Supporting Information for

Synthesis and self-assembly of branched glycopolypeptides: effect of topology and conformation

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Synthesis of glycopolypeptide 2':

Tree-like **2'**, 40 units of benzyl-*L*-glutamate: poly(γ-benzyl-*L*-glutamate–*block*–*DL*-propargylglycine, copolymer **2**) (93 mg, ca. 0.045 mmol of alkyne units), α-azido-dextran (600 mg, 0.09 mmol, 2 equiv. to alkyne groups) and sodium ascorbate (63 mg, 0.32 mmol, 7 equiv. to alkyne groups) were dissolved in 5 mL of anhydrous DMSO in a Schlenk tube. $CuSO_4$ (45 mg, 0.18 mmol, 4 equiv. to alkynes groups) was then added and the Schlenk tube was placed in an oil bath at 30 °C for 16 hours. The reaction medium was then dialyzed 4-5 days against milliQ water (Spectra/Por®6 MWCO 50 kDa membrane), containing EDTA the first 2 days, and lyophilized, then the reaction mixture was purified by ultrafiltration to remove all the unreacted dextran (yield = 349 mg, 89%).
^{1}H-NMR (400 MHz, DMSO, δ, ppm): 7.26 (s broad, benzyl), 5.05 (s broad, C**H**$_2$-benzyl), 4.92 (s broad, C_4O**H**), 4.84 (s broad, C_3O**H**), 4.70 (s broad, C_1**H**$_{anom.}$), 4.55 (s, broad, NH-C**H**-CO), 4.49 (s broad, C_2O**H**), 3.76 (s broad, C_6**H**), 3.53 (s broad, C_5**H**), 3.45 (s broad, C_6**H'**), 3.22 (s broad, C_2**H** + C_4**H**), 2.55 (s broad, CH_2-C**H**$_2$-CO), 2-2.2 (m broad, CH-C**H**$_2$-CH_2).
IR (cm^{-1}): 3100-3600 (peak: 3300); 2920; 1730, 1650, 1545, 1200-1450 (multiple peaks)

Synthesis of glycopolypeptide 3':

Tree-like **3'**, 60 units of benzyl-*L*-glutamate: poly(γ-benzyl-*L*-glutamate–*block*–*DL*-propargylglycine, copolymer **3**) (137 mg, ca. 0.045 mmol of alkyne units), α-azido-dextran (600 mg, 0.09 mmol, 2 equiv. to alkyne groups) and sodium ascorbate (63 mg, 0.32 mmol, 7 equiv. to alkyne groups) were dissolved in 5 mL of anhydrous DMSO in a Schlenk tube. $CuSO_4$ (45 mg, 0.18 mmol, 4 equiv. to alkynes groups) was then added and the Schlenk tube was placed in an oil bath at 30 °C for 16 hours. The reaction medium was then dialyzed 4-5 days against milliQ water (Spectra/Por®6 MWCO 50 kDa membrane), containing EDTA the first 2 days, and lyophilized, then the reaction mixture was purified by ultrafiltration to remove all the unreacted dextran (yield = 369 mg, 85%).

^{1}H-NMR (400 MHz, DMSO/TFA, δ, ppm): 7.26 (s broad, benzyl), 5.05 (s broad, C**H**$_2$-benzyl), 4.92 (s broad, C_4O**H**), 4.84 (s broad, C_3O**H**), 4.70 (s broad, C_1**H**$_{anom.}$), 4.55 (s, broad, NH-C**H**-CO), 4.49 (s broad, C_2O**H**), 3.76 (s broad, C_6**H**), 3.53 (s broad, C_5**H**), 3.45 (s broad, C_6**H'**), 3.22 (s broad, C_2**H** + C_4**H**), 2.55 (s broad, CH_2-C**H**$_2$-CO), 2-2.2 (m broad, CH-C**H**$_2$-CH_2).
IR (cm^{-1}): 3100-3600 (peak: 3300); 2920; 1730, 1650, 1545, 1200-1450 (multiple peaks)

Synthesis of glycopolypeptide 4':

Tree-like **4'**, 80 units of benzyl-*L*-glutamate: Poly(γ-benzyl-*L*-glutamate–*block*–*DL*-propargylglycine, copolymer **4**) (181 mg, ca. 0.045 mmol of alkyne units), α-azido-dextran (600 mg, 0.09 mmol, 2 equiv. to alkyne groups) and sodium ascorbate (63 mg, 0.32 mmol, 7 equiv. to alkyne groups) were dissolved in 5 mL of anhydrous DMSO in a Schlenk tube. $CuSO_4$ (45 mg, 0.18 mmol, 4 equiv. to alkynes groups) was then added and the Schlenk tube was placed in an oil bath at 30 °C for 16 hours. The reaction medium was then dialyzed 4-5 days against milliQ water (Spectra/Por®6 MWCO 50 kDa membrane), containing EDTA the first 2 days, and lyophilized, then the reaction mixture was purified by ultrafiltration to remove all the unreacted dextran (yield = 440 mg, 92%).

^{1}H-NMR (400 MHz, DMSO, δ, ppm): 7.26 (s broad, benzyl), 5.05 (s broad, C**H**$_2$-benzyl), 4.92 (s broad, C_4O**H**), 4.84 (s broad, C_3O**H**), 4.70 (s broad, C_1**H**$_{anom.}$), 4.55 (s, broad, NH-C**H**-CO), 4.49 (s broad, C_2O**H**), 3.76 (s broad, C_6**H**), 3.53 (s broad, C_5**H**), 3.45 (s broad, C_6**H'**), 3.22 (s broad, C_2**H** + C_4**H**), 2.55 (s broad, CH_2-C**H**$_2$-CO), 2-2.2 (m broad, CH-C**H**$_2$-CH_2).
IR (cm^{-1}): 3100-3600 (peak: 3300); 2920; 1730, 1650, 1545, 1200-1450 (multiple peaks)

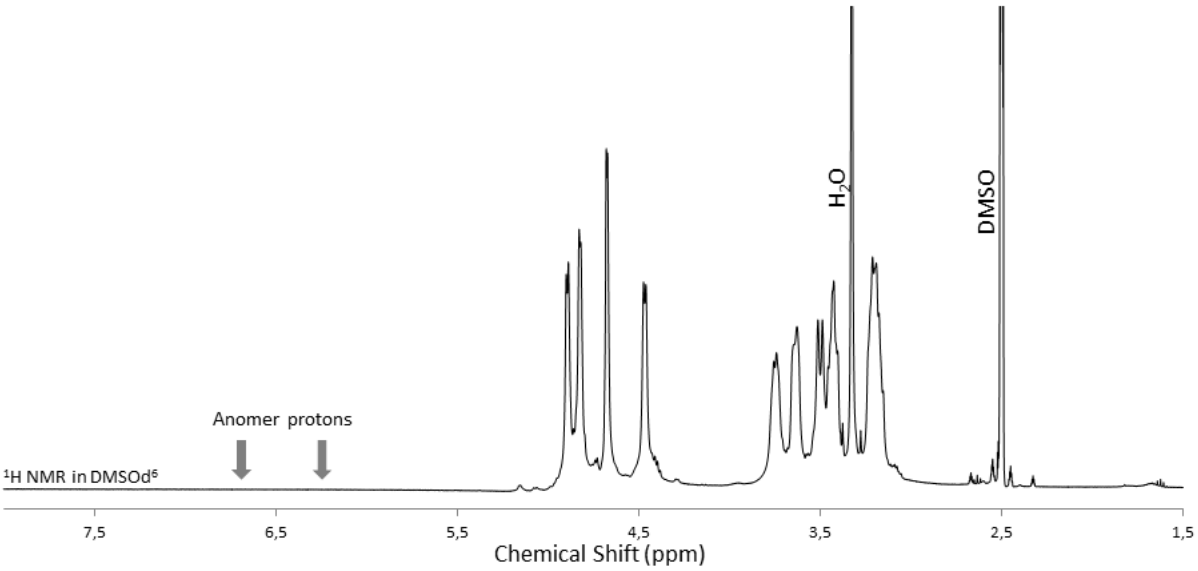

Figure S1. [1]HNMR of azido-dextran after purification in DMSO-d[6].

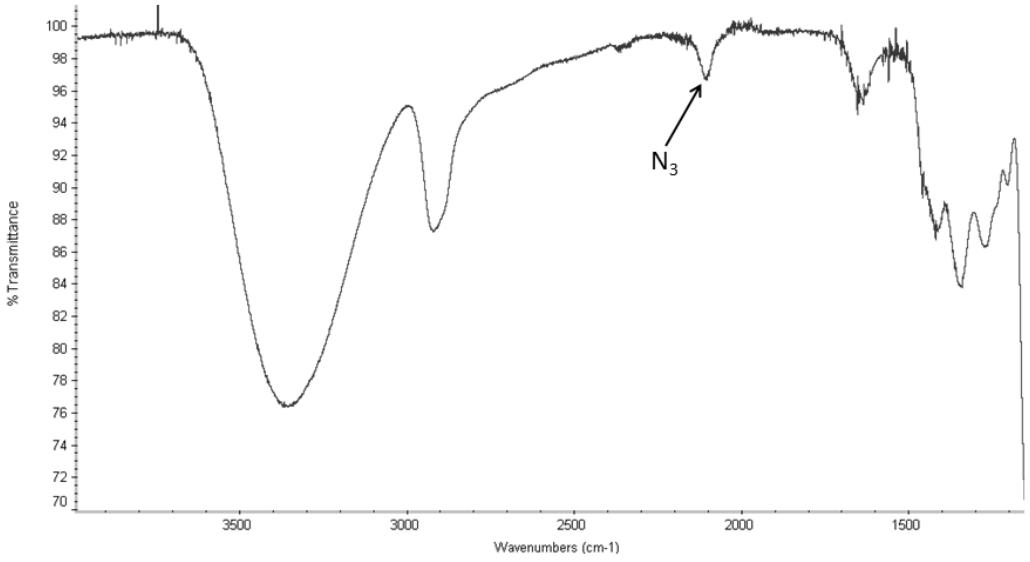

Figure S2. FTIR of azido-dextran after purification.

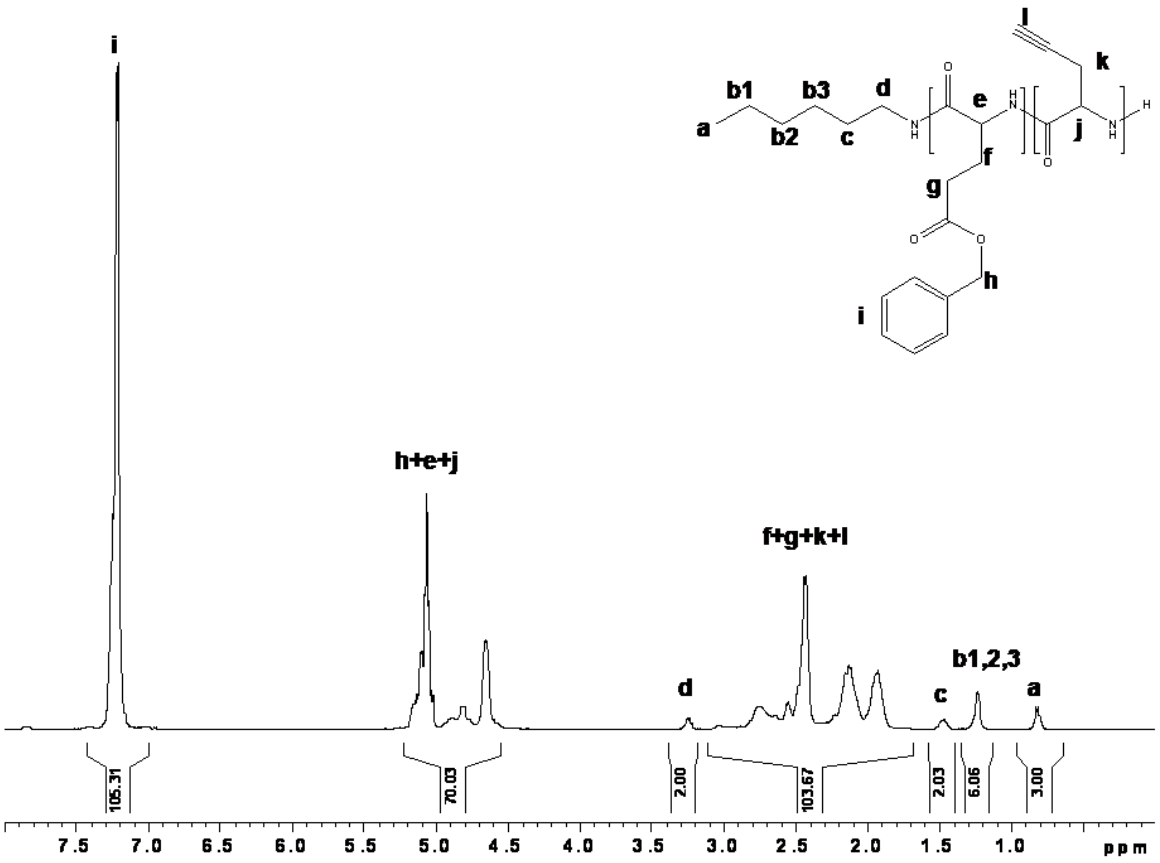

Figure S3. Typical ^{1}HNMR of poly(γ-benzyl-*L*-glutamate–*block*–*DL*-propargylglycine) (copolymer **1**) in TFA-d^{6}

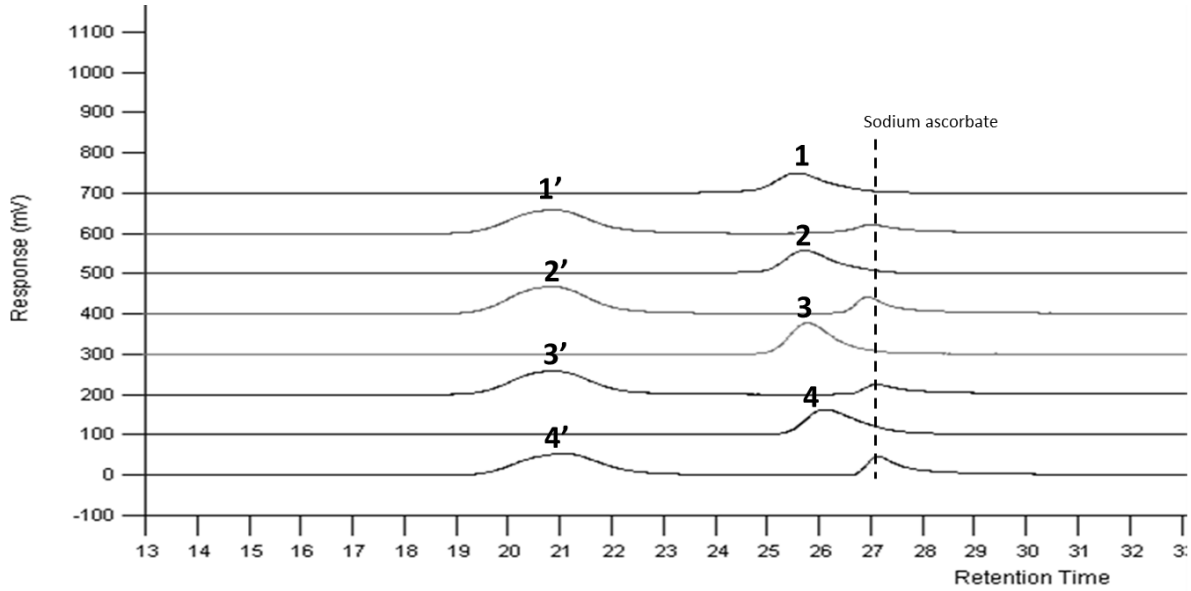

Figure S4. SEC traces of the copolypeptides **1'** to **4'** before and after CuAAc (elution in DMSO containing 1% LiBr, UV detection)

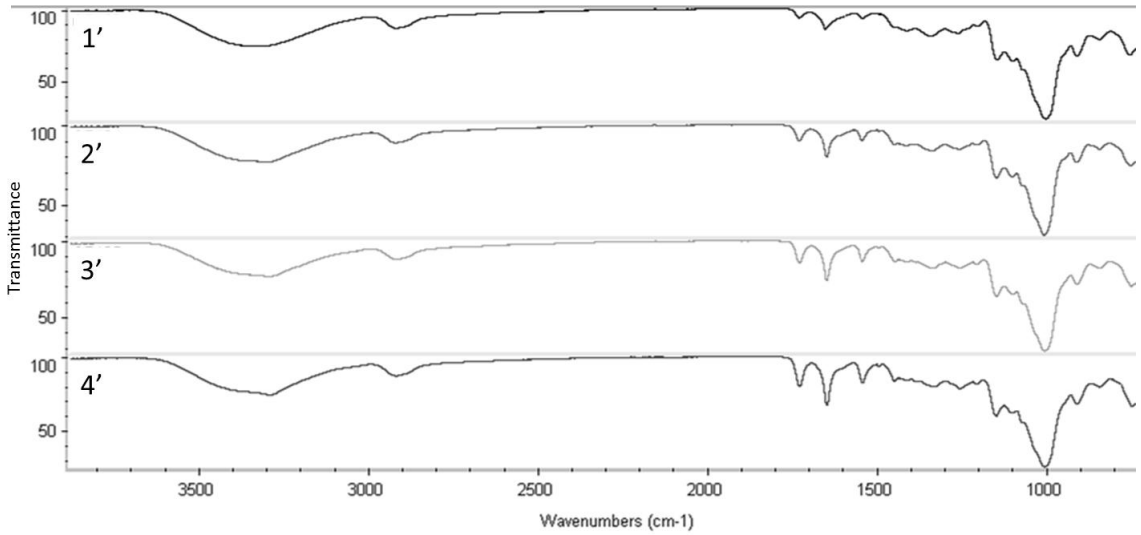

Figure S5. FTIR of glycopolypeptides **1'** to **4'**

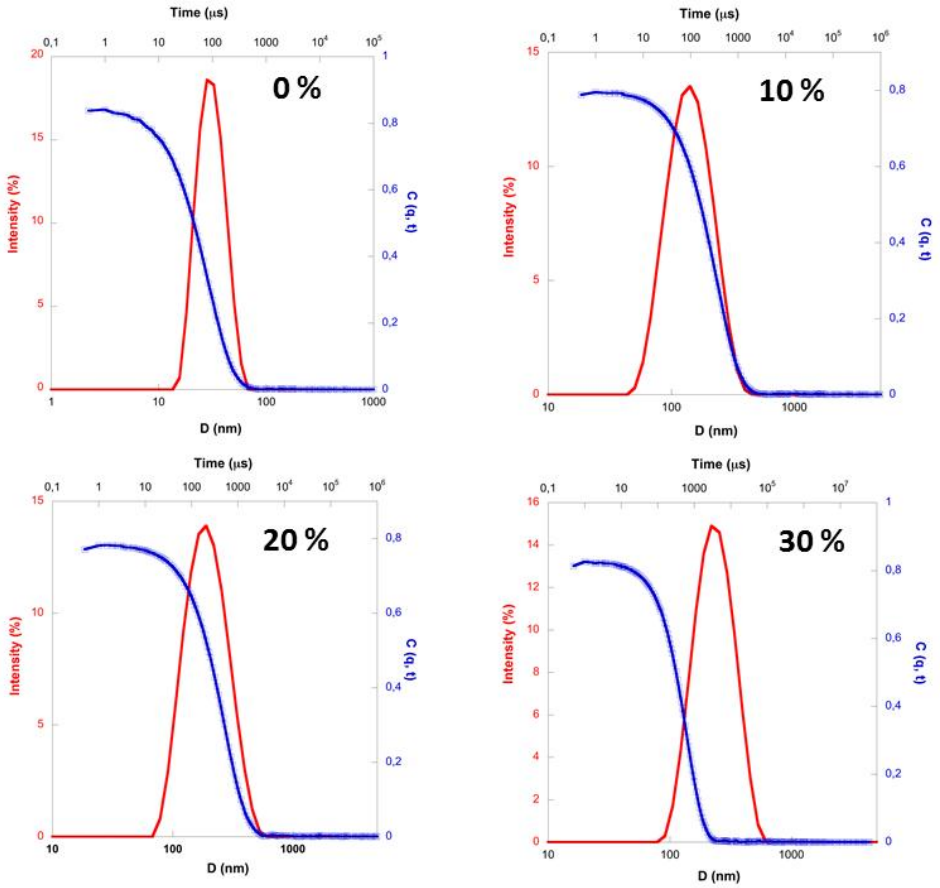

Figure S6 DLS measurements after self-assembly of blends including **3'** and PBLG

Glycopolypeptide	Volume taken by the polypeptide (nm^3)	Volume taken by the oligosaccharides (nm^3)	Total volume (nm^3)	*f* ratio
1'	6.7	54.9	61.7	0.89
2'	13.0	54.9	67.9	0.81
3'	16.7	54.9	71.6	0.77
4'	20.3	54.9	75.2	0.73

Table S1. Volumes in nm^3 calculated for **1'** to **4'**: results were obtained from masses (DP from ^{1}HNMR) by taking densities value of 1.28 $g.cm^{-3}$ for PBLG and 0.98 $g.cm^{-3}$ for dextran.

Blend	Volume taken by the polypeptide (nm3)	Volume taken by the oligosaccharides (nm3)	Total volume (nm3)	f ratio
3' alone	16.7	54.9	71.6	0.77
3' + 10% PBLG	23.2	54.9	78.1	0.70
3' + 20% PBLG	31.4	54.9	86.3	0.64
3' + 30% PBLG	41.9	54.9	96.8	0.57

Table S2. Volumes in nm^3 calculated for the blends made from **3'**: results were obtained from masses by taking densities value of 1.28 $g.cm^{-3}$ for PBLG and 0.98 $g.cm^{-3}$ for dextran.