Synthesis, characterization, and photo-responsive properties of Y-shaped amphiphilic azo triblock copolymer

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ABSTRACT: In this study, we report the synthesis, characterization, and photo-responsive properties of a new Y-shaped amphiphilic azo triblock copolymer composed of two isotropic polyethylene glycol (PEG) blocks and an azobenzene liquid crystalline block. The azo block, with two ending groups suitable for the azo coupling reaction, is polymerized by atom transfer radical polymerization with a synthesized initiator containing two functional terminal groups. The macromolecular diazonium salts are prepared by the diazotization of PEG terminated with an amino group. The triblock copolymer is obtained by the azo coupling reaction between the azo block and macromolecular diazonium salts in DMF under mild condition. The intermediates and the obtained triblock copolymer are characterized by ^{1}H NMR, FT-IR, GPC, POM, DSC, TEM, and UV-vis. The photoinduced isomerization behavior of the azo copolymer is investigated by UV-vis. With the addition of water into the solution of the triblock copolymer, spherical aggregates with an average diameter of about 400 nm can be easily obtained. The aggregates are elongated when irradiated with polarized 365 nm UV light. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43695.

INTRODUCTION

Amphiphilic block copolymers consisting of both hydrophilic and hydrophobic blocks can self-assemble in selected solvents to form various polymeric aggregates such as vesicles,[1,2] nanotubes,[3] spherical micelles, and/or colloids.[3–5] On the other hand, the hydrophobic block are usually immiscible in the hydrophilic block, which results in the segregation to form the microphase-separated morphologies.[6,7] The competition and interaction between these two kinds of blocks can result in many interesting micro/nanostructures like cylinders, lamellae, and/or spheres phases with the increasing ratio of one block in volume.[8–10] Making use of these unique properties, the applications of amphiphilic block copolymers as nanoreactors, drug delivery systems, biodiagnostics, nanolithography, ultrahigh-density storage media, and nanoporous membranes have been actively explored.[11–14]

The synthesis of well-defined amphiphilic block copolymers was achieved by the development of living/controlled polymerization techniques, especially by atom transfer radical polymerization (ATRP),[15–17] ring-opening metathesis polymerization (ROMP),[18]

and reversible addition-fragmentation chain transfer polymerization (RAFT).[19] However, in these typical polymerization techniques, macroinitiators and/or macromolecular chain transfer agents are needed to fabricate the final block copolymers, and in some particular cases, the reactivity of the macroinitiators and/or the second monomer is not high enough to form the required block copolymers completely. In recent years, azo coupling reaction between a polymeric block with an anilino ending group and a macromolecular diazonium salt was used to prepare amphiphilic diblock copolymers with high efficiency.[20–23]

Azobenzene and many of its derivatives can alter their configurations from the more stable *trans* configuration to the less stable *cis* configuration upon irradiation with different lights, while the *cis* configuration can get back to the *trans* configuration when another light is used or heated.[24–29] The changing of configuration induced by light can influence both of the surface and bulk properties of these azo materials, such as photo-induced phase transition,[30] photo-induced chromophore orientation,[31–33] photo-induced mass transport,[34–37] etc. Polymers containing azobenzene and/or its derivatives (azo polymers for

short) have also been intensively investigated in recent years owing to the novel properties of the azo chromophores.[38–40] The photo-responsive properties and possible applications of azo polymers include photo-induced dichroism and birefringence and many others.[41–45]

Compared with linear block copolymers, Y-shaped amphiphilic block copolymers possess three building blocks linked with a single junction point, which will lead to interesting self-assembly properties. The incorporation of photo-responsive azobenzene LC block to such Y-shaped amphiphilic block copolymers will bring some attractive properties to the system. In this study, we report the synthesis, characterization, and photo-responsive properties of a new Y-shaped amphiphilic azo triblock copolymer composed of two isotropic PEG blocks (hydrophilic blocks) and an azobenzene LC block (hydrophobic block). The chemical structure, molecular weight, and polydispersity of the block copolymer are characterized by nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR), and gel permeation chromatography (GPC). The mesomorphic properties of the block copolymer are studied by polarized-light optical microscopy (POM) and differential scanning calorimetry (DSC). The photo-induced isomerization of the polymer is investigated by UV-vis spectroscopy. The morphology of self-assembly aggregates is detected by transmission electron microscopy (TEM).

EXPERIMENTAL

Materials

N-ethyl-N-hydroxyethylaniline (97%) and 3,5-dihydroxybenzenemethanol (97%) were purchased from TCI Chemicals (Shanghai, China). 2-Bromoisobutyryl bromide (97%) and 4-aminobenzonitrile (98%) were purchased from Alfa Aesar (Shanghai, China) and used as received. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, 97%) was bought from J&K Chemical (Beijing, China) and used as received. The azobenzene monomer 6-(4-cyano-azobenzene-4′-oxide)-hexyl methacrylate with a double bond suitable for polymerization was synthesized by the previously reported method.[38] Aniline-functionalized PEG (PEG_{43}-NH_2) was prepared according to the literature procedure.[20,21] Deionized water (resistivity >18 MΩ cm) was obtained from a Milli-Q water purification system. Anisole and tetrahydrofuran (THF) were purified by distillation with sodium and benzophenone. All other reagents and solvents were commercially available products and were used as received without further purification.

N-Ethyl-N-(2-chloroethyl)Aniline (1)

Phosphorus oxychloride (8 mL, 80 mmol) was added drop-wise into N-ethyl-N-hydroxyethylaniline (10.0 g, 60 mmol) in an around-bottom flask with ice bath. After the addition, the mixture was heated to 110 °C and the reaction was carried out at this temperature for 3 h. The reaction was diluted with water (adjusting pH to 10 with $NaHCO_3$) and extracted with dichloromethane (DCM). The organic extracts were dried with $MgSO_4$ and evaporated in a vacuum. Yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.23 (t, 2H, Ar H), 6.69 (m, 3H, Ar H), 3.60 (m, 4H, N-CH_2CH_2-Cl), 3.40 (m, 2H, N-CH_2CH_3), 1.17 (t, 3H, -CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 12.6, 40.5, 45.6, 52.6,

112.1, 116.8, 129.6, and 147.0. IR (KBr): $v = 2970$ (s), 1600, 1500 (s), 1340 (s), and 720 cm^{-1} (s).

3,5-Bis[2-ethyl(phenyl)aminoethoxy]benzenemethanol (2)

N-ethyl-N-(2-chloroethyl)aniline (3.7 g, 20 mmol) and 3,5-dihydroxybenzenemethanol (1.4 g, 10 mmol) were added into a mixture of K_2CO_3 (3.6 g, 26 mmol) and KI (1.3 g, 8 mmol) in N,N-dimethylformamide (DMF, 100 mL) with violent stirring. After reacting at 110 °C for 12 h, the mixture was poured into excess of water. The product was extracted from water with DCM (100 mL). The extracts were dried with $MgSO_4$ and concentrated by rotary evaporation. The final product was obtained by silica gel chromatography with a mixture of ethyl acetate and petroleum ether (1:6) as eluting solvent. Yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.22 (m, 4H, Ar H), 6.70 (m, 6H, Ar H), 6.48 (s, 2H, Ar H), 6.34 (s, 1H, Ar H), 4.58 (s, 2H, OH-CH_2), 4.06 (t, 4H, O-CH_2), 3.68 (t- 4H, N-CH_2), 3.45 (m, 6H, N-CH_2), 1.26 (b, 1H, OH), 1.18 (t, 6H, CH_2-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 12.3, 14.2, 21.0, 45.7, 49.7, 60.4, 65.2, 65.5, 100.5, 105.3, 111.9, 116.1, 129.4, 143.5 and 160.2.

3,5-Bis[2-ethyl(phenyl)amino ethoxy]benzene Methyl 2-Bromo-2-Methyl-Propionate (3)

To a CH_2Cl_2 (30 mL) solution of a mixture of 3,5-bis[2-ethyl-(phenyl)aminoethoxy]benzenemethanol (4.3 g, 10 mmol) and triethylamine (6 mL) under ice bath was added 2-bromoisobutyryl bromide (6.9 g, 30 mmol) in 30 mL CH_2Cl_2. The solution was stirred at room temperature overnight. The resulting solution was added CH_2Cl_2 and washed with water, dried over anhydrous $MgSO_4$. After solvent removal, column chromatography (SiO_2, ethyl acetate: petroleum ether = 1:5) was undertaken to afford the product. Yield: 94%. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.23 (m, 4H, Ar H), 6.71 (m, 4H, Ar H), 6.68 (m, 2H, Ar H), 6.50 (s, 2H, Ar H), 6.37 (s, 1H, Ar H), 5.10 (s, 2H, COO-CH_2), 4.07 (t, 4H, O-CH_2), 3.70 (t-4H, N-CH_2), 3.46 (m, 6H, N-CH_2), 1.93 (s, 6H, CH-CH_3), 1.19 (t, 6H, CH_2-CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 12.3, 30.8, 45.7, 49.6, 55.7, 65.6, 67.2, 101.0, 106.4, 111.9, 116.1, 129.4, 137.8, 147.5, 160.1, and 171.4.

6-(4-cyano-azobenzene-4′-oxide)-Hexyl Methacrylate (6-OCN)

6-OCN was prepared according to the literature.[38] ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.94 (m, 4H, Ar H), 7.79 (d, 2H, Ar H), 7.01 (d, 2H, Ar H), 6.11 (s, 1H, C = CH_2), 5.55 (s, 1H, C = CH_2), 4.18 (t, 2H, OCH_2), 4.07 (t, 2H, OCH_2), 1.94 (s, 3H, CH_3), 1.87–1.48 (m, 8H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 18.4, 25.8, 25.8, 64.7, 68.3, 113.2, 123.1, 125.3, 125.6, 133.2, 136.5, 146.8, 154.9, 162.5, and 167.8. IR (KBr): 2940 (s), 2226 (s), 1726 (s), 1632 (s), 1601, 1581, 1500 (s), 1254 cm^{-1} (s). HRMS (ESI, m/z): [M + Na]$^+$ calcd for $C_{22}H_{25}O_3N_3$, 414.1788; found, 414.1786. UV-vis (chloroform): λ_{max} (ε) = 363 nm.

Tosylate Ended Poly(ethylene glycol) (PEG_{43}-Ts)

PEG_{43}-Ts was prepared according to the literature.[20,21] M_n (NMR) = 2.1 × 10^3, M_n (GPC) = 3.7 × 10^3, PDI = 1.07. ^{1}H NMR (600 MHz, d_6-DMSO, δ): 7.78 (d, 2H, Ar H), 7.48 (d, 2H, Ar H), 4.12 (t, 2H, -SO_3-CH_2-), 3.45-3.60 (m, 180H, -O-CH_2-), 3.23 (s, 3H, -O-CH_3), 2.41 (s, 3H, -Ar-CH_3).

Aniline Functionalized PEG (PEG$_{43}$-NH$_2$)

PEG$_{43}$-NH$_2$ was prepared according to the literature.[20,21] M_n (NMR) = 2.1×10^3, M_n (GPC) = 3.7×10^3, and PDI = 1.07. ^{1}H NMR (600 MHz, d_6-DMSO, δ): 7.63 (d, 2H, Ar H), 6.56 (d, 2H, Ar H), 5.96 (s, 2H, -NH$_2$), 4.26 (t, 2H, -COO-CH$_2$-), 3.45-3.60 (m, 180H, -O-CH$_2$-), 3.24 (s, 3H, -O-CH$_3$).

Atom Transfer Radical Polymerization for P6OCN with Dianilino Functionality (P6OCN$_{16}$)

CuBr (57.4 mg, 0.4 mmol) was added into a schlenk flask, and then the flask was degassed and back-filled with nitrogen for three times. After this step, deoxygenated ATRP initiator 3,5-bis(2-ethyl(phenyl)aminoethoxy)benzenemethyl 2-bromo-2-methyl-propionate (0.116 g, 0.2 mmol), azobenzene monomer 6-(4-cyano-azobenzene-4′-oxide)-hexyl methacrylate (6-OCN) (1.56 g, 4 mmol), 1,1,4,7,10,10-hexamethyl-triethylenetetramine (HMTETA) (110 μL, 0.4 mmol) and anisole (2.0 mL) were added. Following the degassing progress by three freeze-pump-thaw cycles, the reaction was immersed into an oil bath preheated to 85 °C. After the polymerization for 3 days, THF was added to dilute the reaction mixture and then the system was passed through an alumina column to remove catalyst. The filtrate was poured into 500 mL of petroleum ether and the precipitate was collected by filtration, then the product was dried in a vacuum oven for a day. The conversion of the monomers was calculated by eq. (1) based on the integration areas of the peaks located at 6.10 ppm ($I_{6.10}$) and 6.91 ppm ($I_{6.91}$), which were corresponding to the vinyl proton on the methacrylate group coming from the residual monomer and the protons on the phenyl group at the *ortho*-position to the ether group coming from the obtained polymer:

$$\text{Conv } (\%) = (1 - 2I_{6.10}/I_{6.91}) \times 100. \tag{1}$$

The conversion estimated by this method was approximately 80% obtained from the ^{1}H NMR analysis, and the corresponding numbers of the repeat unit of P6OCN was 16 according to the feeding ratio. The crude product was purified by washing it with hot ethanol at least for 5 times and dried in a vacuum oven overnight at room temperature. GPC: $M_n = 1.0 \times 10^4$, and PDI = 1.26. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.81 (m, Ar H), 7.68 (m, Ar H), 6.91 (m, Ar H), 3.94 (m, -CH$_2$), 2.02–0.91 (m, -CH$_2$, -CH$_3$). IR (KBr): 2940, 2862 (s), 2224 (s), 1728 (s), 1599, 1580, 1500 (s), 1256 cm^{-1} (s). DSC: $T_g = 50.5$ °C, T_{LC-I} = 135.0 °C (cooling). UV-vis (chloroform): λ_{max} (ε) = 363 nm.

Macromolecular Azo Coupling Reaction for Y-Shaped Amphiphilic Block Copolymer (P6OCN$_{16}$-*b*-2PEG$_{43}$)

Precursor azo polymer with dianilino functionality (P6OCN$_{16}$) (0.44 g, 0.04 mmol) was dissolved in DMF (60 mL) at 0 °C. A diazonium salt of PEG$_{43}$-NH$_2$ was prepared by adding the aqueous solution of sodium nitrite (15 mg, 0.2 mmol in 0.5 mL of water) to a mixture of PEG$_{43}$-NH$_2$ (0.44 g, 0.2 mmol, $M_n = 2.1 \times 10^3$), H$_2$O (1.0 mL), and HCl (36%, 0.07 mL). The mixture was stirred at 0 °C for 30 min, and then was added drop-wise into the above DMF solution. The solution of the reaction was stirred at 0 °C for 3 days, after that it was poured into 500 mL water. The precipitate was collected through filtration, purified by washing with water, and then dried in a vacuum oven at room temperature for 24 h. Yield: 90%. GPC: $M_n = 1.8 \times 10^4$,

and PDI = 1.28. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.81 (m, Ar H), 7.68 (m, Ar H), 6.91 (m, Ar H), 3.94 (m, -CH$_2$), 3.63 (m, O-CH$_2$-CH$_2$-O), 2.02–0.91 (m, -CH$_2$, -CH$_3$). IR (KBr): 2941, 2861 (s), 2225 (s), 1728 (s), 1599, 1580, 1500 (s), 1255 cm^{-1} (s). DSC: T_{LC-I} = 135.9 °C, $T_g = 54.5$ °C, $T_C = 31.1$ °C (cooling). UV-vis (chloroform): λ_{max} (ε) = 363 nm.

Spherical Aggregates Preparation

0.90 mg P6OCN$_{16}$-*b*-2PEG$_{43}$ was first dissolved in anhydrous THF (3.0 mL) to form a homogeneous solution at the concentration of 0.3 mg mL^{-1}. The solution was mildly stirred with a magneton, and deionized water (2.0 mL) was added slowly into the solution (2.0 mL) through a syringe pump at a predetermined addition rate (7.2 mL h^{-1}) simultaneously, which gave the aggregates of the triblock copolymer dispersed in the mixture solvent. After that process, excessive of water (10.0 mL) was slowly added into the dispersion of the copolymer to dilute it. The aggregates dispersed in water were finally obtained by evaporating of THF slowly in a dust-free condition at room temperature.

Photo-Induced Shape Deformation

The above prepared aggregates dispersed in water were firstly cast on copper grids, which was coated with a polymer film. Then the aggregates together with the copper grids were dried in a vacuum oven at room temperature for 20 h. After that, the sample was irradiated by polarized light at the wavelength of 365 nm (6 h, LED lamp, 60 mW cm^{-2}) to investigate the photo-induced deformation of the aggregates. The UV light was incident perpendicularly to the surface of the grids under an ambient condition at room temperature. After the irradiation, TEM observation was conducted to detect the shape deformation of the aggregates.

Characterization

^{1}H NMR spectroscopies were obtained on JEOL JNM-ECA600 or JEOL JNM-ECA300 NMR spectrometer with tetramethylsilane (TMS) as the internal standard at ambient temperature in CDCl$_3$ or d_6-DMSO. FT-IR spectra were conducted on a Nicolet 560-IR spectrometer: the samples were mixed with KBr, and then pressed into thin transparent disks. Mass spectra were determined using Thermofisher LTQ system, the samples were dissolved in chloroform. UV-vis spectra of the samples were measured in solution by using the Agilent 8453 UV-vis spectrophotometer. The molecular weights and molecular weight distributions were obtained by using a gel permeation chromatographic (GPC) system equipped with a refractive index (RI) detector (Wyatt Optilab rEX) and a PLgel 5 μm mixed-D column. The measurements were conducted at 35 °C and the molecular weights were calibrated by polystyrene standards. THF was used as the eluent in the flow rate of 1.0 mL min^{-1}. Thermal analyses of the compounds and the polymers were carried out using TA Instruments DSC Q2000 systems with a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. Polarizing microscopic (POM) observations were carried out on a Nikon LV 1000 POL microscope equipped with a Nikon DS-U3 digital sight, Nikon DS-Fi2 CCD camera and a Linkam LTS420E hot stage. TEM images were taken by using a JEOL-JEM-1200EX transmission electron microscope under an accelerating voltage
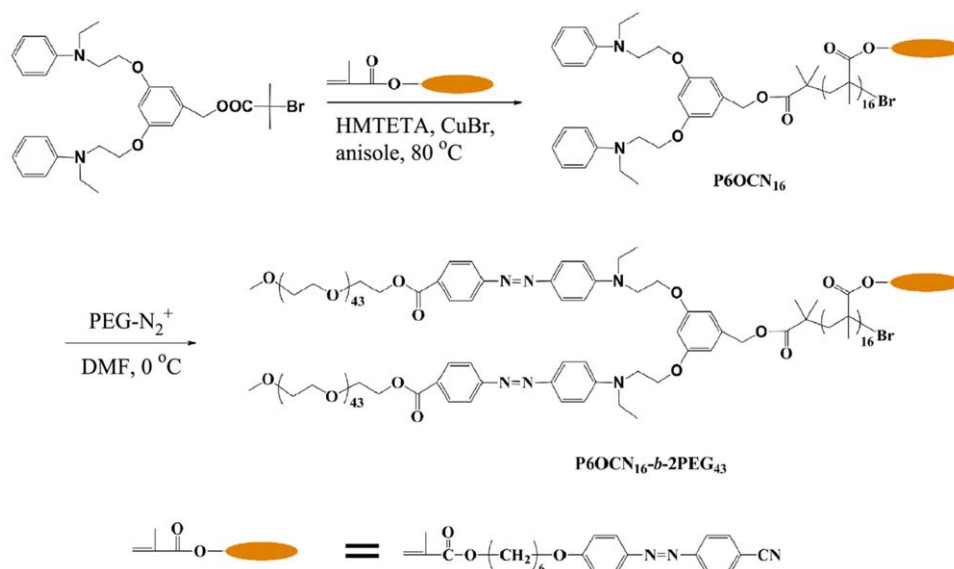
Scheme 1. Synthesis of the amphiphilic azo triblock copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of 120 kV. The samples for TEM observation were prepared by casting the diluted aggregate dispersions of the block copolymer onto the copper grids which was coated with a thin polymer film, then the samples were dried in a 30 °C vacuum oven for 12 h. No staining treatment was conducted for the measurement.

RESULTS AND DISCUSSION

The procedure of the novel Y-shaped amphiphilic azo triblock copolymer prepared by the macromolecular azo coupling reaction is shown in Scheme 1. Firstly, an ATRP initiator with two specific functional groups (N-Ph) is prepared. Then, the precursor azo polymer with dianilino groups (P6OCN$_{16}$) is polymerized through ATRP with the obtained initiator. Finally, the Y-shaped amphiphilic azo triblock copolymer is obtained by the macromolecular azo-coupling reaction between P6OCN$_{16}$ and the diazonium salt of PEG$_{43}$-NH$_2$.

The synthetic route used to prepare the ATRP initiator with two specific functional groups (N-Ph) is shown in Scheme 2, which

includes three reaction steps. In the first step, N-ethyl-N-(2-chloroethyl)aniline is synthesized from N-ethyl-N-hydroxyethylaniline with phosphorus oxychloride. Then 3,5-bis[2-ethyl(phenyl)aminoethoxy]benzenemethanol with dianilino groups is prepared by the nucleophilic substitution reaction between the synthesized N-ethyl-N-(2-chloroethyl)aniline and 3,5-dihydroxybenzenemethanol. Finally, the ATRP initiator 3,5-bis[2-ethyl(phenyl)aminoethoxy]benzenemethyl 2-bromo-2-methyl-propionate is obtained by esterification of the previous intermediate with 2-bromoisobutyryl bromide. Figure 1 shows the ^{1}H NMR spectrum with resonance signal assignments of the newly synthesized ATRP initiator, which confirms that the ATRP initiator is successfully synthesized.

The azobenzene monomer used in this study, 6-(4-cyano-azobenzene-4′-oxide)-hexyl methacrylate is prepared according to the literature method.[38] With the prepared ATRP initiator and monomer, the precursor P6OCN$_{16}$ with two functional groups suitable for the azo coupling reaction is polymerized by ATRP
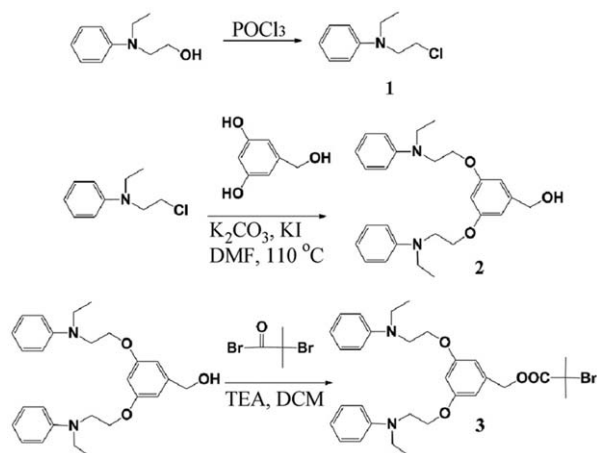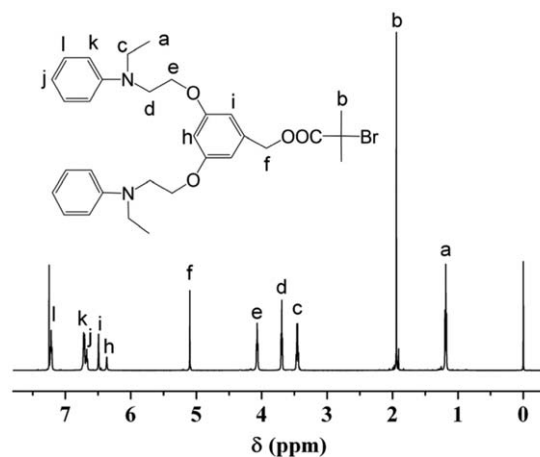

Scheme 2. Synthesis of the ATRP initiator.
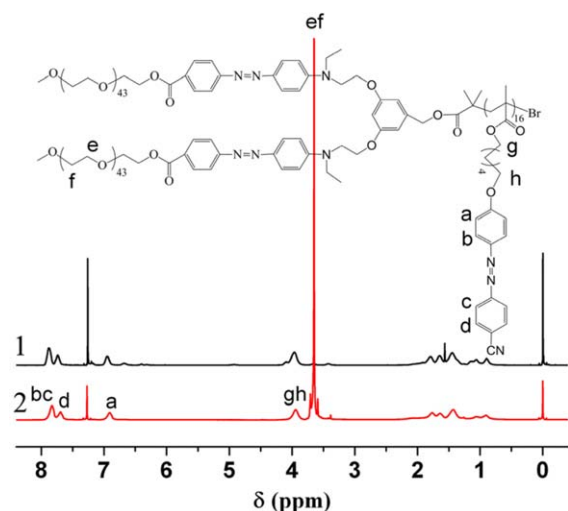

Figure 1. ^{1}H NMR spectrum of the ATRP initiator.

Figure 2. ^{1}H NMR spectra of P6OCN$_{16}$ (line 1) and P6OCN$_{16}$-b-2PEG$_{43}$ (line 2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

according to the literature procedure.[38] The ^{1}H NMR spectrum of the precursor P6OCN$_{16}$ synthesized by ATRP is shown in Figure 2 (line 1). The resonance signals of the spectrum can be readily assigned to the protons of the polymer. Comparing with the spectrum of the azobenzene monomer, the peaks in the low magnetic field range are contributed from the azobenzene chromophores. All of the monomer has been polymerized or washed away as the peaks of the protons of the double bonds from the residual monomer are disappeared. The GPC measurement shows that the ATRP process is well controlled as the PDI of P6OCN$_{16}$ is only 1.26 and the M_n is 1.0×10^4 (Figure 3, line 1).

The aniline-functionalized PEG$_{43}$-NH$_2$ is synthesized according to the literature method.[20,21] The diazonium salt of PEG$_{43}$-NH$_2$ is synthesized by diazotization of PEG$_{43}$-NH$_2$ in the aqueous solution of sodium nitrite and hydrochloric acid. Finally, the macromolecular azo coupling reaction between P6OCN$_{16}$ and the diazonium salt of PEG$_{43}$-NH$_2$ is carried out in DMF under extremely mild conditions. In order to drive the azo coupling reaction to completion, excessive PEG$_{43}$-NH$_2$ is used. PEG can be easily dissolved in water, while the azo containing homopolymer (precursor) P6OCN$_{16}$ prepared by ATRP will be precipitated in water, so that the excess PEG can be easily removed by washing with water.

The ^{1}H NMR spectrum of the amphiphilic azo triblock copolymer P6OCN$_{16}$-b-2PEG$_{43}$ is shown in Figure 2 (line 2). Comparing with P6OCN$_{16}$, similar resonance signals of the protons, coming from the azo block of the polymer, are observed on the ^{1}H NMR spectrum of P6OCN$_{16}$-b-2PEG$_{43}$. In addition, on the ^{1}H NMR spectrum of P6OCN$_{16}$-b-2PEG$_{43}$, the new resonance signal appeared at 3.63 ppm is attributed to the PEG blocks, which confirms the successful reaction between P6OCN$_{16}$ and the diazonium salt of PEG$_{43}$-NH$_2$.

The typical GPC trace of the amphiphilic azo triblock copolymer P6OCN$_{16}$-b-2PEG$_{43}$ is shown in Figure 3 (line 2). Seen

from the figure, GPC trace shows a significant shift towards a higher molecular weight ($M_n = 1.8 \times 10^4$, and PDI = 1.28), after the macromolecular azo coupling reaction. This result demonstrates the formation of the block copolymer linked by azobenzene bridge. Additionally, it is worth noting that no residual mono-block remains after the reaction, indicating that all of the P6OCN$_{16}$ has taken part in the reaction and the excess of PEG has been washed away thoroughly.

According to the spectral feature and isomerization behavior, azo chromophores have been classified into azobenzene type, aminoazobenzene type, and pseudo stilbene type.[46] The azobenzene type, which is the one used in this study, may show liquid crystallinity owing to its structural feature. The liquid crystallinity of the precursor P6OCN$_{16}$ and the triblock copolymer P6OCN$_{16}$-b-2PEG$_{43}$ is studied by POM and DSC after the characterization of the structures of them. For P6OCN$_{16}$, POM observation indicates that the isotropic-LC transition occurs at around 135.0 °C. When cooling from the isotropic phase, batonnet texture appears below that temperature [Figure 4(a)], indicating a smectic phase. After the macromolecular azo-coupling reaction, the obtained copolymer P6OCN$_{16}$-b-2PEG$_{43}$ shows similar texture under POM [Figure 4(b)]. A similar result was also reported before.[38]

The DSC curves of the precursor P6OCN$_{16}$ and the triblock copolymer P6OCN$_{16}$-b-2PEG$_{43}$ on the first cooling scan are shown in Figure 5. P6OCN$_{16}$ shows the glass transition temperature (T_g) at 50.5 °C. An exothermic transition around 135.0 °C (peak value) is observed, which belongs to the isotropic to liquid crystalline transition temperature (T_{I-LC}). After the macromolecular azo-coupling reaction, the obtained triblock copolymer P6OCN$_{16}$-b-2PEG$_{43}$ shows an isotropic to liquid crystalline transition temperature around 135.9 °C (peak value). As PEG cannot form liquid crystals and the melting temperature of the PEG$_{43}$-OH is 53–55 °C, the exothermic peak on the DSC curve of P6OCN$_{16}$-b-2PEG$_{43}$ is coming from the P6OCN block. The value of the liquid crystalline transition temperature of P6OCN$_{16}$-b-2PEG$_{43}$ is around 135.9 °C, which is nearby to that of P6OCN$_{16}$, indicates the strong phase separation between

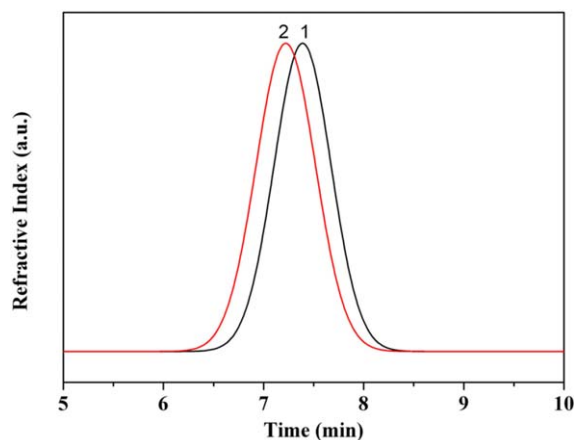**Figure 3.** GPC traces of P6OCN$_{16}$ (line 1) and P6OCN$_{16}$-b-2PEG$_{43}$ (line 2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. Typical polarizing optical micrographs of P6OCN$_{16}$ (a) and P6OCN$_{16}$-b-2PEG$_{43}$ (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
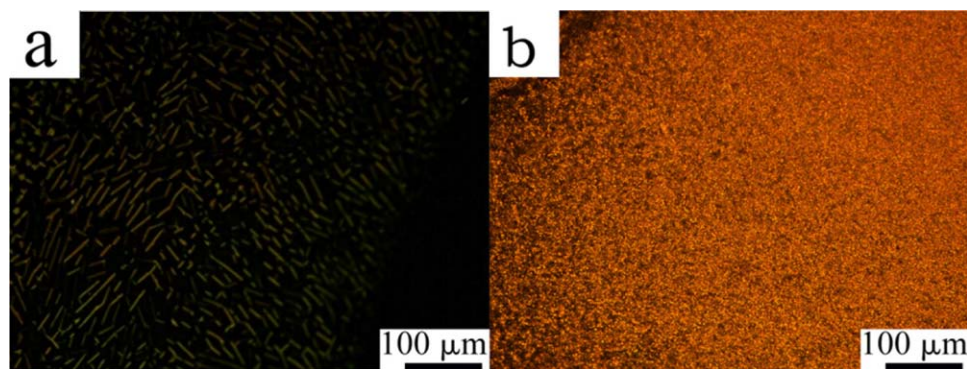
PEG blocks and P6OCN block. Zhu et $al.$[47] reported that the liquid crystalline transition temperature of the diblock copolymer PChEMA$_{50}$-b-PAzoCN$_7$ is lower than that of the homopolymer PChEMA$_{50}$. While the liquid crystalline transition temperature increases with the increase of the length of PAzoCN block, and is even higher than that of the homopolymer PChEMA$_{50}$ when the repeat unit of PAzoCN is higher than 50. Similarly, the liquid crystalline transition temperature of P6OCN$_{16}$-b-2PEG$_{43}$ in this work may be higher than that of the homopolymer P6OCN$_{16}$. In addition, a new crystallization peak on the DSC curve, which is coming from the PEG blocks of P6OCN$_{16}$-b-2PEG$_{43}$, is observed. Due to the strong phase separation between PEG blocks and P6OCN block and the supercooling effect, the crystallization peak of P6OCN$_{16}$-b-2PEG$_{43}$ is centered at 31.1 °C.

The UV-vis spectra of the solution of P6OCN$_{16}$-b-2PEG$_{43}$ irradiated with 365 nm light (1.0 mW cm^{-2}) at different time intervals are shown in Figure 6. It is obvious to see that the max absorption of P6OCN$_{16}$-b-2PEG$_{43}$ is around 363 nm (π–$\pi^\star$ absorption band). Upon irradiating by the light, the absorption intensity at 363 nm decreases while the absorption intensity at 449 nm (n–$\pi^\star$ absorption band) increases gradually. After about 40 s irradiation with the light, the P6OCN$_{16}$-b-2PEG$_{43}$ solution

reaches its photo-stationary state. A similar result was reported before.[22]

The self-assembly of P6OCN$_{16}$-b-2PEG$_{43}$ is studied by adding deionized water into its THF solution. First, homogeneous solution of P6OCN$_{16}$-b-2PEG$_{43}$ (0.3 mg mL^{-1}) is prepared by dissolving it in anhydrous THF. Then, equal volume of deionized water is slowly added through a syringe pump at a predetermined water addition rate (7.2 mL h^{-1}) under mildly stirring, which gives the aggregates of the triblock copolymer dispersed in the mixture solvent. After that, excessive of deionized water is slowly added to dilute it. The aggregates dispersed in water are finally obtained by evaporating of THF slowly in a dust-free condition at room temperature. The aggregates are further cast on copper grids, which was coated with a polymer film, and dried in a vacuum oven at room temperature for 20 h for TEM observation. Figure 7(a) shows the typical image of the spherical aggregates of P6OCN$_{16}$-b-2PEG$_{43}$ with an average diameter of about 400 nm. The formation of the spherical aggregates also confirms the successful preparation of the Y-shaped amphiphilic azo triblock copolymer. The photo-induced deformation of azo aggregates have been well studied. Although the exact mechanism has not yet been fully understand, the photo-induced
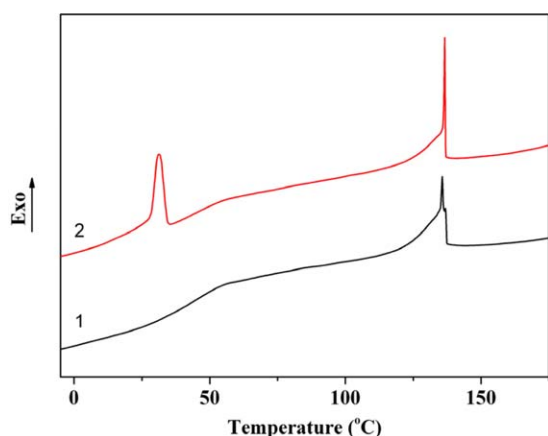

Figure 5. DSC curves of P6OCN$_{16}$ (line 1) and P6OCN$_{16}$-b-2PEG$_{43}$ (line 2) on the first cooling scan. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
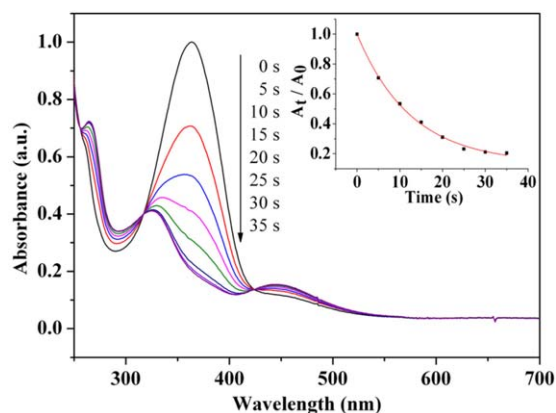

Figure 6. The UV-vis spectra of the solution of P6OCN$_{16}$-b-2PEG$_{43}$ measured after the irradiation with UV light at 365 nm for different time periods. The inset is the relative absorbance at λ_{max} and the corresponding fitted curve. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
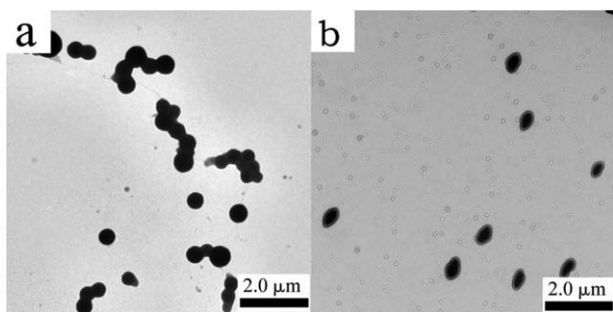
Figure 7. Typical TEM images of the aggregates of P6OCN₁₆-*b*-2PEG₄₃. (a) Original aggregates and (b) irradiated with polarized 365 nm light.

isomerization of azobenzene is believed to play a key role in the light-driven process. In this study, the polarized LED light was used to investigate the photo-induced deformation of the aggregates, the samples are perpendicularly irradiated with 365 nm polarized light (60 mW cm^{-2}). After the irradiation for 6 h, the aggregates are obviously elongated along the polarization direction of the polarizer [Figure 7(b)], with an average major-to-minor axis ratio (l/d) of 1.5 ± 0.3.

CONCLUSIONS

In conclusion, Y-shaped amphiphilic azo triblock copolymer P6OCN$_{16}$-*b*-2PEG$_{43}$ was synthesized by macromolecular azo coupling reaction. The intermediates and P6OCN$_{16}$-*b*-2PEG$_{43}$ were characterized by ^{1}H NMR, FT-IR, GPC, POM, DSC, TEM, and UV-vis. P6OCN$_{16}$-*b*-2PEG$_{43}$ showed a smectic liquid crystalline phase when cooling down from the isotropic state. By irradiating the solution of P6OCN$_{16}$-*b*-2PEG$_{43}$ with UV light, the photo-induced *trans* to *cis* isomerization behavior of the azo triblock copolymer was observed. After the addition of deionized water into the THF solution of P6OCN$_{16}$-*b*-2PEG$_{43}$, spherical aggregates with an average diameter of about 400 nm were obtained. When irradiated with 365 nm polarized light, the aggregates could be obviously elongated along the polarization direction of the irradiation light with axis ratio (l/d) of 1.5 ± 0.3.

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