

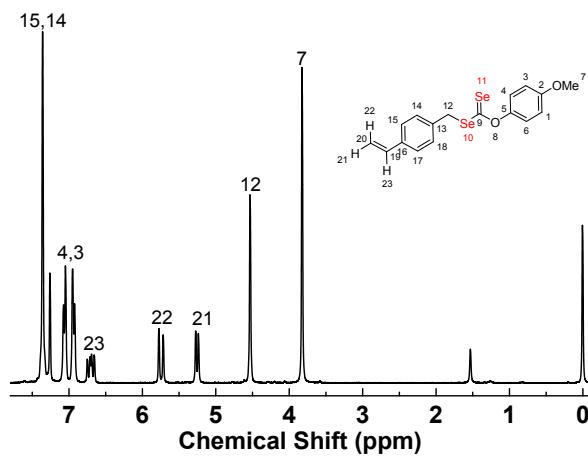
## Supporting Information for

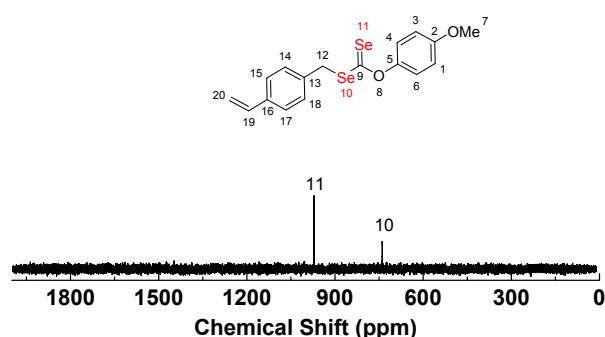
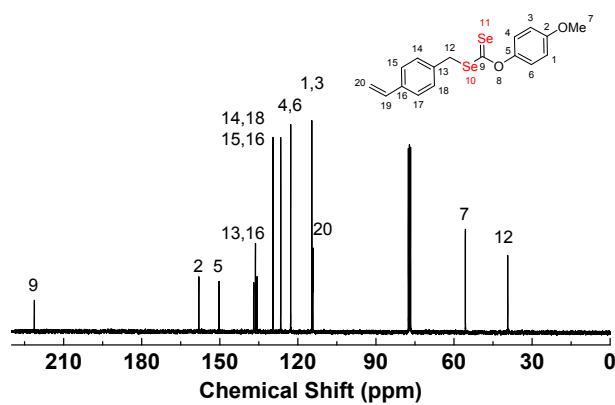
### From seleno-mediated radical polymerization to seleno-containing branched polymer and dynamic hydrogel

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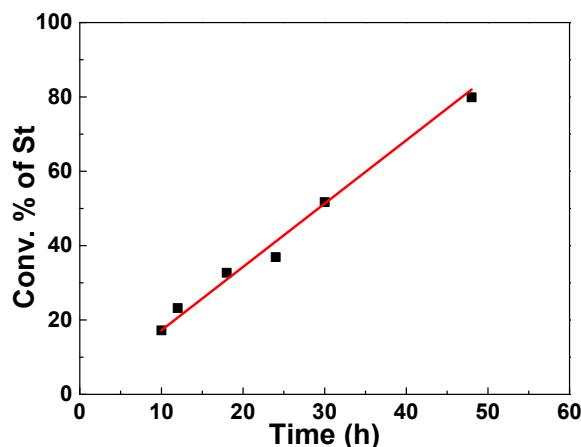
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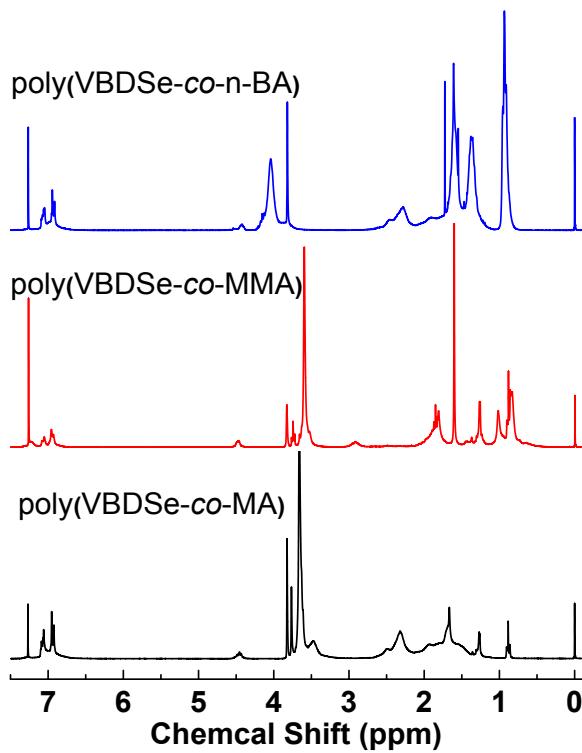




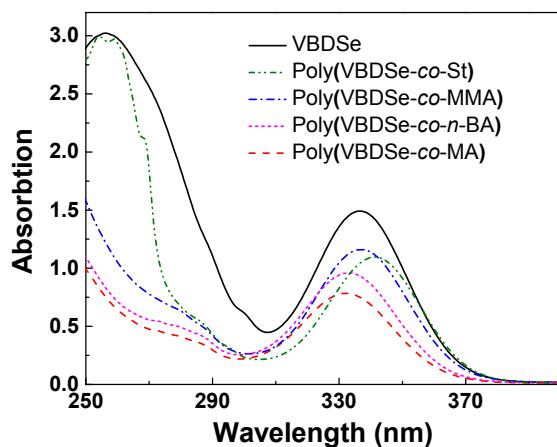
**Fig. S1.** <sup>1</sup>H, <sup>13</sup>C and <sup>77</sup>Se NMR spectra of O-(4-methoxyphenyl) Se-(4-vinylbenzyl) carbonodiselenoate (VBDSe).



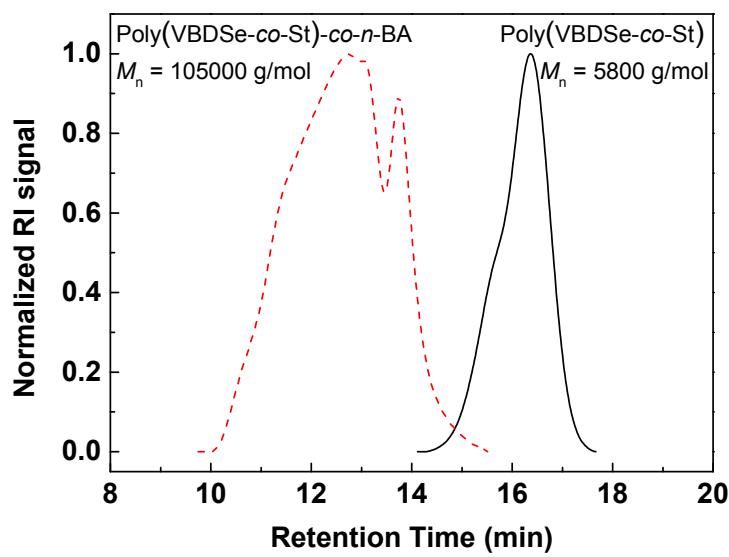
**Fig. S2.** Kinetic plot of Se-RAFT polymerization of St,  $[St]_0:[VBDSe]_0:[AIBN]_0 = 100:1:0.5$  at  $60^\circ\text{C}$ ,  $[M]_0 + [VBDSe]_0 = 3 \text{ mol/L}$  in toluene. The conversions of styrene were determined by <sup>1</sup>H NMR spectra of the crude polymerization mixture by comparing the integrated areas of characteristic signals of monomer and polymer using the following equations:  $C_{St} = 1 - (5 \times I_{5.27-5.23}) / (3 \times I_{7.43-7.12})$ , where  $I_{a-b}$  means the integrated areas from  $a$  to  $b$  ppm in <sup>1</sup>H NMR spectra.



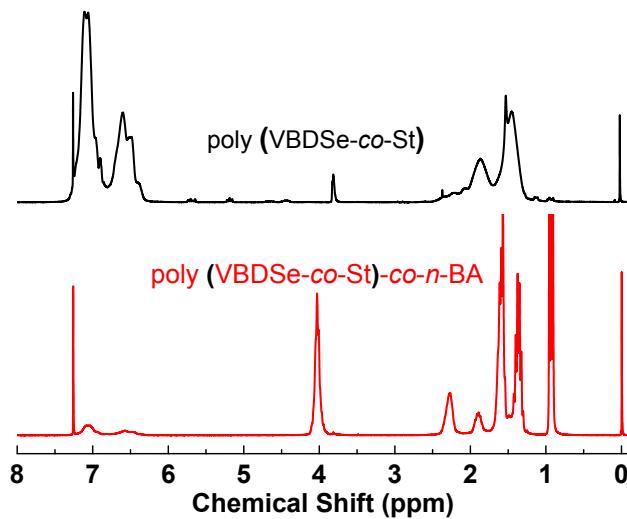
**Fig. S3.**  $^1\text{H}$  NMR spectra of various hyperbranched copolymers obtained from Se-RAFT-SCVP ( $[\text{M}]_0:[\text{VBDSe}]_0 = 10:1$ ), 24 h.



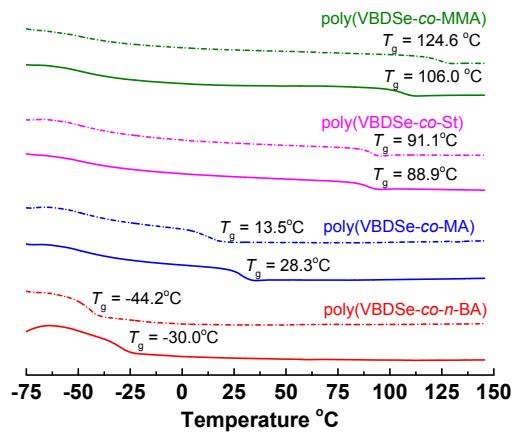
**Fig. S4.** UV-Vis spectra of hyperbranched copolymers,  $[\text{M}_2]_0:[\text{VBDSe}]_0 = 100:1$ , reacted for 24h.  $[\text{M}] = 1 \times 10^{-4}$  mol /L in  $\text{CH}_2\text{Cl}_2$ .



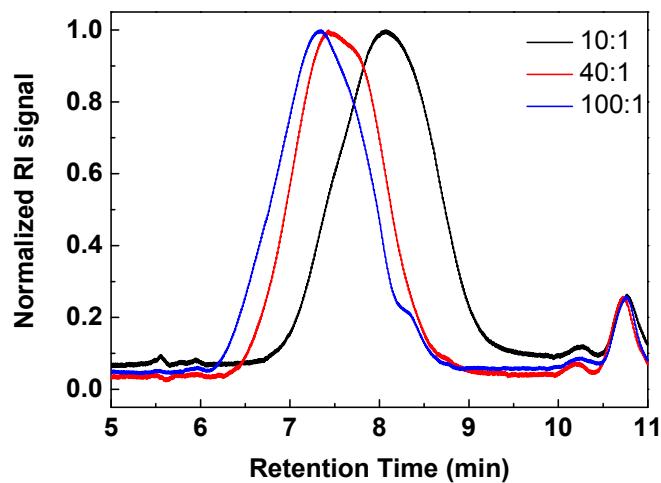
**Fig. S5.** SEC traces of hyperbranched poly(VBDSe-co-St) and poly(VBDSe-co-St)-co-n-BA after chain extension with *n*-BA using a feed ratio:  $[n\text{-BA}]_0:[\text{macro-CTA}]_0:[\text{AIBN}]_0 = 500:1:0.5$ .  $[\text{BA}]_0 + [\text{poly(VBDSe-co-St)}]_0 = 3\text{ mol/L}$ , in toluene at  $60^\circ\text{C}$  for 24h,  $M_{n,\text{macro-CTA}} = 5800$  g/mol.



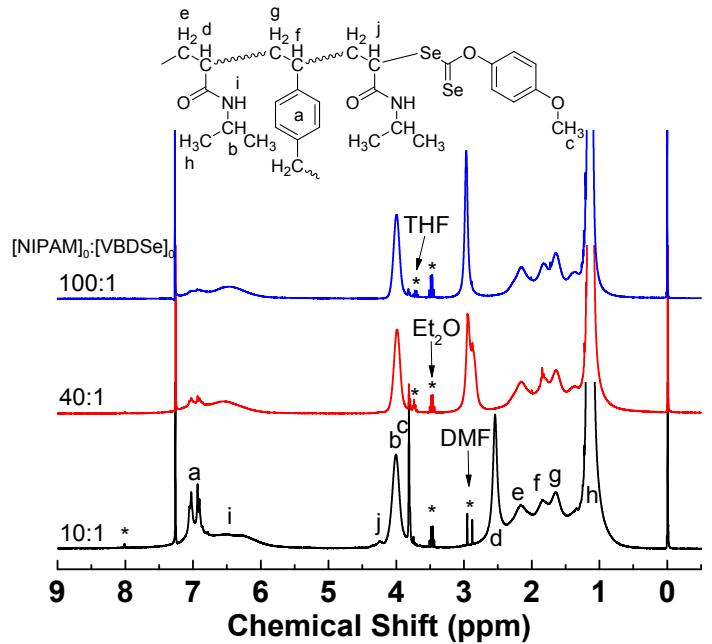
**Fig. S6.**  $^1\text{H}$  NMR spectra of hyperbranched poly(VBDSe-co-St) and poly(VBDSe-co-St)-co-n-BA after chain extension with *n*-BA using a feed ratio:  $[n\text{-BA}]_0:[\text{macro-CTA}]_0:[\text{AIBN}]_0 = 500:1:0.5$ ,  $[\text{n-BA}]_0 + [\text{poly(VBDSe-co-St)}]_0 = 3\text{ mol/L}$ , in toluene at  $60^\circ\text{C}$  for 24h ,  $M_{n,\text{macro-CTA}} = 5800$  g/mol.



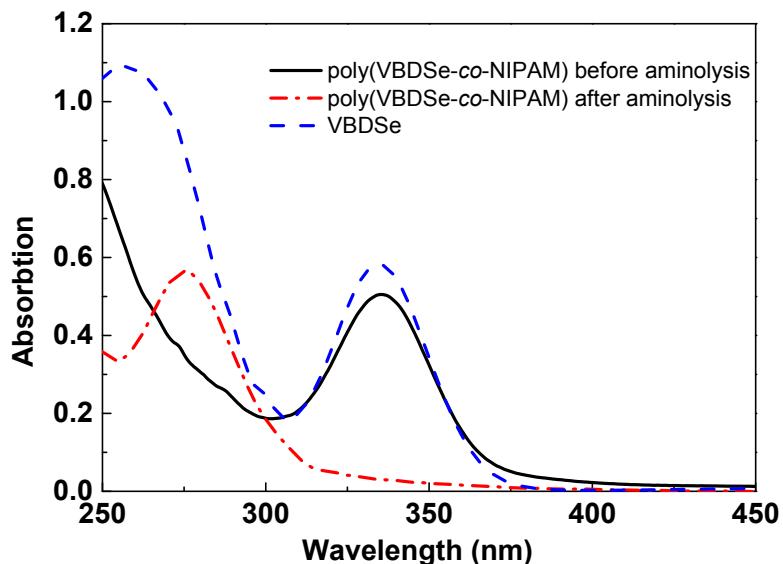
**Fig. S7.** DSC traces of hyperbranched copolymers synthesized by Se-RAFT-SCVP.  $[M]_0:[VBDSe]_0 = 10:1$  (solid line) or 100:1 (dashed line).



**Fig. S8.** SEC chromatograms of hyperbranched poly(VBDSe-co-NIPAM) ( $[NIPAM]_0:[VBDSe]_0 = 10:1$ , 40:1 and 100:1).



**Fig. S9.**  $^1\text{H}$  NMR spectra of hyperbranched poly(VBDSe-*co*-NIPAM) in  $\text{CDCl}_3$ .



**Fig. S10.** UV-vis curves of VBDSe and hyperbranched copolymer before and after aminolysis in THF ( $1 \times 10^{-5}$  mol/L) with 10 eq. *n*-hexylamine.