Dendrimer-like Star Block and Amphiphilic Copolymers by Combination of Ring Opening and Atom Transfer Radical Polymerization

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ABSTRACT: A new type of macromolecular architecture, denoted as dendrimer-like star block copolymers, is reported. These block copolymers are described by a radial geometry where the different generations or layers are comprised of high molecular weight polymer emanating from a central core. A hexahydroxyl functional core was used as an initiator for the "living" ring opening polymerization (ROP) of ϵ-caprolactone producing a hydroxyl terminated six arm star polymer with controlled molecular weight and narrow polydispersities (PD < 1.1). Capping these chain ends with dendrons containing activated bromide moieties produced "macro-initiators" for atom transfer radical polymerization (ATRP). Methyl methacrylate was polymerized from these "macro-initiators" in the presence of an organometallic promoter to produce the requisite dendrimer-like star polymers. High molecular weight was obtained with low polydispersities (<1.2). Alternatively, amphiphilic character could be introduced by designing the different layers or generations to be either hydrophobic or hydrophilic. For example, methyl methacrylate (MMA) with either hydroxyethyl methacrylate (HEMA) or methacrylate functional ethylene oxide macromonomers (EO) were polymerized from these "macro-initiators" to provide a hydrophilic outer layer. The use of macromolecular building blocks allows rapid attainment of high polymer in a limited number of steps with purification between transformation requiring only polymer precipitation.

Introduction

Block copolymers, soaps, lipids, etc. are examples of amphiphiles that are capable of self-assembly into periodic geometries with long-range order. Block copolymers contain at least two distinct polymer chains covalently bound at one point, which promotes the miscibility of the two intrinsically dissimilar materials, and phase separation, when it occurs, is limited to dimensions on the order of 100−400 Å.[1] The amphiphilic nature of many block polymers is manifested by the tendency to phase separate and promote self-assembly or micelle formation in solution.[2] The micellization process results from the selective solublization in the solvent of one of the blocks of the diblock copolymer. Above the critical micelle concentration (cmc), spherical micelles will be formed which consist of two concentric regions; an interior region comprised of the block that is insoluble in the solvent which is collapsed and an outer region formed by the solvent-swollen compatible block. This self-assembly process has facilitated the fabrication of many new nanoscopic structures. For example, Moller[3a,b] and Hilborn[3c] have used the micellization of diblock polymers to organize nanometer-sized particles of either a metal or a semiconductor. In this approach, a suitable inorganic precursor is selectively bound to the core of a micelle, followed by film formation and transformation of the inorganic precursor to the requisite nanoparticle. Stringent control of particle size and separation has been demonstrated from these kinetically controlled assemblies. Alternatively, amphiphilic molecules have been used to template both meso- and nanoporosity in silicates.[4,5] 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 amphiphiles ultimately provides pore sizes under 30 Å after calcination, whereas macromolecular surfactants provides larger pores; in each case, the pores are commensurate with the micelle size. Each of the applications described above involve the development of structures that are kinetically quenched.

The micelle stability and structure depends on many factors including solvent, temperature, concentration, pH, etc. The formation of micelles is a dynamic situation which complicates the ability to engineer macromolecular properties. A noteworthy strategy designed to ameliorate these variables is the preparation of a fully bonded unimolecular micelle exemplified by an appropriately functionalized dendrimer. Dendritic micelles are covalently bound macromolecules that predominately retain their basic overall shape irrespective of their environment and have no critical micelle concentrations.[6] This is a very different situation from the development of structure via the dynamic equilibrium

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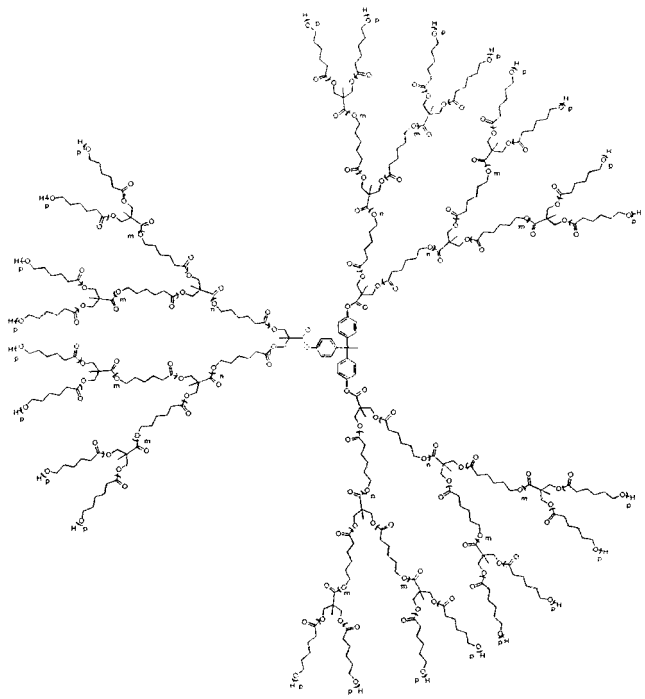
between various small molecules or macromolecules. Fully bonded dendritic micelles can promote molecular inclusion and solublize hydrophobic molecules in aqueous solution.[6j] Likewise, polymers with star molecular architectures have also been shown to be acceptable models for polymeric micelles, provided they have a sufficient number of arms or chains emanating from a central core. There are two general ways to prepare star polymers. The first approach involves the termination of either linear polymers or diblock polymers with a multifunctional reagent.[7] For instance, anionically prepared poly(styrene) can be terminated with silicon tetrachloride to form a four-arm star polymer with a central silicon core. Alternatively, star polymers can be grown from multifunctional initiators attached to a central core. The use of dendritic macromolecules allows the ultimate formation of star polymers with a predictable number of arms, and this concept has been demonstrated by a number of groups.[8] Although this approach can indeed produce star polymers with the requisite number of arms necessary to create micellar structures, these materials have a relatively compact core of defined chemical composition, leaving little latitude for manipulation.

Block copolymers are remarkable self-assembling systems that can assume a wide variety of morphologies including lamellar, hexagonal-packed cylindrical, and body-centered cubic micellar structures, depending on the relative volume fractions of the blocks.[1] This clear picture of the morphology as a function of composition has primarily emerged from the investigation of diblock copolymers. However, the molecular architecture of the polymer chain also has a pronounced affect on the morphology and interfacial activity, and this is of concern in the preparation of dendritic micelles capable of microphase separation. Sanchez et al.[9] predicted that larger values of χ_n, where χ is the Flory interaction parameter and n is the degree of polymerization, will be necessary for phase separation for branched polymers including graft and star architectures than those for the corresponding diblock polymers. Hadjichristidis et al.[10] have studied three-arm star copolymers and terpolymers and found that these phase diagrams were shifted (i.e., cylindrical morphologies were observed at compositions where lamellar structures were observed for the corresponding diblock copolymers) due to steric crowding near the branch point leading to high curvature at the interface of the microphase separated domains. Unfortunately, full examination and explanation of these observations has been hindered due to the difficulty in preparing well defined, branched block copolymers.

In the past decade, significant efforts have been devoted to the development of "living" controlled polymerization based on free radical chemistry.[11] Two main approaches have been developed: the first involves the mediation of the free radical process by stable nitroxide free radicals,[12] while the second, atom transfer radical polymerization (ATRP),[13] mediated by a variety of metal complexes, evolved from the Kharasch reaction. One of the major advantages of "living" free radical chemistry, when compared to other living procedures for vinyl monomers (i.e., anionic and cationic), is the stability of the initiating centers.[14] This has permitted a wide variety of functionalized unimolecular initiators to be prepared and employed in the synthesis of well-defined linear polymers,[15] block copolymers,[16] and other

Scheme 1

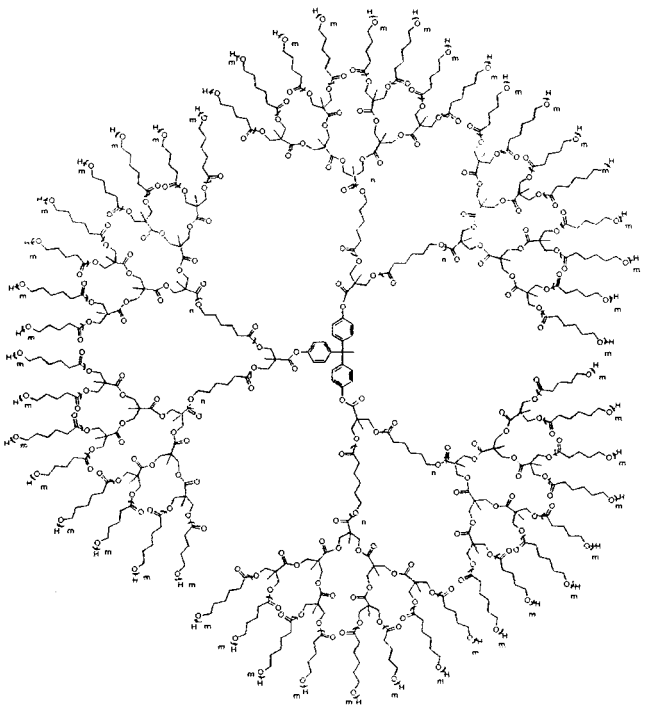


G-3(24 OH)

complex molecular architectures including graft, dendrigraft, and hyperbranched structures.[17] Furthermore, the stability of these umimolecular initiators has allowed the possibility of combining "living" free radical procedures with a wide variety of other living and nonliving polymerization procedures. Concurrent with independent reports from Matyjaszewski[19] and Sogah,[20] we have also demonstrated[18] a dual living polymerization strategy in which two different functional groups on a single initiator were used to initiate "living" ring opening and "living" free radical polymerization requiring minimal steps and no intermediate functionalization transformations.

Our objective is to extend the possibilities of dual living polymerizations (either consecutive or concurrent) to encompass new and complex molecular architectures, ultimately leading to structures that may mimic unimolecular polymeric micelles. In this article, the synthesis of star and dendrimer-like star block copolymers of poly(ϵ-caprolactone) with poly(methyl methacrylate) and related structures by combination of living ROP and controlled ATRP techniques is reported. We have recently demonstrated that the living ROP of ϵ-caprolactone initiated from bis(hydroxymethyl) groups (i.e., 1,3-bis(hydroxymethyl) propionic acid and its derivatives) is a facile process which leads to macromolecules with controlled molecular weights and narrow polydispersities.[21] An important feature of this synthesis is the use of a catalytic amount of $Sn(Oct)_2$ in conjunction with the 1,3-bis(hydroxymethyl) moiety to minimize intermolecular complexation which deleteriously affects the living nature of the polymerization. Three generations of dendrimer-like star poly(ϵ-caprolactones) have been prepared by a divergent growth approach using repetitive ROP coupled with functionalization and deprotection of an AB_2 branching juncture formed at the chain ends between generations (Scheme 1).[22] In this way, the high molecular weight polymer, capable of entanglement, constitutes each generation and provides mechanical integrity to these otherwise brittle dendritic

Scheme 2



materials. In a similar fashion, we have prepared a new molecular architecture, denoted as layered dendritic block copolymers (Scheme 2).[23] These block copolymers are described by a radial geometry where the succeeding layers or generations are comprised of high molecular weight polymer all emanating from a central core. The goal of this paper is to extend this synthetic strategy to hybrid dendritic-linear systems capable of microphase separation using a combination of "living" ROP and ATRP procedures. We describe the use of a hexahydroxyl functional core as an initiator for the ROP of ϵ-caprolactone to produce initially a six-arm star polymer of controlled molecular weight and narrow polydispersity. Capping the chain ends with branching points containing activated bromide moieties produces "macro-initiators" useful for subsequent atom transfer radical polymerization (ATRP).[10c] To study the affects of branching on phase separation, methyl methacrylate was polymerized from these "macro-initiators" to give the requisite dendrimer-like star block copolymers. In addition, we have extended this synthetic approach to include hybrid-linear systems to encompass monomer sets that impart amphiphilic character. The large number of available methacrylate and acrylate monomers allows significant synthetic flexibility in tuning the polarity of the individual layers of the dendrimer-like star polymers. These structures are denoted as amphiphilic, dendrimer-like star polymers.

Experimental Section

Materials. The 1,1,1-tris(p-hydroxyphenyl)ethane (THPE) (Hoechst Celanese) and stannous(II) 2-ethylhexanoate (Sn(Oct$_2$) (Sigma) were used as delivered. 4-(Dimethylamino)-pyridinium 4-toluenesulfonate (DPTS) was synthesized according to a literature procedure.[24] The ϵ-caprolactone was dried over CaH_2 (Mallinckrodt) and distilled and stored under N_2 prior to use. Toluene was dried over Na, distilled, and stored under N_2. The methyl methacrylate and hydroxyethyl methacrylate (HEMA) were distilled under vacuum and refrigerated under N_2 until used. The hexahydroxyl initiator, **1**, was prepared according to a literature procedure.[25] The benzyl 2,2′-bis(hydroxymethyl) propionate was synthesized according to a literature procedure.[23,25] All other compounds were purchased from Aldrich and used as received.

Measurements. Size-exclusion chromatography (SEC) was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer. 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 eluant. The SEC results were calibrated with polystyrene standards. The thermophysical properties (T_g) were recorded on a Perkin-Elmer DSC-7. ^{1}H NMR spectra were recorded in solution with a Bruker AM 250 (250 MHz) spectrometer. ^{13}C NMR spectra were recorded at 62.9 MHz on a Bruker AM 250 spectrometer using the solvent carbon signal as an internal standard.

Synthesis. Benzyl 2,2-Bis(*tert*-butyldimethylsiloxymethyl)benzyl propionate, g1(−TBDMS, −CO$_2$C$_7$H7) (3). **2** (49.8 g, 222 mmol), *tert*-butyldimethylsilyl chloride ((TBDMS)Cl) (80.5 g, 535 mmol) and imidazole (37.8 g, 533 mmol) were dissolved in CH_3CN (150 mL). The mixture was stirred for 12 h and the solvent was then evaporated. The crude product was dissolved in hexane and extracted with H_2O. The organic phase was separated and dried ($MgSO_4$). The hexane was evaporated to a yield of 95.2 g (94%) of a colorless liquid. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 12H, −Si(CH_3)$_2$), 0.83 (s, 18H, −C(CH_3)$_3$), 1.12 (s, 3H, −CH_3), 3.64−3.77 (q, 4H, −CH_2O−), 5.10 (s, 2H, −CH_2Ph−), 7.32 (s, 5H, −CH_2−Ph).

2,2-Bis(*tert*-butyldimethylsiloxymethyl)propionic Acid (4) and a General Procedure for the Removal of the Benzyl and Benzylidene Groups. 3 (210 mmol, 95.2 g) was dissolved in EtOAc (100 mL) and Pd/C (10 wt %) (1.5 g) was added. The apparatus for catalytic hydrogenolysis was evacuated, filled with H_2 and agitated. After completion of the reaction (approximately 4 h), the Pd/C was filtered off. The solvent was evaporated to yield 94.2 g (99%) of a colorless liquid. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 12H, −Si(CH_3)$_2$), 0.82 (s, 18H, −C(CH_3)$_3$), 1.07 (s, 3H, −CH_3), 3.60−3.69 (q, 4H, −CH_2O−). ^{13}C NMR ($CDCl_3$): δ −5.62, 17.05, 18.18, 25.77, 49.69, 64.39, 179.44.

g2(−TBDMS, −CO$_2$C$_7$H7) (5). 2 (23.3 g, 104 mmol), **4** (79.0 g, 218 mmol) and_DPTS (4.87 g, 15.5 mmol) were dissolved and stirred in CH_2Cl_2. DCC (55.7 g, 0.270 mmol) was then added immediately and the mixture was left to react for 12 h. The mixture was filtered, and the filtrate was purified by column chromatography (silica gel, hexane/EtOAc 95:5). The yield was 30 g (32%) of a viscous and colorless liquid. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 24H, −Si(CH_3)$_2$), 0.84 (s, 36H, −C(CH_3)$_3$), 1.09 (s, 6H, CH_3), 1.23 (s, 3H, CH_3), 3.56−3.70 (q, 8H, −CH_2O), 4.15−4.30 (ABq, 4H, −CH_2O−), 5.13 (s, 2 H, −CH_2Ph−), 7.33 (s, 5H, −Ph). ^{13}C NMR ($CDCl_3$): δ −5.58, 16.93, 17.58, 18.20, 25.83, 46.94, 50.38, 64.04, 65.31, 66.77, 128.03, 128.30, 128.60, 135.57, 172.51, 174.19.

g2(−TBDMS, −COOH) (6). 5 (30.0 g, 32.9 mmol) and 10% Pd/C (1.5 g) were dissolved in EtOAc (100 mL) and hydrogenolyzed according to the general procedure for the removal of the benzyl group. The yield was 26.2 g (97%) of a viscous and colorless liquid. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 24H, −Si(CH_3)$_2$), 0.84 (s, 36H, −C(CH_3)$_3$), 1.06 (s, 6H, −CH_3), 1.25 (s, 3H, −CH_3), 3.57−3.72 (q, 8H, −CH_2O−), 4.06−4.29 (m, 4H, −CH_2O−), 5.28 (s, 2H, −CH_2−). ^{13}C NMR ($CDCl_3$): δ −5.59, 16.96, 17.55, 18.18, 25.81, 46.59, 50.41, 64.07, 64.92, 174.17, 178.84.

2,2-Bis(phenyldioxymethyl)propionic Acid (7). Bis-MPA (50.0 g, 347 mmol), benzaldehyde dimethylacetal (85.1 g, 560 mmol) and PTSA (1.39 g, 7.46 mmol) were dissolved in acetone and stirred for 14 h. NH_4OH (aq, 30%) and EtOH (1:1) (8 mL) were then added to neutralize the PTSA. The acetone was evaporated and the crude product was diluted in CH_2Cl_2 and extracted with water. The organic phase was separated, dried ($MgSO_4$) and recrystallized from CH_2Cl_2 to yield of 93.1 g (90%) of white crystals. ^{1}H NMR ($CDCl_3$): δ 1.09 (s, 3H, −CH_3), 3.66−4.64 (q, 4H, −CH_2O)$_2$CH−), 5.47 (s, 1H, −CHPh),

7.31−7.47 (m, 5H, −PH). ^{13}C-NMR (acetone-d_6): δ 18.14, 42.61, 73.96, 102.04, 127.12, 128.67, 129.35, 139.81, 175.70.

G-1 (6 OH) and a General Procedure for the Polymerization of ϵ-Caprolactone. The "initiator" **1** (5.00 g, 7.64 mmol) was dried over $MgSO_4$ in warm THF, and filtered into the pre flamed reaction flask, which was subsequently sealed. The solvent was then evaporated under vacuum at 90 °C. Dry toluene (2 mL) was added and evaporated to remove residual H_2O(3×). The reaction flask was then filled with N_2 and dry toluene (2 mL) to dissolve the initiator. ϵ-Caprolactone (75.0 g, 658 mmol) was added and the temperature was increased to 110 °C before a catalytic amount of $Sn(Oct)_2$ (32 mg, 0.08 mmol) was added. The ratio of catalyst/initiator was 1/400. The polymerization reaction was stirred for 24 h, diluted with THF, and precipitated into cold MeOH to give 72.0 g (90%) of a white crystalline powder. ^{1}H NMR ($CDCl_3$): δ 1.30−1.42 (m, poly, $-CH_2-$), 1.55−1.69 (m, poly, $-CH_2-$), 2.26−2.32 (t, $-CH_2O-$), 3.60−3.65 (t, 12H, $-CH_2OH-$), 4.01−4.07 (t, poly, $-CH_2CO-$), 4.33 (s, 12H, $-CCH_3(CH_2O)_2-$), 6.88−7.24 (dd, 12H, Ph−). ^{13}C NMR ($CDCl_3$): δ 17.74, 24.50, 28.27, 32.20, 34.03, 46.69, 51.58, 62.38, 64.05, 65.07, 120.67, 129.64, 146.22, 148.60, 171.37, 172.78, 173.65.

G-1.5-1(0-OH) and a General Procedure for the Functionalization of PCL. To a stirred solution **G-1(6 OH)** (14.3 g, 1.00 mmol), **7** (2.01 g, 9.00 mmol), TPP (3.17 g, 12.1 mmol) and THF (5 mL) at ambient temperature, DIAD (2.44 g, 12.1 mmol) was slowly added. The reaction mixture was precipitated into cold MeOH after 24 h. The filtered product was a white crystalline powder. Yield: 10.3 g (95%). ^{1}H NMR ($CDCl_3$): δ 1.00 (s, 18H, $-CH_3$), 1.30−1.40 (m, poly, $-CH_2-$), 1.55−1.68 (m, poly, $-CH_2CH_2$), 2.26−2.30 (t, poly, $-COCH_2-$), 3.59−4.64 (q, 24H, $-(CH_2O)_2CH$Ph), 4.00−4.04 (t, poly, $-CH_2O$), 4.15−4.20 (t, 12H, $-CH_2OCO-$), 4.31 (s, 12H, $-CCH_3(CH_2O)_2-$), 5.41 (s, 6H, $-CH$Ph), 6.88−7.24 (dd, 12H, −Ph), 7.28−7.41 (m, 30H, −CH*Ph*). ^{13}C NMR ($CDCl_3$): δ 17.87, 24.53, 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-1.5-1(12 OH). G-1.5-1(0 OH) (12.0 g, 0.77 mmol) was dissolved in THF (10 mL) and diluted with EtOAc (100 mL) before Pd/C (1.0 g) was added according to the general procedure for the removal of the benzylidene protecting groups. After 24 h the Pd/C was filtered off and the filtrate was precipitated in cold methanol. Yield: 10.0 g (86%) of a white crystalline powder. ^{1}H NMR ($CDCl_3$): δ 1.00 (s, 18H, $-CH_3$), 1.29−1.35 (m, poly, $-CH_2-$), 1.50−1.58 (m, poly, $-CH_2CH_2-$), 2.19−2.25 (t, poly, $-COCH_2-$), 3.00 (t, 12H, −OH), 3.61−3.81 (dd, 24H, $-CH_2OH$), 3.91−4.00 (t, poly, $-CH_2O$), 4.03−4.09 (t, 12H, $-CH_2OCO$), 4.26 (s, 12H, $-CCH_3(CH_2O)_2-$), 6.84−7.02 (dd, 12H, Ph−). ^{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-1.5-2(24-OH) and a General Procedure for the Removal of the TBDMS Group. G1.5-2(0 OH) (10.03 g, 0.52 mmol) was added to a flask which was sealed. The flask was evacuated and filled with N_2(g) (3×) to provide an inert atmosphere. Dry CH_2Cl_2 (30 mL) and $BF_3{\cdot}Et_2O$ (0.37 g, 2.6 mmol) were then added in that order. The mixture was stirred for 12 h at 40 °C before it was precipitated into cold MeOH. The filtered, dried product gave 7.1 g (yield: 80%) of a white crystalline powder. ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 36H, $-CH_3$), 1.20 (s, 18H, $-CH_3$), 1.32−1.42 (m, poly, $-CH_2CH_2CH_2-$), 1.57−1.69 (m, poly, $-CH_2CH_2CH_2-$), 2.26−2.32 (t, poly, $-CH_2O-$), 3.63−3.84 (m, 48H, $-CH$2OH), 4.01−4.06 (t, poly, $-CH_2CO-$), 4.13−4.24 (t, 48H, $-CH_2OCO-$), 4.29−4.44 (m, 36H, $-CH_2O-$), 6.91−7.09 (ABq, 12H, −Ph). ^{13}C NMR ($CDCl_3$): δ 17.03, 17.71, 18.00, 24.47, 25.43, 28.24, 34.01, 46.29, 46.68, 49.82, 64.04, 64.79, 65.13, 66.84, 120.66, 129.62, 146.21, 148.59, 171.36, 172.77, 172.94, 173.45, 174.89.

General Procedure for the Modification of the Hydroxy-Functional End Groups of the Poly(ϵ-caprolactone) Initiators for ATRP. G-1 (6-OH) (8.00 g, 3.2 mmol) was dissolved in 50 mL of dry THF. To this solution was added triethylamine (1.40 g, 17.75 mmol). 2-Bromo-2-methylpropionyl bromide (1.580 g, 6.85 mmol) was added dropwise over a 15 min period and stirring continued at room temperature for 48 h. ^{1}H-NMR ($CDCl_3$): d 1.28−1.40 (m, poly, $-CH_2CH_2-CH_2-$), 1.55−1.70 (m, poly, $-CH_2CH_2CH_2-$) 1.89 (s, 6H, CH_3), 2.24−2.35 (t, poly, $-CH_2CO-$), 4.00−4.05 (t, poly, $-CH_2O-$), 4.11−4.16 (t, 18H, $-CH_2OH$), 4.31 (2, 12H, $-CCH_3(CH_2O)_2-$), 6.89−7.07 (dd, 12H, Ph−). ^{13}C-NMR ($CDCl_3$): δ 17.74, 24.51, 25.47, 28.29, 30.70, 34.05, 46.71, 51.61, 55.88, 64.05, 65.11, 65.70, 120.69, 129.65, 146.23, 148.62, 171.37, 171.57, 172.77, 173.43.

General Procedure for the ATRP of Methyl Methacrylate from Functional Polycaprolactone. G-1 (6-Br) (0.40 g 0.15 mmol) and dibromobis(triphenylphosphine)nickel(II) (7.00 mg, 0.009 mmol) were charged into a flask which was evacuated for 12h and then purged with nitrogen and evacuated (4×). Dry methyl methacrylate (2.00 g, 20.00 mmol) was added through a rubber septum and allowed to stir at room temperature until the macroinitiator dissolved. Optionally, toluene or THF could be added to facilitate the dissolution of the initiator and/or reduce the viscosity of the polymerization. The reaction flask was placed in a hot oil bath (110 °C) and allowed to react for 5−8 h. The polymers were isolated in hexane, stirred in methanol, and isolated by filtration.

Scheme 3

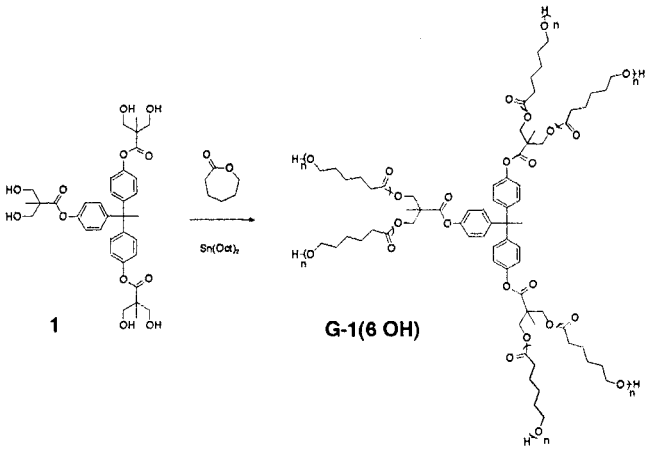


Table 1. Characteristics of Poly(ϵ-Caprolactone) Star Polymers

sample entry	DP target	DP ^{1}H NMR	M_n (^{1}H NMR)	M_w/M_n (SEC)
G-1(6-OH)a	20	21	14 300	1.06
G-1(6-OH)b	80	81	56 000	1.09

Results and Discussion

The dendritic initiator used in this study is the first generation hexahydroxyl functionalized 2,2′-bis(hydroxymethyl)propionic acid (bis-MPA) dendrimer, **1**.[25] The synthesis of the six arm star polymers or "macroinitiators" was accomplished by the reaction of **1** with ϵ-caprolactone in the presence of a catalytic amount of $Sn(Oct)_2$ using bulk conditions, followed by hydrolysis of the active oxy metal bonds to produce the desired hydroxyl chain ends[21a] (Scheme 3). Two star poly(ϵ-caprolactone) polymers were prepared and the characteristics of the polymers are shown in Table 1. The number average molecular weights of the polymers (referred to as **G-1(6-OH)a** and **G-1(6-OH)b**) are 14 300 and 56 000, respectively. This designation denotes the first generation of poly(ϵ-caprolactone) containing six hydroxyl functional groups as confirmed by ^{1}H NMR, and the polydispersities, as measured by size exclusion chromatography, were <1.10. The target degree of polymerization, DP, for each arm of the star polymers

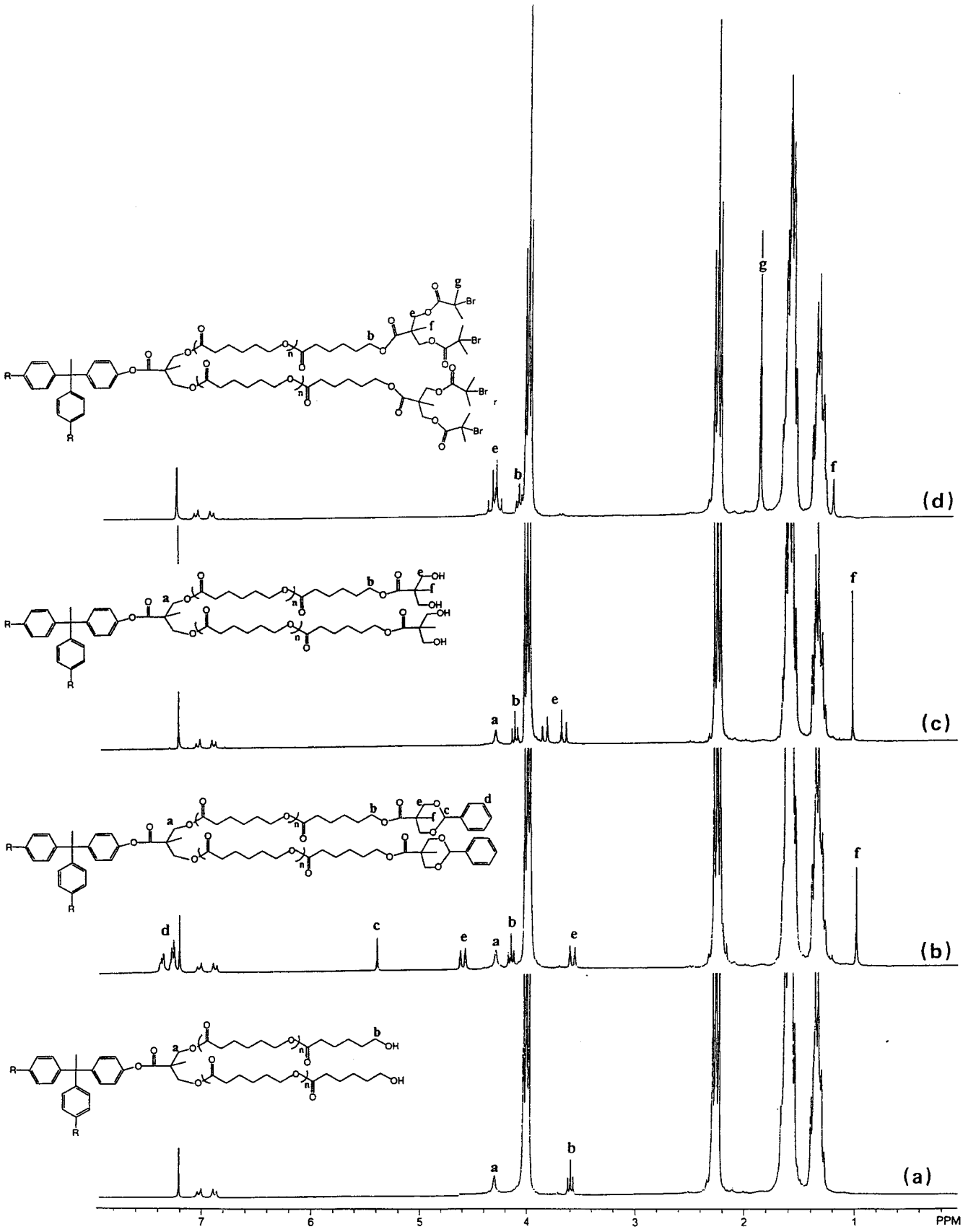
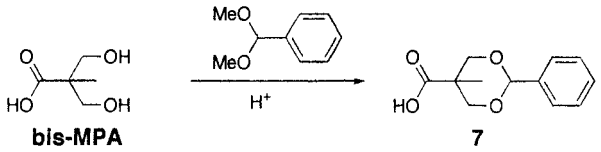


Figure 1. ^{1}H NMR of **G-1(12-Br)a** and intermediates.

G-1(6-OH)a and **b** was 20 and 80, respectively, and the average DP's, calculated by ^{1}H NMR, were 21 and 81 (Table 1). The ^{1}H NMR spectrum of **G-1(6-OH)a** in Figure 1a shows the four major resonances attributed to the repeat unit of poly(caprolactone) as well as peaks associated with the methylene protons adjacent to the hydroxyl chain ends, **b**, and the protons of the initiator, **a**. Examination of the ^{13}C NMR spectrum and comparison with previous studies demonstrated that initiation occurs from each of the hydroxyl groups producing the

Scheme 4



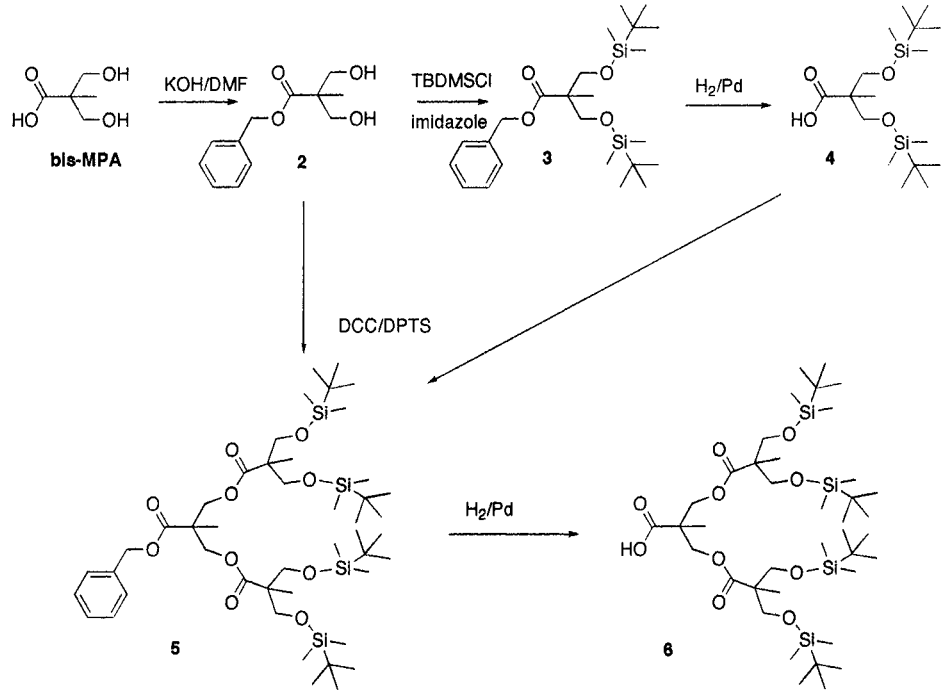
requisite six arm star polymer or "macro-initiator".[21]

In some instances, a branching juncture was introduced at the chain ends by the derivatization with an AB_x monomer or dendron. For example, incorporation of AB_2 or AB_4 protected derivatives produces six-arm polymers with either 12 or 24 hydroxyl groups, respectively.[23,25] The AB_2 moiety is simply bis-MPA where the hydroxyl groups are protected with a benzylidine group, **7** (Scheme 4). The synthesis of the AB_4 dendron was accomplished by the convergent growth approach as shown in Scheme 5. The hydroxy groups of the benzyl ester **2** were protected with *tert*-butyldimethylsilyl chloride (TBDMSCl) to give **3** (Scheme 5). The benzyl group could be readily removed by catalytic hydrogenolysis to give **4**. The coupling of **4** with **2** afforded the second generation **5** which could be transformed by hydrogenolysis to produce **6**. The structures of the branched dendrons were confirmed by both ^{1}H NMR and ^{13}C NMR spectroscopy. Of particular interest is the quaternary carbon signals in the ^{13}C NMR spectra (Figure 2), since they are known to reflect the nature of the substitution on the two alcohols of bis-MPA.[27] Figure 2 shows that the AB_4 branching juncture has quaternary carbons signals assignable to disubstituted bis-MPA units, without any traces of contamination from monosubstitution, validating the proposed structures.

Mitsunobu conditions were used to couple the protected AB_2 and AB_4 monomers to the six arm star poly(ϵ-caprolactone) to produce ultimately **G-1.5(12-OH)a** and **G-1.5(24-OH)a**, respectively (Scheme 6). These transformations were followed by ^{1}H NMR, ^{13}C NMR and SEC measurements.[28] The ^{1}H NMR spectra of **G-1.5(O−OH)a** shows five new peaks denoted as **c**, **d**, **e**, and **f** which can be attributed to the protected bis-MPA end groups, and the peak denoted as **b** shifts (Figure 1b). The benzylidene unit of the AB_2 branching juncture was removed by hydrogenolysis to generate the six arm star polymer with 12 hydroxyl groups, denoted as **G-1.5(12-OH)a.** Deprotection eliminates the **c** and **d** peaks derived from the benzylidene protecting group and shifts the **e** and **f** resonances (Figure 1c). The TMDBS protecting groups of the AB_4 branching juncture were removed with $BF_3{\cdot}Et_2O$, generating 24 hydroxyl groups **(G1.5(24-OH)a)**. Shown in Figure 3 are the SEC traces for the six-arm star poly(ϵ-caprolactone) and the coupled products. The distributions are monomodal with no evidence of either contamination from unreacted dendron or transesterification.

The polymerization of MMA by a controlled atom transfer procedure, requires an initiator with an activated alkyl halide, such as an α-halo ester. Introduction of these initiating centers into the dendritic structure was accomplished by the esterification of the hydroxyl functional chain ends of **G-1(6-OH)** with 2-bromo-2-methylpropionyl bromide in THF in the presence of triethylamine (Scheme 6). Isolation of the chain end functionalized polymers or "macro-initiators" (denoted as **G-1.5(6-Br)a** and **b, G-1.5(12-Br)a,** and **G-1.5(24-Br)a**) and purification from excess reagents were accomplished by a simple precipitation in methanol. The versatility of this pseudo double stage approach has also been recently demonstrated by Hult and Fréchet with their elaboration of dendritic polyesters based on bis-(hydroxymethyl) propionic acid. The ^{1}H NMR spectrum of **G-1.5(12-Br)a** shows a clear shift in the peaks as **e** assigned (see Figure 1c,d) upon the formation of the ester linkage. Furthermore, a new peak, denoted as **g**, from the $-CH_3$ groups of the modified chain end is observed in Figure 1d. ^{13}C NMR was also used to examine the efficiency of this transformation by the examination of the quarternary carbon in the bis-MPA unit (Figure 4). These carbons are known to shift

Scheme 5



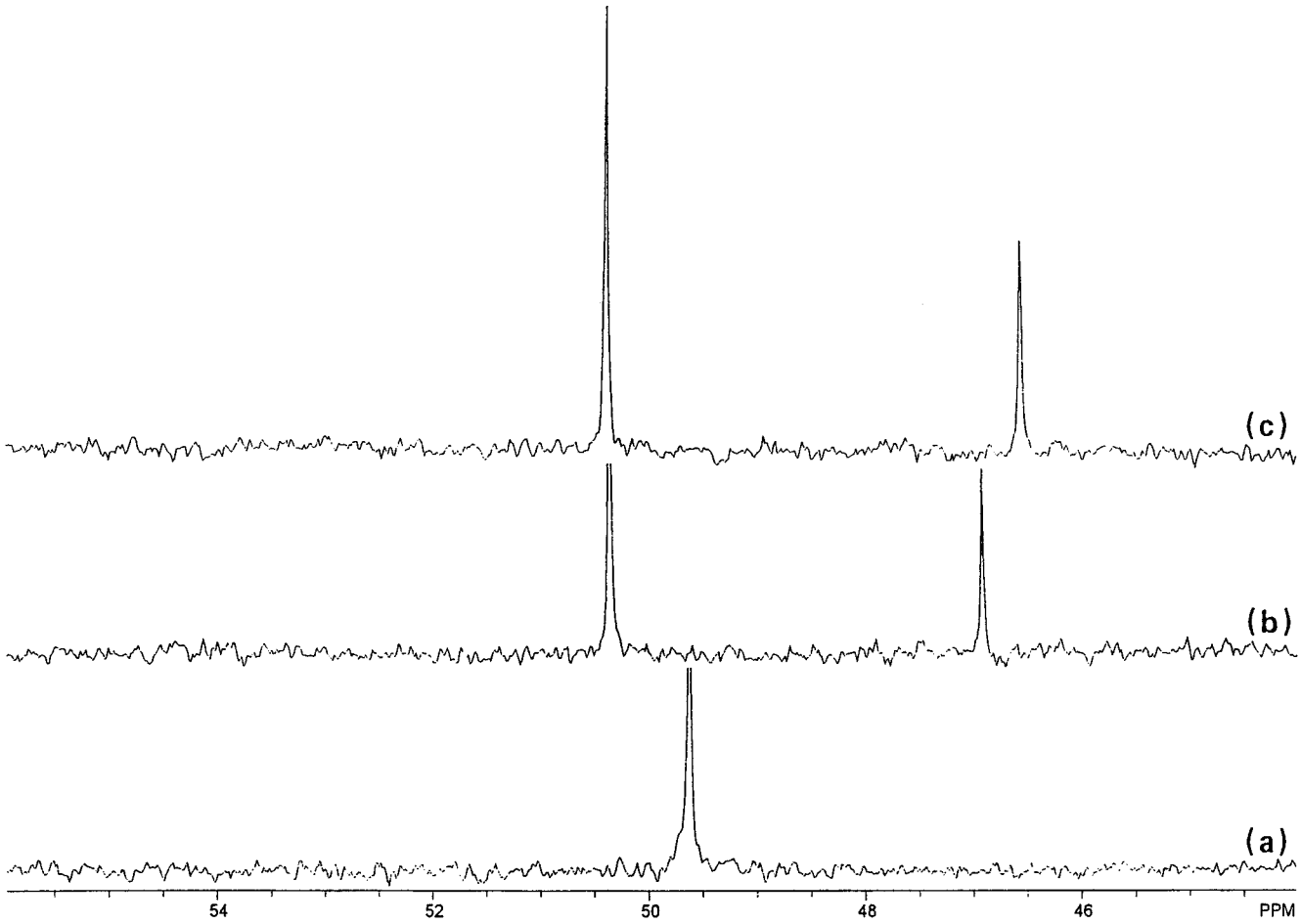


Figure 2. ^{13}C NMR of (a) **3**, (b) **5** and (c) **6**.

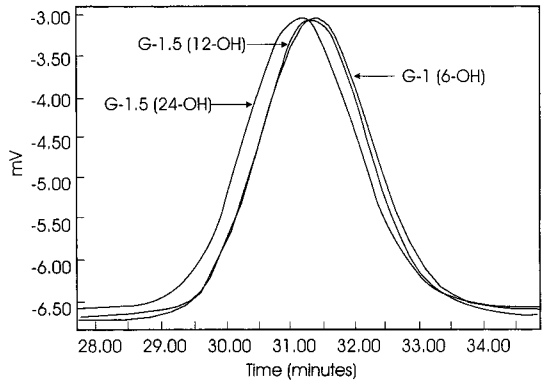


Figure 3. SEC traces of **G-1(6-OH)a** and coupled products.

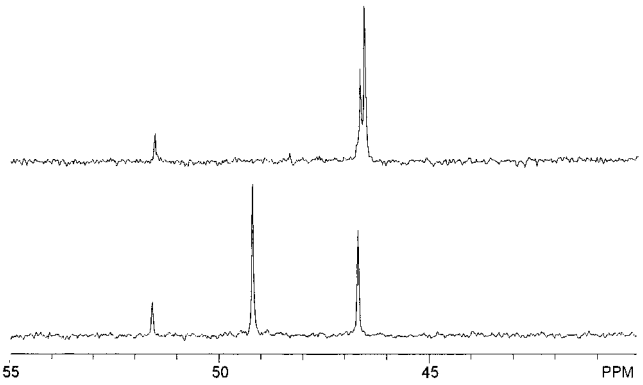
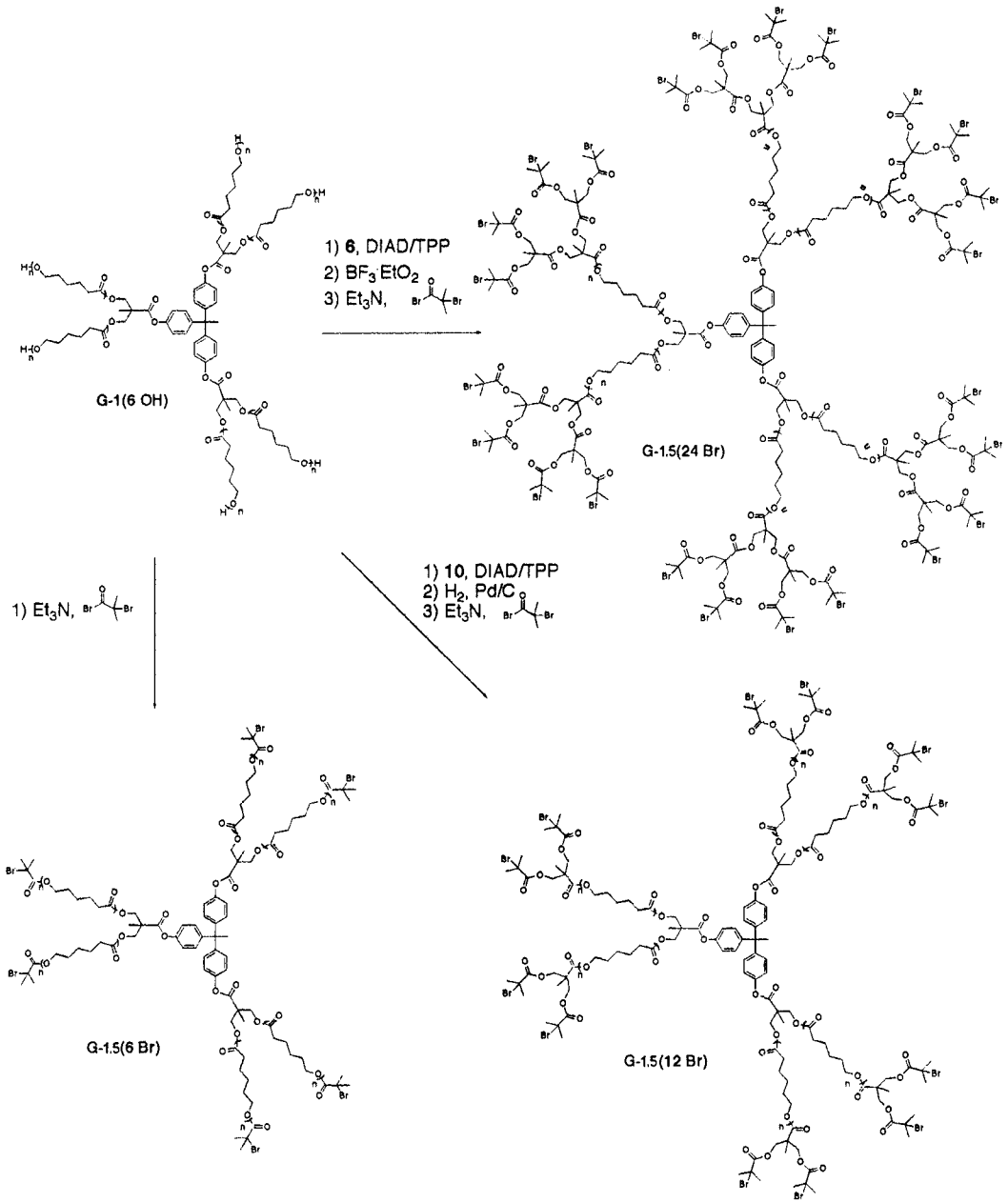


Figure 4. A portion of ^{13}C NMR of **G-1.5(12OH)a** (bottom) and **G-1.5(12-Br)a** (top).

depending on the substitution. Functionalization of the hydroxyl groups with 2-bromo-2-methyl propionoyl bromide or α-bromoisobutyl bromide shifts the quarternary carbon peak from 49.1 to 46.7 ppm, indicating quantitative transformation of the hydroxyl groups (Figure 4).

The homopolymerization of methyl methacrylate (MMA) using a variety of activated bromides as initiators in the presence of metal catalyst such as $NiBr_2(PPh_3)_2$ or $RhBr_2(PPh_3)_2$ has been shown to be a living process.[7,29] While MMA is a good solvent for the poly(ϵ-caprolactone) "macroinitiators" allowing bulk polymerization conditions, polymerization solvents also were surveyed simply to reduce the viscosity of the high molecular weight products (Scheme 7). Likewise, MMA hydroxy ethyl methacrylate (HEMA) mixtures dissolve the poly(caprolactone) "macroinitiators" at moderate HEMA compositions, polymerization of monomer mixtures containing a higher HEMA content (i.e., >20 wt %) requires the use of a polar solvent (e.g., THF) (Scheme 8). Higher concentrations of HEMA in the copolymer required the use of the trimethylsilyl-protected HEMA (Si−HEMA) to avoid "gelation." Upon completion of the bulk polymerization, the polymer was dissolved in a 50/50 (vol) mixture of methanol/THF, and the trimethylsiloxy group was readily removed under acidic conditions. Ethylene oxide macromonomer/MMA mixtures containing moderate amounts of poly(ethylene oxide) macromonomer (i.e., <5 mol %) also solubilize the poly(caprolactone) "macro-initiators" while higher compositions also require a solvent such as THF to facilitate miscibility (Scheme 9). The Ni(II)-based catalyst has been shown to be active under mild conditions in both

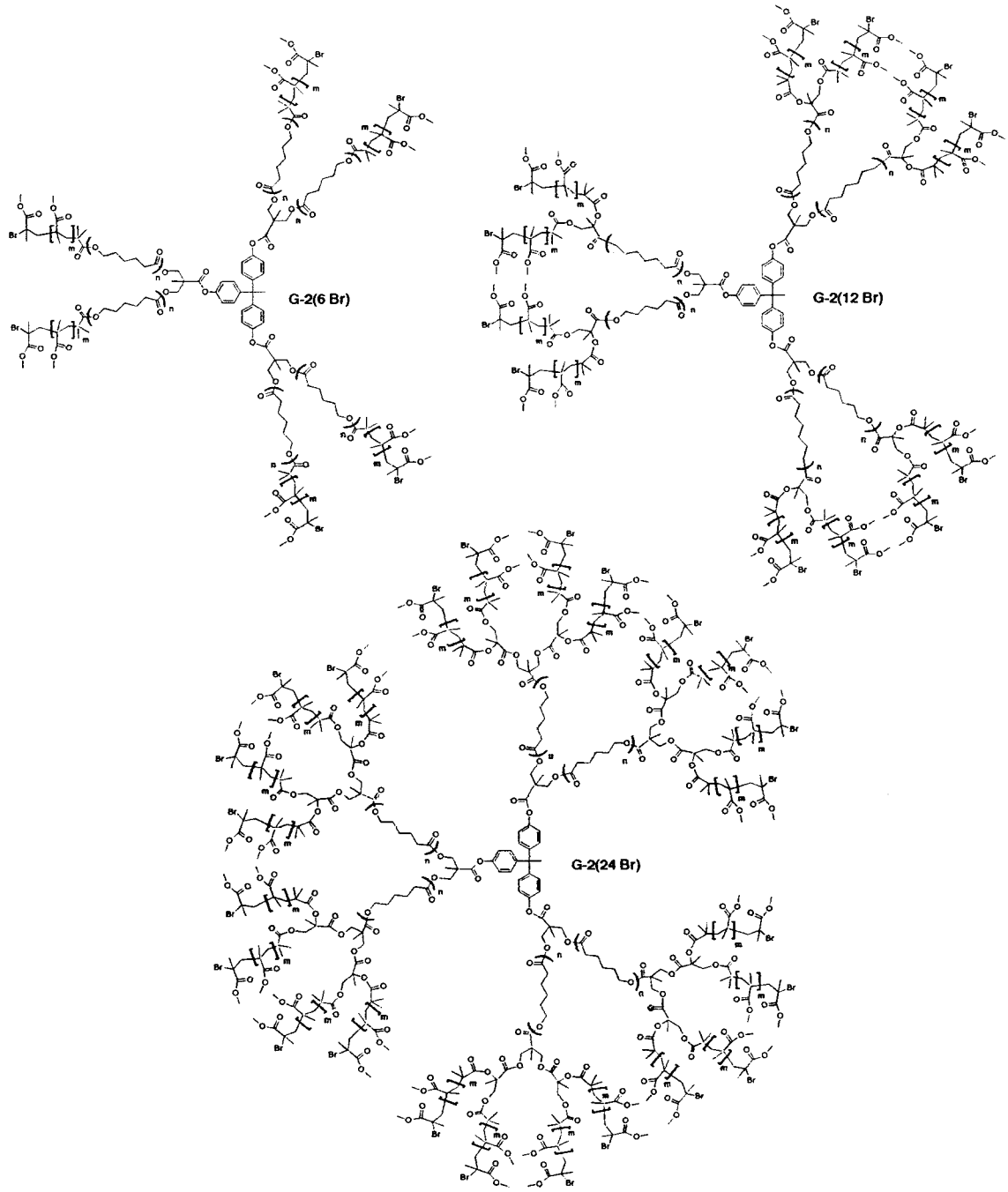
Scheme 6



organic solvents as well as aqueous suspensions. However, these catalysts are extremely sensitive to oxygen, requiring efficient purging of the reaction flask and polymerization under argon or vacuum. Generally, ATRP cataylsts are used in near stoichiometric amounts relative to the activated bromide, however, controlled polymerization is possible with $NiBr_2(PPh_3)_2$ contents as low as 10−20% of the stoichiometric amount. Decreases in the catalyst concentration increase the polymerization time and somewhat broaden the polydispersity of the products. In this study, the poly(ϵ-caprolactone) macroinitiator and $NiBr_2(PPh_3)_2$ (20 mol %) were charged into the flask and evacuated and back filled with nitrogen six times. The flask was then placed in an oil bath heated to 100 °C, where the poly(caprolactone) melted. To this flask, was added MMA or a mixture of MMA and solvent. For the case where THF was used as a solvent, the oil bath temperature was restricted to 80 °C. The polymerization times varied from several hours to overnight depending on the solids and catalyst contents, and completion of polymerization was determined by the point when the reaction mixture either solidified or became extremely viscous. The polymers were dissolved in THF, isolated in either heptane or hexane, and reprecipitated from THF into methanol to afford a white powder.

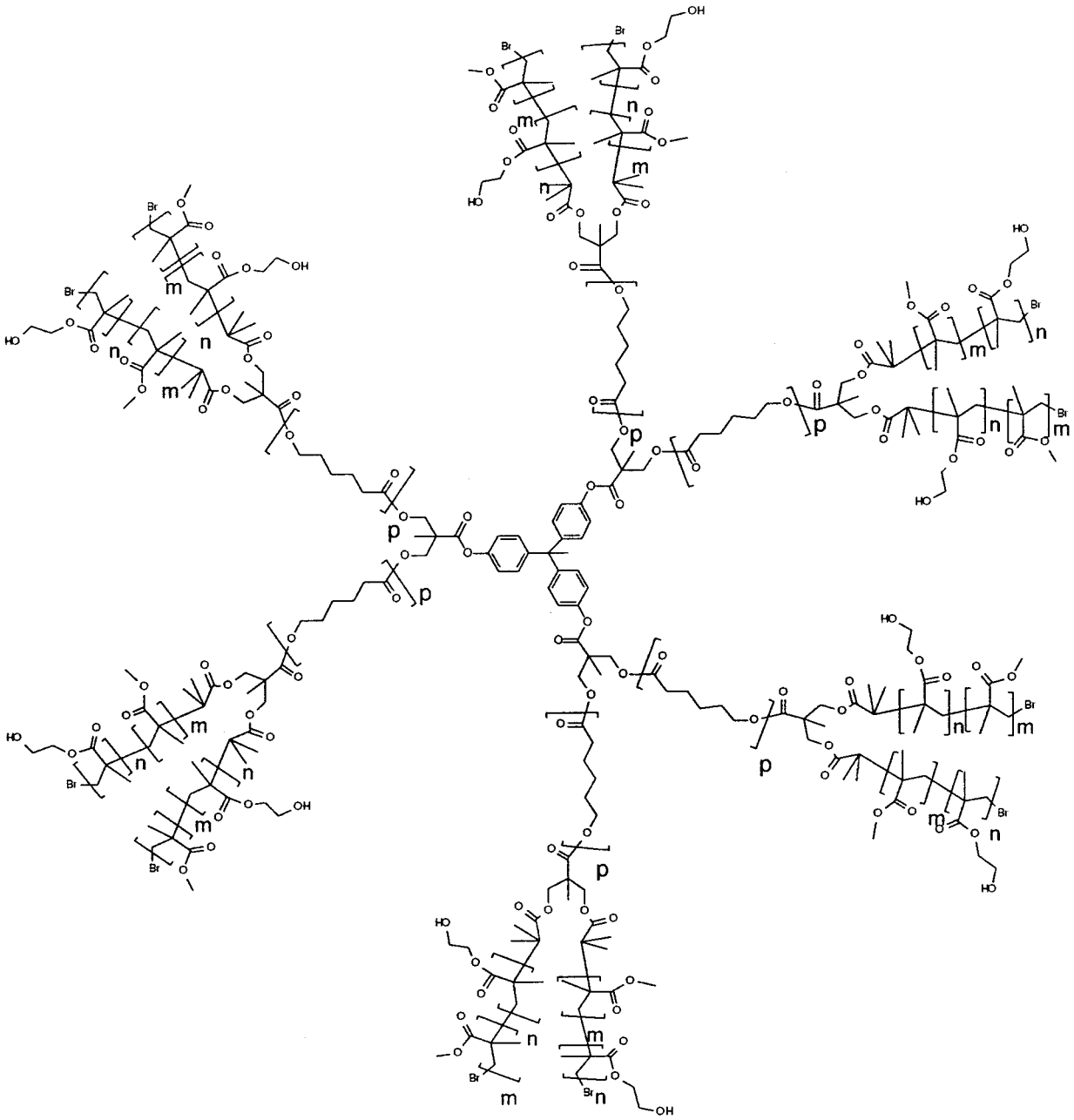
This general polymerization procedure was used to survey each of the macroinitiators, employing various solvents, and catalyst concentrations (Schemes 7−9). The target molecular weight for the poly(methyl methacrylate) blocks ranged from approximately 5000 to 14000 per arm for the six; 12 and 24-arm initiators. Shown in Figure 5 are the SEC traces for the poly(e-caprolactone) "macroinitiator" and the block copolymers derived from 12 and 24-arm initiators, denoted as **G-2(12-Br)a-2** and **G-2(24-Br)a-1**, respectively. Clearly, from these data, high molecular weight, low polydispersity products are obtained, and the total molecular weight increases with the number of arms, as anticipated. The characteristics of the polymers synthesized are shown in Table 2 for the methyl methacrylate based copolymers (Scheme 7) and Table 3 for the HEMA and

Scheme 7



ethylene oxide (EO) based copolymers (Schemes 8 and 9). The number average molecular weights, determined by SEC relative to poly(styrene) standards, range from 49 000 to 247 000 for the star polymers and from 70 000 to 220 000 g/mol for the dendrimer-like star polymers. However, these molecular weight values determined by SEC are difficult to compare since the hydrodynamic volumes will vary with molecular architecture. Polymerization from the **G-1(6-Br)a** and **b** initiators produce six-arm star radial diblock copolymers, whereas polymerization from **G-1.5(12-Br)a** and **G-1.5(24-Br)a** results in a more dendrimer-like star molecular architecture (Scheme 7). The highly branched structures for the latter polymers are expected to result in a more globular molecular shape, reminiscent of traditional dendritic materials. Correlating the solution characteristics of polymers containing the hydrophilic HEMA or the ethylene oxide macromonomers by SEC is even more problematical. In the case of the poly(ethylene oxide) macromonomers, an extremely complex molecular architecture, denoted as dendrimer-like star-graft copolymers, is expected. Nonetheless, a high molecular weight polymer was produced, and the polydispersities were surprisingly narrow and were symmetrical and monomodal. Polymerization in either THF or toluene had minimal effect on the molecular weight of the final polymers, provided the initial solids content was above 20%. Below this concentration, the polymerizations became very sluggish, and it was difficult to obtain high conversion or molecular weight. Similar results have been observed in nitroxide-mediated "living" free radical procedures.[14b] The molecular weight of the polymers was also independent of the Ni(II) concentration in the range 0.20−1.0 mol equiv (relative to the number of initiating

Scheme 8



centers). In all cases, the polydispersities were surprisingly narrow, below 1.2 with most in the range of 1.1. These data are consistent with our previous work on the initiation of poly(styrene) or poly(methyl methacrylate) from linear poly(ϵ-caprolactone) in which the use of a macroinitiator produced products with narrower polydispersities than those obtained from small molecule initiators.[18] Although the polydispersities were narrow, not all of the SEC traces were symmetrical (Figure 6). In fact, all samples prepared using catalyst concentrations near the stoichiometric amount as well as samples prepared in solution showed unsymmetrical SEC peaks. Conversely, samples prepared in bulk with lower catalyst content produced narrow polydispersity products with symmetric and monomodel SEC traces (Figure 6).

To gain further insight into the formation of the copolymer, and in particular, the poly(methyl methacrylate) block, cleavage of the dendrimer-like star polymer to give the methyl methacrylate tethered arms was investigated. The block copolymers were dissolved in either 1,4-dioxane or THF and hydrolyzed with HCl to give the cleaved polymer. Analysis by ^{1}H NMR clearly shows the disappearance of the ϵ-caprolactone resonances (Figure 7), and only the resonances of the poly(methyl methacrylate) remain, consistent with hydrolysis of the caprolactone core (Figure 7). Similar spectra were observed for the copolymers containing HEMA or EO in the outer layer. Consistent with these data is a significant decrease in molecular weight from 90 000 to 15 000 determined by SEC using polystyrene standards (Figure 8). The molecular weight of the cleaved arm is close to the target value. Of particular interest is the narrow polydispersity of the poly(methyl methacrylate) arm (PD = 1.11). As stated before, this has been observed for other samples initiated from poly(caprolactone). The other objective in this study was to examine the poly(methyl methacrylate) obtained after degradation of the caprolactone core to investigate whether radical coupling had indeed occurred. However,

Scheme 9

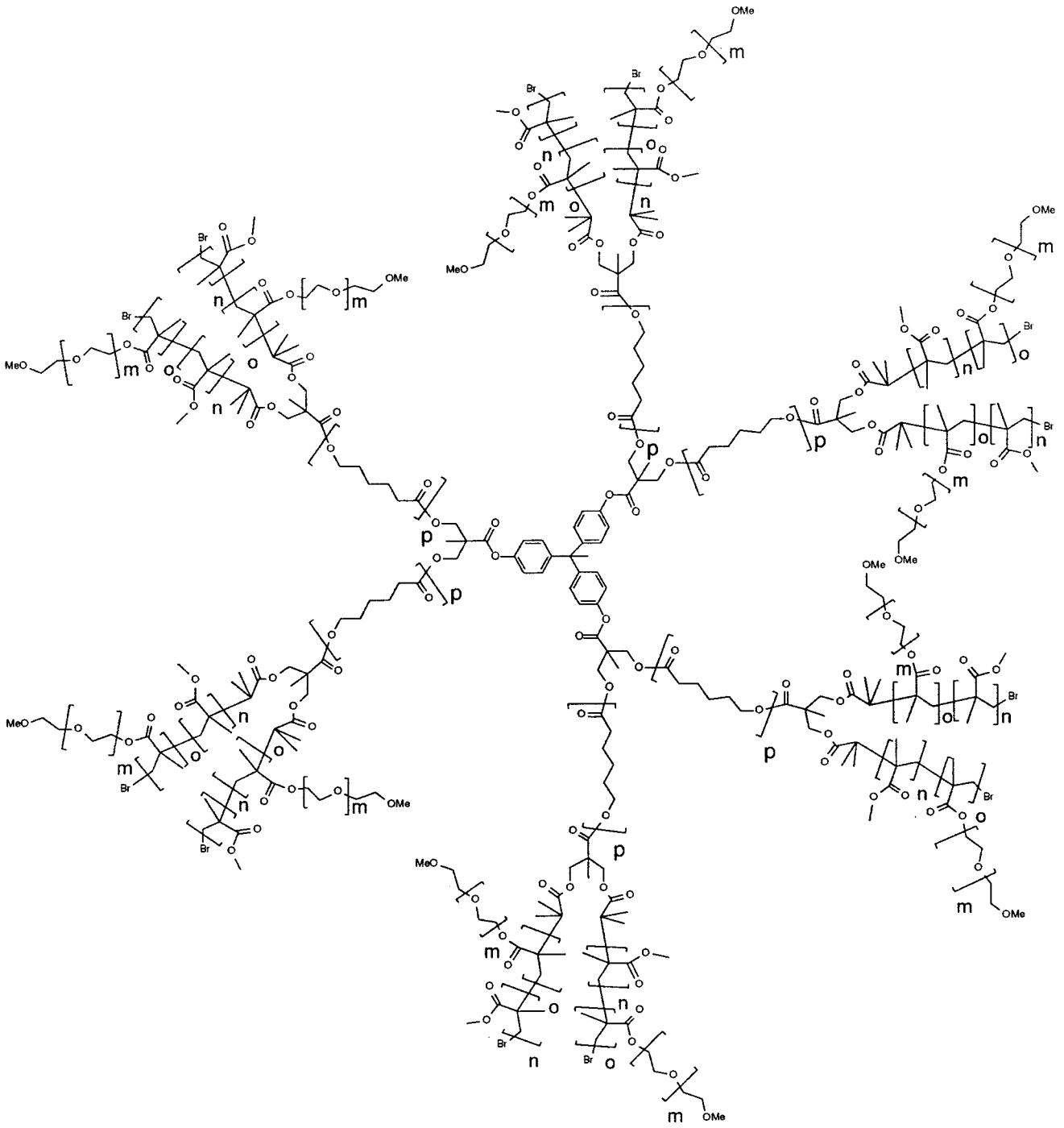


Table 2. Characteristics of Caprolactone−Methyl Methacrylate Dendrimer-like Star Block Copolymers

sample entry	"macro- initiator"	polym conditions	stoichiometric concentration of catal	targeted PMMA DP	$\langle M_n \rangle$ (SEC)	$\langle M_w \rangle / \langle M_n \rangle$
G-2(6-Br)a-1	**G-1.5(6-Br)a**	bulk	1.0	60	37 000	1.13
G-2(6-Br)a-2	**G-1.5(6-Br)a**	THF	1.0	60	34 000	1.18
G-2(6-Br)a-3	**G-1.5(6-Br)a**	toluene	1.0	60	36 000	1.18
G-2(6-Br)a-4	**G-1.5(6-Br)a**	bulk	1.0	130	51 000	1.16
G-2(6-Br)a-5	**G-1.5(6-Br)a**	bulk	0.4	130	50 000	1.11
G-2(6-Br)a-6	**G-1.5(6-Br)a**	bulk	0.2	130	66 000	1.17
G-2(6-Br)b-1	**G-1.5(6-Br)b**	bulk	0.5	200	247 000	1.14
G-2(12-Br)a-1	**G-1.5(12-Br)a**	bulk	0.2	100	70 000	1.19
G-2(12-Br)a-2	**G-1.5(12-Br)a**	THF	0.2	100	76 000	1.11
G-2(12-Br)a-3	**G-1.5(12-Br)a**	toluene	0.2	125	96 000	1.09
G-2(24-Br)a-1	**G-1.5(24-Br)a**	toluene	0.2	130	220 000	1.14

in these cases, the SEC traces were symmetrical and monomodal with no evidence of higher molecular weight product. It should be acknowledged, however, that the concentration of the coupled product, if occurring, would

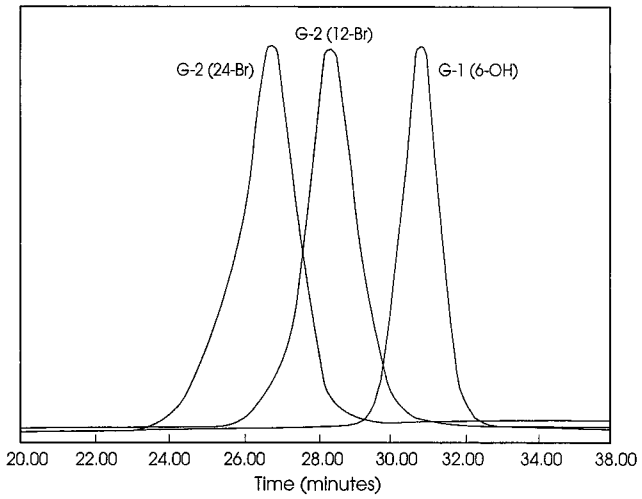


Figure 5. SEC traces of **G-1(6-OH)a**, **G-2(12-Br)a**, and **G-2(24-Br)a**.

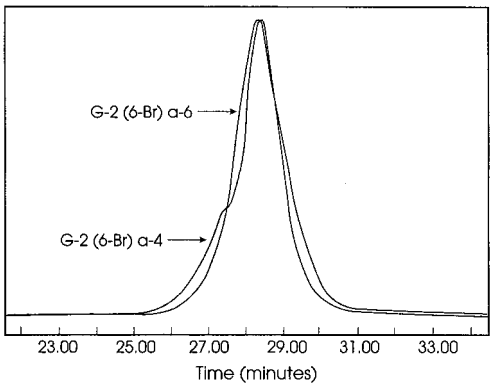


Figure 6. SEC traces of dendrimer-like star polymers prepared with different catalyst concentrations.

be low and may not be detectable by SEC after cleavage.

Of particular interest in the dendrimer-like star polymers is whether the introduction of branching significantly affects the morphology of the copolymers. The two critical issues that will be addressed include the ability of the poly(ϵ-caprolactone) central block to crystallize and the occurrence of phase separation between the poly(ϵ-caprolactone) and poly(methyl methacylate) based coblocks. The dendrimer-like star polymers containing low molecular weight poly(ϵ-caprolactone) blocks showed a single phase morphology, as evidenced by a single T_g for the copolymers irrespective of the number of arms. The T_g was reduced when compared to PMMA (80 °C) and appears to follow the Fox equation for a random or phase mixed copolymer. Conversely, the copolymers containing higher molecular weight poly(ϵ-caprolactone) showed the expected two phase structure, as evidenced by detection of two T_g's (−55 and 100 °C for the poly(caprolactone) and poly(methyl methacrylate, respectively). For these samples, some crystallization of the ϵ-caprolactone block was observed. The star block polymers derived from poly(ϵ-caprolactone) as the central block with an outer block derived from MMA and HEMA also showed a two-phase structure, as evidenced by two T_g's (Table 3), as well as a melting endotherm associated with the poly(ϵ-caprolactone) phase at 40 °C. A typical dynamic mechanical analysis plot is shown in Figure 9, where the two T_g's are clearly observed. The T_g's are sharp and are identical to the analogous homopolymers, a characteristic of high phase purity. Conversely, the dendrimer-like star polymers, e.g., the branched copolymers, showed only a single transition and appears to follow the Fox equation for a random copolymer. As the number of arms increases, the constraints on the system increase, preventing crystallization and microphase separation. Conversely, most of the star and dendrimer-like star polymers derived from a MMA/EO outer block show two T_g's. One transition is at ∼−60 °C, characteristic of the ϵ-caprolactone phase, and the second occurs between 60 and 80 °C, which is presumably due to the random copolymer of MMA and EO which comprises the outer layer. Films of the layered dendrimer-like star polymers were cast from toluene and heated to 125 °C (2 h) to remove solvent. The films were transparent, consistent with the absence of homopolymer contamination. Moreover, the films were tough and ductile, unlike traditional dendrimers.

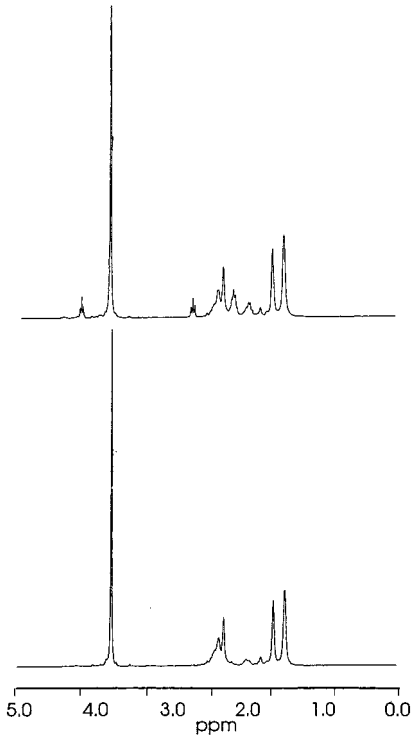


Figure 7. ^{1}H NMR of **G-2(12-Br)a-1** (top) and hydrolyzed product (bottom).

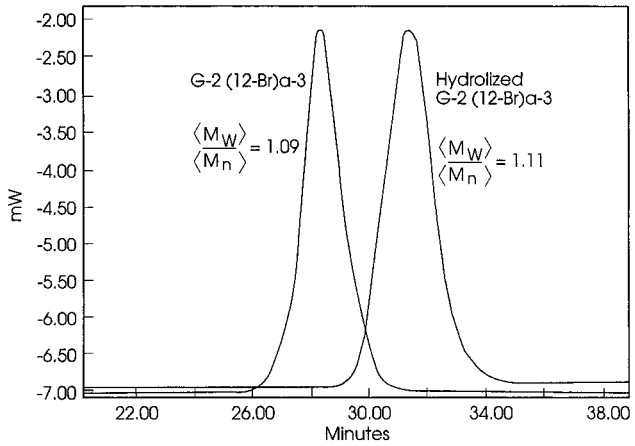


Figure 8. SEC traces of **G-2(12-Br)a-3** and hydrolyzed **G-2(12-Br)a-3**.

Table 3. Characteristics of Amphiphilic Dendrimer-like Star Block Copolymers

sample entry	"macro- initiator"	polym condition	MMA + comonomer (type & wt %)	2nd generation target DP	$\langle M_n \rangle$ (SEC)	$\langle M_w \rangle / \langle M_n \rangle$	thermal analysis: first generation T_g °C	first generation Tm °C	second generation T_g, °C
G-2(6-Br)a-7	**G-1.5(6-Br)a**	bulk	HEMA (10%)	120	60 000	1.45	−65	40	100
G-2(6-Br)a-8	**G-1.5(6-Br)a**	bulk	HEMA (20%)	120	59 000	1.5		41	90
G-2(6-Br)a-9	**G-1.5(6-Br)a**	THF	HEMA (27%)	120	71 000	1.19			
G-2(12-Br)	**G-1.5(12-Br)a**	bulk	HEMA (10%)	120	96 000	1.17			90
G-2(12-Br)a-4	**G-1.5(12-Br)a**	THF	HEMA (20%)	120	92 000	1.18			90
G-2(12-Br)a-5	**G-1.5(12-Br)a**	THF	HEMA (75%)	110	82 000	1.1			
G-2(24-Br)a-2	**G-1.5(24-Br)a**	bulk	HEMA (25%)	110	76 000	1.19			92
G-2(6-Br)a-10	**G-1.5(6-Br)a**	bulk	EO-400 (10%)	113	78 000	1.31			
G-2(6-Br)a-11	**G-1.5(6-Br)a**	toluene	EO-400 (20%)	113	85 000	1.22			
G-2(6-Br)a-12	**G-1.5(6-Br)a**	toluene	EO-400 (30%)	103	75 000	1.34	−65	49	60−80
G-2(12-Br)a-6	**G-1.5(12-Br)a**	toluene	EO-400 (25%)	105	120 000	1.2			45
G-2(6-Br)a-13	**G-1.5(6-Br)a**	bulk	EO-1000 (10%)	100	70 000	1.24			80
G-2(6-Br)a-14	**G-1.5(6-Br)a**	toluene	EO-1000 (30%)	100	60 000	1.17	−55	30	70 (broad)
G-2(12-Br)a-7	**G-1.5(12-Br)a**	toluene	EO-1000 (30%)	105	116 000	1.09	−60	45	60
G-2(12-Br)a-8	**G-1.5(12-Br)a**	toluene	EO-1000 (66%)	105	84 000	1.2	−60		

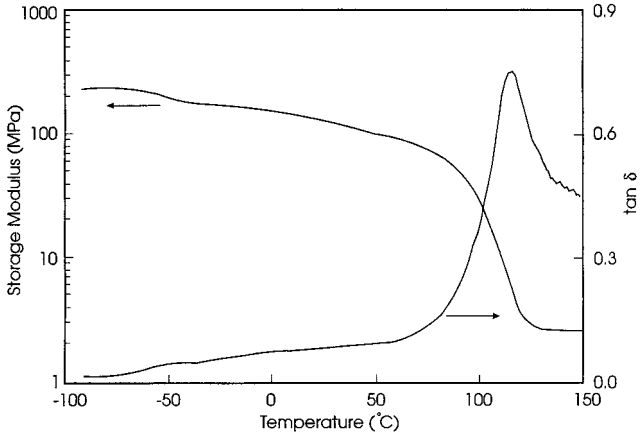


Figure 9. Dynamic mechanical spectra of **G-2(6-Br)a-7**.

One of the key interests in the preparation of the dendrimer-like star polymers containing either HEMA or EO in the outer block is to form structures with amphiphilic character. In particular, the objective is to form unimolecular micelles with the poly(caprolactone) layer existing as a densely packed core surrounded by the HEMA- or EO-based second generation layers, analogous to the dendritic unimolecular micelles reported by Fréchet et al.[6f−g] The ultimate motivation for the preparation of these stimuli-responsive hybrid macromolecules is to template nanostructure in organosilicates, analogous to work from Stucky and others.[4] Since each of the components in the block copolymer were designed to be thermally unstable, subsequent heat treatments of the organosilicate should produce nanoporosity. Preliminary investigations on the materials by ^{1}H NMR showed that the macromolecules responded to changes in the polarity of the solvent used to dissolve them. Figure 10 shows the ^{1}H NMR spectra of **G-2(12-Br)a-5** in $CD_3OH/CDCl_3$ (50/50 vol %) mixture, which solvates each of the blocks, and a CD_3OD/D_2O (50/50 vol %) mixture, which solvates only the outer, hydrophilic layer. In the first spectra (Figure 10, top), each of the layers or blocks are clearly detectable at their expected compositions. Conversely, the signals of the protons for the poly(caprolactone) layer were significantly diminished when the selective solvent system was used. However, the shifts in the peaks are not as clear as those reported by Fréchet et al.,[6] due to peak overlap, nor could the reverse core−shell structure

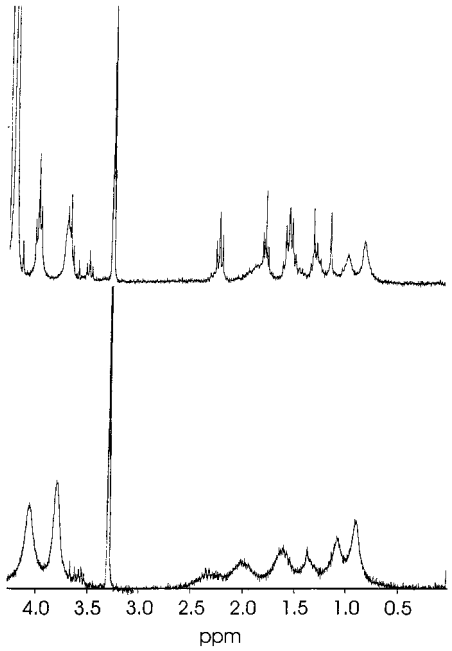


Figure 10. ^{1}H NMR spectra of **G-2(12-Br)a-5** in (top) $CDCl_3/CD_3OD$ (50/50) and (bottom) CD_3OD/D_2O (50/50).

be generated. Nonetheless, this experimental observation is in qualitative agreement with the formation of micelles.

Summary

We have demonstrated that it is possible to combine various living polymerization techniques with traditional dendrimer synthesis to prepare block copolymers with complex molecular architectures. These block copolymers are characterized by a radial geometry where the different layers or generations are comprised of high molecular weight polymer emanating from a central core. A hexahydroxy-functional 2,2-bis(hydroxymethyl) propionic acid derivative was used as the "initiator" for the ROP of poly(ϵ-caprolactone) in the presence of $Sn(Oct)_2$. Poly(ϵ-caprolactone) with a six-arm star molecular architecture were formed, and accurate control of molecular weight and narrow polydispersities were demonstrated (PD < 1.11). Capping the chain ends with activated bromo functional dendrons produced six arm star polymers with either six, 12 or 24 bromide end groups. These macromolecules served as "macro-initiators" for the "living" polymeri-

zation of methyl methacrylate and related monomers via ATRP to form the dendritic-like star block polymers. High molecular weight was achieved with surprisingly low polydispersities (<1.20). Hydrolytic cleavage of the dendrimer-like star polymers released the poly(methyl methacrylate)-based tethered arms which were found to be close to the target molecular weight and manifested extremely narrow polydispersities (PD ~ 1.10). Unlike traditional dendrimer synthesis where the molecular weight buildup is slow and tedious, the use of monodispersed macromolecular building blocks allows a rapid increase in molecular weight in just a few generations. A key advantage to the use of macromolecular building blocks is the simple purification required between transformations. Considerable versatility in the morphology and subsequent properties of these novel block polymers is realized by variation of monomer type and block lengths. For instance, the hydrophilicity of either the "inner" or "outer" block can be designed in such a way as to prepare unimolecular micelles for applications as "nano-reactors" or as templates for nanopore generation in organosilicates.

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