Supporting Information

Polyesters with Inbuilt Photolabile Units for Degradation of PET in the Natural Environment

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Characterisation

NMR experiments were conducted at 298 K on a Bruker DRX-400 MHz, AV-400 MHz and Bruker AV 500 MHz AVANCE III HD spectrometer using TopSpin 3.2 and equipped with a z-gradient bbo/5 mm tunable Smart Probe and a GRASP II gradient spectroscopy accessory providing a maximum gradient output of 53.5G/cm (5.35G/cmA). Unless indicated otherwise, NMR spectra were taken in $CDCl_3$ as the solvent and in 5 mm Norell NMR tubes. Air sensitive compounds were analysed in sealed Young's NMR tubes and prepared inside the glovebox. The following abbreviations are used: b, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet.

IR spectroscopy measurements were conducted on an Agilent Technologies Cary 630 FTIR spectrometer using ATR sampling station.

UV-vis spectroscopy was performed using an Agilent Technologies Cary 60 UV-vis spectrometer in standard 1 cm quartz cuvettes (Hellma).

Differential scanning calorimetry (**DSC**) measurements were performed using a Perkin Elmer DSC 4000 and a sample mass of approximately 5 mg under a nitrogen atmosphere with a heating cycle of 10 ˚C/min from 0 to 200 ˚C and followed by a cooling cycle at the same rate from 200 to 0 ˚C. Then the samples were reheated at the same rate for a second heating cycle to 200 ˚C. Unless indicated otherwise, only the second cycle is reported. An additional heating cycle of 20 ˚C/min from 0 to 200 ˚C was carried in some cases.

Thermal analysis measurements were carried out using Mettler Toledo TGA instrument. 5-10 mg samples were used for each measurement. The temperature was ramped up to 700 °C at a rate of 10 °C/ min under air or nitrogen atmosphere.

Gel Permeation Chromatography (GPC) analysis was performed by the Polymer Characterisation Research Technology Platform, University of Warwick, Gibbet Hill Road, CV4 7AL Coventry. All data for PET and PET copolymers before and after weathering were recorded on an Agilent Infinity II instrument equipped with a differential refractive index (DRI) detector. The system was equipped with 2 x Agilent PLGel Mixed C columns (300 x 7.5 mm) and an Agilent 5 µm PLGel Guard column. The samples were first dissolved in hexafluoro isopropanol (HF^iP) (20 mg/mL) and left overnight at ambient temperature. One drop of each sample was added in vials containing 1 mL of eluent ($CHCl_3$) and the samples were filtered through 0.22 µm filters prior to injection. The mobile phase was $CHCl_3$ and run at a flow rate of 1 mL min^{-1} at 30 °C. All sample analysis was carried out using Agilent

GPC/SEC Software. Agilent polystyrene (PS) EasiVials were used to create a third order conventional calibration from DRI data between 364,000 and 370 g mol^{-1}.

EPR spectroscopy was carried out on a Bruker ELEXYS-E580 spectrometer 100 K, 405 nm (LED ex-situ irradiation). EPR simulations were simulated using EasySpin 5.2.36 for MATLAB 2021a.[1]

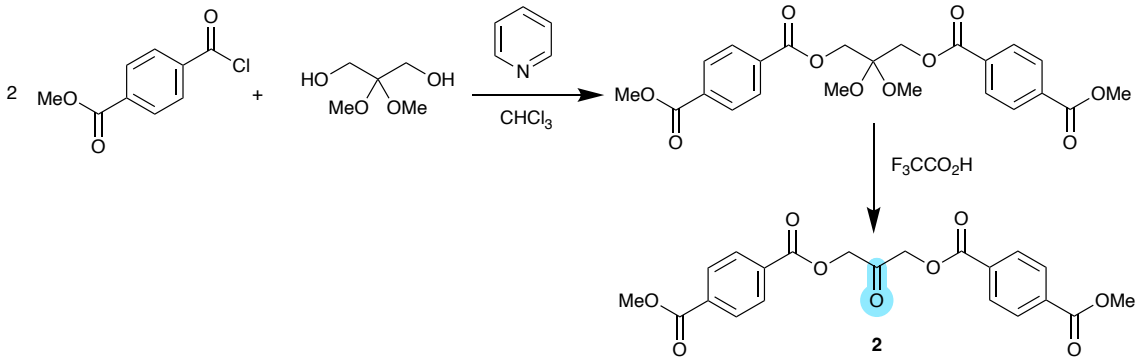
MWFQ: 9.73258400 GHz
MWPW: 1.5 e-06
Sweep width 400 G
Mod Amp: 2 G
Sweep time: 60 s

Synthesis

Compound **1** was synthesised according to a literature procedure.[2]

Synthesis of dihydroxyacetone diterephthalate ester 2

The synthesis was adapted from a procedure described by Putnam and co-workers, which also details the preparation of 2,2-dimethoxy-1,3-propanol.[3]



2,2-Dimethoxy-1,3-propanol (0.67 g, 5.05 mmol) and pyridine (1.01 mL, 12.62 mmol) were dissolved in 50 mL chloroform in a round bottom flask. The solution is cooled within an ice bath. Methyl terephthaloyl chloride (2 g, 10.1 mmol) was dissolved in 50 mL chloroform and added dropwise to the other solution. The mixed solution was left stirring for 24h at room temperature. After filtration, the final product was precipitated in cold methanol and dried in vacuo. The solid product was suspended in water and trifluoracetic acid (8ml) was added and the mixture was left stirring overnight. The deprotected product **2** was obtained by dropwise addition to cold diethyl ether. Yield: 1.67 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22-8.15 (m, 8H, Ar-H), 5.15 (s, 4H, CH_2), 4.00 (s, 6H, OMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 197.2 (C_{quat}, CO), 166.1 (C_{quat}, Ester CO), 165.0 (C_{quat}, Ester CO), 134.6 (C_{quat}, Ar), 132.5 (C_{quat}, Ar), 130.0 (CH, Ar-H), 129.8 (CH, Ar-H), 67.0 (CH_2), 52.6 (CH_3).

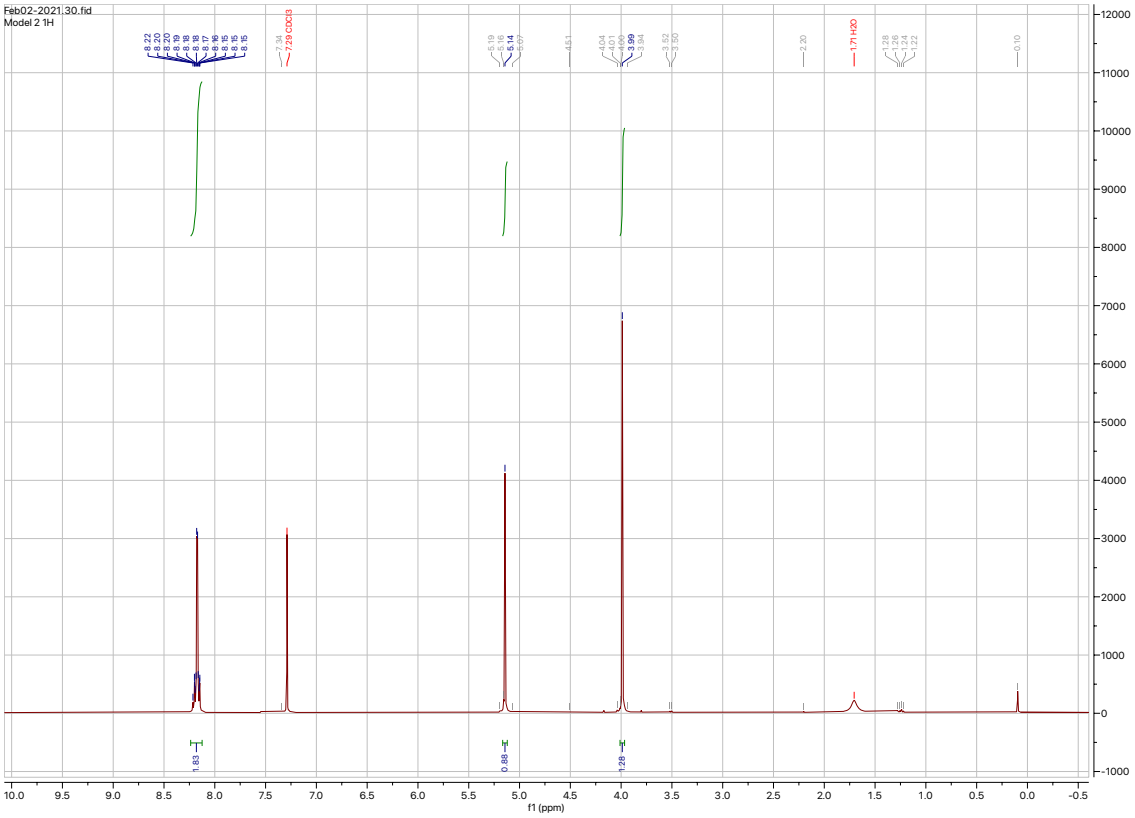


Figure S1. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

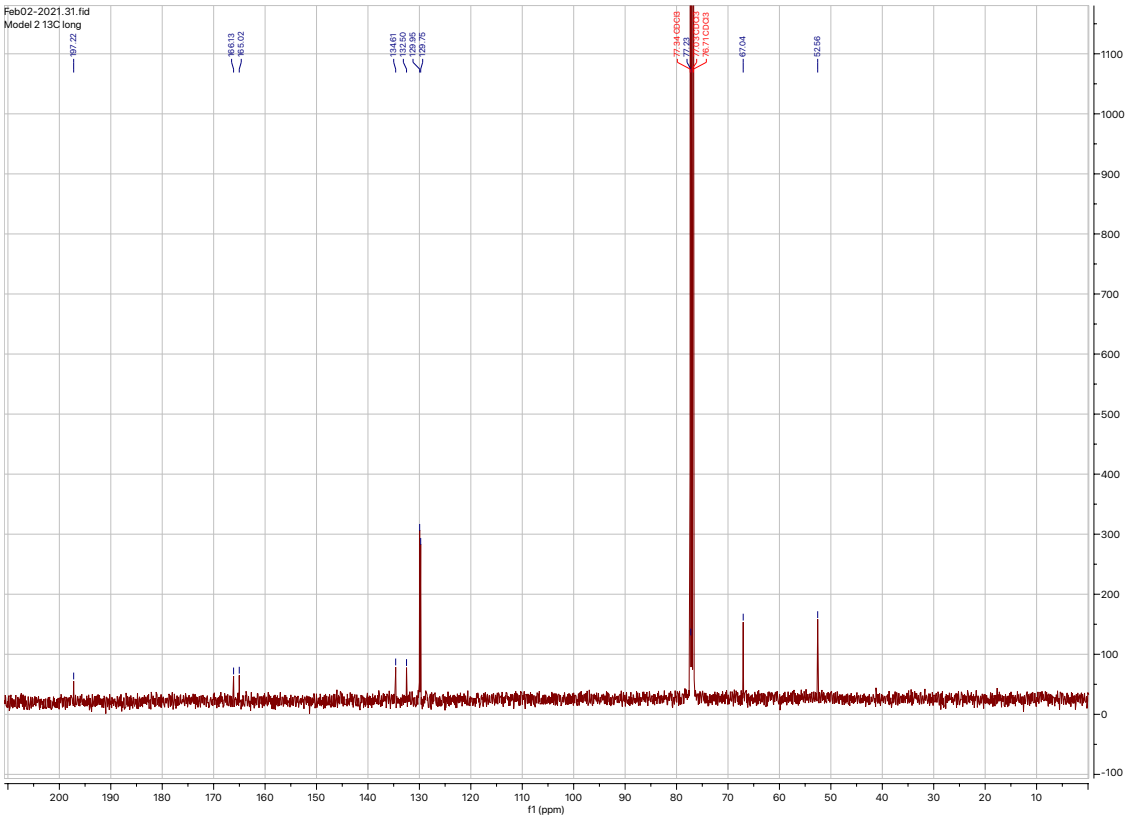


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of compound **2**.

Degradation experiments of compound **2**

All degradation experiments for compound **2** have been carried out on an NMR scale using CD_3CN as the solvent. All samples were prepared in air and reaction conditions (temperature, reaction time, additive amount) are listed in Table 1 in the main text, as well as the use of UV irradiation. Conversions were determined by ^1H NMR analysis. As an example, ^1H and ^{13}C NMR analysis for entry 3 in Table 1 are shown in Figures S3a-c.

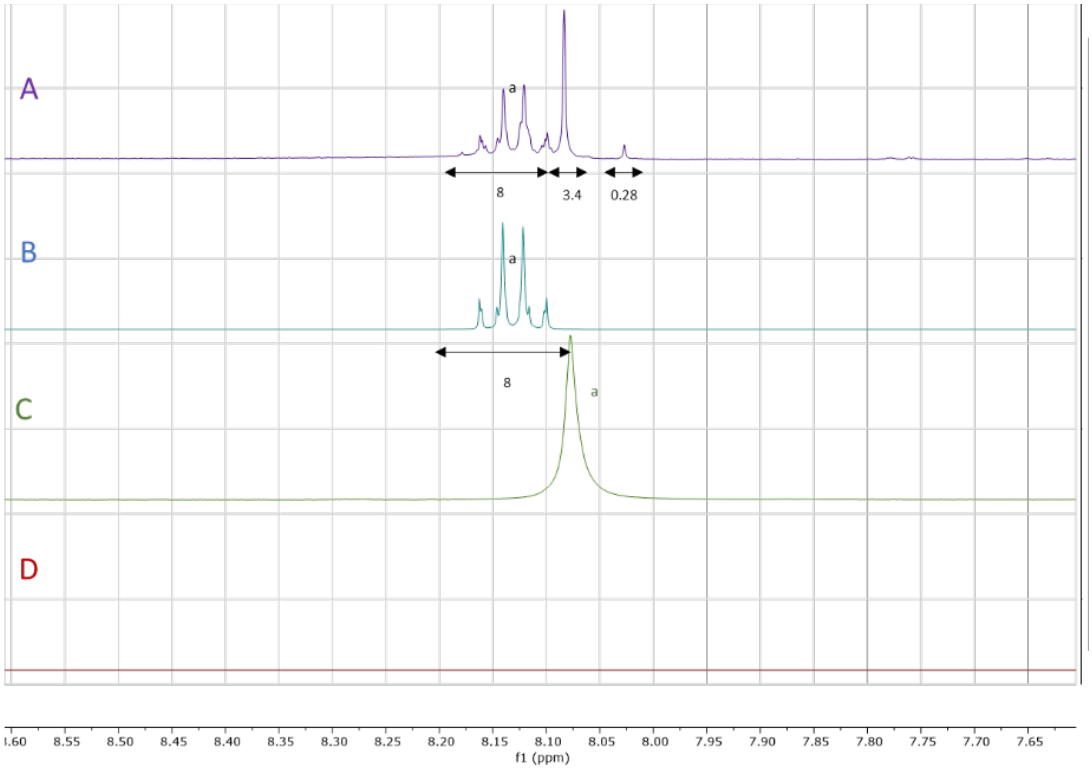


Figure S3a. ^1H NMR spectrum (in CD_3CN at 298K) of the aromatic region during the degradation of compound **2** according to entry 3 in Table 1 (A); pure compound **2** (B); monomethyl terephthalate (C) and 1,3-dihydroxyacetone (D). Conditions: compound **2** and CD_3COOD (1:50) in CD_3CN after 24 hours at 70 ˚C.

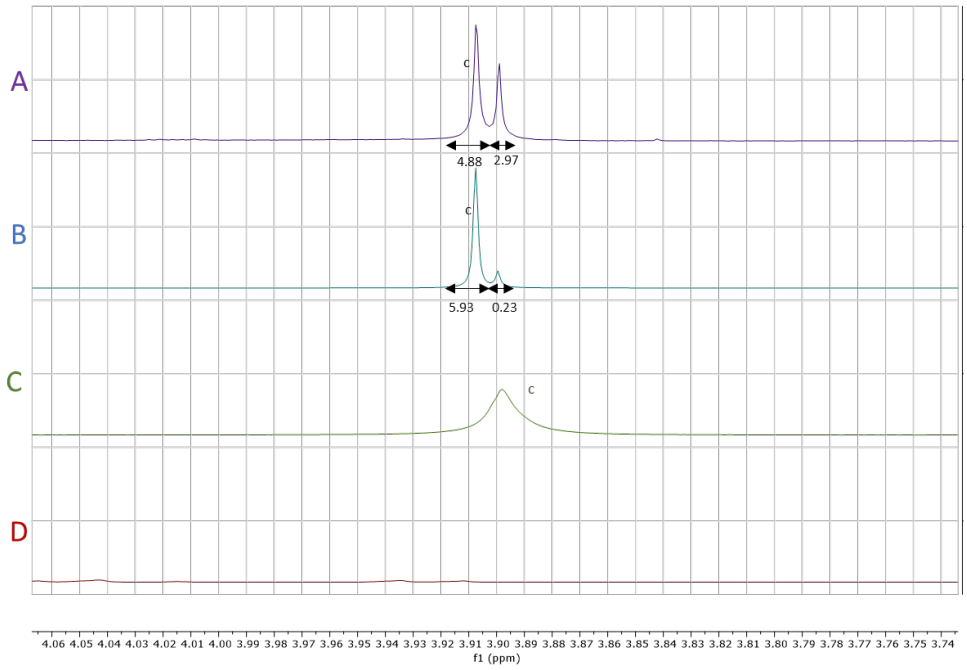


Figure S3b. ^{1}H NMR spectrum (in CD_3CN at 298K) of the aliphatic region (OMe) during the degradation of compound **2** according to entry 3 in Table 1 (A); pure compound **2** (B); monomethyl terephthalate (C) and 1,3-dihydroxyacetone (D). Conditions: compound **2** and CD_3COOD (1:50) in CD_3CN after 24 hours at 70 ˚C.

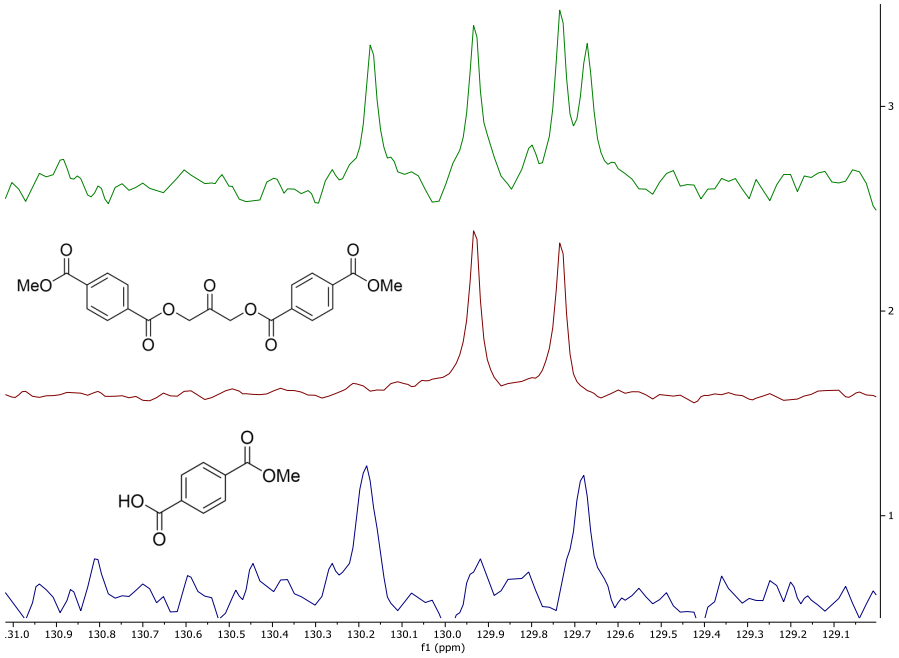


Figure S3c. $^{13}C\{^{1}H\}$ NMR spectrum (in CD_3CN at 298K) of the aromatic signals observed during the degradation of compound **2** according to entry 3 in Table 1 (top), pure compound **2** (centre) and monomethyl terephthalate (bottom). Conditions: compound **2** and CD_3COOD (1:50) in CD_3CN after 24 hours at 70 ˚C.

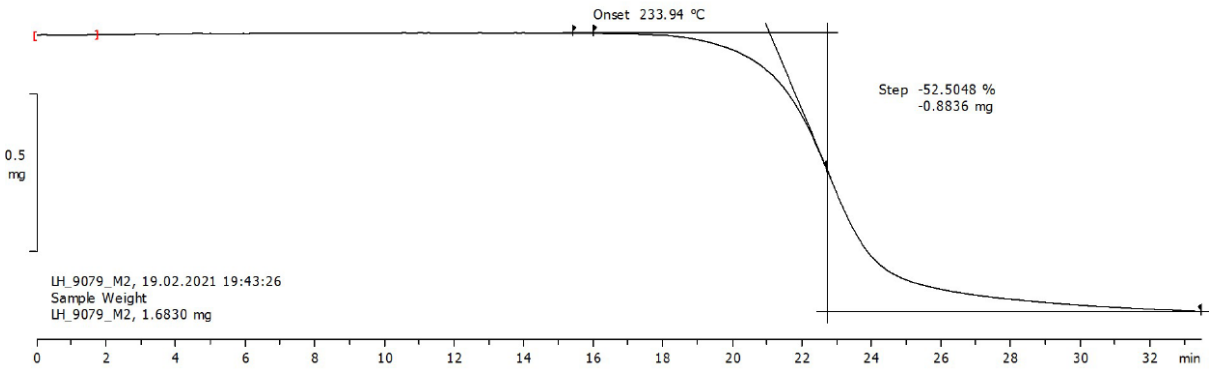
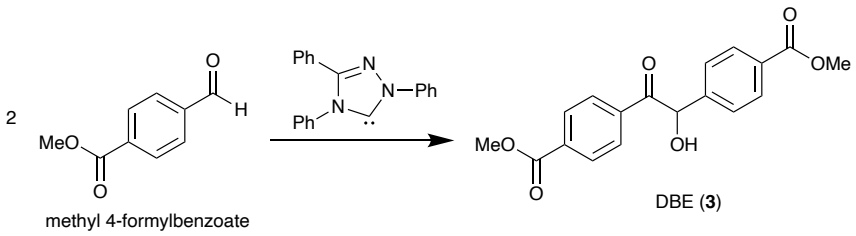


Figure S4. TGA analysis for **2** (Heating rate: 10 °C min^{-1}, Hold temperature: 260 °C; Hold time: 10 min)

Synthesis of dimethyl benzoin ester **3** (DBE)



A Schlenk flask was charged with methyl 4-formylbenzoate (10 g, 61 mmol) and THF (20 mL). To this 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (91 mg, 0.3 mmol) was added and the mixture was stirred to dissolve. The Schlenk flask was sealed, taken out of the glovebox, and heated under N_2 at 60 °C for two hours. The solvent was removed *in vacuo* and the residue recrystallised from ethanol yielding a white solid (8 g, 80 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.08 (d, 2H, Ar-H), 8.02 (d, 2H, Ar-H), 7.95 (d, 2H, Ar-H), 7.42 (d, 2H, Ar-H), 6.04 (d, 1H, OH), 4.55 (d, 1H, CH), 3.94 (s, 3H, CH_3), 3.90 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CD_3CN) δ (ppm): 199.6 (C_{quat}, Ar-CO), 167.1 (C_{quat}, Ester CO), 166.6 (C_{quat}, Ester CO), 144.8 (C_{quat}, Ar), 138.6 (C_{quat}, Ar), 135.3 (C_{quat}, Ar), 131.2 (C_{quat}, Ar), 130.7 (CH, Ar-H), 130.4 (CH, Ar-H), 129.9 (CH, Ar-H), 128.7 (CH, Ar-H), 77.0 (CH, Benzoin), 53.0 (CH_3, Me), 52.7 (CH_3, Me).

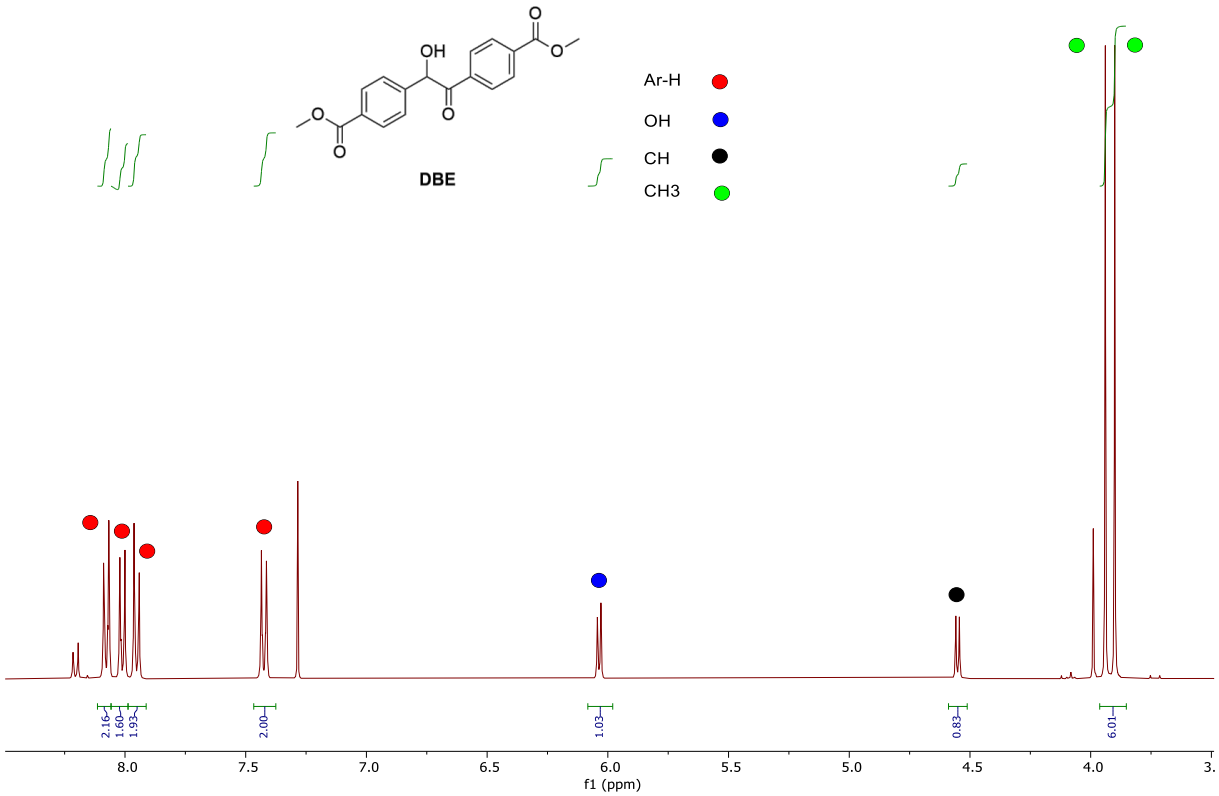


Figure S5. ^{1}H NMR spectrum of dimethyl benzoin ester **3** (DBE) in $CDCl_3$.

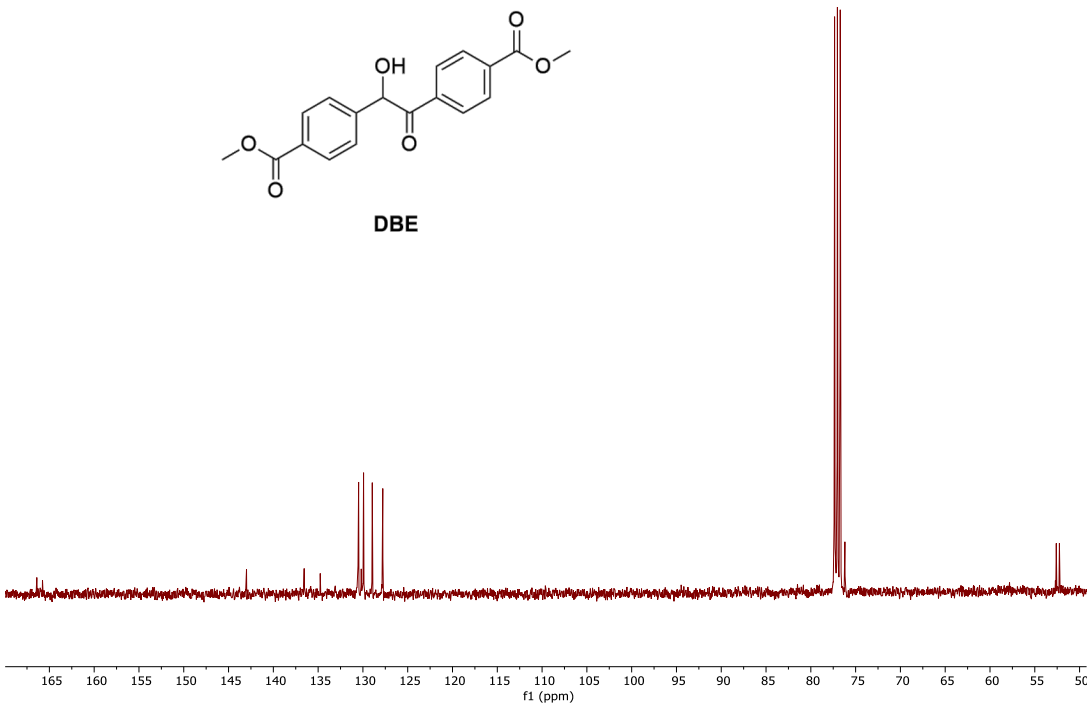


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum in $CDCl_3$ of DBE (**3**).

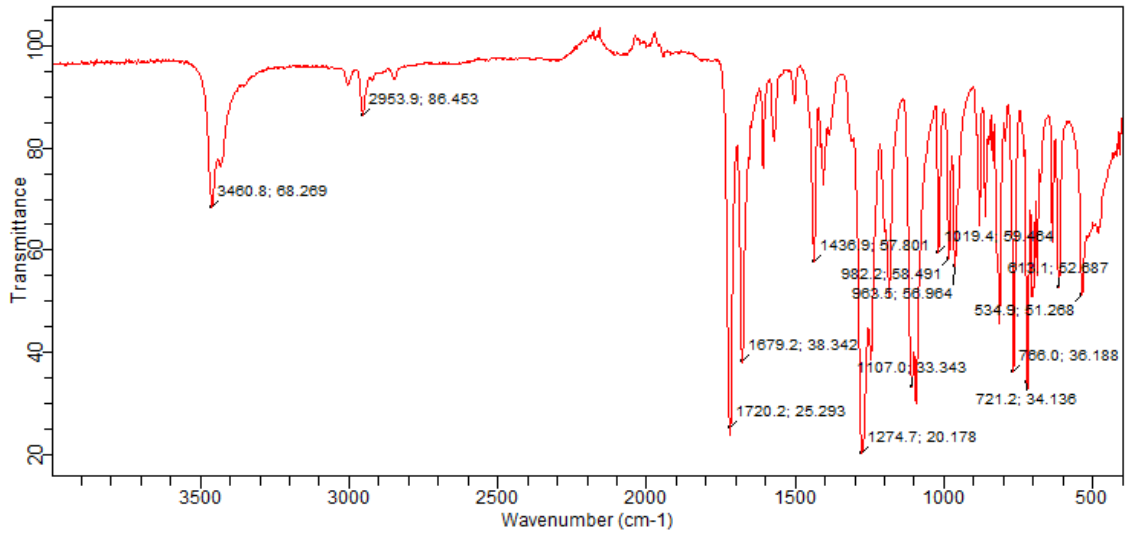


Figure S7. FT-IR spectrum of DBE (**3**).

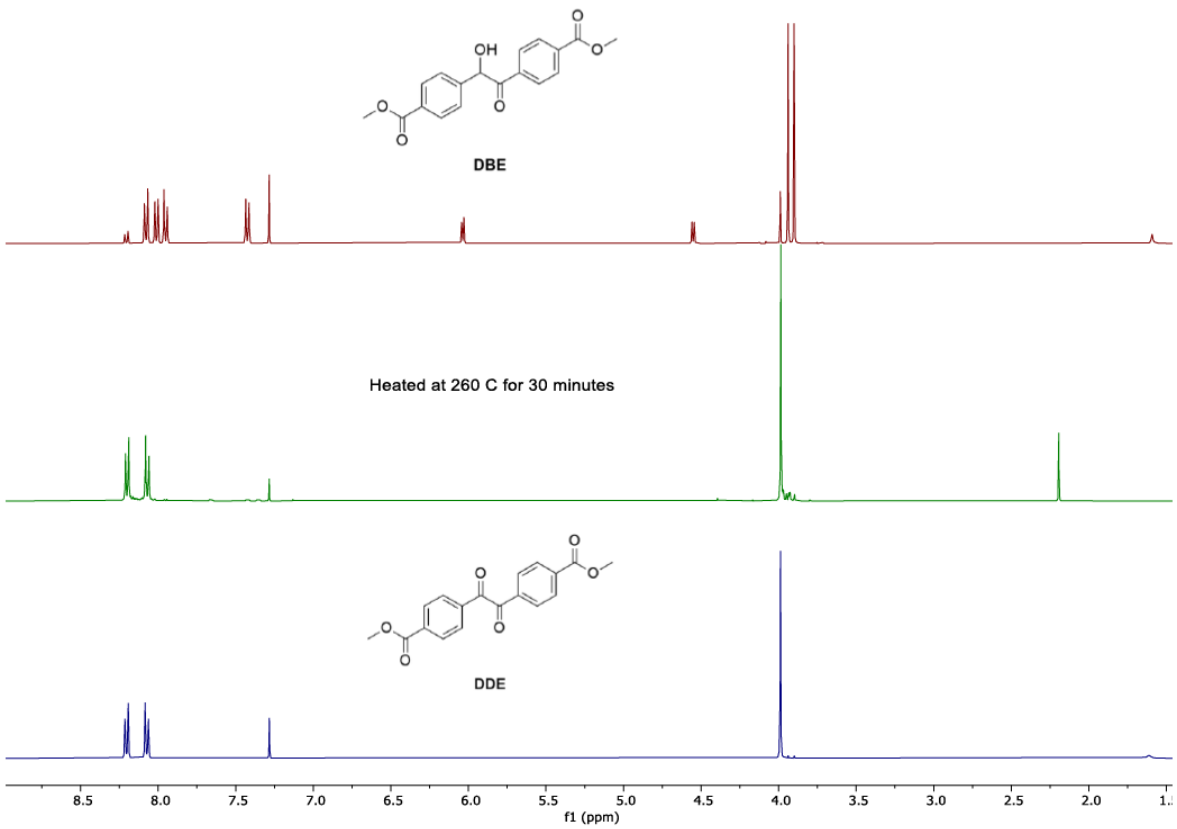


Figure S8. Thermal conversion of benzoin dimethyl ester BDE **3** into DDE (**4**). NMR spectra recorded in $CDCl_3$ at 298 K.

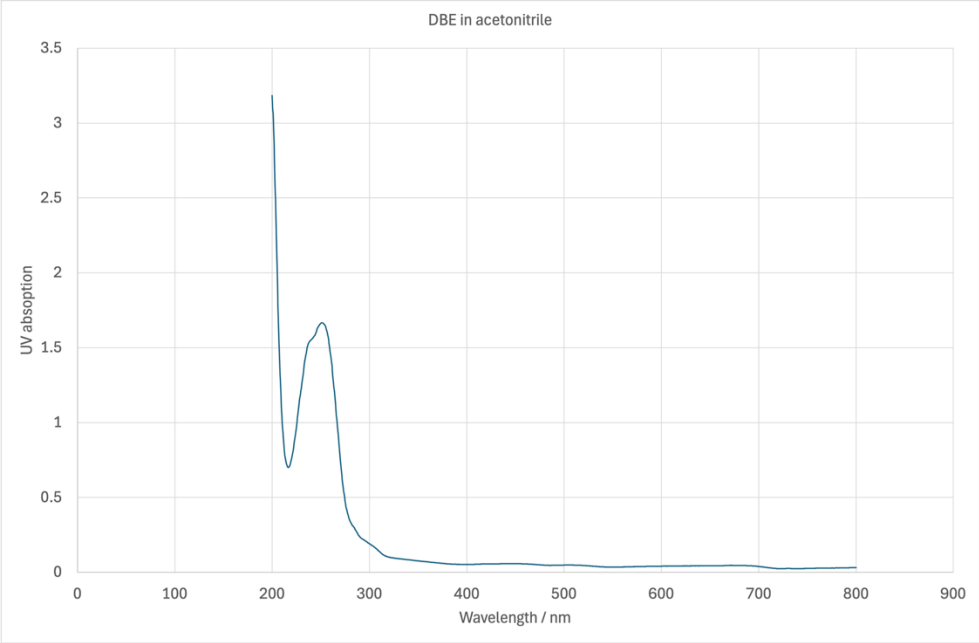
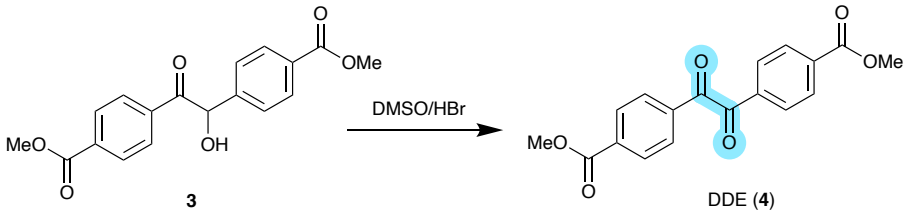


Figure S9. UV-vis spectrum of DBE (**3**) (c = 67 µM in acetonitrile).

Synthesis of dimethyl diketo ester **4** (DDE)



In a 500 mL round-bottom flask, compound **3** (10 g, 30 mmol) was dissolved in DMSO (125 mL). Under stirring, concentrated hydrobromic acid (40 mL, 48 %) was added dropwise after which the mixture was stirred at 60 °C for 24 hours. Deionised water (250 mL) was added and the precipitate was filtered and washed thoroughly with deionised water. A fine yellow powder was obtained after drying (7.3 g, 22 mmol) in 73 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ^{1}H (ppm): 8.18 (d, 4H, Ar-H), 8.05 (d, 4H, Ar-H), 3.97 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) $\delta\,^{13}$C (ppm): 192.9 (C_{quat}, Ar-CO), 165.8 (C_{quat}, Ester CO), 137.5 (C_{quat}, Ar), 135.6 (C_{quat}, Ar), 130.2 (CH, Ar-H), 129.9 (CH, Ar-H), 52.7 (CH_3, Me).

^{1}H NMR (400 MHz, CD_3CN) δ^{1}H (ppm): 8.16 (d, 4H, Ar-H), 8.07 (d, 4H, Ar-H), 3.91 (s, 6H, CH_3). ^{1}H NMR (400 MHz, THF-d_8) δ_{1H} (ppm): 8.17 (d, 4H, Ar-H), 8.10 (d, 4H, Ar-H), 3.91 (s, 6H, CH_3). ^{13}C NMR (100 MHz, THF-d_8) $\delta\,_{13C}$ (ppm): 193.6 (C_{quat}, Ar-CO), 166.2 (C_{quat},

Ester CO), 137.1 (C_{quat}, Ar), 136.6 (C_{quat}, Ar), 130.9 (CH, Ar-H), 130.9 (CH, Ar-H), 52.9 (CH_3, Me)

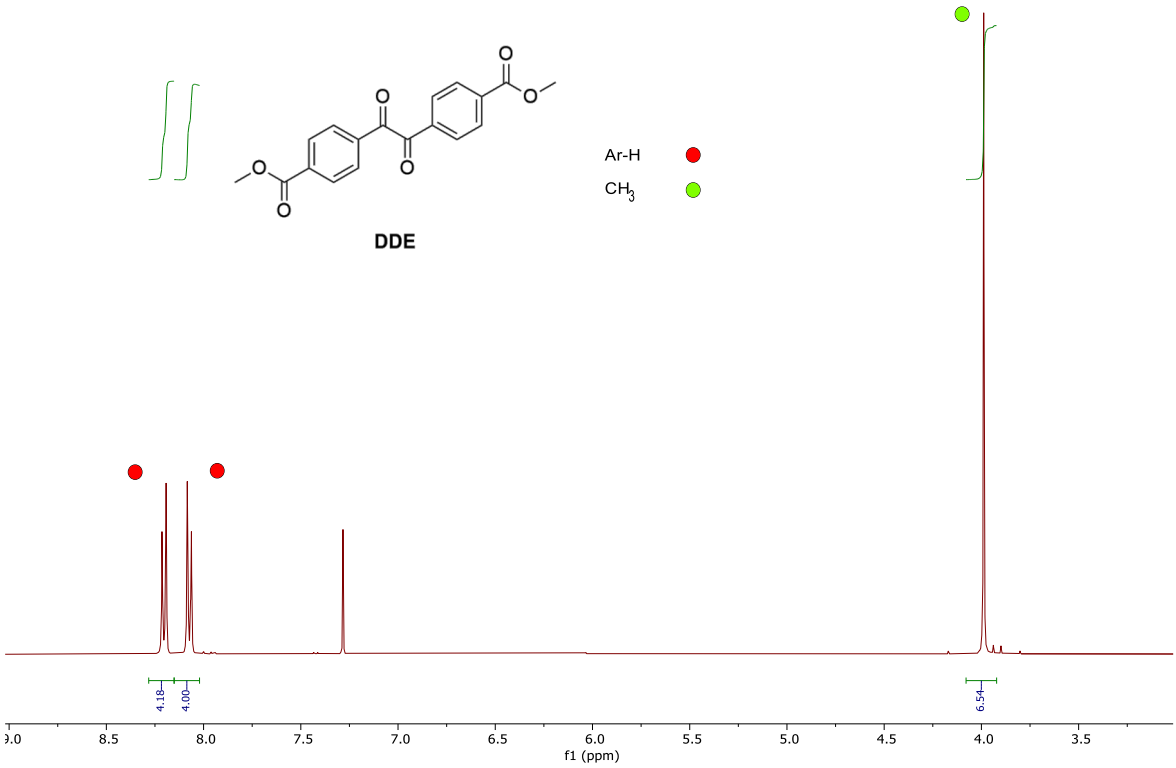


Figure S10. ^{1}H NMR spectrum of compound **4** in $CDCl_3$ at 298K.

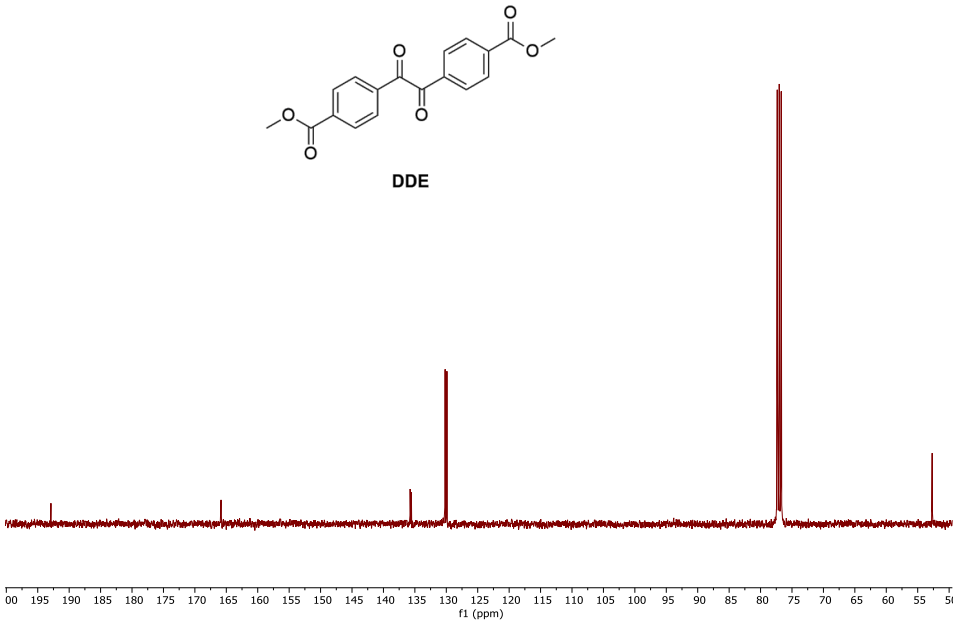


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of DDE (**4**) in $CDCl_3$ at 298K.

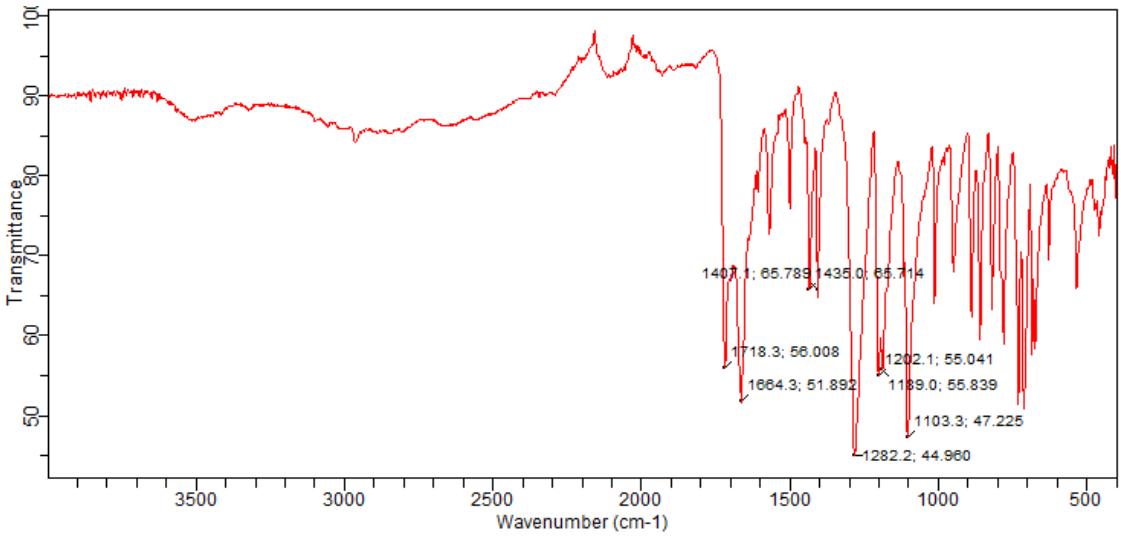


Figure S12: FT-IR spectrum of DDE (**4**).

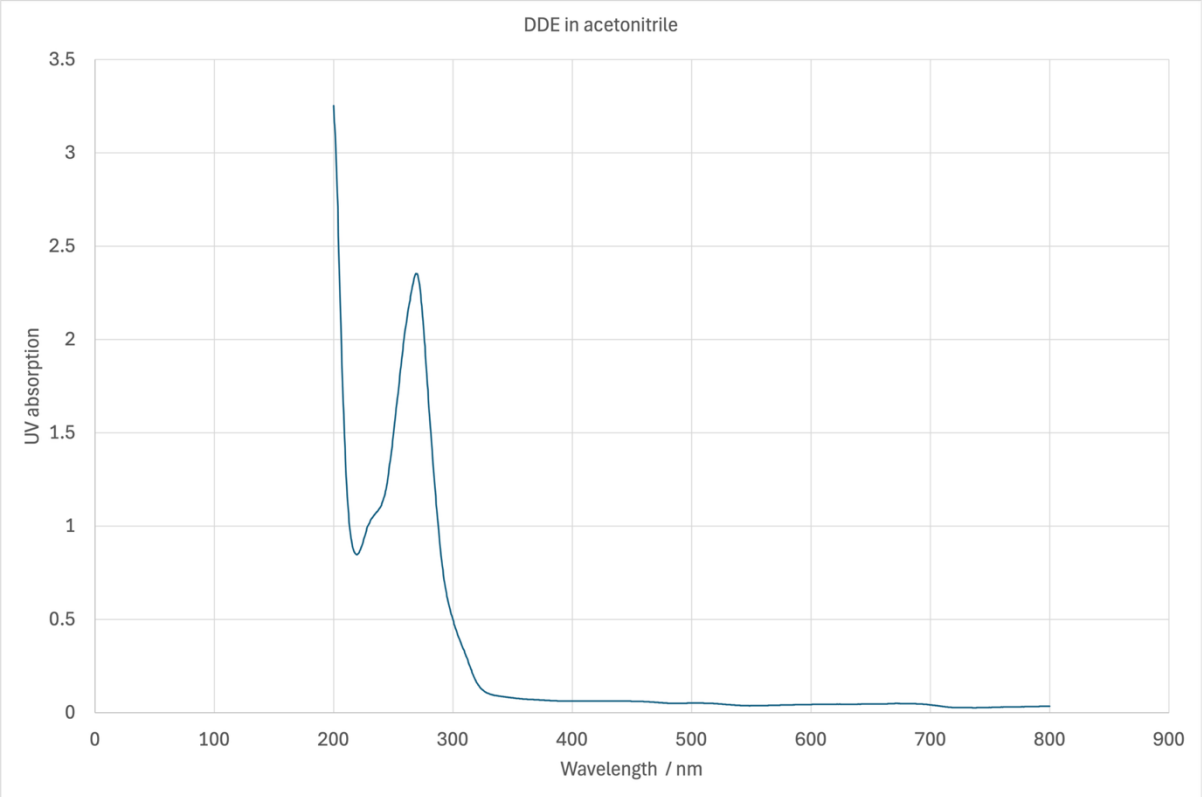
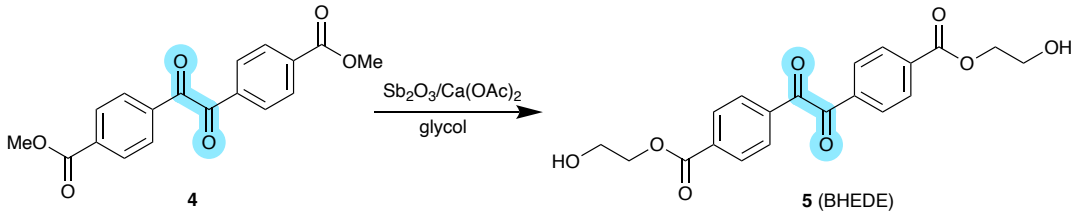


Figure S13. UV-vis spectrum of DDE (**4**) (c = 68 µM in acetonitrile).

Synthesis of bis(hydroxyethyl) diketo ester (BHEDE) **5**



A 50 mL round-bottom flask was charged with DDE **4** (1 g, 3 mmol) and ethylene glycol (10 mL). Sb_2O_3 (40mg) and $Ca(OAc)_2$ (8mg) were added as catalysts, and the solution was stirred at 200 °C for 2 hours. At the end of the reaction, deionised water was added and the pale-orange solid precipitates. The solid was further washed with deionised water and the di(hydroxyethyl) ester **5** (0.79 g, 68% yield) was collected after drying. M.p.: 184-186 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.21 (d, 4H, Ar-H), 8.14 (d, 4H, Ar-H), 4.99 (t, 2H, OH), 4.34 (t, 4H, CH_2), 3.73 (q, 4H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 193.9 (C_{quat}, Ar-CO), 165.4 (C_{quat}, Ester CO), 136.2 (C_{quat}, Ar), 135.8 (C_{quat}, Ar), 130.7 (CH, Ar-H), 130.4 (CH, Ar-H), 67.7 (CH_2, Hydroxyethyl), 59.4 (CH_2, Hydroxyethyl). IR (ATR, neat, in cm^{-1}): 3462 (br, O-H), 2968 (m-w, O-H), 2879 (m-w, O-H), 1725 (s, C=O), 1688 (w, aromatic C-H), 1287 (s, aromatic ester C-O), 1079 (s, primary alcohol C-O), 717 (s, aromatic C-H).

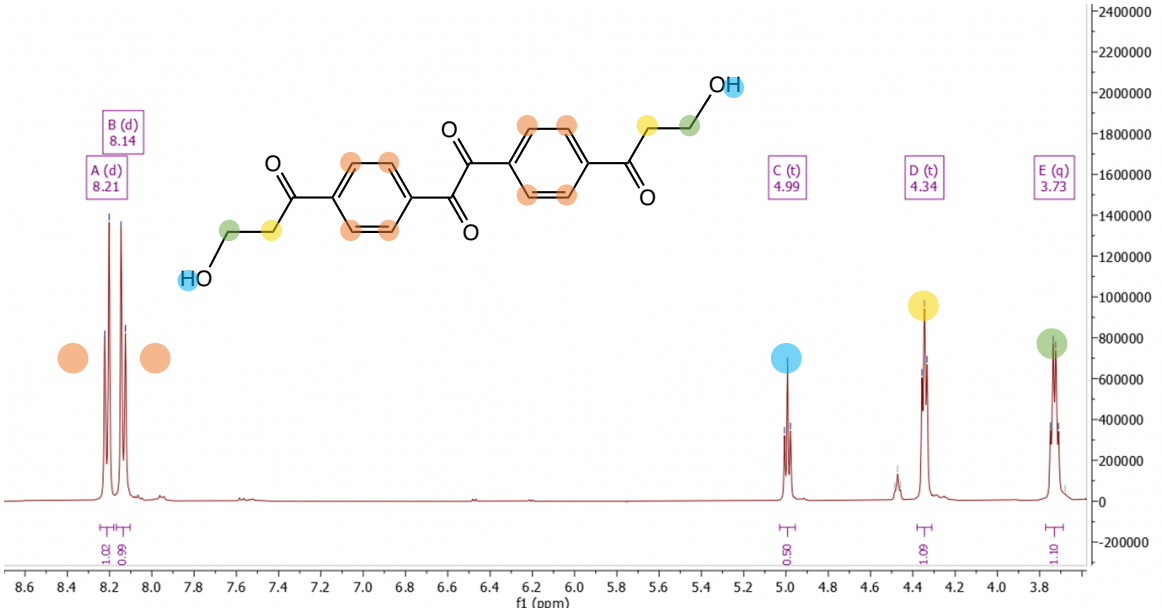


Figure S14. ^{1}H NMR spectrum of compound **5** in d_6-DMSO at 298K.

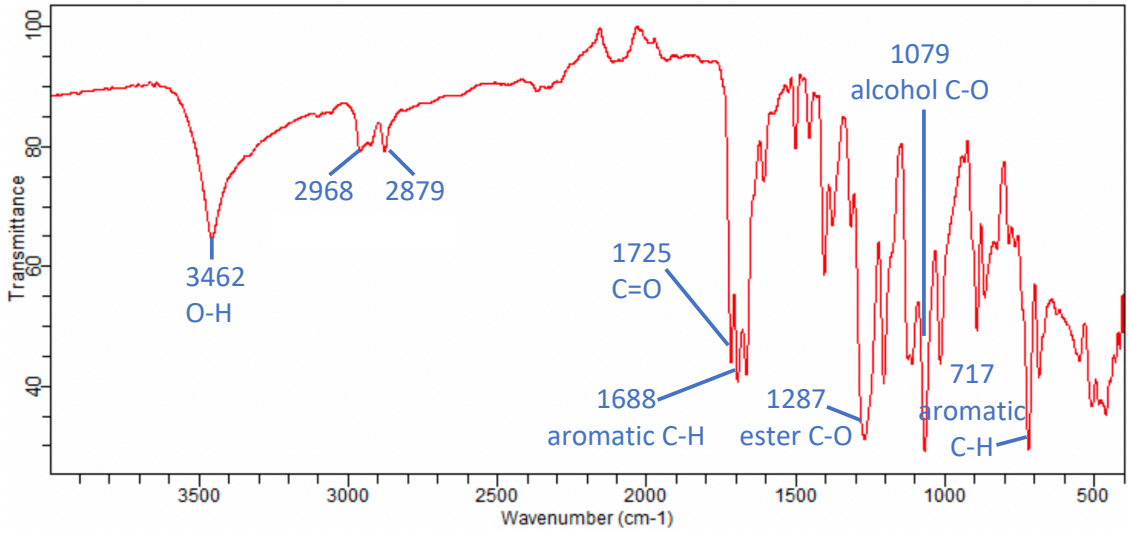


Figure S15. IR spectrum of di(hydroxyethyl) ester **5** (BHEDE).

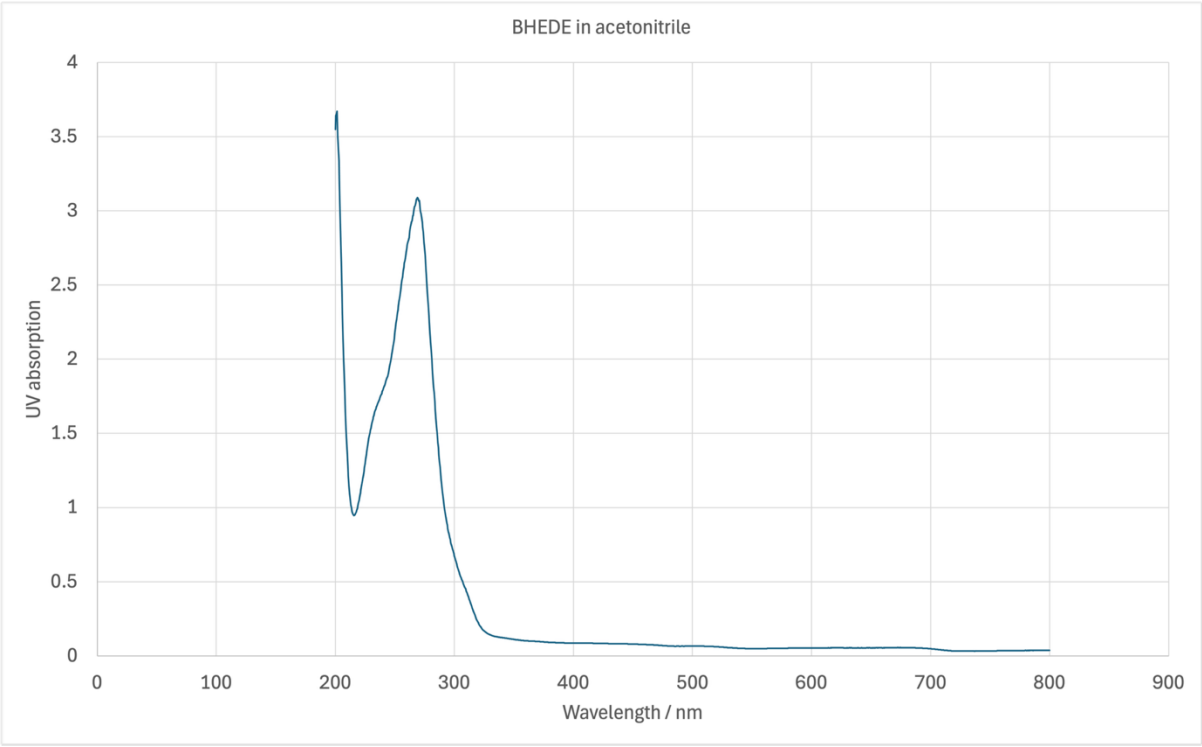


Figure S16. UV-vis spectrum of BHEDE (**5**) (c = 104 µM in acetonitrile).

Reactivity Studies

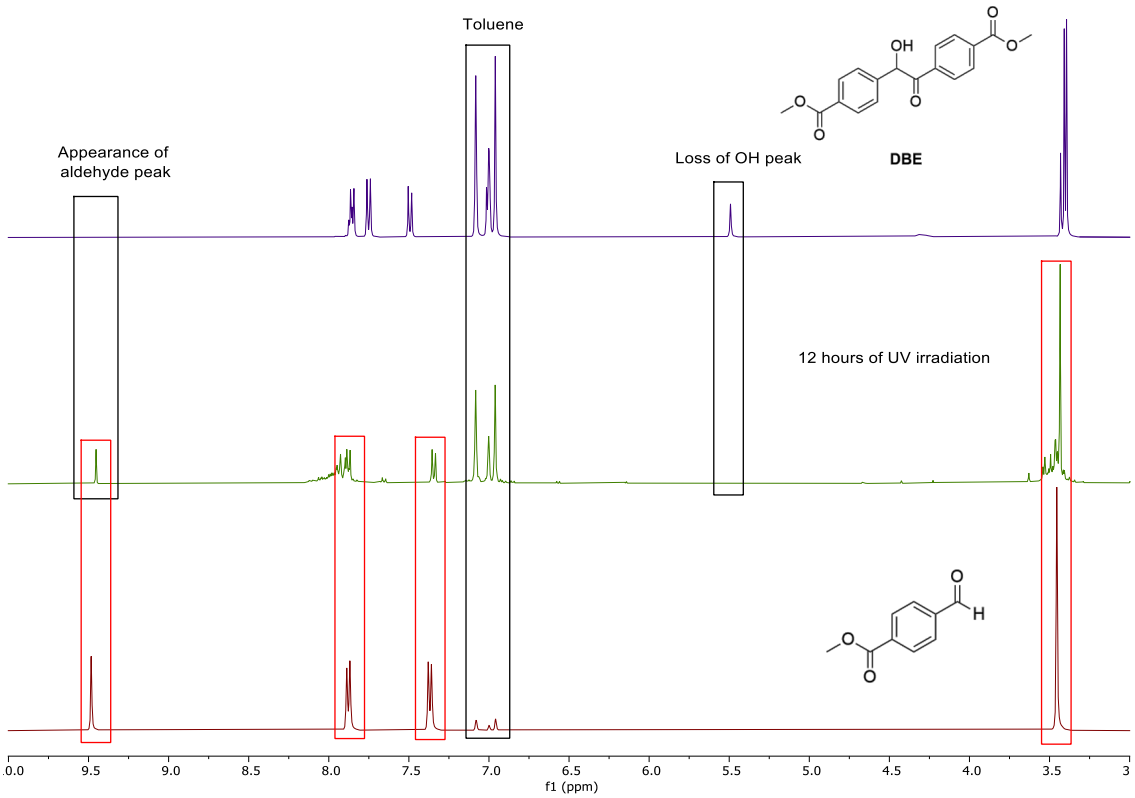


Figure S17. ^{1}H NMR spectrum (toluene-d_8) of DBE (**3**) (top) and after 12 hours of UV irradiation (centre). A spectrum of methyl 4-formylbenzoate was added as reference (bottom).

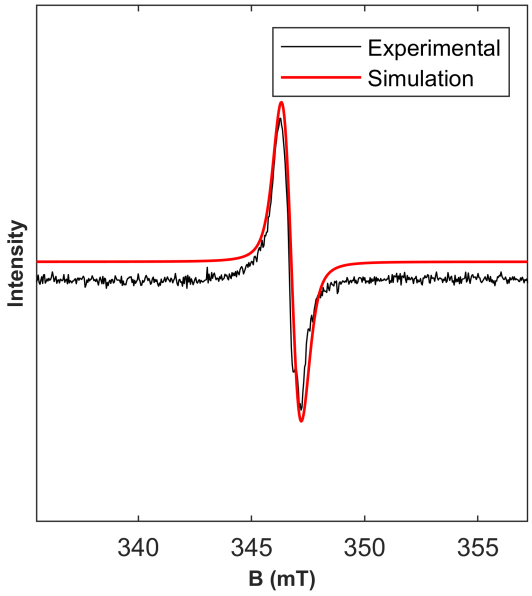


Figure S18. EPR spectrum of DDE (**4**) (neat) at 100 K, after 20 minutes LED irradiation at 405 nm at room temperature. Simulation resulted in g = 2.005328.

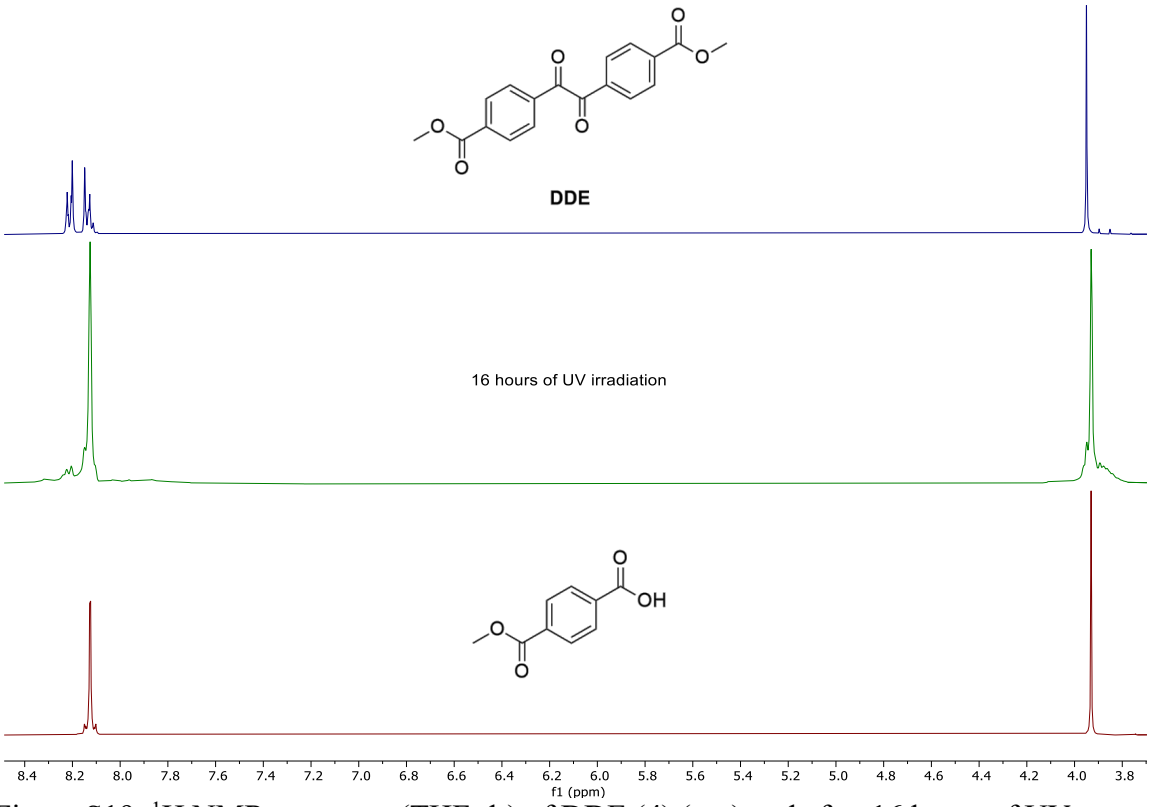


Figure S19. ^{1}H NMR spectrum (THF-d_8) of DDE (**4**) (top) and after 16 hours of UV exposure at 365 nm (centre) in air. A spectrum of monomethyl terephthalate is added as a reference (bottom).

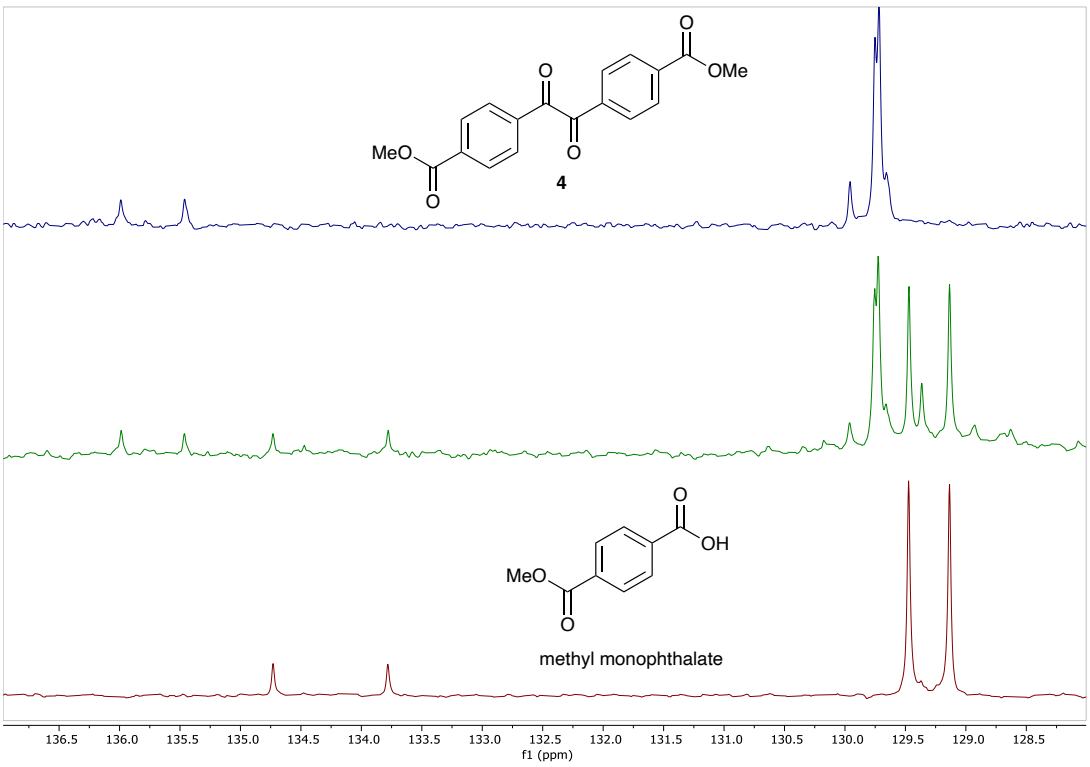


Figure S20. Detail of ^{13}C{^{1}H} NMR spectrum (THF-d_8) of DDE (**4**) (top), after 16 hours UV irradiation (centre) in air. Monomethyl terephthalate is provided as a reference (bottom).

Polymerisation reactions

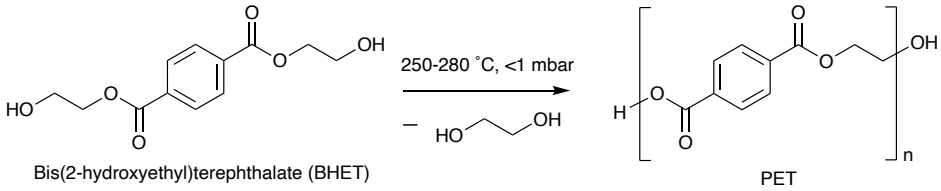


Figure S21. Conventional PET production from BHET via continuous removal of ethylene glycol.

A three-neck 1000 mL flask was charged with a different amounts of BHET together with DDE (**4**) or BHEDE (**5**). A mixture of Sb_2O_3 and $Ca(OAc)_2$ (5:1) was added into the flask (1 wt%). The mixture was stirred under vacuum below 1 mbar using a gastight mechanical stirrer at 270 °C for 1 hour. The copolymer was obtained as a brittle yellow to red solid (depending on DDE content). Purification can be achieved by dissolving the copolymer in hexafluoro isopropanol (1g in 10 mL at 60 ˚C), or more conveniently in N-methylpyrrolidone (NMP) or Cyrene® (1 g in 5 mL at 200 ˚C), followed by precipitation in cold methanol. This results in off-white to yellow powders which were analysed by IR spectroscopy, TGA, GPC and DSC analysis.

Figure S22. Appearance of a BHET/BHEDE copolymer, obtained after polymerisation of BHET and BHEDE (100:1) at 270 ˚C under vacuum.

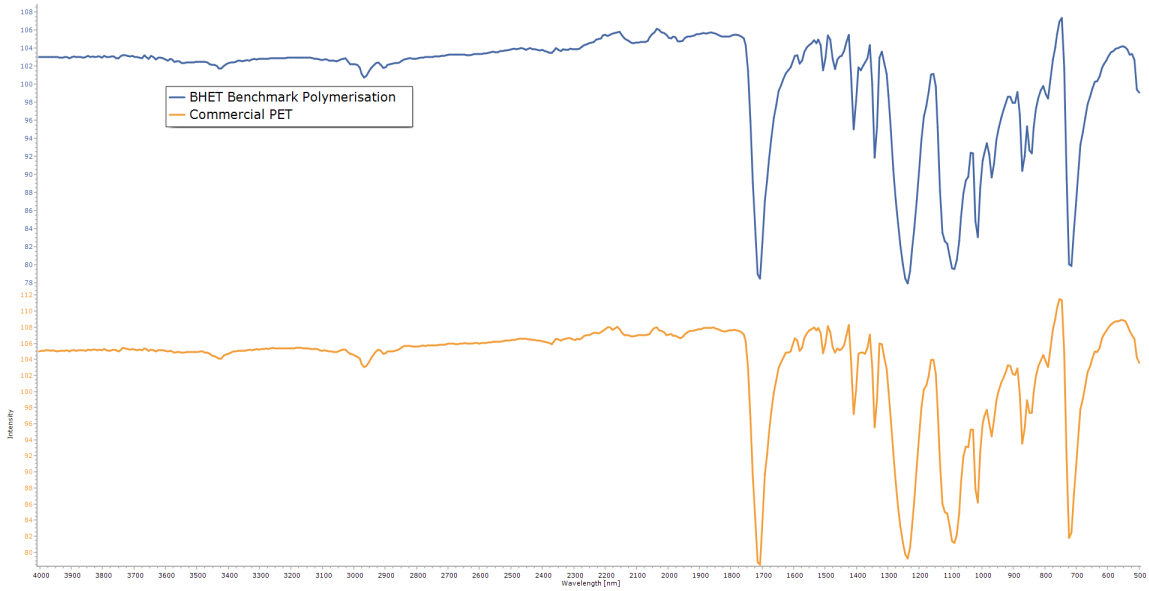


Figure S23. IR spectrum of PET prepared from BHET (blue) and commercial PET (orange).

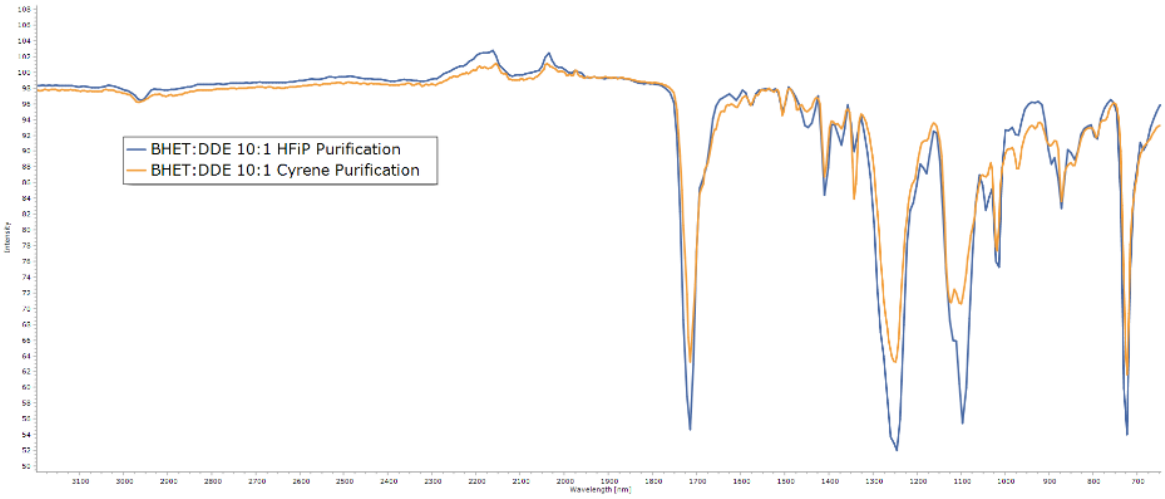


Figure S24. IR spectrum of a BHET:DDE co-polymer (10:1) purified with HFIP (blue) and Cyrene® (orange).

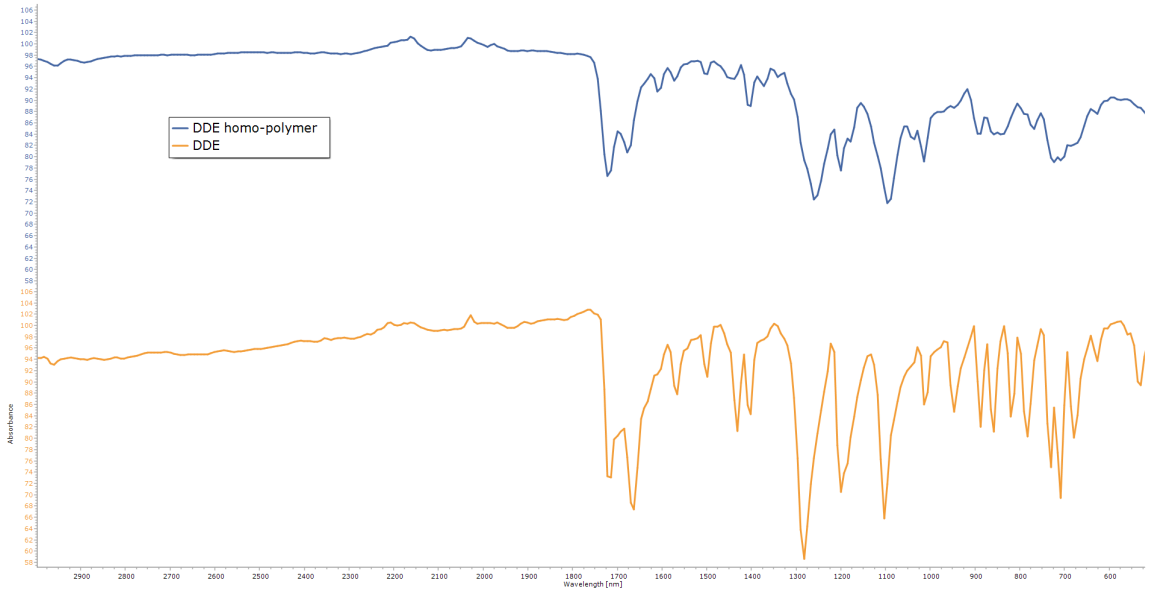


Figure S25. IR spectrum of PDDE obtained from the polymerisation of DDE (**4**) and ethylene glycol at 250 ˚C (top). The IR spectrum of DDE (bottom).

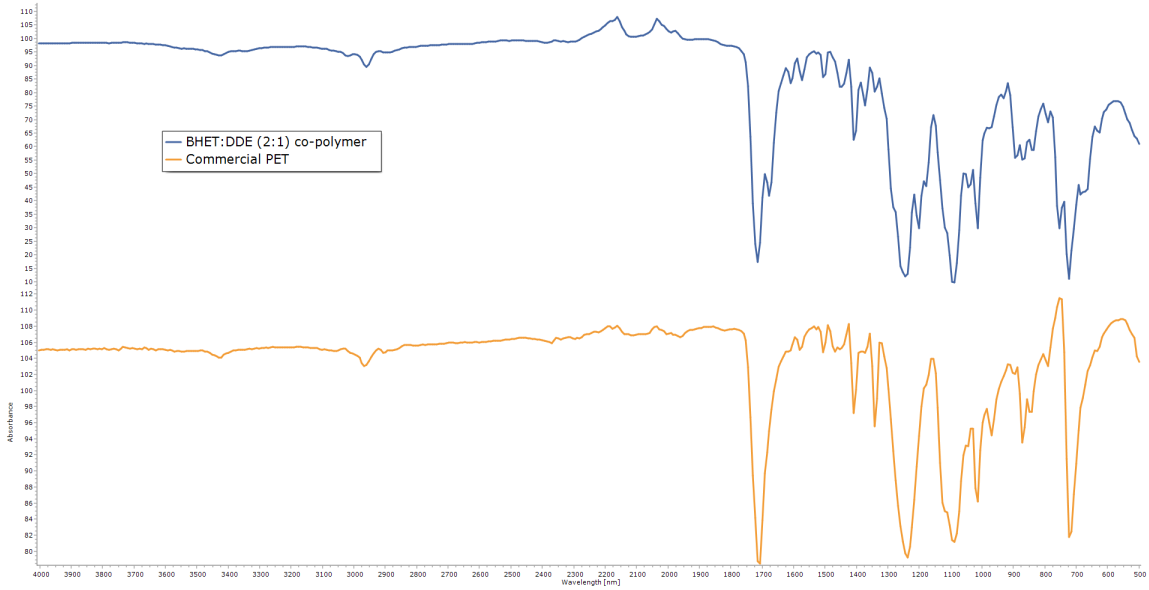


Figure S26a. IR spectrum of BHET/DDE copolymer (2:1) obtained from the polymerisation of BHET and DDE (top). IR spectrum of PET for comparison (bottom).

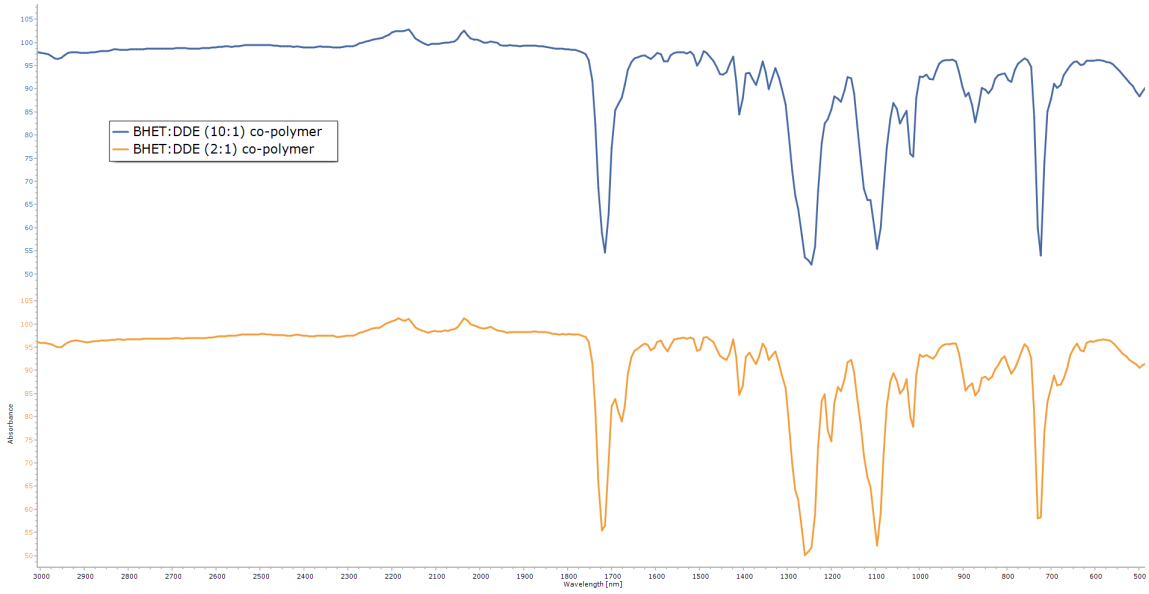


Figure S26b. IR spectrum of the BHET:DDE co-polymer (10:1) (top) and the BHET:DDE co-polymer (2:1) (bottom).

DSC Analysis

The DSC experiments consisted of three phases:

- The sample was heated from 0 to 280 °C at a rate of 10 °C/min
- The sample was cooled from 280 to 0 °C at a rate of -10 °C/min
- The sample was heated again from 0 to 280 °C at a rate of 10 °C/min

Table S1. DSC analysis results for PET compared with BHET/DDE copolymer (10:1)

Entry	BHET eq.	DDE eq.	T_g (°C)	T_{cc} (°C)	T_m (°C)
1	1	0	74.3	107.3	257.4
2	10	1	78.1	128.7	238.0

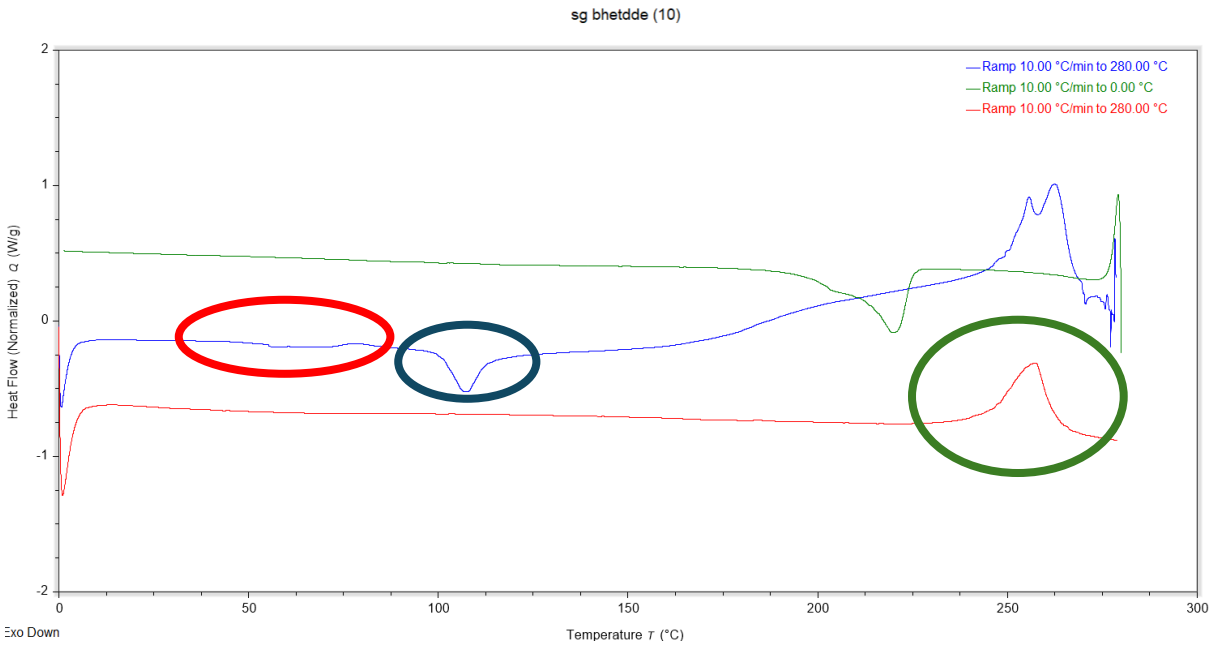


Figure S27. DSC analysis of PET polymer showing T_g (red circle), T_{cc} (blue circle), and T_m (green circle) transition temperatures.

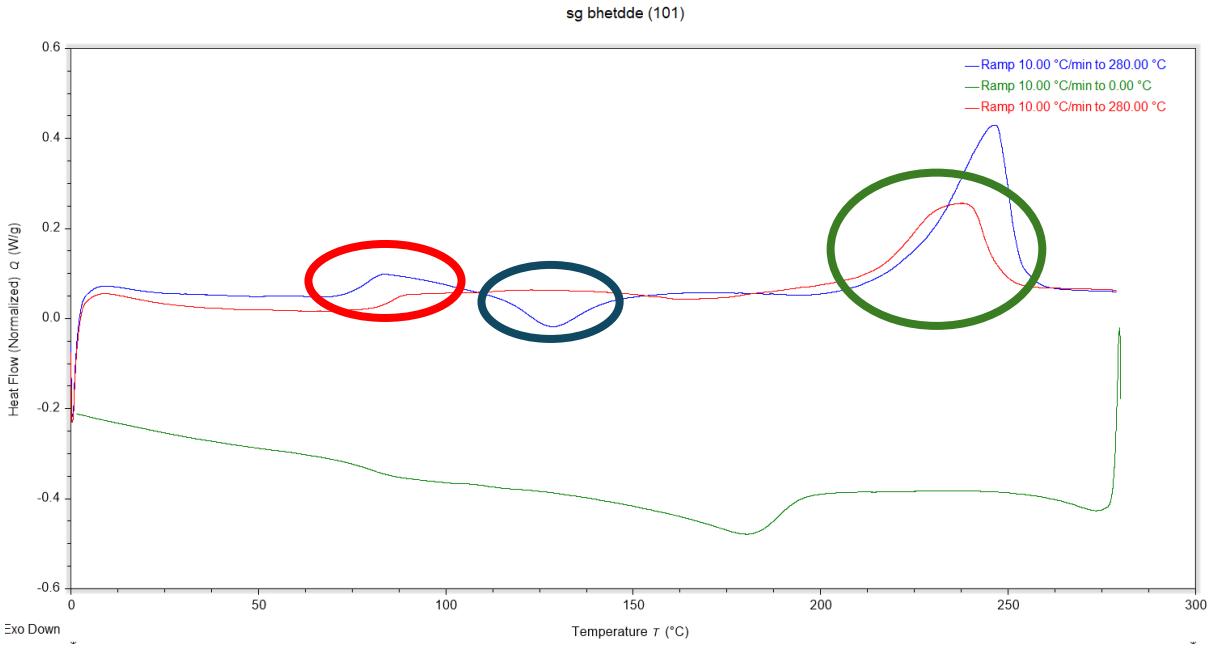


Figure S28. DSC analysis of the BHET/DDE co-polymer (10:1 ratio) showing T_g (red circle), T_{cc} (blue circle), and T_m (green circle) transition temperatures.

DSC Analysis of extruded copolymers

The DSC experiments consisted of four phases:

- The sample was heated from 0 to 280 °C at a rate of 10 °C/min
- The sample was cooled from 280 to 0 °C at a rate of -10 °C/min
- The sample was heated again from 0 to 280 °C at a rate of 10 °C/min
- The sample was heated again from 0 to 280 °C at a rate of 20 °C/min

DSC analysis was performed on all extruded copolymer samples listed below in Table S2. Example traces are shown in Figures S29-S37.

Table S2. DSC analysis of extruded copolymers prepared from PET and DDE or BHEDE.

Sample	**Additive**	**Tg[a]**	**Tm[a]**	**Tg[b]**	**Tc[b]**	**Tm[b]**
G1	DDE 1.7 wt%	79.7	241.1/249.6	80.0	144.0	246.9
G2	DDE 3.4 wt%	80.9	240.4/248.9	78.4	139.9	247.5
G3	DDE 8.4 wt%	80.6	242.0/249.5	78.5	nd.	247.7
G4	DDE 16.8 wt%	80.8	240.5/248.0	79.7	144.3	245.9
G5	BHEDE 2.0 wt %	80.4	240.6/249.4	79.5	146.1	246.9
G6	BHEDE 4.0 wt%	80.4	241.8/249.7	78.5	143.3	247.7

Conditions: a) heating and cooling rate: 10 ˚C/min. 2nd heating cycle. b) heating rate: 20 ˚C/min. (nd = not determinable).

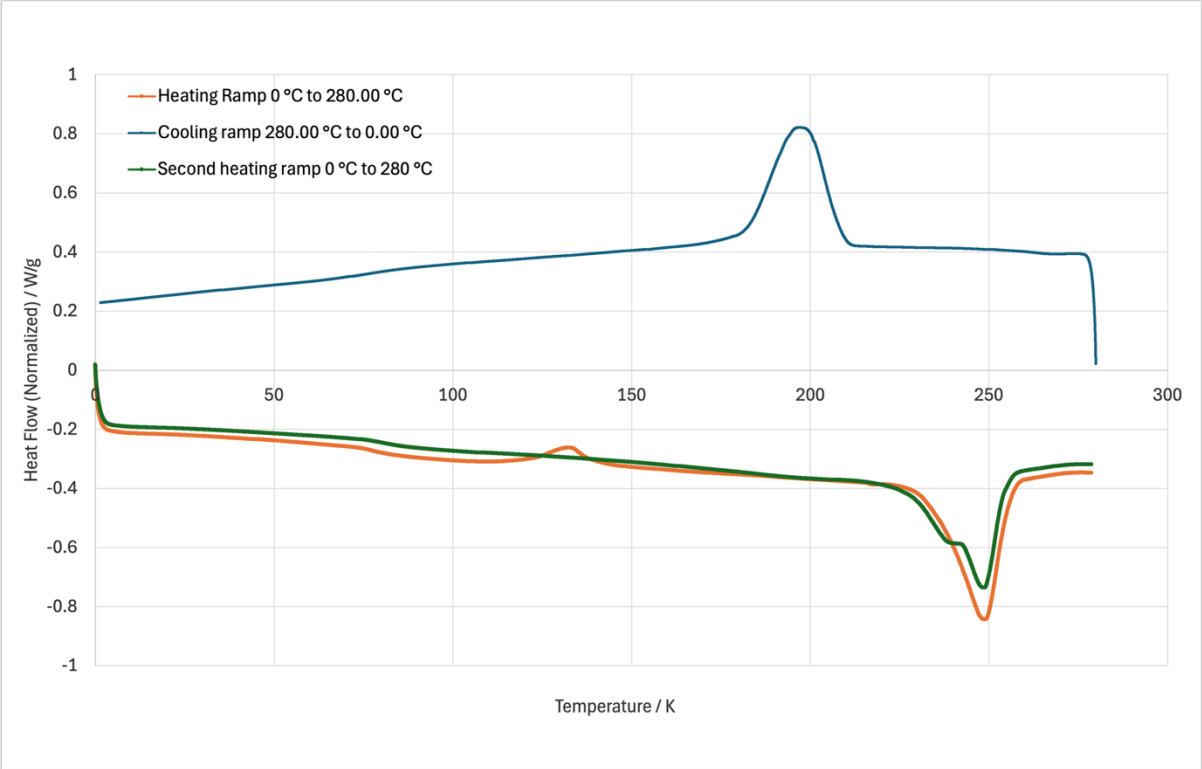


Figure S29. DSC analysis of copolymer G1 (PET/DDE1.7wt%) (Endotherm down).

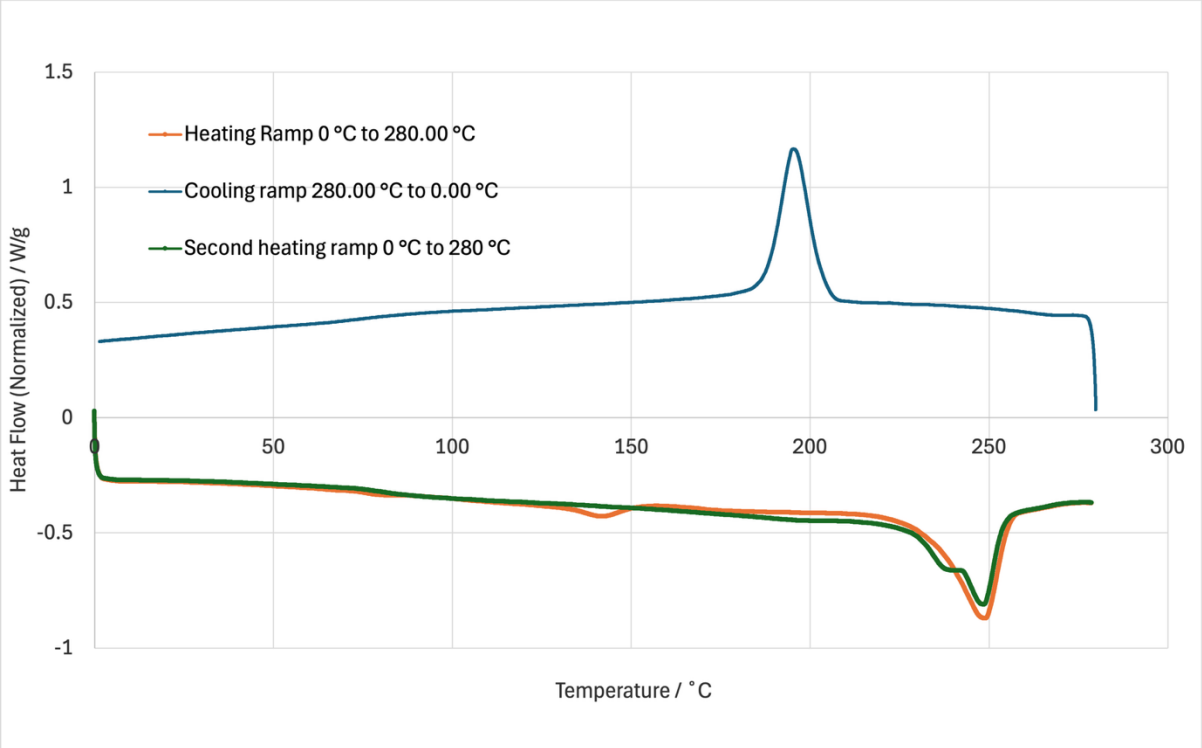


Figure S30. DSC analysis of copolymer G2 (PET/DDE3.4wt%) (Endotherm down).

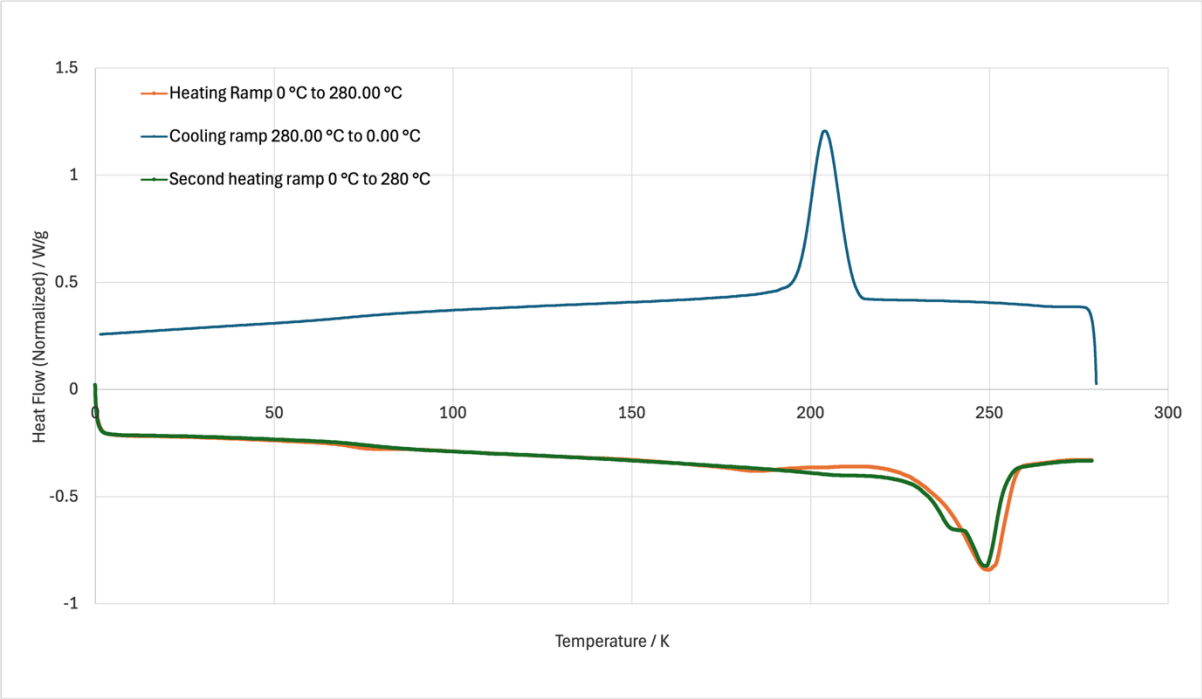


Figure S31. DSC analysis of copolymer G3 (PET/DDE8.4wt%) (Endotherm down).

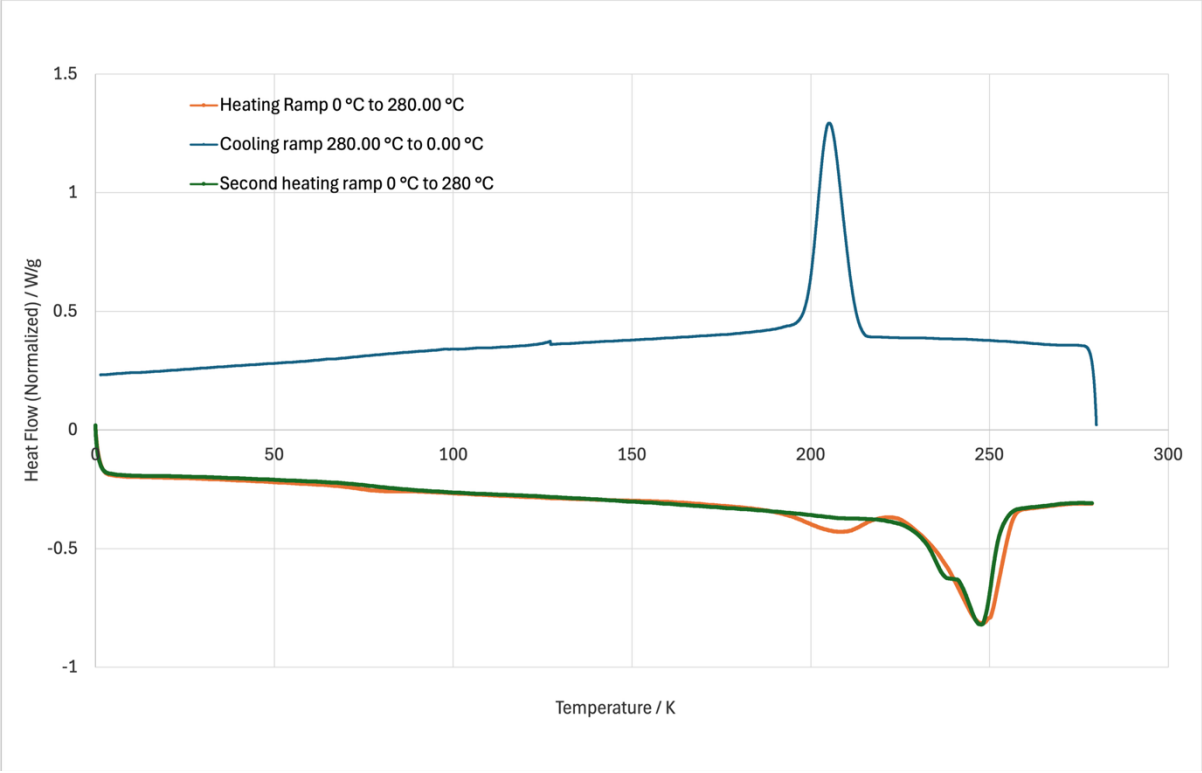


Figure S32. DSC analysis of copolymer G4 (PET/DDE16.8wt%) (Endotherm down).

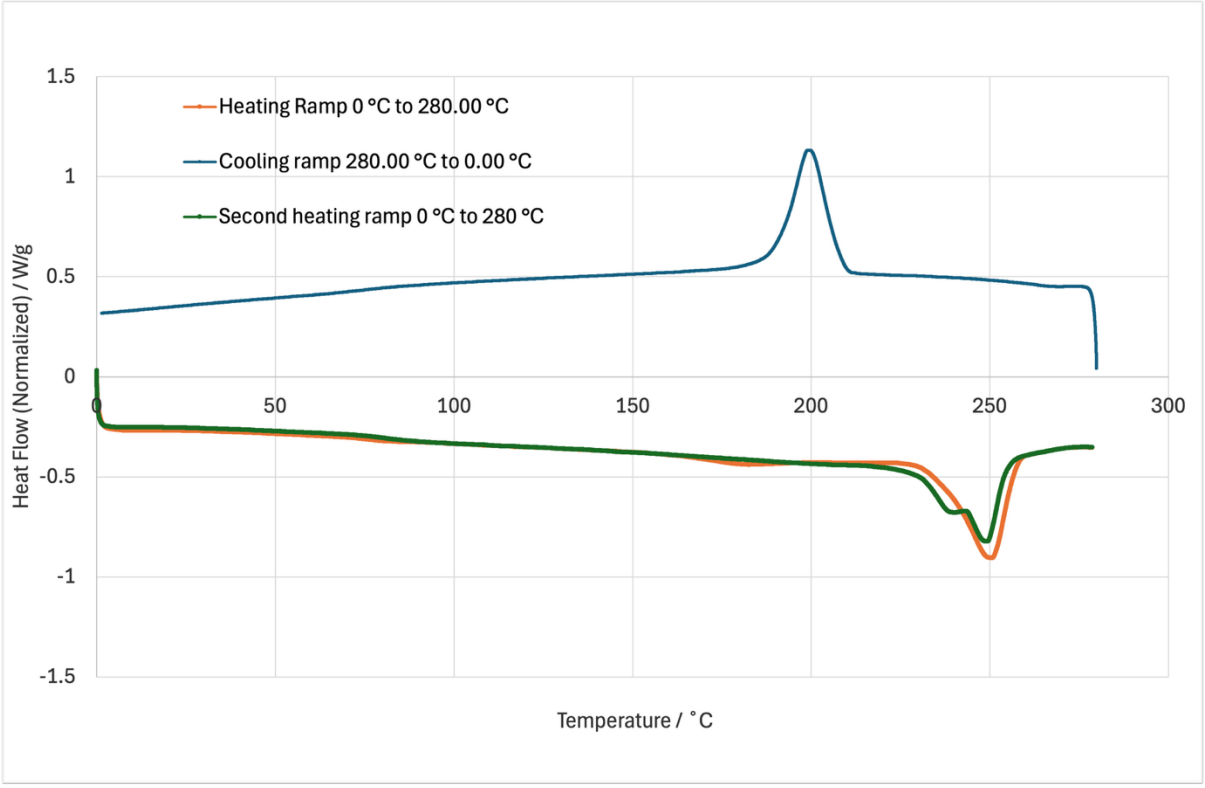


Figure S33. DSC analysis of copolymer G5 (PET/BHEDE2.0wt%) (Endotherm down).

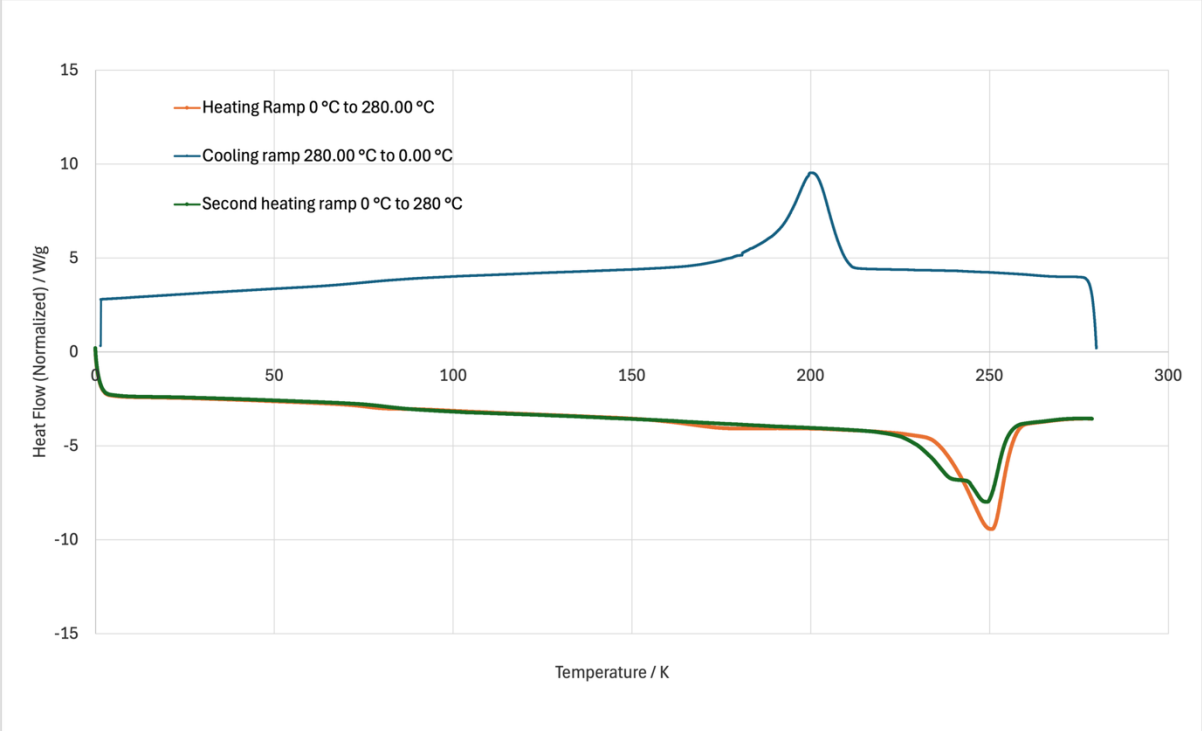


Figure S34. DSC analysis of copolymer G6 (PET/BHEDE4.0wt%) (Endotherm down).

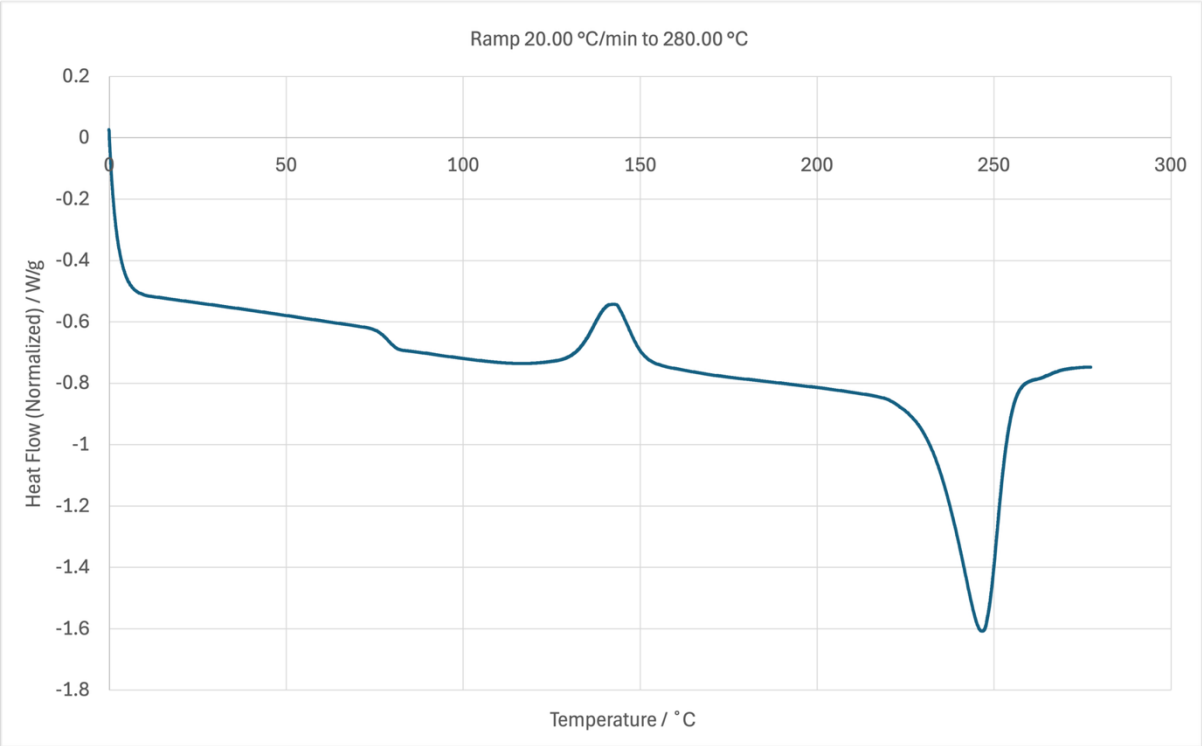


Figure S35. DSC analysis of copolymer G1 (PET/DDE1.7wt%) at 20 ˚C/min (Endotherm down).

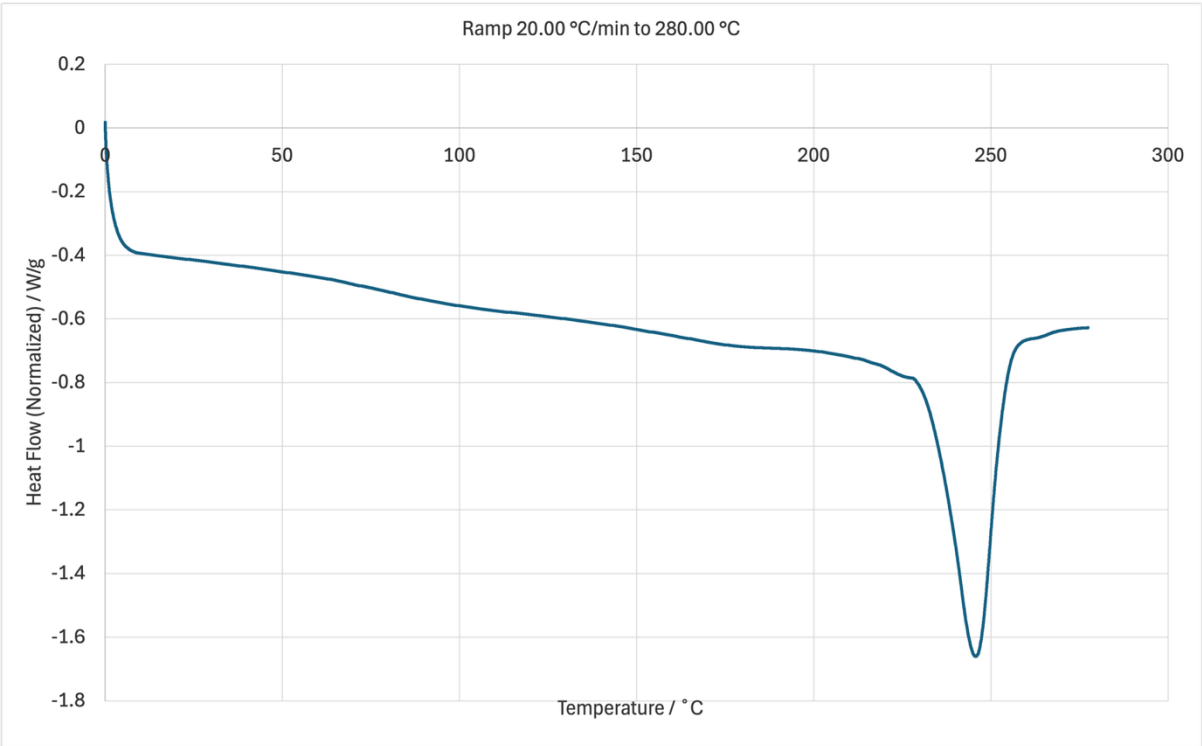


Figure S36. DSC analysis of copolymer G4 (PET/DDE1.7wt%) at 20 ˚C/min (Endotherm down).

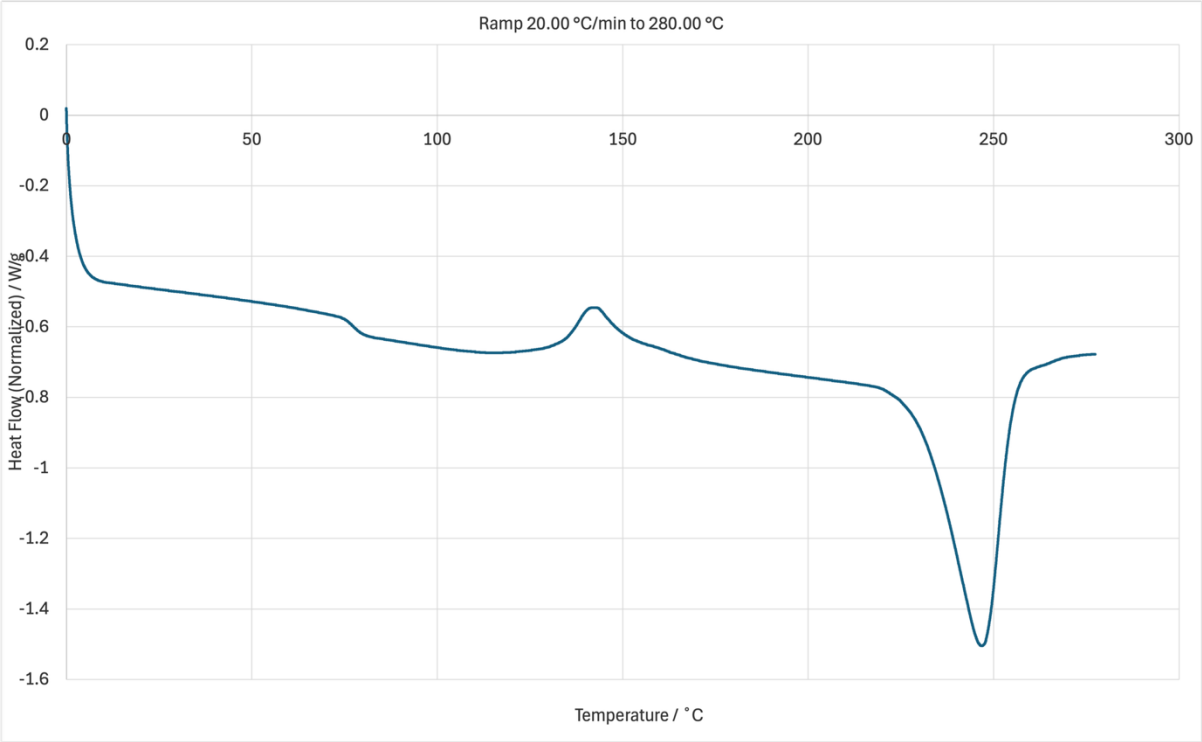


Figure S37. DSC analysis of copolymer G6 (PET/BHEDE4.0wt%) at 20 ˚C/min (Endotherm down).

TGA analysis

TGA analysis were carried under a N_2 atmosphere or under air in which the sample was heated from 25 to 700 °C at a rate of 10 °C/min.

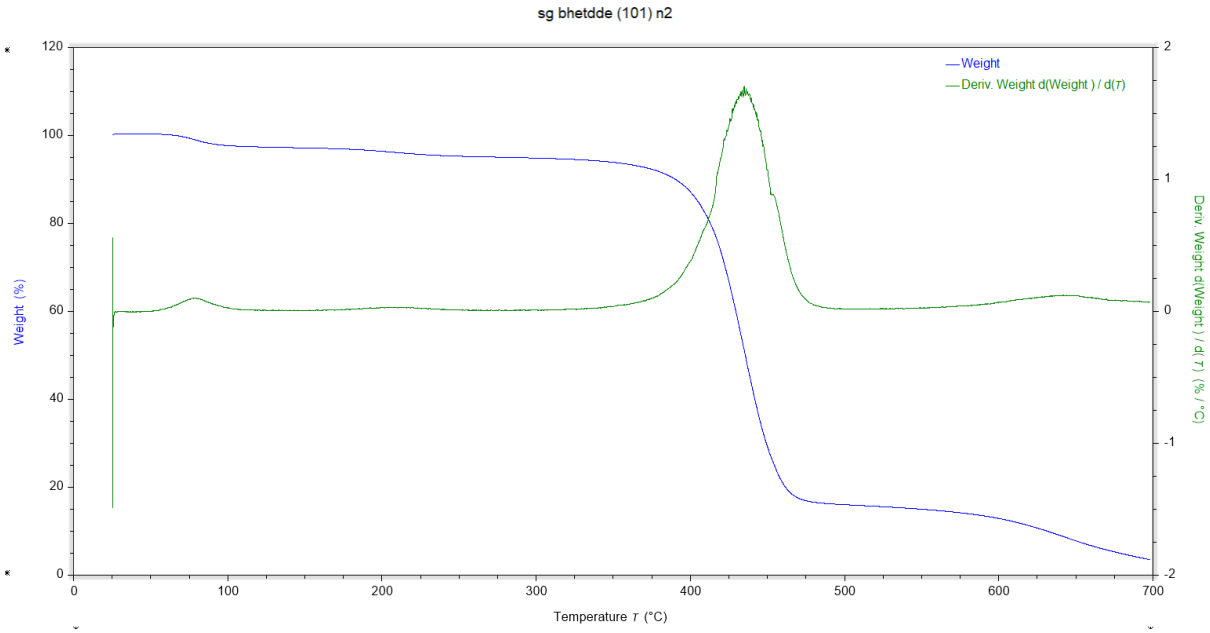


Figure S38. TGA analysis for BHET/DDE co-polymer at a 10:1 ratio under N_2 gas, showing the onset temperature for decomposition at 410 °C.

Polymer processing

Xplore MC15

Reactive extrusion experiments have been carried out using a micro-compounder Xplore MC15 HT (Xplore Instruments BV, The Netherlands). The micro-compounder is a small extrusion unit equipped with co-rotating screws that allows achieving a homogeneous melt compound thanks to its side recirculation channel. The procedure was adapted from the results reported by Bascucci.[4] Pellets of PET dried overnight in an oven at 125 °C were added at a constant screw rate of 100 rpm, under a flow of nitrogen gas and every barrel compartment set at 275 °C. As shown in Figure S30, the force initially fluctuates at high values during feeding as solid pellets are being added via the front feeder (0-40 seconds). The force then decreases steadily during the first 2.5 minutes before stabilizing for the rest of the experiment, suggesting that little polymer degradation occurs after this time. This indicates that PET degradation in the

barrel is slow following the initial 2.5 minute period and suggests that it is not crucial to minimise the recycling time when preparing samples.

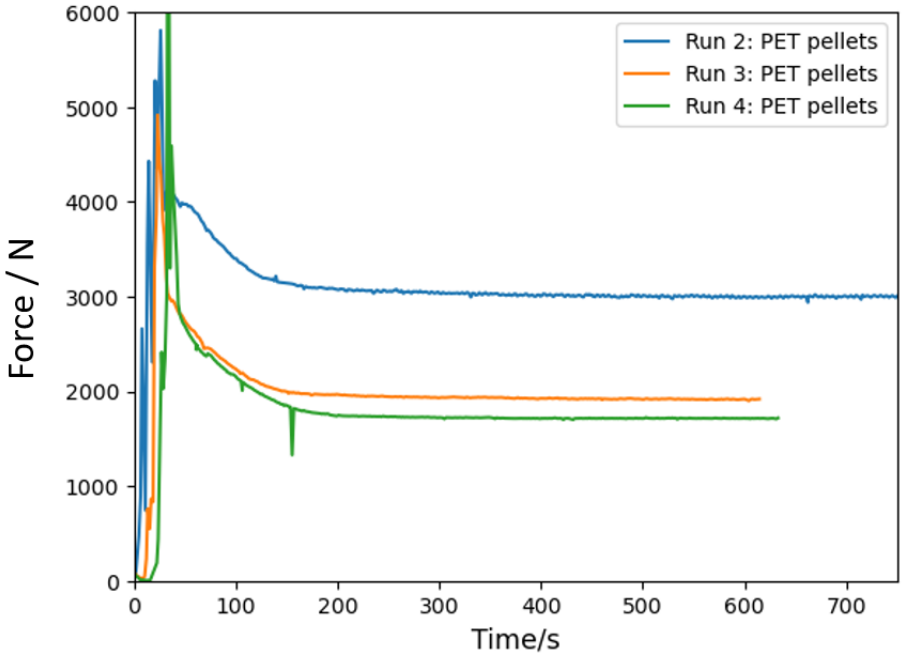


Figure S39: Force vs. time curves for three extrusions of PET pellets without any additive.

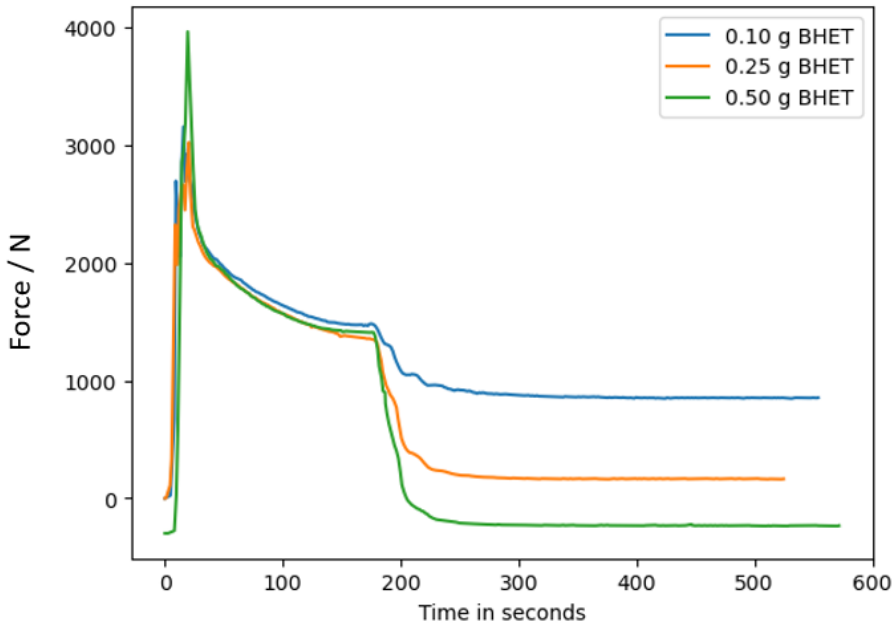


Figure S40: Torque force versus time after the addition of PET (8g, introduced between 0 and 20 seconds), left to stabilize for 3 minutes before the addition of BHET.

Polymer samples were prepared with different additive concentrations for DDE (**4**), DMT, BHEDE (**5**) and BHET. For DDE, a sample was made using the same number of moles of DMT and vice versa for BHEDE and BHET. For simplicity, weight percentages of 1, 2, 5 and 10 were chosen for DMT (based on 13 g PET) and the weights giving the number of moles for DDE. Weights corresponding to the same number of moles as 1 and 2 wt% DMT were also used to prepare samples containing BHEDE and BHET, as shown in Table S3. Higher additive concentrations for BHET and BHEDE were avoided as the resulting polymers would become too brittle for hot-pressing.

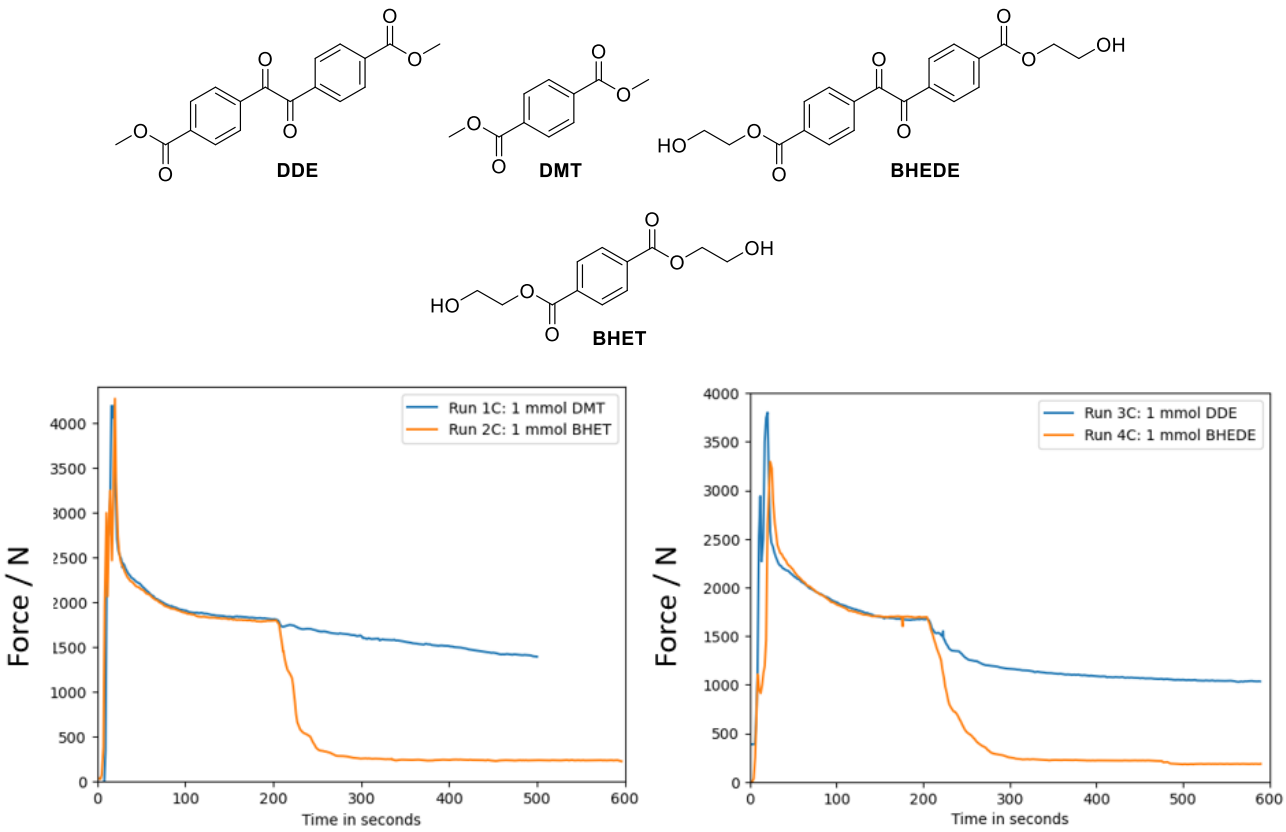


Figure S41. Change in torque force during circulation of PET (13 g) upon the addition of various additives DMT, BHET, DDE and BHEDE (1 mmol) after 200 s.

Table S3. Extrusion experiments using PET (13 g) and different amounts of additives.

Sample	Additive wt%	MW additive / g/mol	Moles additive / mmol	Weight additive / mg	Measured/ mg
G1	DDE 1.7 wt%	326.36	0.67	218.5	219.0
G2	DDE 3.4 wt%	326.36	1.34	436.9	438.1
G3	DDE 8.4 wt%	326.36	3.35	1092.4	1093.5
G4	DDE 16.8 wt%	326.36	6.69	2184.8	2183.8
F2	DMT 1.0 wt%	194.19	0.67	130.0	130.5
F3	DMT 2.0 wt%	194.19	1.34	260.0	260.2
F4	DMT 5.0 wt%	194.19	3.35	650.0	652.0
F5	DMT 10.0 wt%	194.19	6.69	1300.0	1301.7
G5	BHEDE 2.0 wt %	386.36	0.67	258.6	258.3
G6	BHEDE 4.0 wt%	386.36	1.34	517.3	517.3
F6	BHET 1.3 wt%	254.24	0.67	170.2	170.1
F7	BHET 2.6 wt%	254.24	1.34	340.4	340.4

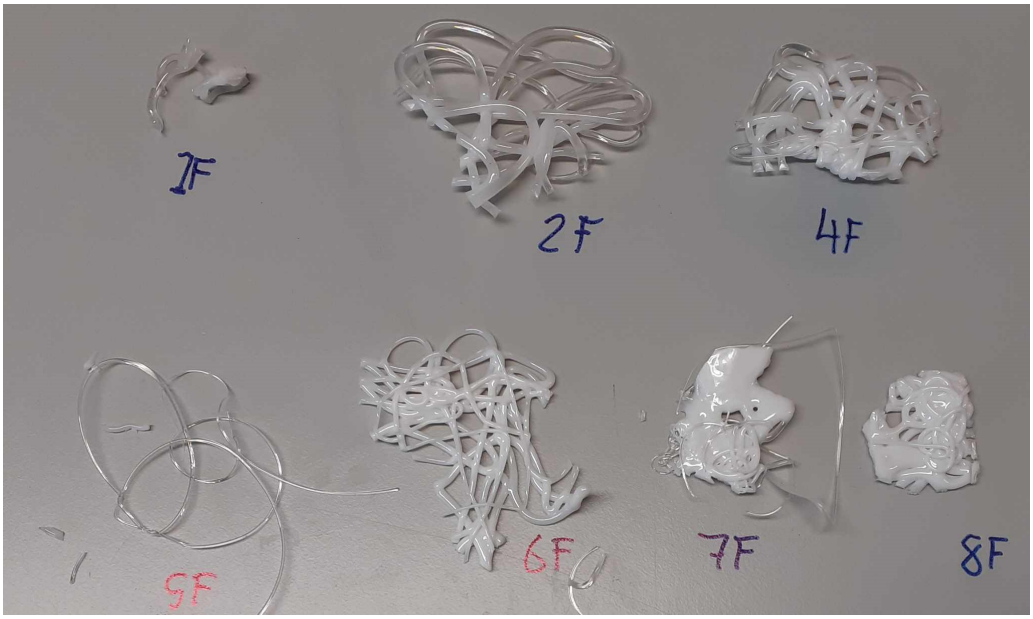


Figure S42. Polymer samples of PET with DMT and BHET additives at various loadings obtained upon extrusion (see Table S2).

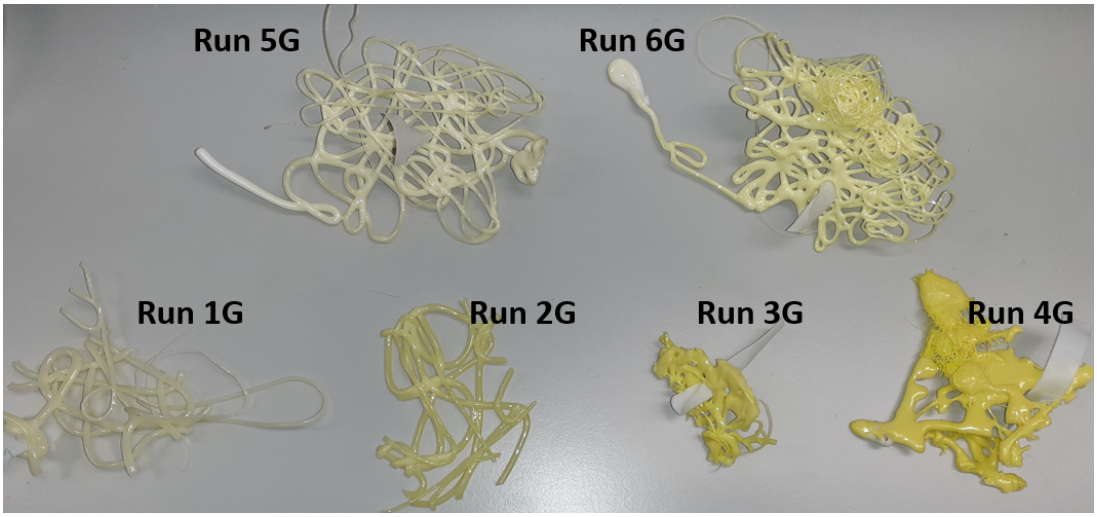


Figure S43. Polymer samples of PET with DDE and BHEDE additives at various loadings obtained upon extrusion (see Table S2).

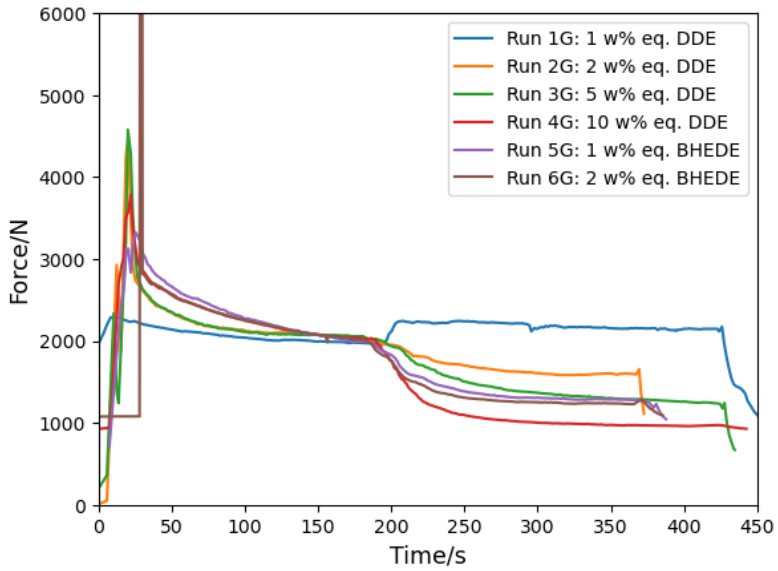


Figure S44. Change in torque force during circulation of PET upon the addition of DDE and BHEDE additives after 200 s.

NMR Analysis of extruded copolymers

PET/DDE and PET/BHEDE copolymers prepared by reactive extrusion as listed in Table S2 have been analysed by solution phase ^{1}H NMR analysis, recorded at 25 ˚C. Approximately 10 mg polymer sample was dissolved in a mixture of hexafluoroisopropanol-d_1 (HFIP-d_1) and $CDCl_3$ (1:9 v/v), kept at 70 ˚C for several hours until completely dissolved.[5]. The spectra for PET, DDE and DMT measured under the same conditions have been included for comparison.

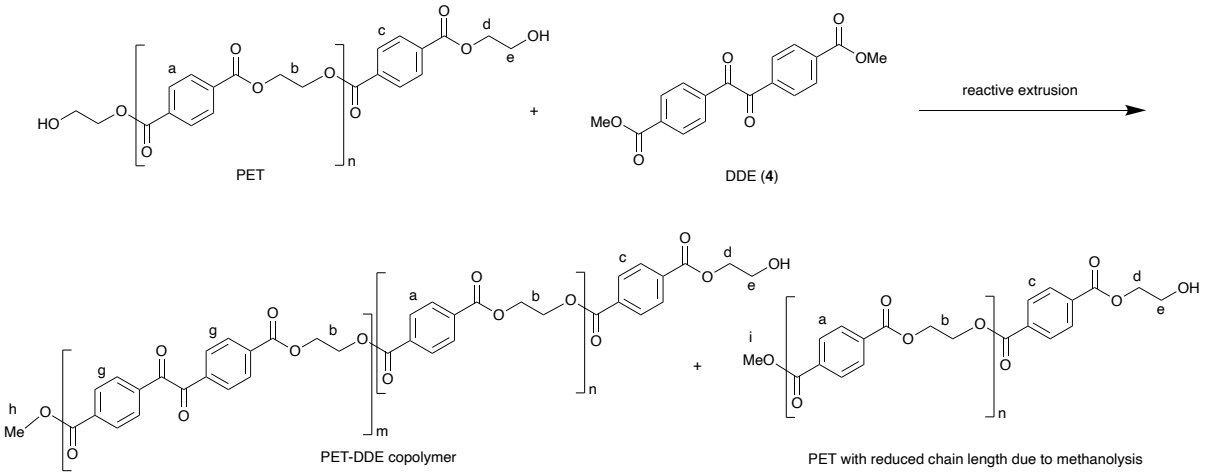


Figure S45. Assignment of ^{1}H NMR signals in PET/DDE copolymers.

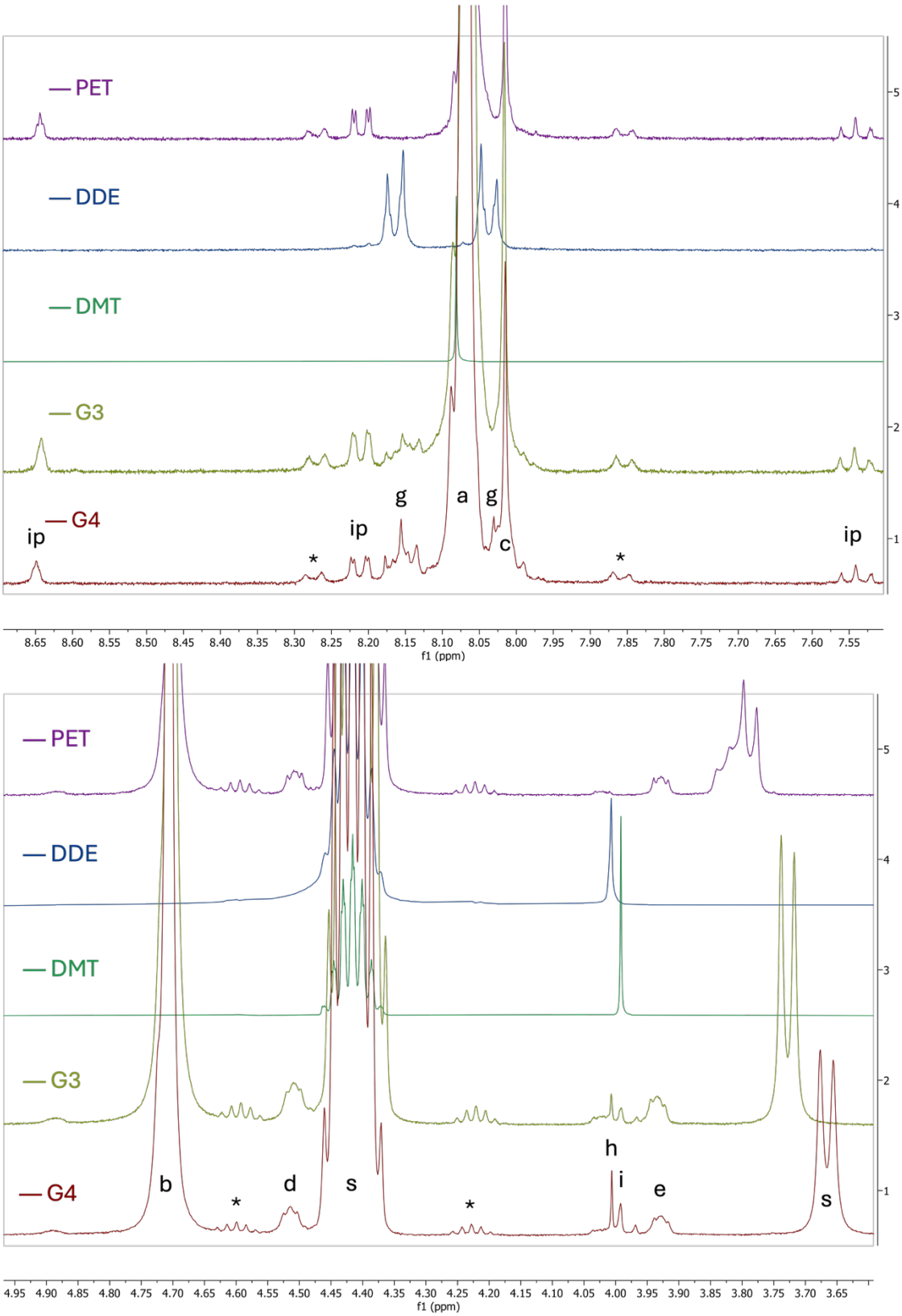


Figure S46. ^{1}H NMR spectrum in HFIP-d_1/$CDCl_3$ of PET/DDE copolymers G3 and G4. Assignments are shown in Figure S45. ip = these signals are due to isophthalic acid. The PET used here is a copolymer of terephthalic acid and ethylene glycol, with small amount of isophthalic acid included for processing. * = ^{13}C satellites; s = HFIP-d_1 solvent.

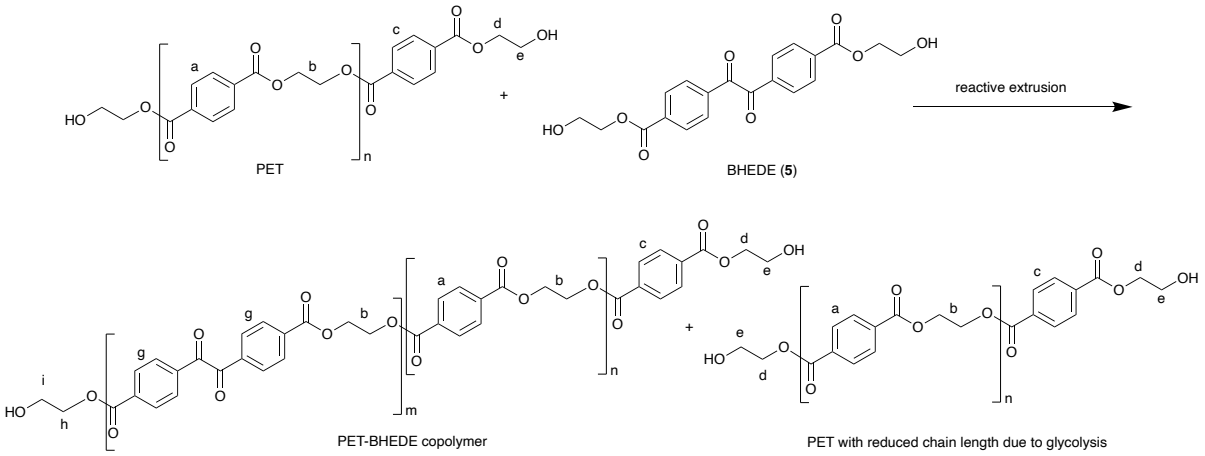
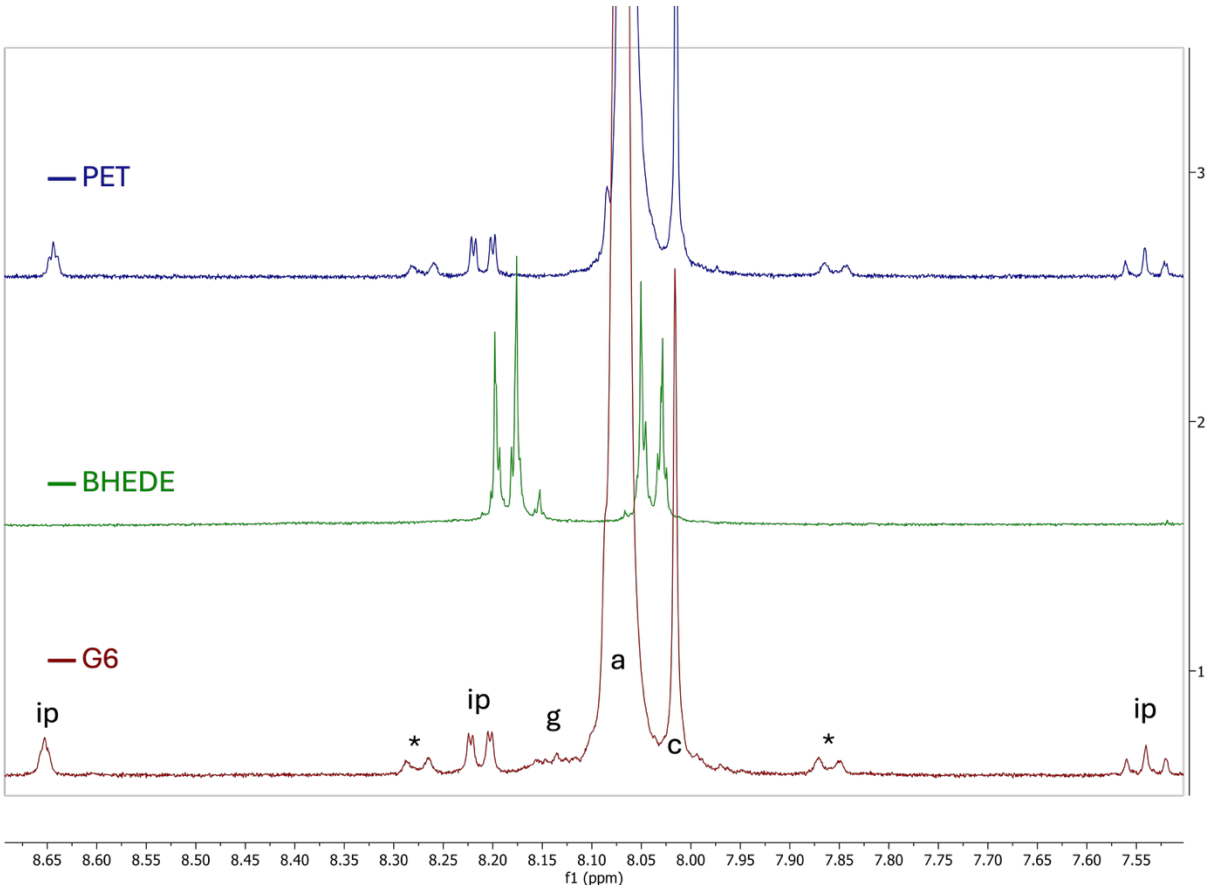


Figure S47. Assignment of ^{1}H NMR signals in PET/BHEDE copolymers.



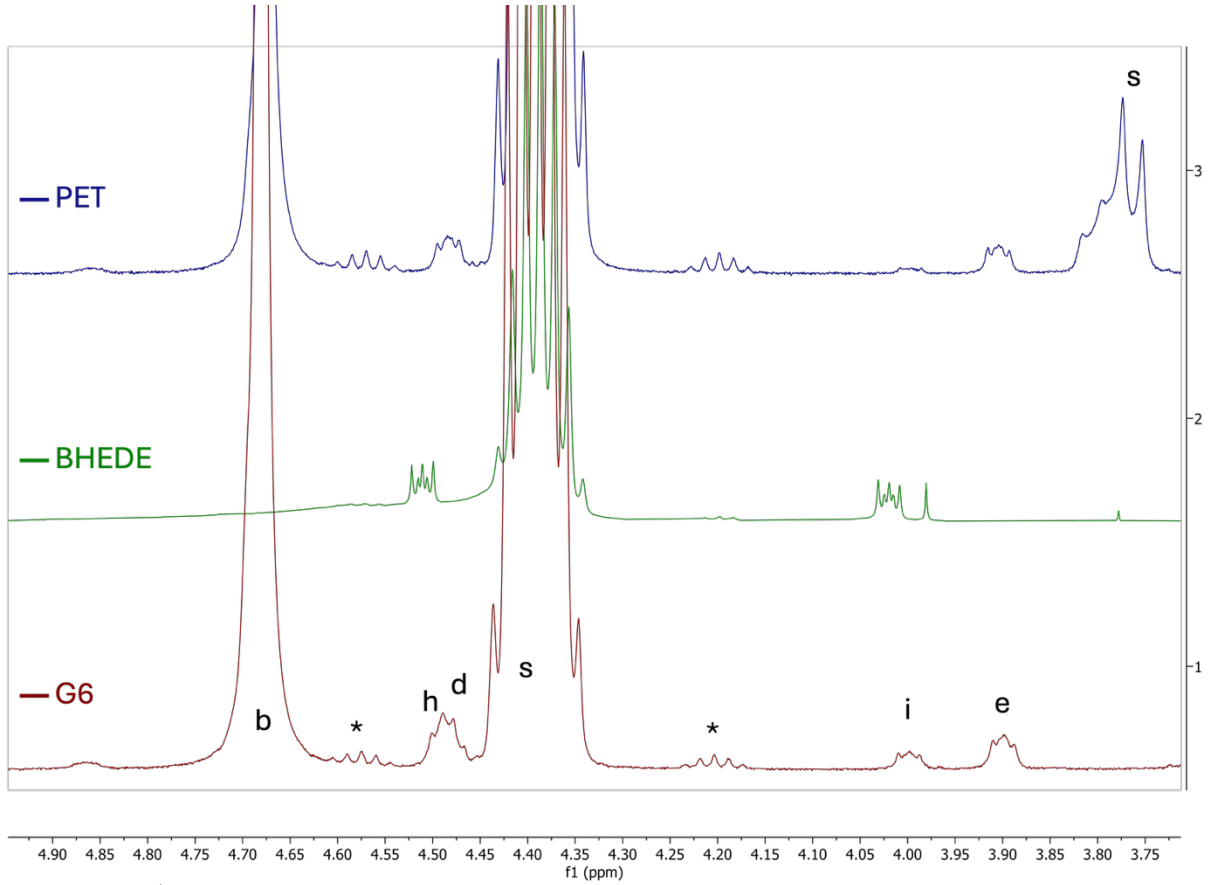


Figure S48. ^{1}H NMR spectrum in HFIP-d_1/$CDCl_3$ of PET/BHEDE copolymer G6. Assignments are shown in Figure S47. ip = these signals are due to isophthalic acid. The PET used here is a copolymer of terephthalic acid and ethylene glycol, with small amount of isophthalic acid included for processing. * = ^{13}C satellites; s = HFIP-d_1 solvent.

Sample preparations using hot press

Hot press Equipment: Temperature controller (A), heating element (B) and press (C).

Procedure: 1) Polyester samples were dried overnight in an oven at 125 ˚C. 2) Extruded sample cut into segments and divided into 1.15 g portions, 3) Samples are melted between Teflon sheets at 270 ºC for 75 sec, 4) Hot press unit placed in the hydraulic press and 2-ton pressure applied at 75 sec mark, 5) The sample is held under pressure for 10 sec before temperature set to 235 ºC, 6): Sample removed from the hot press at 235 ºC and cooled to RT in a water bath.

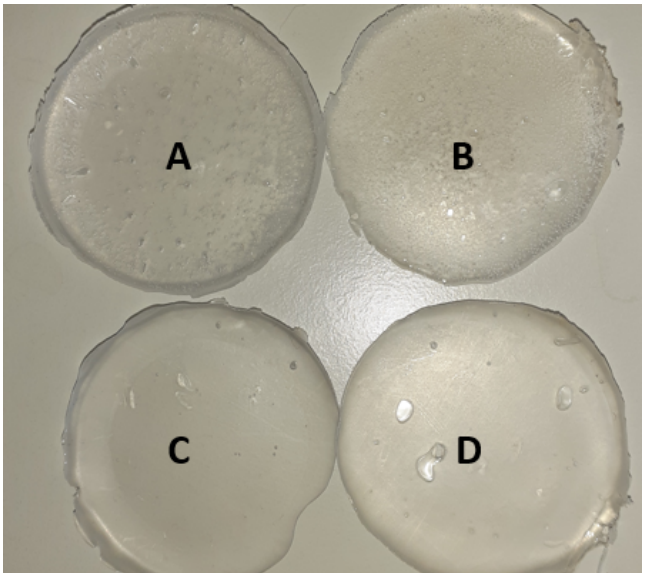


Figure S49: Hot pressed samples from non-dried PET pellets (A) and non-dried extruded PET sample (B) showing bubble formation due to residual moisture. Pre-dried PET pellets (C) and pre-dried extruded PET sample (D).

Weathering Experiments

Accelerated weathering conditions have been carried out using a QUV chamber equipped with UV-B (313 nm) lamps. Copolymer samples were extruded and pressed into plates of 1 mm thickness and were analysed by GPC analysis before and after 14 days of weathering. The weathering cycle used involved irradiation at 0.71±0.02 W/m^2 for 8 hours at 60 °C followed by 4 hours of darkness at 50±2 °C. There was no specific control of the relative humidity (generally 50% at 20 ˚C). Results for copolymers have been compared with pure PET, which was processed under the same conditions. Table S3 contains the original GPC data in duplicate (A and B), with the reference codes that relate to the GPC analysis shown below. In Table S4, the averaged values are tabulated, which are shown in Figure 8.

Control experiments were also performed for DDE (**4**) and BHEDE (**5**), which were dissolved in DCM and the solution adsorbed onto silica TLC plates. After evaporation of the solvent, the plates were placed in the QUV chamber and exposed to the same weathering

conditions as above. After 14 days, the product was redissolved and analysed by NMR. No changes were observed under these conditions.

Table S4. GPC analysis of PET copolymers with different additives, before (T0) and after accelerated weathering (T14).

Additive / wt%	**mmol**	**GPC code**	**M_n**	**M_w**	**M_z**	**Đ**
None		1F T0 A	28,900	56,900	93,800	1.97
None		1F T0 B	31,500	56,200	87,100	1.79
None		1F T14 A	23,400	53,500	93,100	2.28
None		1F T14 B	24,900	52,100	87,900	2.09
DDE (**4**) / 17	6.70	4G T0 A	9,100	21,800	43,200	2.40
DDE (**4**) / 17	6.70	4G T0 B	9,300	22,100	45,000	2.38
DDE (**4**) / 17	6.70	4G T14 A	8,600	21,100	52,000	2.82
DDE (**4**) / 17	6.70	4G T14 B	8,600	23,100	46,600	2.70
DMT / 10	6.70	5F T0 A	22,400	41,400	66,000	1.85
DMT / 10	6.70	5F T0 B	21,900	40,800	64,400	1.86
DMT / 10	6.70	5F T14 A	19,400	42,300	77,800	2.18
DMT / 10	6.70	5F T14 B	21,400	42,300	71,100	1.98
BHEDE (**5**) / 4	1.34	6G T0 A	18,500	35,000	57,400	1.90
BHEDE (**5**) / 4	1.34	6G T0 B	14,900	30,100	53,100	2.05
BHEDE (**5**) / 4	1.34	6G T14 A	14,000	38,300	81,600	2.74
BHEDE (**5**) / 4	1.34	6G T14 B	16,100	40,900	82,800	2.55
BHET / 3	1.34	7F T0 A	15,800	31,400	50,000	1.99
BHET / 3	1.34	7F T0 B	16,900	31,800	51,000	1.88
BHET / 3	1.34	7F T14 A	14,700	30,100	52,100	2.04
BHET / 3	1.34	7F T14 B	16,400	29,100	45,400	1.78

Conditions: weathering experiments. Polymer blends were prepared by extrusion, mixing 13 g PET with the additive (6.70 mmol for DDE and DMT; 1.34 mmol for BHEDE and BHET). All experiments have been carried out in duplicate, indicated as A and B in column 3.

Table S5. GPC analysis of PET copolymers with different additives, before and after accelerated weathering. Averaged molecular weight values, shown graphically in Figure 13 in the main text.

Additive / wt%	Amount mmol	Time days	M_n	M_w	M_z	Đ
none		0	30,200	56,550	90,450	1.88
none		14	24,150	52,800	90,500	2.19
DDE (**4**) / 17	6.70	0	9,200	21,950	44,100	2.39
DDE (**4**) / 17	6.70	14	8,600	22,100	49,300	2.76
DMT / 10	6.70	0	22,150	41,100	65,200	1.86
DMT / 10	6.70	14	20,400	42,300	74,450	2.08
BHEDE (**5**) / 4	1.34	0	16,700	32,550	55,250	1.98
BHEDE (**5**) / 4	1.34	14	15,050	39,600	82,200	2.65
BHET / 3	1.34	0	16,350	31,600	50,500	1.94
BHET / 3	1.34	14	15,550	29,600	48,750	1.91

Conditions: weathering experiments. Polymer blends were prepared by extrusion, mixing 13 g PET with the additive (6.70 mmol for DDE and DMT; 1.34 mmol for BHEDE and BHET). All values are averages from two measurements (see Table S3 for original values).

GPC Analysis

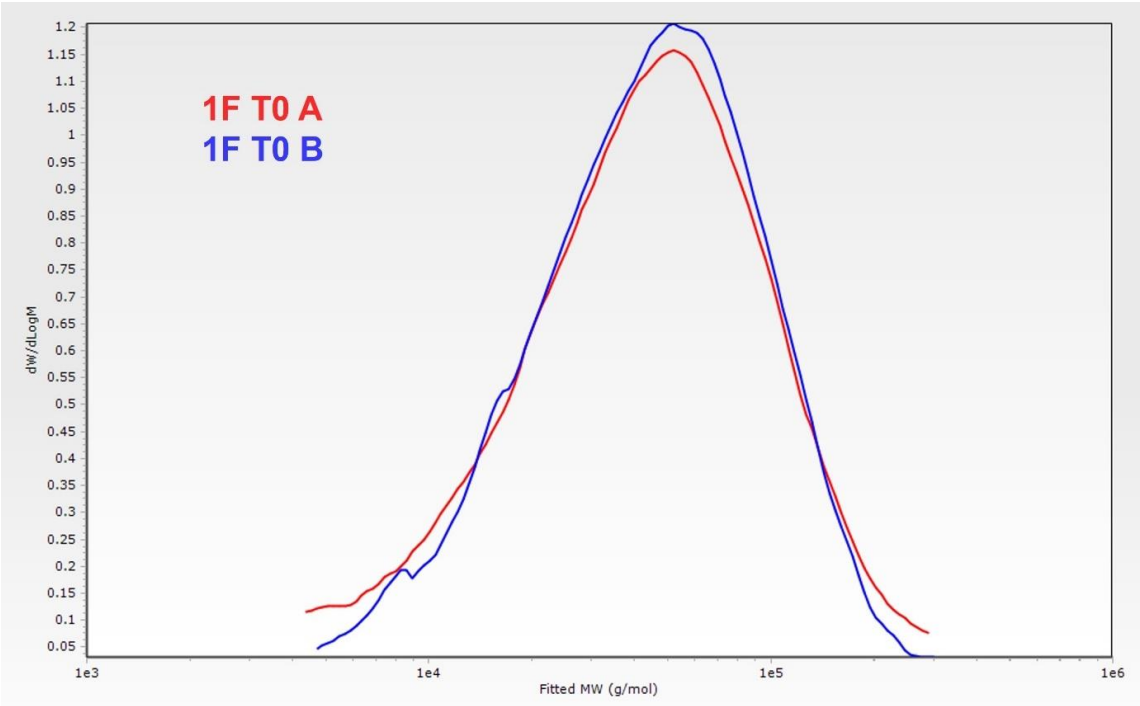


Figure S50. Molecular weight distribution of PET without any additive before weathering (T0). Analysis carried out in duplicate (A and B).

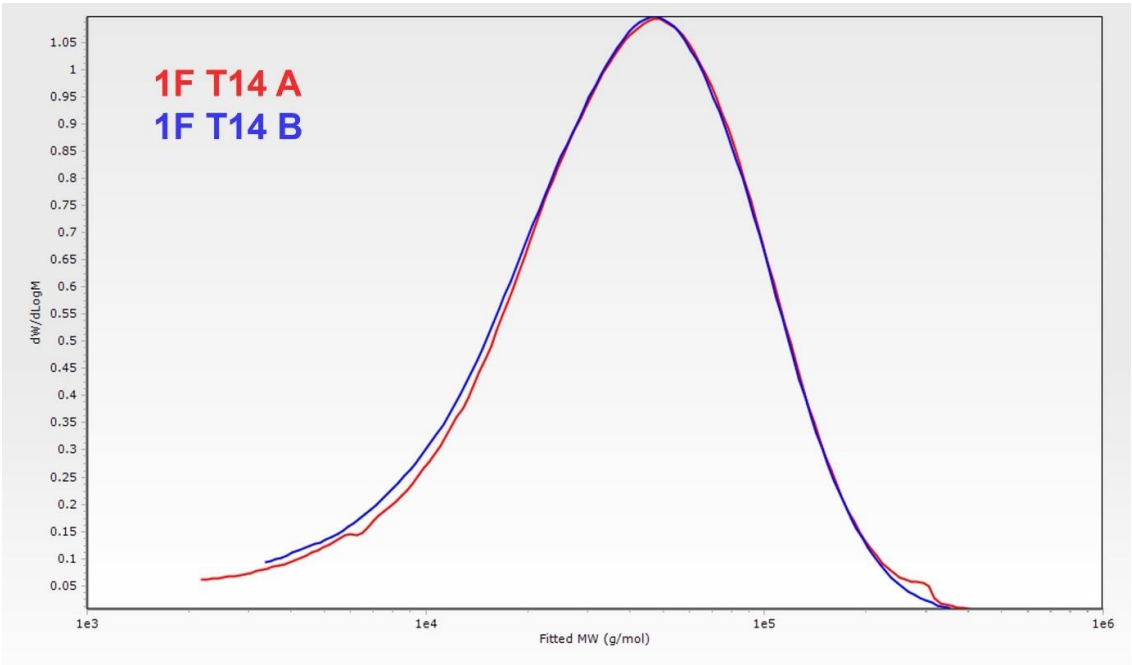


Figure S51. Molecular weight distribution of PET without any additive after weathering (T14). Analysis carried out in duplicate (A and B).

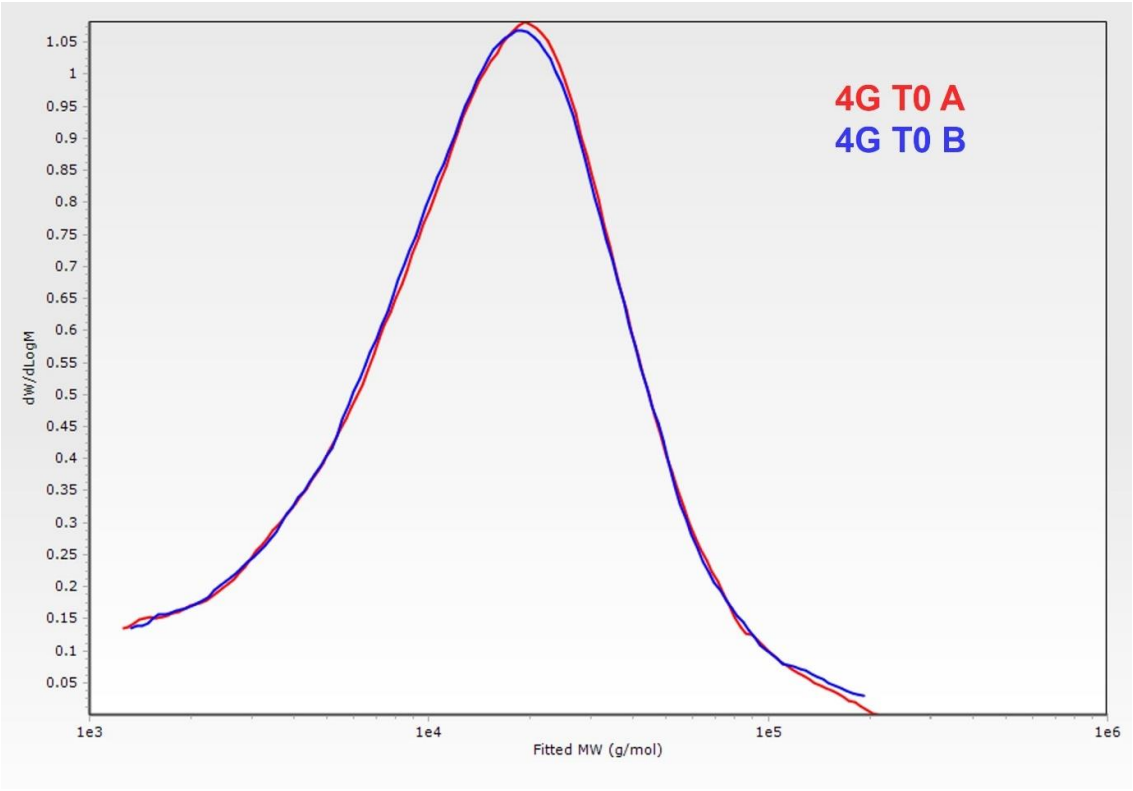


Figure S52. Molecular weight distribution of PET with additive DDE (**4**) before weathering (T0). Analysis carried out in duplicate (A and B).

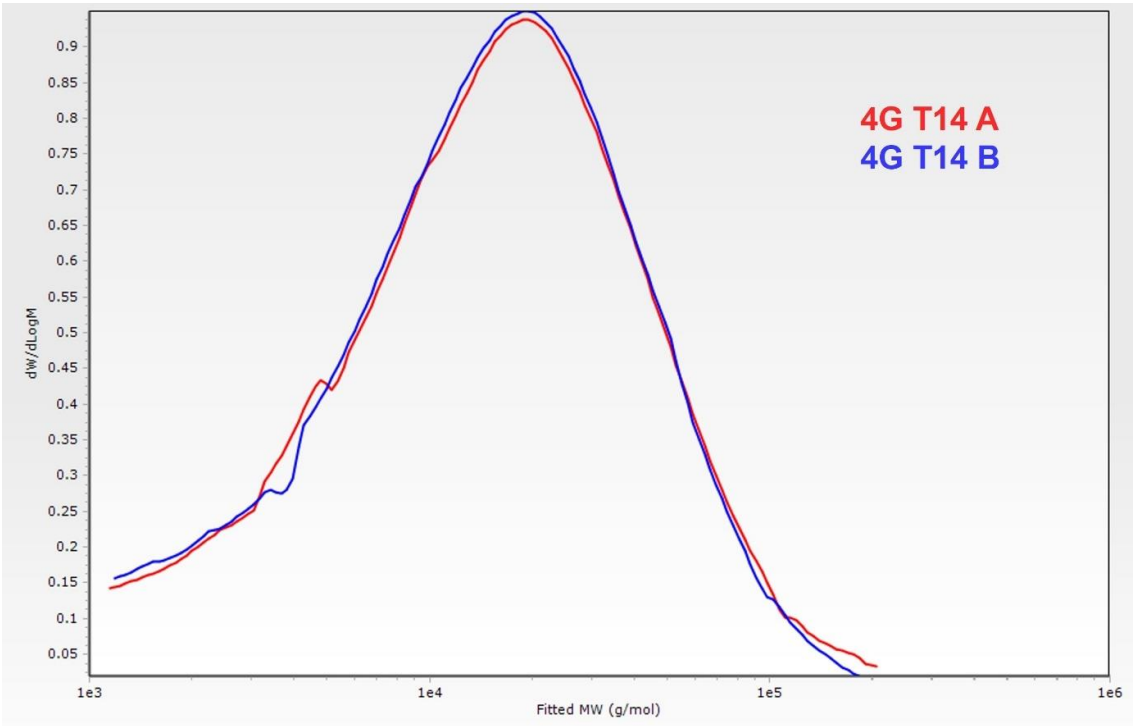


Figure S53. Molecular weight distribution of PET with additive DDE (**4**) after weathering (T14). Analysis carried out in duplicate (A and B).

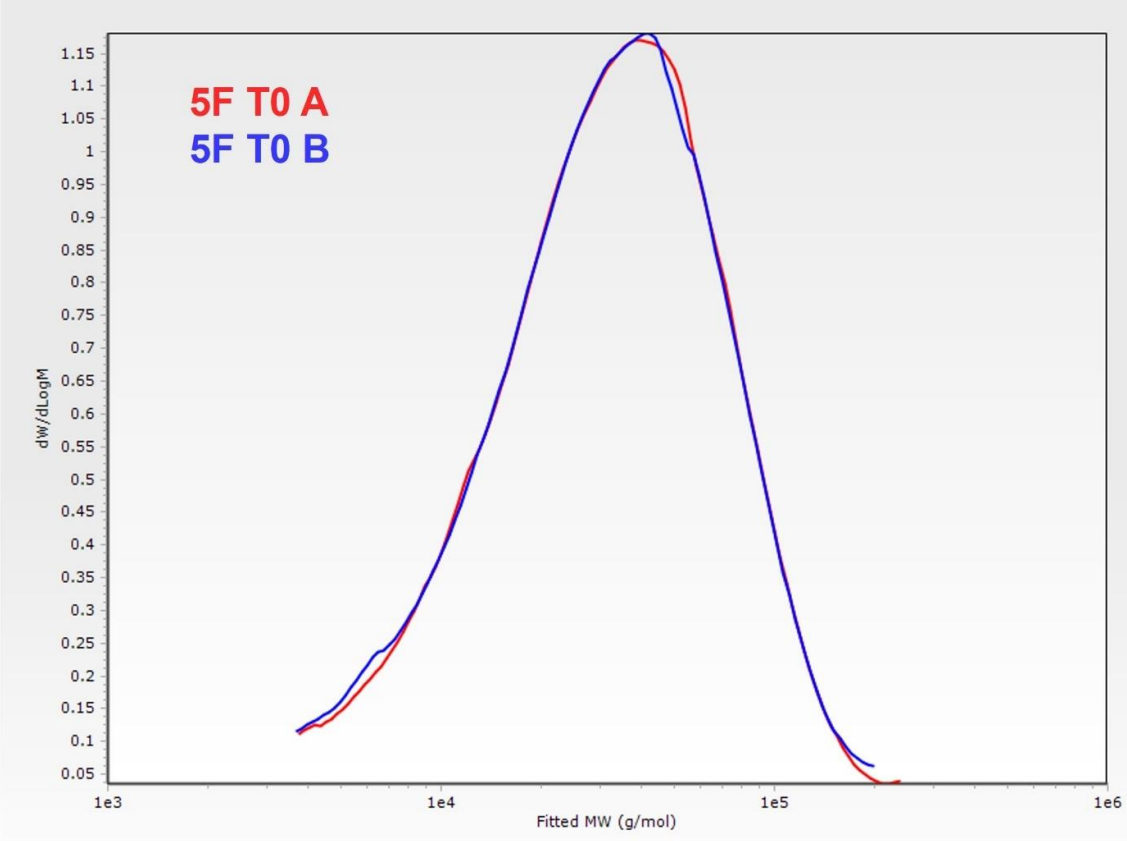


Figure S54. Molecular weight distribution of PET with additive DMT before weathering (T0). Analysis carried out in duplicate (A and B).

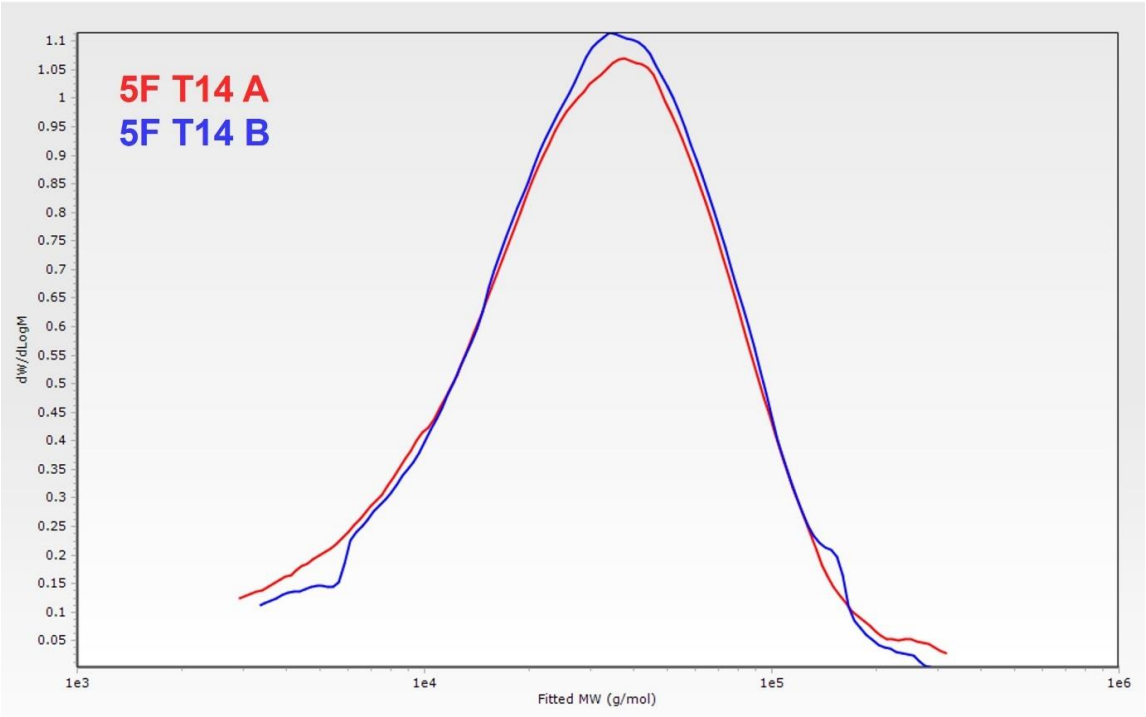


Figure S55. Molecular weight distribution of PET with additive DMT after weathering (T14). Analysis carried out in duplicate (A and B).

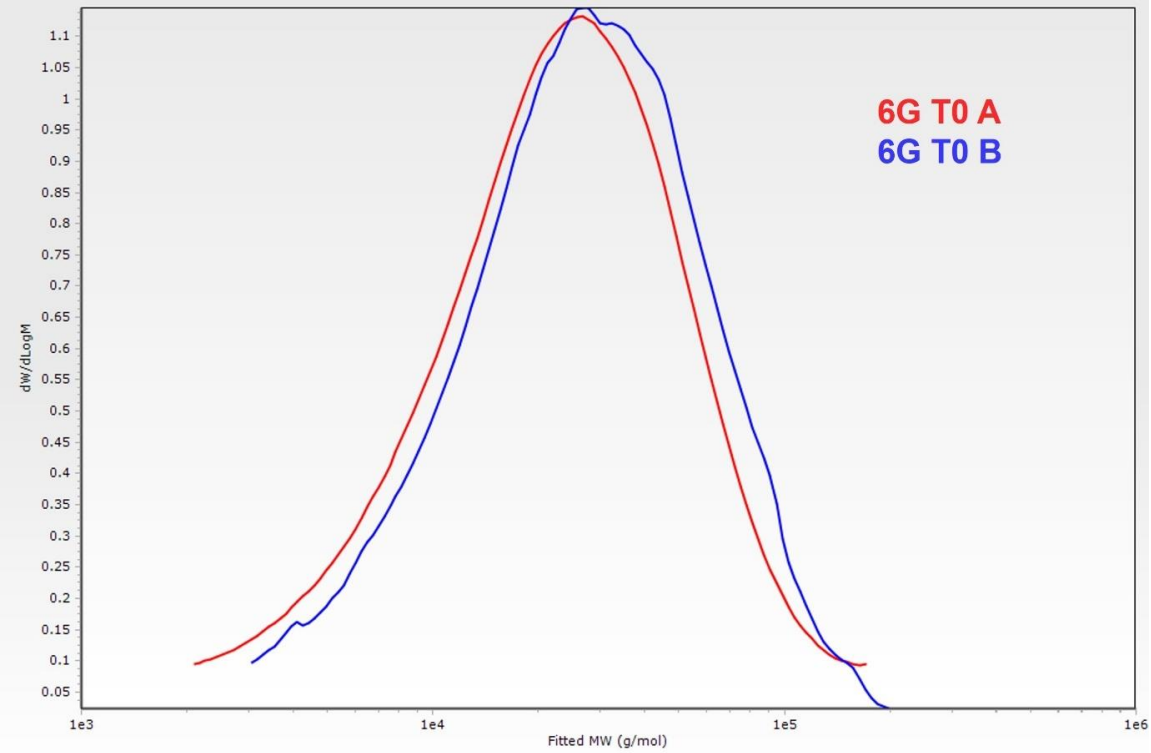


Figure S56. Molecular weight distribution of PET with additive BHEDE before weathering (T0). Analysis carried out in duplicate (A and B).

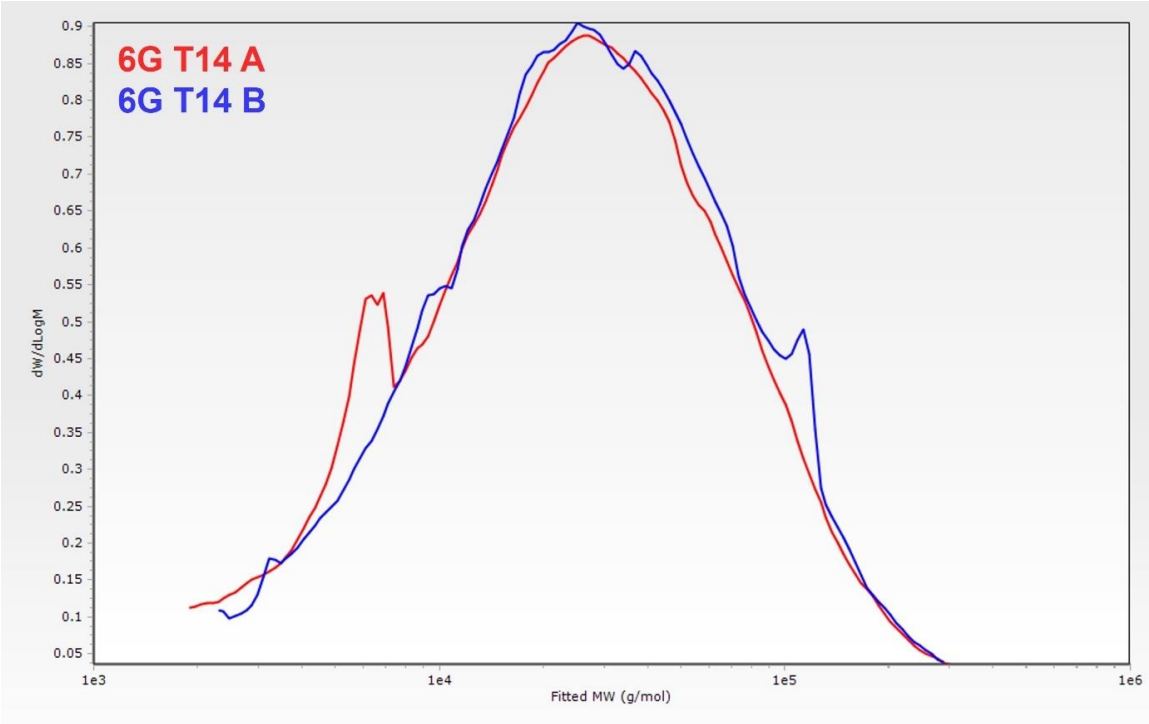


Figure S57. Molecular weight distribution of PET with additive BHEDE after weathering (T14). Analysis carried out in duplicate (A and B).

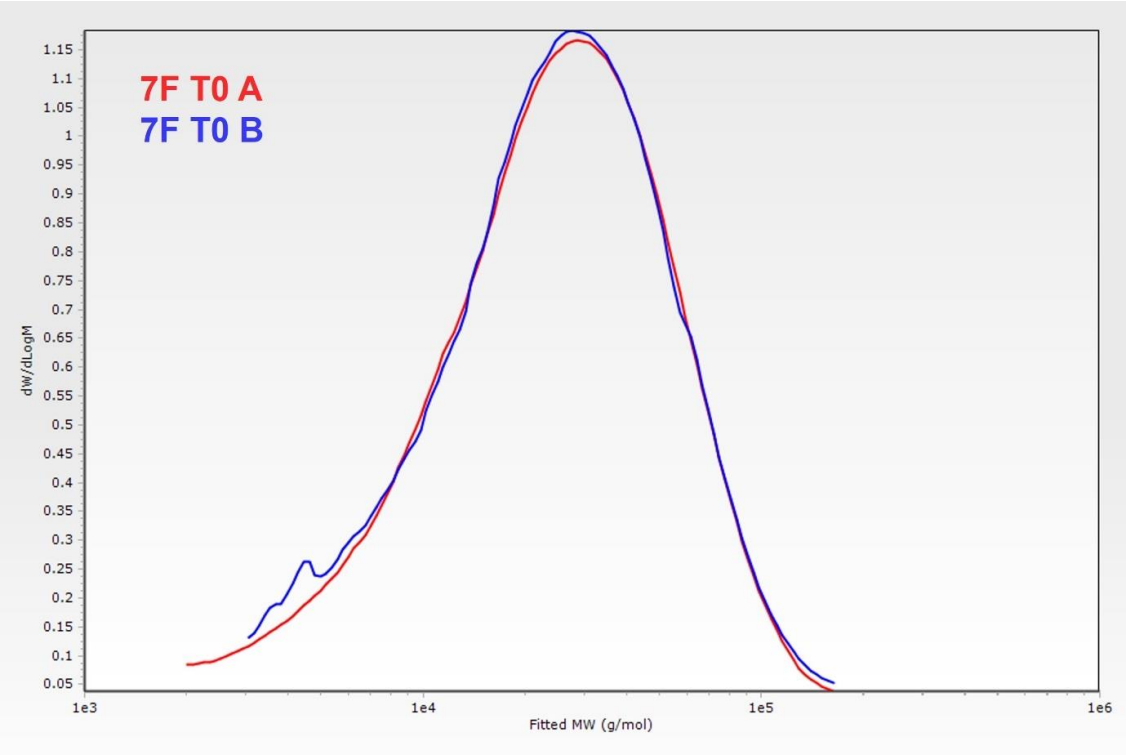


Figure S58. Molecular weight distribution of PET with additive BHET before weathering (T0). Analysis carried out in duplicate (A and B).

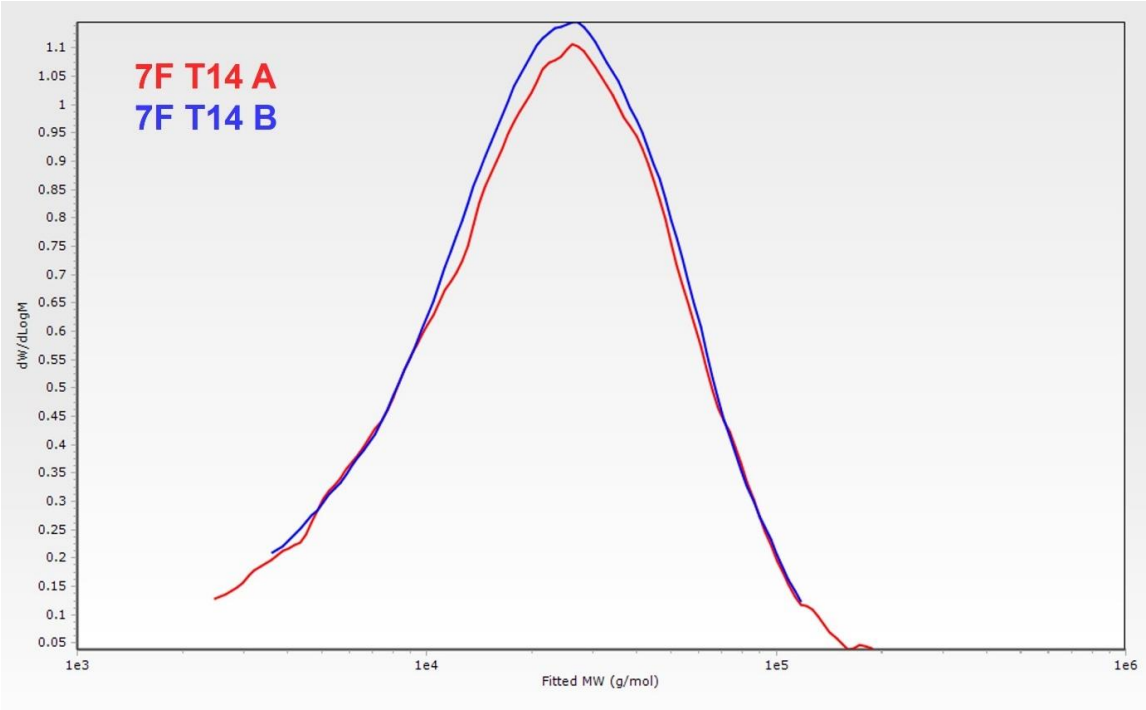


Figure S59. Molecular weight distribution of PET with additive BHET after weathering (T14). Analysis carried out in duplicate (A and B).

Additional GPC Analysis

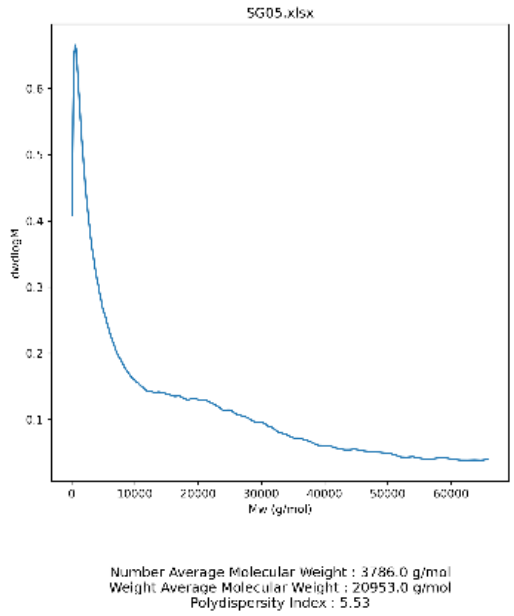


Figure S60. GPC analysis of BHET:DDE (10:1) copolymer obtained through melt polymerisation under vacuum after purification from NMP/methanol.

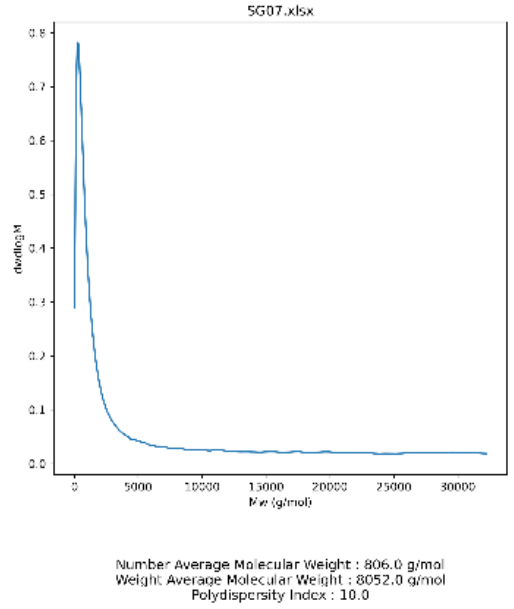


Figure S61. GPC analysis of BHET:DDE (5:1) copolymer obtained through melt polymerisation under vacuum after purification from NMP/methanol.

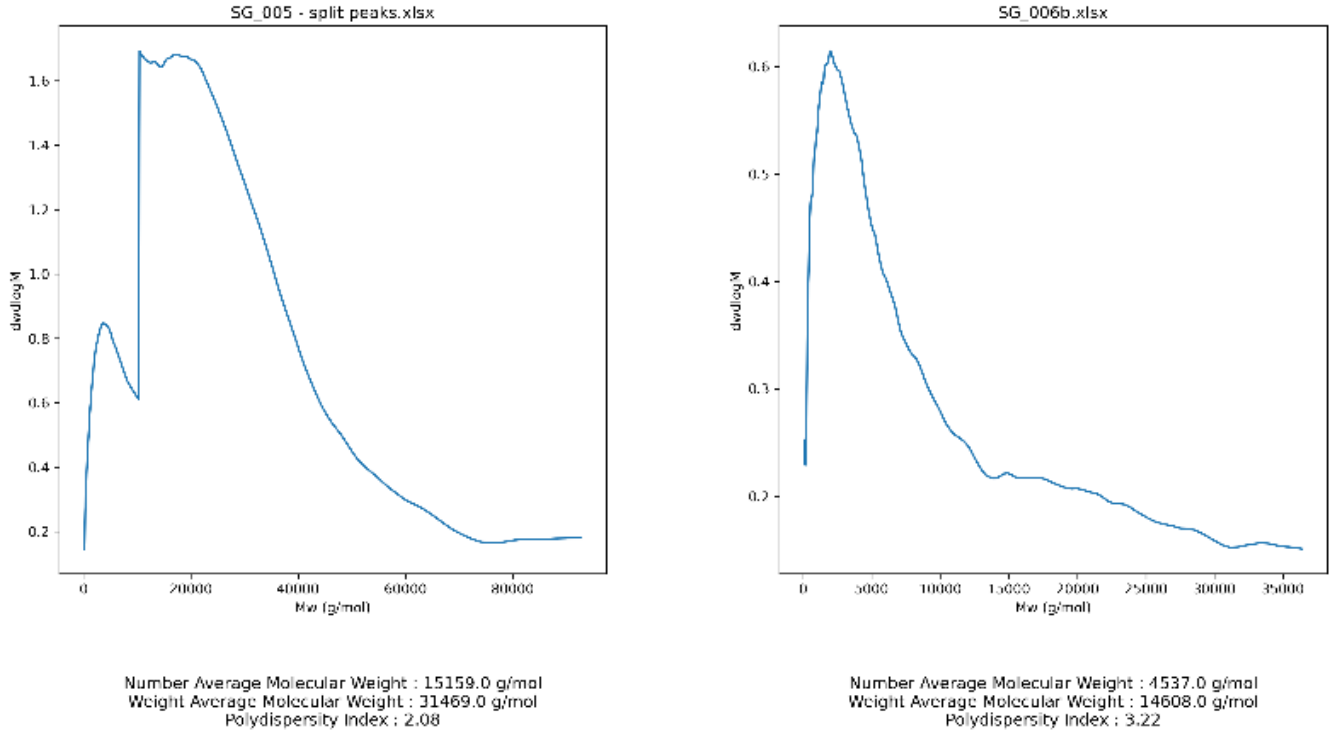


Figure S62. GPC analysis of the BHET:DDE co-polymer (10:1) obtained through extrusion (and pressed into a plate at 270 °C), before (left) and after (right) weathering.

References

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