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ARTICLE

# Thermally Reversible Dendronized Step-Polymers Based on Sequential Huisgen 1,3-Dipolar Cycloaddition and Diels–Alder "Click" Reactions

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ABSTRACT: Thermally labile dendronized AA–BB step polymers are described. First through third generation dendritic bisfuran monomers **6a**–**6c** were prepared in part by the Cu(I)-catalyzed azide–alkyne Huisgen 1,3-dipolar cycloaddition reaction and in turn polymerized by the reversible furan–maleimide Diels–Alder reaction. The Diels–Alder reaction conditions were optimized through end-capping studies with *N*-phenylmaleimide (**7**). Dendronized step polymers **10a**–**10c** were then formed from reaction with bismaleimide **9** and their assembly, disassembly, and reassembly behavior studied by GPC.

## Introduction

Dendritic polymers are an interesting class of macromolecular architectures that have generated much attention in recent years.[1] The ability to readily derivatize these compounds while fine-tuning their properties is highly desirable as it allows for rapid production and screening of novel materials. The efficient and selective nature of cycloaddition (CA) reactions[2] lend themselves well to the synthesis and modification of dendritic and other hyperbranched polymers.[3] Among the CA reactions, the azide–alkyne Huisgen 1,3-dipolar CA[4] has become a useful method for peripheral modification of dendrimers and dendritic polymers,[5] while the [4 + 2] Diels–Alder (DA) CA[6] has been widely used in dendritic polymerizations.[7] Because of their high reliability, selectivity, robust character, and the availability of starting materials, these two CAs have been included in the select group of "click chemistry" reactions.[8]

Stimuli-responsive dendronized polymers[9] hold great potential for the production of "smart" polymeric materials.[10] The reversibility of the furan–maleimide DA reaction[11] has been shown to have utility in the production of thermally responsive systems,[12] including segment block dendrimers,[13] simple linear polymers,[14,15] cross-linking linear polymers,[16] and alternating copolymers.[17] In addition, it has been used to prepare hydrogel,[18] nonlinear optical,[19] self-healing,[20] and interpenetrating network (IPN)[21] materials as well as for nanoscale lithography.[22] Previous work from our group has reported the use of furan–maleimide DA adducts in thermally cleavable foams,[23] encapsulants,[24] surfactants,[25,26] and other dendritic macromolecular assemblies.[27] Herein we report the preparation and characterization of first through third generation linear dendronized step polymers[28] from monomers that were derivatized by the azide–alkyne Huisgen 1,3-dipolar CA and polymerized by the furan–maleimide DA reaction. These materials represent the first examples of linear covalent dendronized polymers with thermal reversibility.

## Results and Discussion

**Synthesis of Dendritic Bisfuran Monomers.** The convergent approach to developing the desired multifunctionalized dendrons began with the synthesis of the general scaffold. By preparing a symmetric molecule containing two furan groups and two terminal alkynes, nonreversible functionalization by way of the azide–alkyne Huisgen 1,3-dipolar CA could first be performed, followed by thermally reversible polymerization using the Diels–Alder reaction between the bisfurans and a bismaleimide.

Furfuryl 4-chlorobutanoate (**1**) was coupled to 2,5-dibromohydroquinone (**2**) in the presence of KI and $K_2CO_3$ in DMF at elevated temperature to give dibromo bisfuran **3** (Scheme 1). Next, **3** was subjected to Sonogashira[29] conditions to couple TMS–acetylene, followed by TMS deprotection with TBAF in THF. The resulting dialkynyl bisfuran **4** was then functionalized with Fréchet dendritic benzyl azides **5a**–**5c**[30] in the presence of $Cu(PPh_3)_3Br$ and Hunig's base. The Huisgen 1,3-dipolar CA reactions proceeded smoothly to give the dendritic bisfurans **6a**–**6c** in high yield. All new compounds were fully characterized by $^1H$ and $^{13}C$ NMR along with ESI or MALDI MS and combustion analysis. Elution volumes of dialkynyl bisfuran **4** and dendritic bisfurans **6a**–**6c**, determined using GPC (Figure 1), confirmed the increasing hydrodynamic size with increasing dendrimer generation.

**$^1H$ NMR Analysis of End-Capping Study with *N*-Phenylmaleimide.** In an effort to optimize the DA reaction conditions, dendritic bisfuran **6a** was first allowed to react with a monomaleimide to yield a bis-DA adduct, the formation of which could be monitored by $^1H$ NMR. The DA reaction of furan and maleimide occurs at temperatures <60 °C,[11] with recent examples utilizing temperatures between 50 and 55 °C.[13,26,27] Hence, 1.0 equiv of [G-1] bisfuran **6a** was combined with 2.0 equiv of *N*-phenylmaleimide (**7**) in a minimal quantity of $CDCl_3$ (Scheme 2). Previous examples of the furan–maleimide DA reaction report repeated solvent concentration as a method for encouraging the progress of the reaction[26,27] along with promoting the formation of the thermodynamically stable exo isomer.[31] Therefore, the reaction vessel was left open, the mixture heated to 50 °C, and a fresh minimal quantity of $CDCl_3$ added every 24 h. Aliquots were removed at regular time intervals and analyzed by $^1H$ NMR.

The formation of DA adduct **8** was monitored by both the disappearance of the free maleimide protons of **7** and the appearance of the bridgehead protons of **8** (Figures S1–S8 of

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Scheme 1

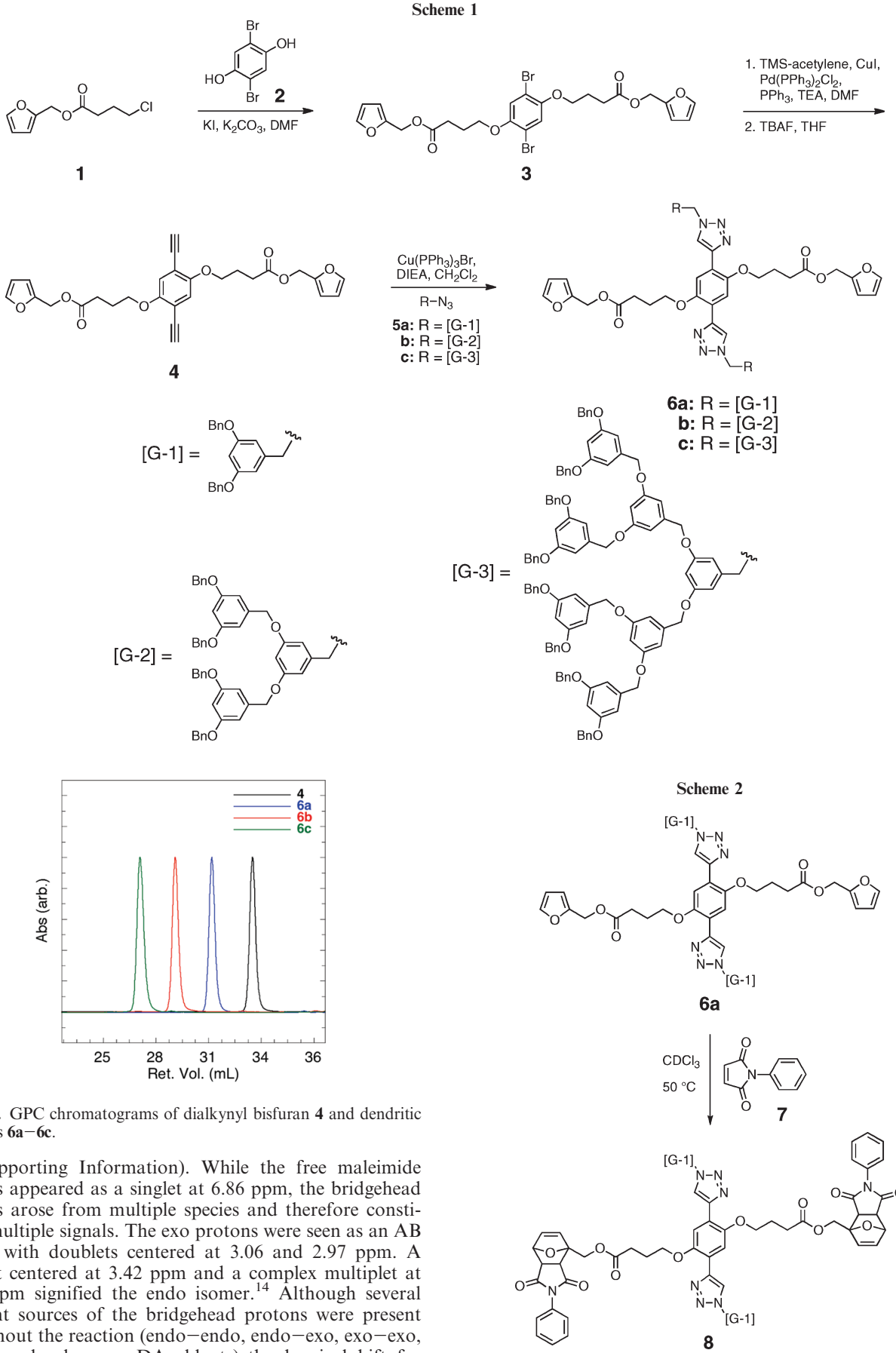



**Figure 1.** GPC chromatograms of dialkynyl bisfuran **4** and dendritic bisfurans **6a**–**6c**.

the Supporting Information). While the free maleimide protons appeared as a singlet at 6.86 ppm, the bridgehead protons arose from multiple species and therefore constituted multiple signals. The exo protons were seen as an AB system with doublets centered at 3.06 and 2.97 ppm. A doublet centered at 3.42 ppm and a complex multiplet at ~3.7 ppm signified the endo isomer.[14] Although several different sources of the bridgehead protons were present throughout the reaction (endo–endo, endo–exo, exo–exo, and exo and endo mono-DA adducts), the chemical shifts for the exo and endo protons were nearly identical throughout, allowing for definitive measurements.

Scheme 2




During the assembly of **8**, the bridgehead proton signals were monitored and plotted as a percentage of the sum of the

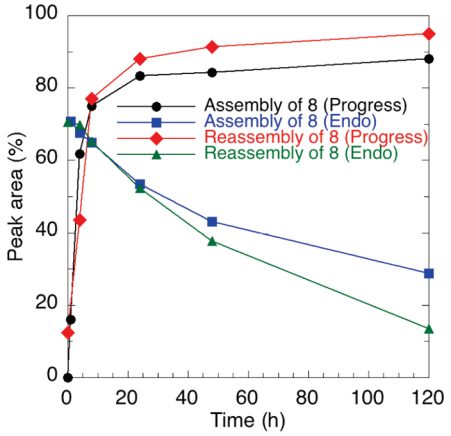



**Figure 2.** Reaction progress and endo composition of the assembly and reassembly of DA adduct **8** heated to 50 °C in $CDCl_3$ for indicated time as monitored by $^1H$ NMR.

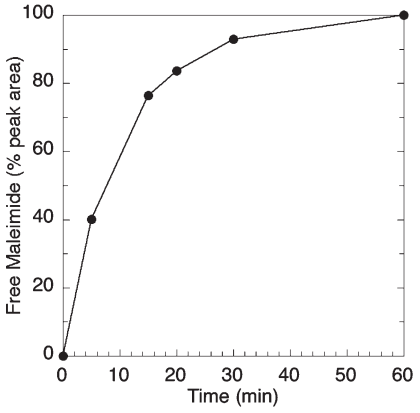



**Figure 3.** Disassembly of DA adduct **8** followed by the appearance of free maleimide protons in the $^1H$ NMR (TCE-$d_2$, 1 mM) at 110 °C.

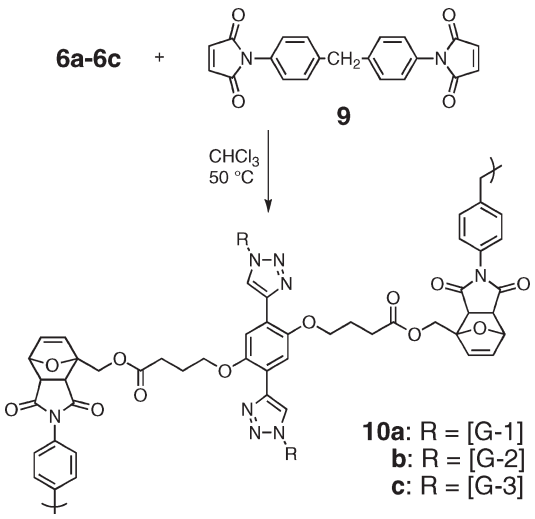
bridgehead and free maleimide proton signal (Figure 2). At time zero, no bridgehead proton signals were observed. Over time, the formation of **8** was evidenced by the appearance of the endo and exo bridgehead protons along with a decrease in the free maleimide proton signal at 6.86 ppm. After 8 h, 75% of maleimide **7** had reacted, and after 120 h, 88% had reacted. An apparent equilibrium appeared to be established by this point, as after 240 h the consumed maleimide **7** increased only slightly to 90%. In addition, the quantity of endo isomer was measured by plotting the endo bridgehead proton signal as a percentage of the sum of the endo and exo bridgehead protons. As expected, the kinetically favored endo isomer initially dominated the mixture (71% after 1 h), while over time the thermodynamically favored exo isomer took precedence (29% endo after 120 h and 11% endo after 240 h).[31]

The disassembly of **8** was investigated by $^1H$ NMR using a purified sample from the assembly experiment described above. The retro-DA reaction of furan−maleimide has been shown to take place at temperatures >60 °C,[11] with temperatures between 90 and 120 °C typically employed.[13,26,27] To achieve these high temperatures, 1,1,2,2-tetrachloroethane-$d_2$ (TCE-$d_2$) was used as the solvent. In this solvent, the free maleimide proton signal of **7** appeared at 6.20 ppm, while the bridgehead proton signals of **8** appeared as an AB system with two doublets centered at 2.41 and 2.33 ppm (exo isomer) and as a doublet centered at 2.78 ppm and a complex multiplet at ~3.0 ppm (endo isomer).[14]

A solution of DA adduct **8** in TCE-$d_2$ (1 mM) was heated to 110 °C and monitored by $^1H$ NMR at regular time intervals. After only 5 min, 40% of the retro-DA reaction had completed (Figure 3). After 30 min, the reaction was 93% complete, and after 60 min, the reaction was complete as evidenced by the absence of the bridgehead protons of **8**. A first-order rate constant[14] of 88 $ms^{-1}$ was determined for the disassembly reaction at this temperature.[32]

Finally, the thermal reassembly of **8** was performed using the disassembled sample from above under similar conditions as the initial assembly. The fragmented reaction mixture was concentrated in vacuo and heated to 50 °C in a minimal quantity of $CDCl_3$. The reaction vessel was left open and a new minimal quantity of $CDCl_3$ was added every 24 h. The reaction progress was monitored by $^1H$ using the chemical shifts as outlined in the initial assembly. The reassembly progressed similarly to the initial assembly, with the reaction 77% complete after 8 h, 91% complete after 48 h, and 95% complete after 120 h (Figure 2). The concentration of endo isomer also progressed similarly, with a composition of 70% after 4 h and 14% after 120 h.

**Scheme 3**




**GPC Analysis of Polymer Assembly, Disassembly, and Reassembly.** With acceptable conditions for the DA reactions in hand, the step polymerizations of dendritic bisfurans **6a**−**6c** and the commercially available 1,1′-(methylenedi-4,1-phenylene)bismaleimide (**9**) were performed. The reactions were carried out similarly to the end-capping study with *N*-phenylmaleimide (**7**). Accordingly, dendritic bisfurans **6a**−**6c** (1.0 equiv) were combined with bismaleimide **9** (1.0 equiv), and the mixtures were dissolved in a minimal quantity of $CHCl_3$ and heated to 50 °C (Scheme 3). The reaction vessels were left open, and a fresh minimal quantity of $CHCl_3$ was added every 24 h.

GPC proved to be an excellent method for qualitatively monitoring the progress of the polymerizations along with estimating their molecular weights using polystyrene standards. During the assembly, aliquots were removed at regular time intervals and monitored by GPC (Figure 4). In each case, a gradual growth of polymer was observed as evidenced by the appearance of peaks at smaller retention volumes. Not surprisingly, the formation of first generation DA polymer **10a** appeared to progress faster than second generation polymer **10b**, which was faster still than third generation polymer **10c**. In the case of **10a**, most of the monomer **6a** and other low molecular weight oligomers were consumed within 240 h, while in the case of third generation polymer **10c**, the

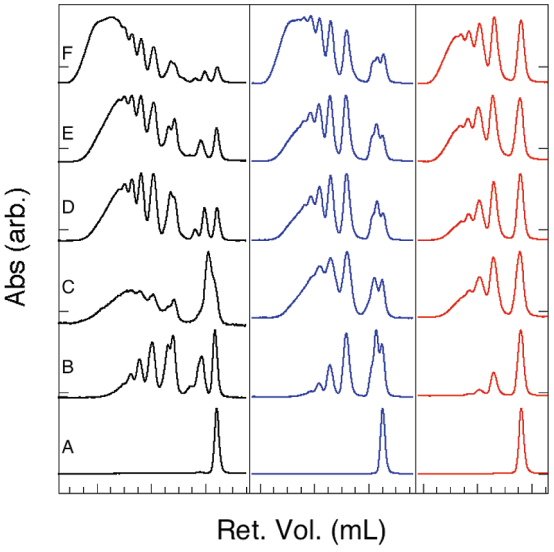



**Figure 4.** Polymer assembly of dendritic DA polymers **10a** (black, left), **10b** (blue, middle), and **10c** (red, right) at 50 °C in $CHCl_3$. (A) $t$ = 0; (B) $t$ = 8 h; (C) $t$ = 24 h; (D) $t$ = 48 h; (E) $t$ = 120 h; (F) $t$ = 240 h.

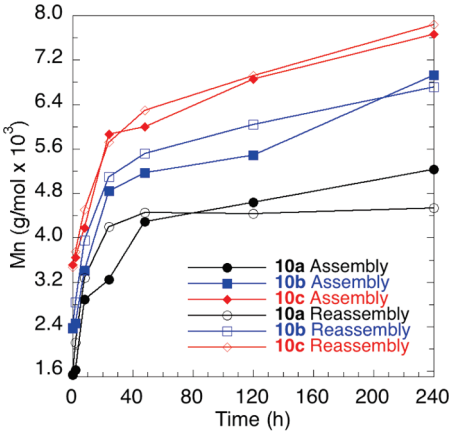



**Figure 5.** Polystyrene-equivalent $M_n$ values for the assembly and reassembly of dendritic DA polymers **10a**−**10c** at 50 °C in $CHCl_3$ for indicated time.

monomer **6c** was still a major contributor to the GPC trace. From the appearance of the GPC traces, there was no evidence for selectivity in product formation.

Polystyrene-equivalent number-average molecular weights ($M_n$) were also derived from the GPC chromatograms for the assembly of **10a**−**10c** (Figure 5). This plot showed a gradual increase in polymer size over time, with the largest increase occurring during the first 48 h. After 240 h of reaction time at 50 °C, the reaction mixtures were divided in half. The first half of the reaction mixtures were precipitated twice from $CH_2Cl_2$ and hexanes to give polystyrene-equivalent $M_n$ values of 9100, 8900, and 9500 g/mol and degrees of polymerization of 5.9, 3.7, and 2.3 for **10a**−**10c**, respectively. The other half of the reaction mixtures were removed from the heat and allowed to stand at room temperature for an additional 35 days. After this time, polystyrene-equivalent $M_n$ values of 8400, 10 000, and 10 800 g/mol and degrees of polymerization of 5.5, 4.2, and 2.6 were found for **10a**−**10c**, respectively.

The precipitated polymers **10a**−**10c** from the assembly experiment described above were then subjected to the disassembly conditions. Hence, TCE solutions of **10a**−**10c**

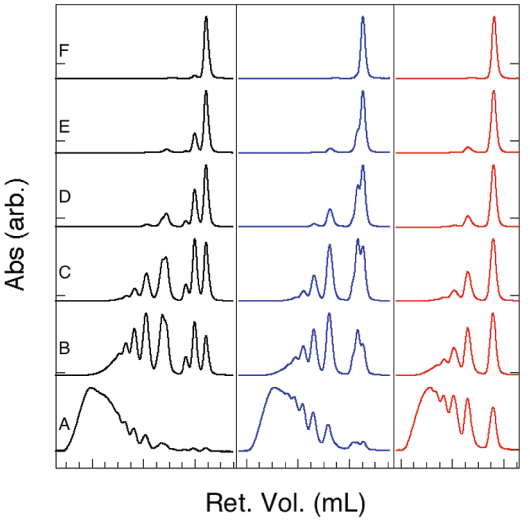



**Figure 6.** Polymer disassembly of dendritic DA polymers **10a** (black, left), **10b** (blue, middle), and **10c** (red, right) at 110 °C in TCE (1 mM based on polystyrene-equivalent $M_n$ values). (A) $t$ = 0; (B) $t$ = 5 min; (C) $t$ = 10 min; (D) $t$ = 20 min; (E) $t$ = 30 min; (F) $t$ = 60 min.

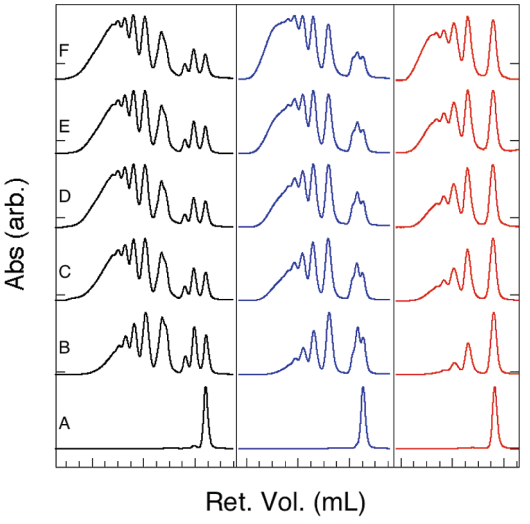



**Figure 7.** Polymer reassembly of dendritic DA polymers **10a** (black, left), **10b** (blue, middle), and **10c** (red, right) at 50 °C in $CHCl_3$. (A) $t$ = 0; (B) $t$ = 8 h; (C) $t$ = 24 h; (D) $t$ = 48 h; (E) $t$ = 120 h; (F) $t$ = 240 h.

(1 mM based on polystyrene-equivalent $M_n$ values) were prepared and heated to 110 °C. After only 5 min, most of the higher molecular weight polymers had degraded to monomer and smaller oligomers (Figure 6). At 30 min, mostly monomers were present, and after 60 min, the polymers had completely disassembled to monomers **6a**−**6c**. The time course of the reaction was nearly identical to the disassembly of *N*-phenylmaleimide DA adduct **8**. In addition, polymers **10a**−**10c** all proceeded similarly, requiring 60 min to complete. This was most likely due to the first-order nature of the retro-DA reaction as opposed to the second-order nature of the polymerization.[14]

To demonstrate the repeatable nature of this thermally reversible system, reassembly of the disassembled polymers from above was performed using the same conditions as for the initial assembly. As expected, the reassembly reactions proceeded in a similar fashion to the initial assembly reactions, with first generation dendritic polymer **10a** growing at a faster initial rate than second generation polymer **10b** (Figure 7). Both **10a**

and **10b** formed considerably faster than third generation polymer **10c**, which still showed considerable amounts of monomer **6c** after 240 h. The crude polystyrene-equivalent $M_n$ values for each polymerization at regular time intervals were also determined (Figure 5). All three polymers increased in size quickly over the first 48 h. At this time, the growth of the polystyrene-equivalent $M_n$ value for first generation polymer **10a** slowed considerably, ending at 4500 g/mol after 240 h. The polystyrene-equivalent $M_n$ values for second and third generation polymer **10b** and **10c** both continued to grow, albeit at a slower rate, reaching values of 6700 and 7800 g/mol, respectively, after 240 h. These polystyrene-equivalent $M_n$ values corresponded to degrees of polymerization of 2.9, 2.8, and 1.9 for **10a**−**10c**, respectively.

## Summary

The synthesis and study of a thermally reversible dendritic step polymer utilizing sequential "click" reactions has been described. First through third generation benzyl aryl ether azide dendrons **5a**−**5c** were added to a central dialkynyl bisfuran scaffold **4** with the Huisgen 1,3-dipolar CA, followed by a $^1$H NMR study of the assembly, disassembly, and reassembly of DA adduct **8**. After acceptable DA reaction conditions were determined, dendritic bisfuran monomers **6a**−**6c** were polymerized with bismaleimide **9**, and the thermal assembly, disassembly, and reassembly reactions were studied by GPC. Both NMR and GPC studies demonstrated that dendritic bisfuran monomers **6a**−**6c** undergo assembly and disassembly cleanly and predictably using relatively mild temperature conditions.

## Experimental Section

**Materials and Methods.** NMR data were collected on Bruker 500 and 600 MHz spectrometers running Xwinnmr (Bruker). Chemical shifts were referenced to the deuterated solvent resonance for $^1$H (7.26 ppm for $CDCl_3$ and 5.32 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, 1000, and 10 000 Å columns in series) with THF as the mobile phase at a flow rate of 1 mL/min. Data were collected with a Waters 2996 photodiode array detector at 323 nm using Empower software (Waters). All chemicals were purchased from commercial suppliers and used as received unless otherwise noted. Commercially available 1,1′-(methylenedi-4,1-phenylene)bismaleimide (**9**) was purchased from Aldrich (95%) and recrystallized from $CH_2Cl_2$/hexanes before use.

**Furfuryl 4-Chlorobutanoate (1).** A round-bottom flask equipped with a stirbar was charged with furfuryl alcohol (5.60 g, 56.7 mmol), triethylamine (8.60 g, 85.1 mmol), and $CH_2Cl_2$ (50 mL). The mixture was cooled to 0 °C in an ice bath, followed by dropwise addition of 4-chlorobutyryl chloride (8.00 g, 56.7 mmol). The mixture was stirred for 1 h at 0 °C and was then allowed to warm to room temperature (rt) over the course of 1 h. The solvent was removed under reduced pressure, and the solid residue was resuspended in hexanes (50 mL). The suspension was filtered and washed several times with hexanes. The filtrate was collected and extracted with 0.5 M HCl (3 × 100 mL), 0.5 M NaOH (3 × 100 mL), and brine (100 mL). The organics were collected, dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure to yield **1** (10.8 g, 94% yield) as a light brown oil. The product was shown to be >95% pure by $^1$H NMR and was carried forward without further purification. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.43−7.42 (m, 1H), 6.42−6.40 (m, 1H), 6.37−6.36 (m, 1H), 5.08 (s, 2H), 3.59 (t, $J$ = 6 Hz, 2H), 2.53 (t, $J$ = 7 Hz, 2H), 2.15−2.05 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 172.2, 149.3, 143.2, 110.6, 110.5, 58.1, 44.0, 31.1, 27.6.

**Bisfurfuryl 4,4′-[(2,5-Dibromo-1,4-phenylene)bisoxy]dibutanoate (3).** To a 500 mL round-bottom flask equipped with a stirbar was added 2,5-dibromohydroquinone (**2**) (5.00 g, 18.7 mmol), furfuryl 4-chlorobutanoate (**1**) (9.20 g, 46.8 mmol), $K_2CO_3$ (12.9 g, 93.3 mmol), KI (1.55 g, 9.35 mmol), and DMF (150 mL). The flask was fitted with a reflux condenser, and the mixture was heated to 140 °C for 2.5 h. After cooling, the solvent was removed under reduced pressure, and the solid residue was resuspended in EtOAc, filtered, and the solid washed several times with EtOAc. The filtrate was collected, and the solvent was removed under reduced pressure, followed by purification by flash chromatography (silica gel, $CH_2Cl_2$) and recrystallization from hexanes:EtOAc to give **3** (5.21 g, 46% yield) as off-white needles: mp 96−98 °C. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.42 (d, $J$ = 1 Hz, 2H), 7.06 (s, 2H), 6.40 (d, $J$ = 3 Hz, 2H), 6.36−6.35 (m, 2H), 5.09 (s, 4H), 3.98 (t, $J$ = 6 Hz, 4H), 2.60 (t, $J$ = 7 Hz, 4H), 2.17−2.08 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 172.6, 149.9, 149.4, 143.2, 118.6, 111.2, 110.6, 110.5, 68.9, 58.1, 30.5, 24.5. MS (ESI) $m/z$ 622.9 $[M + Na]^+$. Anal. Calcd for $C_{24}H_{24}Br_2O_8$: C, 48.02; H, 4.03. Found: C, 47.95; H, 4.10.

**Bisfurfuryl 4,4′-[(2,5-Diethynyl-1,4-phenylene)bisoxy]dibutanoate (4).** To a heavy walled Schlenk flask equipped with a stirbar was added **3** (1.00 g, 1.66 mmol), TMS−acetylene (560 mg, 6.64 mmol), $Pd(PPh_3)_2Cl_2$ (116 mg, 0.166 mmol), CuI (30.0 mg, 0.166 mmol), triethylamine (10 mL), $PPh_3$ (44.0 mg, 0.166 mmol), and DMF (20 mL). Four cycles of freeze−pump−thaw were performed, followed by heating to 55 °C for 16 h. After cooling, the mixture was transferred to a 250 mL round-bottom flask. The solvent was removed under reduced pressure, and the solid residue was resuspended in EtOAc, filtered, and the solid washed several times with EtOAc. The filtrate was collected, and the solvent was removed under reduced pressure, followed by resuspension in THF (50 mL). TBAF (1.0 M in THF, 3.32 mL, 3.32 mmol) was then added dropwise with stirring, and the mixture was allowed to stir for 15 min. The mixture was quenched with a saturated $NH_4Cl$ solution (25 mL), and the organic layer was separated, dried over $MgSO_4$, and filtered. After concentration under reduced pressure, the residue was purified by flash chromatography (silica gel, $CH_2Cl_2$) to give **4** (410 mg, 51% yield) as a yellow-orange solid: mp 82−84 °C. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.40 (s, 2H), 6.91 (s, 2H), 6.38 (d, $J$ = 3 Hz, 2H), 6.34 (s, 2H), 5.07 (s, 4H), 3.98 (t, $J$ = 6 Hz, 4H), 3.32 (s, 2H), 2.57 (t, $J$ = 7 Hz, 4H), 2.13−2.08 (m, 4H). $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 172.6, 153.7, 149.4, 143.2, 117.8, 113.3, 110.53, 110.47, 82.8, 79.4, 68.2, 58.0, 30.3, 24.4. MS (ESI) $m/z$ 513.3 $[M + Na]^+$. Anal. Calcd for $C_{28}H_{26}O_8$: C, 68.56; H, 5.34. Found: C, 68.11; H, 5.85.

**[G-1] Azide (5a)[30].** To a 200 mL round-bottom flask under an $N_2$ atmosphere was added [G-1]-OH[33] (3.00 g, 9.39 mmol), DBU (1.70 g, 11.3 mmol), and $CH_2Cl_2$ (50 mL). The mixture was cooled to 0 °C in an ice bath, followed by dropwise addition of diphenylphosphoryl azide (3.10 g, 11.3 mmol). The reaction was allowed to warm to rt and was stirred for 16 h. The solvent was removed under reduced pressure, followed by purification by flash chromatography (silica gel, 1:1 $CH_2Cl_2$−hexanes) to give **5a** (2.46 g, 76% yield) as a colorless, viscous oil that solidified to a white solid upon standing: mp 67−69 °C, lit.[30] 69 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.45−7.35 (m, 10H), 6.61−6.58 (m, 3H), 5.06 (s, 4H), 4.28 (s, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 160.2, 137.6, 136.6, 128.5, 128.0, 127.5, 107.2, 101.8, 70.1, 54.8.

**[G-2] Azide (5b)[30].** To a 200 mL round-bottom flask under an $N_2$ atmosphere was added [G-2]-OH[33] (4.00 g, 5.37 mmol), DBU (2.22 g, 8.06 mmol), and $CH_2Cl_2$ (50 mL). The mixture was cooled to 0 °C in an ice bath, followed by dropwise addition of diphenylphosphoryl azide (1.23 g, 8.06 mmol). The reaction was allowed to warm to rt and was stirred for 16 h. The solvent was removed under reduced pressure, followed by purification by flash chromatography (silica gel, $CH_2Cl_2$) to give **5b** (2.90 g, 71% yield) as a white foam: mp 108−109 °C, lit.[30] 110 °C. $^1$H

NMR (600 MHz, $CDCl_3$): $\delta$ 7.43−7.31 (m, 20H), 6.68 (d, $J$ = 2 Hz, 4H), 6.59−6.55 (m, 5H), 5.04 (s, 8H), 4.98 (s, 4H), 4.26 (s, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 160.11, 160.07, 139.0, 137.6, 136.7, 128.5, 128.0, 127.5, 107.2, 106.3, 101.8, 101.6, 70.1, 70.0, 54.8.

**[G-3] Azide (5c)[30].** To a 250 mL round-bottom flask under an $N_2$ atmosphere was added [G-3]-OH[33] (2.50 g, 1.57 mmol), DBU (353 mg, 2.35 mmol), and $CH_2Cl_2$ (50 mL). The mixture was cooled to 0 °C in an ice bath, followed by dropwise addition of diphenylphosphoryl azide (645 mg, 2.35 mmol). The reaction was allowed to warm to rt and was stirred for 16 h. The solvent was removed under reduced pressure, followed by purification by flash chromatography (silica gel, $CH_2Cl_2$) to give **5c** (2.46 g, 76% yield) as a white, waxy solid. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.41−7.30 (m, 40H), 6.68−6.66 (m, 12H), 6.58−6.54 (m, 9H), 5.02 (s, 16H), 4.97 (s, 12H), 4.23 (s, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 160.1, 160.0, 139.1, 139.0, 137.6, 136.7, 128.5, 127.9, 127.5, 107.2, 106.4, 101.8, 101.63, 101.59, 70.1, 70.04, 70.00, 54.8.

**[G-1] Bisfuran (6a).** In a small vial equipped with a stirbar, **4** (200 mg, 0.406 mmol), $Cu(PPh_3)_3Br$ (76 mg, 0.0812 mmol), **5a** (308 mg, 0.893 mmol), DIEA (262 mg, 2.03 mmol), and $CH_2Cl_2$ (3.0 mL) were combined. The mixture was stirred at rt for 48 h, at which point the solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 95:5 $CH_2Cl_2$−acetone) to give **6a** (460 mg, 96% yield) as an off-white cotton-like solid: mp 162−164 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.08 (s, 2H), 7.97 (s, 2H), 7.39−7.28 (s, 22H), 6.59−6.56 (m, 6H), 6.34−6.33 (m, 2H), 6.31−6.30 (m, 2H), 5.51 (s, 4H), 5.00 (s, 12H), 4.19 (t, $J$ = 6 Hz, 4H), 2.45 (t, $J$ = 7 Hz, 4H), 2.20−2.10 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 172.4, 160.3, 149.2, 149.1, 143.1, 137.1, 136.4, 128.5, 128.0, 127.4, 123.5, 119.3, 110.8, 110.6, 110.5, 107.0, 102.0, 70.1, 67.8, 58.1, 54.0, 30.8, 24.8. MS (ESI) $m/z$ 1203.4 $[M + Na]^+$. Anal. Calcd for $C_{90}H_{78}N_8O_{16}$: C, 71.17; H, 5.46; N, 7.11. Found: C, 70.91; H, 5.65; N, 7.39.

**[G-2] Bisfuran (6b).** In a small vial equipped with a stirbar, **4** (100 mg, 0.204 mmol), $Cu(PPh_3)_3Br$ (38 mg, 0.0410 mmol), **5b** (346 mg, 0.449 mmol), DIEA (132 mg, 1.02 mmol), and $CH_2Cl_2$ (3.0 mL) were combined. The mixture was stirred at rt for 48 h, at which point the solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 97:3 $CH_2Cl_2$−acetone) to give **6b** (390 mg, 94% yield) as an off-white foam: mp 145−148 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.06 (s, 2H), 7.92 (s, 2H), 7.41−7.29 (m, 42H), 6.64 (d, $J$ = 2 Hz, 8H), 6.56−6.54 (m, 10H), 6.31−6.30 (m, 2H), 6.27−6.26 (m, 2H), 5.49 (s, 4H), 5.01 (s, 16H), 4.97 (s, 4H), 4.94 (s, 8H), 4.09 (t, $J$ = 6 Hz, 4H), 2.41 (t, $J$ = 7 Hz, 4H), 2.15−2.05 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 172.5, 160.3, 160.1, 149.3, 149.1, 143.1, 138.9, 137.2, 136.7, 128.5, 127.9, 127.5, 123.5, 110.9, 110.6, 110.5, 107.2, 106.4, 102.1, 101.7, 70.12, 70.05, 67.8, 58.1, 54.1, 30.9, 29.7, 24.9. MS (MALDI in dithranol) $m/z$ 2030.0 $[M + H]^+$. Anal. Calcd for $C_{126}H_{112}N_6O_{20}$: C, 74.54; H, 5.56; N, 4.14. Found: C, 74.41; H, 5.34; N, 4.11.

**[G-3] Bisfuran (6c).** In a small vial equipped with a stirbar, **4** (50 mg, 0.102 mmol), $Cu(PPh_3)_3Br$ (19 mg, 0.0203 mmol), **5c** (362 mg, 0.224 mmol), DIEA (66 mg, 0.510 mmol), and $CH_2Cl_2$ (3.0 mL) were combined. The mixture was stirred at rt for 48 h, at which point the solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica gel, 98:2 $CH_2Cl_2$−acetone) to give **6c** (340 mg, 90% yield) as an off-white foam: mp 62−64 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.07 (s, 2H), 7.93 (s, 2H), 7.43−7.29 (m, 82H), 6.69 (d, $J$ = 2 Hz, 16H), 6.65−6.64 (m, 8H), 6.58−6.57 (m, 14H), 6.55−6.53 (m, 4H), 6.30−6.29 (m, 2H), 6.26−6.25 (m, 2H), 5.45 (s, 4H), 5.01−4.93 (m, 60H), 4.07 (t, $J$ = 6 Hz, 4H), 2.39 (t, $J$ = 7 Hz, 4H), 2.13−2.05 (m, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 172.5, 160.2, 160.0, 159.9, 149.2, 149.0, 143.1, 139.1, 138.8, 137.1, 136.7, 128.5, 128.31, 128.28, 127.9, 127.6, 127.5, 127.2, 123.5, 119.3, 110.7, 110.6, 110.5, 107.1, 106.3, 102.0, 101.54, 101.49, 70.03, 69.98, 69.91, 67.7, 58.0, 54.0, 30.8, 24.8. MS (MALDI in dithranol) $m/z$ 3728.3 $[M + H]^+$. Anal. Calcd for $C_{238}H_{208}N_6O_{36}$: C, 76.67; H, 5.62; N, 2.25. Found: C, 76.90; H, 6.00; N, 2.20.

**[G-1] DA Adduct (8).** [G-1] bisfuran **6a** (100 mg, 84.6 $\mu$mol) and *N*-phenylmaleimide **7** (14.7 mg, 84.6 $\mu$mol) were dissolved in $CDCl_3$ (500 $\mu$L), and the mixture was heated to 50 °C in an open vial. Every 24 h, fresh $CDCl_3$ (500 $\mu$L) was added. After 10 days, the residue was purified by flash chromatography (silica gel, 9:1 $CH_2Cl_2$−acetone) to give **8** (75 mg, 65% yield,[34] 93% exo isomer) as a white foam. Data for exo−exo isomer: $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 8.04 (s, 2H), 7.93 (s, 2H), 7.41−7.28 (m, 26H), 7.21−7.20 (m, 4H), 6.59−6.57 (m, 2H), 6.55 (d, $J$ = 2 Hz, 4H), 6.50 (d, $J$ = 5 Hz, 2H), 6.32 (d, $J$ = 6 Hz, 2H), 5.49 (s, 4H), 5.31 (s, 2H), 4.99 (s, 8H), 4.85 and 4.50 (AB pattern, $J$ = 13 Hz, 4H), 4.18 (t, $J$ = 6 Hz, 4H), 3.06 and 2.97 (AB pattern, $J$ = 6 Hz, 4H), 2.46 (t, $J$ = 4 Hz, 4H), 2.19−2.10 (m, 4H). $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ 174.7, 173.3, 172.4, 160.3, 149.1, 143.1, 137.6, 137.2, 137.1, 136.4, 131.5, 129.0, 128.7, 128.5, 128.0, 127.5, 126.4, 123.6, 119.4, 110.9, 107.0, 101.9, 89.6, 81.4, 70.1, 67.8, 61.4, 53.9, 49.9, 48.3, 30.8, 29.4, 24.8. MS (ESI) $m/z$ 1550.0 $[M + Na]^+$, 1375.9 $[M - \text{maleimide} + Na]^+$, 1203.3 $[\mathbf{6a} + Na]^+$. Anal. Calcd for $C_{90}H_{78}N_8O_{16}$: C, 70.76; H, 5.15; N, 7.34. Found: C, 70.28; H, 5.38; N, 7.46.

**NMR Studies.** To monitor assembly of DA adduct **8**, [G-1] bisfuran **6a** (100 mg, 84.6 $\mu$mol) and *N*-phenylmaleimide (**7**) (14.7 mg, 84.6 $\mu$mol) were dissolved in $CDCl_3$ (500 $\mu$L), and the mixture was heated to 50 °C in an open vial. Every 24 h, fresh $CDCl_3$ (500 $\mu$L) was added. At time intervals aliquots were removed from the vial, and $^1$H NMR spectra were collected at ambient temperature. To monitor disassembly, a solution of purified bis-DA adduct **8** in TCE-$d_2$ (1 mM) was heated to 110 °C in a sealed NMR tube. At time intervals the reaction was removed from the heating bath, and $^1$H NMR spectra were collected at ambient temperature. To monitor the reassembly, the same disassembled sample of DA adduct **8** was concentrated to dryness and redissolved in a minimal quantity of $CDCl_3$. The sample was heated to 50 °C in an open vial. At time intervals aliquots were removed from the vial, and $^1$H NMR spectra were collected at ambient temperature.

**GPC Studies.** To measure the assembly of dendritic DA polymers **10a**−**10c**, [G-*n*] bisfurans **6a**−**6c** (1.0 equiv) and bismaleimide **9** (1.0 equiv) were dissolved in a minimal quantity 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 **10a**−**10c** was precipitated from $CH_2Cl_2$ and hexanes and heated to 110 °C in TCE (1 mM based on polystyrene-equivalent $M_n$ values). Aliquots were taken out at time intervals, diluted with THF, and analyzed by GPC. To monitor reassembly, the same 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.

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**Supporting Information Available:** $^1$H NMR spectra of the assembly of DA adduct **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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