Synthesis and Characterization of Biobased Polyesters with Tunable T_g by ROCOP of Beta-Elemene Oxides and Phthalic Anhydride

Francesco Della Monica* and Arjan W. Kleij*

* **Francesco Della Monica** – Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute for Science & Technology (BIST), Av. Països Catalans 16, 43007 Tarragona, Spain; orcid.org/0000-0001-6530-7351; Email: fdellamonica@iciq.es

* **Arjan Willem Kleij** – Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute for Science & Technology (BIST), Av. Països Catalans 16, 43007 Tarragona, Spain. Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluis Companys 23, 08010 – Barcelona (Spain); orcid.org/0000-0002-7402-4764; Email: akleij@iciq.es

SUPPORTING INFORMATION

57 pages, 84 figures, 2 tables

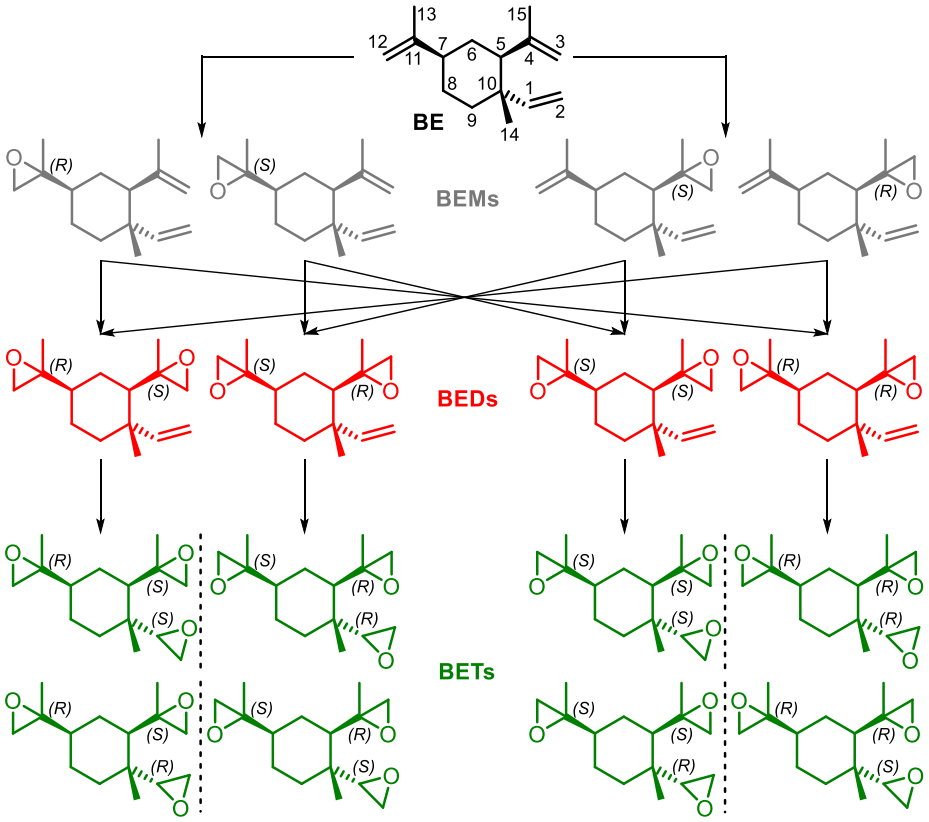
General Considerations

All water-sensitive operations were carried out under a nitrogen atmosphere using an MBraun glovebox, standard vacuum line, and Schlenk techniques. Solvents were purchased from Sigma-Aldrich (HPLC grade) and dried using an MBraun MBSPS800 purification system. NMR spectra were recorded on a Bruker AV-400 spectrometer operating at 400 MHz to collect ^{1}H and 100 MHz for ^{13}C NMR spectral data. ^{1}H NMR spectra are referenced to the residual solvent peak at δ 7.26 ppm for $CDCl_3$. ^{13}C NMR spectra are referenced to the residual solvent peak at δ 77.16 ppm for $CDCl_3$. Differential scanning calorimetry (DSC) analyses for determination of the glass transition temperatures (T_g) were measured under a N_2 atmosphere using a Mettler Toledo equipment (model DSC822e). Samples were weighed into 40 μL aluminum crucibles and subjected to two heating cycles at a heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were recorded under air atmosphere using Mettler Toledo equipment (model TGA/SDTA851). Samples were weighed into 40 µL aluminum crucibles and heated to 600 ºC at a heating rate of 10 °C/min. Gel permeation chromatography (GPC) measurements were performed using an Agilent 1200 series HPLC system, equipped with PSS SDV Analytical linear M GPC column (8 x 300 mm; 5 μm particle size) in tetrahydrofuran at 30 °C at a flow rate of 1 mL·min^{-1}. Samples were analyzed at a concentration of 1 mg·mL^{-1} after filtration through a 0.45 μm pore-size membrane. M_n, M_w, and $Đ$ data were derived from the RI signal by a calibration curve based on polystyrene standards (PS from Polymer Standards Service) for the analysis of the polymers. The crosslinked poly(**BED**-*alt*-**PA**) GPC samples were prepared by extracting the polymer (3-4 mg) with THF (2 mL), shaking the suspension for 10 minutes with an ultrasonic bath at room temperature and filtering the solution through a 0.45 μm pore-size membrane. Gas-chromatography mass (GC-MS) analyses were performed using an Agilent equipment (model 6890N, with MSD model 5973) equipped with a HP5 column (30m x 0.25 mm, 0.25 μm) via direct injection (280 ºC) in MeOH-formic acid 0.1% and ESI as ionization mode with the following temperature program: 80ºC (110') - 325ºC (5') / 20 ºC·min^{-1}, at a flow rate of 1.5 mL·min^{-1}. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) was performed by the on a BRUKER Autoflex spectrometer using the following conditions: sample (4 µL, 1 mg/mL), dithranol as a matrix (20 µL, 10 mg/mL) and CF_3COONa as an additive (1 µL, 1 mg/mL).

Reagents and Complexes

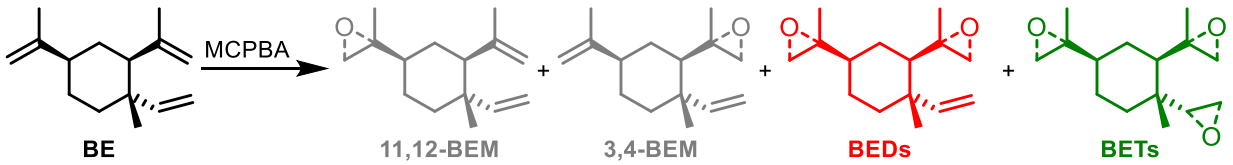
All reagents were purchased from commercial suppliers (Aldrich and Acros) and used as received. Phthalic anhydride (**PA**) is commercially available and was used after recrystallization from hot chloroform and drying under vacuum for 48 h. The additive bis(triphenylphosphine)iminium chloride (PPNCl) is commercially available and was used after recrystallization from dichloromethane and drying under vacuum for 48 h. β-elemene was kindly provided by Isobionics.[1] The complexes **1**[2] and **2**[3] were prepared following previously reported procedures. β-elemene monoxides (**BEM**) and β-elemene dioxides (**BED**) were dissolved in dry hexane or dichloromethane, stirred over CaH for 24 h, filtered through Celite and vacuum-dried prior to use in the copolymerization reactions.

Reaction Conditions Screening for β-elemene Epoxidation



Scheme S1 Possible stereoisomers for **BEM**, **BED** and **BET** obtained after β-elemene epoxidation.

Table S1 Epoxidation of **BE** with *m*CPBA.



Entry	[*m*CPBA]/[**BE**]	Conv[a] (%)	**BED**/**BEM**[a] (%)	Yield **BEM** (%)	Yield **BED** (%)	Yield **BET** (%)	11,12/3,4[a] (%)	Recovered **BE** (%)
1	0.5	47	12/88	41.5	n.d.	n.d.	63/37	95
2	0.75	66	19/81	48.2	n.d.	n.d.	64/36	99
3	1	73	22/78	53.6	n.d.	n.d.	66/34	99
4[b]	1	72	22/78	44.7	n.d.	n.d.	65/35	90
5[c]	1	72	22/78	47 (3.54 g)	n.d.	n.d.	66/34	81
5[d]	1	71	24/76[e]	49.5	17	0	67/33	81
6[f]	2.2	100	99/1	-	97	-	-	-
7[g]	3.2	100	-	-	18	25	-	-
8[h]	3.5	100	-	0	0	32.5	-	0

Reaction conditions: β-elemene = 1.00 g (4.9 mmol); [**BE**] = 0.1 M; temperature = 0 ºC; reaction time = 1 h. Difference between conversion and yield is due to formation of BE dioxide. a) Determined by ^{1}H NMR on the basis of signals of methyl 14 on cyclohexyl ring. b) β-elemene = 3.07 g (15.0 mmol). c) β-elemene = 7.0 g. d) β-elemene = 3.0 g. e) from isolated yields. f) β-elemene = 2.00 g; reaction time = 4 h. g) β-elemene = 1.00 g, reaction time = 20 h, T = from 0 to RT. h) β-elemene = 1.00 g, reaction time = 24 h, T = from 0 to r.t.

Synthesis of β-elemene monoxide (BEM)

BE (3.00 g, 14.68 mmol) was weighed into a vial and transferred to a 250 mL round-bottomed flask. After dissolving in dichloromethane (147 mL, [**BE**] = 0.1 M), the solution was cooled to 0 °C with an ice bath. *Meta*-chloroperbenzoic acid, *m*CPBA (77 % w/w, 3.29 g, 14.68 mmol) was added portion-wise during 15 minutes, and the suspension was stirred for further 45 min. The suspension was then filtered, washed with cold hexane and the filtrate dried by rotary evaporation. The resulting mixture was suspended in cold hexane and filtered again. The filtrate was dried obtaining a clear liquid. The mixture was dissolved into hexane (50 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (50 mL, 4 times). The organic phase was dried over sodium sulfate and dried giving a clear liquid (3.0 g). The mixture was analyzed by ^{1}H NMR to determine the conversion (71%). The product was purified by column chromatography (from Hex:Et_2O = 9:1 to Hex:EtOAc = 9:1) obtaining recovered **BE** (0.72 g, yield = 24%), **BEM** (1.60 g, yield = 49.5%) and **BED** (0.59 g, yield = 17%). APCI-HRMS: $[C_{15}H_{25}O]^+$ calculated = 221.1900; measured = 221.1897.

The same procedure was scaled up to 7.00 g of **BE** (34.25 mmol), yielding 3.54 g of **BEM** (yield = 47%) (entry 5, Table S1).

Spectroscopic data of 11,12-**BEM**.

^{1}H-NMR (400 MHz, $CDCl_3$, rt): δ 5.80 (*dd*, 1H, *J* = 17.8 Hz, *J* = 10.5 Hz, -C*H*=CH_2); 4.91 (*m*, 1H, -CH=C*H*$_2$); 4.87 (*m*, 1H, -CH=C*H*$_2$); 4.83 (*m*, 1H, -C=C*H*$_2$); 4.59 (*m*, 1H, -C=C*H*$_2$); 2.64-2.66 (*m*, 1H, -COC*H*$_2$); 2.55 (*d*, 1H, J = 4.9, -COC*H*$_2$); 1.95 (*m*, 1H, cyclo -C*H*); 1.70 (*m*, 3H, -C*H*$_3$); 1.66-1.35 (overlapped *m*, 6H, cyclo -CH_2-); 1.30 (*m*, 1H, cyclo -C*H*); 1.29 (*m*, 3H, -C*H*$_3$); 0.99 (*s*, 3H, -C*H*$_3$).

^{13}C-NMR (100 MHz, $CDCl_3$, rt): δ 150.13; 147.59; 147.57; 112.36; 110.16; 110.14; 59.59; 53.61; 53.48; 52.47; 52.47; 52.32; 44.68; 44.60; 40.00; 39.97; 39.53; 39.44; 29.97; 29.51; 24.95; 24.90; 23.99; 23.53; 18.61; 18.45; 16.71; 16.88.

Spectroscopic data of 3,4-**BEM**.

^{1}H-NMR (400 MHz, $CDCl_3$, rt): δ 5.97 (*dd*, *J* = 17.5 Hz, *J* = 10.8 Hz, -C*H*=CH_2) and 5.79 (*dd*, *J* = 17.5 Hz, *J* = 10.8 Hz, -C*H*=CH_2) 1H; 5.01-4.93 (*m*, 2H, -CH=C*H*$_2$); 4.73-4.70 (overlapped *m*, 2H, -C=C*H*$_2$); 2.68-2.66 (*m*, -COC*H*$_2$) and 2.59 (*dd*, -COC*H*$_2$) and 2.57 (*d*, *J* = 4.39 Hz, COC*H*$_2$) and 2.41 (*d*, *J* = 4.95 Hz, COC*H*$_2$) 2H; 1.91-1.82 (*m*, 1H, -C*H*); 1.76-1.73 (*m*, 3H, -C*H*$_3$); 1.66-1.35 (overlapped *m*, 6H, cyclo -CH_2-); 1.30 (*m*, 1H, cyclo -C*H*); 1.22 (*m*, 3H, -C*H*$_3$); 1.13-1.09 (*m*, 3H, -C*H*$_3$)

^{13}C-NMR (100 MHz, $CDCl_3$, rt): δ 150.60; 150.20; 149.47; 110.72, 109.78; 58.78, 58.15; 56.34; 53.45; 53.37; 51.52; 45.44; 45.25; 41.77; 41.25; 39.42; 31.74; 29.35; 27.08; 26.80; 22.80; 22.63; 21.27; 21.12; 19.95; 17.58; 17.32.

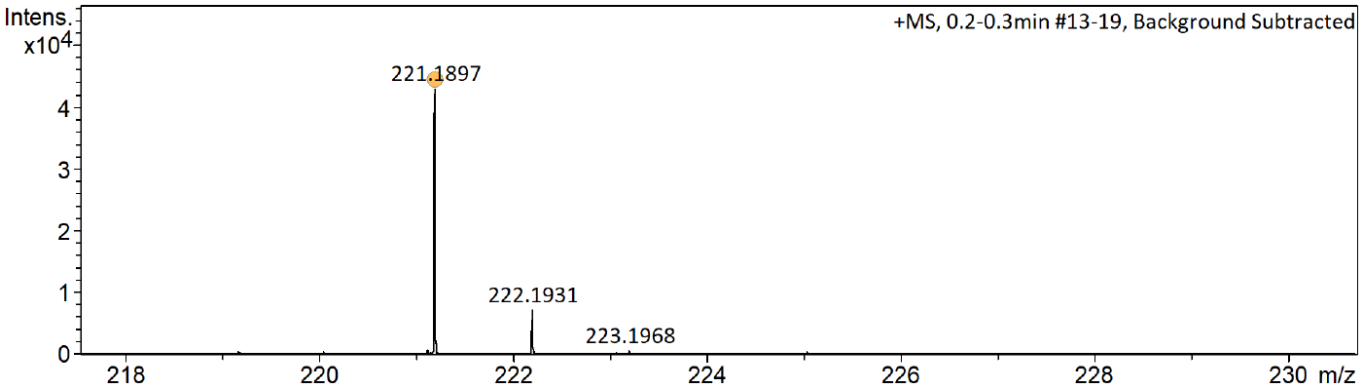


Figure S1 APCI-HRMS spectra of of a 3,4-**BEM**/11,12-**BEM** mixture.

Synthesis of β-elemene dioxide (BED)

BE (2.00 g, 9.79 mmol) was weighed into a vial and transferred to a 250 mL round-bottomed flask. After dissolving it into dichloromethane (98 mL, [**BE**] = 0.1 M), the solution was cooled to 0 °C with an ice bath. *m*CPBA (77 % w/w, 4.83 g, 14.68 mmol) was added portion-wise during 22 minutes, and the suspension was stirred at 0 °C. 4 h After the first addition, the suspension was filtered, washed with cold hexane and the filtrate dried by rotary evaporation. The resulting mixture was suspended into cold hexane and filtered again. The filtrate was dried obtaining a clear liquid. The mixture was dissolved into hexane (50 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (50 mL, 4 times). The organic phase was dried over sodium sulfate and dried giving **BED** as a clear liquid (2.25 g, yield 97%). ESI-HRMS: $[C_{15}H_{25}O_2Na]^+$ calculated = 259.1669; measured = 259.1658.

In some cases, a mixture of **BEM** and **BED** was obtained (up to 85:15), probably due to a lower quality of *m*CPBA. In these cases, the product was re-purified by column chromatography (Hex:EtOAc = 8:2).

Spectroscopic data of **BED**.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 5.96 (*dd*, *J* = 6.4, *J* = 10.8 Hz, -C*H*=CH_2), 5.91 (*dd*, *J* = 6.4 Hz, *J* = 10.8 Hz, -C*H*=CH_2); 5.76 (*dd*, *J* = 10.6, *J* = 17.4 Hz, -C*H*=CH_2); 5.75 (*dd*, *J* = 10.8, *J* = 17.5 Hz, -C*H*=CH_2); 5.01-5.00 (*m*, -CH=C*H*$_2$); 4.98-4.94 (*m*, -CH=C*H*$_2$); 4.93-4.92 (*m*, -CH=C*H*$_2$); 2.70-2.53 (overlapped *m*, -COC*H*$_2$); 2.42 (*dd*, *J* = 4.7 Hz, *J* = 6.1 Hz, -COC*H*$_2$); 1.84-1.66 (overlapped *m*, cyclo -C*H*$_2$); 1.64-1.54 (overlapped *m*, cyclo -C*H*$_2$); 1.52-1.23 (overlapped *m*, cyclo -C*H*$_2$ and -C*H*); 1.31 (*d*, *J* = 0.6, -C*H*$_3$); 1.30 (*d*, *J* = 0.6, -C*H*$_3$); 1.28 (*m*, -C*H*$_3$); 1.27 (*d*, *J* = 0.6, -C*H*$_3$); 1.21 (*d*, *J* = 0.6, -C*H*$_3$); 1.11 (*s*, -C*H*$_3$); 1.10 (*s*, -C*H*$_3$); 1.08(*s*, -C*H*$_3$).

^{13}C NMR (400 MHz, $CDCl_3$, rt): δ 150.37; 150.18; 148.19; 149.08; 110.90; 110.83; 109.99; 109.93; 59.48; 59.43; 59.36; 58.71; 58.57; 58.02; 56.37; 56.18; 53.70; 53.51; 53.48; 53.14; 53.04; 52.86; 52.82; 51.11; 50.87; 44.21; 44.16; 44.12; 43.31; 41.20; 41.16; 40.72; 40.58; 39.99; 39.41; 39.37; 26.54; 26.09; 26.04; 26.02; 24.02; 23.61; 23.48; 23.18; 22.98; 22.38; 20.02; 19.85; 19.32; 18.49; 18.46; 18.38; 17.50; 17.48; 17.32; 17.13.

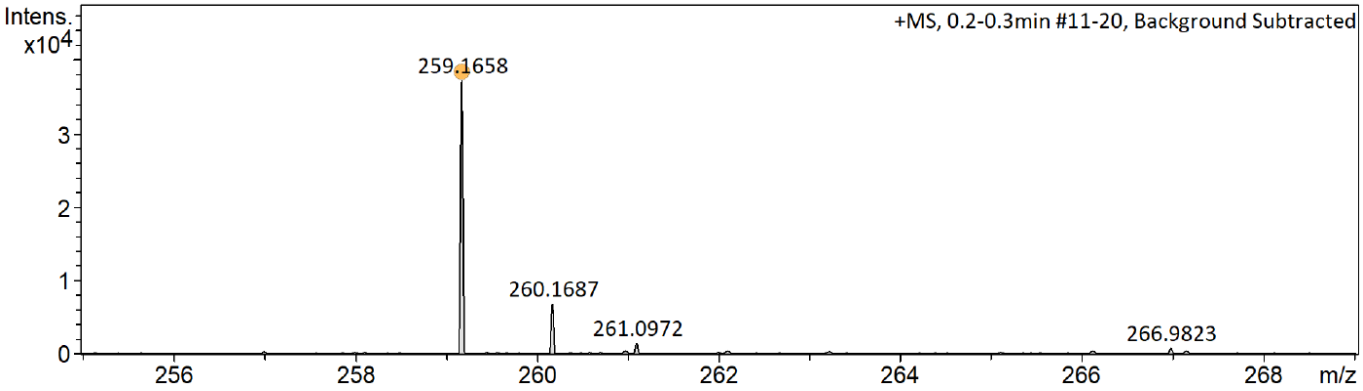


Figure S2 ESI-HRMS spectra of **BED**.

Synthesis of β-elemene trioxide (BET)

BE (1.00 g, 4.89 mmol) was weighed into a vial and transferred to a 100 mL round-bottomed flask. After dissolving it into dichloromethane (49 mL, [**BE**] = 0.1 M), the solution was cooled to 0 °C with an ice bath. *m*CPBA (77 % w/w, 3.51 g, 15.66 mmol) was added portion-wise during 30 minutes, and the suspension was stirred at 0 °C in an ice bath and left warming up to room temperature. After 24 h, the suspension was filtered, washed with cold hexane and the filtrate dried by rotary evaporation. The resulting mixture was suspended into dichloromethane and filtered again two times. The filtrate was dried obtaining a clear liquid, which partially solidified at 0 ºC. The mixture was dissolved into dichloromethane (50 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (50 mL, 4 times). The organic phase was dried over sodium sulfate and dried giving a clear liquid (1.0 g). The mixture was analyzed by ^1H NMR to determine the conversion (100%). The product was purified by column chromatography (from Hex:EtOAc = 8:2 to Hex:EtOAc = 6:4) obtaining **BET** (0.40 g, yield = 32.5%). ESI-HRMS: $[C_{15}H_{24}O_3Na]^+$ calculated = 275.1618; measured = 275.1617.

Spectroscopic data of **BET**.

^1H NMR (400 MHz, $CDCl_3$, rt): δ 2.9-2.46 (overlapped *m*, 7H, -C*H*OCH_2 and -COCH_2); 1.85 (*m*, 1H, cyclo -CH_2); 1.64 (overlapped *m*, 2H, cyclo -CH_2); 1.48-1.20 (overlapped *m*, 3H, cyclo -CH_2); 1.42 (*m*, 1H, cyclo -C*H*); 1.31 (*d*, *J* = 0.7 Hz, -CH_3); 1.29 (*s*, -CH_3); 1.28 (*s*, -CH_3); 1.27 (*s*, -CH_3); 1.27 (*m*, 1H, cyclo -C*H*); 1.26 (*m*, 1H, cyclo -C*H*); 1.23 (*d*, *J* = 0.6 Hz, -CH_3); 1.22 (*s*, -CH_3); 1.15 (*s*, -CH_3); 1.12 (*s*, -CH_3); 1.11 (*s*, -CH_3); 1.10 (*s*, -CH_3); 1.08 (*s*, -CH_3); 1.07 (*s*, -CH_3); 1.06 (*s*, -CH_3); 1.05 (*s*, -CH_3); 0.93 (*s*, -CH_3); 0.91 (*s*, -CH_3); 0.88 (*s*, -CH_3); 0.87 (*s*, -CH_3); 0.85 (*s*, -CH_3); 0.78 (*s*, -CH_3); 0.77 (*s*, -CH_3).

^{13}H NMR (400 MHz, $CDCl_3$, rt): δ 60.06, 60.05, 59.82; 59.40; 59.35; 59.31; 59.24; 58.08; 58.05; 57.40; 56.49; 56.38; 55.51; 55.31; 54.52; 54.14; 53.88; 53.77; 53.63; 53.34; 52.89; 52.67; 52.29; 52.19; 50.48; 50.14; 44.37; 44.09; 43.67; 43.11; 43.05; 42.30; 37.39; 37.34; 37.17; 36.62; 36.53; 36.41; 36.34; 36.15; 35.08; 34.90; 26.87; 26.74; 26.44; 26.35; 25.91; 22.96; 22.87; 22.77; 22.63; 22.56; 20.47; 20.28; 19.48; 19.41; 19.25; 18.60; 18.52; 18.25; 13.15; 13.10.

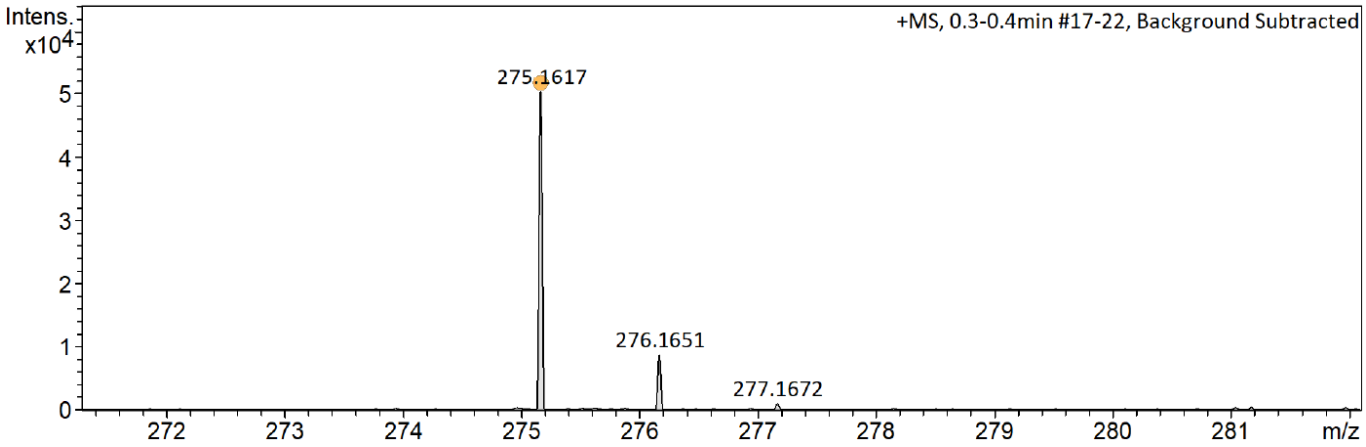


Figure S3 ESI-HRMS spectra of **BET**.

Reaction Conditions Screening for the ROCOP of BEM/PA

Table S2 ROCOP of **BEM** with **PA**

Entry	Cat. (mol%)	[**PA**]/[Cat]	Solvent	T (°C)	Time (h)	Conv.[a] %	Polyester[b] (%)	M_n[c] (kDa)	$Đ$[c]
1	**1** (1)	100	THF	60	36.5	26	n.d.	n.d.	n.d.
2	**2** (1)	100	THF	60	36.5	13	n.d.	n.d.	n.d.
3	**1** (1)	100	Tol	100	24	71(71)	>99	4.72(5.11)	1.18(1.21)
4	**2** (1)	100	Tol	100	24	46(44)	>99	2.22(2.52)	1.16(1.15)
5[d]	**1** (1)	100	neat	60	36.5	81	>99	4.85	1.14
6[d]	**2** (1)	100	neat	60	36.5	17	n.d.	n.d.	n.d.
7[d]	**1** (1)	100	neat	80	24	92	>99	5.41	1.20
8[d]	**2** (1)	100	neat	80	24	24	>99	n.d.	n.d.
9	**1** (0.5)	200	Tol	100	40.5	55	>99	7.05	1.21
10	**1** (0.33)	300	Tol	100	40.5	52	>99	6.52	1.22
11	**2** (0.5)	200	Tol	100	40.5	44	>99	3.93	1.16
12	**2** (0.33)	300	Tol	100	40.5	39	>99	4.53	1.14
13[d]	**1** (0.5)	200	neat	100	24	99	>99	6.01	1.28
14[d]	**1** (0.33)	300	neat	100	2	21	n.d.	n.d.	n.d.
15[d]	**1** (0.33)	300	neat	100	6	50	n.d.	n.d.	n.d.

Reaction conditions: Phthalic anhydride = 100 mg ($6.75 \cdot 10^{-4}$ mol); β-elemene monoxides = 149 mg ($6.75 \cdot 10^{-4}$ mol); solvent = 200 µL; PPNCl/Catalyst = 1/1. a) Determined by ^{1}H NMR on the basis of aromatic proton signals of phthalic anhydride and polyester. b) Determined by ^{1}H NMR of isolated product. c) Determined by GPC in THF calibrated with polystyrene standards. d) β-elemene monoxides = 298 mg ($1.35 \cdot 10^{-3}$ mol).

General Procedure for the ROCOP of BEM/PA in Toluene (entry 1, Table 1)

In a glove-box, PPNCl (3.9 mg, 6.75 *μ*mol), complex **1** (3.7 mg, 6.75 *μ*mol), **PA** (100 mg, 0.68 mmol), **BEM** (149 mg, 0.68 mmol), and toluene (200 *μ*L) were added in this order into a 4 mL glass vial equipped with a magnetic stirring bar. The vial was closed with a Teflon lined cap and sealed with electric insulator tape. Out of the glove-box, the vial was placed in an aluminum heating mantel preheated to 100 °C, and the mixture kept stirring for 17 h. To stop the reaction, the vial was cooled down to room temperature in cold water, opened to air and the mixture dissolved into a minimum amount of dichloromethane. An aliquot was collected to determine the conversion by ^{1}H NMR analysis. The reaction mixture was poured into acidified methanol under stirring and the polymer product was collected by filtration. The polymer was purified by dissolution into dichloromethane and precipitated from methanol. Conversion = 75%. Yield = 67%. M_n = 6.96, $Đ$ = 1.19.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.68 (*bs*, 1H, Ar-C*H*); 7.60 (*bs*, 1H, Ar-C*H*); 7.47-739 (overlapped *m*, 2H, Ar-C*H*); 5.77 (overlapped *m*, 1H, -C*H*=CH_2); 4.89 (*s*, 1H, -CH=C*H*$_2$); 4.88-4.62 (overlapped *m*, 2H, polyester -[O-C*H*$_2$-CR_2]-); 4.86 (*s*, 1H, -CH=C*H*$_2$); 4.80 (*s*, 1H, -C=C*H*$_2$); 4.56 (*s*, 1H, -C=C*H*$_2$); 2.33 (broad *s*, 1H, cyclo-C*H*), 1.99 (*d*, 1H, cyclo-C*H*) 1.68 (*s*, 3H, -C*H*$_3$); 1.66 (*s*, 3H, -C*H*$_3$); 1.65-1.42 (overlapped, 6H, cyclo -C*H*$_2$) 0.97 (*s*, 3H, -C*H*$_3$)

^{13}C NMR (400 MHz, $CDCl_3$, rt): δ 167.02; 166.83; 166.60; 166.40; 150.16; 149.91; 147.64; 147.46; 134.12; 134.00; 133.76; 133.69; 132.01; 131.33; 131.14; 131.06; 130.68; 129.54; 129.25; 128.97; 112.41; 112.35; 110.25; 110.09; 87.00; 86.65; 86.61; 86.52; 86.40; 86.27; 73.65; 73.59; 73.50; 71.23; 67.02; 66.82; 52.75; 52.44; 52.38; 50.99; 45.80; 43.60; 39.82; 39.68; 39.62; 31.04; 28.60; 28.34; 27.91; 27.57; 25.12; 24.95; 24.87; 22.82; 22.45; 22.13; 21.82; 21.62; 21.53; 21.32; 21.18; 19.03; 18.79; 18.72; 16.72; 16.67.

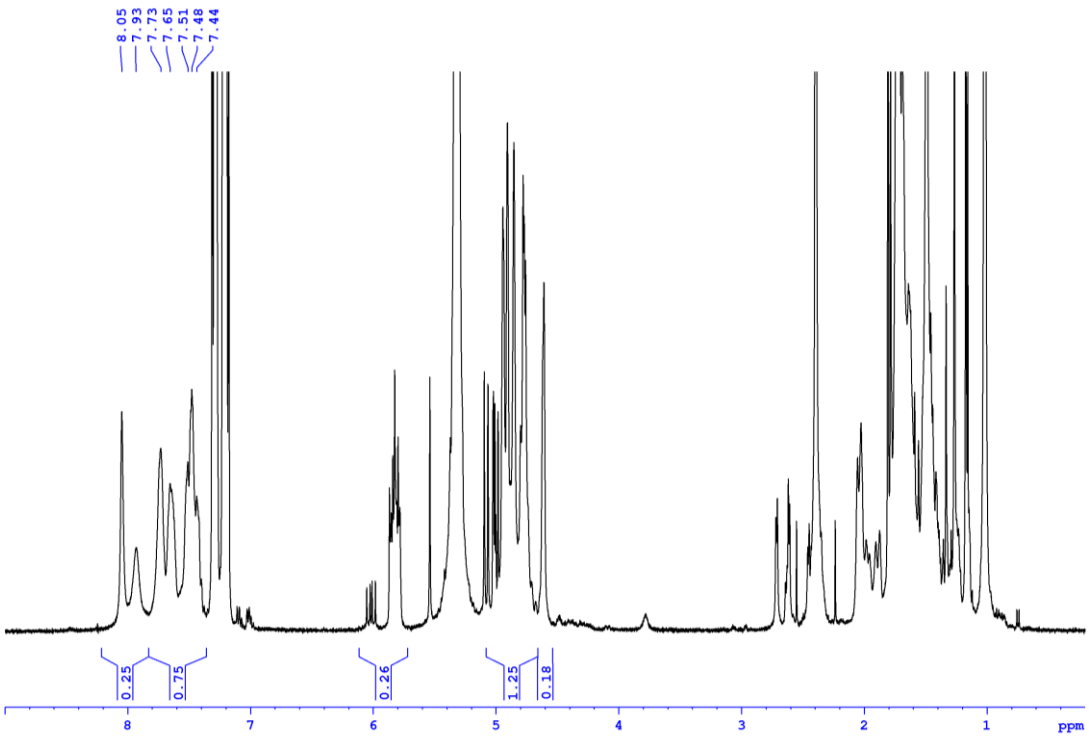


Figure S4 ^{1}H NMR spectra of an aliquot of the reaction mixture for the formation of poly(**BEM**-*alt*-**PA**) to determine the conversion (entry 1, Table 1) ($CDCl_3$, 400 MHz).

General Procedure for the ROCOP of BEM/PA without Solvent (entry 5, Table 1)

In a glove-box, PPNCl (1.3 mg, 2.25 μmol), complex **1** (1.2 mg, 2.25 μmol), **PA** (100 mg, 0.68 mmol) and **BEM** (298 mg, 1.35 mmol) were added in this order into a 4 mL glass vial equipped with a magnetic stirring bar. The vial was closed with a Teflon lined cap and sealed with electric insulator tape. Out of the glove-box, the vial was placed into an aluminum heating mantel, preheated to the desired temperature, and the mixture kept stirring for the desired reaction time. To stop the reaction, the vial was cooled down to room temperature in cold water, opened to air and the mixture dissolved into a minimum amount of dichloromethane. An aliquot was collected to determine the conversion by ^{1}H NMR analysis. The reaction mixture was poured into acidified methanol under stirring and the polymer was collected by filtration. The polymer was purified by dissolution into dichloromethane and precipitated from methanol. Conversion = 98%. Yield = 95%. M_n = 6.39, $Đ$ = 1.25.

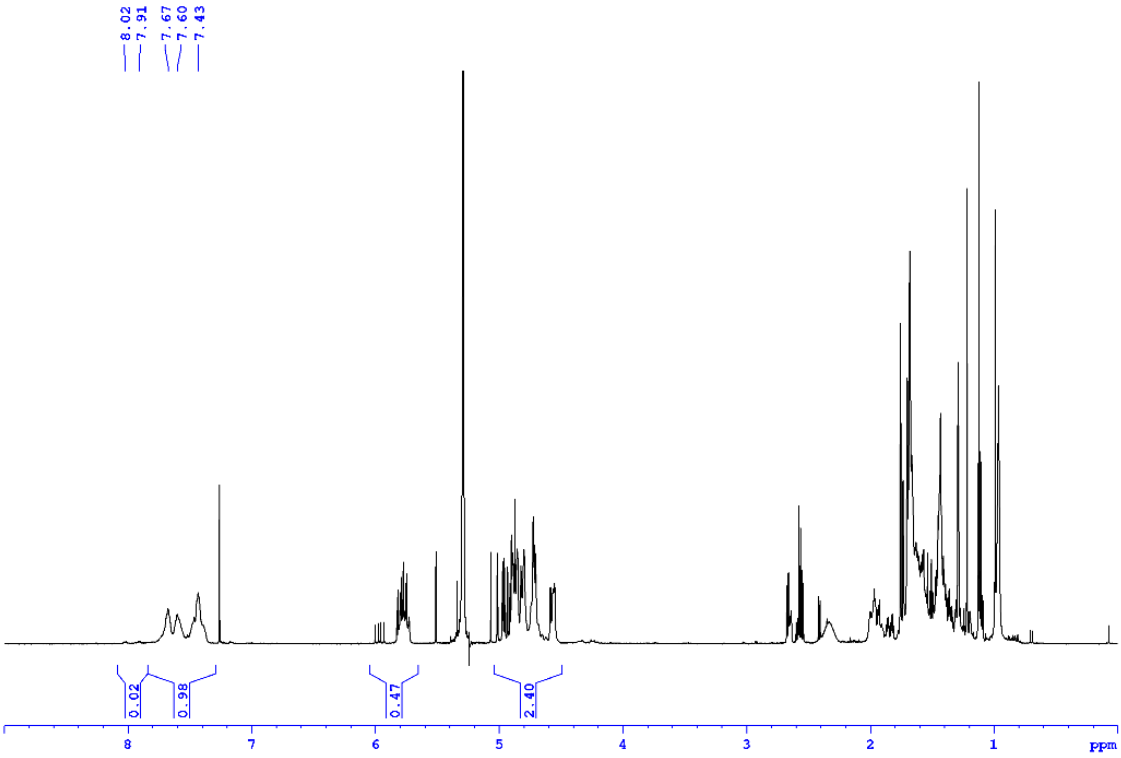


Figure S5 ^{1}H NMR spectra of an aliquot of the reaction mixture for the formation of poly(**BEM**-*alt*-**PA**) to determine the conversion (entry 5, Table 1) ($CDCl_3$, 400 MHz).

Gram-scale ROCOP of BEM/PA in Toluene (entry 6, Table 1)

In a glove-box, PPNCl (38.8 mg, $6.75 \cdot 10^{-5}$ mol), complex **1** (36.8 mg, $6.75 \cdot 10^{-5}$ mol), **PA** (1.00 g, 6.75 mmol), **BEM** (1.49 g, 6.75 mmol), and toluene (2.0 mL) were added in this order into a 10 mL Schlenk tube equipped with a magnetic stirring bar. Out of the glove-box, the tube was placed in an oil bath, preheated to 100 °C, and kept stirring for 24 h. To stop the reaction, the tube was cooled down to room temperature in cold water, opened to air and the mixture dissolved into the minimum amount of dichloromethane. An aliquot was collected to determine the conversion by ^{1}H NMR analysis. The reaction mixture was poured into acidified methanol under stirring and the polymer was collected by filtration. The polymer was purified by dissolution into dichloromethane and precipitated from methanol. Conversion = 55%. Yield = 52%. M_n = 6.88, $Đ$ = 1.21.

Gram-scale ROCOP of BEM/PA without solvent (entry 7, Table 1)

In a glove-box, PPNCl (12.3 mg, $2.14 \cdot 10^{-5}$ mol), complex **1** (11.6 mg, $2.14 \cdot 10^{-5}$ mol), **PA** (0.95 g, 6.41 mmol), and **BEM** (2.83 g, 12.8 mmol) were added in this order into a 10 mL Schlenk tube equipped with a magnetic stirring bar. Out of the glove-box, the tube was placed in an oil bath, preheated to 100 °C and kept stirring for 24 h. To stop the reaction, the tube was cooled down to room temperature in cold water, opened to air and the mixture dissolved into a minimum amount of dichloromethane. An aliquot was collected for to determine the conversion by ^{1}H NMR analysis. The reaction mixture was poured into acidified methanol under stirring and the polymer was collected by filtration. The polymer was purified by dissolution in dichloromethane and precipitated from methanol. Conversion = > 99%. Yield = 94%. M_n = 4.36, $Đ$ = 1.21.

General Procedure for the ROCOP of BED/PA in Toluene (entry 8, Table 1)

In a glove-box, PPNCl (3.9 mg, 6.75 µmol), complex **1** (3.7 mg, 6.75 µmol), **PA** (100 mg, 0.68 mmol), **BED** (160 mg, 0.68 mmol), and toluene (200 µL) were added in this order into a 4 mL glass vial equipped with a magnetic stirring bar. The vial was closed with a Teflon lined cap and sealed with electric insulator tape. Out of the glove-box, the vial was placed in an aluminum heating mantel, preheated to 60 °C, and kept stirring for 48 h. To stop the reaction, the vial was cooled down to room temperature in cold water, opened to air and the mixture dissolved into a minimum amount of dichloromethane. An aliquot was collected to determine the conversion by ^{1}H NMR analysis. The reaction mixture was poured into acidified methanol under stirring and the polymer was collected by filtration. Conversion = 57%. Yield = 52%. M_n = 6.8, $Đ$ = 1.77.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.70 (*bs*, 1H, Ar-C*H*); 7.45 (overlapped *m*, 3H, Ar-C*H*); 6.01 and 5.71 (*bs*, 1H, -C*H*=CH_2); 5.14-4.76 (overlapped *m*, 2H, -CH=C*H*$_2$ and 2H, polyester -[O-C*H*$_2$-CR_2]-); 3.96 (broad *s*, branch polyester -[O-C*H*$_2$-CR_2]-); 2.30 (broad *s*, 2H, -COC*H2*), 2.01 (*d*, 1H, cyclo-C*H*); 1.67 (overlapped *m*, 1H, cyclo -C*H*$_2$); 1.66 (overlapped *m*, 1H, cyclo -C*H*$_2$); 1.64 (overlapped *s*, 3H, -C*H*$_3$); 1.48-144 (overlapped *m*, 2H, cyclo -C*H*$_2$); 1.18 (overlapped *s*, 3H, -C*H*$_3$); 1.03 (overlapped *m*, 1H, cyclo-C*H*); 0.97 (overlapped *s*, 3H, -C*H*$_3$).

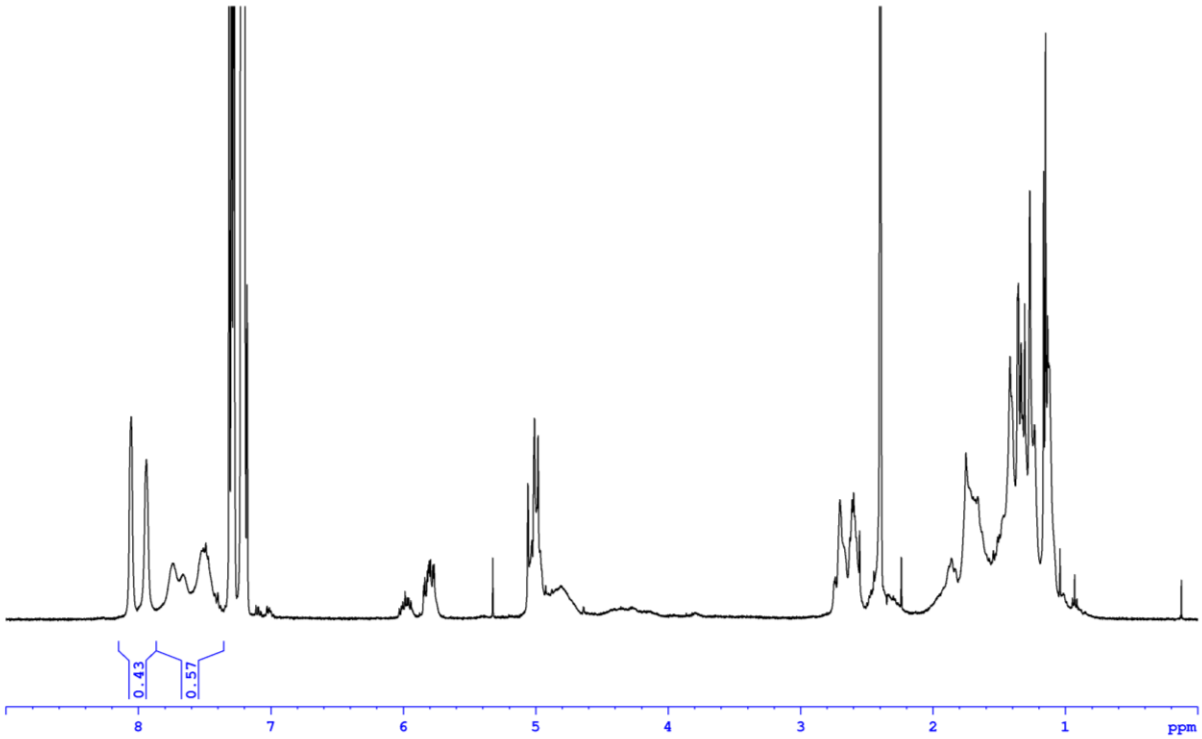


Figure S6 ^{1}H NMR spectra of an aliquot of the reaction mixture for the formation of poly(**BED**-*alt*-**PA**) to determine the conversion (entry 8, Table 1) ($CDCl_3$, 400 MHz).

General Procedure for the ROCOP of BED/PA without Solvent (entry 11, Table 1)

In a glove-box, PPNCl (3.9 mg, 6.75 µmol), complex **1** (3.7 mg, 6.75 µmol), **PA** (100 mg, 0.68 mmol), and **BED** (319 mg, 1.35 mmol) were added in this order into a 4 mL glass vial equipped with a magnetic stirring bar. The vial was closed with a Teflon lined cap and sealed with electric insulator tape. Out of the glove-box, the vial was placed in an aluminum heating mantel, preheated to 80 °C, and kept stirring for 24 h. To stop the reaction, the vial was cooled down to room temperature in cold water, opened to air and the mixture dissolved into a minimum amount of dichloromethane. An aliquot was collected to determine the conversion by ^{1}H NMR analysis. The reaction mixture was poured into acidified methanol under stirring and the polymer was collected by filtration. Conversion = 91%. Yield = 89%. M_n = 4.1, $Đ$ = 2.48.

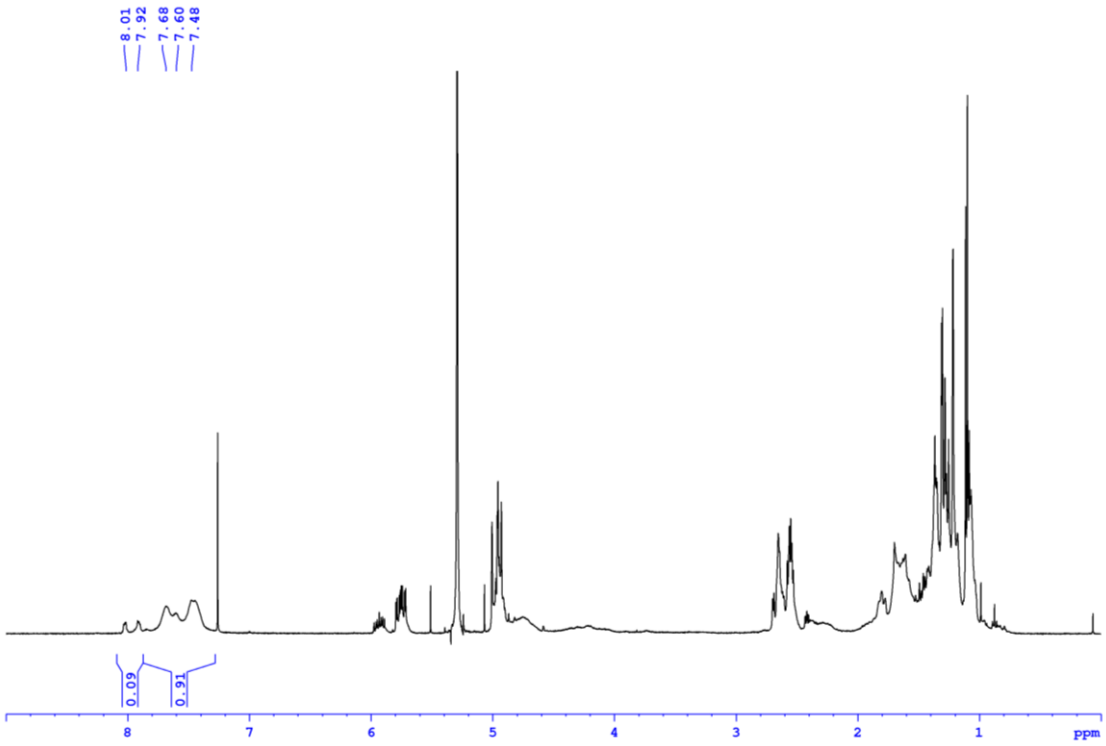


Figure S7 ^{1}H NMR spectra of an aliquot of the reaction mixture for the formation of poly(**BED**-*alt*-**PA**) to determine the conversion (entry 11, Table 1) ($CDCl_3$, 400 MHz).

Epoxidation of Poly(BEM-*alt*-PA) to Poly(BED-*alt*-PA)

In a 50 mL flask, poly(**BEM**-*alt*-**PA**) (400 mg, 1.09 mmol repeating unit, M_n = 4.36 kDa, $Đ$ = 1.21) was dissolved into dichloromethane (22 mL, [repeating unit] = 0.05 M) and positioned in an ice bath. *m*CPBA (77 % w/w, 292 mg, 1.30 mmol, 1.2 eq) was added portion-wise during 5 minutes. The flask was left in the ice bath and warmed up to room temperature under stirring. After 15 h, the solution was washed 3 times with saturated $NaHCO_3$ (aq) and 2 times with water, then the solution was dried using Na_2SO_4. The solid was dissolved into a minimum amount of dichloromethane and poured into methanol under stirring. The polymer was collected by filtration and dried in vacuum. Isolated yield = 0.40 g (96%); M_n = 4.10 kDa, $Đ$ = 1.22. Functionalization degree = 94%.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.69 (*bs*, 1H, Ar-C*H*); δ 7.61 (*bs*, 1H, Ar-C*H*); 7.44 (overlapped *m*, 2H, Ar-C*H*); 5.92 and 5.73 (*dd*, *J* = 10.4 Hz, *J* = 16.9 Hz, and overlapped *m*, 1H, -C*H*=CH_2); 4.98-4.88 (overlapped *m*, 2H, -CH=CH_2); 4.76 (overlapped *bs*, 2H, polyester -[O-CH_2-CR_2]-); 2.57 (m, 2H, -COCH_2); 2.29 (broad *s*, 1H, cyclo-C*H*); 1.90 (overlapped *m*, 1H, cyclo-CH_2); 1.70 (overlapped *s*, 3H, -CH_3); 1.65-1.37 (overlapped *m*, 5H, cyclo -CH_2); 1.36 (overlapped *m*, 1H, cyclo -C*H*); 1.25-0.94 (overlapped *s*, 6H, -CH_3).

^{13}C NMR (400 MHz, $CDCl_3$, rt): δ 167.02; 166.60; 150.06; 149.97; 149.25; 149.00; 147.49; 133.99; 131.46; 130.71; 128.93; 112.41; 110.93; 110.26; 110.00; 86.47; 86.35; 73.50; 71.26; 66.96; 66.60; 59.84; 58.65; 58.13; 58.09; 57.97; 53.55; 53.27; 53.02; 52.43; 51.36; 43.62; 43.33; 41.41; 40.82; 39.87; 39.65; 39.28; 25.12; 24.86; 24.56; 24.29; 22.62; 22.18; 21.86; 20.11; 19.04; 18.86; 18.68; 17.52; 17.33; 16.69.

Epoxidation of Poly(BEM-*alt*-PA) to Poly(BET-*alt*-PA)

In a 50 mL flask, poly(**BEM**-*alt*-**PA**) (400 mg, 1.09 mmol repeating unit, M_n = 4.36 kDa, $Đ$ = 1.21) was dissolved into dichloromethane (22 mL, [repeating unit] = 0.05 M) and positioned in an ice bath. *m*CPBA (77 % w/w, 608 mg, 2.71 mmol, 2.5 eq) was added portion-wise during 5 minutes. The flask was left in the ice bath and warmed up to room temperature under stirring. After 26 h, the solution was washed 3 times with saturated $NaHCO_3$ (aq) and 2 times with water following drying on Na_2SO_4. The solid was dissolved into a minimum amount of dichloromethane and poured into methanol under stirring. The polymer was collected by filtration and dried in vacuum. Isolated yield = 0.41 g (94%); M_n = 4.02 kDa, $Đ$ = 1.26. Functionalization degree = 90%.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.69 (*bs*, 1H, Ar-C*H*); δ 7.61 (*bs*, 1H, Ar-C*H*); 7.45 (overlapped *m*, 2H, Ar-C*H*); 4.76 (*bs*, 2H, polyester -[O-CH_2-CR_2]-); 3.58 (overlapped *m*, 1H, -CHOCH_2); 2.90-2.43 (overlapped *m*, 4H, -CHOCH_2 and -COCH_2); 2.23 (*bs*, 1H, cyclo -C*H*); 1.86 (overlapped *m*, 1H, cyclo -C*H*); 1.85 (overlapped *m*, 1H, cyclo -CH_2); 1.69 (overlapped *s*, 3H, -CH_3); 1.69-133 (overlapped *m*, 5H, cyclo -CH_2); 1.25-0.75 (overlapped *s*, 6H, -CH_3).

^{13}C NMR : δ 166.61; 133.63; 133.30; 132.01; 131.56; 130.79; 128.97; 128.10; 86.29; 66.95; 59.95; 59.76; 58.03; 57.39; 56.27; 55.26; 53.82; 53.55; 50.38; 44.38; 43.17; 42.33; 39.27; 37.46; 37.04; 36.58; 36.26; 36.07; 35.29; 24.74; 24.43; 22.13; 21.95; 21.63; 21.27; 20.32; 20.11; 19.58; 18.92; 18.63; 17.52; 15.68; 15.18; 13.21.

NMR Characterization of BE

NMR characterization of β-elemene is reported to facilitate comparison with the β-elemene oxide products.

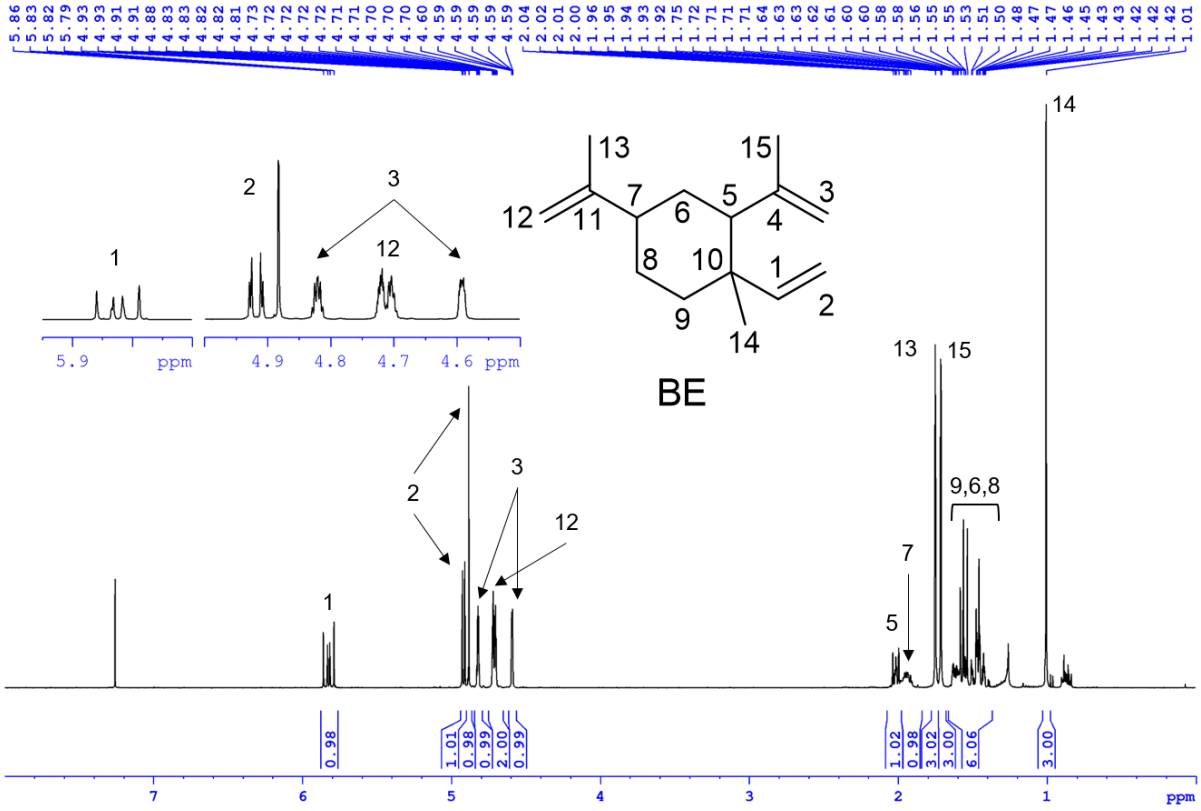


Figure S8 ^{1}H NMR of **BE** (400 MHz, rt, $CDCl_3$).

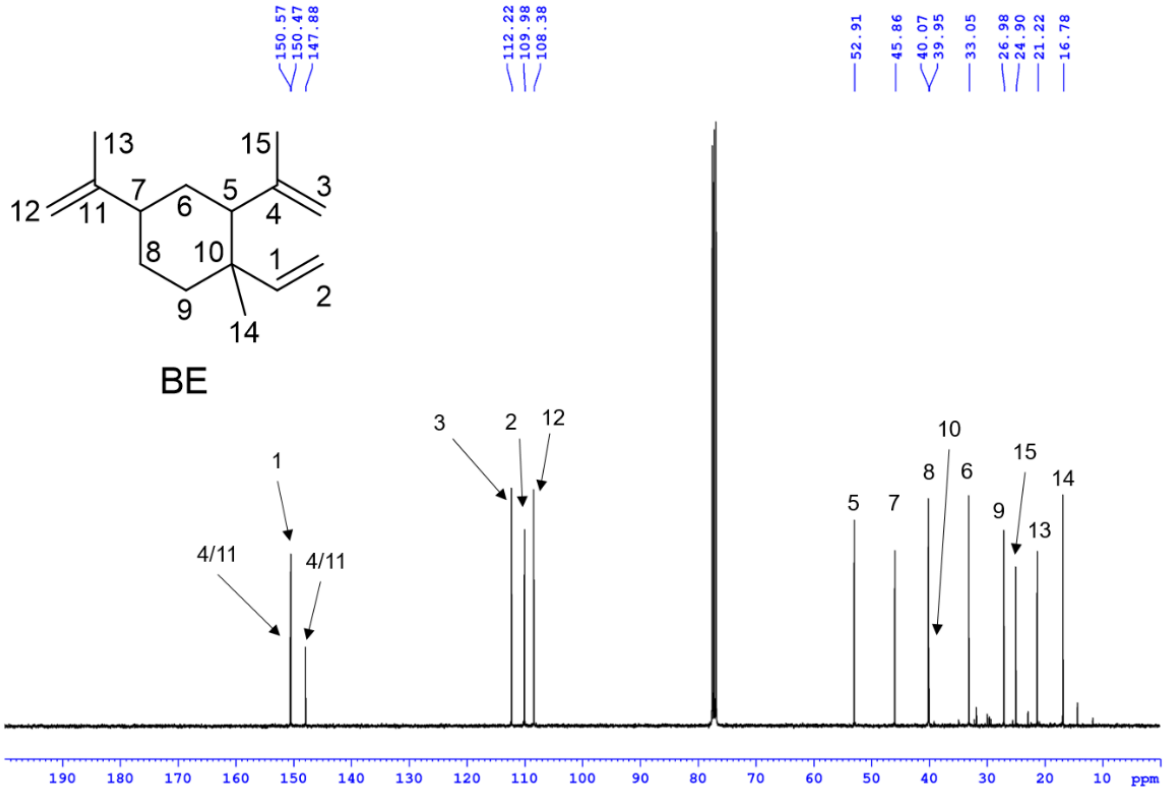


Figure S9 ^{13}C NMR of **BE** (400 MHz, rt, $CDCl_3$).

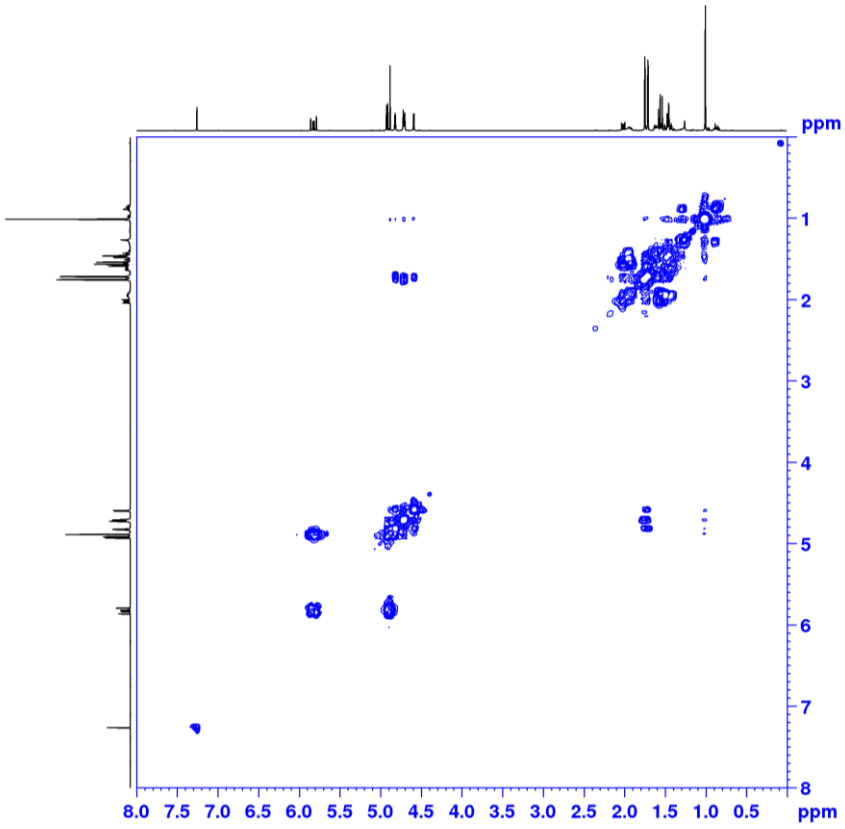


Figure S10 ^{1}H-^{1}H COSY NMR of **BE** (400 MHz, rt, $CDCl_3$).

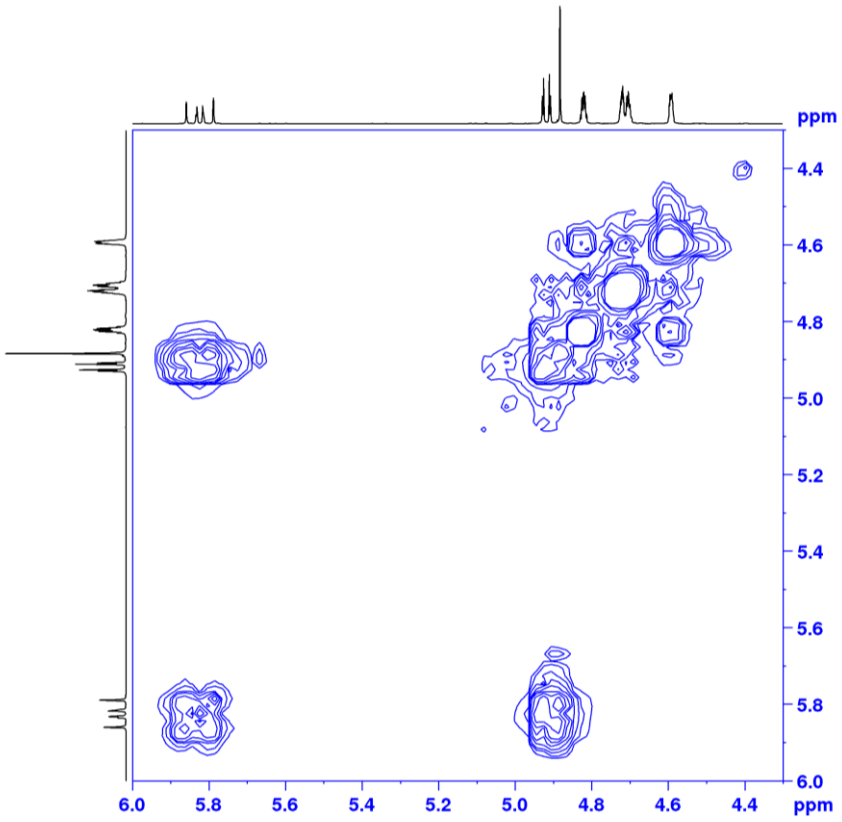


Figure S11 ^{1}H-^{1}H COSY NMR of **BE** from 6.0 to 4.3 ppm (400 MHz, rt, $CDCl_3$).

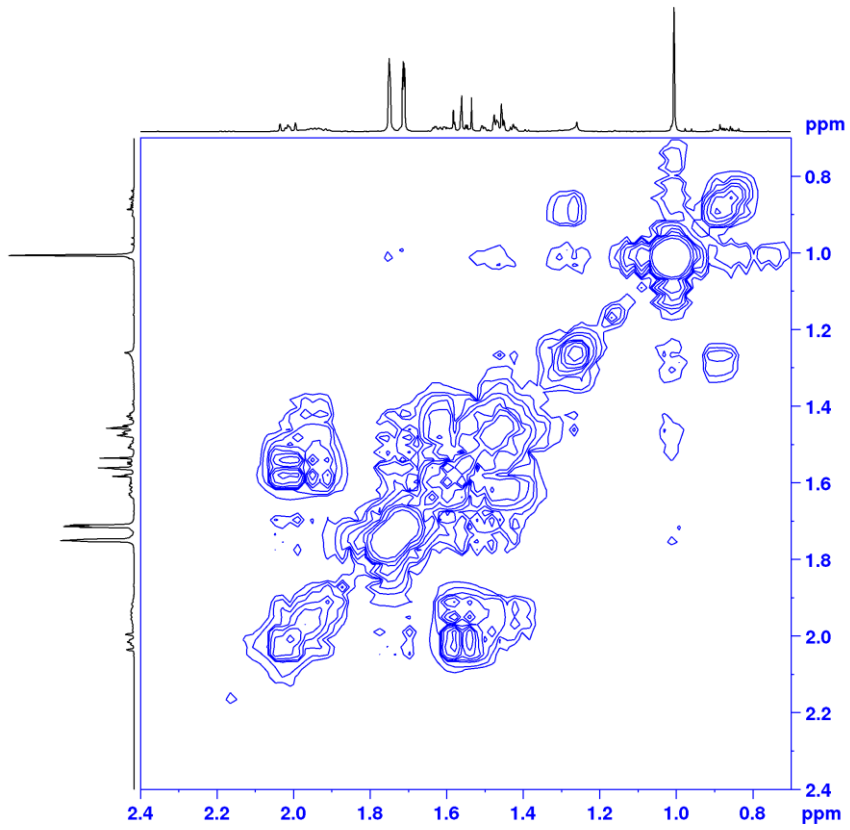


Figure S12 ^{1}H-^{1}H COSY NMR of **BE** from 2.4 to 0.7 ppm (400 MHz, rt, $CDCl_3$).

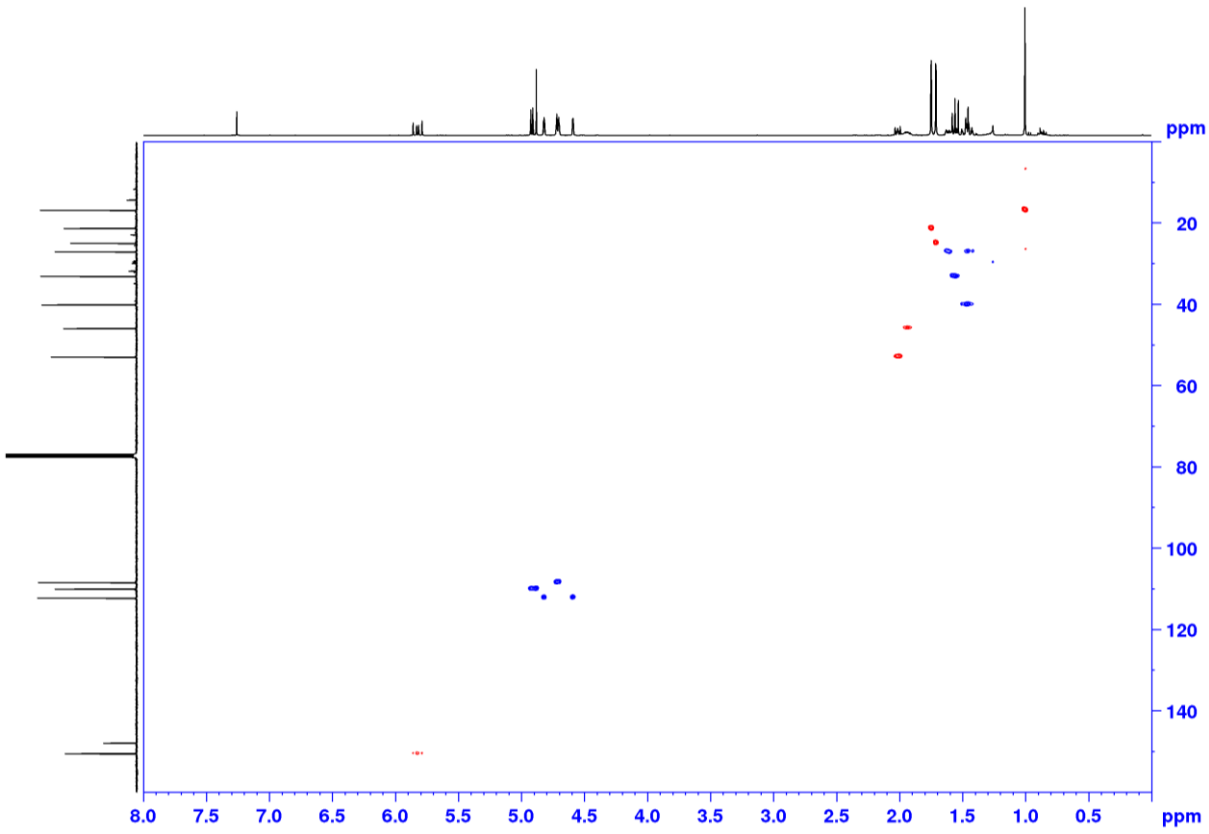


Figure S13 ^{1}H-^{13}C HSQC NMR of **BE** (400 MHz, rt, $CDCl_3$).

NMR Characterization of BEM

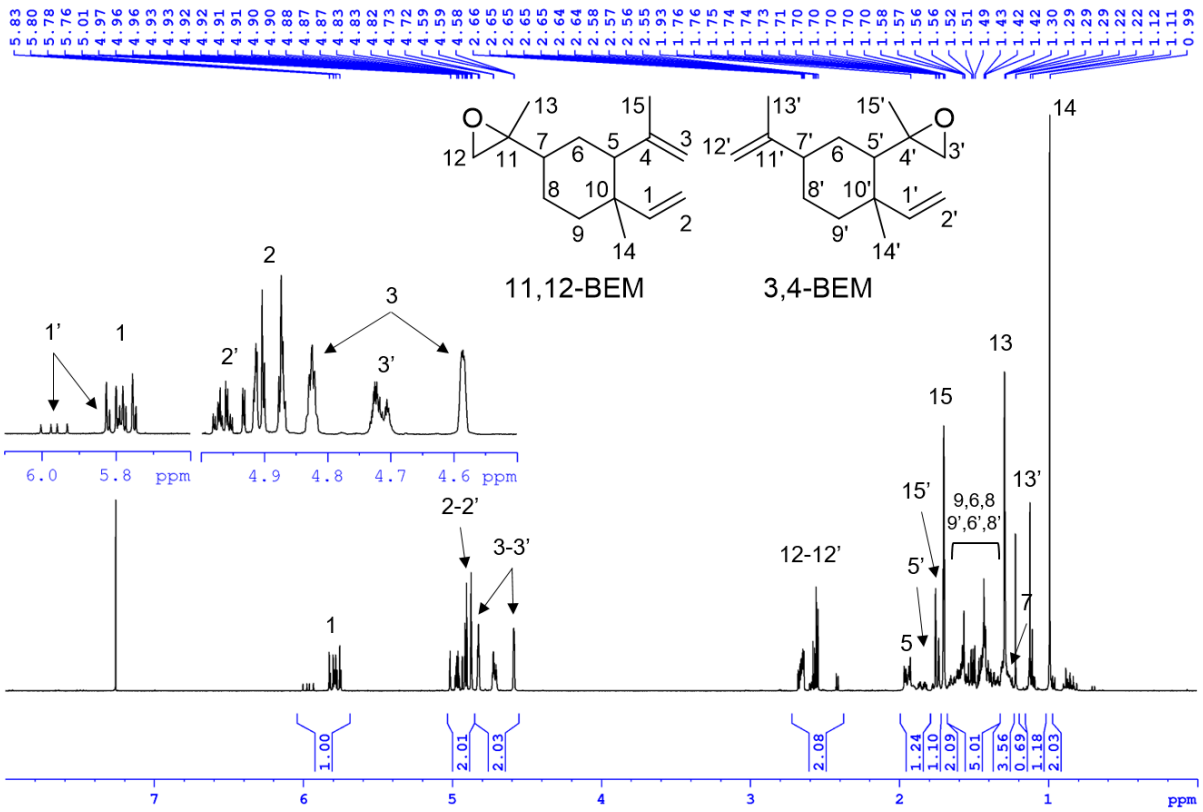


Figure S14 ^{1}H NMR of **BEM** (400 MHz, rt, $CDCl_3$).

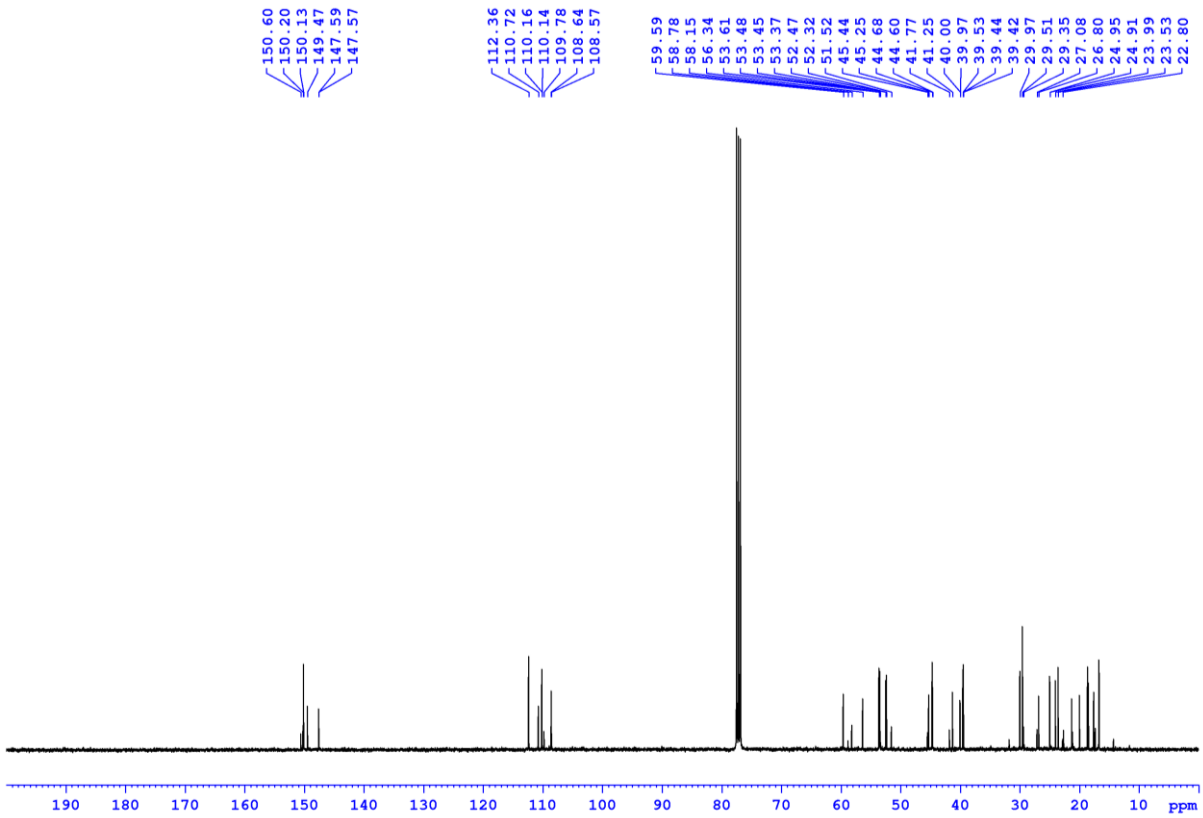


Figure S15 ^{13}C NMR of **BEM** (400 MHz, rt, $CDCl_3$).

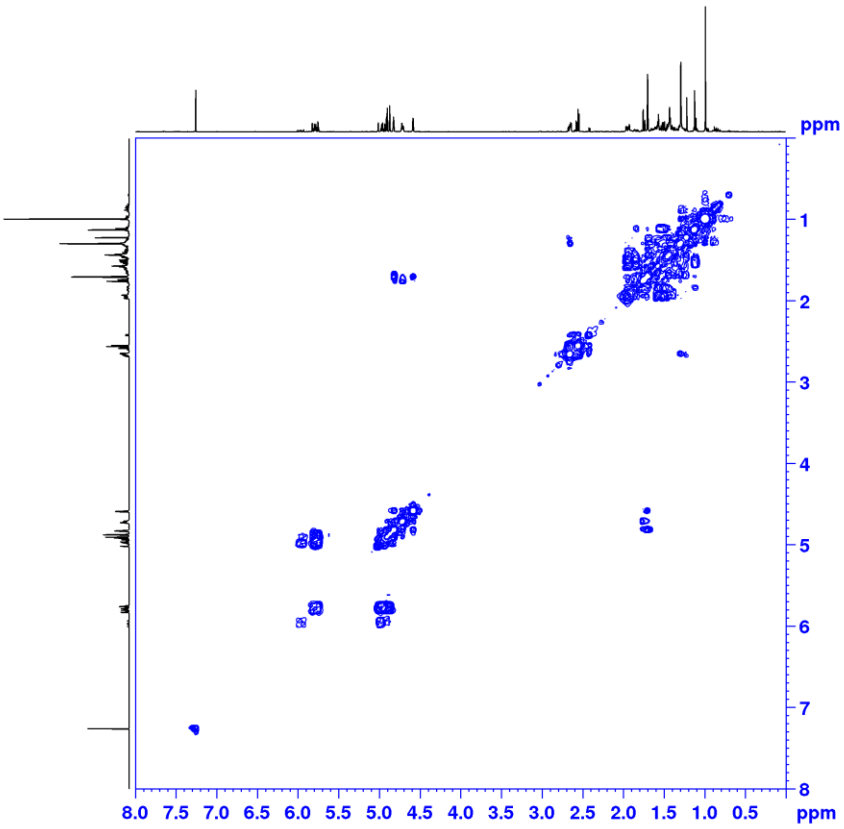


Figure S16 ^{1}H-^{1}H COSY NMR of **BEM** (400 MHz, rt, $CDCl_3$).

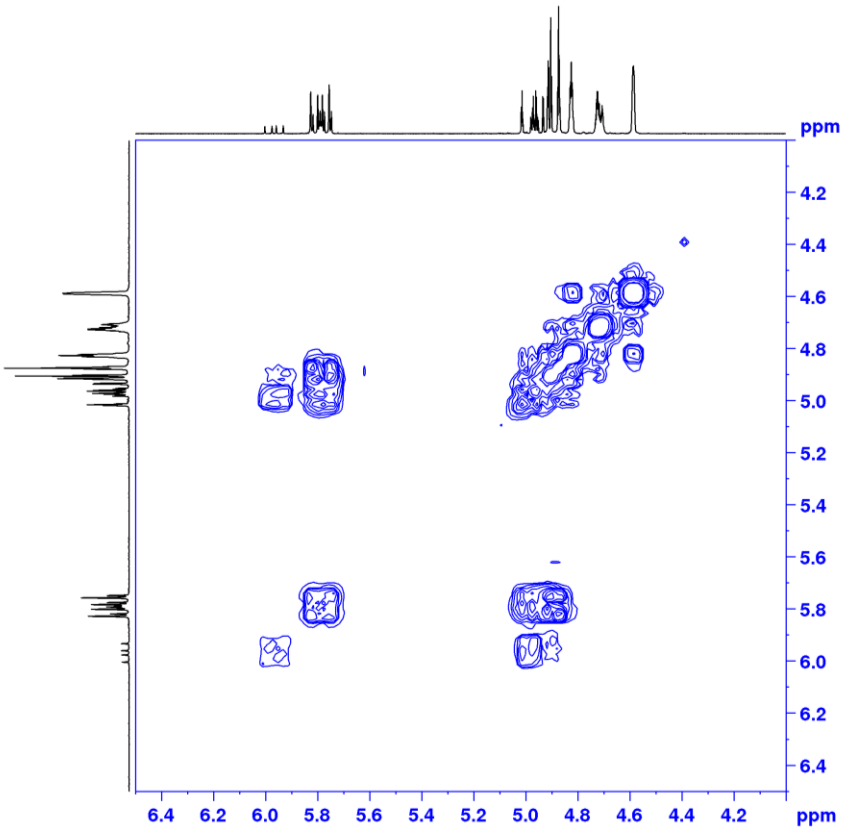


Figure S17 ^{1}H-^{1}H COSY NMR of **BEM** from 6.5 to 4.2 ppm (400 MHz, rt, $CDCl_3$).

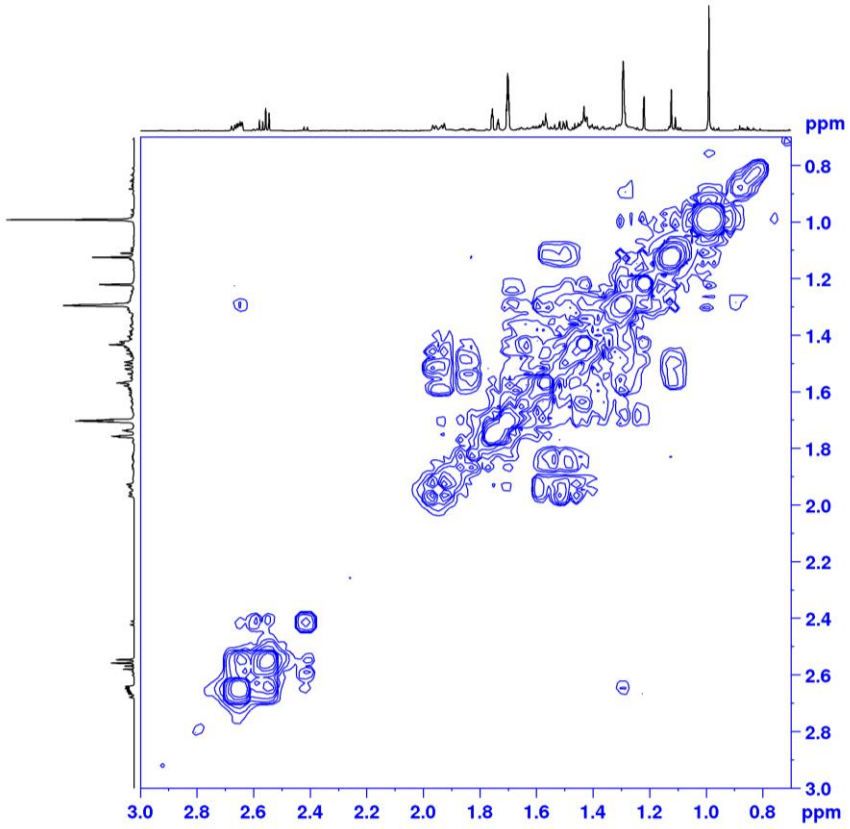


Figure S18 ^{1}H-^{1}H COSY NMR of **BEM** from 3.0 to 0.7 ppm (400 MHz, rt, $CDCl_3$).

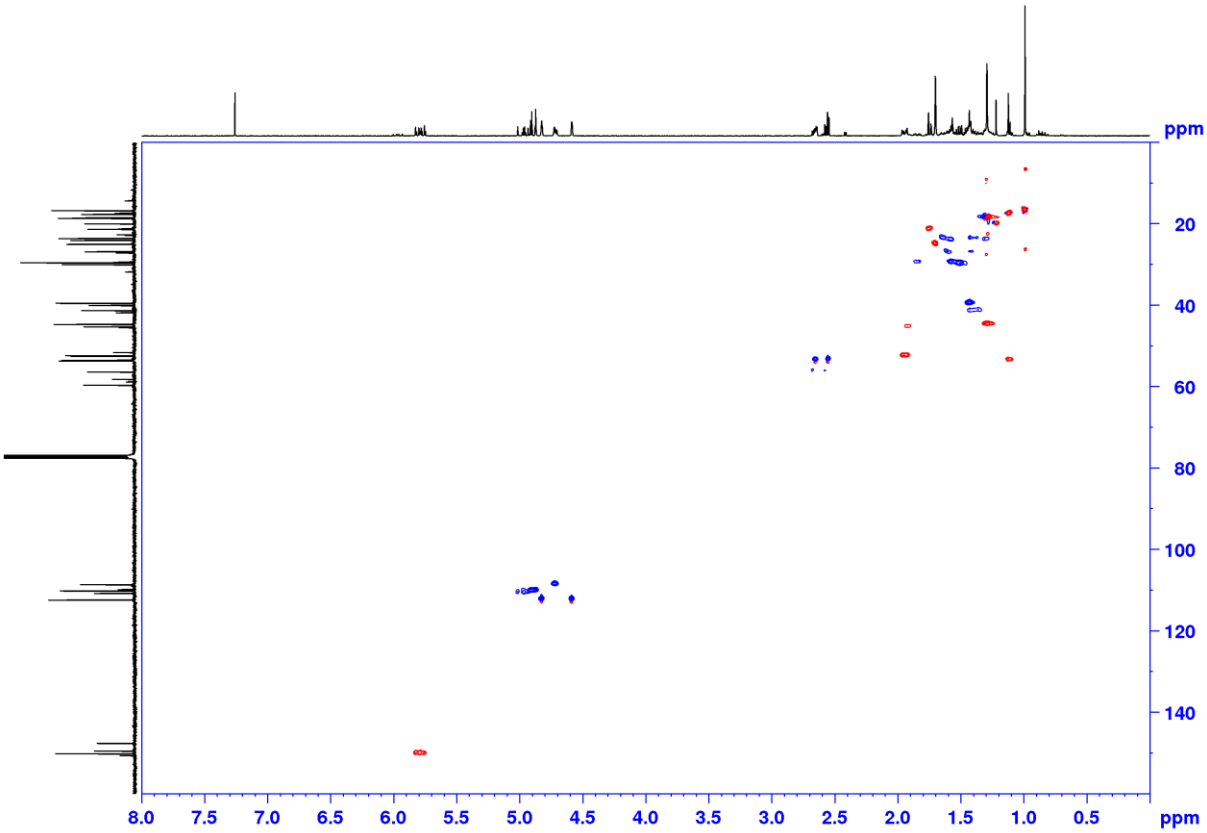


Figure S19 ^{1}H-^{13}C HSQC NMR of **BEM** (400 MHz, rt, $CDCl_3$).

NMR Characterization of 11,12-BEM

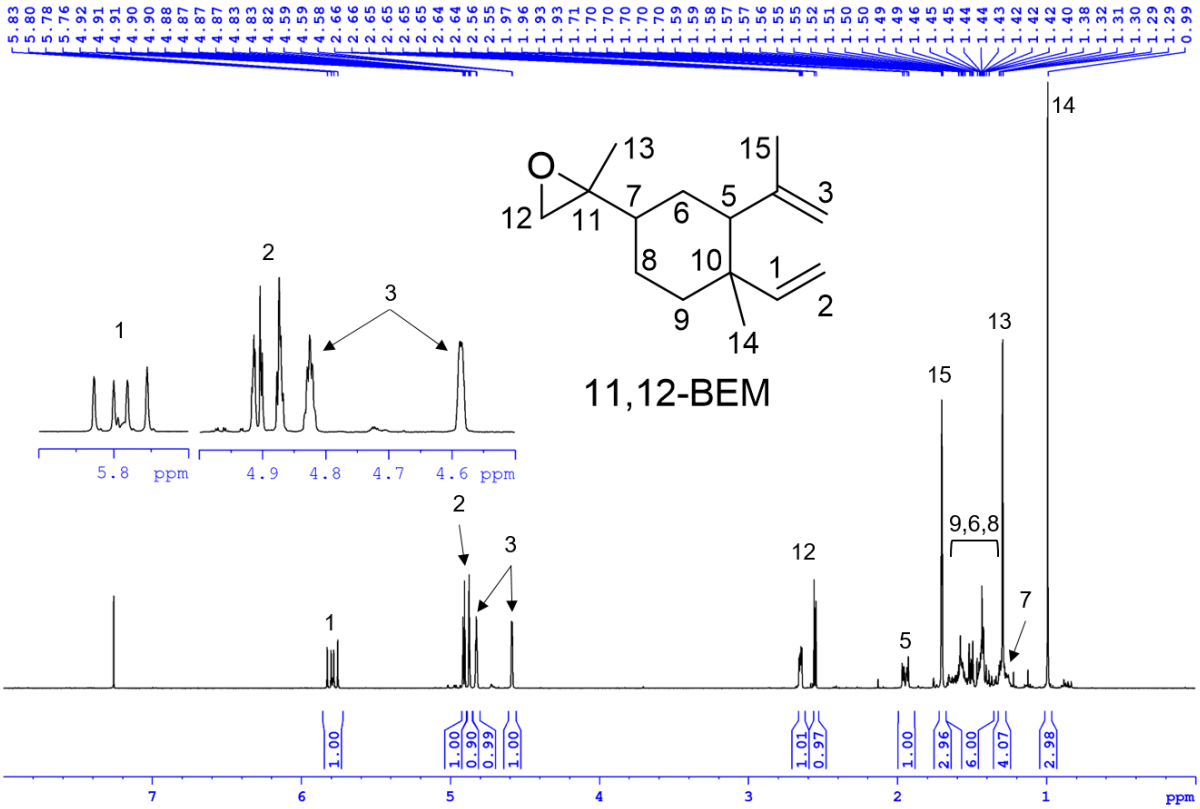


Figure S20 ^{1}H NMR of 11,12-**BEM** (400 MHz, rt, $CDCl_3$).

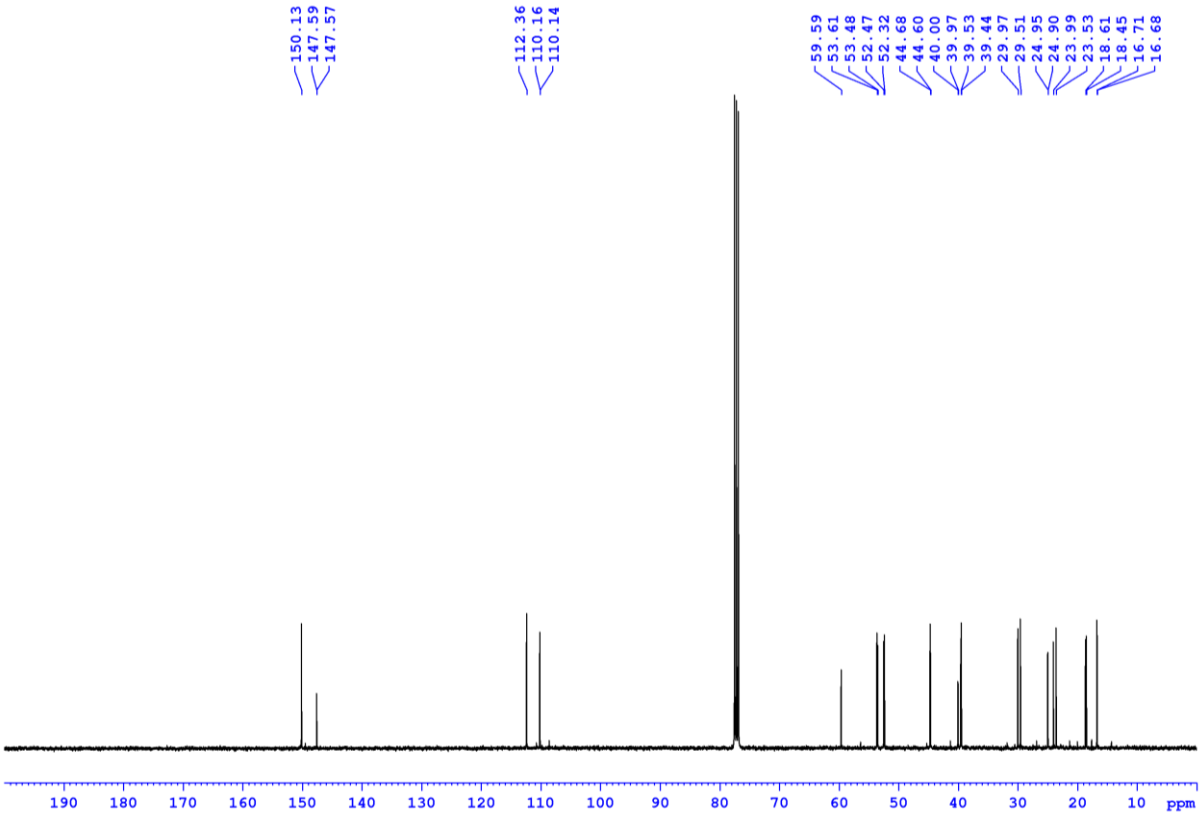


Figure S21 ^{13}C NMR of 11,12-**BEM** (400 MHz, rt, $CDCl_3$).

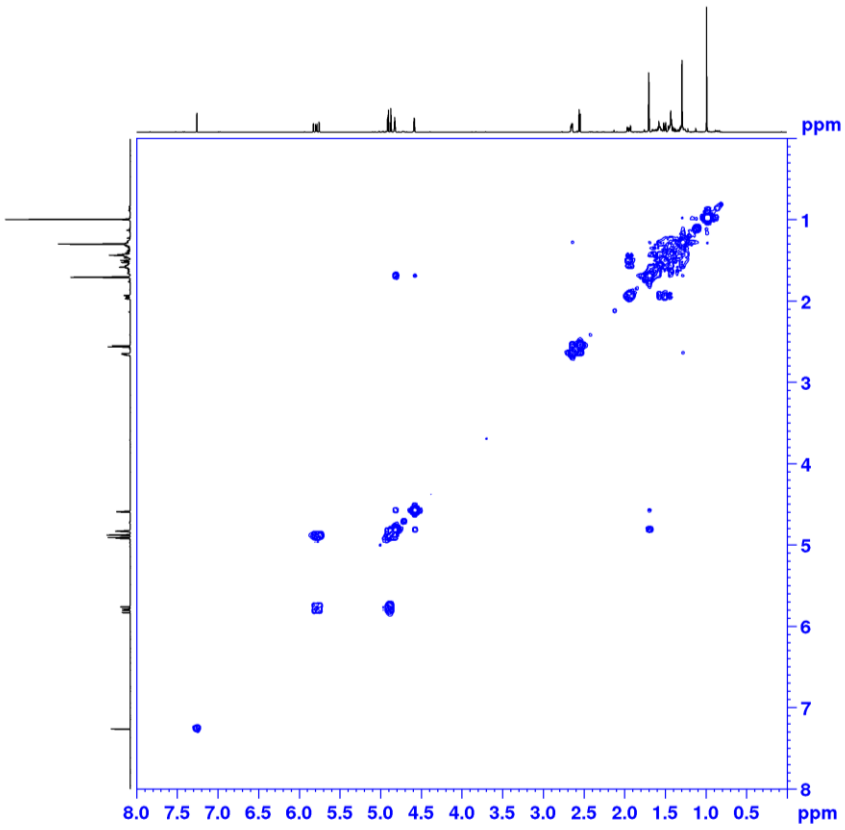


Figure S22 ^{1}H-^{1}H COSY NMR of 11,12-**BEM** (400 MHz, rt, $CDCl_3$).

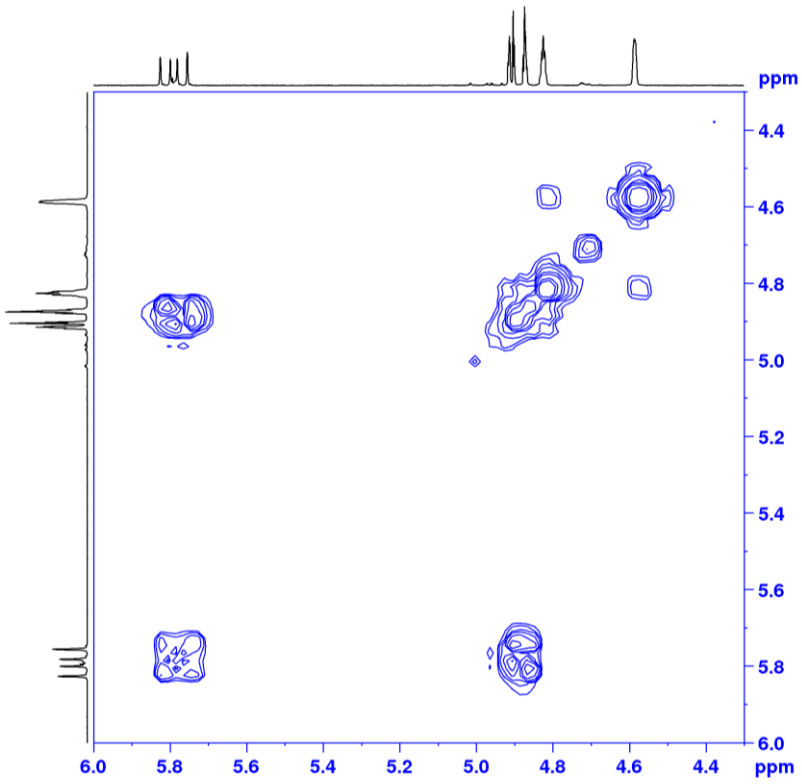


Figure S23 ^{1}H-^{1}H COSY NMR of 11,12-**BEM** from 6.0 to 4.3 ppm (400 MHz, rt, $CDCl_3$).

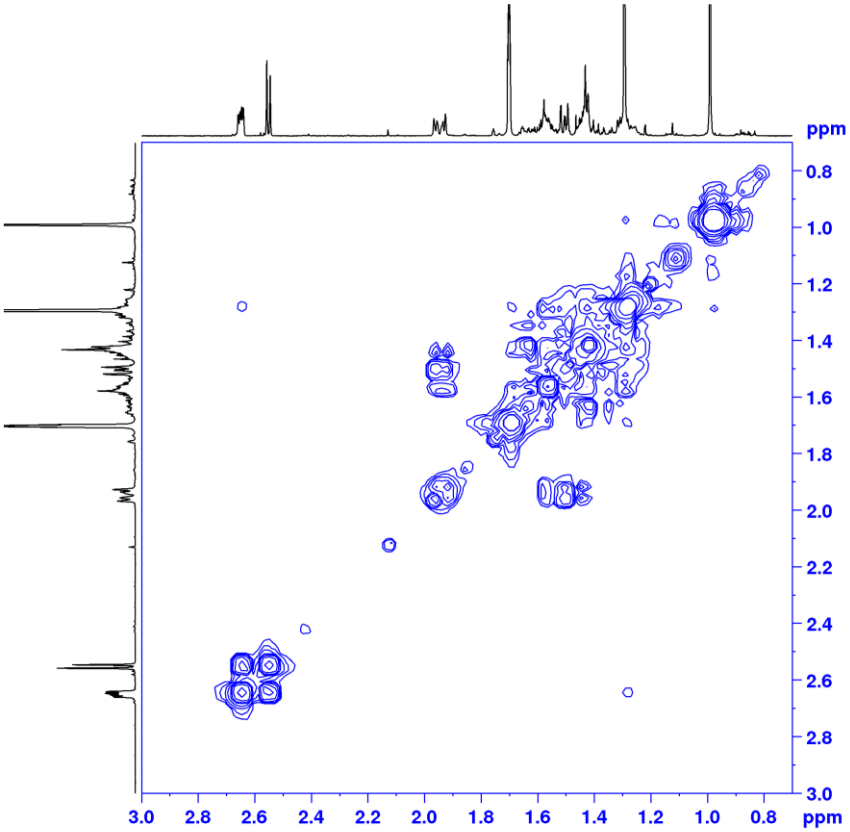


Figure S24 ^{1}H-^{1}H COSY NMR of 11,12-**BEM** from 3.0 to 0.7 ppm (400 MHz, rt, $CDCl_3$).

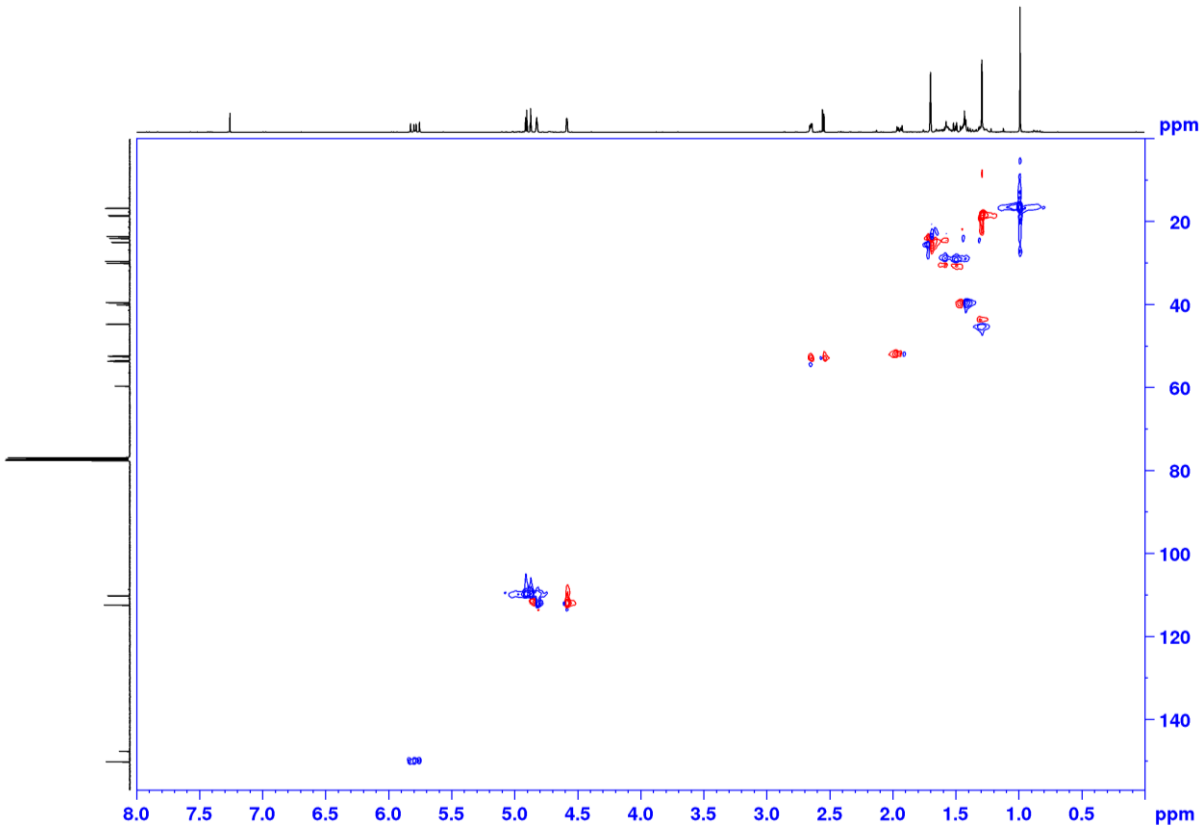


Figure S25 ^{1}H-^{13}C HSQC NMR of 11,12-**BEM** (400 MHz, rt, $CDCl_3$).

NMR Characterization of BED

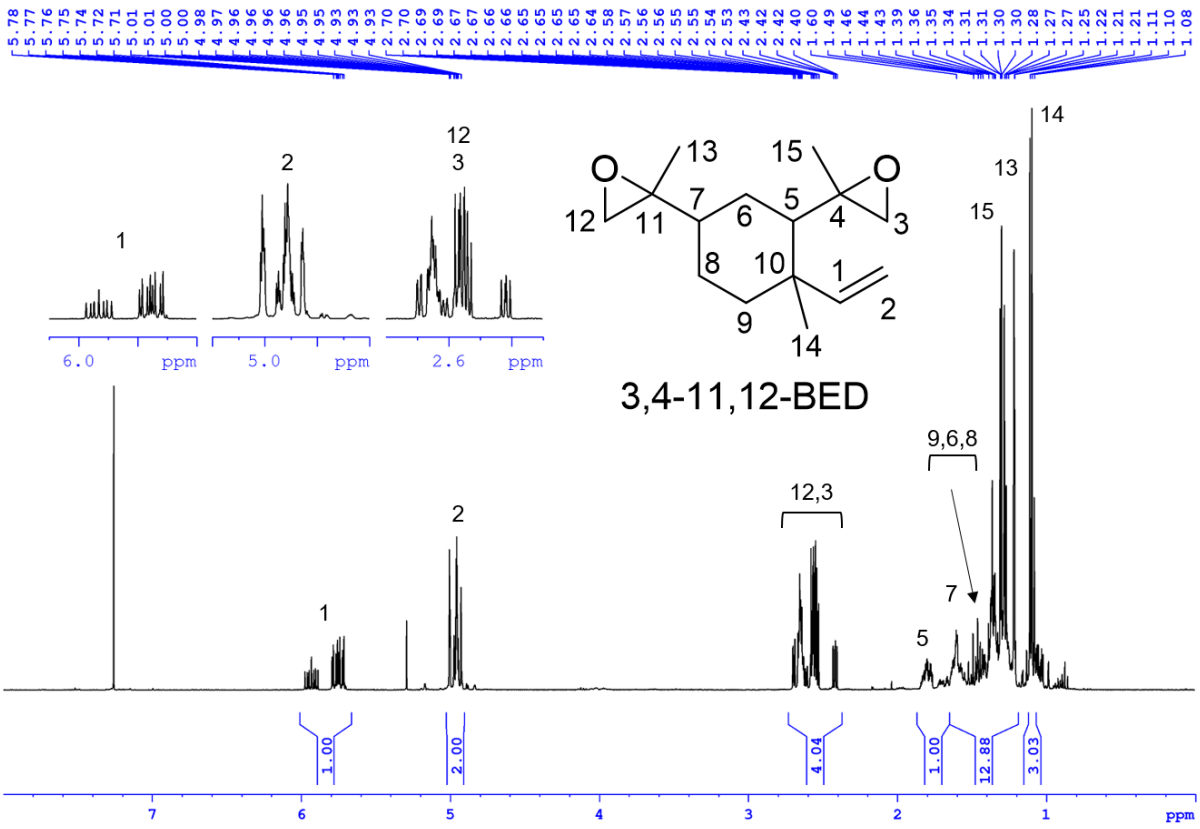


Figure S26 ^{1}H NMR of **BED** (400 MHz, rt, $CDCl_3$).

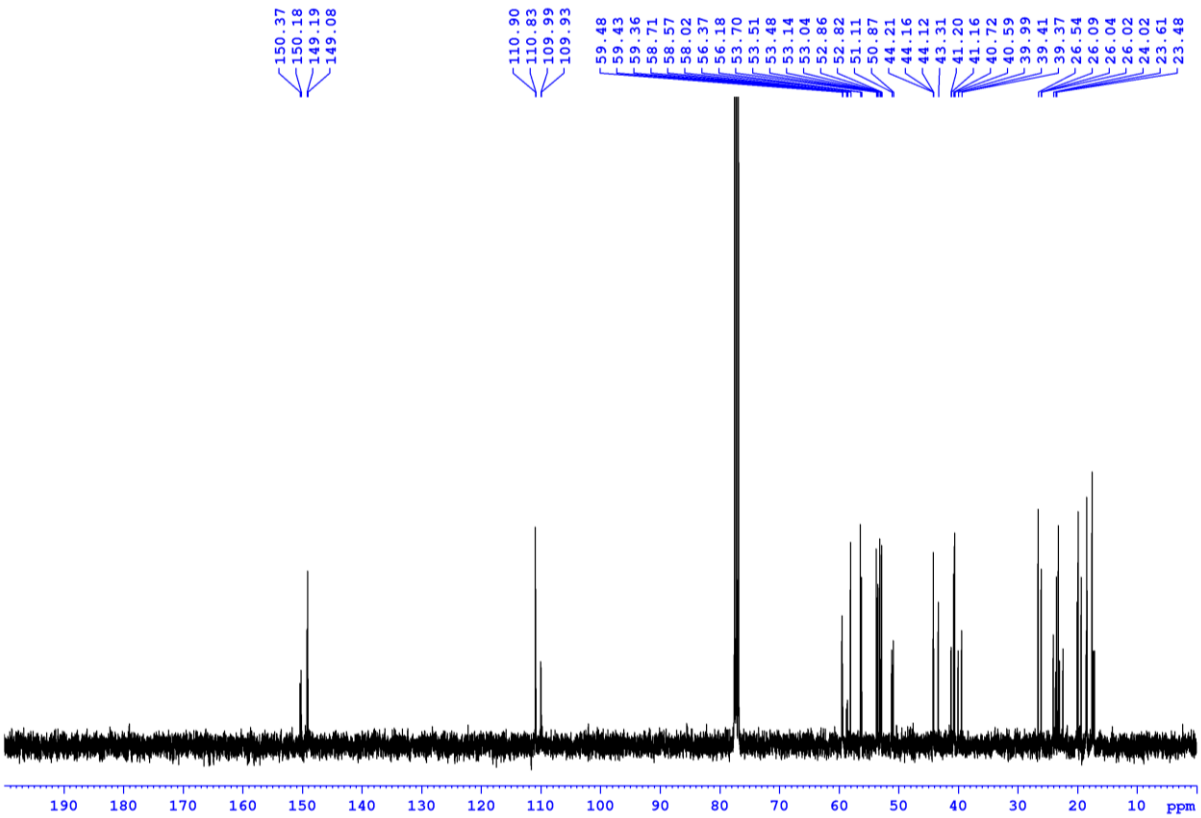


Figure S27 ^{13}C NMR of **BED** (400 MHz, rt, $CDCl_3$).

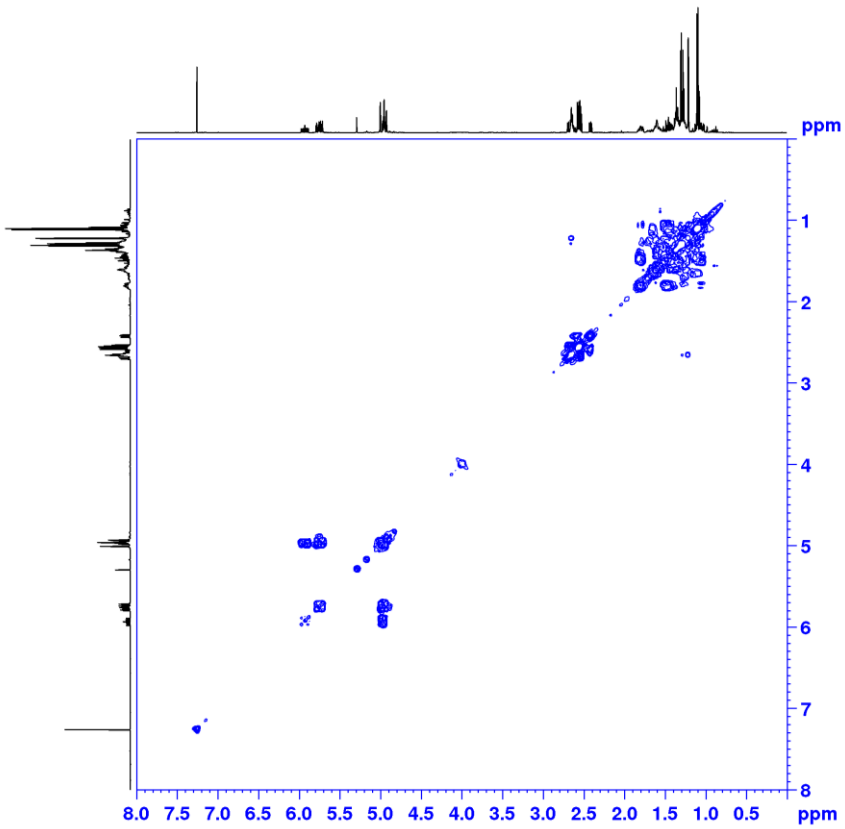


Figure S28 ^{1}H-^{1}H COSY NMR of **BED** (400 MHz, rt, $CDCl_3$).

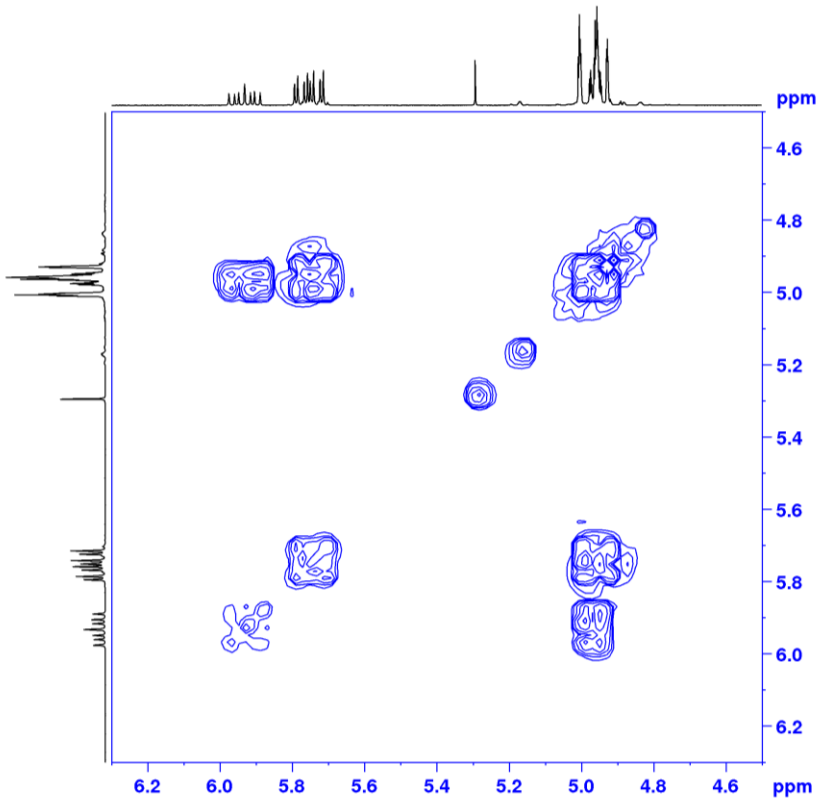


Figure S29 ^{1}H-^{1}H COSY NMR of **BED** from 6.3 to 4.5 ppm (400 MHz, rt, $CDCl_3$).

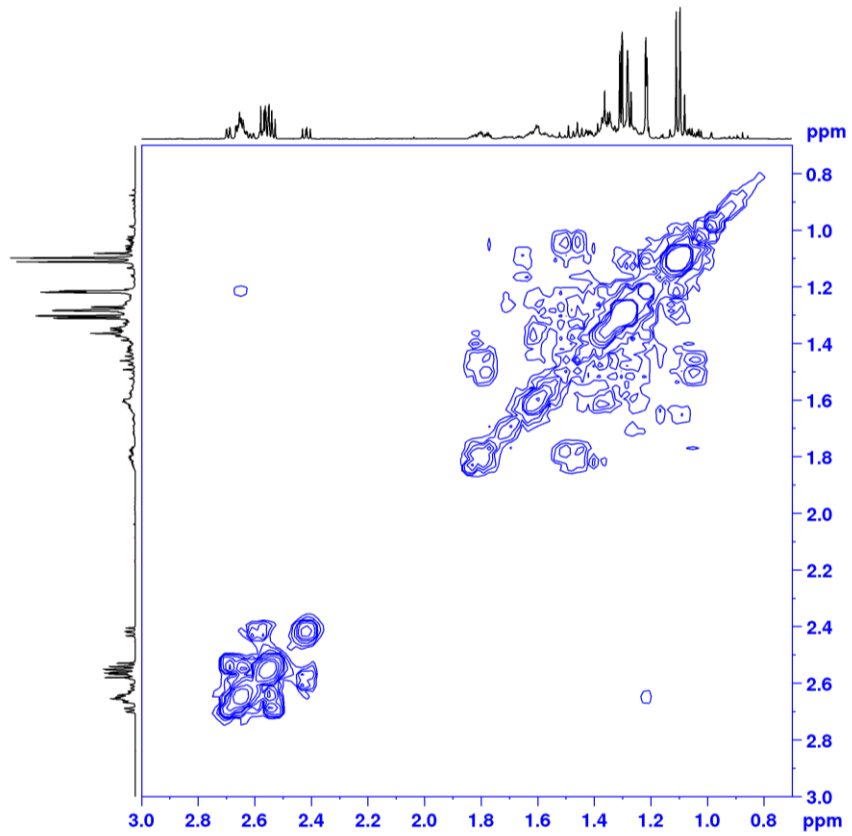


Figure S30 ^{1}H-^{1}H COSY NMR of **BED** from 3.0 to 0.7 ppm (400 MHz, rt, $CDCl_3$).

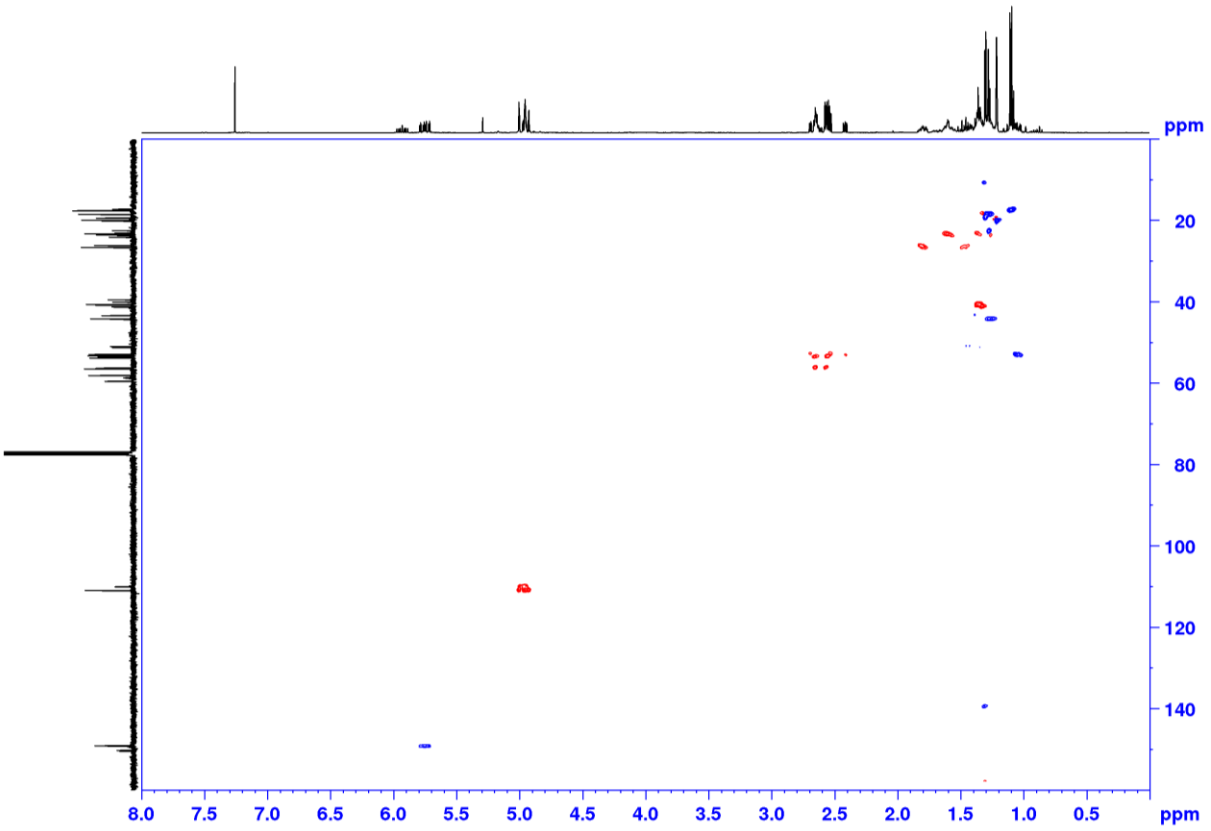


Figure S31 ^{1}H-^{13}C HSQC NMR of **BED** (400 MHz, rt, $CDCl_3$).

NMR Characterization of BET

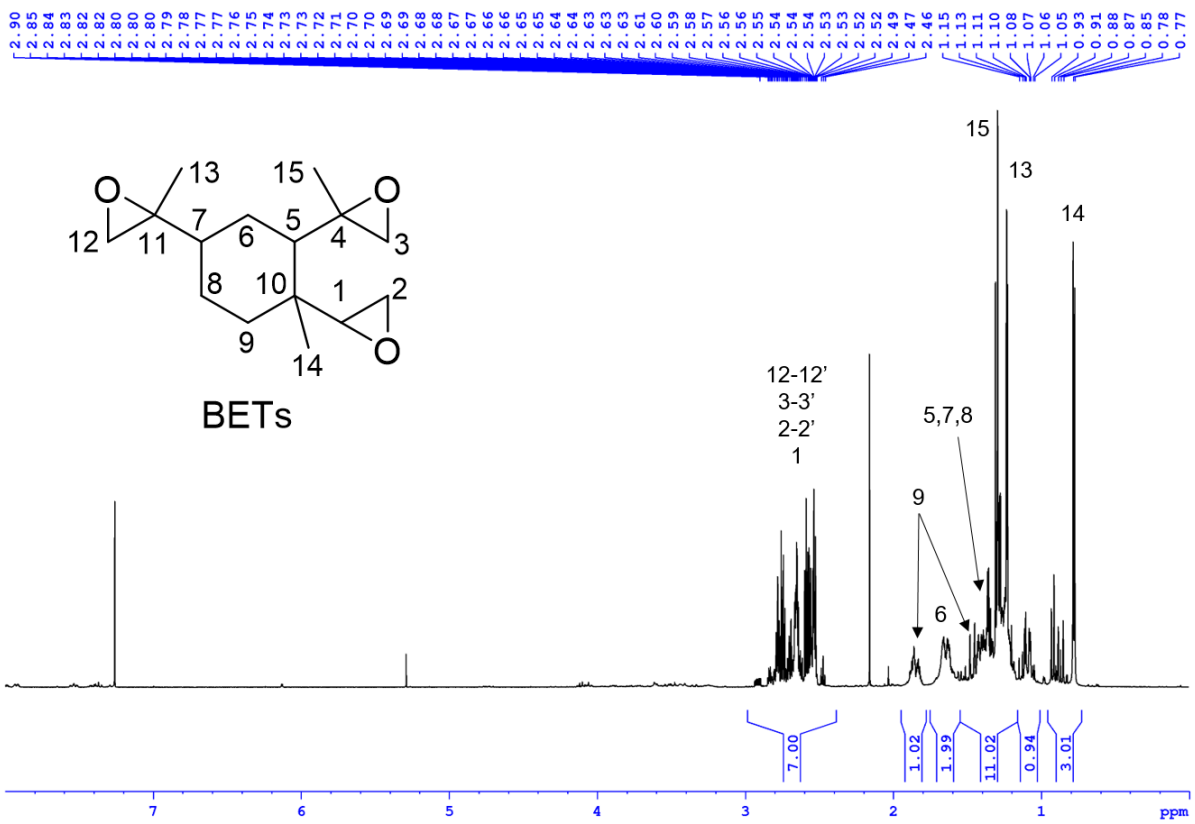


Figure S32 ^{1}H NMR of **BET** (400 MHz, rt, $CDCl_3$).

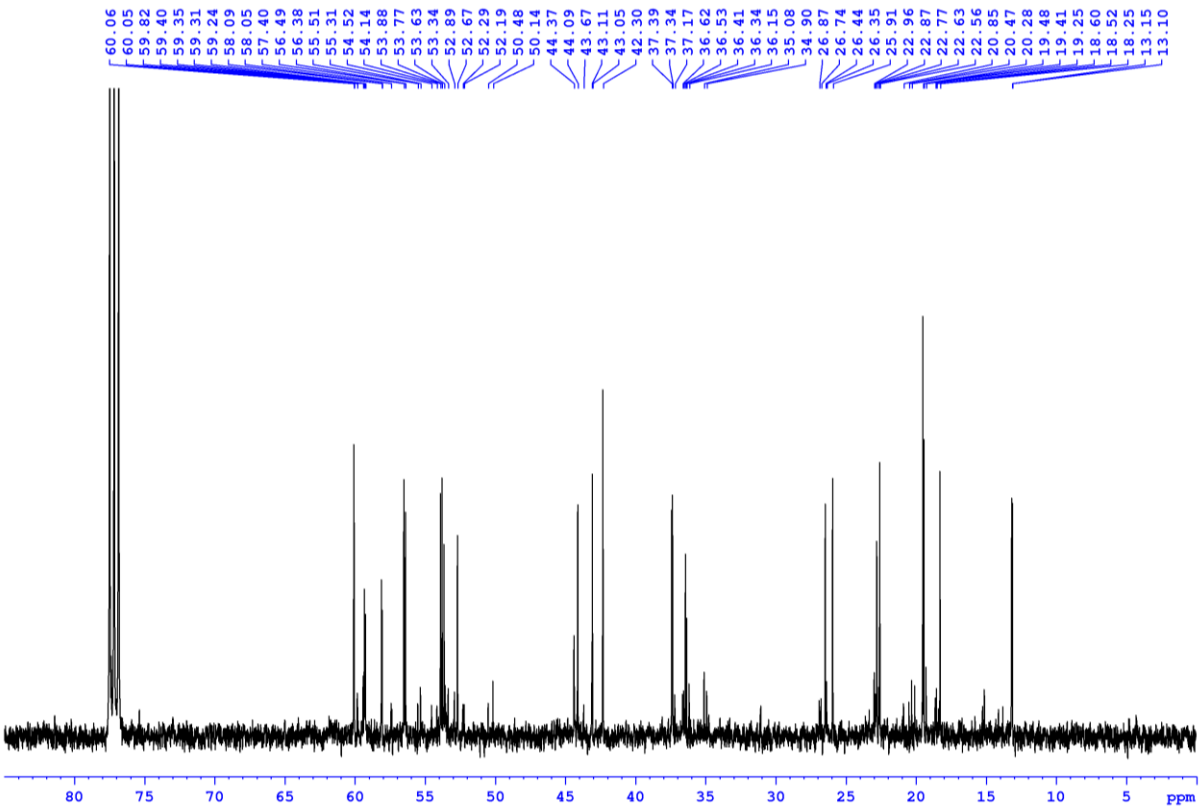


Figure S33 ^{13}C NMR of **BET** (400 MHz, rt, $CDCl_3$).

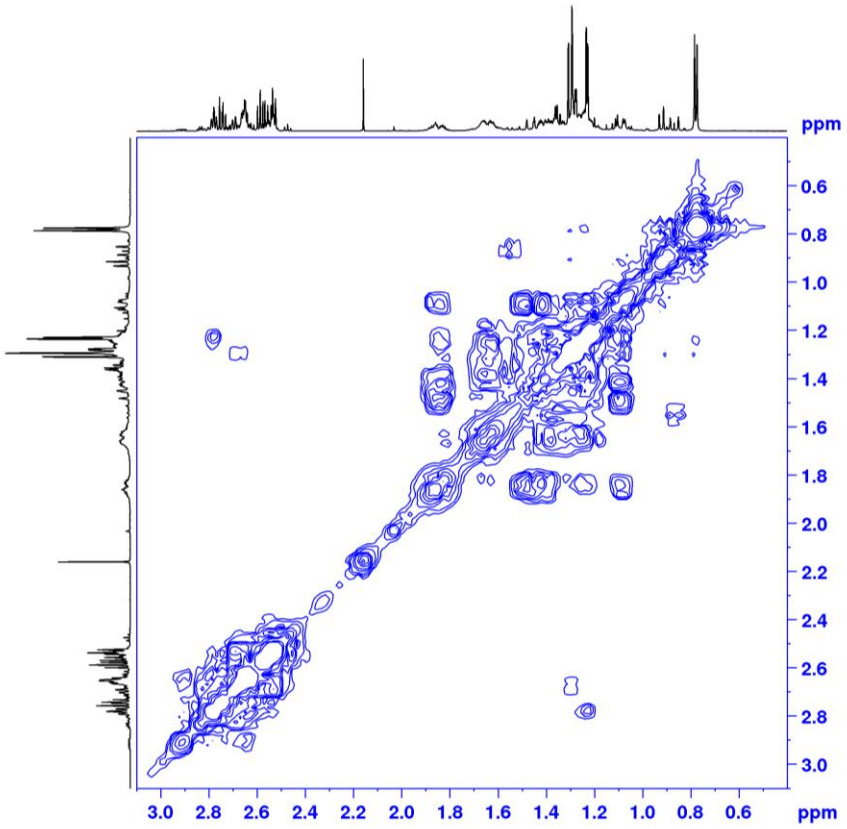


Figure S34 ^{1}H-^{1}H COSY NMR of **BET** (400 MHz, rt, $CDCl_3$).

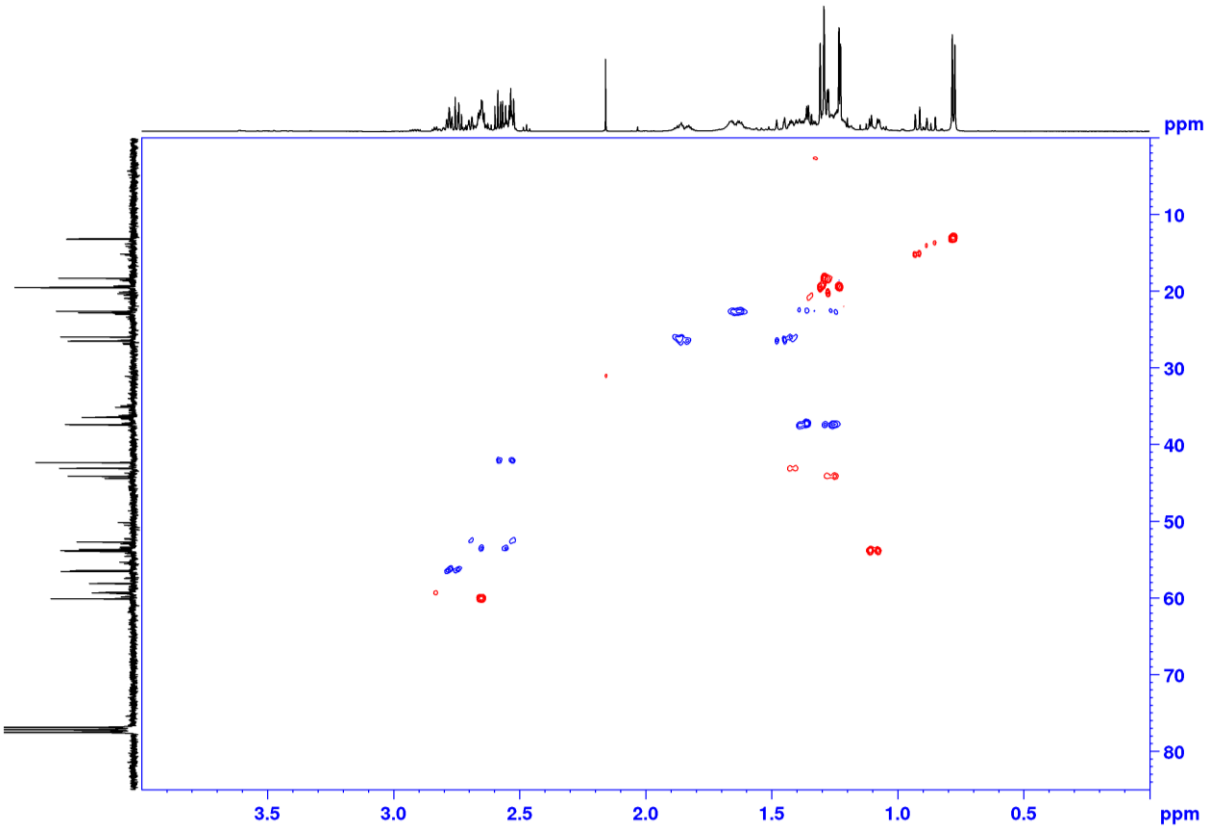


Figure S35 ^{1}H-^{13}C HSQC NMR of **BET** (400 MHz, rt, $CDCl_3$).

NMR Characterization of Poly(BEM-*alt*-PA)

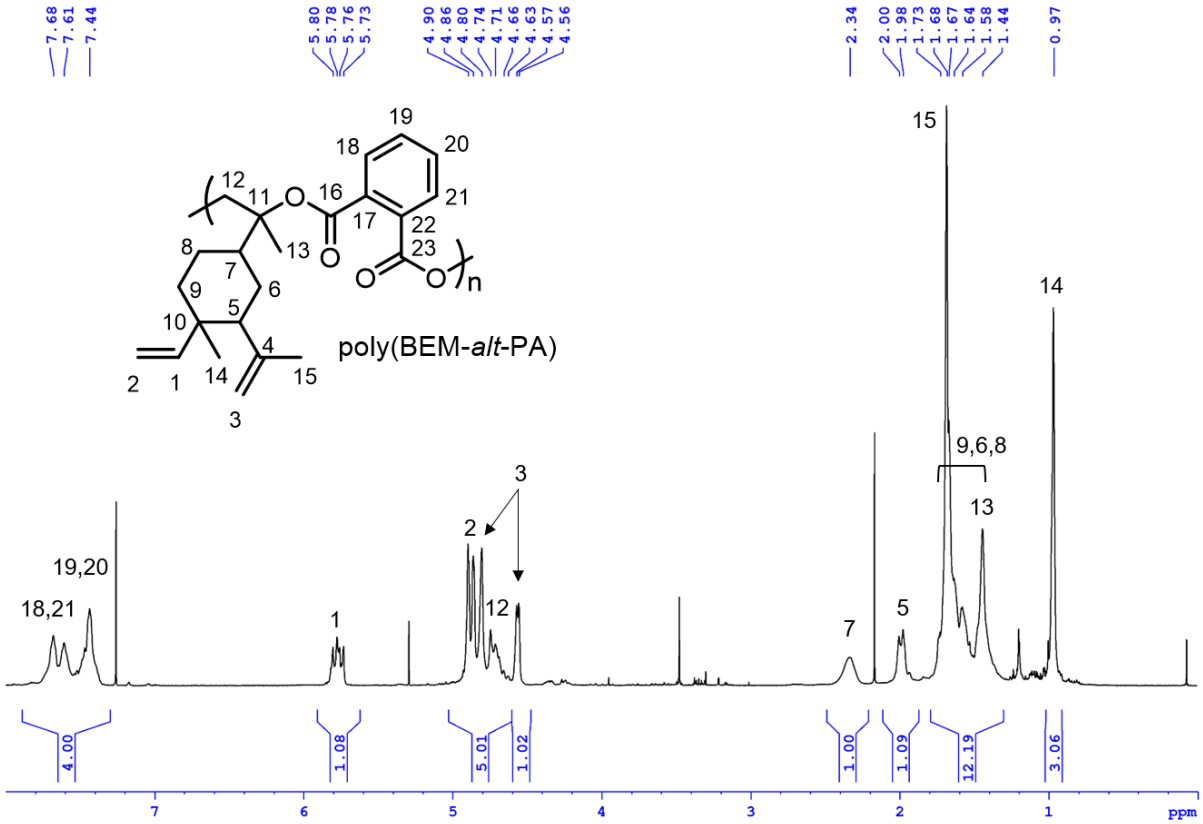


Figure S36 ^{1}H NMR of poly(**BEM**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

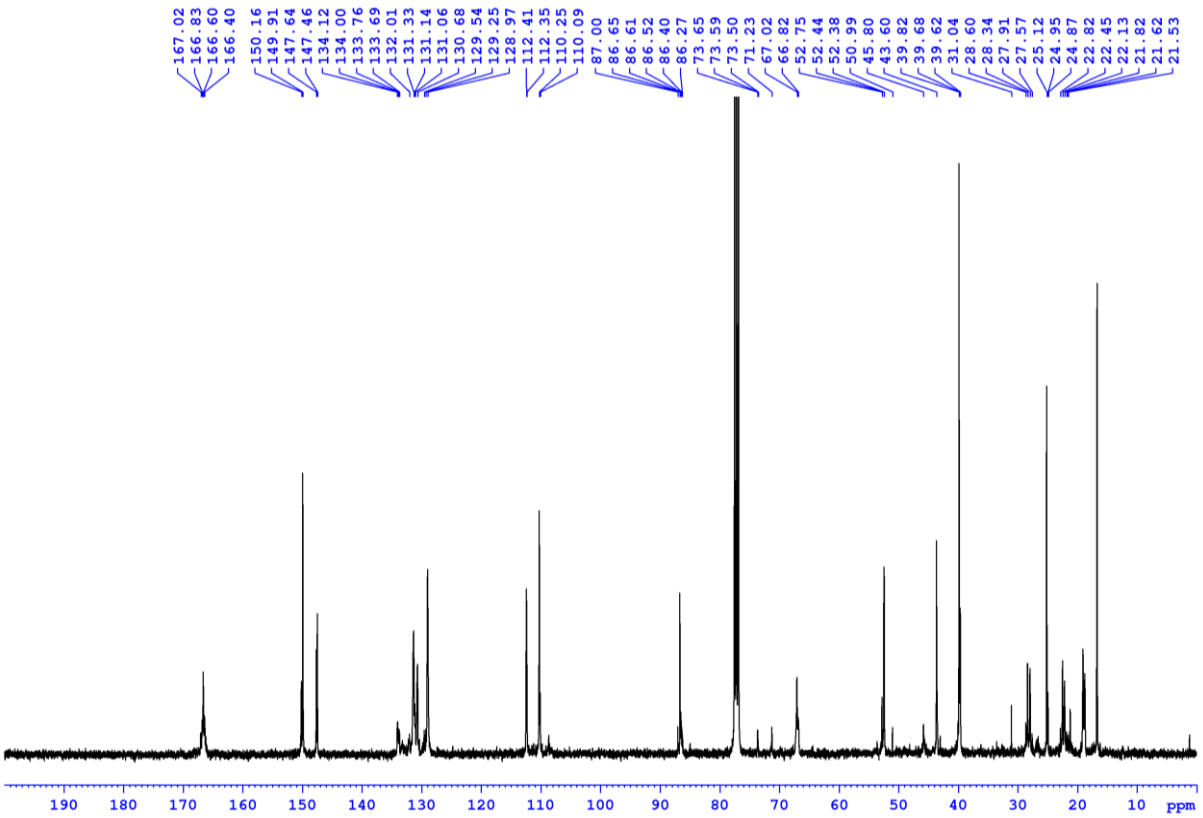


Figure S37 ^{13}C NMR of poly(**BEM**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

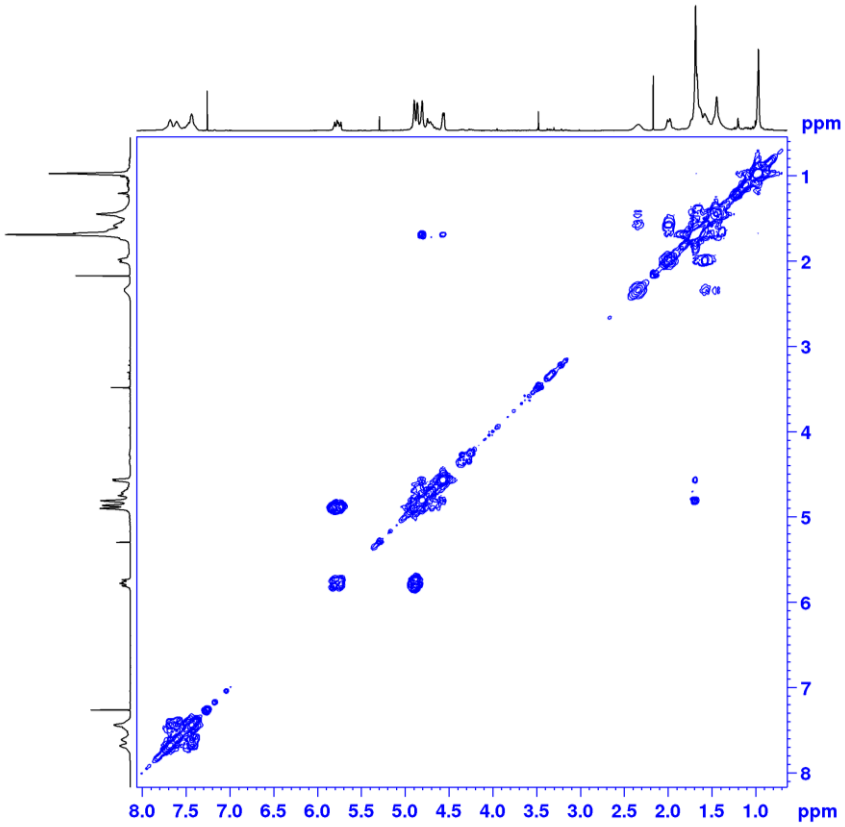


Figure S38 ^{1}H-^{1}H COSY NMR of poly(**BEM**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

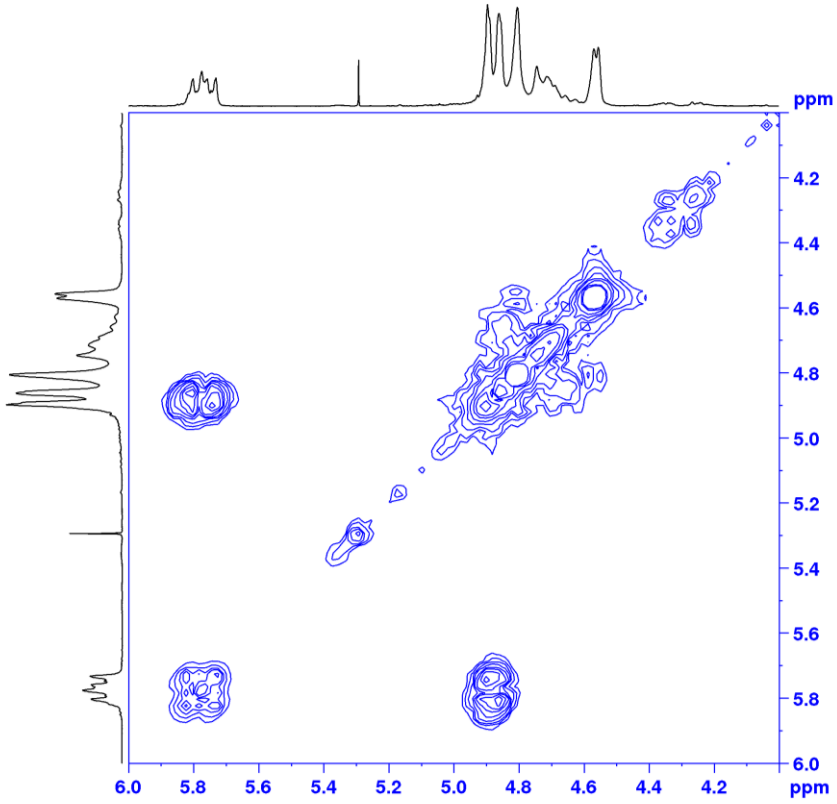


Figure S39 ^{1}H-^{1}H COSY NMR of poly(**BEM**-*alt*-**PA**) from 6.0 to 4.0 ppm (400 MHz, rt, $CDCl_3$).

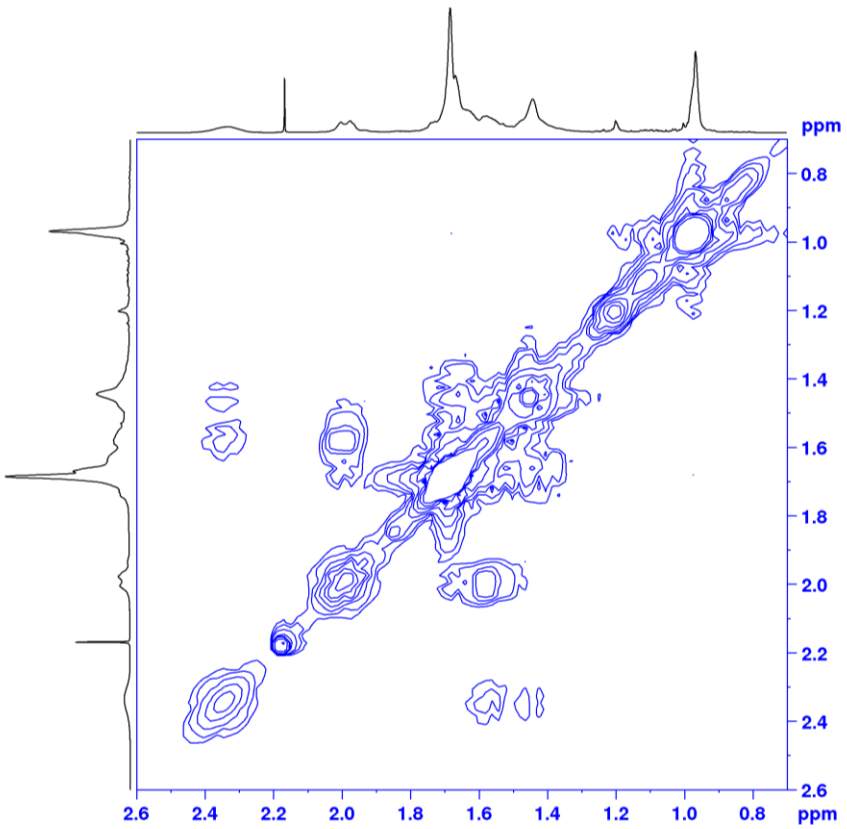


Figure S40 ^{1}H-^{1}H COSY NMR of poly(**BEM**-*alt*-**PA**) from 2.6 to 0.7 ppm (400 MHz, rt, $CDCl_3$).

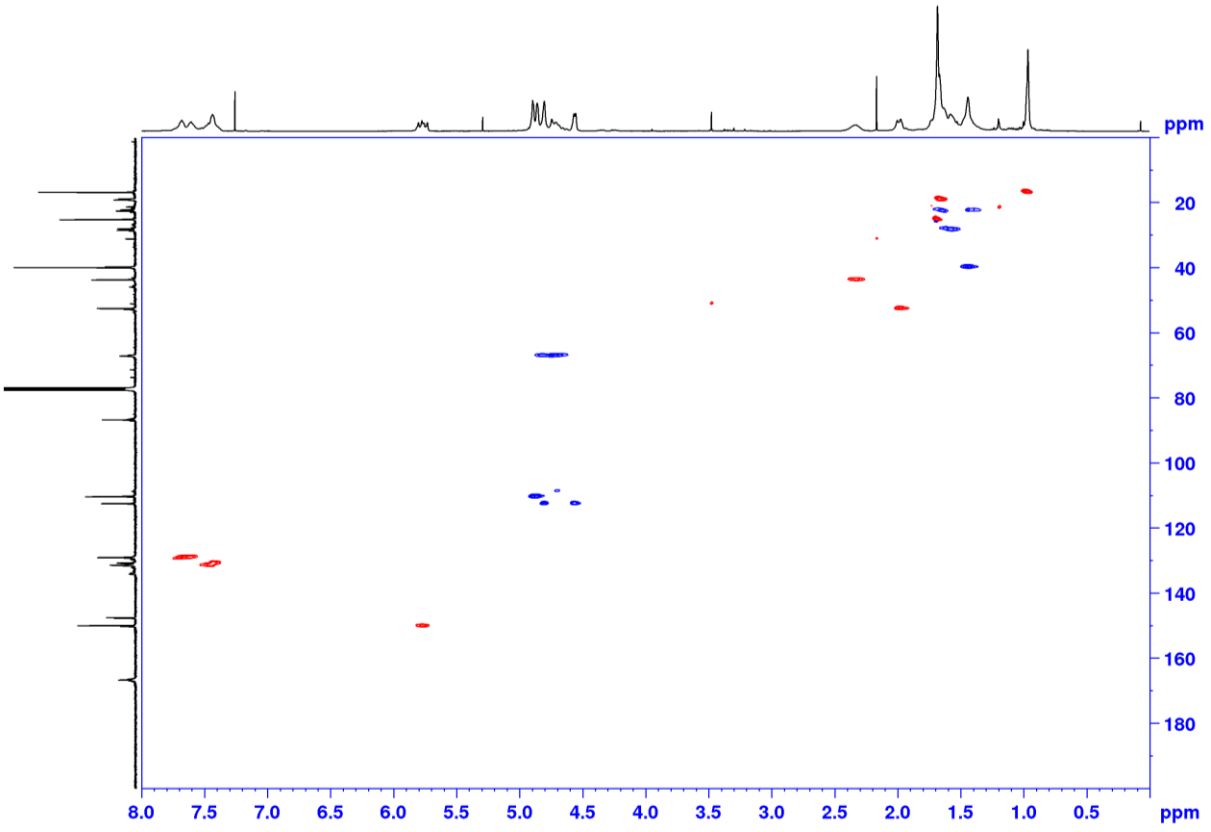


Figure S41 ^{1}H-^{13}C HSQC NMR of poly(**BEM**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

NMR Characterization of Crosslinked Poly(BED-*alt*-PA)

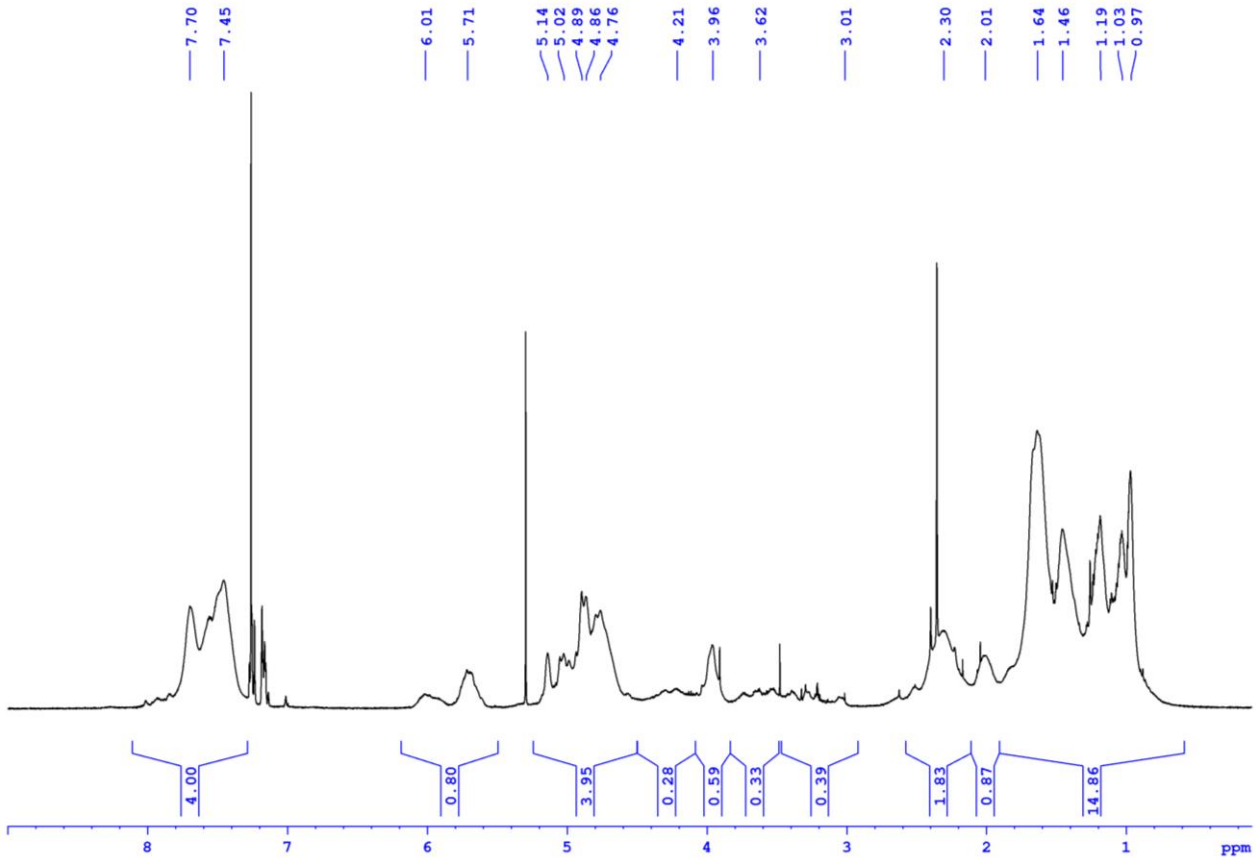


Figure S42 ^{1}H NMR of crosslinked poly(**BED**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

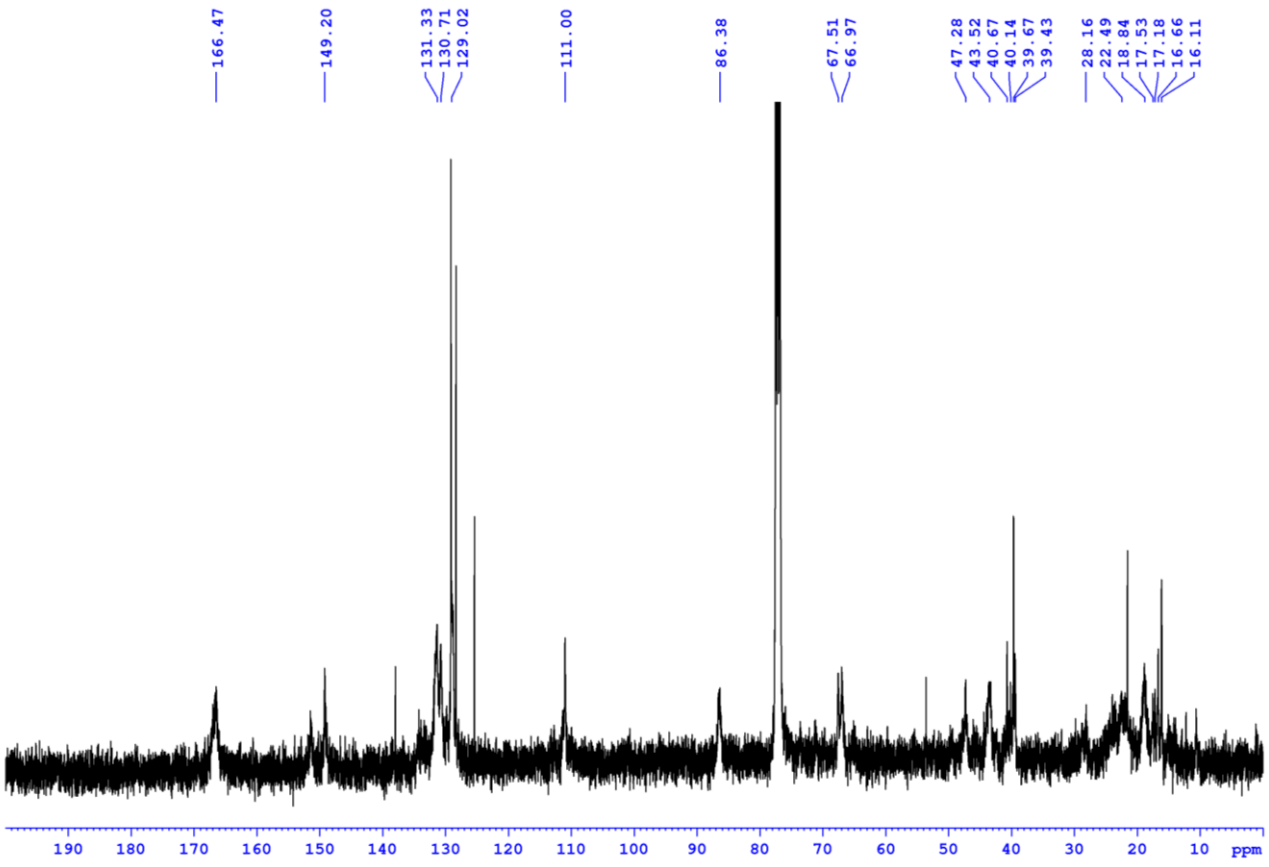


Figure S43 ^{13}C NMR of crosslinked poly(**BED**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

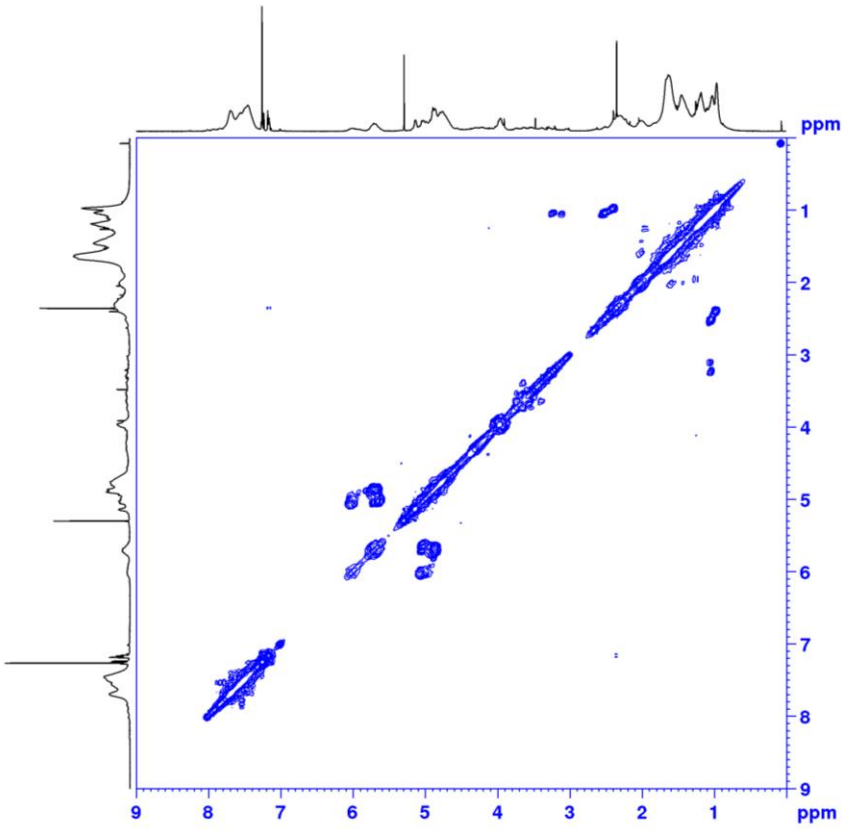


Figure S44 ^{1}H-^{1}H COSY NMR of crosslinked poly(**BED**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

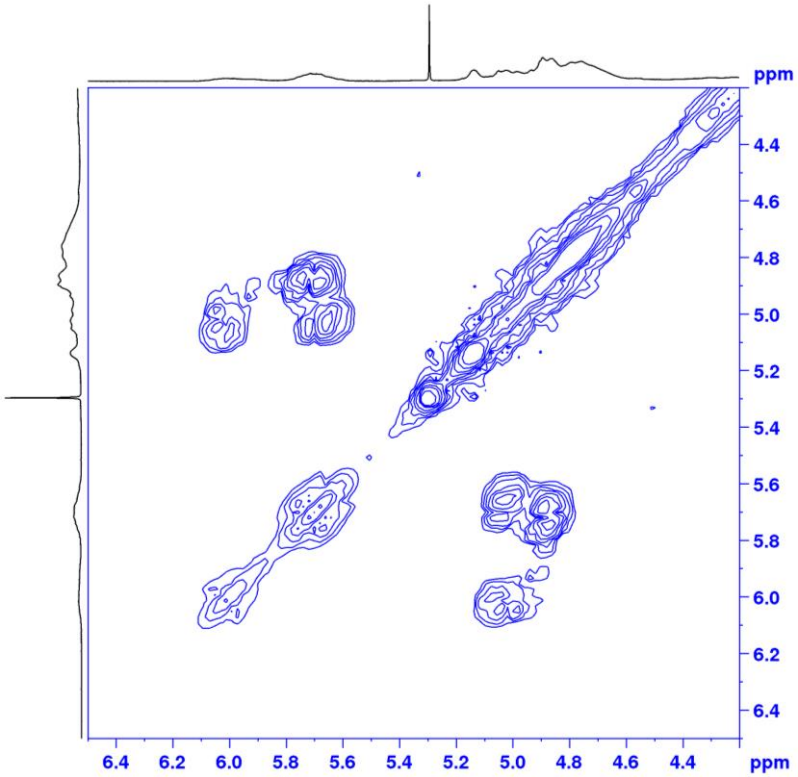


Figure S45 ^{1}H-^{1}H COSY NMR of crosslinked poly(**BED**-*alt*-**PA**) from 6.5 to 4.2 ppm (400 MHz, rt, $CDCl_3$).

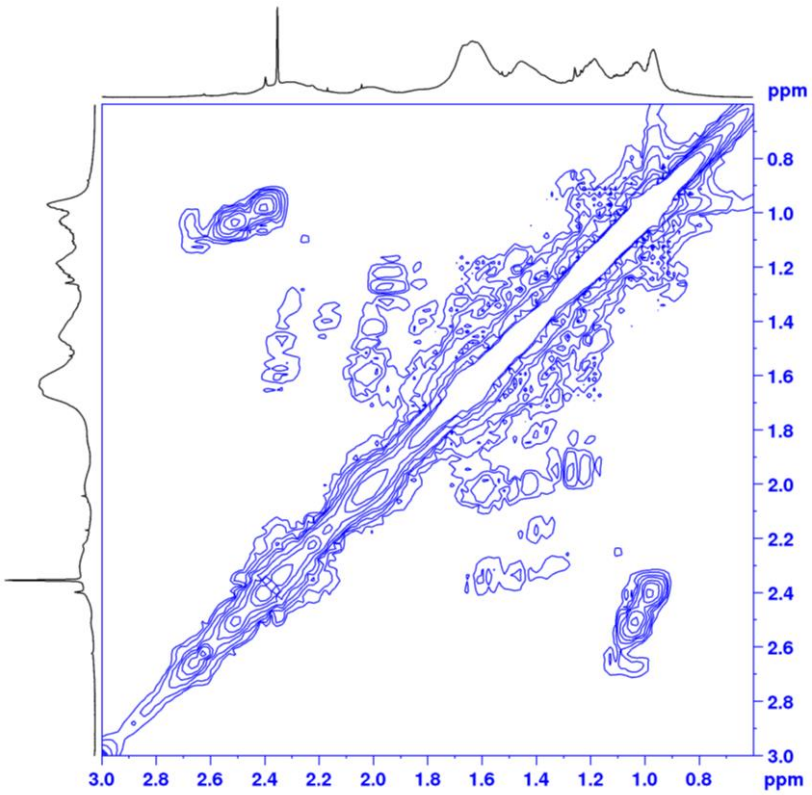


Figure S46 ^{1}H-^{1}H COSY NMR of crosslinked poly(**BED**-*alt*-**PA**) from 3.0 to 0.6 ppm (400 MHz, rt, $CDCl_3$).

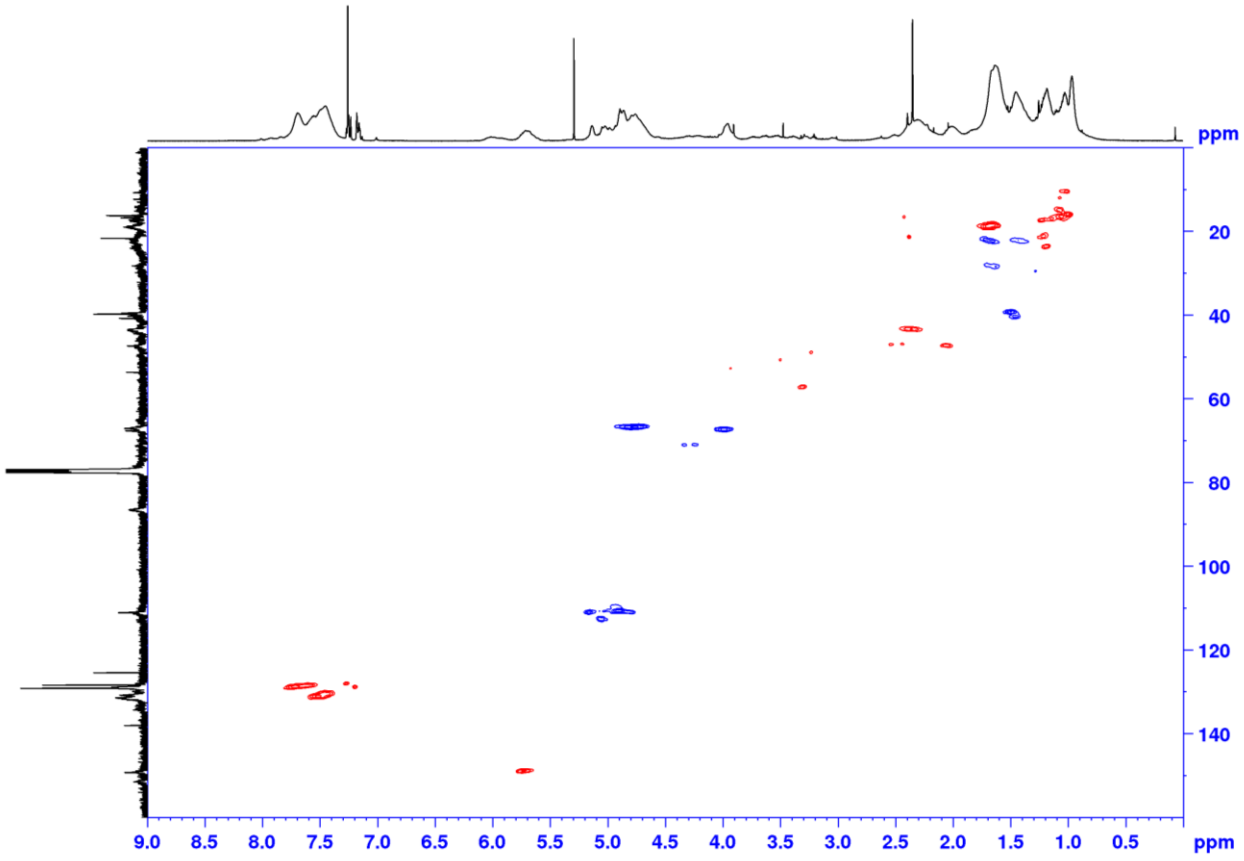


Figure S47 ^{1}H-^{13}C HSQC NMR of crosslinked poly(**BED**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

NMR Characterization of Poly(BED-*alt*-PA)

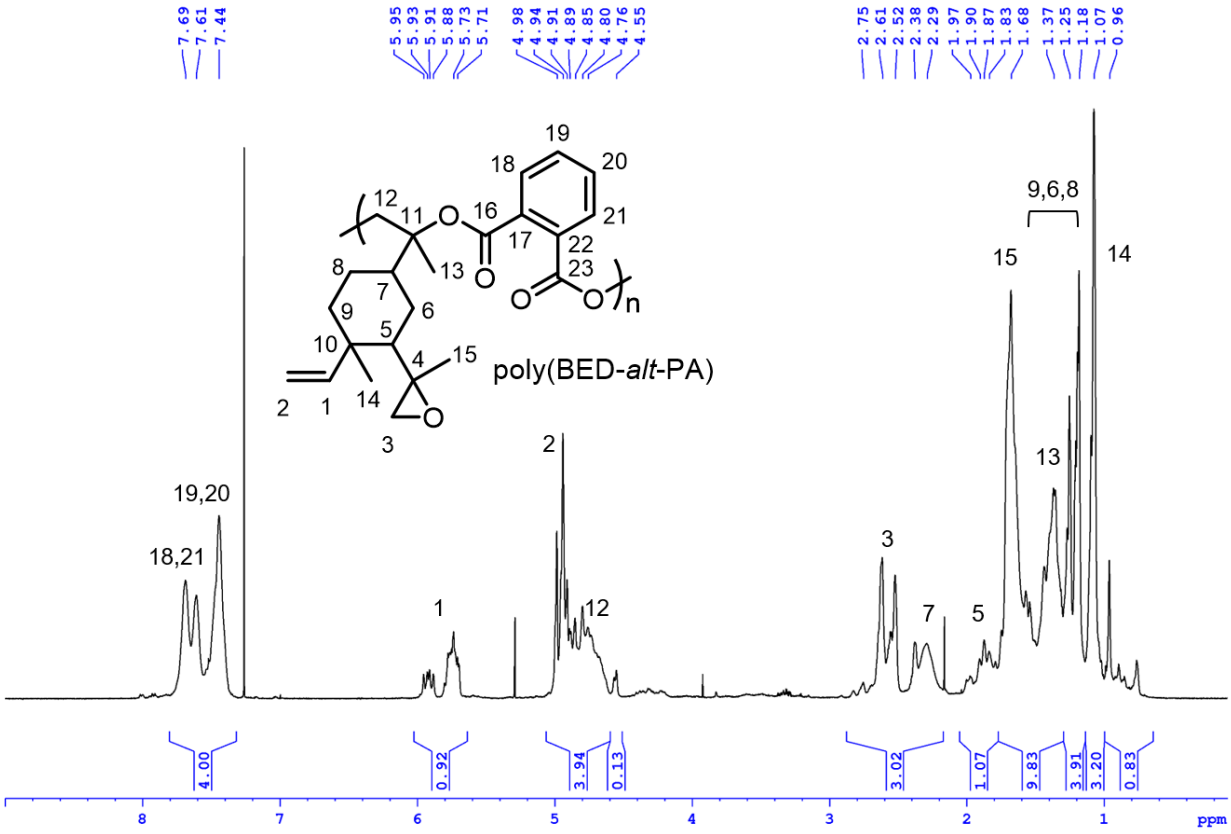


Figure S48 ^{1}H NMR of poly(**BED**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

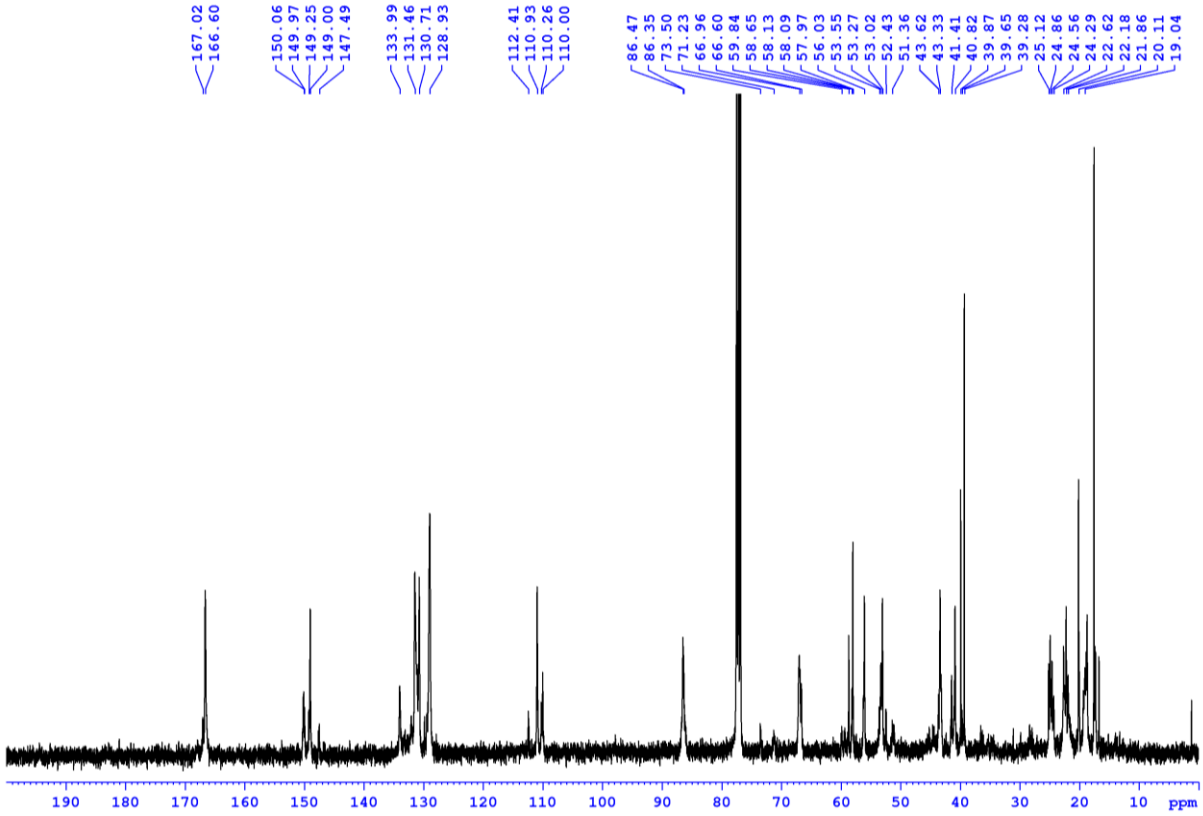


Figure S49 ^{13}C NMR of poly(**BED**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

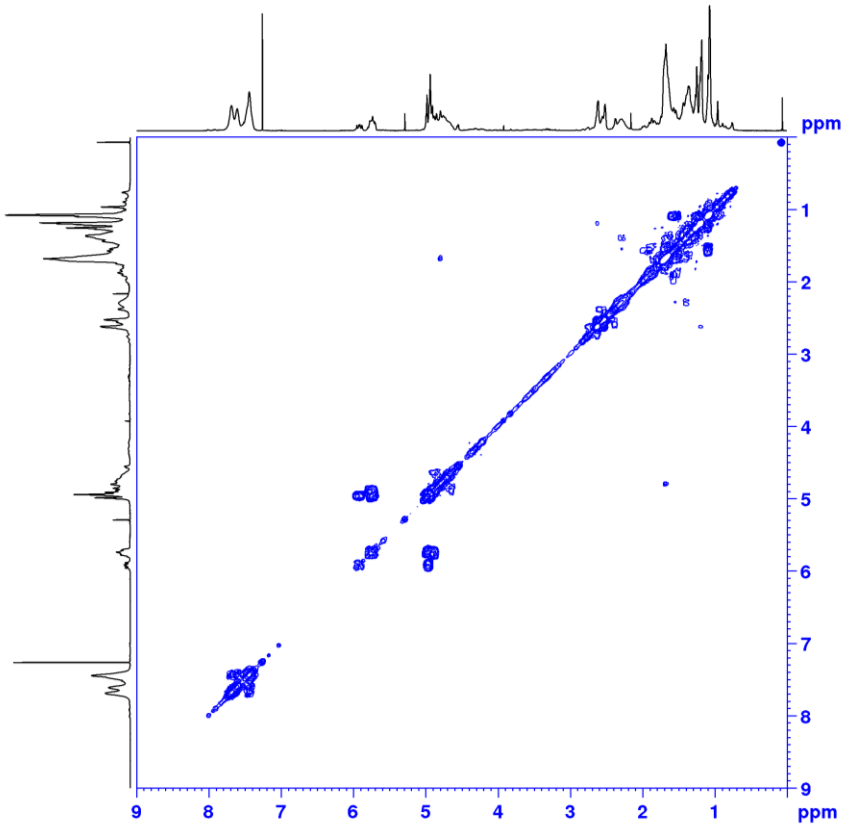


Figure S50 ^{1}H-^{1}H COSY NMR of poly(**BED**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

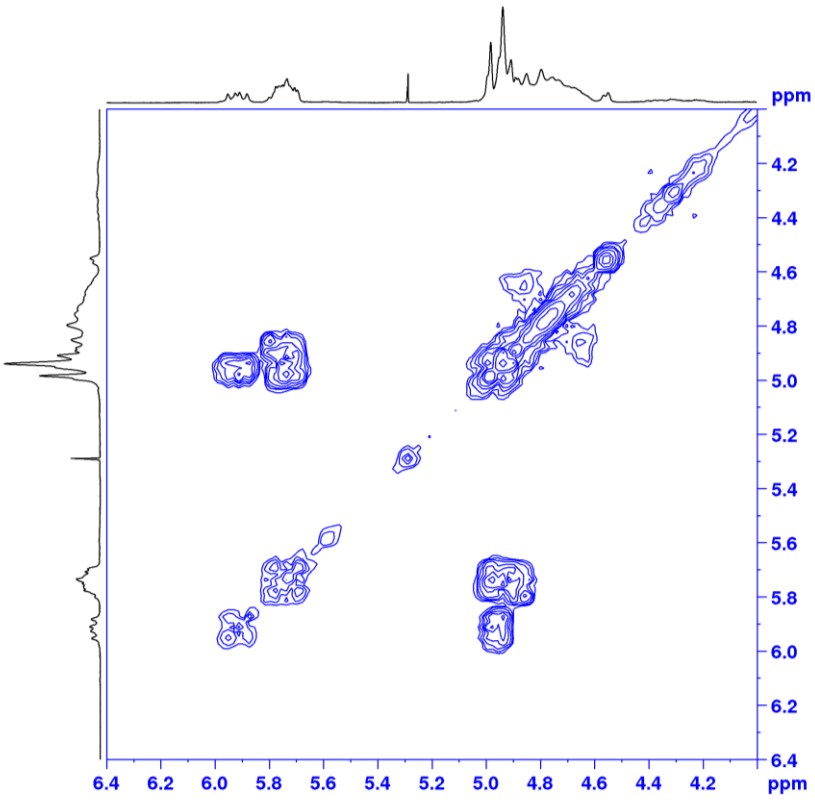


Figure S51 ^{1}H-^{1}H COSY NMR of poly(**BED**-*alt*-**PA**) from 6.0 to 4.0 ppm (400 MHz, rt, $CDCl_3$).

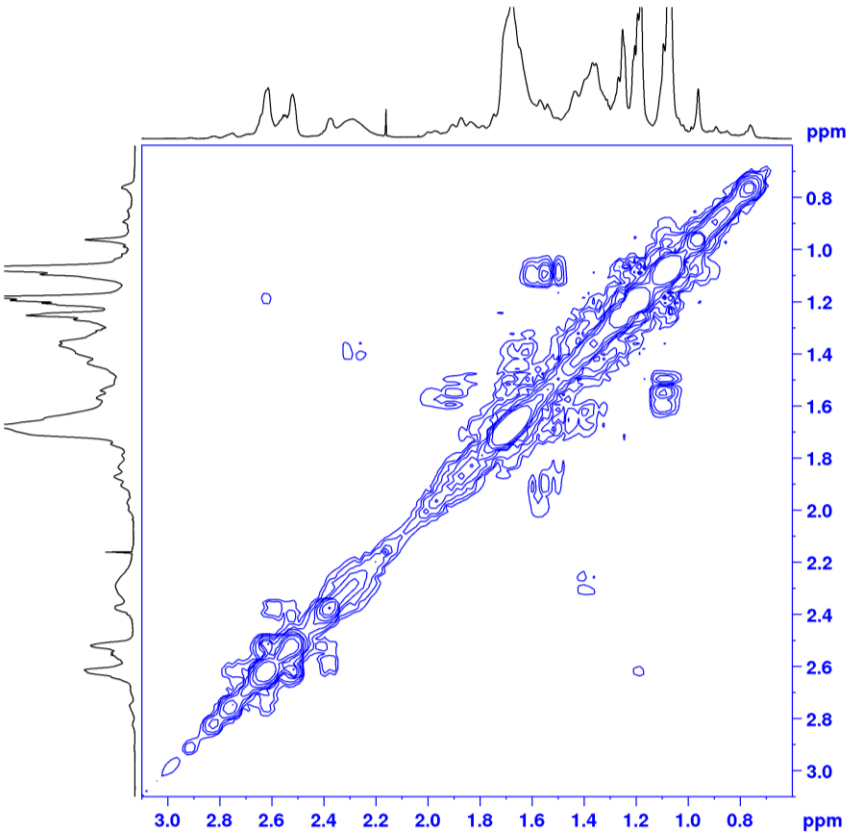


Figure S52 ^{1}H-^{1}H COSY NMR of poly(**BED**-*alt*-**PA**) from 3.1 to 0.6 ppm (400 MHz, rt, $CDCl_3$).

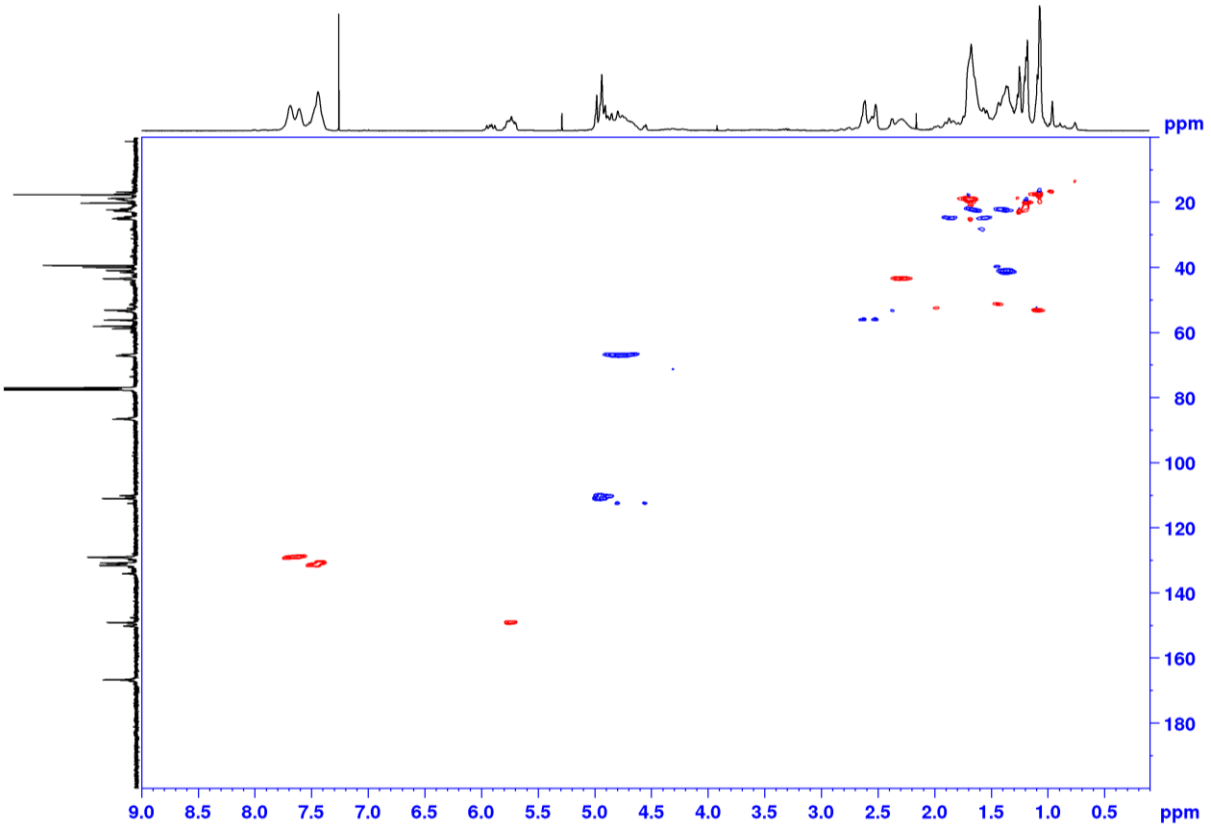


Figure S53 ^{1}H-^{13}C HSQC NMR of poly(**BED**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

NMR Characterization of Poly(BET-*alt*-PA)

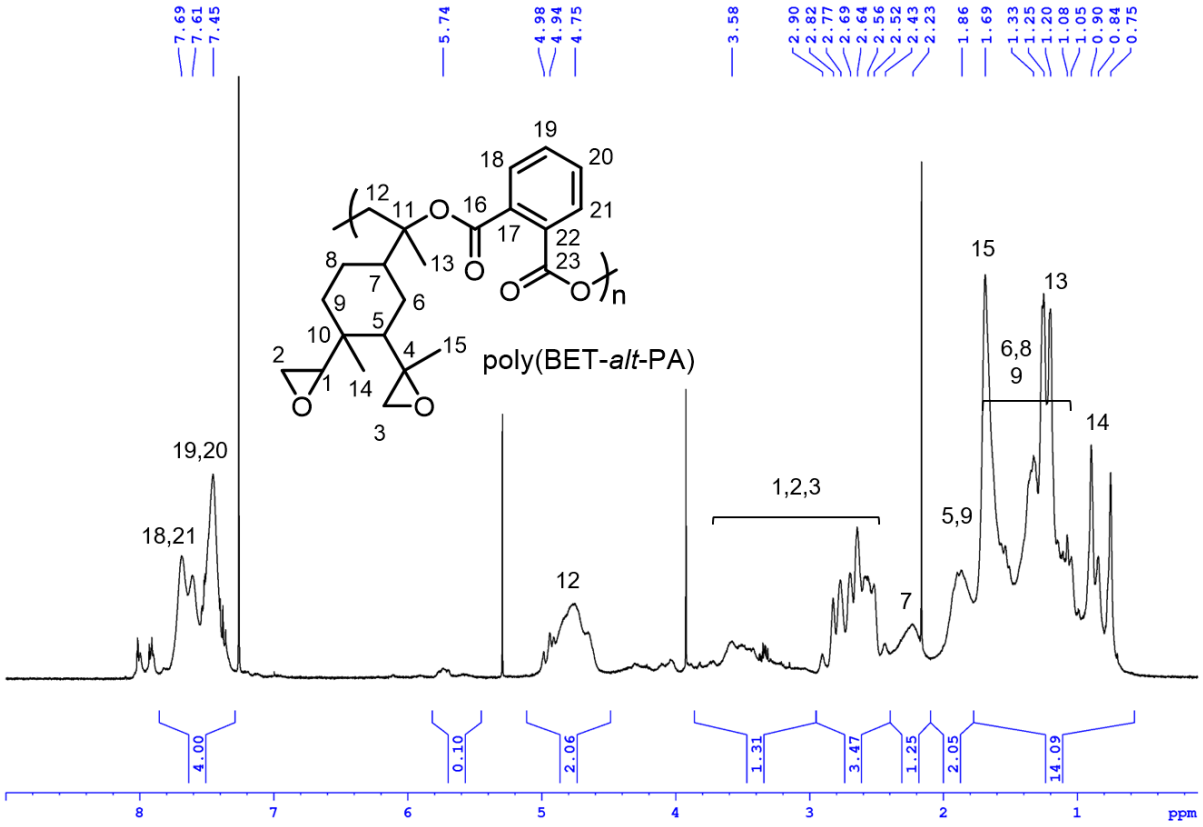


Figure S54 ^{1}H NMR of poly(**BET**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

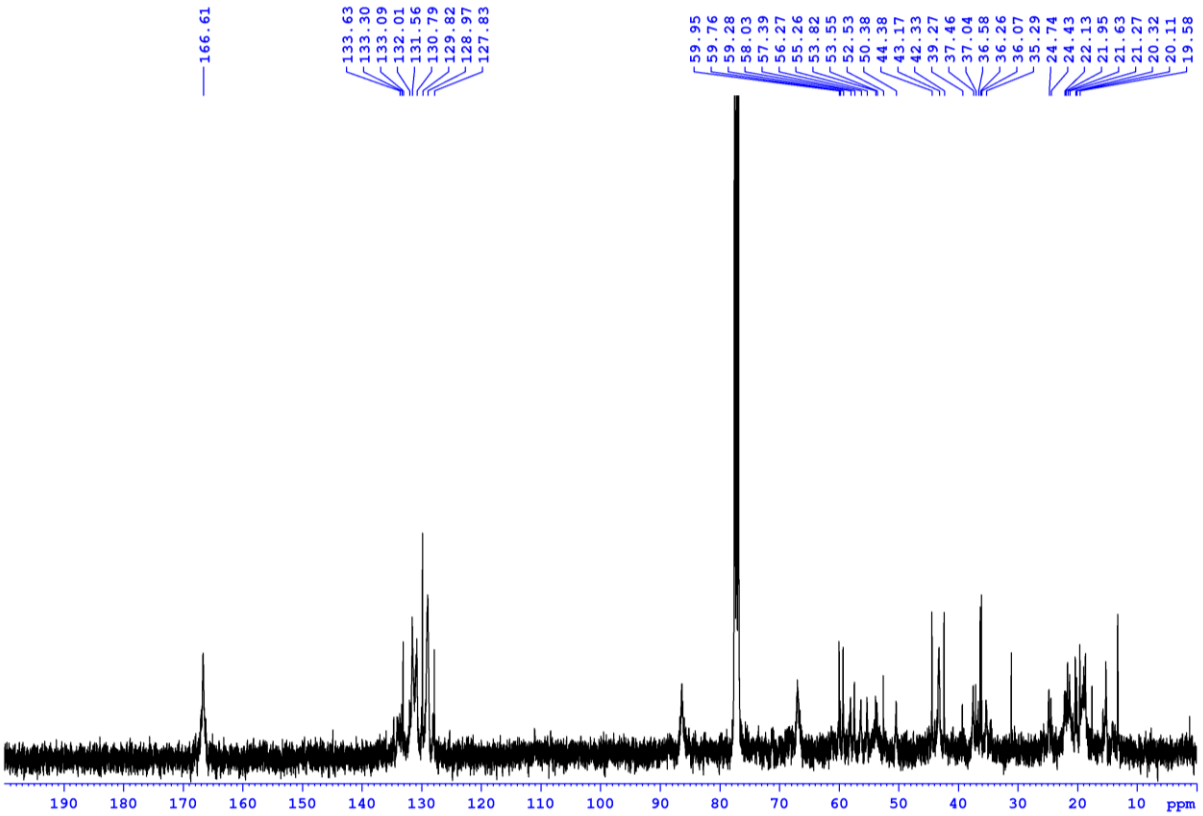


Figure S55 ^{13}C NMR of poly(**BET**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

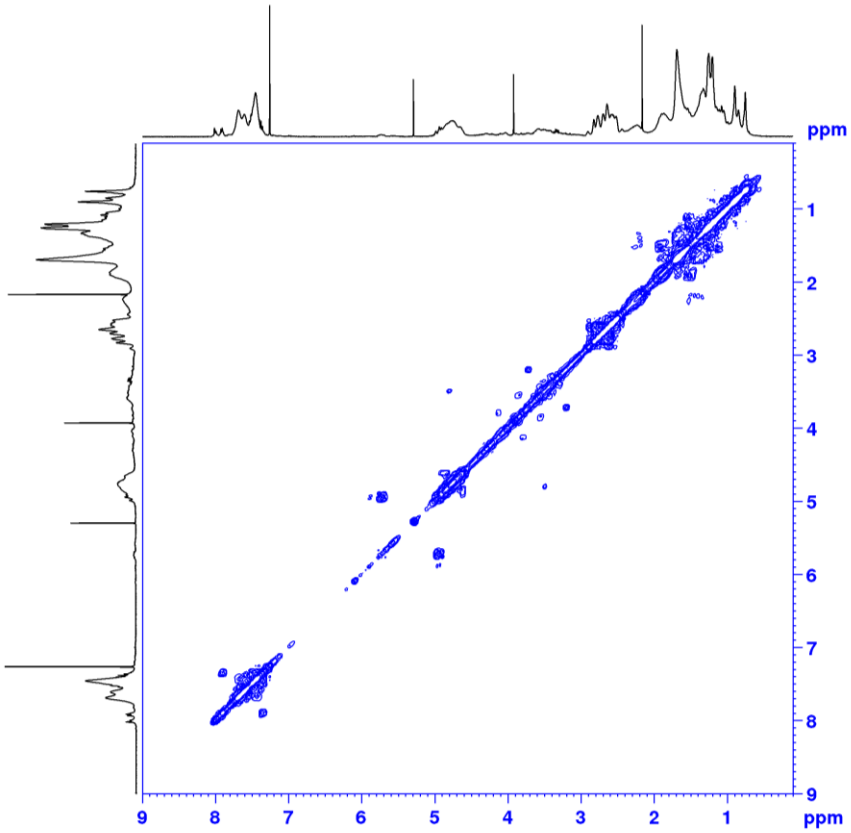


Figure S56 ^{1}H-^{1}H COSY NMR of poly(**BET**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

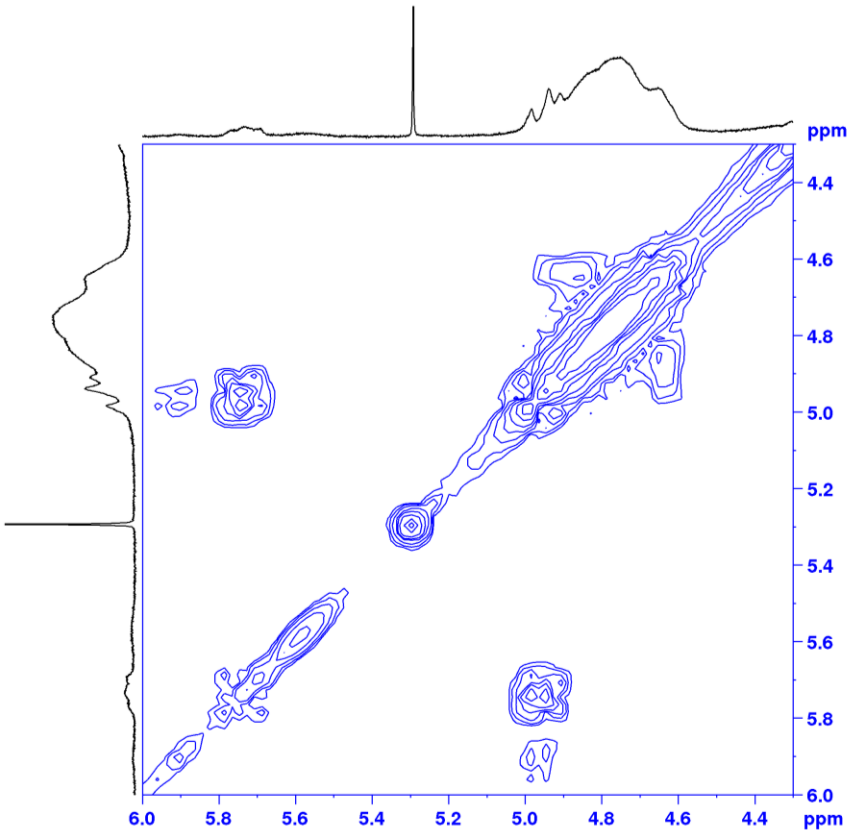


Figure S57 ^{1}H-^{1}H COSY NMR of poly(**BET**-*alt*-**PA**) from 6.0 to 4.3 ppm (400 MHz, rt, $CDCl_3$).

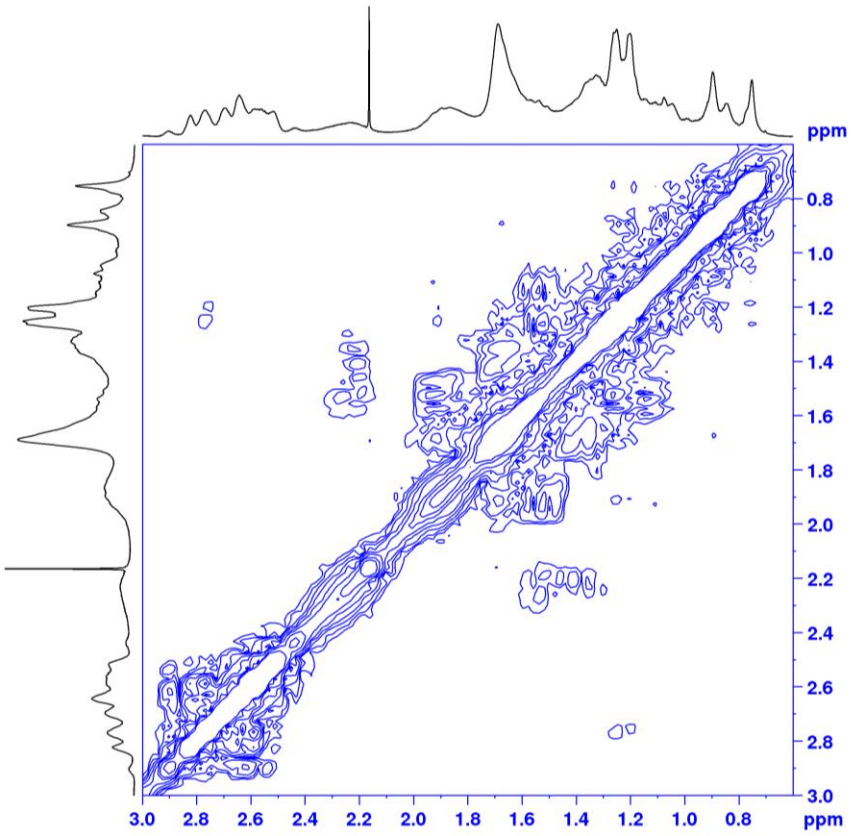


Figure S58 ^{1}H-^{1}H COSY NMR of poly(**BET**-*alt*-**PA**) from 3.0 to 0.6 ppm (400 MHz, rt, $CDCl_3$).

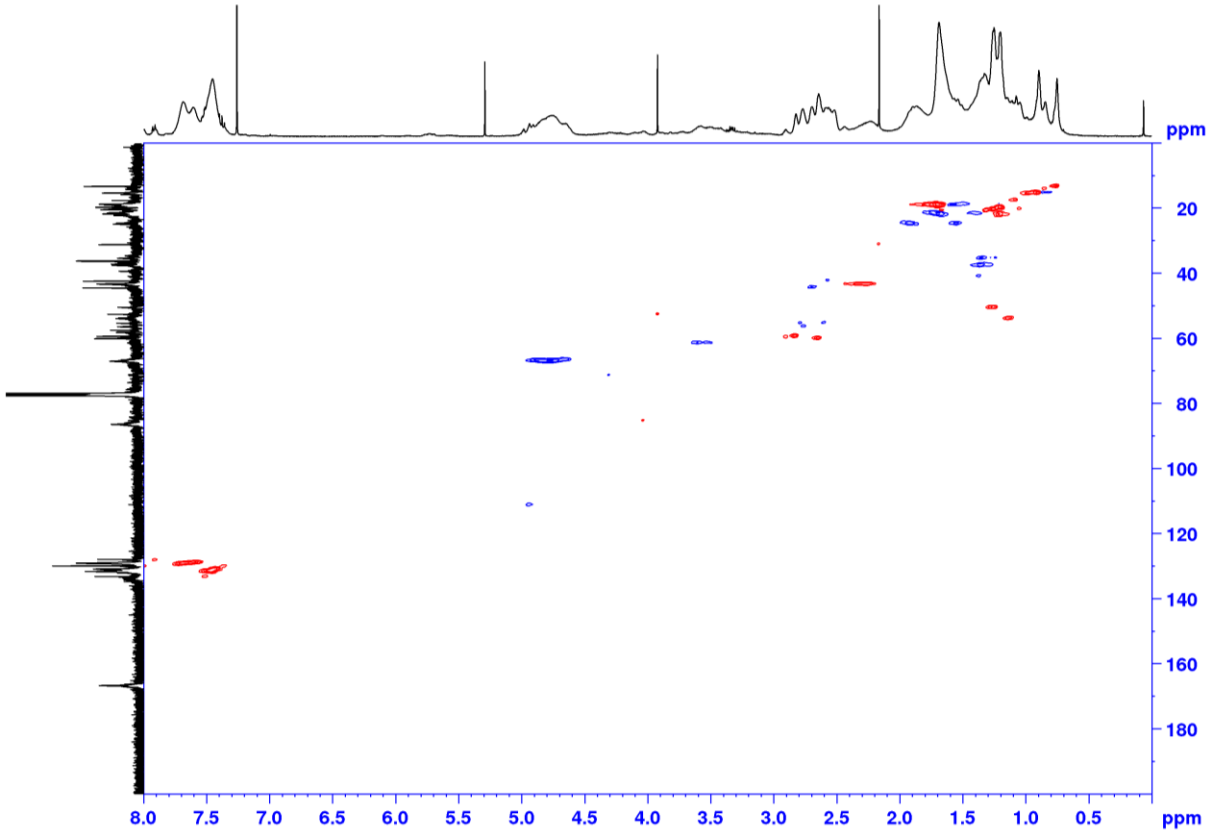
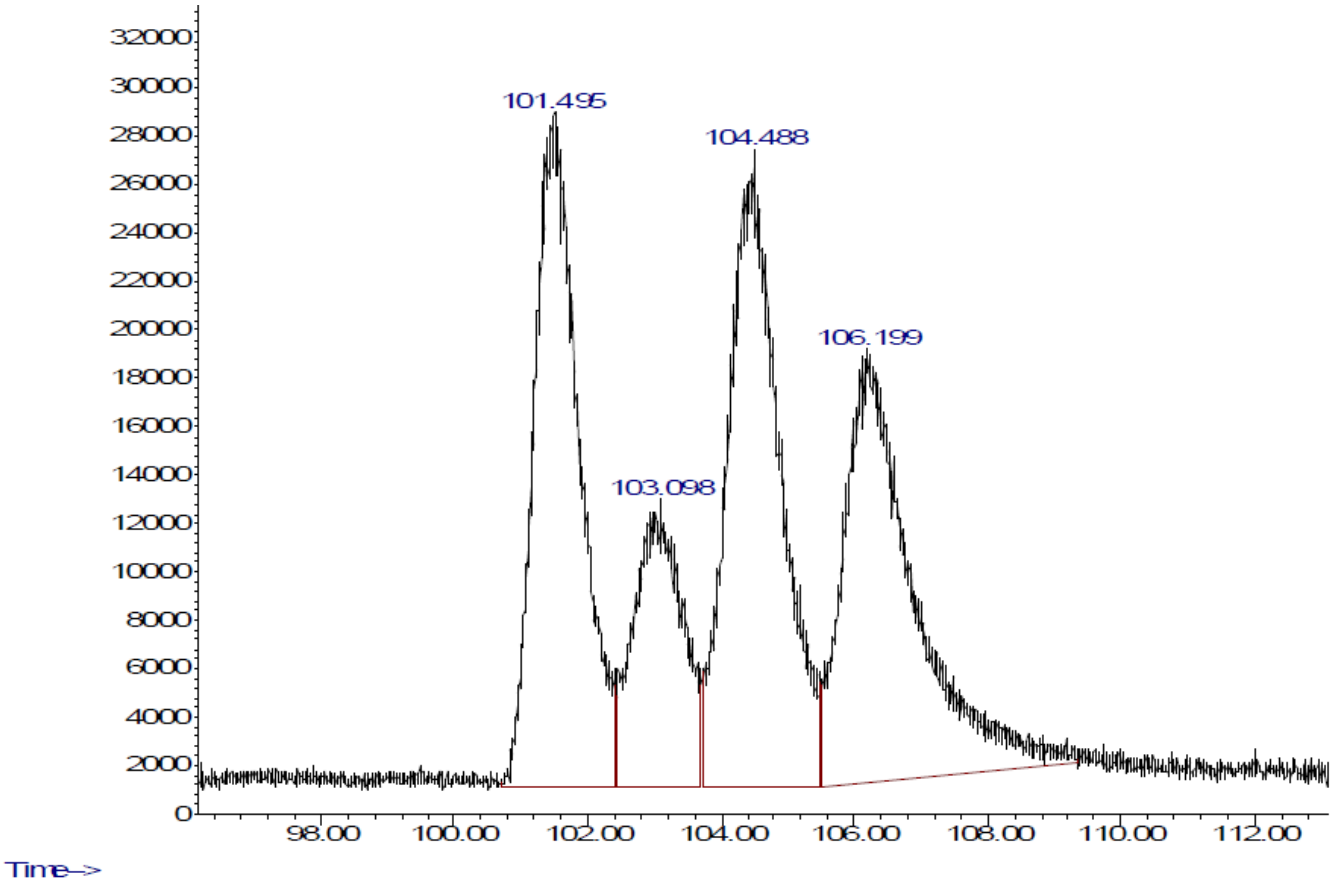


Figure S59 ^{1}H-^{13}C HSQC NMR of poly(**BET**-*alt*-**PA**) (400 MHz, rt, $CDCl_3$).

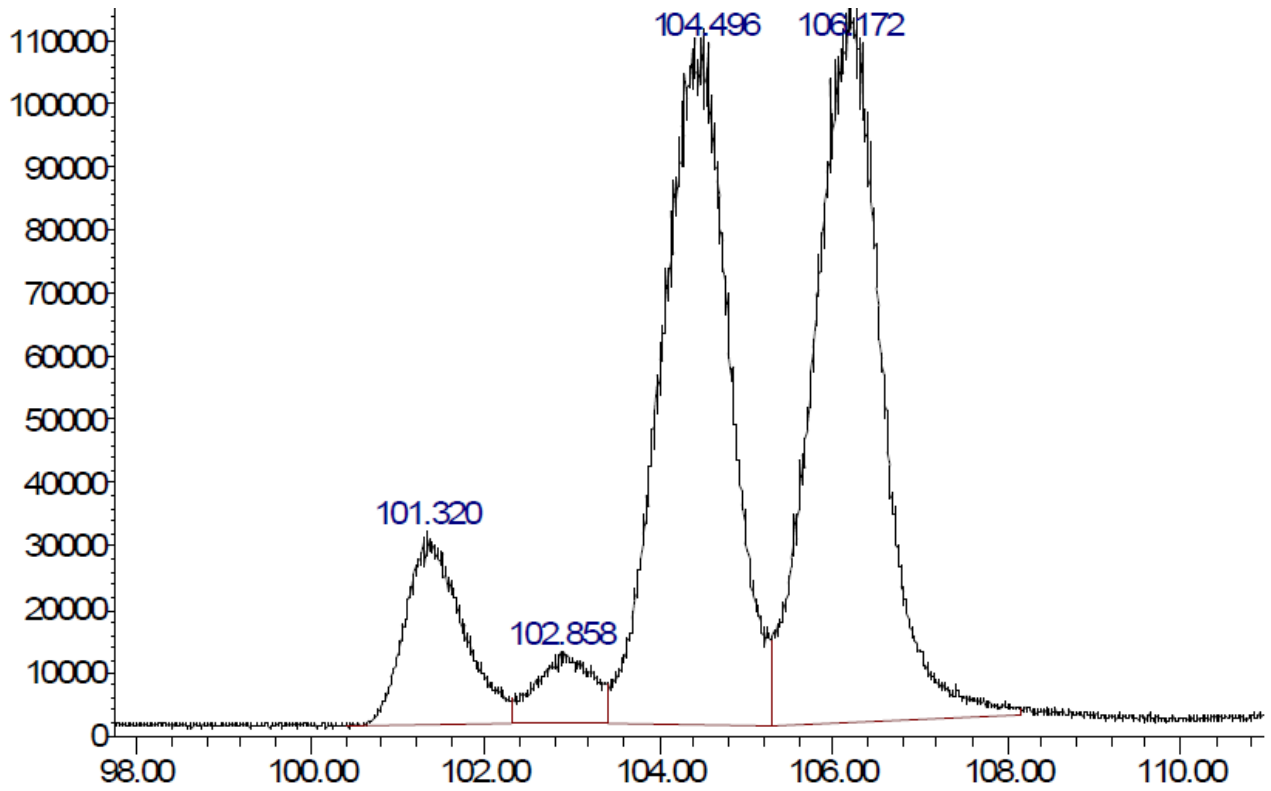
Gas chromatography–mass spectrometry analyses of BEM



peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	101.495	17150	17287	17447	M	28117	12877348	92.14%	28.208%
2	103.098	17449	17567	17674	M	11948	5901370	42.22%	12.927%
3	104.488	17676	17810	17984	M	26581	13976317	100.00%	30.615%
4	106.199	17986	18109	18656	M	17997	12896911	92.28%	28.251%

Sum of corrected areas: 45651945

Figure S60 GC-MS analysis of a 3,4-**BEM**/11,12-**BEM** mixture (49:51 ratio by NMR).
(all peaks show the same mass at m/z = 221.2.)

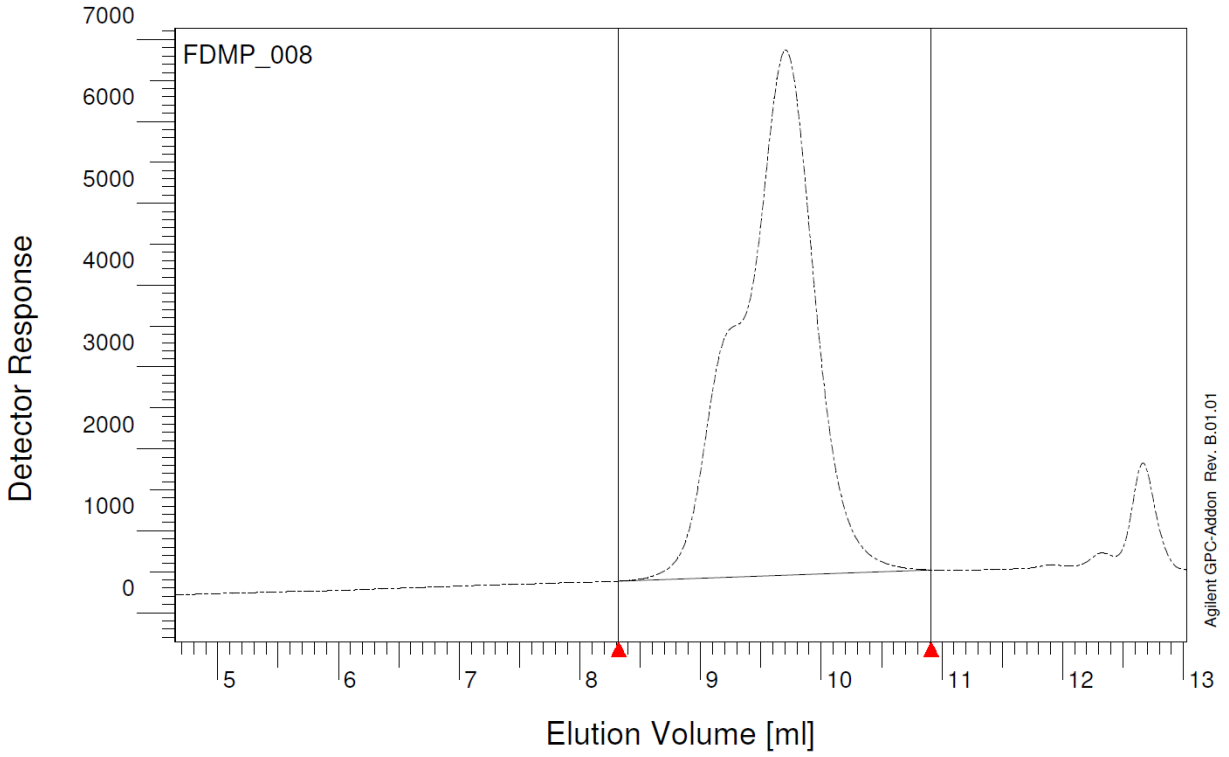


peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	101.320	17095	17256	17430	M	30754	13648528	22.26%	9.884%
2	102.858	17430	17525	17620	M	11155	4757614	7.76%	3.445%
3	104.496	17620	17811	17951	M	110269	58369270	95.19%	42.268%
4	106.172	17951	18104	18452	M	115306	61317358	100.00%	44.403%

Sum of corrected areas: 138092770

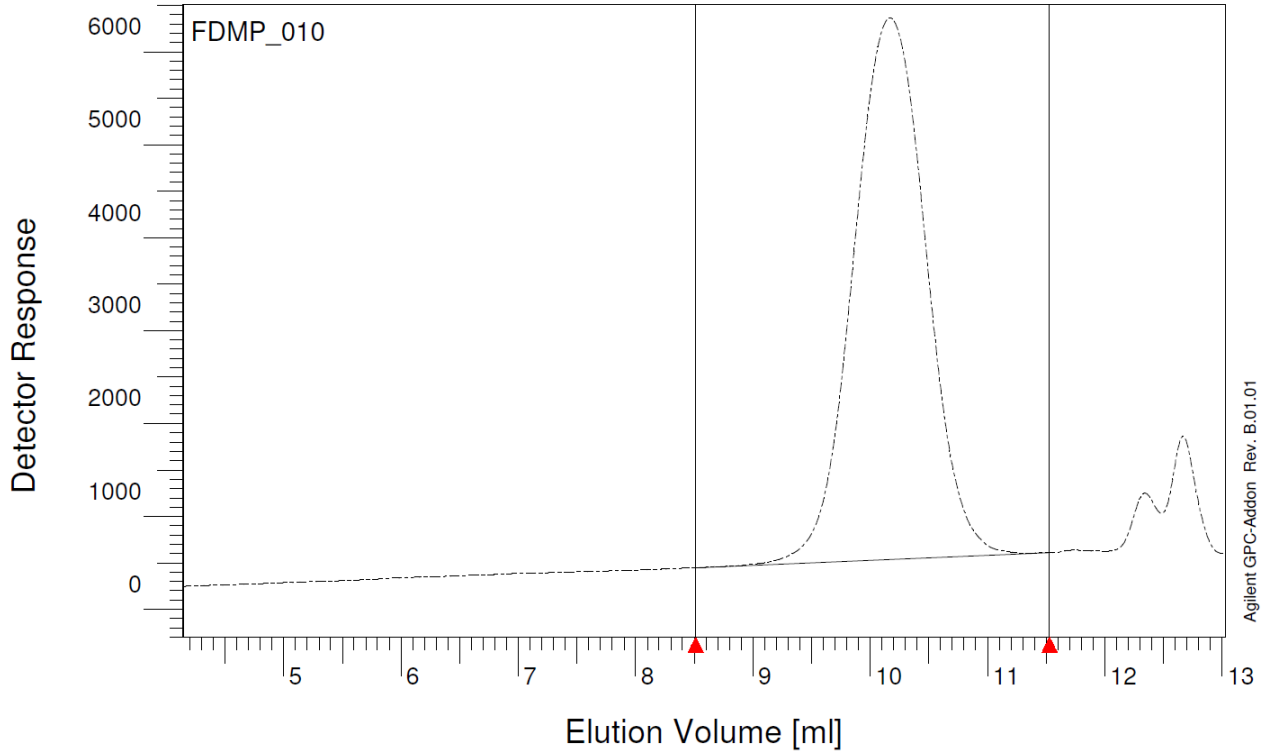
Figure S61 GC-MS analysis of a 3,4-**BEM**/11,12-**BEM** mixture (20:80 ratio by NMR).
(all peaks show the same mass at m/z = 221.2.)

Gel Permeation Chromatography of BE-Based Polyesters



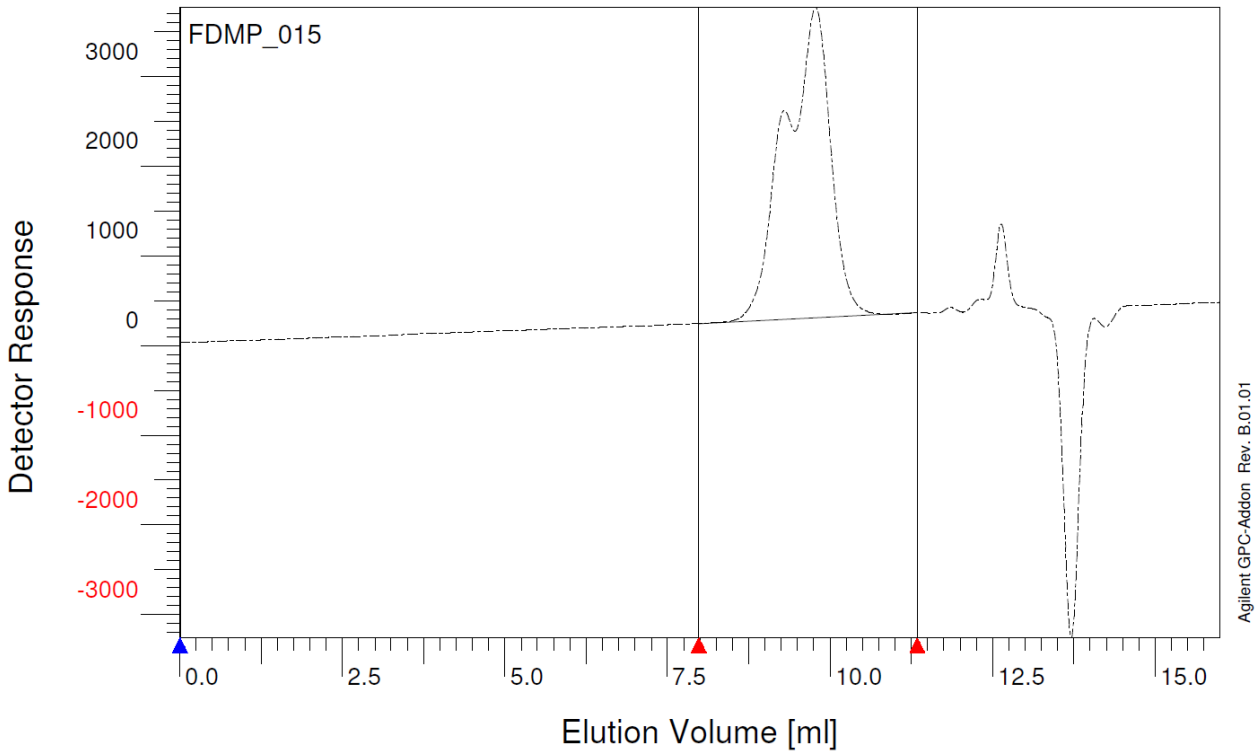
M_n (Da)	M_W (Da)	M_z (Da)	M_p (Da)	*Đ*
6.9586e3	8.2465e3	9.9003e3	6.5865e3	1.1851

Figure S62 GPC trace of poly(**BEM**-*alt*-**PA**) sample related to entry 1 table 1.



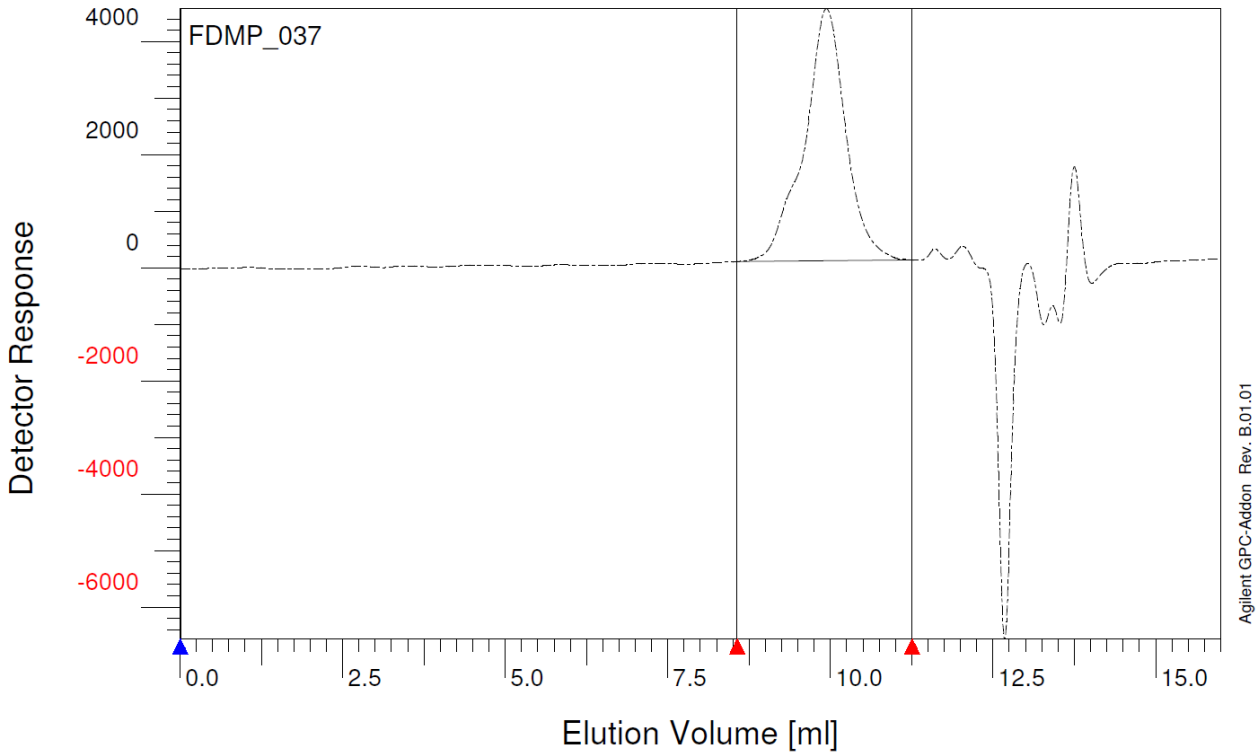
M_n (Da)	M_W (Da)	M_z (Da)	M_p (Da)	*Đ*
3.5119e3	3.9700e3	4.5194e3	3.7574e3	1.1304

Figure S63 GPC trace of poly(**BEM**-*alt*-**PA**) sample related to entry 2 table 1.



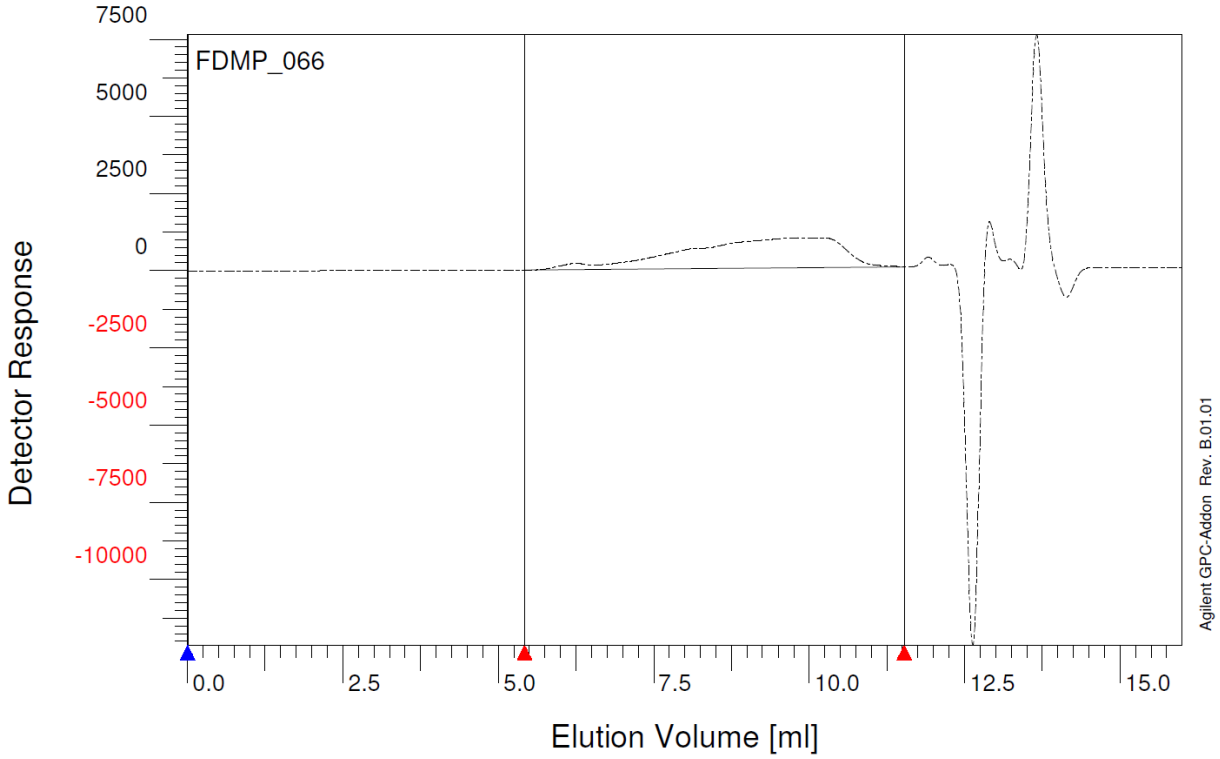
M_n (Da)	M_W (Da)	M_z (Da)	M_p (Da)	*Đ*
6.8755e3	8.3279e3	1.0224e4	6.0224e3	1.2112

Figure S64 GPC trace of poly(**BEM**-*alt*-**PA**) sample related to entry 6 Table 1.



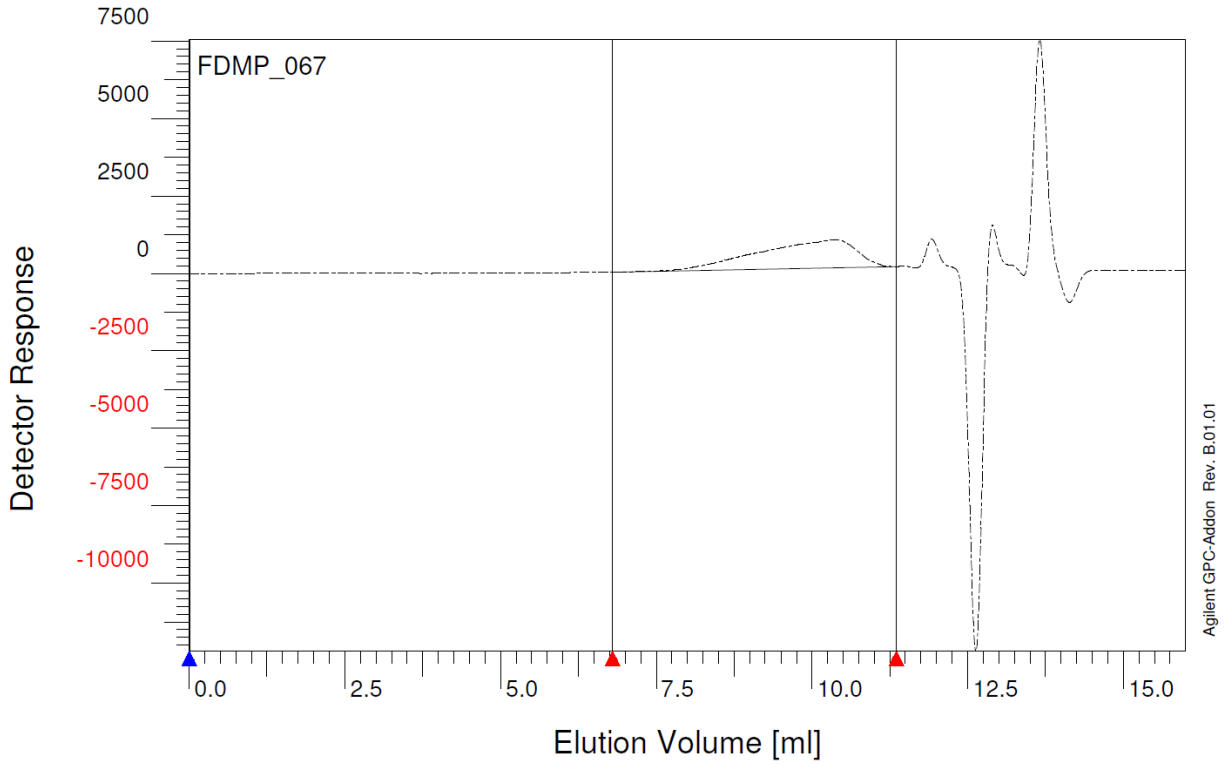
M_n (Da)	M_W (Da)	M_z (Da)	M_p (Da)	*Đ*
4.3597e3	5.2704e3	6.4813e3	4.5723e3	1.2089

Figure S65 GPC trace of poly(**BEM**-*alt*-**PA**) sample related to entry 7 Table 1.



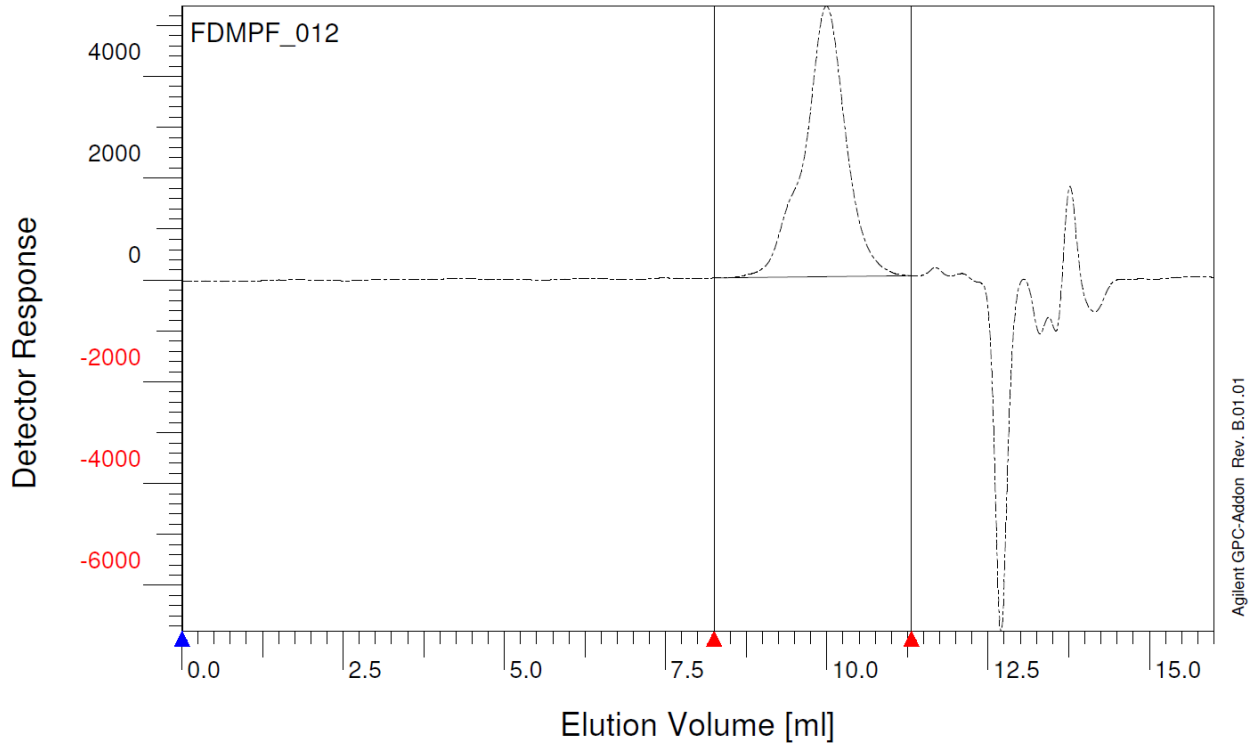
M_n (Da)	M_W (Da)	M_z (Da)	M_p (Da)	*Đ*
6.8044e3	1.2023e5	1.6105e6	5.3193e3	1.7669

Figure S66 GPC trace of THF-soluble fraction of crosslinked poly(**BED**-*alt*-**PA**) sample related to entry 8 Table 1.



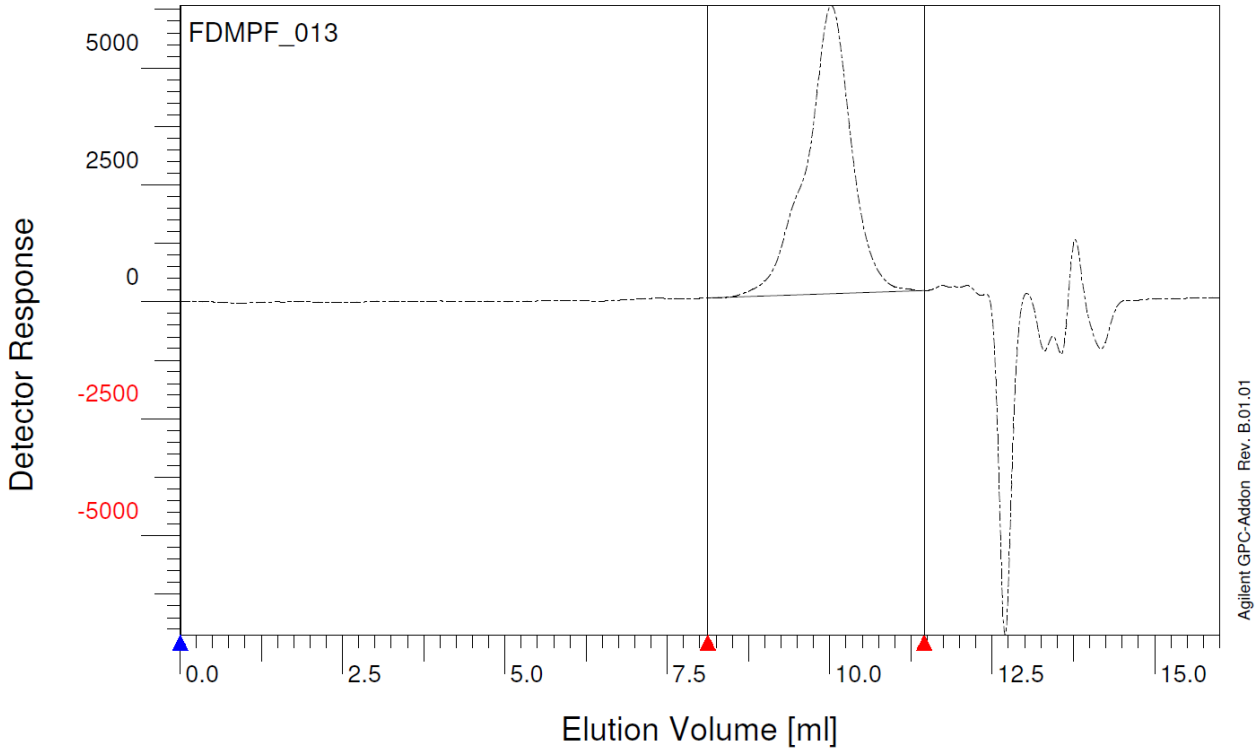
M_n (Da)	M_W (Da)	M_z (Da)	M_p (Da)	*Đ*
4.0995e3	1.0154e4	3.2562e4	2.7459e3	2.4769

Figure S67 GPC trace of THF-soluble fraction of crosslinked poly(**BED**-*alt*-**PA**) sample related to entry 11 Table 1.



M_n (Da)	M_W (Da)	M_z (Da)	M_p (Da)	*Đ*
4.1044e3	5.0182e3	6.3394e3	4.2610e3	1.2226

Figure S68 GPC trace of poly(**BED**-*alt*-**PA**).



M_n (Da)	M_W (Da)	M_z (Da)	M_p (Da)	*Đ*
4.0183e3	5.0758e3	6.7386e3	4.1133e3	1.2632

Figure S69 GPC trace of poly(**BET**-*alt*-**PA**).

Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry of BE-Based Polyesters

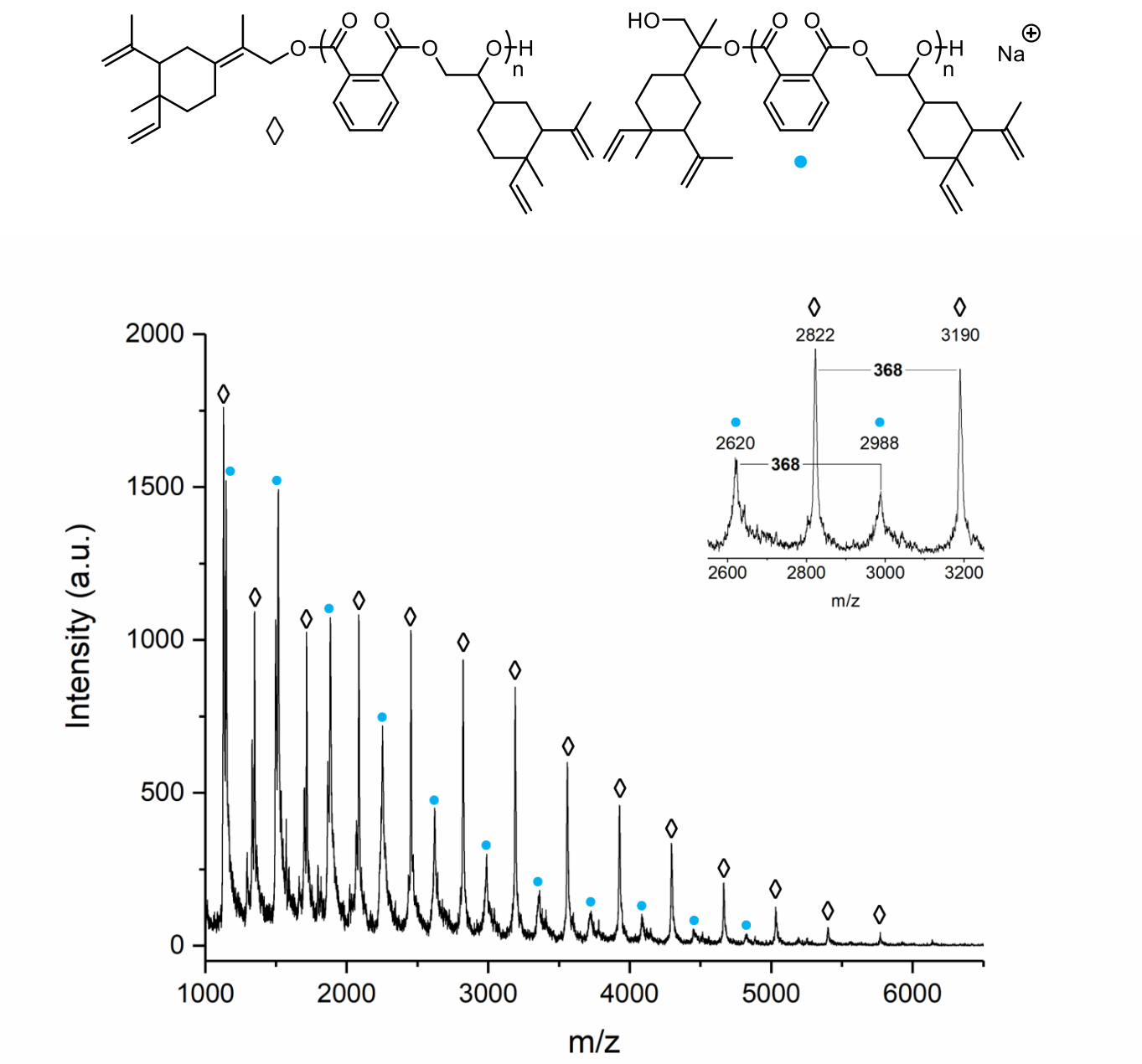


Figure S70 MALDI-TOF spectrum of poly(**BEM**-*alt*-**PA**) sample related to entry 7 table 1.

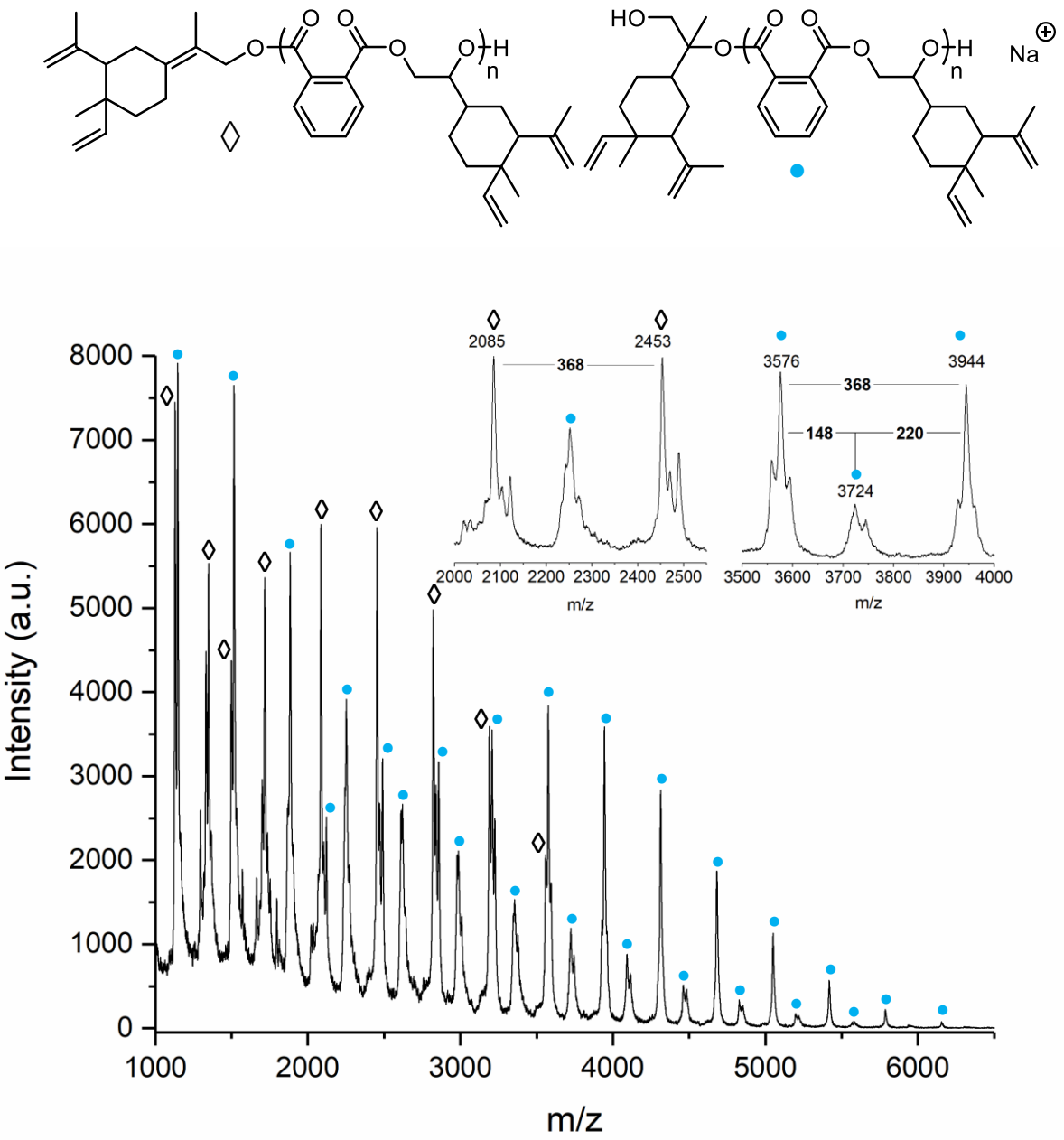


Figure S71 MALDI-TOF spectrum of poly(**BEM**-*alt*-**PA**) sample related to entry 2 Table 1.

Differential Scanning Calorimetry of BE-Based Polyesters

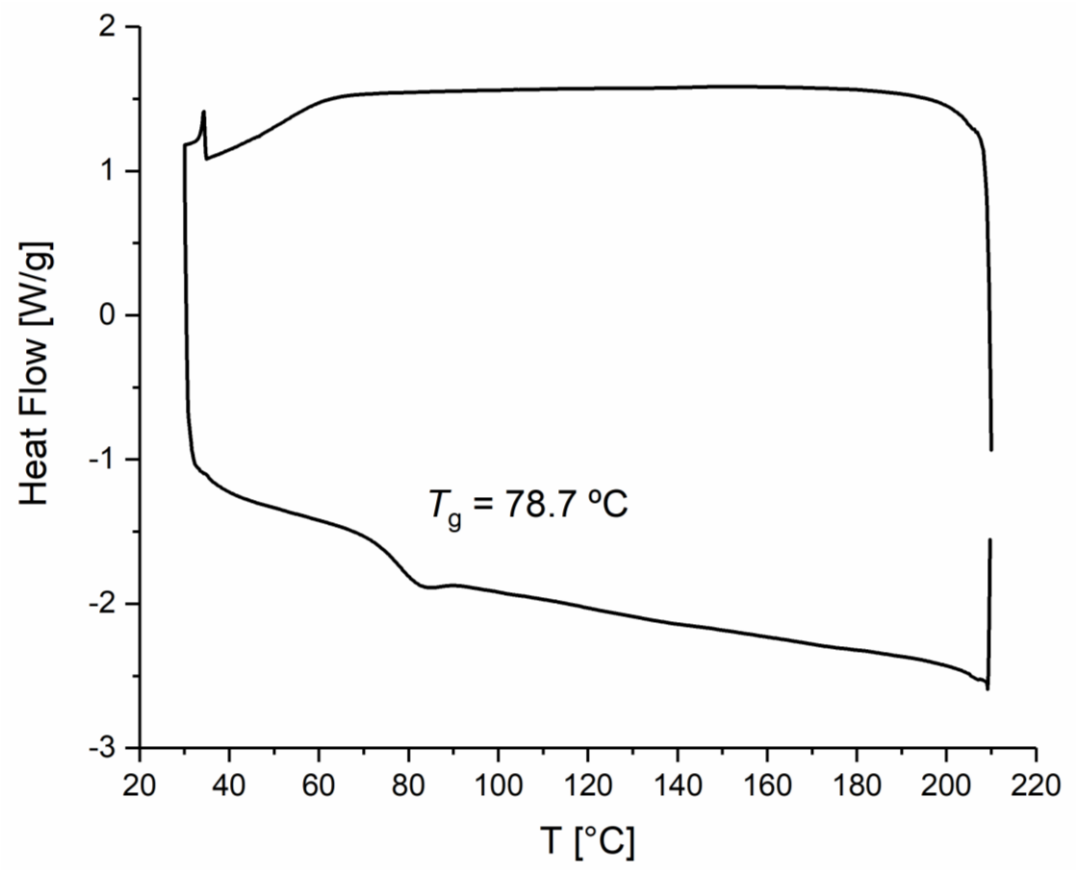


Figure S72 DSC thermogram of poly(**BEM**-*alt*-**PA**) sample related to entry 6 Table 1.

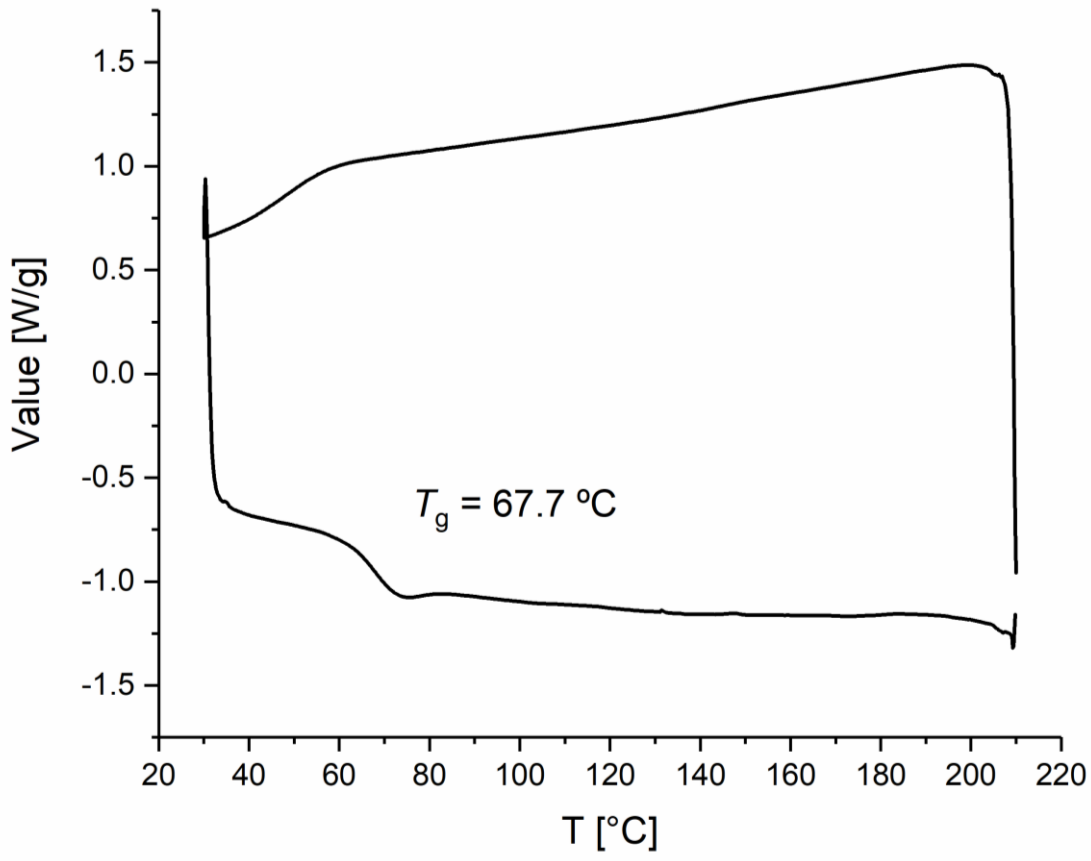


Figure S73 DSC thermogram of poly(**BEM**-*alt*-**PA**) sample related to entry 7 Table 1.

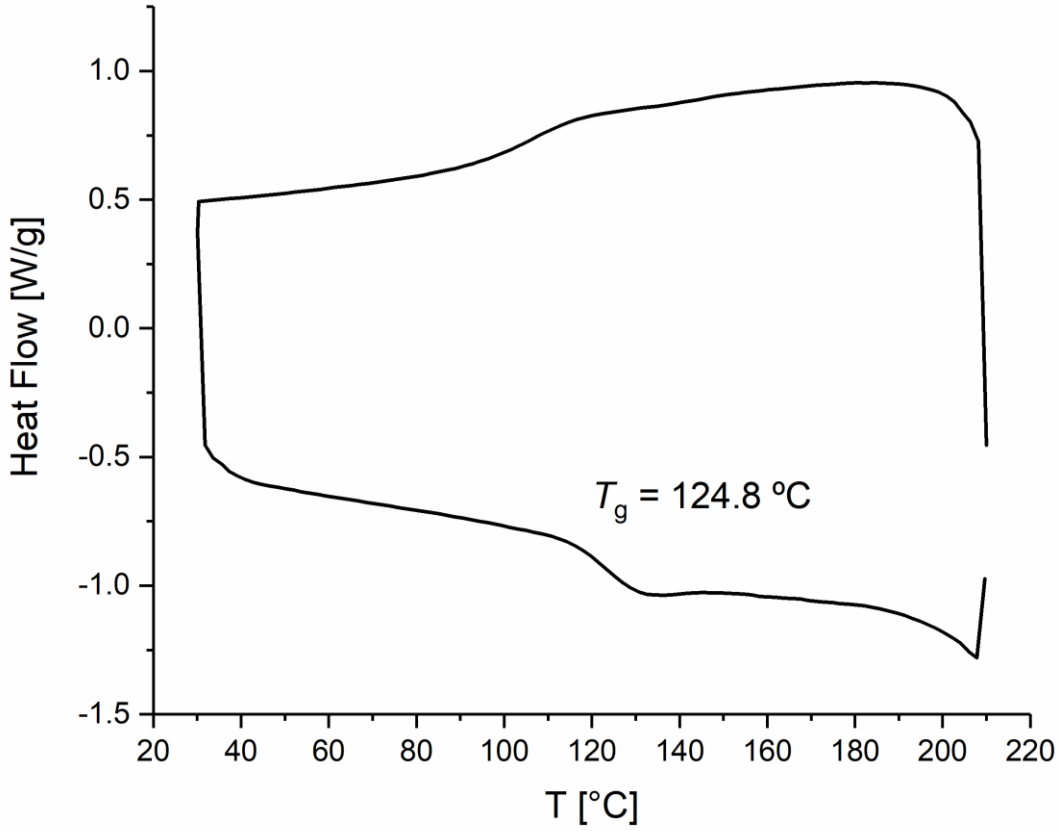


Figure S74 DSC thermogram of crosslinked poly(**BED**-*alt*-**PA**) sample related to entry 8 Table 1.

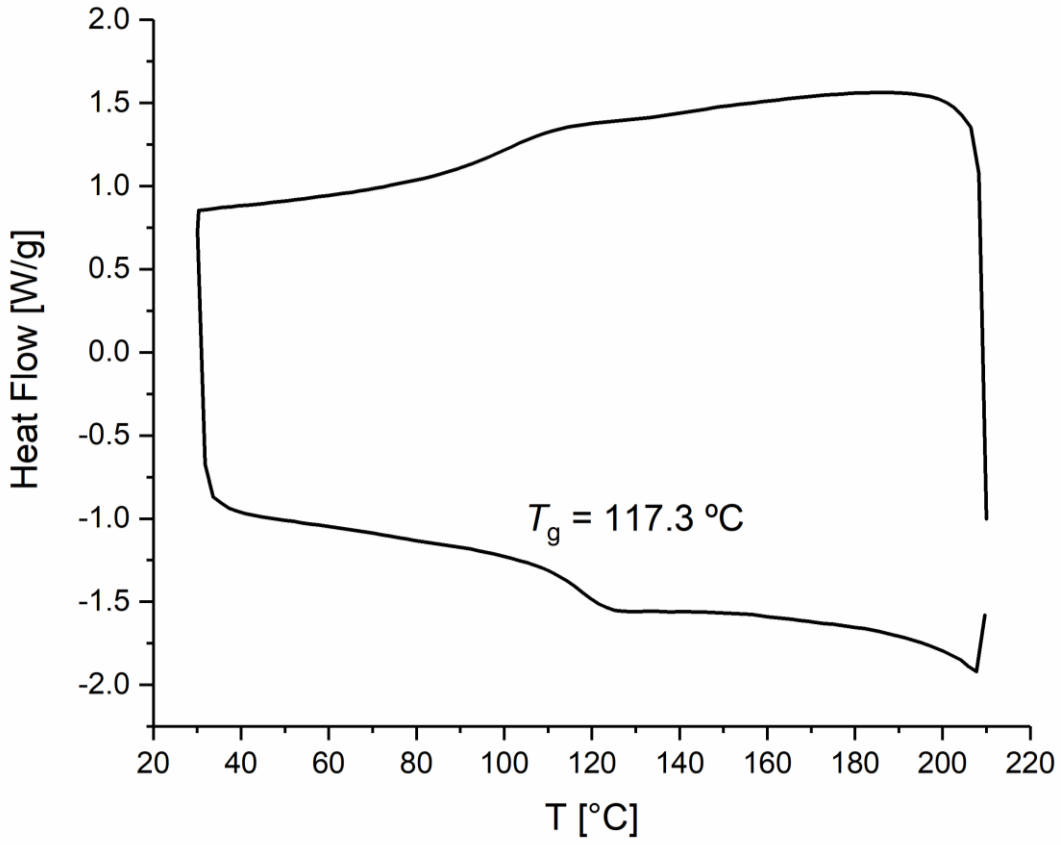


Figure S75 DSC thermogram of crosslinked poly(**BED**-*alt*-**PA**) sample related to entry 11 Table 1.

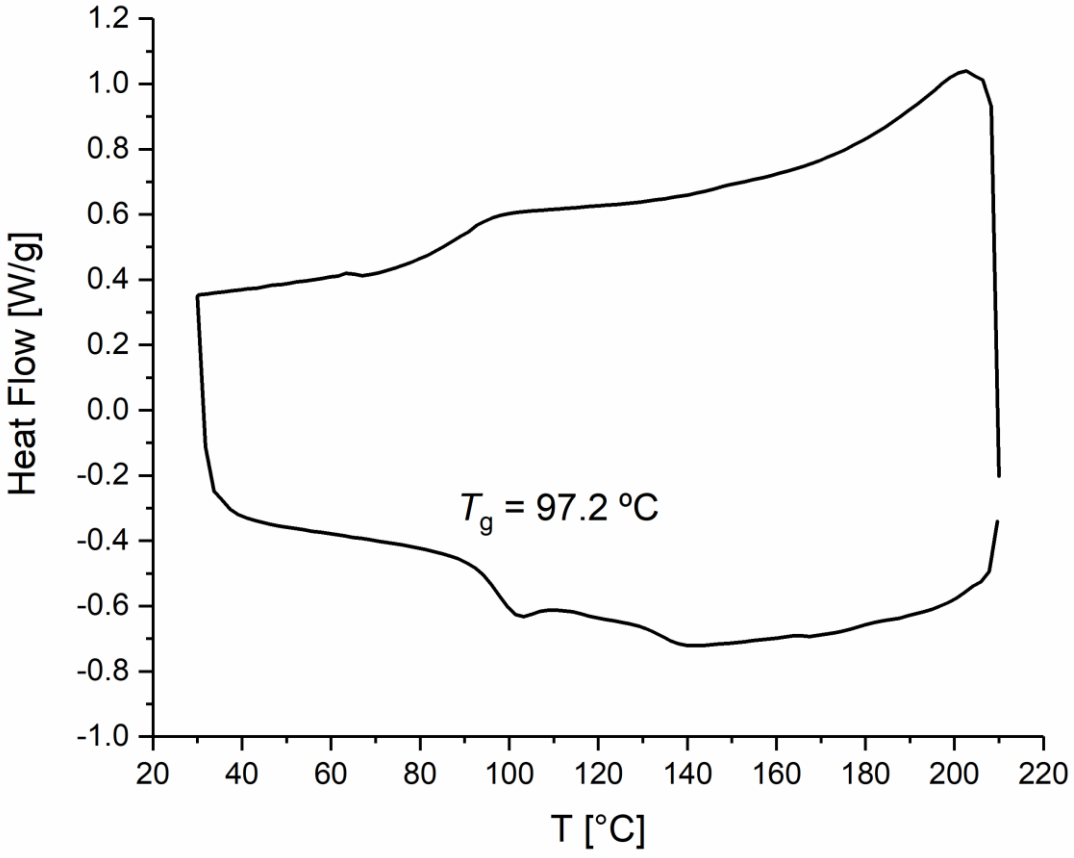


Figure S76 DSC thermogram of poly(**BED**-*alt*-**PA**).

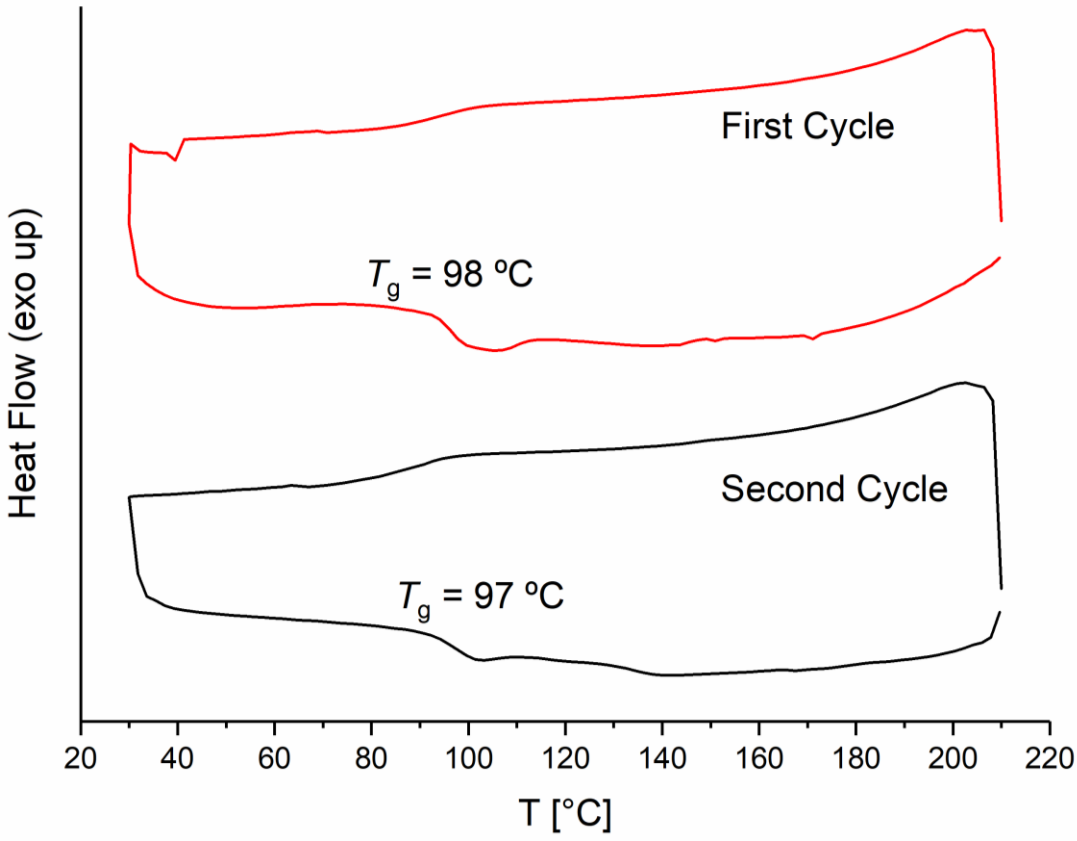


Figure S77 Comparison of first and second cycle of DSC thermogram of poly(**BED**-*alt*-**PA**).

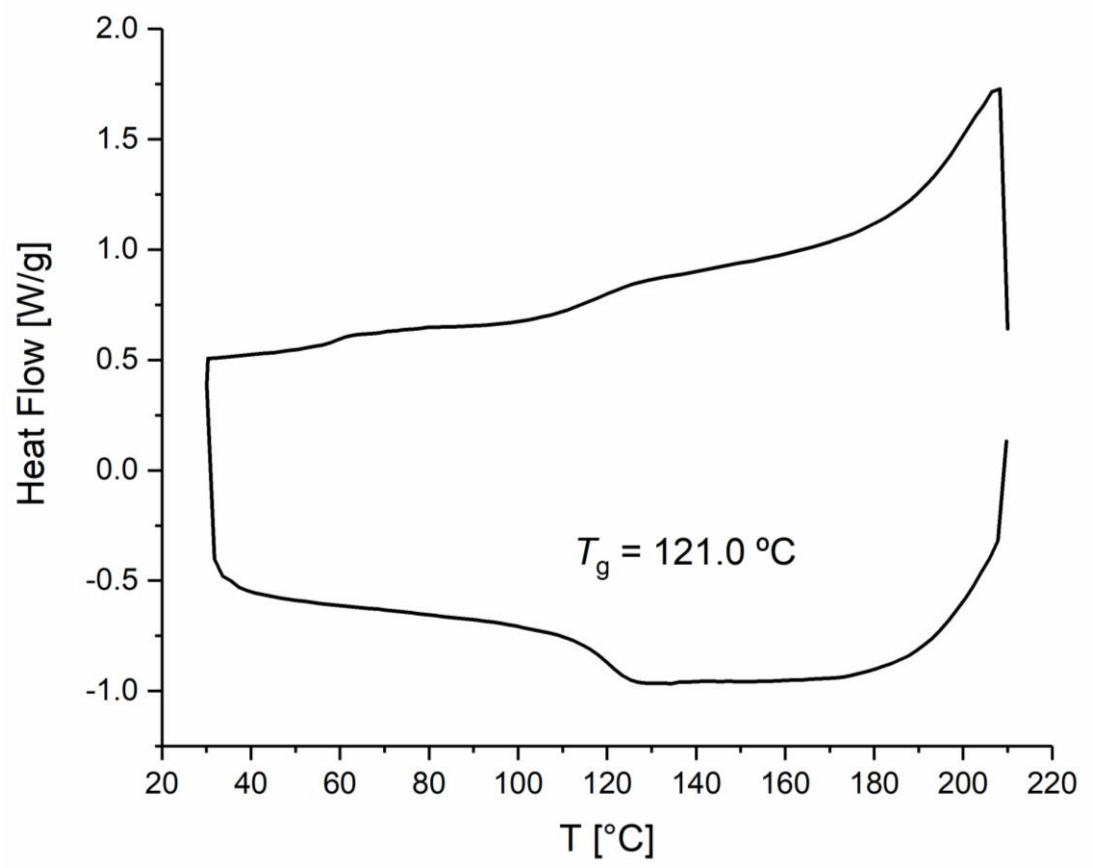


Figure S78 DSC thermogram of poly(**BET**-*alt*-**PA**).

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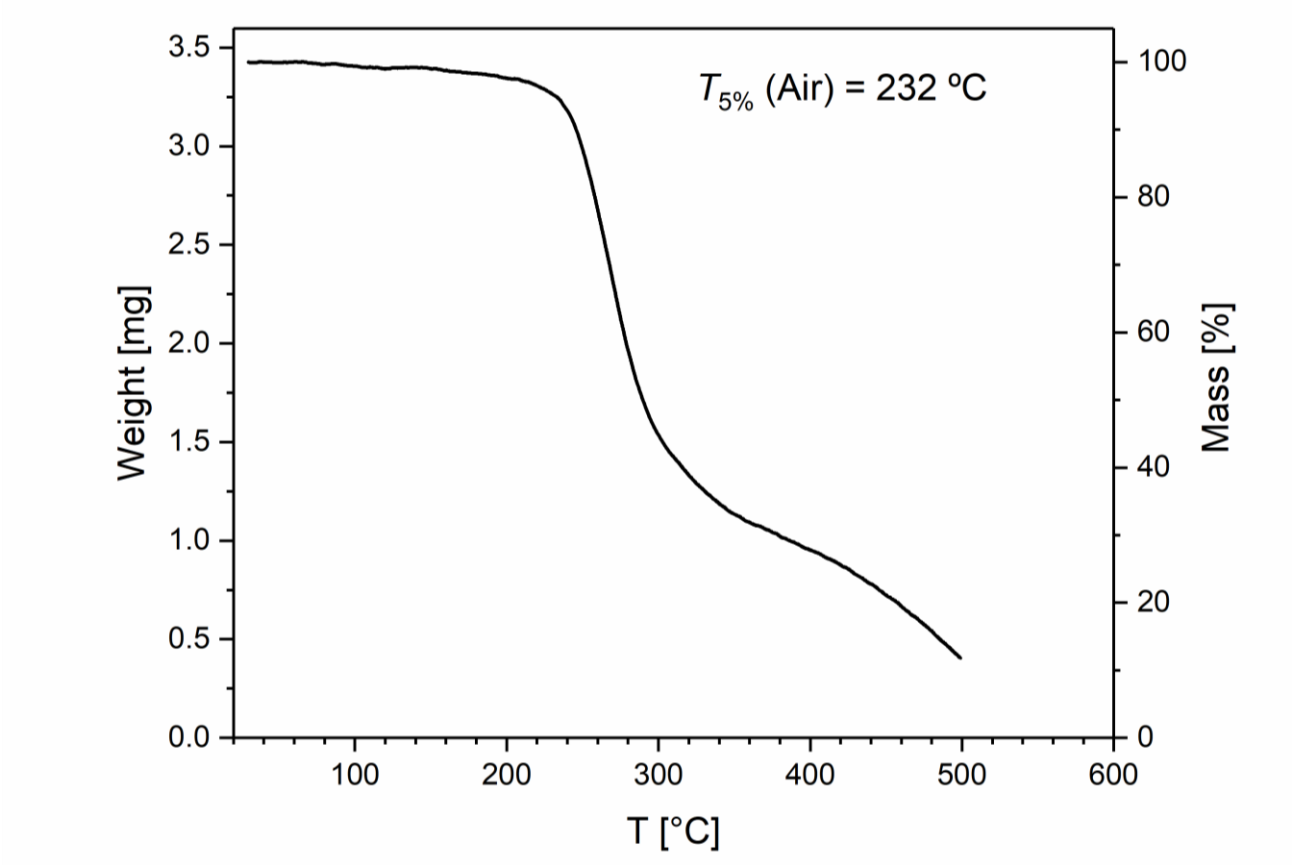

Figure S79 TGA thermogram of poly(**BEM**-*alt*-**PA**) sample related to entry 6 Table 1.

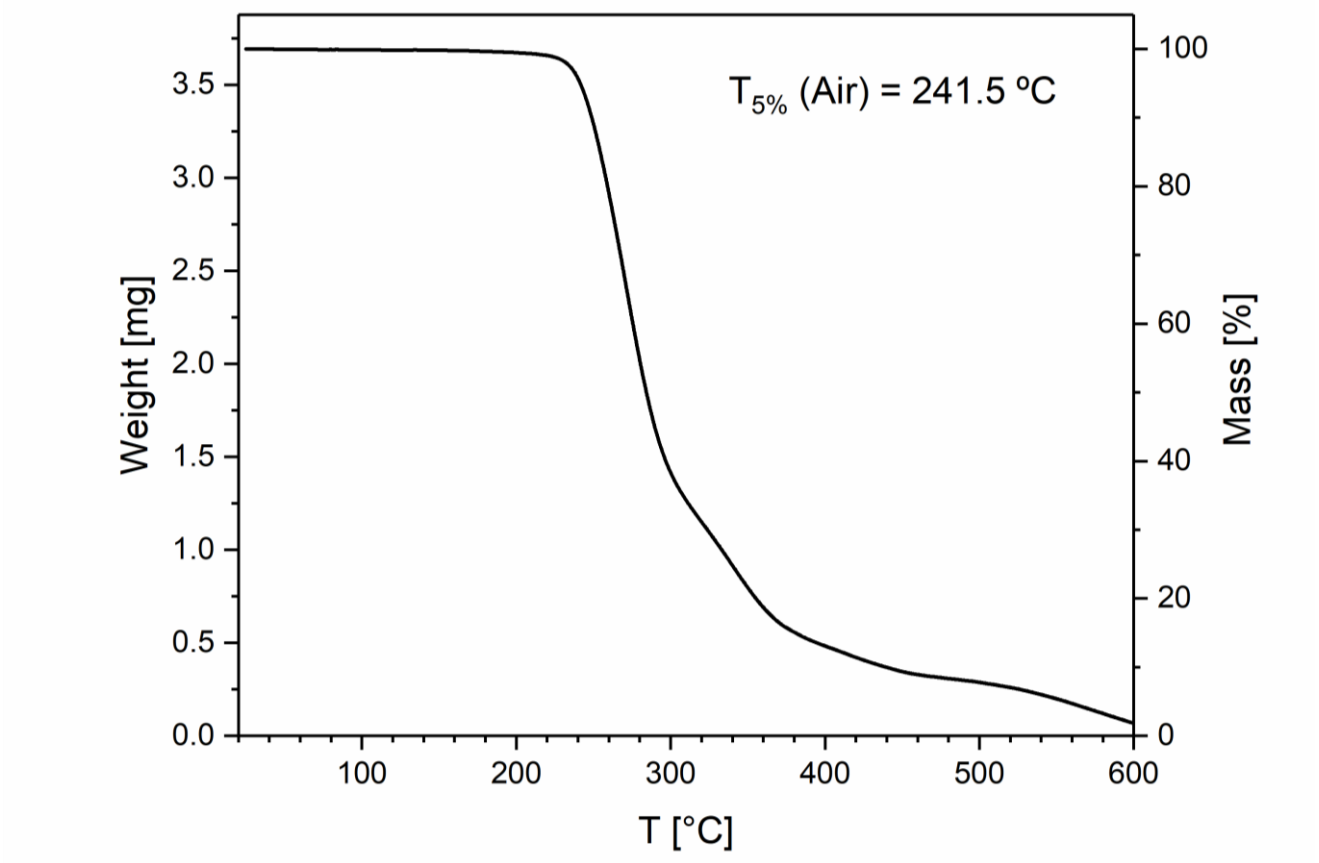

Figure S80 TGA thermogram of poly(**BED**-*alt*-**PA**) sample related to entry 7 Table 1.

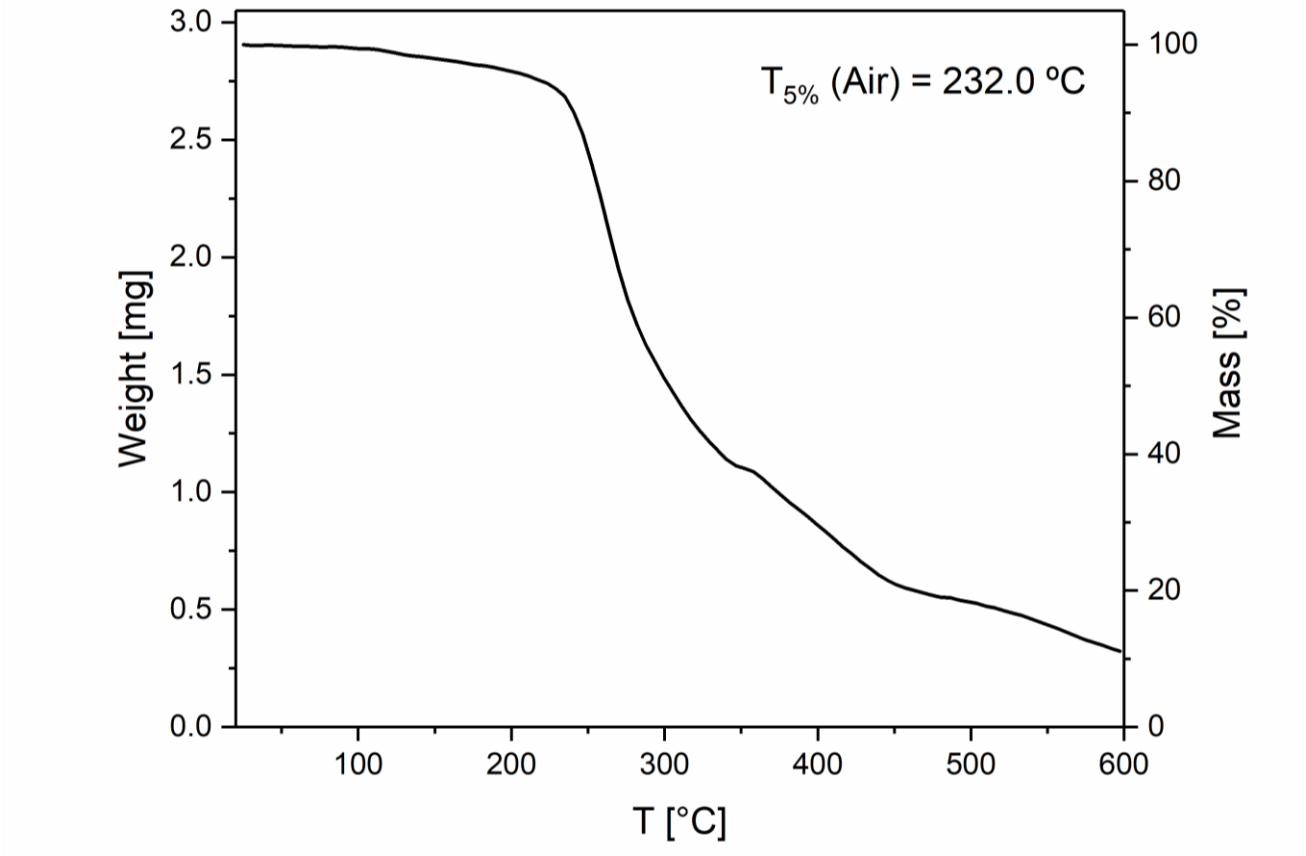

Figure S81 TGA thermogram of crosslinked poly(**BED**-*alt*-**PA**) sample related to entry 8 Table 1.

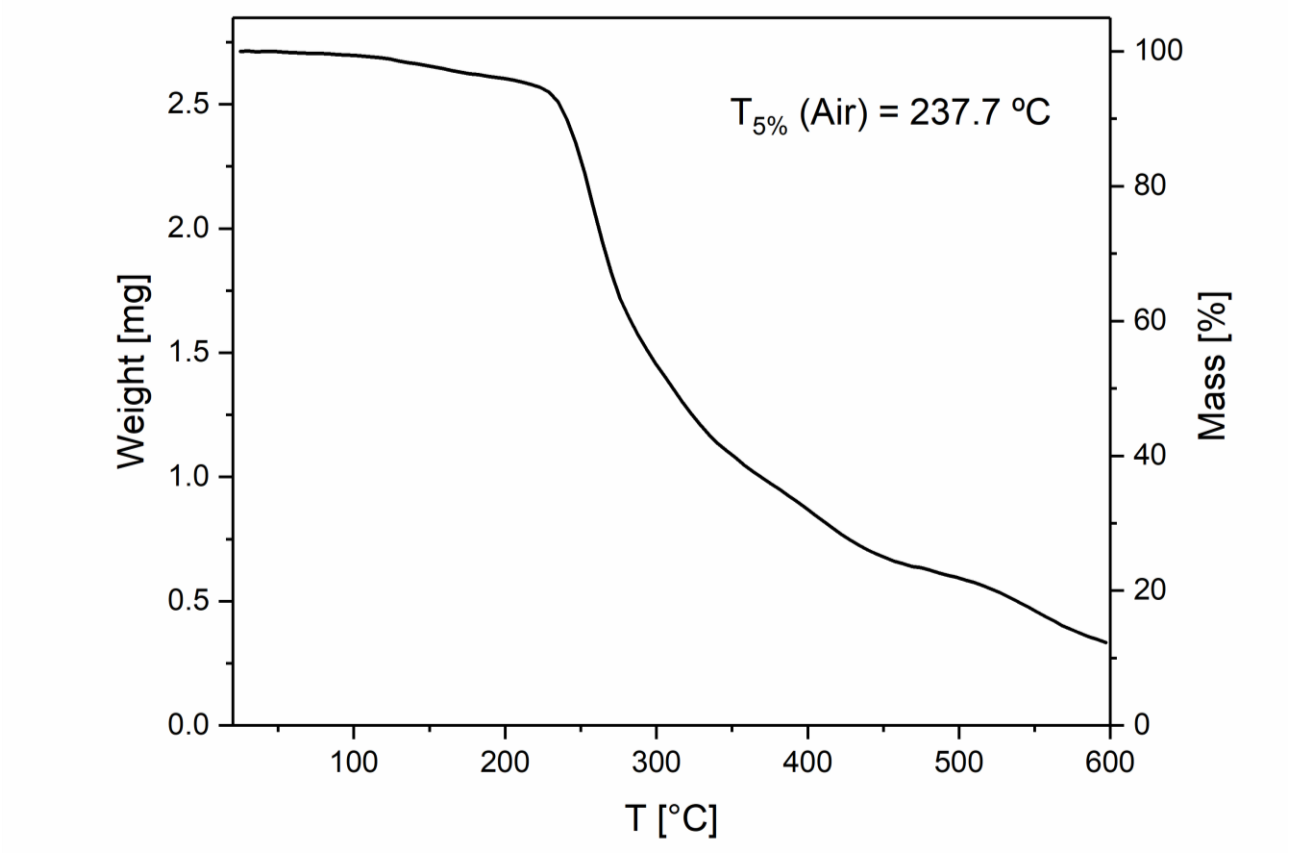

Figure S82 TGA thermogram of crosslinked poly(**BED**-*alt*-**PA**) sample related to entry 11 Table 1.

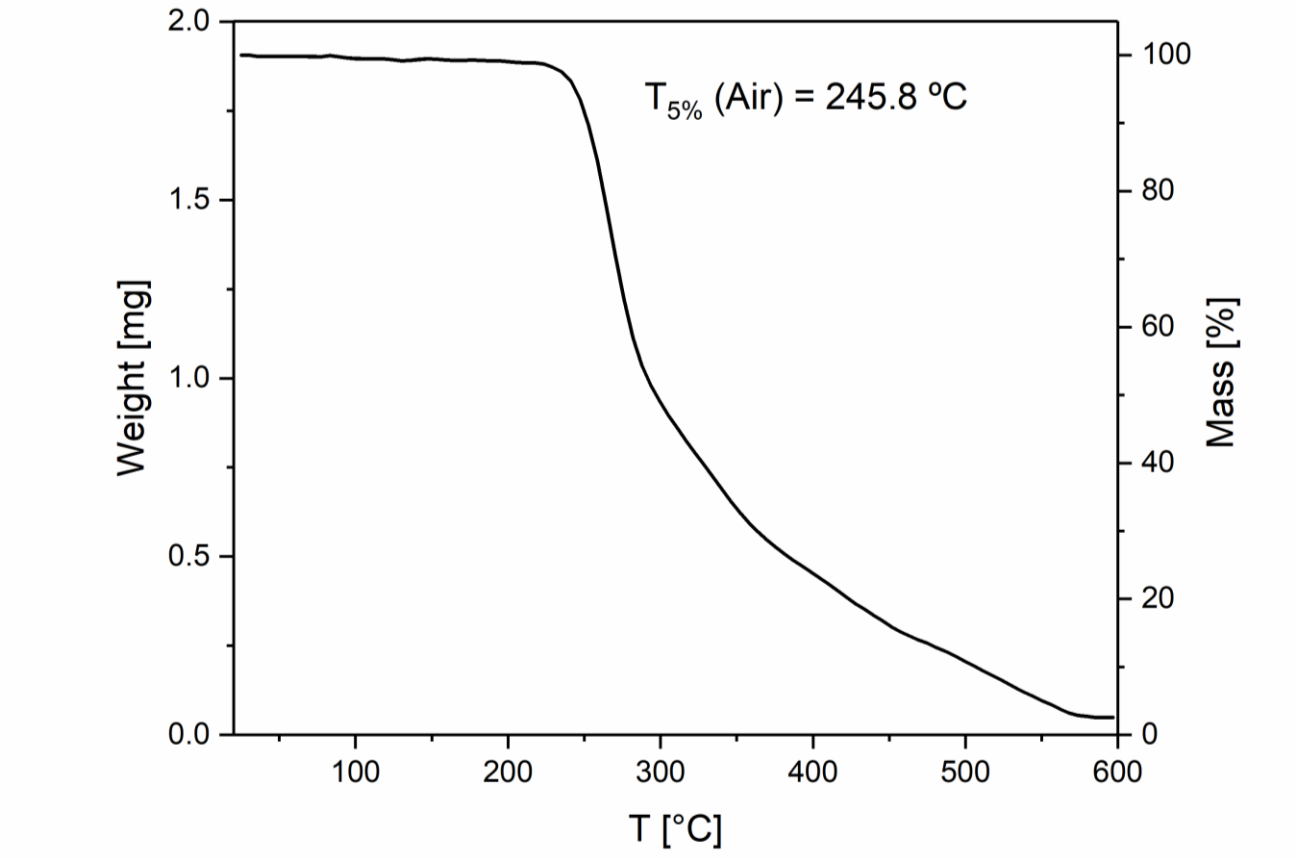

Figure S83 TGA thermogram of poly(**BED**-*alt*-**PA**).

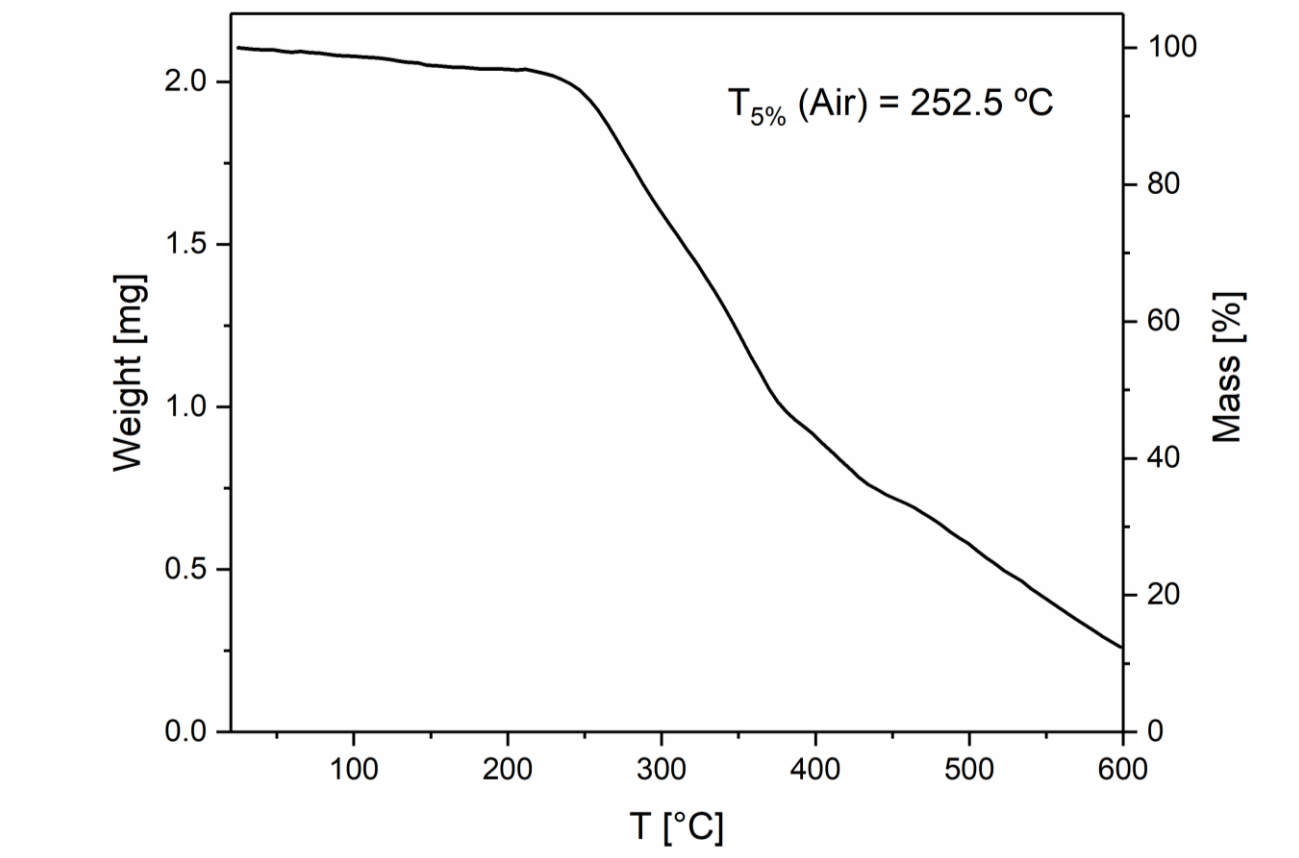

Figure S84 TGA thermogram of poly(**BET**-*alt*-**PA**).

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