

## Supporting Information

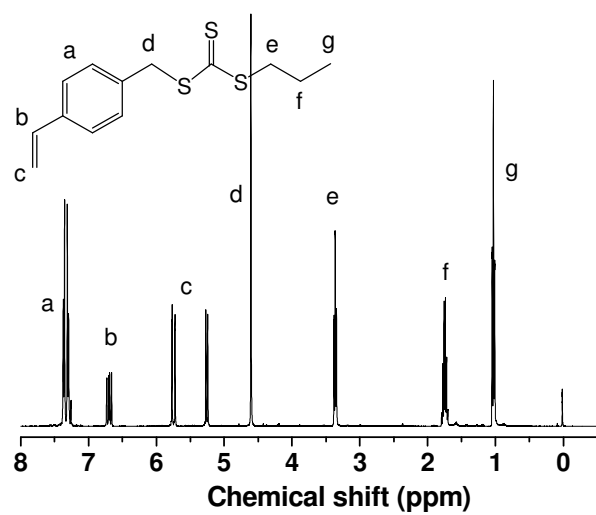
# Facile Synthesis of Hyperbranched and Star-Shaped Polymers by RAFT Polymerization Based on a Polymerizable Trithiocarbonate

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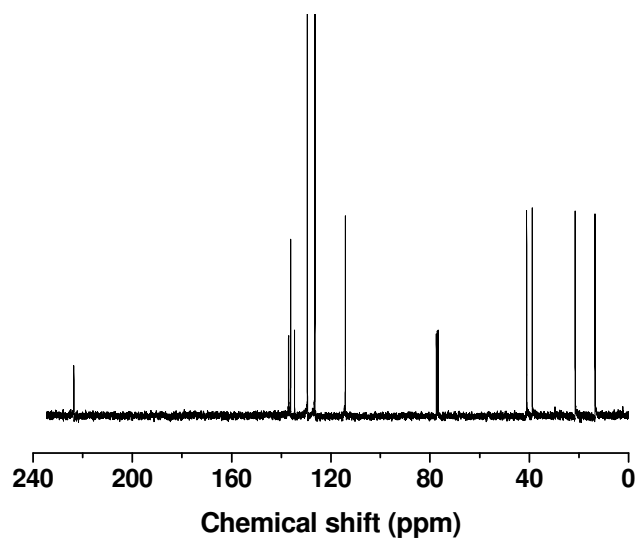
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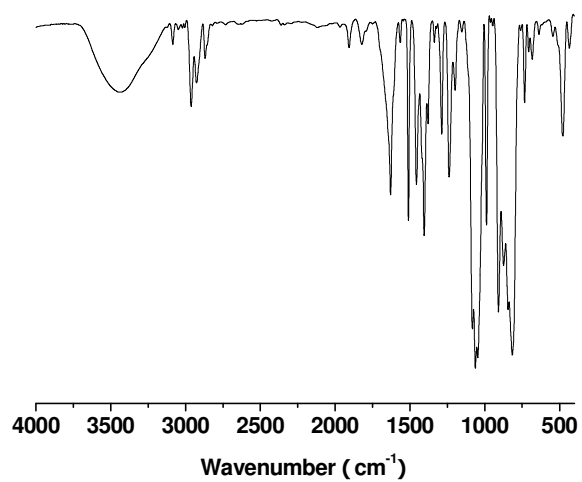
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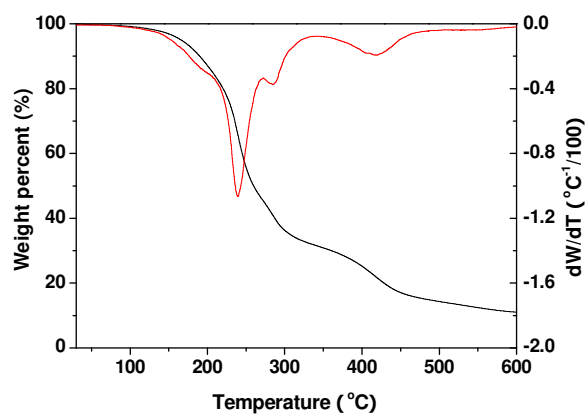
**Figure S1.**  $^1\text{H}$  NMR spectra of VBPT.



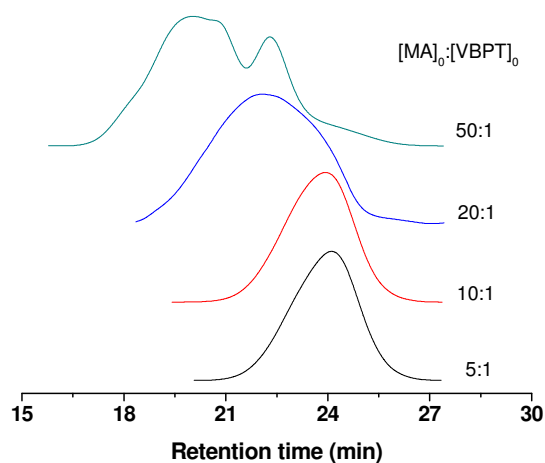
**Figure S2.**  $^{13}\text{C}$  NMR spectra of VBPT.



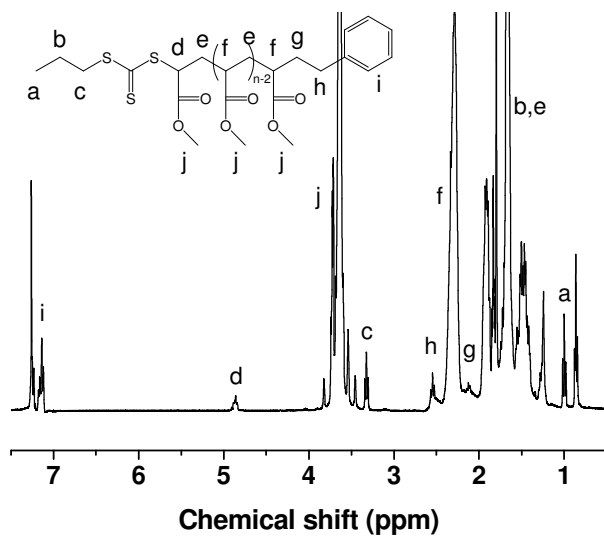
**Figure S3.** IR spectra of VBPT.



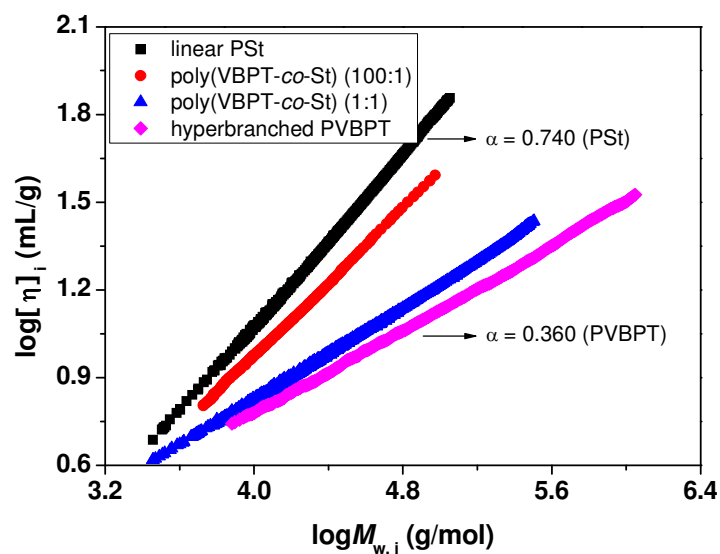
**Figure S4.** Dependence of weight loss and dW/dT of VBPT on temperature.



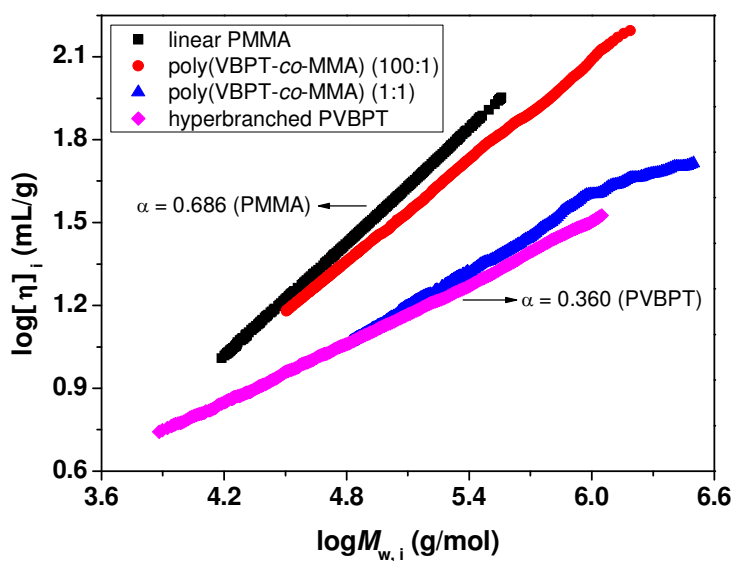
**Figure S5.** GPC traces of poly(VBPT-*co*-MA) branched copolymers synthesized by RAFT copolymerization at constant AIBN concentration ( $[AIBN]_0 = 3.0$  mmol/L). Samples were listed in runs 16 to 19 of Table 1.



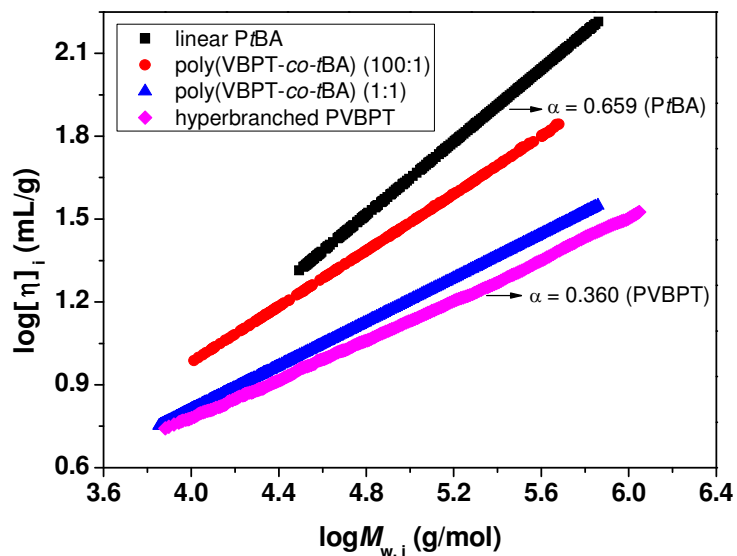
**Figure S6.**  $^1\text{H}$  NMR spectra of PMA synthesized by RAFT polymerization mediated by S-benzyl S'-propyltrithiocarbonate (BPTT) ( $[MA]_0:[VBPT]_0:[AIBN]_0 = 100:1:0.1$ ,  $[MA]_0 = 3.0$  mol/L, in toluene at  $60^\circ\text{C}$  for 18 h,  $M_n(\text{GPC}) = 4870$ ,  $\text{PDI} = 1.20$ ,  $\text{DP}(\text{NMR}) = 54.0$ ,  $M_n(\text{NMR}) = 4890$ ).



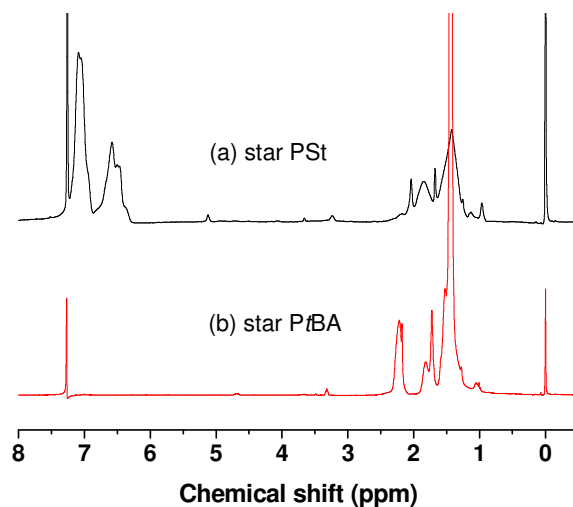
**Figure S7.** Mark-Houwink-Sakurada plots of poly(VBPT-*co*-St) branched copolymers obtained by RAFT copolymerization, hyperbranched PVBPT and linear PSt. The resulting  $\alpha$  values were determined from the slope.



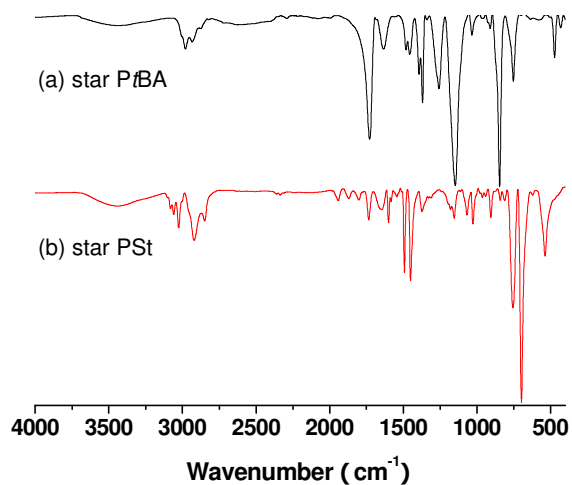
**Figure S8.** Mark-Houwink-Sakurada plots of poly(VBPT-*co*-MMA) branched copolymers obtained by RAFT copolymerization, hyperbranched PVBPT and linear PMMA. The resulting  $\alpha$  values were determined from the slope.



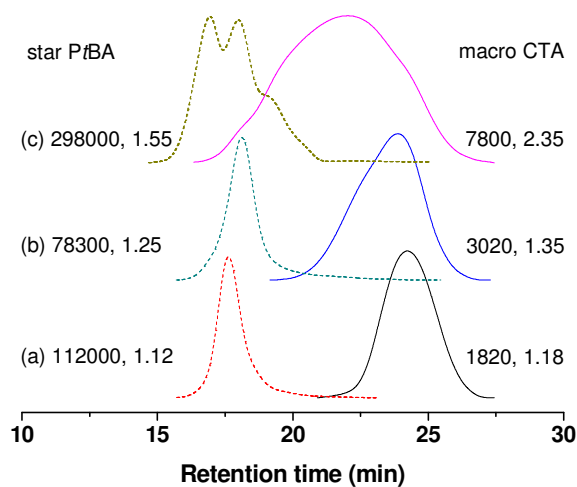
**Figure S9.** Mark-Houwink-Sakurada plots of poly(VBPT-*co*-tBA) branched copolymers obtained by RAFT copolymerization, hyperbranched PVBPT and linear PtBA. The resulting  $\alpha$  values were determined from the slope.



**Figure S10.**  $^1\text{H}$  NMR spectra of star-shaped PSt and PtBA with a poly(VBPT-*co*-MA) branched core.



**Figure S11.** IR spectra of star PtBA (a) and PSt (b) with a branched core of poly(VBPT-*co*-MA).



**Figure S12.** GPC traces of poly(VBPT-*co*-MA) branched macro CTA (solid line) and star-shaped PtBA with a branched core (dashed line) synthesized by runs 9 (a), 7 (b) and 11 (c) as listed in Table 6, and CTA functionality of various macro CTAs were 7.26, 13.0 and 55.8, respectively.