

Supporting information

Table of contents

Section S1: Methods	3
Section S2: Polymerisation procedure.....	4
Section S3: PTA/OX ROCOP	5
Section S4: Mechanistic hypothesis	14
Section S5: Degradation and weathering.....	15
Section S6: References.....	23

Section S1: Methods

Solvents and reagents were obtained from commercial sources and used as received unless stated otherwise. NMR spectra were recorded by using a Jeol JNM-ECA 400II, Bruker Advance 600 and 700 MHz spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ chemical shifts are referenced to the residual proton resonance of the deuterated solvents.

Oxetane was successively dried over calcium hydride and sodium and stored inside an argon filled glovebox prior to use. $\text{LCr}(\text{Na/K/Rb})\cdot\text{H}_2\text{O}$, $\text{L}'\text{Cr}$ and $\text{KOAc}@18\text{-crown-6}$ were prepared following literature methods.^[1,2] Phthalic thioanhydride was synthesized according to the literature procedure and then purified by recrystallisation from $t\text{BuOMe}$ and under dynamic vacuum at 90°C and was stored inside an argon filled glovebox prior to use.^[3]

Infrared spectra were measured using a Thermo-Nicolet Nexus 670 FTIR spectrometer with DuraSampl IR accessory in total reflection at room temperature. TGA data was measured using a Netzsch TG 209. DSC was measured on a Netzsch 204 F1 "Phoenix". Films were prepared by hot-pressing 500 mg of polymer between two aluminium plates covered with Teflon sheets heated with two LLG hotplates (held in place by a 5 kg weight put on top) at 110°C for 5 minutes followed by hardening at 70°C for 2h. Uniaxial tensile testing was performed on a Wick/Roell Z010 instrument (ZwickRoell GmbH & Co., KG, Germany, 500 N load cell class 0.5, extensimeter multixtens class 0.5), 3 specimens were tested per sample.

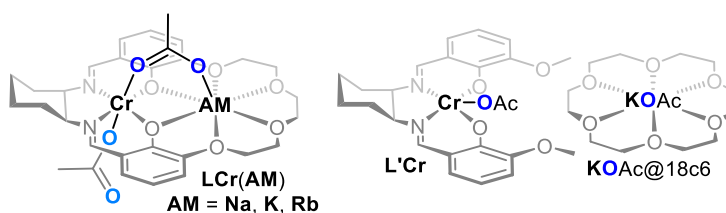
X-ray scattering experiments were performed using by the MOUSE instrument at the Bundesanstalt für Materialforschung und -prüfung (BAM).^[4] X-rays were generated from a microfocused X-ray tube, with a copper target and monochromatized with multi-layered optics to a wavelength of 0.1542 nm ($\text{Cu K}\alpha$). Data were collected using an in-vacuum Eiger 1 M detector (Dectris, Switzerland), which was placed at multiple distances between 57 and 2507 mm from the sample. The samples were mounted free-standing in the X-ray beam. The DAWN software package was used to process the measured data, to absolute intensity, according to standardized procedures also considering the propagation errors.^[5,6] [

The molecular mass and polydispersity of the polymers were determined by a Waters 1515 size exclusion chromatography (SEC) instrument equipped with two linear PLgel columns (Mixed-C) following a guard column and a differential refractive index detector using tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min at 30°C and a series of narrow polystyrene standards for the calibration of the columns. Each polymer sample was dissolved in HPLC-grade THF (6 mg/mL) and filtered through a $0.20\ \mu\text{m}$ porous filter frit prior to analysis.

Section S2: Polymerisation procedure

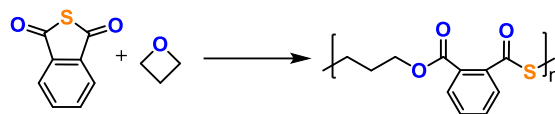
General polymerisation protocol:

The catalyst and the monomers were added to a flame dried vial equipped with a flame dried stirrer bar and sealed with a melamine cap containing a Teflon inlay. The vial was brought outside the glovebox and placed in a pre-heated aluminium block at the specified temperature for the specified time. At the specified end point of the reaction, the polymerisation mixture was cooled down to room temperature and an aliquot was removed and analysed by ^1H NMR for the determination of the conversion. The mixture was solubilized with ca. 5 ml of DCM and then added to 50 mL of MeOH causing the precipitation of the polymer which was isolated by centrifugation and dried in a vacuum oven set to 50 °C for 2 h.



Scheme 1: Catalyst structures.

Section S3: PTA/OX ROCOP



Scheme 2: Synthesis of PTA/OX copolymer.

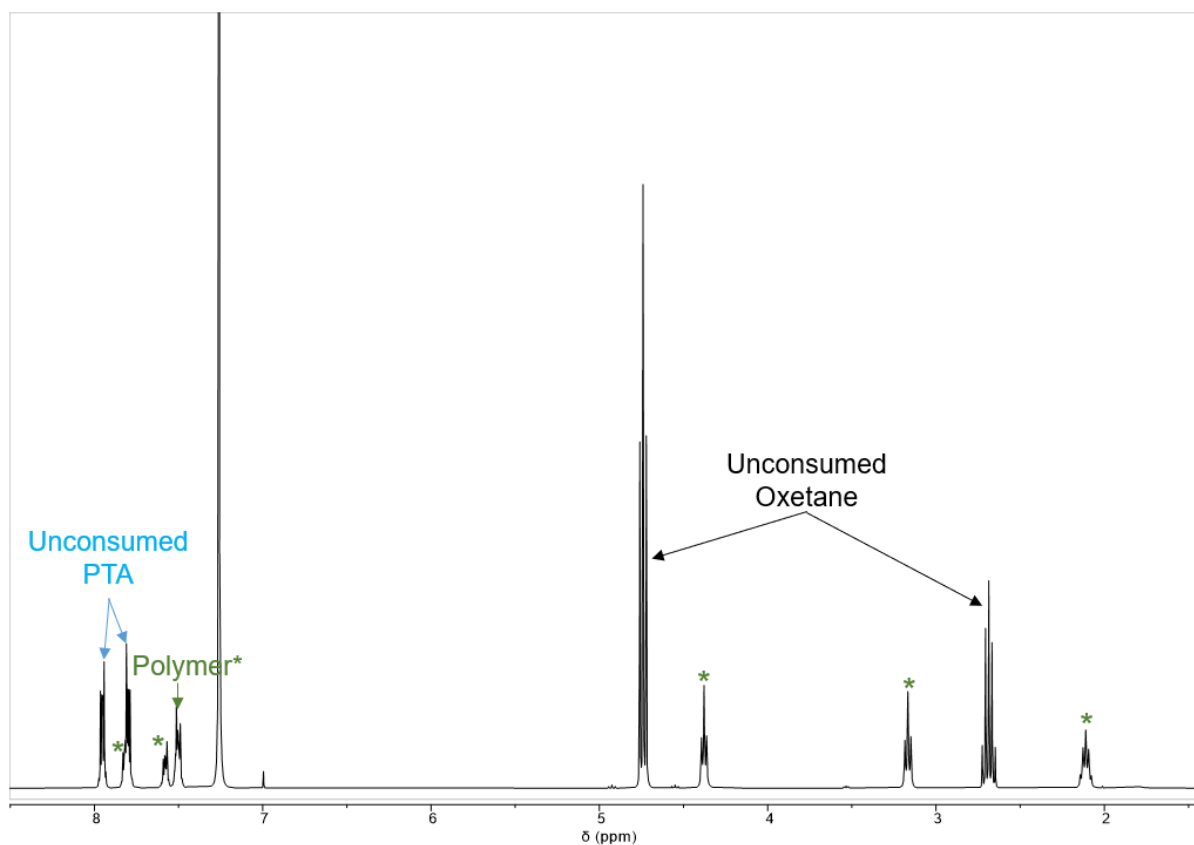


Figure S 1: ¹H NMR spectrum (400 MHz, CDCl₃, 25°C) of crude mixture corresponding to table 1, run #2.

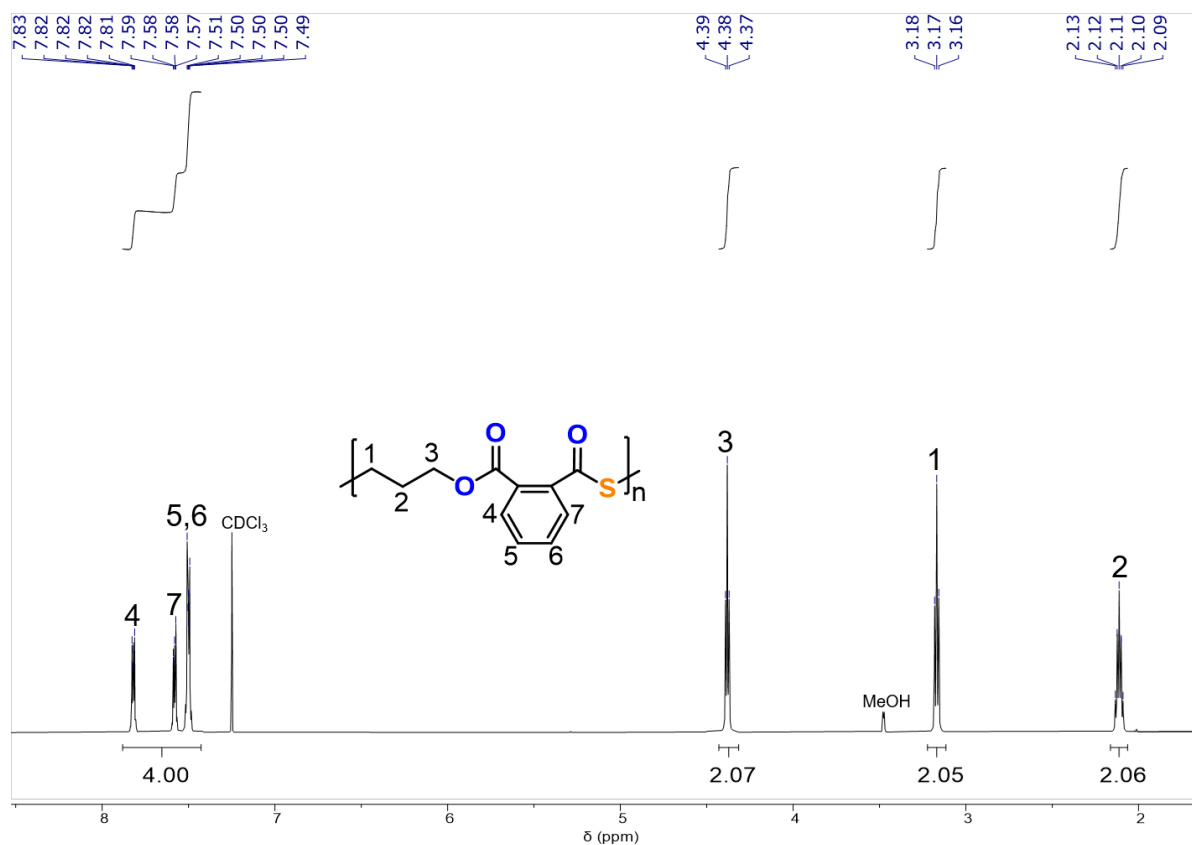


Figure S 2: ^1H NMR spectrum (400 MHz, CDCl_3 , 25°C) of the polymer corresponding to table 1, run #1; residual MeOH at ca. 3.4 ppm.

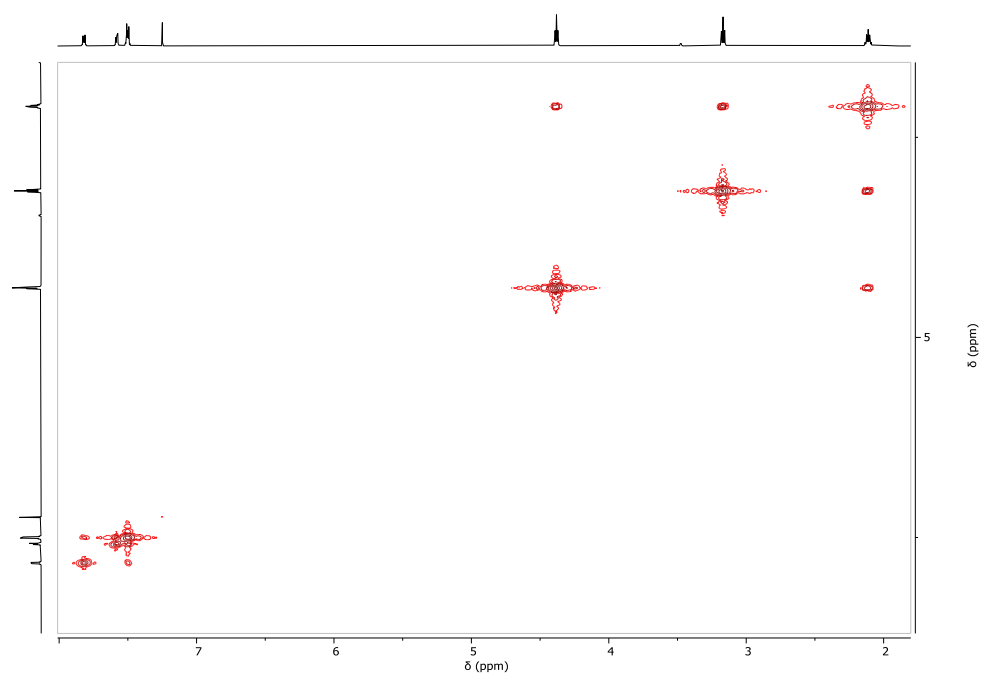


Figure S 3: ^1H - ^1H COSY NMR spectrum (CDCl_3 , 25°C) of the polymer corresponding to table 1, run #1.

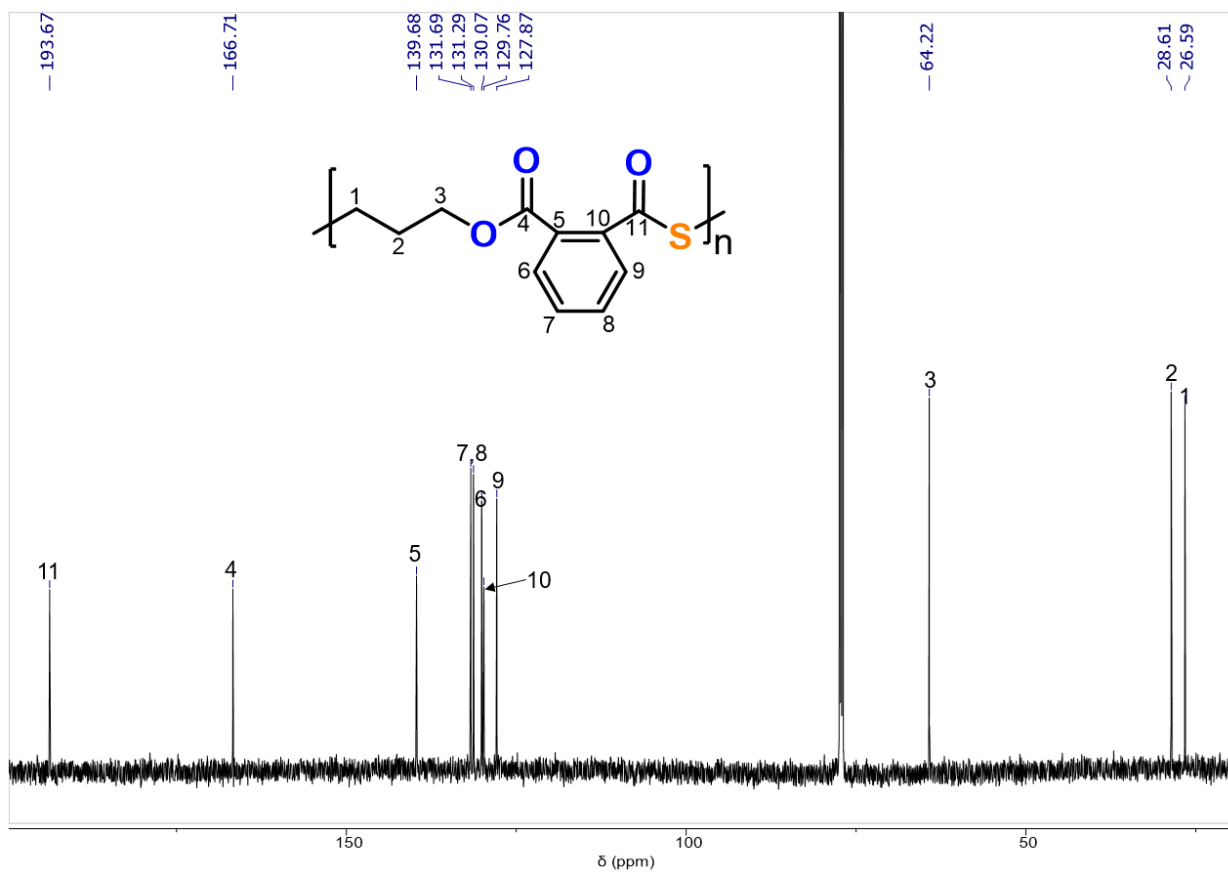


Figure S 4: ^{13}C NMR spectrum (126 MHz, CDCl_3 , 25°C) spectrum of the polymer corresponding to table 1, run #1.

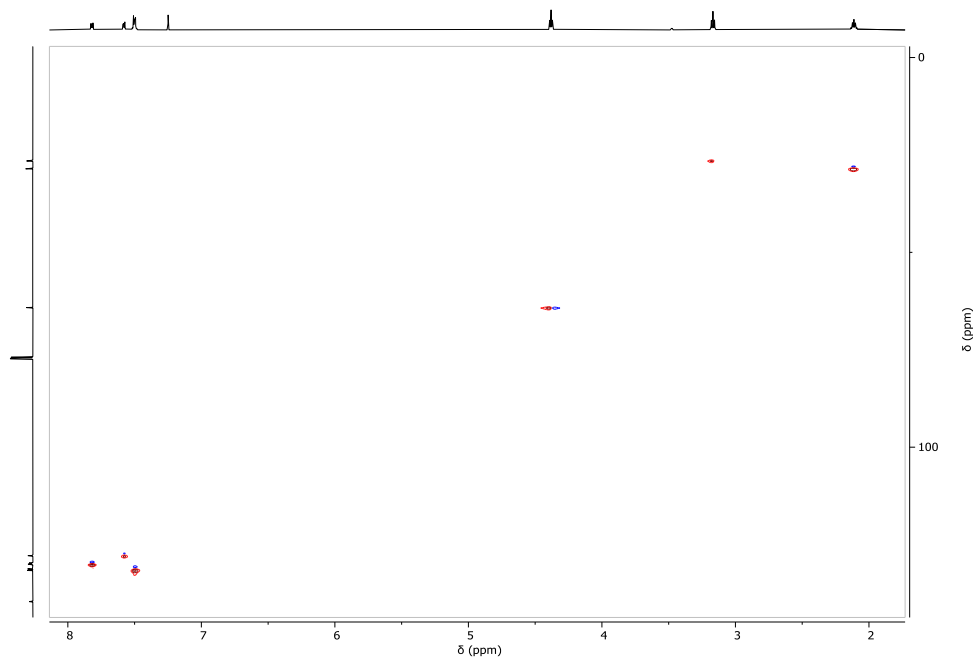


Figure S 5: ^1H - ^{13}C HSQC NMR spectrum (CDCl_3 , 25°C) spectrum of the polymer corresponding to table 1, run #1.

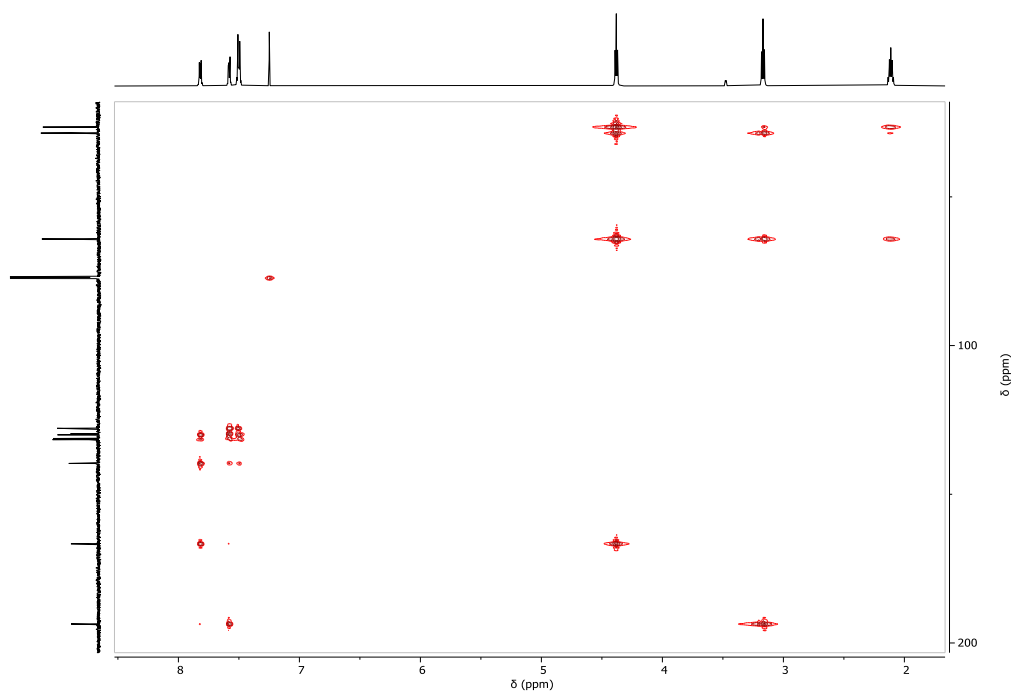


Figure S 6: ^1H - ^{13}C HMBC NMR spectrum (CDCl_3 , 25°C) spectrum of the polymer corresponding to table 1, run #1.

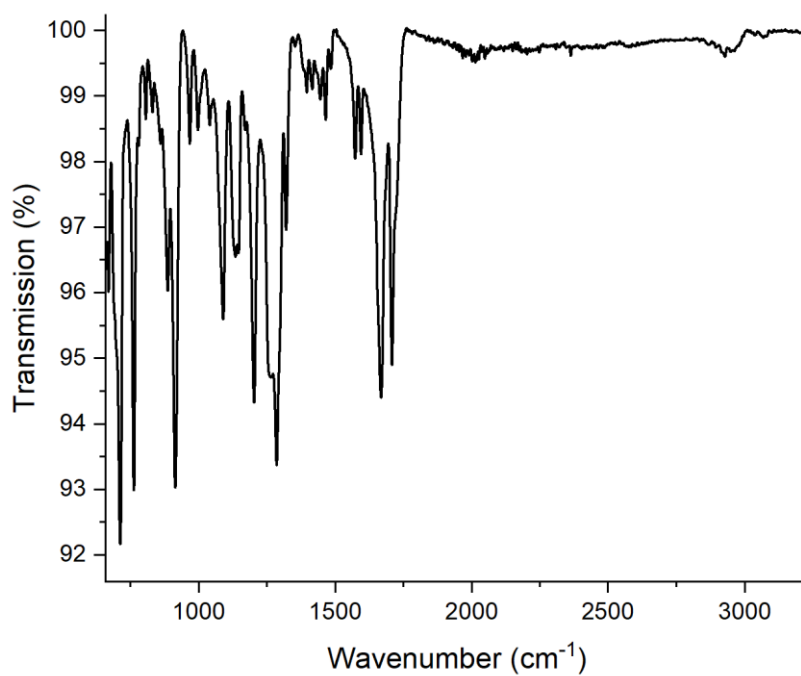


Figure S 7: IR spectrum corresponding to table 1, run #1.

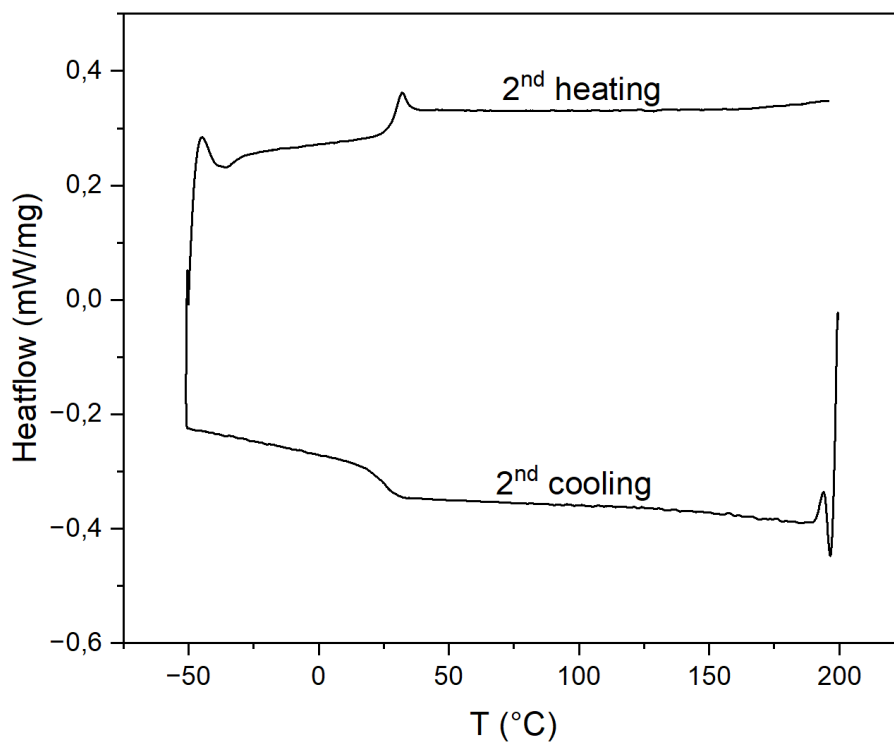
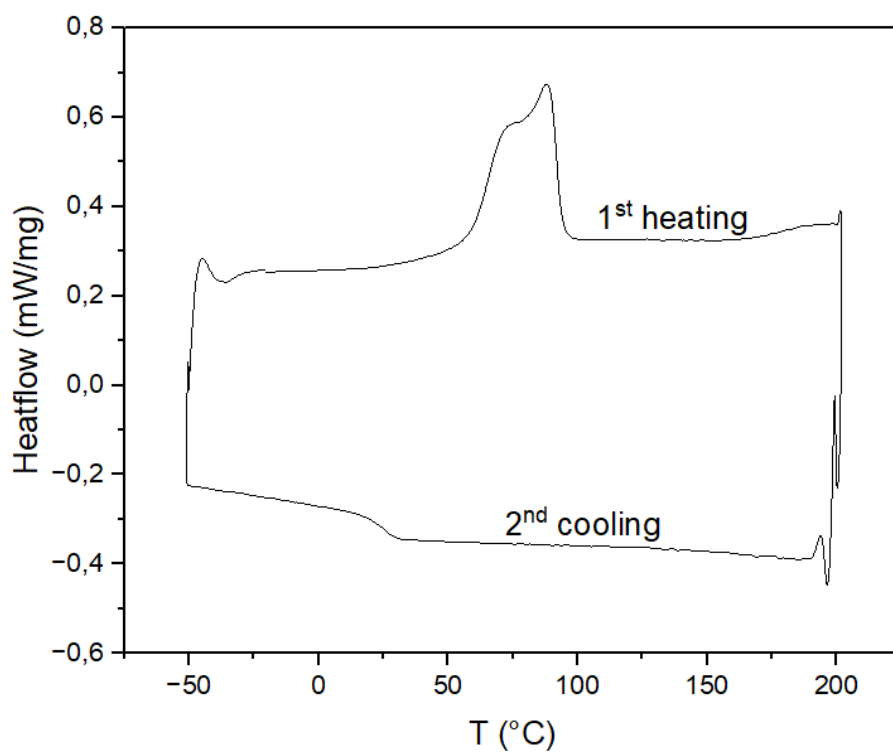


Figure S 8: DSC heating curves of the polymer corresponding to table 1, run #8.

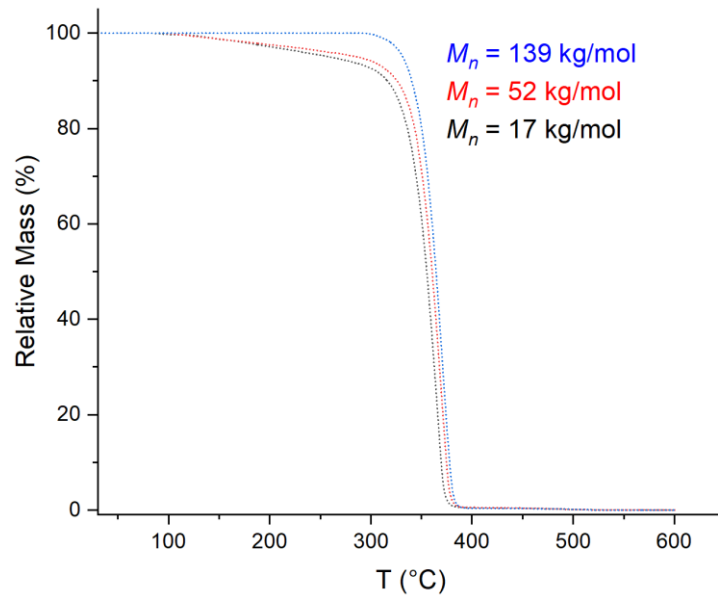
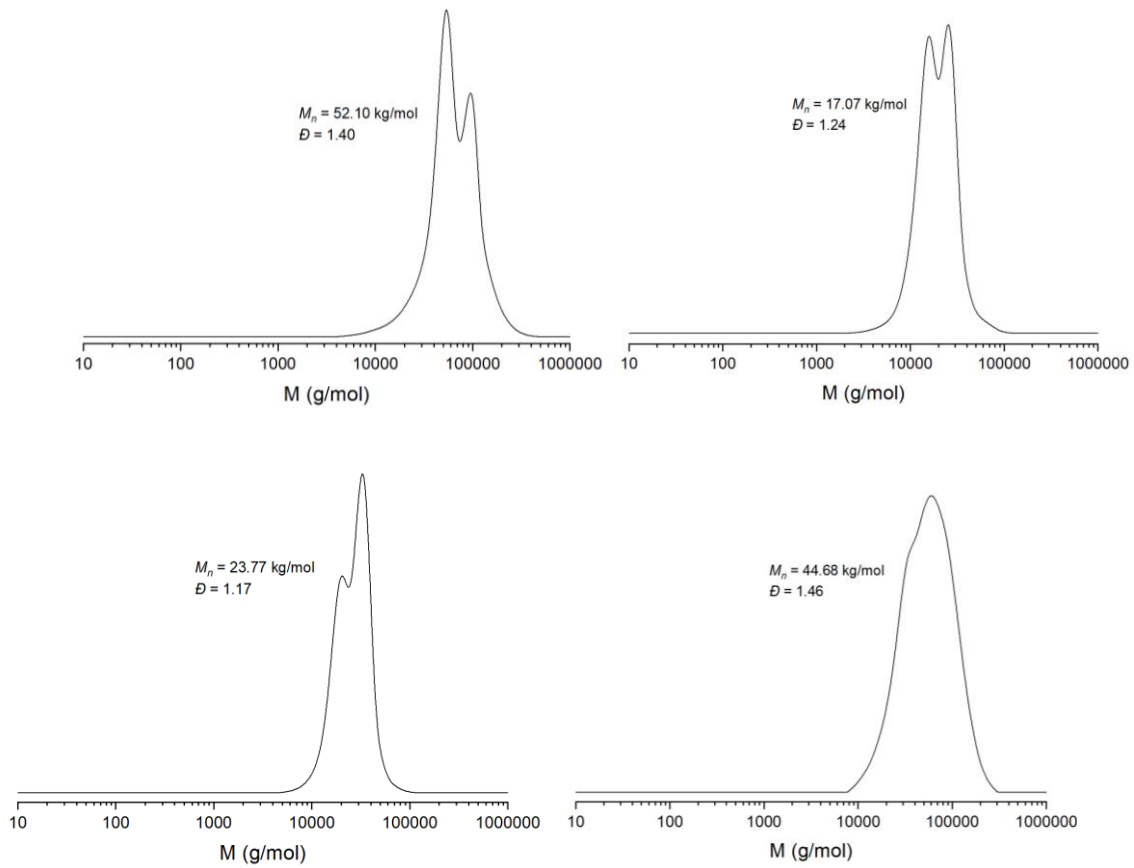


Figure S 9: Overlaid TGA data of copolymer corresponding to table 1, run #1, #7 and #8.



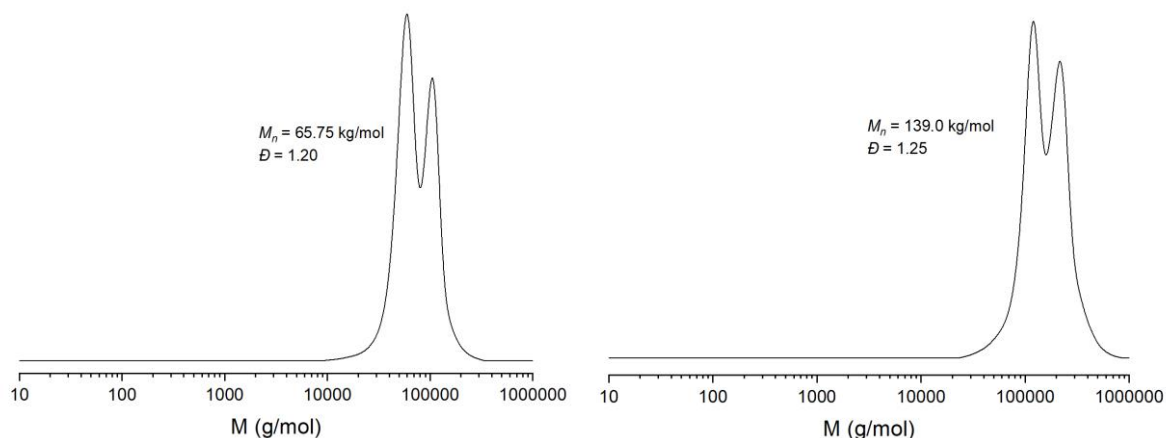


Figure S 10: SEC traces corresponding to table 1.

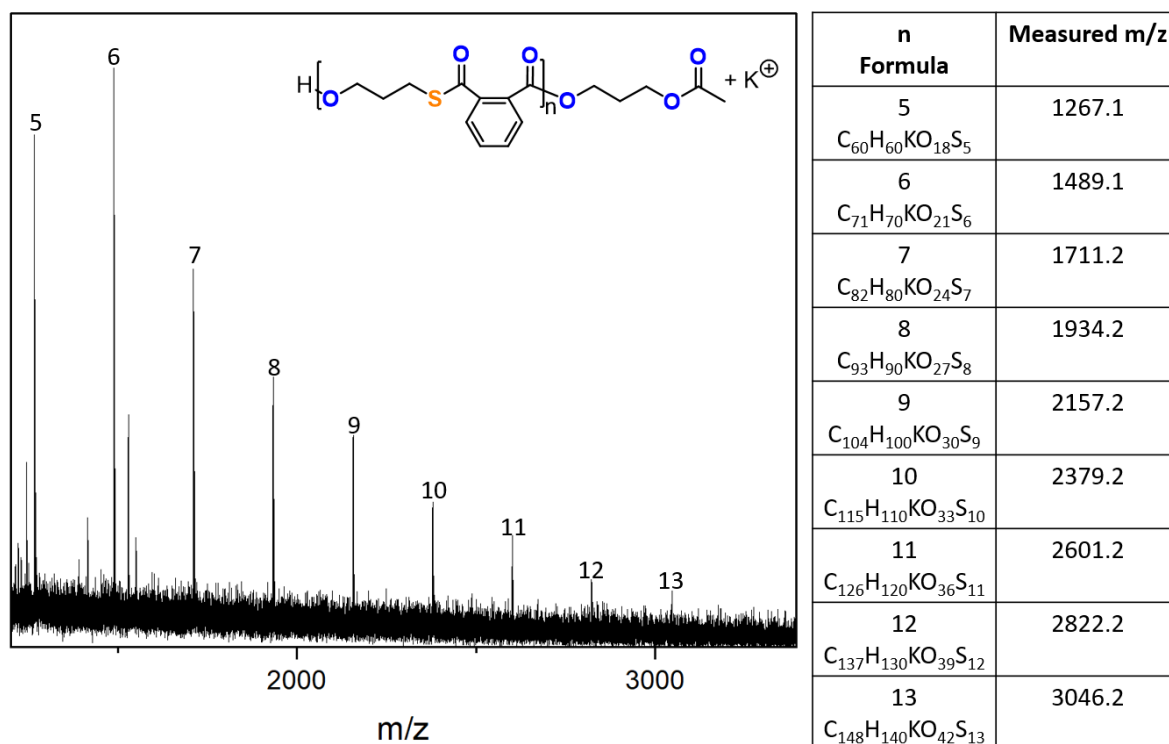


Figure S 11: MALDI-TOF spectrum of polymer at $M_n < 2$ kg/mol as per GPC.

End-group analysis by ³¹P NMR spectroscopy: A reported procedure by Marchessault for the analysis of protic end-groups was followed.^[7] A polymer sample (20 mg of table 1 run #3) and a stock solution (40 μ L, made of bisphenol A (400 mg), chromium(III)acetylacetonate (5.5 mg), and pyridine (10 mL)), in CDCl₃ (0.5 mL), were mixed in an NMR tube. Excess 2-chloro-4,4,5,5-tetramethyldioxaphospholane (40 μ L) was then added to the NMR tube which was then shaken. The mixture was allowed to react for 30 min before analysis by ³¹P NMR.

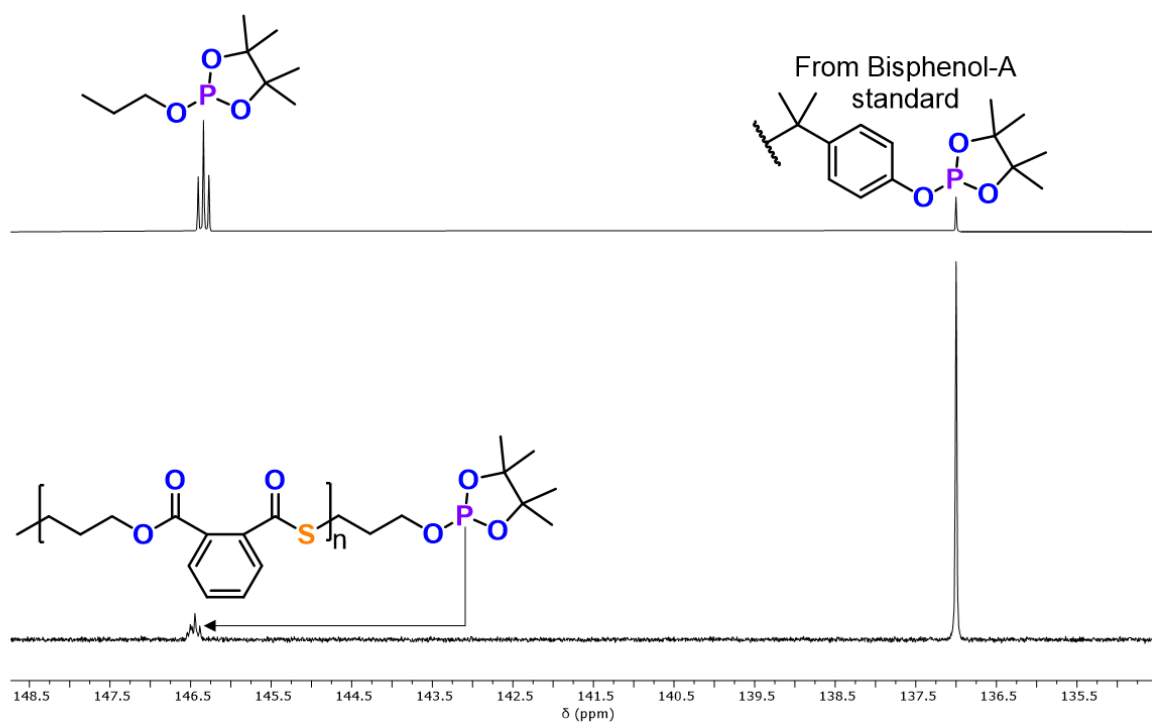


Figure S 12: ^{31}P NMR (162 MHz, CDCl_3 , 25°C) end-group analysis of (top) control experiments with propanol and (bottom) PTA/OX copolymer (table 1, run #2).

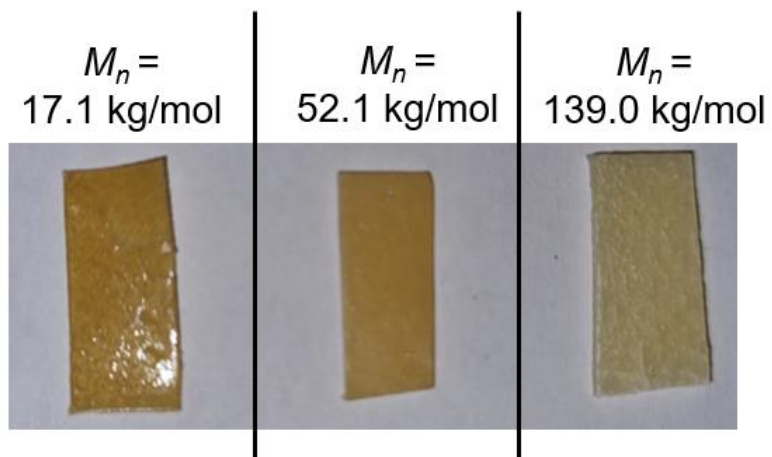


Figure S 13: Photograph of the hot-pressed films employed at different molecular weights.

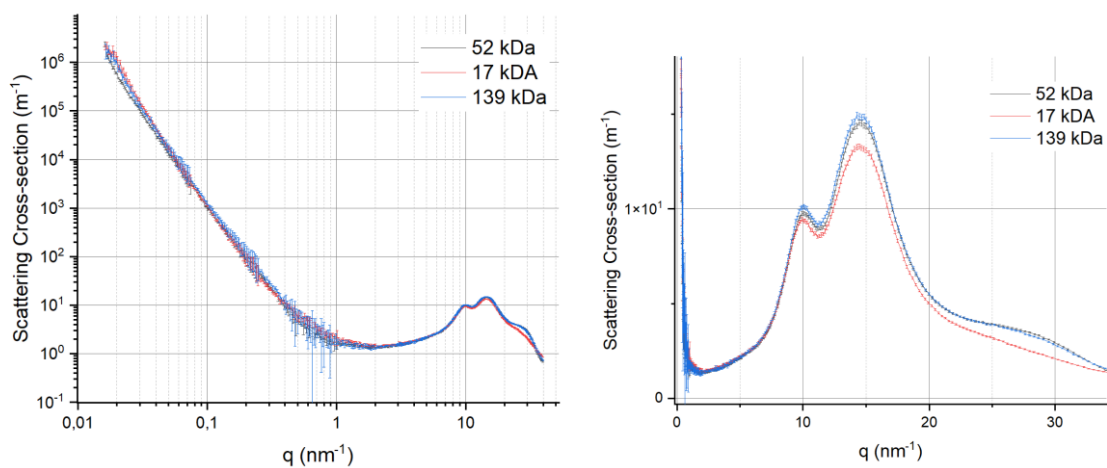
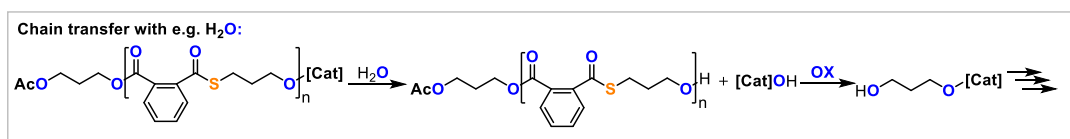
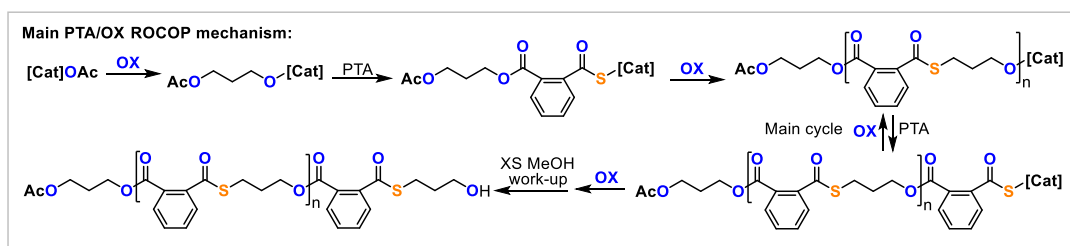


Figure S 14: SAXS/WAXS data of the above polymer films.

Section S4: Mechanistic hypothesis



Scheme 3: Mechanistic hypothesis of main and side reactions.

Section S5: Degradation and weathering

Oxidative degradation: The powdered polymer (50mg of table 1 run #8) was dispersed in aqueous H₂O₂ (3 mL) and stirred for 7d in a glass vial leading to the gradual dissolution of the initially insoluble polymer. Afterwards all volatiles were let evaporated and the solid degradation products were analysed by ¹H NMR spectroscopy. No polymeric products could be identified by GPC after degradation.

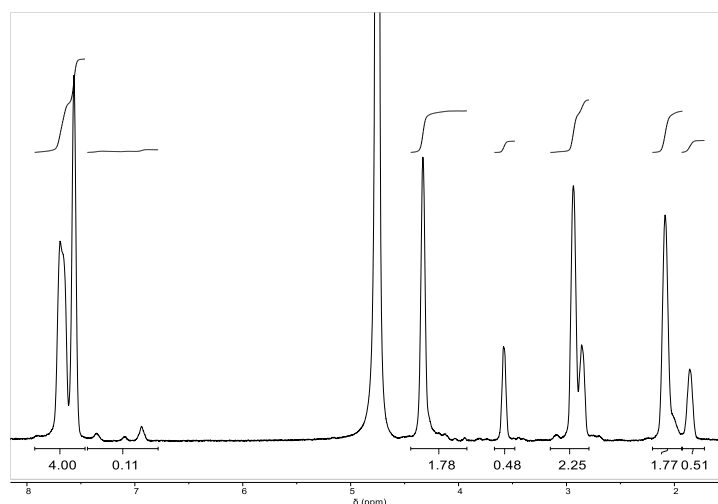


Figure S 15: Zoom into the ¹H NMR spectra (400 MHz, D₂O, 25°C) after oxidative degradation revealing desymmetrisation of the initially symmetric NMR spectrum due to chain cleavage.

UV degradation: The polymer (50mg of table 1 run #8) was dissolved in CDCl₃ (0.75 mL) and irradiated for 16h by a broadband Hg UV 1000W UV lamp inside a J. Youngs NMR tube. Afterwards the sample was analysed by ¹H NMR spectroscopy and GPC.

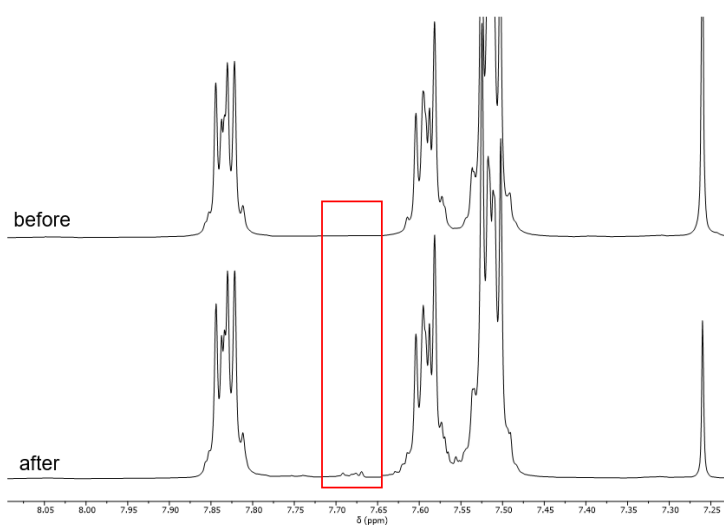


Figure S 16: Zoom into the overlaid ¹H NMR spectra (400 MHz, CDCl₃, 25°C) before and after UV degradation.

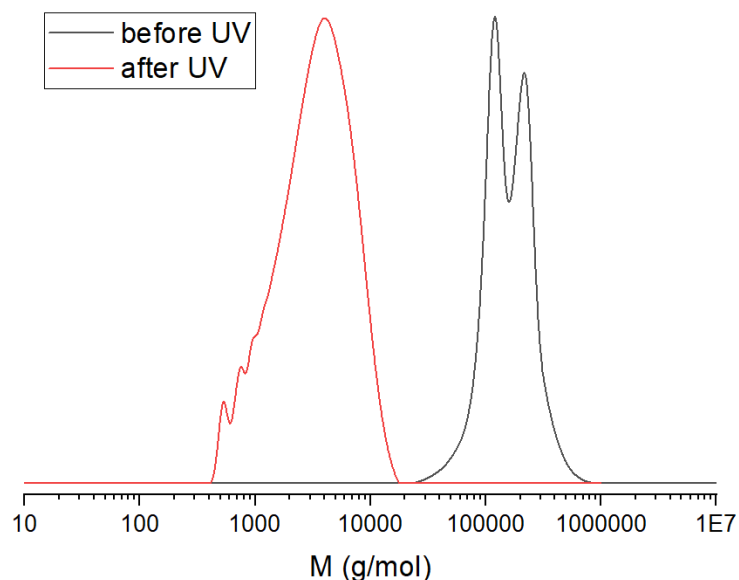


Figure S 17: Overlaid GPC traces of polymer before and after irradiation (5 days, $M_n < 2.5$ kDa) with broadband UV light in CDCl_3 solution for 72 h.

Weathering procedure: Weathering was carried out using a Weiss (Weiss Technik GmbH, Germany) Global UV Test 200 fluorescent lamp weathering device (device “GUT# 1”) according to ISO 4892-3:2016 (Plastics – Methods of exposure to laboratory light sources – Part 3: Fluorescent UV lamps). The UVA-340 fluorescent lamps used comply to Type 1A lamps as defined by ISO 4892-3:2016 and don’t show spectral contribution below the solar cut-off around 290 nm. For the wet cycle water spraying with de-ionised water was used.

The weathering cycle used was adapted from ISO 4892-3:2016, table 4, cycle 3: the maximum temperature of the dry cycle was reduced from the standard’s 50 °C to 30 °C and UV-irradiation with 45 W/m^2 irradiance was kept constant, i.e., also during the rain-phase. The age of the lamps was 458 hours.

The 6 h weathering cycle comprises a 5 h period at 30 °C, followed by a 1 h water-spray rain-phase without temperature regulation, in which the water spraying starts at 21 °C room temperature.

Thioester samples alongside all-ester reference samples of PET and PBT were suspended vertically using on the stainless-steel hooks hung-up in the stainless-steel mesh frame in the back of the samples compartment. Starting with de-ionised water, the rainwater was recycled as long as an electrical conductivity of 5 $\mu\text{S}/\text{cm}$ or a period of 7 days was not exceeded.

Reference Samples: PET: 250 μm transparent film, Hostaphan RN 250, by MITSUBISHI POLYESTER FILM GmbH (Germany), obtained in 2020.

PBT: extruded tiles of 3,0 mm thickness of Ultradur B4500, by BASF Performance Materials (Germany), obtained in 2012.



Figure S 18: Photo of the thioester samples (top row) and the all-ester reference samples (lower row) PET (left) and PBT (right) before and after weathering.

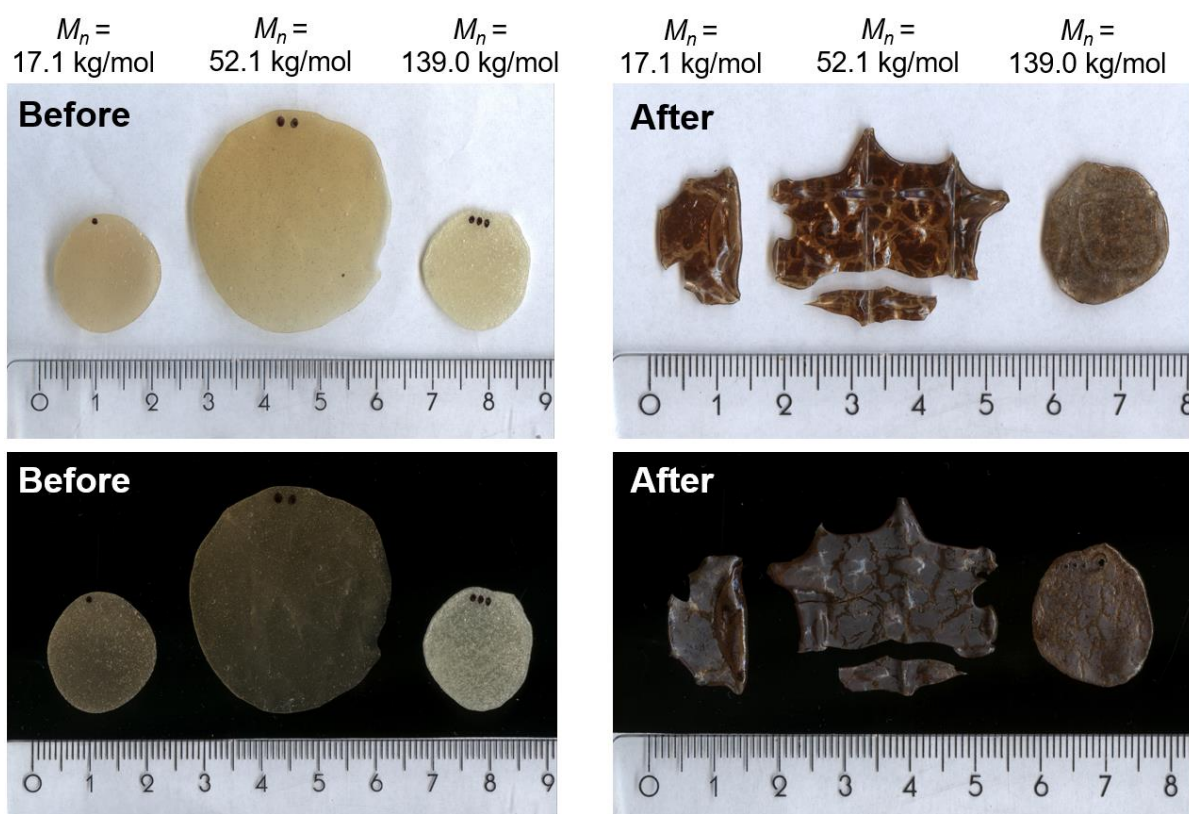


Figure S 19: Scans of polymer films before and after weathering for 336h as outlined above.

ATR-FTIR spectroscopy for weathering section: IR spectroscopy was carried out using a Bruker (Bruker Optik GmbH, Germany) LUMOS II IR-microscope. The spectral range was 600 cm^{-1} to 4000 cm^{-1} . A Germanium ATR tip was used (at 1100 cm^{-1} and 45° angle of incidence the informational depth is about $0,7\text{ }\mu\text{m}$). A liquid nitrogen cooled detector was used. The pressure of the ATR tip was set to low. Resolution was 4 cm^{-1} and for each measurement, 128 scans were accumulated, and a background was measured with 128 scans prior to each sample. Between each measurement the tip was cleaned. Atmospheric correction for CO_2 and water were used and after the measurement an automatic baseline correction (method 2, rubber band) was underdone. Spectra accumulation and manipulation was carried out using the Bruker OPUS software. For each sample investigated IR-measurements on three different sites were carried out.

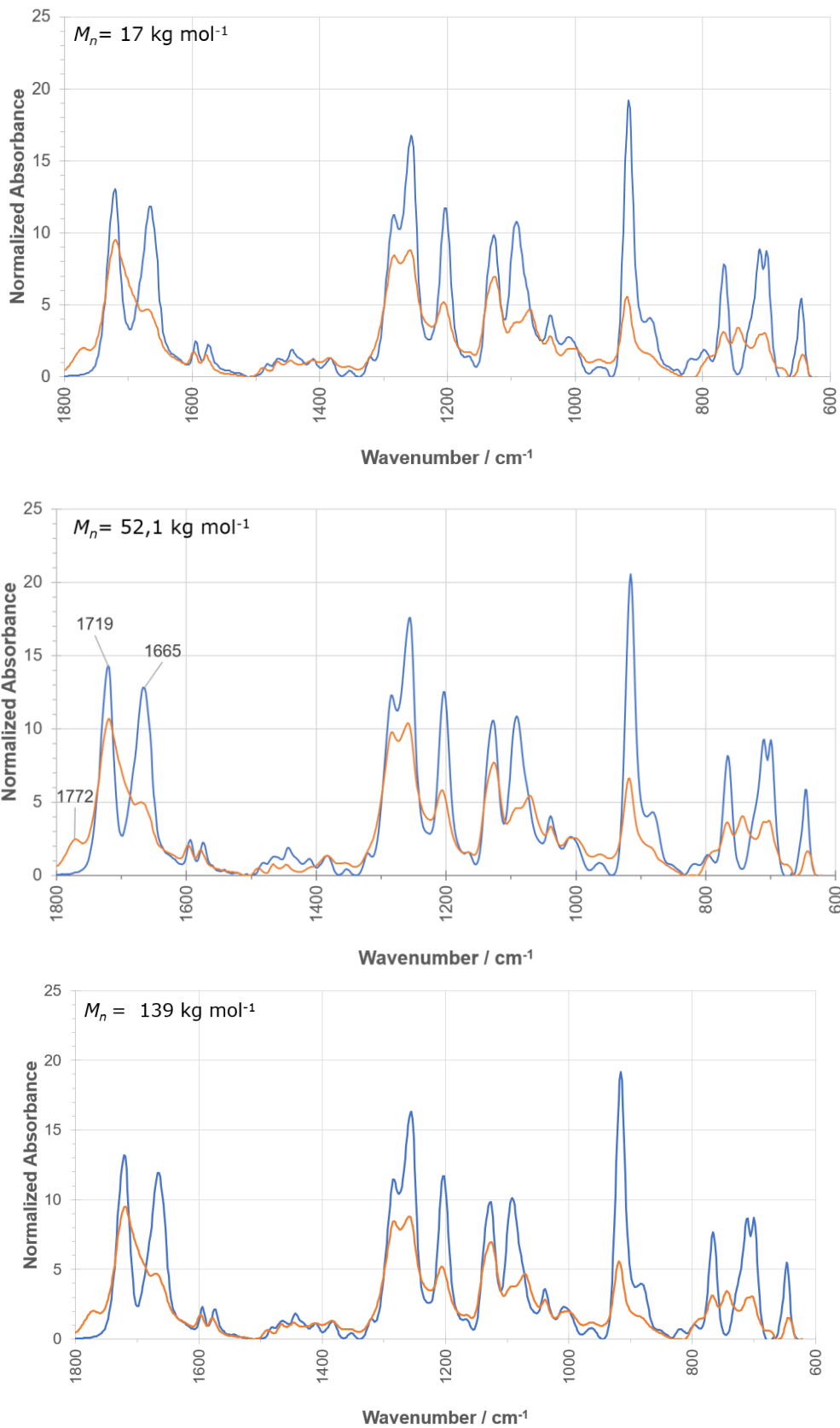


Figure S 20: Normalised ATR-IR spectra of the film surfaces before (blue) and after (orange) weathering.

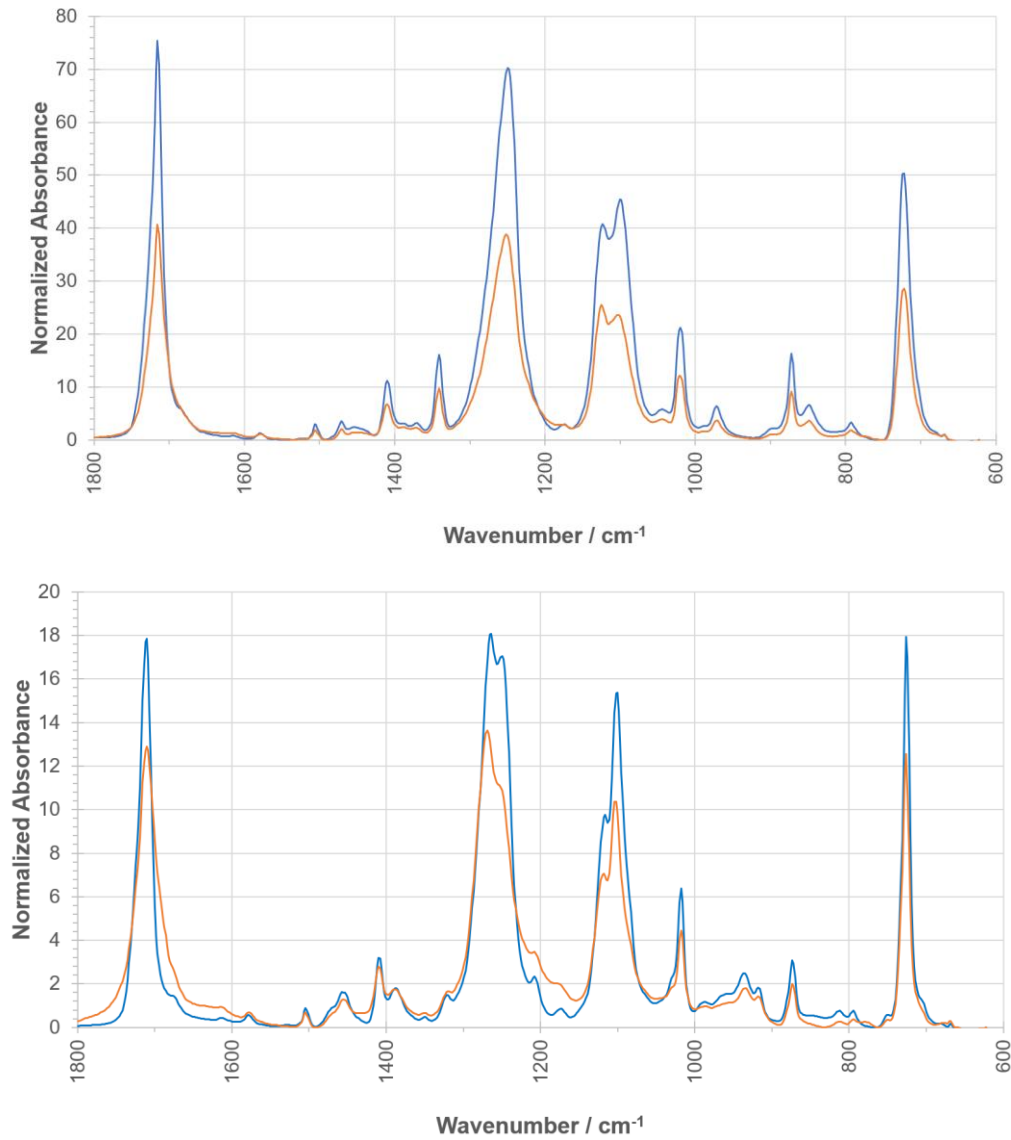


Figure S 21: Normalised ATR-IR spectra of the film surfaces before (blue) and after (orange) weathering. (Top) PET. (Bottom) PBT.

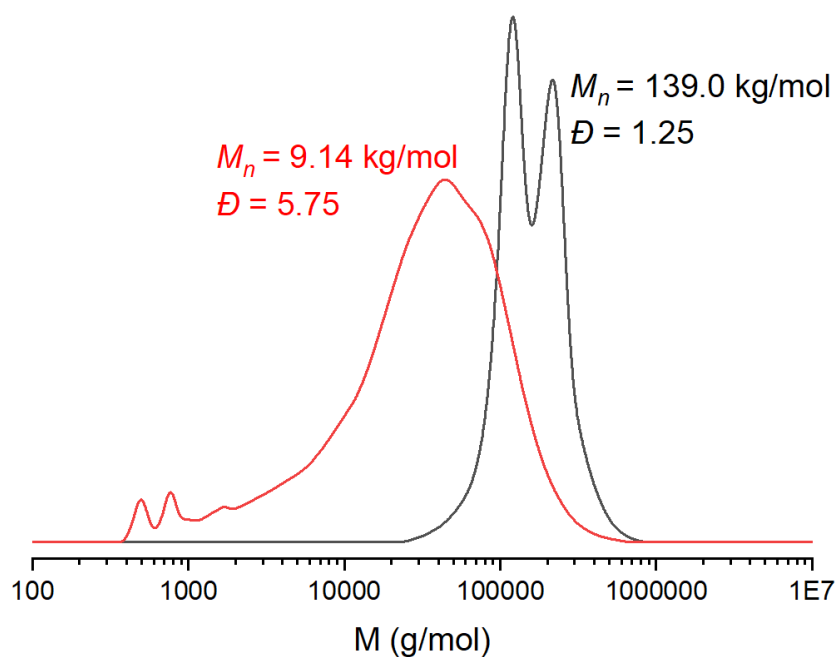


Figure S 22: Overlaid GPC traces of polymer before and after weathering at a starting M_n of 139.0 kg/mol.

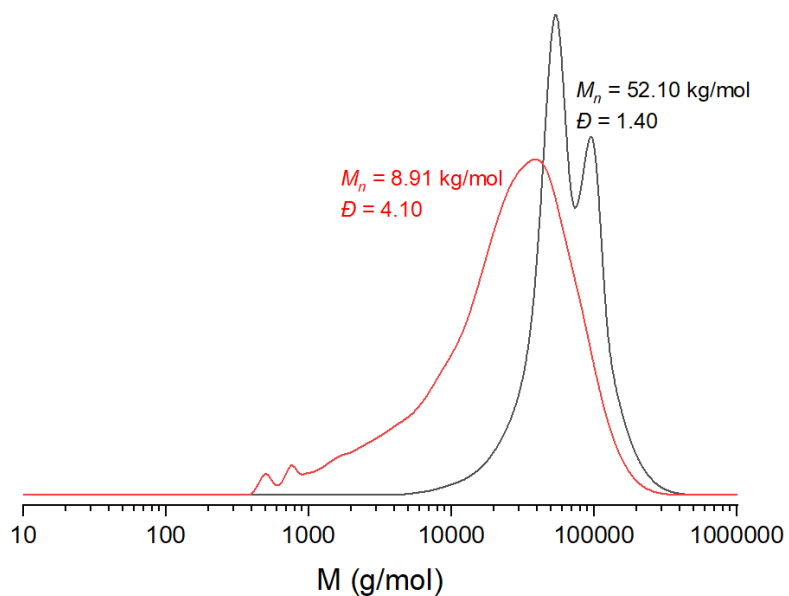


Figure S 23: Overlaid GPC traces of polymer before and after weathering at a starting M_n of 52.1 kg/mol.

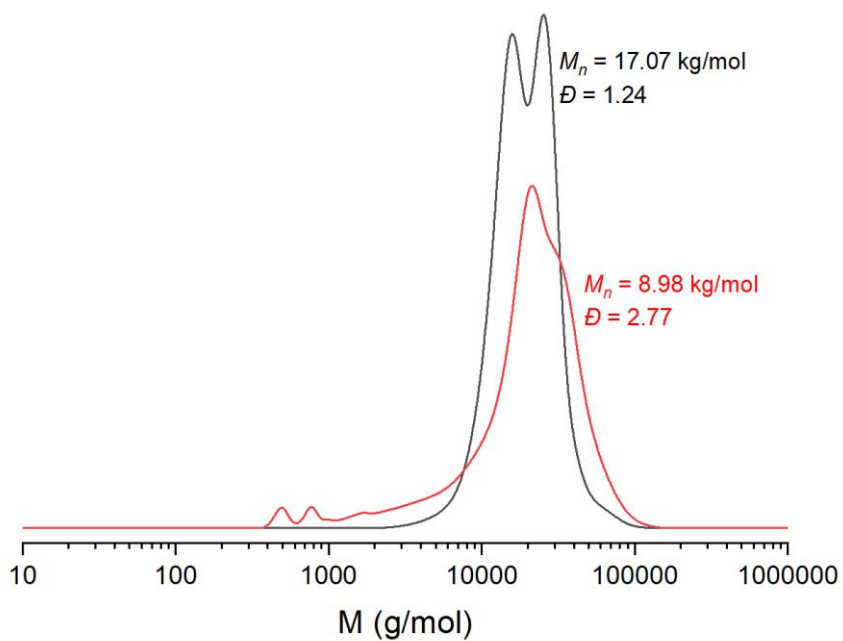


Figure S 24: Overlaid GPC traces of polymer before and after weathering at a starting M_n of 17.07 kg/mol.

Section S6: References

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