Supporting Information

Rational design of a multi-in-one heterofunctional agent for versatile topological transformation of multisite multisegmented polystyrenes

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Experimental

Materials

The chemicals 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 distilled under reduced pressure. ε-Caprolactone (CL, 99%, Sigma-Aldrich) was distilled from CaH_2 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 glacial acetic acid and washing with acetone for three times. Anthracene-9-carboxylic acid (98%, Macklin), *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA, 99%, Aladdin), 2-bromoisobutyryl bromide (97%, Aladdin), stannous octoate ($Sn(Oct)_2$, 97%, Sigma-Aldrich), and other reagents with analytical grade were used directly. The organic solvents such as toluene, acetone, dichloromethane (DCM), tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) were dried and distilled according to standard procedures. *N*,*N*-bis(2-hydroxyethyl)-9-anthracenemethylamine (BHAMA),[1] *N*-(2-hydroxy)ethyl maleimide (HEMI),[2] and *N*-(2-bromopropionyloxy)ethyl maleimide (BEMI)[3] were prepared according to reference methods.

Synthesis of BAMA

BHAMA (1.60 g, 5.42 mmol), triethylamine (1.38 g, 13.6 mmol) and anhydrous DCM (80 mL) were added to a round-bottom flask. Upon cooling with an ice-water bath, 20 mL of DCM solution containing 2-bromoisobutyryl bromine (2.49 g, 10.8 mmol) was slowly added to the reaction mixture. The esterification reaction was further conducted at ambient temperature for 20 h. After filtration, the solution was subjected to rotary evaporation. The crude product was partitioned in DCM and water. The organic phase obtained by extraction was combined, followed by drying with Na_2SO_4 overnight. Flash column chromatography using petroleum ether and ethyl acetate (10:1, *v*/*v*) as the eluent was used to isolate the product, and *N,N*-bis(2-(bromoisobutyryloxy)ethyl)-9-anthracenemethanamine (BAMA, 1.80 g, 56% yield) was obtained as yellow solid powders. ^{1}H NMR ($CDCl_3$): δ 8.46 (t, *J* 8.8, 3H, Ar*H*), 8.01 (d, *J* 8.0, 2H, Ar*H*), 7.52 (t, *J* 6.8, 2H, Ar*H*), 7.46 (t, *J* 6.4, 2H, Ar*H*), 4.69 (s, 2H, ArCH_2N), 4.25 (t, *J* 5.2, 4H, CH_2O), 2.99 (t, *J* 5.2, 4H, NCH_2CH_2O), 1.80 (s, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 171.66 (*C*=O), 131.50, 131.42, 129.19, 128.01, 126.11, 125.01, 124.89 (Ar*C*), 64.43 (*C*H_2O), 55.85 (Ar*C*H_2N), 52.24 (N*C*H_2CH_2O), 51.62 (*C*$(CH_3)_2$Br), 30.74 (*C*H_3).

Synthesis of anthryl-functionalized PSts

BAMA (0.593 g, 1.0 mmol), PMDETA (0.347 g, 2.0 mmol) and St (10.4 g, 0.10 mol) were successively added to a Schlenk tube under nitrogen, and toluene was added to reach a total volume of 22.7 mL. After two freeze-pump-thaw cycles, CuBr (0.288 g, 2.0 mmol) was added to the tube, followed by another two freeze-pump-thaw cycles. The reaction mixture was subjected to polymerization at 110 °C. At time intervals (t = 0.5, 1.0, 1.5, 3.0, 8.0, 15, 20 h), about 1.0 mL of solution was carefully drawn under nitrogen. Partial solution was diluted with $CDCl_3$ and subjected to ^{1}H NMR analysis, and monomer conversion (C) was deduced by the equation $C = (I_{6.10\text{-}6.84} - I_{5.76})/(I_{6.10\text{-}6.84} + I_{5.76})$, in which I denoted integral area. The residual solution was diluted with excess THF and passed through a short column of neutral alumina, concentrated and precipitated into hexane or methanol. The isolated polymers obtained at different times were labelled as P1-P7, in which the number was liable to increase with increasing time. The polymerization was stopped at 26 h, the solution was rapidly cooled to room temperature, followed by further purification to isolate multisite PSt (P8). Various PSt samples were subjected to ^{1}H NMR and GPC analyses.

P1: 15.6% conversion, $M_{n,GPC}$ = 2.91 kDa, and $Đ_M$ = 1.16. ^{1}H NMR ($CDCl_3$): δ 8.34, 7.92, 7.43 (m, Ar*H* of Ant), 6.0-7.2 (m, Ph*H* of PSt), 4.51 (m, terminal C*H*Br), 4.42 (m, ArCH_2N), 3.45 (m, CH_2O), 3.09 and 2.79 (m, NCH_2CH_2O), 0.5-2.6 (m, CH_2C*H* of PSt and CH_3).

P8: 100% conversion, $M_{n,GPC}$ = 48.1 kDa, and $Đ_M$ = 2.84. ^{1}H NMR ($CDCl_3$): δ 8.34, 7.91, 7.43 (m, Ar*H* of Ant), 6.0-7.2 (m, Ph*H* of PSt), 4.41 (m, ArCH_2N), 3.44 (m, CH_2O), 3.26 and 3.07 (m,

NCH_2CH_2O), 0.5-2.6 (m, CH_2CH of PSt and CH_3).

Hydrolysis of anthryl-functionalized PSts

Hydrolysis of P*x* (*x* = 1-8) comprising ester groups in the main chain afforded carboxyl-terminated PSt (denoted as H*x*). In a typical run, KOH (0.20 g), ethanol (1.0 mL) and deionized water (0.15 mL) were added to a round-bottom flask. After stirring for 30 min, 3.0 mL of THF solution comprising P8 (50 mg) was added to the mixture, followed by refluxing for 48 h. The mixture was neutralized with dilute HCl, concentrated, and precipitated into cold methanol. After centrifugation and vacuum drying, H8 (45 mg) was obtained as white solid powders. Other anthryl-functionalized PSts were subjected to hydrolysis according to similar procedures.

H8: GPC and ^{1}H NMR analyses: $M_{n,GPC}$ = 12.3 kDa, $Đ_M$ = 1.30, and l = 95 (calculated by the equation l = [St unit] : [-COOH] = $1.2I_{6.2\text{-}7.2}/I_{0.96}$). ^{1}H NMR ($CDCl_3$): δ 6.2-7.2 (m, PhH of PSt), 0.6-2.4 (m, CH_2CH of PSt and terminal C(CH_3)$_2$COOH).

Fractionation of P8

P8 (4.0 g) was initially dissolved in THF (10 mL), and cyclohexane (200 mL) was slowly added to form dilute solution. Afterwards, hexane was slowly added to the solution under stirring until slightly turbid solution was formed, and the turbid solution was cooled using ice-water bath, followed by stirring for 30 min. After decantation, solid polymer absorbed on the wall of beaker was collected, and the first fraction F1 (0.16 g) was obtained after vacuum drying. According to similar procedures, hexane was carefully added to the clear polymer solution, and fractional precipitation was adopted to isolate other fractions F*x* (*x* = 2-5). The mass of each fraction was about 0.28 g (F2), 0.32 g (F3), 1.80 g (F4) and 0.40 g (F5). ^{1}H NMR ($CDCl_3$): δ 8.34, 7.91, 7.43 (m, ArH of Ant), 6.0-7.2 (m, PhH of PSt), 4.42 (m, ArCH_2N), 3.44 (m, CH_2O), 3.26 and 3.07 (m, NCH_2CH_2O), 0.5-2.6 (m, CH_2CH of PSt and CH_3).

UV-triggered topological transformation from multisite to intrachain folding PSts

Single-chain folding polymers (S*x*, *x* = 1-5) was prepared by UV-induced intrachain anthracene dimerization of anthryl-functionalized F*x*, in which the irradiation intensity of 365 nm UV light was fixed at 150 mW cm^{-2}. F*x* was dissolved in THF to form polymer solution (c_p = 2.0 mg mL^{-1}), followed by UV irradiation at 25 ^{o}C for 3 h. After concentration and vacuum drying, S*x* was obtained in high yield (> 98%). ^{1}H NMR ($CDCl_3$): δ 5.8-7.8 (m, ArH of AntD, and PhH of PSt), 5.12 (m, ArCH of AntD), 3.0-4.2 (m, ArCH_2N and NCH_2CH_2O), 0.5-2.6 (m, CH_2CH of PSt and CH_3).

Synthesis of PSt-*g*-P*t*BA

First, Diels-Alder reaction was conducted to generate bromine-functionalized PSt (PSt-Br). F4 (0.404 g, 0.020 mmol of anthryl group), BEMI (55 mg, 0.20 mmol) and DMF (4.0 mL) were added to a glass

tube. The solution was bubbled with nitrogen for 10 min, followed by heating at 100 °C for 24 h. After precipitation into methanol, PSt-Br (0.368 g, 90% yield) was obtained as white solid powders. ^{1}H NMR ($CDCl_3$): δ 6.0-7.7 (m, Ar*H* of DA unit, and Ph*H* of PSt), 4.62 (m, ArC*H*), 3.9-4.3 (m, C*H*Br and $CONCH_2CH_2O$), 3.2-3.8 (m, C*H*$CONCH_2$ and $COOCH_2CH_2N$), 2.6-3.2 (m, $(CH_2)_3N$), 0.5-2.4 (m, CH_2CH of PSt and CH_3).

Second, PSt-*g*-P*t*BA (G1) was synthesized by ATRP via grafting from approach. PSt-Br (0.205 g, 0.010 mmol of bromine functionality), PMDETA (1.7 mg, 0.010 mmol) and *t*BA (0.115 g, 0.90 mmol) were successively added to a Schlenk tube under nitrogen, and acetone was added to reach a total volume of 0.75 mL. After two freeze-pump-thaw cycles, CuBr (1.4 mg, 0.010 mmol) was added to the tube, followed by another two freeze-pump-thaw cycles. The reaction mixture was subjected to polymerization at 60 °C for 15 h. The solution was diluted with excess THF and passed through a short column of neutral alumina, concentrated and precipitated into methanol. After vacuum drying, G1 (0.251 g, 40% conversion) was obtained as white solid powders. GPC analysis: $M_{n,GPC}$ = 123 kDa, and $Đ_M$ = 1.16. ^{1}H NMR ($CDCl_3$): δ 6.0-7.7 (m, Ar*H* of DA unit, and Ph*H* of PSt), 4.63 (m, ArC*H*), 3.95-4.25 (m, $CONCH_2CH_2O$ and terminal C*H*Br), 3.2-3.8 (m, C*H*$CONCH_2$ and $COOCH_2CH_2N$), 2.6-3.2 (m, $(CH_2)_3N$), 0.5-2.5 (m, CH_2CH of PSt and P*t*BA, CH_3 of P*t*BA and linking group, and C*H*COO).

Synthesis of PSt-*g*-PCL

First, Diels-Alder reaction was conducted to generate hydroxyl-functionalized PSt (PSt-OH). F4 (0.404 g, 0.020 mmol of anthryl group), HEMI (28 mg, 0.20 mmol) and DMF (4.0 mL) were added to a glass tube. The solution was bubbled with nitrogen for 10 min, followed by heating at 100 °C for 24 h. After precipitation into methanol, PSt-OH (0.382 g, 94% yield) was obtained as white solid powders. ^{1}H NMR ($CDCl_3$): δ 6.0-7.7 (m, Ar*H* of DA unit, and Ph*H* of PSt), 4.65 (m, ArC*H*), 3.2-3.9 (m, C*H*$CONCH_2CH_2OH$ and $COOCH_2$), 2.6-3.2 (m, $(CH_2)_3N$), 0.5-2.4 (m, CH_2CH of PSt and CH_3).

Second, ROP of CL using PSt-OH as a macroinitiator gave PSt-*g*-PCL (G2). PSt-OH (0.203 g, 0.010 mmol of hydroxyl functionality), CL (69 mg, 0.60 mmol), $Sn(Oct)_2$ (2.3 mg, 0.005 mmol) and dry toluene were added to a Schlenk tube under nitrogen, and the total volume was 0.60 mL. The mixed solution was subjected to three freeze-vacuum-thaw cycles, followed by polymerization at 100 °C for 24 h. The polymer was purified by precipitation into methanol, and G2 (0.269 g, 96% conversion) was isolated after vacuum drying. GPC analysis: $M_{n,GPC}$ = 143 kDa, and $Đ_M$ = 1.20. ^{1}H NMR ($CDCl_3$): δ 6.0-7.7 (m, Ar*H* of DA unit, and Ph*H* of PSt), 4.67 (m, ArC*H*), 4.24 (m, $CONCH_2CH_2O$), 4.06 (t, *J* 6.6, CH_2O of PCL), 3.33-3.85 (m, C*H*$CONCH_2$, $COOCH_2CH_2N$, and

terminal CH_2OH), 2.80-3.33 (m, (CH_2)$_3$N), 0.5-2.4 (m, CH_2CH of PSt, COCH_2CH_2CH_2CH_2 of PCL, and CH_3 of linking group).

Synthesis of PSt-*g*-PCL/P*t*BA

The combination of quaternization reaction and Diels-Alder reaction was used to prepare bromine- and hydroxyl-functionalized PSt (PSt-OH/Br). F4 (0.404 g, 0.020 mmol of anthryl group), 3-bromo-1-propanol (28 mg, 0.20 mmol) and DMF (4.0 mL) were added to a glass tube. The solution was bubbled with nitrogen for 10 min, followed by heating at 100 °C for 24 h. Afterwards, BEMI (55 mg, 0.20 mmol) in small amount of DMF was added to the solution, and the mixture was further stirred at 100 °C for 24 h. After precipitation into methanol, PSt-OH/Br (0.396 g, 96% yield) was obtained as white solid powders. ^{1}H NMR ($CDCl_3$): δ 6.0-7.8 (m, ArH of DA unit, and PhH of PSt), 4.69 (m, ArCH of DA unit), 4.0-4.5 (m, CH_2OCOCHBr), 3.2-4.0 (m, ArCCH_2, COOCH_2CH$_2$N$^+$, HOCH_2CH$_2$CH$_2$N$^+$, and CHCONCH_2), 2.8-3.2 (m, COOCH$_2$CH_2N$^+$ and HOCH$_2$CH$_2$CH_2N$^+$), 0.5-2.6 (m, CH_2CH of PSt, HOCH$_2$CH_2CH$_2$N$^+$, and CH_3).

On this basis, ATRP of *t*BA was conducted at 60 °C for 20 h to synthesize PSt-*g*-P*t*BA (G3), followed by ROP of CL at 100 °C for 24 h to generate PSt-*g*-PCL/P*t*BA (G4). The synthetic procedures were similar to those of G1 and G2. Monomer conversion was determined to be 46% (for *t*BA polymerization) and 94% (for CL polymerization), respectively.

PSt-*g*-P*t*BA (G3): ^{1}H NMR ($CDCl_3$): δ 6.0-7.8 (m, ArH of DA unit, and PhH of PSt), 4.73 (m, ArCH), 4.0-4.5 (m, CONCH$_2$CH_2O and terminal CHBr), 3.2-4.0 (m, ArCCH_2, COOCH_2CH$_2$N$^+$, HOCH_2CH$_2$CH$_2$N$^+$, and CHCONCH_2), 2.8-3.2 (m, COOCH$_2$CH_2N$^+$ and HOCH$_2$CH$_2$CH_2N$^+$), 0.5-2.6 (m, CH_2CH of PSt and P*t*BA, CH_3 of P*t*BA and linking group, and HOCH$_2$CH_2CH$_2$N$^+$).

PSt-*g*-PCL/P*t*BA (G4): ^{1}H NMR ($CDCl_3$): δ 6.0-7.8 (m, ArH of DA unit, and PhH of PSt), 4.64 (m, ArCH), 3.9-4.4 (m, CH_2O of PCL, CONCH$_2$CH_2O, OCH_2CH$_2$CH$_2$N$^+$, and terminal CHBr), 3.16-3.90 (m, ArCCH_2, COOCH_2CH$_2$N$^+$, CHCONCH_2, and terminal CH_2OH), 2.65-3.16 (m, COOCH$_2$CH_2N$^+$ and HOCH$_2$CH$_2$CH_2N$^+$), 0.5-2.6 (m, CH_2CH of PSt and P*t*BA, CH_3 of P*t*BA and linking group, COCH_2CH_2CH_2CH_2 of PCL, CHCOO, and OCH$_2$CH_2CH$_2$N$^+$).

Thermo-induced self-catalyzed cleavage of various polymers

The polymer was subjected to thermolysis in bulk or DMF solution at a fixed temperature for the desired time. In a typical run, F4 was dissolved in DMF, and the polymer solution (c_p = 16 mg mL^{-1}) was heated at 150 °C. At time intervals (t = 1, 2, 4, 8, 12, 16, 24 and 36 h), about 0.5-1.0 mL of polymer solution was drawn. After cooling down, the polymer solution was subjected to acidification using HCl aqueous solution. Most of solvents were removed by distillation under reduced pressure. Carboxyl-terminated polystyrene (mixtures of PSt-COOH and (PSt-COOH)$_2$) was isolated by

precipitation into methanol, in which protonated BHAMA remained in the solution. The reaction was finally stopped at 48 h, and the resultant polymer was denoted as F4'. ^{1}H NMR ($CDCl_3$): δ 6.2-7.2 (m, Ph*H* of PSt), 0.6-2.4 (m, CH_2C*H* of PSt and terminal C(CH_3)$_2$COOH).

Similarly, S4 and G1 were subjected to thermal treatment in DMF solution at 150 °C for 48 h. After purification, S4' and G1' comprising PSt were obtained. After thermolysis, the resultant P*t*BA was soluble in methanol, and the isolated G1' was carboxyl-terminated polystyrene.

Characterization

^{1}H NMR spectra (400 MHz) of BAMA and polymers, and ^{13}C NMR spectrum (100 MHz) of BAMA were recorded in $CDCl_3$ on a Varian Unity Inova 400 MHz spectrometer at 25 °C. ^{1}H DOSY NMR spectra of F4 and S4 were recorded in CD_2Cl_2 on an Agilent ProPulse 600 MHz spectrometer at 25 °C. Apparent molar mass ($M_{n,GPC}$) and dispersity ($Đ_M = M_w/M_n$) of various polymers were measured on a TOSOH HLC-8320 gel permeation chromatography (GPC) using three TSKgel SuperMultipore HZ-M columns at 40 °C. THF was used as an eluent at a flow rate of 0.35 mL min^{-1}, and the samples were calibrated with PSt standard samples. Differential scanning calorimetry (DSC) was measured on Q200 DSC from TA Instruments using a heating/cooling rate of 10 K min^{-1}. UV-vis absorption spectra were recorded using a Shimadzu UV-1800 spectrophotometer.

References

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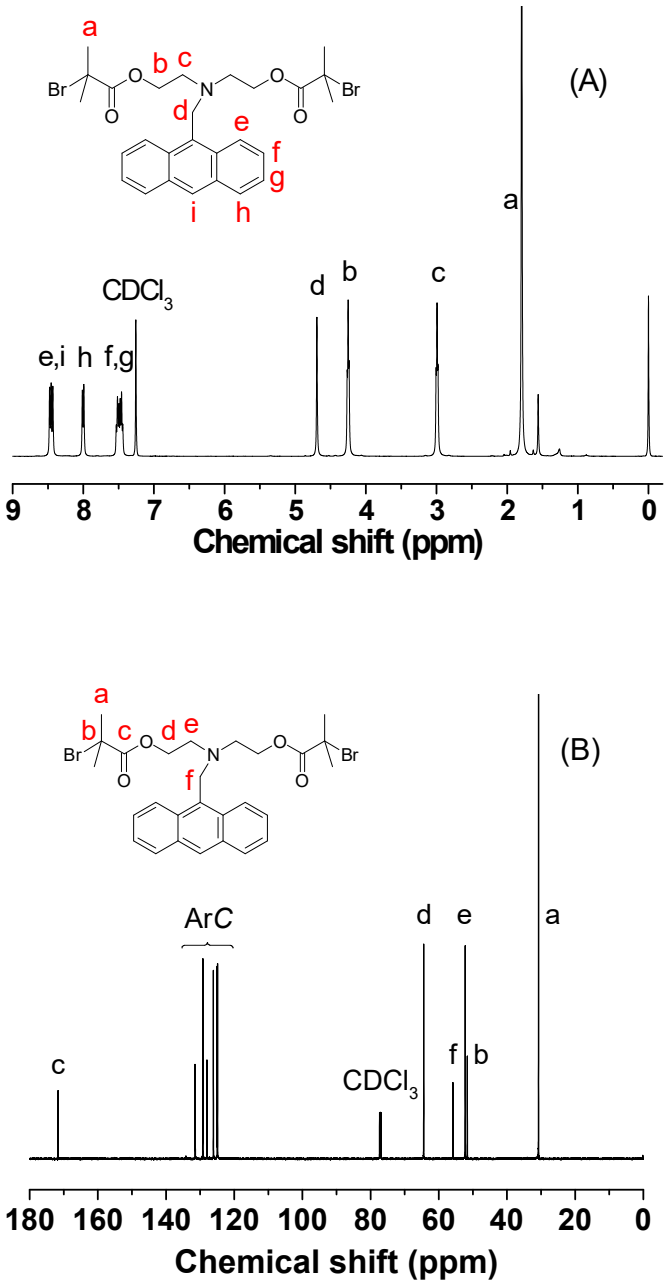

Fig. S1 ^{1}H (A) and ^{13}C (B) NMR spectra of BAMA recorded in $CDCl_3$.

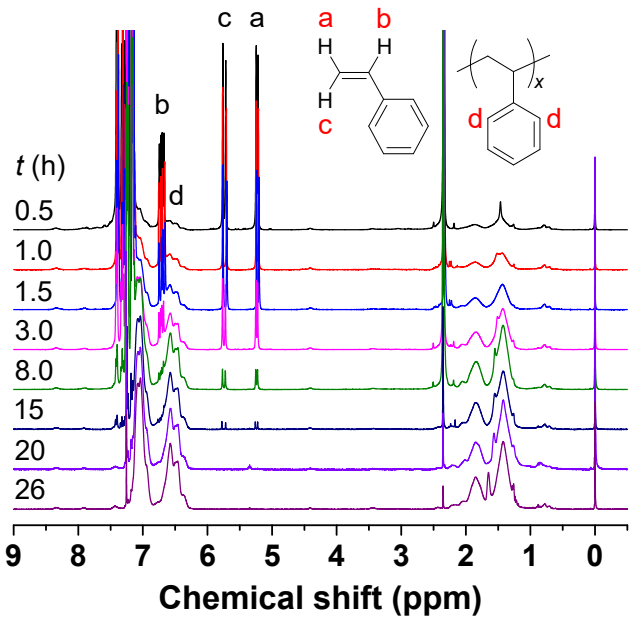

Fig. S2 ^{1}H NMR spectra of PSt-bearing solution recorded in $CDCl_3$, in which the original polymer solution comprising PSt, St and toluene obtained at different times was directly diluted with $CDCl_3$.

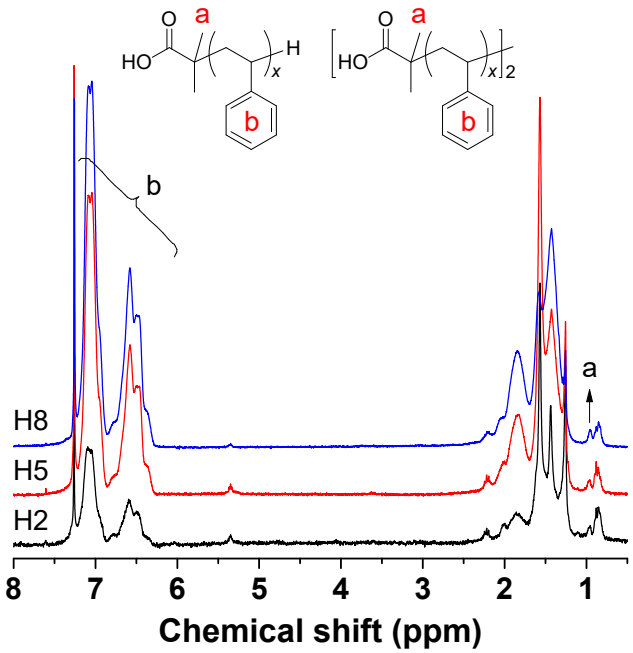

Fig. S3 ^{1}H NMR spectra of typical PSt samples (H*x*, *x* = 2, 5, 8) obtained by hydrolysis of anthryl-functionalized PSts (P*x*) recorded in $CDCl_3$ (*).

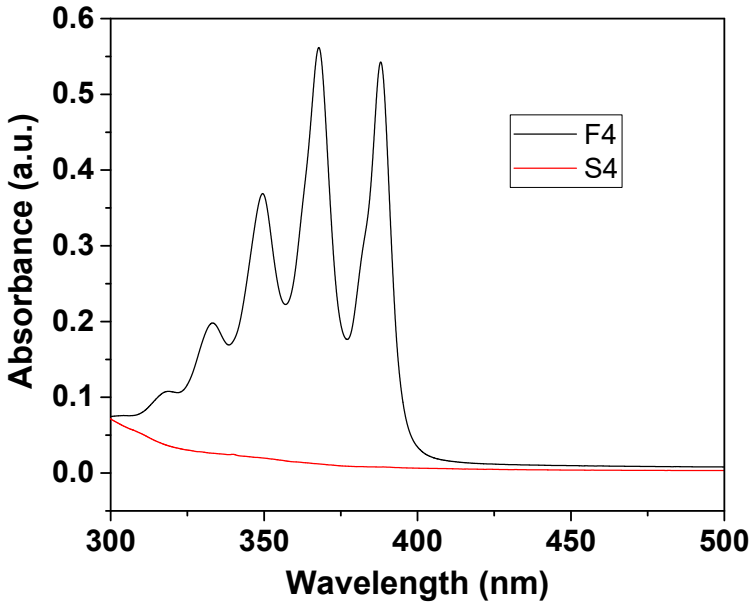

Fig. S4 UV-vis spectra of multisite PSt (F4) and single-chain folding PSt (S4) in THF (c_p = 1.0 mg mL^{-1}).

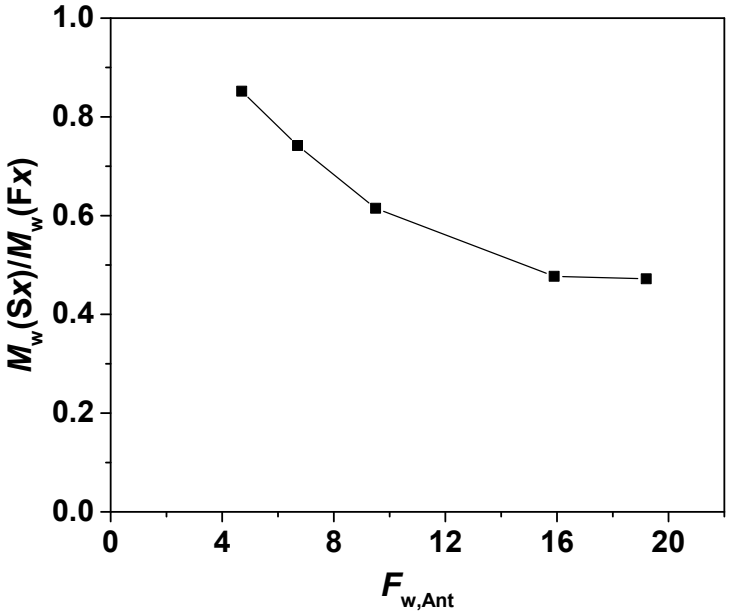

Fig. S5 Dependence of M_w(Sx)/M_w(Fx) on $F_{w,Ant}$ of multisite PSts.

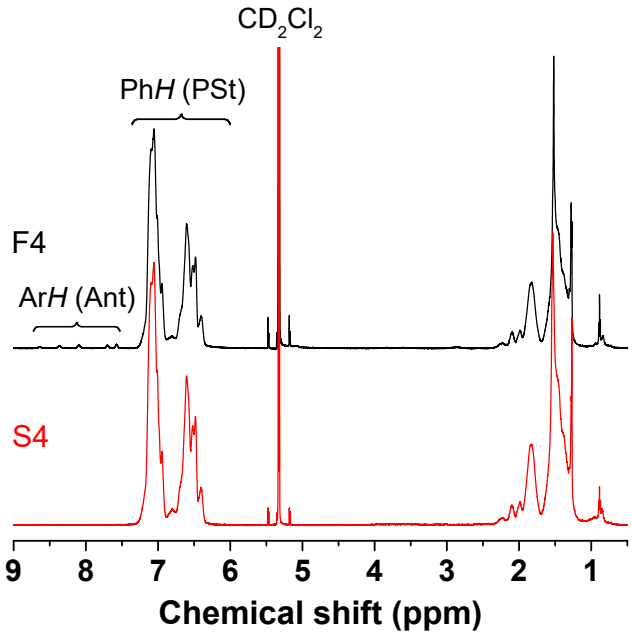

Fig. S6 ^{1}H NMR spectra of AntD-bearing intrachain folding PSt (S4) and its precusor (F4) recorded in CD_2Cl_2 (c_p = 2.0 mg mL^{-1}).

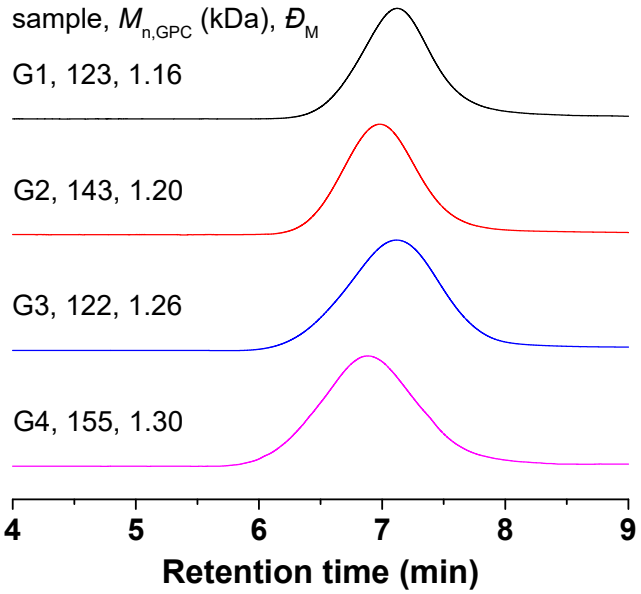

Fig. S7 GPC traces of various graft copolymers.

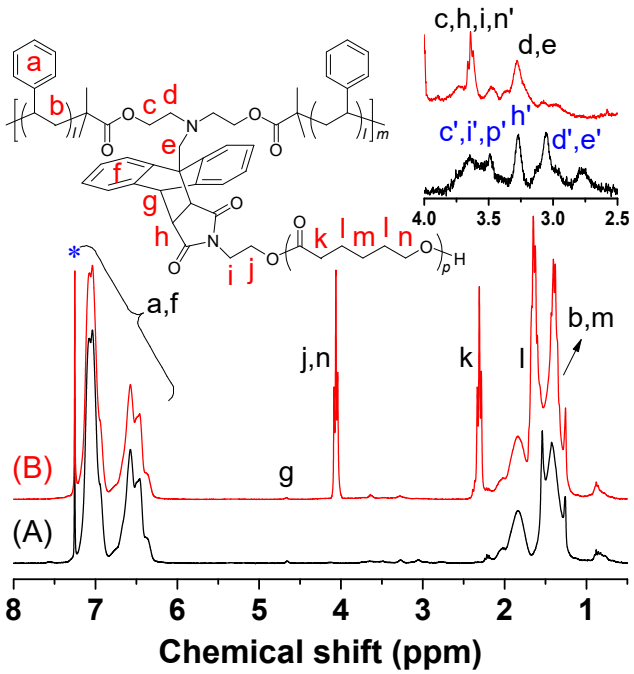

Fig. S8 ^{1}H NMR spectra of hydroxyl-functionalized PSt (PSt-OH, A) and PSt-*g*-PCL (G2, B) recorded in $CDCl_3$ (*), in which n' denoted the signal of terminal CH_2OH of PCL, and c', d', e', h', i' and p' (NCH_2CH_2OH) meant signals of PSt-OH at 2.6-3.9 ppm.

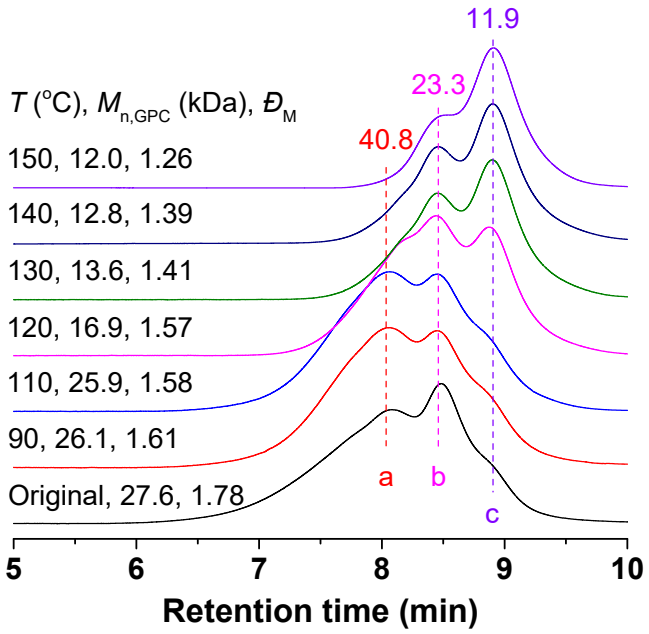

Fig. S9 GPC traces of P6 and its thermally treated samples, in which the thermolysis was conducted in DMF solution (c_p = 16 mg mL^{-1}) at different temperatures for 48 h, and typical peak molar masses were observed at about 40.8 kDa (a), 23.3 kDa (b) and 11.9 kDa (c).

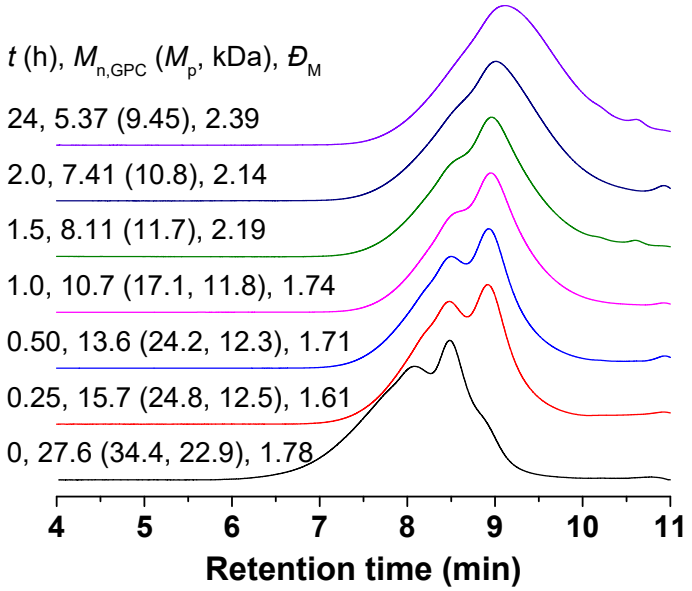

Fig. S10 GPC traces of P6 and its thermally treated samples, in which the thermolysis was conducted in bulk at 150 °C for different times.

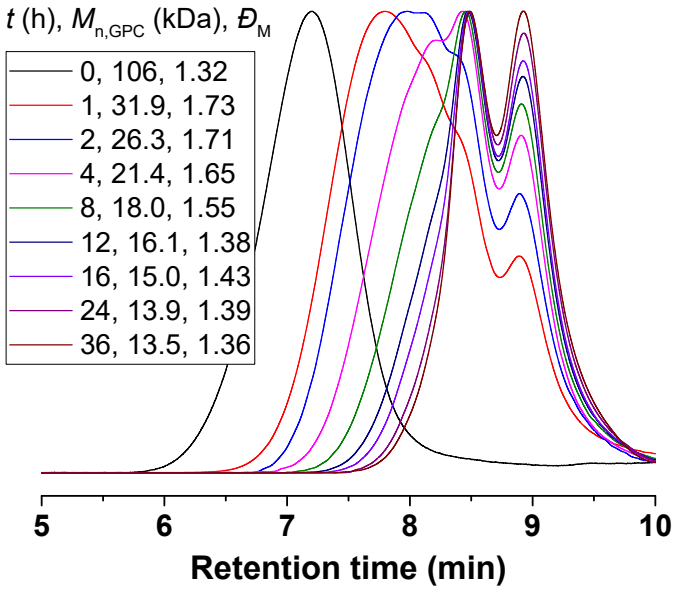

Fig. S11 GPC traces of F4 and its thermally treated samples, in which the thermolysis was conducted in DMF solution (c_p = 16 mg mL^{-1}) at 150 °C for different times.