

## Supplementary data

### Modular synthesis of block copolymers via cycloaddition of terminal azide and alkyne functionalized polymers

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**3-(1,1,1-trimethylsilyl)-2-propynyl 2-bromo-2-methylpropanoate [1]:** A solution of 2-bromoisobutyryl bromide (2.05 g, 8.93 mmol) in THF (20 mL) was added dropwise to a solution of 3-trimethylsilyl-2-propyn-1-ol (776.7 mg, 6.06 mmol) and triethylamine (905.3 mg, 8.95 mmol) in THF (40 mL) at 0°C. After complete addition, the reaction mixture was allowed to stir for 1 hour at room temperature. The excess of the acid bromide was quenched by addition of methanol (5 mL). The formed triethylammonium bromide was filtered off and the solvent was removed *in vacuo*. The crude product was dissolved in dichloromethane and washed two times with a saturated ammonium chloride solution and two times with distilled water. The organic layer was dried with magnesium sulfate and solvent was removed *in vacuo*, yielding a yellow oil which was purified using flash chromatography (heptane/EtOAc 19:1). The product was isolated as a colorless oil which was dried under vacuum (1.59 g, 93%).  $\delta_{\text{H}}$ (CDCl<sub>3</sub>, 300 MHz) 4.75 (s, 2H,  $\equiv\text{-CH}_2\text{-O}$ ), 1.95 (s, 6H, O<sub>2</sub>C-C(CH<sub>3</sub>)<sub>2</sub>Br), 0.18 (s, 9H, (H<sub>3</sub>C)<sub>3</sub>Si). FTIR-ATR/cm<sup>-1</sup> 3800, 3736, 3650, 3001, 2962, 2893, 2180, 2094, 1739

**Atom transfer radical polymerization (typical procedure):** CuBr (57.6 mg, 0.40 mmol) was placed in a Schlenk tube which was fitted with a stopper, evacuated and back-filled with dry nitrogen. This procedure was repeated three times. After the evacuating cycles the stopper was replaced by a septum. Xylene (7 mL), N-(n-propyl)-2-pyridylmethanimine (119.1 mg, 0.80 mmol) and MMA (2.03 g, 20.3 mmol) were added and the reaction mixture was cooled in an ice bath. Subsequently, 3-(1,1,1-trimethylsilyl)-2-propynyl 2-bromo-2-methylpropanoate (111.4 mg, 0.40 mmol) was added and the reaction mixture was purged with dry nitrogen for five minutes and placed in a statically controlled oil bath at 90°C. Samples were taken periodically for

conversion analysis by gas chromatography.  $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$  4.61 (br. s,  $\equiv\text{-CH}_2\text{-CO}_2$ ), 3.63-3.48 (br. s, backbone  $\text{H}_3\text{C-O}_2\text{C}$ ), 2.11-0.73 (br. m, backbone  $\text{CH}_2$ ,  $\text{CH}_3$ ), 0.18 (s,  $(\text{H}_3\text{C})_3\text{Si-}\equiv$ ). SEC:  $M_n = 7.85 \text{ kg/mol}$ .  $M_w/M_n = 1.14$

**Deprotection of trimethylsilyl alkyne functionalized polymers [2, 3]:** Trimethylsilyl protected polymer (PMMA or PS) was dissolved in THF (0.01 M solution) and tetrabutylammonium fluoride (10.00 equiv) was added. The reaction mixture was stirred overnight at room temperature. PMMA samples were purified over a basic alumina column and precipitated in heptane, yielding a white solid which was dried under vacuum. PS was purified by precipitation in methanol, yielding a white solid which was dried under vacuum. **[2]:** (yield: 1.05 g, 83%)  $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$  4.63 (br. m,  $\equiv\text{-CH}_2\text{-O}_2\text{C}$ ), 3.63-3.48 (br. s, backbone  $\text{H}_3\text{C-O}_2\text{C}$ ), 2.45 (br. m,  $\text{H-}\equiv$ ), 2.11-0.73 (br. m, backbone  $\text{CH}_2$ ,  $\text{CH}_3$ ). SEC:  $M_n = 21.28 \text{ kg/mol}$ .  $M_w/M_n = 1.13$  **[3]:** (yield: 0.83 g, 87%)  $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$  7.37-6.34 (br. m, arom. H), 4.61 (br. m,  $\equiv\text{-CH}_2\text{-O}_2\text{C}$ ), 4.48 (br. m,  $\text{CH}_2\text{-CH(Ph)-Br}$ ), 2.25-1.18 (br. m, backbone  $\text{CH}_2$ ,  $\text{CH}$ ), 0.85 (br. m,  $\text{O}_2\text{C-CH(CH}_3\text{)-CH}_2$ ). SEC:  $M_n = 4.82 \text{ kg/mol}$ .  $M_w/M_n = 1.23$

**Alkyne functionalized poly(ethylene glycol) methyl ether [4]:** A solution of EDCI (92.4 mg, 0.48 mmol) in dichloromethane (2 mL) was added dropwise to a solution of poly(ethylene glycol) methyl ether (Aldrich,  $M=2000 \text{ g/mol}$ , 800.4 mg, 0.40 mmol), 4-pentynoic acid (47.4 mg, 0.49 mmol) and DMAP (6.4 mg, 0.052 mmol) in dichloromethane (4 mL) at  $-20^\circ\text{C}$ . After complete addition, the reaction mixture was allowed to stir for 20 hours at room temperature. The reaction mixture was washed twice with a 1 M sodium hydroxide solution and two times with distilled water. The organic layer was dried with anhydrous magnesium sulfate and solvent was removed *in vacuo*, yielding a white solid (0.69 g, 83%).  $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$  4.25 (t,  $J = 4.81 \text{ Hz}$ ,  $\text{O-CH}_2\text{-CH}_2\text{-CO}_2$ ), 3.69 (t,  $J = 4.81 \text{ Hz}$ ,  $\text{O-CH}_2\text{-CH}_2\text{-CO}_2$ ), 3.63 (s,  $\text{O-(CH}_2\text{)}_2\text{-O}$ ), 3.37 (s,  $\text{CH}_3\text{-O}$ ), 2.61-2.46 (m,  $\text{O}_2\text{C-(CH}_2\text{)}_2\text{-}\equiv$ ), 1.99 (t,  $J = 2.41 \text{ Hz}$ ,  $\text{H-}\equiv$ ). FTIR-ATR/ $\text{cm}^{-1}$  3261, 2880, 1960, 1727, 1467, 1338, 1282, 1238, 1143

**Tosylated poly(ethylene glycol) methyl ether:** Poly(ethylene glycol) methyl ether (Aldrich,  $M=2000 \text{ g/mol}$ , 2.00 g, 1.00 mmol) was dissolved in pyridine (10 mL) and toluene-4-sulfonyl chloride (1.91 g, 10.0 mmol) was added. The reaction mixture was stirred for 20 hours at room temperature and then poured into cold distilled

water. The product was extracted with dichloromethane. The organic layer was washed twice with a cold 6 M hydrochloric acid solution and three times with cold distilled water. Afterwards, the organic layer was dried with anhydrous magnesium sulfate and solvent was removed *in vacuo*, yielding a white solid (1.82 g, 85%).  $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$  7.77 (m, arom. H), 7.31 (m, arom. H), 4.14 (t,  $J = 4.80 \text{ Hz}$ ,  $\text{CH}_2\text{-CH}_2\text{-OTs}$ ), 3.63 (s, O- $(\text{CH}_2)_2\text{-O}$ ), 3.37 (s,  $\text{H}_3\text{C-O}$ ), 2.44 (s,  $\text{H}_3\text{C-aryl}$ )

**Azide functionalized poly(ethylene glycol) methyl ether [5]:** Tosylated poly(ethylene glycol) methyl ether (1.72 g, 0.80 mmol) was dissolved in DMF (10 mL) and sodium azide (650.3 mg, 10.00 mmol) was added. The reaction mixture was stirred for 22 hours at room temperature. Dichloromethane (25 mL) was added and the reaction mixture was washed three times with cold distilled water, twice with cold 6 M hydrochloric acid solution and two times with cold distilled water. The organic layer was dried with anhydrous magnesium sulfate and solvent was removed *in vacuo*, yielding a white solid (1.32 g, 82%).  $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$   $\delta$  3.86 (t,  $J = 4.80 \text{ Hz}$ ,  $\text{CH}_2\text{-CH}_2\text{-N}_3$ ), 3.63 (s, O- $(\text{CH}_2)_2\text{-O}$ ), 3.37 (s,  $\text{H}_3\text{C-O}$ ). FTIR-ATR/ $\text{cm}^{-1}$  2881, 2098, 1960, 1463, 1342, 1100

**Polystyrene terminal azide introduction [6, 7]:** PS which was prepared by ATRP using either 1-bromoethylbenzene or 2-[(2-bromopropanoyl)oxy]ethyl 2-bromopropanoate as an initiator, was dissolved in THF (0.01 M solution). Subsequently, azidotrimethylsilane (10.00 equiv) and TBAF (10.0 equiv) were added (4.0 mL, 4.0 mmol). The reaction mixture was stirred overnight at room temperature and the polymer was precipitated in methanol, yielding a white solid which was dried under vacuum. [6]: (yield: 1.35 g, 91%)  $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$  7.36-6.38 (br. m, arom. H), 3.91 (br. m,  $\text{CH}_2\text{-CH}(\text{Ph})\text{-N}_3$ ), 2.17-1.24 (br. m, backbone  $\text{CH}_2$ ,  $\text{CH}$ ), 1.11-1.02 (br, s,  $\text{H}_3\text{C-CH}(\text{Ph})\text{-CH}_2$ ). FTIR-ATR/ $\text{cm}^{-1}$  3019, 2925, 2837, 2090 ( $\nu_{\text{N}_3}$ ), 2008, 1943, 1865, 1796, 1597, 1493, 1450. SEC:  $M_n = 3.66 \text{ kg/mol}$ .  $M_w/M_n = 1.16$  [7]: (yield: 1.65 g, 85%)  $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$  7.38-6.35 (br. m, arom. H), 3.93 (br. m,  $\text{CH}_2\text{-CH}(\text{Ph})\text{-N}_3$ ), 3.36 (br. m,  $\text{O}_2\text{C-}(\text{CH}_2)_2\text{-CO}_2$ ), 2.25-1.18 (br. m, backbone  $\text{CH}_2$ ,  $\text{CH}$ ), 0.85 (br. m,  $\text{O}_2\text{C-CH}(\text{CH}_3)\text{-CH}_2$ ). FTIR-ATR 3023, 2919, 2094 ( $\nu_{\text{N}_3}$ ), 2021, 1939, 1873, 1805, 1731, 1597, 1493, 1450  $\text{cm}^{-1}$ . SEC:  $M_n = 11.69 \text{ kg/mol}$ .  $M_w/M_n = 1.14$

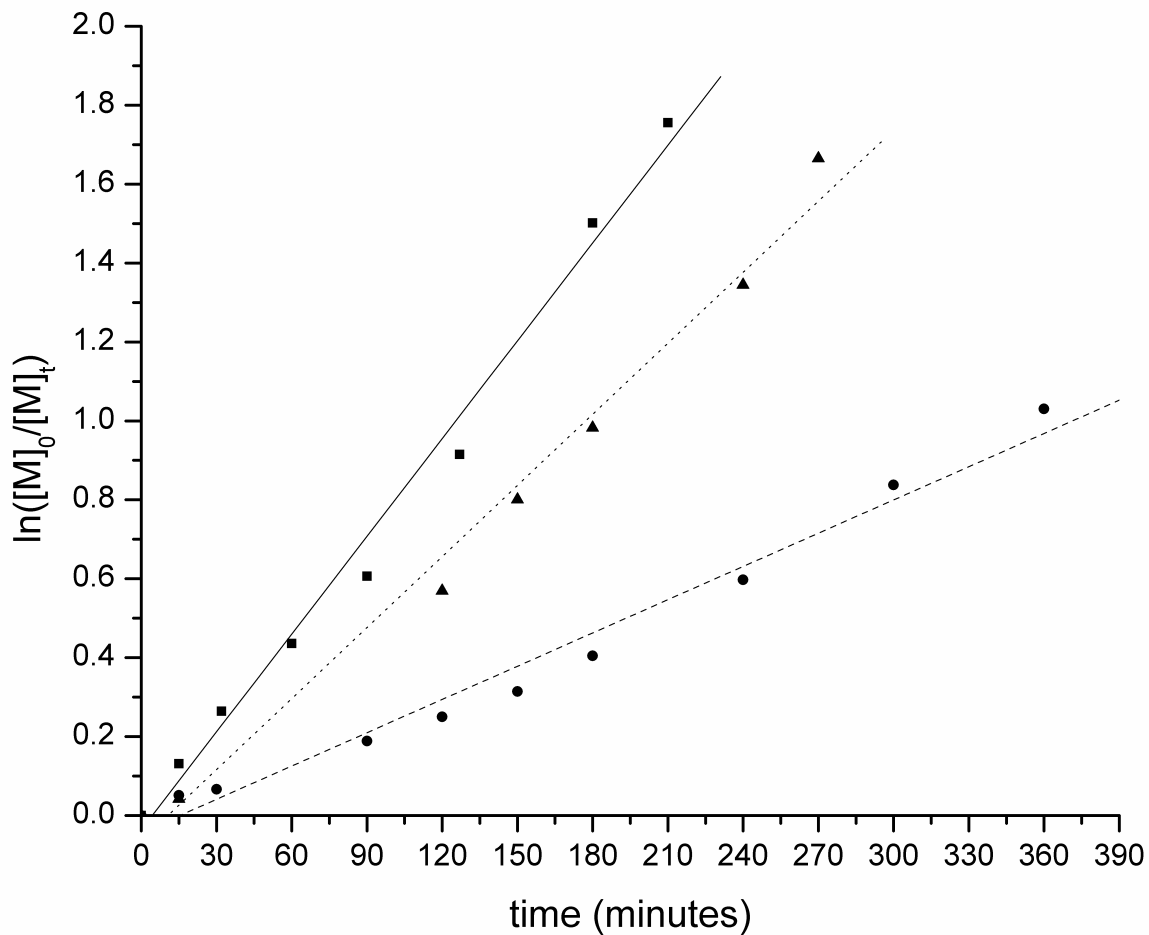
**Azidomethyl polystyrene resin:** Merrifield resin (1.01 g, 1.0-1.5 mmol/g) was reacted with  $\text{NaN}_3$  (974.3 mg,

15.0 mmol) in DMSO at 60°C for 48 hours. The suspension was cooled to room temperature and filtered.

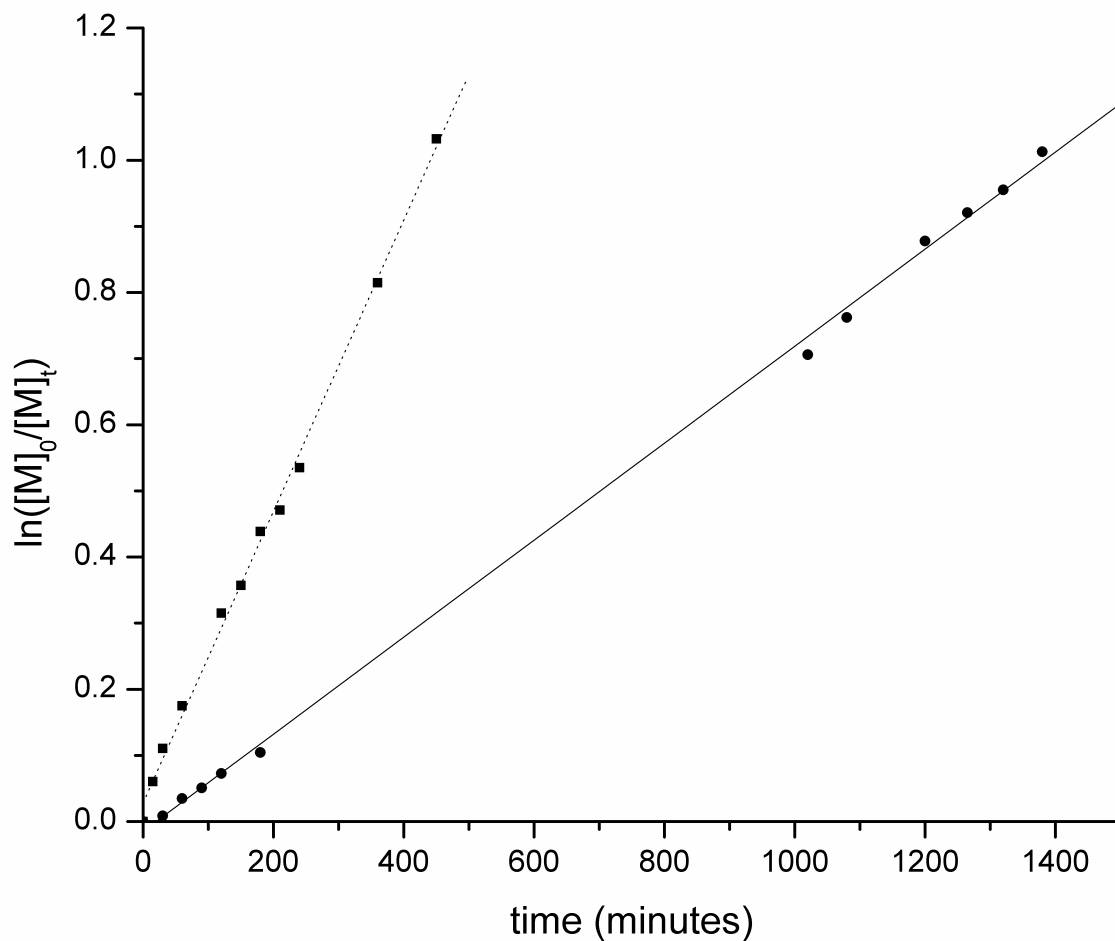
Subsequently, the resin was washed with methanol and dichloromethane to give azidomethyl polystyrene resin.

FTIR-ATR/cm<sup>-1</sup> 3053, 3022, 2915, 2846, 2094 ( $\nu_{N_3}$ ), 1940, 1867, 1798, 1715, 1598 1493, 1453 1262

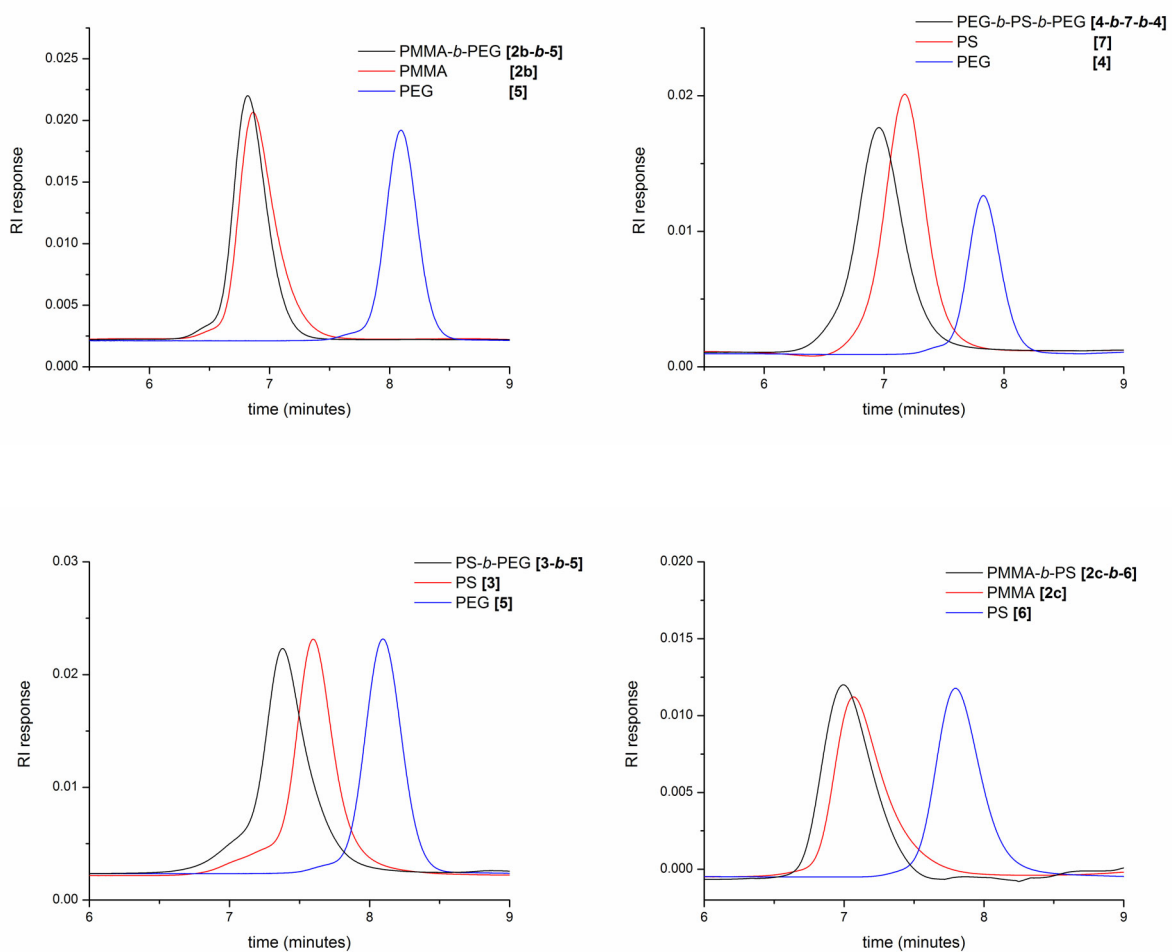
**Cycloaddition reactions (typical procedure):** Alkyne functionalized PMMA (1.71 g, 0.24 mmol), azide functionalized PS (540.6 mg, 0.20 mmol) and CuI (7.78 mg, 0.041 mmol) were placed in a Schlenk tube which was fitted with a stopper, evacuated and back-filled with dry nitrogen. This procedure was repeated three times. After the evacuating cycles, tetrahydrofuran (10 mL) and 1,8-diaza[5.4.0]bicycloundec-7-ene (606.7 mg, 3.98 mmol) were added and the reaction mixture was placed in a statically controlled oil bath at 35°C for 18 hours. Subsequently, azidomethyl polystyrene resin (400.6 mg, 0.4-0.6 mmol theoretically) was added and the reaction mixture was stirred 25 hours. The resin was filtered off and the polymer was precipitated in methanol yielding a slightly blue colored solid. The polymer was dissolved in dichloromethane and washed with a 0.065 M EDTA solution. The organic layer was dried with anhydrous magnesium sulfate and was concentrated *in vacuo*. The polymer was precipitated in methanol yielding a white solid which was dried under vacuum.



**Fig. 1** Semilogarithmic kinetic plots of the polymerization of methyl methacrylate (MMA)[2] and styrene [3] using 3-(1,1,1-trimethylsilyl)-2-propynyl 2-bromo-2-methylpropanoate as initiator; (■)  $[MMA]_0 = 2.78$  M,  $[CuBr]_0 = [N-(n\text{-propyl})\text{-}2\text{-pyridylmethanimine}]_0/2 = [\text{initiator}]_0 = 0.056$  M; (▲)  $[MMA]_0 = 2.21$  M,  $[CuBr]_0 = [N-(n\text{-propyl})\text{-}2\text{-pyridylmethanimine}]_0/2 = [\text{initiator}]_0 = 0.044$  M; (●)  $[styrene]_0 = 7.45$  M,  $[CuBr]_0 = [PMDETA]_0 = [\text{initiator}]_0 = 0.12$  M



**Fig.2** Semilogarithmic kinetic plots of the polymerization of styrene [6, 7]; (■)  $[\text{styrene}]_0 = 6.75 \text{ M}$ ,  $[\text{CuBr}]_0 = [\text{PMDETA}]_0 = [\text{initiator}]_0 = 0.23 \text{ M}$ ; (●)  $[\text{styrene}]_0 = 6.07 \text{ M}$ ,  $[\text{CuBr}]_0/2 = [2,2'\text{-bipyridyl}]_0/4 = [\text{initiator}]_0 = 0.031 \text{ M}$



**Fig. 3** SEC traces of the polymer precursors (—, —) and the subsequently formed block copolymers (—).