

Functionalization of Poly(ϵ -caprolactone) as a Versatile Platform

Using ϵ -(α -Phenylseleno) Caprolactone as Monomer

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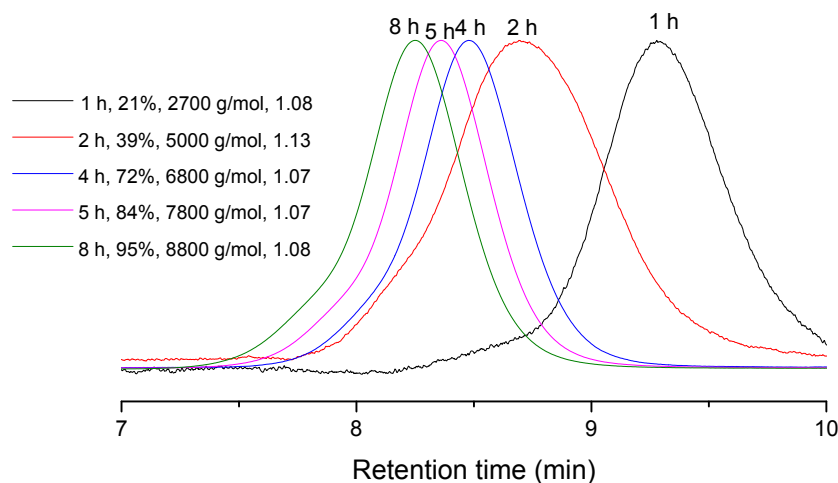


Fig S1 SEC traces of polymers obtained by ring-opening polymerization with $[\text{CLSePh}]_0:[\text{EG}]_0 = 50:1$ at 100°C

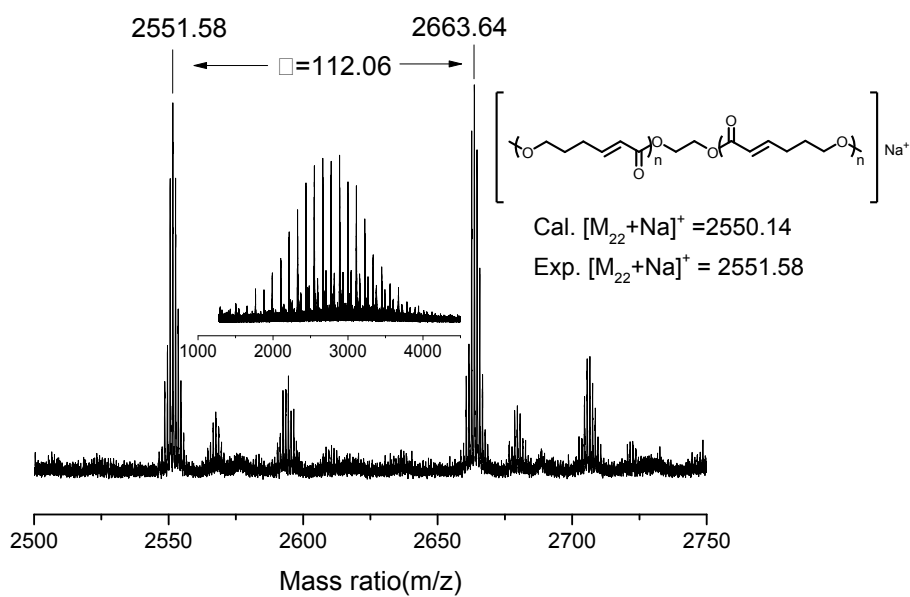


Fig. S2 MALDI-ToF mass spectrum of PCLSePh ($M_{n,SEC} = 5500 \text{ g mol}^{-1}$, $\mathcal{D} = 1.11$) after oxidation.

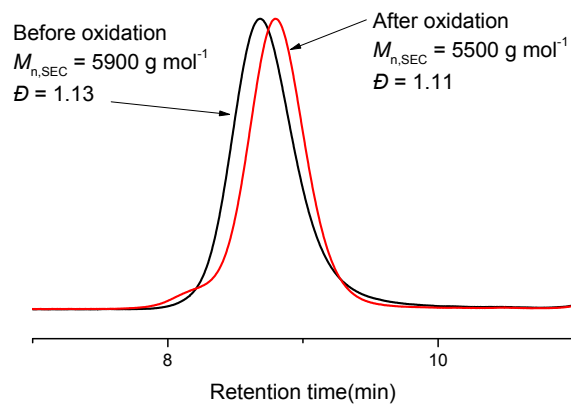


Fig S3 The SEC traces of polymers before and after oxidization.

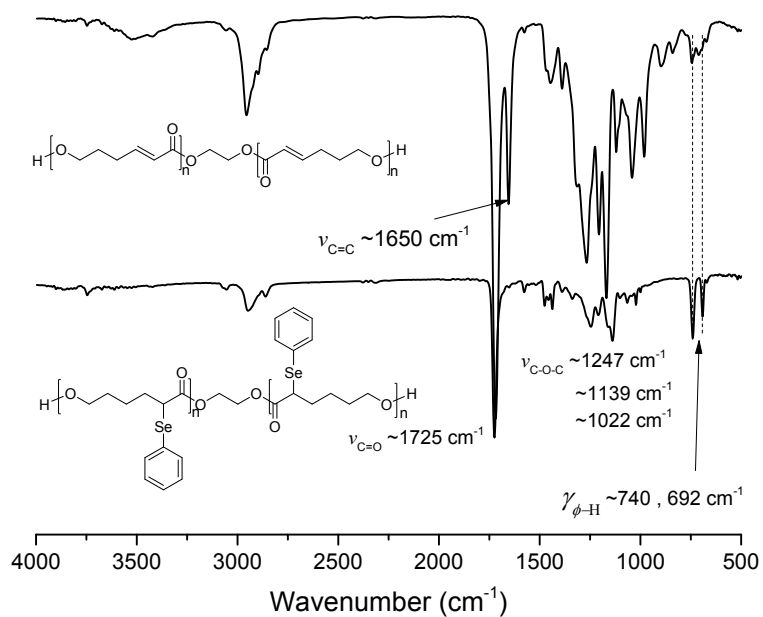


Fig. S4 FTIR spectra of polymer before and after oxidation.

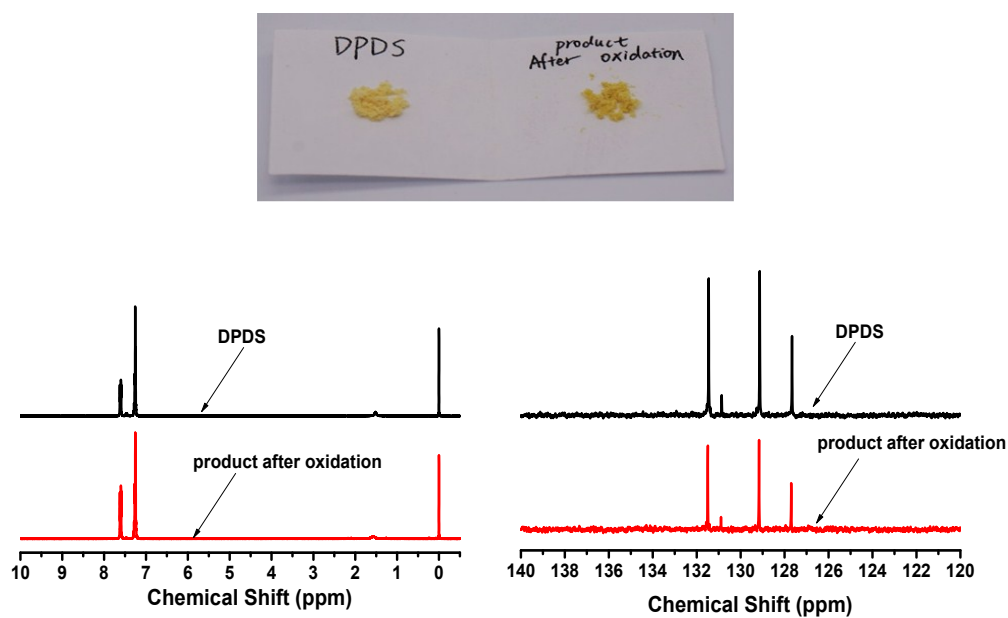


Fig. S5 ^1H NMR and ^{13}C NMR spectra of original and the recycled DPDS after oxidation treatment.

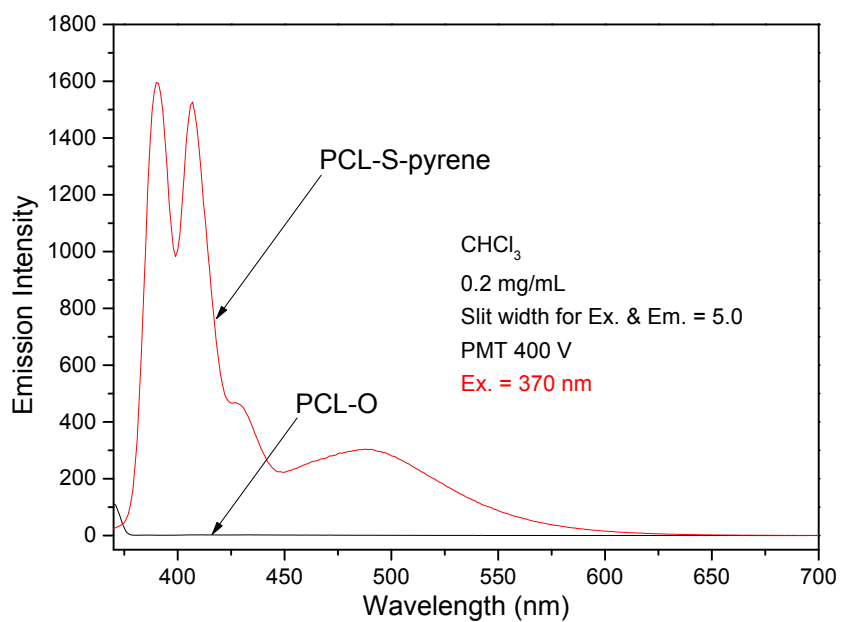
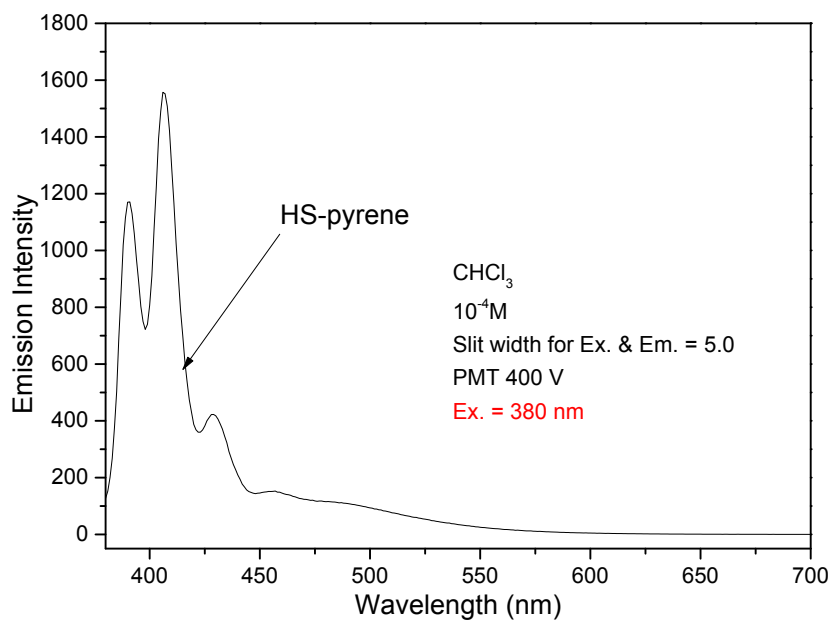


Fig. S6 fluorescence analysis of pyrenemercaptan, PCL-O (polymer after oxidation) and PCL-S-pyrene.

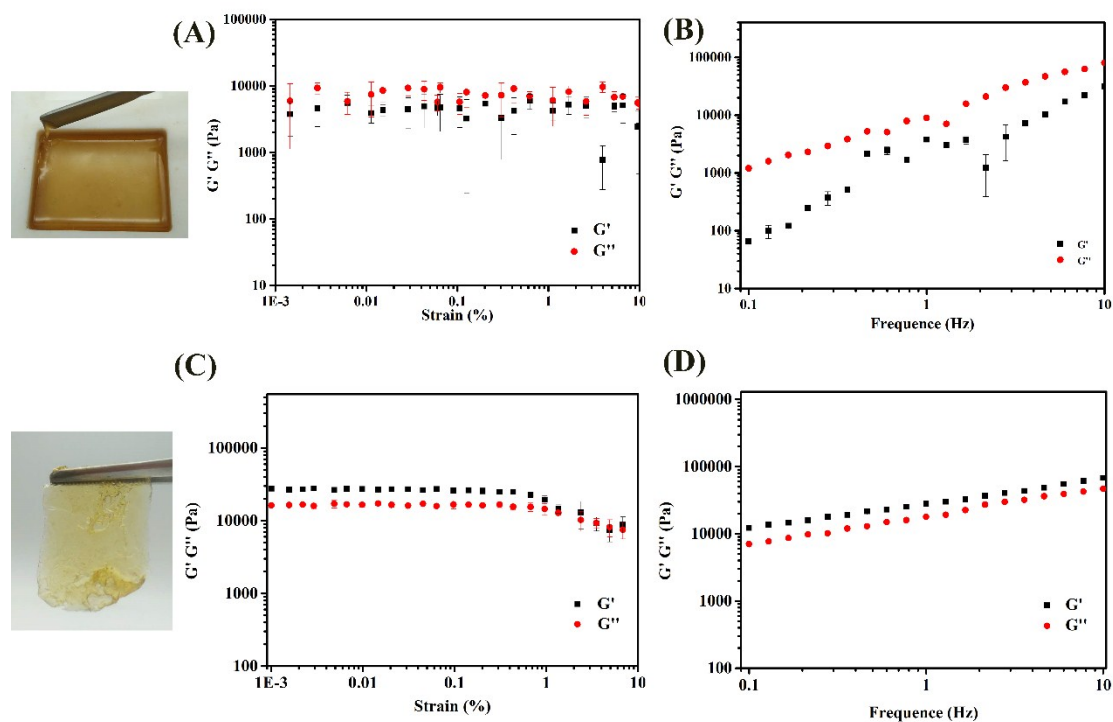


Fig. S7 Influence of strain and frequency on elastic modulus G' and loss modulus G'' of polymer before (A, B) and after (C, D) heating.

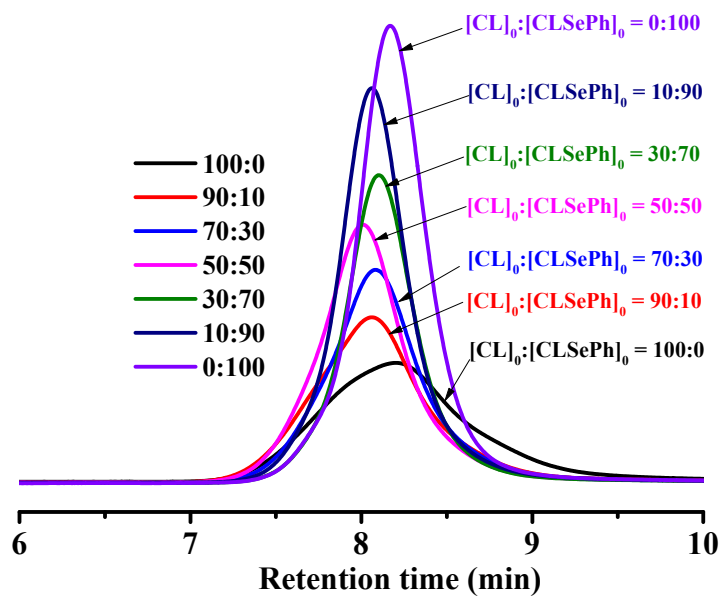


Fig. S8 SEC traces of copolymers prepared by random ring opening copolymerization.

Table S1 T_g values of copolymers before and after oxidation.

Entry	f^a	F^b	T_g (before oxidation) /°C	T_g (after oxidation) /°C
1	1.0	1.0	-8.96	-27.82
2	0.9	0.85	-14.16	-35.21
3	0.7	0.63	-22.08	-48.64
4	0.5	0.44	-33.83	-53.45
5	0.3	0.26	-46.04	-53.72
6	0.1	0.08	-51.01	-
7	0.9	0.0	-60.00	-60.00

^amolar fraction of CLSePh in the comonomer feed. ^bmolar fraction of CLSePh in the random copolymer.

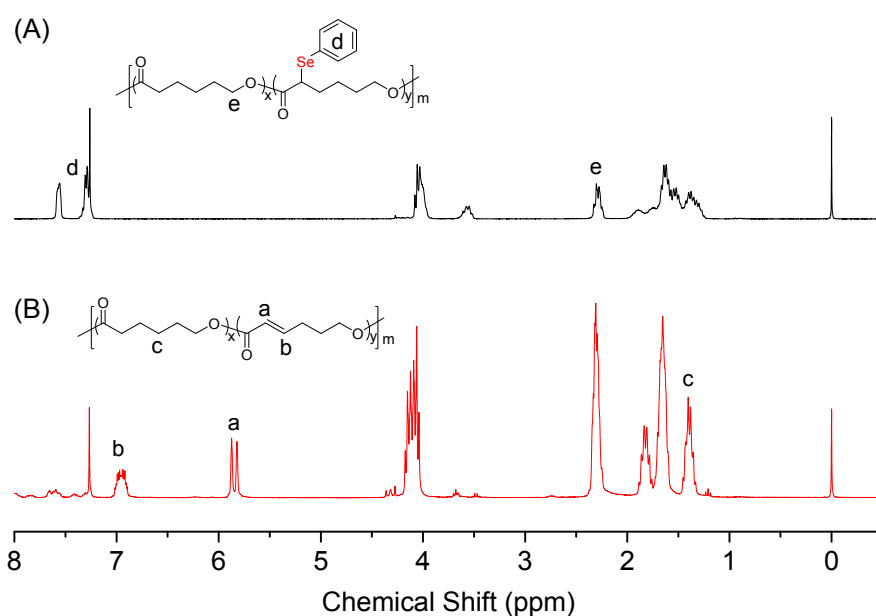


Fig. S9 ^1H NMR of copolymers before and after oxidation. (A) Before oxidation (Table S1, Entry 4, prepared by ring-opening polymerization with $\text{Sn}(\text{Oct})_2$ as catalyst at 100°C in glove box); (B) After oxidation elimination reaction (Table S2, Entry 4).

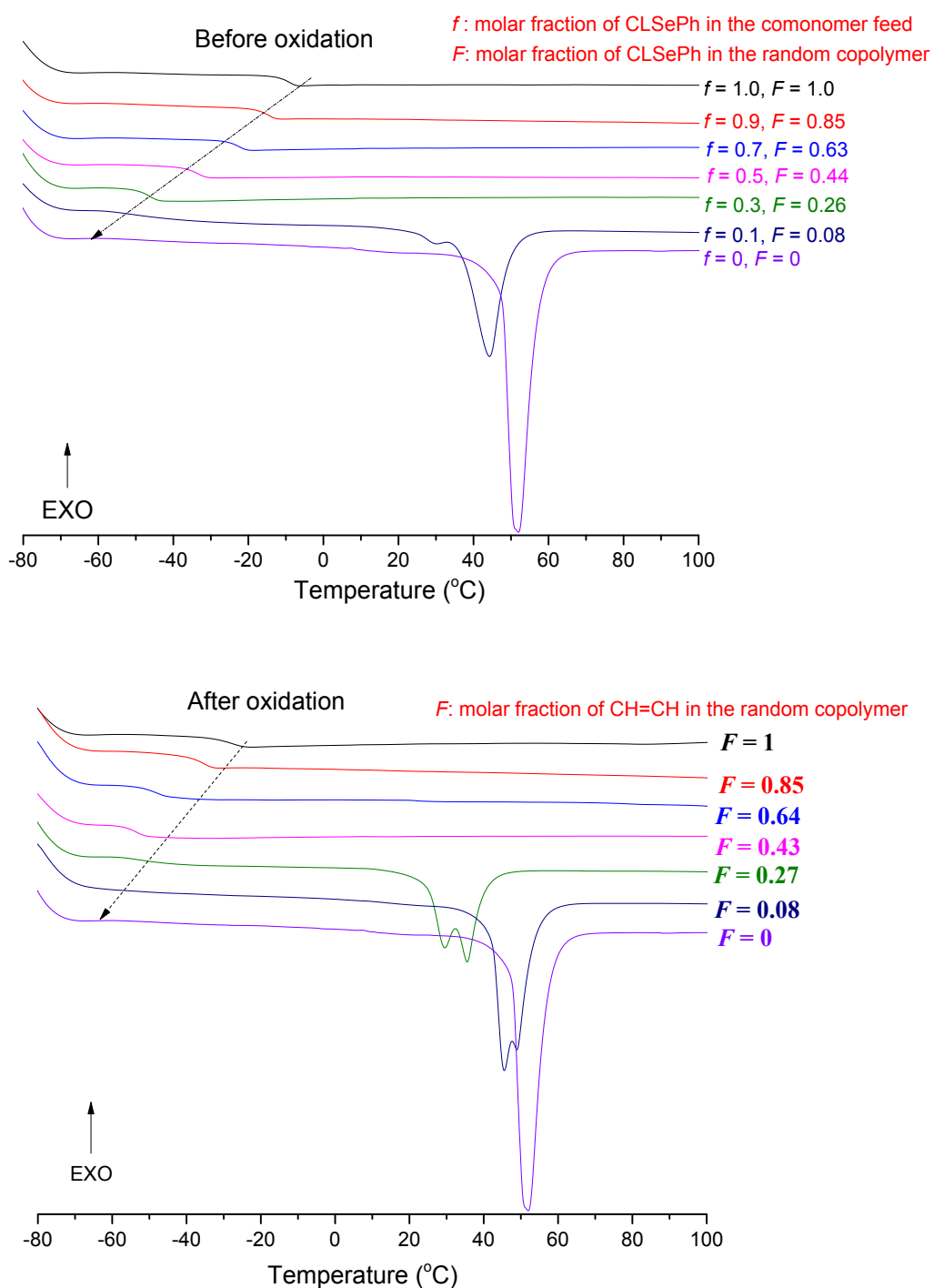


Fig. S10 DSC curves during the second heating process of random copolymers before and after oxidation at the heating rates of 20 °C min⁻¹.

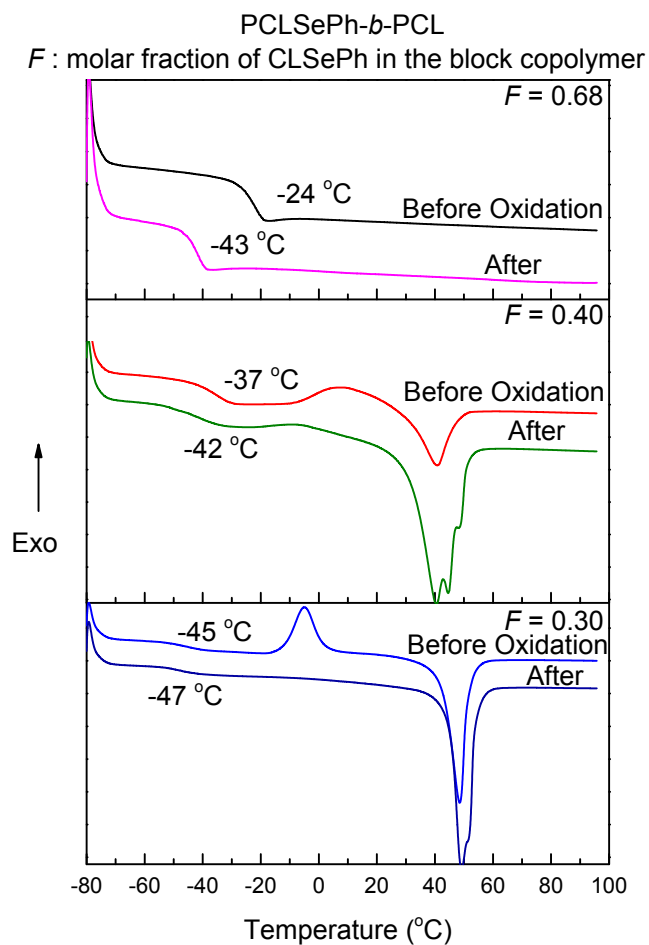


Fig. S11 DSC curves during the second heating process of block copolymers before and after oxidation at the heating rates of 20 °C min^{-1} .

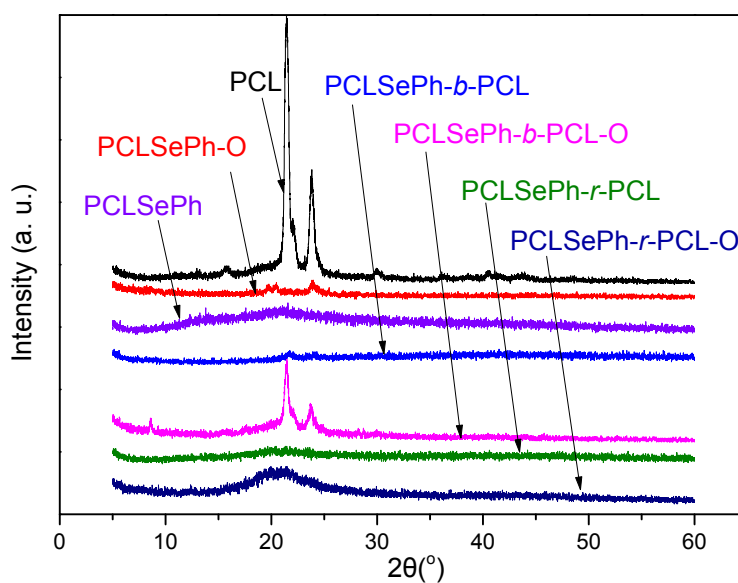


Fig. S12 X-Ray Diffraction (XRD) patterns of polymers including PCL, PCLSePh and its oxidation product (PCLSePh-O), random copolymer (PCLSePh-*r*-PCL) and its oxidation product (PCLSePh-*r*-PCL-O), block copolymer (PCLSePh-*b*-PCL) and its oxidation product (PCLSePh-*b*-PCL-O).

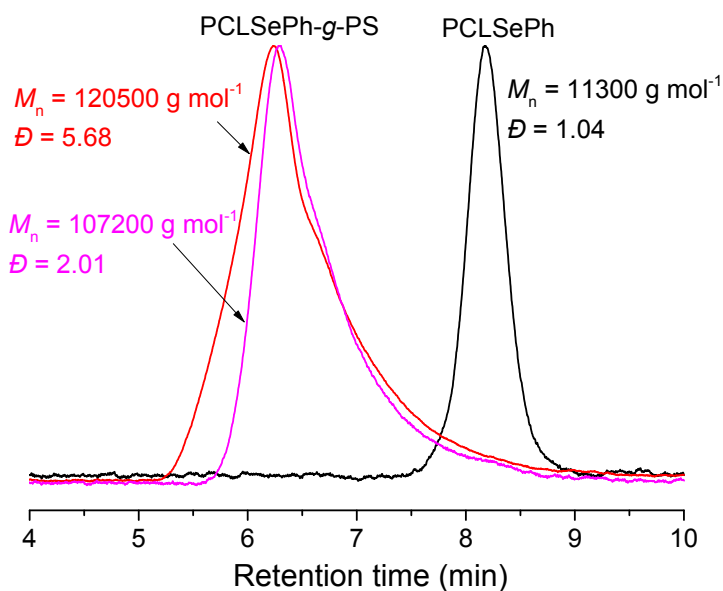


Fig. S13 SEC traces of hybrid polymers prepared from radical polymerization of styrene using PCLSePh as macroinitiator under UV irradiation for 1 hour (pink line) and 2 hours (red line), respectively.

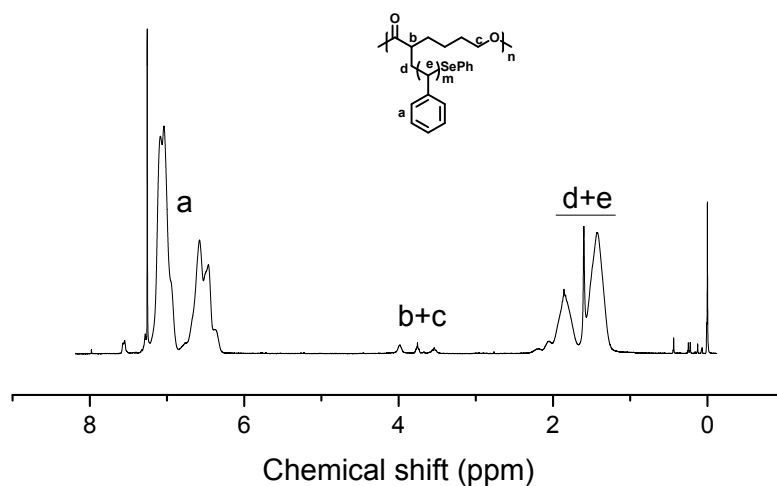


Fig. S14 ^1H NMR of hybrid polymer prepared from radical polymerization of styrene using PCLSePh as macroinitiator under UV irradiation for 1 hour.

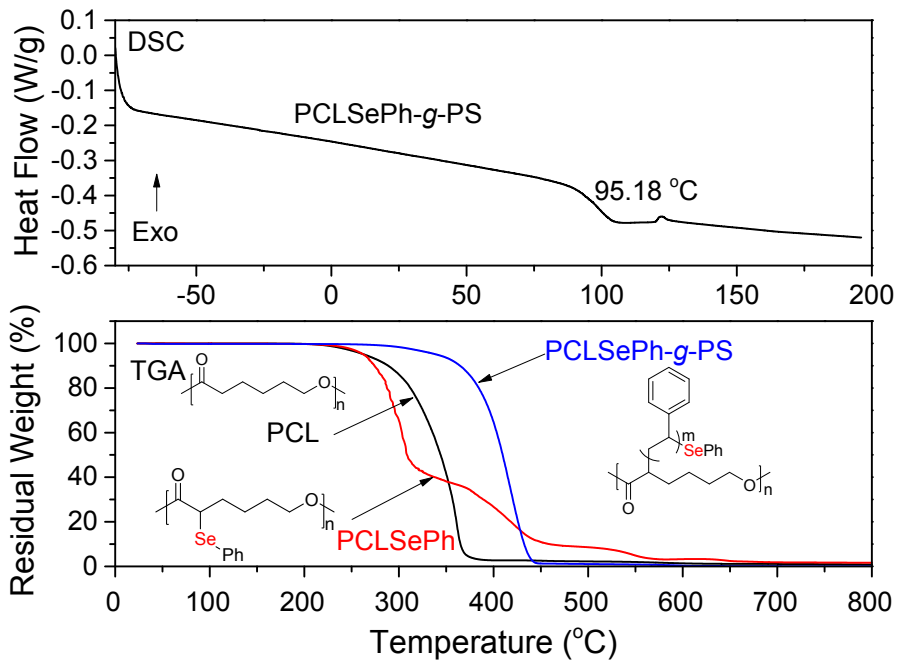


Fig. S15 Thermogravimetric analysis of different functionalized PCLs.