Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

for

One-Step Synthesis of Multi-Alkyne Functional Hyperbranched Polyglycerols by Copolymerization of Glycidyl Propargylether and Glycidol

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Content:

1. Additional Characterization Data for *hb*P(G-GPE)

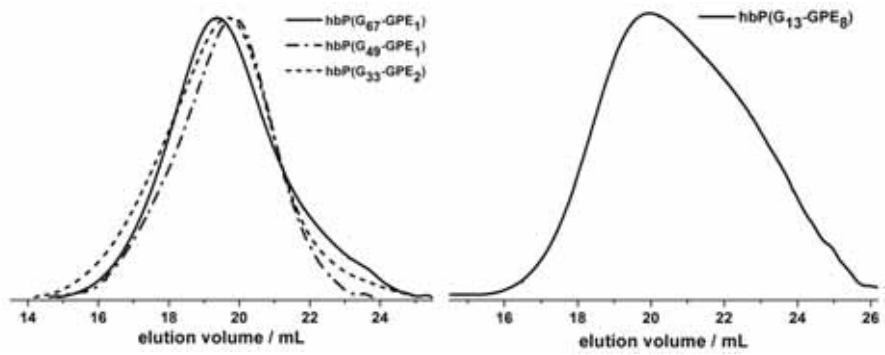


Figure S1. SEC traces (solvent: DMF, refractive index detector) of various *hb*P(G_m-GPE_n) samples. The sample *hb*P(G_{13}-GPE_8) (right) shows a slightly unsymmetrical appearance in the SEC elugram, probably due to interactions of the relatively high amount of alkyne functionalities with the column material.

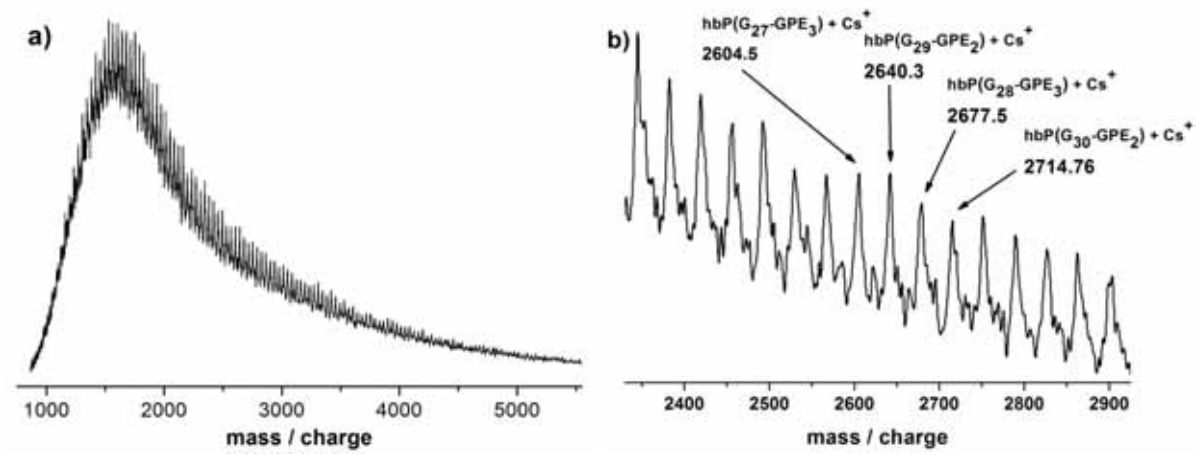


Figure S2. MALDI ToF MS spectrum of *hb*P(G_{33}-PGE_2) (Table 1, entry 5) showing the successful incorporation of the two monomers glycidol (G) and glycidyl propargyl ether (GPE). a) Full spectrum, b) zoomed spectrum with several peaks assigned. The broadening of the signals occurs due to the similar masses of copolymers with varying GPE content, e.g., TMP-*hb*P(G_{27}-GPE_3) ($C_6H_{14}O_3(C_3H_6O_2)_{27}(C_6H_8O_2)_3 \cdot Cs^+$ with calculated average mass: 2603.6) and TMP-*hb*P(G_{30}-GPE_1) ($C_6H_{14}O_3(C_3H_6O_2)_{30}(C_6H_8O_2)_1 \cdot Cs^+$ with calculated average mass: 2601.6).

2. Calculation of the Copolymer Composition and M_n from ^{1}H NMR Data

Figure S4 exemplifies the ^{1}H NMR spectrum of *hb*P(G_{13}-GPE_8) with the corresponding integrated signals.

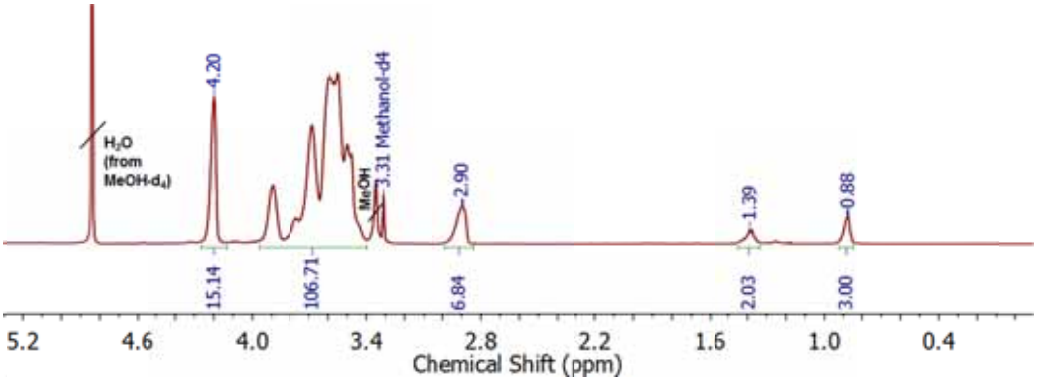


Figure S4. ^{1}H NMR spectrum (600MHz, MeOH-d_4) of *hb*P(G_{13}-GPE_8).

To calculate the copolymer composition, the integrals of the initiator (here: 1,1,1-trimethylol propane, TMP) are assigned (methane and methylene group at 0.88 and 1.39 ppm, respectively). To calculate the average amount of GPE repeat units (n_{GPE}), the methylene signals of the propargyl ether group at 4.20 ppm are used. The composition and the number average molecular weight can subsequently be calculated using the absolute integral of the polyether backbone (4.10-3.40 ppm). First, six protons have to be subtracted from the signal occurring from the methylene carbons of TMP (or other triol-initiator systems). Both monomers, glycidol (G) and GPE contribute with five protons to this signal for each monomer included. Therefore, the number of G repeat units (n_G) is calculated as $n_G = \frac{\text{Integral (polyether backbone)} - 6 - (n_{GPE} \times 5)}{5}$. Knowing n_G and n_{GPE}, the number average molecular weight (M_n) can be determined by multiplying with the molar masses of the monomers.

2. 2D NMR Characterization of *hb*P(G-GPE)

i) Determination of the Propargyl Ether Signals

To determine the signals of the propargyl ether functionalities in *hb*P(G-GPE), HSQC (Heteronuclear Single Quantum Coherence) and HMBC (Heteronuclear Multiple Bond Correlation) NMR spectra were recorded (Figure S5, Full Spectra: Figure S7 and S8). Using the HSQC spectrum (Figure S5a), the ^{13}C signal of the methylene group of the propargyl ether can be assigned at 59.3 ppm. Using the HMBC spectrum, the signals of the acetylene carbons are assigned at 80.7 and 76.3 ppm. Due to the absence of a H/^{13}C corsspeak in the HSQC spectrum for the signal at 80.7 ppm, this signal can be assigned to the quaternary carbon of the acetylene group.

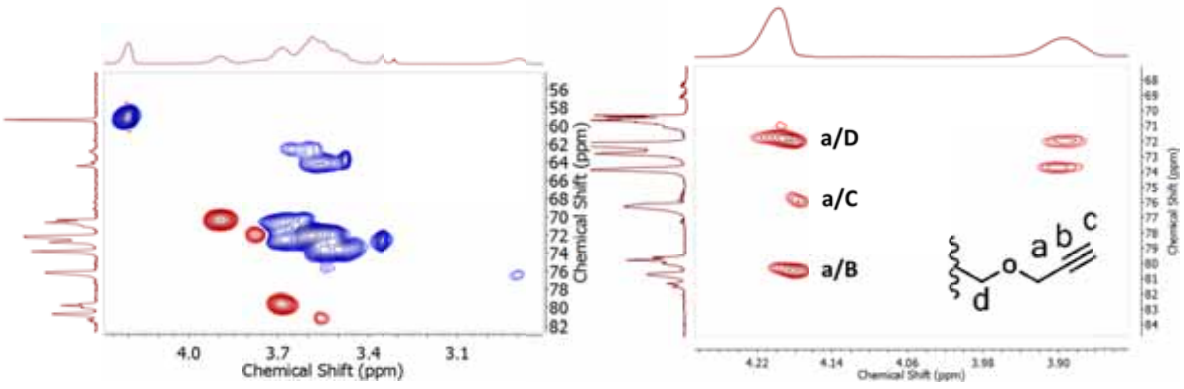


Figure S5: a) HSQC spectrum (CH_2: blue, CH/CH_3: red) and b) HBMC spectrum of *hb*P(G_{13}-GPE_8) and structure of the GPE-repeat units with assigned peaks. Capital letters correspond to the carbon atoms, lowercase letters to the protons.

ii) Peak assignment of the glycerol repeat units L_{13}, D, L_{14} and the GPE repeat units L_{GPE} und L_{GPE}

L_{13}: Due to the fact that the two signals of the L_{13} repeat units at 81.5 ppm and 62.8 ppm show the same integral value in all IG ^{13}C spectra, no overlap with signals from PGE repeat units is concluded. These signals exclusively belong to linear-1,3 glycerol repeat units.

L_{14} vs. T_{GPE}: The ^{13}C signal at 73.9 ppm exclusively belongs to the two carbons (C1 and C3) of the L_{14} repeat unit. In the HSQC-TOCSY spectrum (Figure S7, blue: direct coupling, red: long-range coupling), only two crosspeaks can be found for the signal at 73.9 ppm: The first crosspeak

(73.9 ppm/3.90 ppm) represents the direct C-H coupling, while the other two crosspeaks (73.9 ppm/3.55 ppm and 73.9 ppm/3.48 ppm) correspond to the protons bound to the other two carbons in the L_{14} repeat unit. Moreover, in the HMBC spectrum (Figure S8), in the range of 73.9 ppm, no crosspeak with the propargyl ether group can be found. Using the additional HMBC-crosspeak in the ^{1}H shift range of 3.90 ppm, the C3-carbon of the "glycerol"-part of the T_{GPE}-repeat units can be assigned to the signal at 71.9 ppm.

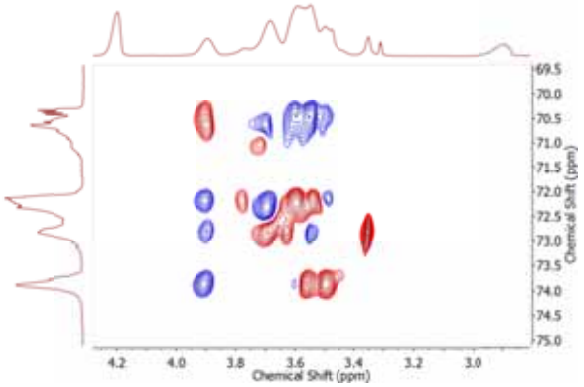


Figure S6. a) HSQC-TOCSY spectrum of *hb*P(G_{13}-GPE_8) with the relevant signal region used to determine the shift of the ^{13}C NMR signals of the L_{14} and the T_{GPE} repeat unit.

D vs. L_{GPE}: Due to the chemical similarity of the C2-atom within the dendritic glycerol repeat unit (D) and the L_{GPE} repeat unit and the absence of additional direct coupling signals in the 2D HSQC-TOCSY spectra in the range of the dendritic repeat unit (79.9 ppm), a peak overlap for the C2 carbon of D and L_{GPE} can be deducted (Figure S7).

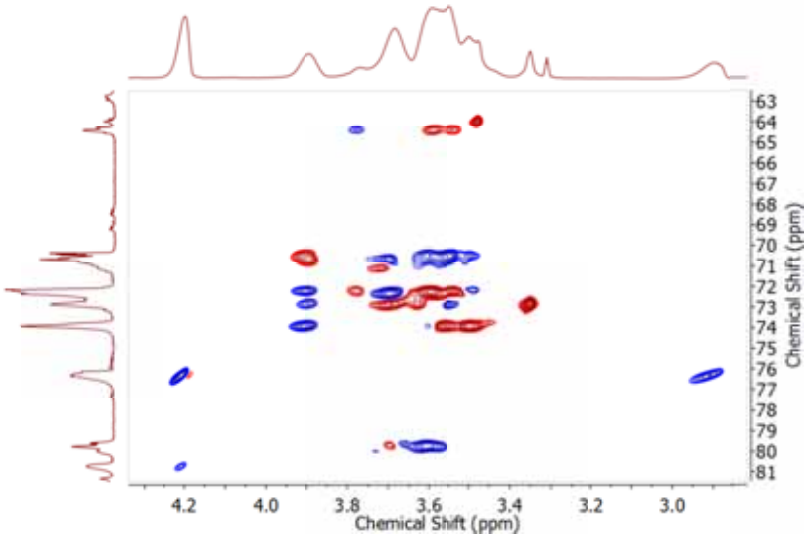


Figure S7. Full HSQC-TOCSY spectrum of *hb*P(G_{13}-GPE_8).

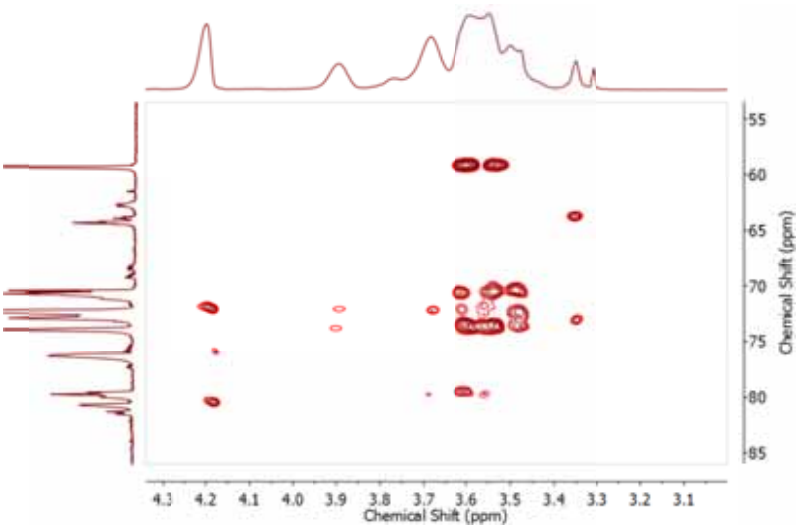


Figure S8. Full HMBC NMR spectrum of *hb*P(G_{13}-GPE_8).

4. Additional Data for Determination of the Degree of Branching

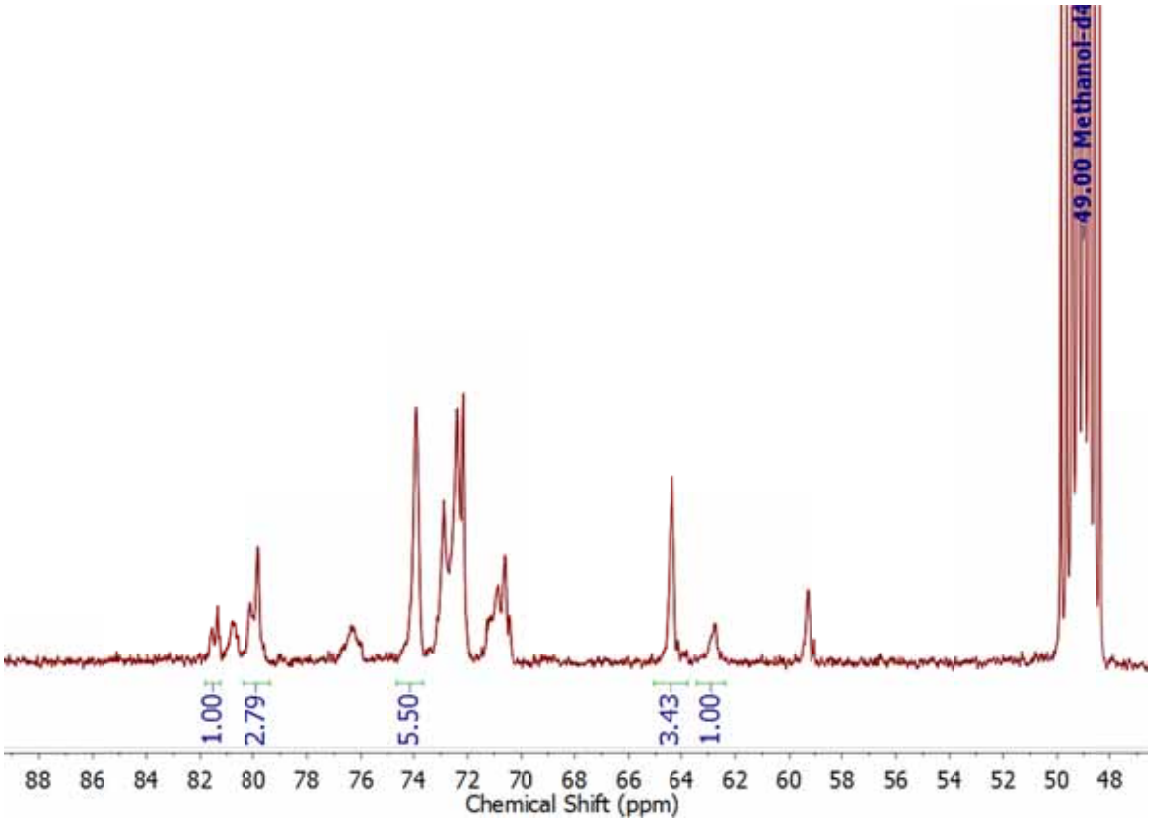
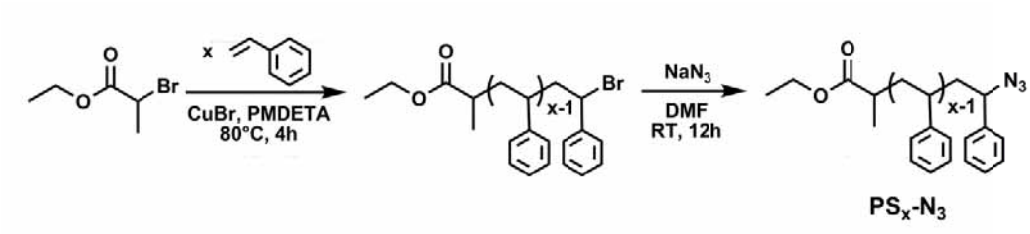


Figure S9. Exemplary full IG ^{13}C NMR spectrum (100 MHz, MeOH-d_4) of *hb*P(G_{27}-GPE_3) with the corresponding integrals.

Table S1. Complete integrals data determined from IG ^{13}C NMR spectroscopy.

	Sample	L_{13}	$2L_{14}$	$D + L_{PGE}$	T	Sum
1	*hb*P(G_{67}-GPE_1)	1.00	6.29	2.95	3.90	11.00
2	*hb*P(G_{49}- GPE_1)	1.00	6.17	2.86	4.13	11.08
3	*hb*P(G_{32}- GPE_1)	1.00	6.28	2.60	3.85	10.59
4	*hb*P(G_{21}- GPE_1)	1.00	6.16	2.58	4.39	11.05
5	*hb*P(G_{33}- GPE_2)	1.00	5.26	2.81	3.12	9.56
6	*hb*P(G_{27}- GPE_3)	1.00	5.50	2.79	3.43	9.97
7	*hb*P(G_{20}- GPE_3)	1.00	6.00	3.21	3.47	10.68
8	*hb*P(G_{28}- GPE_5)	1.00	6.29	3.09	4.00	11.24
9	*hb*P(G_{13}- GPE_8)	1.00	5.54	3.92	1.71	9.40

5. Data for *hb*P(G-GPE)-*g*-PS Copolymers



Scheme S1. Synthesis of azide end-functional polystyrene (PS-N_3) by ATRP. (Tsarevsky et al. *Macromolecules* **2005**, *38 (9)*, 3558–3561)

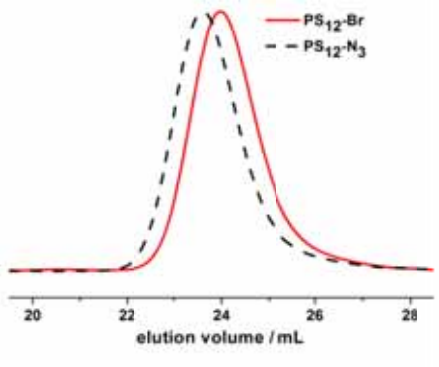


Figure S10. SEC traces (solvent: $CHCl_3$, polystyrene standards) of polystyrene with bromide (red) and azide (black/dashed) end-group, prepared by ATRP. PS_{12}-Br: M_n=1350 g mol^{-1}, PDI=1.16. PS_{12}-N_3: M_n=1430 g mol^{-1}, PDI=1.15.

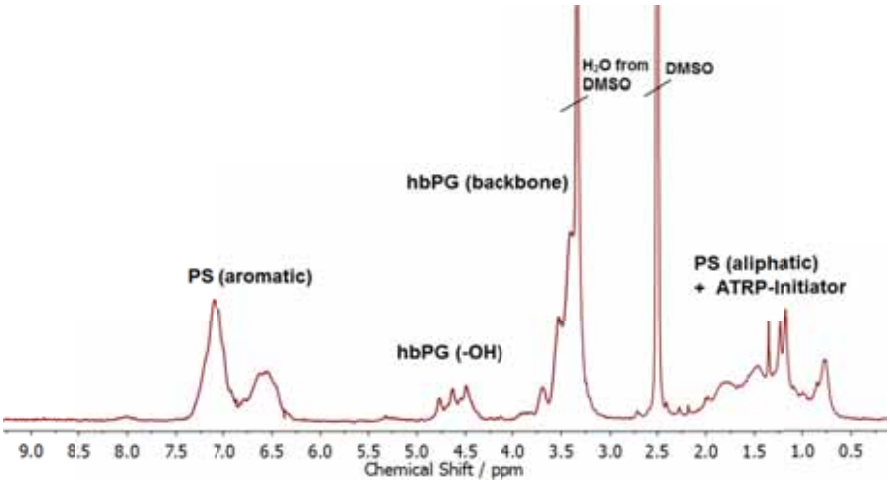


Figure S11. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of *hb*P(G_{33}-GPE_2)-*g*-(PS_{12})$_2$.