SUPPLEMENTARY MATERIAL

Defect-free Hyperbranched Polydithioacetal via Melt Polymerization

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SYNTHESIS OF THE AB_2 MONOMER

4-Hydroxymethylbenzaldehyde. $NaBH_4$ (0.35 g, 9.25 mmol) was added with continuous stirring over 30 min to a cooled solution (at –5 °C) of terepthalaldehyde (5 g, 37.3 mmol) taken in a mixture of EtOH (70 mL) and THF (100 mL). The mixture was stirred for 6 h, while the temperature was maintained 0 °C. After neutralization with 2M HCl to pH 5, the solvents were evaporated, water (200 mL) was added to the residue, and products were extracted with ethylacetate. The combined organic extracts were dried with $MgSO_4$, and the solvent was evaporated. The product was purified by column chromatography using a mixture of ethylacetate and petreoleum ether (2 : 1) as the eluent. The yield was 4.1 g (82%), m.p. 40 °C.

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10 (s, 1H, C**H**O); 7.88 (d, 2H, Ar-**H**'s); 7.54 (d, 2H, Ar-**H**'s); 4.80 (d, 2 H, ArC**H_2**).

4-Bromomethylbenzaldehyde. 4-Hydroxymethylbenzaldehyde (2.5 g, 18.38 mmol) was taken in 10 mL of toluene in a round bottom flask and 5 mL of 48 % aqueous HBr was added to it. The mixture was refluxed for 3 h; 100 mL chroloform was added to it and the organic layer was separated out and washed with aq. sodium bicarbonate solution until it became neutral. The organic layer was dried with anhydrous sodium sulphate, concentrated and dried under reduced pressure to yield the product as pale yellow crystalline solid. The yield was 3 g (82%), m.p 94 °C.

NMR (400 MHz, $CDCl_3$, δ ppm): 10.02 (s, 1H, C**H**O); 7.88 (d, 2H, Ar-**H**'s); 7.57 (d, 2H, Ar-**H**'s); 4.52 (s, 2H, ArC**H_2**).

4-Formylbenzylethanethioate.[2] 4-Bromomethylbenzaldehyde (1.5 g, 7.53 mmol) was taken in 15 mL THF and K_2CO_3 (2 g, 10.1 mmol) was added to it. The flask was flushed with N_2 and thioacetic acid (1.2 g, 15.78 mmol) was added to it. This mixture was stirred at room temperature under a slow stream of nitrogen for 12 h. 20 mL water was added and it was extracted with ethylacetate (30 mL x 3). Organic layer was washed with brine once and passed through anhydrous sodium sulphate. Solvent was removed and the residue was dried under vacuum. Product was obtained as brown liquid. The yield was 1.2 g (83%).

NMR (400 MHz, $CDCl_3$, δ ppm): 9.98 (s, 1H, C**H**O) 7.83 (d, 2H, Ar-**H**'s), 7.47 (d, 2H, Ar-**H**'s), 4.16 (s, 2H, ArC$\mathbf{H_2}$), 2.37 (s, 3H, C$\mathbf{H_3}$).

4-(Dimethoxymethyl)benzylethanethioate. 4-Formylbenzylethanethioate (2 g, 10.39 mmol) was taken in 30 mL of dry methanol and 6 mL of trimethylorthoformate was added to it along with a few drops of methanolic HCl. The mixture was refluxed under N_2 for 12 h. Solid $NaHCO_3$ was then added and the contents were stirred to affect complete neutralization. The mixture was filtered and the filterate was concentrated to leave behind the product which was distilled using a Kugehlrohr at 130 °C under a vacuum of 5 torr to yield a yellow liquid. The yield was 1.4 g (57%).

NMR (400 MHz, $CDCl_3$, δ ppm): 7.38 (d, 2H, Ar-**H**'s), 7.29 (d, 2H, Ar-**H**'s), 5.36 (s, 1H, C**H**$(OMe)_2$), 4.12 (s, 2H, ArC$\mathbf{H_2}$), 3.31 (s, 6H, CH(O**Me**)$_\mathbf{2}$), 2.35 (s, 3H, COC$\mathbf{H_3}$).

(4-(Dimethoxymethyl)phenyl)methanethiol.[2] 4-(Dimethoxymethyl) benzylethanethioate (3.5 g, 14.58 mmol), was taken in 15 mL methanol and dry N_2 gas was bubbled through the solution for 15 min. A solution of sodium hydrogensulphide (1.34 g, 14.58 mmol), in 15 mL methanol was added into it and the reaction mixture was stirred at room temperature for 3 h under a slow N_2 purge. A solution of NH_4Cl (1.54 g, 29.14 mmol) in 15 mL water was added to it and the contents was extracted with ethylacetate (3 X 40 mL). The organic layer was washed with brine, separated and dried using anhydrous sodium sulphate. After solvent removal under reduced pressure the product was obtained as dark yellow liquid. Yield is 2.6 g (90%).

NMR (400 MHz, $CDCl_3$, δ ppm): 7.41 (d, 2H, Ar-**H**'s), 7.34 (d, 2H, Ar-**H**'s), 5.38 (s, 1H, C**H**$(OMe)_2$), 3.76 (d, 2 H, ArC$\mathbf{H_2}$), 3.33 (s, 6 H, CH(O**Me**)$_2$), 1.76 (t, 1H, S**H**).

Benzyl mercaptan. Benzyl chloride (5 g, 39.5 mmol) was taken in 30 mL absolute ethanol containing thiourea (4 g, 52.6 mmol) and refluxed for 4 h. After cooling to room temperature, 30 mL of 10N NaOH solution was added to it; the contents were then refluxed for another 3 h under inert atmoshphere. After lowering the pH to 5 by addition of 4N HCl, the reaction mixture was extracted twice with 50 mL of ethyl acetate. The combined organic layer was

washed with brine, separated and dried using anhydrous sodium sulphate. Removal of the solvent under reduced pressure yielded the product as a colorless oil. Yield is 3.5 g (71 %).

NMR (400 MHz, $CDCl_3$, δ ppm): 7.3-7.2 (m, 5H, Ar-**H**'s), 3.75 (d, 2H, ArC**H_2**), 1.76(t, 1H, S**H**).

1-(Dimethoxymethyl)-4-methylbenzene. p-Tolualdehyde (5 g, 41.6 mmol) was taken in 30 mL dry methanol along with 15 mL trimethylorthoformate and a few drops of methanolic HCl were added to it. The reaction mixture was refluxed for 12 h. Solid $NaHCO_3$ was added to the cooled reaction mixture and the contents were stirred to ensure complete neutralization. The mixture was filtered and the filterate was concentrated to leave behind the product which was distilled using a Kugehlrohr at 120 °C at 10 torr to yield a colorless oil. Yield is 5.2 g (76 %).

NMR (400 MHz, $CDCl_3$, δ ppm): 7.34 (d, 2H, Ar-**H**'s), 7.18 (d, 2H, Ar-**H**'s), 5.36 (s, H, C**H**$(OMe)_2$), 3.3 (s, 6H, CH(O**Me**$)_2$), 2.35(s, 3H, ArC**H_3**).

1-(((Benzylthio)(p-tolyl)methylthio)methyl)benzene.[3] 1-(Dimethoxymethyl)-4-methylbenzene (1 g, 6 mmol) was taken in 20 mL chloroform. Benzyl mercaptan (1.48 g, 12 mmol) was added to it along with a catalytic amount of iodine (0.15 g, 0.6 mmol). The reaction mixture was stirred for 15 min under dry N_2 atmosphere. 5 mL sodium thiosulphate (0.158 g, 1mmol) solution was added to it followed by the addition of 5 mL of 2N NaOH solution. The organic layer was washed with brine, separated and dried using anhydrous sodium sulphate. After removal of the solvent, the product was obtained as colourless liquid. Yield is almost quantitative.

NMR (400 MHz, $CDCl_3$, δ ppm): 7.25-7.14 (m, 14H, Ar-**H**'s), 4.45 (s, 1H, C**H**$(SCH_2Ar)_2$), 3.79 (d, 2H, ArC**H_2**), 3.57 (d, 2H, ArC**H_2**), 2.34 (s, 3H, ArC**H_3**).

Ethyl 3-mercaptopropanoate.[4] 3-Mercaptopropionic acid (6.1 g, 57.6 mmol) was dissolve in 10 mL dry ethanol and 0.4 mL of acetylchloride was added. The reaction mixture was stirred at room temperature overnight. Product was extracted in dichloromethane and the organic layer was washed with $NaHCO_3$ aqueous solution. The organic layer was dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure. The product was obtained as colourless oil. Yield is 4.8 g (63%).

NMR (400 MHz, $CDCl_3$, δ ppm): 4.22 (q, 2H, $CH_3C\mathbf{H_2}O$), 2.81 (m, 2H, $COCH_2C\mathbf{H_2}SH$), 2.69 (t, 2H, $COC\mathbf{H_2}CH_2SH$), 1.7 (t, 1H, $CH_2S\mathbf{H}$), 1.32 (t, 3H, $OCH_2C\mathbf{H_3}$).

General polymerization procedure. (4-(Dimethoxymethyl)phenyl)methanethiol 1 g (5 mmol) was taken in a polymerization flask along with 2 mol % of pyridinium camphorsulphonate. The reaction mixture was degassed by purging N_2 for 15 min and then heated to 60 °C under N_2 atmosphere to ensure homogeneous mixing of the catalyst and monomers. Then the polymerization was carried out at 80 °C for 45 min under N_2 purging. Then the polymerization tube was connected to a Kugehlrohr apparatus and the polymerization was continued at 80 °C under reduced pressure of 20 torr for 45 min. The polymer was dissolved in THF and the solution of the polymer was neutralized by solid $NaHCO_3$ and filtered. The filtrate was concentrated and poured into dry methanol to obtain the polymer. This polymer was further purified through dissolution followed by reprecipitation using THF-methanol. Yield is 0.5 g (60%).

General procedure for postpolymerization functionalization. 100 mg of the polymer was dissolved in 0.3 mL dry 1,2-dichlorobenzene and 0.12 g (1 equivalent with respect to terminal methoxy unit) of dodecanethiol was added. 2 mol-percent of PCS catalyst was added to it and the reaction mixture was stirred for 15 min at 50 °C under slow flow of dry nitrogen for complete homogenization. The contents were stirred at 80 °C under dry N_2 purge for 1h 30 min. The reaction mixture was poured into methanol to obtain polymer. The polymer was further purifiedby dissolution followed by reprecipitation using THF-methanol. The isolated polymer was thoroughly dried at 60 °C under high vacuum. Yield is 170 mg (81%).

NMR (400 MHz, $CDCl_3$, δ ppm): 7.4-7.1 (m, 4H, Ar-**H**'s), 4.85 (m, 1H, C**H**$(SCH_2CH_2)_2$), 4.6 (m, 1H, C**H(**$SCH_2Ar)_2$), 3.79-3.56 (m, 2H, Ar$C\mathbf{H_2}S$), 2.59-2.46 (m, 2H, $CH_2C\mathbf{H_2}S$), 1.5-1.2 (m, $CH_2(C\mathbf{H_2})_{10}CH_3$), 0.87(t, 3H, $CH_2C\mathbf{H_3}$).

Benzyl mercaptan functionalized hyperbranched polydithioacetal: A similar procedure as above was followed using benzyl mercaptan to yield the required polymer. Yield is 73%**.**

NMR (400 MHz, $CDCl_3$, δ ppm): 7.4-7.1 (m, 9H, Ar-**H**'s), 4.6-4.4 (m, 1H, ArC**H**$(ArCH_2S)_2$), 3.8-3.5 (m, 2H, ArC$\mathbf{H_2}$).

Ethylmercaptopropanoate functionalized hyperbranched polydithioacetal: A similar procedure as above was followed using ethylmercaptopropanoate to yield the required polymer. Yield is 59%**.**

NMR (400 MHz, $CDCl_3$, δ ppm): 7.4-7.1 (m, 4H, Ar-**H**'s), 5 (m, 1H, C**H**$(SCH_2CH_2)_2$), 4.6 (m, 1H, C**H(**$SCH_2Ar)_2$), 4.1 (m, 2H, $CH_3C\mathbf{H_2}O$), 3.79-3.56 (m, 2H, ArC$\mathbf{H_2}$S), 2.9-2.5 (m, 4H, COC$\mathbf{H_2}C\mathbf{H_2}$S), 1.25 (m, 3H, $OCH_2C\mathbf{H_3}$).

Triethylene glycol monomethylether monotosylate: Triethyleneglycol monomethylether (10 g, 60 mmol) was taken in 30 mL THF and the contents were cooled in ice bath. Sodium hydroxide (7.2 g, 180 mmol, 50 % aq. solution) was added to it. p-Toluene sulfonylchloride (13.5 g, 72 mmol) in 30 mL was slowly added using a dropping funnel over a period of 1 h. The reaction mixture was stirred overnight. 20 mL of water was added to it and the contents were stirred until two distinct layers were formed. The organic layer was separated and concentrated. 50 mL water was added to it and the mixture was extracted with ethylacetate (60 mL x 3). The ethylacetate layer was washed with brine, separated and dried using anhydrous sodium sulphate. After removal of the solvent, 50 mL of diethyl ether was added and the contents were set aside for few hours, during which time some unreacted tosylchloride precipitated out. The precipitate was filtered and the solvent was removed to give pure product as colourless liquid. The yield is 17.6 g (91%).

NMR (400 MHz, $CDCl_3$, δ ppm): 7.81 (d, 2H, Ar-**H**'s), 7.35 (d, 2H, Ar-**H**'s), 4.15 (t, 2H, -OC$\mathbf{H_2}$), 3.66-3.56 (m, 10H, OC$\mathbf{H_2}C\mathbf{H_2}$O), 3.38 (s, 3H, -OC$\mathbf{H_3}$), 2.45 (s, 3H, ArC$\mathbf{H_3}$).

4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-benzaldehyde: Triethylene glycol monomethyl ether monotosylate (5.7 g, 18 mmol), 4-hydroxybenzaldehyde (2 g, 16.4 mmol) and potassium carbonate (9.1 g, 66 mmol) were taken in a round bottom flask, along with 100 mL of dry acetonitrile. The reaction mixture was refluxed for 48 h under N_2 atmosphere. The acetonitrile was removed and 100 mL water was added. This aqueous layer was extracted with diethylether

(3 x 100 mL). The organic layer was dried over anhydrous sodium sulphate; after removal of the solvent, the product obtained was dried under vacuum dried. Yield is 3.2 g (72%).

NMR (400 MHz, $CDCl_3$, δ ppm): 9.29 (s, 1H, ArC**H**O), 7.86(d, 2H, Ar-**H**'s), 7.07(d, 2H, Ar-**H**'s), 4.26 (t, 2H, ArOC**H_2**), 3.93(t, 2H, $ArOCH_2C$**H_2**O) 3.79-3.59(m, 8H, OC**H_2**C**H_2**O), 3.42(s, 3H, OC**H_3**).

1-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy-4-(dimethoxymethyl)-benzene: 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-benzaldehyde (2 g, 7.4 mmol) was taken in 20 mL dry methanol along with trimethylorthoformate (10 mL). A few drops of dry methanolic HCl were added to it. The reaction mixture was refluxed overnight. Sodium bicarbonate was added to the cooled reaction mixture and the contents were stirred to ensure complete neutralization. The solution was filtered and the filtrate was concentrated under reduced pressure to give the product as light yellow liquid. Yield is 2.1 g (90%).

(400 MHz, $CDCl_3$, δ ppm): 7.35(d, 2H, Ar-**H**'s), 6.89(d, 2H, Ar-**H**'s), 5.34(s, 1H, ArC**H**$(OMe)_2$) 4.14 (t, 2H, ArOC**H_2**), 3.85(t, 2H, $ArOCH_2C$**H_2**O), 3.72-3.54(m, 8H, OC**H_2**C**H_2**O), 3.37(s, 3H, OC**H_3**) 3.30 (s, 6H, $ArCH(OC$**H_3**$)_2$).

1,6-dibromohexane: 1,6-hexanediol (10 g, 84.7 mmol) was taken in a round bottom flask along with 100 mL of aq. HBr (48 wt %) solution and refluxed for 48 h. The aqueous layer was extracted with chloroform and neutralized by washing with aq. sodium bicarbonate solution. After reoval of the solvent, the pure product was distilled at 120 $^{\circ}$C under 10 torr vacuum. Yield is 17 g (83%).

Hexane-1,6-dithiol: Hexane-1,6-dithiol was prepared following the same procedure as benzyl mercaptan. Yield is 67%.

(400 MHz, $CDCl_3$, δ ppm): 2.53(q, 2H, C**H_2**SH), 1.6-1.38(m, 6H, $HSCH_2C$**H_2**C**H_2**C**H_2**C**H_2**CH_2SH), 1.33(t, 2H, CH_2S**H**).

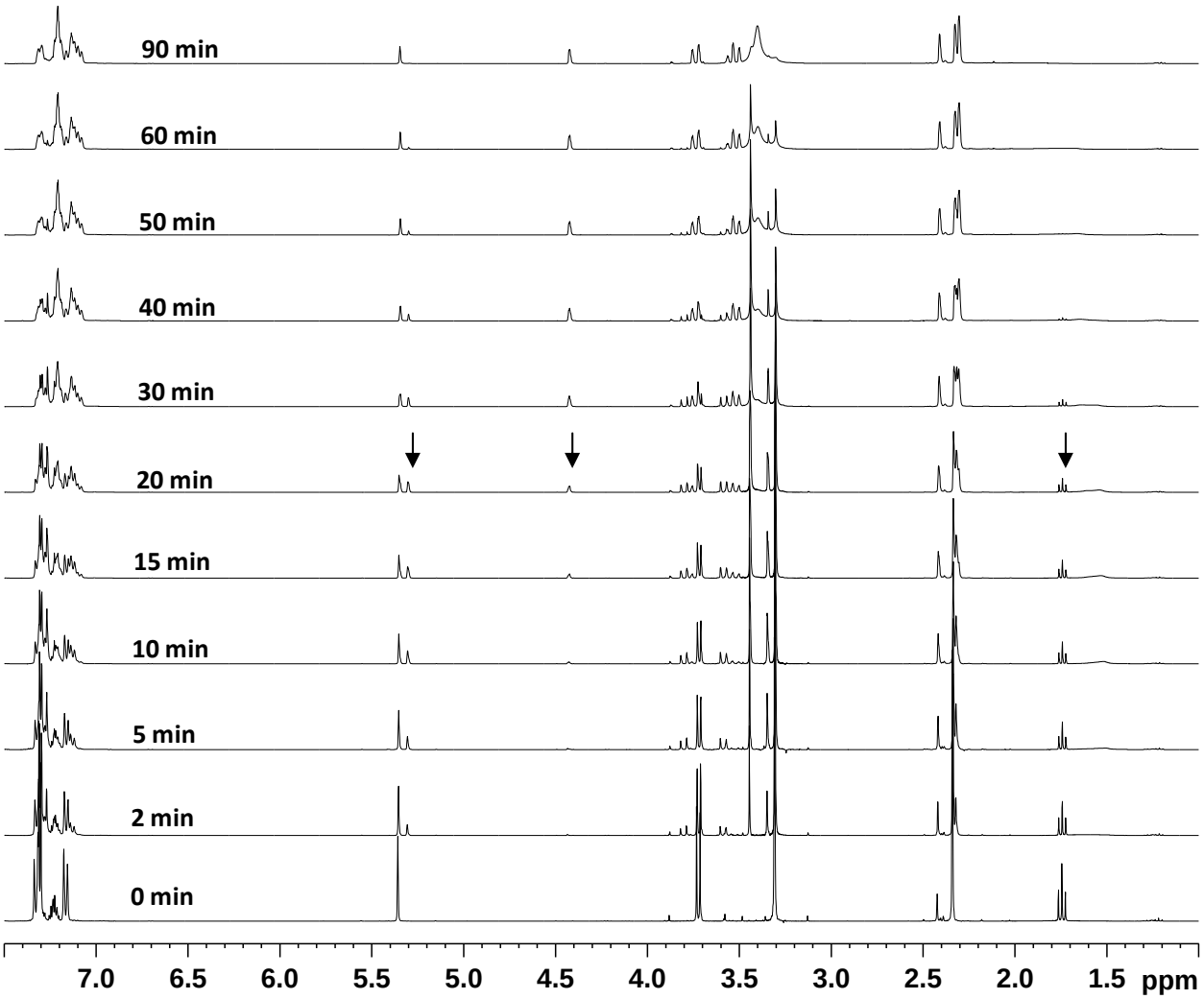

Figure S1: Variation of the ^{1}H-NMR spectra of the reaction mixture containing TDMA and BzSH (with I_2 as catalyst) as a function of reaction time. Note the disappearance of the triplet at 1.75 ppm due to the -S**H** proton, along with the other changes discussed in the main article.

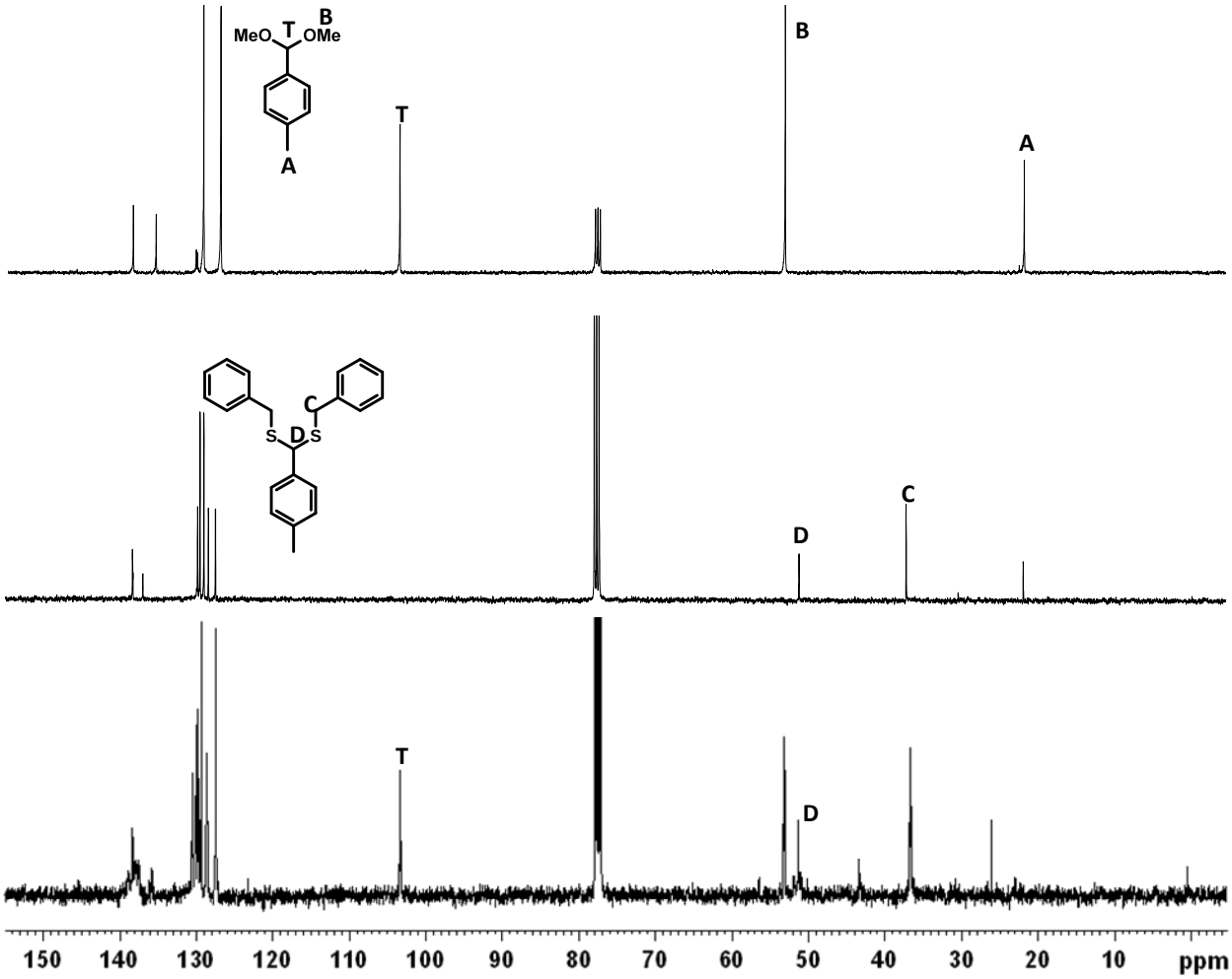

Figure S2: ^{13}C NMR spectra of the parent hyperbranched polydithioacetal along with those of the dendritic and terminal model compounds.[1] The peaks marked **T** and **D** in the bottom most spectrum indicate the positions of the Terminal and Dendritic methine carbons.

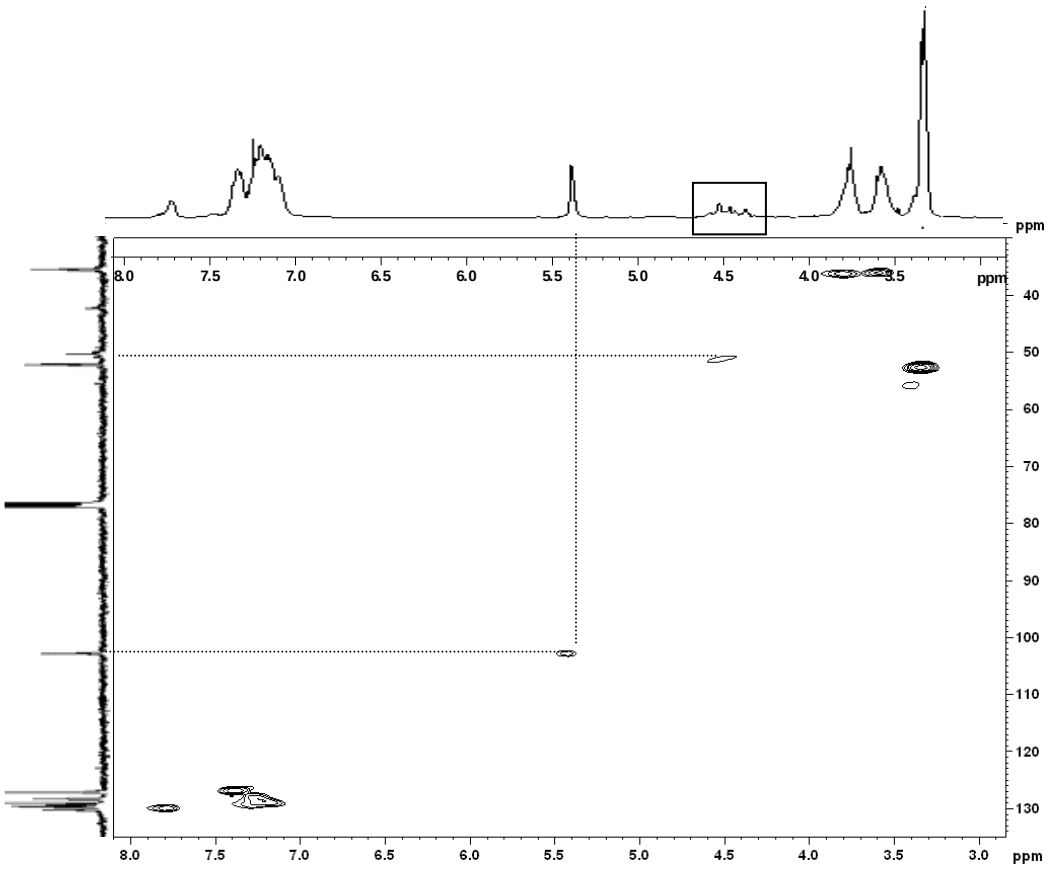

Figure S3: ^{1}H-^{13}C HSQC spectrum of the hyperbranched polythioacetal. All the peaks in the proton NMR spectrum in the boxed region cross-correlates only with the dendritic methine peak in the ^{13}C- NMR spectrum; this confirms that all the peaks in the proton NMR spectrum do correspond to the methine proton of the dendritic units alone. The correlation to the terminal peak is also clearly evident.

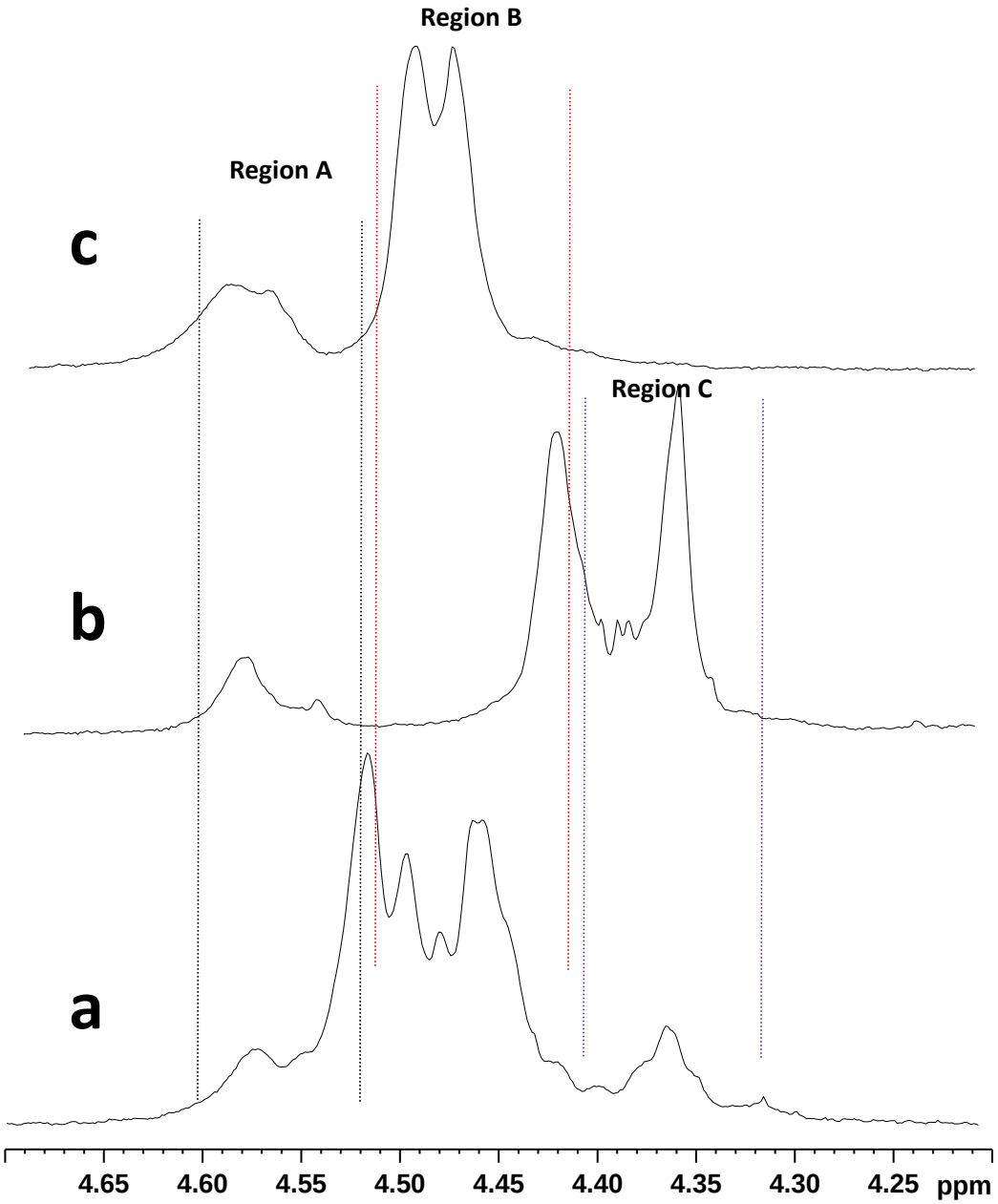

Figure S4: Expanded methine region of the ^{1}H-NMR spectra of: (a) the parent hyperbranched polymer, (b) the polymer wherein all the terminal groups have been hydrolyzed to aldehydes, and (c) the polymer wherein all the terminal groups have been transformed to dithioacetal groups using excess benzyl mercaptan. Region A appears to be common to all the polymers, while region B appears to correspond to the main dithioacetal repeat unit. Region C appears to correspond to the dendritic (D) repeat units that have one or both benzyl units carrying an aldehyde unit in their *para* positions; this expectedly is of very low intensity in the parent polymer spectrum (spectrum **a**). The region B corresponds to the primary repeat unit in the polymer; the multiple peaks in this region (which is the most intense region in spectrum **a**) suggests sensitivity to the nature of the chiral center of the adjacent repeat units, in other words to some form of tacticity.

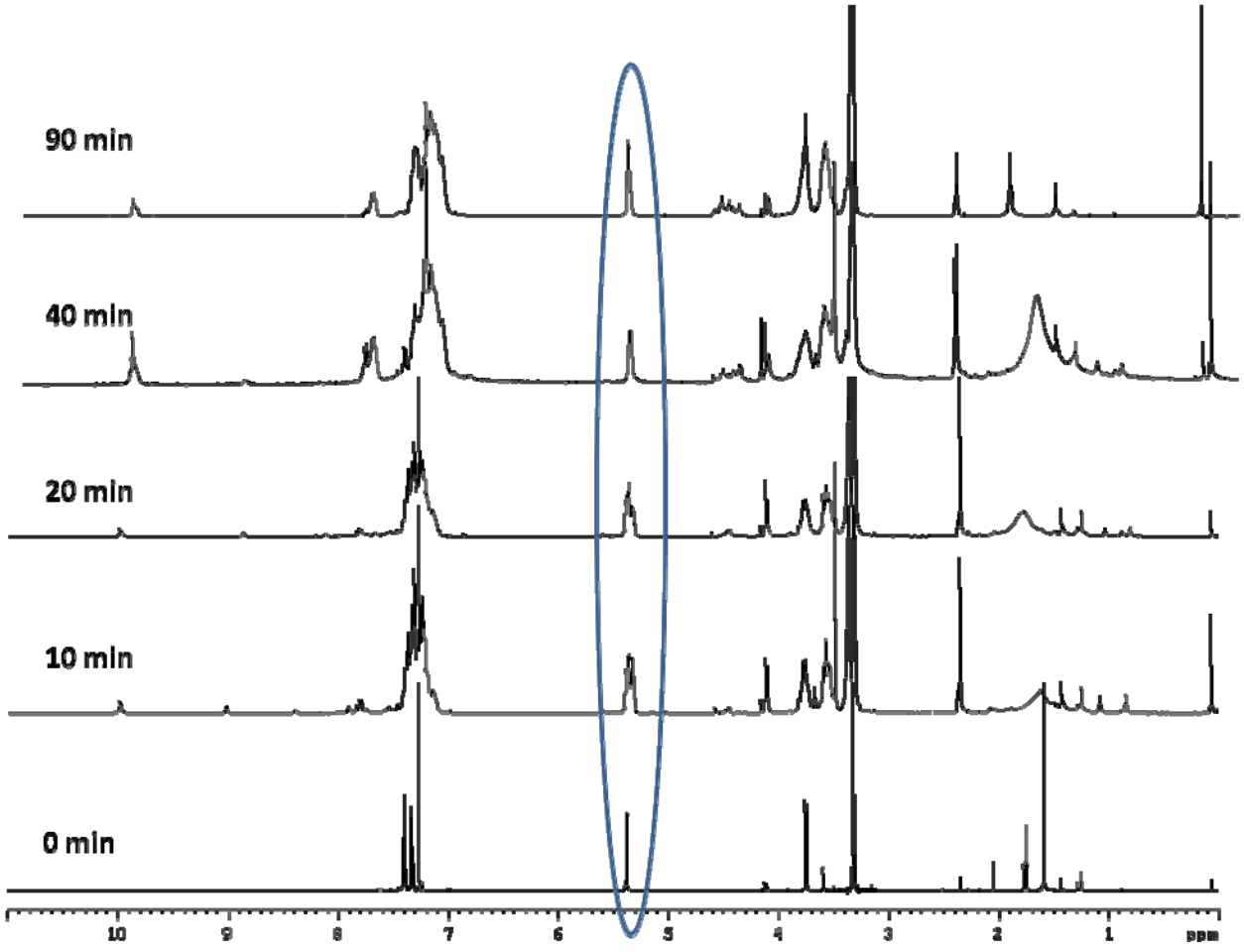

Figure S5: Stack plot of the ^{1}H NMR spectra of aliquots taken after different time intervals during the polymerization of monomer **A**. The polymerization times are listed on the left, while the ellipsoid highlights the appearance subsequently disappearance of the peak due to linear units. An expansion of this region is shown in Figure S6. The increase in the aldehyde peak is also seen as a function of polymerization time, suggesting that the inadvertent hydrolysis of the terminal acetal groups also appears to increase with polymerization time.

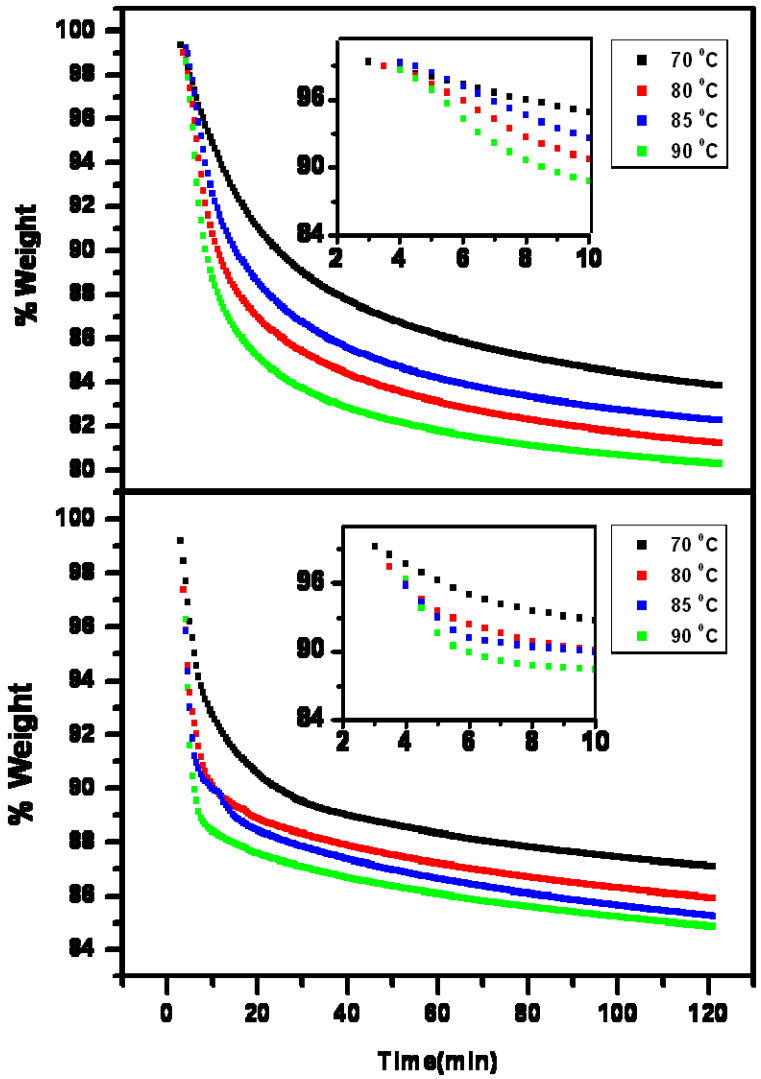

Figure S6: Isothermal TGA plots (at different temperatures) during the formation of HB polyacetal (above) and HB polydithioacetal (below); the loss of methanol during the polymerization is utilized to estimate the percent conversion. Inset shows an expanded region of the early times, that clearly reveals the nonlinear behaviour in the HB polydithioacetal case.

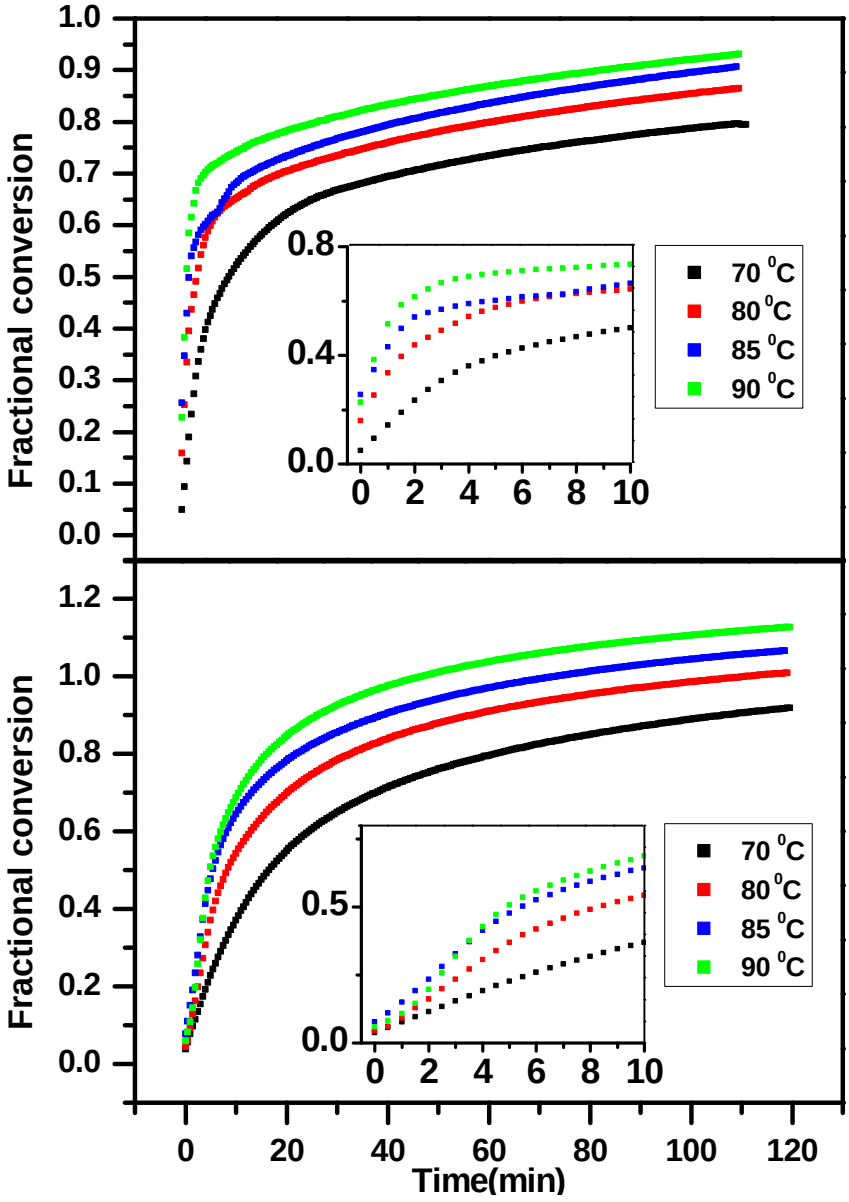

Figure S7: Plot of extent of polymerization (percent conversion) as a function of time. This data were extracted from the isothermal TGA curves by normalization with respect to the theoretically expected weight loss. The top plot corresponds to: (a) polydithioacetal formation and the bottom to (b) polyacetal formation. The insets are expanded region showing the early times of the polymerization. In the case of polydithioacetal (top), the reaction is rapid and begins in many cases before attaining the set isothermal temperatures; this is especially true for the higher temperature runs, as evident from the plots.

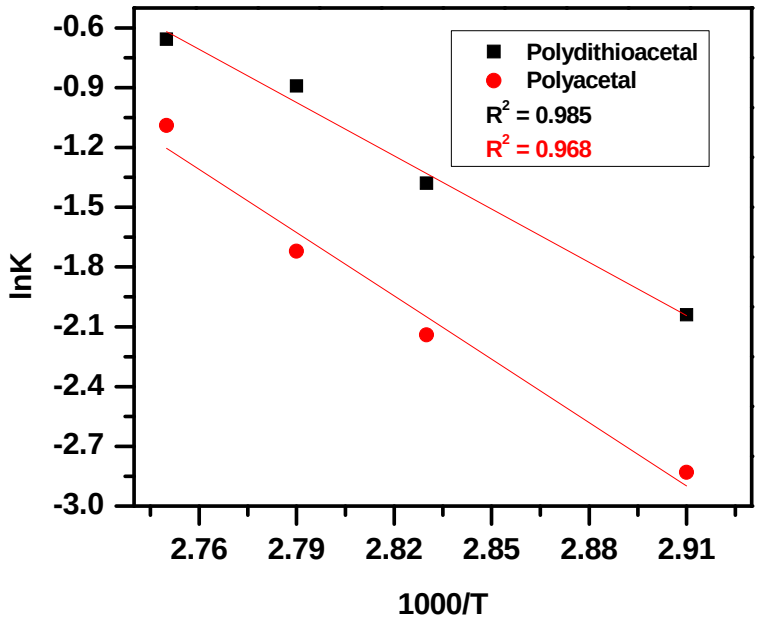

Figure S8: Arrhenius plot of the polymerizations yielding polyacetal (red) and polydithioacetal (black).

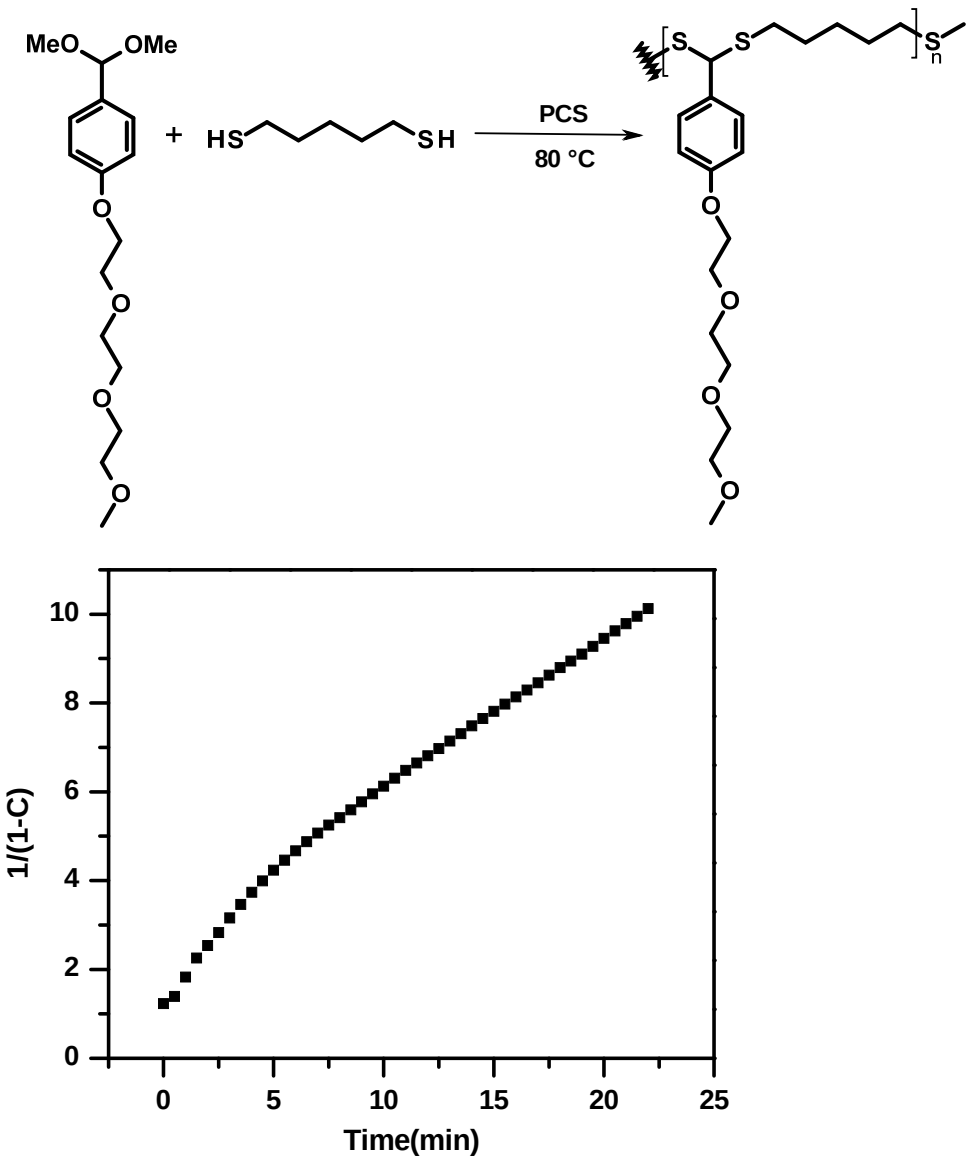

Figure S9: Model reaction to generate the linear polythioacetal (top); 2nd order kinetic plot for the linear polydithioacetal polymerization at 80° C; a clear break in the plot suggests that this feature is not unique to HBPs alone.

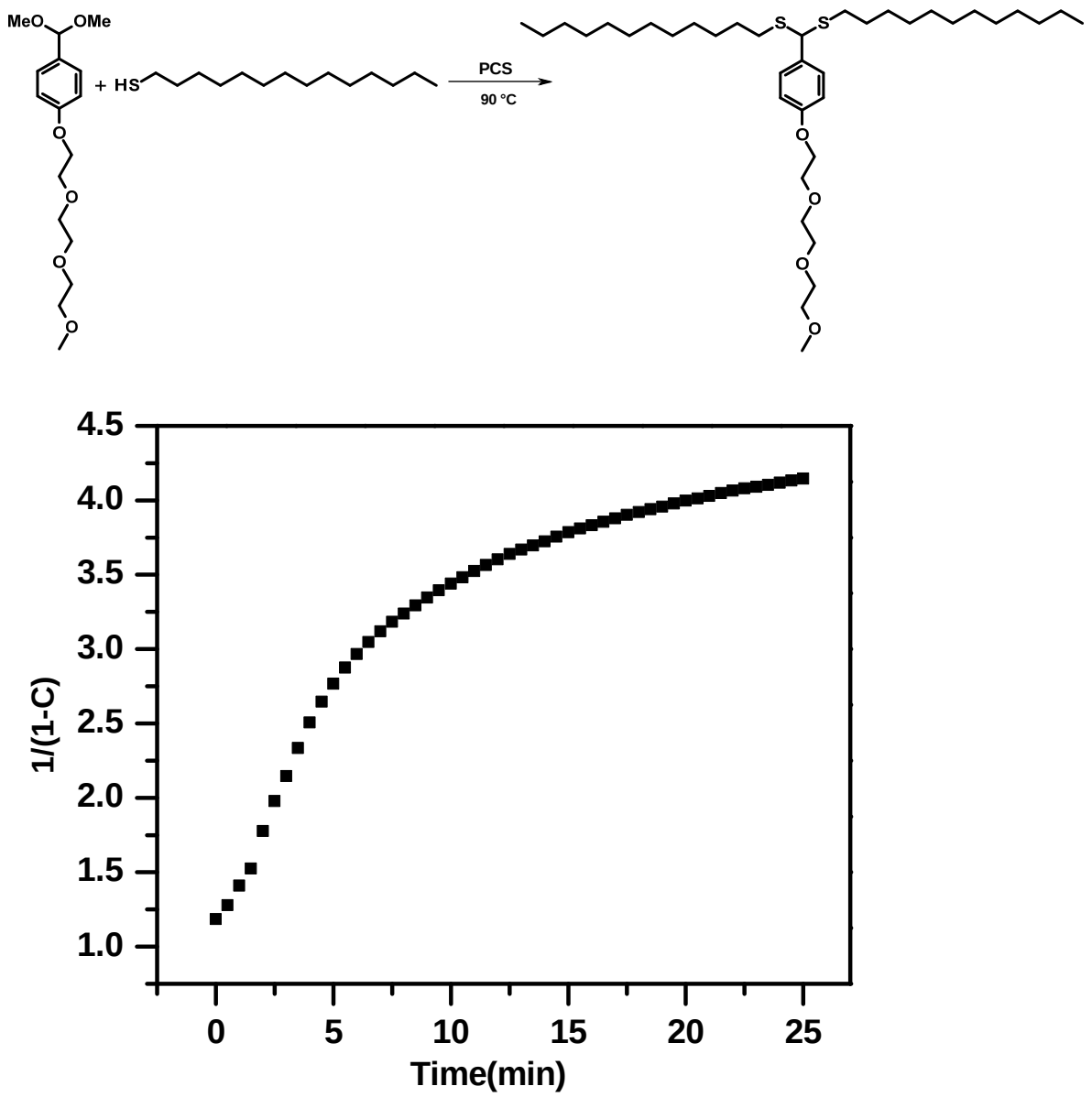

Figure S10: Model reaction wherein the dimethylacetal is transformed to a long chain dithioacetal (top); the use of high-boiling molecules ensures that the TGA method can be utilized to measure the extent of reaction, assuming that the wt-loss is primarily due to the loss of the product methanol alone. 2nd order kinetic plot of the model reaction (bottom); here again a clear break in the curve is seen suggestion that this feature is intrinsic to the dithioactal formation. The break occurs at slightly higher than 60 % conversion; we interpret this as being due to the transformation of the intermediate monothioacetal to the dithioacetal. This is consistent with the NMR experiments, wherein the accumulation of the intermediate monothioacetal occurs before it gets transformed to the final dithioacetal; the NMR studies also suggests a slightly slower rate of disappearance of the intermediate.

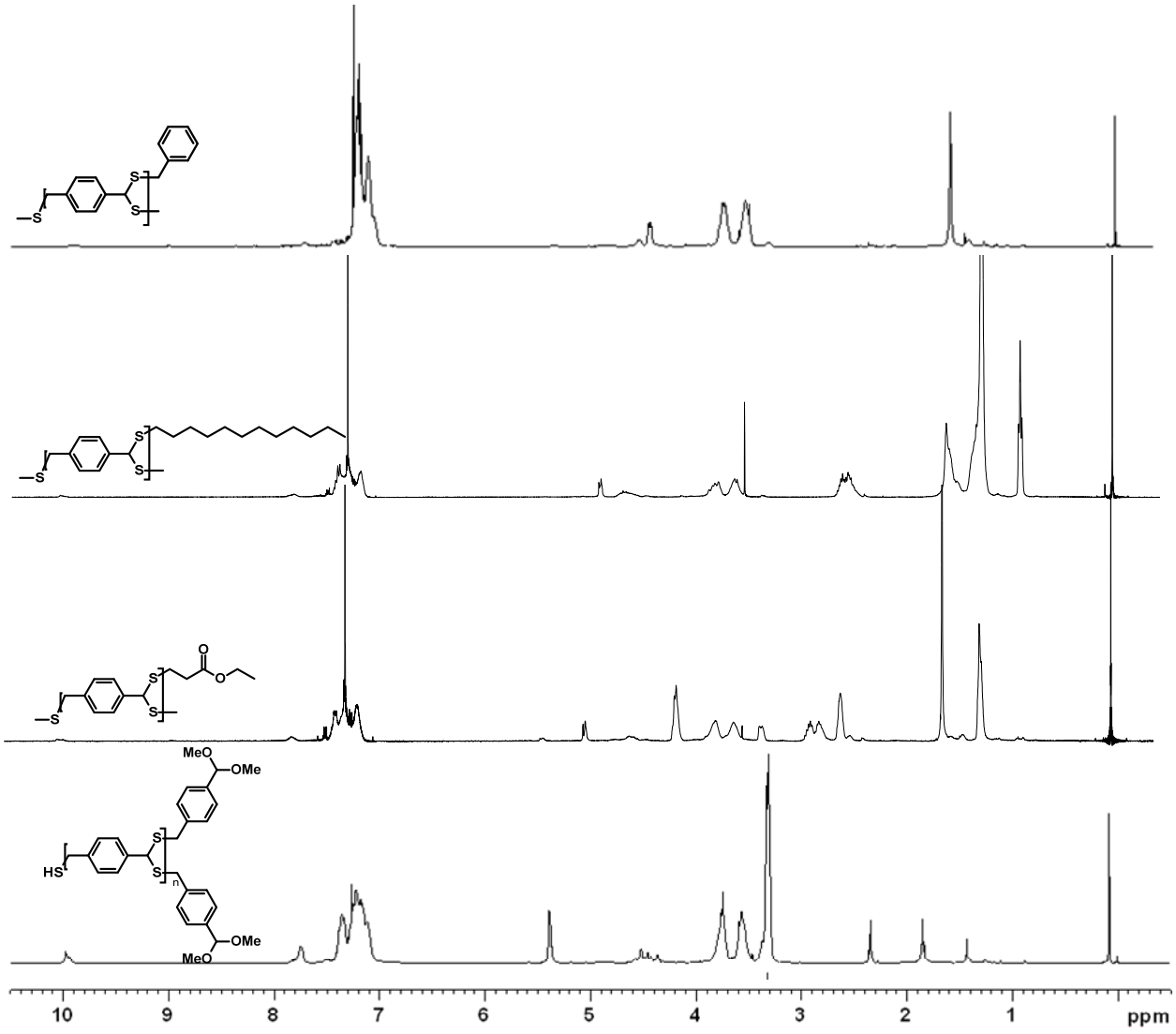

Figure S11: ^{1}H NMR spectra of the parent hyperbranched polydithioacetal and various peripherally derivatized polymers.

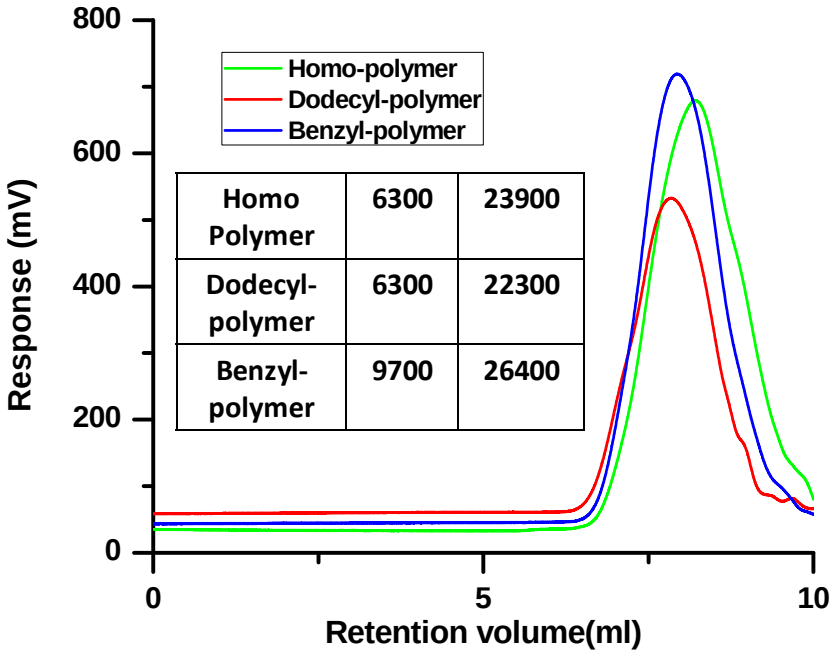

Figure S12: Overlay of GPC chromatograms of polydithioacetal and the various peripherally derivatized polymers.

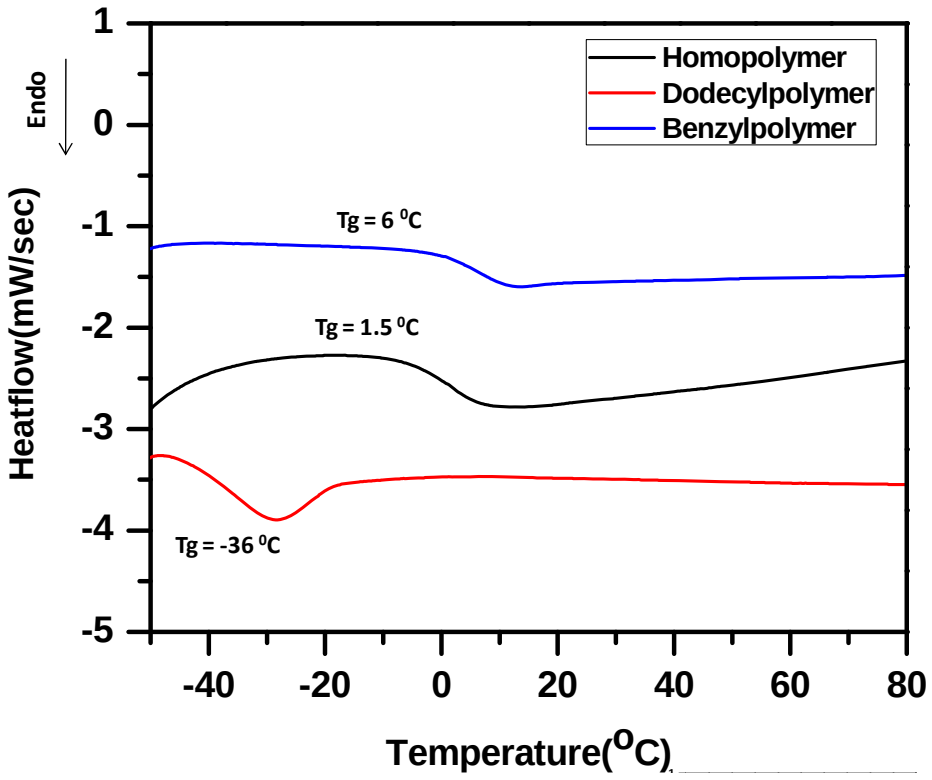

Figure S13: DSC thermograms of the parent hyperbranched polydithioacetal and various peripherally derivatized polymers.

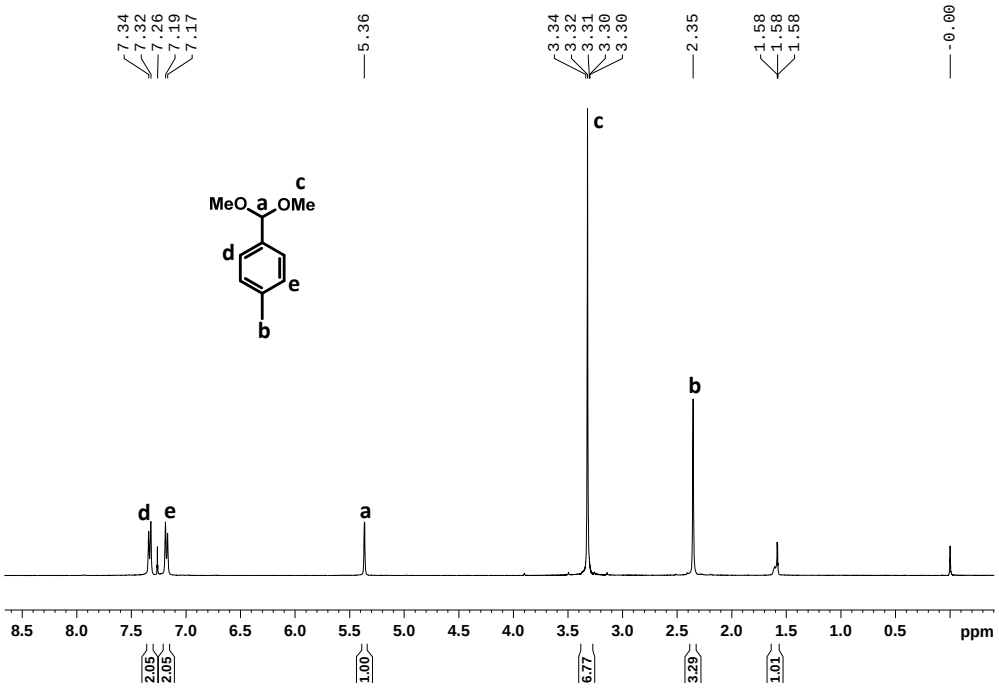

Figure S14: ^{1}H-NMR of the model terminal compound.

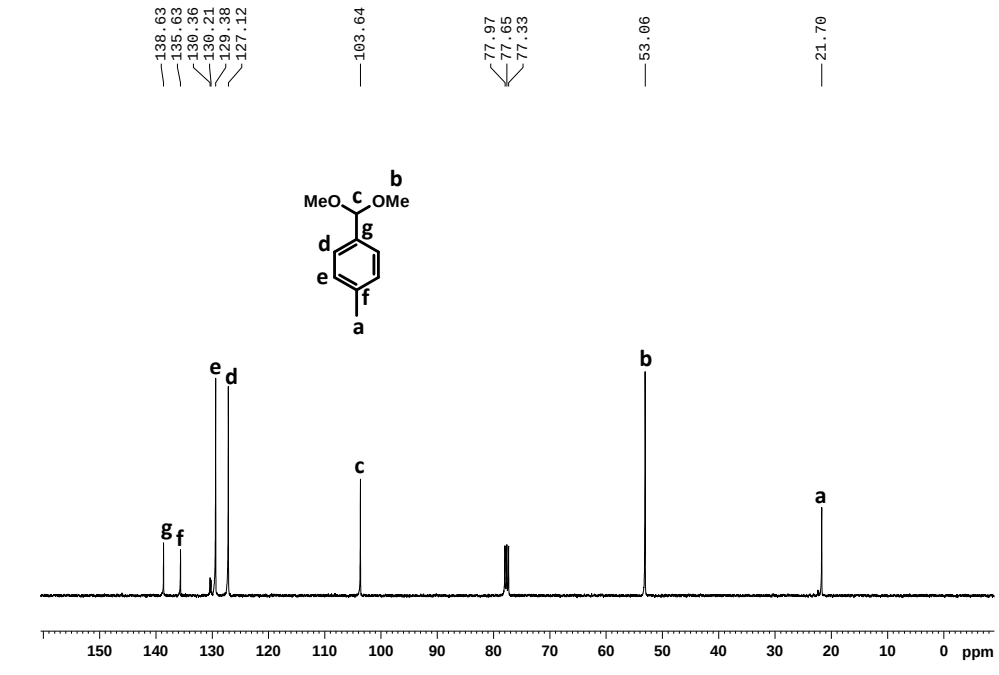

Figure S15: ^{13}C-NMR of the model terminal compound.

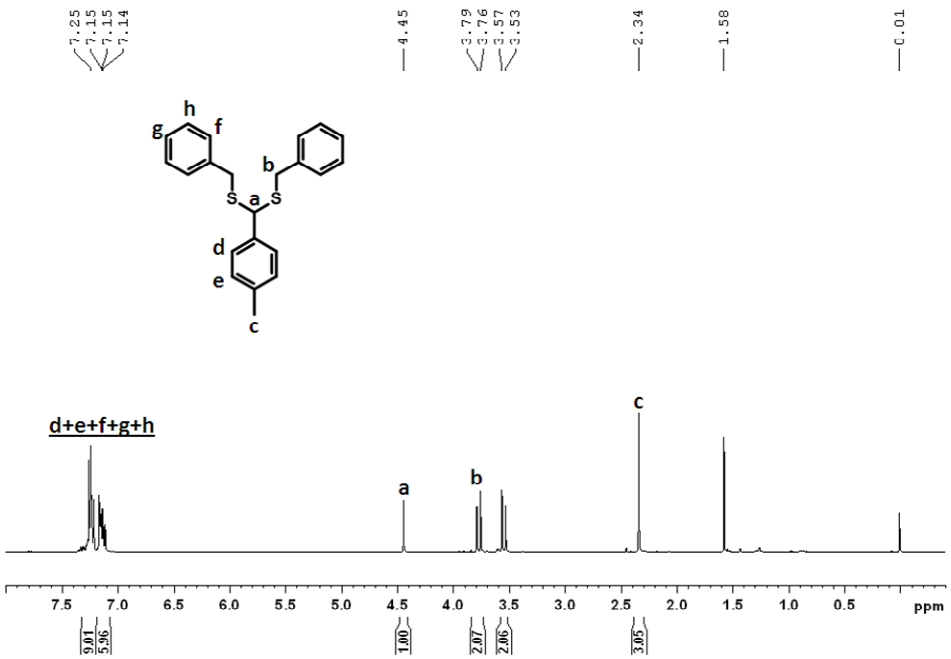

Figure S16: ^{1}H-NMR of the model dendritic compound.

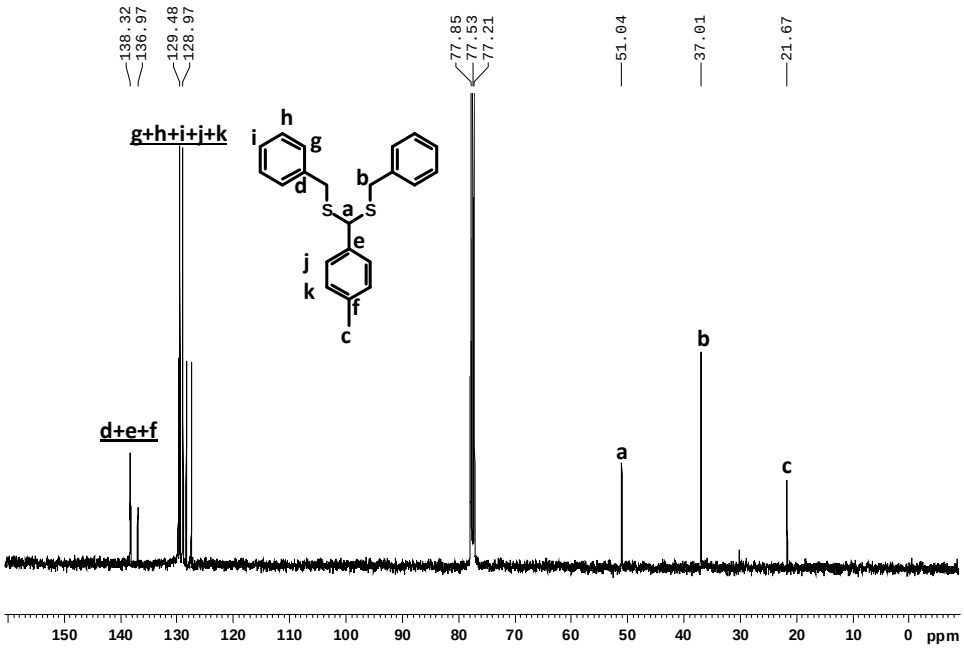

Figure S17: ^{1}H-NMR of the model dendritic compound.

References

1. Numerous efforts to make the model linear compound failed may be due to its instability. Although cyclic oxathiolanes are known but that does not exactly resemble our linear units.
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