Hz, 1 H, HC(3)), 2.95 (br q, J = 7.0 Hz, 1 H, HC(6)), 2.25-2.15 (qd, J_q = 7.2 Hz, J_d = 1-2 Hz, 1 H, HC(5)), 2.34-2.11 (2 qd, J_q = 7.4 Hz, J_d = 16 Hz, 2 H, CH_2). 1.11 (t, J = 7.4 Hz, 3 H, CH_2CH_3), 1.06 (d, J = 7.0 Hz, 3 H, $H_3CC(6)$), 1.00 (d, J = 7.2 Hz, 3 H, H33CC(5)); decoupling experiment, irradiation on $H_3CC(5)$ gave a br s at 2.2 ppm, irradiation on CH_2CH_3 gave two d with J = 16 Hz at 2.34-2.11 ppm; MS m/e (rel intensity) 181 (M^+, 39), 152 (23), 149 (21), 135 (12), 134 (24), 120 (46), 119 (26), 107 (47), 106 (100), 105 (64), 91 (55), 79 (20), 28 (69).

2-Methyl-3-nitrobicyclo[4.4.0^{1,6}]deca-3,5-diene (33): ^{1}H NMR (300 MHz) δ 7.26 (d, J = 6.4 Hz, 1 H, HC(3)), 5.74 (br d, J = 6.4 Hz, 1 H, HC(4)), 2.87 (qd, J_q = 7.0 Hz, 1.4 Hz, 1 H, HC(1)), 1.4-2.4 (m, 10 H), 1.14 (d, J = 7.0, 3 H, CH_3).

***rac*-2,7-Dimethyl-3-nitrobicyclo[4.4.0^{1,6}]deca-3,5-diene (34)**: ^{1}H NMR (300 MHz) δ 7.26 (d, J = 6.4 Hz, 1 H, HC(4)), 5.78 (d, J = 6.4 Hz, 1 H, HC(5)), 2.87 (qd, J_q = 7.0 Hz, J_d = 1.3 Hz, 1 H, HC(2)), 2.70 (m, 1 H, HC(7)), 2.48 (dm, J_d = 12.5 Hz, 1 H, HC(1)), 1.85-1.40 (m, 6 H), 1.20 Hq, J = 7.1 Hz, 3 H, CH_3), 1.11 (q, J = 7.0, 3 H, CH_3); MS m/e (rel intensity) 207 (M^+ + 1, 30), 190 (54), 161 (11), 151 (17), 146 (21), 145 (20), 136 (22), 131 (29), 119 (21), 117 (32), 115 (24), 105 (100), 91 (62), 77 (39), 65 (22), 55 (22), 41 (46). Anal. ($C_{12}H_{16}NO_2$) C, H, N.

***rac*-4-Isopropyl-2,3-dimethyl-1-nitro-1,3-cyclohexadiene (32)**. *rac*-**2c** (870 mg, 5 mmol) was allowed to react with 3-pyrrolidino-2-methylpentene (isomeric mixture of 2- and 3-pentene, 842 mg, 5.5 mmol) according to GP 1 (50 h room temperature, 8 h heating under reflux) to give **32** (364 mg, 37%, d > 90%), which could be recrystallized from pentane at -20 °C to give yellow crystals. Bicyclic products could be detected in trace amounts by NMR: mp 37-38 °C; ^{1}H NMR (300 MHz) 7.34 (dd, J = 6.3, 1.0 Hz, 1 H, HC(6)), 5.80 (dd, J = 6.3, 1.2 Hz, 1 H, HC(5)), 2.96 (qd, J_q = 7.0 Hz, J_d = 1.0 Hz, 1 H, HC(2)), 2.38 (dd, J = 6.9, 6.8 Hz, 1 H), 2.26 (qd, J_q = 7.1 Hz, J_d = 1.2 Hz, HC(3)), 1.15 (d, J = 6.8 Hz, 3 H, CH_3), 1.09 (d, J = 6.9 Hz, 3 H, CH_3) 1.04 (d, J = 7.0 Hz, 3 H, CH_3), 1.00 (d, J = 7.1 Hz, 3 H, CH_3); MS m/e (rel intensity) 195 (M^+, 38), 152 (12), 149 (12), 138 (44), 136 (34), 134 (25), 119 (34), 107 (53), 106 (100), 105 (36), 91 (63), 79 (42), 77 (57), 65 (32), 53 (21), 51 (20), 43 (93), 41 (58), 39 (36), 27 (25). Anal. ($C_{11}H_{17}NO_2$) C, H, N.

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Supplementary Material Available: Listing of in depth IR and/or ^{13}C NMR spectral data for compounds cited in the work, a 2D ^{1}H NMR of **18**, the measurement and interpretation of NOE obtained with **5**, **11b**, and **14b**, and elemental analyses and the coordinates of the X-ray crystal structure of **25** (12 pages). Ordering information is given on any current masthead page.

Preparation of Polymers with Controlled Molecular Architecture. A New Convergent Approach to Dendritic Macromolecules

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Abstract: The novel convergent growth approach to topological macromolecules based on dendritic fragments is described. The polyether dendritic fragments are prepared by starting from what will become the periphery of the molecule and progressing inward. In the first step, 2 mol of a benzylic bromide is condensed with the two phenolic groups of the monomer, 3,5-dihydroxybenzyl alcohol, under phase-transfer conditions. After transformation of the benzylic alcohol functionality of the growing molecule into the corresponding bromide, the procedure is repeated with stepwise addition of the monomer followed again by activation of the benzylic site. After several generations of growth, the resulting dendritic wedges, in their benzylic bromide form, can be coupled to a polyfunctional core such as 1,1,1-tris(4'-hydroxyphenyl)ethane to form the final hyperbranched macromolecule. Unique features of the convergent approach include the control over the nature and placement of the groups that are placed at the periphery of the molecule and the fact that each growth step only involves reaction at a single site of the growing macromolecule. The dendrimers can be purified by normal flash chromatography and are fully characterized by use of a combination of spectroscopic and chromatographic techniques. They double their molecular weight at each generation growth step, become progressively denser and more compact, and have a very low polydispersity. The scope and versatility of the "convergent" approach is compared to the more established "divergent" approach to dendritic macromolecules.

Introduction

The synthesis of polymers with highly controlled molecular architectures has gained increased importance due to the rising demand for specialty polymers that possess novel properties.[1] In particular, a family of hyperbranched polymers prepared by multiplicative growth from a central core has attracted much attention, as the polymers appear to adopt a spherical shape free of the sort of chain entanglement that is so characteristic of other more conventional high polymer systems. While early work on hyperbranched molecules was carried out more than a dozen years ago,[2] it was not until the mid 1980's that Tomalia[3] and Newkome[4] reported their independently conceived approaches to highly branched "starburst" and "arborol" structures. A very extensive review[5] of this and related synthetic[6,7] or theoretical[8,9] work has

(1) Bikales, N. M. *Polym. J.* **1989**, *19*, 11.
(2) Buhleier, E.; Wehner, W.; Vogtle, F.; *Synthesis* **1987**, 155.
(3) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17*, 117. Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466.
(4) Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2004. Newkome, G. R.; Baker, G. R.; Saunders, M. J.; Russo, P. S.; Gupta, V. K.; Yao, Z.; Bouillion, J. E. *J. Chem. Soc., Chem. Commun.* **1986**, 752. Newkome, G. R.; Yao, Z.; Baker, G. R.; Gupta, V. K.; Russo, P. S.; Saunders, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 849.
(5) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.
(6) Denkewalter, R. G.; Kolc, J.; Luskasavage, W. J. U.S. Patent 4,289,872, 1981.
(7) Padias, A. B.; Hall, H. K., Jr.; Tomalia, D. A.; McConnell, J. R. *J. Org. Chem.* **1987**, *52*, 5305. Hall, H. K.; Polis, D. W. *Polymer Bull.* **1987**, *17*, 409.
(8) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718. De Gennes, P. G.; Hervet, H. J. *J. Phys. Lett.* **1983**, *44*, 351. Burchard, W.; Kajaiwara, K.; Nerger, D. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 157. Maciejewski, M. *J. Macromol. Sci., Chem.* **1982**, *A17*, 689.

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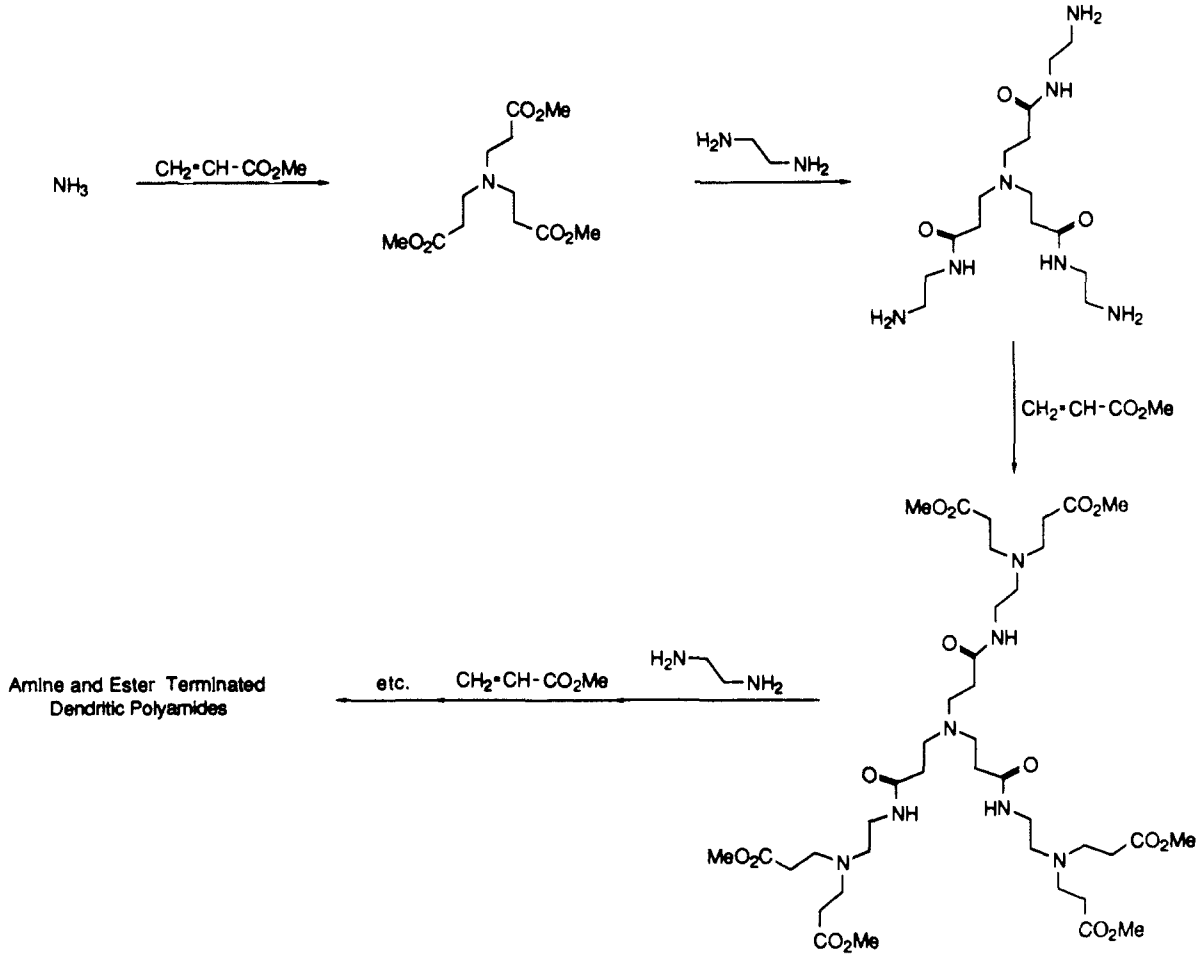
Scheme I



appeared. Previously, the synthesis of dendritic macromolecules has been via a divergent approach that involves the initial reaction of the monomer unit with a polyfunctional core, in Tomalia's case[3] methyl acrylate and ammonia, followed by exhaustive amidation of the resulting esters with large excesses of ethylenediamine to afford the next generation of reactive amine groups. Repetition of the two-step procedure leads to subsequent generations (Scheme I). The rapid increase in the number of reactive groups at the chain ends of the growing macromolecule is a significant feature of all the divergent approaches.[2-7] This leads to a number of potential problems as growth is pursued: Firstly, any incomplete reaction of these terminal groups would lead to imperfections or failure sequences in the next generation; the probability of this occurring increases as the growing macromolecule increases. Secondly, to prevent side reactions and to force reactions to completion, extremely large excess amounts of reagents are required in latter stages of growth, causing some difficulties in purification. In this study, we describe the synthesis of dendritic polyether macromolecules based on 3,5-dihydroxybenzyl alcohol, (**1**) as the monomer unit with a novel "convergent" methodology.

Convergent Growth Strategy. The basic concept of the "convergent" approach utilizes the symmetrical nature of these molecules to advantage. Construction of the macromolecule is started at what will ultimately become its "periphery", and, at each step, growth is designed to occur via reaction of only a very limited number of reactive sites. In the basic approach discussed herein, coupling of a single site of the growing molecule with two sites of the monomer is involved in every generation growth (Scheme II). This is in sharp contrast to the "divergent" approach used for "starburst" and analogous polymers where growth must involve simultaneous additions at a progressively larger number of sites. The starting material, **2**, contains what will eventually constitute surface functionality (s) of the dendritic macromolecule as well as a reactive functional group (f_r); **2** is then condensed with monomer **3**. The monomer itself has at least two coupling sites (c) and a protected functional group (f_p). After coupling, f_p is activated to f_r to give **4** and the process is continued by successive iterations, for example until the dendritic "wedge", **5**, is obtained. Dendrimer **5** has a single reactive group (f_r) at its focal point and may be coupled to a polyfunctional core such as **6** to provide the final dendritic macromolecule **7**, which, in the illustration of Scheme II, has exactly 64 surface functional groups.

Results and Discussion

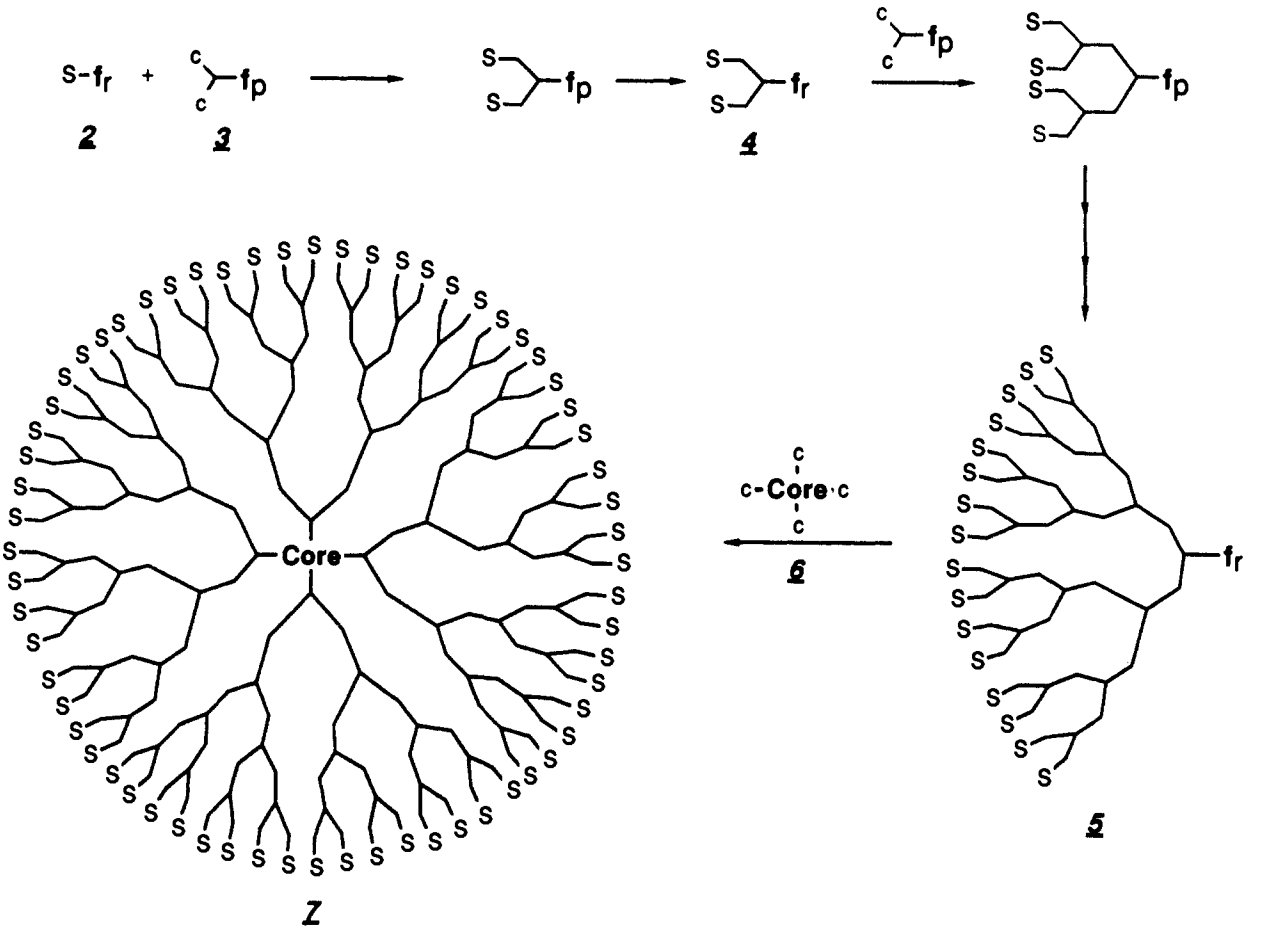
Synthesis of Dendritic Macromolecules. To demonstrate this new "convergent-growth" approach, we chose to explore the synthesis of a family of dendritic polyether macromolecules[10] based on 3,5-dihydroxybenzyl alcohol (**1**) as the monomer unit. This section was made on the basis of the very high yields that can be obtained for the formation of benzyl ethers from phenols and benzylic halides (Scheme III). In the discussion below, the various generation dendritic molecules will be designated by use of the following notation [G-x]-f, in which [G-x] refers to generation number (x = 0, 1, 2, ...) and f refers to the functional group located at the focal point. After coupling to a core, the notation [G-x]$_n$-[C] will be used where n represents the number of dendritic fragments (generation x) coupled to the core. Starting from the known[11] benzylic bromide **8**, which in our case is the first-generation benzylic bromide [G-1]-Br, reaction with **1** was examined in a variety of solvents (DMF, 1,4-dioxane, THF, acetone, 3-

(9) Naylor, A. M.; Goddard, W. A., III; Kiefer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339.

(10) Fréchet, J. M. J.; Jiang, Y.; Hawker, C. J.; Philippides, A. E. *Preprints of the IUPAC International Symposium of Functional Polymers*; The Polymer Society of Korea: Seoul, 1989; 19. Hawker, C. J.; Fréchet, J.M.J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010.

(11) Reimann, E. *Chem. Ber.* **1969**, *102*, 2887.

Scheme II



methylbutan-2-one) and with a variety of bases[12] (Cs_2CO_3, KOH, K_2CO_3) in the presence and absence of phase-transfer agents. The optimum reaction conditions, in terms of yield and synthetic ease, were found to include the use of potassium carbonate and 18-crown-6 in refluxing acetone under vigorous stirring for 48 h. It was found essential to maintain efficient stirring throughout the reaction in order to maintain a high rate of conversion. Reaction of **8** and **1** gave the second-generation benzylic alcohol [G-2]-OH (**9**), which was isolated in 91% yield after recrystallization. The C-alkylation of phenols is a well-known side reaction;[13] however, no evidence of C-alkylation was observed in the crude reaction product by high-field ^1H and ^{13}CNMR spectra. Similarly, no C-alkylation was detected in latter generations.

The reaction of [G-2]-OH (**9**) with a variety of halogenating agents was investigated in order to restore the "reactive" bromomethyl functionality at the focal point of the growing dendritic "wedge". CCl_4[14] and *N*-bromosuccinimide[15] used in combination with triphenylphosphine (PPh_3) gave poor yields of the corresponding halomethyl compounds (45 and 62% respectively). The use of PBr_3[11] or CBr_4/PPh_3[14] led to [G-2]-Br (**10**) in reproducible yields of over 90% after recrystallization.

Reaction of [G-2]-Br (**10**) with **1** gives the next-generation alcohol [G-3]-OH (**11**) in 88% yield after purification by flash chromatography. In this case, as with subsequent generations, it was found that reaction with PBr_3 led to lower yields when compared to brominations with CBr_4/PPh_3 (for **11**, 72% vs 90%). This may be due to the production of trace amounts of acid in the PBr_3 reaction, which would lead to unwanted side reactions. Having obtained the third-generation bromide [G-3]-Br (**12**), by reaction of **11** with CBr_4/PPh_3, we proceeded to generation 4. Reaction of [G-3]-Br (**12**) with **1**, as above, gave the next-generation alcohol [G-4]-OH (**13**), in 92% yield, which was brominated with CBr_4/PPh_3 to give [G-4]-Br (**14**). A larger excess of CBr_4 and PPh_3 (2.5 equiv) was required to force the reaction of completion; even larger excesses, up to 10 equiv for [G-6]-Br, were required in ensuing generations. Though the amounts involved are very small given the high molecular weight of **13**, this excess of CBr_4 must be removed prior to further coupling to monomer **1** in order to avoid the formation of unwanted side products arising from reactions with CBr_4. To remove the excess CBr_4, we first purify the crude product by flash chromatography and then precipitate it into ether to afford pure **14** in 95% yield. Conversion of **14** into fifth-generation [G-5]-OH (**15**) was accomplished in 85% yield, while activation to [G-5]-Br (**16**), which required the use of 5 mol equiv of CBr_4/PPh_3, was only achieved in 83% yield after purification. Similar transformations to [G-6]-OH (**17**) and [G-6]-Br (**18**) also resulted in decreased yields of 78 and 72%, respectively. The nominal molecular formula of [G-6]-Br (**18**) is $C_{889}H_{763}BrO_{126}$ and corresponds to a molecular weight[16] of 13 542. The requirement for high stoichiometric ratios for activation and the decrease in yield observed for the fifth and sixth generation suggest that increased steric congestion around the functional group located at the focal point of the dendritic wedge reduces its reactivity.

After highly pure dendritic wedges were obtained, coupling to a polyfunctional core was carried out as shown in Scheme IV. The polyfunctional core chosen in this case was 1,1,1-tris(4′-hydroxyphenyl)ethane ([C]-$(OH)_3$, **19**). This allowed the use of the same coupling chemistry as was used in building the dendritic wedges, though this need not be the case. In a typical reaction,

(12) Buehler, C. A.; Pearson, D. E. *Survey of Organic Synthetic*; John Wiley and Sons: New York, 1967; p 445 Vol. 2. Weber W. P.; Gokel, G. W. *Phase Transfer Catalysis in Organic Synthesis*; Springer Verlag: New York, 1977; pp 9, 76. Pfeffer P. E.; Silbert, L. S. *J. Org. Chem.*, **1976**, *41*, 1373.

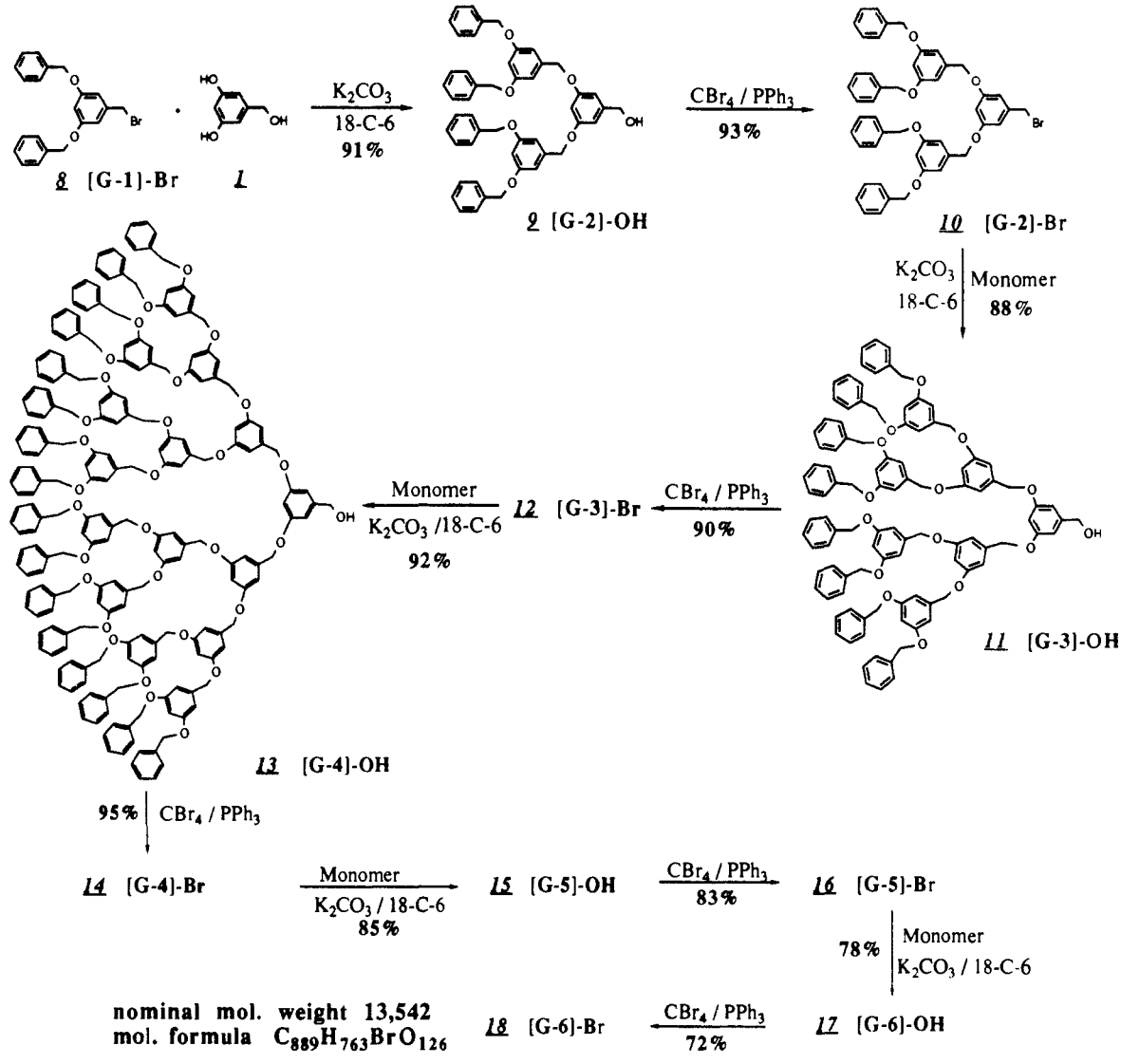
(13) Kornblum, N.; Seltzer, R.; Haberfield, P. *J. Am. Chem. Soc.* **1963**, *85*, 1148.

(14) Hooz, J.; Gilani, S. S. H. *Can. J. Chem.* **1968**, *46*, 86.

(15) Bose, A.; Lal, B. *Tetrahedron Lett.* **1973**, *40*, 3937.

(16) Calculated on the basis of C = 12.01, H = 1.008, and O = 16.00.

Scheme III



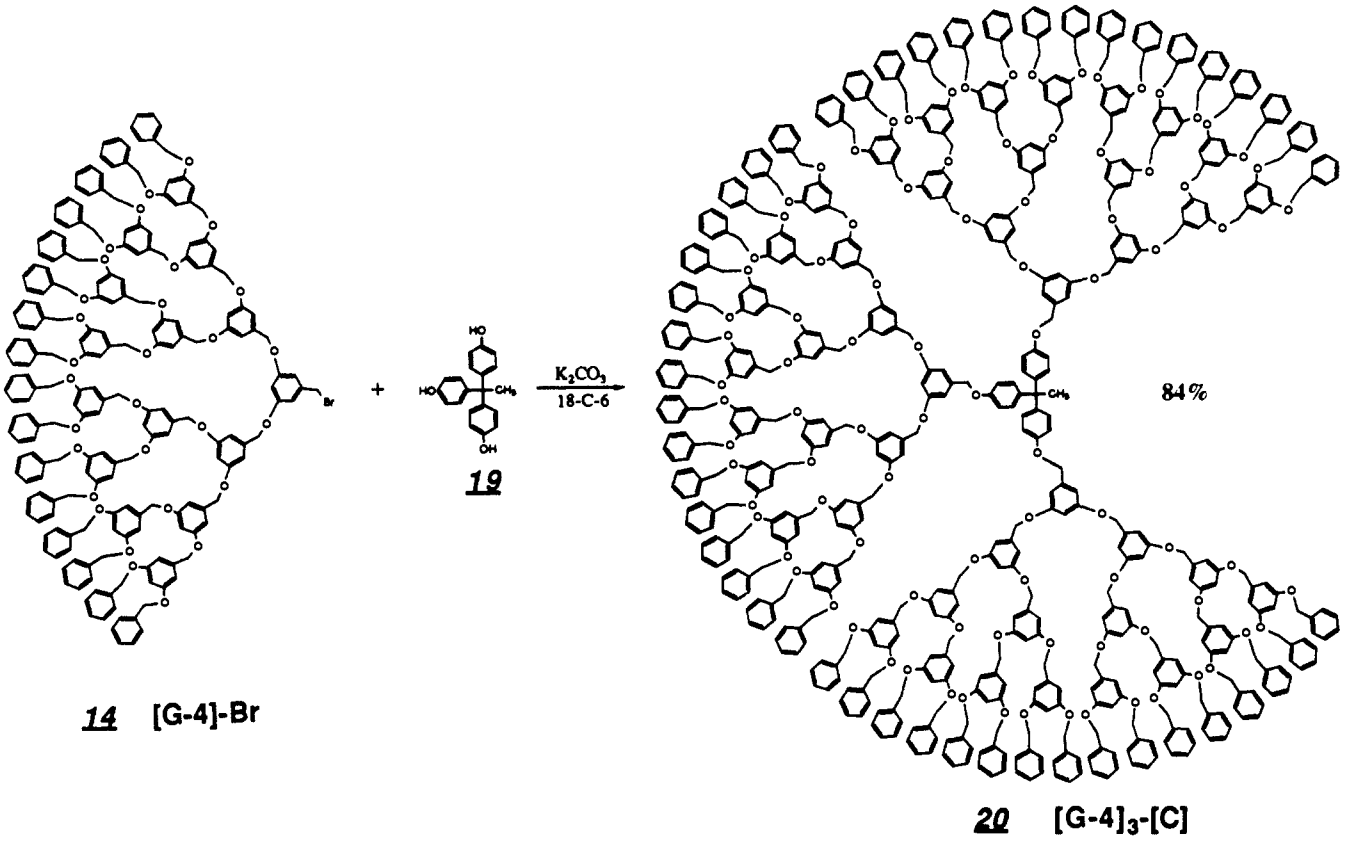
an acetone solution of dendritic bromide [G-4]-Br (**14**) (3.10 equiv) was heated at reflux with 1.00 equiv of the core molecule, **19**, in the presence of potassium carbonate and 18-crown-6. In order to remove the slight excess of bromide used in the coupling step, it was transformed into the easily separated monoalkylated core through addition of a large excess of **19** (5–30 equiv) once the reaction was deemed to be complete. The monoalkylated core [G-4]-[C]-$(OH)_2$ containing two free phenolic groups has a chromatographic mobility that is vastly different from that of the desired trialkylated core $[G\text{-}4]_3$-[C] (**20**), which was obtained in 84% yield. A similar reaction was carried out with each generation of bromide, from benzyl bromide, [G-0]-Br, to **18**, [G-6]-Br. Yields were in the range of 84–91% for [G-0]–[G-4], and, as was observed in the preparation of the dendritic wedges, they declined to 76% for $[G\text{-}5]_3$-[C] and to 51% for $[G\text{-}6]_3$-[C] as purification became progressively more difficult. Again, this can be attributed to increased steric congestion as $[G\text{-}6]_3$-[C] is a highly branched macromolecule of nominal molecular formula $C_{2687}H_{2304}O_{381}$ and molecular weight 40 689.

Despite the apparent limit to the size of the macromolecule that can be obtained by convergent growth from monomer **1**, the approach remains extremely valuable in its ability to produce midsize dendritic macromolecules of up to generations 6–8. With more flexible monomers it is expected that growth inhibition would only be observed at even higher stages of generation growth. Nevertheless, the method is advantageous as the macromolecules that are obtained have an extremely low dispersity of molecular sizes. In addition, the overall process involving coupling of complete dendritic wedges to a central core is highly adaptable to the preparation of unsymmetrical dendritic macromolecules.

Characterization. One of the major problems associated with the synthesis of dendritic macromolecules is the characterization and evaluation of the purity of the products that are obtained. In our "convergent" methodology, infrared spectroscopy offers little information since the spectrum is soon overwhelmed by the dominant functional groups in the molecule (aromatic and ether groups) and the ability to detect accurately the reactive functional group at the focal point quickly becomes impaired. Similarly, elemental analysis is nt accurate enough to reliably detect the subtle changes in the molecular structure, for example [G-3]-OH requires C = 79.12; H = 5.82%, while [G-5]-Br requires C = 78.46; H = 5.66% and $[G\text{-}4]_3$-[C] shows C = 79.57; H = 5.73%. While these are three vastly different molecules in terms of both functional group at the focal point and generation number, the values for % C differ by only 1.11% and those for % H by 0.16%. Fortunately, a number of spectroscopic, chromatographic, and light-scattering techniques are of great value in the detection of impurities and the characterization of products.

^{1}H and ^{13}C NMR Spectroscopy. Unlike the earlier work of Hall et al.,[7] ^{1}H NMR spectroscopy proved invaluable in the characterization of the various products. Figure 1 shows the 300-MHz ^{1}H NMR spectrum of [G-3]-Br (**12**) in which three main regions can be seen. The resonances for the exterior phenyl groups occur at 7.25–7.45 ppm, the resonances for the aromatic protons of the monomer units occur in the region 6.50–6.70 ppm, separate resonances are observed in the appropriate ratio for each "layer"

Scheme IV



of monomer units, and at highest field, resonances for the methylene protons occur in the region 4.90–5.10 ppm. In addition, the methylene resonance for the unique $-CH_2Br$ functional group at the focal point of the dendritic wedge is seen at 4.40 ppm. In all cases, the resonances for the CH_2OH (4.54–4.62 ppm) and CH_2Br (4.35–4.41 ppm) are easily distinguishable for each other (Figure 2). The $Ar'-CH_2Ar$ resonance for the C-alkylated product occurs near 4.00 ppm in similar systems[17] and again is easily distinguishable. When dendritic wedges are attached to the core molecule **19**, the methyl resonance of the core moiety is observed at 2.05–2.08 ppm while two doublets are also seen for the aromatic rings of **19** at 6.80–6.84 and 6.95–6.98 ppm, an area of the spectrum that is not obscured by the aromatic resonances of the dendritic wedges. These factors, which allow easy identification of the functional group at the focal point and the core moiety, contribute greatly to overall characterization of the dendritic macromolecules. Integration data for these groups can also be used to confirm the extent of coupling to either the core **19** or monomer **1**, or to quantify the generation number. Figure 2 shows the 300-MHz ^1H NMR spectra for each type of compound studied; the large differences between resonances for the functional group at the focal point can be seen.

Completely information can be gathered for analysis of the ^{13}C NMR spectra of the various compounds. When compared to the proton spectra, greater differences are found between the resonances for the CH_2OH and CH_2Br functional groups, the former occurring at 64.80–65.29 ppm and the latter at 33.50–33.57 ppm. Similarly, the core group provides unique resonances at ca. 30.75, 50.60, 114.00, and 129.60 ppm to assist in the identification and detection of impurities. For all generations, the slightly different chemical environment of the monomer unit attached to the functional group at the focal point allows it to be distinguished from the other monomer units. Figure 3 shows the region 101–109 ppm of the 75-MHz ^{13}C NMR spectra for the series [G-2]-Br–[G-5]-Br. The resonances for carbons 2 and 4 + 6 of the monomer units are seen in this region; those resonances attributed to the unique monomer unit located at the focal point appear near 102.2 and 108.2 ppm, while the resonances for all other monomer units are near 101.6 and 106.4 ppm. As the generation number increases, these signals for the focal point unit decrease in size when compared to the corresponding resonances of other monomer units.

Mass Spectrometry. The nominal molecular weights of the lower dendritic structures were confirmed by mass spectroscopy. Unfortunately, due to instrument and technique limitations, the molecular ion of dendritic wedges greater than generation 3 could not be observed. The nominal molecular weight for all suitable dendritic wedges was confirmed by the presence of the expected molecular ion in either the EI or FAB spectra. For example, [G-3]-OH (**11**), which has a nominal molecular weight of 1592, showed two prominent peaks in ca 1:1 ratio at m/e = 1592 and 1593 in the FAB spectrum. The M + 1 peak at m/e 1593 is expected in view of the molecular formula of the compound ($C_{105}H_{92}O_{15}$).

Size-Exclusion Chromatography. Size-exclusion chromatography proved to be extremely important in the analysis of the purity of the benzylic alcohols and trialkylated core macromolecules since molecular sizes change dramatically at each generation growth or coupling step. The technique also proved to be sensitive as percentages as low as 0.5% of lower molecular weight impurities were easily observed. A composite of the SEC chromatographs for each generation benzylic bromide, from benzyl bromide [G-0]-Br to sixth-generation bromide [G-6]-Br (**18**), is shown in Figure 4. This shows only a minor amount of broadening as the generation number increases. Similarly, the SEC chromatographs for each trialkylated core molecule, from generation numbers from 0 to 6, are shown in Figure 5. Again, only slightly broadening is observed. The reason for this broadening is unknown at this time but may be due to otherwise undetectable impurities or a change in the rigidity of the macromolecule as it increases in size. A similar phenomenon has previously been reported.[18] Comparison of the retention volumes of the dendrimers with those of narrow molecular weight distribution polystyrene standards in

(17) Wooley, K. L.; Hawker C. J.; Frêchet, J. M. J. Unpublished results.

(18) Aharoni, S. M.; Crosby, C. R.; Walsh, E. K. *Macromolecules* **1982**, *15*, 1093.

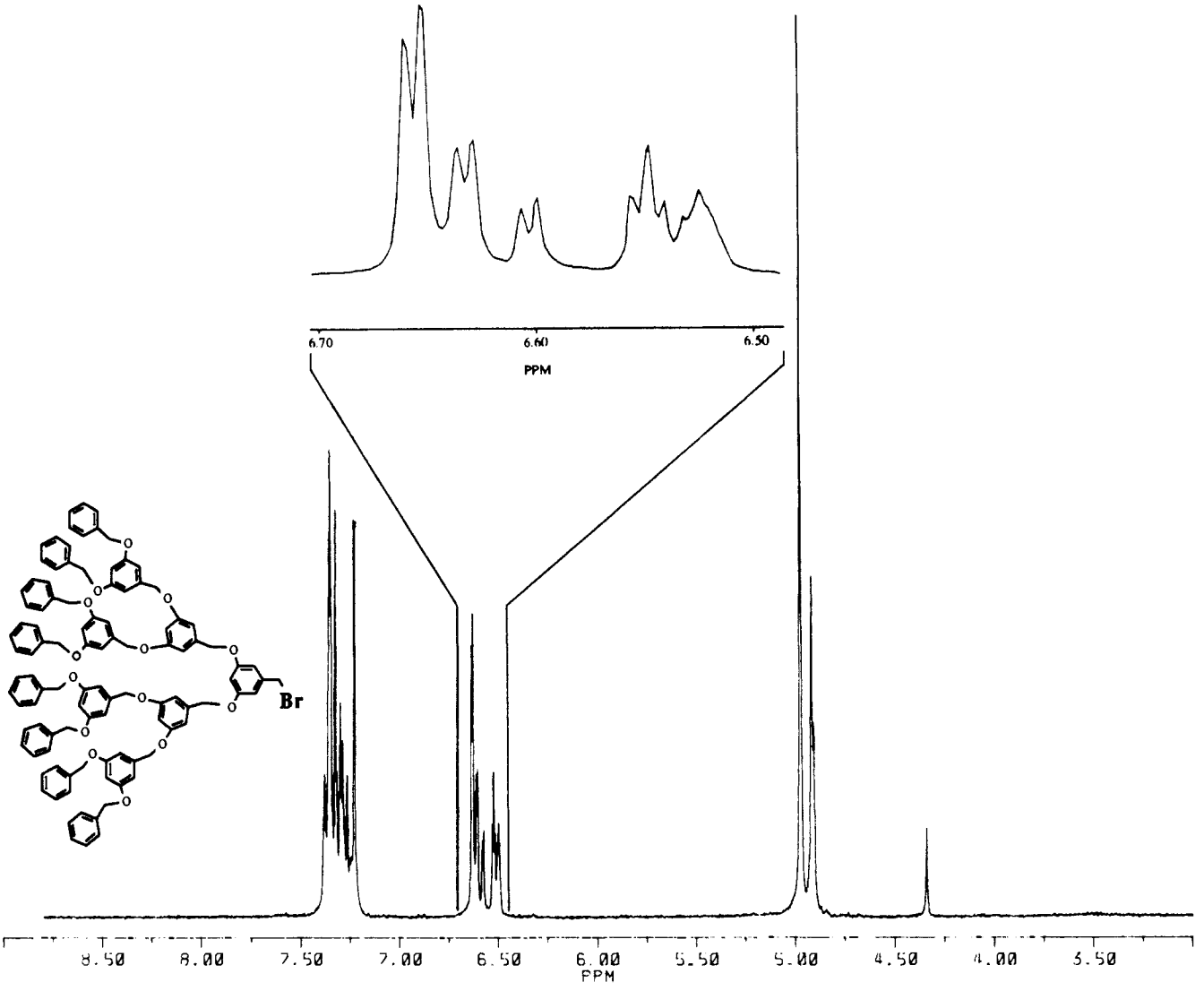


Figure 1. 300-MHz ^{1}H NMR spectrum of third-generation bromide [G-3]-Br (**12**).

Table I. Gel Permeation Chromatography and Low-Angle Light-Scattering Data for the Dendritic Macromolecules

			GPC data[c]		
compd	nominal M_w[a]	LALLS M_w(exact)[b]	M_n	M_w	M_w/M_n
$[G\text{-}3]_3$-[C]	5034		4220	4280	1.01
[G-5]-OH	6687	6560 ± 350	5400	5510	1.02
$[G\text{-}4]_3$-[C]	10127		6820	6890	1.02
[G-6]-OH	13479		7950	8110	1.02
$[G\text{-}5]_3$-[C]	20314	20900 ± 1500	11350	11600	1.02
$[G\text{-}6]_3$-[C]	40689	38500 ± 1900	15050	15400	1.02

[a] Calculated from C = 12.01, H = 1.008, O = 16. [b] Average of four to six runs. [c] Calibrated with narrow-dispersity polystyrene standards.

instructive. A plot of log molecular weight versus retention volume is shown in Figure 6 for both the dendrimers and the polystyrene standards. It can be seen that the points for the dendrimer macromolecules follow a relatively straight line, similar in shape to the universal SEC plots of log $M[n]$ vs retention volume,[19] whereas those for the polystyrene standards follow a curve and increasingly deviate from the dendrimer plot as molecular weight increases. This property of dendritic macromolecules has previously been noted by Aharoni[18] and suggests that the dendrimers progressively become denser and more compact as molecular weight increases as was also observed earlier in the case of Tomalia's starburst polymers.[3,5]

SEC coupled to a low-angle laser light scattering (LALLS) instrument allowed the nominal molecular weights of the larger dendrimers (<3000) to be confirmed within the experimental errors of the LALLS technique. For example, $[G\text{-}5]_3$-[C] (**21**) with a nominal molecular weight of 20314 shows a LALLS M_w value of 20900 ± 1500. Table I reports the results of SEC and LALLS experiments for a variety of dendrimers. It is interesting to note that our largest hyperbranched macromolecule $[G\text{-}6]_3$-[C] with nominal and LALLS M_w values of 40689 and 38500 ± 1900, respectively, only shows a GPC polystyrene equivalent M_w of 15400. This indicates that such molecules are very compact as was observed in the case of starburst and similar dendrimers.[5] Polydispersity data given in Table I for measurements against narrow molecular weight distribution polystyrene standards[20] also suggest that our dendritic macromolecules have a very narrow distribution of molecular weights. This is also illustrated in Figure

(19) Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B* **1967**, *5*, 753. Morena-Bondi, M. C.; Orellana, G.; Turro, N. J., Tomalia, D. A. *Macromolecules* **1990**, *23*, 910.

(20) Polystyrene standards were obtained from Polymer Laboratories, Amherst, MA.

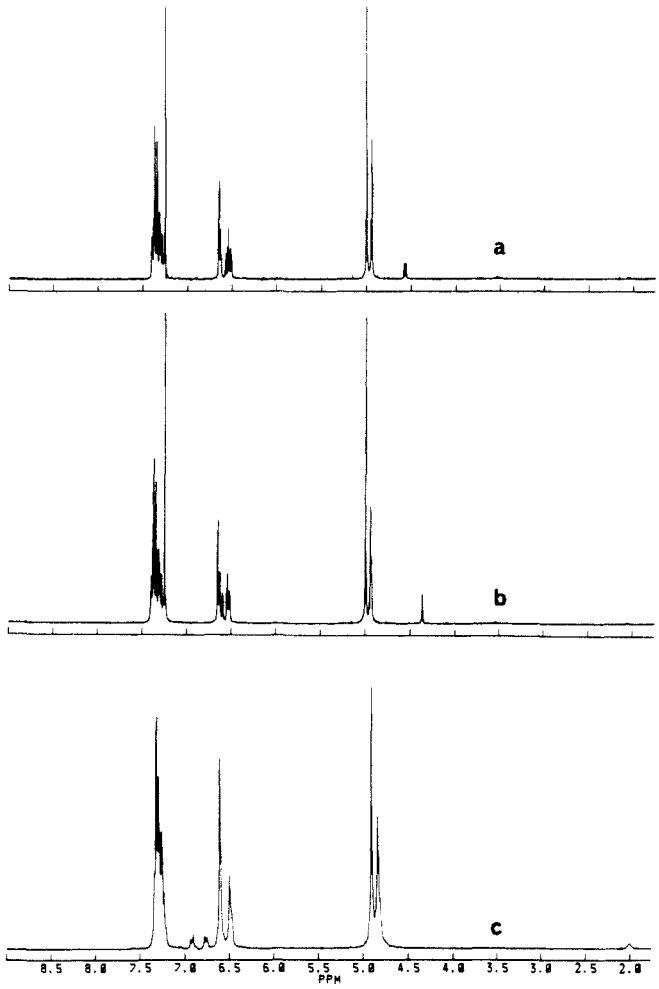


Figure 2. Evolution of ^{1}H NMR spectrum of **11** upon bromination and subsequent coupling to trifunctional core **19**: (a) [G-3]-OH (**11**); (b) [G-3]-Br (**12**); (c) [G-3]$_3$-[C].

7, which shows the elution characteristics of a dendritic "wedge", [G-4]-OH (**13**), and a dendrimer, [G-5]$_3$-[C] (**21**), with narrow molecular weight distribution polystyrene standards of similar elution volumes. The comparisons obtained from runs under identical conditions over a stable set of columns suggest that the dendritic macromolecules have a very low polydispersity index.

Conclusion

The concept of using a "convergent" approach to the synthesis of dendritic macromolecules has a number of potential advantages: the small number of coupling reactions per generation growth step gives greater control over the synthesis, the possibility of failure sequences is minimized, and large excesses of reagents are avoided, which simplifies purification. We have demonstrated, via the synthesis of dendritic macromolecules based on 3,5-dihydroxybenzyl alcohol (**1**), that the "convergent" approach can be realized in practice. The two-step procedure, dialkylation of monomer **1** followed by conversion of the hydroxymethyl group to the corresponding bromomethyl group, was optimized and proved to be highly efficient; yields of over 80% were routinely obtained for the two-step procedure up to generation 4, decreasing to 72% for generation 5, and decreasing to 56% for generation 6. An apparent limitation of the "convergent" approach is in its susceptibility to steric inhibition; as the macromolecules become larger, the functional group at the focal point becomes "masked" by the growing macromolecule and its reactivity is lessened. This problem may be even less significant with monomers that possess more flexible geometries; we are currently exploring the use of several new monomers that do not contain rigid aromatic rings and may lead to even larger monodispersed hyperbranched macromolecules. However, this study involving monomer **1** indicates that the "convergent" approach has a number of advantages at lower

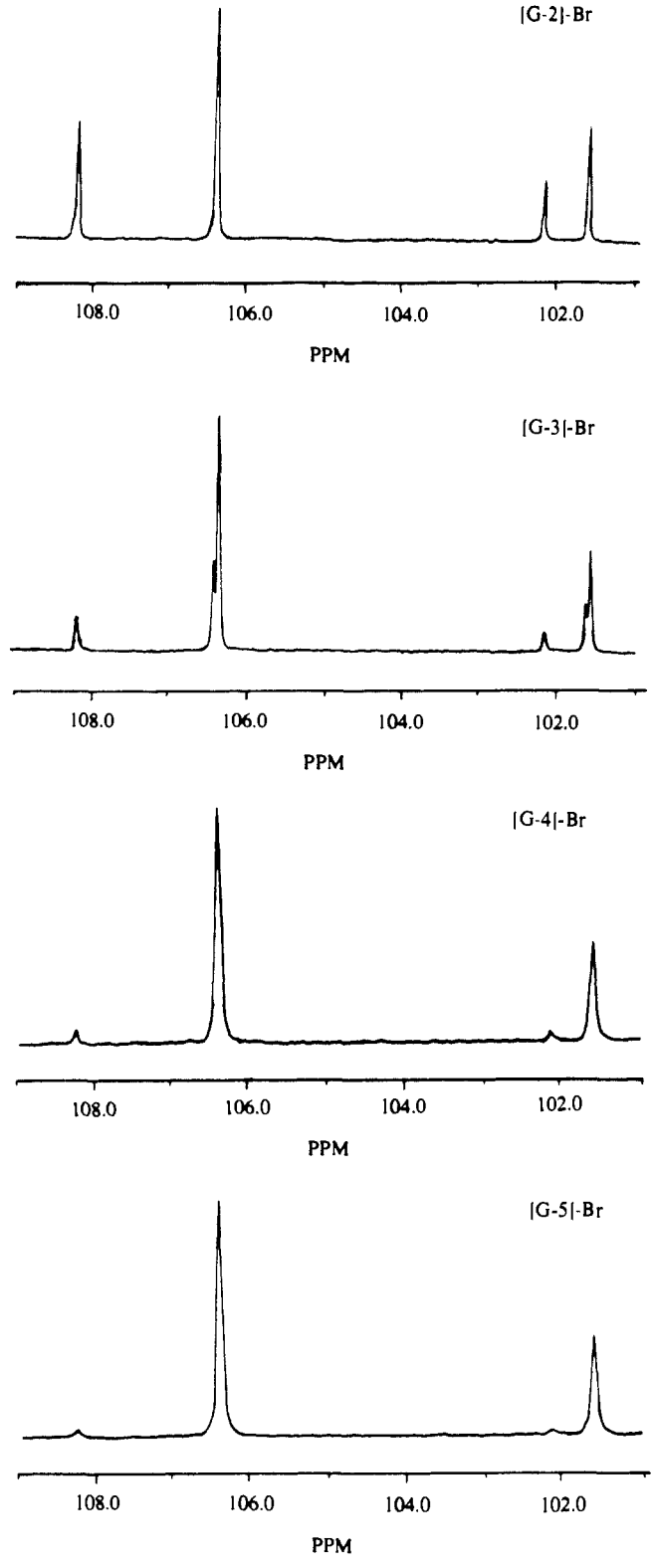


Figure 3. Comparison of 75-MHz ^{13}C NMR spectra for various generation bromides from [G-2]-Br to [G-5]-Br in the region 101–109 ppm.

molecular weights (<50 000), while the "divergent" approach is superior in its ability to reach higher molecular weights. Characterization of the consecutive dendritic wedge and macromolecules is both reliable and sensitive to impurities and defects. A combination of ^{1}H and ^{13}C NMR and SEC allowed every product to be fully characterized and the absence of starting materials or side products to be demonstrated. Mass spectra and LALLS have provided confirmation of the nominal molecular weights for the lower and higher molecular weight products, respectively. Further work in progress in this laboratory will demonstrate the applicability of the convergent growth technique to the preparation

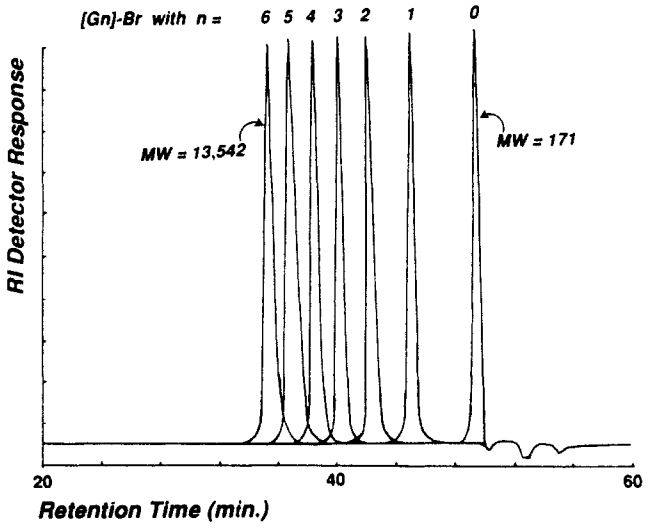


Figure 4. Overlay of SEC traces for dendritic bromides from [G-0] to [G-6]. The *nominal* molecular weight values are shown.

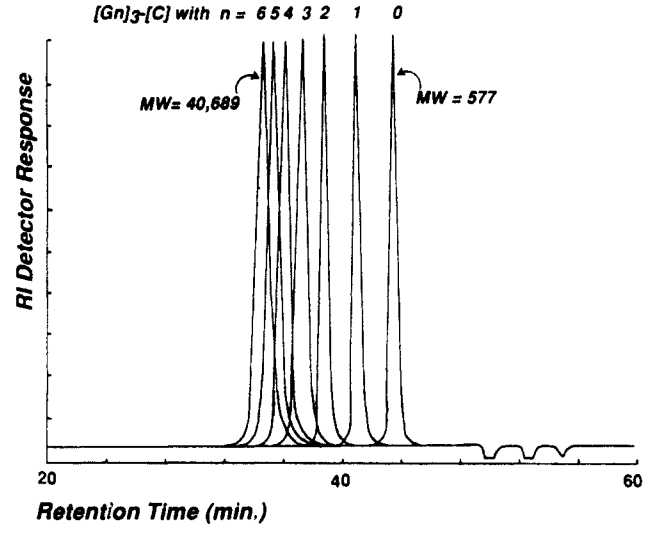


Figure 5. Overlay of SEC traces for the trialkylated cores $[Gn]_3$-[C]. The *nominal* molecular weight values are shown.

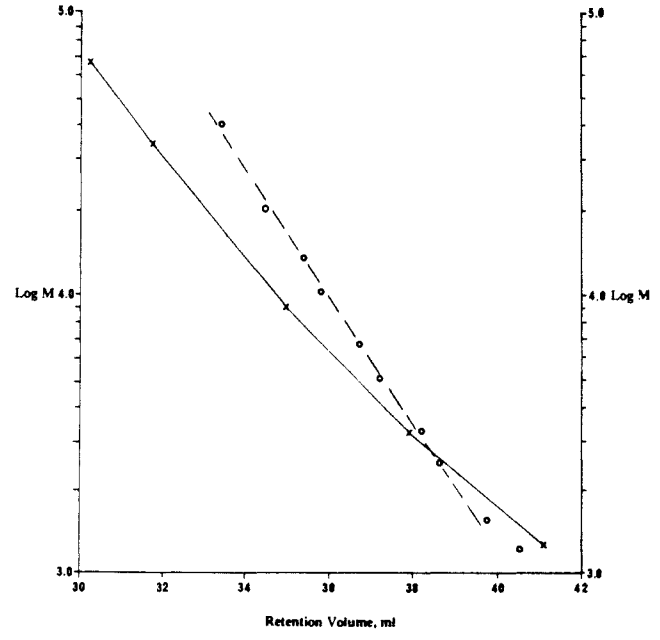


Figure 6. Semilogarithmic plot of SEC weight average molecular weight vs retention volumes for polystyrene standards (×) and dendritic polyether macromolecles (○).

of highly unsymmetrical dendritic macromolecules, an area where the convergent approach provides unmatched control over molecular architecture.

Experimental Section

General Directions. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet 1R/44 spectrophotometer as thin films on NaCl disks. ^{1}H NMR spectra were recorded on solutions in $CDCl_3$ on a Bruker WM 300 (300-MHz) spectrometer with the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 75 MHz on a Bruker WM300 spectrometer with $CDCl_3$ as the solvent and the solvent carbon signal as internal standard. Mass spectra were obtained on a Kratos MS890 with either El or FAB ionization; the latter were run with 3-nitrobenzyl alcohol as the matrix. Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230–400 mesh). Size-exclusion chromatography was carried out on a IBM LC/9560 chromatograph connected to a Milton Roy refractoMonitor 1V refractive index detector; data analysis was performed by an IBM System 9000 computer. Five 10-μm IBM GPC/SEC columns (300 × 7.7 mm) connected in series in order of decreasing pore size (IBM types B–F) were used with THF as solvent. The following abbreviations are used: Ar refer to aromatic rings derived from monomer **1**, Ph refers to aromatic rings derived from benzyl bromide, and Ar′ refers to aromatic rings derived from the core molecule **19**.

General Procedure for the Synthesis of Dendritic Benzyl Alcohols. A mixture of the appropriate dendritic benzyl bromide (2.00 equiv), 3,5-dihydroxybenzyl alcohol (**1**) (1.00 equiv), dried potassium carbonate (2.50 equiv), and 18-crown-6 (0.2 equiv) in dry acetone was heated at reflux and stirred vigorously under nitrogen for 48 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between water and CH_2Cl_2 and the aqueous layer extracted with CH_2Cl_2 (3×). The combined organic layers were then dried and evaporated to dryness. The crude product was purified as outlined in the following text.

General Procedure for the Synthesis of Dendritic Benzyl Bromides. To a mixture of the appropriate dendritic benzyl alcohol (1.00 equiv) and carbon tetrabromide (1.25 equiv) in the minimum amount of dry tetrahydrofuran required to disolve the above reagents was added triphenylphosphine (1.25 equiv), and the reaction mixture was stirred under nitrogen for 20 min. For the latter generations (4–6), larger excesses of CBr_4 and PPh_3 (2.5-, 5.0-, and 10.0-fold, respectively) were required to force the reaction to completion; these were added in 1.25-equiv amounts at 10-min intervals until TLC showed no starting material. The reaction mixture was then poured into water and extracted with CH_2Cl_2 (3×); the combined extracts were dried and evaporated to dryness. The crude product was then purified as outlined in the following text.

[G-2]-OH (9). This was prepared from [*G*-1]-Br[11] (**8**) and purified by recrystallization from 3:1 toluene/hexane to give **9** as a white crystalline solid: yield 91%; mp 110–111 °C; IR 1600, 1430, 1365, 1160, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.62 (d, 2 H, *J* = 6 Hz, C*H*$_2$OH), 4.97 (s, 4 H, ArC*H*$_2$O), 5.02 (s, 8 H, PhC*H*$_2$O), 6.52 (t, 1 H, *J* = 2 Hz, Ar*H*), 6.57 (t, 2 H, *J* = 2 Hz, Ar*H*), 6.59 (d, 2 H, *J* = 2 Hz, Ar*H*), 6.67 (d, 4 H, *J* = 2 Hz, Ar*H*), 7.29–7.42 (m, 20 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 65.29 (*C*H$_2$OH), 69.93, 70.10 (*C*H$_2$O), 101.32, 101.54, 105.74, 106.33 (Ar *C*), 127.54, 127.99, 128.57 (Ph *C*H), 136.75, 137.26, 143.40, 160.05, 160.15 (Ar and Ph *C*); mass spectrum (FAB), *m*/*z* 744. Anal. Calcd for $C_{49}H_{44}O_7$: C, 79.01; H, 5.95. Found: C, 78.86; H: 6.25.

[G-2]-Br (10). This was prepared from [G-2]-OH (**9**) and purified by recrystallization from 4:1 toluene/hexane to give **10** as a white crystalline solid: yield 93%; mp 129–130.5 °C; IR 1595, 1435, 1370, 1160, 1075 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.41 (s, 2 H, C*H*$_2$Br), 4.97 (s, 4 H, ArC*H*$_2$O), 5.04 (s, 8 H, PhC*H*$_2$O), 6.53 (t, 1 H, *J* = 2 Hz, Ar*H*), 6.59 (t, 2 H, *J* = 2 Hz, Ar*H*), 6.63 (d, 2 H, *J* = 2 Hz, Ar*H*), 6.68 (d, 4 H, *J* = 2 Hz, Ar*H*), 7.30–7.44 (m, 20 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 33.57 (*C*H$_2$Br), 69.98, 70.08 (*C*H$_2$O), 101.60, 102.16, 106.35, 108.16 (Ar *C*), 127.53, 127.99, 128.56 (Ph *C*H), 136.71, 139.00, 139.73, 159.92, 160.14 (Ar and Ph *C*); mass spectrum (FAB), *m*/*z* 806/808 (ca. 1:1). Anal. Calcd for $C_{49}H_{43}BrO_6$: C, 72.86; H, 5.36. Found: C, 73.00; H, 5.36.

[G-3]-OH (11). This was prepared from [G-2]-Br (**10**) and purified by flash chromatography, eluting with CH_2Cl_2 to give **11** as a colorless glass: yield 88%, IR 1595, 1470, 1370, 1165, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.57 (d, 2 H, *J* = 6 Hz, C*H*$_2$OH), 4.94 (s, 12 H, ArC*H*$_2$O), 5.00 (s, 16 H, PhC*H*$_2$O), 6.36 (m, 3 H, Ar*H*), 6.39 (t, 4 H, *J* = 2 Hz, Ar*H*), 6.42 (d, 2 H, *J* = 2 Hz, Ar*H*), 6.48 (d, 4 H, *J* = 2 Hz, Ar*H*), 6.50 (d, 8 H, *J* = 2 Hz, Ar*H*), 7.27–7.41 (m, 40 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 65.09 (*C*H$_2$OH), 69.83, 69.88, 70.01 (*C*H$_2$O), 101.15, 101.52, 105.64, 106.31 (Ar *C*), 127.50, 127.93, 128.51 (Ph *C*H), 136.68, 139.17, 139.26, 143.50, 159.97, 160.07 (Ar and Ph *C*); mass spectrum (FAB), *m*/*z* 1592,

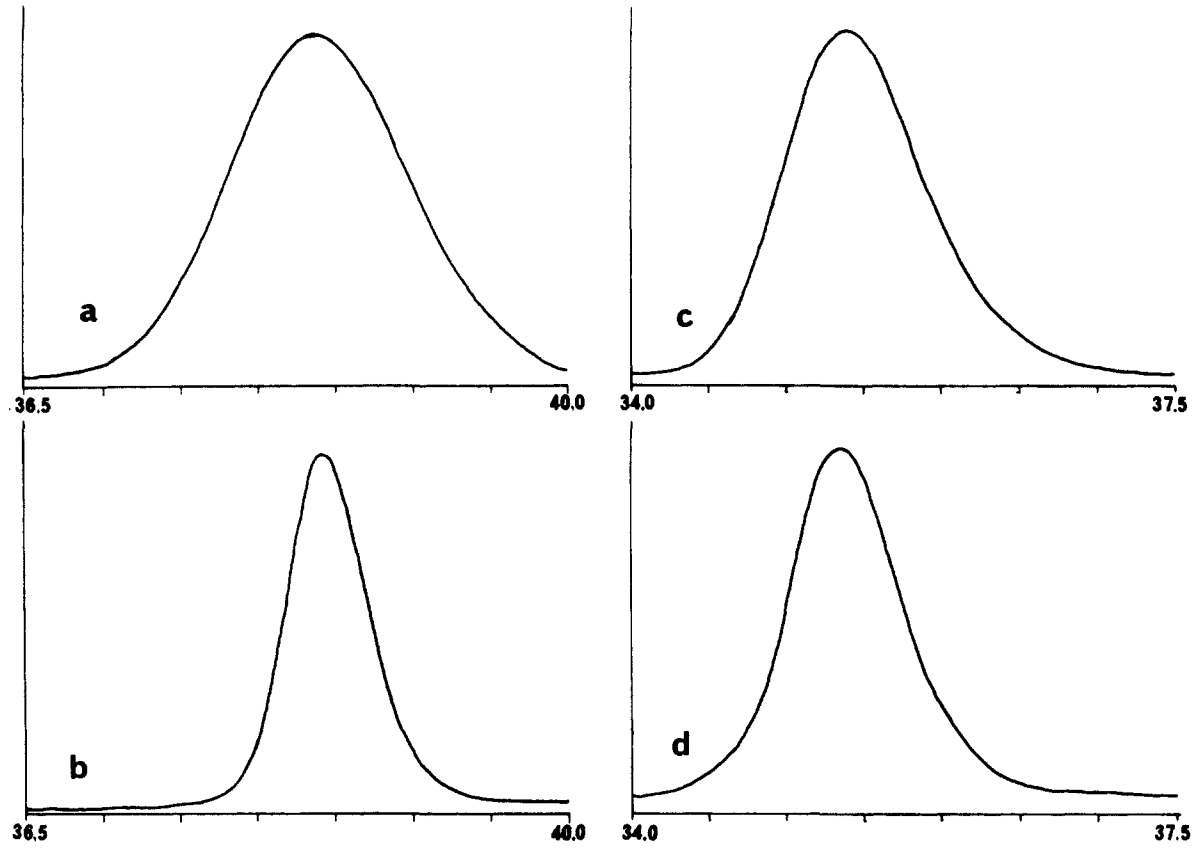


Figure 7. Comparison of polydispersities of dendritic macromolecules and narrow distribution polystyrene standards: (a) polystyrene, M_w/M_n = 1.05, M_n = 3250; (b) [G-4]-OH, with nominal M_n = 3,291; (c) polystyrene, M_w/M_n = 1.03, M_n = 11 700; (d) [G-5]$_3$-[C], with nominal M_n = 20 314.

1593. Anal. Calcd for $C_{105}H_{92}O_{15}$: C, 79.12; H, 5.82. Found: C, 79.02; H, 5.96.

[G-3]-Br (12). This was prepared from [G-3]-OH (**11**) and purified by flash chromatography, eluting with 1:1 hexane/CH_2Cl gradually increasing to 1:5 hexane/CH_2Cl_2; the product was then precipitated into ether (300 mL) from CH_2Cl_2 (minimum amount) to give **12** as a colorless glass: yield 90%; IR 1600, 1460, 1370, 1170, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.36 (s, 2 H, CH_2Br), 4.93 (s, 4 H, ArCH_2O), 4.95 (s, 8 H, ArCH_2O), 5.00 (s, 16 H, PhCH_2O), 6.52 (m, 3 H, Ar*H*), 6.55 (t, 4 H, J = 2 Hz, Ar*H*), 6.60 (d, 2 H, J = 2 Hz, Ar*H*), 6.63 (d, 4 H, J = 2 Hz, Ar*H*), 6.65 (d, 8 H, J = 2 Hz, Ar*H*), 7.27–7.41 (m, 40 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 33.57 (CH_2Br), 69.96, 69.99, 70.07 (CH_2O), 101.56, 101.62, 102.15, 106.34, 106.41, 108.19 (Ar *C*), 127.53, 127.97, 128.55 (Ph CH), 136.73, 139.01, 139.16, 139.77, 159.93, 160.03, 160.13 (Ar and Ph C); mass spectrum (FAB), m/z 1655, 1656, 1657, 1658. Anal. Calcd for $C_{105}H_{91}BrO_{14}$: C, 76.12; H, 5.54. Found: C, 76.18; H, 5.72.

[G-4]-OH (13). This was prepared from [G-3]-Br (**12**) and purified by flash chromatography, eluting with CH_2Cl_2 gradually increasing to 1:19 ether/CH_2Cl_2 to give **13** as a colorless glass: yield 92%; IR 1595, 1470, 1360, 1170, 1065 cm^{-1}; ^{1} NMR ($CDCl_3$) δ 4.54 (d, 2 H, J = 6 Hz, CH_2OH), 4.93 (s, 28 H, ArCH_2O), 5.00 (s, 32 H, PhCH_2O), 6.53–6.57 and 6.63–6.67 (m, 42 H, Ar*H*), 7.29–7.42 (m, 80 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 64.99 (CH_2OH), 69.85, 69.95 (CH_2O), 101.09, 101.51, 105.66, 106.30 (Ar *C*), 127.46, 127.88, 128.47 (Ph *C*H), 136.69, 139.14, 139.18, 139.31, 143.51, 159.92, 159.96, 160.05 (Ar and Ph *C*). Anal. Calcd for $C_{217}H_{188}O_{31}$: C, 79.17; H, 5.76. Found: C, 79.22; H, 6.00.

[G-4]-Br (14). This was prepared from [G-4]-OH (**13**) and purified by flash chromatography, eluting with 1:1 hexane/CH_2Cl_2 gradually increasing to CH_2Cl_2; the product was then precipitated into ether from CH_2Cl_2 to give **14** as a colorless glass: yield 95%; IR 1600, 1470, 1360, 1170, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.36 (s, 2 H, CH_2Br), 4.92 and 4.95 (both s, 28 H, ArCH_2O), 5.01 (s, 32 H, PhCH_2O), 6.48–6.52 (m, 7 H, Ar*H*), 6.53 (t, 8 H, J = 2 Hz, Ar*H*), 6.57 (d, 2 H, J = 2 Hz, Ar*H*), 6.62–6.65 (m, 28 H, Ar*H*), 7.29–7.43 (m, 80 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 33.54 (CH_2Br), 69.90, 69.99 (CH_2O), 101.55, 102.09, 106.33, 108.22 (Ar *C*), 127.48, 127.91, 128.50 (Ph *C*H), 136.72, 139.06, 139.17, 139.71, 159.67, 159.99, and 160.09 (Ar and Ph *C*). Anal. Calcd for $C_{217}H_{187}BrO_{30}$: C, 77.70; 5.61. Found: C, 77.97; H, 5.66.

[G-5]-OH (15). This was prepared from [G-4]-Br (**14**) and purified by flash chromatography, eluting with CH_2Cl_2 gradually increasing to 1:19 ether/CH_2Cl_2 to give **15** as a colorless glass: yield 85%; IR 1600, 1465, 1360, 1170, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.55 (br s, 2 H, CH_2OH), 4.97 (br s, 60 H, ArCH_2O), 5.04 (s, 64 H, PhCH_2O), 6.60–6.76 (m, 93 H, Ar*H*), 7.31–7.45 (m, 160 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 64.81 (CH_2OH), 69.74, 69.84 (CH_2O), 100.98, 101.42, 105.58, 106.23 (Ar *C*), 127.41, 127.83, 128.41 (Ph *C*H), 136.64, 139.11, 139.22, 139.31, 143.54, 159.79, 159.88, 159.97 (Ar and Ph *C*). Anal. Calcd for $C_{441}H_{380}O_{63}$: C, 79.20; H, 5.73. Found: C, 79.21; H, 5.91.

[G-5]-Br (16). This was prepared from [G-5]-OH (**15**) and purified by flash chromatography, eluting with 1:2 hexane/CH_2Cl_2 gradually increasing to CH_2Cl_2; the product was then precipitated into ether from CH_2Cl_2 to give **16** as a colorless glass: yield 83%; IR 1600, 1470, 1360, 1165, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.35 (s, 2 H, C*H2Br*), 4.96 (br s, 62 H, ArCH_2O), 5.02 (s, 64 H, PhCH_2O), 6.60–6.75 (m, 93 H, Ar*H*), 7.30–7.44 (m, 160 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 33.52 (CH_2Br), 69.76, 69.86 (CH_2O), 101.43, 101.97, 106.24, 108.14 (Ar *C*), 127.42, 127.83, 128.42 (Ph *C*H), 136.65, 139.02, 139.11, 139.19, 159.75, 159.89, 159.99 (Ar and Ph *C*). Anal. Calcd for $C_{441}H_{379}BrO_{62}$: C, 78.4; H, 5.66. Found: C, 78.0; H, 5.76.

[G-6]-OH (17). This was prepared from [G-5]-Br (**16**) and purified by flash chromatography, eluting with CH_2Cl_2 gradually increasing to 1:19 ether/CH_2Cl_2 to give **17** as a colorless glass: yield 78%; IR 1595, 1470, 1360, 1170, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.55 (br s, 2 H, CH_2OH), 4.99 (br s, 124 H, ArCH_2O), 5.06 (br s, 128 H, PhCH_2O), 6.60–6.75 (m, 189 H, Ar*H*), 7.35–7.49 (m, 320 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 64.8 (CH_2OH), 69.74, 69.90 (CH_2O), (peak too small to observe), 101.44, 105.60, 106.24 (Ar *C*), 127.41, 127.84, 128.40 (Ph *C*H), 136.67, 139.10, 139.20, 139.31, 143.55, 159.75, 159.87, 160.00 (Ar and Ph *C*). Anal. Calcd for $C_{889}H_{764}O_{127}$: C, 79.21; H, 5.71. Found: C, 79.11; H, 5.77.

[G-6]-Br (18). This was prepared from [G-6]-OH (**17**) and purified by flash chromatography, eluting with 1:2 hexane/CH_2Cl_2 gradually increasing to CH_2Cl_2; the product was then precipitated into ether from CH_2Cl_2 to give **18** as a colorless glass: yield 72%; IR 1600, 1470, 1360, 1170, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.37 (s, 2 H, CH_2Br), 5.00 (br s, 124 H, ArCH_2O), 5.08 (s, 128 H, PhCH_2O), 6.61–6.78 (m, 189 H, Ar*H*), 7.30–7.46 (m, 320 H, Ph*H*); ^{13}C NMR ($CDCl_3$) δ 33.50 (CH_2Br), 69.85, 69.95 (CH_2O), (peak too small to observe), 102.02, 106.28, 108.19 (Ar *C*), 127.46, 127.89, 128.47 (Ph *C*H), 136.69, 139.02, 139.15, 139.40, 159.70, 159.93, 160.03 (Ar and Ph *C*). Anal. Calcd for $C_{889}H_{763}BrO_{126}$: C, 78.84; H, 5.68. Found: C, 78.96; H, 5.70.

General Procedure for the Synthesis of Dendritic Trialkylated Core Molecules. A mixture of the appropriate dendritic benzyl bromide (3.10 equiv), 1,1,1-tris(4′-hydroxyphenyl)ethane (**19**) (1.00 equiv), dried po-

tassium carbonate (4.0 equiv), and 18-crown-6 (0.3 equiv) in dry acetone was heated at reflux and stirred vigorously under nitrogen for 48 h; 1,1,1-tris(4′-hydroxyphenyl)ethane (**19**) (5–30 equiv) was then added, and stirring and heating were continued for 24 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between water and CH_2Cl_2, the aqueous layer was extracted with CH_2Cl_2 (3×), and the combined organic layers were then dried and evaporated to dryness. The crude product was purified as outlined in the following text.

1,1,1-Tris(4′-benzyloxyphenyl)ethane [G-0]$_3$-[C] (22). This was prepared from benzyl bromide and purified by flash chromatography eluting with 1:4 hexane/CH_2Cl_2 to give **22** as a colorless oil: yield 87%; IR 1610, 1505, 1240, 1170, 1000, 820, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3 H, CH_3), 4.98 (s, 6 H, CH_2O), 6.84 (d, 6 H, J = 9 Hz, core Ar′H), 6.98 (d, 6 H, J = 9 Hz, core Ar′H), 7.27–7.41 (m, 15 H, PhH); ^{13}C NMR ($CDCl_3$) δ 30.73 (*C*H$_3$), 50.59 (*C*CH$_3$), 69.91 (PhCH$_2$O), 113.92 (Ar′ *C*), 127.47, 127.87, 128.51 (Ph *C*H), 129.59, 137.08, 141.97, 156.81 (Ar′ and Ph *C*); mass spectrum (EI), m/z 576. Anal. Calcd for $C_{41}H_{36}O_3$: C, 85.38; H, 6.30. Found: C, 85.10; H, 6.42.

[G-1]$_3$-[C] (23). This was prepared from [G-1]-Br (**8**) and purified by flash chromatography eluting with 1:4 hexane/CH_2Cl_2 to give **23** as a colorless gum: yield 91%; IR 1600, 1470, 1365, 1170, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 3 H, CH_3), 4.91 (s, 6 H, ArCH_2O), 4.99 (s, 12 H, PhCH_2O), 6.55 (t, 3 H, J = 2 Hz, ArH), 6.66 (d, 6 H, J = 2 Hz, ArH), 6.82 (d, 6 H, J = 9 Hz, core Ar′H), 6.97 (d, 6 H, J = 9. Hz, core Ar′H), 7.27–7.41 (m, 30 H, PhH); ^{13}C NMR ($CDCl_3$) δ 30.71 (*C*H$_3$), 50.59 (*C*CH$_3$), 69.84 (Ar*C*H$_2$O), 70.02 (Ph*C*H$_2$O), 101.46, 106.33 (Ar *C*), 113.96 (core Ar′ *C*), 127.50, 127.95, 128.53 (Ph *C*H), 129.59 (core Ar′ *C*), 136.72, 139.56, 142.00, 156.71, 160.09 (Ar, Ar′, and Ph *C*); mass spectrum (FAB), m/z 1212, 1213. Anal. Calcd for $C_{83}H_{72}O_9$: C, 82.15; H, 6.00. Found: C, 82.04; H, 6.10.

[G-2]$_3$-[C] (24). This was prepared from [G-2]-Br (**12**) and purified by flash chromatography, eluting with 1:3 hexane/CH_2Cl_2 to give **24** as a colorless glass: yield 89%; IR 1595, 1470, 1360, 1170, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 3 H, CH_3), 4.92, 4.94 (each s, 18 H, ArCH_2O), 5.02 (s, 24 H, PhCH_2O), 6.52 (t, 3 H, J = 2 Hz, ArH), 6.55 (t, 6 H, J = 2 Hz, ArH), 6.64 (d, 6 H, J = 2 Hz, ArH), 6.66 (d, 12 H, J = 2 Hz, ArH), 6.83 (d, 6 H, J = 9 Hz, core Ar′H), 6.97 (d, 6 H, J = 9 Hz, core Ar′H), 7.27–7.41 (m, 60 H, PhH); ^{13}C NMR ($CDCl_3$) δ 30.76 (*C*H$_3$), 50.61 (*C*CH$_3$), 69.86, 69.93, 70.04 (Ar and PhCH$_2$O), 101.54, 106.35, 106.41 (Ar *C*), 113.97 (Core Ar′ *C*), 127.50, 127.95, 128.53 (Ph *C*H), 129.61 (Core Ar′ *C*), 136.72, 139.19, 139.53, 142.04, 156.73, 160.00, 160.12 (Ar, Ar′, and Ph *C*). Anal. Calcd for $C_{167}H_{144}O_{21}$: C, 80.65; H, 5.83. Found: C, 80.89; H, 6.00.

[G-3]$_3$-[C] (25). This was prepared from [G-3]-Br (**12**) and purified by flash chromatography, eluting with 1:3 hexane/CH_2Cl_2 to give **25** as a colorless glass: yield 84%; IR 1600, 1470, 1360, 1170, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 3 H, CH_3), 4.91, 4.94 (each s, 42 H, ArCH_2O), 5.00 (s, 48 H, PhC*H2O*), 6.51–6.55, 6.63–6.66 (m, 63 H, ArH), 6.80 (d, 6 H, J = 9 Hz, Core Ar′H), 6.95 (d, 6 H, J = 9 Hz, core Ar′H), 7.27–7.41 (m, 120 H, PhH); ^{13}C NMR ($CDCl_3$) δ 30.70 (*C*H$_3$), 50.64 (*C*CH$_3$), 69.96, 70.06 (Ar and PhCH$_2$O), 101.59, 106.36, 106.46 (Ar *C*), 113.99 (core Ar′ *C*), 127.52, 127.96, 128.54 (Ph *C*H), 129.63 (Core Ar′ *C*), 136.76, 139.20, 139.57, 142.06, 156.75, 160.04 160.13 (Ar, Ar′, and Ph *C*). Anal. Calcd for $C_{335}H_{288}O_{45}$: C, 79.93; H, 5.76. Found: C, 79.89; H, 5.90.

[G-4]$_3$-[C] (20). This was prepared from [G-4]-Br (**14**) and purified by flash chromatography, eluting with 1:3 hexane/CH_2Cl_2 to give **20** as a colorless glass: yield 84%; IR 1600, 1470, 1360, 1170, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3 H, CH_3), 4.92 (s, 90 H, ArCH_2O), 4.99 (s, 96 H, PhCH_2O), 6.50–6.55, 6.62–6.66 (m, 135 H, ArH), 6.82 (d, 6 H, J = 9 Hz, core Ar′H), 6.97 (d, 6 H, J = 9 Hz, core Ar′H), 7.27–7.42 (m, 240 H, PhH); ^{13}C NMR ($CDCl_3$) δ 30.50 (*C*H$_3$), 50.60 (*C*-CH$_3$), 69.89, 69.99 (Ar and PhCH$_2$O), 101.56, 106.33, 106.45 (Ar *C*), 113.97 (Core Ar′ *C*), 127.50, 127.91, 128.50 (Ph *C*H), 129.60 (Core Ar′ *C*), 136.76, 139.21, 139.54, 142.01, 156.73, 160.00, 160.09 (Ar, Ar′, and Ph *C*). Anal. Calcd for $C_{671}H_{576}O_{93}$ requires C, 79.57; H, 5.75. Found: C, 79.29; H, 6.05.

[G-5]$_3$-[C] (21). This was prepared from [G-5]-Br (**16**) and purified by flash chromatography, eluting with 1:3 hexane/CH_2Cl_2 to give **21** as a colorless glass: yield 76%; IR 1600, 1465, 1365, 1170, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 3 H, CH_3), 4.91 and 5.00 (each br s, 384 H, ArCH_2O and PhCH_2O), 6.51–6.66 (m, 273 H, ArH), 6.82 (d, 6 H, J = 9 Hz, core Ar′H), 6.96 (d, 6 H, J = 9 Hz, core Ar′H), 7.27–7.43 (m, 480 H, PhH); ^{13}C NMR ($CDCl_3$) δ (peak too small to observe) (*C*H$_3$), 50.59 (*C*CH$_3$), 69.76 69.85 (Ar and PhCH$_2$O), 101.44, 106.25, (peak too small to observe) (Ar *C*), 113.81 (core Ar′ *C*), 127.46, 127.86, 128.44 (Ph *C*H), 129.59 (core Ar′ *C*), 136.69, 139.14 (peak too small to observe), 141.95, 156.72, 159.91, 159.99 (Ar, Ar′, and Ph *C*). Anal. Calcd for $C_{1343}H_{1152}O_{189}$: C, 79.40; H, 5.71. Found: C, 79.17; H. 5.62.

[G-6]$_3$-[C] (26). This was prepared from [G-6]-Br (**18**) and purified by flash chromatography, eluting with 1:3 hexane/CH_2Cl_2 to give **26** as a colorless glass: yield 51%; IR 1600, 1470, 1360, 1170, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.04 (s, 3 H, CH_3), 4.93 and 4.99 (each s, 762 H, ArCH_2O and PhCH_2O), 6.51–6.70 (m, 567 H, ArH), 6.80 (d, 6 H, J = 9 Hz, core Ar′H), 6.99 (d, 6 H, J = 9 Hz, core Ar′H), 7.27–7.44 (m, 960 H, PhH); ^{13}C NMR ($CDCl_3$) δ (peaks too small to observe), 69.95, 70.07 (Ar and PhCH$_2$O), (peak too small to observe), 106.36, 106.46 (Ar *C*), 113.99 (core Ar′ *C*), 127.53, 127.90, 128.59 (Ph *C*H), 129.65 (core Ar′ *C*), 136.79, 139.25, 139.55, 142.09, 156.77, 159.96, 160.03 (Ar, Ar′ and Ph *C*). Anal. Calcd for $C_{2687}H_{2304}O_{381}$: C, 79.31; H, 5.70. Found: C, 79.24; H, 5.85.

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