

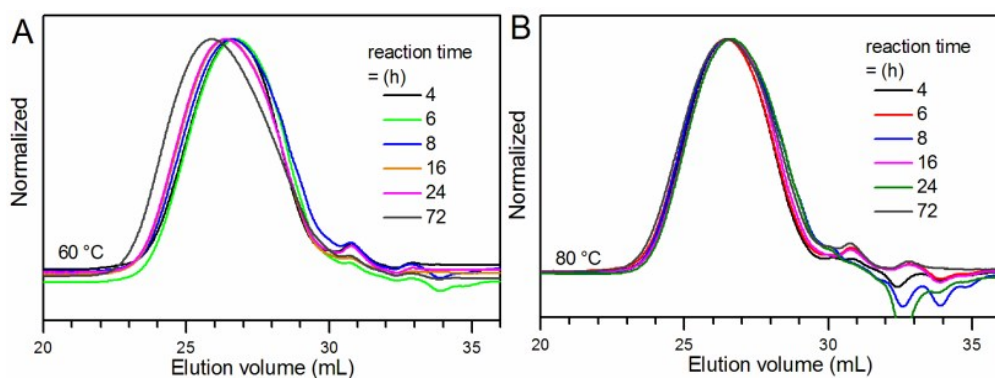
SUPPORTING INFORMATION

Control-Synthesized Multilayer Hyperbranched-Hyperbranched Polyethers with Tunable Molecular Weight and Invariant Degree of Branching

Tuan Liu^{1,2}, Xuepei Miao^{1,2}, Xinxin Geng¹, An Xing¹, Liangdong Zhang², Yan Meng^{1,*} and Xiaoyu Li^{2,*}

1. Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, P. R. China

2. State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, P. R. China



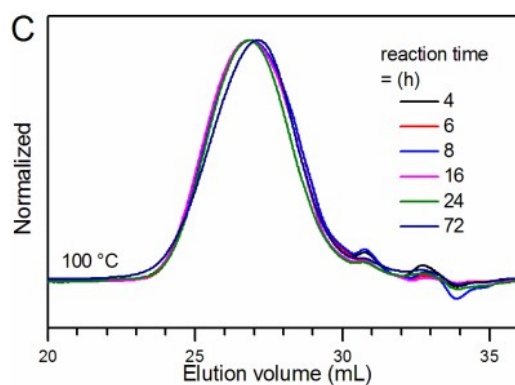


Fig. S1. Normalized GPC results of HBPE-2C as a function of reaction time when polymerization is carried out at (A) 60 °C, (B) 80 °C, and (C) 100 °C.

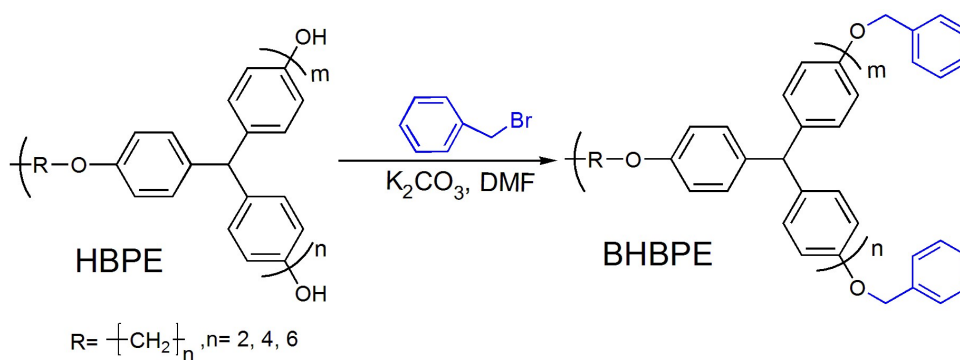


Fig. S2. The reaction route for terminal group modification.

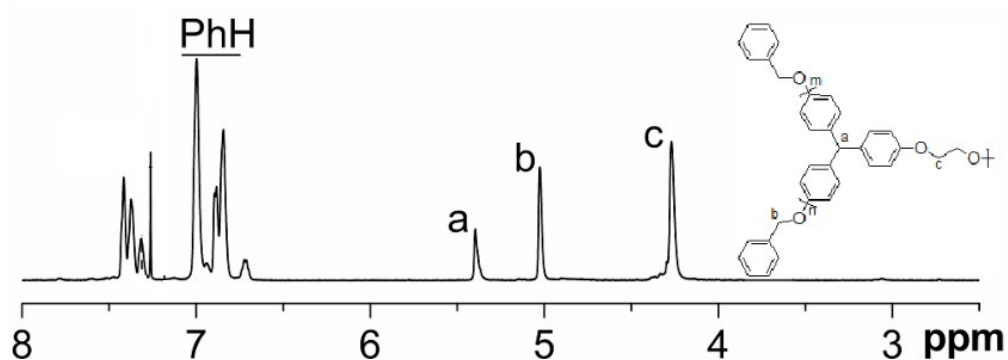


Fig. S3. ^1H NMR spectra of benzyl-terminated HBPE-2C (BHBPE-2C).

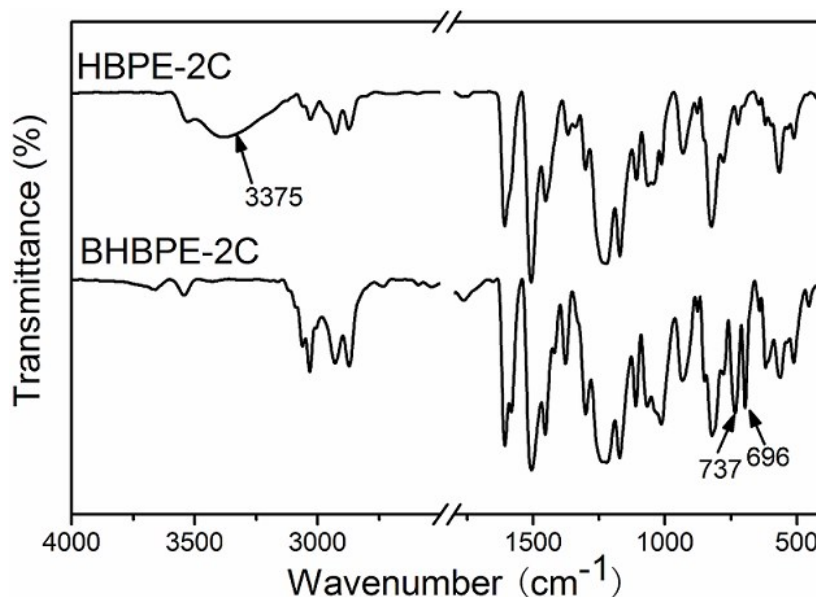


Fig. S4. FTIR spectra of HBPE-2C and BHBPE-2C.

Terminal group modification of HBPE-2C-1. 2 g HBPE-2C-1, 10.4 g benzyl bromide, 3.6 g K_2CO_3 , and 40 mL DMF were added into three-necked flask. Under mechanical stirring, reactants were heated to 80 °C and kept for 24 h under dry nitrogen atmosphere. After cooling to room temperature, the mixture was filtered and precipitated into petroleum ether twice. After the precipitate was dried under vacuum at 90 °C, the obtained benzyl-terminated HBPE-2C (BHBPE-2C) is a light red solid. Yield: 1.8 g, 70%. 1H -NMR (600 MHz, $CDCl_3$, δ): 4.22-4.30 (br, O- CH_2CH_2 -O), 5.00-5.05 (br, Ph_3CH_2 -O), 5.36-5.42 (br, Ph_3CH), 6.80-7.44 (br, C_6H_4 O).

Synthesis of triphenol methane. PHBA (24.4 g, 0.2 mol), phenol (94 g, 1.0 mol), $ZnCl_2$ (2.8 g, 0.02 mol), and PTSA (3.8 g, 0.02 mol) were added into a three-necked flask equipped with mechanical stir and thermometer. After stirring for 1 h, reactants were heated to 45 °C and kept for 24 h. The solution was filtered and washed at least twice using both dichloromethane (200 mL) and hot water (>70 °C). The resultant

mixtures were dried under vacuum at 90 °C. The obtained pure product is a brick-red solid with a yield of 70%. ¹H-NMR (600 MHz, acetone-d₆, δ): 5.33 (s, 1H, Ph₃CH), 6.76 (d, 6H, C₆H₄O), 6.94 (d, 6H, C₆H₄O), 8.15 (s, 3H, PhOH); ¹³C-NMR (600 MHz, acetone, δ): 54.32, 114.75, 130.06, 136.04, 155.50.

Synthesis of model compounds for the terminal unit (T). 2C-AB₂ (8 g, 0.02 mol), phenol (7.52, 0.08 mol), K₂CO₃ (16.58 g, 0.12 mol), and 200 mL DMF were added into a three-necked flask equipped under mechanical stirring. Reactants were heated to 80 °C and kept for 24 h and then cooled to room temperature. The mixture was acidified with hydrochloric acid and then filtered. After removing most DMF using a rotary evaporator, the remanent solution was pure into water. The precipitate was collected and dried under vacuum. The crude product was purified by a silica gel column with 1:1 ethyl acetate/petroleum ether as the eluent, and the obtained the product is a brick red solid with a yield of 90%. ¹H-NMR (600 MHz, (methyl sulfoxide)-d₆, δ): 4.30-4.24 (br, 4H, O(CH₂)₂O), 5.29 (s, 1H, Ph₃CH), 6.68 (d, 4H, C₆H₄O), 6.84-7.00 (m, 11H, C₆H₄O), 7.29 (t, 2H, C₆H₄O). ¹³C-NMR (600 MHz, (methyl sulfoxide)-d₆, δ): 54.02, 66.65, 66.73, 114.60, 114.93, 115.40, 121.19, 129.99, 130.23, 130.33, 135.43, 137.79, 155.93, 156.93, 158.77.

Synthesis of model compounds with well defined linear (L) and the denritic (D)

units. Both compounds were synthesized using the same method. Triphenol methane (11.68 g, 0.04 mol), 2-Phenoxyethylbromide (40.2 g, 0.2 mol), K₂CO₃ (16.6 g, 0.12

mol), and 200 mL DMF was added into a three-necked flask under mechanical stirring. The reactants were heated to 80 °C and kept for 24 h and then cooled to room temperature. The mixture was acidified with hydrochloric acid and then filtered. Most DMF was removed by a rotary evaporator. The crude product was purified by silica gel column chromatography with 1:20 ethyl acetate/petroleum ether as the eluent. The obtained product is a white crystal-like solid. The compounds with well defined linear and dendritic units have yields of 40% (L) and 25% (D), respectively.

Linear unit (L): $^1\text{H-NMR}$ (600 MHz, (methyl sulfoxide)- d_6 , δ): 4.25-4.30 (br, 4H, $\text{O}(\text{CH}_2)_2\text{O}$), 5.37 (s, 1H, Ph_3CH), 6.69 (d, 2H, $\text{C}_6\text{H}_4\text{O}$), 6.86-7.00 (m, 16H, $\text{C}_6\text{H}_4\text{O}$), 7.29 (t, 4H, $\text{C}_6\text{H}_4\text{O}$). $^{13}\text{C-NMR}$ (600 MHz, (methyl sulfoxide)- d_6 , δ): 53.45, 66.20, 114.18, 114.43, 114.96, 120.70, 129.49, 129.77, 129.86, 134.67, 137.02, 155.54, 156.53, 158.29.

Dendritic unit (D): $^1\text{H-NMR}$ (600 MHz, (methyl sulfoxide)- d_6 , δ): 4.30-4.26 (br, 4H, $\text{O}(\text{CH}_2)_2\text{O}$), 5.45 (s, 1H, Ph_3CH), 6.89-7.10 (m, 21H, $\text{C}_6\text{H}_4\text{O}$), 7.29 (t, 6H, $\text{C}_6\text{H}_4\text{O}$).

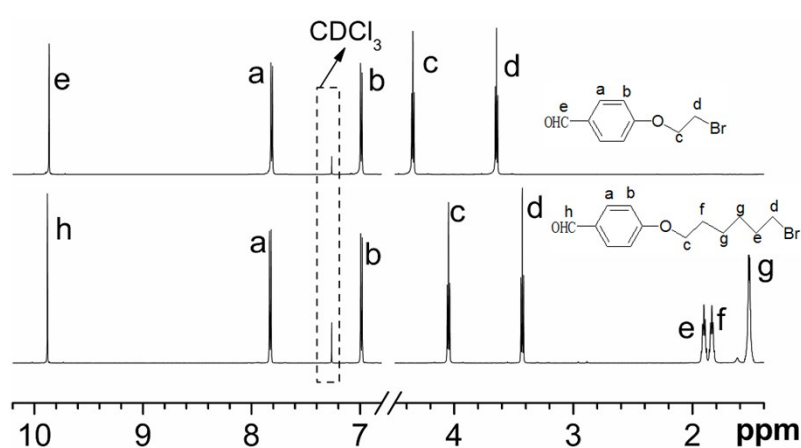


Fig. S5. ^1H NMR spectra of intermediate molecules of AB_2 monomers with different spacer lengths, *i.e.*, $n=2$ and 6.

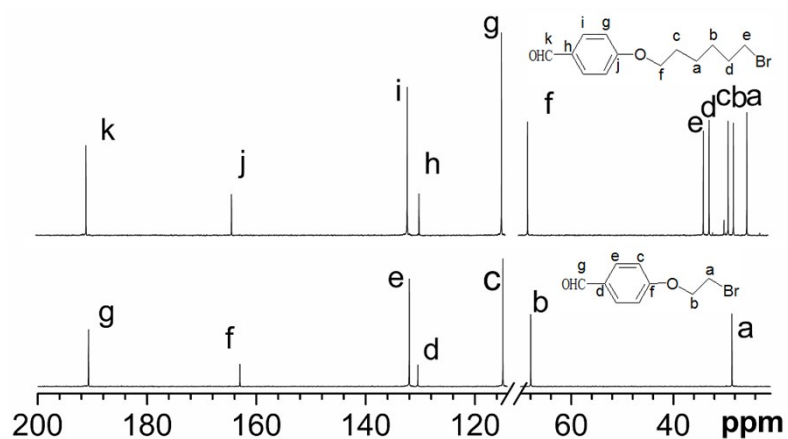


Fig. S6. ^{13}C NMR spectra of intermediate molecules with different spacer lengths, *i.e.*, $n=2$ and 6.

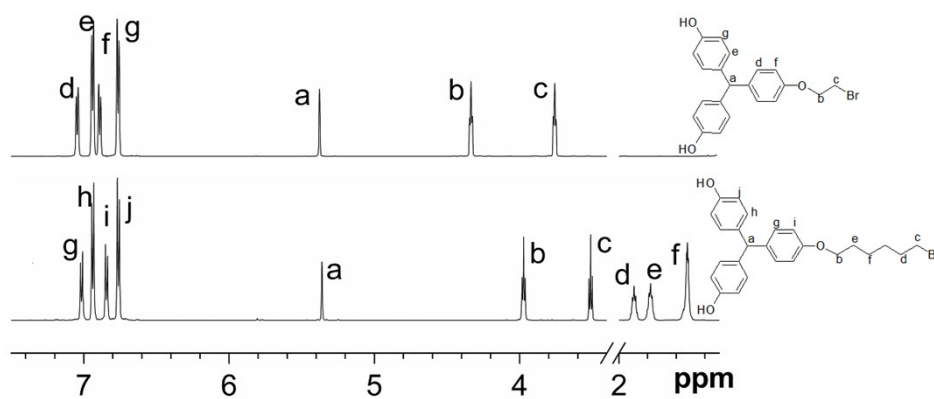


Fig. S7. ^1H NMR spectra of three AB_2 monomers with different spacer lengths, *i.e.*, $n=2$ and 6.

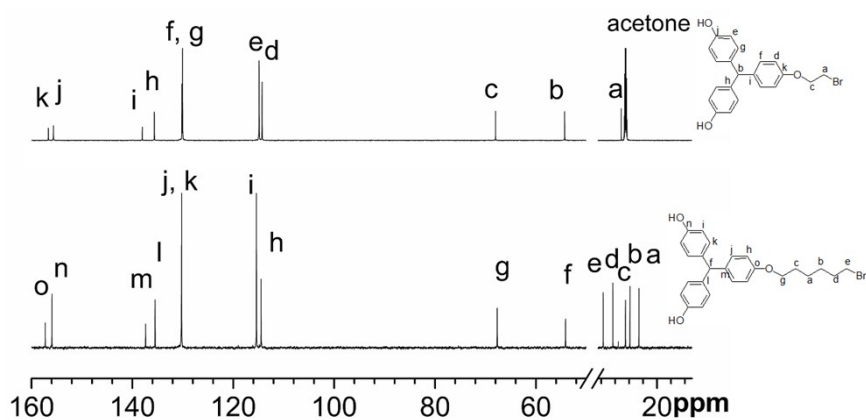


Fig. S8. ^{13}C NMR spectra of three AB_2 monomers with different spacer lengths, *i.e.*, $n = 2$ and 6 .

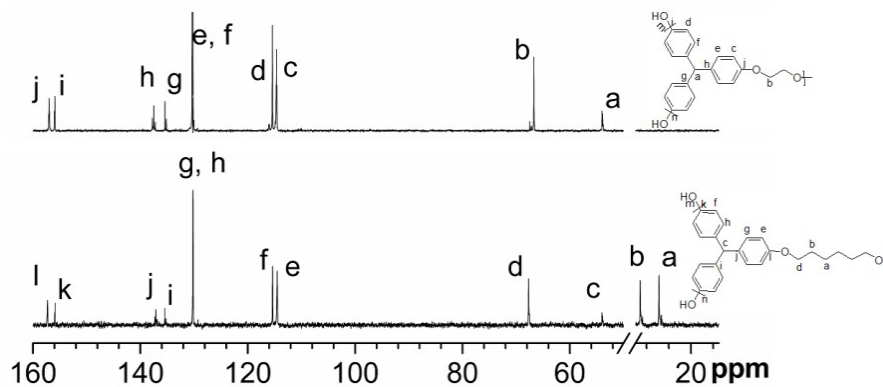


Fig. S9. The ^{13}C NMR spectra of HBPEs (80°C , 0.1 mol/L) obtained from monomers with different spacer lengths, *i.e.*, $n = 2$ and 6 .

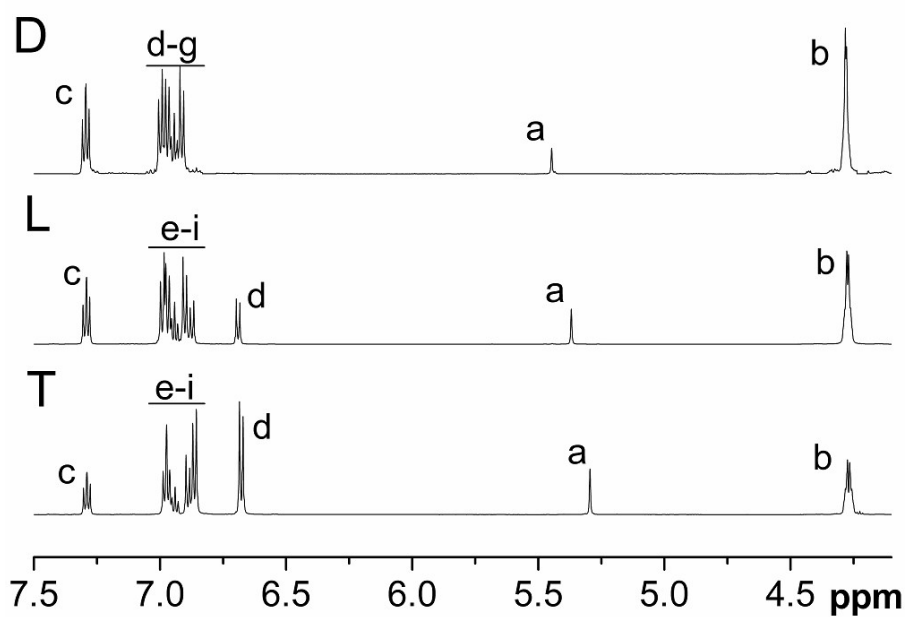


Fig. S10. The ^1H NMR spectra of three model molecules, which can be used to determine the degree of branching of HBPEs.

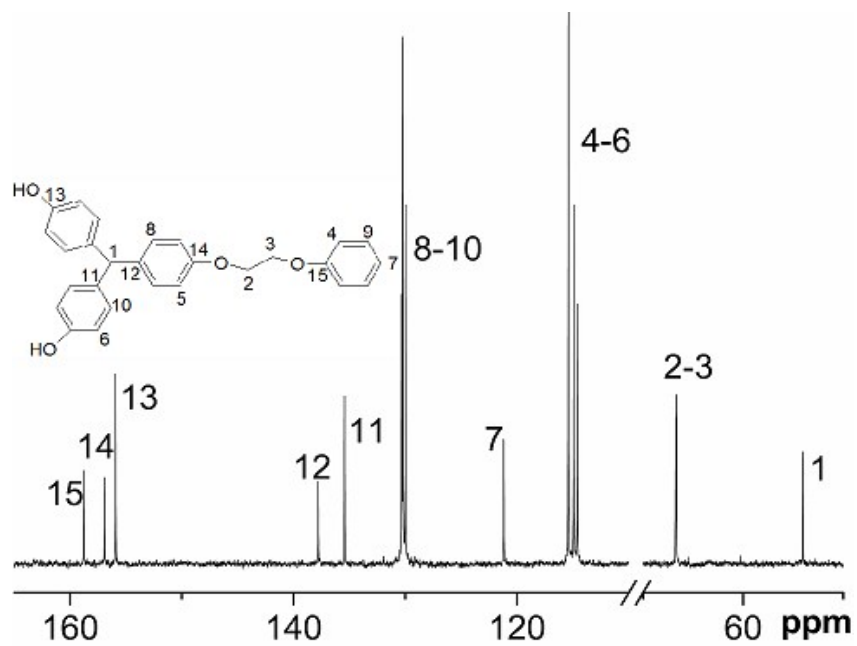


Fig. S11. The ^{13}C NMR spectra of the model molecule showing the peak positions of the terminal unit (T).

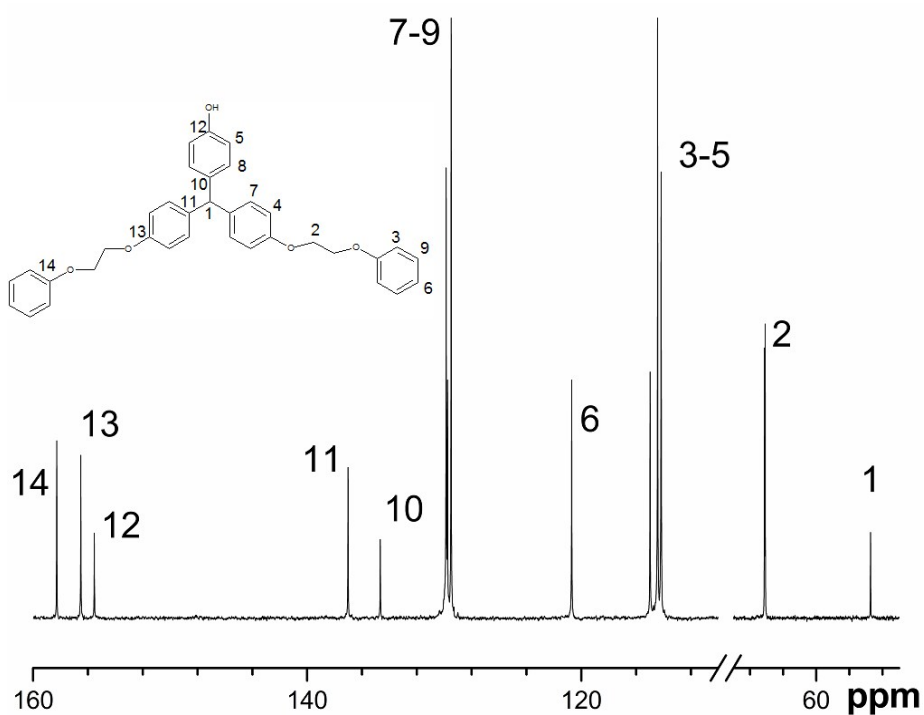


Fig. S12. ^{13}C NMR spectra of the model molecule showing the peak positions of the linear unit (L).

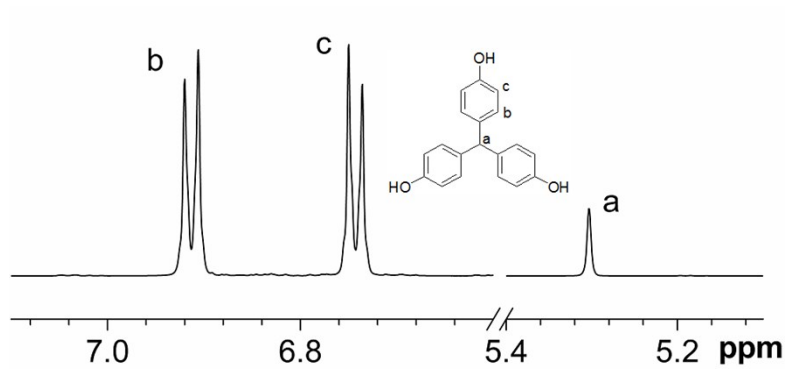


Fig. S13. ^1H NMR spectra of the model molecule, triphenol methane.

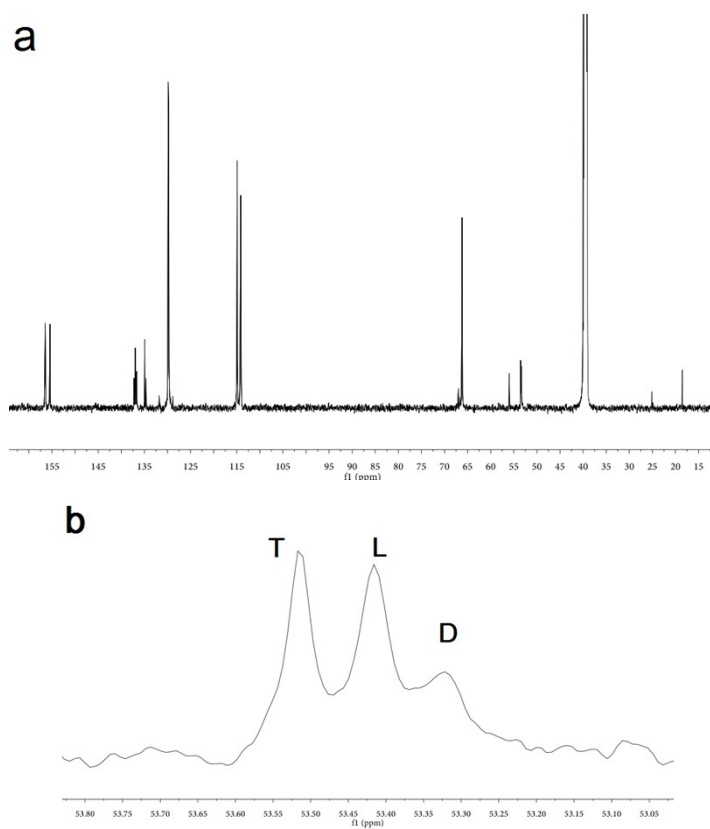


Fig. S14. ^{13}C NMR spectra of HBPE2C-5 (a) and the enlarged view covering 53 to 54 ppm (b).

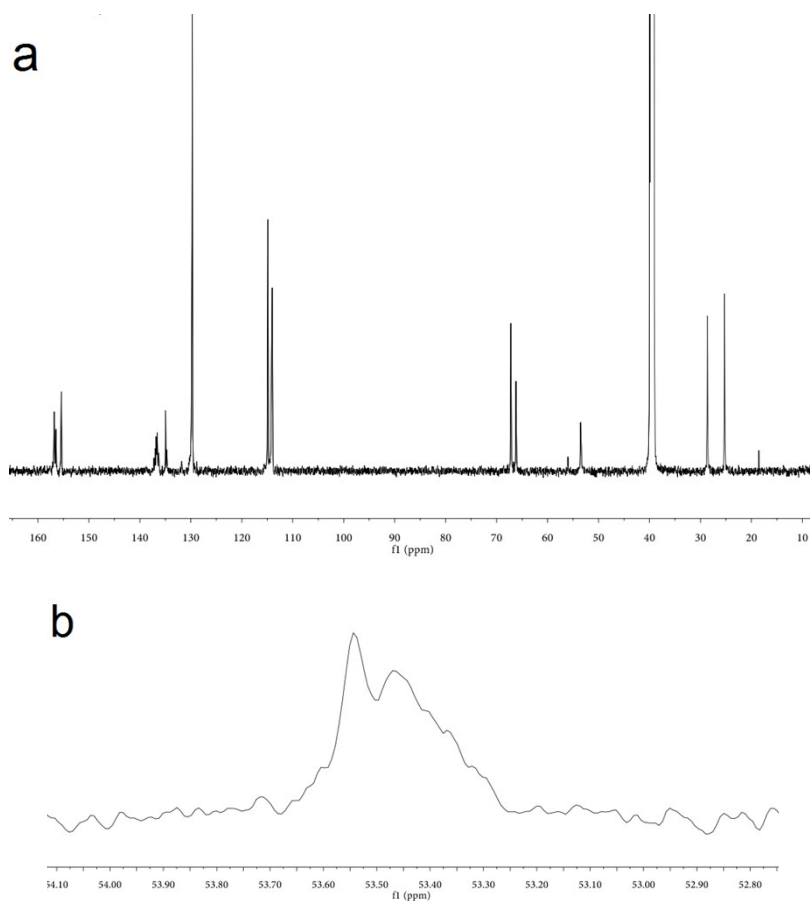


Fig. S15. ^{13}C NMR spectra of C2-C6-C2-C6 (a) and its enlarged views (b).

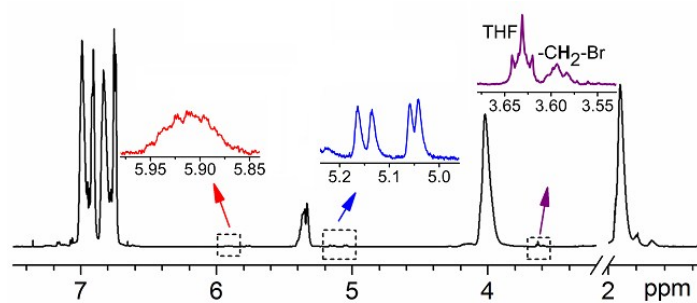


Fig. S16. The ^1H NMR spectrum of HBPE-4C-1 (80 °C, 24 h). Insets show the enlarged views of boxed regions.