentrated solution could further aggregate into 3D colloidal crystal-like close-packed arrays (Fig. S11, ESI†) during the freeze drying process due to the narrow size distribution. Colloidal crystal-like structures have been widely observed in the self-assembly of hard monodisperse colloids, however it has been hardly observed in the self-assembly of vesicles.<sup>4a</sup>

As we know, AZO groups can reversibly switch their molecular conformation between *cis*- and *trans*-forms in response to irradiation with UV and visible light, respectively. The *trans*-form matches the size and hydrophobicity of the  $\beta$ -CD's cavity, thus forming the host–guest complex, while the *cis*-form does not. Therefore, the supramolecular PEG-*b*-HBPO is supposed to be disconnected under UV irradiation, leading to the disassembly of the vesicles as a result. The UV-vis spectrum and DLS results prove this deduction. As shown in UV-vis spectrum (Fig. 1c), with an increase in UV irradiation time, the absorbance peak at  $\lambda = 325$  nm,

corresponding to the  $\pi$ - $\pi^*$  transition of the *trans*-AZO groups, is obviously decreased; while the absorbance peak at  $\lambda = 424$  nm, corresponding to the n- $\pi^*$  transition of *cis*-AZO groups, is increased. Such a result was further supported by a quantitative analysis of the UV-triggered isomerization process (Fig. S12, ESI†). When exposed to visible light for 24 h, the *cis*-AZO groups were transferred back to the *trans*-form again, accompanied with an increase of the absorbance peak for *trans*-AZO at  $\lambda = 325$  nm (Fig. 1d). Furthermore, the absorbance peak for *trans*-AZO was decreased again when the vesicle solution was further exposed to UV irradiation for another 24 h. This process is reversible and can be repeated for several cycles. Herein, a duration of 24 h was selected for the UV and Vis irradiation in order to ensure the complete light-responsive isomerization for the AZO groups.

The disassembly process during the trans-to-cis transition was also monitored. Firstly, a phenomenon should be noticed that after UV irradiation, the solution still exhibited Tyndall scattering, indicating that there were still nanoscaled objects present. Secondly, as shown in the DLS measurements, before UV irradiation, only one peak for vesicles with a  $D_{\rm h} \sim 600$  nm was observed; after UV irradiation for two hours, the peak at  $D_{\rm h} \sim 600$  nm disappeared and two new peaks appeared; after UV irradiation for 12 h, two peaks at  $D_{\rm h} \sim 300$  nm and  $D_{\rm h} > 1$  µm were formed (Fig. 1e). These two peaks were kept consistent with extending the irradiation time further. The DLS results might suggest that the vesicles were disassembled into two other supramolecular structures under UV light. To prove it, samples were taken out immediately after UV irradiation for 24 h and then freeze-dried for SEM and TEM examinations. A mixture of fibrous and sheetlike aggregates were observed (Fig. 2c and Fig. S13a, ESI†), while spherical vesicles totally disappeared. Interestingly, after subsequent exposure to visible light for 24 hours, the nanofibers and nanosheets disappeared and vesicles were re-formed again (Fig. S13b and c, ESI<sup>†</sup>).

In short, the self-assembly of supramolecular PEG-b-HBPOs undergoes an unprecedented reversible "one to two" (i.e., "vesicles to nanofibers plus nanosheets") morphological transition under UV/vis stimuli. So, what is the mechanism for this special transition? To address it, the disassembly process of PEG-b-HBPOs in a molecular scale should be considered. As mentioned above, PEG-b-HBPOs will be disassociated into AZO-PEGs and CD-g-HBPOs under UV light. So, the self-assembly behaviours of AZO-PEGs and CD-g-HBPOs must be investigated. In fact, both AZO-PEG and CD-g-HBPO are amphiphilic in nature. For AZO-PEG, AZO is a hydrophobic head and PEG is a hydrophilic tail; while HBPO is hydrophobic and CD is hydrophilic in CD-g-HBPO. According to the SEM and TEM measurements, CD-g-HBPOs self-assembled into irregular nanosheets in aqueous solution (Fig. 2d, e and Fig. S14, ESI<sup>†</sup>). The nanosheets are not uniform in size and have a  $D_{\rm h} \sim 300$  nm according to the DLS data (Fig. 1f). The height of the nanosheets is measured to be 6.1 nm by AFM (Fig. S14c, ESI<sup>†</sup>). Given that the molecule size of CD-g-HBPO is about 3.1 nm (Fig. S7, ESI<sup>†</sup>), almost 1/2 of 6.1 nm, the nanosheets are supposed to possess a bilayer structure. The <sup>1</sup>H NMR measurement by adding D<sub>2</sub>O gradually into DMSO-d<sub>6</sub> solution of CD-g-HBPOs indicates the nanosheets have a hydrophilic corona of CDs and

hydrophobic cores of HBPOs (Fig. S15, ESI<sup>†</sup>). Thus, a possible structure of the nanosheets can be illustrated as shown in Scheme 1. The CD-*g*-HBPO nanosheets are very stable, and could be kept without changes in morphology and size for at least half a year.

AZO-PEGs self-assemble into well-defined long nanofibers of about 10 nm in diameter and micrometers in length according to the TEM and AFM measurements (Fig. 2f and Fig. S16, ESI†), which agrees well with the results of a similar system reported by Li and coworkers.<sup>7</sup> The nanofibers have a  $D_h$  greater than 1 µm in the DLS measurement (Fig. 1f), which has also been observed by others for the micrometer-long nanofibers.<sup>8</sup> The nanofibers are flexible, and they tend to aggregate together to form thicker nanofibers and even nanofiber balls (Fig. S16, ESI†). The <sup>1</sup>H NMR measurements indicate the hydrophobic AZO groups are in the fibre core and hydrophilic PEG chains are stretched outside as the shell (Fig. S17, ESI†). Given that, the AZO-PEG nanofibers should have a molecular packing model as shown in Scheme 1.

Therefore, CD-g-HBPOs and AZO-PEGs self-assemble into nanosheets and nanofibers, respectively. Thus, the disassembly process of PEG-b-HPBOs is much clearer now. The supramolecular polymers of PEG-b-HPBOs disassociated into CD-g-HBPOs and AZO-PEGs under UV irradiation, and then the disassociated CD-g-HBPOs formed nanosheets and AZO-PEGs formed nanofibers, which consists of the UV-triggered "one to two" morphological transition from PEG-b-HPBO vesicles to CD-g-HBPO nanosheets and AZO-PEG nanofibers.

To further prove the reversibility, the reverse self-assembly process by mixing CD-g-HBPO nanosheets and AZO-PEG nanofibers together in water was also studied under visible light. As shown in the DLS results (Fig. 1f), at the beginning there were two peaks with  $D_{\rm h} \sim 300$  nm assigned to the CD-g-HBPO nanosheets and  $D_{\rm h} > 1$  µm assigned to AZO-PEG nanofibers. Then, with the elapse of time these two peaks gradually disappeared and a new peak at  $D_{\rm h} \sim 600$  nm appeared instead. Further TEM measurements show that the aggregates with the  $D_{\rm h} \sim 600$  nm are spherical vesicles (Fig. S18, ESI†). In other words, CD-g-HBPO nanosheets and AZO-PEG nanofibers did transit into vesicles again under visible light.

In summary, herein, we report an unusual supramolecular polymer structure with "latent double amphiphilicity", which shows a new light-responsive "one to two" morphological transition process from vesicles to nanosheets plus nanofibers. The process is reversible under alternating UV and visible light irradiation. It can be induced from the work that the "latent double-amphiphilic" or even "latent multi-amphiphilic" supramolecular polymers are very promising to generate more complex and multiple-state morphology transitions, and then greatly enhance the controllability on the self-assembly structure and dynamics.

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