Supporting Information

A photo-thermal dual-regulated latent monomer strategy for sequence control of polymers

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Table of Contents

SECTION A. Experimental Section 2

1. Materials 2
2. Analysis Techniques 3
3. Monomer Synthesis and Polymerizations 4
   - 3.1 Synthesis of Compound 1 4
   - 3.2 Synthesis of Compound 2 5
   - 3.3 Synthesis of Compound 4 5
   - 3.4 Synthesis of Compound 5*o* (“ring-open” isomer) 6
   - 3.5 Synthesis of Compound 5*c* (“ring-closed” isomer) 7
   - 3.6 Synthesis of furan-protected hydroxyethyl maleimide (FMOH) and hydroxyethyl maleimide (MOH) 8
   - 3.7 Typical Procedures for RAFT Polymerization of BMA and 5*o* at 120 °C 8
   - 3.8 Typical Procedures for Three-stage RAFT Polymerization of BMA and 5*c* at 120 °C 9
   - 3.9 Polymerization of BMA with dithienylfuran (DTF) 9

SECTION B. Results and Discussions 10

1. The effect of free dithienylfuran on the polymerization 10
2. RAFT Polymerization of BMA and 5*o* at 120 °C 11
3. RAFT Polymerization of BMA and 5*c* at 120 °C in the dark 12
4. Three-stage RAFT Polymerization of BMA and 5*c* at 120 °C 13
5. Five-stage RAFT Polymerization of BMA and 5*c* at 120 °C.....14
6. Three-stage RAFT Polymerization of BMA, MOH and 5*c* at 120 °C 17
7. Three-stage RAFT Polymerization of BMA, FMOH and 5*c* at 120 °C.....19
8. Four-stage RAFT Polymerization of BMA, FMOH and 5*c* at 120 °C.....20

SECTION C. References 21

SECTION A. Experimental Section

1. Materials

Butyl methacrylate (BMA, Sinopharm Chemical Reagent, 99%) was inhibited during storage, and the inhibitor was removed by alkaline aluminum oxide column chromatography. 2,2-Azobisisobutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent, China (98%) and purified by recrystallization from ethanol. Dicumyl peroxide (DCPO, ACROS), 3,4-Dibromofuran (Accela 97%), 2-Cyanoprop-2-yl-1-dithiobenzoate (CPDB, Aldrich, 99%), *N*-Methylmaleimide (MMI, Aldrich, 98%), Ethylene carbonate (EC, Alfa Aesar, 99%), CsF (Macklin, 99%), [1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride (PEPPSI-IPr, energy-chemical, 98%), Sodium (meta)periodate ($NaIO_4$, Meryer, 99.5%), Oxalic acid (macklin, anhydrous, 99.0%), 5-Methyl-2-thiophenecarboxylic Acid (aladdin, 98.0%), Heptane (macklin, 98%), Bis(pinacolato)diboron (B_2pin_2, Amethyst, 98%), (1,5-Cyclooctadiene)(methoxy)iridium(I) dimer ($[Ir(COD)(OMe)]_2$, Meryer, 95%) and 4,4'-Di-tert-butyl-2,2'-dipyridyl (dtbpy, Meryer, 98%) were used as received. Furan, 2-aminoethanol, maleic anhydride, anhydrous ether, methanol, dioxane, acetonitrile, anisole, petroleum ether (PE), ethyl acetate (EA), dimethyl sulfoxide (DMSO), sulfuric acid (H_2SO_4) and all other chemicals were obtained from Sinopharm

Chemical Reagent Co., Ltd. and used as received without any further purification. Tetrahydrofuran (THF), dichloromethane (DCM), *N*, *N*-dimethylformamide (DMF) and toluene were purified by passing through a purification column (Solvent Dispensing System; glass contour).

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 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 × 10^5 g/mol. THF or DMF was used as the eluent at a flow rate of 0.35 mL/min at 40 ^oC. Data acquisition was performed using EcoSEC software and molecular weights were calculated using poly(styrene) (PS) as the standard.

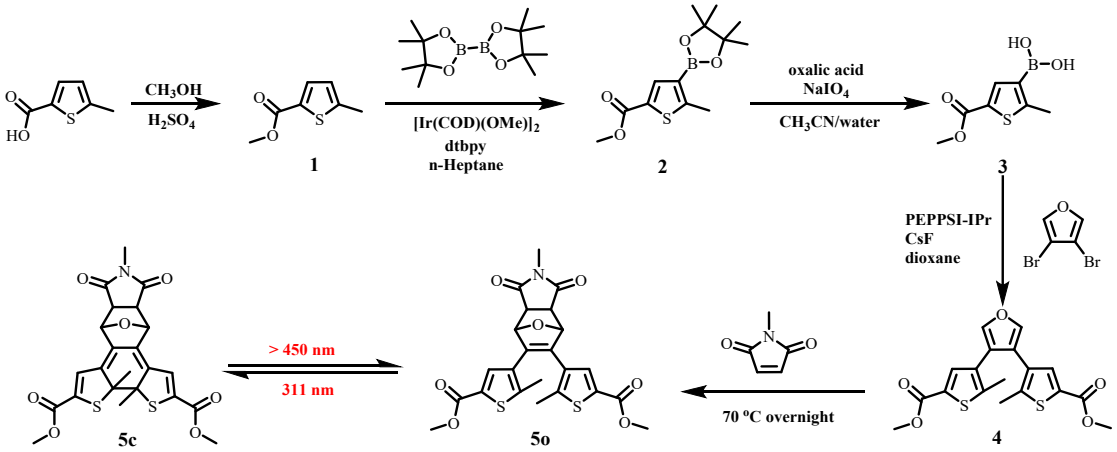
Proton nuclear magnetic resonance (^1H NMR) spectra of all samples were collected in $CDCl_3$ or DMSO-d_6 by a Bruker nuclear magnetic resonance instrument (300 MHz) using tetramethylsilane (TMS) as the internal standard at room temperature. The ^1H NMR spectra were referenced to δ 7.26 ppm in $CDCl_3$ or δ 2.54 ppm in DMSO-d_6.

Crude copolymers were purified by a recycling preparative SEC (Japan Analytical Industry Co., Ltd.) system equipped with a manual injector and a differential refractive index detector. THF was used as the eluent with a flow rate of 10 mL/min. Generally, the dry crude copolymer was dissolved in THF at 100 mg/mL concentration and filtered through a 0.45 μm PTFE syringe filter prior to injection. The target fraction was collected manually, and analyzed using the TOSOH HLC-8320 SEC equipped with a refractive-index and a UV detector.

Ultra-violet visible (UV-vis) absorption spectra of the samples were measured on a Shimadzu UV-2600 spectrophotometer at room temperature. The concentration of dithienylfuran-protected methyl maleimide (DTFMMI) is 0.025 mg/mL in anisole.

All ring-closing reactions, i.e., 5***o***-to-5***c*** isomerization, were carried out using a LED ultraviolet lamp at 311 nm (1.5 W/m^2). The ring-opening reactions, i.e., 5***c***-to-5***o*** isomerization, were performed using the blue light (> 450 nm, 451.9 W/m^2).

3. Monomer Synthesis and Polymerizations



Scheme S1. Synthesis of photo-sensitive latent monomers (**5*o*** and **5*c***)

3.1 Synthesis of Compound 1

5-methylthiophene-2-carboxylic acid (25.0 g, 176.0 mmol) was dissolved in 250 mL methanol, followed by the addition of sulfuric acid (2.5 mL). The reaction was refluxed at 75 °C for 48.0 hours. Afterwards, the solvent was removed by reduced pressure distillation, and 250 mL n-Hexane was added. The mixture was washed with water (75 mL × 4) and saturated brine (75 mL). The combined organic phase was dried with anhydrous sodium sulfate, vacuum filtered and then evaporated to obtain methyl 2-carboxylate-5-methylthiophene (compound **1**).

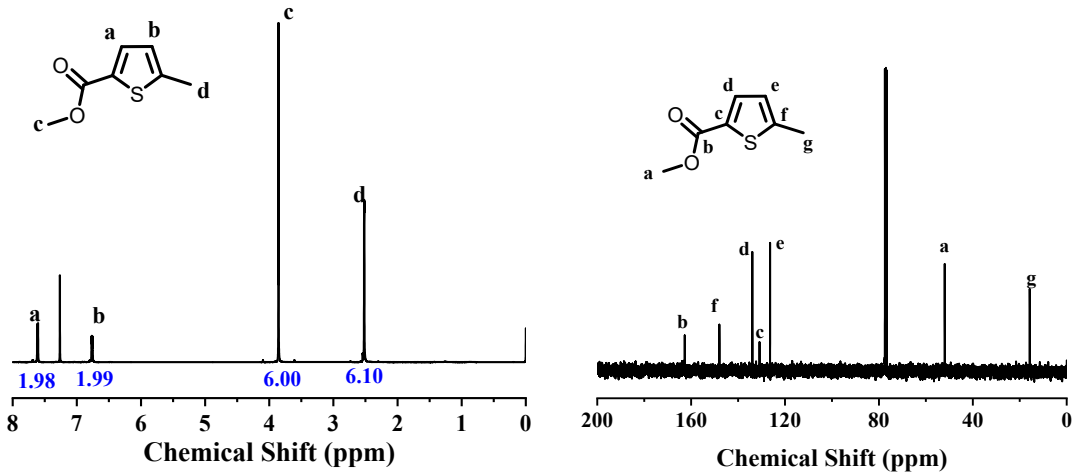


Figure S1. 300 MHz ^{1}H NMR spectrum (a) and ^{13}C NMR spectrum (b) of compound **1** in $CDCl_3$.

3.2 Synthesis of Compound 2

Compound **1** (35.5 g, 227.5 mmol), bis(pinacolato)diboron (B_2pin_2, 34.62 g, 136.2 mmol) and 4, 4-ditert-butyl-bipyridine (dtbpy, 243.4 mg, 0.6829 mmol) were added into a 500 mL three-neck round-bottom flask, and 200 mL n-heptane was added as the solvent. The mixture was degassed by three freeze-pump-thaw cycles. Then the (1,5-Cyclooctadiene) (methoxy)iridium(I) Dimer ($[Ir(COD)(OMe)]_2$ (304.2 mg, 0.4589 mmol) was added rapidly in argon atmosphere, and took three freeze-pump-thaw cycles again. The reaction solution was heated at 100 °C and refluxed for 24.0 h, followed by cooling to room temperature to obtain a white precipitate. The precipitate was collected *via* vacuum filtration and washed with hexane followed by drying to obtain the yellowish solid compound **2**.

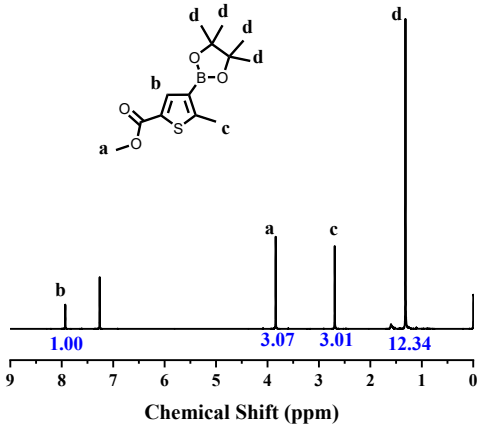


Figure S2. 300 MHz ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

3.3 Synthesis of Compound 4

Compound **4** was synthesized by adapting a reported procedure[1]. Compound **2** (8.6975 g, 30.83 mmol), oxalic acid (7.7748 g, 86.36 mmol), water (37 mL), and acetonitrile (186 mL) were put into a 500 mL three-neck round-bottom flask. After stirring for 5 min, $NaIO_4$ (9.8924 g, 46.25mmol) was added and the resulting mixture was stirred overnight. At this stage, white solids suspended in the reaction mixture were observed. The mixture was diluted with water (300 mL) and extracted with ethyl acetate (5 × 200 mL) in a separatory funnel. The combined organic phase was washed

with brine (200 mL), dried over sodium sulfate, filtered, and dried under reduced pressure. The obtained solid was further suspended in hexanes, and then collected by suction filtration as a yellowish solid (compound **3**).

Compound **3** (18.4911 g, 92.92 mmol), CsF (28.7804 g, 185.8 mmol), 3, 4-dibromofuran (4.0 mL, 8.3956 g, 37.17mmol), and dioxane (200 mL) were put into a 500 mL three-neck round-bottom flask. After three freeze-pump-thaw cycles, [1,3-Bis(2,6-diisopropylphenyl) imidazol-2-ylidene] (3-chloropyridyl) palladium (II) dichloride (PEPPSI-IPr) (1.2637 g, 1.86 mmol) was added. Three freeze-pump-thaw cycles was further applied to the mixture followed by refluxing in an oil bath at 100 ^{o}C for 24.0 h. After completion of the reaction, 300 mL ethyl acetate was added, the organic phase was washed with water, dried with Na_2SO_4, filtered and evaporated, and column chromatography (eluent: PE: EA=10:1) was used to obtain compound **4** as a yellowish liquid.

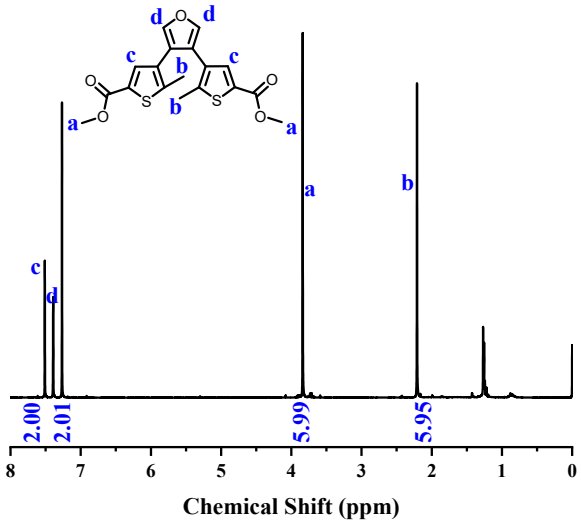


Figure S3. 300 MHz ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

3.4 Synthesis of Compound 5*o* (“ring-open” isomer)

Compound **4** (4.45 g, 11.8 mmol), *N*-methylmaleimide (1.09 g, 9.8 mmol) and 100 mL toluene were added to a 250 mL round-bottom flask at 70 ^{o}C overnight. After completion of the reaction, the solvent was removed by reduced pressure distillation, and the crude product was washed with n-hexane to obtain the pure compound **5*o***.

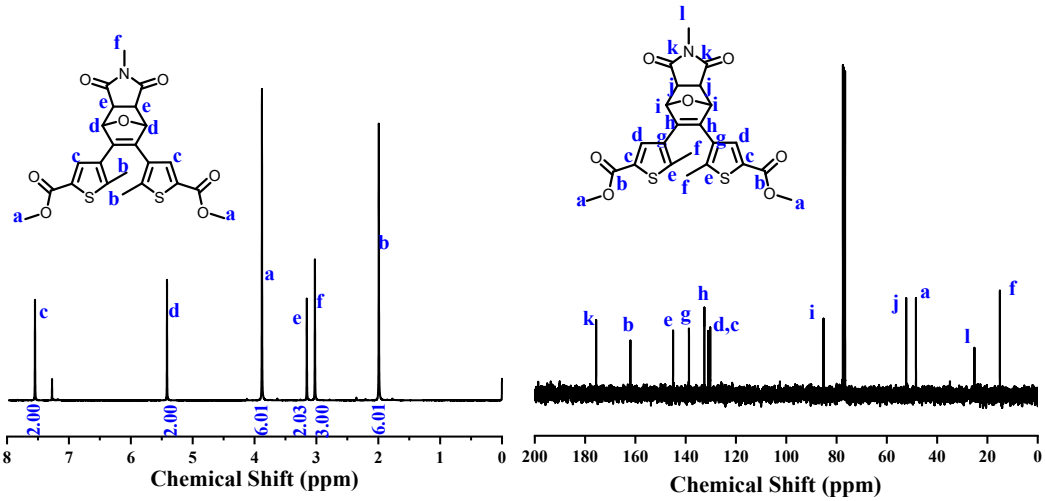


Figure S4. 300 MHz ^{1}H NMR spectrum (a) and ^{13}C NMR spectrum (b) of compound **5*o*** in $CDCl_3$.

3.5 Synthesis of Compound 5*c* ("ring-closed" isomer)

10 mg **5*o*** was dissolved in 0.6 mL DMSO-d_6 and irradiated under 311 nm UV irradiation for 24.0 h. A mixture of 78.3% **5*c*** and 21.7% **5*o*** was obtained.

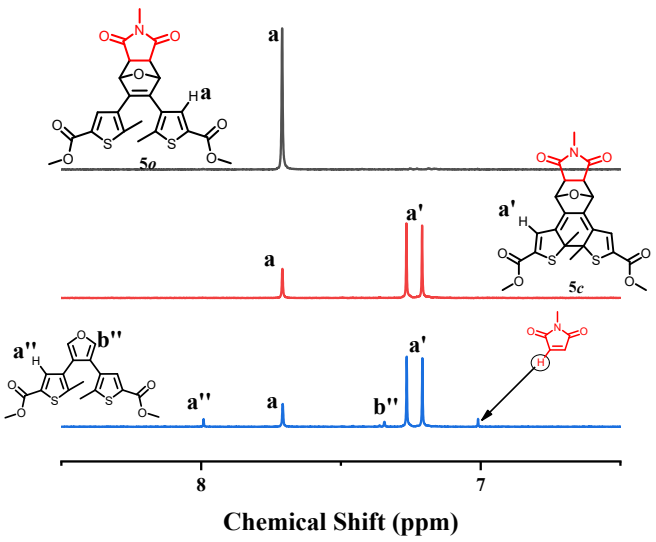


Figure S5. Partial ^{1}H NMR spectra of a DMSO-d_6 solution of (a) **5*o***, (b) **5*o*** after irradiation with 311 UV light until the appropriate ratio of **5*o*** and **5*c*** was reached, and (c) the mixture after heating at 110 °C for 10.5 h

A series of amplification experiments were carried out under the irradiation of 311 UV irradiation. 1.11 g ring-opened isomer (**5*o***) was dissolved in 19.5 mL DMSO

and 3.0 mL EA. The mixture was placed under the 311 nm UV irradiation overnight. An appropriate amount of ethyl acetate (20.0 mL) was added into the reaction solution, followed by washing with water (75.0 mL × 4) and saturated brine (75 mL). The organic layer was combined and dried with anhydrous sodium sulfate followed by filtration. The filtrate was dried and the crude product was further purified by column chromatography (eluent: DCM) to obtain ~583 mg purple-dark solid powder.

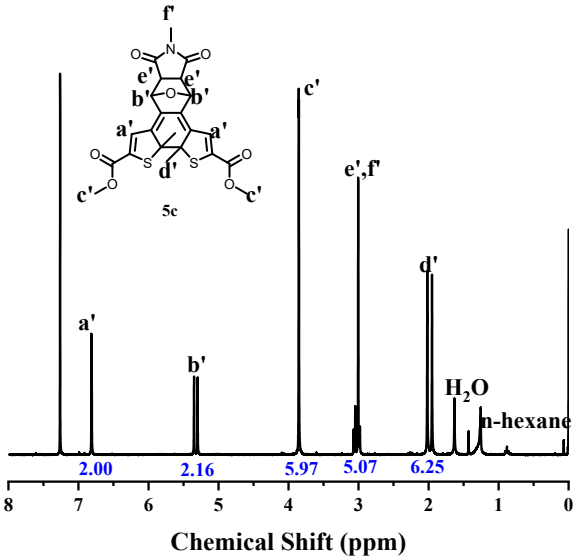
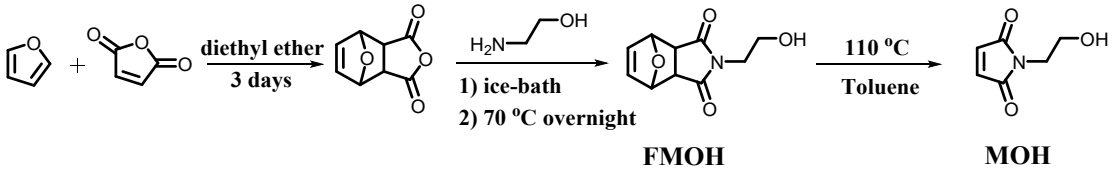


Figure S6. 300 MHz ^{1}H NMR spectrum of compound **5*c*** in $CDCl_3$.

3.6 Synthesis of furan-protected hydroxyethyl maleimide (FMOH) and hydroxyethyl maleimide (MOH)[2, 3]



Scheme S2. Synthesis of distinct monomer units (**FMOH** and **MOH**)

3.7 Typical Procedures for RAFT Polymerization of BMA and 5*o* at 120 °C

The polymerization was carried out in a baked Schlenk tube under argon atmosphere. BMA (2.0 mL, 12.5 mmol), **5*o*** (305.2 mg, 0.627 mmol), CPDB (13.8 mg, 0.0624 mmol) and DCPO (17.0 mg, 0.0624 mmol) were added into a glass tube. Ethylene carbonate (EC) (130.3 mg, 1.48 mmol) was added and used as the internal standard in the polymerization. The solvent (anisole :4.0 mL) was added to increase

the uniformity of the system. Then, the mixture was degassed by three freeze-pump-thaw cycles and placed in an oil bath kept at 120 °C. At determined time interval, an aliquot was taken out with a syringe under argon and quenched by cooling to -24 °C for ^{1}H NMR spectroscopy and SEC analysis to determine the monomer conversion. The crude copolymer was diluted with THF and precipitated in PE to obtain the solid product, which was further purified by preparative SEC to remove the remaining DTF or MMI. Other copolymers were obtained in a similar way.

3.8 Typical Procedures for Three-stage RAFT Polymerization of BMA and 5*c* at 120 °C

The polymerization was carried out in a baked Schlenk tube under argon atmosphere. BMA (2.0 mL, 12.5 mmol), **5*c*** (305.2 mg, 0.627 mmol), CPDB (13.8 mg, 0.0624 mmol) and DCPO (17.0 mg, 0.0624 mmol) were added into a glass tube. Ethylene carbonate (EC) (130.3 mg, 1.48 mmol) was added and used as the internal standard in the polymerization. The solvent (anisole :4.0 mL) was added to increase the uniformity of the system. Then, the mixture was degassed by three freeze-pump-thaw cycles and placed in an oil bath kept at 120 °C. The reaction was irradiated with blue light (> 450 nm) at the designated time for a period of time. At determined time intervals, an aliquot was taken out with a syringe under argon and quenched by cooling to -24 °C for ^{1}H NMR spectroscopy and SEC analysis to determine the monomer conversion. The crude copolymer was diluted with THF and precipitated in PE to obtain the solid product, which was further purified by preparative SEC to remove the remaining DTF or MMI. Other copolymers were obtained in a similar way.

3.9 Polymerization of BMA with dithienylfuran (DTF)

The RAFT polymerization of BMA in the presence of DTF was carried out in a baked Schlenk tube under argon atmosphere. BMA (2.0 mL, 12.5 mmol), DTF (235.8 mg, 0.627 mmol), CPDB (13.8 mg, 0.0624 mmol) and DCPO (17.0 mg, 0.0624 mmol) were added into a glass tube. Ethylene carbonate (EC) (100.5 mg, 1.14 mmol) was added and used as the internal standard in the polymerization. Dioxane (4.0 mL) was added and the mixture was degassed by three freeze-pump-thaw cycles and placed in

an oil bath kept at 70 °C. The polymerization was monitored by ^{1}H NMR spectroscopy. After 24.0 h, the conversion of BMA reached 97.92% and the characteristic NMR peaks of DTF were still clearly observed. The crude copolymer was diluted with THF and precipitated in PE to obtain the solid product, which was then further purified by preparative SEC to remove the remaining DTF. The final purified polymer was analyzed by SEC and ^{1}H NMR spectroscopy.

SECTION B. Results and Discussions

1. Polymerization of BMA with dithienylfuran (DTF)

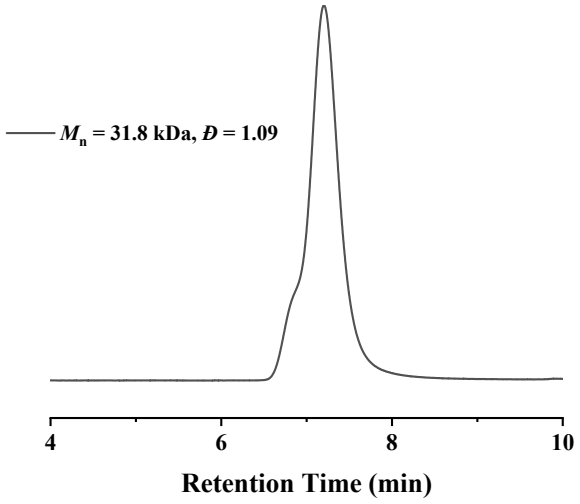


Figure S7. SEC trace of purified polybutyl methacrylate (**PBMA**). $[BMA]_0/[\mathbf{DTF}]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in dioxane, dioxane /BMA (2/1, v/v).

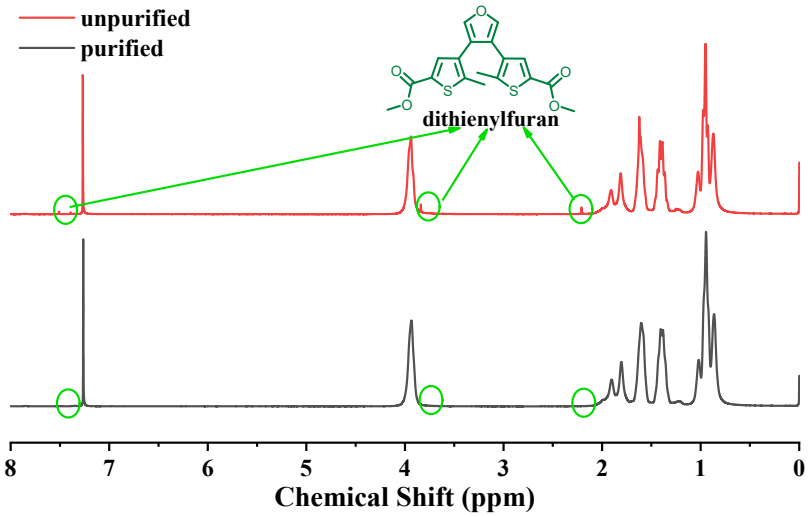


Figure S8. ^{1}H NMR spectra recorded for polybutyl methacrylate (**PBMA**) before and after purification. $[BMA]_0/[\mathbf{5}o]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in dioxane, dioxane/BMA (2/1, v/v).

2. RAFT Polymerization of BMA and 5*o* at 120 °C

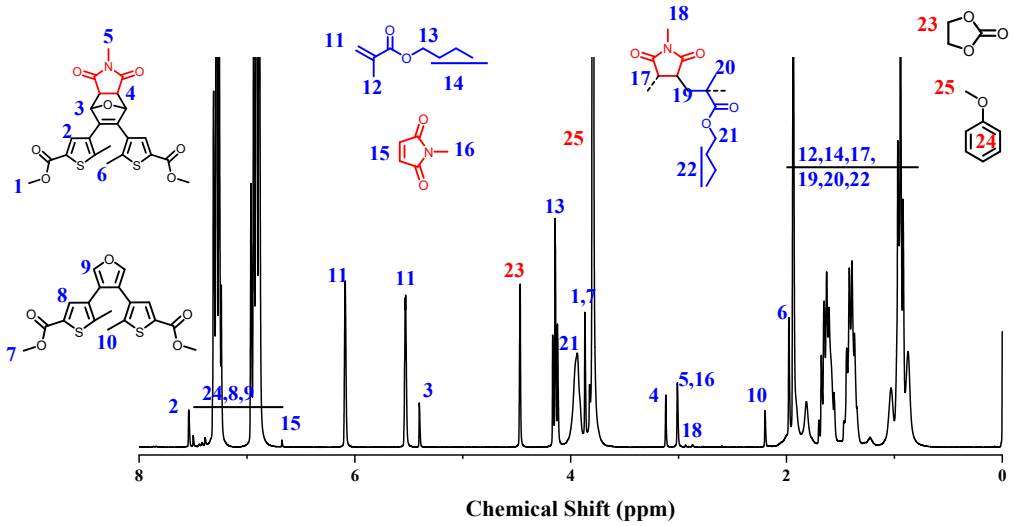


Figure S9. ^{1}H NMR spectrum in $CDCl_3$ recorded for the RAFT polymerization of BMA and **5*o*** after 1.0 h at 120 °C. $[BMA]_0/[\mathbf{5}o]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in anisole, anisole/BMA (2/1, v/v). $Conv._{BMA} = ([I_{6.19\text{-}6.00}]_0 - [I_{6.19\text{-}6.00}])/ [I_{6.19\text{-}6.00}]_0 \times 100\%$. $Conv._{MMI} = ([I_{3.05\text{-}2.96}]_0 - [I_{3.05\text{-}2.96}]) / [I_{3.05\text{-}2.96}]_0 \times 100\%$.

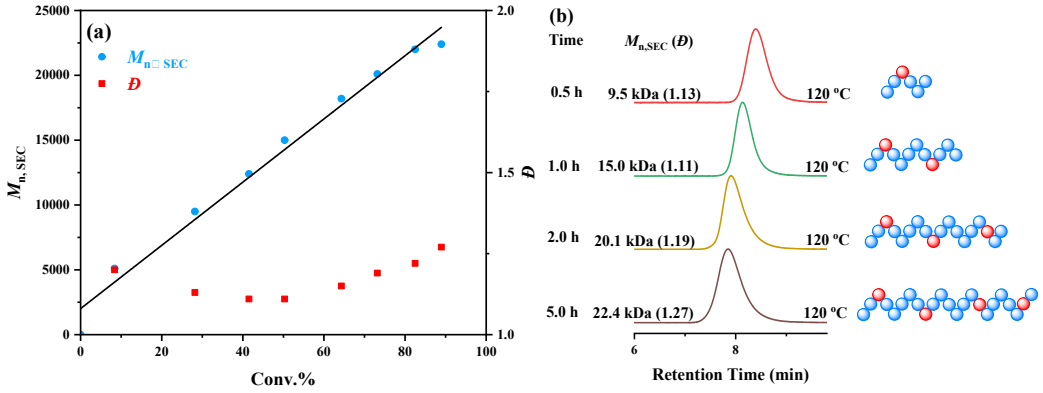


Figure S10. Synthesis of **poly (BO-G)** *via* sequence-controlled RAFT polymerization of BMA and **5*o*** at 120 °C. (a) Plot of $M_{n,SEC}$ with increasing monomer conversion. (b) SEC traces at different polymerization time points. $[BMA]_0/[\mathbf{5}o]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in anisole, anisole /BMA (2/1, v/v). The model diagram of polymer chains is not accurate but is intended to guide the eye.

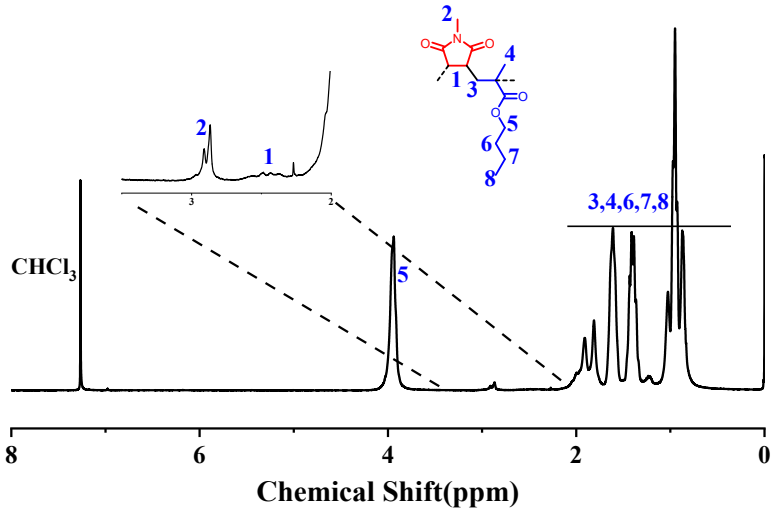


Figure S11. ^{1}H NMR spectrum of purified BMA/MMI copolymer (**poly (BO-G)**). ($[BMA]_0/[\mathbf{5}o]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in anisole, anisole /BMA (2/1, v/v). M_n = 32.9 kDa, $Đ$ = 1.17).

3. RAFT Polymerization of BMA and 5*c* at 120 °C in the dark

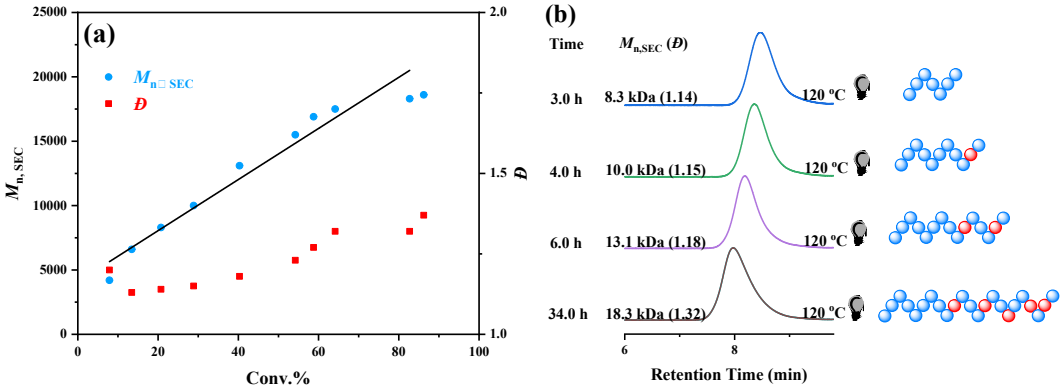


Figure S12. Synthesis of poly (BC-DG-1) *via* sequence-controlled RAFT polymerization of BMA and **5*c*** at 120 °C. (a) Plot of $M_{n,SEC}$ with increasing conversion. (b) SEC traces at different polymerization time points. $[BMA]_0/[\mathbf{5}c]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in anisole, anisole/BMA (2/1, v/v). The model diagram of polymer chains is not accurate but is intended to guide the eye.

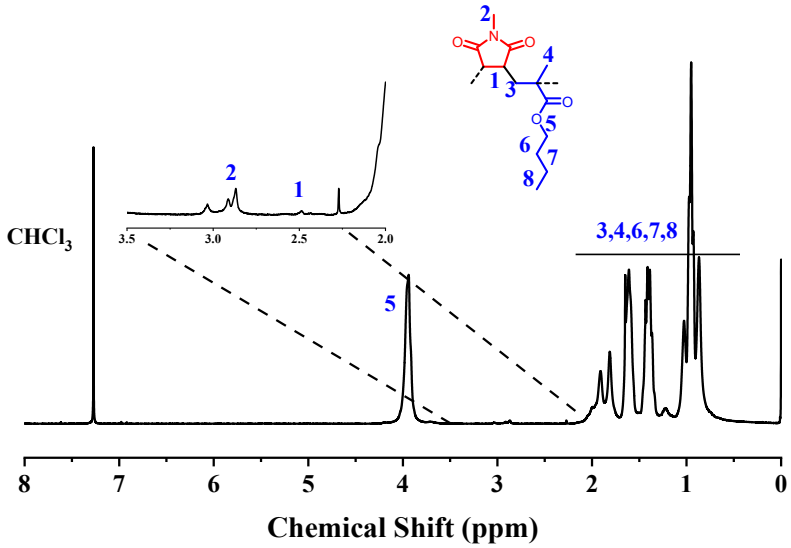


Figure S13. ^{1}H NMR spectrum of purified BMA/MMI copolymer (**poly (BC-DG-1)**). ($[BMA]_0/[\mathbf{5}c]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in anisole, anisole/BMA (2/1, v/v). M_n = 31.4 kDa, $Đ$ = 1.20).

4. Three-stage RAFT Polymerization of BMA and 5*c* at 120 °C

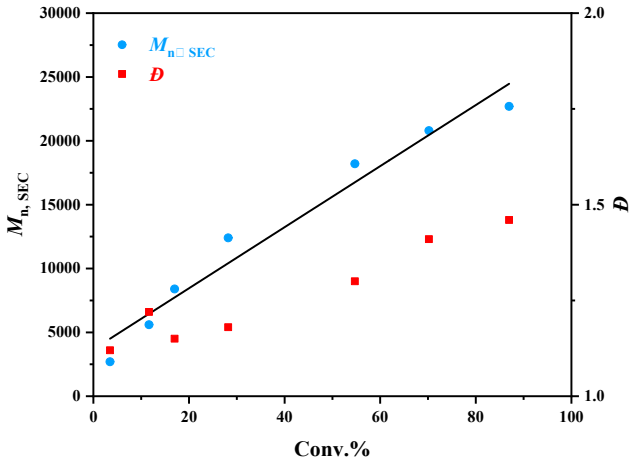


Figure S14. Synthesis of **poly (BC-DG-2)** *via* sequence-controlled, three-stage RAFT polymerization of BMA and **5*c*.** Plot of $M_{n,SEC}$ with increasing conversion. $[BMA]_0/[\mathbf{5}c]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in anisole, anisole/BMA (2/1, v/v).

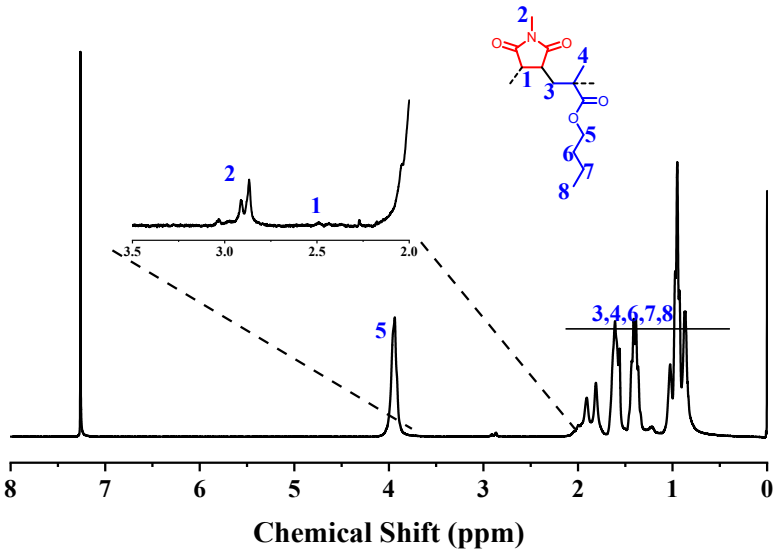


Figure S15. ^{1}H NMR spectrum of purified BMA/MMI copolymer (**poly (BC-DG-2)**). ($[BMA]_0/[\mathbf{5}c]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in anisole, anisole/BMA (2/1, v/v). M_n = 36.1 kDa, $Đ$ = 1.15).

5. Five-stage RAFT Polymerization of BMA and 5*c* at 120 °C

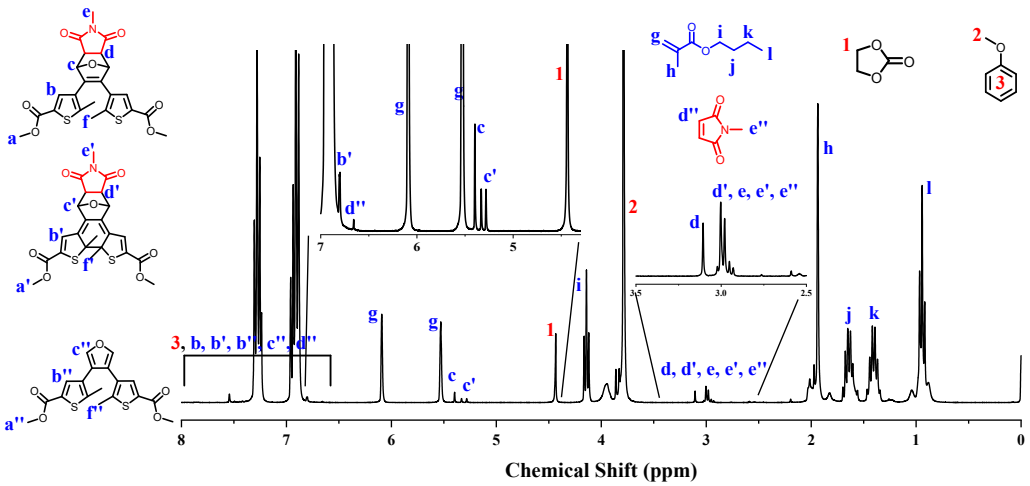


Figure S16. ^{1}H NMR spectrum recorded for the RAFT polymerization of BMA and **5*c*** after heating at 120 °C for 2.0 h followed by blue light (> 450 nm) irradiation for 0.5 h. $BMA]_0/[\mathbf{5}c]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in anisole, anisole/BMA (2.5/1, v/v). $Conv._{BMA} = ([I_{6.19\text{-}6.00}]_0 - [I_{6.19\text{-}6.00}])/ [I_{6.19\text{-}6.00}]_0 \times 100\%$. $Conv._{MMI} = ([I_{3.15\text{-}2.87} - I_{5.44\text{-}5.25}]_0 - [I_{3.15\text{-}2.87} - I_{5.44\text{-}5.25}]) / [I_{3.15\text{-}2.87} - I_{5.44\text{-}5.25}]_0 \times 100\%$.

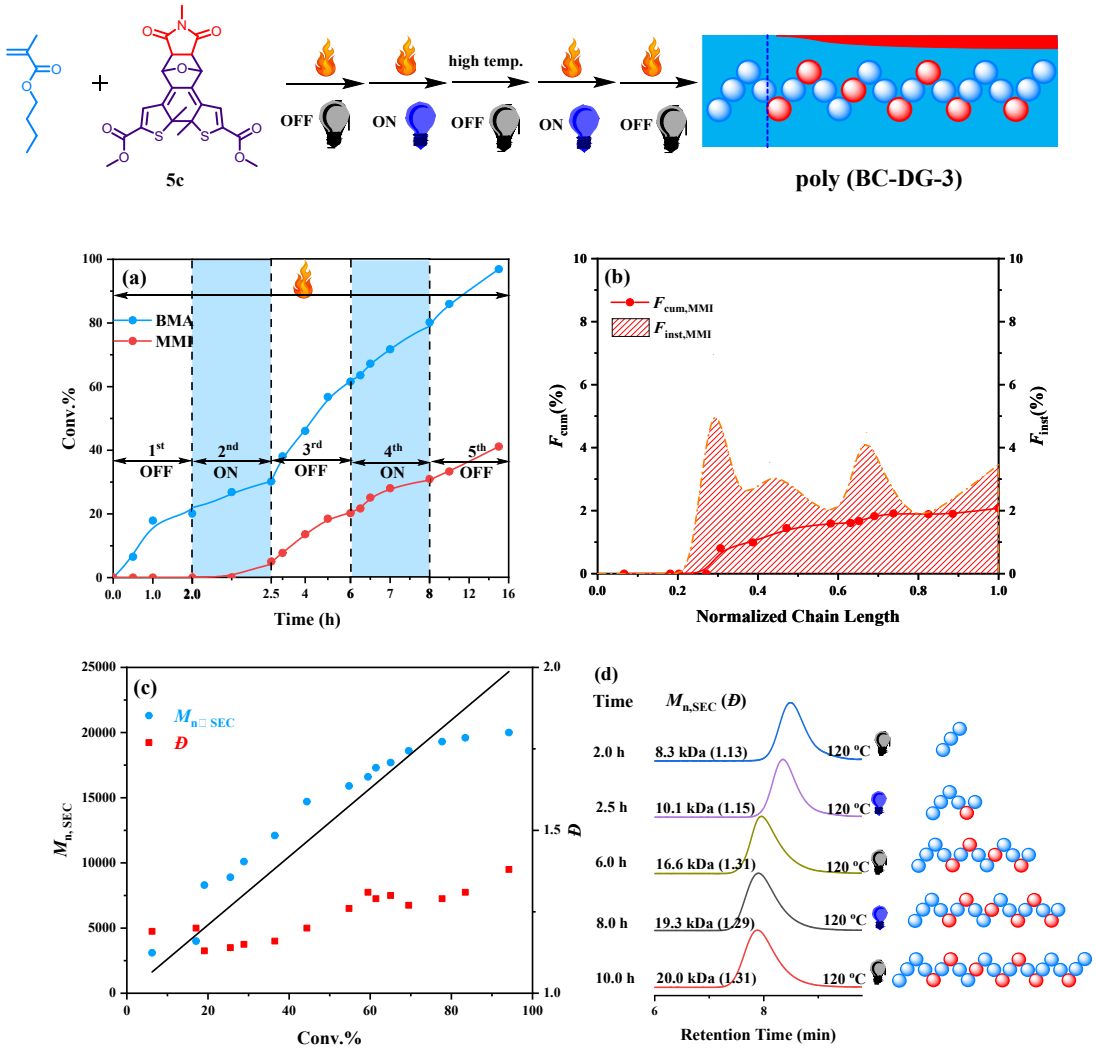


Figure S17. Synthesis of **poly (BC-DG-3)** *via* sequence-controlled, five-stage RAFT polymerization of BMA and **5*c***: (a) kinetic plots; (b) cumulative (F_{cum}) and instantaneous (F_{inst}) contents of MMI in the polymers as a function of the normalized chain length; (c) plot of $M_{n,SEC}$ with increasing conversions; (d) SEC traces at different polymerization time points. $[BMA]_0/[5c]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in anisole, anisole/BMA (2.5/1, v/v). Five-stage polymerization: 120 °C in the dark (2.0 h) - 120 °C with > 450 nm light (0.5 h) - 120 °C in the dark (3.5 h) - 120 °C with > 450 nm light (2.0 h) - 120 °C in the dark (8.0 h). The model diagram of polymer chains is not accurate but is intended to guide the eye. The F_{inst} profile has been smoothed.

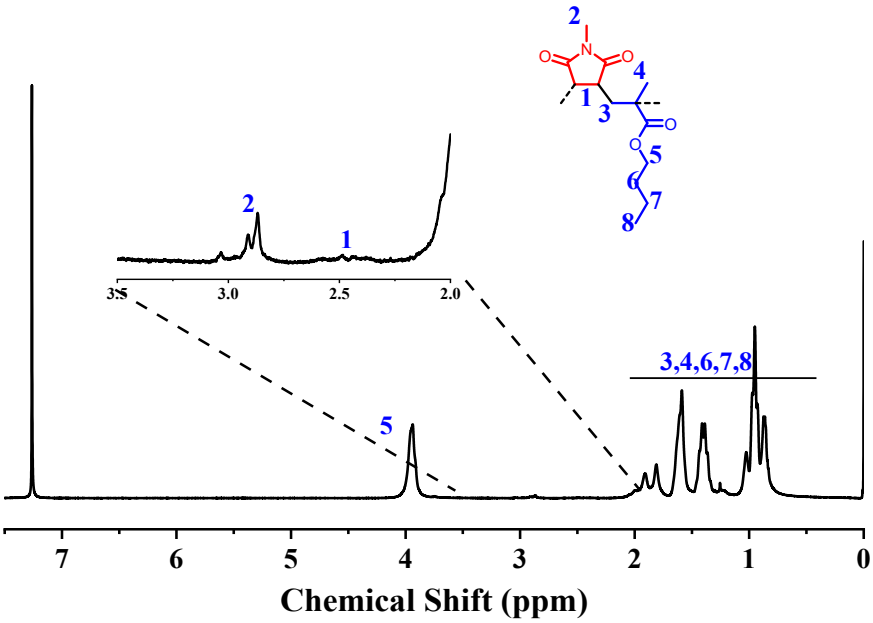


Figure S18. ^{1}H NMR spectrum of purified BMA/MMI copolymer (**poly (BC-DG-3)**). ($[BMA]_0/[5c]_0/[CPDB]_0/[DCPO]_0$ = 200/10/1/1, BMA = 2.0 mL, in anisole, anisole/BMA (2.5/1, v/v). M_n = 28.0 kDa, $Đ$ = 1.17).

6. Three-stage RAFT Polymerization of BMA, MOH and 5*c* at 120 °C

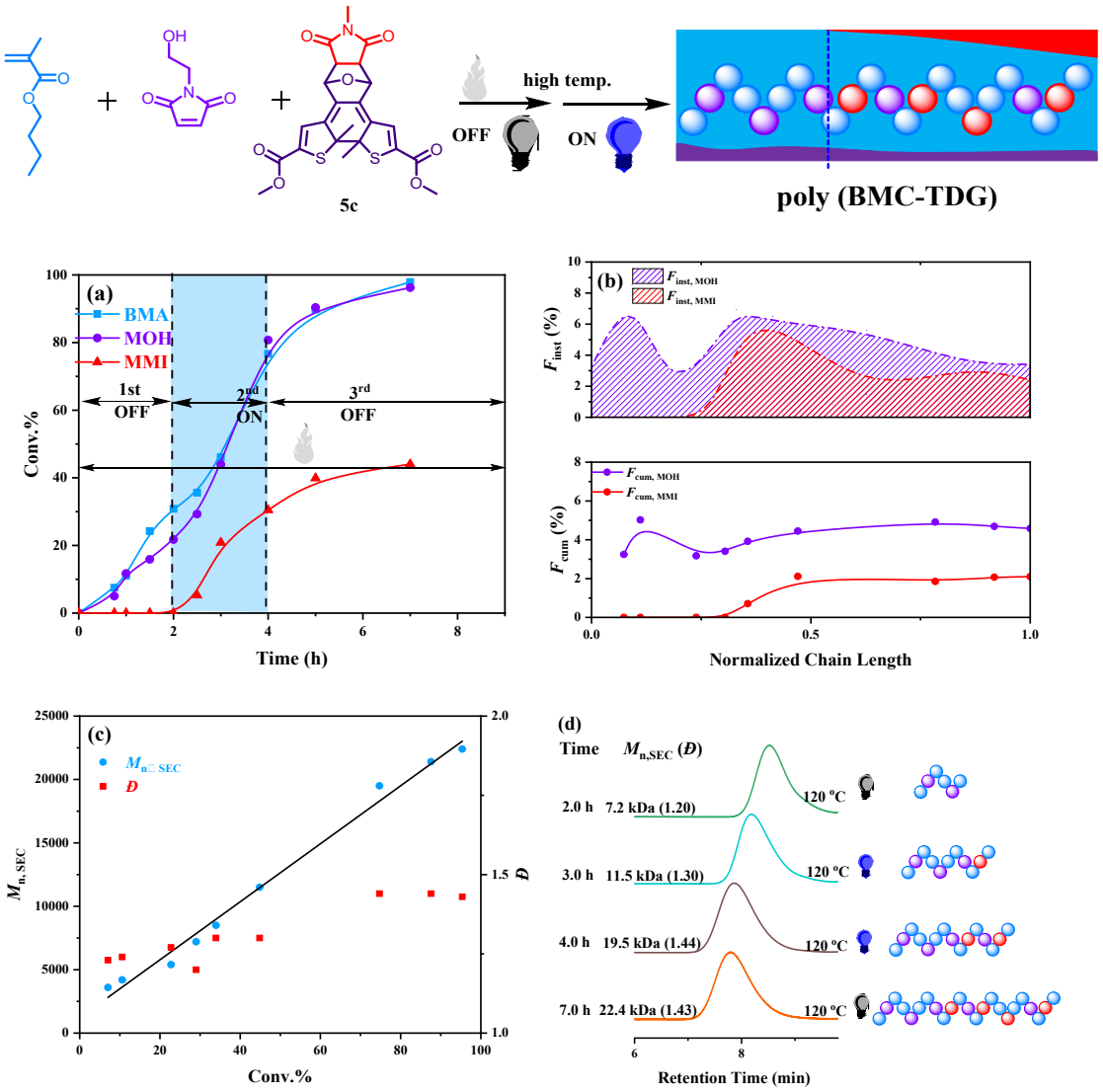


Figure S19. Synthesis of **poly (BMC-TDG)** *via* sequence-controlled, three-stage RAFT polymerization of BMA, MOH and **5*c*** at 120 °C. (a) plots of monomer conversion *versus* time; (b) cumulative (F_{cum}) and instantaneous (F_{inst}) monomer contents in polymers as a function of normalized chain length; (c) plot of $M_{n,SEC}$ with increasing conversions; (d) SEC traces at different polymerization time points. $[BMA]_0/[MOH]_0/[5c]_0/[CPDB]_0/[DCPO]_0$ = 200/10/10/1/1, BMA = 2.0 mL, in anisole, anisole /BMA (2/1, v/v). The model diagram of polymer chains is not accurate but is intended to guide the eye. The F_{inst} profile has been smoothed.

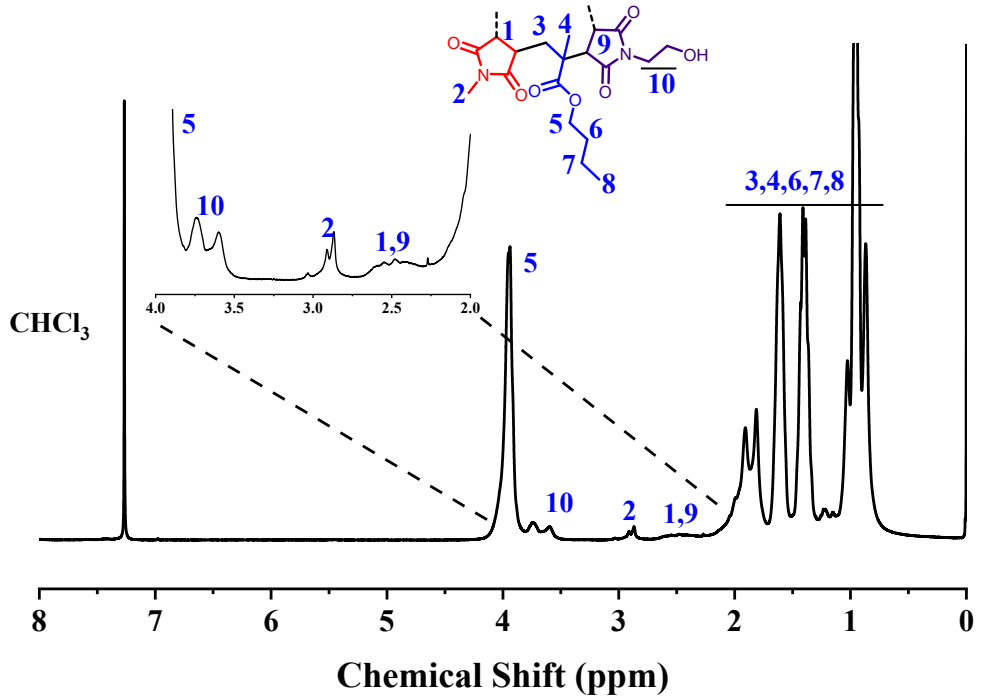


Figure S20. ^{1}H NMR spectrum of purified BMA/MOH/MMI copolymer (**poly (BMC-TDG)**). ($[BMA]_0/[MOH]_0/[5c]_0/[CPDB]_0/[DCPO]_0$ = 200/10/10/1/1, BMA = 2.0 mL, in anisole, anisole /BMA (2/1, v/v). M_n = 27.2 kDa, $Đ$ = 1.31).

7. Three-stage RAFT Polymerization of BMA, FMOH and 5*c* at 120 °C

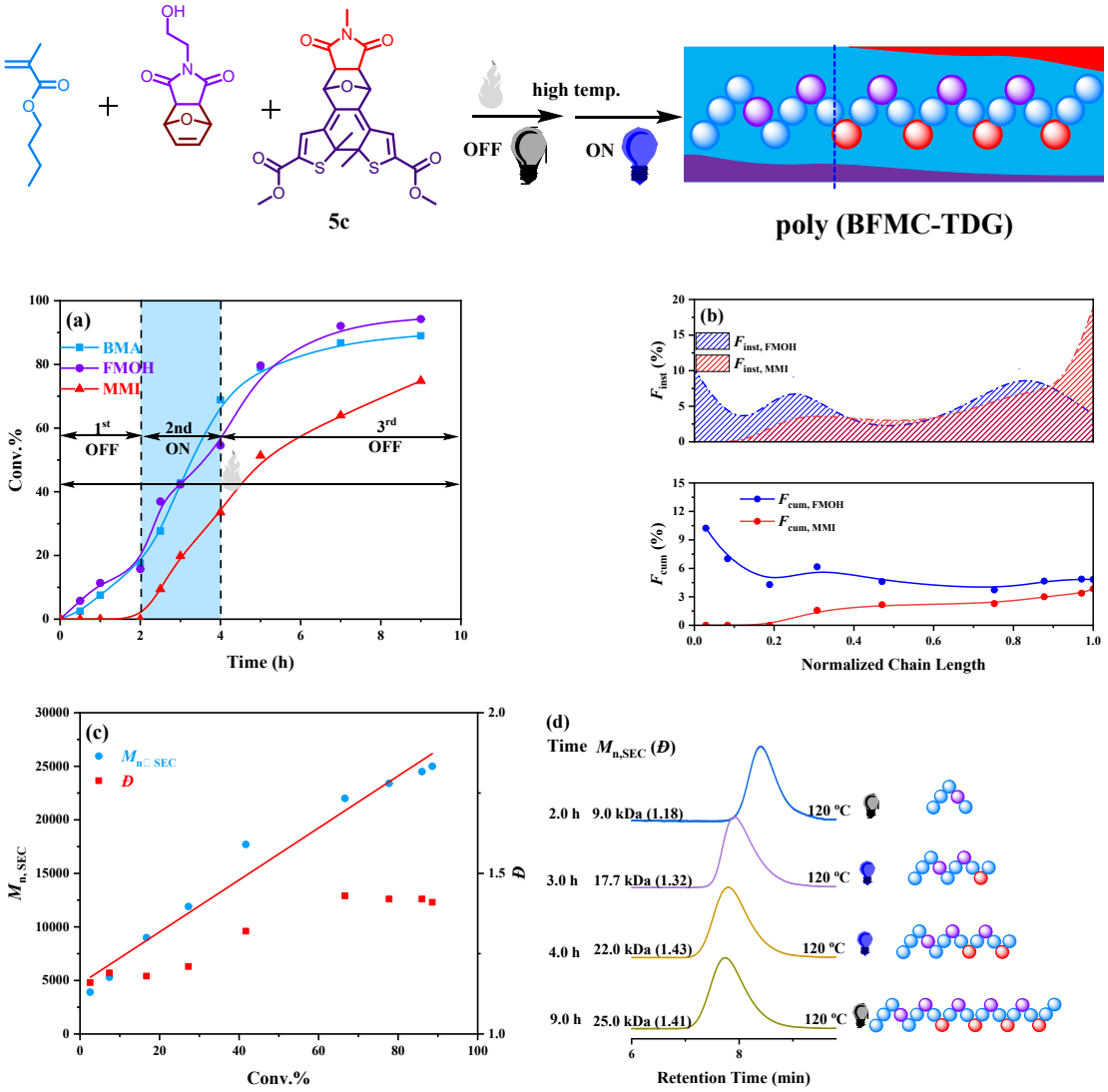


Figure S21. Synthesis of **poly (BFMC-TDG)** *via* sequence-controlled, three-stage RAFT polymerization of BMA, FMOH and **5*c*** at 120 °C. (a) plots of monomer conversion *versus* time; (b) cumulative (F_{cum}) and instantaneous (F_{inst}) monomer contents in polymers as a function of normalized chain length; (c) Plot of $M_{n,SEC}$ with increasing conversions. (d) SEC traces at different polymerization time points. $[BMA]_0/[FMOH]_0/[\mathbf{5}c]_0/[CPDB]_0/[DCPO]_0$ = 200/10/10/1/1, BMA = 2.0 mL, in anisole, anisole/BMA (2/1, v/v). The model diagram of polymer chains is not accurate but is intended to guide the eye. The F_{inst} profile has been smoothed.

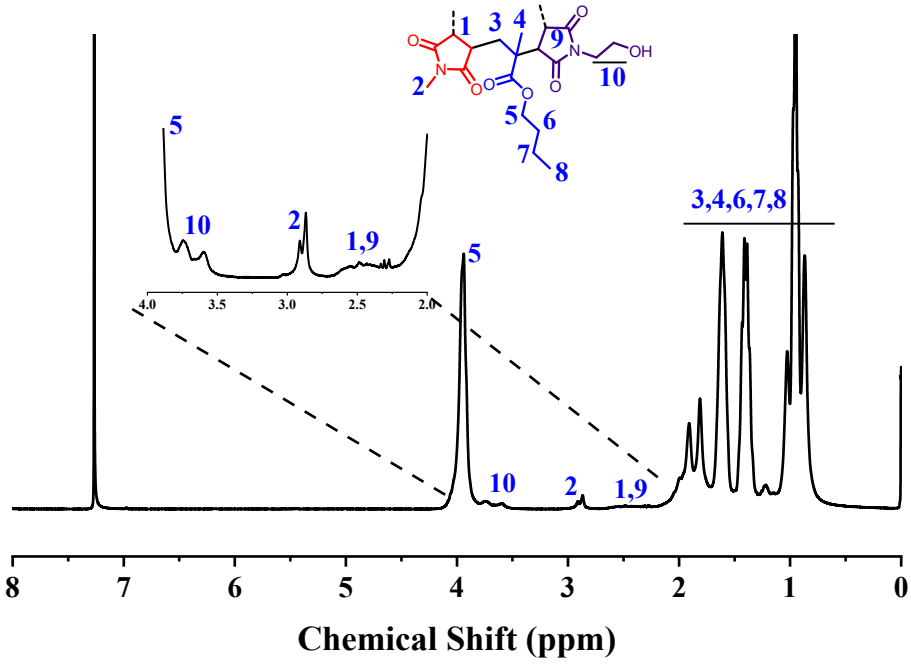


Figure S22. ^{1}H NMR spectrum of purified BMA/MOH/MMI copolymer (**poly (BFMC-TDG)**). ([BMA]$_0$/[FMOH]$_0$/[**5*c***]$_0$/[CPDB]$_0$/[DCPO]$_0$ = 200/10/10/1/1, BMA = 2.0 mL, in anisole, anisole/BMA (2/1, v/v). M_n = 35.1 kDa, $Đ$ = 1.32).

8. Four-stage RAFT Polymerization of BMA, FMOH and 5*c* at 120 °C

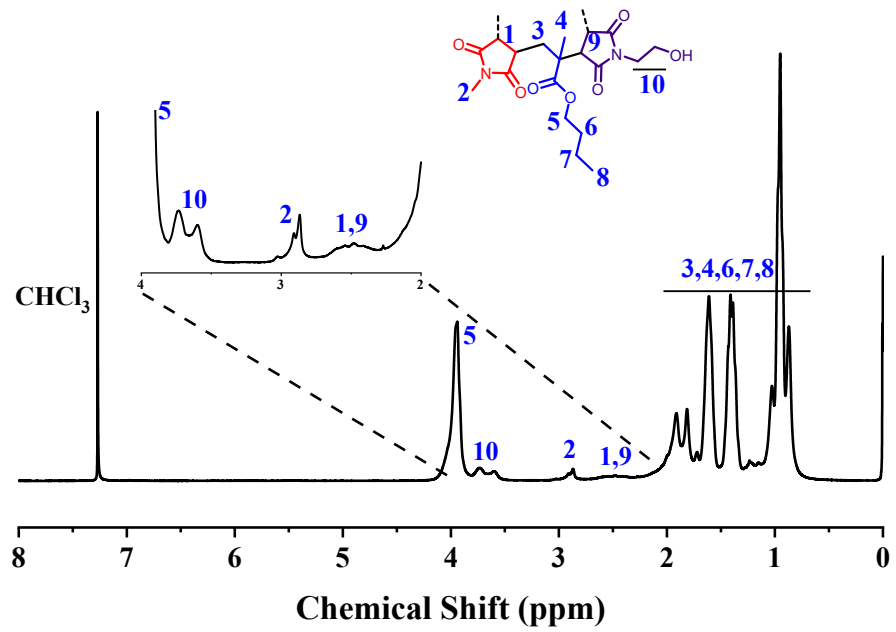


Figure S23. ^{1}H NMR spectrum of purified BMA/MOH/MMI copolymer (**poly (BFMC-TTG)**). ($[BMA]_0/[FMOH]_0/[\mathbf{5}\boldsymbol{c}]_0/[CPDB]_0/[DCPO]_0$ = 200/10/10/1/1, BMA = 2.0 mL, in anisole, anisole/BMA (2/1, v/v). M_n = 23.0 kDa, $Đ$ = 1.23).

SECTION C. References

1. D. G. Patel, T. B. Mitchell, S. D. Myers, D. A. Carter and F. A. Novak, *J. Org. Chem.*, 2020, **85**, 2646-2653.
2. F. Han, Q. Shi, L. Zhang, B. Liu, Y. Zhang, Y. Gao, R. Jia, Z. Zhang and X. Zhu, *Polym. Chem.*, 2020, **11**, 1614-1620.
3. Z. Huang, J. Zhao, Z. Wang, F. Meng, K. Ding, X. Pan, N. Zhou, X. Li, Z. Zhang and X. Zhu, *Angew. Chem. Int. Edit.*, 2017, **56**, 13612-13617.