

## Supplementary Information:

### Synthesis and photochemical properties of spiropyran graft and star polymers obtained by 'click' chemistry

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## 1. Experimental part

### Materials

Pentaerythritol Tetrakis(2-bromoisobutyrate) (4Br<sup>i</sup>Bu) was synthesized following a literature procedure.<sup>1</sup> Methyl methacrylate (99% purity, Sigma–Aldrich) was purified by vacuum distillation. 2-(trimethylsilyloxy) ethyl methacrylate was purified by filtration through neutral alumina. All the other reagents were purchased from Sigma–Aldrich and used without further purification.

### Methods

Molecular weights of polymer were characterized by gel permeation chromatography performed on an Agilent 1200 series equipped with two PL Gel 5 lm Mixed-C 300 x 7.5 mm<sup>2</sup> columns at 40 °C. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 mL min<sup>-1</sup>. Molecular weights were calculated based on PMMA standards. Proton Nuclear Magnetic Resonance spectra were recorded at room temperature with a Bruker Avance 400 (400 MHz) and a Bruker Avance Ultrashield 600 (600 MHz). Deuterated Chloroform (CDCl<sub>3</sub>) was used as solvent, and signals were referred to the signal of the residual protonated solvent signal. Chemical shifts are reported in ppm and coupling constants in Hertz. Carbon NMR spectra were recorded on Bruker Avance Ultrashield 600 (600 MHz) with total proton decoupling. ATR-FTIR spectra were collected on a Perkin Elmer Spectrum 100 in the spectral region of 650-4000 cm<sup>-1</sup> and were obtained from 4 scans with a resolution of 2 cm<sup>-1</sup>. A background measurement was taken before the sample was loaded onto the ATR unit for measurements. Absorption spectra were recorded using a Cary 50 UV–vis spectrophotometer. Emission measurements were carried out with a Perkin Elmer LS 55 Fluorimeter. Quartz cuvettes of 1 cm path length were used. The solutions were irradiated by means of a standard 20W 365 nm UV lamp.

**Synthesis of 1'-(2-acryloxyethyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (BSPA) 6<sup>2</sup>**

A solution of 1'-(2-hydroxyethyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (3.168 g, 9 mmol) and triethylamine (3.6 mL, 25.7 mmol) in dry THF (25 mL) was stirred at 0 °C under N<sub>2</sub> atmosphere for 1 hour. Acryloyl chloride (1 mL, 12.6 mmol) was added dropwise to the mixture. The resulting solution was stirred at 25 °C overnight. After evaporation of the solvent, the residue was dissolved in ethyl acetate and saturated aqueous sodium hydrogen carbonate was added. The aqueous phase was extracted with ethyl acetate. The combined organic phase was washed with brine, dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure to leave the product as a reddish-brown solid. The crude product was purified by silica gel column chromatography (7/3 *n*-hexane/ethyl acetate as eluent) to give the acrylated spirobenzopyran monomer (2.6 g, 6.4 mmol, 71%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm) 1.16 (3H, s, 3'-CH<sub>3</sub>), 1.28 (3H, s, 3'-CH<sub>3</sub>), 3.40-3.59 (2H, m, NCH<sub>2</sub>), 4.30-4.33 (2H, m, OCH<sub>2</sub>), 5.82 (1H, dd, *J* = 10.4 Hz, *J* = 1.5 Hz, CH<sub>2</sub>=CH), 5.87 (1H, d, *J* = 10.4 Hz, 2-CCH=CH), 6.06 (1H, dd, *J* = 17.4 Hz, *J* = 10.4 Hz, CH<sub>2</sub>=CH), 6.38 (1H, dd, *J* = 17.4 Hz, *J* = 1.5 Hz, CH<sub>2</sub>=CH), 6.70 (1H, d, *J* = 7.5 Hz, ArH), 6.75 (1H, d, *J* = 8.5, ArH), 6.88-6.92 (2H, m, ArH, 2-CCH=CH), 7.10 (1H, d, *J* = 7.5, ArH), 7.19-7.23 (1H, m, ArH), 8.00-8.26 (2H, m, ArH); <sup>13</sup>CNMR (400 MHz, CDCl<sub>3</sub>, δ, ppm) δ 19.86, 25.87, 42.43, 52.84, 62.47, 106.49, 106.73, 115.59, 118.42, 119.96, 121.76, 121.86, 122.80, 126.00, 127.88, 128.07, 128.35, 131.29, 135.71, 141.07, 146.63, 159.40, 165.95.

### **Synthesis of Poly(2-bromoisobutyryloxyethyl methacrylate) (PBiBEMA)<sup>3</sup>**

#### **1<sup>st</sup> step - Synthesis of Poly(trimethylsilyloxyethyl methacrylate) (PHEMATMS)**

ATRP was applied for the synthesis of the polymers. All polymerization reactions were carried out in a moisture and oxygen-free glass tube. EBiB (36.8 μL, 0.25 mmol), CuCl (19.8 mg, 0.2 mmol), CuCl<sub>2</sub> (6.7 mg, 0.2 mmol), HMTETA (70 μL, 0.25 mmol) were mixed at a 1:0.8:0.2:1 molar ratio in anisole (50% weight). HEMATMS (1.0 g, 5 mmol) was added to the solution at a molar ratio of 10, 20 or 40 with respect to EBiB. The polymerization were carried out at 60 °C for 45, 60 or 120 minutes, respectively, depending on the desired polymer molecular weight. The polymerizations were stopped by cooling the flask to room temperature and exposing the reaction mixture to air. THF was added to the mixtures and the resulting polymer solutions were filtered through a short column of neutral alumina. After removing solvent under reduced pressure, the products were dried under vacuum, collected and used without further purification. The identical reaction was repeated in larger scale, using EBiB (92.5 μL, 0.625 mmol), CuCl (49.5 mg, 0.5 mmol), CuCl<sub>2</sub> (17 mg, 0.125 mmol), HMTETA (170 μL, 0.625 mmol) and HEMATMS (5.0714 g, 25 mmol). The polymerization was carried out for 110 minutes and identical purification procedure was used.

#### **2<sup>nd</sup> step - Synthesis of Poly(2-bromoisobutyryloxyethyl methacrylate) (PBiBEMA)**

A solution of PHEATMS (1.0 g, assuming 5 mmol of TMS groups) in THF (4 mL) was placed in a two-neck round bottom flask, and KF (0.350 g, 6 mmol) and 2,6-di-tert-butylphenol (10.5 mg, 0.05 mmol) were added under N<sub>2</sub>. A 0.01 M solution of TBAF in THF (0.5 mL, 0.005 mmol) was added to the flask, followed by the dropwise addition of 2-bromoisobutyl bromide (1.4 g, 6 mmol). The resulting solution was stirred at room

temperature overnight. The excess of acid bromide was quenched by adding 0.16 mL of water and 0.16 mL of Et<sub>3</sub>N. The mixture was centrifugated to separate the solid products. The liquid phase was collected, concentrated and purified by dialysis against THF for 48 hours (1000 g/mol average pore size). After removing the solvent under reduced pressure, the product was dried under vacuum to give 0.17 g of polymer in the case of 45 minutes reaction time (PBiBEMA1; M<sub>n</sub> = 3,600 g/mol, PDI = 1.1), 0.23 g of polymer in the case of 60 minutes reaction time (PBiBEMA2; M<sub>n</sub> = 4,900 g/mol, PDI = 1.1) and 0.4 g of polymer in the case of 120 minutes reaction time (PBiBEMA4; M<sub>n</sub> = 7,300 g/mol, PDI = 1.1). Identical synthetic and purification procedures were followed for the larger scale reaction. Reagent: PHEATMS (5.0g, assuming 25 mmol of TMS groups) in THF (20 mL), KF (1.8 g, 30 mmol), 2,6-di-tert-butylphenol (52.6 mg, 0.25 mmol), a solution of TBAF in THF (2.5 mL, 0.025 mmol), 2-bromoisobutyl bromide (3.75 mL, 30 mmol). 1.9 g of polymer were obtained (PBiBEMA3; M<sub>n</sub> = 5,800 g/mol, PDI = 1.2).

### **ATRP of methylmethacrylate (MMA) in the presence of BSP-OH-1 (6)**

All the ATRP tests were performed in a moisture and oxygen-free glass tube. EBiB (18.4 μL, 0.125 mmol), CuCl (9.9 mg, 0.1 mmol), CuCl<sub>2</sub> (3.4 mg, 0.025 mmol), HMTETA (35 μL, 0.125 mmol) were mixed at a 1:0.8:0.2:1 molar ratio in anisole (50% weight). MMA (0.52 g, 2.5 mmol) was added to the solution at a molar ratio 20 with respect to EBiB. The test was carried out at 60 °C for 35 minutes. The reaction was stopped by cooling the flask to room temperature and exposing the mixture to air. THF was added to the mixtures and the resulting polymer solution was filtered through a short column of neutral alumina. After removing solvent under reduced pressure, the products were dried under vacuum and collected. This procedure established the reference. All the other reactions were performed following the standard procedure with the appropriate modification (see Table S1).

### **Synthesis of Poly(2-azidoisobutyryloxyethyl methacrylate) (PAiBEMA)**

Sodium azide (0.1 g, 2.3 mmol) was added to a solution of PBiBEMA3 (0.1 g, 0.4 mmol) in dimethylformamide (DMF) (1 mL). The mixture was stirred overnight at room temperature and extracted several times with dichloromethane (DCM). The organic phase was dried over anhydrous MgSO<sub>4</sub> and filtered. After removing the solvent under reduced pressure the product was dried under vacuum to give 0.52 g of polymer (PAiBEMA1; M<sub>n</sub> = 6,100 g/mol, PDI = 1.2). The identical synthetic and purification procedure was used for the synthesis of PAiBEMA2 and PAiBEMA3, varying the molar ratio (Table S2). A molar ratio PAiBEMA3:NaN<sub>3</sub> = 1:0.46 was used in the case of PAiBEMA2, (M<sub>n</sub> = 6,000 g/mol, PDI = 1.2). A molar ratio PAiBEMA3:NaN<sub>3</sub> = 1:0.18 was used in the case of PAiBEMA3 (M<sub>n</sub> = 6,000 g/mol, PDI = 1.3). In all cases the presence of the azide groups were observed by FT-IR (cm<sup>-1</sup>) 2111.

### **Synthesis of 1'-(propargyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (BSP-alkyne 5)<sup>4</sup>**

#### **1<sup>st</sup> step - Synthesis of 1-propargyl-2,3,3-trimethylindoleninium tosylate**

2,3,3-Trimethylindolenine (1.2 mL, 7 mmol) and 1-tosyl-2-propyne (1.5 mL, 8.7 mmol) were mixed and heated at 78 °C for 3 hours. The reaction mixture was allowed to cool to room temperature. The resulting dark violet crude material was used without further purification.

### **2<sup>nd</sup> step - Synthesis of 1-propargyl-2,3,3-trimethylindolenine**

20 mL of a 0.5 M solution of KOH (11 mmol) in water were added to 1-propargyl-2,3,3-trimethylindoleninium tosylate (2.6 g, assuming 7 mmol). The resulting mixture was stirred for 45 minutes at room temperature and then extracted with Et<sub>2</sub>O. The organic phase was dried over MgSO<sub>4</sub> and filtered. The solvent was removed by rotary evaporation, leading to the desired product as a dark orange oil. The product was immediately used in the following step without further purification.

### **3<sup>rd</sup> step - Synthesis of 1'-(propargyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (BSP-alkyne)**

To a solution of 1-propargyl-2,3,3-trimethylindolenine (2.6 g, assuming 7 mmol) in EtOH (11 mL) 2-hydroxy-5-nitro benzaldehyde (1.64 g, 9.8 mmol) was added. The reaction mixture was heated under reflux for 4 hours. The reaction mixture was allowed to cool to room temperature of its own accord, the solvent was removed under reduced pressure to give the crude product as a dark purple oil. After purification through silica gel column chromatography (7/3 *n*-hexane/ethyl acetate as eluent) the propargyl spirobenzopyran (0.97 g, 2.8 mmol, 40%) was obtained as a bright yellow solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, δ, ppm): 1.20 (3H, s, 3'-CH<sub>3</sub>), 1.30 (3H, s, 3'-CH<sub>3</sub>), 2.08-2.10 (1H, m, HC≡C), 3.88 (1H, dd, *J* = 18.2 Hz, *J* = 2.4 Hz, NCH<sub>2</sub>), 4.03 (1H, dd, *J* = 18.2 Hz, *J* = 2.7 Hz, NCH<sub>2</sub>), 5.09 (1H, d, *J* = 10.2 Hz, 2-CCH=CH), 6.75 (1H, d, *J* = 9.9, ArH), 6.82 (1H, d, *J* = 7.8 Hz, ArH), 6.91-6.99 (2H, m, ArH, 2-CCH=CH), 7.10-7.14 (1H, m, ArH), 7.21-7.26 (1H, m, ArH), 8.00-8.04 (2H, m, ArH); <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>, δ, ppm): 160.2, 146.1, 141.5, 136.8, 129.4, 128.2, 126.5, 123.0, 122.0, 121.4, 121, 119, 116.5, 108.8, 106.4, 80.2, 80.0, 53.2, 33.0, 26.6, 20.5.

### **Click reaction of BSP-alkyne onto PAiBEMA**

PAiBEMA1 (0.52 g, 0.21 mmol) was dissolved in 4 mL of tetrahydrofuran and BSP-alkyne (0.080 g, 0.23 mmol), 13 μL of an aqueous freshly prepared 4M solution of sodium ascorbate (0.05 mmol) were added. CuBr (15.1 mg, 0.1 mmol) and PMDETA (21.9 μL, 0.1 mmol) were used as catalyst. The reaction mixture was stirred at 40 °C for 60 h under nitrogen and then purified through dialysis against THF (cut-off 1000 g/mol). The identical synthetic and purification procedure was used to click BSP-alkyne onto PAiBEMA2 and PAiBEMA3. In all the cases the peak at 2111 cm<sup>-1</sup> due to the azide groups decreased in intensity, as shown by FT-IR, only in the case of PAiBEMA3 the total absence of the peak at 2111 cm<sup>-1</sup> was recorded.

## Synthesis of 6-Azidohexyl Methacrylate (AHMA)<sup>5,6</sup>

### 1<sup>st</sup> step - Synthesis of 6-azido-1-hexanol

6-chloro-1-hexanol (3 mL, 22.5 mmol) was added to a solution of NaN<sub>3</sub> (2.3 g, 36.2 mmol) in DMF (4 mL) and water (4 mL). The mixture was heated to 75 °C for 22 h. The reaction mixture was cooled to room temperature, dissolved in 150 mL of water and extracted with Et<sub>2</sub>O (6 x 100 mL). The combined organic phase was washed twice with 100 mL of aqueous solution of NaCl, dried over anhydrous MgSO<sub>4</sub> and then filtered. After removing the solvent was removed under reduced pressure, the product was dried under vacuum to obtain pure 6-azido-1-hexanol as a yellowish oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 1.33 -1.66 (8H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 3.27 (2H, t, *J* = 6.8 Hz N<sub>3</sub>-CH<sub>2</sub>), 3.64 (2H, t, *J* = 6.8 Hz O-CH<sub>2</sub>); FT-IR (cm<sup>-1</sup>): 2094 (νN<sub>3</sub>).

### 2<sup>nd</sup> step - Synthesis of 6-Azidohexyl Methacrylate (AHMA)

6-azido-1-hexanol (3.2 g, assuming 22.5 mmol), was reacted with methacryloyl chloride (2.6 mL, 27.0 mmol) in dry DCM (70 mL) at 0 °C in the presence of triethylamine (4.4 mL, 31.5 mmol) for 24 h under inert atmosphere. After removing the solvent under reduced pressure, ethyl acetate and saturated aqueous solution of NaHCO<sub>3</sub> were added to the mixture. The aqueous phase was extracted with ethyl acetate (4 x 50 mL) and the combined organic layers were dried over anhydrous MgSO<sub>4</sub> and filtered. The solvent was removed under reduced pressure to leave the product as a yellow oil. After purification through silica gel column chromatography (9/1 *n*-hexane/ethyl acetate as eluent) the 6-azidohexyl methacrylate (AHMA) (1.71 g, 8.1 mmol, 72%) was obtained as transparent oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 1.32-1.75 (8H, m, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.94 (1H, s, CH<sub>3</sub>), 3.27 (2H, t, *J* = 6.8 Hz N<sub>3</sub>-CH<sub>2</sub>), 4.14 (2H, t, *J* = 6.8 Hz O-CH<sub>2</sub>), 5.55 (1 H, m, C=CH<sub>2</sub>), 6.09 (1 H, m, C=CH<sub>2</sub>); FT-IR (cm<sup>-1</sup>): 2094 (νN<sub>3</sub>) and 1714 (νC=O).

### Synthesis of poly(6-azidohexyl methacrylate) (PAHMA)

ATRP was applied for the synthesis of the polymers. All polymerization reactions were carried out in a moisture and oxygen-free glass tube. The initiator used depended on the desired polymer architecture: EBiB (2.6 μL, 0.018 mmol) to obtain the linear polymer, 4BriBu (13.2 mg, 0.018 mmol) to synthesize the star-like polymer and PBiBEMA1 (5 mg, 0.018 mmol) to obtain the molecular brush architecture. The selected initiator (0.018 mmol), CuCl (1.8 mg, 0.018 mmol) and PMDETA (3.8 μL, 0.018 mmol) were mixed at a 1:1:1 molar ratio in isopropyl alcohol (IPA) (50% weight). AHMA (380 mg, 1.8 mmol) was added to the solution at a molar ratio of 100 with respect to EBiB. The polymerization were carried out at 30 °C for 195, 50 or 40 minutes, respectively, depending on the desired polymer architecture. The polymerizations were stopped by cooling the flask to room temperature and exposing the reaction mixture to air. THF was added to the mixtures and the resulting polymer solutions were filtered through a short column of neutral alumina. The linear and star-like polymers were purified through precipitation into methanol, while the molecular brush polymer was purified through dialysis against THF (cut-off 3,500 g/mol). All the products were dried under vacuum to give 170 mg of linear PAHMA (9,200 g/mol, PDI: 1.2), 105 mg of star-like PAHMA

(10,200 g/mol, PDI: 1.2) and 18 mg of molecular brush PAHMA (22,100 g/mol, PDI: 1.2).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.80-1.03 (m, 3H,  $\text{CH}_3$  along the polymer backbone), 1.32-1.83 (m, 10H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$  and  $\text{CH}_2$  along the polymer backbone), 3.34 (m, 2H,  $\text{CH}_2\text{N}_3$ ), 3.96 (m, 2H,  $\text{CH}_2\text{O}$ ). In all the polymers the presence of the azide groups and the carbonyl groups were observed by FT-IR ( $\text{cm}^{-1}$ ) 2095 and 1728, respectively.

### **Synthesis of poly(BSP hexyl methacrylate) (PBSPHMA)**

Linear PBSPHMA (85 mg, 0.4 mmol) was dissolved in 6 mL of THF and BSP-alkyne (153 mg, 0.44 mmol), 25  $\mu\text{L}$  of an aqueous freshly prepared 4M solution of sodium ascorbate (0.1 mmol) were added. CuBr (28.7 mg, 0.2 mmol) and PMDETA (42  $\mu\text{L}$ , 0.2 mmol) were used as catalyst. The reaction mixture was stirred at 40  $^\circ\text{C}$  for 60 h under nitrogen. The reaction mixture was cooled to room temperature, filtered through a short column of neutral alumina, precipitated into methanol and further purified through dialysis against THF (cut-off 1000 g/mol).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.55-2.4 (m, 19 H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ,  $\text{CH}_2$  and  $\text{CH}_3$  along the polymer backbone and  $\text{CH}_3$  of the benzospiropyran unit), 3.58-4.79 (m, 6H,  $\text{CH}_2\text{O}$ ,  $\text{CH}_2\text{N}_3$ ,  $\text{CH}_2\text{N}$ ), 5.9 (br s, 1H, C-CH=CH), 6.46-7.20 (m, 6H, C-CH=CH and ArH), 7.45 (br s, 1H, triazole), 7.93 (br s, 2H, ArH). The identical synthetic and purification procedure was used to click BSP-alkyne onto the star-like and molecular brush PBSPHMA. In all the cases the absence of the azide groups were confirmed by FT-IR.

### **UV-Vis spectroscopic studies on BSP functional polymer obtained after click reaction of BSP-alkyne onto PAiBEMA (40% BSP)**

Approximately,  $1 \times 10^{-4}$  M stock solution of polymer in DCM was prepared [Note: the polymer concentration for the measurements was calculated based on the polymer  $M_n$  from SEC (PMMA standards) and considering the amount of BSP units bonded to the polymer] and stored in the dark at room temperature. The absorbance spectra of 3 ml of solution were recorded before and after exposure to UV light (365 nm) for 1 minute.

### **UV-Vis spectroscopic studies on photochromism of linear, star-like and molecular brush PBSPHMA**

Approximately,  $0.5 \times 10^{-4}$  M stock solutions of linear and molecular brush PBSPHMA and  $0.5 \times 10^{-5}$  M of star-like PBSPHMA in THF were prepared [Note: all polymer concentrations for the measurements were calculated based on the polymer  $M_n$  from SEC (PMMA standards) of the corresponding PAHMA precursor polymer] and stored in the dark at room temperature. Then 3 ml of each solution were exposed to UV light irradiation for 1 minute and the absorbance spectra were recorded. The absorbance decrease at  $\lambda_{\text{max}}$  (580 nm) was monitored, after removal of the irradiating source, for each polymer every 0.05 second for 800 seconds, in order to evaluate the ring closing kinetic over time. The first-order rate constants were estimated by following the decrease of the absorbance at  $\lambda_{\text{max}}$  in time and subsequently examined using the equation  $\ln([A_t]/[A_0]) = -kt$  with  $A_t$  and  $A_0$  denote the absorbance at  $\lambda_{\text{max}}$  at time  $t$  and at the beginning of the thermal relaxation process, respectively.<sup>7</sup>

For studying switching efficiency the value of absorbance was measured after irradiating the sample with UV light (365 nm) for 1 minute several times. After every measurement the BMC form was allowed to completely reverse back to the BSP form and the sample was kept in the dark during the experiment to avoid the interference of ambient light.

## Fluorescence spectroscopic studies on linear, star-like and molecular brush PBSPHMA

Approximately,  $1 \times 10^{-5}$  M stock solutions of linear and molecular brush PBSPHMA and  $1 \times 10^{-6}$  M of star-like PBSPHMA in THF were prepared [Note: all polymer concentrations for the measurements were calculated based on the polymer  $M_n$  from SEC (PMMA standards) of the corresponding PAHMA precursor polymer] and stored in the dark at room temperature. Fluorescence emission spectra of PBSPHMA were recorded before, after photoisomerisation by exposure to UV light for 1 minute and after maintaining the same sample in the dark for 10 minutes with excitation wavelength was set at 580 nm. Excitation spectra were collected after photoisomerisation upon exposure to UV light for 1 minute and after maintaining the same sample in the dark for 10 minutes. Excitation spectra were monitored at 650 nm.

## 2. ATRP of BSP monomers

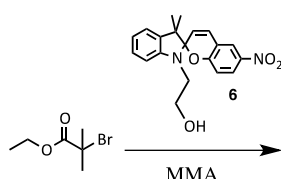


Table S1: Results of MMA ATRP in the presence of **6**.

Entry	<b>6</b> (mmol)	MMA (mmol)	EBiB (mmol)	Double bond consumption <sup>(a)</sup> (%)	$M_n$ (g/mol)	PDI
1	–	20	1	79	2700	1.3
2	0.8	20	1	80	2600	1.2
3	4.0	20	1	100	–	–
4	8.0	20	1	84 <sup>(b)</sup>	–	–
5	0.8	–	1	–	–	–
6	0.8	20	–	74	–	–

(a) Determined by  $^1\text{H}$  NMR spectroscopy from integration of peaks at 5.56 ppm and 6.10 ppm, indicative of the presence of MMA double bonds. (b) At this concentration **6** was only partially soluble in THF.

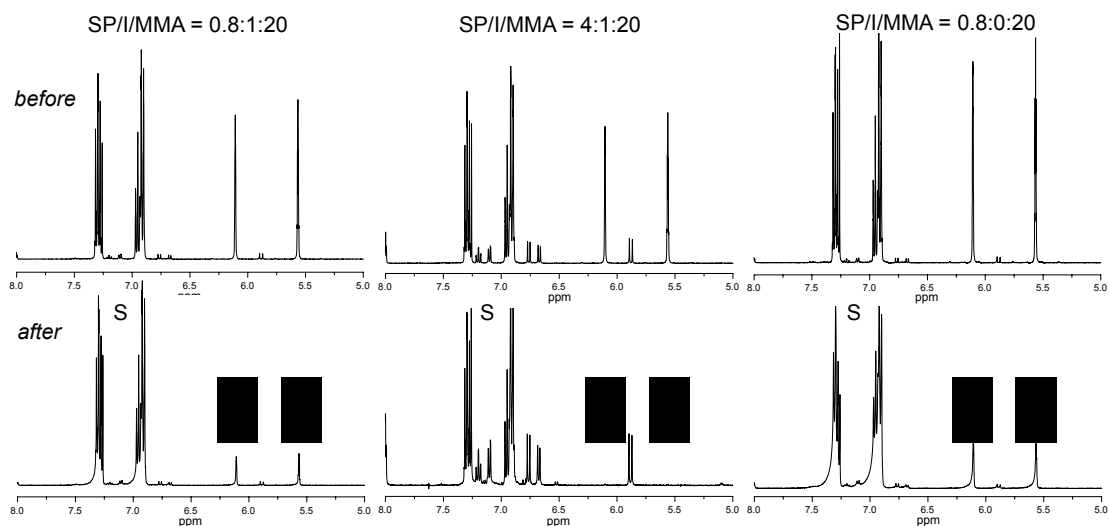


Figure S1: Representative sections of  $^1\text{H}$ -NMR spectra of MMA ATRP in the presence of **6** at different ratios. Top row: spectra of sample taken before the start of the ATRP; bottom row: spectra of samples taken after 35 minutes of reaction. The peaks of the reaction solvent anisole (S) were used as internal standard. Reactant ratios refer to entries in Table S1 (from left to right: entries 2, 3 and 6). Arrows mark the reduced MMA double bond peaks.

**Discussion control experiments:** A set of reactions under the same experimental conditions was carried out in the presence of **6** omitting either monomer or initiator. The  $^1\text{H}$  NMR spectrum of the product obtained after the reaction without monomer (ratio BSP-OH-1 to initiator = 0.8; entry 5, Table S1) matches the  $^1\text{H}$  NMR of BSP-OH-1, suggesting no reaction occurred under these conditions. In contrast, the results of the reaction carried out without initiator but in the presence of MMA (entry 6, Table S1) resembled the results obtained in the presence of an excess of BSP derivative. Indeed, in the  $^1\text{H}$  NMR spectrum of the final product the peaks 5.56 ppm and 6.10 ppm, indicative of the presence of the MMA double bonds, were considerably reduced with respect to the  $^1\text{H}$  NMR of the initial reaction mixture (Figure S1). According to the peak integration, around 75% of the double bonds were consumed without any detectable polymer formation.



### 3. BSP polymers by 'click' chemistry

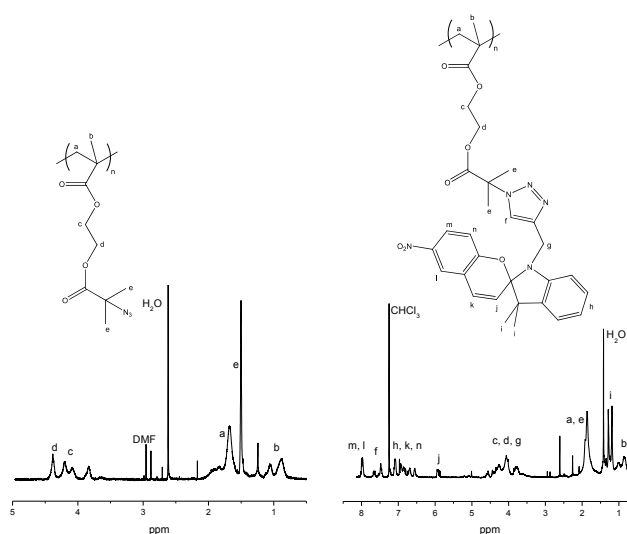


Figure S2: <sup>1</sup>H NMR spectrum of the azide functional polymer entry 1, Table 2 (left) and the same polymer after the addition of SP by cycloaddition (right).

Table S2: Characterization of the polymers bearing an azide functionality in the side chain by bromide substitution on **1** ( $M_n$  of 5800 g/mol,  $D = 1.2$ ) using various ratios of NaN<sub>3</sub> to **1**.

Entry	N <sub>3</sub> /Br ratio <sup>(a)</sup>	$M_n$ (g/mol)	$D$
1	1	6100	1.2
2	0.7	6000	1.2
3	0.4	6000	1.2

(a) Estimated from <sup>1</sup>H NMR spectra using the relative peak intensities at 1.97 ppm (bromide substituted) and 1.46 ppm (azide substituted). Due to a peak overlapping a slight error in the quantification may occur.

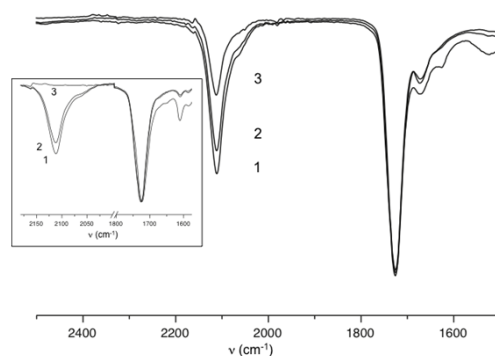


Figure S3: FT-IR spectra of polyazides **5** (entry 1, 2, 3, Table S2). Inset: FT-IR spectra after click reaction of SP-alkyne onto polyazides **5**. The carbonyl peak of the polymer was used to normalize the spectra for both spectra.

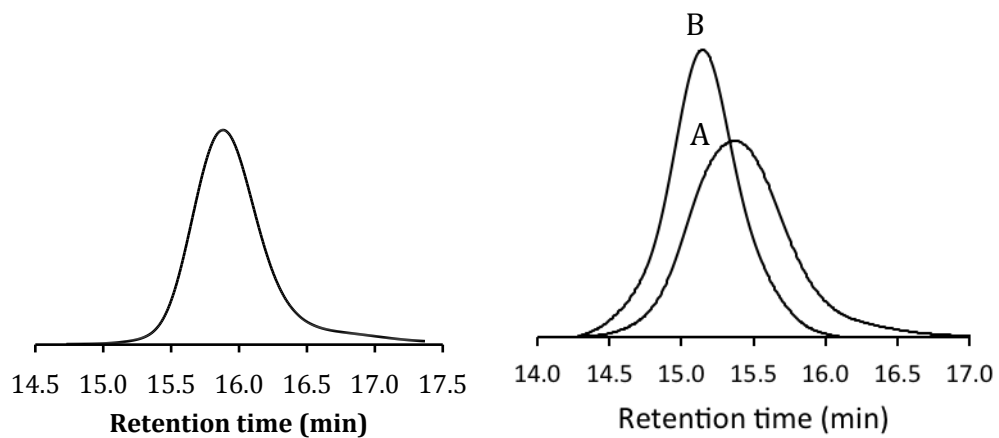


Figure S4: SEC of (A) star-like PAHMA (10,200 g/mol, PDI: 1.2) and (B) molecular brush PAHMA (22,100 g/mol, PDI: 1.2).

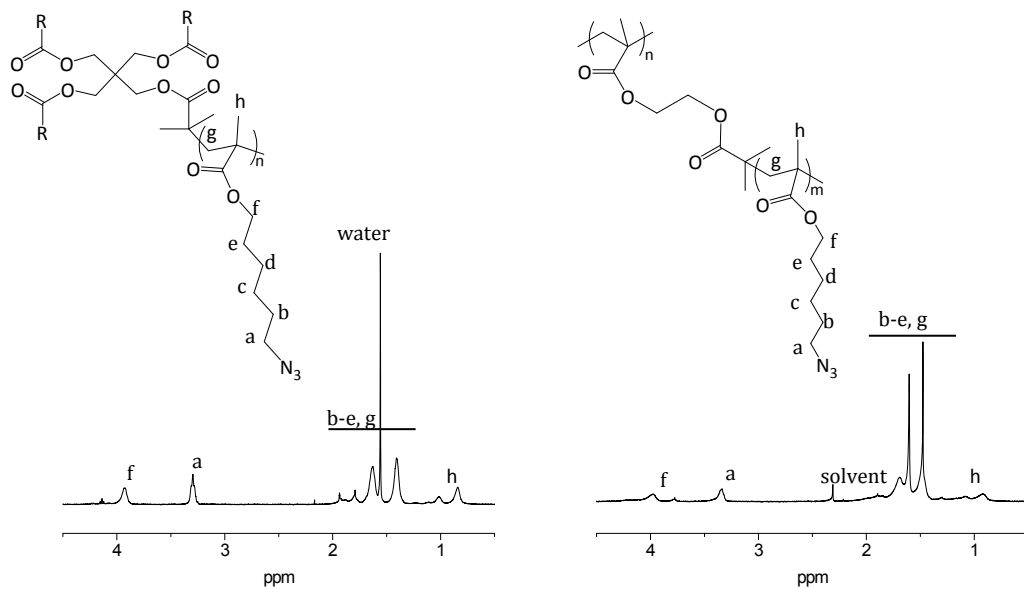


Figure S4: <sup>1</sup>H NMR spectra of star-like PAHMA (left) and molecular brush PAHMA (right) in CDCl<sub>3</sub>.

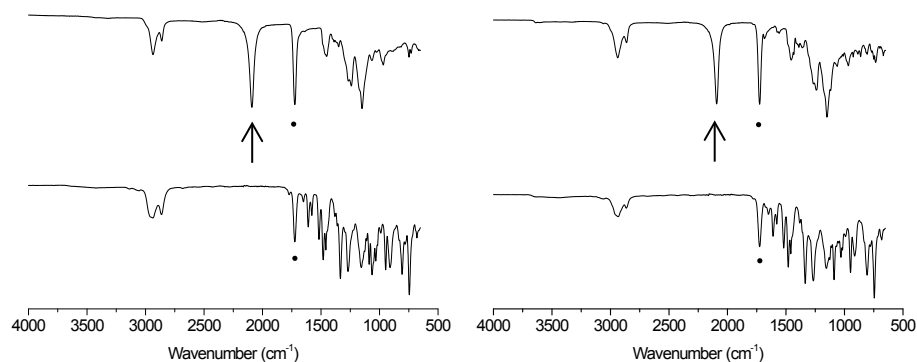


Figure S5: FT-IR spectra of star-like PAHMA (left spectrum) and molecular brush PAHMA (right spectrum) before (top) and after (bottom) click reaction with BSP-alkyne. The arrows mark the azide peaks and the dots mark the carbonyl peaks.

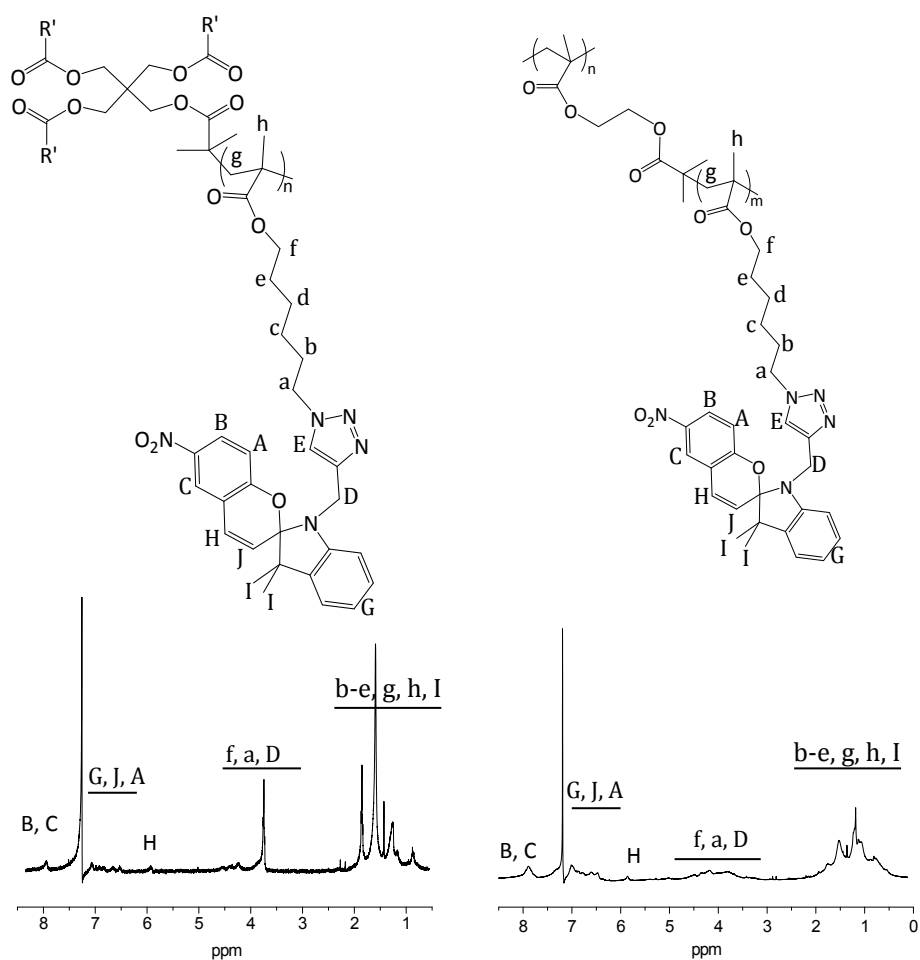


Figure S6:  $^1\text{H}$  NMR spectra of poly (BSP hexyl methacrylate) with star-like (left) and molecular brush (right) architectures in  $\text{CDCl}_3$ .

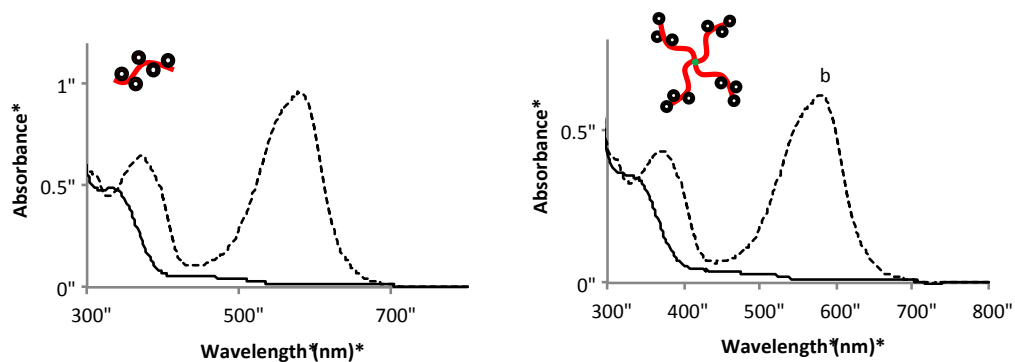


Figure S8: UV-Vis spectra of BSP linear and star-like polymer before (a) and after (b) 1 minute of UV (365 nm) irradiation.

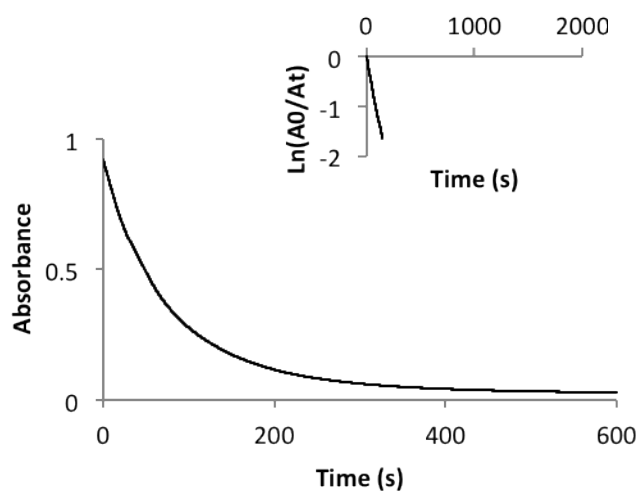
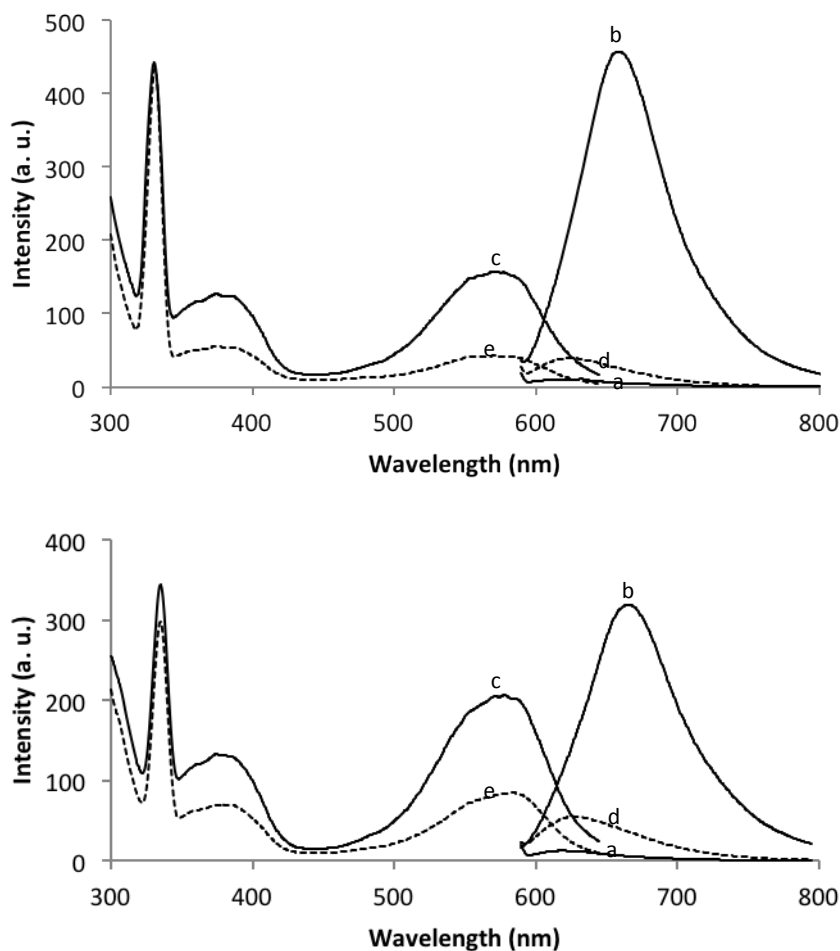


Figure S9: Absorbance decrease at  $\lambda_{\max}$  (580 nm) in THF as a function of time after removing the UV light source, for the transition of BMC to BSP for the linear polymer at room temperature. A linear correlation between BMC ( $\lambda_{\max}$ ) and its rate constant is revealed for this polymer.



**Figure S10:** Fluorescence spectra of star-like (top) and molecular brush (bottom) PBSPHMA. Emission spectra before (a), after (b) irradiation with UV light (365 nm) for 1 minute and the following excitation spectrum (c) (solid lines); Emission (d) and excitation (e) spectra of the same sample kept in the dark for 10 minutes (dashed lines). All the emission spectra were acquired under 580 nm light excitation and all the excitation spectra were obtained by monitoring 650 nm emission.

<sup>1</sup> K. Matyjaszewski, P.J. Miller, J. Pyun, G. Kickelbick, S. Diamanti, *Macromolecules*, 1999, **32**, 6526.

<sup>2</sup> F.M. Raymo, S. Giordani, *J. Am. Chem. Soc.*, 2001, **123**, 4651.

<sup>3</sup> A. Nese, J. Mosnàcek, A. Juhari, J.A. Yoon, K. Koynov, T. Kowalewski, K. Matyjaszewski, *Macromolecules*, 2010, **43**, 1227.

<sup>4</sup> M. Bertoldo, S. Nazzia, G. Zampanò, F. Ciardelli, *Carbohydr. Polym.*, 2011, **85**, 401.

<sup>5</sup> B.S. Sumerlin, N.V. Tsarevsky, G. Louche, R.Y. Lee, K. Matyjaszewski, *Macromolecules*, 2005, **38**, 7540.

<sup>6</sup> N. Cengiz, H. Kabadayioğlu, R. Sanyal, *J. Polym. Sci. A: Polym. Chem.*, 2010, **48**, 4737.

<sup>7</sup> J.B. Flannery, *J. Am. Chem. Soc.*, 1968, **90**, 5660.