

## Supporting Information for

# Facile Synthesis of Gradient Polymers with Advanced Sequence Control by Using Furan Protected Maleimide as a Co-monomer

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## SECTION C. REFERENCE

### SECTION A. Experimental Section

#### 1. Materials

Methyl methacrylate (MMA, Sinopharm Chemical Reagents, 99%) and Benzyl methacrylate (BzMA, Aladdin, 98%) was inhibited during storage, and the inhibitor was removed from it by alkaline aluminum oxide column chromatography. 2,2'-azobis-(2,4-dimethylvaleronitrile) (ABVN), 1,1'-Azobis(cyclohexanecarbonitrile) (ACHN) and 2,2-Azobisisobutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent, China (98%) and purified by recrystallization from ethanol. 2-Cyanoprop-2-yl 1-dithionaphthalate (CPDN) was synthesized according to the method reported elsewhere.<sup>1</sup> 4-cyano-4-[(phenylthioxomethyl)thio]-, 1,1'-(1,2-ethanediyl) ester (BiCPADB) was synthesized according to the literature.<sup>2</sup> Toluene (solvent) was purified before use by passing through a purification column (Solvent Dispensing System; glass contour). N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Energy Chemical, 99%), Copper (Cu(0), 99%, Aldrich) were used as received. Furan, maleic anhydride, anhydrous ether, methanol, N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and all other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. and used as received without any further purification.

#### 2. Analysis Techniques

The number-average molecular weight ( $M_n$ ) and polydispersity ( $D = M_w/M_n$ ) 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 Mutipore HZ-N (4.6 × 150 mm, 3 μm beads size) columns arranged in series, and it can separate polymers in the molecular weight range 500-1.9 × 10<sup>5</sup> g/mol. THF was used as the eluent at a flow rate of 0.35 mL/min at 40 °C. Data acquisition was performed using EcoSEC software and molecular weights were calculated with poly(methyl methacrylate) (PMMA) standards.

All <sup>1</sup>H NMR spectra were collected using a Bruker nuclear magnetic resonance

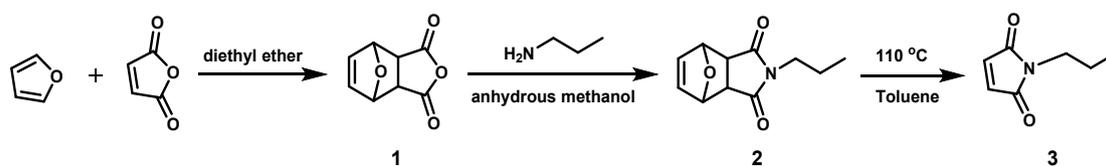
instrument (300 MHz) using tetramethylsilane (TMS) as the internal standard at room temperature. The  $^1\text{H}$  NMR spectra were referenced to  $\delta$  7.26 ppm in  $\text{CDCl}_3$ .

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy were acquired on an UltrafleXtreme MALDI-TOF mass spectrometer equipped with a 1 KHz smart beam-II laser. The instrument was calibrated prior to each measurement with external PMMA at the molecular weight under consideration. The compound trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, >98%) served as the matrix and was prepared in  $\text{CHCl}_3$  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). All samples were dissolved in chloroform at a concentration of 10 mg/mL. After sample preparation and solvent evaporation, the plate was inserted into the MALDI mass spectrometer. The attenuation of the laser was adjusted to minimize undesired polymer fragmentation and to maximize the sensitivity.

Differential scanning calorimetry (DSC) was performed with heating and cooling at a rate of  $10\text{ }^\circ\text{C min}^{-1}$  with a limited temperature from  $0\text{ }^\circ\text{C}$ - $200\text{ }^\circ\text{C}$  on a Q200 differential scanning calorimeter (TA Instruments), and the glass transition temperature ( $T_g$ ) was measured on the third cycle of a heat/cool/heat experiment.

Thermogravimetric analyses (TGA) were performed on a thermogravimetric analyzer (Discovery TGA, USA) at a heating rate of  $10\text{ }^\circ\text{C /min}$  from room temperature to  $800\text{ }^\circ\text{C}$  under a  $\text{N}_2$  atmosphere.

### 3. Monomer synthesis and polymerizations



**Scheme S1.** Synthesis of propyl maleimide (compound 3)

#### 3.1 Synthesis of furan protected maleic anhydride (1)

Maleic anhydride (40.0 g, 408 mmol) was dissolved in 300 mL anhydrous

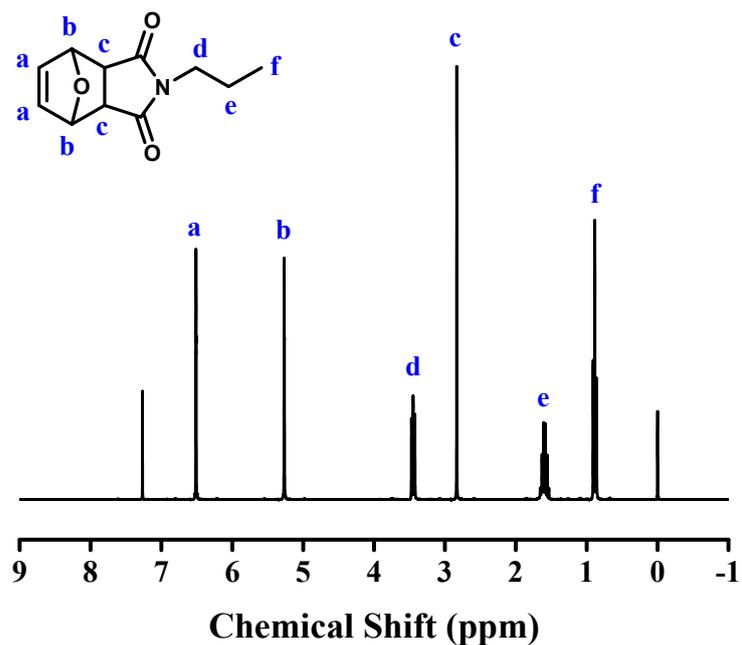
diethyl ether, and then furan (64.0 g, 940 mmol) was added to the above solution. The reaction was stirred at room temperature for 48 hours. The product precipitated out of solution and was collected via vacuum filtration and washed with diethyl ether. After that, the product was added to 300 mL anhydrous diethyl ether again and stirred at room temperature for 24 hours. The mixture was filtered to afford the final product as a white solid (60.0 g, 88.5% yield).

### 3.2 Synthesis of furan protected propyl maleimide (compound 2)

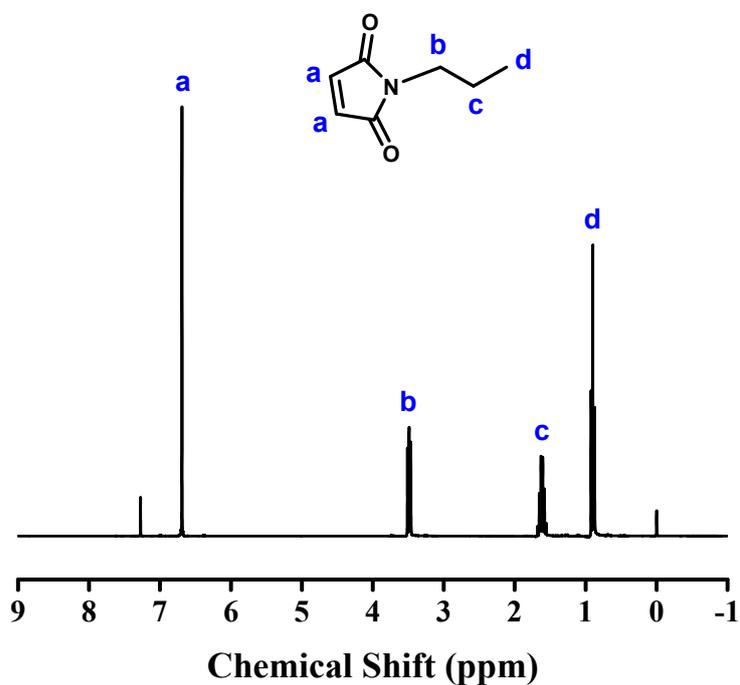
To a 500 mL round-bottom flask, 250 mL anhydrous methanol and compound 1 (35 g, 211 mmol) were added and cooled to 0 °C with stirring. And then, a solution of n-propylamine (21.6 g, 365 mmol) in anhydrous methanol (30.0 mL) was added dropwise to the above mixture. The reaction was allowed to warm to room temperature and then refluxed at 70 °C for 16 hours. Afterwards, the reaction was concentrated by rotovaping and purified by recrystallization from methanol to afford the pure product as a white crystal (20.0 g, 45.7% yield) (**Figure. S1**). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.51 (s, 2H), 5.27 (s, 2H), 3.53 – 3.38 (m, 2H), 2.83 (s, 2H), 1.68 – 1.52 (m, 2H), 0.88 (t, 3H).

### 3.3 Synthesis of propyl maleimide (compound 3)

Compound 2 (14.0 g, 67.6 mmol) was dissolved in 200 mL of toluene, the mixture was refluxed at 110 °C for 24 hours. Then, toluene was removed under vacuum and the residue was subjected to column chromatography (petrol ether/ether acetate, 4/1 (v/v)). The product was obtained as a white crystal (5.45 g, 58.0% yield) (**Figure. S2**). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.69 (s, 2H), 3.57 – 3.42 (m, 2H), 1.69 – 1.55 (m, 2H), 0.90 (t, 3H).



**Figure S1.** 300 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of compound 2



**Figure S2.** 300 MHz <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> of compound 3

### 3.4 Typical procedures for RAFT polymerization of MMA and FPMI with programmable fluctuations of temperature

The polymerization was carried out in a baked Schlenk tube under argon

protection. A typical procedure for a MMA/PMI di-block gradient copolymer was given. Into a glass tube, FPMI (0.9770 g, 4.71 mmol), CPDN (0.0640, 0.236 mmol), MMA (5.0 mL, 47.1 mmol), ABVN (0.0117 g, 0.0471 mmol), and toluene (5.0 mL) were added. Then, the mixture was degassed by three freeze-pump-thaw cycles. The reaction tube was placed in an oil bath kept at 40 °C. After predetermined time, the tube was taken out and was removed to another oil bath pre-stabilized at 100 °C and maintained for predetermined time. In case of the polymer chain loss livingness during the temperature jump, we often add a certain amount of initiator ACHN. At predetermined intervals, an aliquot was taken out with a syringe under argon, and the reaction was terminated by cooling to -24 °C. Immediately, monomer conversion was determined by <sup>1</sup>H NMR spectroscopy. The crude copolymer was diluted with THF and precipitated in methanol to obtain the pure product, which was then analyzed by SEC and MALDI-TOF mass spectroscopy.

### 3.5 RAFT homopolymerization of MMA

The polymerization was carried out in a baked Schlenk tube under argon protection. Into a glass tube, MMA (5.0 mL, 47.1 mmol), ACHN (0.0115 g, 0.0471 mmol), CPDN (0.064 g, 0.236 mmol) and toluene (10.0 mL) were added. Then, the mixture was degassed by three freeze-pump-thaw cycles. The reaction tube was placed in an oil bath kept at 100 °C. At predetermined intervals, an aliquot was taken out with a syringe under argon, and the reaction was terminated by cooling to -24 °C. The crude polymer was diluted with THF and precipitated in methanol to obtain the pure product.

### 3.6 RAFT homopolymerization of PMI

Into a 5 mL ampoule, PMI (0.5 g, 3.59 mmol), AIBN (0.0007 g, 0.004 mmol), CPDN (0.0024 g, 0.009 mmol) and toluene (0.5 mL) were added. Then, the mixture was degassed by three freeze-pump-thaw cycles and stirred at 65 °C for 12.0 h. The reaction was terminated by cooling to -24 °C. The crude polymer was precipitated in methanol to obtain the pure product. ( $M_{n,SEC} = 5200$  Da,  $D = 1.15$ )

## SECTION B. Results and Discussions

### 1. The effect of free furan on the polymerization

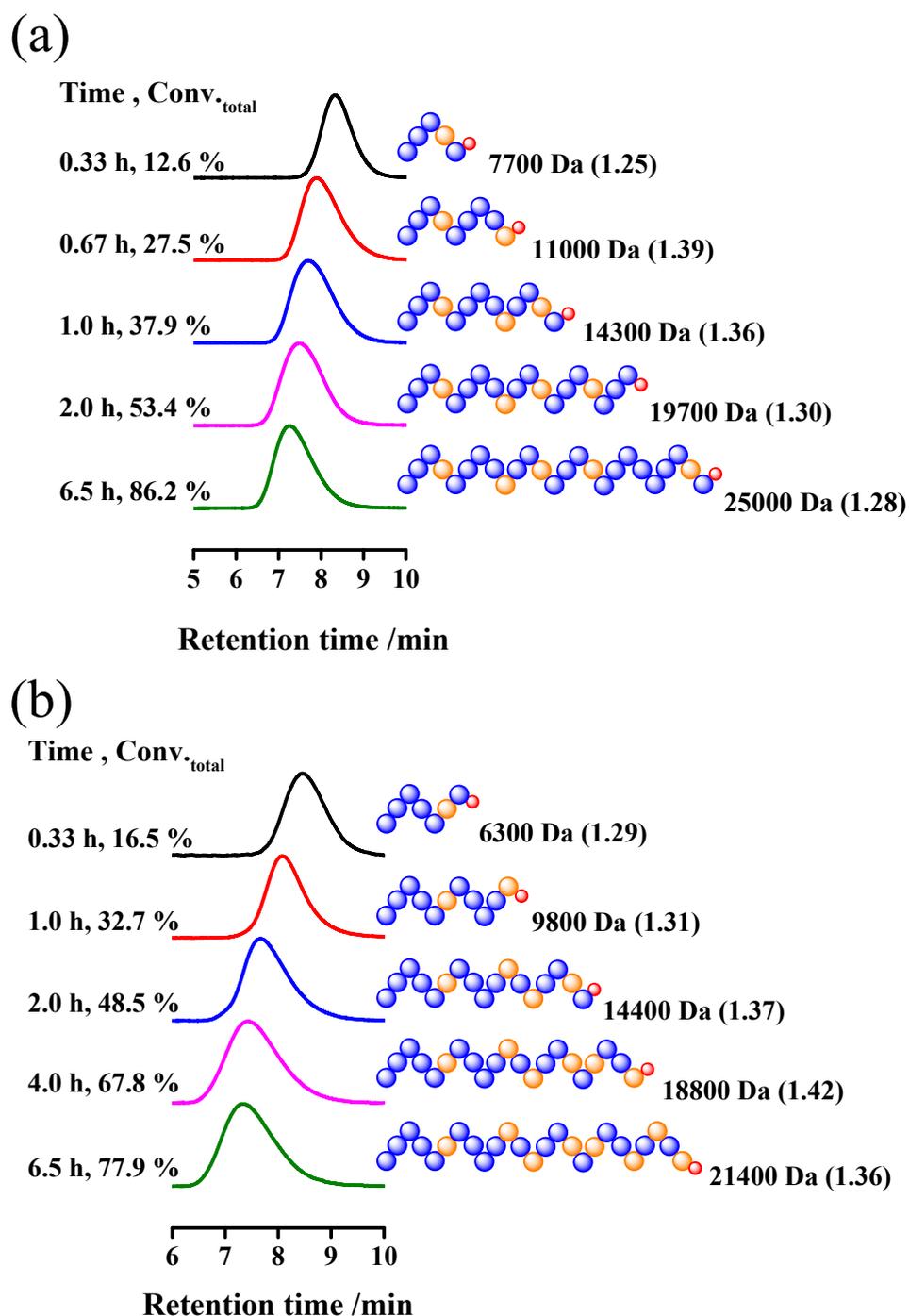
To verify whether furan can polymerize with MMA, the RAFT polymerization was conducted under room temperature since furan has the boiling point of 32 °C.<sup>3</sup> As shown in Table 1, the polymerization of MMA in the absence of furan was carried for in DMSO at 25 °C. Within 22 h, the PMMA ( $M_n = 26900$  Da,  $D = 1.12$ ) can be easily obtained. However, when furan was added ( $[MMA]_0/[furan]_0 = 200/20$ ,  $[MMA]_0/[furan]_0 = 100/100$ ), no polymer yielded. This result validated that furan cannot copolymerize with MMA *via* radical polymerization.

**Table 1.** Polymerizations of MMA and Furan under various conditions<sup>a</sup>

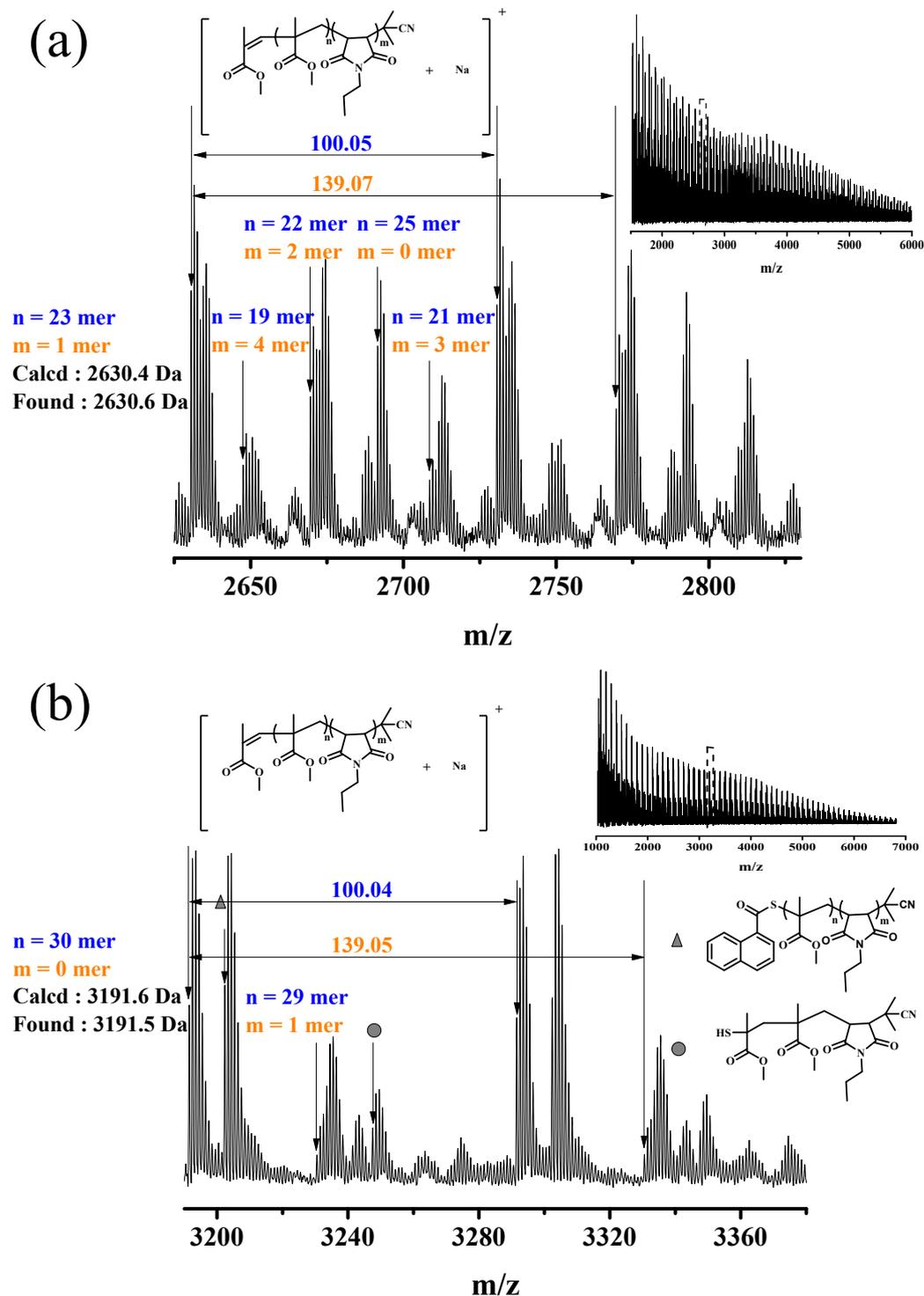
Entry	Contents	Temperature (°C)	Time (h)	Conv. (%)
1	MMA/CPDN/Cu(0)/PMDETA	25	22	85.6
2	MMA/furan/CPDN/Cu(0)/PMDETA	25	22	-
3	MMA/furan/CPDN/Cu(0)/PMDETA	25	22	-

<sup>a</sup>entry 1:  $[MMA]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0 = 200/1/1/1$ , MMA = 5.0 mL, DMSO = 2.84 mL,  $[MMA]_0 = 6.01$  mol/L; entry 2:  $[MMA]_0/[furan]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0 = 200/20/1/1/1$ , MMA = 5.0 mL, DMSO = 2.5 mL,  $[MMA]_0 = 6.01$  mol/L; entry 3:  $[MMA]_0/[furan]_0/[CPDN]_0/[Cu(0)]_0/[PMDETA]_0 = 100/100/1/1/1$ , MMA = 3.0 mL, DMSO = 1.5 mL,  $[MMA]_0 = 4.32$  mol/L.

### 2. SEC traces and MALDI-TOF mass spectra of simultaneous gradient and hierarchical gradient copolymers

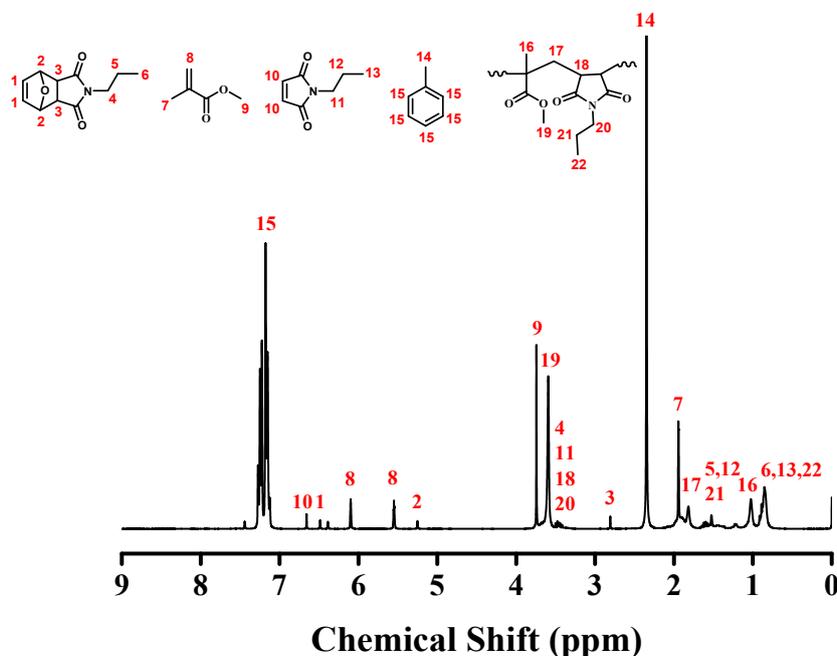


**Figure S3.** SEC curves of the samples during the polymerization with bead model of chain sequence distribution: a) MMA with PMI at 100 °C; b) MMA with FPMI at 100 °C.  $[MMA]_0/[PMI]_0$ (or  $[FPMI]_0$ )/ $[CPDN]_0/[ACHN]_0 = 200/20/1/0.2$ , MMA = 5.0 mL, in toluene/MMA (2/1, v/v). The positions and numbers of both monomer unit beads are not accurate but the illustration is intended to guide the eye.

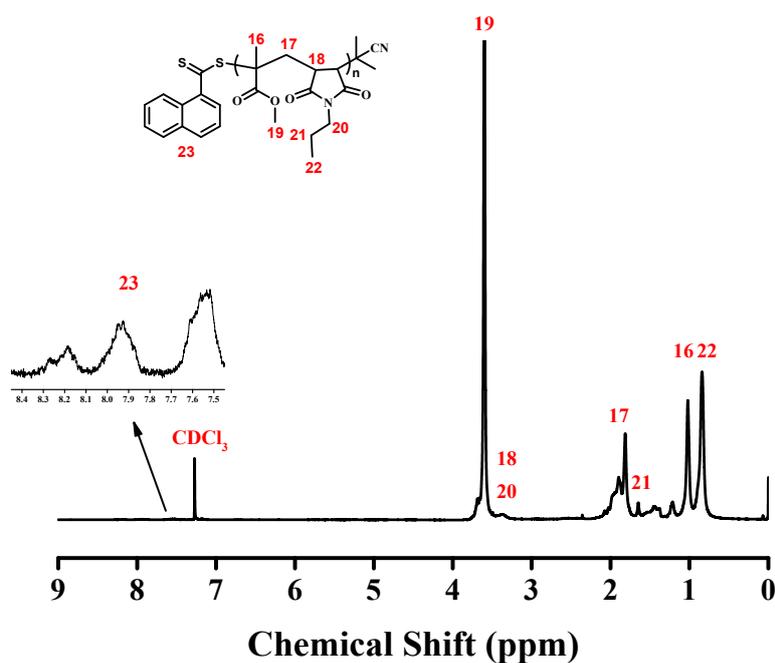


**Figure S4.** MALDI-TOF mass spectra of the polymers from MMA/PMI and MMA/FPMI at 100 °C for producing sequence-controlled polymers by using Na salt as the cationization agent and a DCTB matrix: a) The sample was obtained from the copolymerization of MMA and PMI (7700 Da,  $D = 1.25$ ); b) The sample was obtained from the copolymerization of MMA and FPMI (6300 Da,  $D = 1.29$ ).  $[MMA]_0/[PMI]_0$ (or  $[FPMI]_0$ )/ $[CPDN]_0$ / $[ACHN]_0 = 200/20/1/0.2$ , MMA = 5.0 mL, in toluene/MMA (2/1, v/v).

Figure S5 shows a typical  $^1\text{H}$  NMR spectrum recorded during a sequential radical copolymerization of MMA and FPPI. MMA conversion ( $\text{Conv.}_{\text{MMA}}$ ) was calculated from the raw experimental samples by comparing the integration of one vinyl proton of remaining MMA at 6.10 ppm ( $I_{6.10}$ ) to the initial integration of MMA. The region 2.35 ppm ( $I_{2.35}$ ), which belongs to the 3 methyl protons of toluene was used as an internal standard. The conversion of polymerized PMI was estimated by comparing the integration of 2 protons of remaining FPPI at 6.49 ppm ( $I_{6.49}$ ) and the integration of 2 protons of the released but unpolymerized PMI at 6.66 ppm ( $I_{6.66}$ ) with the initial undeprotected FPPI. By the way, the concentration of free PMI in the system was also calculated.

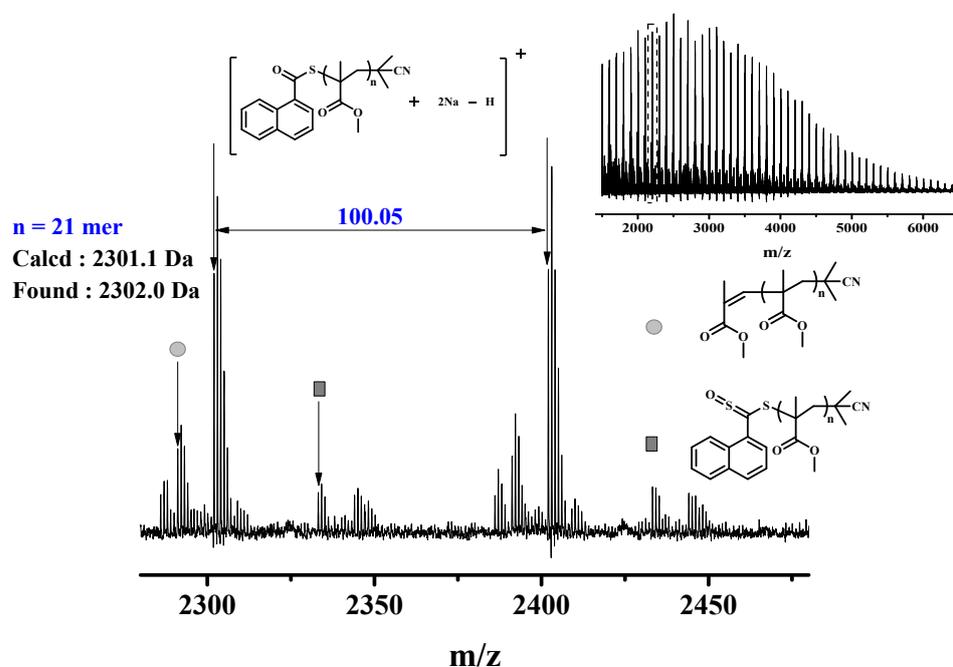


**Figure S5.**  $^1\text{H}$  NMR spectrum recorded for the RAFT polymerization of MMA and FPPI.  $[\text{MMA}]_0/[\text{FPPI}]_0/[\text{CPDN}]_0/[\text{ACHN}]_0 = 200/20/1/0.2$ , MMA = 5.0 mL, in toluene/MMA (2/1, v/v) at 100 °C.  $M_n = 18800$  Da,  $D = 1.42$ .  $\text{Conv.}_{\text{MMA}} = ([I_{6.10}]_0 - I_{6.10})/[I_{6.10}]_0 \times 100\%$ ;  $\text{Conv.}_{\text{PMI}} = ([I_{6.49}]_0 - I_{6.49} - I_{6.66})/[I_{6.49}]_0 \times 100\%$ .  $c_{\text{free,PMI}} = (I_{6.66}/2)/[(I_{2.35} \times M_{\text{toluene}}/3\rho_{\text{toluene}}) + (I_{6.10} \times M_{\text{MMA}}/\rho_{\text{MMA}})] \times 10^3$  mol/L.



**Figure S6.**  $^1\text{H}$  NMR spectrum recorded for MMA/PMI copolymer after precipitation.  $([\text{MMA}]_0/[\text{FPMI}]_0/[\text{CPDN}]_0/[\text{ACHN}]_0 = 200/20/1/0.2, \text{MMA} = 5.0 \text{ mL}, \text{in toluene/MMA} (2/1, v/v) \text{ at } 100 \text{ }^\circ\text{C}. M_n = 18,800 \text{ Da}, D = 1.42).$

### 3. MALDI-TOF mass spectrum of the MMA/PMI di-block gradient copolymer

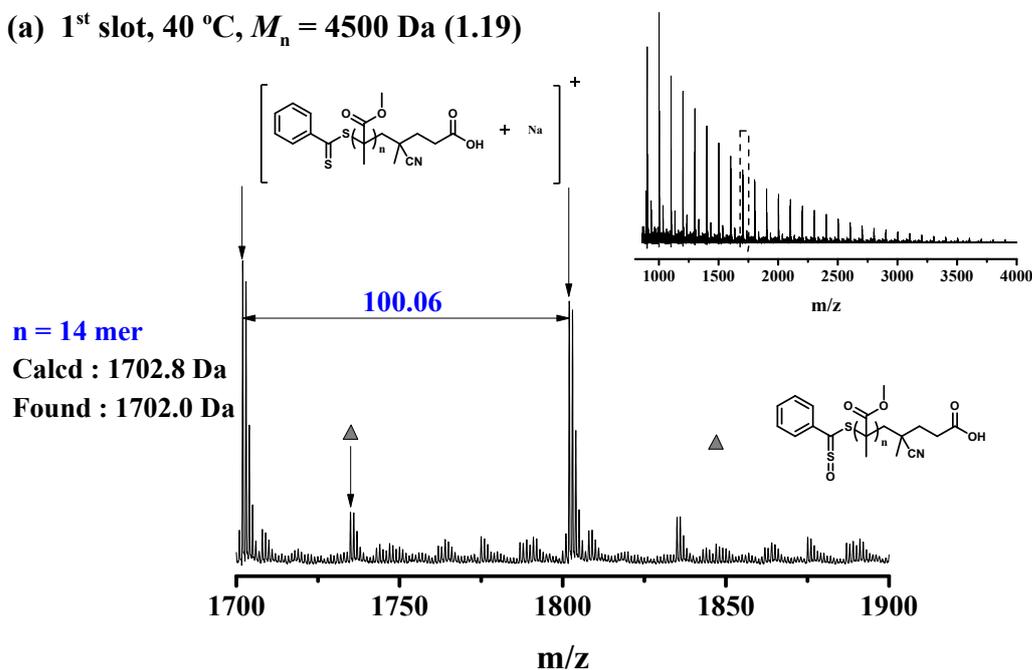


**Figure S7.** MALDI-TOF mass spectrum of MMA/PMI di-block gradient copolymer was obtained in reflection mode by using Na salt as the cationization agent and a DCTB matrix. The sample was obtained from the 1<sup>st</sup> slot (40  $^\circ\text{C}$ , 11.0 h);  $([\text{MMA}]_0/[\text{FPMI}]_0/[\text{CPDN}]_0/[\text{ABVN}]_0 = 200/100/1/0.5, \text{MMA} = 3.0 \text{ mL}, \text{in DMF},$

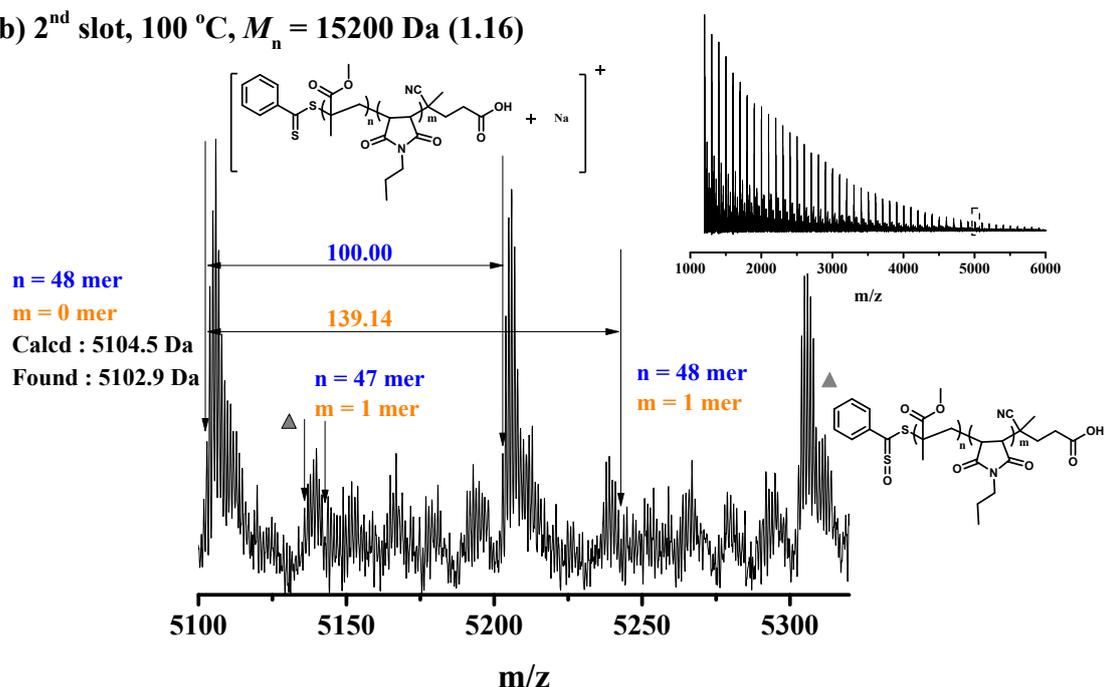
DMF/MMA (2/1, v/v). Temperature sequence: 40 °C (17.5 h) –100 °C (6.0 h).

#### 4. MALDI-TOF mass spectra of the MMA/PMI tri-block gradient copolymer

(a) 1<sup>st</sup> slot, 40 °C,  $M_n = 4500$  Da (1.19)



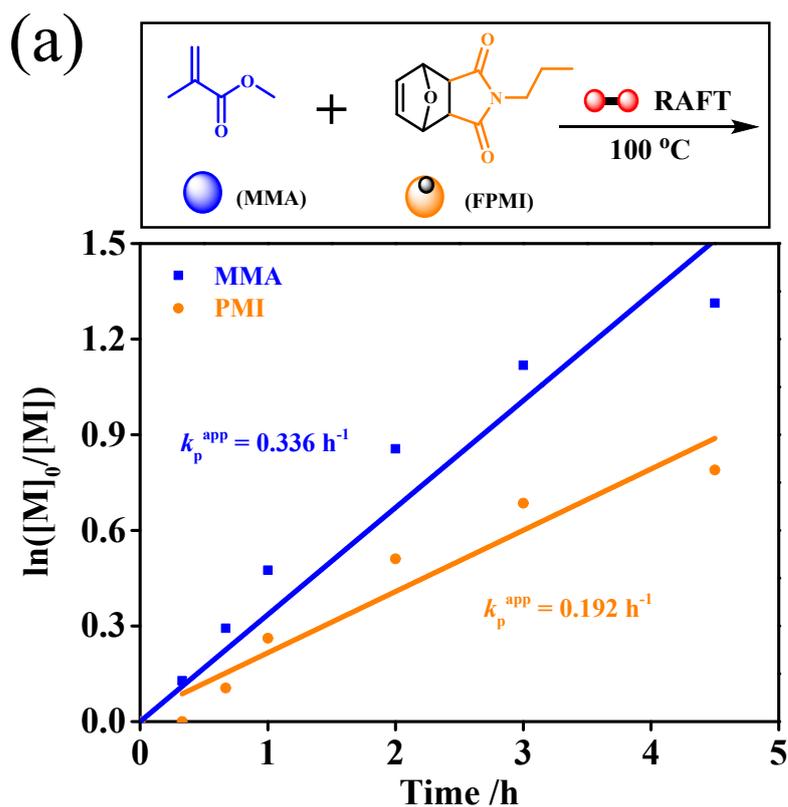
(b) 2<sup>nd</sup> slot, 100 °C,  $M_n = 15200$  Da (1.16)

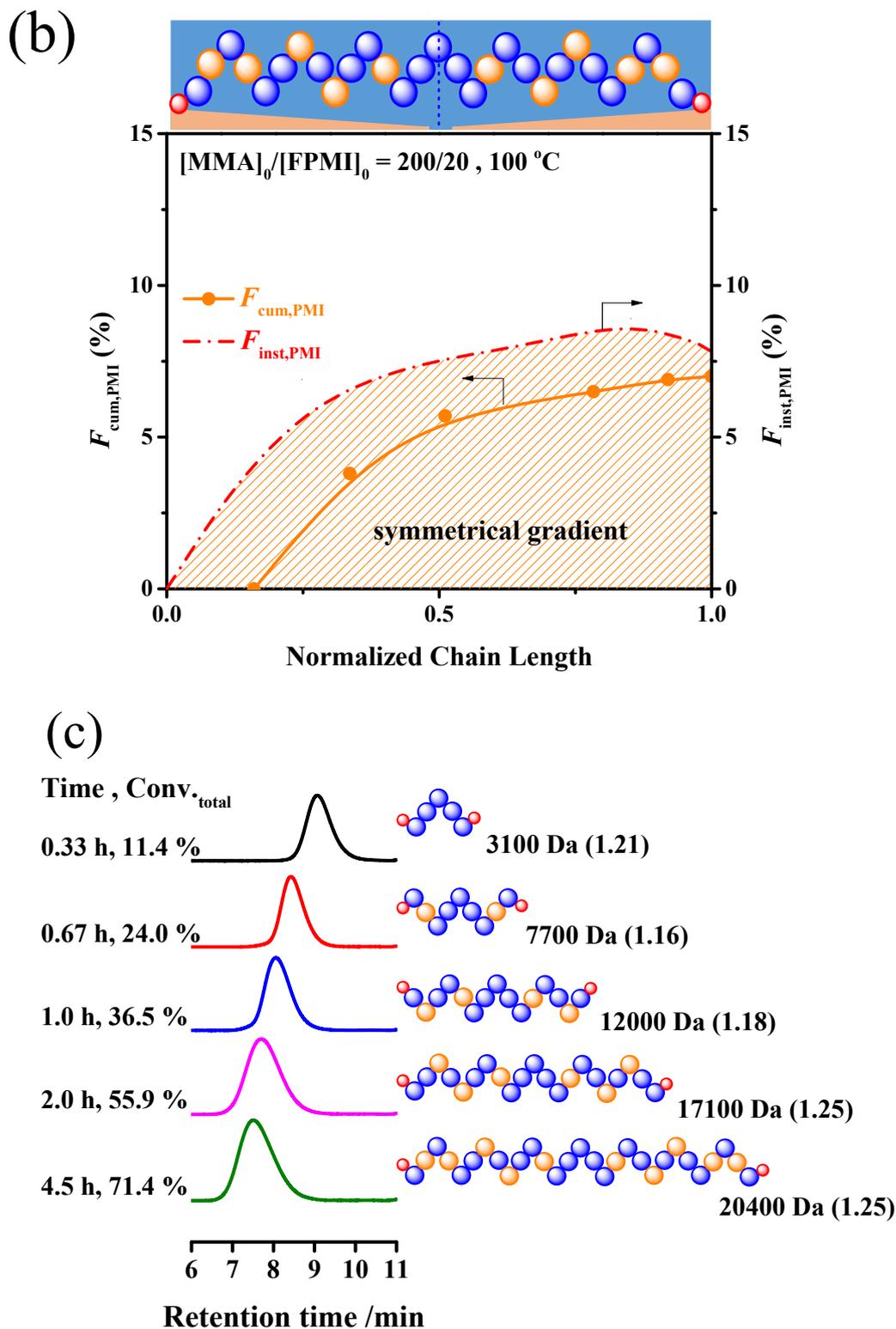


**Figure S8.** MALDI-TOF mass spectrum of MMA/PMI tri-block gradient copolymer was obtained in reflection mode by using Na salt as the cationization agent and a DCTB matrix: a) The sample was obtained from the 1<sup>st</sup> slot (40 °C, 11.0 h); b) The sample was obtained from the 2<sup>nd</sup> slot (100 °C, 0.25 h). [MMA]<sub>0</sub>/[FPMI]<sub>0</sub>/[BiCPADB]<sub>0</sub>/[ABVN]<sub>0</sub> = 200/20/1/0.2, MMA = 5.0 mL, in toluene/MMA (1/1, v/v). Tandem temperature mode = 40 °C (22.5 h)–100 °C (5.0 h).

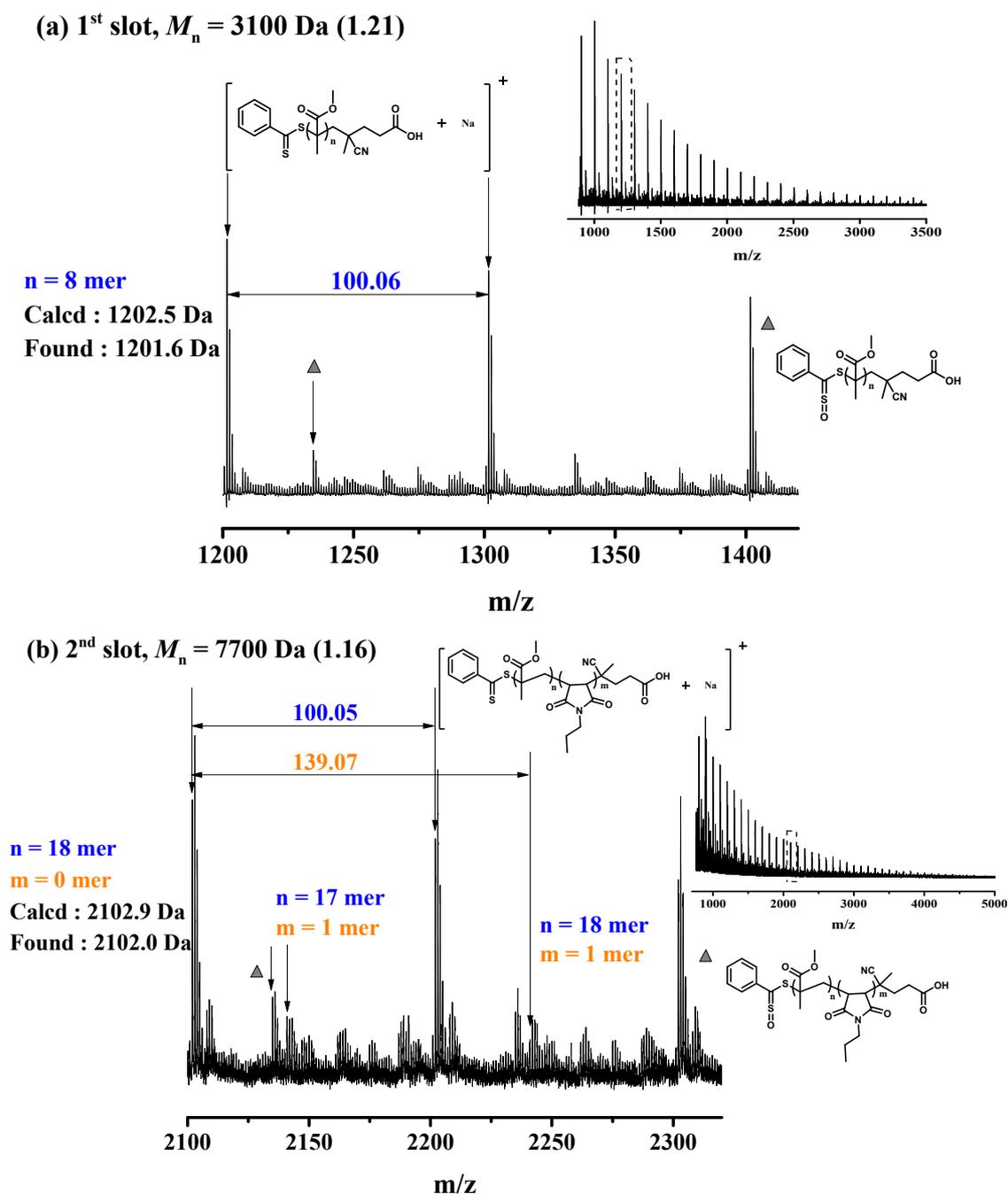
5. Synthesis of symmetrical gradient copolymers from  $[MMA]_0/[FPMI]_0/[BiCPADB]_0/[ACHN]_0 = 200/20/1/0.2$ , MMA = 5.0 mL, in toluene, toluene/MMA (2/1, v/v) at 100 °C

In the case of polymerization of MMA with FPMI at 100 °C, and using BiCPADB as a bi-functional RAFT agent, a symmetrical gradient copolymer can be easily obtained.





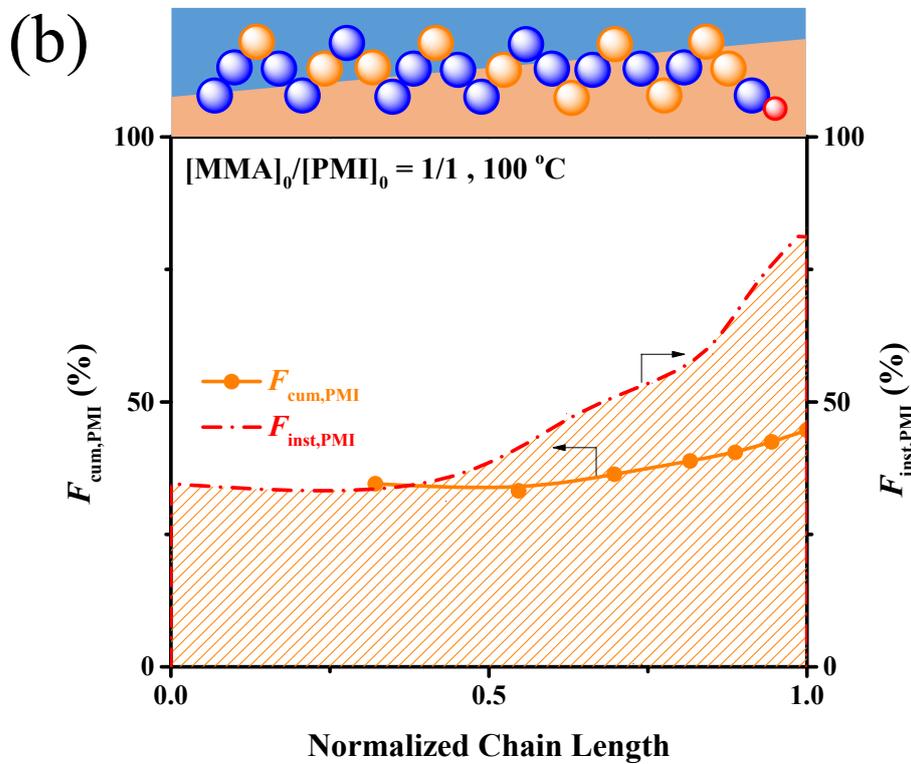
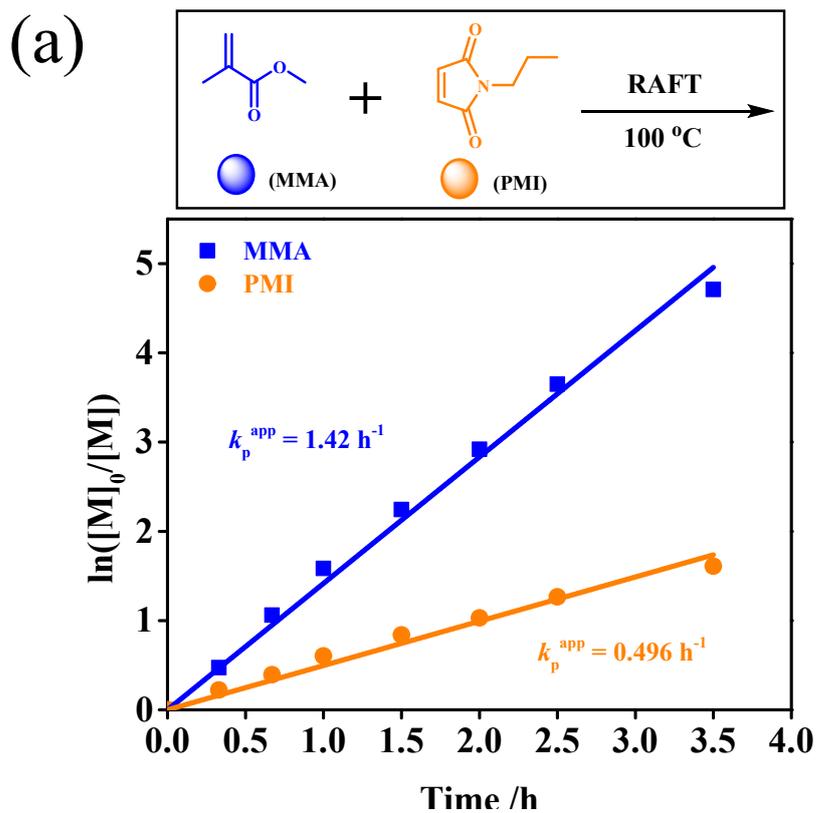
**Figure S9.** Synthesis of MMA/PMI symmetrical gradient copolymers with BiCPADB as RAFT agent: a) Kinetic plots; b) Cumulative ( $F_{cum}$ ) and instantaneous ( $F_{inst}$ ) PMI unit contents in products as a function of normalized chain length; c) SEC traces.  $[MMA]_0/[FPMI]_0/[BiCPADB]_0/[ACHN]_0 = 200/20/1/0.2$ , MMA = 5.0 mL, in toluene, toluene/MMA (2/1, v/v) at 100 °C. The positions and numbers of both monomer unit beads are not accurate but the illustration is intended to guide the eye.

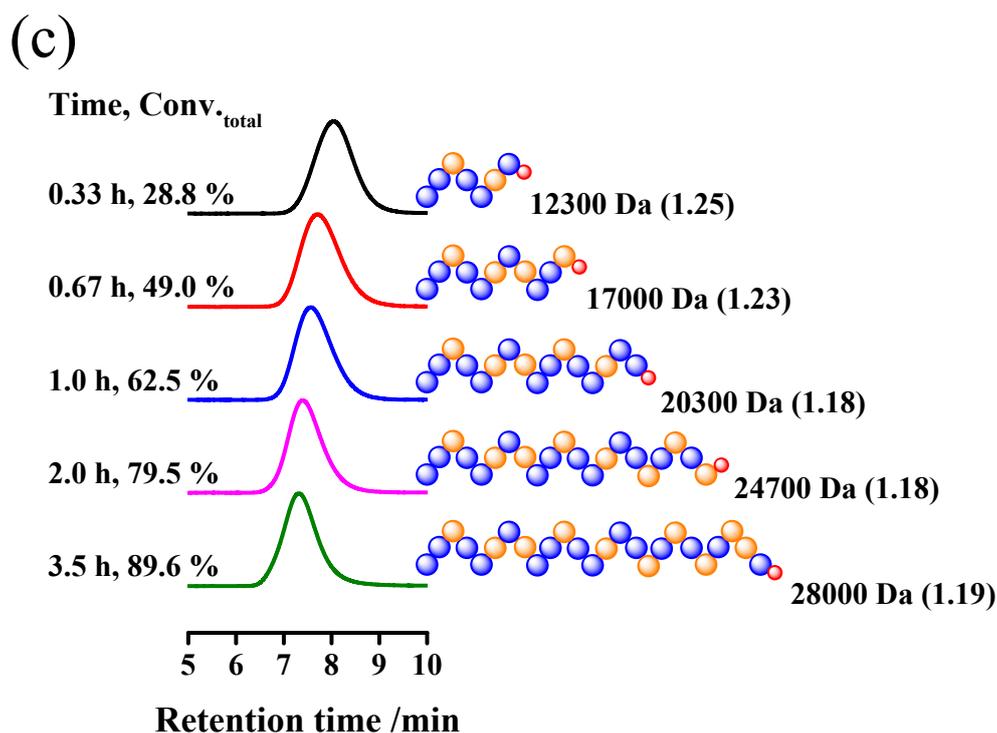


**Figure S10.** MALDI-TOF mass spectrum of MMA/PMI symmetrical gradient copolymer was obtained in reflection mode by using Na salt as the cationization agent and a DCTB matrix: a) The sample was obtained from the 1<sup>st</sup> slot (0.33 h, pure PMMA); b) The sample was obtained from the 2<sup>nd</sup> slot (0.67 h, MMA/PMI copolymer).  $[MMA]_0/[FPMI]_0/[BiCPADB]_0/[ACHN]_0 = 200/20/1/0.2$ , MMA = 5.0 mL, in toluene/MMA (2/1, v/v) at 100 °C.

**6. Synthesis of simultaneous gradient copolymers from  $[MMA]_0/[PMI]_0/[CPDN]_0/[ACHN]_0 = 120/120/1/0.2$ , MMA = 3.0 mL, in toluene,**

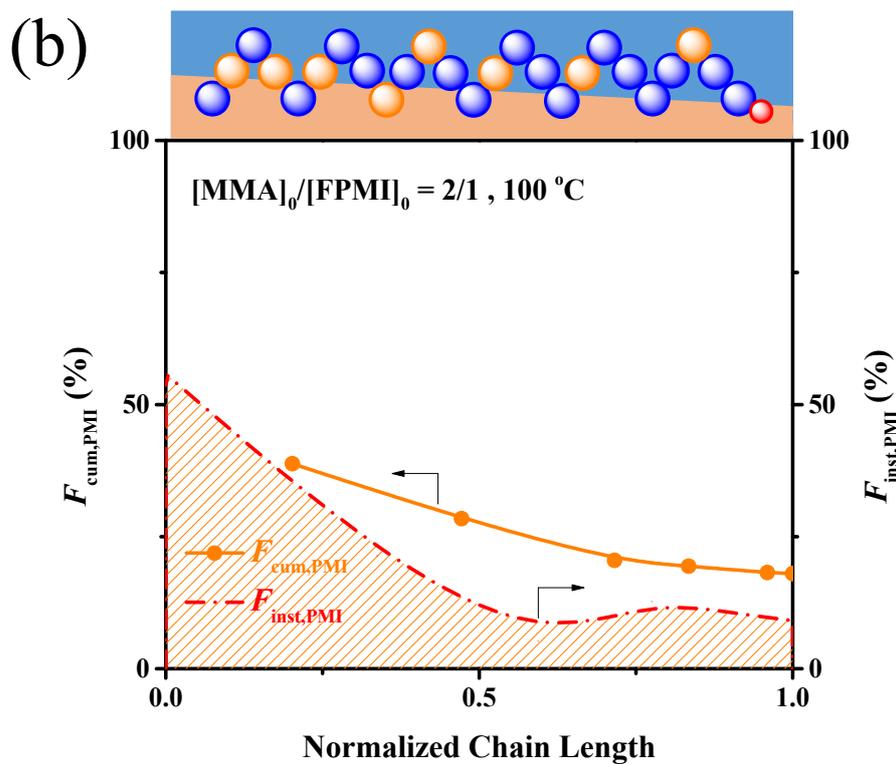
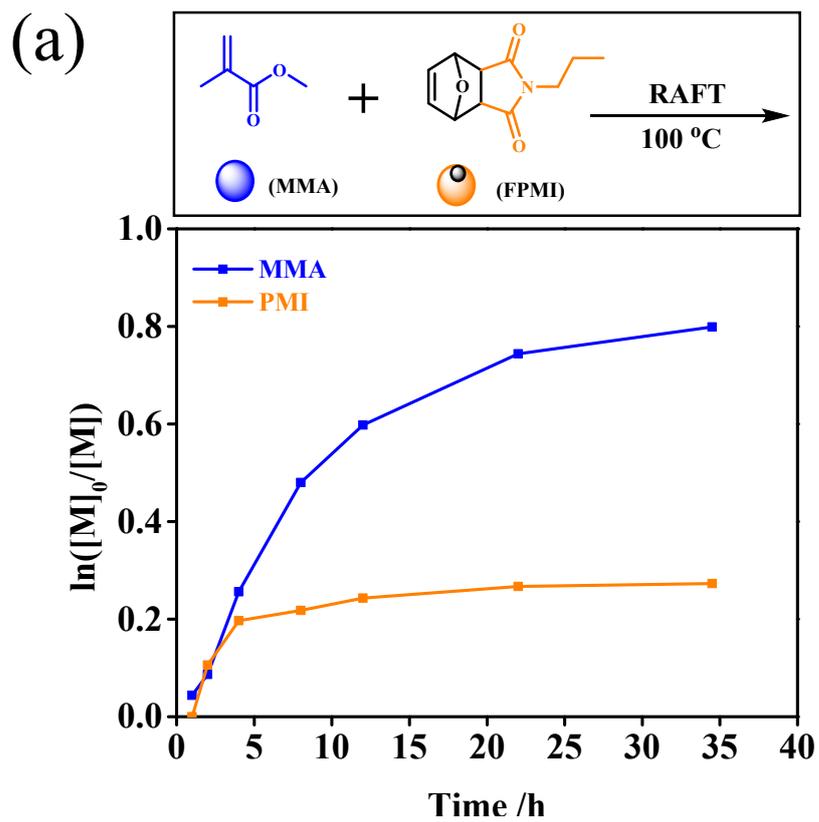
toluene/MMA (2/1, v/v) at 100 °C

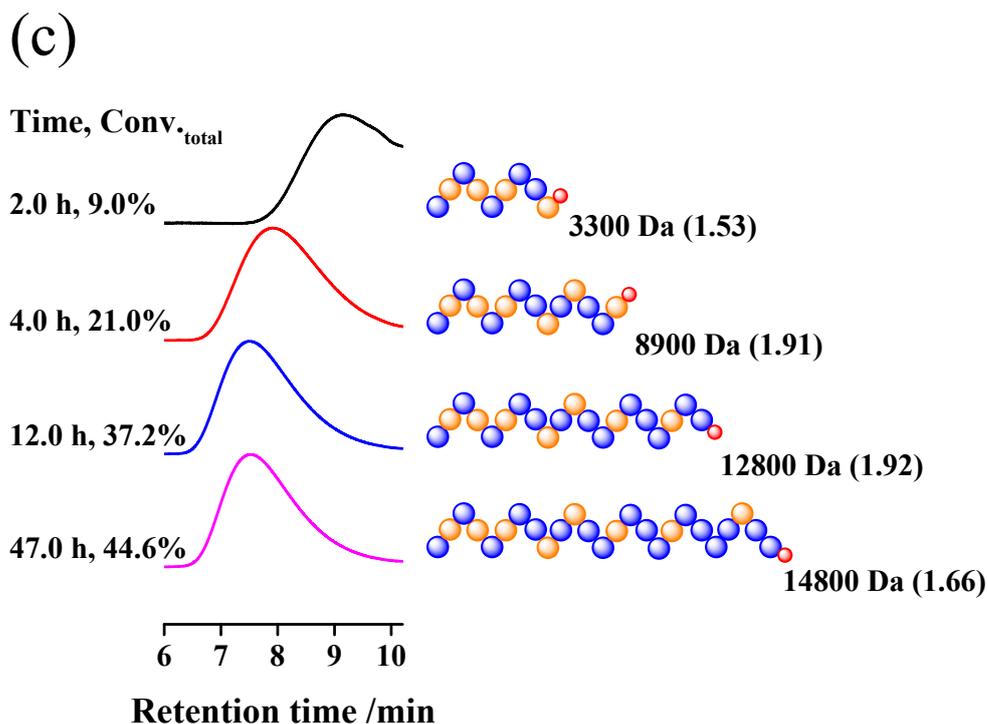




**Figure S11.** Synthesis of MMA/PMI gradient copolymers with CPDN as RAFT agent: a) Kinetic plots; b) Cumulative ( $F_{\text{cum}}$ ) and instantaneous ( $F_{\text{inst}}$ ) PMI unit contents in products as a function of normalized chain length; c) SEC traces.  $[\text{MMA}]_0/[\text{PMI}]_0/[\text{CPDN}]_0/[\text{ACHN}]_0 = 120/120/1/0.2$ , MMA = 3.0 mL, in toluene, toluene/MMA (2/1, v/v) at 100 °C. The positions and numbers of both monomer unit beads are not accurate but the illustration is intended to guide the eye.

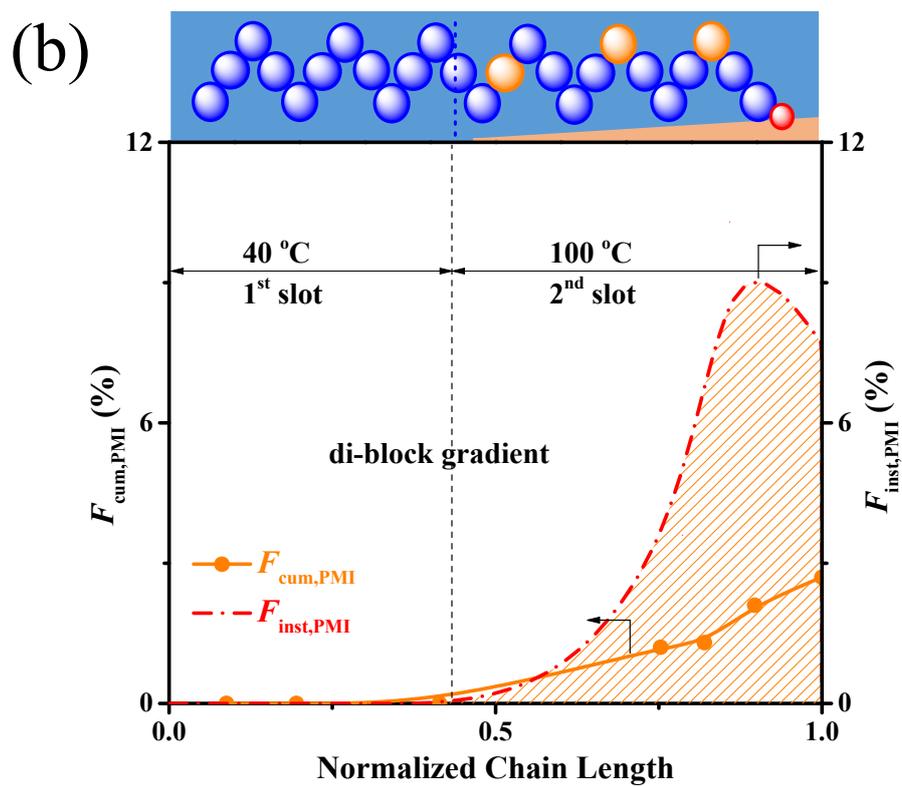
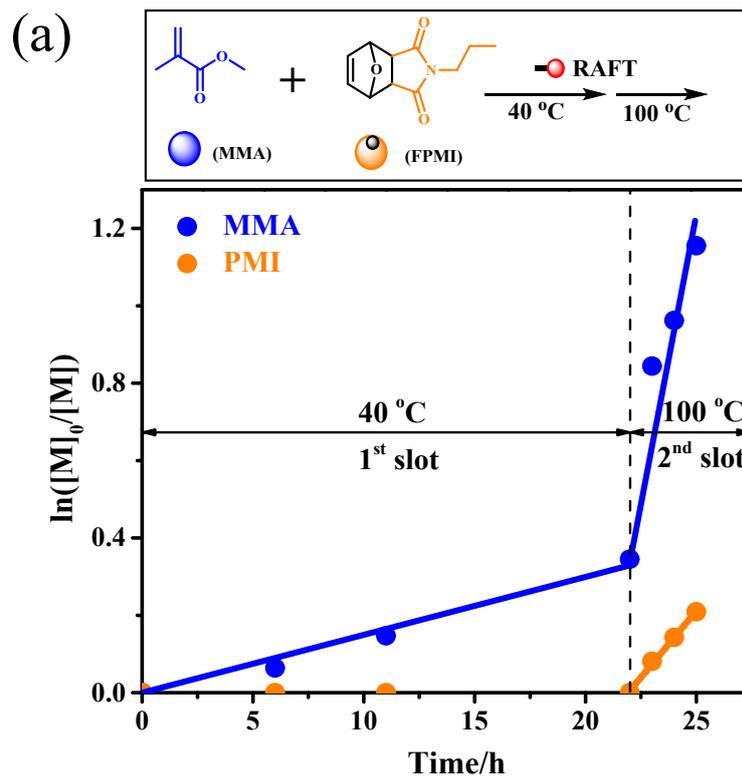
**7. Synthesis of simultaneous gradient polymers from**  
 $[\text{MMA}]_0/[\text{FPMI}]_0/[\text{CPDN}]_0/[\text{ACHN}]_0 = 200/100/1/0.2$ , MMA = 1.0 mL, in toluene, toluene/MMA (3.5/1, v/v) at 100 °C

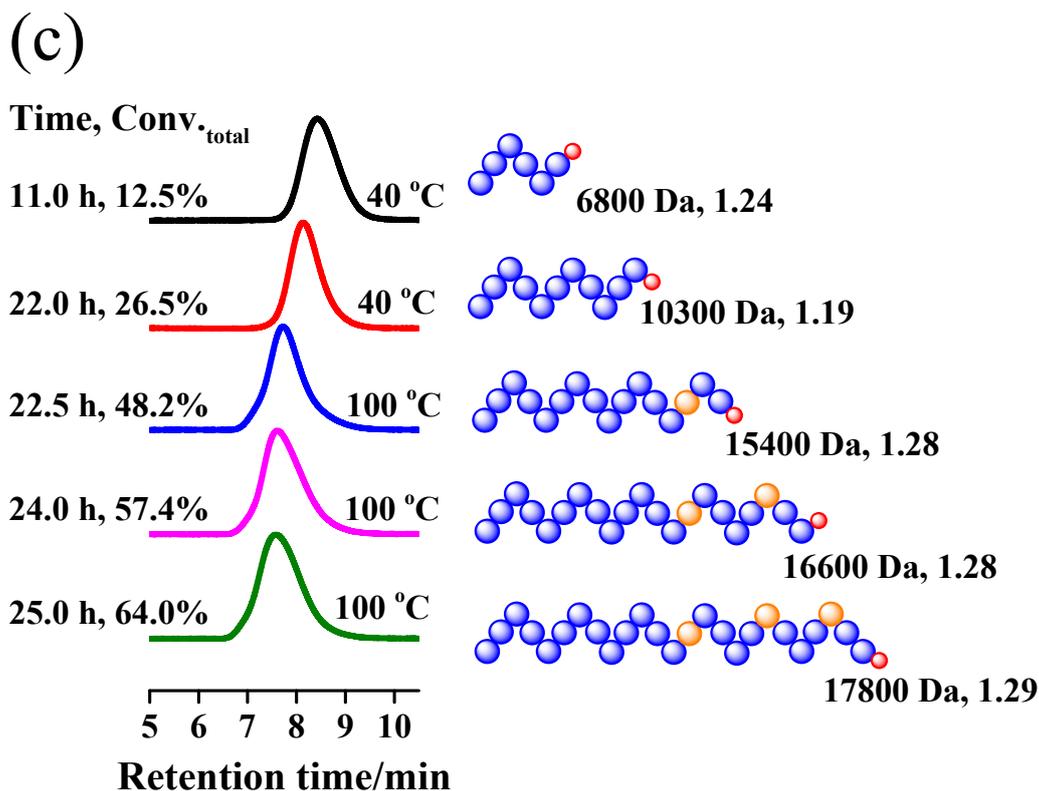




**Figure S12.** Synthesis of MMA/PMI gradient copolymers with CPDN as RAFT agent: a) Kinetic plots; b) Cumulative ( $F_{cum}$ ) and instantaneous ( $F_{inst}$ ) PMI unit contents in products as a function of normalized chain length; c) SEC traces.  $[MMA]_0/[FPMI]_0/[CPDN]_0/[ACHN]_0 = 200/100/1/0.2$ , MMA = 1.0 mL, in toluene, toluene/MMA (3.5/1, v/v) at 100 °C. The positions and numbers of both monomer unit beads are not accurate but the illustration is intended to guide the eye.

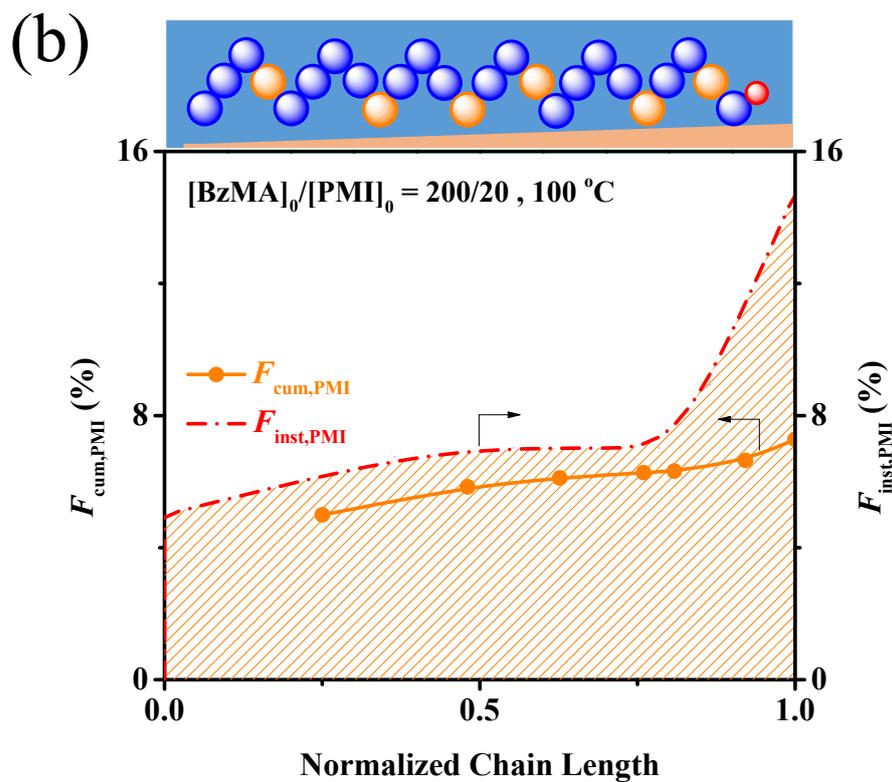
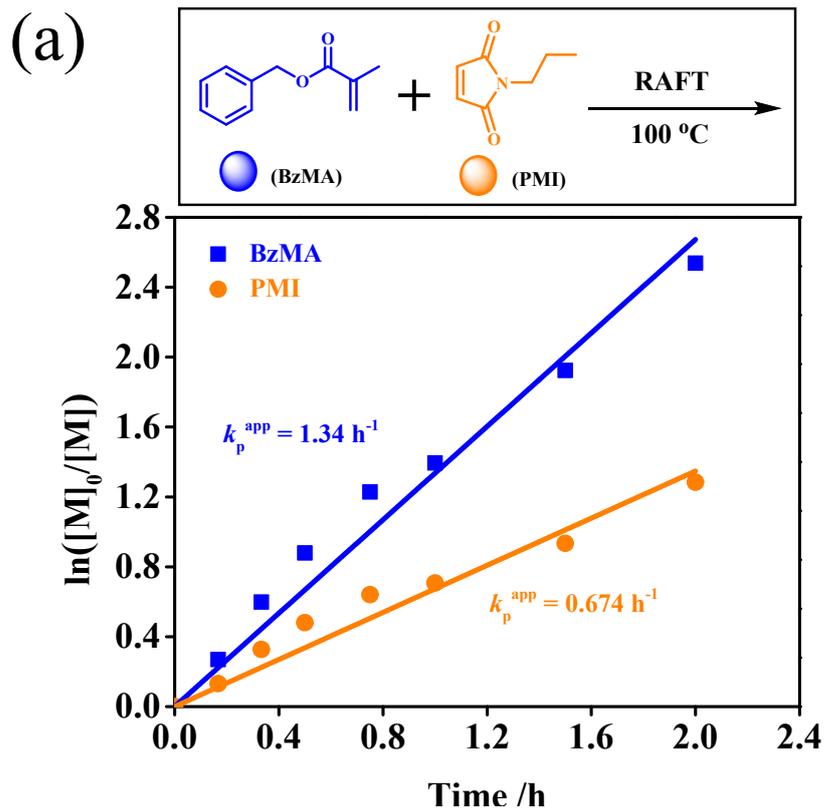
**8. Synthesis of di-block gradient polymers from  $[MMA]_0/[FPMI]_0/[CPDN]_0/[ABVN]_0 = 200/20/1/0.2$ , MMA = 5.0 mL, in toluene toluene/MMA (1/1, v/v). Temperature sequence: 40 °C (22.0 h) – 100 °C (3.0 h)**

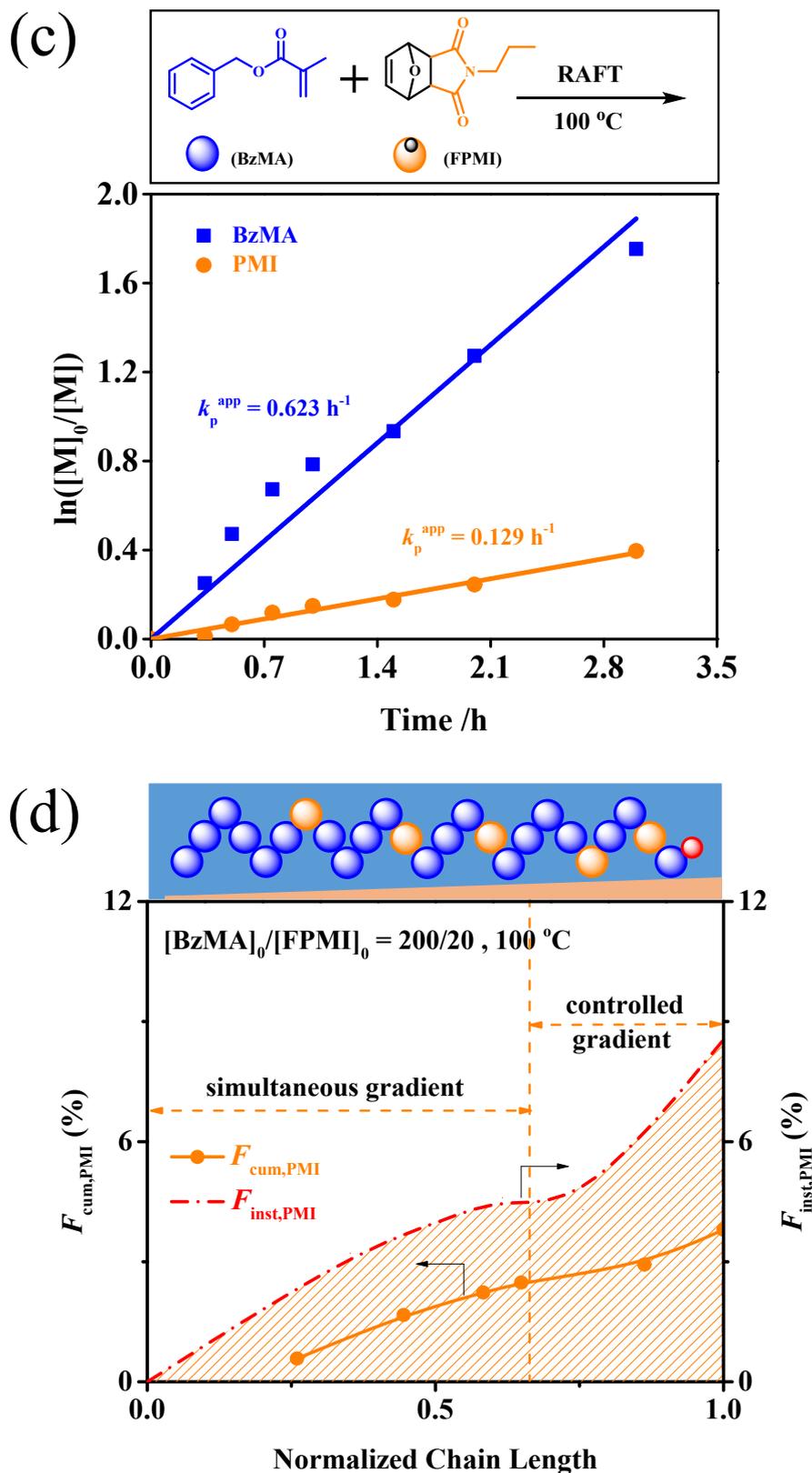




**Figure S13.** Synthesis of MMA/PMI di-block gradient copolymer with CPDN as RAFT agent: a) Kinetic plots; b) Cumulative ( $F_{\text{cum}}$ ) and instantaneous ( $F_{\text{inst}}$ ) PMI unit contents in products as a function of normalized chain length; c) SEC traces.  $[\text{MMA}]_0/[\text{FPMI}]_0/[\text{CPDN}]_0/[\text{ABVN}]_0 = 200/20/1/0.2$ , MMA = 5.0 mL, in toluene, toluene/MMA (1/1, v/v). Temperature sequence: 40 °C (22.0 h) – 100 °C (3.0 h). The positions and numbers of both monomer unit beads are not accurate but the illustration is intended to guide the eye.

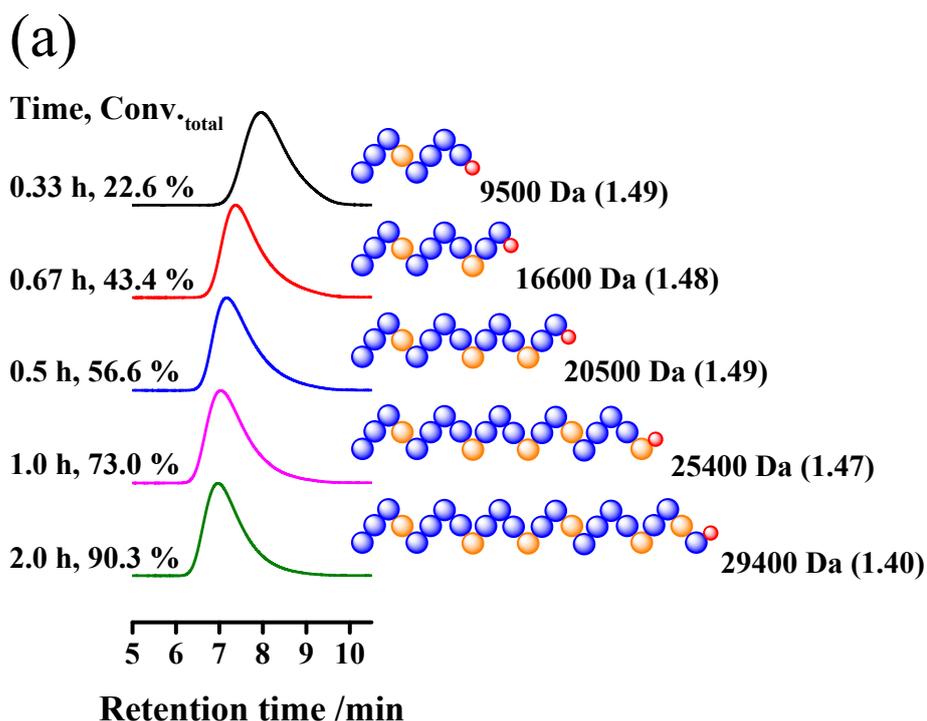
**9. Synthesis of simultaneous gradient copolymers with benzyl methacrylate (BzMA)/PMI (or FPMI) co-monomer pair from  $[\text{BzMA}]_0/[\text{PMI}]_0$  (or  $[\text{FPMI}]_0)/[\text{CPDN}]_0/[\text{ACHN}]_0 = 200/20/1/0.5$ , BzMA = 5.0 mL, in toluene, toluene/BzMA (1/1, v/v)**

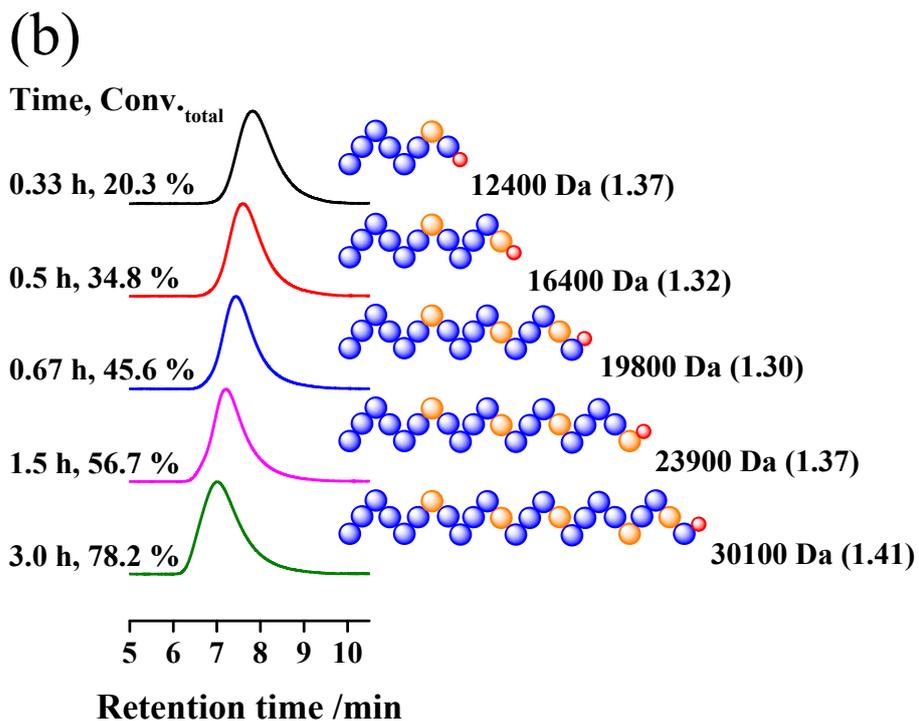




**Figure S14.** Synthesis of BzMA-PMI simultaneous gradient copolymers: a) Kinetic plots of BzMA with PMI at 100 °C; b) Cumulative ( $F_{cum}$ ) and instantaneous ( $F_{inst}$ ) PMI unit contents in products as a function of normalized chain length: BzMA with PMI at 100 °C; c) Kinetic plots of BzMA with FPMI at 100 °C; d) Cumulative ( $F_{cum}$ )

and instantaneous ( $F_{\text{inst}}$ ) PMI unit contents in products as a function of normalized chain length: BzMA with FPMI at 100 °C.  $[\text{BzMA}]_0/[\text{PMI}]_0$  (or  $[\text{FPMI}]_0/[\text{CPDN}]_0/[\text{ACHN}]_0 = 200/20/1/0.5$ , BzMA = 5.0 mL, in toluene, toluene/BzMA (1/1, v/v). Normalized chain length ( $i$ ) =  $\text{Conv}_{\text{total}}(i)/\text{Conv}_{\text{max}}$ ;  $\text{Conv}_{\text{max}}$  equal to the maximum value of  $\text{Conv}_{\text{total}}$ ;  $F_{\text{cum, PMI}}(i) = (1 \times \text{Conv}_{\text{PMI}}) / (1 \times \text{Conv}_{\text{PMI}} + 10 \times \text{Conv}_{\text{BzMA}})$ ;  $F_{\text{inst, PMI}}((i - i-1)) = (1 \times \text{Conv}_{\text{PMI}}(i) - 1 \times \text{Conv}_{\text{PMI}}(i-1)) / [(1 \times \text{Conv}_{\text{PMI}}(i) - 1 \times \text{Conv}_{\text{PMI}}(i-1)) + (10 \times \text{Conv}_{\text{BzMA}}(i) - 10 \times \text{Conv}_{\text{BzMA}}(i-1))]$ . The positions and numbers of both monomer unit beads are not accurate but the illustration is intended to guide the eye.





**Figure S15.** SEC curves of the samples during the polymerization with bead model of chain sequence distribution: a) BzMA with PMI at 100 °C; b) BzMA with FPMI at 100 °C.  $[BzMA]_0/[PMI]_0$  (or  $[FPMI]_0$ )/ $[CPDN]_0/[ACHN]_0 = 200/20/1/0.5$ , MMA = 5.0 mL, in toluene/MMA (1/1, v/v). The positions and numbers of both monomer unit beads are not accurate but the illustration is intended to guide the eye.

## 10. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) curves of the advanced gradient copolymers

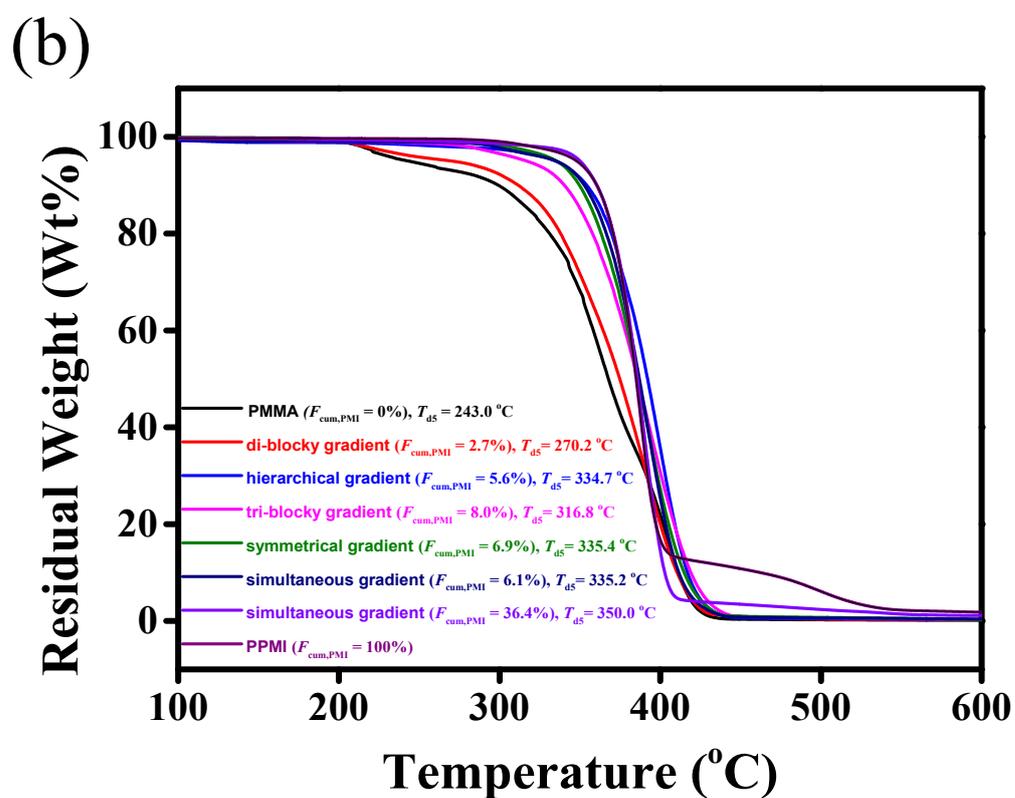
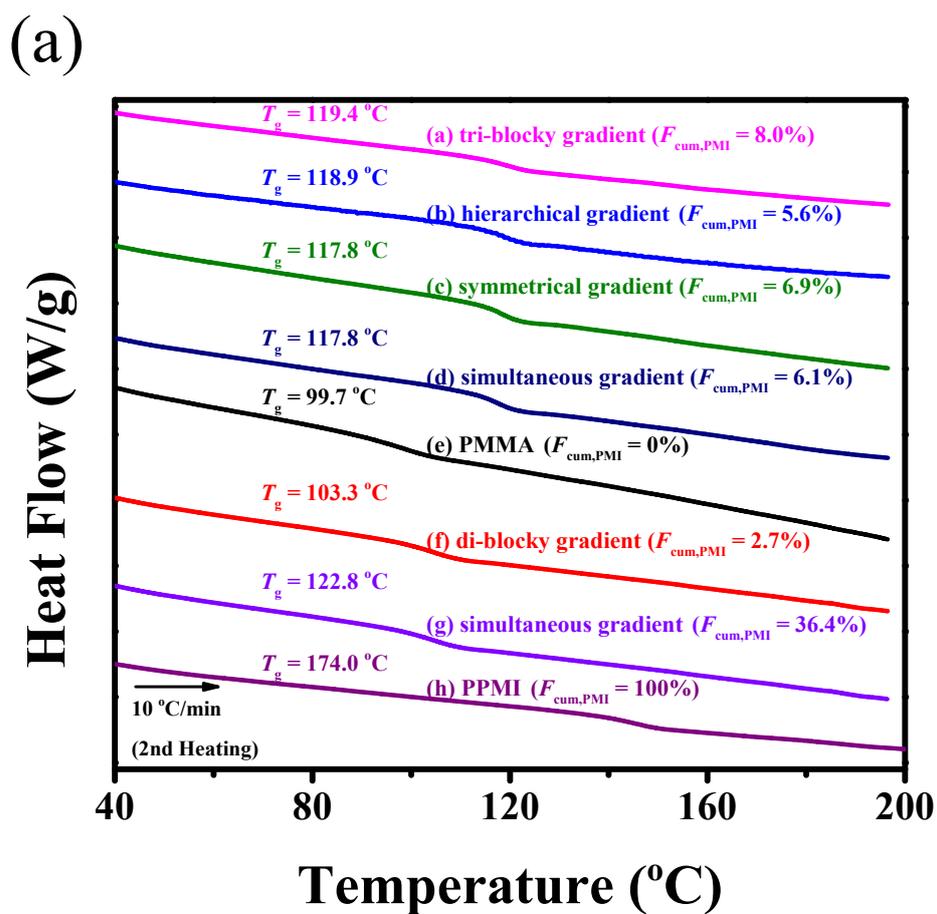


Figure S16. Thermal properties of MMA/PMI advanced gradient polymers: (a)

differential scanning calorimetry thermograms of MMA/PMI advanced gradient polymers; (b) Thermogravimetric analysis curves of MMA/PMI advanced gradient polymers in a nitrogen stream at the heating rate of 10 °C/min. The cumulative PMI content ( $F_{\text{cum,PMI}}$ ) of each sample was determined by  $^1\text{H}$  NMR. The onset temperature of decomposition ( $T_{\text{d5}}$ ) was determined as the 5% weight loss temperature in thermogravimetric curves.

### SECTION C. REFERENCE

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2. Satoh, K.; Lee, D. H.; Nagai, K.; Kamigaito, M., *Macromol. Rapid. Commun.* **2014**, *35*, 161-167.
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