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A dumbbell-like supramolecular triblock copolymer and its self-assembly of light-responsive vesicles

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

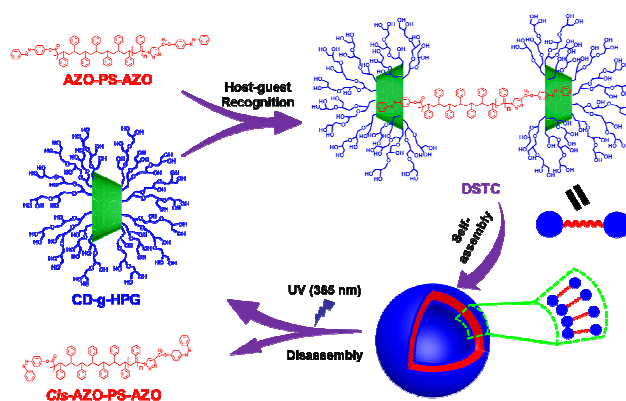
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This work reports the synthesis, self-assembly and light-responsive disassembly of a novel dumbbell-like supramolecular triblock copolymer (DSTC). The DSTC has an amphiphilic hyperbranched-linear-hyperbranched structure and can self-assemble into monolayer vesicles in water. In addition, the vesicles could disassemble into unimers under UV light due to the *trans*-to-*cis* isomerization of the AZO groups.

Recently, supramolecular polymers (SPs) prepared by noncovalent coupling of monomers or polymer segments,¹ have drawn tremendous interest owing to their advantages such as highly dynamic, stimuli responsive and self-adjusting properties over traditional covalent polymers.² The present efforts on SPs are mainly focused on the construction of SPs with different topological structures and functions, as well as their applications in the fields of biochemistry, medicine and material science.³ Various SPs with linear, branched, dendritic or block structures have already been reported up to now.⁴ Dumbbell-like polymer (DLP) is such a kind of polymer with two big “heads” connected by a thin “string”.⁵ There have been several reports on the covalently connected DLPs.⁶ Fréchet and Gitsov have first reported ABA type dumbbell-like linear-dendrimer copolymers.⁷ Kricheldorf and coworkers have reported ABA type dumbbell-like linear-hyperbranched copolymers.⁸ The self-assembly behaviours of covalent amphiphilic DLPs have also been studied.⁹ However, to our knowledge, dumbbell-like SPs have seldom been reported.¹⁰

Herein, in this paper, we report for the first time on the construction of a dumbbell-like supramolecular triblock copolymer (DSTC). As shown in Scheme 1, the DSTC was prepared through noncovalent host-guest coupling between monotelechelic hyperbranched polyglycerol (HPG) grafted from β -cyclodextrin (CD-g-HPG) and ditelechelic azobenzenes-endcapped linear polystyrene (AZO-PS-AZO). Such a “hyperbranched-linear-hyperbranched” DSTC is amphiphilic and can self-assemble into vesicles with a monolayer structure in water under visible light, and the vesicle size depends on the molecular weight of PS block in the DSTC. In addition, the vesicles could disassemble into unimers under the irradiation of UV light.

CD-g-HPG ($M_{n,GPC} = 3,400$ Da, $M_{n,NMR} = 5,300$ Da, $DP_n = 57$, $PDI = 1.29$, $DB = 0.62$) was synthesized according to our previous work



Scheme 1 Preparation, self-assembly and disassembly processes of DSTCs.

(Figures S1-S3, ESI†).^{4f,g} AZO-PS-AZO was prepared by two steps. Firstly, monotelechelic AZO-PS ($M_{n,GPC} = 5,800$ Da, $PDI = 1.20$) was synthesized by atom transfer radical polymerization (ATRP) of styrene with 2-bromo-2-methylpropionic acid-4-phenylazophenol ester (AZO-Br) as the initiator. Secondly, AZO-PS terminated with azide group (AZO-PS-N₃) was reacted with alkyne modified azobenzene (4-propyneoxy-azobenzene, AZO-PP) to get the target ditelechelic polymer of AZO-PS-AZO with two AZO groups at the chain-ends. The detailed synthetic processes of AZO-Br, AZO-PP, AZO-PS, AZO-PS-N₃ and AZO-PS-AZO were summarized in the supporting information (Figures S4-S15 and Table S1, ESI†).

The host-guest complexation ability between the hydrophilic CD-g-HPGs and hydrophobic AZO-PS-AZOs was characterized by UV-Vis titration. A DMF/H₂O mixed solvent (50 v%) and very low polymer concentration (inset of Fig. 1a) were selected for the experiments in order to keep the polymers in a completely unimolecular and soluble state. As shown in Fig. 1a, in the case of keeping the concentration of AZO-PS-AZOs unchanged, the absorption peak at 350 nm ascribed to the characteristic absorption peak of *trans*-AZO increased gradually with the addition of CD-g-HPGs. Such an enhancement of absorbance is attributed to the increase of molar extinction coefficient (ϵ) of *trans*-AZO guests when complexed by CD hosts,¹¹ which supports the occurrence of complexation

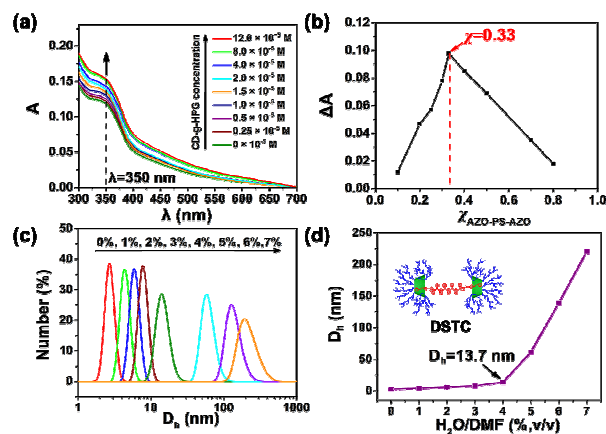


Fig. 1 Complexation and self-assembly of DSTCs. (a) UV-Vis absorption spectra of AZO-PS-AZOs at varied content of CD-g-HPGs in DMF/H₂O (1/1, v/v). The concentration of AZO groups was kept at 1.0×10^{-5} M. (b) A Job plot of AZO-PS-AZOs and CD-g-HPGs in DMF/H₂O (1/1, v/v) mixed solvent. $\chi_{\text{AZO-PS-AZO}}$ is the molar fraction of AZO-PS-AZOs in the mixture of AZO-PS-AZOs and CD-g-HPGs. (c) DLS curves of the mixed solution of CD-g-HPG and AZO-PS-AZO with different water/DMF volume percentage ratios (v/v). (d) Dependence of D_h on the water/DMF volume ratios for CD-g-HPG and AZO-PS-AZO mixtures.

between β -CD groups in CD-g-HPGs and AZO groups in AZO-PS-AZOs. The Benesi-Hildebrand plot was obtained by the quantitative calculation of the absorbance change of AZO groups (ΔA at $\lambda = 350$ nm) in AZO-PS-AZOs versus the concentration of CD groups in CD-g-HPGs (Figure S16, ESI[†]), from which a host-guest CD/AZO complexation constant of 2.81×10^4 M⁻¹ was calculated. To our knowledge, this value is similar with most reported ones,¹² which indicates strong complexation ability between CD-g-HPGs and AZO-PS-AZOs. A Job plot was generated by plotting ΔA at $\lambda = 350$ nm versus the AZO-PS-AZO molar fraction (Fig. 1b), and it was determined that the binding stoichiometry between AZO-PS-AZO and CD-g-HPG is 1:2 ($\chi_{\text{AZO-PS-AZO}} = 0.33$). In other words, the host-guest complexation between AZO-PS-AZOs and CD-g-HPGs did form the target DSTCs as shown in scheme 1.

The obtained DSTCs are amphiphilic, and would undergo self-assembly in water. To prove it, CD-g-HPGs and AZO-PS-AZOs (molar ratio of 2:1) were first dissolved in the cosolvent of DMF, and then water was dropwise added into the solution to induce the self-assembly process. In the dynamic light scattering (DLS) measurements, all the samples had unimodal size distributions (Fig. 1c) and the number-average hydrodynamic diameters (D_h) increased with water content (Fig. 1d). There seemed to be two stages in the D_h versus water content plot (Fig. 1d). In the first stage (water/DMF: 0-4 v%), a small increase of the D_h from 2.8 nm to 13.7 nm was observed. According to our previous work, CD-g-HPG existed as unimers around 2.8 nm.⁴⁸ Meanwhile, the theoretical molecular length of one PS block and DSTC by CPK model of Visual Molecular Dynamics (VMD)¹³ is 10.7 nm and 16.1 nm (Figure S17, ESI[†]), respectively. So the particles with a $D_h = 13.7$ nm should be assigned to the DSTC molecules with some shrinkage or collapse in PS blocks. Therefore, this first stage is attributed to the host-guest

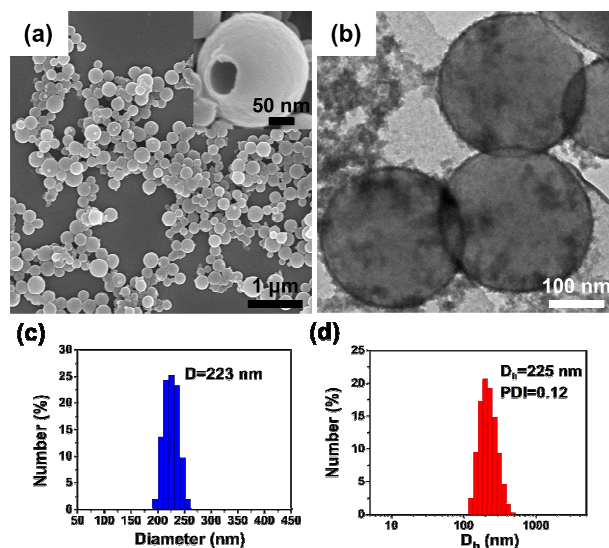


Fig. 2 Characterizations of self-assemblies. (a) The SEM image of the air-dried particles after gold spraying. (b) The TEM image of the particles stained with RuO₄. (c) Statistical analysis of 100 particles from the SEM images. (d) Number-averaged size distribution of the particles in aqueous solution.

complexation process between CD-g-HPGs and AZO-PS-AZOs to form DSTCs. In the second stage (water/DMF: 4-7 v%), the D_h of aggregates in solution increased sharply from 13.7 nm to 220 nm, indicating that the obtained DSTCs further self-assembled into supramolecular aggregates with more water added. Therefore, this stage belongs to the self-assembly stage of DSTCs.

The self-assemblies of DSTCs were carefully characterized by SEM and TEM. To obtain the stable self-assemblies, the polymer solution with a water/DMF volume ratio of 20% (v/v) was dialyzed against water to remove DMF (MWCO: 3,500 Da), and a final opalescent solution with a polymer concentration of 1 mg/mL was obtained. The SEM image in Fig. 2a shows that the self-assemblies are spherical particles with a relatively narrow size distribution. The holes directly seen in some particles (inset of Fig. 2a) indicate that they are vesicles or hollow spheres with a very thin wall thickness. The TEM image of self-assemblies stained with ruthenium tetroxide (RuO₄) in Fig. 2b indicates that the spherical particles are unilamellar vesicles in nature according to a clear contrast difference between the inner pool and the outer thin wall. The vesicle has a wall thickness of around 13.6 ± 0.8 nm through statistical analysis of 30 vesicles from the TEM images. The PS blocks in the vesicles can be selectively stained by RuO₄, which endows the vesicles with good resolution in the TEM measurements. Considering that one DSTC molecule is about 13.7 nm according to the DLS measurements (Fig. 1d), the vesicle should possess a monolayer structure with DSTC molecules spanning the vesicle wall as shown in Scheme 1. The vesicle size through the statistical analysis of 100 particles from the SEM images is around 223 ± 2.6 nm (Fig. 2c), which agrees well with the D_h of the vesicles ($D_h = 225$ nm) through the DLS measurement (Fig. 2d).

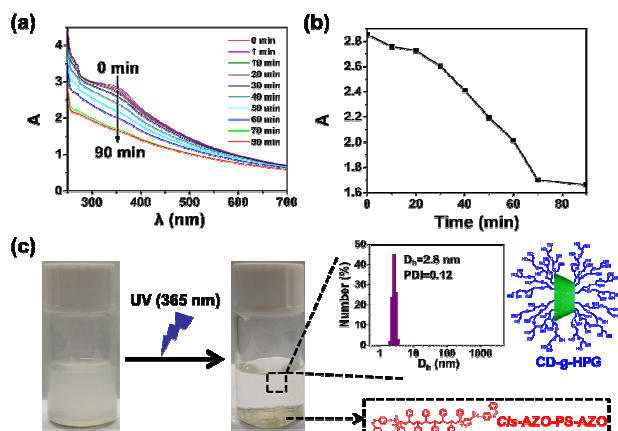


Fig. 3 Disassembly of DSTC vesicles. (a) UV-Vis absorption spectra of the aqueous solution of DSTC vesicles at different UV irradiation time (365 nm, 250 W). (b) Absorbance at $\lambda = 350$ nm as a function of the irradiation time. (c) Digital photos of aqueous vesicle solution before and after UV irradiation. The amplified part of the upper clear liquid shows the number-averaged size distribution of the residual CD-g-HPGs, and the bottom shows the AZO-PS-AZO precipitates.

The polymer vesicles were further collected by dialysis and freeze-drying and then characterized by ^1H NMR measurement in DMF-d_7 . All the proton signals attributed to CD-g-HPGs and AZO-PS-AZOs were observed clearly. In addition, the molar ratio between CD and AZO groups was close to 1:1 (Figure S18, ESI †). These data further prove that the polymer vesicles are composed of DSTCs through the 1:2 complexation between AZO-PS-AZOs and CD-g-HPGs.

The polymer vesicles could undergo disassembly process under UV irradiation. It is well-known that only *trans*-AZO forms host-guest complex with β -CD, whereas *cis*-AZO cannot.¹⁴ Thus, with the continuous UV irradiation on vesicles, the isomerization of AZO groups from *trans*- to *cis*-form occurs, which will certainly lead to disassembly of vesicles. As expected, the absorption peak of *trans*-AZO ($\lambda = 350$ nm) diminished gradually and almost completely disappeared after 90 minutes of UV irradiation (Figs. 3a and 3b). Meanwhile, the solution was transformed from turbid to transparent with a $D_h = 2.8$ nm (Fig. 3c), followed with the appearance of yellow precipitates in the bottom of the bottle. The $D_h = 2.8$ nm is equal to the size of CD-g-HPGs.⁴⁶ In addition, as the further evidence, the residual polymers in the transparent solution was collected by freeze drying and should be attributed to CD-g-HPGs according to the ^1H NMR characterization (Figure S19, ESI †). The precipitates should be the insoluble AZO-PS-AZOs with the AZO groups in the *cis* form (*cis*-AZO-PS-AZOs) according to the ^1H NMR characterization (Figure S20, ESI †). These results proved DSTC vesicles did disassemble into unimers of CD-g-HPGs and AZO-PS-AZOs under UV irradiation. It should be noted that absorption peak at 450 nm ascribed to *cis*-AZO could not be observed during this UV-induced disassembly process (Fig. 3a), which might be due to the precipitation of *cis*-AZO-PS-AZOs.

It was also found the vesicle size depends on the molecular weight of PS block in the DSTC molecule. Generally, vesicle size

increases with the increase of hydrophobic fraction of the vesicle-forming polymers.¹⁵ The same result was found here. When the molecular weight of PS block was increased to 23,000 Da, the vesicle size increased to 556 nm (Figure S21, ESI †) according to the DLS measurement. The reason is that more molecules are needed to stabilize the vesicle if the molecules have a higher hydrophobic fraction, which leads to vesicles with a larger size.

In conclusion, a dumbbell-like supramolecular hyperbranched-linear-hyperbranched triblock copolymer has been prepared through non-covalent host-guest coupling between the monotelechelic CD-functionalized CD-g-HPG and ditelechelic azobenzenes-endcapped AZO-PS-AZO. The obtained supramolecular polymers can self-assemble into vesicles in water, and the size of vesicles increases with the content of hydrophobic PS in DSTCs. Besides, the vesicles have a monolayer structure and can be disassembled under irradiation of UV light (365 nm). The present work will extend the understanding on supramolecular polymers with more complex topologies and intriguing self-assembly behaviours.

The authors thank the National Basic Research Program (2013CB834506), China National Funds for Distinguished Young Scholar (21225420), National Natural Science Foundation of China (2144062, 91127047) and "Shu Guang" project supported by Shanghai Municipal Education commission and Shanghai Education Development Foundation (13SG14) for financial support.

Notes and references

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† Electronic Supplementary Information (ESI) available: Details of synthesis and characterization, and supporting figures composed of ^1H NMR, ^{13}C NMR, GPC, MS, FT-IR results. See DOI: 10.1039/c000000x/

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