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Amphiphilic Stars and Dendrimer-Like Architectures Based on Poly(Ethylene Oxide) and Polystyrene

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ABSTRACT: Newly designed star-shaped and dendrimer-like copolymers made of poly(ethylene oxide) (PEO) and polystyrene (PS) were synthesized by sequential anionic polymerization of ethylene oxide and atom transfer radical polymerization (ATRP) of styrene, the switch from the first to the second mechanism being obtained by selective transformation of "living" oxanionic sites. First, tri- and tetrafunctional initiators were used to anionically polymerize ethylene oxide and produce tri- and tetraarmed PEO stars. Next, the OH end groups of PEO star branches were derivatized into 2-bromopropionate groups giving rise to the corresponding tri- and tetrabromoester ended-PEO stars; the latter served as macroinitiators for the ATRP of styrene at 100 °C in the presence of CuBr/2,2′-bipyridine catalyst system affording amphiphilic star block copolymers PEO_n-*b*-PS_n ($n = 3$ or 4). PEO_n-*b*-PS_{2n} ($n = 3$ or 4) dendrimer-like copolymers constituted of an inner PEO part and an outer PS layer were prepared by introducing a branching agent at the OH termini of the PEO arms before growing the PS generation by ATRP. The same branching agent was used in the preparation of miktoarmed PEO-*b*-PS_2 copolymers and PS_2-*b*-PEO-*b*-PS_2 H-type copolymers, starting from ω-OH and α,ω-di-OH PEO, respectively. The samples obtained were characterized by NMR spectroscopy and size exclusion chromatography equipped with a multiangle laser light scattering detector. These copolymers exhibited the expected structure, as confirmed after cleavage of the ester functions linking the PEO arm ends to PS moieties. Indeed, the hydrolyzed PS arms isolated were of low polydispersity index and their molar masses were in good agreement with the values calculated by NMR on the corresponding star-shaped and dendrimer-like copolymers.

Introduction

Poly(ethylene oxide) (PEO) end-capped with hydrophobic alkyl chains are amphiphilic polymers that exhibit self-associating properties; in aqueous solutions the hydrophobic parts tend to aggregate into microdomains promoting the formation of micelles.[1−3] Amphiphilic macromolecular compounds that are of practical utility generally correspond to a linear arrangement of hydrophilic PEO blocks with hydrophobic sequences based on styrene, propylene oxide, or alkyl chains. Such amphiphiles can be found in miscellaneous applications ranging from the stabilization of dispersions to the encapsulation of drugs or the modification of the rheology of aqueous formulations[1]. In a recent addition, PEO-*b*-poly(propylene oxide) were used as templates for the formation of nanoporous organosilicates.[4] By varying the conditions of the sol−gel process and the concentration of the structure-directing amphiphilic copolymers, an entire array of porosities and morphologies have been obtained.

Among self-associating amphiphilic structures, copolymers based on polystyrene (PS) and PEO were certainly the most extensively investigated. Once the synthesis of linear PS/PEO block copolymers (PS-*b*-PEO or PEO-*b*-PS-*b*-PEO)[1,2] was mastered, efforts were directed toward the diversification of the overall architecture of PS/PEO-based compounds, the two moieties being arranged in miscellaneous assemblies. For instance, graft copolymers,[5,6] star block[7] and miktoarmed stars,[8] and Janus-type[9] as well as hyperbranched[10] species have been derived. In view of the role played by branching points on the conformational entropy of macromolecules, one can expect branched assemblies to behave differently from their corresponding linear counterparts (in solution as well as in the solid state).[1] For instance, graft copolymers provide a better steric stabilization to colloidal suspensions than linear homologues because of their particular architecture.[1]

Synthetic routes based on anionic polymerization are certainly the best suited to assemble PS and PEO subchains in well-defined architectures. However, some recent reports tend to demonstrate that the combination of anionic polymerization of ethylene oxide and controlled radical polymerization of vinylic monomers[11] (styrene, *tert*-butyl acrylate) is not only a viable as well as a simpler alternative to a purely anionic route, but it also allows one to prepare unprecedented copolymer structures. Compared to ionic mechanism, controlled radical polymerization offers the advantage of being applicable to a wide range of vinylic monomers and facile to carry out.[12,13] Well-defined polymeric architectures could be engineered via this novel route.[14] This could be achieved by maintaining a very low steady-state concentration of active sites in dynamic equilibrium with a large reservoir of so-called dormant species.

Among various approaches based on this principle, atom transfer radical polymerization (ATRP) is one of the most attractive methods affording "living"/controlled propagation for numerous vinylic monomers.[13,14] ATRP involves the reversible and repeated transfer of halide from the dormant chain end to ligated transition metal compounds (e.g., CuX with X = Br, Cl), the polymer growing between this back and forth transfer when it is in the free radical form.

Following this route, we have recently described the conditions best suited for the preparation of miscel-

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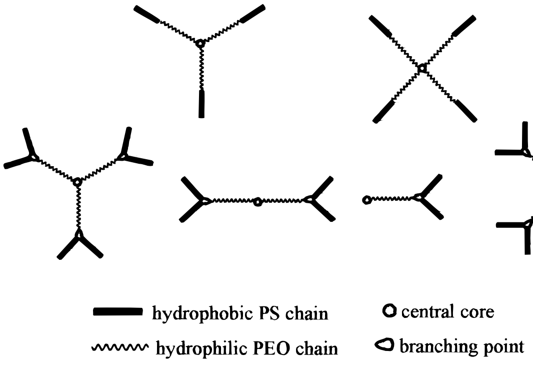
Table 1. Anionic Polymerization of Ethylene Oxide Carried out in DMSO Using Tri- (1) and Tetrafunctional (2) Precursors

type of initiator	$\bar{M}_n$(targeted)[a] (g/mol)	$\bar{M}_n$(SEC)[b] (g/mol)	PDI $_{SEC}$[b]	$\bar{M}_n$(MALL)[c] (g/mol)	$\bar{M}_n$(^{1}H NMR)[d] (g/mol)
1	3000	2200	1.08		2700
	6000	3900	1.10	6500	5800
	20000	11800	1.07	20000	
2	10000	5700	1.10	8900	
	12000	7800	1.10	13100	

[a] On the basis of the monomer to the initiator ratio for 100% conversion. [b] Determined by SEC in a mixture of water/methanol (1/1 in volume) in the presence of 0.1% of NaN_3. [c] Determined by SEC equipped with a MALLS detector using a mixture of water/methanol (1/1 in volume) in the presence of 0.1% of NaN_3. [d] For triarmed PEO stars, the determination of $\bar{M}_n$ was based on the integration of the protons due to the methyl groups of the core compared with those of the protons of ethylene oxide units. This calculation could not be made with the tetraarmed PEO stars because their core did not contain any characteristic proton.

laneous star-shaped polymers of precise functionality using a family of calixarene-based initiators.[15] Hedrick et al. have also contributed to this field with their hexa- and dodecaarmed poly(methyl methacrylates) stars[16] and their dendrimer-like block copolymers,[17] the latter architecture being obtained upon combining anionic polymerization of ϵ-caprolactone for the inner part and ATRP of methyl methacrylate for the external branches.

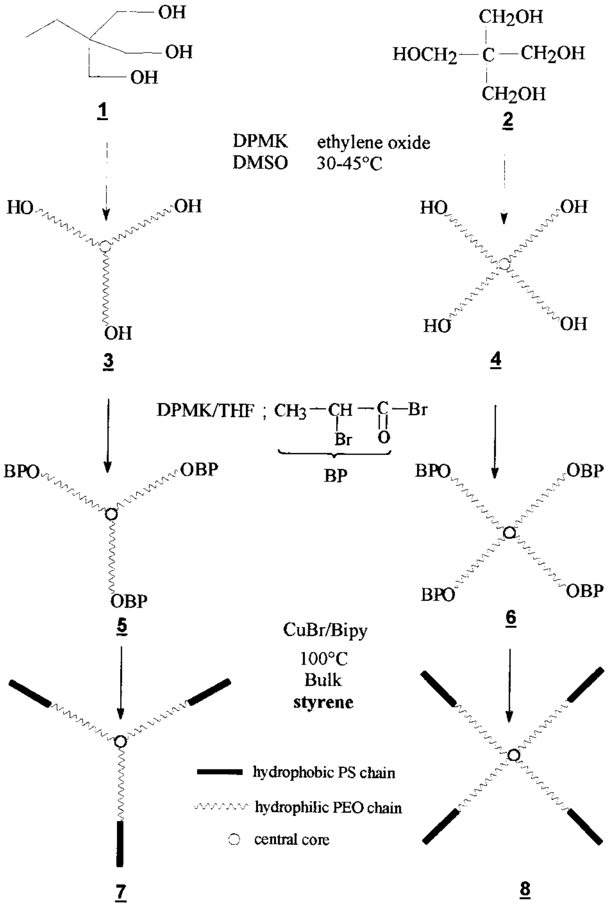
This paper describes the synthesis of three novel classes of branched architectures all based on PEO and PS subchains. As described below, these structures comprised of PEO-*b*-PS_2 miktoarmed stars, PS_2-*b*-PEO-*b*-PS_2 H-type copolymers, PEO_n-*b*-PS_n star-block copolymers and PEO_n-*b*-PS_{2n} dendrimer-like copolymers were obtained upon associating anionic and atom transfer radical polymerizations, the switching from the first mechanism to the second being achieved by transformation of PEO oxanionic "living" sites.



Results and Discussion

(a) Synthesis of Star Block Copolymers PEO_3-*b*-PS_3 and PEO_4-*b*-PS_4. Well-defined PEO triarmed stars (**3**) of expected molar masses were synthesized by the "core first method" using 2-ethyl-2-hydroxymethyl-1,3-propanediol (**1**) as precursor, as previously reported.[18] Samples with polydispersity indices close to unity could be obtained by using dimethyl sulfoxide (DMSO) as solvent instead of tetrahydrofuran (THF) and diphenylmethyl potassium (DPMK) as deprotonating agent of the hydroxylated precursors (Scheme 1). The amount of DPMK introduced was adjusted so as to deprotonate only 20% of the hydroxyl functions carried by **1** as a means to prevent a too fast polymerization of ethylene oxide.

Scheme 1. Synthesis of Tri- and Tetraarmed PEO_n-*b*-PS_n Star Block Copolymers



Under such conditions, all of the three hydroxyl functions of **1** could efficiently initiate the polymerization of ethylene oxide and give rise to samples with a Poisson-type distribution of molar masses, the exchange of protons between the OH groups and alkoxides ($R_{exch} = k_{exch}[O^-][OH]$) being rapid compared to the rate of polymerization ($R_p = k_p[O^-][M]$). The same methodology was applied with pentaerythritol (**2**) as a tetrafunctional precursor that produced four-armed PEO stars. In the latter case, the extent of deprotonation did not exceed 10% of the OH functions of **2** owing to the tendency of the alkoxides formed after deprotonation by DPMK to precipitate out. Upon dilution of the medium with DMSO, this effect was somehow alleviated; obtaining of tetraarmed PEO stars **4** of predicted molar masses and polydispersity indices revolving around 1.1 indicated that the polymerization occurred under controlled conditions (Table 1).

These tri- and tetraarmed PEO star samples were characterized by size exclusion chromatography (SEC) equipped with a multiangle laser light scattering (MALLS) detector, using a mixture of methanol/water (1/1 in volume) as eluent. In such conditions, the polymers did not aggregate in contrast to the situation prevailing in pure water or THF as eluent.

The second step in the synthesis of star block PEO_n-*b*-PS_n consisted in the preparation of the star-type macroinitiators (**5** and **6**, Scheme 1). This was achieved through chemical modification of the OH end groups carried by the branches of these PEO stars into 2-bro-

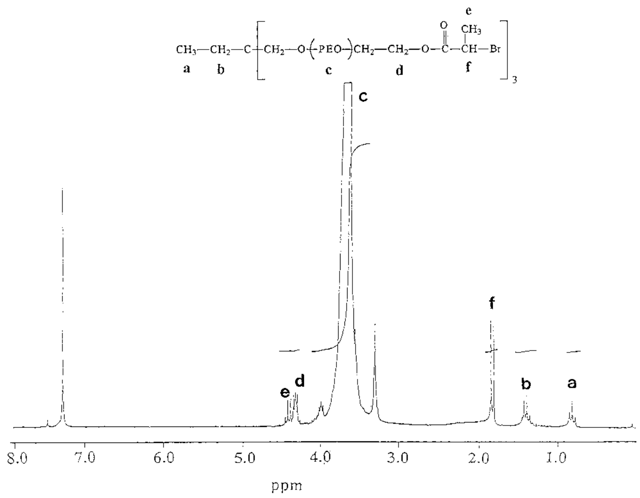


Figure 1. ^{1}H NMR spectrum ($CDCl_3$; 200 MHz) of PEO macroinitiator **5**.

moproprionate functions that bring about controlled ATRP of styrene.[19] For the quantitative derivatization of their OH functions, PEO stars were thoroughly deprotonated using a solution of DPMK, the alkoxides formed being reacted with an excess of 2-bromopropionyl bromide at room temperature. Isolation of **5** and **6** was accomplished by successive precipitations in diethyl ether. The complete substitution of the hydroxyl groups was evidenced by IR and NMR spectroscopies. The former technique showed the presence of the vibration due to the ester band at 1700 cm^{-1}; on the other hand, ^{1}H NMR spectrum in $CDCl_3$ of the trifunctional macroinitiator (Figure 1) revealed the disappearance of the signal of the hydroxyl protons at 5.3 ppm and the presence of a quadruplet at 4.4 ppm as well as a doublet at 1.8 ppm due to the protons of the methine group and of the methyl group of 2-bromopropionate functions, respectively.

The modified PEO stars were then characterized by SEC in order to compare their behavior with that of their precursors. Both hydroxylated and 2-bromopropionate stars exhibited the same SEC traces provided the solutions used for their characterization in THF were dilute enough. Indeed, the SEC traces of the esterified PEO were concentration dependent: peaks appeared in the high molar masses region denoting the tendency of these species to self-assemble probably through their ester functions. In contrast, the molar mass distribution was narrow and monomodal at concentrations lower than 0.5%.

The final step in the synthesis of amphiphilic star copolymers **7** and **8** was the growth of PS blocks from 2-bromopropionate ended PEO stars (Scheme 1). This could be achieved upon polymerizing styrene by ATRP under the same controlled conditions as those determined by us for the preparation of well-defined octaarmed polystyrene stars.[15] These conditions consisted in polymerizing styrene at 100 °C in the presence of CuBr/2,2′-bipyridine as catalyst system and discontinuing the chain growth at rather low monomer conversion. Since styrene is a good solvent for PEO, the polymerization could be performed under bulk conditions. The copolymers' experimental data are given in Table 2. The reaction times were varied from a few hours to overnight depending upon the molar mass targeted. All the polymers obtained were completely soluble, and no insoluble material due to cross-linking was detected.

Table 2. Bulk ATRP of Styrene at 100 °C in the Presence of 2,2′-Bipyridine Using the Tri- (5) and Tetrafunctional (6) PEO Macroinitiators

PEO macroinitiator precursor	run	$\bar{M}_n$(NMR)^a (g/mol)	$\bar{M}_n$(MALLS)^b (g/mol)	PDI^b	% PEO (mol)
trifunctional	1^c	30 500	37 300	1.25	39
star **5**	2^c	20 200	26 000	1.19	53
($\bar{M}_n$ = 6500 g/mol)	3^c	12 500	14 600	1.22	72
tetrafunctional	4^d	36 800	41 300	1.30	43
star **6**	5^d	78 200	89 000	1.25	14
($\bar{M}_n$ = 8900 g/mol)					

[a] Determined by ^{1}H NMR in $CDCl_3$. [b] Determined by SEC equipped with a MALLS detector using THF as eluent. In these calculations it was assumed that the increment of the refractive index of the copolymer is a linear function of their massic composition. [c] $\bar{M}_{n(theo)}$ = 70000 g·mol^{-1} for 100% conversion. [d] $\bar{M}_{n(theo)}$ = 200000 g·mol^{-1} for 100% conversion.

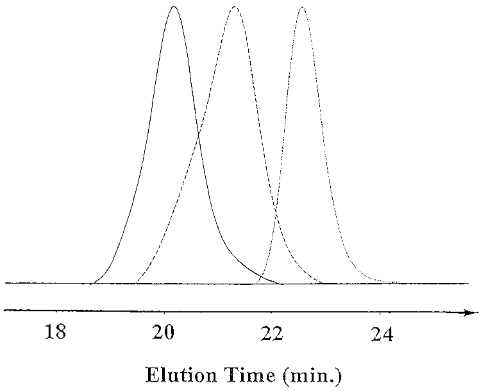


Figure 2. SEC traces (RI detector) of PEO_3-*b*-PS_3 star block copolymers **7** of different composition (- - , run 2, Table 2; —, run 1, Table 2) and PEO star precursor **3** (Table 1).

The copolymers with a low PS content were purified by precipitation in pentane (a nonsolvent for PEO and a relatively good solvent for PS). Samples with a higher PS content (run 1, Table 2) were purified by precipitation in a large excess of ethanol. The solvent that precipitated these copolymers was evaporated and the concentrate was analyzed. SEC traces of a triarmed hydroxylated PEO precursor and of two resulting star block copolymers PEO_3-*b*-PS_3 are displayed in Figure 2.

These chromatograms unambiguously show the formation of the PS blocks. After polymerization of styrene, the SEC trace shifts to the higher molar masses region along with complete disappearance of the peak of the precursor. This means that all the PEO star molecules efficiently initiated the ATRP of styrene and participated in the growth of PS blocks. Batsberg et al. recently reported the synthesis of linear triblock PS-*b*-PEO-*b*-PS by ATRP from a difunctional 2-bromopropionate PEO macroinitiator.[20] In this case, these authors had first to selectively extract homopolystyrene generated by thermal polymerization before isolating the expected copolymers. In our study, no such purification was necessary, provided polymerization did not last longer than 9 h, the copolymers obtained being free of any linear contaminant. Their molar mass distribution remained narrow ($\bar{M}_w/\bar{M}_n$ < 1.2) indicating a controlled polymerization process. This was also confirmed by MALLS/SEC characterization, both light scattering and refractometric detections showing superimposable and monomodal traces (Figure 3).

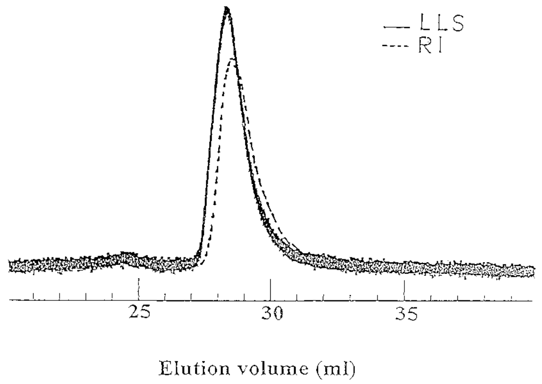


Figure 3. MALLS/SEC trace (RI and LLS detectors) of PEO$_3$-*b*-PS$_3$ star block copolymer **7** (run 3, Table 2).

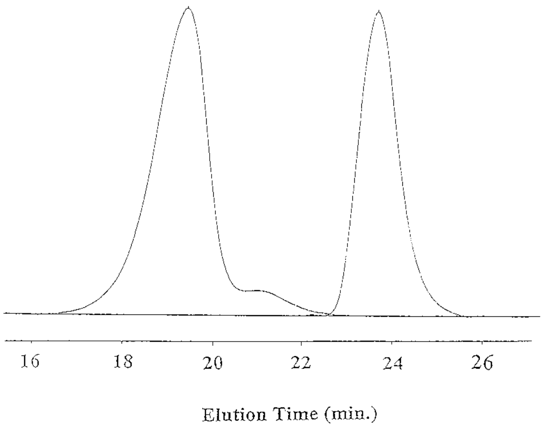


Figure 4. SEC traces of the copolymer **8** derived from the macroinitiator **6** after polymerizing styrene for more than 9 h.

Figure 4 shows the SEC trace of a copolymer sample **8** derived from the tetrafunctional macroinitiator **6**. When the polymerization of styrene lasted longer than 9 h, a second population appeared in the low molar masses area that was assignable to linear PS chains produced by the thermal polymerization process. However, pure PEO$_4$-*b*-PS$_4$ star was isolated from the linear contaminant by selective extraction with cyclohexane, as already reported.[15]

Figure 5 shows the ^{1}H NMR spectrum of a typical PEO$_3$-*b*-PS$_3$ star block copolymer in CDCl$_3$. It shows all the peaks expected for such a structure. The relative content in PEO and PS was calculated by the integration of the aromatic signals and that at 3.5 ppm due to the protons of ethylene oxide repeating units; the values are given in Table 2.

The most reliable method to determine the actual molar mass of such copolymers is by ^{1}H NMR since molecular features of PEO star precursor are already known. However, NMR characterization has to be carried out in a good solvent (CDCl$_3$) for both parts since the use of a selective solvent of one block may result in the formation of micelles. In the latter case, the estimation of the relative proportion of the two blocks would have been misleading, as will be described in the next section. For the calculation of the actual molar mass of these PEO$_n$-*b*-PS$_n$ samples, we assumed that the 2-bromopropionate sites of **4** and **5** efficiently initiated the ATRP of styrene and that the structure of the star copolymers obtained corresponds to the expected one. This was checked by cleaving the ester functions linking the PS blocks to the PEO ones using KOH in a mixture of THF and methanol. The polymers obtained after scission were then recovered by precipitation in a large excess of methanol. Proton NMR analysis of the isolated polymers showed only the resonance of the peaks due to hydrolyzed PS; the protons of the PEO backbone completely disappeared. As expected, the SEC traces of the PS recovered after cleavage (Figure 6) appeared at lower retention volumes than those of the PEO$_n$-*b*-PS$_n$ precursors; in addition these traces were monomodal with polydispersity indices close to 1.2. This confirmed the controlled character of the bulk ATRP of styrene that was triggered by the trifunctional macroinitiator **4**. Should side reactions such as star–star radical coupling have occurred in detectable amount, a shoulder corresponding to twice the molar mass of the hydrolyzed chains would have been detected.

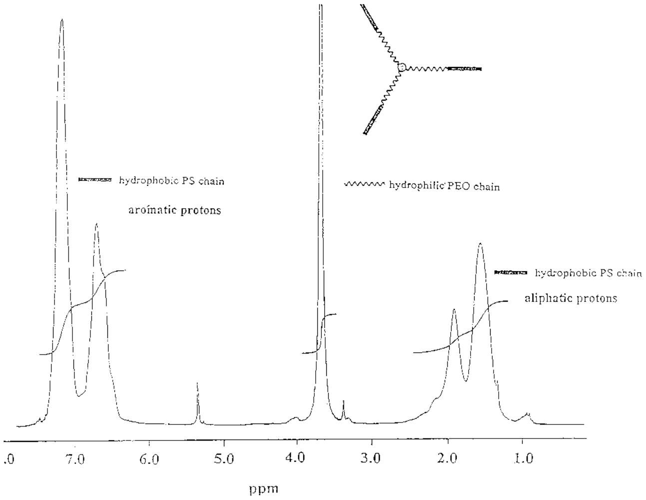


Figure 5. ^{1}H NMR spectrum (CDCl$_3$; 200 MHz) of PEO$_3$-*b*-PS$_3$ star block copolymer **7**.

The molar masses of the PS part of these copolymers were determined by NMR ($\bar{M}_n$ = 8000 g/mol) and compared with those determined by SEC for the hydrolyzed PS blocks ($\bar{M}_n$ = 10000 g/mol). Notwithstanding the probable loss of hydrolyzed PS chains of small size upon precipitation, the $\bar{M}_n$ values drawn from NMR and SEC are rather close confirming that the synthesized copolymer exhibits the expected structure. The ester functions linking PS to PEO blocks in the tetrafunctional copolymers **8** were also cleaved, yielding linear PS chains whose SEC traces exhibited single peaks. The molar masses of the hydrolyzed PS chains matched the values determined by NMR for the PS part of the tetrafunctional copolymer **8**.

These star block copolymers were also characterized by MALLS/SEC and did not aggregate in THF solution. For the calculation of their molar masses, it was assumed that the increment of their refractive index (d*n*/d*c*) is a linear function of their composition which was derived from NMR measurements. The values delivered by LS (Table 2) were close to those derived from ^{1}H NMR indicating that these star block copolymers are homogeneous in size and composition.

(b) Synthesis of PEO$_n$-*b*-PS$_{2n}$ Miktoarm, H-Type, and Dendrimer-Like Copolymers. We prepared such PEO/PS copolymers to investigate the effect of the branching points on the overall properties of amphiphilic architectures and subsequently compare their behavior with that of both linear homologues and the

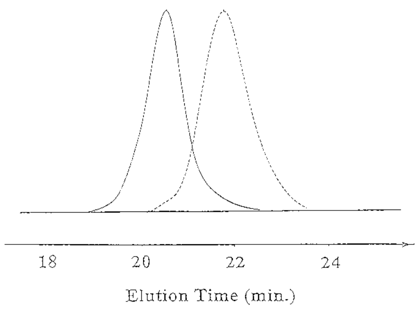
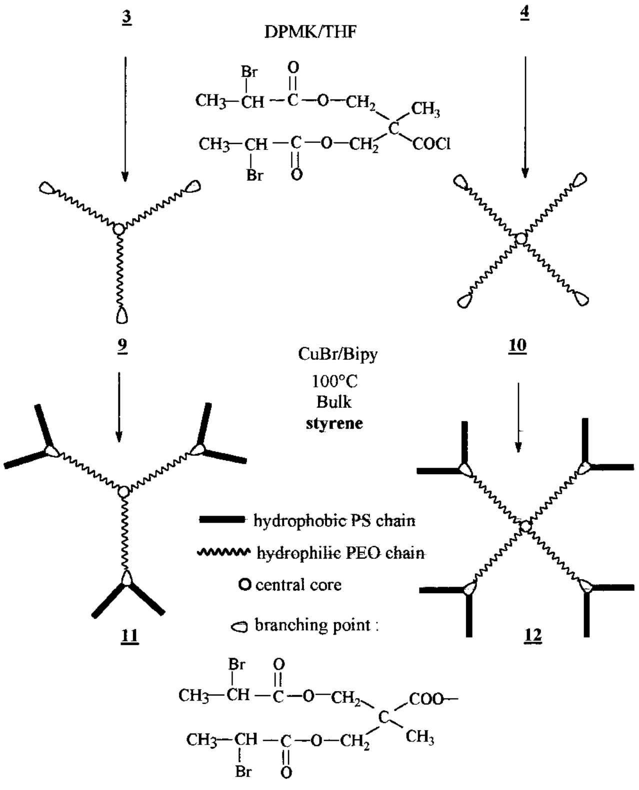


Figure 6. SEC traces (RI detector) of star block copolymer **7** (— run 1, Table 2) and linear PS (- -) obtained after hydrolysis of the ester functions.

Scheme 2. Synthesis of Tri- and Tetraarmed PEO_n-*b*-PS_{2n} Dendritic Copolymers



above PEO_n-*b*-PS_n star block copolymers. The synthetic pathway to these series of PEO_n-*b*-PS_{2n} architectures (with $n = 1, 2, 3$, and 4) is depicted in Schemes 2 and 3. PEO_1-*b*-PS_2 miktoarmed stars and PS_2-*b*-PEO-*b*-PS_2 H-type copolymers were synthesized from monohydroxy and bis(hydroxy) linear PEO's, respectively. The latter were obtained, respectively, from DPMK in THF and a DMSO solution of partially deprotonated 2,2-dimethyl-1,3 propanediol used as initiator. The hydroxyl groups of these PEO precursors were then derivatized into twice as many 2-bromoproprionate groups. The latter were introduced through the condensation of a designed branching agent onto the PEO termini and were subsequently used to initiate the ATRP of styrene.

This branching agent was synthesized in two steps from 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) and 2-bromopropionyl bromide (Scheme 4). The structure of this AB_2 molecule was confirmed by both ^1H and ^{13}C NMR spectroscopy and by mass spectrometry as well (see Experimental Section).

To generate the PEO termini and fit them with two 2-bromopropionate functions, the hydroxyl groups of the PEO precursor were thoroughly deprotonated using DPMK before reacting the alkoxides formed with the acyl chloride function of the branching agent. The resulting PEO's were recovered and purified by successive precipitation in diethyl ether. This modification step

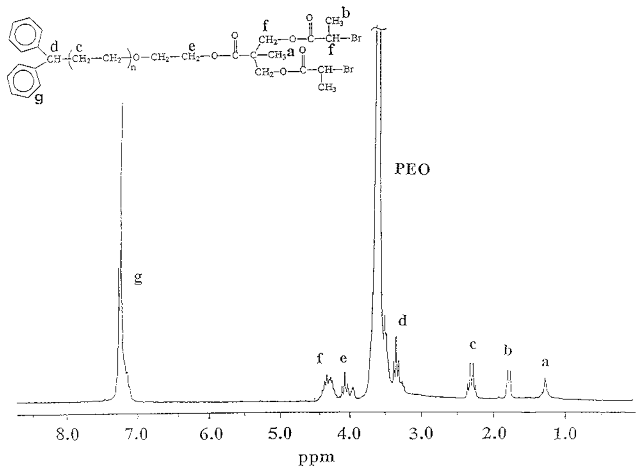
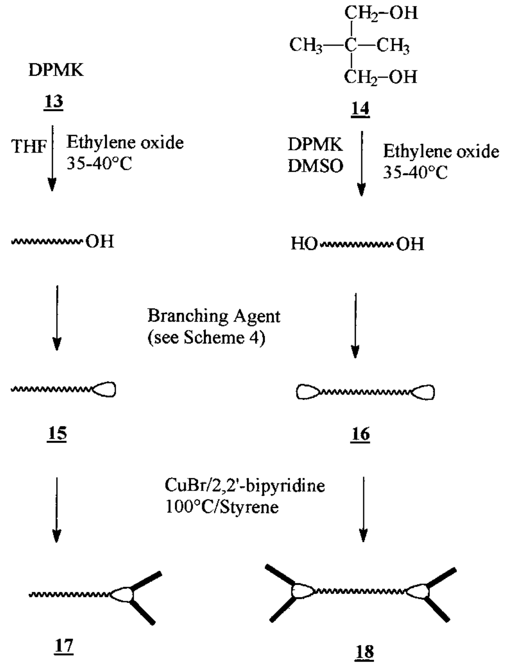


Figure 7. ^1H NMR ($CDCl_3$; 200 MHz) spectrum of the PEO macroinitiator **15**.

Scheme 3. Synthesis of Mono- and Difunctional PEO_n-*b*-PS_{2n} Copolymers



Scheme 4. Synthesis of the Branching Agent

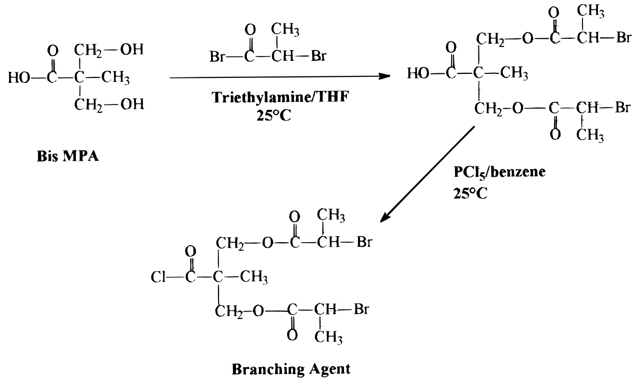


Table 3. Bulk ATRP of Styrene at 100 °C in the Presence of CuBr/2,2′-Bipyridine Using the Mono- (15), Di- (16), Tri- (9), and Tetrafunctional (10) PEO Macroinitiators

PEO macroinitiator precursor	run	$\bar{M}_n$(NMR)[a] (g/mol)	$\bar{M}_n$(MALLS)[b] (g/mol)	PDI[b]	% PEO (mol)
monofunctional	1[c]	10 600	13 800	1.15	41
linear **15**	2[c]	7 600	8 000	1.10	52
($\bar{M}_n$ = 2400 g/mol)					
difunctional	3[d]	10 100	8 200	1.15	50
linear **16**	4[d]	23 600	16 200	1.17	25
($\bar{M}_n$ = 3000 g/mol)	5[d]	29 600	23 000	1.18	21
trifunctional	6[e]	64 700	43 000	1.38	14
star **9**	7[e]	34700	24400	1.40	27
($\bar{M}_n$ = 4700 g/mol)	8[e]	24200	20000	1.27	36
	9[e]	10700	12300	1.33	65
tetrafunctional	10[f]	123000	64000	1.20	11
star **10**	11[f]	41000	24800	1.18	29
($\bar{M}_n$ = 6000 g/mol)					

[a] Determined by ^{1}H NMR in $CDCl_3$. [b] Determined by SEC equipped with a MALLS detector using THF as eluent. [c] $\bar{M}_{n(theo)}$ = 30 000 g·mol^{-1} for 100% conversion. [d] $\bar{M}_{n(theo)}$ = 100 000 g·mol^{-1} for 100% conversion. [e] $\bar{M}_{n(theo)}$ = 200 000 g·mol^{-1} for 100% conversion. [f] $\bar{M}_{n(theo)}$ = 300 000 g·mol^{-1} for 100% conversion.

was monitored by ^{1}H NMR; Figure 7 shows the ^{1}H NMR spectrum of the macroinitiator of the miktoarmed star. The signal at 1.8 ppm is assignable to the CH_3(CH) protons and a broad signal at 4.3 ppm is due to the resonance of CH_2 and CH protons of the branching point, which attests to the efficiency of this derivatization step.

Two PS arms of well-controlled size were grown from each of these branching points using the same conditions described above. Depending upon the structure of the precursor, either miktoarm stars, H-type and dendrimer-like copolymers were obtained from mono- (**15**), di- (**16**) and multigeminate (**9** and **10**) PEO's. The polymerization process was restricted to low monomer conversion and short duration in order to prevent the presence of recombined materials and the formation of linear PS by the thermal autopolymerization of styrene. The hydrophilic/hydrophobic balance was adjusted by the initial feed ratio of styrene to the PEO-based macroinitiators (**9**, **10**, **15**, **16**). The final copolymers were easily recovered by precipitation in pentane after the reaction mixture was filtered through alumina. Table 3 summarizes the characteristics of these PEO_n-*b*-PS_{2n} branched copolymers.

Characterization of the samples by ^{1}H NMR confirmed their expected structure. On the basis of the molar mass of the PEO precursor, the $\bar{M}_n$'s of the resulting copolymers agreed with the expected values. In contrast, molar masses obtained by MALLS/SEC in THF tended to differ from the targeted values, the discrepancy being more pronounced for copolymers with high content in PS. This difference may mirror some fluctuation in the composition of these dendrimer-like copolymers but it may also reflect their very peculiar solution behavior in THF. For instance, the SEC traces of PEO_3-*b*-PS_6 and PEO_4-*b*-PS_8 were concentration dependent, in contrast to star block homologues of approximately the same composition and concentration; a tail was detected in the low molar masses region when increasing the concentration of the solution injected (≥5 mg/mL, Figure 8). Since this side peak totally disappeared from the SEC traces when diluting the injections to 1 mg/mL, this phenomenon may simply be the result of interactions between these dendritic structures and the SEC columns rather than due to the presence of residual PEO macroinitiator or PS chains. Under diluted conditions, the SEC traces of these dendritic copolymers become narrower and shift toward high molar masses compared to that of the PEO precursor (Figure 9); the polydispersity indices of the corresponding copolymers are around 1.2, attesting to the well-defined architecture of the samples obtained. The same is true for PEO_2-*b*-PS_4 H-type copolymers. The difference in elution of the star block and dendritic copolymers through SEC columns indicates that branching strongly affects the overall behavior of these objects.

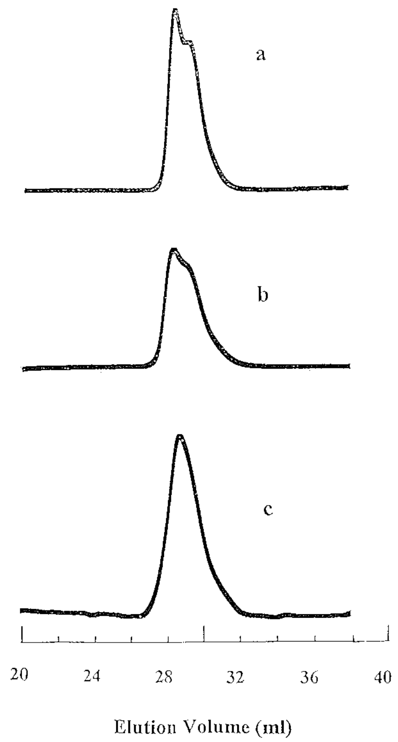


Figure 8. MALLS/SEC traces of a dendrimer-like PEO_4-PS_8 copolymer **12** at different concentrations: (a)10 mg/mL; (b) 5 mg/mL; (c) 1 mg/mL.

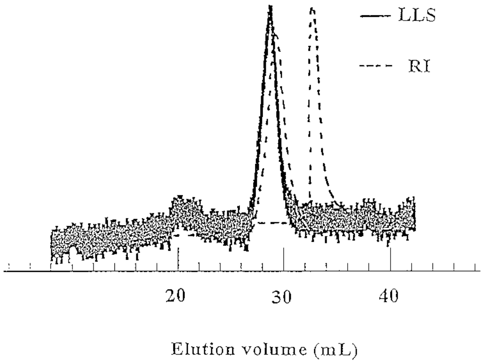


Figure 9. MALLS/SEC traces (RI and LLS detectors) of dendrimer-like copolymers **11** (PEO_n-PS_{2n}) and PEO precursor **3**.

The SEC traces of the PEO_1-*b*-PS_2 miktoarmed copolymers provided by the MALLS detector exhibited a signal of high intensity in the high molar mass region that was not observed with the refractometric detector. This peak was attributed to the self-association of several of these copolymers into micellar structures through the free end of their PEO block, as previously demonstrated for linear PS-*b*-PEO compounds.[1−2]

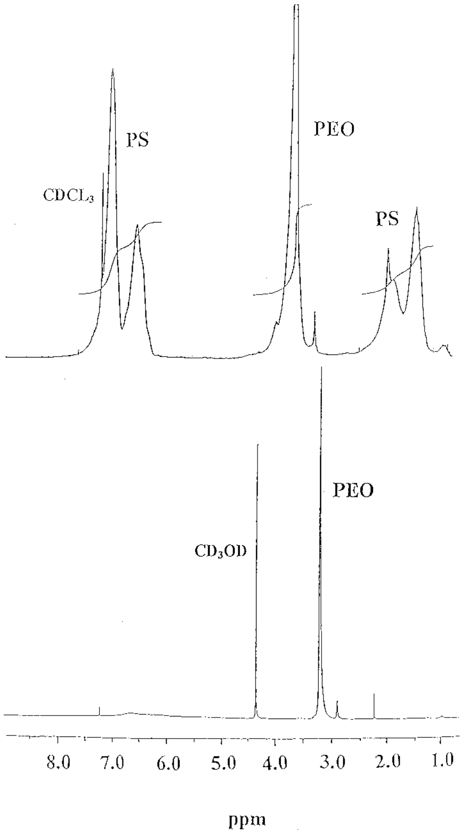


Figure 10. ^{1}H NMR spectrum (200 MHz) in $CDCl_3$ and in a mixture of $CD_3OD/CDCl_3$ (70/30 v/v) of sample **11** (PEO_3-*b*-PS_6).

This amphiphilic character of the PEO/PS copolymers was investigated by NMR spectroscopy with varying solvent polarity. Fréchet and Gitsov[21] demonstrated that amphiphilic star copolymers constituted of four PEO arms bearing hydrophobic dendritic wedges self-organize differently to form either mono and/or multimolecular micelles depending on the solvent and their overall concentration. So-called unimolecular micelles were also recently obtained by Hedrick[17,22] in the case of amphiphilic dendrimers. Figure 10 shows typical ^{1}H NMR spectra of our PEO_3-*b*-PS_6 copolymer obtained in $CDCl_3$ and in a mixture of $CD_3OD/CDCl_3$ (70/30 v/v). $CDCl_3$ being a good solvent of both PEO and PS blocks, well-resolved signals were observed since both PS and PEO chains are soluble in this solvent. With deuterated methanol which is a selective solvent of the inner PEO part, the protons due to the PS chains were no longer detected, suggesting that PEO arms were able to wrap the hydrophobic parts, the latter preferring to stay within the core of the structure. This demonstrated the ability of these systems to form stable micellar structures such as those described by others[16,17,21−23]. In THF, the PEO arms stayed in the inner part in a slightly more compact form than in chlorinated solvent, the dendritic and hydrophobic parts extending outward.

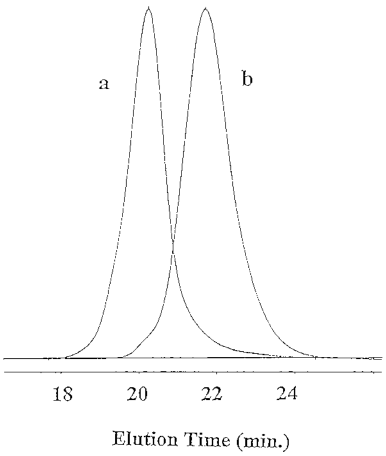


Figure 11. SEC traces obtained (a) before and (b) after cleavage of the ester function of a PEO_3-*b*-PS_6 block copolymer.

Table 4. Determination of the Functionality of Each Type of PEO_n-PS_{2n} Copolymers

type of copolymer	$\bar{M}_n$(NMR) PS[a] copolymer (g/mol)	$\bar{M}_n$(SEC) PS[b] linear (g/mol)	$\bar{M}_n$(SEC) expected (g/mol)	f_{theo}
PEO_1-*b*-PS_2	9400	5500	4700	2
	8200	5000	4100	2
PEO_2-*b*-PS_4	20600	5800	5150	4
	45800	12800	11450	4
PEO_3-*b*-PS_6	70000	13500	11700	6
	60000	12000	10000	6
PEO_4-*b*-PS_8	117000	16200	14600	8

[a] Determined by ^{1}H NMR in $CDCl_3$ before hydrolysis. [b] Determined by SEC using THF as eluent after hydrolysis.

As shown in the section devoted to star block copolymers, one way to account for the well-defined character of these novel branched copolymers was to cleave the ester functions linking the PEO part to the PS one. The size of outer PS arms as well as their actual number in the dendritic structure were thus determined. Hydrolysis was performed under the same basic conditions as those described above, the formation of linear PS being monitored both by ^{1}H NMR and SEC. Typical SEC traces obtained before and after cleavage are shown in Figure 11. The number of PS branches present in the dendritic block copolymers was determined by taking the ratio of the $\bar{M}_n$ values of the hydrolyzed linear PS chains to those of the PS part in the dendritic precursor. As shown in Table 4, the results obtained agree with the calculated values, confirming that these structures have the expected number of PS arms.

Conclusion

Combination of the anionic polymerization of ethylene oxide with the atom transfer radical polymerization of styrene was exploited to engineer block PS/PEO copolymers in original topologies. Two new architectural PEO/PS copolymers were synthesized from the same PEO precursor but they differ by the topological arrangement of their external PS arms. In the first series of experiments, star block copolymers PEO_n-*b*-PS_n ($n = 3$ or 4) were obtained by ATRP of styrene using the 2-bromoproprionate-carrying PEO stars as initiators. Dendrimer-like PEO_n-*b*-PS_{2n} ($n = 3$ or 4) copolymers were also derived from the PEO stars. First, the OH end groups of the PEO precursors were derivatized into geminal 2-bromoproprionate groups which were then used to initiate ATRP of styrene. In addition, PEO-*b*-PS_2 miktoarmed stars and PS_2-*b*-PEO-*b*-PS_2 H-type copolymers were derived using ω-OH−PEO and α,ω-di-OH PEO as precursors and the same derivatization/polymerization sequence as the one described for dendrimer-like copolymers. The synthetic pathway followed to prepare such copolymers enabled us to control both the functionality and the hydrophilic−lipophilic balance.

The well-defined character of these novel branched architectures was verified upon cleavage of the ester functions linking the PEO moiety to the PS part. The hydrolyzed PS arms were of low polydispersity index and their molar masses were in good agreement with the values calculated by NMR on the corresponding star block and dendrimer-like copolymers.

Preliminary investigations by ^{1}H NMR showed that these amphiphilic copolymers self-associate into unimolecular micelles using a selective solvent. Size exclusion chromatography also showed differences in the way dendrimer-like PEO$_n$-*b*-PS$_{2n}$ and star block PEO$_n$-*b*-PS$_n$ homologues were eluted through SEC columns.

Experimental Section

Materials. Ethylene oxide (Fluka, 98%) was transferred from its steel tank into a three-neck flask in which it was dried over sodium at −40 °C during 3 h before being distilled into a graduated buret. 2-Ethyl-2-hydroxymethyl-1,3-propanediol (Aldrich, 99%) and 2,2-dimethyl-1,3-propanediol (Aldrich, 99%) were purified by freeze-drying twice from a dioxane solution. Pentaerythritol (Aldrich, 98%) was dried by heating under vacuum. Dimethyl sulfoxide (Aldrich, 98%) was purified by distillation over calcium hydride into a Schlenk apparatus just before use. 2-Bromopropionyl bromide (97%), 2,2-bis(hydroxymethyl)propionic acid (bis-MPA), triethylamine (TEA), copper bromide (CuBr), 2,2′-bipyridine (Bipy), and pentaphosphorus chloride (PCl$_5$) were used as received from Aldrich. Styrene was stored over CaH$_2$ and then vacuum distilled before polymerization. Tetrahydrofuran (THF) was distilled over CaH$_2$ for esterification reactions. A THF solution of the deprotonating agent, diphenylmethylpotassium (DPMK), was prepared according to a reported procedure.[24] This solution was titrated with a known amount of acetanilide dissolved in DMSO, until the appearance of a persistent red-orange color.

Characterization. NMR spectra were obtained using a Bruker AC200 NMR spectrometer. Apparent molar masses of PEO stars were determined using size exclusion chromatography apparatus equipped with a Varian refractive index detector and a JASCO 875 UV/vis absorption detector, dual detection fitted with three TSK columns (10^4, 1500, and 250 Å) at a flow rate of 0.7 mL/min. Calibration was performed using linear poly(ethylene oxide) standards (Tosoh). The actual molar masses of the PEO stars were calculated from the response of a multiangle laser light scattering detector equipped with a laser source operating at 633 nm (Wyatt technology) that was connected to a size exclusion chromatography (MALLS/SEC) line. The d*n*/d*c* values of PEO stars were measured in both THF and mixture methanol/water (1/1 in volume) at 25 °C, with a laser source operating at 633 nm and was the same as that of linear PEO (see Table 1).

Synthesis of PEO Stars (3 and 4). A typical synthesis of a triarm star was as follows. In a 500 mL four-neck flask equipped with a magnetic stirrer, an inlet, and three graduated burets containing DMSO, ethylene oxide, and DPMK, the anhydrous trifunctional precursor **1** (0.5 g, 3.7 mmol) was dissolved in dry DMSO (150 mL) under a slight nitrogen overpressure. A solution of DPMK in THF (3.3 mmol) was slowly introduced; the orange-red color was lost as the alkoxides were formed. The solution remained homogeneous and took a yellowish color. Ethylene oxide (25 mL, 0.5 mol) was then added. The solution was stirred at 30 °C for 48 h. The alkoxides were deactivated by adding few drops of a concentrated solution of HCl in methanol. The solution was concentrated and precipitated with an excess of diethyl ether. After the first precipitation, as DMSO was still present in the polymer, the latter was reprecipitated twice in a large excess of diethyl ether from a dichloromethane solution. Yield = 90% after three precipitations; $\bar{M}_n = 5800$ as determined by ^{1}H NMR. It should be noted that the higher the molar mass, the easier the precipitation. The molecular characteristics of PEO stars are given in Table 1.

Preparation of Triarmed Star PEO Macroinitiator 5. In a three-neck flask equipped with a reflux condenser, triarm star PEO (4.5 g, 7.5×10^{-4} mol, $\bar{M}_n = 6000$ g/mol) was dissolved in dry THF (100 mL). To this colorless solution was added diphenylmethyl potassium (4 mL, 2.2×10^{-3} mol) dropwise. The solution remained dark red for 1 h indicating the complete deprotonation of the hydroxyl functions. A solution of 2-bromopropionyl bromide (2.4 mL, 2.25×10^{-2} mol) in dry THF (20 mL) was transferred dropwise at 0 °C through a cannula under nitrogen. The solution turned yellow. The mixture was allowed to rise to room temperature and the reaction was stirred overnight. The suspension obtained was filtered and after concentration, the corresponding solution was precipitated in a large excess of diethyl ether (three times). The obtained white powder was dried under vacuum (yield = 72%) and characterized (see Figure 1).

Tetraarmed Star PEO Macroinitiator 6. It was prepared according to the same procedure as that followed for the synthesis of **5** (yield = 67%).

Bulk ATRP of Styrene. In a typical bulk polymerization, a Schlenk flask was charged with tris(bromopropionate) PEO macroinitiator **3** (0.2 g, 3.33×10^{-5} mol), CuBr (13.2 mg, 1×10^{-4} mol), and Bipy (46.8 mg, 3×10^{-4} mol). Styrene (2.1 mL, 2.2×10^{-2} mol) was added. The system was degassed and heated at 100 °C for 4 h. Dichloromethane was added to the crude product and the mixture was filtered over a column of neutral alumina. The solution was precipitated twice in a large excess of pentane. The polymer **5** was dried under vacuum at 30 °C and the conversion (48%) was determined by gravity; $\bar{M}_n$ was equal to 37 300 g·mol^{-1} by MALLS/SEC. The data pertaining to all the block copolymers synthesized are given in Tables 2−4.

Synthesis of the Branching Agent: 2,2-Bis(2-(bromomethyl)propionato)propionyl Chloride. In a 250 mL three-neck flask equipped with a magnetic stirrer, 2,2-bis(hydroxymethyl)propionic acid (5 g, 3.7×10^{-2} mol) was dissolved in dried THF (80 mL). Triethylamine (12.5 mL, 8.9×10^{-2} mol) was added and the solution became homogeneous. The flask was cooled at 0 °C. A solution of 2-bromo propionyl bromide (9.5 mL, 8.9×10^{-2} mol) in THF was added dropwise through a cannula. The mixture was kept under stirring at room temperature overnight. The salts were filtered off and the solvent was removed completely under vacuum. A pale yellow viscous liquid was obtained in 90% yield and used further without purification.

The latter compound (5 g, 1.2×10^{-2} mol) was dissolved in benzene (50 mL). Pentaphosphorus chloride (3 g, 1.4×10^{-2} mol) was then added. The mixture turned immediately to orange color; the solution was kept under stirring at room temperature overnight. The salts were filtered off and benzene was removed by evaporation under vacuum. Hexane was added in order to remove the excess of PCl$_5$. The organic phase was recovered and the solvent evaporated under vacuum. A clearly brown liquid was obtained in 70% yield ($C_{11}H_{15}O_5Br_2Cl = 422.5$ g/mol)

^{1}H NMR (CDCl$_3$), δ_{ppm}: 4.60 (m, 6H, C*H*$_2$ and C*H*), 1.8 (d, 3H, C*H*$_3$−CH−Br, $J = 6.9$ Hz), 1.4 (s, 3H, CH$_3$).

^{13}C NMR (CDCl$_3$), δ_{ppm}: 18.5 (CH$_3$), 22 (*C*H$_3$−CH−Br); 39.8 (CH$_3$-*C*H−Br), 56.6 (C quaternary), 66.3 (CH$_2$) 169.9 (C═O ester function) and 175.4 (C═O acyl chloride function).

Mass Spectrum (FAB): ($M - 35.5 = M_1 = 386.9$ g/mol) and (M_1 − COCH(Br)CH$_3$ = 251 g/mol).

Preparation of the Linear Monofunctional Macroinitiator (15). The procedure was the same as that of the synthesis of macroinitiators **5** and **6**, except that the branching agent was used in place of 2-bromopropionyl bromide. Yield: 62%. The ^{1}H NMR spectrum of **15** is shown in Figure 7.

Hydrolysis of the PEO$_n$-*b*-PS$_n$ and PEO$_n$-*b*-PS$_{2n}$ Copolymers. The procedure was the same whatever the structure of the copolymer. Typically, a copolymer **7** (300 mg, 7.2×10^{-5} mol of ester) was added in a flask and solubilized with THF (30 mL). Then, KOH (2 mL, 1 M in methanol solution) was added via a syringe. The solution was refluxed overnight. The solution was concentrated by evaporation of the THF and precipitated in pure methanol. A linear PS whose SEC trace is shown in Figure 6 was recovered (yield 40%).

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