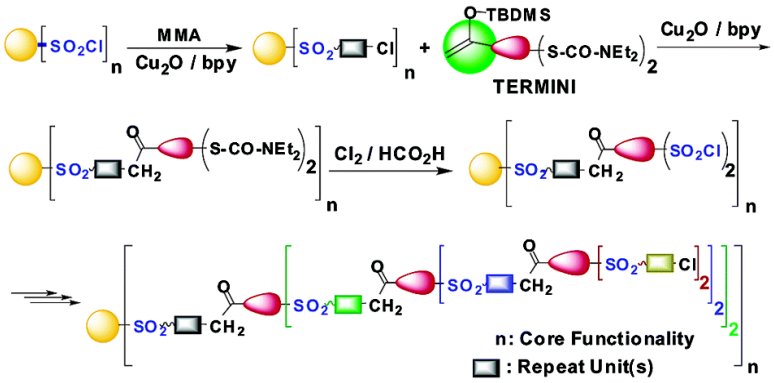
Article

Universal Iterative Strategy for the Divergent Synthesis of Dendritic Macromolecules from Conventional Monomers by a Combination of Living Radical Polymerization and Irreversible TERminator Multifunctional INItiator (TERMINI)

Virgil Percec, Bogdan Barboiu, Cristian Grigoras, and Tushar K. Bera

J. Am. Chem. Soc., **2003**, 125 (21), 6503-6516• DOI: 10.1021/ja034746j • Publication Date (Web): 06 May 2003



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 25 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

J|A|C|S
ARTICLES
Published on Web 05/06/2003

Universal Iterative Strategy for the Divergent Synthesis of Dendritic Macromolecules from Conventional Monomers by a Combination of Living Radical Polymerization and Irreversible TERminator Multifunctional INItiator (TERMINI)

Virgil Percec,* Bogdan Barboiu, Cristian Grigoras, and Tushar K. Bera

Contribution from the Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

Received February 18, 2003; E-mail: percec@sas.upenn.edu

Abstract: A new synthetic concept named TERMINI that stands for irreversible TERminator Multifunctional INItiator is reported. Suitable combinations of TERMINI and living polymerizations provide access to strategies for the design and synthesis of unprecedented complex molecular and macromolecular architectures from a diversity of commercial monomers. TERMINI represents a masked multifunctional initiator designed to quantitatively and irreversibly interrupt a chain organic reaction or a living polymerization. After demasking, the TERMINI repeat unit enables the quantitative reinitiation, in the presence or absence of a catalyst, of the same or a different living polymerization or a chain organic reaction in more than one direction, thus becoming a branching point. The demonstration of this concept was made by using a combination of metal-catalyzed living radical polymerization (LRP) and (1,1-dimethylethyl)[[1-[3,5-bis(*S*-phenyl 4-*N,N*′-diethylthiocarbamate)phenyl]ethenyl]oxy]dimethylsilane as TERMINI, to elaborate a novel iterative divergent method for the synthesis of dendritic macromolecules based on methyl methacrylate (MMA).

Introduction

We have been investigating the design and synthesis of complex architectures that produce self-assembling building blocks which generate supramolecular objects with the shape perfection required to self-organize in novel and known lattices.[1−3] When the supramolecular objects exhibit an internal ordered structure[3] rather than a micelle-like structure, the retrostructural analysis of their lattices enables the formulation of a primary structure−activity relationship that provides access to designed functions. The most powerful architectural motif used in our laboratory is based on monodisperse self-assembling amphiphilic dendrons[1−3] synthesized by an iterative convergent method.[4] Currently we are addressing the following question: what are the similarities and differences between narrow molecular weight distribution dendrons and other complex architectures during the process of self-assembly of supramolecular objects when compared to the self-assembly of similar objects generated from monodisperse building blocks? Toward this goal, we report here the elaboration of a new and universal strategy for the synthesis of complex molecular and macromolecular architectures by a combination of living polymerization reactions and TERMINI.

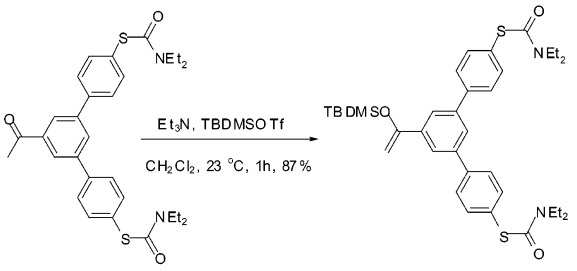
TERMINI is a new synthetic concept that stands for TERminator Multifunctional INItiator. Briefly, TERMINI represents a masked or protected multifunctional compound capable of quantitatively and irreversibly interrupting a living polymerization or a chain organic reaction. After deprotection or demasking the TERMINI functionality should reinitiate with 100% efficiency the same or a different living polymerization or with 100% chemoselectivity an organic reaction in more than one direction. During this reinitiation process the TERMINI repeat unit generates a branching point. In this publication we report the elaboration of a TERMINI that can be used in conjunction with metal-catalyzed living radical polymerization (LRP) and a diversity of conventional monomers. The demonstration of this universal strategy for the design and synthesis of complex macromolecules will be made by developing a novel iterative divergent strategy for the synthesis of dendritic macromolecules from commercial methacrylate monomers.

Results and Discussion

Elaboration of Synthetic Strategies and Analytical Methods. Selected reaction conditions for the control of chain end

(1) Percec, V.; Ahn, C.-H.; Ungar, G.; Yeardley, D. J. P.; Möller, M.; Sheiko, S. S. *Nature* **1998**, *391*, 161.
(2) (a) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855. (b) Balagurusamy, V. S. K.; Ungar, G.; Percec, V.; Johansson, G. *J. Am. Chem. Soc.* **1997**, *119*, 1523. (c) Hudson, S. D.; Jung, H.-T.; Percec, V.; Cho, W.-D.; Johansson, G.; Ungar, G.; Balagurusamy, V. S. K. *Science* **1997**, *278*, 449. (d) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **2001**, *123*, 1302. (e) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *Chem. Eur. J.* **2002**, *8*, 2011. (f) Percec, V.; Bera, T. K.; Glodde, M.; Fu, Q.; Balagurusamy, V. S. K.; Heiney, P. A. *Chem. Eur. J.* **2003**, *9*, 921.
(3) (a) Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Balagurusamy, V. S. K.; Shiyanovskaya, I.; Singer, K. D.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H.-W.; Hudson, S. D.; Duan, H. *Nature* **2002**, *419*, 384. (b) Ungar, G.; Liu, Y.; Zeng, X.; Percec, V.; Cho, W.-D. *Science* **2003**, *299*, 1208.
(4) For a review on convergent synthesis see: (a) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819. For pioneering work on convergent synthesis see: (b) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (c) Miller, T. M.; Neenan, T. X. *Chem. Mater.* **1990**, *2*, 346. (d) Moore, J. S.; Xu, Z. *Macromolecules* **1991**, *24*, 5893.

Scheme 1. Last Step of the Synthesis of (1,1-Dimethylethyl)[[1-[3,5-bis(*S*-phenyl 4-N,N′-diethylthiocarbamate)phenyl]ethenyl]oxy]dimethylsilane TERMINI



functionality, number average molecular weight (M_n), and polydispersity (PD) of linear macromolecules generated by metal-catalyzed LRP initiated with aryl and alkyl sulfonyl chloride initiators have been reported.[5,6] This expertise will be applied to the synthesis of dendritic macromolecules based on methyl methacrylate (MMA) by a combination of metal-catalyzed LRP and TERMINI. *N*,*N*′-Diethylthiocarbamate has been selected as a mask of aryl sulfonyl chloride, since sulfonyl chlorides represent the only available class of universal initiators for the LRP of a variety of monomers.[5,6] Alkyl halide based initiators undergo dimerization reactions during the initiation step[6c−e] of a living radical polymerization. In contrast, aryl sulfonyl chlorides provide 100% initiation efficiency and a much higher rate of initiation than propagation for styrenes, methacrylates, and acrylates.[6b] These two particularities of aryl sulfonyl chlorides warrant their selection as optimum candidates for the introduction of branching points. In addition, a demasking process that transforms the *N*,*N*′-diethylthiocarbamate into the aryl sulfonyl chloride in several minutes under very mild conditions at room temperature was elaborated.[7] Aryl enol ether has been selected as the 1,1-disubstituted olefin fragment of TERMINI that upon addition to radical species interrupts irreversibly their chain growth process.[8] The last step involved in the synthesis of TERMINI selected for the present series of experiments is illustrated in Scheme 1.

The TERMINI employed, (1,1-dimethylethyl)[[1-[3,5-bis(*S*-phenyl 4-*N*,*N*′-diethylthiocarbamate)phenyl]ethenyl]oxy]dimethylsilane, is obtained in five steps (55.3% overall yield) on starting from 4-methoxyphenylboronic acid and 3,5-dibromoacetophenone. The first four steps of this synthesis were reported previously.[7] TBDMSOTf was used for the fifth step (Scheme 1), since it provides the TBDMS enol ether under mild reaction conditions and in high yield.[9] At the same time, the TBDMS group offers sufficient stability to the enol ether both for long time storage and under the metal-catalyzed reaction conditions selected for the end-capping process. Since enol ethers are cleaved under acidic conditions, for this step we have employed our previously developed self-regulated catalytic system based on Cu_2O/bpy.[10] This catalytic system maintains neutral reaction conditions throughout all synthetic steps and creates in situ via a self-regulated mechanism[10] only the required concentration of highly reactive, nascent CuCl species. The small concentration of highly reactive nascent CuCl facilitates the production of an extremely low concentration of radical species and thus minimizes undesirable radical side reactions.[10,11] An important aspect regarding the TERMINI agent is that after end capping the excess of the unreacted enol ether or its precursor is recovered and reused. This provides an economic synthetic method, since an excess of TERMINI is used in each end-capping step.

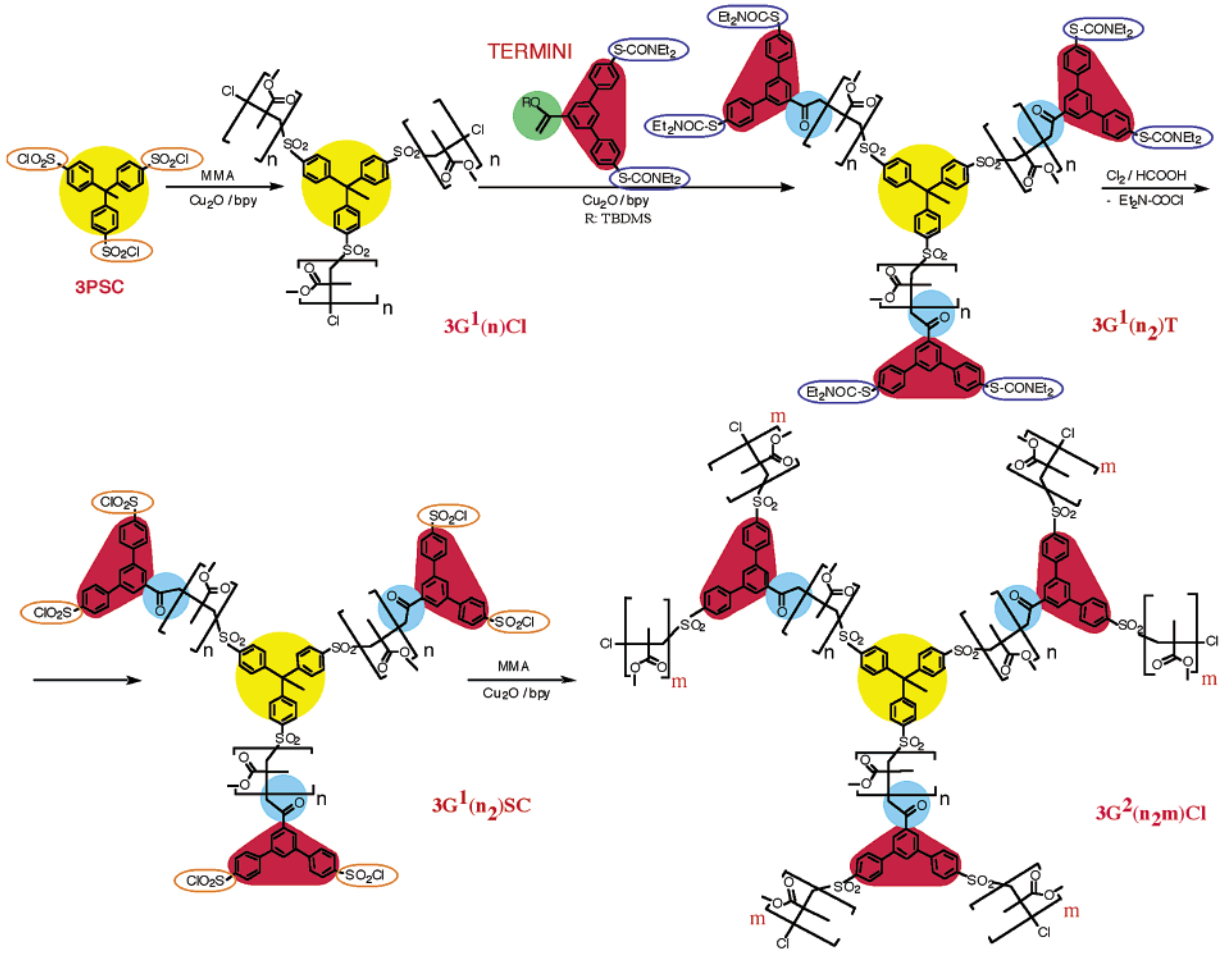
The divergent iterative synthesis elaborated on the basis of this TERMINI in conjunction with the trifunctional initiator 1,1,1-tris(4-chlorosulfonylphenyl)ethane (3PSC)[7] and MMA is outlined in Scheme 2. In the first step 3PSC is used as a trifunctional initiator to initiate the Cu_2O/bpy catalyzed LRP of MMA and produce the three-armed star polymer $3G^1(n)Cl$, where 3 stands for a trifunctional core, G^1 refers to the first generation, *n* is the degree of polymerization per arm (DP), and Cl represents the functionality present at the chain ends of each arm. Previously we have demonstrated by a combination of kinetic and structural analysis experiments that both 3PSC and the disulfonyl chloride resulting from TERMINI initiate the LRP of MMA with 100% efficiency.[11a] During the synthesis of $3G^1(n)Cl$ the conversion of MMA is monitored most conveniently by ^1H NMR spectroscopy.

In the second step of this sequence of reactions the $3G^1(n)Cl$ three-armed star is quantitatively end-capped using a 4× excess of TERMINI agent. This excess is required to avoid radical side reactions and to produce $3G^1(n_2)T$. Subscript 2 from $3G^1(n_2)T$ is the number of new arms generated from each TERMINI branching point located at the end of PMMA of DP = *n*, while T stands for TERMINI chain ends. This reaction step is monitored by a combination of ^1H NMR, gel permeation chromatography (GPC), size exclusion chromatography−multiangle laser light scattering (SEC-MALLS), and, when possible, by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectrometry. For early generations the combination of ^1H NMR, GPC, and MALDI-TOF provides the most efficient method of structural analysis. However, for higher generations or for dendritic macromolecules with a high DP of PMMA per arm, SEC-MALLS becomes the most suitable method of analysis. MALDI-TOF analysis of $3G^1(6_2)T$ is used here as an example to demonstrate the perfect control of the first two reaction steps.

The three series of peaks A−C from Figure 1 contain the initiator and three TERMINI moieties as, respectively, α and

(5) (a) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970. (b) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3635.
(6) For two representative publications that demonstrate the scope and capabilities of sulfonyl chloride initiators see: (a) Percec, V.; Kim, H.-J.; Barboiu, B. *Macromolecules* **1997**, *30*, 8526. (b) Percec, V.; Barboiu, B.; Kim, H.-J. *J. Am. Chem. Soc.* **1998**, *120*, 305. For recent reviews on metal-catalyzed LRP initiated with alkyl halides see: (c) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (d) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689. (e) Fischer, H. *Chem. Rev.* **2001**, *101*, 3581.
(7) Percec, V.; Bera, T. K.; De, B. B.; Sanai, Y.; Smith, J.; Holerca, M. N.; Barboiu, B.; Grubbs, R. B.; Fréchet, J. M. J. *J. Org. Chem.* **2001**, *66*, 2104.
(8) (a) Kamigata, N.; Udodaira, K.; Shimizu, T. *J. Chem. Soc., Perkin Trans. 1* **1997**, 783. (b) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6708. (c) Bon, S. A. F.; Steward, A. G.; Haddleton, D. M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2678. (d) Tokuchi, K.; Ando, T.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4735. (e) Snijder, A.; Klumperman, B.; van der Linde, R. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2350.
(9) (a) Mander, L. N.; Sethi, S. P. *Tetrahedron Lett.* **1984**, *25*, 5953. (b) Corey, E. J.; Cho, H.; Rucker, C.; Hua, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455.
(10) (a) Percec, V.; Barboiu, B.; van der Sluis, M. *Macromolecules* **1998**, *31*, 4053. (b) van der Sluis, M.; Barboiu, B.; Pesa, N.; Percec, V. *Macromolecules* **1998**, *31*, 9409.
(11) (a) Percec, V.; Barboiu, B.; Bera, T. K.; van der Sluis, M.; Grubbs, R. B.; Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4776. (b) Robello, D. R.; Andre, A.; McCovick, T. A.; Kraus, A.; Mourey, T. H. *Macromolecules* **2002**, *35*, 9334.

Scheme 2. Divergent Iterative Synthetic Strategy Elaborated for Synthesis of Dendritic PMMA by a Combination of LRP and TERMINI



ω chain ends of PMMA branches. The difference between these peaks in the same series equals the corresponding molar mass of the MMA unit, which is 100.12. Therefore, this MALDI-TOF analysis demonstrates the quantitative end capping of $3G^1(6_2)Cl$ with TERMINI groups.

The third step of this strategy involves the demasking that transforms the *N*,*N*′-diethylthiocarbamate groups of $3G^1(n_2)T$ into sulfonyl chloride groups. This step is accomplished by oxidative chlorination of $3G^1(n_2)T$ under mild conditions (7 min, at 23 °C) to transform quantitatively the masked sulfonyl chlorides of the TERMINI fragment into the active aryl sulfonyl chloride initiator groups. Details of this reaction step were reported previously.[7] The resulting $3G^1(n_2)SC$, where SC stands for sulfonyl chloride, represents a hexafunctional initiator capable of initiating the metal-catalyzed LRP of MMA to produce the second generation $3G^2(n_2m)Cl$, where *m* stands for the DP per arm of PMMA from the second generation. The instability of sulfonyl chlorides under the MALDI-TOF analysis conditions does not allow the use of this method for the structural analysis of $3G^1(n_2)SC$. Therefore, a combination of GPC, 500 MHz ^{1}H NMR, SEC-MALLS, and kinetic analysis was employed for the structural analysis of $3G^1(n_2)SC$ and for the demonstration of its structure. After the synthesis of $3G^1(n_2)$-SC, the previous sequence of these reaction steps that involves the metal-catalyzed LRP of MMA, end capping with TERMINI, and demasking was reiterated to produce four generations of dendritic macromolecules. For each generation each of these reaction steps is monitored by a combination of 500 MHz ^{1}H NMR spectroscopy, MALDI-TOF, GPC, and SEC-MALLS.

We will describe an example of ^{1}H NMR analysis for the synthesis of $3G^2(20_227)Cl$, starting from $3G^1(20)Cl$. The 500 MHz ^{1}H NMR spectrum of $3G^1(20)Cl$ (Figure 2) exhibits the resonance of methoxy protons from the PMMA main chain (signal c) at 3.57 ppm and the resonance of the methoxy protons of terminal MMA unit capped with an ω-end chlorine (signal d) at 3.73 ppm. The methoxy protons of the PMMA vicinal to the aryl sulfonyl moiety from 3PSC initiator (signal b) are observed at 3.67 ppm. In addition, the 3PSC initiator fragment exhibits the aromatic resonance a_1 at 7.23 ppm and a_2 at 7.8 ppm. The ratio between the integrals of a_1, a_2, d, and b is used to demonstrate not only the quantitative initiation but also the perfect degree of functionalization with chlorine chain ends. The ratio between the integrals of c and a_1, a_2, d, and b is used to calculate the DP of PMMA per branch (i.e., DP_{NMR}). DP_{NMR} is calculated with high accuracy up to values of about 100. DP_{NMR} agrees with the theoretical DP determined from the kinetic experiments that monitor the monomer conversion over time by NMR and with the values determined gravimetrically after the dendritic macromolecule was separated by precipitation in hexanes. Since there is excellent agreement between DPs determined by all these methods, in the sixth column of Table 1 we report the values of M_{th} that correspond to the M_n of the dendritic macromolecule calculated with the aid of $DP_{th/grav}$. M_{th} is calculated by using the following equation: $M_{th} = M_{init} + C$

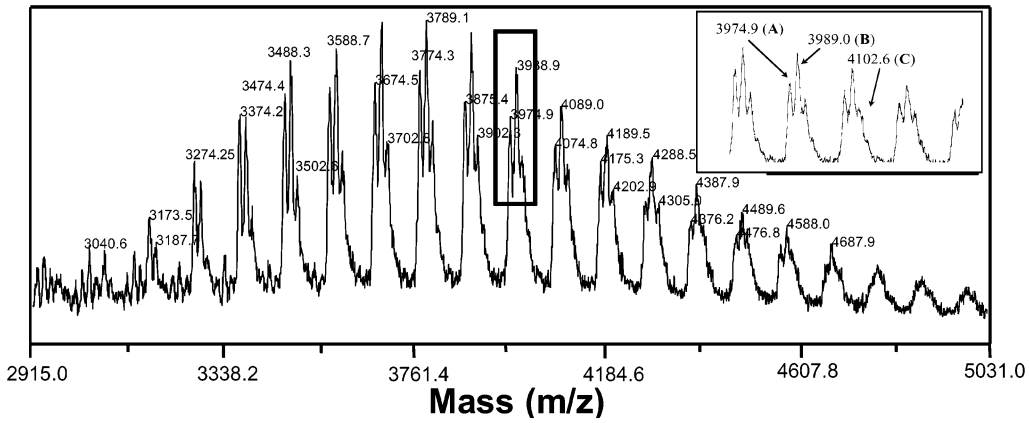


Figure 1. MALDI-TOF analysis of $3G^1(6_2)T$ synthesized by in situ Cu_2O/bpy catalyzed end capping of the MMA polymerization initiated with 3PSC (method B). Three homologous series of peaks have been identified: (**A**) $3G^1(6_2)T + Na^+$; (**B**) $3G^1(6_2)T + K^+$; (**C**) $3G^1(6_2)T + Ag^+ - H^+$.

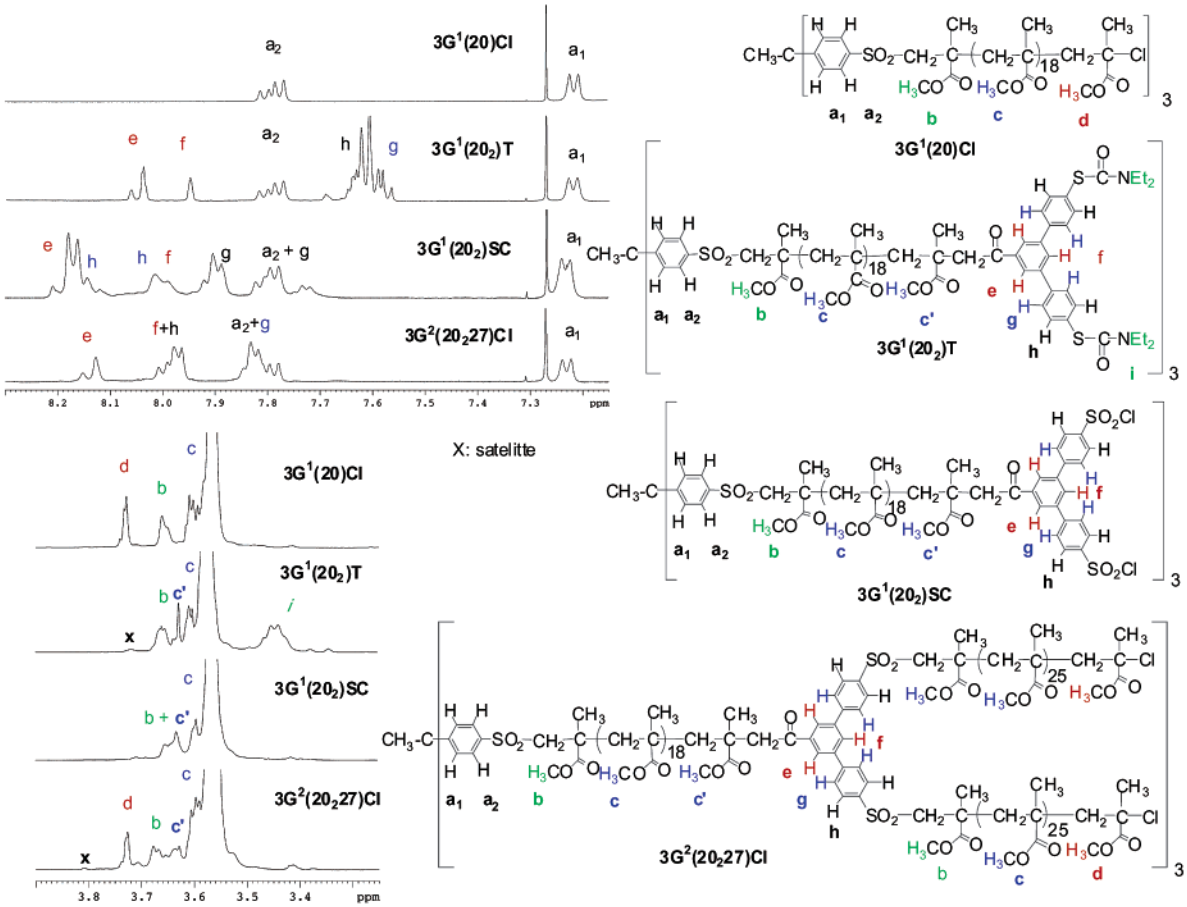


Figure 2. 500 MHz ^1H NMR analysis of the intermediary products generated during the synthesis of $3G^2(20_227)Cl$ starting from $3G^1(20)Cl$.

$\times M_{MMA} \times 3 \times 2^{n-1} \times DP$, where M_{init} represents the molar mass of the initiator employed in the polymerization, C represents the monomer conversion, M_{MMA} is the molar mass of MMA, n is the generation number (i.e., 1, 2, 3, 4), and DP is equal to the molar ratio of the initial monomer and sulfonyl chloride initiating groups (i.e., $DP = [M]_0/[-SO_2Cl]_0$. The end capping of $3G^1(20)Cl$ with TERMINI was qualitatively monitored by the disappearance of the resonance d at 3.73 ppm of the parent $3G^1(20)Cl$ (terminal methoxy group next to the Cl-chain end) and the appearance of a new resonance, c′, at 3.63 ppm (terminal methoxy group next to TERMINI chain end) and resonance i at 3.44 ppm (methylene protons of thiocarbamate group) of $3G^1(20_2)T$. However, quantitative end capping was established by the integration of the e, f, g, and h resonances of $3G^1(20_2)T$ versus its a_1 and a_2 resonances, since all these aromatic protons are well separated and have identical relaxation times. The demasking step of $3G^1(20_2)T$ is accomplished by the oxidative chlorination of $3G^1(20_2)T$ to transform the thiocarbamate groups into sulfonyl chloride groups and thus to provide $3G^1(20_2)SC$. During this step resonance i disappears and the signal e is shifted upfield, while f is shifted downfield. This reaction is most conveniently monitored by the decrease

Table 1. Synthesis of Three Series of Three-Armed Core Dendritic PMMA, Each Containing Four Generations, by Using Method A[a]

						GPC		SEC-MALLS	
	[MMA], M	10^2[–SO_2Cl], M	10^2[Cu_2O],M	conversn, %/time, h	$10^{-3}M_{th}$	$10^{-3}M_n$	M_w/M_n	dn/dc	$10^{-3}M_n$
$3G^1(15)Cl$	6.71	42.90	5.00	96/14	5.20	4.70	1.15		
$3G^2(15_226)Cl$	4.00	13.10	5.00	85/21	22.10	18.20	1.06	0.110	20.00
$3G^3(15_226_230)Cl$	3.48	6.50	4.40	56/36	60.70	36.40	1.08	0.120	55.75
$3G^4(15_226_230_280)Cl$	4.64	2.90	2.80	50/52	258.10	81.00	1.13	0.130	187.50
$3G^1(20)Cl$	3.10	9.30	1.76	60/12	7.70	6.10	1.12		
$3G^2(20_227)Cl$	2.17	4.00	1.37	50/14	24.46	20.10	1.08	0.090	24.53
$3G^3(20_227_223)Cl$	1.68	4.00	1.15	56/12	57.54	35.40	1.05	0.093	56.21
$3G^4(20_227_223_230)Cl$	0.77	1.33	1.15	52/22	140.07	65.20	1.09	0.135	149.40
$3G^1(100)Cl$	4.78	2.40	1.59	50/14	30.59	26.00	1.12	0.083	29.11
$3G^2(100_2100)Cl$	4.22	2.11	1.56	50/18	91.00	59.00	1.12	0.085	88.30
$3G^3(100_2100_2112)Cl$	3.42	1.71	1.54	56/7	213.76	102.20	1.19	0.085	191.20
$3G^4(100_2100_2112_2102)Cl$	1.69	0.84	1.36	51/9	464.08	168.20	1.23	0.087	456.20

[a] Definitions and conditions: DP_{ARM} = (conversn)$[M]_0/([I]_0/n)$, $[Cu_2O]/[bpy]$ =1/2, T = 90 °C, *p*-xylene, d*n*/d*c* in $cm^3\ g^{-1}$.

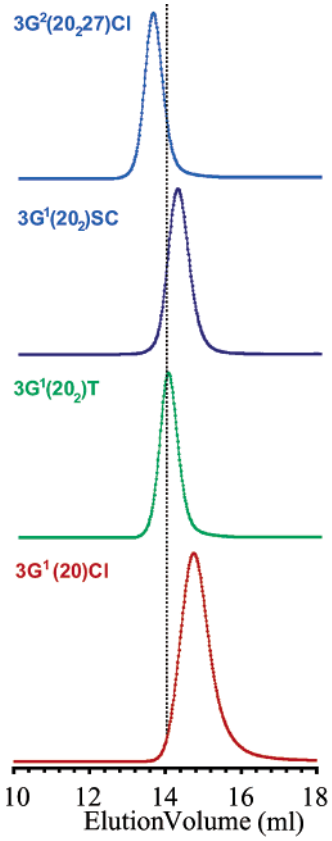


Figure 3. GPC analysis of the intermediary products generated during the synthesis of $3G^2(20_227)Cl$ starting from $3G^1(20)Cl$.

of signal i. The ^1H NMR spectrum of $3G^2(20_227)Cl$ shows again the signal d that is due to the terminal methoxy group containing a chlorine end. This resonance has the same chemical shift as the one from $3G^1(20)Cl$. As expected, the resonance corresponding to protons e of $3G^2(20_227)Cl$ is shifted upfield from the corresponding protons of $3G^2(20_2)SC$ and downfield from those of $3G^2(20_2)T$. The DP of PMMA per branch in $3G^2(20_227)Cl$ is calculated by the combination of techniques that was described for the analysis of $3G^1(20)Cl$. The sequence of reactions analyzed with the aid of the 500 MHz ^1H NMR spectra is also supported by the GPC analysis of $3G^1(20)Cl$, $3G^1(20_2)T$, $3G^1(20_2)SC$, and $3G^2(20_227)Cl$ (Figure 3).

As expected, end capping of $3G^1(20)Cl$ with TERMINI increases its molecular weight and as a consequence a shift toward lower elution volumes (V_e) is observed. Oxidative chlorination of $3G^1(20_2)T$ decreases the molecular weight of the newly formed $3G^1(20_2)SC$, and this is indeed observed in Figure 3. Finally, $3G^2(20_227)Cl$ has a higher molar mass than its precursor $3G^1(20_2)SC$, and this is demonstrated by the GPC trace from Figure 3. The quantitative transition between these four reaction steps without any detectable side reactions is demonstrated by the monomodal molecular weight distribution of these GPC traces.

Two methods have been elaborated to perform this iteration, consisting of three reaction steps (Scheme 3). The first method is based on an iterative process in which the required sequence of three reaction steps, i.e., LRP, end capping, and demasking, are executed separately (method A). In the second method (method B) the LRP and end capping are combined in a two-step one-pot process. Subsequently, in method B TERMINI is added to the reaction at a predetermined conversion during the LRP process. As a consequence, the first two steps of method A are combined, thus eliminating the need for the isolation and purification of the resulted dendritic macromolecule after the first reaction step. Therefore, method B reduces the time involved for the synthesis of one generation. These two methods complement each other in terms of controlled architecture, functionality of the chain ends, and number of purification steps.

New Dendritic Architectural Motifs Accessible by a Combination of LRP and TERMINI. A detailed inspection of Chart 1 reveals the capabilities of the new iterative strategy from Scheme 3 for the synthesis of dendritic macromolecules. We begin this discussion by following the structure of the fourth-generation $3G^4(n_2m_2p_2q_2)Cl$ from Chart 1a.

When the DP of PMMA in each generation is zero, the resulting dendritic macromolecule (Chart 1b) has a perfect monodisperse structure that resembles the structure of conventional dendrimers prepared by traditional divergent methods.[12,13]

(12) (a) Fréchet, J. M. J.; Tomalia, D. A. *Dendrimers and Dendritic Polymers*, Wiley: New York, 2001. (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons*; Wiley-VCH: Weinheim, Germany, 2001. (c) Tomalia, D. A.; Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2719.

(13) For some representative and pioneering examples of divergent strategies to dendrimers see: (a) Buhleier, E.; Wehner, W. I.; Vögtle, F. *Synthesis* **1978**, 155. (b) Tomalia, D. A.; Baker, H.; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Polym. J.* **1985**, *17*, 117. (c) Newkome, G. R.; Yao, Z.; Baker, R. G.; Gupta, V. K. *J. Org. Chem.* **1985**, *50*, 2003. (d) de Brabander-van den Berg, E.-M. M.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1308. (e) Wörner, C.; Mülhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1306. (f) Ihre, H.; De Jesus, L. P.; Fréchet, J. M. J.; *J. Am. Chem. Soc.* **2001**, *123*, 5908. (g) Peerlings, H. W. I.; van Benthem, R. A. T. M.; Meijer, E. W. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3112.

Scheme 3. The Two Methods Elaborated for the Synthesis of Dendritic Macromolecules by a Combination of LRP and TERMINI: (a) Method A: Consisting of Three Steps, Three Pots per Iteration; (b) Method B: Consisting of Three Steps, Two Pots per Iteration

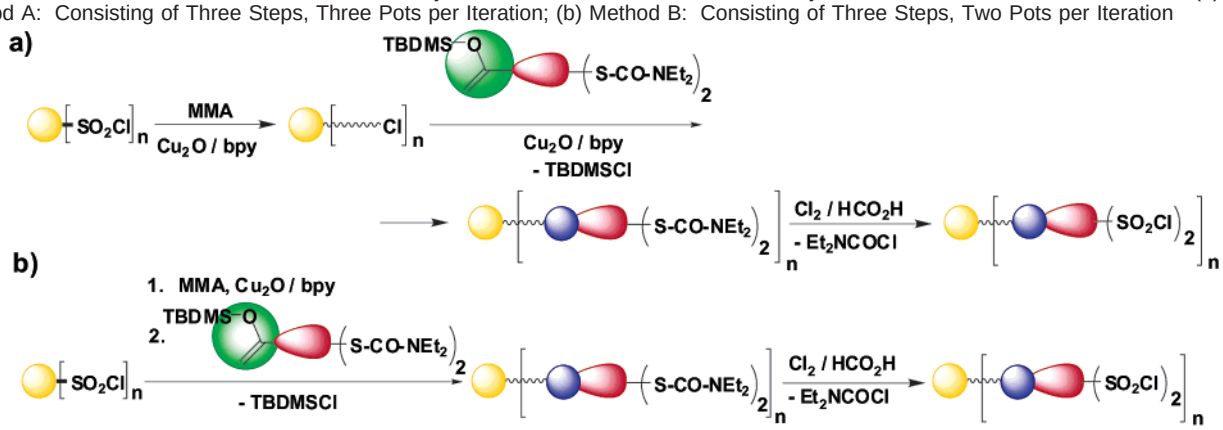
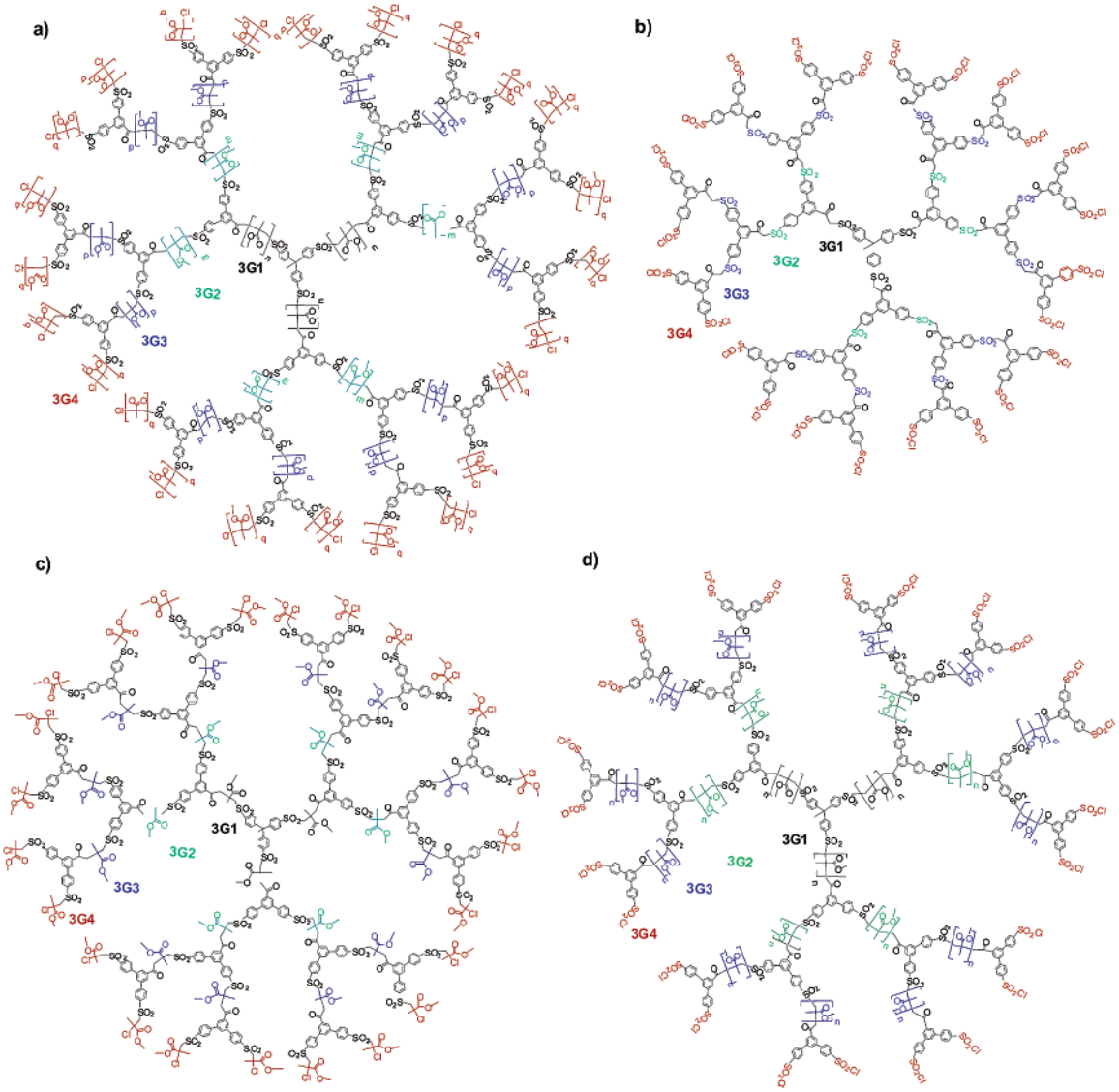


Chart 1. Dendritic Macromolecules Accessible by the Combination of LRP of MMA and the Bifunctional TERMINI Starting from the 3PSC−Trifunctional Iniatiator: (a) Containing Various DP of the PMMA per Arm and PMMA Chain Ends; (b) Containing DP of PMMA Equal to Zero and Sulfonyl Chloride Chain Ends; (c) Containing DP of PMMA Equal to 1 and MMA Adduct as Chain Ends; (d) Containing Various DP of the PMMA per Arm and Sulfonyl Chloride as Chain Ends



This structure can be synthesized by eliminating the polymerization step from Scheme 3 and is envisioned by deleting the PMMA branches from the structure of $3G^4(n_2m_2p_2q_2)Cl$ in Chart 1a and of $3G^4(n_2m_2p_2q_2)SC$ from Chart 1d. A monodisperse structure is also obtained for the case in which the DP of PMMA from each branch is equal to 1 in each generation (Chart 1c).

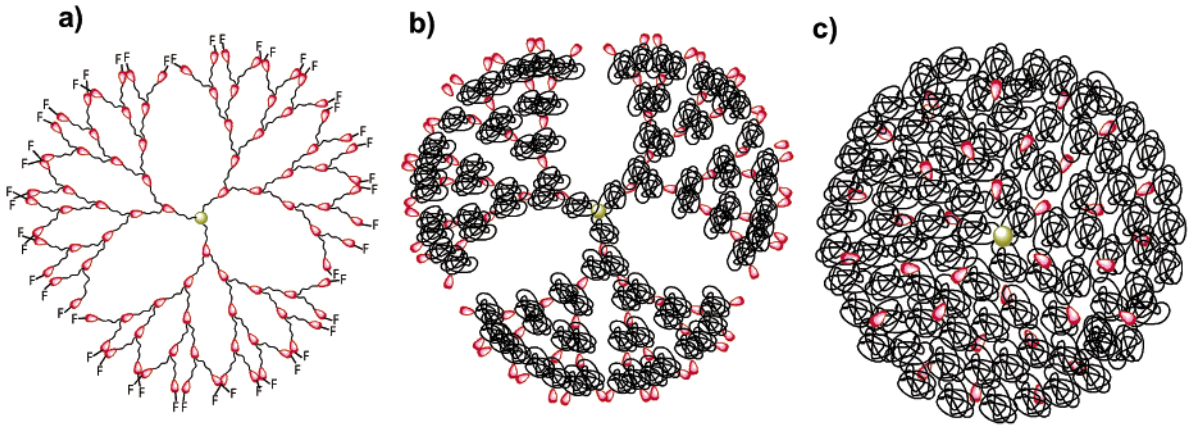


Figure 4. Depictions of dendritic macromolecules containing (a) small DP of PMMA to provide short and stiff chains between branching points, (b) medium DP of PMMA to provide flexible random coil conformation between the branching points, and (c) large DP of PMMA to provide long entangled chains between branching points. F denotes a functional group.

We have previously elaborated synthetic methods for the addition of only one monomer unit to any sulfonyl chloride initiator, and thus, the synthesis of the structures illustrated in Chart 1c is synthetically accessible.[6a] The last two methods for the synthesis of monodisperse dendrimers will be reported in future publications.

At least three different classes of dendritic macromolecules can be envisioned when the DP of PMMA per branch is larger than 1. In all cases the resulting dendritic macromolecules have a perfect degree of branching with a branching multiplicity equal to 2, and therefore, they differ from hyperbranched polymers,[14,15] for which the degree of branching (DB) is less controlled. At the same time they have a narrow molecular weight distribution (M_w/M_n) of the PMMA segments. As a consequence, these dendritic macromolecules differ from conventional monodisperse dendrimers synthesized by either divergent[12,13] or convergent methods.[4] In the first class of dendritic macromolecules accessible by the combination of LRP and TERMINI (Figure 4a) the DP per branch is larger than 1 but lower than the DP that defines the persistence length of PMMA. In this case the PMMA repeat units between branches are stiff, and as a consequence, each branch is fully elongated. The second class (Figure 4b) refers to DPs larger than the one corresponding to the persistence length of PMMA but lower than the DP which corresponds to the M_n that produces entangled chains. In this case the PMMA branches adopt a random-coil conformation. The third case refers to DPs which correspond to M_n values that are larger than the entanglement molecular weight (Figure 4c).

These three classes of dendritic macromolecules have no precedent and should exhibit completely different physical properties both between themselves and in comparison with classic dendrimers.[12] In addition to these three classes, combinations of different DP values per branch such as those described in the cases from parts a−c of Figure 4 can be incorporated within a single dendritic macromolecule. Finally, within any of the above-mentioned architectures, the structure of each generation can be changed by simply employing a different monomer. In addition, the structure of the outer shell of these dendritic macromolecules can be functionalized with different groups, shown as F in Figure 4a. Last but not least, the structures of these dendritic macromolecules can be modified by performing a diversity of chemical reactions on their repeat units.

Synthesis and Structural Analysis of Four Series, Each Containing Four Generations of Dendritic PMMA, Using Method A. The sequence of three iterative reactions combined as in method A was used to demonstrate the TERMINI concept for the synthesis of three series of dendritic PMMA. Each of these series of dendritic PMMA contains four generations, and the most representative data referring to their synthesis and structural characterization are summarized in Table 1. Table 1 reports data on the synthesis and the structure of these dendritic PMMA that include the DP of PMMA per branch in each generation (column 1), the most relevant reaction conditions employed in their synthesis (columns 2−5 and footnote), the molecular weights of the dendritic macromolecules determined by three different methods (columns 6, 7, and 10), their molecular weight distribution determined from GPC analysis (column 8), and the specific incremental refractive index, d*n*/d*c*, values (column 9) used in the determination of the average molecular weight (column 10) by SEC-MALLS.

The DP of PMMA per branch reported in the first column of Table 1 corresponds to the theoretical molecular weight from the sixth column and was calculated by the combination of kinetic, ^{1}H NMR, and gravimetric analysis described in the previous section.

This value is determined by multiplying the theoretical DP at 100% conversion, i.e., $[MMA]_0/[-SO_2Cl]_0$ obtained from columns 2 and 3, with the monomer conversion reported in column 5. The M_n values reported in column 7 were determined by GPC calibrated with PMMA standards. Since dendritic macromolecules have a hydrodynamic volume smaller than the corresponding linear PMMA, these $M_{n,GPC}$ values are, as expected, only relative and their dependence versus the real molecular weight (M_{th}) is strongly influenced by generation number.

(14) For recent reviews on hyperbranched polymers see: (a) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685. (b) Voit, B. I. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505. (c) Sunder, A.; Heinemann, J.; Frey, H. *Chem. Eur. J.* **2000**, *6*, 2499. (d) Kubisa, P. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 457.

(15) For recent conceptual advances in hyperbranched polymers see: (a) Emrick, T.; Chang, H.-T.; Fréchet, J. M. J. *Macromolecules* **1999**, *32*, 6380. (b) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059. (c) Markowski, L. J.; Thompson, J. L.; Moore, J. S. *Macromolecules* **2002**, *35*, 1599. (d) Guan, Z. *J. Am. Chem. Soc.* **2002**, *124*, 5616.

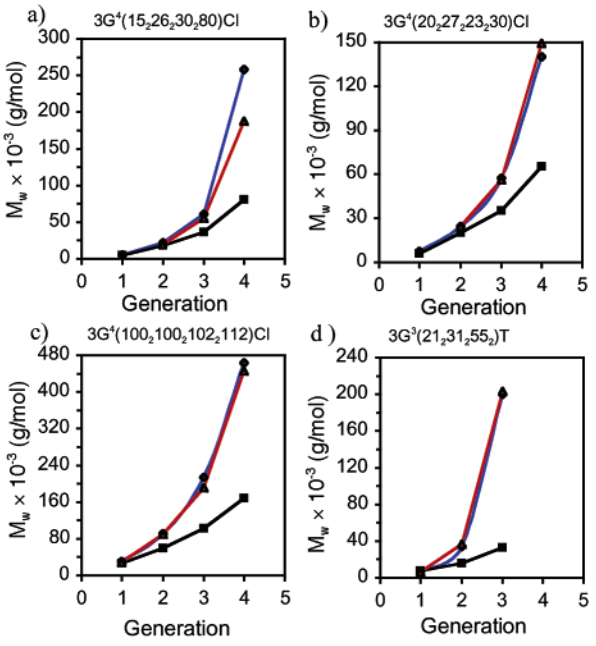


Figure 5. Dependence of M_{th} (◆), $M_{n,GPC}$ (■), and $M_{n,SEC-MALLS}$ (▲) on the generation number for four series of dendritic PMMA: (a) $3G^4(15_2$-$26_2 30_2 80)Cl$; (b) $3G^4(20_2 27_2 23_2 30)Cl$; (c) $3G^4(100_2 100_2 102_2 112)Cl$; (d) $3G^3(21_2 31_2 55_2)T$.

For example, at the first and, depending on DP, even at the second generation there is a relatively good agreement between $M_{n,GPC}$ and M_{th}. However, at higher generations $M_{n,GPC}$ values are lower than the absolute values. The difference between $M_{n,GPC}$ and M_{th} increases by increasing the generation number. This trend demonstrates that at and above generation 2 or 3 the dendritic macromolecules adopt the expected globular shape. This trend can be best observed by inspecting Figure 5a−c, which displays the dependence of M_{th}, $M_{n,GPC}$ and $M_{n,SEC-MALLS}$ from Table 1 versus generation number, *n*, for all three series of dendritic macromolecules synthesized by method A and for a set of dendritic PMMA prepared by method B (Figure 5d).

It is rewarding to see that the present series of dendritic macromolecules adopts the dendritic globular shape depending on DP per branch at generation 2 or 3. For example, these generations are lower than those at which Fréchet type[16] and other dendrimers undergo the transition to a globular shape. A careful inspection of Figure 5 shows that the onset of the globular shape is indicated by the deviation of the absolute molecular weight from the GPC molecular weight. This deviation is observed at generation 2 for dendritic PMMA with DP = 100 per branch (Figure 5c) and, respectively, 21 and 31 per branch (Figure 5d). At lower DP's per branch (Figure 5a,b) this deviation is observed at generation 3. This trend demonstrates that the larger DP per branch facilitates a globular shape at lower generations. This trend is most probably associated with the flexibility of PMMA branches, which increases with the increase in DP and, therefore, facilitates a globular shape more than the corresponding stiffer branches of lower DPs. This result will permit the design of dendritic macromolecules with globular shapes determined not only by the generation number[12,16] but also by the flexibility of their branches that in the synthetic strategy elaborated here can be controlled both by the structure of the monomer and by its DP per branch. In addition, the molecular weight distribution of the dendritic macromolecules reported in Table 1 is about as narrow as that reported for conventional "monodisperse" dendritic macromolecules that were prepared by either convergent or divergent methods.[2,4,13,16b]

The d*n*/d*c* values of all dendritic PMMA for which the absolute molecular weights were determined by SEC-MALLS experiments are reported in column 9 of Table 1. As expected, and observed experimentally, the d*n*/d*c* values of these dendritic macromolecules depend on the generation number, and for each generation their d*n*/d*c* value is determined by the DP of PMMA per branch. The strongest dependence of d*n*/d*c* on generation number is for the series of dendritic macromolecules with the lowest DP per branch. For dendritic macromolecules with the largest DP per branch the d*n*/d*c* values are close to the value reported for PMMA (d*n*/d*c* = 0.086 $cm^3\ g^{-1}$).[17] Finally, the last column in Table 1 summarizes the absolute molecular weight determined from SEC-MALLS experiments.

We will discuss very briefly the capabilities of the synthetic method A and of the most significant reaction parameters on the structure of the dendritic macromolecules from Table 1. The first series from Table 1 has DPs of PMMA per branch of 15, 26, 30, and 80. Attempts to produce a series of dendritic macromolecules with DP equal to 10 in each generation number was less successful because of the low solubility at the sulfonyl chloride stage of the dendritic structure. This is an expected behavior, since a DP equal to 10 produces a dendritic macromolecule with stiff branches. However, this solubility problem can be alleviated by small changes of the DP per branch in each generation. This explains the selection of DP per branch for the first series of dendritic macromolecules from Table 1. GPC traces of this series are presented in Figure 6a. All these GPC traces show a monomodal and narrow molecular weight distribution, despite the very high monomer conversions employed (96 and 85%) during the synthesis of the first and second generations.

It is expected that at very high conversions termination reactions that are second order in growing radicals are favored, since the monomer concentration is very low. However, neither GPC traces obtained with UV/RI detectors nor SEC-MALLS traces were able to detect any side reactions. In addition, at generations 3 and 4 there is an excellent agreement between the absolute molecular weight determined by SEC-MALLS and the M_{th} value (Table 1). Although the monomer conversion was lowered during the synthesis of generations 3 and 4, the first discrepancy between the M_{th} and $M_{n,SEC-MALLS}$ values occurs at generation 4. A more detailed inspection of the GPC trace of $3G^4(15_2 26_2 30_2 80)Cl$ from Figure 6a shows a very small deviation from the symmetric shape of the curve at lower elution volumes and, therefore, at higher molecular weights. We believe that a small amount of sample with higher molecular weight is obtained via termination by combination most probably during the first and second generation and becomes visible by GPC and SEC-MALLS analysis only at generation 4. This provides the discrepancy between the M_{th} and $M_{n,SEC-MALLS}$ values from

(16) (a) Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401. (b) Hawker, C. J.; Malmström, E. E.; Frank, K. W.; Kampf, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 9903. (c) Naylor, A. M.; Goddard, W. A., III; Kiefer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339. (d) Percec, V.; Cho, W.-D.; Mosier, P. E.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 11061.

(17) Anton, G. R. M.; Horta, A.; Fuentes, H. I. *Polym. Commun.* **1986**, *27*, 5.

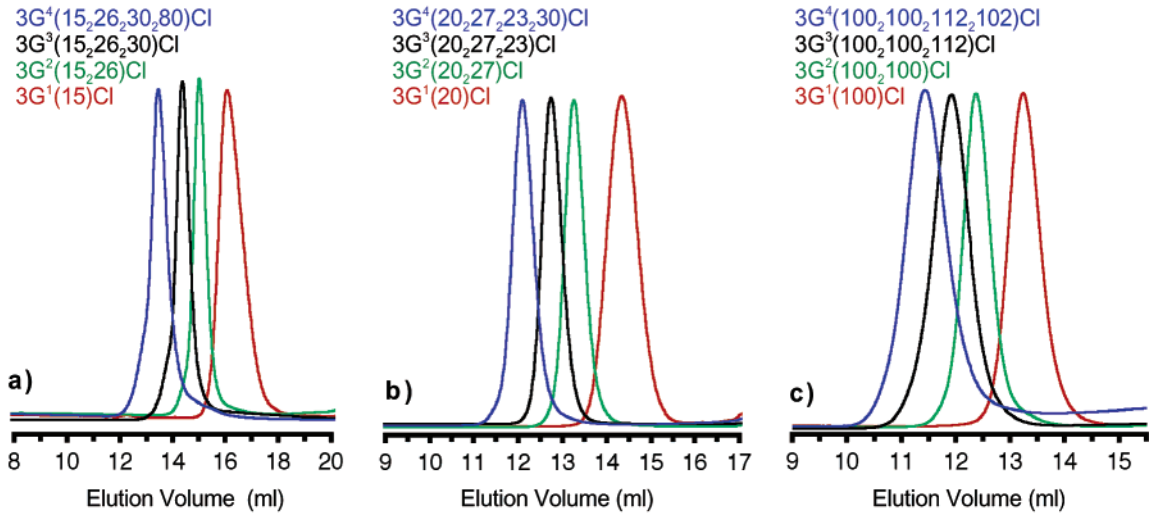


Figure 6. GPC analysis of dendritic PMMA synthesized by a combination of LRP and TERMINI by using method A: (a) $3G^4(15_226_230_280)Cl$; (b) $3G^4(20_2-27_223_230)Cl$; (c) $3G^4(100_2100_2102_2112)Cl$.

Table 1. The conclusion derived from this analysis is that in each generation the monomer conversion should be limited to about 50%.

The second series of dendritic macromolecules from Table 1 was synthesized with DPs of 20, 27, 23, and 30 per arm, at monomer conversions maintained between 50 and 60%. Dendritic macromolecules with excellent monomodal GPC traces were obtained (Figure 6b). The agreement between M_{th} and $M_{n,SEC-MALLS}$ for this series is excellent (Table 1), and this demonstrates that our decision to interrupt the polymerization at lower conversions eliminated the previously observed deviations of the experimental absolute molecular weights ($M_{n,SEC-MALLS}$) from the theoretical weight (M_{th}). The GPC traces from Figure 6b and ^{1}H NMR analysis discussed in the previous section (Figure 2) for the first two generations demonstrate excellent control during the synthesis of all four generations. The third series of dendritic macromolecules contains DPs of 100, 100, 112, and 102 per branch. This series was obtained at monomer conversions between 50 and 56%. No solubility problems were encountered at any generation and functional chain end when the PMMA dendritic macromolecules have a DP of at least 50 per branch. Excellent agreement between M_{th} and $M_{n,SEC-MALLS}$ in addition to narrow M_w/M_n values (Table 1 and Figure 6c) was observed for all generations when the DP per branch was about 100.

SEC-MALLS traces (Figure 7) confirm the monomodal character of the GPC chromatograms from Figure 6c. It is well-known that SEC-MALLS detects the presence of small concentrations of high-molecular-weight fractions, and their absence from the SEC-MALLS traces shows that there are no intermolecular secondary reactions or, if they occur, their extent is so small that it is not detectable by any of the analytical methods used.

In conventional size exclusion chromatography (SEC) or GPC the highest molecular weights elute at the lowest elution volume (V_e), and the radius of gyration (R_g) increases with molecular weight.[18] Therefore, both the values of molecular weight and

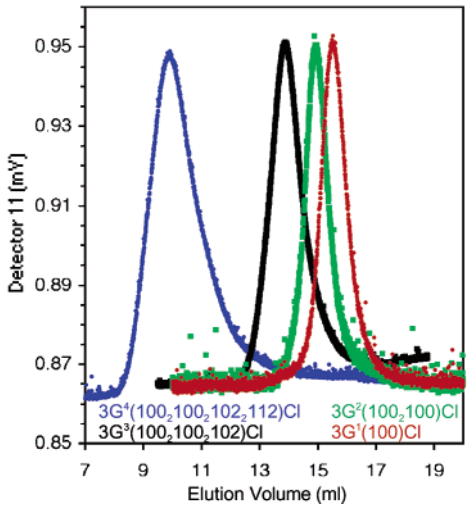


Figure 7. SEC-MALLS analysis of dendritic PMMA during the synthesis of $3G^4(100_2100_2102_2112)Cl$.

R_g should show a linear decrease with an increase of V_e.[19] A linear PMMA standard has been used to test this linearity and compare it to that of the dendritic PMMA (Figure 8).

Absence of aggregation in solution is detected by a monomodal shape of the SEC-MALLS curve (Figure 9) and a concentration-independent shape (Figure 10).

An interesting effect of the concentration on the shape of the peak obtained by SEC-MALLS (Figure 10) was observed. Although the GPC analysis of the first-generation $3G^1(100)Cl$ did not reveal the presence of any low-molecular-weight fraction, the more sensitive SEC-MALLS analysis demonstrated a deviation from the symmetry observed as a shoulder at higher V_e and, therefore, is expected to be of lower molecular weight on the curve obtained with $c = 38 \times 10^{-4}$ g/mL.

The plot of molecular weight versus V_e from Figure 10a shows that this shoulder is due to a higher molecular mass sample that does not elute via size exclusion principles.[18a] This shoulder disappears at lower concentrations ($c = 20 \times 10^{-4}$ g/mL), and at this concentration the molecular weight of the

(18) (a) Percec, V.; Ahn, C.-H.; Cho, W.-D.; Jamieson, A. M.; Kim, J.; Leman, T.; Schmidt, M.; Gerle, M.; Möller, M.; Prokhorova, S. A.; Sheiko, S. S.; Cheng, S. Z. D.; Zhang, A.; Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **1998**, *120*, 8619. (b) Wyatt, P. J. *Anal. Chim. Acta* **1993**, *272*, 1.

(19) Motherwell, W. B.; Crich, D. *Free Radical Reactions in Organic Synthesis*; Academic Press: New York, 1992.

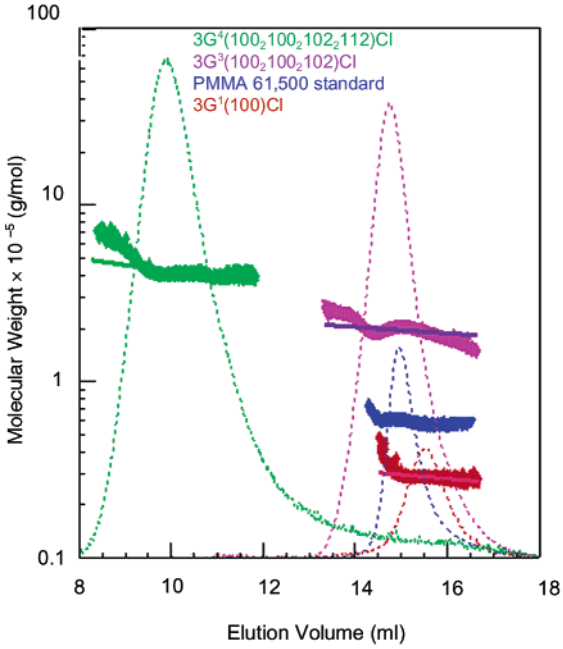


Figure 8. Comparative molar mass evolution for a linear PMMA standard and three generations of dendritic PMMA synthesized by a combination of LRP and TERMINI.

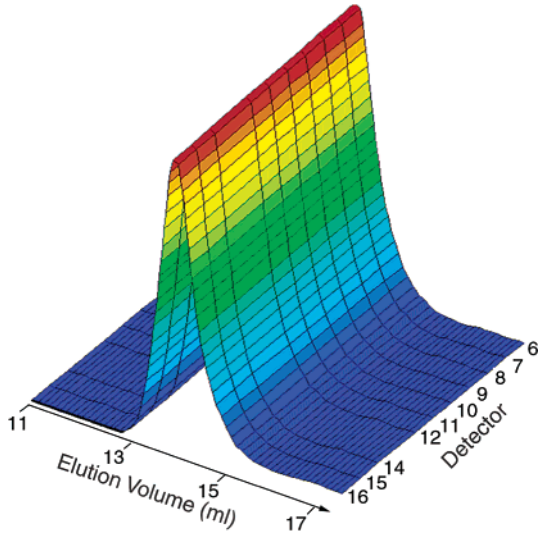


Figure 9. 3-D visualization of the SEC-MALLS chromatogram of $3G^3(100_2100_2102)Cl$.

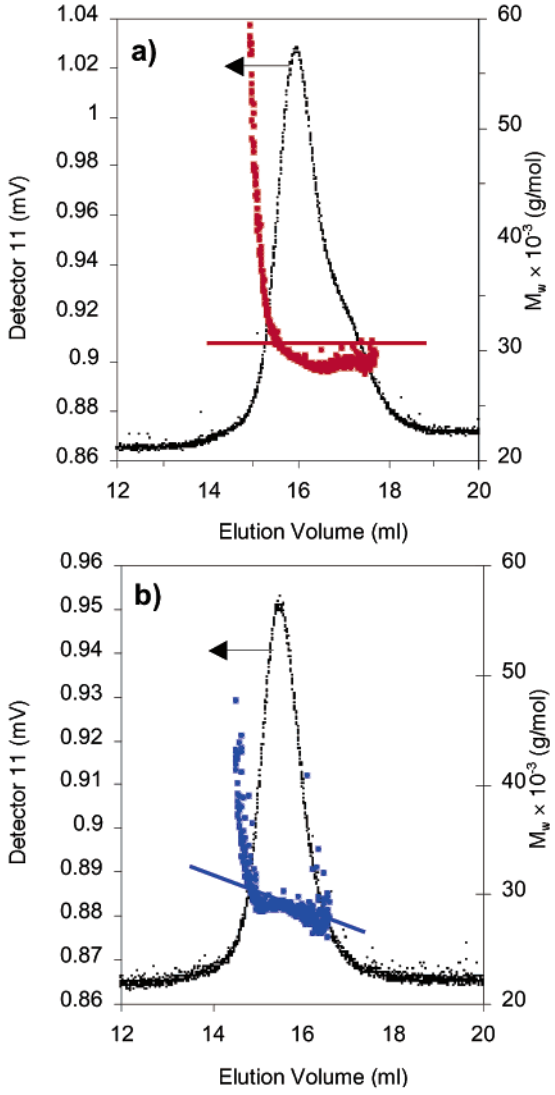


Figure 10. Effect of concentration on the SEC-MALLS and the dependence of absolute molecular weight on elution volume (V_e) for (a) $3G^1(100)Cl$ ($c = 38 \times 10^{-4}$ g/mL) and (b) $3G^1(100)Cl$ ($c = 20 \times 10^{-4}$ g/mL).

sample displays the expected trend in V_e (Figure 10b). Therefore, the shoulder from Figure 10a is associated with an intermolecular aggregate of dendritic macromolecules that is concentration dependent and does not form below a certain concentration. The determination of the molecular weight of the dendritic macromolecules by SEC-MALLS experiments was performed on monomodal samples prepared by dilution experiments such as the one described above, exhibiting a dependence of molecular weight on V_e similar to that shown in Figures 9 and 10b. The d*n*/d*c* values used in the calculation of the absolute molecular weights reported in Tables 1 and 2 were determined by successive dilution of the sample until the value remained constant.

Synthesis and Structural Analysis of a Series of Dendritic PMMA Containing Three Generations by Using Method B. An additional series of three generations of dendritic PMMA was prepared by method B. In this case, at a predetermined reaction time, corresponding to a certain monomer conversion, TERMINI was injected as a benzene solution, and then benzene was distilled and the polymerization process was monitored until the molecular weight of the dendritic macromolecule did not change with additional reaction time.

The competitive process between end capping with TERMINI and polymerization is expected to produce a molecular weight distribution of the dendritic macromolecule broader than that obtained by method A. However, at the same time method B reduces the extent of the radical side reaction, since both the excess of MMA and TERMINI are available throughout the entire synthesis. The end of end capping with TERMINI is monitored by GPC analysis, which follows the change in the molecular weight of the dendritic macromolecule as a function of time. When the molar mass value does not change over time, the end-capping process is completed. The complete end capping was also supported by MALDI-TOF analysis (Figure 1) and by ^{1}H NMR spectroscopy. Therefore, after in situ end capping (method B) the dendritic macromolecule has a TERMINI group on each chain end. The structure of the dendritic PMMA

Table 2. Synthesis of Three-Armed Core Dendritic PMMA Containing Three-Generations by Using Method B[a]

	[MMA], M	10^2[$-SO_2Cl$], M	10^2[Cu_2O],M	conversn, %/time, h	$10^{-3}M_{th}$	GPC $10^{-3}M_n$	GPC M_w/M_n	SEC-MALLS d*n*/d*c*	SEC-MALLS $10^{-3}M_n$
$3G^1(21_2)T$	5.16	21.62	2.17	88/20	7.20	7.30	1.09	0.149	
$3G^2(21_231_2)T$	4.13	6.66	3.88	50/18	34.40	16.00	1.15	0.106	36.67
$3G^3(21_231_255_2)T$	3.73	4.55	2.30	67/25	199.80	32.70	1.32	0.103	203.10

[a] Definitions and conditions: $DP_{ARM} = (\text{conversn})[M]_0/([I]_0/n)$, $[Cu_2O]/[bpy] = 1/2$, $T = 90$ °C, *p*-xylene, d*n*/d*c* in $cm^3\ g^{-1}$.

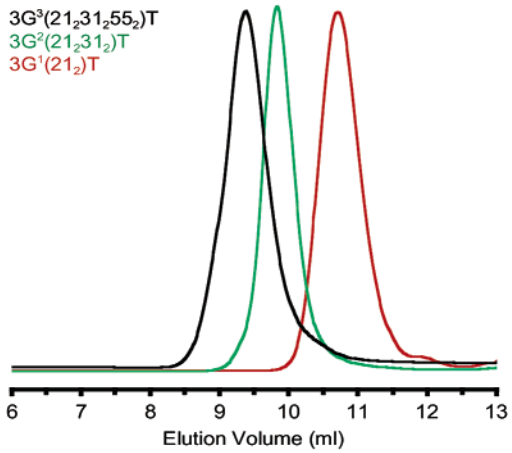


Figure 11. GPC analysis of the $3G^3(21_231_255_2)T$ series of dendritic PMMA synthesized by a combination of LRP and TERMINI by using method B.

obtained by method B explains the large values reported for d*n*/d*c* values reported in Table 2. However, the effect of the DP of PMMA on the d*n*/d*c* values of the dendritic macromolecule increases with DP per arm, and consequently, d*n*/d*c* values decrease with the increase of the generation number.

Symmetric GPC traces were obtained for all three generations (Figure 11), and good agreement between M_{th} and $M_{n,SEC-MALLS}$ was observed in all cases.

The only deficiency of method B is that the exact monomer conversion at which the end capping with TERMINI is completed cannot be predicted in advance of the kinetic experiment, since the reactivity of TERMINI does not seems to be much larger than the reactivity of MMA. Nevertheless, the reduction of the number of reactions and purification steps compensates for this deficiency.

The strategy elaborated here provides the first example of iterative synthesis of a complex organic molecule in which two main steps, from a total of three for each iteration, consist of a metal-catalyzed radical reaction. The third step represents a "demasking" which involves a quantitative oxidative chlorination that takes place under mild conditions in very short reaction time. Therefore, this strategy opens novel synthetic capabilities for free radical chain reactions[19] and living radical polymerizations[20] in complex organic synthesis.

The divergent strategy elaborated here resembles a method based on metal-catalyzed living ring-opening polymerization of ϵ-caprolactone[21] that was reported while our work was in progress.[22] However, the previously reported method is limited in scope to aliphatic polyesters as branches,[21] while the presently reported strategy is universal in scope, since it can be applied to a large diversity of methacrylates, acrylates, acrylonitrile,[23] methacrylonitrile, and styrenes. Therefore, our strategy will endow for the first time a direct comparison between the physical properties of well-established and well-understood linear polymers and their dendritic homologues. The understanding of their physical properties will allow the elaboration of novel technological concepts and applications based on conventional monomers. Last but not least, the synthetic capabilities demonstrated here for aryl sulfonyl chlorides as initiators for metal-catalyzed LRP are raising the fundamental question: when is the negligible level of radical dimerization required to induce the persistent radical effect[6e] taking place in their case, and what is the extent of this reaction that could not be detected during the synthetic experiments described here? Given the reversible character of the radical initiation with sulfonyl chlorides,[6b] this is a very challenging question. Research directed to answer this question is in progress in our laboratory.

Conclusions

A new synthetic concept named TERMINI, which stands for irreversible TERminator Multifunctional INItiator, was elaborated. A strategy based on a difunctional TERMINI molecule and metal-catalyzed LRP endows novel divergent methods for the synthesis of monodisperse dendrimers and dendritic macromolecules with narrow molecular weight distribution. Four series of dendritic macromolecules containing PMMA branches were reported in this publication. They have been synthesized by two different iterative methods: method A, involving three reaction steps in three pots, and method B, involving three reaction steps in two pots. The structural analysis of these dendritic macromolecules demonstrated the formation of the globular shape at generations that are determined by a tandem consisting of generation number and DP of the PMMA per branch. This result opens unprecedented strategies for the design and synthesis of dendritic macromolecules of predetermined shapes that are controlled by a combination of generation number, DP per branch and the chemical structure of the monomer repeat unit. The combination of TERMINI and metal-catalyzed LRP can be applied to a diversity of methacrylates, acrylates, acrylonitrile, methacrylonitrile, and styrenes, and therefore, it has a universal character. This strategy provides access to dendritic macromolecules with unprecedented structural complexity that are derived from the largest and the simplest class of commercial olefins. The design of more complex architectures based on this TERMINI concept and metal-catalyzed LRP and the development of libraries of TERMINI molecules suitable for nucleophilic and electrophilic

(20) (a) Webster, O. W. *Science* **1991**, *251*, 887. (b) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.
(21) (a) Trollsas, M.; Hedrick, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 4644. (b) Hedrick, J. L.; Magbitang, T.; Connor, E. F.; Glauser, T.; Volksen, W.; Hawker, C. J.; Lee, V. Y.; Miller, R. D. *Chem. Eur. J.* **2002**, *8*, 3308.
(22) Percec, V. Invited Lecture Presented at the IUPAC International Symposium on Ionic Polymerizations, Kyoto, Japan, July 19−23, 1999; Book of Abstracts, p 37; IUPAC: Kyoto, 1999.
(23) Barboiu, B.; Percec, V. *Macromolecules* **2001**, *34*, 8626.

reactions as well as for combinations of different chain organic and living polymerization reactions are in progress in our laboratory.

Experimental Section

General Methods. ^{1}H NMR (200, and 500 MHz) and ^{13}C NMR (50 and 106 MHz) spectra were recorded on Bruker spectrometers at 20 °C in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Column chromatographic purifications were conducted using 200−400 mesh silica gel obtained from Natland International Corp. Gel permeation chromatography (GPC) analyses were performed on a Shimadzu LC-10AT high-pressure liquid chromatograph equipped with a CTO-10A column oven (30 °C) containing four AM gel columns (10 μm, 500 Å, 10^4 Å, 10^5 Å, and 10^6 Å), a PE Nelson Analytical 900 Series integrator data station, a Shimadzu RID-10A RI detector, and a SPD-10A UV−vis detector (254 nm). Dichloromethane (Fisher) was used as eluent at a flow rate of 2 mL/min. M_n and M_w were determined using calibration plots constructed with PMMA standards. Size exclusion chromatography multiangle laser light scattering (SEC-MALLS) analysis was performed on a Wyatt EOS system (18 angles) equipped with Polymer Standard columns (10 μm, 500 Å, 10^4 Å, and 10^5 Å) and THF as eluent. A flow rate of 1 mL/min and 23 °C were set for these experiments. The light source was a 30 mW linear polarized GaAs (gallium arsenide) laser with $\lambda = 690$ nm. A Wyatt Optilab DSP (RI detector) was used as the concentration detector. The concentrations of the injected solutions were in the range of 1−4 g/L. Solutions of dendritic macromolecules in THF for light scattering and d*n*/d*c* experiments were made by dissolving weighted quantities (Shimadzu microbalance, Model AW 220, with an accuracy of 0.1 mg) in a known volume of filtered solvent (0.22 μm Millipore filters). Stock solutions for d*n*/d*c* experiments were equilibrated for 1 h before analysis and dilutions were made on a volumetric basis, by addition of known amounts of filtered solvent. The specific refractive index (d*n*/d*c*) values were determined on a Wyatt Optilab DSP polarimeter at 690 nm in THF at 23 °C. This was calibrated against NaCl−H_2O mixtures. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) spectrometry analysis was performed on a Voyager-DE instrument (Applied Biosystems) with a 337 nm nitrogen laser (pulse width 3 ns), an accelerating potential of 24 kV, and positive ionization. The sample preparation was done by using the dried droplet method:[24] 4.30 mg of (4-hydroxybenzylidene)malononitrile was dissolved in 400 μL of MeCN (HPLC grade) containing 0.1% TFA (v/v). A 2.20 mg amount of 3G^1-(6_2)T was dissolved in 40 μL of THF (HPLC grade). A 2.00 mg amount of NaCl was dissolved in 1 mL of freshly distilled H_2O. Successively, 0.5 μL from each of the prepared solutions described above was spotted on the target and allowed to dry for 20 min in the air.

Materials. All materials, unless otherwise noted, were purchased from Aldrich and used as received. Methyl methacrylate (MMA; 99+% purity) was passed through a basic Al_2O_3 chromatographic column (flash). A lecture bottle with chlorine gas (Aldrich, 99.5+%, 454 g) was equipped with a CGA-180 valve (Aldrich) and Teflon tubing (GPC type from Shimadzu, diameter 3 mm) to bubble the Cl_2 for oxidative chlorination experiments at a flow rate of 2 g/min. CuCl (Fisher, 96%) was purified by grinding and stirring with H_2SO_4 (1 N), followed by filtration and successive washing with glacial HOAc (four times), EtOH, and Et_2O. The white CuCl powder was dried at 100 °C for 30 min and stored in an airtight bottle. Benzene was purified on activated alumina columns. Copper(I) oxide (95+%) was used as received from Alfa. The 1,1,1-tris(4-chlorosulfonylphenyl)ethane (3PSC)[7] initiator and the 3,5-bis(*S*-phenyl 4-*N*,*N*′-diethylthiocarbamate)acetophenone[7] precursor to TERMINI were synthesized as reported previously.

Synthesis of (1,1-Dimethylethyl)[[1-[3,5-bis(*S*-phenyl 4-*N*,*N*′-diethylthiocarbamate)phenyl]ethenyl]oxy]dimethylsilane (TER-MINI). A two-necked 250 mL flask fitted with a magnetic stirring bar and N_2 inlet was charged with 3,5-bis(*S*-phenyl 4-*N*,*N*′-diethylthiocarbamate)acetophenone[7] (6.50 g, 12.21 mmol), triethylamine (4.94 g, 48.85 mmol), and 50 mL of dry CH_2Cl_2. To the ice−water bath cooled reaction mixture was added *t*BuMe$_2$SiOTf (7.3 mL, 32.00 mmol) dropwise, and the solution was warned to 23 °C. After 30 min a sample was taken, the solvent was evaporated, and the white solid was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR. When the acetyl protons (2.66 ppm) were absent in the ^{1}H NMR spectrum, the reaction mixture was diluted with 250 mL of CH_2Cl_2, washed with 100 mL of 10% KOH two times and then washed with brine, and dried over Na_2SO_4. Solvent was removed on a rotary evaporator, and the yellow solid was purified by column chromatography (silica gel, 30% EtOAc in hexanes as eluent) to produce 6.90 g (87%) of white crystals. $R_f = 0.44$ (7/3 hexanes/EtOAc). Mp: 143−145 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.83−7.58 (m, 11H), 5.31(s, 1H), 4.52 (s, 1H), 3.52 (q, 8H), 1.27 (b, 12H), 1.03 (s, 9H), 0.26 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 165.95, 155.97, 142.08, 141.24, 139.29, 136.44, 129.11, 126.42, 123.81, 91.93, 42.72, 26.21, 18.66, 14.13, −4.22.

Synthesis of 3G^1(6_2)T. MMA (2.00 g, 19.97 mmol), *p*-xylene (5 mL), initiator (3PSC, 0.50 g, 0.90 mmol), catalyst (Cu_2O, 80.00 mg, 0.56 mmol), ligand (bpy, 170.00 mg, 1.09 mmol), and benzene (1 mL) were weighed directly into a 25 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated at 90 °C in an oil bath. The reaction was monitored by ^{1}H NMR, and when conversion reached 81%, 2 mL of polymerization mixture was removed and a solution of TERMINI (2.90 g, 4.49 mmol) in a previously degassed 10 mL mixture of *p*-xylene and benzene (1/1) was added via cannula. The temperature was raised to 120 °C, and the benzene azeotrope was distilled under Ar. The reaction was continued for 3 days, and then the mixture was diluted with CH_2Cl_2 and passed through a short basic alumina column to remove the catalyst and TERMINI. The solvent was removed on a rotary evaporator to yield 0.80 g of 3G^1(6_2)T, which was dried under vacuum for 24 h and then analyzed by MALDI-TOF. No purification by precipitation was involved. Therefore, all the species formed during polymerization and end capping were available to be analyzed by MALDI-TOF (M_n = 3873 and $M_w/M_n = 1.02$, $M_{th} = 3834$). All the ions were accounted for, and no evidence of termination was found. The assigned spectrum is presented in Figure 1.

Synthesis of 3G^1(20)Cl. MMA (11.5 mL, 106.8 mmol), *p*-xylene (23 mL), initiator (3PSC, 0.50 g, 0.90 mmol), catalyst (Cu_2O, 87.00 mg, 0.61 mmol), and ligand (bpy, 192.00 mg, 1.23 mmol) were weighed directly into a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 90 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove samples at predetermined times using an airtight syringe. Samples were dissolved in $CDCl_3$, and the conversion was measured by ^{1}H NMR spectroscopy. After the desired conversion (61%, $M_{th} = 7700$) was reached, the reaction mixture was diluted with CH_2Cl_2, passed through a short basic alumina column to remove the catalyst, and then precipitated twice in cold hexanes. The product was separated by filtration and dried under vacuum to yield 6.20 g of 3G^1(20)Cl (58%). $M_{n,NMR} = 7400$, $M_{n,GPC} = 6100$, and $M_w/M_n = 1.12$. Due to the low molecular weight, SEC-MALLS analysis of this sample was not accessible.

Synthesis of 3G^1(20_2)T. 3G^1(20)Cl (2.30 g, 0.30 mmol), *p*-xylene (5 mL), TERMINI (2.31 g, 3.57 mmol), catalyst (CuCl, 44.35 mg, 0.44 mmol), ligand (bpy, 140.00 mg, 0.90 mmol), and benzene (6 mL) were placed in a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 110 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove the water−benzene azeotrope and prevent TERMINI hydrolysis. The reaction was monitored for the disappearance of the corresponding Cl-chain end using ^{1}H NMR spectroscopy. After 2.5 h the reaction mixture was opened to the

(24) Linnemayr, K.; Vana, P.; Allmaier, G. *Rapid Commun. Mass. Spectrom.* **1998**, *12*, 1344.

atmosphere, diluted with CH_2Cl_2, and then passed through a short column containing basic alumina to remove the catalyst and TERMINI. The solvent was distilled, and the concentrated polymer solution was precipitated twice in cold hexanes and once in acidic methanol to yield 2.50 g (87%) of $3G^1(20_2)$T.

Synthesis of $3G^1(20_2)$SC. A dilute solution of $3G^1(20_2)$T (3.00 g, 0.33 mmol) in 300 mL of CH_2Cl_2 was vigorously stirred with 100 mL of an aqueous solution of HCO_2H (1% v/v) at 23 °C, and Cl_2 gas was passed through until the emulsion had a stable pale yellow color. The CH_2Cl_2 phase was separated, washed with H_2O, $NaHCO_3$, and brine, dried over Na_2SO_4, concentrated, and precipitated three times in acidic MeOH to give 2.31 g (78%) of product.

Synthesis of $3G^2(20_227)$Cl. MMA (7.10 g, 70.90 mmol), *p*-xylene (25 mL), initiator ($3G^1(20_2)$SC, 1.80 g, 0.23 mmol), catalyst (Cu_2O, 64.00 mg, 0.45 mmol), and ligand (bpy, 140.00 mg, 0.89 mmol) were placed in a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 90 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove samples at predetermined times using an airtight syringe. Samples were dissolved in $CDCl_3$, and the conversion was measured by ^{1}H NMR spectroscopy. After the desired conversion (56%, $M_{th} = 24\,460$) was reached, the reaction mixture was diluted with CH_2Cl_2 and passed through a short basic alumina column to remove the catalyst, The product was precipitated twice in cold hexanes, filtered, and dried under vacuum to yield 4.00 g (70%) of $3G^2(20_227_2)$Cl. $M_{n,NMR} = 24\,400$, $M_{n,GPC} = 20\,100$, $M_w/M_n = 1.08$, and $M_{n,SEC-MALLS} = 24\,530$.

Synthesis of $3G^2(20_227_2)$T. $3G^2(20_227)$Cl (3.00 g, 0.12 mmol), *p*-xylene (15 mL), TERMINI (2.36 g, 3.65 mmol), catalyst (CuCl, 36.21 mg, 0.36 mmol), ligand (bpy, 114.00 mg, 0.73 mmol), and benzene (6 mL) were weighed into a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 110 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove the water−benzene azeotrope. The reaction was monitored for the disappearance of the Cl-chain end using ^{1}H NMR spectroscopy. After 4 h, the reaction mixture was opened to the atmosphere, diluted with CH_2Cl_2, and then passed through a short basic alumina column to remove the catalyst and TERMINI. The solvent was removed on a rotary evaporator, and the concentrated polymer solution was precipitated twice in cold hexanes and once in acidic methanol to yield 2.70 g (88%) of $3G^2(20_227_2)$T.

Synthesis of $3G^2(20_227_2)$SC. A dilute solution of $3G^2(20_227_2)$T (2.60 g, 0.10 mmol) in 200 mL of CH_2Cl_2 was vigorously stirred with 100 mL of an aqueous solution of HCO_2H (1% v/v) at 23 °C, and Cl_2 gas was passed through until the emulsion had a stable pale yellow color. The CH_2Cl_2 phase was separated, washed with H_2O, $NaHCO_3$, and brine, dried over Na_2SO_4, concentrated, and precipitated three times in acidic MeOH to give 2.50 g (96%) of $3G^2(20_227_2)$SC.

Synthesis of $3G^3(20_227_223)$Cl. MMA (6.15 g, 61.40 mmol), *p*-xylene (30 mL), initiator $3G^2(20_227_2)$SC (2.47 g, 0.09 mmol), catalyst (Cu_2O, 64.00 mg, 0.42 mmol), and ligand (bpy, 140.00 mg, 0.83 mmol) were weighed into a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated at 90 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove samples at predetermined times using an airtight syringe. Samples were dissolved in $CDCl_3$, and the conversion was measured by ^{1}H NMR spectroscopy. After the desired conversion (40%, $M_{th} = 57\,540$) was reached, the reaction mixture was diluted with CH_2Cl_2, passed through a short basic alumina column to remove the catalyst, and then precipitated twice in cold hexanes. The product was recovered by filtration and dried under vacuum to yield 3.70 g (76%) of $3G^3(20_227_223)$Cl. $M_{n,NMR} = 57\,450$, $M_{n,GPC} = 35\,400$, $M_w/M_n = 1.05$, and $M_{n,SEC-MALLS} = 56\,210$.

Synthesis of $3G^3(20_227_223_2)$T. $3G^3(20_227_223)$Cl (2.40 g, 0.04 mmol), *p*-xylene (25 mL), TERMINI (1.93 g, 3.00 mmol), catalyst (CuCl, 30.00 mg, 0.30 mmol), ligand (bpy, 94.50 mg, 0.61 mmol), and benzene (6 mL) were placed in a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 110 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove the water−benzene azeotrope and prevent TERMINI hydrolysis. The reaction was monitored for the disappearance of the Cl-chain end using ^{1}H NMR. After 5.5 h the reaction mixture was opened to the atmosphere, diluted with CH_2Cl_2, and passed through a short basic alumina column to remove the catalyst and excess of TERMINI. The solvent was removed on a rotary evaporator and the concentrated polymer solution precipitated twice in cold hexanes and once in acidic methanol to yield 2.30 g (87%) of $3G^3(20_227_223_2)$T.

Synthesis of $3G^3(20_227_223_2)$SC. A dilute solution of $3G^3(20_227_223_2)$T (2.25 g, 0.03 mmol) in 200 mL of CH_2Cl_2 was vigorously stirred with 100 mL of an aqueous solution of HCO_2H (1% v/v) at 25 °C, and Cl_2 gas was passed through until the emulsion had a stable pale yellow color. The CH_2Cl_2 phase was separated, washed with H_2O, $NaHCO_3$, and brine, dried over Na_2SO_4, concentrated, and precipitated three times in acidic MeOH to give 2.00 g (91%) of dendritic PMMA initiator.

Synthesis of $3G^4(20_227_223_230)$Cl. MMA (2.66 g, 26.60 mmol), *p*-xylene (30 mL), initiator $3G^3(20_227_223_2)$SC (1.00 g, 0.01 mmol), catalyst (Cu_2O, 54.00 mg, 0.37 mmol), and ligand (bpy, 117.00 mg, 0.74 mmol) were weighed into a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 90 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove samples at predetermined times using an airtight syringe. Samples were dissolved in $CDCl_3$, and the conversion was measured by ^{1}H NMR spectroscopy. After the desired conversion (46%, $M_{th} = 140\,070$) was reached, the reaction mixture was diluted with CH_2Cl_2, passed through a short basic alumina column to remove the catalyst, and then precipitated twice in cold hexanes. The product was recovered by filtration and dried under vacuum to yield 2.10 g (89%) of $3G^4(20_227_223_230)$Cl. $M_{n,NMR} = 136\,800$, $M_{n,GPC} = 65\,200$, $M_w/M_n = 1.09$, and $M_{n,SEC-MALLS} = 149\,400$.

Synthesis of $3G^1(100)$Cl. MMA (10.85 g, 108.00 mmol), *p*-xylene (11 mL), initiator (3PSC, 0.10 g, 0.18 mmol), catalyst (Cu_2O, 51.70 mg, 0.34 mmol), and ligand (bpy, 112.80 mg, 0.72 mmol) were weighed directly into a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 90 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove samples at predetermined times using an airtight syringe. Samples were dissolved in $CDCl_3$, and the conversion was measured by ^{1}H NMR spectroscopy. After the desired conversion (50%, $M_{th} = 30\,590$) was reached, the reaction mixture was diluted with CH_2Cl_2, passed through a short basic alumina column to remove the catalyst, and then precipitated twice in cold hexanes. The product was recovered by filtration and dried under vacuum to yield 5.00 g (91%) of $3G^1(100)$Cl. $M_{n,GPC} = 26\,000$, $M_w/M_n = 1.12$, and $M_{n,SEC-MALLS} = 29\,100$.

Synthesis of $3G^1(100_2)$T. $3G^1(100)$Cl (3.00 g, 0.10 mmol), *p*-xylene (10 mL), TERMINI (0.48 g, 0.75 mmol), catalyst (Cu_2O, 30.00 mg, 0.02 mmol), ligand (bpy, 65.00 mg, 0.04 mmol), and benzene (6 mL) were added to a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 110 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove the water−benzene azeotrope. The reaction was monitored for the disappearance of the Cl-chain ends using ^{1}H NMR spectroscopy. After 50 h the reaction mixture was opened to the atmosphere, diluted with CH_2Cl_2, and passed through a short basic alumina column to remove the catalyst and excess TERMINI; the solvent was then distilled and the concentrated polymer solution was precipitated twice in cold hexanes and once in acidic methanol to yield 2.80 g (91%) of $3G^1(100_2)$T.

Synthesis of $3G^1(100_2)$SC. A dilute solution of $3G^1(100_2)$T (2.70 g, 0.08 mmol) in 200 mL of CH_2Cl_2 was vigorously stirred with 100

mL of an aqueous solution of HCO_2H (1% v/v) at 25 °C, and Cl_2 gas was passed through until the emulsion had a stable yellow color. The CH_2Cl_2 phase was separated, washed with H_2O, $NaHCO_3$, and brine, dried over Na_2SO_4, concentrated, and precipitated three times in acidic MeOH to give 2.60 g (98%) of $3G^1(100_2)$SC.

Synthesis of $3G^2(100_2100)$Cl. MMA (9.80 g, 0.97 mmol), *p*-xylene (12 mL), initiator $3G^1(100_2)$SC (2.50 g, 0.08 mmol), catalyst (Cu_2O, 49.00 mg, 0.34 mmol), and ligand (bpy, 106.00 mg, 0.68 mmol) were weighed into a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 90 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove samples at predetermined times using an airtight syringe. Samples were dissolved in $CDCl_3$, and the conversion was measured by ^{1}H NMR spectroscopy. After the desired conversion (50%, $M_{th} = 91\,000$) was reached, the reaction mixture was diluted with CH_2Cl_2, passed through a short basic alumina column to remove the catalyst, and then precipitated twice in cold hexanes. The product was recovered by filtration and dried under vacuum to yield 6.20 g (80%) of $3G^2(100_2100)$Cl. $M_{n,GPC} = 59\,000$, $M_w/M_n = 1.12$, and $M_{n,SEC-MALLS} = 88\,300$.

Synthesis of $3G^2(100_2100_2)$T. $3G^2(100_2100)$Cl (4.00 g, 0.04 mmol), *p*-xylene (14 mL), TERMINI (0.43 g, 0.66 mmol), catalyst (Cu_2O, 42.00 mg, 0.29 mmol), ligand (bpy, 91.50 mg, 0.58 mmol), and benzene (6 mL) were weighed into a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 110 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove the water−benzene azeotrope. The reaction was monitored for the disappearance of the Cl-chain ends using ^{1}H NMR spectroscopy. After 16 h the reaction mixture was opened to the atmosphere, diluted with CH_2Cl_2, then passed through a short basic alumina column to remove the catalyst and excess TERMINI. The solvent was distilled on a rotary evaporator, and the concentrated polymer solution was precipitated twice in cold hexanes and once in acidic methanol to yield 3.20 g (77%) of $3G^2(100_2100_2)$T.

Synthesis of $3G^2(100_2100_2)$SC. A dilute solution of $3G^2(100_2100_2)$T (3.10 g, 0.03 mmol) in 200 mL of CH_2Cl_2 was vigorously stirred with 100 mL of an aqueous solution of HCO_2H (1% v/v) at 23 °C, and Cl_2 gas was passed through until the emulsion had a stable pale yellow color. The CH_2Cl_2 phase was separated, washed with H_2O, $NaHCO_3$, and brine, dried over Na_2SO_4, concentrated, and then precipitated three times in acidic MeOH to give 2.60 g (98%) of dendritic PMMA initiator.

Synthesis of $3G^3(100_2100_2112)$Cl. MMA (6.40 g, 64.10 mmol), *p*-xylene (12 mL), initiator $3G^2(100_2100_2)$SC (2.50 g, 0.03 mmol), catalyst (Cu_2O, 42.00 mg, 0.29 mmol), and ligand (bpy, 91.10 mg, 0.58 mmol) were weighed into a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 90 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove samples at predetermined times using an airtight syringe. Samples were dissolved in $CDCl_3$, and the conversion was measured by ^{1}H NMR spectroscopy. After the desired conversion (56%, $M_{th} = 213\,760$) was reached, the reaction mixture was diluted with CH_2Cl_2, passed through a short basic alumina column to remove the catalyst, and then precipitated twice in cold hexanes. The product was recovered by filtration and dried under vacuum to yield 4.70 g (77%) of $3G^3(100_2100_2112)$Cl. $M_{n,GPC} = 102\,200$, $M_w/M_n = 1.19$, and $M_{n,SEC-MALLS} = 191\,200$.

Synthesis of $3G^3(100_2100_2112_2)$T. $3G^3(100_2100_2112)$Cl (3.50 g, 0.01 mmol), *p*-xylene (20 mL), TERMINI (0.62 g, 0.96 mmol), catalyst (Cu_2O, 10.00 mg, 0.10 mmol), ligand (bpy, 31.50 mg, 0.21 mmol), and benzene (6 mL) were placed in a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 110 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove the water−benzene azeotrope. The reaction was monitored for the disappearance of the corresponding Cl-chain end using ^{1}H NMR spectroscopy. After 8 h the reaction mixture was opened to the atmosphere, diluted with CH_2Cl_2, and then passed through a short basic alumina column to remove the catalyst and excess of TERMINI. The solvent was distilled, and the concentrated polymer solution was precipitated twice in cold hexanes and once in acidic methanol to yield 2.90 g (90%) of $3G^3(100_2100_2112_2)$T.

Synthesis of $3G^3(100_2100_2112_2)$SC. A dilute solution of $3G^3(100_2100_2112_2)$T (2.80 g, 0.01 mmol) in 200 mL of CH_2Cl_2 was vigorously stirred with 100 mL of an aqueous solution of HCO_2H (1% v/v) at 25 °C, and Cl_2 gas was passed through until the emulsion had a stable pale yellow color. The CH_2Cl_2 phase was separated, washed with H_2O, $NaHCO_3$, and brine, dried over Na_2SO_4, concentrated, and precipitated three times in acidic MeOH to give 2.60 g (92%) of $3G^3(100_2100_2112_2)$SC.

Synthesis of $3G^4(100_2100_2112_2102)$Cl. MMA (5.48 g, 54.80 mmol), *p*-xylene (27 mL), initiator $3G^3(100_2100_2112_2)$SC (2.50 g, 0.01 mmol), catalyst (Cu_2O, 64.00 mg, 0.44 mmol), and ligand (bpy, 139.50 mg, 0.89 mmol) were added in a 50 mL Schlenk tube. After four freeze−pump−thaw cycles, the tube was filled with Ar and the reaction mixture was heated to 90 °C. The sidearm of the tube was purged with Ar for at least 5 min before it was opened to remove samples at predetermined times using an airtight syringe. Samples were dissolved in $CDCl_3$, and the conversion was measured by ^{1}H NMR spectroscopy. After the desired conversion (51%, $M_{th} = 464\,080$) was reached, the reaction mixture was diluted with CH_2Cl_2, passed through a short basic alumina column to remove the catalyst, and then precipitated twice in cold hexanes. The product was recovered by filtration and dried under vacuum to yield 4.60 g (87%) of $3G^4(100_2100_2112_2102)$Cl. $M_{n,GPC} = 168\,200$, $M_w/M_n = 1.23$, and $M_{n,SEC-MALLS} = 456\,200$.

Acknowledgment. Financial support by the ARO-MURI (No. DAAG-55-97-1-0126) and NSF (Nos. DMR-99-96288, DMR-01-02459, and DMR-00-79909) is gratefully acknowledged.

JA034746J