

## Supporting Information

### **Dual Gated Chain-Shattering Based on Light Responsive Benzophenones and Thermally Reversible Diels-Alder Linkages**

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## Materials

All solvents for synthesis were obtained from Sigma-Aldrich, Acros Organics or Fischer and used without further purification. The benzophenone-2,4'-dicarboxylic acid monohydrate (TCI, >98%), *trans,trans*-2,4-hexadien-1-ol (Alfa Aesar, 98%),  $\alpha,\alpha'$ -dibromo-*p*-xylene (Sigma Aldrich, 98%), carbon disulfide (VWR, 99.9%), diethyl phosphite (Fluka, >95%), sodium hydride (Sigma Aldrich, 95%) and zinc chloride (Sigma Aldrich, >98%) were used as received. THF (Scharlau, GPC grade), MeOH (Roth, HPLC ultra gradient grade) and NaI (Sigma-Aldrich, 99%) for SEC-ESI MS analysis were used without further treatment.

## Characterization Methods

**Electrospray ionization-Orbitrap mass spectrometry (ESI-Orbitrap MS).** Mass spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the  $m/z$  range 1000-6000 Th using ammonium hexafluorophosphate (Thermo Scientific). All spectra were recorded in the negative mode, using isopropyl alcohol/acetonitrile = 1:1 (v/v) as ESI solvent. The spectra were recorded in a concentration of 0.5 mg·mL<sup>-1</sup>. Prior to the time-dependent irradiation of P1 with light ( $\lambda_{\text{max}} = 365$  nm), the solvent was degassed by purging nitrogen for 15 min. The FT resolution was set to 140000 employing 3 microscans during an acquisition time between 2 and 5 min measuring with a capillary temperature of 320 °C. The aux gas flow was (dimensionless) 0.00, the sheath gas 10.00, and the spare gas 1.00. The flow rate was set to 5  $\mu\text{L}\cdot\text{min}^{-1}$ . The spray voltage was set to 4.6 kV and kept constant throughout the irradiation study.

**Size exclusion chromatography coupled with electrospray ionization mass spectrometry (SEC-ESI MS).** Spectra were recorded on a LTQ Orbitrap XL Q Exactive mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the  $m/z$  range 74-1822 using premixed calibration solutions (Thermo Scientific). A constant spray voltage of 4.6 kV, a dimensionless sheath gas of 8, and a dimensionless auxiliary gas flow rate of 2 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 62.0, respectively. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), autosampler (WPS 3000TSL), and a thermostated column department (TCC 3000SD). Separation was performed on two mixed bed size exclusion chromatography columns (Polymer Laboratories, Mesopore 250  $\times$  4.6 mm, particle diameter 3  $\mu\text{m}$ ) with precolumn (Mesopore 50  $\times$  4.6 mm) operating at 30 °C. THF at a flow rate of 0.30 mL·min<sup>-1</sup> was used as eluent. The mass spectrometer was coupled to the column in parallel to a RI-detector (RefractoMax520, ERC, Japan) in

a setup described earlier.<sup>1</sup> 0.27 mL·min<sup>-1</sup> of the eluent were directed through the RI-detector and 30 µL·min<sup>-1</sup> infused into the electrospray source after postcolumn addition of a 100 µM solution of sodium iodide in methanol at 20 µL·min<sup>-1</sup> by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 50 µL aliquot of a polymer solution with a concentration of 2 mg·mL<sup>-1</sup> was injected onto the HPLC system.

**Size exclusion chromatography (SEC).** Size exclusion chromatography (SEC) measurements were performed on a Polymer Laboratories PLGPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 µm bead-size guard column (50×7.5 mm) followed by three PLgel 5 µm MixedC columns (300×7.5 mm) and a differential refractive index detector using *N,N*-dimethylacetamide (DMAc) containing 0.03 wt% LiBr as eluent at 50 °C with a flow rate of 1.0 mL min<sup>-1</sup>. The SEC system was calibrated against linear poly(styrene) standards with molecular weights ranging from 700 to 2·10<sup>6</sup> g mol<sup>-1</sup>.

**Nuclear magnetic resonance (NMR) spectroscopy.** Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded on a Bruker AM 400 (400 MHz) spectrometer. The chemical shifts are expressed in parts per million (ppm) and calibrated on characteristic solvent signals as internal standards. All coupling constants are absolute values and *J* values are expressed in Hertz (Hz). The description of signals include: s = singlet, bs = broad singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet. The carbon nuclear magnetic resonance (<sup>13</sup>C{<sup>1</sup>H} NMR) spectra were recorded on a Bruker AM 400 (100 MHz) spectrometer.

**UV-visible spectroscopy (UV-vis).** UV-visible spectroscopy was performed using a Cary 300 Bio spectrophotometer (Varian) featuring a thermostated (298 K) sample cell holder. Absorption spectra of the samples were recorded with a resolution of 1 nm and a slit width of 2 nm in a quartz glass cuvette (VWR, quartz glass, SUPRASIL®). Polymer P1 was dissolved in DMSO in a concentration of 5·10<sup>-3</sup> mol·L<sup>-1</sup>.

## Experimental Part

**(2E,4E)-hexa-2,4-dienyl 2-(4-((((2E,4E)-hexa-2,4-dienyl)oxy)carbonyl)benzoyl)benzoate (M1).** To a stirred solution of 500 mg benzophenone-2,4'-dicarboxylic acid monohydrate (1.74 mmol, 1.00 eq) (protected from ambient light) in 1.2 mL anhydrous DMF (1.5 M), 106.0 mg DMAP (0.867 mmol, 0.50 eq) and 426 mg sorbin alcohol (4.34 mmol, 2.50 eq) are added. 831 mg EDC·HCl (4.33 mmol, 2.50 eq) is added to the reaction mixture at 0 °C, which is then stirred for 5 min at 0 °C and 48 h at ambient temperature. The mixture was subsequently diluted with 200 mL dichloromethane, washed twice with water and once with brine solution. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated at reduced pressure. The product was obtained as colorless oil (322 mg, 0.746 mmol, 43%) after flash chromatography using cyclohexane:ethyl acetate = 10:1 as eluent.

R<sub>f</sub> = 0.54 (cyclohexane:ethyl acetate = 2:1)

<sup>1</sup>H NMR (400 MHz, 298 K, DMSO-d<sub>6</sub>): δ = 8.05 (m, 3H), 7.88 – 7.64 (m, 4H), 7.54 (dd, <sup>3</sup>J = 7.5 Hz, <sup>4</sup>J = 0.9 Hz, 1H), 6.38 (m, 1H), 6.17 – 6.01 (m, 2H), 5.96 – 5.59 (m, 4H), 5.41 – 5.26 (m, 1H), 4.83 (d, <sup>3</sup>J = 6.4 Hz, 2H), 4.50 (d, <sup>3</sup>J = 6.4 Hz, 2H), 1.71 (m, 6H).

<sup>13</sup>C NMR (101 MHz, 298 K, DMSO-d<sub>6</sub>) δ = 195.55 (C), 165.00 (C), 164.76 (C), 140.54 (C), 140.08 (C), 134.64 (CH), 134.57 (CH), 133.34 (CH), 133.16 (CH), 131.08 (CH), 130.97 (CH), 130.48 (CH), 130.42 (CH), 130.34 (CH), 129.82 (CH), 129.57 (CH), 129.08 (CH), 128.55 (CH), 127.86 (CH), 123.84 (CH), 122.98 (CH), 65.45 (CH<sub>2</sub>), 65.39 (CH<sub>2</sub>), 17.90 (CH<sub>3</sub>), 17.84 (CH<sub>3</sub>).

HR ESI MS: [M<sub>2</sub>+Na]: *m/z* 453.1669 (*m/z*(theo) 453.1672)

**1,4-phenylenebis(methylene) bis((diethoxyphosphoryl)methanedithioformate) (M2):** The synthesis was adapted from the literature.<sup>2</sup>

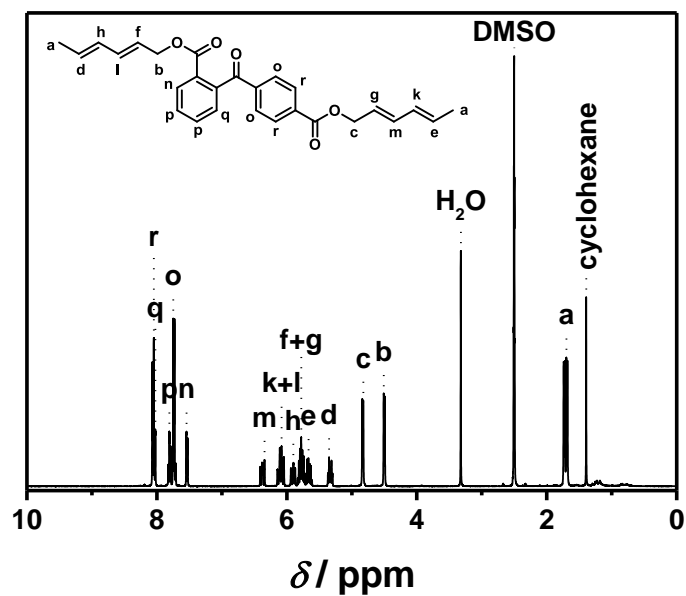
**Hetero Diels-Alder step-growth polymerization to yield polymer P1.** 100 mg (2E,4E)-hexa-2,4-dienyl 2-(4-((((2E,4E)-hexa-2,4-dienyl)oxy)carbonyl)benzoyl)benzoate (M1) (0.232 mmol, 1.00 eq), 123.2 mg 1,4-phenylenebis(methylene) bis((diethoxyphosphoryl)methanedithioformate) (M2) (0.232 mmol, 1.00 eq) and 34.8 mg ZnCl<sub>2</sub> (0.256 mmol, 1.10 eq) were stirred in 780 μL ethyl acetate at 50 °C. After 24 h, the solids were filtered, washed with cold ethyl acetate and dried under a high vacuum. P1 was obtained as pale brown solid (quantitative yield).

**Light-Triggered Degradation of P1:** 10 mg P1 (*M<sub>w</sub>* = 14 kDa; *M<sub>n</sub>* = 7 kDa; *Đ* = 2.0) was dissolved in 5 mL isopropyl alcohol:acetonitrile = 1:1 (v/v) in a concentration of 2 mg·mL<sup>-1</sup> and portioned equally to 5 sealed vials. The solution was degassed by purging with nitrogen for 15 min and subsequently irradiated using a Philips Cleo Cleo Compact PL-L (36 Watt, λ<sub>max</sub> = 350 nm) in a self-made photo reactor.

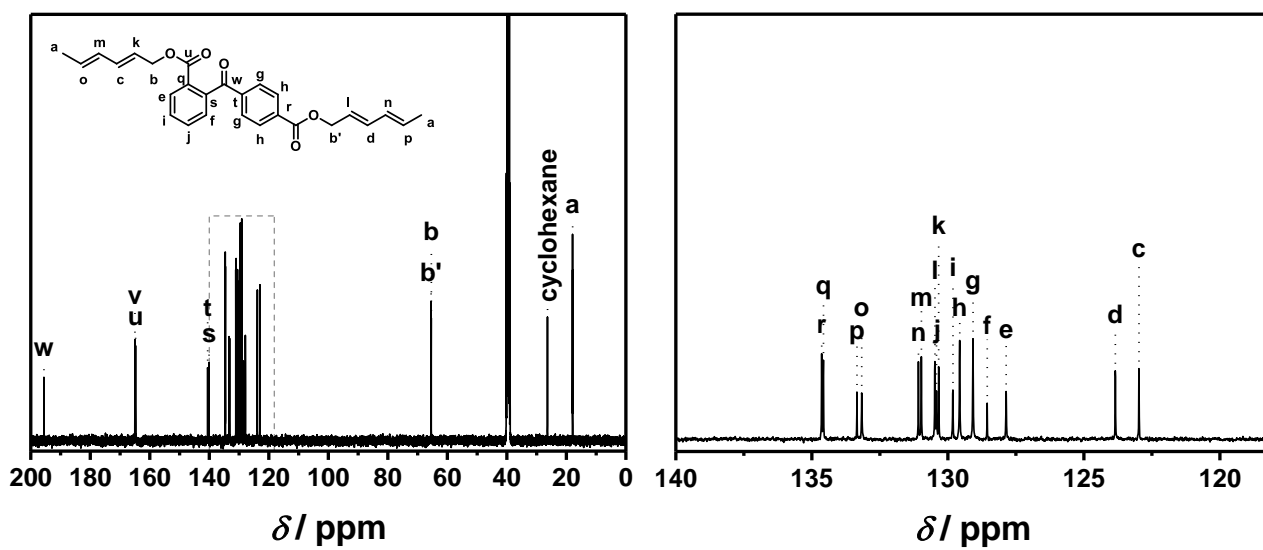
After 1, 2, 3, 4 and 24 h, respectively, an aliquot was taken, and the solvent was removed under reduced pressure prior analytical characterization.

**Thermally-Triggered Degradation of P1:** 20 mg P1 ( $M_w = 14$  kDa;  $M_n = 7$  kDa;  $\bar{D} = 2.0$ ) was placed in a pressure tube and dissolved in 0.5 mL acetonitrile. The red color indicates the formation of the thiocarbonyl group (Figure S10). After 40 min, the reaction was rapidly cooled in liquid nitrogen to prevent potential Diels-Alder reactions.

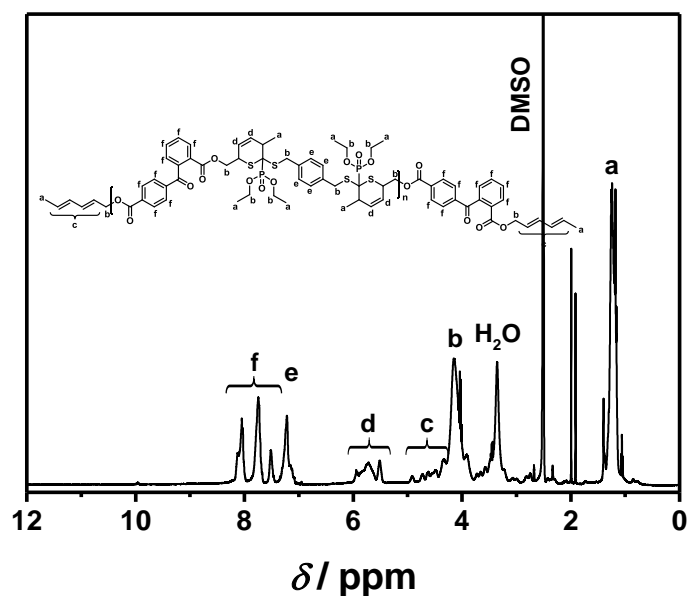
## NMR data



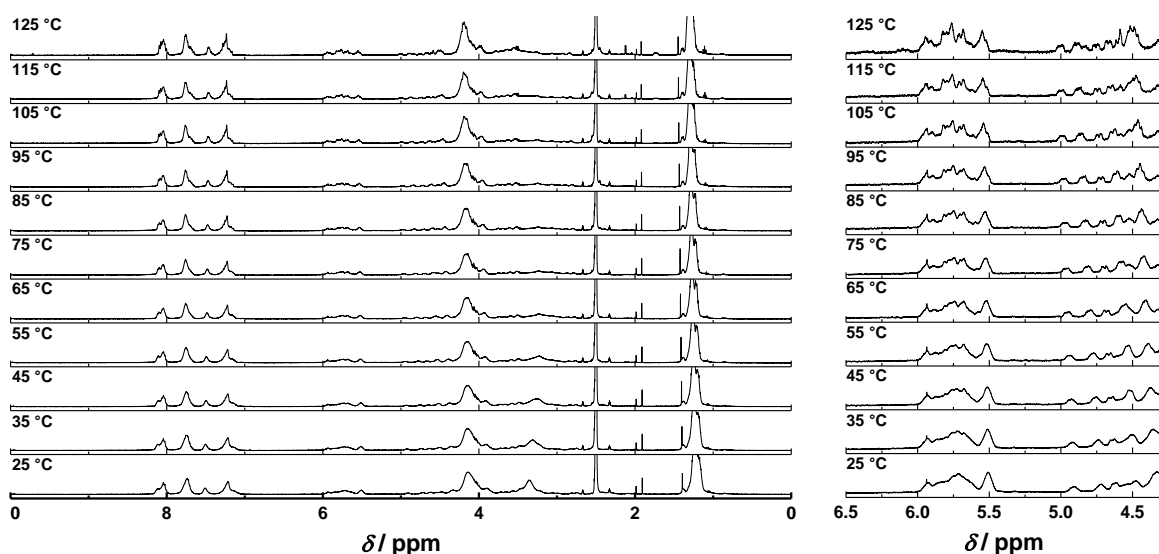
**Figure S1**  $^1\text{H}$  NMR (400 MHz, 298 K) spectrum of monomer (M1) in  $\text{DMSO-d}_6$ .



**Figure S2**  $^{13}\text{C}$  NMR (101 MHz, 298 K) spectrum of monomer (M1) in  $\text{DMSO-d}_6$ .



**Figure S3**  $^1\text{H}$  NMR (400 MHz, 298 K) spectrum of polymer (P1) in  $\text{DMSO-d}_6$ . All potential isomers are not depicted and assigned.



**Figure S4** Overview spectra of the online HT NMR (400 MHz,  $\text{DMSO-d}_6$ ) experiment of P1 in a temperature range between 298 and 398 K, respectively.

### Debonding percentage

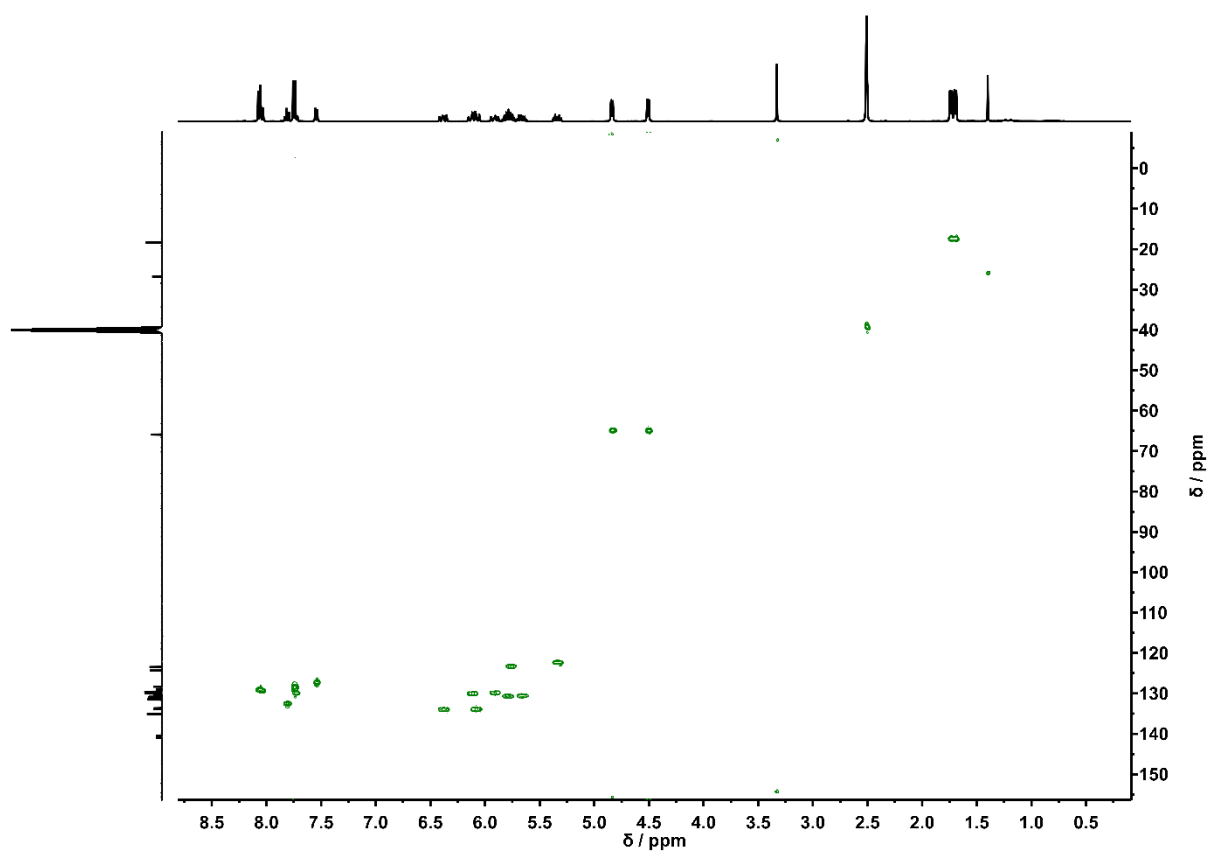
The percentage of debonding was calculated as follows: The aromatic region (6.945 – 8.303 ppm) was normalized to 12 H; the olefin region (4.400 – 6.500 ppm) was integrated with constant set borders. For 0% debonding: the thiopyrane ring is represented by 4 H, whereas the free diene resonance integrals is 0 H. Thus:

$$\begin{aligned}
 0\%: 4 &= (4H - 4 \cdot XH) + 12 \cdot XH \\
 &\rightarrow 4 = 4H + 8 \cdot XH \\
 &\rightarrow \frac{4}{4H} = 1 + 2X
 \end{aligned}$$

During the polymerization reaction, not 100% of all dienes have been consumed and for 25 °C:

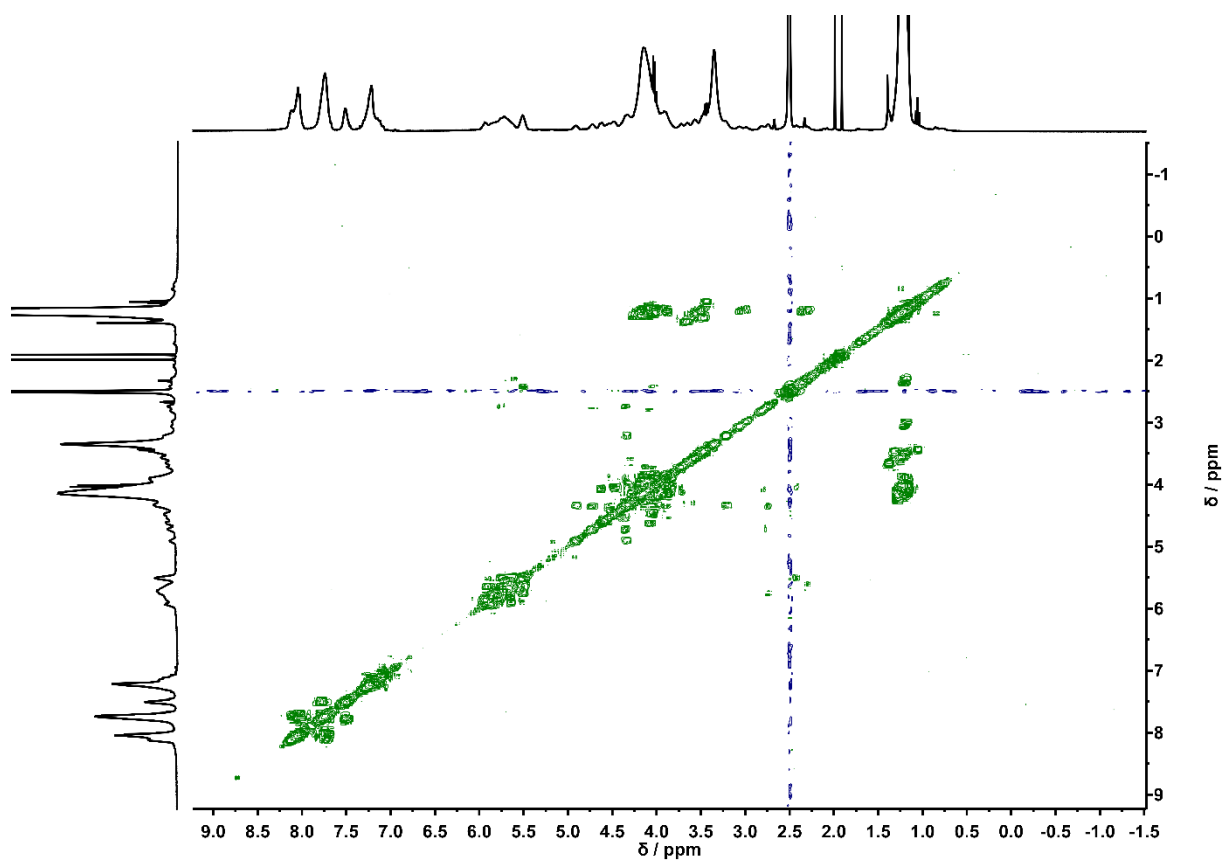
$$25\text{ }^{\circ}\text{C}: \frac{5.87}{4H} = 1 + 2X$$

$$\rightarrow X = 0.23$$

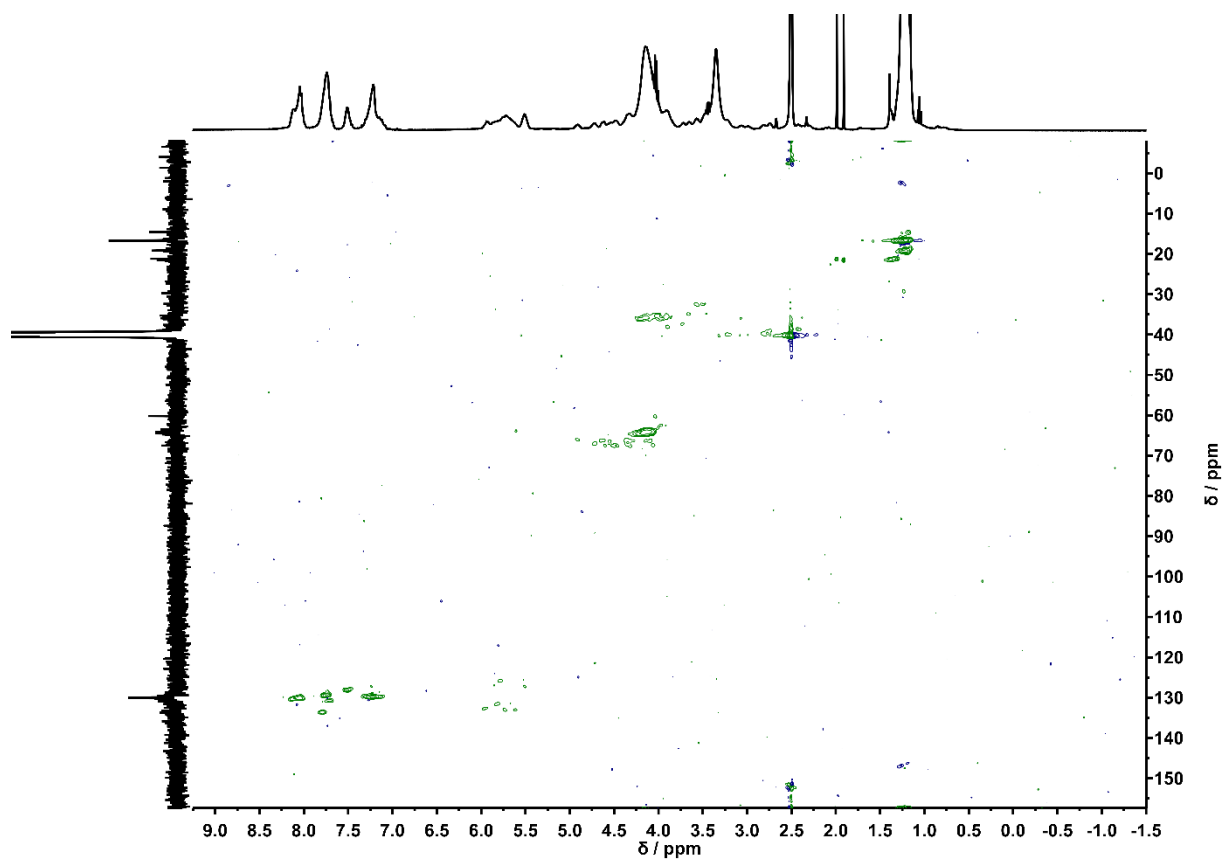


**Figure S5**  $^1\text{H}$ - $^{13}\text{C}$  HSQC (298 K) spectrum of M1 in DMSO- $\text{d}_6$ .



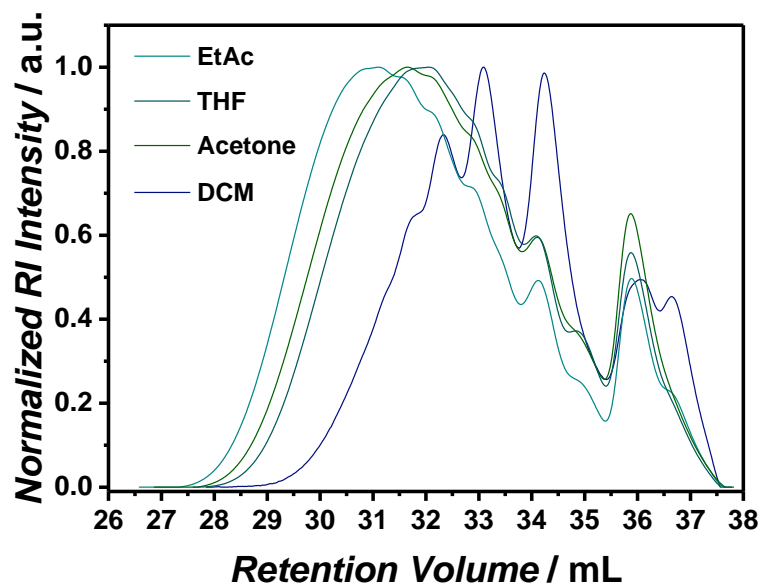


**Figure S6**  $^1\text{H}$ - $^1\text{H}$  COSY (298 K) spectrum of P1 in  $\text{DMSO-d}_6$ .



**Figure S7**  $^1\text{H}$ - $^{13}\text{C}$  HSQC (298 K) spectrum of P1 in  $\text{DMSO-d}_6$ .

## Miscellaneous SEC Data

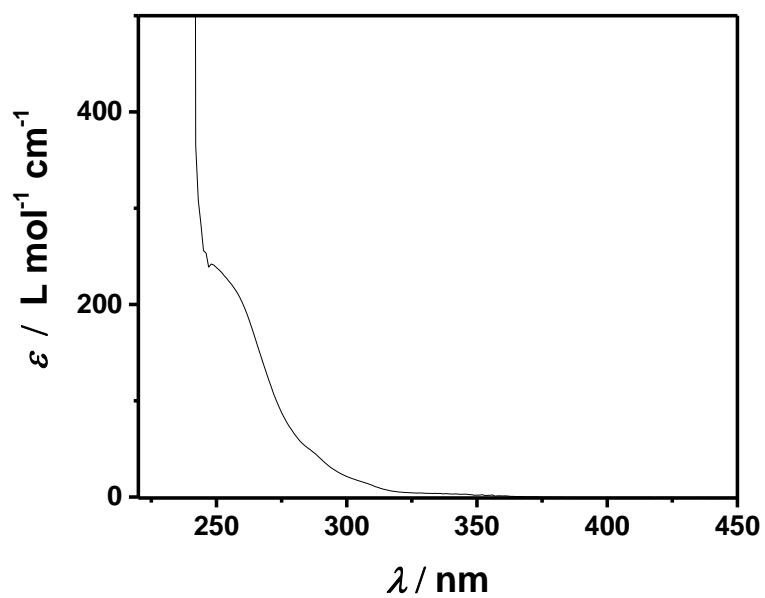


**Figure S8** SEC traces for P1 after 8 h polymerization in ethyl acetate (EtAc) (bright cyan), THF (dark cyan), acetone (green) and dichloromethane (DCM) (blue). Conditions: THF SEC performing at 30 °C and a flow rate of 1 mL·min<sup>-1</sup>.

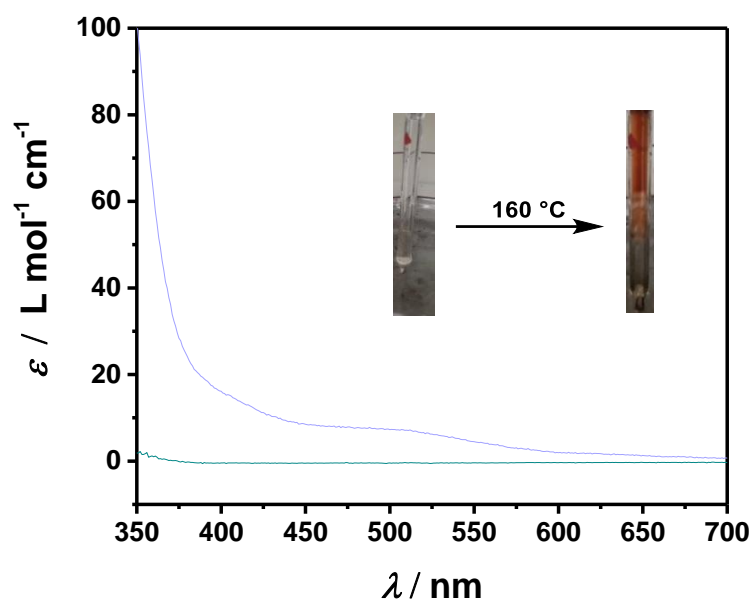
**Table S1** Polymer characterization ( $M_n$ ,  $M_w$  and  $\mathcal{D}$ ) obtained from SEC measurements (conditions: THF SEC conducted at 30 °C and a flow rate of 1 mL·min<sup>-1</sup>) in different solvents. Calibration was relative to poly(styrene) standards.

| Solvent | $M_n / \text{g} \cdot \text{mol}^{-1}$ | $M_w / \text{g} \cdot \text{mol}^{-1}$ | $\mathcal{D}$ |
|---------|--|--|---------------|
| EtAc    | 2500                                   | 5600                                   | 2.19          |
| THF     | 2200                                   | 4300                                   | 1.95          |
| Acetone | 2200                                   | 4600                                   | 2.09          |
| DCM     | 1500                                   | 2800                                   | 1.82          |

## UV/Visible Measurement

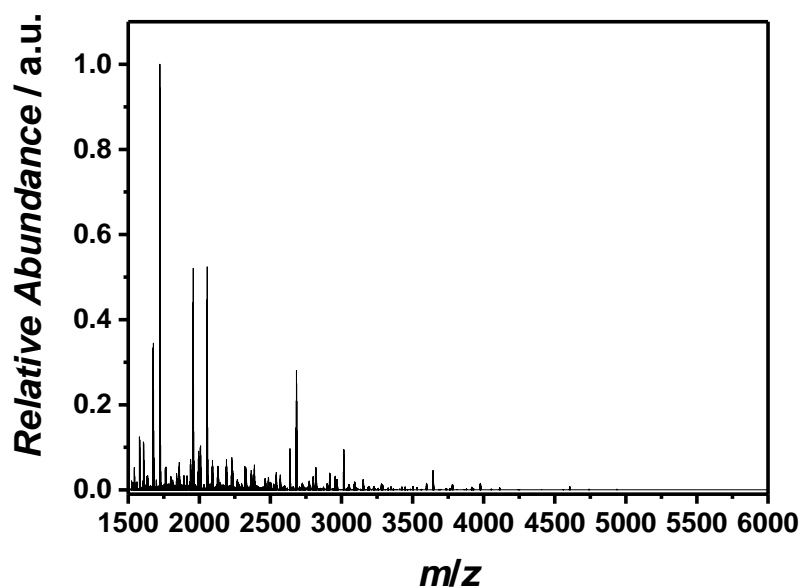


**Figure S9** UV/visible measurement of P1 in DMSO (298 K) at a concentration of  $5 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ .

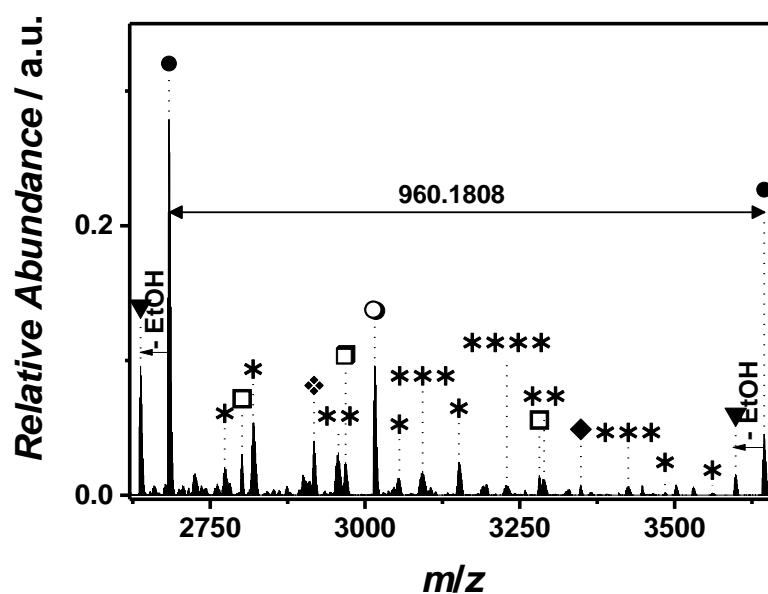


**Figure S10** UV/visible measurement of P1 in acetonitrile (298 K) before (cyan line) and after temperature increase to 160 °C for 40 min (light purple line).

## MS Data

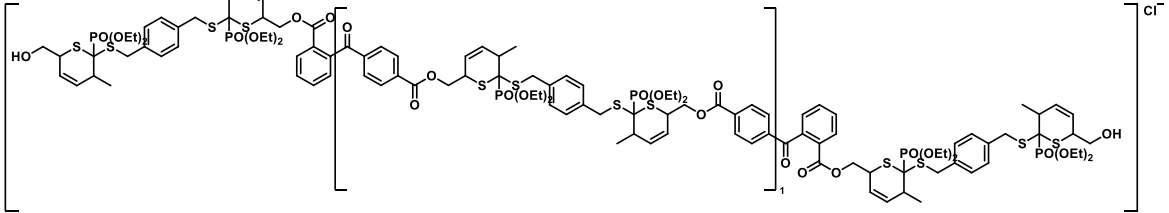
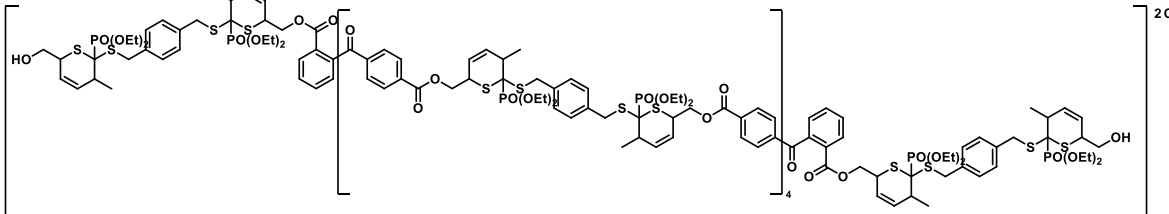
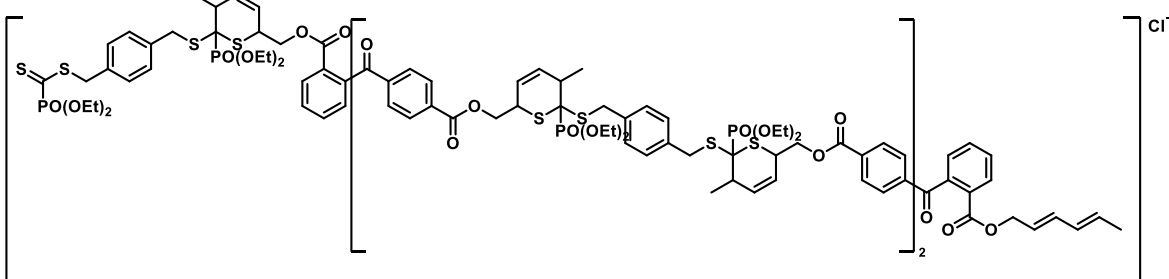


**Figure S11** ESI-Orbitrap mass spectrum of P1 ( $M_n = 2200 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w = 5600 \text{ g}\cdot\text{mol}^{-1}$ ,  $\bar{D} = 2.19$ ) recorded in negative ion mode in DCM:MeOH = 3:1 (v/v) from  $m/z$  1500 to  $m/z$  6000.

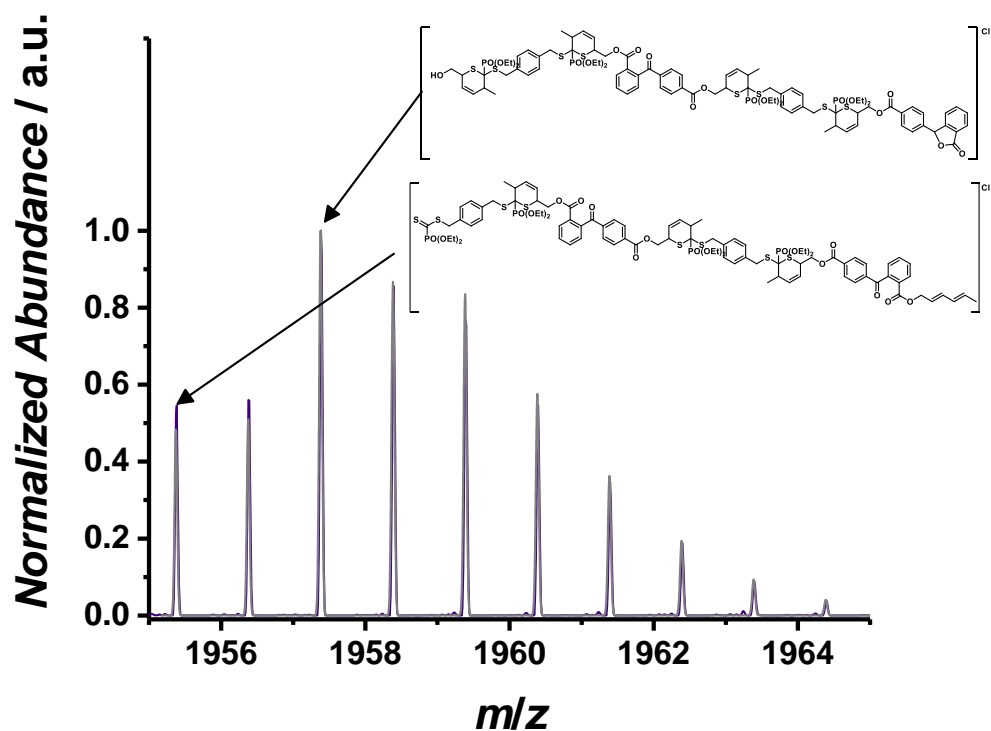


**Figure S12** Zoomed ESI-Orbitrap mass spectrum of P1 ( $M_n = 2200 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w = 5600 \text{ g}\cdot\text{mol}^{-1}$ ,  $\mathcal{D} = 2.19$ ) displayed in a range between  $m/z$  2620 to  $m/z$  3660 depicting the repeating unit ( $m/z(\text{exp})$  960.1808;  $m/z(\text{theo})$  960.2024). Labeled are the most abundant species. Species labeled with \* stem from (multiple) attachment of  $\text{ZnCl}_2$ .

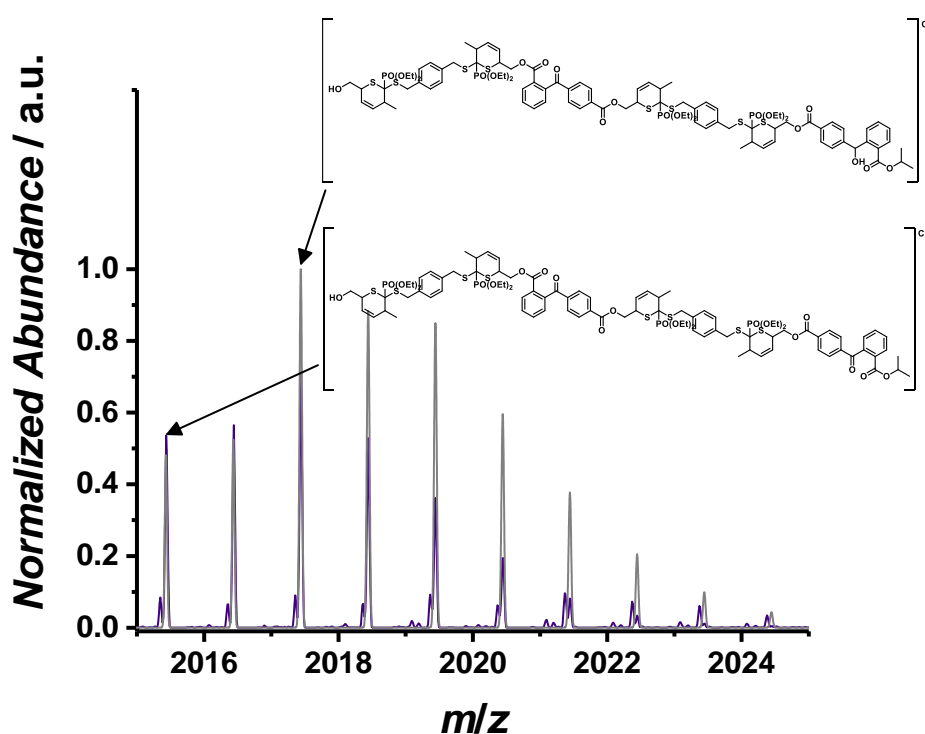
**Table S2** Peak assignment of the SEC-ESI Orbitrap mass spectrum of P1 showing the labels (corresponding to the species in **Figure S9**), the resolution (obtained by the Xcalibur software), the experimental  $m/z$  and theoretical  $m/z$  values,  $\Delta m/z$  and the proposed chemical structures. Minor species stemming from (multiple) attachment of  $\text{ZnCl}_2$  or by elimination of  $\text{EtOH}$  are not depicted.

| Label | Resolution | $m/z(\text{exp})$ | $m/z(\text{theo})$ | $\Delta m/z$ | Structure   |
|-------|------------|-------------------|--------------------|--------------|---|
| ●     | 40000      | 2681.5327         | 2681.5450          | 0.0122       |   |
| □     | 37000      | 2798.5490         | 2798.5608          | 0.0118       |   |
| ❖     | 40000      | 2915.5644         | 2915.5767          | 0.0123       |  |

|   |       |           |           |        |  |
|---|-------|-----------|-----------|--------|--|
| □ | 38000 | 2964.6035 | 2964.6132 | 0.0097 |  |
| ○ | 38000 | 3013.6313 | 3013.6498 | 0.0185 |  |
| ◆ | 35000 | 3345.7293 | 3345.7574 | 0.0254 |  |



**Figure S13** Isotopic simulation of a selected degradation species at  $m/z$  1955 comparing the experiment (purple line) and the simulation (grey line) of degraded P1. The ion abundance of the lactone at  $m/z$  1957 indicates the successful degradation.

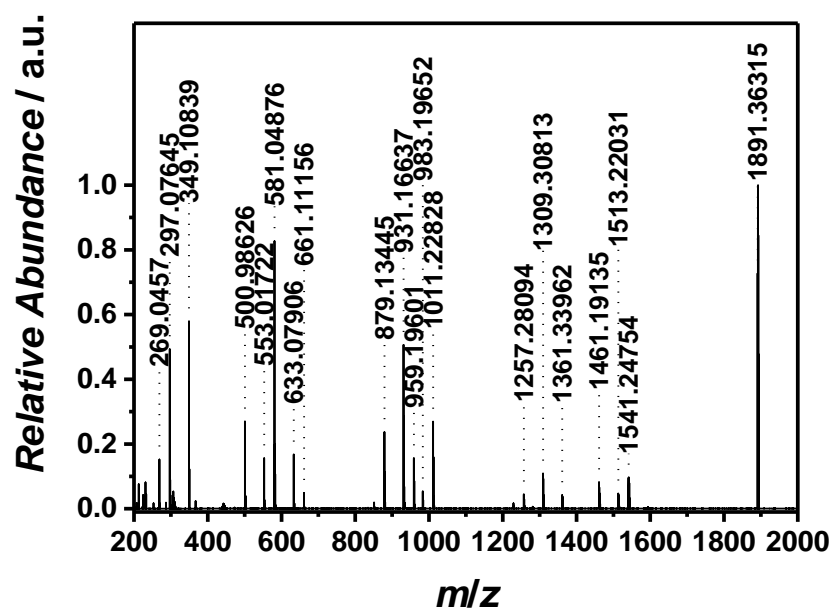


**Figure S14** Isotopic simulation of a selected degradation species at  $m/z$  2015 comparing the experiment (purple line) and the simulation (grey line) of degraded P1. Since  $\text{ZnCl}_2$  coordinates strongly to P1, the slightly shifted low abundant peaks stem from polymer/ $\text{ZnCl}_2$  complexes and are not assigned.





# Tandem MS experiments on P1



**Figure S16** ESI MS/MS (tandem MS in negative ion mode) of P1 isolating a species at 1955  $m/z$  with a higher-energy collision dissociation (HCD) of 14 eV in the relevant range from 200  $m/z$  and 2000  $m/z$ .

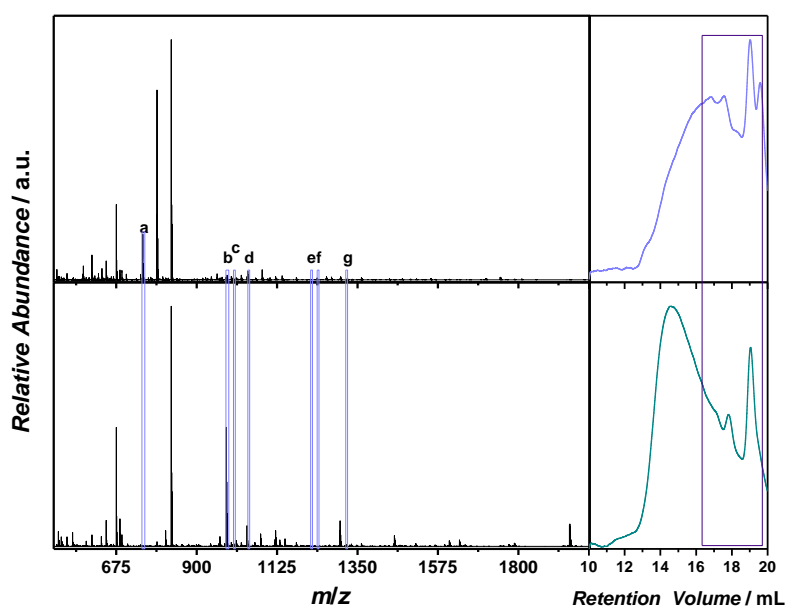
**Table S3** Peak assignment of ESI MS/MS experiment of P1 at 1955  $m/z$  with a higher-energy collision dissociation (HCD) of 14 eV showing the experimental  $m/z$ , the theoretical  $m/z$  values, and  $\Delta m/z$  and the proposed structure.

| $m/z(\text{exp})$ | $m/z(\text{theo})$ | $\Delta m/z$ | Structure |
|-------------------|--------------------|--------------|-----------|
| 269.0457          | 269.0455           | 0.0002       |           |
| 297.0765          | 297.0768           | 0.0003       |           |
| 349.1084          | 349.1081           | 0.0003       |           |
| 500.9863          | 500.9858           | 0.0005       |           |
| 553.0172          | 553.0171           | 0.0001       |           |
| 581.0488          | 581.0484           | 0.0004       |           |

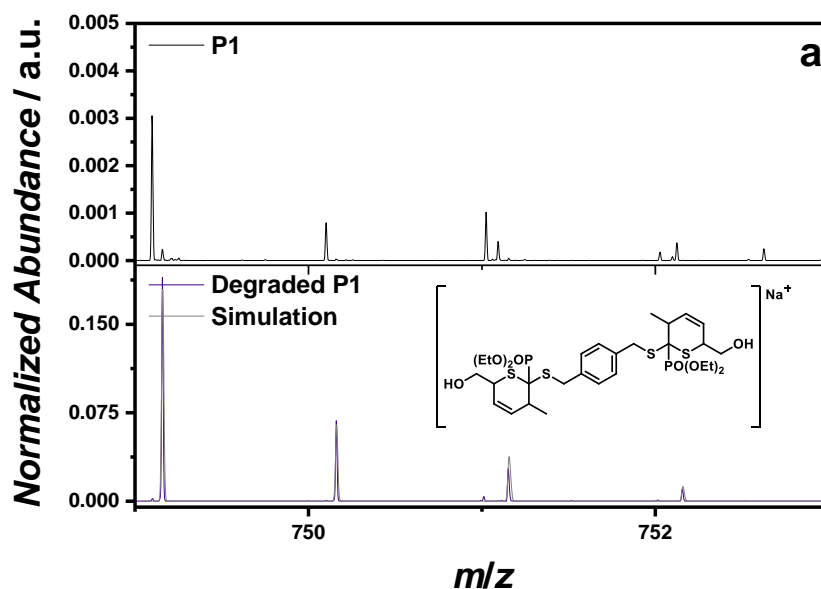
|           |           |        |  |
|-----------|-----------|--------|--|
| 633.0791  | 633.0797  | 0.0006 |  |
| 661.1116  | 661.1110  | 0.0006 |  |
| 879.1345  | 879.1325  | 0.0020 |  |
| 931.1664  | 931.1638  | 0.0026 |  |
| 959.1960  | 959.1951  | 0.0009 |  |
| 983.1965  | 983.1951  | 0.0014 |  |
| 1011.2283 | 1011.2264 | 0.0019 |  |
| 1257.2809 | 1257.2793 | 0.0016 |  |
| 1309.3081 | 1309.3106 | 0.0025 |  |
| 1361.3396 | 1361.3419 | 0.0023 |  |



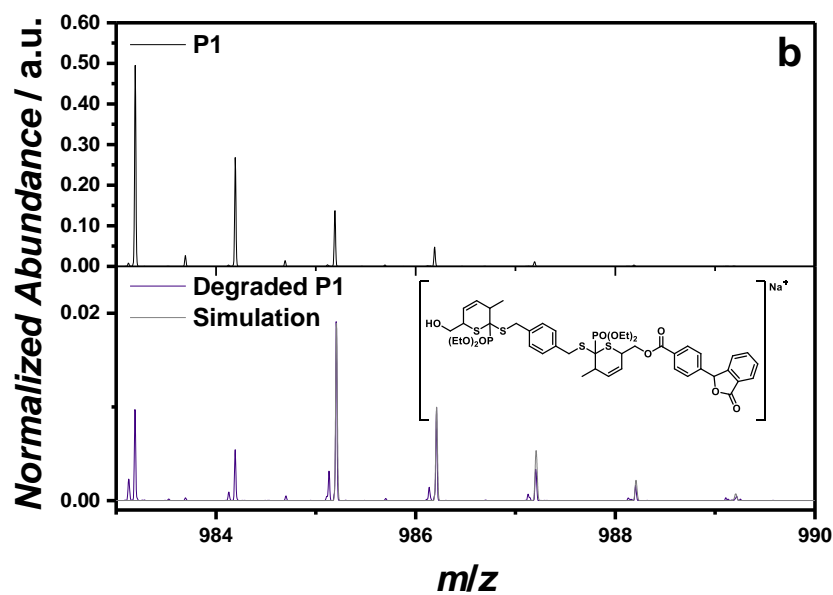
## SEC-ESI MS data of initial P1 and degraded P1



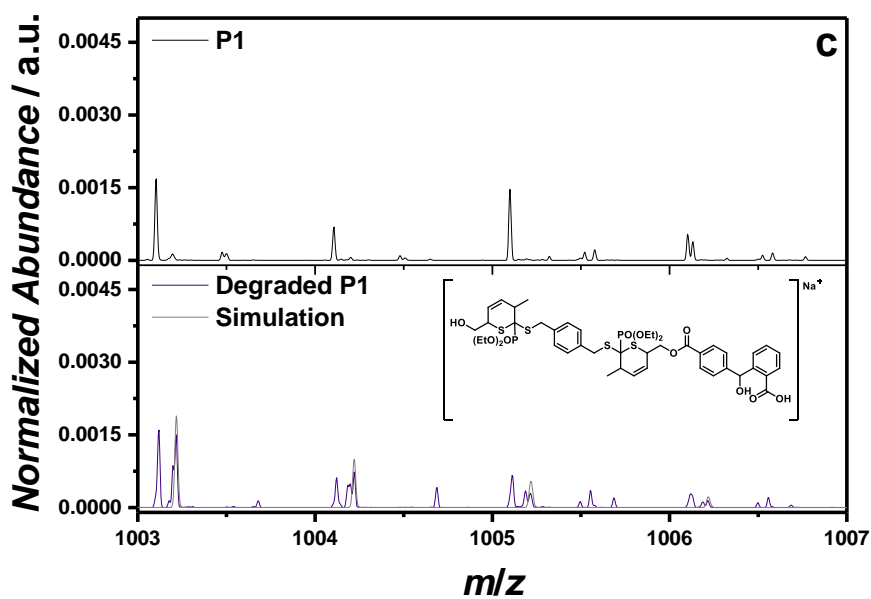
**Figure S17** SEC-ESI Orbitrap mass spectrum (positive mode) of P1 (bottom) and the degraded P1 (top) between  $m/z$  500 and  $m/z$  2000 obtained by summing all species between 16.33 mL and 19.70 mL retention volume. Labeled are the important degradation species (left). SEC traces obtained from the RI detector implemented in the SEC-ESI MS system of P1 (bottom) and the degraded P1 (top).



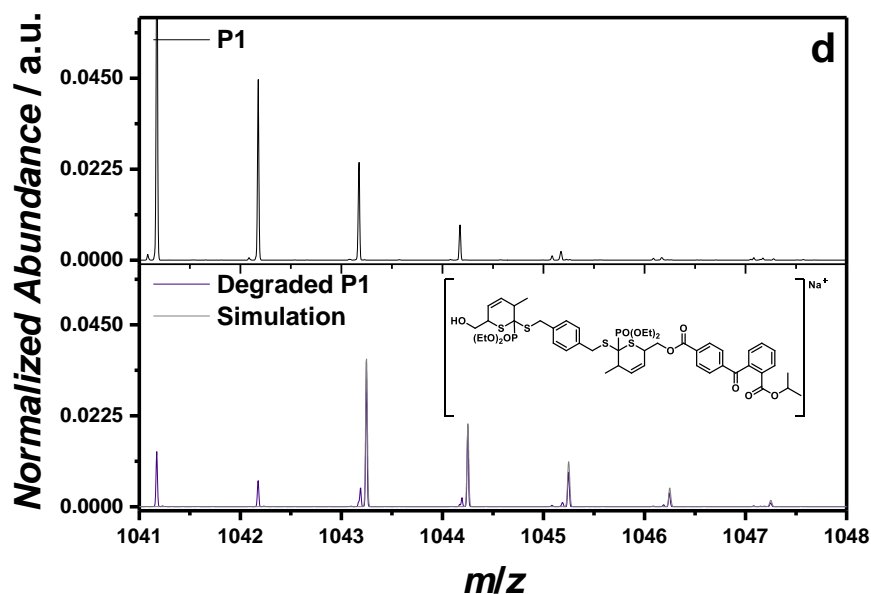
**Figure S18** Isotopic simulation of a selected degradation species at  $m/z$  749 comparing the experiment (purple line) and the simulation (grey line) of degraded P1 (bottom) with the intact polymer P1 (top).



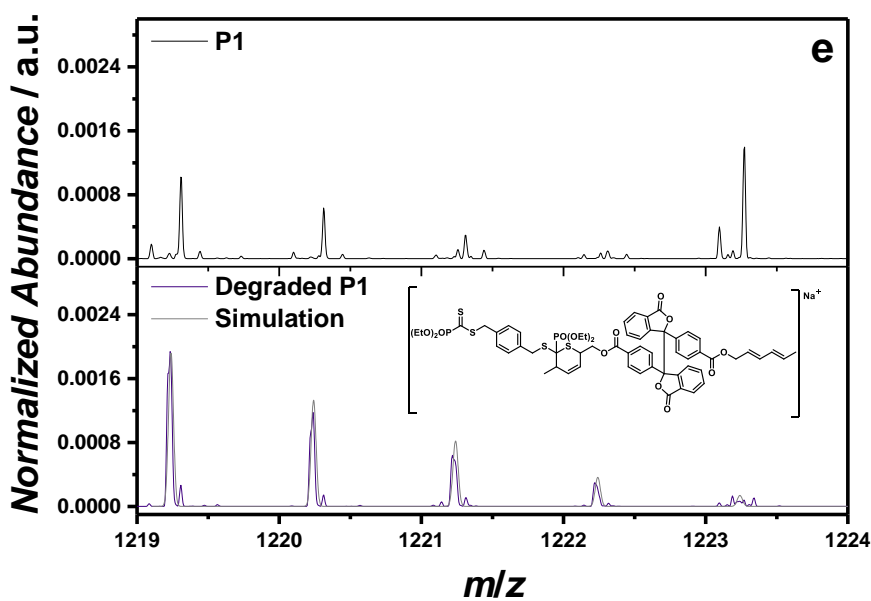
**Figure S19** Isotopic simulation of a selected degradation species at  $m/z$  985 comparing the experiment (purple line) and the simulation (grey line) of degraded P1 (bottom) with the intact polymer P1 (top).



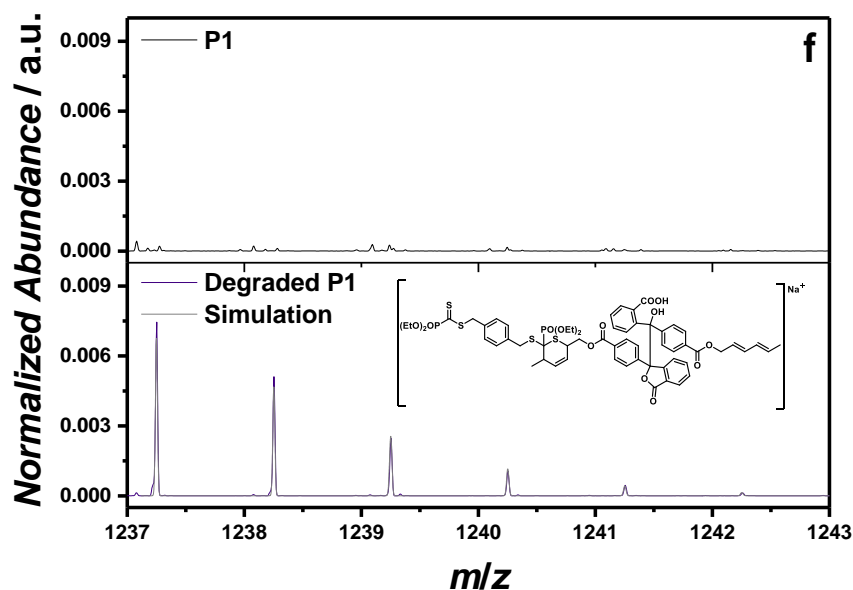
**Figure S20** Isotopic simulation of a selected degradation species at  $m/z$  1003 comparing the experiment (purple line) and the simulation (grey line) of degraded P1 (bottom) with the intact polymer P1 (top).



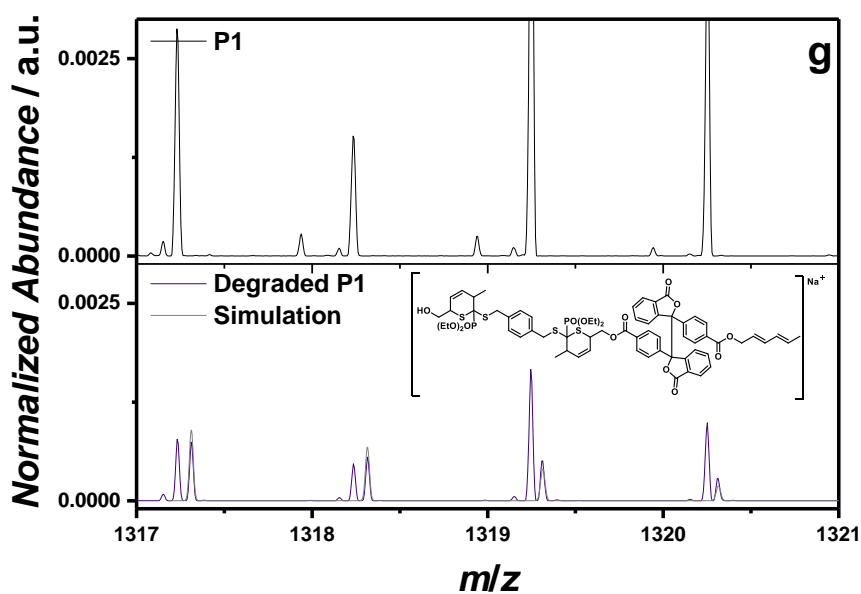
**Figure S21** Isotopic simulation of a selected degradation species at  $m/z$  1043 comparing the experiment (purple line) and the simulation (grey line) of degraded P1 (bottom) with the intact polymer P1 (top).



**Figure S22** Isotopic simulation of a selected degradation species at  $m/z$  1219 comparing the experiment (purple line) and the simulation (grey line) of degraded P1 (bottom) with the intact polymer P1 (top).



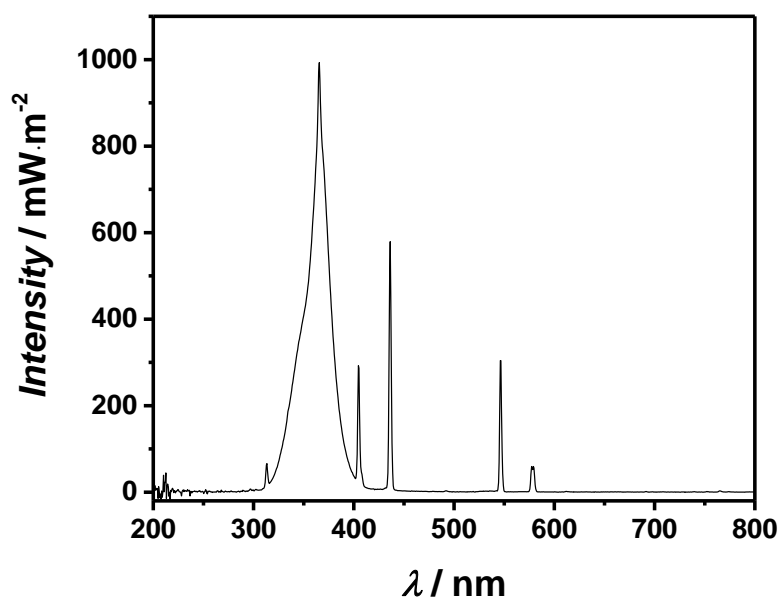
**Figure S23** Isotopic simulation of a selected degradation species at  $m/z$  1237 comparing the experiment (purple line) and the simulation (grey line) of degraded P1 (bottom) with the intact polymer P1 (top).



**Figure S24** Isotopic simulation of a selected degradation species at  $m/z$  1317 comparing the experiment (purple line) and the simulation (grey line) of degraded P1 (bottom) with the intact polymer P1 (top).

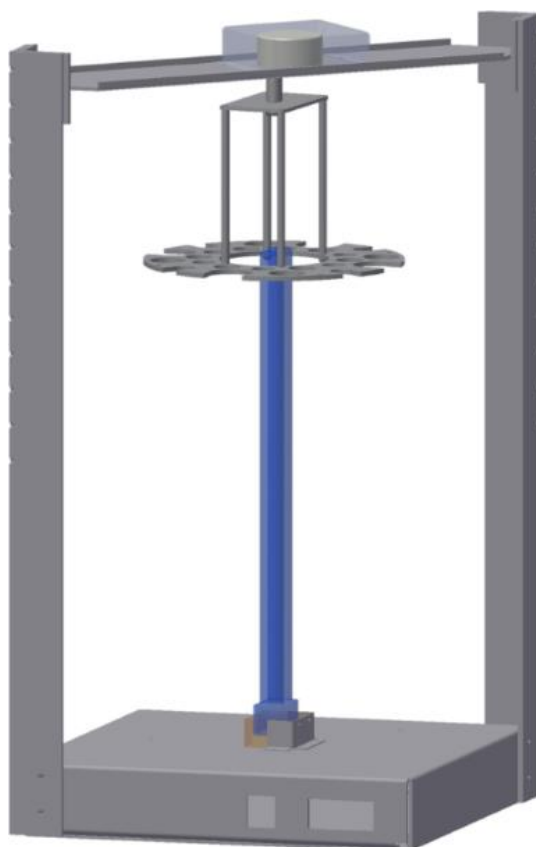
### Set-up for irradiation experiments

The samples to be irradiated were placed on a metallic disc revolving around a compact low-pressure fluorescent lamp (Cleo PL-L, Philips Deutschland GmbH) emitting at 365 nm ( $\pm 50$  nm, 36 W) at a distance of 40-50 mm in a custom built photoreactor (Figure S26).



**Figure S25** Emission spectrum of the employed compact low-pressure fluorescent lamp PL-L (36 W,  $\lambda_{\text{max}} = 365$  nm). The emission spectrum was recorded with a UV sensor (Opsytec Dr. Gröbel GmbH; Ettlingen, Germany).





**Figure S26** Drawing of the custom-built photoreactor employed in the current study. The angular velocity is  $0.5 \text{ rad}\cdot\text{s}^{-1}$ . The samples do not spin while revolving around the light source. The emitted intensity of the applied light sources are sufficient in order to guarantee a sufficient photon penetration of the samples.

## References

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