4644 *J. Am. Chem. Soc.* **1998,** *120,* 4644−4651

Dendrimer-like Star Polymers

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Received October 23, 1997

Abstract: Dendrimer-like star polymers, a novel type of molecular architecture, have been synthesized. The architecture of the new polymers resembles that of three-dimensional spherical dendrimers as well as classical star polymers. The controlled structures, based on aliphatic polyesters, are synthesized by a divergent growth approach. A hexa hydroxy-functional 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) derivative was used as the "initiator" for the stannous-2-ethylhexanoate ($Sn(Oct)_2$) catalyzed living ring opening polymerization of ϵ-caprolactone. The polymerization generated a six-arm polymer with a molecular weight of 14 300 (M_n) and a M_w/M_n of 1.06. The new polymer was functionalized with a protected bis-MPA, deprotected, and used as the "macroinitiator" for the polymerization of a second generation 12 armed poly(ϵ-caprolactone) ($M_n = 42\,300$, $M_w/M_n = 1.16$). Another iteration of the same procedure generated a third generation 24 arm dendrimer-like star polymer with a M_n of 96 000 and M_w/M_n of 1.14. The complete initiation and functionalization was carefully investigated by ^{1}H and ^{13}C NMR. These novel polymers are different from traditional dendritic materials in that this synthetic strategy allows these well defined highly branched polymers to reach a high molecular weight in only a few steps. In addition these materials are semicrystalline.

Introduction

In 1983 Tomalia[1] reported the divergent preparation of highly symmetrical layered dendrimers prepared from AB_x monomers whose globular structures are known to influence the basic physical and chemical properties of these unusual macromolecules.[2] For example, dendrimers are believed to be essentially free of chain entanglement in contrast to most linear polymers, and the unique microenvironment of these molecules have stimulated research in areas ranging from drug delivery to nanofabrication.[3] One limitation of dendrimers is their time-consuming synthesis, and significant effort has been devoted to improving the preparation of these polymers through use of alternative monomers[4] and other synthetic strategies.[4b,5] The divergent synthesis usually involves the sequential addition of AB_x monomers to a core, for generation growth, followed by an activation to allow further growth. After a number of iterations, a macromolecule of respectable size is obtained. A radical variation in the synthesis of dendrimers, denoted the convergent growth approach, was reported by Hawker and Frechet.[4b] This approach starts at the periphery, and well-defined dendrons are prepared and coupled to a multifunctional core molecule. The convergent approach has been shown to be a useful synthetic strategy in the synthesis of dendrimers with more than one type of end groups at the surface of the globular macromolecules.[3]

Another class of dendritic macromolecules known as hyperbranched polymers were first reported by Kim and Webster.[6] Hyperbranched polymers have a less perfect structure than dendrimers but offer the advantage of a one-step synthesis. This attractive feature has led to the development of a number of different architectures involving a huge number of different building blocks.[7] The third class of dendritic macromolecules are the hybrid-linear macromolecules,[8] where one or more dendritic components are randomly or exactly coupled to one or more linear polymers. For example, a linear polymer might be attached to some or all of the terminal groups of a dendrimer to give a hyperstar macromolecule.[9] Alternatively, attachment of a single linear polymer to the focal point of a dendrimer may lead to AB[10] or ABA[11] block copolymers in which the dendrimer and the linear polymer are the A and B blocks, respectively. In addition, hybrid-linear macromolecules have

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been used to simplify the purification of intermediate generations of dendrimers.[12] Dendritic macromolecules have also been constructed by successive grafting of polymeric building blocks. These so-called comb-burst polymers utilize narrow polydispersity linear polymers as building blocks in the construction of highly and randomly branched structures.[13] For example, Gnanou et al.[14] prepared a branched poly(ethylene oxide) by iterative AB_2 functionalization and polymerization from an hydroxy-functional polymer. With this method it was possible to prepare polymers with a more or less exact size and functionality in up to three generations and six end-groups.

A new type of well-defined dendritic macromolecules is reported here. The new polymers, Scheme 1, are first, second, and third generation dendrimer-like poly(ϵ-caprolactone) synthesized by a divergent approach using repetitive living ring-opening polymerization (ROP), followed by functionalization and deprotection of an AB_2 branching-point, Scheme 2. The concept was developed in order to obtain structures that combine classical properties of linear polymers such as entanglements and crystallinity with those of dendritic macromolecules, in particular, the high functionality resulting from the many end-groups.[3] The novel polymers reported here are different from classical dendrimers because a high molecular weight material is obtained in only a few steps. In addition, the new approach is flexible since the degree of polymerization (DP) as well as the monomer selection allows one to tailor-design a wide variety of properties. Poly(ϵ-caprolactone) was used as the polymeric building block, a concept that has been reported earlier for the generation of hyperbranched polymers.[7h] The “living” ROP produces polymers with accurate control of molecular weight, molecular weight distribution, and end-group functionality. The choice of 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) as the branching point was based both on its aliphatic structure as well as its documented use as building block in the synthesis of dendritic macromolecules.[4e,7c,h,15] Furthermore, the possibility exists of developing semicrystalline morphologies.

Experimental Section

Materials. Stannous-2-ethylhexanoate (Sigma) and all other chemicals (Aldrich) were purchased and used without any further purification except the ϵ-caprolactone which was dried over CaH_2 for 24 h and then distilled under high vacuum before use. The hexahydroxy-functional initiator **1** was synthesized according to a procedure developed by Ihre et al.[15b,c]

Techniques. ^1H NMR were recorded in $CDCl_3$ solution, on a Bruker AM 250 (250 MHz) apparatus with the solvent proton signal for reference. ^{13}C NMR spectra were recorded at 62.9 MHz on the same instrument using the solvent carbon signal as a reference. All polymer ^{13}C NMR spectra were recorded on 250 mg of sample using 16384 scans. The number average molecular weights of the polymers were calculated from the ^1H NMR data. The molecular weight distributions were determined by size exclusion chromatography (SEC) using a Waters chromatograph connected to a Waters 410 differential refractometer and an UV-detector. Four 5 μm Waters columns (300 × 7.7 mm) connected in series in order of increasing pore size (100, 1000, 10^5, 10^6 Å) were used with THF as solvent at 25 °C. Poly(styrene) standard samples were used for calibration.

Calculation of the Degree of Polymerization by the Use of ^1H NMR. The ^1H NMR spectra of **G-1(6 OH)**, **G-2(12 OH)**, and **G-3(24 OH)** were used to calculate the degree of polymerization (DP) of the different generations of the synthesized polymers and hence also the molecular weights of these polymers. The DP of **G-1(6 OH)** was calculated as the ratio of the integrated area of the peak corresponding to one of the repeating units of PCL (**C**, Figure 1) to the integrated area of the peak originating from the chain ends (**a**, Figure 1). The DP of the second generation (DP_2) and the third generation (DP_3) were then calculated from the following equation

$$\boldsymbol{x} = \boldsymbol{a}\mathrm{DP}_1 + \boldsymbol{b}\mathrm{DP}_2 + \boldsymbol{c}\mathrm{DP}_3... \qquad (1)$$

where $\boldsymbol{x}$ is the summed integrated area of any specific repeating unit of the monomer for all generations in the specific polymer, and $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ are the integrated areas of the chain ends of the first, second, and third generations, respectively. To calculate the DP of the second and third generation, it was assumed that the DP of the inner generations were unchanged and that all chain ends had initiated polymerization. These assumptions lead to the relation, $\boldsymbol{a} = \boldsymbol{b}/2 = \boldsymbol{c}/4$. In addition, it was assumed that the protons of the chain ends and the protons of the repeating units have equivalent relaxation times (τ). The results of these calculations are listed in Table 1.

Synthesis. 2,2-Bis(phenyldioxymethyl)propionic Acid (2). 2,2-Bis(hydroxymethyl)propionic acid (bis-MPA) (25.0 g, 187 mmol), benzaldehyde dimethyl acetal (42.6 g, 280 mmol), and *p*-toluenesulfonic acid (*p*-TSA) (0.69 g) were all dissolved and stirred in acetone (100 mL) at ambient temperature. After 2 h, a few drops of NH_4OH (aq, 30%)/EtOH (1:1) solution was added to neutralize the *p*-TSA. The reaction mixture was then diluted with 400 mL of CH_2Cl_2 and extracted once with H_2O (25 mL). The organic phase was separated, filtered, and concentrated. The residue was recrystallized from CH_2Cl_2 to give the product as a white powder. Yield: 37.3 g (90%). Mp: 197−198 °C. ^1H NMR ($CDCl_3$) δ 1.09 (s, 3H, $-CH_3$), 3.66−4.64 (2d, 4H, $-(CH_2O)_2CH-$, $J = 9.0$ Hz), 5.46 (s, 1H, $-CH$Ph), 7.31−7.47 (m, 5H, −Ph). ^{13}C NMR (DMSO-d_6) δ 22.75, 46.73, 77.81, 105.52, 131.25, 133.17, 133.85, 143.56, 180.71.

G-1(6 OH) and a General Procedure for Poly(ϵ-caprolactone) Formation. The hexahydroxy-functional initiator **1** (3.50 g, 5.35 mmol) was dissolved in dry THF and dried with $MgSO_4$. The liquid was filtered into the reaction flask where the solvent was evaporated under a nitrogen atmosphere. Toluene (3 mL) was added, and the temperature was raised to 90 °C under high vacuum to remove the toluene and residual H_2O. The reaction flask was then filled with N_2(g) and toluene (1.5 mL) to dissolve the initiator. ϵ-Caprolactone (73.2 g, 642 mmol) was added, and the temperature was raised 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 of the initiator. The reaction was stirred for 24 h, diluted with THF, and precipitated into MeOH to give 70.0 g (yield: 91.2%) of a white crystalline powder. Mp: 49.9 °C. ^1H NMR ($CDCl_3$) δ 1.30 (m, poly, $-CH_2-$), 1.60 (m, poly, $-CH_2CH_2CH_2-$), 2.26 (t, poly, $-COCH_2-$, $J = 5.2$ Hz), 3.60 (t, 12H, $-CH_2OH$, $J = 5.0$ Hz), 4.01 (t, poly, $-CH_2O-$, $J = 5.2$ Hz), 4.31 (s, 12H, $-CCH_3(CH_2O)_2-$), 6.88 (dd, 6H, Ph−, $J = 6.9$ Hz), 7.06 (dd, 6H, Ph−, $J = 6.9$ Hz). ^{13}C NMR ($CDCl_3$) δ 17.66, 24.43, 25.39, 28.20, 32.20, 33.96, 46.64, 51.52, 62.23, 63.97, 65.07, 120.62, 129.57, 146.17, 148.56, 171.29, 172.69, 173.35.

G-1.5(0 OH) and a General Procedure for AB_2 Functionalization. To a stirred solution of **G-1(6 OH)** ($M_n = 14\,300$ g/mol) (14.3 g, 1.00 mmol), **2** (2.01 g, 9.00 mmol), triphenylphosphine (TPP) (3.17 g, 12.1 mmol), and THF (5 mL) at room temperature was slowly added diisopropyl azodicarboxylate (DIAD) (2.44 g, 12.1 mmol). The reaction mixture was precipitated into cold methanol after 24 h. The filtered product was a white crystalline powder. Yield: 14.4 g (94%). Mp: 46.3 °C. ^1H NMR ($CDCl_3$) δ 0.96 (s, 18H, $-CH_3$), 1.30 (m, poly, $-CH_2-$), 1.60 (m, poly, $-CH_2CH_2CH_2-$), 2.26 (t, poly, $-COCH_2-$, $J = 6.0$ Hz), 3.55−4.60 (2d, 24H, $-(CH_2O)_2CHPh$, $J = 9.2$ Hz), 4.01 (t, poly, $-CH_2O-$, $J = 5.3$ Hz), 4.14 (t, 12H, $-CH_2OCO$), 4.31 (s, 12H, $-CCH_3(CH_2O)_2-$), 5.37 (s, 6H, $-CH$Ph), 6.88 (dd, 6H, Ph−, *J*

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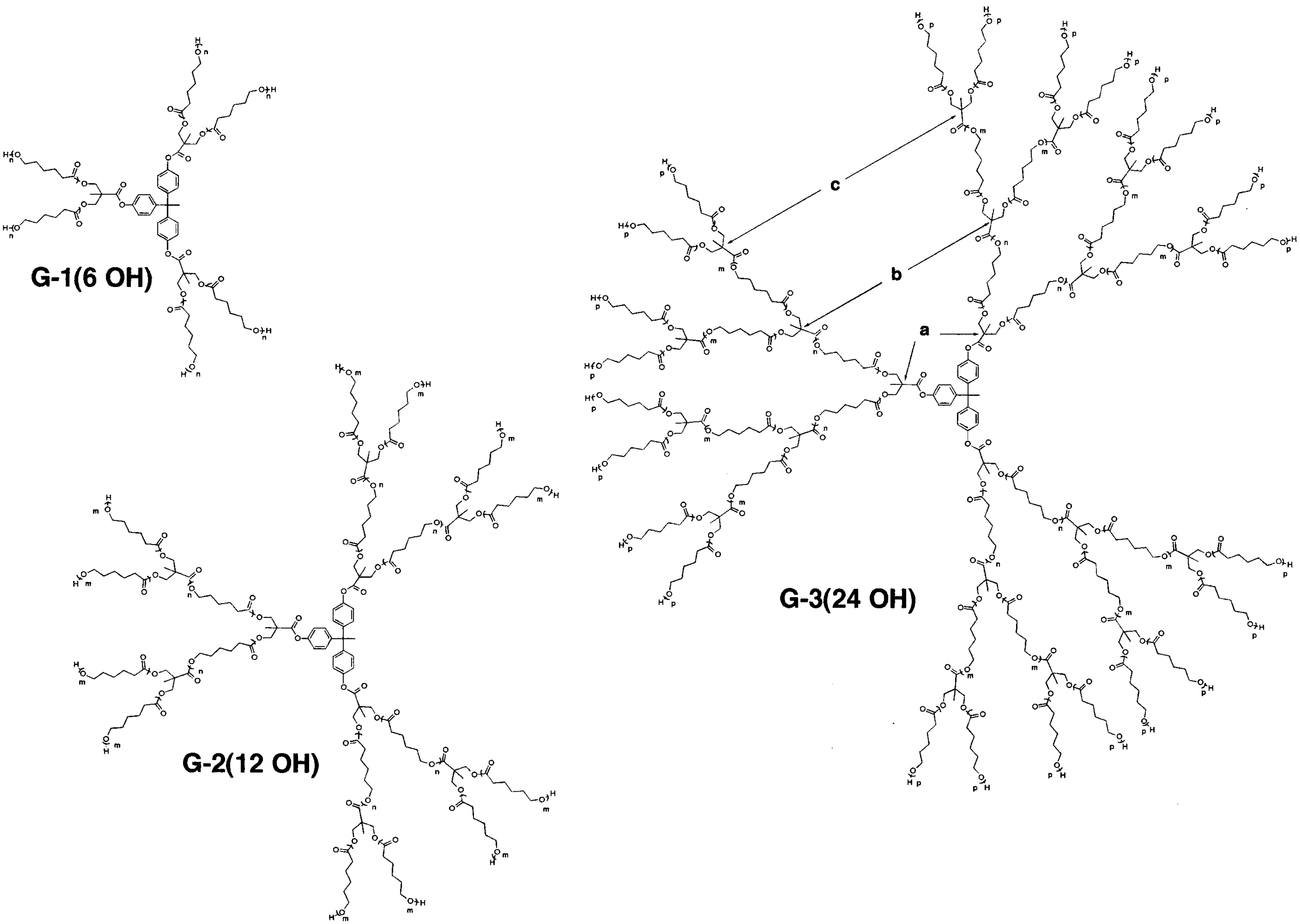
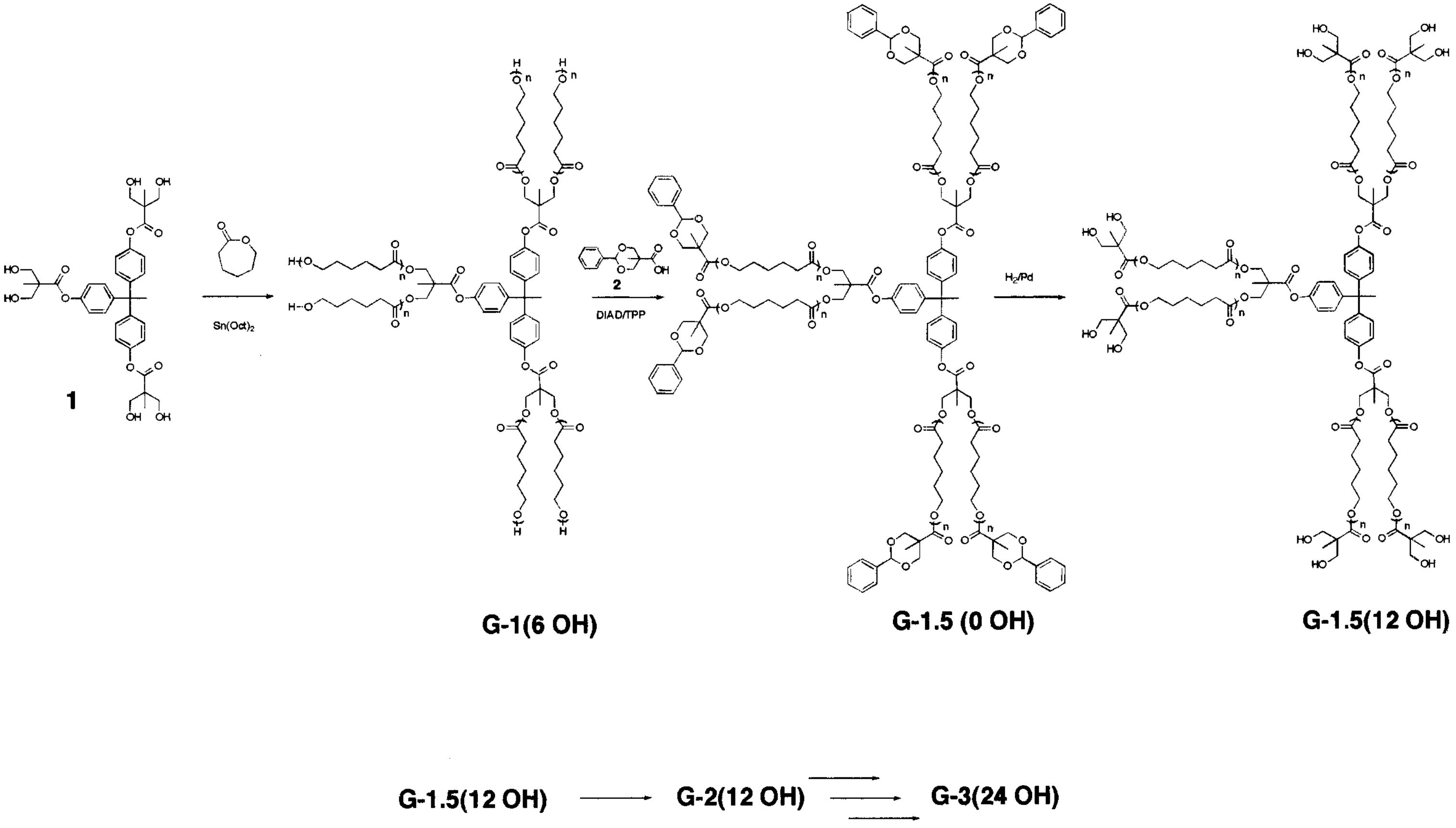
Scheme 1. Molecular Structures of the First, the Second and the Third Generation Dendrimer-like Poly(ϵ-caprolactone)



Scheme 2. Synthetic Route for the Preparation of Dendrimer-like Poly(ϵ-caprolactone)



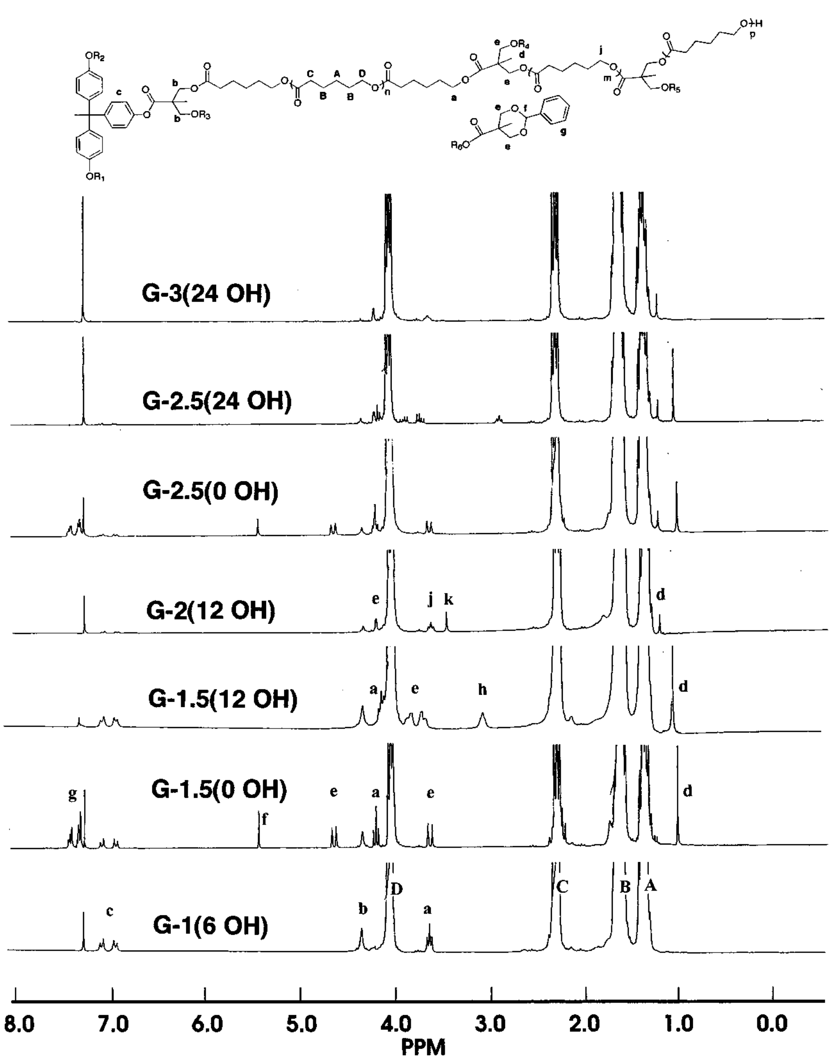


Figure 1. ^{1}H NMR spectra for the dendrimer-like star poly(ϵ-caprolactone)s.

Table 1. Experimental Molecular Weights and Thermal Transitions of the Dendrimer-like Polymers and Their Intermediates

sample	M_n (NMR)	M_n (GPC)	M_w/M (GPC)	DP (NMR)	phase-transition temp^d (°C)/ enthalpy changes (kJ·mol^{-1})
G-1(6 OH)	14 300	25 700	1.06	20.1^a	49.9 (74.0)
G-1.5(0 OH)		28 100	1.05	20.1^a	46.3 (57.8)
G-1.5(12 OH)		28 400	1.06	20.1^a	49.7 (54.9)
G-2(12 OH)	42 300	88 100	1.16	20.1^a 21.3^b	55.9 (41.8)
G-2.5(0 OH)		96 300	1.16	20.1^a 21.3^b	51.8 (55.1)
G-2.5(24 OH)		99 500	1.15	20.1^a 21.3^b	51.7 (57.3)
G-3(24 OH)	96 000	158 000	1.14	20.1^a 21.3^b 21.5^c	51.9 (68.1)

^{a} DP of the first generation. ^{b} DP of the second generation. ^{c} DP of the third gneration. ^{d} Data are from second heating scan.

= 6.8 Hz), 7.24 (dd, 6H, Ph−, J = 6.8 Hz), 7.25−7.36 (m, 30H, Ph−). ^{13}C NMR (CDCl$_3$) δ 17.87, 24.52, 25.48, 28.30, 34.06, 42.36, 46.73, 51.62, 64.06, 64.77, 65.14, 73.51, 101.69, 120.71, 126.17, 128.11, 128.87, 129.67, 137.92, 146.25, 148.64, 171.39, 172.78, 173.44, 173.95.

G-1.5(12 OH) and a General Procedure for Removal of the Benzylidene Group. G-1.5(0 OH) (M_n = 15 600 g/mol) (12.0 g, 0.77 mmol) was dissolved in THF (10 mL) and diluted with EtOAc (100 mL) before 1.0 g of Pd/C (10%) was added. The apparatus for catalytic hydrogenolysis was evacuated and filled with H$_2$(g). The reaction mixture was stirred for 24 h, and the Pd/C was removed by filtration. The filtrate was precipitated into cold MeOH. The filtered solid was a white crystalline powder. Yield 10.0 g (86%). Mp: 49.7 °C. ^{1}H NMR (CDCl$_3$) δ 0.99 (s, 18H, −CH_3), 1.29 (m, poly, −CH_2−), 1.56 (m, poly, −CH_2CH$_2$CH_2−), 2.21 (t, poly, −COCH_2−, J = 5.9 Hz), 3.00 (t, 12 OH, −OH), 3.61−3.81 (2d, 24H, −CH_2OH, J = 5.2 Hz), 4.01 (t, poly, −CH_2O−, J = 5.2 Hz), 4.06 (t, 12H, −CH_2OCO), 4.26 (s, 12H, −CCH$_3$(CH_2O)$_2$−), 6.84 (dd, 6H, Ph−, J = 6.9 Hz),(dd, 6H, Ph−, J = 6.9 Hz). ^{13}C NMR (CDCl$_3$) δ 17.13, 17.74, 24.50, 25.46, 28.14, 34.04, 46.69, 49.20, 51.60, 64.06, 64.56, 65.12, 67.68, 120.68, 129.65, 146.23, 148.61, 171.37, 172.78, 173.45, 175.77.

G-2(12 OH). G-1.5(12 OH) (M_n = 15 100 g/mol) (2.7 g, 0.18 mmol), ϵ-caprolactone (4.91 g, 43.1 mmol), and a catalytic amount of Sn(Oct)$_2$ were reacted according to the general procedure for poly(ϵ-caprolactone) formation to give **G-2(12 OH)** as a white crystalline powder. Yield: 7.55 g (99%). Mp: 55.9 °C. ^{1}H NMR (CDCl$_3$) δ 1.22 (s, 18H, −CH_3), 1.34 (m, poly, −CH_2−), 1.57 (m, poly, −CH_2-CH$_2$CH_2−), 2.26 (t, poly, −COCH_2−, J = 6.0 Hz), 3.59 (t, 24H, −CH_2-OH, J = 5.0 Hz), 4.01 (t, poly, −CH_2O−, J = 5.3 Hz), 4.17 (s, 24H, −CCH$_3$(CH_2O)$_2$−), 4.30 (s, 12H, −CCH$_3$(CH_2O)$_2$−), 6.84 (dd, 6H, Ph−, J = 6.8 Hz), 7.02 (dd, 6H, Ph−, J = 6.8 Hz). ^{13}C NMR (CDCl$_3$) δ 17.69, 24.42, 25.37, 28.20, 32.20, 33.94, 46.16, 46.65, 62.17, 63.94, 64.78, 65.09, 120.62, 129.55, 172.54, 172.69, 173.30.

G-2.5(0 OH). G-2(12 OH) (M_n = 42 300 g/mol) (4.50 g, 0.11 mmol), **2** (0.40 g, 1.81 mmol), TPP (0.68 g, 2.57 mmol), and DIAD (0.52 g, 2.57 mmol) were reacted according to the general procedure for AB$_2$ functionalization to give **G-2.5(0 OH)** as a white crystalline powder. Yield: 4.40 g (93%). Mp: 51.8 °C. ^{1}H NMR (CDCl$_3$) δ 0.99 (s, 36H, −CH_3), 1.19 (s, 18H, −CH_3), 1.30 (m, poly, −CH_2−), 1.61 (m, poly, −CH_2CH$_2$CH_2−), 2.26 (t, poly, −COCH_2−, J = 6.0 Hz), 3.58−4.63 (2d, 48H, −(CH_2O)$_2$CHPh, J = 9.0 Hz), 4.01 (t, poly,

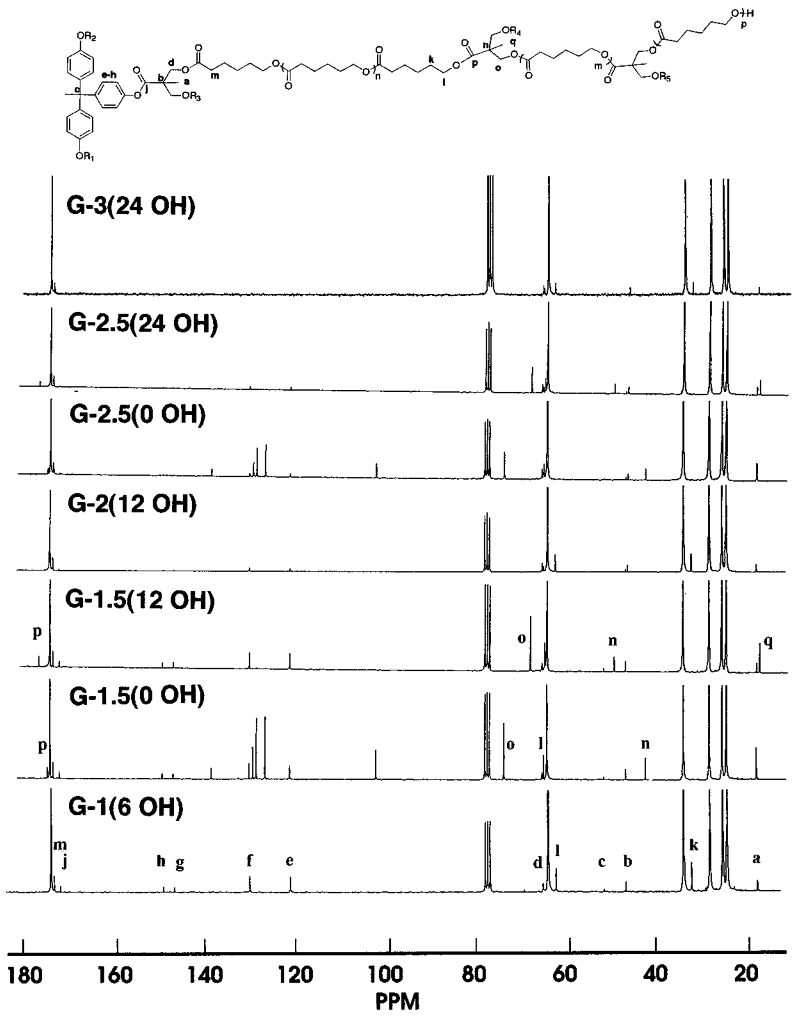


Figure 2. ^{13}C NMR spectra for the dendrimer-like star poly(ϵ-caprolactone)s.

$-CH_2O-$, $J = 5.3$ Hz), 4.17 (t, 24+24H, $-CCH_3(CH_2O)_2-$ and $-CH_2$-OCO), 4.31 (s, 12H, $-CCH_3(CH_2O)_2-$), 6.91 (dd, 6H, Ph$-$, $J = 6.8$ Hz), 7.03 (dd, 6H, Ph$-$, $J = 6.8$ Hz), 7.27$-$7.39 (m, 60 H, Ph$-$). ^{13}C NMR (CDCl$_3$) δ 17.77, 24.44, 25.39, 28.21, 33.95, 42.26, 46.16, 46.65, 63.94, 64.64, 64.78, 65.09, 101.56, 120.63, 126.07, 127.99, 128.75, 129.57, 137.87, 172.66, 173.29, 173.83.

G-2.5(24 OH). G-2.5(0 OH) ($M_n = 44\,800$ g/mol) (3.50 g, 0.08 mmol) and 0.6 g of Pd/C (10%) were reacted according to the general procedure for the removal of the benzylidene group to give **G-2.5(24 OH)** as a white crystalline powder. Yield: 3.20 g (94%). Mp: 51.7 °C. ^{1}H NMR (CDCl$_3$) δ 1.03 (s, 36H, $-CH_3$), 1.20 (s, 18H, $-CH_3$), 1.31 (m, poly, $-CH_2-$), 1.64 (m, poly, $-CH_2CH_2CH_2-$), 2.26 (t, poly, $-COCH_2-$, $J = 6.0$ Hz), 2.86 (t, 24 H, $-OH$), 3.65$-$3.90 (2dd, 48H, $-CH_2OH$, $J = 4.9$ and 9.0 Hz), 4.02 (t, poly, $-CH_2O-$, $J = 5.3$ Hz), 4.17 (m, 24+24H, $-CH_2OH$ and $-CH_2OCO$), 4.32 (s, 12H, $-CCH_3$-$(CH_2O)_2-$), 6.91 (dd, 6H, Ph$-$, $J = 6.8$ Hz), 7.03 (dd, 6H, Ph$-$, $J = 6.8$ Hz). ^{13}C NMR (CDCl$_3$) δ 17.10, 17.72, 24.46, 25.42, 28.11, 33.99, 46.19, 46.67, 49.21, 64.00, 64.47, 64.84, 65.12, 67.46, 120.65, 129.60, 172.59, 172.74, 173.38, 175.69.

G-3(24 OH). G-2.5(24 OH) ($M_n = 43\,700$ g/mol) (1.50 g, 0.034 mmol), ϵ-caprolactone (1.90 g, 16.7 mmol), and a catalytic amount of Sn(Oct)$_2$ were reacted according to the general procedure for the formation of poly(ϵ-caprolactone) to give **G-3(24 OH)** ($M_n = 98\,400$ g/mol) as a white crystalline powder. Yield: 3.20 g (95%). Mp: 51.9 °C. ^{1}H NMR (CDCl$_3$) δ 1.20 (s, 54 H, $-CH_3$), 1.35 (m, poly, $-CH_2-$), 1.64 (m, poly, $-CH_2CH_2CH_2-$), 2.28 (t, poly, $-COCH_2-$, $J = 6.0$ Hz), 3.62 (t, 48H, $-CH_2OH$, $J = 5.3$ Hz), 4.02 (t, poly, $-CH_2O-$, $J = 5.2$ Hz), 4.18 (s, 72H, $-CCH_3(CH_2O)_2-$), 4.32 (s, 12H, $-CCH_3(CH_2O)_2-$). ^{13}C NMR (CDCl$_3$) δ 17.77, 24.51, 25.47, 28.29, 32.28, 34.05, 46.24, 62.45, 64.06, 64.89, 65.18, 172.80, 173.45.

Results and Discussion

In this study, a hexa hydroxy functionalized first generation 2,2-bis-(hydroxymethyl)propionic acid (bis-MPA) dendrimer **1** was synthesized and used as the "initiator" to generate a six-arm star poly(ϵ-caprolactone) **G-1(6 OH)**, Scheme 2. The hexa hydroxy functional polymer was prepared in the melt at 110 °C using stannous-2-ethylhexanoate (Sn(Oct)$_2$) as the catalyst. The number average molecular weight of **G-1(6 OH)** was 14 300 as determined by ^{1}H NMR and the molecular weight distribution as measured by size exclusion chromatography (SEC) was 1.06. The hydroxy functional arms had an average degree of polymerization (DP) of 20.1 (target DP = 20). The **G-1(6 OH)** was further functionalized with benzylidene protected bis-MPA **2** to generate **G-1.5(0 OH)** using diisopropyl azodicarboxylate (DIAD) and triphenylphosphine (TPP) in dry THF. The benzylidene protecting groups were removed by hydrogenolysis to generate **G-1.5(12 OH)** containing 12 hydroxyl groups. This polymer was used as a "macroinitiator" for the ring-opening polymerization of ϵ-caprolactone to give the dendrimer-like star polymer **G-2(12 OH)**. The average DP of the 12 arms in the second layer of **G-2(12 OH)** was determined to be 21.3 by ^{1}H NMR a value which corresponds well with the target value of 20. This gave a total molecular weight for polymer **G-2(12 OH)** of 42 300, and the molecular weight distribution as measured by SEC was 1.16. Each arm was again functionalized with a branching site to give **G-2.5(0 OH)**. The functionalization was completed after 48 h. **G-2.5-**

(0 OH) was then deprotected over 48 h to generate **G-2.5(24 OH)** which was used as an "initiator" to form the third generation dendrimer-like star polymer **G-3(24 OH)**. The degree of polymerization for each of the 24 arms in the third layer was determined to be 21.5 by ^{1}H NMR, a value which once again agrees well with the target value of 20. The total number average molecular weight of **G-3(24 OH)** as determined by ^{1}H NMR was calculated to be 96 000, and the molecular weight distribution, measured by SEC, was found to be 1.14. It should be pointed out that the only purification required after polymerization, functionalization, and deprotection was a simple precipitation into cold methanol.

All polymers were carefully investigated by both ^{1}H NMR and ^{13}C NMR. The degree of polymerizations were calculated by ^{1}H NMR and are in all cases close to the target values. The calculated values range between 20.1 and 21.5, while the target value for all of the polymerizations was 20. It can thus be concluded that the assumptions made to calculate these values are valid and that eq 1 is correct. Figure 1 shows the ^{1}H NMR of all polymers and their intermediates after only one precipitation into methanol. One may conclude that the polymers are satisfactorily pure materials. A more thorough interpretation of these spectra reveals more details about the complexities of these structures. All the spectra show four large peaks that originate from the repeating units of ϵ-caprolactone (**A**−**D**). In addition, the spectrum of **G-1(6 OH)** shows one peak assigned to the chain ends (**a**) and two small peaks from the initiator (**b**, **c**). Upon transformation of the chain ends from alcohols into esters, the **a** peak shifts and five new peaks appear (**d**, **e**, **e**, **f**, and **g**) originating from the protected bis-MPA. Deprotection of **G-1.5(0 OH)** removes the **f** and the **g** peaks derived from the benzylidene part of the protected bis-MPA and shifts the **e** ($-CH_2-$ in bis-MPA) and **d** ($-CH_3$ in bis-MPA) resonances. In addition, a new peak **h** appears around 3.1 ppm originating from the −OH protons. The use of **G-1.5(12 OH)** as the "initiator" to form **G-2** upon polymerization merges the **e** peaks into a singlet which corresponds to the **b** peak in **G-1** originating from the "initiator". In addition, the **d** peak shifts again and a new peak **j** appears which arises from the chain ends and corresponds to the **a** peak of **G-1**. The peak detected at around 3.5 ppm originates from MeOH which was used as the precipitation solvent. Functionalization of **G-2** generates **G-2.5(0 OH)** which shifts the **j** peak quantitatively, and five new peaks appear corresponding to the peaks in **G-1.5(12 OH)**. The deprotection to form **G-2.5(24 OH)** as well as the polymerization to form **G-3** generate spectra which correspond to **G-1.5(12 OH)** and **G-2**, respectively. The ^{1}H NMRs show that the functionalization and deprotection steps are quantitative. They also show that the polymerization is controllable; however, it is not clear from the ^{1}H NMR whether all the hydroxyl groups have initiated the polymerization or not.

Figure 2 shows the ^{13}C NMR of all of the polymers and their intermediates. All spectra were recorded in CDCl$_3$ using 16 384 scans to ensure that all desired carbons were detected. The spectra show the same trends observed in the ^{1}H NMR but requires a thorough analysis to demonstrate that the polymers formed and their intermediates have the suggested structures. All the spectra show the CDCl$_3$ peaks and six major resonances from the repeating units of ϵ-CL. In addition, **G-1(6 OH)** displays nine smaller peaks (**a**−**j**) derived from the initiator and three peaks (**k**−**m**) that arise from the chain ends. Quantitative functionalization of **G-1(6 OH)** shifts the peaks (**k** and **l**) that originate from the −OH chain ends. In addition, one new peak (**n**) appears in the quarternary region (45−50 ppm), one (**o**) in

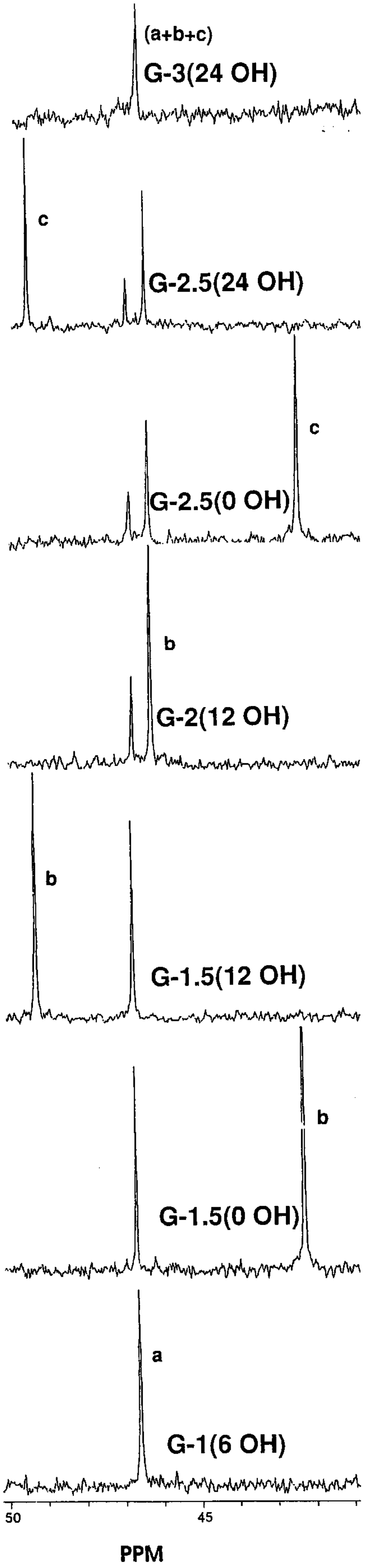


Figure 3. ^{13}C NMR spectra showing the quaternary carbon region of the different bis-MPA units in the dendrimer-like starpolymers. The origin of **a**, **b**, and **c** are show in Scheme 1.

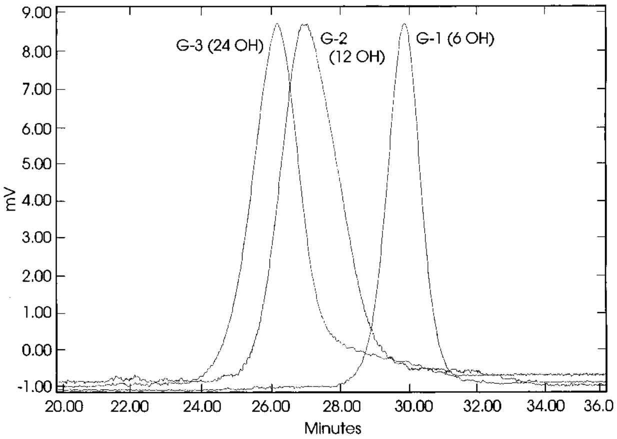


Figure 4. Size exclusion chromatography (SEC) of the three polymers **G-1(6 OH)**, **G-2(12 OH)**, and **G-3(24 OH)**.

the ether/alcohol region (60−80 ppm), and one in the methine region (100−110 ppm). Five new peaks also appear in the aromatic region (120−160 ppm) and one new peak **p** appears in the carbonyl region (170−180 ppm). All these new peaks are derived from the benzylidene protected bis-MPA. The methine peak and the new aromatic signals disappear quantitatively upon deprotection of **G-1.5(0 OH)**. The other three new peaks (**n**−**p**) are shifted in **G-1.5(12 OH)**. Furthermore, the **a** peak splits into two peaks (**a** and **q**) representing the $-CH_3$ carbon of the bis-MPA in the core and the $-CH_3$ carbon of the deprotected bis-MPA, respectively. Upon polymerization to form **G-2** the **a** and the **q** peaks merge into one. In addition, the two peaks (**n** and **o**) derived from the quaternary carbon and the $-CH_2-$ of the bis-MPA, respectively, are quantitatively shifted. Furthermore, a few peaks disappear, due to their low concentrations. Iterative functionalization (**G-2.5(0 OH)**), deprotection (**G-2.5(12 OH)**) and polymerization (**G-3(24 OH)**) reveal new peaks that all correspond to the peaks of the earlier generations.

The ^{13}C NMR spectra show, as the ^1H NMR spectra did, that the functionalization and deprotection steps are quantitative. In contrast to the ^1H NMR spectra, the ^{13}C NMR show that the polymerization reactions have been quantitatively "initiated" from all the hydroxyl groups. The quaternary carbon in the bis-MPA as revealed by ^{13}C NMR studies has been shown to be a very effective tool in determining whether the structures are mono-, di-, or unsubstituted.[15a,c] Figure 3 shows the expanded quaternary region of the ^{13}C NMR spectra of **G-1(6 OH)**, **G-2(12 OH)**, and **G-3(24 OH)** and their intermediates within the sensitivity of NMR detection. **G-1(6 OH)** displays only one peak **a** in that region indicating that all hydroxyl groups have "initiated" the polymerization. After functionalization a second peak **b** appears which shifts upon deprotection and polymerization. The two peaks (**a** and **b**) in the quaternary region of the spectrum of **G-2(12 OH)** indicate that even the second polymerization has been "initiated" by all the hydroxyl groups. After the second functionalization a third peak, **c**, appears which shifts upon deprotection and polymerization. The final polymer **G-3(24 OH)** shows only one peak (**a**+**b**+**c**) which suggests that the initiation of even the third layer poly(ϵ-caprolactone) is complete.

Figure 4 shows the SEC-chromatograms for the three polymers **G-1(6 OH)**, **G-2(12 OH)**, and **G-3(24 OH)** as obtained after one precipitation into cold methanol. The SEC data do not exclude that some transesterification which is often observed in stannous-2-ethylhexanoate catalyzed polymerizations has occurred,[16] but these data clearly indicate that transesterification side reactions are minimal or absent. In addition, it should be mentioned that no homopolymer formation could be detected in any of the three polymerization steps, provided the initiating species were properly dried. It can be concluded from the results of the ^{13}C NMR studies in combination with ^1H NMR and SEC data that the novel polymers **G-1(6 OH)**, **G-2(12 OH)**, and **G-3(24 OH)** have highly branched and controlled molecular structures which correspond very well to the idealized structures in Scheme 1.

The dendrimer-like polymers and their intermediates are semicrystalline as measured by DSC. The calorimetry data for the polymers are given in Table 1. The ability to form semicrystalline morphologies group these materials with only a small set of dendrimers and hyperbranched polymers which have been reported liquid crystalline[4d,f,7b,17] or partially crystalline either intrinsically[4f,5] or after functionalization with long chain alkyl groups.[15d,18] A more thorough discussion of these results will be reported separately. It should be mentioned, that amorphous dendrimer-like star polymers have been prepared by replacing one or more of the poly(ϵ-caprolactone) layers with layers of other polymerized monomers, e.g., D,L-lactides.

Conclusion

A new type of molecular architecture, denoted as dendrimer-like star polymers, has been synthesized. These dendrimer-like star polymers offer an attractive synthetic route to well defined, highly branched, and functional polymers of high molecular weight. In addition, the "solid phase" synthesis provides a convenient and time efficient route for the preparation of these complex structures. Furthermore, the synthetic strategy described allows the preparation of architectures with significant variation in polymer morphology by simply varying either the degree of polymerization in the different generations or by replacing one of the dendrimer-like layers with an alternative monomer. For instance, thermoplastic elastomers can be prepared by replacing one of the ϵ-caprolactone layers with a D,L-lactide layer.

Acknowledgment. The authors gratefully acknowledge financial support from the NSF funded Center for Polymeric Interfaces and Macromolecular Assemblies (CPIMA) under cooperative agreement DMR-9400354. Mikael Trollsås also acknowledges fellowships from the Wenner-Gren Foundation and the Frans Georg and Gull Liljenroths Foundation.

JA973678W

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