Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information to

Light Induced Polyethylene Ligation

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Content

A. Experimental Procedures

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A.1. Materials

Unless otherwise stated, all chemicals were used as received. Acetone (VWR, normapur), acetonitrile (ACN, Acros, 99.9 %, extra dry over molecular sieves), aluminium chloride (Roth, ≥ 98 %, anhydrous, sublimated), aluminium oxide (basic, Acros, Brockmann I for chromatography), aluminium oxide (neutral, Acros, Brockmann I for chromatography), 2-bromo isobutyric bromide (Alfa Aesar, 97 %), 4-bromomethyl benzoate (Alfa Aesar, 98 %), copper (II) bromide (Acros, 99+ %, extra pure, anhydrous), copper sulfate pentahydrate ($CuSO_4$ $5H_2O$, Merck, for synthesis), 18-crown-6 (Acros, 99 %), dichloromethane (DCM, Acros, 99.8 %, extra dry over molecular sieves), 4-(dimethylamino)-pyridine (DMAP, Aldrich, ≥ 99 %), dimethylformamide (DMF, HPLC Biosolve), dimethylsulfoxide (DMSO, Acros, 99.7 %, extra dry), ethanol (Acros, 99.7 %, extra dry), ethanolamine (Acros, 99 %), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC HCl, Roth, ≥ 99 %), *N*-ethyl maleimide (Sigma Aldrich, 98 %), furane (Acros, 99+ %, stabilized), iron powder (Fisher, general purpose grade), magnesium sulfate hydrate ($MgSO_4$ H_2O, Roth, ≥ 99 %, dried), maleic anhydride (Acros, 99 %), potassium carbonate (K_2CO_3, Alfa Aesar, 99 %, anhydrous), potassium peroxodisulfate ($K_2S_2O_8$, Sigma Aldrich, 97 %), propargyl alcohol (Acros, 99 %), sodium ascorbate (Sigma Aldrich, 98 %), sodium azide (NaN_3, Sigma Aldrich ≥ 99 %), sodium hydroxide (NaOH, Roth, ≥ 99 %), tetrahydrofurane (THF, Acros, 99.5 %, extra dry over molecular sieves, stabilized), tetrahydrofurane (THF, VWR, normapur), toluene (VWR, normapur), trimethylamine (Et_3N, Acros, 99 %), tris(2-(dimethylamino)ethyl)amine (Me_6TREN, Alfa Aesar, 99+ %).

Azobisisobutyronitrile (AIBN, Fluka, 98 %) was recrystallized from MeOH. Styrene (Merck, ≥ 99%) and methyl methacrylate (MMA, Sigma Aldrich, 99 %) were passed over a column of basic aluminium oxide prior to polymerization. 2-Bromo-2-methyl propionic acid 2-(3,5-dioxo-10-oxa-4- azatricyclo[5.2.1.02,6]dec-8-en-4-yl) ethyl ester (PG-mal initiator) was synthesized according to literature.[1]

A.2. Nuclear Magnetic Resonance (NMR) Spectroscopy. Ambient temperature NMR measurements were performed on a Bruker AM 400 spectrometer (^{1}H: 400 MHz) for hydrogen. The δ-scale was referenced to the respective solvent resonance 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).

High temperature NMR measurements. High-resolution liquid NMR spectroscopy was carried out with a Bruker DRX 400 spectrometer operating at 400 MHz for the ^{1}H nucleus. Spectra were recorded at 363 K using a 5 mm QNP probe. Polymer samples were examined as 5-15 % (w/v) solutions. A mixture of tetrachloroethylene (TCE) and deuterated benzene (C_6D_6) (2/1 v/v) was used as solvent. Chemical shift values are given in units of ppm, relative to an internal reference of tetramethylsilane.

A.3. Size Exclusion Chromatography (SEC). The apparent number-average molar mass (M_n) and the molar mass distribution [$Đ$ (dispersity) = M_w/M_n] of the polymers were determined *via* SEC measurements performed on a Polymer Laboratories (Varian) PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 mm bead-size guard column (50 x 7.5 mm), one PLgel 5 mm Mixed E column (300 x 7.5 mm), three PLgel 5 mm Mixed C columns (300 x 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 $2.5 \cdot 10^6$ g mol^{-1} and linear poly(methyl methacrylate) standards ranging from 700 to $2.0 \cdot 10^6$ 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., $K = 13.63 \cdot 10^{-3}$ mL·g^{-1}, $\alpha = 0.714$ and for poly(methyl methacrylate) in THF at 35 °C, $K = 12.8 \cdot 10^{-3}$ mL·g^{-1}, $\alpha = 0.69$.[2]

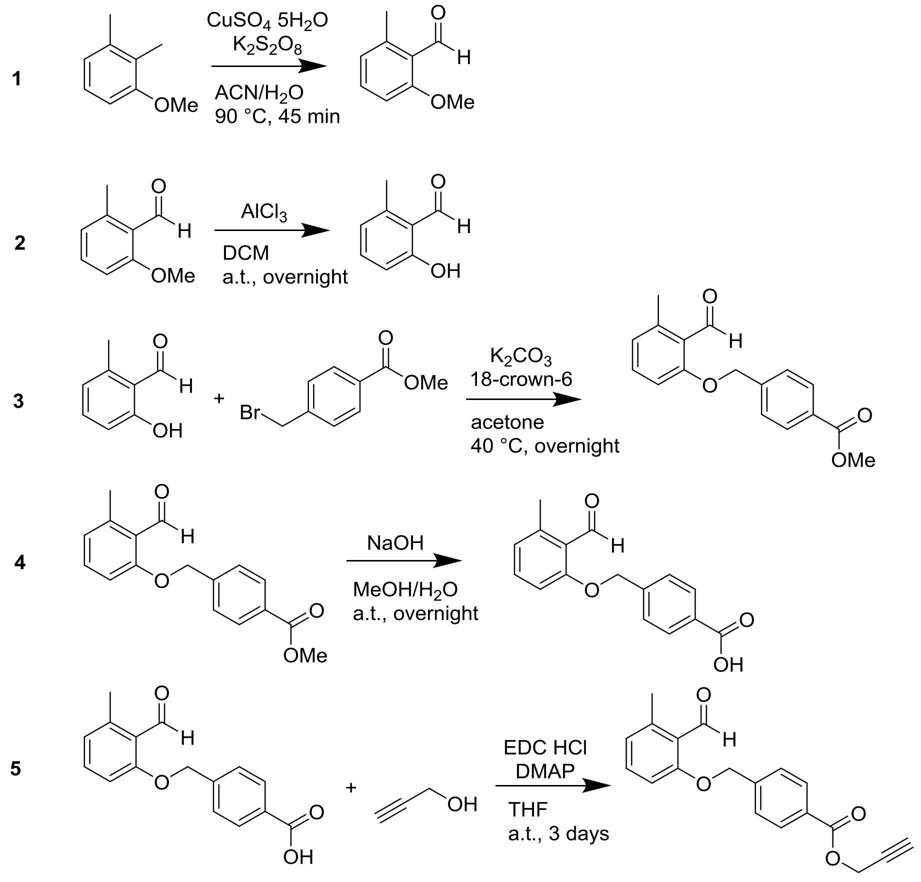
High temperature SEC measurements (SEC(TCB)). The high temperature SEC measurements were performed on a triple detection unit from Viscotek - Malvern Instrument. The system is equipped with a refractive index detector, static light scattering RALS (90 °) and LALS (7 °) and a viscometer detector. The set is equipped with a combination of three columns (Polefin 300 mm x 8 mm I.D porosity of 1 000, 100 000 and 1 000 000 Å) from Polymer Standards Service. The mobile phase is 1,2,4-trichlorobenezene (TCB) at 150 °C at a flow rate of 1 mL min^{-1}. The solvent is stabilized by butylhydroxytoluol at 0.2 g L^{-1} in order to prevent oxidative degradation of the polymer. The samples were dissolved in TCB at a concentration of 5 mg mL^{-1} at 150 °C for about one hour. Samples were injected through a 200 µL loop and filtered in-line before separation on the columns. A conventional calibration curve, obtained with linear polyethylene standards (Polymer Standard Service) in the range of 338 to 78 000 g mol^{-1} was used for the calculation of the molar mass and the molar mass distribution of the samples. The results were acquired and processed using the software "OmniSEC" version 5.12 from Malvern Instrument.

A.4. 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 spectrum was recorded in positive mode and the analyt was dissolved in a THF/MeOH solution (3:2, doped with 100 µmol sodium trifluoroacetate, c = 0.01 g mL^{-1}). The instrument was calibrated in the *m*/*z* range 74–1822 using premixed calibration solutions (Thermo Scientific). The Fourir-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}.

A.5. Synthesis of the Small Molecules

Synthesis of prop-2-yn-1-yl 4-((2-formyl-3-methylphenoxy)methyl)benzoate (Ph-alkyne)

The synthesis consists of five steps, and the steps 1-4 were accomplished according to the literature: step 1,[3] step 2,[4] step 3[5] and step 4.[5]



For the fifth step, 2.00 g 4-((2-formyl-3-methylphenoxy)methyl)benzoic acid (7.40 mmol, 1.0 eq.), 4.28 mL propargyl alcohol (4.15 g, 74.00 mmol, 10.0 eq., dried over sodium sulfate prior to reaction) and 45.2 mg DMAP (0.37 mmol, 0.05 eq.) were dissolved in 30 mL dry THF. After cooling down to 0 °C, 2.13 g EDC HCl (11.1 mmol, 1.5 eq.) was added and the mixture was stirred for three days at ambient temperature. The solvent was removed under reduced pressure, and the residue was dissolved in DCM and water. The organic phase was washed with 1N HCl, sat. $NaHCO_3$ solution, water and brine, respectively, and dried over magnesium sulfate. The product was obtained after removal of the solvent under reduced pressure (2.21 g, 7.18 mmol, 97 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ / ppm = 10.76 (1 H, s, CO*H*), 8.10 (2 H, d, J = 8.4 Hz, $H_{arom.}$), 7.52 (2 H, d, J = 8.6 Hz, H_{arom}), 7.36 (1 H, t, J = 7.8 Hz, H_{arom}), 6.85 (2 H, d, J = 8.4 Hz, H_{arom}), 5.23 (2 H, s, CH_2Ph), 4.94 (2 H, d, ^4J = 2.5 Hz, CH_2CCH), 2.59 (3 H, s, CH_3), 2.53 (1 H, d, ^4J = 2.5 Hz, CH_2CC*H*).

ESI-MS: $[M+Na^+]^+/z_{exp.}$ = 331.0932, $[M+Na^+]^+/z_{theo..}$ = 331.0941.

Refer to Figures S1 and S2 for the ^{1}H NMR and ^{13}C NMR spectrum of prop-2-yn-1-yl 4-((2-formyl-3-methylphenoxy)methyl)benzoate (Ph-alkyne), respectively.

A.6. Synthesis of the Parent Polymers

Synthesis of PE-N_3

PE-N_3 was obtained according to a previously described strategy,[6] starting from iodo end functionalized PE (PE-I). 5 g of PE-I and 400 mg of NaN_3 were suspended in 50 mL of DMF and heated at 150°C under argon for two hours. After cooling down to ambient temperature, 10 mL of MeOH were added to precipitate the resulting functionalized PE. PE-N_3 was obtained after filtration and dried up to constant weight.

SEC(TCB): M_n = 1100 g mol^{-1}, $Đ$ = 1.28

Table S1 Summary of the results for PE-N_3. For $M_{n,SEC(TCB)}$, a PE calibration was used for calculation (refer to Figure 1B for SEC trace). $M_{n,NMR}$ was obtained via referencing the resonance of the protons adjacent to the azide group at 3.00 ppm to the backbone resonances between 1.55 and 0.95 ppm (refer to Figure 1A for the HT ^{1}H NMR spectrum).

Species	$M_{n,SEC(TCB)}$/ g mol^{-1}	$Đ$	$M_{n,SEC(THF)}$/ g mol^{-1}	$Đ$	$M_{n,NMR}$/ g mol^{-1}
PE-N_3	1100	1.28	-	-	1200

Modification of PE-N_3

0.1 g PE-N_3 (0.091 mmol, 1.00 eq.), 35.9 mg Ph-alkyne (0.116 mmol, 1.29 eq.), 1.9 mg $CuSO_4$ $5H_2O$ (0.0076 mmol, 0.08 eq.) and 1.8 mg sodium ascorbate (0.0091 mmol, 0.10 eq.) were suspended in 10 mL of a toluene-DMF mixture (toluene:DMF = 7:3) in a pressure tube. The mixture was deoxygenated via bubbling with argon for 10 min, and subsequently heated at 100 °C for 3 days. After cooling to ambient temperature, 10 mL of MeOH were added and the functionalized PE species were precipitated. PE-Ph was obtained by filtration and drying.

SEC(TCB): M_n = 1200 g mol^{-1}, $Đ$ = 1.25

Table S2 Summary of the results for PE-Ph. For $M_{n,SEC(TCB)}$, a PE calibration was used for calculation (refer to Figure 1B for SEC trace). $M_{n,NMR}$ was obtained via referencing the resonance of the benzyl CH_3 protons at 2.50 ppm to the backbone resonances between 1.55 and 0.95 ppm (refer to Figure 1A for the HT ^{1}H NMR spectrum).

Species	**$M_{n,SEC(TCB)}$/** g mol^{-1}	**$Đ$**	**$M_{n,SEC(THF)}$/** g mol^{-1}	**$Đ$**	**$M_{n,NMR}$/** g mol^{-1}
PE-Ph	1200	1.25	-	-	1600

Synthesis of PS

The presented polymerization procedure was adapted from the literature.[7] In a Schlenk flask, 88.0 mg Fe(0) powder (1.570 mmol, 10.0 eq.), 35.0 mg $CuBr_2$ (0.157 mmol, 1.0 eq.) and 451.0 µL Me_6TREN (389.0 mg, 1.730 mmol, 11.0 eq.) in 1.6 mL DMSO were degassed via bubbling with argon for 20 min. A solution of 40.3 mg PG-mal initiator (0.157 mmol, 1.0 eq.) dissolved in 3.1 mL styrene (2.809 g, 27.0 mmol, 240.0 eq.) was added to the Schlenk flask, and the reaction mixture was deoxygenated via three freeze-pump-thaw cycles. After stirring at 30 °C for 22 h, the polymerization was stopped by dilution with THF, and the copper catalyst was removed by filtration with neutral aluminium oxide. The final polymer (700 mg) was obtained via two-fold precipitation in ice-cold methanol and subsequent drying.

SEC(THF): M_n = 5000 g mol^{-1}, $Đ$ = 1.08

Table S3 Summary of the results for the furane-protected maleimide bearing PS. $M_{n,SEC(THF)}$ is obtained by employing a PS calibration (refer to Figure S5A for SEC trace). $M_{n,NMR}$ was received via referencing the resonances d and e to the aromatic backbone resonances between 7.20 and 6.20 ppm (refer to Figure S3 for the ^{1}H NMR spectrum).

Species	**$M_{n,SEC(TCB)}$/** g mol^{-1}	**Đ**	**$M_{n,SEC(THF)}$/** g mol^{-1}	**Đ**	**$M_{n,NMR}$/** g mol^{-1}
PS (pro)	-	-	5000	1.08	5100

Synthesis of PMMA

The presented polymerization procedure is adapted from the literature.[7] In a Schlenk flask, 8.8 mg Fe(0) powder (0.157 mmol, 1.0 eq.), 3.5 mg $CuBr_2$ (0.0157 mmol, 0.1 eq.) and 45.1 µL Me_6TREN (38.9 mg, 0.173 mmol, 1.1 eq.) in 1.8 mL acetonitrile were degassed via bubbling with argon for 20 min. A solution of 40.3 mg PG-mal initiator (0.157 mmol, 1.0 eq.) dissolved in 3.6 mL MMA (3.400 g, 27.0 mmol, 222 eq.) was added to the Schlenk flask, and the reaction mixture was deoxygenated via three freeze-pump-thaw cycles. After stirring at 30 °C for 5 h, the polymerization was stopped by dilution with THF, and the copper catalyst was removed by filtration with neutral aluminium oxide. The final polymer (800 mg) was obtained via two fold precipitation in ice-cold water and drying.

SEC(THF): M_n = 5500 g mol^{-1}, *Đ* = 1.23

Table S4 Summary of the results for the furane-protected maleimide bearing PMMA. $M_{n,SEC(THF)}$ is obtained by employing a PMMA calibration (refer to Figure S5B for SEC trace). $M_{n,NMR}$ was received via referencing the resonance k at 6.25 ppm to the backbone resonance e at 3.53 ppm (refer to Figure S4 for the ^{1}H NMR spectrum).

Species	**$M_{n,SEC(TCB)}$/** g mol^{-1}	**Đ**	**$M_{n,SEC(THF)}$/** g mol^{-1}	**Đ**	**$M_{n,NMR}$/** g mol^{-1}
PMMA (pro)	-	-	5500	1.23	3800

Deprotection of the Maleimide-Endgroups of PS and PMMA

The deprotection step was accomplished in bulk in a drying oven under vacuum using elevated temperatures. Refer to Figures S3 and S4 for the ^{1}H NMR spectra of the polymers before and after the removal of the furane protecting group. In Figure S5 a comparison of SEC traces before and after the deprotection is presented.

Table S5 Details of the removal of the furane protecting endgroups of PS and PMMA.

Species	**Time/ h**	**Temperature/ °C**
PS (depro)	24	110
PMMA (depro)	24	110

Table S6 Summary of the results after deprotection of the maleimide polymers PS and PMMA. For $M_{\mathrm{n,SEC(TCB)}}$, a PE calibration was used for calculation. $M_{\mathrm{n,SEC(THF)}}$ is obtained by employing a PS calibration for PS or a PMMA calibration for PMMA. For PS, $M_{\mathrm{n,NMR}}$ was received via referencing the resonances d and e to the aromatic backbone resonances between 7.20 and 6.20 ppm (refer to Figure S3 for the ^{1}H NMR spectrum). For PMMA, $M_{\mathrm{n,NMR}}$ was obtained by comparison of the integral of the resonance l at 6.71ppm to the backbone resonance e at 3.53 ppm (refer to Figure S4 for the ^{1}H NMR spectrum).

Species	$M_{\mathrm{n,SEC(TCB)}}$/ g mol^{-1}	**Đ**	$M_{\mathrm{n,SEC(THF)}}$/ g mol^{-1}	**Đ**	$M_{\mathrm{n,NMR}}$/ g mol^{-1}
PS (depro)	2300	1.10	5000	1.10	5000
PMMA (depro)	1500	1.38	5300	1.20	4000

A. 7. Modification and Block Copolymer Formation via UV Light Triggered Cycloaddition

1.0 eq. of PE-Ph and 5.0 eq. of *N*-ethyl maleimide (or 1.0 eq. of a maleimide-terminal polymer (PS or PMMA)) were dissolved in a 1:1 mixture of ACN : toluene ($4*10^{-5}$ mol L^{-1}). The reaction mixture was heated up to 100 °C and placed in a custom-build photoreactor.[8] The solution was irradiated while stirring employing a compact lamp (Philips PL-L cleo, for emission spectra refer to Figure S7) for an hour. Subsequently, the mixture was again heated to 100 °C and irradiated in the photoreactor for an additional hour. In total, the heating-irradiating cycle was repeated five times. After removal of close to 90 % of the solvent, the amount of solvent left was doubled by adding the same amount of MeOH in order to precipitate the block copolymer. The final polymer species were directly analyzed after filtration and drying.

Table S7 Summary of the results after UV irradiation of PE-Ph and *N*-ethyl maleimide, PS or PMMA. For $M_{n,SEC(TCB)}$, a PE calibration was used, and for $M_{n,SEC(THF)}$, a PS calibration for PS, and a PMMA calibration for PMMA was employed for the calculation. For PE-Et, $M_{n,NMR}$ was obtained by referencing resonance h at 4.88 ppm to the backbone resonance between 1.40 and 1.10 ppm (refer to Figure 1). For PS, in the ^{1}H NMR spectra of the block copolymer the integral of resonance i at 4.87 ppm was compared to the aromatic backbone resonances of PS in the range of 7.20 to 6.20 ppm for the value of PS and to the polymer resonance of PE in the area between 1.35 and 1.10 ppm for the value of the PE block (refer to Figures 1 and 2). For the calculation of $M_{n,NMR}$ of PMMA, resonance l which appears in the area between 5.12 and 4.90 ppm in the spectrum of PE-*b*-PMMA was compared to the backbone resonance of PMMA at 3.44 ppm and to the backbone resonance of PE between 1.30 and 1.15 ppm (refer to Figure 2), respectively. For $M_{n,NMR}$ of the block copolymers, the values for the individual blocks were summed up.

Species	Block	$M_{n,SEC(TCB)}$/ g mol^{-1}	Đ	$M_{n,SEC(THF)}$/ g mol^{-1}	Đ	$M_{n,NMR}$/ g mol^{-1}
PE-Et	-	1200	1.38	-	-	2000
	PE	1200	1.25			1600
PE-*b*-PS		3200	1.08	-	-	7500
	PE	850	1.22	-	-	1400
	PS	2300	1.10	5000	1.10	6100
PE-*b*-PMMA		1800	1.34	-	-	5800
	PE	850	1.22	-	-	1200
	PMMA	1500	1.38	5300	1.20	4900

B. Additional Data and Figures

B.1 ^{1}H NMR Spectra

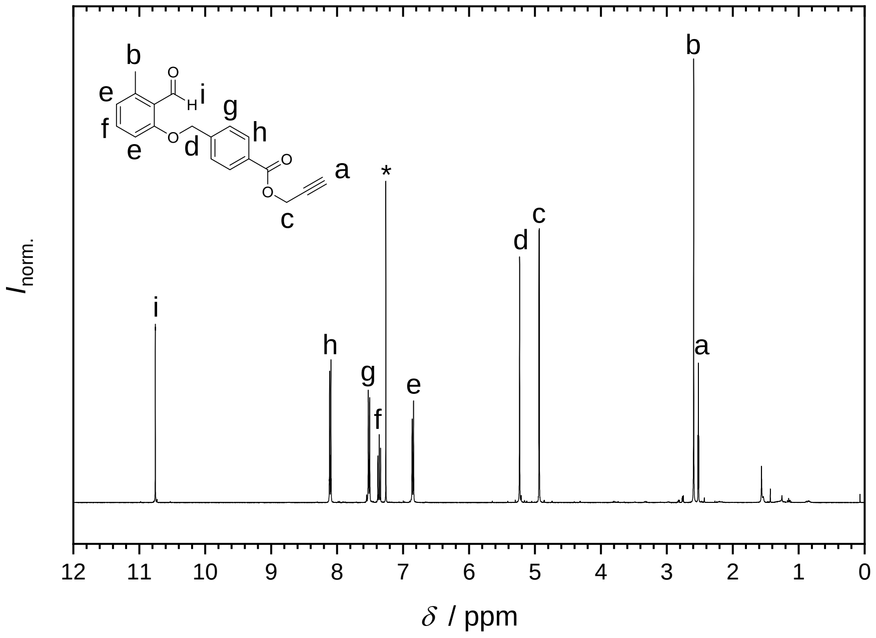


Figure S1 ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) spectrum of prop-2-yn-1-yl 4-((2-formyl-3-methylphenoxy)methyl)benzoate (**Ph-alkyne**).

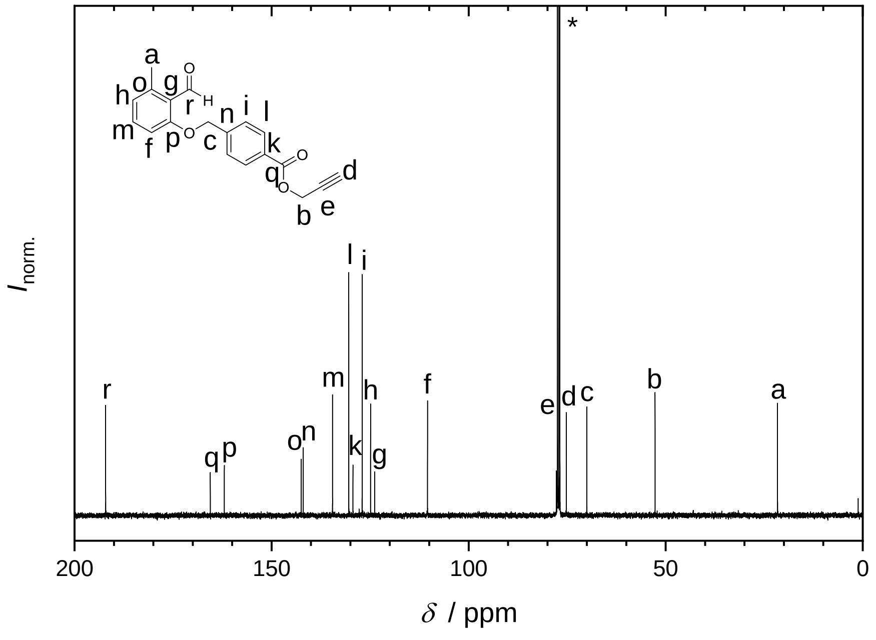


Figure S2 ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) spectrum of prop-2-yn-1-yl 4-((2-formyl-3-methylphenoxy)methyl)benzoate (**Ph-alkyne**).

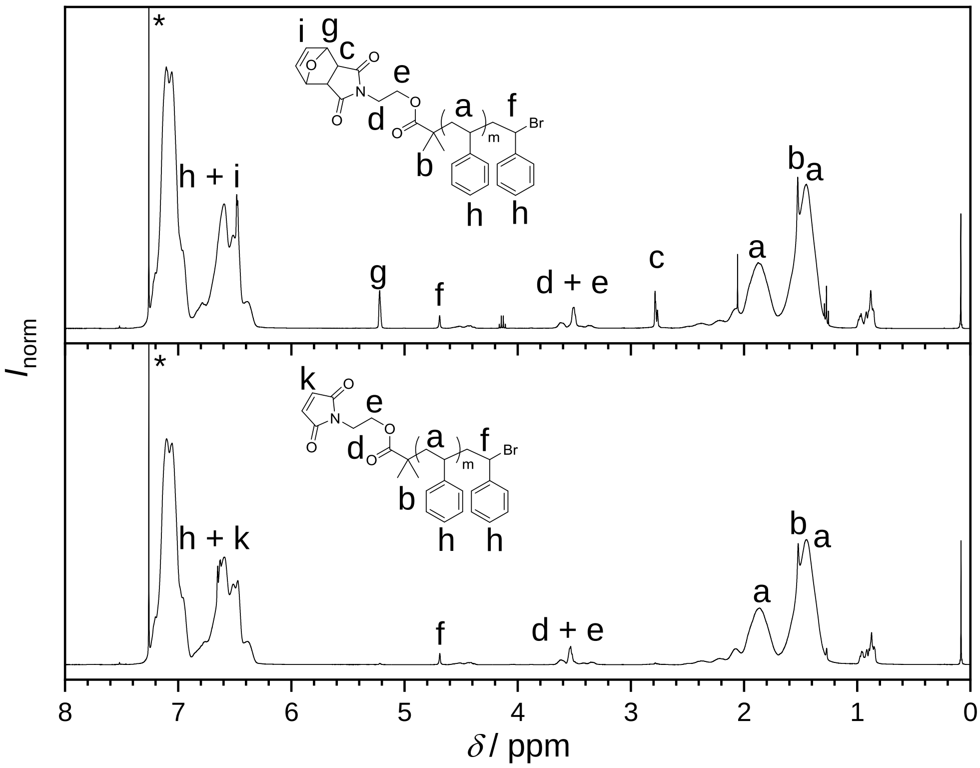


Figure S3 ^{1}H NMR spectra (400 MHz, CDCl$_3$, 25 °C) of **PS** with the furane protected maleimide endgroup (top) and the same species after deprotection (bottom).

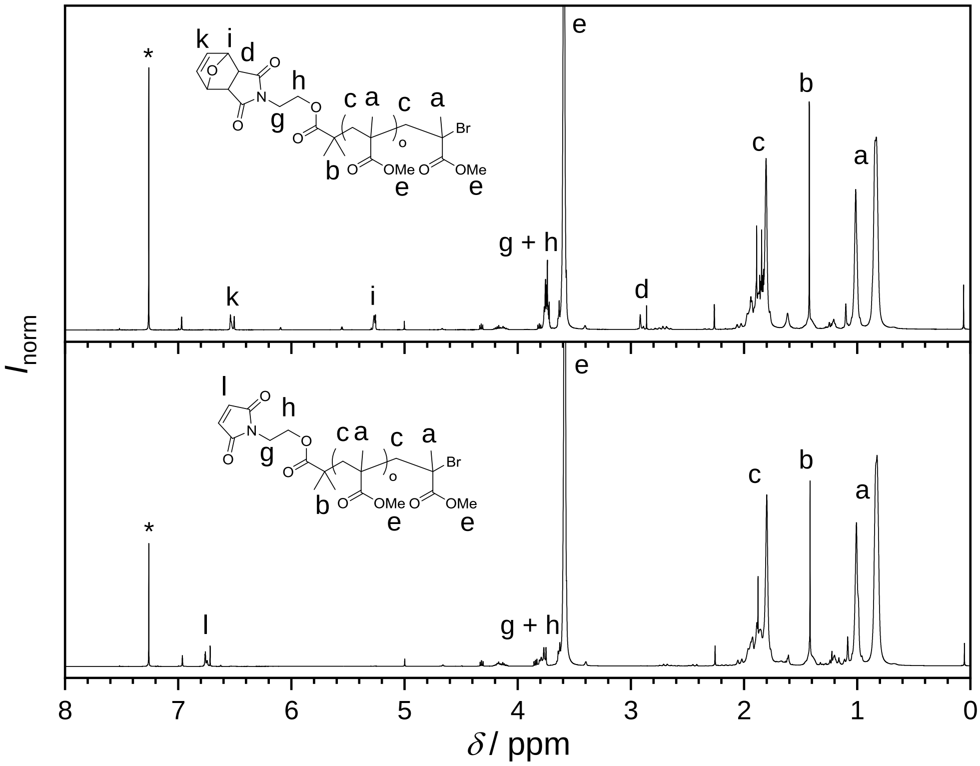


Figure S4 ^{1}H NMR spectra (400 MHz, CDCl$_3$, 25 °C) of **PMMA** with the furane protected maleimide endgroup (top) and the same species after deprotection (bottom).

B.2 SEC Data

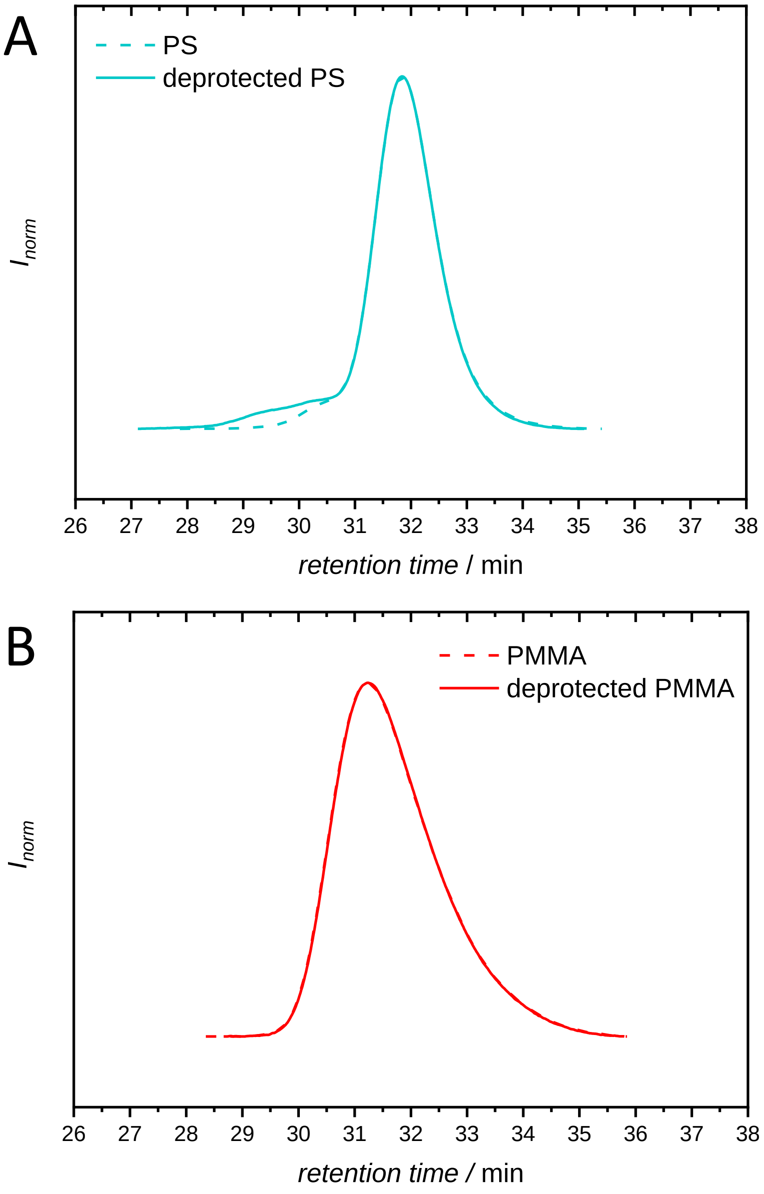


Figure S5 Overview of the results of the deprotection of the maleimide polymer endgroup obtained via SEC (THF, 35 °C, RI, A: **PS**, B: **PMMA**). The polymers with the furane protected end group are displayed as dashed lines, while the deprotected counterparts are represented by solid lines.

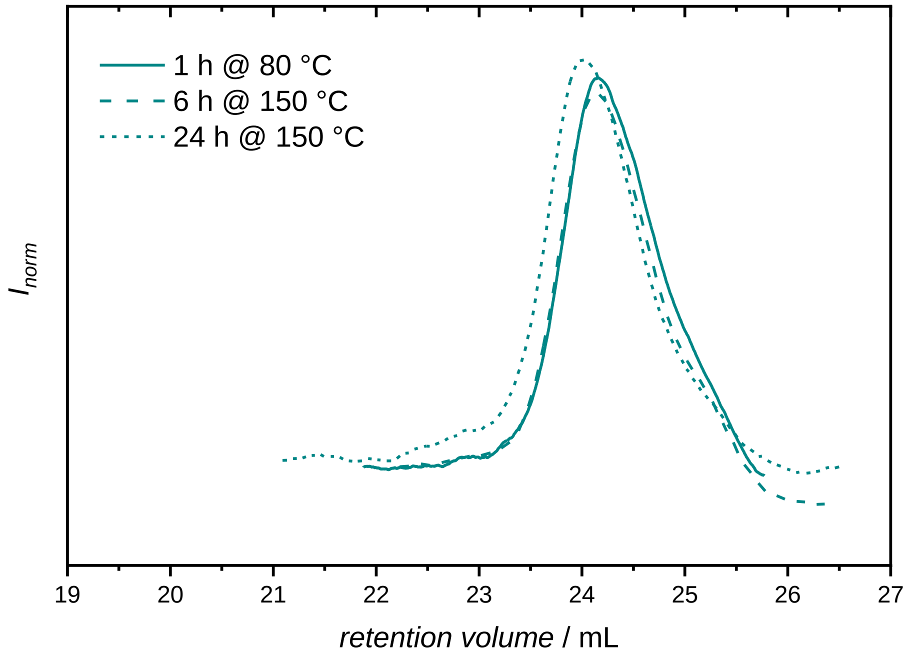


Figure S6 Analysis of the temperature stability of **PE-*b*-PS** in TCB via HT SEC (TCB, 150 °C, RI).

B.3. Further Information

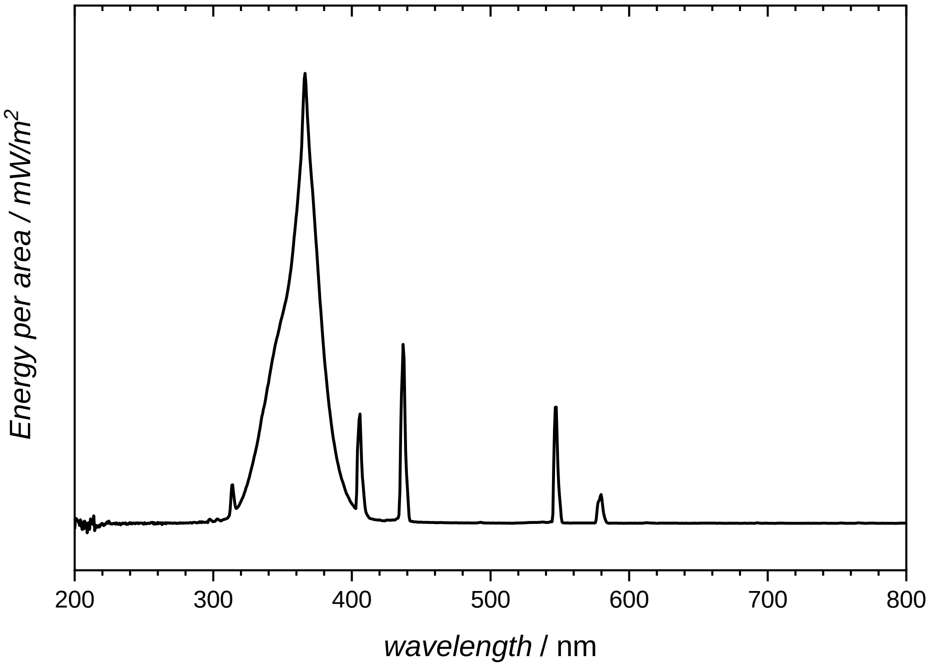


Figure S7 Emission spectrum of the employed compact lamp Philips PL-L cleo for PE ligation.

C. References

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