

## SUPPORTING INFORMATION FOR

# Aqueous Phase Separation Behavior of Highly Syndiotactic High Molecular Weight Polymers with Hydroxy-Containing Side Groups

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## Synthetic procedures

### General.

The silyl-protected diazoacetates  $^s\mathbf{M}_x$  and ethylene glycol based diazoacetates  $\mathbf{SiN}_2\text{-DEG}$  were prepared according to the literature.<sup>1</sup>  $N,N'$ -ditosylhydrazine ( $\text{TsNH}$ )<sub>2</sub> necessary for the monomer synthesis was prepared according to the method published by Toma and coworkers.<sup>2</sup> Rh-catalyst **I** was synthesized according to previously published methods.<sup>3,4</sup> All other starting materials were purchased from commercial sources and were used as received. All reactions were performed under an inert atmosphere ( $\text{N}_2$ ) using dry solvents. Solvents were dried and freshly distilled prior to use.  $\text{Et}_2\text{O}$ , pentane and THF were distilled from sodium wire. Dichloromethane and acetonitrile were distilled from  $\text{CaH}_2$ .  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded at appropriate frequencies on a Bruker AV 300 ( $^1\text{H}$ , 300.10 MHz), a Bruker DRX300 ( $^1\text{H}$ , 300.13 MHz), a Bruker AMX 400 ( $^1\text{H}$ , 400.13 MHz) and a Bruker DRX 500 ( $^1\text{H}$ , 499.91 MHz) spectrometers. Molecular mass distributions were measured using size exclusion chromatography (SEC) on a Shimadzu LC-20AD system with two PLgel  $5\mu\text{m}$  MIXED-C columns (Polymer Laboratories) in series and a Shimadzu RID-10A refractive index detector, using dichloromethane as mobile phase at 1 mL/min and  $T = 35\text{ }^\circ\text{C}$ . Polystyrene standards in the range of 760-1 880 000  $\text{g mol}^{-1}$  (Aldrich) were used for calibration. UV-Vis measurements were measured on a Shimadzu UV-1800 and UV-2600 Double Beam spectrophotometer in a wavelength range of 190-1100 nm equipped with a TCC-100 Electronically Thermo-Controlled Homothermal cell holder that uses a Peltier element for electronic cooling.

*Caution! Although diazoacetates are not known as unstable compounds, always be aware that diazo compounds in general are potentially explosive.*

## General procedure for the synthesis of polycarbenes with hydroxyl-containing side chains

### Synthesis of hydroxyl-containing diazoacetates **M**<sub>2</sub>-**M**<sub>5</sub>.

As an example, the synthesis of **M**<sub>5</sub> is described. To a cooled mixture (0 °C) of 1,5-pentanediol (4.67 g, 45 mmol) and NaHCO<sub>3</sub> (1.58 g, 19 mmol) in dry acetonitrile (MeCN, 30 mL), bromoacetyl bromide (1.31 mL, 15 mmol) was added in a dropwise manner. The reaction mixture was allowed to warm to room temperature and after stirring for 16 h the mixture was quenched with H<sub>2</sub>O. Almost all MeCN was evaporated prior to the extraction with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to yield **Br-M**<sub>5</sub> as colorless oil (3.49 g, ~100%).

Subsequently, **Br-M**<sub>5</sub> (2.0 g, 8.9 mmol) and (TsNH)<sub>2</sub> (6.0 g, 17.6 mmol) were dissolved in 20 mL of dry THF and cooled to 0 °C. DBU (6.6 mL, 44 mmol) was added in a dropwise manner to the cooled mixture and stirring was continued for 16 h while the reaction mixture was allowed to warm up to room temperature.

The reaction mixture was quenched with a saturated solution of NaHCO<sub>3</sub> and almost all THF was evaporated prior to extraction with Et<sub>2</sub>O. The organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated to yield **M**<sub>5</sub> as yellow oil. Yield: (1.28 g, 84%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300.1 MHz), δ (ppm): 4.76 (s, 1H, -CH=N<sub>2</sub>), 4.19 (t, 2H, <sup>3</sup>J=6.6 Hz, -OCH<sub>2</sub>-), 3.67 (q, 2H, <sup>3</sup>J=6.3 Hz, -CH<sub>2</sub>OH), 1.65 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.47 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-).

**M**<sub>2</sub>. Yield: 48% <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300.1 MHz), δ (ppm): 4.84 (s, 1H, -CH=N<sub>2</sub>), 4.32 (t, 2H, <sup>3</sup>J=6 Hz, -OCH<sub>2</sub>-), 3.84 (t, 2H, <sup>3</sup>J=6 Hz, -CH<sub>2</sub>OH), 2.35 (broad, 1H, OH).

**M**<sub>3</sub>. Yield 58% <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300.1 MHz), δ (ppm): 4.77 (s, 1H, -CH=N<sub>2</sub>), 4.34 (t, 2H, <sup>3</sup>J=6 Hz, -OCH<sub>2</sub>-), 3.70 (broad 2H, -CH<sub>2</sub>OH), 2.25 (broad, 1H, -OH), 1.89 (q, 2H, <sup>3</sup>J=6 Hz, -CH<sub>2</sub>CH<sub>2</sub>-).

CH<sub>2</sub>-).

**M<sub>4</sub>**. Yield 74% <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300.1 MHz), δ (ppm): 4.81 (s, 1H, -CH=N<sub>2</sub>), 4.20 (t, 2H, <sup>3</sup>J=6.3 Hz, -OCH<sub>2</sub>-), 3.66 (q, 2H, <sup>3</sup>J=6 Hz, -CH<sub>2</sub>OH), 1.72 (q, 2H, <sup>3</sup>J=6.3 Hz, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.65 (q, 2H, <sup>3</sup>J=6 Hz, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-).

### Synthesis of the silyl-protected diazoacetates <sup>s</sup>M<sub>2</sub>-<sup>s</sup>M<sub>5</sub>.

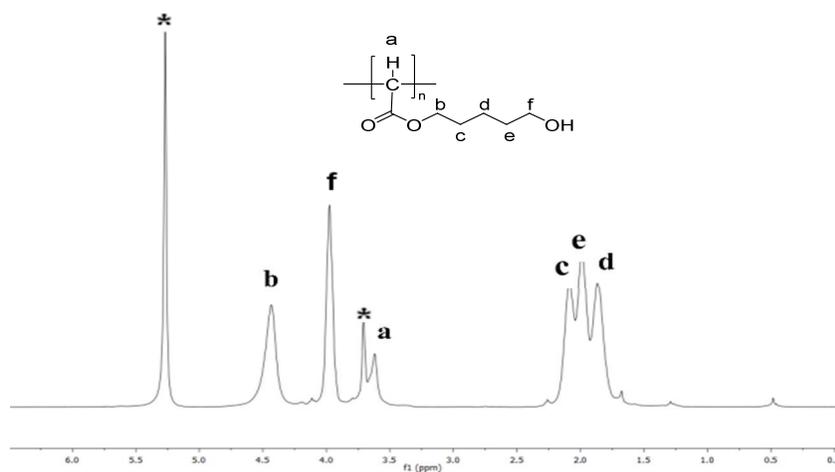
As an example, the synthesis of <sup>s</sup>M<sub>5</sub> is described. **M<sub>5</sub>** (0.84 g, 4.88 mmol) and imidazole (0.99 g, 14.6 mmol) were dissolved in 25 mL dry THF and cooled to 0°C. TBDMS (1.47 g, 9.8 mmol) was dissolved in 5 mL dry THF and this solution was added dropwise via a syringe to the solution of **M<sub>5</sub>**. The reaction mixture was stirred overnight at room temperature and was quenched with H<sub>2</sub>O. Almost all THF was evaporated prior to extraction with Et<sub>2</sub>O. The organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated to yield <sup>s</sup>M<sub>5</sub> as pale yellow oil. Yield: 1.24 g (72%). If necessary, the excess of TBDMS can be removed by purifying the compound with flash column chromatography on silica. (PE 40-60°C then PE 40-60°C/ethylacetate 15:1).

<sup>s</sup>M<sub>5</sub> <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300.1 MHz), δ (ppm): 4.75 (s, 1H, -CH=N<sub>2</sub>), 4.18 (t, 2H, <sup>3</sup>J=6 Hz, -OCH<sub>2</sub>-), 3.63 (t, 2H, <sup>3</sup>J=6 Hz, -CH<sub>2</sub>OSi-), 1.66 (q, 2H, <sup>3</sup>J=6 Hz -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.54 (q, 2H, <sup>3</sup>J=6 Hz -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.47 (q, 2H, <sup>3</sup>J=6 Hz -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 0.91 (s, 9H, -Si<sup>t</sup>Bu), 0.07 (s, 6H, -Si(CH<sub>3</sub>)<sub>2</sub>-).

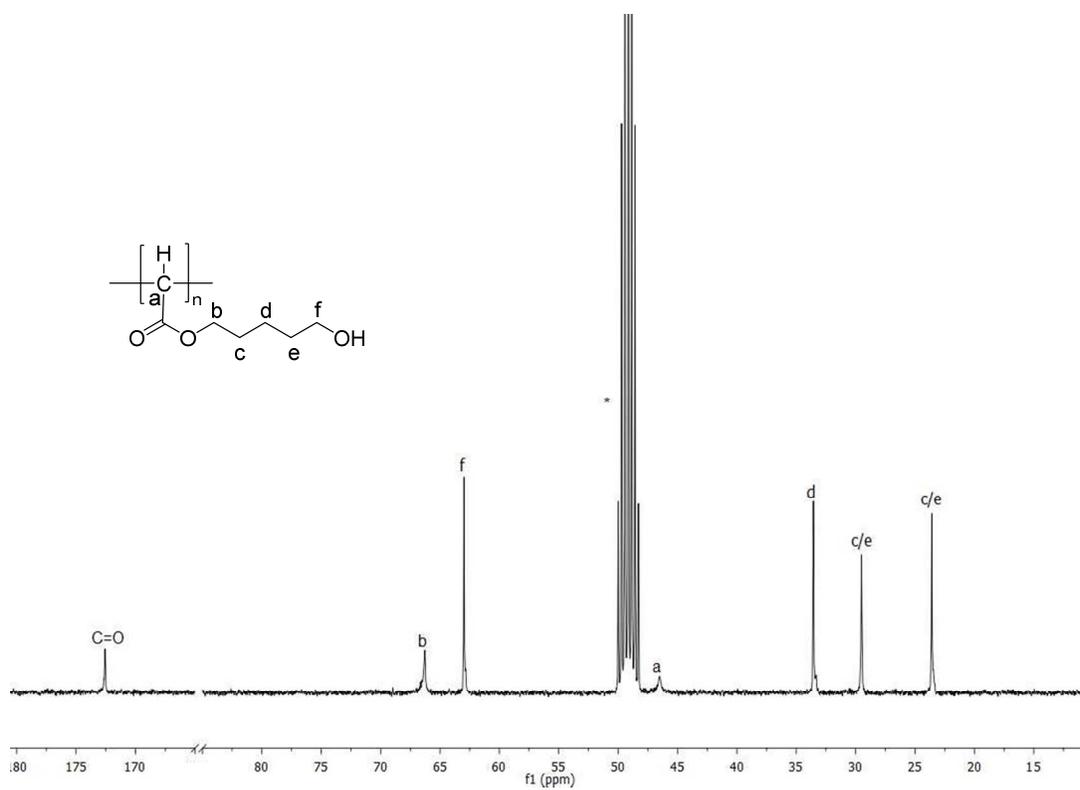
<sup>s</sup>M<sub>2</sub>. Yield: 69% <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400.13 MHz), δ (ppm): 4.77 (s, 1H, -CH=N<sub>2</sub>), 4.23 (t, 2H, <sup>3</sup>J=6 Hz, -OCH<sub>2</sub>-), 3.82 (t, 2H, <sup>3</sup>J=6 Hz, -CH<sub>2</sub>OSi-), 0.90 (s, 9H, -Si<sup>t</sup>Bu), 0.07 (s, 6H, -Si(CH<sub>3</sub>)<sub>2</sub>-).

<sup>s</sup>M<sub>3</sub>. Yield: 41% <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300.1 MHz), δ (ppm): 4.79 (s, 1H, -CH=N<sub>2</sub>), 4.26 (t, 2H, <sup>3</sup>J=6 Hz, -OCH<sub>2</sub>-), 3.72 (t, 2H, <sup>3</sup>J=6 Hz, -CH<sub>2</sub>OSi-), 1.86 (q, 2H, <sup>3</sup>J=6 Hz -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 0.93 (s, 9H, -Si<sup>t</sup>Bu), 0.07 (s, 6H, -Si(CH<sub>3</sub>)<sub>2</sub>-).

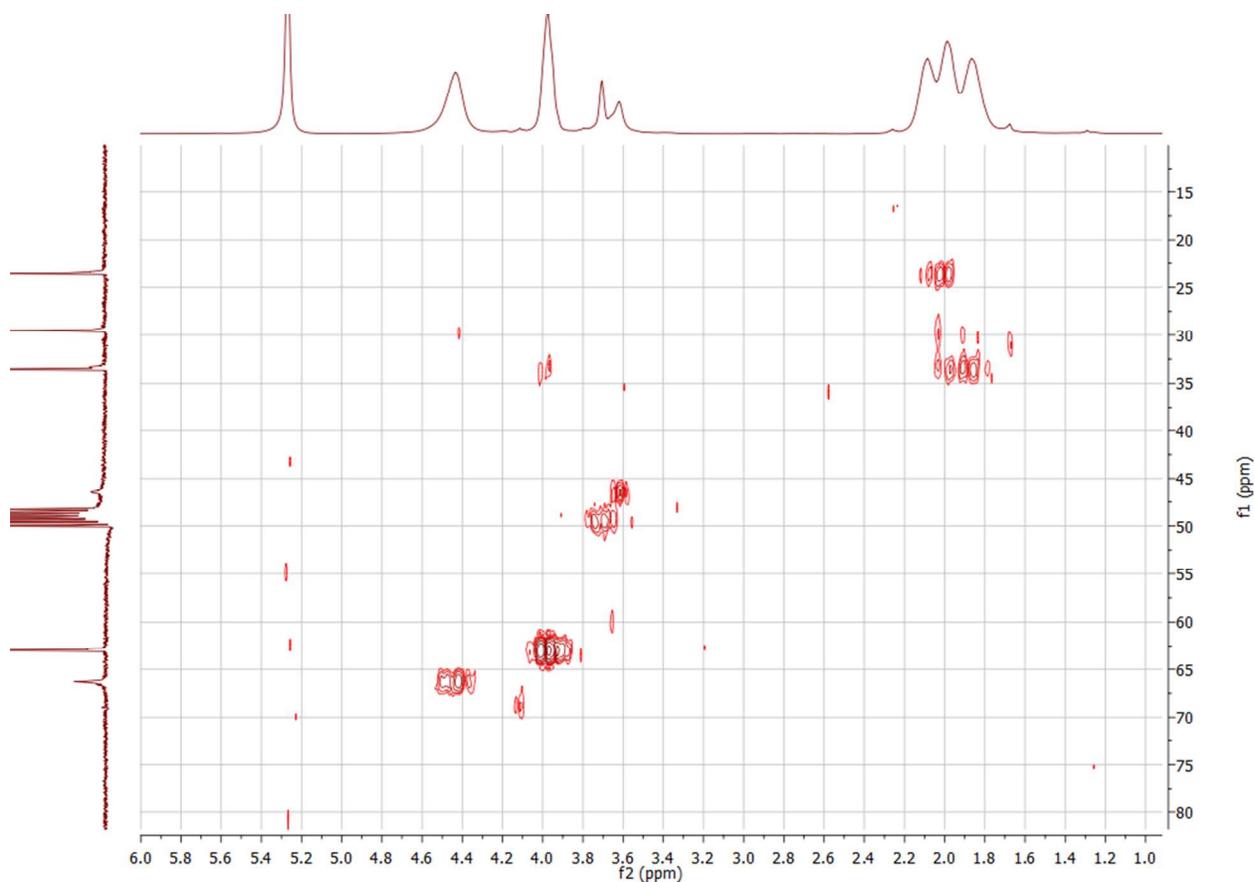
<sup>s</sup>**M**<sub>4</sub>. Yield: 69% <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400.13 MHz), δ (ppm): 4.75 (s, 1H, -CH=N<sub>2</sub>), 4.21 (t, 2H, <sup>3</sup>J=6 Hz, -OCH<sub>2</sub>-), 3.65 (t, 2H, <sup>3</sup>J=6 Hz, -CH<sub>2</sub>OSi-), 1.73 (q, 2H, <sup>3</sup>J=6 Hz -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.60 (q, 2H, <sup>3</sup>J=6 Hz -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 0.91 (s, 9H, -Si<sup>t</sup>Bu), 0.07 (s, 6H, -Si(CH<sub>3</sub>)<sub>2</sub>-).



**Figure S1.** <sup>1</sup>H-NMR spectrum (methanol-*d*<sub>4</sub>) of **pM**<sub>5</sub>. Signals marked with an asterisk (\*) correspond to the solvent and traces of water.



**Figure S2.**  $^{13}\text{C}$ -NMR spectrum (methanol- $d_4$ ) of  $\text{pM}_5$ . Signals marked with an asterisk (\*) correspond to the solvent.



**Figure S3.** HSQC-NMR of **pM<sub>5</sub>** in methanol-*d*<sub>4</sub>.

## **Synthesis of polycarbenes with diazoacetates bearing diethylene glycol (DEG) based side chains**

The synthesis of diazoacetates bearing a DEG-based side chain and the synthesis of the corresponding polymers are largely based on the methods described for the synthesis of **M<sub>5</sub>** and **pM<sub>5</sub>**.

### **Synthesis of DEG-based diazoacetate N<sub>2</sub>-DEG.**

Diethylene glycol (5.54 g, 52.89 mmol) and NaHCO<sub>3</sub> (1.57 g, 18.69 mmol) were dissolved in 40

mL dry MeCN and the solution was cooled to 0 °C. Bromoacetyl bromide (1.92 mL, 22.04 mmol) was added in a dropwise manner. The reaction mixture was stirred overnight, while warming up to room temperature. The thus obtained white suspension was quenched with H<sub>2</sub>O and most of the MeCN was evaporated before extraction with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to yield **Br-DEG** as a light yellow oil (~100%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300.1 MHz), δ (ppm): 4.33 (t, 2H, <sup>3</sup>J=6 Hz, -OCH<sub>2</sub>), 3.87 (s, 2H, Br-CH<sub>2</sub>), 3.72 (q, 4H, <sup>3</sup>J=6 Hz, CH<sub>2</sub>OCH<sub>2</sub>), 3.59 (t, 2H, CH<sub>2</sub>OH), 2.96 (b, 1H, OH).

**Br-DEG** (5g, 22.02 mmol) and (TsNH)<sub>2</sub> (15 g, 44.05 mmol) were dissolved in dry THF and cooled to 0 °C. DBU (16 mL, 107 mmol) was added in a dropwise manner using a syringe. The reaction mixture was slowly warmed up to room temperature, and stirred for 16 h. Subsequently the mixture was quenched with a saturated NaHCO<sub>3</sub> solution, after which THF was evaporated before extraction with Et<sub>2</sub>O. The organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated, yielding **N<sub>2</sub>-DEG** as a yellow oil (1.61 g, 42%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300.1 MHz), δ (ppm): 4.83 (br s, 1H, -CH=N<sub>2</sub>), 4.35 (m, 2H, <sup>3</sup>J=6.6 Hz, -OCH<sub>2</sub>-), 3.71 (m, 4H, -CH<sub>2</sub>OCH<sub>2</sub>-), 3.63 (m, 2H, -CH<sub>2</sub>OH).

### **Synthesis of the silyl-protected diazoacetate SiN<sub>2</sub>-DEG.**

**N<sub>2</sub>-DEG** (1.47 g, 8.44 mmol) and imidazole (1.15 g, 16.89 mmol) were dissolved in dry THF and a solution of TBDMS (3.8 g, 25.3 mmol) in 5 mL dry THF was added dropwise. The reaction mixture was stirred for 16 h and quenched with H<sub>2</sub>O. THF was evaporated before extraction with Et<sub>2</sub>O. The organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated to yield the crude product. Purification by flash column chromatography (silica, gradient 100% PE, followed by PE:EtOAc 50:1→30:1→20:1→15:1→10:1→6:1) gave **SiN<sub>2</sub>-DEG** (0.83 g, 34%) as a yellow oil. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300.1 MHz), δ (ppm): 4.81 (br s, 1H, CH=N<sub>2</sub>), 4.34 (m, 2H,

-OCH<sub>2</sub>-), 3.79 (t, 2H, <sup>3</sup>J=6 Hz, -OCH<sub>2</sub>-), 3.74 (m, 2H, -CH<sub>2</sub>O-), 3.58 (t, 2H, <sup>3</sup>J=6 Hz -CH<sub>2</sub>OSi-), 0.92 (s, 9H, -Si<sup>t</sup>Bu), 0.09 (s, 6H, -Si(CH<sub>3</sub>)<sub>2</sub>-).

### Polymerization of SiN<sub>2</sub>-DEG.

In a dry Schlenk flask, 19.7 mg (0.046 mmol) of Rh-catalyst **I** was dissolved in 5 mL dry CH<sub>2</sub>Cl<sub>2</sub> and cooled to 0 °C. In another dry Schlenk flask, **SiN<sub>2</sub>-DEG** (0.67 g, 2.32 mmol) was dissolved in 2 mL of dry CH<sub>2</sub>Cl<sub>2</sub> and added dropwise using a syringe, to the solution of Rh-catalyst. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The solution was concentrated to a volume of ca. 1 mL and MeOH was added to precipitate the polymer. The polymer was isolated from the mixture by centrifugation and three washing steps with dry MeOH. The precipitate was dried to yield **pSi-DEG** (0.14 g, 23%) as a white solid. M<sub>w</sub> =114 kDa, M<sub>n</sub>=26 kDa, M<sub>w</sub>/M<sub>n</sub> =4.4. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300.1 MHz assigned from <sup>1</sup>H,<sup>1</sup>H-COSY), δ (ppm): 4.17 (br, 2H, -OCH<sub>2</sub>-), 3.76 (b, 2H, .OCH<sub>2</sub>-), 3.68 (br, 2H, -CH<sub>2</sub>O-), 3.56 (br, 2H, -CH<sub>2</sub>OSi-), 3.19 (br s, 1H, -[CH]<sub>n</sub>-), 0.93 (s, 9H, -Si<sup>t</sup>Bu), 0.12 (s, 6H, -Si(CH<sub>3</sub>)<sub>2</sub>-).

### Deprotection procedure of pSi-DEG.

**pSi-DEG** was dissolved in THF (3 mL) and MeOH was added until the solution started to turn into a suspension. Subsequently a concentrated aqueous HCl solution (37%, 0.66 mL, 8 mmol) was added dropwise and the solution was stirred for 1 h. The solvents were evaporated until a volume of ca. 1 mL was left and new THF (2 mL) was added after which evaporation was repeated, resulting in a sticky solid. A small amount of MeOH was added and the solution was stirred until the solid dissolved completely. Subsequently an excess of THF was added to precipitate the desilylated polymer **pDEG-OH**. The supernatant was removed and the precipitate was dried under vacuum. Yield: 0.02 g of a white solid (25%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300.1 MHz), δ

(ppm): 4.18 (br, 2H, -OCH<sub>2</sub>-), 3.62 (b, 4H, -CH<sub>2</sub>OCH<sub>2</sub>-), 3.54 (br, 2H, -CH<sub>2</sub>OH), 3.19 (br s, 1H, -[CH]<sub>n</sub>-).

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