SUPPORTING INFORMATION

Hyperbranched polyethers with tunable glass transition temperature: controlled synthesis and mixing rules

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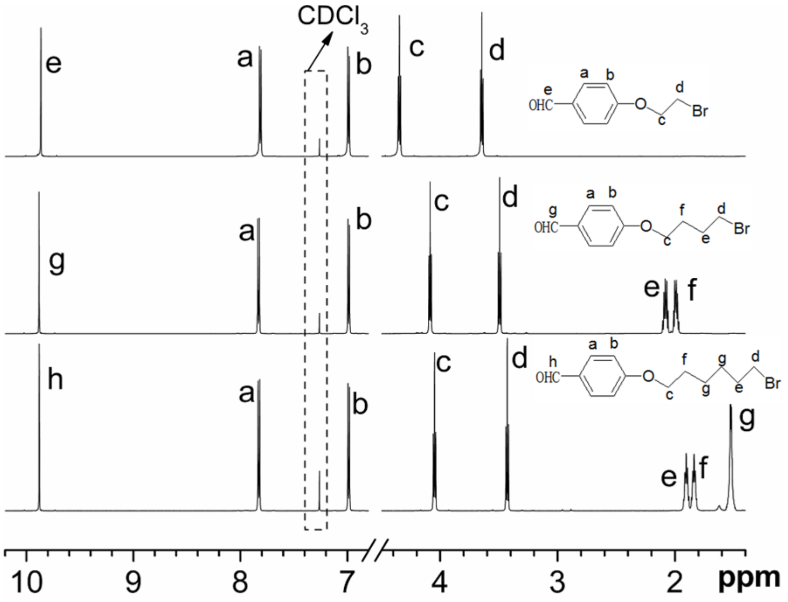

Fig. S1 ^{1}H NMR spectra of monomers with different spacer lengths, *i.e.*, n =2, 4, and 6.

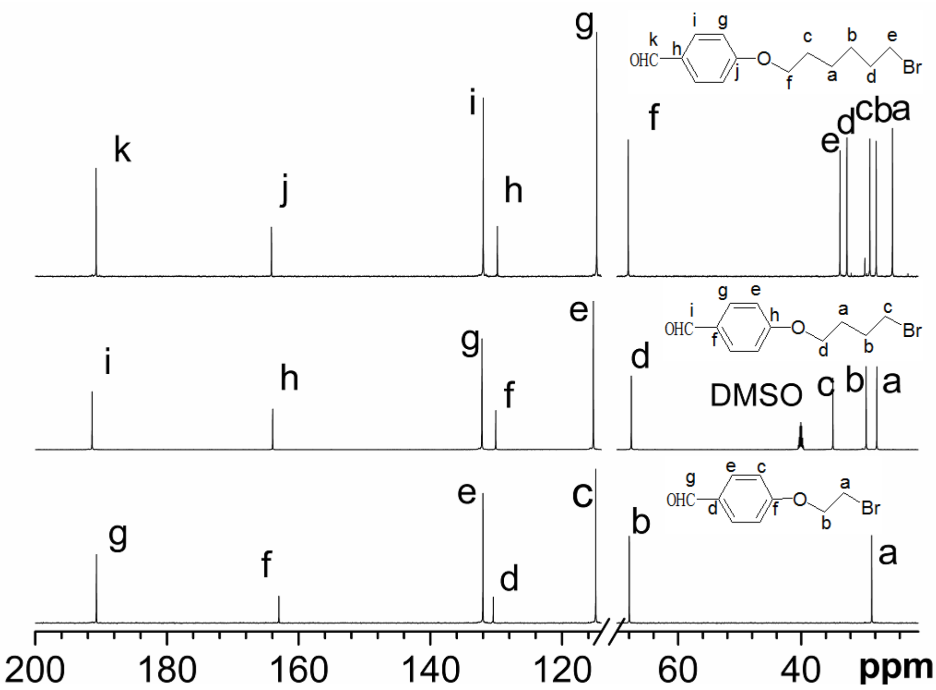

Fig. S2 ^{13}C NMR spectra of monomers with different spacer lengths, *i.e.*, n=2, 4, and 6.

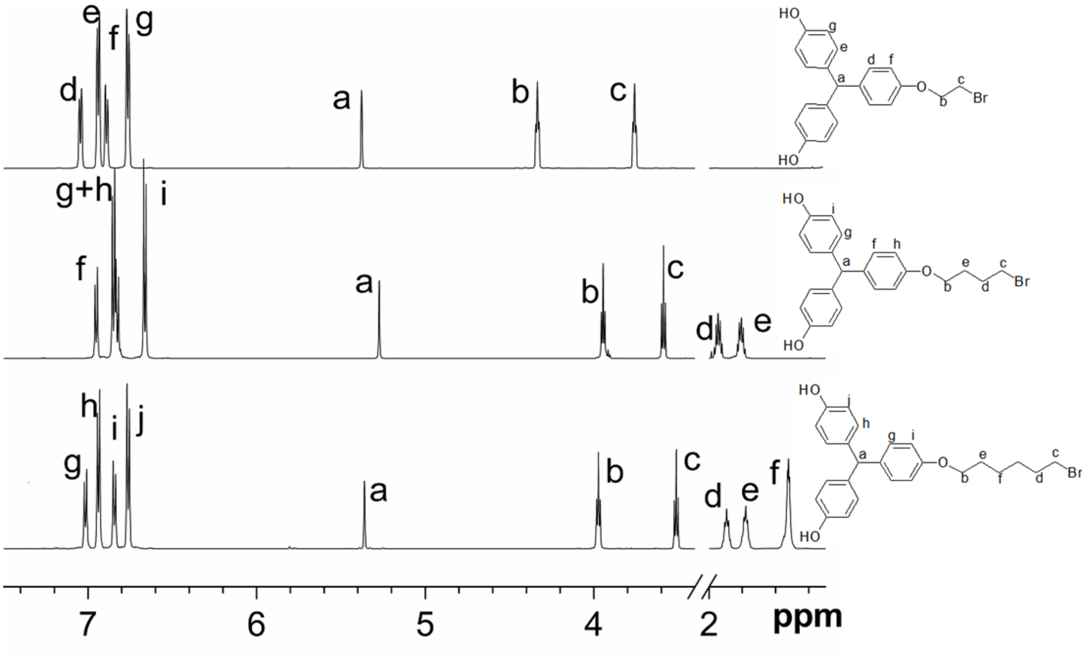

Fig. S3 ^{1}H NMR spectra of three AB_2 monomers with different spacer length, *i.e.*, n = 2, 4, and 6.

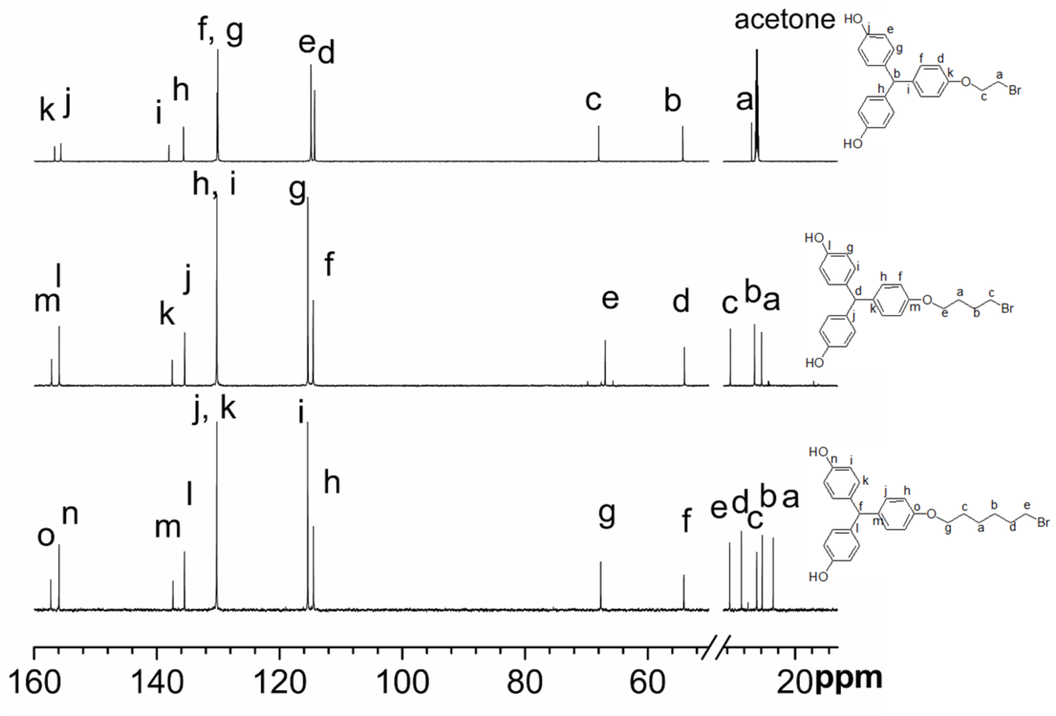

Fig. S4 ^{13}C NMR spectra of three AB_2 monomers with different spacer length, *i.e.*, n = 2, 4, and 6.

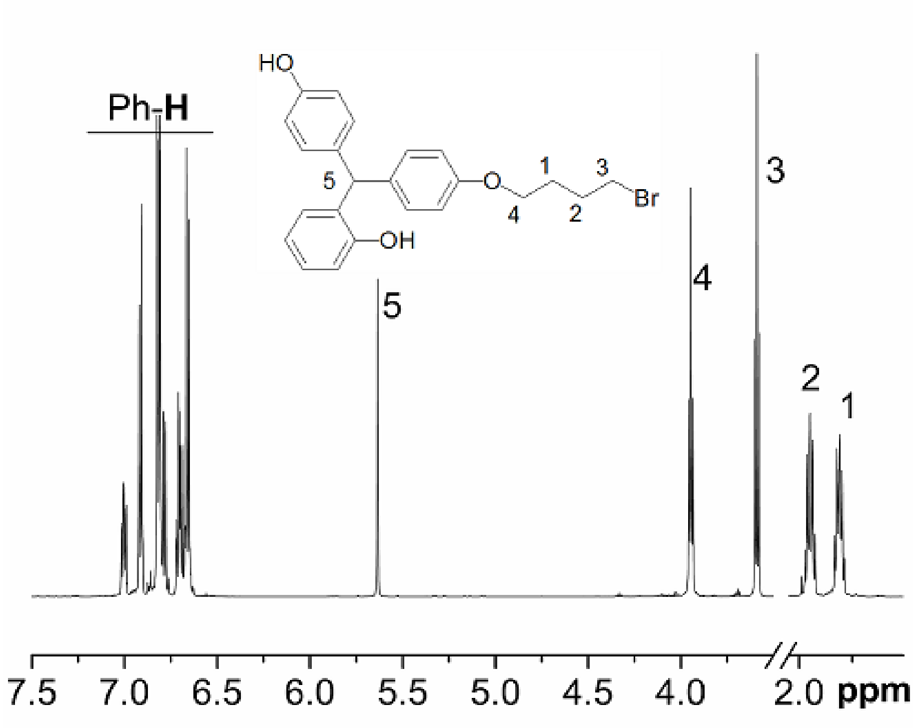

Fig. S5 ^{1}H NMR spectrum of the byproduct (n=2) in Scheme 1.

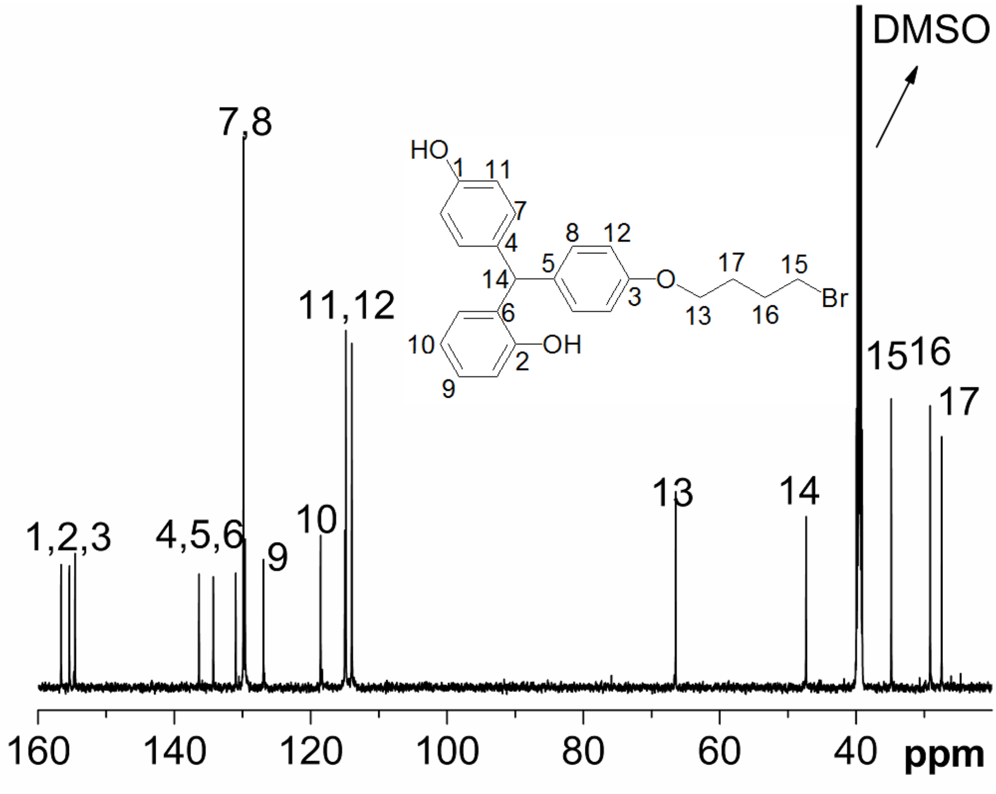

Fig. S6 The ^{13}C NMR spectrum of the byproduct (n=2) in Scheme 1.

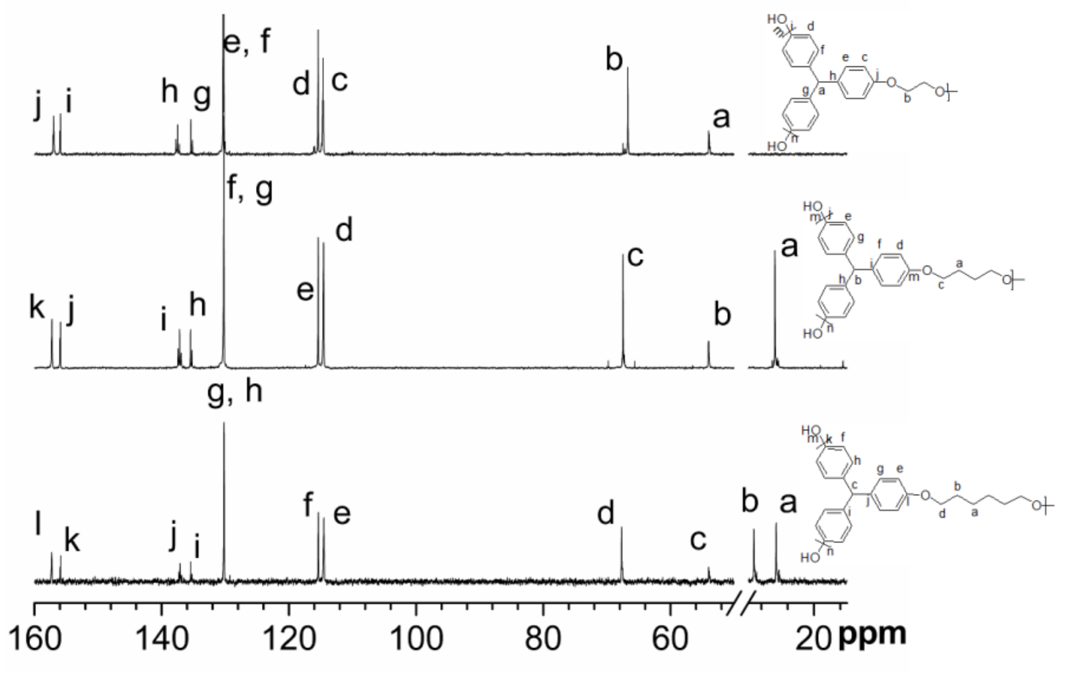

Fig. S7 The ^{13}C NMR spectra of HBPEs (80 °C, 0.1 mol/L) obtained from monomers with different spacer lengths, *i.e.*, n =2, 4 and 6.

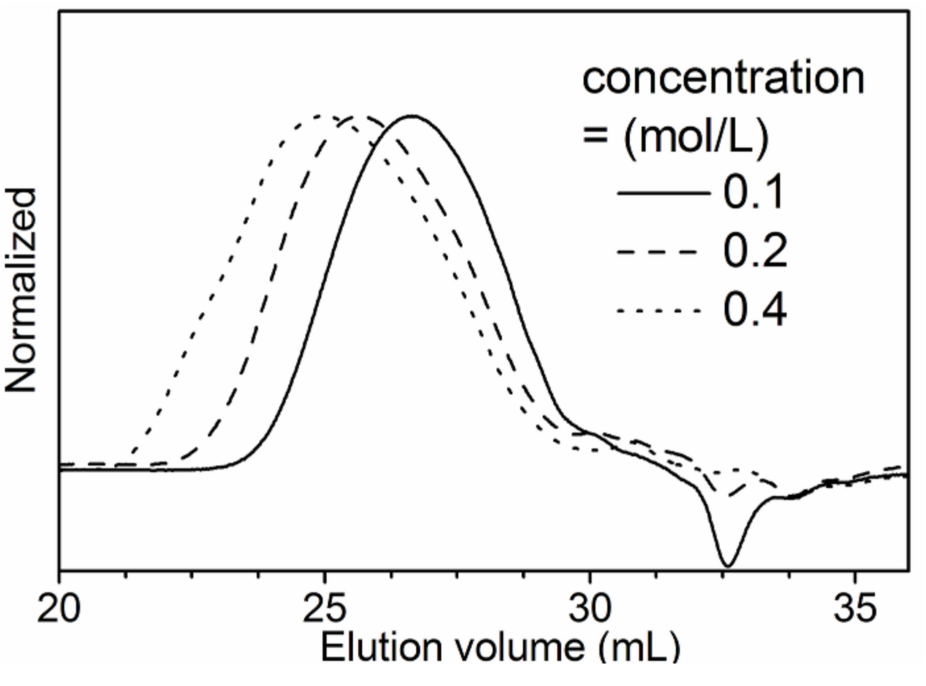

Fig. S8 The variation of GPC curves with concentration from 0.1 mol/L to 0.4 mol/L when polymered for 24 h.

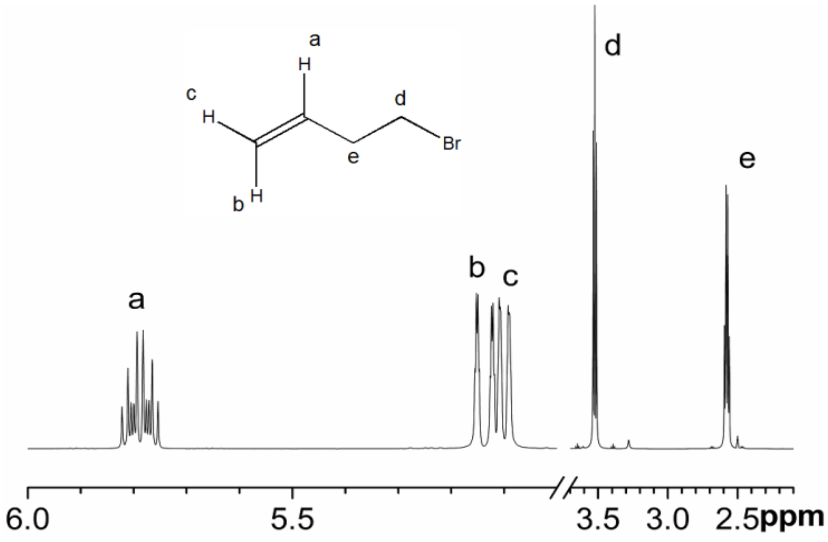

Fig. S9 The ^{1}H NMR spectrum of model compound 4-bromo-1-butene.

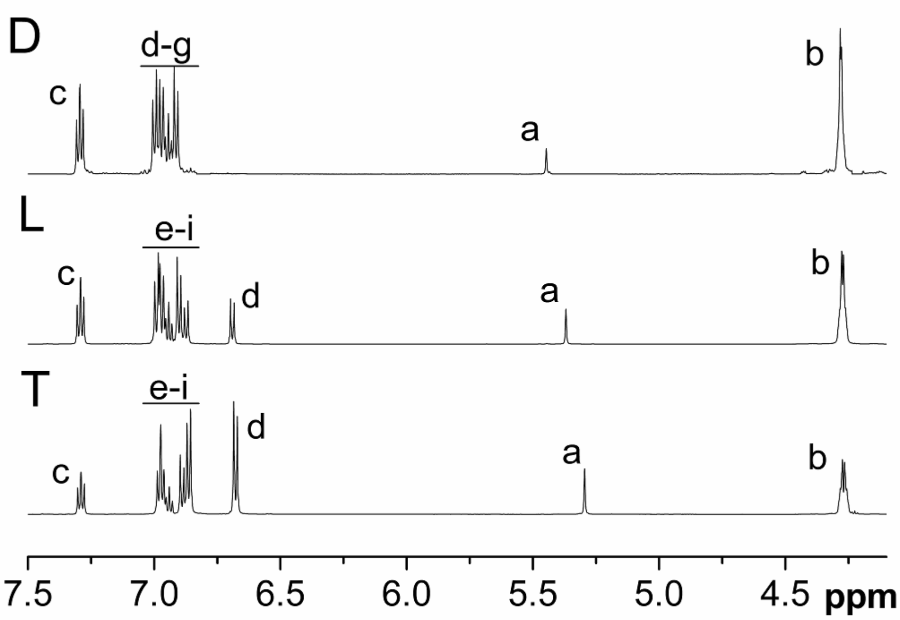

Fig. S10 The ^{1}H NMR spectra of three model molecules which are used to determine the degree of branching in HBPEs.

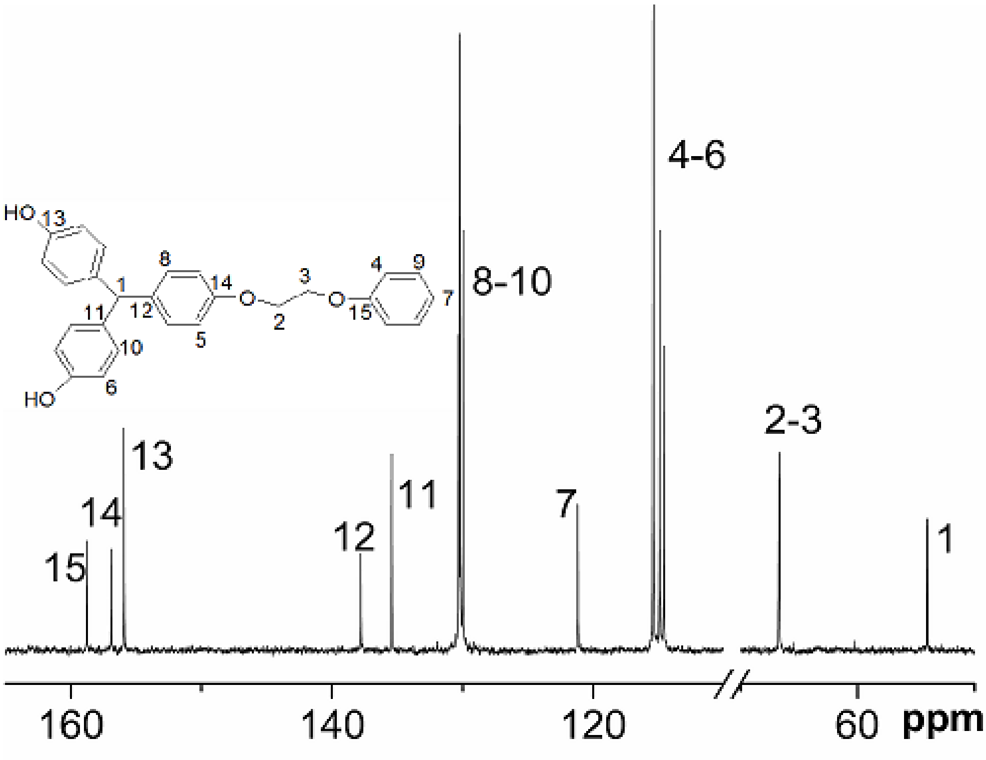

Fig. S11 The ^{13}C NMR spectra of the model molecule showing the peak position of the terminal unit (T).

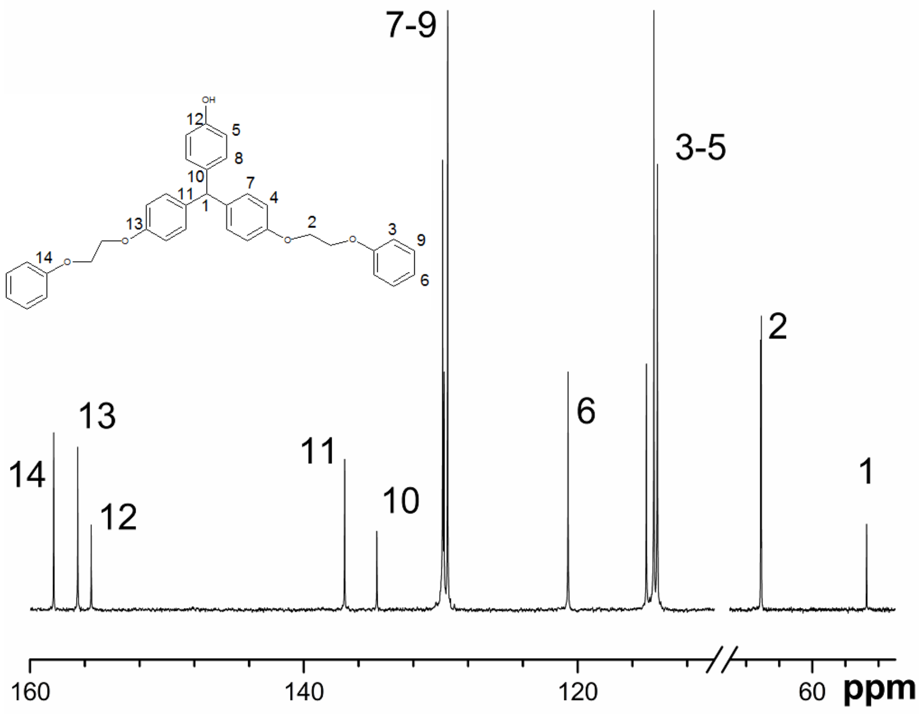

Fig. S12 ^{13}C NMR spectra of the model molecule showing the peak position of the linear unit (L).

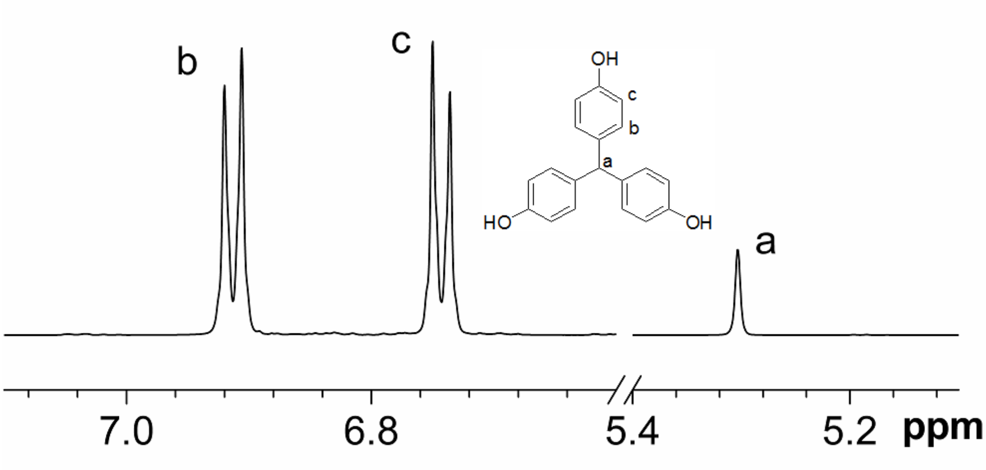

Fig. S13 ^{1}H NMR spectra of the model molecule, triphenol methane.

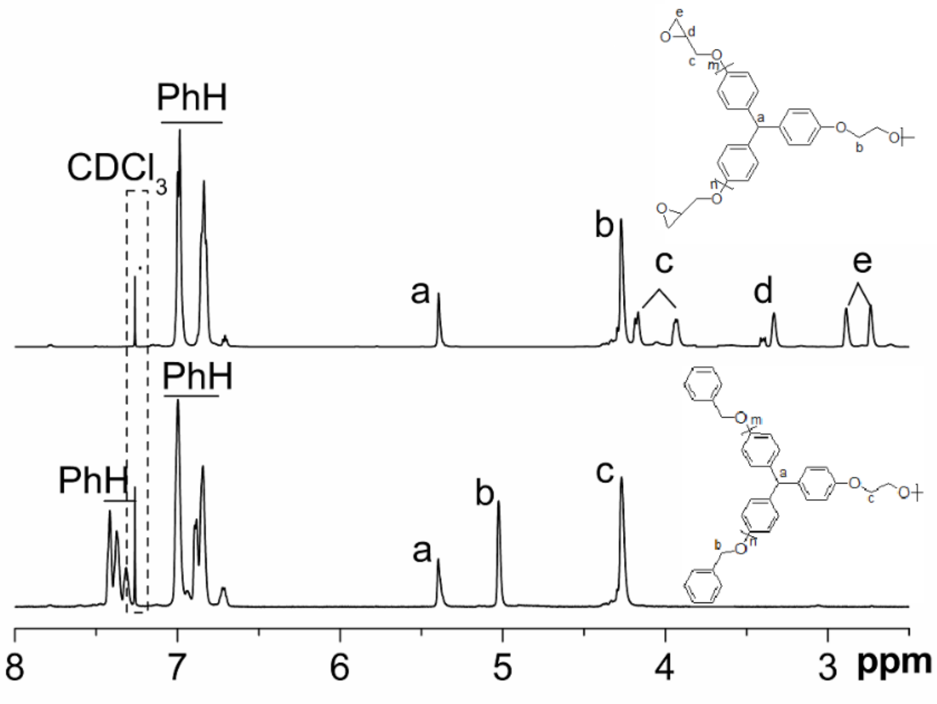

Fig. S14 ^{1}H NMR spectra of epoxide-terminated HBPE-2C-1 (EHBPE-2C-1) and benzyl-terminated HBPE-2C-1 (BHBPE-2C-1).

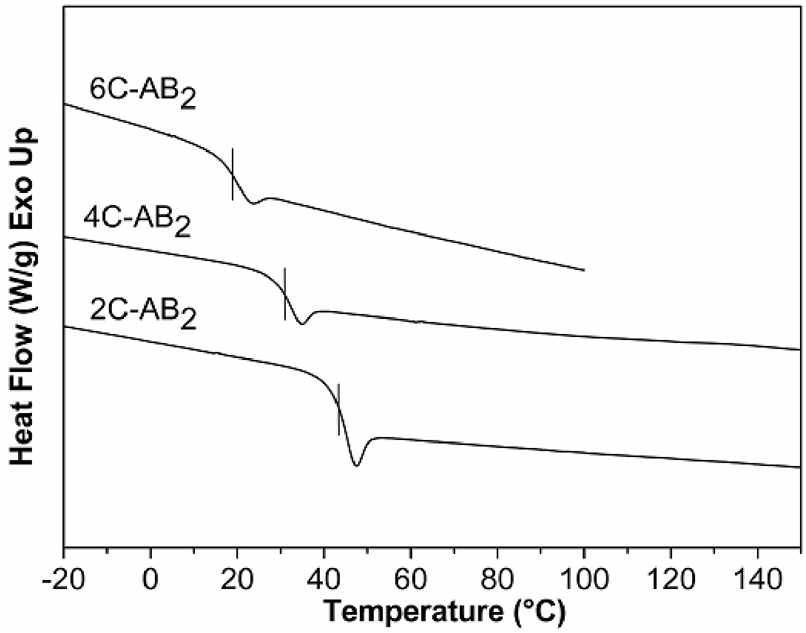

Fig. S15 DSC traces of three AB_2 monomers (n=2, 4, and 6).

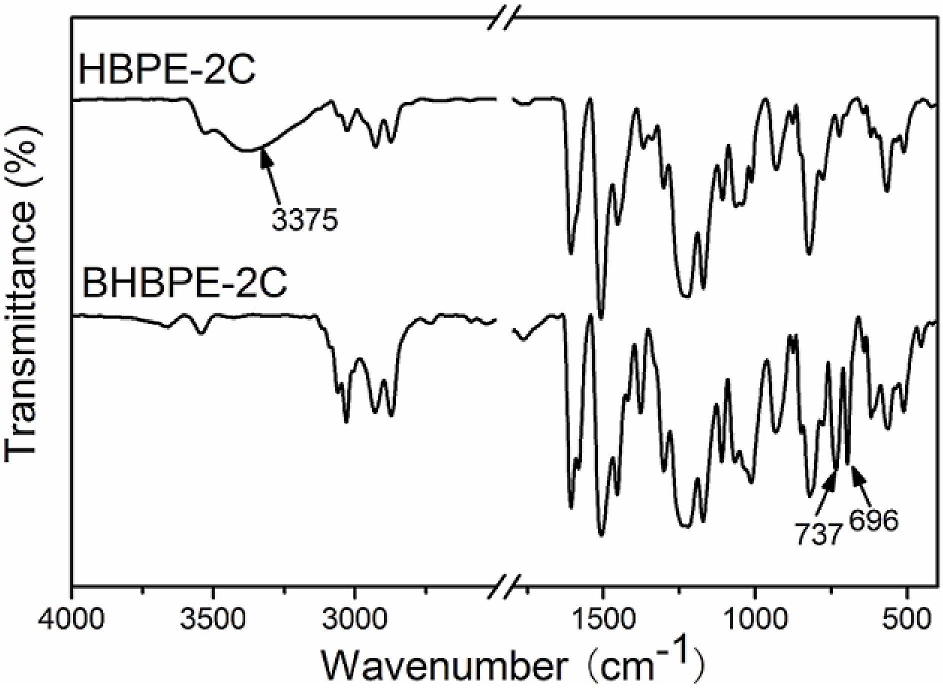

Fig. S16 FTIR spectra of HBPE-2C and BHBPE-2C-1.

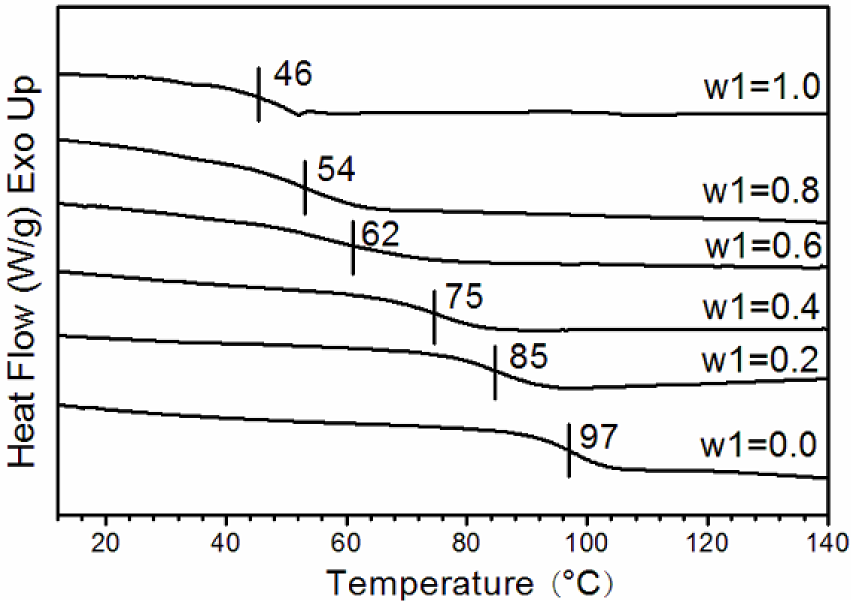

Fig. 17 T_gs of binary blends of benzyl-terminated BHBPE-2C-1 and BHBPE-6C-1 as a function of the weight fraction of BHBPE-6C-1.

HBPE-2C:^{1}H-NMR (600 MHz, (methyl sulfoxide)-d6, *δ*): 4.22-4.36 (br, O(C**H**$_2$)$_2$O), 5.30-5.47 (br, C**H**Ph$_3$), 6.75-7.10 (br, C$_6$**H**$_4$O). ^{13}C-NMR (600 MHz, (methyl sulfoxide)-d6, δ): 53.90, 66.72, 114.65, 115.40, 130.21, 130.34, 135.45, 137.50, 155.95, 156.98.

HBPE-4C: ^{1}H-NMR (600 MHz, (methyl sulfoxide)-d6, *δ*): 1.84-1.97 (br, OCH$_2$(C**H**$_2$)$_2$CH$_2$O), 3.92-4.08 (br, OC**H**$_2$(CH$_2$)$_2$C**H**$_2$O), 5.30-5.44 (br, C**H**Ph$_3$), 6.72-7.04 (br, C$_6$**H**$_4$O). ^{13}C-NMR (600 MHz, (methyl sulfoxide)-d6, δ): 25.95, 54.00, 67.49, 114.56, 115.42, 130.22, 130.25, 135.44, 137.21, 155.89, 157.28.

HBPE-6C:^{1}H-NMR (600 MHz, (methyl sulfoxide)-d6, *δ*): 1.40-1.58 (br, O(CH$_2$)$_2$(C**H**$_2$)$_2$(CH$_2$)$_2$O), 1.64-1.82 (br, OCH$_2$C**H**$_2$(CH$_2$)$_2$C**H**$_2$CH$_2$O), 3.80-4.00 (br, OC**H**$_2$(CH$_2$)$_4$C**H**$_2$O), 5.28-5.41 (br, C**H**Ph$_3$), 6.70-7.08 (br, C$_6$**H**$_4$O). ^{13}C-NMR (600

MHz, (methyl sulfoxide)-d6, δ): 25.78, 29.14, 52.95, 67.70, 114.57, 115.36, 130.22, 135.50, 137.10, 155.90, 157.30.

Synthesis of 4-(4-bromine-butoxy)benzaldehyde and 4-(6-bromine-hexyloxy) -benzaldehyde

Both 4-(4-bromine-butoxy)-benzaldehyde and 4-(6-bromine-hexyloxy)-benzaldehyde were synthsized using the same procedure as that of 4-(2-bromine-oxethyl)-benzaldehyde. The obtained product is a brown viscous liquid with a yield of 80%.

4-(4-bromine-butoxy)-benzaldehyde: ^{1}H-NMR (600 MHz, $CDCl_3$, *δ*): 1.96-2.02 (m, 2*H*, $OCH_2C\mathbf{H}_2(CH_2)_2Br$), 2.06-2.12 (m, 2*H*, $O(CH_2)_2C\mathbf{H}_2CH_2Br$), 3.50 (t, 2*H*, $O(CH_2)_3C\mathbf{H}_2Br$), 4.09 (t, 2*H*, $OC\mathbf{H}_2(CH_2)_3Br$), 6.99 (d, 2*H*, $C_6\mathbf{H}_4O$), 7.83 (d, 2*H*, $C_6\mathbf{H}_4O$), 9.88 (s, 1*H*, PhC**H**O). ^{13}C-NMR (600 MHz, (methyl sulfoxide)-d6, δ): 27.73, 29.46, 34.87, 67.62, 115.24, 130.07, 132.16, 163.95, 191.36.

4-(6-bromine-hexyloxy)-benzaldehyde: ^{1}H-NMR (600 MHz, $CDCl_3$, *δ*): 1.48-1.56 (m, 4*H*, $O(CH_2)_2(C\mathbf{H}_2)_2(CH_2)_2Br$), 1.81-1.87 (m, 2*H*, $OCH_2C\mathbf{H}_2(CH_2)_4Br$), 1.88-1.96 (m, 2*H*, $O(CH_2)_4C\mathbf{H}_2CH_2Br$), 3.45 (t, 2*H*, $O(CH_2)_5C\mathbf{H}_2Br$), 4.05 (t, 2*H*, $OC\mathbf{H}_2(CH_2)_5Br$), 6.99 (d, 2*H*, $C_6\mathbf{H}_4O$), 7.83 (d, 2*H*, $C_6\mathbf{H}_4O$), 9.88 (s, 1*H*, PhC**H**O).^{13}C-NMR (600 MHz, $CDCl_3$, δ): 25.19, 27.84, 28.86, 32.59, 33.72, 68.12, 114.73, 129.10, 131.97, 164.13, 190.75.

Synthesis of 4-(4-bromine-butoxy)-4',4''- dihydroxy triphenylmethane (4C-AB_2) and 4-(6-bromine-hexyloxy)-4',4''- dihydroxy triphenylmethane (6C-AB_2)

Both 4C-AB_2 and 6C-AB_2 were synthsized using the same procedure as 2C-AB_2, and the obtained product is a pink crytal-like solid with a yield of 40%.

4C-AB_2: ^{1}H-NMR (600 MHz, (methyl sulfoxide)-d6, *δ*): 1.78-1.84 (m, 2*H*, $OCH_2C\mathbf{H}_2(CH_2)_2Br$), 1.91-1.98 (m, 2*H*, $O(CH_2)_2C\mathbf{H}_2CH_2Br$), 3.59 (t, 2*H*, $O(CH_2)_3C\mathbf{H}_2Br$), 3.94 (t, 2*H*, $OC\mathbf{H}_2(CH_2)_3Br$), 5.27 (s, 1*H*, $C\mathbf{H}Ph_3$), 6.66 (d, 4*H*, $C_6\mathbf{H}_4O$), 6.83 (d, 2*H*, $C_6\mathbf{H}_4O$), 6.85 (d, 4*H*, $C_6\mathbf{H}_4O$), 6.95 (d, 2*H*, $C_6\mathbf{H}_4O$), 9.21 (s, 2*H*, $PhO\mathbf{H}$). ^{13}C-NMR (600 MHz, (methyl sulfoxide)-d6, δ): 27.91, 29.59, 35.29, 54.03, 66.94, 114.53, 115.39, 130.21, 130.26, 135.46, 137.50, 155.91, 157.13.

By product: ^{1}H-NMR (600 MHz, (methyl sulfoxide)-d6, *δ*): 1.78-1.84 (m, 2*H*, $OCH_2C\mathbf{H}_2(CH_2)_2Br$), 1.93-1.98 (m, 2*H*, $O(CH_2)_2C\mathbf{H}_2CH_2Br$), 3.59 (t, 2*H*, $O(CH_2)_3C\mathbf{H}_2Br$), 3.95 (t, 2*H*, $OC\mathbf{H}_2(CH_2)_3Br$), 5.64 (s, 1*H*, $C\mathbf{H}Ph_3$), 6.65-7.03 (br, $C_6\mathbf{H}_4O$).^{13}C-NMR (600 MHz, (methyl sulfoxide)-d6, δ): 27.47, 29.15, 34.87, 47.36, 66.47, 113.97, 114.85, 118.56, 126.92, 129.62, 129.87, 131.00, 134.30, 136.38, 154.57, 155.39, 156.62.

6C-AB_2: ^{1}H-NMR (600 MHz, acetone-d_6, *δ*): 1.48-1.58 (m, 4*H*, $O(CH_2)_2(C\mathbf{H}_2)_2(CH_2)_2Br$), 1.75-1.82 (m, 2*H*, $OCH_2C\mathbf{H}_2(CH_2)_4Br$), 1.87-1.93 (m, 2*H*, $O(CH_2)_4C\mathbf{H}_2CH_2Br$), 3.51 (t, 2*H*, $O(CH_2)_5C\mathbf{H}_2Br$), 4.97 (t, 2*H*, $OC\mathbf{H}_2(CH_2)_5Br$), 5.36 (s, 1*H*, $C\mathbf{H}Ph_3$), 6.76 (d, 4*H*, $C_6\mathbf{H}_4O$), 6.85 (d, 2*H*, $C_6\mathbf{H}_4O$), 6.95 (d, 4*H*, $C_6\mathbf{H}_4O$), 7.03 (d, 2*H*, $C_6\mathbf{H}_4O$), 8.14 (s, 2*H*, $PhO\mathbf{H}$). ^{13}C-NMR (600 MHz, (methyl sulfoxide)-d6, δ):

25.19, 27.79, 29.06, 32.66, 35.44, 54.12, 67.66, 114.48, 115.41, 130.22, 130.25, 135.49, 137.37, 155.94, 157.27.

Synthesis of triphenol methane

PHBA (12.2 g, 0.1 mol), phenol (47 g, 0.5 mol), $ZnCl_2$ (1.4 g, 0.01mol), and PTSA (1.9 g, 0.01 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 for 24 h. Then the solution was filtered and washed at least twice with 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%. ^{1}H-NMR (600 MHz, acetone-d_6, δ): 5.33 (s, 1*H*, $Ph_3C\mathbf{H}$), 6.76 (d, 6*H*, $C_6\mathbf{H}_4O$), 6.94 (d, 6*H*, $C_6\mathbf{H}_4O$), 8.15 (s, 3*H*, PhO**H**); ^{13}C-NMR (600 MHz, acetone, δ): 54.32, 114.75, 130.06, 136.04, 155.50.

Synthesis of a model compound for the terminal unit (T)

2C-AB_2 (4 g, 0.01 mol), phenol (3.76, 0.04 mol), K_2CO_3 (8.29 g, 0.06 mol), and 100 mL DMF were added into a three-necked flask equipped under mechanical stirring. Reactants were heated to 80 °C for 24 h and then cooled to room temperature. The mixture was acidified with hydrochloric acid and then filtered. After removing most of DMF by a rotary evaporator, the remanent solution was pure into water. The precipitate was collected and dried under vacuum. The crude pruduct was purified by silica gel column chromatography with 1:1 ethyl acetate/petroleum ether as the eluent, and the obtained the product was a brick red solid with a yield of 90%. ^{1}H-NMR (600 MHz, (methyl sulfoxide)-d6, δ): 4.30-4.24 (br, 4H, O(C$\mathbf{H}_2$)$_2$O), 5.29 (s, 1H, Ph$_3$C$\mathbf{H}$), 6.68 (d, 4H, $C_6\mathbf{H}_4O$), 6.84-7.00 (m, 11H, $C_6\mathbf{H}_4O$), 7.29 (t, 2H, $C_6\mathbf{H}_4O$). ^{13}C-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 dedinfed linear (L) and the dendric (D) units

Both compounds were sysnthesized using the same method. THTPM (5.84 g, 0.02 mol), 2-Phenoxyethylbromide (20.1 g, 0.1 mol), K_2CO_3 (8.3 g, 0.06 mol), and 100 mL DMF was added into a three-necked flask under mechanical stirring. The reactants were heated to 80 °C for 24 h and then cooled to room temperature. The mixture was acidified with hydrochloric acid and then filtered. Most of 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 dendric units have yields of 40% (L) and 25% (D), respectively.

Linear unit (L): ^{1}H-NMR (600 MHz, (methyl sulfoxide)-d6, δ): 4.25-4.30 (br, 4H, O(C$\mathbf{H}_2$)$_2$O), 5.37 (s, 1H, Ph$_3$C$\mathbf{H}$), 6.69 (d, 2H, $C_6\mathbf{H}_4O$), 6.86-7.00 (m, 16H, $C_6\mathbf{H}_4O$), 7.29 (t, 4H, $C_6\mathbf{H}_4O$). ^{13}C-NMR (600 MHz, (methyl sulfoxide)-d6, 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.

Dendric unit (D): ^{1}H-NMR (600 MHz, (methyl sulfoxide)-d6, δ): 4.30-4.26 (br, 4*H*, $O(C\mathbf{H}_2)_2O$), 5.45 (s, 1*H*, $Ph_3C\mathbf{H}$), 6.89-7.10 (m, 21*H*, $C_6\mathbf{H}_4O$), 7.29 (t, 6*H*, $C_6\mathbf{H}_4O$).