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Synthesis of Dendrimer-Like Polystyrene by Atom Transfer Radical Polymerization and Investigation of Their Viscosity Behavior

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ABSTRACT: The synthesis of dendrimer-like polystyrene (PS) of second and third generations by combination of atom transfer radical polymerization (ATRP) and chain end modifications is reported. Calixarene-based cores were used as initiators for ATRP of styrene yielding star polymers containing precisely 4, 6, or 8 arms. The latter were modified in two steps so as to generate PS stars carrying 8, 12, or 16 terminal bromoisobutyrate groups, respectively. These precursors served as multifunctional macroinitiators for the formation of the second generation of dendrimer-like PS. Reiteration of the aforementioned sequence of reactions allowed to derive dendrimer-like polystyrene of third generation that were constituted of 16, 24, or 32 outer arms, respectively. The chain end modification was monitored by ^{1}H NMR spectroscopy. The dendrimer-like PS were also characterized by size exclusion chromatography equipped with a multiangle laser light scattering detector (SEC/MALLS). The actual polymer architecture and the functionality of the stars were confirmed by analysis of the individual arms obtained upon hydrolysis of the ester links present at the core of the stars and at the branching points. The intrinsic viscosities of these dendrimer-like polystyrenes are similar to those reported for regular dendrimers.

Introduction

In recent years, a number of original branched polymer architectures including stars,[1] comb-type,[2] graft,[2,3] or hyperbranched polymers[4−8] have been developed following the literature surge witnessed in the 1990s on the synthesis and characterization of regular dendrimers.[6,9−12] Because of the tedious sequence of protection, condensation and deprotection of AB$_n$-type monomers required in the synthesis of dendrimers and the necessity to repeat this cycle several times to obtain high molar mass samples, synthetic approaches have been designed to construct dendritic macromolecules of large size by simpler means.[13] Dendrigrafts,[14−17] comb−burst polymers,[18] polymers with dendritic branching,[19−21] and dendrimer-like polymers[13,22,23] comprise dendritically branched architectures that could be grown to very high molar masses in just a few generations. Dendrimer-like polymers resemble regular dendrimers by the presence of a central core and a precise number of branching points and outer terminal functions and differ only by the size of the generation and their mode of polymerization—living chain processes against condensation reactions.[13,22,23] Although coined by Hedrick et al.[23] the synthesis of dendrimer-like polymers was first contemplated by Six et al.[22] who grew generations of poly(ethylene oxide) from branching points located at the end of the previous generation. Such a synthesis relies on the reiteration of two same steps that are the anionic polymerization of ethylene oxide from multifunctional alkoxides and the chemical modification of the chain ends in order to introduce the branching points and the initiating sites for the next generation. The same group adopted a similar approach to prepare PS$_n$-*b*-PEO$_{2n}$ and PEO$_n$-*b*-PS$_{2n}$ dendrimer-like amphiphilic copolymers by atom transfer radical polymerization (ATRP) of styrene and anionic polymerization of ethylene oxide.[24,25] Using a variation of this divergent "grafting from" approach, the Hedrick group derived an entire array of dendrimer-like polyesters and related copolymers by successive grafting of polylactones and polylactides obtained by ring-opening polymerization and polymethacrylic blocks by ATRP.[23,26−28] Not fundamentally different either was the synthetic scheme followed by Percec et al. for the synthesis of dendrimer-like polymethacrylates of third generation.[29,30] Starting from a trifunctional initiator for the copper-catalyzed living radical polymerization of methyl methacrylate, they developed multipurpose compounds—named TERMINI—acting as chain terminators as well as reinitiators and served to introduce branching points. In contrast, Hadjichristidis et al. followed a convergent approach to assemble their dendrimer-like copolymers of styrene and isoprene, the central core being built in this case in the last instance.[31] Such dendritic copolymers were obtained via anionic polymerization using a dual-functionality compound as a branching agent and trichloromethylsilane or tetrachlorosilane as deactivators to build the central core. Very recently, Hirao et al. also proposed a convergent approach involving coupling reactions of living anionic poly(methyl methacrylate)s and functionalization of chain ends to derive dendrimer-like polymethacrylate-based systems.[32]

In this report, we describe the synthesis and the characterization of a series of dendrimer-like polystyrenes (PS) of first, second, and third generations by a divergent methodology. Depending on the functionality of the initiator that served to form the core, these dendritic structures include 4, 6, or 8 branches for the inner core, 8, 12, and 16 branches for the second generation and 16, 24, or 32 outer arms (third generation) (Scheme 1). They were obtained by repetition of ATRP of styrene and a sequence of two chain end modifications to introduce the branching points and at

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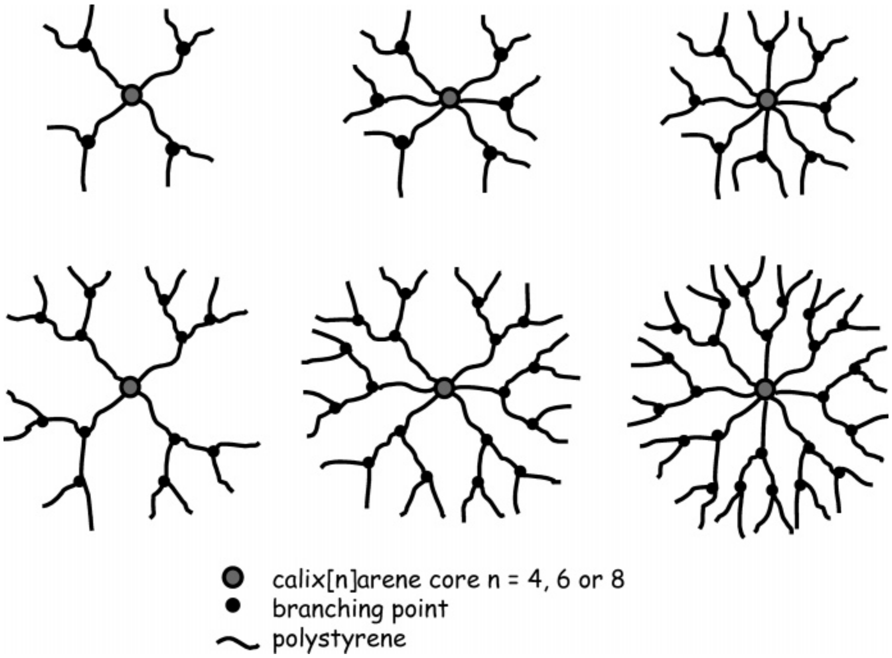
Scheme 1. Sketch of the Different Dendrimer-Like Polystyrenes Prepared by ATRP



the same time multiply by a factor of 2 the number of initiating sites for the next generation. The viscosity behavior of these dendrimer-like PS is also presented.

Results and Discussion

Recently, we described a strategy of synthesis of asymmetric and miktoarm stars by combination of atom transfer radical polymerization (ATRP) and chemical modification of chain ends.[33] This approach consisted in the prior preparation of ω-bromo-terminated PS by ATRP followed by a two-step derivatization of the bromo end groups into twice as many halogenoester functions that subsequently served for the initiation of either the same monomer or another by ATRP. These modification reactions were monitored by ^{1}H NMR spectroscopy and MALDI−TOF and proved quantitative.[33] The same procedure was followed here for the preparation of dendrimer-like polymers, but in this case multifunctional initiators were used instead of monofunctional ones (Scheme 2).

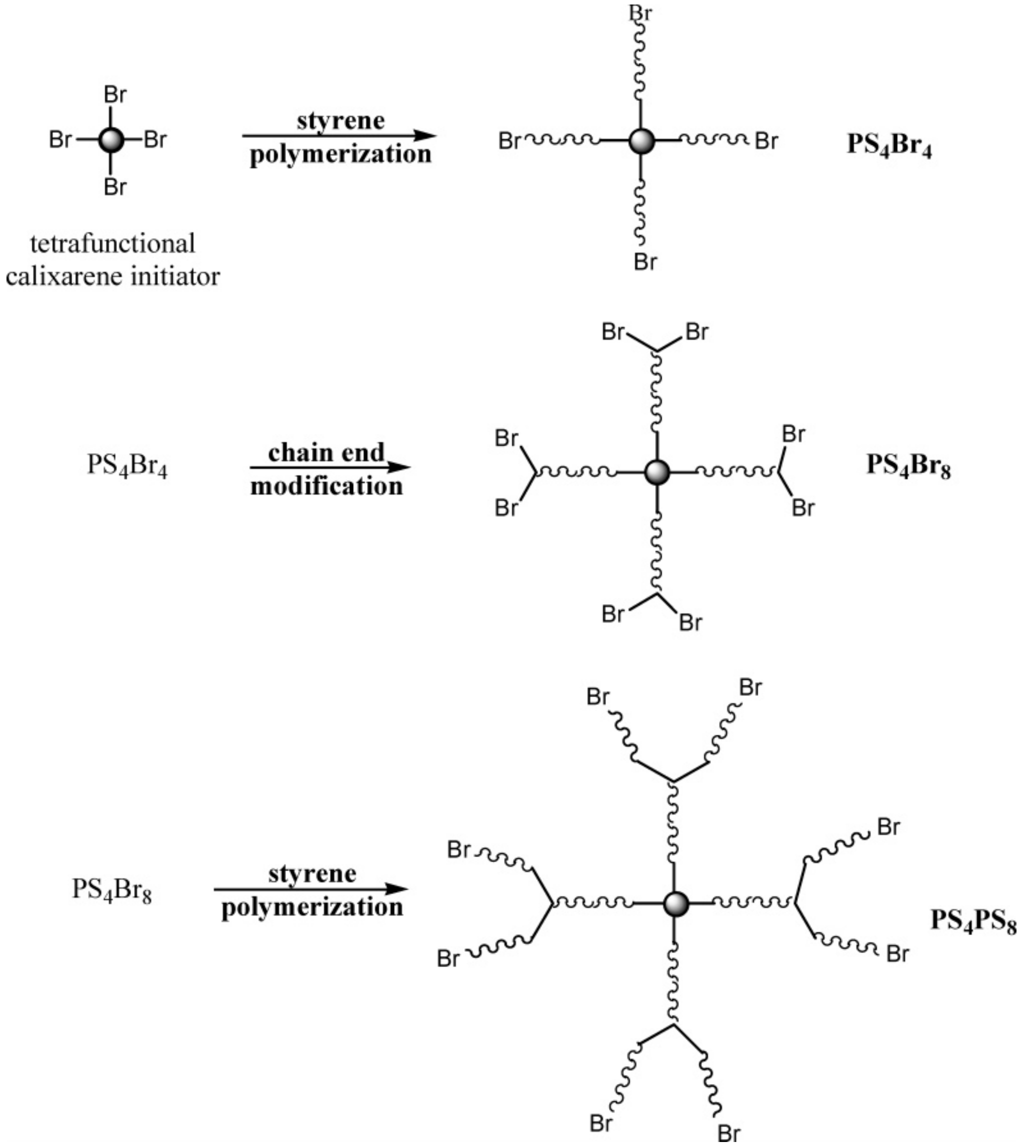
Synthesis of Star-Shaped Polystyrene Precursors (First Generation). The first step in our procedure was the synthesis of polystyrene stars (PS$_n$, n = 4, 6, or 8) with precisely four, six, or eight arms obtained by the core-first method using calixarene-based multifunctional initiators (Scheme 3). These initiators were prepared in one step from commercially available *tert*-butylcalix[n]arene (n = 4, 6, or 8) that were esterified using bromoisobutyryl bromide, as previously reported.[34]

Styrene was polymerized in bulk at 100 °C in the presence of CuBr/2,2′-bipyridyl (bipy) (1/3) as the catalytic system. Star polymers with four (PS$_4$), six (PS$_6$), and eight (PS$_8$) arms were prepared and their molecular characteristics are listed in Table 1. A multiangle laser light scattering (MALLS) detector coupled to a size exclusion chromatography (SEC) line was used to determine the actual molar mass of such samples. The degree of polymerization targeted for each arm of the stars was kept low (between 10 and 30) in order to better monitor the end group modification by ^{1}H NMR spectroscopy. A high [monomer]/[initiator] ratio was also chosen in order to minimize the extent of irreversible termination between stars. Indeed, we previously showed that too high the monomer conversion irreversible couplings gain in probability and may eventually affect the functionality of the samples.[34] When discontinuing the polymerization at low conversion (<15% for a functionality of 8), star samples exhibiting narrow polydispersity (M_w/M_n < 1.2) and experimental molar masses closed to theoretical values could be obtained (see Table 1).

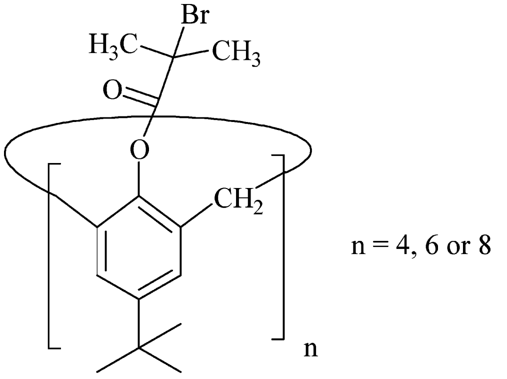
Introduction of the Branching Points at Each Arm End. The next step in the synthesis of these dendrimer-like polymers was the introduction of a branching point and thus two geminal ATRP initiating sites at each chain end of the stars. This was achieved in two steps (Scheme 4): first, a nucleophilic substitution of the ω-bromo end groups using 2-amino-1,3-propanediol (also called serinol) followed by an esterification reaction. The first reaction was carried out in DMF at 30 °C for 72 h and the final polystyrene (PS$_n$(OH)$_{2n}$) was recovered by precipitation using methanol. No side reaction occurred as attested by ^{1}H NMR analysis. Indeed, the ^{1}H NMR spectra of the precursor PS$_n$Br$_n$ star exhibit a signal at δ = 4.5 ppm assignable to the protons carried by secondary terminal carbons groups C$\boldsymbol{H}$(Ph)−Br (Figure 1A). After reaction with serinol, this signal vanished and a new one appeared at δ = 3.3 ppm that was attributed to C$\boldsymbol{H_2}$−OH protons (Figure 1B) of the PS$_n$(OH)$_{2n}$. This result corroborates previous observations made while preparing asymmetric and miktoarm stars as to the selectivity of this reaction.[33]

The modification of the hydroxy functions into ATRP initiating sites was accomplished in a second step by esterification using 2-bromoisobutyryl bromide in dry THF, in the presence of triethylamine. Purification of the corresponding macroinitiators (PS$_n$Br$_{2n}$ with n = 4, 6 or 8) from excess reagents was performed by two precipitations using methanol. The ^{1}H NMR spectra of these PS$_n$Br$_{2n}$ show a clear shift of the signal due to the −CH$_2$O− protons upon formation of the ester linkage (δ = 4 ppm) attesting to the formation of the expected structure (Figure 1C).

Scheme 2. Strategy for the Synthesis of Dendrimer-Like Polystyrenes Using a Tetrafunctional Initiator



Scheme 3. Chemical Structure of *tert*-Butylcalix[*n*]arenes (n = 4, 6 or 8) that Were Esterified Using Bromoisobutyryl Bromide



Synthesis of Second Generation (G-2) Dendrimer-Like Polystyrenes. The polymerization of styrene using PS$_n$Br$_{2n}$ as macroinitiator was performed in bulk at 100 °C with CuBr/bipy as catalytic system in order to obtain second generation dendrimer-like polystyrenes (PS$_n$PS$_{2n}$ with n = 4, 6 or 8). Table 2 gives the data pertaining to these dendrimer-like PS obtained from macroinitiators with different core functionalities and molar masses obtained by SEC/MALLS ranging between 19 600 and 103 700 g/mol.

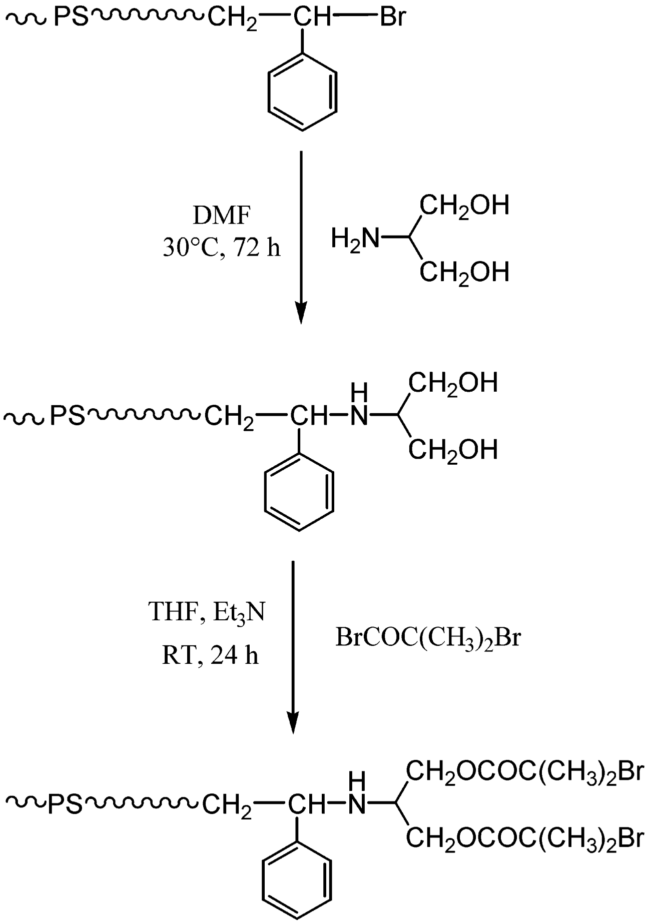
Here also, the polymerization was stopped at low monomer conversion in order to prevent irreversible couplings between the growing species. Figures 2 and 3 showed the evolution of molar masses for the second generation dendrimer-like PS grown from hexafunctional and octafunctional cores, respectively. Samples of narrow molar mass distribution ($1.1 < M_w/M_n < 1.4$) were obtained and their molar mass increases with conversion. The complete disappearance of the peak of the PS$_n$Br$_{2n}$ precursor on the chromatogram meant that all precursor chains participated in the polymerization. The molar mass values drawn from SEC/MALLS agreed well with the theoretical values attesting that two PS arms of well-controlled size could be grown from each of these branching points. As to the characterization by ^{1}H NMR spectroscopy of the second generation PS$_8$PS$_{16}$Br$_{16}$ dendrimer-like polymers, it revealed the presence of a signal at 4.5 ppm due to the protons carried by terminal secondary carbons which was not present in the ^{1}H NMR spectrum of the parent PS$_8$Br$_{16}$ macroinitiator. The ratio of 13.5 found between the intensities of the signal appearing at 4.5 ppm and the

Table 1. Synthesis of Multiarm Polystyrene Stars Using Calix[n]arene-Based Initiators[a]

run	n	$[M]_o/[I]_o$	$M_{n,SEC}$[b] (g mol^{-1})	$M_{n,MALLS}$[c] (g mol^{-1})	M_w/M_n[c]	convn[d] (%)	$M_{n,th}$[e] (g mol^{-1})	$[\eta]$ (dL/g)
1	4	800	6300	12 600	1.14	14	12 900	0.0914
2	4	470	3900	7000	1.35	13	7600	
3	6	530	8000	16 100	1.28	25	15 600	
4	6	530	7800	15 700	1.25	23	14 500	0.0934
5	8	790	16 100	27 000	1.11	31	28 000	
6	8	790	13 400	25 000	1.19	27	25 000	
7	8	770	11 200	22 200	1.2	25	23 000	
8	8	770	6600	13 300	1.22	15	14 500	0.0703

[a] Conditions: [−Br]/[CuBr]/[bipy] = 1/1/3, T = 100 °C in bulk. [b] Determined by standard SEC in THF (calibration with linear PS standards). [c] Determined by SEC/MALLS in THF. [d] Monomer conversion measured gravimetrically. [e] $M_{n,th} = (\%\text{ convn} \times [M]_o/[I]_o \times M_{styrene}) + M_{initiator}$.

Scheme 4. Branching Reaction of PS Branches



one at 0.5−1.0 ppm—due to the methyl protons of the calixarene core and of the ester linkages of PS_8Br_{16} indicated that initiation occurred—if not quantitatively—with high efficiency (Figure 4).

In some cases, the presence of a second population could be detected by MALLS in the high molar mass region of the SEC traces due to couplings between growing radicals. Only for monomer conversion above 40% could the effect of such irreversible coupling reactions be seen in the chromatogram. The probability for two radicals to couple is function of the equilibrium constant K_{eq} ($K_{eq} = k_a/k_d$) between dormant and active species and the ratio $k_p[M]/k_t[M°]$. Upon comparing both light scattering and refractometric SEC traces for a PS_6PS_{12} dendrimer-like sample corresponding to 39% monomer conversion (Figure 5), a shoulder hardly detectable by refractometry appears pronounced with the MALLS detector in the high molar mass region. Because ATRP of styrene is associated with a rather high equilibrium constant K_{eq} and low k_p/k_t ratio (in comparison with alkyl acrylates),[35] bimolecular coupling reaction could not be avoided above a threshold (>30%) that var-

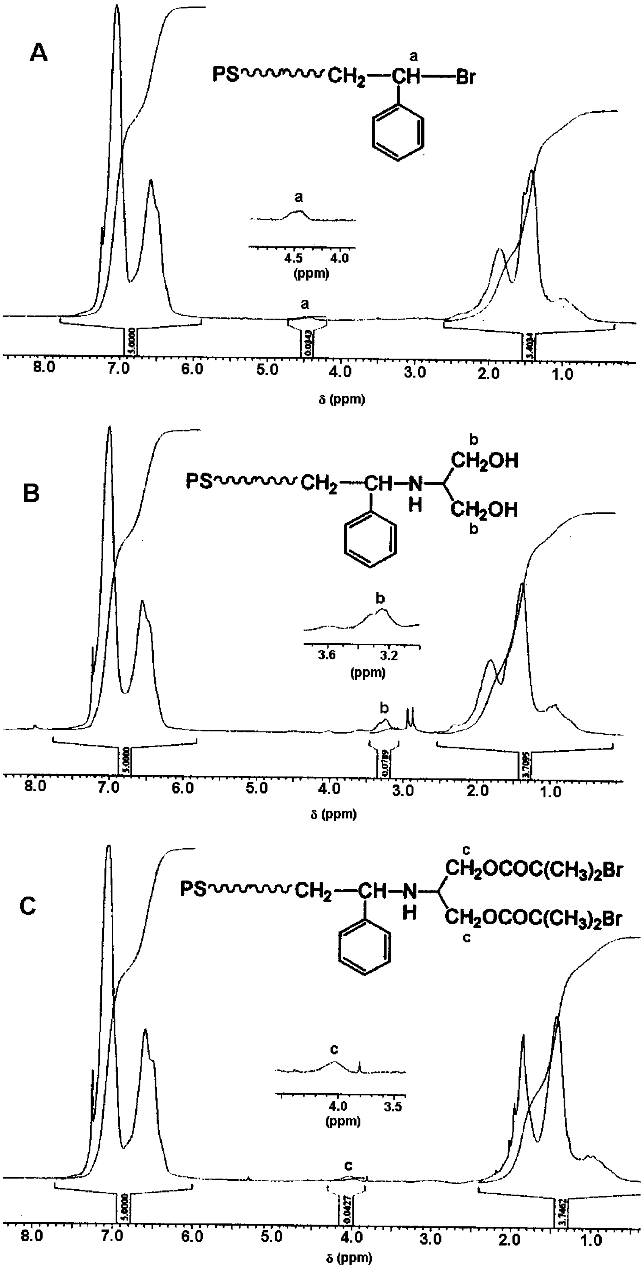


Figure 1. ^1H NMR ($CDCl_3$; 200 MHz) of PS_6Br_6 hexafunctional star polystyrene (A), $PS_6(OH)_{12}$ (B), and PS_6Br_{12} (C) (run 3, Table 1).

Table 2. Synthesis and Solution Properties of $PSnPS_{2n}$ Second Generation Dendrimer-Like Polystyrenes Prepared Using PS_nBr_{2n} as Macroinitiator[a]

PS_nBr_{2n}			PS_nPS_{2n}						
run	n	M_n[b]	$[M]_o/[I]_o$	$M_{n,SEC}$[c] (g mol^{-1})	$M_{n,MALLS}$[b] (g mol^{-1})	M_w/M_n[b]	convn[d] (%)	$M_{n,th}$[e] (g mol^{-1})	$[\eta]$ (dL/g)
9	4	7000	3000	11 400	23 900	1.27	5	22 600	0.136
10	4	12 600	3000	10 000	19 600	1.20	3	21 900	
11	4	12 600	3000	15 800	31 500	1.19	6	31 300	0.1819
12	4	12 600	3000	26 000	38 600	1.22	9	40 100	0.2116
13	6	16 100	2400	16 300	36 400	1.19	8	35 500	
14	6	15 700	2400	16 400	38 900	1.23	10	40 700	0.1659
15	6	15 700	2400	20 000	46 600	1.22	11.5	44 400	0.1515
16	6	16 100	2400	20 900	51 300	1.19	17	58 000	
17	6	16 100	2400	28 100	63 400	1.21	21	68 000	0.1908
18	6	16 100	2400	40 000	103 700	1.26	39	113 000	0.2564
19	8	13 300	6000	22 600	36 800	1.29	4	38 300	0.1018
20	8	13 300	6000	21 500	52 200	1.40	6	50 700	
21	8	13 300	6000	33 000	69 100	1.26	10	75 700	0.1363
22	8	13 300	6000	55 100	88 200	1.28	12	88 100	0.188
23	8	22 200	4800	28 000	56 000	1.23	6.5	54 700	0.1202
24	8	22 200	4800	32 500	57 000	1.16	8	62 000	0.1122
25	8	22 200	4800	49 000	95 000	1.31	18	111 900	0.1750

[a] Conditions: $[-Br]/[CuBr]/[bipy] = 1/1/3$, $T = 100$ °C in bulk. [b] Determined by SEC/MALLS in THF. [c] Determined by standard SEC in THF (calibration with PS standards). [d] Monomer conversion measured gravimetrically. [e] $M_{n,th} = (\%\ \text{convn} \times [M]_0/[I]_0 \times M_{styrene}) + M_{macroinitiator}$.

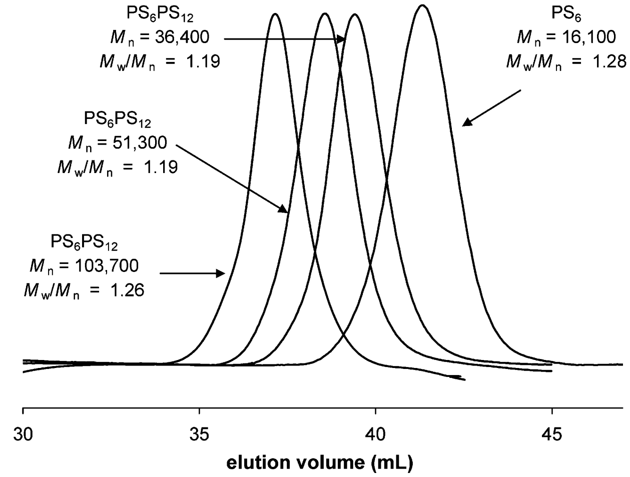


Figure 2. SEC traces (RI detector) of dendrimer-like polystyrenes PS_6PS_{12} (runs 13, 16 and 18, Table 2) and its precursor PS_6 (run 3, Table 1). Conditions: $[-Br]/[CuBr]/[bipy] = 1/1/3$, $T = 100$ °C, in bulk.

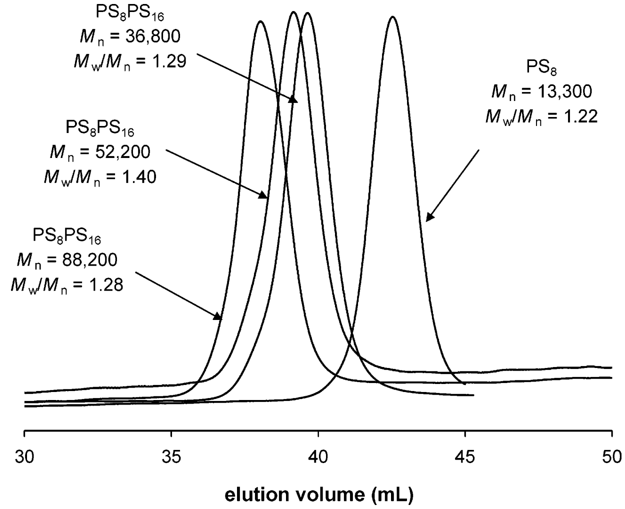


Figure 3. SEC traces (RI detector) of dendrimer-like polystyrenes PS_8PS_{16} (runs 19, 20 and 22, Table 2) and its precursor PS_8 (run 8, Table 1). Conditions: $[-Br]/[CuBr]/[bipy] = 1/1/3$, $T = 100$ °C, in bulk.

ied with the functionality (8, 12, 16) of the sample considered.

SEC even equipped with MALLS detection is not suitable for revealing possible intramolecular couplings that might have occurred and formed loops.

Synthesis of Third Generation (G-3) Dendrimer-Like Polystyrenes. For the synthesis of dendritic PS of higher generation, the same sequence of reactions as that described above was repeated (i.e., styrene polymerization and chain end modification). Scheme 1 shows the different G-3 dendritic structures prepared. Nucleophilic substitution with serinol followed by esterification reaction with 2-bromoisobutyryl bromide performed on PS_nPS_{2n} dendrimers gave $PS_nPS_{2n}Br_{4n}$ macroinitiators with 16, 24, or 32 ATRP initiating sites depending on the functionality of the initial calixarene core ($n = 4$, 6, or 8). Then, styrene was polymerized in bulk under the same conditions as those previously described. Table 3 reports the molecular characteristics of G-3 dendrimer-like PS and Figure 6 presents the SEC traces of PS_8, PS_8PS_{16}, and $PS_8PS_{16}PS_{32}$ samples grown from the octafunctional calixarene core.

As clearly indicated in Table 3, all of these samples exhibited a symmetrical and monomodal distribution of molar masses and moderate polydispersity ($M_w/M_n < 1.4$). Molar masses increased linearly with the monomer conversion and the experimental molar masses determined by light scattering were very closed to the expected ones, provided the polymerization was discontinued at low monomer conversion (<20%) to avoid irreversible couplings. As in the case of the second generation sample, initiation of the third generation was monitored by ^1H NMR spectroscopy. The fact that protons carried by terminal secondary carbons could be clearly seen at 4.5 ppm and that methyl protons due to ester linkages increased in intensity (0.5−1 ppm) indicated that initiation occurred as expected.

Determination of the Functionality of the Dendrimer-Like PS. Being either linked to the calixarene core or to the branching points through an ester function, the PS arms could be easily detached by hydrolysis under basic conditions (KOH in mixture of THF and methanol). Indeed, the comparison of molar masses

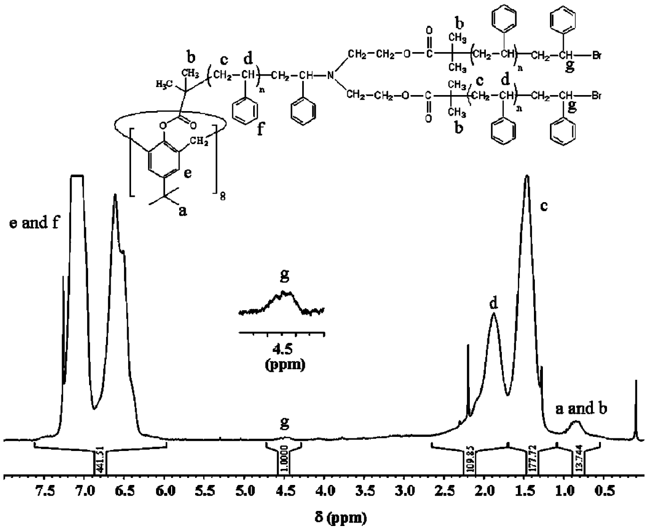


Figure 4. ^{1}H NMR spectrum (CDCl$_3$; 200 MHz) of a dendrimer-like polystyrene PS$_8$PS$_{16}$ (run 22, Table 2).

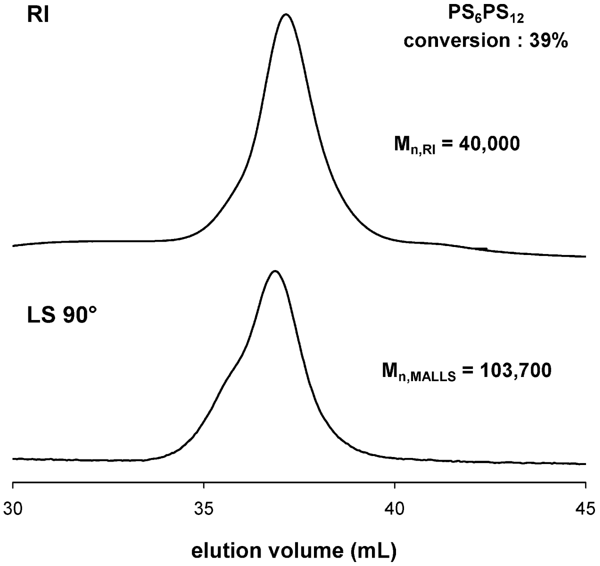


Figure 5. SEC traces obtained either by RI (top) or by LS at 90° (down) of a second generation PS$_6$PS$_{12}$ dendrimer-like polystyrene obtained at high conversion (run 18, Table 2). Conditions: [−Br]/[CuBr]/[bipy] = 1/1/3, T = 100 °C, in bulk.

before and after hydrolysis proved useful to determine the exact number of branches in star structures.[34,36] In the present case, the SEC trace of a well-defined PS$_6$PS$_{12}$ sample (run 32 in Table 4) is compared with that of the resulting hydrolyzed polymer (Figure 7). The latter trace is monomodal with relatively low polydispersity ($M_w/M_n = 1.37$). The ratio of the molar masses of the parent PS$_6$PS$_{12}$ sample (M_n = 38 900 g/mol) to that of the hydrolyzed polymer (M_n = 2400 g/mol) falls close (16.8) to the expected value of 18 (6 arms for G-1 and 12 arms for G-2 with molar masses, respectively, equal to 2600 and 1900 g/mol), providing additional evidence for the expected dendritic architecture (Table 4). Hydrolysis of a second sample (run 33) resulted in a ratio value falling in the same range (16.2), the slightly larger departure from the expected value (18) being certainly due to the difference between the molar masses of the two generations hydrolyzed.

Viscosity of Dendrimer-Like Polystyrenes. An accurate and convenient means to determine the extent of shrinkage due to branching in polymeric samples and evaluate their overall shape is to measure their intrinsic viscosity [η].[12,37] It was preferred to the determination of the radii of gyration by light scattering which would have required samples of high molar mass in all generations and/or a laser for MALLS of shorter wavelength. In the literature, several papers deal with the viscometric behavior of star polymers,[38,39] hyperbranched polymers,[8] dendrigrafts,[40] and regular dendrimers,[8,41] but to the best of our knowledge, no one has so far addressed the case of dendrimer-like polymers. Gauthier et al. observed that their arborescent polystyrenes behave in a first approximation like dense globular objects whose intrinsic viscosity remains independent of the molar mass.[40] As shown by the relation between [η]—which is also inversely proportional to the hydrodynamic density—and the hydrodynamic volume (V_H)

$$[\eta] = 2.5N_aV_H/M = (10\Pi/3)N_aR_H{}^3/M \qquad (1)$$

where R_H is the hydrodynamic radius and N_a the Avogadro number, such a constant [η] in the particular case of arborescent polymers merely reflects the fact that both V_H of the sample and its mass (M) vary approximately in the same proportion upon increasing the number of generations.

In the case of hyperbranched poly(α,ε-L-lysine) also, spherelike behaviors were reported by Aharoni et al. who observed independent [η] with respect to the molar mass.[42] Although also spherical in shape, regular dendrimers exhibit completely different behaviors, whether obtained by convergent or divergent synthesis. Their intrinsic viscosity first increases as a function of molar mass/generation, passes through a maximum to eventually decreases (bell-shaped curve).[8,41] Unlike the cases of arborescent or hyperbranched polymers, such a variation mirrors the different dependence of hydrodynamic volumes and molar masses with the number of generations (g). Molar masses in regular dendrimers increase exponentially with g according to 2^{g-1} and their hydrodynamic volume grows with g^3; [η] varying proportionally to $g^3/2^{g-1}$, it passes therefore through a maximum with increasing g.

The intrinsic viscosity of our dendrimer-like PS were determined at 35 °C using toluene as a solvent. To our surprise, their viscosity behavior was not different from that found for regular dendrimers, at least for the family of PS$_4$, PS$_4$PS$_8$, and PS$_4$PS$_8$PS$_{16}$ samples. The progression of molar masses with the number of generations for dendrimer-like polymers is expected to follow the same exponential trend in 2^{g-1} as the one unveiled for regular dendrimers, since the two families of dendrimers share common molecular features. To determine how vary hydrodynamic volumes as a function of g, we resorted to expression 2 given below, using [η] and M determined experimentally.

$$R_H = [3M[\eta]/10\pi N_a]^{1/3} \qquad (2)$$

As shown in Figure 8, R_H increases nearly linearly with g for the three families of dendrimer-like PS, indicating that V_H thus grows in g^3 like regular dendrimers.

The fact that [η] passes through a maximum for the PS$_4$PS$_8$PS$_{16}$ sample is thus fully accounted for; in contrast, no maximum of [η] could be observed for the

Table 3. Characteristics and Solution Properties of Third Generation Dendrimer-Like Polystyrenes $PS_nPS_{2n}PS_{4n}$[a]

		G-1		G-2		G-3				
run	n	$M_{n,MALLS}$[b] (g mol^{-1})	M_w/M_n[b]	$M_{n,MALLS}$[b] (g mol^{-1})	M_w/M_n[b]	$M_{n,MALLS}$[b] (g mol^{-1})	M_w/M_n[b]	convn[c] (%)	$M_{n,th}$[d] (g mol^{-1})	[η] (dL/g)
26	4	12 600	1.14	31 500	1.19	51 100	1.26	4	56 400	0.124
27	6	15 700	1.25	38 900	1.23	52 000	1.36	5	63 800	
28	6	15 700	1.25	38 900	1.23	103 700	1.43	8	119 000	0.200
29[e]	6	15 700	1.25	38 900	1.23	149 700	1.29	15	151 200	0.347
30	8	13 300	1.22	69 100	1.26	103 600	1.28	1	94 100	0.2218
31	8	13 300	1.22	69 100	1.26	141 100	1.27	4	168 900	0.2049

[a] Conditions: [−Br]/[CuBr]/[bipy] = 1/1/3, T = 100 °C in bulk. [b] Determined by SEC/MALLS in THF. [c] Monomer conversion measured gravimetrically. [d] $M_{n,th} = (\%\ \text{convn} \times [M]_0/[I]_0 \times M_{\text{styrene}}) + M_{\text{macroinitiator}}$. [e] For this sample, a shoulder due to irreversible coupling reactions is observed in the high molar mass region.

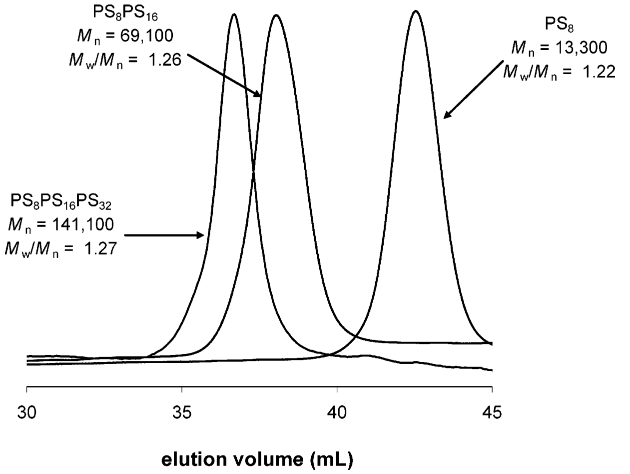


Figure 6. SEC traces (RI detector) of (a) PS_8 octafunctional star (run 8, Table 1), (b) G-2 dendritic polystyrene (run 21, Table 2) and (c) G-3 dendrimer-like polystyrene (run 31, Table 3). Conditions: [−Br]/[CuBr]/[bipy] = 1/1/3, T = 100 °C, in bulk.

Table 4. Determination of the Functionality of Dendrimer-Like Polystyrenes by Cleavage of Their Branches[a]

dendrimer-like PS				linear PS		
run	dendrimer	f(theo)	M_n[b] (g mol^{-1})	M_n[c] (g mol^{-1})	M_w/M_n[c]	f(calcd)[d]
32	PS_6PS_{12}	18	38 900	2300	1.37	16.9
33	PS_6PS_{12}	18	103 700	6400[e]	1.46	16.2

[a] Conditions: [ester linkage]/[KOH] = 14.5, in THF at reflux, t = 24 h. [b] Determined by SEC/MALLS in THF. [c] Linear products obtained after cleavage of ester functions present in the core and at the branching points. [d] f (functionality) corresponding of the number of branches and calculated by the relation f = $M_{n(SEC/MALLS)dendrimer}/M_{n(SEC)linear}$. [e] Presence of a shoulder in the low molar mass region (dendrimer arms molar mass of 2600 and 8000 for G-1 and G-2 respectively).

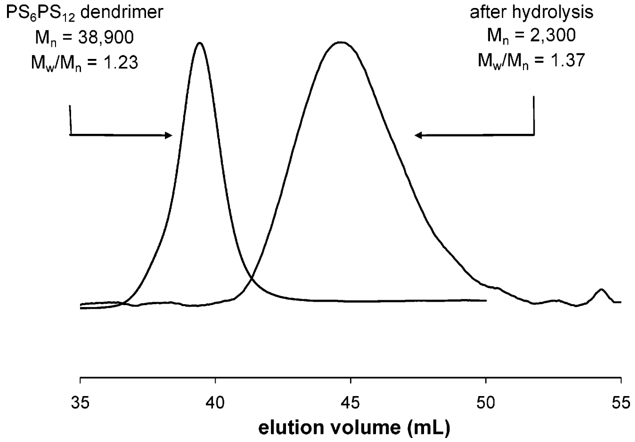


Figure 7. SEC traces (RI detector) (a) before and (b) after hydrolysis of the ester functions present in the core and in the branching points of a PS_6PS_{12} dendrimer-like polystyrene (run 32, Table 4).

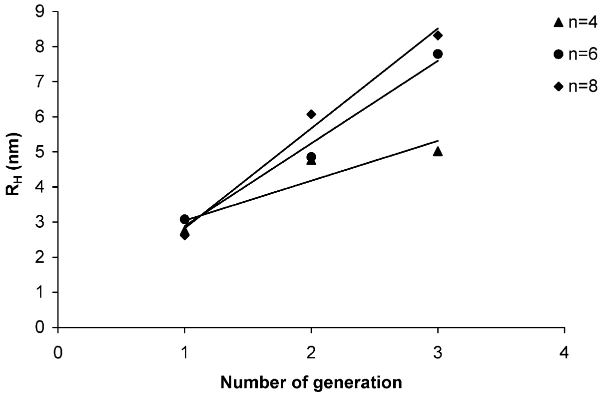


Figure 8. Evolution of the hydrodynamic radius (R_H) as a function of the number of generation (G) for dendrimer-like polystyrenes prepared using tetrafunctional (n = 4; G-1, run 1, Table 1; G-2, run 11, Table 2; G-3, run 26, Table 3), hexafunctional (n = 6; G-1, run 4, Table 1; G-2, run 14, Table 2; G-3, run 28, Table 3), or octafunctional (n = 8; G-1, run 8, Table 1; G-2, run 21, Table 2; G-3, run 31, Table 3) initiators.

other families of dendrimer-like PS but the trend exhibited by their log[η] vs g curves seems to indicate that such a maximum—if it exists—is likely shifted toward higher generations (>3) (Figure 9).

The evolution of log[η] as a function of log M_w was also plotted (Figure 10). The same trend as the one observed for the log[η] vs g plot is seen here, indicating that [η] is not independent of the molar mass for dendrimer-like polystyrenes as in the case of hyperbranched polymers.

Samples of dendrimer-like PS of generation higher than 3 could not be obtained although precursors fitted with 48 and 64 ATRP initiating sites were prepared; well-defined samples carrying, respectively, 48 and 64 outer branches could not be isolated because of a too high probability of star−star couplings even when the polymerization was discontinued at very low conversion. As a matter of fact, the properties found for these dendrimer-like polymers distinguish them from highly dense globular structures such as hyperbranched polymers or other highly branched systems; indeed, the peculiar profile of hydrodynamic density—reciprocal to that of [η]—with respect to the number of generations/molar mass and their globally spherical shape reminds one of the properties exhibited by regular dendrimers.

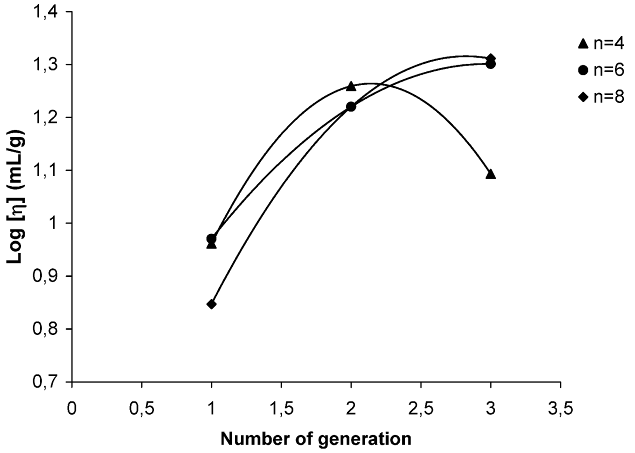


Figure 9. Evolution of log[η] as a function of the number of generation (G) for dendrimer-like polystyrenes prepared using tetrafunctional ($n = 4$; G-1, run 1, Table 1; G-2, run 11, Table 2; G-3, run 26, Table 3), hexafunctional ($n = 6$; G-1, run 4, Table 1; G-2, run 14, Table 2; G-3, run 28, Table 3), or octafunctional ($n = 8$; G-1, run 8, Table 1; G-2, run 21, Table 2; G-3, run 31, Table 3) initiators.

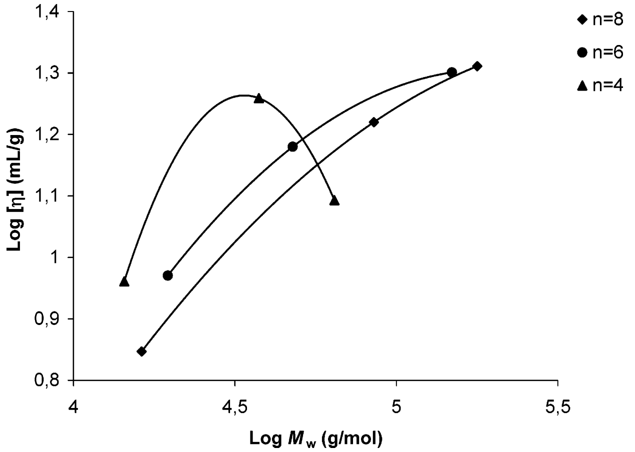


Figure 10. Evolution of log[η] as a function of log M_w for dendrimer-like polystyrenes prepared from tetrafunctional ($n = 4$; G-1, run 1, Table 1; G-2, run 11, Table 2; G-3, run 26, Table 3), hexafunctional ($n = 6$; G-1, run 4, Table 1; G-2, run 14, Table 2; G-3, run 28, Table 3), or octafunctional ($n = 8$; G-1, run 8, Table 1; G-2, run 21, Table 2; G-3, run 31, Table 3) initiators.

Conclusions

Dendrimer-like polystyrenes of precise functionality and low polydispersity have been prepared for the first time by atom transfer radical polymerization and chain end modification reactions in a divergent manner, using multifunctional calixarene-based initiators. Second and third generation dendrimer-like polystyrenes carrying up to 32 outer arms have been prepared. Their well-defined character was checked by different means including the cleavage of the ester groups present at the core and the branching points. The molar masses of the hydrolyzed PS arms were in good agreement with the calculated values. The study of their solution properties showed that these dendrimer-like polystyrenes behave as solvated spheres whose intrinsic viscosity is much lower than that of linear homologues and whose density is unevenly distributed from the core to the external corona. Samples of high generations would be needed to fully corroborate the finding disclosed in this contribution and a new synthetic scheme is currently developed to this end.

Experimental Section

Materials. All reagents were purchased from Aldrich. Styrene (99%) was stirred overnight over CaH_2 and distilled prior to use. Copper(I) bromide (CuBr, 98%), and 2,2′-bipyridyl (bipy, 99%) were used as received. Triethylamine, tetrahydrofuran and acetone were distilled over CaH_2 prior to use. 4-*tert*-Butylcalix[4]arene (95%), 4-*tert*-butylcalix[6]arene (95%), 4-*tert*-butylcalix[8]arene (95%), 2-amino-1,3-propanediol (serinol, 98%), 2-bromoisobutyryl bromide (98%), sodium hydroxide (1 M solution in methanol), and *N*,*N*-dimethylformamide (DMF, 99%) were used as received.

Instrumentation. ^{1}H NMR spectra were obtained using a Bruker AC 200 NMR spectrometer. $CDCl_3$ was used as solvent. Apparent molar masses of polymers were determined using a size exclusion chromatography (SEC) apparatus equipped with a refractive index (RI) (Varian RI-4) and UV−vis (Varian 2550 variable λ) detectors and with four TSK-gel columns (7.8 × 300 mm, 5 μm, G 2000, 3000, 4000, 5000 HR with pore sizes of 250, 1500, 10000, and 100000 Å, respectively) using tetrahydrofuran as eluent (0.7 mL/min) at 25 °C. Calibration was carried out using linear polystyrene standards. Molar masses of starlike and dendrimer-like polystyrenes were also determined in THF at 25 °C from a SEC line including four TSK-gel columns (300 × 7.7 mm, 250, 1,500, 10^4, and 10^5 Å), an RI detector (Varian), and a multiangle laser light scattering detector (Wyatt Technology). The flow rate was 0.7 mL/min and the wavelength of the laser source was 632.8 nm. The d*n*/d*c* values of starlike and dendrimer-like polystyrenes were measured in THF at 25 °C with a laser source operating at 633 nm and were found to be the same as that of linear polystyrene (d*n*/d*c* = 0.183 cm^3/g at 633 nm).[43] Viscometric measurements were performed in toluene at 35 °C using an Ubbelohde viscometer (CT 52 Schott). Samples were filtered through glass filters (200 μm) before measurements.

Synthesis of Multifunctional Initiators. Tetra-, hexa-, and octafunctional initiators were prepared by reaction of 4-*tert*-butylcalix[n]arene ($n = 4$, 6 or 8) with 2-bromoisobutyryl bromide according to a procedure described previously.[34,39]

ATRP of Styrene. The same procedure was followed for the preparation of stars (G-1) and dendrimer-like PS (G-2 and G-3). All polymerizations were performed in a Schlenk apparatus. The reaction mixtures were degassed by three freeze−pump−thaw cycles and placed in a thermostated oil bath prior to the polymerization. In a typical experiment, a Schlenk flask was flame dried under vacuum and filled with 4-*tert*-butylcalix[4]arene (0.074 g, 0.06 mmol), 2,2′-bipyridyl (0.168 g, 1.08 mmol), copper bromide (0.051 g, 0.36 mmol), and styrene (5 g, 48 mmol) under a N_2 atmosphere. After 3 h of polymerization, the reaction mixture was cooled to room temperature and the content was diluted with THF and passed through a column of neutral alumina to remove the copper salts. The polymer was precipitated from an excess of methanol, filtered, and dried at 50 °C under vacuum to give 0.7 g of a crude product (convn = 14%). SEC/MALLS (THF): M_n = 12 600 g/mol, M_w/M_n = 1.14. ^{1}H NMR ($CDCl_3$), δ, ppm: 7.3−6.3 (m, 5H, aromatic), 4.5 (s, C***H***Br), 1.3−2.5 (m, C$\boldsymbol{H_2}$ and C***H*** of PS), 0.2−1.2 (m, C$\boldsymbol{H_3}$ of initiator).

Chain End Modifications. The same procedure was followed for chain end modifications of G-1, G-2, and G-3 samples, irrespective of the core functionality. A typical experiment is as follows. A PS_6Br_6 star polystyrene (3 g, 1.92 × 10^{-4} mol, M_n = 16 100 g/mol, M_w/M_n = 1.28) was dissolved in DMF (18 mL), and 3.15 g (3.46 × 10^{-2} mol) of serinol (2-amino 1,3-propanediol) was added. After the reaction was stirred for 72 h at 30 °C, the polymer was precipitated in methanol, filtered, and dried at 35 °C under vacuum for 24 h to give 2.4 g of a PS with 12 hydroxyl functions ($PS_6(OH)_{12}$) (80%). ^{1}H NMR ($CDCl_3$), δ, ppm: 7.3−6.3 (m, 5H, aromatic), 3.1−3.4 (m, C***H***(Ar)NHC***H***(C$\boldsymbol{H_2}$OH)$_2$), 1.3−2.5 (m, C$\boldsymbol{H_2}$ and C***H*** of PS), 0.2−1.2 (m, C$\boldsymbol{H_3}$ of initiator).

Next, $PS_6(OH)_{12}$ (2.2 g, 1.41×10^{-4} mol, M_n = 16 100 g/mol, M_w/M_n = 1.28) was dissolved in dry THF (17 mL) along with triethylamine (1.18 mL, 8.46×10^{-3} mol). The solution was cooled to 0 °C, and 2-bromoisobutyryl bromide (1.05 mL, 8.46×10^{-3} mol) dissolved in 10 mL of THF was added dropwise over a period of 15 min. The reaction mixture was stirred at room temperature for 24 h. The precipitated salts were removed by filtration, and the polymer recovered after two precipitations from an excess of methanol was filtered and dried at 50 °C under vacuum for 12 h. Such a procedure gave 1.8 g of $PS_6(Br)_{12}$ (yield = 82%). ^{1}H NMR ($CDCl_3$), δ, ppm: 7.3−6.3 (m, 5H, aromatic), 4.0−3.7 (m, $C\boldsymbol{H_2}OCO$), 3.1−3.4 (m, $C\boldsymbol{H}(Ar)NHC\boldsymbol{H}$), 1.3−2.5 (m, $C\boldsymbol{H_2}$ and $C\boldsymbol{H}$ of PS), 1.9 (s, $C(C\boldsymbol{H_3})_2Br$), 0.2−1.2 (m, $C\boldsymbol{H_3}$ of initiator).

Hydrolysis of Stars and Dendrimer-Like Polymers. A typical procedure is as follows. A dendrimer-like polymer PS_6PS_{12} (0.150 g, M_n = 38 900 g/mol, M_w/M_n = 1.28) was dissolved in 15 mL of THF in a 100 mL round-bottomed flask equipped with a condenser and a N_2 inlet. To this solution was added 1 mL of KOH (1 M solution in methanol), and the mixture was refluxed for 24 h. The solution was evaporated to dryness and redissolved in THF, and the polymer was precipitated from methanol and dried under vacuum to give 0.135 g of linear PS (yield = 90%). SEC (THF vs PS standard): M_n = 2300 g/mol, M_w/M_n = 1.37.

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