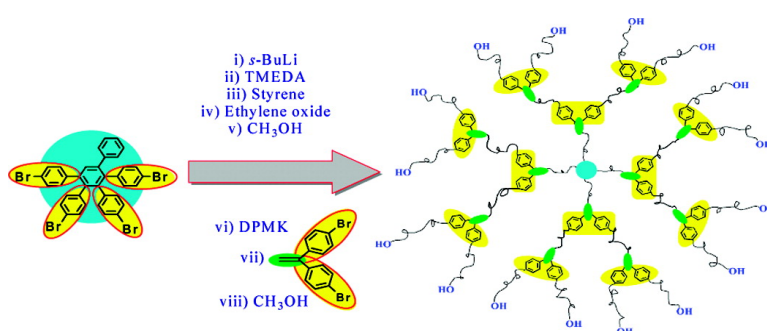## Article

Combination of an Anionic Terminator Multifunctional Initiator and Divergent Carbanionic Polymerization: Application to the Synthesis of Dendrimer-Like Polymers and of Asymmetric and Miktoarm Stars

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A R T I C L E S

Combination of an Anionic Terminator Multifunctional Initiator and Divergent Carbanionic Polymerization: Application to the Synthesis of Dendrimer-Like Polymers and of Asymmetric and Miktoarm Stars

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Abstract: A new and versatile synthetic strategy that provides access to precisely defined and totally soluble multicarbanionic initiators has been implemented to obtain by divergent growth dendrimer-like samples of polystyrene (PS) (up to the seventh generation) or polybutadiene (PB) (up to the third generation) and also asymmetric and miktoarm stars. This strategy rests on lithium−halide exchange reactions to generate multicarbanionic species and on the design of an original reagent that can concomitantly react with living carbanionic chains/arms to deactivate them and produce multicarbanionic sites after exchange of its bromides against lithium. This reagent, 4,4′-dibromodiphenylethylene (**1**), functions as a TERminating agent and a Multifunctional INItiator (TERMINI), according to a concept first proposed by Percec in another context. Upon using this anionic TERMINI in living carbanionic polymerization and repeating the two steps of chain end derivatization by **1** and divergent arm growth from the multifunctional sites generated, perfectly defined dendrimer-like polystyrene and polybutadiene could be obtained up to the seventh generation for the former and up to the third generation for the latter. Each step, i.e., chain end modification and arm growth, was carefully monitored, and the dendrimer-like samples of PS and PB were all characterized by size exclusion chromatography equipped with a multiangle laser light scattering detector (SEC/LS) and high-temperature size exclusion chromatography equipped with a viscometric detector (HT-SEC). The viscosity behavior of these dendrimer-like polystyrenes−bell-shaped variation versus the number of generation−was found to be similar to that reported for regular dendrimers. This chemistry, namely this anionic TERMINI, was also exploited to derive three-arm asymmetric and miktoarm stars.

1. Introduction

We have been investigating the design and synthesis of complex architectures that exhibit the shape and structure perfection required to accomplish certain high-value functions.[1] For instance, we recently reported the synthesis of dendrimer-like poly(ethylene oxide) (PEO) that revealed anti-inflammation properties upon modification of their outer functions with glycosidic units.[2] Likewise dendrimer-like PEO of radial symmetry and spherical shape were shown to expand and shrink upon modification of their inner part with short poly(acrylic acid) segments.[3] Such dendrimers are designed to transport encapsulated species and deliver them in high pH media.

The chemistry used to construct these dendritic scaffolds was based on a divergent iterative approach combining "living" ring-opening polymerization of ethylene oxide (EO) from a pluri-oxanionic initiator and subsequent branching reactions meant to multiply by a factor of 2 the number of initiating sites for the growth of the generation to come. Hedrick and co-workers followed a similar approach to generate dendrimer-like aliphatic polyesters of the third generation including 24 arms.[4]

Very convenient when the generations to be grown require active species such as alkoxides, this divergent approach proves also very useful in atom transfer radical polymerization (ATRP). For instance, Hedrick and co-workers end-capped six-arm polyester stars with 12 or 24 ATRP initiating sites and grew a second generation of poly(methyl methacrylate) (PMMA) and poly(hydroxyethyl methacrylate) (PHEMA) arms to eventually obtain dendrimer-like star block copolymers.[5−7] More recently Percec et al. also resorted to a combination of "living" radical polymerization (LRP) and chain end derivatization to prepare by divergent growth dendritic PMMAs of the third generation.[8,9]

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In that work, these authors elaborated a new concept for the functionalization/derivatization of growing arms. Named TER-MINI for irreversible TERmination Multifunctional INITiator, a specific molecule was designed by Percec and co-workers that could interrupt the growth of "living" radical species and generate at the same time a branching point and twice as many initiating sites for the growth of the next generation. From calixarenes of various functionalities (4, 6, and 8) that were derivatized to accommodate ATRP sites, our team derived dendrimer-like polystyrenes of the third generation by resorting to the same iterative divergent method based on generation growth and chain end derivatization.[10] In the same vein, amphiphilic dendrimer-like copolymers including polystyrene (PS) and poly(acrylic acid) (PAA) generations (PS_n-b-PAA_{2n} and PAA_n-b-PS_{2n}) were obtained by us.[11] One of the difficulties encountered while applying this divergent strategy to active species such those of ATRP is the risk of spoiling the architecture formed due to inevitable termination reactions: when growing arms outward from a core, the probability of dendrimer–dendrimer coupling is not negligible and our attempts to prepare dendrimer-like polystyrene of a generation higher than three all failed.[10]

This prompted us to turn toward chemistries and chain polymerizations that are defect-free and truly "living" to construct dendrimer-like polymers of high generation from regular monomers such as styrene, dienes, or methacrylates. From that standpoint anionic polymerization fulfills ideally all the criteria of livingness and is certainly the most appropriate chain polymerization for monomers such as those mentioned above. However, due to the difficulty to generate pluricarbanionic initiators suitable for the latter monomers, and more generally soluble species that carry a precise number of carbanions, anionic polymerization has essentially been utilized in a convergent manner in macromolecular engineering. Unlike the divergent approach, the convergent synthesis entails the coupling of "living" linear chains with multifunctional deactivating agents. Dendrimer-like polymers resulting from the convergent approach have been obtained by iteration of the two steps of linear chain growth followed by their deactivation on the antagonist sites of the previous generation. Knauss,[12–14] Hadjichristidis,[15,16] and Hirao[17,18] applied this strategy of convergent deactivation of "living" carbanionic chains, using either chlorosilane containing electrophilic reagents or diphenylethylene derivatives including masked electrophilic benzyl bromide functions. Knauss and Hadjichristidis limited the synthesis of their dendrimer-like samples to small generations, but Hirao and co-workers succeeded in obtaining well-defined polymethacrylate dendritic samples up to the seventh generation.

As multifunctional electrophilic deactivating reagents are easier to generate and handle than multicarbanionic initiators,

as illustrated in the examples cited above, anionic polymerization was long thought as only suitable for the convergent methodology in the synthesis of stars and dendrimer-like polymers. Indeed, even regular, miktoarm, and asymmetric stars have been obtained by this deactivating convergent approach.[19–23]

The necessity in the latter approach to use a large excess of "living" linear chains for a complete coupling with the electrophilic moieties and thus the need to carefully fractionate the architecture formed from the precursor is a tedious and painstaking work that incited us to investigate an original divergent anionic route of dendrimer synthesis. The strategy of synthesis reported here capitalizes on a chemistry that we recently disclosed and exploited to design perfectly defined di- and pluricarbanionic initiators soluble in apolar media.[24,25] This chemistry is based on lithium–halide exchange reactions with pluribromoaryls as precursors and BuLi as a lithium source. After the first step which corresponds to the synthesis of "living" stars including a precise number of arms, the construction of dendrimer-like architectures requires the introduction of branching points at the end of the first generation and twice as many active initiating sites for the next generation to grow. Inspired by Percec's TERMINI concept, we thus designed and report here a compound that can interrupt the growth of "living" carbanionic chains and concomitantly introduce at their end two initiating sites that can get activated by lithium–halide reactions. This report actually describes a novel method of generating on a single (macro)molecule carbanionic species in a high and yet precise number through an anionic TERMINI. Combining a pluricarbanionic initiator with such an anionic TERMINI agent, repeatedly used generation after generation, affords well-defined dendrimer-like samples as it will be shown subsequently. The living character of the anionic polymerization of styrene and butadiene was undoubtedly an asset that helped us to obtain dendrimer-like PS of the seventh generation and polybutadiene of the third generation.

Prior to the synthesis of these dendrimer-like samples, the TERMINI concept was tested through the synthesis of asymmetric stars and miktoarm stars by combining the TERMINI developed in this work with "living" linear carbanionic chains.

2. Results and Discussion

2.1. Introduction of a Branching Point at the Chain End of Linear Carbanionic Polymers by the Means of a TER-MINI. 4,4′-Dibromodiphenylethylene (**1**) is the anionic TER-MINI designed to deactivate and functionalize "living" carbanionic chains. It contains a bromide in the para position of its two phenyl rings to allow subsequently an easy lithium–bromide exchange after its incorporation at the chain ends. The

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Scheme 1. Synthesis of Asymmetric and "Miktoarm" Star (Co)Polymers

⌇⌇ : PS, PB or PI

∿∿ : PEO, PS, PB or PI
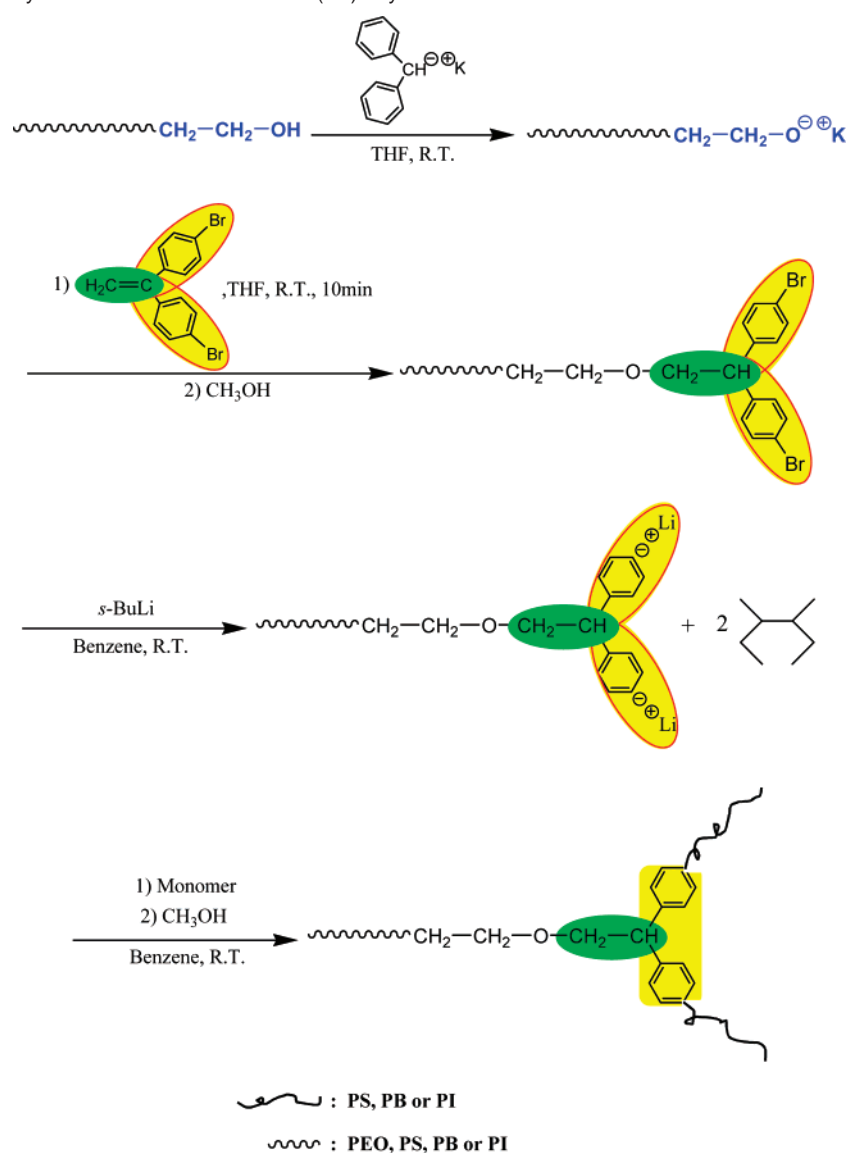
two bromides are also meant to impoverish the electron density on the unsaturation and facilitate its selective attack by nucleophiles, even weak ones. **1** is obtained in just two steps from commercial dibromobenzophenone with an excellent yield (see Experimental Section, Supporting Information).

Before reacting **1** with the growing carbanionic arms of a "living" star to generate the precursor of the second generation dendrimer-like sample, its ability to terminate and functionalize carbanionic stars was thus tested using "living" polystyryl lithium chains. Upon adding an excess of 4,4′-dibromodiphenylethylene to such chains, we expected to end-cap these chains with two bromophenyl moieties and utilize subsequently the latter to generate lithiated carbanions by exchange reaction with a lithium source. As shown in the size exclusion chromatogram (SEC) of the PS sample isolated (Figure S1), the reaction between the "living" polystyryl lithium and 4,4′-dibromodiphenylethylene did not occur as expected. Three different populations could actually be observed corresponding for the first peak (**1**) to the expected nucleophilic addition of "living" PS chains on the unsaturation of **1** and for the two others (**2** and **3**) to a combination of both addition and coupling with either one or

two arylbromide sites of **1** (Figure S1). This demonstrates that the polystyryl lithium chain end is too nucleophilic and therefore not selective enough to react only with the unsaturation of the TERMINI agent so as to generate pure ω,ω'-dibromo end-functionalized chain polymer.

For better selectivity, the reactivity of the living polystyrene chains was reduced and their alkyl lithium chain ends were replaced by less nucleophilic potassium alkoxide ends. To this end, hydroxyl-terminated linear PS or PB synthesized by deactivation of living lithiated polymers with an excess of ethylene oxide and also hydroxyl-terminated commercial linear PEO served as precursors. Upon characterization by ^{1}H NMR spectroscopy, these ω-hydroxy precursors exhibited a quantitative chain end functionalization. The hydroxyl functions of these linear polymer chains were then deprotonated in the presence of a stoichiometric amount of diphenylmethyl potassium (DPMK) in THF to afford potassium alkoxide living chain ends, and then a solution containing an excess of 4,4′-dibromodiphenylethylene (4 equiv per hydroxyl group) in THF was added to the mixture (Scheme 1). The SEC analysis of the polymer isolated after methanol quenching showed the presence of only
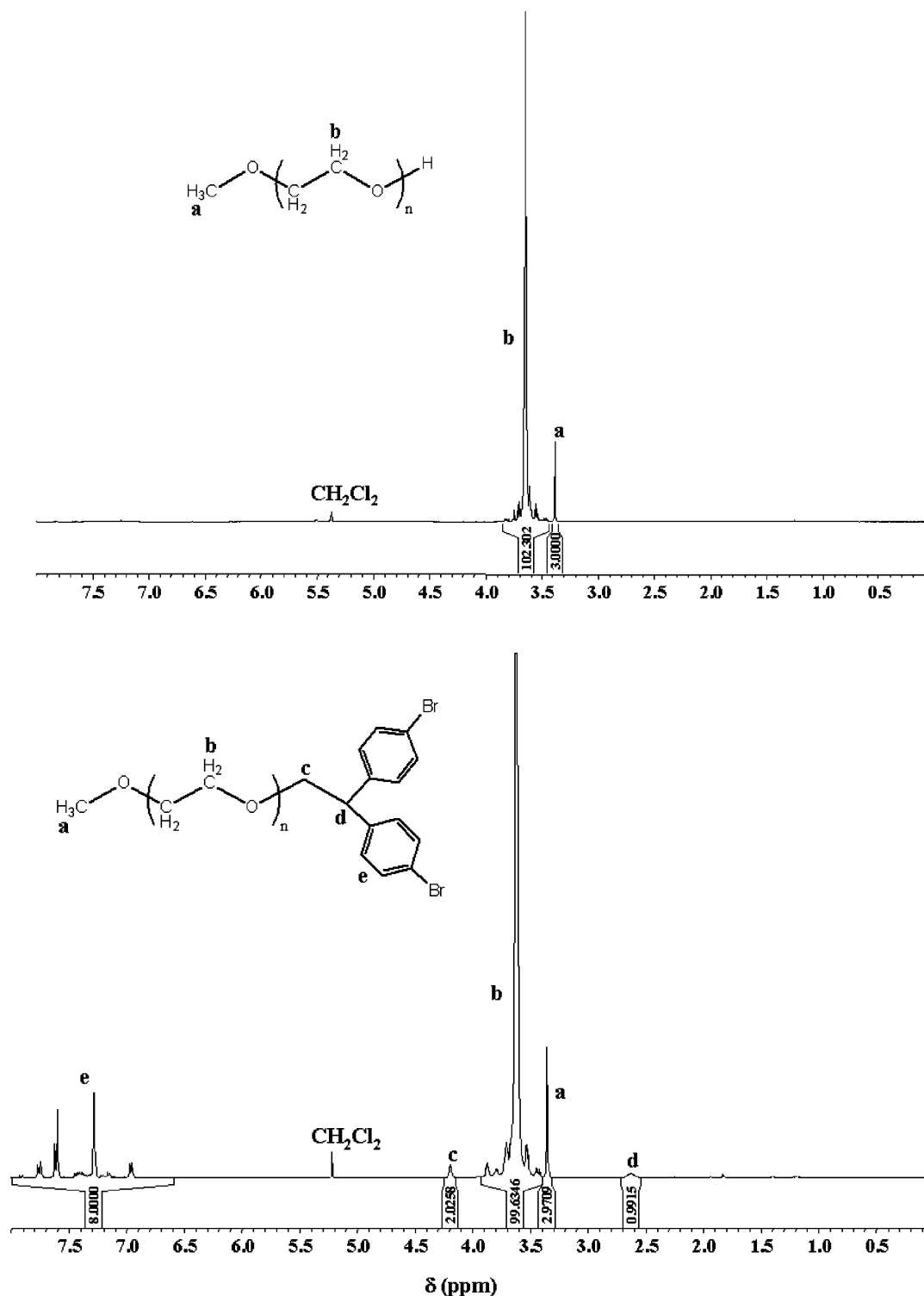
Figure 1. ^{1}H NMR spectra (CD$_2$Cl$_2$; 400 MHz) of PEO(Br)$_2$ aryl bromide-terminated poly(ethylene oxide) (run 4, Table 1) and its precursor PEO-OH hydroxyl-terminated poly(ethylene oxide) (run 3, Table 1).

one single peak slightly shifted with respect to that of the precursor toward the high molar mass region after the functionalization with **1** (Figure S2). The ^{1}H NMR spectra of the three PEO-(PhBr)$_2$, PS-(PhBr)$_2$, and PB-(PhBr)$_2$ functionalized samples revealed the total disappearance of the signal at $\delta = 5.4$ ppm corresponding to the unsaturation of **1**; in addition the signals appearing at $\delta = 6.9-8.0$ ppm and at $\delta = 4.2$ ppm (in the case of PEO) or $\delta = 3.7$ ppm (in the case of PS or PB) assignable, respectively, to the end-standing aromatic protons

$-$CH$_2-$CH(**Ph**Br)$_2$ and to the protons of the terminal primary carbon groups $-$C**H$_2$**$-$CH(PhBr)$_2$ could be clearly seen (Figures 1 and S3). For the determination of the experimental functionality we based our calculation on the ratios of the resonance signals appearing at $\delta = 3.3$ and 0.9 ppm (methyl protons of the initiator $-$C**H$_3$** in the cases of PEO and PS and PB, respectively) to those seen at $\delta = 6.9-8.0$ ppm and assignable to the aromatic protons at the chain end: all fall close to 1. Another means of checking the functionality of the same

Table 1. Characteristics of Asymmetric and "Miktoarm" Star (Co)Polymers

		$M_n \times 10^{-3}$ (g·mol^{-1})			$M_{w \text{ SEC/LS}}$ $\times 10^{-3}$ (g·mol^{-1})		functionality[a]		
run	type	theor	SEC/RI	^{1}H NMR		M_w/M_n	theor	OH	PhBr
1	PS-OH	2.4	2.4	2.3		1.04	1.0	1.0	
2	PS-(PhBr)$_2$	2.8	2.7	2.7		1.06			1.9
3	PEO-OH	1.1	1.0	1.1		1.05	1.0	1.0	
4	PEO-(Br)$_2$	1.4	1.3	1.4		1.06			1.9
5	PB-OH	3.0	3.1	3.1		1.03	1.0	1.0	
6	PB-(PhBr)$_2$	3.4	3.5	3.5		1.0			2.0
7	(PS)-b-(PS)$_2$(OH)$_2$	6.0	3.9		6.2	1.06	2.0	1.9	1.9
8	(PS)-b-(PS)$_2$(OH)$_2$	27.8	21.0		28.2	1.03	2.0	1.8[b]	
9	(PS)-b-(PS)$_2$(OH)$_2$	30.0	24.5		31.8	1.02	2.0	1.8[b]	
10	(PB)-b-(PB)$_2$(OH)$_2$	17.8	9.7		18	1.04	2.0	1.8	
11	(PS)-b-(PB)$_2$(OH)$_2$	30.0	19.7		30.4	1.01	2.0	1.9[b]	
12	(PS)-b-(PI)$_2$(OH)$_2$	12.5	9.6	12.8	12.7	1.05	2.0	1.9	
13	(PB)-b-(PS)$_2$(OH)$_2$	51.0	47.0	51.8	52.2	1.04	2.0	1.9[b]	

[a] Estimated by ^{1}H NMR spectroscopy. [b] Estimated by titration of the hydroxyl end groups by DPMK ([DPMK] = 0.521 mol·L^{-1}).

samples is to calculate the ratios of the resonance signals appearing at $\delta = 3.6$ ppm ((OC**H$_2$**C**H$_2$**)$_n$ methylene protons of the PEO chains) or at $\delta = 4.9-5.8$ ppm (protons of the double bonds of the PB chains) to those assignable to the aromatic protons of the chain end at $\delta = 6.9-8.0$ ppm: again the extent of functionalization calculated by this method is close to 1. One of the most striking features about this anionic TERMINI is the peculiar reactivity exhibited by its disubstituted unsaturation and in particular its faculty to undergo selective addition when reacted with alkoxides. The presence of the two bromides on separate phenyl rings explains the high electroaffinity exhibited by this unsaturation. For instance in the reaction between the potassium alkoxide carried by PEO chains with regular 1,1′-diphenylethylene, no addition on the latter compound could be observed by ^{1}H NMR spectroscopy. On the other hand, these potassium alkoxides carried by these polymers are too weak nucleophiles to react with the bromophenyl sites of **1**, paving the way for the synthesis of perfectly defined $\omega,\omega′$-dibromophenyl end-functionalized PEO, PS, and PB chains, which can now serve to generate polylithium macroinitiators by halogen–lithium exchange reaction.

2.2. Synthesis of Miktoarm and Asymmetric Star Polymers from Dicarbanionic Macroinitiators. These $\omega,\omega′$-dibromophenyl PS and PB chains were then treated with stoichiometric amounts of *sec*-butyllithium used here as a lithium provider; this reaction was carried out in benzene or cyclohexane and resulted in the formation of the corresponding dilithiated species, reflected by the red color taken by the medium, and of 2-bromobutane (Scheme 1). The two phenyl lithiums carried by PS and PB chains were found to be totally soluble in apolar solvents such as cyclohexane or benzene. To neutralize 2-bromobutane, which might subsequently deactivate the chains that are expected to grow from these carbanionic sites upon monomer addition, 1 equiv of *sec*-butyllithium was added which resulted in the formation of 3,4-dimethylhexane (Scheme 1). This sequence of reactions, i.e., lithium–bromide exchange reaction followed by 2-bromobutane neutralization, was successfully brought about with the polyarylbromide precursor.[24,25] The polymerization of monomers such as styrene, butadiene, or isoprene was then performed in cyclohexane or benzene and at room temperature using these PS-(Ph$^-$Li$^+$)$_2$, or PB-(Ph$^-$Li$^+$)$_2$ dilithiated macroinitiators. After polymerization, the living carbanionic species were deactivated with EO to functionalize the two grown arms with terminal hydroxyl
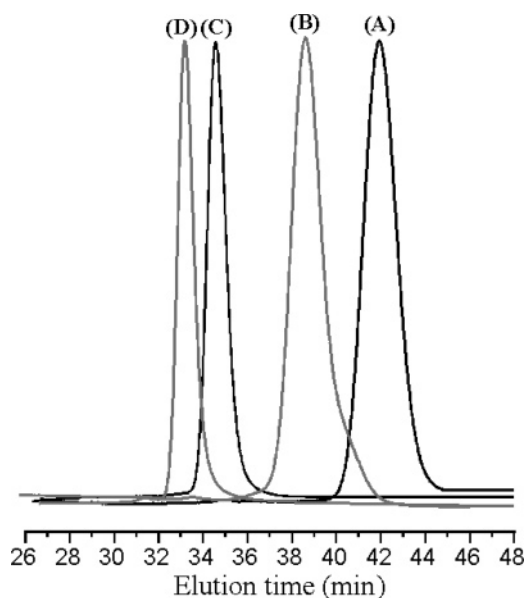
Figure 2. SEC traces (RI detector) of asymmetric star polystyrenes PS-b-PS$_2$ (runs 7 (B), 8 (C), and 9 (D), Table 1) and its precursor PS-(Br)$_2$ (run 2(A), Table 1). Conditions: [Li$^+$] = 5×10^{-3} mol·L^{-1}, at RT in benzene.

functions. Depending upon the monomer-macroinitiator couple considered, either asymmetric or miktoarm star samples were isolated and analyzed by size exclusion chromatography with a light scattering detector (SEC/LS) and ^{1}H NMR spectroscopy. Table 1 gives the data pertaining to these three-arm asymmetric and miktoarm copolymer stars grown from these dilithiated macroinitiators. Samples of narrow molar mass distribution (1.01 < M_w/M_n < 1.15) were obtained in all cases. The complete disappearance of the peak due to the PS-(PhBr)$_2$ and PB-(PhBr)$_2$ precursors from the chromatograms meant that all precursor chains participated in the initiation process (Figures 2, S4, and S5). The absolute molar mass values drawn from the SEC/LS detector were found to agree almost perfectly with theoretical values but were higher than those obtained from the refractive index (RI) detector relative to linear standards which mirrors their compact architecture (Table 1). The nature of the architectures formed and especially the star character was also characterized by ^{1}H NMR using to this end asymmetric and miktoarm star samples of low degrees of polymerization (Figure 3 and Table 1). From the ratio of the integrals of the signal of the methyl protons $-C$**H$_3$** of *sec*-BuLi the initiator at $\delta = 0.9$
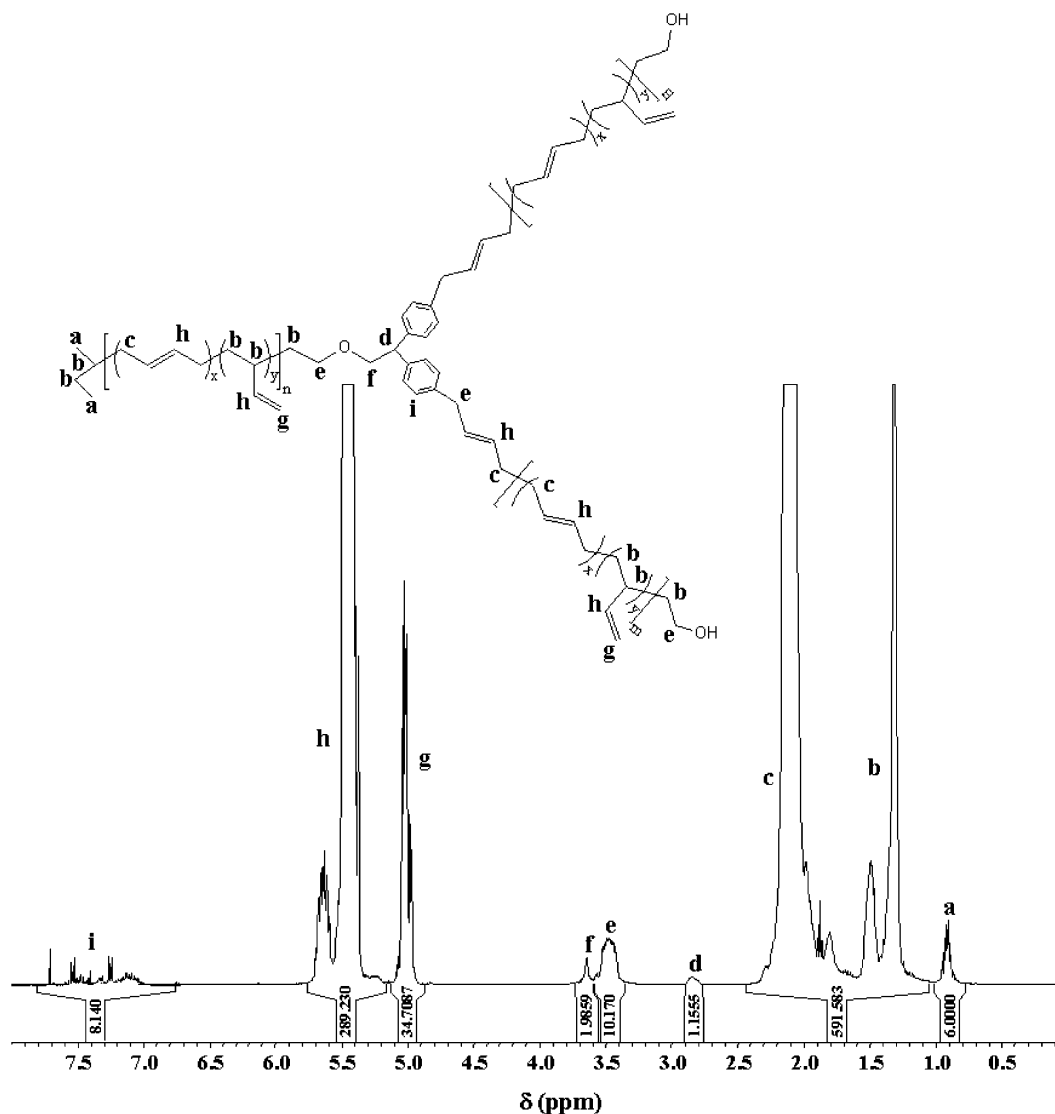
Figure 3. ^{1}H NMR spectrum (CD$_2$Cl$_2$; 400 MHz) of an asymmetric star polybutadiene PB-*b*-PB$_2$(OH)$_2$ (run 10, Table 1).

ppm to that of the methylene protons due to the −C*H₂*OH star arm ends and −CH₂−O−CH₂−CH(Ph)₂− branching points (δ = 3.6 ppm), the actual functionality of several samples was determined and values close to 2 were obtained for the number of arms grown from each branching point of these asymmetric and miktoarm star (co)polymers (Figure 3 and Table 1). The functionality of the branching points was also double checked by titration of the hydroxyl end groups carried by these asymmetric and miktoarm stars, using a solution of diphenyl-methyl potassium (DPMK) of known concentration ([DPMK] = 0.521 mol·L^{-1}). Again functionalities close to 2 were found in all cases (Table 1).

2.3. Synthesis of Dendrimer-Like Polystyrene and Polybutadiene. As mentioned in the introduction, dendrimer-like polymers constructed by the divergent approach described here are grown by repeating generation after generation the two following steps: polymerization from phenyl lithium carbanionic sites derived by lithium−bromide exchange and end-functionalization of the growing sites with 4,4′-dibromodiphenylethylene. The first step in such an endeavor is thus the synthesis of living stars by divergent growth. We described recently the preparation of a new category of tri- and tetracarbanionic initiators obtained by halogen−lithium exchange reaction

between a tri- and tetrabromoaryl compound and *sec*-butyl-lithium as the lithium source.[25] The tri- and tetracarbanionic species formed were shown to be excellent initiators for the anionic polymerization of styrene and butadiene, and well-defined tri- and tetraarmed polystyrene and polybutadiene stars exhibiting monomodal and narrow molar mass distribution could be obtained in this way.[25] These pluricarbanionic initiators were also employed to prepare (PB-*b*-PEO)$_4$ amphiphilic diblock and P(S-*b*-B-*b*-MMA)$_n$ (n = 3 or 4) triblock star copolymers.[25,29] Upon neutralizing and derivatizing the living stars described above, in particular their four growing carbanionic sites with EO and then 4,4′-dibromodiphenylethylene, the precursors of the second generation would then be generated in the form of dibromoaryl ended star polymers. The growth in a second step of the second generation would then require a lithium−bromide exchange before twice as many arms could be grown upon monomer addition.

2.3.1. Synthesis of Star-Shaped (G-1) Polystyrene and Polybutadiene Precursors (Number Following G Stands for Number of Generation). Tetraarmed star polymers were thus prepared from the tetrabromoaryl compound shown in Scheme

(29) Matmour, R.; Francis, R.; Duran, R. S.; Gnanou, Y. *Macromolecules* **2005**, *38*, 7754.

Scheme 2. Synthesis of Third Generation Dendrimer-Like Polystyrene
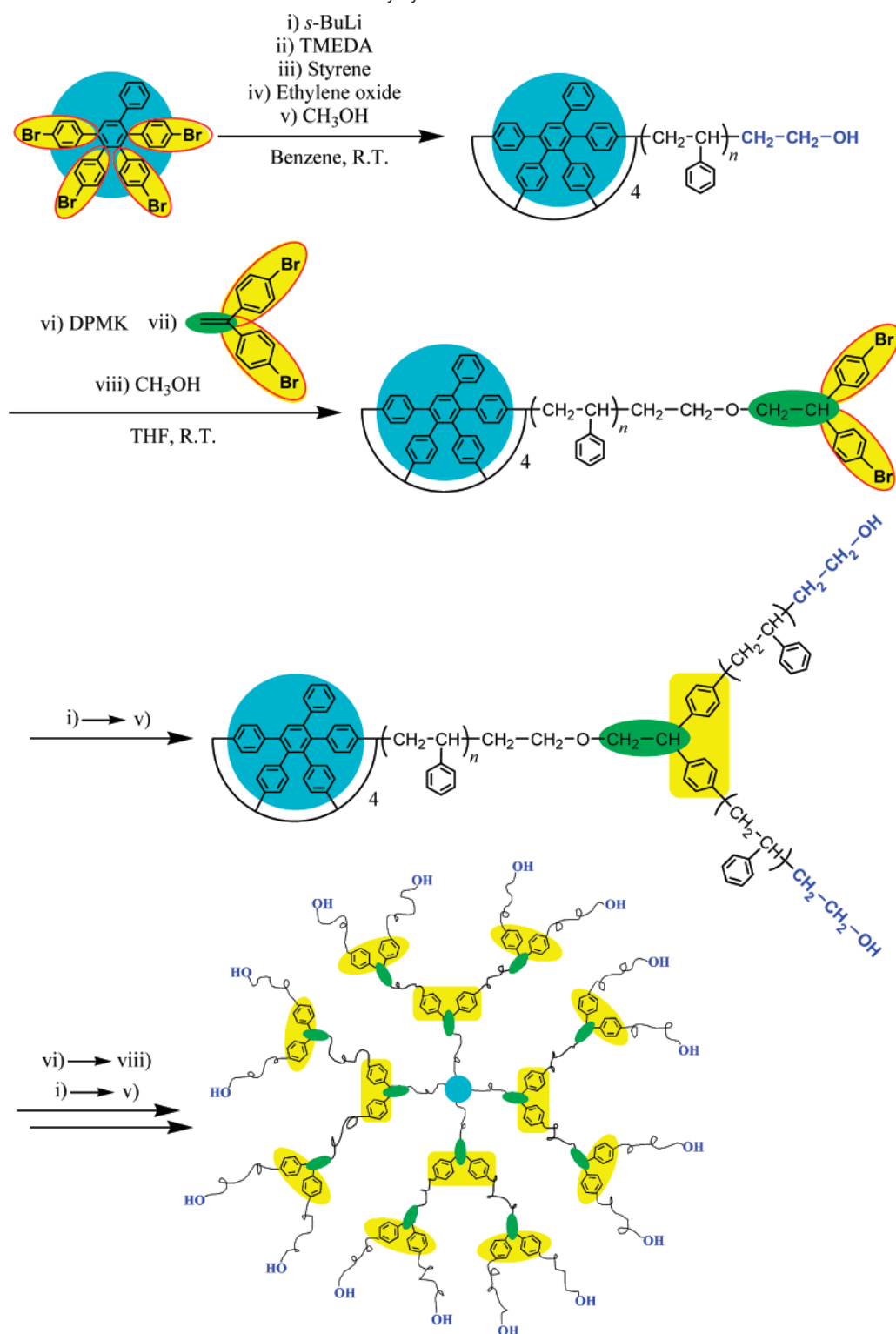
2 which was first subjected to a lithium–halide exchange reaction. The latter precursor was prepared in excellent yields (>90%) by a Diels–Alder reaction of 2,3,4,5-tetrakis(*p*-bromophenyl)cyclopentadienone and phenylacetylene with extrusion of carbon monoxide; it was treated with stoichiometric amounts of *sec*-butyllithium to generate the corresponding tetraalkyllithium agent in benzene (Scheme 2).[25,28] The resulting tetralithiated species being insoluble in the latter solvent, tetramethylethylene diamine (TMEDA) (ratio of [TMEDA]/[Li]

= 2) was utilized to solubilize the tetraphenyllithium formed, both ligand and lithium species forming a soluble complex. These complexes give stable species and enough steric bulk precluding the tetralithiated initiators from aggregating. As previously mentioned, this lithium–bromide exchange reaction produces 2-bromobutane that has to be neutralized before growing carbanionic chains. *sec*-Butyllithium (1 equiv) was thus added next, yielding 3,4-dimethylhexane as an inert byproduct. The anionic polymerization of styrene and butadiene could then

Table 2. Characteristics and Solution Properties of Dendrimer-Like Polystyrenes and Polybutadienes

| | | $M_{n\ theor} \times 10^{-3}$ (g·mol^{-1}) | | | | functionality[a] | | | [η] | |
run	type	theor	SEC	SEC/HT	M_w/M_n	theor	OH	PhBr	(dL/g)	g'^{b}
14	PSG-1	8.0	3.08	7.9	1.1	4	3.8		0.0608	0.84
15	PSG-1Br	9.4	4.3	9.3	1.1	8		7.9		
16	PSG-2	55.9	40.3	57.0	1.07	8	7.8		0.1848	0.63
17	PSG-2Br	58.6	41.7	59.4	1.1	16		15.8		
18	PSG-3	151.0	91.2	153.6	1.08	16	15.9[c]		0.2218	0.374
19	PSG-3Br	156.4	95.6	158.9	1.1	32		31.8		
20	PSG-4	373.6	189.9	375.3	1.05	32	31.8[c]		0.2156	0.193
21	PSG-4Br	384.4	198.5	387.4	1.07	64		64.1		
22	PSG-5	695.3	363.3	710.5	1.04	64	64.7[c]		0.2047	0.116
23	PSG-5Br	716.9	382.3	730.6	1.08	128		127.0		
24	PSG-6	1212.5	586.0	1301.0	1.04	128	127.7[c]		0.1679	0.062
25	PSG-6Br	1255.7	628.2	1345.4	1.08	256		255.0		
26	PSG-7	1822.0	610.4	1920.2	1.04	256	255.6[c]		0.1228	0.034
27	PBG-1	14.0	7.6	14.5	1.03	4	3.8			
28	PBG-1-Br	15.9	7.8	15.2	1.03	8		7.9		
29	PBG-2	36.7	28.4	38.6	1.05	8	7.8			
30	PBG-2-Br	41.3	29.0	41.9	1.05	16		15.8		
31	PBG-3	121.9	72.6	129.6	1.05	16	15.7[c]			
32	PBG-3-Br	135.0	74.0	131.4	1.05	32		31.7		

[a] Estimated by ^{1}H NMR spectroscopy. [b] $g' = [\eta]_{dendri}/[\eta]_{linear}$; ($[\eta] = 1.23 \times 10^{-2}\ M_n^{0.71}$). [c] Estimated by titration of the hydroxyl end groups by DPMK ([DPMK] = 0.521 mol·L^{-1}).

be carried out in benzene and at room temperature from this solubilized tetralithiated initiator. After complete conversion of the monomer, end capping was accomplished through addition of a large excess of ethylene oxide which introduced terminal hydroxyl functions. The characteristics of such ω-hydroxyl star samples are listed in Table 2. The characterization of all the samples obtained by SEC showed the disappearance of the peak due to the tetrafunctional initiator in the low molar mass region, implying its total consumption in the initiation of styrene and butadiene polymerization (Figure S6). The actual molar masses of such ω-hydroxyl polystyrene and polybutadiene stars were determined using an SEC/LS detector; they were found to be in good agreement with the calculated values, and their distributions were narrow (M_w/M_n < 1.1). The tetrafunctionality of the resulting polystyrene and polybutadiene stars was then demonstrated by ^{1}H NMR characterization of the star samples of low degrees of polymerization (Figure S7). The experimental functionality values calculated from the ratios of the resonance signals appearing at $\delta = 6.8-8.0$ ppm (aromatic protons of the tetrafunctional initiators) to those seen at $\delta = 3.6$ ppm ($-CH_2-$ OH chain end protons) were found to be always close to 4 for the four-armed stars. Further evidence of the star character and the four-arm star structure was obtained by comparing the intrinsic viscosity [η] of our samples with that of linear polymers, as previously demonstrated.[25]

2.3.2. Introduction of Branching Points at Each Arm End by the Means of 1. The next step in the synthesis of these dendrimer-like polymers was the introduction of a branching point and thus of two aryl bromide groups at each arm end of these stars. The same procedure as that used for the preparation of asymmetric and miktoarm star polymers was followed. The hydroxyl functions carried by the arm ends of these polystyrene and polybutadiene stars were deprotonated in the presence of a stoichiometric amount of DPMK in THF, and then a THF solution of 4,4′-dibromodiphenylethylene was added. After protonation of the functionalized chain ends by methanol addition, the resulting functionalized star polymers were analyzed by SEC and ^{1}H NMR spectroscopy (Figures S6 and S7).

First, as in the case of linear chain polymers, it can be observed that the SEC trace of these functionalized stars is unimodal and sharp, attesting to the absence of any coupling reactions on the bromide positions; a small shift of the peak can even be seen toward the high molar mass region, indicating the addition of **1** at the arm ends. The functionalization of each arm end with dibromodiphenylethylene was checked by ^{1}H NMR on PB$_4$-(PhBr)$_8$ star samples of low degrees of polymerization (Figure S7). Indeed, the ^{1}H NMR spectrum exhibits signals at $\delta = 6.9-8.0$ ppm assignable to the aromatic protons of the star core and of its arm tips $-CH_2-CH(PhBr)_2$ and other signals at $\delta = 3.7$ ppm and $\delta = 3.5$ ppm corresponding to the protons carried by the terminal primary carbon groups $-CH_2-CH(PhBr)_2$ and $-CH_2-O-CH_2-CH(PhBr)_2$, respectively (Figure S7). The experimental functionality was determined by comparing the integration values of the signals of the aromatic protons due to the polyphenylene core and to the dibromophenyl end groups ($\delta = 6.5-8.0$ ppm; 54H) with that of the signals of the protons carried by the terminal primary carbon groups $-CH_2-CH-(PhBr)_2$ ($\delta = 3.7$ ppm; 8H) and $-CH_2-O-CH_2-CH(PhBr)_2$ ($\delta = 3.5$ ppm; 8H). The ratio of 6.7 found between the intensities of the signals appearing at $\delta = 6.5-8.0$ ppm and the one at $\delta = 3.7$ ppm indicated that functionalization occurred quantitatively (Figure S7).

2.3.3. Preparation of Pluricarbanionic Initiators for the Synthesis of Second-Generation (G-2) Dendrimer-Like Polystyrene and Polybutadiene. From the eight bromophenyl sites of PS$_4$(PhBr)$_8$ and PB$_4$(PhBr)$_8$ polystyrene and polybutadiene stars, eight arms were grown anionically after lithium−bromide exchange reaction and monomer addition. These stars were thus first treated with stoichiometric amounts of *sec*-butyllithium in benzene to generate the corresponding polylithiated species PS$_4$(Ph$^-$Li$^+$)$_8$ and PB$_4$(Ph$^-$Li$^+$)$_8$, and 2-bromobutane was neutralized into 3,4-dimethylhexane upon addition of a further equivalent of BuLi. The presence of TMEDA (ratio of [TMEDA]/[Li] = 2) was necessary to solubilize the polylithiated species formed in benzene. The polymerizations of styrene and butadiene were performed in a second step in benzene at room
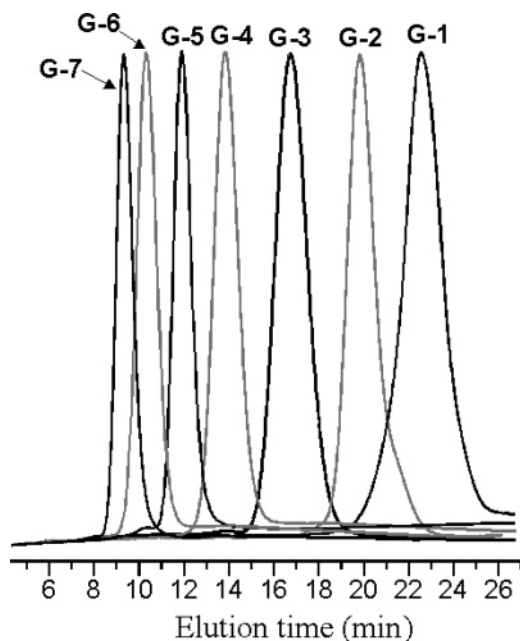
Figure 4. HTSEC traces (RI detector) of dendrimer-like polystyrenes (runs 14, 16, 18, 20, 22, 24, and 26, Table 2). Conditions: [TMEDA]/[−PhLi] = 2, at RT, in benzene.

**Figure 5.** HTSEC traces (RI detector) of dendrimer-like polybutadienes (runs 27, 29, and 31, Table 2). Conditions: [TMEDA]/[−PhLi] = 2, at RT, in benzene.

temperature using $PS_4(Ph^-Li^+)_8$ and $PB_4(Ph^-Li^+)_8$ octalithiated species, as initiators, respectively. After polymerization of the monomer the living chain ends were deactivated by addition of an excess of ethylene oxide; the dendrimer-like polystyrene and polybutadiene of the second generation isolated were then analyzed by SEC and ^{1}H NMR spectroscopy (Figures 4, 5, S8, and S9). First, the SEC traces of the second generation PS_4-$PS_8(OH)_8$ and $PB_4PB_8(OH)_8$ dendrimer-like samples indicate the complete disappearance of the peaks of the $PS_4(PhBr)_8$ and $PB_4(PhBr)_8$ precursors (Figures 4, 5, and S9), confirming that all precursor chains participated in the initiation−polymerization process. In the SEC chromatograms of the $PS_4PS_8(OH)_8$ and

$PB_4PB_8(OH)_8$ samples, two other small peaks can however be observed next to the main peak toward the high molar mass region whose presence results from the aggregation of the eight hydroxyl end groups of these dendrimer-like samples in THF (Figure S9). To break the aggregation between these peripheral hydroxyl end groups, the different samples were characterized by high-temperature size exclusion chromatography (HT-SEC) running at 130 °C in dichlorobenzene as solvent and equipped with a viscometer detector giving the absolute molar mass. In this case, no peak due to aggregates could be seen and only one peak exhibiting a monomodal and narrow molar mass distribution ($1.01 < M_w/M_n < 1.2$) could be observed (Figures 4 and 5, Table 2). Indeed, the molar mass values determined by HT-SEC characterization agreed well with the expected values confirming that two PS or PB arms of well-controlled size could be grown from each branching point. As to the characterization by ^{1}H NMR carried out on the second generation $PB_4PB_8(OH)_8$ dendrimer-like polybutadiene (Figure S8), it clearly revealed the presence of four signals: at $\delta = 6.5−8.0$ ppm the signals of the aromatic protons of the polyphenylene core (22H) and the branching points (32H at the branching points) could be clearly seen as well as the signals of the methylene protons carried by the branching points and at arm ends $−CH_2−CH−(PhCH_2)_2−$ at $\delta = 3.7$ ppm (8H), $−CH_2−$ $O−CH_2−CH−(PhCH_2)_2−$ and $−CH_2−OH$ at $\delta = 3.4$ ppm (24H), and $−CH_2−CH−(PhCH_2)_2−$ at $\delta = 2.8$ ppm (4H). The ratios of 6.8, 2.2, and 13.8 found between the intensities of the signal appearing at $\delta = 6.5−8.0$ ppm (54H) and the ones at $\delta = 3.7$ ppm (8H), at $\delta = 3.4$ ppm (24H), and at $\delta = 2.8$ ppm (4H), respectively, indicated that initiation occurred with excellent efficiency (Figure S8). Indeed, the titration of the hydroxyl end groups at the periphery of the PS and PB dendrimer-like polymers in THF by a solution of DPMK of known concentration ([DPMK] = 0.521 mol·L^{-1}) gave in the case of both PS or PB dendrimer-like polymers values of functionality close to 8 (Table 2). The excellent definition of these second generation $PS_4PS_8(OH)_8$ and $PB_4PB_8(OH)_8$ dendrimer-like polymers prompted us to prepare dendritic PS and PB of a higher generation.

2.3.4. Third-Generation (G-3) Dendrimer-Like Polystyrene and Polybutadiene. The synthetic methodology described above which is based on an iterative divergent approach was repeated here (i.e., chain end modification and polymerization of styrene or butadiene) for the synthesis of dendritic PS and PB of a higher generation. Similarly to the cases of **G-1** and **G-2**, the peripheral hydroxyl end groups of $PS_4PS_8(OH)_8$ and $PB_4PB_8(OH)_8$ dendrimer-like polymers were deprotonated by reaction with stoichiometric amounts of DPMK, and a solution of 4,4′-dibromodiphenylethylene was added in excess (4 equiv per −OH group). After protonation of the living chain ends by addition of methanol, the resulting $PS_4PS_8(PhBr)_{16}$ and PB_4-$PB_8(PhBr)_{16}$ dendrimer-like polymers were isolated and characterized by SEC, HT-SEC, and ^{1}H NMR spectroscopy. As previously shown, no substitution reaction implying terminal phenylbromide positions could be observed (Figures 4 and 5). Indeed, the ^{1}H NMR analysis of the chain ends of the PB_4PB_8-$(PhBr)_{16}$ dendrimer-like polybutadiene clearly indicates four distinct signals corresponding to the aromatic protons of the polyphenylene core and the aryl rings of the branching points ($\delta = 6.8−8.0$ ppm; 118H), to the methylene protons carried by
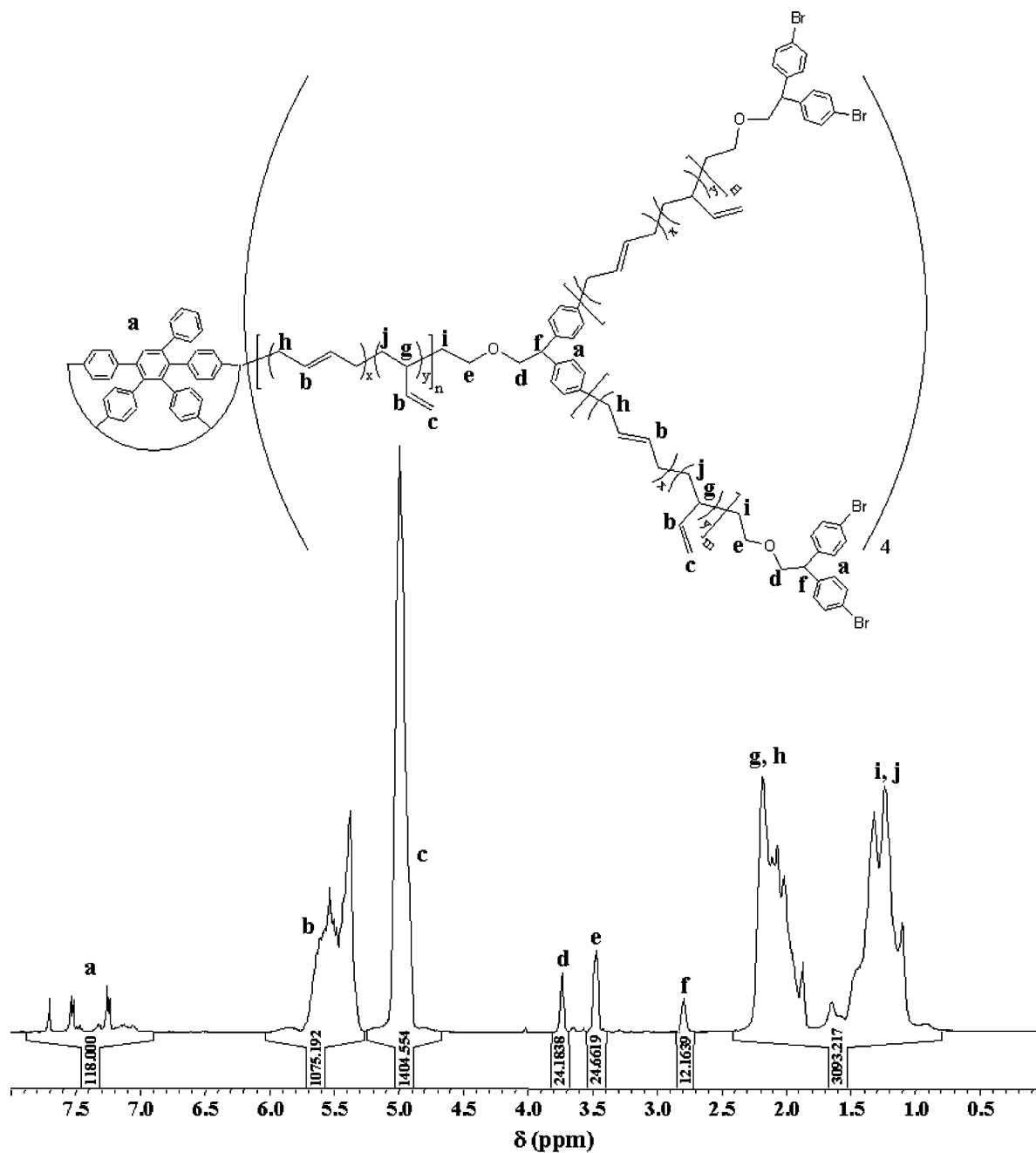
Figure 6. ^{1}H NMR spectrum (CD$_2$Cl$_2$; 400 MHz) of an aryl bromide-terminated dendrimer-like polybutadiene PB$_4$-*b*-PB$_8$(Br)$_{16}$ (run 30, Table 2).

the branching points −C**H**$_2$−CH−(PhCH$_2$)$_2$− and appearing at δ = 3.7 ppm (24H), −C**H**$_2$−O−CH$_2$−CH−(PhCH$_2$)$_2$− at δ = 3.4 ppm (24H), and −CH$_2$−C**H**−(PhCH$_2$)$_2$− at δ = 2.8 ppm (12H) (Figure 6). In addition, the experimental −PhBr functionality, determined from the ratios of the integration values of the different signals occurring at δ = 6.8−8.0 ppm, at δ = 3.7 ppm, at δ = 3.4 ppm, and at δ = 2.8 ppm were found to correspond to the expected value of 16 groups per polymer. Next, the resulting PS$_4$PS$_8$(PhBr)$_{16}$ and PB$_4$PB$_8$(PhBr)$_{16}$ dendrimer-like polymers were treated with stoichiometric amounts of *sec*-butyllithium in benzene to generate the corresponding PS$_4$PS$_8$(Ph$^-$Li$^+$)$_{16}$ and PB$_4$ PB$_8$(Ph$^-$Li$^+$)$_{16}$ polylithiated species. At this stage 16 carbanionic sites per polymer formed a physical gel due to the stronger aggregation between these polylithiated species in benzene. Upon addition of 2 equiv of TMEDA per −PhLi, the polylithiated species became totally soluble in

benzene and monomer−either styrene or butadiene depending upon the precursor−was polymerized. The living chain ends were deactivated by addition of an excess of ethylene oxide, and the resulting dendritic polystyrene and polybutadiene were characterized by SEC and HT-SEC. As shown in Figures 4 and 5, the HT-SEC profiles of the PS$_4$PS$_8$PS$_{16}$(OH)$_{16}$ and PB$_4$PB$_8$-PB$_{16}$(OH)$_{16}$ third-generation dendrimer-like polymers exhibit only one sharp monomodal and narrow (1.05 < M_w/M_n < 1.08) peak, corresponding, respectively, to the dendritic polystyrene and polybutadiene, with in each case the total disappearance of the second generation macroinitiator. As in the case of the second generation sample, the hydroxyl end groups at the periphery of the PS$_4$PS$_8$PS$_{16}$(OH)$_{16}$ and PB$_4$PB$_8$PB$_{16}$(OH)$_{16}$ dendrimer-like polymers were titrated in THF by a solution of DPMK of known concentration ([DPMK] = 0.521 mol·L^{-1}) which gave for both PS and PB dendrimer-like polymers values

of functionality close to 16 indicating that initiation occurred as expected (Table 2).

2.3.5. From the Fourth (G-4) to the Seventh Generation (G-7) Dendrimer-Like Polystyrene. The same iterative divergent approach as that used for the synthesis of the third generation dendrimer-like polymers was applied for the preparation of the fourth (G-4), fifth (G-5), sixth (G-6), and seventh generation (G-7) dendrimer-like polystyrenes. Successively, the hydroxyl end groups standing at the periphery of the precursors of these dendrimer-like polystyrenes were deprotonated by a solution of DPMK and functionalized by reaction with 4,4′-dibromodiphenylethylene; the dibromophenyl end-functionalized dendrimer-like polystyrenes eventually obtained were subsequently used after reaction with *s*-BuLi as pluricarbanionic macroinitiators for the polymerization of styrene in the presence of TMEDA as an additive. After deactivation of the living polystyryl lithium chain ends by an excess of ethylene oxide and degassed methanol, all the dendritic polystyrene samples of different generations (G-4, G-5, G-6, and G-7) were successively characterized by SEC and HT-SEC (Figures 4, 5, and S9). As in the previous cases, the same peaks corresponding to the aggregates were observed in the high molar mass region by SEC. However, the latter were not observed at high temperature as shown in the HT-SEC chromatograms of fourth (G-4), fifth (G-5), sixth (G-6), and seventh generation (G-7) dendrimer-like polystyrenes (Figure 4). As can be seen in Figure 4, the HT-SEC peak of each generation of PS is monomodal and narrow and shifts to the high molar mass region with the total disappearance of the precursor as the iterative steps proceed. Indeed, the experimental degree of −OH functionality was determined by titration of hydroxyl end groups by reaction with a solution of DPMK of known concentration ([DPMK] = 0.521 mol·L^{-1}). As seen in Table 2, the results showed experimental functionalities very close to the expected values. From the fourth generation onward, this last method, that is the titration of hydroxyl end groups, was found to be more efficient than ^{1}H NMR spectroscopy, because of the weak intensity of the resonance signals due to the end groups compared to that of the aromatic protons of the styrene repeating units. Thus, upon iteration of the two sequences of styrene polymerization and branching reaction of this divergent approach, a seventh-generation dendrimer-like PS (G-7) sample was synthesized with an absolute molar mass M_n of 1920×10^3 g·mol^{-1}, including no less than 256 OH end groups and 508 PS segments.

2.4. Viscosity Behavior of Dendrimer-Like Polystyrenes. In the literature, several studies deal with the viscometric behavior of star polymers, hyperbranched polymers, dendrigrafts, and regular dendrimers. However to the best of our knowledge, we were the first to demonstrate, in the case of third generation dendrimer-like polystyrenes synthesized by atom transfer radical polymerization, that the latter dendritic architecture exhibits a behavior in solution similar to that of regular dendrimers.[10] In contrast to hyperbranched polymers, whose intrinsic viscosity remains independent of the molar mass, the variation of log[η] against the generation or the molar mass of dendrimer-like PS exhibits a bell-shaped curve with an increase of [η], followed eventually by a decrease after reaching a maximum for the third generation as observed in the case of regular dendrimers.[30,31] In fact molar masses in regular den-
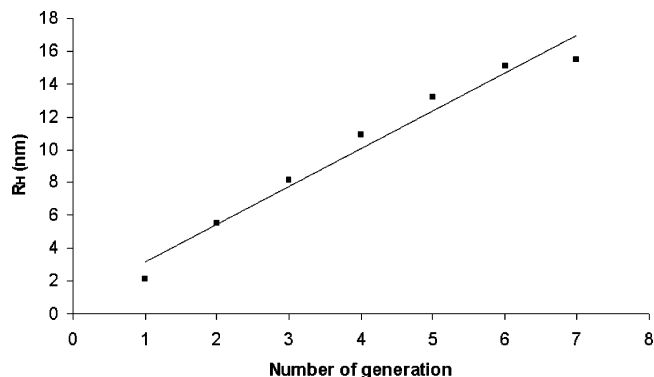
Figure 7. Evolution of the hydrodynamic radius (R_H) as a function of the number of generation (G) for dendrimer-like polystyrenes obtained from an initial tetrafunctional initiator (runs 14, 16, 18, 20, 22, 24, and 26, Table 2).

drimers increase exponentially with g with a variation in 2^{g-1}, and their hydrodynamic volume grows with g^3; [η] varying proportionally to $g^3/2^{g-1}$, it experiences a maximum as g increases.

For a better comparison with the results that we previously obtained on samples prepared by ATRP up to the third generation, the intrinsic viscosities of our anionically prepared dendrimer-like PS were determined at 35 °C using toluene as solvent. First, from the experimental [η]$_{dendritic}$ (measured at 35 °C in toluene) and the [η]$_{linear}$ values (calculated from eq 1 for linear PS of same molar mass under the same conditions),[32] the g' ratio [η]$_{dendritic}$/[η]$_{linear}$ could be determined and is listed in Table 2. The intrinsic viscosity of these dendritic samples is found to be lower than that of linear PS (until 30 times lower than that of linear PS), and the g' parameter decreases with the generation, confirming that the dendritic structure becomes more and more compact as the number of generations and branched segments increases.

$$[\eta]_{linear} = 1.23 \times 10^{-2} M_w^{0.71} \tag{1}$$

As shown by the relation between [η], which is also inversely proportional to the hydrodynamic density, and the hydrodynamic volume (V_H)

$$[\eta] = 2.5 N_a V_H / M = (10\pi/3) N_a R_{H,app}^3 / M \tag{2}$$

where $R_{H,app}$ is the apparent hydrodynamic radius and N_a is the Avogadro number, such a constant [η] in the particular case of hyperbranched 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.

To determine how hydrodynamic volumes vary as a function of the number of generations (g) we resorted to the eq 3 given below, using [η] and M determined experimentally.

$$R_{H,app} = [3M[\eta]/10\pi N_a]^{1/3} \tag{3}$$

As shown in Figure 7, $R_{H,app}$ increases nearly linearly with the number of generation for polystyrene dendrimer-like polymers, indicating that V_H thus grows in g^3 like regular dendrimers.

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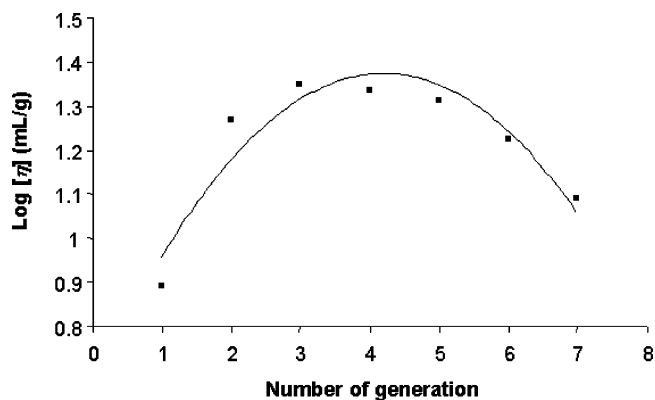
Figure 8. Evolution of log[η] as a function of the number of generation (*G*) for dendrimer-like polystyrenes prepared using a tetrafunctional initiator (runs 14, 16, 18, 20, 22, 24, and 26, Table 2).
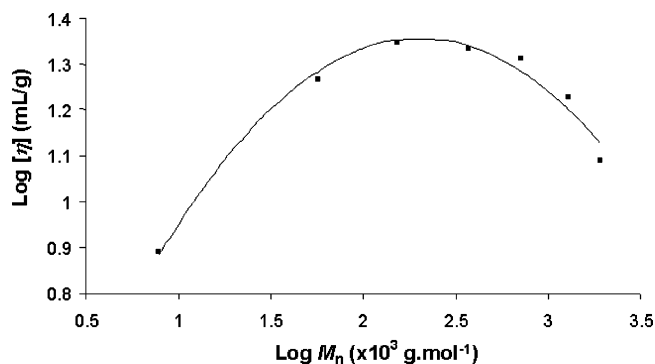
Figure 9. Evolution of log[η] as a function of log M_w for dendrimer-like polystyrenes prepared from a tetrafunctional initiator (runs 14, 16, 18, 20, 22, 24, and 26, Table 2).

From the variation of log[η]$_{\text{dendritic}}$ with the number of generations, we observe that [η] reaches a maximum corresponding to the third generation dendrimer-like PS and then decreases gradually until the seventh generation (Figure 8). The evolution of log[η]$_{\text{dendritic}}$ as a function of log M_n was also plotted (Figure 9). The same trend as the one observed previously for the plot of log[η]$_{\text{dendritic}}$ against the number of generations is seen here, indicating that [η] is not independent of the molar mass for dendrimer-like PS in contrast to some hyperbranched polymers or highly dense globular structures. The peculiar

profile of [η] and that reciprocal of hydrodynamic density, the latter being the reciprocal of [η], resemble those exhibited by regular dendrimers indicating that the twin architectures possess the same "signature".

Conclusion

The methodology of synthesis of dendrimer-like samples described in this paper is based on an original chain end modification, involving the reaction of a potassium alkoxide living chain/arm with the unsaturation of 4,4′-dibromodiphe-nylethylene which affords ω,ω'-ended dibromophenyl chains/arms. The latter bromophenyl functions carried by separate aryl rings were then subjected to a halogen−lithium exchange reaction to prepare the corresponding polylithiated species, providing an efficient synthetic route to asymmetric and "miktoarm" star (co)polymers including polystyrene, polybutadiene, and/or polyisoprene arms. Starting from a tetracarbanionic initiator and upon repeating this sequence of reactions, dendrimer-like PS and PB up to the seventh and third generations, respectively, could be successfully synthesized. The characterization of dendrimer-like PS samples confirmed that regular dendrimers and the macromolecular architectures described in this study belong to the same family, the two types of dendritic structures exhibiting a similar viscosity behavior with regards to the number of generations.

This chemistry could be successfully implemented only after the design of an original reagent, 4,4′-dibromodiphenylethylene, that functions successfully as a TERminator for living carbanionic chains and as a precursor for the Multifunctional INItiator. Applied to styryl and dienyl carbanions, this chemistry is versatile enough to be applied to other anionic species such as enolates, etc.

Supporting Information Available: Experimental details concerning the synthesis of hydroxyl- and ω,ω'-dibromodiphenyl-terminated polymers and their characterization by ^{1}H NMR and GPC. This material is available free of charge via the Internet at http://pubs.acs.org.

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