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Copper(I) Bromide/*N*-(*n*-Octyl)-2-pyridylmethanimine−Mediated Living-Radical Polymerization of Methyl Methacrylate Using Carbosilane Dendritic Initiators

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ABSTRACT: The zeroth ($Si\{(CH_2)_3SiMe_2(C_6H_4CH_2OC(O)CMe_2Br)\}_4$), **2**, and first ($Si\{(CH_2)_3Si((CH_2)_3$-$SiMe_2(C_6H_4CH_2OC(O)CMe_2Br))_3\}_4$), **3**, generation of 2-bromoisobutyryl functionalized carbosilane dendrimers have been successfully applied as initiators for the copper(I) bromide/*N*-(*n*-octyl)-2-pyridylmethanimine-mediated living-radical polymerization of methyl methacrylate. The overall rate of polymerization are comparable for the two dendritic initiators studied, **2** (3.4×10^{-5} mol L^{-1} s^{-1}) and **3** (4.8×10^{-5} mol L^{-1} s^{-1}) with the benzylic model compound $C_6H_5CH_2OC(O)CMe_2Br$ (**1**) showing a lower rate of polymerization for both dendritic initiators, (7.3×10^{-5} mol L^{-1} s^{-1}) where [initiator sites] = 1.87×10^{-2} mol L^{-1}. We postulate that this is caused by initial intramolecular termination. The molecular weight distribution is less than 1.3 after 3 h reaction time. Initiator **3**, however, produces star−star coupling throughout the polymerization. When the dendritic periphery is partialy functionalized (statistically two and six arms of the first generation dendrimer, respectively, **4** and **5**) the control of the molecular weight distribution was lost (PDI > 3) for **4** as a result of too low of a value for [initiator site], i.e., 3.12×10^{-3} mol L^{-1}.

Introduction

Living-radical polymerization of vinyl monomers giving polymers predictable average molecular weights (e.g. M_n), narrow polydispersity indices (PDI), and controlled geometries/topology is of continuing interest.[1] Although many polymerization systems have been proposed, including nitroxide-mediated living-radical polymerization[2] and reversible addition−fragmentation (RAFT),[3] metal-mediated living-radical polymerization is currently the most widely used technique to prepare well-defined polymers from a variety of monomers including styrenes, acrylates, methacrylates and acrylonitrile.[1] This type of transition metal-mediated living polymerization was pioneered by Sawamoto[4] and Matyjaszewski[5] utilizing $[Ru_2Cl_2(PPh_3)_2]$ and [CuX(bipy)] catalysts, respectively, in conjunction with appropriate initiators.

We have developed catalysts based on Cu^IX and *N*-alkyl-2-pyridylmethanimine Schiff base ligands for the living-radical polymerization of methacrylates.[6] Schiff base ligands are attractive in that they are easy to synthesize with a variety of catalyst properties available, e.g., varying solubility as a function of the alkyl substituent chain-length.

Dendrimers[7] are well-defined polymers with precise molecular composition and topology. Some exciting potential applications are being developed in areas such as micelle mimicry,[8] catalysis,[9] and supported synthesis.[10] Roovers et al.[11] and others[12] resently prepared regular dendritic star polymers from carbosilane dendrimers using poly(butadienyl)lithium as a coupling reagent. The resulting polymeric stars are good models for polymeric micelles.

Combining dendrimer synthesis and living-radical polymerization may yield novel polymeric materials with controlled topology. For example, Fréchet et al.[13] used convergent polyether dendrons possessing benzylic halides at their focal point as initiators for metal mediated living-radical polymerization to produce hybrid dendritic-linear block copolymers. Hedrick et al.[14] prepared dendrimer-like star block and amphiphilic copolymers by combination of ring-opening polymerization of ϵ-caprolactone and living-radical polymerization of methacrylates.

Herein, carbosilane dendrimers (zeroth and first generation) which have been fully or partially functionalized with a tertiary-alkyl bromide species are investigated as initiators for the Cu^IBr/*N*-(*n*-octyl)-2-pyridylmethanimine-mediated living-radical polymerization of MMA. Evolution of the molecular weight distribution throughout the polymerization as well as the overall rate of polymerization was investigated.

Results and Discussion

The esterification of carbosilane dendritic polyols with 2-bromoisobutyryl bromide proceeds at ambient temperature in the presence of triethylamine as base; see Scheme 1. This is a versatile route that proceeds in quantitative yield to synthesize dendritic initiators for living-radical polymerization.[15]

The reaction of both $G_0-SiMe_2C_6H_4CH_2OH$ and $G_1-SiMe_2C_6H_4CH_2OH$ with 2-bromoisobutyroyl bromide in the presence of pyridine afforded the corresponding initiators $G_0-CH_2OC(O)CMe_2Br$, **2**, and $G_1-CH_2OC(O)$-CMe_2Br, **3.** Quantitative reaction of both **2** and **3** is confirmed by ^1H NMR by a shift of the benzylic resonances to lower field (from ca. 4.6 to 5.2 ppm) and the appearance of methyl resonances, 1.9 ppm, in the

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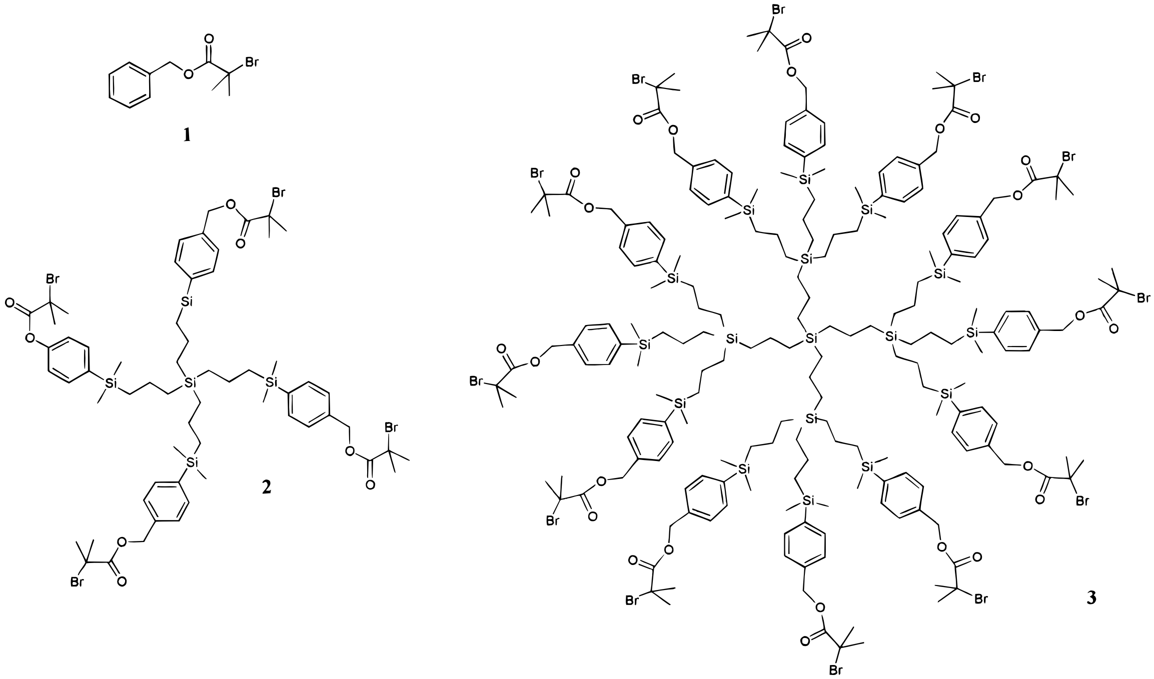
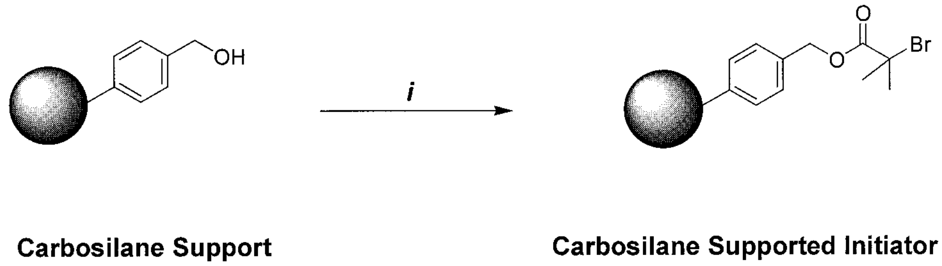
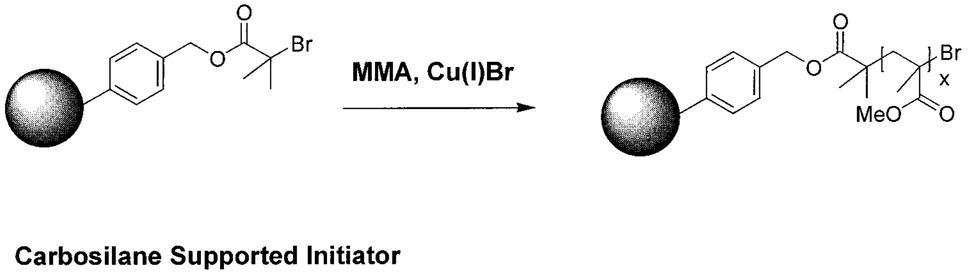


Figure 1. Synthesis of MMA star polymers from a derivatized G_1 carbosilane dendrimer.

Scheme 1. Reagents and Conditions: (i) $BrC(O)CMe_2Br$, Pyridine, THF, room temperature



Scheme 2. Schematic Representation of Dendritic Initiator 3



expected ratios. The characteristic $C{=}O$ and $C{-}Br$ resonances appear at 171.6 and 55.9 ppm in the ^{13}C NMR spectra, respectively. The MALDI−TOF−MS spectrum of initiator **3** (see Figure 1 for a schematic structure) shows signals at *m*/*z* 4592.6 corresponding to $[G_1{-}CH_2OC(O)CMe_2Br + Na]^+$ (calcd 4591.9) (see Supporting Information).[16]

Atom transfer polymerization reactions of MMA in xylene (20% v/v) using *N*-octyl-2-pyridylmethanimine (NN′) as a bidentate ligand in conjunction with Cu^IBr and either **1**, **2**, or **3** as initiator (see Scheme 2), were carried out at 90 °C. A different series of living-radical polymerization reactions were also carried out using partly functionalized generation one dendrimer with two and six initiator groups at the periphery (G_1−(two initiators)), **4**, and (G_1−(six initiators)), **5**.[17] This is achieved by the addition of a very dilute solution of 2-bromoisobutyroyl bromide in THF to G_1 polyol. MALDI−TOF−MS of **4** showed a signal at *m*/*z* 3115.1 (see supplementary information) assigned to $[G_1{-}(CH_2OH)_{10}(CH_2OC(O)CMe_2Br)_2 + Na]^+$ (calculated 3118.2). MALDI−TOF−MS of **5** showed a broad signal between *m*/*z* 3700−4100 corresponding to a dendritic species with between five and seven initiator groups at the periphery. The ^1H NMR spectra confirmed the average amount of initiator groups at the periphery of the carbosilane dendritic species.

The monomer conversion and the cumulative MWD of the polymer product were analyzed every 30 min. In Figure 2, $\langle M_n \rangle$ vs conversion of polymerizations using **1**, **2**, and **3** are shown. Table 1 reports the concentration of **1**, **2**, and **3** and the actual concentration of initiating sites as well as the $\langle M_n \rangle$ and PDI values of the final polymeric product after 3 h reaction time.

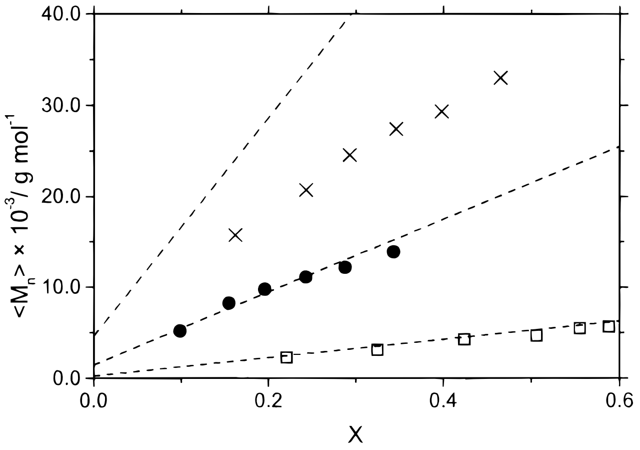


Figure 2. $\langle M_n \rangle$ vs conversion of the polymerization of MMA with initiators **1** (□), **2** (●), and **3** (×) at [initiator sites] = 1.87×10^{-2} mol L^{-1}.

Table 1. Polymerization of MMA with Functional Initiators[a]

initiator	[dendrimer], mol L^{-1}	[initiator sites], mol L^{-1}	$\langle M_n \rangle$	PDI[b]
1	1.87×10^{-2}	1.87×10^{-2}	5700	1.17
2	4.69×10^{-3}	1.87×10^{-2}	13900	1.18
3	1.56×10^{-3}	1.87×10^{-2}	33000	1.29

[a] Reaction time 3 h. [b] Determined using GPC with linear poly(MMA) standards.

Table 1 demonstrates that living-radical polymerization reactions were successful, which produced reasonably narrow MWDs. Polymerization was carried out under identical conditions with **1**, a nondendritic initiator, as a control reaction for comparison purposes. This model compound produced a linear polymer and thus accurate values for the molecular weights were obtained by GPC. As can be seen in Figure 2 the experimental and theoretical values of $\langle M_n \rangle$ correspond well. The same is true for the G_0 dendritic initiator **2**, which produces a four-armed star polymer. As the number of branching points is only one the difference in hydrodynamic volume, compared to that of a free random linear polymer coil, seems small and hence the apparent molecular weights determined with GPC are a good estimate. An alternative explanation might be that only two sites initiate the production of the linear polymer. However, this explanation is not favored, since in all previous related work all initiator sites in multifunctional initiators have been found to be active, so we have no reason to suspect the current initiators to differ.

Conventional GPC analysis of the generation one dendritic initiator, **3**, yields incorrect values for the molecular weight. The presence of five branching points in the dendritic structure (see Figure 1) restricts its conformational freedom and lowers its hydrodynamic volume, which results in lower GPC determined molecular weights (Figure 2).

A closer look at the entire MWD development throughout the atom transfer polymerization reaction for initiator **3** reveals that higher molecular weight species are formed continuously during reaction (Figure 3). This is ascribed to termination via combination of two growing polymer chains from different dendritic molecules (a conventional free radical polymerization of MMA shows ca. 30% termination via combination under these conditions).[18]

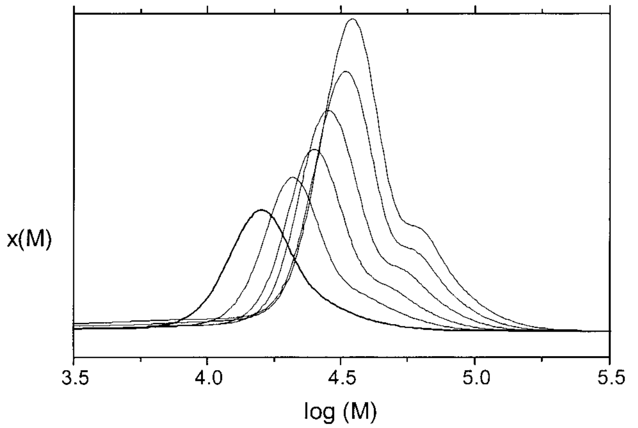


Figure 3. $x(M)$ vs. $\log(M)$ of the polymerization of MMA using dendritic initiator **3** at different stages of monomer conversion, i.e., 16.2, 24.3, 29.3, 34.6, 39.8, and 46.5%, respectively from left to right.

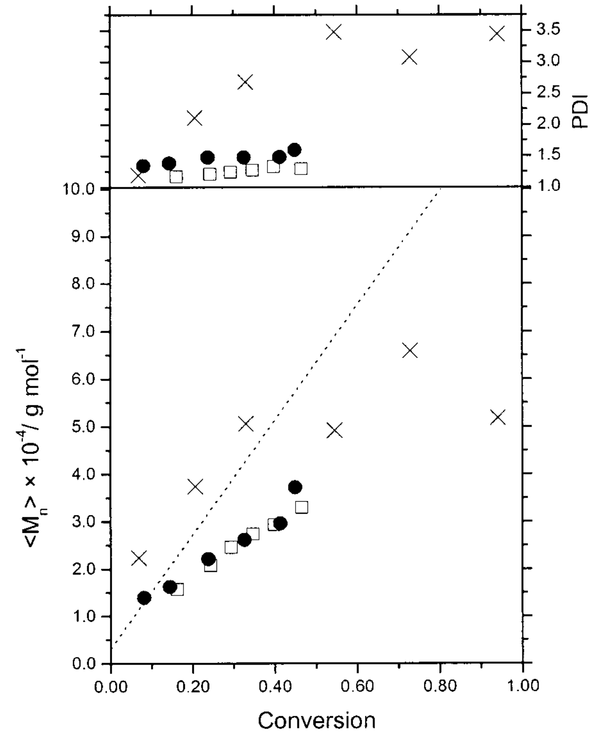


Figure 4. $\langle M_n \rangle$ and PDI vs conversion of the polymerization reactions using dendritic initiators of generation one with two initiating sites **4** (×), six initiating sites **4** (●), and 12 initiating sites **3** (□), at [dendrimer] = 1.56×10^{-3} mol L^{-1}.

The second polymerization series comprised the use of partly functionalized dendritic species of generation one. Hereby, initiators with two and six initiating groups at the periphery of a first generation dendrimer, **4**, and **5**, were used. In these experiments, the concentration of the dendritic initiator was kept constant with the concentration of actual initiator sites increased from 3.12×10^{-3} to 9.37×10^{-3} and finally 1.87×10^{-2} mol L^{-1}. The theoretical M_n at low conversion, 6.9% for the two-arm star initiator is ca. 5.2×10^3 as compared to the measured value of 22.4×10^3 (PDI = 1.19). At increasing conversion complete loss of control of the molecular weight distribution was observed with an increase in PDI to values above 3. This is attributed to too low a concentration of initiator, Figure 4 where M_n vs conversion shows nonlinear behavior. In contrast both the six- (**5**) and 12-arm (**3**) initiators produced

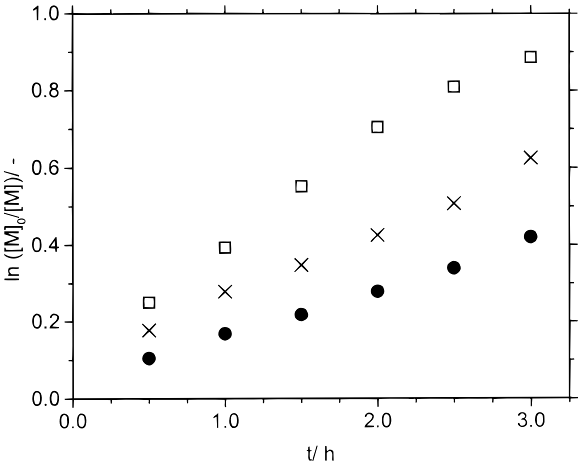


Figure 5. ln([M]$_0$/[M]) vs time of the polymerization reactions using initiators **1** (□), **2** (●), and **3** (×) at [initiator sites] = 1.87×10^{-2} mol L^{-1}.

dendritic molecules of similar molecular weight (Figure 4). The PDI for the polymerization with the six-arm initiator showed values between 1.3 and 1.6 whereas the values for the 12-armed initiator were all below 1.3.

The overall rate of polymerization was studied with [MMA]:[Cu^{I}Br]:[ligand]:[initiator sites] constant, (100:1:2:1). Thus, the [dendrimer] decreases in the polymerization systems using compounds **1**, **2**, and **3** with factors of 1, 4, and 12, respectively. The assumption that the reversible activation process is in equilibrium entails that the number of active propagating species can be calculated from

$$[\mathrm{R}] = \frac{\mathrm{k}_{\mathrm{act}}[\mathrm{Cu(I)}][\mathrm{I}]}{\mathrm{k}_{\mathrm{deact}}[\mathrm{Cu(II)}]}$$

wherein [R/g L^{-1}], [I/g L^{-1}], [Cu(I)/g L^{-1}], and [Cu(II)/g L^{-1}] are the concentration of activated propagating sites, dormant sites, copper(I) bromide species, and copper(II) bromide species and k_{act}/L mol^{-1} s^{-1} and k_{deact}/L mol^{-1} s^{-1} are the rate coefficients for the reversible activation and deactivation processes, respectively. From the above equation, it would seem that a constant concentration of initiator sites would yield identical initial overall rates of polymerization (i.e. $R_{\mathrm{p}} = k_{\mathrm{p}}[\mathrm{M}][\mathrm{R}]$; $t = 0$ s). First-order behavior in monomer concentration is observed (Figure 5). However, the dendritic structure of initiators **2** and **3** create a nonrandom distribution of C−Br chain ends at low conversion. This leads to a higher probability of permanent bimolecular termination, a process which is diffusion-controlled, relative to chain-deactivation by the Cu(II) complex, the latter of which is randomly distributed over the system. Ultimately, a higher concentration of Cu(II) species is generated during the initial stages of polymerization, leading to a reduction of the overall rate of polymerization according to eq 1. This effect is seen in Figure 5 where a first-order fit gives rates of polymerization of 7.3×10^{-5}, 3.4×10^{-5}, and 4.8×10^{-5} mol L^{-1} s^{-1} for initiators **1**, **2**, and **3**, respectively ([initiator sites] = 1.87×10^{-2} mol L^{-1}).The present investigation illustrates the difference between the model compound with random distribution of the initiator sites and the dendritic species inducing a nonrandom distribution. Comments on the exact amount of both intra- and intermolecular bimolecular termination will not be given, since a more detailed kinetic investigation is required and is the subject of our further studies.

Concluding Remarks

We have successfully applied functionalized carbosilane dendrimers as initiators in copper(I) mediated living-radical polymerization. The star polymers thus formed have M_{n} close to those predicted by the amount of consumed monomer with related narrow molecular weight distributions (PDI < 1.3). The overall rate of the polymerizations was lower when dendritic initiators were applied most likely as a result of initial intramolecular termination.

Experimental Section

General Data. All reactions were carried out using standard Schlenk techniques under an inert atmosphere of dry, oxygen-free nitrogen unless otherwise stated. Et_2O and THF were carefully dried and distilled from Na/benzophenone prior to use. Methyl methacrylate was passed over a short column of activated basic alumina to remove its inhibitor before use. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller and Wycoff.[17] All other standard chemicals were purchased from ACROS Chimica or Aldrich Chemical Co. and used without further purification. *N*-Octyl-2-pyridylmethanimine was prepared according to a literature procedure.[19] The functionalized carbosilane dendrimers were prepared according to literature procedures. Molecular weight distributions were measured using gel permeation chromatography (GPC), on a system equipped with a guard column and two mixed C columns (Polymer Laboratories) with differential refractive index detection using tetrahydrofuran at 1.0 mL min^{-1} as an eluent. Poly(MMA) standards in the range 1×10^6 to 200 g mol^{-1} were used to calibrate the GPC. ^{1}H and ^{13}C spectra were recorded on a Bruker AC 200 and AC 300 spectrometers in chloroform-*d* at ambient temperatures. Chemical shifts (δ) are given in ppm relative to $SiMe_4$ as an external standard, and the coupling constants are presented in hertz (Hz). Mass spectra obtained under electron ionization (EI) conditions (70 eV), were recorded by linear scanning from m/z 50−500. MALDI−TOF−MS spectra were acquired using a Voyager-DE BioSpectrometry workstation (PerSeptive Biosystems Inc., Framingham, MA) mass spectrometer equipped with a nitrogen laser emitting at 337 nm. The instrument was operated in the linear mode at an accelerating voltage in the range 23000−25000 V. External calibration was performed using insulin (bovine) and detection was done by means of a linear detector and a digitizing oscilloscope operating at 500 MHz. Sample solutions with (~30 mg/mL) in THF were used, and the matrix was 3,5-dihydroxybenzoic acid in THF (36 mg/mL). A solution of sodium acetate in THF was added to the sample in order to improve the peak resolution. The sample solution (0.2 μL) and the matrix solution (0.2 μL) were combined and placed on a gold MALDI target and analyzed after evaporation of the solvents. Elemental microanalysis were obtained from Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

Synthesis of Initiators, $PhCH_2OC(O)CMe_2Br$ (1). A solution of 2-bromoisobutyryl bromide (6.39 g, 27.8 mmol) in THF (20 mL) was added dropwise to a solution of benzyl alcohol (2.00 g, 18.5 mmol) and pyridine (1.58, 20 mmol) in THF (50 mL). After being stirred overnight at room temperature, the reaction mixture was poured onto aqueous HCl (50 mL, 4 M). The aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were extracted with aqueous solution of NaOH (3 × 50 mL, 1 M). The organic layer was dried with Na_2SO_4, and the solvent was removed in vacuo. The product was purified by column chromatography on basic alumina and isolated as a colorless oil in 61% yield (2.91 g, 11.3 mmol). Anal. calcd for $C_{11}H_{13}BrO_2$ (257): C, 51.38; H, 5.10. Found: C, 51.41; H, 5.12. ^{1}H NMR ($CDCl_3$): δ 7.39 (m, 5 H, Ph(*H*)), 5.23 (s, 2 H, PhC*H*$_2$O), 1.98 (s, 6 H, C*Me*$_2$). ^{13}C{^{1}H}

NMR ($\mathrm{CDCl_3}$): δ 171.6 (C(O)), 135.7 (1 C, Ar, $C{-}\mathrm{CH_2}$), 128.8, 128.6, 128.1 (5 C, ArC), 67.8 (Ar$C\mathrm{H_2}$), 56.0 ($C\mathrm{Me_2}$), 31.1 (CMe_2). GC−MS (rel intensity): *m*/*z* 257 ($\mathrm{M^+}$, 5); 177 ($\mathrm{M^+} - \mathrm{Br}$, 50); 91 ($\mathrm{C_7H_7^+}$, 100).

$\mathbf{G_0\text{-}CH_2OC(O)CMe_2Br,\ Si\{(CH_2)_3SiMe_2(C_6H_4\text{-}4)CH_2OC\text{-}(O)\text{-}Me_2Br\}_4}$ (2). The synthetic procedure is identical to that described for **1**, starting from $\mathrm{G_0{-}SiMe_2C_6H_4CH_2OH}$ (1.27 g, 1.48 mmol), pyridine (0.79 g, 10.0 mmol), and 2-bromoisobutyryl bromide (2.04 g, 8.88 mmol) in THF (25 mL). The product was purified by column chromatography on basic alumina and isolated as viscous slightly yellow oil in 59% yield (1.27 g, 0.78 mmol). Anal. Calcd for $\mathrm{C_{64}H_{96}Br_4O_8Si_5}$ (1453.5): C, 52.89; H, 6.66; Si, 9.66. Found: C, 53.10; H, 6.74; Si, 9.58. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.51 (d, $J = 8.1$, 8 H, ArH), 7.36 (d, 8 H, $J = 7.8$, ArH), 5.21 (s, 8 H, ArCH_2O), 1.97 (s, 24 H, C(CH_2)$_2$), 1.29 (m, 8 H, SiCH$_2$CH_2), 0.79 (t, $J = 8.4$, 8 H, CH_2SiAr), 0.58 (t, $J = 8.1$, 8 H, CH_2SiCH_2), 0.22 (s, 24 H, Si(CH_3)$_2$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 171.7 (C(O)), 140.2 (4 C, Ar, C−Si), 136.1 (4 C, Ar, C−CH$_2$), 134.0 (8 C, ArC), 127.2 (8 C, ArC), 67.8 (ArCH$_2$), 55.9 (CMe$_2$), 31.1 (CMe_2), 20.8 (4 C, CH$_2$SiAr), 18.8 (4 C, SiCH$_2$$CH_2$), 17.7 (4 C, CH$_2$SiCH$_2$), −2.6 (SiMe_2). MALDI−TOF−MS: 1472.2 $(\mathrm{M + Na})^+$ (calculated 1471.3 $(\mathrm{M + Na})^+$).

$\mathbf{G_1{-}CH_2OC(O)CMe_2Br,\ Si\{(CH_2)_3Si((CH_2)SiMe_2(C_6H_4\text{-}4)CH_2O{-}C(O)Me_2Br)_3\}_4}$ (3). The synthetic procedure is identical to that described for **1**, starting from $\mathrm{G_1{-}SiMe_2C_6H_4\text{-}CH_2OH}$ (0.21 g, 0.075 mmol), pyridine (0.11 mL, 1.35 mmol), and 2-bromoisobutyryl bromide (0.23 g, 1.0 mmol) in THF (25 mL). The product was purified by column chromatography on basic alumina and isolated as a viscous slightly yellow oil in 68% yield (0.23 g, 0.051 mmol). Anal. Calcd for $\mathrm{C_{204}H_{312}Br_{12}O_{24}\text{-}Si_{17}}$ (4585.0): C, 53.44; H, 6.86; Si, 10.41. Found: C, 53.60; H, 6.94; Si, 10.33. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.48 (d, $J = 7.8$, 24 H, ArH), 7.34 (d, 24 H, $J = 7.2$, ArH), 5.18 (s, 24 H, ArCH_2O), 1.95 (s, 72 H, C(CH_2)$_2$), 1.23 (m, 32 H, CH$_2$SiCH$_2$CH_2 CH$_2$-SiCH$_2$ and CH_2CH$_2$SiAr), 0.81 (t, $J = 8.4$, 24 H, CH_2SiAr), 0.58 (m, 40 H, CH_2SiCH_2), 0.22 (s, 72 H, Si(CH_3)$_2$). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 171.6 (C(O)), 140.1 (12 C, Ar, C-Si), 136.1 (12 C, Ar, C-CH$_2$), 134.0 (24 C, ArC), 127.2 (24 C, ArC), 67.7 (ArCH$_2$); 55.9 (CMe$_2$), 31.0 (CMe_2); 20.8 (12 C, CH$_2$SiAr), 18.9 (16 C, two signals overlapping, CH$_2$CH$_2$SiAr and CH$_2$SiCH$_2$$CH_2CH_2$-SiCH$_2$), 18.5 (4 C, CH$_2$SiCH$_2CH_2$$CH_2$SiCH$_2$), 18.1 (4 C, CH$_2$-Si$CH_2CH_2CH_2$SiCH$_2$), 17.7 (12 C, CH$_2SiCH_2CH_2CH_2$SiAr), −2.5 (Si$Me_2$). MALDI−TOF−MS: 4592.5 $(\mathrm{M + Na})^+$ (calculated 4591.9 $(\mathrm{M + Na})^+$).

Typical Polymerization. Methyl methacrylate was polymerized using **3** as initiator (MMA/Cu$^{\mathrm{I}}$Br/*n*-octyl-2-pyridylmethanimine/actual initiator = 100/1/2/1) in 20% xylene solution. Typically initiator **3** (148.5 mg, 3.2×10^{-5} mol) was added to a Schlenk tube under nitrogen containing Cu$^{\mathrm{I}}$Br (55.7 mg, 3.88×10^{-4} mol), *n*-octyl-2-pyridylmethanimine (169.7 mg, 7.78×10^{-4} mol), deoxygenated inhibitor free MMA (4.15 mL), and deoxygenated xylene (16.6 mL). The solution was deoxygenated by three freeze−pump−thawed prior to being heated to 90 °C. Samples were removed periodically for 3 h for gravimetrical and GPC analysis, via syringe. All molecular weight distribution data were recorded on unprecipitated polymer. MMA was also polymerized with **1** and **2** as initiators under similar conditions.

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Supporting Information Available: Tables giving full data sets for polymerization reaction and figures showing selected MALDI−TOF spectra. This material is available free of charge via the Internet at http://acs.pubs.org.

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(16) Note that the use of too high energies in MALDI−TOF−MS for the analysis of polymers/small molecules containing tertiary bromide groups, results in fragmentation of the bromides thereby complicating interpretation. Waterson, C. Ph.D. Thesis; The University of Warwick, 1999.

(17) Partially functionalized $\mathrm{G_1}$ dendrimers (two and six initiators at the periphery of a first generation dendrimer, respectively ($\mathrm{G_1}$-(2 initiators)), **4**, and ($\mathrm{G_1}$-(6 initiators)), **5**, were prepared according to the same procedure as described for the preparation of compound **3**. The ^{1}H and ^{13}C NMR spectra of compounds **4** and **5** showed the respective resonances at the expected chemical shifts and in the correct ratios. MALDI−TOF−MS of **4**: 3116.5 $(\mathrm{M + Na})^+$ corresponds to $[\mathrm{G_1{-}(CH_2\text{-}OH)_{10}(CH_2OC(O)CMe_2Br)_2 + Na}]^+$ (calculated 3118.2). The MALDI−TOF−MS of **5**: 3700−4100 corresponds to a dendritic species with five to seven initiator groups at the periphery.

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