

Supporting information
for
Biomass-derived poly(ether-amides) incorporating hydroxycinnamates

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TABLE OF CONTENTS

Coumaryl tert-butyl ester dimer (3a) NMR characterization.....	Fig S1-2
Ferulyl tert-butyl ester dimer (3a) NMR characterization.....	Fig S3-4
Sinapyl tert-butyl ester dimer (3a) NMR characterization.....	Fig S5-6
Coumaryl diacid ester dimer (3a) NMR characterization.....	Fig S7-8
Ferulyl diacid ester dimer (3a) NMR characterization.....	Fig S9-10
Sinapyl diacid ester dimer (3a) NMR characterization.....	Fig S11-12
Side product formation in dimer synthesis.....	Scheme S1
Poly(ether amide) characterization	
Infrared spectroscopy.....	Fig S13-14
Gel permeation chromatography.....	Fig S15-17
Polymer insolubility.....	Table S1
Thermogravimetric Analysis.....	Fig S18-20

Differential Scanning Calorimetry.....	Fig S21-23
Decomposition studies method	

Figure S1: ^1H spectrum of **3a**

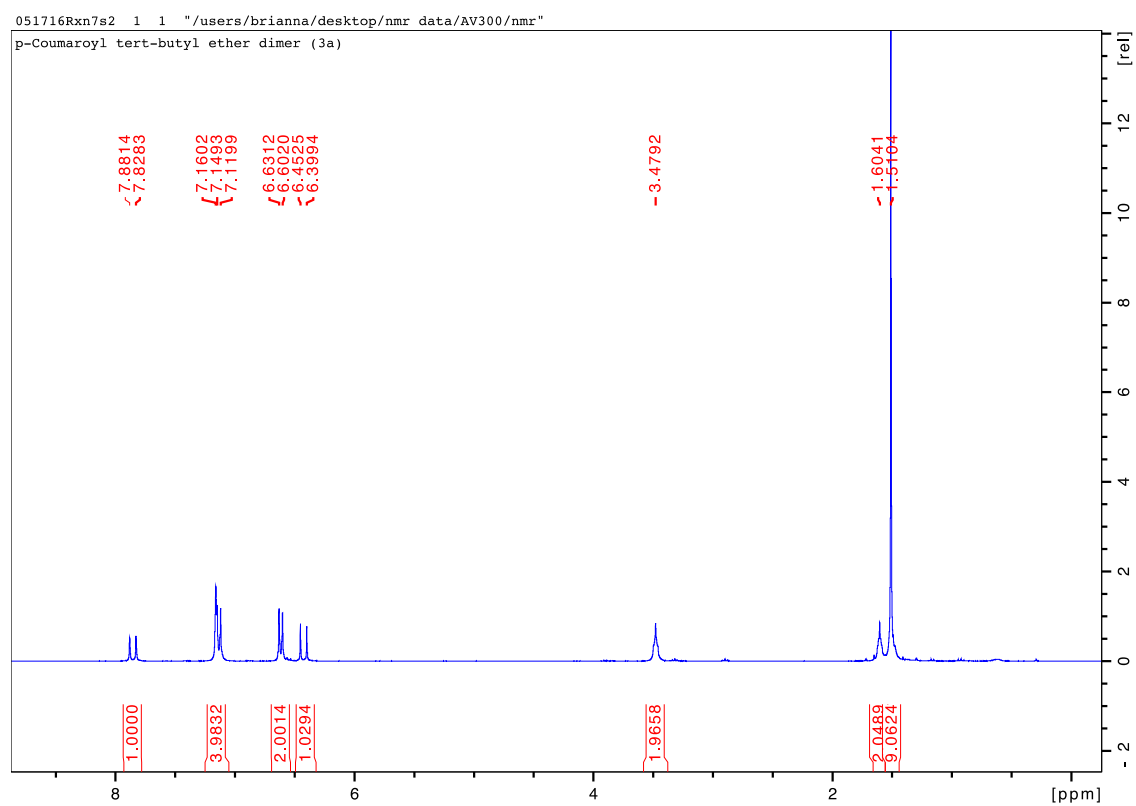


Figure S2: ^{13}C spectrum of **3a**

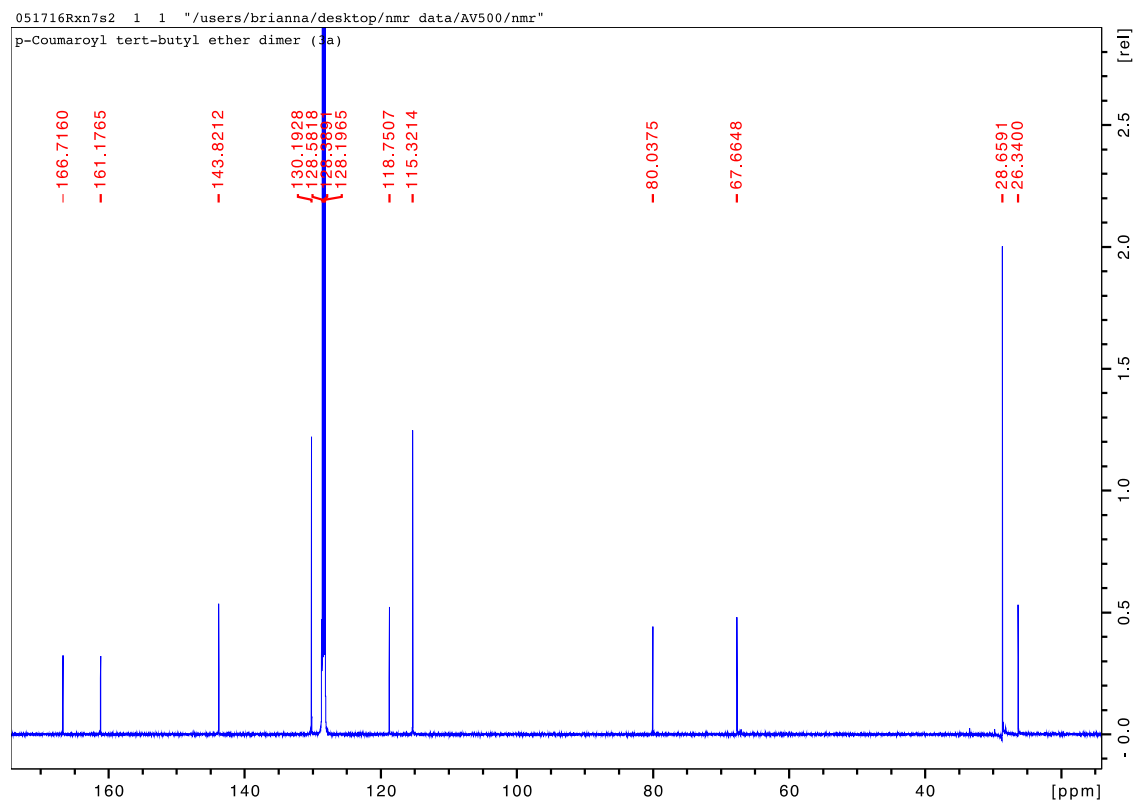


Figure S3: ^1H spectrum of **3b**

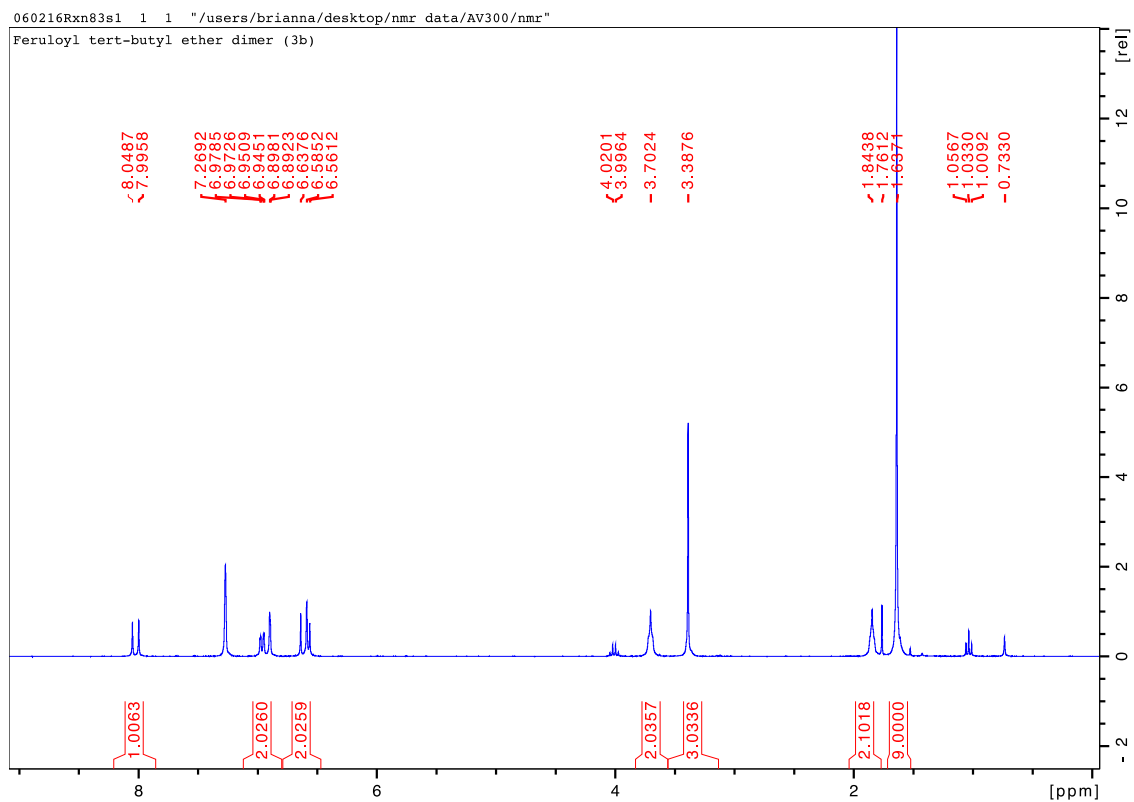


Figure S4: ^{13}C spectrum of **3b**

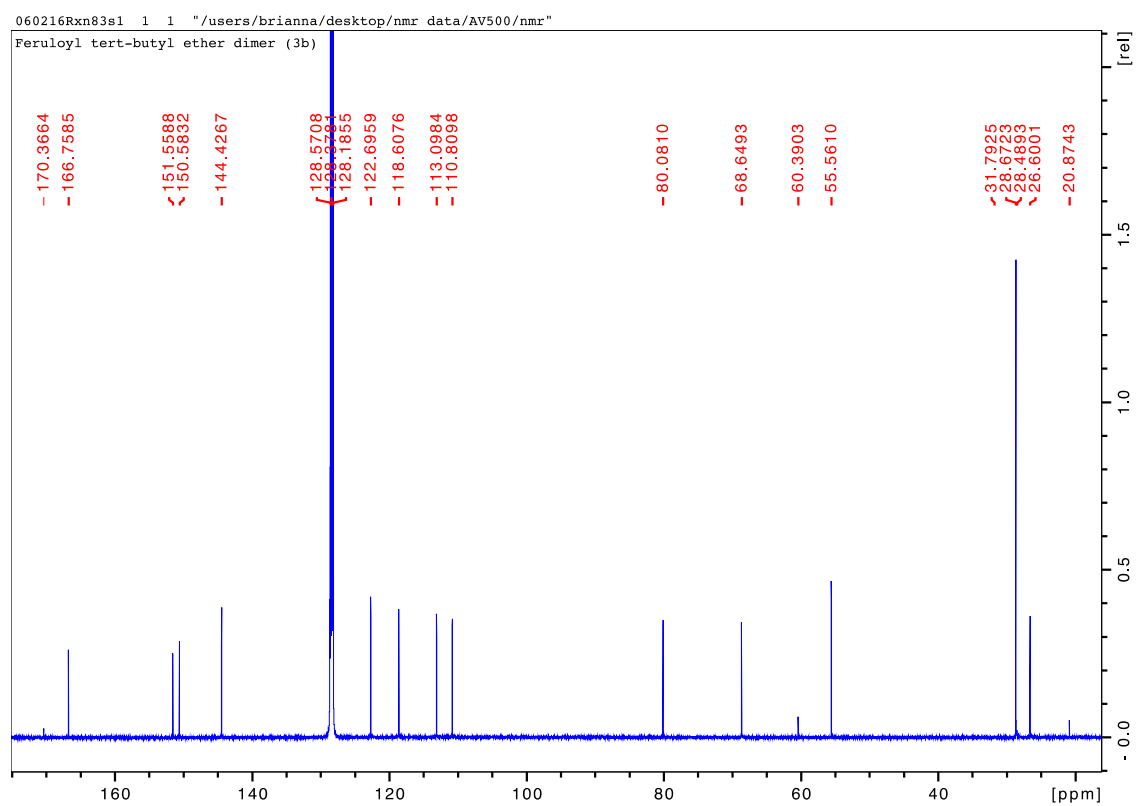


Figure S5: ^1H spectrum of **3c**

051416Rxn143s1 1 1 "/users/brianna/desktop/nmr data/AV300/nmr"
Sinapoyl tert-butyl ether dimer (3c)

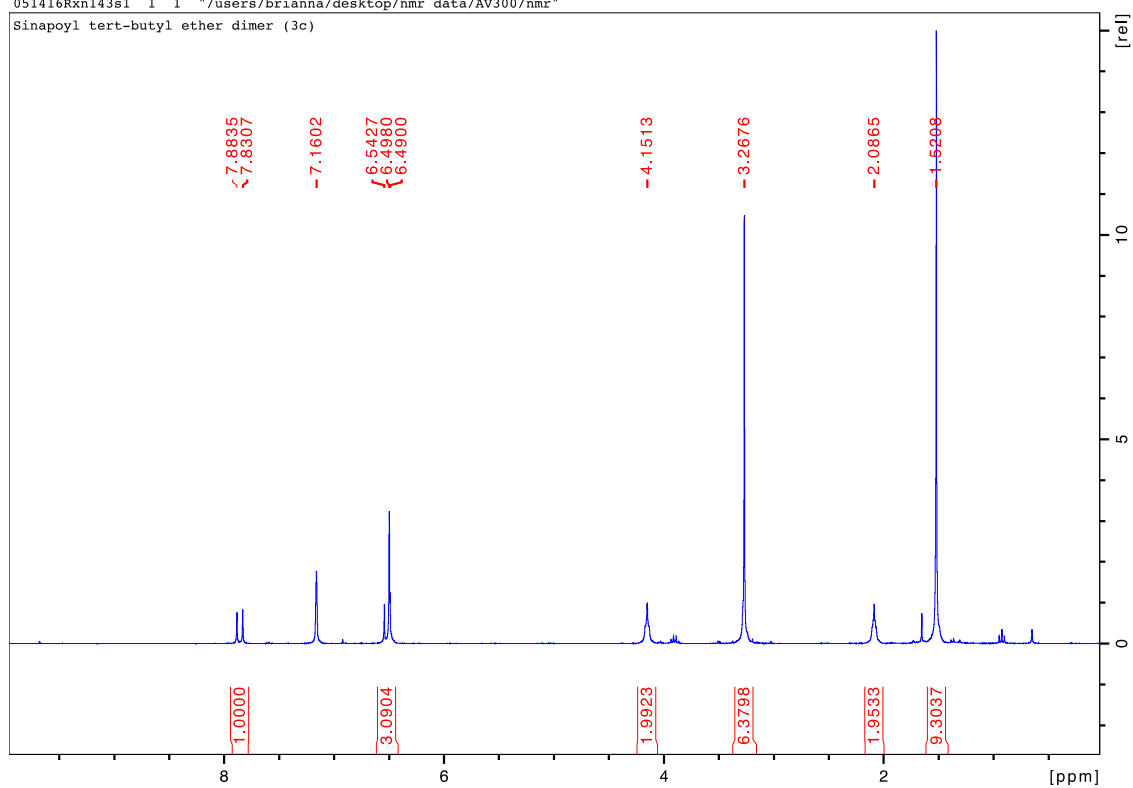


Figure S6: ^{13}C spectrum of **3c**

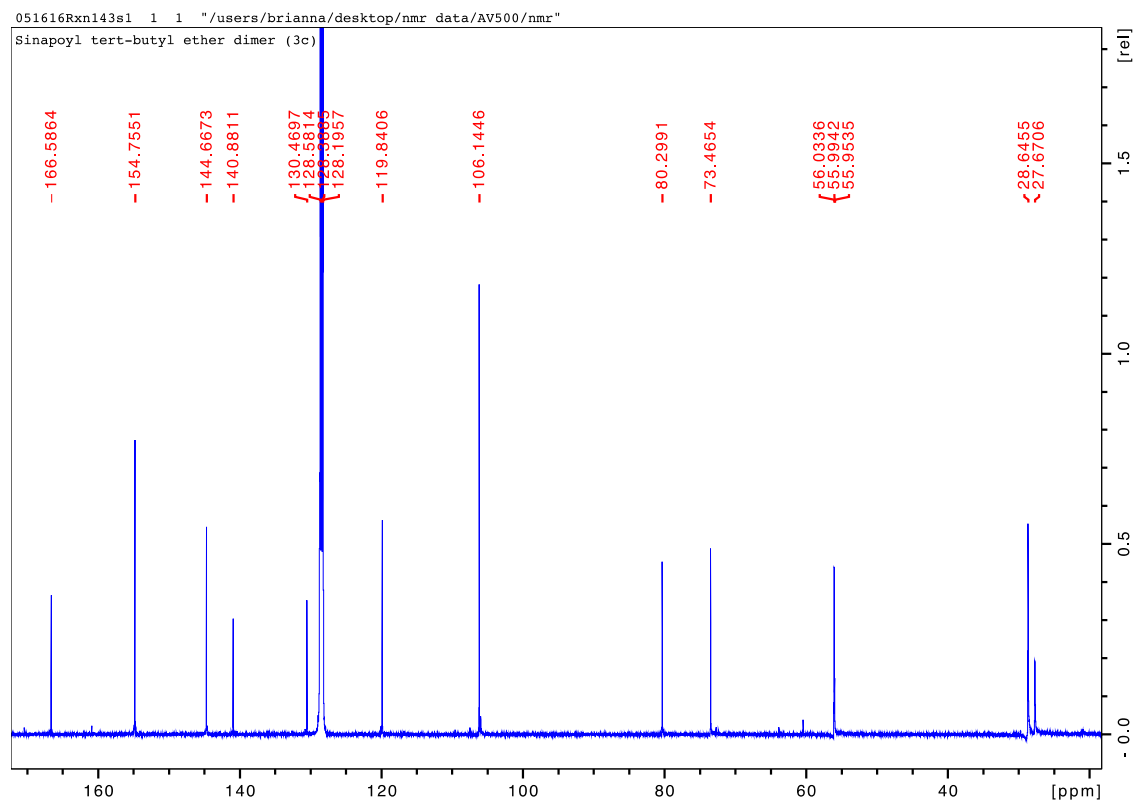


Figure S7: ^1H spectrum of **4a**

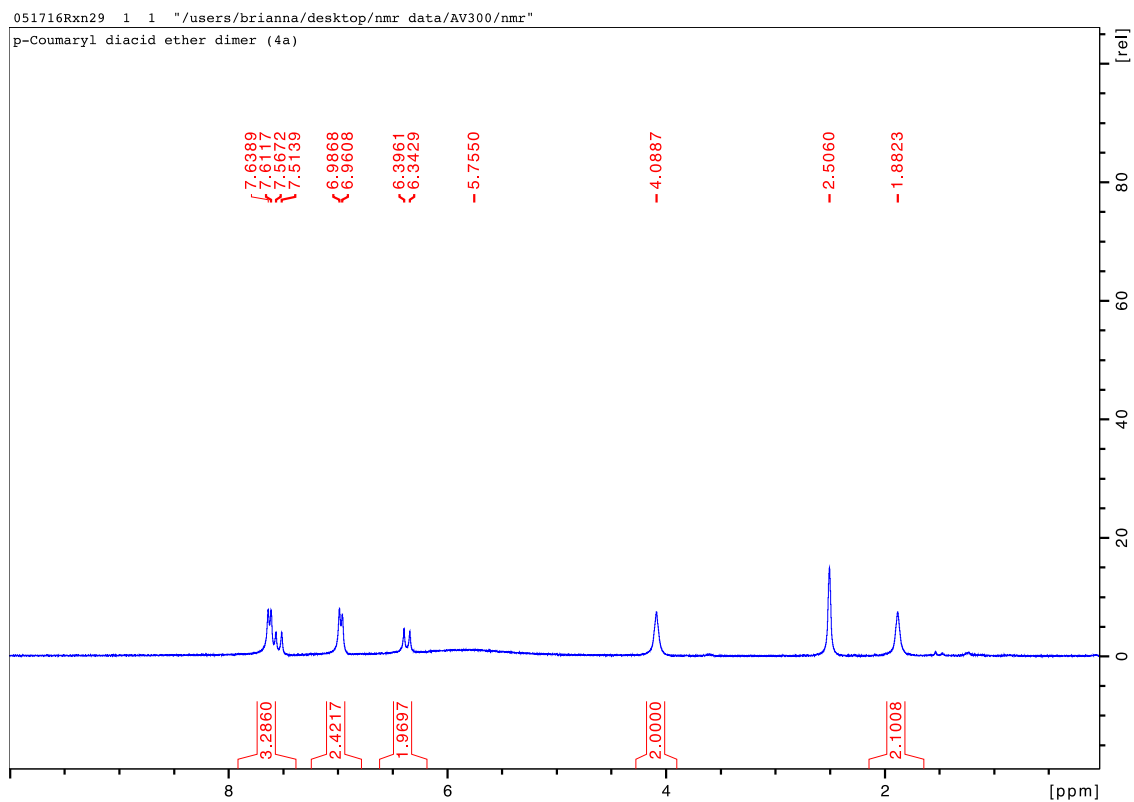


Figure S8: ^{13}C spectrum of **4a**

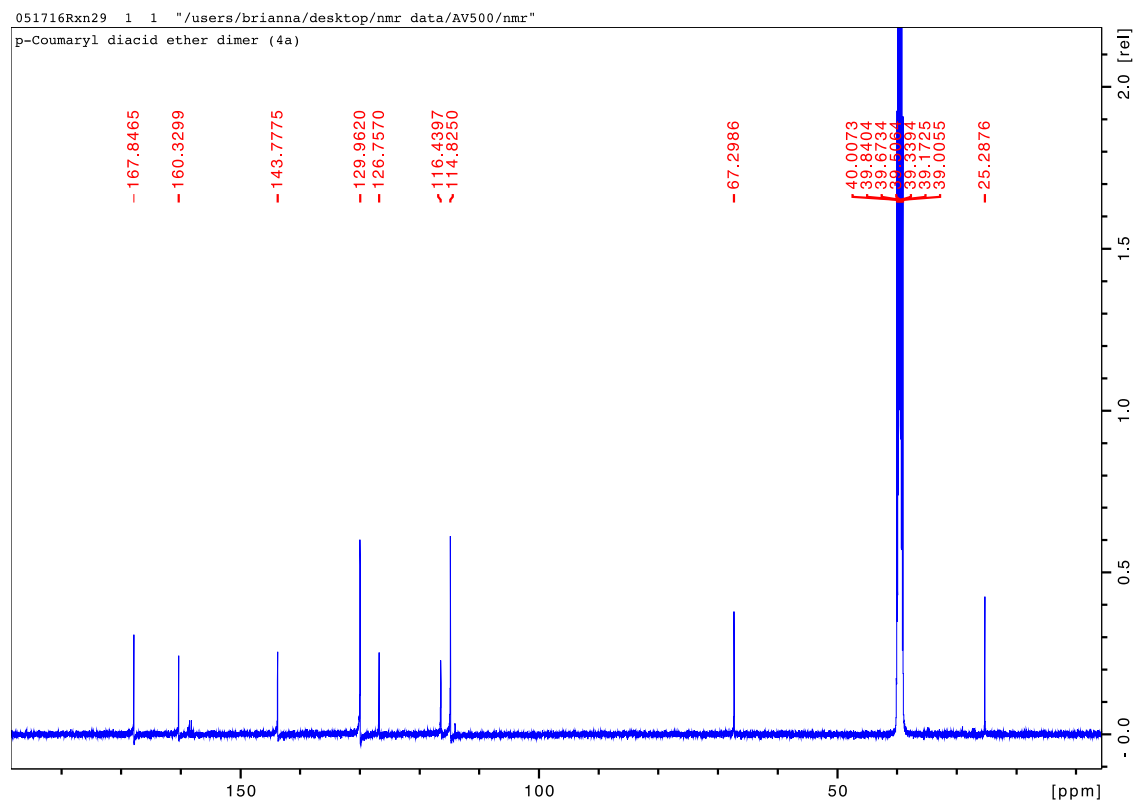


Figure S9: ^1H spectrum of **4b**

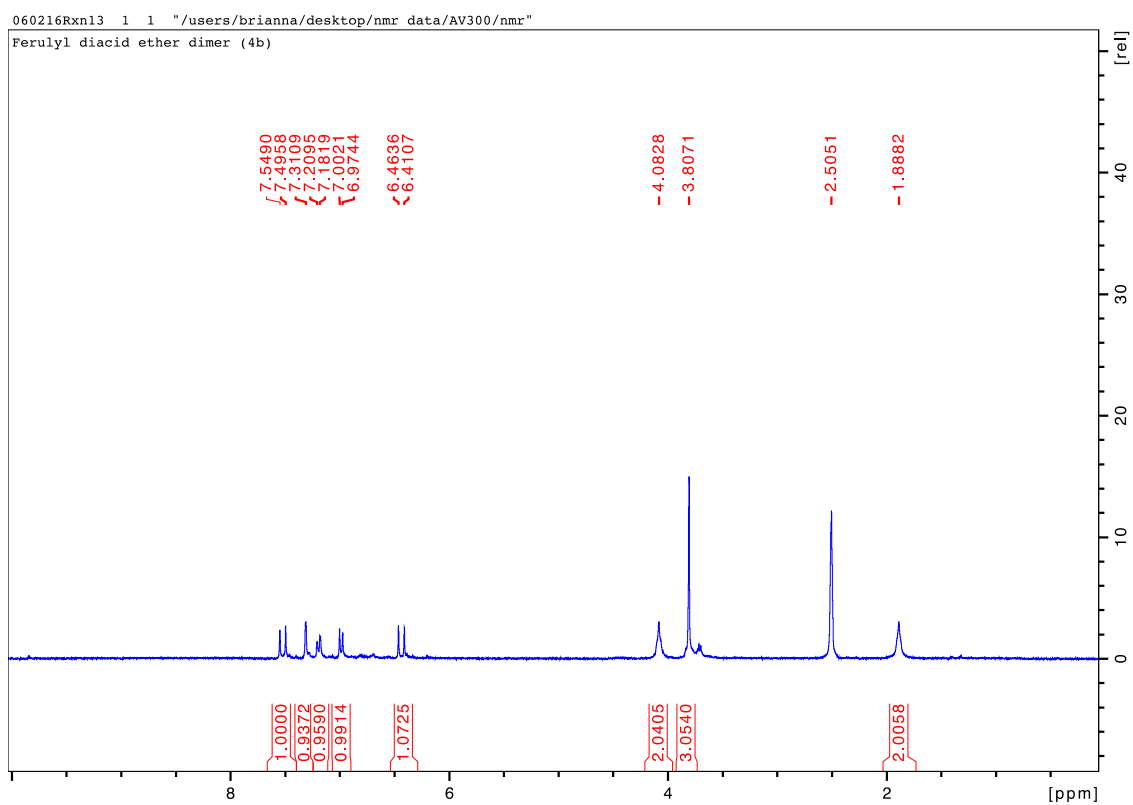


Figure S10: ^{13}C spectrum of **4b**

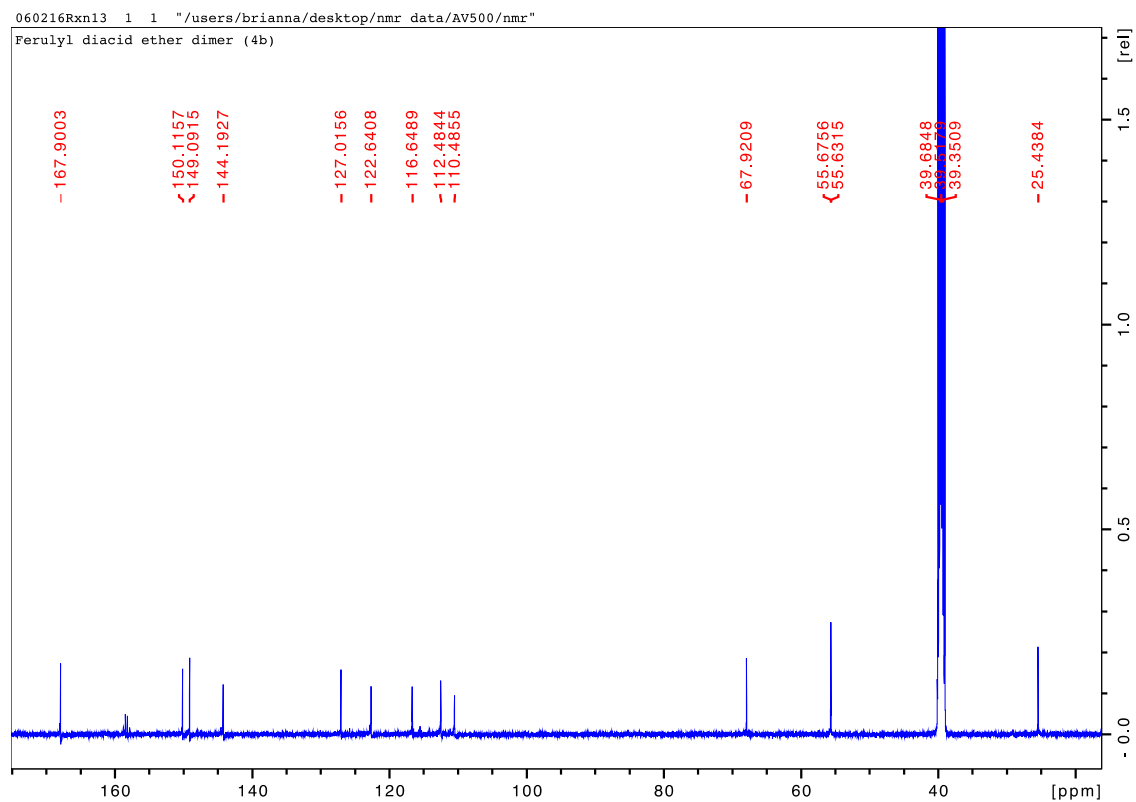


Figure S11: ^1H spectrum of **4c**

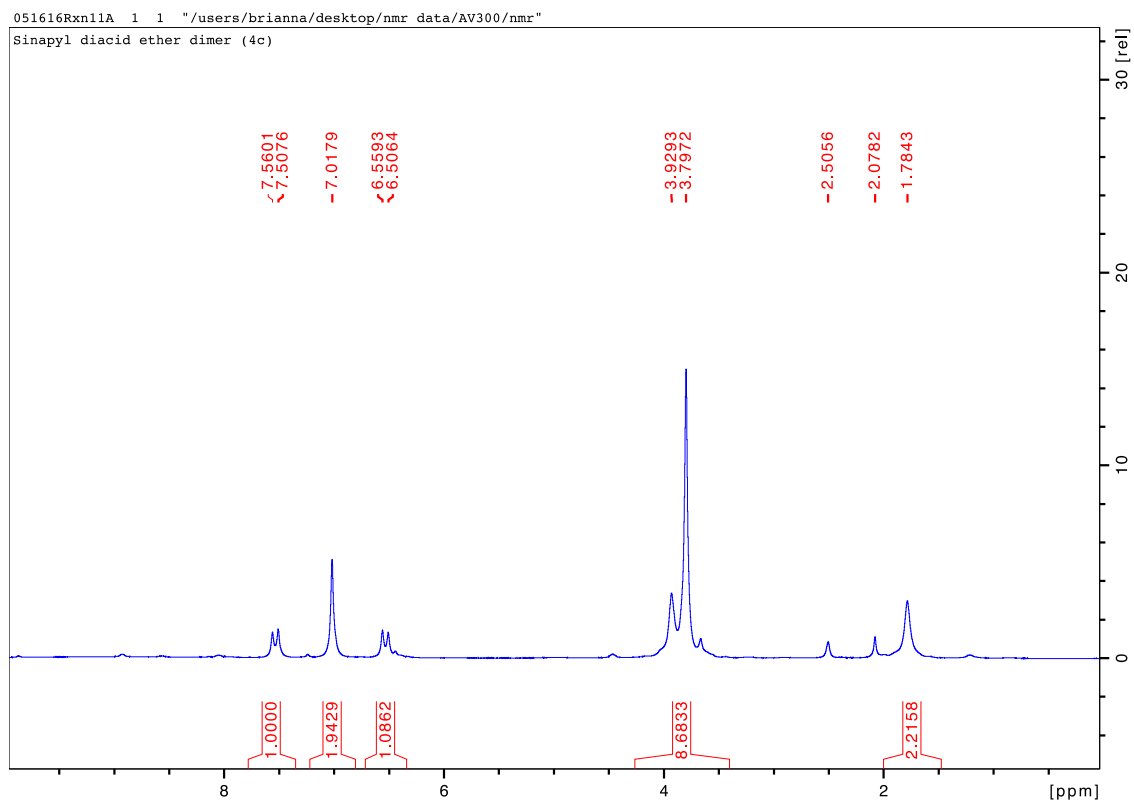
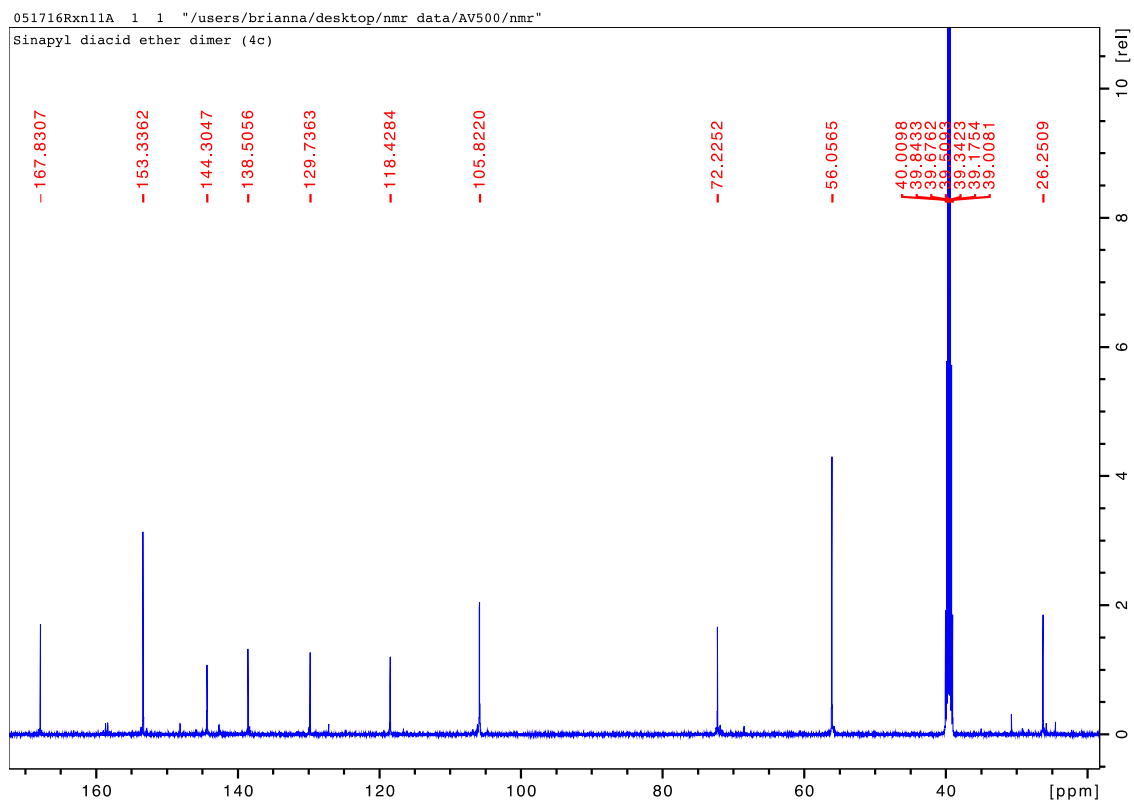
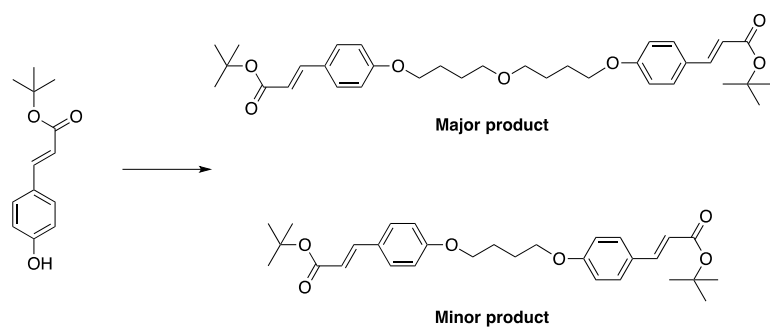


Figure S12: ^{13}C spectrum of **4c**





Scheme S1: Non-optimized reaction conditions led to the formation of side products over the desired ether dimer

Polymer Characterization

p-Coumaryl diacid + ethylenediamine (**P1**). Yield 0.2321 g, 77.2%

p-Coumaryl diacid + 1,4-diaminobutane (**P2**). Yield 0.2346 g, 71.6%

p-Coumaryl diacid + 1,6-diaminohexane (**P3**). Yield 0.2486 g, 68.7%

p-Coumaryl diacid + 1,8-diaminooctane (**P4**). Yield 0.2161 g, 55.2%

p-Coumaryl diacid + 1,10-diaminodecane (**P5**). Yield 0.2622 g, 64.5%

p-Coumaryl diacid + *m*-phenylenediamine (**P6**). Yield 0.2604 g, 70.6%

p-Coumaryl diacid + *p*-phenylenediamine (**P7**). Yield 0.2994 g, 81.9%

Ferulic diacid + ethylenediamine (**P8**). Yield 0.1977 g, 56.3%

Ferulic diacid + 1,4-diaminobutane (**P9**). Yield 0.1789 g, 51.0%

Ferulic diacid + 1,6-diaminohexane (**P10**). Yield 0.2637 g, 70.6%

Ferulic diacid + 1,8-diaminooctane (**P11**). Yield 0.2529 g, 62.8%

Ferulic diacid + 1,10-diaminodecane (**P12**). Yield 0.3104 g, 73.9%

Ferulic diacid + *m*-phenylenediamine (**P13**). Yield 0.1892 g, 51.3%

Ferulic diacid + *p*-phenylenediamine (**P14**). Yield 0.2494 g, 68.4%

Sinapyl diacid + ethylenediamine (**P15**). Yield 0.2228 g, 65.1%

Sinapyl diacid + 1,4-diaminobutane (**P16**). Yield 0.2549 g, 68.6%

Sinapyl diacid + 1,6-diaminohexane (**P17**). Yield 0.2219 g, 56.5%

Sinapyl diacid + 1,8-diaminooctane (**P18**). Yield 0.4804 g, 87.9%

Sinapyl diacid + 1,10-diaminodecane (**P19**). Yield 0.4164 g, 74.4%

Sinapyl diacid + *m*-phenylenediamine (**P20**). Yield 0.4564 g, 78.7%

Sinapyl diacid + *p*-phenylenediamine (**P21**). Yield 0.3877 g, 78.8%

Infrared (IR) Spectroscopy

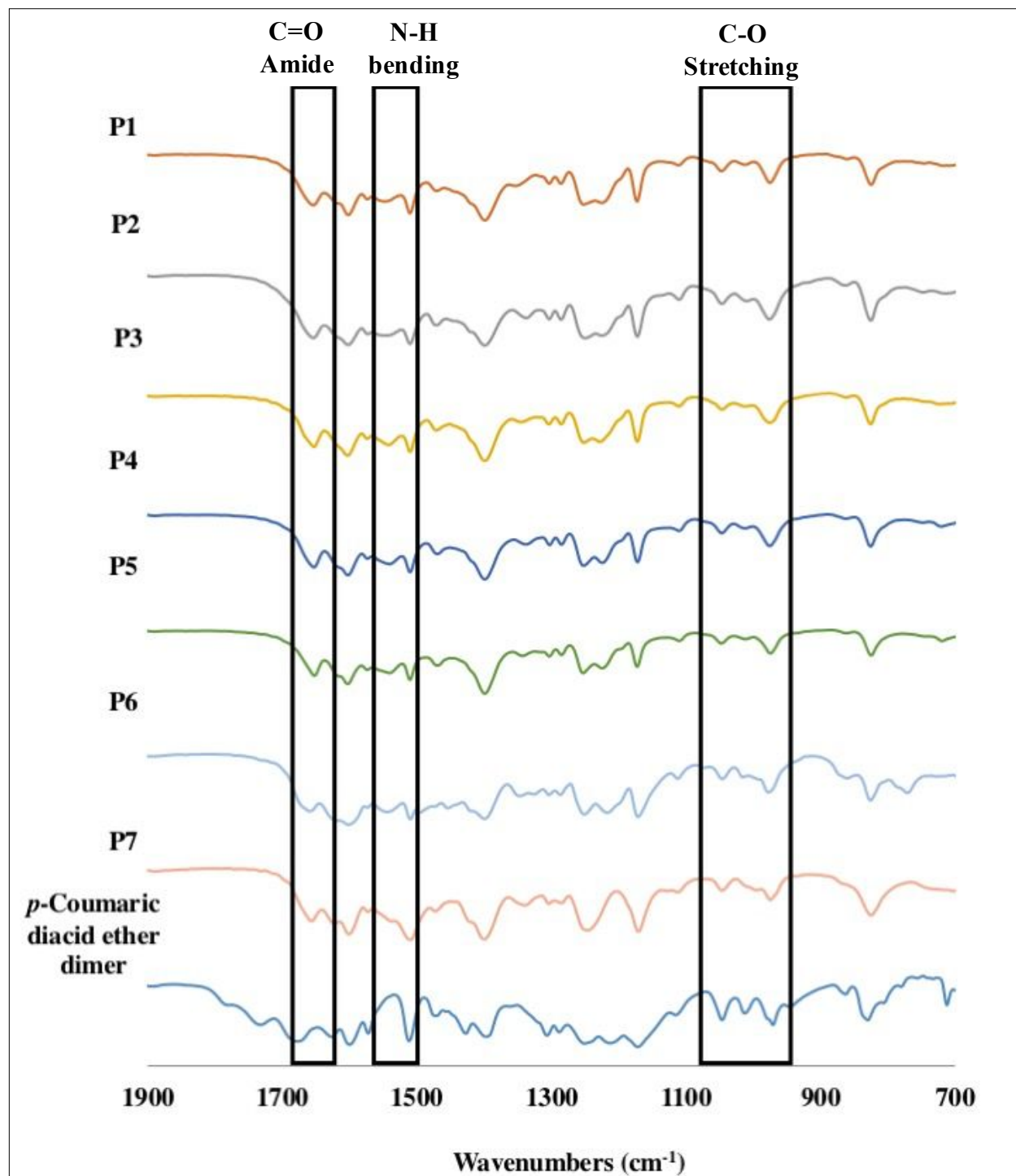


Figure S13: IR fingerprint region of *p*-Coumaric-based poly(ether-amide)s (P1-P7)

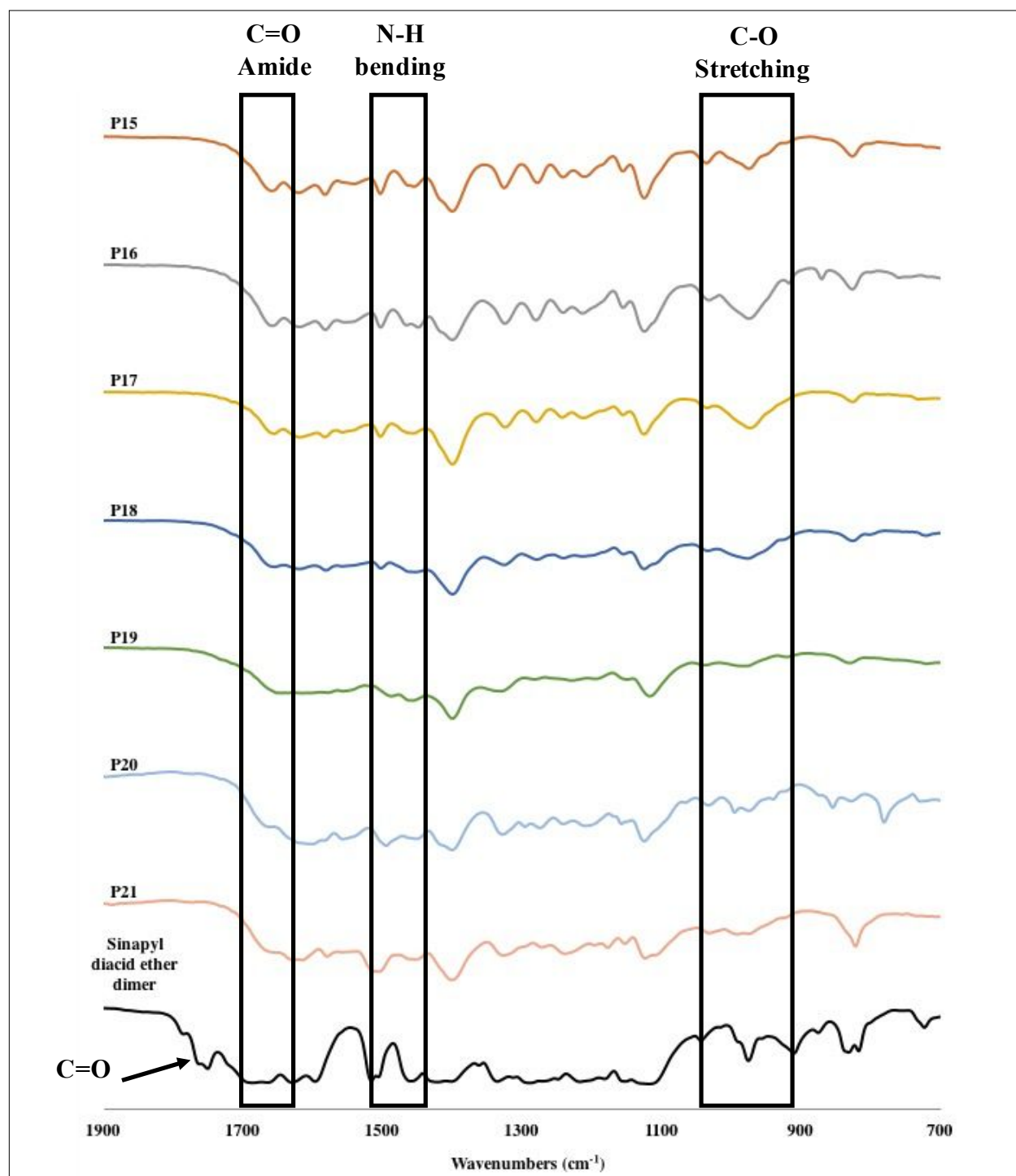


Figure S14: IR fingerprint region of Sinapyl-based poly(ether-amide)s (**P15-P21**)

Gel Permeation Chromatography (GPC)

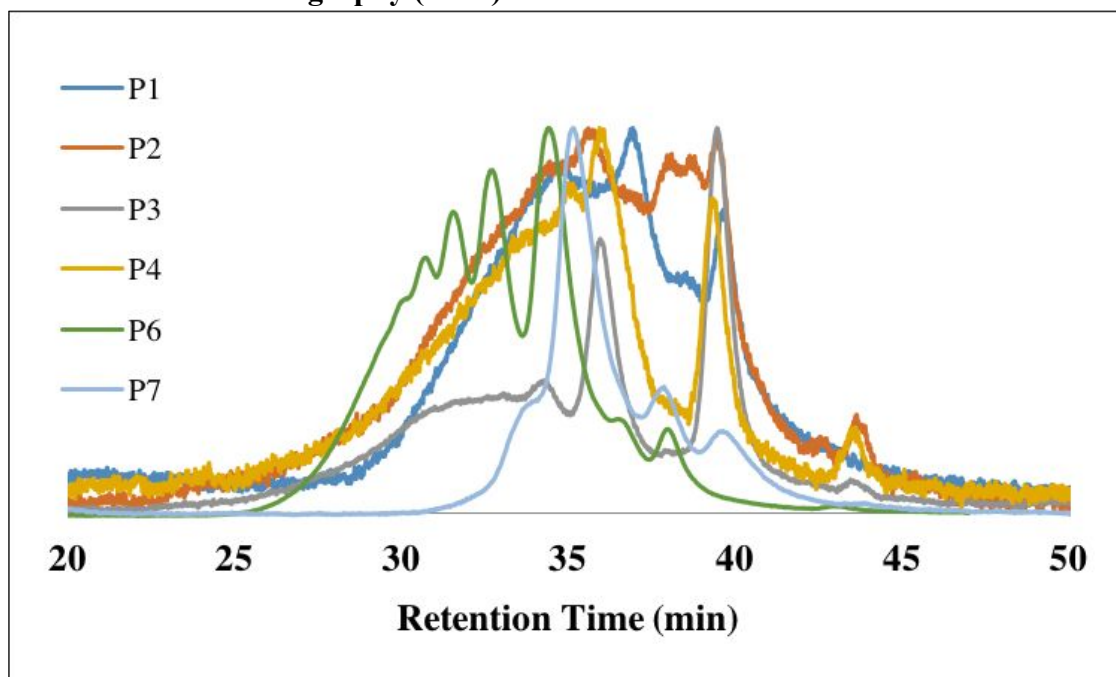


Figure S15: Stacked GPC traces of *p*-Coumaryl-based poly(ether-amide)s (**P1-P7**)

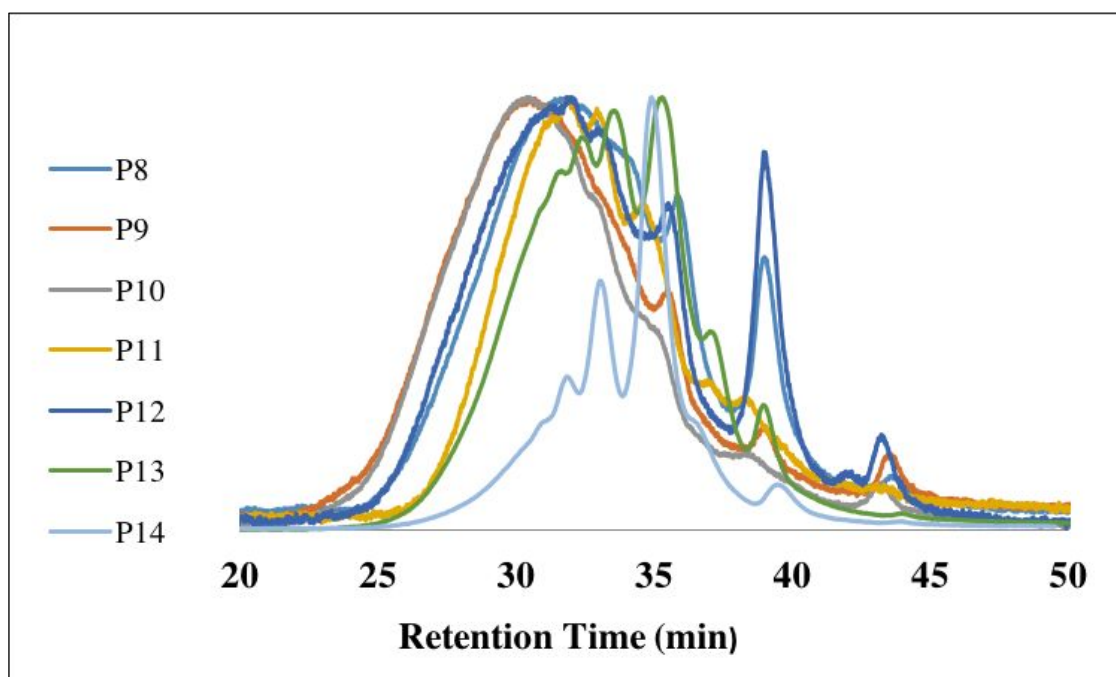


Figure S16: Stacked GPC traces of ferulyl-based poly(ether-amide)s (**P8-P14**)

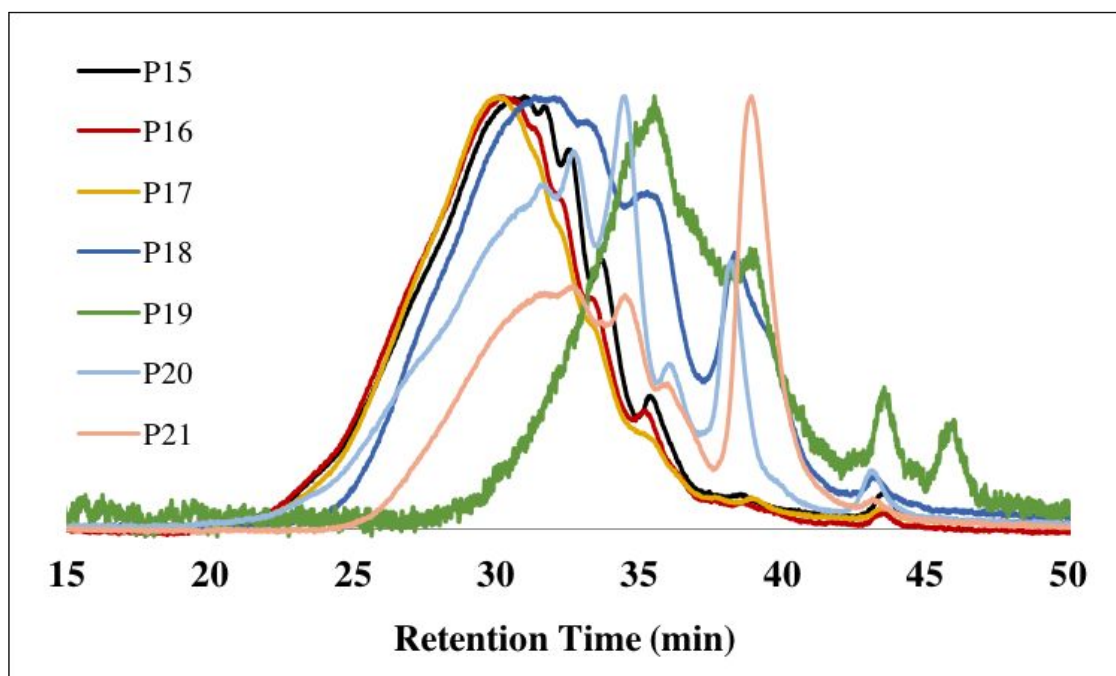


Figure S17: Stacked GPC traces of sinapyl-based poly(ether-amide)s (**P15-P21**)

Table S1 Insolubility of poly(ether-amide)s in DMF after 24h^a

	Polymer	Wt% insoluble ^a
<i>p</i> -coumaryl	P1	78.7
	P2	75.6
	P3	73.0
	P4	77.3
	P5	81.7
	P6	34.6
	P7	63.6

ferulyl	P8	19.8
	P9	31.3
	P10	50.5
	P11	54.1
	P12	38.5
	P13	22.5
	P14	36.0
sinapyl	P15	40.7
	P16	29.5
	P17	42.5
	P18	56.5
	P19	23.7
	P20	33.8
	P21	43.3

^a1.0 mL of 10 mM LiBr in DMF was added to weighed polymer samples (10 mg) and allowed to sit at room temperature for 24 h. Solvent was decanted and the residual solid was dried in a vacuum oven overnight. Solid was weighed to determine wt% insoluble.

Thermogravimetric Analysis (TGA)

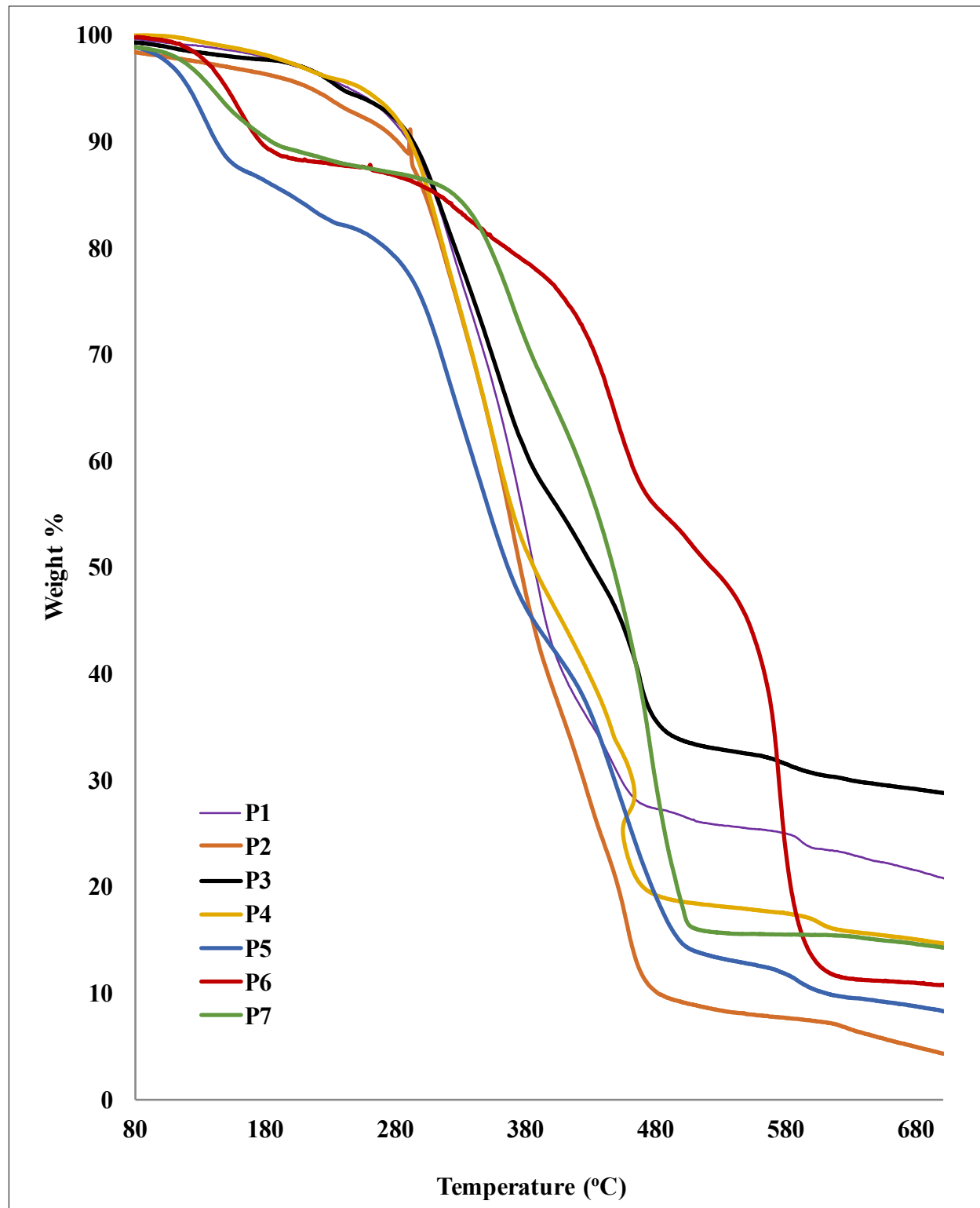


Figure S18: Stacked TGA traces of *p*-Coumaryl-based poly(ether-amide)s (**P1-P7**)

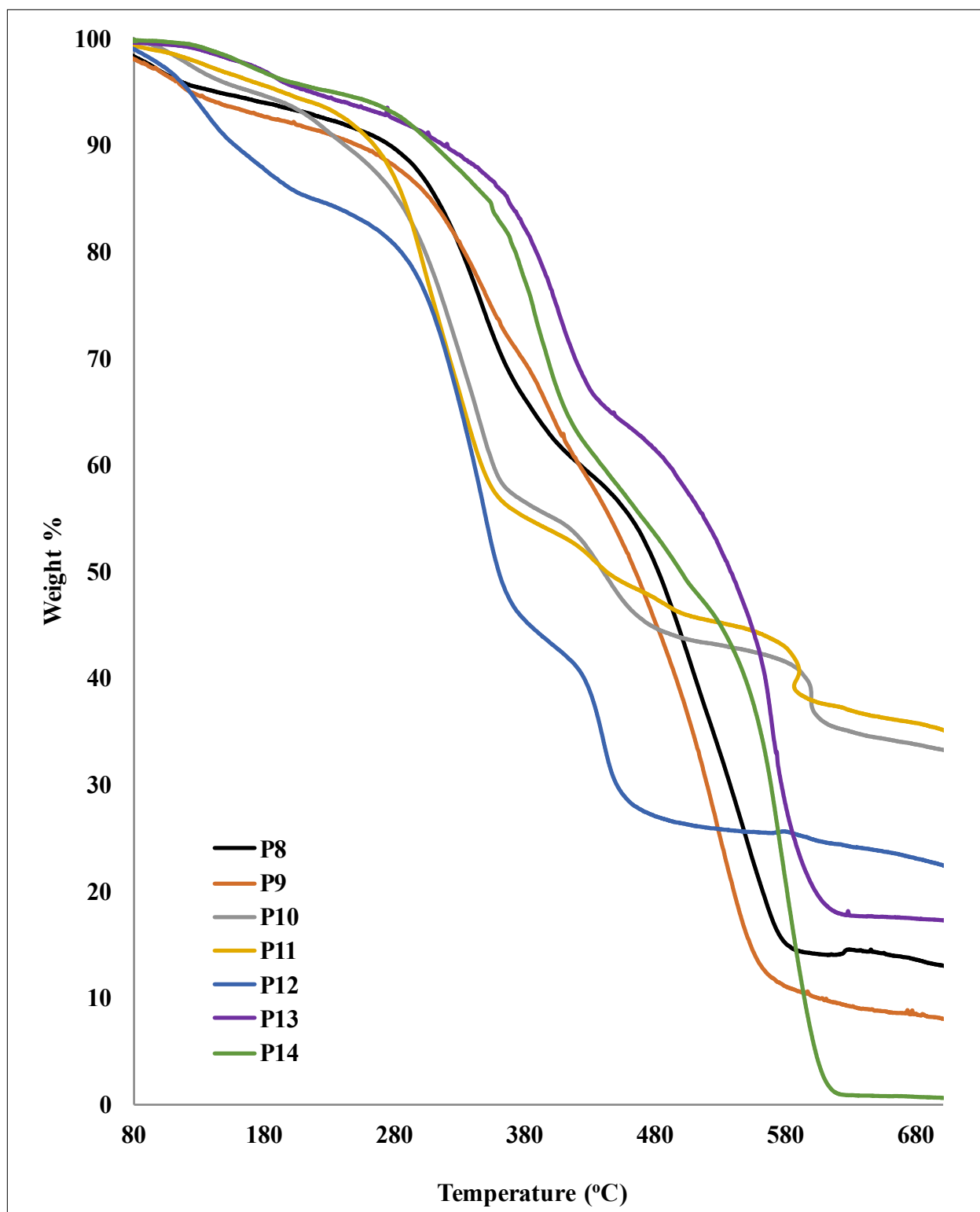


Figure S19: Stacked GPC traces of ferulyl-based poly(ether-amide)s (P8-P14)

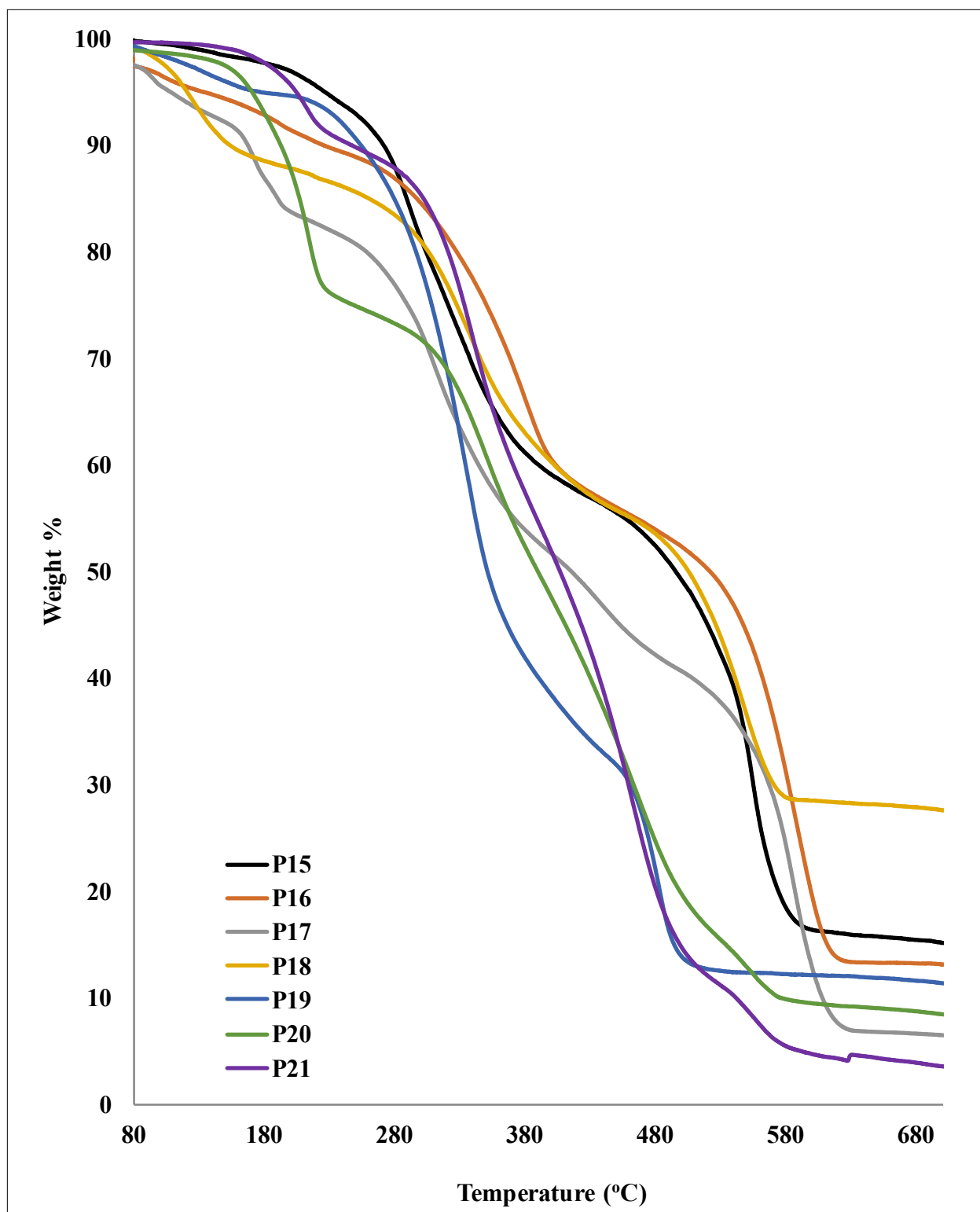


Figure S20: Stacked GPC traces of sinapyl-based poly(ether-amide)s (**P15-P21**)

Differential Scanning Calorimetry

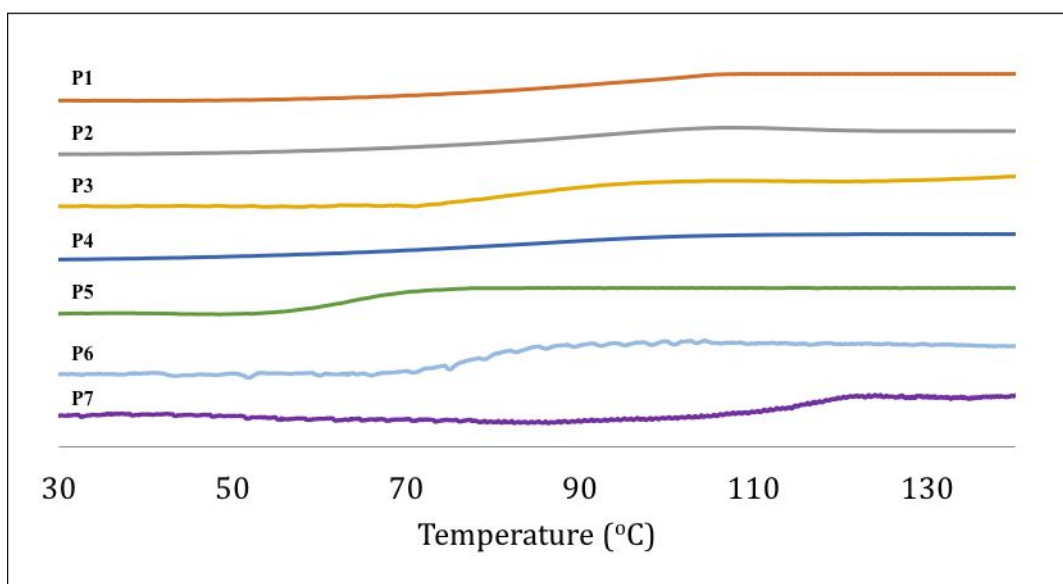


Figure S21: Stacked DSC traces of *p*-Coumaryl-based poly(ether-amide)s (**P1-P7**)

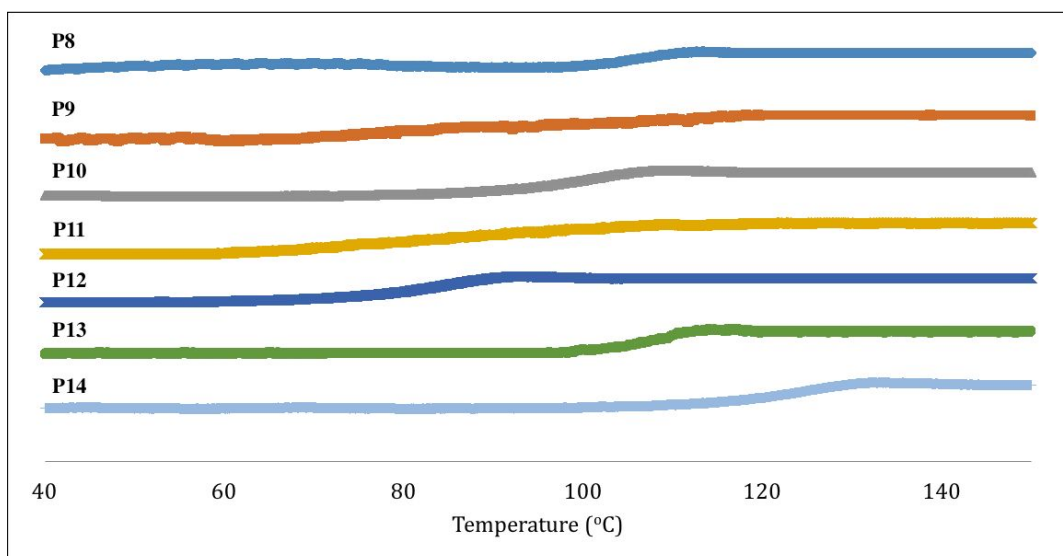


Figure S22: Stacked DSC traces of ferulyl-based poly(ether-amide)s (**P8-P14**)

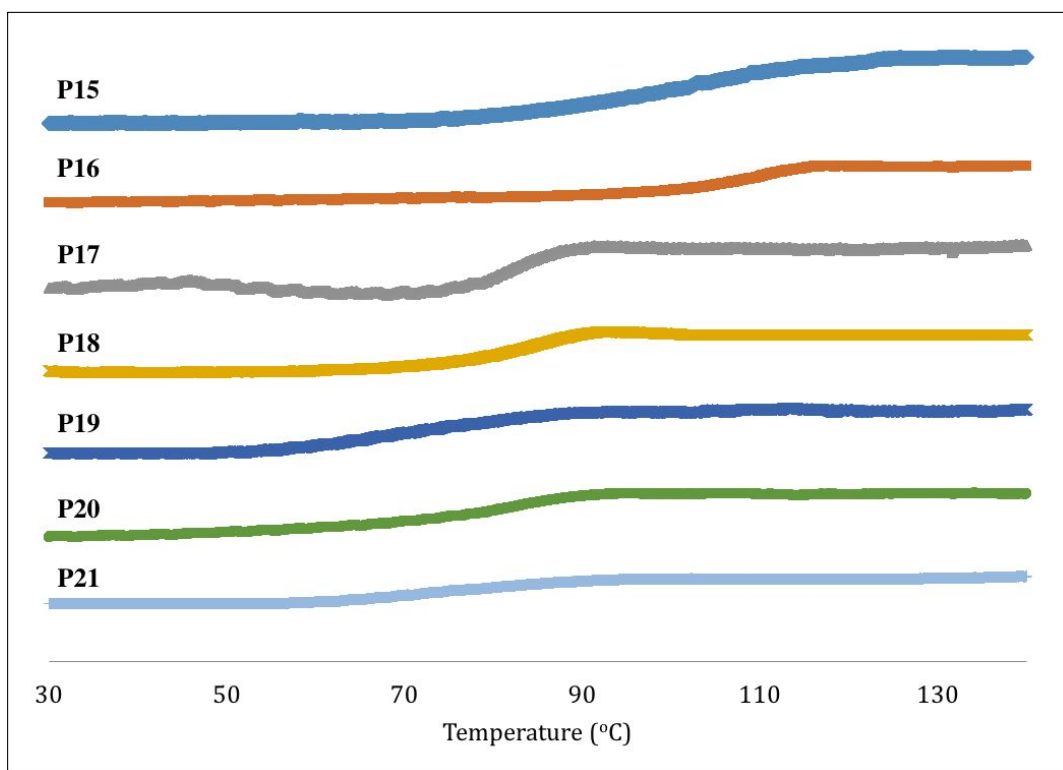


Figure S23: Stacked DSC traces of sinapyl-based poly(ether-amide)s (**P15-P21**)

Decomposition Studies

Method

Polymer samples (10-20 mg) were weighed and added to 20 mL scintillation vials (two vials were prepared for each polymer sample). An aliquot of 1 M HCl was added to each vial (one solution of each for each polymer) to reach a final concentration of 10 mg/mL. A small stir bar was added to each vial, the vials were capped, and the resulting suspensions were allowed to stir for 30 days. 0.1 mL aliquots of solution were taken on Day 7, 14, and 21 and stored in a -80 °C freezer until analysis by gel permeation chromatography (GPC). Samples were warmed to room temperature, diluted to 1.0 mL total volume with 10 mM LiBr in *N,N*-dimethylformamide (DMF), and passed through a 0.20 µm PTFE filter before injection. GPC for all polymers was conducted on a Jasco system equipped with a refractive index detector, a UV detector, a Waters Styragel guard column, and four Waters HR Styragel 5 µm columns (100-5K, 500-30K, 50-100K, 5-600 K) using 10 mM LiBr in *N,N*-dimethylformamide (DMF) at 40 °C and a flow rate of 1.0 mL min⁻¹. Calibration was performed using nine near-monodisperse polystyrene standards (M_n =1,250 to 549,000 Da) from Jordi Laboratories and chromatograms were analyzed using ChromNAV chromatography software. Due to the low sample concentration in each aliquot, raw GPC traces were smoothed using a median filter (n=15) and normalized in Microsoft Excel to minimize noise due to the absorptivity of DMF.