Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Facile topological transformation of ABA triblock copolymers into multisite, single-chain-folding and branched multiblock copolymers via sequential click coupling and anthracene chemistry

Yanzhe He,[a] Zhigang Wang,[a] Peng Liu,[a] Xiangdong Zhou[b] and Youliang Zhao*[a]

[a] Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China. E-mail: ylzhao@suda.edu.cn.

[b] College of Textile and Clothing Engineering, Soochow University, Suzhou 215123, China.

Experimental

Materials

All the starting materials were purchased from Sinopharm Chemical Reagent Co., Ltd. unless otherwise stated. Styrene (St, 99%, Meryer) was purified by successive washing with 5% NaOH aqueous solution and water, drying over Na_2SO_4 and distillation under reduced pressure, and *tert*-butyl acrylate (*t*BA, 99%, Alfa-Aesar) was purified by passing through a basic alumina column. CuBr (98%) was purified by stirring in acetic acid and washing with ethanol. Anthracene-9-carboxylic acid (98%, Macklin), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99%, Aladdin), glycidol (97%, J&K Chemicals), 2-bromopropionyl bromide (97%, Aladdin) and other reagents were used as received. Clickable *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (DBA) was synthesized according to the literature procedure.[1] Toluene, acetone, tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were dried over CaH_2 and distilled according to standard procedures.

Synthesis of DBPAC

Anthracene-9-carboxylic acid (4.45 g, 20.0 mmol), glycidol (1.80 g, 24.3 mmol), triphenylphosphine (0.105 g, 0.40 mmol) and toluene (50 mL) were added to a round-bottom flask under nitrogen. The mixture was reacted at 110 °C for 30 h, and most of toluene was removed by evaporation. The crude product comprising 2,3-dihydroxylpropyl anthracene-9-carboxylate (DHPAC) was partitioned between dichloromethane and water, followed by washing with deionized water and drying the organic phase with Na_2SO_4. After removing the solvent under reduced pressure, 80 mL of THF was added to dissolve DHPAC. To the solution cooled with ice water bath was added triethylamine (4.55 g, 45.0 mmol), followed by slow addition of 30 mL of THF solution bearing 2-bromopropionyl bromide (9.71 g, 45.0 mmol). Afterwards, the reaction mixture was warmed to room temperature and further stirred for 24 h. The salt was removed by filtration, and the solvent was removed by evaporation. After extraction and drying, the mixture was further subjected to flash column chromatography. As mixtures of hexane and ethyl acetate (20:1, *v*/*v*) were used as the eluent, DBPAC (8.50 g, 75% yield) was isolated as yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (s, 1H, Ar*H* of anthryl group), 8.05 (d, *J* 8.4, 4H, Ar*H* of anthryl group), 7.57 (t, *J* 8.4, 2H, Ar*H* of anthryl group), 7.51 (t, *J* 7.6, 2H, Ar*H* of anthryl group), 5.58 (m, 1H, $CH_2C\mathit{H}O$), 5.04 and 4.69 (m, 2H, $AntCOOC\mathit{H}_2$), 4.34-4.58 (m, 4H, $CHCOOC\mathit{H}_2$ and $C\mathit{H}Br$), 1.82 (m, $C\mathit{H}_3$).

Synthesis of α,ω-azido-functionalized P*t*BA-*b*-PSt-*b*-P*t*BA copolymers

First, anthracene-mid-functionalized PSt (P1) was synthesized by ATRP of St using DBPAC initiator. To a round-bottom flask were added DBPAC (0.151 g, 0.533 mmol of bromide functionality), St (16.7 g, 160 mmol), CuBr (57.6 mg, 0.40 mmol), PMDETA (69.3 mg, 0.40 mmol) and dry toluene under nitrogen, and the total volume was 80 mL. The reaction mixture was degassed with three freeze-pump-thaw cycles, followed by polymerization at 100 °C for 7 h. After cooling down, the mixture was diluted with excess THF. The copper salt was removed by passing through a short column of neutral alumina. The solution was concentrated and precipitated into methanol. After vacuum drying, 2.45 g (14% conversion) of PSt was obtained. GPC and ^{1}H NMR analyses: $M_{n,GPC} = 8350$ Da, $Đ_M = 1.24$, and $M_{n,NMR} = 9310$ Da. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51, 7.98 and 7.44 (each s, Ar*H* of anthryl group), 6.0-7.2 (m, Ph*H* of PSt), 5.15 (m, $CH_2C\mathit{H}O$), 3.7-4.8 (m, $C\mathit{H}_2O$ and terminal $C\mathit{H}Br$), 0.6-2.6 (m, $C\mathit{H}_2C\mathit{H}$ of PSt and $C\mathit{H}_3C\mathit{H}COO$ connecting with PSt).

Second, five examples of dibromide-terminated P*t*BA-*b*-PSt-*b*-P*t*BA (P2-P6) copolymers were obtained by chain extension polymerization of *t*BA initiated with PSt macroinitiator. In a typical run, P1 (0.210 g, 0.045 mmol of bromide functionality), CuBr (4.9 mg, 0.034 mmol), *t*BA (115 mg, 0.90 mmol) and PMDETA (5.8 mg, 0.034 mmol) were successively added to a Schlenk tube, and then toluene was added to reach a total volume of 0.45 mL. After degassing with three freeze-pump-thaw cycles, the reaction mixture was subjected to polymerization at 60 °C for 6 h. The copper salt was removed by dilution and passing through an alumina column. The crude product was isolated by repetitive precipitation from THF solution into methanol. After vacuum drying, 233 mg (20% conversion) of copolymer P2 was obtained as solid powders. Other triblock copolymers P3-P6 with longer P*t*BA blocks were prepared according to similar procedures. GPC and ^{1}H NMR analyses of P2: $M_{\text{n,GPC}}$ = 9840 Da, $Đ_{\text{M}}$ = 1.17, and $M_{\text{n,NMR}}$ = 10500 Da. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51, 7.98, 7.43 (m, Ar*H* of anthryl group), 6.0-7.2 (m, Ph*H* of PSt), 5.14 (m, $CH_2C\mathit{H}O$), 3.5-4.8 (m, $C\mathit{H_2}O$ and terminal $C\mathit{H}Br$), 0.6-2.6 (m, $C\mathit{H_2}C\mathit{H}$ of PSt, $C\mathit{H_2}C\mathit{H}$ and $C\mathit{H_3}$ of P*t*BA, and $C\mathit{H_3}C\mathit{H}COO$ connecting with PSt).

Last, five examples of diazido-functionalized P*t*BA-*b*-PSt-*b*-P*t*BA (P2'-P6') copolymers were generated by azidation reaction. In a typical run, P2 (200 mg, 0.019 mmol), NaN_3 (124 mg, 1.9 mmol) and NH_4Cl (102 mg, 1.9 mmol) were added to a glass tube, and then DMF was added to reach a total volume of 2.0 mL. The contents were stirred at 50 °C for 48 h. After filtration, most of the solution was removed by reduced pressure. The crude polymer was dissolved in THF, followed by precipitation into methanol to isolate the polymer. After purification, 194 mg (97% yield) of P6 was obtained as solid powders. Other copolymers P2'-P6' were isolated using similar procedures. GPC analysis: $M_{\text{n,GPC}}$ = 9870 Da, $Đ_{\text{M}}$ = 1.17 (P2'); $M_{\text{n,GPC}}$ = 11100 Da, $Đ_{\text{M}}$ = 1.18 (P3'); $M_{\text{n,GPC}}$ = 14000 Da, $Đ_{\text{M}}$ = 1.23 (P4'); $M_{\text{n,GPC}}$ = 17200 Da, $Đ_{\text{M}}$ = 1.19 (P5'); $M_{\text{n,GPC}}$ = 20100 Da, $Đ_{\text{M}}$ = 1.20 (P6'). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51, 7.98, 7.44 (m, Ar*H* of anthryl group), 6.0-7.2 (m, Ph*H* of PSt), 5.14 (m, $CH_2C\mathit{H}O$), 3.5-4.8 (m, $C\mathit{H_2}O$ and terminal $C\mathit{H}N_3$), 0.6-2.6 (m, $C\mathit{H_2}C\mathit{H}$ of PSt, $C\mathit{H_2}C\mathit{H}$ and $C\mathit{H_3}$ of P*t*BA, and $C\mathit{H_3}C\mathit{H}COO$ connecting with PSt).

Synthesis of multisite multiblock copolymers

First, the dependence of molar mass and dispersity of multiblock copolymers on reaction time was investigated. P4' was chosen as a typical copolymer to reveal the reaction kinetics. P4' (100 mg, 6.9 μmol), DBA (13.8 mg, 6.9 μmol) and THF (1.0 mL) were added to a reaction flask, and then the solution was stirred in dark at room temperature. At time intervals (t = 0.5, 1 and 2 h), about 50 μL of polymer solution was drawn. After dilution with THF, the polymer solution was immediately subjected to GPC analysis. The sample obtained at 6 h was labelled as P9.

Second, multiblock copolymers with distinct length of P*t*BA segments were synthesized. In a typical run, P2' (105 mg, 10 μmol), DBA (20 mg, 0.10 mmol) and THF were added to a reaction flask, and the total volume was 1.05 mL. The mixture was stirred in dark at ambient temperature for 6 h. After purification, 98 mg (93% yield) of P7 was obtained as brown solid powders. Other copolymers P8, P10 and P11 were synthesized according to similar procedures, and their precursor polymers were P3', P5' and P6', respectively. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51, 7.98, 7.43 (m, Ar*H* of anthryl group), 6.0-7.2 (m, Ph*H* of PSt), 3.5-5.2 (m, $C\mathit{H_2}O$, $C\mathit{H}O$ and $C\mathit{H}N$), 0.6-2.6 (m, $C\mathit{H_2}C\mathit{H}$ of PSt, $C\mathit{H_2}C\mathit{H}$ and $C\mathit{H_3}$ of P*t*BA, and $C\mathit{H_3}C\mathit{H}COO$ connecting with PSt), 4.8-5.2 ($C\mathit{H}O$ and $C\mathit{H}N$), 4.61 ($AntCOOC\mathit{H_2}$).

Multiblock copolymers with tunable block number obtained by fractional precipitation

Fractional precipitation using THF/hexane mixtures was adopted to obtain various (P*t*BA-*b*-PSt-*b*-P*t*BA)$_n$ samples with different n_w values. P8 (100 mg) and THF (20 mL) were stirred overnight to form clear solution, followed by slow addition of hexane. As the solution became turbid, the mixture was subjected to centrifugation, and the solid sample was collected to afford the first fraction (denoted as F1). Afterwards, hexane was carefully added to the collected solution until turbid solution was formed, and the second fraction F2 was isolated. On this basis, other fractions F*x* (*x* = 3-5) were obtained according to similar procedures. After vacuum drying, the fractionalized copolymers were subjected to GPC analysis.

Photo-triggered topological transformation from MMP to SMP

At low concentration, the intrachain dimerization of anthryl groups induced by 365 nm UV irradiation afforded SMPs comprising anthracene dimer, and the radiation intensity was fixed at 150 mW cm^{-2}. In a typical run, P7 (25 mg) was dissolved in 25 mL of THF, followed by UV irradiation at 365 nm for 4 h. After purification, P12 were isolated as yellowish solid powders. As other MMPs P8-P11 were used as raw materials, various SMPs P13-P16 were obtained. Similarly, UV irradiation of F*x* gave F*x*' with relatively low dispersity. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65, 7.43 (m, Ar*H* of AntD), 6.0-7.2 (m, Ph*H* of PSt and Ar*H* of AntD), 5.52 (m, ArC*H* of AntD), 5.02 (m, C*H*O and C*H*N), 3.5-4.8 (m, COOCH_2), 0.6-2.6 (m, CH_2C*H* of PSt, CH_2C*H* and CH_3 of P*t*BA, and CH_3C*H*COO connecting with PSt).

Photo-triggered topological transformation from MMP to BMP

P9 was used as an initial copolymer to synthesize branched multiblock copolymer via UV-induced linking reaction. P9 (0.10 g) was dissolved in THF, and the total volume was 1.0 mL. The solution was exposed to UV irradiation at 365 nm for 4 h. After purification, P17 was obtained as yellowish solid powders. GPC analysis: $M_{n,GPC}$ = 48.8 kDa, $Đ_M$ = 13.5. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65, 7.48 (m, Ar*H* of AntD), 6.0-7.2 (m, Ph*H* of PSt and Ar*H* of AntD), 5.60 (m, ArC*H* of AntD), 5.12 (m, C*H*O), 3.5-5.0 (m, COOCH_2 and C*H*N), 0.6-2.6 (m, CH_2C*H* of PSt, CH_2C*H* and CH_3 of P*t*BA, and CH_3C*H*COO connecting with PSt).

Characterization

The apparent number-average molar mass ($M_{n,GPC}$) and dispersity ($Đ_M$) of various polymers were measured on a TOSOH HLC-8320 gel permeation chromatography (GPC) with three TSKgel SuperMultipore HZ-M columns at 40 °C, in which THF with a flow rate of 0.35 mL min^{-1} was used as the eluent and PSt homopolymers with low dispersity acted as standard samples. Gel permeation chromatography equipped with multiple angle laser scattering detector (GPC-MALLS) was used to determine weight-average molar mass ($M_{w,LS}$) and solution viscosity of various polymers. GPC was conducted in THF at 35 °C with a flow rate of 1.0 mL min^{-1}, molar mass was determined by a triple detection method, and the intrinsic viscosity of polymer solutions in THF was measured using a viscosimetric detector connected to GPC system. ^{1}H (400 MHz) NMR spectra were measured on a Varian spectrometer at 25 ^{o}C using CDCl$_3$. Fourier transform infrared (FT-IR) spectra were recorded on Bruker Vertex 70 FT-IR instrument. Differential scanning calorimetry (DSC) was measured on Q200 DSC from Waters TA Instruments using a heating rate of 10 K min^{-1}. UV-vis absorption spectra were recorded using a Shimadzu UV-1800 spectrophotometer.

Reference

1 J. Q. Chen, L. Xiang, X. F. Liu, X. P. Liu and K. Zhang, *Macromolecules*, 2017, **50**, 5790–5797.

Table S1 GPC results of anthryl-functionalized (P*t*BA-*b*-PSt-*b*-P*t*BA)$_n$ (P8) and its typical fractionalized samples (F*x*, *x* = 1-5)

sample	$M_{\mathrm{n,GPC}}$ (kDa)	$Đ_{\mathrm{M}}$	n_{w}
P8	41.8	4.07	13.0
F1	596	1.61	71.5
F2	359	1.43	38.3
F3	176	1.23	16.1
F4	118	1.40	12.3
F5	62.1	1.31	6.1

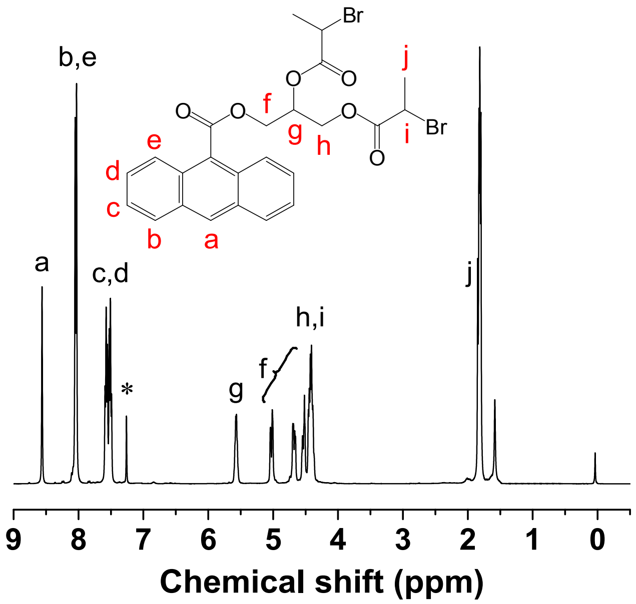

Fig. S1 ^{1}H NMR spectrum of DBPAC recorded in $CDCl_3$.

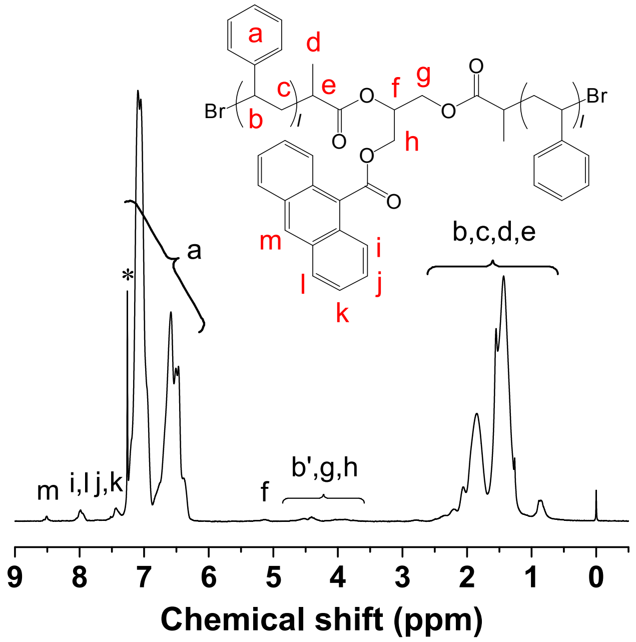

Fig. S2 ^{1}H NMR spectrum of PSt (P1) recorded in $CDCl_3$, in which b' denotes terminal C*H*Br.

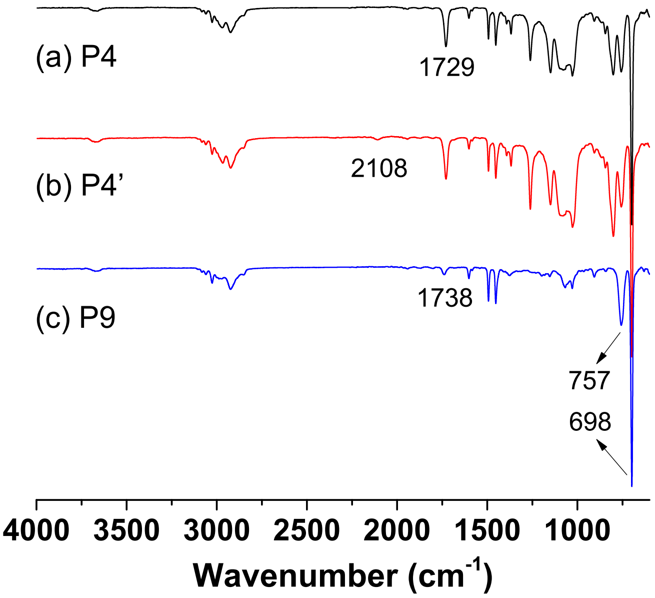

Fig. S3 FT-IR spectra of dibromide-functionalized P*t*BA-*b*-PSt-*b*-P*t*BA (P4), diazido-functionalized P*t*BA-*b*-PSt-*b*-P*t*BA (P4') and click-generated (P*t*BA-*b*-PSt-*b*-P*t*BA)$_n$ (P9).

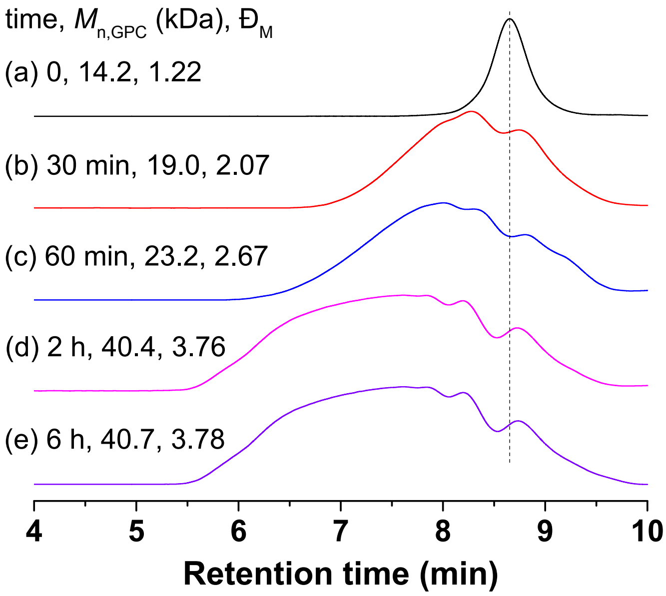

Fig. S4 GPC traces of P9 (t = 6 h) and its precursor polymers obtained by DSPAAC between diazido-functionalized P*t*BA-*b*-PSt-*b*-P*t*BA (P4') and DBA.

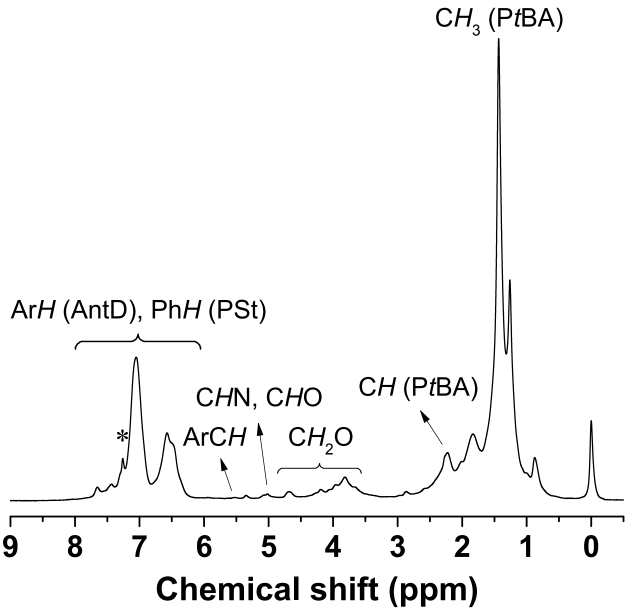

Fig. S5 ^{1}H NMR spectrum of AntD-bearing single-chain-folding copolymer P14 recorded in $CDCl_3$.

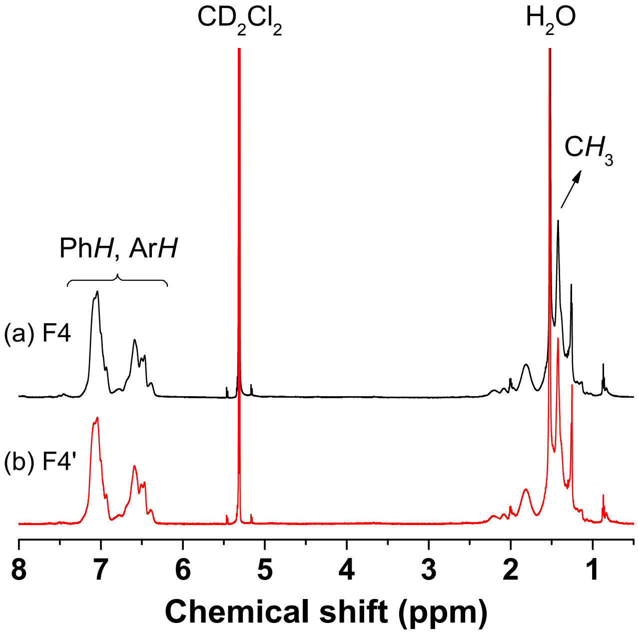

Fig. S6 ^{1}H NMR spectra of (P*t*BA-*b*-PSt-*b*-P*t*BA)$_n$ copolymers before (a, F4) and after (b, F4') UV-induced sing-chain folding recorded in CD_2Cl_2 (c_p = 2.0 mg mL^{-1}).

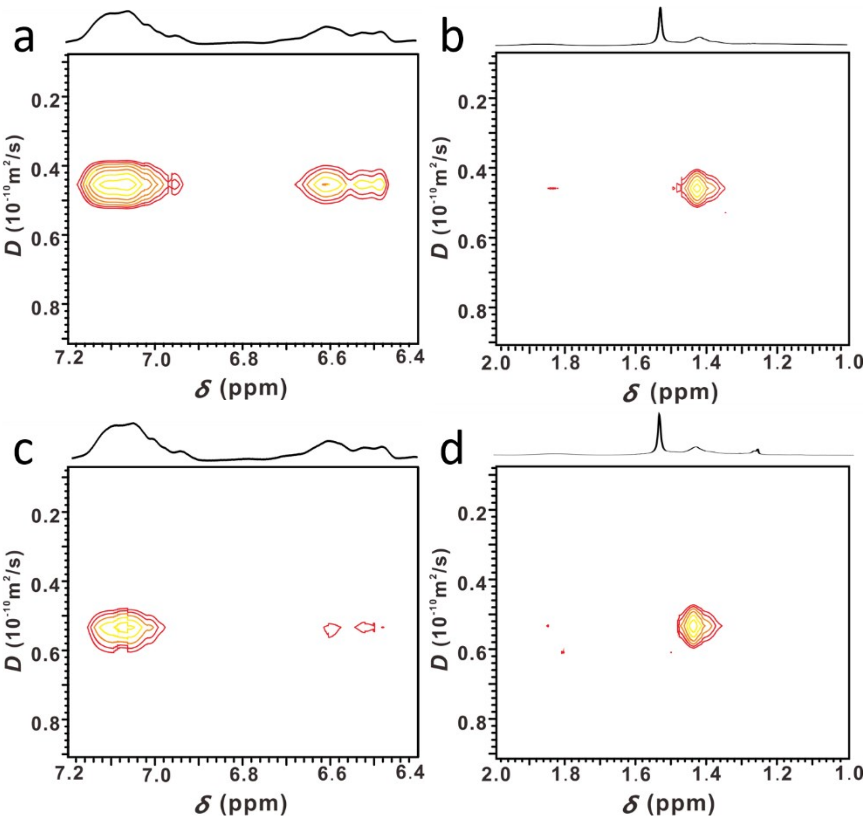

Fig. S7 DOSY spectra of (P*t*BA-*b*-PSt-*b*-P*t*BA)$_n$ copolymers before (F4, a and b) and after (F4', c and d) UV-induced sing-chain folding recorded in CD_2Cl_2 (c_p = 2.0 mg mL^{-1}), in which the *x*-axis is the ^{1}H resonances and *y*-axis denotes the diffusion coefficient.

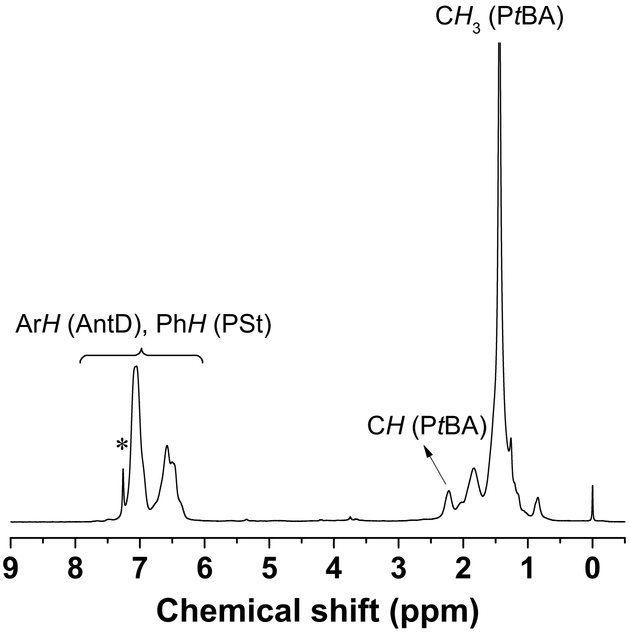

Fig. S8 ^{1}H NMR spectrum of AntD-bearing branched copolymer P17 recorded in $CDCl_3$.

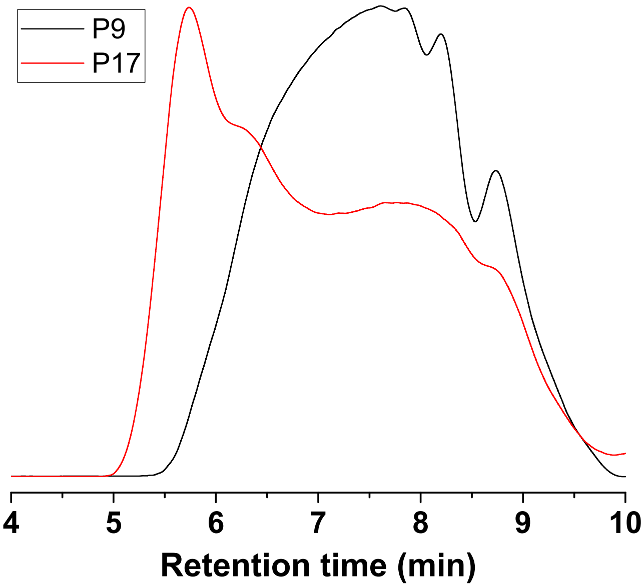

Fig. S9 GPC traces of MMP (P9, M_p = 121 kDa) and BMP (P17, M_p = 549 kDa).