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Photocontrolled reversible supramolecular assemblies of a diblock azo-copolymer based on β-cyclodextrin–Azo host–guest inclusion complexation†

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The double hydrophobic block copolymer, poly[6-(4-(phenyldiazenyl)phenoxy)hexyl acrylate]-*b*-polystyrene (PAzo-*b*-PS), was synthesized by reversible addition–fragmentation chain transfer (RAFT) polymerization. This hydrophobic block copolymer can self-assemble into spherical micelles through β-cyclodextrin–azobenzene (β-CD–Azo) host–guest inclusion. Furthermore, the spherical micelles can be dissociated and reassembled by alternating irradiation of UV/visible light. These supramolecular self-assembly and disassembly procedures were studied by dynamic light scattering (DLS), atomic force microscopy (AFM), transmission electron microscopy (TEM) and UV-Vis spectra.

Introduction

Block copolymers in selective solution can self-assemble into various morphologies such as micelles,[1–3] vesicles[4–6] and rods,[7,8] which have attracted much attention because of their potential applications in drug delivery systems, sensor systems, and functional nanomaterials.[9–12] Although a number of works have been devoted to the self-assembly studies of block copolymers in recent years, it is still an attractive subject for scientists to build up the nanoarchitectures with well-defined morphologies and advantageous functions.

Recently, there has been a growing interest in azobenzene (Azo)-containing block copolymers because of their unique reversible photo-isomerization between the *trans*-to-*cis* isomers of the chromophore, which could induce changes in several physicochemical properties such as the size and polarity. Triggered by this photo-responsive property, Azo-containing block polymers are promising for applications in many fields. In particular, the self-assembly behaviours of Azo-containing block copolymers have been well investigated due to their potential applications in drug release systems and smart materials.[13–16] Zhao *et al.* constructed the Azo-containing block copolymers composed of a hydrophilic poly(acrylic acid) (PAA) block and a side-chain liquid crystalline hydrophobic Azo-containing polymethacrylate block, and these block copolymers showed a photo-induced reversible change in the morphology of micellar aggregates.[17] Wang *et al.* found photo-induced mass-migration behavior of two amphiphilic Azo-containing diblock copolymers.[18] Recently, Ji *et al.* observed the self-assembled morphology transitions of Azo-containing amphiphilic block copolymers from spherical vesicle to irregular vesicle transitions by facilely adjusting the chain length of hydrophilic and hydrophobic blocks, and the vesicular morphology was further transformed into micelles and even dissociated by addition of different amounts of β-cyclodextrin (β-CD).[19] However, it is worth noting that all of them were focused on amphiphilic Azo-containing block copolymers. To the best of our knowledge, the self-assembly behaviour of hydrophobic Azo-containing block copolymers in aqueous solution has never been reported.

In the past few years, inclusion complexation between Azo and CD has been widely investigated. CDs are a class of cyclic oligosaccharides with six (α-), seven (β-), or eight (γ-) glucose units linked by 1,4-α-glucosidic bonds.[20,21] CDs have a hydrophobic cavity that can accommodate guest molecules such as adamantane, ferrocene and *trans*-Azo *via* host–guest inclusion complexation.[22–28] The host–guest interaction between CDs and *trans*-Azo is mainly governed by hydrophobic and van der Waals interactions.[29–31] On the other hand, it is very difficult to form an inclusion complex between CDs and *cis*-Azo since they are non-matched host–guest pairs. Therefore, this unique photo-controlled host–guest interaction has been extensively used to construct light-responsive supramolecular assemblies such as micelles,[32,33] vesicles,[29] nanotubes[34] and hydrogels.[35]

Herein, we prepared a series of double hydrophobic Azo-containing diblock copolymers of poly[6-(4-(phenyldiazenyl)phenoxy)hexyl acrylate]-*b*-polystyrene (PAzo-*b*-PS) using reversible addition–fragmentation chain transfer (RAFT) polymerization. PAzo-*b*-PS diblock copolymers can self-assemble into micelles in water through β-CD–Azo host–guest interaction (Scheme 1). The self-assembly behaviour was further studied by dynamic light

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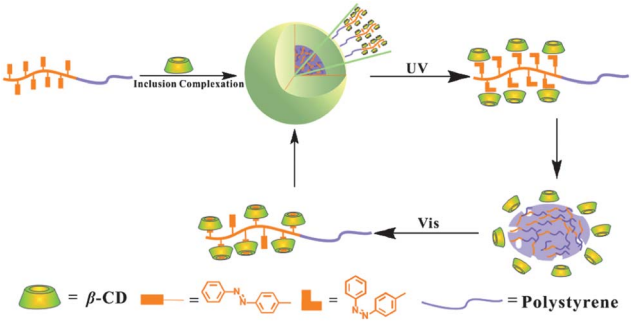

Scheme 1 The formation of PAzo-*b*-PS with β-CD micelles and their reversible photo-responsive self-assembly and disassembly procedures.

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scattering (DLS), atomic force microscopy (AFM), transmission electron microscopy (TEM) and UV-Vis spectra. Their reversible photo-responsive property of self-assembled aggregates was also evaluated by alternating irradiation of UV/visible light.

Experimental

Materials

β-CD (Shanghai Seebio Biotechnology, Inc., China) was recrystallized three times from deionized water. Styrene (Shanghai LingFeng Chemical Reagent Co., China) was washed with an aqueous solution of sodium hydroxide (5 wt%) three times, and then washed with pure water until neutralization. After drying with anhydrous magnesium sulphate overnight, the styrene monomer was obtained by distillation under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN, Shanghai LingFeng Chemical Reagent Co., China) was recrystallized twice from acetone solution. Cumyl dithiobenzoate (CDB) was synthesized according to literature procedures.[36] Details on the preparation of 6-(4-(phenyldiazenyl)phenoxy)hexyl acrylate monomer are given in the ESI.† Unless otherwise mentioned, all other chemicals were obtained commercially and used directly as received.

Characterization

^{1}H-NMR spectra were recorded at 400 MHz, using a BRUKER AV400 Spectrophotometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal reference. The number average weight (M_n) and polydispersity index (PDI) were determined using a gel permeation chromatograph (GPC) equipped with an LC1120 HPLC pump (polymer laboratories, UK), a differential refractive index (DRI) detector (Shodex, RI-101), a 5.0 μm bead-sized guard column (50 × 7.5 mm), and two PLgel 5.0 μm MIXED-C columns (300 × 7.5 mm) in series (Polymer laboratories, UK). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL min^{-1}, and toluene was used as a flow marker. The GPC system was calibrated using polystyrene as the standards. The UV-Vis spectra of the samples were measured over different irradiation time intervals by using a Thermo Scientific Evolution 220 spectrophotometer. Fluorescence spectra were measured on a Thermo Scientific Lumina Fluorescence Spectrometer. Dynamic light scattering (DLS) measurements were carried out on a BECKMAN COULTER Delasa Nano C particle analyser at a fixed angle (165°). All the measurements were carried out at room temperature. AFM observation was carried out on a Veeco's NanoScope III Multimode Atomic Force Microscope by drying a 10 μL droplet of solution onto freshly cleaved mica. Transmission electron microscopy (TEM) analysis was performed on a JEOL JEM1400 electron microscope operated at 100 kV with a carbon coated copper grid. Sample was prepared by dropping the micelle solution onto a carbon-coated copper grid and then dried at room temperature. Irradiation with UV light (365 nm) and visible light (450 nm) of the sample was respectively performed on a 500 W Xe light equipped with 365 nm and 450 nm cutoff filters (E = 2000 mW cm^{-2}, CEL-HXF300/CEL-HXUV300, China), and the distance between the UV-lamp and the sample is about 70 cm.

Synthesis of poly[6-(4-(phenyldiazenyl)phenoxy)hexyl acrylate] (PAzo)

The typical procedure for the synthesis of poly[6-(4-(phenyldiazenyl)phenoxy)hexyl acrylate] *via* RAFT polymerization is described below: 6-(4-(phenyldiazenyl)phenoxy)hexyl acrylate (2.112 g, 6 mmol), AIBN (10 mg, 0.06 mmol), and CDB (30 mg, 0.11 mmol) were dissolved in 8 mL anisole in a 25 mL flask. After purging with nitrogen for 40 min to eliminate the oxygen, the flask was sealed under a nitrogen atmosphere and placed in an oil bath (70 °C) for 24 h. At the end of the reaction, the flask was cooled in ice water and opened. The product was precipitated twice from THF to methanol and dried in a vacuum oven overnight at 50 °C.

Synthesis of poly[6-(4-(phenyldiazenyl)phenoxy)hexyl acrylate]-*b*-polystyrene diblock copolymer (PAzo-*b*-PS)

The PAzo-*b*-PS diblock copolymer was prepared using a similar procedure to that of RAFT polymerization of PAzo, except that PAzo was used as the macro-RAFT agent. Typically, styrene (0.52 g, 5 mmol), PAzo (0.12 g, 0.032 mmol), and AIBN (9 mg, 0.05 mmol) were dissolved in 5 mL 1,4-dioxane in a 25 mL flask. After purging with nitrogen for 40 min to eliminate the oxygen, the flask was sealed under a nitrogen atmosphere and placed in an oil bath (70 °C) to polymerize for 24 h. At the end of the reaction, the flask was cooled in ice water and opened. The product was precipitated twice from THF to methanol and dried in a vacuum oven overnight at 50 °C.

Preparation of the micelle solutions

The PAzo-*b*-PS diblock copolymer was first dissolved in THF to obtain solutions with a concentration of 1 mg mL^{-1}. Then a 0.4 mL PAzo-*b*-PS THF solution was slowly injected into 4 mL of β-CD in water solution (1 : 1 molar ratio compared to the Azo group) at room temperature. The mixture solution was stirred for 30 min at 60 °C to evaporate the THF and sonicated for 5 min to get the micelle solution. Finally, the concentration of the micelle solution was 0.1 mg mL^{-1}.

Results and discussion

Synthesis of Azo-containing diblock copolymers

The Azo-containing diblock copolymer (PAzo-*b*-PS) was synthesized *via* RAFT polymerization as shown in Scheme 2. The PAzo

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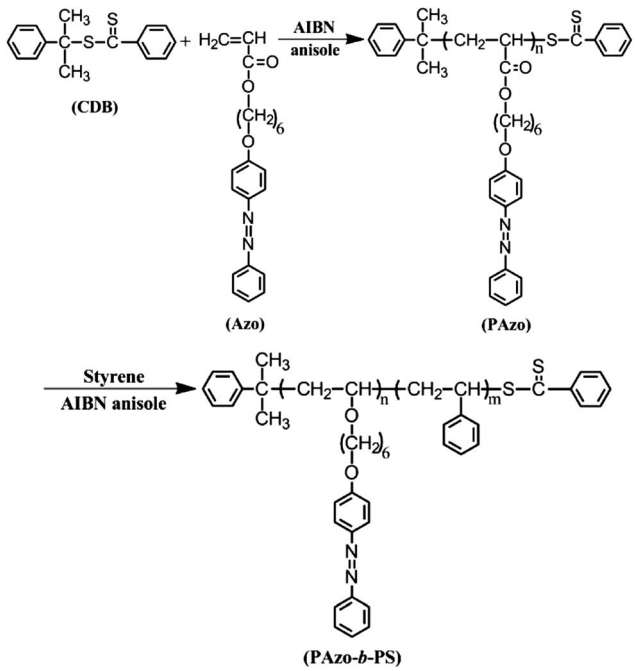

Scheme 2 The synthetic route of the hydrophobic PAzo-*b*-PS diblock copolymer.

homopolymer and PAzo-*b*-PS block copolymers were all successfully synthesized, which were confirmed by GPC and ^{1}H NMR. Fig. 1 shows the GPC traces of the PAzo homopolymer and PAzo-*b*-PS diblock copolymers. The polymerization results are also listed in Table 1. It can be seen that the molecular weights of block copolymers increased with the molar ratio of the styrene monomer to the macro-RAFT agent. Fig. 2 shows the ^{1}H NMR spectra of the PAzo homopolymer and the $PAzo_{10}$-*b*-PS_{130} diblock copolymer in $CDCl_3$. The signals (a, b, c) from 6.92 to 7.85 ppm are assigned to the resonance of the aromatic protons of the Azo group. The resonance signal (d) from 3.94 to 4.06 ppm is ascribed to the methylene group of $-CH_2-O-$ in the

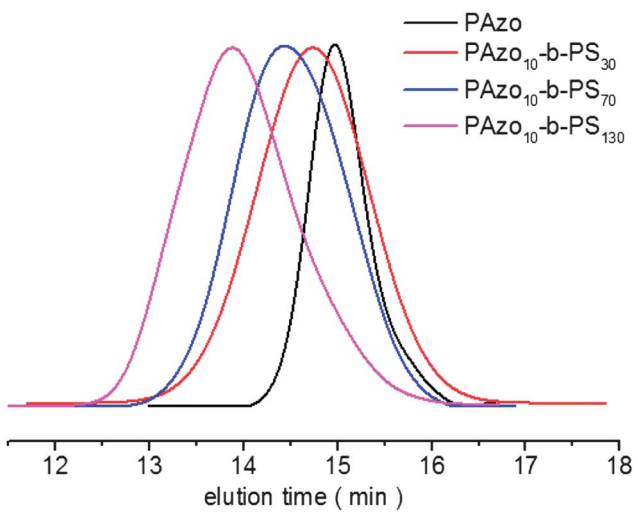

Fig. 1 GPC traces of the PAzo homopolymer and PAzo-*b*-PS diblock copolymers with THF as the eluent.

Table 1 Characterization of the PAzo homopolymer and PAzo-*b*-PS diblock copolymers

Sample	$M_{n,GPC}$ [a]	$M_{n,NMR}$ [b]	M_w/M_n [a]	Wt% (PAzo block)
$PAzo_{10}$	3700	—	1.16	92.6%
$PAzo_{10}$-*b*-PS_{30}	4300	6800	1.48	50.4%
$PAzo_{10}$-*b*-PS_{70}	5900	11 000	1.45	31.2%
$PAzo_{10}$-*b*-PS_{130}	10 300	17 200	1.53	19.9%

[a] The number-average molecular weight ($M_{n,GPC}$) and polydispersities (M_w/M_n) were measured by GPC with PS standards. [b] The number-average molecular weight ($M_{n,NMR}$) was determined by ^{1}H NMR.

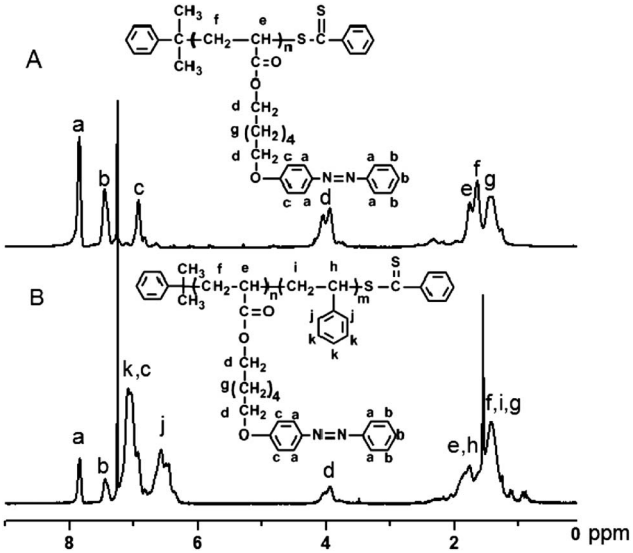

Fig. 2 ^{1}H NMR spectra of (A) the $PAzo_{10}$ and (B) the $PAzo_{10}$-*b*-PS_{70} diblock copolymer.

side chains. The signal (j) from 6.42 to 6.70 ppm corresponds to the aromatic protons of the styrene unit. Therefore, GPC and ^{1}H NMR results indicate that the PAzo-*b*-PS diblock copolymer was successfully synthesized.

Self-assembly of PAzo-*b*-PS with β-CD in water

It is well known that an amphiphilic polymer can self-assemble into micelles in aqueous solution. The morphologies and sizes of the micelles are mainly determined by the block length and the hydrophilic-to-hydrophobic ratio.[6] Here, we converted the hydrophobic PAzo-*b*-PS diblock copolymer into a PAzo-*b*-PS–β-CD complex by host–guest inclusion complexation between β-CD and Azo, after which we carried out their further self-assembly in water. PAzo-*b*-PS diblock copolymers with different molecular weights have been constructed to study the self-assembly behaviour in aqueous solution. Samples were prepared by adding the PAzo-*b*-PS diblock copolymer THF solution into β-CD in aqueous solution with a molar ratio of 1 : 1 (compared to the Azo group) to form PAzo-*b*-PS–β-CD amphiphilic complexes, and the trace of THF in the solution was removed by stirring for 30 min at 60 °C. PAzo-*b*-PS with β-CD can self-assemble to micelles in

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aqueous solution. The critical micelle concentration (CMC) of the amphiphilic complex was measured by using pyrene as a hydrophobic fluorescent probe, since pyrene could be used to estimate the CMC of the β-CD micelle.[37–39] Pyrene will preferentially partition into hydrophobic microdomains showing strong fluorescence intensity while weak fluorescence intensity in water. In addition, the rapid rise in the intensity ratio of peaks at 383 and 371 nm (I_3/I_1) of pyrene in the excitation spectra indicates the formation of micelles. As shown in Fig. 3, the CMC value is determined to be around 0.89 mg L^{-1}, which is rather lower in comparison to those of general amphiphilic block copolymer micelles.[40,41] Further evidence of micelle formation was evaluated by DLS. As shown in Fig. 4, the $PAzo_{10}$-*b*-PS_{70} diblock copolymer with β-CD aggregates into particles of bigger size (D_h = 256 nm, PDI = 0.115) than the aggregates of $PAzo_{10}$-*b*-PS_{30} with β-CD, which has D_h = 212 nm (PDI = 0.128). When the polymerization degree of styrene units increases to 130, the particle size increases around 314 nm (PDI = 0.198). The result indicates the polymerization degree of hydrophobic PS block plays an important role in the size of the aggregates. We also studied the influence of the different molar ratio of β-CD–Azo (from 0.5 : 1 to 5 : 1) on the formation of PAzo-*b*-PS–β-CD micelles, and found that the self-assembled micelle can form even at a low molar ratio of 0.5 : 1 (cyclodextrin–Azo group). Moreover, DLS results showed that the concentration of β-CD has little impact on the size of the micelles (see ESI†). A similar phenomenon was also reported by previous literature.[42,43] In our case, we choose the 1 : 1 molar ratio of the β-CD–Azo group to study the self-assembly behavior. Atomic force microscopy (AFM) was used for the direct visualization of the size and morphology of the micelles. In Fig. 5, it can be seen that the micelles formed from the 0.1 mg mL^{-1} solution of $PAzo_{10}$-*b*-PS_{70}–β-CD complexes have a spherical shape, with sizes in the range of 70–130 nm. The self-assembly micelles of the $PAzo_{10}$-*b*-PS_{70}–β-CD complexes were also observed by TEM. Spherical micelles can clearly be seen in Fig. 6A. The number-average size calculated based on TEM images was in the range of 60–160 nm. However, the sizes of the micelles observed in AFM and TEM are smaller than those obtained from DLS studies. This may be caused by the shrinkage of micelles upon drying procedure. Besides the spherical morphology, the TEM measurements also provide useful information on the self-assembly structure. To observe the structure of the self-assembly spherical micelle in more

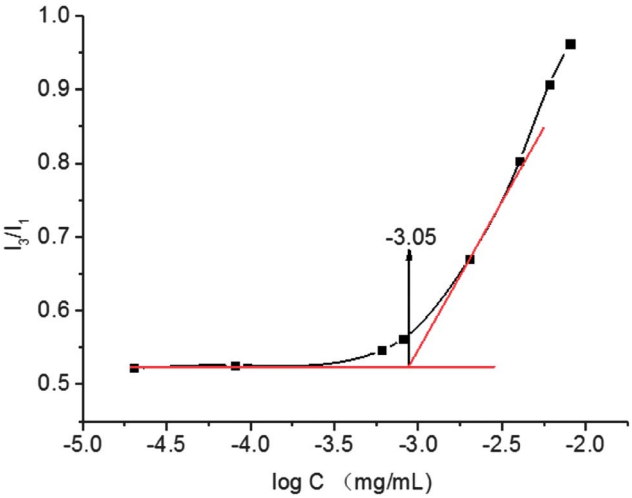

Fig. 3 Plots of the fluorescence intensity ratio I_3/I_1 from pyrene excitation spectra *vs.* the log of concentration (mg mL^{-1}) of $PAzo_{10}$-*b*-PS_{70}–β-CD.

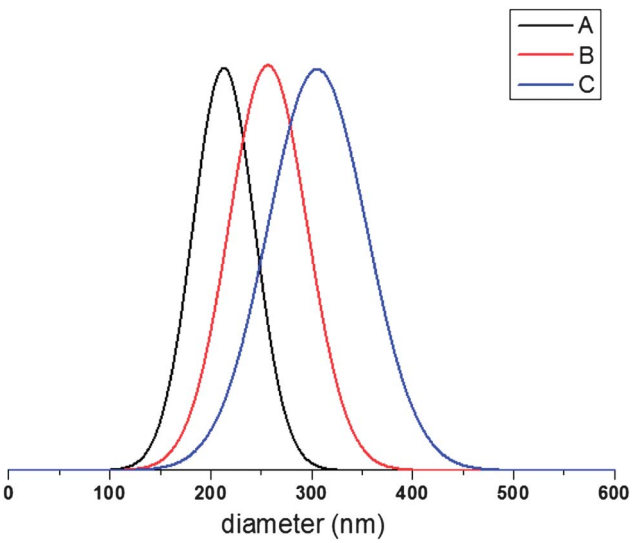

Fig. 4 The size distribution of PAzo-*b*-PS–β-CD complexes in aqueous solution: (A) $PAzo_{10}$-*b*-PS_{30}–β-CD, (B) $PAzo_{10}$-*b*-PS_{70}–β-CD, and (C) $PAzo_{10}$-*b*-PS_{130}–β-CD.

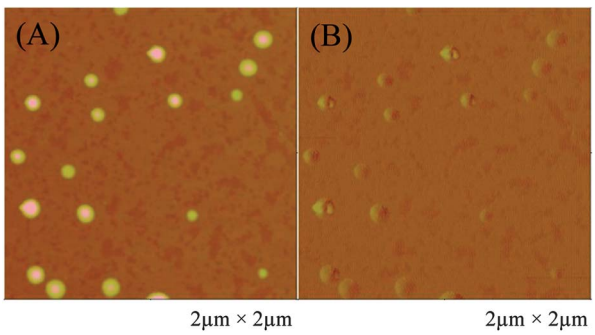

Fig. 5 The AFM images of $PAzo_{10}$-*b*-PS_{70}–β-CD complexes in aqueous solution: height image (A) and phase image (B). The concentration of the sample is 0.1 mg mL^{-1}.

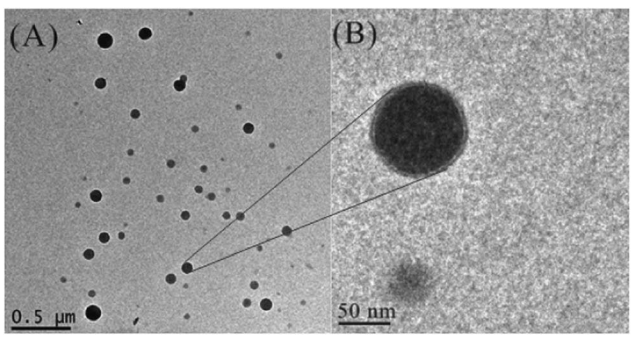

Fig. 6 TEM images of $PAzo_{10}$-*b*-PS_{70}–β-CD complexes (C = 0.1 mg mL^{-1}).

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detail, a single micelle image is enlarged in Fig. 6B. We find that the assembled structure should be a core–shell structure composed of grey shells and black inner cores. In addition, the shell thickness of the micelle was 6 nm, which is larger than the size of a single β-CD molecule. The result indicates that the outer shell is composed of hydrophilic β-cyclodextrin-capped azobenzene parts. Additionally, the micelle core is more than 80 nm, which is larger than those of the extended chain of the $PAzo_{10}$-*b*-PS_{70} copolymer (0.25 nm × DP, *i.e.* 20 nm). Thus the inner core of the micelle should be the aggregation of hydrophobic PS and part of PAzo segments. We have shown the formation mechanism of the micelles in Scheme 1.

Photocontrolled reversible self-assembly and disassembly

Photo-controlled supramolecular self-assembly and disassembly of PAzo-*b*-PS–β-CD complexes in aqueous solution were also investigated. Many studies have reported that *trans*-Azo has a stronger binding affinity in aqueous solution with β-CD while a weaker binding force between *cis*-Azo and β-CD,[44–47] which indicates that the inclusion complexation between β-CD and Azo is reversible by Azo photo-isomerization. Therefore, the self-assembly micelles of PAzo-*b*-PS with β-CD can be disassociated and reassembled under different light irradiation. DLS measurements and TEM were used to study the photo-responsive behavior of the aggregates. As shown in Fig. 7, without irradiation, the Azo-containing $PAzo_{10}$-*b*-PS_{70} diblock copolymer with β-CD could form spherical micelles in aqueous solution with a size of 256 nm (Fig. 8A). After 365 nm UV light irradiation for 30 minutes, the size of the micelles decreased to 223 nm, which also can be clearly observed by TEM. As shown in Fig. 8B, the spherical micelle structure disappeared and particles with irregular shapes formed. After 365 nm UV irradiation, β-CD will leave the *trans*-Azo group of the PAzo-*b*-PS block copolymer because of the photo-isomerization of Azo from the *trans* to the *cis* state. As a result, the hydrophilic–hydrophobic balance of the diblock copolymers has been changed and spherical micelles were dissociated. The subsequent 450 nm visible irradiation (30 min) made the size return to 260 nm and the spherical micelles reassembled again as shown in Fig. 8C. This is because the *cis*-Azo was transformed to *trans*-Azo and the inclusion complexation between β-CD and Azo was rebuilt again. This reversible self-assembly and disassembly process was also traced by UV-Vis spectra. From Fig. 9A we can see that the absorption bands at around 350 nm decreased remarkably with the increase of irradiation time. At the same time, the absorption band at 455 nm slightly increased. The absorption bands at 350 nm are ascribed to the π–π* transition of the *trans* form, and the absorption bands at 455 nm are ascribed to the n–π* transition of the *cis* form of the Azo group. This result indicates the photo-isomerization of the *trans*-Azo group to the *cis*-Azo group. As a result, the *cis*-Azo groups in PAzo-*b*-PS left the β-CD cavities, and spherical micelles were dissociated. With further 450 nm visible light irradiation (Fig. 9B), the absorption band near 350 nm increased again with a slight decrease in the 455 nm absorption band, which indicates that the *cis*-Azo group is transformed to a *trans* state. So, the inclusion complexation of Azo groups and β-CD occurred again and the spherical micelles reassembled. Moreover, this reversible self-assembly and disassembly of the Azo-containing PAzo-*b*-PS diblock copolymers with β-CD complexes can be recycled many times by alternatively irradiating the sample with UV and visible light (Fig. 10). We also

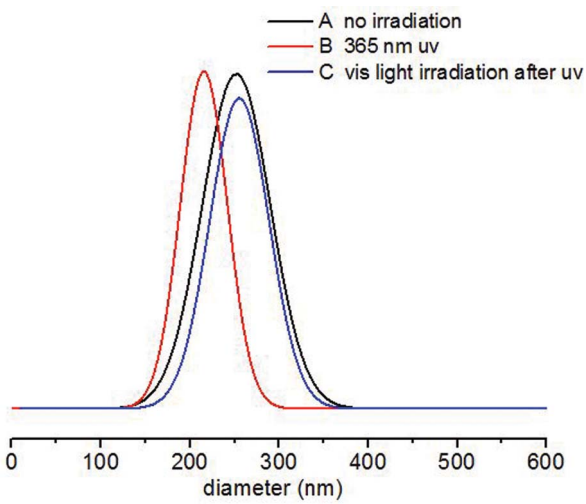

Fig. 7 The size distribution of the $PAzo_{10}$-*b*-PS_{70}–β-CD sample: (A) self-assembled micelles, (B) irregular aggregates after 30 min UV irradiation and (C) reassembled micelles by visible light irradiation after UV irradiation.

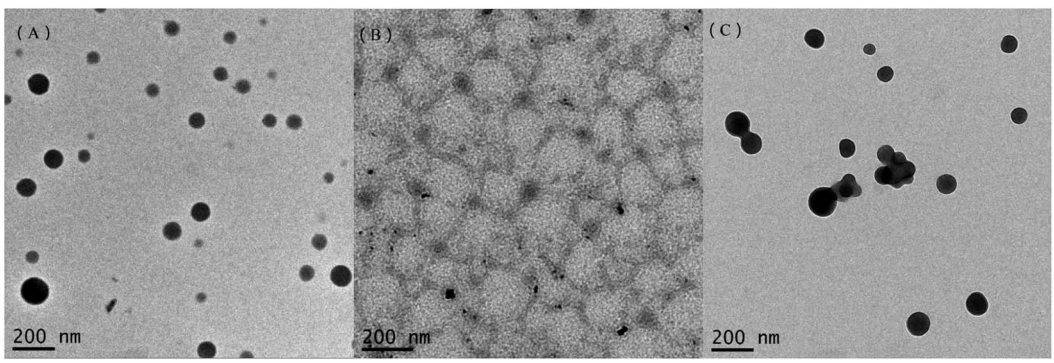

Fig. 8 TEM images of $PAzo_{10}$-*b*-PS_{70} with β-CD at a 1 : 1 molar ratio. The concentration of the sample is at 0.1 mg mL^{-1}: (A) without irradiation; (B) after 365 nm UV irradiation for 30 min and (C) subsequent 450 nm visible light for 30 min.

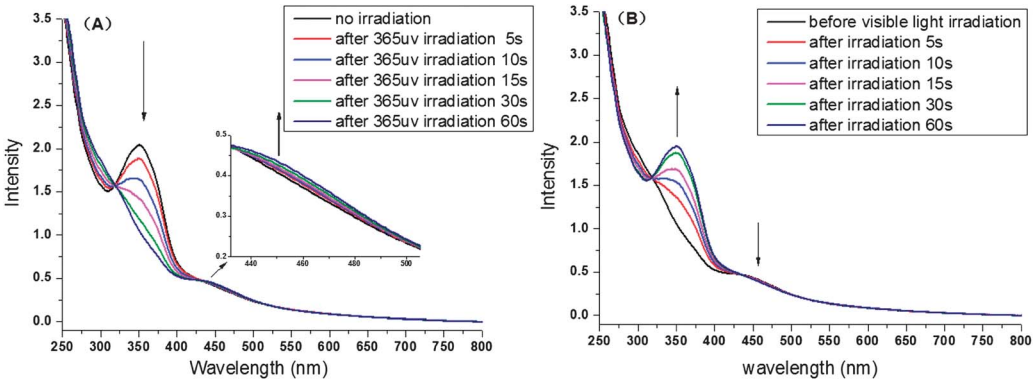

Fig. 9 UV-Vis spectra of the mixtures of $PAzo_{10}$-*b*-PS_{70} and β-CD at a 1 : 1 molar ratio: (A) at 365 nm UV irradiation induced *trans*-to-*cis* transition and (B) 450 nm visible light irradiation induced *cis*-to-*trans* transition. The concentration of the sample is 0.1 mg mL^{-1}.

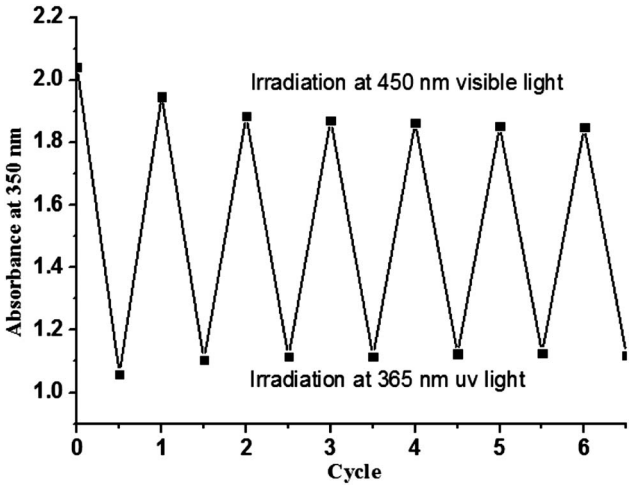

Fig. 10 Photo-isomerization cycles of $PAzo_{10}$-*b*-PS_{70}–β-CD complexes (1 : 1 molar ratio) at 350 nm.

tried to study the self-assembly and disassembly process using NMR (500 MHz). However, we did not get the resonance signal of Azo since the concentration of polymer is very low (0.1 mg mL^{-1}), which is not enough for the NMR characterization.

Conclusions

The double hydrophobic PAzo-*b*-PS block copolymers were synthesized *via* RAFT polymerization. The hydrophobic block copolymers can self-assemble into spherical micelles by the inclusion complexation between β-CD and Azo side groups on the block copolymers. The spherical micelles can be reversibly disassembled and reassembled by alternating UV and visible light irradiation. This non-covalently connected photo-responsive supramolecular assemblies system might have potential applications in many fields.

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