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Thermally Reversible Dendronized Linear AB Step-Polymers via "Click" Chemistry

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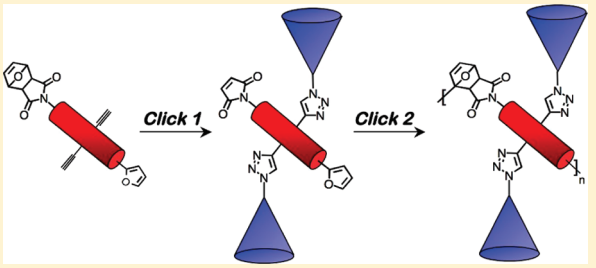
Supporting Information

ABSTRACT: The synthesis and characterization of thermally labile dendronized linear AB step-polymers is described. First through third generation dendritic AB monomers **14a**−**c** containing both a furan and furan-protected maleimide functionality were prepared by the Cu(I)-catalyzed azide−alkyne cycloaddition reaction followed by polymerization via the thermally reversible furan-maleimide Diels−Alder reaction. The assembly, disassembly, and reassembly behavior of linear dendronized step-polymers **16a**−**c** was studied by GPC.



INTRODUCTION

Dendronized polymers, also referred to as denpols,[1,2] are linear polymers containing pendant dendrimers[3] as side groups in the polymer repeat unit. The molecular architecture of these macromolecules can be tailored with respect to dendron size and generation, providing a high level of control over nanoscopic size, rigidity, and functionality.[2] This tunability has led to potential applications of denpols including molecular containers,[4] catalyst carriers,[5] molecular scaffolds,[6] and electrolytes for Li-ion batteries.[7] The development of the denpol field is highly dependent on the ability to synthesize these molecules in a highly efficient and selective manner. As a result, "click" reactions[8] including the Cu(I)-catalyzed azide−alkyne Huisgen 1,3-dipolar[9] and the Diels−Alder (DA)[10] cycloadditions have been extensively used in the preparation of dendrimers, denpols, and other polymers.[11]

Stimuli responsive denpols[12,13] exhibit significant and abrupt physical changes (shape, volume, phase state, material properties, etc.) in response to small variations in the local environment. The thermal reversibility of the furan−maleimide DA reaction[14] make it an ideal candidate for the production of temperature responsive systems. The ability to undergo both the forward and retro furan-maleimide DA reaction at relatively mild temperatures (room temperature to 60 °C for forward DA and 90−120 °C for retro DA)[14] has resulted in a wide variety of architectures including linear polymers,[13,15−17] alternating copolymers,[18] and cross-linked networks,[19] providing useful applications for nanoscale lithography,[20] hydrogels,[21] nonlinear optics,[22] interpenetrating networks (IPNs),[23] optically active films,[24] and self-healing[25] materials. Previously, our group has demonstrated the preparation of thermally degradable foams[26] encapsulants,[27] and surfactants,[28,29] as well as covalently reversible dendritic macromolecular assemblies[30] and AA−BB dendronized step-polymers[13] utilizing furan−maleimide DA adducts. Complementary to this last work, herein we report the preparation and characterization of AB[17] dendronized step-polymers derivatized by the Cu(I)-catalyzed azide−alkyne cycloaddition (CuAAC) reaction and polymerized by the furan−maleimide DA reaction. These materials represent the first examples of thermally reversible dendronized polymers originating from a single monomeric species.

RESULTS AND DISCUSSION

Synthesis of Dendritic AB Monomers. In designing thermally reversible dendritic AB monomers, we envisioned a tetrakis-substituted benzene core containing symmetric opposing terminal alkyne quadrants, along with asymmetric opposing terminal furan and maleimide quadrants. Such a molecule would be capable of both peripheral modification of the alkynes via the CuAAC reaction and thermally reversible linear polymerization via the furan-maleimide DA reaction. The synthesis of the dendritic AB monomers started from commercially available 2,5-dibromohydroquinone (**1**) (Scheme 1). Reaction with methyl 4-chlorobutanoate (**2**) under basic conditions at elevated temperature gave bis-substituted methyl ester **3** in 40% yield. Sonagashira coupling[31] of **3** with TIPS-acetylene realized compound **4** in a yield of 90% (method A). Alternatively, we prepared compound **4** by a different route. 2,5-Dibromohydroquinone (**1**) was treated with *p*-methoxybenzyl (PMB) chloride under basic conditions to give bis-PMB-protected compound **5** in 93% yield. Sonagashira coupling with TIPS−acetylene, followed by deprotection of the PMB groups with 10% TFA in CH_2Cl_2 gave the

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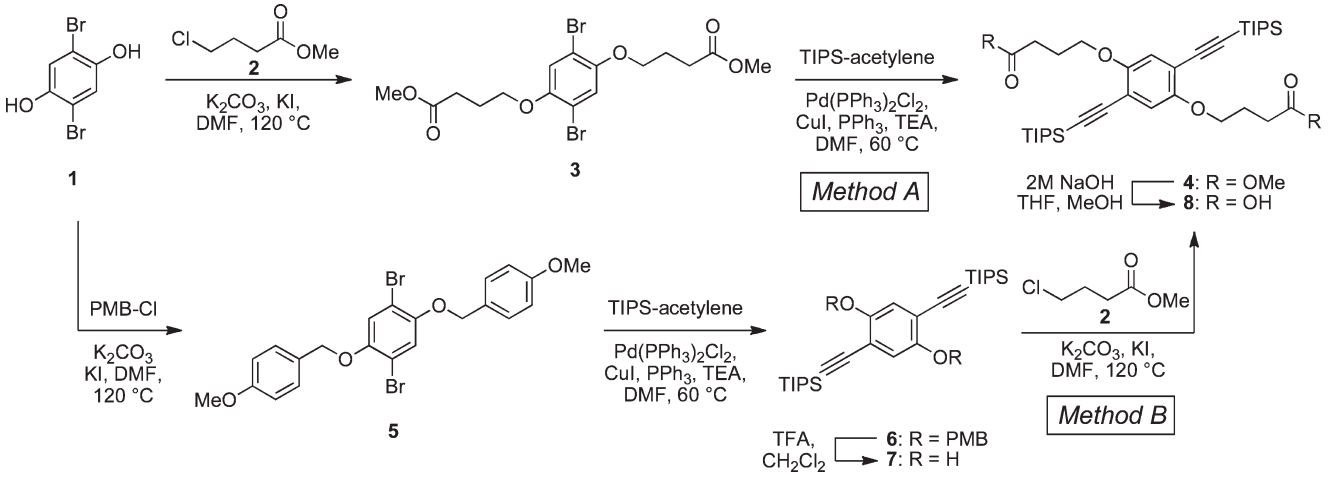
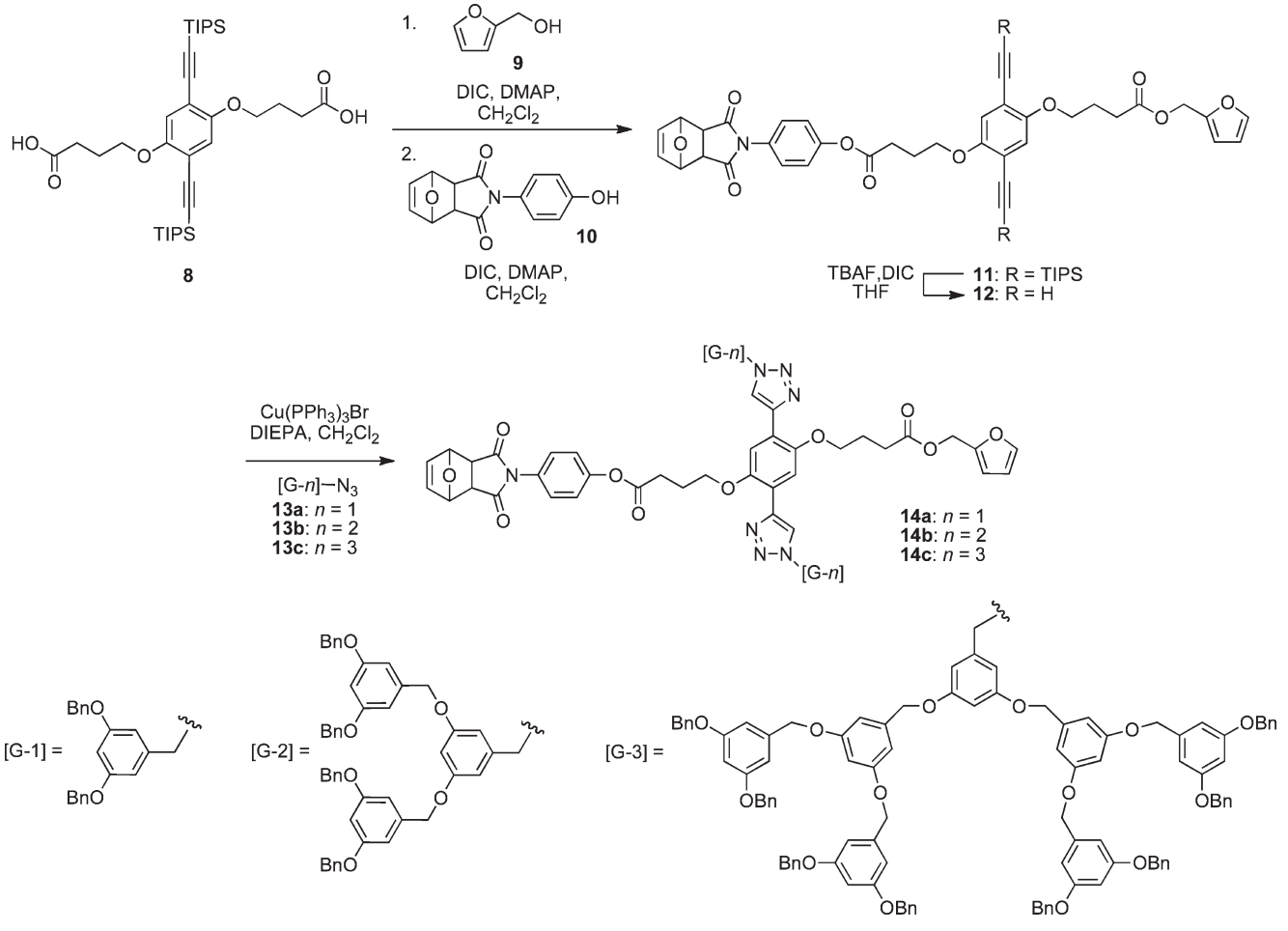
Scheme 1. Two Methods for the Synthesis of Diacid 8



Scheme 2. Synthesis of Dendritic AB Monomers 14a−c



TIPS-protected acetylenic hydroquinone **7** in 60% yield from **5**. Upon reaction with methyl 4-chlorobutanoate (**2**) under similar conditions as described above, **7** was converted to compound **4** in a yield of 86% (method B). With bis-methyl ester **4** in hand, hydrolysis of the methyl ester with 2 M NaOH gave bis-carboxylic acid **8** in near quantitative yield.

The TIPS-protected AB furan−maleimide monomer **11** was then prepared in moderate yield via statistical *N,N′*-diisopropylcarbodiimide

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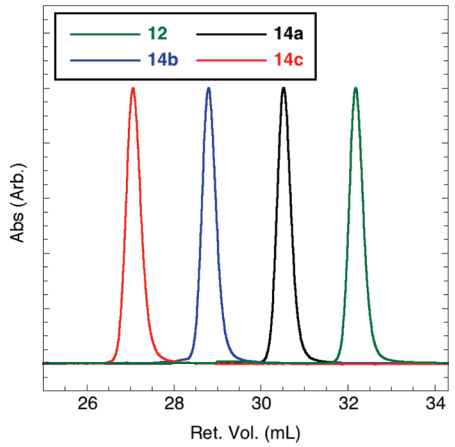


Figure 1. GPC chromatograms of dialkynyl AB monomer **12** (green, far right) and dendritic AB monomers **14a** (black, second from right), **14b** (blue, second from left), and **14c** (red, far left).

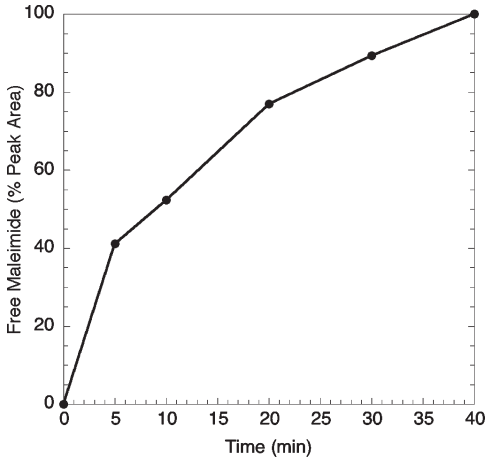
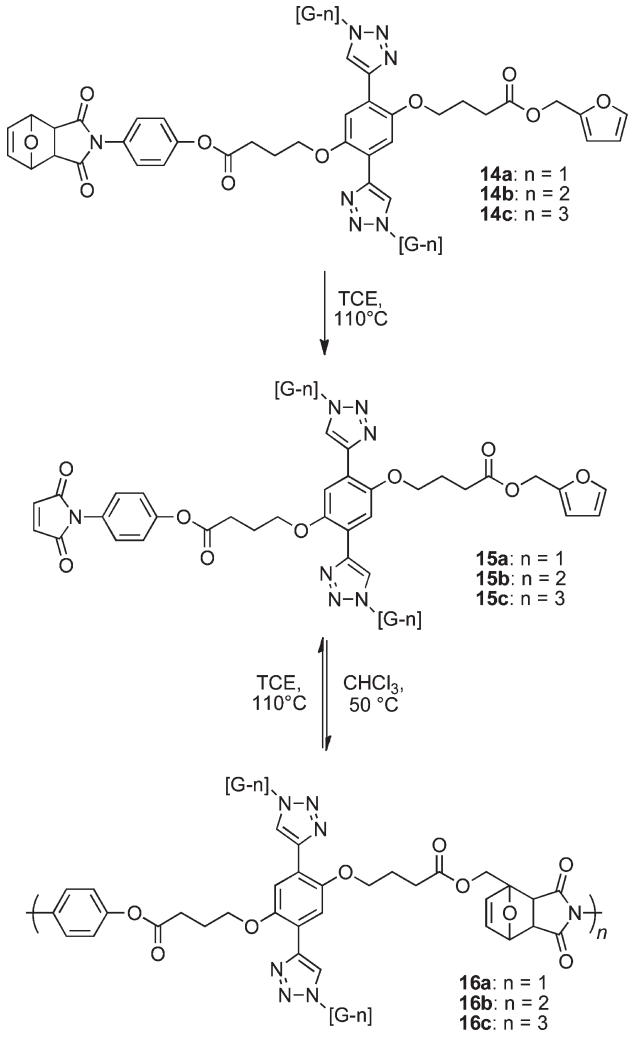


Figure 2. Maleimide deprotection of [G-1] dendritic monomer **14a** followed by the appearance of free maleimide protons in the ^{1}H NMR (TCE-d_2, 1.0 mM) at 110 °C.

Scheme 3. Maleimide Deprotection of 14a−c and Subsequent Polymerization



(DIC) coupling of **8** with furfuryl alcohol (**9**), followed by DIC coupling of the crude monofurfuryl product with furan-protected *N*-(4-hydroxyphenyl)maleimide **10** (Scheme 2). Deprotection of the TIPS groups with TBAF proved to be a challenge, as the maleimide ester was found to be extremely sensitive to the cleavage conditions. Ultimately, it was discovered that stoichiometric addition of DIC to the reaction mixture resulted in selective cleavage of the TIPS groups with TBAF, giving the bis-acetylenic AB monomer **12** in 56% yield. Finally, dendritic AB monomers **14a−14c** were prepared in good yield via the CuAAC reaction of **12** with dendritic azides **13a−c**.[13] All new compounds were fully characterized by ^{1}H and ^{13}C NMR, along with ESI or MALDI MS and combustion analysis. Elution volumes of dialkynyl AB monomer **12** and dendritic AB monomers **14a−c**, determined using GPC (Figure 1), confirmed the increasing hydrodynamic size with increasing dendrimer generation.

^{1}H NMR Analysis of Maleimide Deprotection. Before the dendritic AB monomers could be polymerized, suitable conditions for the maleimide deprotection had to be determined in order to fully "activate" the monomers (Scheme 3). The retro-DA of furan-maleimide adducts is known to occur at temperatures >60 °C,[14] with temperatures between 90 and 120 °C typically employed.[13,29,30,32] We chose to perform the test reaction on [G-1] AB monomer **14a** at 110 °C in 1,1′,2,2′-tetrachloroethane-d_2 (TCE-d_2) so that reaction progress could be monitored by ^{1}H NMR. Hence, a solution of [G-1] AB monomer **14a** in TCE- d_2 (1.0 mM) was prepared for evaluation by NMR spectroscopy. An NMR tube containing the AB monomer solution was sealed, heated in an oil bath maintained at 110 °C, and monitored by ^{1}H NMR at regular time intervals.

The progress of the retro-DA reaction was followed by both the formation of the free maleimide singlet of **15a** at 6.92 ppm and the disappearance of the bridgehead protons of **14a** at 3.07 ppm (Figures S1−S6, Supporting Information).[16] The free maleimide proton signal was plotted as a percentage of the sum of the free maleimide and bridgehead proton signals (Figure 2). Initially, no free maleimide signal was observed, but after only 5 min the reaction was shown to be 41% complete. Within 20 min, 77% completion was observed, and after 40 min the bridgehead proton signals were no longer visible, indicating reaction completion.

GPC Analysis of Polymer Assembly, Disassembly, and Reassembly. After determining suitable retro-DA conditions,

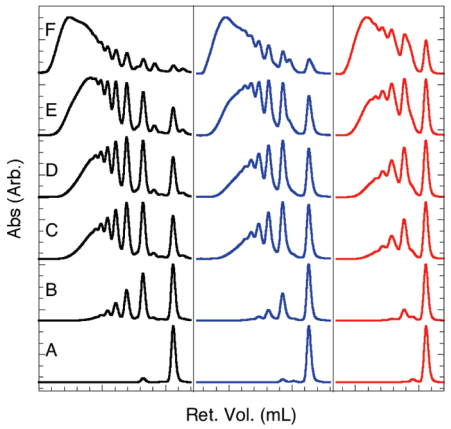


Figure 3. Assembly of dendritic AB DA step-polymers **16a** (black, left), **16b** (blue, middle), and **16c** (red, right) at 50 °C in $CHCl_3$. Key: (A) $t = 0$; (B) $t = 8$ h; (C) $t = 24$ h; (D) $t = 48$ h; (E) $t = 120$ h; (F) $t = 288$ h.

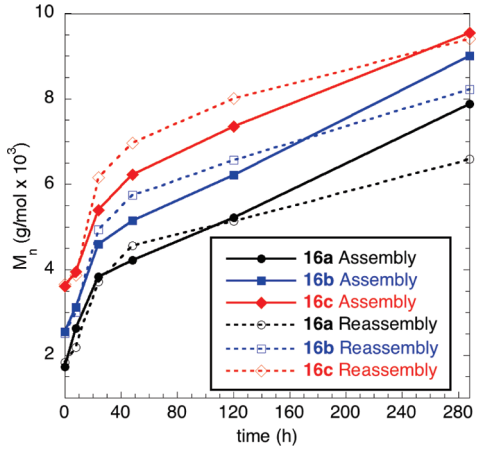


Figure 4. Polystyrene-equivalent M_n values for the assembly and reassembly of dendritic AB DA polymers **16a**−**c** at 50 °C in $CHCl_3$ for indicated time.

step-polymerizations were performed with dendritic AB monomers **14a**−**c** (Scheme 2). Accordingly, **14a**−**c** were dissolved in TCE (1.0 mM) and heated in an oil bath set to 110 °C for 40 min, at which point TLC suggested complete maleimide deprotection. The solvent was then removed under reduced pressure, followed by redissolving in a minimal quantity of $CHCl_3$ and heating to 50 °C. The reaction vessels were left open and a fresh minimal quantity of $CHCl_3$ was added every 24 h. Aliquots were removed at regular time intervals and reaction progress was monitored using GPC.

During the formation of dendritic step-polymers **16a**−**c**, a gradual increase of higher molecular weight compounds was observed as evidenced by the appearance of peaks at lower GPC retention volumes (Figure 3). At $t = 0$ for each reaction, some degree of progress could be seen, suggesting that the polymerization actually began during the maleimide deprotection of **14a**−**c**, most likely while removing the TCE under reduced pressure. Similarly to our previously published results on AA − BB sysems,[13] the formation of [G-1] DA polymer **16a** appeared to progress at a faster rate than [G-2] DA polymer **16b**, which was faster still than [G-3] DA polymer **16c**. After 288 h, monomers **15a**−**c** were still detected in the reaction mixtures,

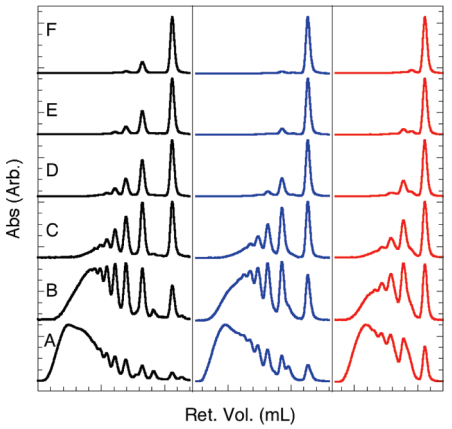


Figure 5. Disassembly of dendritic AB DA polymers **16a** (black, left), **16b** (blue, middle), and **16c** (red, right) at 110 °C in TCE (1.0 mM based on **14a**−**c** from assembly experiments). Key: (A) $t = 0$; (B) $t = 5$ min; (C) $t = 10$ min; (D) $t = 20$ min; (E) $t = 30$ min; (F) $t = 40$ min.

with the formation of **16c** showing the most monomer, followed by **16b** and **16a**, respectively. The presence of monomer is consistent with the inefficiency of the DA reaction rather than retro-DA events, as isolated DA adducts are stable at 50 °C. A peak in the GPC at greater elution volume than monomer appeared in the assembly of **16c**. It is likely that this peak is cyclized monomer,[33] although definitive evidence is absent. This peak disappeared upon disassembly and reappeared upon reassembly (vide infra).

Polystyrene equivalent number-average molecular weight (M_n) values were also determined during the formation of dendritic polymers **16a**−**c** (Figure 4). After 288 h, M_n values of 7900, 9000, and 9500 g/mol were determined for DA polymers **16a**−**c**, respectively. These M_n values correlated to degrees of polymerization of 6.2, 4.2, and 2.5 for **16a**−**c**, respectively. An additional time point taken after 456 h showed no measurable enhancement in polymer growth with respect to polystyrene equivalent M_n values, suggesting that near-maximal M_n values had been achieved within 288 h under these conditions.

The crude polymers **16a**−**c** from the assembly experiments were then subjected to disassembly conditions (Figure 5). The polymer solutions were concentrated under reduced pressure, followed by dissolving in TCE (1.0 mM based on **14a**−**c** from assembly experiments) and heating in an oil bath set to 110 °C. Aliquots were removed at regular times intervals and monitored by GPC. Within 5 min, significant disassembly appeared to take place, and after 20 min the polymers had been reduced to monomers **15a**−**c** and lower molecular weight oligomers. After 40 min, all disassembly GPC traces appeared nearly identical to the initial trace from the respective assembly experiments. These results suggest relatively clean disassembly with minimal decomposition. In addition, all disassemblies occurred at approximately the same rate, likely as a result of the first order nature of the retro-DA reaction.

The crude disassembled DA polymers were also assembled a second time to demonstrate the repeatable nature of the thermally reversible system. This reassembly was carried out under identical conditions as the initial assembly. Not surprisingly, the reassembly reactions proceeded similarly to the initial assemblies, with [G-1] DA polymer **16a** growing at the fastest rate, followed

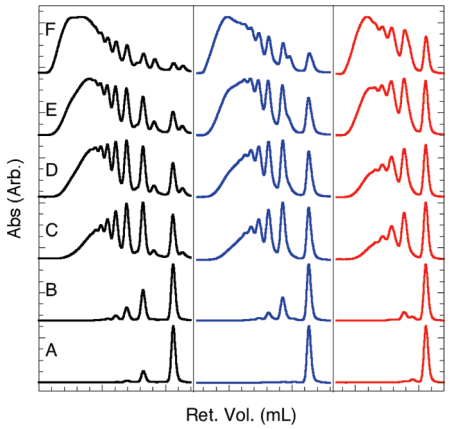


Figure 6. Reassembly of dendritic AB DA step-polymers **16a** (black, left), **16b** (blue, middle), and **16c** (red, right) at 50 °C in $CHCl_3$. Key: (A) t = 0; (B) t = 8 h; (C) t = 24 h; (D) t = 48 h; (E) t = 120 h; (F) t = 288 h.

by [G-2] DA polymer **16b** and finally [G-3] DA polymer **16c** (Figure 6). Polystyrene equivalent M_n values were also determined during the reassembly of dendritic polymers **16a**−**c** (Figure 4). After 288 h, M_n values of 6600, 8200, and 9400 g/mol were determined for DA polymers **16a**−**c**, respectively. These M_n values correlated to degrees of polymerization of 5.2, 3.9, and 2.5 for DA polymers **16a**−**c**, respectively. During both assembly and reassembly, qualitative assessment of GPC traces did not indicate any selectivity of product formation.

■ SUMMARY

The synthesis, characterization, and study of polymerization behavior of a thermally reversible AB step-polymer utilizing sequential CuAAC and furan−maleimide DA "click" reactions has been described. Compound **12**, a tetrakis-substituted benzene core containing symmetric opposing terminal alkyne quadrants along with asymmetric opposing terminal furan and maleimide quadrants, was prepared and derivatized via the CuAAC reaction with first through third generation benzyl aryl ether azide dendrons **13a**−**c**[13] to give dendritic AB monomers **14a**−**c**. After optimization of the retro-DA conditions using [G-1] dendritic AB monomer **14a**, monomers **14a**−**c** were polymerized and assembly, disassembly, and reassembly behavior monitored by GPC. Initial results suggest that polymer formation and degradation occur in a repeatable manner with minimal degradation under mild reaction conditions. Methods to increase polymer size and reaction rates are currently under investigation.

■ EXPERIMENTAL SECTION

Materials and Methods. NMR data was collected on Bruker 500 and 600 MHz Spectrometers running Topspin (Bruker). Chemical shifts were referenced to the deuterated solvent resonance for ^{1}H (7.26 ppm for $CDCl_3$ and 6.00 ppm for TCE-d_2) and ^{13}C NMR (77.0 ppm for $CDCl_3$). GPC studies were performed using a Waters Alliance 2695 separations module with Jordi DVB columns (500, 1,000, 10 000 Å columns in series) with THF as the mobile phase at a flow rate of 1 mL/min. Data was collected with a Waters 2996 photodiode array detector at 330 nm using Empower software (Waters). All chemicals were purchased from commercial suppliers and used as received unless otherwise noted.

Dimethyl 4,4′-((2,5-Dibromo-1,4-phenylene)bisoxy)dibutanoate (3). A round-bottom flask was charged with 2,5-dibromohydroquinone (**1**) (5.9 g, 22 mmol), methyl 4-chlorobutanoate (**2**) (7.5 g, 55 mmol), K_2CO_3 (15 g, 110 mmol), and DMF (50 mL). The reaction mixture was then placed in an oil bath and heated to 100 °C for 1 h. After allowing it to cool to room temperature, the reaction mixture was poured into brine (500 mL). The suspension was filtered and the resulting solid purified by flash chromatography (silica gel; CH_2Cl_2) to give **3** as a white solid (4.2 g, 40% yield): mp 82−84 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (s, 2H), 4.00 (t, J = 6 Hz, 4H), 3.70 (s, 6H), 2.58 (t, J = 8 Hz, 4H), 2.13 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.5, 149.9, 118.5, 111.2, 68.9, 51.7, 30.4, 24.5. MS (ESI) m/z 489.2 $[M + Na]^+$; $C_{16}H_{20}Br_2NaO_6$ requires 489.1. Anal. Calcd for $C_{16}H_{20}Br_2O_6$: C, 41.05; H, 4.31. Found: C, 40.69; H, 4.62.

Dimethyl 4,4′-((2,5-Bis((triisopropylsilyl)ethynyl)-1,4-phenylene)bisoxy)dibutanoate (4). (Method A) A round-bottom flask was charged with **7** (2.50 g, 5.33 mmol), K_2CO_3 (3.70 g, 26.8 mmol), KI (445 mg, 2.68 mmol), and DMF (50 mL). Methyl 4-chlorobutanoate (**2**) (2.18 g, 16.0 mmol) was then added, followed by heating in an oil bath set to 100 °C with stirring for 3 h. The reaction mixture was allowed to cool to room temperature, followed by pouring into brine (450 mL). The resulting brown precipitate was collected by vacuum filtration and purified by recrystallization from MeOH to give **4** as off-white needles (3.03 g, 86% yield). (Method B) A heavy-walled Schlenk flask was charged with **3** (6.33 g, 13.5 mmol), TIPS−acetylene (7.40 g, 40.6 mmol), $Pd(PPh_3)_2Cl_2$ (950 mg, 1.35 mmol), CuI (260 mg, 1.35 mmol), triphenylphosphine (350 mg, 1.35 mmol), triethylamine (35 mL), and DMF (70 mL). The flask was sealed, followed by four cycles of freeze−pump−thaw. The sealed vessel was then placed in an oil bath heated to 60 °C and stirred for 72 h. The reaction mixture was then allowed to cool to room temperature and was poured on H_2O (500 mL). The suspension was extracted with EtOAc (500 mL), followed by collecting the EtOAc layer and washing with 1 M HCl (2 × 500 mL) and brine (250 mL). The EtOAc layer was collected, dried over $MgSO_4$, filtered, the filtrate collected and the solvent removed under reduced pressure. The residue was purified by flash chromatography (silica gel; hexanes:CH_2Cl_2 (1:1)) followed by recrystallization from MeOH to give **4** as white needles (8.12 g, 90% yield): mp 102−104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.84 (s, 2H), 4.03 (t, J = 6 Hz, 4H), 3.68 (s, 6H), 2.55 (t, J = 8 Hz, 4H), 2.09 (m, 4H), 1.13 (s, 42H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.7, 153.8, 117.1, 114.1, 102.7, 96.7, 67.9, 51.5, 30.4, 24.6, 18.7, 11.3. MS (ESI) m/z 671.1 $[M + H]^+$; $C_{38}H_{63}O_6Si_2$ requires 671.4. Anal. Calcd for $C_{38}H_{62}O_6Si_2$: C, 68.01; H, 9.31. Found: C, 67.67; H, 9.62.

4,4′-(((2,5-Dibromo-1,4-phenylene)bis(oxy))bis(methylene))bis(methoxybenzene) (5). A round-bottom flask was charged with 2,5-dibromohydroquinone (**1**) (5.00 g, 18.7 mmol), 4-methoxybenzyl chloride (7.31 g, 46.7 mmol), K_2CO_3 (12.9 g, 93.3 mmol), and DMF (50 mL). The reaction mixture was purged with N_2, followed by heating to 120 °C with stirring for 1 h. After allowing the reaction mixture to cool to room temperature, the suspension was poured onto H_2O (450 mL). The solution was then placed in the freezer (−35 °C) for 30 min, at which point an off-white precipitate was observed. The precipitate was collected by vacuum filtration and washed several times with H_2O. The solid was air-dried, then recrystallized from 1,2-dichloroethane to give **5** as a white solid (8.85 g, 93% yield): mp 194−196 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 9 Hz, 4H), 7.17 (s, 2H), 6.92 (d, J = 9 Hz, 4H), 5.00 (s, 4H), 3.82 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.5, 150.0, 129.0, 128.2, 119.4, 114.0, 111.6, 71.9, 55.3. MS (EI) m/z 264.9 $[M + H - 2PMB]^+$; $C_6H_3Br_2O_2$ requires 264.9. Anal. Calcd for $C_{22}H_{20}Br_2O_4$: C, 51.99; H, 3.97. Found: C, 51.60; H, 3.71.

2,5-Bis(triisopropylsilyl)ethynyl)hydroquinone (7). A heavy-walled Schlenk flask was charged with **5** (4.00 g, 7.86 mmol),

TIPS−acetylene (4.30 g, 23.6 mmol), $Pd(PPh_3)_2Cl_2$ (551 mg, 0.786 mmol), CuI (150 mg, 0.786 mmol), triphenylphosphine (206 mg, 0.786 mmol), triethylamine (25 mL), and DMF (50 mL). The flask was sealed and then degassed by four freeze−pump−thaw cycles. The sealed vessel was then placed in an oil bath maintained at 60 °C and stirred for 40 h. The reaction mixture was then allowed to cool to room temperature and was poured on H_2O (300 mL). The suspension was extracted with CH_2Cl_2 (3 × 300 mL), followed by addition of Celite and $MgSO_4$. The suspension was filtered and the filtrate collected. After removal of solvent under reduced pressure, the solid residue was redissolved in CH_2Cl_2 (200 mL), and washed with 1 M HCl (2 × 200 mL) and brine (1 × 100 mL). The organic layer was collected, dried over $MgSO_4$, filtered, and the filtrate concentrated under reduced pressure to give a yellow solid. The solid was suspended in CH_2Cl_2 (50 mL), followed by dropwise addition of TFA (5 mL). The mixture was stirred for 30 min, followed by dilution with toluene (50 mL) and removal of solvent under reduced pressure. The resulting yellow solid was suspended in hexanes and filtered. The filtrate was concentrated under reduced pressure, followed by purification by flash chromatography (silica gel; hexanes:CH_2Cl_2 (9:1)) to give **7** as a white solid (2.20 g, 60% yield): mp 124−125 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 2H), 5.47 (s, 2H), 1.13 (s, 42H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.4, 116.4, 111.7, 100.7, 100.4, 18.7, 11.2. MS (ESI) m/z 469.5 $[M - H]^-$; $C_{28}H_{45}O_2Si_2$ requires 469.3. Anal. Calcd for $C_{28}H_{46}O_2Si_2$: C, 71.43; H, 9.85. Found: C, 71.07; H, 9.47.

4,4′-((2,5-Bis((triisopropylsilyl)ethynyl)-1,4-phenylene)-bisoxy)dibutanoic Acid (8). Compound **4** (7.00 g, 10.5 mmol) was suspended in a mixture of THF (100 mL), MeOH (50 mL), and 2 M NaOH (50 mL). The mixture was stirred vigorously at room temperature for 16 h. The reaction mixture was then acidified with 6 M HCl until the solution reached pH ∼ 2. The suspension was reduced to ∼75 mL under reduced pressure, at which point a thick precipitate formed. The solid was collected by vacuum filtration and was washed several times with H_2O. The resulting solid was dried under high-vac to give **8** as a white solid (6.45 g, 96% yield): mp 180 °C (dec.). ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.94 (s, 2H), 3.97 (t, J = 5 Hz, 4H), 2.39 (t, J = 6 Hz, 4H), 1.88 (m, 4H), 1.08 (s, 42H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 174.3, 153.6, 116.4, 113.3, 102.9, 96.3, 67.9, 30.2, 24.5, 18.6, 10.9. MS (ESI) m/z 641.2 $[M - H]^-$; $C_{36}H_{57}O_6Si_2$ requires 641.4. Anal. Calcd for $C_{36}H_{58}O_6Si_2$: C, 67.24; H, 9.09. Found: C, 67.60; H, 8.85.

2,(4-Hydroxyphenyl)-3a,4,7,7a-tetrahydro-1*H*-4,7-epoxy-isoindole-1,3(2*H*)-dione (10). A heavy-walled Schlenk flask was charged with *N*-(4-hydroxyphenyl)maleimide[34] (20.0 g, 106 mmol), furan (72.0 g, 1.06 mol), and acetone (50 mL). The flask was sealed and placed in an oil bath heated to 75 °C. After 30 min, the reaction mixture formed a thick precipitate. The mixture was allowed to cool to room temperature and was then placed in the freezer (−35 °C) for 30 min. The solid was collected by vacuum filtration and was washed with cold acetone to give the exo-isomer of **10** as a gray solid (15.5 g, 57% yield): mp 168 °C (dec.), lit.[35] 172 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ 7.04 (d, J = 9 Hz, 2H), 6.89 (d, J = 9 Hz, 2H), 6.62 (s, 2H), 5.22 (s, 2H), 3.03 (s, 2H), 2.81 (s, 1H). ^{13}C NMR (150 MHz, acetone-d_6): δ 176.5, 158.1, 137.5, 135.5, 128.9, 116.1, 82.1, 48.3. MS (ESI) m/z 256.1 $[M - H]^-$; $C_{14}H_{10}NO_4$ requires 256.1. Anal. Calcd for $C_{14}H_{11}NO_4$: C, 65.37; H, 4.31; N, 5.44. Found: C, 65.39; H, 4.51; N, 5.60.

4-(1,3-Dioxo-3a,4,7,7a-tetrahydro-1*H*-4,7-epoxyisoindol-2(3*H*)-yl)phenyl 4-(4-(4-(furan-2-ylmethoxy)-4-oxobutoxy)-2,5-bis((triisopropylsilyl)ethynyl)phenoxy) Butanoate (11). A flask was charged with **8** (5.00 g, 7.82 mmol) and DMAP (480 mg, 3.91 mmol), followed by addition of CH_2Cl_2 (200 mL). DIC (490 mg, 3.91 mmol) was then added dropwise, followed by dropwise addition of furfuryl alcohol (**9**) (380 mg, 3.91 mmol). The reaction mixture was allowed to stir at room temperature for 2 h, at which point the solution was extracted with 1 M HCl (3 × 200 mL) followed by 1 M NaOH (3 × 200 mL). The 1 M NaOH layers were combined, acidified to pH∼2 with concentrated HCl, and reduced to ∼100 mL under reduced pressure. The solid was collected by vacuum filtration and washed several times with H_2O to give recovered **8** as a white solid (1.95 g, 39% yield). The procedure was repeated twice more with the recovered **8**. The CH_2Cl_2 layers from the three extractions were dried over $MgSO_4$, filtered, and the filtrate concentrated under reduced pressure to give crude monofurfuryl coupled product as an off-white low-melting solid (3.60 g). The solid was dissolved in CH_2Cl_2 (100 mL), followed by addition of DMAP (919 mg, 7.5 mmol). DIC was then added dropwise, followed by portionwise addition of **10** (1.92 g, 7.50 mmol). The reaction mixture was stirred at room temperature for 4 h. The mixture was then washed with 1 M HCl (2 × 100 mL) and brine (100 mL). The organic layer was collected, dried over $MgSO_4$, filtered, and the filtrate concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel; hexanes:EtOAc (3:2)) to give **11** as an off-white glass that turned into a brittle foam upon drying on high-vac (3.09 g, 41% yield): mp 94−95 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (m, 1H), 7.32−7.30 (m, 2H), 7.19−7.18 (m, 2H), 6.87 (s, 1H), 6.85 (s, 1H), 6.57 (s, 2H), 6.40−6.35 (m, 2H), 5.39 (s, 2H), 5.07 (s, 2H), 4.07 (t, J = 6 Hz, 2H), 3.99 (t, J = 6 Hz, 2H), 3.01 (s, 2H), 2.84 (t, J = 8 Hz, 2H), 2.59 (t, J = 8 Hz, 2H), 2.20 (m, 2H), 2.10 (m, 2H), 1.15−1.11 (m, 42H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.2, 172.9, 171.3, 153.8, 153.7, 150.5, 149.5, 143.2, 136.7, 129.0, 127.5, 122.2, 117.1, 114.1, 114.0, 110.6, 110.5, 102.7, 96.79, 96.72, 81.4, 67.8, 67.7, 58.0, 47.5, 30.8, 30.5, 24.7, 24.6, 18.73, 18.67, 11.35, 11.32. MS (ESI) m/z 984.1 $[M + Na]^+$; $C_{55}H_{71}NNaO_{10}Si_2$ requires 984.5. Anal. Calcd for $C_{55}H_{71}NO_{10}Si_2$: C, 68.65; H, 7.44; N, 1.46. Found: C, 68.61; H, 7.80; N, 1.67.

4,(1,3-Dioxo-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-epoxyisoindol-2(3*H*)-yl)phenyl 4-(2,5-Diethynyl-4-(4-(furan-2-ylmethoxy)-4-oxobutoxy)phenoxy)butanoate (12). A flask was charged with **11** (2.00 g, 2.08 mmol), DIC (794 mg, 6.23 mmol), and THF (50 mL). The mixture was cooled in an ice bath, followed by dropwise addition of TBAF (1 M solution, in THF, 4.36 mL, 4.36 mmol) with stirring. After stirring for 15 min, 1 M HCl (100 mL) was added, and the resulting mixture extracted with CH_2Cl_2 (3 × 150 mL). The organics were combined, dried over $MgSO_4$, filtered, and the filtrate concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel; CH_2Cl_2:acetone (97:3)) to give **12** as a colorless glass that turned into a brittle foam upon drying under high-vacuum (755 mg, 56% yield): mp 44−47 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42−7.41 (m, 1H), 7.32−7.30 (m, 2H), 7.21−7.19 (m, 2H), 6.97 (s, 1H), 6.95 (s, 1H), 6.57 (s, 2H), 6.40−6.35 (m, 2H), 5.39 (s, 2H), 5.08 (s, 2H), 4.10 (t, J = 6 Hz, 2H), 4.02 (t, J = 6 Hz, 2H), 3.34 (s, 1H), 3.32 (s, 1H), 3.01 (s, 2H), 2.84 (t, J = 8 Hz, 2H), 2.60 (t, J = 8 Hz, 2H), 2.27−2.18 (m, 2H), 2.17−2.08 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.1, 172.7, 171.1, 153.8, 153.7, 150.4, 149.4, 143.2, 136.7, 129.0, 127.5, 122.2, 118.0, 117.9, 113.5, 110.6, 110.5, 82.9, 81.4, 79.4, 68.29, 68.24, 58.1, 47.5, 30.7, 30.5, 24.50, 24.4. MS (ESI) m/z 649.9 $[M + H]^+$; $C_{37}H_{32}NO_{10}$ requires 650.2. Anal. Calcd for $C_{37}H_{31}NO_{10}$: C, 68.41; H, 4.81; N, 2.16. Found: C, 68.80; H, 5.19; N, 2.25.

4-(1,3-dioxo-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-epoxyisoindol-2(3*H*)-yl)phenyl 4-(2,5-Bis(1-(3,5-bis(benzyloxy)benzyl)-1*H*-1,2,3-triazol-4-yl)-4-(4-(furan-2-ylmethoxy)-4-oxobutoxy)-phenoxy)butanoate (14a). A small vial was charged with **12** (200 mg, 0.308 mmol), [G-1]-azide **13a**[13] (320 mg, 0.924 mmol), Cu-$(PPh_3)_3Br$ (56 mg, 0.0616 mmol), DIPEA (200 mg, 1.54 mmol) and CH_2Cl_2 (1.0 mL). The vial was left at room temperature for 16 h, at which point the reaction mixture was directly purified by flash chromatography (silica gel; CH_2Cl_2:acetone (92:8)) to give **14a** an off-white glass. The product became a brittle white foam after drying overnight under high-vacuum (340 mg, 82% yield): mp 65 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 8.05 (s, 1H), 8.01 (s, 1H), 7.96 (s, 1H), 7.39−7.28 (m, 21H), 7.24−7.22 (m, 2H), 7.08−6.92 (m, 2H),

6.57−6.51 (m, 8H), 6.33−6.29 (m, 2H), 5.50 (s, 2H), 5.38 (s, 2H), 5.36 (s, 2H), 4.99 (s, 6H), 4.97 (s, 4H), 4.27 (t, J = 6 Hz, 2H), 4.19 (t, J = 6 Hz, 2H), 2.99 (s, 2H), 2.68 (t, J = 7 Hz, 2H), 2.45 (t, J = 8 Hz, 2H), 2.30−2.20 (m, 2H), 2.16−2.15 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.1, 173.7, 172.6, 171.3, 160.35, 160.30, 150.3, 149.27, 149.23, 149.13, 143.22, 143.19, 143.0, 137.3, 137.1, 136.56, 136.49, 136.46, 134.6, 129.1, 128.55, 128.53, 128.03, 127.99, 127.59, 127.52, 127.4, 123.8, 123.6, 122.3, 122.2, 119.43, 119.38, 111.0, 110.8, 110.7, 110.5, 107.01, 106.97, 102.0, 101.9, 81.4, 79.8, 77.3, 77.0, 76.8, 70.10, 70.07, 68.2, 67.8, 58.1, 54.0, 53.9, 31.4, 30.8, 24.8, 24.7. MS (ESI) m/z 1361.9 $[M + Na]^+$; $C_{79}H_{69}N_7NaO_{14}$ requires 1362.6. Anal. Calcd for $C_{79}H_{69}N_7O_{14}$: C, 70.79; H, 5.19; N, 7.31. Found: C, 70.79; H, 5.42; N, 7.04.

4-(1,3-dioxo-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-epoxyisoindol-2(3*H*)-yl)phenyl 4-(2,5-Bis(1-(3,5-bis((3,5-bis(benzyloxy)-benzyl)oxy)benzyl)-1*H*-1,2,3-triazol-4-yl)-4-(4-(furan-2-yl-methoxy)-4-oxobutoxy)phenoxy)butanoate (14b). A small vial was charged with **12** (100 mg, 0.154 mmol), [G-2]-azide **13b**[13] (356 mg, 0.462 mmol), $Cu(PPh_3)_3Br$ (29 mg, 0.0308 mmol), DIPEA (99 mg, 0.770 mmol) and CH_2Cl_2 (1.0 mL). The vial was left at room temperature for 64 h, at which point the reaction mixture was directly purified by flash chromatography (silica gel; CH_2Cl_2:acetone (95:5) followed by EtOAc:hexanes (3:2)) to give **14b** an off-white glass. The product became a brittle white foam after drying overnight on high-vac (182 mg, 54% yield): mp 63 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (s, 1H), 8.05 (s, 1H), 7.97 (s, 1H), 7.93 (s, 1H), 7.41−7.32 (m, 41H), 7.32−7.30 (m, 2H), 7.05−6.95 (m, 2H), 6.65−6.63 (m, 8H), 6.56−6.52 (m, 12H), 6.31−6.26 (m, 2H), 5.50 (s, 2H), 5.34 (s, 2H), 5.33 (s, 2H), 5.03−4.96 (m, 16H), 4.97 (s, 2H), 4.94 (s, 4H), 4.91 (s, 4H), 4.18 (t, J = 6 Hz, 2H), 4.10 (t, J = 6 Hz, 2H), 2.93 (s, 2H), 2.64 (t, J = 7 Hz, 2H), 2.41 (t, J = 8 Hz, 2H), 2.27−2.16 (m, 2H), 2.15−2.05 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.1, 173.7, 172.6, 171.5, 160.33, 160.26, 160.18, 160.16, 150.3, 149.33, 149.25, 149.16, 143.3, 143.1, 139.03, 138.97, 137.4, 137.3, 136.79, 136.77, 136.69, 134.65, 129.1, 128.6, 128.02, 128.01, 127.64, 127.58, 127.4, 123.8, 123.6, 122.3, 119.5, 119.4, 111.0, 110.8, 110.7, 110.6, 107.2, 107.1, 106.4, 102.0, 101.9, 101.6, 81.4, 79.8, 70.12, 70.05, 70.01, 68.2, 67.8, 58.1, 54.1, 53.9, 47.5, 45.9, 31.5, 30.9, 29.8, 24.9, 24.7. MS (MALDI) m/z 2121.4 $[M + H - furan]^+$, $C_{131}H_{114}N_7O_{21}$ requires 2120.8. Anal. Calcd for $C_{135}H_{117}N_7O_{22}$: C, 74.06; H, 5.39; N, 4.48. Found: C, 73.68; H, 5.74; N, 4.33.

4-(1,3-Dioxo-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-epoxyisoindol-2(3*H*)-yl)phenyl 4-(2,5-Bis(1-(3,5-bis((3,5-bis((3,5-bis(benzyloxy)benzyl)oxy)benzyl)oxy)benzyl)-1*H*-1,2,3-triazol-4-yl)-4-(4-(furan-2-ylmethoxy)-4-oxobutoxy)phenoxy)butanoate (14c). A small vial was charged with **12** (50 mg, 0.0770 mmol), [G-3]-azide **13c**[13] (374 mg, 0.231 mmol), $Cu(PPh_3)_3Br$ (14 mg, 0.0154 mmol), DIPEA (50 mg, 0.385 mmol) and CH_2Cl_2 (1.0 mL). The vial was left at room temperature for 64 h, at which point the reaction mixture was directly purified by flash chromatography (silica gel; CH_2Cl_2:acetone 97:3) to give **14c** an off-white glass. The product became a brittle white foam after drying overnight on high-vac (230 mg, 77% yield): mp 63 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (s, 1H), 8.04 (s, 1H), 7.96 (s, 1H), 7.92 (s, 1H), 7.56−7.22 (m, 81H), 7.18−7.14 (m, 2H), 6.97−6.92 (m, 2H), 6.70−6.42 (m, 44H), 6.28−6.22 (m, 2H), 5.44 (s, 2H), 5.32−5.26 (m, 4H), 5.02−4.85 (m, 58H), 4.12 (t, J = 6 Hz, 2H), 4.06 (t, J = 6 Hz, 2H), 2.87 (s, 2H), 2.60 (t, J = 7 Hz, 2H), 2.38 (t, J = 8 Hz, 2H), 2.23−2.13 (m, 2H), 2.12−2.02 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.0, 172.5, 171.4, 160.09, 160.00, 159.98, 143.2, 139.18, 139.16, 138.9, 136.7, 136.6, 128.5, 128.0, 127.5, 122.2, 110.7, 110.5, 107.10, 107.05, 106.4, 101.5, 81.3, 70.0, 69.9, 68.1, 67.7, 58.0, 54.0, 53.8, 47.4, 31.4, 30.8, 24.8, 24.6. MS (ESI) m/z 3817.9 $[M + H]^+$; $C_{243}H_{210}N_7O_{37}$ requires 3817.5. Anal. Calcd for $C_{247}H_{213}N_7O_{38}$: C, 76.32; H, 5.52; N, 2.52. Found: C, 76.11; H, 5.90; N, 2.52.

NMR Studies. To monitor the retro-DA reaction during maleimide deprotection of [G-1] monomer **14a** to form **15a** (Scheme 2), [G-1] monomer **14a** (1.3 mg, 1.0 μmol) was dissolved in TCE-d_2 (1.0 mL) in an NMR tube. The tube was sealed, followed by heating in an oil bath set to 110 °C. A time intervals the reaction was removed from the heating bath and ^{1}H NMR spectra were collected at ambient temperature. Reaction progress was determined by plotting the free maleimide proton (6.92 ppm) signal as a percentage of the sum of the free maleimide and bridgehead proton (3.07 ppm) signals.[16]

GPC Studies. To monitor the assembly of dendritic DA polymers **16a**−**c**, [G-n] AB monomers **14a**−**c** were dissolved in TCE (1.0 mM) and heated to 110 °C in open flasks. After 1 h, the reaction mixtures were concentrated under reduced pressure, the residues dissolved in a minimal quantities of $CHCl_3$ and heated to 50 °C in open vials. Every 24 h, a fresh minimal quantity of $CHCl_3$ was added to each vial. At time intervals aliquots were taken, dissolved in THF, and analyzed by GPC. To monitor disassembly, each crude polymer mixture of **16a**−**c** was heated to 110 °C in TCE (1.0 mM based on **14a**−**c** from assembly experiments). Aliquots were taken out at time intervals, diluted with THF, and analyzed by GPC. To monitor reassembly, the disassembled polymer samples were concentrated to dryness and dissolved in a minimal quantity of $CHCl_3$. Every 24 h, a fresh minimal quantity of $CHCl_3$ was added to each vial. At time intervals aliquots were taken, dissolved in THF, and analyzed by GPC.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{1}H NMR spectra of the disassembly of [G-1] AB monomer **14a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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