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Star Block Copolymers and Hexafullerene Stars via Derivatization of Star-Shaped Polystyrenes

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ABSTRACT: The end-functionalization of hexaarm star-shaped polystyrene (PS), prepared via "living" cationic polymerization, by organosilicon compounds was investigated. The presence of a *sec*-chlorine atom at each branch end was first confirmed by ^{1}H NMR. After activation of these chain ends by $TiCl_4$, both allylic and azido groups were introduced through the use of their trimethylsilyl derivatives (allyltrimethylsilane and trimethylsilyl azide, respectively), particularly taking advantage of the high affinity of silicon compounds toward electrophilic reagents. These end-standing allyl and azide functions on the hexaarm PS stars were then transformed into hydroxyl and amino groups with use of classical organic chemistry reactions. PS stars carrying six fullerenes on their periphery were also generated from hexaazido star samples. The presence of these six C_{60} entities was confirmed by miscellaneous characterization methods, including ^{1}H NMR, size-exclusion chromatography, thermal gravimetry, and cyclic voltammetry. Besides the synthesis of these ω-functionalized stars, PS_6-*b*-PEO_6 star block copolymers were also prepared with use of the hexahydroxy samples as macroinitiators of ethylene oxide polymerization.

I. Introduction

Polymers with terminal functional groups have gained much importance because of the versatility of the applications they afford. Such polymers can be used to perform two main operations: (1) chain extension or cross-linking via condensation reactions with a bi- or multifunctional linking agent fitted with antagonist functions and (2) formation of block copolymers by condensation with other polymers or via initiation of a monomer chain polymerization. A very important requirement of ω-functional polymers is their perfect terminal functionality: for example, step-growth processes are very sensitive to precise end-group stoichiometry, and polycondensates of high molar mass can be prepared only if the functionality of precursors corresponds to a known whole number. Similarly, for the synthesis of block copolymers by chain addition, it is of paramount importance that all chains serving as macroinitiators be fitted with the required function.

Reactive functions can be introduced at chain extremities by initiation with a functional initiator, end-capping, or transfer. The most efficient procedure to prepare ω-functionalized polymers is to quench "living" chains with an appropriate deactivating agent used under selective conditions. This approach was applied with great success in "living" anionic polymerization to generate a variety of ω-functional polymers such as macromonomers and telechelics. A variant of the end-quenching methodology is the chemical transformation of the end groups carried by preformed polymers. The latter approach is found particularly useful in carbocationic polymerization, in which direct quenching of "living" chains by nucleophiles does not necessarily yield the expected functions. Except for poly(vinyl ether)s, which were found amenable to the end-quenching technique, the functionalization by chemical transformation of isolated polymers was preferred in polyisobutylene (PIB) and polystyrene (PS). Kennedy and Ivan[1] described various quantitative transformations of *tert*-chlorine groups of PIB into miscellaneous reactive groups. Likewise, Miyashita et al.[2] reported the derivatization of chloro end functions of cationically prepared PS samples using organosilicon compounds, after noting that direct end-quenching of living polystyrene chains by the same reagents is effective only in certain experimental conditions (low concentration of Lewis acids). More recently, Matyjaszewski et al.[3] showed how to derivatize PS chains obtained by atom transfer radical polymerization.

In this article, we report the end-functionalization of hexaarm PS stars that were grown by carbocationic polymerization from a hexafunctional initiator. Using organosilicon compounds, we describe how to obtain hexaallyl and hexaazido PS stars from *sec*-chlorine-ended PS stars. Herein, we also unveil the successive transformation reactions and the treatment that were undertaken to synthesize new materials such as C_{60} end-capped PS stars and amphiphilic PS_6-*b*-PEO_6 star block copolymers.

II. Experimental Section

A. Materials. All reactions were carried out under a dry nitrogen atmosphere by use of Schlenk techniques. All the anhydrous solvents were deaerated before use. Tetrahydrofuran (THF) and 1,4-dioxane were purified by distillation from sodium/benzophenone. Dichloromethane was refluxed overnight on calcium hydride and distilled before use. Allyltrimethylsilane (ATMS) and azidotrimethylsilane (AzTMS) were distilled over CaH_2 under a nitrogen atmosphere just before use. Chlorobenzene was distilled over CaH_2 under vacuum. 9-Borabicyclo[3.3.1]nonane (9-BBN), C_{60}, hydrogen peroxyde in water (H_2O_2), triphenylphosphine (PPh_3), sodium hydroxide,

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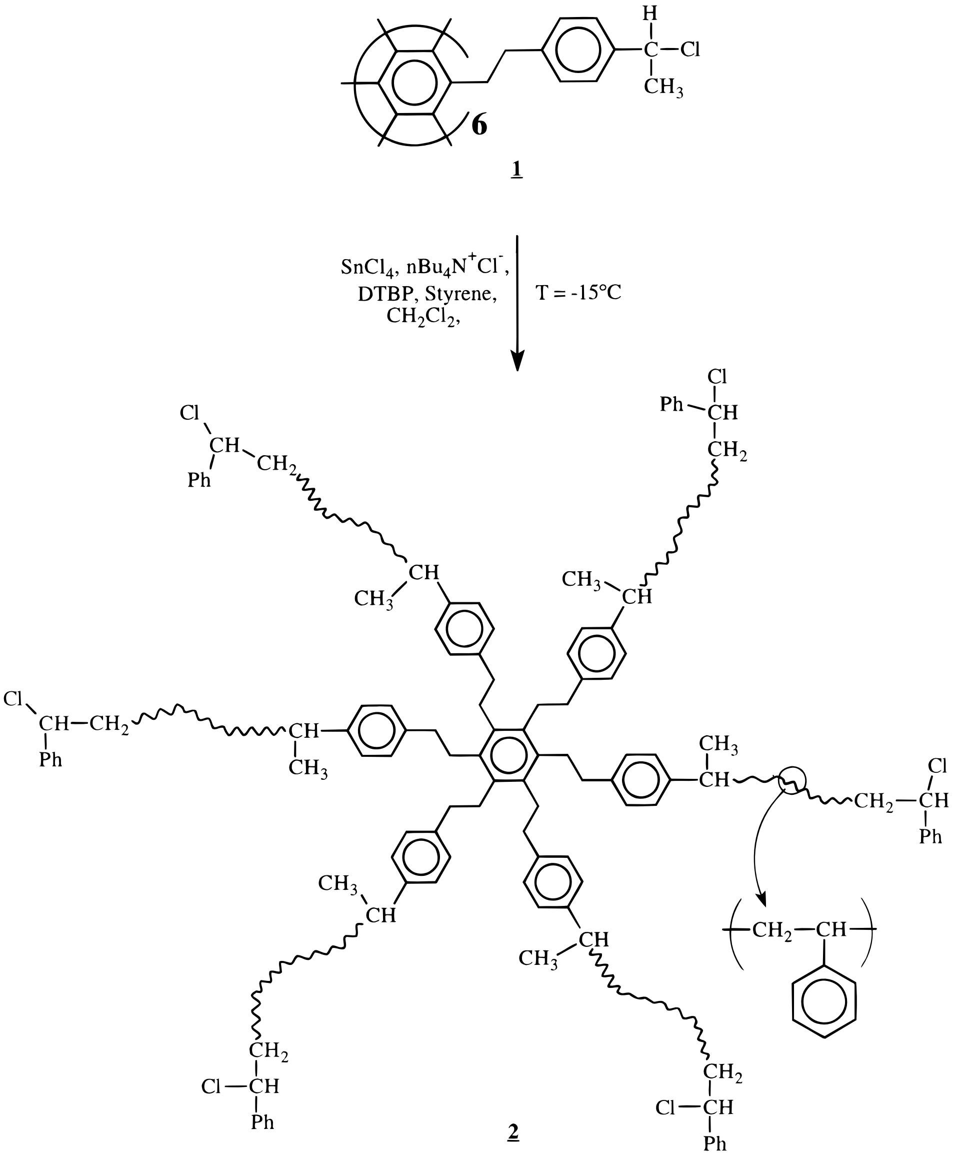
Scheme 1. Synthesis of Hexaarm PS Star Molecules[4]



and $TiCl_4$ (1.0 M solution in CH_2Cl_2) were used as received from Aldrich. Ethylene oxide (EO) was stirred over sodium for 5 h at −40 °C and was purified by cryodistillation. Diphenylmethyl potassium (DPMK) in THF was prepared following known procedures. All other reagents were purchased from Aldrich and were used after distillation for the liquids or drying for the solids.

B. Synthesis of Hexaarm PS Star and Linear PS by "Living" Cationic Polymerization. The general procedure for the preparation of hexaarm star-shaped PS has already been reported in detail.[4] Linear chains of short size and stars of short arm size were prepared with $\bar{M}_n$ ranging from 2000 g/mol to 3000 g/mol to characterize their end groups under good conditions. For this purpose the following system of polymerization was used: hexafunctional initiator **1** or PhEtCl/$SnCl_4$/2,6-di-*tert*-butylpyridine/*n*-Bu_4NCl in CH_2Cl_2 at −15 °C.

C. Functionalization at the PS Star Periphery with Allyl (a), Azido (b), Hydroxyl (c), and Amino (d) Groups. (a) Synthesis of the Hexaallyl PS Star, 3. CH_2Cl_2 (17 mL) was added to a 100-mL three-necked flask containing 500 mg (0.04 mmol) of freeze-dried hexachloro PS star (**2**). The solution was stirred and cooled to −20 °C. After addition of 4 mL (25 mmol) of ATMS, 3.8 mL (3.8 mmol) of $TiCl_4$ was introduced to trigger the reaction; the solution then turned suddenly from pale yellow to dark orange. The reaction mixture was stirred for 12 h and quenched by addition of 5 mL of $MeOH-NH_3$. The mixture was diluted in CH_2Cl_2, filtered, concentrated with use of a rotary evaporator, and precipitated twice from MeOH. By ^1H NMR (in $CDCl_3$) the resonance signals characteristic of the protons of the allylic group of **3** were assigned as follows: δ (in ppm) = 5.4−5.6 ($CH{=}CH_2$) and = 4.8−5.0 ($CH{=}CH_2$).

(b) Synthesis of the Hexaazido PS Star, 5. CH_2Cl_2 (17 mL) was added to a 100-mL three-necked flask containing 500 mg (0.04 mmol) of freeze-dried hexachloro PS star (**2**). The solution was stirred and cooled to −20 °C. After addition of 3.3 mL (25 mmol) of AzTMS, 3.8 mL (3.8 mmol) of $TiCl_4$ was introduced to trigger the azidation reaction; as mentioned above, the solution suddenly turned from yellow pale to dark orange. The reaction mixture was stirred for 12 h and quenched by addition of 5 mL of $MeOH-NH_3$. The quenched reaction mixture was dissolved in CH_2Cl_2, filtered, concentrated using a rotary evaporator, and precipitated twice from MeOH. By ^1H NMR (in $CDCl_3$, δ in ppm), the resonance signal (δ = 3.8−4.0) characteristic of the methine protons adjacent ($-CH(Ph)-N_3$) to N_3 which are present at the arm ends of **5** was observed. A strong absorption band characteristic of the vibration of the azido group could also be observed in the Fourier transform infrared (FTIR) (KBr) spectrum of the sample at ν (cm^{-1}) = 2097.

(c) Synthesis of the Hexahydroxyl PS Star, 4. Anhydrous THF (50 mL) was added to a 250-mL three-necked flask containing 500 mg (0.04 mmol) of freeze-dried hexaallyl PS

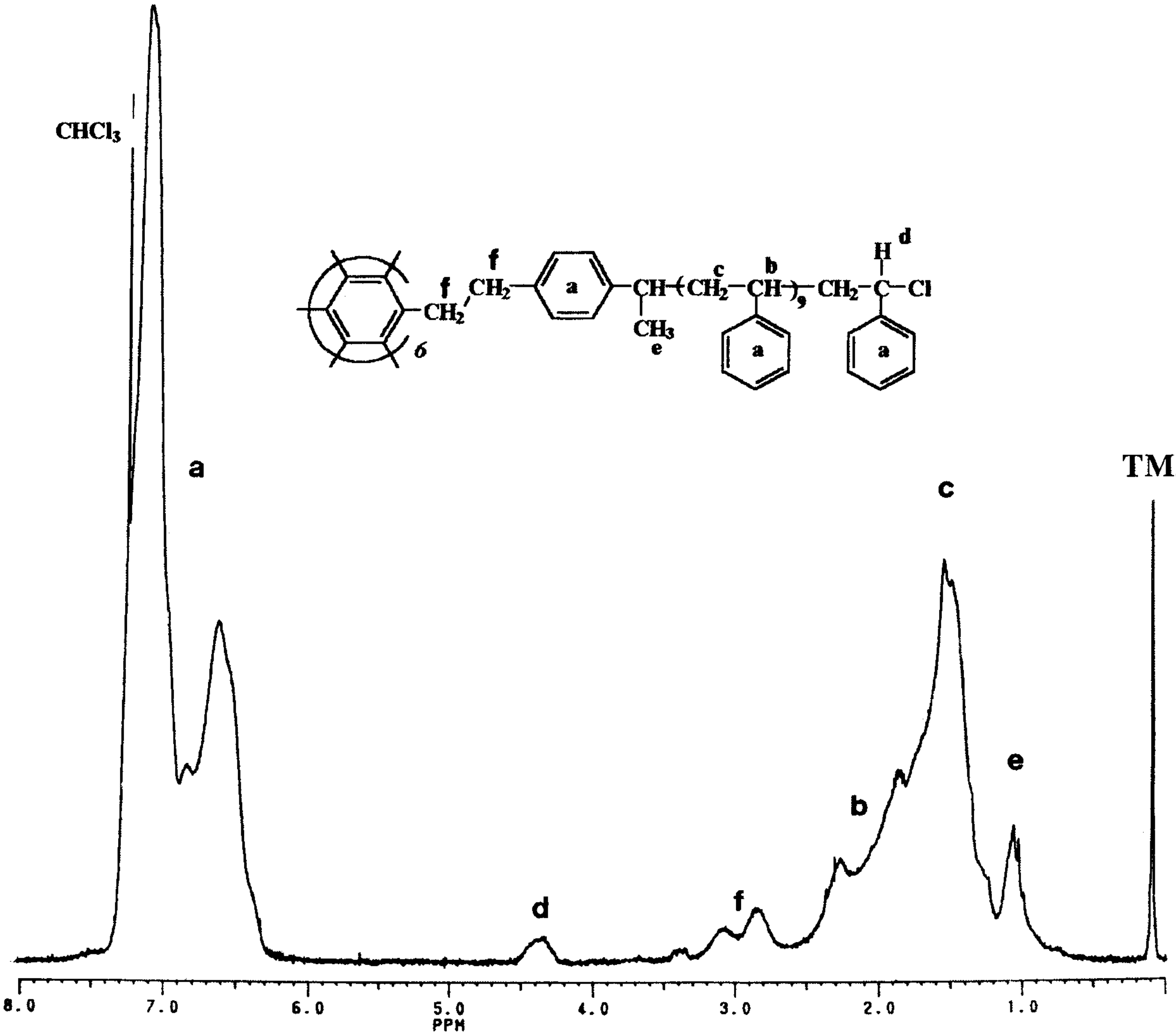


Figure 1. ^{1}H NMR (200 MHz, in $CDCl_3$) spectrum of a PS star sample of $\bar{M}_n$ ≈12000 g/mol as determined by SEC-MALLS and ≈13000 g/mol as evaluated from the NMR integrations.

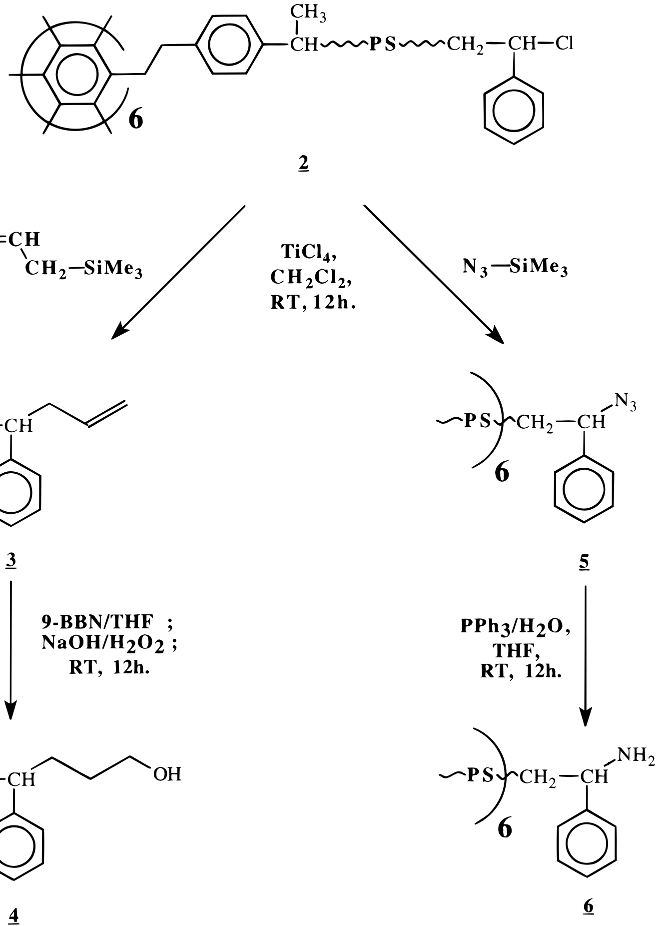
star (**3**). The solution was stirred and cooled to −30 °C and, at this temperature, 10 mL (5 mmol) of 9-BBN (0.5 M solution in THF) was added. After 2 h, 1 mL (5 mmol) of NaOH (5N) and 0.6 mL (5 mmol) of aqueous H_2O_2 (33% in volume) were introduced into the mixture under nitrogen. The temperature was maintained at −30 °C for one additional hour and was allowed to slowly reach 25 °C. The mixture was stirred for 16 h at 25 °C, then heated at 50 °C for 3 h. The mixture was diluted with THF, filtered, concentrated with a rotary evaporator, and precipitated twice from methanol. The resonance signal caused by the hydroxyl groups of **4** was found in the ^{1}H NMR spectrum (in $CDCl_3$, δ in ppm) at 3.4−3.6 (CH_2−OH). Moreover, a large infrared band relative to the absorption of the hydroxyl group was found at ν (cm^{-1}) = 3100−3700 cm^{-1} in the FTIR spectrum.

(d) Synthesis of the Hexaamino PS Star, 6. The solid mixture containing 500 mg (0.04 mmol) of freeze-dried hexaazido PS star (**5**) and 656 mg (2.5 mmol) of PPh_3 was deaerated under vacuum in a 250-mL two-necked flask. After dissolution of the mixture with 30 mL of anhydrous THF, 70 mL (3.8 mmol) of distilled and deaerated water was added at room temperature. The reaction mixture was stirred for 12 h. The mixture was concentrated and precipitated twice from MeOH. No resonance signal characteristic of the amino group could be detected in the ^{1}H NMR spectrum (in $CDCl_3$); however, the disappearance of the signal corresponding to the resonance of the methine proton in a position to the azido group $-CH(Ph)-N_3$ (at 3.8−4.0 ppm) could be noticed. On the other hand (on KBr), a medium band absorption relative to the vibration of the amino group was observed at ν (cm^{-1}) = 3300−3500 in the FTIR spectrum, whereas the disappearance of the strong absorption at ν (cm^{-1}) = 2097 relative to the azido group could be noticed concomitantly.

D. Synthesis of the Hexafullerene PS Star. To a 250-mL two-necked flask were introduced 500 mg (0.04 mmol) of freeze-dried hexaazido PS star (**5**) and 360 mg (0.5 mmol) of C_{60} under a nitrogen atmosphere (in a glovebox). After flaming/deaerating the flask containing the mixture of solids, 100 mL of anhydrous chlorobenzene was added to solubilize these solids. The reaction mixture was stirred and allowed to reflux for 1 day under nitrogen, and the solution turned from magenta to dark brown. After removing the solvent under vacuum, the product was redissolved in THF, filtered (to remove unreacted C_{60} that is insoluble in THF), concentrated, and precipitated twice from cold hexane; a brown powder was eventually obtained. Resonance signals characteristic of monosubstituted C_{60} were observed by ^{13}C NMR (in $CDCl_3$, at δ in ppm = 135−145). The strong infrared band at 2097 cm^{-1} relative to the azido group (on KBr) disappeared. Thermal gravimetry (heat rate = 10 °C/min) showed only two plateaus: decomposition of the PS part between 200 and 450 °C (weight % ≃77.3) and decomposition of the C_{60} part between 470 and 570 °C (weight % ≃22.7).

Finally, cyclic voltammetry showed three waves corresponding to the three first reduction waves of C_{60}-monofunctionalized compounds: $E° = -1.00$ V, −1.40 V, and −1.90 V vs ferrocene/ferricinium (Pt cathode, n-$Bu_4N^+BF_4^-$: 10^{-3} M in toluene−acetonitrile (1/4, v/v), sweep rate = 100 mV s^{-1}; $T = -15$ °C).

Scheme 2. Functionalization Reactions at the Periphery of PS Star 2: Left Side, Allylation/Oxidation To Obtain 3 and 4, Respectively; Right Side, Azidation/Reduction To Obtain 5 and 6, Respectively



E. Synthesis of (PS-*b*-PEO)$_6$ Star Block Copolymers. After two precipitations of their CH_2Cl_2 solutions by MeOH, hexahydroxy-terminated PS star samples (**4**) were first dried (in a vacuum oven) and then freeze-dried from their 1,4-dioxane solution. Polymerization of ethylene oxide was carried out under a dry nitrogen atmosphere in a 250-mL three-necked flask reactor equipped with a magnetic stirrer and containing 200 mg (0.02 mmol) of **4** previously freeze-dried. To this polymer was added 30 mL of anhydrous THF. The six alcoholic functions of **4** were first deprotonated using DPMK (0.2 mL; <0.1 mmol) in slight imbalance to avoid the formation of linear PEO chains. This metallation took from several minutes to 1 h. Ethylene oxide (2.3 mL) was then added to the solution containing the hexaalkoxide initiator. The reaction medium was acidified, after 12 h of polymerization at 40 °C, by some drops of acetic acid (Aldrich). The mixture was stirred for a few minutes and precipitated from Et_2O. The (PS-*b*-PEO)$_6$ star block copolymer was filtered, diluted with THF, and precipitated again from Et_2O. The product was obtained as a white powder, dried in a vacuum oven, and freeze-dried before characterization by ^{1}H NMR and size-exclusion chromatography (SEC) (THF and water were used as eluents).

F. Characterization. ^{1}H NMR spectra were recorded in solution in $CDCl_3$ with a Brucker AC-200 MHz- spectrometer, with tetramethylsilane (TMS) proton signal as an internal standard. All chemical shifts are reported in parts per million (δ in ppm) with reference to TMS and were measured relative to TMS. ^{13}C NMR spectra were recorded at 62.90 MHz on a Brucker AC 200 spectrometer with the solvent carbon signal as internal standard ($CDCl_3$).

Infrared spectra were recorded on a Nicolet 320 FT spectrophotometer as thin film of polymer on KBr.

Molar mass distributions were measured by SEC with a JASCO HPLC-pump type 880-PU, a Varian 5500 apparatus equipped with a refractive index (RI)/UV dual detection, and three TSK gel columns calibrated with PS standards. Absolute molar masses of star polymers were obtained by SEC equipped with a RI/UV dual detection coupled with a multiangle laser light scattering (MALLS) detector (DAWN-F laser photometer, Wyatt Technology Inc.). The flow rate of THF (used as eluent) was 0.7 mL/min. Refractive index increment (d*n*/d*c*) of 0.185 mL/g for linear PS was assumed to be the same for PS star samples.

III. Results and Discussion

Recently, we described the synthesis of hexaarm star-shaped polystyrenes **2** that were obtained by “living” cationic polymerization using a newly designed hexafunctional initiator **1** fitted with six 1-phenylethyl chloride groups (Scheme 1).[4]

Well-defined and precisely controlled PS stars with absolute molar masses up to 100 000 g/mol and molar mass dispersities (MMD) of about 1.1 could be obtained by this approach. The synthesis of such well-defined stars by a divergent process was possible because of the “living” character of the cationic polymerization which was established with use of a monofunctional model. On the other hand, the hexafunctionality of the PS stars was checked by growing simultaneously linear chains and stars from a mixture of mono- and hexafunctional initiators; the values obtained for the ratio of the star molar mass to that of the linear chains being close to 6, it was concluded that the stars obtained by this method do exhibit the same functionality of 6 as that of the initiator.

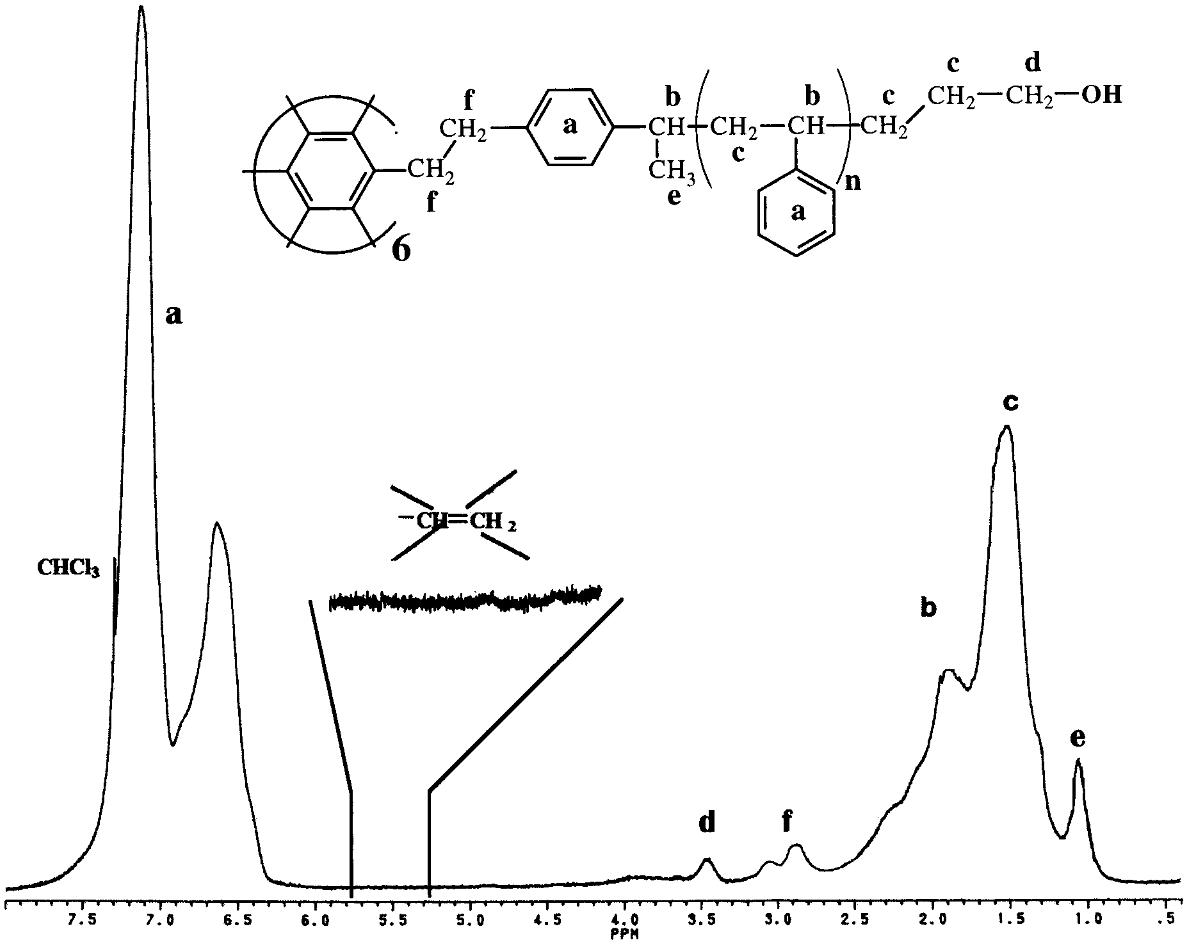
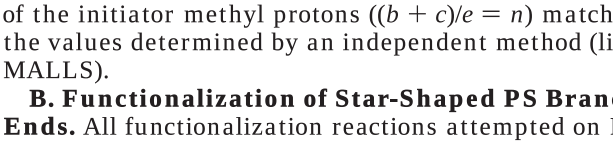


Figure 2. ^1H NMR (200 MHz, in $CDCl_3$) spectrum of a PS ω-OH **4**.

A. Determination of the Actual Branch End Structure of the Hexaarm PS Stars. For the sake of characterization of the branch end structure before and after carrying out the functionalization reactions, PS star samples of "low" molar masses with values ranging from 12 000 to 18 000 g/mol (the average molar mass of the arms therefore ranging from 2000 to 3000 g/mol) were prepared. Because they are synthesized by "living" cationic polymerization from a phenylethyl chloride type/$SnCl_4$ initiating system, these stars should be ended by a terminal secondary chlorine atom upon quenching by methanol. The presence of the chlorine atom at the star branch end was checked by ^1H NMR (Figure 1).

The peaks caused by the methyl and the methine protons adjacent to the chlorine atom that were observed in the ^1H NMR spectrum of the initiator also appear in the same ratio in ^1H NMR spectrum of the stars, in addition to the resonance of the protons of the polymer repeating units. Thus, the terminal function in these stars is a secondary chlorine atom, and their functionality is exactly that of the initiator. The results confirm those previously reported by Miyashita et al.,[2] who also observed the presence of a secondary chlorine atom (broad signal at $\delta = 4.3-4.5$ ppm) at the end of their cationically prepared linear PS chains. As already mentioned by these authors, the quenching of growing chains by methanol does not afford an end-standing methoxide, but rather a *sec*-chlorine atom. Because the time-average concentration of carbocations in equilibrium (eq 1) is very low, most growing ends therefore exist under the dormant and stable C—Cl form that is unaffected by the addition of methanol.



(1)

^1H NMR spectroscopy was also used to determine the number-average molar mass of the PS star samples; the $\bar{M}_n$ values obtained by comparing the integrated peak due to the protons of the PS repeating units with that of the initiator methyl protons ($(b + c)/e = n$) matched the values determined by an independent method (like MALLS).

B. Functionalization of Star-Shaped PS Branch Ends. All functionalization reactions attempted on PS stars were first performed on linear PS homologues.

Because of the relative inertness of the end-standing C—Cl bond, conventional bases could not be used for the substitution reactions. In contrast, organosilicon reagents readily react with alkyl chlorides, provided the latter are activated by appropriate Lewis acids.[2,5] Advantage was thus taken of the affinity of these organosilicon compounds toward chlorine atoms to derivatize the PS branch ends. As mentioned in the introduction, Miyashita et al.[2] adopted the same synthetic strategy as ours to end-functionalize their cationically prepared PS chains and compared the

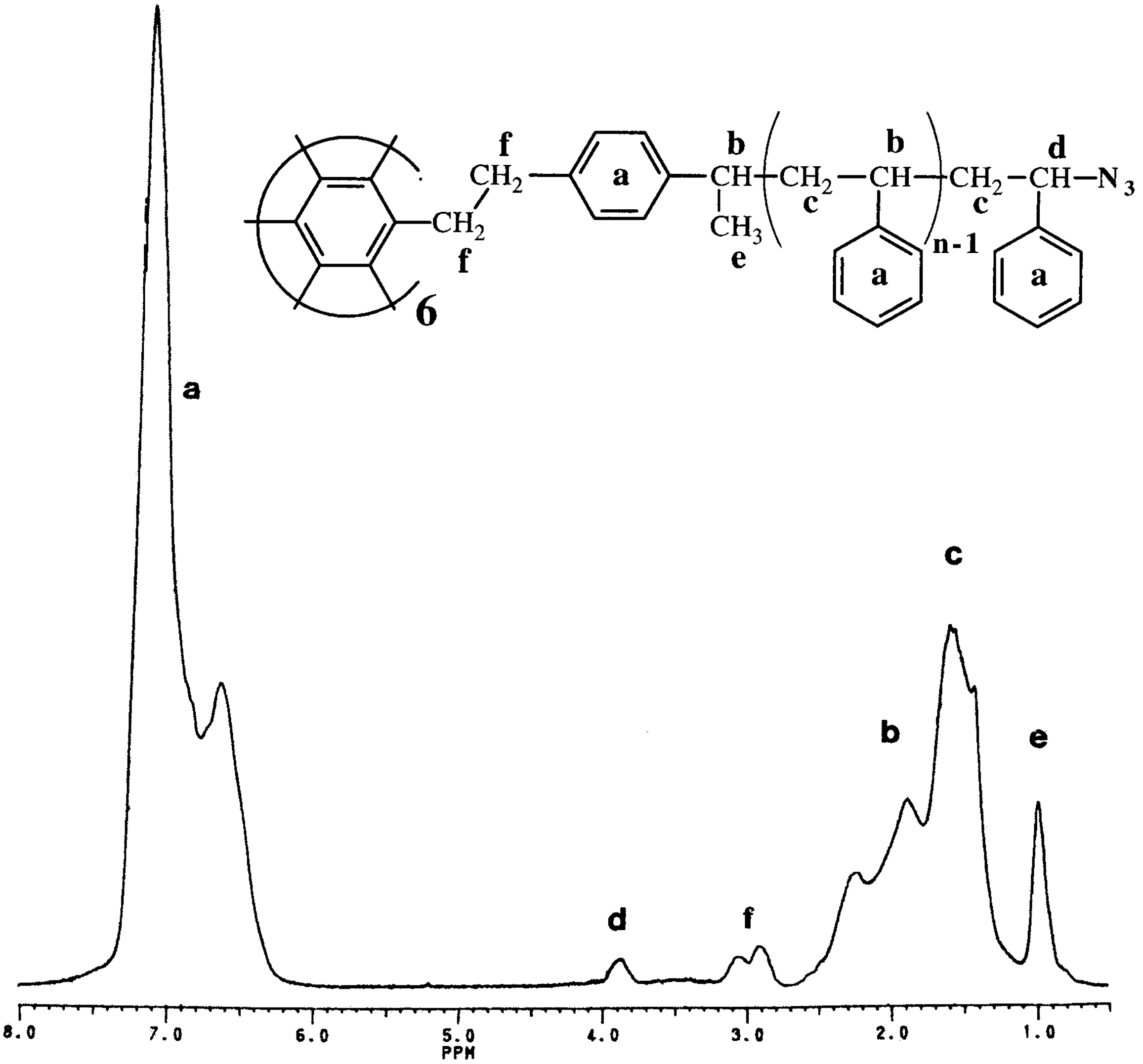


Figure 3. ^{1}H NMR (200 MHz, in CDCl$_3$) spectrum of a PS ω-N$_3$ **5**.

direct end-quenching of growing chains with the derivatization of isolated polymers. They noticed that the quenching reaction yields a satisfactory extent of functionalization, only when low concentrations of Lewis acid were used to polymerize styrene. Because we came to use much higher concentrations of Lewis acid in our experiments to prepare our star samples, we therefore gave preference to the synthetic route based on the derivatization of isolated polymers. We then used a 20-fold excess of Lewis acid but did not resort to n-Bu$_4$N$^+$-Cl$^-$ salts as Miyashita et al. did.[2] The silyl compounds were introduced in 100-fold molar excess over the chlorinated end. Two types of derivatization were carried out with a view of ultimately deriving hexahydroxy- and hexaamino-terminated PS stars (Scheme 2):

(a) Synthesis of Hexahydroxy PS Stars. The transformation of the chlorine atoms in **2** into hydroxyl groups was achieved in two steps. The use of ATMS provided us with the opportunity to convert the end-standing [∼CH(Ph)—Cl] group into allylic groups (carried by the last styrene unit), TiCl$_4$ being used as activator. Not only Miyashita et al.[2] (see above) but also Kennedy and co-workers[6] used ATMS as a means to functionalize their chlorine-ended polymers. In a second step, these allyl functions were reduced in a classical manner to obtain end-standing hydroxyl groups. Star-shaped PS **2** ($\bar{M}_n$ = 2000 g/mol per branch) were thus treated with ATMS (100-fold excess per chlorine content) in the presence of a 20-fold excess of TiCl$_4$. Characterization of the resulting polymer **3** by ^{1}H NMR spectroscopy showed that the functionalization reaction occurred quantitatively as confirmed by the total disappearance of the signal (δ = 4.3−4.5 ppm) caused by the protons in the α-position to the chlorine atoms and by the presence of the signals that can be assigned to the resonances of allylic protons [at 4.8−5.0 ppm (CH−CH_2) and 5.4−5.7 ppm (CH—CH$_2$)]. The extent of functionalization ($\bar{F}_n$) was checked by comparing the integrated peak area of the methyl [see signal e in Figure 1] carried by the initiator fragment with those of the allylic groups: $\bar{F}_n$ was found close to 1, indicating that functionalization had occurred without side reactions.

The six end-standing hydroxyl groups of PS **4** were obtained upon treating the allylic groups above with 9-BBN, and afterward with a mixture of NaOH/H$_2$O$_2$, with use of the classical hydroboration/oxidation procedure.[7] The efficiency of the reaction was checked again by ^{1}H NMR. The ^{1}H NMR spectrum of **4** (Figure 2) showed a broad signal characteristic of the resonance of the protons in the α-position to the hydroxyl groups at 3.5 ppm, whereas that caused by allylic protons completely disappeared. The $\bar{F}_n$ for these hydroxyl groups, as determined by ^{1}H NMR from the peak area

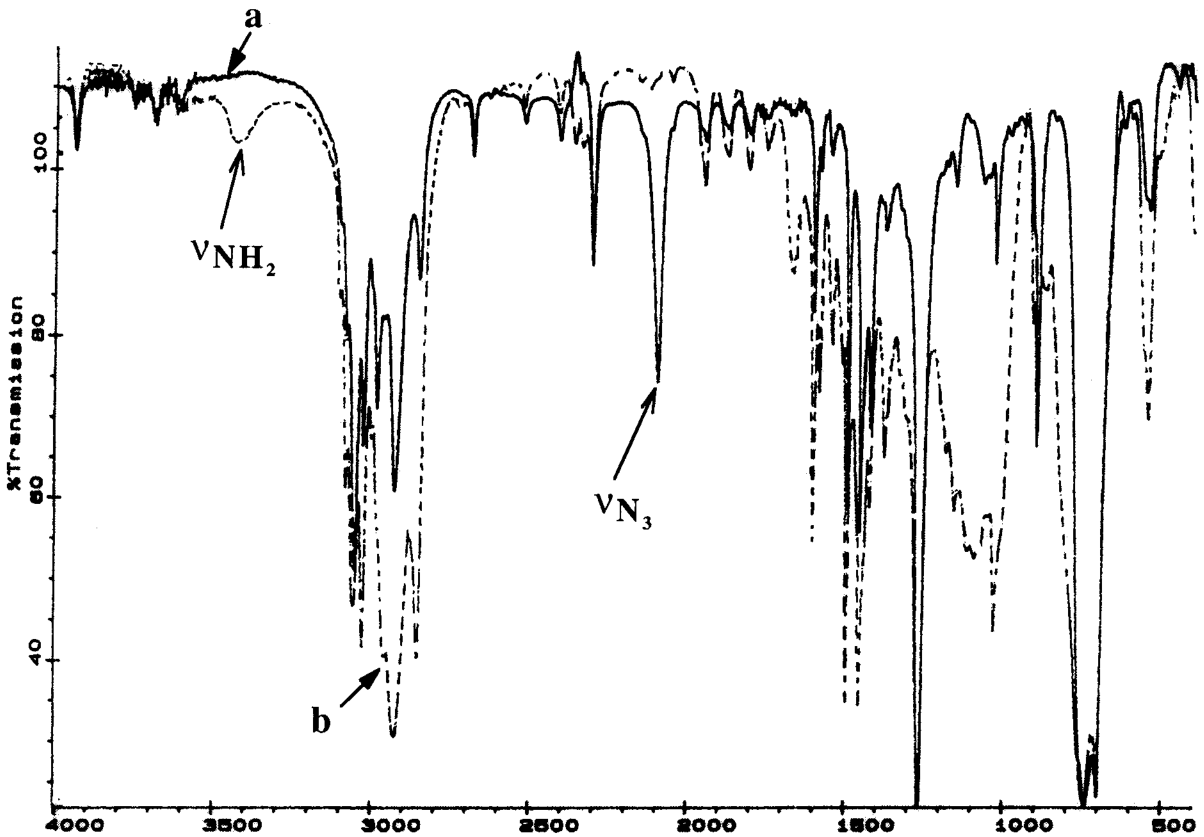
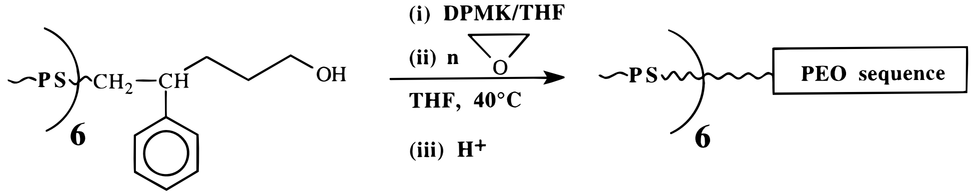


Figure 4. FTIR spectra of a star PS-ω-N_3 (a) —, and ω-NH_2 (b) – – –.

Scheme 3. Synthesis of Star-Shaped Block Copolymers (PS-*b*-PEO)$_6$



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ratio of 3*d*/2*e*, was close to 1, indicating that all branches of the star were functionalized.

Characterization of these samples by FTIR showed the presence of a broad medium band centered at 3300 cm^{-1} caused by the vibration of the hydroxyl groups (thin film on KBr).

(b) Synthesis of Hexaamino PS Stars. Similar in its principle to the functionalization by the allylic groups, the derivatization of [~CH(Ph)—Cl] arm ends with azido groups was also attempted. With use of the same Lewis acid ($TiCl_4$), polymer **2** was reacted with another organosilicon derivative, namely AzTMS. The reaction between polymer **2** and AzTMS (100-fold excess per chlorine content) was carried out in CH_2Cl_2 for 12 h at −15 °C after the activation of the C—Cl covalent bonds by $TiCl_4$ (20-fold excess per chlorine content) (Scheme 2). The complete replacement of the chlorine atoms by azido groups was monitored by ^1H NMR through the shift of the resonance corresponding to the methine protons of the terminal unit [~C*H*(Ph)~] from $\delta_H = 4.3-4.5$ ppm to $\delta_H = 3.8-4.0$ ppm (Figure 3).

The $\bar{F}_n$ for these azido groups, which was calculated using the peak area ratio of 3*d*/*e*, was close to the expected value of 1.

In addition, the infrared spectrum of the star polymer **5** exhibited a strong absorbance band at 2105 cm^{-1} characteristic of the $\nu(N_3)$ vibration of the hexaazide compound formed.

To obtain the hexaamine **6**, **5** was reduced with use of a 10-fold excess of PPh_3/H_2O[8]; the reaction was carried out at 20 °C in THF for 12 h and was again monitored by ^1H NMR through the shift of the resonance due to the methine proton d [~C*H*(Ph)~] of the terminal unit from $\delta_H = 3.8-4.0$ ppm to the region $\delta_H = 2.5-3.0$ ppm. Again quantitative functionalization was obtained for this latter reaction. The reduction of the hexaazide **5** to the hexaamine **6** was also monitored by infrared spectroscopy. In the following spectrum (in absorbance), the disappearance of the characteristic band at 2105 cm^{-1} mentioned above and the appearance of a new (medium) band at 3430 cm^{-1} characteristic of the $\nu(NH_2)$ vibration of the hexaamine **6** formed are shown (Figure 4).

B. Preparation of Materials with Potential Applications. Because PS star samples can now be fitted with either 6-azido and 6-hydroxyl groups, we took advantage of the latter and derived new materials whose characteristics and hence properties could be

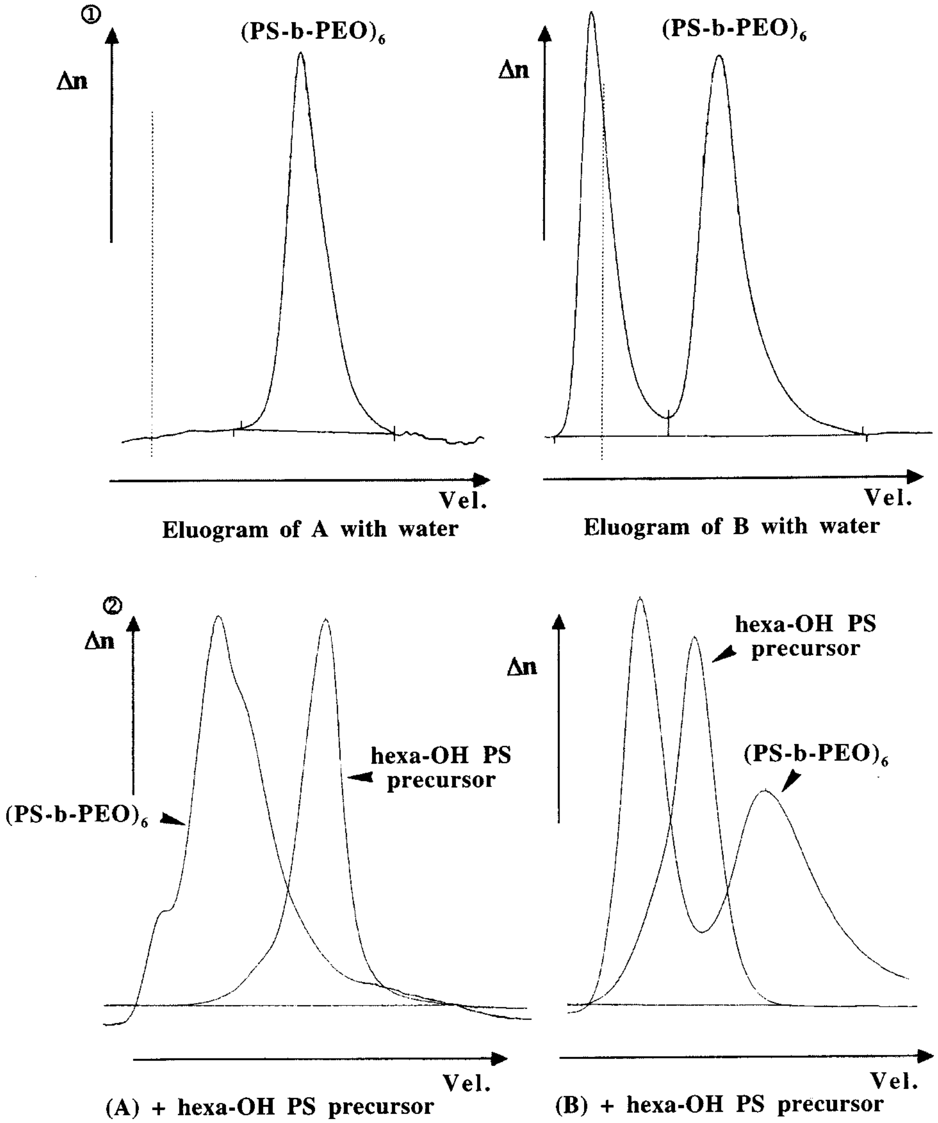


Figure 5. SEC traces of two (PS-*b*-PEO)$_6$ copolymers: A (PS content = 3%) and B (PS content = 10%), using water (1) and THF (2) as eluents.

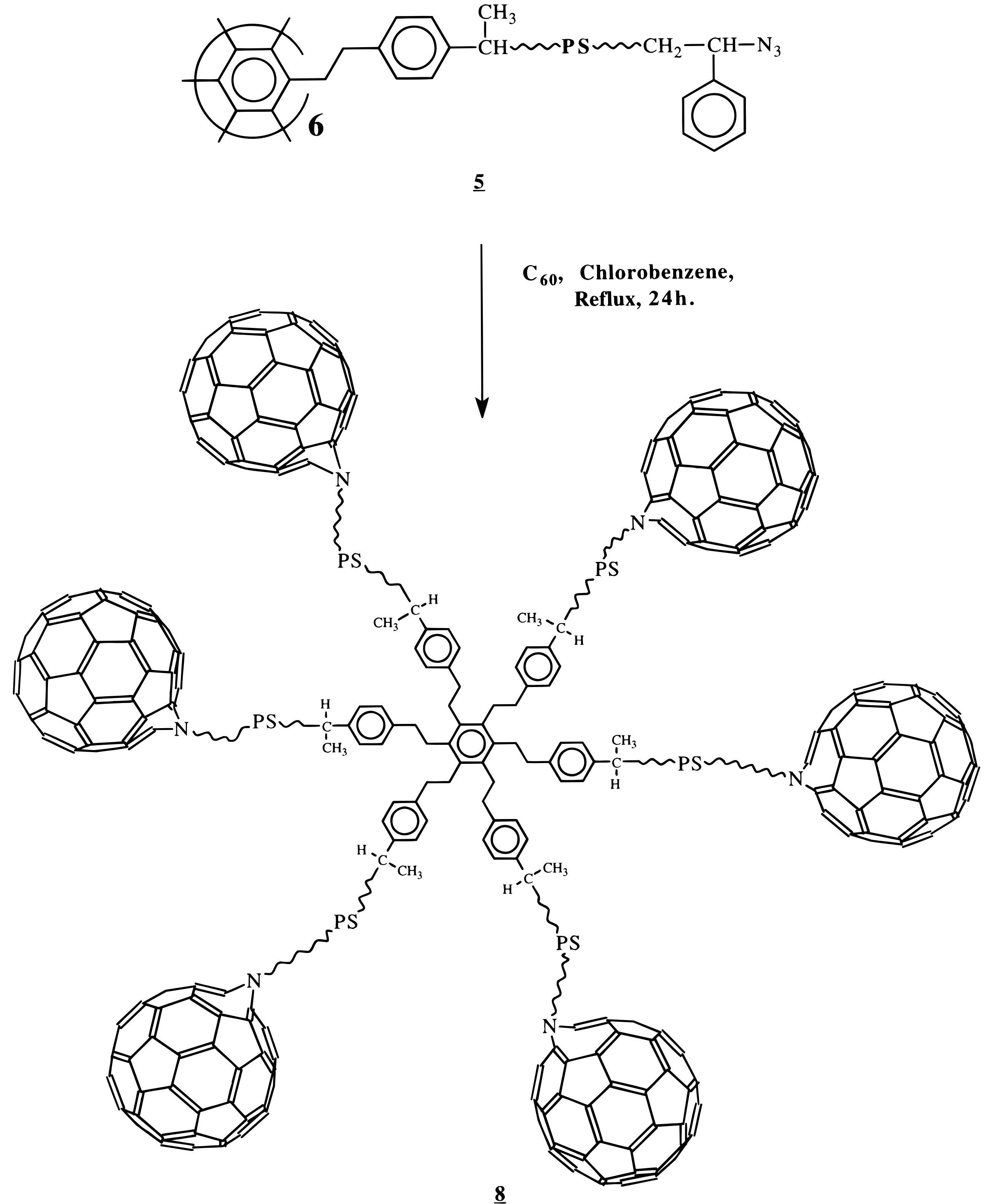
used afterward. On one hand amphiphilic star block copolymers made of PS-*b*-PEO branches were synthesized from **4** used as macroinitiator, and on the other hand six C_{60} molecules were grafted at the periphery of PS stars using **5** as precursor.

(a) Synthesis of Block Copolymers (PS-*b*-PEO)$_6$ (Scheme 3). The end-standing alcohol functions of PS **4** were first deprotonated by use of a default of DPMK. In fact, as reported by Gnanou et al.,[9] DPMK does not need to be used in stoichiometry with respect to the concentrarion of alcohol functions for the ethylene oxide polymerization to occur because alkoxide and hydroxyl termini slowly exchange during the growth process. The alkoxides generated in this way were then subsequently used to polymerize ethylene oxide, the "living" character of the latter polymerization allowing precise control of the size of the hydrophilic outer PEO layer. Two samples were actually synthesized with a hydrophobic PS content varying from 3% in A to 10% in B (mass %). ^{1}H NMR was used to characterize the PS/PEO star samples obtained. The comparison of the signals characteristic of the PS part at δ(aromatic C*H*) = 6.2−7.3 ppm and δ(C*H* and CH_2) = 1.0−2.3 ppm with that corresponding to the PEO block at δ(CH_2−O) = 3.0−4.5 ppm confirmed that the PS/PEO ratios in A and B were those targeted (3% in A, 10% in B).

Despite the slight difference in their respective compositions, A and B exhibited different behaviors in water or THF (Figure 5).

The amphiphilic copolymer whose PS content is the richest (10%) gave two populations both in water and THF. In the latter solvent (2), the population that was eluted at low volumes was followed unexpectedly by a second population with an even higher retention time than the hexahydroxy PS precursor. The comparison of the eluogram obtained for this copolymer with that of the precursor proves that ethylene oxide has polymerized effectively. As to the formation of two populations, it is certainly the result of the aggregation of PEO blocks in THF. Because THF is not a good solvent for the latter polymer, the tendency of branched PEO to aggregate is a well-known feature and has been reported by several authors. In particular, Gauthier and co-workers[10] made the same observation when studying the behavior of PS−PEO copolymers in THF. In our case, it appears that this aggregation occurs both intra- and intermolecularly, hence the formation of two populations that are eluted at different times. In water (1) the same

Scheme 4. Synthesis of C_{60}-Terminated PS Star Molecules [$\bar{M}_w$ (PS Branch Precursor) = 3000 g/mol]



pattern was observed, the copolymer B giving two discrete populations that correspond to intra- and intermolecularly aggregation of the PS part, respectively.

In contrast to sample B, the amphiphilic copolymer A with its 3% of PS content was eluted as a unimodal distribution both in water and in THF. In the latter solvent (2) the SEC traces appeared to be shifted (with respect to those of the precursor), indicating that the polymerization of ethylene oxide did occur, but the SEC traces were broad and at least three populations could be distinguished. The fact that these populations corresponded to a much higher molar mass than expected indicates that PEO blocks also tend to aggregate intermolecularly in the presence of THF. In water (1), the same amphiphilic copolymer A gave only one population of species that can be identified with an unimicellar system. Indeed, the lower content in PS did not allow

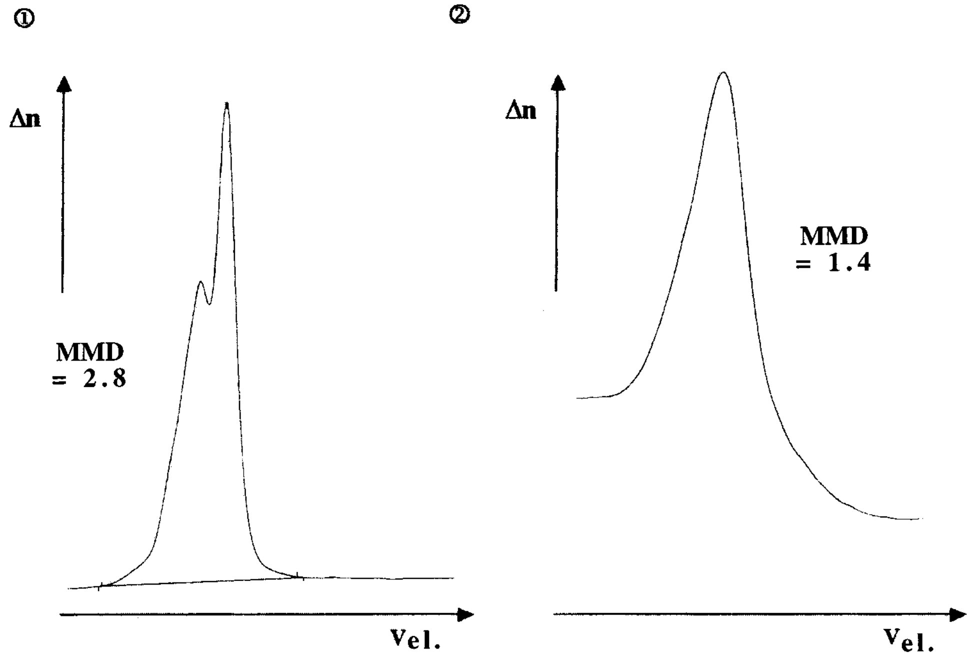


Figure 6. Chromatograms of a C_{60}-terminated PS star: with THF as eluent in (1) and chlorobenzene as eluent in (2).

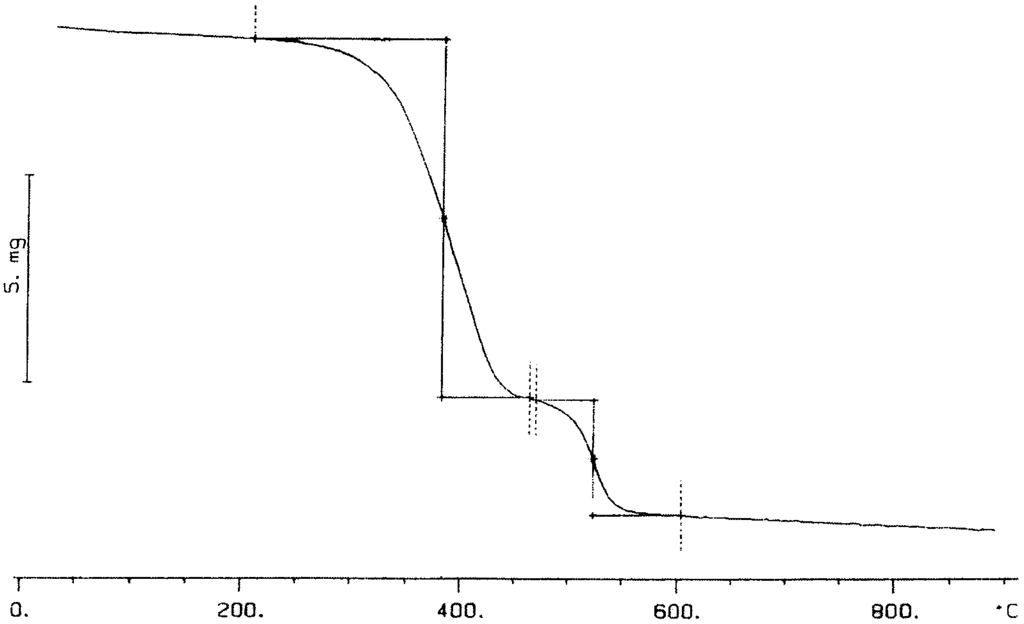


Figure 7. Thermogravimetric analysis of C_{60}-terminated PS star **8** (heating rate, 10 °C/min, under N_2).

the PS central core to aggregate intermolecularly; each of these macromolecules can therefore be considered as a stable micelle.

(b) Synthesis of Fullerene-Terminated Hexa-Branched PS Stars (Scheme 4). The synthesis of polymers containing fullerene as side groups or in the main chain is usually carried out in the context of "smart" materials.[11] Recently, many studies have indeed been devoted to the grafting of C_{60} molecules onto miscellaneous polymers to get access to processable C_{60}-containing polymers.[12,13] In particular, Hawker et al.[12c] recently described the preparation of C_{60}-modified dendrimers that were obtained by one-step cycloaddition of azido-functionalized polyether dendrimers to C_{60}. Actually, they followed the same procedures as those reported by Wudl and co-workers,[14] who described the synthesis of azafulleroid compounds via reaction of C_{60} with organic azides.

Herein we report the synthesis of a polymeric architecture consisting of six fullerene moieties linked to a star structure whose precursor is the hexaazido PS **5**[15] (Scheme 4). This hexaazide polymer **5** was allowed to react with a 2-fold excess of C_{60} per azide function for 1 day in chlorobenzene at 130 °C. The starting magenta solution turned deep brown after a few hours. After removal of the solvent under vacuum, THF was added to solubilize the hexafullerene PS star, whereas the insoluble C_{60} was filtered off. The THF solution was then concentrated and the functionalized polymer was isolated by precipitation with methanol. The product was purified by repeated precipitations of its CH_2Cl_2 solution from cooled hexane.

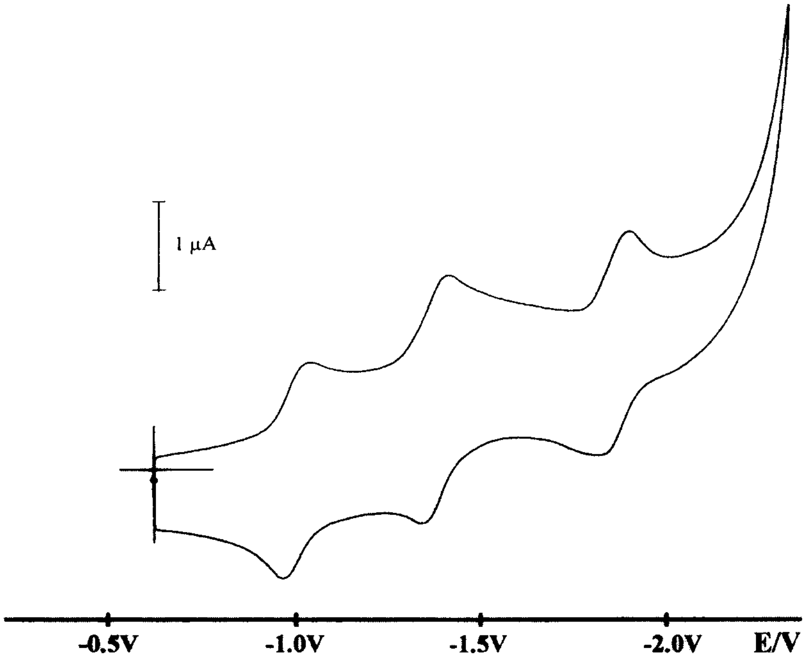


Figure 8. Cyclic voltammogram of **8** (9×10^{-5} M) using a toluene/acetonitrile mixture (1/5), Pt as the cathode, n-Bu_4NBF_4 (10^{-3} M) as the electrolyte, ferrocene/ferricinium as the redox couple internal reference, and a scan rate of 100 mV/s.

These newly built "star-balls" architectures have been characterized by SEC (Figure 6), ^1H and ^{13}C NMR, FTIR, thermal gravimetry (Figure 7), and cyclic voltammetry (Figure 8).

The eluograms of an hexafullerene PS star sample are presented in Figure 6 with use of THF and chlorobenzene as eluents. The SEC trace (1) in THF exhibits a shoulder in the high molar mass region with a broad distribution of 2.8, whereas the eluogram (2) obtained with PhCl as eluent shows a smooth monomodal distribution (MMD = 1.4). We can therefore infer that the shoulder observed in THF is likely caused by the aggregation of C_{60} termini, THF being a nonsolvent for the C_{60} parts.

In the ^1H NMR spectrum of **8**, the signal caused by the methine protons adjacent to the azido group ($\sim CH(Ph)-N_3$) at $\delta = 3.8-4.0$ ppm totally disappeared, and at the same time no new signal was observed. The signal of the methine proton in the α-position to the C_{60} ($\sim CH(Ph)-N < C_{60}$) probably is now shifted under the two broad multiplets appearing at $\delta = 0.8-2.4$ ppm and $\delta = 2.5-3.5$ ppm that are associated with the resonance of the $[-CH_2-CH-]$ of the repeating units and the protons $[-CH_2-CH_2-]$ of the star core, respectively. The ^{13}C NMR spectrum showed characteristic multiplets associated with the resonance of the carbon atoms of the PS backbone ($\delta = 41$ ppm $[-CH-]$, $\delta = 44-46$ ppm $[-CH_2-]$, $\delta = 126-129$ ppm [aromatic$-CH-$], and $\delta = 146-148$ ppm [aromatic $-Cq-$]) and the signals corresponding to monosubstituted C_{60} between 140 and 146 ppm. These latter peaks are in good agreement with the known opened annulene structure of monosubstituted C_{60} azafulleroids as described by Wudl and coworkers.[14] In the infrared spectrum of **8**, we observed the total disappearance of the characteristic strong band at $\nu = 2105$ cm^{-1} associated with the vibration of the azido groups (ν_{N3}).

All these characterizations effectively confirmed the presence of C_{60} molecules at the PS periphery in lieu of azido groups. Further characterizations of these "star-balls" structures **8** were nevertheless carried out to determine their actual C_{60} content (Figure 7) and their electrochemical behavior (Figure 8).

The thermal gravimetric analysis of **8** shows as expected two plateaus, the PS part being first decomposed between 200 and 450 °C and the C_{60} units between 470 and 570 °C. This technique allowed us to determine the actual content of C_{60} in these materials; the relative heights (mass %) found for the two transitions (77.9:22.1) appear to be in good agreement with the calculated values of the relative mass of the PS part and of C_{60} (80.6:19.4), assuming a quantitative functionalization of PS stars by C_{60}.

The cyclic voltammogram of **8** in CH_3CN/toluene (20/80) on a Pt cathode at −15 °C with use of n-Bu_4NBF_4 (10^{-3} M) as the electrolyte shows three waves at $E° =$ −1.00 V, −1.40 V, and −1.90 V vs ferrocene/ferricinium before the solvent front, corresponding to the three first reduction waves of C_{60}. These values agree closely with those reported for monosubstituted C_{60} compounds.[16] Moreover, the shape of the waves shows that the six C_{60} redox centers are independent, each wave behaving as a one-electron exchange.[17,18] It is reasonable to state that these C_{60} termini are not encapsulated in the PS matrix and do not interact among themselves. The important effect, however, is the solubilization of the C_{60} units via the PS inner part. Finally, the comparison of the height of the first cyclic voltammetry wave with that of C_{60} itself provided the number (n) of C_{60} units in **8**; with the Bard formula,[18] a value of $n = 5 \pm 1$ was found in satisfactory agreement with the expected number of 6:

$$n_p = \frac{I_p/C_p}{I_m/C_m}\left(\frac{M_p}{M_m}\right)^{0.275}$$

where I, C, and M are the intensity, concentration, and molar mass, respectively; the subscripts p and m refer to **8** and C_{60}, respectively.

Conclusion

In this article we report selective and quantitative chemical modifications of hexaarm PS stars with controlled arm size and well-defined end-functionality. The six terminal secondary chlorine atoms were first functionalized using ATMS in the presence of $TiCl_4$; the latter reaction was followed by the hydroboration and oxidation of the terminal allylic entities to give the hexaalcohol-terminated PS star which served as a hexafunctional initiator for the anionic polymerization of ethylene oxide after being deprotonated by a strong base. Characterization of both the end-functionalized PS stars and the star block copolymers $(PS\text{-}b\text{-}PEO)_6$ clearly indicated that functionalization and subsequent copolymerization occurred as expected and were quantitative. In the second part of this study, the transformation of the chlorinated termini of the starting PS star **2** into azido ends using AzTMS in the presence of $TiCl_4$ was described; the hexaazido PS star obtained was then reacted with an excess of C_{60} (2:1) to give the "star-balls" architecture **8**. The derivatization of the six-branch termini into as many C_{60} moieties was not hindered by steric constraints, because the size of the PS arms was large enough, the space induced by the PS branches being large enough to accommodate the six C_{60} molecules. Indeed, the different characterizations (SEC, ^1H and ^{13}C NMR, thermal gravimetry, and cyclic voltammetry) performed on the fullerene derivatives **8** not only confirmed the effectiveness of the reaction between the azide functions and C_{60}, but also allowed us to determine the actual content of C_{60} in the "star-balls" **8**. For instance, the three first reversible waves in the cyclic voltammogram (Figure 8) were shown to involve 5 ± 1 C_{60} end groups.

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