Synthesis and Surface Properties of Amphiphilic Star-Shaped and Dendrimer-like Copolymers Based on Polystyrene Core and Poly(ethylene oxide) Corona

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ABSTRACT: Polystyrene (PS)/poly(ethylene oxide) (PEO) amphiphilic star-block copolymers and dendrimer-like architectures were prepared using a core-first method. PS stars were first obtained by atom transfer radical polymerization using three and four functional benzyl halides. The chain ends of these star polymers were subsequently modified to generate either the same or twice the number of hydroxyl groups that served to grow the PEO blocks by anionic polymerization of ethylene oxide. Well-defined PS_n-*b*-PEO_n ($n = 3$ or 4) stars and PS_3-*b*-PEO_6 dendrimer-like copolymers exhibiting a monomodal and narrow molar mass distribution were obtained in this way. When spread at the air/water interface, these stars proved to be surface active, forming stable reproducible films. Isotherms yielded A_0 (theoretical surface area occupied by a film at zero pressure) values, allowing for quantitative comparisons between the stars and linear diblock analogues. Both structures demonstrated similar behavior, passing from liquid expanded regions to highly compressed structures at comparable molecular areas.

Introduction

Recent advances in the area of controlled radical polymerization (CRP),[1] viz. atom transfer radical polymerization (ATRP),[1−3] nitroxide-mediated polymerization (NMP),[4] and reversible addition−fragmentation chain transfer (RAFT),[5,6] allow for better definition and ease in the synthesis of complex macromolecular architectures. These methodologies provide powerful tools to design tailor-made linear and branched polymers.[7,8] The area of amphiphilic block copolymers has significantly benefited from the current momentum created by CRP methodologies.[1−8] Many of them were not accessible before the advent of CRP, which offers better opportunities to exploit their unique features, such as their interfacial properties or their ability to self-assemble in various morphologies (spheres, cylinders, vesicles, etc.) in a selective solvent.[9−15]

Besides linear copolymers, branched amphiphiles have also been prepared using these novel synthetic tools.[7,8] For instance, star-block copolymers as well as dendrimer-like copolymers comprising a poly(ethylene oxide) (PEO) core and a polystyrene (PS) corona are two examples of such amphiphilic architectures recently reported by us.[16] These structures were derived by a combination of anionic polymerization of ethylene oxide, appropriate derivatization of chain ends, and ATRP of styrene.[16] More recently, we also reported the synthesis of PS and poly(acrylic acid)-based amphiphilic miktoarm stars, obtained by ATRP and chain-end derivatization.[17] Several other groups have described the preparation of amphiphilic star copolymers by CRP or related methodologies as well.[7,8] In most cases, two vinylic blocks based on styrene or alkyl (meth)acrylates, on one hand, and *tert*-butyl acrylate, on the other, were associated in a star structure whose amphiphilic character was unveiled upon hydrolysis of *tert*-butyl ester side groups.[7,8]

In this contribution, we describe the core-first synthesis of three- and four-arm amphiphilic stars and dendrimer-like copolymers that include an inner PS core and an outer PEO shell. As the growth of the outer PEO layer by anionic polymerization of ethylene oxide required the absence of any electrophilic functions (such as ester groups) in the PS precursor, a novel synthetic scheme was developed to this end. First, ATRP of styrene was initiated using three and four functional initiators. The ω-bromo ends of the PS stars thus obtained were then modified to either equal or double the number of hydroxyl groups that were subsequently used to initiate ethylene oxide polymerization. This simple method leads to well-defined amphiphilic star-block and dendrimer-like copolymer structures. Initial characterization of the surface properties of these systems at the air/water interface and a comparison of their behavior with linear diblock systems are also presented.

Experimental Section

Materials. Styrene (St) was purchased from Aldrich (99%), stirred with CaH_2 overnight, and distilled prior to use. Copper bromide (CuBr), 2,2′-dipyridyl (bipy), 1,3,5-tris(bromomethyl)-mesitylene, and 1,2,4,5-tetrakis(bromomethyl)benzene (Aldrich) were used as received. Ethylene oxide (EO) (Fluka, 99.8%) was stirred over sodium for 2 h and then distilled before use. Dimethylformamide (99%), dimethyl sulfoxide, and all other common solvents were purified using standard procedures; sodium and naphthalene were used as received. Double distilled water was used to purify the samples.

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AC 200 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Apparent molar masses were determined with a size exclusion chromatography (SEC) equip-

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Table 1. Experimental Parameters and Molar Mass Determination in the Synthesis of PS_3-*b*-PEO_3 and PS_3-*b*-PEO_6 Stars

compound	code	t (h)	yield (%)	$M_{n,th}$ (g mol^{-1})	$M_{n,SEC,DMF}$ (g mol^{-1}) (PDI)	$M_{n,SEC,THF}$ (g mol^{-1}) (PDI)	$M_{n,NMR}$ (g mol^{-1})	$M_{w,DLS}$ (g mol^{-1}) (PDI)
$(PSBr)_3$[a]	**2a**[b]	3	49.5	20 000[e]	13 400 (1.1)	12 200 (1.2)	19 600[f]	19 100 (1.2)
	2b[c]	3	44	31 000[e]	22 800 (1.1)	23 200 (1.1)	32 400[f]	30 800 (1.1)
	2c[d]	3	41.2	32 000[e]	20 500 (1.1)	19 800 (1.1)	31 600[f]	32 000 (1.3)
$(PSOH)_3$[g]	**3a**	164	88		14 200 (1.1)	nd	20 800[h]	nd
	3b	164			23 500 (1.1)	nd	33 800[h]	nd
PS_3-*b*-PEO_3	**4a**[i]	4		25 550[k]	19 500 (1.1)	16 000 (1.1)	26 600	nd
	4b[j]	7		59 000[k]	51 600 (1.1)		60 600	nd
	4c[l]	7	35	20 700	20 600 (1.1)	nd	27 000	nd
	4d[m]	164	98	62 000	52 600 (1.2)	nd	62 150	nd
PS_3-*b*-PEO_6	**10**	164	65	65 000	47 100 (1.2)	nd	63 650	nd

[a] [I]:[CuBr]:[bipy] = 1:1:2, where I is the trifunctional initiator; T = 110 °C. [b] [St]/[I] = 250. [c] [St]/[I] = 500. [d] [St]/[I] = 500. [e] $M_{n,th}$ = (([St]/[initiator]) × conversion) × 104.15) + 398, where [St] and [initiator] represent the molar concentration of styrene and initiator, respectively. [f] $M_{n,NMR}$ = (no. of units of styrene per arm × 104.15 × 3) + 398, where 104.15 and 398 stand for the molar mass of styrene and initiator, respectively. [g] Temperature = 30 °C. [h] $M_{n,NMR}$ = total no. of units of EO × 44 + molar mass of $(PSOH)_3$ (^{1}H NMR). [i] [EO]/[$(PSOH)_3$] = 382. [j] [EO]/[$(PSOH)_3$] = 2469, ambient temperature where [EO] and [$(PSOH)_3$] stand for the number of moles of EO and $(PSOH)_3$, respectively. [k] $M_{n,th}$ = (([EO]/[$(PSOH)_3$]) × [EO] (conversion) × 44) + $M_{n,th}$($(PSOH)_3$). [l] [EO]/[$(PSOH)_3$] = 589. [m] Chain extension: [EO]/[PS_3-*b*-PEO_3] = 821, ambient temperature, where [EO], [$(PSOH)_3$], and [PS_3-*b*-PEO_3] stand for the number of moles of EO, $(PSOH)_3$, and PS_3-*b*-$PEO_3^{(1)}$, respectively. [n] [EO]/[DPMK] = 2564, ambient temperature.

ped with three TSK-gel columns (7.8 × 30 cm, 5 μm, G 2000, 3000, and 4000 HR with pore sizes of 250, 1500, and 10 000 Å, respectively) and a refractive index (RI) detector (Jasco, RI-1530) with DMF as eluent (0.7 mL/min). Comparison was made with a second SEC apparatus fitted with four TSK-gel columns (7.8 × 30 cm, 5 μm, G 2000, 3000, 4000, and 5000 HR with pores of 250, 1500, 10 000, and 1 × 10^5 Å, respectively) and THF as the mobile phase (1 mL/min). This instrument was equipped with a refractive index (RI) detector (Varian RI-4) and a UV−vis detector (Varian 2550 variable λ detector). Both SECs were calibrated using linear polystyrene samples. Some absolute molar masses of $(PSBr)_3$ and $(PSBr)_4$ stars were calculated using a multiangle laser light scattering (MALLS) detector (DLS) (Wyatt Technology) connected to an SEC line. The dn/dc values for $(PSBr)_3$ and $(PSBr)_4$ stars were measured in THF at 25° C with a laser source and found to be the same as that of linear polystyrene (dn/dc = 0.183 cm^3/g).

Surface film characterization was conducted using a Teflon Langmuir KSV trough equipped with two moving barriers and a Wilhelmy plate for measuring surface pressure. Isotherm, hysteresis, and viscometry experiments were performed at least three times to verify reproducibility. Between runs, the troughs were cleaned with ethanol and rinsed several times with Millipore filtered water of resistivity ≥18.2 MΩ cm. Solutions were prepared by dissolving 5 mg of polymer in 5 mL of chloroform and spread dropwise on a layer of Millipore water with a gastight Hamilton syringe. The chloroform was then allowed to evaporate for 30 min to ensure no residual solvent remained. The subphase temperature was controlled at 25 °C through water circulating under the troughs. Experiments were run with barrier movement not exceeding ±10 mm min^{-1} and a linear compression rate of 0.5 mN m^{-1} min^{-1}.

1. Synthesis of ω-Bromopolystyrene Three-Arm Star ($(PSBr)_3$) by ATRP (2). Using a Schlenk apparatus flamed and dried under vacuum, styrene (10 mL, 8.72 × 10^{-2} mol), 1,3,5-tris(bromomethyl)mesitylene (**1**) (69 mg, 1.74 × 10^{-4} mol), bipy (163 mg, 1.04 × 10^{-3} mol), and CuBr (75 mg, 5.22 × 10^{-4} mol) were added in this order under nitrogen flow. Two freeze−thaw−pump cycles followed by nitrogen backfilling ensured an inert atmosphere for the reaction. The vessel was placed in an oil bath maintained at 110 °C for 4 h. The solution was then cooled to room temperature, diluted with dichloromethane, and passed through a column of neutral alumina. After evaporation, the polymer was precipitated in methanol, filtered, washed, and dried at 40 °C under vacuum for 24 h to give a colorless powder (**2**) (58%) (sample **2b** in Table 1). ^{1}H NMR ($CDCl_3$) δ ppm: 7.3−6.3 (m, 5H, aromatic), 4.5 (broad, s, 1H, C*H*(Ph)−Br), 2.2−1.3 (m, 3H, aliphatic main). SEC (DMF): M_n = 22 800 g/mol, M_w/M_n = 1.1; M_w(DLS in THF) = 30 800 g/mol; M_w/M_n = 1.1; M_n(^{1}H NMR) = 32 400 g/mol; $M_{n,th}$ = 31 000 g/mol.

2. Synthesis of ω-Hydroxypolystyrene Three-Arm Star ($(PSOH)_3$) (3). $(PSBr)_3$ (3.5 g, 1.1 × 10^{-4} mol) was dissolved in a minimum quantity of DMF (∼ 25 mL) with ethanolamine (4 mL, 6.62 × 10^{-2} mol) in a Schlenk flask. The content was stirred at room temperature for 7 days under a nitrogen atmosphere. The polymer was purified by repeated precipitation in methanol and then filtered, washed, and dried at room temperature in a desiccator. Yield **3**: 88% (sample **3b** in Table 1). ^{1}H NMR ($CDCl_3$) δ ppm: 7.3−6.3 (m, 5H, aromatic), 3.3 (broad, s, 2H, CH_2OH), 3.1 (broad, s, 2H, C*H*(Ph)−N*H*), 2.2−1.3 (m, 3H, aliphatic main chain). SEC (DMF): M_n = 23 500 g/mol; M_w/M_n = 1.1; M_n(^{1}H NMR) = 33 800 g/mol.

3. Synthesis of Diphenylmethylpotassium (DPMK). In a flame-dried 250 mL round-bottomed flask, pieces of potassium (4.1 g, 1.05 × 10^{-1} mol) were introduced followed by the addition of dry THF (60 mL). Naphthalene (6.72 g, 5.25 × 10^{-2} mol) was added, turning the solution dark green (due to the dissolution of potassium). The remaining THF (115 mL) was added along with diphenylmethane (17.6 mL, 0.105 mol). All of these additions were performed under dry and inert conditions. The resulting solution was stirred for 1 week and then used as such for the anionic polymerization of EO.

4. Determination of the Concentration of DPMK. A flame-dried 100 mL round-bottomed flask was charged with dry DMSO (10 mL) followed by a few grains (end of spatula) of triphenylmethane. More DPMK was then added until the solution just turned red-orange. Acetanilide (∼0.2 g, 1.48 × 10^{-3} mol) was added, instantly turning the solution a clear light yellow. The resulting solution was titrated with DPMK from a buret. Upon further addition of acetanilide, the titration was repeated. Each addition and titration was carried out under dry and inert conditions with the average concentration of DPMK determined be 5.162 × 10^{-4} mol/mL.

5. Synthesis of PS_3-*b*-PEO_3 Amphiphilic Three-Arm Star Polymer (4). A two-neck 250 mL flask was flamed, dried under vacuum, and charged with the macroinitiator ($(PSOH)_3$) (1 g, 4.8 × 10^{-5} mol). The flask was again dried carefully before adding dry THF (15 mL) to dissolve the polymer. DPMK (0.5 mL, 3 × 10^{-4} mol) was introduced through one neck while keeping the flask in liquid nitrogen. The temperature was raised slowly to room temperature and stirred for 24 h. The flask was again chilled in a liquid nitrogen bath, and ethylene oxide (EO) (3 mL, 6.014 × 10^{-2} mol) was added through the second neck. After addition, the content was stirred at −40 °C for 2 h, followed by 2 h at 0 °C, and finally at room temperature. After 6 h, the propagation reaction was quenched with methanol. Excess solvent was removed, and the polymer was washed with diethyl ether (2 × 30 mL) and water (2 × 20 mL). Polymer was obtained as a colorless solid (1.92 g, 35% EO conversion). ^{1}H NMR ($CDCl_3$): δ ppm: 7.3−6.3 (m, 5H, aromatic), 3.6 (s, 4H, $(CH_2CH_2O)_n$, PEO block), 2.2−1.3 (m, 3H, aliphatic main chain). SEC (DMF): M_n = 19 500 g/mol; M_w/M_n = 1.1; M_n(^{1}H NMR) = 26 000 g/mol; $M_{n,th}$ = 25 600 g/mol.

6. Chain Extension of PEO Block Present in PS_3-*b*-PEO_3 Star. DPMK was added to a dry THF (15 mL) solution

containing PS_3-*b*-PEO_3 (1.3 g, 4.87×10^{-5} mol) (0.4 mL, 2.06×10^{-4} mol), and the resulting mixture was stirred continuously for 24 h. Following the procedure outlined for **4**, EO (2 mL, 4×10^{-2} mol) was then introduced and stirred for 20 h at −40 °C. The polymerization was stopped and purified according to the procedure for compound **4**. Yield: 98%. ^{1}H NMR ($CDCl_3$): δ ppm: 7.3−6.3 (m, 5H, aromatic), 3.6 (s, 4H, (CH_2CH_2O)$_n$, PEO block), 2.2−1.3 (m, 3H, aliphatic main chain). SEC (DMF): M_n = 52 600 g/mol; M_w/M_n = 1.2; M_n(^{1}H NMR) = 62 100 g/mol.

7. Synthesis of ω,ω'-bis(hydroxy)polystyrene Three-Arm Star ($(PS(OH)_2)_3$) (9). $(PSBr)_3$ (3 g, 9.36×10^{-5} mol) and diethanolamine (1 g, 9.5×10^{-3} mol) were dissolved in a minimum amount of DMF (∼20 mL) and continuously stirred for 7 days at room temperature in a nitrogen atmosphere. The solution was then precipitated thrice in excess methanol, filtered, and dried in a vacuum desiccator for 24 h. Yield (76%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.3−6.3 (m, 5H, aromatic), 3.3 (broad, s, 4H, CH_2OH (×2)), 3.1 (broad, s, 2H, CH(Ph)−NH), 2.2−1.3 (m, 3H, aliphatic main chain). SEC (DMF): M_n = 19 700 g/mol.; M_w/M_n = 1.1; M_n(^{1}H NMR) = 19 600 g/mol.

8. Synthesis of PS_3-*b*-PEO_6 Dendrimer (10). This PS_3−PEO_6 dendrimer was prepared by the same procedure employed for the synthesis of PS_3-*b*-PEO_3 (**4**). DPMK (0.5 mL, 2.5×10^{-4} mol/mL) was mixed with a dry THF (15 mL) solution containing $(PS(OH)_2)_3$ (0.5 g, 2.53×10^{-5} mol). EO (2 mL, 4×10^{-2} mol) was added slowly and the solution stirred for 8 h. The polymer was isolated by precipitation in ether (yield = 65%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.3−6.3 (m, 5H, aromatic), 3.6 (s, 4H, (CH_2CH_2O)$_n$, PEO block), 2.2−1.3 (m, 3H, aliphatic main chain). SEC (DMF): M_n = 47 100 g/mol; M_w/M_n = 1.2; $M_{n,th}$ = 65 000 g/mol. M_n(^{1}H NMR) = 63 600 g/mol.

9. Synthesis of ω-Bromopolystyrene Four-Arm Star ($(PSBr)_4$) (6). $(PSBr)_4$ was synthesized according to the same procedure used for $(PSBr)_3$, with the exception of 1,2,4,5-tetrakis(bromomethyl)benzene (**5**) as the multifunctional ATRP initiator. Styrene (5 mL, 4.36×10^{-2} mol) was mixed with **5** (39.2 mg, 8.72×10^{-5} mol), bipy (108.9 mg, 6.97×10^{-4} mol), and CuBr (50 mg, 3.48×10^{-4} mol) in a flame-dried flask. The solution was stirred in an oil bath at 110 °C for 4 h, diluted, and then passed through neutral alumina, removing copper complexes. Polymer was recovered by precipitating in methanol. Yield (70%). ^{1}H NMR ($CDCl_3$) δ ppm: 7.3−6.3 (m, 5H, aromatic), 4.5 (broad, s, 1H, CH(Ph)−Br), 2.2−1.3 (m, 3H, aliphatic main). SEC (DMF): M_n = 25 500 g/mol, M_w/M_n = 1.1. LS: M_w = 38 200 g/mol; M_w/M_n = 1.2; M_n(^{1}H NMR) = 36 200 g/mol; $M_{n,th}$ = 37 000 g/mol.

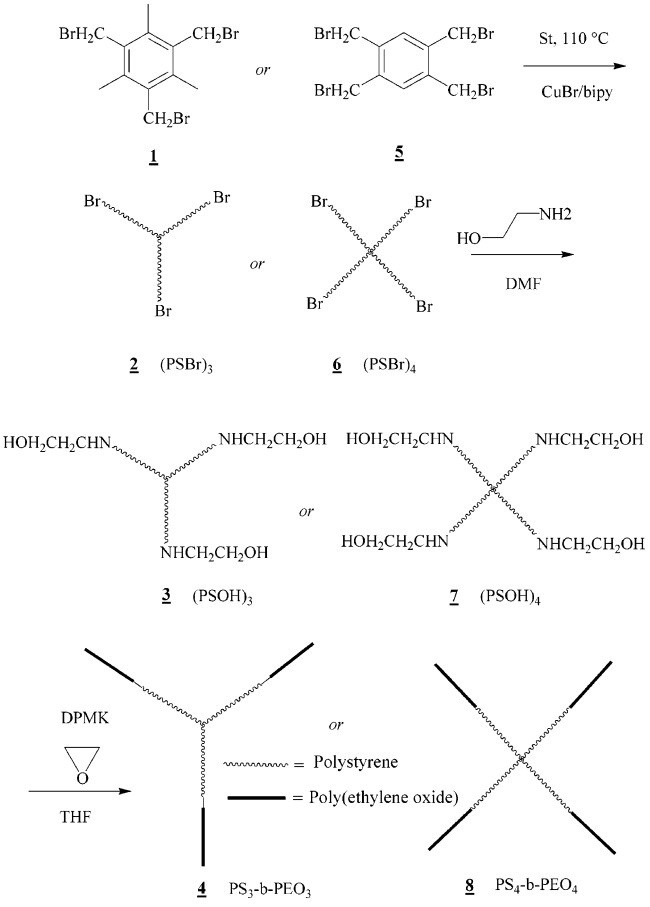
10. Synthesis of ω-Hydroxypolystyrene Four-Arm Star ($(PSOH)_4$) (7). The same procedure described for **3** is used for $(PSOH)_4$. A DMF (20 mL) solution containing $(PSBr)_4$ (2.3 g, 6×10^{-5} mol) and ethanolamine (3.5 mL, 5.8×10^{-2} mol) was continuously stirred for 7 days. The polymer was isolated by precipitating in methanol. Yield 100%. ^{1}H NMR ($CDCl_3$) δ ppm: 7.3−6.3 (m, 5H, aromatic), 3.3 (broad, s, 2H, CH_2OH), 3.1 (broad, s, 2H, CH(Ph)−NH), 2.2−1.3 (m, 3H, aliphatic main chain). SEC (DMF): M_n = 24 100 g/mol; PDI = 1.1; M_n(^{1}H NMR) = 38 000 g/mol.

11. Synthesis of PS_4-*b*-PEO_4 Amphiphilic Four-Arm Star Polymer (8). The same procedure as that for the synthesis of PS_3-*b*-PEO_3 amphiphilic three-arm star (**4**) was employed. $(PSOH)_4$ (500 mg, 1.31×10^{-5} mol) and DPMK (0.4 mL, 2.06×10^{-4} mol/mL) were mixed with dry THF (15 mL) and stirred for 24 h. To this solution, EO (2 mL, 4×10^{-2} mol) was added and stirring continued for 3 h. The polymer was recovered by precipitating in ether. Yield: 600 mg (6%). ^{1}H NMR ($CDCl_3$): δ ppm: 7.3−6.3 (m, 5H, aromatic), 3.6 (s, 4H, (CH_2CH_2O)$_n$, PEO block), 2.2−1.3 (m, 3H, aliphatic main chain). SEC (DMF): M_n = 29 500 g/mol; M_w/M_n = 1.1; $M_{n,th}$ = 46 000 g/mol; M_n(^{1}H NMR) = 45 500 g/mol.

Results and Discussion

The synthetic method described here to obtain amphiphilic three- and four-arm star-block and dendrimer-like copolymers rests on a sequence of reactions starting with the ATRP of styrene followed by the chemical modification of chain ends and ending with the anionic polymerization of ethylene oxide.

Scheme 1. Synthesis of Three- and Four-Arm Star-Block Copolymers: PS_3-*b*-PEO_3 and PS_4-*b*-PEO_4



Synthesis of Amphiphilic Three- and Four-Arm Star-Block Copolymers: PS_3-*b*-PEO_3 (4) and PS_4-*b*-PEO_4 (8). Tris(bromomethyl)mesitylene was chosen as the initiator for the ATRP of styrene. In addition to efficiently triggering the polymerization of styrene,[18] benzyl halides, unlike haloesters or halonitriles, do not introduce electrophilic functions in the initiated chains that might subsequently interfere with the anionic polymerization of ethylene oxide. ATRP was performed at 110 °C in bulk using CuBr/bipy as the metal/ligand system (Scheme 1). 2,2′-Dipyridyl was preferred to pentamethyldiethylenetriamine (PMDETA) as the ligand because tris(bromomethyl)mesitylene precipitated out in the presence of PMDETA. This initiating system yielded samples with low polydispersities. A typical SEC trace shown in Figure 1a (see Table 1) clearly indicates a monomodal distribution without any trace of star−star coupling and unreacted precursor. The use of linear PS standards for molar mass determination of these samples resulted in lower values than expected, likely because of the difference in the hydrodynamic volumes of the two types of architectures.[19] On the other hand, their absolute molar masses determined both from light scattering-coupled SEC and from ^{1}H NMR end-group analysis agree with the theoretical values ($M_{n,th}$).

In the next step, these $(PSBr)_3$ stars underwent a nucleophilic substitution reaction to generate hydroxyl groups at their chain ends (Scheme 1), following a procedure reported by Matyjaszewski[18] and by us.[17] Sub-

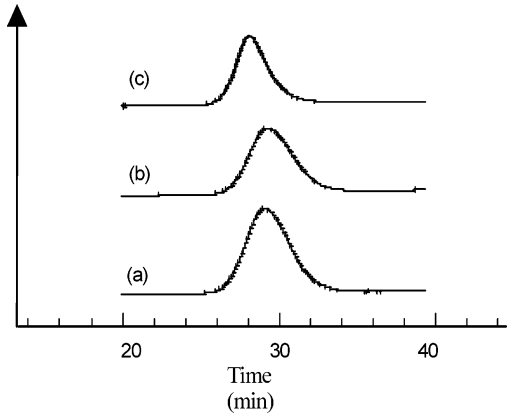


Figure 1. SEC traces in DMF (RI detector) of (a) $(PSBr)_3$ (**2**), (b) $(PSOH)_3$ (**3**), and (c) PS_3-*b*-PEO_3 (**4**), corresponding to samples **2a**, **3a**, and **4a** in Table 1.

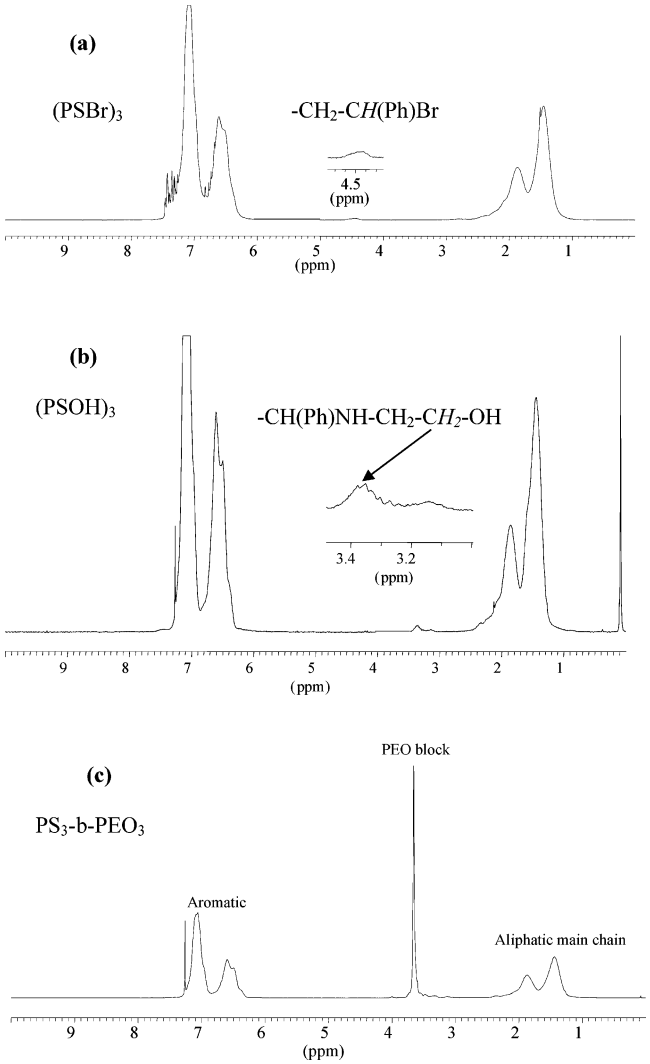


Figure 2. ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of (a) $(PSBr)_3$ (**2**), (b) $(PSOH)_3$ (**3**), and (c) PS_3-*b*-PEO_3 (**4**).

stitution was achieved using ethanolamine as both a base and the nucleophile. In contrast, using triethylamine as the base and ethanolamine as the nucleophile resulted in a partial functionalization only. Complete substitution occurred with ethanolamine used alone and in large excess, as confirmed by ^{1}H NMR. Figure 2b shows that the signal due to C*H*(Ph)−Br proton at δ 4.5 ppm completely disappeared, and new signals assigned to CH_2OH at δ 3.3 ppm and to C*H*(Ph)N− at 3.1 ppm appear. Table 1 lists the characteristics of these $(PSOH)_3$ star polymers. DMF was preferred to THF as eluent for their SEC characterization due to possible self-association of such samples in THF. For the determination of the molar mass by ^{1}H NMR (see Table 1), the resonance signals at δ 3.3 ppm (CH_2OH) and δ 3.1 ppm (C*H*(Ph)−N*H*) were compared with those at δ 7.3−6.3 (aromatic protons).

These $(PSOH)_3$ stars were then used as precursors for the anionic polymerization of ethylene oxide. Under dry and inert conditions, the terminal hydroxyl groups were partially deprotonated (60−80%) by DPMK (Scheme 1). If the hydroxyl groups were fully deprotonated, the $(PSOH)_3$ precursor exhibited a tendency to precipitate in organic medium, leading to an uncontrolled polymerization. Thorough deprotonation of hydroxyls was not necessary for PEO blocks to grow uniformly because of the fast exchange between oxanions and free hydroxyl groups.[20,21] For this reason, we chose 60−80% deprotonation, a range that prevented precursor precipitation but led to fast polymerization. After adding DPMK, the solution turned pale yellow. Ethylene oxide was then introduced, instantly turning the solution colorless and less viscous. With time, however, the viscosity increased, indicating the growth of PEO blocks. The reaction was stopped by adding methanol. The characteristics of the corresponding star-block copolymers, noted PS_3-*b*-PEO_3, are presented in Table 1. SEC characterization (DMF) of the stars yielded monomodal peaks and polydispersity indices close to unity. Figure 1c shows a clear shift in molar mass when compared to 1b, indicating the formation of a well-defined amphiphilic three-arm star-block structure. With THF as eluent, lower molar mass values were obtained (M_n = 6000 g mol^{-1}). Since SEC molar masses were calibrated using linear PS standards, we turned to ^{1}H NMR to determine the actual molar masses of these star-block copolymers. Knowing the molar mass of the $(PSOH)_3$ precursor, we calculated that of the copolymer by comparing the resonance signal at δ 3.6 ppm (O$CH_2CH_2)_n$ (PEO block)) with that at δ 7.3−6.3 (aromatic protons (PS block)) (Figure 2c). Through this method, we obtained excellent agreement between experimental and targeted molar mass.

A successful chain extension reaction from these PS_3-*b*-PEO_3 stars demonstrated that the chain ends can be further reactivated and propagated. Table 1 presents the results of a chain extension, and Figure 3 depicts the controlled increase in molar mass, where (a), (b), and (c) represent $(PSOH)_3$, PS_3-*b*-$PEO_3^{(1)}$, and PS_3-*b*-$PEO_3^{(2)}$, respectively, the latter being an amphiphilic star obtained by chain extension of PS_3-*b*-$PEO_3^{(1)}$.

A four-arm star-block copolymer, PS_4-*b*-PEO_4, was also synthesized following a strategy similar to that described above. In this case, the ATRP of styrene was accomplished using tetrakis(bromomethyl)benzene and CuBr/bipy as the tetrafunctional initiator and metal/catalyst system, respectively (see Scheme 1). The $(PSBr)_4$ samples thus obtained were characterized by SEC and ^{1}H NMR, as shown in Table 2. Experimental values were determined using ^{1}H NMR ($M_{n,NMR}$) and light scattering. The expected values agreed with those determined from light scattering and ^{1}H NMR, as seen in Table 2. The SEC trace (DMF) shown in Figure 5a demonstrates a well-defined star of narrow molar mass distribution. The ^{1}H NMR spectrum (not shown) yielded peaks similar to those for $(PSBr)_3$, demonstrating the expected star structure.

Table 2. Experimental Parameters and Molar Mass Determination in the Synthesis of PS_4-*b*-PEO_4

compound	code	yield	$M_{n,th}$ (g mol^{-1})	$M_{n,SEC,DMF}$ (g mol^{-1}) (PDI)	$M_{n,SEC,THF}$ (g mol^{-1}) (PDI)	$M_{n,NMR}$ (g mol^{-1})	$M_{w,DLS}$ (g mol^{-1}) (PDI)
$(PSBr)_4$[a]	**6**	70	37 000	25 500 (1.1)	25 500 (1.1)	36 200	38 150 (1.2)
PS_4-*b*-PEO_4	**8a**[b]	nd	31 250	29 550 (1.1)	nd	46 000	nd
	8b[c]	nd	88 600	67 300 (1.2)	32 100 (1.1)	87 300	nd

[a] [St]/[I] = 500; [I]:[CuBr]:[bipy] = 1:1:2 per chain, temperature = 110 °C. [b] [EO]/[$(PSOH)_4$] = 3053, time = 3 h, EO conversion (%) = 3. [c] [EO]/[$(PSOH)_4$] = 4590, time = 15 h, EO conversion = 25%.

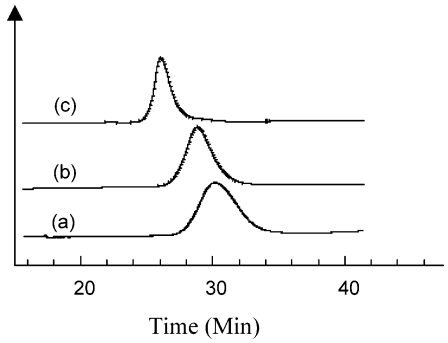


Figure 3. SEC traces in DMF (RI detector) of (a) $(PSOH)_3$ (**3**), (b) PS_3-*b*-$PEO_3^{(1)}$ (**4**), and (c) PS_3-*b*-$PEO_3^{(2)}$ (**4**) corresponding to samples **3a**, **4c**, and **4d** in Table 1.

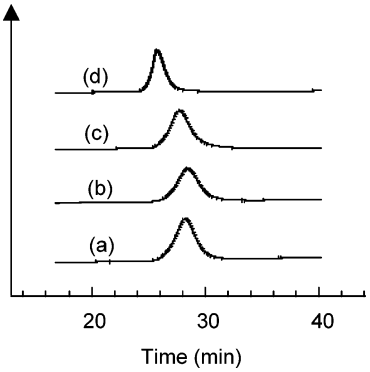


Figure 4. SEC traces in DMF (RI detector) of (a) $(PSBr)_4$, (b) $(PSOH)_4$, (c) PS_4-*b*-$PEO_4^{(1)}$, and (d) PS_4-*b*-$PEO_4^{(2)}$, corresponding to samples **6**, **8a**, and **8b** in Table 2.

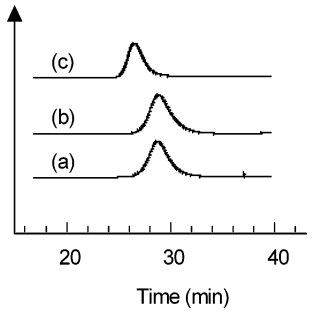
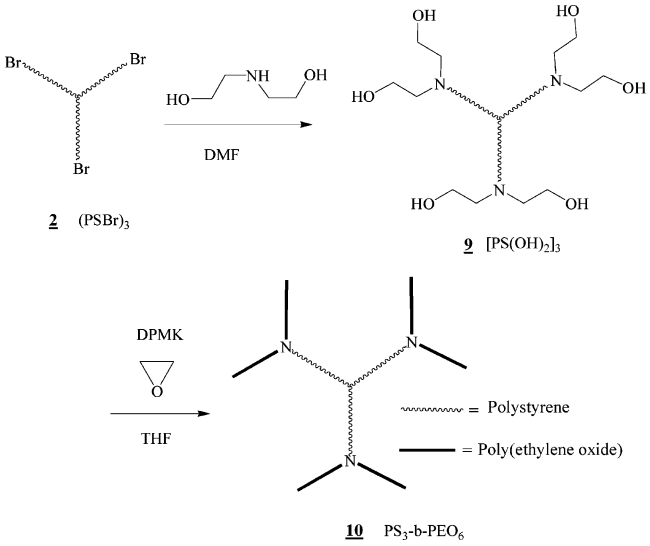


Figure 5. SEC traces in DMF (RI detector) of (a) $(PSBr)_3$ (**2**), (b) $(PSOH)_3$ (**3**), and (c) PS_3−PEO_6 (**10**), corresponding to samples **2a** and **10** in Table 1.

The chain-end bromine atoms of the $(PSBr)_4$ samples were subsequently replaced with hydroxyl groups by treating the stars with excess ethanolamine, as explained above. The formation of four peripheral hydroxyls was confirmed by ^{1}H NMR analysis of $(PSOH)_4$. The signal representing C*H*(Ph)−Br at δ 4.5 ppm completely disappeared while new signals due to CH_2-OH and CH(Ph)N− appeared at δ 3.3−3.1 ppm.

The final step in preparing a four-arm PS_4-*b*-PEO_4 star involved polymerizing ethylene oxide using the macroinitiator $(PSOH)_4$ in dry THF and a limited degree of hydroxyl deprotonation (<60%) (Scheme 2). This reaction yielded well-defined amphiphilic four-arm star-block copolymers, PS_4-*b*-PEO_4, as illustrated by SEC (DMF) in Figure 4c. The characteristics of PS_4-*b*-PEO_4 are presented in Table 2. Figure 4d shows another sample of PS_4-*b*-PEO_4 star with a longer PEO block length obtained by a longer polymerization time. As can be seen, there is a shift toward larger molar mass in the SEC trace, demonstrating controlled chain growth.

Scheme 2. Synthesis of Dendrimer-like Copolymers PS_3-*b*-PEO_6



Synthesis of Dendrimer-like Copolymers (PS_3-*b*-PEO_6). In this case, the three-arm precursor $(PSBr)_3$ (sample **2c** in Table 1) (Scheme 2) was chemically modified to generate two geminal hydroxyl functions at each arm end. Nucleophilic substitution of the chain-end bromides (CH(Ph)−*Br*) was achieved with diethanolamine (Scheme 2), in a fashion similar to that recently reported by our group.[17] Excess diethanolamine was used to ensure a fast, complete reaction. The quantitative substitution was confirmed by ^{1}H NMR where the signal representing C*H*(Ph)−Br completely disappeared and a new signal due to CH_2OH (×2) appeared.

PEO blocks were then grown from these hydroxyl-terminated PS chains after partial deprotonation (60%) by DPMK and addition of ethylene oxide (Scheme 2). We selected a ratio of [EO]/[PS] that ensured a resulting PEO block of comparable length with that of the PS block. Upon polymerization of ethylene oxide, an increase in viscosity was observed. The copolymer obtained was characterized by SEC (DMF) and ^{1}H NMR (Table 1). Figure 5c shows a clear shift in molar mass from the parent PS stars (Figure 5a,b), indicating the formation of the expected dendrimer-like structure. ^{1}H NMR analysis involved the comparison of the aromatic and PEO signals. Both the targeted and the experimental molar masses obtained from ^{1}H NMR are in good agreement. In contrast, a poor agreement is seen be-

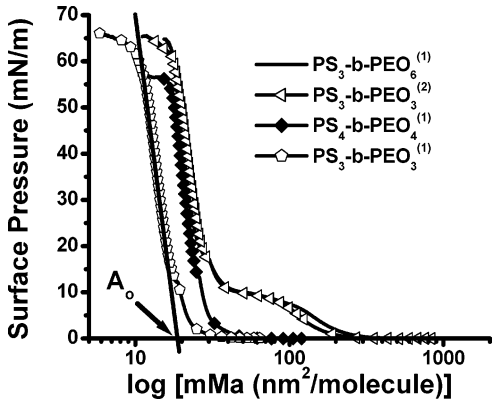


Figure 6. Surface pressure vs log(mean molecular area) ($\pi-$mMa) plots of representative PS−PEO stars at 25 °C. Because of limitations in the trough dimensions, the isotherms are composed of several overlapping parts (obtained from independent experiments). While surface pressure (π) reflects the change in the surface tension of the water subphase, mean molecular area (mMa) refers to the average area a molecule in the monolayer occupies at the air/water interface.

tween the theoretical values and those drawn from SEC using a RI detector. Again, this discrepancy is due to differences between the elution of stars and of the calibration standards.

Surface Characterization. The surface pressure−area ($\pi-A$) isotherms of several of the star copolymers are presented in Figure 6, with a log scale on the *x*-axis for convenient visualization. Upon compression, the star copolymers pass through several regions: one at high surface areas and low pressure, a plateaulike section, and a region of significantly lower compressibility at smaller surface areas. These surface films were reproducible and could be compressed up to surface pressures as high as 60 mN m^{-1}. Initial experiments involving canal viscometry,[22] where the flow rate of a monolayer forced through a canal or slit is measured, showed that the PS−PEO stars flow at the air/water interface at $\pi \leq 10$ mN m^{-1} ($\Delta\pi$ being 2 mN m^{-1} between the two sides of the canal). In addition, hysteresis experiments conducted at low pressures of $\pi \leq 5$ mN m^{-1} demonstrated the stars to be elastic. These data are consistent with those of classical insoluble monolayer-forming surfactants with low molar mass, indicating that the star copolymers are highly surface active.

Despite their original architecture, the behavior of our star-block copolymers as surface films compares qualitatively to that of linear PS-*b*-PEO systems. Within the literature, these linear diblock copolymers have been viewed as passing through different conformations upon compression. At high areas, where the pressure increases slowly, surface films of linear systems exist in a liquid-expanded state. Here, both polymer blocks remain at the air/water interface, with the hydrophobic PS collapsed into globules and the hydrophilic PEO spread out into what is described as a pancake structure.

As compression continues, a gradual increase in pressure occurs until around 8−11 mN m^{-1}, at which point a pseudoplateau is observed. So named for the almost constant pressure maintained over a significant change in area, an extended pseudoplateau generally represents a biphasic state. Analogous to linear diblock copolymers, both PS_3-*b*-$PEO_3^{(2)}$ and PS_3-*b*-$PEO_6^{(1)}$ demonstrate this pseudoplateau, as seen in Figure 6. In linear diblock systems, this region remains a point of disagreement. Citing the collapse and hydration of homopolymer PEO monolayers at 8.5−10.2 mN m^{-1},[23] Goncalves da Silva et al.[24] interprets this feature as PEO dissolving into the water subphase. As compression continues, they consider the sharp increase in pressure as the result of the formation of a brushlike conformation, where the PEO chains stretch into the water subphase. This tempting idea of a monolayer PEO-*b*-PS brush can also be found in several other studies.[25] Lennox, however, disagrees with this view, claiming instead that PEO dehydration followed by a change in conformation occurs.[26]

Table 3. Isotherm Characteristics of PS-*b*-PEO Diblock Copolymer Stars[a]

compound	$M_{n,NMR}$ (g mol^{-1})	A_0 (nm^2/molecule)	A_0/St (Å^2/St unit)
PS_3-*b*-$PEO_3^{(1)}$	27 000	17.9	8.5
PS_3-*b*-$PEO_3^{(2)}$	62 150	30.0	9.0
PS_4-*b*-$PEO_4^{(1)}$	46 000	25.8	6.2
PS_3-*b*-PEO_6	63 650	27.4	9.4

[a] A_0 values were obtained from both surface film isotherms (Figure 6) and isotherms normalized with respect to the number of styrene units (Figure 7).

While our preliminary data on star diblocks cannot confirm one interpretation over the other, the following analysis can be made. Extrapolation of the linear, high-pressure portion of an isotherm to $\pi = 0$ mN m^{-1} yields A_0, the theoretical surface area that a perfectly compact surface film would occupy at zero pressure. In the case of PS-*b*-PEO diblock copolymers, such a film is traditionally seen as a hydrophobic surface, with the PEO pushed into the water subphase while remaining anchored to the interfacial region by the hydrophobic PS. As a result, A_0 is typically considered representative of the area the PS occupies at the interface.

Listed in Table 3, the A_0 values demonstrate that for stars of the same architecture (e.g., the PS_3-*b*-PEO_3 stars) A_0 increases with increasing molar mass. Though PS_3-*b*-PEO_6 has the highest molar mass, this dendritic star occupies less space than PS_3-*b*-$PEO_3^{(2)}$, a triarm linear star of similar molar mass and PS chain length. While PS_3-*b*-PEO_6 contains twice the number of PEO arms found in PS_3-*b*-$PEO_3^{(2)}$, these chains are shorter. Such results indicate that PEO chain length plays a greater role than the number of branches in determining surface film area.

The effect of architecture can be seen upon normalizing the isotherms with respect to the number of styrene (St) repeat units. If the mMa is divided by the total number of St units, the triarm stars (PS_3-*b*-$PEO_3^{(1)}$, PS_3-*b*-$PEO_3^{(2)}$, and PS_3-*b*-PEO_6) occupy ca. 9 Å^2/St while the tetraarm star (PS_4-*b*-$PEO_4^{(1)}$) is smaller (6.2 Å^2/St) (Figure 7, Table 3). These normalized isotherms thus indicate that the number of PS branches influences the film area. The stars with three PS arms are equivalent with respect to area occupied by styrene while the four-arm PS star is more compact. The magnitude of such surface areas is much lower than the smallest cross-sectional area of a St repeat, and therefore, the close-packed surface film cannot be considered a monolayer in the same sense as insoluble low molar mass amphiphiles. Rather than lying perfectly flat at the air/water interface, the PS likely forms three-dimensional coils at high compression.

To compare the A_0 values obtained for our stars with those of linear diblock copolymer systems, we divided the star A_0 values by the number of arms. Possessing 111 St units/branch, the triarm star PS_3-*b*-$PEO_3^{(2)}$, for

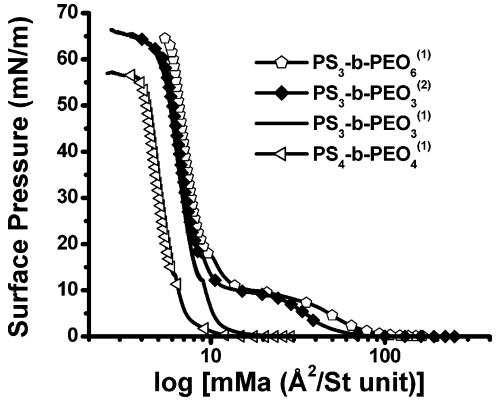


Figure 7. Isotherms of the PS−PEO stars normalized with respect to the total number of styrene units.

example, compares to a linear PS-*b*-PEO sample of 125 St units that was investigated by Lennox.[26] On the basis of an isotherm figure from this work, we estimated Lennox's sample to have an A_0 of 8 nm^2/molecule, a value comparable to the 10.0 nm^2/molecule that the separate branches of PS_3-*b*-$PEO_3^{(2)}$ were determined to occupy. Lennox's A_0 is also similar to the area that branches in PS_4-*b*-$PEO_4^{(1)}$ and PS_3-*b*-PEO_6 occupy (6.5 and 9.1 nm^2/molecule, respectively). Variations in these values are most likely due to differences in the amount of PEO present.

The importance of PEO can also be seen in the pseudoplateau region. While the exact nature of the surface film in this region remains a matter of debate, the pseudoplateau clearly reflects PEO behavior. Our own preliminary data indicate this observation in that only two of our stars contain a pseudoplateau region. Both PS_3-*b*-$PEO_3^{(2)}$ and PS_3-*b*-PEO_6 contain significantly longer chains of PEO than the other stars, PS_3-*b*-$PEO_3^{(1)}$ and PS_4-*b*-$PEO_4^{(1)}$. When compressed, the latter two block copolymers undergo only a minimal increase in pressure prior to the steep pressure rise seen at small molecular areas. To better define the role of PEO, we are further investigating surface film behavior for these and other stars.

Conclusion

We report here an efficient and easy way to synthesize three- and four-arm amphiphilic PS_3-*b*-PEO_3 and PS_4-*b*-PEO_4 star-block copolymers as well as PS_3−PEO_6 dendrimer-like copolymers. In all cases, well-defined samples with polydispersities close to 1.1 could be obtained. Compared to our previous reports on PS-*b*-PEO branched polymers,[16,27] those described in this contribution represent the inverse structure, consisting of a PS core and a PEO corona.

These novel PS-*b*-PEO diblock copolymer architectures are also shown to be surface active at the air−water interface, forming stable and reproducible surface films. When normalized with respect to PS, the isotherms indicated that the PS in the tetraarm star was more compact than the triarm star PS. Our preliminary studies indicate that the amount of PEO present exerts the greatest influence on surface film behavior.

We have already reported the monolayer behavior of a PEO_3-*b*-PS_3 system at the air/water interface through transferring onto a substrate followed by atomic force microscope (AFM).[27] Thus, this new breed of PS_n-*b*-PEO_n (n = 3 and 4) and PS_n-*b*-PEO_{2n} (n = 3) amphiphilic star polymers can also be studied in this manner. This work as well as additional surface film characterization at the air/water interface is currently under investigation. Varying compositions and architectures may lead to an entirely different and interesting morphology and will be the topic of a subsequent report.

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