Supporting Information

Self-Reporting Visible Light-Induced Polymer Chain Collapse

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A. Experimental procedures

A.1 Materials

Unless otherwise stated all chemicals were used as received. Cyclohexane (VWR, normapur), 1,2 dichlorobenzene (Acros, 99 %, extra pure), dichloromethane (DCM, VWR, normapur), dichloromethane (DCM, Acros, 99.8 %, extra dry), 4-dimethylaminopyridine (DMAP, Acros organics, 99 %), *N*,*N*-dimethylformamide (DMF, Acros, 99.8 %, extra dry), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrogenchloride (EDC·HCl, Roth, ≥99 %), hydroxylamine hydrochloride (Alfa Aesar, 99 %), magnesium sulfate (MgSO4, Roth, ≥99 %), methanol (MeOH, VWR, normapur), methanol (MeOH, Acros, 99.9 %, extra dry), 1-pyrenecarboxaldehyde (Alfa Aesar, 99 %), sodium acetate (Roth, ≥98.5 %, pure, anhydrous), 4-vinylbenzoic acid (TCI, ≥97.0 %, stabilized with BHT).

Azobisisobutyronitrile (AIBN, Fluka, 98 %) was recrystallized from MeOH. Styrene (Merck, ≥99 %) and 1,2-dichlorobenzene (Acros, 99 %, extra pure) were passed over a column of basic and neutral aluminium oxide prior to polymerization, respectively.

1-Pyrenecarbaldehyde oxime was synthesized according to literature.[1]

A.2. Synthesis of pyrene-1-carbaldehyde *O*-(4-vinylbenzoyl) oxime (PyOHSty)

1.94 g of 1-pyrenecarboxaldehyde oxime (7.92 mmol, 1.0 eq.), 1.29 g of 4-vinylbenzoic acid (8.71 mmol, 1.1 eq.) and 4.8 mg of DMAP (0.40 mmol, 0.05 eq.) were dissolved in a 1:1 mixture of DCM and THF (50 mL). After cooling down to 0 °C, 1.82 g of EDC·HCl (9.50 mmol, 1.2 eq.) were added, and the reaction mixture was stirred at ambient temperature overnight. After removal of the solvent under reduced pressure, the residue was dissolved in DCM. The organic phase was washed with sat. $NaHCO_3$, 1H HCl, water and brine. Drying over MgSO4 and removal of the solvent afforded the crude product which was further purified via column chromatography (cyclohexane: DCM = 1:4). The targeted compound was received as pale yellow solid (2.82 g, 7.54 mmol, 95 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ / ppm = 9.55 (s, 1 H, CO*H*), 8.76 (d, 1 H, J = 8.0 Hz, H_{Py}), 8.62 (d, 1 H, J = 8.0 Hz, H_{Py}), 8.29-8.05 (m, 7 H, H_{Py}), 8.19 (d, 2 H, J = 8.4 Hz, H_{Ph}), 7.56 (d, 2 H, J = 8.2 Hz, H_{Ph}), 6.81 (dd, 1 H, J = 17.8 Hz, J = 11.2 Hz, C*H*CH_2), 5.93 (d, 1 H, J = 17.6 Hz, CHCH_2), 5.45 (d, 1 H, J = 10.8 Hz, CHCH_2). ^{13}C NMR (CDCl3, 100 MHz): δ / ppm = 164.06 (s, 1 C), 155.99 (s, 1 C), 142.65 (s, 1 C), 136.13 (s, 1 C), 133.94 (s, 1 C), 131.34 (s, 1 C), 130.68 (s, 1 C), 130.30 (s, 2 C), 129.68 (s, 1 C), 129.47 (s, 1 C), 127.95 (s, 1 C), 127.53 (s, 1 C), 126.94 (s, 1 C), 126.58 (s, 2 C), 126.51 (s, 2 C), 126.28 (s, 1 C), 125.16 (s, 1 C), 125.03 (s, 1 C), 124.58 (s, 1 C), 122.88 (s, 2 C), 117.07 (s, 1 C).

ESI-MS:

$[M+H^+]^+/z_{exp.}$ = 376.1325, $[M+H^+]^+/z_{theo.}$ = 376.1332.

$[M+Na^+]^+/z_{exp.}$ = 398.1143, $[M+Na^+]^+/z_{theo.}$ = 398.1151.

A.3. Copolymerization of PyOHSty

1.5 mg of AIBN ($9.13\cdot10^{-3}$ mmol, 1.0 eq.), 10.0 mg of CDB ($36.71\cdot10^{-3}$ mmol, 4.0 eq.), 3.0 g of styrene (28.80 mmol, 3154.4 eq.) and a variable amount of PyOHSty (1.33/0.80/0.27 mmol) were dissolved in *o*-chlorobenzene (2 mL), and subsequently degassed via purging with argon for 30 min. The polymerization was conducted at 60 °C for 26.5 h. Chain growth was stopped via cooling with liquid nitrogen and the final polymer was purified via three-fold precipitation into ice-cold methanol.

Table S1 Summary of the conditions and results of the RAFT-mediated copolymerization of styrene and **PyOHSty**. Each polymerization procedure was performed at 60 °C for 26.5 h employing *o*-chlorobenzene as solvent. A polystyrene calibration was used for the calibration of $M_{n,SEC(THF)}$.

Species	**AIBN:CTA:Sty:PyOHSty**	**yield / g**	$M_{n,SEC(THF)}$/ g mol^{-1}	**Đ**
1	1:4:3154:146	0.45	17.000	1.22
2	1:4:3154:88	0.35	12.000	1.15
3	1:4:3154:30	0.30	13.000	1.20

A.4. LED-irradiation of CDB PS PyOHSty 1-3

8.0 mg of CDB PS PyOHSty 1-3 were dissolved in DCM (400 mL) and the solution was deoxygenated via purging with argon for 1 h. Subsequently, the polymer solutions were irradiated with an LED setup (430-435 nm, 3 × 3W, refer to Figure S6 for the emission spectrum) for 2.5 h. Subsequently, the solvent was removed under reduced pressure, and the irradiated polymer species were purified via precipitation into ice-cold methanol.

B. Measurements and analytical methods

B.1. Nuclear magnetic resonance (NMR) spectroscopy

NMR measurements were performed on a Bruker AM 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz) for hydrogen and carbon nuclei. The δ-scale was referenced to the respective solvent signal of chloroform-d$_1$ which was employed as deuterated solvent. Abbreviations used in the description of the materials synthesis include singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), and multiplet (m).

The number of photoreactive PyOHSty unit per chain was calculated by comparing the integral of the magnetic resonance of the aldehyde proton between 9.60 and 9.20 ppm with the value of the integral associated with the magnetic resonance of the aromatic backbone in the region of 7.40 to 6.20 ppm minus the number of protons of PyOHSty, which appear in the same area. $M_{\mathrm{n,SEC}}$ was taken as the molecular weight of the polymeric species as $M_{\mathrm{n,NMR}}$ cannot be obtained due to overlap of the magnetic resonances of the backbone and the protons of the end group.

B.2. Size exclusion chromatography (SEC)

The apparent number average molar mass (Mn) and the molar mass distribution [$Đ$ (polydispersity index) = $M_{\mathrm{w}}/M_{\mathrm{n}}$] of the polymers were determined via SEC measurements, which were performed on a Polymer Laboratories (Varian) PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5mm bead-size guard column (50 × 7.5 mm), one PLgel 5mm Mixed E column (300 × 7.5 mm), three PLgel 5mm Mixed C columns (300 × 7.5 mm) and a differential refractive index detector using tetrahydrofuran (THF) as the eluent at 35 °C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated using linear polystyrene standards ranging from 476 to 2.5·106 g mol^{-1}. Calculation of the molecular weight proceeded via the Mark-Houwink-Sakurada (MHS) parameters for polystyrene (PS) in THF at 35 °C, i.e., K = 13.63·10−3 mL g^{-1}, α = 0.714.

B.3. High Resolution/Orbitrap Electrospray Ionization Mass Spectrometry (ESI-MS)

Mass spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fischer Scientific, San Jose, CA, USA) equipped with a HESI II probe. The spectra were recorded in positive mode and the analyte was dissolved in a DCM/MeOH solution (3:1, doped with 100 µmol sodium trifluoroacetate, c = 0.01 g mL^{-1}). The instrument was calibrated in the m/z range 74 to 1822 using premixed calibration solutions (Thermo Scientific). The Fourier-Transform resolution was set to 140 000. A constant spray voltage of 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 and 68.0, respectively. The flow rate was set to 5 µL min^{-1}.

B.4. Ultraviolet-visible (UV-Vis) spectroscopy

The UV-Vis spectra were recorded on a Cary 100 UV-Visible Spectrophotometer (Agilent Technologies, USA) equipped with a tungsten halogen light source (190 to 900 nm, accuracy +/- 2 nm) and a R928 PMT detector. Spectra were recorded in DCM at 20 °C with a concentration of $1.23 \cdot 10^{-5}$ mmol mL^{-1} and $6.25 \cdot 10^{-2}$ mg mL^{-1} for PyOHSty and the copolymer species, respectively, and collected between 200 and 800 nm. Samples were baseline corrected with respect to the pure solvent.

B.5. Fluorescence spectroscopy

Fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence Spectrometer using quartz cuvettes loaded with 400 µL of samples. An excitation wavelength of 344 nm was used and the emission was recorded from 355 to 800 nm. All spectra were recorded in DCM (PyOHSty: $c = 3.98 \cdot 10^{-7}$ mmol mL^{-1}, copolymer species: $c = 1.04 \cdot 10^{-2}$ mg mL^{-}) at 20 °C.

B.6. Diffusion-Ordered Spectroscopy (DOSY NMR)

DOSY experiments based on ^{1}H NMR were performed in $CDCl_3$ ($c = 8.9$ mg mL^{-1}) at 298.00 K on a Bruker AM 400 spectrometer at an operating frequency of 400 MHz (^{1}H) using a stimulated echo sequence incorporating bipolar gradient pulses and a longitudinal eddy current delay (BPP-LED) with the standard Bruker pulse program, ledbpgp2s. The gradient strength was linearly incremented in 96 steps from 5 % up to 95 % of the maximum gradient strength. Diffusion times and gradient pulse durations were optimized for each experiment in order to achieve a 95% decrease in the signal intensities at the largest gradient amplitude. After Fourier transformation and phase correction, the diffusion dimension of the 2D DOSY spectra was processed by means of the Bruker Topspin software package (version 3.2), and analyzed with the Bruker Dynamic Center. Spectra for the polymer and the corresponding single-chain nanoparticle were measured and mean values were taken from the experimentally determined diffusion coefficients D of the characteristic NMR-peaks. The hydrodynamic diameter d was obtained *via* the application of the Stokes-Einstein equation (with $k_B = 1.38 \cdot 10^{-23}$ m^2 kg s^{-2} K^{-1}, $T = 298$ K, $\eta = 0.536$mPa s, d = diameter, D = diffusion coefficient)

$$d = \frac{k_B T}{3\, \pi\, \eta\, D}$$

C. Additional data and figures

C.1. Characterization of PyOHSty

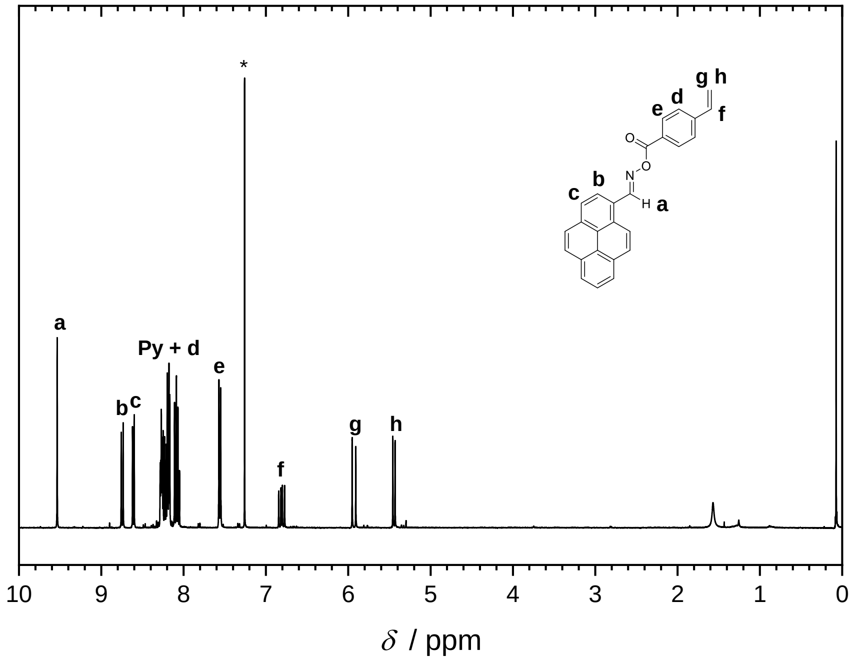


Figure S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **PyOHSty**. The magnetic resonance marked with an asterisk is assigned to $CHCl_3$.

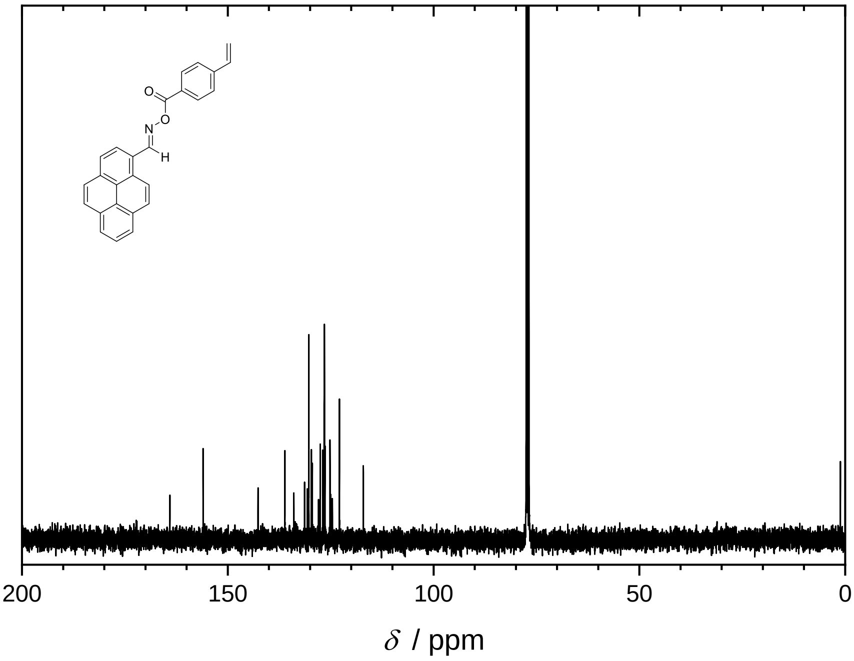
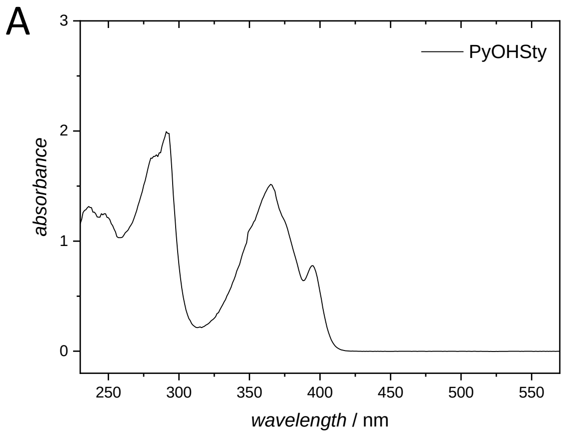
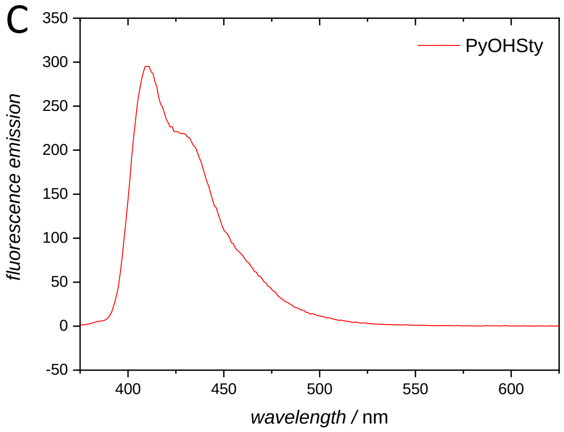


Figure S2 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **PyOHSty**.



B

Species	$\lambda_{abs.max}$ / nm	ε / L mol^{-1} cm^{-1}
PyOHSty	395	63.000
	365	120.000
	291	160.000



D

Species	$\lambda_{em.max}$ / nm
PyOHSty	409

Figure S3 A: UV/Vis spectrum of **PyOHSty** in DCM at ambient temperature (c = 1.23·10^{-5} mmol mL^{-1}). B: Corresponding table with the absorption maxima $\lambda_{abs.max}$ and the molar extinction coefficient ε. **C**: Fluorescence spectrum ($\lambda_{exc.}$ = 344 nm) of **PyOHSty** in DCM at ambient temperature (c = 3.98^{-7} mmol mL^{-1}). **D**: Corresponding table displaying $\lambda_{em.max}$.

C.2. Characterization of the Copolymers

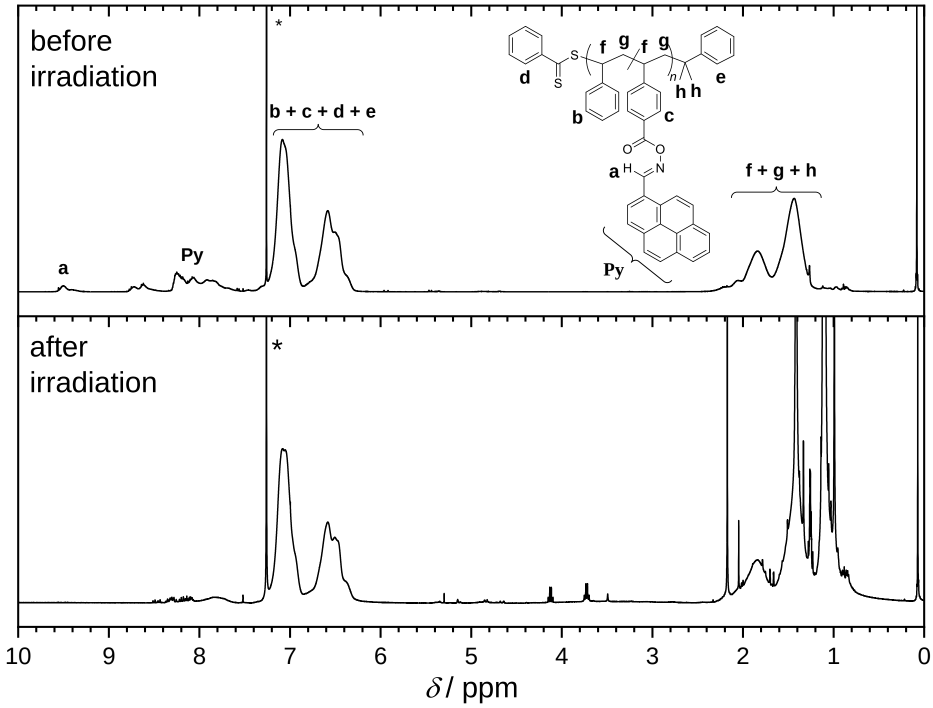


Figure S4 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **CDB PS PyOHSty 2** before and after LED irradiation (430 – 435 nm). The magnetic resonance marked with an asterisk is assigned to $CHCl_3$.

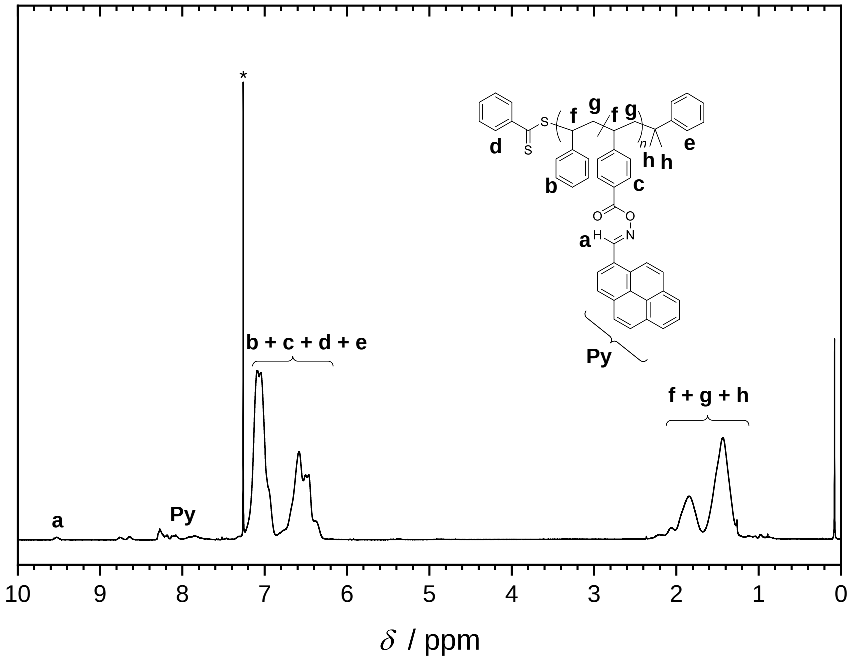


Figure S5 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **CDB PS PyOHSty 3**. The magnetic resonance marked with an asterisk is assigned to $CHCl_3$.

C.3. Emission spectrum

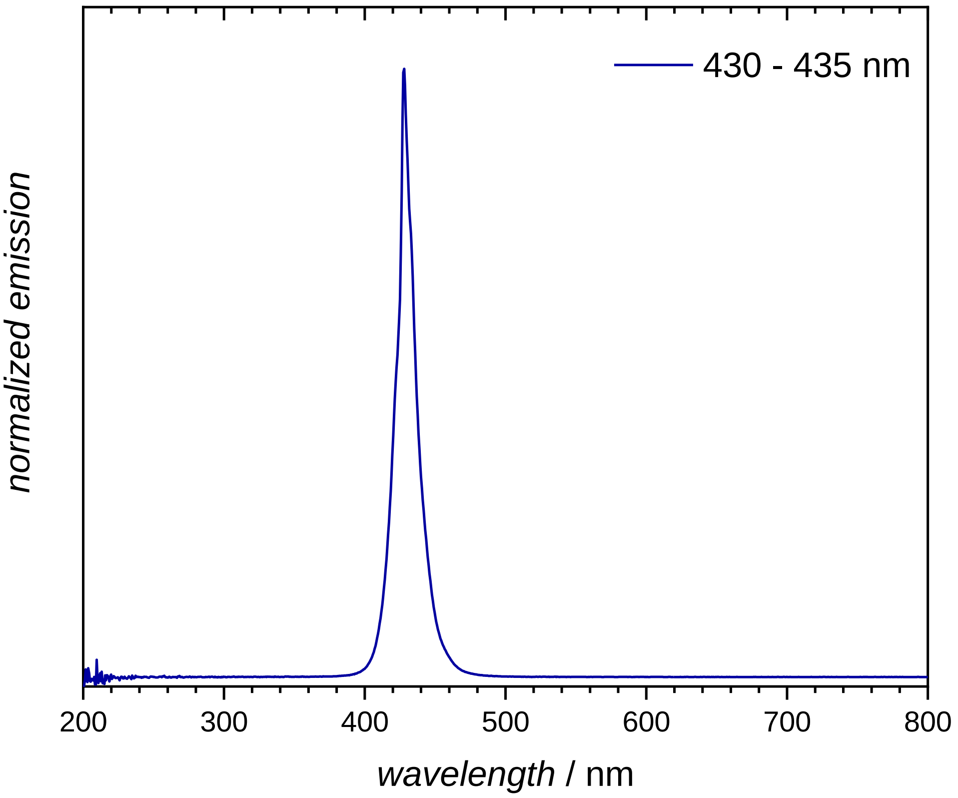


Figure S6 Emission spectrum of the LED setup employed in the current study.

C.4. DOSY NMR Data

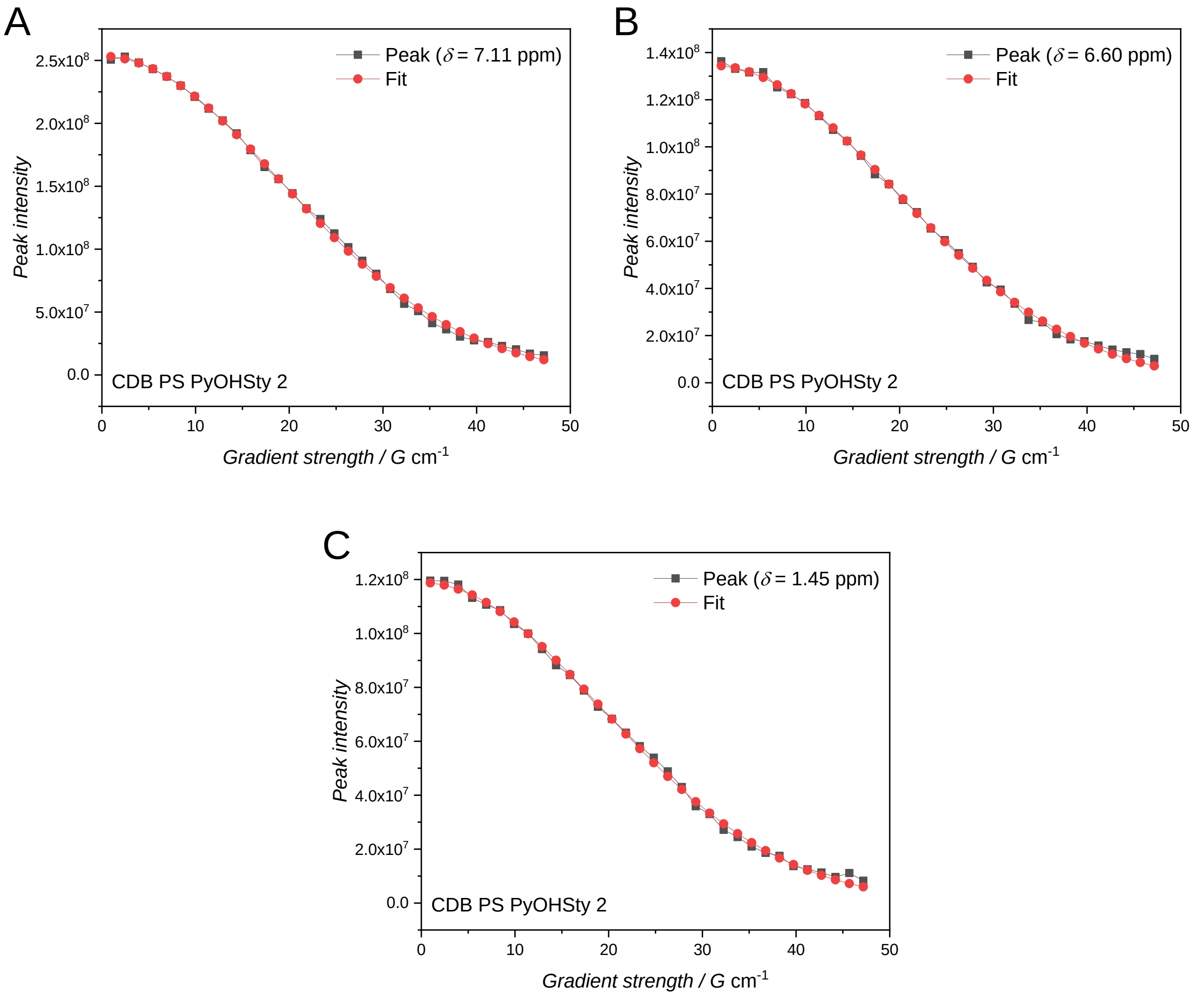


Figure S7 DOSY data fit of the pristine polymeric species **CDB PS PyOHSty 2**.

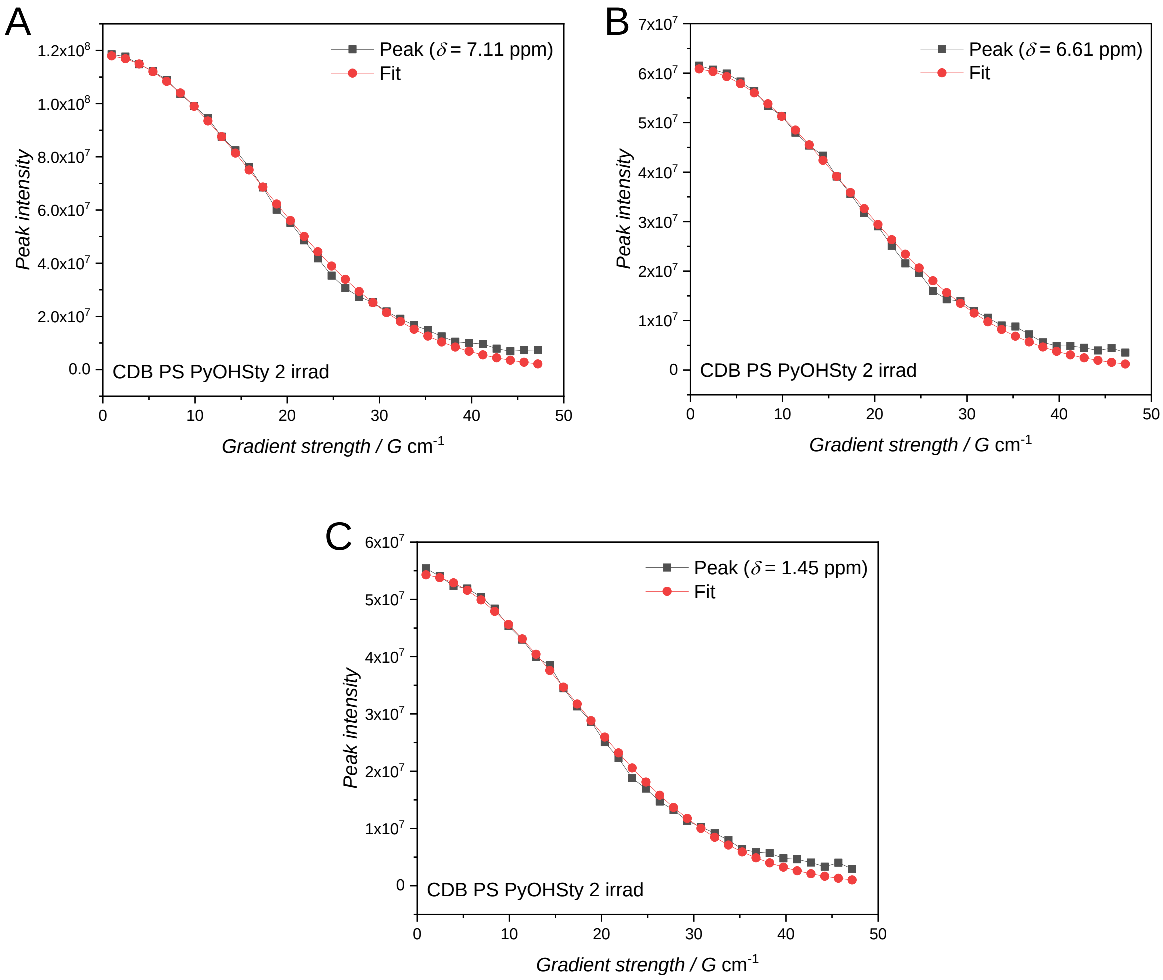


Figure S8 DOSY data fit of **CDB PS PyOHSty 2** after LED irradiation.

Table S2 DOSY NMR (400 MHz, $CDCl_3$, 298 K) results of **CDB PS PyOHSty 2** including diffusion coefficients and diameter of three signals.

Species	***Diffusion Coefficient D/*** **m^{2}s^{-1}**	***Signal/*** **ppm**	***Diameter d/*** **nm**
CDB PS PyOHSty 2	$1.95\ 10^{-10}$	7.11	4.18
	$1.88\ 10^{-10}$	6.60	4.33
	$1.91\ 10^{-10}$	1.45	4.26
CDB PS PyOHSty 2 (irrad)	$2.83\ 10^{-10}$	7.11	2.88
	$2.76\ 10^{-10}$	6.61	2.95
	$2.80\ 10^{-10}$	1.45	2.91

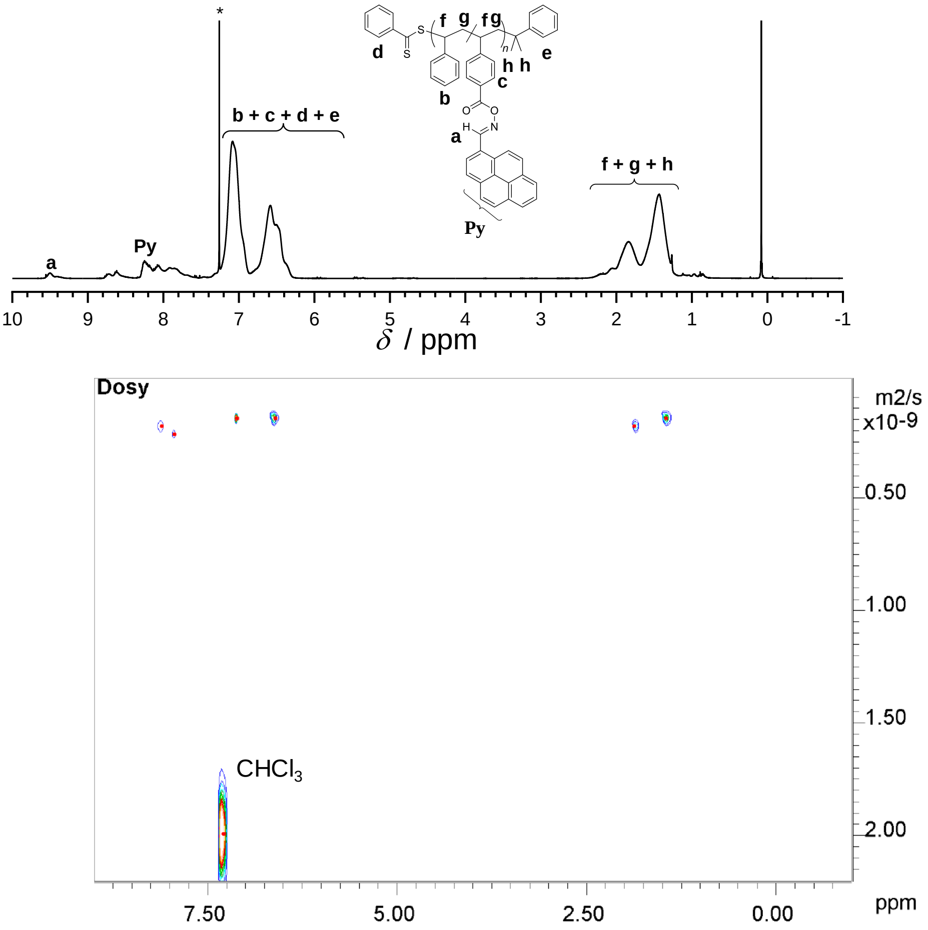


Figure S9 DOSY spectrum (400 MHz, CDCl$_3$, 298 K) of **CDB PS PyOHSty 2**.

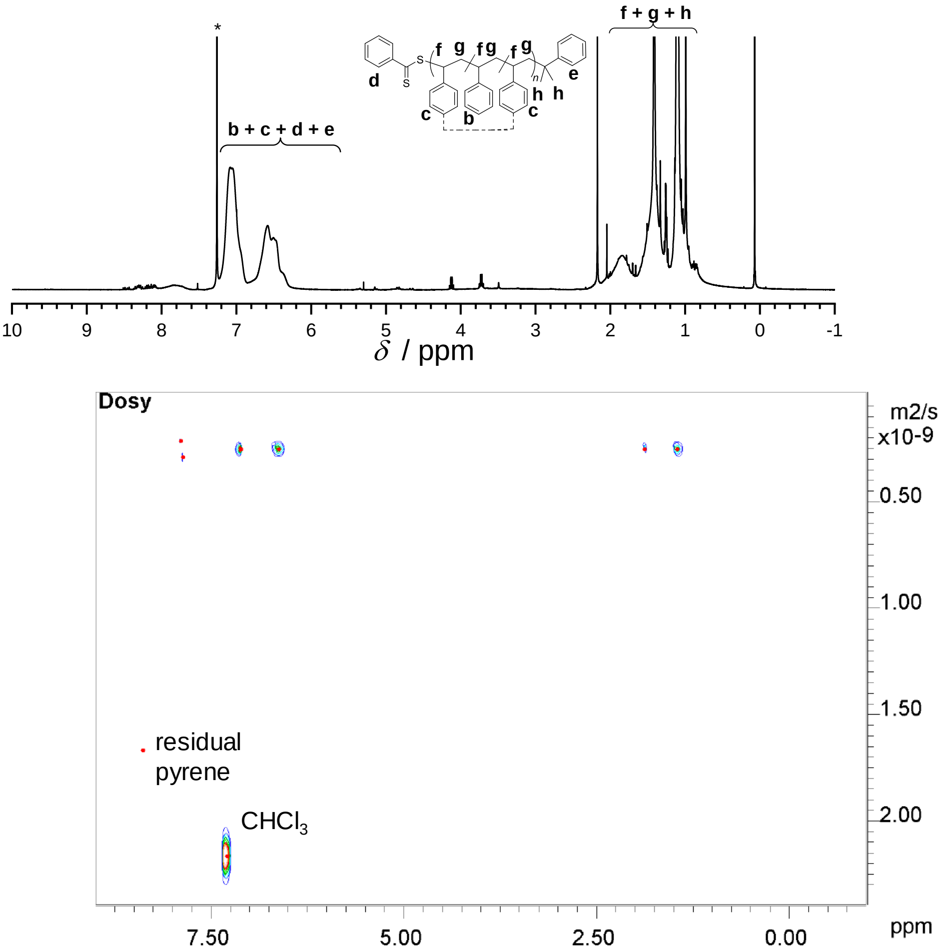


Figure S10 DOSY spectrum (400 MHz, CDCl$_3$, 298 K) of **CDB PS PyOHSty 2** after LED-irradiation.

D. References

[1] J. T. Offenloch, M. Gernhardt, J. P. Blinco, H. Frisch, H. Mutlu, C. Barner-Kowollik, *Chem. Eur. J.* **2019**, *25*, 3700–3709.