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# Supporting Information

## Inverse Vulcanization of Elemental Sulfur with 1,4-Diphenylbutadiyne for Cathode Materials in Li-S Batteries

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## I. Materials

Sulfur ($S_8$, refined, 99.5%, Acros), 1,4-Diphenylbutadiyne (DiPhDY, 99%, Alfa Aesar), 1,2-Dichlorobenzene (99%, Acros), Phenylacetylene (98%, Pfaltz & Bauer), *N,N,N',N",N"*-Pentamethyldiethylenetriamine (PMDETA, 99 %, Aldrich), Copper (II) chloride (anhydrous, 98%, Alfa Aesar), (ethylenedinitrilo)tetraacetic acid disodium salt, dihydrate (EDTA, ACS grade, EMD), Chloroform (anhydrous, Aldrich), Dichloromethane (ACS grade, Fischer Scientific), Copper(I) iodide (Aldrich, 98%), N,N-Dimethylformamide (DMF, ACS grade, EMD), Sodium sulfide nonahydrate (Acros, 98%), 1,10-Phenanthroline (Sigma, ACS grade), Chloroform-d ($CDCl_3$, 0.01 % v/v TMS Cambridge Isotope Laboratories), Polyethylene (Aldrich, $M_w$ ~4000 g/mol), Conductive carbon (Super C65, Timcal), Lithium bis(trifluoromethane)sulfonimide (Aldrich), Lithium nitrate (Aldrich), Polypropylene separator (Celgard), Lithium foil (FMC), 1,3-Dioxolane (Novolyte) and 1,2-Dimethoxy ethane (Novolyte) were commercially available and used as received without further purification. Tetrabutylammonium hexafluorophosphate (TBAFP, 99 %, Fluka) was recrystallized from absolute ethanol and dried *in* vacuo before use.

## II. Instrumentation and Methods

$^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DRX 500 MHz or a BrukerAvance III 400 MHz spectrometer. Chemical shifts are referenced to $Me_4Si$ (δ 0.00 ppm) for $^1$H NMR and residual $CHCl_3$ (δ 77.0 ppm) in $CDCl_3$ for $^{13}$C NMR. Size exclusion chromatography (SEC) was performed in a tetrahydrofuran (THF) mobile phase with a Waters 1515 isocratic pump running three 5-µm PLgel columns (Polymer Labs, pore size $10^4$, $10^3$ and $10^2$ Å) at a flow rate of 1 mL/min with a Waters 2414 differential refractometer and a Waters 2487 dual-wavelength UV-vis spectrometer. Molar masses were calculated using the Empower software (Waters), calibrated against low polydispersity linear polystyrene standards. Thermal gravimetric analysis (TGA) was performed with a Q50 TGA (TA instruments) from 25 °C to 600 °C at a rate of 20 °C/min under nitrogen atmosphere and data was analyzed with TA Universal Analysis software. XPS data were collected with monochromatic Al(Kα) radiation using a KRATOS 165 Ultra photoelectron spectrometer. Differential scanning calorimetry (DSC) characterization was carried out using a 2920 Modulated DSC (TA Instruments) running Thermal Solution 1.4E (TA Instruments) software, or a Discovery DSC (TA instruments) under nitrogen atmosphere. Cyclic voltammetry (CV) was performed with a Zahner Zennium Electrochemical Workstation utilizing a three electrode electrochemical cell with a platinum button working electrode (1 mm$^2$), a platinum mesh counter electrode, and a $Ag/AgNO_3$ reference. Battery cycling was performed at ambient temperature ($T_{average}$ = 23 °C) with an Arbin BT2000 battery tester controlled with MITS Pro 2.0 software.

## III. Experimental Procedures

### A. Preparation of Poly(Sulfur-*co*-1,4-Diphenylbutadiyne) (poly(S-*co*-DiPhDY))

### 1. General Synthetic Procedure (Inverse Vulcanization)

A general procedure for the preparation of poly(S-*co*-DiPhDY) is presented below and followed by specific conditions for different copolymer compostions. It was found that the inverse vulcanization of sulfur with DiPhDY at feed ratios of DiPhDY $\geq$ 20 wt% resulted in a very vigorous, exothermic reaction and necessitated lower reaction temperatures accompanied by longer reaction times.

A typical polymerization was conducted as follows: To a 5 mL glass vial equipped with a magnetic stir bar was added elemental sulfur and 1,4-diphenylbutadiyne. The mixture was heated with rapid stirring

(500 rpm) until vitrification of the reaction mixture occurred or for a specified time. The resulting copolymer was then rapidly cooled in a dry ice/acetone bath for 2 min. The reaction product was extracted by breaking the glass vial.

**a. Preparation of Poly(S-*co*-DiPhDY) with 10 wt% DiPhDY:**

The copolymerization was conducted according to the general procedure *vide supra* with $S_8$ (900 mg, 3.51 mmol) and DiPhDY (100 mg, 0.49 mmol) at 175 °C for 10 min yielding a dark reddish purple glass. (0.91 g yield)

**b. Preparation of Poly(S-*co*-DiPhDY) with 20 wt% DiPhDY**

The copolymerization was conducted according to the general procedure *vide supra* with $S_8$ (800 mg, 3.12 mmol) and DiPhDY (200 mg, 0.99 mmol) at 175 °C for 10 min yielding a purple glass. (0.93 g yield)

**c. Preparation of Poly(S-*co*-DiPhDY) with 40 wt% DiPhDY**

The copolymerization was conducted according to the general procedure *vide supra* with $S_8$ (600 mg, 2.34 mmol) and DiPhDY (400 mg, 1.98 mmol) at 125 °C for 1 hr yielding a dark purple glass. (0.95 g yield)

**d. Preparation of Poly(S-*co*-DiPhDY) with 60 wt% DiPhDY:**

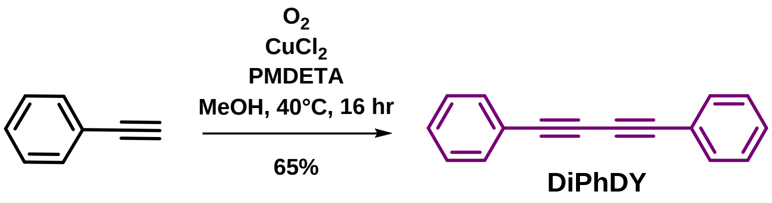
The copolymerization was conducted according to the general procedure *vide supra* with $S_8$ (400 mg, 1.56 mmol) and DiPhDY (600 mg, 2.97 mmol) at 125 °C for 1 hr yielding a dark purple glass. (0.87 g yield)

### 2. Isolation of Higher Molecular Weight Fraction

Poly(S-*co*-DiPhDY) (60 wt% DiPhDY) (1.0 g) was dissolved in dichloromethane (20 ml) and added dropwise to an excess of rapidly stirred methanol (ca. 200 mL). The resulting precipitate was recovered via vacuum filtration. This was repeated for a total of three precipitations. The remaining small molecule contaminants were removed via flash silica gel chromatography with 5 % v/v $CH_2Cl_2$ in hexanes as the eluent. After elution of the small molecule component the remaining polymer was eluted with 100 % $CH_2Cl_2$. The solvent was removed *in vacuo* affording poly(S-*co*-DiPhDY) as a glassy purple solid. (456 mg yield) $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.7 – 6.7 (br). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 131 – 126 (br). Found: C, 65.08; H, 3.95; S, 31.77

## B. Synthesis of 1,4-Diphenylbutadiyne (DiPhDY)

Commercially available 1,4-diphenylbutadiyne was principally used for the synthesis of poly(sulfur-*co*-1,4-diphenylbutadiyne) but preliminary experiments were conducted with DiPhDY synthesized according to a procedure adapted from Nielsen et al.[1]



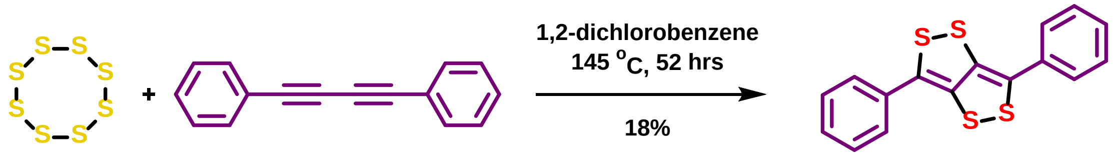
**DiPhDY**

(1,4-diphenybutadiyne)

To a 25 mL round bottomed flask equipped with a magnetic stir bar was added phenylacetylene (0.204 g, 2.00 mmol), copper(II) chloride (0.538 g, 4.00 mmol) and methanol (4 mL). N, N, N’, N’’, N’’-Pentamethyldiethylenetriamine (0.930 g, 5.4 mmol) was then added to the stirred mixture which was subsequently bubbled with oxygen for 5 minutes. The reaction was stirred at 40°C overnight and then cooled to room temperature. The resulting solution was diluted with dichloromethane and washed with saturated EDTA $_{(aq)}$ (3x20 mL) followed by 1N HCl (2x20 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo.* The product was isolated by passing a solution of the crude mixture in dichloromethane through a short plug of silica and removing the solvent *in vacuo* yielding a white solid. (0.1313 g, 65%). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.55 (m, 4H), 7.32 – 7.40 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 132.52, 129.22, 128.46, 121.82, 81.57, 73.93.

## C. Synthesis of Diphenyldithiolodithiole

3,6-Diphenyl-[1,2]dithiolo[4,3-c][1,2]dithiole (diphenyldithiolodithiole) was prepared using a procedure adapted from Blum *et. al.*[2]

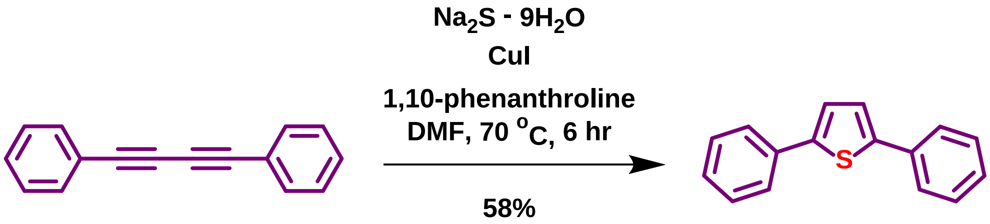


**1, diphenyldithiolodithiole**
(3,6-diphenyl-[1,2]dithiolo[4,3-*c*][1,2]dithiole)

To a 50 mL round bottom flask equipped with a magnetic stirbar was added $S_8$ (800 mg, 3.13 mmol), 1,4-diphenylbutadiyne (1.01 g, 5 mmol), and 1,2-dichlorobenzene (20 mL). The mixture was heated to 145 °C with stirring for 52 hrs. The product was isolated via silica gel chromatography with hexanes as the eluent affording a dark red crystalline solid (297 mg, 18%). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.53 (m), 7.53 – 7.43 (m). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.40, 137.92, 132.62, 130.09, 129.20, 128.60.

## D. Synthesis of 2,5-Diphenylthiophene

2,5-Diphenylthiophene was prepared using a procedure adapted from Fu *et. al.*[3]



To a 100 mL round bottom flask equipped with a magnetic stirbar was added 1,4-diphenylbutadiyne (505 mg, 2.5 mmol), copper(I) iodide (71 mg, 0.375 mmol), 1,10-phenanthroline (90 mg, 0.50 mmol), sodium sulfide nonahydrate (6.0 g, 25 mmol), and DMF (25 mL). The mixture was stirred at 70 °C for 6 hrs. After cooling to room temperature the mixture was diluted with water (75 ml) and extracted with ethyl acetate (3 x 25 mL). The organic layers were combined and washed with saturated EDTA$_{(aq)}$ (2 x 50 mL), brine (50 mL), dried over anhydrous sodium sulfate and the solvent was removed *in vacuo* to afford the product as a light yellow solid that was used without further purification. (342 mg, 58%) $^1$H NMR (500 MHz, $CDCl_3$) δ 7.67 (m, 4H), 7.43 (m, 4H), 7.33 (s, 2H), 7.32 (tt, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 143.64, 134.34, 128.94, 127.53, 125.66, 124.01.

## E. Procedures for Diphenyldithiolodithiole Reactivity Control Experiment

### 1. Reactivity of Dithiolodithiole (Neat) at Inverse Vulcanization Temperature

Dithiolodithiole (6.0 mg, 18 μmol) was added to an NMR tube. The sample was heated to 175 °C for 30 min affording a clear red liquid and then allowed to cool to room temperature. $CDCl_3$ (0.6 mL) was added and the resulting red solution was analyzed via NMR spectroscopy. The solvent was then removed *in vacuo* and the residue was dissolved in THF for SEC analysis.

### 2. Reactivity of Dithiolodithiole with $S_8$ at Inverse Vulcanization Temperature

Dithiolodithiole (5.4 mg, 16 μmol) and $S_8$ (5.4 mg, 21 μmol) were briefly ground in a mortar and pestle to ensure adequate mixing. The mixture was transferred to an NMR tube and heated to 175 °C for 30 min affording a clear orange solution and then allowed to cool to room temperature. $CDCl_3$ (0.6 mL) was added and the resulting red solution was analyzed via NMR spectroscopy. The solvent was then removed *in vacuo* and the residue was dissolved in THF for SEC analysis.

### 3. Reactivity of Dithiolodithiole with DiPhDY at Inverse Vulcanization Temperature

Dithiolodithiole (5.7 mg, 17 μmol) and 1,4-diphenylbutadiyne (3.4 mg, 17 μmol) were briefly ground in a mortar and pestle to ensure adequate mixing. The mixture was transferred to an NMR tube and heated to 175 °C for 30 min affording a clear dark red solution and then allowed to cool to room temperature. $CDCl_3$ (0.6 mL) was added and the resulting red solution was analyzed via NMR spectroscopy. The solvent was then removed *in vacuo* and the residue was dissolved in THF for SEC analysis

## F. Fabrication and Testing of Lithium-Sulfur Coin Cell Batteries

A mixture of poly(S-*co*-DiPhDY) (10 wt% DiPhDY), conductive carbon, and poly(ethylene) in a 75:20:5 mass ratio respectively were ballmilled with chloroform to afford a slurry. The slurry was blade cast onto conductive carbon coated aluminum foil and allowed to dry under ambient conditions yielding an active layer with sulfur loading of ca. 0.75 mg/cm$^2$. Circular cathodes (1 cm$^2$) were punched and assembled with a poly(propylene) separator, lithium foil anode, and electrolyte (0.38 M lithium bis(trifluoromethane)sulfonimide, 0.38 M lithium nitrate in 1:1 v/v 1,3-dioxolane : 1,2-dimethoxyethane) into a CR2032 coin cell. Batteries were then cycled from 1.7 V to 2.6 V vs. Li/Li$^+$. Note: All capacity measurements reported are specific capacity based on total

# IV. Results and Discussion

## A. Characterization of Poly(S-*co*-DiPhDY) and Investigation of the Course of Polymerization

### 1. Isolation of Higher MW Poly(S-*co*-DiPhDY) Fraction

The isolation of a higher molecular weight fraction of poly(S-*co*-DiPhDY) from any oligomeric and small molecule components of the inverse vulcanizate was completed in order to interrogate the repeating unit structure of poly(S-*co*-DiPhDY). The majority of lower molecular weight species present in a sample of poly(S-*co*-DiPhDY) prepared with 60 wt% DiPhDY were able to be removed with a series of precipitations into hexanes. Residual small molecule contaminants were then easily separated by flash chromatography affording a higher molecular weight fraction of poly(S-*co*-DiPhDY) which was highly soluble in polar aprotic solvents allowing for characterization by SEC (Figure S1) and CV (Figure 1). SEC indicated that the polymer had a low apparent molecular weight and fairly broad polydispersity ($M_{n\ apparent}$ = 2300 g/mol, $M_w/M_n$ = 1.8) consistent with previous high sulfur content copolymers prepared *via* inverse vulcanization.

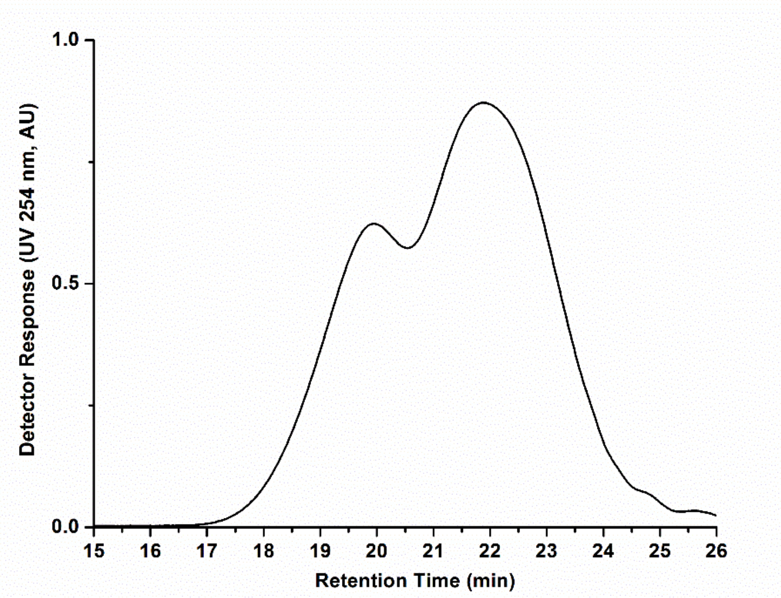


**Figure S1.** SEC Trace of higher molecular weight poly(S-*co*-DiPhDY) ($M_{n\ apparent}$ = 2300 g/mol, $M_w/M_n$ = 1.8)

## 2. Diphenyldithiolodithiole Reactivity Control Experiments

Diphenyldithiolodithiole (**1**, Scheme 1) was identified as a soluble component of the crude copolymerization mixture resulting from the inverse vulcanization of sulfur with low DiPhDY (5 wt%) feed ratios. To investigate the role of diphenyldithiolodithiole in the copolymerization it was synthesized and isolated according to a previously reported method.[2] The interaction of diphenyldithiolodithiole with the various components of the inverse vulcanization reaction was interrogated applying inverse vulcanization conditions (*i.e.* thermal treatment in the melt) to diphenyldithiolodithiole in the bulk, with additional sulfur, and with another equivalent of DiPhDY. SEC revealed that no significant homopolymerization of **1** occurred upon heating to 175 °C nor was copolymerization with additional sulfur observed (Figure S2). However, analysis of the thermally treated samples via NMR (Figures S3 and S4) revealed the appearance of an second small molecule component with resonances characteristic of a 2,5-diphenylthiophene derivatives reported in the literature.[4] 2,5-Diphenylthiophene was also synthesized to serve as a model compound for further comparison of the NMR spectra (Figure S5). The splitting patterns of the $^1$H NMR signals and their relative chemical shifts were found to be similar to the small molecule that was formed upon thermal treatment of diphenyldithiolodithiole serving to further corroborate the proposed copolymerization pathway.

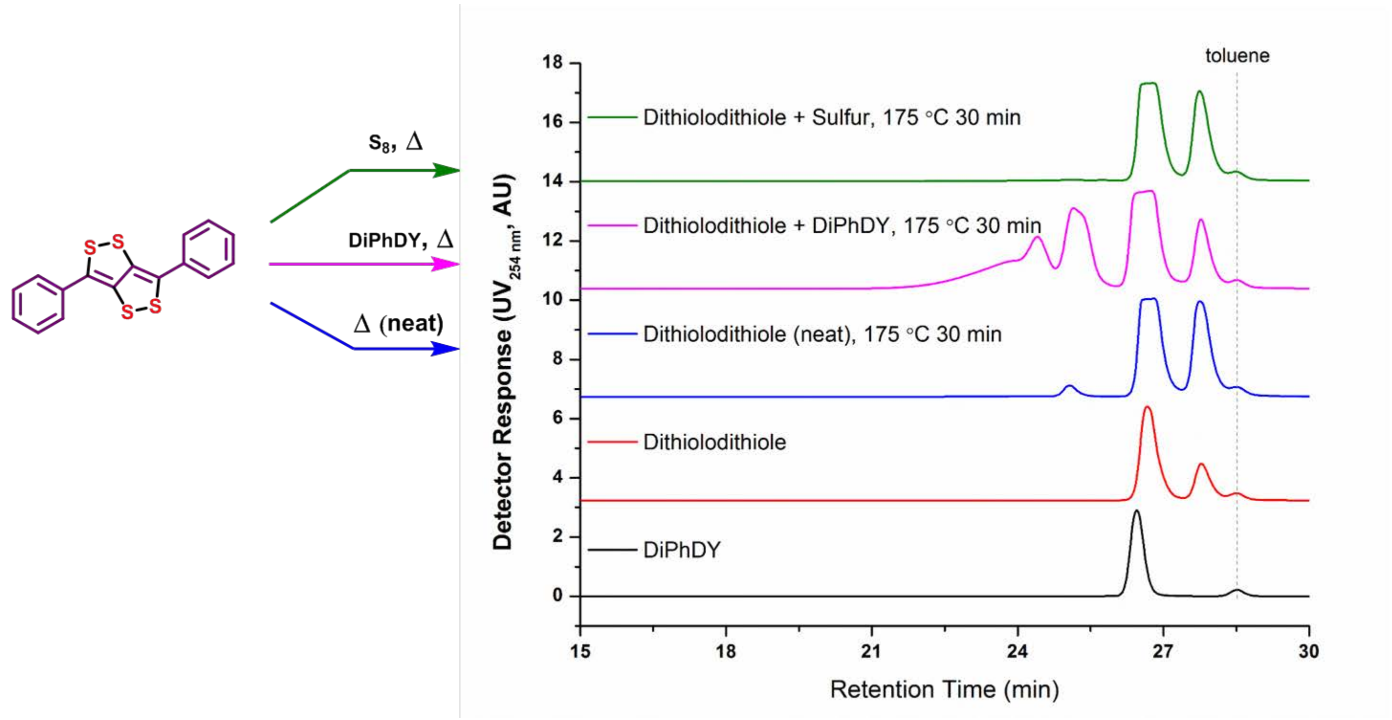


**Figure S2.** SEC traces of 1,4-diphenylbutadiyne, diphenyldithiolodithiole, reaction mixture of thermally treated (T = 175 °C) diphenyldithiolodithiole neat, with DiPhDY, and with elemental sulfur (bottom to top respectively).

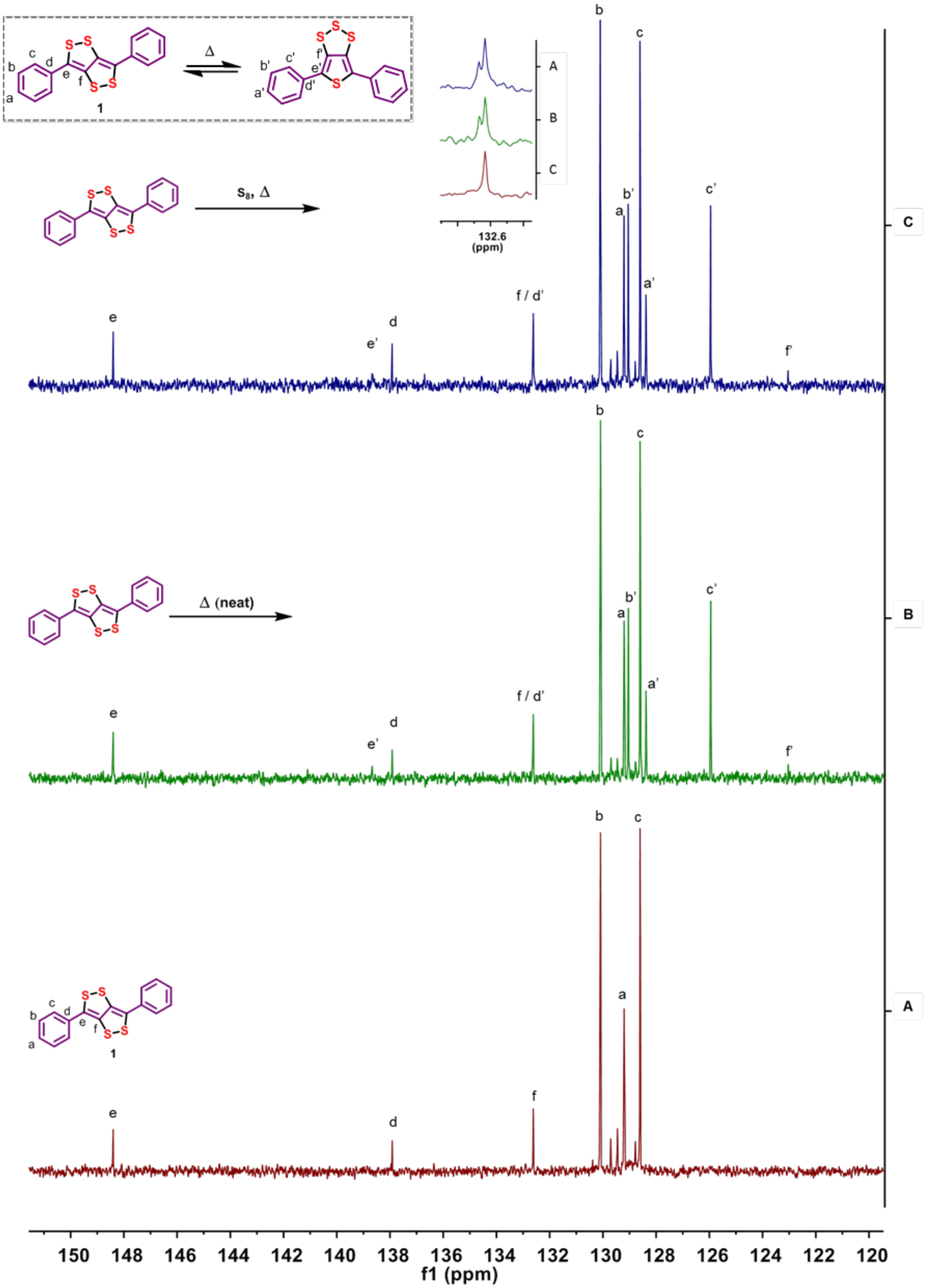


**Figure S3.** Annotated $^{13}$C NMR (100 MHz, $CDCl_3$) spectra of diphenyldithiolodithiole **1** (A, bottom) and reaction mixtures resulting from the thermal treatment (175 °C) of **1** neat (B, middle) and with $S_8$ (C, top).

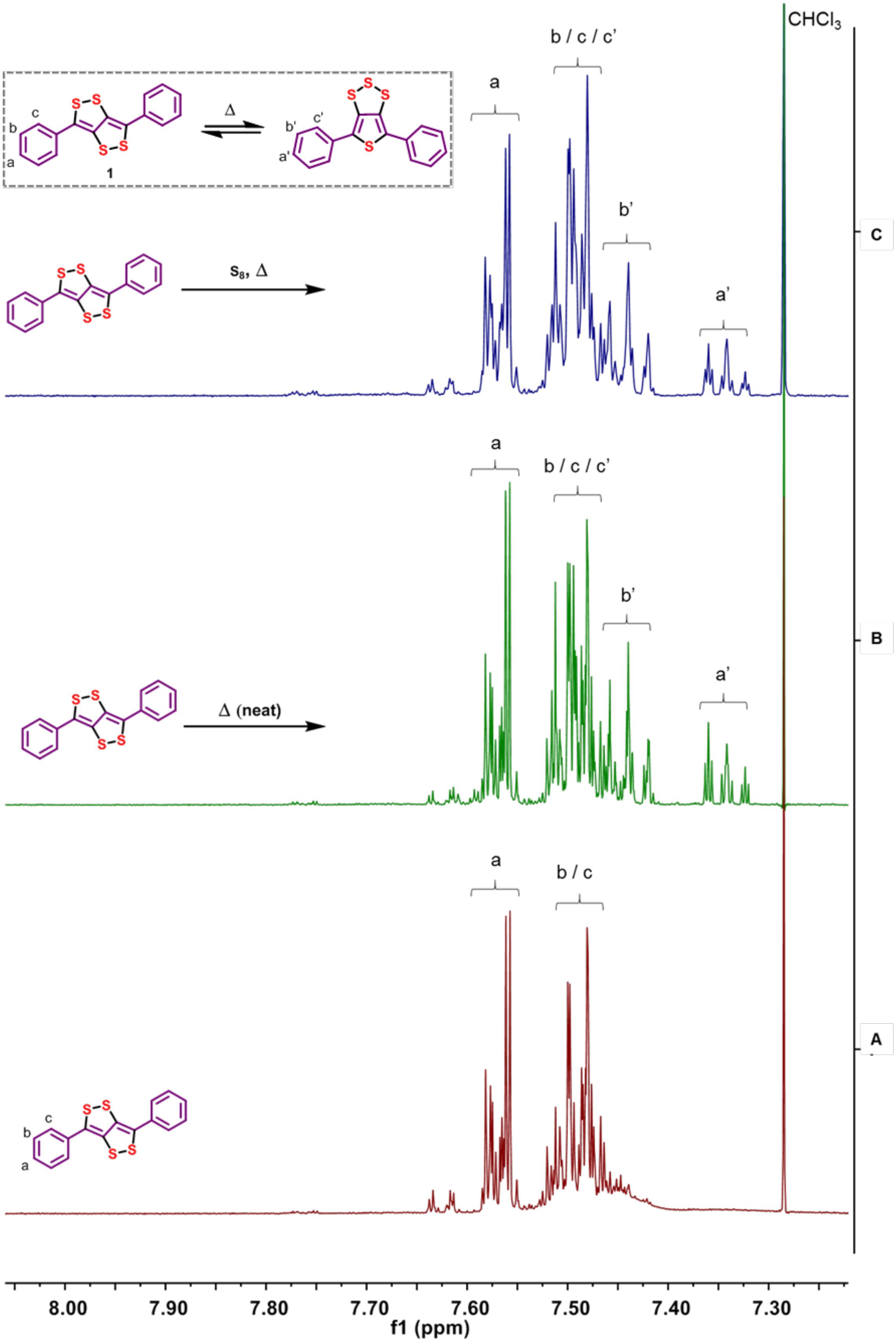


**Figure S4.** Annotated $^{1}$H NMR (400 MHz, $CDCl_3$) spectra of diphenyldithiolodithiole **1** (A, bottom) and reaction mixtures resulting from the thermal treatment (175 °C) of **1** neat (B, middle) and with $S_8$ (C, top).

## 3. 2,5-Diphenylthiophene as a Model Compound for NMR Comparison

2,5-Diphenylthiophene was prepared to serve as a model compound for comparison of NMR analysis of the sulfur / DiPhDY inverse vulcanization reaction mixture. $^1$H NMR (Figure S5) revealed similar signals, notably the triplet of triplets like signal at 7.32 ppm and second order multiplet at 7.43 ppm, to the new signals observed upon thermal treatment of diphenyldithiolodithiole at 7.34 and 7.43 ppm respectively (Figure S4). The signal observed further downfield at 7.68 ppm could not be directly compared due to overlap of the diphenyldithiolodithiol signals.

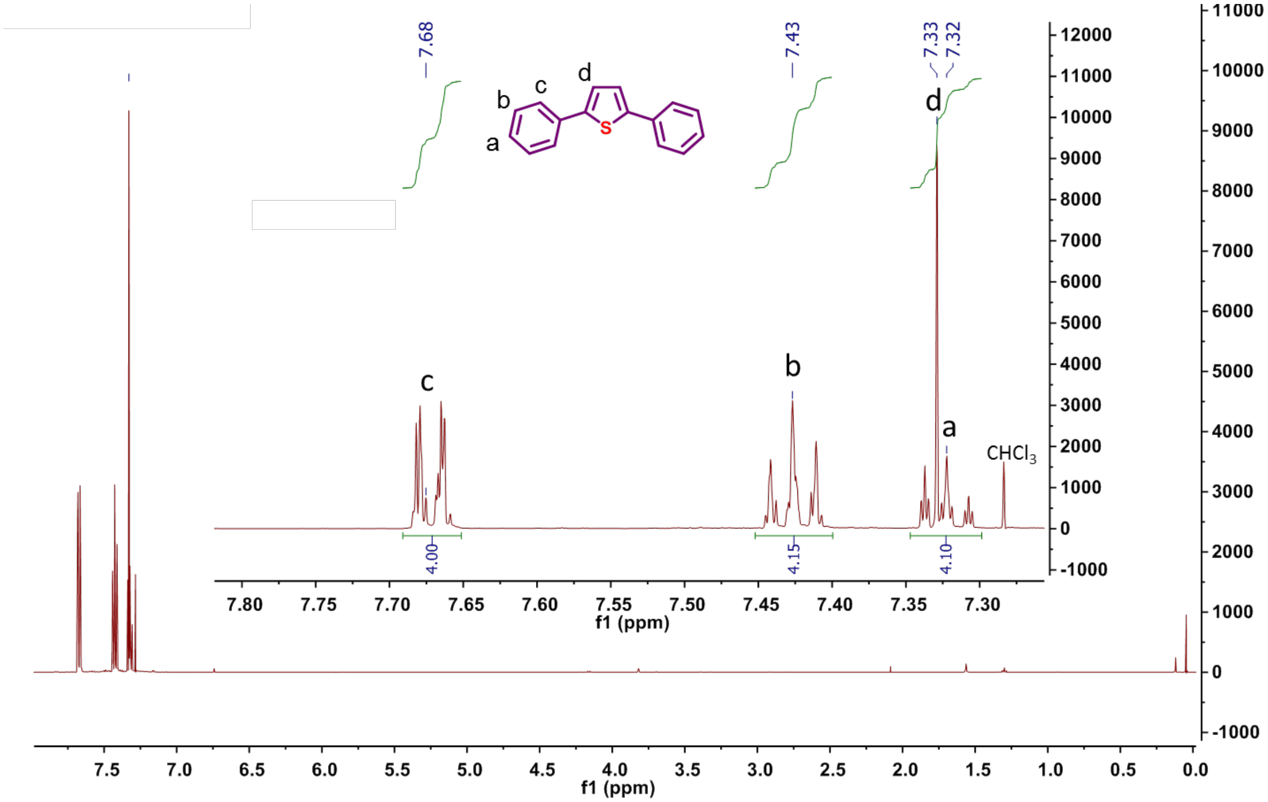


**Figure S5.** Annotated $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2,5-diphenylthiophene.

## 4. Laser Desorption Ionization Mass Spectrometry (LDI-MS)

LDI-MS was performed to confirm the presenence of polysulfane connectivity in the poly(S-*co*-DiPhDY) inverse vulcanizate. The LDI-MS spectrum (Figure SS6) showed the presence of a complex mixture of polymeric species with the notable feature of distrubutions spaced by 32 m/z units corresponding to cantentated S-S connectivity in poly(S-*co*-DiPhDY).

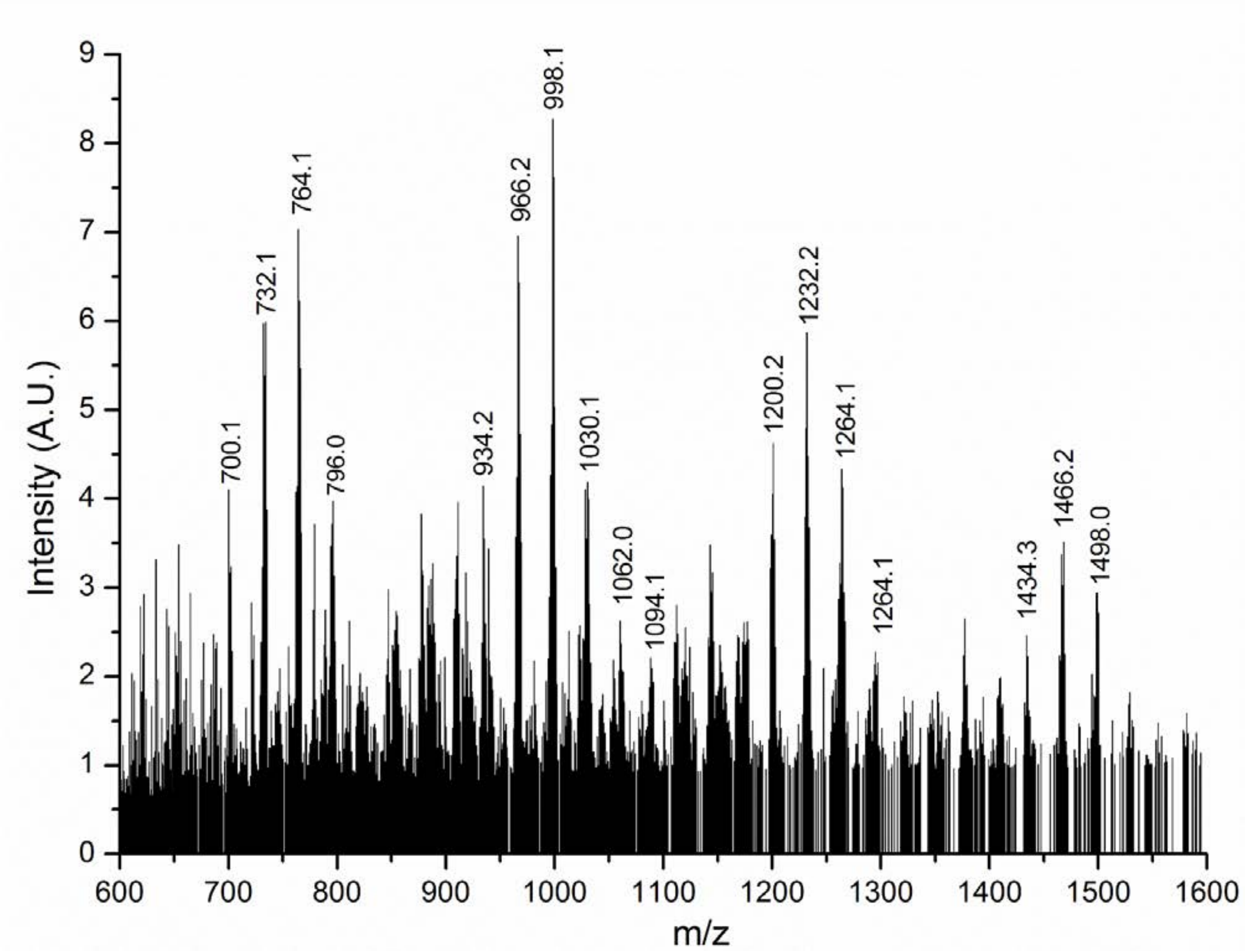
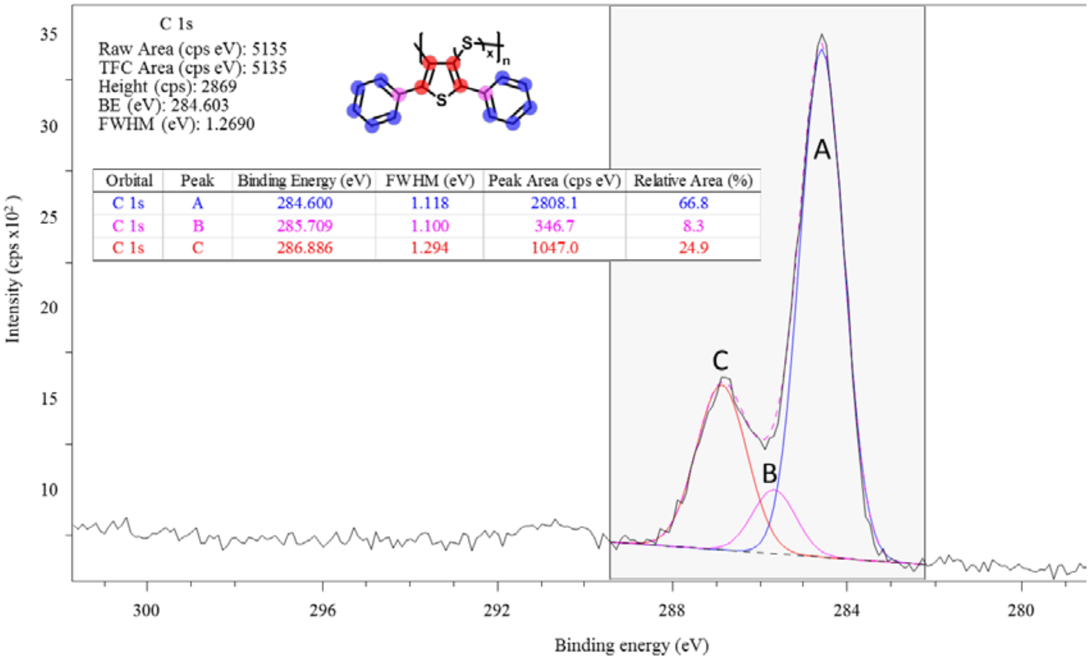


**Figure S6.** LDI Mass Spectrum of poly(S-*co*-DiPhDY) (20 wt% DiPhDY)

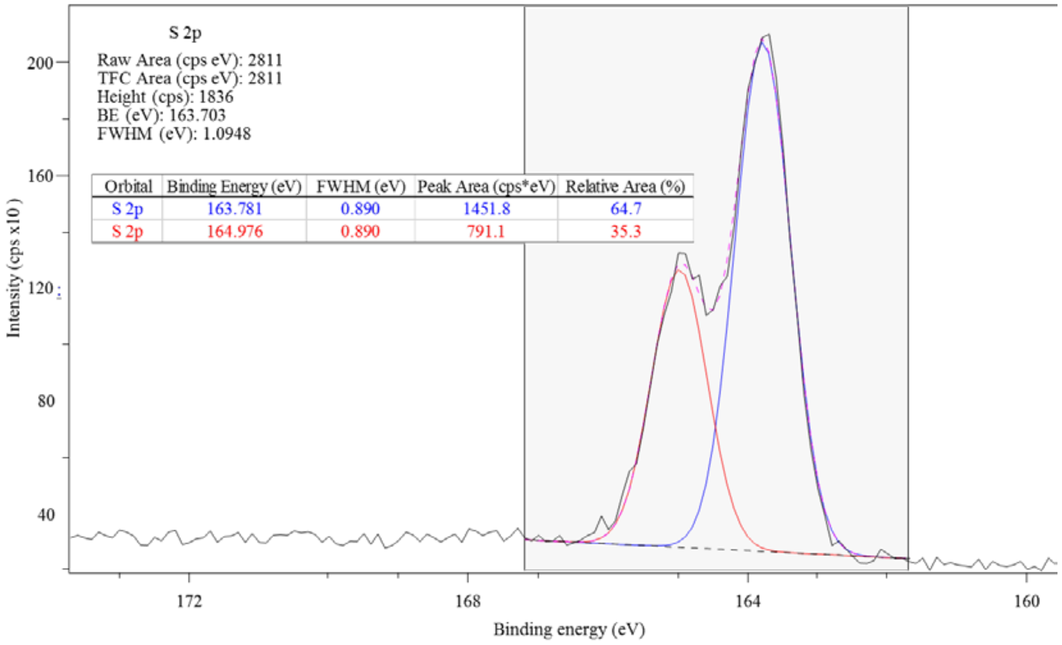
## 5. X-Ray Photoelectron Spectroscopy (XPS)

X-Ray photoelectron spectroscopy revealed three discernable C species present in relative abundances that corroborate the proposed structure of the organosulfur component of poly(S-*co*-DiPhDY) (Figure S7). XPS also served to corroborate the electrochemical evidence that the oxidation state of the S contained within poly(S-*co*-DiPhDY) is similar to elemental sulfur (Figure S8) with the S 2p region observed to be analogous with the XPS spectra of $S_8$.[5]



| Orbital | Peak | Binding Energy (eV) | FWHM (eV) | Peak Area (cps eV) | Relative Area (%) |
|---|---|---|---|---|---|
| C 1s | A | 284.600 | 1.118 | 2808.1 | 66.8 |
| C 1s | B | 285.709 | 1.100 | 346.7 | 8.3 |
| C 1s | C | 286.886 | 1.294 | 1047.0 | 24.9 |

**Figure S7.** XPS Spectra of poly(S-*co*-DiPhDY) (20 wt% DiPhDY) highlighting C 1s



| Orbital | Binding Energy (eV) | FWHM (eV) | Peak Area (cps*eV) | Relative Area (%) |
|---|---|---|---|---|
| S 2p | 163.781 | 0.890 | 1451.8 | 64.7 |
| S 2p | 164.976 | 0.890 | 791.1 | 35.3 |

**Figure S8.** XPS Spectra of poly(S-*co*-DiPhDY) (20 wt% DiPhDY) highlighting S 2p

## B. Thermogravimetric Analysis of 1,4-Diphenylbutadiyne

TGA of DiPhDY (Figure S9) was performed to provide a reference thermogram for the weight loss processes observed with poly(S-*co*-DiPhDY) prepared with various S:DiPhDY feed ratios.

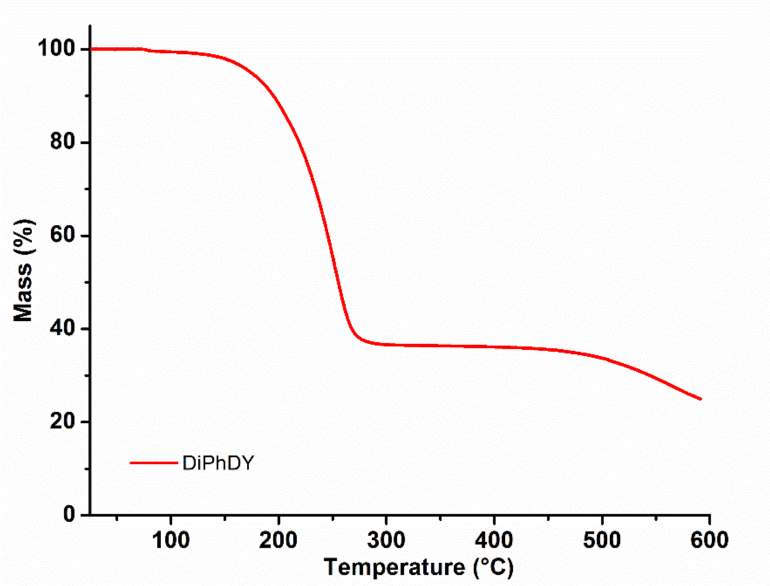


**Figure S9.** TGA thermogram of 1,4-diphenylbutadiyne

## C. Li-S Battery Performance of Poly(S-*co*-DiPhDY) with Various S:DiPhDY Compositions

Lithium-sulfur coin cells (2032 type) were fabricated with poly(S-*co*-DiPhDY) of various S:DiPhDY compositions as the active cathode material and cycled at a rate of C/5 from 1.7 V to 2.6 V vs. Li/Li$^+$. Comparison of the cycling performance revealed improved performance (*i.e.* higher capacity) with copolymer compositions prepared with higher sulfur content (lower DiPhDY loading). Excellent capacity retention was observed with copolymers prepared with 10, 20, and 40 wt% DiPhDY while the isolated higher molecular weight poly(S-*co*-DiPhDY) suffered from more pronounced capacity fading.

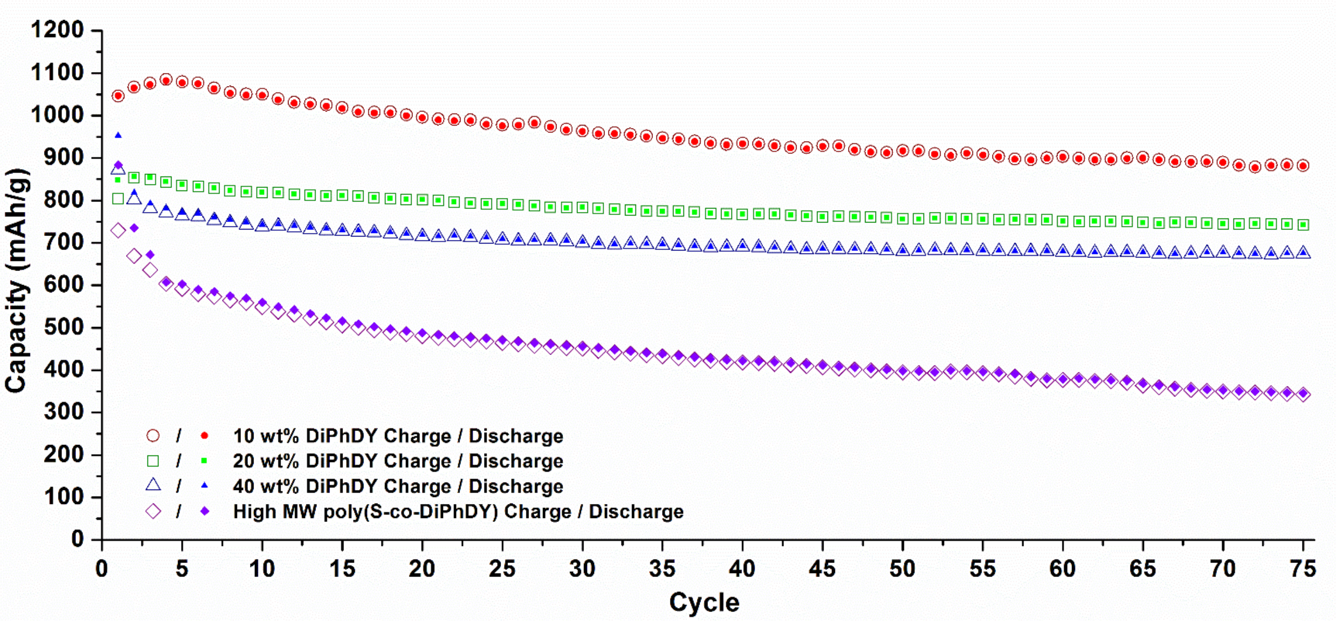


**Figure S10.** Cycling performance at C/5 of Li-S batteries fabricated with poly(S-*co*-DiPhDY) of various compositions. All capacities based on sulfur content.

## V. References

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