Supporting information

Temperature switchable alternating copolymerization of epoxides and lactones via pre-sequenced spiroorthoester intermediates

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Contents

A. Experimental section

General Considerations. Unless otherwise indicated, all air- and/or water-sensitive reactions were carried out under dry nitrogen using either an MBraun glove box or standard Schlenk line techniques. NMR spectra were recorded on a Bruker Avance 300 MHz and 400 MHz spectrometer. ^{1}H NMR chemical shifts are reported in ppm versus residual protons in deuterated solvents as follows: δ 7.27 $CDCl_3$ and 7.16 C_6D_6, $^{13}C\{^{1}H\}$ NMR chemical shifts are reported in ppm versus residual ^{13}C in the solvents: δ 77.2 $CDCl_3$ and 128.39 C_6D_6. $^{19}F\{^{1}H\}$ NMR chemical shifts are reported in ppm and externally referenced to neat $CFCl_3$ at 0 ppm. X-ray diffraction measurements were carried out on a Bruker APEX DUO or Bruker X8 APEX II diffractometer equipped with graphite monochromated Mo-K_α radiation. Bruker SAINT software package[1] was used to integrate images. Absorption correction was done using SADABS.[2] Structure solutions were obtained using SHELXT[3] and refined using SHELXL[4] via the Olex2 interface.[5] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were constrained to geometrically calculated positions. EA CHN analysis was performed using a Carlo Erba EA1108 elemental analyzer. The elemental composition of unknown samples was determined by using a calibration factor. The calibration factor was determined by analyzing a suitable certified organic standard (OAS) of a known elemental composition. Infrared (IR) spectra were recorded using a PerkinElmer Frontier IR Single-Range Spectrometer with a resolution of 1 cm^{-1} and a scan speed of 0.2 cm/s in the absorbance mode. Samples for FTIR measurement were prepared by coating approximately 10 mg of the polymers on the diamond/ZnSe crystal at room temperature. Molecular weights were determined by triple-detection gel permeation chromatography (GPC-LLS) using a Malvern OMNISEC GPC instrument equipped with Viscotek T3000 and T6000 GPC columns packed with poly(styrene-co-divinylbenzene) particles and used at a temperature of 25 °C. The response was measured with a built-in differential refractometer, a differential viscometer, and twoangle light-scattering detectors. A flow rate of 1.0 mL min^{-1} was used and samples were dissolved in THF (concentrations up to 5 mg mL^{-1}). Narrow-molecular weight polystyrene standards were used for calibration purposes. The dn/dc (differential refractive index increment) values of the polymers studied were determined assuming the 100% mass recovery method from Malvern OMNISEC software version 10.2. Differential scanning calorimetry (DSC) measurements were performed to detect the glass transition , crystallization temperature, and melting temperature of the polymers using a differential scanning calorimeter NETZCH DSC214 Polyma. Experiments were carried out under nitrogen atmosphere with approximately 5-10 mg of the polymer samples sealed in an aluminum pan with a punctured lid. The samples were heated from -100 to 200 °C with a 10 °C /min heating rate. Thermal degradation studies were performed on a NETZCH TG 209 F1 Libra instrument. Samples were placed in an alumina crucible and heated under nitrogen at a rate of 10 °C/min from 30 to 800 °C.

Materials. Solvents (THF, toluene, hexane and diethyl ether) were collected from a Solvent Purification System from Innovative Technology, Inc. whose columns were packed with activated alumina and dried and vacuum-distilled over sodium, using benzophenone as an indicator and degassed through a series of freeze-pump-thaw cycles. Deuterated solvents ($CDCl_3$ and C_6D_6) were dried over CaH_2, collected by vacuum distillation and degassed through a series of freeze-pump-thaw cycles. $InCl_3$ was purchased from Tokyo Chemical Industries (TCI) and used without further purification. (Trimethylsilyl)methylmagnesium chloride (1.0 M in Et_2O) and dimethylanilinium tetrakis(pentafluorophenyl)borate ($[HNMe_2Ph][B(C_6F_5)_4]$) were purchased from Aldrich and Alfa Aesar, respectively, and used as received. 1,2-epoxy-7-octene and ε-caprolactone were purchased from Aldrich and dried over CaH_2, distilled and stored under molecular sieves. Proligand

$H(NN_iO_{tbu})$[6] and $In(CH_2Si(CH_3)_3)_3$[7] were synthesized according to previously reported procedures. **1** and **2** were synthesized according to a previous report.[8]

Synthesis of spiroorthoester (SOE1) with 1. In a glovebox, a 100 mL schlenk flask was charged with 7.5 mL and 22.5 mL solution of a 1,2-epoxy-7-octene and ε-caprolactone stock solution, respectively (1,2-epoxy-7-octene: 12.5 mmol; [1,2-epoxy-7-octene] = 1.67 M; ε-caprolactone: 12.5 mmol; [ε-caprolactone] = 0.556 M). 7.5 mL solution of a catalyst stock solution (**1**: 0.1875 mmol; [**1**] = 0.025 M) were added to the schlenk flask. 12.5 mL solution of toluene was used to make up to the total volume of 50 mL. The resulting mixture was placed in an oil bath preheated to 60 °C and stirred. A sample of the crude mixture (ca. 0.05 mL) was dissolved in C_6D_6 to be analyzed by ^1H NMR spectroscopy to determine conversion. The solvent was removed under vacuum after 24 h. The residue was dissolved in hexane and filtered through silica flash column to remove catalyst. The collected solution was dried over vacuum to obtain the desired spiro orthoester (SOE1) as colourless oil in 92% isolated yield. The product was dried under high vacuum for 4 h prior to analysis.

One-pot synthesis of poly(ether-*alt*-ester) with 1. In a glovebox, a schlenk flask was charged with 0.6 mL and 1.8 mL solution of a 1,2-epoxy-7-octene and ε-caprolactone stock solution, respectively (1,2-epoxy-7-octene: 1.0 mmol; [1,2-epoxy-7-octene] = 1.67 M; ε-caprolactone: 1.0 mmol; [ε-caprolactone] = 0.556 M). 0.6 mL solution of a catalyst stock solution (**1**: 0.015 mmol; [**1**] = 0.025 M) were added to the schlenk flask. 1.0 mL solution of toluene was used to make up to the total volume of 4 mL. The resulting mixture was placed in an oil bath preheated to 60 °C and stirred for 24 h. A sample of the crude mixture (ca. 0.05 mL) was dissolved in C_6D_6 to be analyzed by ^1H NMR spectroscopy to determine conversion of epoxide and ε-caprolactone and confirm the formation of corresponding SOE. The solvent was removed under high vacuum. The residue was stirred in an oil bath preheated to 110 °C for 24 h. The resulting viscous liquid was cooled down to room temperature. Some of the crude mixture was dissolved in C_6D_6 to be analyzed by $^{13}C\{^1H\}$ NMR spectroscopy to determine conversion of monomer. Cold methanol (0 °C, 15 mL) was added to the remaining polymeric product. The methanol-insoluble product was separated and dried under high vacuum for 4 h prior to analysis.

Homopolymerization of spiroorthoester (SOE1) with 1. In a glovebox, a Schlenk flask was charged with a catalyst (0.00416 mmol) and monomer SOE1 (0.832 mmol) was added directly to the flask. The mixture was stirred in an oil bath preheated to corresponding temperature for corresponding time. The resulting viscous liquid was cooled down to room temperature. Some of the crude mixture was dissolved in C_6D_6 to be analyzed by $^{13}C\{^1H\}$ NMR spectroscopy to determine conversion of monomer. Cold methanol (0 °C, 15 mL) was added to the remaining polymeric product. The methanol-insoluble product was separated and dried under high vacuum for 4 h prior to analysis.

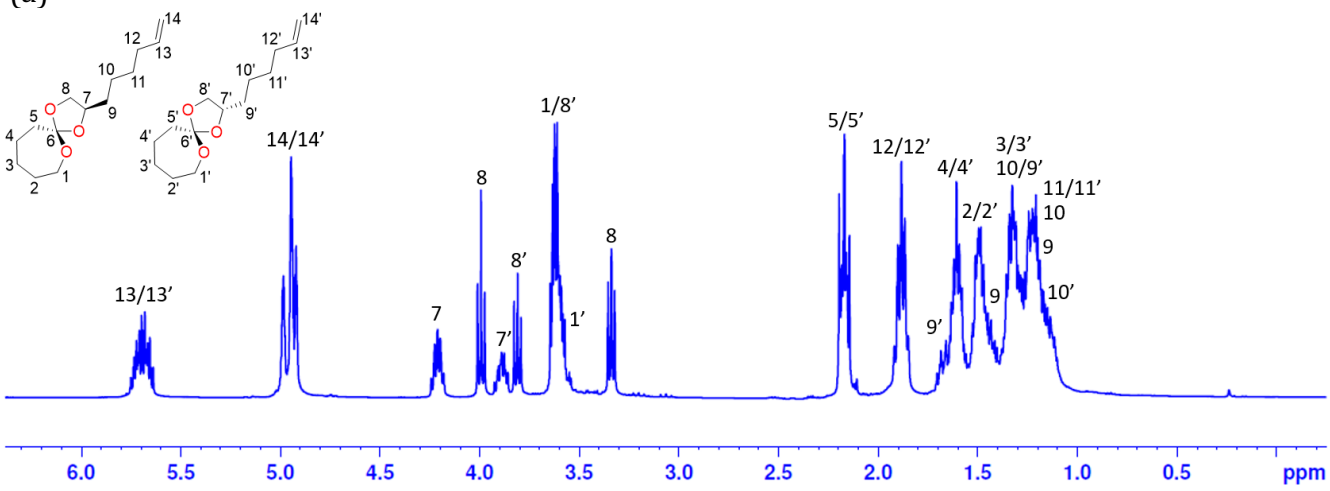
Synthesis of cross-linked poly(ether-*alt*-ester). In a glovebox, a vial was charged with poly(ether-ester) (0.416 mmol), 2,2'-(ethylenedioxy)diethanethiol (0.208 mmol), and 2,2'-azobis(2-methylpropionitrile) (0.0298 mmol) in minimal amount of toluene. The mixture was stirred in an oil bath preheated to 80 °C for 5 min. The resulting soft solid was cooled down to room temperature. The insoluble product was washed with cold methanol and dried under high vacuum for 4 h prior to analysis.

Degradation of poly(ether-*alt*-ester). A vial was charged with poly(ether-ester) (0.416 mmol) and 10 mL of 0.1 M of tetrabutylammonium hydroxide in MeOH/DCM. The mixture was stirred at room temperature for 2 h. Subsequently, 1 M HCl in diethyl ether was added to neutralize the reaction. The resulting mixture was dried under high vacuum for 4 h prior to analysis.

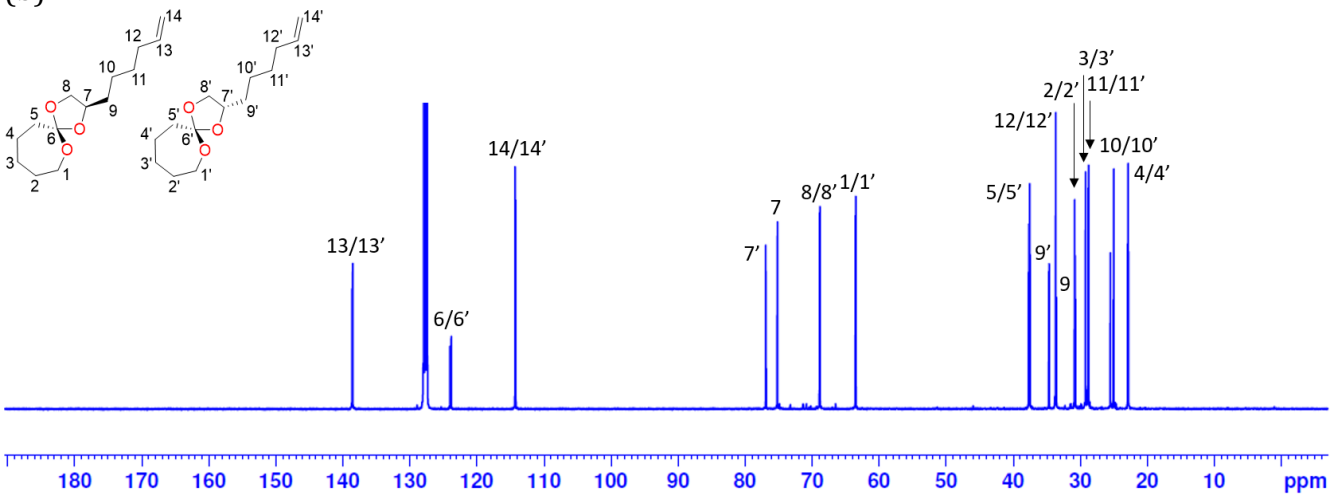
Lewis acidity study. We used a modified Gutmann–Beckett method to determine relative acidity of catalysts for SOE polymerization. This method involves the addition of 0.8 eq triethylphosphine oxide ($OPEt_3$) to form an adduct with the metal complexes. The free triethylphosphine oxide shift is determined by the addition of a sealed capillary tube containing a solution of triethylphosphine oxide in $CDCl_3$ into the NMR tube. The downfield shift of the phosphorus peak of the adducts are used to determine the relative strength of the Lewis acidity of each species.

B. Spiroorthoester (SOE) monomer

(a)



(b)



(c)

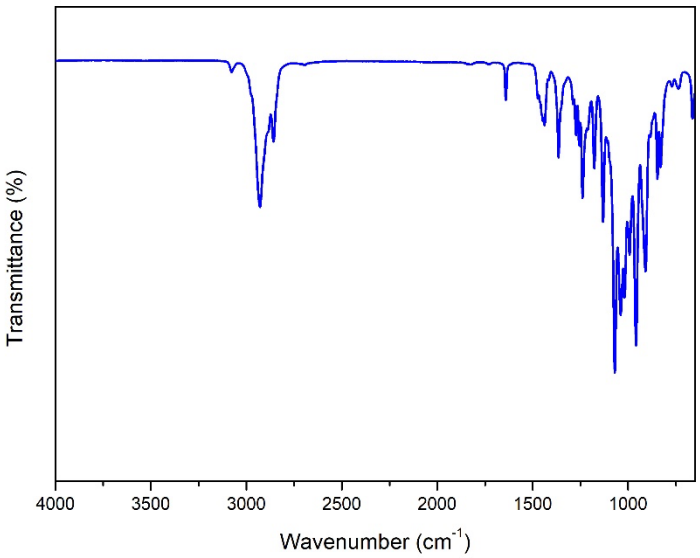
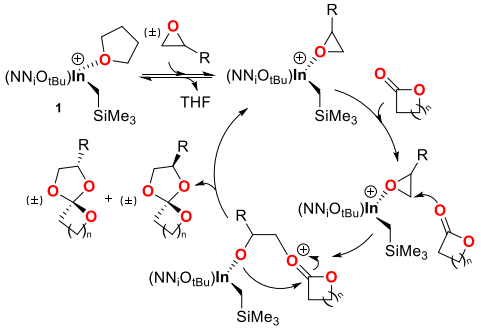
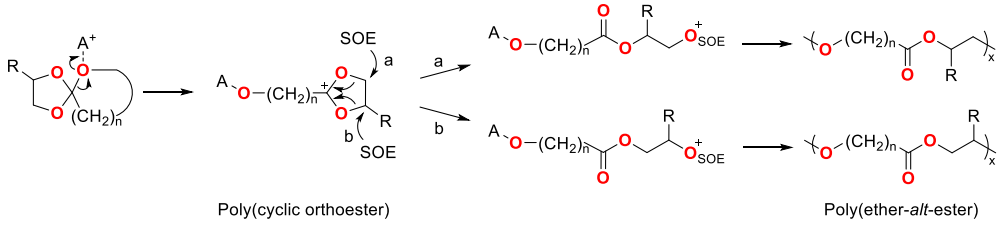


Figure S1. (a) ^{1}H NMR (400 MHz, C_6D_6, 25 °C), (b) $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6, 25 °C), and (c) FTIR spectrum of SOE1.

Scheme S1. Proposed mechanism for the synthesis of SOEs by **1**.



Scheme S2. Proposed mechanism for the cationic polymerization of SOEs by Lewis acid catalyst.[9]



C. Homopolymerization of SOE1 with 1

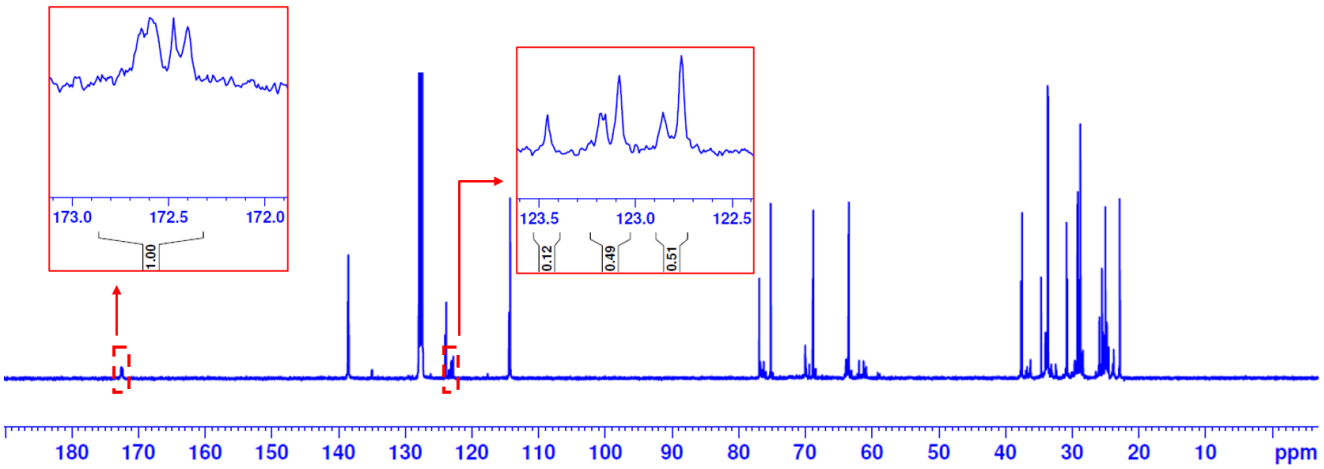


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of the crude product (poly(cyclic orthoester 53% and poly(ether-*alt*-ester) 47%) from the homopolymerization of 200 equiv SOE1 at 80 °C for 24 h (Table 1, entry 3) (151 MHz, C_6D_6, 25 °C).

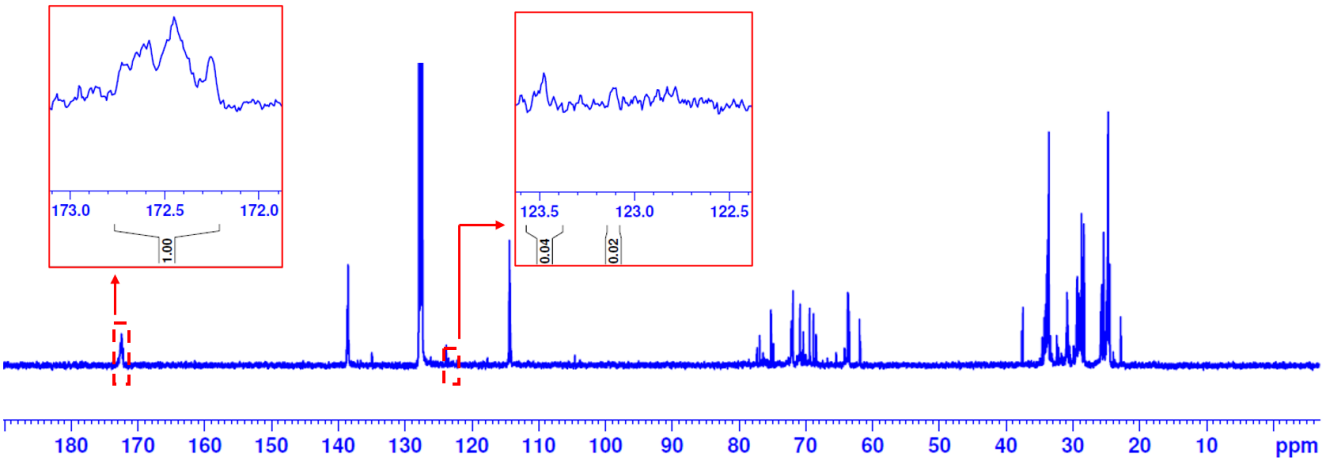


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of the crude product (poly(cyclic orthoester 6% and poly(ether-*alt*-ester) 94%) from the homopolymerization of 200 equiv SOE1 at 80 °C for 48 h (Table 1, entry 4) (151 MHz, C_6D_6, 25 °C).

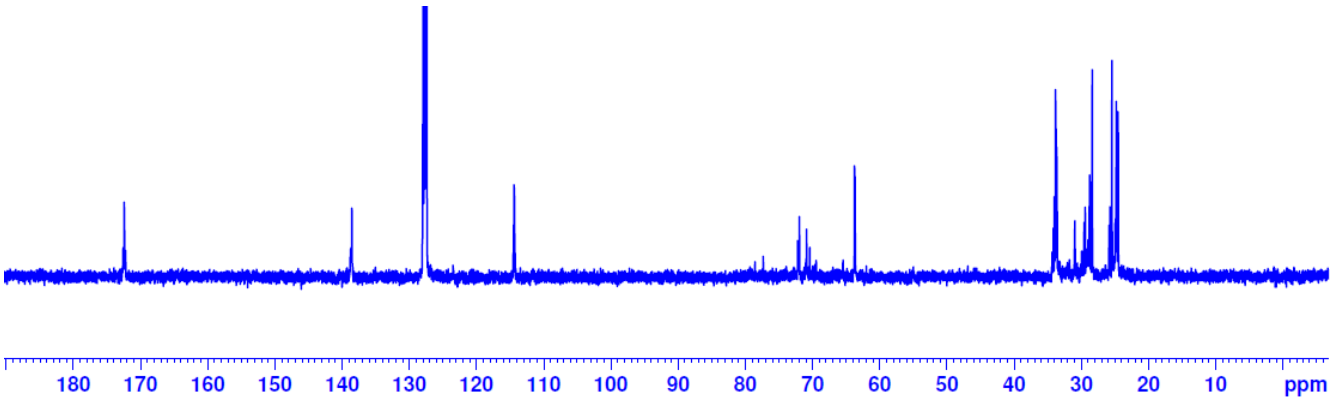


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of poly(ether-*alt*-ester) (100%) from the one-pot reaction of SOE1 (Table 1, entry 1) (151 MHz, C_6D_6, 25 °C).

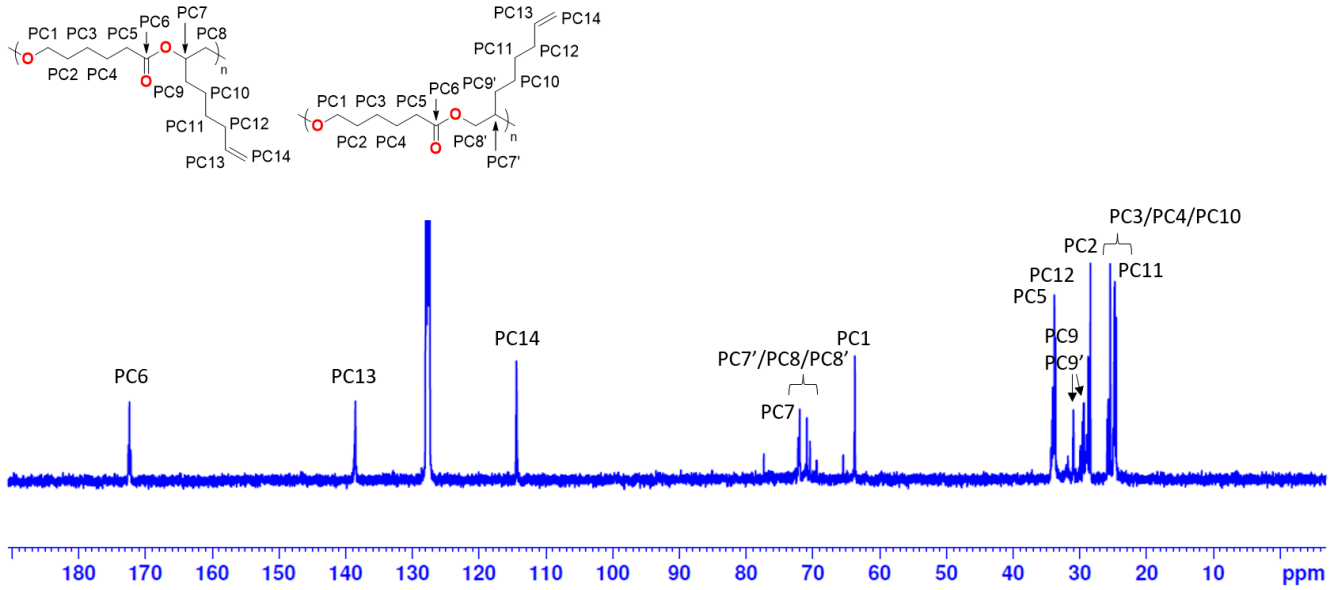


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of poly(ether-*alt*-ester) (100%) from the homopolymerization of 200 equiv SOE1 at 110 °C for 24 h (Table 1, entry 5) (151 MHz, C_6D_6, 25 °C).

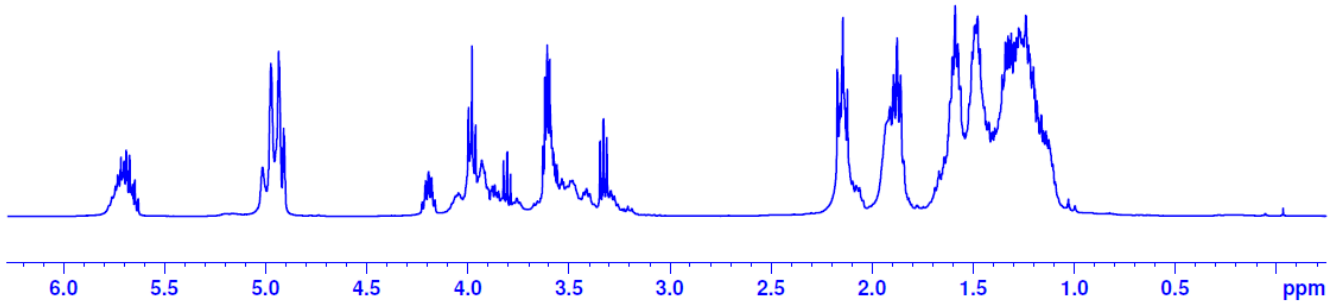


Figure S6. ^{1}H NMR spectrum of the crude product (poly(cyclic orthoester 53% and poly(ether-*alt*-ester) 47%) from the homopolymerization of 200 equiv SOE1 at 80 °C for 24 h (Table 1, entry 3) (400 MHz, C_6D_6, 25 °C).

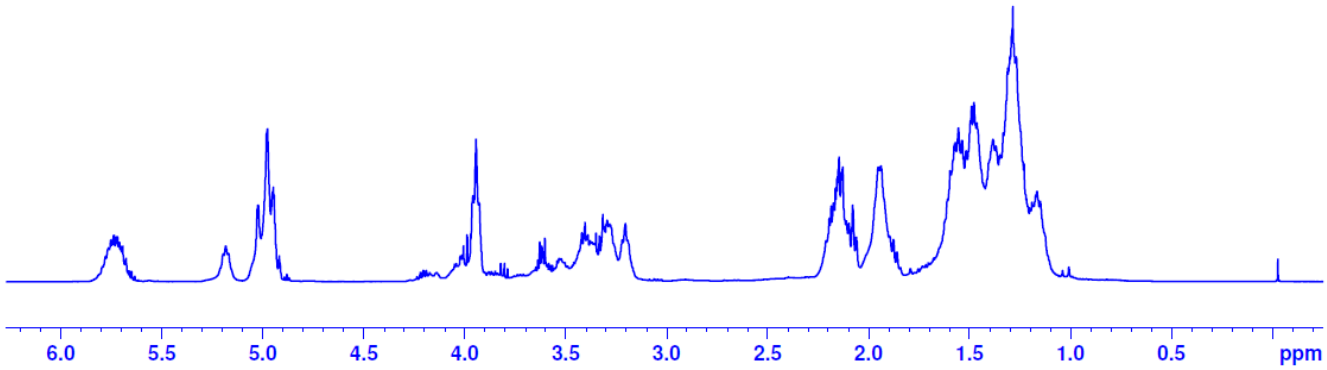


Figure S7. ^{1}H NMR spectrum of the crude product (poly(cyclic orthoester 6% and poly(ether-*alt*-ester) 94%) from the homopolymerization of 200 equiv SOE1 at 80 °C for 48 h (Table 1, entry 4) (400 MHz, C_6D_6, 25 ℃).

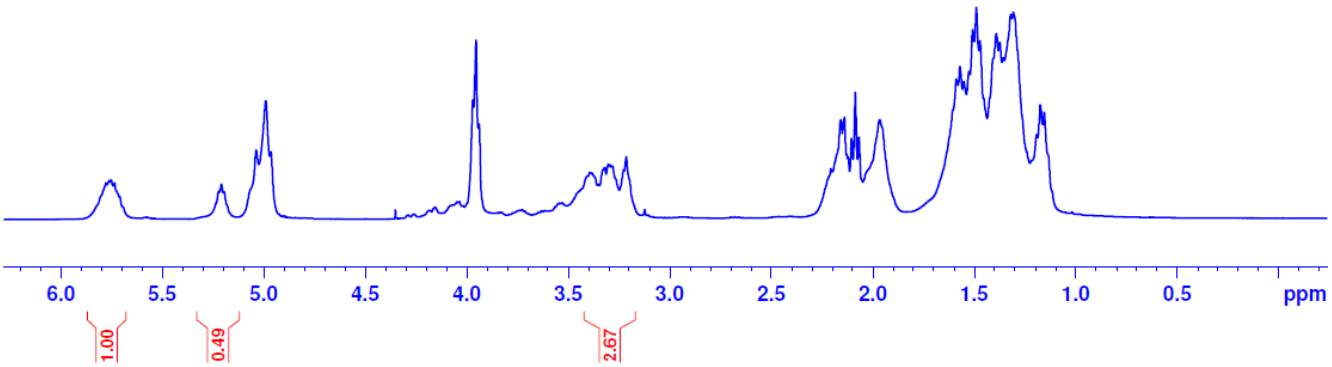


Figure S8. ^{1}H NMR spectrum of poly(ether-*alt*-ester) (100%) from the one-pot reaction of SOE1 (Table 1, entry 1) (400 MHz, C_6D_6, 25 ℃).

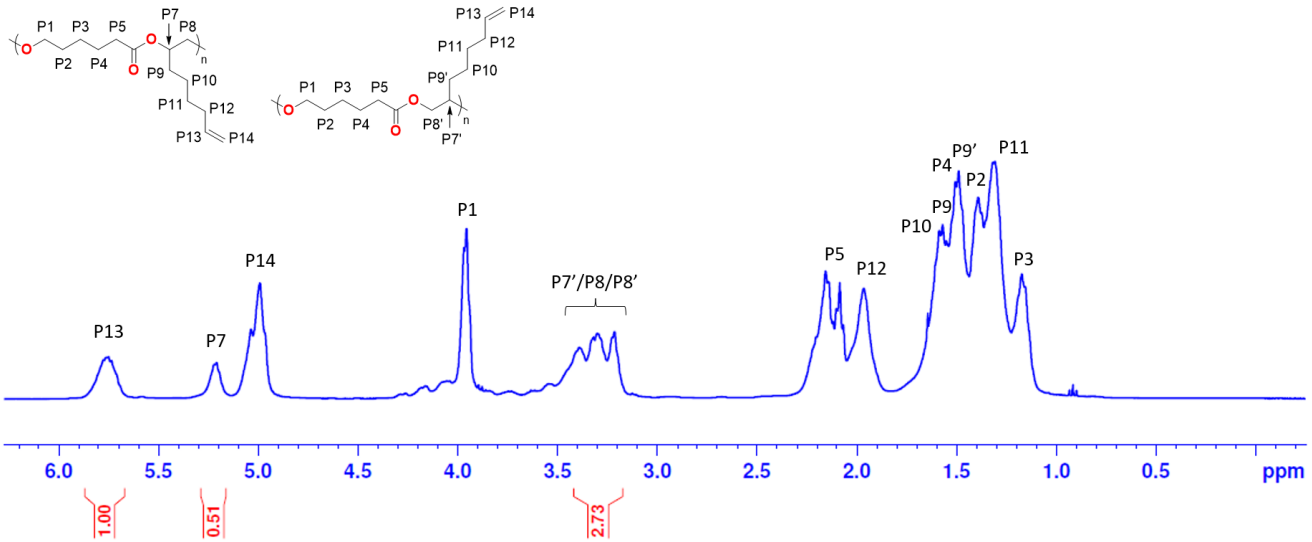


Figure S9. ^{1}H NMR spectrum of poly(ether-*alt*-ester) (100%) from the homopolymerization of 200 equiv SOE1 at 110 °C for 24 h (Table 1, entry 5) (400 MHz, C_6D_6, 25 ℃).

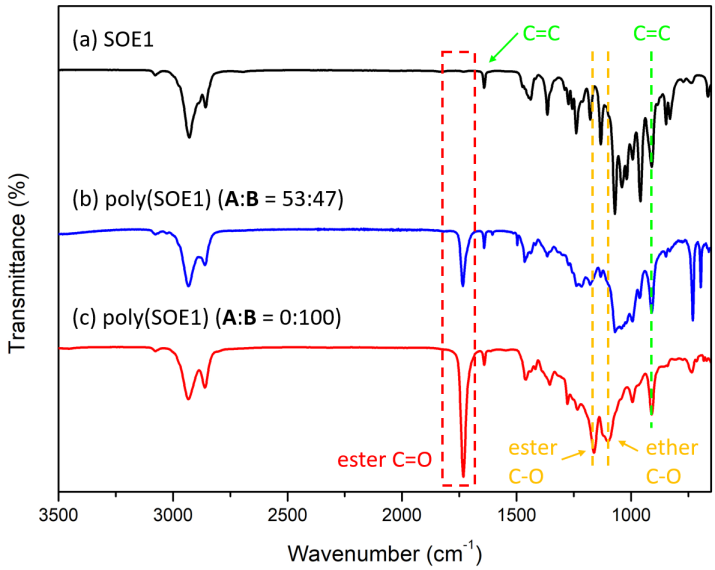


Figure S10. Overlaid FTIR spectra of (a) monomer SOE1, (b) structurally mixture of poly(cyclic orthoester) (**A**, 53%) and poly(ether-ester) (**B**, 47%) (Table1, entry 3), and (c) structurally pure poly(ether-ester) (**B**, 100%) (Table1, entry 1).

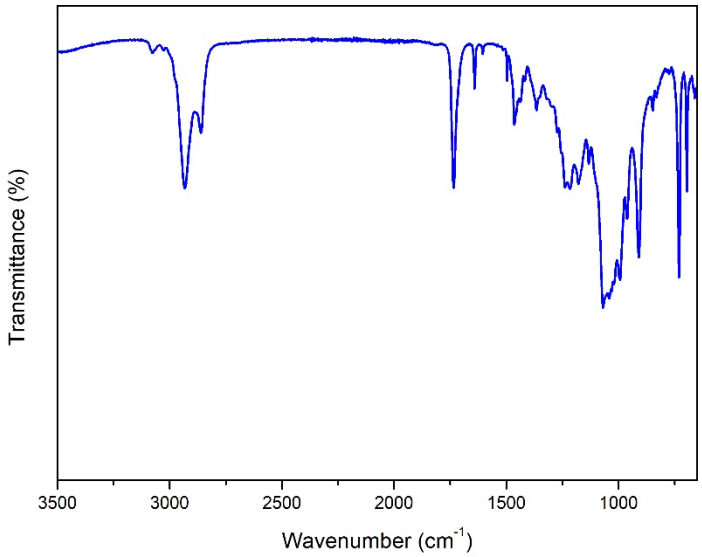


Figure S11. FTIR spectrum of the product (poly(cyclic orthoester 53% and poly(ether-*alt*-ester) 47%) from the homopolymerization of 200 equiv SOE1 at 80 °C for 24 h (Table 1, entry 3).

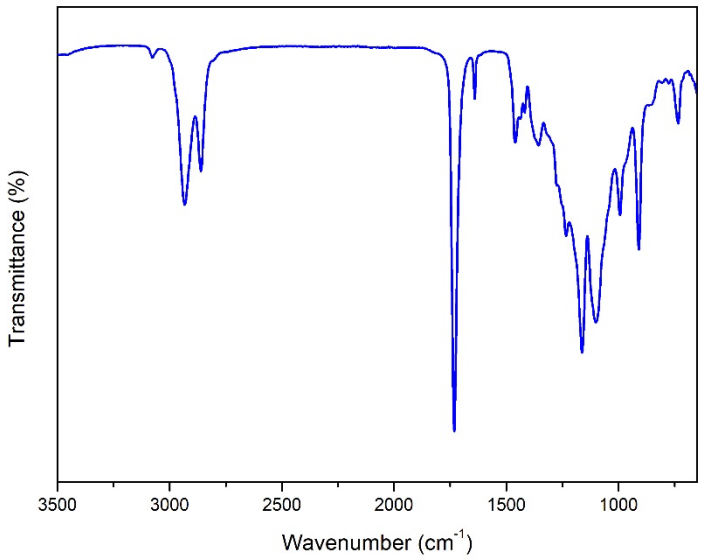


Figure S12. FTIR spectrum of the product (poly(cyclic orthoester 6% and poly(ether-*alt*-ester) 94%) from the homopolymerization of 200 equiv SOE1 at 80 °C for 48 h (Table 1, entry 4).

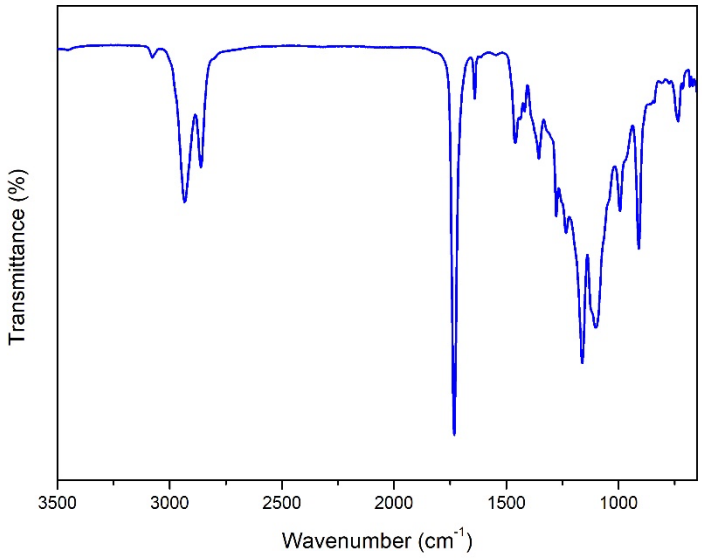


Figure S13. FTIR spectrum of poly(ether-*alt*-ester) (100%) from the one-pot reaction of SOE1 (Table 1, entry 1).

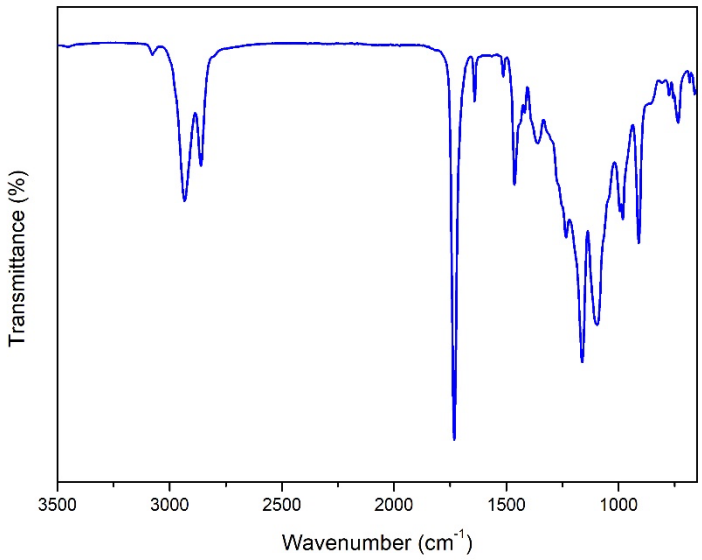


Figure S14. FTIR spectrum of poly(ether-*alt*-ester) (100%) from the homopolymerization of 200 equiv SOE1 at 110 °C for 24 h (Table 1, entry 5).

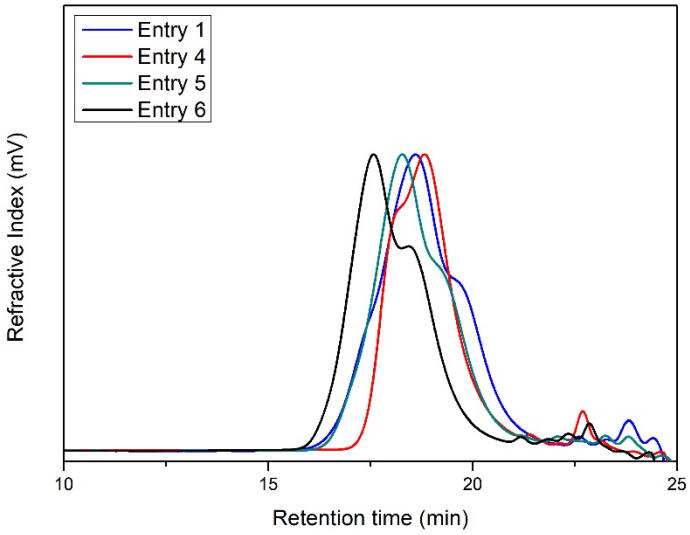


Figure S15. Overlaid GPC trace of poly(ether-*alt*-ester).

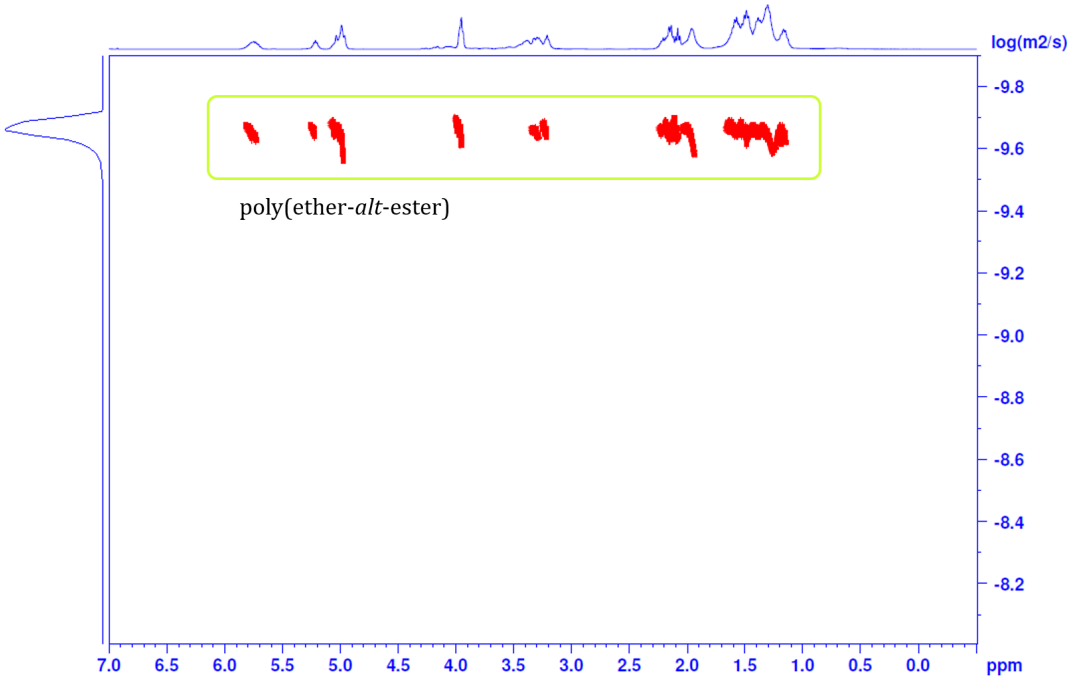


Figure S16. DOSY-NMR spectrum of poly(ether-*alt*-ester) (100%) from the homopolymerization of 200 equiv SOE1 at 110 °C for 24 h (Table 1, entry 5) (400 MHz, C_6D_6, 25 °C).

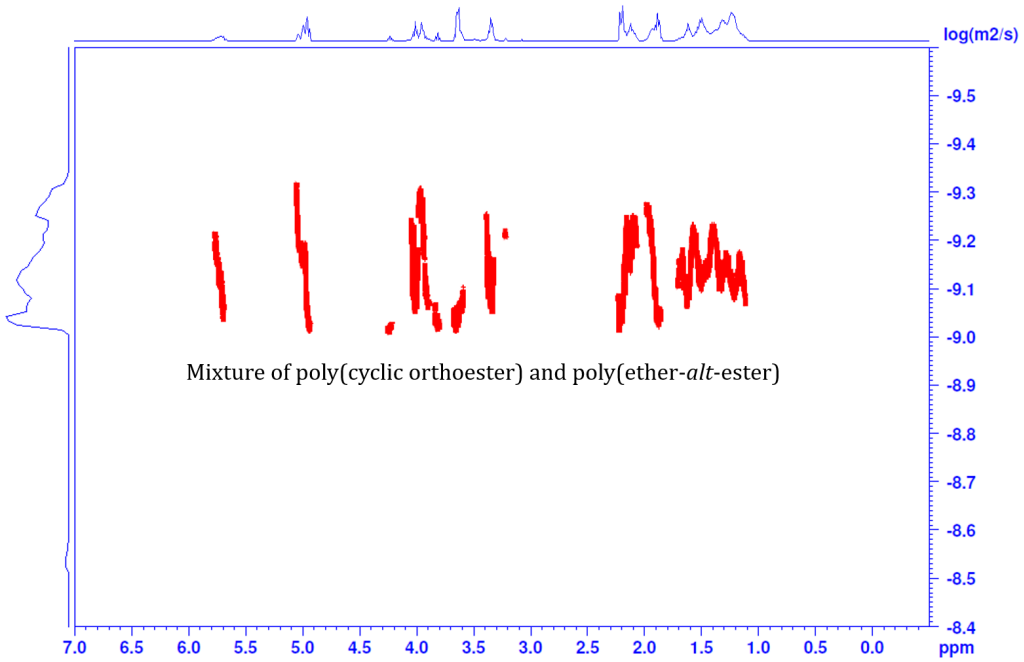


Figure S17. DOSY-NMR spectrum of mixture of poly(cyclic orthoester) 53% and poly(ether-*alt*-ester) 47% from the homopolymerization of 200 equiv SOE1 at 80 °C for 24 h (Table 1, entry 3) (400 MHz, C_6D_6, 25 °C).

D. Thermal properties of poly(ether-*alt*-ester)

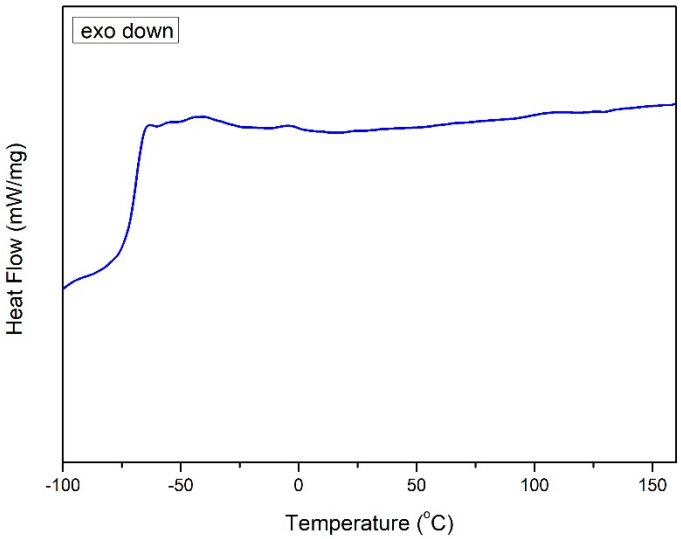


Figure S18. DSC thermogram of poly(ether-*alt*-ester) (100%) from the one-pot reaction of SOE1 (Table 1, entry 1).

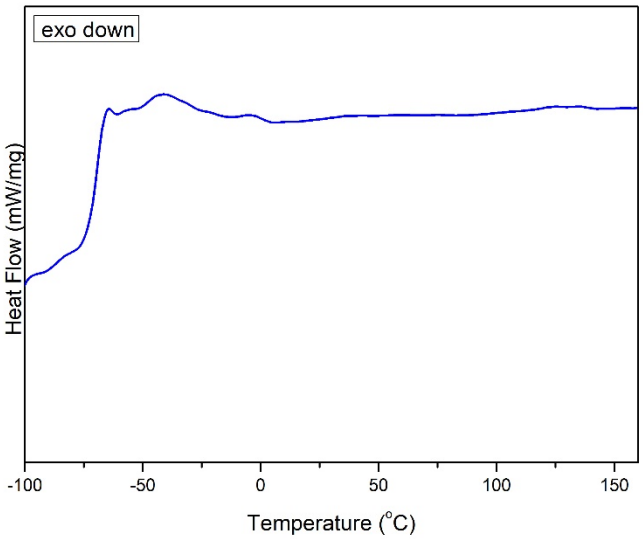


Figure S19. DSC thermogram of poly(ether-*alt*-ester) (100%) from the homopolymerization of 200 equiv SOE1 at 110 °C for 24 h (Table 1, entry 5).

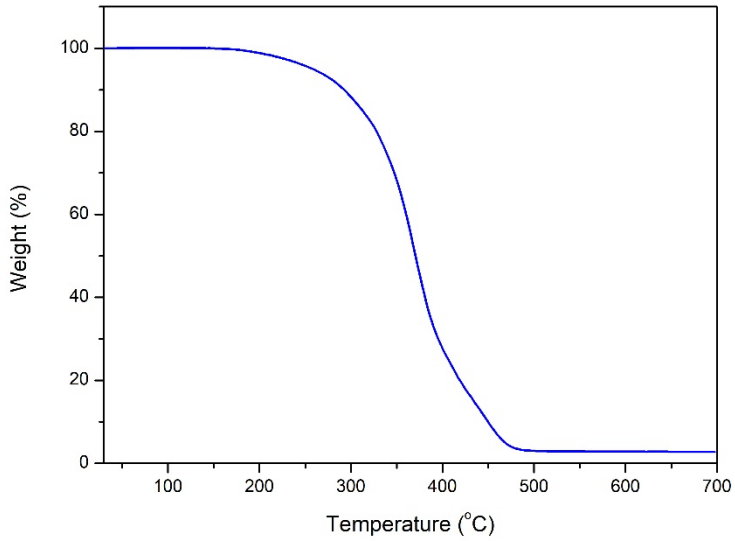


Figure S20. TGA plot of poly(ether-*alt*-ester) (100%) from the one-pot reaction of SOE1 (Table 1, entry 1).

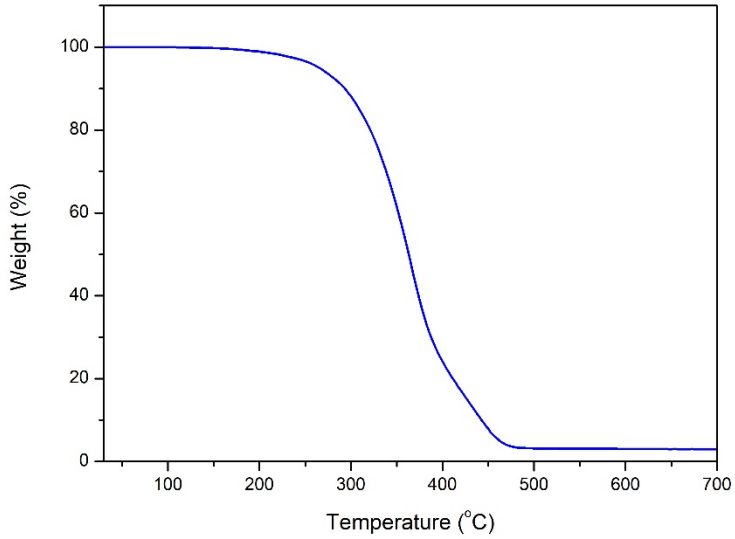
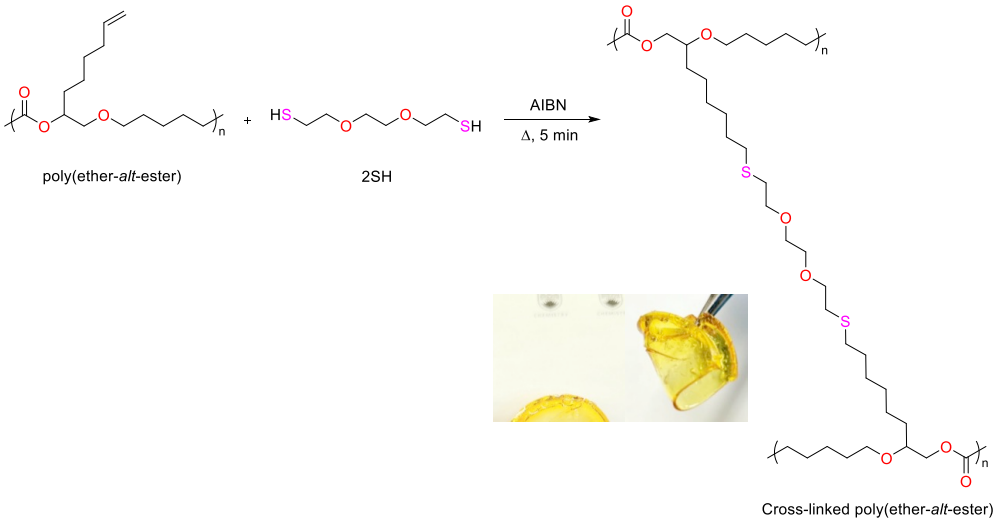


Figure S21. TGA plot of poly(ether-*alt*-ester) (100%) from the homopolymerization of 200 equiv SOE1 at 110 °C for 24 h (Table 1, entry 5).

E. Cross-linking of poly(ether-*alt*-ester)



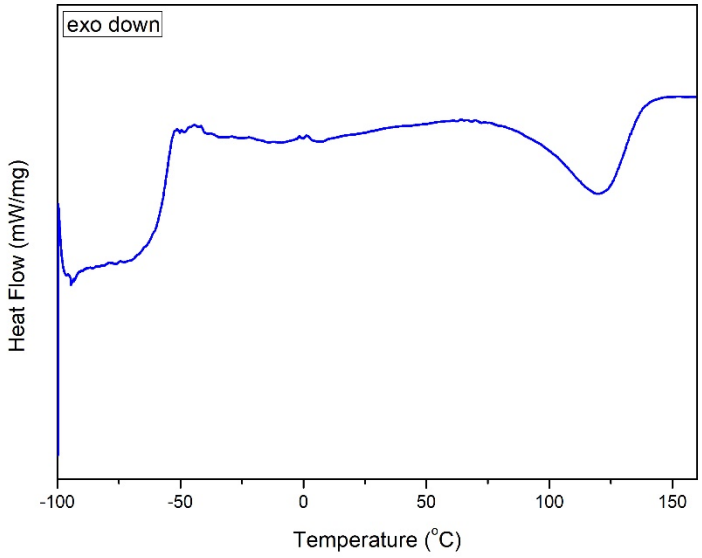


Figure S22. DSC thermogram of the cross-linked poly(ether-*alt*-ester).

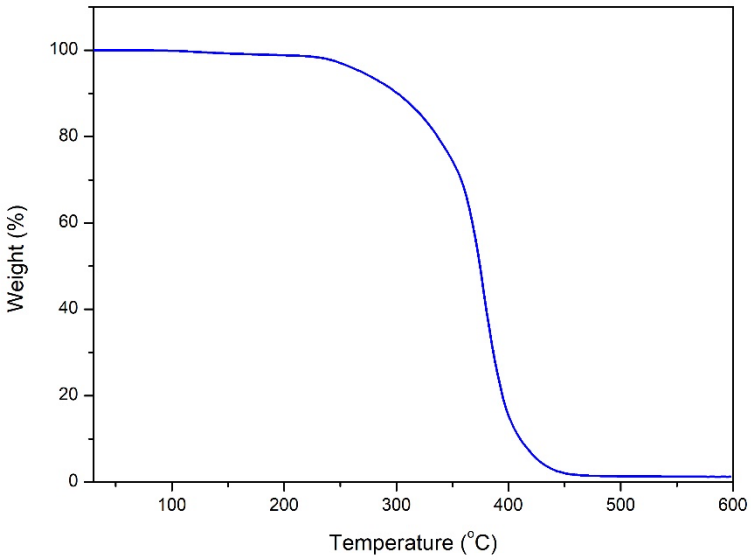


Figure S23. TGA plot of the cross-linked poly(ether-*alt*-ester).

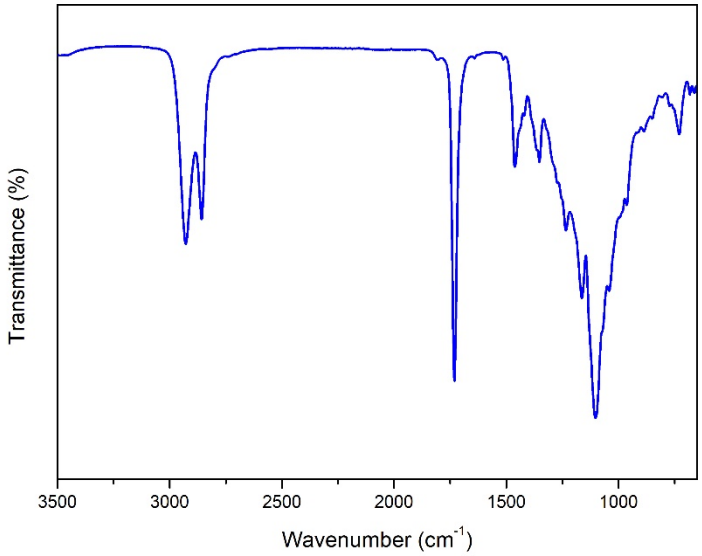


Figure S24. FTIR spectrum of the cross-linked poly(ether-*alt*-ester).

Table S1. Thermal properties of non-cross-linked and cross-linked poly(ether-*alt*-ester)s.

	Polymer	Glass transition temperature (°C)	Crystallization temperature (°C)	Decomposition temperature (°C)
1	Poly(ether-*alt*-ester) (Table 1, entry 1)	-68.8	-	176
2	Poly(ether-*alt*-ester) (Table 1, entry 5)	-68.7	-	177
3	Cross-linked Poly(ether-*alt*-ester)	-52	120	240

F. Degradation of poly(ether-*alt*-ester) and cross-linked poly(ether-*alt*-ester)

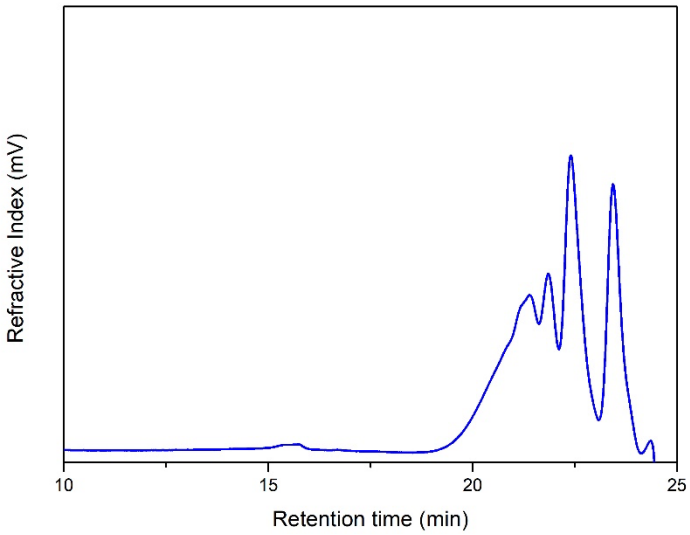


Figure S25. GPC trace of the product of poly(ether-*alt*-ester) degradation.

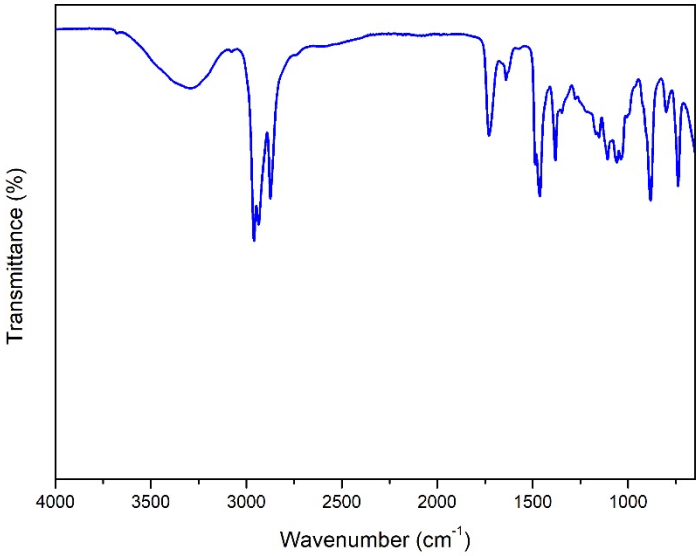


Figure S26. FTIR spectrum of the product of poly(ether-*alt*-ester) degradation.

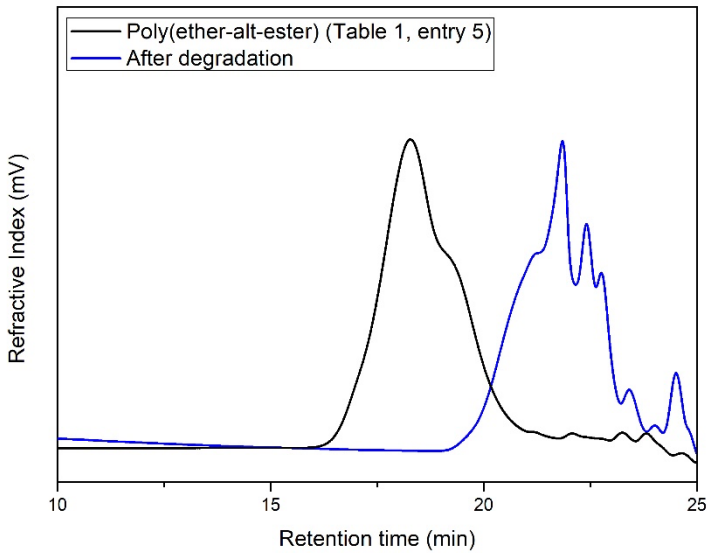


Figure S27. GPC trace of the product of cross-linked poly(ether-*alt*-ester) degradation.

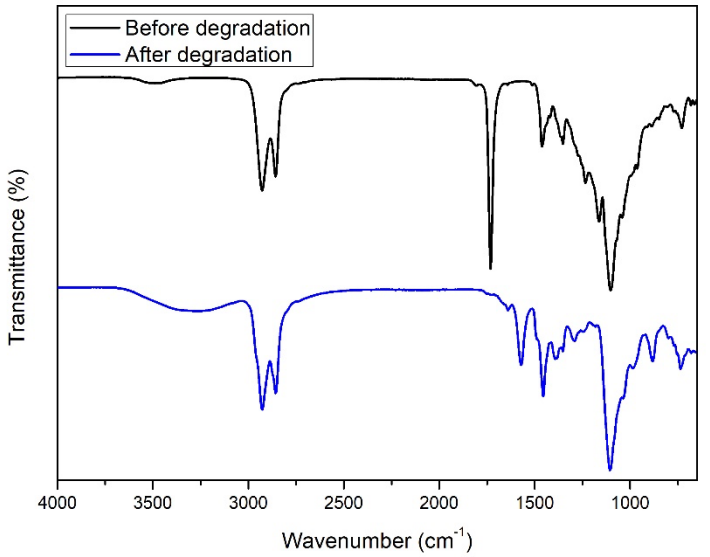


Figure S28. FTIR spectrum of the product of cross-linked poly(ether-*alt*-ester) degradation.

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