

Supplementary Materials

Scheme S1. Model reactions of atom transfer radical with TEMPO trapping (AT-TEMPO) of mixed initiators (R_y-X ($y = 1$ or 2)).

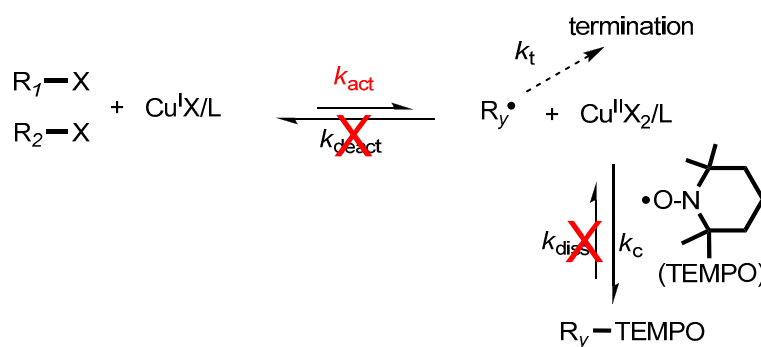


Figure S1. 1H NMR (600 MHz, $CDCl_3$) spectra of (i) linear PVBC and (ii) hyperbranched PVBC polymers.

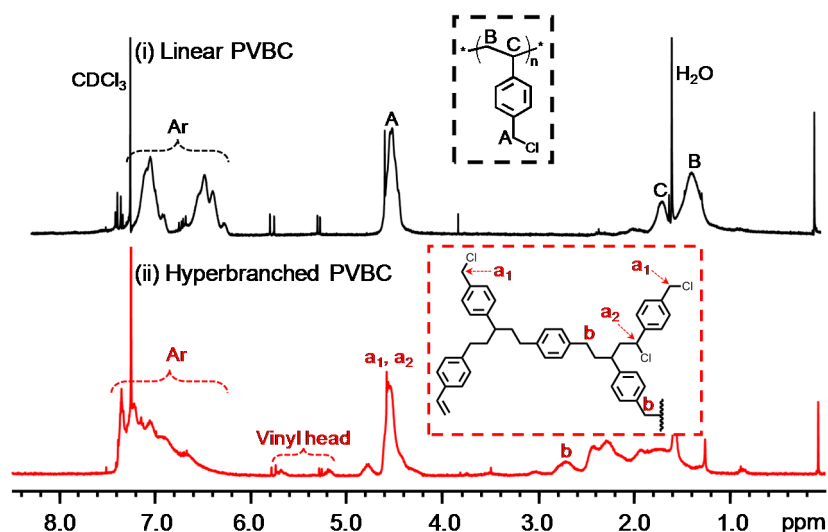


Figure S2. Kinetic plot of conversion vs time for one-pot reactions performed with an increase in temperature: (a) from 70 $^{\circ}C$ /1 h to 110 $^{\circ}C$ /+23 h and (b) from 70 $^{\circ}C$ /24 h to 110 $^{\circ}C$ /+24 h (St/VBC/EBiB/CuBr/Bpy = 160/80/5/1/2; $[St]_0 = 3.5$ M).

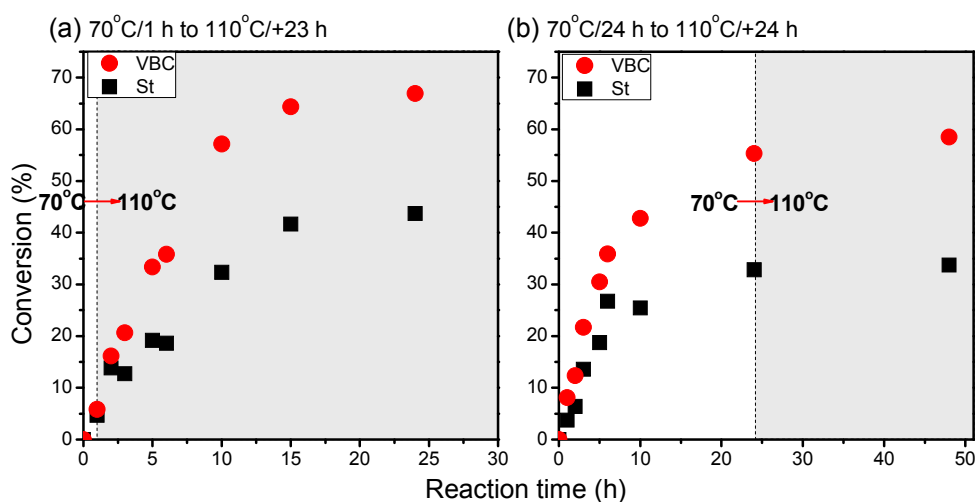


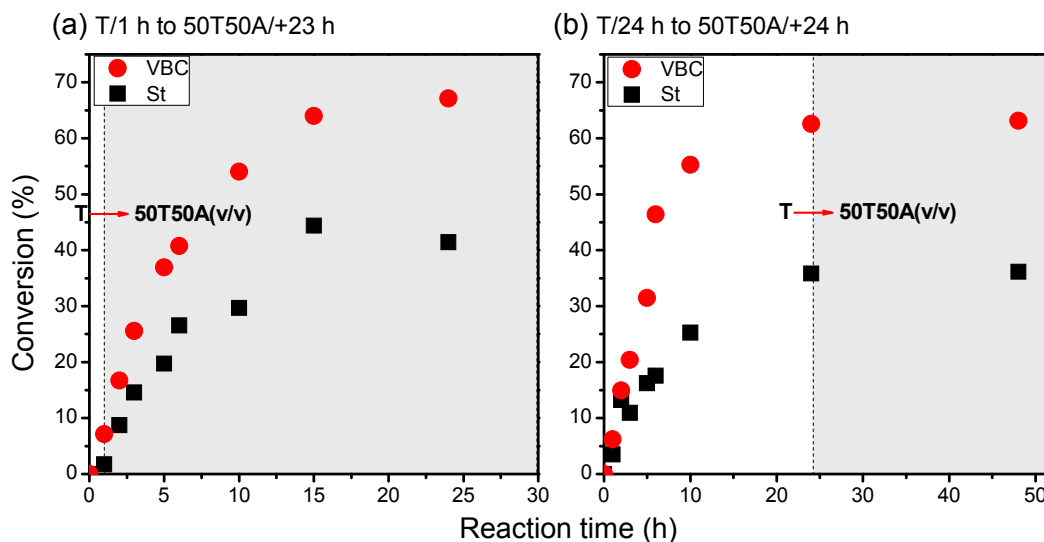
Table S1. Values of M_n determined through GPC/refraction index ($M_{n,\text{GPC-RI}}$) and GPC/light scattering ($M_{n,\text{GPC-LS}}$) of the products obtained using the temperature varying procedure.

Values	70 °C/1 h to 110 °C/+23 h ^a	70 °C/5 h to 110 °C/+19 h ^a	70 °C/24 h to 110 °C/+24 h ^a
$M_{n,\text{GPC-RI}}$	1575	1600	1550
$M_{n,\text{GPC-LS}}$	2740	2814	2430
BI ^b	0.57	0.58	0.64

^a Starting condition: St/VBC/CuBr/Bpy/EBiB= 160/80/1/2/5 at 70 °C in A ($[\text{St}]_0 = 3.5 \text{ M}$);

^b BI = $M_{n,\text{GPC-RI}}/M_{n,\text{GPC-LS}}$ (for linear polymer BI = 1.0; for branched polymer BI < 1.0).

Figure S3. Kinetic plot of conversion vs. time for one-pot reactions performed with increased solvent polarity at 70 °C: (a) from T/1 h to 50T50A (v/v)/+23 h and (b) from T/24 h to 50T50A/+24 h (St/VBC/EBiB/CuBr/Bpy = 160/80/5/1/2; $[\text{St}]_0 = 3.5 \text{ M}$).



Scheme S2. (i) Chain extension of *t*BA with hbPSt MI and (ii) hydrolysis of hbPSt-*g*-*t*BA to form hbPSt-*g*-PAA.

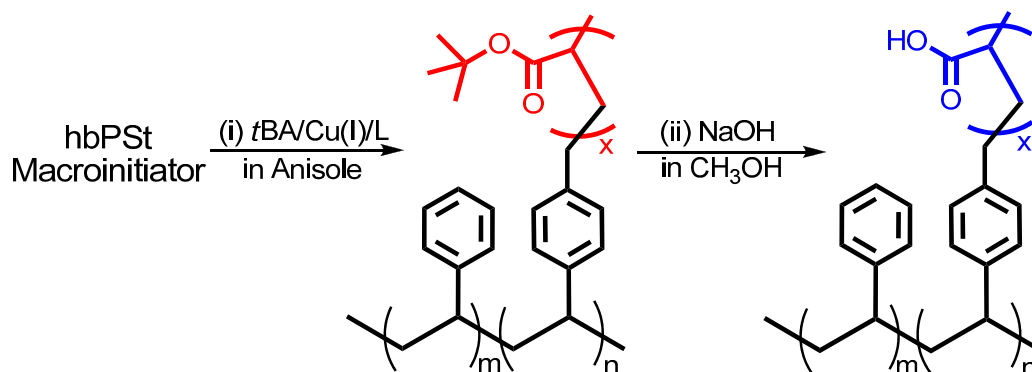


Figure S4. FT-IR spectra (KBr plate) of (a) hbPSt-*g*-PtBA and (b) hbPSt-*g*-PAA.

