

Dendritic Initiators for “Living” Radical Polymerizations: A Versatile Approach to the Synthesis of Dendritic-Linear Block Copolymers

Marc R. Leduc,[†] Craig J. Hawker,^{*,‡} Julian Dao,[‡] and Jean M. J. Fréchet^{*,†}

Contribution from Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, New York 14853-1301, and Almaden Research Center, IBM Research Division, 650 Harry Road, San Jose, California 95120-6099

Received June 26, 1996[⊗]

Abstract: The first use of polyether dendrons as macromolecular initiators for the controlled free radical polymerization of vinyl monomers has been demonstrated. Dendrons containing either a single benzylic TEMPO or halide functionality at their focal point have been used for the nitroxide mediated and atom transfer radical polymerizations, respectively. In both cases, hybrid dendritic-linear block copolymers with well-controlled molecular weights and low polydispersities can be obtained. The structure of the hybrid block copolymers is supported by SEC and spectral data. All the copolymers exhibit a single T_g , indicating that both blocks are miscible. Hybrid block copolymers difficult or impossible to prepare by previous techniques have been synthesized to demonstrate the versatility of this approach.

Introduction

Polymers and copolymers with complex, yet well-defined architectures are drawing increasing attention in the search for novel materials with unconventional and/or improved properties.¹ Of these macromolecular structures, hybrid dendritic-linear copolymers, which consist of covalently bound linear and dendritic segments, have been shown to exhibit interesting solution and solid-state properties.² These novel copolymers have previously been prepared by a variety of different synthetic strategies. The first involves coupling of pre-formed linear polymers functionalized at one or both chain-ends with reactive dendrons having a complimentary functionality at their focal point. Examples of this strategy include the block copolymers obtained by the reaction of hydroxy-terminated poly(ethylene glycol) and poly(ethylene oxide) linear fragments with aromatic polyether dendrons having a single bromobenzyl group at their focal point.³ The synthesis of polystyrene–aromatic polyether dendron block copolymers by termination of anionically prepared “living” polystyrene has also been accomplished in a similar fashion.⁴ The main advantage of this fragment coupling method is that the hybrid macromolecule is obtained in a single step from well-defined starting materials. However, the approach is limited to a few systems with suitable coupling chemistries, and problems may arise as a result of both sterically inhibited coupling, and a less than favorable entropy term for the coupling reaction. In addition, this approach generally prohibits the synthesis of hybrids in which highly reactive groups are located at the periphery of the dendrons. An alternative route to dendritic-linear block copolymers has been successfully demonstrated by Meijer,⁵ Chapman,⁶ and their co-workers. In

this approach the dendritic segment is grown via a divergent⁷ strategy from a suitably end-functionalized linear polymer. This process has the advantage of producing hybrids with reactive groups located at the periphery of the dendritic block. However, the presence of the linear block throughout the stepwise divergent synthesis increases somewhat the complexity of the purification procedure.

In a complementary approach that is easily implemented, Fréchet and co-workers⁸ have recently demonstrated that well-defined hybrid dendritic-linear block copolymers can also be obtained using reactive dendrons as macromolecular initiators in the anionic polymerization of ϵ -caprolactone. It was therefore envisaged that this concept of dendritic macroinitiators could be coupled with recent advances in the “living”/controlled free radical polymerization of vinyl monomers^{9–15} to afford a new and general synthetic methodology for the preparation of hybrid dendritic-linear block copolymers. In contrast to living ionic polymerizations and polycondensations, free-radical polymerizations have the advantage of being relatively insensitive to functional groups located either in the initiator¹⁶ or the monomer¹⁷ and are also much less demanding experimentally. Furthermore, the “living” nature of these free radical polymerizations affords both relatively low polydispersities (M_w/M_n) and excellent control over molecular weight.^{9–15} We now report the first use of dendrons as macroinitiators in controlled free-radical polymerizations that lead to a variety of hybrid dendritic-linear block copolymers.

(5) (a) van Hest, J. C. M.; Delnoye, D. A. P.; Baars, M. W. P. L.; van Genderen, M. H. P.; Meijer, E. W. *Science* **1995**, *268*, 1592. (b) van Hest, J. C. M.; Baars, M. W. P. L.; Elissen-Román, C.; van Genderen, M. H. P.; Meijer, E. W. *Macromolecules* **1995**, *28*, 6689.

(6) Chapman, T. M.; Hillyer, G. L.; Mahan, E. J.; Shaffer, K. A. *J. Am. Chem. Soc.* **1994**, *116*, 11195.

(7) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

(8) Gitsov, I.; Ivanova, P. T.; Fréchet, J. M. J. *Macromol. Rapid Commun.* **1994**, *15*, 387.

(9) (a) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185. (b) Hawker, C. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1456. (c) Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763.

[†] Cornell University.

[‡] IBM Research Division.

[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1996.

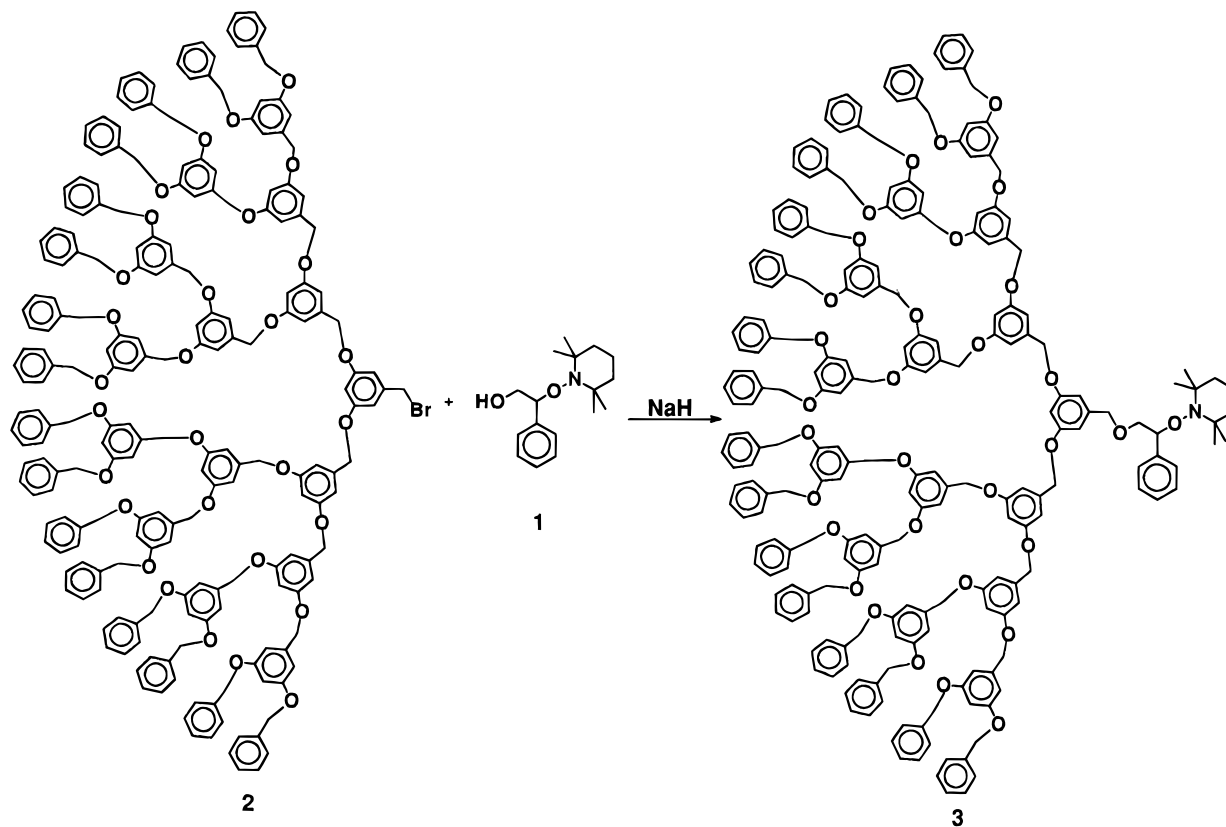
(1) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.

(2) (a) Gitsov, I.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 6536. (b) Fréchet, J. M. J.; Gitsov, I. *Macromol. Symp.* **1995**, *98*, 441.

(3) (a) Gitsov, I.; Wooley, K. L.; Hawker, C. J.; Ivanova, P. T.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 5621. (b) Gitsov, I.; Wooley, K. L.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1200. (c) Gitsov, I.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 6536.

(4) Gitsov, I.; Fréchet, J. M. J. *Macromolecules* **1994**, *27*, 7309.

Scheme 1



Results and Discussion

Of the various “living”/controlled free radical polymerization techniques,^{9–15} two were selected to investigate the proposed dendritic macroinitiator concept. Following the seminal work of Rizzardo,¹⁰ Georges,¹¹ and their co-workers, Hawker has shown that well-defined unimolecular initiators can be used to

initiate a stable nitroxide (such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO)) mediated “living” free radical polymerization.⁹ The concept¹⁴ of atom transfer radical polymerization (ATRP), based on early work by Curran et al.,¹⁸ involves initiation through a benzylic halide used in conjunction with a coordinative Cu(I)/Cu(II) redox system to perform the “living” free radical polymerizations of various monomers.¹⁴ An analogous approach has been developed by Sawamoto and co-workers¹³ while improved ATRP methods based on the premise of increased solubility of the “catalyst” have been introduced recently.^{14c,d,15} Both the nitroxide mediated polymerization and the ATRP provide fairly accurate control over the molecular weights, polydispersities and chain ends and, importantly, both use a discrete unimolecular initiating system.

(a) TEMPO Mediated Polymerizations. A series of polyether dendrons containing a single, initiating styrene/TEMPO functionality at the focal point were prepared by reaction of the hydroxy-containing TEMPO derivative, **1**, with the corresponding dendritic fragments¹⁹ having a bromobenzyl groups at their focal point. For example, reaction of the fourth generation dendrimer, [G-4]-Br **2**, with 1.5 equiv of the sodium salt of **1** was found to give the corresponding dendritic initiator, **3**, in 82% yield after purification by flash chromatography (Scheme 1). Using this synthetic strategy, TEMPO-functionalized dendrimers were prepared with generation numbers ranging from 0 to 4 in purified yields of between 75 and 90%. The introduction of a single styrene-TEMPO group at the focal point of the dendritic fragments was confirmed by a variety of spectroscopic techniques. Comparison of the 300 MHz ¹H NMR spectra for the third-generation dendritic initiator, [G-3]-TEMPO **4**, with the starting materials, [G-3]-Br **5**, revealed a

(10) (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987. (b) Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316. (c) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K.; Saban, M. *Macromolecules* **1994**, *27*, 7228. (d) Georges, M. K.; Kee, R. A.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. *J. Phys. Org. Chem.* **1995**, *8*, 301. (e) Kazmaier, P. M.; Moffat, K. A.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K. *Macromolecules* **1995**, *28*, 1841. (f) Veregin, R. P. N.; Georges, M. K.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 4391. (g) Keoshkerian, B.; Georges, M. K.; Boils-Boissier, D. *Macromolecules* **1995**, *28*, 6381. (h) Saban, M. D.; Georges, M. K.; Veregin, R. P. N.; Hamer, G. K.; Kazmaier, P. M. *Macromolecules* **1995**, *28*, 7032. (i) Odell, P. G.; Veregin, R. P. N.; Michalak, L. M.; Brousmiche, D.; Georges, M. K. *Macromolecules* **1995**, *28*, 8453. (j) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 3346.

(11) (a) Rizzardo, E. *Chem. Aust.* **1987**, *54*, 32. (b) Moad, G.; Rizzardo, E. Abstract from 35th IUPAC International Symposium on Macromolecules, Akron, OH, 1994; p 9. (c) Moad, G.; Rizzardo, E. *Macromolecules* **1995**, *28*, 8722.

(12) (a) Otsu, T.; Yoshida, M.; Tazaki, T. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127. (b) Otsu, T.; Yoshida, M.; Tazaki, T. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 133.

(13) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.

(14) (a) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901. (b) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (c) Patten, T. E.; Xia, J.; Matyjaszewski, K. *Polym. Prepr.* **1995**, *37* (1), 577. (d) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.

(15) (a) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665. (b) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.

(16) Hawker, C. J.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993.

(17) Hawker, C. J.; Elce, E.; Dao, J.; Russel, T.; Volksen, W.; Barclay, G. G. *Macromolecules* **1996**, *29*, 2686.

(18) Curran, D. P. *Synthesis* **1988**, 489.

(19) (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010.

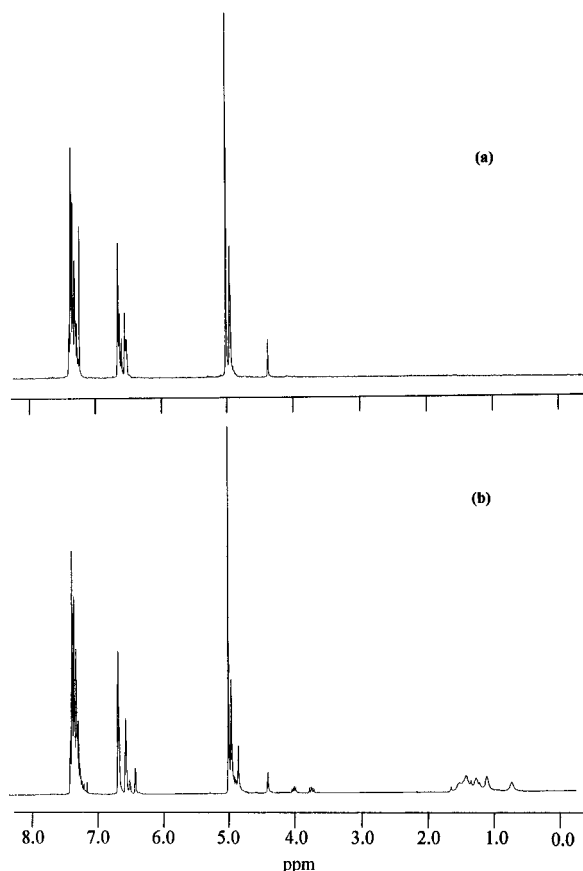


Figure 1. ^1H NMR spectra of [G-4]-Br **2** (a) and [G-4]-TEMPO **3** (b).

number of characteristic features (Figure 1). The resonance for the unique bromobenzyl group of **5** at 4.36 ppm is replaced by new resonances at 0.50–1.50, 3.55, 3.88, and 4.30 ppm which are due to the styrene-TEMPO group of **4**. Subtle changes in the resonances for the internal building blocks (6.40–6.70 ppm) and the methylene protons (4.90–5.00 ppm) of **4** are also fully consistent with the introduction of the TEMPO fragments at the focal point. Integration of the unique resonances for the dendrimer (ca. 5.00 ppm) and comparison with those of the styrene-TEMPO fragment confirms that a single TEMPO functional group has been introduced. This finding is also supported by the ^{13}C and infrared spectral data.

The ability of these dendritic initiators to polymerize vinyl monomers was investigated under the bulk polymerization conditions typically associated with “living” free radical procedures.^{9,10} For example, the third generation dendrimer, **4**, was dissolved in 150 molar equiv of styrene and heated at 123 °C under argon for 48 h to give the hybrid dendritic-linear polymer, **6**, which is isolated in 87% yield after purification by precipitation (Scheme 2). Examination of the ^1H NMR spectrum for **6** reveals resonances for both the dendritic and the polystyrene blocks and confirms the copolymer structure in which the polystyrene chain is attached to the focal point of the polyether dendrimer (Figure 2). Integration of the unique resonances for the dendrimer (ca. 5.00 ppm) and comparison with the other resonances allows the relative percentage of dendrimer and linear polystyrene blocks in the copolymer to be determined. Comparison of the size exclusion chromatography (SEC) traces for the hybrid block copolymer **6** and the starting dendrimer, **4**, clearly demonstrate that the purified hybrid block copolymer is free of dendritic impurities (Figure 3). Of particular note is the relatively low polydispersity of the hybrid polymer, **6**, ($M_w/M_n = 1.16$) and the excellent agreement between the experi-

mentally determined (SEC) number average molecular weight (M_n) of 14 000 amu and the theoretical number average molecular weight of 15 500. These results indicate that the styrene/TEMPO group at the focal point of the dendrimer is initiating the growth of a single polystyrene chain, the molecular weight of which is controlled by the molar ratio of dendritic initiator to styrene. As shown in Table 1 similar results were obtained for all the dendritic initiators (generations 1–4) and a number of trends can be observed. At molecular weights below 30 000 amu, the agreement between experimental and calculated M_n values is excellent, with low polydispersities being observed. However, as the molecular weight increases, both the polydispersity and the difference between experimental and calculated molecular weights increase. Similar behavior has also been observed for low molecular weight unimolecular initiators.^{9a} It should be noted that minor amounts of impurities that appear to consist of the dendritic block only could be detected in the crude polymerization mixture for both the third- and fourth-generation dendritic initiators only. However, the low levels of these impurities, typically less than 1–2%, did not appear to affect the course of the polymerization reaction or present any difficulties during purification.

Two unique features associated with “living” free radical polymerizations are the unusual tolerance for reactive functional groups or monomers¹⁶ coupled to the ability to prepare well-defined random copolymers.¹⁷ These features allow the synthesis of novel hybrid dendritic-linear copolymers which are either difficult to prepare, or cannot be prepared, by existing techniques. To demonstrate the versatility of “living” free radical polymerizations the use of dendritic initiators in the polymerization of 4-acetoxystyrene and the copolymerization of styrene with methyl methacrylate were investigated. In the case of 4-acetoxystyrene, initiation with either **3** or **4** afforded well defined hybrid block copolymers with low polydispersities (ca. 1.25–1.30) and controlled molecular weights. Subsequent deprotection of the acetoxy groups with ammonium hydroxide led to the unusual block copolymer, **7**, in which a strongly hydrogen-bonding linear poly(vinylphenol) block is attached to a relatively hydrophobic polyether dendron (Scheme 3). Similarly, copolymerization of a 1:9 mixture of methyl methacrylate and styrene using **4** as the initiator also afforded a defined hybrid dendritic-linear block copolymer, **8**. Analysis of **8** by ^1H NMR spectroscopy confirmed its structure as a block copolymer as well as the “random copolymer” nature of the linear poly(methyl methacrylate-*r*-styrene) block. It should be noted that the preparation of **8** is not possible by the previously reported anionic route.⁴

(b) Atom Transfer Radical Polymerization (ATRP). The high degree of control associated with the convergent growth approach allows ready access to polyether dendrons that contain a single benzylic halide at their focal point.¹⁹ As was the case for the TEMPO derivatives discussed above, the single bromobenzyl or chlorobenzyl²⁰ focal point group can act as an initiating site for the polymerization of vinyl monomers under atom transfer radical polymerization (ATRP) conditions. For example, a bulk polymerization of styrene was initiated by a third-generation dendritic chloride, [G-3]-Cl **9**, using the $\text{Cu}^{\text{I}}\text{-Cl}/4,4'-(\text{di-}n\text{-heptyl})\text{-2,2'-dipyridyl}$ ²¹ **10** complex. Heating this mixture to 130 °C under argon in a sealed tube for 8 h afforded the block copolymer **11** in 95% yield after purification by precipitation (Scheme 4). The molecular weight as determined by SEC ($M_n = 9540$) is in excellent agreement with the calculated value of 9460 while the polydispersity remains low

(20) Lee, J. B.; Nolan, T. J. *Can. J. Chem.* **1966**, *44*, 1331.

(21) Kramer, R.; Lehn, J. M.; Cian, A. D.; Fisher, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 703.

Scheme 2

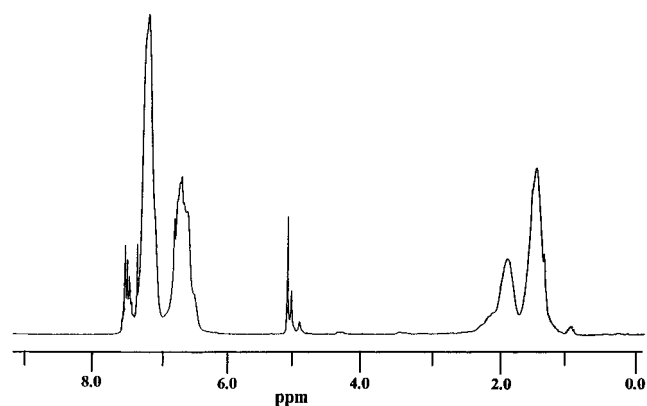
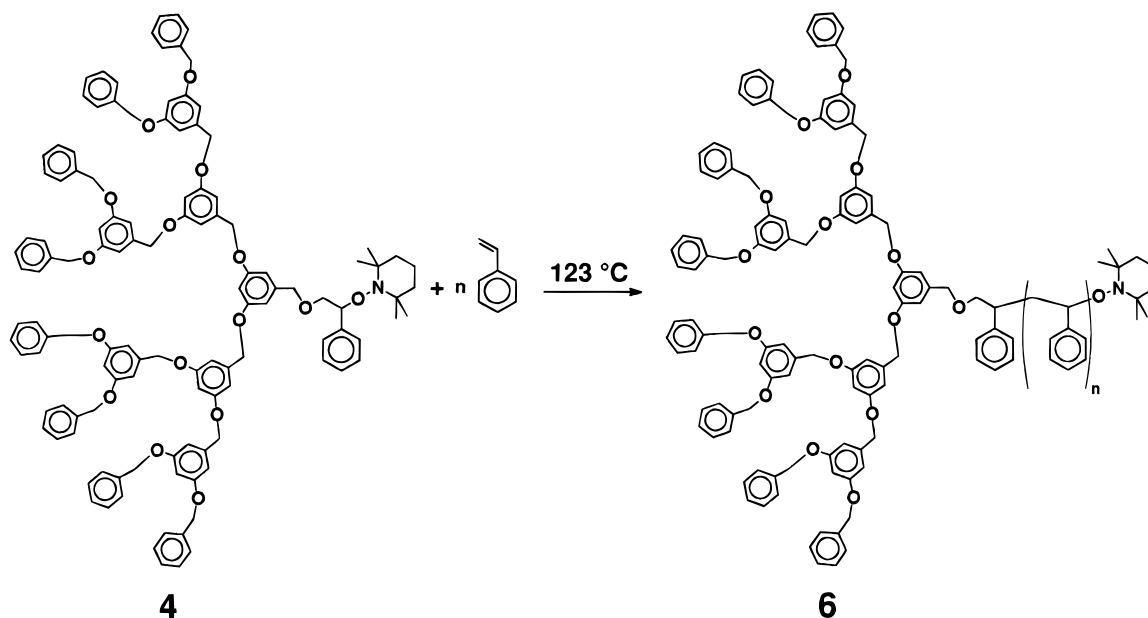


Figure 2. ^1H NMR spectrum (300 MHz, CDCl_3) of [G-3]-PS-TEMPO **6**.

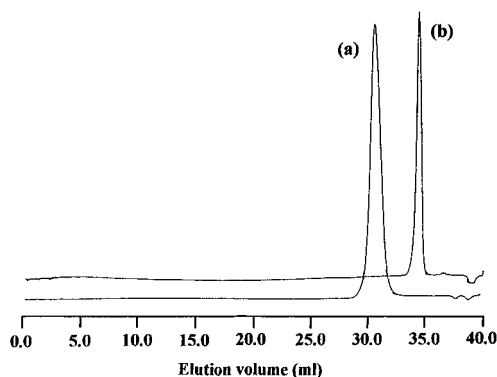


Figure 3. SEC traces of [G-3]-PS-TEMPO **6** (a) and [G-3]-TEMPO **4** (b).

($M_w/M_n = 1.10$). Once again, ^1H NMR analysis of block copolymer **11** confirms the presence of both the dendritic and polystyrene blocks (Figure 4). Furthermore, the molecular weight (10 500) determined by the relative integrations of resonances for the dendritic and polystyrene blocks' protons in the ^1H NMR spectrum is consistent within experimental errors with the peak molecular weight obtained by SEC ($M_p = 10\,300$). It has previously been shown⁴ that the ultraviolet (UV) spectrum of polyether dendron–polystyrene block copolymers possess λ_{max} at 229, 262, and 283 nm. The pure polyether dendrons

Table 1. Polymerization of Styrene by Dendritic-TEMPO Initiators

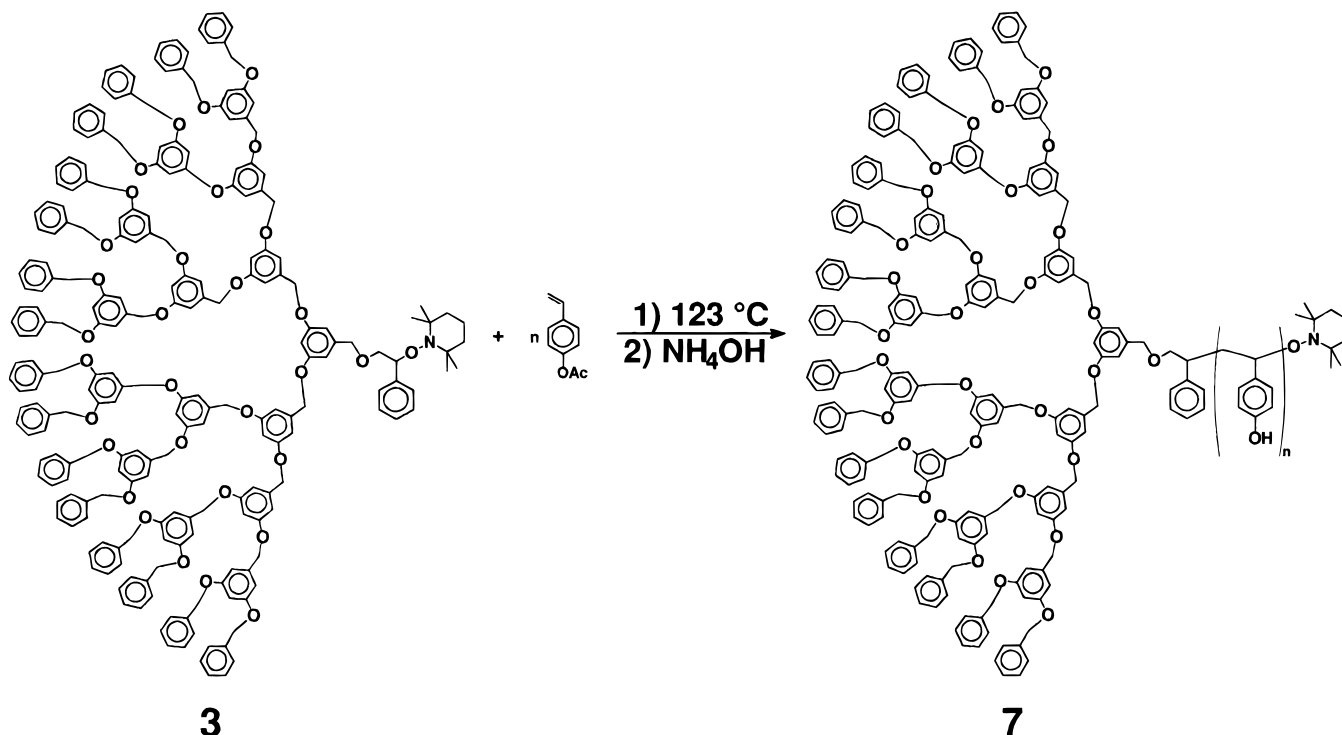
initiator	M_n (SEC)	M_n (calcd)	M_w/M_n
[G-0]-TEMPO	14 000	15 500	1.15
[G-0]-TEMPO	21 000	22 500	1.23
[G-1]-TEMPO	13 500	15 500	1.19
[G-1]-TEMPO	25 000	27 000	1.27
[G-2]-TEMPO	14 500	15 500	1.21
[G-2]-TEMPO	24 500	27 000	1.24
[G-3]-TEMPO	14 000	15 500	1.16
[G-3]-TEMPO	24 000	27 000	1.28
[G-3]-TEMPO	41 000	45 000	1.34
[G-3]-TEMPO	14 000	16 500	1.25 ^a
[G-3]-TEMPO	19 000	21 000	1.19 ^b
[G-4]-TEMPO	14 000	16 000	1.14
[G-4]-TEMPO	24 500	28 000	1.25
[G-4]-TEMPO	42 000	46 000	1.33
[G-4]-TEMPO	91 000	110 000	1.42
[G-4]-TEMPO	22 500	25 000	1.28 ^a
[G-4]-TEMPO	21 500	25 000	1.20 ^b

^a 4-Acetoxystyrene used as the monomer. ^b 1:9 mixture of methyl methacrylate and styrene used as the monomer feed.

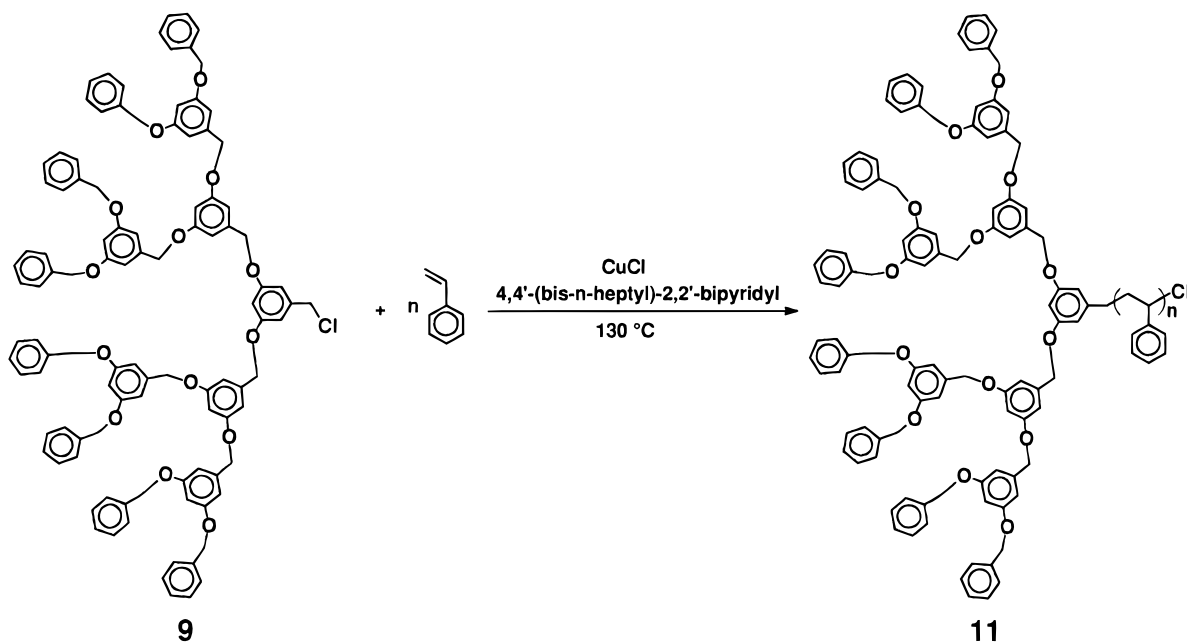
exhibit λ_{max} at 288 nm whereas linear polystyrene absorbs minimally above 280 nm (λ_{max} are observed at 223 and 259 nm). Hence, a spectroscopic difference between the linear polystyrene and the dendritic building blocks can be used to confirm the presence of the dendritic component in the block copolymer. Indeed, dual-detector SEC—differential refractive index (DRI) and ultraviolet at 283 nm—of the hybrid block copolymer **11** reveals that both the DRI and UV traces are superimposable (Figure 5), suggesting that the dendron is homogeneously incorporated into the polymer. These SEC results in conjunction with the ^1H NMR spectroscopic evidence, reaffirm that initiation of the polymerization occurs from the dendritic macroinitiator.

In Table 2, SEC results for dendritic initiators of generations 1–4 are presented. Several trends similar to those observed for the TEMPO-functionalized dendrons are observed for this initiating system. At molecular weights higher than ca. 30 000, the polydispersity of the hybrid block copolymers increases from ca. 1.1–1.2 to 1.3–1.5 and the experimentally determined molecular weight deviates increasingly from the calculated value. Similar behavior has been reported for the ATRP of styrene at high molecular weights and reveals the limitations

Scheme 3



Scheme 4



of this method.^{14d} The discrepancies between the calculated and apparent molecular weights might be attributed to side reactions, such as chain transfer and thermal initiation, inherent to the ATRP process. Also, the specific solution behavior of the copolymers as observed in previous investigations of similar copolymer systems must be considered.⁴ Polymerizations carried out with 2,2'-dipyridyl instead of 4,4'-(di-*n*-heptyl)-2,2'-dipyridyl were heterogeneous and afforded polymers with slightly increased polydispersities, consistent with previous observations.^{14c,d,15}

SEC analyses of the crude ATRP polymerization mixtures at high conversions with the third and fourth generation dendritic initiators reveal the presence of small quantities of impurities with molecular weight and UV characteristics consistent with those of the dendritic initiators. These impurities are readily

removed by precipitation. This behavior is similar to that observed with the TEMPO-based dendritic initiators. We have observed that dendritic initiators having bromobenzyl groups at the focal point gave slightly higher levels of this "starting dendron-like" impurity than the corresponding chlorobenzyl initiators. This observation suggests that some termination reaction, perhaps the result of HX elimination (X = Br or Cl), occurs after additions of one or even a few styrene units. Such thermal elimination leading to chain transfer would indeed be expected to be more prevalent for bromo-substituted derivatives than for the chloro analogues. Alternately a minor amount of radical chain transfer could be responsible for the partial deactivation of the initiator.

The well-defined nature of these hybrid dendritic-block copolymers allowed their phase behavior to be studied using

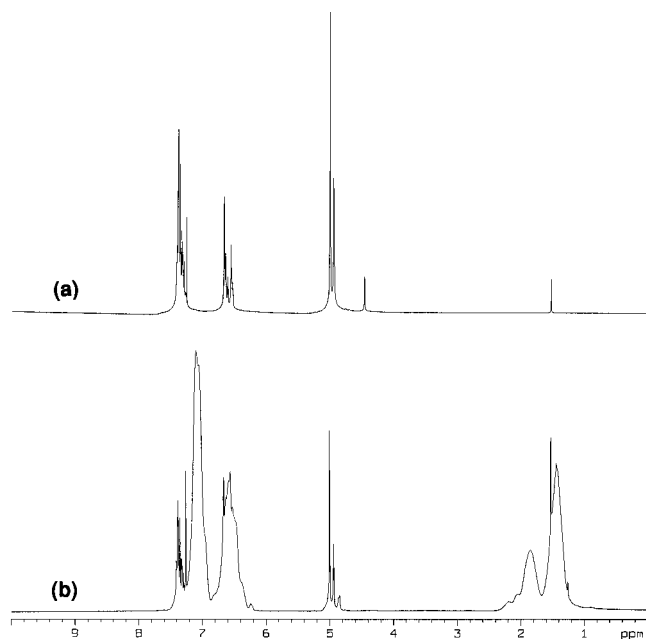


Figure 4. ^1H NMR spectra (300 MHz, CDCl_3) of [G-3]-Cl **9** (a) and [G-3]-PS-Cl **11** (b).

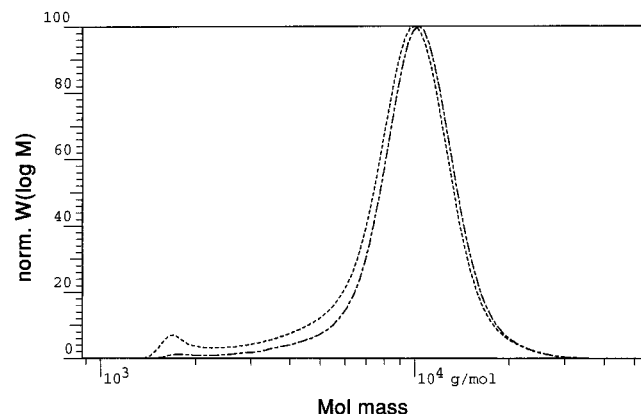


Figure 5. SEC traces of the crude [G-3]-PS-Cl mixture before purification: (---) UV at 283 nm; (—) DRI.

differential scanning calorimetry (DSC). Interestingly, a single glass transition temperature (T_g) was observed for all of the block copolymers, regardless of the method of preparation. In contrast, physical mixtures of the starting dendritic initiators and narrow polydispersity polystyrene of the same overall composition as the hybrids exhibited two glass transitions corresponding to the T_g 's of the individual components. This indicates that, in the hybrid block copolymers, the dendritic block is still compatible with the linear block even at generation 4. For example, the hybrid block copolymer [G-4]-PS-Cl, **12**, exhibited a T_g at 347 K while a mixture of 34 wt % [G-4]-Cl and polystyrene, **14**, prepared by ATRP ($M_n = 6200$, $M_w/M_n = 1.2$) has two glass transitions at 314 K (dendron) and 367 K (polystyrene). Examination of the glass transition temperature for the hybrid copolymers composed of various generation dendrons and polystyrene segments of approximately the same molecular weight shows a decrease in T_g with increasing generation number. For example, the glass transition temperature decrease from 373 to 350 K on going from generation 0 to generation 4. These experimental T_g values are consistent with those calculated using the FOX equation.^{22,23} A similar

(22) Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 1514.

(23) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

Table 2. ATRP of Styrene Initiated by Dendron/CuX/Ligand^a

initiator	ligand ^b	M_n (SEC)	M_n (calcd) ^c	M_w/M_n
benzyl chloride	C ₇ -Bipy	10 800	10 700	1.16
benzyl chloride	C ₇ -Bipy	41 200	50 000	1.29
[G-1]-Cl	Bipy	10 700	10 460	1.30
[G-1]-Cl	Bipy	41 000	47 000	1.36
[G-1]-Cl	C ₇ -Bipy	10 540	9 750	1.10
[G-1]-Cl	C ₇ -Bipy	40 300	41 400	1.23
[G-1]-Br	Bipy	10 770	9 365	1.24
[G-1]-Br	C ₇ -Bipy	9 720	9 400	1.07
[G-2]-Cl	Bipy	10 200	9 300	1.31
[G-2]-Cl	C ₇ -Bipy	10 560	10 190	1.13
[G-2]-Cl	C ₇ -Bipy	35 770	48 700	1.32
[G-2]-Br	Bipy	9 860	8 780	1.25
[G-2]-Br	C ₇ -Bipy	11 700	10 760	1.10
[G-3]-Cl	Bipy	11 500	11 100	1.24
[G-3]-Cl	C ₇ -Bipy	9 540	9 460	1.10
[G-3]-Cl	C ₇ -Bipy	32 500	49 000	1.34
[G-3]-Br	C ₇ -Bipy	10 100	8 800	1.19
[G-4]-Cl	Bipy	13 100	13 200	1.14
[G-4]-Cl	C ₇ -Bipy	9 200	8 700	1.10
[G-4]-Cl	C ₇ -Bipy	28 300	28 000	1.27
[G-4]-Cl	C ₇ -Bipy	57 000	91 400	1.51
[G-4]-Cl	C ₇ -Bipy	40 000	50 200	1.34

^a Polymerization temperature: X = Cl, 130 °C; X = Br, 100 °C.
^b Bipy: 2,2'-bipyridyl. C₇-Bipy: 4,4'-(di-*n*-heptyl)-2,2'-bipyridyl.²¹ ^c M_n (calcd) = $[(\text{[styrene]}/\text{[dendron]}) \times \text{MW}_{\text{styrene}}] \times \text{conversion} + \text{MW}_{\text{initiator}}$.

thermal behavior has been observed for dendron-polystyrene-dendron triblocks prepared by living anionic polymerization.⁴

Conclusion

Polyether dendrons have been used successfully as macro-initiators for the "living"/controlled free radical polymerization of vinyl monomers. The dendron-TEMPO method affords greater control over the polymerization at high molecular weights and appears to be somewhat less prone to chain-transfer processes or other side reactions than the dendritic halide ATRP approach. However, both techniques give excellent control of the molecular weight and low polydispersity at molecular weights below ca. 30 000 amu. The versatility of the macro-initiator approach toward hybrid dendritic-linear copolymer synthesis has been demonstrated by the use of various monomers and initiators. Further investigations into the use of this free radical methodology for the preparation of functionalized dendritic-linear block copolymers useful for surface modification and hybrid dendritic-linear stars²⁴ useful for rheology control are currently in progress.

Experimental Section

General Directions. Styrene was distilled over CaH_2 immediately prior to use. All reagents were purchased from Aldrich and were used as received without purification. The dendritic alcohols and bromides used throughout this study were synthesized according to the literature.¹⁹ Analytical thin layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel GF₂₅₄ (0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230–400 mesh). Infrared spectra were recorded on a Nicolet IR/44 spectrophotometer in KBr pellets or neat. Monomer conversion was determined gravimetrically and/or by ^1H NMR of the crude reaction mixtures using CDCl_3 as solvent. Both methods gave comparable results. ^1H NMR spectra were recorded on solutions in CDCl_3 on a Bruker AF300 (300 MHz) spectrometer with the use of the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 75 MHz on a Bruker AF300 spectrometer on solutions in CDCl_3 with the use of the solvent carbon signal as standard. Size exclusion chromatography (SEC) was performed at 45 °C on a line consisting of a M510 pump,

(24) Gitsov, I.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1996**, *118*, 3785.

an U6K universal injector, an UV 486 detectors (all Waters), a differential refractive index detector—DRI (Milton Roy), and a Model 110 differential viscometer (Viscotek). The separation was achieved across a set of four 5 μ m PL Gel columns (Polymer Laboratories) with porosities of 100 Å, 500 Å, 1000 Å, and Mixed C. The mobile phase was THF eluting at a nominal flow rate of 1 mL/min. The molecular weight characteristics of the polymers were calculated by a polystyrene calibration curve constructed with 23 monodisperse polystyrene standards. The glass transition temperature (T_g) for each sample was measured by differential scanning calorimetry using a Mettler DSC 30 low-temperature cell coupled to a TC10A processor. Heating rates were 10 K/min. T_g was taken as the midpoint of the inflection tangent of the second heating run.

Preparation of 4,4'-(Di-*n*-heptyl)-2,2'-bipyridyl (10).²¹ Into a precooled (−78 °C) 100 mL two-neck round bottom flask with a magnetic stir bar and septa were placed THF (20 mL) and lithium diisopropylamide (LDA) (2.0 M solution in heptane/tetrahydrofuran/ethylbenzene, 5.7 mL, 11 mmol). A solution of 4,4'-dimethyl-2,2'-dipyridyl (1.00 g, 5.43 mmol) in THF (25 mL) was added dropwise to the LDA/THF solution. After the addition was complete, the reaction mixture was stirred at −78 °C for 1 h. A solution of 1-bromohexane (1.81 g, 10.9 mmol) in THF (5 mL) was added dropwise to the reaction mixture after which it was allowed to warm to room temperature overnight. The reaction was quenched by addition of water (ca. 20 mL) and evaporated under reduced pressure to give a viscous yellow residue in water. Upon addition of saturated aqueous sodium chloride solution (ca. 10 mL), a yellow precipitate was obtained which was filtered, dried, and crystallized twice from ethanol to obtain 4,4'-(di-*n*-heptyl)-2,2'-bipyridyl as fine white crystals (1.23 g, 64%): IR (KBr) 3054, 1597, 1550, 1463, 1379, 1255, 993, 897, 851, 826 cm^{−1}; ¹H NMR (CDCl₃) δ 0.86 (t, 6 H, J = 6.8 Hz, CH₃), 1.20–1.38 (m, 16 H, (CH₂)₄), 1.66 (m, 4 H, CH₂CH₃), 2.68 (t, 4 H, J = 7.9 Hz, ArCH₂), 7.14 (dd, 2 H, J = 5.02 and 1.66 Hz, ArH), 8.24 (br s, 2 H, ArH), 8.55 (dd, 2 H, J = 5.02 and 0.57 Hz, ArH); ¹³C NMR (CDCl₃) δ 14.03, 22.59, 29.05, 29.25, 30.43, 31.70, 35.50, 121.26, 123.86, 148.92, 152.87, 156.13.

General Procedure for Synthesis of Dendritic Initiators, [G-3]-TEMPO (4). To a solution of the alcohol, **1** (392 mg, 1.50 mmol), in dry tetrahydrofuran (25 mL) was added sodium hydride (80 mg, 60% dispersion in oil, 2.0 mmol), and the reaction mixture was stirred under argon at room temperature for 15 min. The dendritic bromide, [G-3]-Br, **5** (1.70 g, 1.02 mmol), dissolved in dry tetrahydrofuran (10 mL) was then added dropwise and the reaction mixture heated at reflux under argon for 6 h. The reaction mixture was then cooled, evaporated to dryness, and partitioned between dichloromethane (100 mL) and water (100 mL). The aqueous layer was extracted with dichloromethane (2 \times 50 mL), and the combined organics were dried and evaporated to dryness. The crude product was purified by flash chromatography eluting with dichloromethane gradually increasing to 1:9 diethyl ether/dichloromethane to afford the dendritic initiator, **4**, as a colorless foam (1.61 g, 86%): IR (neat) 2950, 1500, 1380, 1030 cm^{−1}; ¹H NMR (CDCl₃) δ 0.54 (br s, 3 H, CH₃), 0.91–1.50 (br m, 15 H, CH₂ and CH₃), 3.55 (ABq, 1 H, CHH), 3.88 (ABq, 1 H, CHH), 4.36 (s, 2 H, CH₂), 4.85, 4.92, and 5.00 (each s, 28 H, ArCH₂O), 4.89 (ABq, 1 H, CH), 6.35–6.60 (m, 21 H, ArH), 7.25–7.35 (45 H, ArH); ¹³C NMR (CDCl₃) δ 17.30, 20.49, 34.10, 39.76, 40.58, 60.06, 70.09, 70.18, 72.93, 85.51, 101.35, 101.71, 106.00, 106.50, 127.18, 128.05, 128.70, 136.90, 139.37, 139.50, 141.31, 142.10, 159.96, 160.17, 160.28. Anal. [G-3]-TEMPO C₁₂₂H₁₁₇NO₁₆ requires C, 79.07; H, 6.36; N, 0.76. Found: C, 79.34; H, 6.58; N, 0.93%.

[G-0]-TEMPO (15). This was prepared from benzyl bromide and **1** using the procedure outlined above. The crude product was purified by flash chromatography eluting with dichloromethane to give the [G-0] initiator, **15**, as a colorless foam (82%): IR (neat) 3050, 2970, 1495, 1380, 1030 cm^{−1}; ¹H NMR (CDCl₃) δ 0.56 (br s, 3 H, CH₃), 0.93–1.50 (br m, 15 H, CH₂ and CH₃), 3.58 (ABq, 1 H, CHH), 3.91 (ABq, 1 H, CHH), 4.37 (s, 2 H, CH₂), 4.92 (ABq, 1 H, CH), 7.25–7.35 (m, 10 H, ArH); ¹³C NMR (CDCl₃) δ 17.35, 20.52, 34.11, 39.76, 40.60, 60.02, 70.21, 85.53, 127.19, 128.12, 128.65, 130.12, 141.31, 142.22. Anal. [G-0]-TEMPO C₂₄H₃₃NO₂ requires C, 78.43; H, 9.05, N, 3.81. Found: C, 78.25; H, 8.80; N, 4.03%.

[G-1]-TEMPO (16). This was prepared from [G-1]-Br and **1** using the procedure outlined above. The crude product was purified by flash

chromatography eluting with dichloromethane gradually increasing to 1:19 diethyl ether/dichloromethane to give the dendritic initiator, **16**, as a colorless foam (76%): IR (neat) 3050, 2970, 1490, 1375, 1010 cm^{−1}; ¹H NMR (CDCl₃) δ 0.58 (br s, 3 H, CH₃), 0.90–1.50 (br m, 15 H, CH₂ and CH₃), 3.59 (ABq, 1 H, CHH), 3.90 (ABq, 1 H, CHH), 4.39 (s, 2 H, CH₂), 4.91 (s, 2 H, ArCH₂O), 4.93 (ABq, 1 H, CH), 6.50 (t, 1 H, J = 6 Hz, ArH), 6.60 (d, 1 H, J = 6 Hz, ArH), 7.25–7.35 (m, 15 H, ArH); ¹³C NMR (CDCl₃) δ 17.38, 20.50, 34.23, 39.88, 40.62, 59.93, 70.24, 72.95, 85.55, 101.50, 106.38, 127.19, 127.30, 127.91, 128.12, 128.65, 136.56, 141.3, 160.10. Anal. [G-1]-TEMPO C₃₈H₄₅NO₄ requires C, 78.72; H, 7.82; N, 2.42. Found: C, 78.86; H, 8.04; N, 2.27%.

[G-2]-TEMPO (17). This was prepared from [G-2]-Br and **1** using the procedure outlined above. The crude product was purified by flash chromatography eluting with dichloromethane gradually increasing to 1:19 diethyl ether/dichloromethane to give the dendritic initiator, **17**, as a colorless foam (90%): IR (neat) 3050, 2975, 1495, 1380, 1020 cm^{−1}; ¹H NMR (CDCl₃) δ 0.57 (br s, 3 H, CH₃), 0.90–1.50 (br m, 15 H, CH₂ and CH₃), 3.61 (ABq, 1 H, CHH), 3.90 (ABq, 1 H, CHH), 4.33 (s, 2 H, CH₂), 4.83 (s, 4 H, ArCH₂O), 4.86 (ABq, 1 H, CH), 4.92 (s, 8 H, ArCH₂O), 6.30 (d, 2 H, J = 6 Hz, ArH), 6.38 (t, 1 H, J = 6 Hz, ArH), 6.49 (t, 2 H, J = 6 Hz, ArH), 6.58 (d, 4 H, J = 6 Hz, ArH), 7.25–7.45 (m, 25 H, ArH); ¹³C NMR (CDCl₃) δ 17.17, 20.45, 34.30, 39.90, 40.46, 60.10, 69.86, 70.12, 72.84, 85.37, 101.27, 101.53, 105.87, 106.41, 127.28, 127.59, 127.91, 128.03, 128.61, 136.79, 139.36, 141.13, 141.97, 159.79, 160.14.

[G-4]-TEMPO (3). This was prepared from [G-4]-Br, **2**, and **1** using the procedure outlined above. The crude product was purified by flash chromatography eluting with dichloromethane gradually increasing to 1:9 diethyl ether/dichloromethane to give the dendritic initiator, **3**, as a colorless foam (79%): IR (neat) 3040, 2970, 1490, 1385, 1030 cm^{−1}; ¹H NMR (CDCl₃) δ 0.56 (br s, 3 H, CH₃), 0.90–1.50 (br m, 15 H, CH₂ and CH₃), 3.60 (ABq, 1 H, CHH), 3.88 (ABq, 1 H, CHH), 4.34 (s, 2 H, CH₂), 4.83 (s, 4 H, ArCH₂O), 4.86 (ABq, 1 H, CH), 4.90 and 4.95 (each s, 56 H, ArCH₂O), 6.30–6.60 (complex m, 45 H ArH), 7.25–7.50 (m, 85 H, ArH); ¹³C NMR (CDCl₃) δ 17.28, 20.46, 34.09, 39.76, 40.61, 60.02, 70.10, 70.17, 70.22, 72.87, 85.48, 101.30, 101.71, 106.05, 106.54, 127.20, 127.99, 128.09, 128.66, 136.90, 139.41, 139.53, 141.40, 142.13, 159.95, 160.19, 160.30. Anal. [G-4]-TEMPO C₂₃₄H₂₁₃NO₃₂ requires C, 79.14; H, 6.05; N, 0.39. Found: C, 79.28; H, 6.31; N, 0.67%.

General Procedure for the Synthesis of Chlorobenzyl Dendrons.²⁰

Synthesis of [G-4]-Cl, 13. To a solution of [G-4]-OH (1.93 g, 0.586 mmol) in dry tetrahydrofuran (8 mL) were added carbon tetrachloride (0.64 g, 4.2 mmol) and triphenylphosphine (0.20 g, 0.76 mmol). The reaction mixture was heated to reflux under argon atmosphere. After 40 min, additional triphenylphosphine (0.20 g, 0.76 mmol) was required to push the reaction to completion. The reaction was quenched by addition of water and CH₂Cl₂ upon complete disappearance of starting material as shown by TLC (CH₂Cl₂). The phases were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 \times). The combined organic extracts were dried (MgSO₄) and evaporated to dryness. The crude product was purified by flash chromatography, eluting with 2:1 hexanes/CH₂Cl₂ gradually increasing to CH₂Cl₂ to give **13** as a colorless glass (1.75 g, 90%): IR (KBr) 1596, 1452, 1374, 1158, 1055 cm^{−1}; ¹H NMR (CDCl₃) δ 4.44 (s, 2 H, CH₂Cl), 4.91 and 4.93 (both s, 28 H, ArCH₂O), 4.99 (s, 32 H, ArCH₂O), 6.50–6.55 (m, 7 H, ArH), 6.56 (t, 8 H, J = 2 Hz, ArH), 6.59 (d, 2 H, J = 2 Hz, ArH), 6.62–6.68 (m, 28 H, ArH), 7.28–7.45 (m, 80 H, PhH); ¹³C NMR (CDCl₃) δ 46.16, 69.94, 69.99, 97.01, 99.25, 101.52, 106.30, 107.70, 127.49, 127.92, 128.50, 136.70, 139.07, 139.14, 139.48, 159.90, 159.98, 160.00, 160.06. MALDI-TOF mass spectrum: 3325 (theory: 3333, M + Na). Anal. [G-4]-Cl C₂₁₇H₁₈₇O₃₀Cl requires C, 78.74; H, 5.70. Found: C, 78.66; H, 5.80.

[G-1]-Cl (18). This was prepared from [G-1]-OH using the procedure outlined above. The crude product was purified by recrystallization from methanol to give **18** as a white needles in 80% yield: IR (KBr) 1596, 1449, 1370, 1166, 1047 cm^{−1}; ¹H NMR (CDCl₃) δ 4.51 (s, 2 H, CH₂Cl), 5.03 (s, 4 H, PhCH₂O), 6.57 (t, 1 H, J = 2.2 Hz, ArH), 6.64 (d, 2 H, J = 2.2 Hz, ArH), 7.32–7.43 (m, 10 H, PhH); ¹³C NMR (CDCl₃) δ 46.28, 70.14, 102.02, 107.64, 127.53, 128.06, 128.60,

136.61, 139.54, 160.08. Anal. [G-1]-Cl $C_{21}H_{19}O_2Cl$ requires C, 74.53; H, 5.66; Cl, 10.34. Found: C, 74.60; H, 5.61; Cl, 10.96.

[G-2]-Cl (19). This was prepared from [G-2]-OH using the procedure outlined above. The crude product was purified by flash chromatography eluting with CH_2Cl_2 to give **19** as a white powder in 91% yield: IR (KBr) 1598, 1472, 1375, 1172, 1055 cm^{-1} ; 1H NMR ($CDCl_3$) δ 4.50 (s, 2 H, CH_2Cl), 4.97 (s, 4H, $ArCH_2O$), 5.03 (s, 8 H, $PhCH_2O$), 6.54 (t, 1 H, $J = 2.2$ Hz, ArH), 6.58 (t, 2 H, $J = 2.2$ Hz, ArH), 6.62 (d, 2 H, $J = 2.2$ Hz, ArH), 6.68 (d, 4 H, $J = 2.2$ Hz, ArH), 7.29–7.44 (m, 20 H, PhH); ^{13}C NMR ($CDCl_3$) δ 46.28, 70.04, 70.09, 101.60, 102.05, 106.35, 107.67, 127.53, 128.00, 128.56, 136.71, 139.04, 139.52, 159.96, 160.14. MALDI-TOF mass spectrum: 790 (theory: 786, $M + Na$), 807 (theory: 802, $M + K$). Anal. [G-2]-Cl $C_{49}H_{43}O_6Cl$ requires C, 77.14; H, 5.69; Cl, 4.59. Found: C, 77.33; H, 5.72; Cl, 4.80.

[G-3]-Cl (9). This was prepared from [G-3]-OH using the procedure outlined above. The crude product was purified by flash chromatography eluting with 2:1 hexanes/ CH_2Cl_2 gradually increasing to CH_2Cl_2 to give **9** as a colorless glass in 93% yield: IR (KBr) 1597, 1450, 1375, 1158, 1056 cm^{-1} ; 1H NMR ($CDCl_3$) δ 4.43 (s, 2 H, CH_2Cl), 4.93 (s, 12 H, $ArCH_2O$), 5.00 (s, 8 H, $ArCH_2O$), 6.5–6.7 (m, 21 H, ArH), 6.727–7.43 (m, 40 H, PhH); ^{13}C NMR ($CDCl_3$) δ 46.20, 69.87, 69.92, 69.97, 101.49, 101.54, 101.94, 106.28, 106.34, 107.61, 127.46, 127.91, 128.49, 136.68, 138.99, 139.12, 139.50, 159.90, 159.96, 160.05. MALDI-TOF mass spectrum: 1632 (theory: 1635, $M + Na$), 1648 (theory: 1651, $M + K$). Anal. [G-3]-Cl $C_{105}H_{91}O_{14}Cl$ requires C, 78.23; H, 5.69. Found: C, 77.60; H, 5.67.

General Procedure for “Living” Free Radical Polymerizations via the Nitroxide Method (TEMPO). A mixture of the dendritic initiator, [G-3]-TEMPO, **4**, (463 mg, 0.25 mmol) and styrene (3.90 g, 37.5 mmol) was heated at 123 °C under argon for 48 h. During this time the polymerization mixture became progressively more viscous and eventually solidified. The crude polymerization mixture was then dissolved in dichloromethane and precipitated into a 1:3 mixture of isopropyl alcohol and acetone; the precipitate was then redissolved in dichloromethane and precipitated into methanol. The purified hybrid dendritic-linear polymer, **6**, was obtained as a white solid (3.58 g, 82%): IR (neat) 3050, 2950, 1600, 1385, 1035 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.20–2.10 (br m, aliphatic H's of polystyrene), 4.86, 4.98, 5.04 (each s, CH_2O dendron), 6.30–7.20 (br m, aromatic H's of polystyrene and

dendron), 7.30–7.45 (complex m, PhH 's of dendron); ^{13}C NMR ($CDCl_3$) δ 40–42 (br m), 69.5, 70.1, 101.6, 106.4, 125.6–128.2 (br m), 136.7, 139.2, 144.8–145.3 (br m), 160.02, 160.15.

General Procedure for “Living” Free Radical Polymerizations (ATRP). Synthesis of [G-3]-PS-Cl (11). [G-3]-Cl, **9** (0.0872 g, 5.41×10^{-5} mol), 4,4'-(bis-*n*-heptyl)-2,2'-bipyridyl (0.0406 g, 11.5×10^{-5} mol), Cu^I Cl (0.0057 g, 5.7×10^{-5} mol), and styrene (0.447 g, 4.29×10^{-3} mol) were placed in a dry glass tube. The homogeneous dark brown mixture was thoroughly degassed to remove traces of oxygen, and the tube was sealed under dry argon atmosphere. The tube was wrapped in aluminum foil and submerged into an thermostated oil bath at 130 °C. The contents of the tube became progressively more viscous and completely hardened into a dark brown solid after ca. 3 h. The tube was removed from the oil bath after 8 h and cooled to room temperature. The brown solid was dissolved in THF and passed through a short column of neutral alumina to give a clear and slightly yellow solution. Copolymer **11** was obtained as a white powder after precipitation from THF into methanol (0.509 g, 95%); conversion 95% (by 1H -NMR of crude mixture); IR (KBr) 3060, 3026, 2920, 1597, 1493, 1452, 1375, 1155 cm^{-1} ; 1H NMR (after precipitation, $CDCl_3$) δ 0.9–2.4 (br m, CH and CH_2 polystyrene), 4.2–4.5 (br m, CH_2Cl), 4.85 (s, $ArCH_2O$ dendron), 4.9 (s, $ArCH_2O$ dendron), 5.0 (s, $ArCH_2O$ dendron), 6.2–7.2 (m, ArH polystyrene and dendron), 7.28–7.43 (m, PhH dendron); ^{13}C NMR ($CDCl_3$) δ 30.9, 40–42 (br m), 69.9, 70.1, 99.2, 106.4, 125.6–128.5 (br m), 136.7, 139.2, 145.1 and 160.1; SEC (crude mixture, relative to polystyrene) $M_n = 9540$, $M_w = 10\,560$, $M_w/M_n = 1.10$, M_n (calcd for 95% conversion) = 9460.

Acknowledgment. Financial support for this project by the AFOSR MURI program (USC), the National Science Foundation (DMR-9641291, NSF Center for Polymeric Interfaces and Macromolecular Assemblies), Bayer Corp., Loctite Corp., and IBM Corp. is gratefully acknowledged. The SEC analyses were made in the Polymer Characterization Facility of the Cornell Materials Science Center supported by the NSF (Grant DMR-9121654). M.R.L. also acknowledges the support of NSERC (Canada) through a postgraduate fellowship.

JA962159A