Dendritic−Linear A_xB_x Block Copolymers Prepared via Controlled Ring-Opening Polymerization of Lactones from Orthogonally Protected Multifunctional Initiators

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ABSTRACT: A new concept in initiator design using orthogonal protecting groups provides a versatile synthetic route to novel dendritic−linear AB, A_2B, AB_2, A_2B_2, and A_3B_3 amphiphilic block copolymers. The A blocks are composed of the first- through third-generation dendrons from 2,2-bis(hydroxymethyl)-propionic acid (bis-MPA), and the B blocks are poly(ϵ-caprolactone) prepared by living ring-opening polymerization (ROP). The enabling feature in the preparation of these dendritic−linear block copolymers is the synthesis of orthogonally protected multifunctional initiators. These initiators allow for the selective coupling of the dendritic fragments and, upon selective and quantitative deprotection of the initiating species, controlled ROP of ϵ-caprolactone from this central core molecule. Because of the sensitivity of the poly(ϵ-caprolactone) and dendrons toward hydrolysis, protection and deprotection schemes for the initiators as well as the dendrons were judiciously designed to be performed under mild conditions. Libraries of new initiators were prepared, composed of the first- through third-generation protected dendrons and hydroxyl groups protected with either benzyl ether or benzylidene acetal groups. Deprotection of these hydroxyl groups by catalytic hydrogenolysis yielded the requisite nucleophilic initiators for the controlled ROP of ϵ-caprolactone in the presence of a suitable organometallic promoter. Narrowly dispersed products with predictable molecular weights were obtained. NMR and GPC studies of the block copolymers confirmed the versatility of the orthogonally protected multifunctional initiator approach to dendritic−linear copolymers. Upon deprotection of the surface hydroxyl groups on the dendrons, the macromolecules became amphiphilic, with a polar, hydrophilic head and a nonpolar, hydrophobic tail. These materials provide a new class of polymeric surfactants, which might lead to novel supramolecular architectures in the constrained geometry of a monolayer film or in solution as self-assembled micelles.

Introduction

The tailoring of the mechanical, thermal, rheological, and solution properties of macromolecules through the introduction of controlled branching and/or block copolymerization has continued to assume an increasingly important position in polymer science.[1] Accordingly, the synthesis of branched molecular architectures, such as hyperbranched, dendritic, star, and comb-burst macromolecules has been the goal of many research groups.[2] The interest in these mesoscopic systems and nanostructures is driven by the potential interesting properties and emerging technological applications. Dendrimers provide the standard of a material with a precisely defined structure, while hyperbranched, dendri-graft and related architectures are less perfect elaborations of branched macromolecules.[3] Further variation in structure includes the use of different monomers, molecular weights, polydispersities, and block and graft copolymers. Advances in living/controlled polymerization techniques have given, in part, the tools to facilitate the preparation of such materials.[4,5] Of particular interest is the unique combination of controlled polymerization procedures with a precisely defined branch structure. One class of materials that manifest such a complex architecture is dendritic polymers, which are generally characterized as having generations of high-molecular-weight polymer between branching junctures.[6] Dendritic polymers can be prepared as either the hyperbranched version through the self-polymerization of an AB_x macromonomer or the dendrimer analogue (dendrimer-like star polymers) by a genealogically directed synthesis comprising generations of high-molecular-weight polymer between AB_x branching junctures using a convergent growth method. These materials have abundant functionality and improved solubility, as well as the other desirable features of dendritic-type materials, yet with the mechanical integrity of linear macromolecules.

However, the overwhelming majority of the reports are on the design, synthesis, and characterization of dendritic−linear block, graft, and star-shaped copolymers.[7] For instance, Schlüter et al.,[8] Hawker et al.,[9] Percec et al.,[10] and others[11] have shown that a linear backbone decorated with dendritic wedges can produce

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nanostructured materials with unusual properties. These dendritic−linear graft block copolymers are prepared by either the reaction of dendrons with a functional linear backbone, polymerization of dendritic macromonomers, or the growth of dendritic grafts from the backbone. In another example, dendritic−linear star-shaped macromolecules have been prepared from the initiation of living/controlled ring-opening,[12] radical,[13] or anionic[14] polymerization procedures from the surface functionality of dendrimers. The presence of the unique and accessible focal point in dendrons prepared by the convergent growth approach allows for the synthesis of AB and ABA di- and triblock copolymers. In this approach, the focal point can be used to either initiate, terminate, or couple reactive linear and star-shaped polymer chains.[15] Appropriately designed dendritic−linear hybrid block copolymers are amphiphilic and shape-responsive in properly chosen solvents, forming either monomolecular or supramolecular micelles. Dendritic−linear block copolymers of polystyrene chains with poly(propylene imine) dendrimers were found to be amphiphilic, with the size and shape of the organization in solution dependent on dendron generation. In a similar manner, Percec et al.[16] designed and synthesized spherical and cylindrical supramolecular structures from monodendrons that self-assemble through various recognition mechanisms. Supramolecular systems with complex architectures were also formed with monodendritic building blocks by both homo- and copolymerizations.[16]

Applications of such dendritic−linear hybrid copolymer systems are becoming pervasive in many emerging technologies.[17] For example, considerable attention has focused on a new electrically insulating material, that has a low dielectric constant for on-chip applications to replace the current SiO_2.[18] The use of macromolecules with complex architectures has proven to be an effective means of introducing nanoporosity in organosilicates (silsesquioxanes, SSQ). The reduction in dielectric constant is simply achieved by replacing a portion of the film with air, which has a dielectric constant of 1.[19] In this approach, polymeric organic−inorganic hybrids with controlled morphologies were demonstrated in which the function of the macromolecule was to template the vitrification of the SSQ precursor. Ensuring the compatibility of the organic template and the SSQ materials on the nanoscopic scale is critical and was accomplished using highly branched, minimally entangled star-shaped or hyperbranched[20] macromolecules derived from poly(ϵ-caprolactone) (PCL). The dendritic−linear star-shaped copolymers were initially soluble in the organosilicate prepolymer; however, upon network formation, the consumption of the abundant end group dramatically changes the solubility and molecular weight of the SSQ, leading to phase separation. Stringent control of the size and shape of the phase-separated macromolecule and subsequent pore size was demonstrated in these kinetically controlled assemblies. Alternatively, amphiphilic or surfactant molecules have been used as structure-directing agents that template both meso- and nanoporosity in organosilicates.[21] The structure-directing capabilities of these amphiphilic molecules, which include van der Waals, electrostatic, and hydrogen-bonding interactions, have been exploited to promote silica−surfactant self-assembly concurrent with the sol−gel condensation of the reactive inorganic species. The use of low-molar-mass surfactants ultimately provides pore sizes less than 30 Å after calcination, whereas macromolecular surfactants provide larger pores. In each case, the pores are commensurate with the micelle size. Block copolymers offer the possibility of optimizing the polymer−solvent sol−gel mixture phase behavior by adjusting the block lengths and types, composition, and architecture. Although the higher-molecular-weight surfactants (i.e., amphiphilic block copolymers) permit the organization of larger structural features, it is often at the sacrifice of the periodicity or regularity of the desired nanoscale features.

In this paper, the synthesis of new amphiphiles intermediate between those of conventional low-molar-mass surfactants (i.e., compact polar head with hydrophobic alkyl chains) and block copolymers (i.e., distinct polymer chains chemically bound at one point) with the shape of the former and the size of the latter is described with the motivation of eventually templating nanoporosity in silicates via surfactant−silica self-assembly. The design of these molecules was inspired by nature, in the form of phospholipids. Naturally occurring phospholipids are functional amphiphiles that spontaneously assemble into various structures such as the bilayers of living cells. One of the important properties to control is the ability to form assemblies with tailored stability. Cell membranes undergo an order−disorder transition above physiological temperature.[22] At lower temperatures, these membranes crystallize to inhibit their fluidity. Attempts to increase the stability of liposomes or vesicles include the incorporation of specific substances such as cholesterol[22] or cholesterol polysaccharides[23] into the bilayer system, the incorporation of polymerizable functional groups,[24] the increase of the number of hydrophobic chains from two to three,[25] and/or the increase of the number of hydrophilic groups. In the latter case, Ikeda et al. and others[25] showed that an increase in the hydrophobic chain number had a pronounced effect on the amphiphiles' ability to form and stabilize micelles. Toward this goal, dendritic−linear hybrid A_xB_x amphiphilic block copolymers have been prepared, where the A blocks are hydrophilic dendrimers derived from 2,2-bis(hydroxymethyl) propionic acid and the B blocks are linear chains of poly(ϵ-caprolactone). The design of these copolymers is versatile, allowing the molecular weight, composition, and number of poly(ϵ-caprolactone) blocks or tails to be varied along with the generation and number of dendrons. The versatility in the design stems from the various libraries of building blocks employed in the construction of the copolymers. These libraries include different generations of hydrophilic functional dendrons; poly(ϵ-caprolactone); and, the enabling feature, novel orthogonally protected multifunctional initiators. Although the use of orthogonal protecting groups is common in organic synthesis, it is rarely employed as a tool in polymer synthesis. The protecting group must react selectively and in good yield to generate a stable, protected substrate for the projected reactions. Second, it must also be selectively and quantitatively removed under mild reaction conditions in the presence of other functional groups and, in this instance, in the presence of the polyester backbone. The synthesis of numerous orthogonally protected multifunctional initiators is described herein, together with the other libraries of building blocks, as a route to new amphiphilic A_xB_x dendritic−linear copolymers.

Experimental Section

Materials. Stannous-2-ethylhexanoate (Sigma) and all other chemicals (Aldrich) were purchased and used without any further purification unless otherwise stated. ϵ-Caprolactone (Aldrich) was dried over CaH_2 for 24 h and then distilled under high vacuum prior to use. 2-Benzyloxy ethanol, **1**, was used without further purification. $Sn(OTf)_2$ was purchased from Aldrich and dried by three azeotropic distillations from toluene, and a stock solution of the catalyst was prepared (150 mg of catalyst dissolved in 10 mL of a toluene/THF [80:20] solvent mixture). 4-(Dimethylamino)pyridinum-4-toluenesulfonate (DPTS) was prepared according to a literature procedure.[26]

Measurements. ^{1}H NMR spectra were recorded with a Bruker AM 250 (250 MHz) spectrometer with the solvent proton signal as the internal standard. The number-average molecular weight of the poly(ϵ-caprolactones) was calculated from the ^{1}H NMR spectra from the ratio of the $-OCH_2-$ methylene proton signals ($\delta = 4.05$) and the $-CH_2OH$ methylene proton signals ($\delta = 3.65$). ^{13}C NMR spectra were recorded at 62.9 MHz on a Bruker AM 250 spectrometer with the solvent carbon signal as the internal standard. Size-exclusion chromatography was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer, using polystyrenes of known molecular weights as calibration standards. Four 5-μm Waters columns (300 × 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5, and 10^6) were used with reagent-grade THF as the solvent (25 °C, 1 mm/min flow rate). Analytical TLC was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). For DSC measurements, a Perkin-Elmer DSC 7 instrument was used.

Initiator Synthesis. *(5-Methyl-2-phenyl-[1,3]dioxan-5-yl)-methanol,* ***2***. 1,1,1-Tris(hydroxymethyl)ethane (92.0 g, 766 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TSA; 5.6 g, 29 mmol) were dissolved in 1.5 L of THF, and the mixture was stirred at room temperature (RT) for 2 h. Benzaldehyde dimethyl acetal (120.0 mL, 800 mmol) was added dropwise and allowed to react overnight. The solution was neutralized with NH_4OH/EtOH, diluted with 800 mL of CH_2Cl_2, and washed twice with 200 mL of water. The combined organic phases were dried over $MgSO_4$ and concentrated to yield 159.0 g (99%) of a colorless powder. The crude product (15.0 g) was purified by column chromatography on silica gel with ethyl acetate/hexane (1:1) to yield 11.1 g (50 mmol; 74%) of the desired product. ^{1}H NMR ($CDCl_3$, δ): 0.71 (s, 3H, $-CH_3$), 3.57 (d, 2H, $-COCH_2-$, $J = 11.7$ Hz), 3.78 (s, 2H, CH_2OH), 3.99 (d, 2H, $-COCH_2-$, $J = 11.7$ Hz), 5.40 (s, 1H, $-CH$Ph), 7.30−7.503 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 16.9, 34.9, 65.3, 73.3, 101.8, 126.1, 128.3, 129.0, 138.6.

(5-Hydroxymethyl-2-phenyl-[1,3]dioxan-5-yl)-methanol, ***3***. Pentaerythritol (68.0 g, 500 mmol) was dissolved in 500 mL of water. A catalytic amount of concentrated HCl and benzaldehyde (54.0 mL, 525 mmol) were added dropwise. Stirring continued for 3 h at RT. The white precipitate was washed twice with slightly alkaline cold water, and then refluxed with water to 100 °C and hot filtered. The powder was purified via crystallization from toluene to yield 40.7 g (182 mmol; 36%) of a white powder. ^{1}H NMR ($CDCl_3$, δ): 3.52 (s, 2H, $-CH_2$-OH), 3.75 (d, 2H, $-COCH_2-$, $J = 11.9$ Hz), 4.12 (s, 2H, $-CH_2$-OH), 4.15 (d, 2H, $-COCH_2-$, $J = 12.4$ Hz), 5.42 (s, 1H, $-CH$Ph), 7.34−7.46 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 38.9, 64.2, 65.6, 70.0, 102.1, 126.0, 128.3, 129.0, 138.1.

tert-Butyldimethyl-(5-methyl-2-phenyl-[1,3]dioxan-5-yl-methoxy)-silane, ***4***. (5-Methyl-2-phenyl-[1,3]dioxan-5-yl)-methanol (**2**) (105.0 g, 500 mmol), dissolved in 1.0 L of CH_2Cl_2, was added to dry triethylamine (77.5 mL, 550 mmol) and a catalytic amount of dimethylaminopyridine (12.0 g, 98 mmol). *tert*-Butyldimethylsilyl chloride (115.0 g, 760 mmol) was added, and the mixture was stirred for 48 h. The reaction solution was diluted with 500 mL of CH_2Cl_2 and washed with 200 mL of saturated NH_4Cl (4×) and with 200 mL of water (2×). The organic phase was dried over $MgSO_4$ and concentrated to yield 179.6 g of an orange transparent liquid. The crude product was subdivided into six smaller portions and purified by column chromatography on silica gel with ethyl acetate/hexane (1:40) to yield **4** as a transparent liquid in 77% yield. ^{1}H NMR ($CDCl_3$, δ): −0.02 (s, 6H, $-SiCH_3$), 0.67 and 1.16 (s, 3*H*, $-CH_3$), 0.82 (s, 9*H*, $-CH_3$), 3.24 and 3.74 (s, 2*H*, $-CH_2O-$), 3.49−3.96 (m, 4*H*, $-CH_2O-$), 5.31 (s, 1H, $-OCH-$), 7.23−7.44 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): −5.7, 17.2, 19.0, 25.8, 35.2, 65.3, 73.2, 101.9, 126.1, 128.3, 128.8, 138.6.

2-(tert-Butyldimethylsilanyloxymethyl)-2-methylpropane-1,3-diol, ***5***. Approximately 1.0 g of palladium/carbon (10 wt %) was added to **4** (11.2 g, 35 mmol) dissolved in a THF/methanol (50:50) solvent mixture under a nitrogen blanket. The apparatus for the catalytic hydrogenolysis was filled with H_2(g). The reaction mixture was shaken for 6 h, and afterward, the Pd/C was removed by filtration. The solvent was concentrated to yield 8.2 g (35 mmol; 100%) of a colorless viscous liquid. No further purification was necessary, and the product (**5**) was used directly for subsequent reactions. ^{1}H NMR ($CDCl_3$, δ): 0.00 (s, 6H, $-SiCH_3$), 0.71 (s, 3*H*, $-CH_3$), 0.82 (s, 9H, $-CH_3$), 2.28−2.35 (m, 2H, −OH), 3.41 and 3.53 (s, 2H, $-CH_2O-$), 3.47−3.66 (m, 4H, $-CH_2OH$). ^{13}C NMR ($CDCl_3$, δ): −5.7, 16.8, 18.1, 25.8, 41.0, 67.9, 68.8.

3-Benzyloxy-2-(tert-butyldimethylsilanyloxymethyl)-2-methylpropan-1-ol, ***6***. A solution of **5** (3.7 g, 16 mmol) dissolved in 200 mL of dry THF (0.6 g, 16 mmol), sodium hydride (60 wt % dispersion in mineral oil), benzylbromide (1.9 mL, 16 mmol), and tetrabutylammonium iodide (0.6 g) was added to a round-bottom flask and stirred for 3 h. After dilution with 200 mL of CH_2Cl_2, the solution was washed with 100 mL of saturated NH_4Cl (2×) solution. The organic phase was separated and dried over $MgSO_4$, and the solvent was reduced to yield 5.8 g (18 mmol) of a yellow transparent liquid. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:10) to yield a total of 3.9 g of **6** (12 mmol; 76%) as a transparent viscous liquid. ^{1}H NMR ($CDCl_3$, δ): 0.00 (s, 6H, $-SiCH_3$), 0.79 (s, 3H, $-CH_3$), 0.84 (s, 9H, $-CH_3$), 2.96 (m, 1H, −OH), 3.41 (s, 2H, $-CH_2O-$), 3.54 (d, 2H, $-CH_2OH$), 3.56 (d, 2H, $-CH_2O-$), 4.46 (s, 2H, $-OCH_2$Ph), 7.20−7.27 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): −5.7, 17.2, 18.2, 25.8, 41.0, 67.6, 69.5, 73.6, 74.5, 127.4, 127.5, 138.5.

Benzene-1,3,5-tricarboxylic Acid 1-[3-Benzyloxy-2-(tert-butyldimethylsilanyloxymethyl)-2-methylpropyl] Ester 3,5-Bis-[2-benzyloxymethyl-3-(tert-butyldimethylsilanyloxy)-2-methylpropyl] Ester, ***7***. Compound **6** (1.92 g, 5.0 mmol, 3.3 equiv) was dissolved in 15 mL of THF and triethylamine (0.7 mL, 5.0 mmol, 3.3 equiv) at RT. The solution was stirred for 30 min, and then 1,3,5-benzenetricarbonyl trichloride (0.40 g, 1.50 mmol) in 20 mL of THF was added dropwise. The reaction mixture was stirred for 3 h, and 15 mL of ammonium chloride solution was added. After dilution with 100 mL of diethyl ether, the mixture was extracted three times with 100 mL of an ammonium chloride solution. The water phase was re-extracted with diethyl ether, and the combined organic phases were dried over magnesium sulfate. The solution was concentrated, and the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:9). ^{1}H NMR (δ): 0.00 (s, 18H, $-CH_3$), 0.86 (s, 27H, $-CH_3$), 1.05 (s, 9H, $-CH_3$), 3.41 (s, 6H, $-CH_2-$), 3.56 (d, 6H, $-CH_2-$), 4.31 (s, 6H, $-CH_2-$), 4.47 (s, 6H, $-CH_2-$), 7.15−7.26 (m, 15H, $-Ph$), 8.72 (s, 3H, $-Ph-$). ^{13}C NMR (δ): −5.6, 17.2, 18.2, 25.8, 41.1, 65.2, 67.8, 72.4, 73.4, 127.4, 128.2, 131.5, 134.2, 138.5, 164.8

Benzene-1,3,5-tricarboxylic Acid 1-(3-Benzyloxy-2-hydroxymethyl-2-methylpropyl) Ester 3,5-Bis-(2-benzyloxymethyl-3-hydroxy-2-methylpropyl) Ester, ***8***. Compound **7** (0.98 g, 0.92 mmol) was dissolved in 30 mL of dichloromethane, and BF_3·Et_2O (0.52 mL) was added dropwise; the mixture was then stirred at RT for 3.5 h. An ammonium chloride solution was added to quench the reaction and the mixture was diluted with 150 mL of chloroform and washed three times with 30 mL of a sodium bicarbonate solution and two times with 30 mL of water. The water phase was extracted with 50 mL of chloroform and the combined organic phases were dried over magnesium sulfate and concentrated. The crude product was purified by column chromatography over silica gel with ethyl

acetate/hexane (1:1) to yield 0.38 g of product **8**. ^{1}H NMR (δ): 0.93 (s, 9H, $-CH_3$), 2.62 (bs, 3H, $-OH$), 3.37 (s, 6H, $-CH_2-$), 3.57 (s, 6H, $-CH_2-$), 4.35 (d, 6H, $-CH_2-$), 4.44 (s, 6H, $-CH_2-$), 7.10−7.25 (m, 15H, $-Ph$), 8.68 (s, 3H,$-Ph-$). ^{13}C NMR (δ): 17.3, 40.6, 67.8, 73.7, 74.6, 127.5, 127.8, 128.4, 131.4, 134.5, 137.8, 164.8.

Dendron Synthesis. 3-Hydroxy-2-hydroxymethyl-2-methylpropionic Acid Benzyl Ester, $_p$(g-1), **9**. (See the Results and Discussion section for a description of the initiator nomenclature.) Bis-MPA (50.0 g, 373 mmol), 2,2-dimethoxypropane (58.0 g, 557 mmol), and p-toluenesulfonic acid monohydrate (p-TSA) (1.4 g, 7.0 mmol) were mixed together in 200 mL of acetone. The mixture was stirred for 2 h and neutralized with NH_3/EtOH. After evaporation of the acetone, the mixture was dissolved in CH_2Cl_2 and washed three times with 75 mL of water. The combined organic phases were dried over $MgSO_4$ and concentrated to yield 55.0 g (316 mmol; 85%) of **9**. ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 3H, $-CH_3$), 1.38 (s, 3H, $-CH_3$), 1.41 (s, 3H, $-CH_3$), 3.64 (d, 2H, $-COCH_2-$, J = 11.9 Hz), 4.16 (d, 2H, $-COCH_2-$, J = 11.9 Hz). ^{13}C NMR ($CDCl_3$) δ 18.4, 22.3, 24.9, 41.7, 65.8, 98.3, 180.1.

2,2,5-Trimethyl-[1,3]dioxane-5-carboxylic Acid, (g-1)$_p$, ***10***. Bis-MPA (75.0 g, 559 mmol) and KOH (31.8 g, 567 mmol) were dissolved in 100 mL of dimethylformamide (DMF), and the mixture was heated to 110 °C (1 h). Benzyl chloride (75.1 g, 592 mmol) was slowly added and allowed to react for 14 h. The DMF was distilled off, and the residue was redissolved in CH_2Cl_2 and extracted (3×) with 75 mL of water. The crude product was purified by recrystallization from toluene. After evaporation of the toluene, the product was purified by column chromatography on silica gel with ethyl acetate/hexane to yield a total of 68.8 g (307 mmol; 59%) of **10** in the form of white crystals. ^{1}H NMR ($CDCl_3$, δ): 1.06 (s, 3H, $-CH_3$), 3.70 (d, 2H, $-CH_2OH$, J = 11.3 Hz), 4.90 (d, 2H, $-CH_2OH$, J = 11.3 Hz), 5.18 (s, 2H, $-COOCH_2Ph$), 7.27−7.39 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.1, 49.3, 66.7, 68.1, 127.8, 128.3, 128.6, 135.7, 175.7.

Acetonide- and Benzyl-Protected Second-Generation Dendron, $_p$(g-2)$_p$, ***11****, and a General Procedure for DCC/DPTS Coupling.* The (g-1)$_p$ (22.4 g, 100 mmol) and $_p$(g-1) (40.0 g, 230 mmol) were dissolved in 500 mL of CH_2Cl_2 and 5 mL of dried pyridine, and the mixture was heated until they dissolved completely.[26] 1,3-Dicyclohexylcarbodiimide (DCC) (47.4 g, 230 mmol) and (21.5 g, 69 mmol) 4-(dimethylamino)pyridinum-4-toluenesulfonate (DPTS) were added, and the mixture was stirred for 16 h at 35 °C. The solution was filtered, diluted with CH_2Cl_2, and washed three times with 300 mL of saturated NH_4Cl solution. The organic phase was dried over $MgSO_4$ and evaporated. The viscous oil was redissolved in ethyl acetate, cooled in liquid nitrogen, and cold filtered. Evaporation of the organic solvent yielded 54.0 g of a transparent, slightly yellow oil. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexane. The column was neutralized with 10% triethylamine/hexane to prevent the cleavage of the acetonide protection group. The yield was 45.4 g (85 mmol; 85%) as a clear oil that crystallized after several days. ^{1}H NMR ($CDCl_3$, δ): 1.07 (s, 6H, $-CH_3$), 1.23 (s, 3H, $-CH_3$), 1.32 (s, 6H, $-CH_3$), 1.38 (s, 6H, $-CH_3$), 3.55 (d, 4H, $-COCH_2-$, J = 11.8 Hz), 4.08 (d, 4H, $-COCH_2-$, J = 11.9 Hz), 4.36 (s, 4H, $-COOCH_2-$), 5.13 (s, 2H, $-COOCH_2Ph$), 7.23−7.31 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.7, 18.5, 22.4, 24.8, 42.0, 46.8, 65.4, 65.9, 66.9, 98.1, 128.2, 128.4, 128.6, 135.5, 172.4, 173.5.

Acetonide-Protected Second-Generation Dendron, $_p$(g-2), ***12****, and a General Procedure for Deprotection of the Benzyl Group.* The $_p$(g-2)$_p$ (**11**) (13.6 g, 25 mmol) was dissolved in 200 mL of a THF/ethyl acetate (50:50) solvent mixture. Under a blanket of nitrogen, 1.0 g of Pd/C (10 wt %) was added to the reaction flask. The apparatus for catalytic hydrogenolysis was filled with H_2(g) at 30 psi, and the reaction mixture was shaken for 6 h. The Pd/C was removed by filtration, and the solvents were evaporated to yield 11.5 g of $_p$(g-2) (**12**) (25 mmol; 100%) as a clear viscous oil that crystallized after several days. No further purification was necessary. ^{1}H NMR ($CDCl_3$, δ): 1.13 (s, 6H, $-CH_3$), 1.26 (s, 3H, $-CH_3$), 1.33 (s, 6H, $-CH_3$), 1.39 (s, 6H, $-CH_3$), 3.60 (d, 4H, $-COCH_2-$, J = 11.9 Hz), 4.14 (d, 4H, $-COCH_2-$, J = 11.8 Hz), 4.31 (s, 4H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 17.6, 18.5, 22.3, 24.9, 42.1, 46.5, 65.1, 65.9, 98.2, 173.5, 176.8.

Acetonide- and Benzyl-Protected Third-Generation Dendron, $_p$(g-3)$_p$, ***13****.* The (g-1)$_p$ (**10**) (2.5 g, 11 mmol) and $_p$(g-2) (**12**) (11.5 g, 26 mmol) were esterified using the standard DCC/DPTS coupling procedure to yield, after purification, 9.4 g (9 mmol; 78%) of a transparent oil that crystallized after several days. No pyridine was used for this reaction. ^{1}H NMR ($CDCl_3$, δ): 1.11 (s, 12H, $-CH_3$), 1.17 (s, 6H, $-CH_3$), 1.24 (s, 3H, $-CH_3$), 1.32 (s, 12H, $-CH_3$), 1.38 (s, 12H, $-CH_3$), 3.58 (d, 8H, $-COCH_2-$, J = 11.9 Hz), 4.16 (d, 8H, $-COCH_2-$, J = 11.5 Hz), 4.23−4.29 (m, 12H, $-COOCH_2-$), 5.13 (s, 2H, $-COOCH_2$-Ph), 7.24−7.32 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.6, 18.5, 22.3, 24.9, 42.0, 46.7, 46.8, 64.9, 65.9, 67.2, 98.1, 128.4, 128.5, 128.7, 135.4, 171.8, 171.9, 173.4.

Acetonide-Protected Third-Generation Dendron, $_p$(g-3), ***14****.* The standard deprotection of benzyl group was used to give **14** in near-quantitative yield. ^{1}H NMR ($CDCl_3$, δ): 1.07 (s, 12H, $-CH_3$), 1.26 (s, 9H, $-CH_3$), 1.34 (s, 12H, $-CH_3$), 1.40 (s, 12H, $-CH_3$), 3.60 (d, 8H, $-COCH_2-$, J = 11.9 Hz), 4.15 (d, 8H, $-COCH_2-$, J = 11.8 Hz), 4.22−4.38 (m, 12H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 17.3, 17.7, 18.5, 21.3, 25.7, 42.2, 46.5, 46.7, 65.2, 65.9, 66.3, 98.4, 171.7, 173.0, 173.4.

Synthesis of Initiators with *One* Dendritic Head and *One* Polymeric Tail. 2-Benzyloxymethanol was esterified with the respective dendrons using the DCC/DPTS coupling reaction. The products were purified by column chromatography on silica gel neutralized with NEt_3. Deprotection of the benzyl group was achieved by catalytic hydrogenolysis.

$_p$(g-1)-M$_p$, ***15****.* ^{1}H NMR ($CDCl_3$, δ): 1.21 (s, 3H, $-CH_3$), 1.36 (s, 3H, $-CH_3$), 1.41 (s, 3H, $-CH_3$), 3.65 (d, 2H, $-COCH_2-$, J = 12.0 Hz), 3.67 (t, 2H, $-OCH_2CH_2OCH_2Ph$, J = 4.9 Hz), 4.11 (d, 2H, $-COCH_2-$, J = 12.0 Hz), 4.29 (t, 2H, $-OCH_2CH_2OCH_2$-Ph, J = 4.9 Hz), 4.55 (s, 2H, $-OCH_2Ph$), 7.31−7.23 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.8, 22.4, 24.7, 42.0, 64.4, 65.9, 67.6, 73.1, 98.1, 128.2, 128.4, 128.6, 135.5, 174.1.

$_p$(g-1)-M, ***16****.* ^{1}H NMR ($CDCl_3$, δ): 1.11 (s, 3H, $-CH_3$), 1.36 (s, 3H, $-CH_3$), 1.43 (s, 3H, $-CH_3$), 3.65 (d, 2H, $-COCH_2-$, J = 11.8 Hz), 3.80 (t, 2H, $-OCH_2CH_2OH$, J = 4.6 Hz), 4.20 (d, 2H, $-COCH_2-$, J = 11.9 Hz). 4.30 (t, 2H, $-OCH_2CH_2OH$, J = 4.6 Hz). ^{13}C NMR ($CDCl_3$, δ): 17.8, 22.4, 24.7, 42.0, 60.8, 66.1, 67.3, 98.1, 174.1.

$_p$(g-2)-M$_p$, ***17****.* ^{1}H NMR ($CDCl_3$, δ): 1.11 (s, 6H, $-CH_3$), 1.28 (s, 3H, $-CH_3$), 1.33 (s, 6H, $-CH_3$), 1.39 (s, 6H, $-CH_3$), 3.58 (d, 4H, $-COCH_2-$, J = 12.0 Hz), 3.65 (t, 2H, $-OCH_2CH_2OCH_2$-Ph, J = 4.8 Hz), 4.15 (d, 4H, $-COCH_2-$, J = 12.0 Hz), 4.26 (t, 2H, $-OCH_2CH_2OCH_2Ph$, J = 4.9 Hz), 4.30 (s, 4H, $-COOCH_2-$), 4.52 (s, 2H, $-OCH_2Ph$), 7.29−7.33 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.7, 18.5, 22.4, 24.7, 42.0, 46.7, 64.3, 65.3, 65.9, 67.6, 73.1, 98.1, 127.6, 127.7, 128.4, 137.8, 172.4, 173.5.

$_p$(g-2)-M, ***18****.* ^{1}H NMR ($CDCl_3$, δ): 1.08 (s, 6H, $-CH_3$), 1.30 (s, 3H, $-CH_3$), 1.34 (s, 6H, $-CH_3$), 1.40 (s, 6H, $-CH_3$), 3.61 (d, 4H, $-COCH_2-$, J = 11.7 Hz), 3.76 (t, 2H, $-OCH_2CH_2OH$, J = 4.1 Hz), 4.15 (d, 4H, $-COCH_2-$, J = 11.9 Hz), 4.23 (t, 2H, $-OCH_2CH_2OH$, J = 4.3 Hz), 4.35 (s, 4H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 17.8, 18.4, 21.4, 25.8, 42.2, 47.0, 60.8, 65.6, 66.1, 67.3, 98.3, 172.9, 173.7.

$_p$(g-3)-M$_p$, ***19****.* ^{1}H NMR ($CDCl_3$, δ): 1.10 (s, 12H, $-CH_3$), 1.21 (s, 6H, $-CH_3$), 1.24 (s, 3H, $-CH_3$), 1.31 (s, 12H, $-CH_3$), 1.37 (s, 12H, $-CH_3$), 3.57 (d, 8H, $-COCH_2-$, J = 11.4 Hz), 3.64 (t, 2H, $-OCH_2CH_2OCH_2Ph$, J = 4.7 Hz), 4.10 (d, 8H, $-COCH_2-$, J = 11.8 Hz), 4.26−4.37 (s, 12H, $-COOCH_2-$; t, 2H, $-OCH_2$-CH_2OCH_2Ph), 4.50 (s, 2H, $-OCH_2Ph$), 7.23−7.29 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.6, 18.5, 22.3, 24.9, 42.0, 46.6, 46.8, 64.4, 64.9, 65.9, 67.6, 73.0, 98.1, 127.6, 127.7, 128.4, 137.9, 171.8, 172.1, 173.4.

$_p$(g-3)-M, ***20****.* ^{1}H NMR ($CDCl_3$, δ): 1.11 (s, 12H, $-CH_3$), 1.25 (s, 6H, $-CH_3$), 1.27 (s, 3H, $-CH_3$), 1.32 (s, 12H, $-CH_3$), 1.39 (s, 12H, $-CH_3$), 3.59 (d, 8H, $-COCH_2-$, J = 12.0 Hz), 3.80 (t, 2H, $-OCH_2CH_2OH$), 4.12 (d, 8H, $-COCH_2-$, J = 11.8 Hz), 4.19 (t, 2H, $-OCH_2CH_2OH$), 4.29 (s, 12H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 17.6, 18.5, 22.0, 25.2, 42.1, 46.7, 46.9, 60.7, 65.0, 65.9, 66.2, 98.1, 171.9, 172.4, 173.6.

Synthesis of Initiators with *One* Dendritic Head and *Two* Polymeric Tails. The orthogonally protected compound **2** was esterified to the respective dendrons with a DCC/DPTS coupling reaction. The products were purified by column chromatography on silica gel neutralized with NEt_3. Deprotection of the benzyl group was achieved by catalytic hydrogenolysis.

$_p$(g-1)-D$_p$, ***21***. ^{1}H NMR ($CDCl_3$, δ): 0.82 (s, 3H, $-CH_3$), 1.18 (s, 3H, $-CH_3$), 1.36 (s, 3H, $-CH_3$), 1.42 (s, 3H, $-CH_3$), 3.64 (d, 2H, $-COCH_2-$, $J = 11.8$ Hz), 3.66 (d, 2H, $-OCH_2-$, $J = 11.8$ Hz), 3.88 (s, 1H, $-COOCH_2-$), 4.05 (d, 2H, $-COCH_2-$, $J = 11.8$ Hz), 4.19 (d, 2H, $-COCH_2-$, $J = 11.8$ Hz), 4.47 (s, 1H, $-COOCH_2-$), 5.42 (s, 1H, $-CH$Ph), 7.33−7.46 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.2, 17.8, 22.4, 24.7, 33.8, 42.1, 65.3, 65.9, 73.2, 98.1, 102.0, 128.1, 128.4, 128.6, 135.5, 174.1.

$_p$(g-1)-D, ***22***. ^{1}H NMR ($CDCl_3$, δ): 0.84 (s, 3H, $-CH_3$), 1.09 (s, 3H, $-CH_3$), 1.36 (s, 3H, $-CH_3$), 1.43 (s, 3H, $-CH_3$), 3.57 (s, 4H, $-CH_2$OH), 3.66 (d, 2H, $-COCH_2-$, $J = 11.9$ Hz), 4.19 (d, 2H, $-COCH_2-$, $J = 12.0$ Hz), 4.25 (s, 2H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ) 17.0, 18.2, 20.5, 26.7, 40.5, 42.5, 65.5, 66.3, 67.6, 98.3, 175.1.

$_p$(g-2)-D$_p$, ***23***. ^{1}H NMR ($CDCl_3$, δ): 0.80 (s, 3H, $-CH_3$), 1.11 (s, 6H, $-CH_3$), 1.30 (s, 3H, $-CH_3$), 1.32 (s, 6H, $-CH_3$), 1.38 (s, 6H, $-CH_3$), 3.58 (d, 4H, $-COCH_2-$, $J = 12.0$ Hz), 3.66 (d, 2H, $-COCH_2-$, $J = 12.0$ Hz), 4.01 (d, 2H, $-COCH_2-$, $J = 11.8$ Hz), 4.13 (d, 4H, $-COCH_2-$, $J = 11.9$ Hz), 4.34 (s, 4H, $-COOCH_2-$), 4.42 (s, 2H, $-COOCH_2-$), 5.41 (s, 1H, $-CH$Ph), 7.32−7.46 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.1, 17.8, 18.5, 22.4, 24.8, 33.8, 42.1, 47.0, 65.3, 65.9, 67.5, 73.2, 98.1, 102.0, 126.1, 128.2, 129.0, 137.9, 172.3, 173.5.

$_p$(g-2)-D, ***24***. ^{1}H NMR ($CDCl_3$, δ): 0.82 (s, 3H, $-CH_3$), 1.07 (s, 6H, $-CH_3$), 1.29 (s, 3H, $-CH_3$), 1.33 (s, 6H, $-CH_3$), 1.39 (s, 6H, $-CH_3$), 3.49−3.54 (m, 4H, $-CH_2$OH), 3.60 (d, 4H, $-COCH_2-$, $J = 11.5$ Hz), 4.13 (d, 4H, $-COCH_2-$, $J = 12.0$ Hz), 4.15 (s, 2H, $-COOCH_2-$), 4.31 (s, 4H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 16.9, 17.7, 18.4, 21.3, 25.8, 40.5, 42.2, 47.1, 65.5, 66.0, 67.0, 67.2, 98.3, 172.8, 173.6.

$_p$(g-3)-D$_p$, ***25***. ^{1}H NMR ($CDCl_3$, δ): 0.80 (s, 3H, $-CH_3$), 1.08 (s, 12H, $-CH_3$), 1.20 (s, 6H, $-CH_3$), 1.25 (s, 3H, $-CH_3$), 1.30 (s, 12H, $-CH_3$), 1.36 (s, 12H, $-CH_3$), 3.56 (d, 8H, $-COCH_2-$, $J = 11.9$ Hz), 3.64 (d, 2H, $-COCH_2-$, $J = 11.8$ Hz), 3.98 (d, 2H, $-COCH_2-$, $J = 11.5$ Hz), 4.09 (d, 8H, $-COCH_2-$, $J = 11.8$ Hz), 4.25 (s, 12H, $-COOCH_2-$), 4.39 (s, 2H, $-COOCH_2-$), 5.38 (s, 1H, $-CH$Ph), 7.28−7.43 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.1, 17.4, 17.6, 18.5, 22.3, 24.9, 33.8, 42.0, 46.9, 64.9, 65.9, 67.6, 73.1, 98.1, 102.0, 126.1, 128.2, 129.0, 137.9, 171.8, 172.6, 173.4.

$_p$(g-3)-D, ***26***. ^{1}H NMR ($CDCl_3$, δ): 0.85 (s, 3H, $-CH_3$), 1.11 (s, 12H, $-CH_3$), 1.26 (s, 6H, $-CH_3$), 1.27 (s, 3H, $-CH_3$), 1.33 (s, 12H, $-CH_3$), 1.39 (s, 12H, $-CH_3$), 3.56 (s, 4H, $-CH_2$OH), 3.60 (d, 8H, $-COCH_2-$, $J = 12.0$ Hz), 4.13 (d, 8H, $-COCH_2-$, $J = 11.8$ Hz), 4.19 (s, 2H, $-COOCH_2-$), 4.30 (s, 12H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 16.9, 17.7, 18.5, 22.0, 25.2, 40.5, 42.1, 46.9, 65.0, 65.9, 66.2, 67.4, 98.2, 171.9, 172.4, 173.6.

Synthesis of Initiators with *Two* Dendritic Heads and *Two* Polymeric Tails. The orthogonally protected compound **3** was coupled to the respective dendrons with a DCC/DPTS esterification. The $_p$(g-1)$_2$-D$_p$ was purified by column chromatography on silica gel neutralized with NEt_3. Column chromatography with $_p$(g-2)$_2$-D$_p$ and $_p$(g-3)$_2$-D$_p$ was not successful. Purification was achieved by precipitation in cold hexane. Deprotection of the benzyl protection group was achieved by catalytic hydrogenolysis.

$_p$(g-1)$_2$-D$_p$, ***27***. ^{1}H NMR ($CDCl_3$, δ): 1.11 (s, 3H, $-CH_3$), 1.15 (s, 3H, $-CH_3$), 1.33 (s, 3H, $-CH_3$), 1.36 (s, 3H, $-CH_3$), 1.40 (s, 3H, $-CH_3$), 1.42 (s, 3H, $-CH_3$), 3.63 (d, 2H, $-COCH_2-$, $J = 11.9$ Hz), 3.64 (d, 2H, $-COCH_2-$, $J = 11.9$ Hz), 3.90 (d, 2H, $-COCH_2-$, $J = 11.9$ Hz), 4.04 (s, 2H, $-COOCH_2-$), 4.17 (d, 2H, $-COCH_2-$, $J = 11.9$ Hz), 4.18 (d, 4H, $-COCH_2-$, $J = 11.9$ Hz), 4.59 (s, 2H, $-COOCH_2-$), 5.43 (s, 1H, $-CH$Ph), 7.33−7.47 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 18.4, 18.6, 21.3, 22.1, 25.1, 26.0, 38.0, 42.2, 62.6, 63.1, 66.1, 69,5, 98.2, 102.1, 126.1, 128.3, 129.1, 137.7, 173.8.

$_p$(g-1)$_2$-D, ***28***. ^{1}H NMR ($CDCl_3$, δ): 1.03 (s, 6H, $-CH_3$), 1.30 (s, 6H, $-CH_3$), 1.37 (s, 6H, $-CH_3$), 3.56 (s, 4H, $-CH_2$OH), 3.61 (d, 4H, $-COCH_2-$, $J = 11.9$ Hz), 4.13 (d, 4H, $-COCH_2-$, $J = 11.9$ Hz), 4.21 (s, 4H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 18.2, 20.4, 26.8, 42.5, 45.5, 62.6, 63.7, 66.4, 98.3, 174.8.

$_p$(g-2)$_2$-D$_p$, ***29***. ^{1}H NMR ($CDCl_3$, δ): 1.08 (s, 6H, $-CH_3$), 1.11 (s, 6H, $-CH_3$), 1.28 (s, 3H, $-CH_3$), 1.30 (s, 9H, $-CH_3$), 1.33 (s, 6H, $-CH_3$), 1.37 (s, 6H, $-CH_3$), 1.39 (s, 6H, $-CH_3$), 3.56 (d, 4H, $-COCH_2-$, $J = 10.8$ Hz), 3.61 (d, 4H, $-COCH_2-$, $J = 11.3$ Hz), 3.86 (d, 2H, $-COCH_2-$, $J = 11.6$ Hz), 3.96 (s, 2H, $-COOCH_2-$), 4.06 (d, 2H, $-COCH_2-$, $J = 11.2$ Hz), 4.11 (d, 4H, $-COCH_2-$, $J = 11.6$ Hz), 4.13 (d, 4H, $-COCH_2-$, $J = 11.8$ Hz), 4.32 (s, 4H, $-COOCH_2-$), 4.33 (s, 4H, $-COOCH_2-$), 4.50 (s, 2H, $-COOCH_2-$), 5.41 (s, 1H, $-CH$Ph), 7.32−7.42 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.5, 18.3, 21.6, 22.0, 24.8, 25.3, 37.4, 41.9, 46.9, 63.1, 63.6, 64.8, 65.8, 69.0, 97.9, 101.8, 125.9, 128.0, 128.9, 137.4, 171.9, 173.3.

$_p$(g-2)$_2$-D, ***30***. ^{1}H NMR ($CDCl_3$, δ): 1.04 (s, 12H, $-CH_3$), 1.25 (s, 6H, $-CH_3$), 1.29 (s, 12H, $-CH_3$), 1.36 (s, 12H, $-CH_3$), 3.49 (s, 4H, $-CH_2$OH), 3.57 (d, 8H, $-COCH_2-$, $J = 10.8$ Hz), 4.09 (d, 8H, $-COCH_2-$, $J = 11.8$ Hz), 4.09 (s, 4H, $-COOCH_2-$), 4.29 (s, 8H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 17.7, 18.4, 21.2, 25.9, 42.2, 45.0, 47.1, 61.0, 63.0, 65.3, 66.0, 67.8, 98.3, 172.5, 173.6.

$_p$(g-3)$_2$-D$_p$, ***31***. ^{1}H NMR ($CDCl_3$, δ): 1.10 (s, 12H, $-CH_3$), 1.10 (s, 12H, $-CH_3$), 1.26 (s, 18H, $-CH_3$), 1.31 (s, 24H, $-CH_3$), 1.38 (s, 24H, $-CH_3$), 3.57 (d, 8H, $-COCH_2-$, $J = 12.0$ Hz), 3.59 (d, 8H, $-COCH_2-$, $J = 11.4$ Hz), 3.91 (d, 2H, $-COCH_2-$, $J = 11.8$ Hz), 3.98 (s, 2H, $-COOCH_2-$), 4.07 (d, 2H, $-COCH_2-$, $J = 11.4$ Hz), 4.10 (d, 8H, $-COCH_2-$, $J = 11.8$ Hz), 4.12 (d, 8H, $-COCH_2-$, $J = 11.7$ Hz), 4.26 (s, 12H, $-COOCH_2-$), 4.30 (s, 12H, $-COOCH_2-$), 4.50 (s, 2H, $-COOCH_2-$), 5.43 (s, 1H, $-CH$Ph), 7.31−7.43 (m, 5H, $-Ph$). ^{13}C NMR ($CDCl_3$, δ): 17.6, 17.7, 18.5, 22.0, 22.4, 24.8, 25.1, 37.5, 42.0, 42.1, 46.9, 63.2, 64.0, 64.8, 65.9, 69.0, 98.1, 102.0, 126.1, 128.2, 129.0, 137.5, 171.8, 173.4, 173.5.

$_p$(g-1)$_2$-D, ***32***. ^{1}H NMR ($CDCl_3$, δ): 1.07 (s, 24H, $-CH_3$), 1.22 (s, 12H, $-CH_3$), 1.22 (s, 6H, $-CH_3$), 1.28 (s, 24H, $-CH_3$), 1.35 (s, 24H, $-CH_3$), 3.55 (d, 16H, $-COCH_2-$, $J = 12.0$ Hz), 3.62 (s, 4H, $-CH_2$OH), 4.08 (d, 16H, $-COCH_2-$, $J = 11.8$ Hz), 4.13 (s, 4H, $-COOCH_2-$), 4.21 (s, 8H, $-COOCH_2-$), 4.26 (s, 16H, $-COOCH_2-$). ^{13}C NMR ($CDCl_3$, δ): 17.6, 17.7, 18.5, 22.0, 25.2, 42.1, 44.7, 46.9, 61.8, 63.7, 64.9, 65.9, 98.1, 171.9, 173.5, 173.6.

Synthesis of $_p$(g-2)$_3$-T$_p$, 33. Compound **8** (1.5 g, 2.0 mmol) and $_p$(g-2) (**12**) (4.00 g, 9.0 mmol) were dissolved in 100 mL of dichloromethane, and the mixture was stirred at RT for 1 h. DCC (1.86 g, 9.0 mmol) and DPTS (0.85 g, 2.7 mmol) were added to the reaction mixture, which was then stirred at 30 °C for 12 h. Ammonium chloride solution (30 mL) was added to quench the reaction; the solution was then diluted with 100 mL of dichloromethane, extracted with 50 mL of ammonium chloride solution (3×) and 50 mL of water, dried with magnesium sulfate, and concentrated. The crude product was dissolved in warm ethyl acetate and cooled to precipitate and remove by filtration the byproducts from the DCC/DPTS coupling reaction. The remaining ethyl acetate was evaporated to yield 5.3 g of crude product. Purification was accomplished by column chromatography over silica gel with ethyl acetate/hexane (1:1) to yield 2.5 g of the desired product $_p$(g-2)$_3$-T$_p$, (**33**). ^{1}H NMR (δ): 1.04 (s, 27H, $-CH_3$), 1.19 (s, 9H, $-CH_3$), 1.25 (s, 18H, $-CH_3$), 1.31 (s, 18H, $-CH_3$), 3.37 (s, 6H, $-CH_2$-OCH$_2$Ph), 3.52 (d, 12H, $-COCH_2-$, $J = 12.0$ Hz), 4.05 (d, 12H, $-COCH_2-$, $J = 12.0$ Hz), 4.12 (s, 6H, $-CH_2-$), 4.25 (s, 6H, $-$PhCOOCH_2-), 4.25 (s, 12H, $-COCH_2-$), 4.42 (s, 6H, $-CH_2$-Ph), 7.10−7.20 (m, 15H, $-Ph$), 8.63 (s, 3H, $-Ph-$). ^{13}C NMR ($CDCl_3$, δ): 14.2, 17.4, 17.6, 18.5, 22.2, 25.0, 39.7, 42.0, 46.9, 65.0, 65.9, 67.1, 73.4, 98.1, 127.5, 127.6, 128.3, 131.2, 137.9, 164.3, 172.1, 173.5.

Synthesis of $_p$(g-2)$_3$-T, 34. Carbon on palladium (10 wt %) (1 g) was added to compound **33** (1.16 g, 0.56 mmol) dissolved in an ethyl acetate/THF (1:1) mixture. Hydrogen was charged into the reaction flask, which was then shaken vigorously at RT for 4.5 h. The Pd/C was removed by filtration, and the solution was concentrated to yield 0.76 g (75%) of pure **34**. For ring-opening polymerization reactions, the initiator **34** was purified and dried by short column chromatography over silica gel with an ethyl acetate/hexane (1:1) mixture. The solvents

were removed by distillation, and **34** was dried under high vacuum for 12 h. ^{1}H NMR ($CDCl_3$, δ): 1.02 (s, 9H, $-CH_3$), 1.04 (s, 18H, $-CH_3$), 1.25 (s, 9H, $-CH_3$), 1.28 (s, 18H, $-CH_3$), 1.34 (s, 18H, $-CH_3$), 3.50 (s, 6H, $-CH_2OCH_2Ph$), 3.56 (d, 12H, $-COCH_2-$, J = 12.0 Hz), 4.08 (d, 12H, $-COCH_2-$, J = 12.0 Hz), 4.10 (s, 6H, $-CH_2-$), 4.26 (s, 6H, $-PhCOOCH_2-$), 4.29 (s, 12H, $-COCH_2-$), 8.63 (s, 3H, $-Ph-$). ^{13}C NMR ($CDCl_3$, δ): 14.4, 16.9, 17.7, 18.4, 21.5, 25.6, 40.4, 42.1, 47.0, 65.2, 66.5, 67.8, 86.3, 98.2, 131.3, 134.5, 151.7, 164.6, 172.6, 173.6.

Polymerization: General Procedure for Poly(ϵ-caprolactone) Formation. The multifunctional hydroxyl initiator **24** (0.96 g, 1.75 mmol) was charged into a previously flamed round-bottom flask and purged with nitrogen. ϵ-Caprolactone (2.00 g, 1.75 mmol) was charged into the flask, and the mixture was heated to 110 °C before a catalytic amount of $Sn(Oct)_2$ (32 mg, 0.08 mmol) was added. The molar amount of catalyst is 1/400 relative to the initiator. The bulk reaction mixture was stirred for 24 h, diluted with THF, and precipitated in cold hexanes to give 95% yield of a white crystalline powder. Melting point: 50 °C.

The monohydroxyl initiator, **16** (0.04 g, 0.89 mmol), was charged into a round-bottom flask equipped with a nitrogen inlet and septum, which was carefully flamed under nitrogen and purged with nitrogen (3×). The initiator and a stock solution of $Sn(OTf)_2$ (150 mg of catalyst dissolved in 10 mL of a THF/toluene (20:80) solvent mixture) were charged, and the mixture was stirred for 20 min. The molar amount of catalyst used was 1% of the amount of initiator. The ϵ-caprolactone (2.00 g, 1.75 mmol) was added, and the mixture was heated to 65 °C and allowed to stir for 20 h. The bulk polymerization solution was diluted with THF and precipitated in cold hexanes to give 90% yield of a white crystalline powder. Melting point: 52 °C.

Endcapping: General Procedure for the Formation of an Acetate End Group from Capping of the Hydroxyl Chain Ends. The dendritic−linear copolymer $_p(g\text{-}2)_2\text{-}di(PCL)_{28}$ (2.00 g, 0.80 mmol) dissolved in 5 mL of THF was added to a round-bottom flask, together with triethylamine (0.10 g, 1.00 mmol). Acetic anhydride (0.79 g, 1.00 mmol) was added, and the mixture was allowed to stir for 40 h. The polymer solution was concentrated, redissolved in methylene chloride and extracted (4×) with ammonium chloride. The polymer solution was concentrated, redissolved in THF, precipitated in either hexanes or methanol, and dried to a constant weight.

General Procedure for the Deprotection of the Dendrons. Poly(ϵ-caprolactone) (0.5 g) was dissolved in 3 mL of a THF/methanol mixture and was charged, along with Dowex 50WX8-200 ion-exchange resin (0.4 g), into a round-bottom flask equipped with a septum. The reaction mixture was stirred at 48 °C for 50 h to effect the deprotection reaction. The mixture was cooled, filtered (to remove the Dowex), and concentrated.

Results and Discussion

New multifunctional initiators were prepared using an orthogonal protecting group approach. These initiators enabled the design and synthesis of dendritic−linear hybrid block copolymers having A_xB_x topologies, where the A blocks are composed of hydrophilic dendrons and the B blocks are composed of hydrophobic poly(ϵ-caprolactone) chains. These amphiphilic copolymers are similar in shape to traditional low-molecular-weight surfactants and in size and chain conformation to block copolymers. They mimic in many ways biosynthetic molecules such as phospholipids. The general design strategy for the synthesis of dendritic−linear block copolymers is shown in Figure 1. These A_xB_x topological isomers differ in the number and generation of dendrons, generically illustrated as cones, and the number of poly(ϵ-caprolactone) chains that emanate from the multifunctional initiators, denoted as the dark circle in the structure (Figure 1). The versatility in the

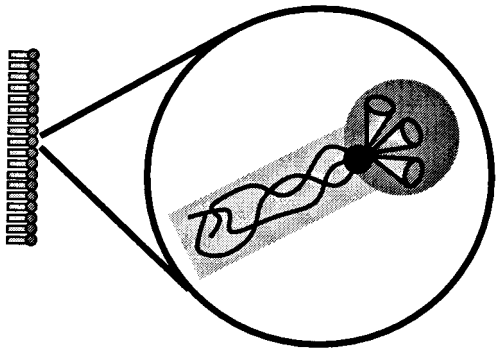
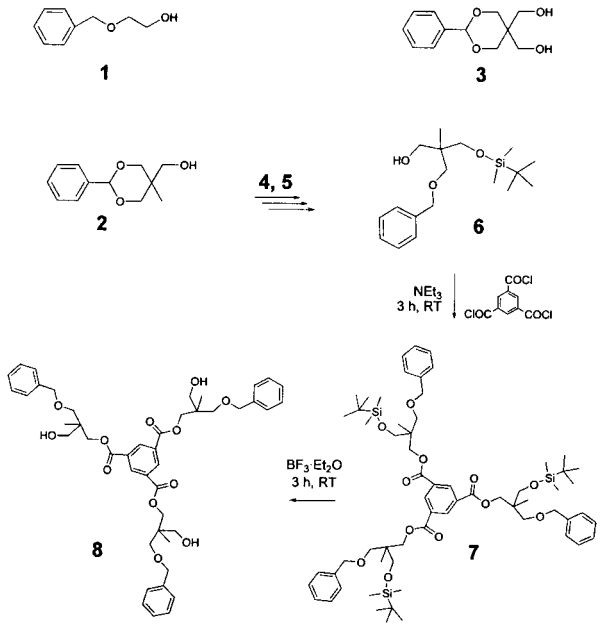


Figure 1. General schematic for assembly of dendritic−linear hybrids.

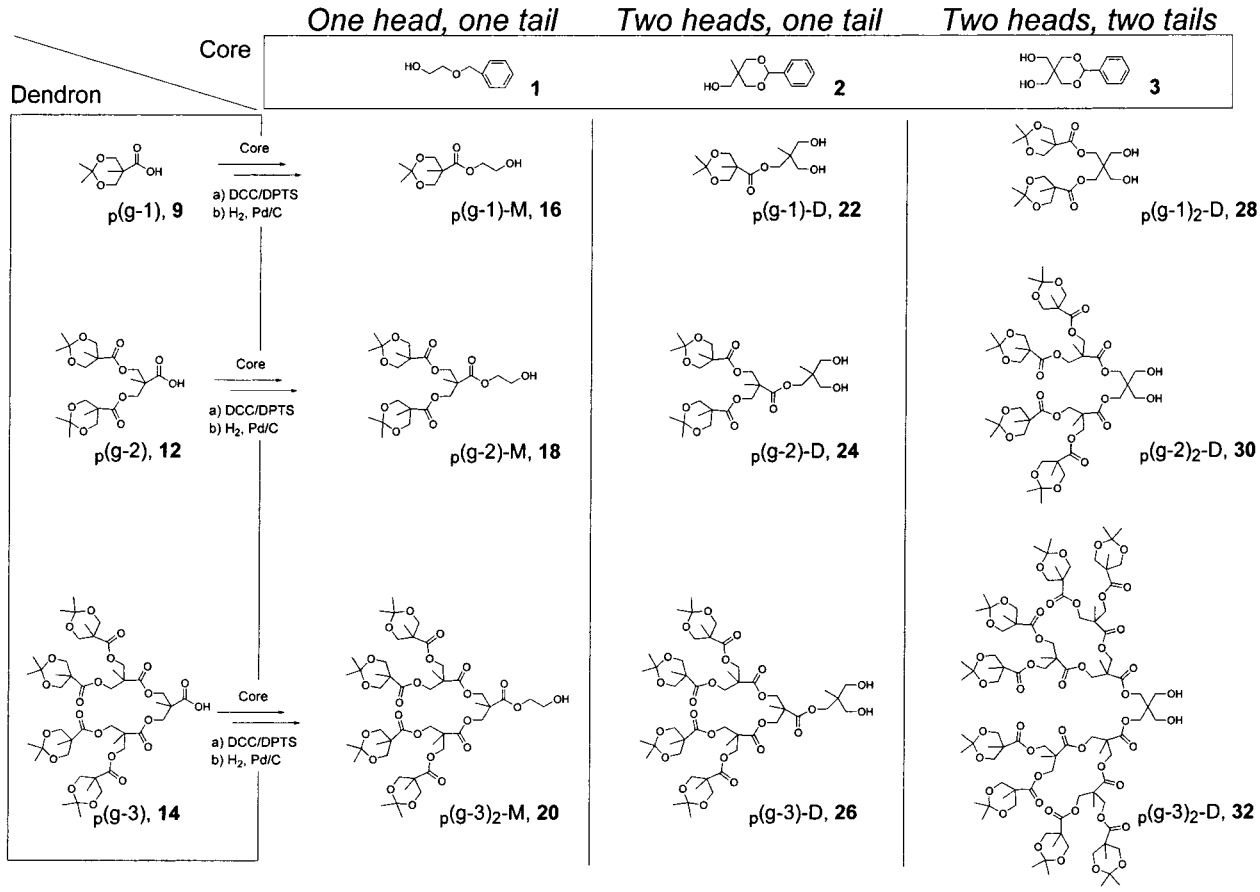
Scheme 1



design stems from the various libraries of "building blocks" employed in the construction of the copolymers. These libraries include various generations of hydrophilic dendrons; poly(ϵ-caprolactone) prepared by controlled/living ring-opening polymerization (ROP) techniques; and, most importantly, new multifunctional initiators. The novelty employed in the synthesis of this library of initiators is the use of orthogonal protecting groups. The initiators serve as the central core molecule from which each of the other libraries is sequentially assembled through consecutive deprotection and transformation steps. These combined libraries of building blocks provide the requisite tools necessary to synthesize new dendritic−linear hybrid amphiphilic copolymers.

Four series of initiators were prepared from orthogonally protected building blocks for the synthesis of the dendritic−linear copolymers. The general synthetic routes to these orthogonally protected compounds are shown in Scheme 1. First, 2-benzyloxyethanol was used as a monohydroxyl-protected compound, **1**. In the second-general synthetic route, selected hydroxyl groups of 1,1,1-tris(hydroxymethyl)ethane and pentaerythritol were protected with benzaldehyde dimethyl acetal by a procedure described by Issidorides and Gulen[27] to form the benzylidene acetal-protected compounds **2** and **3**. The last general synthetic route to the orthogonally protected initiator **8**, also shown in Scheme 1, is directed toward the synthesis of A_3B_3 dendritic−linear copolymer

Scheme 2



architectures. The synthetic route to this initiator is considerably more involved than the other three. The critical feature in this approach is the selective functionalization of 1,1,1-tris(hydroxyethyl)methane with protecting groups that can be selectively removed after subsequent transformations. This was accomplished by the reaction of **3** with *tert*-butyldimethylsilyl chloride to give **4**.[28] The benzylidene acetal group was then selectively removed by catalytic hydrogenolysis over Pd/C to give **5**. This compound was reacted with 1 equiv of sodium hydride and benzyl bromide to give **6**. Reaction of **6** with 1,3,5-benzenetricarbonyl trichloride in the presence of triethylamine yielded the multifunctional orthogonally protected compound **7** in high yields. The *tert*-butyldimethylsilyl group was selectively deprotected with $BF_3{\cdot}Et_2O$ quantitatively to yield **8**.

An important feature in the construction of the amphiphilic copolymers is the judicious choice of the dendritic fragments, which provide the requisite hydrophilic character. Dendrimers derived from 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) are reportedly water-soluble. The first- through third-generation dendrons derived from bis-MPA were prepared by procedures developed by Hult et al.[29] The benzyl ester of bis-MPA was prepared by forming the potassium salt of bis-MPA and reacting the salt with benzyl bromide to give **10**. The hydroxyl groups of bis-MPA were reacted with 2,2-dimethoxypropane to form the acetonide-protected bis-MPA, **9**. The second-generation dendron **11** was prepared by coupling 2 equiv of **9** with 1 equiv of **10** in high yield. The benzyl ester group of **11** was then selectively removed by catalytic hydrogenolysis over Pd/C to give **12** in high yield. The third-generation dendron **14** was synthesized by coupling **12** with a 0.5 equiv of **10** to give **13**, and the benzyl ester group was removed by hydrogenolysis to give the acid functionality at the focal point in **14**. The first- through third-generation acid-functional dendrons were used as components in the synthesis of the multifunctional orthogonal initiators.

The unprotected hydroxyl groups of the orthogonally protected compounds **1**−**3** were coupled to the first- through third-generation acid-functional dendrons using 1,3-dicyclohexylcarbodiimide (DCC) with 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS)[26] in high yields. From the three protected starting compounds (**1**−**3**), esterification of the first- through third-generation dendrons (**9**, **12**, **14**) produced nine dendron-functionalized initiators. Scheme 2 shows the general two-step pathway to these nine compounds, including the coupling and deprotection step to yield the primary alcohols capable of polymerizing cyclic esters. Initiators giving rise to polymers having either one head and one tail (**16**, **18**, **20**), one head and two tails (**22**, **24**, **26**), or two heads and two tails (**28**, **30**, **32**) can be realized from this approach (Scheme 2). A simple and straightforward nomenclature was employed to describe the functionality of the initiators. For example, compound **30** is also denoted as $_p(g\text{-}2)_2$-D. In this case, (g-2) denotes the generation of the dendron used, which can range from g-1 to g-3. The following subscript indicates the number of dendrons used, which once again can range from 1 to 3, and the subscript p indicates that the dendrons are protected. The following value, in this case D for di-, denotes the number of unprotected hydroxyl groups. Alternatively, this latter value could be M for monofunctional or T for trifunctional hydroxyl groups. Prior to the deprotection of the benzylidene acetal group to

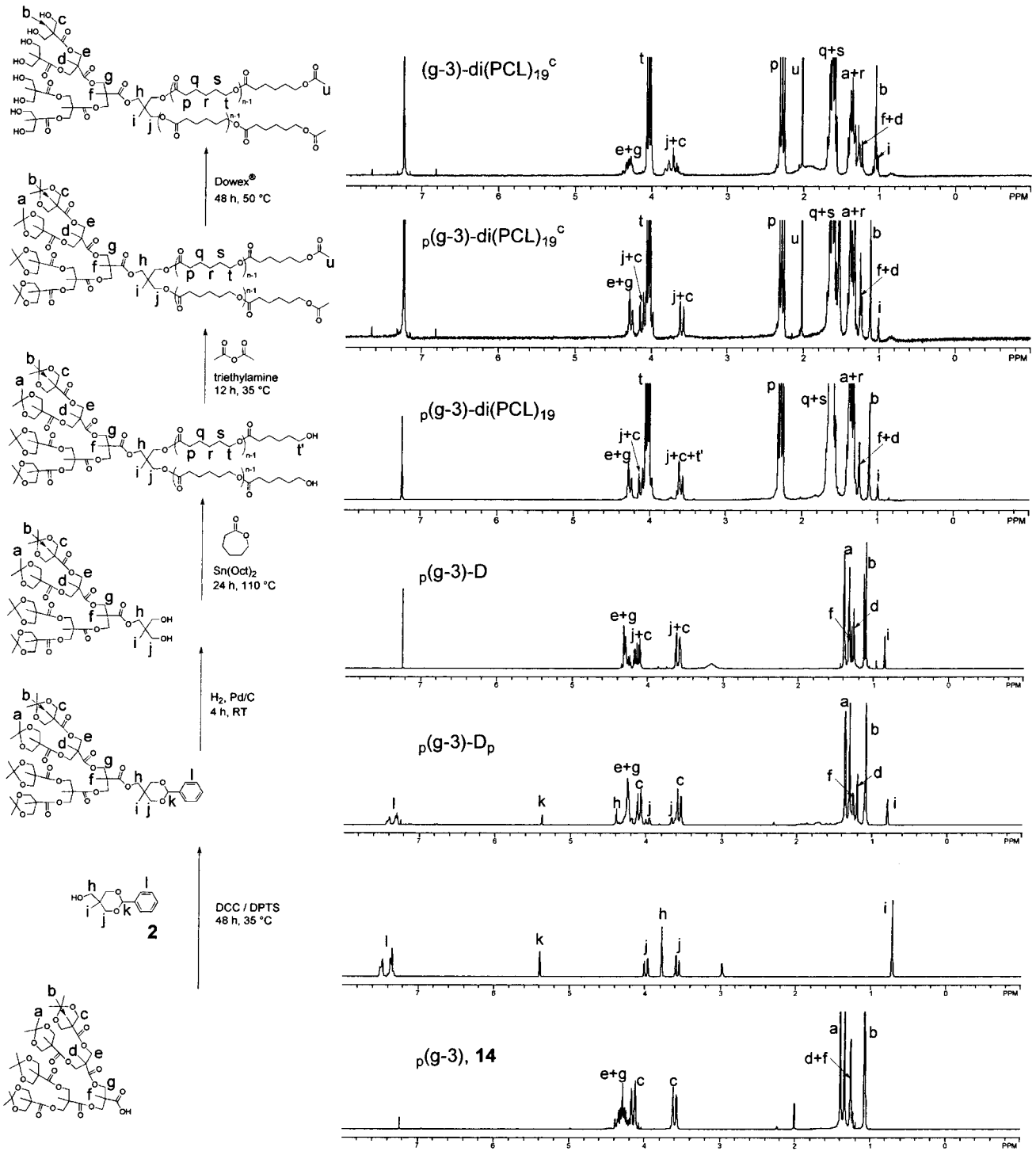
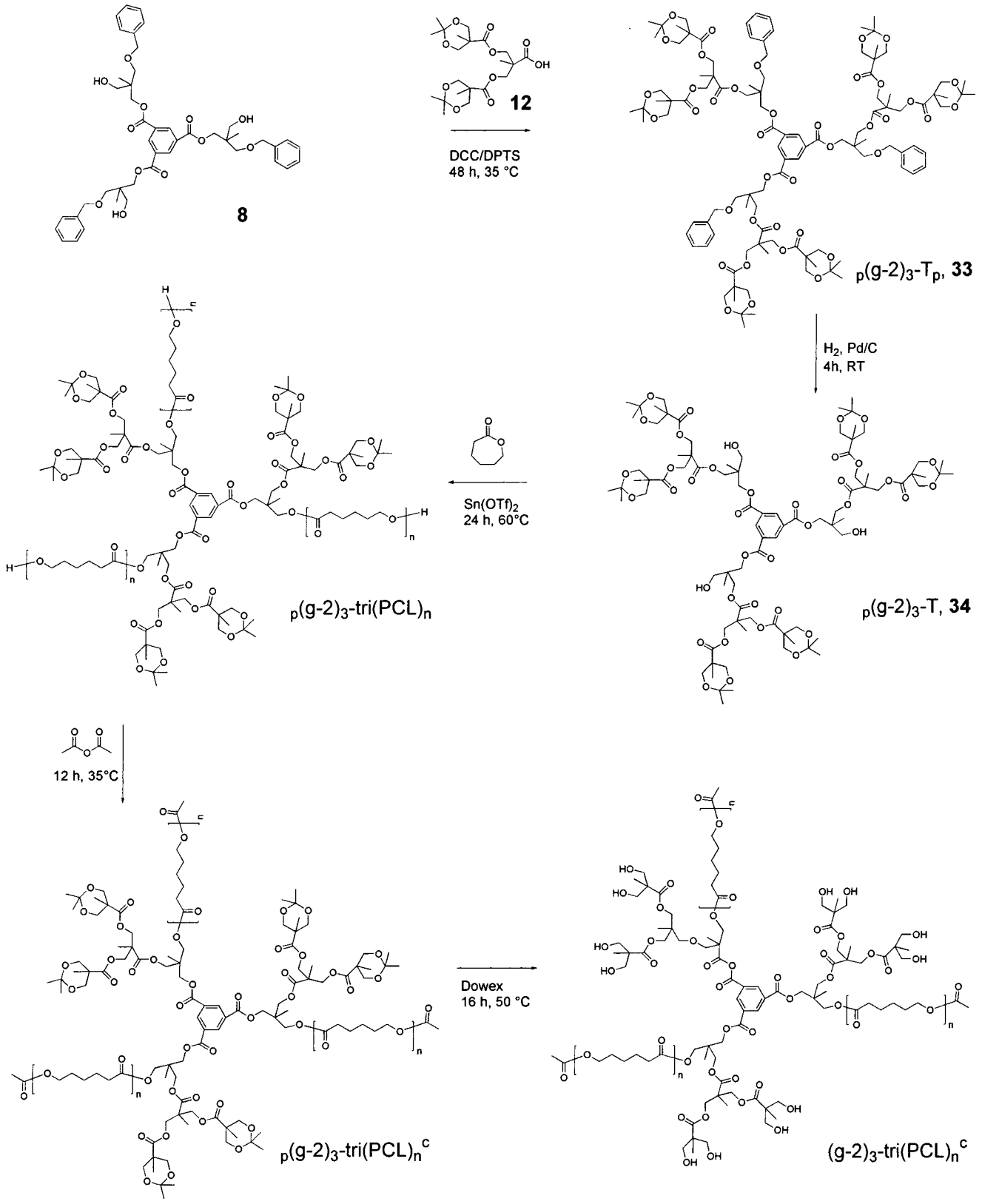


Figure 2. Synthesis and ^{1}H NMR spectra of (g-3)-di(PCL)$_{19}^{c}$.

yield **30**, compound **29** was referred to as $_p$(g-2)$_2$-D$_p$ and once the deprotection was accomplished, the p subscript was removed. Figure 2 shows the general reaction scheme and the ^{1}H NMR spectra of (g-3), **3**, the esterified product $_p$(g-3)$_2$-D$_p$, and the product of the deprotection step $_p$(g-3)$_2$-D. Clearly, the spectra demonstrate pure products with the requisite structure, and the removal of the benzylidene acetal group by catalytic hydrogenolysis regenerated the hydroxyl groups in quantitative yields with no detectable side reactions.

The last general route to the dendron-substituted orthogonally protected initiator **34** was, once again, considerably more involved (Scheme 3). Reaction of **8** with the second-generation acid-functional dendron **12** using DCC/DPTS produced compound **33**. Deprotection of the benzyl ether groups was accomplished by catalytic hydrogenolysis using palladium over carbon to produce the hydroxyl group required to initiate the ROP of ϵ-caprolactone from initiator **34**. Figure 3 shows the ^{1}H NMR spectra of compounds **8**, **33**, and **34**. For each of these compounds, selective and quantitative deprotection transformations are clearly, seen together with the esterification of the dendron on the core. These four series of dendron-substituted initiators collectively comprise the key building blocks from which the dendritic−linear copolymers are prepared.

Scheme 3



The controlled/living ring-opening polymerization of ϵ-caprolactone from each of the new initiators was accomplished using bulk conditions, as ϵ-caprolactone is a good solvent for all of the initiators. Although high selectivity with minimal side reactions has been demonstrated in the ROP of cyclic esters using aluminum- and lanthanide-based initiators,[30−32] most aliphatic polyesters are prepared from tin-based catalysts, of which stannous(II) 2-ethylhexanoate [$Sn(Oct)_2$] is the most effective and versatile.[33−35] $Sn(Oct)_2$ is commercially available, easy to handle, and soluble in common organic solvents as well as in cyclic ester monomers. The $Sn(Oct)_2$ catalyst must be used in combination with a nucleophilic compound such as the hydroxyl groups on

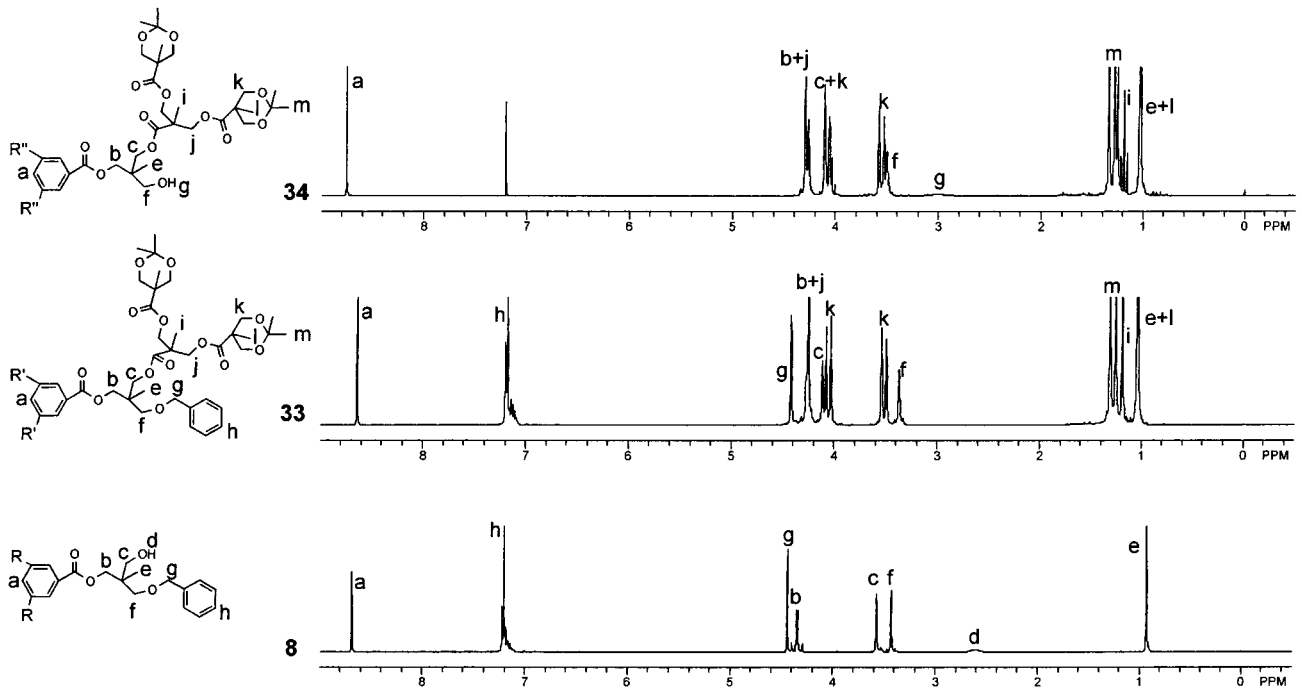


Figure 3. ^{1}H NMR spectra of **8**, **33**, and **34**.

the new initiators.[36−38] The generally accepted coordination−insertion mechanism for ROP has been demonstrated by Duda et al.[39−41] and Kricheldorf et al.[42] The $Sn(Oct)_2$ catalyst is generally only active at elevated temperatures, leading to some inter- and intramolecular transesterification, as described by Penczek et al.,[43] with the expected broadening of the molecular weight distribution. However, polyesters with complex architectures with extremely narrow polydispersities have been demonstrated from the ROP of ϵ-caprolactone and lactide initiated from the surface functionality of dendrimers. For example, the ROP of ϵ-caprolactone initiated from the peripheral-surface hydroxyl-functional groups of dendrons, dendrimers, and hyperbranched polymers derived from 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) in the presence of $Sn(Oct)_2$ has been demonstrated as an efficient means of preparing star-shaped macromolecules.[6a−c] Quantitative conversion of monomer to polymers was reported, and the molecular weight increase with conversion was linear, suggesting "living" character to the bulk polymerizations. The molecular weight closely tracked the monomer-to-initiator ratio, and the polydispersities were inordinately narrow for both the caprolactone and lactide polymerizations. Conversely, polymerization from monofunctional primary alcohols produced polymers with broad and often bimodal polydispersities. These data clearly indicate that the efficiency of initiation is considerably higher for the diol initiators. With this in mind, polymerization from the multifunctional alcohols was carried out in the presence of $Sn(Oct)_2$ at 100 °C (Figure 2), whereas polymerization from the monoalcohols was accomplished using $Sn(OTf)_2$ as the organometallic promoter at 40 °C. When compared to more traditional tin-based catalysts, the triflate-substituted catalysts are considerably more active and allowed low polymerization temperatures with accurate control of molecular weight and narrow polydispersities, even for monoalcohols.[44] Furthermore, polymerization in the presence of the triflate catalyst did not cause deprotection of the orthogonally protected initiators or protected dendrons, or transesterification side reactions of the polyester chains with the polyester dendrons.

These general polymerization procedures were applied to each of the initiators. The four series of initiators produced dendritic−linear block copolymers with four different A_xB_x architectures. The nomenclature used to describe the four polymer series is similar to that used for the initiators. For example, copolymer $(g\text{-}2)_2$-di$(PCL)_n^c$ corresponds to an initiator that has two second-generation dendrons $[(g\text{-}2)_2]$ with two chains of poly(ϵ-caprolactone) [di(PCL)] emanating from this central core. Alternatively, the values $(PCL)_n$ and tri$(PCL)_n$ are the nomenclature for one and three poly(ϵ-caprolactone) chains emanating from the central hub, respectively. The value *n* at the end of the name denotes the number of PCL repeat units per chain, while the superscript c denotes that the PCL hydroxyl chain ends are protected or capped. The molecular weights of the polymers were deliberately designed to be low so that the shape of the amphiphile would be comparable to that of a low-molar-mass surfactant. The targeted average degrees of polymerization (DPs) ranged between 10 and 40. In this way, the relative concentrations of the hydrophilic "head" to the hydrophobic "tail" were similar for each of the copolymer series. Table 1 shows the general characteristics of the polymers prepared. For each of the initiators, two different molecular weights of poly(ϵ-caprolactone) were generated. The DPs, as calculated from end-group analysis using ^{1}H NMR measurements, agree closely with the targeted values from the monomer-to-initiator ratios. Furthermore, the polydispersities were modestly low and consistent with a controlled polymerization process for both catalysts surveyed [$Sn(Oct)_2$ and $Sn(OTf)_2$]. For comparative purposes, the molecular weights of the hydrophobic components or initiators are also included. In addition to accurate control of molecular weight, control of the end groups was possible, irrespective of the organometallic promoter used. Shown in Figure 2 is the ^{1}H NMR spectrum of poly(ϵ-caprolactone) initiated from initiator **26** in the presence of $Sn(OTf)_2$. Resonances

Table 1. Characteristics of Dendritic−Linear Hybrid Copolymers

	dendritic linear polymer	DP target	DP (^{1}H-NMR)	PDI	$M_n \cdot 10^{-3}$
	$_p$(g-1)-(PCL)$_n$	10	8	1.26	11.3
		20	19	1.35	23.8
	$_p$(g-2)-(PCL)$_n$	10	21	1.18	28.8
		20	36	1.21	45.9
	$_p$(g-3)-(PCL)$_n$	10	10	1.29	21.8
		20	22	1.46	35.4
	$_p$(g-1)-di(PCL)$_n$	10	11	1.25	15.3
		20	11	1.27	15.3
	$_p$(g-2)-di(PCL)$_n$	10	11	1.19	18.0
		20	20	1.19	28.3
	$_p$(g-3)-di(PCL)$_n$	10	11	1.31	23.5
		20	19	1.21	32.6
	$_p$(g-1)$_2$-di(PCL)$_n$	10	12	1.40	18.2
		20	23	1.35	30.7
	$_p$(g-2)$_2$-di(PCL)$_n$	20	28	1.37	41.9
		40	58	1.38	76.1
	$_p$(g-3)$_2$-di(PCL)$_n$	20	18	1.33	41.3
		40	31	1.35	56.2
	$_p$(g-2)$_3$-tri(PCL)$_n$	20	18	1.24	108.7
	$_p$(g-2)-(PCL)$_n$-(g-2)$_p$	30	36	1.21	50.9
	$_p$(g-3)-di[(PCL)$_n$-di(PCL)$_m$]	40 40	n = 47 m = 48	1.28 1.30	129.1

associated with the initiating diol are clearly observed, together with the resonances associated with a hydroxyl chain end. These data are consistent with a coordination−insertion mechanism where an exchange process occurs with the initiating alcohol and the tin compound, producing the tin alkoxide active species. By this process, the α-chain end bears the ester from the initiating alcohol, and hydrolysis of the active tin alkoxide chain end leads to the formation of an ω-hydroxyl group. To ensure the hydrophobic character of these chains, the hydroxyl chain ends of each of the polymers were modified with acetic anhydride in the presence of triethylamine to form the acetate. This clean and quantitative transformation occurred without degradation to the aliphatic polyester chains, as evidenced by the retention in molecular weight and narrow polydispersities. The ^{1}H NMR spectrum of this transformation is shown in Figure 2, where the resonances associated with the acetate chain ends are observed.

The last step in the preparation of the A_xB_x amphiphilic block copolymers is the deprotection of the acetonide-protected dendrons. Because of the sensitivity of the polyester chains toward hydrolysis, extremely mild conditions are required to deprotect the acetonide-decorated dendrons. This transformation was accomplished by stirring the block copolymers, dissolved in a THF/methanol (50:50) solvent mixture, in the presence of Dowex, a solid-supported acidic medium, for 48 h at 50 °C. Deprotection was clean and quantitative with no detectable degradation of the polyester backbone. Figure 2 shows the ^{1}H NMR spectrum of this deprotection step for copolymer (g-2)-di(PCL)$_{19}$[c]. Interestingly, dendrimers and dendritic polymers derived from bis-MPA have exquisite ^{1}H NMR handles to follow transformations on the neighboring hydroxyl groups, as the protons on the $-CH_3$ group are very sensitive to the substitution of these groups. The ^{1}H NMR spectra clearly show a shift from 1.12 to 1.05 ppm that is consistent with deprotection of the hydroxyl groups. Similarly, the $-CH_2$ protons adjacent to the hydroxyl groups are also very sensitive to the substitution of the hydroxyl groups, and this transformation is clearly manifested in the spectra (c peak). Likewise, the quaternary carbons on the acetonide group at 98.1 ppm can no longer be detected after the deprotection transformation. Similar spectra were generated from the ROP of ϵ-caprolactone from **34**, and the various transformations are shown in Scheme 3.

The synthetic approach to the dendritic−linear hybrids is extremely versatile. As demonstrated from the orthogonally protected multifunctional initiator approach to these block copolymers, the generation and number of the dendritic blocks can be varied, together with the number and molecular weight of the poly(ϵ-caprolactone) blocks or tails. Moreover, considerable versatility exists in the sequence of the transformations to form the dendritic−linear hybrid copolymers. For example, the reverse sequence is possible where polymerization from the orthogonally protected compounds is performed first, followed by selective deprotection and attachment of the dendrons. In this way, the only purification step required is a polymer precipitation. The synthetic strategy to use a divergent growth approach to grow generations of high-molecular-weight poly(ϵ-caprolactone) between branching junctions generates amphiphiles with starlike space-filled poly(ϵ-caprolactone) tails. Figure 4 shows the target dendritic−linear hybrid, which is composed of two third-generation dendrons with two generations of poly(ϵ-caprolactone). In this case, the coupling of dendrons to the two generations of poly(ϵ-caprolactone) is the preferred synthetic route to allow for the characterization of the branching juncture and related transformations introduced to the poly(ϵ-caprolactone) chain to form the macroinitiator for the growth of subsequent generations.

The dendritic−linear hybrid with two generations of poly(ϵ-caprolactone) was prepared by a multistep process shown in Figure 4. First, ϵ-caprolactone was initiated from **3** to produce a two-arm poly(ϵ-caprolactone) polymer with an average DP of 47 (target 40) and a polydispersity of 1.28. Quantitative initiation from each of the hydroxyl groups was observed by ^{13}C NMR measurements, and the hydroxyl chain ends were easily detected by ^{1}H NMR spectroscopy (Figure 4). The hydroxyl chain ends were esterified with *tert*-butylsilyl-(TBDMS-) protected bis-MPA using Mitsunobu conditions.[45] The transformation was quantitative by ^{1}H NMR spectroscopy, and four new peaks appeared in the spectrum (Figure 4ii). The TBDMS groups were deprotected quantitatively ($BF_3 \cdot Et_2O$), as judged by the appearance of the peaks denoted i and h, and the requisite hydroxyl-functional macroinitiator was formed. This transformation was accomplished without affecting either the other protecting group or the polyester backbone. Polymerization of ϵ-caprolactone from the macroinitiator was accomplished in bulk at 100 °C in the presence of Sn(Oct)$_2$. The target DP per arm was 40, and ^{1}H NMR analysis, from the ratio of the methylene protons adjacent to the hydroxyl chain ends (δ =

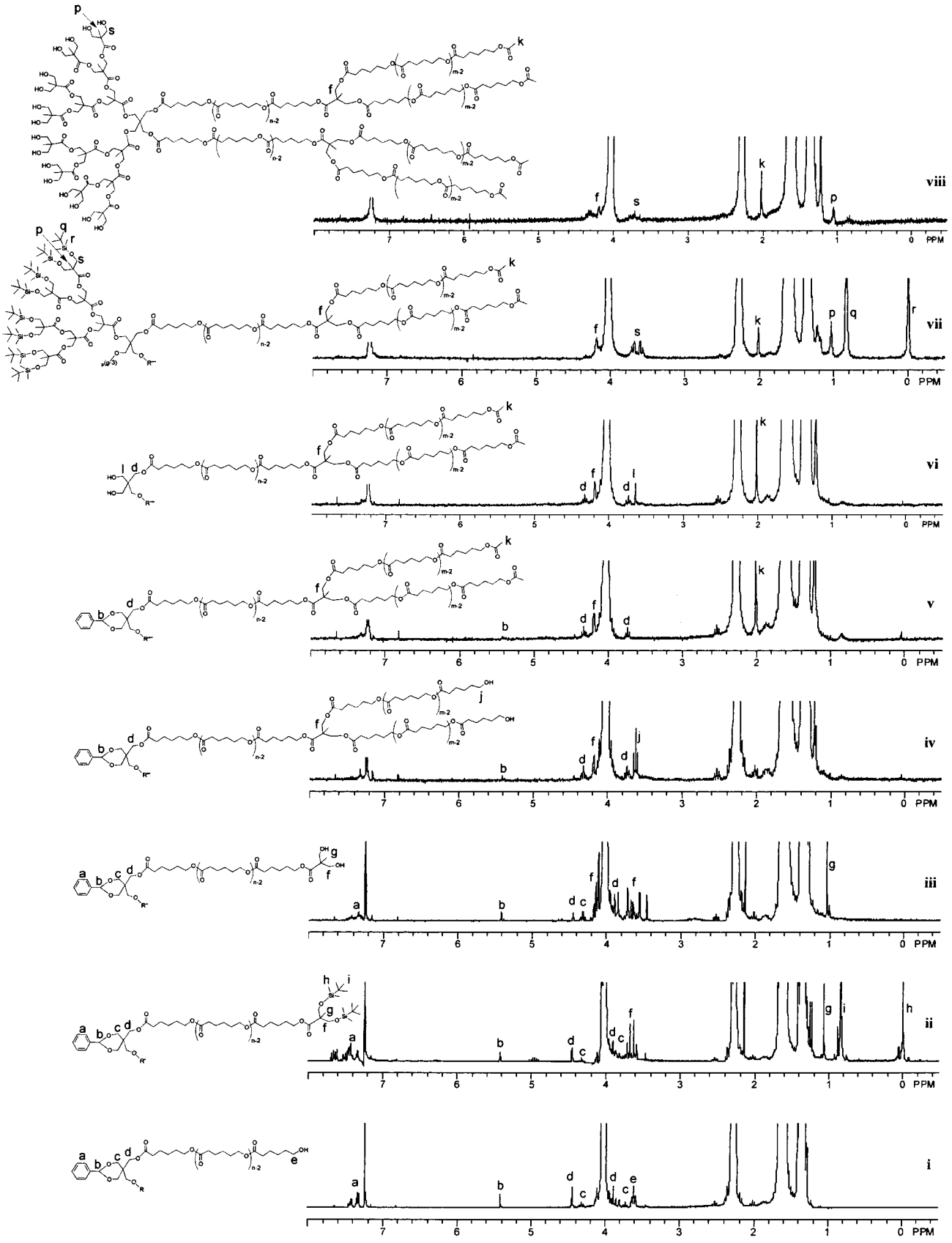


Figure 4. ^{1}H NMR spectra and synthesis of dendritic−linear hybrid with second-generation poly(ϵ-caprolactone) tails.

4.05) (Figure 4iv), permitted an average DP of 48 per arm to be calculated ($M_w/M_n = 1.30$). The hydroxyl chain ends were capped by esterification with acetyl chloride in the presence of triethylamine, as indicated by the disappearance of the peak denoted j and the appearance of peak k (Figure 4v). Deprotection of the benzylidene acetal protecting group by hydrogenolysis produced an α-dihydroxyl functionality. The ^{1}H NMR spectra clearly

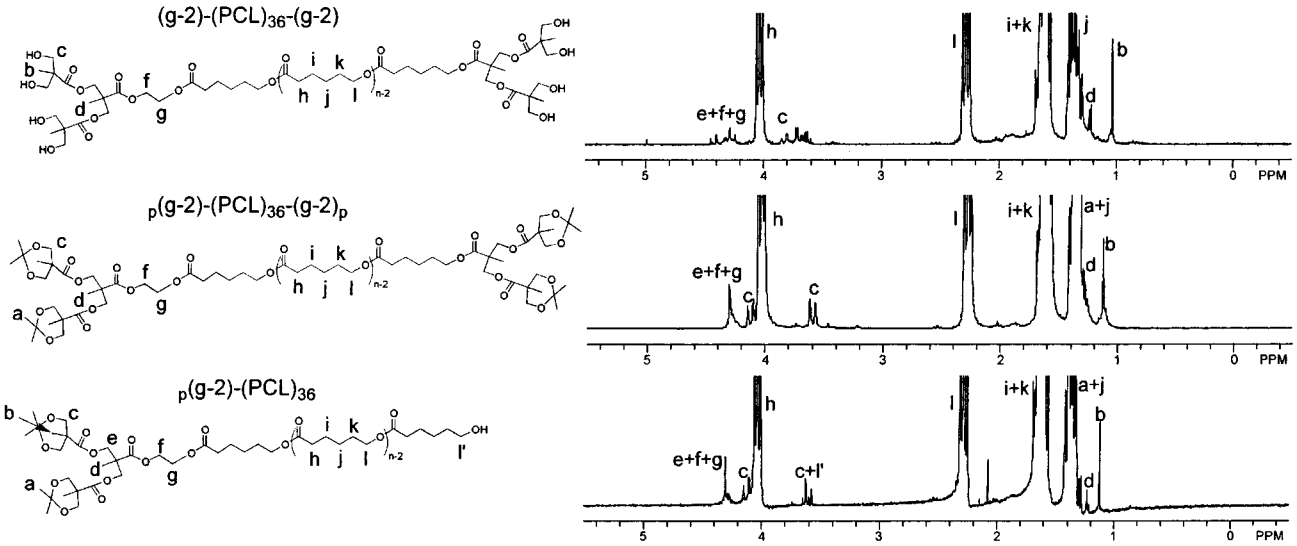


Figure 5. ^{1}H NMR spectra of dendritic linear ABA diblock copolymer.

show the disappearance of the benzylidene acetal group and the appearance of the methylene peaks adjacent to the hydroxyl groups, denoted l. Attachment of the $_p$(g-3) dendron was accomplished using Mitsunobu[45] conditions and produced four new peaks in the ^{1}H NMR spectra. Integration of the resonances associated with the TBMDS protecting groups with those of the poly(ϵ-caprolactone) backbone indicated, within the limits of the sensitivity of the NMR technique, quantitative conversion. Deprotection of the TBDMS groups with $BF_3{\cdot}Et_2O$ produced the requisite dendritic−linear hybrid.

The last example, which demonstrates the versatility of this approach to dendritic−linear hybrid block copolymers, is the preparation of ABA triblock copolymers. This macromolecular architecture is readily accessible through transformations at the hydroxyl functionalized poly(ϵ-caprolactone) chain ends. For example, the hydroxy functionality of $_p$(g-2)-(PCL)$_n$ can be readily esterified using Mitsunobu conditions with $_p$(g-2) to form a symmetric ABA dendritic−linear triblock copolymer. This polymer has an average degree of polymerization of 36 and a polydispersity of 1.26. Figure 5 shows the ^{1}H NMR spectra of the functionalization of the hydroxy end groups with $_p$(g-2). The resonances associated with the protons adjacent to the end groups (3.60 ppm) are shifted upon esterification with $_p$(g-2). Purification was accomplished by a simple polymer precipitation. Deprotection of the acetonide using Dowex in a methanol/THF solvent mixture for 48 h at 50 °C produced the requisite amphiphilic dendritic−linear ABA triblock copolymer. The resonances associated with the $-CH_3$ of the bis-MPA, as well as the $-CH_2-$ adjacent to the hydroxyl groups, are very sensitive to the substitution of the neighboring hydroxyl groups and are shifted in a way that is consistent with quantitative deprotection.

Summary

A new concept in initiator design provided an efficient and versatile route to dendritic−linear amphiphilic block copolymers with a variety of A_xB_x topologies. The A blocks were composed of hydrophilic dendrons of various generations, while the B blocks were composed of hydrophobic chains of poly(ϵ-caprolactone). The versatility in the design stems from the various libraries of building blocks used in the construction of the copolymers. These libraries include various generations of hydrophilic dendrons; poly(ϵ-caprolactone) prepared by controlled/living polymerization techniques; and, most importantly, new initiators. The novelty in the synthesis of the library of initiators is the use of orthogonal protecting groups. These compounds serve as the central core from which each of the other libraries were sequentially assembled through selective deprotection and transformations. Because of the sensitivity of the poly(ϵ-caprolactone) and polyester dendrons toward hydrolysis, protection and deprotection schemes were performed under neutral or mild conditions. ^{1}H NMR and GPC studies of the A_xB_x amphiphilic block copolymers confirm the efficiency of the orthogonally protected multifunctional initiator approach to dendritic−linear copolymers, as evidenced by controlled end groups, predictable molecular weights, and narrow polydispersities. These new amphiphiles resemble, in many ways, low-molar-mass surfactants such as phospholipids, yet with many of the characteristics of block copolymers. The numerous A_xB_x topologies possible using these multifunctional initiators will provide unique possibilities from nano- to supramolecular structures. Future publications will describe the amphiphilic character of these macromolecules, together with their ability to organize silica-vitrificates into nanostructures through self-assembly.

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