Supporting Information

Photoresponsive Amphiphilic Block Macrocycles Bearing Azobenzene Side Chains

Lishan Li,[a] Ye Cai,[a] Zhengbiao Zhang,[a] Wei Zhang,[a] Nianchen Zhou,*[a] and Xiulin Zhu*[a]

[a] State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials; Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, P. R. China.

*Corresponding authors. E-mail: nczhou@suda.edu.cn (N. C. Zhou); xlzhu@suda.edu.cn (X. L. Zhu).

Materials. Unless otherwise specified, all chemicals were purchased from Shanghai Chemical Reagent Co. Ltd., Shanghai, China. *Tert*-butyl acrylate (*t*-BA, 99%, Aldrich) was passed twice through basic alumina column to remove inhibitor and then distilled over CaH_2 in vacuum before use. *N, N, N′, N″, N″*-Pentamethyldiethylenetriamine (PMDETA) (98%, Jiangsu Liyang Jiangdian Chemical Factory, China) was dried with 4Å molecular sieves and distilled under vacuum. Copper (I) bromide (CuBr; chemical pure) was purified via washing with acetic acid and ethanol and then dried in vacuum. 4-Vinylbenzyl chloride (4-VBC) was passed twice through neutral alumina column to remove inhibitor. Tetrahydrofuran (THF) (≥99%) was refluxed with sodium and a small amount of benzophenone and distilled. 4-Aminoanisole (analytical reagent). 6-Chlorohexanol (≥98%; Aldrich), propargyl alcohol (≥99%), 2-bromoisobutyryl bromide (≥98%;

Aldrich) and sodium azide (≥ 99.5%; Aldrich), trifluoroacetic acid (TFA) (≥99%; Aldrich) were used as received.

Characterizations. The conventional GPC: the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the polymers were determined using an Agilent PL-50 gel permeation chromatograph (GPC) equipped with refractive-index detector using PL Mixed gel D (5 μm beads size) columns with molecular weights ranging from 200 ~ 4×10^5 g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min and 40 °C. GPC samples were injected using a PL-AS RT autosampler and calibrated with PS standards. Detection of TD-GPC consisted of a RI detector (Optilab rEX), a multi-angle (14-145°) laser light scattering detector (DAWN HELEOS) with the He-Ne light wave length at 658.0 nm, and on-line viscosity detector (viscoSTAR). Three detectors were calibrated with PS standard. THF was used as the eluent at a flow rate of 1.0 mL/min at 35 °C. Three TSK-GEL type columns (pore size 15, 30 and 200Å, with molecular weight range of 100-1000, 300-2000 and 500-400000 g/mol, respectively) with 5 nm bead size were used. The refractive index increment (dn/dc) values were measured offline by using an Optilab rEX refractive index detector (λ=658 nm) at 25 °C, which were conducted in THF at 25 °C with a flow rate of 0.5 mL/min. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian Inova 400 MHz NMR instrument with deuterium chloroform ($CDCl_3$) with tetramethylsilane (TMS) as the internal standard for chemical shifts. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolette-6700 FT-IR spectrometer. Differential scanning calorimetry (DSC) was performed using a TA instruments DSC2010 with a heating/cooling rate of 10 °C min^{-1} from 25 °C to 200 °C under a continuous nitrogen flow. The DSC2010 instrument was calibrated by pure indium for temperature and enthalpy changes. Samples (about 6.00 mg) were crimped in standard aluminum pans. First-order transitions were taken at the maximum point of endothermic or exothermic peaks and the glass transition temperature (T_g) at the midpoint of the heat capacity jump. Elemental analysis of C, H and N were conducted with an EA1110 CHNO-S instrument. The purity of compounds was determined on HPLC (mode 515 high-performance liquid chromatograph, Waters) with a mixed solvent of methanol and water as eluent at the ratio of 80: 20 (v/v) at 30 ^{o}C. Ultraviolet visible (UV-vis) absorption spectra were determined on a Hitachi U-3900 spectrophotometer at room temperature. Transmission electron microscopy (TEM) was recorded on HITACHI HT7700 at a 120 kV accelerating voltage. The size of the micelles aggregates were measured by dynamic light scattering (DLS) using an Malvern Zetasizer Nano-ZS90 at 25 ^{o}C at a scattering angle of 90^{o}. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry measurement was performed using a Bruker Autoflex III (MALDI-TOF) mass spectrometer equipped with a 337 nm nitrogen laser. Both matrix, 4-hydroxy-a-cyanocinnamic acid, and sample were dissolved in 1:1 (v/v) acetonitrile:water with 1% trifuoroacetic acid. This mixture solution (0.5l) was placed on a metal sample plate. The sample was air-dried at ambient temperature.

Synthesis of ATRP Initiator: Propargyl-2-bromoisobutyrate (PBB)

PBB was prepared according to reference.[S1] ^{1}H NMR (400 MHz, $CDCl_3$, δ), (TMS, ppm): 4.81 (s, 2H, $COOCH_2$); 2.50 (s, 1H, C≡CH); 1.96 (s, 6H, $C(CH_3)_2Br$). HPLC measurement indicated that the purity of PBB was above 96 %.

Synthesis of styrene monomer bearing a pendant azobenzene group (BHME)

BHME was prepared according to previous work.[S2] The BHME was characterized by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, δ), (TMS, ppm): 1.45-1.52 (m, 4H, -CH_2CH_2-), 1.60-1.72 (m, 2H, AzoOCH$_2$-C$\underline{H_2}$), 1.78-1.88 (m, 2H, ArOCH$_2$-C$\underline{H_2}$), 3.46-3.50 (m, 2H, -CH_2OAr), 3.89 (s, 3H, -OCH_3), 4.02-4.05 (m, 2H, AzoOCH$_2$), 5.21-5.25 (d, 1H, =CH_2), 5.71-5.33 (d, 1H, =CH_2), 6.66-6.76 (m, 1H, ArCH=), 6.97-7.02 (m, 4H, phenyl), 7.29-7.31 (d, 2H, phenyl), 7.38-7.40 (d, 2H, phenyl), 7.87-7.91 (m, 4H, phenyl)；Elemental analysis: Calculated (%): C 75.65, H 7.26, N 6.30; Found(%): C 75.70, H 7.30, N 6.20. The purity of BHME determined by HPLC was above 96%.

Synthesis of the PBHME with α-alkyne-ω-bromine (Scheme 1)

A typical procedure for the preparation of PBHME with α-alkyne-ω-bromine was as following: BHME (1.13 g, 2.50 mmol), CuBr (12.30 mg， 0.08 mmol), PBB

(18.00 mg，0.08 mmol), and anisole (3.5mL) were added to a 10 mL flask equipped with a magnetic stirrer. The reaction mixture was degassed using two freeze/pump/thaw cycles to eliminate oxygen. Immediately following a 3rd freeze, PMDETA (0.13 mmol, 21.06 mg) was carefully added to the solution, followed by a pump/thaw cycle. Upon thawing, the flask was placed into preheated oil bath maintained at 90 °C for a scheduled time interval. The flask was taken out from oil bath and then cooled by ice-bath and opened. The polymerization mixture was diluted with THF and passed through a column of neutral alumina to remove the metal salt. The polymer were purified by precipitating twice from THF to methanol and dried in a vacuum oven overnight at 40 °C. By feeding different molar ration of $[BHME]_0/[PBB]_0/[CuBr]_0/[PMDETA]_0$, the $PBHME_{10}$ with α-alkyne-ω-bromine was obtained, in which $[BHME]_0/[PBB]_0/[CuBr]_0/[PMDETA]_0$ was 30:1:1:1.5.

Synthesis of *linear*-$PBHME_m$-*b*-P*t*-BA_n-Br

A typical procedure for the preparation was as following: *t*-BA (3.45 mmol, 0.44 g), CuBr (0.08 mmol, 12.30 mg), macro-ATRP initiator, $PBHME_{10}$ (0.08 mmol, 0.37 mg), and anisole (6.00mL) were added to a 10 mL flask. The operation in detail was the same as above mentioned preparation of PBHME. The characterization of the polymers is listed in Table 1.

Synthesis of *linear*-$PBHME_{10}$-*b*-P*t*-BA_3-N_3

Linear-$PBHME_{10}$-*b*-P*t*-BA_3-Br (0.09 mmol, 0.43 g)，NaN_3(0.86 mmol, 0.56 g), and DMF (5 mL) were added into a 50 mL round-bottom flask with a magnetic stirrer, and the reaction mixture was stirred for 24 h at 50 °C. After most of the DMF was extracted by ethyl acetate and water, the solvent was removed in vacuum, and then diluted with THF and precipitated into an excess of methanol. The polymer was obtained by filtration and purified by re-dissolved in THF followed by passing through a neutral alumina column to remove residual sodium salts. The final product was collected and dried for 24 h in a vacuum oven (yield, 99%).

Synthesis of *cyclic*-$PBHME_{10}$-*b*-P*t*-BA_3

A typical synthetic procedure is as follows: DMF (700 mL) was added into a 1000mL three-necked round-bottomed flask with a dynamoelectric stirrer and degassed by bubbling with argon for 5h, and then CuBr (0.15g, 1.04 mmol) and PMDETA (0.27g, 1.56 mmol) were introduced. The *linear*-PBHME$_3$-*b*-P*t*-BA$_3$-N$_3$ (0.15g, 3.00×10^{-2} mmol) in 10.0 mL of DMF was added to into the 1000 mL flask CuBr/PMDETA at 80 °C via a syringe pump at a rate of 0.6 mL/h under the protection of argon. After the addition of polymer solution was completed, the reaction was allowed to proceed for an additional 48 h at 80 °C. The highest weight concentration of the *linear*-PBHME$_m$-*b*-P*t*-BA$_n$-Br in DMF during the ring-closure reaction was adopted as about 2.1×10^{-4}g/mL. The mixture was then cooled to room temperature, and then DMF was removed under reduced pressure. The obtained product was dissolved in THF and then precipitated to an excess methanol. The crude product was respectively purified by using azide- and alkyne-terminated polystyrene resin. The final product was dried in a vacuum oven for 24h (yield: 72.3 %).

Selective hydrolysis of *linear*-PBHME$_{10}$-*b*-P*t*-BA$_3$-N$_3$ and *cyclic*-PBHME$_{10}$-*b*-P*t*-BA$_3$

In a typical procedure, the *linear*-PBHME$_{10}$-*b*-P*t*-BA$_3$-N$_3$ (0.45 g, 0.09 mmol, $M_{n,GPC}$ = 5500 g/mol) were dissolved in 3 mL dichloromethane and treated with excess trifluoroacetic acid (20 times in molar excess relative to the repeat units of *tert*-butyl acrylate in the copolymer) at room temperature for 12 h. The solution was concentrated and precipitated into an excess n-hexane. The product was collected by filtration and dried in a vacuum oven. About 0.43 g of *linear*-PBHME$_{10}$-*b*-PAA$_3$-N$_3$ was obtained.

Self-assembly of the linear-PBHME$_{10}$-b-PAA$_3$-N$_3$ and cyclic-PBHME$_{10}$-b-PAA$_3$ in THF/water solvent.

Self-assembly of the *cyclic*-PBHME$_{10}$-*b*-PAA$_3$ and *linear* precursor was performed by gradually adding water (3ml) to the THF solution of polymers (10 ml) at room temperature. The initial concentrations of both *linear*- and *cyclic*- polymers were 0.20 mg/mL. The water addition was performed using a syringe pump at the rate of 2.5 ml/h. When water addition was completed, the suspensions were stocked for 1 day to stabilize the aggregates. To investigate the effects of photoisomerization of azobenzene on self-assembled behavior, the above obtained aggregates solutions of copolymers were exposed to UV light and then the irradiated solutions were placed in dark until the photo-stationary state of *trans*-to-*cis* and *cis*-to-*trans* was respectively reached.

Estimating of the repeated units of BHME(m) and *t*-BA (n) in the *linear*- and *cyclic*-PBHME$_m$-*b*-PAA$_n$

The numbers of AA unit are supposing to be equal to the *t*-BA unit for the near-quantitative hydrolysis of *t*-BA. The ^{1}H NMR spectra of the PBHME and block copolymers *linear*-PBHME$_{10}$-*b*-*t*-BA$_3$-Br prepared *via* ATRP chain-extension are shown in Figure S1. The average number (m) of BHME units was calculated based on the integral values of protons (b) at 3.3-3.6 ppm and the protons (a,h,k) at 0.8-1.0 ppm. The average number (n) of *t*-BA units of the block copolymer was calculated based on the integral difference between the integral of both protons of BHME and *t*-BA in copolymer (b1) and the integral of BHME units in PBHME (a1) at 1.0-2.4 ppm. The calculation formulas are as followings:

BHME unit (m) = $(I_{(3.3\text{-}3.6)\ \mathrm{PBHME}}/2)/(I_{(0.8\text{-}1.0)\ \mathrm{PBHME}}/6)$ (Formula S1)

t-BA unit (n) = $(I_{(1.0\text{-}2.4)\ linear\text{-}\mathrm{PBHME}\text{-}b\text{-}\mathrm{P}t\text{-}\mathrm{BA\text{-}Br}} - I_{(1.0\text{-}2.4)\ \mathrm{PBHME}})/12$ (Formula S2)

where $I_{3.3\text{-}3.6}$: integral of the protons in PBHME at $_{3.3\text{-}3.6}$ ppm, $I_{0.8\text{-}1.0}$: integral of the protons in PBHME at $_{0.8\text{-}1.0}$ ppm and $I_{1.0\text{-}2.4:}$ integral of the protons both protons of BHME and *t*-BA in copolymer at $_{1.0\text{-}2.4}$ ppm

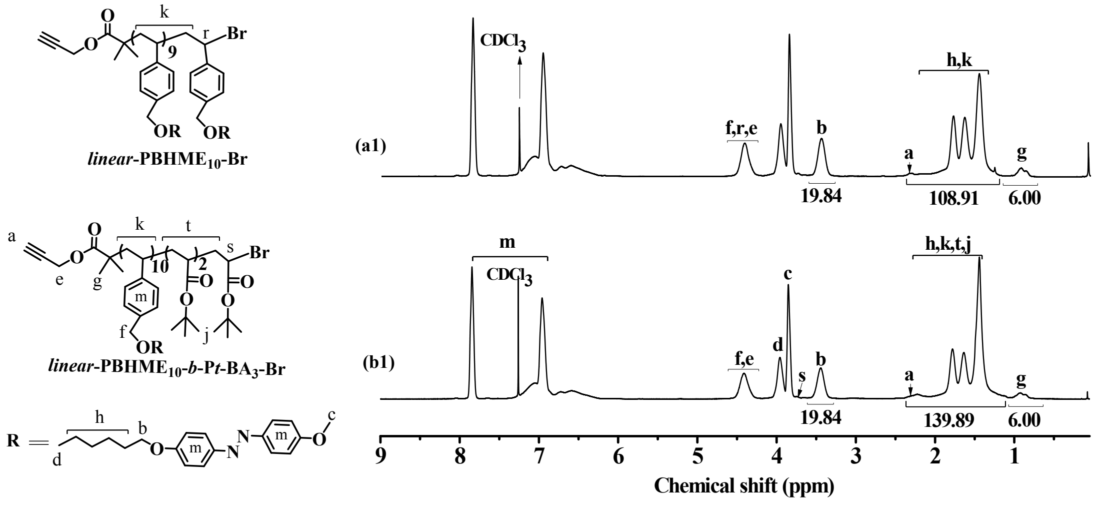

Figure S1. ^{1}H NMR spectra for the $PBHME_{10}$ with α-alkyne-ω-bromine and block copolymer *linear*-$PBHME_{10}$-*b*-*t*-BA_3-Br prepared via ATRP chain-extension using $PBHME_{10}$ as the macro-ATRP initiator

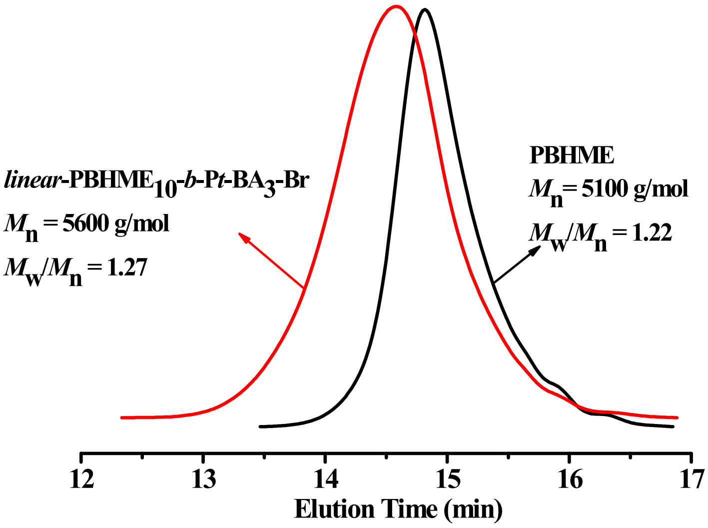

Figure S2 GPC curves of homopolymer $PBHME_{10}$, block copolymers *linear*-$PBHME_{10}$-*b*-P*t*-BA_3-Br with α-alkyne-ω-bromine prepared via ATRP chain-extension using $PBHME_{10}$ as the macro-ATRP initiator

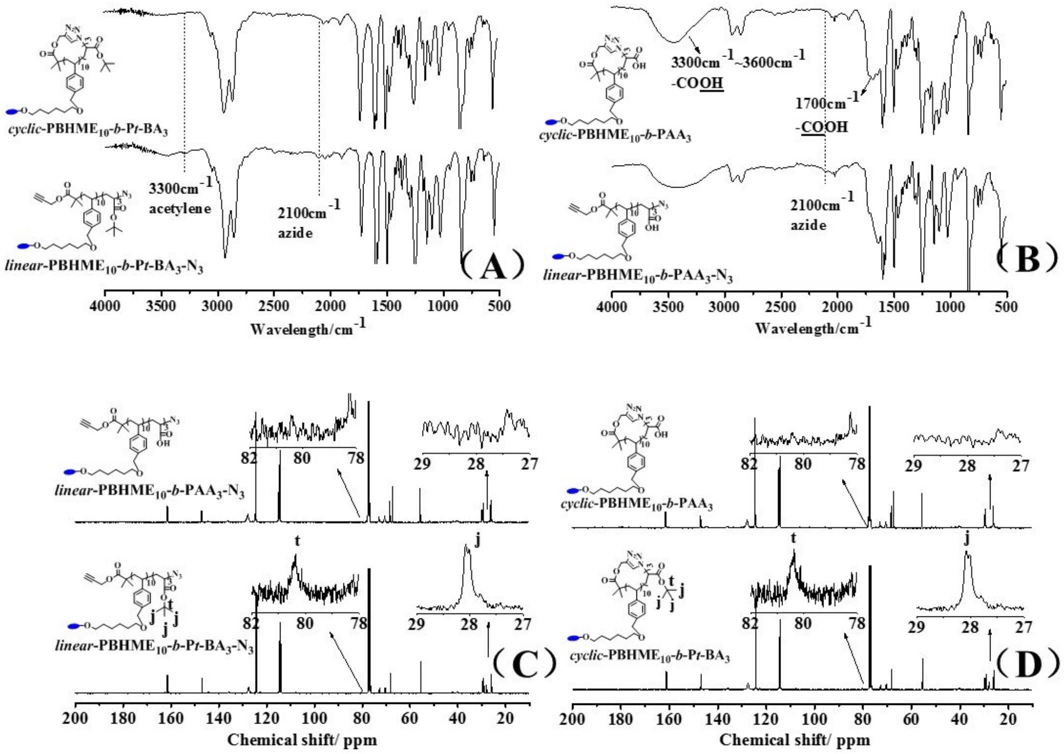

Figure S3. FT-IR spectra (A) of the *linear*-PBHME$_{10}$-*b*-*t*-BA$_3$-N$_3$ and *cyclic*-PBHME$_{10}$-*b*-*t*-BA$_3$ as well as the *linear*-PBHME$_{10}$-*b*-*t*-AA$_3$-N$_3$ and *cyclic*- PBHME$_{10}$-*b*-AA$_3$-N$_3$; ^{13}C NMR spectra of the *linear*-PBHME$_{10}$-*b*-*t*-BA$_3$-N$_3$ and *linear*- PBHME$_{10}$-*b*-AA$_3$-N$_3$ (C) as well as the *cyclic*-PBHME$_{10}$-*b*-*t*-BA$_3$ and *cyclic*- PBHME$_{10}$-*b*-AA$_3$ (D).

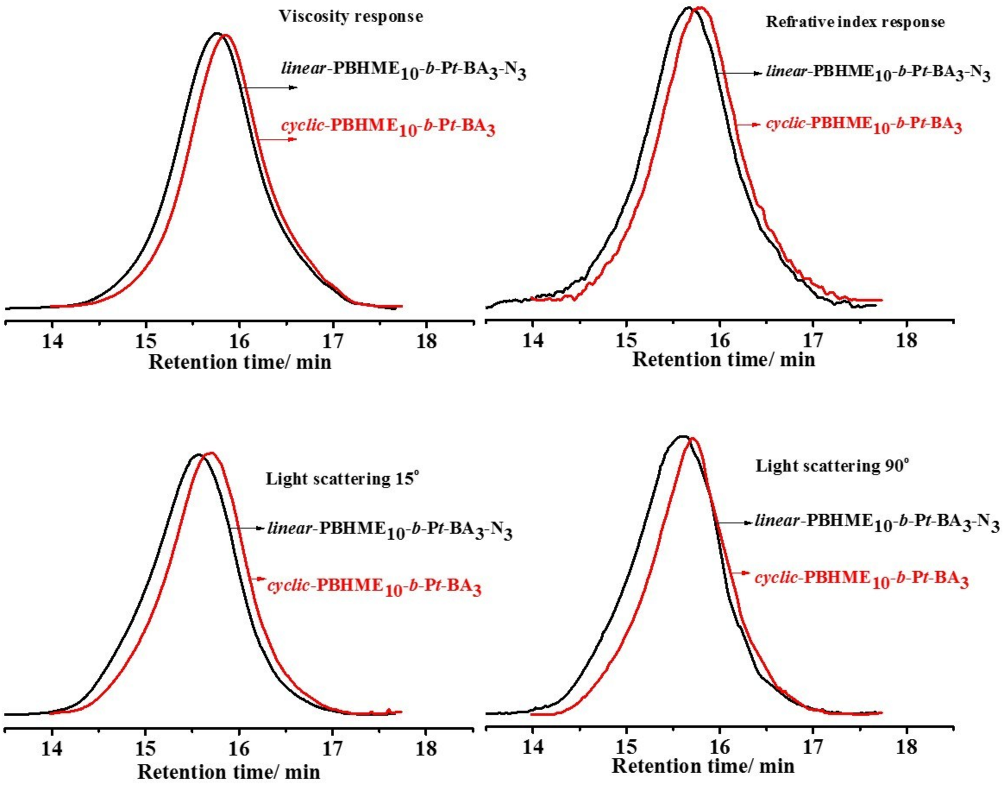

Figure S4. TD-GPC traces of the *linear*-PBHEM$_{10}$-*b*-P*t*-BA$_3$-N$_3$ ($M_{\mathrm{n,GPC}}$ = 5500 g/mol, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.27) and *cyclic*-PBHEM$_{10}$-*b*-P*t*-BA$_3$ ($M_{\mathrm{n,GPC}}$ = 5300 g/mol, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.27).

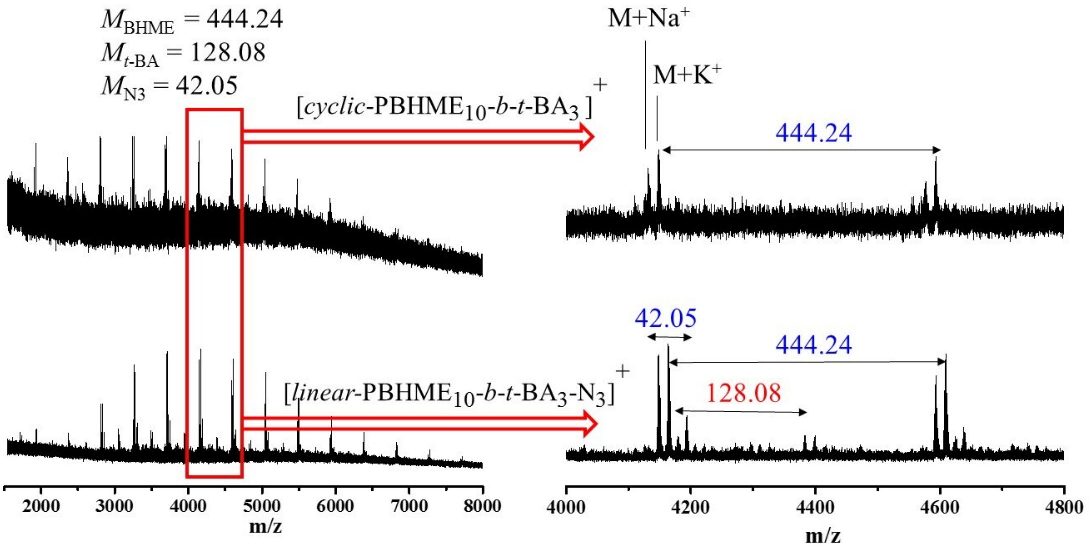

Figure S5. MALDI-TOF mass spectra of the *linear*-PBHME$_{10}$-*b*-*t*-BA$_3$-N$_3$ ($M_{n,GPC}$ = 5500 g/mol, M_w/M_n = 1.27) and *cyclic*-PBHME$_{10}$-*b*-*t*-BA$_3$ ($M_{n,GPC}$ = 5300 g/mol, M_w/M_n = 1.27)

Table S1. Data of corresponding to mass peaks in MALDI-TOF mass spectra (**Figure S5**) for the *linear*-PBHME$_{10}$-*b*-*t*-BA$_3$-N$_3$ (*L*) and *cyclic*-PBHME$_{10}$-*b*-*t*-BA$_3$ (*C*)

N	Theoretical $(L)^+$	Obesrved $(L)^+$	mM_{BHME}-(m-1)M_{BHME}	n$M_{t\text{-}BA}$-(n-1)$M_{t\text{-}BA}$	M_{end}	m	n
1	4173.20	4173.088	444.24	128.08	167.07	7	6
2	4145.17	4145.095	444.24	128.08	139.06	7	6
3	4617.40	4617.651	444.24	128.08	167.07	8	6
4	4589.37	4588.936	444.24	128.08	139.06	8	6
5	4301.30	4301.542	444.24	128.08	167.07	7	7

N	Theoretical $(C)^+$	Obesrved $(C)^+$	mM_{BHME}-$(m\text{-}1)M_{\mathrm{BHME}}$	$nM_{t\text{-BA}}$-$(n\text{-}1)M_{t\text{-BA}}$	M_{end}	m	n
1	4128.23	4129.084	444.24	128.08	167.07	8	3
2**	4144.23	4145.983	444.24	128.08	167.07	8	3
3	4572.47	4572.208	444.24	128.08	167.07	9	3
4**	4588.47	4589.279	444.24	128.08	167.07	9	3

Theoretical $(C)^+$ and $(L)^+$: theoretical molecular weight (g/mol);

Observed $(C)^+$ and $(L)^+$ (g/mol) : mass obtained by MALDI-TOF mass spectra(g/mol).

Non-starred theoretical weight = M_{end} +444.2 × m +128.1 × n + 23 ($M_{\mathrm{Na}} = 23$);

Starred "*" theoretical weight = M_{end} +444.2 × m +128.1 × n + 23 ($M_{\mathrm{Na}} = 23$) + 39 ($M_{\mathrm{K}} = 39$);

Starred "**" theoretical weight = M_{end} +444.2 × m +128.1 × n + 39 ($M_{\mathrm{K}} = 39$);

M_{end} : the molecular weight of end group;

444.2: the molecular weight of monomer BHME;

128.1 : the molecular weight of monomer *t*-BA;

The M_{end} of the *linear*-polymer with azide group or *cyclic*-polymer = 167.07;

The M_{end} of the *linear*-polymer with azide group- M_{N2}(28.04) =139.06;

The M_{end} of the *linear*-polymer with azide group- M_{N3}(42.05) =125.06;

The M_{end} of the *linear*-polymer with azide group- M_{N} (14.00) = 153.07;

m : the number of repeating unit of monomer BHME;

n : the number of repeating unit of monomer *t*-BA;

The M_{end} for 139.06 can be assigned to the expulsion of N_2 of the *linear*-polymer with azide group in testing procedure. [S3]

The first-order rate constant (k_e) of *trans*-to-*cis* photoisomerization was determined by the Formula S3:

$$\mathrm{Ln}[(A_\infty - A_t)/(A_\infty - A_0)] = -k_e t \qquad \text{(Formula S3)}$$

Where A_∞, A_0, and A_t are absorbance at about 358 nm corresponded to the π-π^* transition of *trans* isomers of azobenzene at infinite time, time zero and time t with irradiation of 365nm UV light (1mW/cm^2) at room temperature, respectively.

The first-order rate constants k_Hs of *cis*-to-*trans* photoisomerization were determined by the Formula S4:

$$\mathrm{Ln}[(A_\infty - A_t)/(A_\infty - A_0)] = -k_H t \qquad \text{(Formula S4)}$$

Where A_∞, A_0, and A_t are absorbance at about 450 nm corresponded to the n-π* transition of *cis* isomers of azobenzene at infinite time, time zero and time t with irradiation of 435 nm UV light (60 mW/cm^2) at room temperature, respectively.

References

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[S3] a) P. Na Songkhla, J. Wootthikanokkhan, *J. Polym. Sci., Part B: Polym. Phys.* **2002**, 40, 562; b) J. L. Gao, Z. B. Zhang, N. C. Zhou, Z. P. Cheng, J. Zhu, X. L. Zhu, *Macromolecules* **2011**, 44, 3227.