

## Electronic Supplementary Information

# A versatile strategy for the synthesis of block copolymers bearing a photocleavable junction

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### Materials and methods

Flash chromatography was performed on silica gel (0.040-0.063  $\mu\text{m}$  grade). Tris(2-(dimethylamino)ethyl)amine (Me<sub>6</sub>-Tren) was synthesized as described in the literature<sup>1</sup>. Poly(ethylene oxide) mono methyl ether (PEO<sub>113</sub>-OH, Polymer Source,  $M_n=5,000$  g/mol, PDI=1.04) was dried by azeotropic cycles with toluene prior to use. Styrene (sty, Aldrich, 99%), tert-butylacrylate (tBA, Acros, 99%) and methyl methacrylate (MMA, Aldrich, 99%) were passed through activated basic alumina (Acros) columns prior to use. *N,N*-dimethylformamide (DMF, Aldrich, 99.8%) and tetrahydrofuran (THF, Aldrich, 99.9 %) were distilled on CaH<sub>2</sub> prior to use. Triethylamine was dried over KOH. Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, 99%) was dried 24 h in a vacuum oven at 100°C. 5-hydroxy-2-nitrobenzyl alcohol (Aldrich, 97%), propargyl bromide (Aldrich, 80 wt% in toluene), 1-bromoethylbenzene (Aldrich, 97%), sodium azide (NaN<sub>3</sub>, Acros, 99%), tosyl chloride (TsCl, Fluka, 99 %), 4,4'-dinonyl-2,2'-dipyridyl (dNPyl, Aldrich, 97%), CuBr (Aldrich, 99.999%), ethyl 2-

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<sup>1</sup> Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules*, 2000, **33**, 8629.

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bromoisobutyrate (EBiB, Acros, 98%), anisole (Acros, 99%), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich, 98%), ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA, Fluka, 97%), and all the other chemicals were used as received.

Proton and carbon nuclear magnetic resonance spectra were recorded on a 300 MHz or 500 MHz (Bruker Avance II). Infrared (IR) spectra were recorded on thin films deposited from a dichloromethane solution on a ATR accessory with a Shimadzu FTIR-8400S FT-IR spectrometer. Mass spectra were obtained using chemical ionization (100 eV, ionization gas: methane). Molar masses and polydispersity indices of the polymers were measured on a Waters SEC system equipped with a Waters 510 pump and a 410 differential refractometer (40 °C; eluent: DMF; flow rate of 0.5 mL/min). The calibration was performed using polystyrene standards. UV-vis spectra were recorded on a Varian spectrophotometer (Cary, 50 Conc).

## Experimental Section

**Synthesis of 5-propargylether-2-nitrobenzyl alcohol (3):** A mixture of 5-hydroxy-2-nitrobenzyl alcohol (856 mg, 5.2 mmol, 1 equiv.) and  $K_2CO_3$  (2163 mg, 15.6 mmol, 3 equiv.) was stirred in DMF (10.4 mL) for 1 hour at 60 °C. Propargyl bromide (80 % in toluene, 0.7 mL, 6.3 mmol, 1.2 equiv.) was added dropwise. The mixture was stirred for 24 hours at 60 °C. DMF was removed under reduced pressure. The residue was dissolved in AcOEt and washed with water. The organic phases were combined, dried over  $MgSO_4$ , filtered and the solvent was removed *in vacuo*. The yellow-brown solid was recrystallized in AcOEt/cyclohexane, affording slightly iridescent white crystals (860 mg, 80 %).  $^1H$  NMR (300 MHz,  $(CD_3)_2SO$ ):  $\delta$  8.15 (d, 1H,  $^3J = 9.0$  Hz,  $H_{Ar}$ ), 7.41 (s, 1H,  $H_{Ar}$ ), 7.10 (d, 1H,  $^3J = 9.0$  Hz,  $H_{Ar}$ ), 5.60 (t, 1H,  $^4J = 5.4$  Hz,  $C\equiv C-H$ ), 4.98 (s, 2H,  $-CH_2-OH$ ), 4.85 (d, 2,  $^4J = 5.1$  Hz,  $C\equiv C-CH_2-$ ), 3.67 (s, 1H,  $-OH$ ).  $^{13}C$  NMR (75 MHz,  $(CD_3)_2SO$ ):  $\delta$  161.5 ( $C_{Ar}-O-$ ), 142.2 ( $C_{Ar}-NO_2$ ), 139.9 ( $C_{Ar}-CH_2-$ ), 127.4 ( $H-C_{Ar}$ ), 113.8 ( $H-C_{Ar}$ ), 113.1 ( $H-C_{Ar}$ ), 79.1 ( $H-C\equiv C-$ ), 78.3 ( $H-C\equiv C-$ ), 60.1 ( $C\equiv C-CH_2$ ), 56.1 ( $H_2C-OH$ ). FTIR (film,  $cm^{-1}$ ): 3265 b, 3182 b, 2123 w, 1608 s, 1587 s, 1508 s, 1248 s, 1336 s, 858,

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w. MS (CI) :  $m/z = 208$  ( $[M+H]^+$ , 56), 190 ( $[C_{10}H_8NO_3]^+$ , 100). Anal. Calcd. For  $C_{10}H_9NO_4$ : C, 57.97; H, 4.38; N, 6.76. Found : C, 58.27; H, 4.44; N, 6.84.

**Synthesis of 5-propargylether-2-nitrobenzyl bromoisobutyrate (1):** A solution of bromoisobromoisobutyrate (538  $\mu$ L, 4.35 mmol, 1.2 equiv.) in dry THF (4 ml) was added dropwise to a stirred solution of 5-propargylether-2-nitrobenzyl alcohol **3** (700 mg, 3.62 mmol) and dry  $Et_3N$  (606  $\mu$ L, 4.35 mmol, 1.2 equiv.) in dry THF (8 mL) at 0 °C and under argon. The mixture was slowly brought to 20 °C and stirred overnight. Distilled water (100  $\mu$ L) was added dropwise to quench the reaction. THF was removed under reduced pressure and the residue was dissolved in  $CH_2Cl_2$  and washed with water. The organic phases were combined, dried over  $MgSO_4$ , filtered and the solvent was removed *in vacuo*. The yellow-brown residue was purified on flash chromatography (eluent:  $CHCl_3$ ) affording a light yellow solid (1202 mg, 91 %).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  8.19 (d, 1H,  $^3J = 9.1$  Hz,  $H_{Ar}$ ), 7.26 (s, 1H,  $H_{Ar}$ ), 7.02 (d, 1H,  $^3J = 9.1$  Hz,  $H_{Ar}$ ), 5.64 (s, 2H,  $-CH_2-OCO-$ ), 4.80 (d, 2H,  $^4J = 2.1$  Hz,  $C\equiv C-CH_2-$ ), 2.60 (d, 1H,  $-C\equiv CH$ ), 2.01 (s, 6H,  $CH_3$ ).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  170.8 (C=O), 161.8 ( $C_{Ar}-O-$ ), 140.4 ( $C_{Ar}-NO_2$ ), 135.3 ( $C_{Ar}-CH_2-$ ), 127.9 (H- $C_{Ar}$ ), 114.5 (H- $C_{Ar}$ ), 113.4 (H- $C_{Ar}$ ), 77.1 (H- $C\equiv C-$ ), 77.0 (H- $C\equiv C-$ ), 64.4 ( $-CH_2-OCO-$ ), 56.4 ( $C\equiv C-CH_2$ ), 55.7 ( $C-Br$ ), 30.8 ( $CH_3$ ). FTIR (film,  $cm^{-1}$ ): 3290 m, 2123 w, 1737 s, 1610 s, 1581 s, 1514 s, 1336 s, 1249, s, 1151 s, 858 w. MS (CI) :  $m/z = 356$  ( $[M+H]^+$ , 2), 190 ( $[C_{10}H_8NO_3]^+$ , 100). Anal. Calcd. For  $C_{10}H_9NO_4$ : C, 47.21; H, 3.96; N, 3.93. Found : C, 47.55; H, 3.94; N, 4.08.

**Synthesis of PEO<sub>113</sub>-OTs:** To a solution of PEO-OH (2.60 g, 0.52 mmol) in dry THF (25 mL, 0.2 M), dry triethylamine (1.45 mL, 10.4 mmol, 20 equiv.) and tosylate chloride (1.98 g, 10.4 mmol, 20 equiv.) were added. The light yellow solution was stirred under argon at 35°C for 24 h. THF was removed under reduced pressure. The residue was diluted in  $CH_2Cl_2$  and washed with water. The organics phases were combined, dried over  $Na_2SO_4$ , filtered and the solvent was removed under reduced pressure. The

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light yellow solid was precipitated in Et<sub>2</sub>O, filtered and dried one night *in vacuo* at 30°C, affording a white powder (2.45 g, Yield:91 %, FD: 100 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.77 (d, 2H, <sup>3</sup>J = 8.0 Hz, H<sub>Ar</sub>), 7.32 (d, 2H, <sup>3</sup>J = 8.0 Hz, H<sub>Ar</sub>), 4.31 (t, 2H, <sup>3</sup>J = 4.5 Hz, -CH<sub>2</sub>-OTs), 3.62 (s, 449H, CH<sub>2</sub>(PEO)), 3.36 (s, 3H, CH<sub>3</sub>-O), 2.43 (s, 3H, CH<sub>3</sub>(Ar)).

**Synthesis of PEO<sub>113</sub>-N<sub>3</sub>:** To a solution of PEO-OTs (996 g, 0.19 mmol, 1 equiv.) in dry DMF (9.66 mL, 0.02 M), sodium azide (251 mg, 3.86 mmol, 20 equiv.) was added. The solution was stirred under argon at 20 °C for 24 h. DMF was removed under reduced pressure. The residue was diluted in CH<sub>2</sub>Cl<sub>2</sub> and washed with water. The organics phases were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was precipitated in Et<sub>2</sub>O, filtered and dried one night *in vacuo* at 30°C, affording a white powder (850 mg, Yield: 87 %, Functionalization degree: >92 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 3.62 (s, 452H, CH<sub>2</sub>(PEO)), 3.36 (m, 5H, CH<sub>3</sub>-O ; CH<sub>2</sub>-N<sub>3</sub>).

**Synthesis of PS<sub>52</sub>-Br:** Under argon, a round bottom flask with a side stopcock containing CuBr (35 mg; 0.24 mmol; 1 equiv.) was filled with a solution containing 1-bromoethylbenzene (45 mg; 0.24 mmol, 1 equiv.), styrene (5.08 g; 48.8 mmol; 200 equiv.), dNPy (299mg; 0.73 mmol; 3 equiv.) and anisole (1.27g; 20 wt%) previously degassed by three freeze-pump-thaw cycles. The mixture was degassed by three freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 100 °C for 20 h (styrene conversion = 30 %). The polymerization was quenched by quickly cooling the tube in a water-ice bath. The reaction mixture was filtered on neutral Al<sub>2</sub>O<sub>3</sub> (eluent: CH<sub>2</sub>Cl<sub>2</sub>). The organic phase was dried over MgSO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was precipitated in hexane (2 ×), filtered and dried *in vacuo* at 30 °C for 24 h, affording a white powder (844 mg, 54 %). *M<sub>n</sub>* (SEC) = 5,400 g/mol; PDI (SEC) =1.08. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.50-6.30 (m, 296H, H<sub>Ar</sub>), 4.65-4.35 (m, 1H, CH-Br), 2.60-1.20 (190H, H<sub>backbone</sub>).

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**Synthesis of PS<sub>97</sub>-Br:** Under argon, a round bottom flask with a side stopcock containing CuBr (47 mg; 0.32 mmol; 1.5 equiv.) was filled with a solution containing EBiB (43 mg; 0.22 mmol, 1 equiv.), styrene (9.10 g; 87.37 mmol; 400 equiv.), PMDETA (68 mg; 0.39 mmol; 1.8 equiv.) and anisole (3.90 g; 30 wt%) previously degassed by three freeze-pump-thaw cycles. The mixture was degassed by three freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 90 °C for 5 h (styrene conversion = 23 %). The polymerization was quenched by quickly cooling the tube in a water-ice bath. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with an aqueous solution of EDTA (0.04 M). The organic phase was dried over MgSO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was precipitated in hexane, filtered and dried *in vacuo* at 30 °C for 24 h, affording a white powder (2.01 g, 96 %).  $M_n$  (SEC) = 10,100 g/mol; PDI (SEC) = 1.06. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.20-6.10 (m, 549H, H<sub>Ar</sub>), 4.60-4.0 (m, 1H, CH-Br), 3.65-3.49 (m, 2H, CH<sub>3</sub>-CH<sub>2</sub>-O, ester), 2.40-1.10 (343H, H<sub>backbone</sub>).

**General procedure for the synthesis of PS-N<sub>3</sub>:** To a solution of PS<sub>52</sub>-Br (800 mg, 0.15 mmol, 1 equiv.) in dry DMF (7.41 mL, 0.02 M), sodium azide (193 mg, 2.96 mmol, 20 equiv.) was added. The solution was stirred under argon at 20 °C for 24 h. Distilled H<sub>2</sub>O (50 mL) was added to the mixture inducing the precipitation of the polymer which was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phases were combined, dried over MgSO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was precipitated in MeOH, filtered and dried one night *in vacuo* at 30°C, affording a white powder (707 mg, Yield: 95 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.50-6.30 (m, 324H, H<sub>Ar</sub>), 4.20-3.80 (m, 1H, CH-N<sub>3</sub>), 2.60-1.20 (190H, H<sub>backbone</sub>).

**General procedure for the synthesis of PEO-hv-PS (PEO<sub>113</sub>-hv-PS<sub>133</sub>, entry 2 table SP1)**

Under argon, a schlenk tube containing CuBr (4.5 mg; 0.031 mmol; 1 equiv.) was filled with a solution containing styrene (sty; 980 mg; 9.41 mmol; 300 equiv.), PMDETA (8.2 mg; 0.042 mmol; 1.5 equiv.),

PEO<sub>113</sub>-N<sub>3</sub> (158 mg; 0.031 mmol, 1 equiv.) and anisole (545 μL) previously degassed by three freeze-pump-thaw cycles. The mixture was stirred for 10 minutes and was then frozen. Under argon, a solution of the photocleavable initiator **3** in anisole (112 μL (C = 100 g/L), 0.031 mmol, 1 equiv.) was added. The mixture was degassed by three freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 90 °C for 15 h (styrene conversion = 40 %). The polymerization was quenched by quickly cooling the tube in a water-ice bath. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with an aqueous solution of EDTA (0.04 M). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was precipitated in hexane (2 ×), filtered and dried *in vacuo* at 30 °C for 24 h, affording a white powder (372 g, 68 %). Residual homo-PEO and/or homo-PS was/were removed by extraction with selective solvents (Et<sub>2</sub>O for PS and H<sub>2</sub>O:MeOH (90:10) for PEO). *M<sub>n</sub>* (SEC) = 30,100 g/mol; PDI (SEC) = 1.15. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.12 (m, 1H, H<sub>Ar</sub> in ortho position of NO<sub>2</sub>, junction), 7.86 (s, 1H, =CH triazole; junction) 7.40-6.20 (m, 665H, H<sub>Ar</sub>; PS + junction), 5.23 (s, 2H, CH<sub>2</sub>-O, ester; junction), 4.6-4.3 (m, 3H, CH<sub>2</sub>-O, ether; junction + CH-Br, end chain), 3.62 (s, 452H, CH<sub>2</sub>; PEO), 3.39 (s, 3H, CH<sub>3</sub>-O; PEO), 2.3-1.2 (m, 399 H, H<sub>backbone</sub>; PS).

#### **Procedure for the synthesis of PEO<sub>113</sub>-hv-PtBA<sub>305</sub> (entry 4 table SP1)**

Under argon, a schlenk tube containing CuBr (4.1 mg; 0.029 mmol; 1 equiv.) was filled with a solution containing tert-butyl acrylate (tBA; 1099 mg; 8.57 mmol; 300 equiv.), Me<sub>6</sub>Tren (9.9 mg; 0.043 mmol; 1.5 equiv.), PEO<sub>113</sub>-N<sub>3</sub> (143 mg; 0.29 mmol, 1 equiv.) and anisole (634 μL) previously degassed by three freeze-pump-thaw cycles. The mixture was stirred for 10 minutes and was then frozen. Under argon, a solution of the photocleavable initiator **3** in anisole (102 μL (C = 100 g/L), 0.29 mmol, 1 equiv.) was added. The mixture was degassed by three freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 80 °C for 2 h (tBA conversion = 90 %). The polymerization was quenched by quickly cooling the tube in a water-ice bath. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with an aqueous solution of EDTA (0.04 M). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the

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solvent was removed under reduced pressure. The residue was precipitated in MeOH:H<sub>2</sub>O 50:50, filtered and dried *in vacuo* at 30 °C for 24 h, affording a white solid (1.045 g, 92 %). Residual homo-PEO and/or homo-PtBA was/were removed by extraction with selective solvents (hexane for PtBA and H<sub>2</sub>O:MeOH (90:10) for PEO).  $M_n$  (SEC) = 63,100 g/mol; PDI (SEC) = 1.15. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.16 (d, 1H, <sup>3</sup>J = 9.0 Hz, H<sub>Ar</sub>; junction), 7.87 (s, 1H, =CH triazole; junction), 7.15 (s, 1H, H<sub>Ar</sub>; junction), 7.12 (m, 1H, H<sub>Ar</sub>; junction), 5.49 (s, 2H, CH<sub>2</sub>-O, ester; junction), 4.29 (s, 2H, CH<sub>2</sub>-O, ether; junction), 3.63 (s, 452H, CH<sub>2</sub>; PEO), 3.39 (s, 3H, CH<sub>3</sub>-O; PEO), 2.4-2.1 (s, 305 H, CH<sub>backbone</sub>; PtBa). 1.9-1.2 (m, 3355 H, CH<sub>2backbone</sub> + CH<sub>3</sub> ; PtBa).

#### General procedure for the synthesis of PS-hv-PMMA (PS<sub>97</sub>-hv-PMMA<sub>35</sub>, entry 6 table SP1)

Under argon, a schlenk tube containing CuBr (5.0 mg; 0.035 mmol; 1.2 equiv.) was filled with a solution containing methyl methacrylate (MMA; 349 mg; 3.49 mmol; 125 equiv.), PMDETA (9.1 mg; 0.052 mmol; 1.8 equiv.), PS<sub>97</sub>-N<sub>3</sub> (352 mg; 0.035 mmol, 1.2 equiv.) and anisole (6.53 mL) previously degassed by three freeze-pump-thaw cycles. The mixture was stirred for 10 minutes and was then frozen. Under argon, a solution of the photocleavable initiator **3** in anisole (100 μL (C = 100 g/L), 0.028 mmol, 1 equiv.) was added. The mixture was degassed by three freeze-pump-thaw cycles, filled with argon and stirred in an oil bath at 60 °C for 2 h (MMA conversion = 33 %). The polymerization was quenched by quickly cooling the tube in a water-ice bath. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with an aqueous solution of EDTA (0.04 M). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The residue was precipitated in hexane (2 ×), filtered and dried *in vacuo* at 30 °C for 24 h, affording a white powder (373 mg, 80 %). Residual homo-PS and/or homo-PMMA was/were removed by extraction with selective solvents (Et<sub>2</sub>O:hexane (50:50) for PS and CH<sub>3</sub>-NO<sub>2</sub>:MeOH (30:70) for PMMA..  $M_n$  (SEC) = 15,700 g/mol; PDI (SEC) = 1.12. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.13 (m, 1H, H<sub>Ar</sub> in ortho position of NO<sub>2</sub>, junction), 7.30-6.20 (m,

585H, H<sub>Ar</sub>; PS + junction), 5.45 (m, 2H, CH<sub>2</sub>-O, ester; junction), 4.20 (m, 2H, CH<sub>2</sub>-O, ether; junction), 3.62 (s, 105H, CH<sub>3</sub>-O; PMMA), 2.2-0.8 (m, 331H, H<sub>backbone</sub>; PS + PMMA).

### General procedure for the irradiation of the photocleavable block copolymers

The copolymers were dissolved in dichloromethane at a concentration of 2 g/L. The solutions were placed in a quartz cell and were exposed to UV irradiation (three *Rayonet* photochemical lamps having the maximum emission at 300 nm) for different times. When no more changes were detected on the UV/vis. spectra, the solvent was evaporated and the samples were re-dissolved in DMF for the SEC analysis.

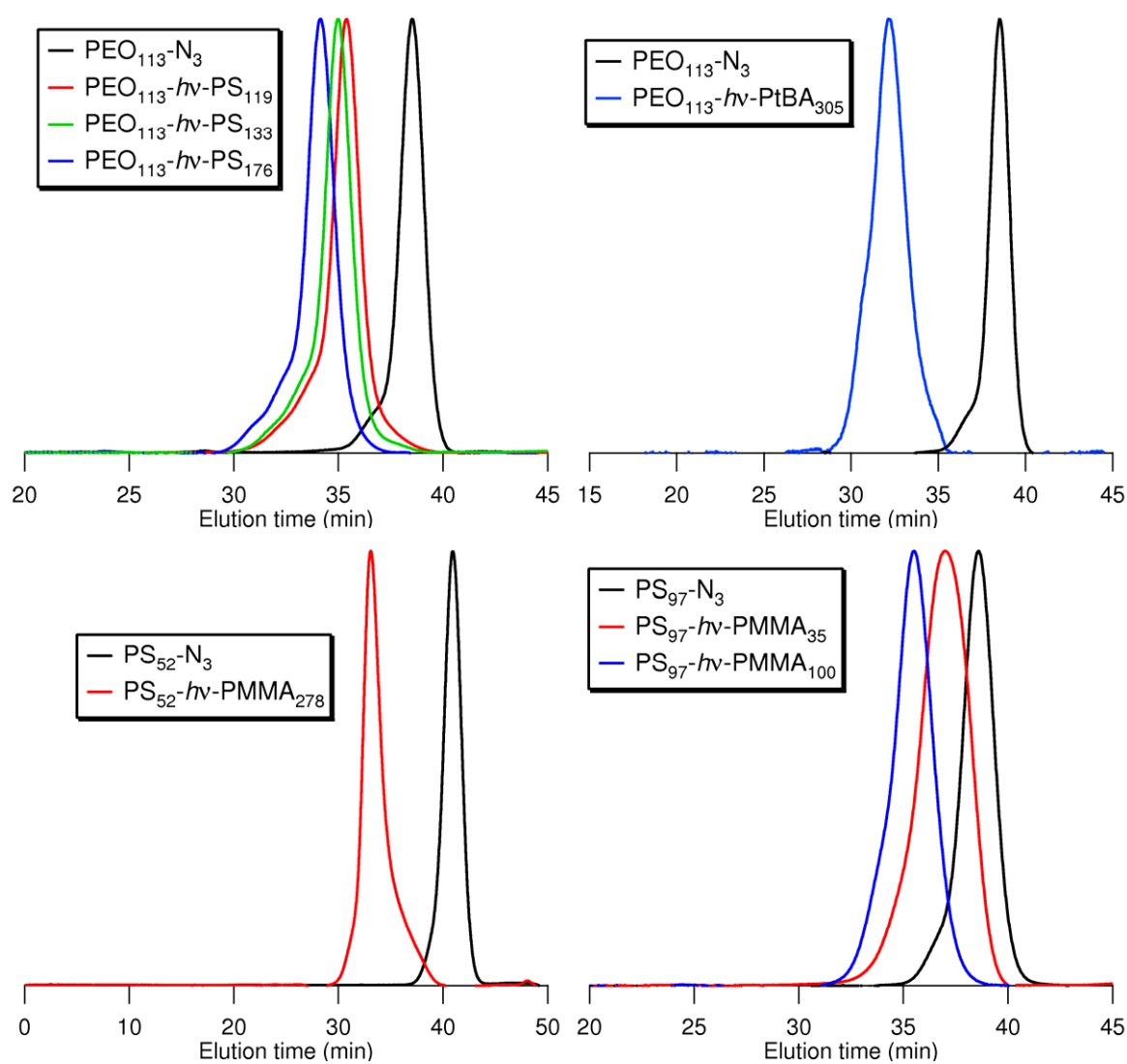
**Table SP1. Conditions for the synthesis of the photocleavable block copolymers<sup>a</sup>.**

entry	polymer	3/CuBr/L <sup>a</sup>	R-N <sub>3</sub>	R-N <sub>3</sub> equiv.	monomer	monomer equiv.	Anisole (wt%)	T (°C)	t (h)	conv. (%) <sup>b</sup>
1	PEO <sub>113</sub> -hv-PS <sub>119</sub>	1:1:1.5	PEO <sub>113</sub> -N <sub>3</sub>	1	sty	300	40	90	15	35
2	PEO <sub>113</sub> -hv-PS <sub>133</sub>	1:1:1.5	PEO <sub>113</sub> -N <sub>3</sub>	1	sty	300	40	90	20	40
3	PEO <sub>113</sub> -hv-PS <sub>176</sub>	1:1.5:2.25	PEO <sub>113</sub> -N <sub>3</sub>	1	sty	400	30	90	20	44
4 <sup>c</sup>	PEO <sub>113</sub> -hv-PtBA <sub>305</sub>	1:1:1.5	PEO <sub>113</sub> -N <sub>3</sub>	1	tBA	300	40	80	2	90
5	PS <sub>52</sub> -hv-PMMA <sub>278</sub>	1:1:1.5	PS <sub>52</sub> -N <sub>3</sub>	1	MMA	300	40	90	2	72
6	PS <sub>97</sub> -hv-PMMA <sub>35</sub>	1:1.2:1.8	PS <sub>97</sub> -N <sub>3</sub>	1.2	MMA	125	95	60	2	33
7	PS <sub>97</sub> -hv-PMMA <sub>100</sub>	1:1.2:1.8	PS <sub>97</sub> -N <sub>3</sub>	1.2	MMA	250	88	60	4	43

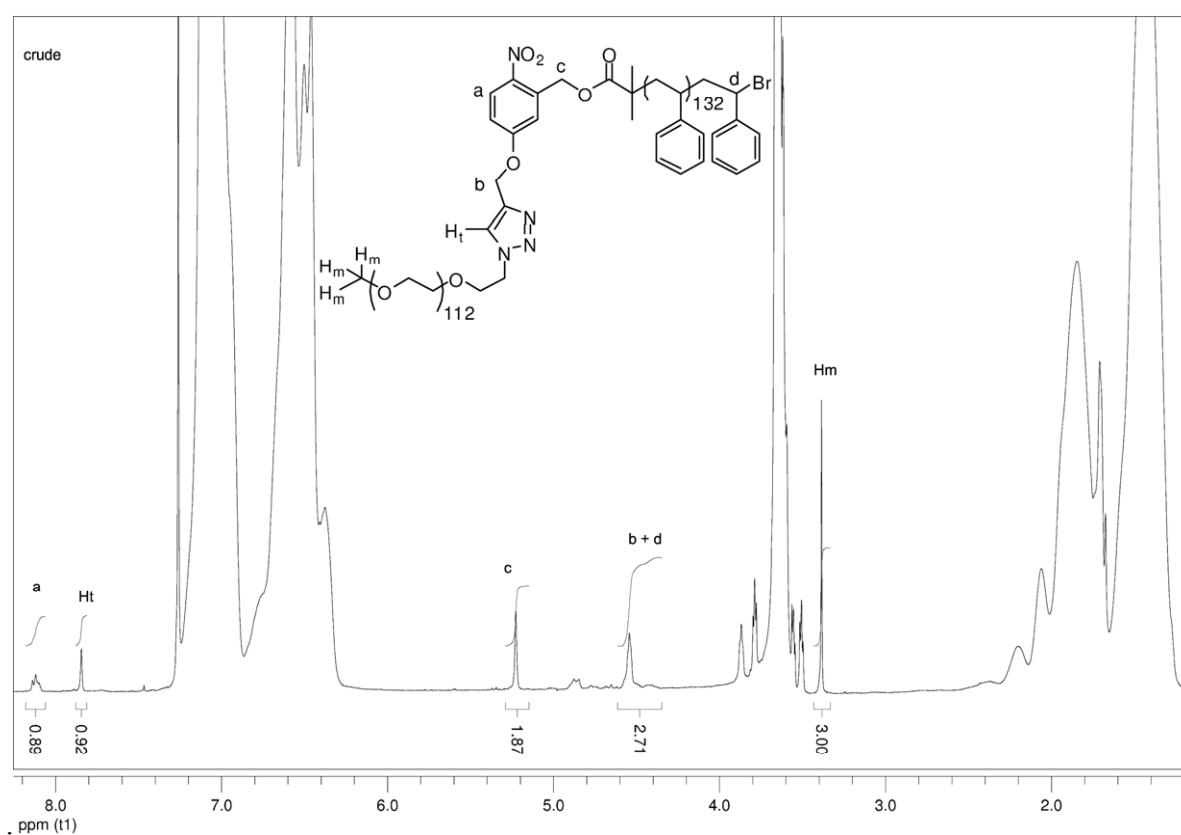
<sup>a</sup> L=Ligand = PMDTA <sup>b</sup> Monomer conversion determined by <sup>1</sup>H NMR <sup>c</sup> L=Ligand=Me<sub>6</sub>Tren instead of PMDETA.



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**GPC chromatograms of the photocleavable copolymers**



The estimation of the click efficiency is determined by  $^1\text{H}$  NMR (500 MHz) on the crude copolymer before removal of the residual(s) homopolymer(s) by comparing the integrations of the chain ends. Here we describe an example for  $\text{PEO}_{113}\text{-hv-PS}_{133}$ . We compare the integration of the triazole proton ( $\text{H}_t$ ) with the methoxy protons (PEO chain-end). Efficiency (%) =  $\text{H}_t * 100 = 92$  when  $\text{H}_m$  is calibrated on 3 (see Figure SP1 below).



**Figure SP1.**  $^1\text{H}$  NMR of the crude  $\text{PEO}_{113}\text{-hv-PS}_{133}$ .