Electronic Supplementary Material (ESI) for Polymer Chemistry.


# Electronic Supplementary Information

## Fine Control of Molecular Weight and Polymer Dispersity *via* Latent Monomeric Retarder

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# SECTION A. Experimental Section

## 1. Materials

Styrene (St, Sinopharm Chemical Reagent, 99%) and Methyl methacrylate (MMA, Sinopharm Chemical Reagents, 99%) was inhibited during storage, and the inhibitor was removed by alkaline aluminum oxide column chromatography. 2-Cyanoprop-2-yl-dithiobenzoate (99%) was purchased from Aldrich. 2,2′-azobis-(2,4-dimethylvaleronitrile) (ABVN) and 1,1′-Azobis (cyclohexanecarbonitrile) (ACCN) were purchased from Sinopharm Chemical Reagent, China (98%) and purifed by recrystallization from ethanol. EC (99.0%) were purchased from Alfa Aesar. 2-Cyanoprop-2-yl dithiobenzoate (CPDB, 99%) was purchased from Aldrich.

Deuterated solvents were obtained from Deutero GmbH. Furan, maleimide, sodium sulfate anhydrous (99%), n-hexane (97%), methanol (99.7%), diethyl ether anhydrous (99.7%), dichloromethane (99.5%), ethyl acetate (99.5%), acetone were purchased from commercial supplier named Sinopharm Chemical Reagent Co.,Ltd. N, N-dimethylformamide (DMF, 99.9%) were purchased from Sigma-Aldrich. All reagents were used directly as received without further purification unless otherwise stated.

## 2. Analysis techniques

The number-average molecular weight ($M_n$) and polydispersity ($Đ = M_w / M_n$) of the polymers were determined using a size exclusion chromatograph (SEC) TOSOH HLC-8320 equipped with refractive index and UV detectors, using two TSKgel Super 20 Multipore HZ-N (4.6 × 150 mm, 3μm bead size) columns arranged in a series with a molecular weight separation ranging from 500 to 1.9 × 105 g/mol. DMF containing lithium bromide was used as the mobile phase (flow rate 0.7 mL/min at 40 °C). Poly(styrene)(PS) standards were provided by PSS for calibration. The dried crude copolymers were dissolved in DMF containing lithium bromide at 20 mg/mL concentration and filtered through a 0.45 μm PTFE syringe filter prior to inject. Data acquisition was performed using Eco SEC software, and molecular weights were calculated according to PS standards.

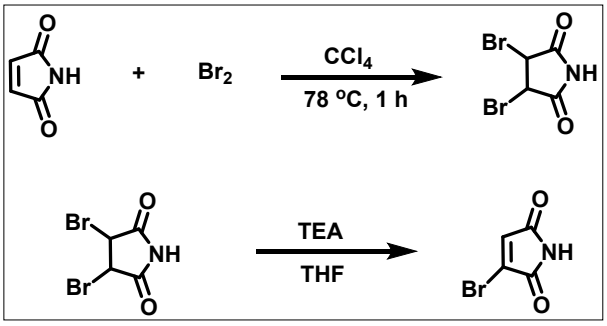
Proton nuclear magnetic resonance ($^1$H NMR) spectra of the samples were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz) by using tetramethylsilane as the internal standard at room temperature. All spectra are referenced internally to residual proton signals of the deuterated solvent. The $^1$H NMR spectra were referenced to δ 2.50 ppm in DMSO-$d_6$.

$^1$H DOSY experiments were performed on an Agilent Direct-Drive II 600 MHz spectrometer (USA) equipped with four broad-band rf channels and a 5mm 1H-19F/15N-31P triple-resonance pulse field gradient (PFG) probe tuned to the recording frequency of 599.829 MHz. All experiments were run without spinning to avoid convection. The DOSY bipolar pulse pair stimulated echo with convection compensation (Dbppste_cc) sequence was utilized with 1s relaxation delay, 9.6 kHz spectral window, 32 transients and 10.3μs 90° pulse width. Diffusion time was 40 ms and gradient duration was 2 ms, The number of gradient steps was set to be 15 and the diffusion encoding pulse strength (gzlvl1) value were linearly increased from 1130 to 28260. DOSY spectra were processed by Vnmrj 3.2 software and the results were mathematically treated by the continuous type using peak height in.

MALDI-TOF mass spectrum (MS) were acquired on an UltrafleXtreme III MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) equipped with an Nd:YAG smart beam-II laser with 355-nm wavelength and 200 Hz firing rate. The MALDI sample spots were prepared onto the MTP 384 target plate. The compound trans-2-[3-(4-tert-butyl-phenyl)-2-methyl- 2-propenylidene]-malononitrile (DCTB, Aldrich, >98%), served as the matrix, was prepared in $CHCl_3$ at a concentration of 20 mg/mL. The cationizing agent sodium trifluoroacetate was prepared in ethanol at a concentration of 10 mg/mL. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). The instrument was calibrated prior to each measurement with external PMMA at the molecular weight under consideration. All samples were dissolved in $CHCl_3$ at a concentration of 10 mg/mL. After sample preparation and solvent evaporation, the target plate was inserted into the MALDI-TOF mass spectrometer. For high resolution mass analysis, the instrument was operated in the reflector mode.

## 3. Retarder and latent retarder design and synthesis

### 3.1 Synthetic route of MBr




**Scheme S1.** Synthesis of MBr.

Maleimide (33.0 g, 0.34 mol) and 400 mL $CCl_4$ was added to a 1.0 L three-neck round-bottom flask equipped with a condenser. The mixture was stirred at room temperature under argon atmosphere. Bromine (20.0 mL, 0.39 mol) was added subsequently and then the mixture was refluxed at 78 ºC for about 1 h. Crude products were crystallized and filtered after cooling to room temperature. The filter cake was washed with 3×100 mL petrol ether (PE) and dried under vacuum at 25 ºC overnight to afford crude 1,2-dibromosuccinimide (75.0 g, yield 86.3%) as a yellow crystal without any further purification.

Crude 1,2-dibromosuccinimide (75.0 g, 0.29 mol) was dissolved to anhydrous THF (750 mL) in a 1.0 L three-neck round-bottom flask equipped with a 250.0 mL slow-addition apparatus and cooled to 0 ºC under argon atmosphere. Triethylamine (TEA, 45 mL, 0.32 mol) was dissolved in anhydrous THF (100 mL) and dropped in the stirred reaction system slowly at 0 ºC and maintained for at least 20 minutes. Then the mixture was moved to room temperature and stirred for about 2 h. The insoluble substance was filtered and the filter cake was washed with 3×200 mL ethyl acetate (EA). The residue was redissolved in 500 mL EA and then washed with 3×250 mL brine. The organic phase was dried with anhydrous $Na_2SO_4$ and the solvent was evaporated, and the crystal was dried under vacuum to afford crude product (42 g, yield 82.4%). Crude product (10.0 g) was then purified by silica gel column chromatography eluting with PE/EA (v/v = 4/1 to 2/1) and recrystallized to afford MBr (8.4 g, yield

84.0%) as a yellow powder. $^1$H NMR (300 MHz, DMSO-$d_6$, ppm): δ 11.29 (s, 1H), 7.32 (s, 1H).

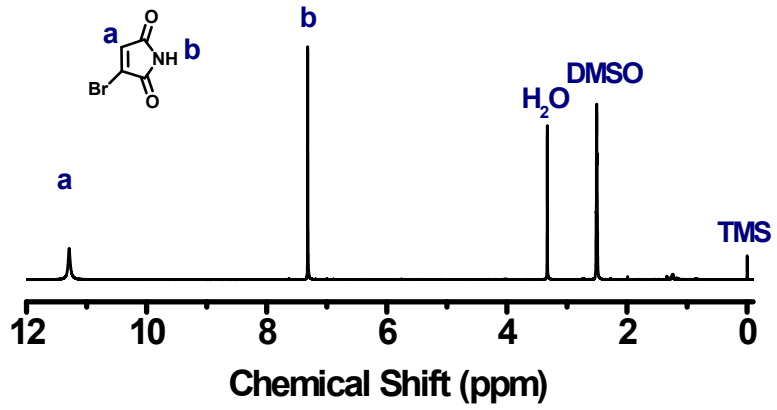
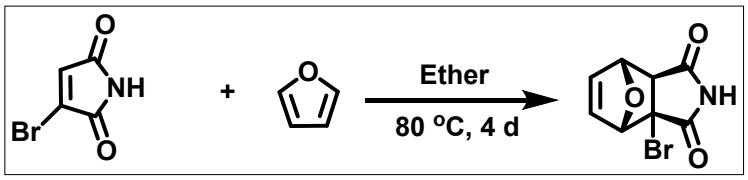



**Fig. S1** 300 MHz $^1$H NMR spectrum in DMSO-$d_6$ of MBr.

### 3.2 Synthetic route of FMBr




**Scheme S2.** Synthesis of FMBr.

To a 350 mL thick-wall pressure flask were added with MBr (12.0 g, 68.2 mmol), furan (46.4 g, 0.68 mol) and anhydrous diethyl ether (18.0 mL). The flask was sealed and the mixture was stirred at 78 ºC for 4 days. After cooling to room temperature, the mixture was filtered. The filter cake was washed with 3×50 mL PE and the products were dried under vacuum at 25 ºC overnight to afford crude product. Crude product was then purified by silica gel column chromatography eluting with PE/EA (v/v = 4/1 to 2/1) and recrystallized to afford FMBr (14.2 g, yield 85.3%) as a light gray powder. $^1$H NMR (300 MHz, DMSO-$d_6$, ppm): δ 11.82 (s, 1H), 6.76 – 6.65 (m, 2H), 5.26 (d, $J$ = 5.9 Hz, 2H), 3.05 (s, 1H).

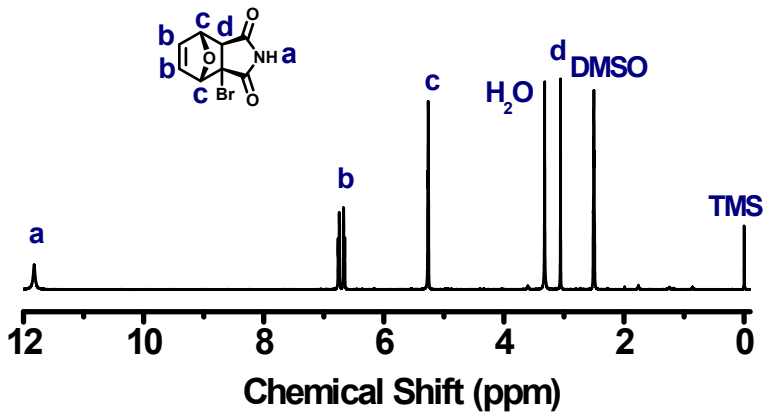



**Fig. S2** 300 MHz $^{1}$H NMR spectrum in DMSO-$d_6$ of FMBr.

## 4. Kinetic profile for the mono-deprotection of FMBr

Temperature plays a vital role in the polymerization rate as well as the deprotection of latent terminator. FMBr (42.6 mg, 0.18 mmol) were respectively dissolved in DMF (1.5 mL) in a 10 ml dry reaction vial with a magnetic stir bar. The closed vial was stirred at 40 $^{o}$C, 60 $^{o}$C, 100 $^{o}$C, 100 $^{o}$C. Aliquots were taken intermittently taken to determine the percent deprotection of furan protecting groups by $^{1}$H NMR spectroscopy using formyl protons of DMF as an internal standard.

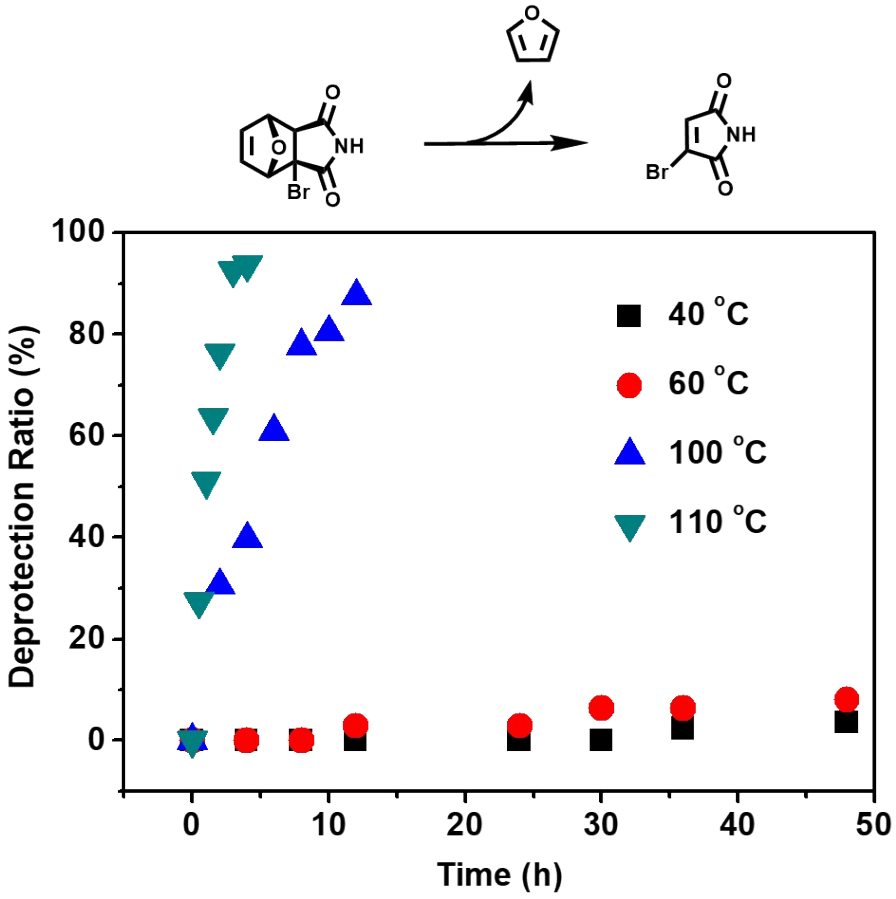



**Fig. S3** Kinetic profile for the mono-deprotection.

## 5. General Polymerization Procedure for RAFT polymerization *via* MBr

All polymerization reactions were performed in 25 mL baked Schlenk flasks equipped with a magnetic stir bar and Teflon stopper under argon protection. A small amount of DMF was added to improve the solubility. Take the preparation of PMMA with adjusted dispersity by MBr as an example. The general procedure is as follows. MMA (2 mL, 18.86 mmol), MBr (0.0830 g, 0.47 mmol), CPDB (0.0209 g, 0.094 mmol), ACCN (0.0046 g, 0.019 mmol), EC (0.06 g, 0.68 mmol) were added into a baked Schlenk flask, and then 2.0 mL DMF was added to improve the solubility. The mixture was then degassed to use by four freeze-pump-thaw cycles prior and was placed in an oil bath kept at 110 °C subsequently. At predetermined intervals, an aliquot was taken out with a syringe under argon. The polymerization was stopped by opening the flask to the air and quenched to -30 °C. The polymers reaction mixtures were dissolved

in DMSO-$d_6$ and determined by $^1$H NMR spectroscopy meanwhile were dissolved in DMF containing lithium bromide and analyzed by SEC. The crude copolymer was diluted with THF and precipitated in methanol to obtain the pure product. Other polymers via using MBr were obtained in a similar way.

## 6. General Polymerization Procedure for RAFT polymerization *via* FMBr

All polymerization reactions were performed in 25 mL baked Schlenk flasks equipped with a magnetic stir bar and Teflon stopper under argon protection. A small amount of DMF was added to improve the solubility. Take the preparation of PMMA with adjusted dispersity by MBr as an example. The general procedure is as follows. MMA (2 mL, 18.86 mmol), FMBr (0.2281 g, 0.93 mmol), CPDB (0.0209 g, 0.094 mmol), ACCN (0.0046 g, 0.019 mmol), ABVN (0.0046 g, 0.019 mmol), EC (0.06 g, 0.68 mmol) were added into a baked Schlenk flask, and then 2.0 mL DMF was added to improve the solubility. The mixture was then degassed to use by four freeze-pump-thaw cycles prior and was placed in an oil bath kept at 40 $^o$C subsequently. After predetermined time, the tube was taken out and was removed to in another oil bath pre-stabilized at 110 $^o$C and maintained for predetermined time. At predetermined intervals, an aliquot was taken out with a syringe under argon. The polymerization was stopped by opening the flask to the air and quenched to -30 $^o$C. The polymers reaction mixtures were dissolved in DMSO-$d_6$ and determined by $^1$H NMR spectroscopy meanwhile were dissolved in DMF containing lithium bromide and analyzed by SEC. The crude copolymer was diluted with THF and precipitated in methanol to obtain the pure product. Other polymers via using FMBr were obtained in a similar way.

## SECTION B. Results and Discussions

### 1. Conversion calculation of RAFT polymerization of MMA with adjusted *Đ* by using MBr

Fig. S4 shows a typical $^1$H NMR spectrum recorded during polymerization of MMA adjusted by MBr. MMA conversion (Conv. $_{MMA}$) was calculated from the raw experimental samples by comparing the integration of one vinyl proton of remaining MMA at 6.05-5.99 ppm (I6.05-5.99) to the initial integration of MMA. MBr conversion (Conv. $_{MBr}$) was calculated from the raw experimental samples by comparing the integration of one vinyl proton of remaining MBr at 7.32-7.30 ppm (I7.32-7.30) to the initial integration of MBr. The region 4.50-4.45 ppm (I4.50-4.45), which belonged to EC was used as an internal standard.

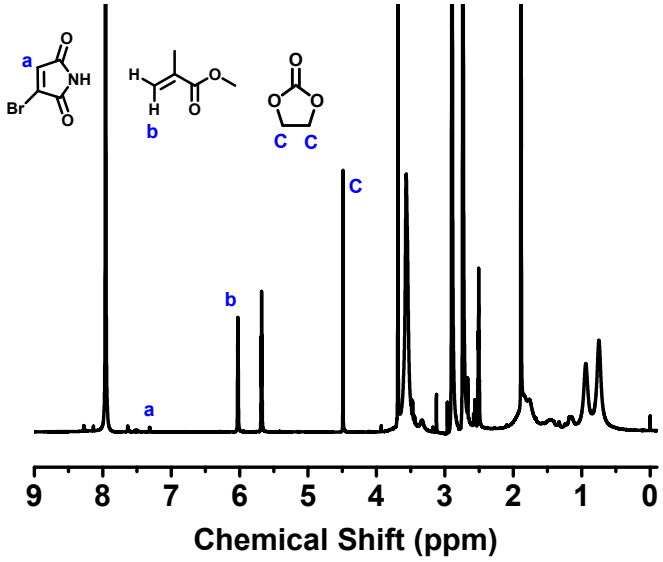



**Fig. S4** 300 MHz $^1$H NMR spectrum in DMSO-$d_6$ recorded for the RAFT polymerization of MMA adjusted by MBr. $[MMA]_0/[MBr]_0/[CPDB]_0/[ACCN]_0$ = 200/5/1/0.2, 110 °C; MMA = 2.0 mL, MMA /DMF = 1/1 (v/v). Conv. $_{MMA}$ = ($[I6.05\text{-}5.99]_0$ - [I6.05-5.99])/ $[I6.05\text{-}5.99]_0 \times 100$ %; Conv. $_{MBr}$ = ($[I7.32\text{-}7.30]_0$ - [I7.32-7.30])/ $[I7.32\text{-}7.30]_0 \times 100$ %.

### 2. Conversion calculation of RAFT polymerization of St with adjusted *Đ* by using

**MBr**

Fig. S5 shows a typical $^{1}$H NMR spectrum recorded during polymerization of St adjusted by MBr. St conversion (Conv. $_{St}$) was calculated from the raw experimental samples by comparing the integration of one vinyl proton of remaining St at 5.90-5.75 ppm (I5.90-5.75) to the initial integration of St. MBr conversion are affected by PSt and cannot be calculated. The region 4.50-4.45 ppm (I4.50-4.45), which belonged to EC was used as an internal standard.

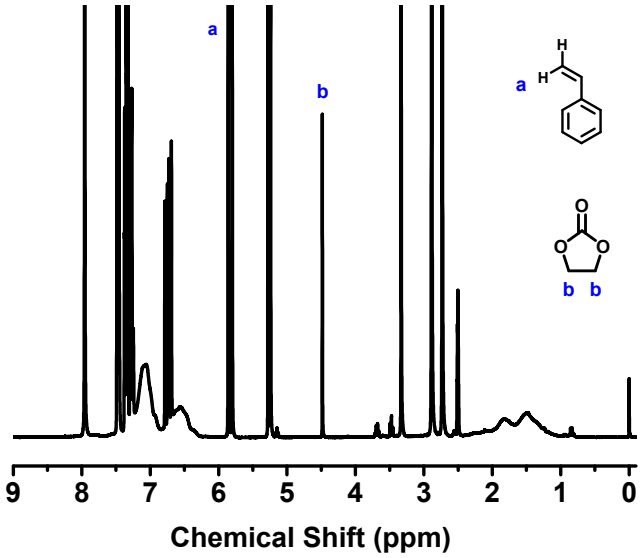



**Fig. S5** 300 MHz $^{1}$H NMR spectrum in DMSO-$d_6$ recorded for the RAFT polymerization of St adjusted by MBr. $[St]_0/[MBr]_0/[CPDB]_0/[ACCN]_0$ = 200/3/1/0.2, 110 °C; St = 2.0 mL, St /DMF = 2/1 (v/v). Conv. $_{St}$ = ($[I5.90\text{-}5.75]_0$ - [I5.90-5.75])/ $[I5.90\text{-}5.75]_0$ × 100 %.

## 3. Conversion calculation of RAFT polymerization of MMA with adjusted *Đ* by using FMBr

Fig. S6 shows a typical $^{1}$H NMR spectrum recorded during polymerization of MMA adjusted by FMBr. MMA conversion (Conv. $_{MMA}$) was calculated from the raw experimental samples by comparing the integration of one vinyl proton of remaining MMA at 6.05-5.99 ppm (I6.05-5.99) to the initial integration of MMA. FMBr conversion (Conv. $_{FMBr}$) was calculated from the raw experimental samples by

comparing the integration of two vinyl protons of remaining FMBr at 6.77-6.64 ppm (I6.77-6.64) to the initial integration of FMBr. MBr conversion (Conv. $_{MBr}$) was calculated from the raw experimental samples by comparing the integration of two vinyl protons of remaining FMBr at 6.77-6.64 ppm (I6.77-6.64) and one vinyl proton of remaining MBr at 7.32-7.30 ppm (I7.32-7.30) to the initial integration of FMBr. The region 4.50-4.45 ppm (I4.50-4.45), which belonged to EC was used as an internal standard.

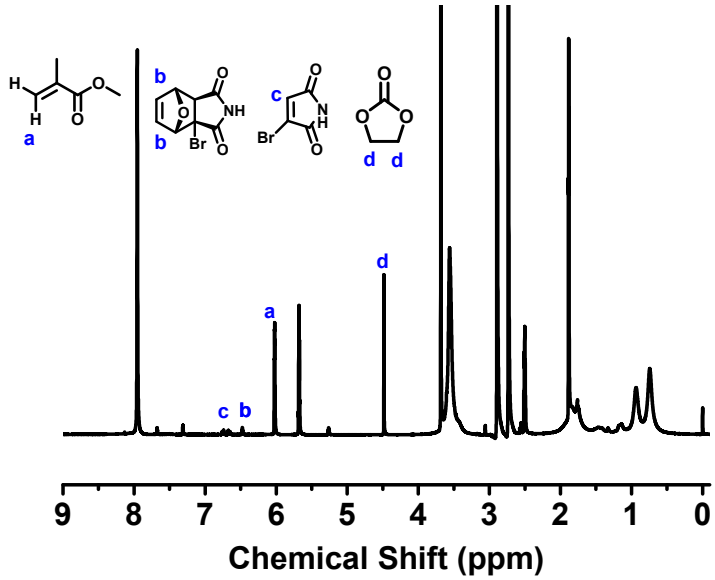



**Fig. S6** 300 MHz $^{1}$H NMR spectrum in DMSO-$d_6$ recorded for the RAFT polymerization of MMA adjusted by FMBr. $[MMA]_0/[FMBr]_0/[CPDB]_0/[ACCN]_0/[ABVN]_0$ = 400/10/1/0.2/0.2, temperature sequence: 40 °C (46.0 h)-110 °C (5.0 h); MMA = 2.0 mL, MMA /DMF = 1/1 (v/v). Conv. $_{MMA}$ = ($[I6.05\text{-}5.99]_0$ - [I6.05-5.99])/ $[I6.05\text{-}5.99]_0$ × 100 %; Conv. $_{FMBr}$ = ($[I6.77\text{-}6.64]_0$ - [I6.77-6.64])/ $[I6.77\text{-}6.64]_0$ × 100 %; Conv. $_{MBr}$ = ($[I6.77\text{-}6.64]_0$ - [I6.77-6.64] – 2 × [I7.32-7.30])/ $[I6.77\text{-}6.64]_0$ × 100 %.

## 4. Supplementary Figures

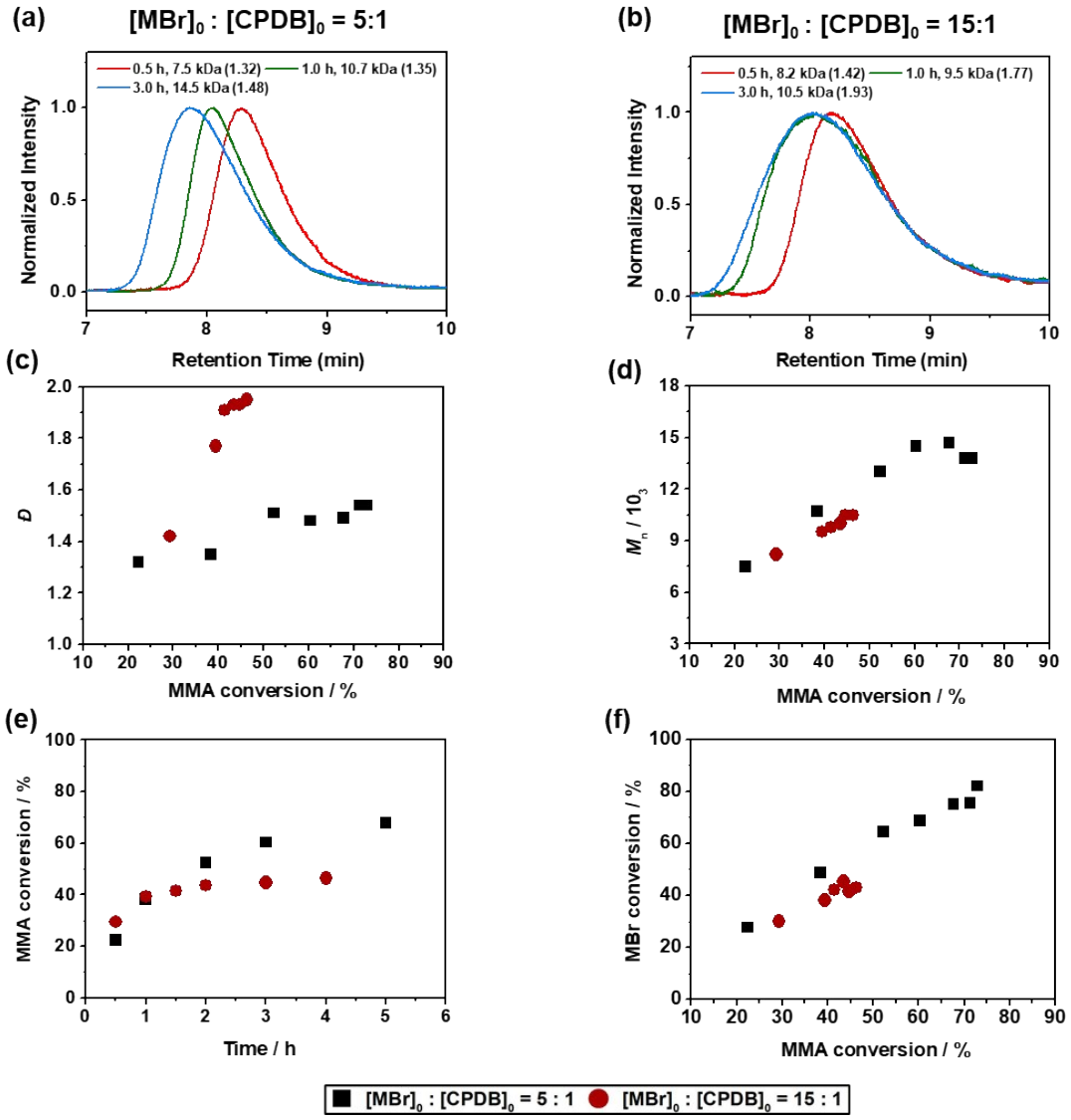



**Fig. S7** Investigation of *Đ* regulation by using MBr in RAFT polymerization. (a-b) SEC traces. (c) *Đ* vs. MMA conversion; (d) $M_n$ vs. MMA conversion; (e) MMA conversion vs. time; (f) MBr conversion vs. MMA conversion. $[MMA]_0/[MBr]_0/[CTA]_0/[ACCN]_0$ = 200/x/1/0.2, 110 °C, MMA = 2.0 mL, MMA/DMF = 1/1 (v/v).

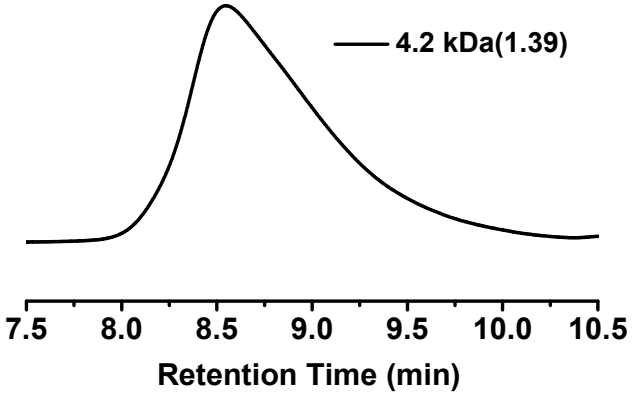



**Fig. S8** SEC traces of PSM-1. $[St]_0/[MBr]_0/[CPDB]_0/[ACCN]_0$ = 200/3/1/0.2, 110 °C; St = 2.0 mL, MMA /DMF = 2/1 (v/v).

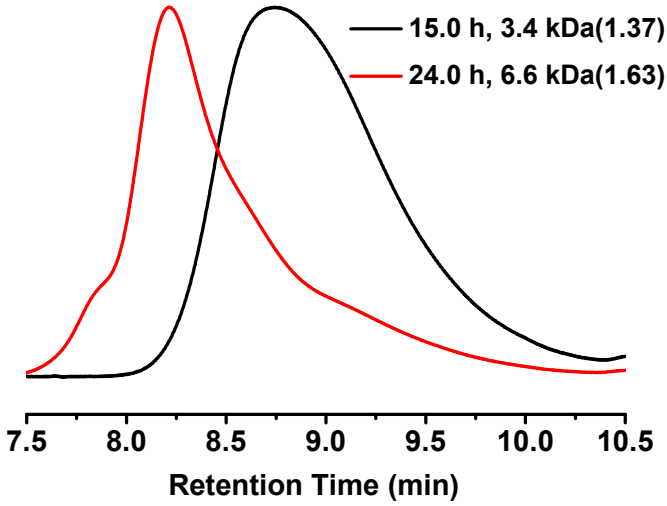



**Fig. S9** SEC traces of PSM-2. $[St]_0/[MBr]_0/[CPDB]_0/[ACCN]_0$ = 200/5/1/0.2, 110 °C; St = 2.0 mL, MMA /DMF = 2/1 (v/v). The same amount of initiator is added after 15 h.

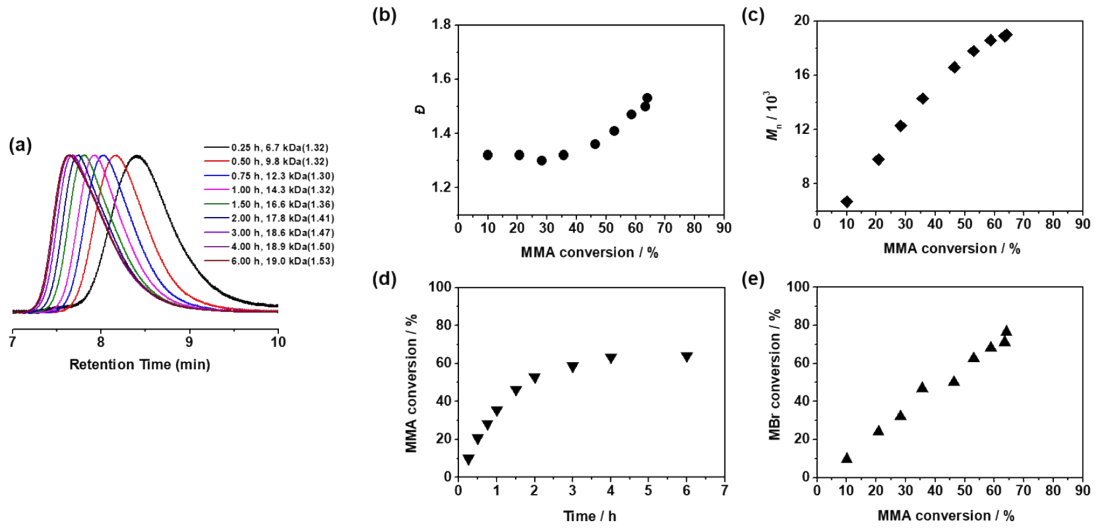



**Fig. S10** Investigation of *Đ* regulation by using MBr in RAFT polymerization. (a) SEC traces; (b) *Đ* vs. MMA conversion; (c) $M_n$ vs. monomer conversion; (d) MMA conversion vs. time; (e) MBr conversion vs. MMA conversion. $[MMA]_0/[MBr]_0/[CPDB]_0/[ACCN]_0$ = 400/5/1/0.2, 110 °C; MMA = 2.0 mL, MMA /DMF = 1/2 (v/v).

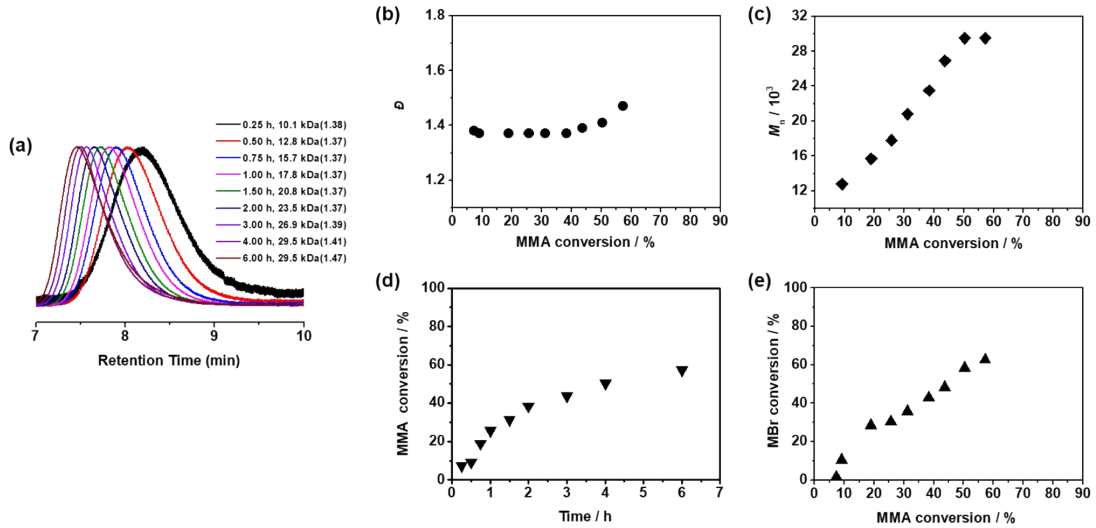



**Fig. S11** Investigation of *Đ* regulation by using MBr in RAFT polymerization. (a) SEC traces; (b) *Đ* vs. MMA conversion; (c) $M_n$ vs. monomer conversion; (d) MMA conversion vs. time; (e) MBr conversion vs. MMA conversion. $[MMA]_0/[MBr]_0/[CPDB]_0/[ACCN]_0$ = 800/5/1/0.2, 110 °C; MMA = 2.0 mL, MMA /DMF = 1/2.5 (v/v).

**Table S1.** RAFT polymerization with adjusted *Đ* by using MBr

| Entry | monomer | $[monomer]_0/[MBr]_0/[CTA]_0/[initiator]_0$[a,b,c] | t(h) | Conversion(%)[d] | $M_{n,SEC}$(Da)[e] | *Đ*[f] |
|---|---|---|---|---|---|---|
| 1 | MMA | 200/0/1/0.2 | 3 | 84.4 | 16,000 | 1.21 |
| 2 | MMA | 200/5/1/0.2 | 5 | 67.7 | 14,700 | 1.49 |
| 3 | MMA | 200/10/1/0.2 | 5 | 51.8 | 13,400 | 1.77 |
| 4 | MMA | 200/15/1/0.2 | 4 | 46.5 | 10,500 | 1.95 |
| 5 | MMA | 200/30/1/0.2 | 2 | 29.0 | 8,000 | 1.85 |
| 6 | MMA | 400/5/1/0.2 | 6 | 64.1 | 19,000 | 1.53 |
| 7 | MMA | 800/5/1/0.2 | 6 | 57.2 | 29,500 | 1.47 |
| 8 | St | 200/3/1/0.2 | 15 | 17.5 | 4,200 | 1.39 |
| 9 | St | 200/5/1/0.2 | 15 | 6.2 | 3,400 | 1.37 |

[a] CTA is 2-Cyanoprop-2-yl dithiobenzoate (CPDB).
[b] Initiator is 1,1′-Azobis (cyclohexanecarbonitrile) (ACCN).
[c] Reaction temperature is 110 °C.
[d] Monomer conversion determined by $^1$H NMR.
[e, f] Determined by SEC in DMF with St standard calibration.

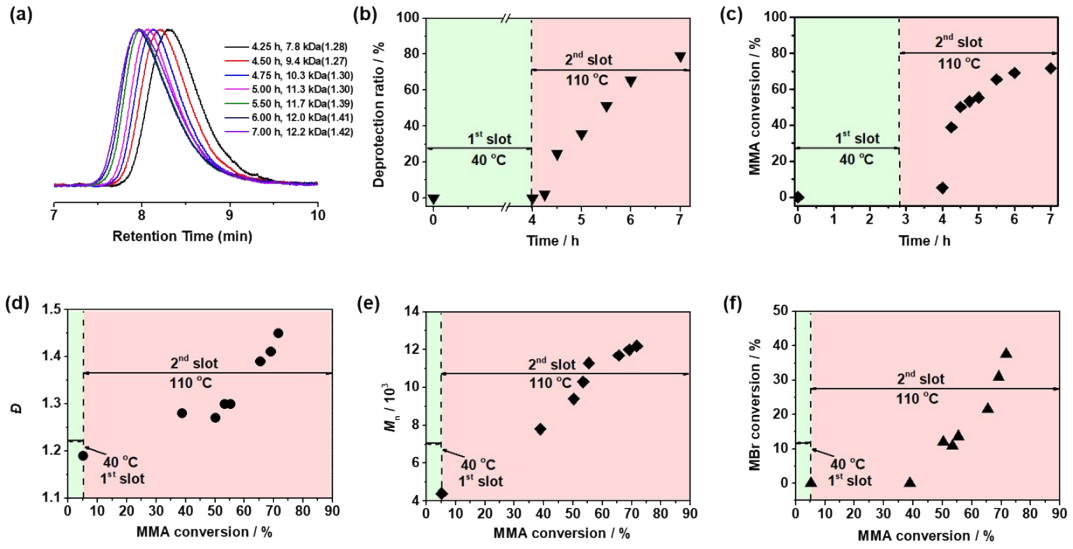



**Fig. S12** Investigation of *Đ* regulation by using FMBr in RAFT polymerization. (a) SEC traces; (b) Deprotection ratio vs. time; (c) MMA conversion vs. time; (d) *Đ* vs. MMA conversion; (e) $M_n$ vs. MMA conversion; (f) MBr conversion vs. MMA conversion. $[MMA]_0/[FMBr]_0/[CPDB]_0/[ACCN]_0/[ABVN]_0$ = 200/10/1/0.2/0.2, MMA = 2.0 mL, MMA /DMF = 1/1 (v/v). Temperature sequence: 40 °C (4.0 h)–110 °C (4.0 h). MMA conversion, MBr conversion and deprotection ratio were determined by 300 MHz $^1$H NMR. $M_n$ and *Đ* were determined by SEC in DMF with St standard calibration.

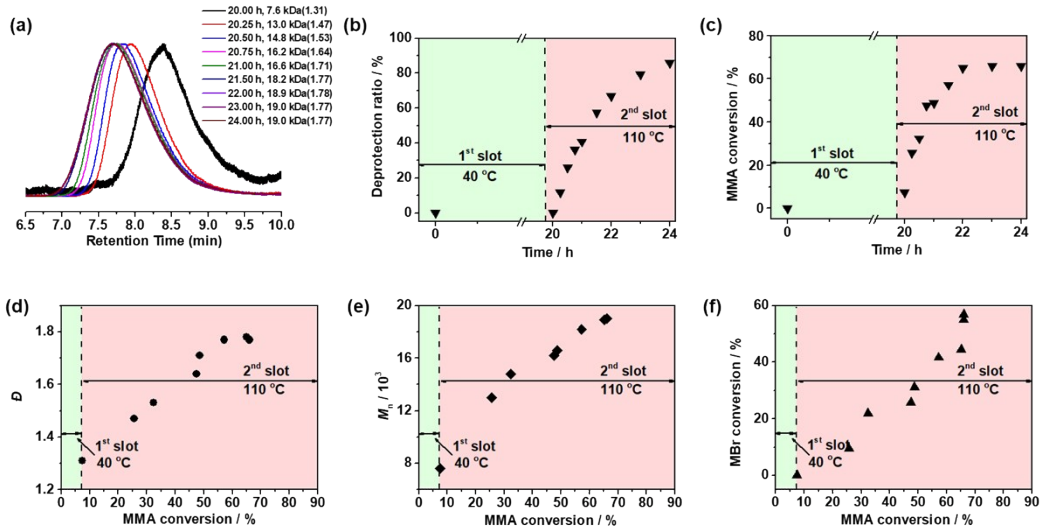



**Fig. S13** Investigation of *Đ* regulation by using FMBr in RAFT polymerization. (a) SEC traces; (b) Deprotection ratio vs. time; (c) MMA conversion vs. time; (d) *Đ* vs. MMA conversion; (e) $M_n$ vs. MMA conversion; (f) MBr conversion vs. MMA conversion. $[MMA]_0/[FMBr]_0/[CPDB]_0/[ACCN]_0/[ABVN]_0$ = 400/20/1/0.2/0.2, MMA = 2.0 mL, MMA /DMF = 1/2 (v/v). Temperature sequence: 40 °C (48.0 h)–110 °C (3.0 h). MMA conversion, MBr conversion and deprotection ratio were determined by 300 MHz $^1$H NMR. $M_n$ and *Đ* were determined by SEC in DMF with St standard calibration.

**Table S2.** RAFT polymerization with adjusted *Đ* by using FMBr

| Entry | $[MMA]_0/[FMBr]_0/[CTA]_0/[initiator_1]_0/[initiator_2]_0$[a,b] | T(°C) | t(h) | Conversion(%)[c] | $M_{n,SEC}$(Da)[d] | *Đ*[e] |
|---|---|---|---|---|---|---|
| 1 | 200/10/1/0.2/0.2 | 40 | 4 | 5.2 | 4,400 | 1.19 |
| | | ↓ 110 | 3 | 71.7 | 12,200 | 1.42 |
| 2 | 400/10/1/0.2/0.2 | 40 | 20 | 34.6 | 18,900 | 1.16 |
| | | ↓ 110 | 3 | 75.2 | 25,800 | 1.40 |
| 3 | 400/20/1/0.2/0.2 | 40 | 20 | 7.4 | 7,600 | 1.31 |
| | | ↓ 110 | 4 | 66.0 | 19,000 | 1.77 |

[a] CTA is 2-Cyanoprop-2-yl dithiobenzoate (CPDB).
[b] $Initiator_1$ is 2,2′-azobis-(2,4-dimethylvaleronitrile) (ABVN) used at 40 °C, $initiator_2$ is 1,1′-Azobis (cyclohexanecarbonitrile) (ACCN) used at 110 °C.
[c] Determined by $^1$H NMR.
[d, e] Determined by SEC in DMF with St standard calibration.

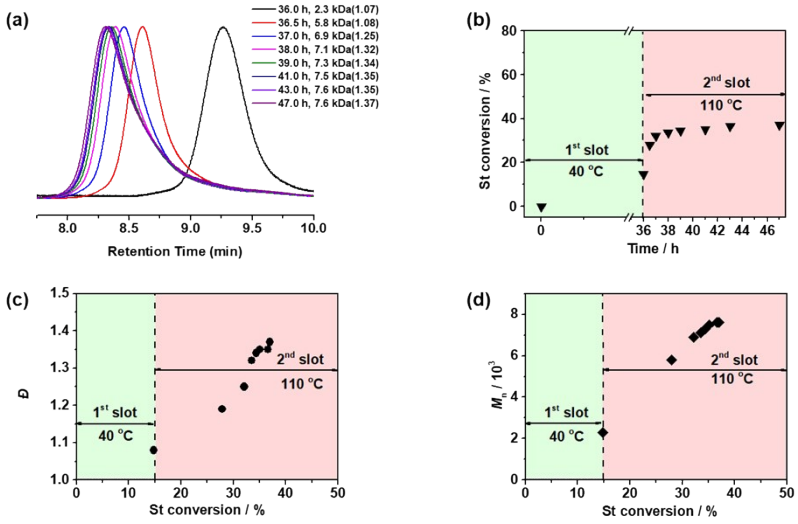



**Fig. S14** Investigation of *Đ* regulation by using FMBr in RAFT polymerization. (a) SEC traces; (b) Deprotection ratio vs. time; (c) MMA conversion vs. time; (d) *Đ* vs. MMA conversion; (e) $M_n$ vs. MMA conversion; (f) MBr conversion vs. MMA conversion. $[MMA]_0/[FMBr]_0/[CPDB]_0/[ACCN]_0/[ABVN]_0$ = 400/20/1/0.2/0.2, MMA = 2.0 mL, MMA /DMF = 1/2 (v/v). Temperature sequence: 40 °C (48.0 h)–110 °C (3.0 h). MMA conversion, MBr conversion and deprotection ratio were determined by 300 MHz $^1$H NMR. $M_n$ and *Đ* were determined by SEC in DMF with St standard calibration.

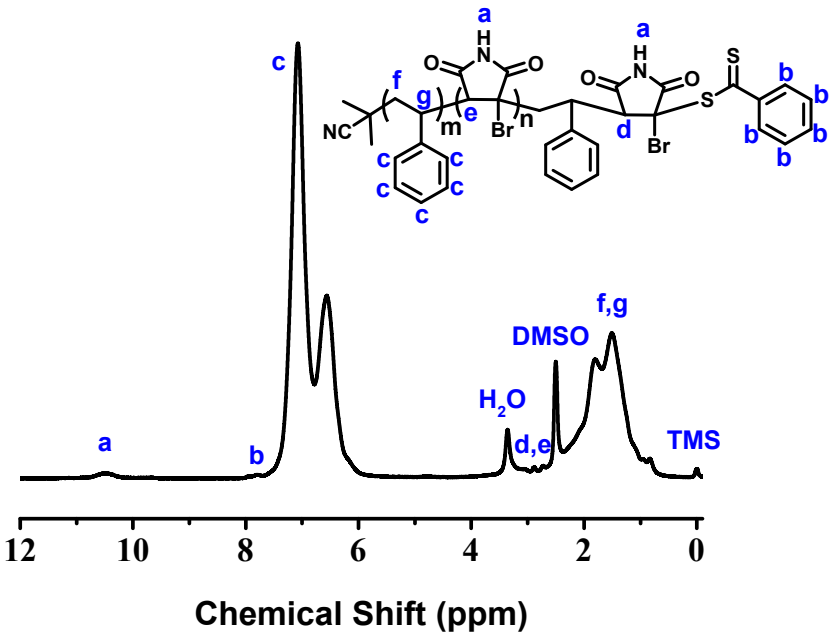



**Fig. S15** 300 MHz $^1$H NMR spectrum in DMSO-$d_6$ recorded for PSt adjusted by MBr.

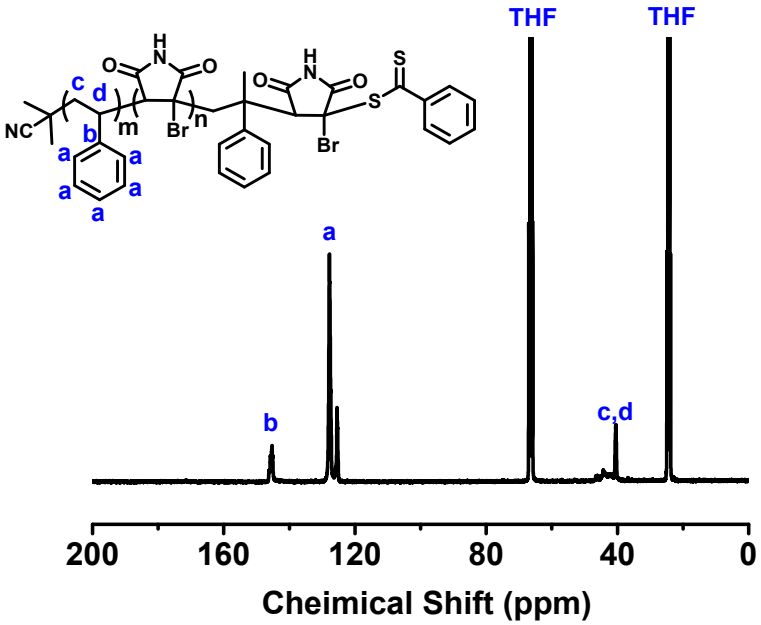



**Fig. S16** 300 MHz $^{13}$C NMR spectrum in THF-$d_8$ recorded for PSt adjusted by MBr.

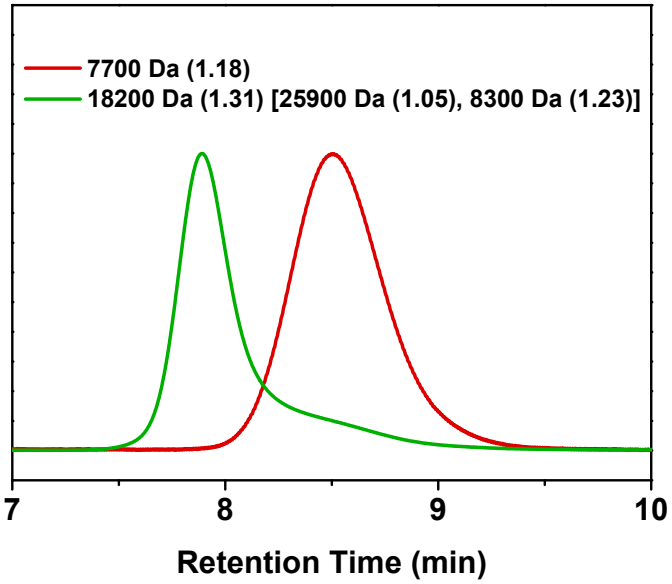



**Fig. S17** SEC traces of PMM-B (red line) and products after chain extension (green line). Reaction condition of synthesizing PMM-B: $[MMA]_0/[MBr]_0/[CTA]_0/[ACCN]_0$ = 200/5/1/0.2, 110 °C, 15 min, MMA = 2.0 mL, MMA/DMF = 1/1 (v/v). Reaction condition of chain extension: $[MMA]_0/[PMM\text{-}B]_0/[ACCN]_0$ = 200/1/0.2, 110 °C, 5 h, MMA = 0.29 mL, MMA/DMF = 1/1 (v/v). Before chain extension, $M_n$ = 7700 Da, $Đ$ = 1.18, and after chain extension, $M_n$ = 18200 Da, $Đ$ = 1.31. There is a significant tailing on the SEC traces, $M_n$ of main peak is 25900 Da, and $M_n$ of tailing part is 8300 Da, so that we can achieve the conclusion that the living chains are extended while the MBr capped chains are retarded.

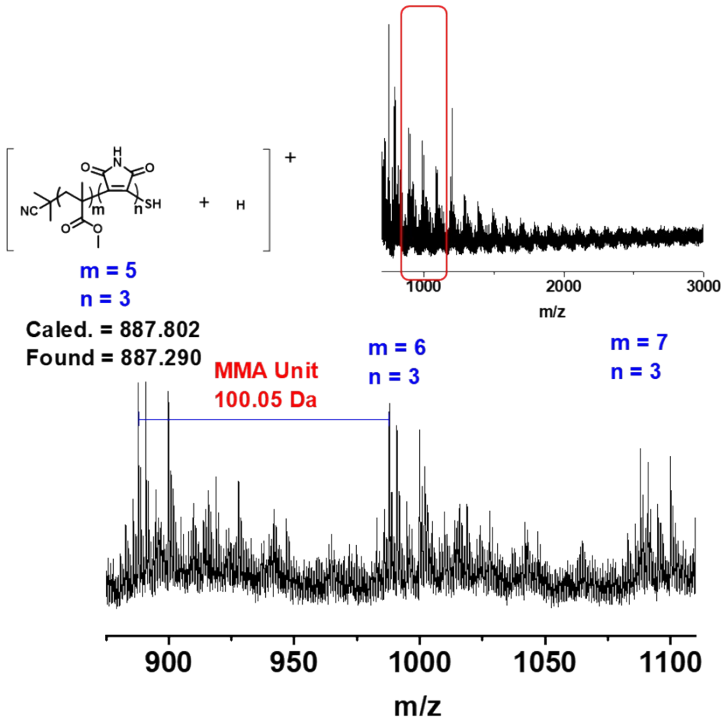



**Fig. S18** MALDI-TOF mass spectrum of PMMA. Reaction condition of synthesizing PMMA: $[MMA]_0/[MBr]_0/[CTA]_0/[ACCN]_0$ = 100/30/1/0.2, 110 °C, 15 min, MMA = 2.0 mL, MMA/DMF = 1/2 (v/v). It should be noted that the MBr units in the chemical structure were distributed along the polymer chain and were not all attached at the end.

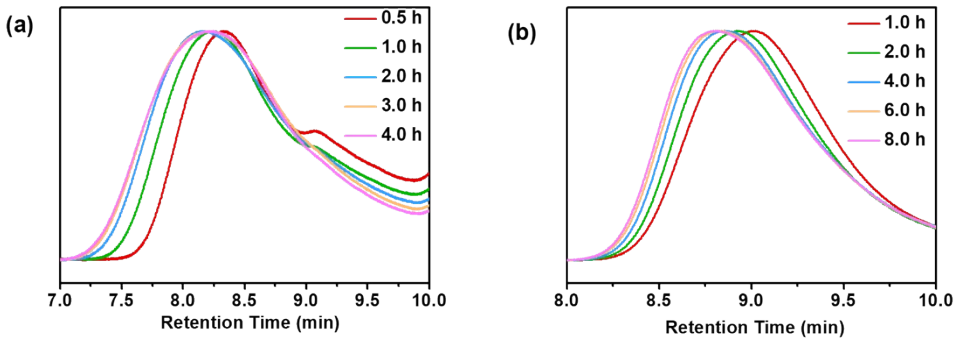



**Fig. S19** SEC traces of completely terminated (a) PMMA and (b) PSt. (a) $[MMA]_0/[MBr]_0/[CPDB]_0/[ACCN]_0$ = 200/60/1/0.2, 110 °C; MMA = 2.0 mL, MMA/DMF = 1/1 (v/v); (b) $[St]_0/[MBr]_0/[CPDB]_0/[ACCN]_0$ = 200/10/1/0.2, 110 °C; St= 2.0 mL, St/DMF = 2/1 (v/v). Determined by SEC in DMF with St standard calibration.