

Electronic Supporting Information (ESI)

Stability of Diels-Alder Photoadducts in Macromolecules

C. Petit,^{ab} L. D. Bangert,^{ab} M. Abbasi,^c M. Wilhelm,^c A. S. Goldmann,^{*ab} C. Barner-Kowollik^{*ab}

^aSchool of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George Street, Brisbane, QLD 4000, Australia. E-Mail: a.goldmann@qut.edu.au; christopher.barnerkowollik@qut.edu.au

^bMacromolecular Architectures, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany. E-Mail: anja.goldmann@kit.edu; christopher.barner-kowollik@kit.edu

^cPolymeric Materials, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany.

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1. Materials

Styrene (99% extra pure, Acros) was destabilized by passing through a basic alumina column and stored at -18 °C, anisole (99.8%, Acros), copper(II) bromine (CuBr₂) (99.9%, Acros), tris[2-(dimethylamino)ethyl]amine (Me₆TREN) (97%, Aldrich), tin(II) 2-ethylhexanoate (Sn(EH)₂) (95%, Aldrich), potassium carbonate (K₂CO₃) (99.0%, VWR), 18-crown-6 (99%, Alfa Aesar), *N*-ethylmaleimide (> 98%, Sigma Aldrich), acetone (extra dry 99.8%, Acros), acetonitrile (extra dry 99.8%, Acros), diethyl ether (VWR/Normapur), cyclohexane (VWR/Normapur), ethyl acetate (VWR/Normapur) were used as received. 2-Hydroxy-6-methylbenzaldehyde¹ and 1,1'-(hexane-1,6-diyl)bis(1H-pyrrole-2,5-dione)² were synthesized following the reported procedures.

2. Instrumentation

2.1. Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR measurements were carried out on a Bruker Avance III 400 spectrometer (¹H: 400 MHz and ¹³C: 100 MHz). The δ scale was referenced to deuterated solvents, indicated in the respective measurement. All spectra were measured at room temperature (298 K) in chloroform-d¹ (unless specified). Chemical shifts δ are expressed in parts per million (ppm) downfield from tetramethylsilane (TMS) as internal standard and are referenced to chloroform-d¹ (¹H: δ = 7.26 ppm, ¹³C: δ = 77.16 ppm).

2.2. Size Exclusion Chromatography (SEC)

Size exclusion chromatography analysis were performed on an Agilent 1200 system, comprising an autosampler, a Plgel 5 μ m bead-size guard column (50 \times 7.5 mm), one Plgel 5 μ m Mixed E column (300 \times 7.5 mm), three Plgel 5 μ m Mixed C columns (300 \times 7.5 mm) and a differential refractive index detector as well as an UV detector using THF as eluent at 35°C with a flow rate of 1 mL·min⁻¹. The SEC system was calibrated using linear poly(styrene) standards ranging from 160 to 6 \times 10⁶ g·mol⁻¹. The SEC calculations were carried out relative to poly(styrene) calibration (Mark-Houwink parameters for PS at 35 °C: $K = 13.63 \times 10^{-3} \text{ mL}\cdot\text{g}^{-1}$; $\alpha = 0.714$).³

2.3. (SEC)- Electrospray Ionisation Mass Spectrometry ((SEC)-ESI MS)

2.3.1. Precursor Materials

Mass spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the *m/z* range 200-6000 using premixed calibration solutions (Thermo Scientific). A spray voltage between 3.6 kV and a dimensionless sheath gas of 5 were applied. The capillary temperature and the S-lens RF level were set to 320 °C. The samples were dissolved with a concentration of 0.05 mg·mL⁻¹ in a mixture of THF and MeOH (3:2) containing 100 μ mol of sodium trifluoroacetate and infused with a flow of 5 μ L·min⁻¹. The spectra were recorded in positive mode.

2.3.2. Thermally Challenged Polymers

The above-cited high resolution mass spectrometer has also been employed for analysing the polystyrenes. All spectra were recorded in negative mode, using a mixture of DCM:MeOH (3:2) doped with 0.1% (w/w) NaCl. Polystyrenes were recorded at a concentration of $0.1 \text{ mg}\cdot\text{mL}^{-1}$. The FT resolution was set to 140 000 with 3 microscans during an acquisition time of 90s. The sheath gas was set to 10.00, and the spare gas 1.00. The flow rate was set to $15 \text{ }\mu\text{L}\cdot\text{min}^{-1}$. The spray voltage was set to 4.5 V and kept constant during the whole experiment.⁴

2.4. Flash Chromatography

Flash chromatography was performed on a PuriFlash Rf+ from Teledyne ISCO company (Lincoln, USA) using a 120 g-RediSep Rf column loaded with silica gel and a pre-column loaded with the crude product deposited on Celite. The run starts after a purge of the system with the solvents used for the separation, followed by a purge with air. The details for each run can be found within each procedures described below requiring a purification via flash chromatography.

2.5. Photoreactor Setup

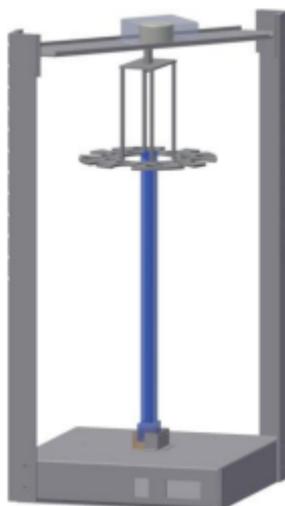


Figure S1 Scheme of the employed photoreactor. The photovials are suspended on the carrousel and surrounded by 5 PL-L lamps.

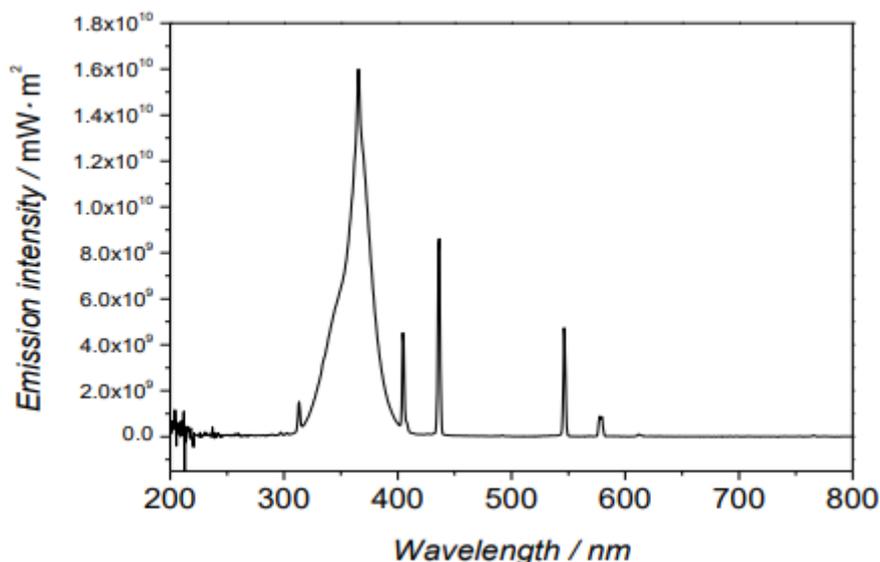


Figure S2 Emission spectrum of the lamp PL-L 36 W (iSOLde Cleo Compact) used in our study.

3. Synthetic Procedures and Analytical Data

3.1. Precursor Materials Synthesis

3.1.1. Synthesis of 2-(4-(bromomethyl)benzyloxy)-6-methylbenzaldehyde (**1**)



The procedure was adapted from literature⁵: 1,4-Bis(bromomethyl)benzene (5.93 g, 2.9 equiv), K_2CO_3 (1.38 g, 1.3 equiv) and 18-crown-6 (36 mg, 0.18 equiv) were stirred in 65 mL of dry acetone at 40 °C. 2-Hydroxy-6-methylbenzaldehyde (1.05 g, 1.0 equiv.) dissolved in 5 mL of acetone was added dropwise and the mixture was stirred at 40 °C overnight. After precipitation of the excess of 1,4-bis(bromomethyl)benzene in cold diethyl ether the filtrate containing the desire product was recovered, the solvent was removed under reduced pressure and the crude product was purified via flash chromatography (silica gel, cyclohexane/ethyl acetate 19:1, $R_f = 0.25$, 30 column volumes and a flow rate of 60 mL·min⁻¹ needed for a complete separation) to afford a white solid.

¹H-NMR ($CDCl_3$, 400 MHz) δ /ppm: 10.73 (s, ¹H, CHO), 7.4 (m, 5H, para and para to CHO), 6.8 (m, 2H, meta to CHO), 5.15 (s, 2H, OCH₂), 4.51 (s, 2H, BrCH₂), 2.59 (s, 3H, CH₃).

¹³C-NMR ($CDCl_3$, 100 MHz) δ /ppm: 192.2 (CHO), 162.1 (OC_{arom}), 142.2 (OCH₂C_{arom}), 137.8 (CH₃C_{arom}), 136.5 (BrCH₂C_{arom}), 134.4 (CH₃CCH), 129.4 (BrCH₂CCH), 127.6 (OCH₂CCH), 124.5 (CH₃CCH), 123.6 (CHOC_{arom}), 110.3 (OCCH), 70.1 (OCH₂), 33.0 (BrCH₂), 21.5 (CH₃).

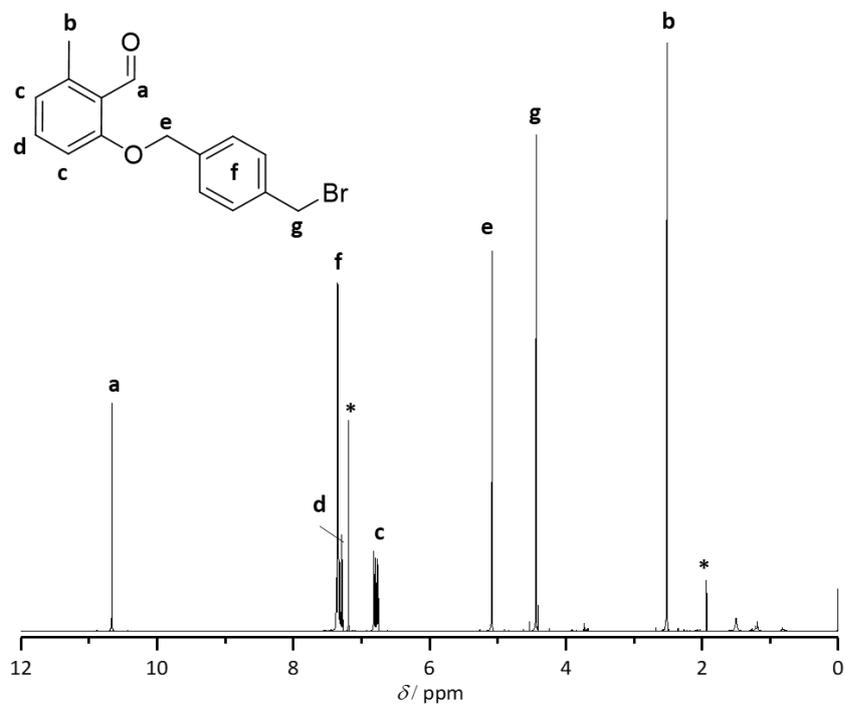


Figure S3 ¹H NMR spectrum of 2-((4-(bromomethyl)benzyl)oxy)-6-methylbenzaldehyde **1**, *residual CHCl₃ (CDCl₃, 400 MHz).

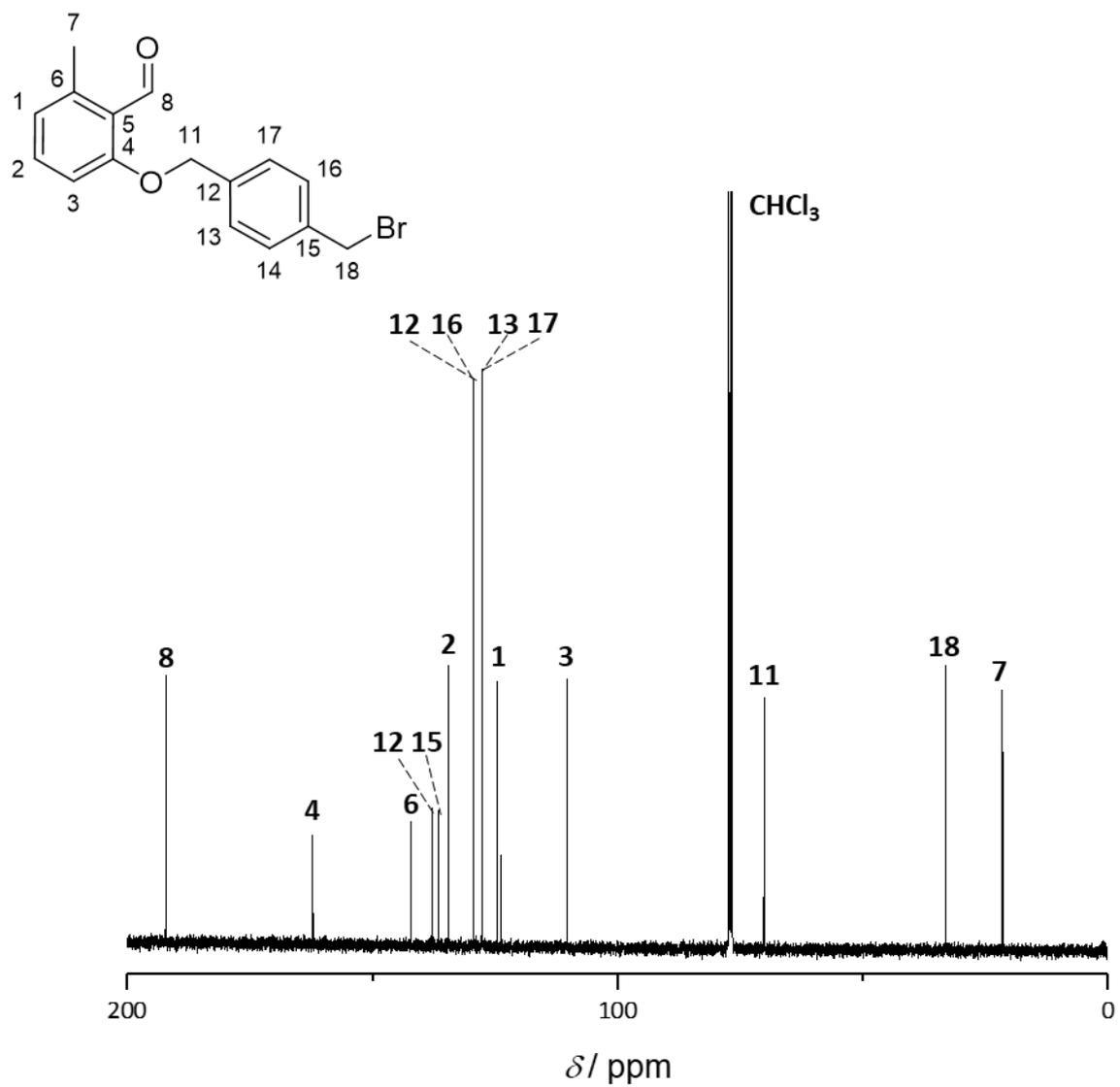


Figure S4 ^{13}C NMR spectrum of 2-((4-(bromomethyl)benzyl)oxy)-6-methylbenzaldehyde **1** (CDCl_3 , 400 MHz).

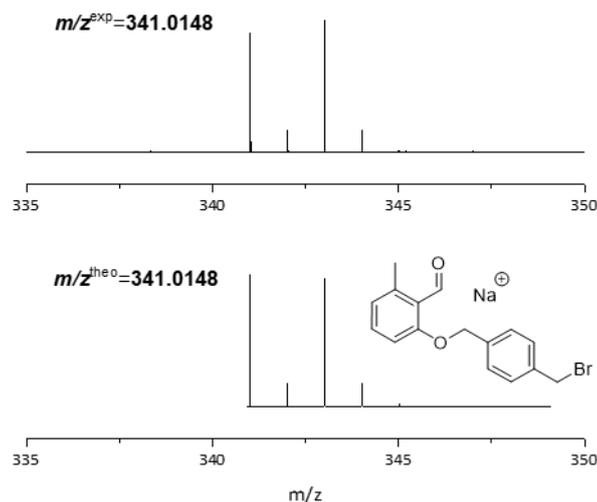


Figure S5 ESI Orbitrap mass spectrum of 2-((4-(bromomethyl)benzyl)oxy)-6-methylbenzaldehyde **1** in positive ion mode via direct infusion. Top: experimental spectrum; Bottom: Simulated isotopic pattern. (Solvent THF:MeOH (3:1) doped with NaOTf).

3.1.2. Synthesis of 5-((4-(bromomethyl)benzyl)oxy)-2-ethyl-4-hydroxy-3a,4,9,9a-tetrahydro-1H-benzof[f]isoindole-1,3(2H)-dione (**2**)

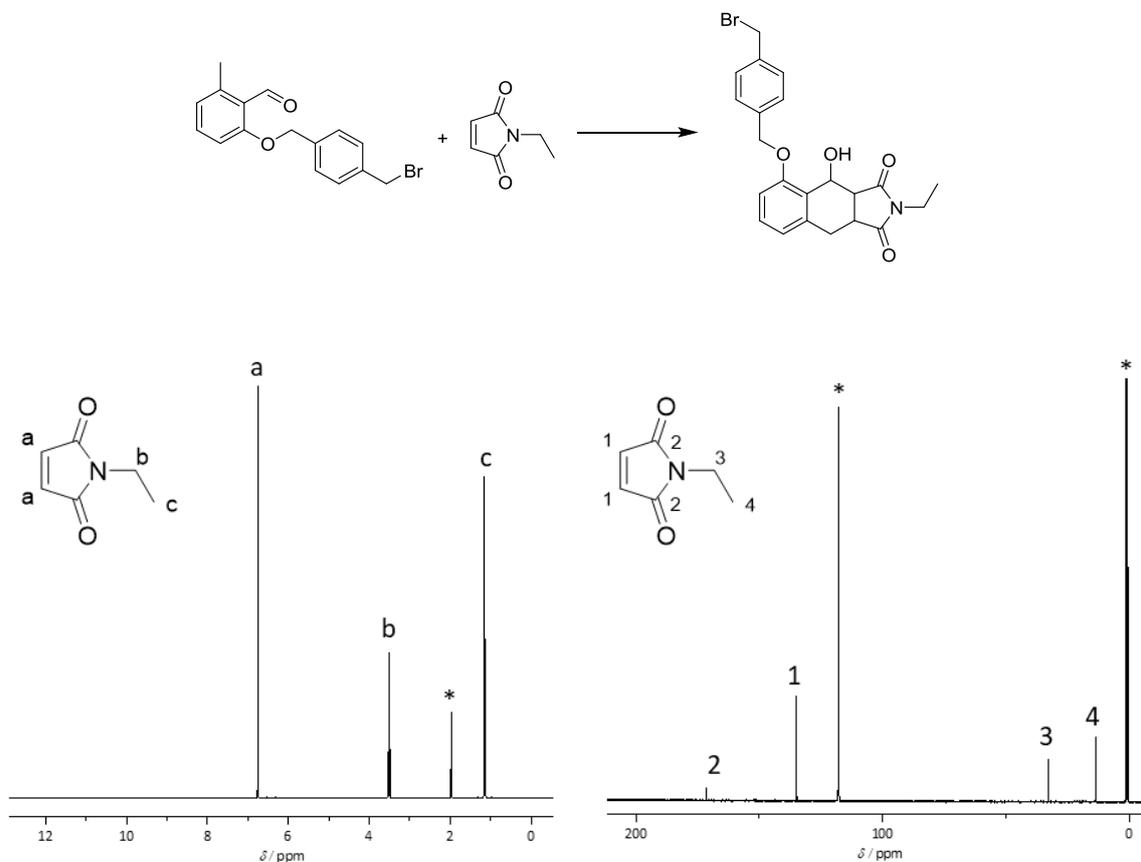


Figure S6 ^1H (left) and ^{13}C (right) NMR spectra of *N*-ethyl maleimide, *residual acetonitrile ($\text{d}_3\text{-ACN}$, 400 MHz).

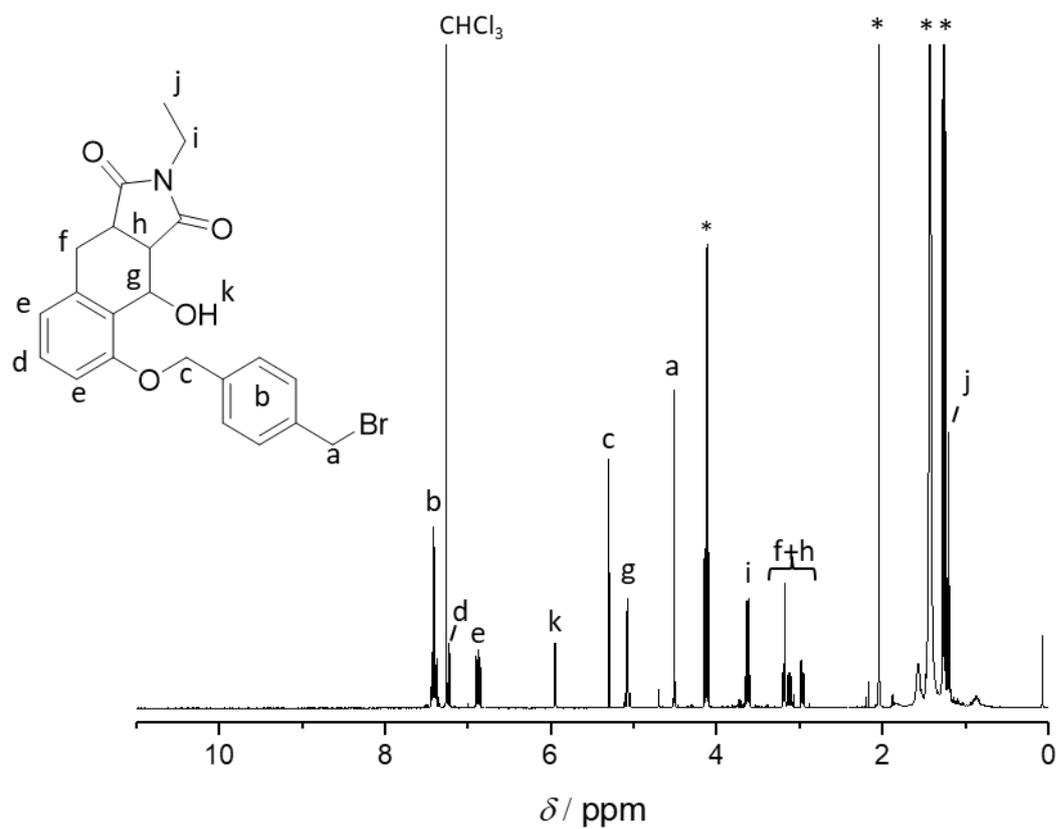


Figure S7 ¹H NMR spectrum of 5-((4-(bromomethyl)benzyl)oxy)-2-ethyl-4-hydroxy-3a,4,9a-tetrahydro-1H-benzo[f]isoindole-1,3(2H)-dione (**3**), *residual solvents (ethyl acetate and cyclohexane) (CDCl₃, 400 MHz).

3.1.3. Synthesis of 1,1'-(hexane-1,6-diyl)bis(1H-pyrrole-2,5-dione)

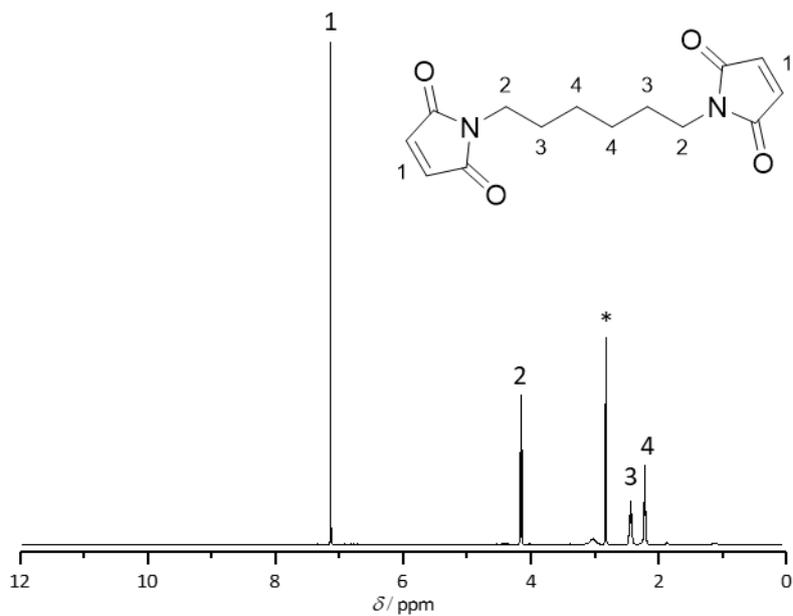


Figure S8 ^1H NMR spectrum of 1,1'-(hexane-1,6-diyl)bis(1H-pyrrole-2,5-dione) *residual acetonitrile ($\text{d}_3\text{-ACN}$, 400 MHz). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ /ppm: 6.68 (s, 4H, CH=CH), 3.46 (t, 4H, N-CH₂), 1.61 (t, 4H, -CH₂), 1.29 (m, 4H, -CH₂);

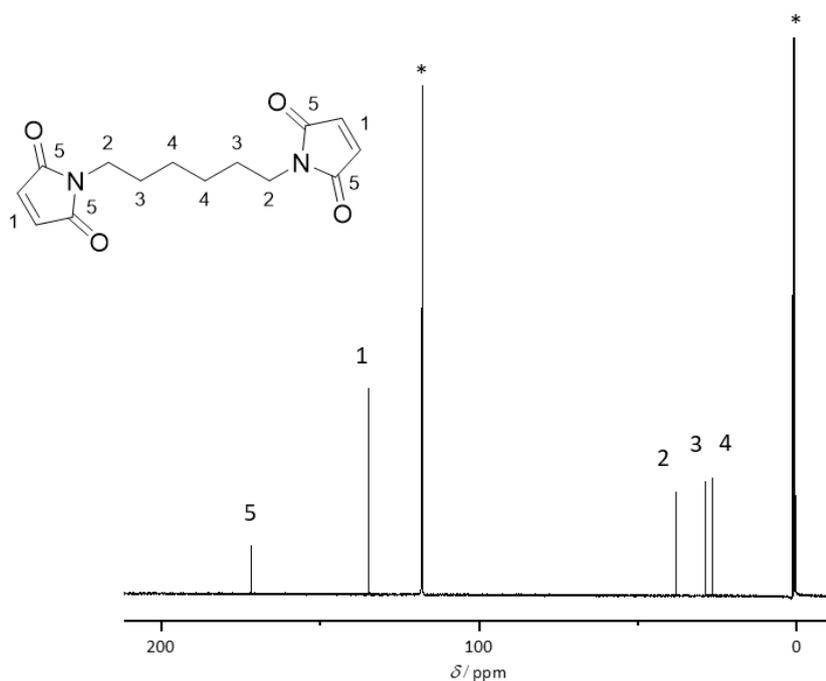
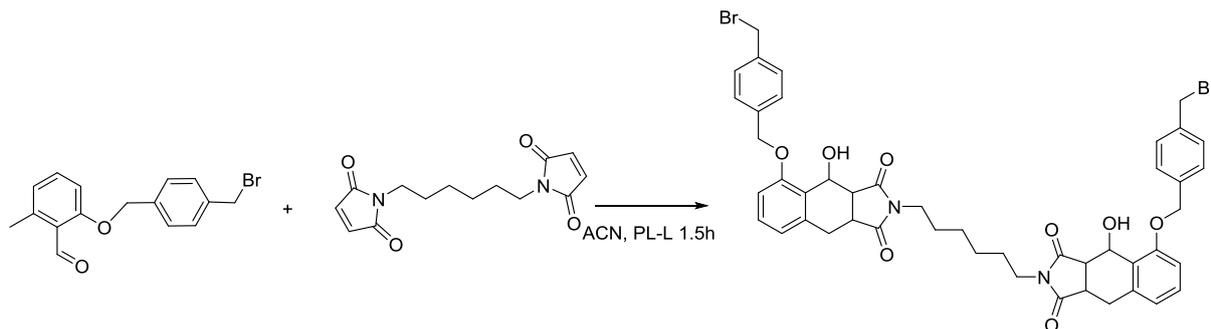


Figure S9 ^{13}C NMR spectrum of 1,1'-(hexane-1,6-diyl)bis(1H-pyrrole-2,5-dione) *residual acetonitrile ($\text{d}_3\text{-ACN}$, 400 MHz). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ /ppm: 170.5 (C=O), 135.8 (C=C), 41.7 (CH₂), 30.2 (CH₂), 26.4 (CH₂).

3.1.4. Synthesis of 2,2'-(hexane-1,6-diyl)bis(5-((4-(bromomethyl)benzyl)oxy)-4-hydroxy-3a,4,9,9a-tetrahydro-1H-benzo[f]isoindole-1,3(2H)-dione) (5)



2-((4-(bromomethyl)benzyl)oxy)-6-methylbenzaldehyde (**1**) and 1,1'-(hexane-1,6-diyl)bis(1H-pyrrole-2,5-dione) were dissolved in 200 mL of dry acetonitrile and mixed until completed dissolution. The mixture was separated in 10 different photovials and each of them was purged 15 min under nitrogen. The vials were then placed in the photoreactor and irradiated for 1.5 h with 5 PL-L lamps. The solvent was removed under reduced pressure and the crude product was collected to afford a yellowish solid.

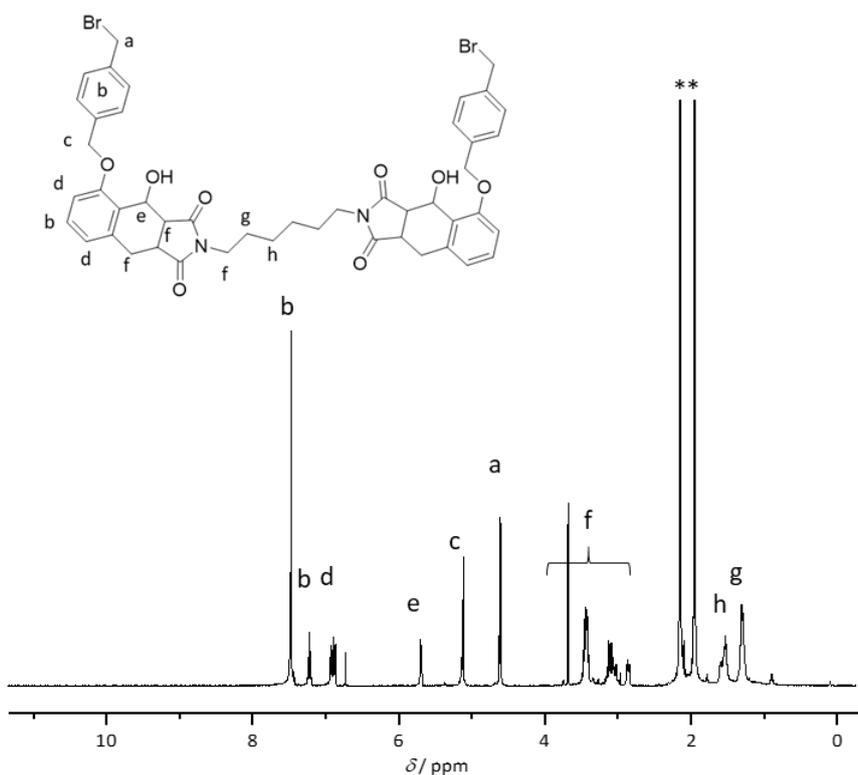


Figure S10 ^1H NMR spectrum of 2,2'-(hexane-1,6-diyl)bis(5-((4-(bromomethyl)benzyl)oxy)-4-hydroxy-3a,4,9,9a-tetrahydro-1H-benzo[f]isoindole-1,3(2H)-dione) **5** *residual acetonitrile and water ($\text{d}_3\text{-ACN}$, 400 MHz). $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ/ppm : 4.1 (2H, OH), 2.84 (4H, $-\text{CH}_{\text{Maleimide}}$), 5.25 (2H, $-\text{CH-OH}$), 3.21/2.96 (4H, $-\text{CH}_2_{\text{cycloadduct}}$), 6.55-6.90 (6H, $-\text{CH}_{\text{Photoenol}}$), 7.2-7.3 (8H, $-\text{CH}_{\text{Benzyl}}$), 4.56 (4H, $-\text{CH}_2\text{-Br}$), 3.18 (4H, $-\text{CH}_2\text{-N}$), 1.4-1.6 (8H, $-\text{CH}_2\text{-N-hexyl}$).

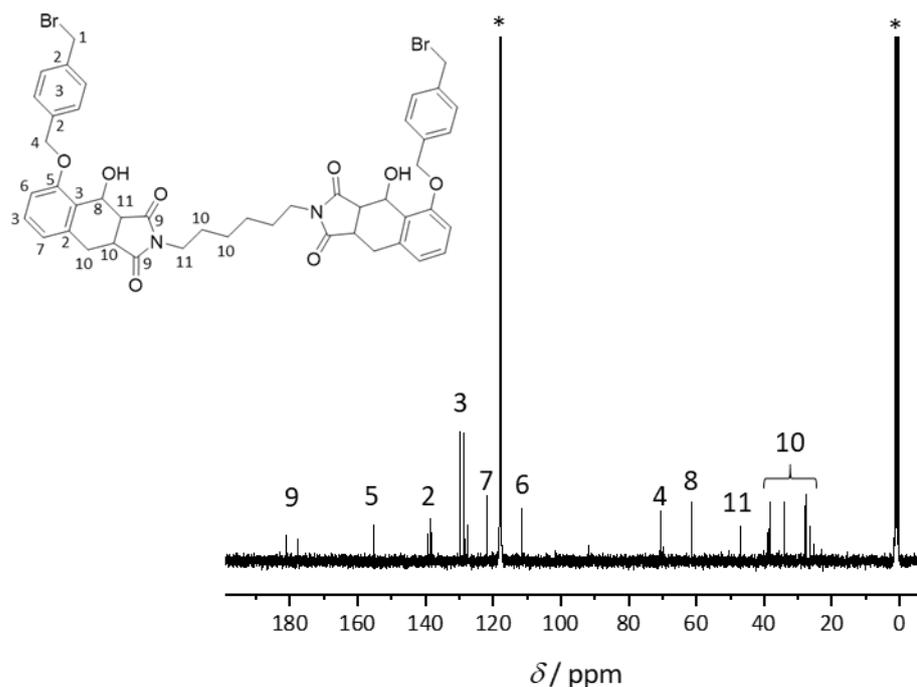


Figure S11 ^{13}C NMR spectrum of 2,2'-(hexane-1,6-diyl)bis(5-((4-(bromomethyl)benzyl)oxy)-4-hydroxy-3a,4,9,9a-tetrahydro-1H-benzo[f]isoindole-1,3(2H)-dione) **5** *residual acetonitrile and water ($\text{d}_3\text{-ACN}$, 400 MHz). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ/ppm : 175.7 (C=O), 50.7 ($\text{CH}_{\text{maleimide}}$), 33.2 (C-Br), 136.9 ($\text{C}_{\text{para-benzylBr}}$), 127-129 ($\text{C}_{\text{ortho-m\`e}ta\text{-benzylBr}+\text{C}_{\text{photoenol-ligation}}}$), 109.3 ($\text{CH}_{\text{ortho-photoenol}}$), 30-34 ($\text{C}_{\text{ligation}}$), 71.1 (C-O), 59.1 (C-OH), 46.8 ($\text{CH}_2\text{-N}$), 26-30 ($\text{CH}_2\text{-hexylMaleimide}$).

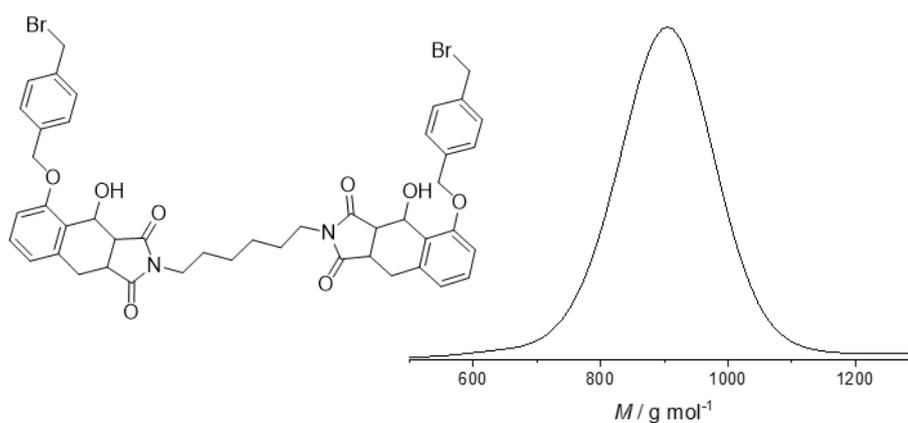


Figure S12 SEC trace of 2,2'-(hexane-1,6-diyl)bis(5-((4-(bromomethyl)benzyl)oxy)-4-hydroxy-3a,4,9,9a-tetrahydro-1H-benzo[f]isoindole-1,3(2H)-dione) **5** (in THF with PS calibration).

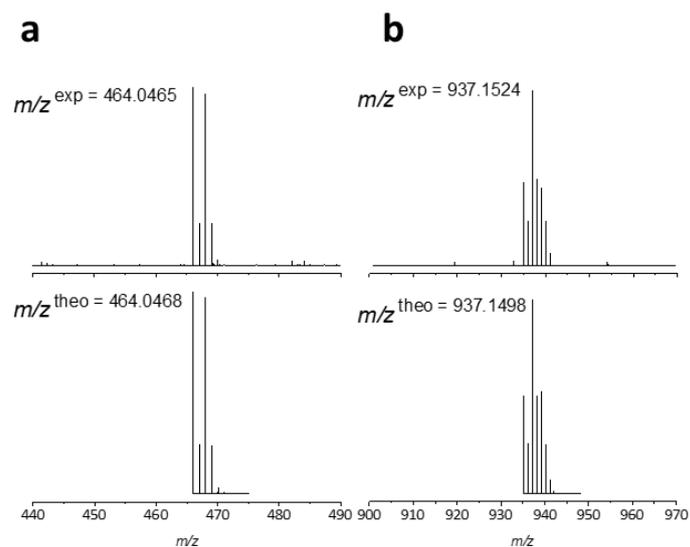


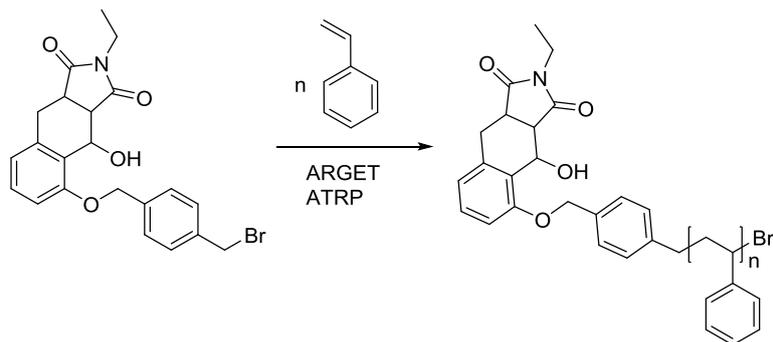
Figure S13 ESI Orbitrap mass spectra of (a) 5-((4-(bromomethyl)benzyl)oxy)-2-ethyl-4-hydroxy-3a,4,9,9a-tetrahydro-1H-benzo[f]isoindole-1,3(2H)-dione (**2**) and of (b) 2,2'-(hexane-1,6-diyl)bis(5-((4-(bromomethyl)benzyl)oxy)-4-hydroxy-3a,4,9,9a-tetrahydro-1H-benzo[f]isoindole-1,3(2H)-dione) (**5**) in positive ion mode via direct infusion (Solvent THF:MeOH (3:1) doped with NaOTf). Top: experimental spectra. Bottom: simulated isotopic patterns.

3.2. Polymers synthesis

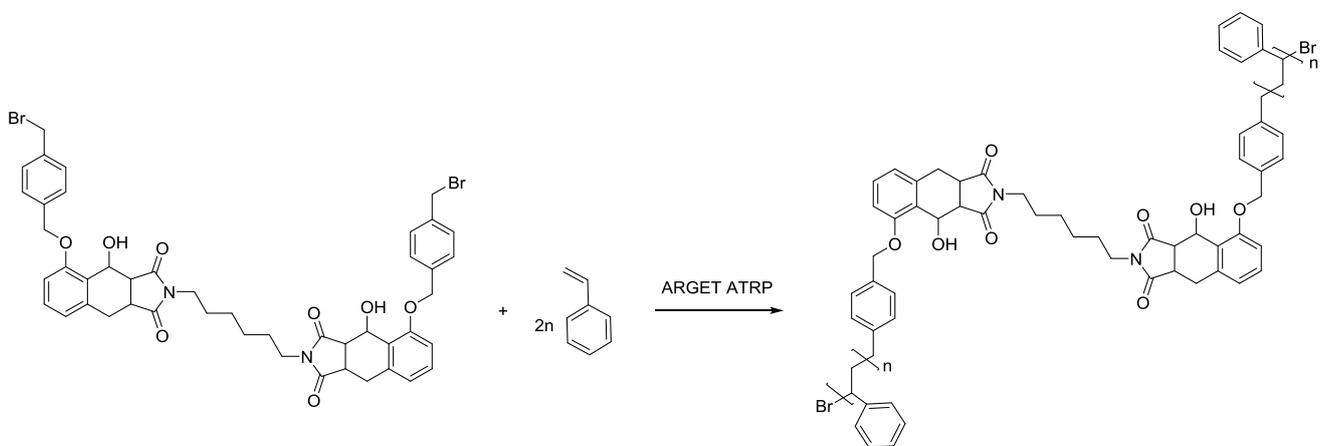
3.2.1. General procedure of ARGET ATRP

The initiator (Initiator **2**: 0.14 mmol; Initiator **5**: 0.07 mmol) and tin(II) 2-ethylexanoate ($\text{Sn}(\text{EH})_2$) (45 μL , 0.14 mmol) were separately dissolved in anisole (1 mL) in round bottom flasks and purged with argon for 30 min. In a Schlenk flask, equipped with a stirring bar, styrene (25 mL, 0.2 mol), CuBr_2 (14 mg, 64.9 μmol) and tris[2-(dimethylamino)ethyl]amine (Me6TREN) (6 μL , 22.4 μmol) were dissolved in anisole (50 mL) and purged with argon for 30 min. After removing oxygen, the initiator- and reducing agent-solution were transferred to the reaction flask via a cannula. The reaction mixture was subsequently placed into an oil bath tempered at 90 $^\circ\text{C}$ for the appropriate reaction time. To stop the polymerization process, the flask was opened to the atmosphere and cooled to ambient temperature in a water bath. The copper catalyst was removed by passing the solution over a short column of neutral alumina oxide. The purified polymer was obtained by two fold precipitations into methanol. The precipitate was filtered off and dried under high vacuum to afford the polymers as white powders.

3.2.2. General schemes



Scheme S1 Polymerization of styrene via ARGET ATRP initiated by 5-((4-(bromomethyl)benzyl)oxy)-2-ethyl-4-hydroxy-3a,4,9,9a-tetrahydro-1H-benzo[f]isoindole-1,3(2H)-dione (**2**).



Scheme S2 Polymerization of styrene via ARGET ATRP initiated by 2,2'-(hexane-1,6-diyl)bis(5-((4-(bromomethyl)benzyl)oxy)-4-hydroxy-3a,4,9,9a-tetrahydro-1H-benzo[f]isoindole-1,3(2H)-dione).

3.2.3. SEC-ESI MS spectra

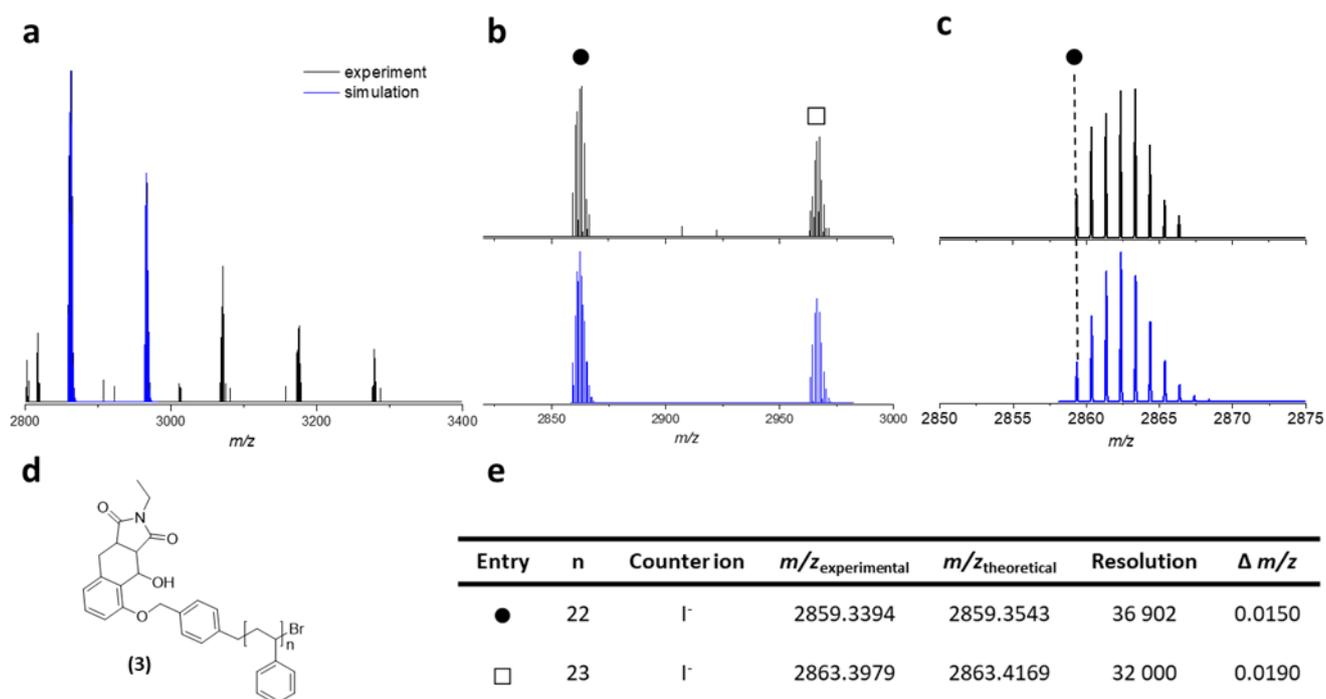


Figure S14 SEC-ESI-MS spectra of polymer **3** in negative ion mode (doped with NaI). **a**: Full spectrum; **b**: Zoom on two repetitive units with the experimental data obtained in black and the simulated spectra in blue; **c**: Zoom into one repeat unit with the experimental data obtained in black and the simulated spectra in blue; **d**: Structure assigned to the spectrum; **e**: Table containing the experimental and theoretical m/z values for both isotopic patterns.

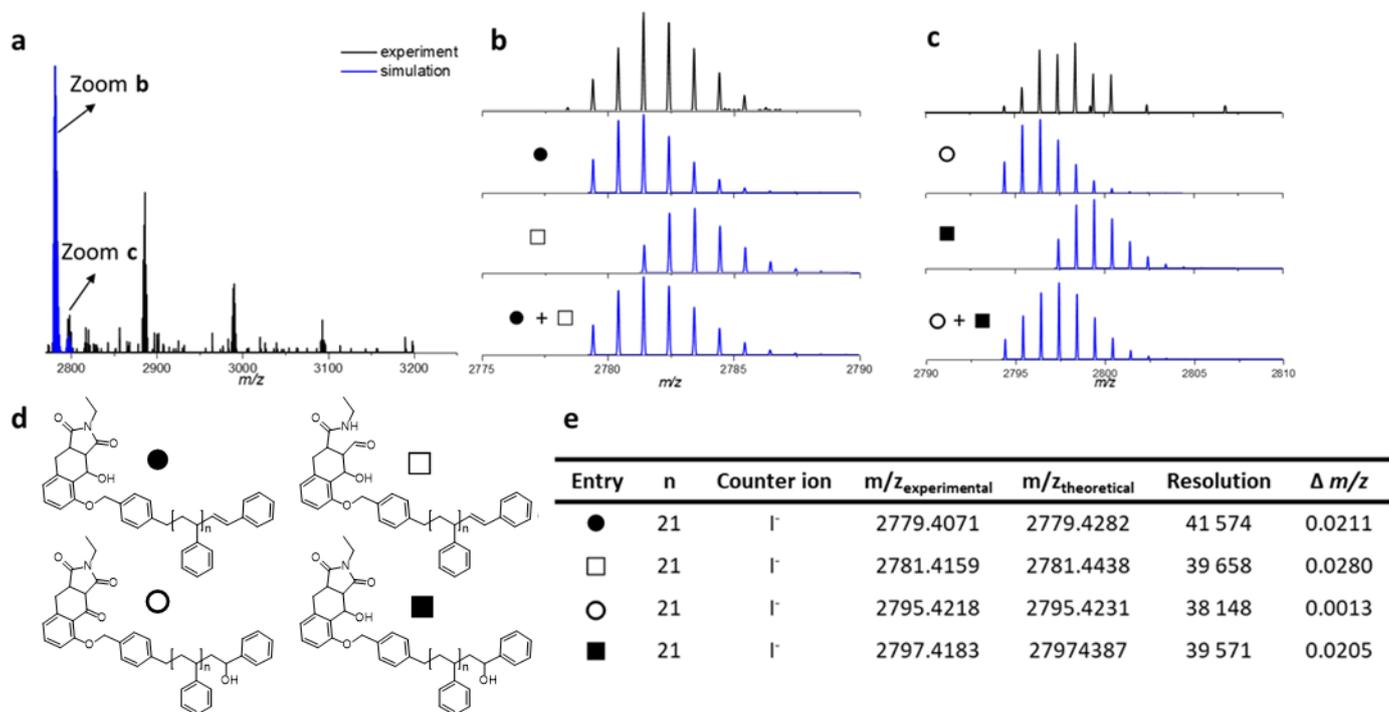


Figure S15 SEC-ESI-MS spectra of polymer **3** after degradation at 150°C for 8h under N₂ atmosphere in negative ion mode (doped with NaI). **a**: Full spectrum; **b**: Zoom on the main peak with the experimental data obtained in black and the simulated spectra in blue (e.g. simulated structure ●, □ and both ● and □ together); **c**: Zoom into the second peak with the experimental data obtained in black and the simulated spectra in blue (e.g. simulated structure ○, ■ and both ○ and ■ together); **d**: Structures assigned to the spectra; **e**: Table containing the experimental and theoretical m/z values.

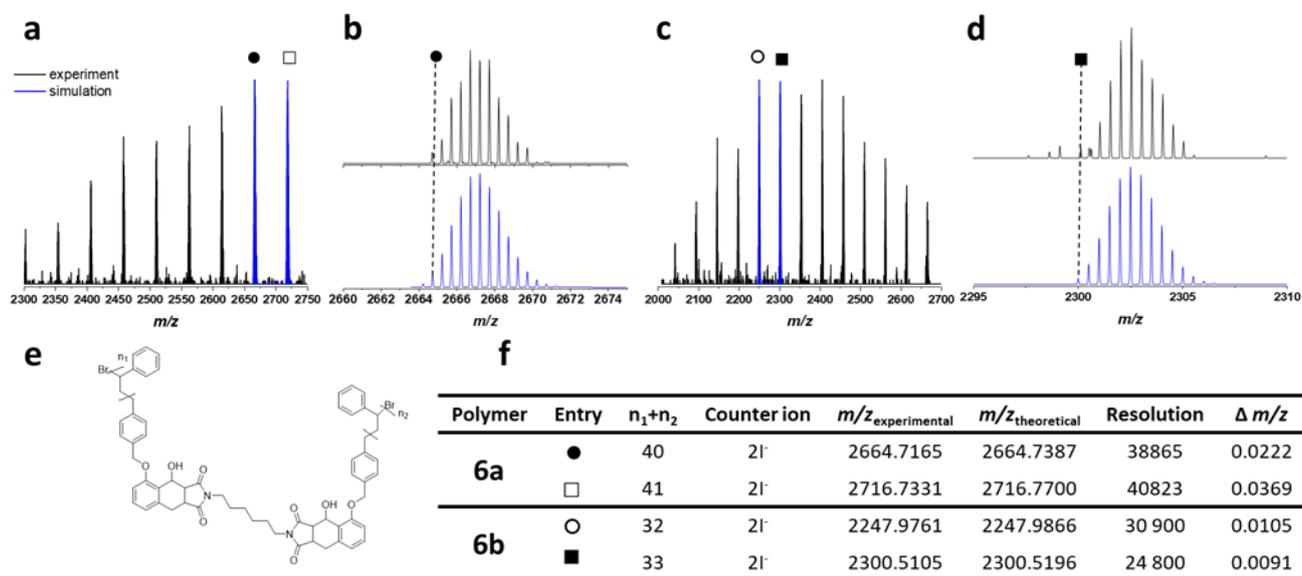


Figure S16 SEC-ESI-MS spectra of the polymers **6a** and **6b** in negative ion mode (doped with NaI). Full spectra and zoom on one unit of the polymer **6a** (respectively **a** and **b**) and **6b** (respectively **c** and **d**) the experimental data obtained in black and the simulated spectra in blue; **e**: Structures assigned to the spectra; **f**: Table containing the experimental and theoretical m/z values for both units of both polymers.

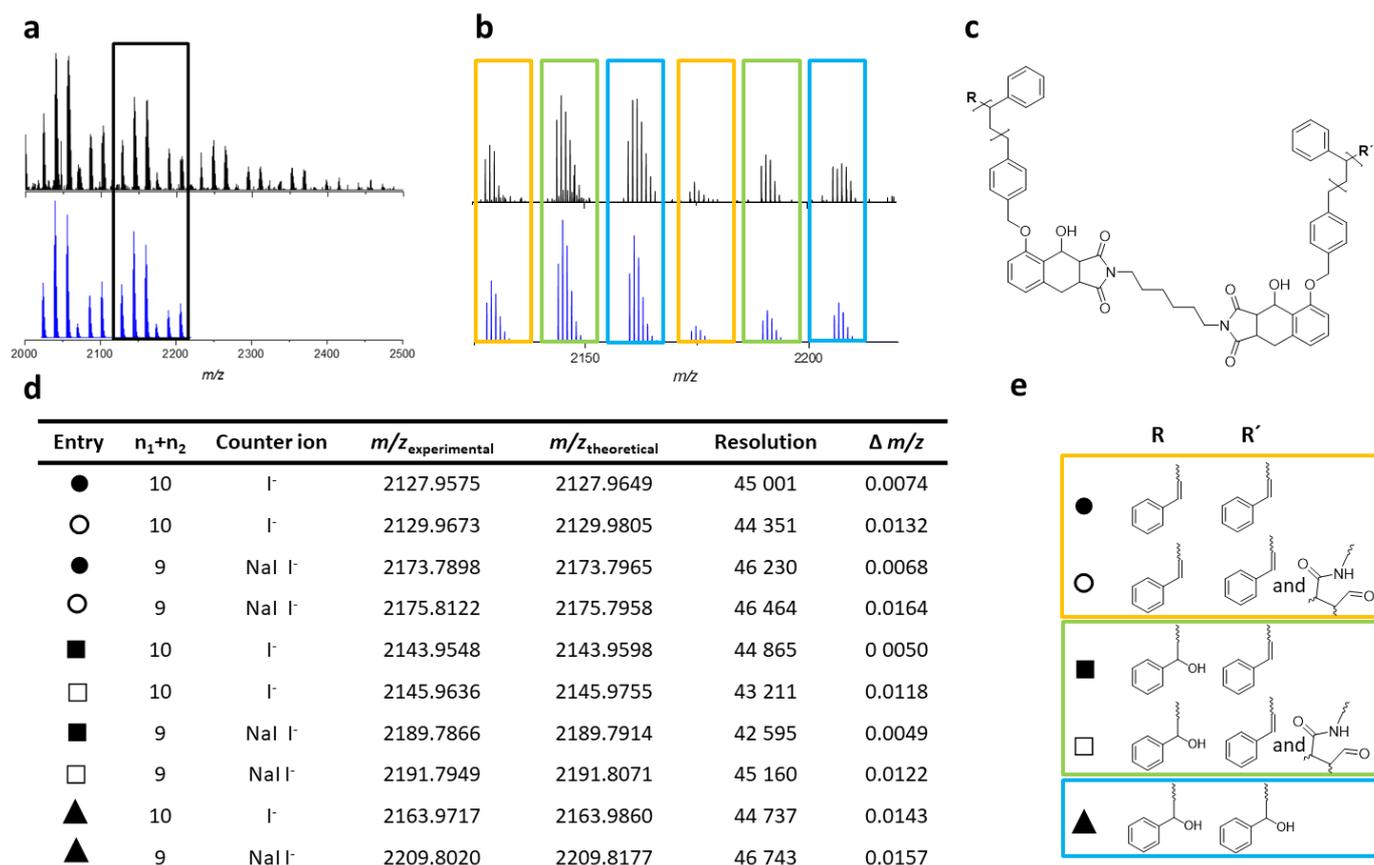


Figure S17 SEC-ESI-MS spectra of **6a** after heating at 150°C for 8h within a N₂ atmosphere in negative ion mode (doped with NaI). Full spectra and zoom on one unit (respectively **a** and **b**), with the obtained experimental data in black and the simulated spectra in blue. The entries under the yellow and green squares are the result of the coaddition of the structures (**e**) ● + ○ and ■ + □ respectively; **c**: general structure assigned to the spectra; **d**: Table containing the experimental and theoretical m/z values as well as the $\Delta m/z$ values for the assigned structures, each structure appears twice, with and without additional NaI, the values of n_1+n_2 were adapted to have all assigned isotopic patterns on the same graphs; **e**: End-groups R and R' of each species found.

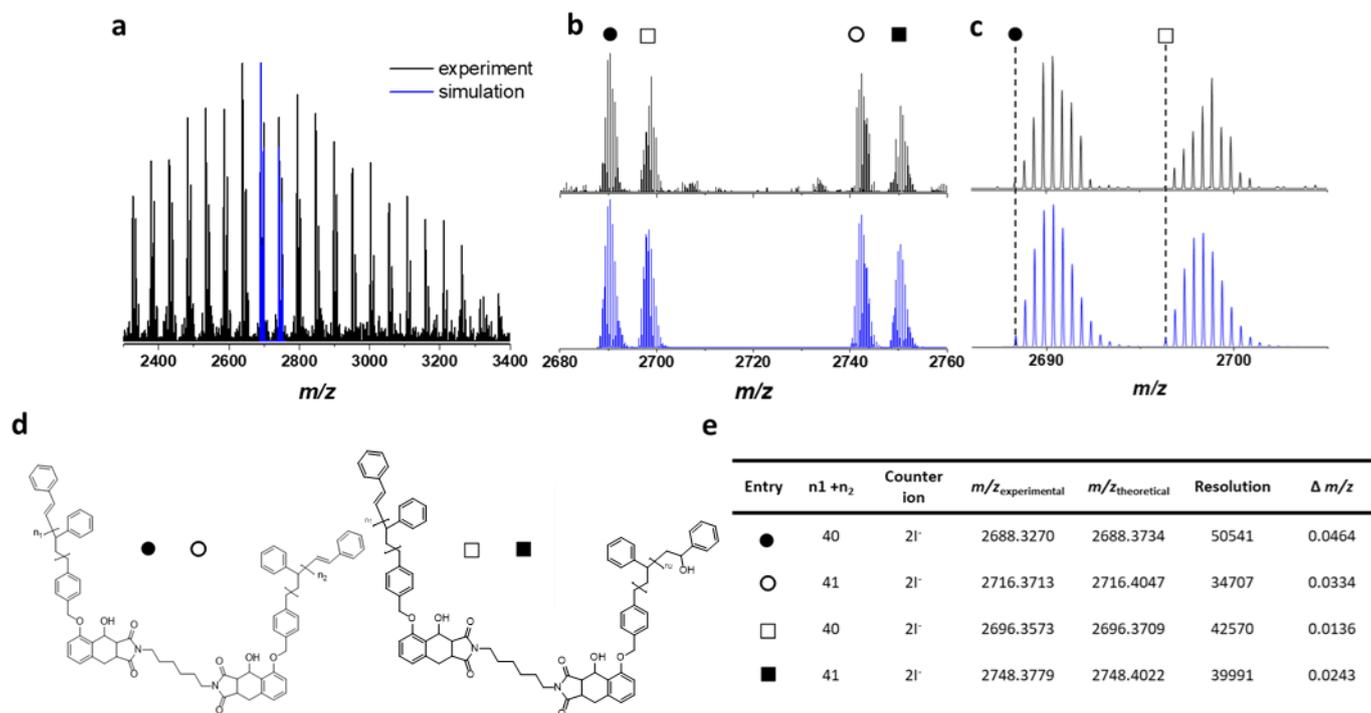


Figure S18 SEC-ESI-MS spectra of **6b** after degradation at 150°C for 8h within a N₂ atmosphere in negative ion mode (doped with NaI). Full spectra, zoom on two repeat units and zoom on one unit (respectively **a**, **b** and **c**) with the experimental data obtained in black and the simulated spectra in blue. **d**: Structures assigned to the spectra; **e**: Table containing the experimental and theoretical m/z values as well as the $\Delta m/z$ values for the assigned structures.

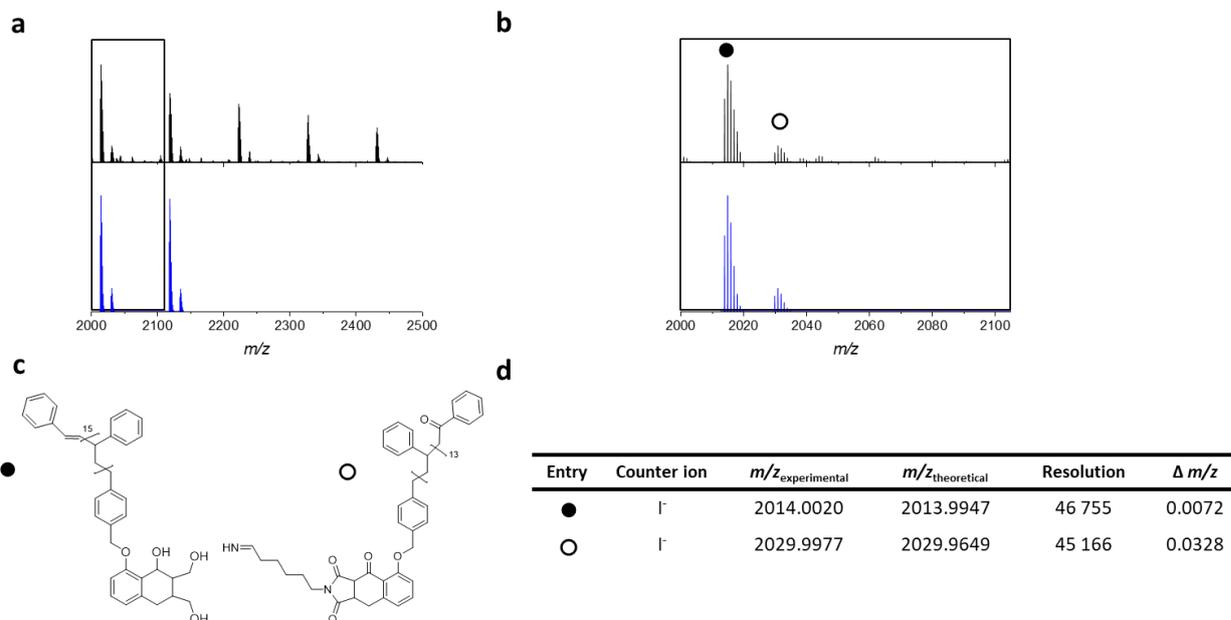


Figure S19 SEC-ESI-MS spectra of **6b** after thermal impact at 180°C for 8h under N₂ atmosphere in negative ion mode (doped with NaI). Full spectra and zoom on one unit (respectively **a** and **b**) with the obtained experimental data in black and the simulated spectra in blue; **c**: Structures assigned to the spectra; **d**: Table containing the experimental and theoretical m/z values as well as the $\Delta m/z$ values for the assigned structures.

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