

## 2D-LC/SEC-(MALDI)-MS characterization of symmetric and nonsymmetric biocompatible PEO<sub>m</sub>-PIB-PEO<sub>n</sub> block copolymers

*Haitham Barqawi<sup>†</sup>, Matthias Schulz<sup>†</sup>, Adekunle Olubummo<sup>†</sup>, Volker Sauerland<sup>‡</sup> and Wolfgang H. Binder<sup>†,\*</sup>*

*<sup>†</sup>Faculty of Natural Sciences II (Chemistry, Physics, Mathematics), Institute of Chemistry, Chair of Macromolecular Chemistry, Martin-Luther University Halle-Wittenberg, D-06120 Halle (Saale), Germany.*

*<sup>‡</sup>Bruker Daltonik GmbH, Fahrenheitstrasse 4, 28359 Bremen, Germany.*

### Supporting Information

## 1 Synthetic part

### S1.1 Synthesis of $\alpha$ -hydroxymethyl- $\omega$ -bromo telechelic PIB (2).

A representative procedure for the preparation of  $\alpha$ -hydroxymethyl- $\omega$ -bromo telechelic PIB (2) with  $M_n = 5,000 \text{ g.mol}^{-1}$  was achieved by a combined method of Puskas<sup>1</sup> and Storey<sup>2</sup> as published previously by our group.<sup>3</sup> Under an argon atmosphere, dichloromethane and n-hexane (40/60 mixture), di-*tert*-butyl pyridine (DtBP) (0.005 mol/L), and MSE initiator (0.049 mol/L) were cooled down to -60°C in a three-necked round-bottom flask equipped with a septum and a mechanical stirrer. To the mixture a solution of TiCl<sub>4</sub> (0.034 mol/L) was added and subsequently the polymerization was started by adding condensed isobutylene (1 mol/L) into the reaction mixture via syringe. After complete conversion of the monomer (~20 minutes), the polymerization mixture was cooled further to -70°C and a quantitative end-capping reaction was achieved by using an excess of 3-bromopropoxybenzene (BPB) (2.5 equiv per chain end). Finally, after 3 hours, the catalyst was destroyed by addition of methanol (large excess), and the polymer was isolated by repeated precipitation from hexane into methanol. The resulting  $\alpha$ -hydroxymethyl- $\omega$ -bromo telechelic PIB (2) was obtained in a yield of 95%.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.82 (d, J = 8.79 Hz, 2H), 4.08 (t, J = 5.78 Hz, 2H), 3.64 (d, J = 10.77 Hz, 1H), 3.58 (t, J = 6.53 Hz, 2H), 3.41 (d, J = 10.78 Hz, 1H), 2.29 (t, J = 6.23 Hz, 2H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 154, 148.5, 141.6, 128.4, 125.7, 125.1, 114, 70.1, 67.3, 53.4, 43.8, 32.6, 30, 28, 20.5. (<sup>1</sup>H- and <sup>13</sup>C- NMR data represent the end group structure of the polymer chains)

**Table S1.** Experimental results of isobutylene polymerization using MSE/TiCl<sub>4</sub> as initiator system.

Entry	Sample	M <sub>n</sub> <sup>1)</sup> (theory)	Characterization				Yield <sup>2)</sup> [%]
			M <sub>n</sub> <sup>1)</sup> (GPC)	M <sub>w</sub> <sup>1)</sup> (GPC)	PDI	M <sub>n</sub> <sup>1)</sup> (NMR)	
1	HO-PIB <sub>57</sub> -Br ( <b>2a</b> )	3000	3190	4950	1.25	3540	92
2	HO-PIB <sub>70</sub> -Br ( <b>2b</b> )	4000	3920	5060	1.29	4260	89
3	HO-PIB <sub>85</sub> -Br ( <b>2c</b> )	5000	4760	5980	1.25	5080	95

<sup>1)</sup> Number average molecular weight in [g/mol].

<sup>2)</sup> Isolated mass of the polymers.

### S1.2 Synthesis of $\alpha$ -alkyne- $\omega$ -bromo-telechelic PIB (**3**)

NaH (1.2 equiv.; 17 mg, 0.714 mmol) was washed three times with dry THF under an argon atmosphere to remove mineral oil and was afterwards cooled down to 0°C via an ice bath.  $\alpha$ -Hydroxymethyl- $\omega$ -bromo-telechelic PIB (**2**) (2.5 g, 0.595 mmol) and 15-crown-5 (1 equiv. 0.131 g, 0.595 mmol) were added drop-wise to the sodium hydride solution. The reaction mixture was allowed to stir for 30 min at 0°C. Subsequently, propargyl bromide (80% in toluene, 2 equiv. 0.141 g, 1.2 mmol) was added slowly to the reaction mixture. The ice bath was removed and the reaction was further stirred at 35°C for 48 hours. Finally, THF was removed via rotary evaporation under reduced pressure. The residue was dissolved in hexane, washed three times with water, once with brine and after separation the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The  $\alpha$ -alkyne- $\omega$ -bromo telechelic PIB (**3**) was isolated by precipitation from hexane into a mixture of methanol/ acetone (1/1) yielding a slight yellow product (90% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.81 (d, J = 8.46 Hz, 2H), 4.08 (m, 4H), 3.64 (d, J = 10.77 Hz, 1H), 3.58 (t, J = 6.53 Hz, 2H), 3.41 (d, J = 10.78 Hz, 1H), 2.35 (m, 1H) 2.29 (t, J = 6.23 Hz, 2H). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 154, 148.5, 141.6, 128.4, 125.7, 125.1, 114, 82.3, 75.6, 73.4, 71.7, 67.3, 53.4, 43.8, 32.6, 30, 28, 20.5. (<sup>1</sup>H- and <sup>13</sup>C- NMR data represent the end group structure of the polymer chains)

### S1.3 Synthesis of $\alpha$ -TEO- $\omega$ -bromo-telechelic PIB (**5**)

The azide/alkyne-click reaction between  $\alpha$ -methoxy- $\omega$ -azido-telechelic triethylene oxide (TEO) (**4**) and  $\alpha$ -alkyne- $\omega$ -bromo-telechelic PIB (**3**) was conducted under Cu<sup>I</sup> mediated conditions as follows: Compound (**3**) (1 equiv.), azido-telechelic TEO (**4**) (1 equiv.), tris-(benzyl triazolylmethyl) amine (TBTA) (0.1 equiv.) and Cu<sup>I</sup> (Cu(I) iodide, 0.1 equiv.) were

dissolved in an argon bubbled toluene (oxygen free) and heated up to 90°C. After 48 hours the solvent was removed via rotary evaporation and the crude product was purified by column chromatography on silica gel using a particular procedure ( $\text{CHCl}_3$  to remove the unreacted  $\alpha$ -alkyne- $\omega$ -bromo-telechelic PIB (**3**),  $R_f = 1$  and followed by  $\text{CHCl}_3/\text{CH}_3\text{OH} = 30:1$ ,  $R_f = 0.1$  to remove the unreacted azido-telechelic TEO) yielding the pure  $\alpha$ -TEO- $\omega$ -bromo-telechelic PIB (**5**) (82% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.47 (s, 1H), 6.82 (d,  $J = 8.41$  Hz, 2H), 4.64-4.46 (m, 2H), 4.08 (t,  $J = 5.78$  Hz, 2H), 3.86 (t,  $J = 4.76$  Hz, 1H), , 3.72-3.47 (m, 12H), 3.37 (s, 3H), 2.29 (t,  $J = 6.23$  Hz, 2H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 154.4, 158.8, 145.4, 142.8, 128.8, 125.7, 125.1, 120.9, 114.2, 81.3, 71.8, 70.6, 69.8, 64.8, 63.5, 59.3, 52.9, 43.1, 29.3, 27.6. ( $^1\text{H}$ - and  $^{13}\text{C}$ - NMR data represent the end group structure of the polymer chains)

#### S1.4 Synthesis of $\alpha$ -TEO- $\omega$ -azido-telechelic PIB (**6**)

The bromo-telechelic compound (**5**) was converted into the azido-telechelic product as follows: Compound (**5**) (1 g, 0.238 mmol) was dissolved in 100 ml of 50/50 (v/v) mixture of heptane and DMF (two-phase) and treated with sodium azide (14 mg, 2.5 equiv.). The final mixture was heated up to 90°C, upon which it changed to a single phase. Quantitative end group conversion was completed after 5 hours as judged via tlc and NMR-spectroscopy. Afterwards, the reaction mixture was cooled down to room temperature changing back to two-phase system. The heptane phase separated and washed three times with deionized water. Finally, the polymer was precipitated into methanol. The obtained product was dried under high vacuum yielding 87% of (**6**).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.47 (s, 1H), 6.82 (d,  $J = 8.41$  Hz, 2H), 4.64-4.46 (m, 2H), 4.08 (t,  $J = 5.78$  Hz, 2H), 3.86 (t,  $J = 4.76$  Hz, 1H), 3.72-3.47 (m, 12H), 3.37 (s, 3H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 154.4 (C18), 158.8, 145.4, 142.8, 128.8, 125.7, 125.1, 120.9, 114.2, 81.3, 71.8, 70.6, 69.8, 64.8, 63.5, 59.3, 52.9, 44.3, 43.1, 29.3, 27.6. FT-IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 3000-2700 (C-H),  $\sim 2100$  ( $\text{N}_3$ ).

#### S1.5 Synthesis of alkyne-telechelic PEOs

Alkyne-telechelic triethylene oxide (**7**) or the poly(ethylene oxide)s (**8**, **9**) were prepared according to literature.<sup>4, 5</sup> A flame dried glass tube was charged with hydroxy-telechelic triethylene oxide or poly(ethylene oxide) monomethyl ether ( $M_n = 550$  Da or  $M_n = 750$  Da,  $M_w/M_n = 1.09$ ) (1.0 g, 1.8 mmol, 1.0 equiv.) and sodium hydroxide (0.7 g, 18.0 mmol, 10.0 equiv.) in toluene (10 ml). A solution of propargyl bromide in toluene (2.0 ml, 18.0 mmol, 10.0 equiv.) was added and the resulting mixture was stirred over night at 50°C. Afterwards, the liquid was decanted and the solvent was removed. The crude product was dissolved in

water (10 ml) and extracted three times with DCM (20 ml). Finally, the separated organic phase was dried over sodium sulfate, filtered and the solvent evaporated to achieve (7) as pale yellow, viscose liquid (88% yield).

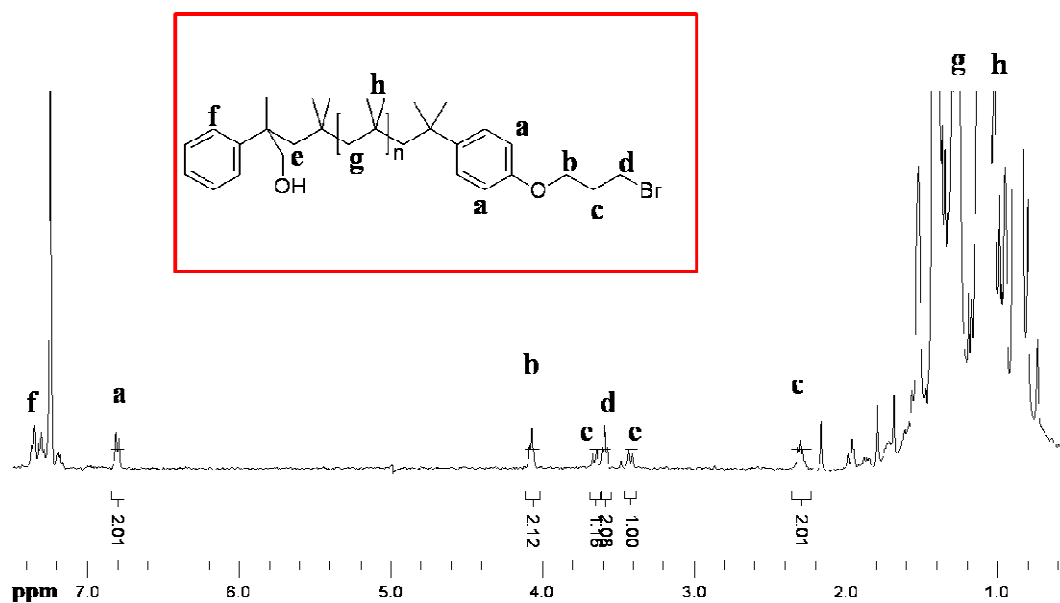
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 4.19 (d,  $J = 2.35$  Hz, 2H), 3.70-3.51 (m, n\*4H), 3.36 (s, 3H), 2.41 (t,  $J = 2.34$  Hz, 1H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 79.67 (C), 74.4 (C), 58.4 (C) (only propargyl-resonances are given).

#### **S1.6 Synthesis of $\alpha$ -methoxy- $\omega$ -azido telechelic triethylene oxide (TEO) (4)**

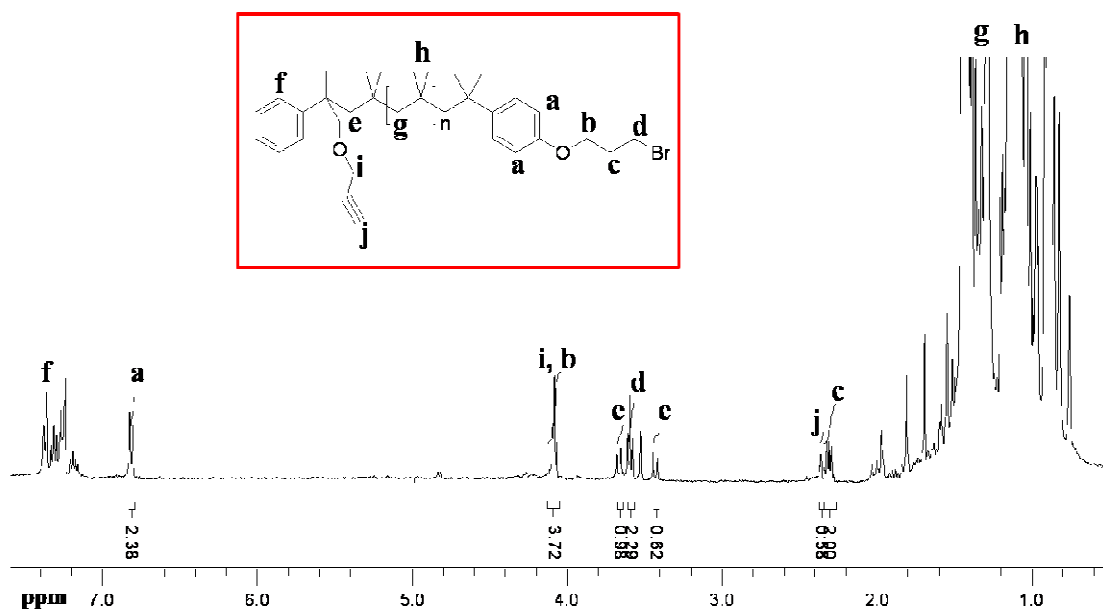
Azido-telechelic triethylene oxide (4) was prepared in a two step reaction starting with the mesylation of the hydroxyl end group, as reported in literature.<sup>3, 6</sup> In a two-necked flask, which was flame dried and flushed with argon several times, predried hydroxyl-telechelic TEO ( $M_n = 164$  Da, PDI = 1.08) (1 g, 6.1 mmol) dissolved in anhydrous THF (20 ml) was charged and subsequent treated with fresh distilled anhydrous triethyl amine (TEA) (1.2 g, 12.2 mmol, 2 equiv.). A solution of mesyl chloride (1.4 g, 12.2 mmol, 2 equiv.) in THF (10 ml) was carefully dropped to the reaction mixture and the reaction proceeded over night at room temperature. After removal of the solvent, the residue was dissolved in water and five times extracted with dichloromethane. The combined DCM phases were dried over sodium sulfate, filtered and subsequent the solvent removed under reduced pressure. Finally, the achieved product was short dried in high vacuum yielding a yellow liquid (72% yield). The conversion into the azido-telechelic TEO was done as follows: a round bottomed flask was charged with the mesylated TEO (1.0 g, 1 equiv.) and dry DMF (20 ml). The stirred solution was slowly treated with sodium azide (1.2 g, 5 equiv.) and the temperature raised to 40°C. The reaction mixture was stirred for 48 hours, further the solution was decanted and the solvent removed. The residue was dissolved in water (50 ml), stirred and three times extracted with DCM (40 ml). Afterwards, the organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered and the solvent removed via rotary evaporation. Finally, the azido-telechelic TEO (4) was received as orange, viscose liquid (90% yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 3.65-3.60 (m, 12 H), 3.35 (t,  $J = 5.3$  Hz, 2H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 70.7 (C), 70.0 (C), 50.7 (C- $\text{N}_3$ ).

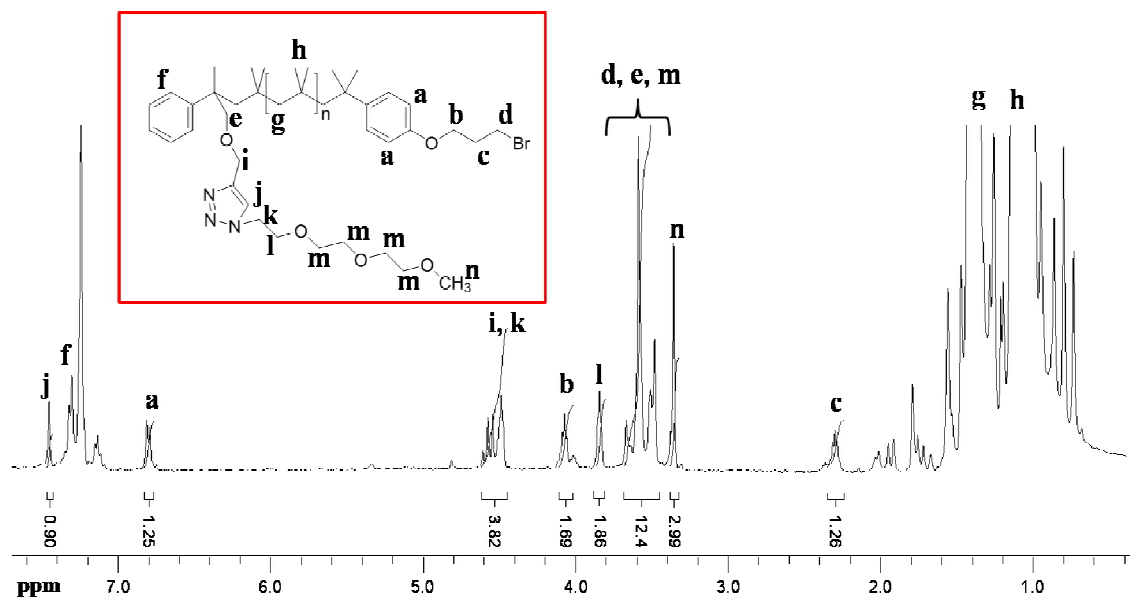
## 2 Figures and Schemes



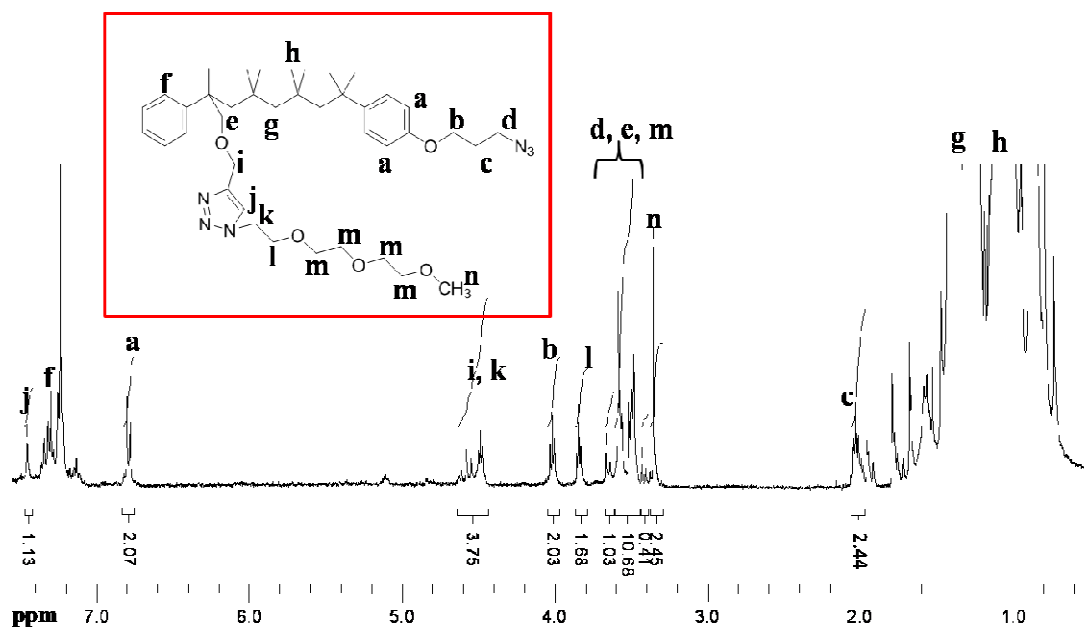
**Figure S1.**  $^1\text{H}$ -NMR of  $\alpha$ -hydroxyl- $\omega$ -bromo-telechelic polyisobutylene (2).



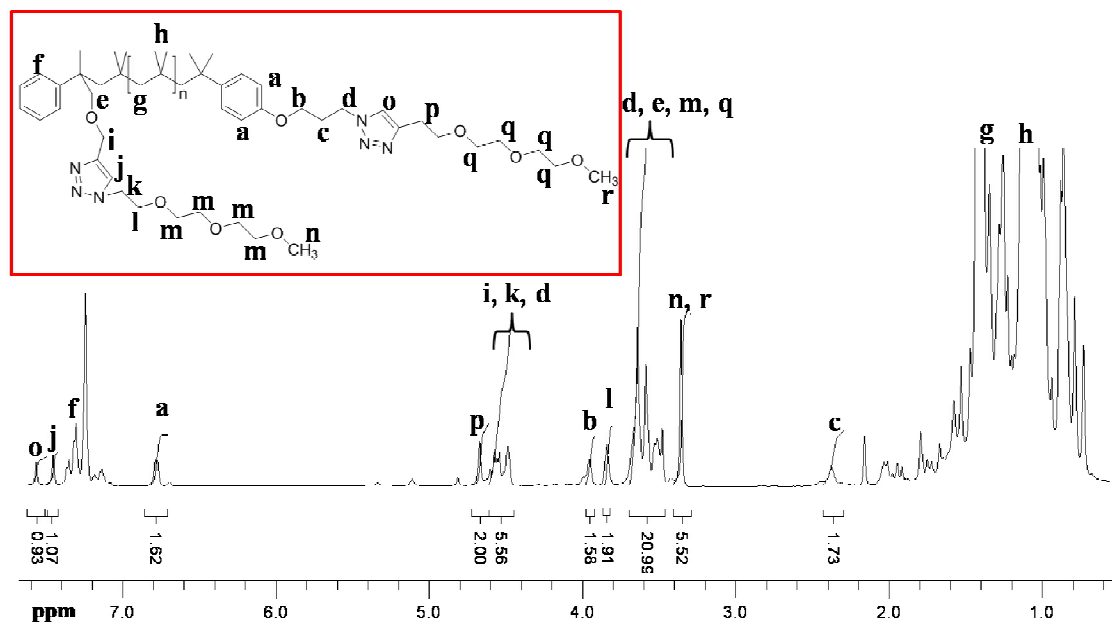
**Figure S2.**  $^1\text{H}$ -NMR of  $\alpha$ -alkyne- $\omega$ -bromo-telechelic polyisobutylene (3).



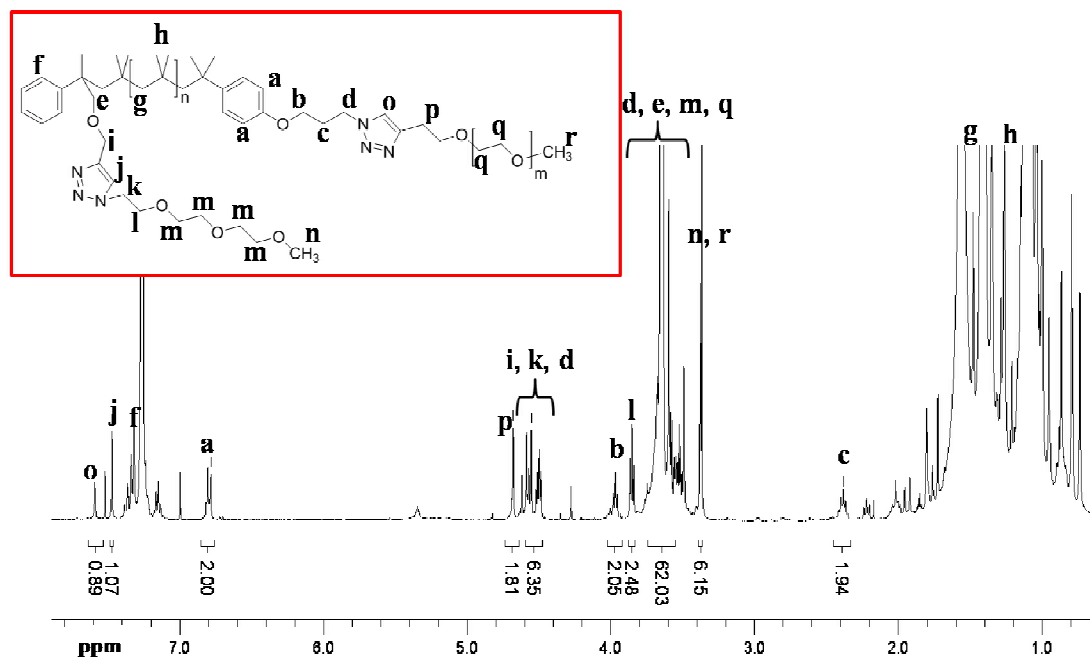
**Figure S3.**  $^1\text{H-NMR}$  of  $\alpha$ -TEO- $\omega$ -bromo-telechelic polyisobutylene (**5**).



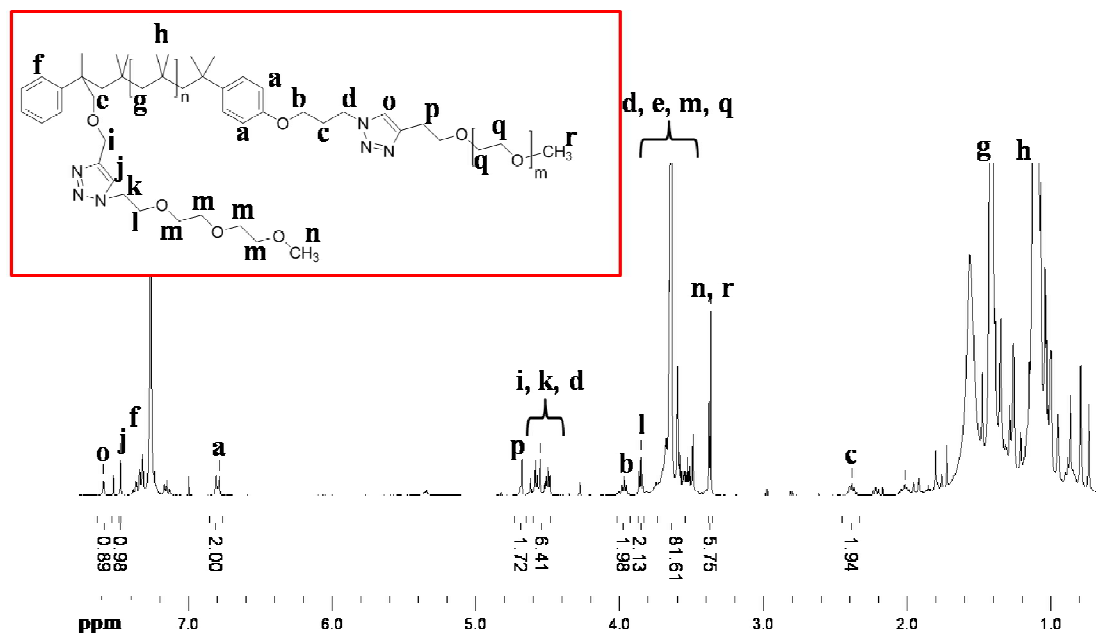
**Figure S4.**  $^1\text{H-NMR}$  of  $\alpha$ -TEO- $\omega$ -azido-telechelic polyisobutylene (**6**).



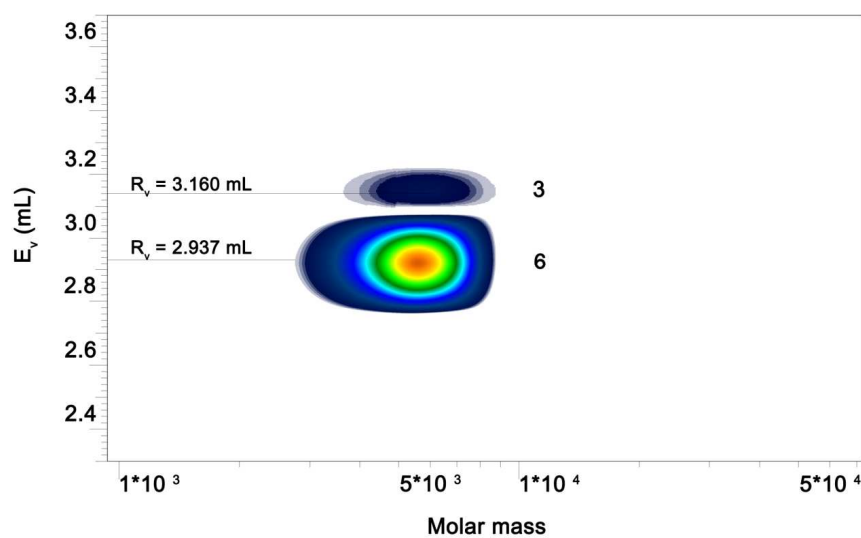
**Figure S5.** <sup>1</sup>H-NMR of symmetric TEO-PIB<sub>85</sub>-TEO block copolymer (**1a**).



**Figure S6.** <sup>1</sup>H-NMR of nonsymmetric TEO-PIB<sub>85</sub>-PEO<sub>12</sub> block copolymer (**1b**).

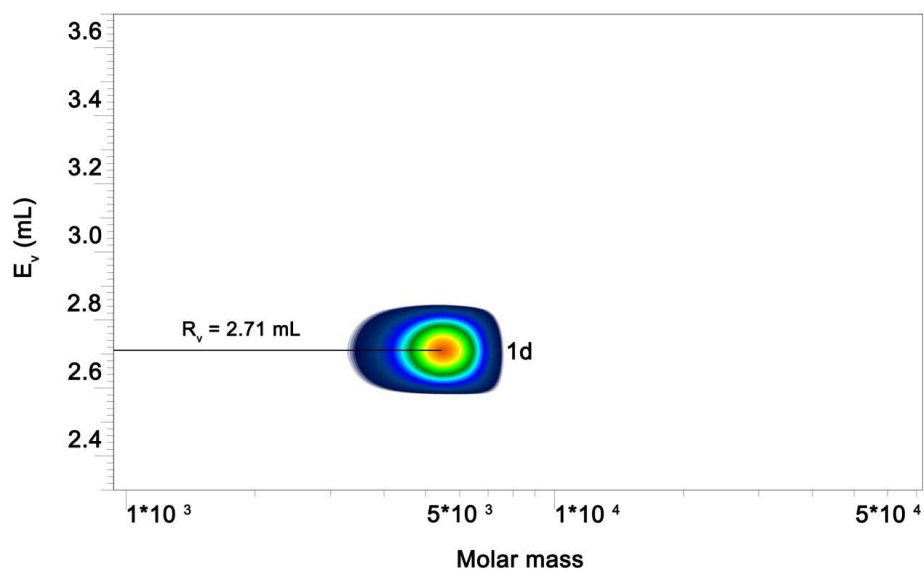


**Figure S7.** <sup>1</sup>H-NMR of nonsymmetric TEO-PIB<sub>85</sub>-PEO<sub>17</sub> block copolymer (**1c**).

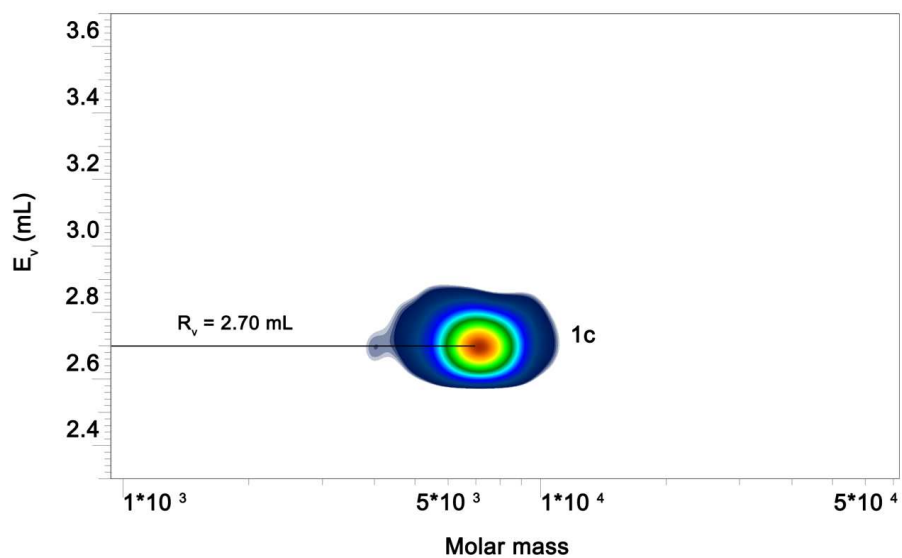


**Figure S8.** 2D-LC/SEC spectrum of unpurified compound **6** after click-reaction demonstrating the presence of impurities within the alkyne-telechelic PIB (**3**).





**Figure S9.** 2D-LC/SEC spectrum of symmetric TEO-PIB<sub>57</sub>-TEO block copolymer (**1d**).



**Figure S10.** 2D-LC/SEC spectrum of nonsymmetric TEO-PIB<sub>85</sub>-PEO<sub>17</sub> block copolymer (**1c**).

## References

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