Supporting Information for

A multifunctional silicon-containing hyperbranched epoxy: controlled synthesis, toughening bismaleimide and fluorescent properties

Song Niu*, Hongxia Yan*, Song Li, Cheng Tang, Zhengyan Chen, Xiaoli Zhi, Peilun Xu

Key Laboratory of Polymer Science and Technology, Shaanxi Province, School of Science, Northwestern Polytechnical University, Xi'an 710129, China

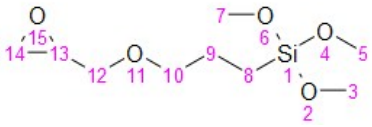
Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, School of Science, Northwestern Polytechnical University, Xi'an 710129, China

*Corresponding author, Tel.: +862988431657.
E-mail: niusong84@163.com (S. Niu), hongxiayan@nwpu.edu.cn (H. Yan).

Contents

1. Spectral characteristics for raw materials

A-187



^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.60 (dd, *J* = 11.5, 3.0 Hz, H^{12}), 3.46 (s, H^{3}, H^{5}, H^{7}), 3.41 – 3.31 (m, H^{10}, H^{12}), 3.29 – 3.24 (m, H^{10}) 3.02 (ddt, *J* = 5.8, 4.1, 2.8 Hz, H^{13}), 2.67 (dd, *J* = 5.1, 4.1 Hz, H^{14}), 2.49 (dd, *J* = 5.1, 2.7 Hz, H^{14}), 1.65 – 1.52 (m, H^{9}), 0.63 – 0.51 (m, H^{8}).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 73.33 (C^{10}), 71.27 (C^{12}), 50.68 (C^{13}), 50.29 (C^{3}, C^{5}, C^{7}), 44.02 (C^{14}), 22.69 (C^{9}), 5.09 (C^{8}).

NPG

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.02 (d, *J* = 1.0 Hz, H^{1}, H^{7}), 3.40 (s, H^{2}, H^{6}), 0.84 (s, H^{4}, H^{5}).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 70.50 (C^{2}, C^{6}), 36.44 (C^{3}), 21.32 (C^{4}, C^{5}).

2. Molecular weights of HPHEp and HPHEp-Polyether

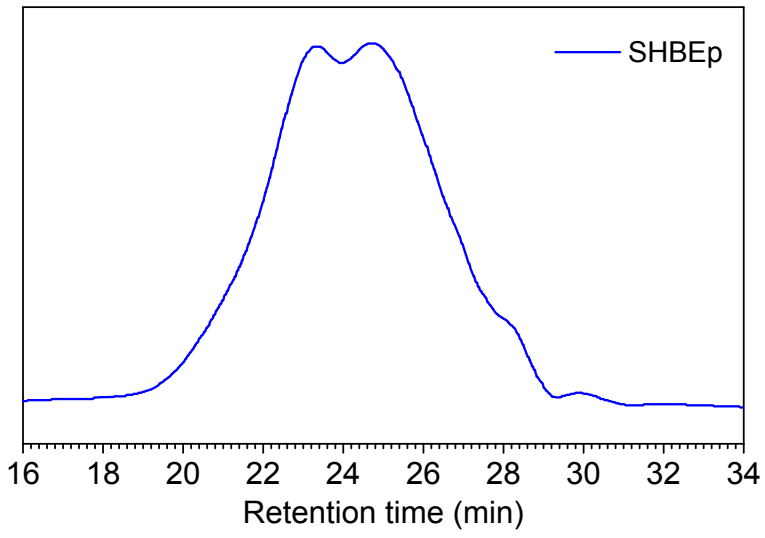


Fig. S1 The molecular weight of SHBEp by GPC.

Table S1 Characterization Data of the Three Samples

Samples	M_p	M_n	M_w	M_z	PDI
HPHEp	1864	846	9998	77069	11.80

3. The predicted ^{29}Si NMR of SHBEp

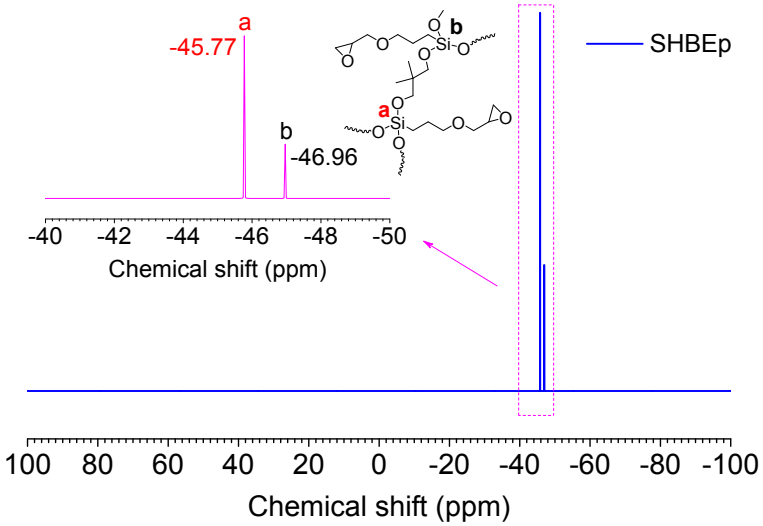


Fig. S2 The ^{29}Si NMR spectra of SHBEp predicted by the software MestReNova v10.0.2.

4. TG and DSC curves of SHBEp

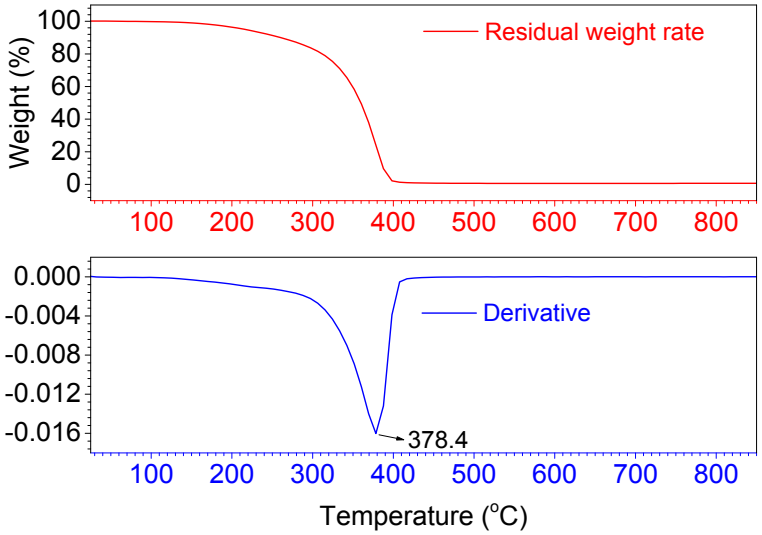


Fig. S3 TG analysis of SHBEp.

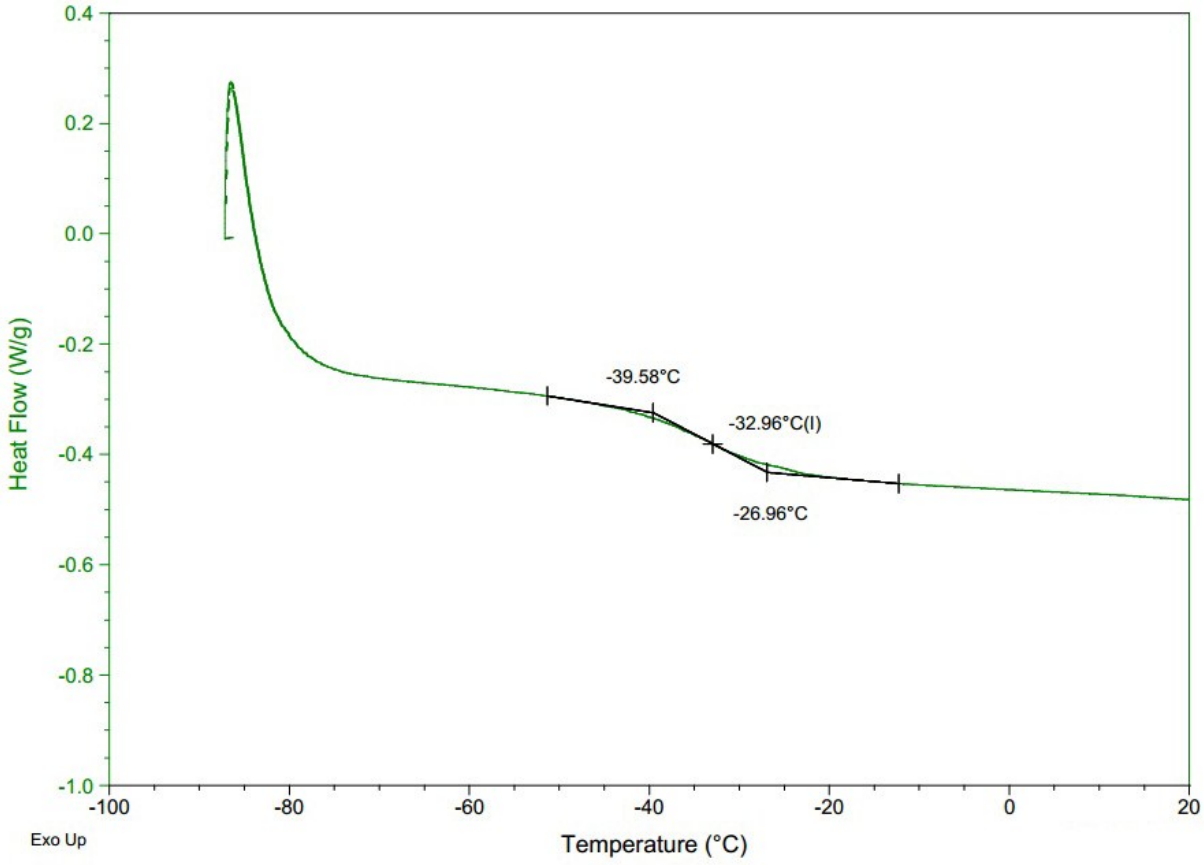
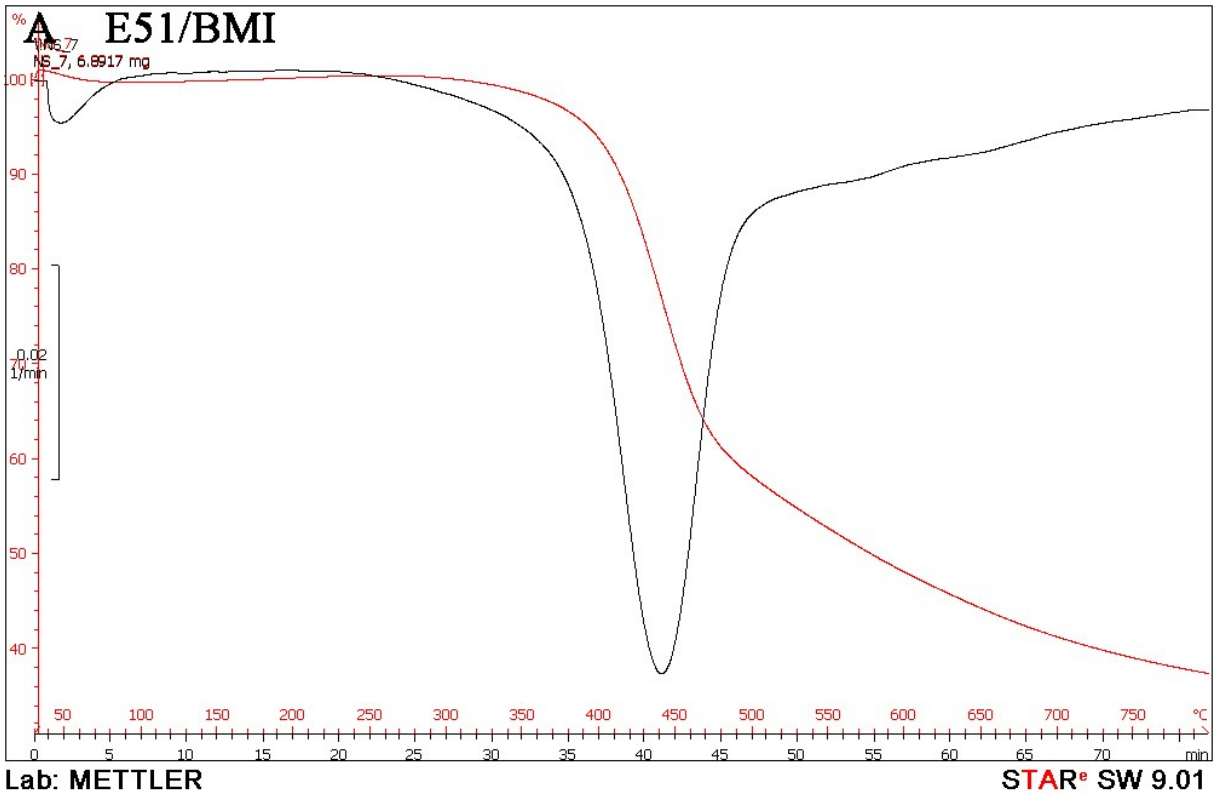
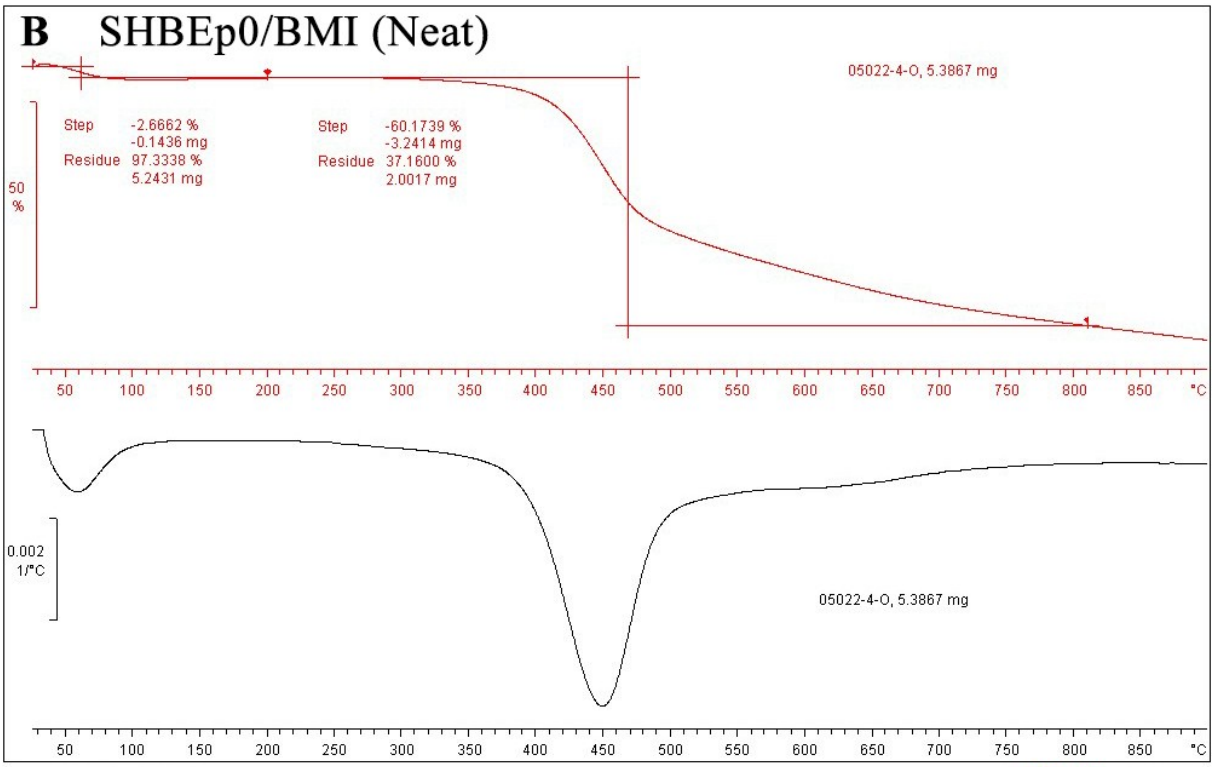


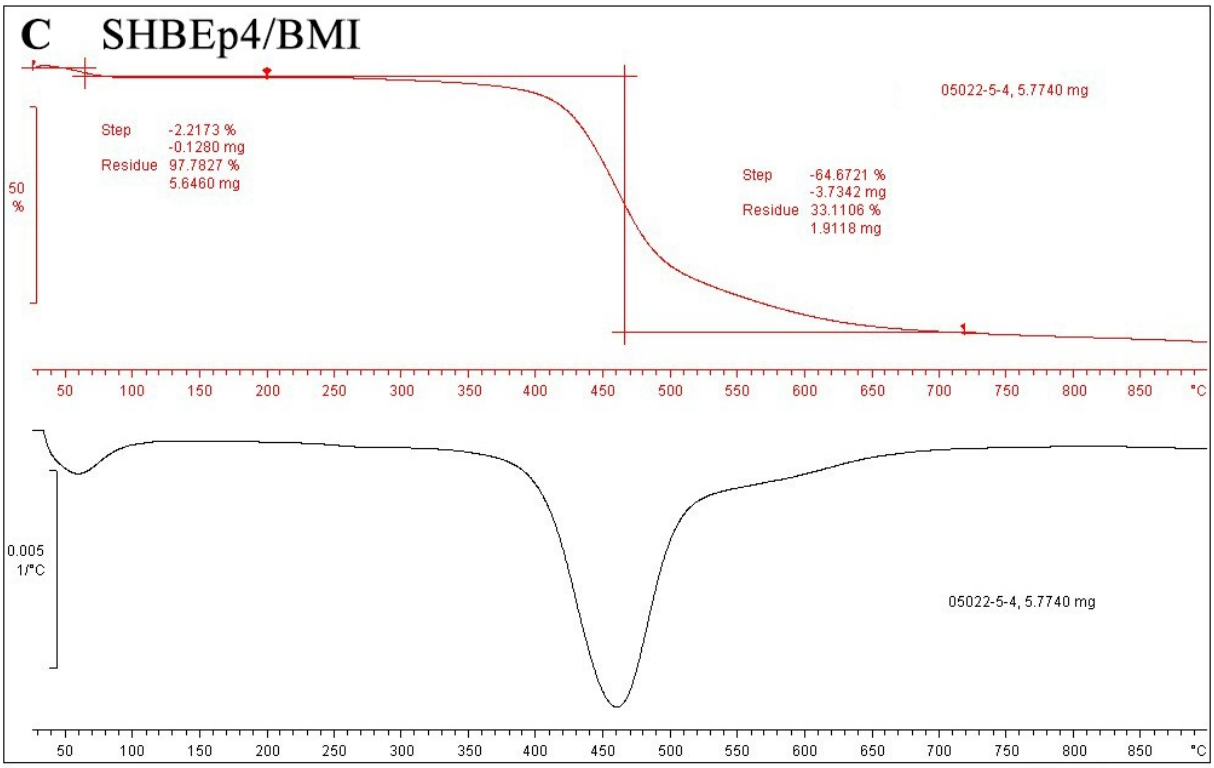
Fig. S4 The DSC curve of SHBEp.

5. TGA and DTG curves of E51/BMI and SHBEp/BMI thermosets

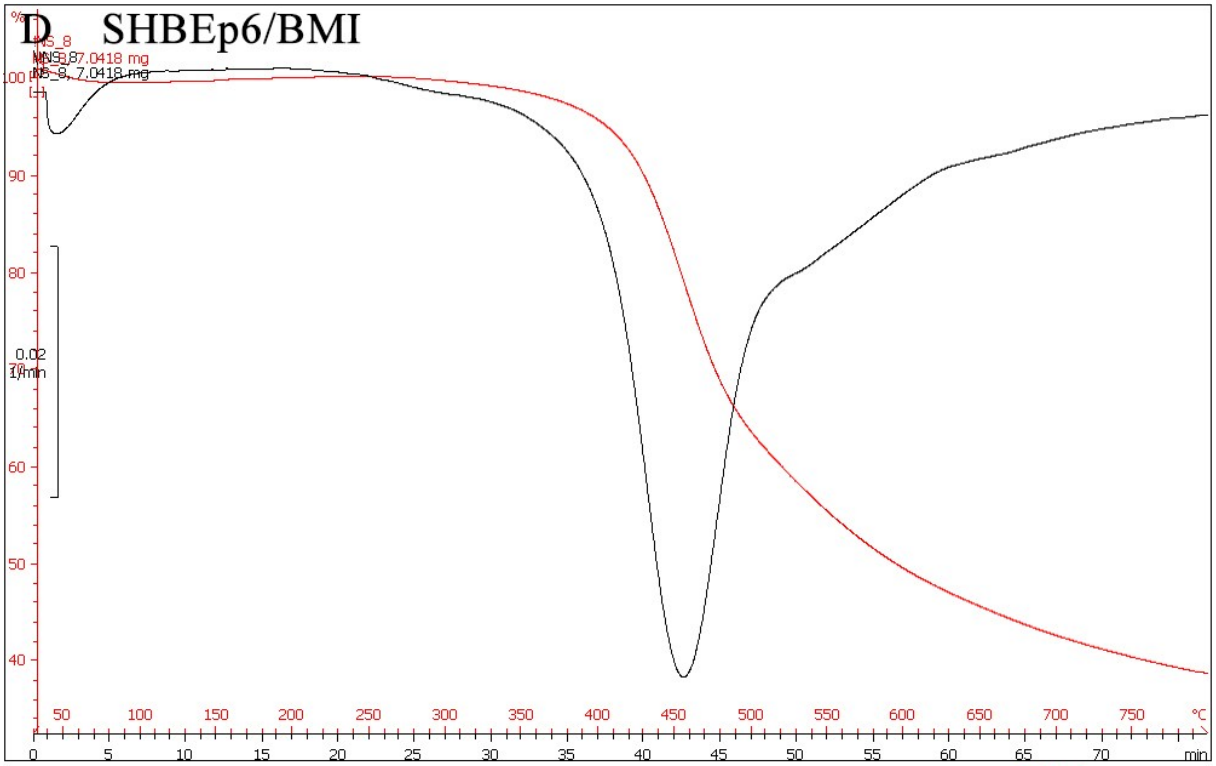




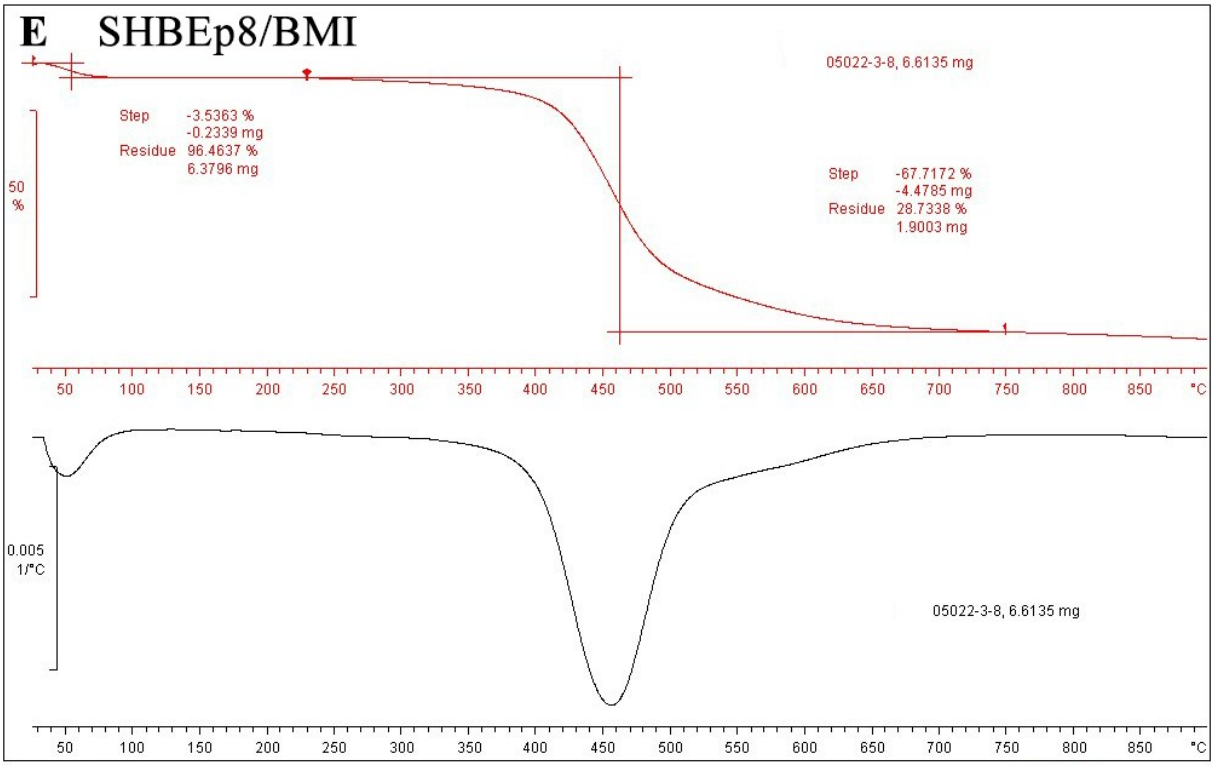
Lab: METTLER STARe SW 8.10



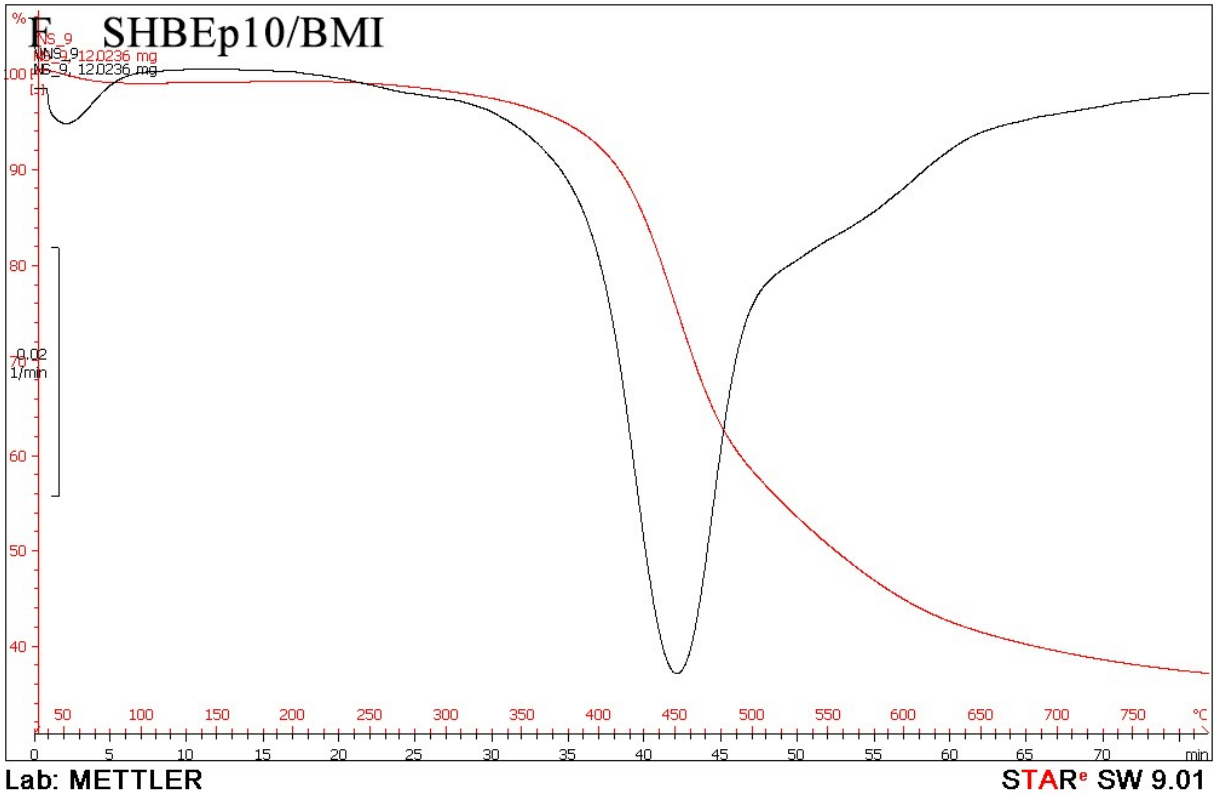
Lab: METTLER STARe SW 8.10



Lab: METTLER STARe SW 9.01



Lab: METTLER STARe SW 8.10



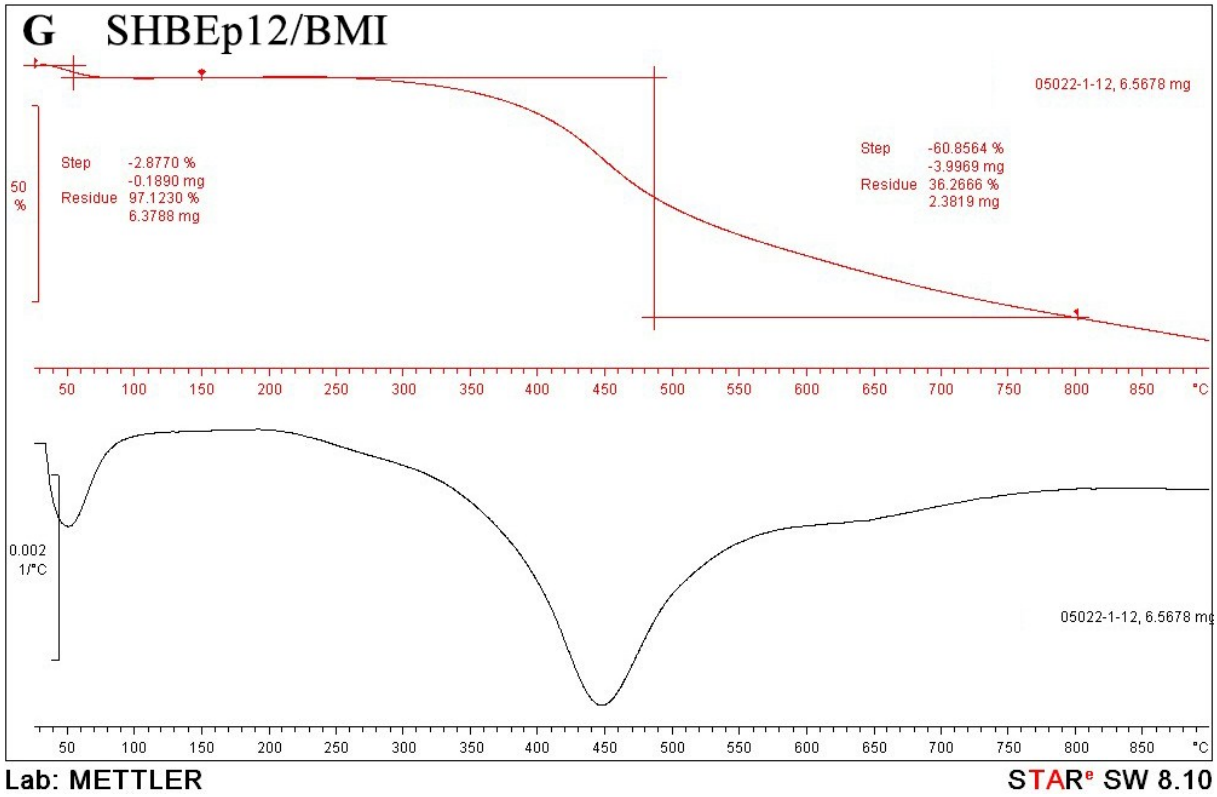


Fig. S5 TGA and DTG curves of A) E51/BMI thermoset and SHBEp/BMI thermosets respectively with B) 0 wt%, C) 4 wt %, D) 6 wt%, E) 8 wt %, F) 10 wt% and G) 12 wt % SHBEp.

6 Hyperbranched polysiloxanes

Polymer a:

In this polymerization, $–OCH_3$ is excess compared to –OH. The mole ratio of A-187 and NPG is 1:1.36, that is, the mole ratio of $–OCH_3$ and –OH is 3:2.72. The polymer (**a**) (Fig. S6a) was obtained using 0.592 mol A-151 (142.769 g) and 0.805 mol NPG (83.853 g) based on the synthesis procedure of SHBEp (**b**) (Fig. S6b);

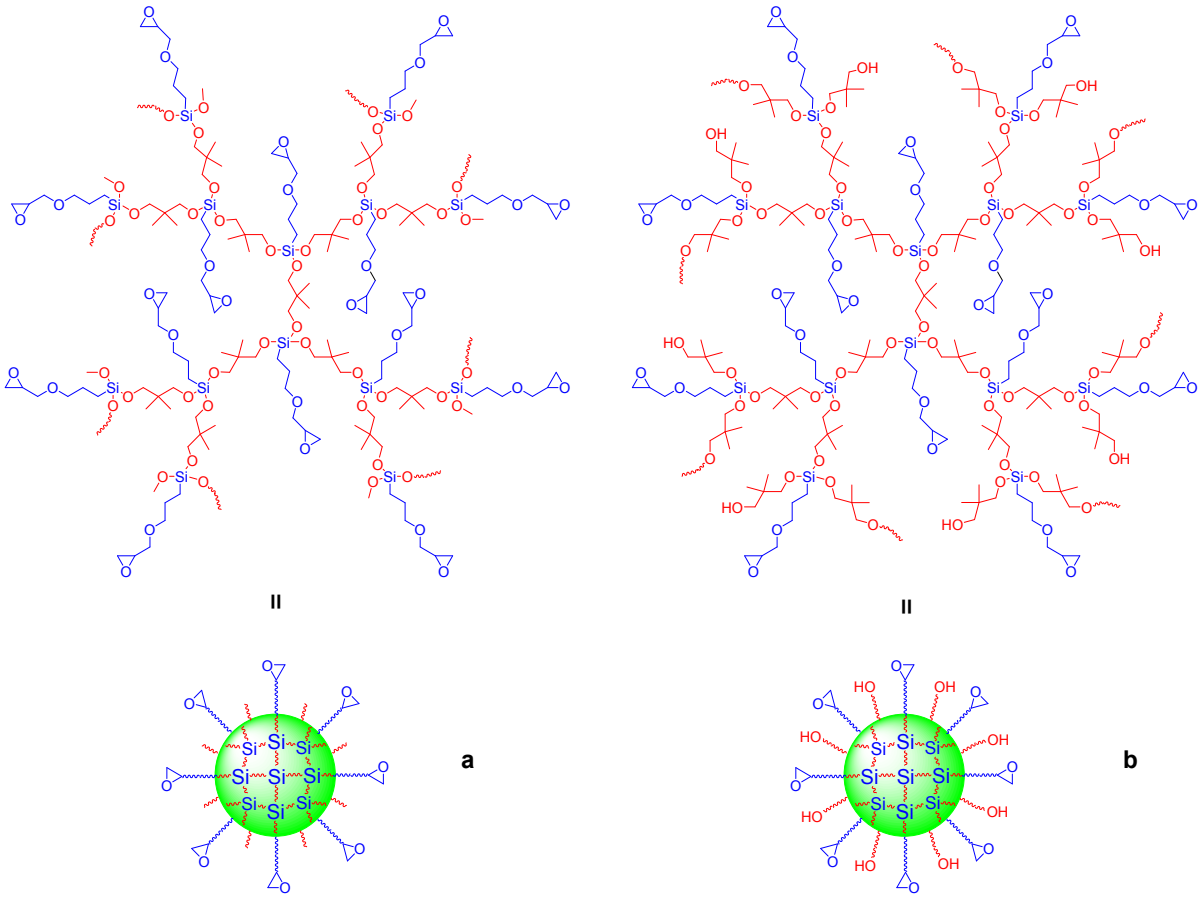


Fig. S6 a) Hyperbranched polysiloxanes with excessive –OCH3 and b) hyperbranched polysiloxanes with excessive –OH groups.

Polymer c and d:

(1) 0.27 mol TEOS (99.5%, 56.53 g), 0.87 mol NPG (90.44 g), and 0.05 g *p*-TSA were charged into a four-necked flask equipped with a thermometer, a top stirrer, a gas inlet, and a distilling setup at room temperature. N_2 protection was provided by supplying N_2 gas through the gas inlet. Then the reaction mixture was heated to about 110 °C, and kept at this

temperature till some distillate was distilled off. Thereafter the heating was continued to raise the temperature of the reaction mixture to about 160 °C and keep the temperature of the distillate at 78 ± 2 °C. The reaction mixture was maintained at 160 °C till the distillate temperature dropped below 55 °C. Finally, the silicone-based polymer terminated with hydroxyl groups (**c**) (Fig. S7c) was prepared;

(2) 0.643 mol TBAA (98.5%, 103.027 g) was further added to the reaction mixture after its temperature was dropped below 100 °C. Then the reaction mixture was heated to about 120 °C, and kept at this temperature till some distillate was distilled off. After that, the temperature of the reaction mixture was raised to about 160 °C while the temperature of the distillate was kept at 82 ± 2 °C. The reaction temperature was kept at 160 °C till the distillate temperature dropped below 55 °C. Finally, the silicone-based polymer containing acetoacetyl groups (**d**) (Fig. S7d) was obtained.

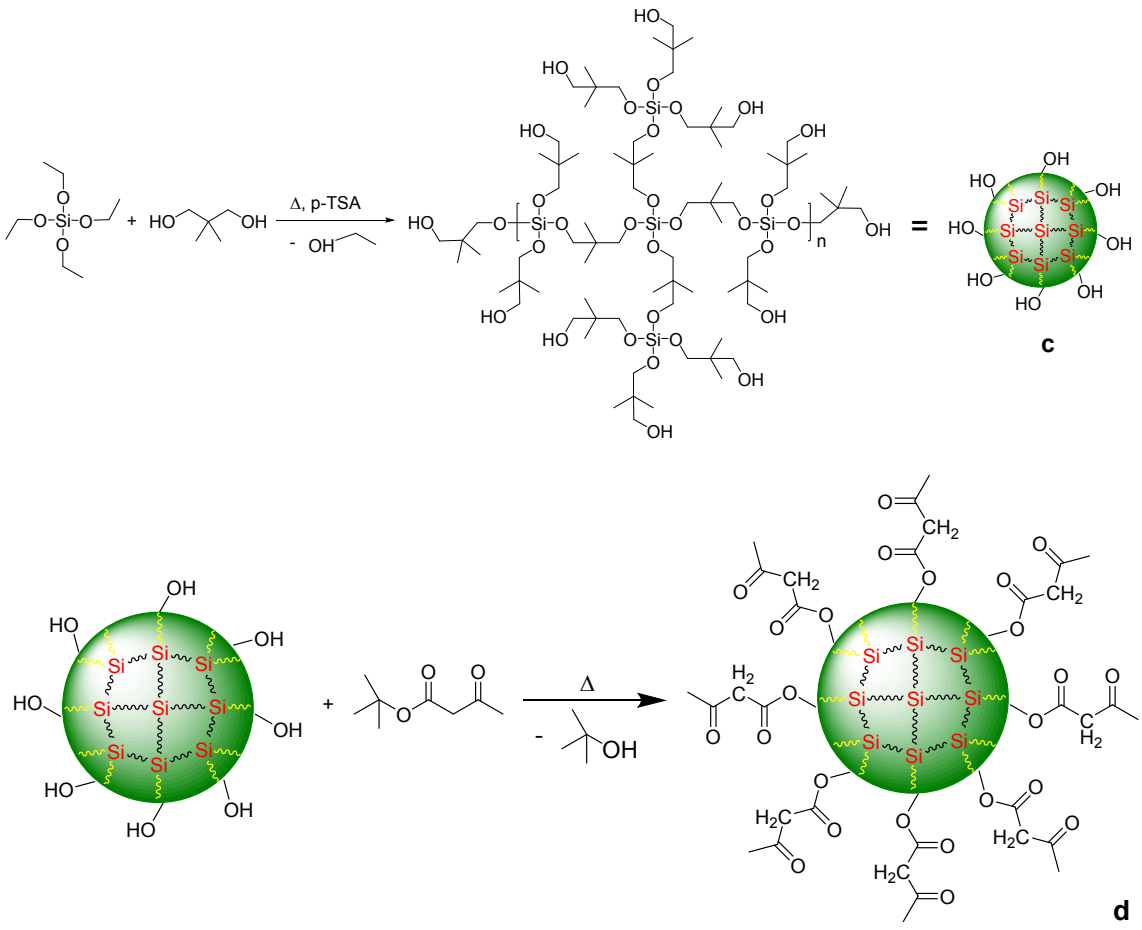


Fig. S7 c) Hyperbranched polysiloxanes terminated with –OH groups and d) hyperbranched polysiloxanes terminated with acetoacetyl groups.

7 The fluorescent lifetime and the absolute fluorescence quantum yield of the SHBEp

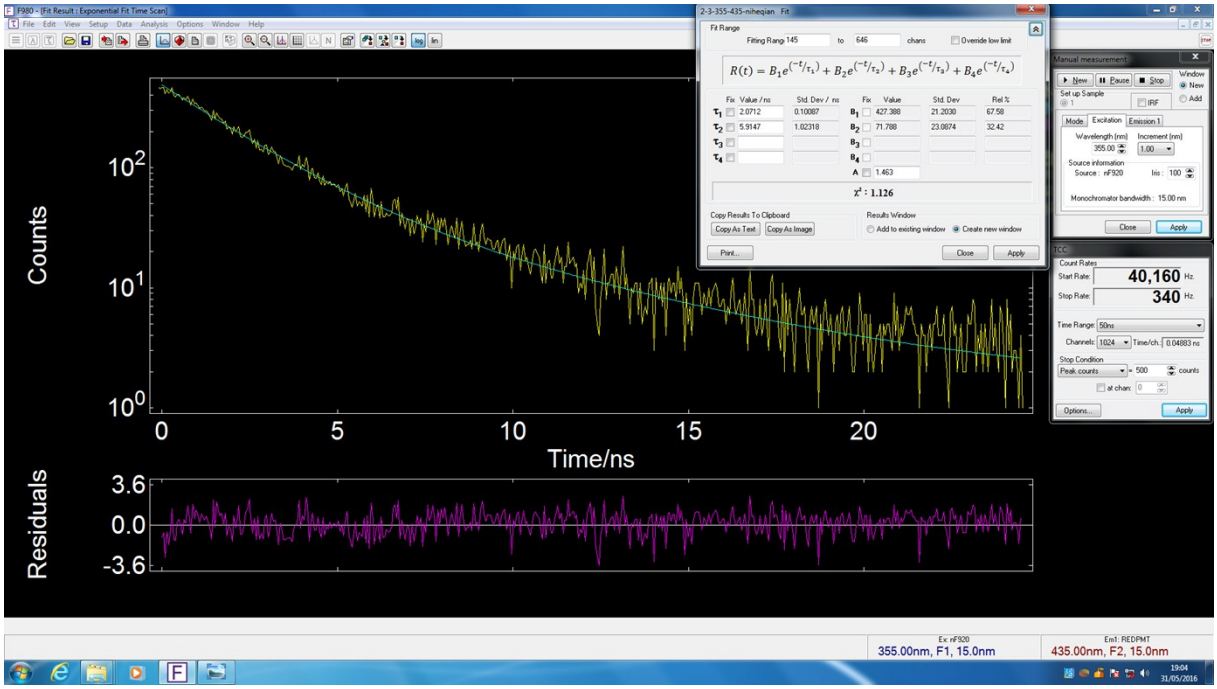


Fig. S8 The printscreen of transient photoluminescence decay curve of the SHBEp from a steady/transient-state fluorescence spectrometer coupled with an integrating sphere (FLS980, Edinburgh Instruments).

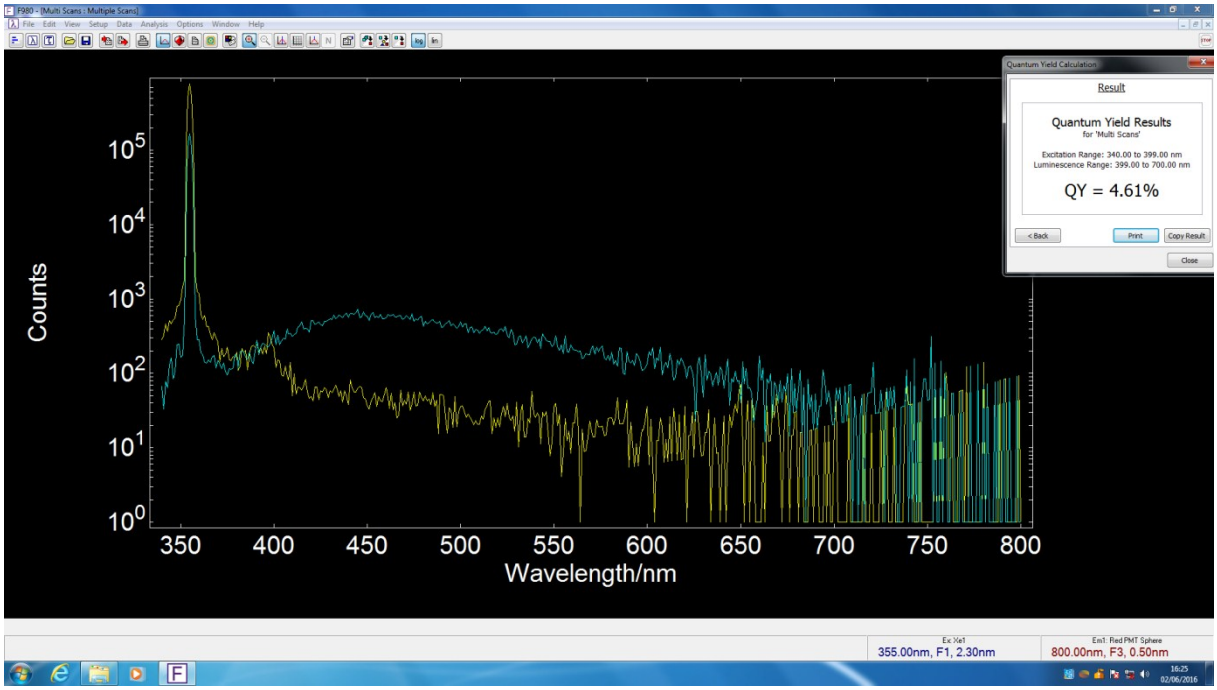


Fig. S9 The printscreen of absolute fluorescence quantum yield of the SHBEp from a steady/transient-

state fluorescence spectrometer coupled with an integrating sphere (FLS980, Edinburgh Instruments).