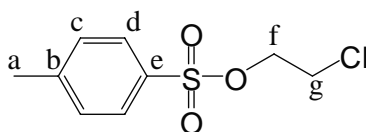


## SUPPLEMENTARY INFORMATION

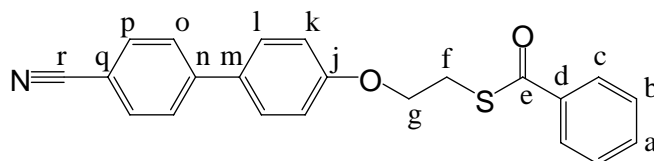
### 1. $^{13}\text{C}$ NMR Resonances of Select Compounds

All  $^{13}\text{C}$  NMR spectra were obtained using a Varian Mercury 300 spectrometer (corresponding to 74.5 MHz for  $^{13}\text{C}$ ), recorded in  $\text{CDCl}_3$ , and referenced to tetramethylsilane. The authors referred to information compiled in the Spectral Database for Organic Compounds (available online at [http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct\\_frame\\_top.cgi](http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi)) in the process of assigning  $^{13}\text{C}$  NMR resonances.

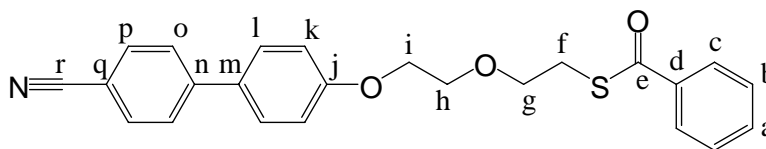
**2-Chloroethyl-*p*-toluenesulfonate (1).**  $^{13}\text{C}$  NMR:  $\delta$  = 145.30 (e), 132.44 (b), 130.00 and 127.97 (c and d), 69.02 (f), 40.83 (g), 21.67 (a).



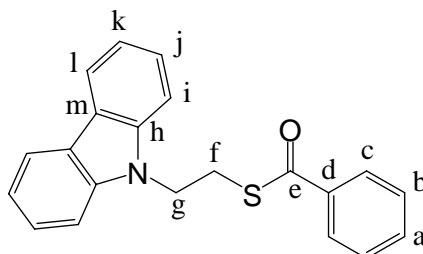
**4'-(2-(Benzoylthio)ethoxy)[1,1'-biphenyl]-4-carbonitrile (3).**  $^{13}\text{C}$  NMR:  $\delta$  = 191.40 (e), 159.00 (j), 145.11 (n), 136.64 (d), 133.69 (a), 132.57 (p), 131.89 (m), 128.70 and 127.30 (b and c), 128.43 (l), 127.13 (o), 119.09 (r), 115.21 (k), 110.14 (q), 66.70 (g), 28.13 (f).



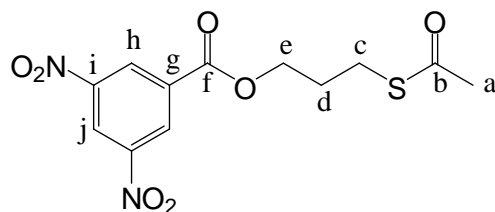
**4'-(2-(2-(Benzoylthio)ethoxy)ethoxy) [1,1'-biphenyl]-4-carbonitrile (6).**  $^{13}\text{C}$  NMR:  $\delta$  = 191.54 (e), 159.35 (j), 145.12 (n), 136.82 (d), 133.48 (a), 132.54 (p), 131.63 (m), 128.61 and 127.23 (b and c), 128.30 (l), 127.07 (o), 119.10 (r), 115.22 (k), 110.06 (q), 70.05 and 69.38 (h and i), 67.50 (g), 28.65 (f).



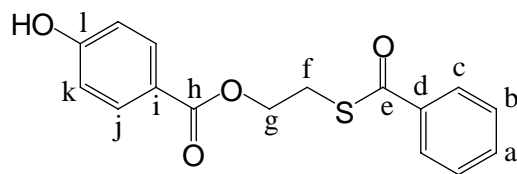
**Thiobenzoic acid S-[2-(9-carbazolyl)ethyl] ester (8).**  $^{13}\text{C}$  NMR:  $\delta$  = 191.73 (e), 140.07 (h), 136.71 (d), 133.73 (a), 128.74 and 127.35 (b and c), 125.91 (j), 122.98 (m), 120.40 (l), 119.26 (k), 108.74 (i), 42.42 (g), 27.28 (f).



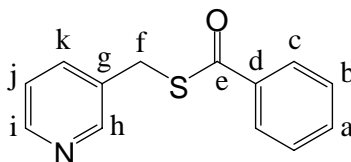
**3,5-Dinitrobenzoic acid 3-(acetylthio)propyl ester (10).**  $^{13}\text{C}$  NMR:  $\delta$  = 195.36 (b), 162.49 (f), 148.67 (i), 133.81 (g), 129.52 (h), 122.47 (j), 65.21 (e), 30.64 (a), 28.68 and 25.50 (c and d).



**4-Hydroxybenzoic acid 2-(benzoylthio)ethyl ester (12).**  $^{13}\text{C}$  NMR:  $\delta$  = 191.42 (e), 166.27 (h), 160.24 (l), 136.65 (d), 133.68 (a), 132.09 (j), 128.70 and 127.32 (b and c), 122.13 (i), 115.28 (k), 63.11 (g), 27.86 (f).

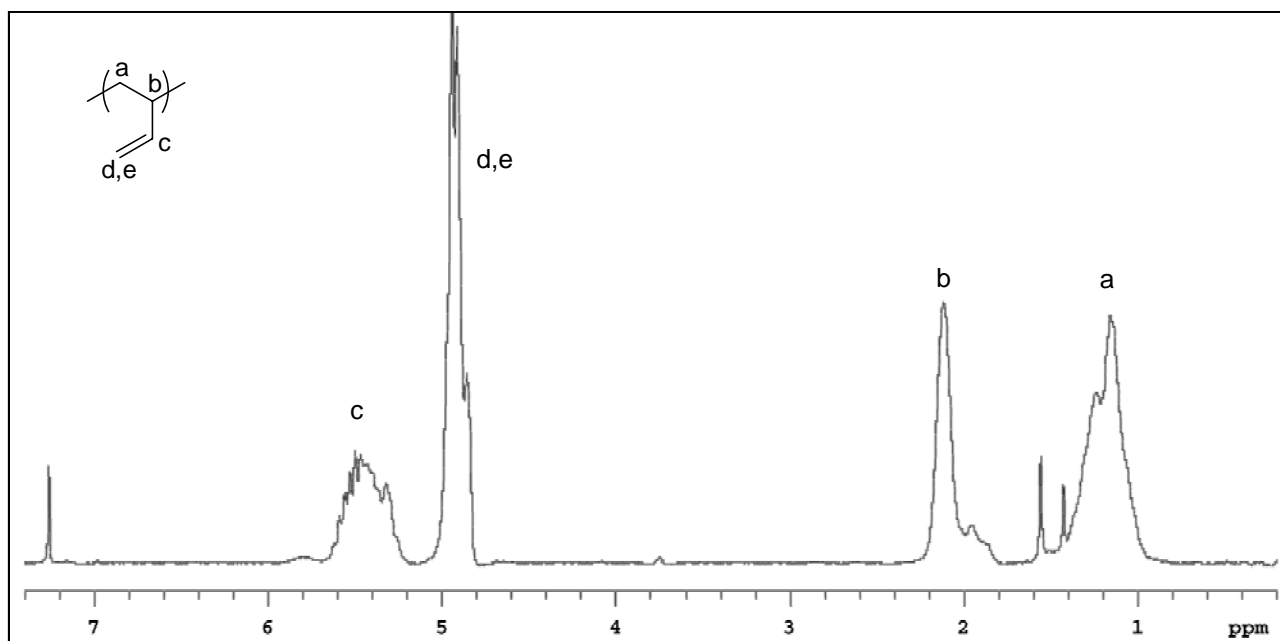


**Thiobenzoic acid S-[3-pyridinylmethyl] ester (13).**  $^{13}\text{C}$  NMR:  $\delta$  = 190.74 (e), 150.14 (h), 148.62 (i), 136.48 and 136.42 (d and k), 133.70 and 133.65 (a and g), 128.71 and 127.31 (b and c), 123.46 (j), 30.38 (f).

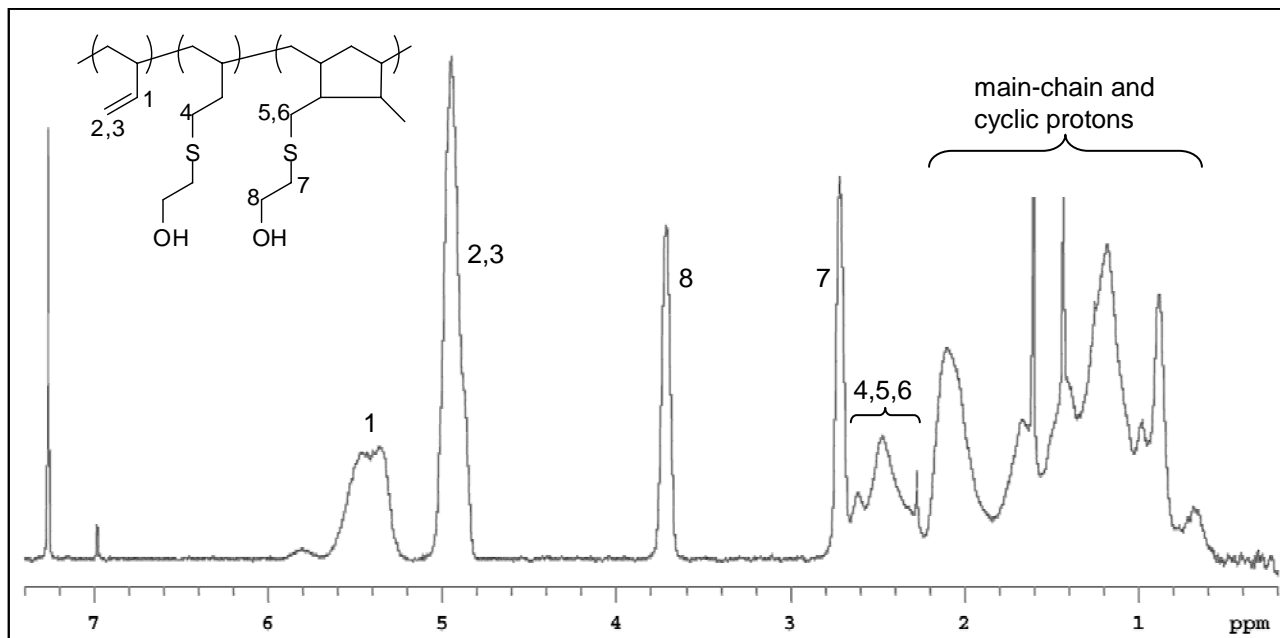


## 2. $^1\text{H}$ NMR Spectra of Select Functionalized Polymers

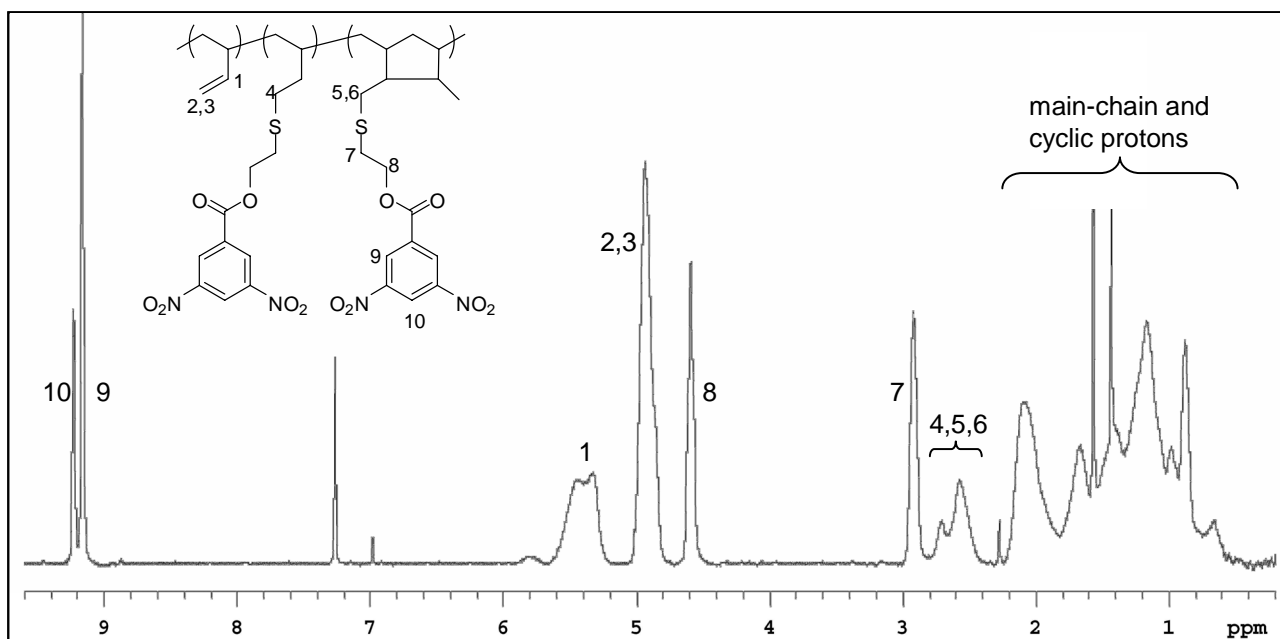
All spectra were taken in  $\text{CDCl}_3$ , resulting in a solvent peak in each case at  $\delta = 7.24$  ppm. Peaks near 1.6 ppm correspond to water, and visible peaks at  $\delta = 6.97$ , 2.27, and 1.43 ppm belong to BHT.



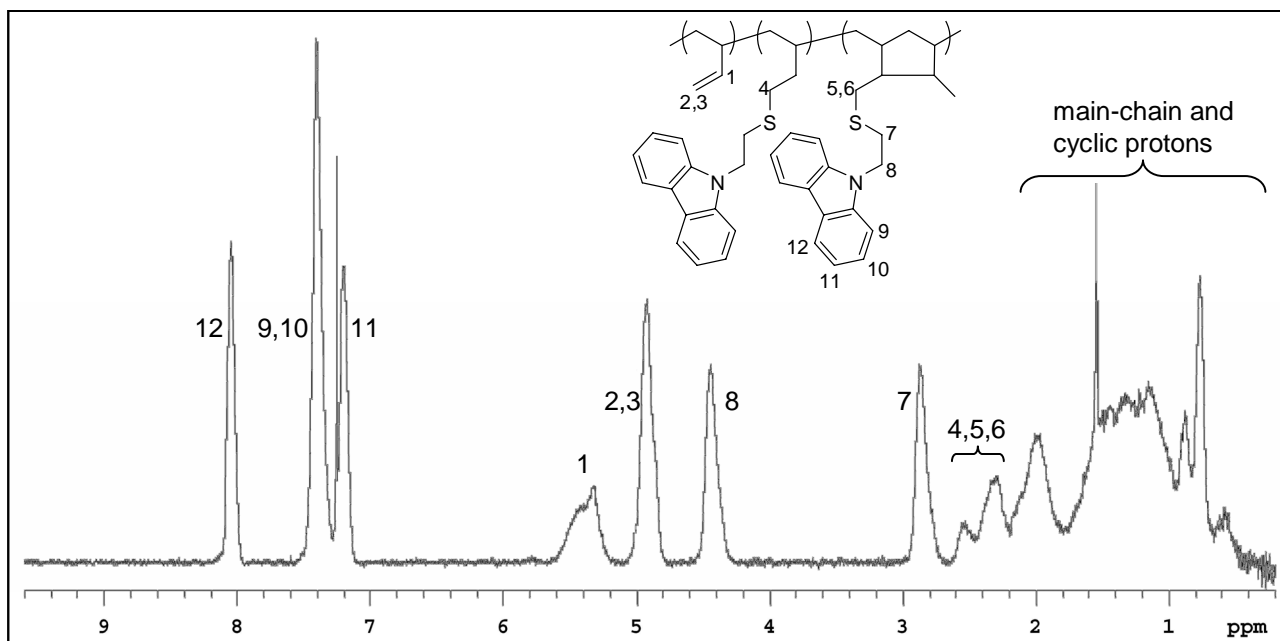
**Figure A.1.**  $^1\text{H}$  NMR trace of unfunctionalized prepolymer 92 kg/mol 1,2-PB.



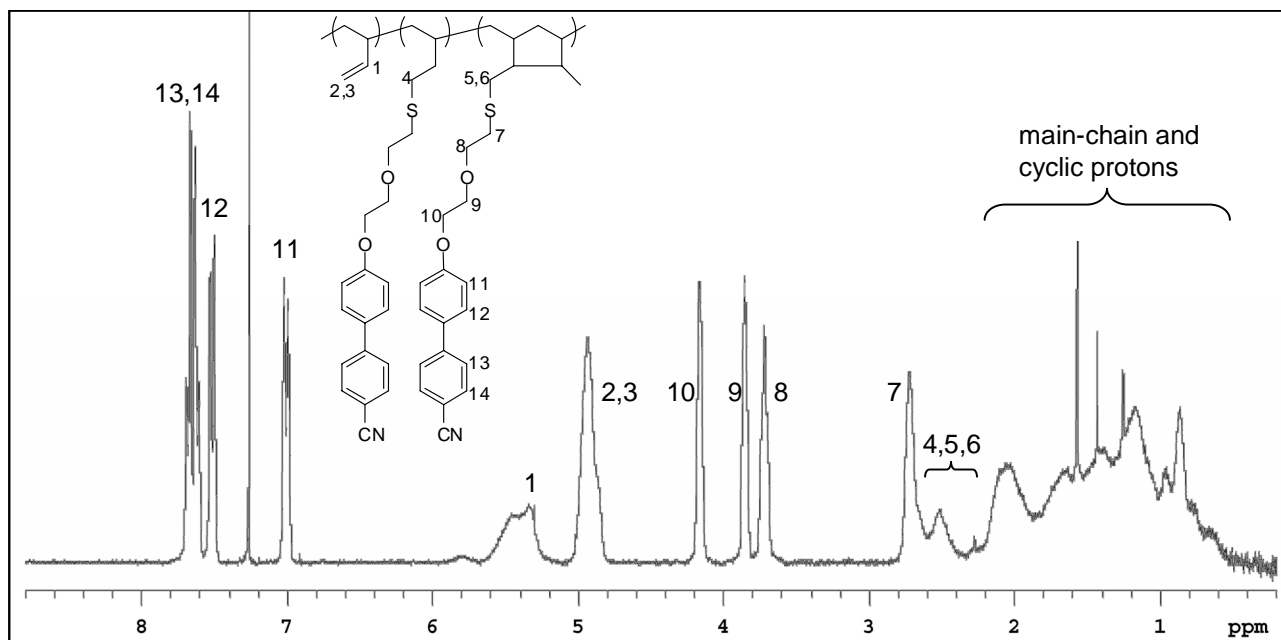
**Figure A.2.**  $^1\text{H}$  NMR trace of functionalized 1,2-PB polymer 92kPB-OH (experimental conditions are given in Table 2).



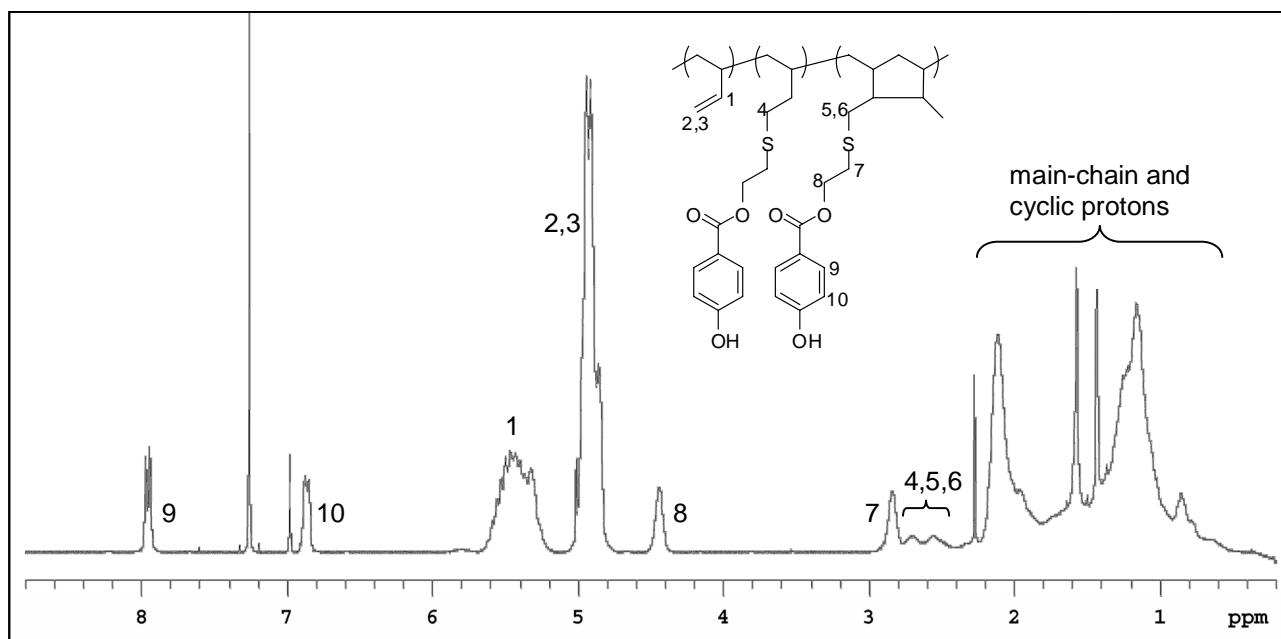
**Figure A.3.**  $^1\text{H}$  NMR trace of functionalized 1,2 PB polymer 92kPB-DNB (experimental conditions are given in Table 2).



**Figure A.4.**  $^1\text{H}$  NMR trace of functionalized 1,2 PB polymer 820kPB8 (experimental conditions are given in Table 1).



**Figure A.5.**  $^1\text{H}$  NMR trace of functionalized 1,2 PB polymer 92kPB6 (experimental conditions are given in Table 1).



**Figure A.6.**  $^1\text{H}$  NMR trace of functionalized 1,2 PB polymer 820kPB12 (experimental conditions are given in Table 1).

### 3. 1,2-Polybutadiene Functionalization using 9-[2-[(Triphenylmethyl)thio]ethyl]carbazole (**14**)

**Synthesis of 9-(2-Chloroethyl)carbazole (**7**).** The procedure was outlined in the description of the preparation of **8**.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.09 (d, 2 carbazole H,  $J$  = 7.8 Hz), 7.50-7.37 (m, 4 carbazole H), 7.29-7.20 (m, 2 carbazole H), 4.60 (t,  $\text{NCH}_2$ ,  $J$  = 7.2 Hz), 3.83 (t,  $\text{CH}_2\text{Cl}$ ,  $J$  = 7.2 Hz).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 140.07, 125.91, 123.07, 120.50, 119.50, 108.43, 44.64, 40.99.

**Synthesis of 9-[2-[(Triphenylmethyl)thio]ethyl]carbazole (**14**).** Potassium carbonate (4.4 g, 32 mmol), triphenylmethyl mercaptan (Alfa Aesar, 98%, 3.1 g, 11 mmol), and 9-(2-chloroethyl)carbazole (2.1 g, 9.1 mmol) were stirred at r.t. in 50 mL DMF for 5 hrs, after which the reaction mixture was transferred to a 500 mL separatory funnel containing 100 mL water and extracted with 50 mL chloroform. The organic layer was washed twice with 100 mL water, the solvent was evaporated under reduced pressure, and the crude product was purified by washing 3 times in 75 mL hot ethanol. Filtration of the solids and removal of remaining solvent under reduced pressure gave analytically pure **14** as ultra-fine, white needles (3.1 g, 6.6 mmol, 72% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.03 (d, 2 carbazole H,  $J$  = 7.8 Hz), 7.43-7.14 (m, 4 carbazole H and 15 phenyl H), 7.00 (d, 2 carbazole H,  $J$  = 8.1 Hz), 4.06 (t,  $\text{NCH}_2$ ,  $J$  = 8.1 Hz), 2.75 (t,  $\text{SCH}_2$ ,  $J$  = 8.1 Hz).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 144.61, 139.76, 129.69, 128.01, 126.86, 125.56, 122.79, 120.27, 119.00, 108.54, 67.39, 42.37, 30.22.

**Functionalization Procedure and Results.** To compound **14** (0.25 g, 0.5 mmol) dissolved in 10 mL chloroform in a 100 mL Schlenk tube were added triethylsilane (Alfa Aesar, 98%, 0.08 g, 0.7 mmol) and trifluoroacetic acid (TFA, 0.5 mL, 5 % vol), and the mixture was stirred 1-2 hrs at r.t. After addition of 1,2-PB (0.2 g, 4 mmol vinyl groups, dissolved in 10 mL chloroform) and AIBN (0.03 g, 0.2 mmol), the contents of the Schlenk tube were degassed in 3 freeze-pump-thaw cycles, then allowed to react at 55 °C for 3 hrs. Following reaction, the polymer solution was transferred to a 100 mL jar containing a small amount of BHT, concentrated by evaporation of all but the last 10 mL solvent under an argon stream, and precipitated in cold methanol. Final purification of the polymer was achieved by reprecipitation from a DCM solution with cold methanol (2-3 times), followed by drying to constant weight under vacuum at r.t. Reaction conditions and results for a specific example are given in Table A.1 (first entry).

### 4. 1,2-Polybutadiene Functionalization Using Thiobenzoic acid S-[3-(9-carbazolyl)propyl] ester (**16**)

**Synthesis of 9-Allylcarbazole (**15**).** Carbazole (10.1 g, 0.057 mol) and potassium hydroxide (88 % wt pellets, crushed, 7.1 g, 0.11 mol) were stirred in 100 mL DMSO at 50 °C for 30 min before dropwise addition of allyl bromide (14.7 g, 0.118 mol). After 15 min the reaction mixture was poured into a 500 mL separatory funnel containing 100 mL chloroform and washed 5 times with 200 mL water to give, after solvent evaporation at 60 °C under reduced pressure, compound **15** in > 99% purity as a dark brown, viscous syrup which solidified upon cooling (11.9 g, 0.057 mol, 100% yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.14-8.06 (m, 2 carbazole H), 7.49-7.32 (m, 4 carbazole H), 7.28-7.19 (m, 2 carbazole H), 6.04-5.90 (m,  $\text{CH}=\text{CH}_2$ ), 5.19-5.10 (m,  $\text{Z-HCH}=\text{CH}$ ), 5.07-4.97 (m,  $\text{E-HCH}=\text{CH}$ ), 4.92-4.85 (m,  $\text{NCH}_2$ ).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 140.34, 132.27, 125.67, 122.90, 120.33, 119.00, 116.74, 108.74, 45.21.

**Synthesis of Thiobenzoic acid S-[3-(9-carbazolyl)propyl] ester (16).** Thiobenzoic acid (30 g, 0.20 mol) was added to 9-allylcarbazole (11.9 g, 0.057 mol) in 100 mL toluene, and the reaction was carried out at 90 °C with argon purge via radical mechanism using AIBN as the initiator (1.8 g, 11 mmol, in 300 mg increments at 1 hr intervals). After 6 hrs the reaction mixture was poured into a 1 L separatory funnel containing 20 g sodium bicarbonate (NaHCO<sub>3</sub>, 0.24 mol) in 250 mL water, extracted with 100 mL chloroform, and the organic phase was washed twice with 200 mL water before solvent removal under reduced pressure. The crude product was subsequently washed in 100 mL hot hexane, 150 mL ethanol, and finally 150 mL of 15:1 ethanol:chloroform. Evaporation of leftover solvent at 80 °C under reduced pressure yielded compound **16** in ca. 90% purity as a dark brown, viscous syrup which solidified upon cooling (9.35 g, 0.024 mol, 42% yield, ~ 10 %wt dibenzoyl disulfide). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.10 (d, 2 carbazole H, *J* = 8.1 Hz), 8.00-7.95 (m, 2 aromatic H *ortho* to COS), 7.62-7.41 (m, 3 aromatic H *meta* and *para* to COS plus 4 carbazole H), 7.27-7.19 (m, 2 carbazole H), 4.43 (t, NCH<sub>2</sub>, *J* = 6.9 Hz), 3.06 (t, SCH<sub>2</sub>, *J* = 6.9 Hz), 2.26 (tt, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S, *J* = 6.9, 6.9 Hz). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ = 191.56, 140.25, 136.88, 133.50, 128.65, 127.23, 125.75, 122.91, 120.41, 119.00, 108.55, 41.65, 28.95, 26.41.

**Functionalization Procedure and Results.** The functionalization procedure followed the general method outlined in the experimental section. Reaction conditions and results for a specific example are given in Table A.1 (second entry).

**Table A1. Reaction Conditions and Results for 1,2-PB Functionalization Using Compounds 14 and 16**

Entry <sup>a</sup>	[PB] (g/mL)	[Thiol] <sup>b</sup>	[AIBN] (g/mL)	Rxn time (hrs)	X <sub>funct</sub> <sup>c</sup> %	M <sub>w</sub> <sup>d</sup> (kg/mol)	PDI <sup>d</sup>	New H NMR peaks above 2.2 ppm for modified PB (all peaks are broad)
820kPB14	0.011	0.1	0.002	2.9	6	945	2.08	8.12-8.04 (2H), 7.52-7.39 (4H), 7.27-7.19 (2H), 4.56-4.43 (2H), 2.97-2.83 (2H)
92kPB16	0.003	1.1	0.003	3.0	19	187	1.34	8.15-8.03 (2H), 7.56-7.37 (4H), 7.28-7.15 (2H), 4.50-4.27(2H), 2.62-2.30 (4H)

<sup>a</sup>) Modified PB polymers were named so that the prefix corresponds to the molecular weight of the starting 1,2-PB chain, and the suffix represents the reagent used. <sup>b</sup>) In molar equivalents of 1,2-PB monomer units. <sup>c</sup>) The fraction of reacted 1,2-PB units that bear functional groups (refer to text). <sup>d</sup>) Measurements as described in Experimental section using the Waters setup (the 1,2-PB prepolymers had PDI values of 1.07 and 1.26 for the 92 kg/mol and 820 kg/mol chains, respectively).