Supporting Information for

Self-Assembly of a Condensation Homopolymer: With an Application in Fractionation

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Materials

All commercial reagents were used without additional purification, unless otherwise stated. Anhydrous solvent was purchased from commercial sources and transferred under argon atmosphere.

Instrumentation

Nuclear Magnetic Resonance (NMR): The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker 400 or 500 MHz spectrometer. The chemical shifts are expressed in ppm in reference to the residual deuterated solvent and the coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

Electrospray Ionization Mass Spectrometry (ESI-MS): ESI-MS spectra were acquired on a Bruker AmaZon SL configured with an ESI source in both negative and positive ionization mode.

Size-Exclusion Chromatography (SEC): SEC analyses were performed on a Polymer Laboratories PL-GPC 50 system equipped with a PL gel 5 μm guard column, two PL gel 5 μm Mixed-D columns, and a refractive index (RI) detector (Agilent Technologies). HPLC-grade tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min at 30 °C. The system was calibrated with polystyrene standards. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity ($Đ = M_w/M_n$) were determined.

Thermal Analysis: Thermal gravimetric analysis (TGA) was performed on a TA Instruments SDT Q600 analyzer under a nitrogen atmosphere. Samples were heated from 25 to 600 °C at a rate of 10 K/min. Differential scanning calorimeter (DSC) was performed on (Mettler Toledo DSC1, Switzerland) in nitrogen atmosphere. An indium standard was used for temperature and enthalpy calibrations. All the samples were first heated from 25 to 200 ºC at a rate of 10 K/min and held at this temperature for 2 min to eliminate the thermal history, then they were cooled to -30 ºC and heated again from -30 to 200 ºC at a heating or cooling rate of 10 K/min. The glass transition temperature (T_g) was determined from the second heating scan.

Transmission Electron Microscopy (TEM): TEM images were obtained using a JEOL JEM-2100 microscope operating at an acceleration voltage of 80 kV. Cryo-TEM imaging was performed on a Talos F200C G2 microscope operating at an acceleration voltage of 200 kV.

Dynamic Light Scattering (DLS): The hydrodynamic diameter (D_h) and size distribution (PDI, Polydispersity Index) of the micelles in DMF/methanol were determined by DLS. The measurements were performed on a Brookhaven BI-200SM

goniometer system (Brookhaven Instruments Corp., USA) equipped with a solid-state laser operating at a wavelength of 532 nm. The data were collected at a fixed scattering angle of 90°. The sample temperature was maintained at 25 °C by a circulating water bath.

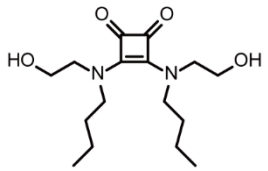
Zeta Potential Analysis: Zeta potential measurements were performed on a Brookhaven Instruments 90PLUS PALS Zeta Potential and Particle Size Analyzer at 25 °C. The polymer samples were dispersed in DMF/methanol mixed solvents (1:1 and 1:3, v/v) at a concentration of 1.0 mg/mL. The measurements were conducted directly in the mixed solvents without the addition of any extra background electrolytes.

Fluorescence Spectroscopy: Fluorescence emission spectra for the dye encapsulation experiments were recorded on a Hitachi F-7000 fluorescence spectrophotometer at room temperature.

Experimental Procedures

Synthesis of Monomers.

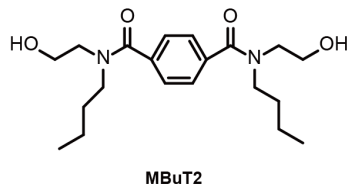
Synthesis of *n*-Butyl Squaramide Diol (**MBuS2**)



MBuS2

The compound was prepared following a procedure slightly modified from our previous work.[1] To a solution of 3,4-diethoxy-3-cyclobutene-1,2-dione (10.0 g, 58.8 mmol, 1.0 eq.) in ethanol (40 mL) was added 2-(butylamino)ethanol (27.6 g, 235.1 mmol, 4.0 eq.) and triethylamine (TEA, 23.8 g, 235.1 mmol, 4.0 eq.). The mixture was stirred at room temperature for 12 h. After completion, the solvent was removed under reduced pressure. The resulting residue was washed with *n*-hexane (2 × 50 mL) and dried under vacuum to afford MBuS2 (17.2 g, 92.6% yield) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.80 (t, J = 5.0 Hz, 4H), 3.67 (t, J = 5.0 Hz, 4H), 3.55 (t, J = 7.4 Hz, 4H), 1.64 - 1.54 (m, 4H), 1.38 - 1.25 (m, 4H), 0.92 (t, J = 7.4 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 184.79, 170.76, 60.39, 52.43, 51.48, 30.81, 19.87, 13.86. **HRMS (ESI)** Calcd. for $C_{16}H_{29}N_2O_4^+$: $[M+H]^+$, 313.2122. Found: m/z 313.2115.

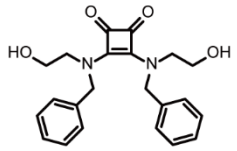
Synthesis of *n*-Butyl Terephthalamide Diol (**MBuT2**)



MBuT2

Under a nitrogen atmosphere, 2-(butylamino)ethanol (6.1 g, 51.7 mmol, 2.1 eq.) and triethylamine (TEA, 5.2 g, 51.7 mmol, 2.1 eq.) were dissolved in 20 mL of anhydrous dichloromethane (DCM). The solution was cooled to 0 °C in an ice bath. A solution of terephthaloyl chloride (5.0 g, 24.6 mmol, 1.0 eq.) in 10 mL of anhydrous DCM was then added dropwise to the mixture. After the addition was complete, the reaction was stirred at 0 °C for 1 h, and then allowed to warm to room temperature and stirred for an additional 12 h. Upon completion, the reaction mixture was washed sequentially with saturated aqueous sodium bicarbonate solution and brine. The organic layer was collected, dried, and concentrated under reduced pressure to afford MBuT2 (6.2 g, 69% yield) as a colorless viscous liquid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 - 7.30 (m, 4H), 3.95 - 3.74 (m, 4H), 3.73 - 3.40 (m, 6H), 3.32 - 3.16 (m, 4H), 1.68 - 1.02 (m, 8H), 0.99 - 0.64 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.81, 171.52, 138.30, 137.57, 137.06, 127.19, 126.88, 61.76, 61.60, 59.72, 50.74, 50.56, 48.91, 45.01, 30.96, 29.57, 20.29, 19.73, 13.98, 13.69.

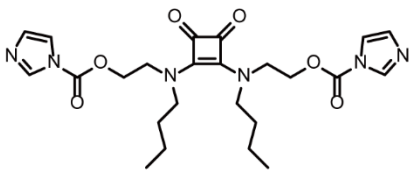
Synthesis of *n*-Benzyl Squaramide Diol (**MBnS2**)



MBnS2

To a solution of 3,4-diethoxy-3-cyclobutene-1,2-dione (10.0 g, 58.8 mmol, 1.0 eq.) in ethanol (40 mL) was added *n*-benzylethanolamine (35.5 g, 235.1 mmol, 4.0 eq.) and triethylamine (TEA, 23.8 g, 235.1 mmol, 4.0 eq.). The mixture was stirred at room temperature for 12 h. After completion, the solvent was removed under reduced pressure. The resulting residue was washed with *n*-hexane (2 × 50 mL) and dried under vacuum to afford MBnS2 (18.5 g, 80.7% yield) as a white solid. **^{1}H NMR (500 MHz, DMSO-d_6)** δ 7.39 - 7.33 (m, 4H), 7.32 - 7.28 (m, 2H), 7.28 - 7.24 (m, 4H), 4.95 (t, J = 5.3 Hz, 2H), 4.87 (s, 4H), 3.58 (q, J = 5.5 Hz, 4H), 3.47 (t, J = 5.6 Hz，4H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 183.90, 169.81, 136.70, 128.71, 127.55, 58.53, 53.16, 51.74. **HRMS (ESI)** Calcd. for $C_{22}H_{25}N_2O_4^+$: $[M+H]^+$, 381.1809. Found: m/z 381.1800.

Synthesis of Imidazole-Functionalized *n*-Butyl Squaramide (**MBuS1**)

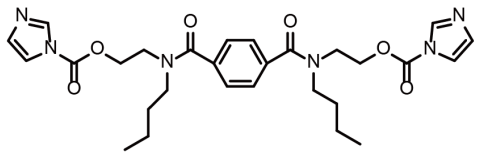


MBuS1

The compound was prepared following a procedure slightly modified from the literature.[2] Under a nitrogen atmosphere, *n*-butyl squaramide diol (**MBuS2**, 10.0 g, 32.0 mmol, 1.0 eq.) was dissolved in 15 mL anhydrous DMF. To this solution, 1,1'-carbonyldiimidazole (CDI, 15.6 g, 96.0 mmol, 3.0 eq.) was added portionwise over 20

min. The reaction mixture was stirred at room temperature for 12 h. Upon completion, the solution was treated with 100 mL anhydrous diethyl ether, resulting in the formation of an oily precipitate. The mixture was stirred at 0 °C for 1 h to induce solidification. The resulting white precipitate was collected by filtration, washed with diethyl ether (2 × 50 mL), and dried under vacuum to afford **MBuS1** (14.8 g, 88.1% yield) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.09 (s, 2H), 7.34 (s, 2H), 7.07 (s, 2H), 4.57 (t, J = 5.2 Hz, 4H), 4.09 (t, J = 5.2 Hz, 4H), 3.33 (t, J = 7.6 Hz, 4H), 1.62 - 1.52 (m, 4H), 1.33 - 1.19 (m, 4H), 0.88 (t, J = 7.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 185.11, 170.40, 148.66, 137.08, 131.22, 117.03, 65.94, 52.43, 47.71, 30.47, 19.79, 13.68. **HRMS (ESI)** Calcd. for $C_{24}H_{33}N_6O_6^+$: $[M+H]^+$, 501.2457. Found: m/z 501.2448.

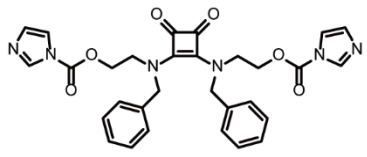
Synthesis of Imidazole-Functionalized *n*-Butyl Terephthalamide (**MBuT1**)



MBuT1

Under a nitrogen atmosphere, *n*-butyl terephthalamide diol (**MBuT2**, 5.0 g, 13.7 mmol, 1.0 eq.) was dissolved in 10 mL anhydrous DMF. To this solution, 1,1'-carbonyldiimidazole (CDI, 6.7 g, 41.2 mmol, 3.0 eq.) was added portionwise over 20 min. The reaction mixture was stirred at room temperature for 12 h. Upon completion, the DMF was removed under vacuum. The resulting residue was dissolved in DCM and washed with a saturated aqueous citric acid solution. The organic layer was collected, and the solvent was removed under reduced pressure. The product was dried under vacuum to afford MBuT1 (6.2 g, 81.8% yield) as a colorless viscous oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.25 - 7.94 (m, 2H), 7.53 - 7.32 (m, 6H), 7.09 (s, 2H), 4.80 - 4.33 (m, 4H), 3.99 - 3.66 (m, 4H), 3.61 - 3.17 (m, 4H), 1.76 - 1.07 (m, 8H), 1.07 - 0.67 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.64, 148.77, 137.55, 137.20, 131.05, 126.90, 117.20, 65.40, 50.14, 44.09, 31.09, 19.74, 13.73.

Synthesis of Imidazole-Functionalized *n*-Benzyl Squaramide (**MBnS1**)



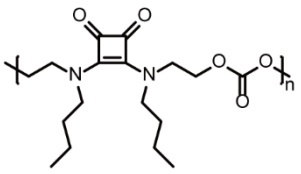
MBnS1

Under a nitrogen atmosphere, *n*-benzyl squaramide diol (**MBnS2**, 10.0 g, 26.3 mmol, 1.0 eq.) was dissolved in 15 mL anhydrous DMF. To this solution, 1,1'-carbonyldiimidazole (CDI, 12.8 g, 78.9 mmol, 3.0 eq.) was added portionwise over 20 min. The reaction mixture was stirred at room temperature for 12 h. Upon completion, the solution was treated with 100 mL anhydrous diethyl ether, resulting in the formation of an oily precipitate. The mixture was stirred at 0 °C for 1 h to induce solidification.

The resulting white precipitate was collected by filtration, washed with diethyl ether (2 × 50 mL), and dried under vacuum to afford **MBnS1** (12.1 g, 80.3% yield) as a white solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.09 (s, 2H), 7.40 (t, J = 1.5 Hz, 2H), 7.29 - 7.23 (m, 6H), 7.26 - 7.17 (m, 4H), 7.07 - 7.02 (m, 2H), 4.74 (s, 4H), 4.52 (t, J = 5.0 Hz, 4H) , 3.91 (t, J = 4.9 Hz, 4H). **^{13}C NMR (101 MHz, DMSO-d_6)** δ 184.37, 170.25, 148.07, 137.07, 135.93, 130.38, 128.74, 127.79, 127.30, 117.27, 65.51, 54.32, 47.71. **HRMS (ESI)** Calcd. for $C_{30}H_{29}N_6O_6^+$: $[M+H]^+$, 569.2144. Found: m/z 569.2139.

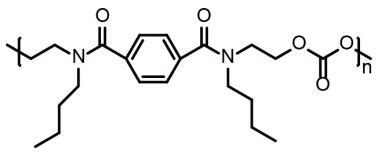
General Procedure for Polymer Synthesis

In a flame-dried 10 mL Schlenk flask, **MBuS1** (1.0 eq.), **MBuS2** (1.0 eq.), and dried cesium fluoride (CsF, 0.05 eq. relative to **MBuS2**) were combined. The flask was evacuated and refilled with nitrogen three times to ensure an inert atmosphere. Anhydrous DMF was then added to achieve a total monomer concentration of 2.0 M. The reaction mixture was stirred at 60 °C under nitrogen overnight. A series of **PBuS** with distinct chain lengths was synthesized through parallel polymerizations by varying the molar ratio of **MBuS1** to **MBuS2** (1.0:1, 1.1:1, 1.2:1, 1.3:1, 1.5:1). **PBuT** was synthesized following the general procedure using an equimolar ratio of **MBuT1** (1.0 eq.) and **MBuT2** (1.0 eq.). **PBuBuS** was synthesized following the general procedure using an equimolar ratio of **MBuS1** (1.0 eq.) and 1,4-butanediol (1.0 eq.). **PBnS** was synthesized following the general procedure using an equimolar ratio of **MBnS1** (1.0 eq.) and **MBnS2** (1.0 eq.).



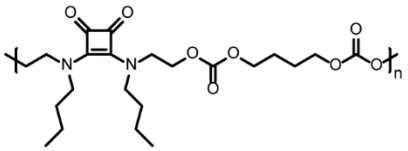
PBuS

PBuS ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (t, J = 5.3 Hz, 4H), 3.88 (t, J = 5.3 Hz, 4H), 3.44 (t, J = 7.4 Hz, 4H), 1.64 - 1.54 (m, 4H), 1.38 - 1.25 (m, 4H), 0.92 (t, J = 7.3 Hz, 6H).



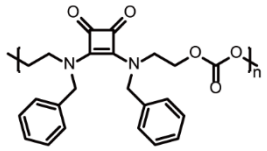
PBuT

PBuT ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 4H), 4.66 - 3.99 (m, 4H), 3.85 - 3.19 (m, 8H), 1.70 - 1.08 (m, 8H), 1.04 - 0.73 (m, 6H).



PBuBuS

PBuBuS ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.35 - 4.29 (m, 4H), 4.18 - 4.15 (m, 4H), 3.96 - 3.90 (m, 4H), 3.47 (t, J = 7.6 Hz, 4H), 1.79 - 1.70 (m, 4H), 1.63 (t, J = 7.4 Hz, 4H), 1.40 - 1.29 (m, 4H), 0.95 (t, J = 7.3 Hz, 6H).



PBnS

PBnS ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 6H), 7.17 - 7.08 (m, 4H), 4.61 (d, J = 6.2 Hz, 4H), 4.18 (t, J = 5.1 Hz, 4H), 3.74 (d, J = 4.8 Hz, 4H).

Isolation and Characterization of the Cyclic Dimer

Following the polymerization, the crude reaction mixture was diluted with dichloromethane and directly subjected to silica gel column chromatography. The cyclic dimer was isolated using ethyl acetate as the eluent. The purified product was obtained as a white solid after removal of the solvent under reduced pressure. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.30 (t, J = 5.0 Hz, 8H), 3.81 (t, J = 4.9 Hz, 8H), 3.51 (t, J = 7.4 Hz, 8H), 1.65 - 1.52 (m, 8H), 1.39 - 1.26 (m, 8H), 0.93 (t, J = 7.3 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 185.29, 170.75, 154.87, 65.30, 50.94, 48.79, 30.68, 19.84, 13.84. **HRMS (ESI)** Calcd. for $C_{34}H_{52}N_4NaO_{10}^+$: $[M+Na]^+$, 699.3576. Found: m/z 699.3575.

General Procedure for Self-Assembly Fractionation

An as-synthesized DMF solution of **PBuS** 200 mg was diluted first with DMF and then further with methanol to a solvent volume ratio of 1:3/1:5/1:10 (a formal polymer concentration of 30.0 mg/mL), then the mixture was added under vigorous vortex mixing for 1 min. The mixture was immediately centrifuged at 10000 *g* for 3 min to separate phases. The supernatant was carefully decanted, and the resulting solid was dried under vacuum at 25 °C for 2 h to yield the purified polymer. The product was characterized by ^{1}H NMR and SEC.

Polymerization Kinetics

The polymerization reactions were conducted according to the **General Procedure for Polymer Synthesis**. At predetermined time intervals, aliquots (50 μL) were withdrawn from the crude reaction mixture and immediately quenched by dilution with deuterated chloroform ($CDCl_3$, 0.45 mL). Monomer conversion was determined by ^1H NMR spectra. Simultaneously, molecular weight distributions were analyzed by SEC.

Recovery of Imidazole Byproduct

Following the polymerization of **PBuS**, the crude reaction mixture was precipitated in methanol. The supernatant, which contained the imidazole byproduct, was collected and concentrated under reduced pressure. The resulting residue was dissolved in dichloromethane (DCM) and extracted with water three times (imidazole is highly water-soluble). The combined aqueous layers were evaporated to dryness under vacuum to afford the recovered imidazole as a white solid. The purity was confirmed by ^1H NMR spectroscopy, and the recovery yield was calculated.

Procedure for a Long Chain Length Fraction of PBuS

The crude polymer 2.0 g was placed in a 50 mL polypropylene centrifuge tube and diluted with 6.7 mL DMF. To this solution, 33.3 mL of methanol (resulting in a 1:5 DMF/methanol ratio, v/v) was added under vigorous vortex mixing for 1 min. The mixture was immediately centrifuged (10000 *g*, 3 min) to induce phase separation. The supernatant was carefully decanted and discarded. The polymer-rich lower phase (precipitate) was redissolved in 6.7 mL of DMF, and the precipitation process was repeated by adding 33.3 mL of methanol with vortexing, followed by centrifugation under the same conditions. After decanting the supernatant, the final solid precipitate was collected and dried under vacuum at 25 °C for 2 h. This procedure yielded the purified, high molecular weight fraction of **PBuS** (0.54 g, 44% yield), which was subsequently characterized by SEC/TEM/DLS.

Determination of Critical Micelle Concentration (CMC)

The Critical Micelle Concentration (CMC) was determined using Dynamic Light Scattering (DLS). A series of polymer solutions (fractionated sample, M_n: 22.7 k, $Đ$: 1.08) in DMF/methanol (1:3, v/v) with concentrations ranging from 0.0001 to 5.0 mg/mL were prepared. The scattering intensity (count rate) was recorded for each sample at 25 °C. The CMC was identified as the intersection point of the two extrapolated linear segments on the plot of count rate versus the logarithm of polymer concentration.

Dye Encapsulation Experiments

Dye loading experiments were performed using hydrophobic dyes (Coumarin 6, Nile Red, 1,6-Diphenyl-1,3,5-hexatriene (DPH)) and a hydrophilic dye (Rhodamine B). Briefly, the polymer (1.0 mg/mL) and the respective dye were mixed in a DMF/methanol (1:3, v/v) solvent mixture. The solution was then dialyzed against the same solvent mixture to remove free, unencapsulated dye. A control experiment containing only the dye (without polymer) in the solvent mixture was performed under identical dye concentration and dialysis conditions. After dialysis, the fluorescence intensity of the solutions was measured to confirm dye retention. The fluorescence emission spectra were recorded using specific excitation wavelengths.

Time-Dependent Evolution of Micelles

The fractionated high molecular weight (HMW, M_n: 22.7 k, $Đ$: 1.08) and low molecular weight (LMW, M_n: 12.0 k, $Đ$: 1.08) samples were dissolved in DMF/methanol (1:3, v/v) at a concentration of 1.0 mg/mL. The hydrodynamic diameter (D_h) and size distribution (PDI) were monitored by DLS at predetermined time intervals (e.g., 0 h, 12 h).

Sample Preparation for Electron Microscopy

For Transmission Electron Microscopy (TEM): A 10 μL aliquot of the respective sample (i.e., solution, suspension, or the bottom fraction after centrifugation) was deposited onto a carbon-coated copper grid and allowed to sit for 1 min. The excess liquid was carefully removed by blotting with filter paper. For staining, the grid was then treated with a 1% (w/v) aqueous solution of phosphotungstic acid (PTA) for 10 s, blotted again, and allowed to air-dry completely before imaging.

For Cryo-Transmission Electron Microscopy (Cryo-TEM): The polymer **PBuS** was dissolved in a DMF/methanol (1:1, v/v) mixture to a final concentration of 1.0 mg/mL. A 3 μL aliquot of this solution was applied to a glow-discharged, carbon-coated copper grid. The grid was then blotted for 5 s and immediately vitrified by plunge-freezing into liquid ethane using a cryo-plunger device.

Four-Step Sequential Fractionation of PBuS

The crude polymer solution (200 mg) was transferred to a 50 mL polypropylene centrifuge tube. First precipitation: DMF/methanol (1:3, v/v, 4 mL, 30 mg/mL) was added as a precipitant under vigorous vortex mixing (1 min). The mixture was immediately centrifuged at 10000 *g* for 3 min. The polymer-rich lower phase was collected, dried under vacuum at 25 °C for 2 h, and analyzed by SEC.

Subsequent fractionations: The supernatant from the first step was transferred to a new 50 mL centrifuge tube. Methanol was incrementally added to adjust the precipitant ratio as follows: Second fraction (DMF/methanol 1:5, v/v): Methanol (2 mL) was added to the supernatant. The mixture was vortexed, centrifuged (10000 *g*, 3 min), and the precipitate was collected. Third fraction (DMF/methanol 1:10, v/v): Additional methanol (5 mL) was added to the remaining supernatant. The precipitation and collection steps were repeated. Fourth fraction (DMF/methanol 1:100, v/v): Methanol (95 mL) was added to the final supernatant. The precipitate was isolated as above. All fractions were dried under vacuum and characterized by SEC.

Degradation of PBuS

A long chain length fraction of **PBuS** from twice fractionation (1:5 DMF/methanol, M_n/22.7k,$Đ$/1.08) was dissolved in a DMF/methanol (1:1, v/v) mixed solvent (66.7 mg/mL) and subjected to degradation at room temperature. At each designated time point (2 h, 4 h, 6 h, 12 h, 24 h, and 36 h): **Before Fractionation**: An aliquot was directly analyzed by SEC without further treatment. **After Fractionation**: A parallel aliquot was precipitated with DMF/methanol (1:10, v/v) then analyzed by SEC.

Table S1. Optimization of polymerization conditions.

Entry [a]	MBuS1: MBuS2	Solvent	Catalyst	Temperature (℃)	Yield [b]	M_n [c] (kDa)	M_w [c] (kDa)	$Đ$ [c]
1	1:1	EA	CsF	60	82%	4.7	6.5	1.38
2	1:1	$CHCl_3$	CsF	60	62%	9.4	10.9	1.16
3	1:1	DMF	CsF	60	73%	14.9	18.1	1.22
4	1:1.05	DMF	CsF	60	56%	10.0	11.5	1.16
5	1:1	DMF	CsF	80	64%	9.9	11.6	1.17
6	1:1	DMF	DBU	60	25%	5.9	7.0	1.18
7	1:1	DMF	None	60	/	/	/	/

[a] All polymerization reactions were conducted at a total monomer concentration of 2.0 M using 5 mol% of CsF as the catalyst, with the molar loading calculated relative to the imidazole-functionalized monomer (MBuS1). [b] Isolated yield after purification by methanol precipitation. [c] M_n and $Đ$ were determined by SEC in THF, calibrated with polystyrene standards.

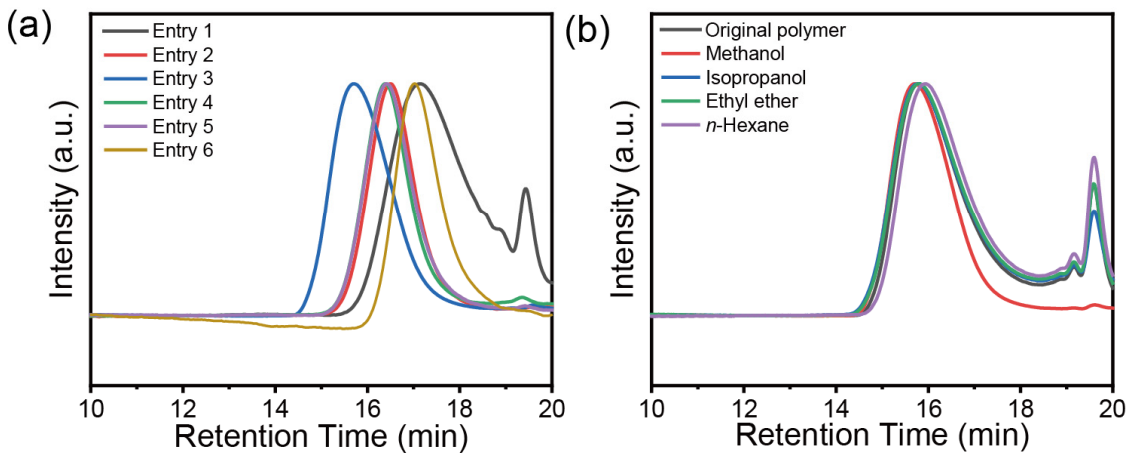


Figure S1. SEC traces for the (a) optimization of polymerization conditions and (b) screening of precipitants.

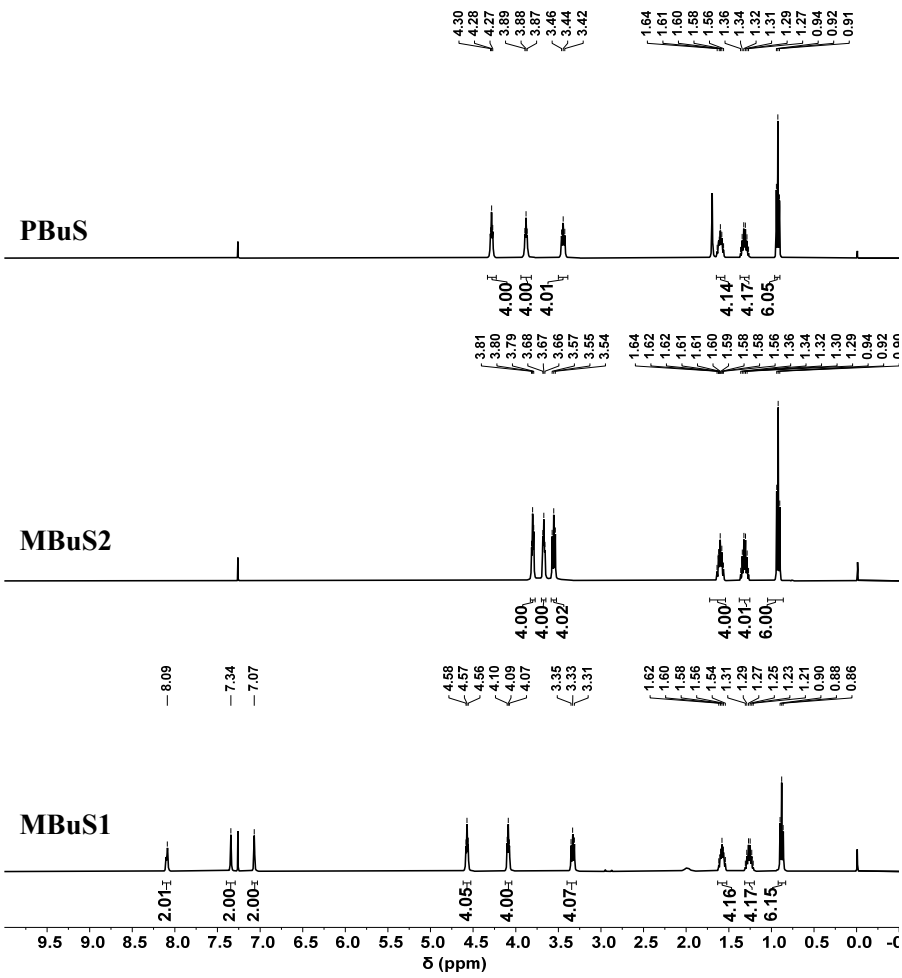


Figure S2. ^{1}H NMR ($CDCl_3$, 400 MHz) spectroscopy of **MBuS1**, **MBuS2** and **PBuS**.

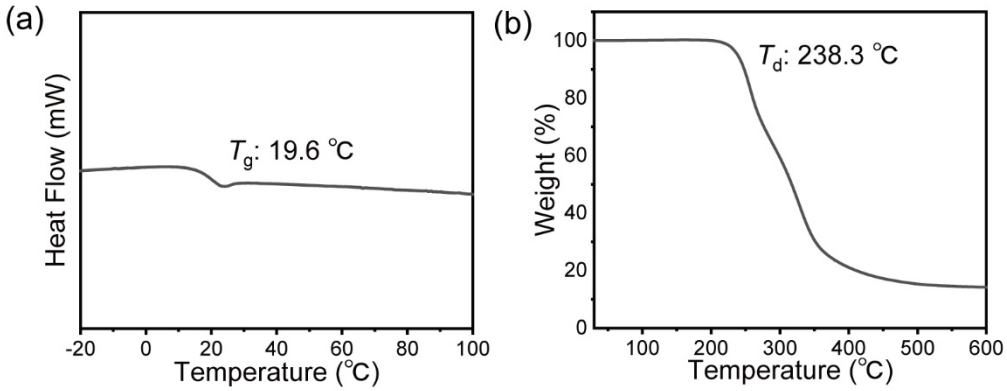


Figure S3. (a) DSC thermogram of **PBuS** from the second heating scan under N_2 at a heating rate of 10 K/min. (b) TGA thermogram of **PBuS**.

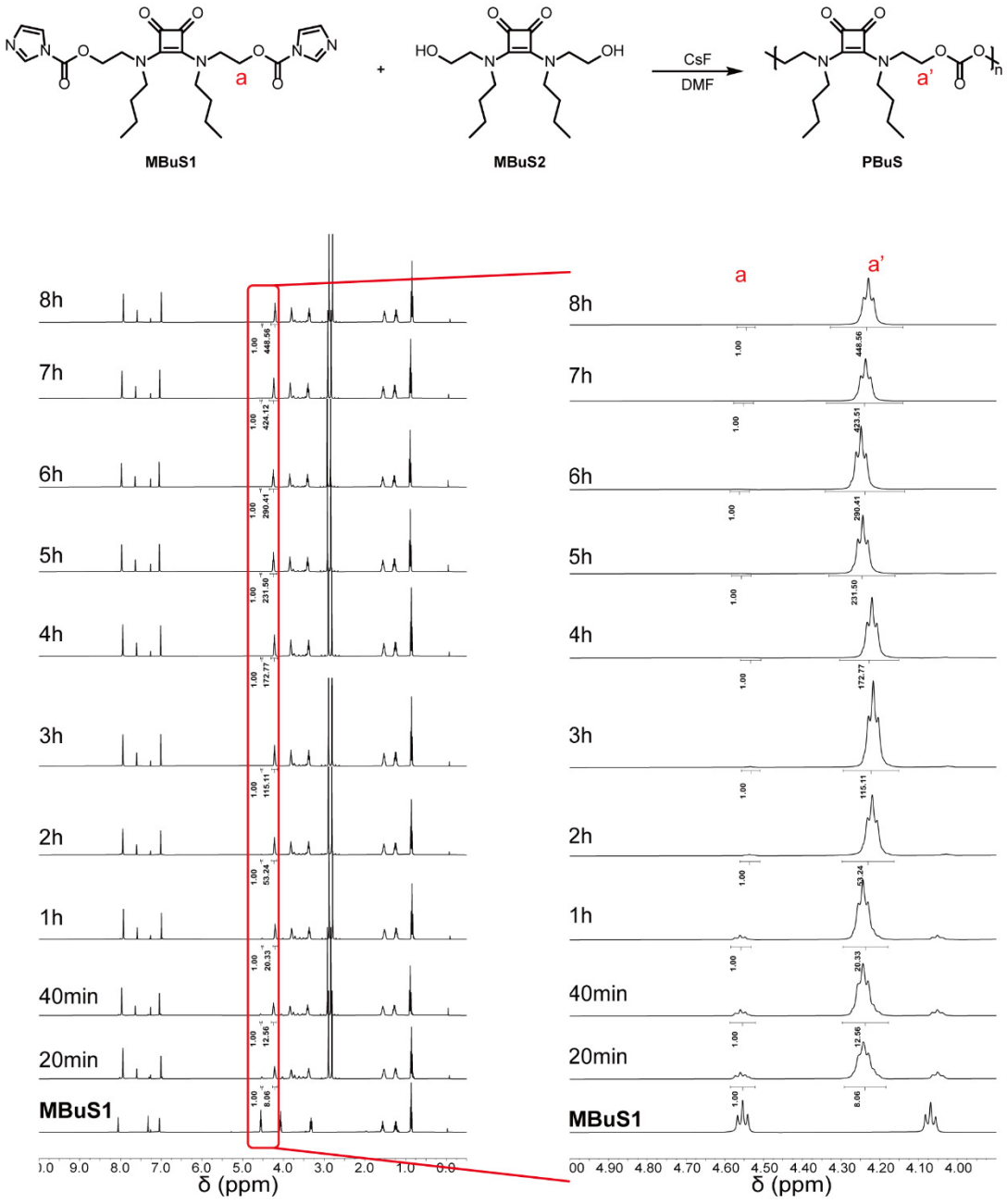


Figure S4. Monitoring of the polymerization kinetics by ^{1}H NMR spectroscopy ($CDCl_3$, 400 MHz).

Table S2. Monitoring of the polymerization kinetics by ^{1}H NMR spectroscopy.

Entry	Time	Conversion (^{1}H-NMR)	M_n （kDa）	$Đ$
1	20 min	88.96%	3.7	1.51
2	40 min	92.63%	4.4	1.59
3	1 h	95.31%	5.2	1.63
4	2 h	98.16%	7.8	1.65
5	3 h	99.14%	8.6	1.76
6	4 h	99.42%	9.2	1.80
7	5 h	99.57%	9.4	1.85
8	6 h	99.66%	9.5	1.87
9	7 h	99.76%	9.6	1.87
10	8 h	99.78%	10.3	1.88

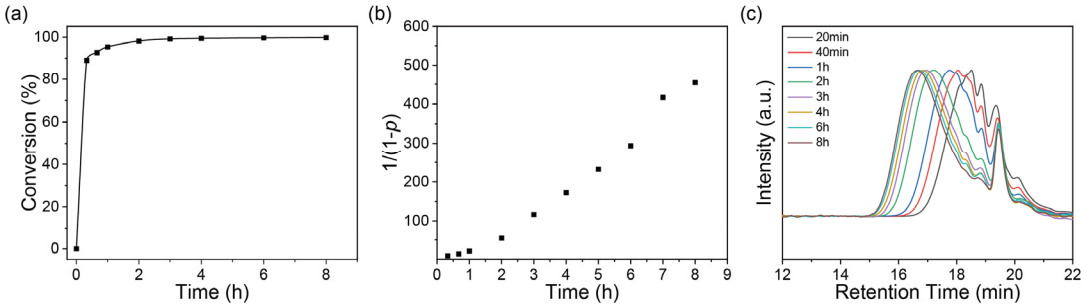


Figure S5. Polymerization kinetics of **PBuS** catalyzed by CsF. (a) Monomer conversion versus time. (b) Second-order kinetic plot of $1/(1-p)$ versus time. (c) Evolution of SEC traces over time.

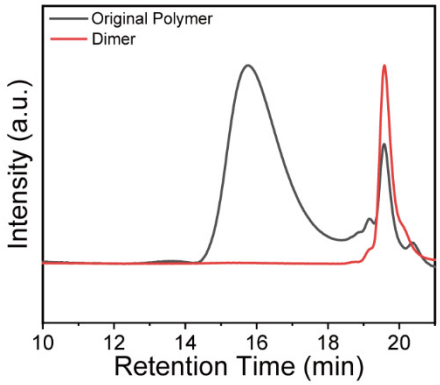


Figure S6. SEC trace of the isolated dimer.

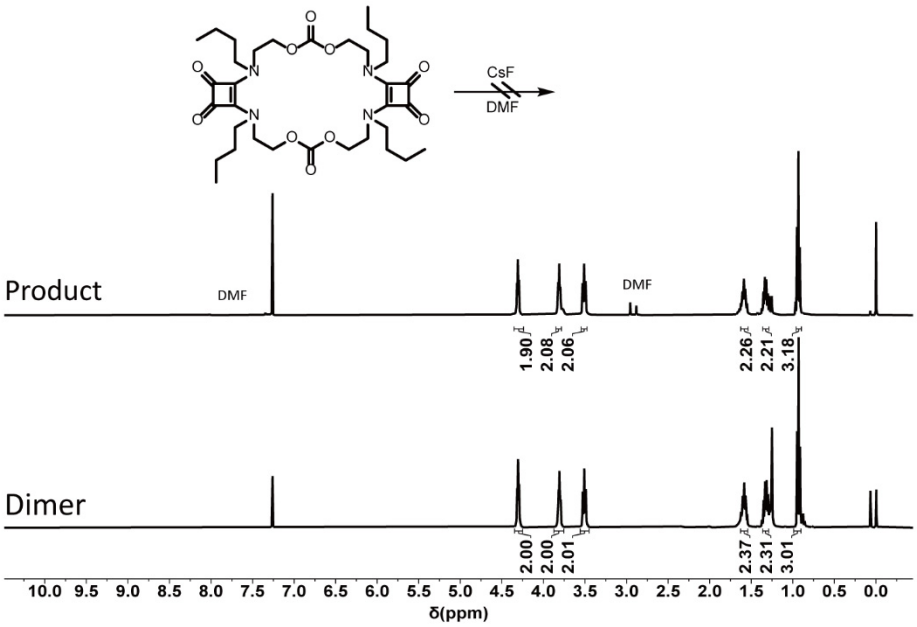


Figure S7. ^{1}H NMR spectrum confirming the CsF-catalyzed repolymerization of the dimer.

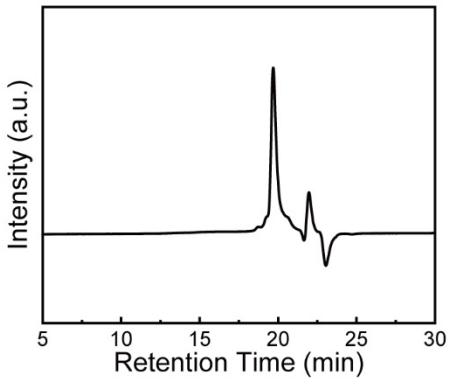


Figure S8. SEC trace of the polymer obtained from the CsF-catalyzed repolymerization of the dimer.

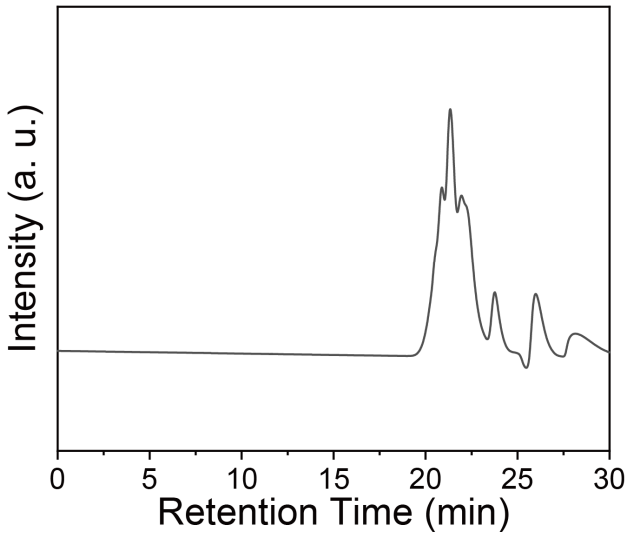


Figure S9. SEC trace of the crude reaction mixture obtained under catalyst-free conditions after 12 h.

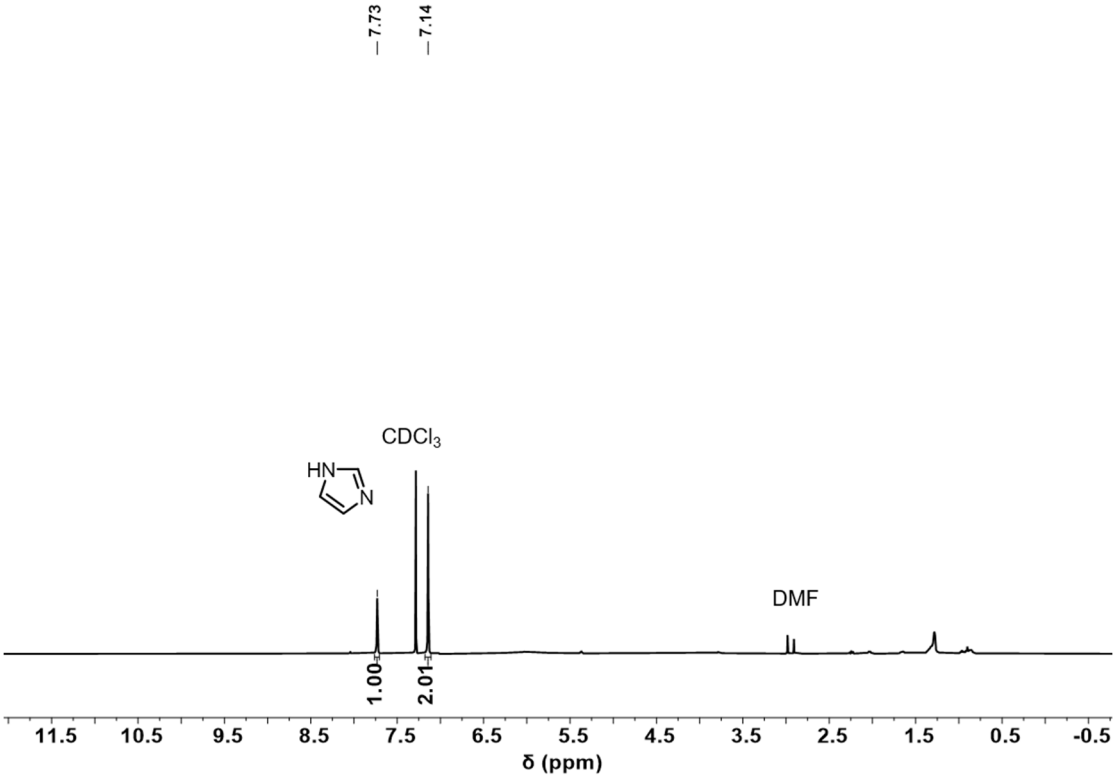


Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the imidazole byproduct recovered from the methanol precipitation supernatant.

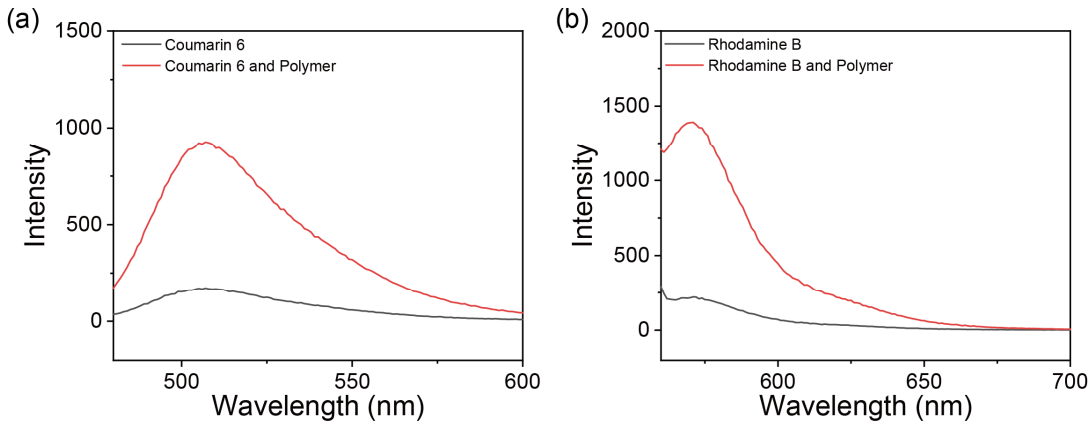


Figure S11. Fluorescence emission spectra of dye loading experiments after dialysis in DMF/methanol (1:3, v/v). (a) Encapsulation of the hydrophobic dye Coumarin 6. (b) Retention of the hydrophilic dye Rhodamine B.

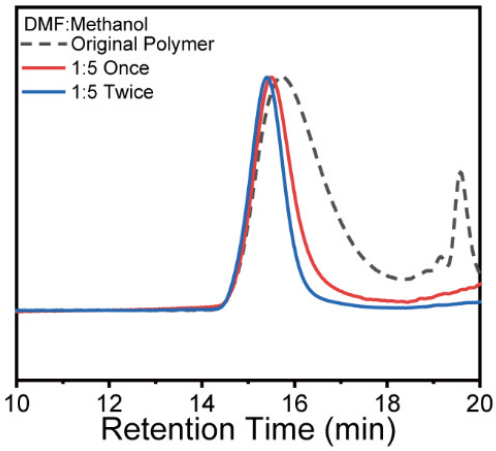


Figure S12. SEC trace of a long chain length fraction of **PBuS** from the twice fractionation with the 1:5 DMF/methanol combination.

Table S3. SEC date of a long chain length fraction of **PBuS** from the twice fractionation with the 1:5 DMF/methanol combination.

Entry	Yield (%)	M_n (kDa)	M_w (kDa)	$Đ$
Original Polymer	/	12.1	17.7	1.45
1:5 Once	52	20.1	22.2	1.10
1:5 Twice	44	22.7	24.4	1.08

Table S4. Zeta potential of **PBuS** assemblies in different solvent mixtures.

Entry	DMF/Methanol	Concentration (mg/mL)	Zeta (mV)
1	1:1	1	-19.65
2	1:3	1	-11.28

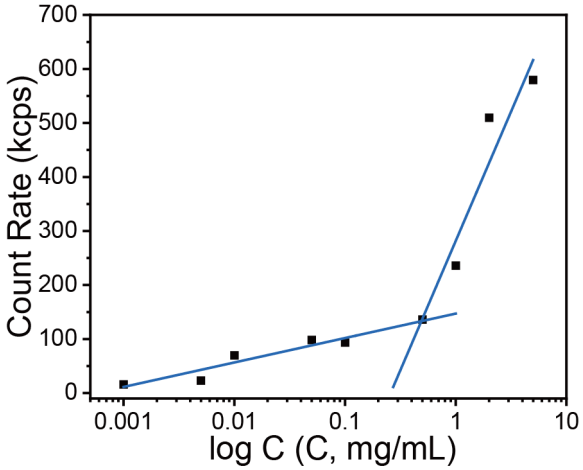


Figure S13. Determination of the Critical Micelle Concentration (CMC) of the fractionated PBuS (M_n/22.7k,$Đ$/1.08) in DMF/methanol (1:3, v/v) using DLS. The CMC is identified as 0.49 mg/mL from the inflection point of the scattering count rate versus polymer concentration plot.

Table S5. Time-dependent evolution of the hydrodynamic diameter (D_h) and polydispersity index (PDI) for the fractionated **PBuS** samples in DMF/methanol (1:3, v/v), determined by DLS.

Entry	Fraction	Time	D_h	PDI
1	M_n/22.7k,$Đ$/1.08	1 min	938.3	0.171
2		12 h	123.7	0.150
3	M_n/12.0k,$Đ$/1.08	1 min	/	/
4		12 h	127.2	0.112

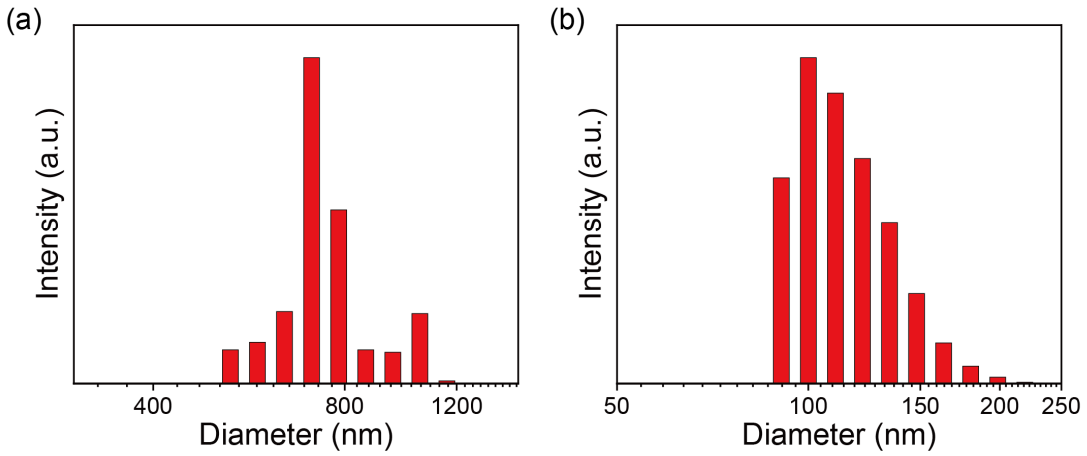


Figure S14. Dynamic light scattering (DLS) size distribution profiles of the long-chain fraction (M_n/22.7k,$Đ$/1.08) in DMF/methanol (1:3, v/v) at (a) 1 min and (b) 12 h.

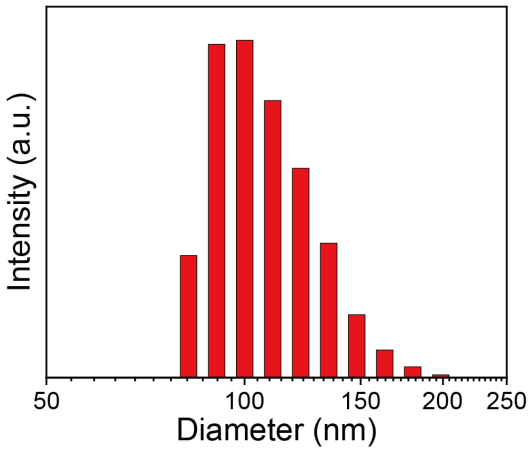


Figure S15. Dynamic light scattering (DLS) size distribution profile of the short-chain fraction (M_n/12.0k, $Đ$/1.08) in DMF/methanol (1:3, v/v) at 12 h.

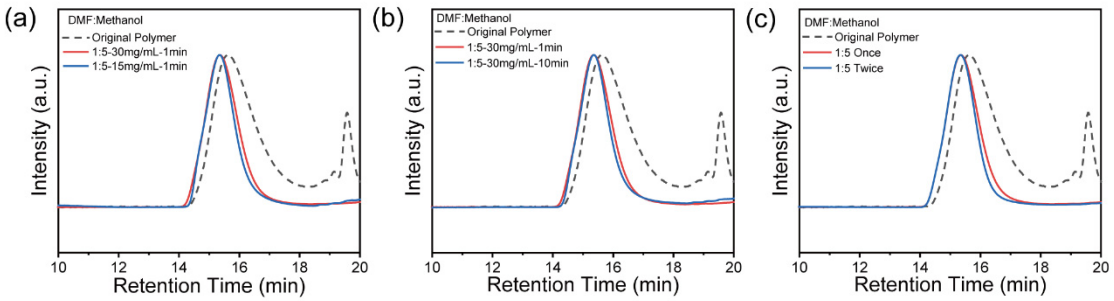


Figure S16. SEC traces of the one-step self-assembly fractionation of **PBuS** under various experimental conditions. (a) polymer concentration, (b) duration of time, and (c) repetition times.

Table S6. Summary of the one-step self-assembly fractionation of **PBuS** under various experimental conditions.

Entry	DMF/methanol (v/v)	C (mg/mL)	Time （min）	Yield (%)	M_n （kDa）	M_w （kDa）	*Đ*
1	1:3	30	1	13	26.3	28.9	1.10
2	1:5	30	1	53	22.4	24.9	1.11
3	1:10	30	1	65	18.6	22.0	1.18
4	1:5	15	1	49	22.2	24.5	1.10
5	1:5	30	10	56	22.3	24.9	1.12
6 [a]	1:5	30	1	50	22.4	24.7	1.10

All data corresponds to the bottom (precipitated) fraction. [a] The precipitate from the first fractionation was redissolved and subjected to a second fractionation under the same conditions.

Table S7. Summary of four-step sequential fractionation.

Entry	DMF/methanol (v/v)	Yield (%)	M_n （kDa）	M_w （kDa）	*Đ*
1	1:3	14	25.2	27.9	1.11
2	1:5	41	18.9	20.6	1.09
3	1:10	9	13.9	15.2	1.09
4	1:100	4	12.1	13.1	1.08

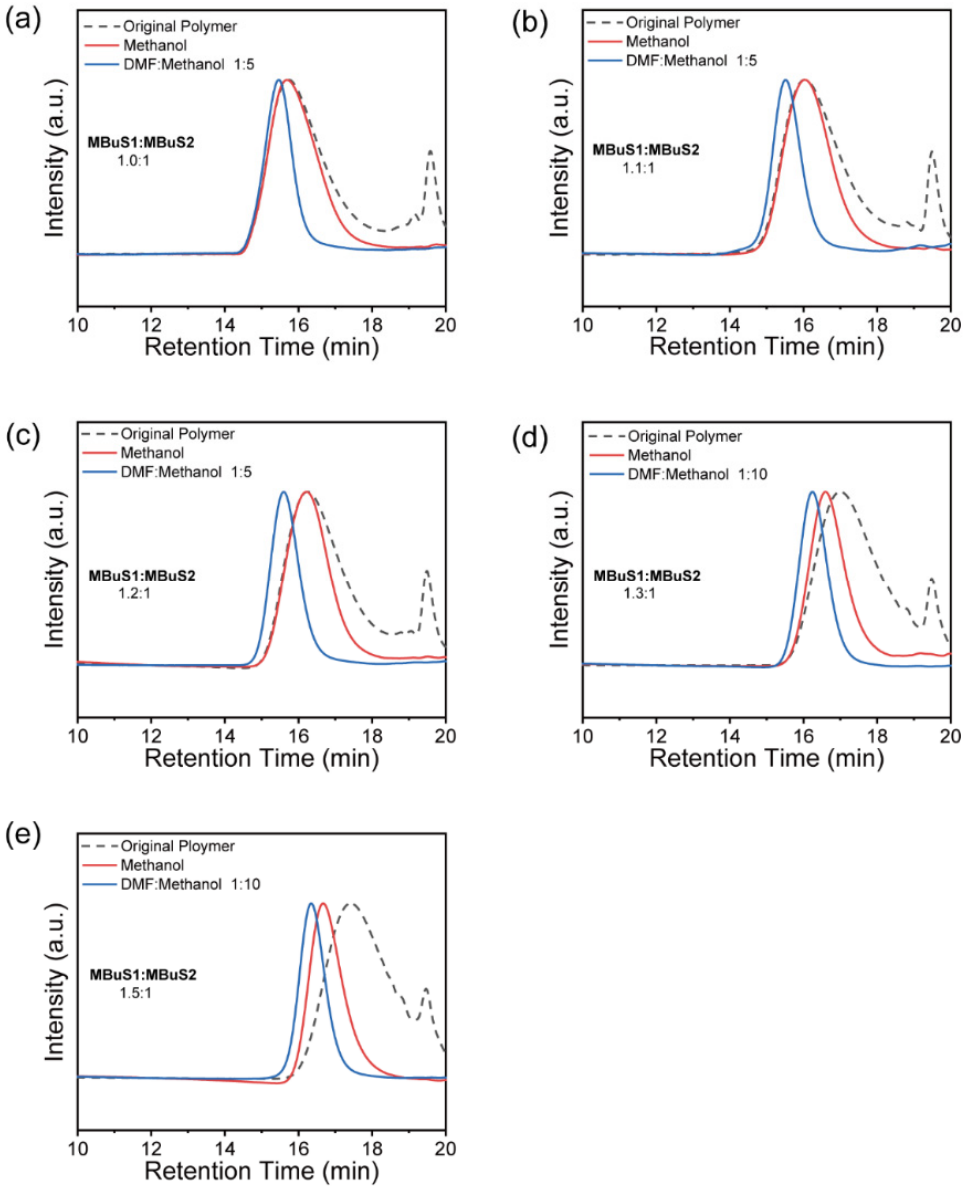


Figure S17. SEC traces for a series of **PBuS** samples, synthesized with varying molar ratios of **MBuS1** to **MBuS2**, after undergoing a crude one-step methanol purification followed by a one-step DMF/methanol fractionation.

Table S8. Summary of a series of **PBuS** samples, synthesized with varying molar ratios of **MBuS1** to **MBuS2**, after undergoing a crude one-step methanol purification followed by a one-step DMF/methanol fractionation.

Entry	MBuS1: MBuS2	Fractionation Condition	Yield (%)	M_n (kDa)	M_w (kDa)	$Đ$
1	1.0:1	Original polymer	/	12.0	17.1	1.43
2		Methanol	79	16.3	20.1	1.23
3		DMF: Methanol 1:5	42	21.8	23.6	1.08
4	1.1:1	Original polymer	/	9.2	13.7	1.48
5		Methanol	76	12.4	15.1	1.22
6		DMF: Methanol 1:5	35	20.4	22.2	1.09
7	1.2:1	Original polymer	/	8.6	11.9	1.39
8		Methanol	65	11.5	13.6	1.18
9		DMF: Methanol 1:5	27	18.9	20.5	1.09
10	1.3:1	Original polymer	/	4.6	7.0	1.53
11		Methanol	56	8.7	9.9	1.14
12		DMF: Methanol 1:10	18	12.0	12.9	1.08
13	1.5:1	Original polymer	/	3.6	5.2	1.48
14		Methanol	36	7.9	8.9	1.13
15		DMF: Methanol 1:10	15	10.9	11.8	1.08

Table S9. SEC data for **PBuS** samples before and after one-step fractionation following degradation for various durations.

Entry	Time (h)	Before Fractionation		DMF: Methanol	After Fractionation	
		M_n (kDa)	$Đ$		M_n (kDa)	$Đ$
1	0	22.7	1.08	/	22.7	1.08
2	2	19.1	1.13	1:10	20.9	1.09
3	4	18.9	1.12	1:10	19.7	1.09
4	6	17.2	1.13	1:10	18.6	1.09
5	12	16.6	1.18	1:10	17.6	1.09
6	24	13.9	1.24	1:10	15.7	1.10
7	36	12.8	1.26	1:10	13.4	1.09

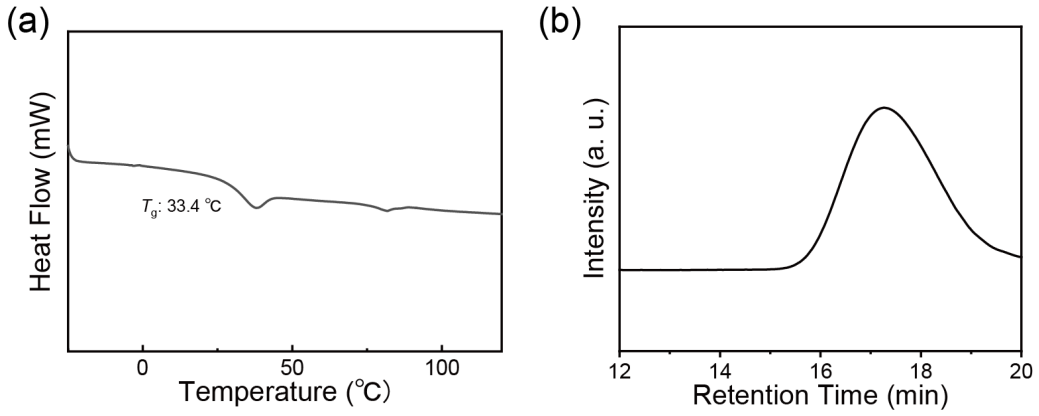


Figure S18. Characterization of the control polymer **PBuT**. (a) DSC thermogram from the second heating scan (10 K/min) under N_2. (b) SEC trace of **PBuT** (M_n/4.0k,$Đ$/1.55).

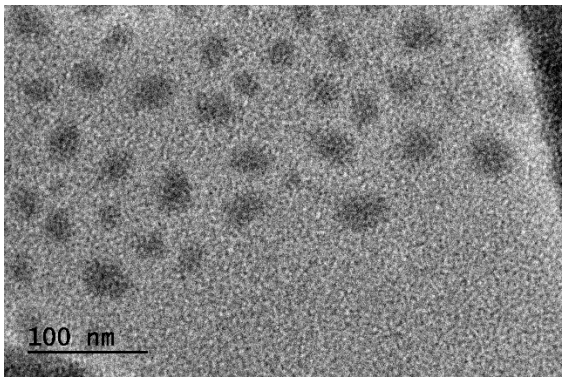


Figure S19. TEM image of **PBuBuS** assemblies prepared from a 1.0 mg/mL solution in a DMF/methanol (1:3, v/v).

Table S10. SEC data and yields for **PBuBuS** and **PBnS** before and after one-step fractionation with a 1:5 DMF/methanol combination.

Entry	Polymer	Fractionation Condition	Yield (%)	M_n （kDa）	M_w （kDa）	$Đ$
1	**PBuBuS**	Original polymer	/	7.2	10.1	1.41
2		DMF: Methanol 1:5	32	11.1	14.1	1.27
3	**PBnS**	Original polymer	/	6.1	8.6	1.40
4		DMF: Methanol 1:5	56	6.4	8.3	1.31

NMR Spectra

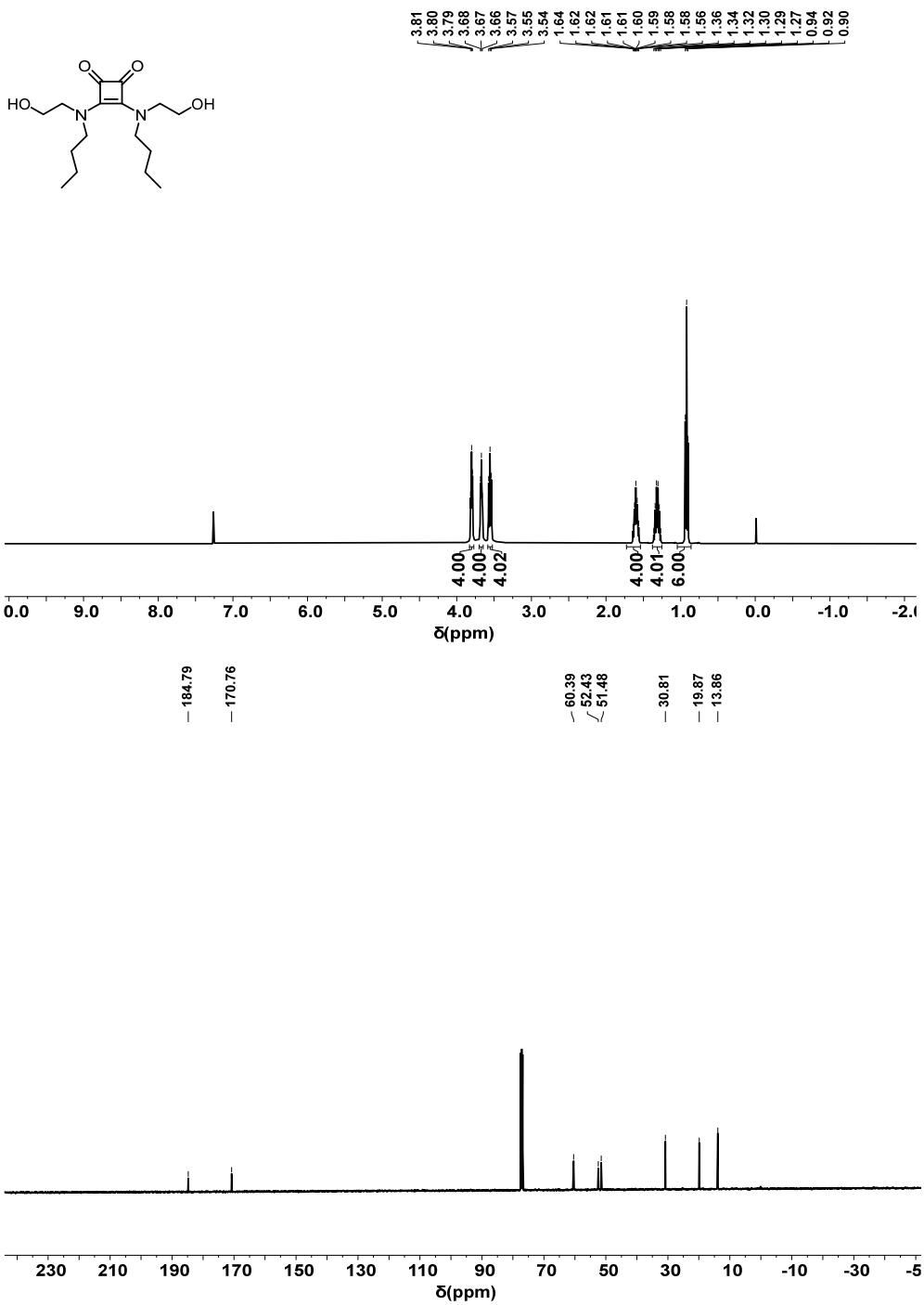


Figure S20. ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 101 MHz) spectra of **MBuS2**.

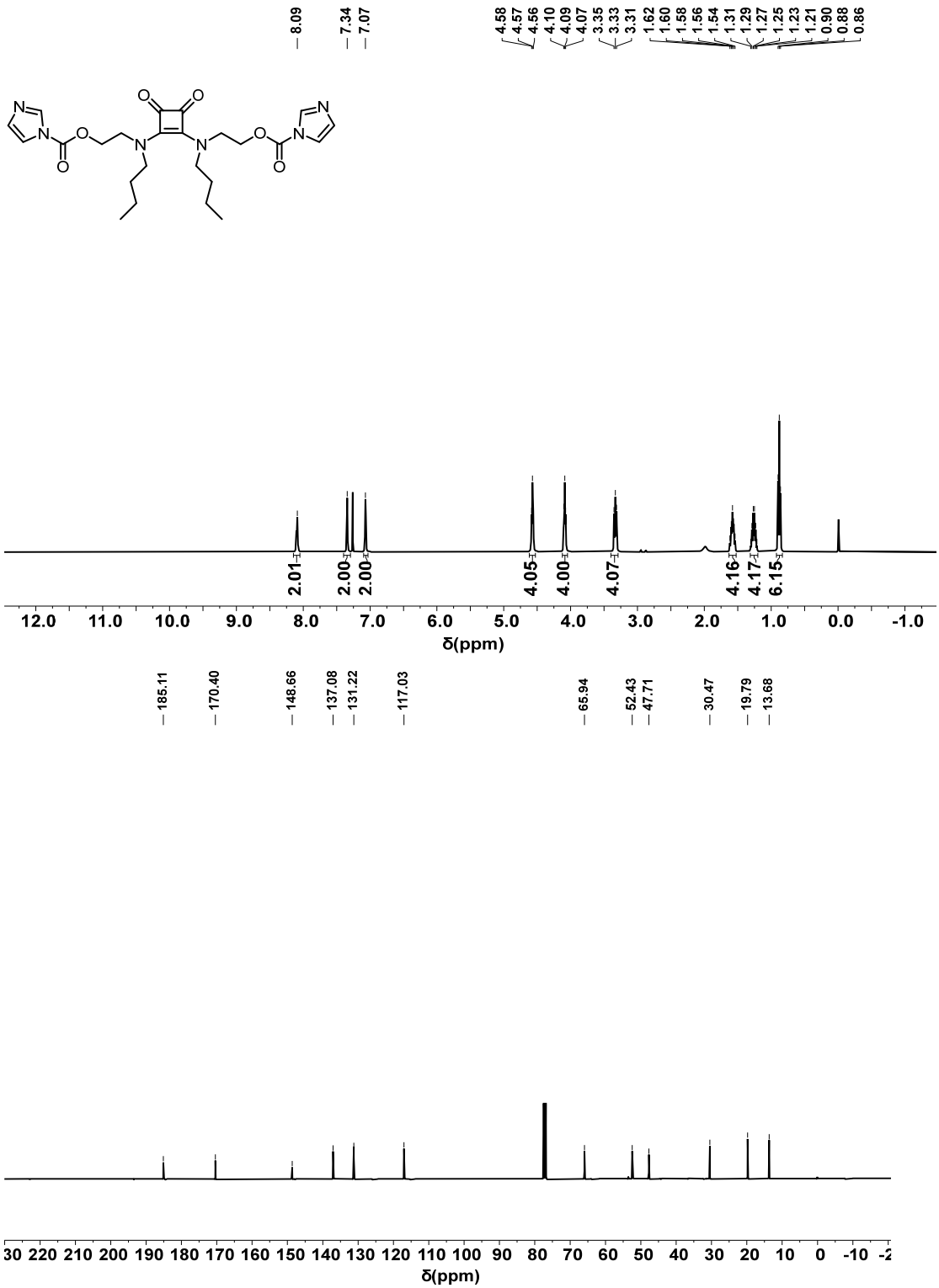


Figure S21. ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 101 MHz) spectra of **MBuS1**.

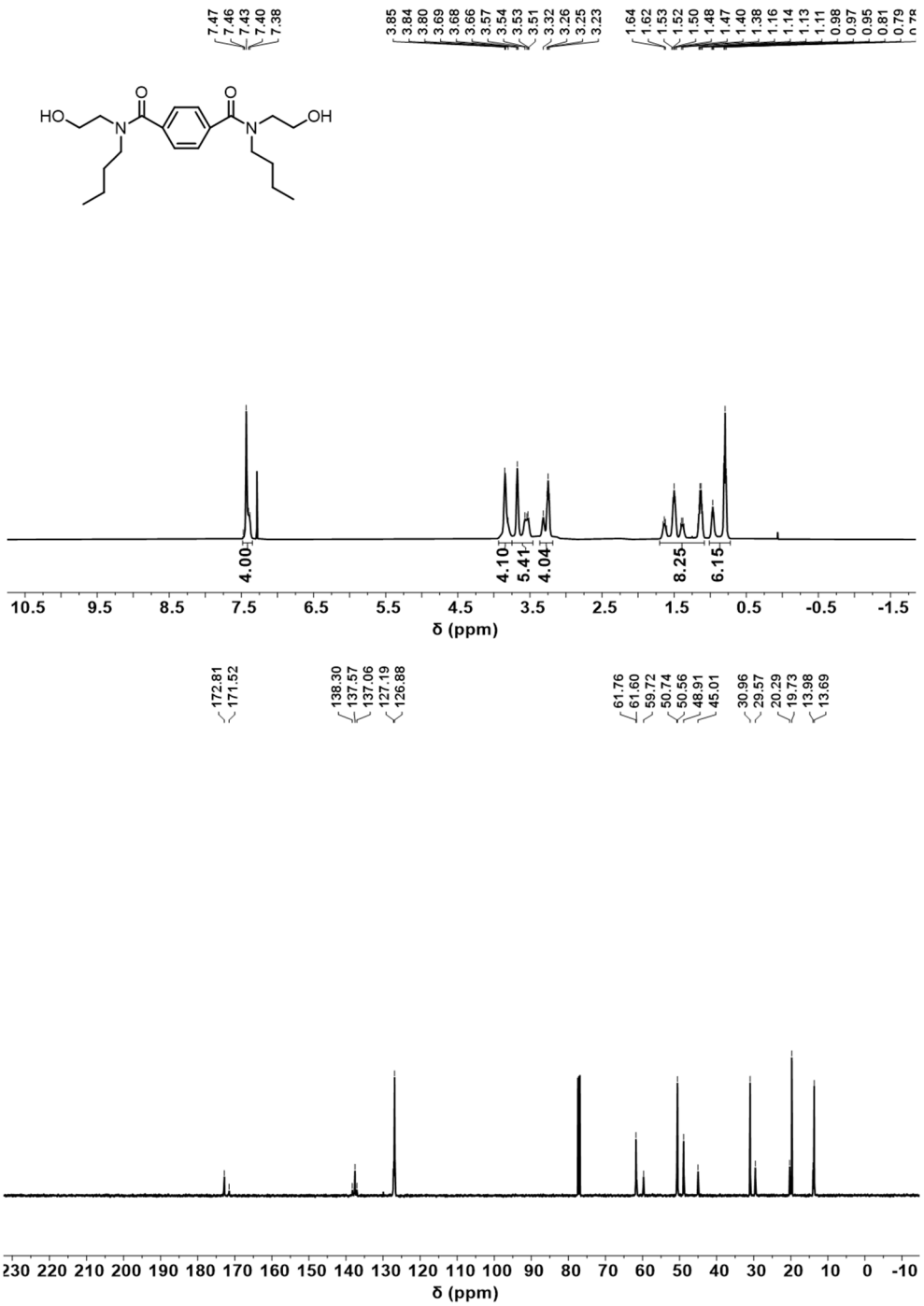


Figure S22. ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 101 MHz) spectra of **MBuT2**.

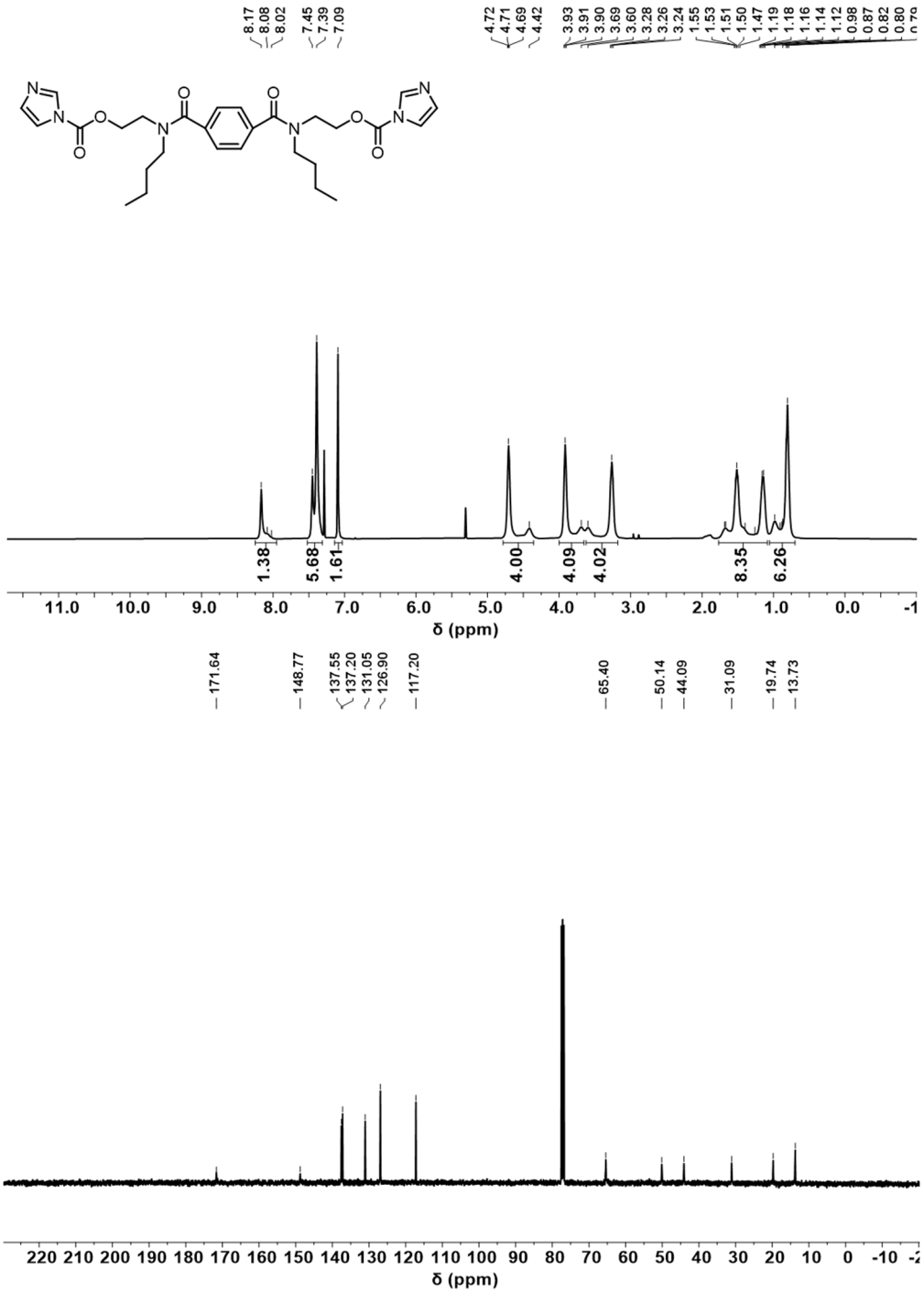


Figure S23. ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 101 MHz) spectra of **MBuT1**.

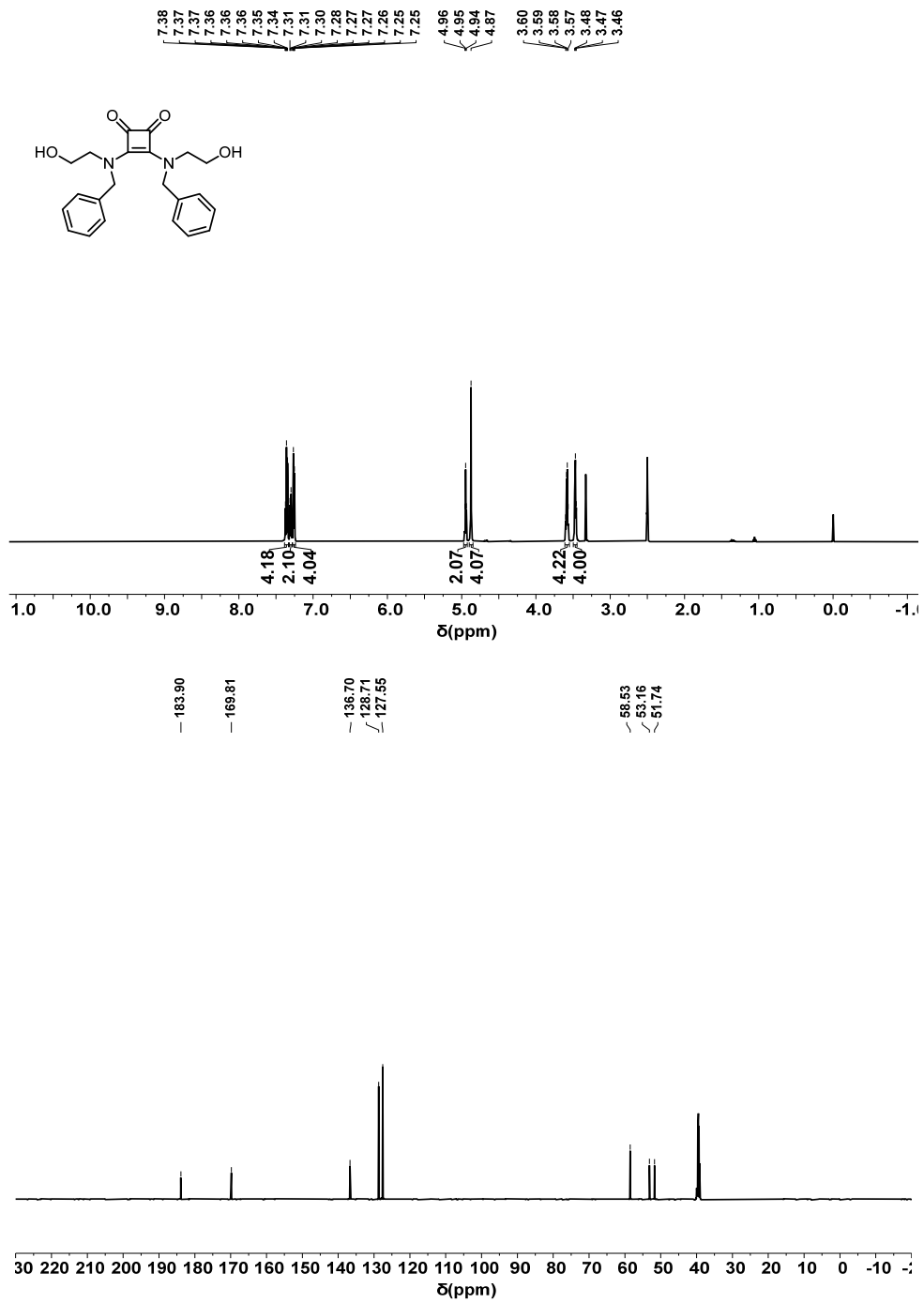


Figure S24. ^{1}H NMR (DMSO-d_6, 500 MHz) and ^{13}C NMR (DMSO-d_6, 126 MHz) spectra of **MBnS2**.

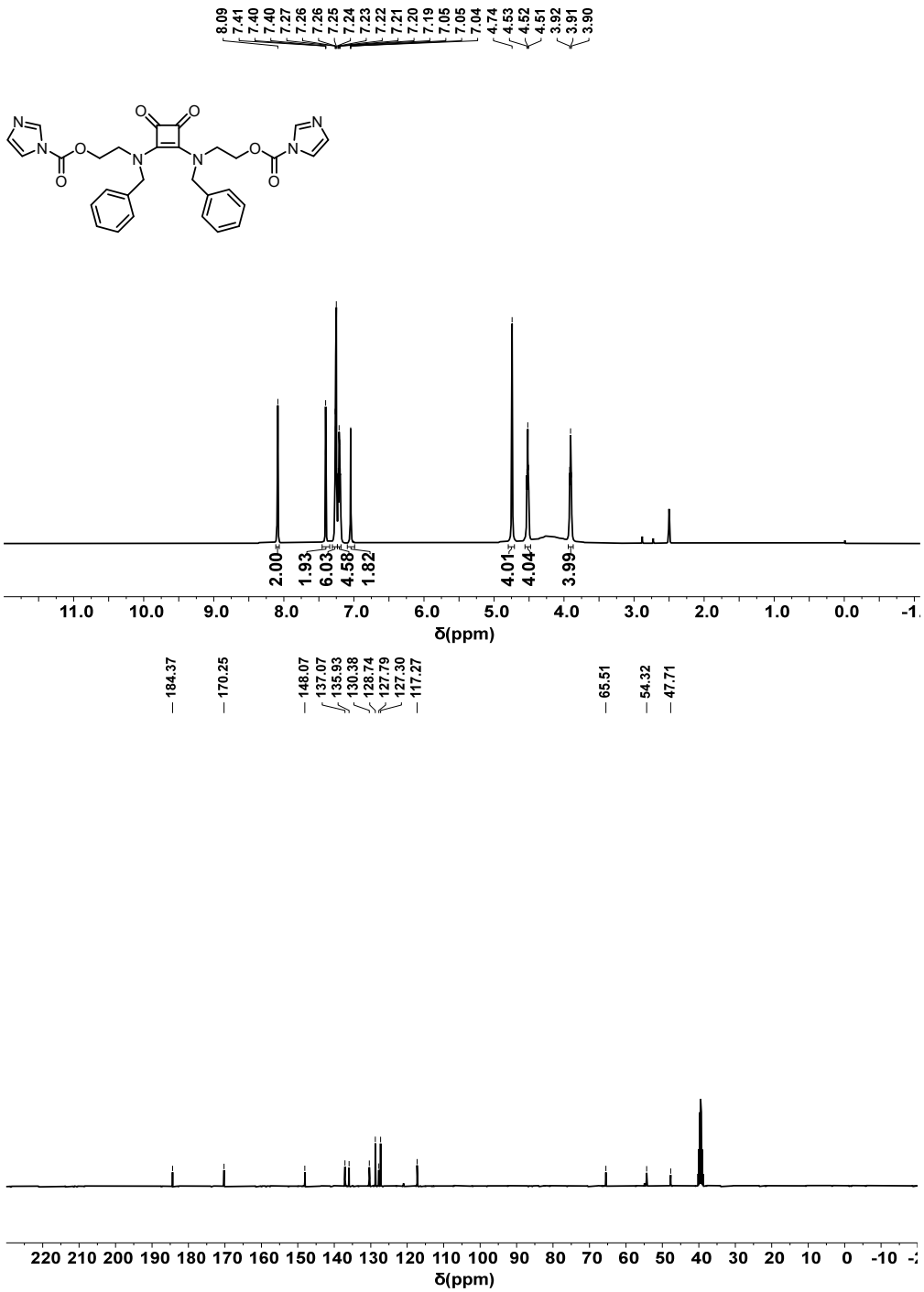


Figure S25. ^{1}H NMR (DMSO-d_6, 400 MHz) and ^{13}C NMR (DMSO-d_6, 101 MHz) spectra of **MBnS1**.

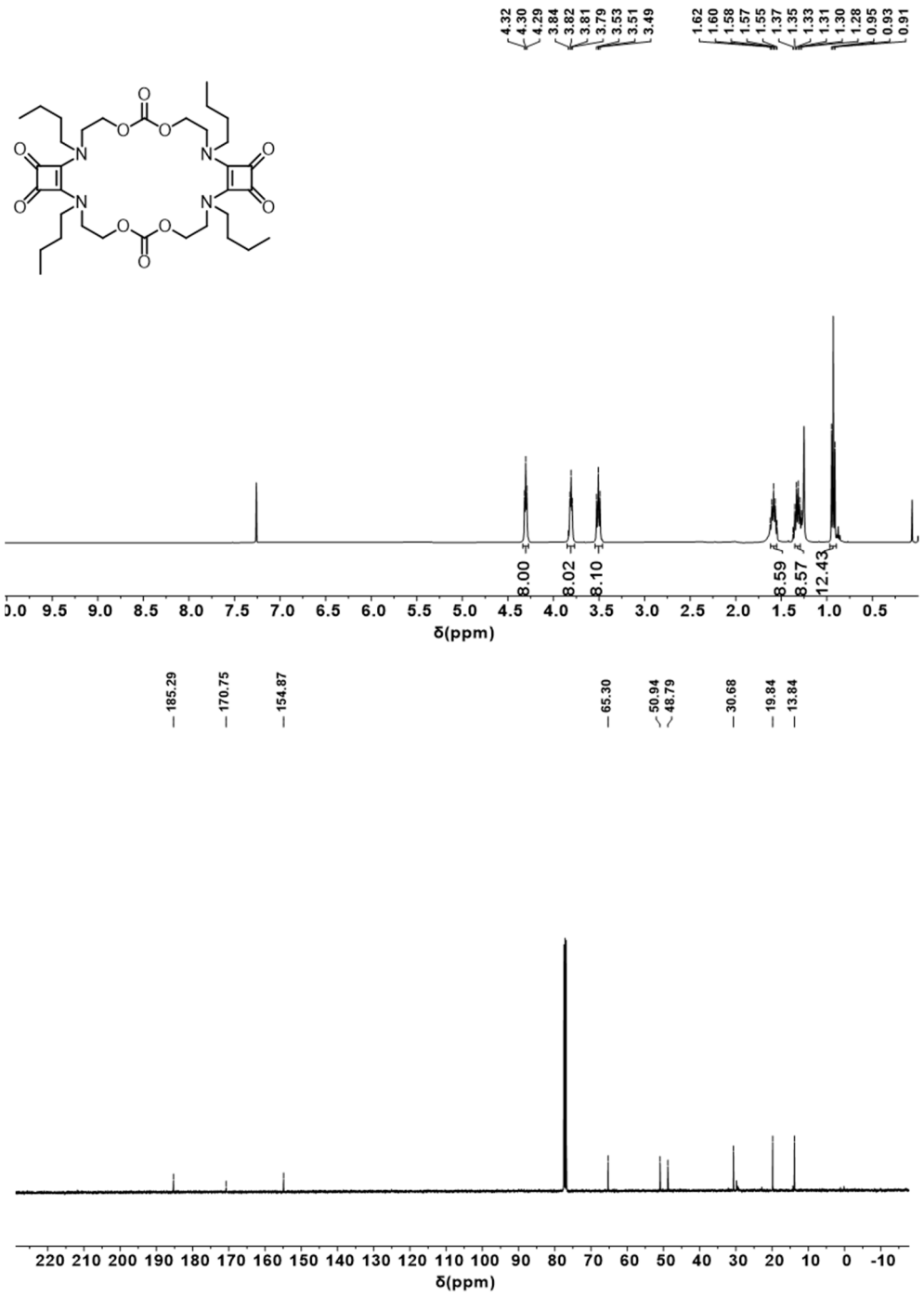


Figure S26. ^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 101 MHz) spectra of Dimer.

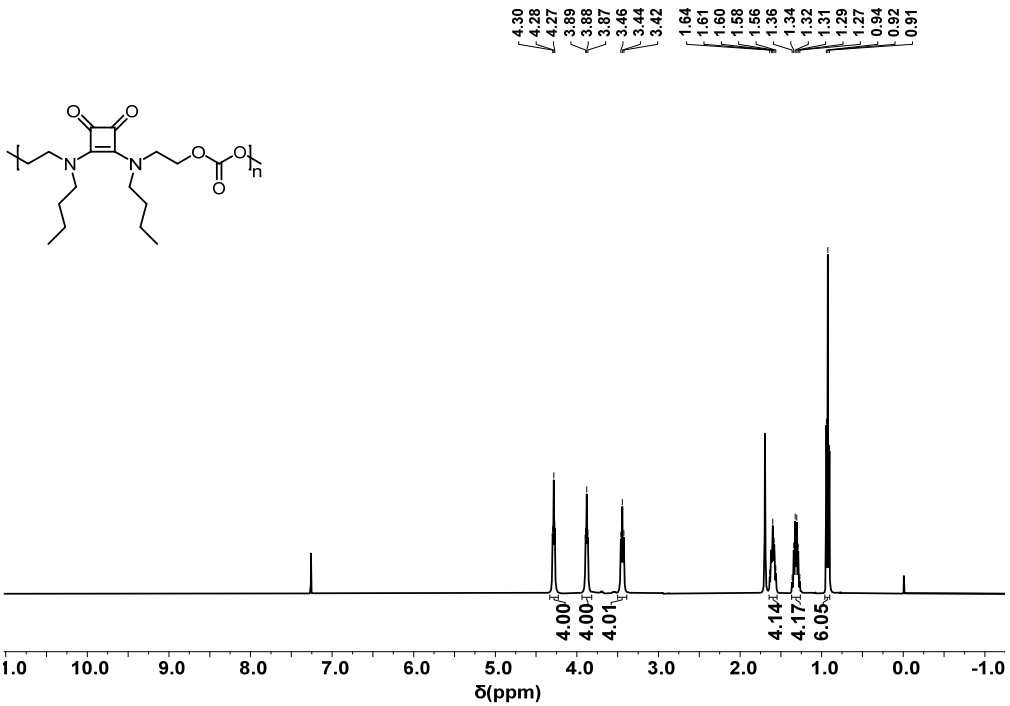


Figure S27. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of **PBuS**.

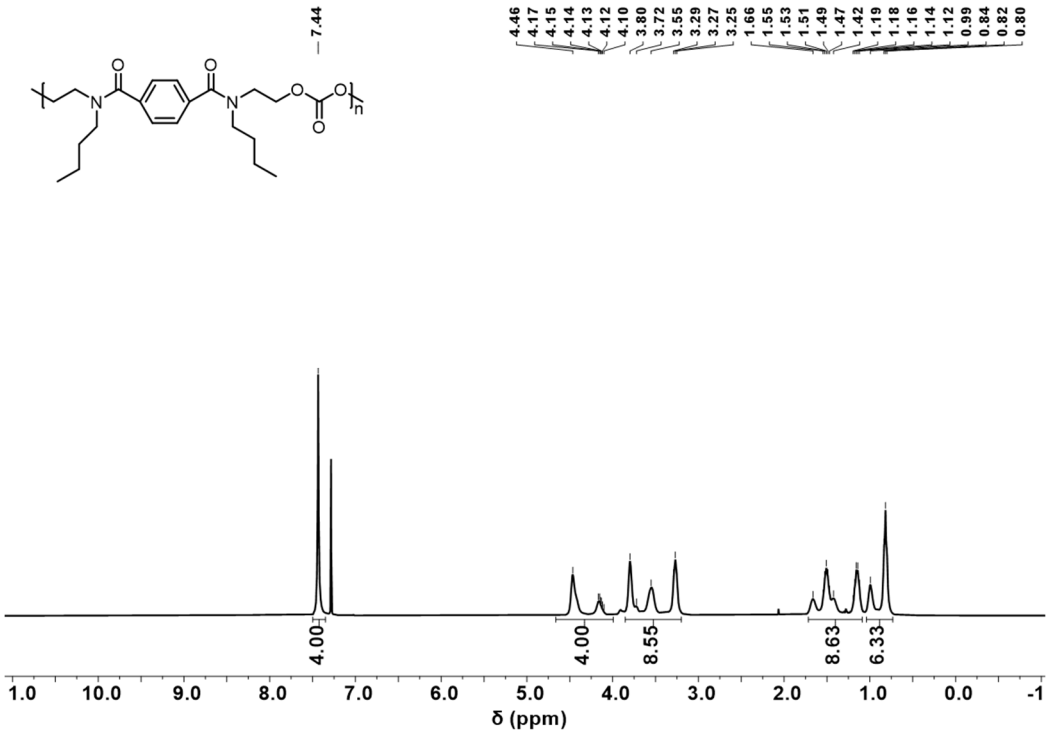


Figure S28. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of **PBuT**.

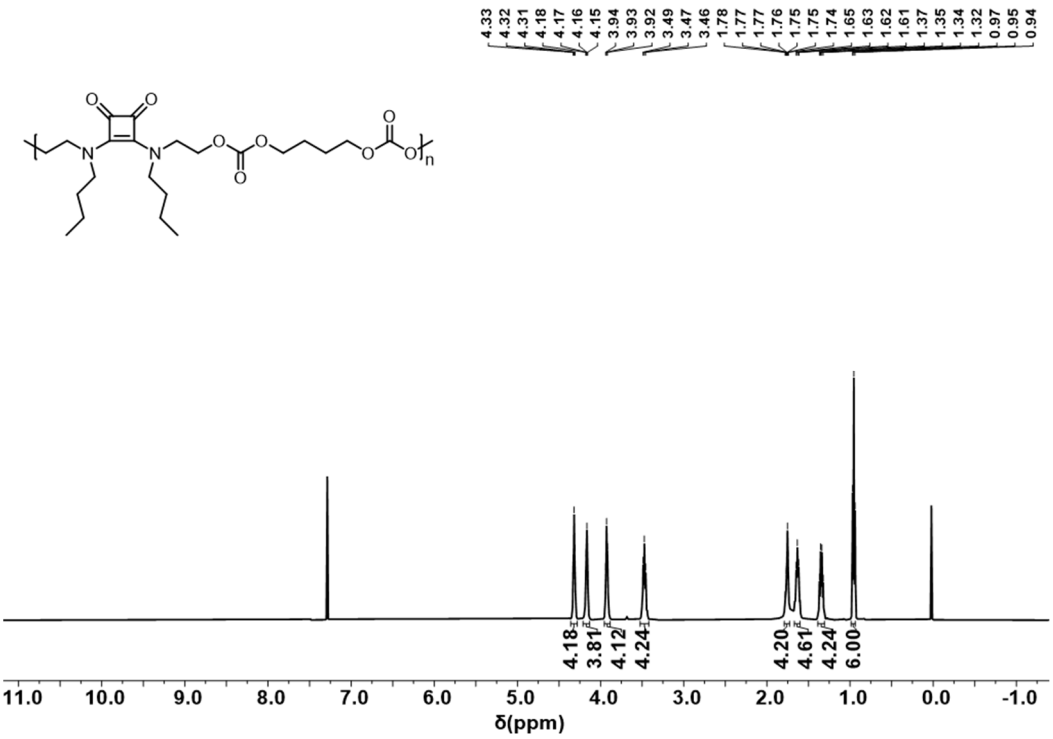


Figure S29. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra of **PBuBuS**.

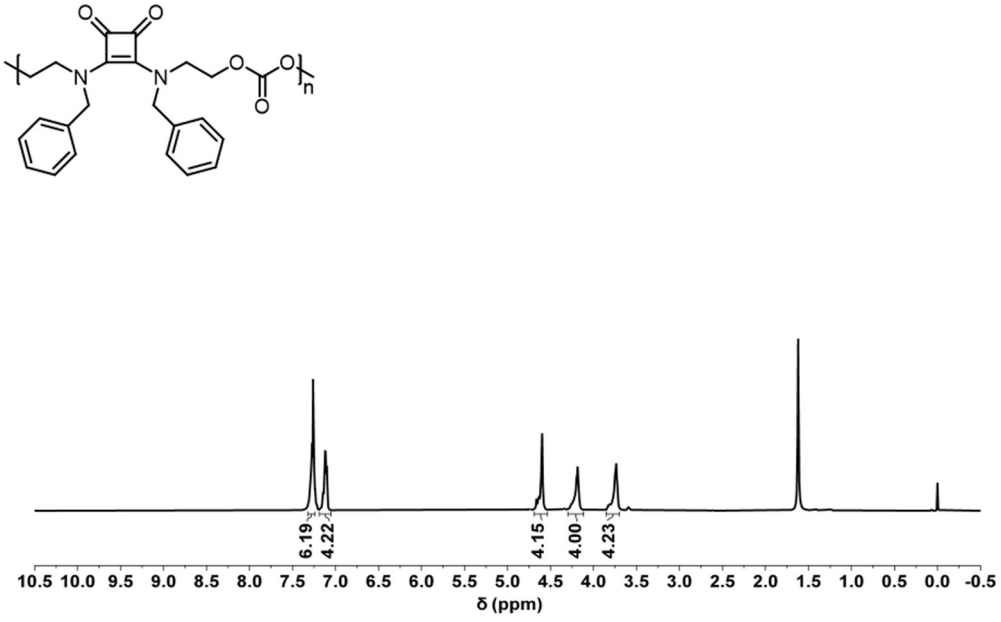


Figure S30. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra of **PBnS**.

References

(1) Li, T.; Wang, B.; Chu, B.; Zhu, J. Molecular Plastics Programming: Squaramide as a Building Block. *Macromolecules* **2024**, *57*, 2306-2316.
(2) Olsson, J. V.; Hult, D.; García-Gallego, S.; Malkoch, M. Fluoride-Promoted Carbonylation Polymerization: A Facile Step-Growth Technique to Polycarbonates. *Chem. Sci.* **2017**, *8*, 4853-4857.