Supplemental Information for:

Doubly-Dendronized linear polymers

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General. THF was distilled from Na / benzophenone before use. Triethylamine was distilled from CaH_2. All other solvents used were reagent grade. All reagents were used as supplied. All ^1H NMR spectra were measured with a Bruker DRX-500 spectrometer at 500 MHz. Analytical size exclusion chromatography (SEC) in N,N-dimethylformamide (DMF) HPLC grade with 0.2% wt LiBr was performed at 70 °C at a nominal flow rate of 1.0 mL/min on a chromatography line calibrated with linear poly(methylmethacrylate) (PMMA) standards (1,280 – 910,500 Da) and fitted with two 7.5 x 300 mm PSS SDV linear (5-μm paticle size). The SEC system used when determining PMMA-equivalent molecular weights consists of a Waters 510 pump, a Waters U6K injector, and a RI Waters 410. Preparative SEC in DMF was performed at ambient temperature at a nominal flow rate of 2 mL/min and fitted with a 600 x 20 mm PSS SDV linear "prep" (10-μm paticle size). THE SEC prep system consists of a Waters 510 pump, a Rheodyne injector with 1 mL sample loop, RI Waters 410, and a Waters fraction collector II.

SEC-multi-angle laser light scattering (MALLS) measurements with DMF as the mobile phase was performed using a system composed of a Waters 510 pump, Rheodyne injector with 50 μL sample loop, two PSS SDV linear (7.8 x 300 mm) columns thermostated at 70 °C, Dawn EOS MALLS, and Optilab DSP differential refractometer thermostated at 35 °C. Flow rate was 1 mL/min. The light source was GaAs laser with 690 nm wavelength and 30 mW output power at 685 nm. Scattering signals were collected at 17 different angels from 28 to 147°. The data were analyzed using ASTRA for Windows software (Ver. 4.90.07, Wyatt Technology). Zimm plot (K*c/R) was used for the detector fitting method. Absolute molecular weight of the dendronized polymer was determined using the MALLS data and two additional parameters, RI detector calibration constant and an assumption of 100% mass recovery of the injected polymer sample. An exact known amount of polymer was injected. For both SEC and SEC-MALLS, typically 1-2 mg/mL of polymer solution was pre-filitered through a 0.2 μm pore size PTFE filters (Whatman) before injection.

PHS-60K-[G2]-yne. PHS-60K-[G2]-OH (50.0 mg, 100 μmol) PDI = 1.19, 4-pentynoic acid (78.7 mg, 0.80 mmol), 1,3-dicyclohexylcarbodiimide (165 mg, 0.80 mmol), 4-(dimethylamino)-pyridinium-*p*-toluene sulfonate (11.9 mg, 40.9 μmol) and 4-(dimethlyamino)-pyridine (5.00 mg, 40.9 μmol) were dissolved in 2 ml of DCM and 1 ml of DMF and stirred for 24 hours. The mixture was then filtered and precipitated into diethylether yielding 34 mg of a clear oil (38%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.90-6.30 (br, ~4H) 4.50-3.80 (br, ~12H), 3.70-3.50 (br,

~3H) 2.60-2.40 (br, 16H), 2.10-1.90 (br, 4H), 1.50-0.70 (br, ~9H). IR (thin film): 3303, 3055, 2985, 2933, 1741, 1471, 1422, 1377, 1265, 1203, 1164, 1129, 1047, 1000, 896, 853, 738. PDI = 1.20

PHS-60K-[G3]-yne. PHS-60K-[G3]-OH (50.0 mg, 52.3 μmol) PDI = 1.29, 4-pentynoic acid (82.0 mg, 0.84 mmol), 1,3-dicyclohexylcarbodiimide (173 mg, 0.84 mmol), 4-(dimethylamino)-pyridinium-*p*-toluene sulfonate (12.9 mg, 44.2 μmol) and 4-(dimethylamino)-pyidine (5.4 mg, 44.2 μmol) were dissolved in 2 ml of DCM and 1 ml of DMF and stirred for 24 hours. The mixture was then filtered and precipitated into diethylether yielding 39.8 mg of a clear solid (44%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.70-3.80 (br, ~28H), 2.70-2.40 (br, 32H), 2.10-1.90 (br, 8H), 1.50-0.70 (br ~21H). IR (thin film): 3287, 2981, 2923, 1738, 1473, 1376, 1287, 1238, 1155, 1129, 1000, 759. PDI = 1.24

General synthesis of doubly dendronized polymers. An equimolar amount of dendritic azide to acetylenic residues in PHS-60K-[G2]-yne (PHS-60K-[G3]-yne) was determined using the THF-SEC calculated molecular weight. The materials were then combined in a scintillation vial equipped with a magnetic stir bar and dissolved in THF (1 mL per 100 mg of reaction mixture). To this solution, an equivalent volume of water to THF was added while stirring vigorously at 25 °C. Sodium ascorbate (10 mol%) and $CuSO_4 \bullet 5H_2O$ (5 mol %) were added to the reaction mixture from freshly prepared aqueous solutions (1.0 M). Upon the addition of copper, the reaction mixture turned brown for a few seconds and then

changed to a yellow-orange color, which persisted for several hours. Reactions that had reached completion, usually overnight, had become blue-green. THF was removed *in vacuo* leaving a polymeric residue on the side of the vial. The aqueous layer was then decanted and the residue washed several times with water. The residue was subjected to the click conditions several times until the yellow-orange colour did not appear. The dendronized polymers were precipitated into hexanes from THF. After precipitation, pseudo-G5 and pseudo-G6 required preparative GPC to remove the excess dendritic azide.

Pseudo-G5. PHS-60K-[G2]-yne (5.6 mg, 3.6 μmol), G3-azide (22 mg, 28 μmol). The precipitate was filtered and collected to yield 12 mg of a white solid (44%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20-6.70 (br, 40H), 6.60-6.00 (br, 21H), 4.70-4.20 (br, 30H). IR (thin film): 3064, 3034, 2922, 2870, 1738, 1675, 1595, 1497, 1449, 1374, 1325, 1297, 1153, 1049, 832, 755, 740, 696. DMF SEC MALLS: M_w= 3,490,000 Da PDI = 1.33

Pseudo-G6. PHS-60K-[G3]-yne (4.9 mg, 3.1 μmol), G3-azide (41 mg, 25 μmol). The residue was purified by preparatory GPC to yield 7.0 mg of a white solid (10%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10-6.70 (br, 40H), 6.50-5.90 (br, 21), 4.80-4.00 (br, 30H). IR (thin film): 3064, 3032, 2925, 2871, 1739, 1675, 1596, 1497, 1450, 1376, 1343, 1296, 1155, 1043, 832, 743, 696. DMF SEC MALLS: M_w= 7,020,000 Da PDI = 1.29