

Supporting Information

Photo-Reversible Bonding and Cleavage of Amphiphilic Block Copolymers

Siham Telitel,^b Eva Blasco,^b Lukas D. Bangert,^b Felix H. Schacher,^{*c,d} Anja S. Goldmann,^{*a,b} and Christopher Barner-Kowollik^{*a,b}

^a*School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George Street, QLD 4000, Brisbane, Australia. a.goldmann@qut.edu.au, christopher.barnerkowollik@qut.edu.au*

^b*Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76131 Karlsruhe, Germany. anja.goldmann@kit.edu, christopher.barner-kowollik@kit.edu*

^c*Institute of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstr. 10, 07743 Jena, Germany. felix.schacher@uni-jena.de*

^d*Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany*

Instruments

Nuclear Magnetic Resonance (NMR)

¹H-NMR. All ¹H-NMR spectra were recorded on a Bruker Ascend 400 (400 MHz) spectrometer and 100 MHz (¹³C), respectively. The calibration was carried out using the internal standard from the solvent peak of 400 MHz (¹H). The NMR solvent used was deuterated-chloroform.

DOSY NMR. All spectra were recorded on a Bruker Ascend 400 (400 MHz) spectrometer. The NMR solvent used was deuterated-chloroform. The solutions were prepared with a concentration of 5mg mL⁻¹. All spectra were recorded at 298 K. Processing was achieved using Topspin 3.1 with the Dynamics Center 2.0.4. The resulting diffusion coefficients (D_{DOSY}) of the polymer signals and the solvent are the result of the fitting procedure.

Size Exclusion Chromatography

SEC measurements were performed on a Polymer Laboratories (Varian) PL-GPC 50 Plus Integrated System and a differential refractive index detector using THF as the eluent at 35 °C with a flow rate of 1 mL min⁻¹. Linear poly(styrene) standards ranging from 476 to 2.5·10⁶ g mol⁻¹ and linear poly(methyl methacrylate) standards ranging from 700 to 2·10⁶ g mol⁻¹ were used for the calibration. The resulting molar mass distributions were determined by universal calibration using Mark-Houwink parameters.

Ultraviolet-Visible (UV/Vis) Spectroscopy

UV/Vis spectra were recorded on a Varian Cary 300 spectrometer with a range from 200 nm to 500 nm. All samples were dissolved in toluene and filled in 1 cm quartz cuvettes.

Tunable Laser System

Laser 270 nm: Laser system Innolas SpitLight 600 OPO laser system operated by a diode-pumped Nd:YAG-laser and use an Optical Parametric Oscillator (OPO) to produce a tunable output between 410 to 670 nm and a second modular unit between 270 to 410 nm. The maximum output energy is about 8 – 15 mJ in the visible range and 1.3 - 2.5 mJ in the UV range.

Electrospray Ionisation Mass Spectrometry (ESI MS)

ESI-MS (Electrospray Ionization Mass Spectrometry) was performed on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument calibration was carried out in the m/z range 74 – 1822 using calibration solutions from Thermo Scientific. A constant spray voltage of 4.7 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 62.0, respectively. The samples were dissolved on a THF:MeOH mixture (3:2) containing 100 μmol of sodium triflate and injected with a flow of 5 $\mu\text{L}\cdot\text{min}^{-1}$.

Materials

9-Anthracenemethanol (Sigma Aldrich, 97%), 2-bromoisobutyl bromide (Alfa Aesar, 97%), Copper(I) bromide (CuBr, Fluka), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA; Sigma Aldrich 99 %), *d*-chloroform (CDCl_3 ; Sigma Aldrich, 99.8 %), dry tetrahydrofuran (THF; Acros Organics, AcrosSeal®, 99.95). All chemicals were purchased from Sigma Aldrich and used as received. Copper(I)bromide was purified by sequential washing with acetic acid, ethanol, and diethyl ether, followed by drying under reduced pressure and stored under inert gas. Styrene and butyl acrylate were purchased from Sigma Aldrich and the inhibitors were removed by passing through a basic alumina column.

Synthesis

Synthesis of 9-anthrylmethyl 2-bromo-2-methyl propanoate

The synthesis was adapted from reference 1.

9-anthracenemethanol (1 g, 4.8 mmol, 1 eq) and triethylamine (0.98 mL, 0.72 g, 7 mmol, 1.45 eq) were dissolved in 20 mL dry THF. The solution was cooled in an ice bath. A solution of 0.87 mL 2-bromoisobutyl bromide (1.62 g, 7 mmol, 1.45 eq) in 10 mL of dry THF was added dropwise under nitrogen atmosphere. The ice bath was removed and the reaction was stirred at ambient temperature overnight. The precipitate was filtered off and the solvent was evaporated. The raw product was dissolved in dichloromethane, subsequently washed with NaHCO_3 solution, and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the yellow oil was recrystallized from hexane to yield 9-anthrylmethyl 2-bromo-2-methyl propanoate (1.49 g, 4.18 mmol, 87%) as light yellow crystals.

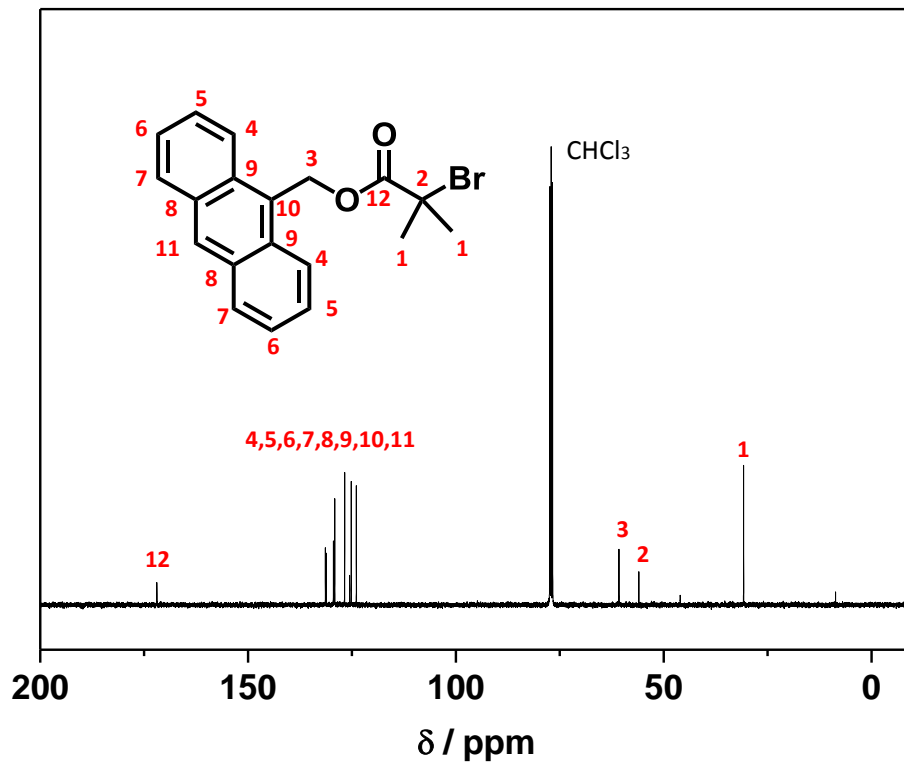
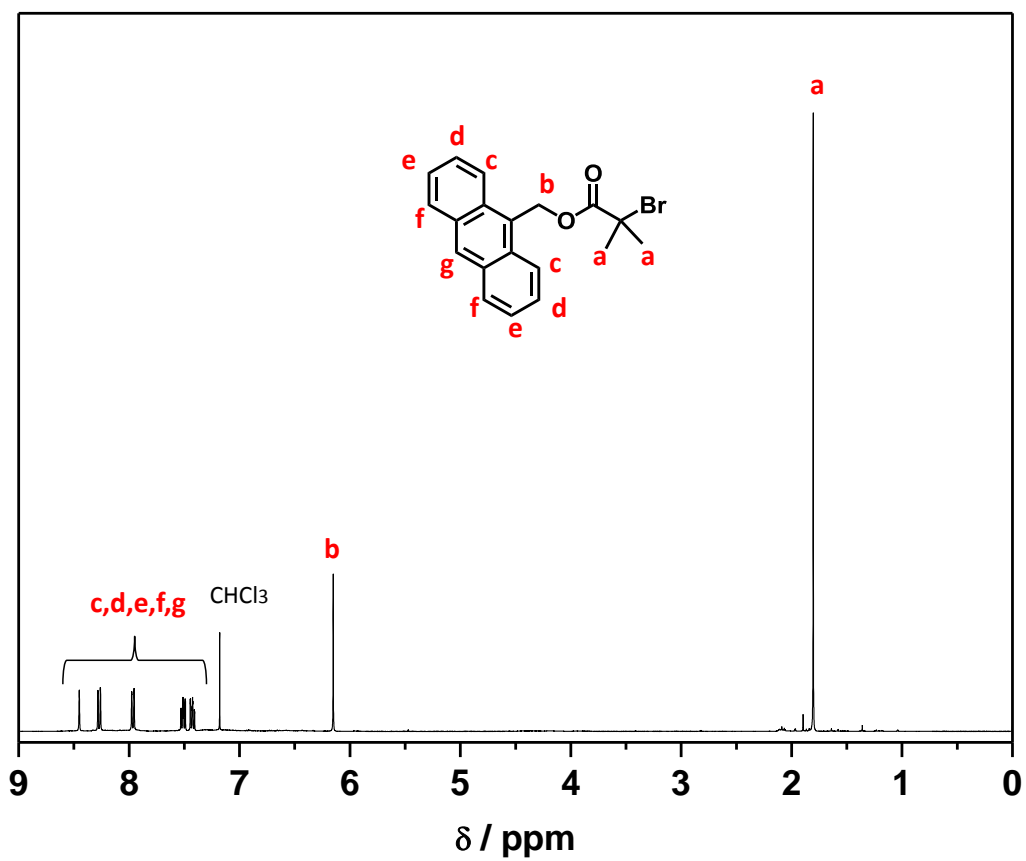
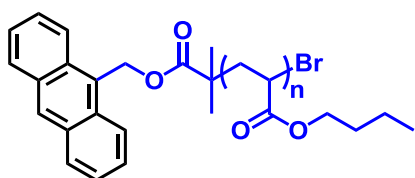


Fig. S1 $^1\text{H NMR}$ (Top) and $^{13}\text{C NMR}$ (Bottom) spectra of the ATRP initiator 9-anthrylmethyl 2-bromo-2-methyl propanoate.¹

Synthesis of Anthracene Functionalized Poly(*n*-butyl acrylate) (PBA)

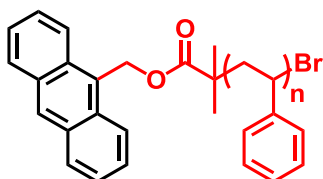
This synthesis procedure is adapted from reference 2.



In a Schlenk tube, 9-anthrylmethyl 2-bromo-2-methyl propanoate (78 mg, 0.219 mmol), PMDETA (46 μ L, 38.2 mg, 0.219 mmol) and Cu(I)Br (31.3 mg, 0.219 mmol) were dissolved in *n*-butylacrylate (6.27 mL, 5.61 g, 43.7 mmol) and deoxygenated by three freeze-pump-thaw cycles. The polymerization reaction was performed at 110°C under nitrogen atmosphere. After 15 min the reaction was quenched by cooling in an ice bath and the solution was precipitated in a methanol/water mixture. The polymer was then dissolved in THF and purified by passing through a short alumina column. The polymer was dried under vacuum. The molecular mass was determined by SEC (PMMA calibration).

Synthesis of Anthracene Functionalized Polystyrene (PS)

This synthesis procedure is adapted from reference 2.



In a Schlenk tube, 9-anthrylmethyl 2-bromo-2-methyl propanoate (78 mg, 0.219 mmol), PMDETA (46 μ L, 38.2 mg, 0.219 mmol) and Cu(I)Br (31.3 mg, 0.219 mmol) were dissolved in styrene (5.0 mL, 4.54 g, 43.7 mmol) and deoxygenated by three freeze-pump-thaw cycles. The polymerization reaction was performed at 110°C under nitrogen atmosphere. After 40 min the reaction was quenched by cooling in an ice bath and the solution was precipitated in methanol. The polymer was then dissolved in THF and purified by passing through a short alumina column. The polymer was dried under vacuum. The molecular mass was determined by SEC (PS calibration).

Table S1: Reaction conditions for the synthesis of polystyrene and poly(*n*-butyl acrylate), *T*: 110°C (^aPS calibration, ^bPMMA calibration)

Polystyrene (PS)						Poly(<i>n</i> -butyl acrylate) (PBA)					
Label	Time [min]	$M_{n,NMR}$ [$g \cdot mol^{-1}$]	$M_{n,SEC}^a$ [$g \cdot mol^{-1}$]	M_n^b [$g \cdot mol^{-1}$]	\mathcal{D}	Label	Time [min]	$M_{n,NMR}$ [$g \cdot mol^{-1}$]	$M_{n,SEC}^a$ [$g \cdot mol^{-1}$]	M_n^b [$g \cdot mol^{-1}$]	\mathcal{D}
PS ₂₂₀₀	40	2,500	2,200	2,600	1.11	PBA ₁₂₀₀	10	1,300	1,200	1,500	1.55
PS ₃₂₀₀	60	2,900	3,200	2,600	1.12	PBA ₃₄₀₀	13	3,800	3,400	4,200	1.26
						PBA ₄₃₀₀	15	3,700	4,300	3,000	1.34

^arelative to the molecular weight (M_n) determined by SEC.

^b M_n determined by using Lambert-Beer's law: $A = \epsilon \cdot l \cdot c$ and molar extinction coefficient of anthracene ($\epsilon_{351nm} = 3,600 \text{ mol} \cdot \text{L}^{-1} \cdot \text{cm}^{-1}$). Please refer to the calculations below.

$$A = \varepsilon \cdot l \cdot c \quad (1)$$

l: path length (cm)

A: absorbance

c: concentration ($\text{mol} \cdot \text{L}^{-1}$)

ε : molar extinction coefficient of anthracene ($\text{mol} \cdot \text{L}^{-1} \cdot \text{cm}^{-1}$)

$$c = \frac{n}{V} \Rightarrow c = \frac{m}{M_n \cdot V} \quad (2)$$

V: volume of solvent (L)

m: masse of polymer (g)

M_n : molecular weight ($\text{g} \cdot \text{mol}^{-1}$)

$$A = \frac{\varepsilon \cdot l \cdot m}{M_n \cdot V} \Rightarrow M_n = \frac{\varepsilon \cdot l \cdot m}{A \cdot V} \quad (3)$$

Photoreactions

Philips PL-L: The respective polymers were dissolved in benzene (respectively at $c = 6 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ for the preparation of the homopolymers (PS-PS and PBA-PBA) as well as $c_{\text{PS}} = 1 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $c_{\text{PBA}} = 6 \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ for the preparation of the block copolymers) in a headspace vial (Pyrex, diameter 20 mm) which was crimped airtight. The solution was deoxygenated by purging with nitrogen. The flask was irradiated under stirring by revolving around a 36 W compact low-pressure fluorescent lamp (Philips PL-L, $\lambda_{\text{max}} = 350 \text{ nm}$, see **Fig. S2 right**) at a distance of 40-50 mm in a custom built photo reactor (see **Fig. S2 left**). The reaction was stopped after 5 h of irradiation. Then, the benzene was removed by evaporation and the polymer was redissolved in THF and analyzed by SEC.

Laser 270 nm: The homopolymer/block copolymer were redissolved in benzene and deoxygenated. The flask was irradiated 3h at $\lambda_2 = 270 \text{ nm}$, 4 mW (100 Hz) using Innolas SpitLight 600 OPO. The sample was analyzed by SEC after the evaporation of the benzene.

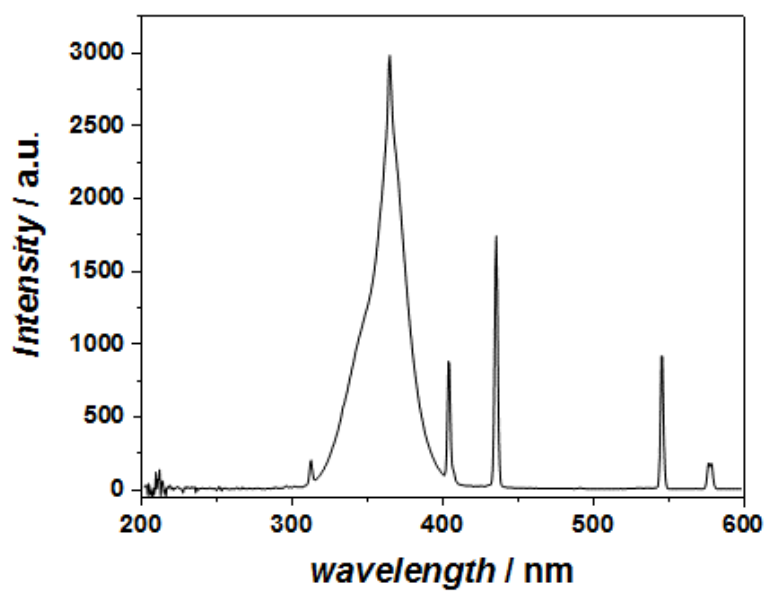
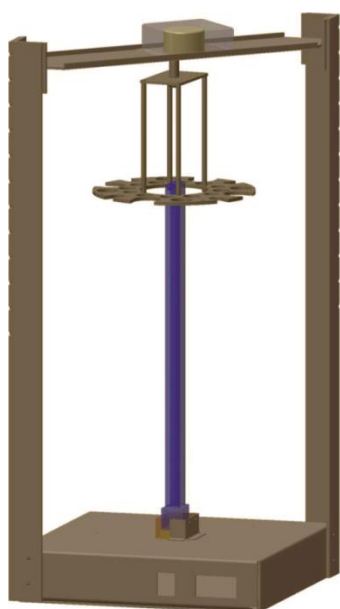


Fig. S2 Left: Schematic setting of the photo-reactor. The lamp is located in the middle (blue). The samples are situated in the wheel-shaped disc in the upper part of the reactor, which rotates while the samples are irradiated. The picture was drawn by Till Gruending. Right: Emission spectra of the used Philips PL-L lamp, $\lambda_{max} = 350$ nm.

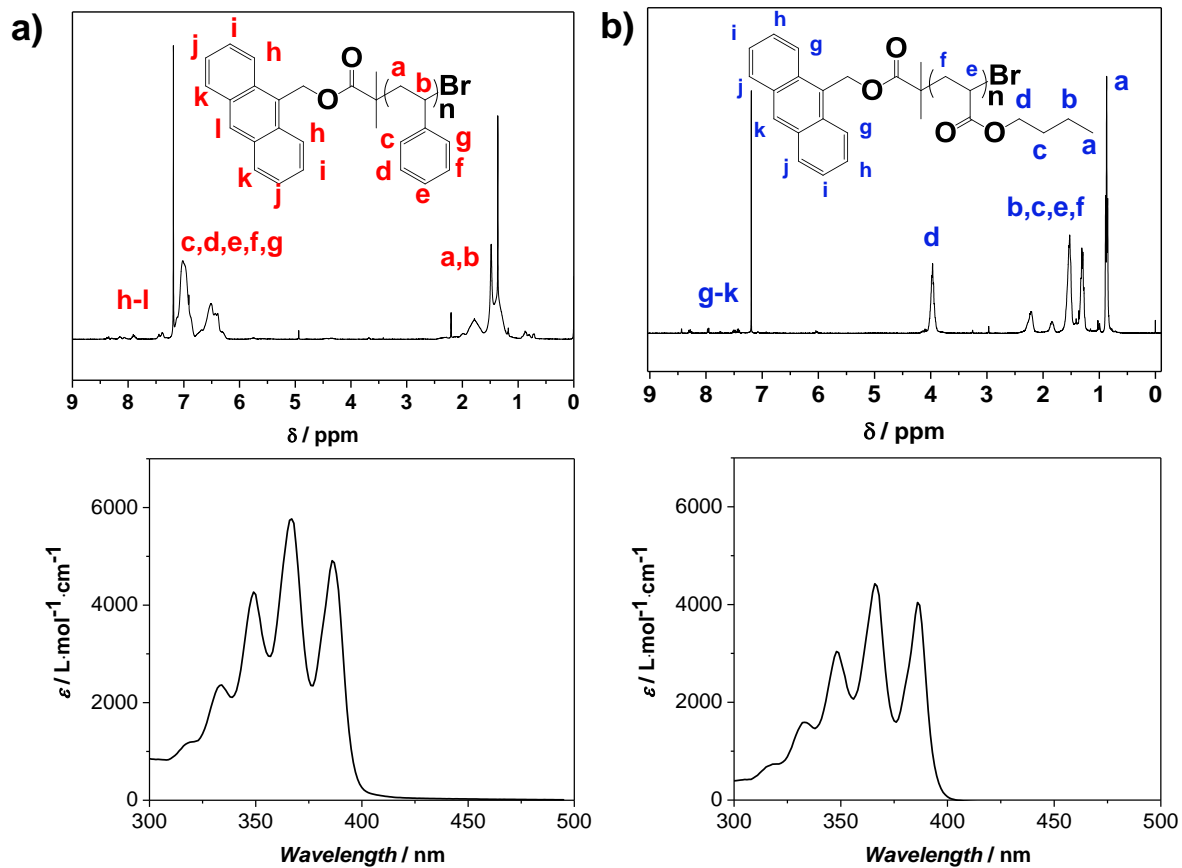
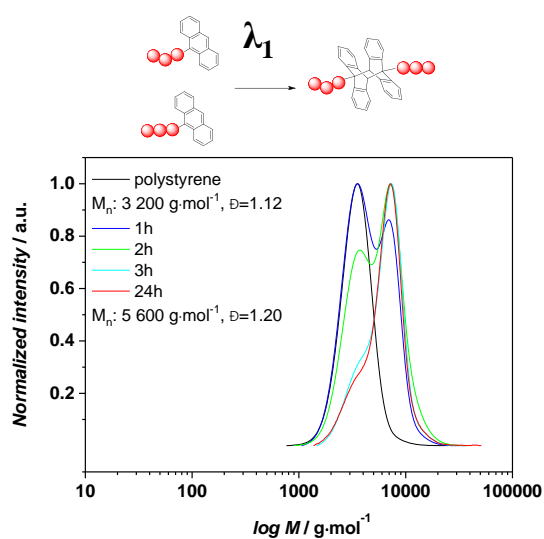
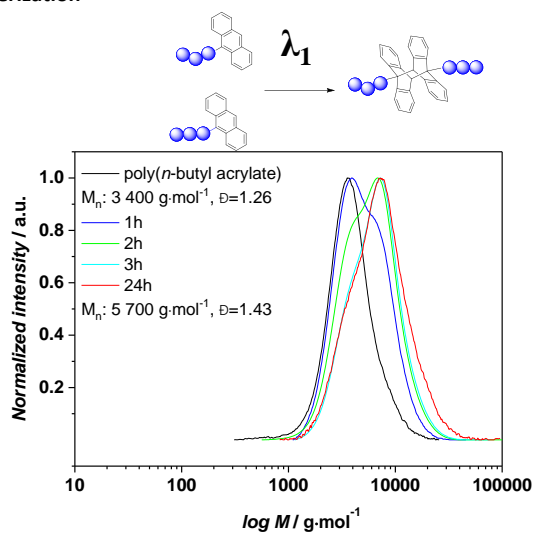


Fig. S3 $^1\text{H-NMR}$ and UV/visible spectra of a) PS₂₂₀₀, $M_n = 2,200 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D} = 1.11$. b) PBA₄₃₀₀, $M_n = 4,300 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D} = 1.34$. Calibration with PS and PMMA standard.

a) dimerization



b) reverse reaction

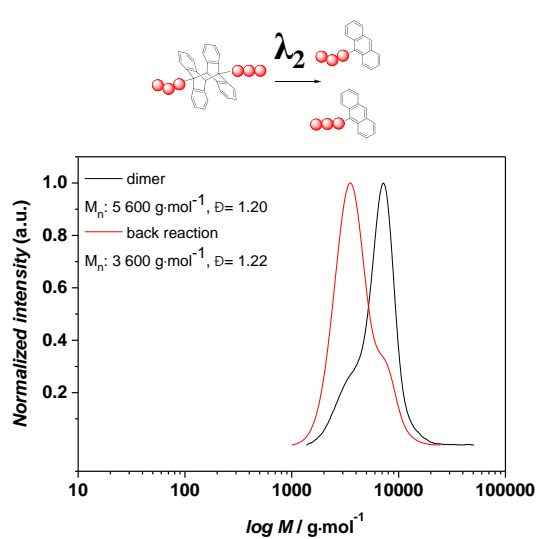
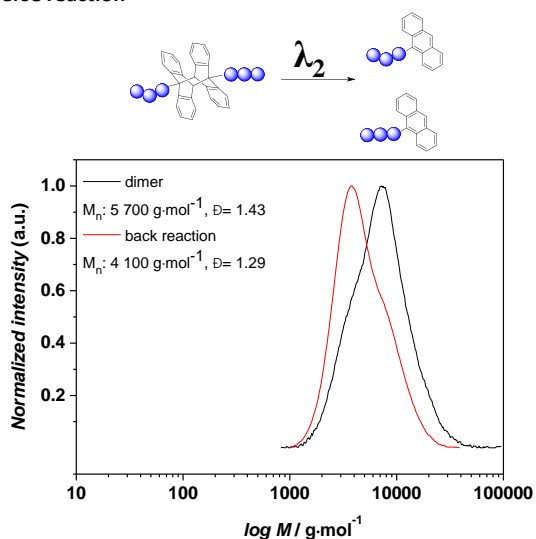


Fig. S4 Kinetic investigations of the homocoupling anthracene dimerization reactions of PBA (left) and PS (right) (a) forward reaction at $\lambda_1 = 350$ nm; (b) back reaction at $\lambda_2 = 270$ nm.

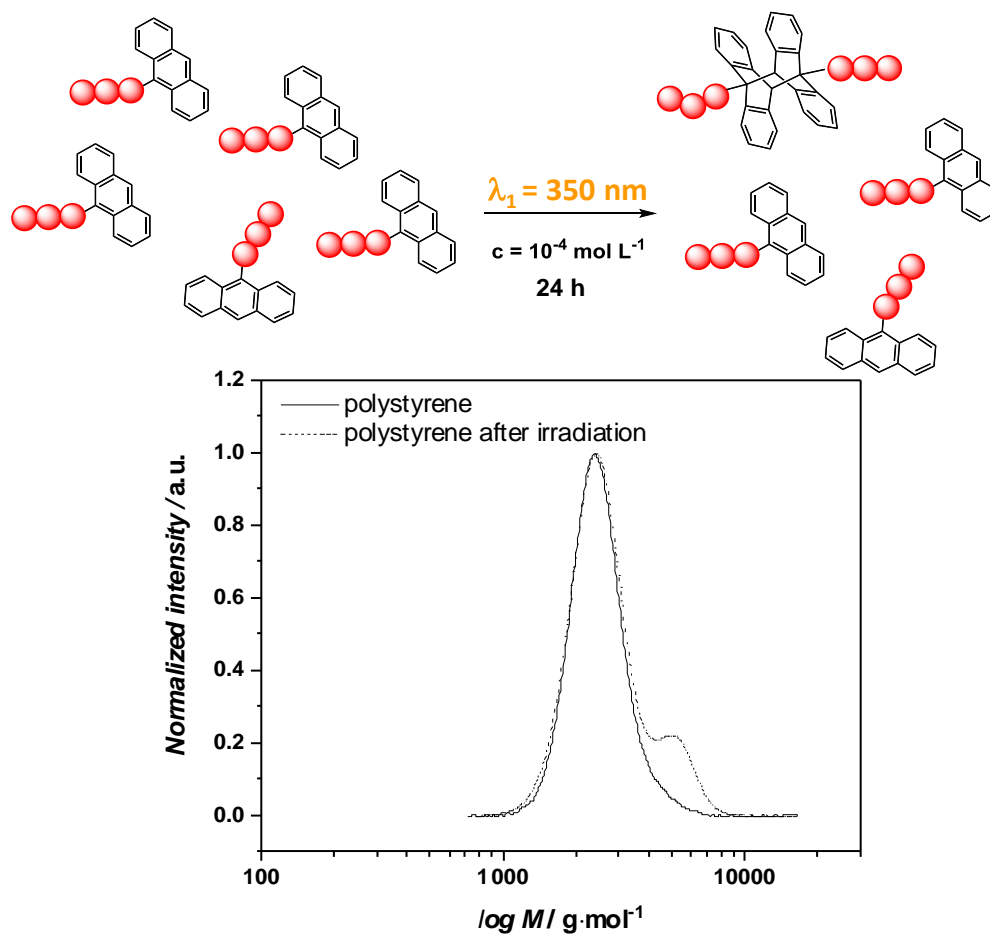


Fig. S5 Test reaction of the dimerization of PS₂₅₀₀ irradiated at 350 nm, $c = 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ in benzene under N₂, $M_n = 2,400 \text{ g}\cdot\text{mol}^{-1}$, $\mathcal{D} = 1.08$; $M_{n,\text{PS}} = 2,500 \text{ g}\cdot\text{mol}^{-1}$, $\mathcal{D} = 1.14$ after 24h of irradiation at $\lambda = 350 \text{ nm}$.

Table S2 Molecular weights (M_n), polydispersities (\mathcal{D}) and diffusion coefficients (D_{DOSY}) of PS, PBA and the resulting block copolymer after irradiation at $\lambda_{\text{max}} = 350 \text{ nm}$.

Entry	Polymer	$M_{n,\text{SEC}}$ [$\text{g}\cdot\text{mol}^{-1}$]	\mathcal{D}	Diffusion coefficient D_{DOSY} [$\text{m}^2\cdot\text{s}^{-1}$]
1	PBA ₄₃₀₀	4,300	1.34	$2.30\cdot 10^{-10}$
2	PS ₂₂₀₀	2,200	1.11	$3.50\cdot 10^{-10}$
3	PS ₂₂₀₀ - <i>b</i> -PBA ₄₃₀₀	7,000	1.46	$1.65\cdot 10^{-10}$
4	PBA ₁₂₀₀	1,200	1.55	$3.40\cdot 10^{-10}$
5	PS ₂₂₀₀	2,200	1.11	$3.50\cdot 10^{-10}$
6	PS ₂₂₀₀ - <i>b</i> -PBA ₁₂₀₀	3,500	1.15	$2.50\cdot 10^{-10}$

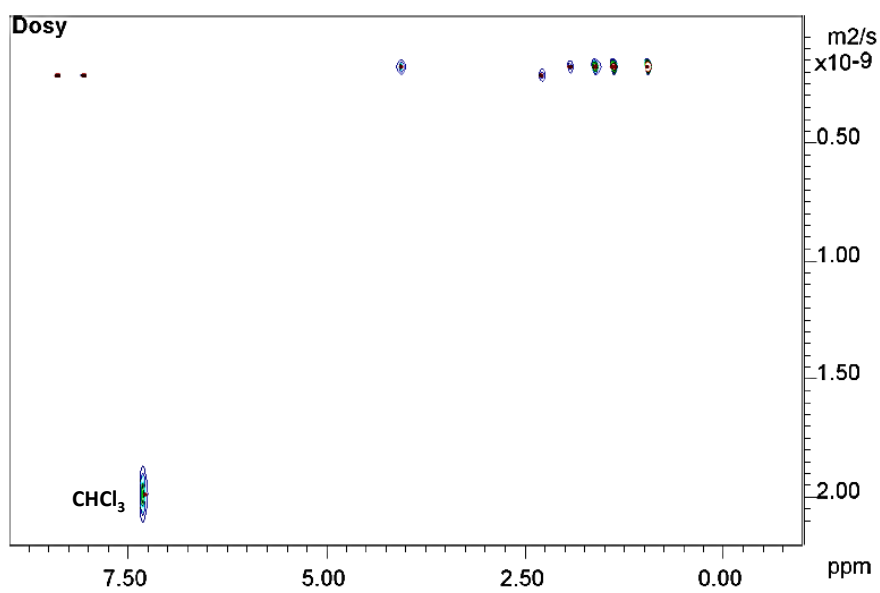
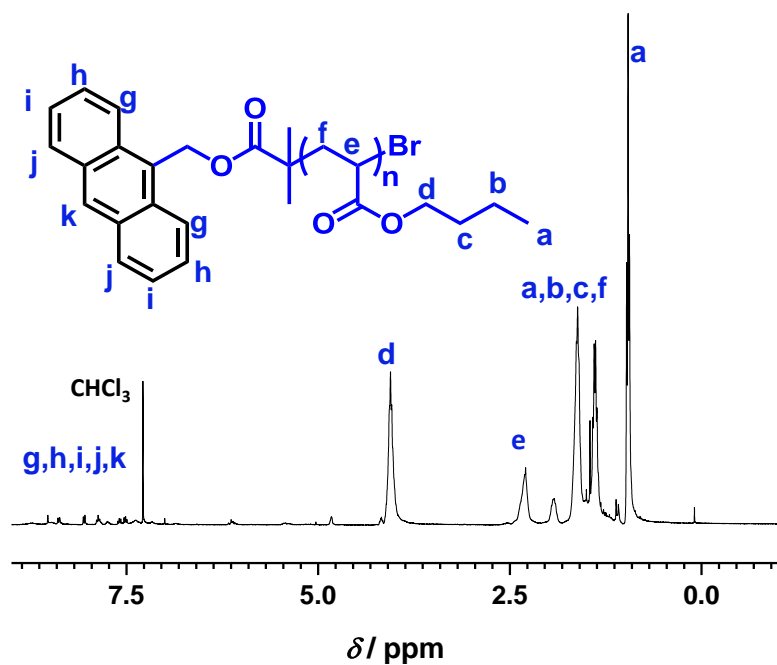


Fig. S6 DOSY spectrum of PBA₄₃₀₀, $M_n = 4,300 \text{ g}\cdot\text{mol}^{-1}$, $D = 1.34$, $D_{\text{DOSY}} = 2.30 \cdot 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$.

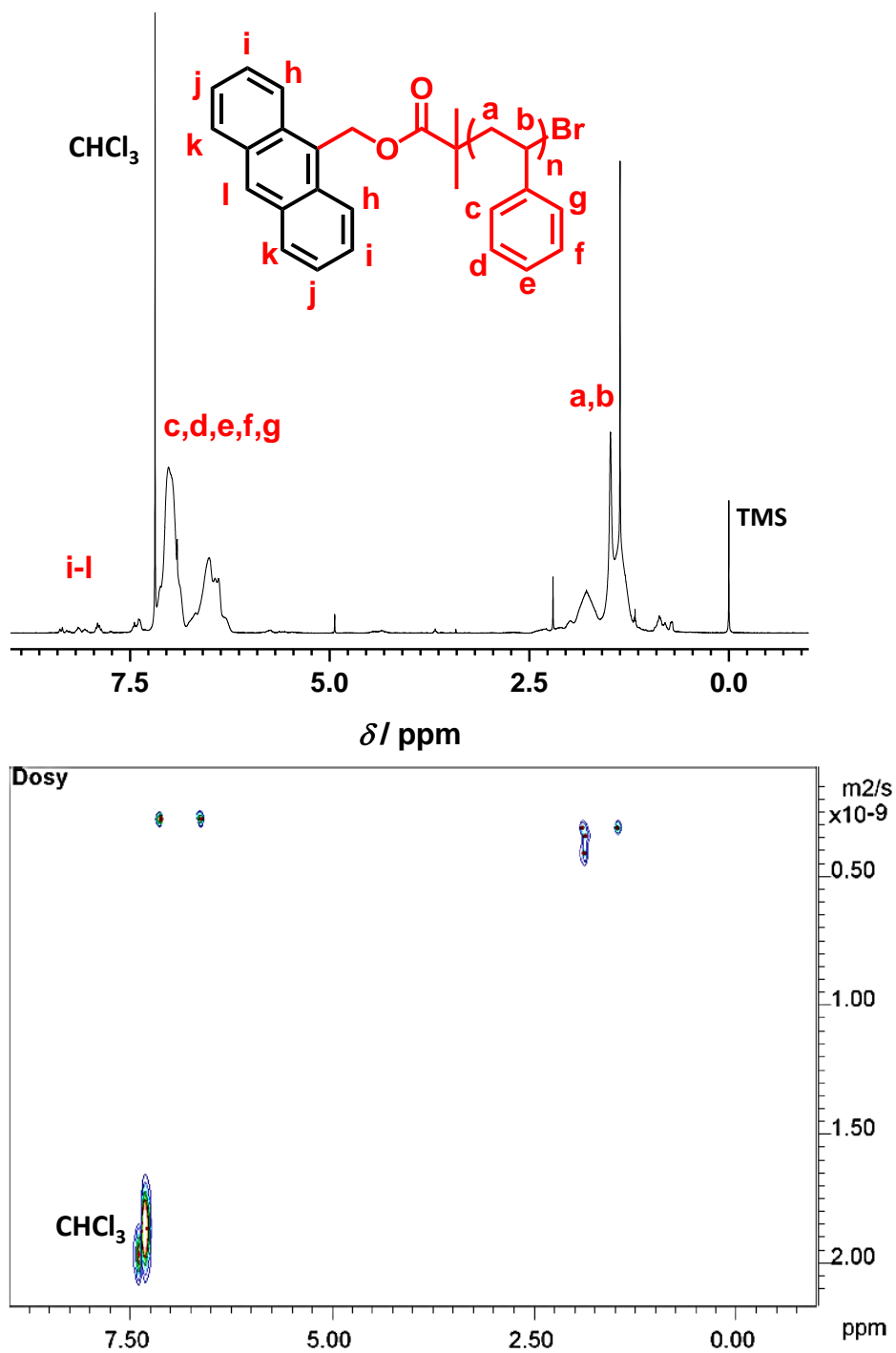


Fig. S7 DOSY spectrum of PS₂₂₀₀, $M_n = 2,200 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D} = 1.11$, $D_{\text{DOSY}} = 3.20 \cdot 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$.

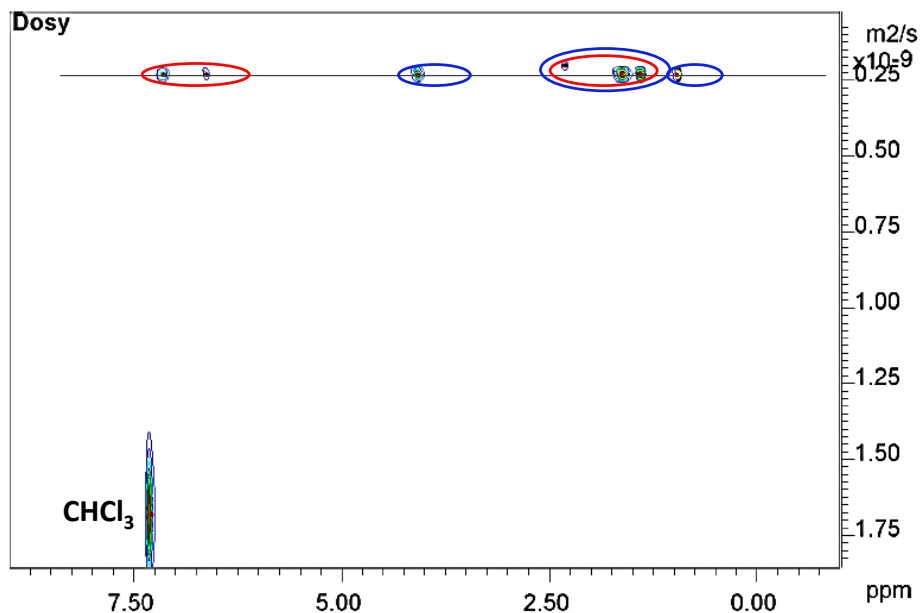
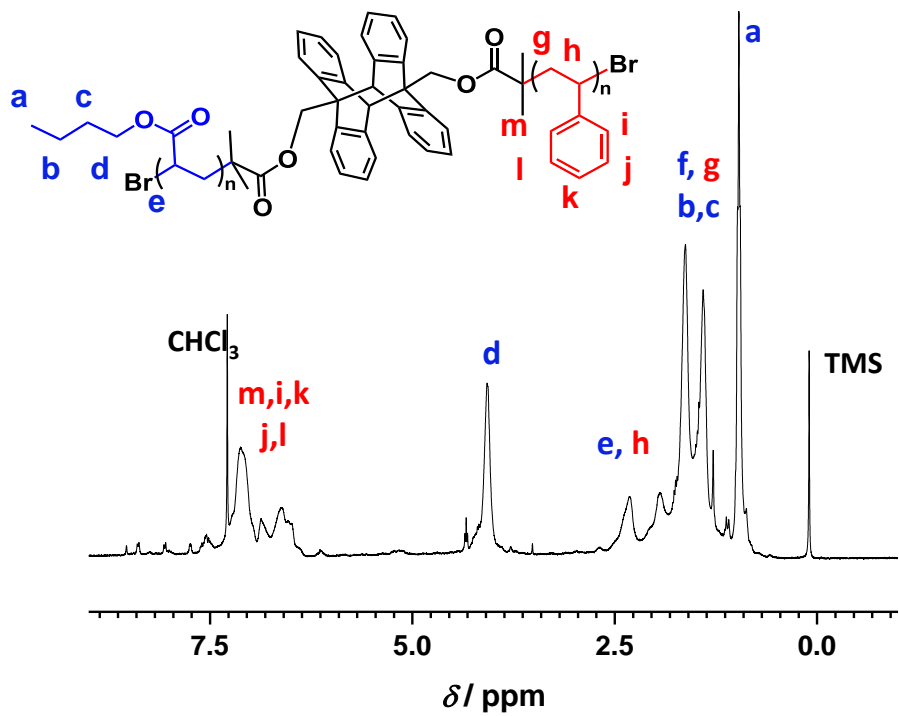


Fig. S8 DOSY spectrum of PS₂₂₀₀-*b*-PBA₁₂₀₀, $M_n = 3,500 \text{ g}\cdot\text{mol}^{-1}$, $\bar{D} = 1.15$, $D_{\text{DOSY}} = 2.50 \cdot 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$.

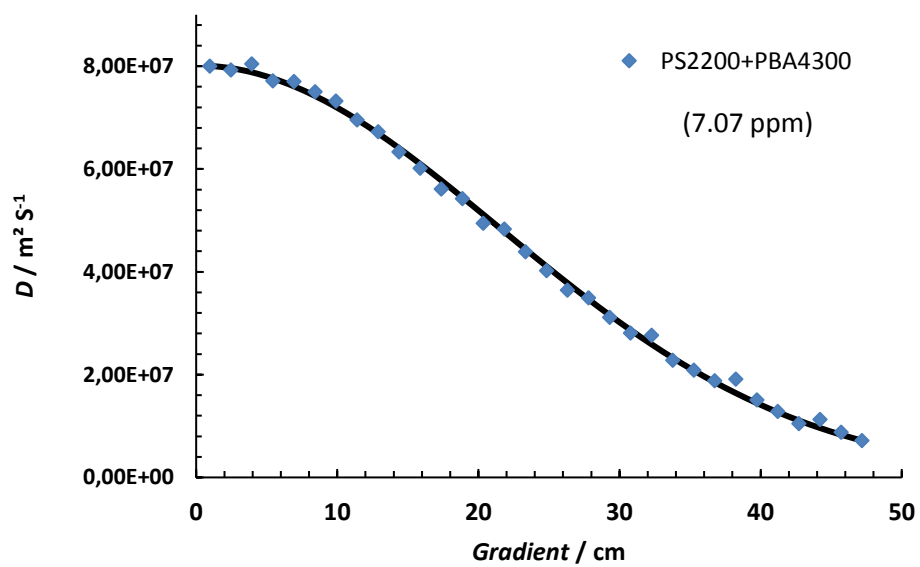
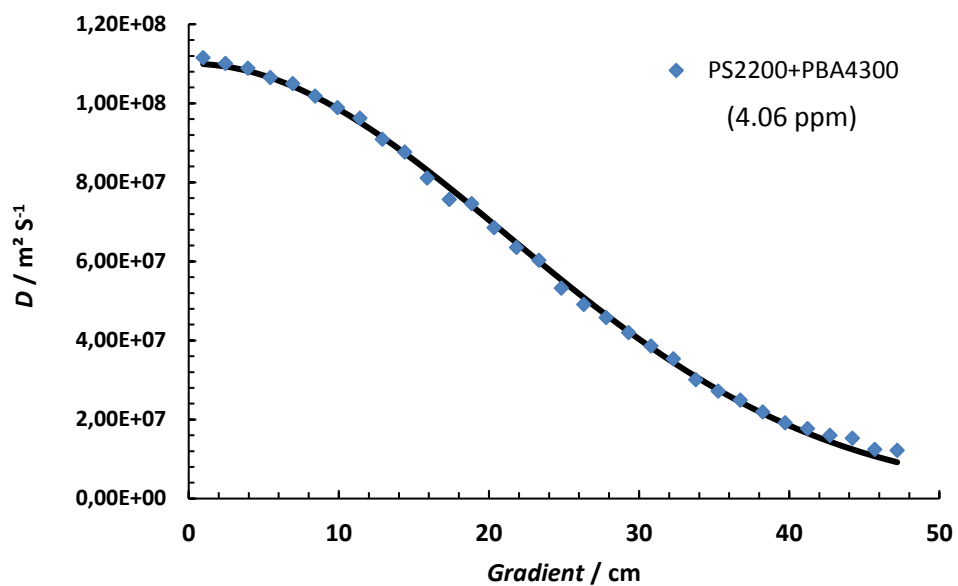


Fig. S9 Exemplary DOSY data fit PS₂₂₀₀-*b*-PBA₄₃₀₀, $D_{\text{DOSY}} = 1.65 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, M_n : 7,000 g·mol⁻¹, \bar{D} =1.46.

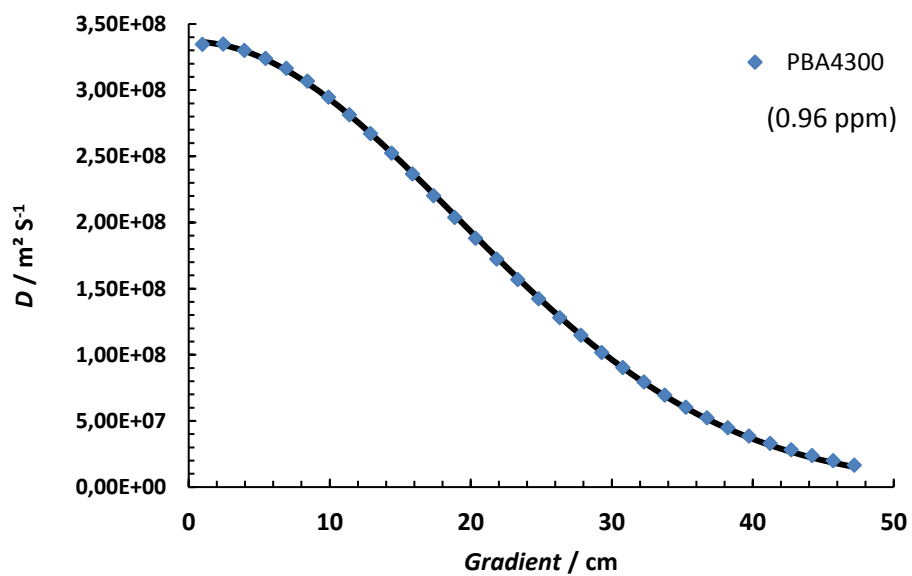
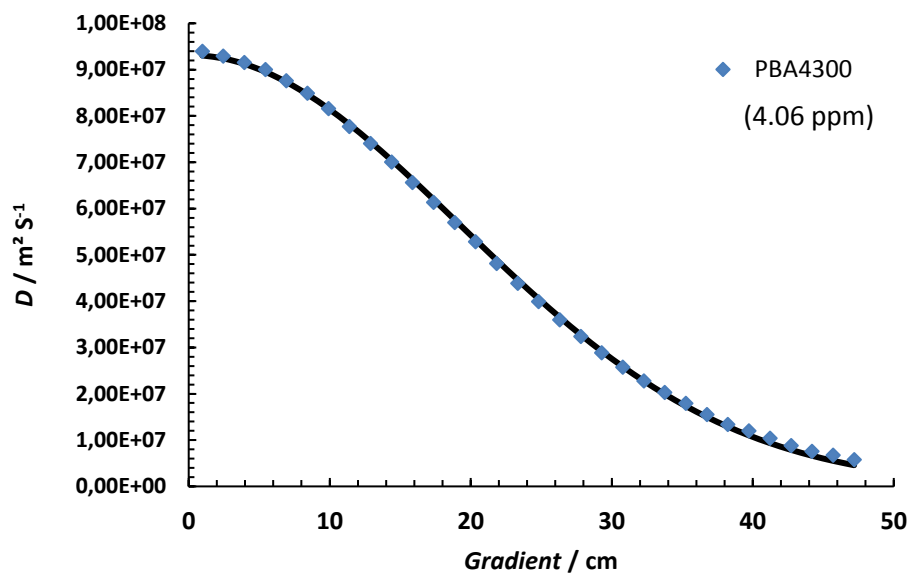


Fig. S10 Exemplary DOSY data fit of PBA₄₃₀₀ M_n : 4,300 g·mol⁻¹, \bar{D} =1.34, D^{DOSY} (PBA₄₃₀₀) = 2.30·10⁻¹⁰ m²·s⁻¹.

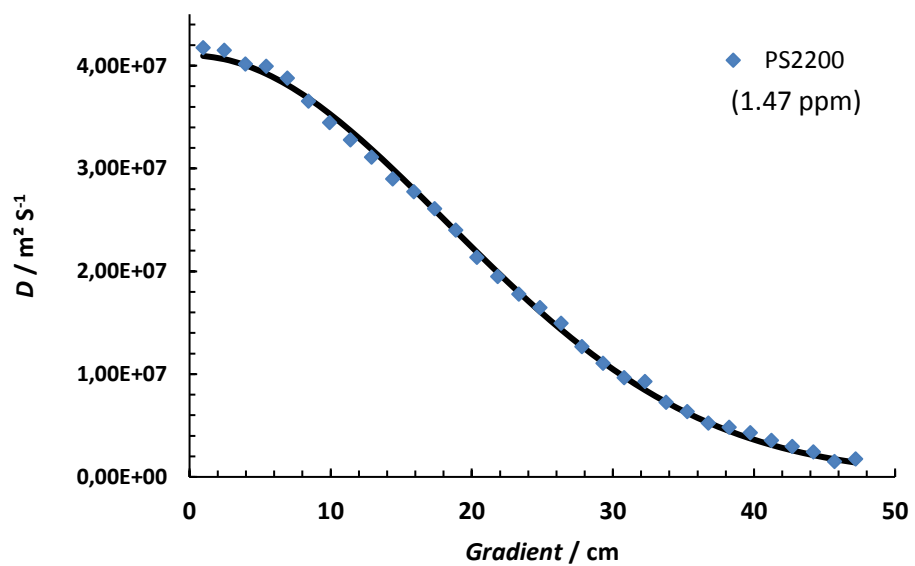
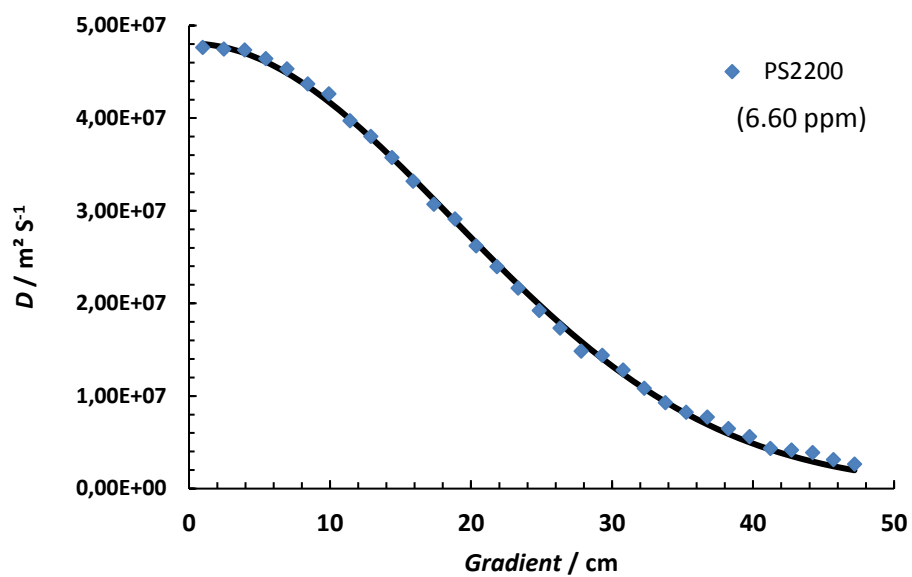


Fig. S11 Exemplary DOSY data fit of PS₂₂₀₀, $D^{\text{DOSY}}(\text{PS}_{2200}) = 3.20 \cdot 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$, M_n : 2,200 g·mol⁻¹, $\bar{D}=1.11$.

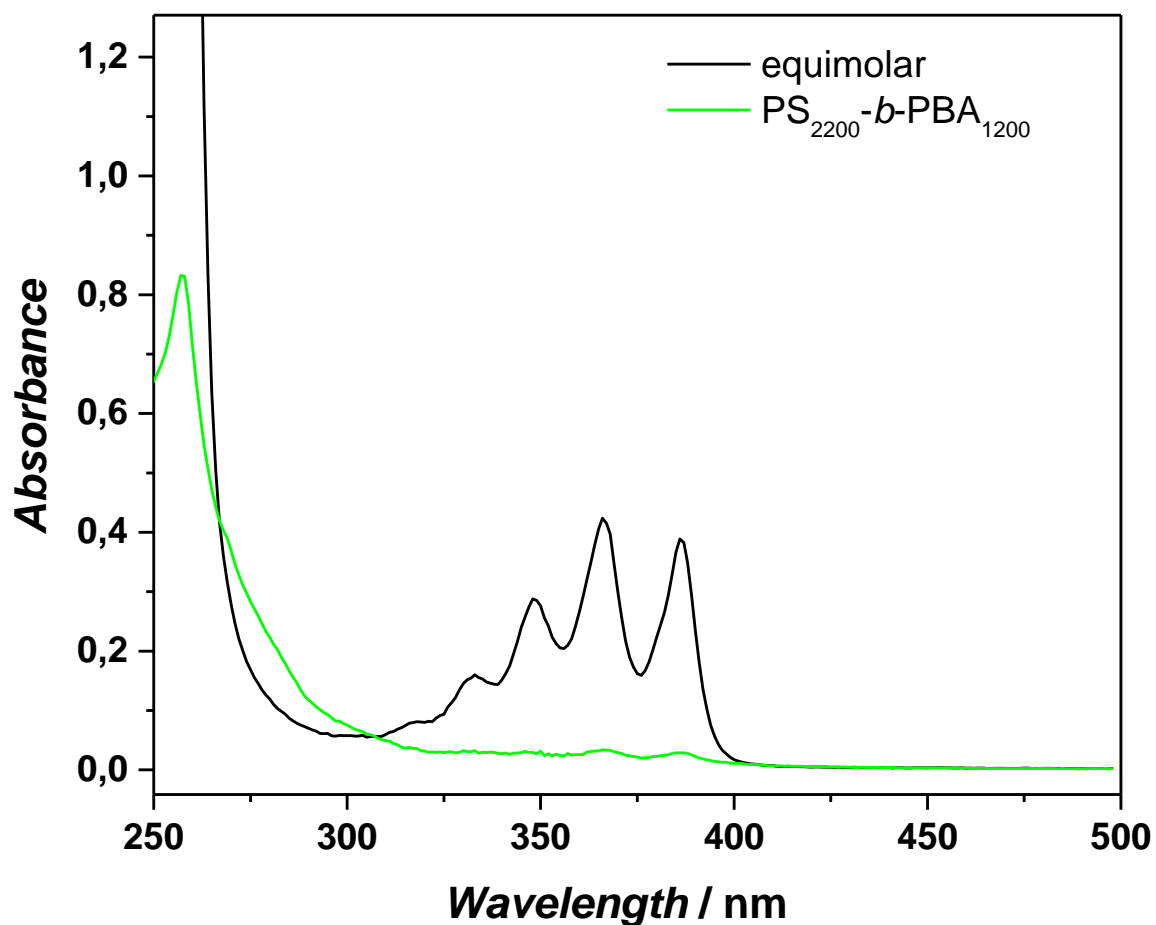


Fig. S12 Comparison of the absorbance spectra of PS₂₂₀₀-*b*-PBA₁₂₀₀ (green) and the physical mixture of PS₂₂₀₀ and PB₁₂₀₀ (black) at a concentration of 0.75 mol·L⁻¹, respectively.

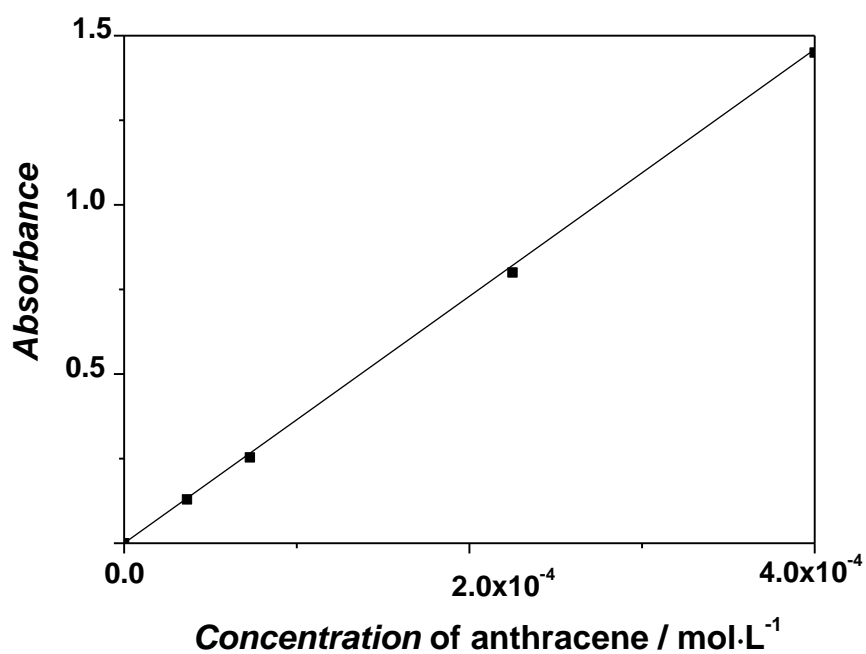
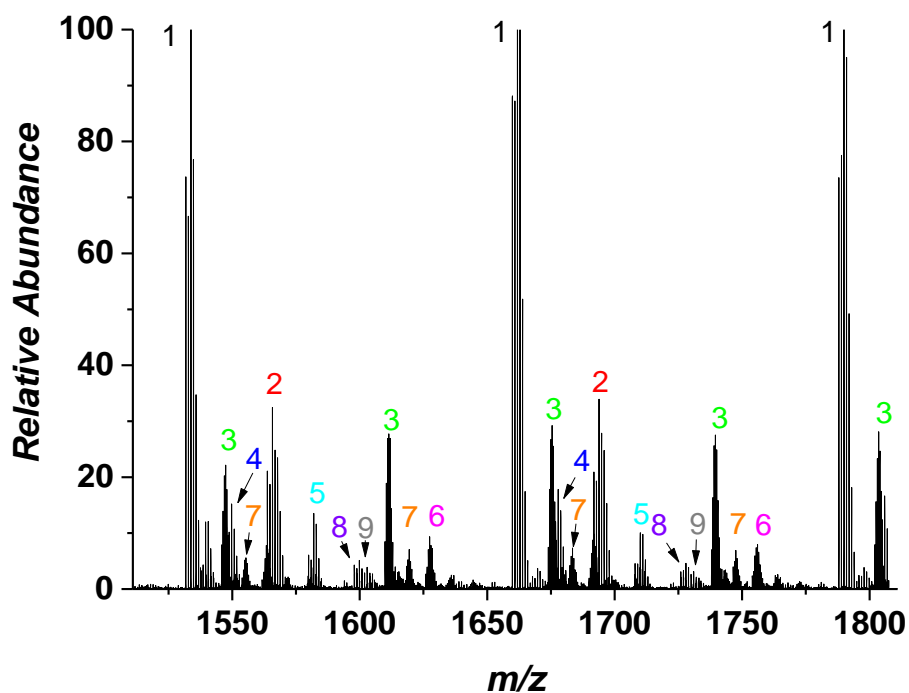


Fig. S13 Calibration curve to quantify the percentage of anthracene moieties per polymer chain.



Label	Resolution	m/z (exp)	m/z (theo)	$\Delta m/z$	Structure
1	55000	1661.8748	1661.8687	0.0061	
2	52000	1693.8661	1693.8585	0.0076	
3	53000	1739.5223	1739.5175	0.0048	
4	54000	1711.0480	1711.0443	0.0037	
5	52000	1755.5193	1755.5124	0.0069	

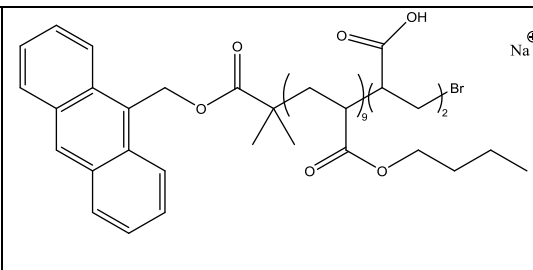
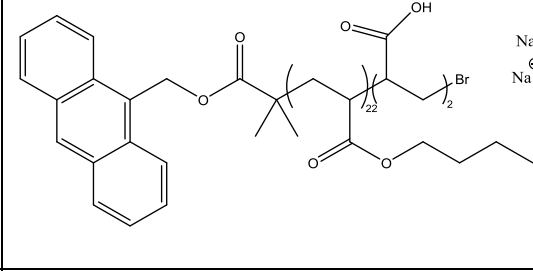
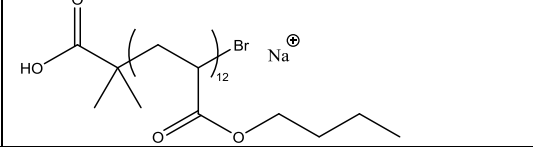
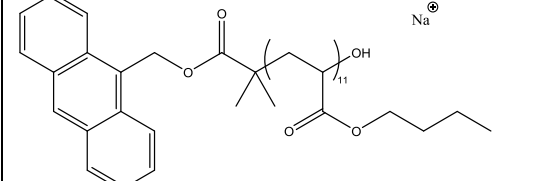
6	53000	1677.8473	1677.8272	0.0201	
7	53000	1683.4675	1683.4548	0.0127	
8	52000	1727.9634	1727.9581	0.0053	
9	42000	1727.0385	1727.0393	0.0008	

Fig. S14 Mass spectrometric analysis of the starting homopolymer PBA₁₂₀₀ showing the expected repeating units of PBA carrying the anthracene endgroup. The peak assignments are shown in the table below.

References

¹Erdoğan, M.; Hizal, G.; Tunca, Ü.; Hayrabetyan, D.; Pekcan, Ö. *Polymer* **2002**, *43*, 1925.

²Claus, T. K., Telitel, S., Welle, A., Bastmeyer, M., Vogt, A., Delaittre, G., Barner-Kowollik, C. *Chem. Commun.* **2017**, *53*, 1599.