Unusual Macromolecula Architectures: The Convergent Growth Approach to Dendritic Polyesters and Novel Block Copolymers

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Abstract: A versatile approach to dendritic polyesters and their use in the preparation of two different types of novel macromolecular architectures represent dendritic block copolymers is described. The chemistry developed for the synthesis of dendritic polyesters involves generation growth through an esterification step using dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) followed by activation of the focal point through removal of its trichloroethyl ester group with zinc in acetic acid. Unusual globular block architectures are then obtained by the controlled placement of different ether and ester chemistries in radial or concentric fashion around a central polyfunctional core. Therefore, a dendritic *segment-block* copolymer is obtained through the attachment of radially alternating dendritic segments incorporating polyester and polyether chemistry to the polyfunctional core. Similarly, a dendritic *layer-block* is obtained by the concentric alternation of ether- and ester-linked layers in the preparation of the dendritic fragments that are finally coupled to the core moiety. The monomer unit used for the preparation of ether-linked fragments was 3,5-dihydroxybenzyl alcohol, while 2,2,2-trichloroethyl 3,5-dihydroxybenzoate was used for the ester-linked fragments. Analysis of the new block copolymers by NMR spectrometry and size-exclusion chromatography suggests that they are pure and monodispersed. In the absence of large differences in the nature of their chain ends, the glass transition temperatures for the various block copolymers appear to be controlled only by the relative proportion of the ether and ester building blocks rather than by the exact geometry.

Introduction

Increasingly important considerations in polymer science are the improvement of polymer properties through the accurate control of macromolecular architecture. The preparation of highly defined dendritic macromolecules by the convergent growth or the starburst (divergent growth) approaches has been well documented.[1-5] These dendritic macromolecules have a unique architecture which is characterized by a high degree of branching that originates from a central point, a branch point at each monomer unit, and a large number of chain ends or "surface" functional groups. Due to these factors, globular, three-dimensional, structures are obtained which possess new and unusual characteristics such as the absence of the classical entanglements found in linear polymers and a bell-shaped relationship between viscosity and molecular weight.[1,6] The convergent growth approach has also been demonstrated[7] to have a high degree of control over the number and placement of functional groups at the periphery (or chain ends) of the dendritic macromolecules. However, the synthetic blueprint of the convergent growth approach also allows precise control over the monomer units in the interior of the dendritic macromolecule. These combined abilities permit the synthesis of novel dendritic *block* copolymers, which extend further the increasingly important fields of both dendritic macromolecules and block copolymers. Traditional block copolymers are important, since they often exhibit unique and useful properties in solution and in the solid state. This is a consequence of the general thermodynamic incompatibility of the blocks, which results in microphase separation and, depending on certain factors, the possibility of obtaining a variety of different morphologies.[8] Traditional block copolymers are normally composed of *linear* blocks; however, due to the three-dimensional globular nature of dendritic macromolecules, there are a number of different architectures which can result in dendritic *block* copolymers. This study describes the extension of the convergent growth approach to the synthesis of dendritic polyesters and the subsequent combination of this ester chemistry with ether chemistry in the production of two novel macromolecular architectures. Dendritic *segment-block* copolymers are characterized by a radial geometry in which dendritic segments of differing chemistry emanate from a polyfunctional core as shown schematically in Figure 1. A different macromolecular architecture, dendritic *layer-block* copolymers, results from the placement of concentric layers of segments of differing chemistry around the central core moiety (Figure 1).

Results and Discussion

Dendritic Polyester Macromolecules. The synthesis of dendritic *segment-block* copolymers requires the preparation of dendritic fragments composed of different building blocks followed by coupling of these fragments to the same polyfunctional core. One dendritic fragment was chosen to be a polyether based on 3,5-dihydroxybenzyl alcohol which is prepared by the published[4] procedure. It was envisaged that the other dendritic fragment would incorporate polyester chemistry based on 3,5-dihydroxybenzoic acid and benzoate esters as chain ends. Taking into account the reactivity and chemistry used in the preparation of dendritic polyethers, a protection/deprotection strategy employing the trichloroethyl ester group, introduced by Woodward,[9] was employed. Deprotection can be achieved in high yield by reaction with zinc in glacial acetic acid, a process that is expected to leave

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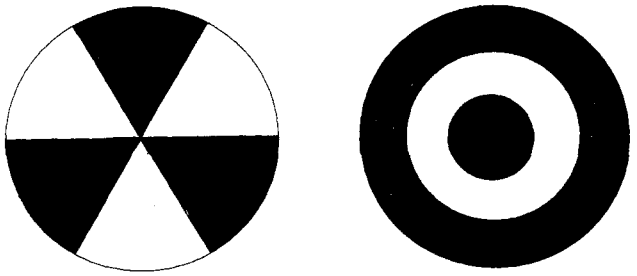

DENDRITIC SEGMENT-BLOCK COPOLYMER

DENDRITIC LAYER-BLOCK COPOLYMER

Figure 1. Graphical representation of dendritic *segment-block* and dendritic *layer-block* copolymers.

both the dendritic polyether and phenyl ester repeating units untouched. Therefore, the monomer unit chosen was 2,2,2-trichloroethyl 3,5-dihydroxybenzoate (**1**), which is prepared in 61% yield by reaction of 3,5-dihydroxybenzoic acid with a mixture of 2,2,2-trichloroethanol and concentrated sulfuric acid.

A key step in the synthesis of dendritic fragments is generation growth, which requires that the coupling step, in this case an esterification reaction, be optimized. Initially, standard chemistry was investigated as follows. Reaction of benzoyl chloride with the monomer unit **1** in the presence of 4-(dimethylamino)pyridine under a variety of conditions gave only poor yields of the first-generation ester **2**, contaminated by a number of side products. In order to overcome this, and avoid the added step of acid chloride formation, the direct coupling of the acid to the phenol was investigated. The condensation of benzoic acid with **1** in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)-pyridine (DMAP) under a variety of reaction conditions gave, at best, a 51% yield of **2** contaminated with a significant amount of the rearranged urea. As the formation of the urea is known to be favored at high pH, 4-(dimethylamino)pyridine was replaced by its *p*-toluenesulfonic acid salt,[10] as described by Moore and Stupp. Reaction of benzoic acid and **1** with DCC and 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) in tetrahydrofuran gave only a 54% yield of product; however, no trace of the urea side product was observed. Optimization of the reaction conditions showed that the solvent of choice was dichloromethane, which is surprising, since both benzoic acid and **1** are only very sparingly soluble in dichloromethane. Therefore addition of DCC to a mixture of benzoic acid, dihydroxybenzoate **1**, and DPTS in dichloromethane gave the desired first-generation ester **2** in 89% yield after chromatographic purification (Scheme I).

Activation of the trichloroethyl ester with zinc in glacial acetic acid gave only starting material due to the insolubility of **2**. Repetition of the reaction in a 1:1 mixture of tetrahydrofuran and glacial acetic acid resulted in removal of the trichloroethyl group to give the acid **3**, which was obtained in 92% yield after purification. Repetition of this two-step process gave the second-generation ester **4** and subsequently the corresponding acid **5** in 73% yield over both steps (Scheme I). Reaction of **5** with the monomer unit **1**, as above, gave a 71% yield of the third-generation trichloroethyl ester **6**, which was deprotected with zinc in HOAc/THF to give the acid **7** in 88% yield. The polyfunctional core molecule employed was 1,1,1-tris(4′-hydroxyphenyl)ethane (**8**), which allowed the same DCC/DPTS chemistry to be used for ester formation. Therefore coupling of 3.30 equiv of the acid **7** with 1 equiv of the core **8** in the presence of DCC and DPTS in dichloromethane gave the polyester dendrimer **9** in 72% yield after purification (Scheme II). After extension of the convergent growth approach to the synthesis of dendritic polyesters, the preparation of novel dendritic block copolymers was attempted.

Dendritic *Segment-Block* Macromolecules. The strategy for control of the location of the inner building blocks was similar to that employed in the synthesis of dendritic macromolecules with

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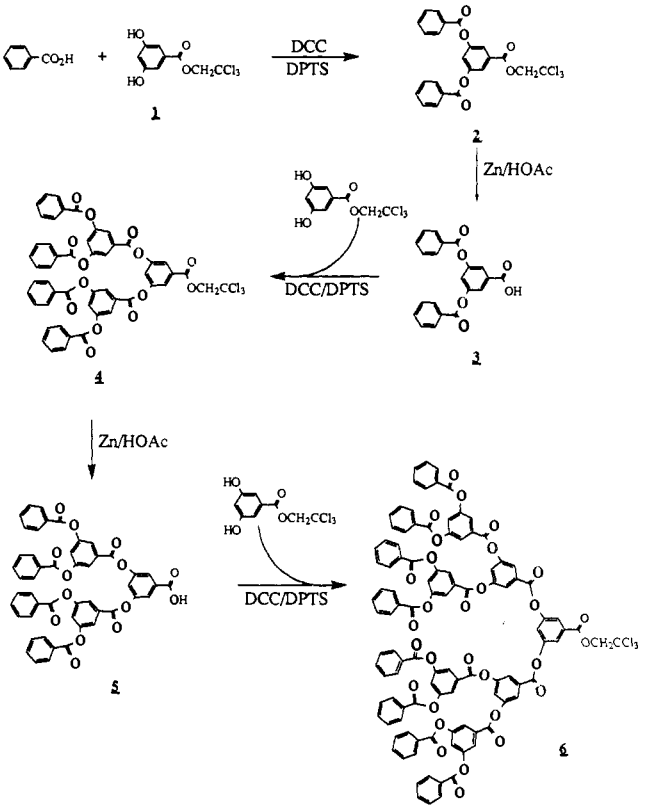
Scheme I



controlled surface functionalization.[11] By stepwise attachment of the different dendritic polyether and polyester fragments to the same monomer unit, a unique type of dendritic fragment can be prepared. After activation of the focal point and coupling of several hybrid ether/ester dendritic fragments to a polyfunctional core, a novel dendritic *segment-block* copolymer is obtained. It should be noted that the only requirements governing the choice of the different monomer units is that they be compatible with the reaction conditions used to couple the fragments to the monomer unit, and subsequently, the polyfunctional core molecule.

To obtain the hybrid ester/ether dendritic segment, the ester fragment was initially coupled to the monomer unit. Reaction of an excess of the monomer unit **1** with the acid **5** under the standard DCC/DPTS esterification conditions gave a mixture of the monophenol **10** and the diacylated derivative **11**. Purification by flash chromatography gave pure **10** in 60% yield. The second step required coupling of a dendritic ether fragment to the monophenolic polyester fragment **10**. However, reaction of **10** with the corresponding second-generation polyether bromide[4] **12** and potassium carbonate under various conditions resulted in a complex product mixture from which the target molecule could not be isolated. This is not a surprising result, since it has been shown that phenolic esters may be cleaved under the conditions used for the alkylation of phenols.[12] The synthetic strategy was then reversed, monomer unit **1** being monoalkylated with the polyether fragment **12** under standard conditions[11] to give the monophenol **13**. The polyester fragment **5**, containing a single acid functionality at its focal point, was then condensed with the monophenol **13** using DCC and DPTS to afford the copolymer **14** in 83% yield after purification (Scheme III). As defined by the synthetic blueprint, the copolymer **14** is itself a block copolymer having both an ether block and an ester block attached to the same, unique focal point monomer unit.

The presence of the trichloroethyl ester at the focal point of **14** allowed the same activation chemistry to be employed. Re-

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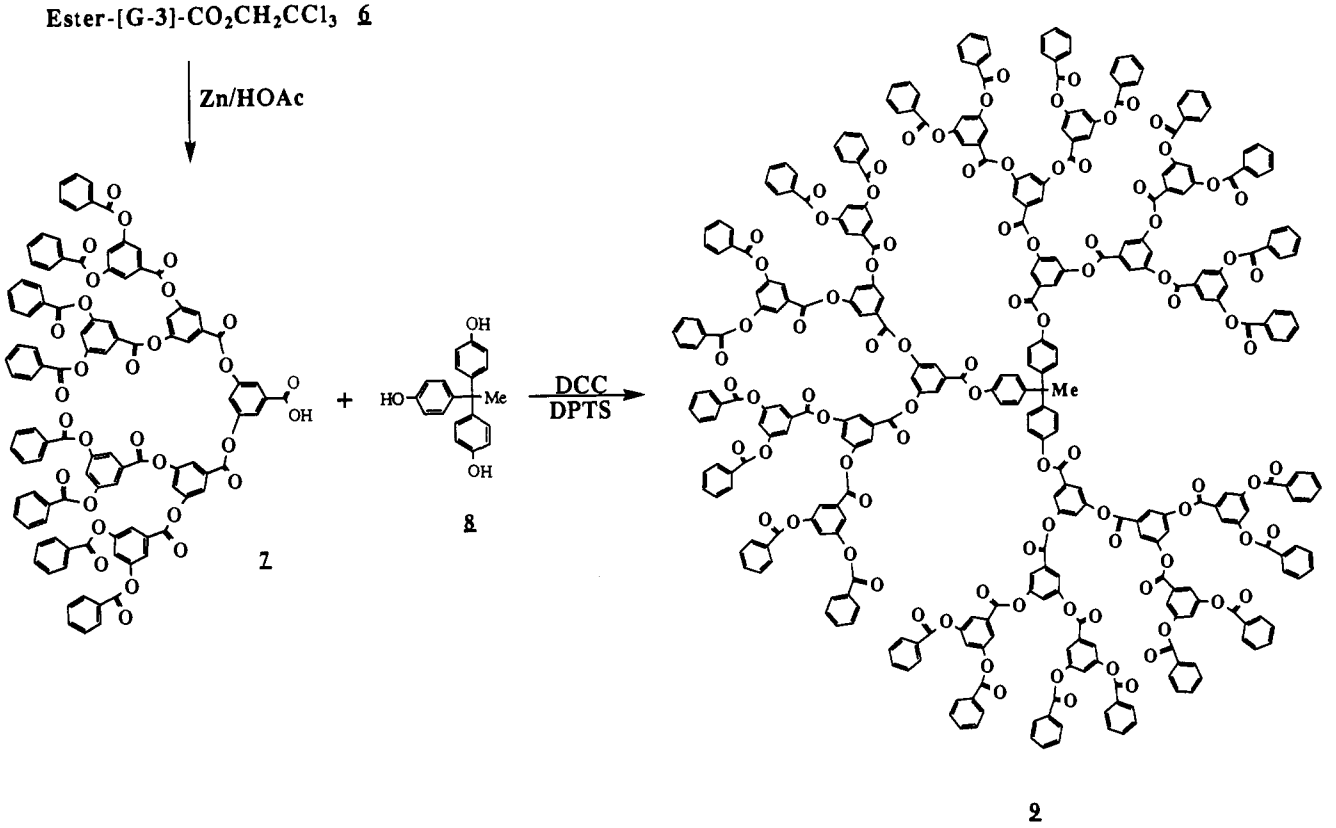
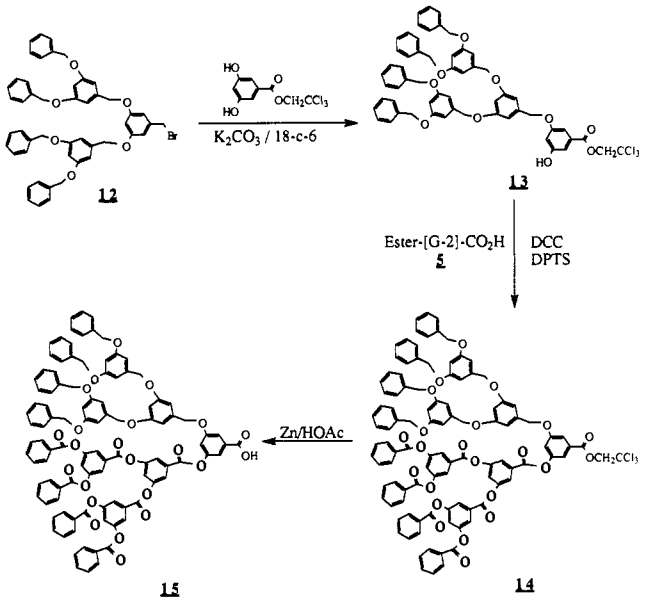
Scheme II



Scheme III



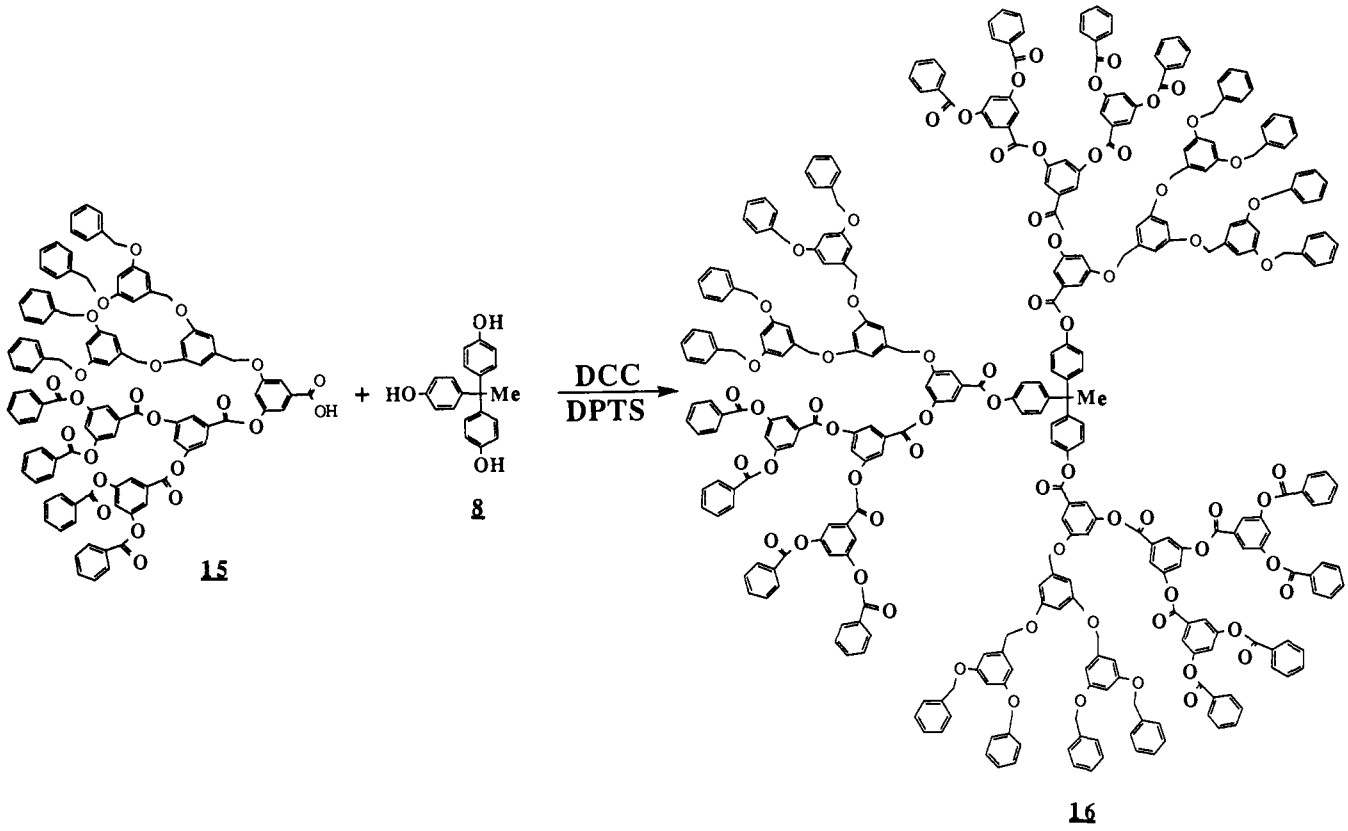
action of **14** with Zn gave the acid **15**, which could then be coupled with the polyfunctional core molecule, 1,1,1-tris(4′-hydroxyphenyl)ethane (**8**). Standard DCC/DPTS conditions led to the formation of ester bonds and gave the first example of a novel dendritic *segment-block* macromolecule **16** (nominal molecular formula $C_{335}H_{240}O_{69}$; nominal molecular weight 5370 amu) (Scheme IV). After purification by flash chromatography, **16** was obtained in 76% yield. Scheme IV shows a planar representation of one of the several possible conformations for the *segment-block* copolymer **16**. Conformations such as this in which several like fragments are in close proximity may be favored due to their lower energies, but numerous other conformations are possible due to free rotation about the many single bonds. However, constraints arising from the branching sequence do not allow a structural isomer where all three polyester fragments are adjacent.

The macromolecule **16** is the first example of a new class of dendritic *segment-block* copolymers. Only slight changes in the synthetic strategy allow a large number of different structures to be prepared where the number and/or size of the fragments can be greater or smaller, the same or different. The basic approach described above is the same in each case.

Dendritic *Layer-Block* Macromolecules. As shown in Figure 1, dendritic *layer-block* copolymers are characterized by concentric layers of different building blocks. Once again the convergent growth approach can be used to prepare these novel macromolecular architectures, the only requirement being that the chemistries associated with generation growth for the inner layers must be compatible with the existing outer layers. The monomer units chosen were 3,5-dihydrobenzyl alcohol and 2,2,2-trichloroethyl 3,5-dihydroxybenzoate (**1**). This leads to dendritic macromolecules composed of the same ether and ester building blocks as those in **16** above, but arranged in a totally different manner. The structure of dendritic *layer-block* macromolecules can be varied with respect to the width, number, and structure of the layers. For this study we chose to synthesize dendritic *layer-block* copolymers which had an outer ether layer and an inner ester layer.

Employing the convergent growth approach meant that the target for the outer ether layer was a low-generation dendritic ether fragment which could be successively attached to the monomer unit for the inner ester layers. Therefore the dendritic fragment used for the outer ether layer was the second-generation bromide **12**, prepared according to the previously published[4] procedures. Reaction of 2.10 equiv of **12** with the ester monomer unit **1** under the standard conditions for ether formation gave the third-generation polyether **17** in 85% yield after purification. The presence of the unique trichloroethyl ester at the focal point of **17** allows the chemistry of generation growth to be switched from ether to ester bond formation. Deprotection of **17** with zinc in acetic acid/tetrahydrofuran gave the acid **18**, which was condensed with the polyfunctional core **8** using DCC and DPTS to give the dendritic *layer-block* macromolecule **19** in 74% yield after purification by flash chromatography (Scheme V). The dendrimer

Scheme IV



15 8 16

19 has three outer layers of ether functional groups and only one inner layer of ester functional groups. Alternatively, **18** could be coupled with the monomer unit **1** in the presence of DCC and DPTS. Again this results in the formation of ester functional groups and gives the fourth-generation fragment **20**, containing both ether and ester linkages, in 78% yield. Removal of the trichloroethyl group with Zn in HOAc/THF yields the corresponding acid **21**. Coupling of **21** with the polyfunctional core **8** using DCC and DPTS gave the next generation dendritic *layer-block* macromolecule **22** in 71% yield after purification by flash chromatography (Scheme VI). The difference between the dendrimers **19** and **22** is that **22** has two inner concentric layers of ester functional groups compared to one for **19**. Both macromolecules have three outer concentric layers of ether functional groups.

The versatility of the convergent growth approach allows the size and number of blocks in dendritic *layer-block* macromolecules to be varied. A large number of macromolecular architectures are theoretically possible, the only requirement being compatibility of the dendritic fragments with the reaction conditions used for each respective generation growth step.

Characterization and Physical Properties of the Block Copolymers. The characterization of the ester and ether dendritic fragments required for the preparation of the *segment-block* copolymer **16** was performed using the techniques described previously.[4,9] Again a combination of ^1H and ^{13}C NMR spectroscopy, size-exclusion chromatography, and mass spectrometry proved to be invaluable in detecting impurities and defects. For the dendritic polyesters, the trichloroethyl group at the focal point provided unique resonances in the ^1H NMR spectrum at 4.98–5.00 ppm and in the ^{13}C NMR spectrum at ca. 74.50 and 94.60 ppm. Integration of the resonance due to the methylene protons and comparison to other resonances in the spectrum allowed the generation number of the fragment to be confirmed and any unreacted trichloroethyl ester to be readily detected. The large R_f difference between the fragments with an acid group at the focal point versus those with an ester group allowed easy purification and also helped confirm the absence of unreacted starting materials. As with the dendritic polyether macromolecules, coupling to the polyfunctional core could be readily detected, since discrete resonances were observed in both the ^1H and ^{13}C spectra for the core group. In addition, our earlier work in which one, two, or three dendritic fragments were coupled to a trifunctional core has demonstrated that these related macromolecules can easily be distinguished as well as separated by chromatographic techniques.[7]

On coupling of the different dendritic fragments to the monomer unit **1**, copolymers such as the fragments **14** and **15** or the *segment-block* macromolecule **16** are obtained. For these macromolecules, unique resonances in the ^1H and ^{13}C NMR spectra are observed for each block. The expanded 200-MHz ^1H NMR spectrum (from 3–9 ppm) of **16** is shown in Figure 2, and unique resonances are found for the ether block at 4.98–5.06, 6.53–6.56, and 6.68–6.74 ppm, for the ester block at 8.03–8.05 and 8.20–8.25 ppm, and for the core molecule at 7.11–7.13 ppm (also 2.25 ppm). These resonances confirm the attachment of the different blocks to the same polyfunctional core, and comparison of the integration data allows the relative number of each type of monomer unit to be determined, thus confirming the synthetic strategy. Complimentary information was obtained from the ^{13}C NMR spectra. Size-exclusion chromatograms for the dendritic *segment-block* macromolecule **16** were comparable in peak width to those for commercial polystyrene standard, and as was previously shown,[4,7] this is indicative of the monodisperse character of the dendrimers produced above.

Similar results were obtained for the dendritic *layer-block* macromolecules. When the second-generation ether block was attached to the monomer unit **1**, the resonances for the trichloroethyl group appeared in areas of the ^1H and ^{13}C NMR spectra that are not obscured by resonances for the ether block. Subsequent buildup of the ester layers could be readily followed by ^1H NMR; for the *layer-block* macromolecule **22** a triplet is observed at ca. 6.80 ppm due to the H-4 proton of a 3,5-bis(benzyloxy)benzoate building block, while a doublet is observed at ca. 7.95 ppm for the H-2 and H-6 protons of the corresponding 3,5-bis(benzoyloxy)benzoate building block (Figure 3). Therefore, the different layers of ester building blocks can be distinguished and the relative number of ether and ester building blocks de-

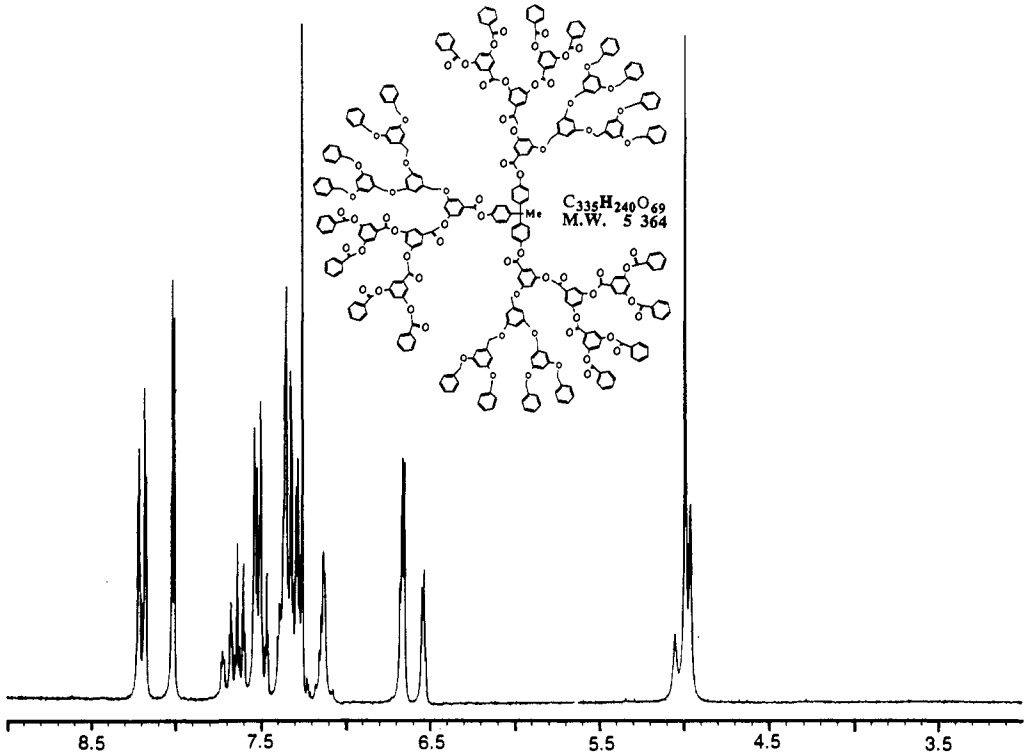


Figure 2. 200-MHz ^{1}H NMR spectrum (3.0–9.0 ppm) of the dendritic *segment-block* macromolecule **16**.

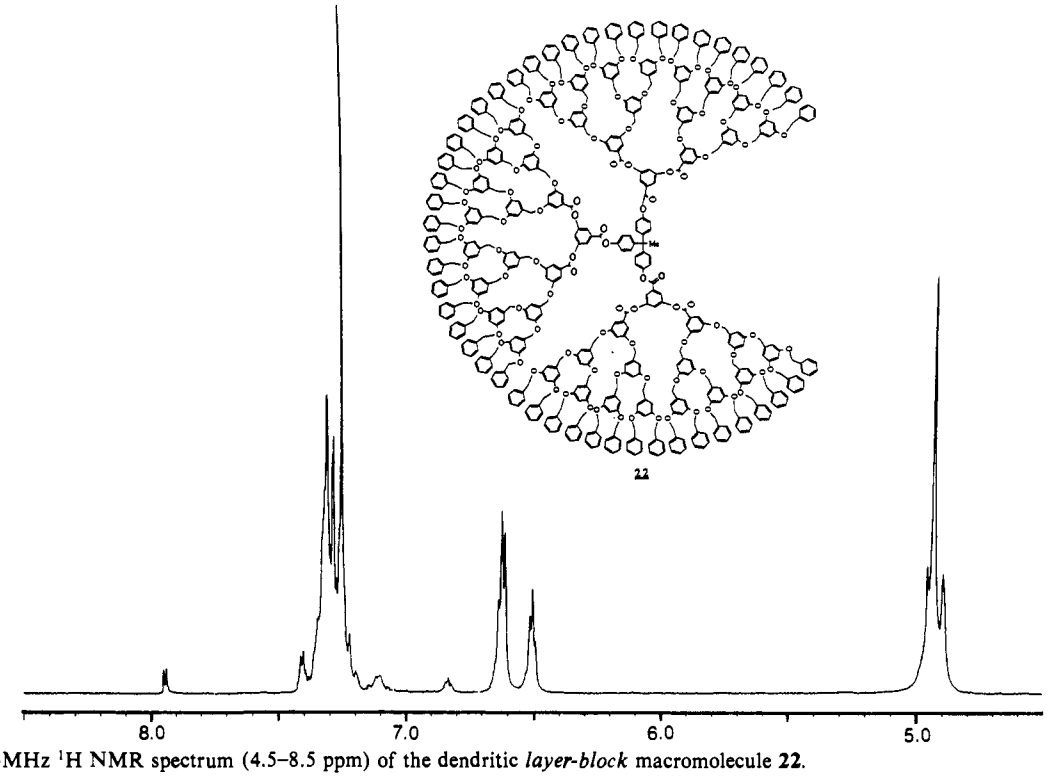
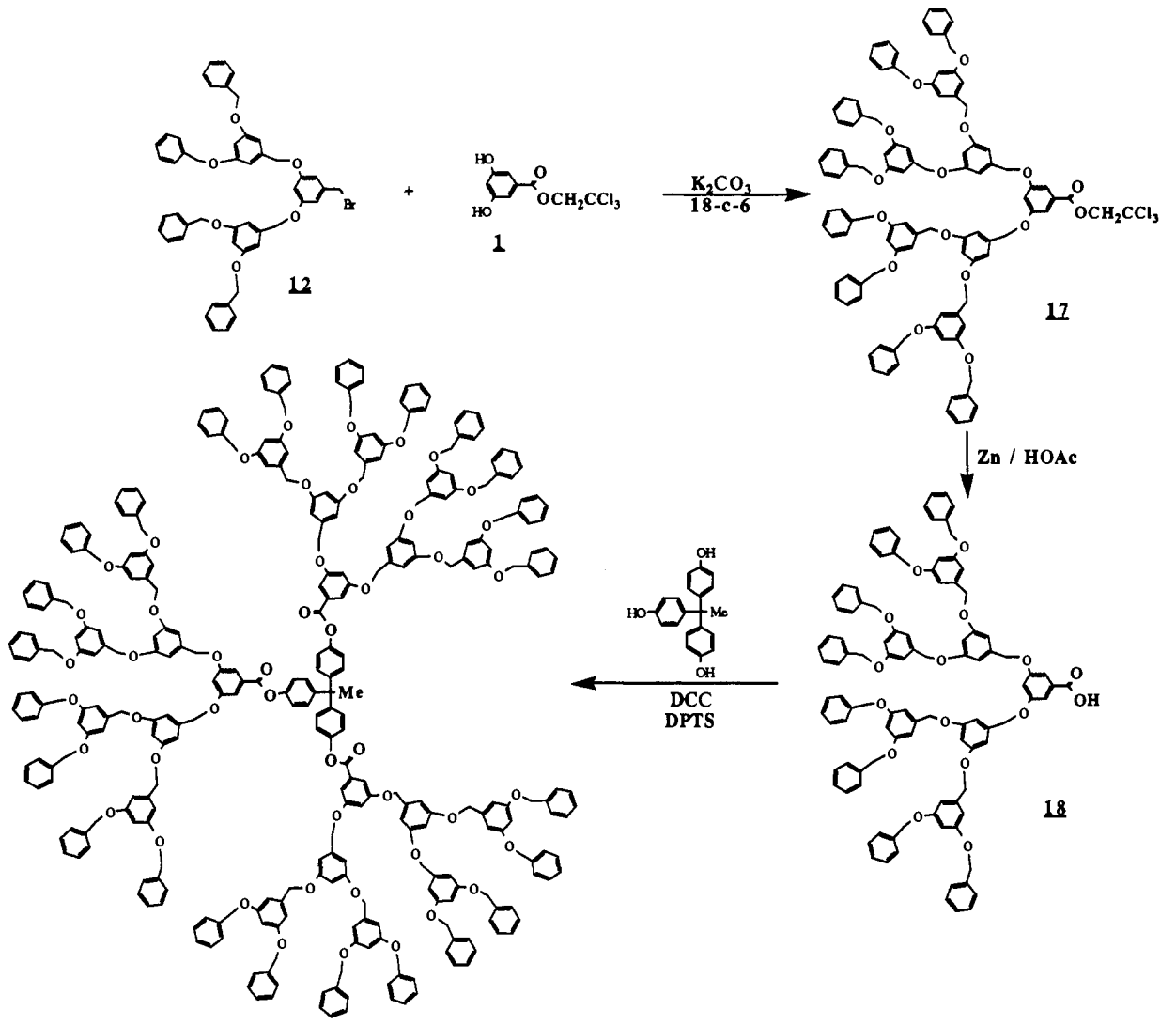


Figure 3. 200-MHz ^{1}H NMR spectrum (4.5–8.5 ppm) of the dendritic *layer-block* macromolecule **22**.

termined by comparison of the integration data. Discrete resonances were also observed for the core molecule at 2.25 and 7.10 ppm. Complimentary information was obtained from the ^{13}C NMR spectra and helped to confirm the validity of the synthetic strategy.

Comparison of the differential scanning calorimetry (DSC) data for the dendritic block copolymers to that for the parent polyether and polyester macromolecules of comparable molecular weight is shown in Figure 4. The third-generation polyether macromolecule, ether-[G-3]$_3$-[C] (**23**), has a glass transition temperature of 312 K, while the corresponding polyester macromolecule, ester-[G-3]$_3$-[C] (**2**), has a much higher glass transition temperature of 399 K. In comparison, the dendritic block copolymers have intermediate glass transition temperatures which show a strong dependence on the relative number of ether and ester building blocks. The *layer-block* copolymer **22** shows a glass transition temperature of 319 K, only 7 K higher than that for the polyether **23**, demonstrating the dominant influence of the larger ether blocks (ratio of ether to ester functional groups in **22** is 28:3). Whereas for the dendritic *segment-block* macromolecule **16** an intermediate glass transition temperature of 351 K is observed, which correlates with the ratio of ether to ester groups of 7:8. When the polyether and polyester homopolymers **23** and **9**, respectively, were physically mixed, the DSC trace showed only a single transition, demon-

Scheme V



strating that phase separation is not occurring in these systems.

Conclusion

The usefulness of the convergent growth approach for the preparation of dendritic macromolecules with highly controlled architectures is demonstrated via the preparation of dendritic polyesters and novel as well as highly unusual dendritic block copolymers. Such structures are not readily accessible through the procedures currently in use for divergent syntheses such as the starburst[1] approach. The stepwise convergent growth process allows the preparation of block copolymers in almost traditional fashion using size monodispersed fragments that contain a single reactive group at their focal point. A difference may arise in some cases as coupling of these blocks usually involves the attachment of several fragments to a polyfunctional core rather than two fragments to one another. The basic concepts described above allow for the synthesis of a wide range of possible dendritic macromolecules where the structure, functional groups, and three-dimensional architecture can be precisely controlled. The high degree of symmetry of the macromolecules and their monodispersity facilitate their analysis using a combination of standard spectroscopic and chromatographic techniques. In particular, ^1H NMR spectroscopy allows the relative number of each different building block to be determined and subtle structural changes to be detected.

While other work[13] has shown that the thermal properties of dendritic macromolecules are greatly affected by the nature of their chain ends, this study shows that the glass transition temperature of the block copolymers is also a good reflection of their internal structure and building blocks.

A large number of different architectures are possible for dendritic block copolymers, including other hybrid structures in which dendritic blocks and linear macromolecules are connected.[14]

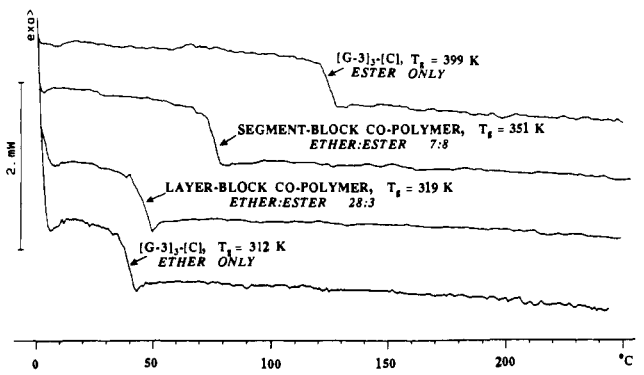


Figure 4. Variation of glass transition temperature for dendritic polymers and copolymers based on ether and ester units.

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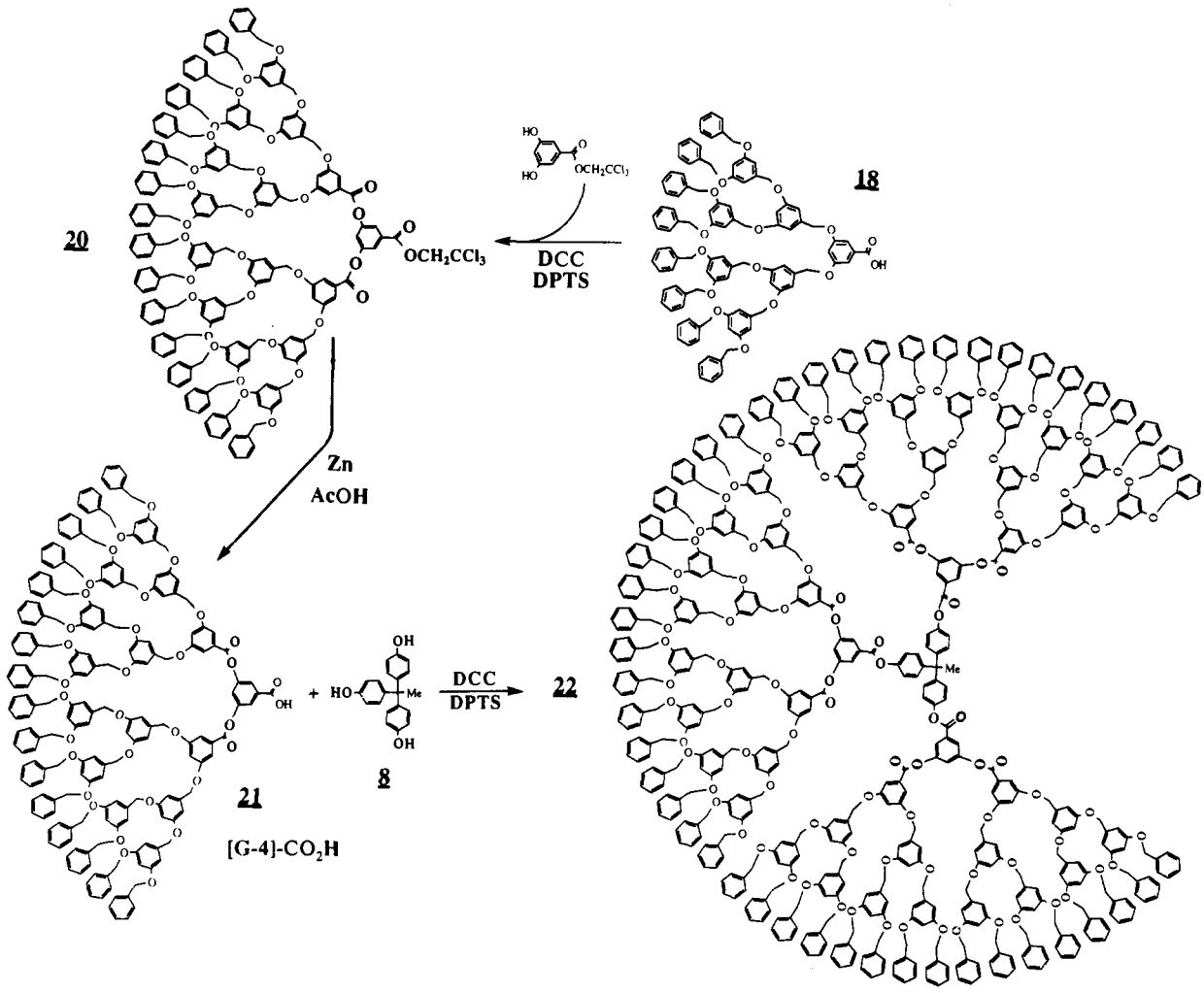
(14) Gitsov, I.; Wooley, K. L.; Hawker, C.; Frêchet, J. M. J. *ACS Polym. Prep.* **1991**, *32* (3), 631.

Scheme VI



We are continuing our exploration of these new architectures, their syntheses, and their properties.

Experimental Section

General Directions. Melting points and glass transition temperatures were determined on a Mettler DSC 30 thermal analysis unit. Infrared spectra were recorded on a Nicolet IR/44 spectrophotometer as thin films on NaCl disks. ^{1}H NMR spectra were recorded of solutions in $CDCl_3$, D_6-acetone, or D_6-DMSO on a Bruker WM 200 (200-MHz) spectrometer using the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 50 MHz on a Bruker WM 200 spectrometer using $CDCl_3$, D_6-acetone, or D_6-DMSO as the solvent and the solvent carbon signal as internal standard. Mass spectra were obtained on a Kratos MS890 using either EI or FAB ionization; the latter were run with 3-nitrobenzyl alcohol as the matrix. Analytical TLC was performed on commercial 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 an IBM LC/9560 chromatography connected to a Milton Roy refractoMonitor IV refractive index detector; data analysis was performed using GPC-PRO software, version 3.12 (Viscotek Corp.). Three 5-μm Hewlett Packard columns (300 × 7.7 mm) connected in series in order of increasing pore size (500 A, 1000 A, and mixed bed C) were used with THF as solvent. The following abbreviations are used: Ar refers to aromatic rings derived from monomer **1**, Ph refers to aromatic rings derived from benzyl chloride, and Ar′ refers to aromatic rings derived from the core molecule **8**.

2,2,2-Trichloroethyl 3,5-Dihydroxybenzoate (1). To freshly distilled 2,2,2-trichloroethanol (25 mL) was added 3,5-dihydroxybenzoic acid (4.50 g, 29.2 mmol) followed by concentrated sulfuric acid (1.0 mL), and the mixture was stirred vigorously and heated at 90 °C for 48 h under nitrogen. The reaction mixture was cooled and evaporated to dryness under reduced pressure. The crude product was purified by flash chromatography eluting with CH_2Cl_2 gradually increasing to 1:10 diethyl ether/CH_2Cl_2 to give the trichloroethyl ester **1** as a viscous oil: 5.12 g, 61.4%; IR 3600–3200, 1705, 1600, 1350, 1220, and 750 cm^{-1}; ^{1}H NMR (D_6-acetone) δ 5.00 (s, 2 H, CH_2CCl_3), 6.68 (t, 1 H, J = 3 Hz, Ar*H*), 7.06 (d, 2 H, J = 3 Hz, Ar*H*), and 8.07 (br s, 2 H, O*H*); ^{13}C NMR (D_6-acetone) δ 74.17, 76.07, 95.60, 108.50, 130.74, 158.87, and 164.63; mass spectrum (EI) m/z 283/285/287/289 (ca. 27:27:9:1); accurate mass $C_9H_7{}^{35}Cl_3O_4$ requires 283.9415, found 283.9413. Anal. Calcd for $C_9H_7Cl_3O_4$: C, 37.25; H, 2.47; Cl, 37.86. Found: C, 37.11; H, 2.54; Cl, 38.02.

Dendritic Polyester Macromolecules. A. 2,2,2-Trichloroethyl 3,5-Bis(benzoyloxy)benzoate (Ester-[G-1]-$CO_2CH_2CCl_3$, 2) and General Procedure for Ester Formation. To a solution of benzoic acid (2.21 g, 18.1 mmol) in dry dichloromethane (20 mL) was added the diphenolic monomer unit **1** (2.25 g, 7.88 mmol) followed by 4-(dimethylamino)-pyridinium *p*-toluenesulfonate (DPTS) (600 mg, 2.1 mmol), and the mixture was stirred at room temperature under nitrogen for 15 min. Dicyclohexylcarbodiimide (DCC) (3.73 g, 18.1 mmol) was then added and stirring continued at room temperature until the reaction had reached completion (ca. 15 min; during this time, a heavy precipitate of dicyclohexylurea appeared. The reaction mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by flash chromatography eluting with 1:1 hexane-/CH_2Cl_2 increasing to 1:3 hexane/CH_2Cl_2 to give the triester **2** as a colorless solid: 3.46 g, 89.0%; IR 1715, 1600, 1350, 1220, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.99 (s, 2 H, CH_2CCl_3), 7.48–7.69 (m, 7 H, 6 × Ph*H* and 1 × Ar*H*), 7.93 (d, 2 H, J = 2 Hz, Ar*H*), and 8.19–8.25 (m, 4 H, 4 × Ph*H*); ^{13}C NMR ($CDCl_3$) δ 74.53, 94.62, 120.79, 121.50, 128.60, 130.17, 130.77, 133.93, 151.36, 163.18, and 164.37; mass spectrum (EI) m/z 491/493/495/497 (ca. 27:27:9:1). Anal. Calcd for $C_{23}H_{15}Cl_3O_6$: C, 55.9; H, 3.06. Found: C, 56.2; H, 2.94.

B. 3,5-Bis(benzoyloxy)benzoic Acid (Ester-[G-1]-CO_2H, 3) and General Procedure for the Removal of the Trichloroethyl Protecting Groups. To the trichloroethyl ester **2** (6.00 g, 12.1 mmol) dissolved in tetrahydrofuran (20 mL) was added glacial acetic acid (20 mL), and the solution was stirred at room temperature under nitrogen. Zinc dust (5.00 g, 76 mmol) was added and the reaction stirred vigorously at room temperature for 15 minutes. The reaction mixture was filtered and the

filtrate poured into water (300 mL) and extracted with diethyl ether (4 × 50 mL). The combined extracts were washed with water (2 × 50 mL), dried, and evaporated to dryness under reduced pressure. The crude product was purified by flash chromatography (dry loading recommended) eluting with CH_2Cl_2 increasing to 1:10 ether/CH_2Cl_2 to give the acid **3** as a colorless solid: 4.05 g, 92%; IR 3600–2600, 1715, 1600, 1350, 1220, and 750 cm^{-1}; ^1H NMR (D_6-acetone) δ 7.50–7.79 (m, 7 H, 6 × Ph*H* and 1 × Ar*H*), 7.93 (d, 2 H, J = 2 Hz, Ar*H*), and 8.20–8.25 (m, 4 H, 4 × Ph*H*); ^{13}C NMR (D_6-acetone) δ 121.16, 121.26, 129.37, 129.69, 130.58, 133.39, 134.53, 152.21, 164.87, and 165.79; mass spectrum (EI) m/z 362 (ca. 100%). Anal. Calcd for $C_{21}H_{14}O_6$: C, 69.6; H, 3.89. Found: C, 69.5; H, 3.72.

C. **Ester-[G-2]-$CO_2CH_2CCl_3$ (4).** This compound was prepared from 3,5-bis(benzoyloxy)benzoic acid, ester-[G-1]-CO_2H (**3**) (3.60 g, 9.94 mmol), the dihydroxybenzoate monomer unit (**1**) (1.34 g, 4.69 mmol), 4-(dimethylamino)pyridinium p-toluenesulfonate (DPTS) (600 mg, 2.1 mmol), and dicyclohexylcarbodiimide (DCC) (2.10 g, 10.3 mmol) and purified by flash chromatography eluting with 1:1 hexane/CH_2Cl_2 increasing to CH_2Cl_2 to give the second-generation ester **4** as a colorless solid: 3.70 g, 81%; IR 1720, 1595, 1365, 1230, and 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.00 (s, 2 H, CH_2CCl_3), 7.48–7.70 (m, 15 H, 12 × Ph*H* and 3 × Ar*H*), 7.95 (d, 6 H, J = 2 Hz, Ar*H*), and 8.20–8.24 (m, 8 H, 8 × Ph*H*); ^{13}C NMR ($CDCl_3$) δ 74.61, 94.57, 120.94, 121.09, 121.63, 128.63, 130.20, 130.80, 131.00, 133.97, 151.09, 151.47, 162.79, 163.01, and 164.42; mass spectrum (FAB) m/z 971/973/975/977 (ca. 27:27:9:1). Anal. Calcd for $C_{51}H_{31}Cl_3O_{14}$: C, 62.9; H, 3.21. Found: C, 62.6; H, 2.97.

D. **Ester-[G-2]-CO_2H (5).** This compound was prepared from the trichloroethyl ester **4** (4.10 g, 4.67 mmol) and was purified by flash chromatography (dry loading recommended) eluting with CH_2Cl_2 increasing to ether to give the acid **5** as a colorless solid: 3.19 g, 90%; IR 360–2600, 1710, 1600, 1330, 1220, and 765 cm^{-1}; ^1H NMR (D_6-acetone), δ 7.57–7.80 (m, 15 H, 12 × Ph*H* and 3 × Ar*H*), 8.00 (d, 2 H, J = 2 Hz, Ar*H*), 8.11 (d, 4 H, J = 2 Hz, Ar*H*), and 8.20–8.26 (m, 8 H, 4 × Ph*H*); ^{13}C NMR (D_6-acetone) δ 121.14, 121.35, 121.71, 122.42, 129.37, 129.59, 130.62, 131.88, 133.53, 134.58, 151.98, 152.38, 163.50, 164.87, and 165.71; mass spectrum (FAB) m/z 842 (M^+, ca. 100%). Anal. Calcd for $C_{49}H_{30}O_{14}$: C, 69.8; H, 3.59. Found: C, 70.0; H, 3.43.

E. **Ester-[G-3]-$CO_2CH_2CCl_3$ (6).** This compound was prepared from ester-[G-2]-CO_2H (**5**) (2.10 g, 2.49 mmol), the dihydroxybenzoate monomer unit **1** (337 mg, 1.19 mmol), 4-(dimethylamino)pyridinium p-toluenesulfonate (DPTS) (175 mg, 0.612 mmol), and dicyclohexylcarbodiimide (DCC) (612 mg, 3.00 mmol) and purified by flash chromatography eluting with 1:1 hexane/CH_2Cl_2 increasing to CH_2Cl_2 to give the third-generation ester **6** as a colorless solid: 1.63 g, 71%; IR 1725, 1360, 1230, and 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.98 (s, 2 H, CH_2CCl_3), 7.45–7.75 (m, 3 1H, 24 × Ph*H* and 7 × Ar*H*), 7.93 (d, 14 H, J = 2 Hz, Ar*H*), and 8.20–8.27 (m, 16 H, 16 × Ph*H*); ^{13}C NMR ($CDCl_3$) δ 74.64, 94.60, 120.90, 121.01, 121.17, 121.66, 128.65, 130.23, 130.74, 130.84, 130.98, 133.90, 151.05, 151.12, 151.47, 162.82, 162.96, 163.05, and 164.39. Anal. Calcd for $C_{107}H_{63}Cl_3O_{30}$: C, 66.4; H, 3.28. Found: C, 66.1; H, 3.13.

F. **Ester-[G-3]-CO_2H (7).** This compound was prepared from the trichloroethyl ester **6** (1.50 g, 0.775 mmol) and was purified by flash chromatography (dry loading recommended) eluting with CH_2Cl_2 increasing to ether to give the acid **7** as a colorless solid: 1.23 g, 88%; IR 3600–2600, 1710, and 760 cm^{-1}; ^1H NMR (D_6-acetone), δ 7.50–7.80 (m, 31 H, 24 × Ph*H* and 7 × Ar*H*), 8.02 (d, 2 H, J = 2 Hz, Ar*H*), 8.08–8.13 (m, 12 H, J = 2 Hz, Ar*H*), and 8.18–8.29 (m, 16 H, 8 × Ph*H*); ^{13}C NMR (D_6-acetone) δ 121.11, 121.24, 121.36, 121.71, 122.40, 129.32, 129.53, 129.62, 130.64, 131.87, 133.50, 134.69, 151.88, 152.42, 163.53, 163.67, 164.81, and 165.71. Anal. Calcd for $C_{105}H_{62}O_{30}$: C, 69.9; H, 3.46. Found: C, 69.7; H, 3.62.

G. **Ester-[G-3]$_3$-[C] (9).** This compound was prepared from ester-[G-3]-CO_2H (**7**) (1.00 g, 0.55 mmol), the triphenolic core molecule **8** (51 mg, 0.17 mmol), 4-(dimethylamino)pyridinium p-toluenesulfonate (DPTS) (17 mg, 0.06 mmol), and dicyclohexylcarbodiimide (DCC) (122 mg, 0.60 mmol) and purified by flash chromatography eluting with 1:1 hexane/CH_2Cl_2 increasing to CH_2Cl_2 to give the polyester macromolecule **9** as a colorless solid: 690 mg, 72%; IR 1720, 1365, and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3 H, C–C*H*$_3$), 7.15 and 7.20 (AB q, 12 H, J = 6 Hz, core-Ar*H*), 7.45–7.77 (m, 93 H, 72 × Ph*H* and 21 × Ar*H*), 8.00 (d, 42 H, J = 2 Hz, Ar*H*), and 8.21–8.28 (m, 48 H, 48 × Ph*H*); ^{13}C NMR ($CDCl_3$) δ 30.85, 51.67, 120.91, 120.97, 121.11, 121.63, 128.65, 129.79, 130.21, 130.24, 130.89, 131.22, 133.96, 146.32, 148.83, 151.09, 151.15, 151.48, 162.81, 162.86, 163.05, 163.21, and 164.47. Anal. Calcd for $C_{335}H_{198}O_{90}$: C, 71.1; H, 3.52. Found: C, 71.2; H, 3.42.

Dendritic *Segment-Block* Macromolecules. A. Ester-[G-2]-[M]-$CO_2CH_2CCl_3$ (10). This compound was prepared from the acid ester-[G-2]-CO_2H (**5**) (450 mg, 0.53 mmol), the dihydroxybenzoate monomer unit **1** (814 mg, 2.85 mmol), 4-(diethylamino)pyridinium p-toluenesulfonate (DPTS) (200 mg, 0.70 mmol), and dicyclohexylcarbodiimide (DCC) (620 mg, 3.00 mmol) and was purified by flash chromatography eluting with CH_2Cl_2 increasing to 1:4 ether/CH_2Cl_2 to give the monophenol **10** as a colorless glass: 330 mg, 60%; IR 1720, 1595, 1365, 1230, and 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.98 (s, 2 H, CH_2CCl_3), 6.89 (m, 1 H, Ar*H*), 7.32 (m, 1 H, Ar*H*), 7.51–7.80 (m, 16 H, 12 × Ph*H* and 4 × Ar*H*), 7.98 (d, 2 H, J = 2 Hz, Ar*H*), 8.10 (d, 4 H, J = 2 Hz, Ar*H*), and 8.20–8.26 (m, 8 H, 8 × Ph*H*); ^{13}C NMR ($CDCl_3$) δ 74.28, 94.63, 108.74, 121.11, 121.29, 121.66, 122.38, 129.54, 130.41, 130.76, 131.39, 133.61, 134.75, 151.73, 152.33, 162.94, 163.47, 164.82, and 165.18. Anal. Calcd for $C_{58}H_{35}Cl_3O_{17}$: C, 62.7; H, 3.18. Found: C, 62.5; H, 3.31.

B. **Ether-[G-2]-[M]-$CO_2CH_2CCl_3$ (13).** A mixture of ether-[G-2]-Br (**12**) (4.00 g, 4.96 mmol), 2,2,2-trichloroethyl 3,5-dihydroxybenzoate (**1**) (1.42 g, 4.96 mmol), potassium carbonate (970 mg, 7.00 mmol), and 18-crown-6 (50 mg, 0.19 mmol) in acetone (50 mL) was heated at reflux under nitrogen for 24 h. The reaction mixture was then evaporated to dryness and the residue partitioned between CH_2Cl_2 (50 mL) and water (50 mL); the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:1 hexane/CH_2Cl_2 increasing to CH_2Cl_2 to give the monophenol **13** as a colorless glass: 2.30 g, 46%; IR 3400–3000, 1720, 1590, 1370, 1210, and 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.97 (s, 2 H, CH_2CCl_3), 5.03 and 5.08 (each s, 14 H, OCH_2Ph), 6.68–6.70 and 6.78–6.81 (each m, 9 H, 9 × Ar*H*), 6.87 (m, 1 H, Ar*H*), 7.32 (m, 1 H, Ar*H*), and 7.38–7.52 (m, 21 H, 20 × Ph*H* and 1 × Ar*H*); ^{13}C NMR ($CDCl_3$) δ 69.71, 69.83, 74.22, 94.77, 101.42, 106.24, 107.95, 108.13, 109.76, 127.38, 127.81, 128.12, 128.36, 130.18, 136.47, 138.64, 138.97, 142.71, 157.19, 159.62, 159.85, and 164.56. Anal. Calcd for $C_{58}H_{49}Cl_3O_{10}$: C, 68.8; H, 4.88. Found: C, 68.7; H, 4.96.

C. **Ester/Ether-[G-3]-$CO_2CH_2CCl_3$ (14).** This compound was prepared from this acid ester-[G-2]-CO_2H (**5**) (1.14 g, 1.53 mmol), the monophenol ether-[G-2]-[M]-$CO_2CH_2CCl_3$ (**13**) (1.41 g, 1.40 mmol), 4-(dimethylamino)pyridinium p-toluenesulfonate (DPTS) (460 mg, 1.56 mmol), and dicyclohexylcarbodiimide (DCC) (321 mg, 1.56 mmol) and was purified by flash chromatography eluting with 1:1 hexane/CH_2Cl_2 increasing to 1:3 hexane/CH_2Cl_2 to give the third-generation ester/ether fragment **14** as a colorless glass: 2.13 g, 83%; IR 1710, 1590, 1370, 1250, and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.99, 5.02, 5.05, and 5.08 (each s, 16 H, 7 × CH_2O and 1 × CH_2CCl_3), 6.61–6.63 and 6.74–6.76 (each m, 9 H, 9 × ether-Ar*H*), 7.22 (t, 1 H, J = 2 Hz, Ar*H*), 7.33–7.73 (complex m, 37 H, 20 × Ph*H* and 17 × Ar*H*), 8.10 and 8.11 (each d, 6 H, J = 2 Hz, ester-Ar*H*), and 8.24–8.29 (m, 8 H, 8 × ester-Ar*H*); ^{13}C NMR ($CDCl_3$) δ 69.84, 70.30, 74.39, 94.68, 101.41, 101.65, 106.15, 106.26, 113.88, 114.22, 115.70, 121.01, 121.57, 127.37, 127.69, 128.14, 128.39, 129.72, 130.65, 131.21, 133.91, 136.59, 138.13, 138.98, 151.07, 151.37, 159.39, 159.96, 162.72, 162.82, 163.61, and 164.33. Anal. Calcd for $C_{107}H_{77}Cl_3O_{23}$: C, 69.9; H, 4.22. Found: C, 69.6; H, 4.46.

D. **Ester/Ether-[G-3]-CO_2H (15).** This compound was prepared from the trichloroethyl ester ester/ether-[G-3]-$CO_2CH_2CCl_3$ (**14**) (1.00 g, 0.57 mmol) and purified by flash chromatography (dry loading recommended) eluting with CH_2Cl_2 increasing to 1:1 ether/CH_2Cl_2 to give the acid **15** as a colorless solid: 733 mg, 79%; IR 3600–2600, 1715, 1595, 1340, 1210, and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.98 and 5.01 (each s, 14 H, 7 × CH_2O), 6.55–6.57 and 6.68–6.70 (each m, 9 H, 9 × ether-Ar*H*), 7.14 (t, 1 H, J = 2 Hz, Ar*H*), 7.26–7.70 (complex m, 37 H, 20 × Ph*H* and 17 × Ar*H*), 8.03 (d, 6 H, J = 2 Hz, ester-Ar*H*), and 8.20–8.24 (m, 8 H, 8 × ester-Ar*H*); ^{13}C NMR ($CDCl_3$) δ 70.01, 70.42, 101.57, 101.89, 106.26, 106.42, 113.52, 113.95, 115.47, 121.17, 121.70, 127.50, 127.93, 128.51, 128.68, 130.28, 130.89, 131.45, 134.02, 136.69, 138.27, 139.11, 151.17, 151.35, 151.52, 159.45, 160.03, 162.90, 164.51, and 170.07. Anal. Calcd for $C_{105}H_{76}O_{23}$: C, 73.9; H, 4.49. Found: 74.0; H, 4.54.

E. **(Ester/Ether-[G-3])$_3$-[C] (16).** This compound was prepared from the acid ester/ether-[G-3]-CO_2H (**15**) (800 mg, 0.47 mmol), the triphenolic core molecule [C]-$(OH)_3$ (**8**) (40 mg, 0.13 mmol), 4-(dimethylamino)pyridinium p-toluenesulfonate (DPTS) (140 mg, 0.47 mmol), and dicyclohexylcarbodiimide (DCC) (100 mg, 0.47 mmol) and purified by flash chromatography eluting with 1:2 hexane/CH_2Cl_2 increasing to CH_2Cl_2 to give the dendritic *segment-block* copolymer **16** as a colorless glass: 533 mg, 76%; IR 1710, 1590, 1370, 1250, and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.21 (br s, 3 H, C–C*H*$_3$), 4.98, 5.00, and 5.06 (each s, 42 H, 21 × CH_2O), 6.53–6.56 and 6.68–6.74 (each m, 27 H, 27 × ether-Ar*H*), 7.11–7.13 (m, 15 H, 12 × Ar′*H* and 3 × Ar*H*), 7.26–7.66 (complex m, 111 H, 60 × Ph*H* and 51 × Ar*H*), 8.03 and 8.05 (each d, 18 H, J = 2 Hz, ester-Ar*H*), and 8.20–8.25 (m, 24 H, ester-Ar*H*); ^{13}C NMR ($CDCl_3$) δ 31.50, 50.56, 69.88, 70.35, 101.45, 101.79, 106.16, 106.34, 113.95, 115.93, 120.92, 121.05, 121.60, 127.39, 127.82, 128.41, 128.55, 129.06, 130.15, 130.75, 131.32, 131.65, 133.93, 136.61, 138.19, 139.02, 146.16, 148.88, 151.10, 151.43, 159.44, 159.98, 162.75, 162.90,

163.86, and 164.37. Anal. Calcd for $C_{335}H_{240}O_{69}$: C, 74.9; H, 4.50. Found: C, 74.9; H, 4.61.

Dendritic *Layer-Block* Macromolecules. A. Ether-[G-3]-$CO_2CH_2CCl_3$ (17). A mixture of ether-[G-2]-Br (**12**) (4.00 g, 4.96 mmol), 2,2,2-trichloroethyl 3,5-dihydroxybenzoate (**1**) (710 mg, 2.48 mmol), potassium carbonate (830 mg, 6.00 mmol), and 18-crown-6 (50 mg, 0.19 mmol) in acetone (50 mL) was heated at reflux under nitrogen for 24 h. The reaction mixture was then evaporated to dryness, and the residue was partitioned between CH_2Cl_2 (50 mL) and water (50 mL); the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:1 hexane/CH_2Cl_2 increasing to 1:3 hexane/CH_2Cl_2 to give the monoester **17** as a colorless glass: 3.67 g, 85%; IR 3400–3000, 1720, 1590, 1370, 1210, and 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.90 (s, 2 H, CH_2CCl_3), 4.97 and 5.03 (each s, 28 H, OCH_2Ph and OCH_2Ar), 6.56–6.60 and 6.68–6.71 (each m, 18 H, 18 × ether-Ar*H*), 6.87 (t, 1 H, J = 2 Hz, ester-Ar*H*), and 7.26–7.42 (m, 42 H, 8 × Ph*H* and 2 × ester-Ar*H*); ^{13}C NMR ($CDCl_3$) δ 69.82, 74.32, 94.82, 101.51, 101.66, 106.27, 106.39, 107.10, 108.35, 127.44, 127.88, 128.25, 131.08, 136.71, 138.72, 139.10, 159.71, 159.93, 160.06, and 164.71. Anal. Calcd for $C_{107}H_{91}Cl_3O_{16}$: C, 73.9; H, 5.27. Found: C, 74.2; H, 5.47.

B. Ether-[G-3]-CO_2H (18). This compound was prepared from the trichloroethyl ester ether-[G-3]-$CO_2CH_2CCl_3$ (**17**) (4.20 g, 2.42 mmol) and purified by flash chromatography (dry loading recommended) eluting with CH_2Cl_2 increasing to 1:3 ether/CH_2Cl_2 to give the acid **18** as a colorless solid: 3.42 g, 88%; IR 3600–2600, 1715, 1595, 1340, 1210, and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.01 and 5.05 (each s, 28 H, 14 × CH_2O), 6.61–6.64 and 6.73–6.76 (each m, 18 H, 18 × ether-Ar*H*), 6.91 (t, 1 H, J = 2 Hz, ester-Ar*H*), and 7.30–7.50 (complex m, 42 H, 40 × Ph*H* and 2 × ester-Ar*H*); ^{13}C NMR ($CDCl_3$) δ 69.92, 101.47, 101.61, 106.25, 106.37, 107.51, 108.79, 127.44, 128.08, 128.46, 131.08, 136.65, 138.67, 139.08, 159.62, 159.96, 160.01, and 171.31. Anal. Calcd for $C_{105}H_{90}O_{16}$: C, 78.4; H, 5.64. Found: C, 78.1; H, 5.61.

C. {(Ether-[G-2])$_2$-Ester-[G-1]}$_3$-[C] (19). This compound was prepared from the acid ether-[G-3]-CO_2H (**18**) (620 mg, 0.40 mmol), the triphenolic core molecule [C]-$(OH)_3$ (**8**) (34 mg, 0.11 mmol), 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) (130 mg, 0.44 mmol), and dicyclohexylcarbodiimide (DCC) (90 mg, 0.44 mmol) and purified by flash chromatography eluting with 1:2 hexane/CH_2Cl_2 increasing to CH_2Cl_2 to give the dendritic layer-block copolymer **19** as a colorless glass: 417 mg, 74%; IR 1710, 1590, 1370, 1250, and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.22 (br s, 3 H, C–CH_3), 5.01 and 5.06 (each s, 84 H, 42 × CH_2O), 6.61–6.64 and 6.70–6.74 (each m, 54 H, 54 × ether-Ar*H*), 6.89 (t, 3 H, J = 2 Hz, Ester-Ar*H*), 7.14 (m, 12 H, 12 × Ar'*H*), 7.28–7.52 (complex m, 120 H, 120 × Ph*H*), and 7.76 (d, 6 H, J = 2 Hz, ester-Ar*H*); ^{13}C NMR ($CDCl_3$) δ 30.78, 51.59, 69.91, 101.44, 106.36, 107.32, 108.87, 120.99, 127.43, 127.87, 128.45, 129.68, 130.82, 131.32, 136.63, 138.64, 139.06, 146.11, 149.02, 159.70, 160.02, and 164.65. Anal. Calcd for $C_{335}H_{282}O_{48}$: C, 79.3; H, 5.60. Found: C, 79.3; H, 5.64.

D. {(Ether-[G-2])$_4$-Ester-[G-2]}$_2$-$CO_2CH_2CCl_3$ (20). This compound was prepared from the acid ether-[G-3]-CO_2H (**18**) (3.00 g, 1.87 mmol), the dihydroxybenzoate monomer **1** (257 mg, 0.90 mmol), 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) (588 mg, 2.00 mmol), and dicyclohexylcarbodiimide (DCC) (412 mg, 2.00 mmol) and purified by flash chromatography eluting with 1:1 hexane/CH_2Cl_2 increasing to 1:5 hexane/CH_2Cl_2 to give the fourth-generation ester/ether fragment **20** as a colorless glass: 2.43 g, 78%; IR 1710, 1590, 1370, 1250, and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.97 and 5.01 (each s, 58 H, 28 × CH_2O and 1 × CH_2CCl_3), 6.55–6.58 and 6.67–6.70 (each m, 36 H, 36 × ether-Ar*H*), 6.88 (t, 2 H, J = 2 Hz, Ester-Ar*H*), 7.25–7.88 (complex m, 85 H, 80 × Ph*H* and 5 × Ar*H*), and 7.90 (d, 2 H, J = 2 Hz, ester-Ar*H*); ^{13}C NMR ($CDCl_3$) δ 70.01, 70.22, 74.60, 94.65, 101.50, 101.69, 106.29, 106.42, 108.04, 109.02, 120.90, 121.52, 127.51, 127.95, 128.53, 130.54, 130.85, 136.67, 138.57, 139.09, 151.35, 159.84, 160.05, 160.59, 163.21, and 164.12. Anal. Calcd for $C_{219}H_{183}Cl_3O_{34}$: C, 75.9; H, 5.19. Found: C, 76.1; H, 5.32.

E. {(Ether-[G-2])$_4$-Ester-[G-2]}$_2$-CO_2H (21). This compound was prepared from the trichloroethyl ester {(ether-[G-2])$_4$-ester-[G-2]}$_2$-$CO_2CH_2CCl_3$ (**20**) (1.90 g, 0.55 mmol) and purified by flash chromatography (dry loading recommended) eluting with $CHCl_3$ increasing to 1:5 ether/$CHCl_3$ to give the acid **21** as a colorless solid: 1.71 g, 93%; IR 3600–2600, 1715, 1595, 1340, 1210, and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.06 (each s, 56 H, CH_2O), 6.64–6.67 and 6.77–6.81 (each m, 36 H, ether-Ar*H*), 7.00 (t, 2 H, J = 2 Hz, ester-Ar*H*), 7.30–7.54 (complex m, 81 H, 80 × Ph*H* and 1 × ester-Ar*H*), 7.62 (d, 4 H, J = 2 Hz, ester-Ar*H*), and 8.05 (d, 2H, J = 2 Hz, ester-Ar*H*); ^{13}C NMR ($CDCl_3$) δ 69.79, 101.35, 101.62, 106.16, 107.83, 108.84, 127.36, 128.04, 128.37, 130.51, 131.45, 136.01, 136.57, 137.16, 138.54, 139.00, 151.10, 159.23, 159.68, 159.93, 163.96, and 169.43. Anal. Calcd for $C_{217}H_{182}O_{34}$: C, 78.2; H, 5.50. Found: C, 78.3; H, 5.78.

F. {(Ether-[G-2])$_4$-Ester-[G-2]}$_3$-[C] (22). This compound was prepared from the acid {(Ether-[G-2])$_4$-Ester-[G-2]}$_2$-CO_2H (**21**) (900 mg, 0.27 mmol), the triphenolic core molecule [C]-$(OH)_3$ (**8**) (22 mg, 0.07 mmol), 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) (90 mg, 0.30 mmol), and dicyclohexylcarbodiimide (DCC) (62 mg, 0.30 mmol) and purified by flash chromatography eluting with 1:2 hexane/CH_2Cl_2 increasing to CH_2Cl_2 to give the dendritic *layer-block* copolymer **22** as a colorless glass: 523 mg, 71%; IR 1710, 1590, 1370, 1250, and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.22 (br s, 3 H, C–CH_3), 4.98, 5.01, and 5.04 (each s, 168 H, CH_2O), 6.57–6.61 and 6.68–6.72 (each m, 108 H, ether-Ar*H*), 6.91 (t, 9 H, J = 2 Hz, Ester-Ar*H*), 7.18 (m, 12 H, 12 × Ar'*H*), 7.28–7.50 (complex m, 240 H, Ph*H*), 7.53 (d, 12 H, J = 2 Hz, ester-Ar*H*), and 8.03 (d, 6 H, J = 2 Hz, ester-Ar*H*); ^{13}C NMR ($CDCl_3$) δ 30.66, 51.50, 69.82, 101.37, 101.55, 106.17, 106.29, 107.85, 108.90, 120.89, 127.38, 127.81, 128.06, 128.39, 129.68, 130.50, 130.78, 131.67, 132.14, 136.58, 138.53, 139.01, 146.18, 148.79, 151.25, 159.72, 159.96, 163.25, 164.04, and 167.54. Anal. Calcd for $C_{671}H_{558}O_{102}$: C, 78.6; H, 5.48. Found: C, 78.8; H, 5.33.

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