

Supporting Information

for

Multi-Arm Polycarbonate Star Polymers with Hyperbranched Polyether Core from CO₂ and Common Epoxides

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A Materials and Instrumentation

Materials. TsOH·H₂O was dried using benzene. Propylene oxide (PO, 98%, Aldrich), 1,2-butylene oxide (BO, 99%, Aldrich) and glycidol (96%, Aldrich) were distilled over CaH₂ under reduced pressure prior to use. Carbon dioxide (>99.99%) and all other solvents and reagents were used as received.

NMR experiments. ¹H and ¹³C NMR spectra were recorded on a Bruker AC 300 and a Bruker 400 spectrometer, operated at 300, 400, 75,4 and 100 MHz respectively, at 21 °C and the

chemical shifts are given in parts per million (ppm). All spectra are referenced to residual solvent signal.

Size Exclusion Chromatography. For size exclusion chromatography (SEC) measurements in DMF (containing $0.25 \text{ g}\cdot\text{L}^{-1}$ of lithium bromide as an additive) an Agilent 1100 Series was used as an integrated instrument, including a PSS HEMA column ($10^6/10^5/10^4 \text{ g}\cdot\text{mol}^{-1}$), a RI and a UV detector. Calibration was carried out using poly(ethylene oxide) standards provided by Polymer Standards Service.

Preparative Size Exclusion Chromatography. For preparative size exclusion chromatography measurements in CHCl_3 , a LC-91XX Next Series Recycling Preparative HPLC Anlage by *Japan Analytical Industry Co. Ltd.*, equipped with a Jaigel-2H column (upper exclusion limit $5 \cdot 10^4 \text{ g}\cdot\text{mol}^{-1}$) and a UV and RI detector, was used. Sample fractionation was performed at 25°C and a flow rate of $3.5 \text{ mL}\cdot\text{min}^{-1}$.

Differential Scanning Calorimetry. Differential Scanning Calorimetry (DSC) curves were recorded with a Perkin-Elmer DSC 7 CLN2 in the temperature range from -70 to $+20^\circ\text{C}$ at heating rates of 10 K min^{-1} under nitrogen.

IR-Spectroscopy. FT-IR spectra were recorded using a Thermo Scientific iS10 FT-IR spectrometer, equipped with a diamond ATR unit.

On-line Viscometry. On-line viscometry measurements were performed using a PSS GRAM column ($30/100/1000 \text{ \AA}$ porosity) with a SECcurity GPC1260 Refractive Index RI detector as well as a SECcurity on-line viscometer DVD1260. As solvent DMF with $5 \text{ g}\cdot\text{mol}^{-1}$ LiBr was used. Samples with a concentration of $20 \text{ mg}\cdot\text{mL}^{-1}$ and a volume of $100 \text{ }\mu\text{L}$ were measured after

8 h at 70 °C. Each sample was measured three times and the average of the data obtained was calculated. As a universal standard, well-defined PMMA samples were used.

B Synthesis and Characterization

Synthesis of (*R,R*)-(salcy)-CoCl. (*R,R*)-(salcy)-CoCl was prepared as described by Ford *et al.*¹ A flame dried 250 mL flask was charged with (salen)Co(II) (1.00 g, 1.65 mmol) and 87 mL CH₂Cl₂. To this red suspension TsOH·H₂O (0.33 g, 1.74 mmol) was added. The mixture was stirred for 1.5 h until it became a dark green solution. This solution was washed three times with 30 mL brine, dried over Na₂SO₄ and concentrated in vacuum. The dark solid was suspended in cold pentane, filtered over Celite[®] and washed with cold pentane. The (salen)Co(III)Cl complex was obtained as a dark green solid and was stored under inner gas atmosphere. (360 mg, 30% yield).

Synthesis of *hb*PEO and *hb*PBO Copolymers. General procedure:² In a Schlenk flask equipped with a septum and a magnetic stirrer, 44 mg (0.33 mmol, 1.0 eq.) trimethylolpropane (TMP) and 17 mg (0.10 mmol, 0.3 eq.) CsOH monohydrate were dissolved in MeOH. The partly deprotonated initiator salt was isolated by azeotropic removal of MeOH with benzene and subsequent drying in high vacuum overnight.

The dried initiator salt was dissolved in 1 mL dimethyl sulfoxide. The flask was immersed in liquid nitrogen and glycidol was added via a syringe. Ethylene oxide was added via distillation (amount of monomers combined: 100 mmol, 300 eq.). The flask was sealed under vacuum and heated to 80 °C for 18 h. MeOH was added to terminate the reaction and the solution was neutralized by filtration over DOWEX WX8 resin. After removal of the solvents in vacuum and

the removal of formed oligomers by precipitation in cold diethyl ether, the polymer was isolated as a brown oil and dried in vacuum at 85 °C for 24 h. Yield 80-90%.

For the synthesis of high molecular weight *hb*PEO, the initiator salt was dissolved in 10 mL dioxane instead of DMSO. The resulting copolymer was purified by dialysis (MWCO = 3500 Da).

Caution: In very few cases the pressure evolving in the early stages of the reaction in the flask may lead to the spontaneous removal of the septum and release of ethylene oxide. Thus, the reaction has to be carried out in an appropriate fume hood, and the respective safety precautions should be taken. In general, the amount of EO used did not exceed 5 g per batch in a 250 mL flask to guarantee a safe reaction.

Table S 1. Overview of the characterization data of all hyperbranched polyether polyols.

Sample ^{a)c)}	M_n / g·mol ^{-1 a)}	\bar{D} ^{a)}	M_n / g·mol ^{-1 b)}	\bar{D} ^{b)}	$[G]$ % ^{c)}	T_g / °C ^{d)}	$[\eta]$ / cm ³ ·g ^{-1 a)}
<i>hb</i> (PG ₅ - <i>co</i> -PEO ₅₇)	3,000	2.12	2,500	1.58	8	-56	7.4
<i>hb</i> (PG ₄ - <i>co</i> -PEO ₄₅) ^{e)}	n.d.	n.d.	2,300	1.35	9	-62	n.d.
<i>hb</i> (PG ₄ - <i>co</i> -PEO ₁₅)	980	2.03	1,900	1.31	21	-62	4.6
<i>hb</i> (PG ₅ - <i>co</i> -PEO ₁₀)	800	2.00	1,600	1.33	30	-64	3.9
<i>hb</i> (PG ₉ - <i>co</i> -PEO ₁₆)	1,400	2.16	1,100	1.51	35	-61	5.1
<i>hb</i> (PG ₁₂₅₀ - <i>co</i> -PEO ₆₇₅₀)	389,000	2.81	53,000	1.18	16	-60	5.5
<i>hb</i> (PG ₄ - <i>co</i> -PBO ₁₀)	1,100	3.40	1,100	1.69	29	-53	3.8

^{a)} Terminology: Indices represent the absolute number of the respective repeating unit (rounded to integer), determined by on-line viscometry with universal calibration ^{b)} determined by SEC in DMF calibrated with a PEO standard, ^{c)} determined by invers gated ¹³C NMR spectroscopy, ^{d)} determined by DSC, ^{e)} no on-line viscometry data available; M_n approximated from SEC and the on-line viscometry data of the other samples. n.d. = not determined.

¹H NMR (DMSO-*d*₆, 400 MHz): δ (ppm) = 4.81 – 4.35 (m, br, OH); 4.10 – 3.06 (m, O-CH, O-CH₂); 1.36 – 1.18 (m, 2H, CH₃-CH₂ (TMP)); 0.89 – 0.68 (m, 3H, CH₃ (TMP)).

^{13}C NMR (DMSO- d_6 , 100 MHz): δ (ppm) = 80.25 – 79.45 (m, CH $G_{1,3\text{-Linear}}$); 78.52 – 77.42 (m, CH $G_{\text{Dendritic}}$); 73.22 – 72.10 (m, 2 CH₂ $G_{1,4\text{-Linear}}$); 72.04 – 69.62 (m, 2 CH₂ $G_{\text{Dendritic}}$, 2 CH₂ EO_{Linear}, CH₂-CH₂-OH EO_{Terminal}, CH G_{Terminal} , CH₂ G_{Terminal}); 69.61 – 68.37 (m, CH₂ $G_{1,3\text{-Linear}}$, CH-OH $G_{1,4\text{-Linear}}$); 63.39 – 62.96 (CH₂-OH G_{Terminal}); 60.87 – 60.07 (m, CH₂-OH EO_{Terminal}, CH₂-OH $G_{1,3\text{-Linear}}$).

Copolymers based on glycidol and BO were obtained by changing the reaction conditions to solvent-free copolymerization at 120 °C for 2 days.³ Both comonomers were added via a syringe before polymerization (amount of monomers combined: 50 mmol, 150 eq.). The resulting copolymers were precipitated in a cold mixture of diethyl ether and hexane.

^1H NMR (DMSO- d_6 , 400 MHz): δ (ppm) = 4.55 – 4.33 (m, br, OH); 4.08 – 3.02 (m, O-CH, O-CH₂); 1.56 – 1.12 (m, CH₃-CH₂ (BO & TMP)); 0.87 (t, CH₃ (BO)); 0.79 (t, CH₃ (TMP)).

^{13}C NMR (DMSO- d_6 , 100 MHz): δ (ppm) = 80.6 – 79.0 (CH $G_{1,3\text{-Linear}}$, CH BO_{Linear}); 78.8 – 77.4 (CH $G_{\text{Dendritic}}$); 75.8 – 75.0 (CH₂ BO_{Terminal}); 74.6 – 73.6 (CH₂ BO_{Linear}); 73.2 – 72.1 (2 CH₂ $G_{1,4\text{-Linear}}$); 72.0 – 69.9 (2 CH₂ $G_{\text{Dendritic}}$, CH G_{Terminal} , CH G_{Terminal} , CH₂ BO_{Terminal}); 69.9 – 68.3 (CH₂ $G_{1,3\text{-Linear}}$, CH-OH $G_{1,4\text{-Linear}}$); 63.5 – 62.8 (CH₂-OH G_{Terminal}); 61.4 – 60.6 (CH₂-OH $G_{1,3\text{-Linear}}$).

Synthesis of poly(propylene carbonate) and poly(butylene carbonate): General procedure:

Propylene oxide was dried over CaH₂. A 100 mL Roth autoclave was dried under vacuum at 50 °C. Propylene oxide (6 mL, 0.09 mol), (*R,R*)-(salcy)-CoCl (11 mg, 0.02 mmol) and [PPN]Cl (10 mg, 0.01 mmol) were combined with a stir bar inside the autoclave. The mixture was stirred under 50 bar and 30 °C for 1 d. The crude product was dissolved in 5 mL acetone and quenched with 1.0 mL 5% HCl solution in methanol. Subsequently, the solution was precipitated in cold methanol. The solid product was dried in vacuum for 24 h; yield 95% for PPC and 46% for PBC.

Functionalization with Phenylisocyanate. For the functionalization with phenylisocyanate, 150 mg *hb*(PG₉-*co*-PEO₁₆)-*g*-PBC₉₂ and 2 mL phenylisocyanate were mixed under argon atmosphere. The mixture was stirred at RT for 4 h. The solution was precipitated two times in cold methanol and once in pentane to remove unreacted phenylisocyanate. The solid product was dried under reduced pressure over night. ¹H NMR (CD₃CN-*d*₃, 400 MHz): δ (ppm) = 7.88 – 7.70 (NH), 7.49 – 7.42 (arom. *o*-H), 7.36 – 7.28 (arom. *m*-H), 7.10 – 7.03 (arom. *p*-H), 4.87 – 4.76 (CH PBC backbone), 4.38 – 3.92 (CH₂ PBC backbone), 3.79 – 3.40 (polyether core), 3.01 (OH PBC) 1.74 – 1.55 (CH₂), 1.53 – 1.32 (CH₂ terminal unit), 1.09 – 0.83 (CH₃).

Investigation of the Weight-depending Composition: To investigate the weight depending composition of the synthesized multiarm star polymers 300 mg polymer were dissolved in 3 mL CHCl₃ and then fractionated by preparative SEC. The solvent was removed under reduced pressure, and the fractionated polymers were investigated by ¹H NMR spectroscopy and SEC.

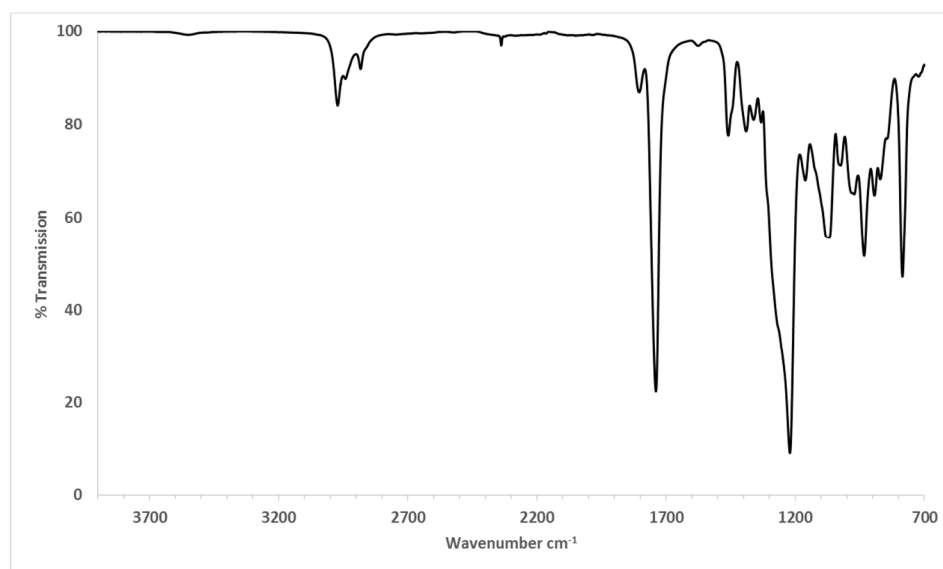


Figure S1. FT-IR spectrum of *hb*(PG₉-*co*-PEO₁₆)-*g*-PBC₉₂ (Table 1, sample 2).

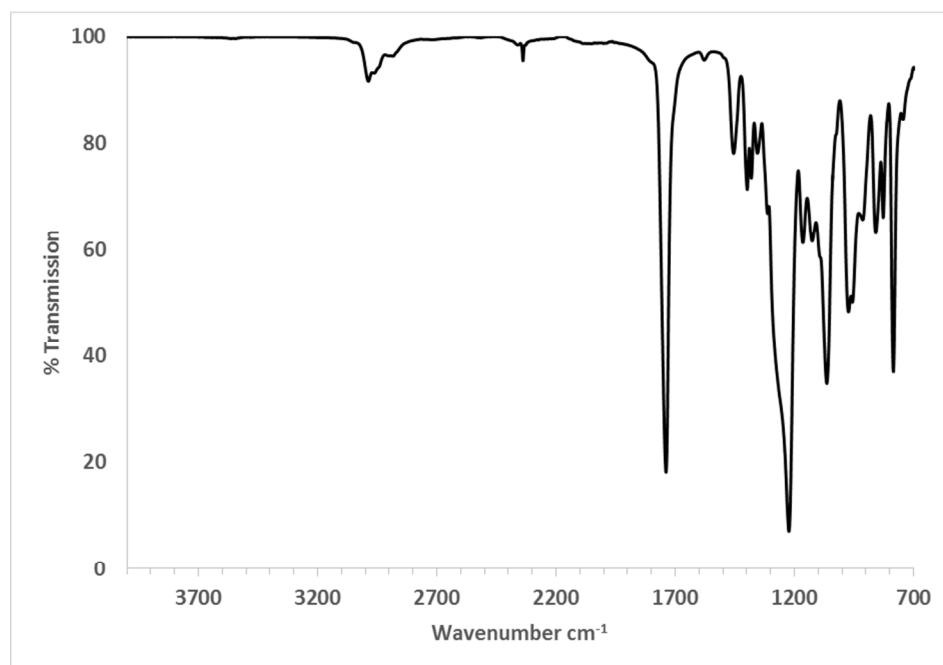


Figure S2. FT-IR spectrum of *hb*(PG₄-*co*-PEO₄₅)-*g*-PPC₃₄₉ (Table 1, sample 7).

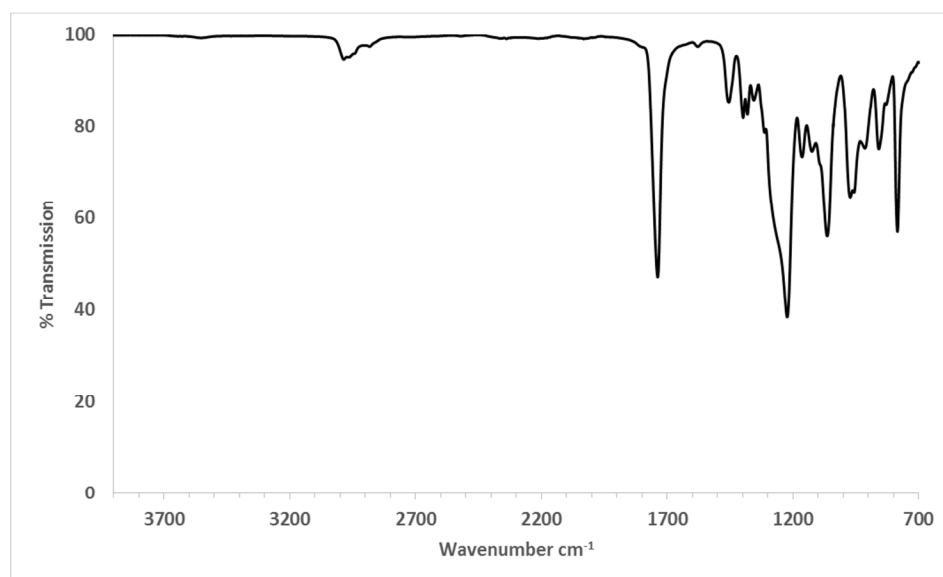


Figure S3. FT-IR spectrum of *hb*(PG₄-*co*-PBO₁₀)-*g*-PPC₁₄₆ (Table 1, sample 8).

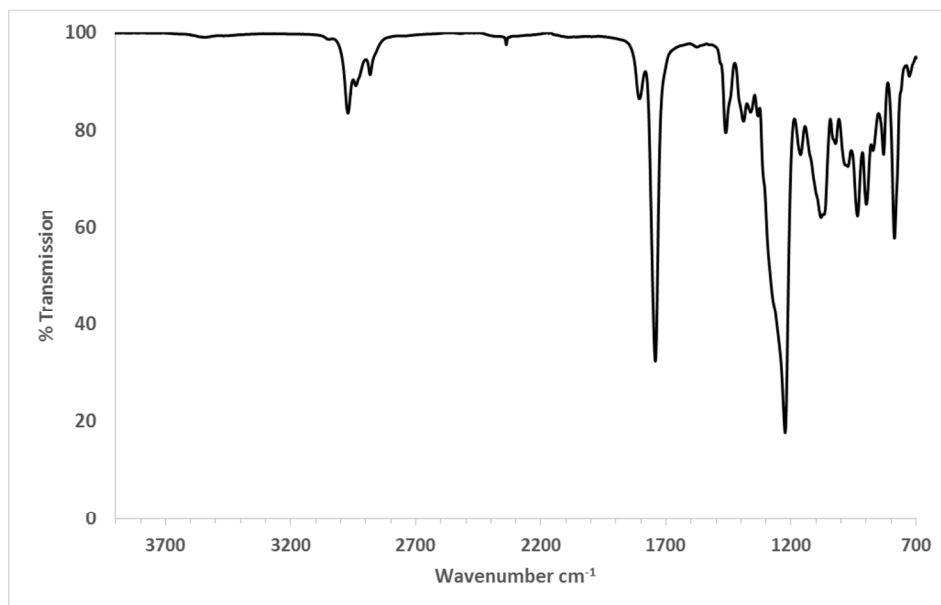


Figure S4. FT-IR spectrum of *hb*(PG₄-*co*-PBO₁₀)-*g*-PBC₆₆ (Table 1, sample 9).

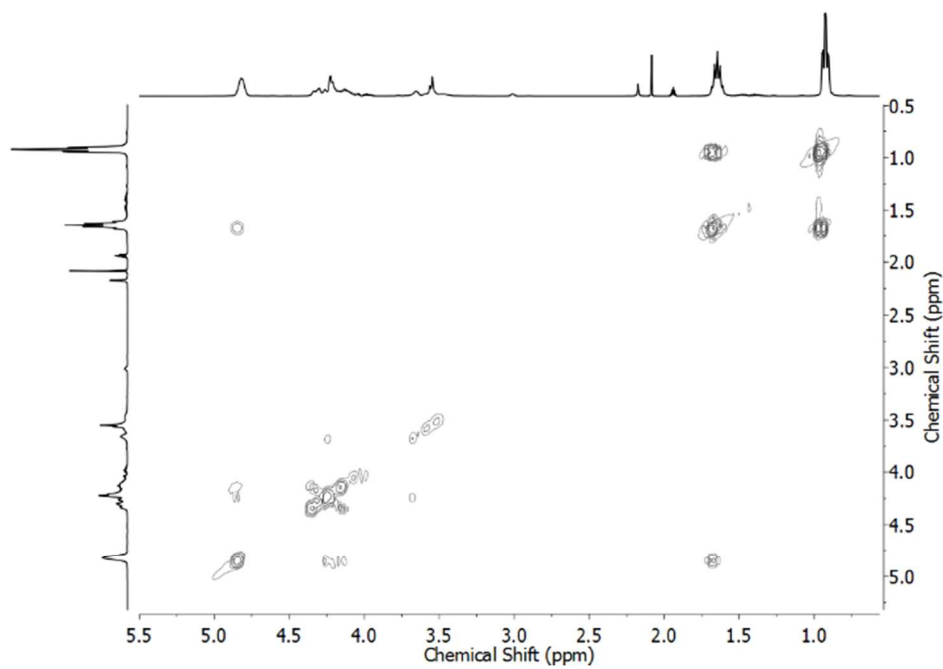


Figure S5. COSY spectrum of *hb*(PG₉-*co*-PEO₁₆)-*g*-PBC₉₂ (Table 1, sample 2) (400 MHz, CD₃CN).

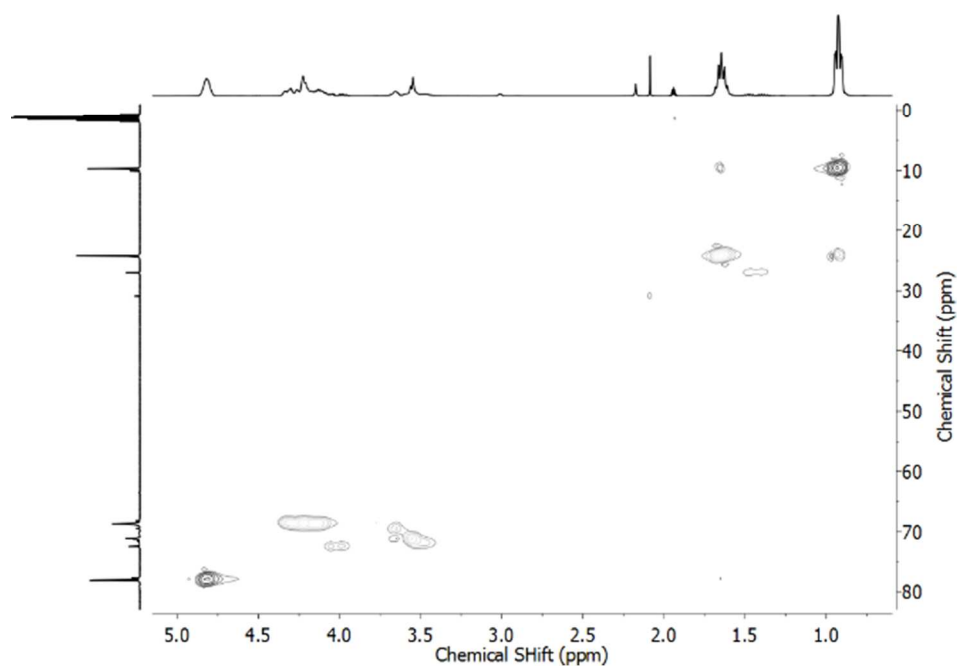


Figure S 1. HSQC spectrum of *hb*(PG₉-*co*-PEO₁₆)-g-PBC₉₂ (Table 1, sample 2) (400 MHz, CD₃CN).

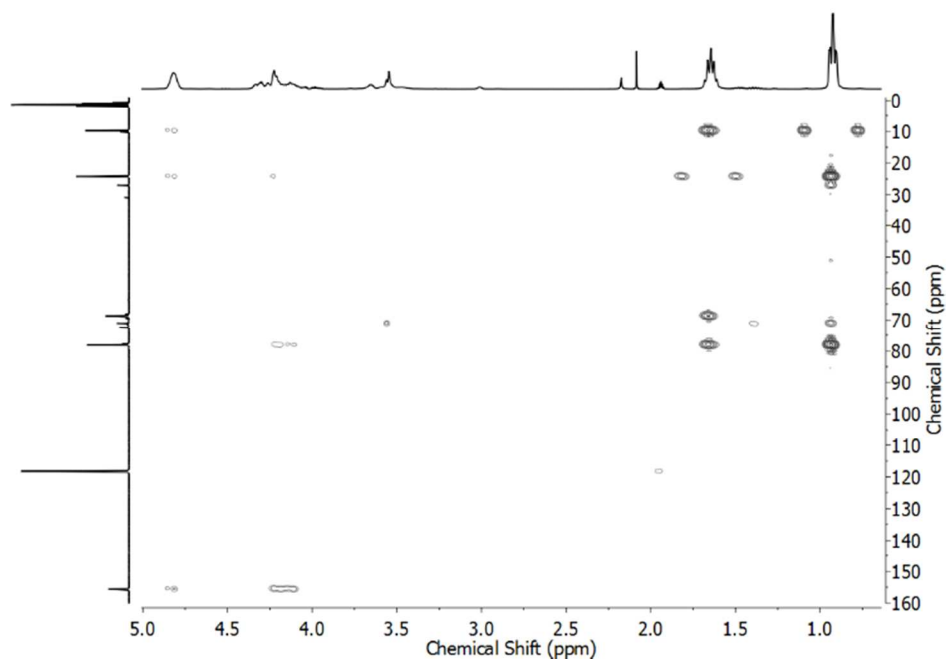


Figure S 2. HMBC spectrum of *hb*(PG₉-*co*-PEO₁₆)-g-PBC₉₂ (Table 1, sample 2) (400 MHz, CD₃CN).

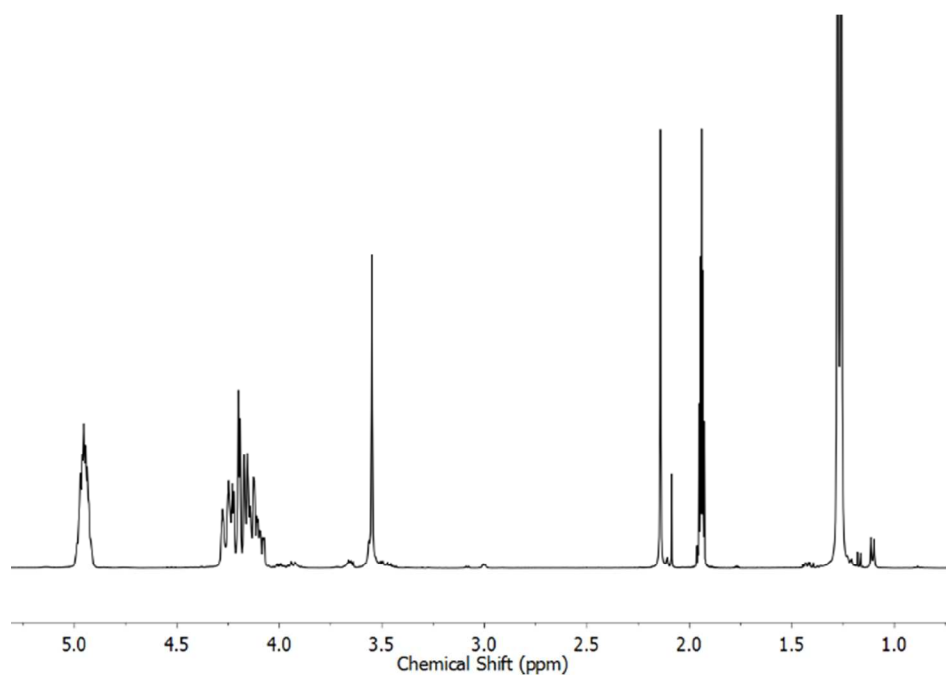


Figure S 3. ^1H NMR spectrum of *hb*(PG₄-*co*-PEO₄₅)-*g*-PPC₃₄₉ (Table 1, sample 7) (400 MHz, CD₃CN).

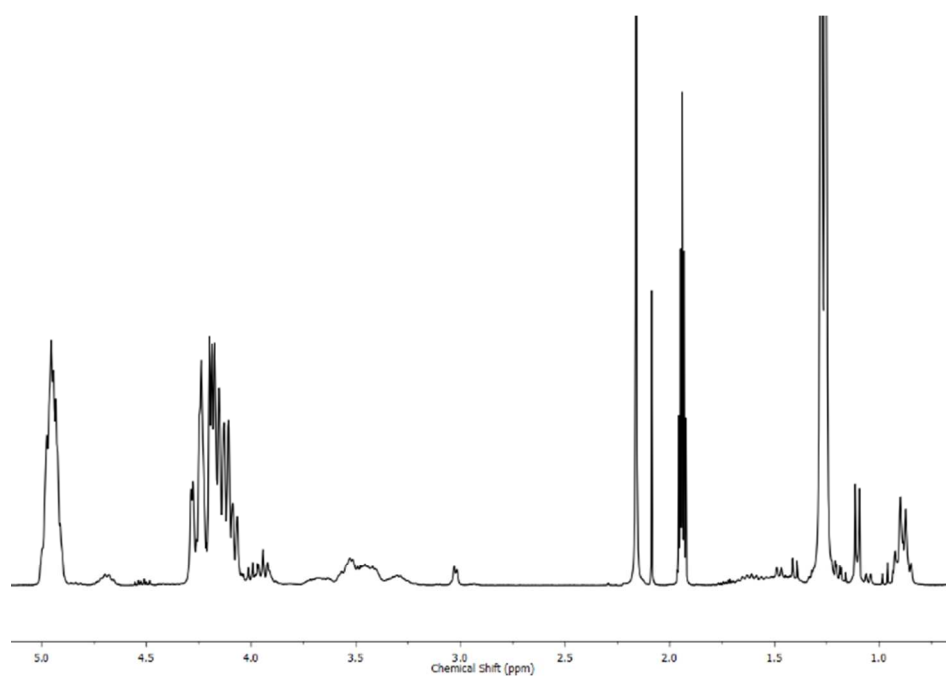


Figure S 4. ^1H NMR spectrum of *hb*(PG₄-*co*-PBO₁₀)-*g*-PPC₁₄₆ (Table 1, sample 8) (300 MHz, CD₃CN).

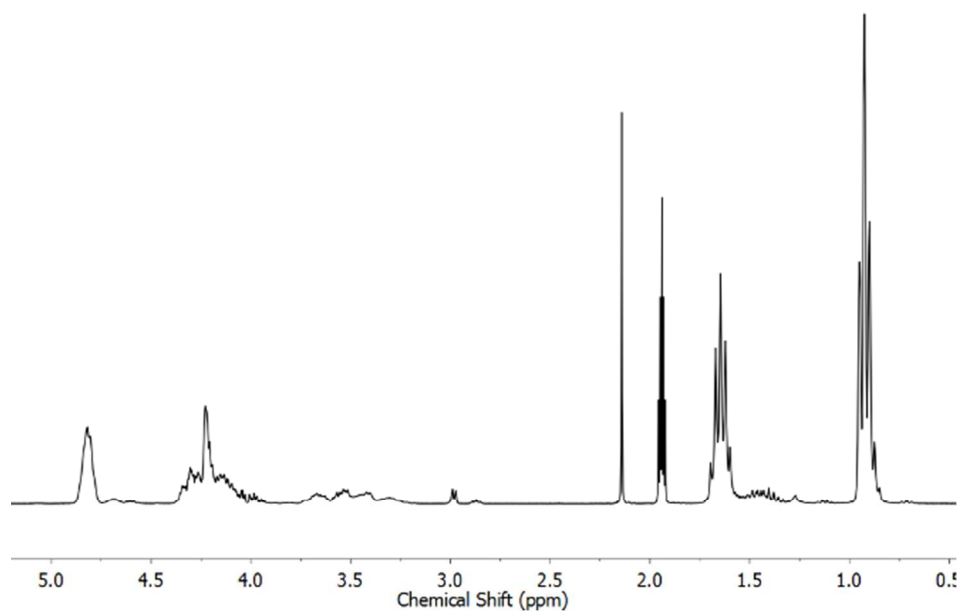


Figure S 5. ¹H NMR spectrum of *hb*(PG₄-*co*-PBO₁₀)-*g*-PBC₆₆ (Table 1, sample 9) (300 MHz, CD₃CN).

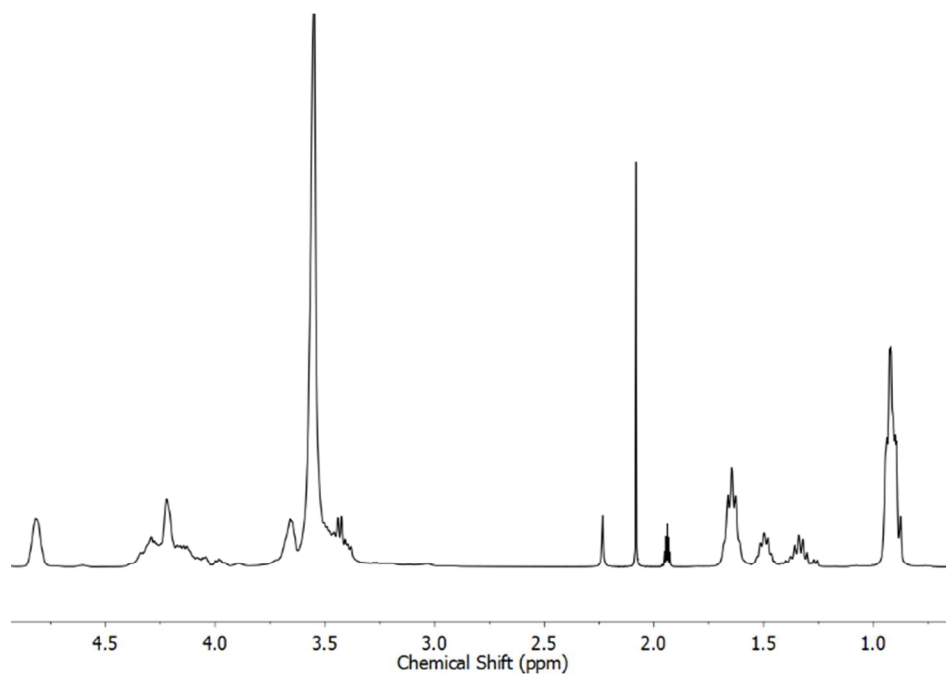


Figure S 6. ¹H NMR spectrum of *hb*(PG₁₂₅₀-*co*-PEO₆₇₅₀)-*g*-PBC₃₆₄₀ (Table 1, sample 6) (400 MHz, CD₃CN).

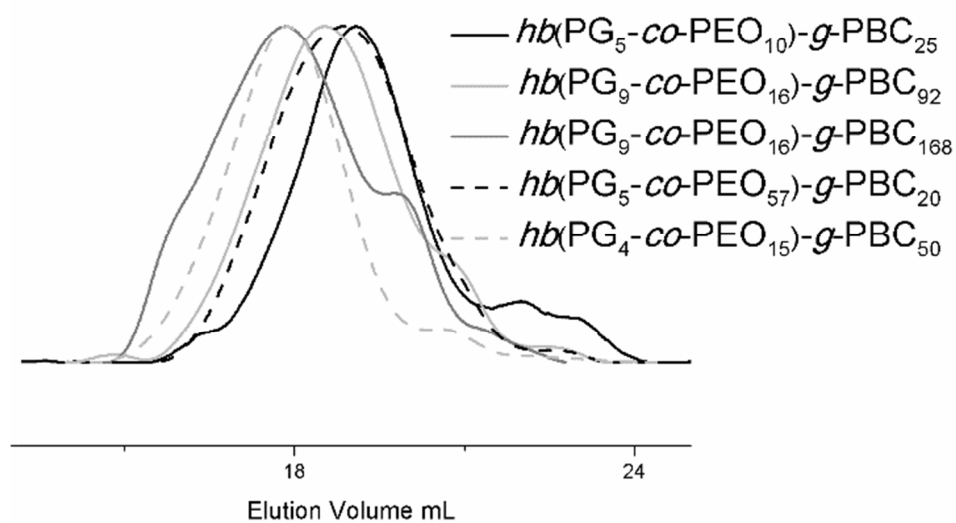


Figure S 7. SEC results of all *hb*PEO-*g*-PBC samples in DMF with PEG calibration.

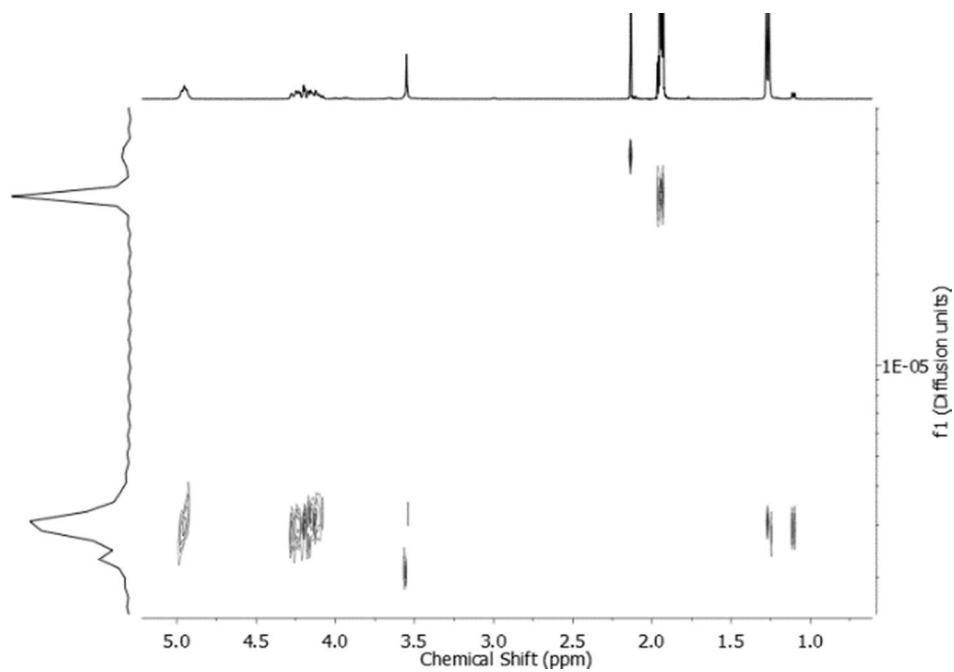


Figure S 8. DOSY spectrum of *hb*(PG₄-*co*-PEO₄₅)-*g*-PPC₃₄₉ (Table 1, sample 7) (CD₃CN, 400 MHz).

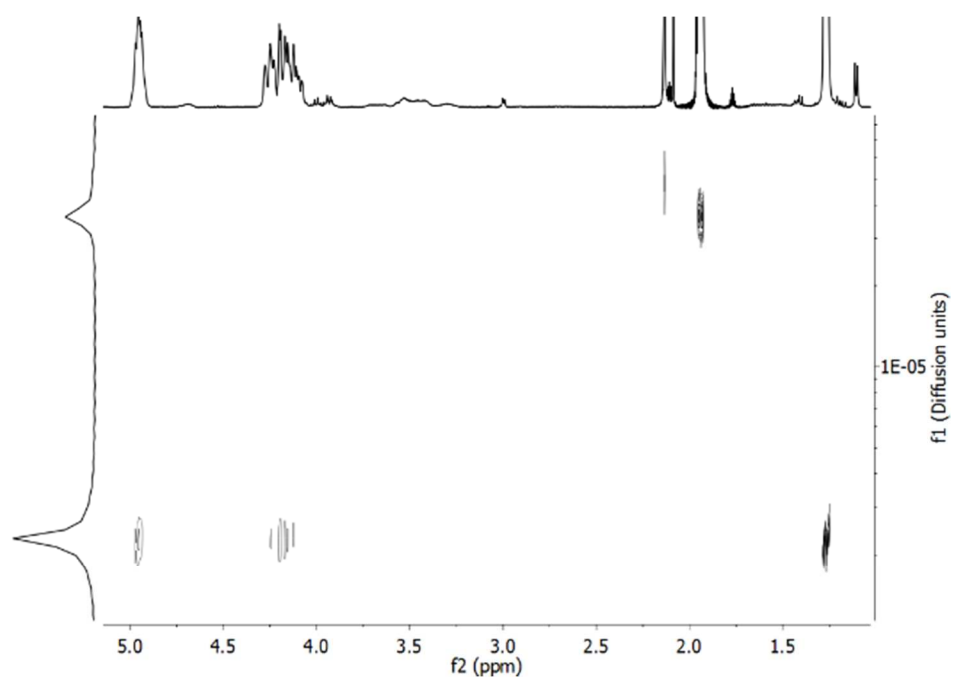


Figure S 9. DOSY spectrum of *hb*(PG₄-*co*-PBO₁₀)-*g*-PPC₁₄₆ (Table 1, sample 8) (CD₃CN, 400 MHz).

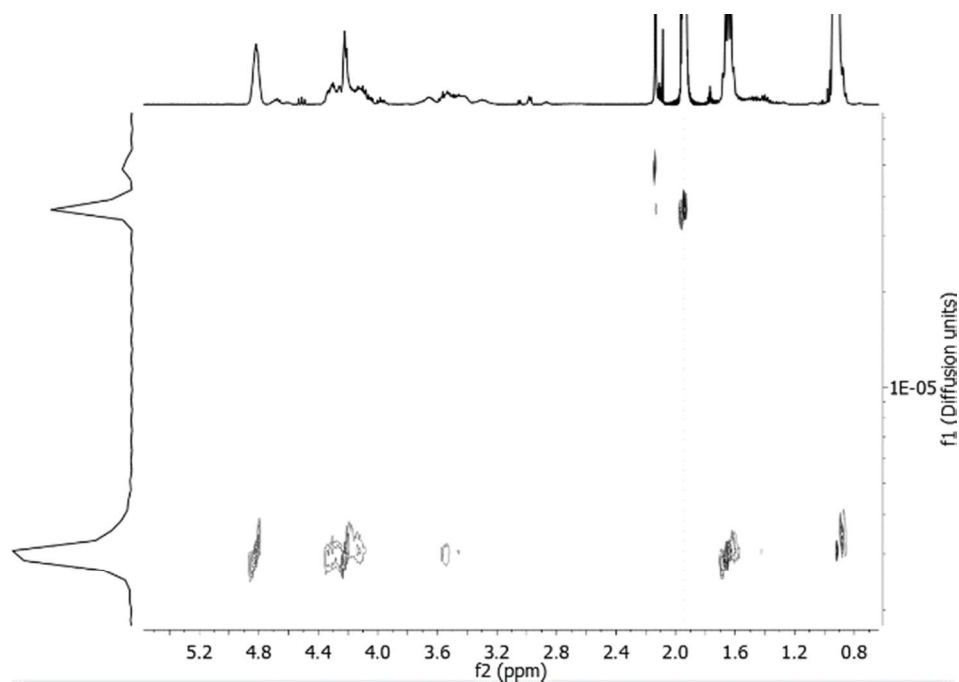


Figure S 10. DOSY spectrum of *hb*(PG₄-*co*-PBO₁₀)-*g*-PBC₆₆ (Table 1, sample 9) (CD₃CN, 400 MHz).

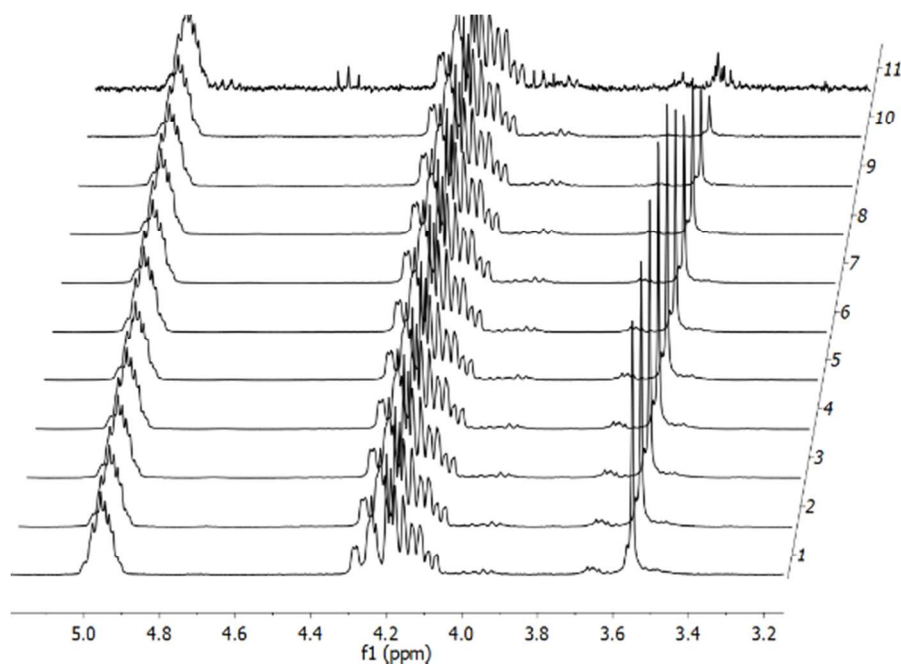


Figure S 11. ^1H NMR spectra of $hb(\text{PG}_4\text{-co-PEO}_{45})\text{-g-PPC}_{349}$ (Table 1, sample 7) after separation with a preparative SEC. (300 MHz, CD_3CN .)

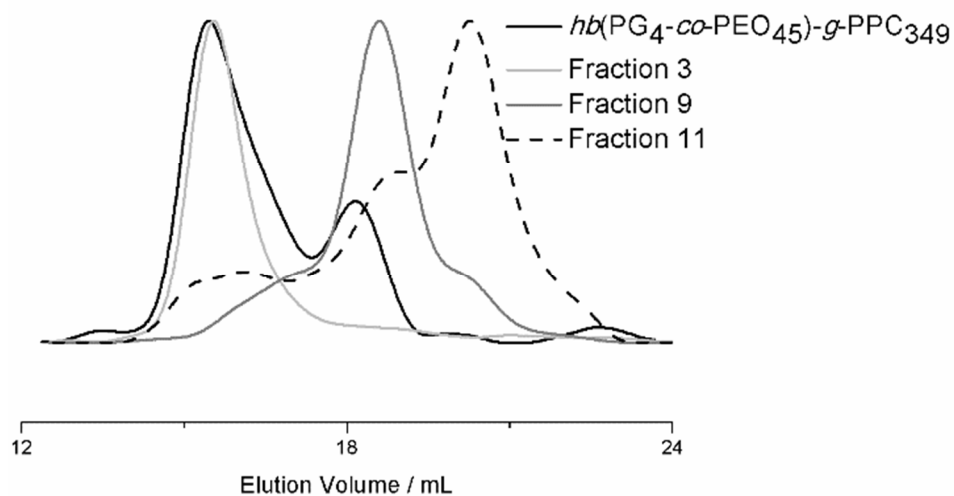


Figure S 12. SEC results for selected fractions of $hb(\text{PG}_4\text{-co-PEO}_{45})\text{-g-PPC}_{349}$ (Table 1, sample 7) star polymers in DMF with PEG calibration.

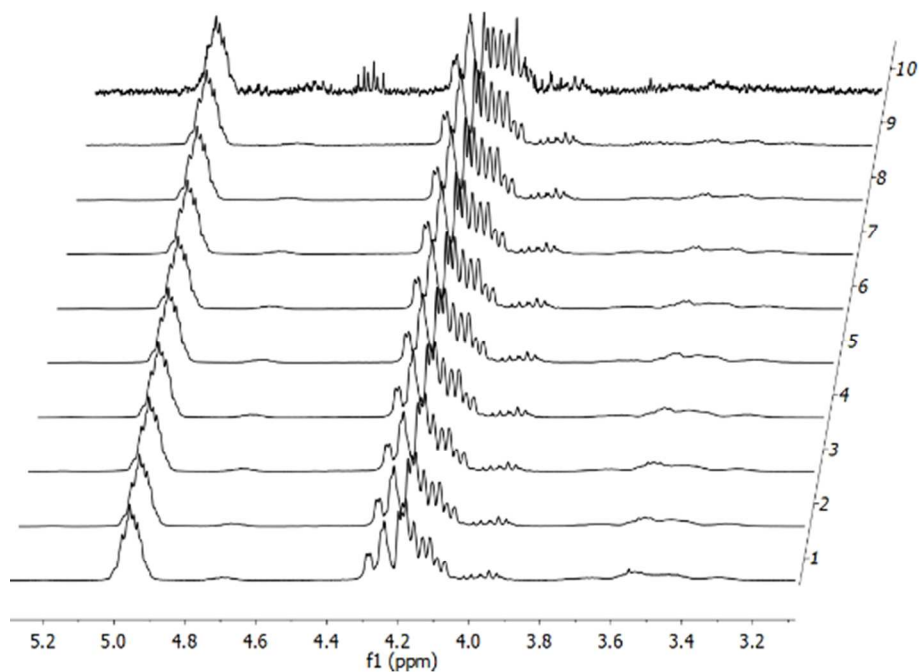


Figure S 13. ^1H NMR spectra of $hb(\text{PG}_4\text{-co-PBO}_{10})\text{-g-PPC}_{146}$ (Table 1, sample 8) after separation with a preparative SEC. (300 MHz, CD_3CN .)

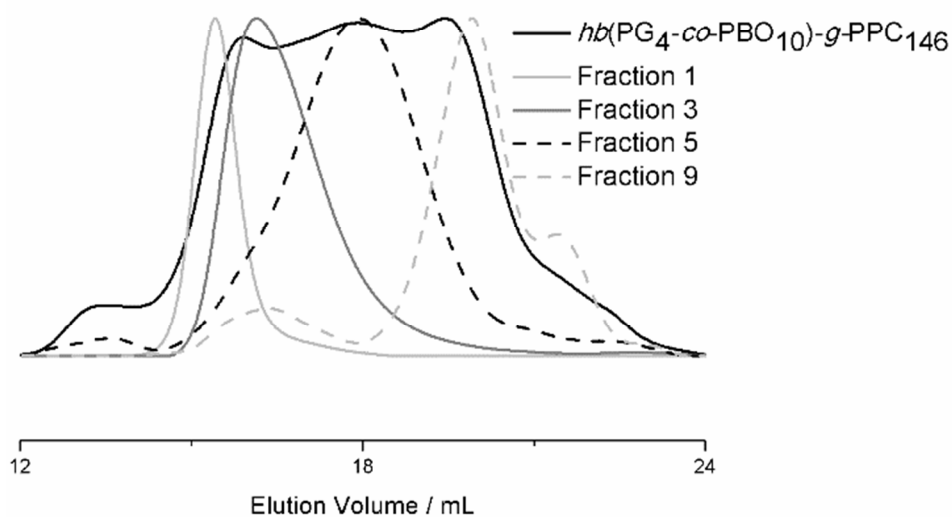


Figure S 14. SEC results for some fraction of $hb(\text{PG}_4\text{-co-PBO}_{10})\text{-g-PPC}_{146}$ (Table 1, sample 8) star polymers in DMF with PEG calibration.

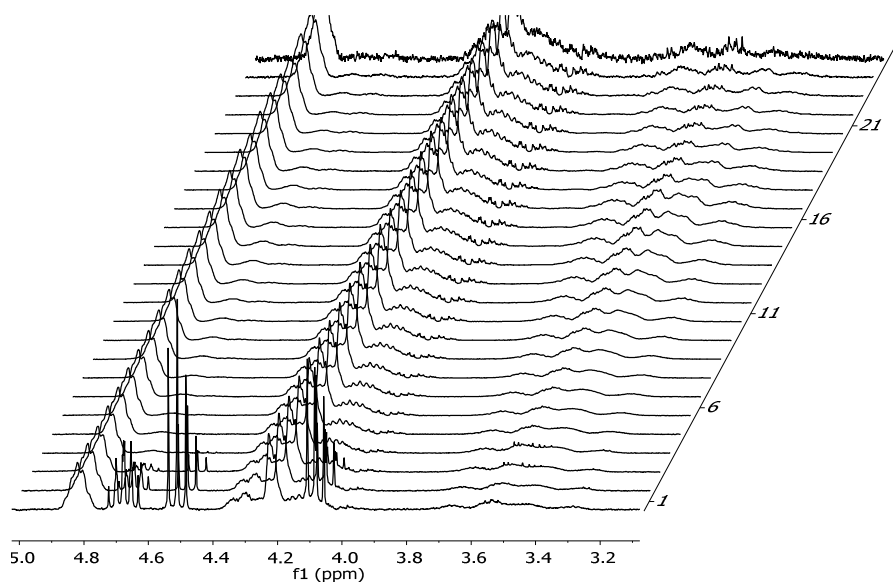


Figure S 15. ^1H NMR spectra of $hb(\text{PG}_4\text{-co-PBO}_{10})\text{-g-PBC}_{66}$ (Table 1, sample 9) after separation with preparative SEC. (300 MHz, CD_3CN .)

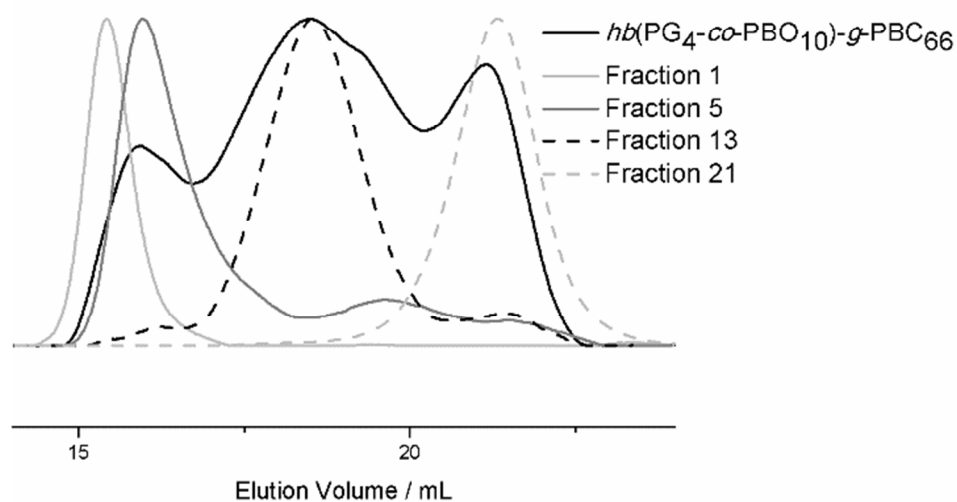


Figure S 16. SEC results for selected fractions of $hb(\text{PG}_4\text{-co-PBO}_{10})\text{-g-PBC}_{66}$ (Table 1, sample 9) star polymers in DMF with PEG calibration.

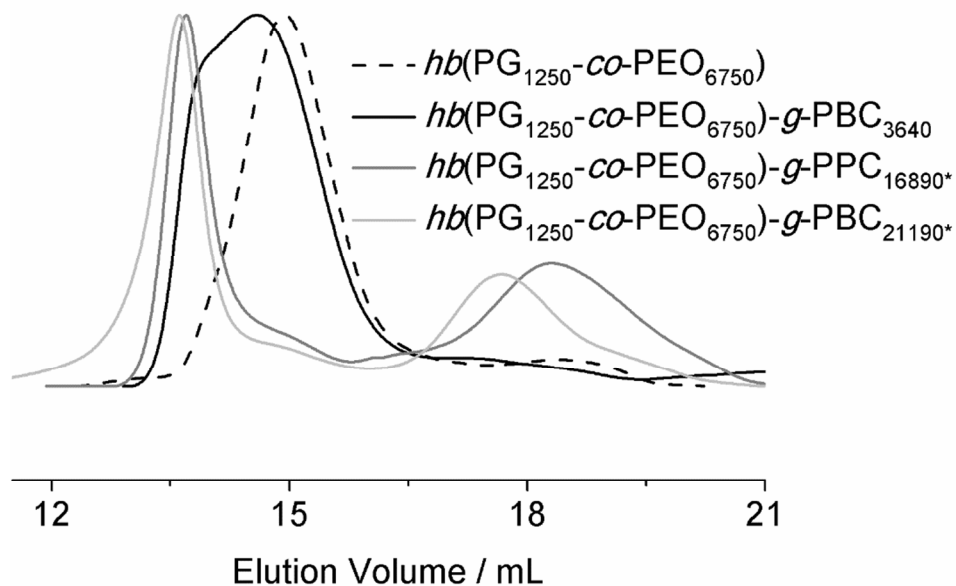


Figure S 17. SEC results for multiarm star copolymers based on the macroinitiator $hb(PG_{1250}-co-PEO_{6750})$ in DMF with PEG calibration. Repeating units of the polycarbonate are marked with a star, if the separation of star-copolymer and homopolymer was not possible. These numbers combine the polycarbonate in the stars and the homopolymer.

C Mark-Houwink α -parameter and Functionalization

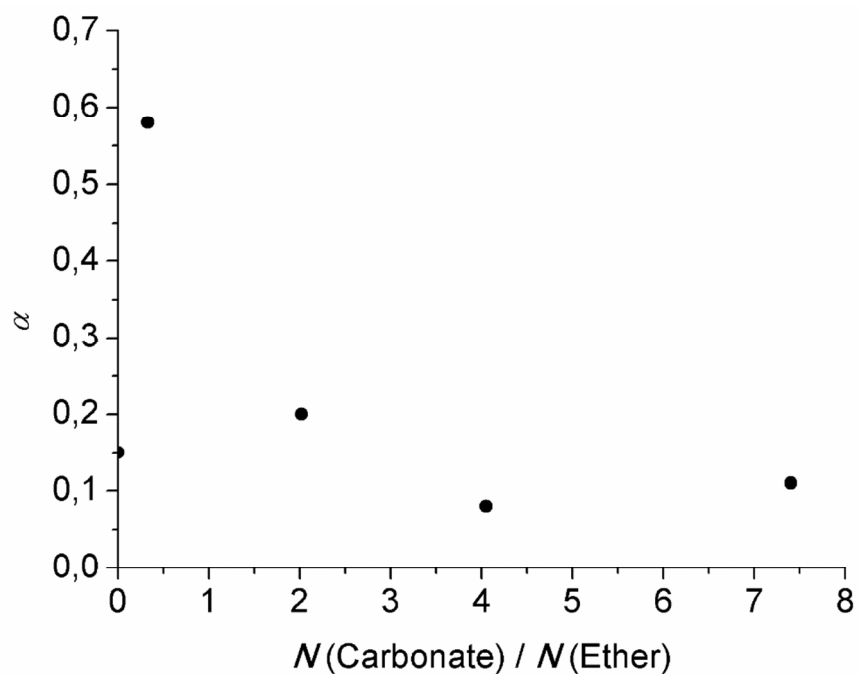


Figure S 18. α -parameters of the series of *hb*(PG-*co*-PEO)-*g*-PBC copolymers plotted versus monomer unit ratio $N(\text{Carbonate}) / N(\text{Ether})$.

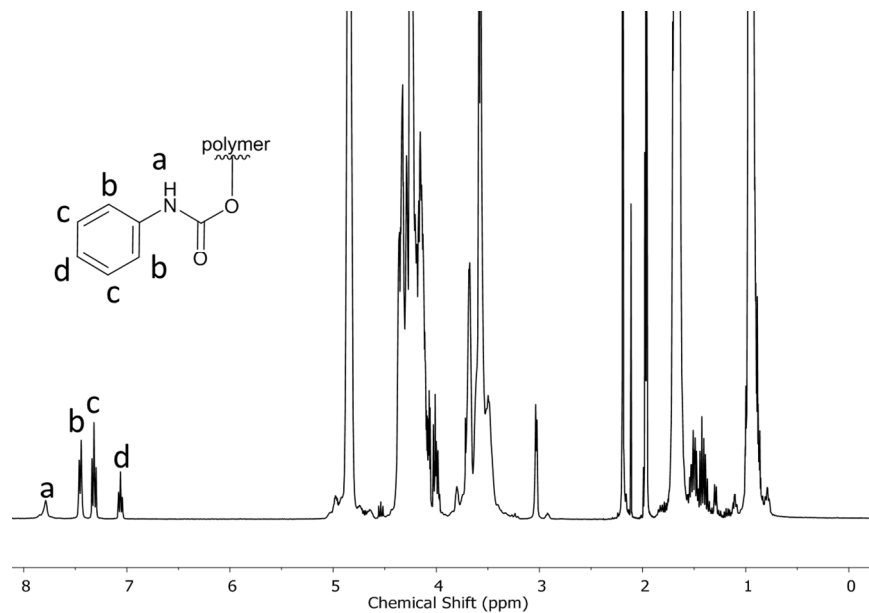


Figure S 19. ¹H NMR spectrum of *hb*(PG₉-*co*-PEO₁₆)-*g*-PBC₉₂ (Table 1, sample 2) after reaction with phenylisocyanate (400 MHz, CD₃CN).

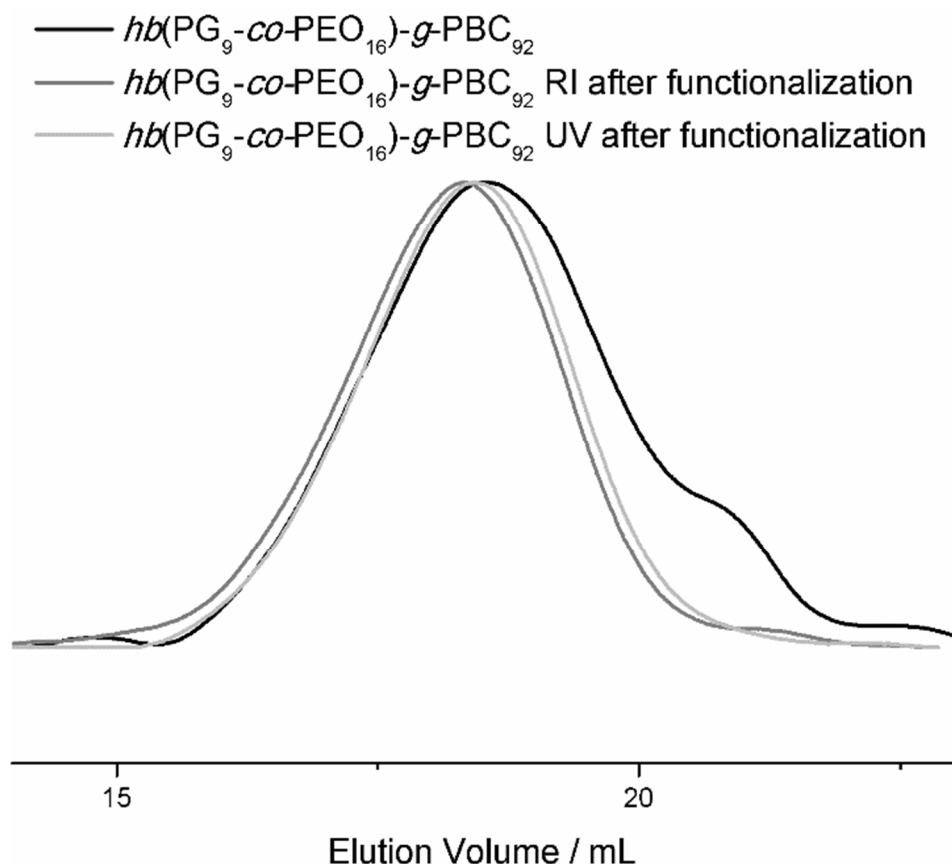


Figure S 20. SEC results $hb(PG_9-co-PEO_{16})-g-PBC_{92}$ (Table 1, sample 2) in DMF with PEG calibration before and after functionalization with phenylisocyanate.

- (1) Ford, D. D.; Nielsen, Lars P C; Zuend, S. J.; Musgrave, C. B.; Jacobsen, E. N. Mechanistic basis for high stereoselectivity and broad substrate scope in the (salen)Co(III)-catalyzed hydrolytic kinetic resolution. *J. Am. Chem. Soc.* **2013**, *135* (41), 15595–15608. DOI: 10.1021/ja408027p.
- (2) Perevyazko, I.; Seiwert, J.; Schömer, M.; Frey, H.; Schubert, U. S.; Pavlov, G. M. Hyperbranched Poly(ethylene glycol) Copolymers: Absolute Values of the Molar Mass, Properties in Dilute Solution, and Hydrodynamic Homology. *Macromolecules* **2015**, *48* (16), 5887–5898. DOI: 10.1021/acs.macromol.5b01020.
- (3) Seiwert, J.; Leibig, D.; Kemmer-Jonas, U.; Bauer, M.; Perevyazko, I.; Preis, J.; Frey, H. Hyperbranched Polyols via Copolymerization of 1,2-Butylene Oxide and Glycidol: Comparison of Batch Synthesis and Slow Monomer Addition. *Macromolecules* **2016**, *49* (1), 38–47. DOI: 10.1021/acs.macromol.5b02402.