Synthesis of Cyclic Dendronized Polymers via Divergent "Graft-from" and Convergent Click "Graft-to" Routes: the Preparation of Modular Toroidal Macromolecules

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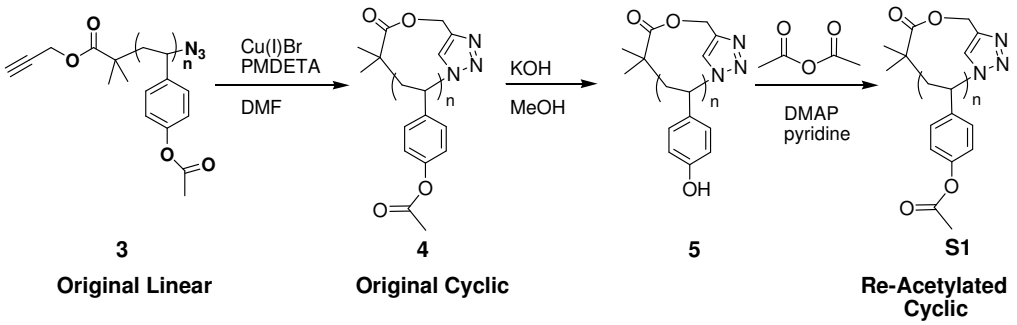
Supporting Information



Scheme S1: Control experiment designed to determine the architecture of the polymer chain after hydrolysis of the pendant acetoxy-group ensuring the structural integrity of the internal lactone.

Since *c*-PAS **4** was deacetylated via an acid/ base catalyzed hydrolysis of the phenolic esters to form the *c*-PHS precursor, **5**, it is also possible that a side reaction hydrolyzing the internal lactone in the polymer backbone could occur during this step. Thus, a control experiment was performed to definitively prove that the linking pivilate lactone ester in the backbone of the cyclic polymer was unhydrolyzed and that ring scission had not occurred to regenerate the linear hydrolyzed polymer precursor. Since the hydrolyzed PHS polymer produced contained different functionality along the polymer backbone resulting in a different conformation in solution and

thus a different retention time via GPC, this sample was not able to be directly comparable to the "linear" precursor to effectively determine the architecture. Structural integrity of the hydrolyzed polymer **5** was proven by subsequent re-acetylation of the PHS pendant alcohols on the backbone and overlaying the resultant GPC trace onto the original cyclic polymer (Figure S1). The resulting PAS polymer **S1** exhibited a monomodal GPC trace that overlaid exactly onto *c*-PAS **4**, but was distinctly more compact than the *l*-PAS **3**, proving the cyclic architecture was retained throughout hydrolysis of the pendant acetate functionalities. It is believed the observed selective hydrolysis of ester side chains results from their phenolic nature as well as the substantial steric hinderance around the pivilate linker of the internal lactone on the macrocyclic backbone.

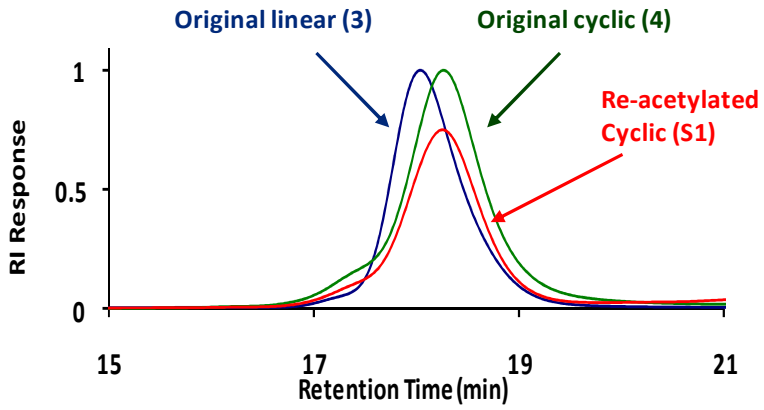


Figure S1: GPC traces of original linear (**3**) (blue) and cyclic (**4**) (green) poly(4-acetoxystyrene) products and subsequent re-acetylation (**S1**) of the hydrolyzed product to confirm structural integrity of the internal cyclic lactone.

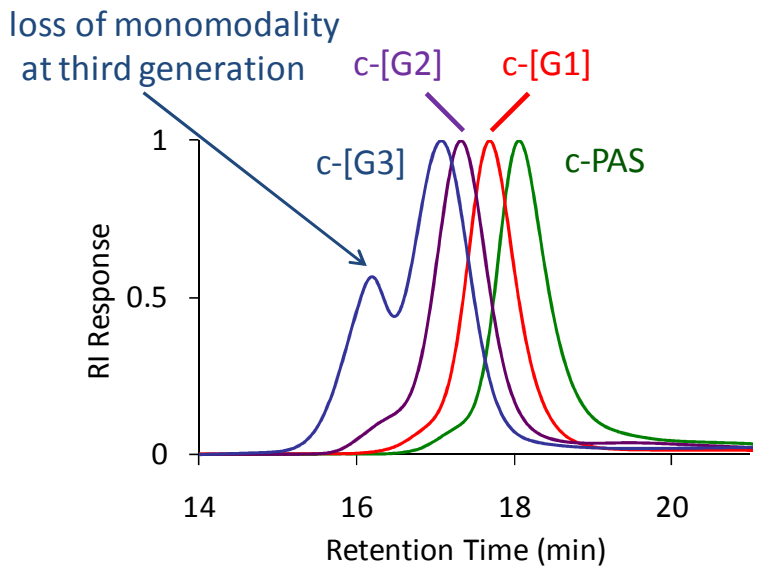


Figure S2: SEC traces of differing generations of polyester-based cyclic dendronized polymers with a DP = 38 showing evidence of undesired high MW impurity at 3rd generation of dendronization.

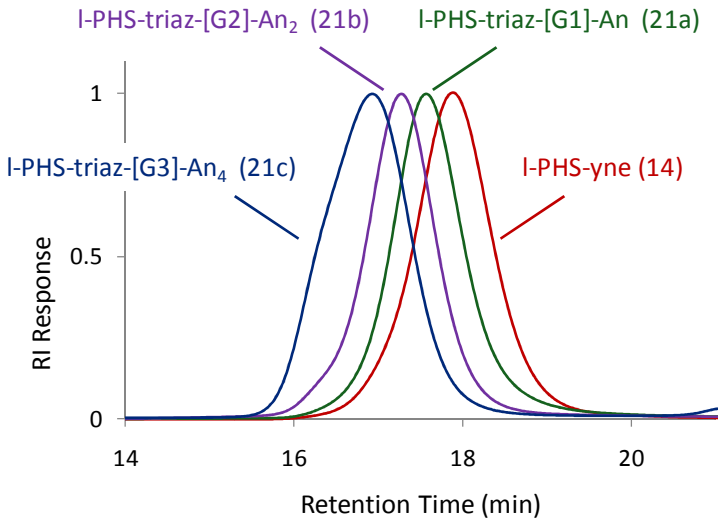


Figure S3: GPC traces of linear "click" dendronized polymers **21a-c**: *l*-PHS-alkyne **14** (red), *l*-PHS-triaz-[G1]-An **21a** (green), *l*-PHS-triaz-[G2]-$(An)_2$ **21b** (purple), and *l*-PHS-triaz-[G3]-$(An)_4$ **21c** (orange).

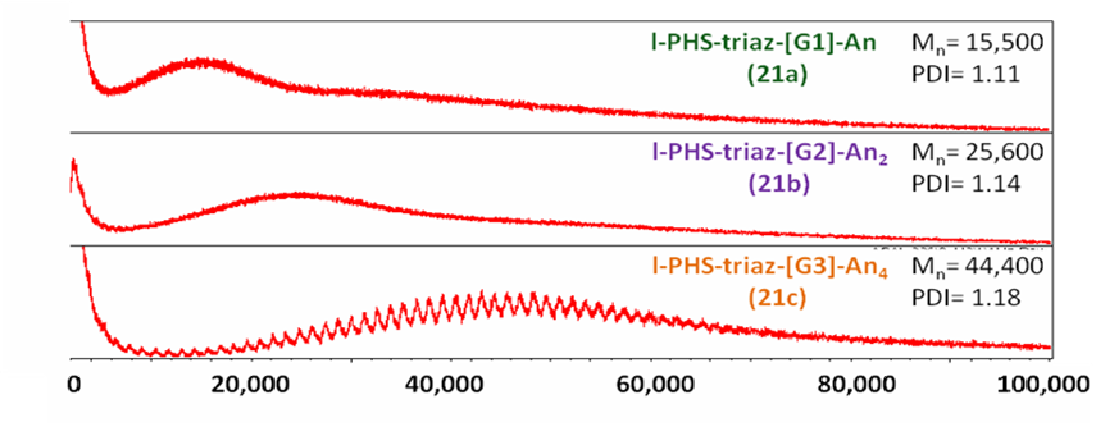


Figure S4: MALDI-TOF MS of first [G1] **21a** (top), second [G2] **21b** (middle), and third **21c** [G3] (bottom) generation linear "graft to" dendronized polymers.

Experimental

Materials: All reagents were purchased from Aldrich or Alfa Aesar and were used without further purification unless noted otherwise. DOWEX acid exchange resin hydrogen form was washed with MeOH and dried under high vacuum before use. THF was distilled from CaH_2 and stored under dry N_2 gas before use. All other solvents were used directly from the bottle without additional purification. *l*-PAS-Br (**2**), *l*-PAS-N_3 (**3**), and *c*-PAS (**4**) were prepared exactly as described previously by our labs.[1] Benzylidene protected bis-MPA acid anhydride (**6**),[2] 3-azido-propanol (**16**),[3] and Acetonide protected bis-MPA acid anhydride (**17**)[4] were prepared exactly as previously reported.

Nomenclature: In order to simplify the identification of compounds, the following nomenclature was used: A prefix *l*- was assigned to linear polymers and *c*- was assigned to cyclic polymers, PAS was used as an abbreviation for Poly(4-AcetoxyStyrene) and PHS was used as an abbreviation for Poly(4-HydroxyStyrene), the divergently "graft from" grown dendronized

polymers are described as PHS-[GX]-$(Ph)_y$ with [GX] representing the generation of dendronization, Ph represents the aromatic end-groups of the benzylidene acetal protecting group, and "y" identifying the amount of end groups present on each dendronized repeat unit of the polymer. Also, the use of (OH) in the place of (Ph) represents the deprotected form of the acetal as shown previously with subscripted the amount of hydroxyls present on the periphery of each repeat unit. For the azido-functionalized dendrons, N_3- was used to describe the 3-azidopropoxy group at the focal point of the dendron with [GX] once again describing the generation of dendronization and $(An)_y$ representing the acetonide acetal protecting group and "y" once again identifying the amount of end-groups present on the periphery of the dendron. PHS-*yne* is used to describe the alkynyl functionalized repeat unit of PHS. For the "graft to" approach for synthesis of dendronized polymers, the same nomenclature scheme is used as the "graft from" constructed dendrons, but with the word *–triaz* embedded in the abbreviation as a means to indicate the formation of the triazole species post "click" coupling.

Characterization: Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. ^{1}H-NMR (400MHz) and ^{13}C (100MHz) spectra were recorded on Varian Mercury spectrometer at room temperature. Chemical shifts are reported in parts per million (ppm) relative to $CDCl_3$ (7.26 ppm for ^{1}H and 77.16 for ^{13}C) and CD_3OD (3.31 ppm for ^{1}H and 49.00 for ^{13}C) as internal standard for calibration. Mass spectral data were collected using a Bruker-Daltonics matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) Autoflex III mass spectrometer in linear mode with positive ion detection. Mass spectral data were also obtained with a Bruker MicroTOF electrospray ionization (ESI) mass spectrometer with an Agilent 1200 series binary pump. Typical sample preparation for MALDI-TOF MS data was

performed by making stock solutions in THF of matrix (20mg/mL), polymer analyte (2mg/mL), and counter-ion (2mg/mL) followed by mixing of the three components in a 20/5/2 ratio and depositing onto the MALDI plate and allowing evaporation of solvent. For poly(4-acetoxystyrene) derivatives, dithranol was used as the matrix with Ag^+ Trifluoroacetate as counterion and the dendronized polymer derivatives were analyzed with α-cyano-4-hydroxycinnamic acid matrix and Na^+ Trifluoroacetate counterion. All MALDI-TOF MS data were calibrated against SpheriCal dendritic calibrants from Polymer Factory (Stockholm, Sweden). M_n and PDI of the resultant spectra were calculated using PolyTools software. Size Exclusion Chromatography (SEC) data were acquired on a Waters model 1515 isocratic pump (Milford, MA) with THF as the mobile phase with a 1 mL/min flow rate with columns at a constant 30°C. This system was operated with a three-series column set from Polymer Laboratories, Inc. consisting of PLgel 5μm MIXED-D (300mm x 7.5mm), PLgel 5μm 500 Å (300mm x 7.5mm), and PLgel 5μm 50 Å (300mm x 7.5mm) columns. The system was also equipped with a Model 2487 differential refractometer detector. The resulting molecular weights were calculated based on linear poly(styrene) standards using Waters Breeze software. Infrared (IR) spectroscopy was implemented using a NEXUS 670 FT-IR ESP. Samples were made using ~1-3 mg of analyte and 10 mg of KBr which was ground into a fine powder by mortar and pestle and compacted into a pellet.

***c*-PAS (4):** *l*-PAS-N_3 (**3**) (0.134 g, 0.022 mmol) was weighed out into a 250mL 2-neck round bottomed flask under N_2 atmosphere before dissolving into 100mL of DMF. In a separate 250mL 2-neck round bottomed flask, PMDETA (0.211 g, 1.22 mmol) was weighed out and then dissolved into 120mL of DMF. Both flasks were passed through 3 successive freeze-pump-thaw

cycles in order to degas. While frozen, the flask containing PMDETA ligand was added Cu(I)Br (0.159 g, 1.11 mmol) before evacuating and back flushing with N_2 gas twice and allowing to thaw. Once both reaction solutions had reached room temperature, the linear polymer solution was placed into a syringe whereupon it was added to the Cu(I) catalyst solution at 110°C at a rate of 2 ml/hr. Once addition was completed, the solution was cooled to room temperature and exposed to oxygen atmosphere, diluted with CH_2Cl_2, and washed with aqueous NH_4Cl x 3 to remove copper salts. The organic phase was then dried over $MgSO_4$, concentrated *in vacuo*, and precipitated into an excess of hexanes to give a slightly brown solid (82% yield). ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.77-2.14 (br m, 3H), 2.16-2.42 (s, 3H), 6.20-7.25 (br m, 4H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 21.33, 40.07, 41.20-47.55 (br), 121.19, 128.47, 142.54, 148.75, 169.45. SEC: M_n = 5000, PDI = 1.29. MS (MALDI-TOF MS): M_n = 5400, PDI = 1.05.

***c*-PHS (5):** *c*-PAS (**4**) (0.271 g, 1.67 mmol/repeat unit) was weighed out directly into a 50mL round-bottomed flask and dissolved into 28mL of a 4/3 THF/MeOH solution before the addition of conc. H_2SO_4 (0.56 mL, 2% v/v) and allowing the reaction to proceed for 24 hours at room temperature. The reaction was then diluted with EtOAc and aqueous $NaHCO_3$ was added to neutralize. The organic fraction was then washed twice more with $NaHCO_3$ solutions before drying over $MgSO_4$ and concentration *in vacuo*. The crude polymer product was then precipitated into hexanes and collected via a glass fritted funnel to give the hydrolyzed product as a white solid (96% yield). ^{1}H-NMR (CD_3OD, δ, ppm): 1.07-2.37 (b, 3H), 6.17-7.00 (b, 4H). ^{13}C-NMR (CD_3OD, δ, ppm): 39-40.25, 42-46, 114.20-115.50, 128.10-129.60, 136.20-138.51, 154.10-155.18. MS (MALDI-TOF): M_n = 4700, PDI = 1.05.

General Procedure for Anhydride Esterification: To a solution of the cyclic poly(hydroxylated) polymer dissolved in pyridine solvent was added benzylidene protected acid anhydride **6** (1.5 eq./ -OH) and dimethylaminopyridine (0.3 eq/ -OH) (DMAP). The reaction was allowed to proceed at least 12h. at room temperature before adding a small amount of H_2O in order to quench any unreacted anhydride. After stirring with H_2O and for an additional 6hrs, the reaction mixture was then diluted with CH_2Cl_2 and washed with aqueous solutions of $NaHSO_4$, $NaHCO_3$, and NaCl before drying over $MgSO_4$ and concentrating *in vacuo*. The crude reaction mixture was precipitated into hexanes and then passed through a plug of silica gel with CH_2Cl_2 solvent to give the pure product as a white solid.

General Procedure for Deprotection of Benzylidene Protecting Group: To a solution of the benzylidene protected dendronized polymer dissolved in a 1/1 mixture of CH_2Cl_2/ MeOH was added 10 wt.% Pd/C (~0.020 g/ 0.100 g polymer) and H_2 gas (10-15psi) was provided via a pressurized soccer ball connected to the flask via a stop-flow adapter. The reaction flask was evacuated and then sealed via the stop-flow adapter before attachment to the H_2 pressurized soccer ball and re-opening of the adapter. The reaction was stirred vigorously at room temperature for 24h. while maintaining H_2 pressure. The crude reaction mixture was then filtered over Celite and the Celite rinsed with approximately 100 mL of a 1/1 mixture of CH_2Cl_2/ MeOH. The filtrate was then concentrated *in vacuo* and placed under high vacuum to remove any residual solvents to give the pure deprotected product. ^{1}H-NMR confirmed the complete removal of the benzylidene protecting group (7.20-7.60 ppm).

***c*-PHS-[G1]-Ph (7):** This polymer was prepared by esterification of c-PHS (**5**) with the benzylidene protected acid anhydride **6** (82% yield). ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.72-1.17 (b, 3H), 1.17-2.15 (b, 3H), 3.41-3.75 (b, 2H), 4.53-4.81 (b, 2H), 5.32-5.52 (b, 1H), 6.13-7.03 (b, 4H), 7.22-7.55 (b, 5H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 17.7, 40, 42-45, 42.7, 73.5, 101.9, 121.1, 126.4, 128.3, 128.5, 129.1, 138.1, 142-143.5, 148.8, 172.5. SEC: M_n = 10,100 Da, PDI = 1.13. SEC: M_n = 4400, PDI= 1.16. MALDI-TOF MS (*m/z*): M_n = 6800, PDI = 1.14.

***c*-PHS-[G1]-$(OH)_2$ (8):** This polymer was prepared by hydrogenolysis of c-PHS-[G1]-Ph (**7**) (86% yield). ^{1}H-NMR (CD_3OD, δ, ppm): 1.05-1.36 (b, 3H), 1.36-2.20 (b, 3H), 3.62-3.92 (b, 4H), 6.31-7.05 (b, 4H). ^{13}C-NMR (CD_3OD, δ, ppm): 17.6, 41.5, 45, 52, 66, 122.6, 129.7, 144.2, 150.5, 175.4.

***c*-PHS-[G2]-Ph_2 (9):** This polymer was prepared by esterification of c-PHS-[G1]-$(OH)_2$ (**8**) with the benzylidene protected acid anhydride (**6**) (94% yield). ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.62-0.96 (b, 6H), 0.96-2.00 (b, 6H), 3.35-3.75 (b, 4H), 4.26-4.72 (b, 8H), 5.27-5.44 (b, 2H), 5.91-6.92 (b, 4H), 7.09-7.46 (b, 10H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 17.9, 40, 42.7, 47, 65.4, 73.5, 101.7, 121.2, 126.3, 128.2, 128.9, 138, 148, 171.4, 173.3. SEC: M_n = 6500, PDI = 1.13. MALDI-TOF MS (*m/z*): M_n = 12800, PDI = 1.08.

***c*-PHS-[G2]-$(OH)_4$ (10):** This polymer was prepared by hydrogenolysis of c-PHS-[G2]-Ph_2 (**9**) (93% yield). ^{1}H-NMR (CD_3OD, δ, ppm): 0.8-1.24 (b, 6H), 1.24-2.25 (b, 6H), 3.46-3.91 (b, 8H), 4.24-4.64 (b, 4H), 6.26-7.31 (b, 4H). ^{13}C-NMR (CD_3OD, δ, ppm): 17.5, 18.5, 41-42, 47, 51.8, 65.9, 66.3, 122.3, 129.9, 143-146, 150, 173.4, 176.

***c*-PHS-[G3]-Ph$_4$ (11):** This polymer was prepared by esterification of c-PHS-[G2]-OH$_4$ (**10**) with benzylidene protected acid anhydride (**6**) in a 1/1 mixture of pyridine/DMF (52% yield). ^{1}H-NMR ($CDCl_3$, δ, ppm): 0.53-0.93 (b, 12H), 0.93-1.75 (b, 12H), 3.23-3.60 (b, 8H), 4.00-4.71 (b, 20H), 5.17-5.41 (b, 4H), 6.05-6.95 (b, 4H), 7.05-7.50 (b, 20H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 17.4, 17.8, 39-41, 42.5, 46.7, 46.9, 65.1, 73.4, 101.6, 121.1, 126.3, 128.2, 128.9, 138.1, 140-144, 148.4, 170.93, 172, 173.3. SEC: M_n = 9600, PDI = 1.13. MALDI-TOF MS (*m/z*): M_n = 28800, PDI = 1.06.

***c*-PHS-yne (12):** *c*-PHS (**5**) (0.210 g, 1.75 mmol/ repeat unit) was dissolved into 20mL of DMF. To this solution was added pentynoic acid (0.259 g, 2.62 mmol), *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (0.503 g, 2.62 mmol), and DMAP (0.021 g, 0.175 mmol) sequentially. The reaction was allowed to proceed for 48h. and then diluted with methylene chloride. The resulting organic solution was then washed twice each with aqueous solutions of $NaHSO_4$, $NaHCO_3$, and NaCl, drying over $MgSO_4$, filtering, and concentrating *in vacuo*. The crude polymer was then dissolved into a minimal amount of methylene chloride and precipitated into hexanes. The product was isolated by filtration to yield a light brown powder (80% yield). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.10-2.00 (br m, 3H), 2.00-2.15 (br s, 1H), 2.51-2.70 (br s, 2H), 2.70-2.89 (br s, 2H), 6.25-7.04 (br m, 4H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 14.5, 33.6, 40.0, 42.2-46.5, 69.6, 82.4, 121.2, 128.5, 142.4, 148.6, 170.2. SEC: M_n = 7660, PDI = 1.30. MALDI-TOF MS (*m/z*): M_n = 6800, PDI = 1.05.

***l*-PHS (13):** $LiAlH_4$ (0.351 g, 9.24 mmol) was weighed out directly into a 100 mL 2-neck round-bottomed flask equipped with N_2 inlet and magnetic stir bar. To this was added 5mL of freshly distilled THF and the solution placed into an ice-water bath at 0°C. *l*-PAS-Br (**2**) (0.300 g, 1.850 mmol/repeat unit) was then weighed out into a separate 25mL RBF under N_2 atmosphere and dissolved into 20mL of freshly distilled THF before adding dropwise to the $LiAlH_4$ slurry over 20min. The reaction was then allowed to warm to room temperature and proceed for 16 hours before cooling to 0°C and the adding sequentially 0.4mL of H_2O, 0.4mL of a 15% NaOH solution, and finally the addition of 1.2mL of H_2O. The reaction mixture was then re-acidified by the addition of dilute HCl and then filtered over Celite and the Celite cake washed with approximately 100mL of EtOAc. The filtrate was then placed into a separatory funnel and washed with aqueous $NaHCO_3$ twice, dried over $MgSO_4$, and concentrated *in vacuo.* The product was the precipitated from a minimal amount of EtOAc into an excess of hexanes to give a white solid (79% yield). ^{1}H-NMR (CD_3OD, δ, ppm): 1.07-2.24 (b, 3H), 6.14-6.90 (b, 4H). ^{13}C-NMR (CD_3OD, δ, ppm): 40.4-41.2, 43-46, 115.7, 129.8-131, 137-140, 155.8. MALDI-TOF MS (*m/z*): M_n = 5100, PDI = 1.03.

***l*-PHS-yne (14):** This compound was produced using an identical procedure as that for *c*-PHS-yne (**12**), except that *l*-PHS (**13**) was used as the starting material for the reaction (88% yield). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.13-1.19 (b, 3H), 2.01-2.13 (b, 1H), 2.51-2.67 (b, 2H), 2.68-2.86 (b, 2H), 6.22-7.04 (b, 4H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 14.5, 33.5, 39.7-40.6, 42.1-46.2, 69.6, 82.3, 121.3, 128.4, 141.9-143.7, 148.6, 170.1. SEC: M_n = 8090, PDI = 1.23. MALDI-TOF MS (*m/z*): M_n = 6700, PDI = 1.09.

General Procedure for Acetonide Anhydride Esterification N_3-[G1]-An (18a): To a solution of 3-azido-propan-1-ol (**16**)[3] (3.0 g, 29.6 mmol) dissolved in 60mL of a 1/1 pyridine/CH_2Cl_2 solvent was added acetonide protected bis-MPA acid anhydride (**17**) (13.723 g, 41.53 mmol) (1.4 eq./ -OH) and dimethylaminopyridine (0.544 g, 4.45 mmol). The reaction was allowed to proceed for 48h. at room temperature before adding 5mL of H_2O in order to quench any unreacted anhydride and allowing it to stir vigorously for an additional 5h. The reaction mixture was then diluted with CH_2Cl_2 and washed with aqueous solutions of $NaHSO_4$, $NaHCO_3$, and NaCl before being dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude reaction mixture was then purified by column chromatography over silica gel eluting with 100% hexanes and gradually increasing the polarity to a 85/15 hexanes/EtOAc mobile phase. The pure product was recovered as a clear liquid (94% yield). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.14 (s, 3H), 1.36 (s, 3H), 1.41 (s, 3H), 1.92 (p, 2H, J=6.8Hz), 3.40 (t, 2H, J=6.8Hz), 3.64 (d, 2H, J=12Hz), (d, 2H, J=12Hz), 4.23 (t, 2H, J=6.4Hz). ^{13}C-NMR ($CDCl_3$, δ, ppm): 18.57, 22.05, 25.40, 28.23, 42.04, 48.14, 61.76, 66.15, 98.16, 174.21. IR (KBr, ν, cm^{-1}): 1080, 1730, 2100, 2800-3000. ESI MS exact mass calculated for (*m/z*) $[C_{11}H_{19}O_4N_3Na]^+$: 280.127. Observed: 280.122. Analysis calculated for $C_{11}H_{19}O_4N_3$: C, 51.35; H, 7.44; O, 24.87; N, 16.33. Observed: C, 51.74; H, 7.55; N, 15.93.

General Procedure for Acetonide Deprotection using DOWEX-H Acid Exchange Resin N_3-[G1]-$(OH)_2$ (19a): To a solution of N_3-[G1]-An protected dendron (**18a**) (5.472 g, 21.26 mmol) dissolved in 165mL of MeOH was added 0.800 g of the dried DOWEX resin. The reaction mixture was then placed into a preheated oil bath set at 40°C and allowed to proceed uncovered. The reaction was monitored via ^{1}H and ^{13}C-NMR by the loss of the acetonide

protons at 1.4 ppm and the quaternary carbon at 98 ppm, respectively. When complete deprotection was verified, the reaction mixture was removed from the oil bath and filtered immediately to remove acid catalyst. The filtrate was then concentrated *in vacuo* to give the pure product as a clear oil (96% yield). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.50 (s, 3H), 1.94 (p, 2H, J=6.4Hz), 2.88 (br s, 2H), 3.42 (t, 2H, J=6.8Hz), 3.71 (d, 2H, J=11.6Hz), 3.90 (d, 2H, J=11.2Hz), 4.27 (t, 2H, J=6Hz). ^{13}C-NMR ($CDCl_3$, δ, ppm): 17.21, 28.12, 48.31, 49.33, 62.05, 68.14, 175.82. IR (KBr, ν, cm^{-1}): 1015, 1700, 2100, 2800-3000, 3050-3650. Analysis calculated for $C_8H_{15}O_4N_3$: C, 44.23; H, 6.96; O, 29.46; N, 19.34. Observed: C, 44.48; H, 7.05; N, 18.13.

N_3-[G2]-$(An)_2$ (18b): This dendron was prepared by dendronization of N_3-[G1]-$(OH)_2$ (**19a**) with acetonide protected bis-MPA acid anhydride (**17**) and was purified via column chromatography over silica gel with a 70/30 hexanes/EtOAc mobile phase to give a clear oil (94% yield). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.12 (s, 6H), 1.28 (s, 3H), 1.34 (s, 6H), 1.40 (s, 6H), 1.91 (p, 2H, J=6.4Hz), 3.38 (t, 2H, J=6.8Hz), 3.61 (d, 4H, J=12.4Hz), 4.14 (d, 4H, J=12Hz), 4.20 (t, 2H, J=6.4Hz), 4.32 (s, 4H). ^{13}C-NMR ($CDCl_3$, δ, ppm):17.81, 18.59, 21.92, 25.48, 28.13, 42.18, 46.92, 48.11, 62.31, 65.36, 66.06, 66.10, 98.21, 172.56, 173.66. IR (KBr, ν, cm^{-1}): 1075, 1110-1175, 1740, 2100, 2800-3000. ESI MS exact mass calculated for (*m/z*) $[C_{24}H_{39}O_{10}N_3Na]^+$: 552.25; Observed (ESI-MS): 552.30. Analysis calculated for $C_{24}H_{39}O_{10}N_3$: C, 54.43; H, 7.42; O, 30.21; N, 7.93. Observed: C, 54.42; H, 7.46; N, 7.78.

N_3-[G2]-$(OH)_4$ (19b): This dendron was prepared by deprotection of N_3-[G2]-$(An)_2$ (**18b**) (97% yield). ^{1}H-NMR, (CD_3OD, δ, ppm): 1.15 (s, 6H), 1.30 (s, 3H), 1.93 (p, 2H, J=6.4Hz), 3.43 (t, 2H,

J=6.4Hz), 3.59 (d, 4H, J=10.8Hz), 3.67 (dd, 4H, J=2.4Hz, 10.8Hz), 4.22 (t, 2H, J=6.4Hz), 4.27 (d, 2H, J=11.2Hz), 4.31 (d, 2H, J=11.2Hz). ^{13}C-NMR ($CDCl_3$, δ, ppm): 17.20, 18.20, 28.04, 46.48, 48.09, 49.87, 50.81, 62.52, 64.86, 67.32, 67.34, 173.01, 175.16. IR (KBr, ν, cm^{-1}): 1050, 1125, 1725, 1735, 2100, 2800-3000, 3010-3600. ESI MS exact mass calculated for (*m/z*) $[C_{18}H_{31}O_{10}N_3Na]^+$: 472.19; Observed: 472.23. Analysis calculated for $C_{18}H_{31}O_{10}N_3$: C, 48.10; H, 6.95; O, 35.60; N, 9.35. Observed: C, 48.13; H, 6.88; N, 9.10.

N_3-[G3]-$(An)_4$ (18c): This dendron was prepared by dendronization of N_3-[G2]-$(OH)_4$ (**19b**) with acetonide protected bis-MPA acid anhydride (**17**) and was purified via column chromatography over silica gel with a 60/40 hexanes/EtOAc mobile phase to give a clear oil (89% yield). ^{1}H-NMR (CD_3Cl_3, δ, ppm): 1.10 (s, 12H), 1.25 (s, 9H), 1.32 (s, 12H), 1.39 (s, 12H), 1.92 (p, 2H, J=6.4Hz), 3.38 (t, 2H, J=6.4Hz), 3.59 (d, 8H, J=12.8Hz), 4.12 (d, 8H, J=12Hz), 4.12 (t, 2H, J=6.4Hz), 4.22-4.30 (m, 12H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 17.61, 17.70, 18.49, 21.92, 25.36, 28.00, 42.06, 46.67, 46.87, 48.08, 62.59, 64.91, 65.94, 65.99, 98.11, 171.87, 172.00, 173.53. IR (KBr, ν, cm^{-1}): 1745, 2100, 2800-3000. MALDI-TOF MS exact mass calculated for (*m/z*) $[C_{50}H_{79}O_{22}N_3Na]^+$: 1096.50. Observed: 1096.47. Analysis calculated for $C_{50}H_{79}O_{22}N_3$: C, 55.91; H, 7.41; N, 3.91; O, 32.77. Observed: C, 56.19; H, 7.49; N, 3.87.

N_3-[G3]-$(OH)_8$ (19c): This dendron was prepared by deprotection of N_3-[G3]-$(An)_4$ (**18c**) (93% yield). ^{1}H-NMR (CD_3OD, δ, ppm): 1.15 (s, 12H), 1.29 (s, 6H), 1.31 (s, 3H), 1.96 (p, 2H, J=6.4Hz), 3.45 (t, 2H, J=6.4Hz), 3.59 (d, 8H, J=10.8Hz), 3.68 (dd, 8H, J=2.4Hz, 12Hz), 4.22-4.35 (m, 14H). ^{13}C-NMR (CD_3OD, δ, ppm): 17.28, 18.05, 18.24, 29.05, 47.90, 47.95, 51.79, 63.86, 65.78, 66.14, 67.25, 173.73, 173.86, 175.87. MALDI-TOF MS exact mass calculated for

(*m/z*) $[C_{38}H_{63}O_{22}N_3Na]^+$: 936.38, Observed: 936.40. Analysis calculated for $C_{38}H_{63}O_{22}N_3$: C, 49.94; H, 6.95; N, 4.60; O, 38.51. Observed: C, 49.69; H, 6.98; N, 4.44.

N_3-[G4]-(An)$_8$ (18d): This dendron was prepared by dendronization of N_3-[G3]-$(OH)_8$ (**19c**) with acetonide protected bis-MPA acid anhydride (**17**) and was purified via column chromatography over silica gel with a 50/50 hexanes/EtOAc mobile phase to give a clear oil (80% yield). ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.13 (s, 24H), 1.27 (m, 21H), 1.34 (s, 24H), 1.40 (s, 24H), 1.94 (p, 2H, J=6.4Hz), 3.41 (t, 2H, J=6.4Hz), 3.61 (d, 16H, J=13.2Hz), 4.14 (d, 16H, J=12Hz), 4.19-4.35 (m, 30H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 17.55, 17.62, 17.80, 18.60, 22.06, 25.43, 28.07, 42.14, 46.80, 46.92, 48.16, 62.74, 64.91, 65.62, 66.03, 66.09, 66.48, 98.21, 17.54, 171.93, 171.96, 173.61. MALDI-TOF MS exact mass calculated for (*m/z*) $[C_{102}H_{159}O_{46}N_3Na]^+$: 2185.009; Observed (MALDI-TOF MS): 2185.005. Analysis calculated for $C_{102}H_{159}O_{46}N_3$: C, 56.63; H, 7.41; N, 1.94; O, 34.02. Observed: C, 56.74; H, 7.43; N, 1.92.

***c*-PHS-triaz-[G1]-An (20a):** *c*-PHS-yne (**12**) (0.043 g, 0.215 mmol/ repeat unit), N_3-[G1]-An dendonized azide (**18a**) (0.061 g, 0.236 mmol), and PMDETA (0.037 g, 0.215 mmol) were weighed out directly into a 10mL single-neck round bottomed flask equipped with magnetic stir bar and N_2 inlet adapter. The mixture was dissolved into 5mL of DMF and passed through 3 successive freeze-pump-thaw cycles for degassing. While frozen, Cu(I)Br (0.031 g, 0.215 mmol) was quickly added before evacuating the flask and back flushing with N_2 gas three additional times. The reaction was allowed to thaw and proceed at room temperature for 18h. before exposing to air, diluting with CH_2Cl_2, and washing with an aqueous solution of NH_4Cl to remove copper salts. The organic phase was then dried with $MgSO_4$, filtered, concentrated *in vacuo*, and

passed through a short silica plug with CH_2Cl_2 as the mobile phase. The solution was concentrated *in vacuo* to give a brown solid. ^{1}H-NMR showed a coupling efficiency of 84%. ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.10 (br s, 3H), 1.35 (br s, 3H), 1.41 (br s, 3H), 2.26 (br s, 2H), 2.80-3.03 (br s, 2H), 3.03-3.22 (br s, 2H), 3.54-3.72 (br, 2H), 4.04-4.24 (br, 4H), 4.42 (br s, 2H), 6.06-6.98 (br m, 4H), 7.52 (br s, 1H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 18.6, 21.1, 26.5, 29.6, 34, 39-41, 42.3, 46.9, 61.5, 66.4, 98.4, 115.5, 121.3, 122.3, 128.6, 142-144, 146.2, 148.8, 171.4, 174.4. SEC: M_n = 8720, PDI = 1.25. MALDI-TOF MS (*m/z*): M_n = 14700, PDI = 1.14.

***l*-PHS-triaz-[G1]-An (21a):** Synthetic procedure was identical as for the synthesis of *c*-PHS-triaz-[G1]-An (**20a**) above except that *l*-PHS-yne (**14**) was used as the starting polymer precursor. ^{1}H-NMR showed a coupling efficiency of 86%. ^{1}H- and ^{13}C-NMR are identical as above. SEC: M_n = 10320, PDI = 1.22. MALDI-TOF MS (*m/z*): M_n = 15500, PDI = 1.11.

***c*-PHS-triaz-[G2]-$(An)_2$ (20b):** *c*-PHS-yne (**12**) (0.031 g, 0.155 mmol/ repeat unit), N_3-[G2]-$(An)_2$ dendonized azide (**18b**) (0.090 g, 0.171 mmol), and PMDETA (0.029 g, 0.171 mmol) were weighed out directly into a 10mL single-neck round bottomed flask equipped with magnetic stir bar and N_2 inlet adapter. The mixture was dissolved into 5mL of DMF and passed through 3 successive freeze-pump-thaw cycles for degassing. While frozen, Cu(I)Br (0.022 g, 0.155 mmol) and Cu(0) (0.010 g, 0.155 mmol) were quickly added before evacuating the flask and back flushing with N_2 gas three times. The reaction was allowed to thaw and proceed at room temperature for 24h before exposing to air, dilution with CH_2Cl_2, and washing with an aqueous solution of NH_4Cl to remove copper salts. The organic portion was then dried with $MgSO_4$, filtered, concentrated *in vacuo*, and passed through a short silica plug with CH_2Cl_2 as

the mobile phase. The solution was concentrated in vacuo to give a brown solid. ^{1}H-NMR showed a coupling efficiency of 76%. ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.09 (s, 6H), 1.29 (s, 3H), 1.31 (s, 6H), 1.39 (s, 6H), 2.24 (br s, 2H), 2.95 (br s, 2H), 3.03-3.22 (br s, 2H), 3.56-3.66 (br d, 4H, J=12Hz), 4.08-4.19 (br d, 6H, J=11.2Hz), 44.28-4.48 (br m, 6H), 6.14-6.94 (br m, 4H), 7.41-7.64 (br s, 1H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 17.8, 18.5, 21, 21.4, 25.9, 29.4, 33.8, 39.2-40.4, 42.2, 46.9, 62, 65.2, 66, 98.2, 115.4, 121.1, 121.8, 128.4, 142-144, 146.1, 148.6, 171.2, 172.5, 173.7. SEC: M_n = 12800, PDI = 1.20. MALDI-TOF MS (*m/z*): M_n = 21600, PDI = 1.16.

***l*-PHS-triaz-[G2]-(An)$_2$ (21b):** Synthetic procedure was identical as for the synthesis of *c*-PHS-triaz-[G2]-(An)$_2$ (**20b**) above except that *l*-PHS-yne (**14**) was used as the starting polymer precursor. ^{1}H-NMR showed a coupling efficiency of 93%. ^{1}H- and ^{13}C-NMR are identical as above. SEC: M_n = 14200, PDI = 1.19. MALDI-TOF MS (*m/z*): $M_{n,lin}$ = 25600, PDI = 1.14.

***c*-PHS-triaz-[G3]-(An)$_4$ (20c):** *c*-PHS-yne (**12**) (0.015 g, 0.075 mmol/ repeat unit), N_3-[G3]-(An)$_4$ dendonized azide (0.088 g, 0.082 mmol), and PMDETA (0.014 g, 0.082 mmol) were weighed out directly into a 10mL single-neck round bottomed flask equipped with magnetic stir bar and N_2 inlet adapter. The mixture was dissolved into 4mL of DMF and passed through 3 successive freeze-pump-thaw cycles for degassing. While frozen, Cu(I)Br (0.011 g, 0.075 mmol) and Cu(0) (0.005 g, 0.075 mmol) were quickly added before evacuating the flask and back flushing with N_2 gas three times. The reaction was allowed to thaw and proceed at room temperature for 24h. before exposing to air, dilution with CH_2Cl_2, and washing with an aqueous solution of NH_4Cl to remove copper salts. The organic portion was then dried with $MgSO_4$, filtered, concentrated *in vacuo*, and passed through a short silica plug with CH_2Cl_2 as the mobile

phase. The solution was concentrated *in vacuo* again to give a brown solid. ^{1}H-NMR showed a coupling efficiency 88%. ^{1}H-NMR ($CDCl_3$, δ, ppm): 1.10 (s, 12H), 1.26 (s, 9H), 1.31 (s, 12H), 1.37 (s, 12H), 2.28 (s, 2H), 2.94 (s, 2H), 2.81-3.20 (br, 4H), 3.54-3.64 (br d, 8H, J=11.6Hz), 4.07-4.18 (br d, 10H, J=11.6Hz), 4.20-4.35 (br m, 12H), 4.42 (br s, 2H), 6.11-6.95 (br, 4H), 7.45-7.68 (br s, 1H). ^{13}C-NMR ($CDCl_3$, δ, ppm): 17.7, 17.8, 18.5, 21.1, 21.8, 25.6, 29.4, 33.9, 42.1, 46.7, 46.9, 62.5, 64.9, 65.8, 66, 98.2, 121.1, 121.7, 128.5, 146.2, 148.7, 170.8-171.6, 172, 172.1, 173.6. SEC: M_n = 19300, PDI = 1.22. MALDI-TOF MS (*m/z*): M_n = 48400, PDI = 1.14.

***l*-PHS-triaz-[G3]-(An)$_4$ (21c):** Synthetic procedure was identical as for the synthesis of *c*-PHS-triaz-[G3]-(An)$_4$ (**20c**) above except that *l*-PHS-yne (**14**) was used as the starting polymer precursor. ^{1}H-NMR showed a coupling efficiency of 90%. ^{1}H- and ^{13}C-NMR are identical as above. SEC: M_n = 19700, PDI = 1.18. MALDI-TOF MS (*m/z*): M_n = 44400, PDI = 1.18.

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