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Synthesis and Investigation of Surface Properties of Dendrimer-like Copolymers Based on Polystyrene and Poly(*tert*-butylacrylate)

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ABSTRACT: The synthesis of well-defined second-generation PS$_n$P*t*BA$_{2n}$ dendrimer-like copolymers based on polystyrene (PS) and poly(*tert*-butylacrylate) (P*t*BA) is described. The synthetic procedure involves a combination of atom transfer radical polymerization (ATRP) using multifunctional initiators and chain end modification reactions. These structures are composed of a PS core with 2, 4, 6, or 8 arms and a corona of P*t*BA with 4, 8, 12, or 16 arms, respectively. Third-generation PS$_n$PS$_{2n}$P*t*BA$_{4n}$ dendrimer-like copolymers were also derived by repetition of chain end modification and ATRP. Characterization was carried out by size exclusion chromatography online with multiangle laser light scattering and by ^{1}H NMR spectroscopy. PS$_n$PAA$_{2n}$ amphiphilic structures based on PS and poly(acrylic acid) (PAA) were subsequently generated by hydrolysis of the *tert*-butylester groups. Langmuir monolayer studies of PS$_n$P*t*BA$_{2n}$ showed the formation of stable films. AFM images demonstrated a significant change in morphology upon increasing surface pressures.

Introduction

The need for amphiphilic block copolymers containing separate hydrophobic and hydrophilic portions has led scientists to a new realm of polymer synthesis. Because of their self-assembling properties that originate from the incompatibility between blocks, such amphiphilic macromolecules attract interest and are currently used in a variety of applications, ranging from dispersion stabilization in drug encapsulation to the modification of aqueous solution rheology.[1−6] Among amphiphilic block copolymers, stimuli-responsive systems, sometimes named intelligent materials, can respond by a change of their size or their shape to a variation of medium pH, ionic strength, or temperature. For obvious environmental concerns, it is highly desirable to derive stimuli-responsive copolymers that are soluble in aqueous media.[7]

For example, the Armes group[8−11] reported the synthesis and the solution properties of a wide range of water-soluble block copolymers, including different alkyl methacrylates for the hydrophobic block and poly(2-dimethylamino) ethyl methacrylate, poly(sulfobetaine), poly(4-vinylbenzoate), and many others for the hydrophilic block. Block copolymers based on polystyrene (PS) and poly(acrylic acid) (PAA) represent another family of amphiphilic systems that exhibit self-associating properties in aqueous media, forming micelle-like structures in the submicron size range, (e.g., spherical micelles, vesicles, or rodlike micelles).[12−15] Eisenberg and co-workers described the synthesis of PS-*b*-PAA diblock copolymers by anionic polymerization and the formation of a vast array of crew-cut aggregate structures in selective solvents such as spheres, rods, and vesicles[12] Studies about the synthesis and, in some cases, about the micellar properties in aqueous media of more complex polymer architectures based on PS and PAA have also been carried out.[16−22]

Numerous amphiphilic block copolymers exhibiting either a linear or a branched topology, including those based on PS and PAA, are now accessible using controlled radical polymerization techniques.[23,24] Among the various approaches that have been developed to control radical polymerization,[25−28] atom transfer radical polymerization (ATRP) represents certainly the most versatile tool owing to its applicability to a large range of vinyl monomers and its aptitude to deliver well-defined polymers.[23−26]

For instance, the synthesis[29,30] of diblock, triblock, and star-block copolymers composed of PS and PAA by ATRP, their aqueous solution properties,[31] and their use as stabilizers in emulsion polymerization under alkaline conditions[20] were described by Matyjaszewski, Charleux, and their respective co-workers. Jiang et al.[18] prepared amphiphilic block-graft copolymers [poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene)-*g*-poly(acrylic acid)] by ATRP. These copolymers were found to form a variety of morphologies in water. They determined these morphologies to be concentration dependent, observing spherical morphologies at lower concentration and quadrilateral shapes at higher ones. Webber et al.[17] examined the preparation and characterization of micelles based on PAA-*g*-PS polymers while Tsitsilianis et al.[19] reported the synthesis and aggregation behavior in water/1,4-dioxane mixtures and in pure 1,4-dioxane of PS/PAA heteroarm star copolymers.

While stars represent a distinct group of polymers,[32] an even more intriguing class of compounds is that of dendrimers.[33] Dendrimers are perfectly branched molecules that are characterized by high end-group functionality and compact molecular structures.[34,35] These

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macromolecules have been extensively investigated for a wide range of applications including catalysis, encapsulation, drug delivery, and other techniques.[36,37] Some years ago, Six et al.[38] first, and then the Hedrick team,[39,40] described the synthesis of a new class of macromolecules called dendrimer-like polymers. These structures share with regular dendrimers some characteristic molecular features but differ from the latter by the macromolecular nature of their successive generations. In subsequent studies, Hedrick and co-workers even prepared amphiphilic dendrimer-like copolymers composed of poly(ϵ-caprolactone) inner blocks and poly(hydroxyethyl methacrylate) outer blocks.[40,41] Synthetic strategies of highly branched architectures whose branching points are separated by polymeric chains, including dendrigrafts, comb-burst, polymers with dendritic branching, and dendrimer-like polymers were recently reviewed by Teerstra et al.[42]

In light of the above studies, we have examined additional ways to prepare amphiphilic dendrimer-like copolymers based on PS and PAA. Previously, we have successfully synthesized amphiphilic dendrimer-like architectures based on poly(ethylene oxide) and polystyrene.[43,44] These systems were obtained by sequential anionic polymerization of ethylene oxide and ATRP of styrene or vice versa, the switch from the first to the second polymerization mechanism occurring through selective transformation of the multiple chain ends. Very recently, we also reported the synthesis of dendrimer-like polystyrenes using multifunctional cores as initiators for ATRP and selective branching reactions.[45] The objective of this report is to expand this methodology to the preparation of dendrimer-like copolymers based on PS and P*t*BA or PAA and examine their behavior at the air/water interface.

Experimental Section

Materials. THF, styrene (99%), and *tert*-butyl acrylate (98%) were stirred overnight with CaH_2 and distilled prior to use. Copper(I) bromide (CuBr, 98%), 2,2′-bipyridyl (bipy, 99%), ethylene carbonate (98%), 4,4′-biphenol (99%), 4-*tert*-butylcalix[4]arene (95%), 4-*tert*-butylcalix[6]arene (95%), 4-*tert*-butylcalix[8]arene (95%), triethylamine (99%), 2-bromoisobutyryl bromide (98%), diethanolamine (99%), serinol (98%), DMF (99%), trifluoroacetic acid (99%), methanol, and dichloromethane were used as received. All reagents were HPLC grade and purchased from Aldrich.

Instrumentation. ^{1}H NMR spectra were obtained with a Bruker AC 200 NMR spectrometer with $CDCl_3$, DMSO-d_6, and D_2O as solvents. Polymer molar masses were determined using a size exclusion chromatography (SEC) apparatus at RT with tetrahydrofuran as eluent (0.7 mL/min). The instrument is equipped with a refractive index (RI) detector (Varian RI-4) and fitted with four TSK-gel columns (7.8 × 300 mm, 5 μm, G 2000, 3000, 4000, and 5000 Hr with pores of 250, 1500, 10 000 and 1×10^5 Å, respectively). This instrument was calibrated using linear polystyrene standards. The actual molar masses of PS star-shaped and dendrimer-like samples were calculated from the response of a multiangle laser light scattering (MALLS) detector (Wyatt technology) that was connected to the SEC line. The d*n*/d*c* values for PS stars were measured in THF at 25 °C with a laser source (633 nm) and were found to be the same as linear PS ($dn/dc = 0.183$ cm^3/g). Infrared (IR) measurements were performed on a 320 FT-IR spectrometer (Nicolet). In a typical experiment, the polymer was spread as a solution on a NaCl pellet and was analyzed after evaporation of the solvent.

Surface film characterizations were conducted using a Teflon Langmuir KSV trough equipped with two moving barriers and a Wilhelmy plate for measuring surface pressure. Isotherm and hysteresis experiments were repeated at least three times with three separately prepared solutions to ensure reproducibility. Between runs, the troughs were cleaned with ethanol and rinsed several times with Millipore filtered water of resistivity ≥ 18.2 MΩ cm^{-1}. Solutions were prepared by dissolving 5 mg of polymer using a Sartorius microbalance for precise mass measurements, in ~5 mL of chloroform. The samples were spread dropwise on a layer of Millipore water with a 100 μL gas-tight Hamilton syringe. Chloroform was 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 trough. Typical experiments were run with barrier speeds of ±5 mm min^{-1}.

Surface films of the dendrimer-like copolymers were transferred onto freshly cleaved mica at various pressures (25 °C). The desired surface pressure was attained at rates of ±5 mm min^{-1}. Once the film had equilibrated at a constant π (surface pressure) for at least 15 min, the mica was pulled through the interface at a rate of 1 mm min^{-1}. The transferred film was scanned in tapping mode with a Nanoscope III atomic force microscope (AFM) (Digital Instruments, Inc., Santa Barbara, CA) with silicon probes (Nanosensor dimensions: $T = 3.8-4.5\mu$m, $W = 27.6-29.2$ μm, $L = 131$ μm). Digital Instruments software was used to process the images with a second-order flattening routine.

Synthesis of Multifunctional Initiators. Bi-, tetra-, hexa-, and octafunctional initiators were prepared by reaction of 4,4′-biphenol or 4-*tert*-butylcalix[*n*]arene ($n = 4$, 6, or 8) with 2-bromoisobutyryl bromide according to a procedure described previously.[46,47]

ATRP of Styrene and *tert*-Butylacrylate. All polymerizations were performed in a Schlenk apparatus. The reaction mixtures were degassed by three freeze−pump−thaw cycles and placed in a thermostated oil bath maintained at 100 °C prior to the polymerization. In a typical experiment, a Schlenk flask was flame dried under vacuum and filled with 4-*tert*-butylcalix[4]arene (0.074 g, 0.06 mmol), 2,2′-bipyridyl (0.168 g, 1.08 mmol), copper bromide (0.051 g, 0.36 mmol), and styrene (5 g, 48 mmol) under a N_2 atmosphere (for the *tert*-butylacrylate polymerization, 10 wt % of ethylene carbonate relative to the mass of *tert*-butylacrylate was also added). After 3 h of polymerization, the reaction mixture was cooled to room temperature, and the content was diluted with THF and passed through a column of neutral alumina to remove the copper salts. The polymer was precipitated from an excess of methanol, filtered, and dried at 50 °C under vacuum to give 0.75 g of a crude product (conv = 15%). SEC/MALLS (THF): $M_n = 13\,400$ g/mol, $M_w/M_n = 1.28$. PS: ^{1}H NMR ($CDCl_3$) δ 7.3−6.3 (m, 5H, aromatic), 4.5 (s, C***H***Br), 2.1−1.3 (m, C$\boldsymbol{H_2}$ and C***H*** of PS). P*t*BA: ^{1}H NMR ($CDCl_3$) δ 2.3−2.1 (s, C***H*** of P*t*BA), 1.7−1.0 (m, C$\boldsymbol{H_2}$, C$\boldsymbol{H_3}$ of P*t*BA).

Chain End Modification Reactions. a. Branching PS Chain Ends. A typical chain end modification experiment is as follows. PS_8Br_8 star polymer (3 g, $M_n = 13\,350$ g/mol) was dissolved in DMF (20 mL) and 0.65 g (6.19×10^{-3} moles) of diethanolamine (serinol was also successfully used under similar experimental conditions) were added. The reaction was stirred for 24 h at 80 °C. The polymer was precipitated twice in cold methanol, filtered, and dried under vacuum overnight at 35 °C to give 2.4 g of a PS with 16 hydroxyl functions ($PS_6(OH)_{12}$) (yield = 80%).^{1}H NMR ($CDCl_3$) δ 7.3−6.3 (m, 5H aromatic), 3.4−3.1 (m, $NR_1(CH_2C\boldsymbol{H_2}OH)_2$, and $R_2C\boldsymbol{H}ArN(R_3)_2$), 2.7−2.4 (m, $NR_1(C\boldsymbol{H_2}CH_2OH)_2$), 2.1−1.3 (m, C$\boldsymbol{H_2}$ and C***H*** of PS).

b. Functionalization of Branched PS Chain Ends. The $PS_8(OH)_{16}$ star (2.15 g, $M_n = 13\,350$ g/mol) was dissolved in dry THF (20 mL) along with triethylamine (1.8 mL, 1.29×10^{-2} mol), and the solution was cooled to 0 °C in an ice bath. Then, 2-bromoisobutyryl bromide (1.6 mL, 1.29×10^{-2}mol) was dissolved in 10 mL of THF and added dropwise over a period of an hour to the mixture. The reaction was stirred at RT for 24 h. The precipitated salts were removed by filtration, and the polymer recovered after two precipitations from an excess of methanol was filtered and dried at 50 °C under vacuum overnight. Such a procedure gave 1.76 g of $PS_6(Br)_{12}$ (yield =

82%). ^{1}H NMR (CDCl$_3$) δ 7.3−6.3 (m, 5H, aromatic), 4.0−3.7 (m, $NR_1(CH_2C\boldsymbol{H_2}OC(=O)R_4)_2$), 3.4−3.1 (m, $R_2C\boldsymbol{H}ArN(R_5)_2$), 2.7−2.4 (m, $NR_1(C\boldsymbol{H_2}CH_2OC(=O)R_4)_2$), 2.1−1.3 (m, $C\boldsymbol{H_2}$ and $C\boldsymbol{H}$ of PS), 1.9 (s, $R_6C(C\boldsymbol{H_3})_2Br$).

Synthesis of PS$_n$PAA$_{2n}$ Amphiphilic Copolymers. PS$_6$P*t*BA$_{12}$ dendritic copolymer (0.40 g, M_n = 49 400 g/mol, 8.1 × 10^{-6} mol) was dissolved in dichloromethane (9 mL). Trifluoroacetic acid (TFA) (0.82 mL, 0.01 mol, 5 equiv to *tert*-butyl ester) was then added, and the mixture was stirred at RT for 24 h. The solvent and excess TFA were removed by vacuum evaporation, and the polymer was washed with CH$_2$Cl$_2$ and dried under vacuum for 12 h at RT to give 0.35 g of a PS$_6$-PAA$_{12}$ amphiphilic copolymer (yield = 87%). ^{1}H NMR (DMSO-*d*$_6$) δ 11.0−9.0 (1H, $COO\boldsymbol{H}$), 7.3−6.3 (m, 5H, aromatic), 2.2 (s, $C\boldsymbol{H}$ of PAA), 2.0−1.1 (m, $C\boldsymbol{H_2}$ of PS and PAA, $C\boldsymbol{H}$ of PS). IR ν_{max} (film) 3050−3500 cm^{-1} (broad peak): COOH.

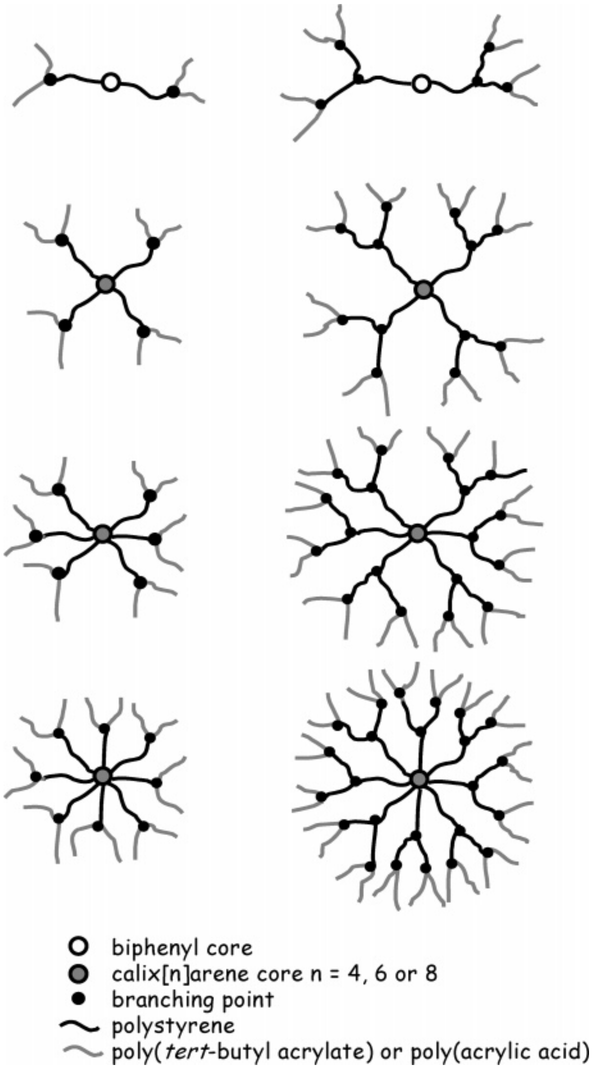
Preparation of PS$_n$PANa$_{2n}$ Amphiphilic Copolymers. In a 100 mL two-neck flask equipped with a magnetic stirrer, the PS$_8$PAA$_{16}$ dendritic copolymer sample (0.40 g, M_n = 48 000 g/mol) was suspended in water (40 mL). Sodium hydroxide (144 mg, 3.6 × 10^{-3} mol) was then added, and the solution was stirred for 24 h until complete solubilization of the copolymer. Water was removed by vacuum evaporation, and the polymer was dried under vacuum at RT. Such a procedure gave 0.30 g of PS$_8$PANa$_{16}$ (yield = 75%). ^{1}H NMR (D$_2$O) δ 2.0 (s, $C\boldsymbol{H}$ of PANa), 1.7−1.2 (m, $C\boldsymbol{H_2}$ of PANa).

Results and Discussion

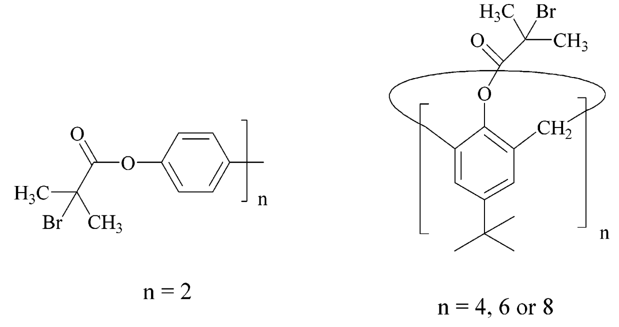
The objective of this study is to successfully construct dendrimer-like copolymers based on PS and P*t*BA or PAA by a combination of ATRP and selective chemical modifications. Using a similar approach, our group has previously described the synthesis of dendrimer-like polystyrenes[45] and asymmetric polystyrene stars.[22] This method is based on a sequence of reactions consisting of the preparation of ω-bromo-terminated linear or star PS by ATRP followed by a two-step derivatization of the bromo end groups into twice as many halogenoester functions from which a new generation of PS could be grown by ATRP. Following this route, we report here the synthesis of dendrimer-like copolymers based on either styrene and *tert*-butylacrylate or styrene and acrylic acid units (Scheme 1).

Synthesis of Star-shaped Polystyrene Precursors: First Generation. The first step in our procedure was the synthesis of linear and star-shaped polystyrenes (denoted as PS$_n$, n = 2, 4, 6, or 8) via ATRP, with precisely two, four, six, or eight arms. PS stars were obtained by the "core first" method using *tert*-butylcalix[*n*]arene-based multifunctional initiators (n = 4, 6, or 8) prepared in just one step, as previously reported (Scheme 2).[46,47]

Scheme 1. Schematic Sketch of the Different Amphiphilic Dendritic Structures



Scheme 2. Multifunctional Initiators Used in the Synthesis of PS/P*t*BA and PS/PAA Star Copolymers.



The optimal conditions for controlling ATRP of styrene using such initiators are reported in previous publications.[45−47] Styrene polymerization was performed in bulk at 100 °C in the presence of CuBr/bipy (1:3) as a catalytic system. The polymers were characterized with size exclusion chromatography online with a multiangle laser light scattering detector (MALLS/SEC). For the first generation, low molar masses between 5000 and 20 000 g/mol were targeted to monitor the chemical transformation of chain ends by ^{1}H NMR spectroscopy. Star and linear polystyrene samples exhibiting narrow molar mass distributions (M_w/M_n < 1.3) were obtained. In addition, the functionality of the stars was checked by comparing their molar mass with that of their individual arms, the latter being isolated after hydrolysis of the ester functions at the central core. Experimental results were in excellent agreement with theoretical values, indicating that the expected structures were obtained. However, the polymerization had to be limited to low conversion to prevent the formation of high molar mass species by irreversible star−star coupling reactions. Indeed, we have previously shown that by using high [monomer]/[initiator] ratios and by limiting the conversion below 30%, the possibility for the star branches to undergo intermolecular termination is negligible.[46,47]

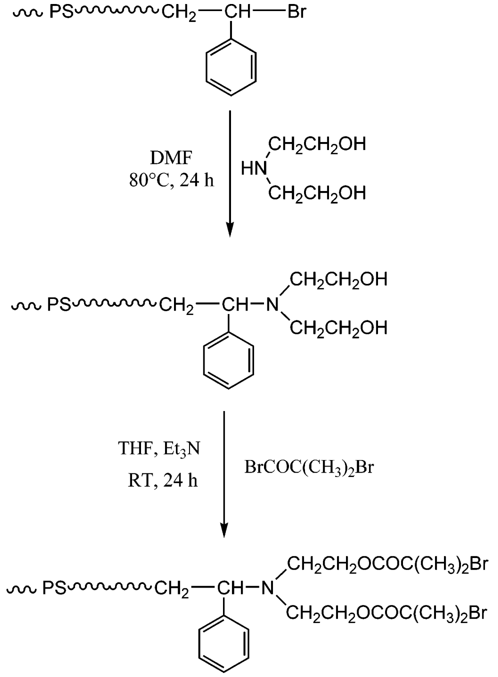
The next step in the synthesis of these dendrimer-like copolymers was the introduction of a branching point at each chain end. This part was achieved in two steps, as depicted in Scheme 3. First, we resorted to

Table 1. Synthesis of Second-generation PS_nPtBA_{2n} Dendrimer-like Copolymers Using PS_nBr_{2n} as Macroinitiators[a]

	PS_nBr_{2n} macroinitiator			PS_nPtBA_{2n}				
run	n	M_n[b] (g mol^{-1})	M_w/M_n[b]	$[M]/[I]$	M_n[c] (g mol^{-1})	M_w/M_n[c]	conv[d] (%)	M_nth[e] (g mol^{-1})
1	2	3100	1.29	400	15 400	1.38	28	17 400
2	2	4800	1.20	1000	17 300	1.23	8.5	15 500
3	2	4800	1.20	1000	21 900	1.16	12	20 300
4	4	7000	1.35	3000	23 200	1.27	5	22 600
5	4	13 400	1.23	1600	44 422	1.28	5	30 000
6	6	15 600	1.28	2400	48 000	1.16	7.5	38 600
7	6	15 600	1.28	2400	57 300	1.10	11	49 400
8	6	15 600	1.28	2400	64 900	1.15	15	58 600
9	6	18 240	1.20	2400	42 300	1.22	7	54 000
10	8	27 000	1.20	4000	82 400	1.26	11	83 400
11	8	27 000	1.20	4000	131 000	1.24	15	104 000
12	8	13 300	1.20	1600	74 700	1.35	32	78 900

[a] Conditions: $[-Br]/[CuBr]/[bipy] = 1:1:3$, 10 wt % of ethylene carbonate, $T = 100$ °C in bulk. [b] Determined by MALLS/SEC in THF. [c] Determined by combination of MALLS/SEC for first generation and ^1H NMR for second generation. [d] Monomer conversion measured gravimetrically. [e] $M_n\text{th} = (\% \text{ conv} \times [M]/[I] \times 128.17) + M_m$ where M_m is the molar mass of the PS_nBr_{2n} macroinitiator.

Scheme 3. Chain End Modification Reactions



nucleophilic substitution to replace the bromo end groups of the PS precursors with two hydroxyl functions. This reaction was carried out using an aminodiol, either diethanolamine (DMF/80 °C/24 h), or serinol (2-amino 1,3-propanediol) (DMF/RT/72 h). The ATRP initiating sites were subsequently generated by esterification of the hydroxyl chain ends with 2-bromoisobutyryl bromide. Purification of these macroinitiators (denoted as PS_nBr_{2n} with $n = 2$, 4, 6, or 8) from excess reagents was performed by three precipitations in methanol. The two reaction products were checked by ^1H NMR analysis (see Experimental Section).

Synthesis of PS_n-$PtBA_{2n}$, H-type, and Dendrimer-like Copolymers: Second and Third Generations. The third step in the synthesis of dendrimer-like copolymers of second generation was ATRP of *tert*-butylacrylate using PS_nBr_{2n} as macroinitiators. This was performed in bulk at 100 °C using CuBr/bipy (1:3) as the catalytic system in the presence of ethylene carbonate (10% in weight relative to *t*BA). The use of this additive proved beneficial in better controlling the polymerization of alkyl acrylates.[48] The reaction times were varied from thirty minutes to a few hours according to the molar mass targeted. Table 1 gives the data pertaining to the second generation of PS_nPtBA_{2n} dendrimer-like copolymers. Figure 1 shows the SEC traces of H-type PS_2PtBA_4 copolymers prepared from the difunctional initiator derived from 4,4′-biphenol (runs 2 and 3).

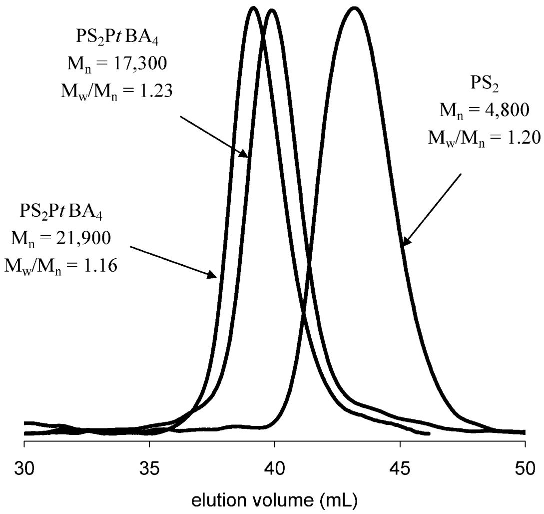


Figure 1. SEC traces (RI detector) of second-generation PS_2PtBA_4 dendrimer-like copolymers (runs 2 and 3, Table 1) and the linear precursor prepared from a difunctional initiator.

In Figures 2 and 3 are given the SEC traces of PS_6PtBA_{12} (runs 6 and 8) and PS_8PtBA_{16} (runs 10 and 11) second-generation dendrimer-like copolymers derived from hexa- and octafunctional calixarene-based initiators. These chromatograms show the formation of the P*t*BA blocks; after the polymerization of *tert*-butylacrylate, the SEC traces shift to higher molar mass regions along with a disappearance of the peak because of the PS precursor. All of the obtained dendritic architectures exhibit narrow molar mass distributions with symmetric and monomodal SEC traces. The actual molar mass was obtained through ^1H NMR by comparison of the integrations of aromatic and *tert*-butyl protons (knowing the molar mass of the PS_n star precursor as obtained by MALLS/SEC). Good correlation between the experimental and theoretical molar masses was obtained.

In contrast to styrene, ATRP of *tert*-butylacrylate is associated with a lower equilibrium constant K_{eq} ($K_{eq} = k_a/k_d$) between active and dormant species and a higher k_p/k_t ratio (k_p is the propagation rate constant and k_t is the termination rate constant).[25] Therefore, the probability of two species to couple irreversibly is

Table 2. Synthesis of the First- (G-1), Second- (G-2), and Third- (G-3) Generation $PS_nPS_{2n}PtBA_{4n}$ Dendrimer-like Copolymers Using PS_nPS_{2n} as Macroinitiator[a]

		G-1 PS_n		G-2 PS_nPS_{2n}		G-3 $PS_nPS_{2n}PtBA_{4n}$			
run	n	M_n[b]	M_w/M_n[b]	M_n[b]	M_w/M_n[b]	M_n[c]	M_w/M_n[b]	conv[d] (%)	M_nth[e]
13	2	4900	1.20	12 750	1.23	17 800	1.28	1	17 000
14	2	4900	1.20	12 750	1.23	38 700	1.22	4	29 000
15	4	12 600	1.14	31 500	1.19	61 000	1.30	2.4	57 300
16	6	15 700	1.25	38 900	1.23	128 400	1.25	8.8	147 000

[a] Conditions: [−Br]/[CuBr]/[bipy] = 1:1:3, 10 wt % of ethylene carbonate, $T = 100$ °C in bulk. [b] Determined by MALLS/SEC in THF. [c] Determined by ^{1}H NMR knowing molar mass of G-2 dendritic precursor by MALLS/SEC. [d] Monomer conversion measured gravimetrically. [e] $M_n\text{th} = (\%\ \text{conv} \times [M]/[I] \times 128.17) + M_m$ where M_m is the molar mass of the $PS_nPS_{2n}Br_{4n}$ dendritic macroinitiator.

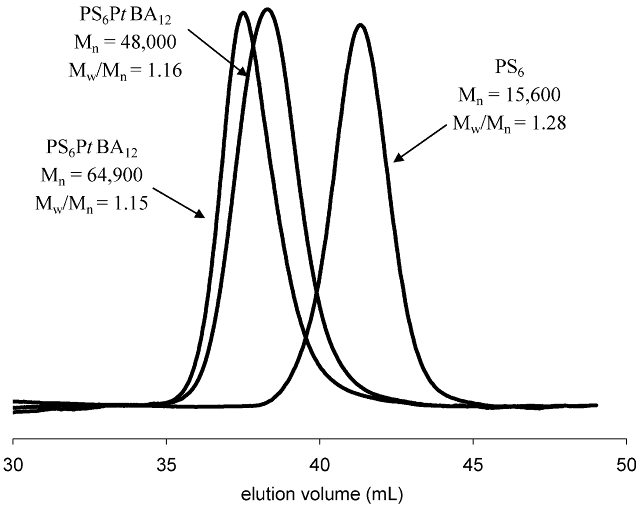


Figure 2. SEC traces (RI detector) of second-generation PS_6PtBA_{12} dendrimer-like copolymers (runs 6 and 8, Table 1) and the PS_6 polystyrene star precursor prepared using a hexafunctional calixarene-based initiator.

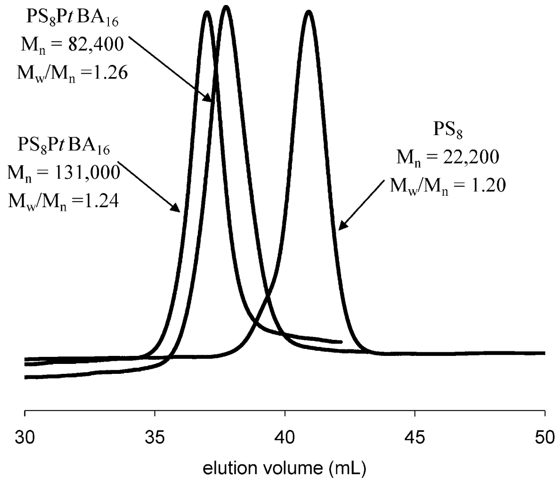


Figure 3. SEC traces (RI detector) of second-generation PS_8PtBA_{16} dendrimer-like copolymers (runs 10 and 11, Table 1) and the PS_8 polystyrene star precursor prepared with an octafunctional calixarene-based initiator.

lower than that for polystyryl radical species.[47] The MALLS/SEC characterization of the dendrimer-like copolymers shows unimodal and symmetrical traces even for conversion higher than 30%, in sharp contrast with the synthesis of dendrimer-like polystyrenes.[45] As indicated in Figure 4, the MALLS trace of a PS_8PtBA_{16} sample (run 11 in Table 1) did not reveal the presence of high molar mass side populations resulting from intermolecular couplings between branches of two dendritic macromolecules.

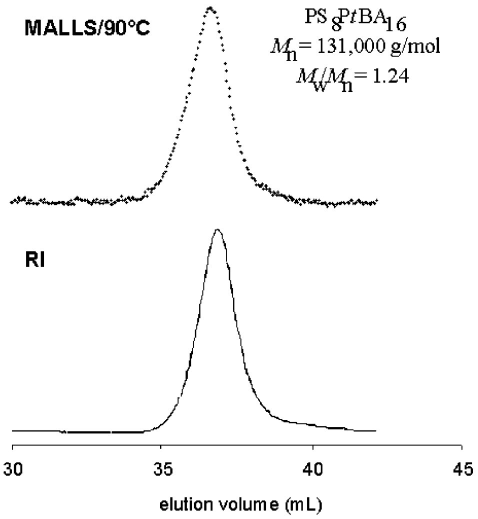


Figure 4. Comparison of SEC traces (MALLS and RI detectors) of a second-generation PS_8PtBA_{16} dendritic copolymer (run 11 in Table 1).

Third-generation dendrimer-like copolymers based on polystyrene for the first and second generations and poly(*tert*-butyl acrylate) for the third generation were derived by combination of chain end modifications and ATRP. For this purpose, second-generation dendrimer-like PS macroinitiators (denoted as $PS_nPS_{2n}Br_{4n}$ with $n = 2$, 4, 6, and 8) were synthesized by the core first methodology following a procedure recently described by us.[45] The growth of the P*t*BA blocks was carried out from $PS_nPS_{2n}Br_{4n}$ macroinitiators using the conditions described above. The copolymers' experimental data are given in Table 2, and the SEC traces of a $PS_6PS_{12}PtBA_{24}$ copolymer and its PS_6 and PS_6PS_{12} precursors are displayed in Figure 5.

The data and the chromatograms unambiguously show an efficient crossover reaction from PS blocks to P*t*BA ones, these third-generation dendritic samples being also free of any polystyrene precursor. Their molar mass distributions remained narrow ($M_w/M_n < 1.3$) and were close to the expected values, indicating a controlled polymerization process. Symmetric and narrow MALLS/SEC traces were indicative of the absence of high molar mass side products.

Synthesis of Amphiphilic PS_n-*b*-PAA_{2n} Dendrimer-like Copolymers. Dendrimer-like copolymers based on PS and P*t*BA generations subsequently serve as precursors for the synthesis of water-soluble dendrimer-like copolymers based on poly(acrylic acid) (PAA). Our aim is to eventually investigate the 2D and 3D self-assembly of such PS_n-*b*-PAA_{2n} dendritic copolymers at air/water interface and in water. Deprotection of the *tert*-butyl ester functions of the P*t*BA blocks gave

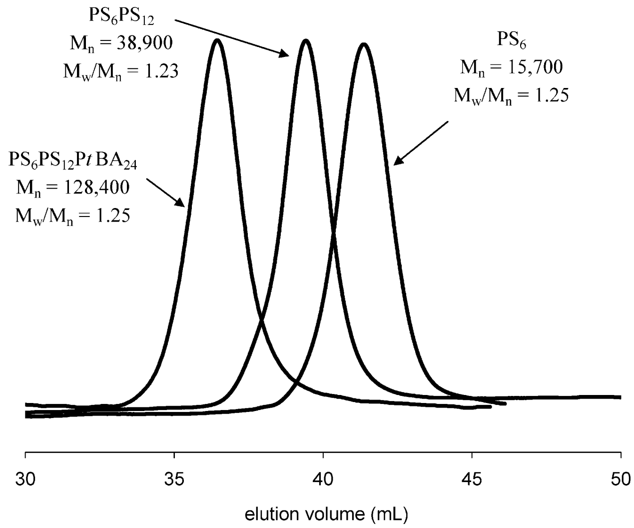


Figure 5. SEC traces (RI detector) of a third-generation PS_6-PS_{12}P*t*BA_{24} dendrimer-like copolymer, its dendritic polystyrene precursor PS_6PS_{12}, and its star precursor PS_6 prepared using a hexafunctional calixarene-based initiator (run 16, Table 2).

dendritic structures composed of PS-based hydrophobic cores and PAA-based hydrophilic coronas. This selective cleavage reaction was performed by adding an excess of trifluoroacetic acid (TFA) in dichloromethane at room temperature for 24 h, according to a well-established procedure.[49] Analysis by ^1H NMR spectroscopy in DMSO-d_6 clearly showed the disappearance of the *tert*-butyl protons (decrease in the signal at 1.5 ppm). Comparison of the integrations in the 1.5−2 ppm region before and after cleavage (Figure 6A and B) indicates a quantitative hydrolysis. Monitoring the reaction by infrared spectroscopy showed that *tert*-butyl ester functions of the copolymer were all removed upon hydrolysis (no band at 1728 cm^{-1}) and replaced by carboxylic acid units (broad band in the 3050 cm^{-1} region). Following this method, second-generation amphiphilic dendrimer-like samples with 2, 4, 6, or 8 polystyrene branches at the core and 4, 8, 12, or 16 poly(acrylic acid) arms in the corona were obtained.

However, dendrimer-like copolymers based on PS and PAA could hardly be solubilized in water. Upon addition of an equimolar solution of sodium hydroxide (with respect to the carboxylic acid units), poly(sodium acrylate) (PANa) blocks were formed helping the resulting copolymer (denoted as PS_nPANa_{2n}) to solubilize in water. Figure 6C shows the ^1H NMR spectrum of PS_n-$PANa_{2n}$ in D_2O. While signals corresponding to sodium acrylate blocks can be seen ($\delta = 1.2{-}2.0$ ppm), aromatic signals corresponding to PS blocks cannot, indicating that the PS part collapsed into the micellar core, the hydrophilic PANa blocks extending outward. For the sake of comparison, Figure 6B shows the ^1H NMR spectrum of PS_8PAA_{16} in DMSO-d_6, a good solvent for both PS and PAA blocks, resulting in well-resolved signals for the two blocks.

Surface Characterizations of PS/P*t*BA Copolymers at the Air/Water Interface. As an introduction to future work, initial Langmuir−Blodgett (LB) surface characterizations were conducted on PS_4P*t*BA_8 (Table 1, run 5), PS_6P*t*BA_{12} (Table 1, run 9), and PS_8P*t*BA_{16} (Table 1, run 11). The amphiphilicity of these PS_n-*b*-PtBA_{2n} samples (containing slightly hydrophilic P*t*BA and strongly hydrophobic PS) allowed these materials to be spread at the air/water interface to form Langmuir monolayers. Surface pressure isotherms of PS_4P*t*BA_8 (run 5), PS_6P*t*BA_{12} (run 9), and PS_8P*t*BA_{16} (run 11) monolayers are presented in Figure 7 with the ordinate scale expressed in units of mean molecular area (MMA in Å^2/molecule) for easy comparison. The reproducible baselines and onset pressures at high surface areas indicate that the films are very expanded at the air/water surface. While these three isotherms are similar in shape, there is a clear shift to larger surface areas with the eight-arm PS core material. The six-arm core may be slightly more compact because it was the most hydrophobic (42% PS, compared to ~30% for the others) of the samples. In addition, three distinct regions are observed. For the high MMA region, the surface pressure slowly increases as the film is compressed (MMA decreased) until it reaches a pseudoplateau region for all of the samples at ~24 mN/m. This second region occurs at intermediate MMA and represents a “pseudo” plateau because of the slight increase in pressure that is observed. The presence of the pseudoplateau in the isotherms suggests a change in the surface aggregation of the polymers within this region, and it is qualitatively consistent with the behavior of other nonelectrolyte copolymer systems such as PS-*b*-PEO,[50−52] Poly(styrene-*b*-*n*-butylacrylate) (P*n*BA),[53] and poly(butadiene-*b*-ethylene oxide) block copolymers.[54]

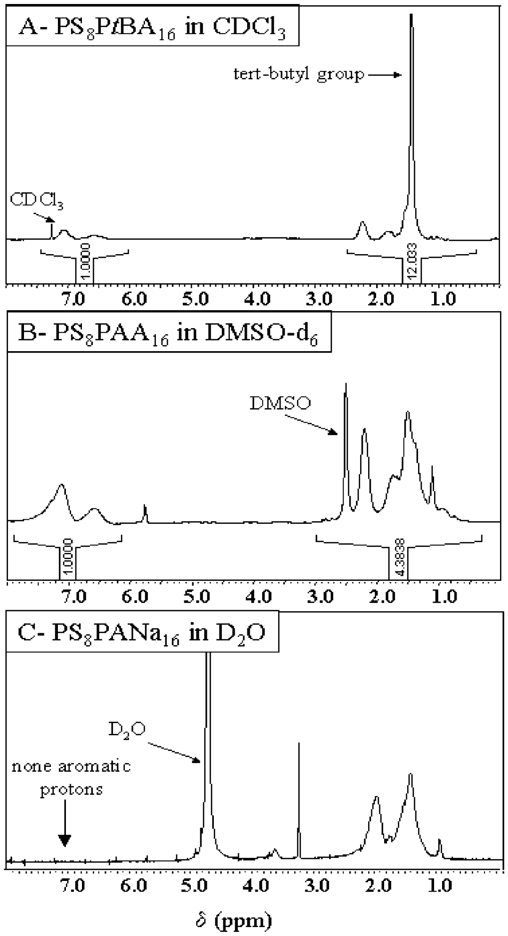


Figure 6. ^1H NMR spectra (200 MHz) of (A) the PS_8P*t*BA_{16} precursor in $CDCl_3$ (run 10, Table 1), (B) PS_8PAA_{16} amphiphilic dendrimer-like polymer in DMSO-d_6, and (C) PS_8PANa_{16} in D_2O.

As the compression continues (lower MMA region), the surface pressure sharply increases, reaching elevated values and highly compacted films. The facile

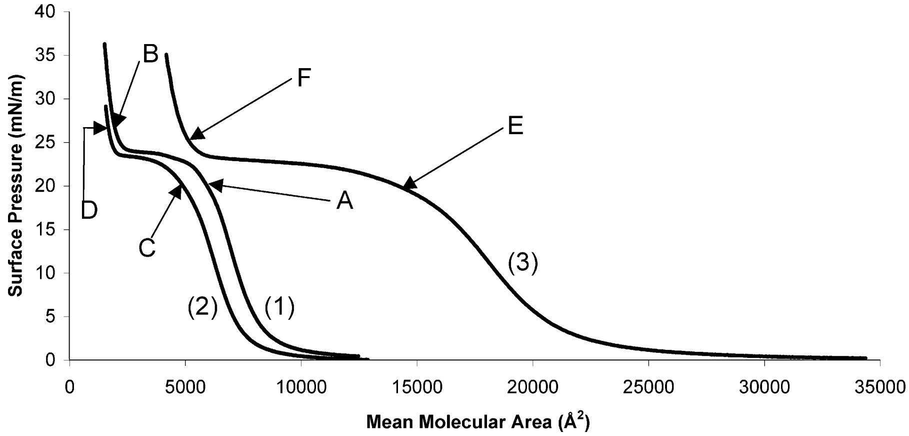


Figure 7. Isotherms at 25 °C of (1) PS_4PtBA_8 (run 5, Table 1), (2) PS_6PtBA_{12} (run 9, Table 1), and (3) PS_8PtBA_{16} (run 11, Table 1). The isotherms are labeled with solid arrows, which correspond to points at which the film was transferred to mica (transfers A, C, and E at 20 mN/m, transfers B and D at 27 mN/m, and transfer F at 25 mN/m).

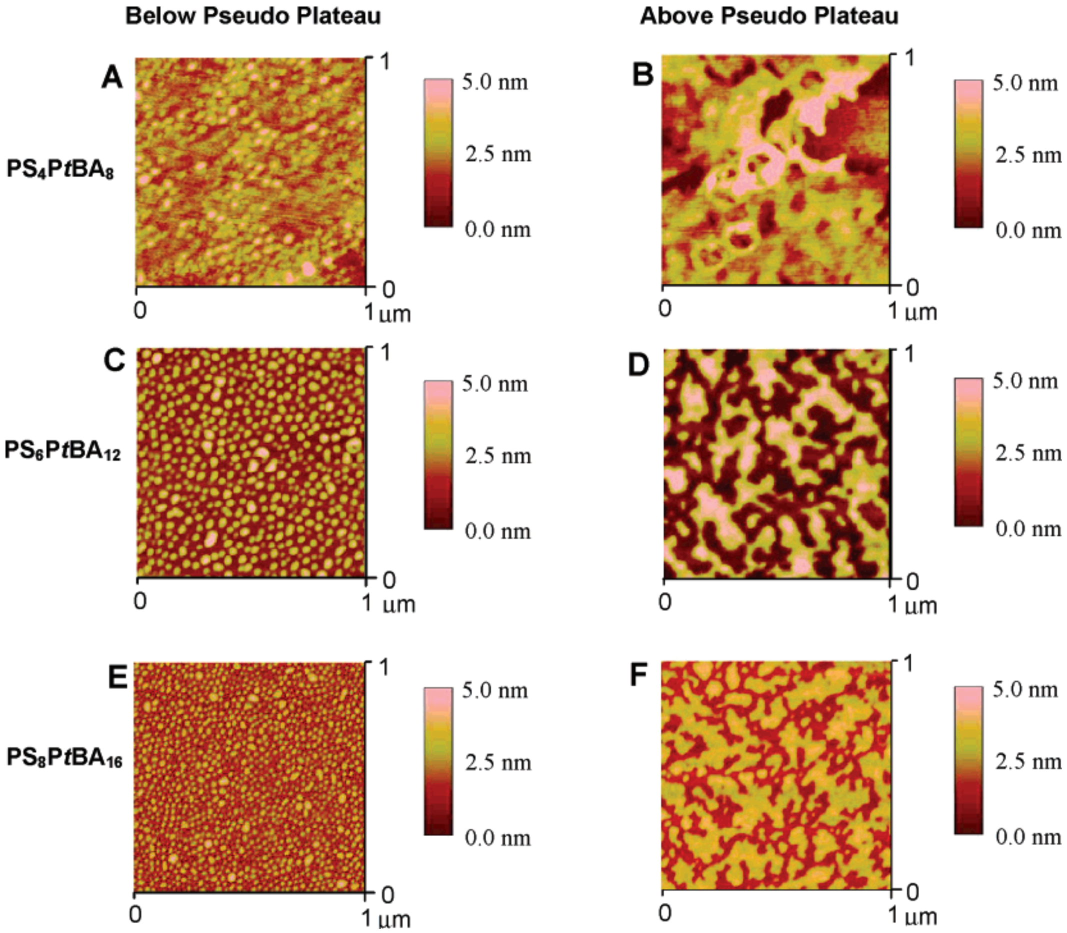


Figure 8. AFM images of PS_4PtBA_8 (A) (run 5, Table 1) before the plateau, 20 mN/m (transfer ratio (*TR*) = 1.2), (B) after the plateau, 27 mN/m (*TR* = 1.5), of PS_6PtBA_{12} (C) (run 9, Table 1) before the plateau, 20 mN/m, (*TR* = 1.9), (D) after the plateau, 27 mN/m (*TR* = 1.6), and of PS_8PtBA_{16} (E) (run 11, Table 1) before the plateau, 20 mN/m, (*TR* = 1.9), and (F) after the plateau, 25 mN/m, (*TR* = 1.7).

synthesis of this type of copolymer allows for architecture to be systematically varied over a wide range and, therefore, should lead to a more quantitative interpretation of the role of copolymer composition on the monolayer behavior.

Compression−expansion hysteresis experiments were also performed with target pressures, covering the entire range obtained in the isotherm experiments ($\pi = 0 \leftrightarrow 35$ mN/m). For any target pressure, every subsequent recompression isotherm was superimposable on the previous compression isotherms. This reproducibility indicates that the surface film formation is macroscopically reversible.

The copolymers were successfully transferred onto mica substrates as Langmuir−Blodgett (LB) films. The morphology of the LB films transferred at a range of applied surface pressures was then studied using atomic force microscopy (AFM). The main change in the surface aggregation of the copolymers occurred around the pseudoplateau pressure of 24 mN/m. Figure 8 shows the height AFM images of three samples at characteristic pressures below (20 mN/m) and above (25, 27 mN/m) the pseudoplateau. The figure caption shows transfer ratios obtained after film transfer ranged from 1.2 to 1.9. These values indicate that the surface film is slightly densifying, likely due to the lower surface energy of the mica surface compared to water. The instantaneous transfer ratio was also constant, indicating homogeneous macroscopic deposition, while AFM scans revealed homogeneous deposition at the submicron scale and successful LB transfer. As expected from the isotherm experiments, the polymer films demonstrate a significant change in surface aggregation within the plateau region. Figure 8A, C, and E indicate that, for pressures lower than 24 mN/m, the AFM images of all three dendrimer-like block copolymers have circular domains of polydisperse sizes and widths in the range of 50−100 nm and heights in the range of 2−4 nm consistent with domains described as surface micelles by Eisenberg and co-workers.[55] Below the pseudoplateau, the domain size decreases as the molar mass and number of arms increase, indicating that the aggregation number increases for more complex architectures. We suppose that the surface micelles in Figure 8 consist of the hydrophobic PS chains aggregating on the top of a layer of hydrophilic P*t*BA that covers the mica surface.

While well-defined though polydisperse, domains are seen at pressures below the pseudoplateau, pressures higher than 24 mN/m yield nonhomogeneous films. The circular surface micelles initially formed at lower pressures (Figure 8A, C, and E) aggregate significantly. This leads to the nonhomogeneous surface morphologies shown in Figure 8B, D, and F. If the films were not significantly modified during transfer, this nonuniform aggregation would indicate either film collapse or local formation of multiple layers on the aqueous surface.

Conclusion

Dendrimer-like copolymers composed of polystyrene and poly(*tert*-butylacrylate) generations and of polystyrene and poly(acrylic acid) ones were prepared using a divergent approach. This procedure is based on sequential atom transfer radical polymerization of styrene and *tert*-butyl acrylate using multifunctional cores combined with chemical transformations of chain ends, resulting in dendrimer-like copolymers of low polydispersity index and molar masses in good agreement with the theoretical ones. Amphiphilic copolymers made of a polystyrene core and poly(acrylic acid) corona were derived by hydrolysis of *tert*-butyl groups under acidic conditions. Preliminary investigations by ^{1}H NMR spectroscopy using water as selective solvent showed that these amphiphilic dendrimer-like copolymers self-associate into aggregates. Langmuir monolayer studies indicated that several of the obtained structures spread at the air/water interface to form stable monolayers that transferred to solid substrates and revealed surface micelle morphology by AFM scans. Further study of the morphology of these copolymers by dynamic light scattering measurements, their viscosity in solution, and morphology studies via AFM imaging and TEM should provide more detailed insight into their assembly characteristics.

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