Supplementary Information

Green polymerisation of renewable lignin-derived vinyl ketone monomer to form UV-degradable polymer

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General information:

Reactions: All inert atmosphere reactions were carried out under an argon atmosphere by standard syringe and septa techniques. Purifications by flash column chromatography were performed using silica gel Merck Geduran® SI 60 (40-63 µm). Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise mentioned.

Reagents and solvents: Reagents and solvents were purchased from commercial sources and generally used as received. Commercially available reagents were purchased at Alfa Aesar, Acros Organics, Sigma Aldrich, TCI Chemicals and Fluorochem suppliers. Solvents were purchased at Sigma Aldrich or/and Fluorochem. 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, 97%) was prepared in house as reported previously.[1]

TLC: Reactions were magnetically stirred and monitored by thin layer chromatography using MerckKieselgel 60F254 plates or Marcherey-nagel Alugram Xtra SIL G/UV254 and analysed with an ultra-violet lamp (λ = 254 nm) and an appropriate stain, either using potassium permanganate or p-anisaldehyde.

NMR: Small molecule NMR spectra (^{1}H and ^{13}C) were recorded on a Bruker AM 300 MHz or a Bruker AVANCE 400 MHz spectrophotometer. NMR experiments were conducted at room temperature in $CDCl_3$. Chemical shifts are given in parts per million (ppm) using the $CDCl_3$ residual non-deuterated signals as reference (δ ^{1}H = 7.26 ppm; δ ^{13}C = 77.16 ppm). The terms m, s, d, t, and q correspond to multiplet, singulet, doublet, triplet, and quartet, respectively. The terms br. and app. are respectively used when the peak is broad or apparent, and in the latter case when the correct real multiplicity cannot be surely assigned. Coupling constants (J) are given in Hertz (Hz). For previously unknown compounds, a combination of ^{13}C DEPT, JMOD, and 2D experiments (COSY, HSQC, HMBC) were used to complete the assignment of ^{1}H and ^{13}C signals when characterization was uncertain. Polymer ^{1}H NMR spectra were recorded on a Bruker 300 MHz spectrometer in 5 mm diameter tubes. Chemical shifts were noted on the δ scale in parts per million (ppm). ^{1}H NMR spectra were recorded with deuterated acetone or chloroform ($CDCl_3$) using the residual signal 2.05 ppm and 7.26 ppm, respectively.

IR: IR spectra were recorded with a Tensor 27 (ATR Diamond) Bruker spectrophotometer. IR spectra were reported as characteristic bands (cm^{-1}).

HRMS: High resolution mass spectra (HRMS) were obtained using a mass spectrometer MicroTOF from Bruker with an electron spray source (ESI) or an atmospheric pressure chemical ionization (APCI) source and a TOF detector at Institut Parisien de Chimie Moléculaire (FR 2769).

Melting points: Melting points were measured in capillary tubes on a Stuart Scientific SMP3 apparatus and are uncorrected.

TGA: Thermogravimetric analysis (TGA) measurements were performed on a TGA Q50 from TA Instruments to investigate the thermal stability of the samples. Measurements were carried out by heating the sample at 40 °C/min from room temperature (RT) to 600 °C under a nitrogen atmosphere.

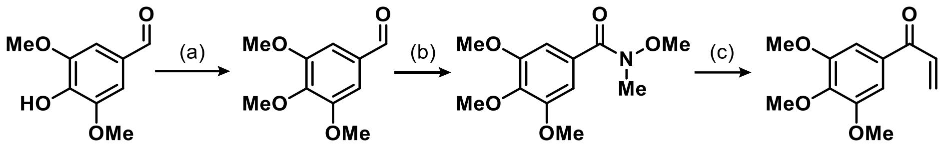
DSC: Differential scanning calorimetry (DSC) measurements were carried out on a DSC Q2000 from TA Instruments with refrigerated cooling accessory (RCS90). In all experiments, the DSC cell was purged with nitrogen at 60 mL/min. Materials were sealed in Tzero aluminium pans. The DSC scans were performed at a heating/cooling rate of 10 °C/min from −50 to 200 °C.

SEC: Polymer samples (2 – 10 mg) were dissolved in SEC grade THF (1 mL) and filtered using a 0.45 µm PTFE syringe filter. SEC analyses of the filtered polymer samples were carried out in SEC grade THF at a flow rate of 1 mL min^{-1} at 40 °C. Size exclusion chromatography (SEC) measurements were carried out on three PL Gel Mixed C 5µm columns (7.5 x 300 mm; separation limits: 0.2 to 2000 kg mol^{-1}) maintained at 40 °C coupled with a solvent and sample delivery module Viscotek GPCmax and 2 modular detectors: a differential refractive index (RI) detector Viscoteck 3580 and a Diode Array UV Detector Shimadzu SPD20-AV set to a wavelength of 305 nm. Molar masses (Mn, the number-average molar mass, Mw, the weight-average molar mass) and dispersity ($Đ = M_w/M_n$) were derived from a calibration curve based on polystyrene (PS) or poly(methyl methacrylate) (PMMA) standards from Polymer Standards Service. The OmniSEC 5.12 software was used for data acquisition and data analysis.

MALDI-TOF: All spectra were acquired on an ultrafleXtreme instrument (Bruker, Bremen, Germany) equipped with a 2000 Hz Smartbeam Nd:YAG laser (355 nm). The spectra were acquired in the positive reflectron mode with a minimum 7000 laser shots and a random walk. The generated ions were accelerated to the kinetic energy of 20.0 kV. The matrix used was DCTB trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile at a concentration of 40mg/ml in THF. Silver trifluoroacetate (AgTFA) was used as a cationization agent. Theoretical isotope patterns were generated using EnviPat Web software.

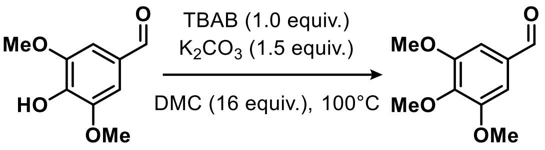
Starting Material synthesis

The enone starting materials were prepared according to the following reaction sequence.

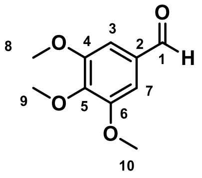


(a) *n*-tetrabutylammonium bromide (1.0 equiv.), K_2CO_3 (1.5 equiv.) and dimethyl carbonate (16 equiv.); (b) *N*,*O*-dimethylhydroxylamine hydrochloride (1.2 equiv.), $CuSO_4 \cdot 5H_2O$ (5 mol%), $CaCO_3$ (1,1 equiv.) and tert-butyl hydroperoxide (70 wt% in water,1,1 equiv.) (c) vinylmagnesium bromide (1.2 equiv.), THF, 0°C then hydrolysis.

Procedure for the methylation of syringaldehyde



In a round bottom flask equipped with a stirring bar was charged syringaldehyde (1.82 g, 10.0 mmol, 1.00 equiv.) with *n*-tetrabutylammonium bromide (3.22 g, 10.0 mmol, 1.00 equiv.) and potassium carbonate (2.07 g, 15.0 mmol, 1.50 equiv.). The flask was placed under inert atmosphere and backfilled with argon. The vacuum/argon cycles were repeated twice and dimethyl carbonate (13.5 mL, 160 mmol, 16.0 equiv.) was added to the flask and an air condenser was placed on top the flask. The mixture was heated at 100°C until complete conversion, as monitored by TLC. Once the reaction is completed, the excess of K_2CO_3 was removed by filtration, 1M HCl (15 mL) was added, and the mixture was diluted with ethyl acetate. The layers were separated and the organic layer was dried with $MgSO_4$ and concentrated under reduced pressure to give 3,4,5-trimethoxybenzaldehyde as a white-yellow solid (1.93 g, 98% yield) without further purification. The characterization data are in accordance with the ones reported in the literature.[2]



mp: 73.6°C

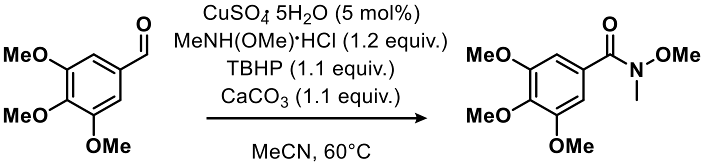
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H, H-1), 7.13 (s, 2H, H-3/H-7), 3.94 (s, 3H, H-9), 3.93 (s, 6H, H-8/H-10).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2 (C-1), 153.8 (2C, C-4/C-6), 143.8 (C-5), 131.9 (C-2), 106.9 (2C, C-3/C-7), 61.2 (C-9), 56.5 (2C, C-8/C-10).

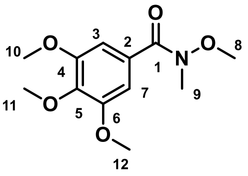
HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{10}H_{12}O_4H$ 197.0808, Found 197.0809

IR (cm^{-1}): 2944, 2842, 1684, 1587, 1143, 1126, 992, 846, 731, 657, 628

Procedure for the synthesis of the Weinreb amide from the corresponding aldehyde



In a round bottom flask equipped with a stirring bar was charged 3,4,5-trimethoxybenzaldehyde (392mg, 2mmol, 1.0 equiv.), $CuSO_4 \cdot 5H_2O$ (25mg, 0.1mmol, 5mol%), *N*,*O*-dimethylhydroxylamine hydrochloride (234.1mg, 2.4mmol, 1.2 equiv.) and $CaCO_3$ (220mg, 2.2mmol, 1.1 equiv.). The flask was placed under vacuum before being backfilled with argon, the vacuum/argon cycles were repeated twice, then acetonitrile (0.8mL) was added to the flask followed by *tert*-butyl hydroperoxide (70% in water, 0.3mL, 2.2mmol, 1.1 equiv.). An air condenser was placed on top the flask and the mixture was heated to 60°C for 48h. The mixture was then, concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/AcOEt 7:3) to give *N*,3,4,5-tetramethoxy-*N*-methylbenzamide as a yellow oil (194mg, 38% yield). The characterization data are in accordance with the ones reported in the literature.[3]



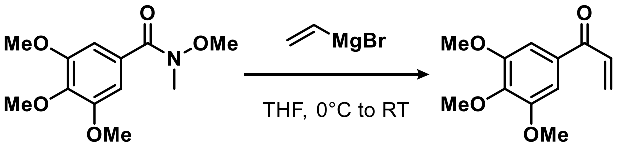
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (s, 2H, H-3/H-7), 3.88 (s, 3H, H-11), 3.88 (s, 6H, H-10/H-12), 3.59 (s, 3H, H-8), 3.36 (s, 3H, H-9).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5 (C-1), 152.9 (2C, C-4/C-6), 140.3 (C-5), 129.2 (C-2), 106.1 (2C, C-3/C-7), 61.3 (C-8), 61.0 (C-11), 56.4 (2C, C-10/C-12), 34.1 (C-9).

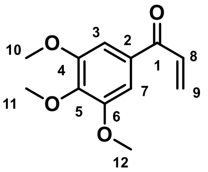
HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{12}H_{17}NO_5H$ 256.1179, found 256.1180.

IR(cm^{-1}): 2939,2837, 1639, 1583, 1413,1237,1126, 750

Procedure for the synthesis of BioPVK



In a round bottom flask equipped with a stirring bar was charged with the Weinreb amide (2.55 g, 10.0 mmol). The flask was placed under inert atmosphere before being backfilled with argon. The vacuum/argon cycles were repeated twice and dry THF (50 mL,) was added. The solution was cooled down to 0°C (ice/water bath) and a solution of vinylmagnesium bromide in THF (17mL, C = 0.7M, 1,2 equiv.) was then added dropwise. The reaction mixture was stirred at room temperature until complete conversion, as monitored by TLC. The reaction mixture was then quenched with an aqueous 1M solution of hydrochloric acid until pH=1. The layers were separated, and the aqueous layer was extracted with ethyl acetate. The organic layer was then dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure. The crude residue was then purified by a short flash column chromatography on silica gel (petroleum ether/AcOEt 8:2) giving 1-(3,4,5-Trimethoxyphenyl)-2-propen-1-one as pale yellow/brown solid (1.82 g, 82% yield). The characterization data are in accordance with the ones reported in the literature.[4]



mp: 45°C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (s, 2H,H-3/H-7), 7.14 (dd, *J* = 17.1, 10.6 Hz, 1H, H-8), 6.44 (dd, *J* = 17.1, 1.7 Hz, 1H, H-9$_{trans}$), 5.91 (dd, *J* = 10.6, 1.8 Hz, 1H,H-9$_{cis}$), 3.92 (s, 9H,H-10/H-11/H-12).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9 (C-1), 153.3 (2C, C-4/C-6), 142.8 (C-5), 132.6 (C-2), 132.3 (C-8), 130.1 (C-9), 106.4 (2C, C-3/C-7), 61.1 (C-11), 56.5 (2C, C-10/C-12).

HRMS (ESI) m/z: $[M+H]^+$ Calculated for $C_{12}H_{14}O_4H$ 223.0965, found 223.0967

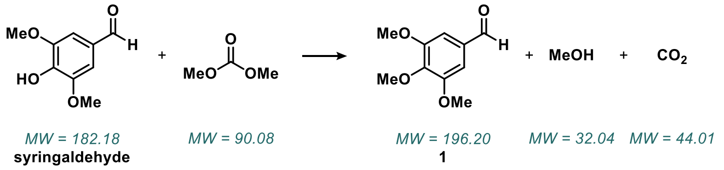
IR: 2361, 1666, 1609, 1456, 1165, 1128, 777

Calculation of the simplified efficiency metrics

Calculation of each AE% and sE-factor$_{(MW)}$ was done according to the following equations:

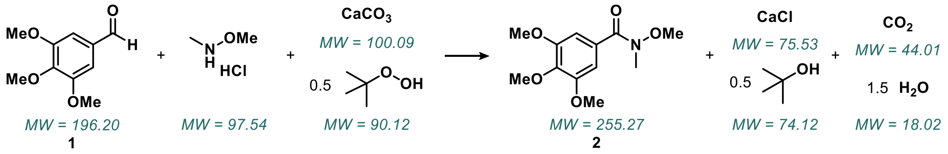
$$AE\% = \frac{MW_{(product)}}{\sum MW_{(reagents)}} \qquad sE\text{–}factor_{(MW)} = \frac{\sum MW_{(byproducts)}}{MW_{(product)}}$$

Syringaldehyde → 1



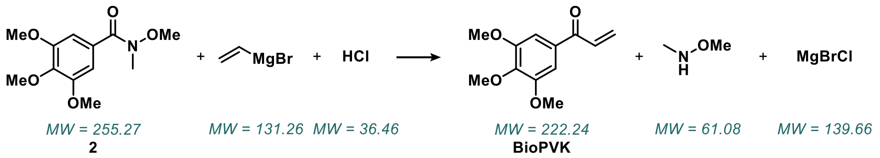
ΣMW$_{(reagents)}$ = 272.26
MW$_{(product)}$ = 196.20
ΣMW$_{(byproducts)}$ = 76.05

1 → 2



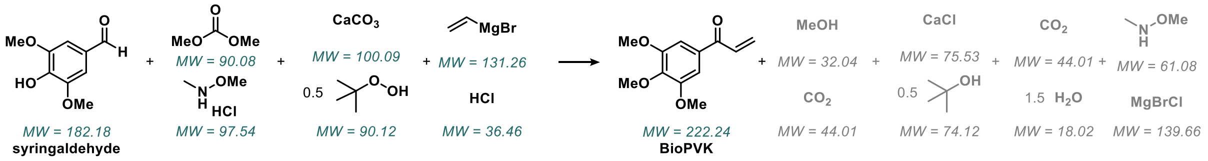
ΣMW$_{(reagents)}$ = 438.89
MW$_{(product)}$ = 255.27
ΣMW$_{(byproducts)}$ = 183.62

2 → BioPVK



ΣMW$_{(reagents)}$ = 422.99
MW$_{(product)}$ = 222.24
ΣMW$_{(byproducts)}$ = 200.74

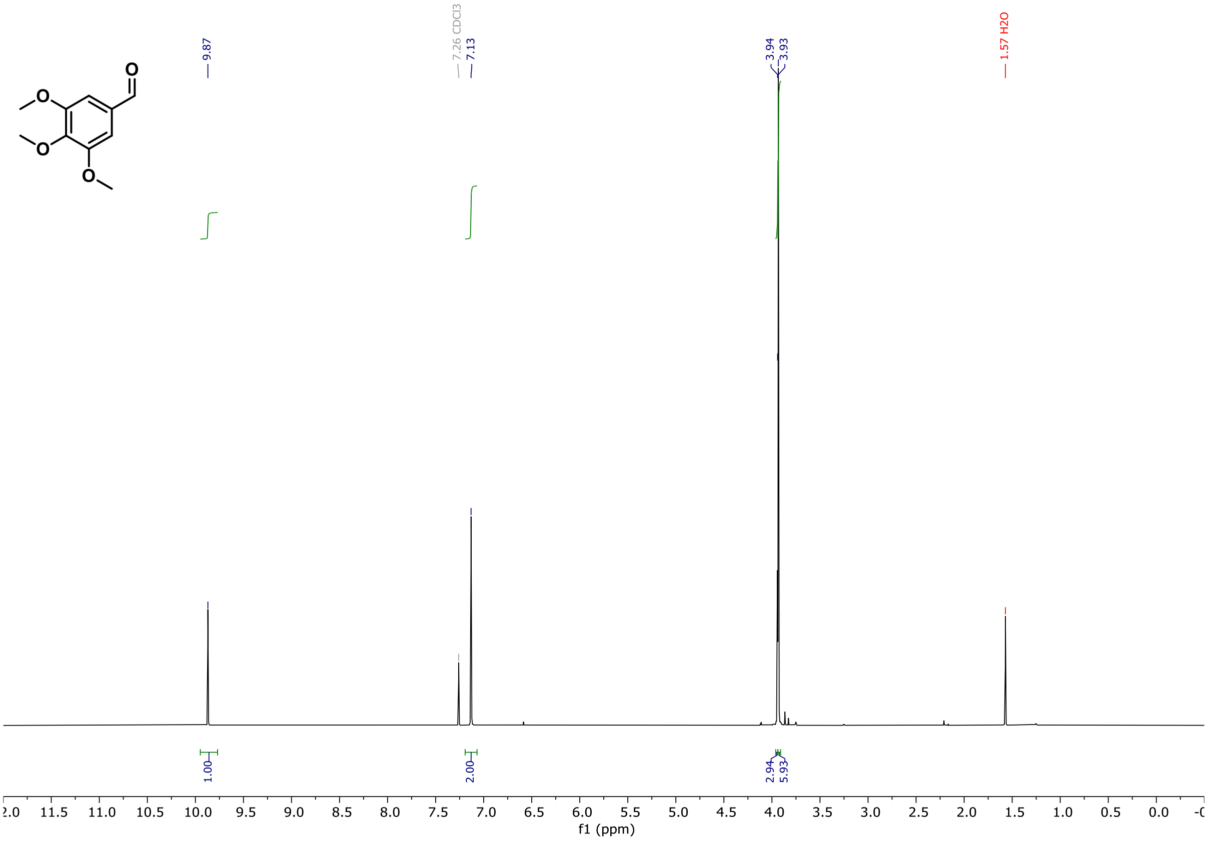
Calculation of the global AE% for the three steps of the synthesis was done by considering a general equation from syringaldehyde to BioPVK.

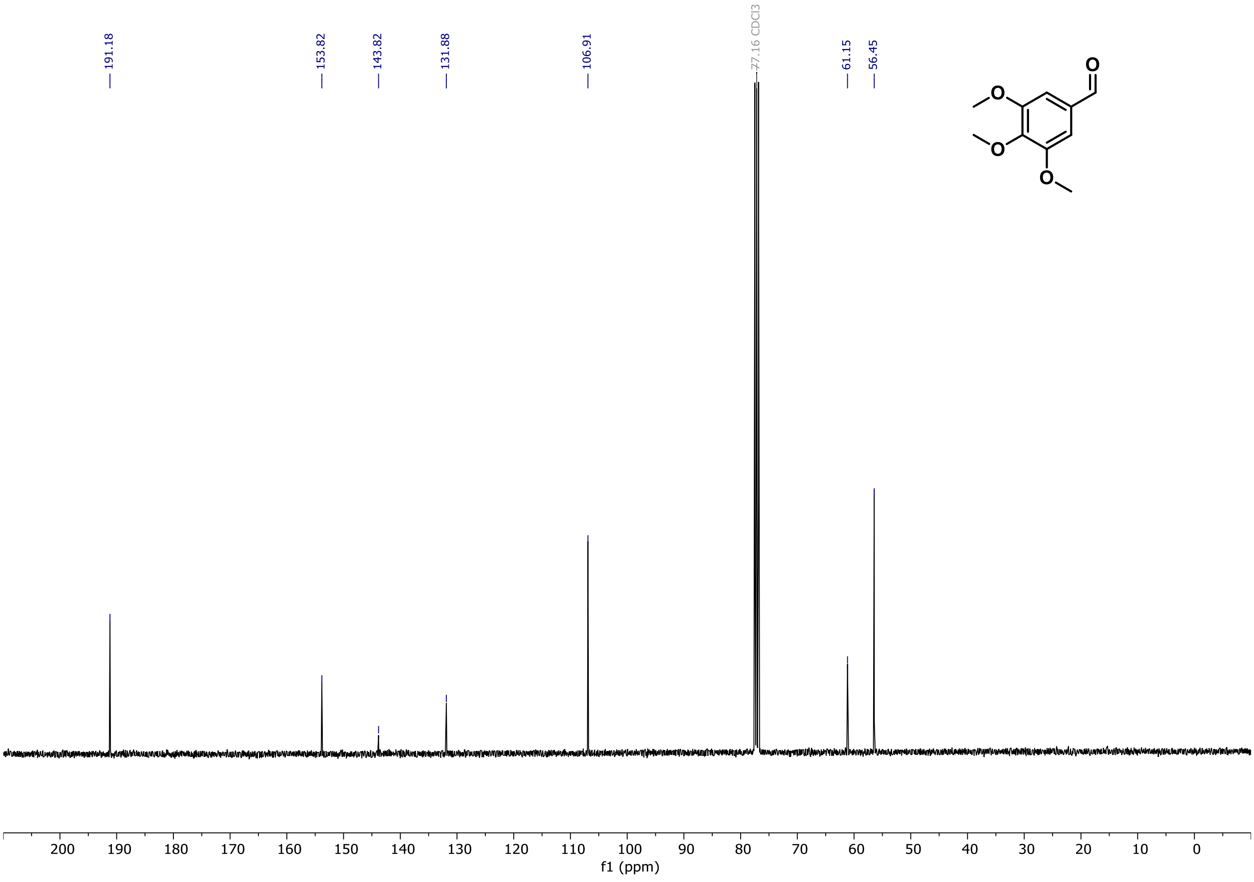


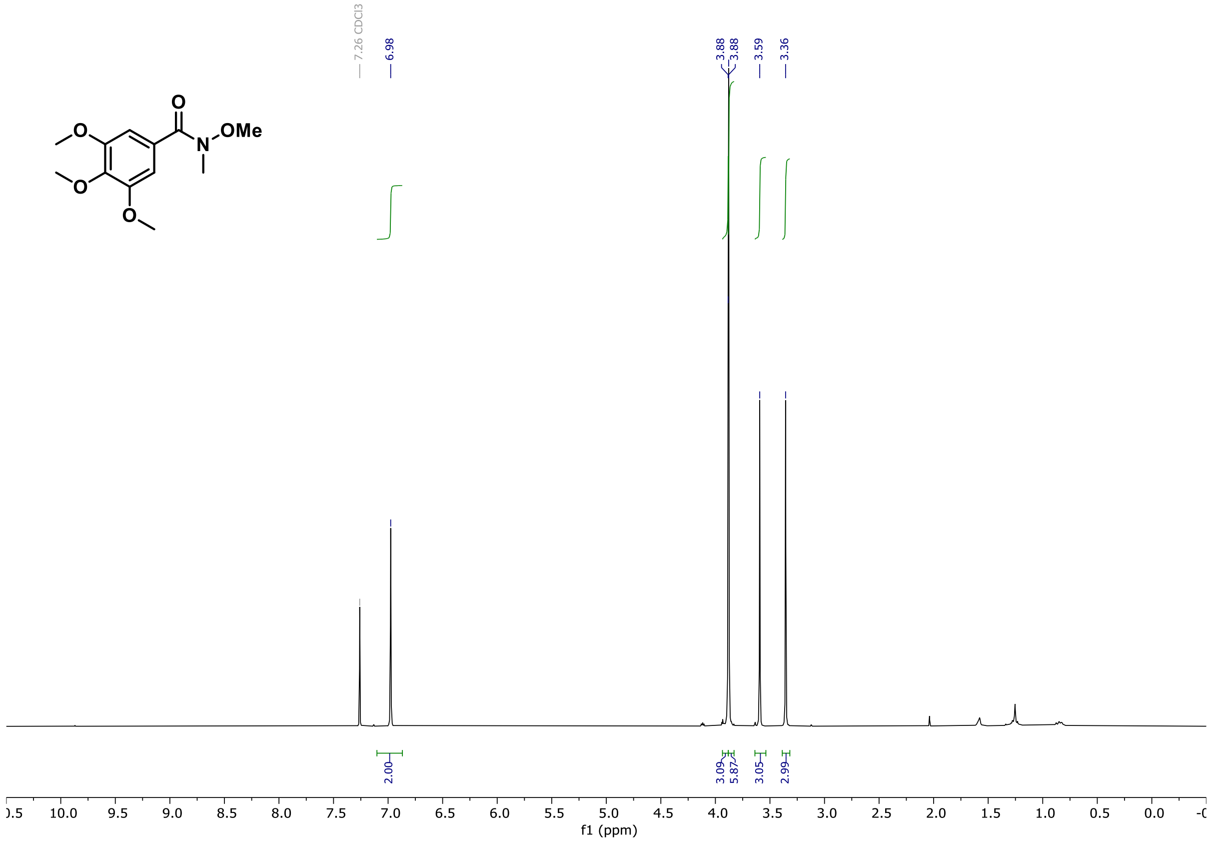
$$AE\% = \frac{100 \times MW_{BioPVK}}{MW_{S} + MW_{DMC} + MW_{amine.HCl} + MW_{CaCO3} + 0.5\ MW_{TBHP} + MW_{Grignard} + MW_{HCl}}$$

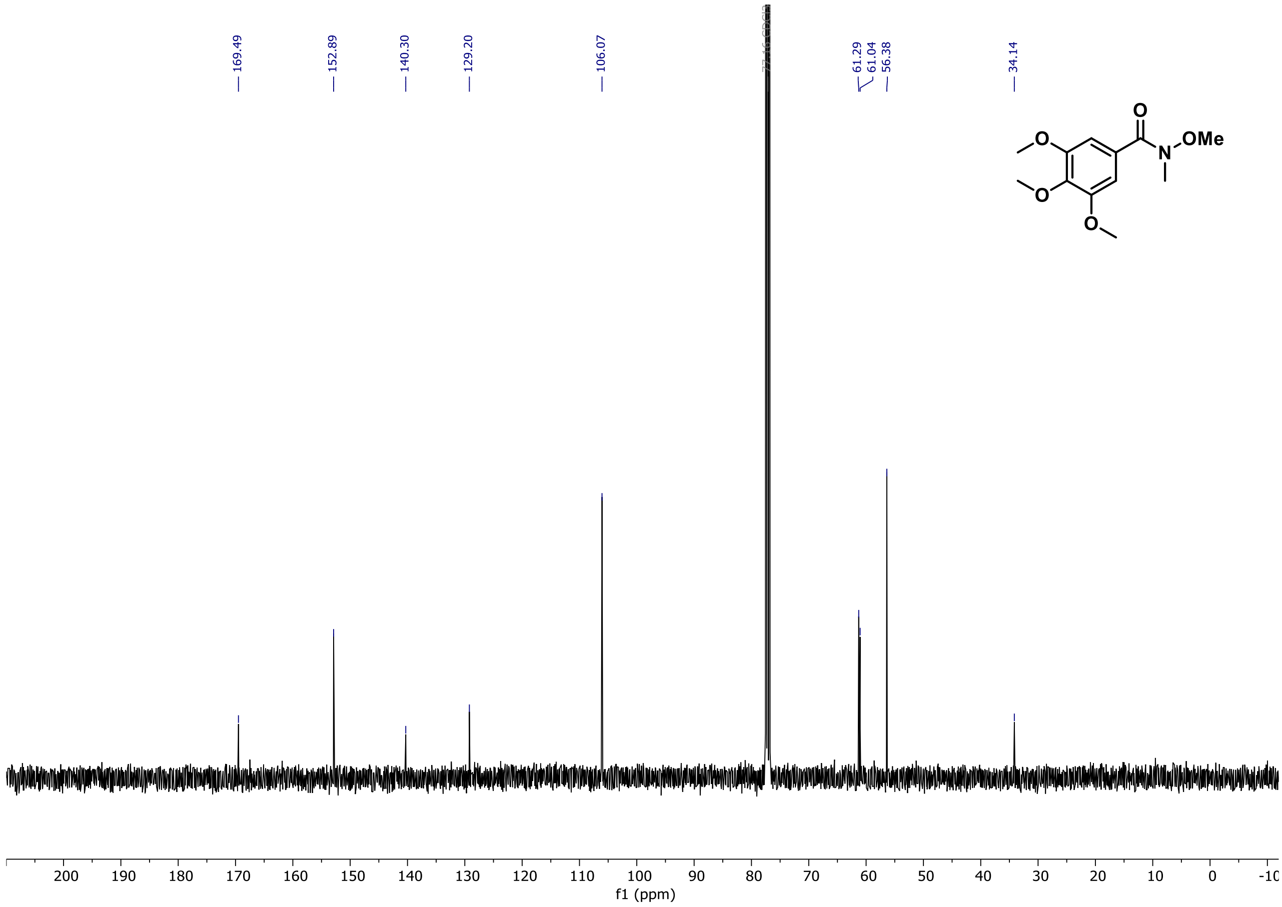
$$AE\% = \frac{100 \times 222.24}{182.18 + 90.08 + 97.54 + 100.09 + 45.06 + 131.26 + 36.46} = \frac{22224}{682.67} = 32.6\ \%$$

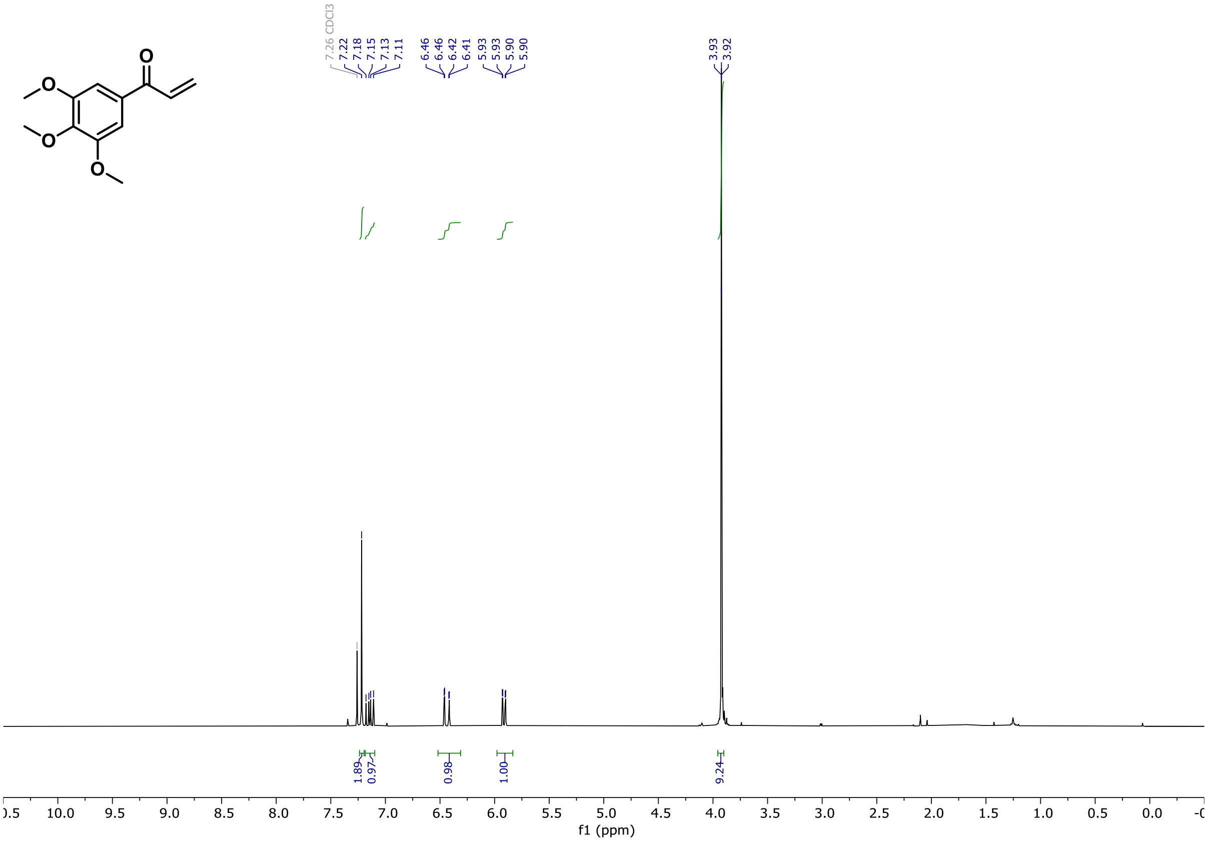
The E factor given, refers to *simple E Factor* (sE-factor$_{(MW)}$), which considers the balanced reaction, disregards excess of reagents, solvents, and water washing in workups.

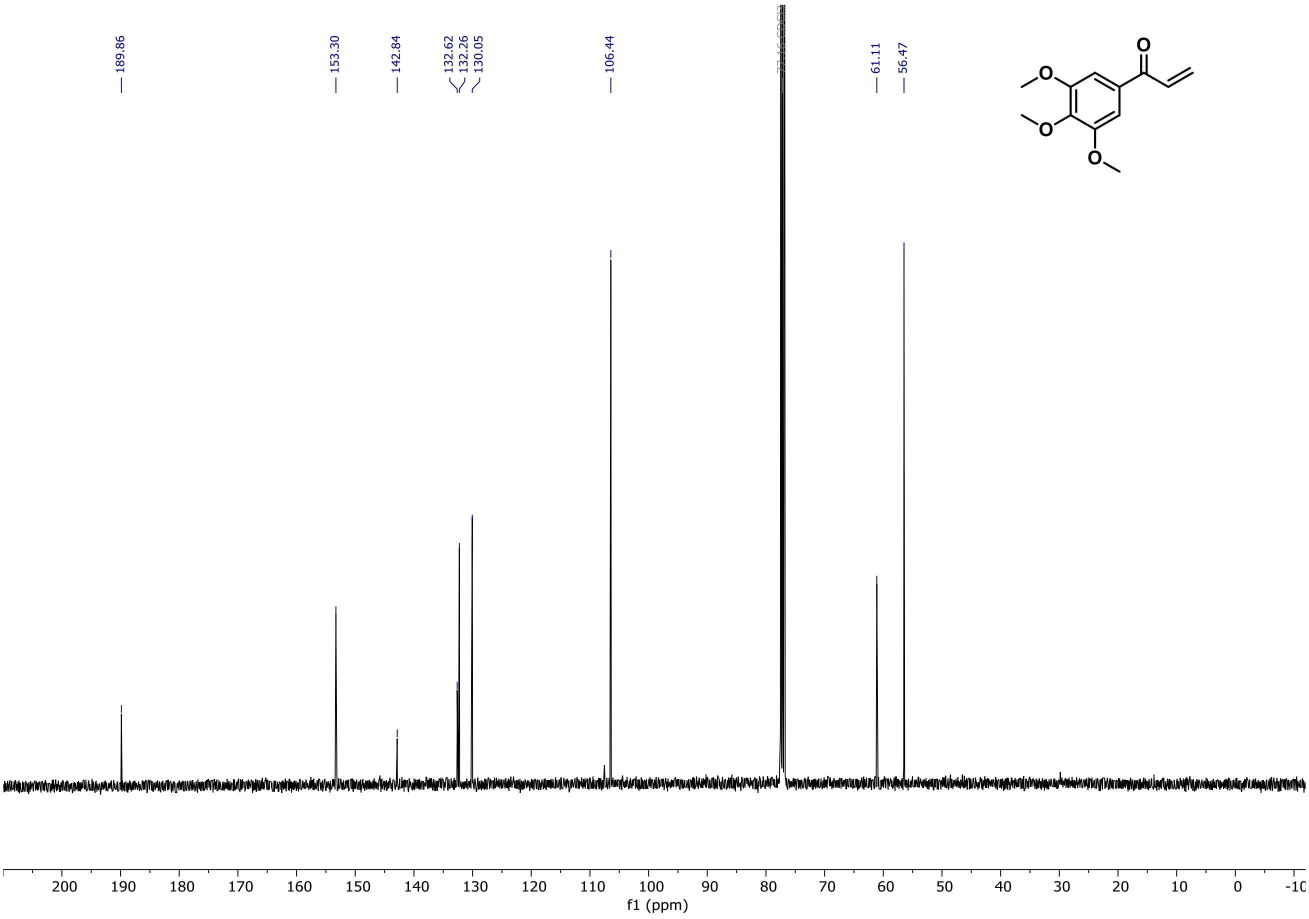

9.87
7.26 CDCl3
7.13
3.94
3.93
1.57 H2O
1.00
2.00
2.94
5.93
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O


191.18
153.82
143.82
131.88
106.91
77.16 CDCl3
61.15
56.45
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
OMe
O
O
O
7.26 CDCl3
6.98
3.88
3.88
3.59
3.36
2.00
3.09
5.87
3.05
2.99
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.49
152.89
140.30
129.20
106.07
77.16 CDCl3
61.29
61.04
56.38
34.14
O
N
OMe
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
O
O
7.26 CDCl3
7.22
7.18
7.15
7.13
7.11
6.46
6.46
6.42
6.41
5.93
5.93
5.90
5.90
3.93
3.92
1.89
0.97
0.98
1.00
9.24
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


189.86
153.30
142.84
132.62
132.26
130.05
106.44
61.11
56.47
O
O
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Polymer synthesis and degradation

Synthesis of P(BioPVK) via FRP

In a typical procedure, BioPVK (150 mg, 0.68 mmol) and trioxane (1.8 mg, 0.02 mmol) was added to a 10 mL vial and dissolved in ethyl lactate (0.35 mL). AIBN (0.6 mg, 3 µmol) was added from a 6 mg/mL stock solution (0.1 mL). The reaction was sealed then degassed by bubbling argon through the solution for 20 min. The flask was then placed in an oil bath at 72 °C and left to react for 3.5 h. The polymerisation was terminated by exposure to air and cooling to ambient temperature. The copolymer was isolated by precipitation in cold ethanol and dried under vacuum. The resultant copolymer was analysed by ^{1}H NMR in deuterated acetone.

Synthesis of P(St-*co*-BioPVK) via FRP

In a typical procedure, styrene (110 mg, 1.08 mmol), BioPVK (0.17 mmol), and trioxane (7 mg, 0.08 mmol) was added to a 10 mL vial and dissolved in ethyl lactate (0.45 mL). AIBN (2.2 mg, 13 µmol) was added from a 22 mg/mL stock solution (0.1 mL). The reaction was sealed then degassed by bubbling argon through the solution for 20 min. The flask was then placed in an oil bath at 72 °C and left to react for 16 h. The polymerisation was terminated by exposure to air and cooling to ambient temperature. The copolymer was isolated by precipitation in cold ethanol and dried under vacuum. The resultant copolymer was analysed by ^{1}H NMR in deuterated acetone.

Synthesis of P(BioPVK) via RAFT polymerisation

In a typical procedure, BioPVK (100 mg, 0.68 mmol), DDMAT (4.1 mg, 11 µmol) and trioxane (4 mg, 0.04 mmol) was added to a 10 mL vial and dissolved in ethyl lactate (0.30 mL). AIBN (0.9 mg, 6 µmol) was added from a 9 mg/mL stock solution (0.1 mL). The reaction was sealed then degassed by bubbling argon through the solution for 20 min. The flask was then placed in an oil bath at 72 °C and left to react for 16 h. The polymerisation was terminated by exposure to air and cooling to ambient temperature. The copolymer was isolated by precipitation in cold ethanol and dried under vacuum. The resultant copolymer was analysed by ^{1}H NMR in deuterated acetone.

Synthesis of P(St-*co*-BioPVK) via conventional emulsion polymerisation

In a typical procedure, a 5% w/v SDS solution was prepared, where 0.75 equivalents of $NaHCO_3$ was added to ensure deprotonation of the sulfoxide groups. KPS (8 mg, 0.03 mmol) was added to a 5 mL RBF and dissolved in 0.27 mL of SDS solution and 1 mL of deionised water. BioPVK (34 mg, 0.15 mmol) was dissolved in styrene (300 mg, 2.88 mmol) and then added to the reaction flask. The concentration of SDS and KPS in the polymerisation were 1% w/w and 0.6% w/w, respectively. The reaction was sealed then degassed by bubbling argon through the solution for 20 min. The flask was then placed in an oil bath at 80 °C and left to react for 2 h. The polymerisation was terminated by exposure to air and cooling to ambient temperature. A sample of dried copolymer was analysed by ^{1}H NMR in deuterated chloroform.

Degradation via irradiation with UV light

In a typical procedure, solid polymer was dissolved in a solvent (e.g., THF) at 4 mg mL^{-1} in a sealed glass vial. The polymer solution was then irradiated with a Dymax 2000-PC modular UV lamp light-curing flood (maximal emission between 315 and 400 nm, 75 mW.cm^{-2}) at a distance of 24 cm from the source. The samples were irradiated for various amounts of time and subsequently analysed by GPC and MALDI-TOF. The sample temperature was controlled at ca. 40 °C (measured by an adjacent thermal couple) by using a steady stream of compressed air (Figure S15a). Without cooling with compressed air the sample environment rises to ca. 70 °C (Figure S15a). Unless stated otherwise, the degradation experiments were performed at ca. 40 °C.

Additional figures

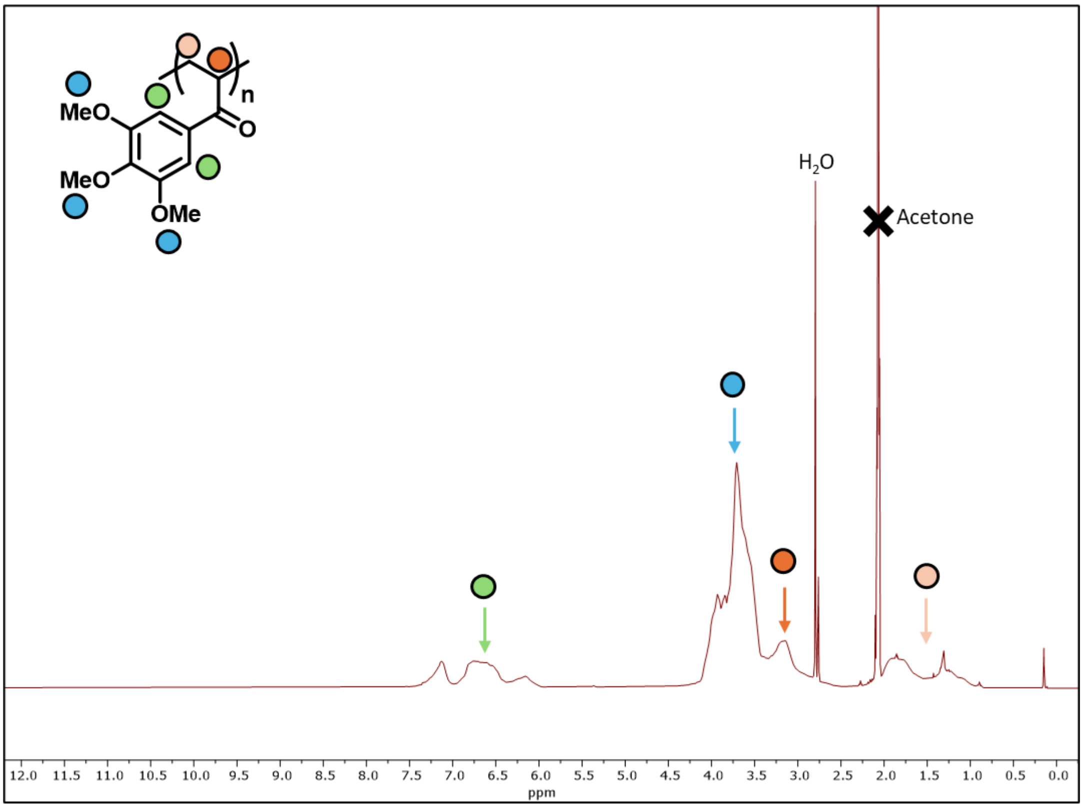


Figure S1. ^{1}H NMR spectra of P(BioPVK) synthesised by free-radical polymerisation (polymer **1**, Table 1) performed in deuterated acetone.

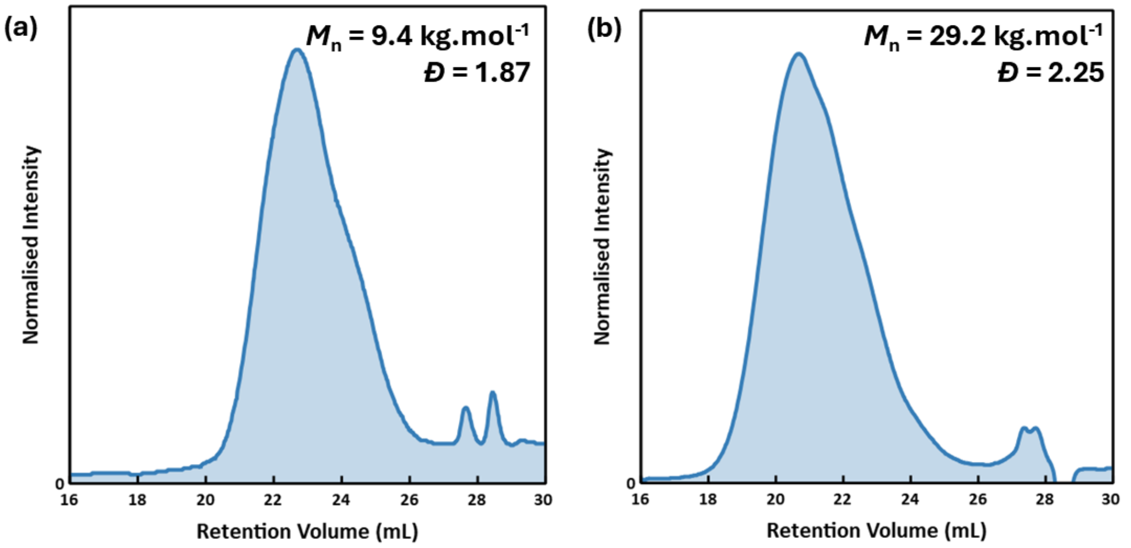


Figure S2. RI- SEC chromatograms of P(BioPVK) by free-radical polymerisation in (a) ethyl lactate (polymer **1**, Table 1) and (b) dioxane.

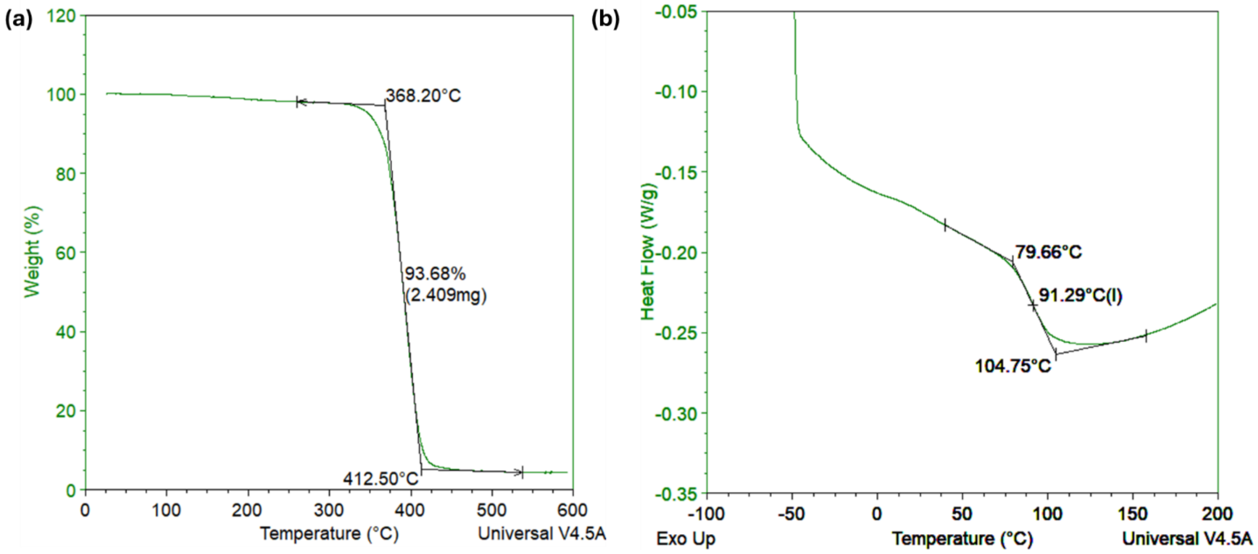


Figure S3. The (a) TGA and (b) DSC thermograms for polymer **1** (Table 1) with the degradation temperature and T_g indicated on the graph.

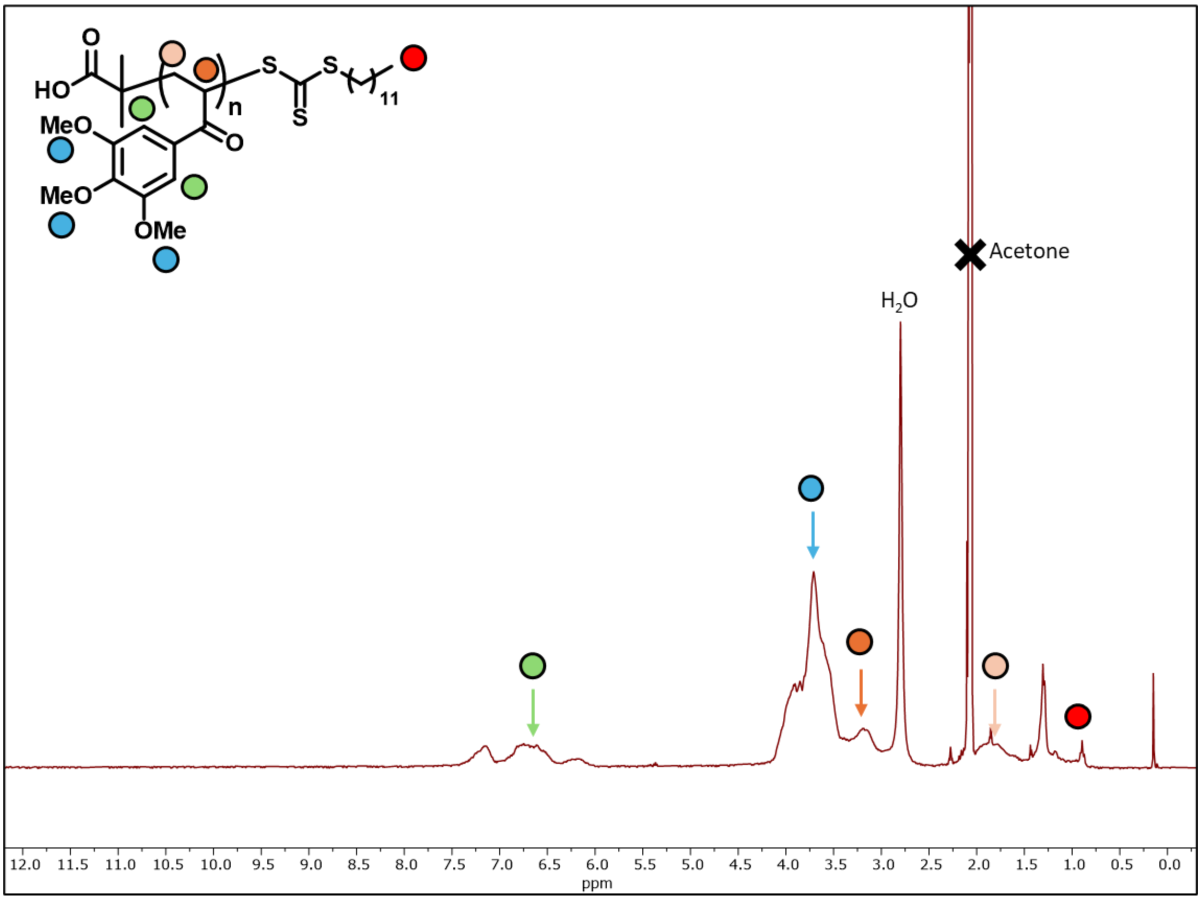


Figure S4. ^{1}H NMR spectra of P(BioPVK) synthesised by RAFT polymerisation (polymer **3**, Table 1) performed in deuterated acetone.

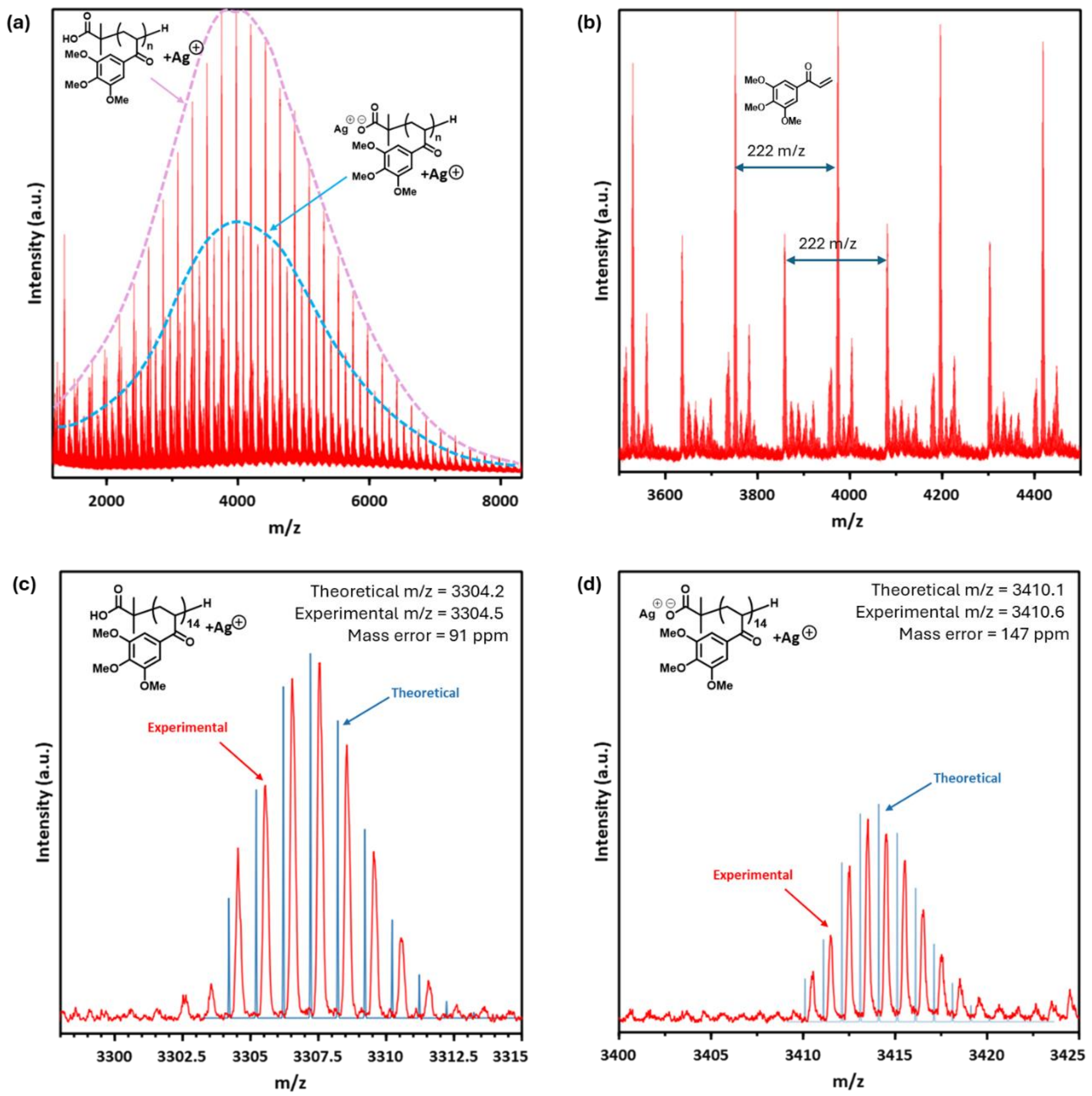


Figure S5. MALDI-TOF spectra of P(BioPVK) synthesised by RAFT polymerisation (polymer **3**, Table 1), where (a) is the full spectra and (b) is an expanded segment of the full spectra. (c) and (d) show expanded segments of the MALDI-TOF spectra along with the theoretical isotope pattern (blue) for the molecule shown in the top left corner of the figures.

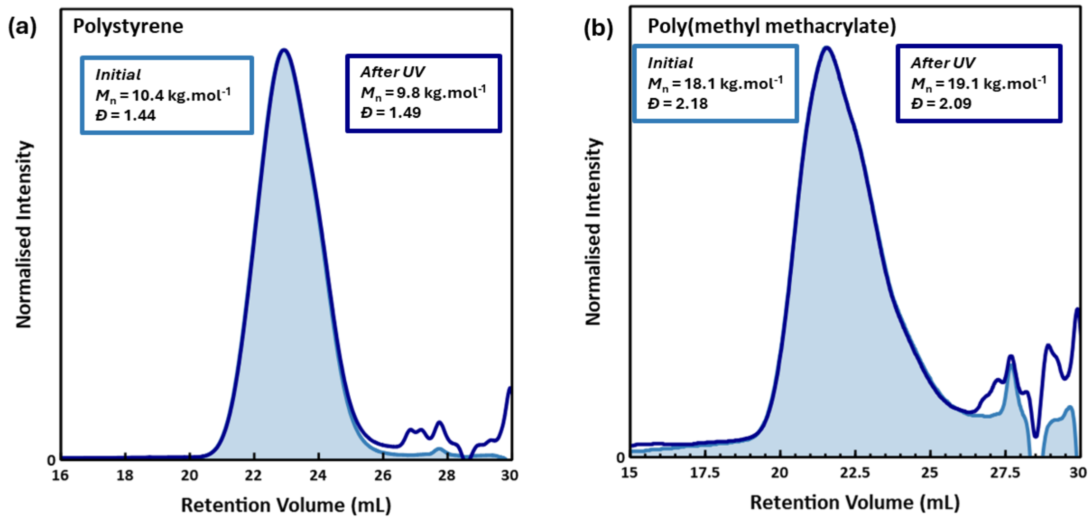


Figure S6. RI SEC chromatograms of (a) PSt and (b) PMMA before and after irradiation with UV light for 30 min.

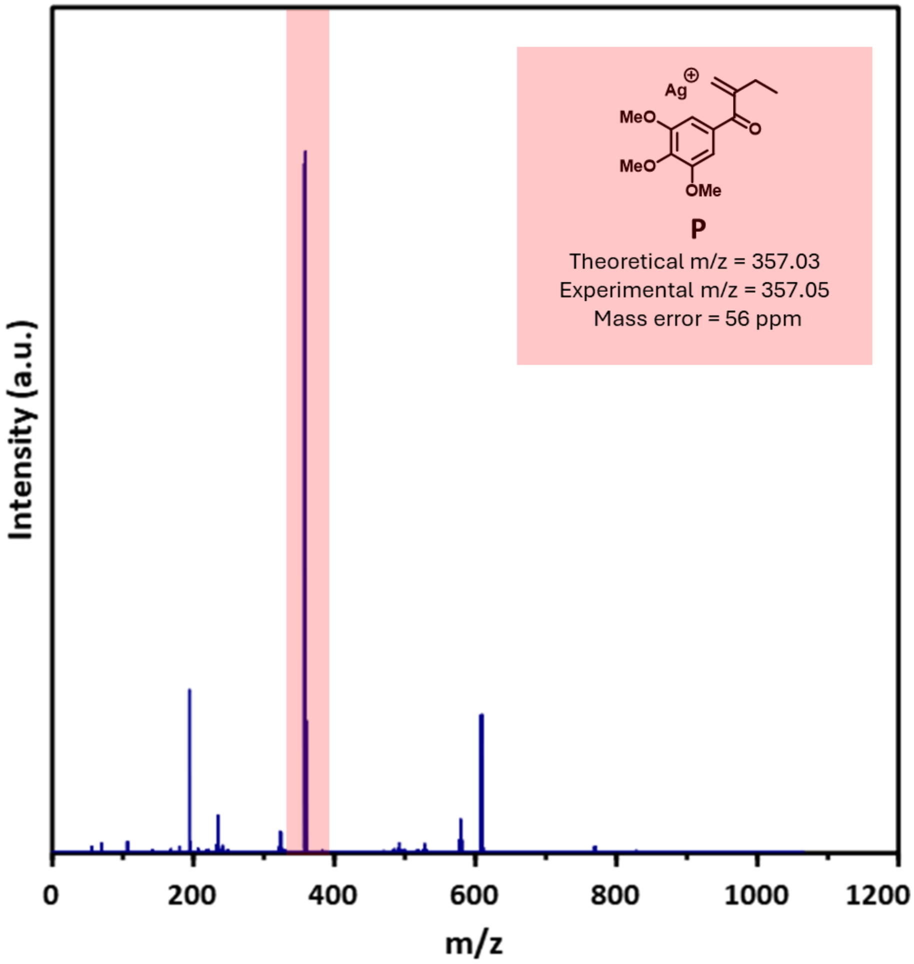


Figure S7. MALDI-TOF spectra of P(BioPVK) synthesised by RAFT polymerisation (polymer **3**, Table 1) after irradiation with UV light.

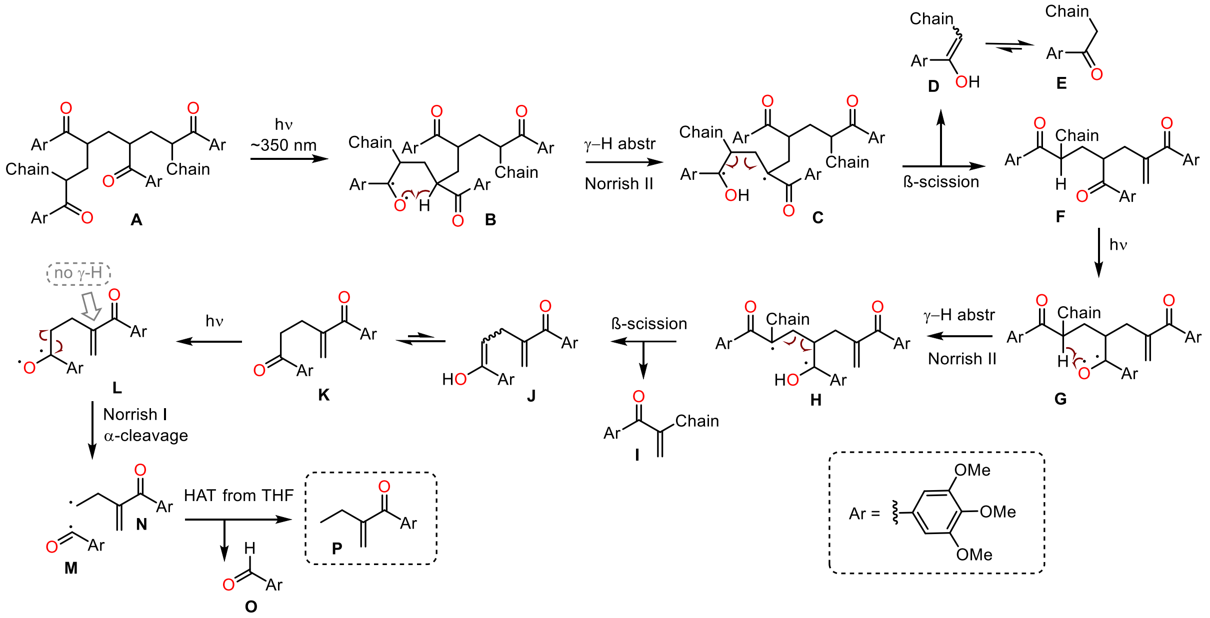


Figure S8. A tentative mechanism for the degradation of polymer **3** is given here below. UV irradiation excites the carbonyl function of the polymer to give intermediate **B**, which undergoes Norrish II reaction. Cleavage via γ-H abstraction / β-scission gives **C**, then **D**, which equilibrate to **E**, and **F**. A second Norrish II reaction involves excitation of the saturated carbonyl function to give **G**, then **H**, and this latter cleaves to **I** and **J**, which equilibrates to **K**. Notice that the second Norrish II reaction involves the saturated rather than the unsaturated one. At a first glance, this selectivity seems counterintuitive, as the excitation of a conjugated carbonyl is expected to be more favorable than that of saturated one. However, it is possible that only excitation of the saturated carbonyl gives a productive intermediate. Further irradiation of **K** gives the excited state **L**. This latter, being devoid of γ-hydrogens at the excited carbonyl function, cannot evolve through a Norrish II reaction. On the other hand, α-cleavage according to a Norrish I reaction gives the free alkyl and acyl radicals **N** and **M**. Final quench of the latter radicals, likely via H-atom transfer (HAT) from THF,[5] gives aldehyde **O** and the conjugated carbonyl **P**, whose mass spectrum coordinated with silver ion corresponds to the parent peak (molecular ion).

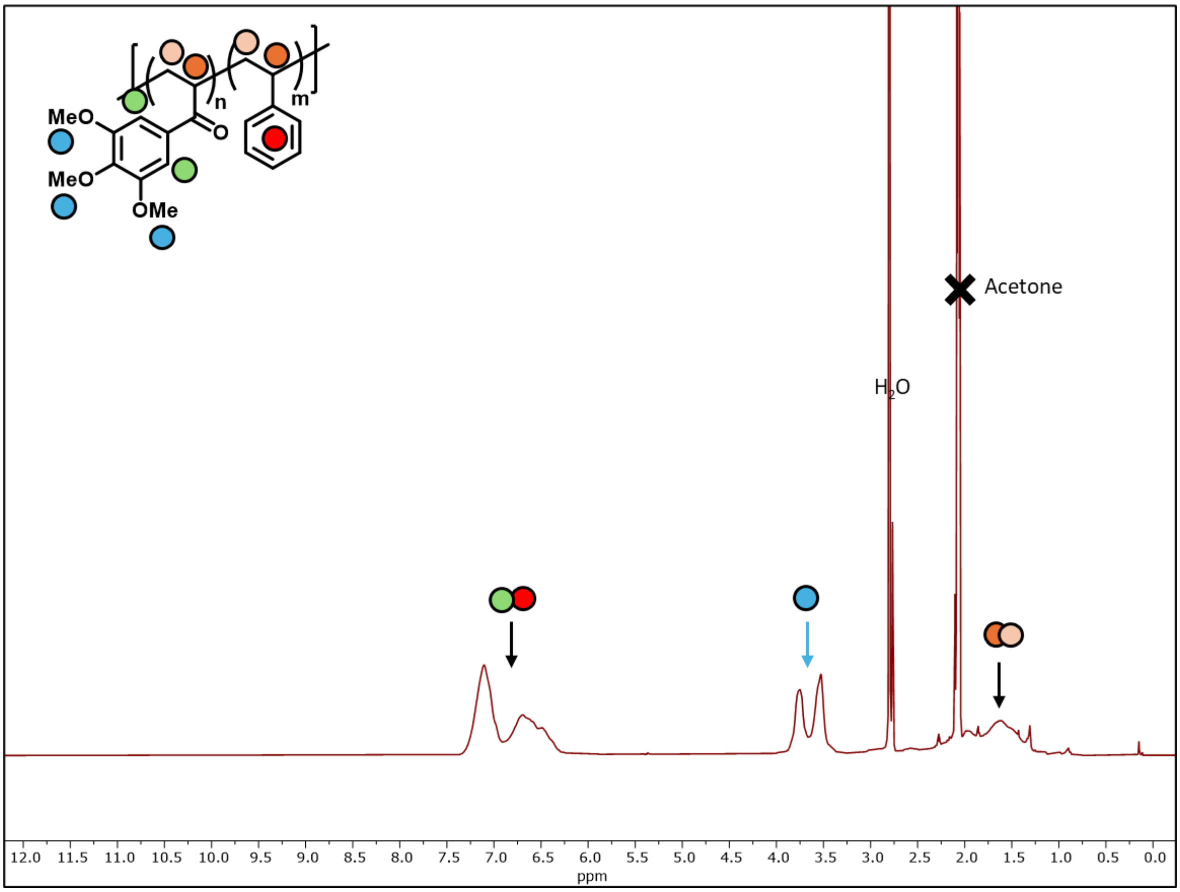


Figure S9. ^{1}H NMR spectra of P(St-*co*-BioPVK) synthesised by free-radical polymerisation (polymer **4**, Table 2) performed in deuterated acetone.

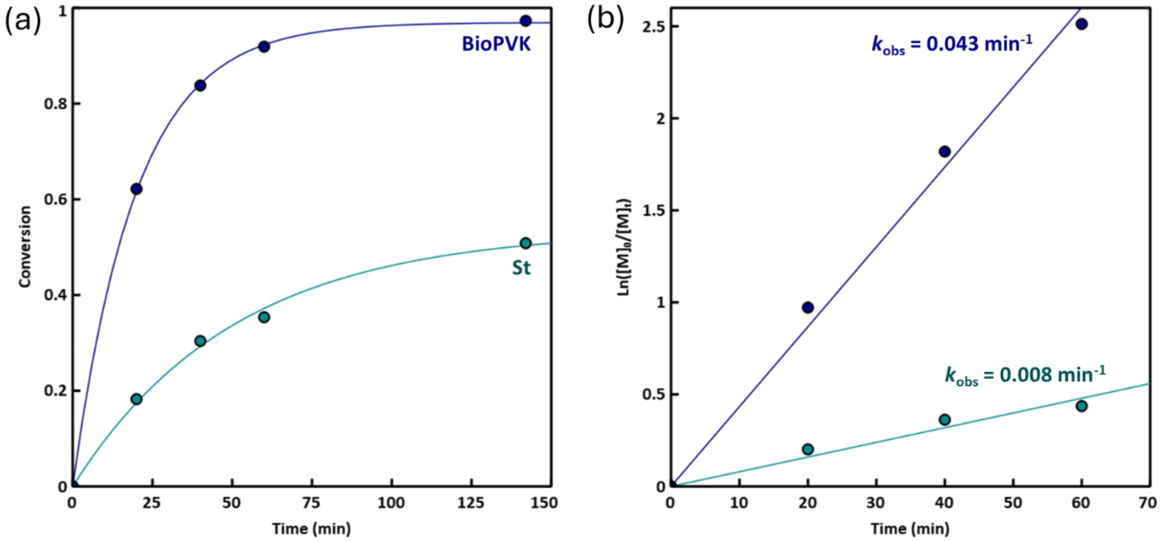


Figure S10. (a) Monomer conversion vs time plot of the copolymerization of St and BioPVK free-radical polymerisation (polymer **4**, Table 2) and (b) the corresponding first order kinetic plots.

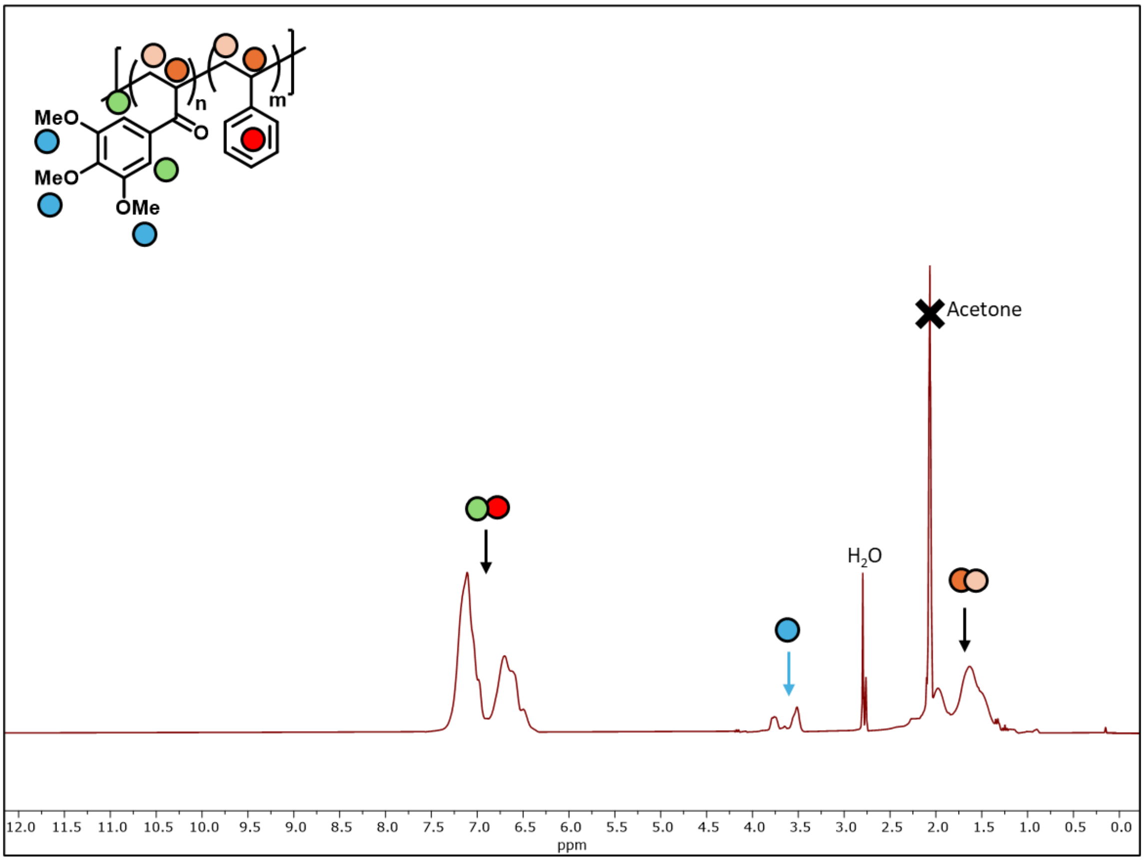


Figure S11. ^{1}H NMR spectra of P(St-*co*-BioPVK) synthesised by free-radical polymerisation (polymer **5**, Table 2) performed in deuterated acetone.

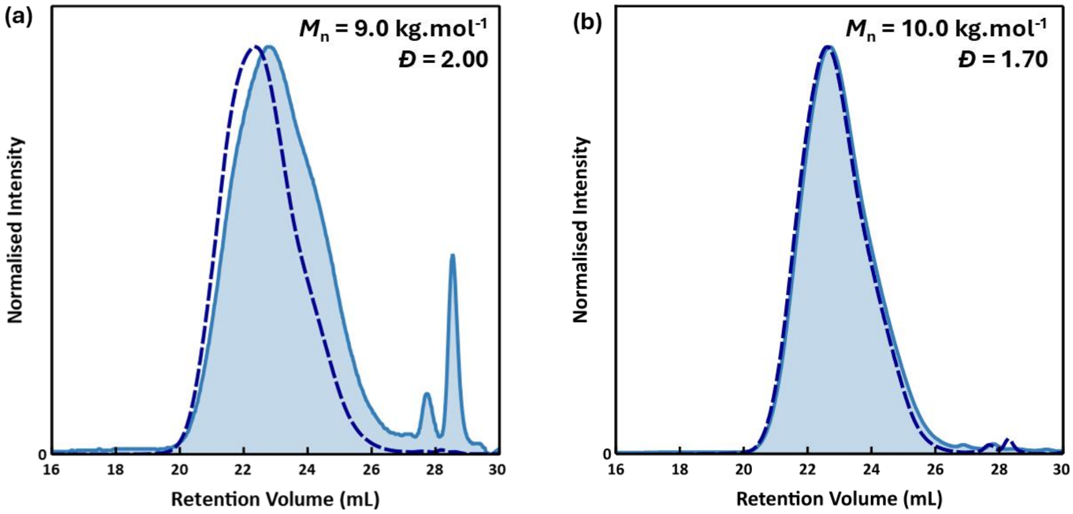


Figure S12. RI and UV SEC chromatograms of P(St-*co*-BioPVK) copolymers synthesised by free-radical polymerisation, where (a) is polymer **4** (Table 2) and (b) is polymer **5** (Table 2).

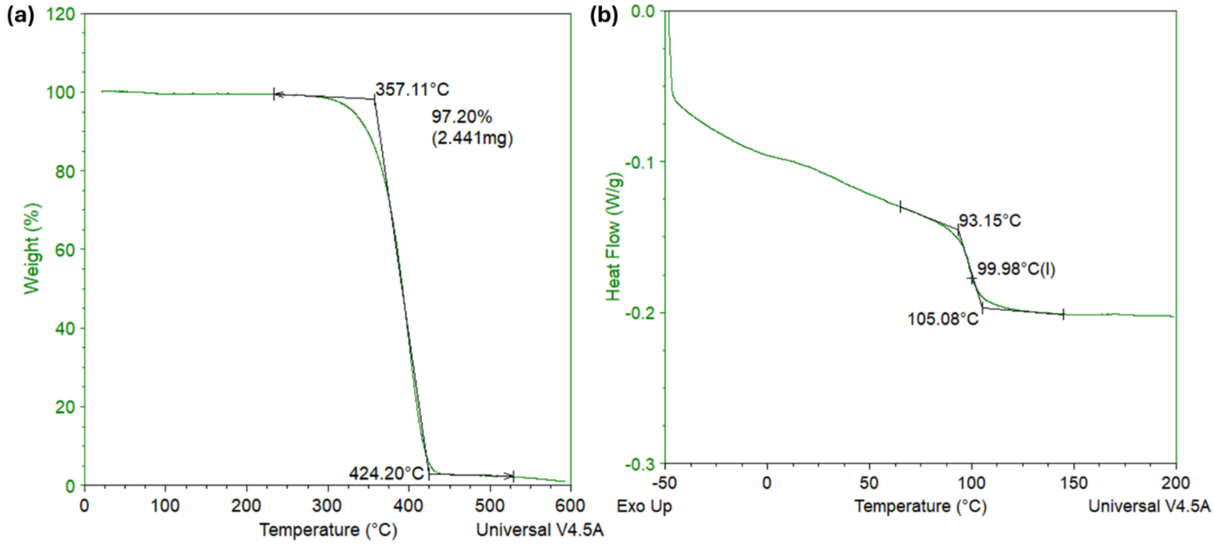


Figure S13. The (a) TGA and (b) DSC thermograms for copolymer **4** (Table 1) with the degradation temperature and T_g indicated on the graph.

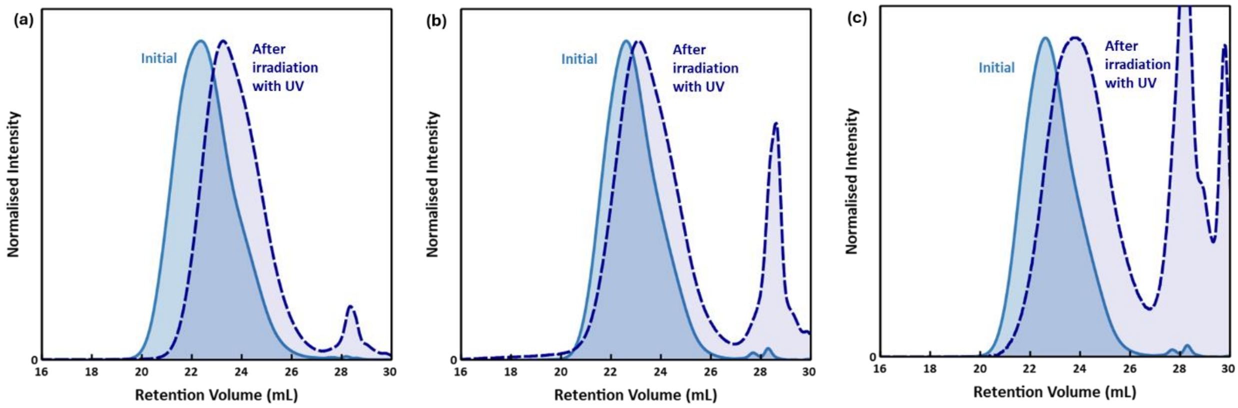


Figure S14. UV SEC chromatograms at 305 nm of (a) P(St-*co*-BioPVK) (polymer **4**, Table 2) before and after irradiation with UV light for 30 min, (b) P(St-*co*-BioPVK) (polymer **5**, Table 2) before and after irradiation with UV light for 30 min, and (c) P(St-*co*-BioPVK) (polymer 5, Table 2) before and after irradiation with UV light for 120 min.

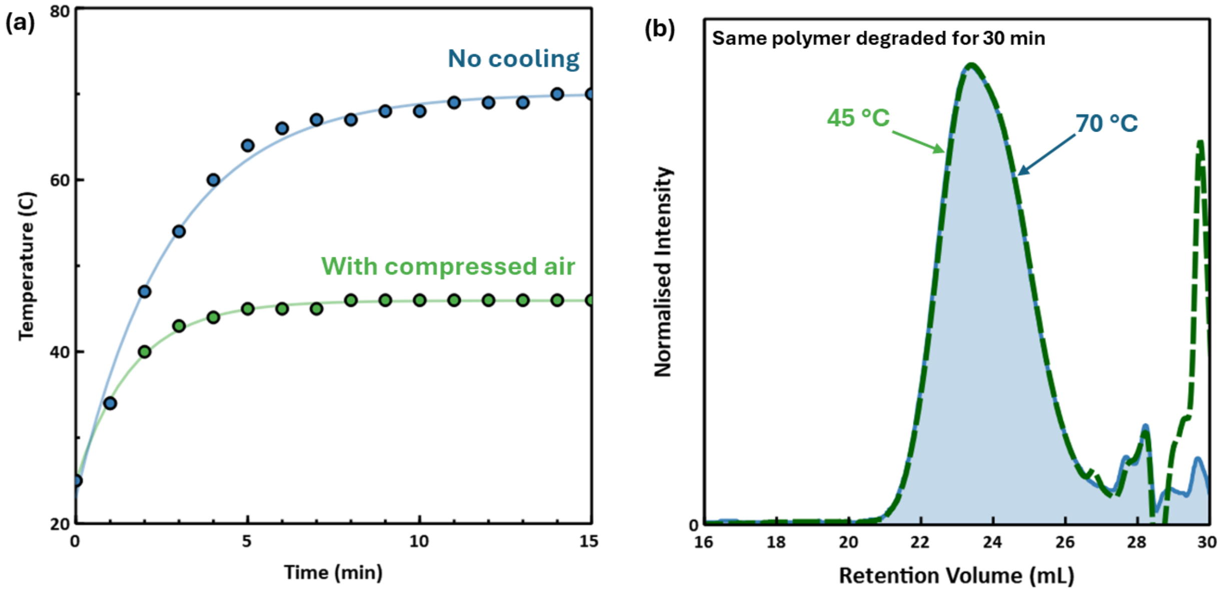


Figure S15. (a) A graph of temperature within the UV chamber against time and (b) UV SEC chromatograms of polymer **4** after irradiation with UV light for 30 min at 70 °C (blue curve) and at 40 °C (dashed green curve).

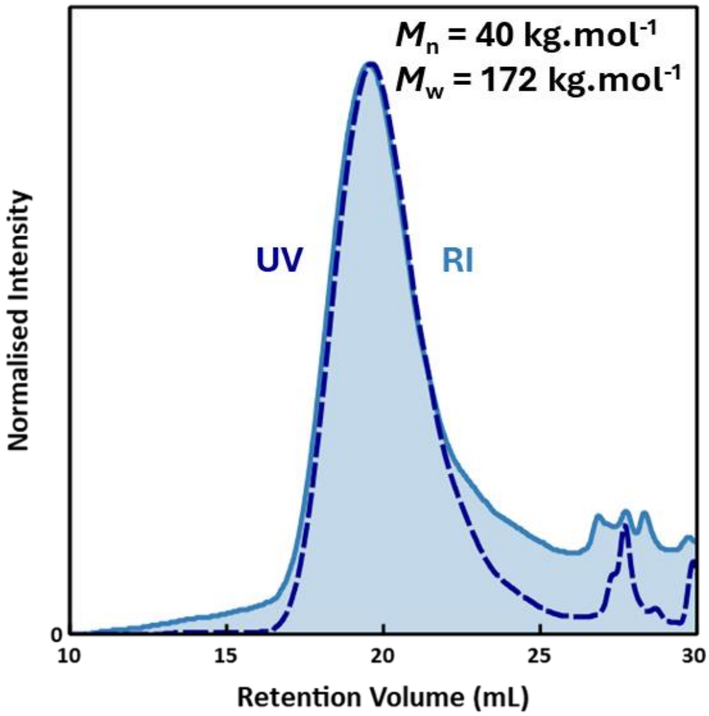


Figure S16. RI and UV SEC chromatograms of P(St-*co*-BioPVK) synthesised by conventional emulsion polymerisation (polymer **6,** Table 2).

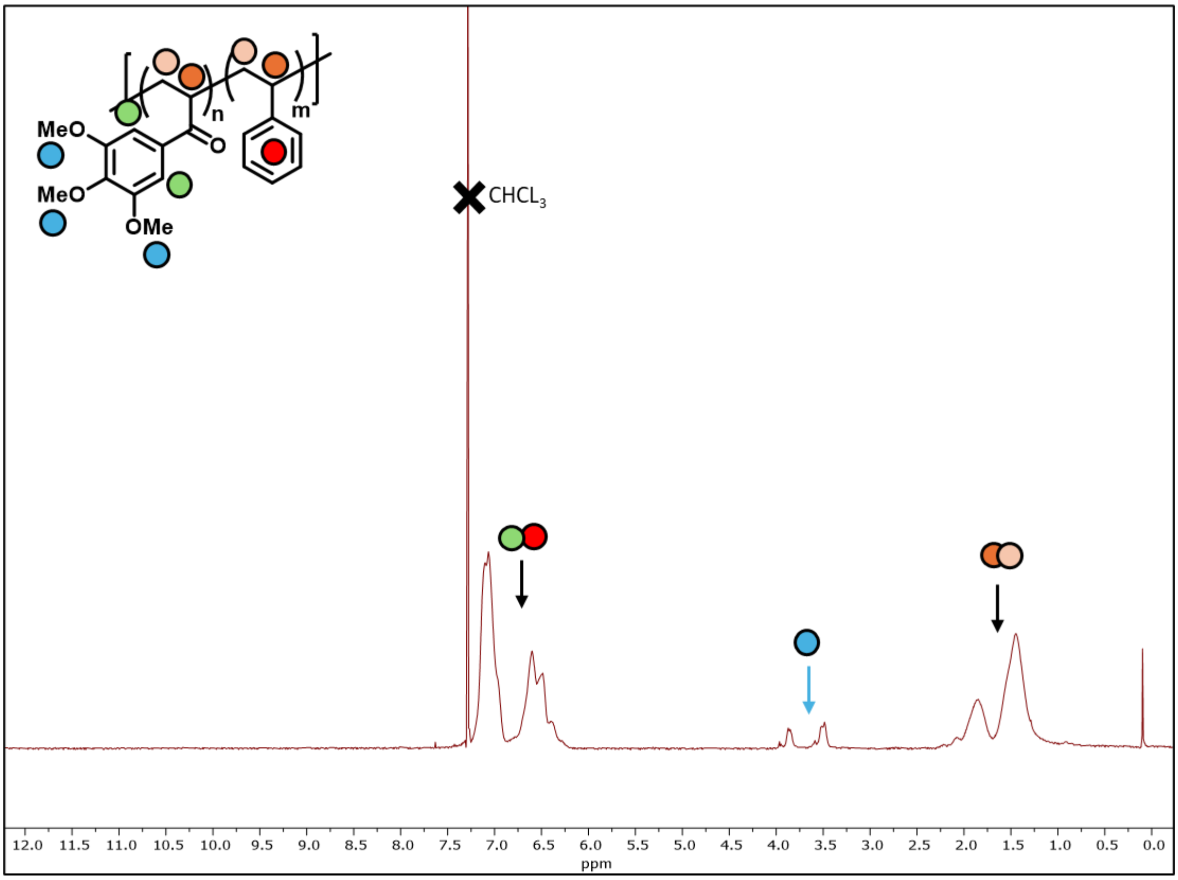


Figure S17. ^{1}H NMR spectra of P(St-*co*-BioPVK) synthesised by conventional emulsion polymerisation (polymer **6**, Table 2) performed in deuterated chloroform.

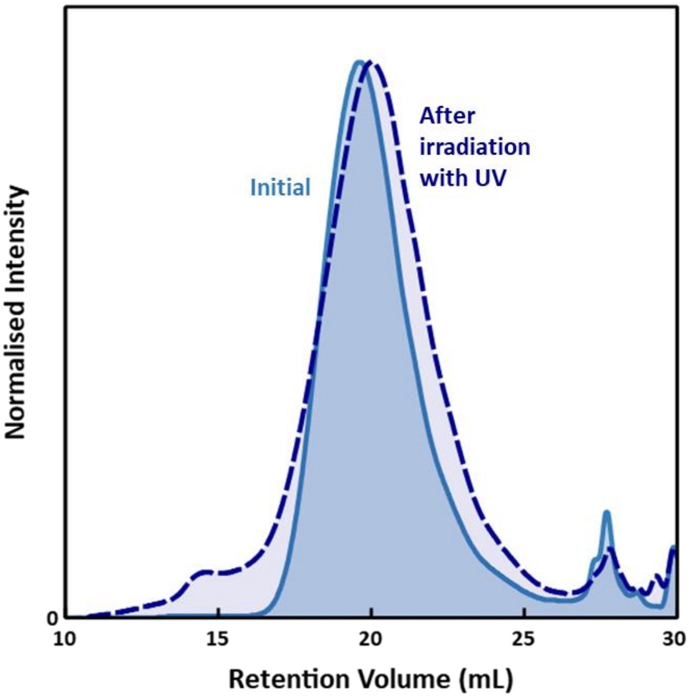


Figure S18. UV SEC chromatograms at 305 nm of P(St-*co*-BioPVK) synthesised by emulsion polymerisation (polymer **6**, Table 2) before and after irradiation with UV light for 30 min as a solid film.

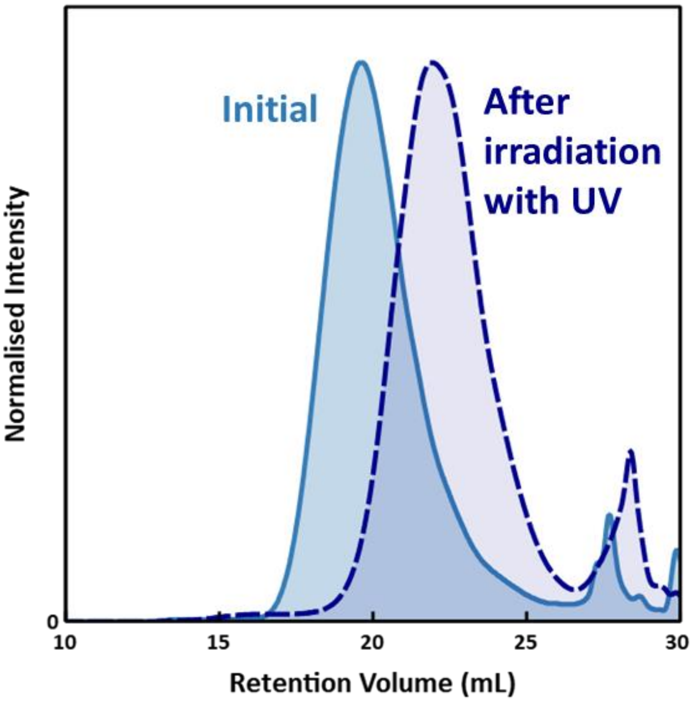


Figure S19. UV SEC chromatograms at 305 nm of P(St-*co*-BioPVK) synthesised by emulsion polymerisation (polymer **6**, Table 2) before and after irradiation with UV light for 30 min as a dilute solution in THF.

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