

## Supporting Information

### High Refractive Index Polyvinylsulfide Materials

#### Prepared By Selective Radical Mono-Addition Thiol-Yne Chemistry

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#### Syntheses:

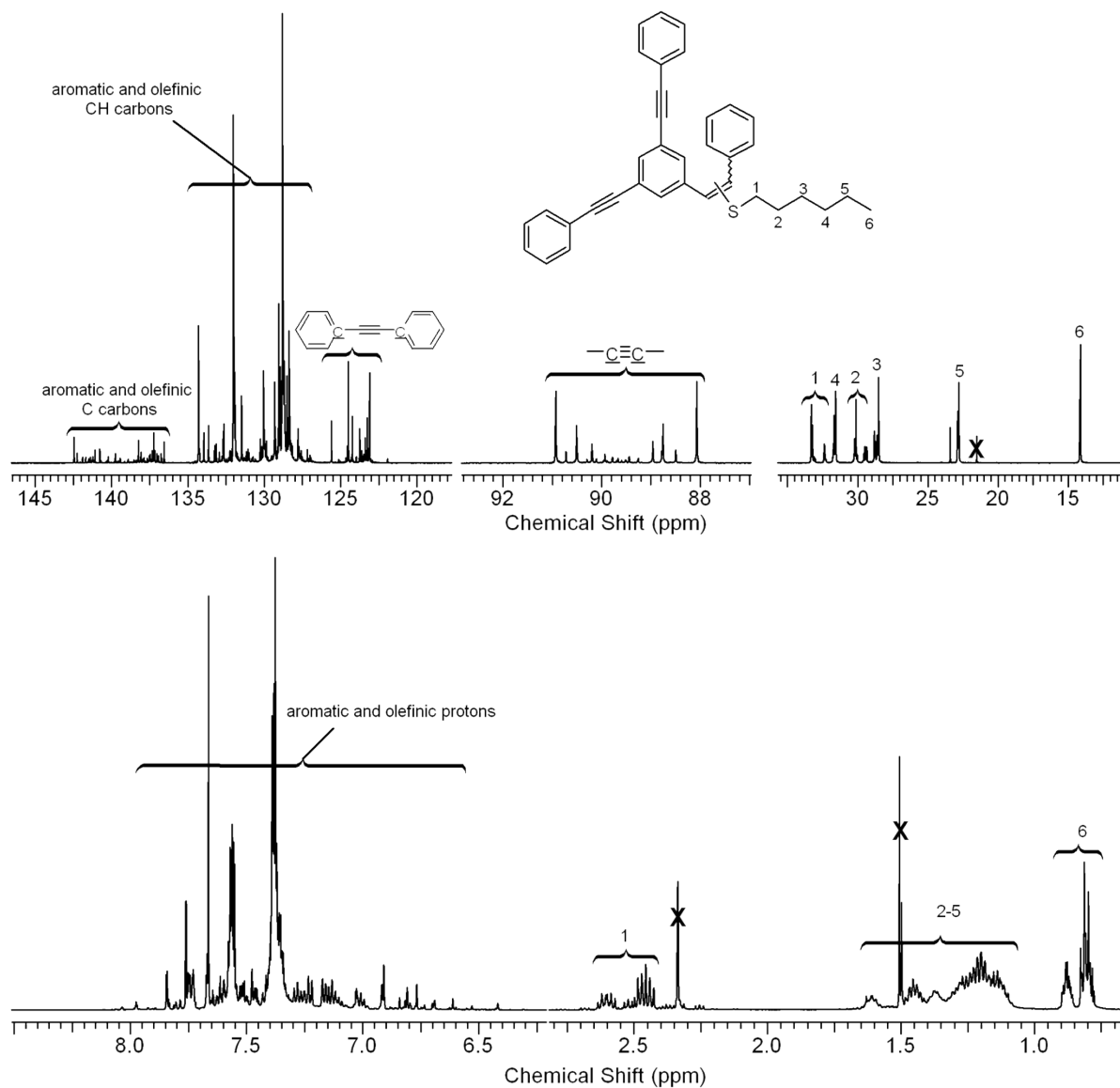
##### *Synthesis of model compounds **B<sub>2b</sub>** and **b<sub>3</sub>**:*

1,3,5-Tris(phenylethynyl)benzene (189 mg, 0.5 mmol), hexanethiol (65 mg, 0.525 mmol or 196 mg, 1.575 mmol), AIBN (12.3 mg, 0.075 mmol) and dry toluene (1.5 ml) were mixed together, stirred and purged with argon for 10 min. The reaction mixture was heated at 90°C for 2 hours. The solvent was then removed by rotary evaporation and the sample was analyzed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

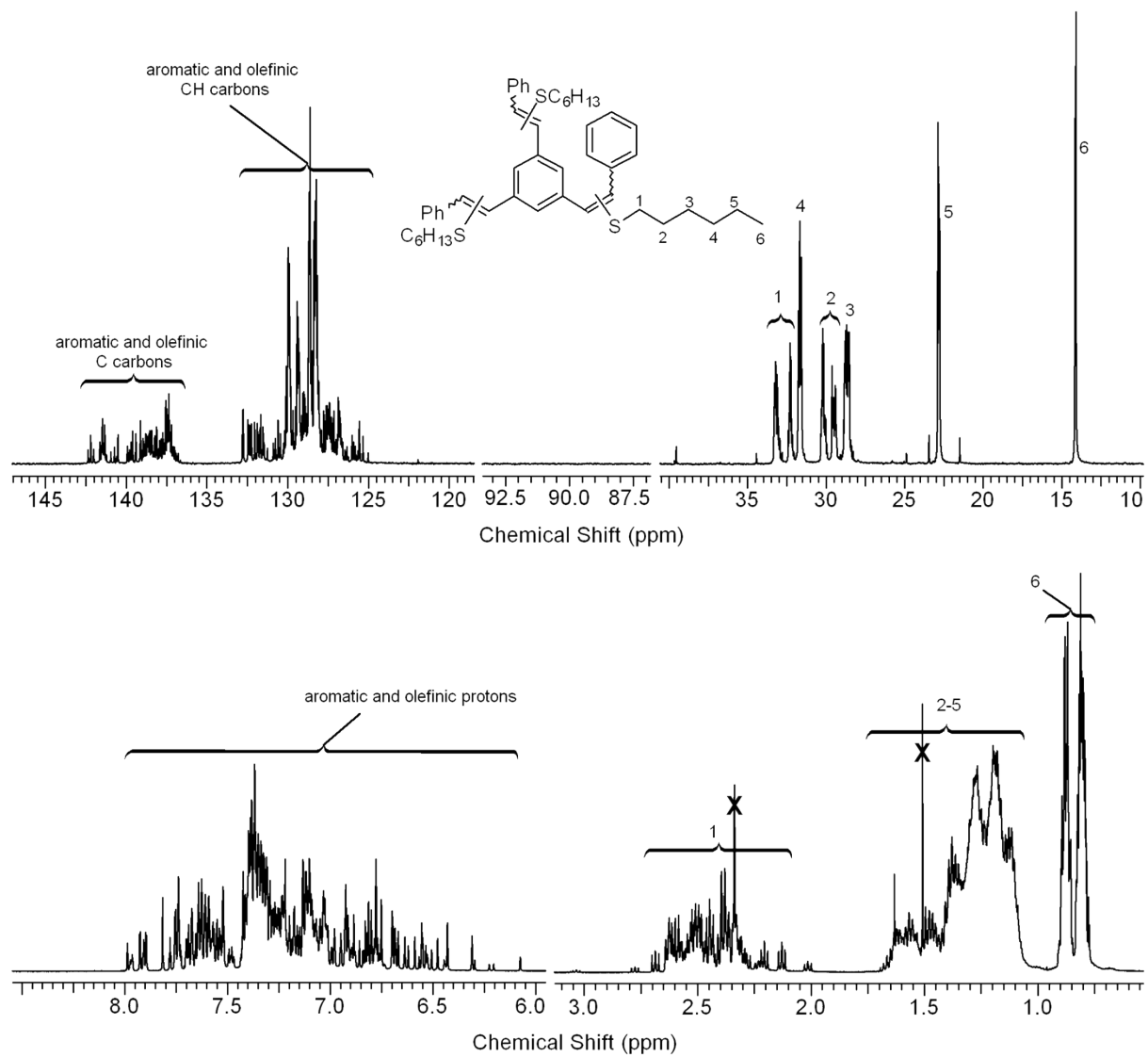
##### *Synthesis of the model compound 1,2-dihexyldisulfide:*

One drop of hexanethiol was dissolved in 0.6 ml of deuterated dichloromethane in a NMR tube. A few drops of triethylamine and a few chips of iodine were added. The oxidation of the thiol to disulfide was followed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

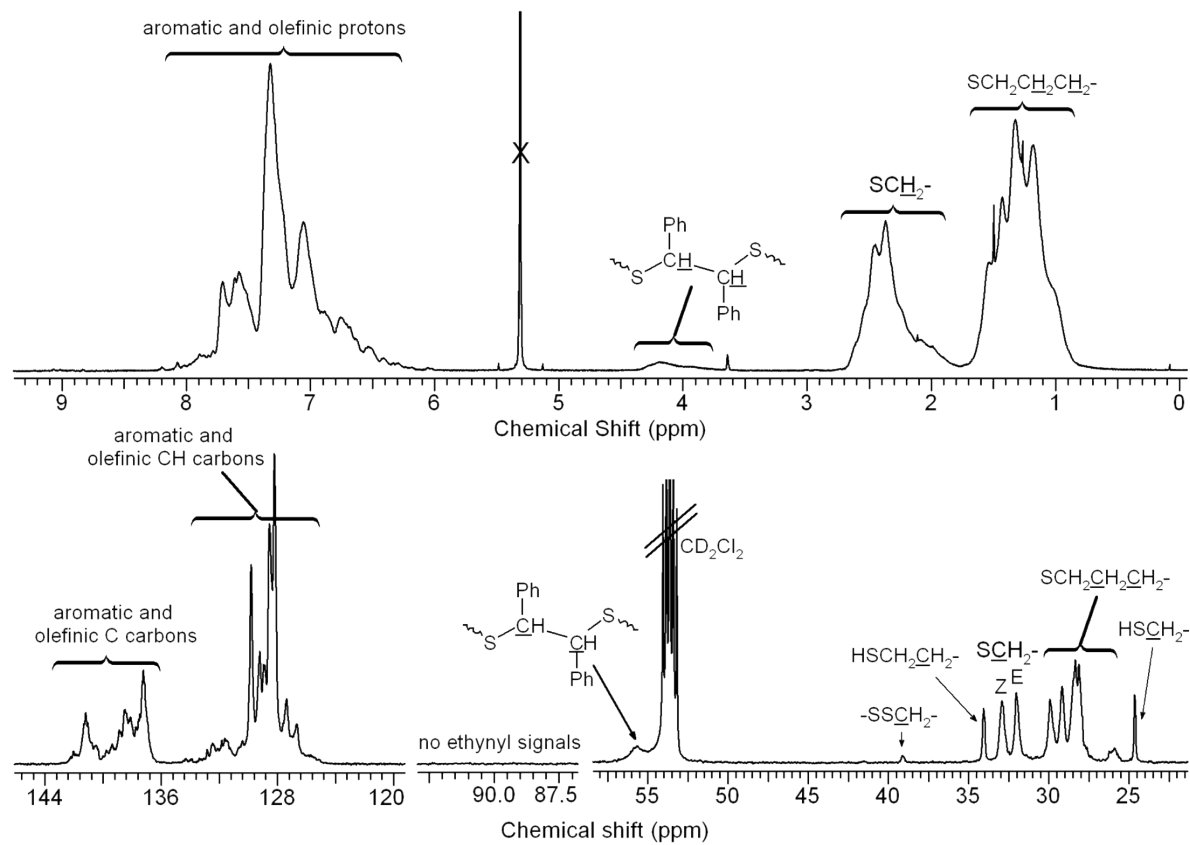
**NMR spectra:**



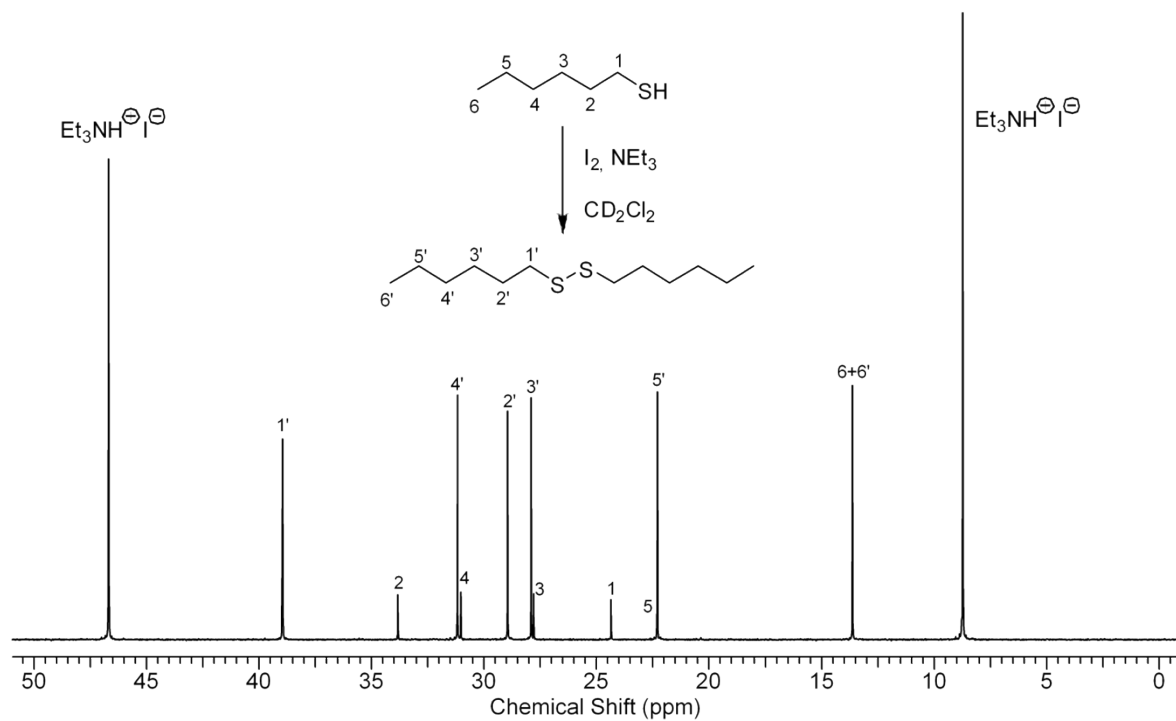
**Figure S1.** <sup>13</sup>C and <sup>1</sup>H NMR spectra of the model compound **B<sub>2b</sub>** (solvent: CD<sub>2</sub>Cl<sub>2</sub>). The reaction product is not pure **B<sub>2b</sub>** as intended from monomer stoichiometry but also contains unreacted **B<sub>3</sub>** and higher substituted compounds (**Bb<sub>2</sub>** and **b<sub>3</sub>**) but in low amounts.



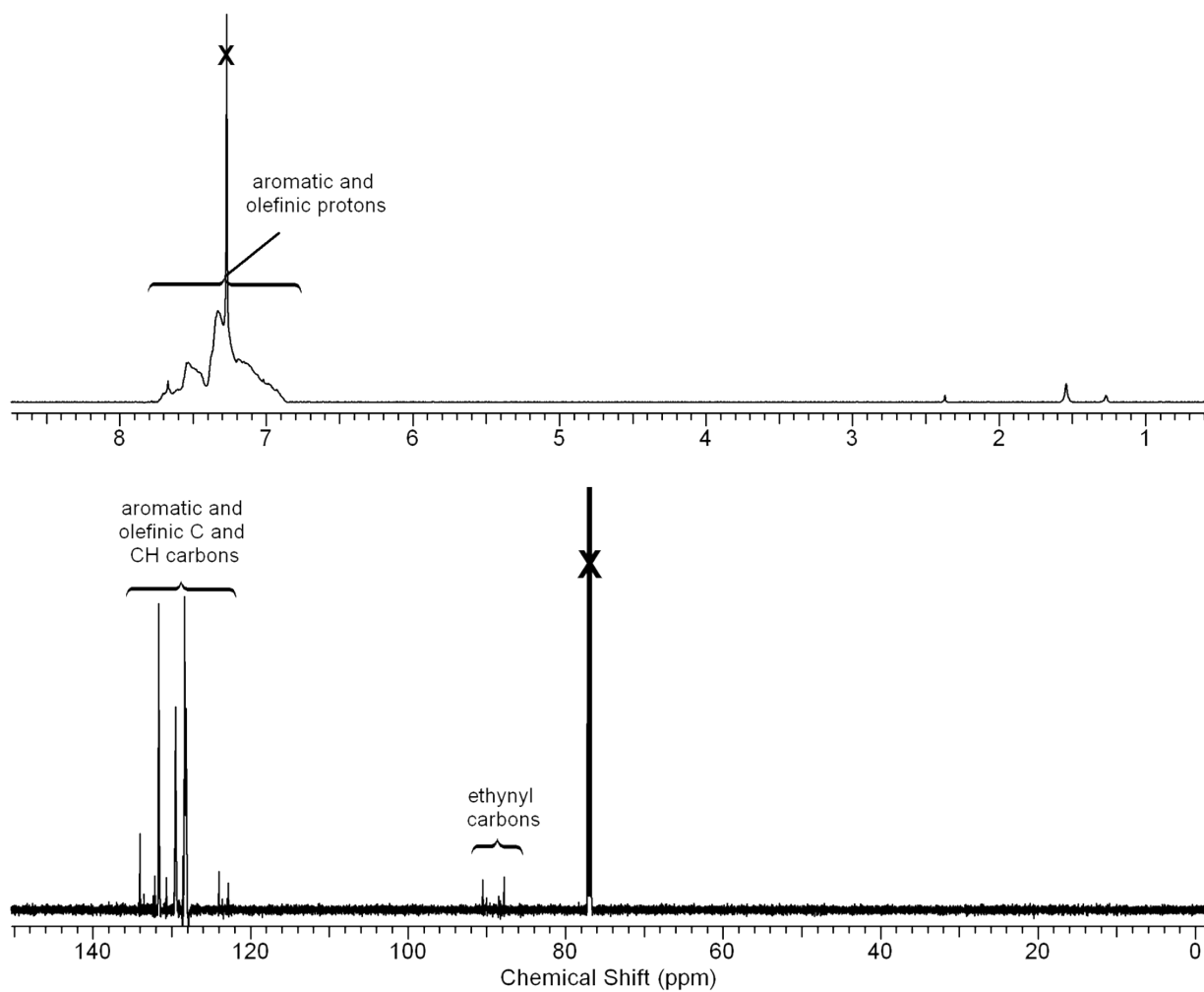
**Figure S2.** <sup>13</sup>C and <sup>1</sup>H NMR spectrum of the model compound **b**<sub>3</sub> (solvent: CD<sub>2</sub>Cl<sub>2</sub>).



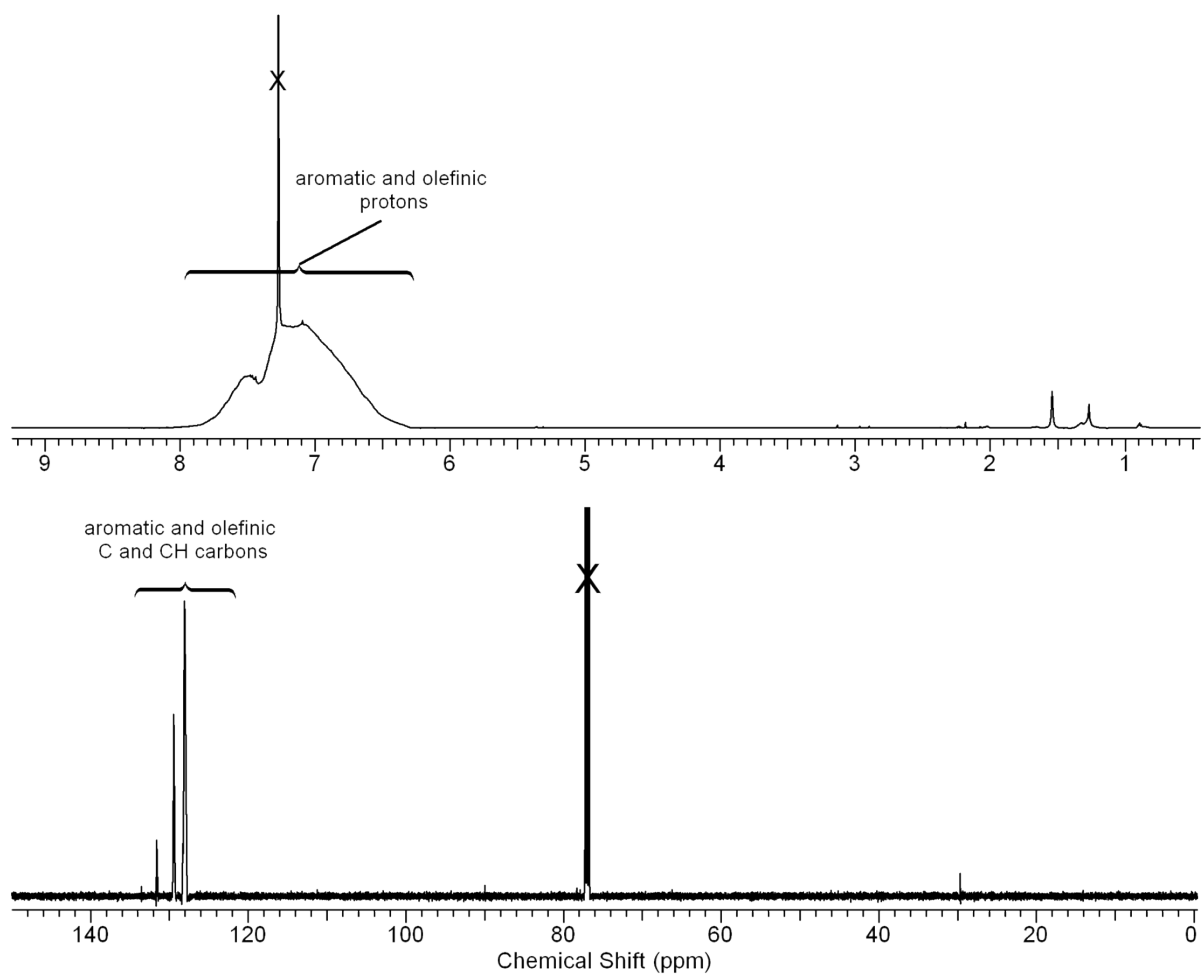
**Figure S3.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of **hb-P8** (solvent:  $\text{CD}_2\text{Cl}_2$ ).



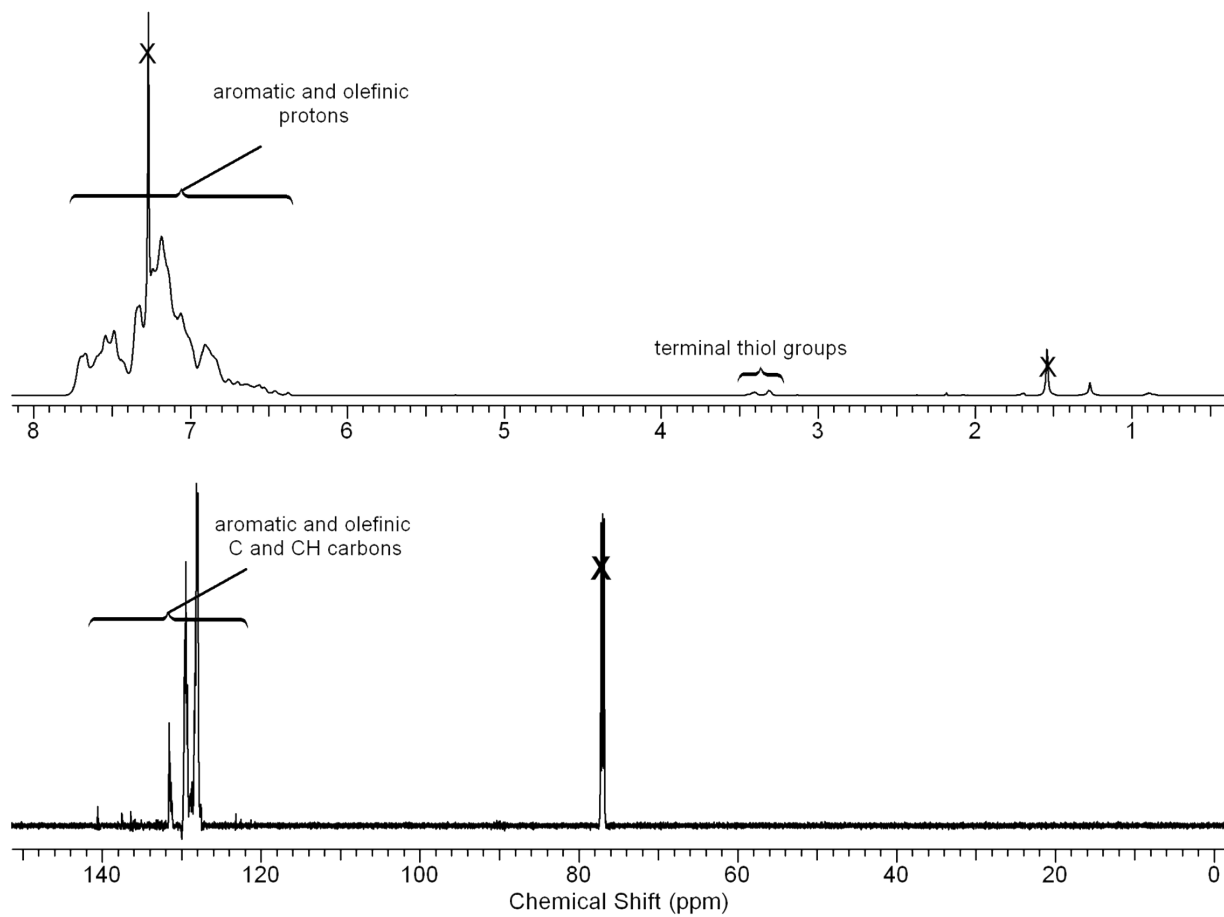
**Figure S4.**  $^{13}\text{C}$  NMR spectrum of the model compound 1,2-dihexyldisulfide (solvent:  $\text{CD}_2\text{Cl}_2$ ).



**Figure S5.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of **hb-P9** (solvent:  $\text{CDCl}_3$ ).



**Figure S6.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of **hb-P10** (solvent:  $\text{CDCl}_3$ ).



**Figure S7.** <sup>1</sup>H and <sup>13</sup>C NMR spectrum of lin-P4 (solvent: CDCl<sub>3</sub>).

Miscellaneous:

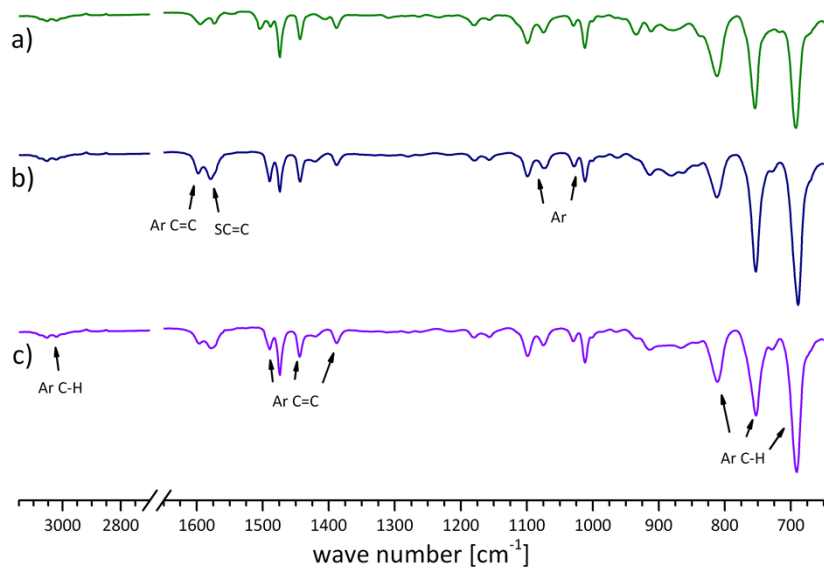


Figure S8. IR spectra of lin-P4 (A), hb-P9 (B) and hb-P10 (C).

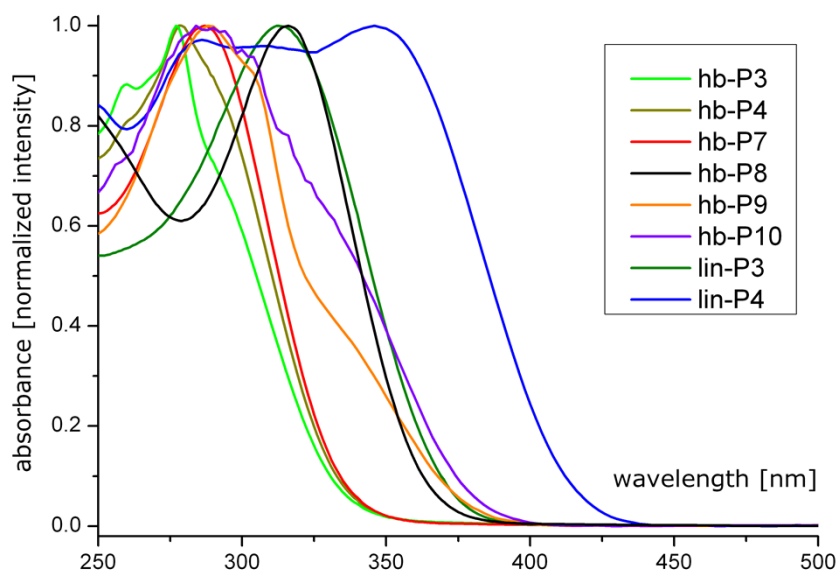


Figure S9. UV-Vis spectra of PVS materials in CH<sub>2</sub>Cl<sub>2</sub>.



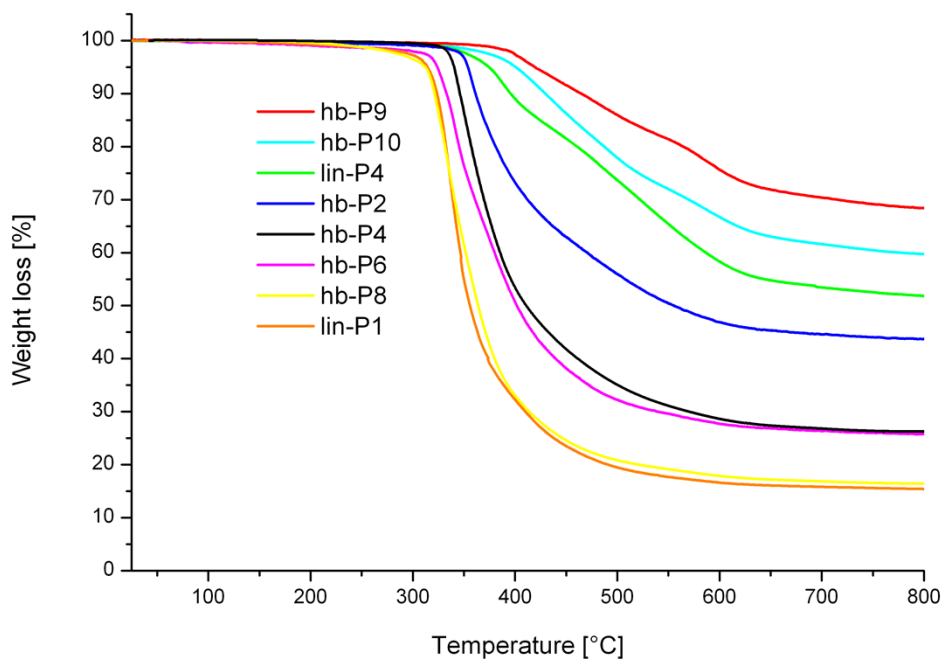


Figure S10. TGA curves of linear and hb-PVS materials in nitrogen atmosphere.

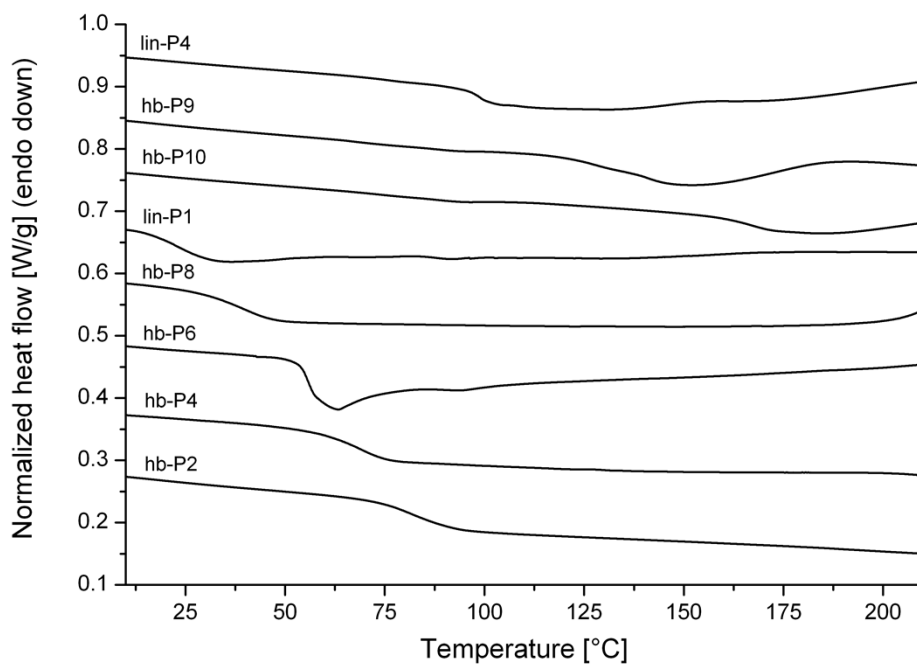
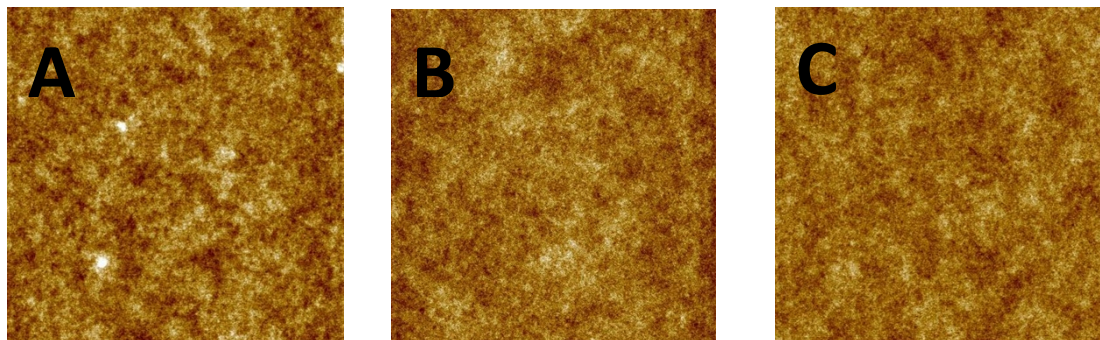


Figure S11. DSC traces of linear and hyperbranched PVS materials.



**Figure S12.** AFM height images ( $10\ \mu\text{m} \times 10\ \mu\text{m}$ ) of thin films of **lin-P3** (A), **hb-P3** (B) and **hb-P7** (C).