

## Electronic Supplementary Information

# Green Synthesis of Sulfur-Containing Polymers by Carbon Disulfide-based Spontaneous Multicomponent Polymerization

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## Materials and Instruments

All experiments were carried out in a glove box or with the standard Schlenk techniques under dry nitrogen. Monomer 1,1'-(oxybis(4,1-phenylene))bis(3-phenylprop-2-yn-1-one) (**1a**), oxybis(4,1-phenylene)bis(3-phenylpropiolate) (**1b**), 3,3'-(oxybis(4,1-phenylene))bis(1-(thiophen-2-yl)prop-2-yn-1-one) (**1c**), 1,1'-((hexane-1,6-diylbis(oxy))-bis(4,1-phenylene))-bis(*N*-benzylmethanamine) (**2b**) and *N*-ethyl-4-(4-(2-(4-(3-(ethylamino)propoxy)phenyl)-1,2-diphenylvinyl) phenoxy)butan-1-amine (**2c**) were prepared following previously reported methods.<sup>1-7</sup> *N,N*-Diethylethylenediamine (**2a**), ethyl phenylpropiolate (**9**) and CS<sub>2</sub> were purchased from TCI (Shanghai, China) Co. Ltd., and used without further purification. Anhydrous dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMAc) were purchased from Energy Chemical (Shanghai, China) and used directly. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen before use. All other chemicals and reagents were commercially available and used as received without further purification. Water was purified with a Millipore filtration system.

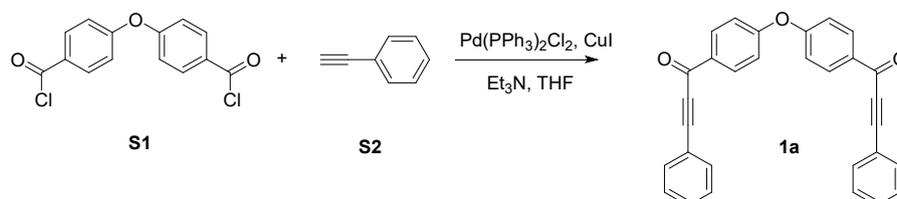
<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a Bruker AVANCE 400 (400 MHz) or AVANCE DRX 500 (500 MHz) NMR spectrometer (Bruker, Germany) using deuterated chloroform (CDCl<sub>3</sub>) or deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) as solvent and tetramethyl silane (TMS,  $\delta = 0$ ) as internal reference. The weight-average molecular weights ( $M_w$ ) and polydispersity indices ( $D = M_w/M_n$ ) of the polymers were measured by Waters 1515 gel permeation chromatography (GPC, Waters Associates, USA) system equipped with a RI detector. DMF containing 0.05 M LiBr was used as the eluent at a flow rate of 1.0 mL min<sup>-1</sup>. A set of linear polymethyl methacrylate (PMMA) standards covering the  $M_w$  range of 10<sup>3</sup>~10<sup>7</sup> were utilized for  $M_w$  and  $D$  calibration. Fourier transform infrared (FT-IR) spectra were measured on a Vector 33 FT-IR (Bruker, Germany) spectrometer (KBr disk). Kinetic data analysis was obtained through in situ IR technique, and the polymerization spectra were recorded on a ReactIR 15 from Mettler Toledo AutoChem. Thermogravimetric analysis (TGA) was carried out on a TG 209 F3 (Netzsch, Germany) at a heating

rate of 20 °C/min in a nitrogen flow. The glass transition temperature ( $T_g$ ) of polymers was characterized by differential scanning calorimetry (DSC 200 F3 Maia, NETZSCH, Germany) in nitrogen flow at a heating rate of 10 °C/min. The light transmittance and absorption were measured by UV-2600 spectrophotometer (Shimadzu, Japan). The polymer film samples were prepared by spinning the solution of polymers (50 mg/mL in dichlorobenzene) on quartz. Refractive index ( $n$ ) curve was measured in air in the spectral range of 400-1700 nm by a V-VASE rotating analyzer ellipsometer (J. A. Woolam, USA). The polymer film samples were prepared by spinning the solution of polymers (50 mg/mL in dichlorobenzene) on plasma treated single-crystal silicon. The static water contact angle of polymer film on silica was measured by a sessile drop method using JC2000D1 (POWEREACH, Shanghai, China). The stretch curve of polymers was tested by electronic universal testing machine (Shimadzu AGS-X-50N, Japan). Confocal laser scanning microscopy (CLSM) (LSM 710, Zeiss, Germany) and scanning electron microscope (SEM) (Regulus8100, Hitachi, Japan) were used for morphological observation. The thickness of ultrathin membrane on silica were determined by a Innova atomic force microscopy (AFM) (Bruker, Germany).

## Preparation of Monomer 1

### Preparation of monomer 1a

Monomer **1a** was synthesized according to the reported procedures.<sup>1</sup> The synthetic route is shown in Scheme S1.



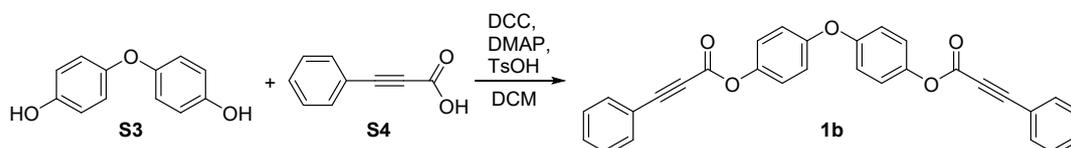
**Scheme S1.** Synthetic routes to monomer **1a**.

**1,1'-(Oxybis(4,1-phenylene))bis(3-phenylprop-2-yn-1-one) (1a):** Pd ( $\text{PPh}_3$ )<sub>2</sub>Cl<sub>2</sub> (140 mg, 0.2 mmol), CuI (114 mg, 0.6 mmol), **S1** (2.95 g, 10 mmol), and distilled THF (100 mL) were added to a

250 mL two-necked round-bottom flask under nitrogen. Triethylamine (1.39 mL, 10 mmol) and phenylacetylene (**S2**, 2.84 mL, 25 mmol) were slowly injected into the solution. The mixture was stirred at room temperature for 6 h, and the formed precipitates were removed by filtration. After concentrated by a rotary evaporator under reduced pressure, the crude product was purified by a silica gel column chromatography using petroleum ether (PE)/ethyl acetate (EA) (10:1, v/v) as eluent. Off-white solid of **1a** was obtained in 77 % yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (TMS, ppm): 8.33 – 8.22 (m, 4H), 7.87 – 7.77 (m, 4H), 7.67 – 7.58 (m, 2H), 7.58 – 7.49 (m, 4H), 7.37 – 7.30 (m, 4H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (TMS, ppm): 176.08, 161.06, 133.63, 132.91, 132.52, 132.01, 129.61, 119.80, 119.43, 93.32, 86.86. FT-IR (KBr disk),  $\nu$  (cm<sup>-1</sup>): 3061, 2195, 1628, 1582, 1493, 1418, 1307, 1289, 1242, 1207, 1156, 1025, 994, 877, 844, 756, 684, 609, 539, 498.

#### Preparation of monomer **1b**

Monomer **1b** was synthesized according to the reported procedures,<sup>2,3</sup> and the synthetic route is shown in Scheme S2.



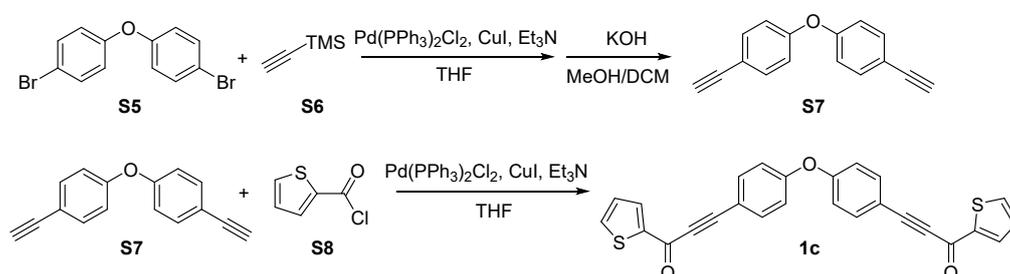
**Scheme S2.** Synthetic routes to monomer **1b**.

**Oxybis(4,1-phenylene) bis(3-phenylpropiolate) (1b):** **S3** (10 mmol, 2.02 g), *N,N*-dicyclohexylcarbodiimide (DCC, 30 mmol, 6.19 g), 4-dimethylaminopyridine (DMAP, 4 mmol, 489 mg) and 4-methylbenzenesulfonic acid (TsOH, 4 mmol, 689 mg) were added into a 250 mL two-necked round bottom flask. The flask was evacuated under vacuum and flushed with dry nitrogen for three times and 80 mL dichloromethane (DCM) was added. Then **S4** (30 mmol, 4.38 g) in 20 mL DCM was injected into the system dropwise. After finishing the addition, the mixture was stirred at room temperature overnight. Afterward, the solvent was evaporated and the crude product was purified by a silica gel column chromatography using PE/EA (10:1 v/v) as eluent. White solid of **1b** was obtained in 98% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.64 (d, *J* = 7.2 Hz, 4H),

7.49 (t,  $J = 7.5$  Hz, 2H), 7.41 (t,  $J = 7.6$  Hz, 4H), 7.17 (d,  $J = 8.9$  Hz, 4H), 7.05 (d,  $J = 9.0$  Hz, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 155.04, 152.45, 145.70, 133.20, 131.10, 128.70, 122.78, 119.70, 119.21, 88.90, 80.16. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3106, 3065, 2232, 1721, 1594, 1491, 1444, 1284, 1250, 1183, 1146, 1099, 1006, 947, 925, 857, 760, 734, 687, 614, 587, 534, 512.

### Preparation of monomer **1c**

Monomer **1c** was synthesized in similar procedure as **1a**.<sup>4</sup> The synthetic routes are shown in Scheme S3.



**Scheme S3.** Synthetic routes to monomer **1c**.

**4,4'-Oxybis(ethynylbenzene) (S7):**  $\text{PdCl}_2(\text{PPh}_3)_2$  (701.9 mg, 1 mmol),  $\text{CuI}$  (380.9 mg, 2 mmol), **S5** (3.28 g, 10 mmol) were added into a 250 mL two-necked round bottom flask, and dissolved with 60 mL triethylamine and 10 mL distilled THF under nitrogen. After addition of trimethylsilylacetylene (**S6**, 5.65 mL, 40 mmol), the mixture was refluxed for 12 h. After evaporating the solvent and purified by silica gel column chromatography using petroleum as eluent, white solid of TMS protected product was obtained. The above solid was dissolved together with  $\text{KOH}$  (3.366 g, 60 mmol) in  $\text{DCM}$  and methanol, and stirred at room temperature for 4 h. A white solid of **S7** can be obtained after purification by silica gel column chromatography using PE as eluent (yield 83%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.47 (d,  $J = 8.8$  Hz, 4H), 6.95 (d,  $J = 8.8$  Hz, 4H), 3.05 (s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 157.04, 133.90, 118.89, 117.37, 83.04.

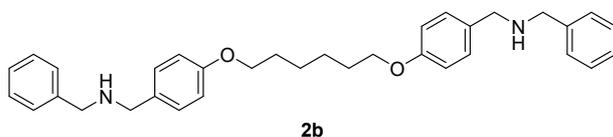
**3,3'-(Oxybis(4,1-phenylene))bis(1-(thiophen-2-yl)prop-2-yn-1-one) (1c):**  $\text{PdCl}_2(\text{PPh}_3)_2$  (7 mg, 0.01 mmol),  $\text{CuI}$  (3.8 mg, 0.02 mmol), **S7** (109 mg, 0.5 mmol), and distilled THF (10 mL) were added into a 50 mL two-necked round-bottom flask under nitrogen. Then triethylamine (173  $\mu\text{L}$ ,

1.25 mmol) and **S8** (134  $\mu$ L, 1.25 mmol) was injected into the solution. The mixture was stirred at room temperature for 6 h. After reaction, the precipitates were removed by filtration, and the solution was concentrated by a rotary evaporator under reduced pressure to get the crude product, which can be purified by a silica gel column chromatography using PE/EA (10:1, v/v) as eluent. 177 mg off-white solid of was obtained in 81% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 8.01 (m, 2H), 7.74 (m, 2H), 7.69 (d,  $J = 8.8$  Hz, 4H), 7.20 (m, 2H), 7.08 (d,  $J = 8.8$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 169.70, 158.36, 144.94, 135.26, 135.25, 134.97, 128.37, 119.36, 115.45, 91.22, 86.70. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3054, 2937, 2870, 2813, 1604, 1572, 1507, 1473, 1446, 1386, 1586, 1243, 1176, 1132, 1113, 1052, 1028, 972, 820, 743, 700, 612, 573, 512.

## Preparation of Monomers 2

### Preparation of monomer **2b**

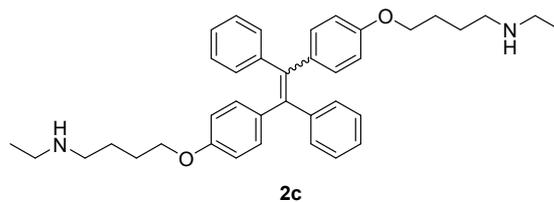
Monomer **2b** was synthesized according to the method reported before.<sup>5,6</sup>



**1,1'-((Hexane-1,6-diylbis(oxy))-bis(4,1-phenylene))-bis(*N*-benzylmethanamine) (**2b**):** White solid in 87% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.33 (m, 8H), 7.24 (m, 6H), 6.86 (d,  $J = 8.7$  Hz, 4H), 3.96 (t,  $J = 6.8$  Hz, 4H), 3.79 (s, 4H), 3.74 (s, 4H), 1.81 (m, 4H), 1.61 (s, 2H), 1.54 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 158.14, 140.39, 132.30, 129.30, 128.37, 128.15, 126.89, 114.39, 67.84, 53.06, 52.58, 29.25, 25.89. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3341, 3058, 3026, 2938, 2868, 2821, 1609, 1581, 1510, 1474, 1448, 1289, 1250, 1165, 1105, 1025, 824, 730, 697, 609, 513.

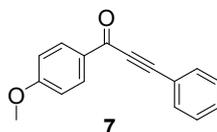
### Preparation of monomer **2c**

Monomer **2c** was synthesized according to the reported method.<sup>5,7</sup>



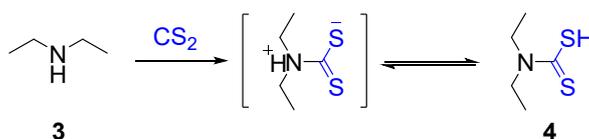
**N-ethyl-4-(4-(2-(4-(3-(ethylamino)propoxy)phenyl)-1,2-diphenylvinyl)phenoxy)butan-1-amine (2c):** Yellow-green viscous product in 89% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.13 – 6.97 (m, 10H), 6.96 – 6.82 (m, 4H), 6.66 – 6.54 (m, 4H), 3.87 (t,  $J = 6.3$  Hz, 4H), 2.76 – 2.60 (m, 8H), 1.84 – 1.72 (m, 4H), 1.66 (m, 4H), 1.13 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 157.33, 144.29, 139.59, 136.25, 132.49, 131.35, 127.62, 126.11, 113.48, 67.40, 49.25, 43.96, 27.08, 26.40, 26.39, 14.93, 14.92. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3054, 2937, 2870, 2813, 1604, 1572, 1507, 1473, 1446, 1386, 1586, 1243, 1176, 1132, 1113, 1052, 1028, 972, 820, 743, 700, 612, 573, 512.

### Model Reactions



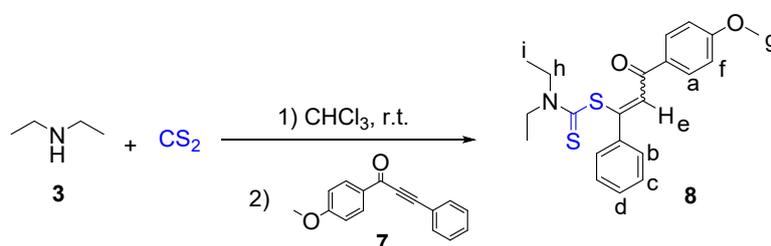
**1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one (7):** compound **7** was synthesized in a similar procedure as **1a** to obtain white solid in 86% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 8.26 – 8.16 (m, 2H), 7.72 – 7.64 (m, 2H), 7.52 – 7.37 (m, 3H), 7.04 – 6.94 (m, 2H), 3.90 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 176.71, 164.51, 132.98, 132.01, 130.60, 130.36, 128.67, 120.40, 113.91, 92.34, 86.95, 55.62.

In order to verify the structure of the intermediate produced by secondary amines with  $\text{CS}_2$ , diethyldithiocarbamic acid (**4**) was prepared according to the route shown in Scheme S4:



**Scheme S4.** Synthetic route to intermediate **4**.

After slowly mixed diethylamine (515  $\mu\text{L}$ , 5 mmol) with excess  $\text{CS}_2$  (604  $\mu\text{L}$ , 10 mmol), the system began to release heat and finished after 10 min. By removing the remaining  $\text{CS}_2$  with rotary evaporation, the colorless crystal of compound **4** was obtained equivalently. The compound was unstable and needed to be stored at low temperature under nitrogen atmosphere.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 8.57 (s, 1H), 4.10 (q,  $J = 7.0$  Hz, 2H), 3.16 (q,  $J = 7.3$  Hz, 2H), 1.38 (t,  $J = 7.3$  Hz, 3H), 1.26 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 208.68, 47.88, 40.79, 12.39, 11.10.

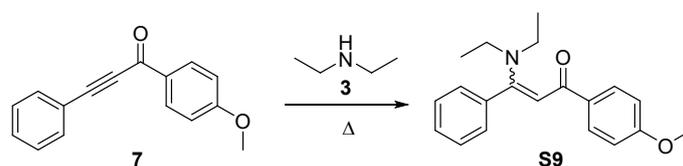


**Scheme S5.** Synthetic route to model compound **8**.

**3-(4-Methoxyphenyl)-3-oxo-1-phenylprop-1-en-1-yl diethylthiocarbamic acid (8):** Model compound **8** was prepared in a similar procedure as the literature (Scheme S5).<sup>8</sup> Diethylamine (15.5  $\mu\text{L}$ , 0.15 mmol) was dissolved with 0.2 mL chloroform in a 25 mL Schleck tube, then  $\text{CS}_2$  (27.2  $\mu\text{L}$ , 0.45 mmol) was added and heat release can be observed. The mixture was stirred until it recovered to room temperature, then compound **7** (35.4 mg, 0.15 mmol) dissolved in 0.2 mL chloroform was injected. Subsequently, the wall of the tube was washed with another 0.1 mL of chloroform. The reaction was conducted at room temperature for 8 h. Following the completion of the reaction, the organic solvent was removed by rotary evaporator. The product was purified by silica gel column using PE/EA (10:1  $v/v$ ) as eluent. Compound **8** was obtained in 86% yield as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ),  $\delta$  (TMS, ppm): 8.11 – 8.04 (d,  $Z\text{-H}_a$ ), 7.98 (d,  $E\text{-H}_a$ ), 7.72 – 7.66 (m,  $Z\text{-H}_c$ ), 7.62 (s,  $Z\text{-H}_e$ ), 7.43 – 7.36 (m,  $Z\text{-H}_b$ ,  $H_d$ ), 7.33 – 7.29 (m,  $E\text{-H}_c$ ), 7.28 (s,  $E\text{-H}_e$ ), 7.22 – 7.17 (m,  $E\text{-H}_b$ ,  $H_d$ ), 7.10 – 7.04 (d,  $Z\text{-H}_f$ ), 7.02 (d,  $E\text{-H}_f$ ), 3.86 (s,  $Z\text{-H}_g$ ), 3.84 – 3.78 (m,  $E\text{-H}_g$ ,  $H_h$ ), 3.74 (q,  $Z\text{-H}_h$ ), 0.94 (t,  $Z\text{-H}_i$ ), 0.85 (m,  $E\text{-H}_i$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ),  $\delta$  (TMS, ppm): 190.97, 189.90,

189.13, 164.05, 163.93, 145.07, 141.09, 139.86, 139.72, 138.24, 132.19, 131.84, 131.65, 130.25, 129.74, 129.35, 128.87, 128.68, 128.44, 128.09, 114.58, 114.51, 56.09, 49.30, 48.77, 48.67, 48.23, 31.43, 22.54, 14.56, 13.64, 13.40, 11.73, 11.40. FT-IR (KBr disk),  $\nu$  (cm<sup>-1</sup>): 3056, 2974, 2932, 2838, 1652, 1598, 1487, 1458, 1444, 1418, 1304, 1245, 1205, 1168, 1073, 1022, 947, 915, 834, 766, 696, 563, 517.

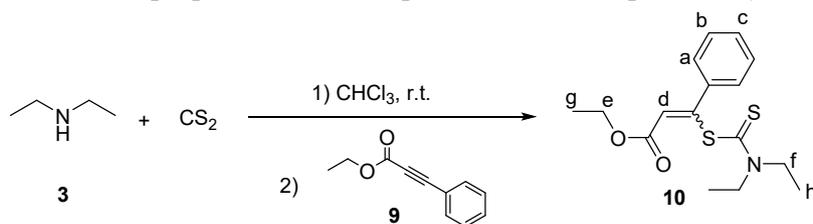
Model compound **S9** was prepared to compare with model compound **8**, and prove that there is no by-product of direct amino-yne reaction in the multicomponent reaction of this work. The synthetic routes to compound **S9** are show in Scheme **S6**:



**Scheme S6.** Synthetic routes to model compound **S9**.

**3-(Diethylamino)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (S9):** Compound **7** (35.4 mg, 0.15 mmol) was dissolved in 2 mL methanol, then diethyl amine (20.6  $\mu$ L, 0.2 mmol) was added. The mixture was heat to 60  $^{\circ}$ C for 8 h. The product was obtained by solvent evaporation and purification by a silica gel column using PE/EA (10:1, v/v) as eluent. Yellow oily liquid of **S9** was obtained in 96% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.89 (d,  $J$  = 8.8 Hz, 0.08H), 7.83 (d,  $J$  = 8.8 Hz, 1.92H), 7.51 – 7.33 (m, 3H), 7.28 – 7.17 (m, 2H), 6.84 (d,  $J$  = 8.9 Hz, 2H), 5.94 (s,  $Z$ -C=CH-S, 0.96H), 5.67 (s,  $E$ -C=CH-S, 0.04H), 3.80 (s, 3H), 3.26 (s, 4H), 1.18 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 186.07, 162.73, 161.53, 137.39, 134.78, 129.45, 128.40, 128.09, 127.82, 113.04, 92.92, 55.28, 44.16, 13.38.

Model compound **10** was prepared in similar procedure as compound **8** (Scheme S7):

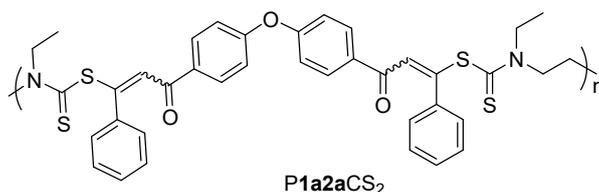


**Scheme S7.** Synthetic route to model compound **10**.

**Ethyl 3-((diethylcarbamothioyl)thio)-3-phenylacrylate (10):** Yellow oil, yield 91%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 7.63 – 7.56 (m, Z- $\text{H}_a$ ), 7.51 – 7.45 (m, E- $\text{H}_a$ ), 7.38 – 7.32 (m, Z- $\text{H}_b$ ,  $\text{H}_c$ ), 7.32 – 7.28 (m, E- $\text{H}_b$ ,  $\text{H}_c$ ), 6.55 (s, Z- $\text{H}_d$ ), 6.47 (s, E- $\text{H}_d$ ), 4.23 (q, Z- $\text{H}_e$ ), 4.06 (q, E- $\text{H}_e$ ), 3.89 (m, Z- $\text{H}_f$ ), 3.78 (m, E- $\text{H}_f$ ), 1.42 – 1.35 (m, Z- $\text{H}_g$ ), 1.34 – 1.25 (m, Z- $\text{H}_h$ ), 1.20 – 1.06 (m, E- $\text{H}_g$ ,  $\text{H}_h$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta$  (TMS, ppm): 190.71, 190.12, 164.68, 164.53, 149.22, 149.14, 139.85, 137.20, 130.04, 129.29, 128.83, 128.34, 128.24, 127.83, 127.18, 125.20, 60.63, 60.52, 49.01, 48.84, 48.51, 48.11, 14.26, 13.92, 13.38, 13.22, 11.38, 11.32.

### Typical Procedures for Polymerization

Without additional notes, all the polymerizations were performed under nitrogen atmosphere following standard Schlenk technique. A representative process for the polymerization of **P1a2aCS<sub>2</sub>** is presented in the following section.



**P1a2aCS<sub>2</sub>**. Monomer **2a** (21.5  $\mu\text{L}$ , 0.15 mmol) in 0.2 mL DMSO was firstly added into a 25 mL Schleck tube and mixed with  $\text{CS}_2$  (27.2  $\mu\text{L}$ , 0.45 mmol). After a heat release process, monomer **1a** (63.9 mg, 0.15 mmol) dissolved in 0.2 mL DMSO was injected, and then the wall of tube was washed with another 0.1 mL of DMSO. The reaction was conducted at room temperature for 8 h, then quenched with 20 mL water. The reaction mixture was extracted thrice with saturated brine and DCM. The organic phase was dried with anhydrous sodium. The polymer was precipitated by adding the solution dropwise into 125 mL of hexane under vigorous stirring. The precipitates were filtered, washed with hexane, and dried in vacuum at 40  $^\circ\text{C}$  to a constant weight. The product was obtained as a yellow solid in 76% yield.  $M_w$ : 31 600,  $D$ : 2.13. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3055, 2976, 2930,

1657, 1587, 1497, 1443, 1411, 1233, 1163, 1009, 942, 875, 838, 763, 695. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (TMS, ppm): 8.13 (s, 2.3H), 7.97 (s, 1.7H), 7.69 (s, 4H), 7.47 – 6.62 (m, 12H), 3.83 (m, 8H), 1.42 – 0.57 (m, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (TMS, ppm): 191.87, 191.22, 189.21, 188.84, 160.23, 160.15, 139.43, 139.13, 137.86, 133.60, 133.18, 132.75, 132.48, 131.95, 131.55, 130.08, 129.57, 129.07, 128.75, 128.61, 128.08, 119.44, 119.25, 100.00, 50.25, 49.73, 13.29, 13.12, 11.23, 10.86.

### Optimization of Polymerization Conditions

**Table S1.** Effect of CS<sub>2</sub> amount on the spontaneous polymerization of **1a**, **2a** and CS<sub>2</sub>.<sup>a</sup>

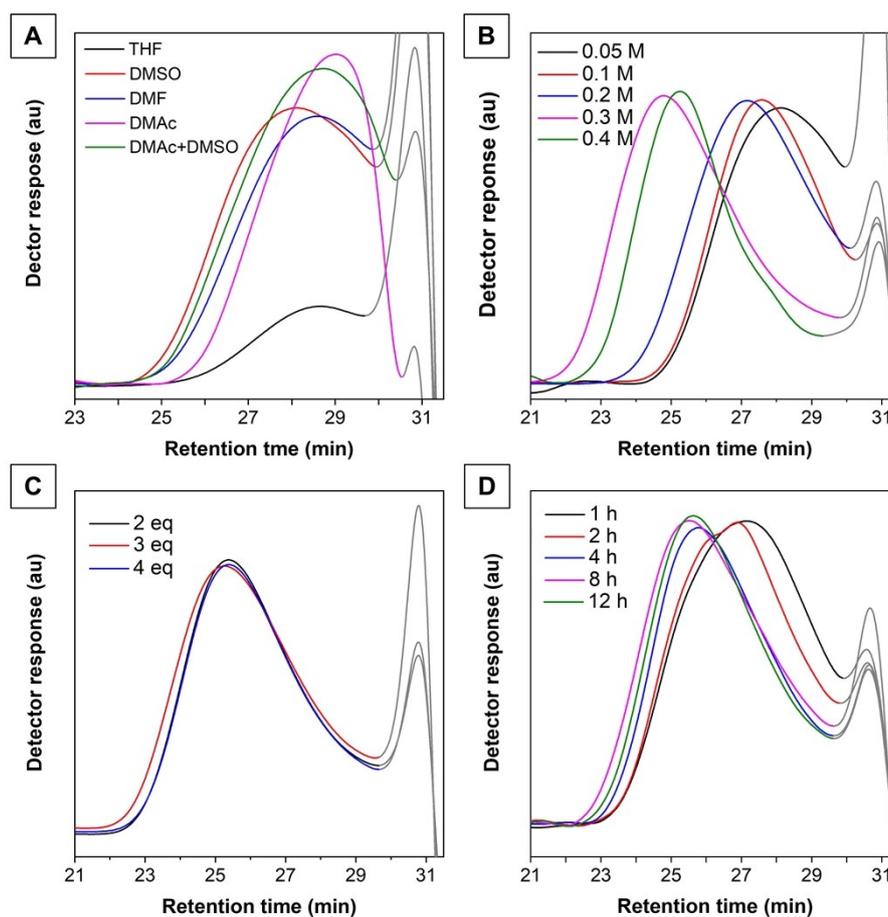
entry	equivalent of CS <sub>2</sub> (eq)	yield (%)	<i>M</i> <sub>w</sub> <sup>b</sup>	<i>D</i> <sup>b</sup>
1	2	73	25 600	1.83
2	3	74	28 300	1.99
3	4	74	25 300	1.89

<sup>a</sup> Carried out under nitrogen in anhydrous DMSO at 25 °C, [**1a**] = [**2a**] = 0.3 M. <sup>b</sup> Determined by GPC in DMF containing 0.05 M LiBr using linear PMMA for calibration.

**Table S2.** Time course of the spontaneous polymerization of **1a**, **2a** and CS<sub>2</sub>.<sup>a</sup>

entry	time (h)	yield (%)	<i>M</i> <sub>w</sub> <sup>b</sup>	<i>D</i> <sup>b</sup>
1	1	56	14 000	1.84
2	2	67	15 100	1.79
3	4	76	19 400	1.82
4	8	76	31 600	2.13
5	12	75	28 100	1.93

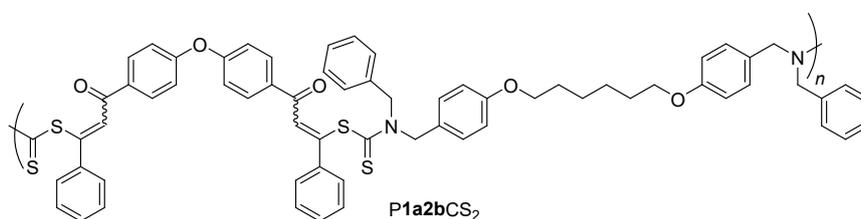
<sup>a</sup> Carried out under nitrogen in anhydrous DMSO at 25 °C, [**1a**] = [**2a**] = 0.3 M, [CS<sub>2</sub>] = 0.9 M. <sup>b</sup> Determined by GPC in DMF containing 0.05 M LiBr using linear PMMA for calibration.



**Figure S1.** GPC traces of the products during polymerization condition optimization. (A) GPC traces of **P1a2aCS<sub>2</sub>** prepared in different solvent. (B) GPC traces of **P1a2aCS<sub>2</sub>** prepared under different concentration. (C) GPC traces of **P1a2aCS<sub>2</sub>** prepared with different CS<sub>2</sub> equivalent. (D) GPC traces of **P1a2aCS<sub>2</sub>** at different time intervals. The gray part is the peaks caused by the solvent.

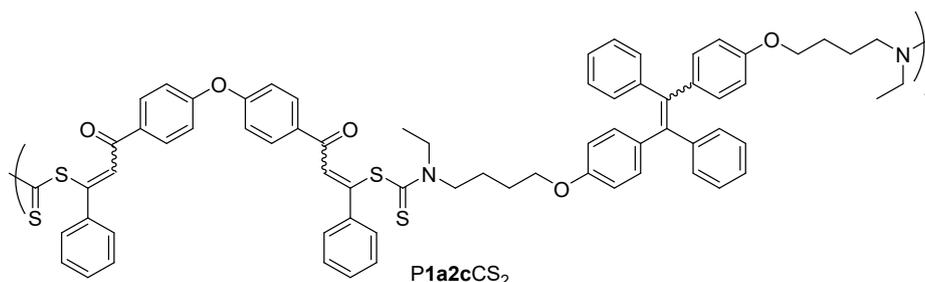
### Characterization Data for PADDCS

The other polymers were prepared according to the method similar to that of **P1a2aCS<sub>2</sub>**. The characterization data of the polymer are as follows:

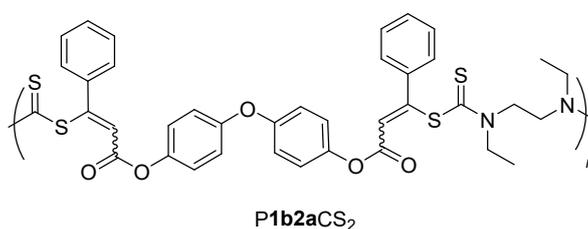


**P1a2bCS<sub>2</sub>**. The polymer was obtained as a yellow solid in 92% yield.  $M_w$ : 21 200,  $D$ : 1.81. FT-IR (KBr disk),  $\nu$  (cm<sup>-1</sup>): 3058, 3031, 3935, 2862, 1658, 1608, 1585, 1511, 1495, 1470, 1407, 1351, 1303, 1235, 1612, 1111, 1076, 1028, 1011, 968, 942, 874, 838, 762, 734, 696, 593. <sup>1</sup>H NMR (400

MHz, DMSO- $d_6$ ),  $\delta$  (TMS, ppm): 8.15 (s, 2H), 7.94 (s, 2H), 7.67 (d, 4H), 7.47 – 6.68 (m, 30H), 5.28 – 4.84 (m, 8H), 3.91 (d, 4H), 1.68 (s, 4H), 1.34 (s, 4H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ),  $\delta$  (TMS, ppm): 194.00, 193.69, 191.11, 189.14, 160.25, 158.81, 139.50, 137.69, 135.55, 131.98, 130.21, 129.31, 128.87, 128.81, 128.06, 127.66, 127.22, 119.30, 115.22, 114.78, 67.90, 56.17, 55.94, 29.08, 25.78.

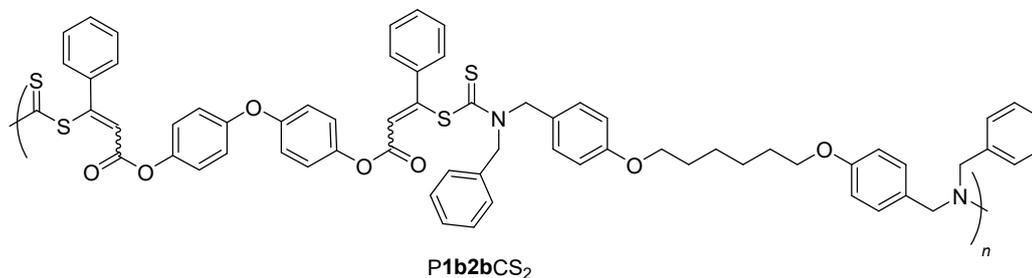


**P1a2cCS<sub>2</sub>**. The polymer was obtained as a yellow solid in 55% yield.  $M_w$ : 7100,  $D$ : 1.39. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3055, 2934, 2870, 2197, 1656, 1605, 1587, 1507, 1491, 1443, 1416, 1374, 1239, 1163, 1071, 1029, 1009, 874, 835, 761, 700, 612, 569.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ),  $\delta$  (TMS, ppm): 8.03 (d, 4H), 7.61 (d, 4H), 7.41 – 6.52 (m, 32H), 3.99 – 3.59 (m, 12H), 1.59 (d, 6H), 1.21 (d, 4H), 0.86 (t, 6H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ),  $\delta$  (TMS, ppm): 190.25, 190.08, 189.02, 160.16, 157.42, 144.18, 139.71, 136.10, 133.60, 133.25, 132.37, 131.88, 131.22, 129.97, 129.56, 128.67, 128.50, 128.12, 126.70, 119.22, 114.18, 67.38, 53.60, 49.00, 31.44, 26.30, 25.07, 23.04, 22.55, 14.45, 13.62, 11.28.

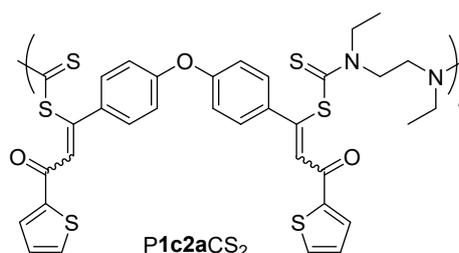


**P1b2aCS<sub>2</sub>**. The polymer was obtained as a white solid in 55% yield.  $M_w$ : 11 200,  $D$ : 1.59. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3056, 2978, 2931, 1735, 1594, 1571, 1491, 1444, 1413, 1353, 1300, 1242, 1185, 1126, 1011, 989, 897, 847, 764, 696, 516.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ),  $\delta$  (TMS, ppm): 7.65 (d, 4H), 7.55 – 6.88 (m, 14H), 6.51 (d, 2H), 4.29 – 3.56 (m, 8H), 1.36 – 0.77 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ),  $\delta$  (TMS, ppm): 188.72, 163.44, 162.61, 154.80, 154.53, 146.23, 138.40,

136.30, 133.50, 130.27, 129.67, 129.20, 128.98, 128.67, 128.32, 128.16, 123.71, 123.48, 119.97, 119.83, 54.32, 52.20, 50.10, 13.21, 11.55, 11.05. 155.04, 152.45, 145.70, 133.20, 131.10, 128.70, 122.78, 119.70, 119.21, 88.90, 80.16.



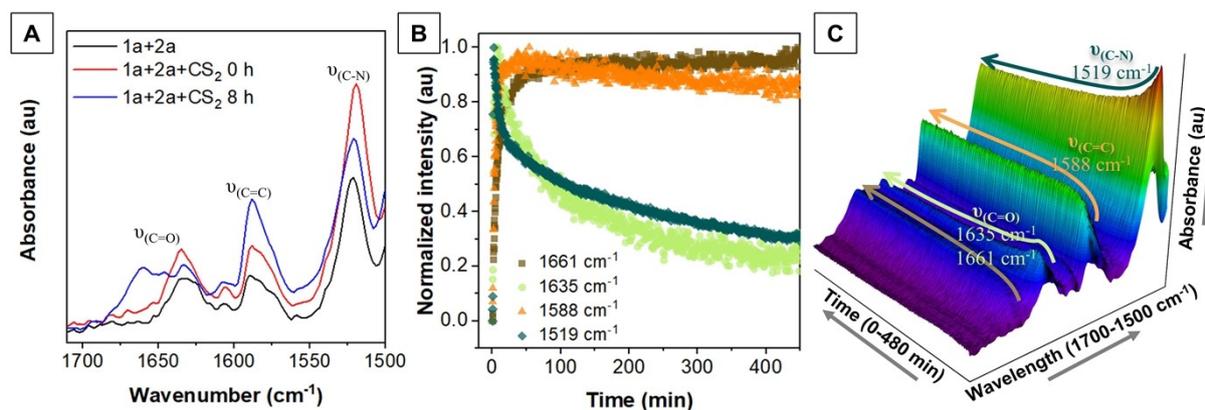
**P1b2bCS<sub>2</sub>**. The polymer was obtained as a white solid in 80% yield.  $M_w$ : 14 900,  $D$ : 1.67. FT-IR (KBr disk),  $\nu$  (cm<sup>-1</sup>): 3059, 2937, 2864, 1733, 1608, 1511, 1491, 1470, 1408, 1351, 1301, 1247, 1182, 1126, 1012, 964, 847, 764, 734, 696, 517. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (TMS, ppm): 7.76 – 6.63 (m, 38H), 5.06 (s, 8H), 3.89 (s, 4H), 1.67 (s, 4H), 1.41 (s, 4H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (TMS, ppm): 193.47, 193.28, 163.20, 158.81, 158.63, 154.73, 150.53, 146.26, 139.13, 135.59, 133.48, 130.64, 130.32, 129.65, 129.46, 129.35, 128.99, 128.91, 128.88, 128.78, 128.23, 127.88, 127.71, 127.63, 127.24, 124.60, 123.70, 123.47, 119.88, 119.79, 115.24, 114.79, 67.82, 56.38, 29.08, 25.78.



**P1c2aCS<sub>2</sub>**. The polymer was obtained as a yellow solid in 65% yield.  $M_w$ : 10 600,  $D$ : 1.52. FT-IR (KBr disk),  $\nu$  (cm<sup>-1</sup>): 3091, 2977, 2930, 2194, 1635, 1589, 1492, 1411, 1354, 1237, 1167, 1079, 1058, 1011, 927, 857, 831, 724. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (TMS, ppm): 8.02 (m, 4H), 7.78 – 7.47 (m, 4H), 7.47 – 6.63 (m, 8H), 4.30 – 3.57 (m, 8H), 1.40 – 0.72 (m, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>),  $\delta$  (TMS, ppm): 188.71, 181.96, 181.26, 157.61, 156.91, 145.43, 145.30, 136.27, 135.00, 134.42, 132.29, 130.86, 129.37, 118.77, 50.47, 49.73, 13.38, 13.24, 10.91.

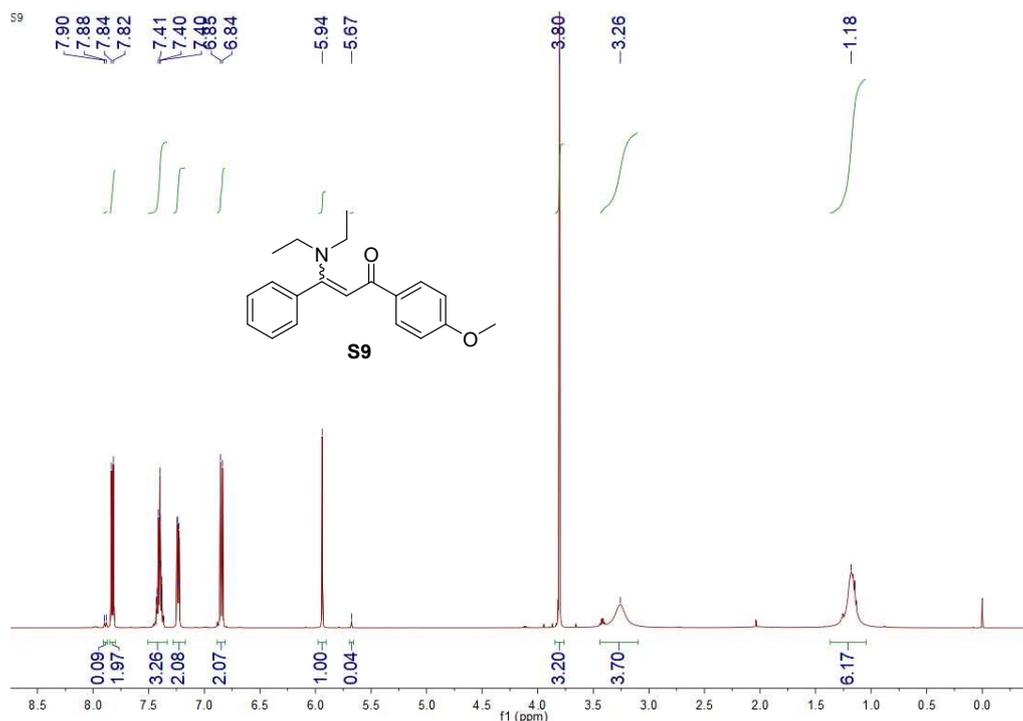


## FT-IR Spectra of Polymers

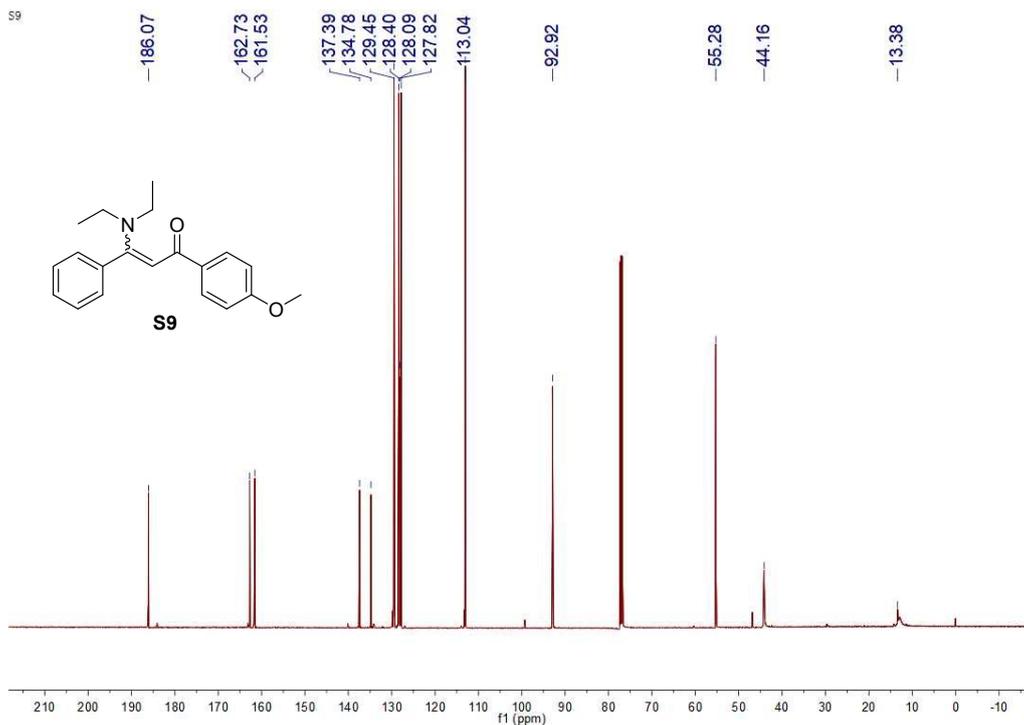


**Figure S3.** (A) *In situ* IR spectra of the polymerization of P1a2aCS<sub>2</sub> in DMSO before and after adding CS<sub>2</sub>. (B) Time-dependent peak intensity at 1661, 1635, 1588, and 1519 cm<sup>-1</sup>, respectively. (C) 3D Fourier transform *in situ* IR profiles of the peaks at 1661, 1635, 1588, and 1519 cm<sup>-1</sup> for the polymerization of 1a, 2a, and CS<sub>2</sub> in DMSO at room temperature.

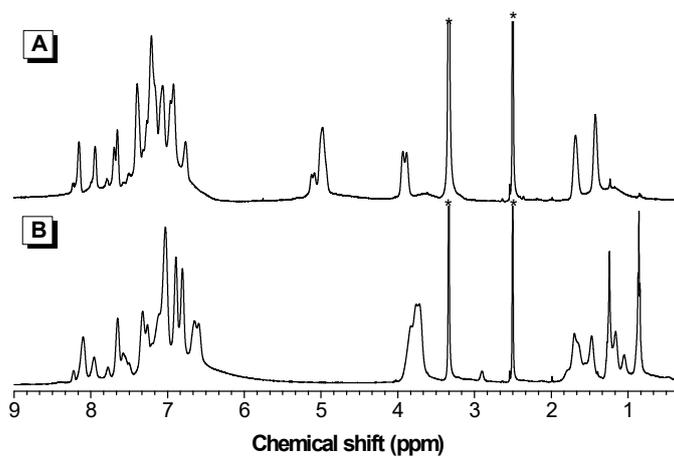
## NMR Spectra of Compound S9 and Polymers



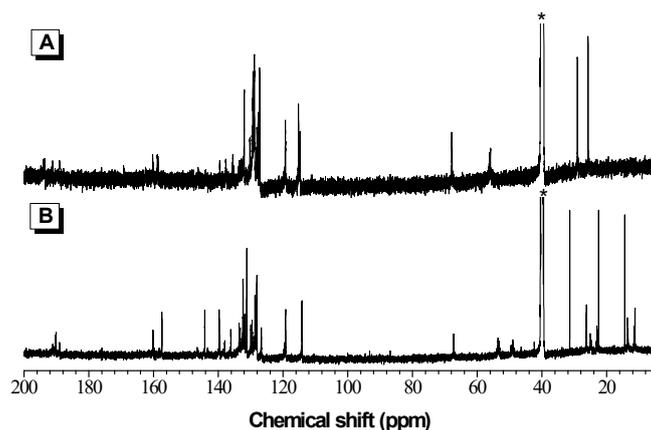
**Figure S4.** <sup>1</sup>H NMR spectrum of S9 in CDCl<sub>3</sub>.



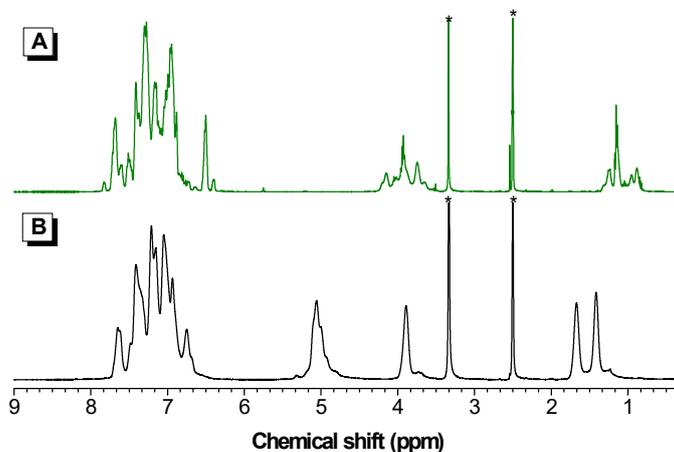
**Figure S5.**  $^{13}\text{C}$  NMR spectrum of **S9** in  $\text{CDCl}_3$ .



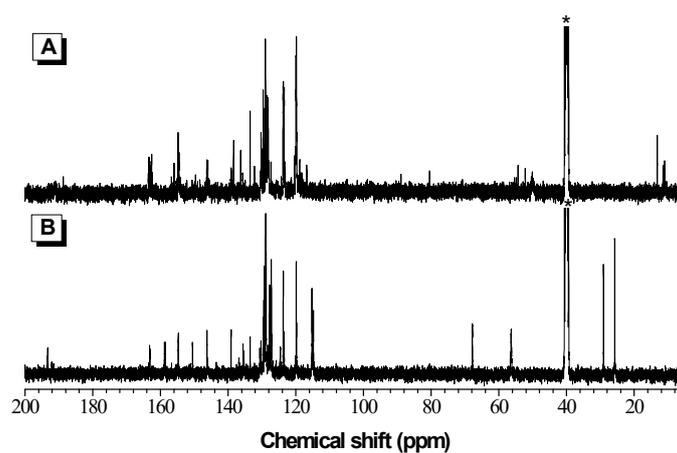
**Figure S6.**  $^1\text{H}$  NMR spectra of (A) **P1a2bCS<sub>2</sub>** and (B) **P1a2cCS<sub>2</sub>** in  $\text{DMSO-}d_6$ . The solvent peaks are marked with asterisks.



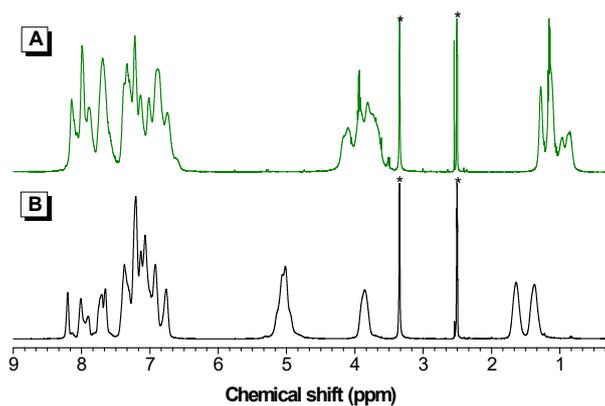
**Figure S7.**  $^{13}\text{C}$  NMR spectra of (A) P1a2bCS<sub>2</sub> and (B) P1a2cCS<sub>2</sub> in DMSO-*d*<sub>6</sub>. The solvent peaks are marked with asterisks.



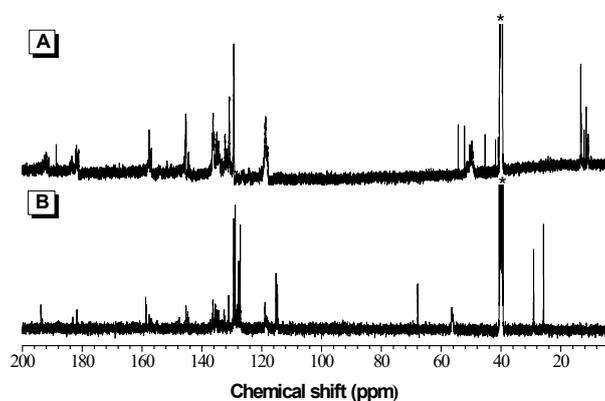
**Figure S8.**  $^1\text{H}$  NMR spectra of (A) P1b2aCS<sub>2</sub> and (B) P1b2bCS<sub>2</sub> in DMSO-*d*<sub>6</sub>. The solvent peaks are marked with asterisks.



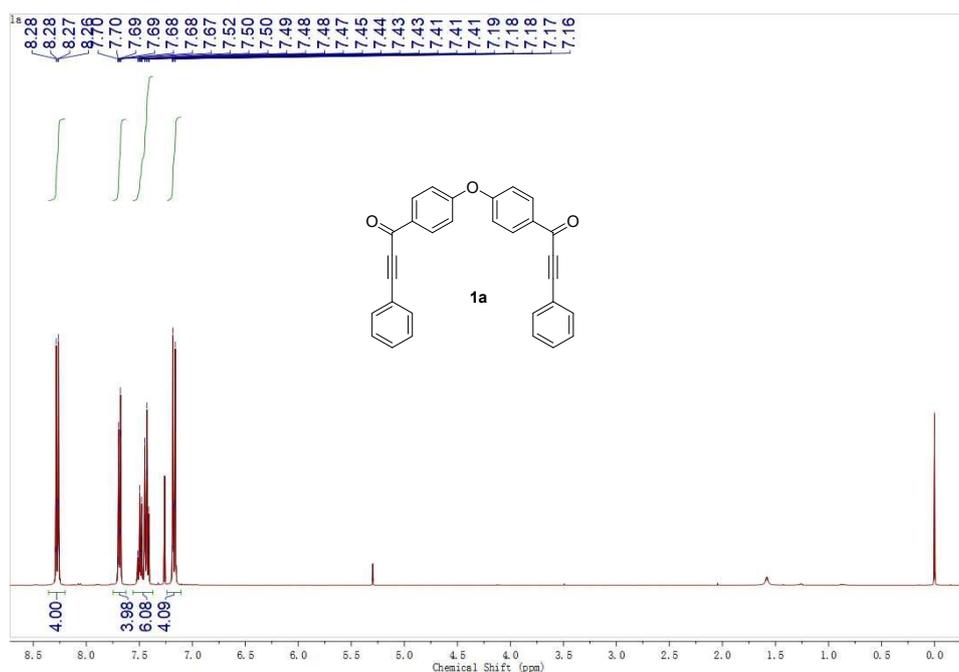
**Figure S9.**  $^{13}\text{C}$  NMR spectra of (A) P1b2aCS<sub>2</sub> and (B) P1b2bCS<sub>2</sub> in DMSO-*d*<sub>6</sub>. The solvent peaks are marked with asterisks.



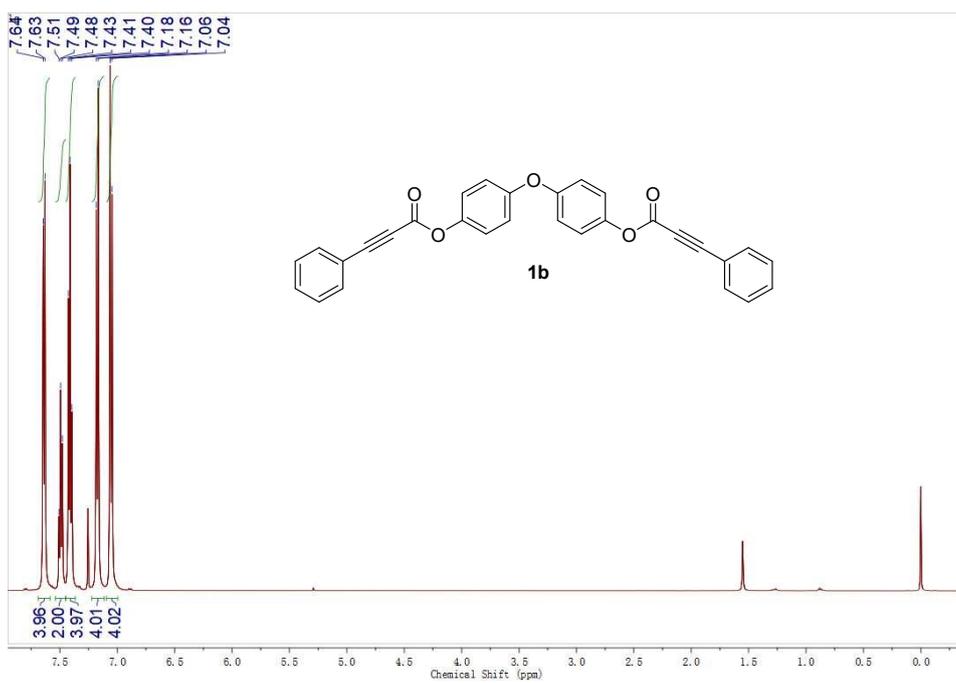
**Figure S10.**  $^1\text{H}$  NMR spectra of (A)  $\text{P1c2aCS}_2$  and (B)  $\text{P1c2bCS}_2$  in  $\text{DMSO-}d_6$ . The solvent peaks are marked with asterisks.



**Figure S11.**  $^{13}\text{C}$  NMR spectra of (A)  $\text{P1c2aCS}_2$  and (B)  $\text{P1c2bCS}_2$  in  $\text{DMSO-}d_6$ . The solvent peaks are marked with asterisks.

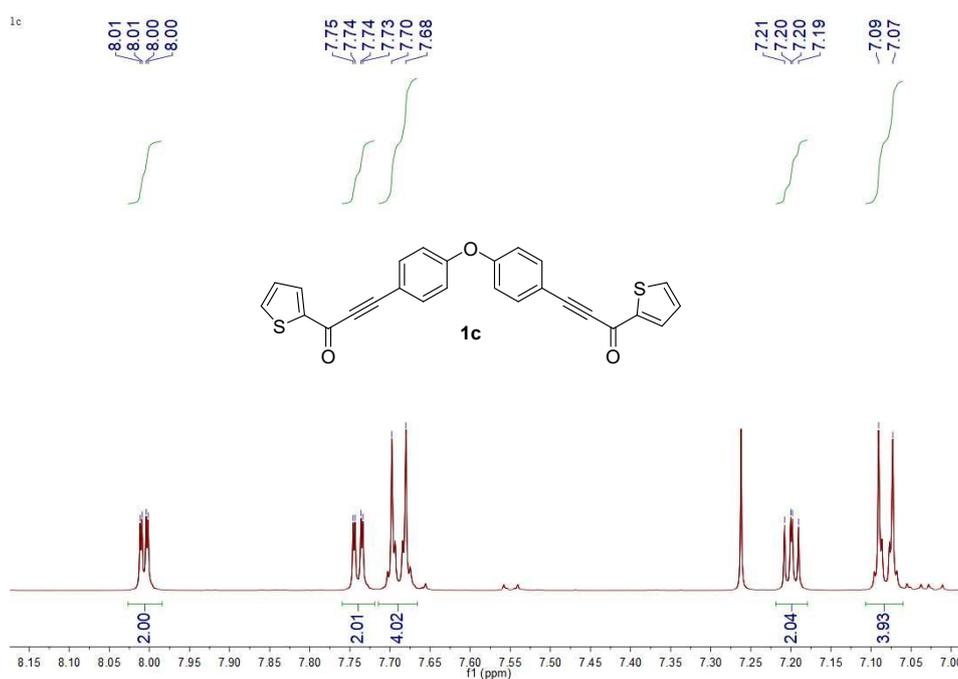


**Figure S12.**  $^1\text{H}$  NMR spectrum of **1a** in  $\text{CDCl}_3$ .

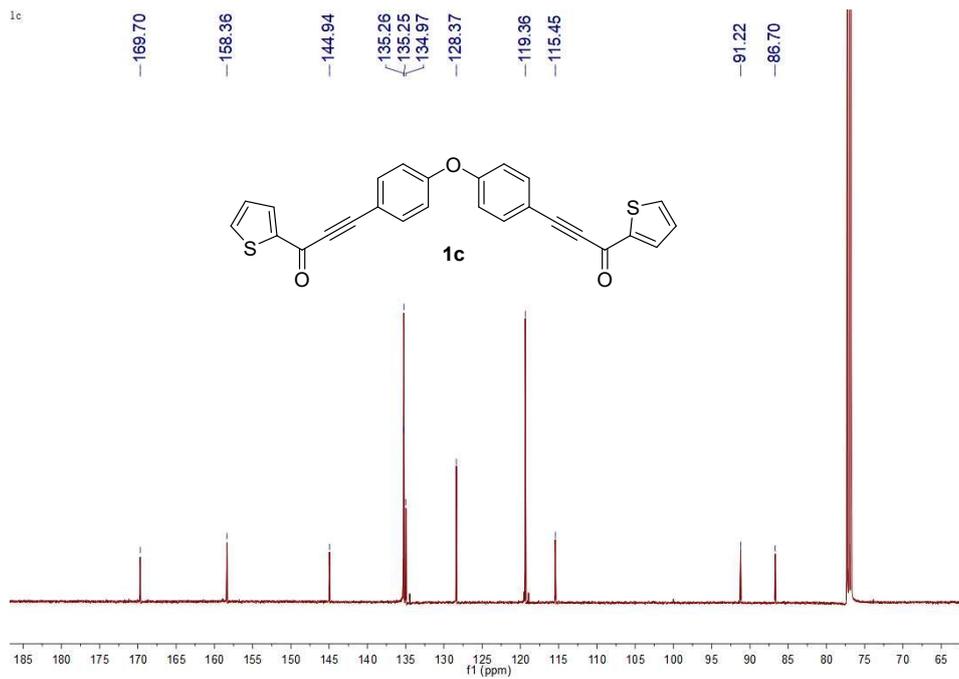




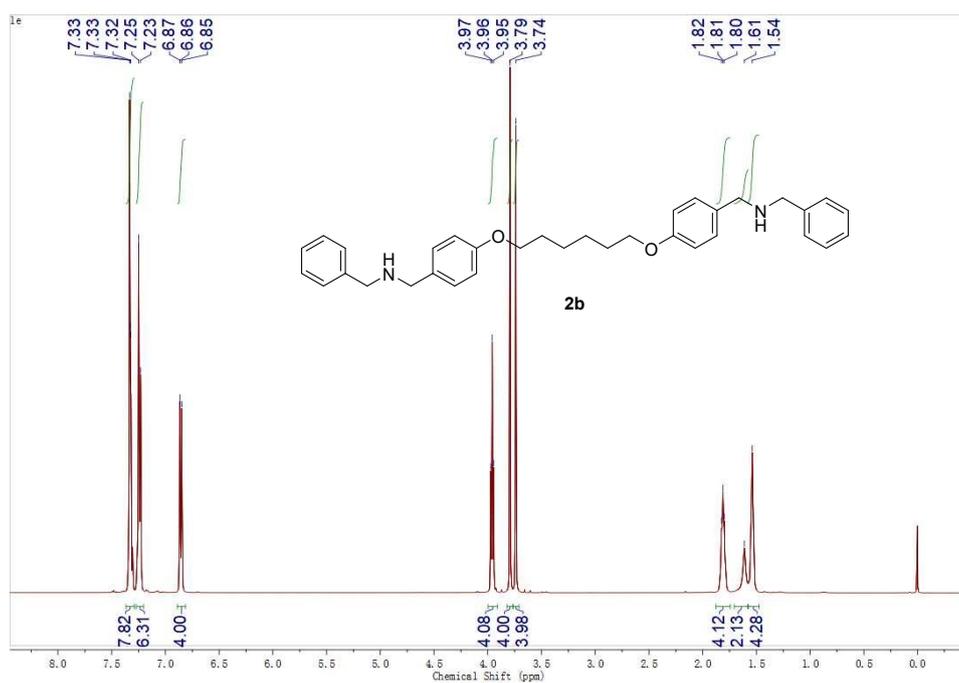
**Figure S15.**  $^{13}\text{C}$  NMR spectrum of **1b** in  $\text{CDCl}_3$ .



**Figure S16.**  $^1\text{H}$  NMR spectrum of **1c** in  $\text{CDCl}_3$ .



**Figure S17.**  $^{13}\text{C}$  NMR spectrum of **1c** in  $\text{CDCl}_3$ .



**Figure S18.**  $^1\text{H}$  NMR spectrum of **2b** in  $\text{CDCl}_3$ .

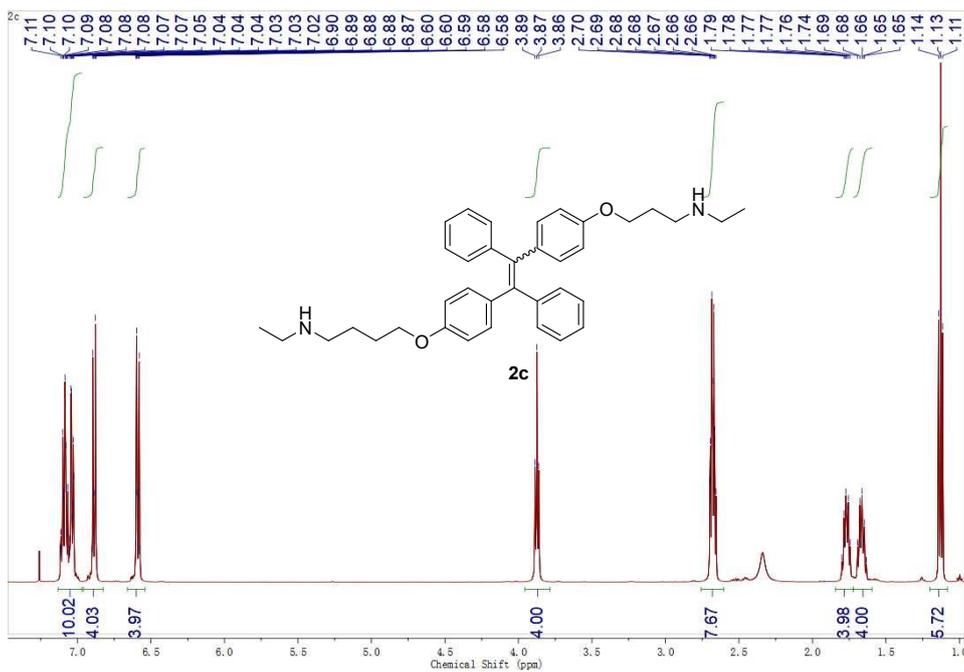
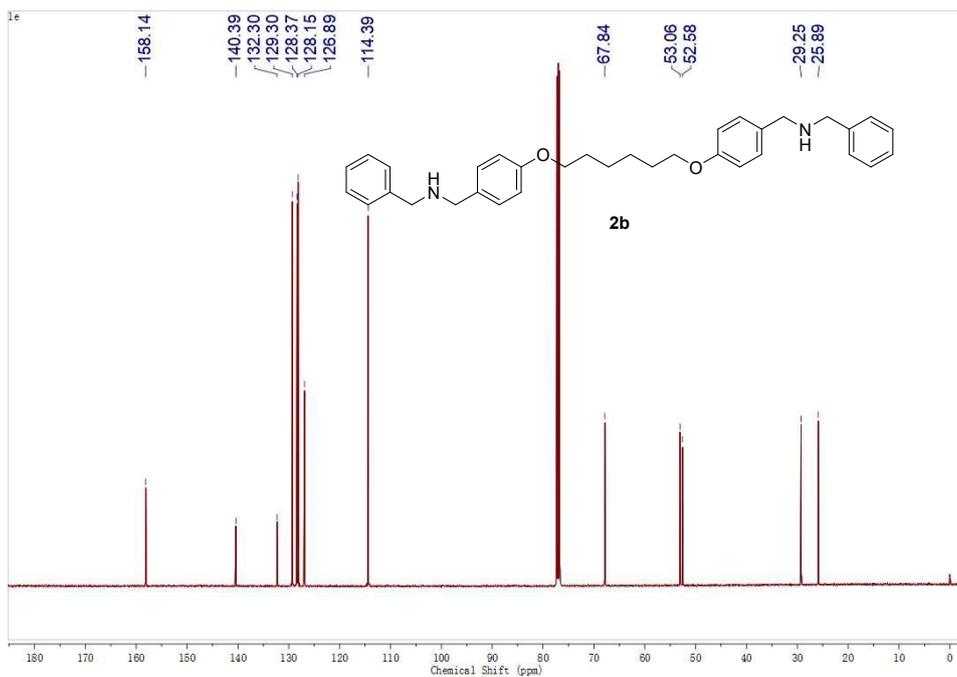




Figure S21.  $^{13}\text{C}$  NMR spectrum of **2c** in  $\text{CDCl}_3$ .

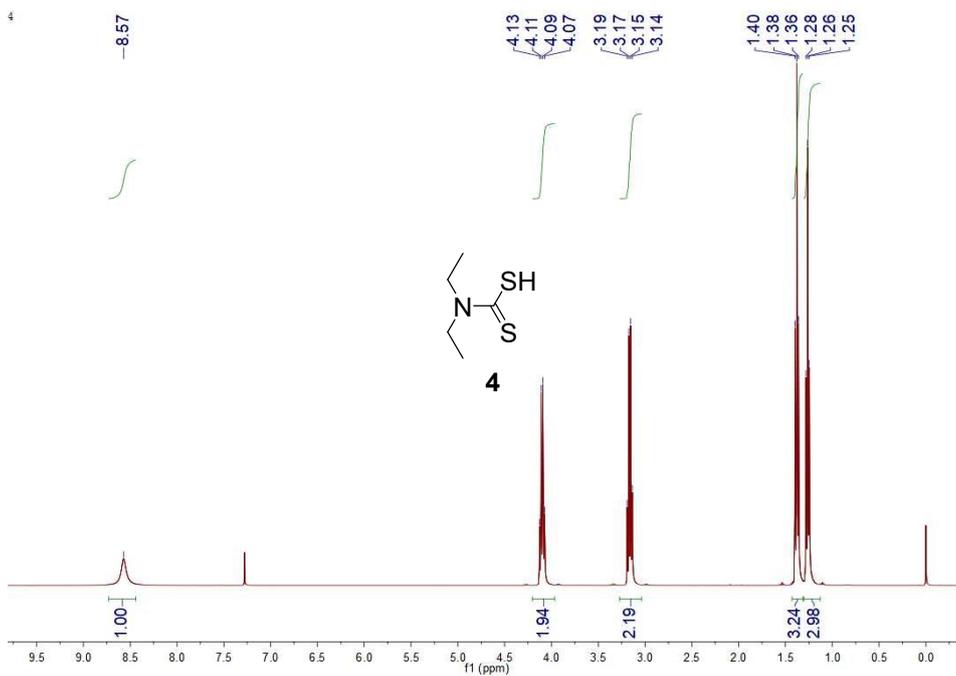


Figure S22.  $^1\text{H}$  NMR spectrum of **4** in  $\text{CDCl}_3$ .

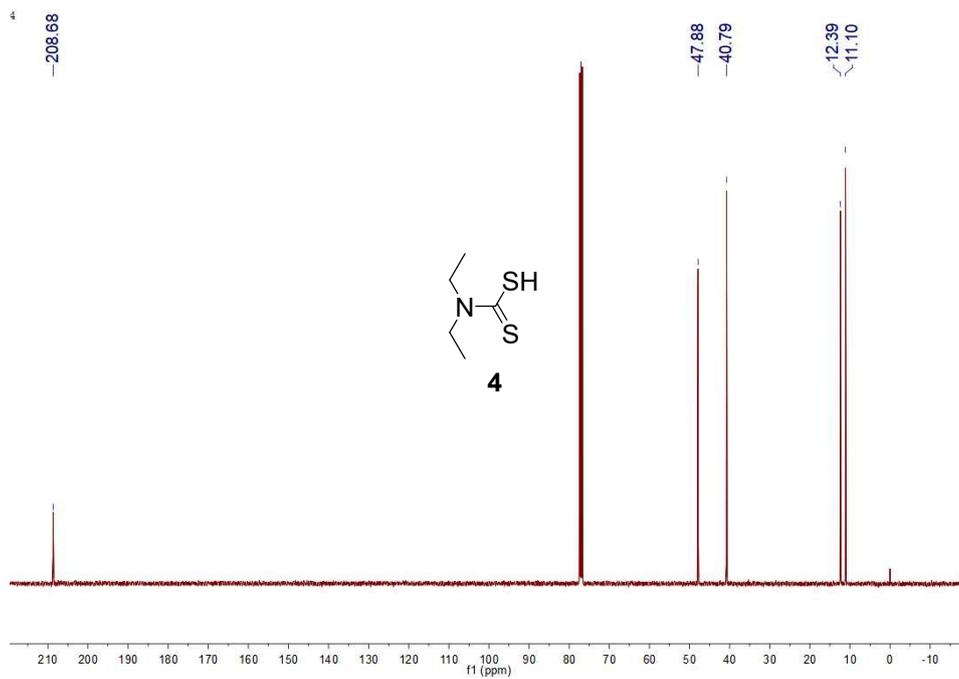


Figure S23. <sup>13</sup>C NMR spectrum of **4** in CDCl<sub>3</sub>.

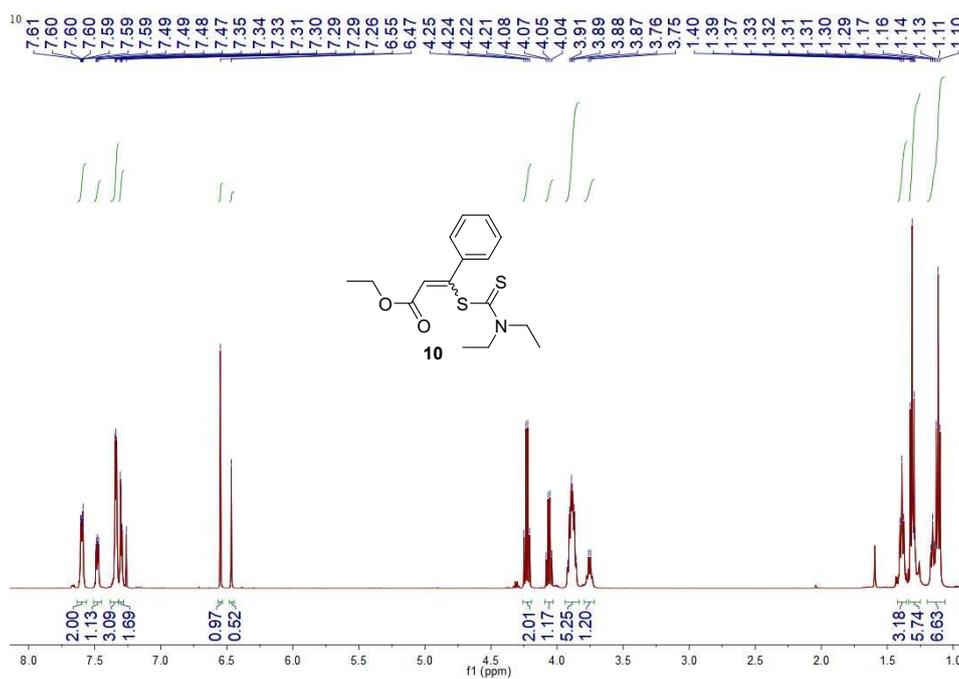


Figure S24. <sup>1</sup>H NMR spectrum of **10** in CDCl<sub>3</sub>.

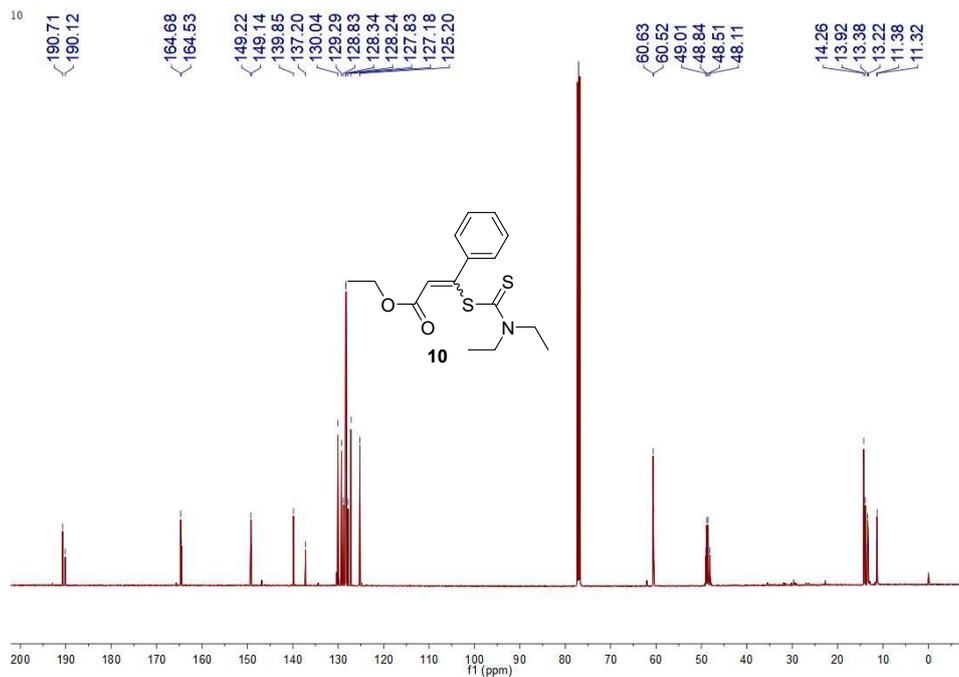


Figure S25.  $^{13}\text{C}$  NMR spectrum of **10** in  $\text{CDCl}_3$ .

## Optical Properties of Polymers

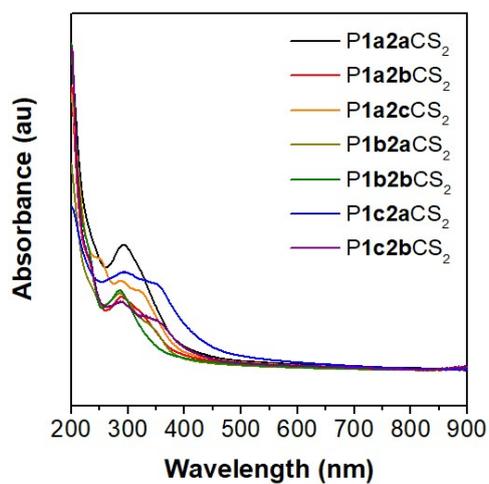


Figure S26. UV-vis spectra of polymer films.

Table S3. The refractive indices and chromatic dispersions of PADDs.

polymer	$n_{632.8}$	$n_{1550}$	$\nu_D^b$	$\nu_D'^c$	$D^d$	$D'^e$
P1a2aCS <sub>2</sub>	1.6966	1.6594	15.8	82.8	0.063	0.012
P1a2bCS <sub>2</sub>	1.6575	1.6385	19.7	266.6	0.051	0.004

P1a2cCS <sub>2</sub>	1.6638	1.6388	15.5	164.1	0.065	0.006
P1b2aCS <sub>2</sub>	1.6737	1.6291	15.3	67.2	0.065	0.015
P1b2bCS <sub>2</sub>	1.6712	1.6283	18.5	66.5	0.054	0.015
P1c2aCS <sub>2</sub>	1.7471	1.6982	9.46	97.3	0.106	0.010
P1c2bCS <sub>2</sub>	1.6998	1.6525	12.0	73.6	0.083	0.014

<sup>a</sup> Refractive index ( $n$ ) and dispersion constant of the polymer for different wavelengths are all obtained from the refractive index curve. <sup>b</sup> Abbé number ( $v_D$ ) =  $(n_{589.2}-1)/(n_{486.1}-n_{656.3})$ . <sup>c</sup> Corrected Abbé number ( $v_D'$ ) =  $(n_{1319}-1)/(n_{1064}-n_{1559})$ . <sup>d</sup> Dispersion of polymers in visible light region ( $D$ ) =  $1/v_D$ . <sup>e</sup> Dispersion of polymers in infrared light region ( $D'$ ) =  $1/v_{D'}$ .

### Mechanical Properties of P1a2aCS<sub>2</sub> and Preparation of Ultrathin Membranes

P1a2aCS<sub>2</sub> is taken as a representative example to illustrate the process of preparation of the membranes: 100  $\mu$ L of P1a2aCS<sub>2</sub> dissolved with DCM (10  $\mu$ M) was slowly drop onto a plate of water. Being driven by the surface tension of flowing water, the polymer can spread and float on water, and DCM volatilized at the same time. Following this, the membranes could be transferred to other substrates, for example, silicon or quartz before further characterization.



**Figure S27.** Mechanical properties of P1a2aCS<sub>2</sub>. (A) The stretch curve of P1a2aCS<sub>2</sub> tested by electronic universal testing machine. (B) The continuous fiber of P1a2aCS<sub>2</sub> prepared through solution processing and (C) the scanning electron microscope image of this fiber.

### References

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