Supplementary information for

Synergistic interaction of renewable nipagin and eugenol for high performance aromatic copoly(ether ester) materials

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1. Experimental Section

Chemical Reagents and Materials

Nipagin (99%), eugenol (99%), methyl thioglycolate (99%), methyl chloroacetate (98%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%) and tetrabutyl titanate (TBT, 99.5%) were purchased from Sigma-Aldrich (St. Louis, USA). 1,4-dibromobutane (98%) and 1,6-hexanediol (98%) were supported by Shanghai Aladdin Chemical Reagent Corporation (Shanghai, China). Other common-used chemical reagents with high purity grade were provided by Tianjin Chemical reagent Corporation (Tianjin, China) and used as received without further purification steps. Silica-gel slices used for thin-layer chromatography (TLC) were purchased from Qingdao Haiyang Chemical Co. Ltd (Qingdao, China).

General Instrumentation and Methods

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C on a Bruker AVANCE III NMR spectrometer operating at 400 MHz and 100.6 MHz, respectively. Tetramethyl silane was used as the internal reference. Fourier transform infrared spectra (FTIR) were recorded on a Bio-Rad FTS6000 spectrophotometer at 25 °C. Polymer samples were prepared by grinding the polymeric materials adequately with KBr powder, followed by compressing the mixture to form a pellet. The molecular weights and polydispersity (D) values of the samples were determined by size exclusion chromatography (SEC, Waters 2414 differential refraction detector) at 35 °C. THF was used as the eluent at a flow rate of 1.0 mL/min. The average molecular weights were calibrated against monodisperse polystyrene (PS) standards. Thermogravimetric analysis (TGA) was carried out using a NETZSCH TG209 instrument. In a typical run, polymer sample was heated from 25 to 800 °C under a nitrogen atmosphere at a rate of 10 °C/min. The temperature leading to 5% weight loss, temperature for maximum degradation rate, and residue weight (%) at 800 °C were recorded. Differential scanning calorimetric (DSC) analysis was carried out by a Mettler-Toledo DSC Q100 calorimeter from TA Instruments. Polymer sample after precipitation from methanol was first heated from room temperature to 150 °C and hold at this temperature for 10 min to erase thermal history, then cooled to -30 °C. Glass transition temperature (T_g) was observed from the second heating run. All runs were carried out at a rate of 10 °C/min. Indium was used as the calibration standards for temperature. Wide X-ray diffraction (WXRD) patterns were recorded on a D/max-2500 diffractometer using CuKα radiation with a wavelength of 0.1542 nm for powder samples precipitated from methanol. Tensile assays were carried out in triplicates on dumb-bell shaped specimens (12 × 2 × 0.5 mm^3) obtained from the casting of chloroform solutions at concentrations of 0.1 g mL^{-1} at a stretching rate of 50 mm/min at 25 °C on a Testometric AX Universal Strength Testing Machine. Young's modulus, tensile strength and elongation at break were calculated by averaging the data from three parallel test.

Synthesis of Nipagin and Eugenol-derived Dimethyl Esters

The preparation methods for nipagin and eugenol-derived dimethyl esters **N1**, **E1** and **E2** have been reported previously (Figure S1-S8).[1,2]

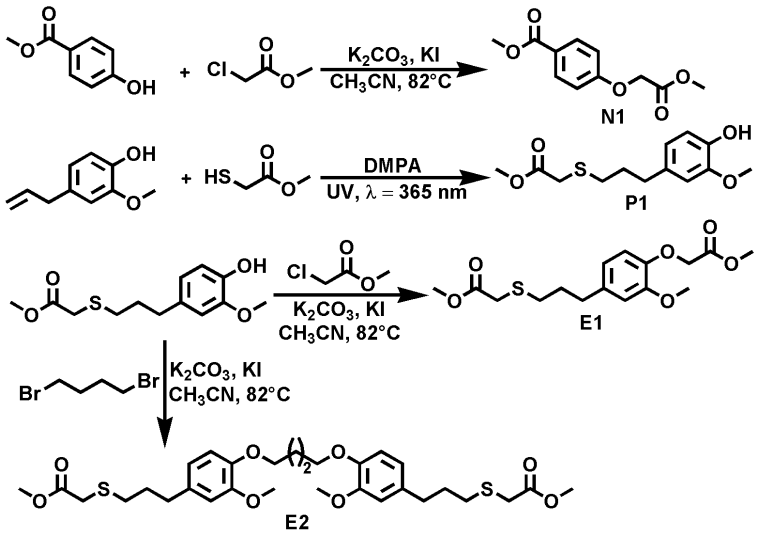

Figure S1. Synthetic routes for the preparation of nipagin and eugenol-derived dimethyl esters **N1**, **E1** and **E2**.

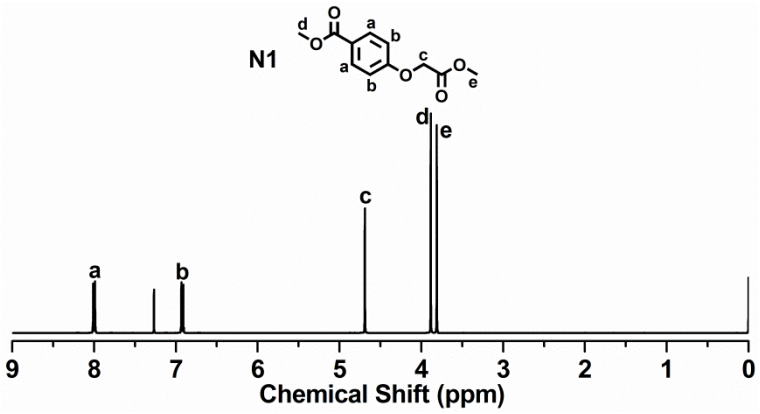

Figure S2. ^{1}H NMR spectrum of **N1**.

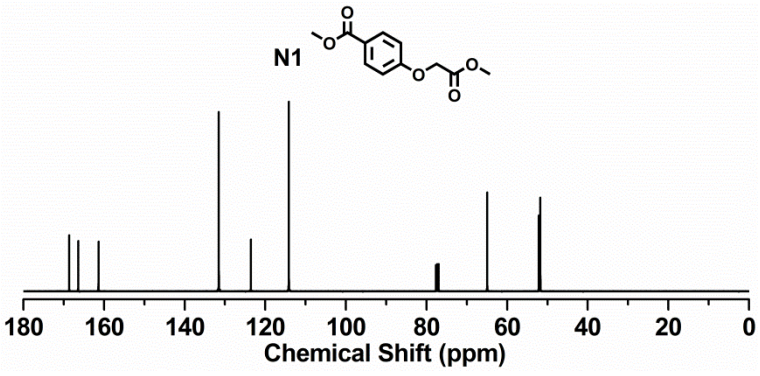

Figure S3. ^{13}C NMR spectrum of **N1**.

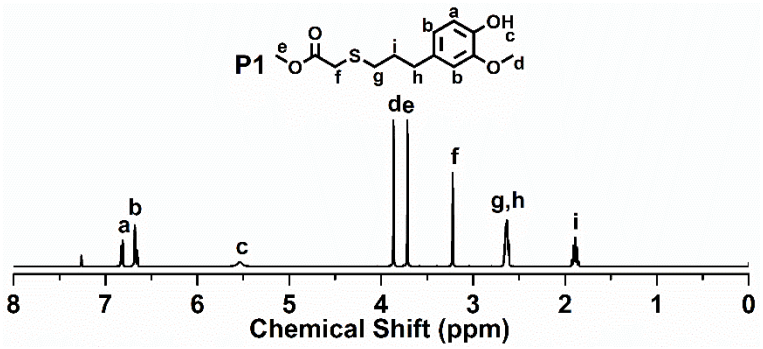

Figure S4. ^{1}H NMR spectrum of **P1**.

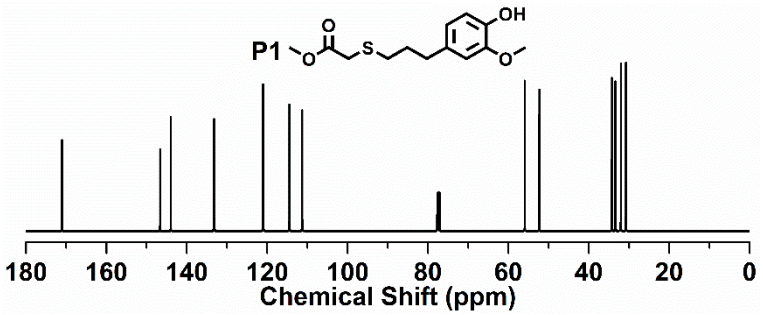

Figure S5. ^{13}C NMR spectrum of **P1**.

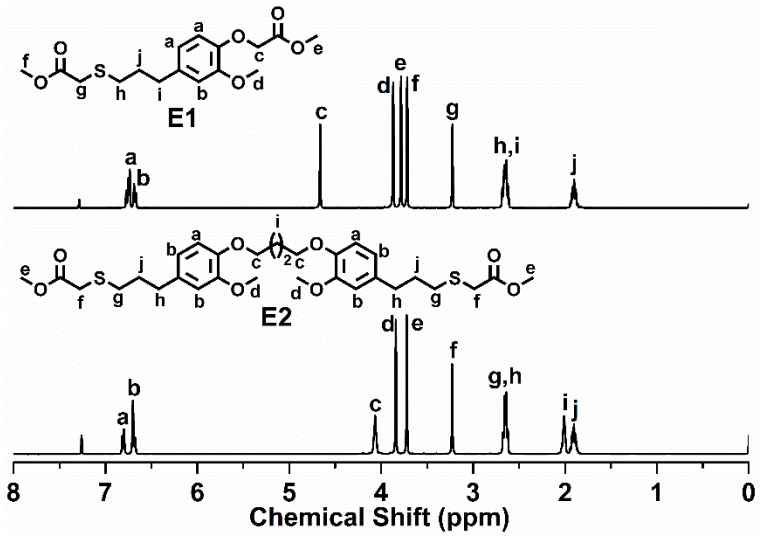

Figure S6. ^{1}H NMR spectra of **E1** and **E2**.

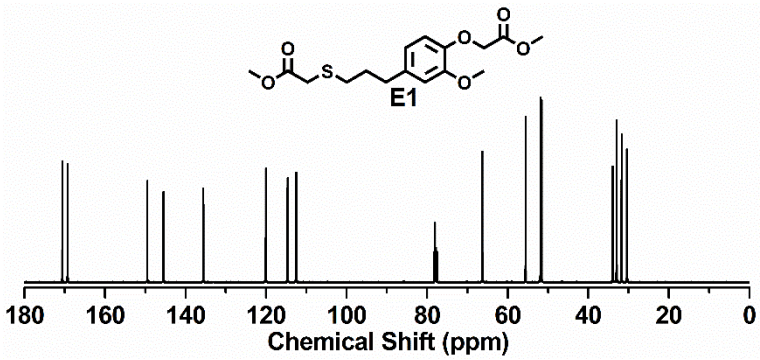

Figure S7. ^{13}C NMR spectrum of **E1**.

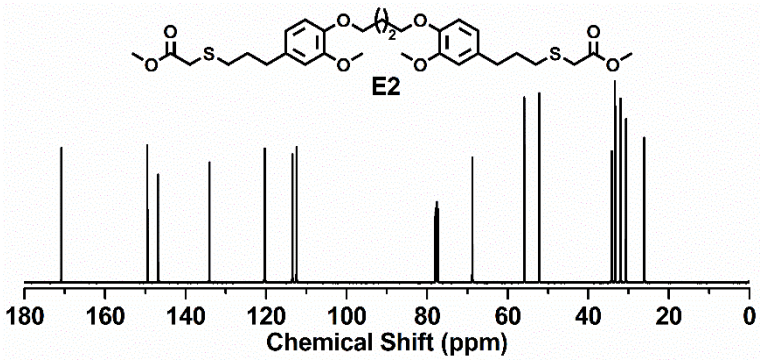

Figure S8. ^{13}C NMR spectrum of **E2**.

2. Experimental Results

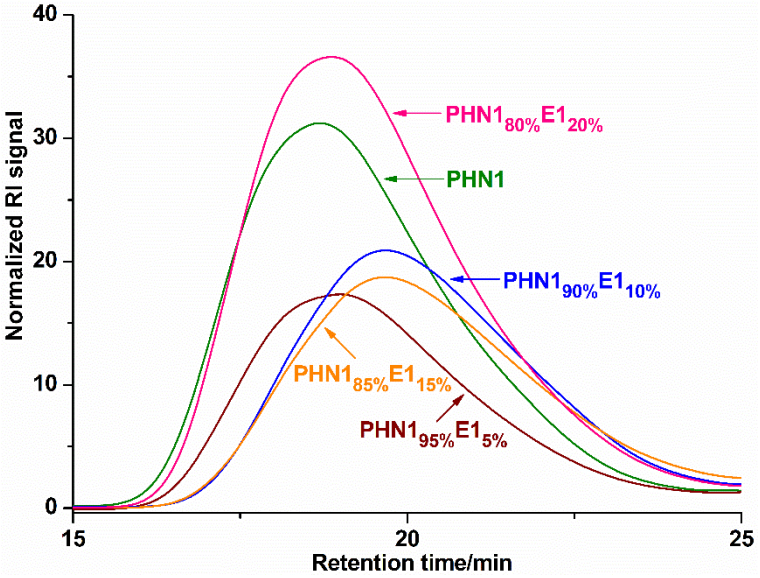

Figure S9. SEC traces of **PHN1$_{1-x}$E1$_x$** copoly(ether ester)s.

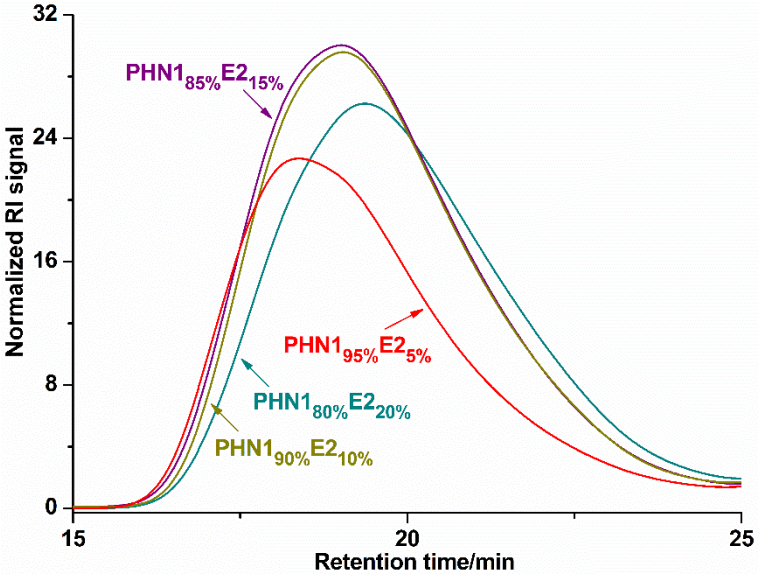

Figure S10. SEC traces of **PHN1$_{1-x}$E2$_x$** copoly(ether ester)s.

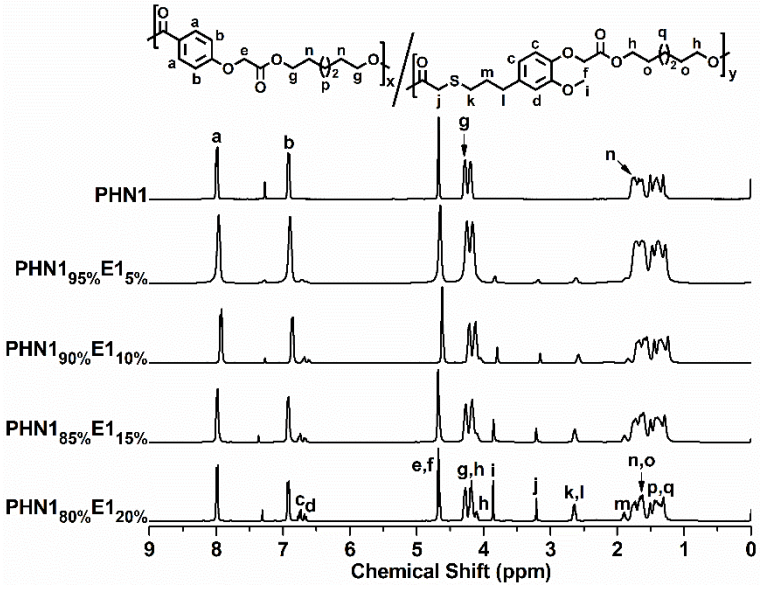

Figure 11. ^{1}H NMR spectra of **PHN1$_{1-x}$E1$_{x}$** copoly(ether ester)s.

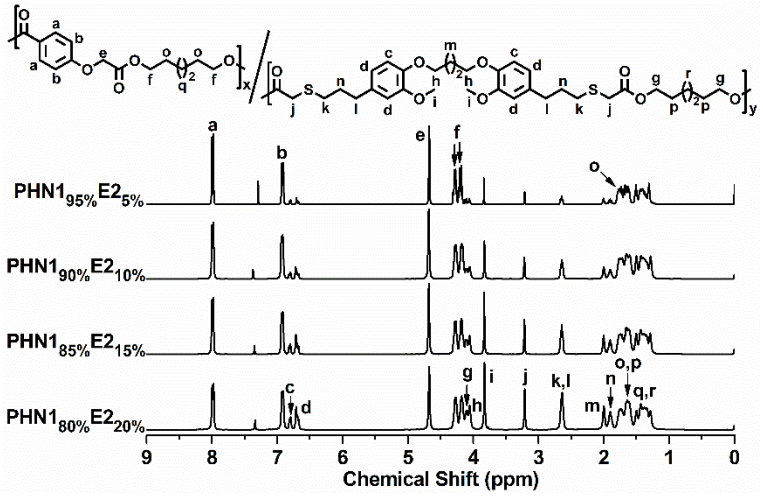

Figure S12. ^{1}H NMR spectra of **PHN1$_{1-x}$E2$_{x}$** copoly(ether ester)s.

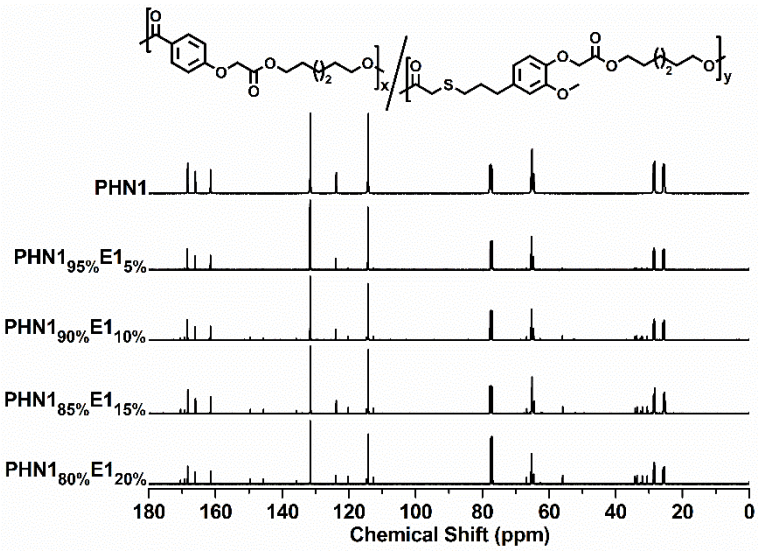

Figure S13. ^{13}C NMR spectra of **PHN1$_{1-x}$E1$_x$** copoly(ether ester)s.

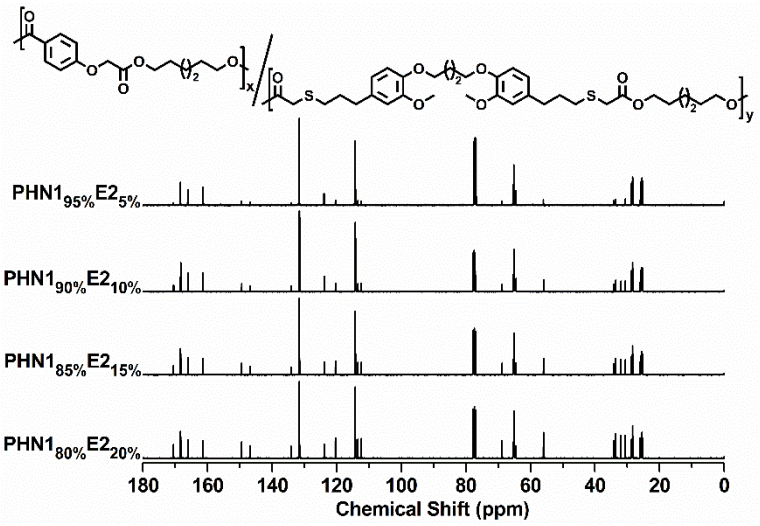

Figure S14. ^{13}C NMR spectra of **PHN1$_{1-x}$E2$_x$** copoly(ether ester)s.

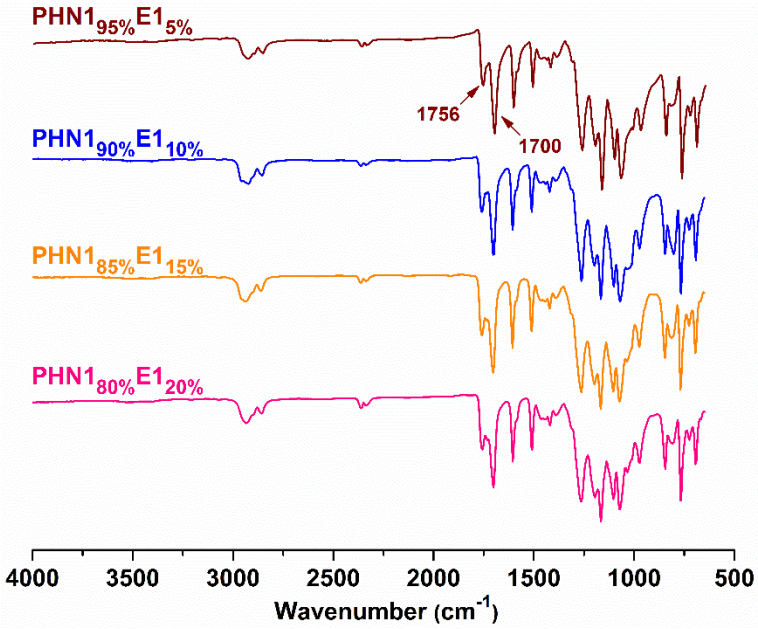

Figure S15. FTIR spectra of **PHN1$_{1-x}$E1$_x$** copoly(ether ester)s.

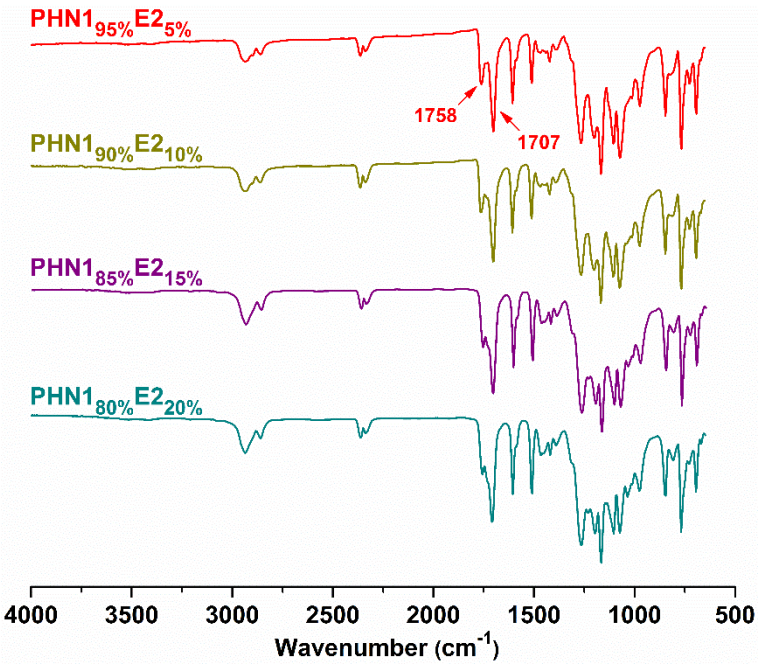

Figure S16. FTIR spectra of **PHN1$_{1-x}$E2$_x$** copoly(ether ester)s.

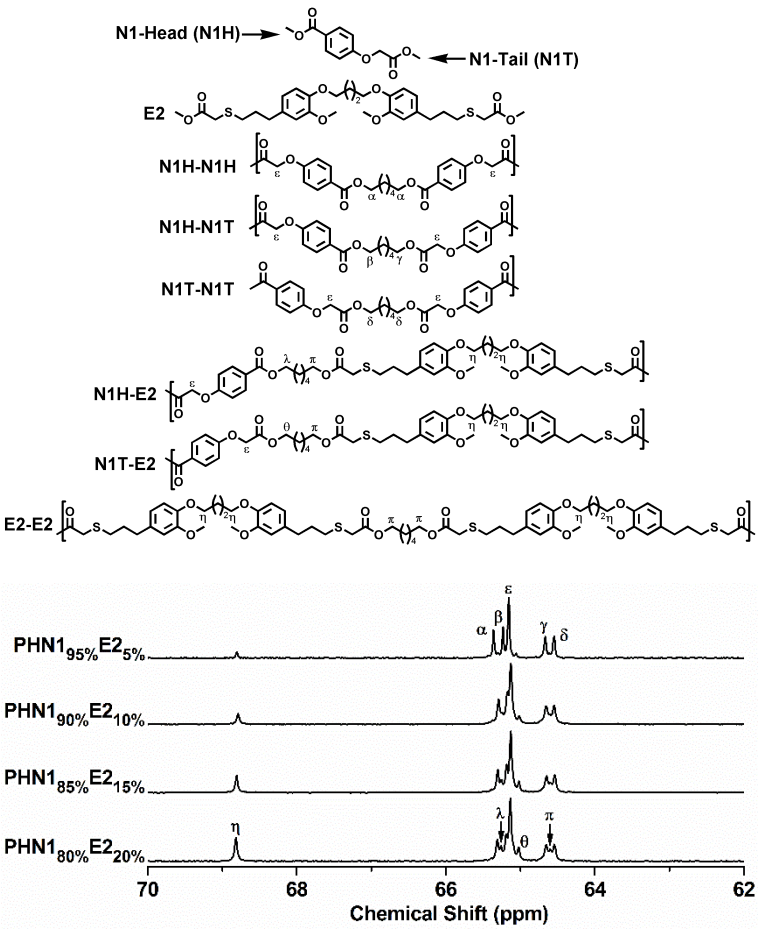

Figure S17. The splitting situations of the methylenes adjacent to the hydroxy-oxygen with the indications of the dyads to which they are assigned in **PHN1$_{1-x}$E2$_x$** copoly(ether ester)s.

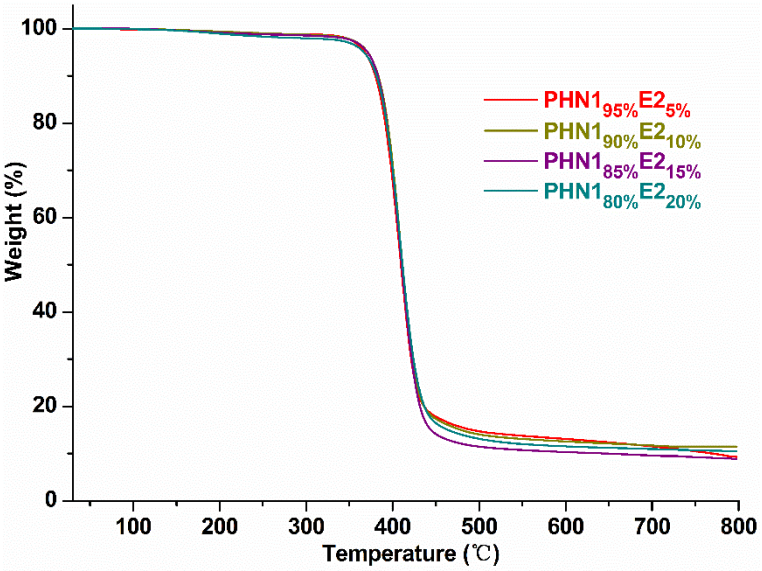

Figure S18. TGA curves of **PHN1$_{1-x}$E2$_x$** copoly(ether ester)s.

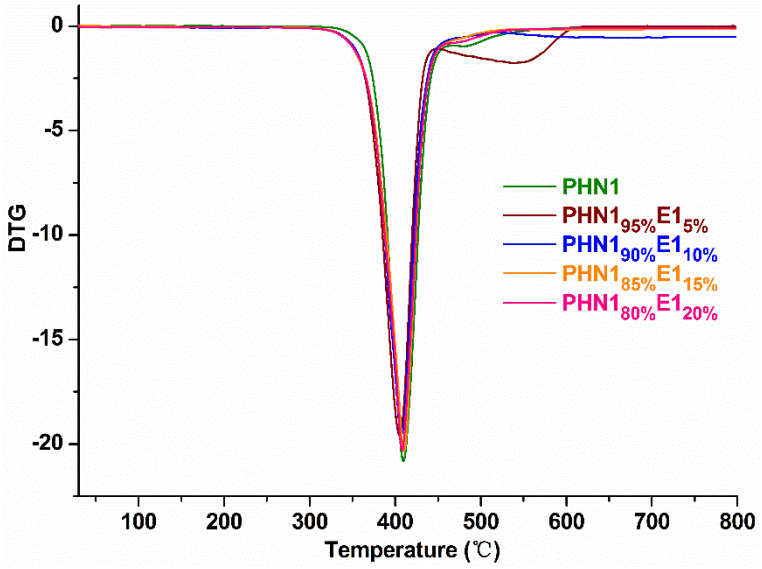

Figure S19. TGA derivative curves of **PHN1$_{1-x}$E1$_x$** copoly(ether ester)s.

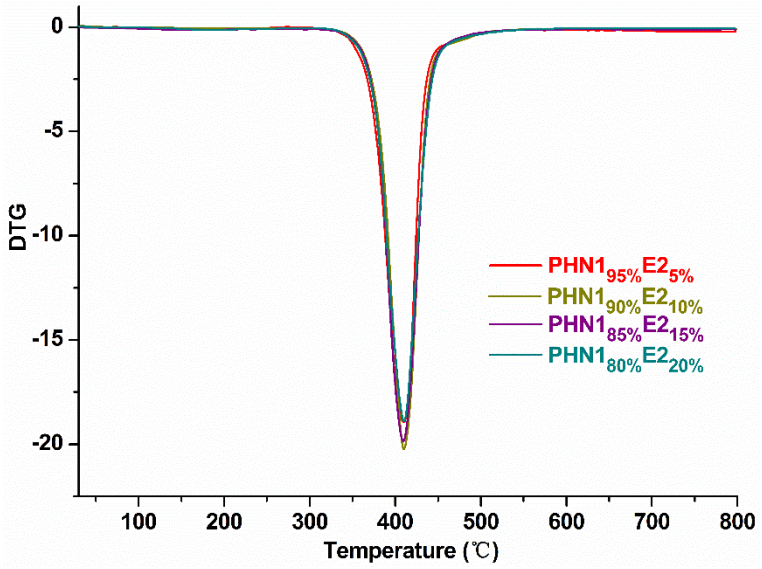

Figure S20. TGA derivative curves of **PHN1$_{1-x}$E2$_x$** copoly(ether ester)s.

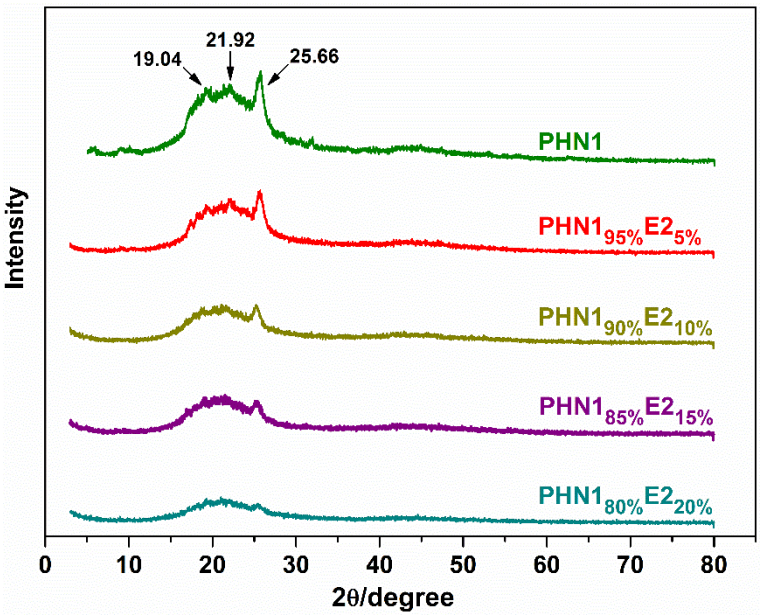

Figure S21. Powder WXRD profiles for **PHN1$_{1-x}$E1$_x$** copoly(ether ester)s.

3. References

1. Hu, K., Zhao, D., Wu, G. & Ma, J. *Polym. Chem.* **6**, 7138-7148 (2015).

2. Hu, K., Zhao, D., Wu, G. & Ma, J. *J. Polym. Sci., Part A: Polym. Chem.* **54**, 2171-2183 (2016).