Macromolecules **2002,** *35,* 9001−9008

Toward an Easy Access to Asymmetric Stars and Miktoarm Stars by Atom Transfer Radical Polymerization

Raju Francis,[†] Bénédicte Lepoittevin, Daniel Taton, and Yves Gnanou*

Laboratoire de Chimie des Polymères Organiques, ENSCPB-CNRS-Université Bordeaux 1, 16, Avenue Pey Berland, 33607 Pessac Cedex, France

Received June 4, 2002; Revised Manuscript Received August 20, 2002

ABSTRACT: AA'_2-type asymmetric stars and AB_2-type miktoarm star polymers were prepared by combination of atom transfer radical polymerization (ATRP) and chemical modification of the termini of ATRP-derived polymers. The first step involved the preparation of ω-bromopolystyrene (PS) chains by ATRP using ethyl 2-bromoisobutyrate as initiator. Styrene was polymerized in bulk at 100 °C in the presence of Cu(I)Br and pentamethyldiethylenetriamine (PMDETA) as catalytic system. Next, the bromo end groups of the resulting PS chains were derivatized into twice as many bromoisobutyrates in order to obtain ω,ω'-bis(bromo)-PS chains. The last step consisted of growing either two additional PS or two poly(*tert*-butyl acrylate) (P*t*BA) blocks by ATRP, following the same polymerization conditions as those mentioned above. This methodology enabled us to synthesize AA'_2 triarm PS stars with asymmetry in the molar mass of their branches and PS(P*t*BA)$_2$ stars with chemically different PS and P*t*BA arms. According to the evolution of molar masses with conversion during growth of both the precursors and the stars using size exclusion chromatography and characterization of the end groups by ^{1}H NMR and matrix-assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectrometry, the structures are well-defined. Finally, the selective cleavage of *tert*-butyl groups from stars containing P*t*BA blocks was performed under acidic conditions. This resulted in the formation of novel amphiphilic PS(PAA)$_2$ miktoarm stars carrying one hydrophobic PS branch and two ionizable poly(acrylic acid) (PAA) arms. Characterization of the latter species by ^{1}H NMR and IR confirmed the expected structure.

Introduction

Controlled/living radical polymerizations combine the advantages offered by truly living systems with the experimental easiness characterizing free radical processes. Whatever the methodology considered, the control of chain growth in controlled/living radical polymerization is achieved through repeated deactivation of growing polymeric radicals into dormant species and activation of the latter. Depending upon the nature of the group capping these dormant species, these methodologies are referred to as atom transfer radical polymerization[1] (ATRP) for ω-halide polymers, nitroxide-mediated polymerization for ω-alkoxyamine polymers[2] (NMP), and reversible addition−fragmentation chain transfer[3] (RAFT) for ω-dithioester polymers. Among these three methodologies, ATRP appears to be the most versatile and powerful tool for engineering macromolecular architectures,[4−6] including ω-functionalized homopolymers, gradient, alternating, block copolymers, and also branched architectures such as graft copolymers, combs, stars, hyperbranched polymers, and dendrimer-like copolymers that are now accessible by ATRP.[7,8] To take the case of star polymers, they were derived by both the arm-first[1] and core-first methods via ATRP. Various families of initiators of precise functionality were for instance designed to serve as central cores, including cyclophosphazene,[9] calixarene derivatives,[10,11] glucose,[12] sucrose,[13] carbosilane-based dendritic cores[14] or other dendritic moieties,[4,5] multifunctional aromatic sulfonyl chlorides,[15] and halogeno-2,2′-bipyridyl-based metallic complexes.[16] These initiators were used in conjunction with either copper, ruthenium, or nickel halides and miscellaneous ligands to grow stars of either polystyrene, poly(alkyl methacrylate), or poly(alkyl acrylate) with a number of arms ranging from 3 to 21. Many other synthetic routes based on either anionic, cationic, or ring-opening metathesis polymerizations have also been designed to obtain star architectures.[17]

In contrast to the situation prevailing for regular stars, methodologies that describe the synthesis of asymmetric stars and miktoarms are mostly based on anionic polymerization.[18] Indeed, both asymmetric and miktoarms stars are traditionally prepared by the arm-first approach through deactivation of living carbanions by chlorosilanes or reaction of the same carbanions with divinylbenzene or diphenylethylene derivatives.[18] This synthetic route is well-suited to living carbanionic polystyryl or polydienyl chains, but it can hardly be applied to engineer polymeric architectures based on other polymers. In very recent contributions, however, Hedrick's team[19] and Pan's group[20] established an alternate method to synthesize miktoarm stars and resorted to multifunctional A_nB_m dual precursors to trigger the tandem ATRP of methyl methacrylate and the ring-opening polymerization of either ϵ-caprolactone or tetrahydrofuran.

This paper reports an original methodology and alternate synthetic route that can afford AA'_2-type asymmetric stars and AB_2-type miktoarm stars in just four steps. The stars can be derived by a two-step chemical modification of ATRP-derived ω-halogeno precursors into twice as many ATRP initiating sites, from which either two dissimilar or similar branches are grown.

Experimental Section

Materials. Styrene (99%) and *tert*-butyl acrylate (*t*BA, 98%) were stirred overnight over CaH_2 and distilled prior to use.

[†] Permanent address: Department of Chemistry, St. Joseph's College, University of Calicut, Calicut 673008, Kerala, India.

* To whom all correspondence should be addressed: e-mail gnanou@enscpb.fr.

10.1021/ma020872g CCC: $22.00

Copper(I) bromide (CuBr, 98%), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA, 99%) and ethyl 2-bromoisobutyrate (98%) were used as received. Triethylamine and tetrahydrofuran were distilled over CaH_2 prior to use. 2-Amino-1,3-propanediol (serinol, 98%), 2-bromoisobutyryl bromide (98%), trifluoroacetic acid (TFA, 99%), and *N,N*-dimethylformamide (DMF, 99%) were used as received. All reagents were purchased from Aldrich.

Synthesis of ω-Bromo-PS Precursor (PS(Br)). In a typical experiment, a Schlenk apparatus that was first flamed and dried under vacuum was charged with 0.83 g (5.8×10^{-3} mol) of CuBr, 1.0 g (5.8×10^{-3} mol) of PMDETA, 1.13 g (5.8×10^{-3} mol) of ethyl 2-bromoisobutyrate, and 80 mL (0.69 mol) of styrene under a N_2 atmosphere. The reaction mixture was degassed by three freeze−pump−thaw cycles, back-filled with N_2, and stirred at room temperature for 10 min. It was then placed in an oil bath thermostated at 100 °C. After 25 min polymerization time, it was cooled to room temperature, and the contents were dissolved in THF and then 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 for 12 h. ^{1}H NMR (monomer conversion and overall yield: 16%) ($CDCl_3$) δ (ppm): 7.3−6.3 (m, 5H, aromatic), 4.5 (broad s, 1H, C*H*(Ph)−Br), 3.6 (broad, 2H, C*H*$_2$ initiator), 2.2−1.3 (m, aliphatic main chain), 1 (m, 2 × C*H*$_3$ initiator). SEC (THF): $M_n = 2150$ g mol^{-1}, $M_w/M_n = 1.14$; MALDI−TOF MS: initiator−(styrene)$_n$−CH=CH-(C_6H_5),Na^+; average molar mass of an experimental peak: 1803.1; calculated value: 1803.9.

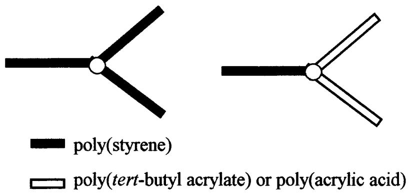
Synthesis of ω,ω′-Bis(hydroxy)-PS (PS(OH)$_2$). Polystyrene (1.0 g, 4.7×10^{-4} mol, $M_n = 2150$, $M_w/M_n = 1.14$) with bromine end groups was dissolved in DMF (5.5 mL), and 1.3 g (1.4×10^{-2} mol) of serinol (2-amino-1,3-propanediol) was added. After stirring for 72 h at 30 °C, the polymer was precipitated in methanol, filtered, and dried at 35 °C under vacuum for 24 h (yield: 85%). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.3−6.3 (m, 5H, aromatic), 3.6 (broad, 2H, C*H*$_2$ initiator), 3.3 (m, 4H, 2 C*H*$_2$OH), 2.2−1.3 (m, aliphatic main chain), 1 (m, 2 × C*H*$_3$ initiator). MALDI−TOF MS: initiator−(styrene)$_n$−NHCH-(CH_2OH)$_2$,Na^+; average molar mass of an experimental peak: 2205.9; calculated value: 2206.5.

Synthesis of ω,ω′-Bis(bromo)-PS (PS(Br)$_2$). In a 100 mL round-bottom flask flame dried under vacuum, the PS sample with two hydroxy groups, PS(OH)$_2$ (1 g, $M_n = 2100$, $M_w/M_n = 1.14$), was dissolved in dry THF (15 mL) along with triethylamine (0.5 mL). A THF solution of 2-bromoisobutyryl bromide (0.50 mL, 2.4×10^{-3} mol in 2 mL of THF) was added dropwise at 0 °C, over a period of 10 min. After stirring for 24 h at room temperature, the polymer was precipitated twice in methanol followed by drying at 35 °C under vacuum for 24 h (yield: 88%). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.3−6.3 (m, 5H, aromatic), 4.1−3.9 (m, C*H*$_2$OCO), 3.7−3.2 (broad, C*H*−NH−C*H* and C*H*$_2$ initiator), 2.2−1.3 (m, aliphatic main chain), 1 (s, 2 × C*H*$_3$ initiator). SEC (THF): $M_n = 2600$, $M_w/M_n = 1.10$.

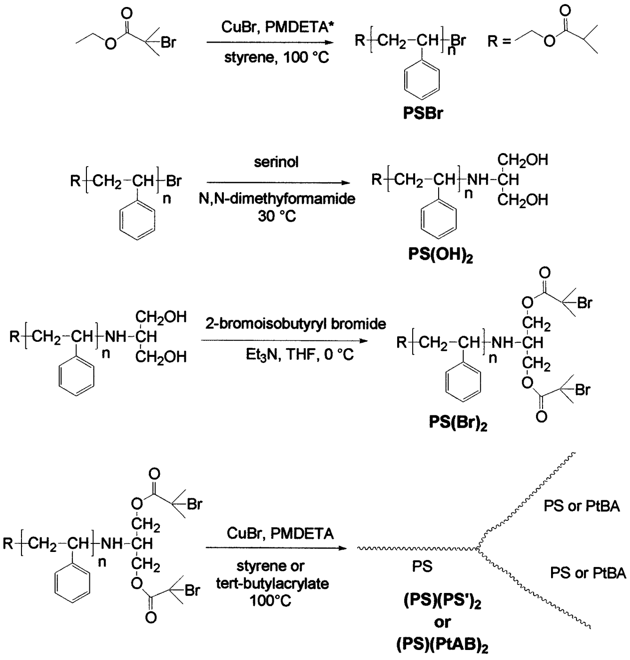
Synthesis of PS(PS′)$_2$ Asymmetric Stars and PS(PtBA)$_2$ Miktoarm Stars. CuBr (27 mg, 1.9×10^{-4} mol), PMDETA (66 mg, 3.8×10^{-4} mol), polystyrene with two active sites PS(Br)$_2$ (0.25 g, 9.6×10^{-5} mol), and styrene (4.4 mL, 3.8×10^{-2} mol) (or *tert*-butyl acrylate (6.0 mL, 3.8×10^{-2} mol)) were added under a N_2 atmosphere to a Schlenck flask which was flamed and dried under vacuum. The mixture was degassed, and the Schlenck was backfilled with N_2. It was then placed in an oil bath thermostated at 100 °C (or 80 °C) for 45 min. Polystyrene samples were precipitated from methanol and then dried in a vacuum at 35 °C for 24 h (overall yield: 16%). In the case of copolymers, the samples were precipitated from a mixture of methanol/water (90/10). The molar masses were analyzed by size exclusion chromatography: PS(PS)$_2$ $M_n = 8600$, $M_w/M_n = 1.26$. ^{1}H NMR ($CDCl_3$) of PS(P*t*BA)$_2$: δ (ppm): 7.3−6.3 (m, aromatic), 2.2 (s, C*H*COOtBu), 1.8 (m, C*H*$_2$ of P*t*BA and C*H* of PS), 1.5−1.3 (m, C*H*$_2$ of PS and C(C*H*$_3$)$_3$). IR ν_{max} (film): 1728.4 cm^{-1} (C=O, ester).

Core Destruction of the PS(PS′)$_2$ Asymmetric Star. Polystyrene star (0.15 g, $M_n = 8600$, $M_w/M_n = 1.26$, prepared using PS(Br) with $M_n = 2100$) was dissolved in THF (8 mL) in a Schlenck flask fitted with a condenser and N_2 inlet. Then ethanol (2.25 mL), water (0.25 mL), and KOH (0.50 g, 8.9×10^{-3} mol) were added, and the mixture was refluxed for 72 h. The solution was concentrated under reduced pressure, neutralized with dilute HCl, and precipitated from methanol. The polymer was filtered and dried under vacuum. SEC (THF): $M_n = 4000$, $M_w/M_n = 1.14$.

Scheme 1. Schematic Description of AA′$_2$ Asymmetric and AB$_2$ Miktoarm Stars



Scheme 2. Reaction Pathway for the Synthesis of Asymmetric and Miktoarm Star Polymers



* PMDETA: N,N,N',N'',N''-pentamethyldiethylenetriamine

Synthesis of PS(PAA)$_2$ Amphiphilic Miktoarm Star. PS(P*t*BA)$_2$ star polymer (0.40 g, $M_n = 19{,}300$, 2.07×10^{-5} mol) was dissolved in dichloromethane (5 mL). Then, trifluoroacetic acid (TFA) (1.0 mL, 1.29×10^{-2} mol, 5 equiv of *tert*-butyl ester) was added, and the mixture was stirred at room temperature for 24 h. The solvent and excess TFA were removed by evaporation; the polymer was washed with CH_2Cl_2 and dried under vacuum for 12 h. ^{1}H NMR (DMSO-*d*$_6$) δ (ppm): 7.3−6.3 (m, 5H, aromatic), 2.2 (s, C*H* of PAA), 2−1.1 (m, C*H*$_2$ of PS and PAA, C*H* of PS). IR: ν_{max} (film) 3050−3500 cm^{-1} (broad peak) (COOH).

Characterization. ^{1}H NMR spectra were obtained using a Bruker AC 200 NMR spectrometer. $CDCl_3$ was used as the solvent. In the case of copolymers polystyrene/poly(acid acrylic), DMSO-*d*$_6$ was used.

The polymer molar masses were determined using size exclusion chromatography (SEC) with tetrahydrofuran as eluent (1 mL/min) at 25 °C. This apparatus was equipped with a refractive index detector (Varian RI-4) and a PSS column (8 × 300 mm, 5 μm) provided by PSS. Molar masses were determined from a calibration curve based on linear polystyrene standards. The actual molar masses of the polystyrene stars were calculated from the response of a multiangle laser light scattering detector (Wyatt Technology) that was connected to a SEC (MALLS/SEC) line. The d*n*/d*c* values for polystyrene star were measured in THF at 25 °C with a laser

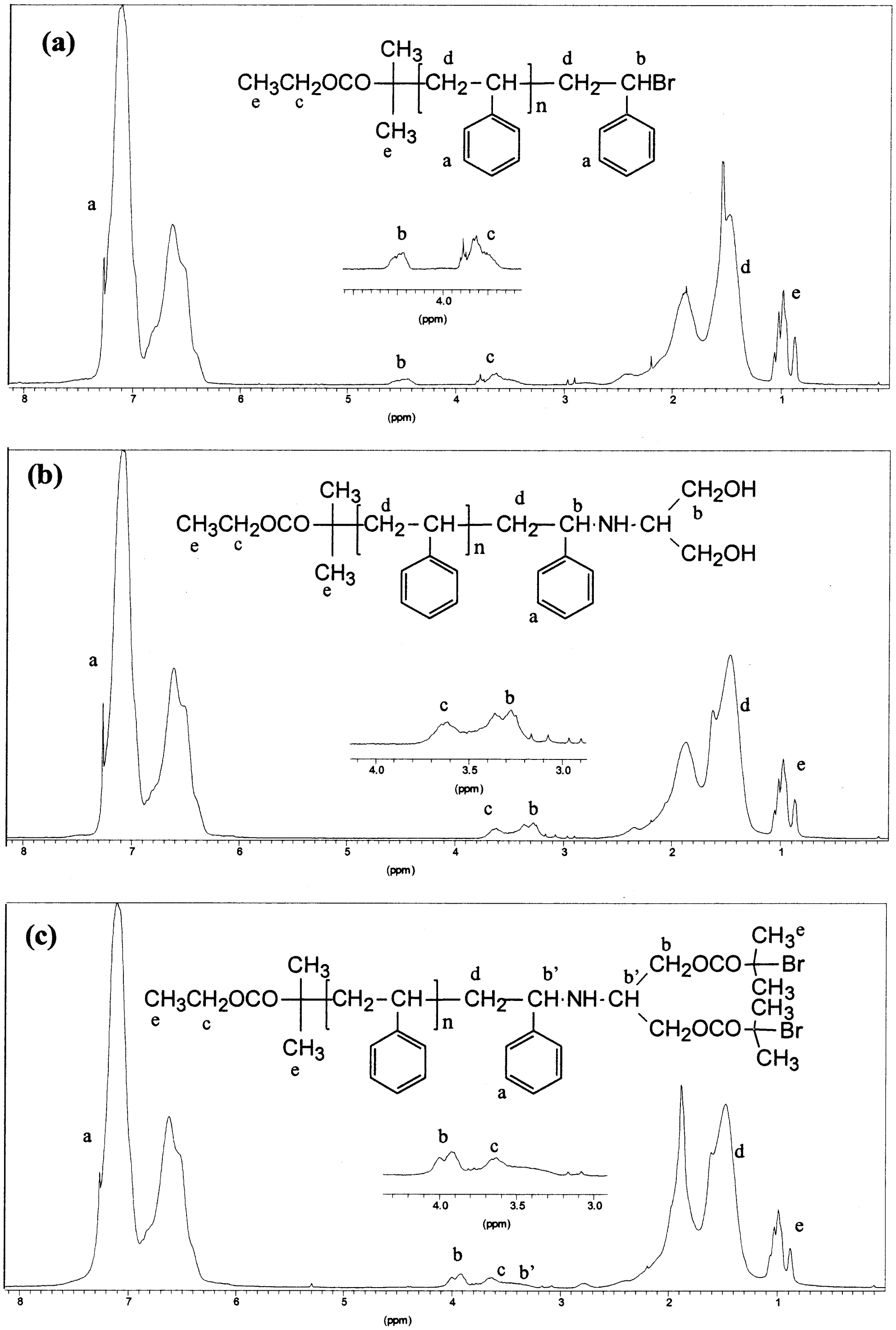


Figure 1. ^{1}H NMR spectra of various precursors: (a) PS(Br), (b) PS(OH)$_2$, and (c) PS with two ATRP sites PS(Br)$_2$.

source (633 nm) and were found to be the same as that of linear polystyrene (dn/dc = 0.183 cm^3/g).

MALDI−TOF mass spectrometry was performed using a Micromass TofSpec E spectrometer equipped with a nitrogen laser (337 nm), a delay extraction, and a reflector. The MALDI mass spectra represent averages over 100 laser shots. This instrument operated at an accelerating potential of 20 kV. The polymer solutions (10 g L^{-1}) were prepared in THF. The matrix solution (1,8-dithranol-9(10*H*)-anthracenone, dithranol) was dissolved in THF. The polymer solution (2 μL) was mixed with 20 μL of the matrix solution, and 2 μL of a sodium iodide solution (10 g L^{-1} in methanol) was added to favor ionization by cation attachment. The final solution (1 μL) was deposited onto the sample target and allowed to dry in air at room temperature. Internal standards (poly(ethylene oxide)) were used to calibrate the mass scale. Infrared measurements were performed using a 320 FT-IR spectrometer (Nicolet). A solution of polymer in CH_2Cl_2 was deposited on a NaCl pellet, and the polymer was analyzed after evaporation of solvent.

Results and Discussion

Synthesis and Derivatization of Linear Polystyrene Precursors to Both Asymmetric and Miktoarm Stars. Our approach to preparing asymmetric and miktoarm stars (Scheme 1) is based on a four-step sequence consisting in the synthesis (i) of well-defined ω-halogen-terminated polystyrene by ATRP followed by derivatization (ii and iii) of the halogen end groups of these polymers into twice as many halogenester func-

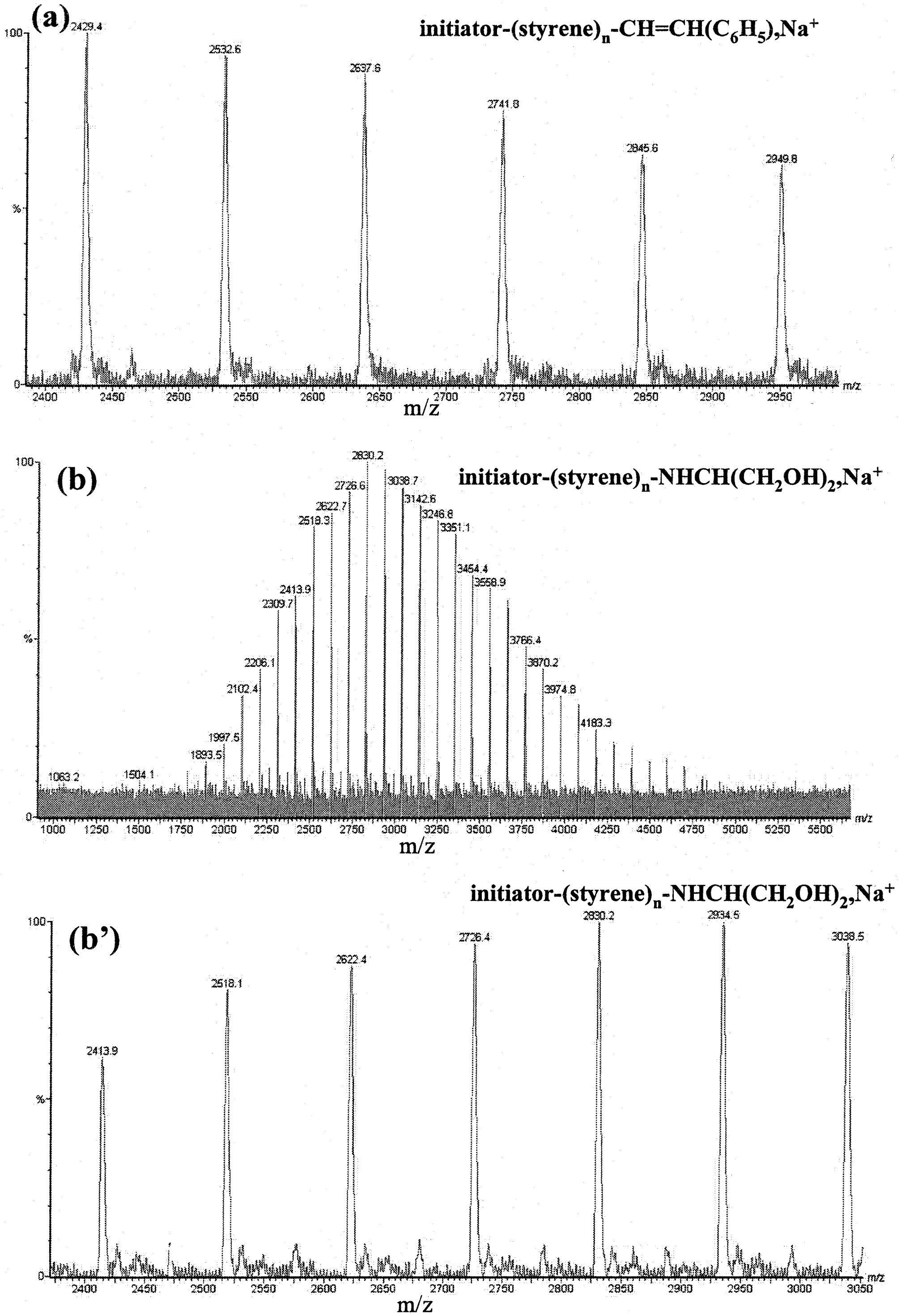


Figure 2. MALDI−TOF mass spectra of PS(Br) (a) and PS(OH)$_2$ (b and b′): $M_n = 2100$, $M_w/M_n = 1.14$; initiator: $CH_3CH_2OCOC(CH_3)_2$.

tions serving subsequently (iv) to initiate the ATRP of either styrene or another monomer (e.g., *tert*-butyl acrylate).

Thus, well-defined ω-bromopolystyrenes (PS) were first synthesized on a large scale by ATRP. To accurately monitor the subsequent chemical modification of the bromo end groups by ^{1}H NMR, low molar mass PS samples were targeted. Ethyl 2-bromoisobutyrate was used as the initiator for the polymerization of styrene, which was performed in bulk at 100 °C with CuBr/PMDETA (1/1) as the catalytic system (Scheme 2). The theoretical ($M_n = 2100$ g/mol) and experimental ($M_n = 2150$ g/mol) molar masses of the obtained PS, denoted PS(Br) in the following part, agreed well (conversion of 17% and polymerization time of 25 min), and the molar mass distribution was narrow ($M_w/M_n = 1.14$).

The next steps (ii) and (iii) in the synthesis of both asymmetric and miktoarm stars consisted in the preparation of ω,ω'-bis(bromo) macroinitiators, which are linear polymers functionalized with two gemini initiating sites for ATRP. Previous means to end-functionalize ATRP-derived polymers include the displacement of halogen end groups by electrophilic substitution described by Matyjaszewski et al.[21,22] to introduce azide end groups. The same team also resorted to nucleophilic substitution to replace the halogen end groups of either polystyrene or poly(methyl acrylate) by hydroxyl functions, using either ethanolamine or 4-aminobutanol.[23] More recently, Macosko et al.[24] described the synthesis of mid-phthalic anhydride polymers by ATRP: they synthesized a novel α-bromoester initiator in six steps, including derivatization of a bromide intermediate with diethanolamine and its subsequent esterification in the last two steps. We followed a similar, though less complicated, strategy than the aforementioned to introduce two bromo ester groups at the ω-end of our PS(Br) chains. 2-Amino-1,3-propanediol (serinol) was reacted in excess with PS(Br) in dimethylformamide at 30 °C for 72 h. The final polymer, denoted $PS(OH)_2$, was pure by ^1H NMR analysis and by MALDI−TOF mass spectroscopy. Figure 1 shows that the CH(Ph)−Br signal at δ 4.5 ppm totally vanished and that a new signal assignable to the CH_2OH protons appears at δ 3.3 ppm.

The efficiency of functionalization was confirmed by analysis of PS(Br) and $PS(OH)_2$ by MALDI−TOF mass spectrometry. The MALDI−TOF spectrum of the parent PS(Br) is presented in Figure 2a. A single distribution is observed with a peak-to-peak mass increment of 104 g mol^{-1}, corresponding to the molar mass of styrene. This series of peaks can be attributed to the following chemical structure: (initiator−(styrene)$_n$−CH=CH-(C_6H_5),Na^+); the experimental and calculated molar masses agree very well. Elimination of HBr obviously occurred during MALDI−TOF characterization, in agreement with the results published by Pascual et al.[25] The MALDI−TOF spectrum of $PS(OH)_2$ is presented in Figure 2b,b′. The previous distribution corresponding to PS(Br) has totally vanished, and the new distribution perfectly matches the expected one (initiator−(styrene)$_n$−NHCH($CH_2OH)_2$),Na^+).

Two gemini ATRP sites were introduced in a second step at the termini of the PS chains by esterification of the hydroxyl functions of $PS(OH)_2$ with 2-bromoisobutyryl bromide in the presence of triethylamine. ^1H NMR spectroscopy (Figure 1c) showed the appearance of a broad signal between δ 3.9 ppm and 4.1 ppm due to the protons of the CH_2OCOC($CH_3)_2$Br group and the disappearance of the upfield CH_2OH peak (δ 3.3 ppm). A small signal assignable to the protons of the −CHNHCH− group was observed around δ 3.2−3.5 ppm. According to SEC, the average molar mass of this PS sample, denoted $PS(Br)_2$, is 2600 g mol^{-1} (M_w/M_n = 1.10), in agreement with the 450 increase due to the modification of PS(Br) into $PS(Br)_2$ (Figure 3, chromatograms a and b). The MALDI−TOF spectrum of $PS(Br)_2$ was complicated by the partial elimination of HBr and is therefore not presented here.

Synthesis of $PS(PS')_2$ Asymmetric Stars. The synthesis of asymmetric stars was achieved upon using $PS(Br)_2$ as a gemini macroinitiator for ATRP of styrene. CuBr/PMDETA complex was employed as the catalytic system, and all the polymerization experiments were conducted in bulk at 100 °C. On the basis of our experience in the synthesis of core-first stars by copper-mediated ATRP,[10] the polymerization was discontinued at rather low monomer conversion (<50%) to minimize the occurrence of side reactions such as star−star coupling. Another way to reduce the probability for growing radicals to undergo irreversible terminations was to maintain a low concentration of propagating radicals. This could be achieved by taking high ratios of monomer to the initiator or by using low transition metal catalyst loading. Table 1 summarizes the data of our asymmetric star synthesis.

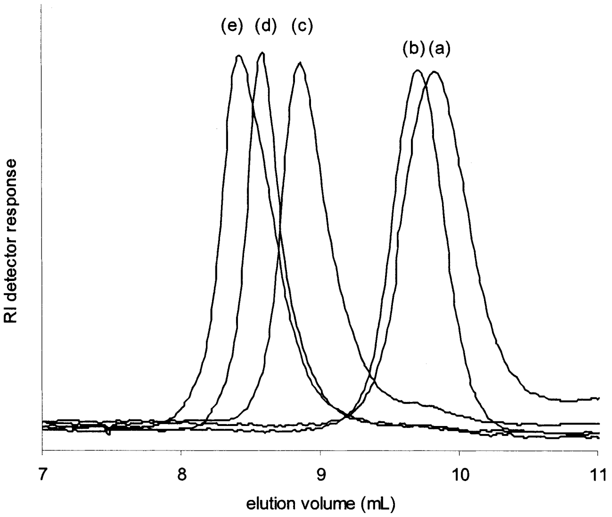


Figure 3. Size exclusion chromatograms of $PS(PS')_2$ polystyrene asymmetric stars and its precursors (RI response): (a) PS(Br) M_n = 2100, M_w/M_n = 1.14; (b) $PS(Br)_2$ M_n = 2600, M_w/M_n = 1.10; (c) $PS(PS')_2$ M_n = 8600, M_w/M_n = 1.26; (d) $PS(PS')_2$ M_n = 18 800, M_w/M_n = 1.14; (e) $PS(PS')_2$ M_n = 19 500, M_w/M_n = 1.21.

Table 1. $PS(PS')_2$ Asymmetric Polystyrene Stars Prepared by ATRP at 100 °C with CuBr/PMDETA in the Presence of $PS(Br)_2$ Macroinitiator

	macroinitiator $PS(Br)_2$		$PS(PS')_2$ star			
run	M_n	M_w/M_n	conv (%)	$M_{n,th}$[a]	M_n[b]	M_w/M_n
1	2100	1.14	16	9 200	8 600	1.26
2	2100	1.14	35	16 700	18 800	1.14
3	2100	1.14	43	21 000	19 500	1.21
4	2800	1.12	10	7 150	7 200	1.24
5	2800	1.12	33	16 500	17 100	1.19
6	2800	1.12	56	26 400	41 800[c]	1.25

[a] Theoretical molar mass: $M_{n,th}$ = (conversion × [styrene]/[macroinitiator] × M_m) + Mi, where M_m and Mi are the molar masses of styrene (104 um) and macroinitiator, respectively. The ratio [styrene]/[macroinitiator] is equal to 400 in this case. [b] Molar mass determined by MALLS. [c] For high conversion (>50%), irreversible coupling reaction occurs as attested by a shoulder in the high molar masses region of the SEC chromatogram and deviation from the expected M_n value.

Figure 3 shows that the average molar mass increased with monomer conversion in the case of styrene polymerization, attesting to the formation of additional PS blocks. The disappearance of the peak of the $PS(Br)_2$ precursor meant that the majority of the precursor chains efficiently participated in the initiation of subsequent PS blocks. In this way, samples denoted $PS(PS')_2$ with molar mass between 8000 and 50 000 g mol^{-1} could be obtained with narrow distribution (1.1 < M_w/M_n < 1.3) and free of any $PS(Br)_2$ precursor. In addition, we checked that no shoulder appeared in the high molar mass region by using SEC equipped with a multiangle laser light scattering detector (MALLS). Both light scattering and refractometric detections proved superimposable, and monomodal traces were observed. This indicated the absence of side populations due to irreversible couplings between stars. The characterization by MALLS/SEC allowed to calculate the absolute molar masses of the samples. The values delivered by MALLS matched the theoretical values,

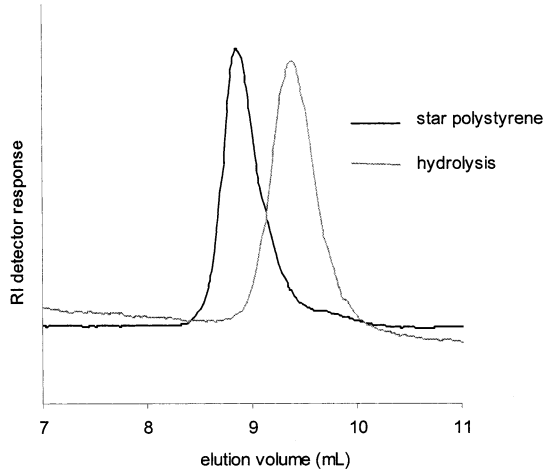


Figure 4. Size exclusion chromatograms of PS polymers (RI response): (A) PS(PS′) asymmetric star before hydrolysis (M_n = 17 100 and M_w/M_n = 1.19, run 8 in Table 1) and (B) after hydrolysis (M_n = 8400 and M_w/M_n = 1.28).

Table 2. Arm Hydrolysis of (PS)(PS′)$_2$ Asymmetric Star by Reaction with KOH

run	M_n of PS precursor	before hydrolysis		after hydrolysis	
		M_n	M_w/M_n	M_n	M_w/M_n
7	2100	8600	1.26	4000	1.14
8	2800	17100	1.19	8400	1.28

thus indicating that these asymmetric PS stars were homogeneous in size and functionality.

One way to account for the quality of such PS stars was to detach the arms from the core for analysis purpose. The PS(PS′)$_2$ samples were thus submitted to hydrolysis by treatment under basic conditions (KOH in THF/ethanol solution) to cleave the ester functions linking the three PS arms. The results are presented in Table 2, and the SEC chromatograms obtained before and after hydrolysis are given in Figure 4. For example, hydrolysis of the star sample of 17 100 g/mol that was grown from the polystyrene precursor (run 8 in Table 2) of 2800 g/mol afforded chains of 8400 g/mol molar mass, which is a value rather close to the expected molar mass for the PS arms of second generation.

Synthesis of PS(PtBA)$_2$ and PS(PAA)$_2$ Miktoarms Stars. Poly(*tert*-butyl acrylate) arms were grown by ATRP from the same PS(Br)$_2$ precursors as those used for the synthesis of PS asymmetric stars. Similar conditions to those applied for the synthesis of PS(PS′)$_2$ were used except for temperature, which was varied from 80 to 100 °C. The data pertaining to these experiments and the molecular features of the samples recovered are presented in Table 3. As expected for ATRP of an acrylate-type monomer, the polymerization was very fast in contrast to the styrene case under the same conditions. Characterization by SEC confirmed the growth of the P*t*BA blocks from the PS(Br)$_2$ precursor and the efficiency of the crossover reaction. Moreover, the low polydispersity values (<1.3) indicated a controlled growth of the P*t*BA arms. A small shoulder in the low molar mas region (Figure 5c) attributable to unreacted PS(Br)$_2$ could, however, be detected in the SEC traces of the first aliquot, indicating a rather slow initiation. The relative content of PS and P*t*BA was calculated by ^{1}H NMR upon comparing the intensity of the signals due to aromatic protons to that at 1.5 ppm attributable to the protons of P*t*BA *tert*-butyl groups (see note *b* in Table 3). Knowing the accurate molar mass of the PS(Br)$_2$ precursor, NMR analysis was reliable enough to determine the actual molar mass of these copolymers, noted PS(P*t*BA)$_2$. In this calculation, however, it was assumed that the 2-isobutyrate sites of PS(Br)$_2$ efficiently initiated the ATRP of *tert*-butyl acrylate. It can be seen in Table 3 that the theoretical and experimental molar masses are in good agreement. This further supported the well-defined architecture of these new miktoarm stars.

Table 3. Synthesis of (PS)(P*t*BA)$_2$ Miktoarm Star Starting from PS(Br)$_2$ Precursor

run	PS(Br)$_2$ precursor		miktoarm star PS(P*t*BA)$_2$			
	M_n	M_w/M_n	conv (%)	$M_{n,th}$[a]	M_n[b]	M_w/M_n
9	2100	1.14	24	15 000	14 000	1.16
10[c]	2600	1.10	3	11 300	9 300	1.30
10[c]	2600	1.10	15	46 300	38 500	1.30
12	2500	1.19	36	21 400	17 100	1.19
13	2500	1.19	57	32 000	27 200	1.26
14	2500	1.19	70	38 700	36 200	1.28

[a] Theoretical molar mass: $M_{n,th}$ = (conversion × [*tert*-butyl acrylate]/[macroinitiator] × M_m) + Mi, where M_m and Mi are the molar masses of monomer (128 um) and the macroinitiator, respectively. The ratio [*tert*-butyl acrylate]/[macroinitiator] is equal to 400 in this case. [b] Molar mass determined by ^{1}H NMR knowing the molar mass of PS(Br) precursor: the relative content in P*t*BA was calculated by integration of the peak between 1 and 2 ppm after subtracting the integration of the methylene and methyne protons of the polymer chains. The following expression was used: $I_{7\ \mathrm{ppm}}/I_{1-3\ \mathrm{ppm}} = 3n + 9m + 3m/5n$, where n and m are the degree of polymerization of the PS block and P*t*BA block, respectively. [c] These polymerizations of *tert*-butyl acrylate were performed at 80 °C, and the ratio [*tert*-butyl acrylate]/[macroinitiator] is equal to 2200; all other polymerizations were performed at 100 °C.

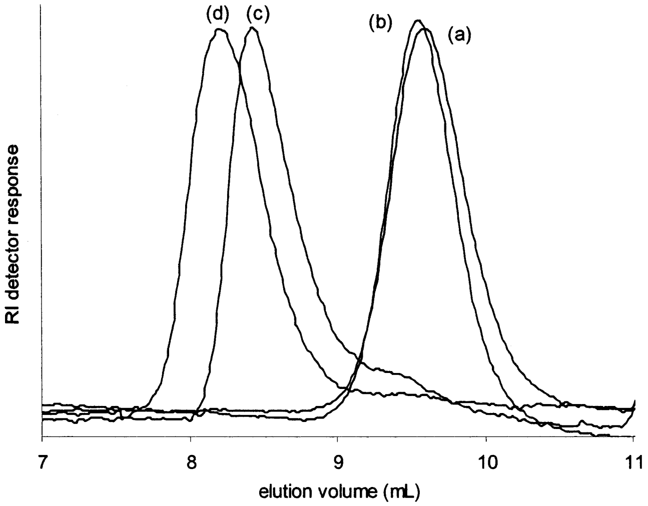


Figure 5. Size exclusion chromatograms of PS(P*t*BA)$_2$ miktoarm stars and its precursors (RI response): (a) PS precursor PS(Br) M_n = 2500, M_w/M_n = 1.14; (b) PS difunctional macroinitiator PS(Br)$_2$ M_n = 2900, M_w/M_n = 1.16; (c) PS(P*t*BA)$_2$ M_n = 17 400, M_w/M_n = 1.19; (d) PS(P*t*BA)$_2$ M_n = 28 800, M_w/M_n = 1.28.

The obtainment of PS(P*t*BA)$_2$ miktoarm stars offered the opportunity to hydrolyze the P*t*BA *tert*-butyl ester groups in order to derive PS(PAA)$_2$ stars. The cleavage reaction of the *tert*-butyl groups was performed by adding an excess of trifluoroacetic acid in dichloromethane at room temperature for 24 h, following a well-established procedure.[26] The reaction was monitored by ^{1}H NMR and by infrared (IR). The ^{1}H NMR spectra showed a decrease of the signal at 1.5 ppm due to the removal of the *tert*-butyl protons of the PtBA

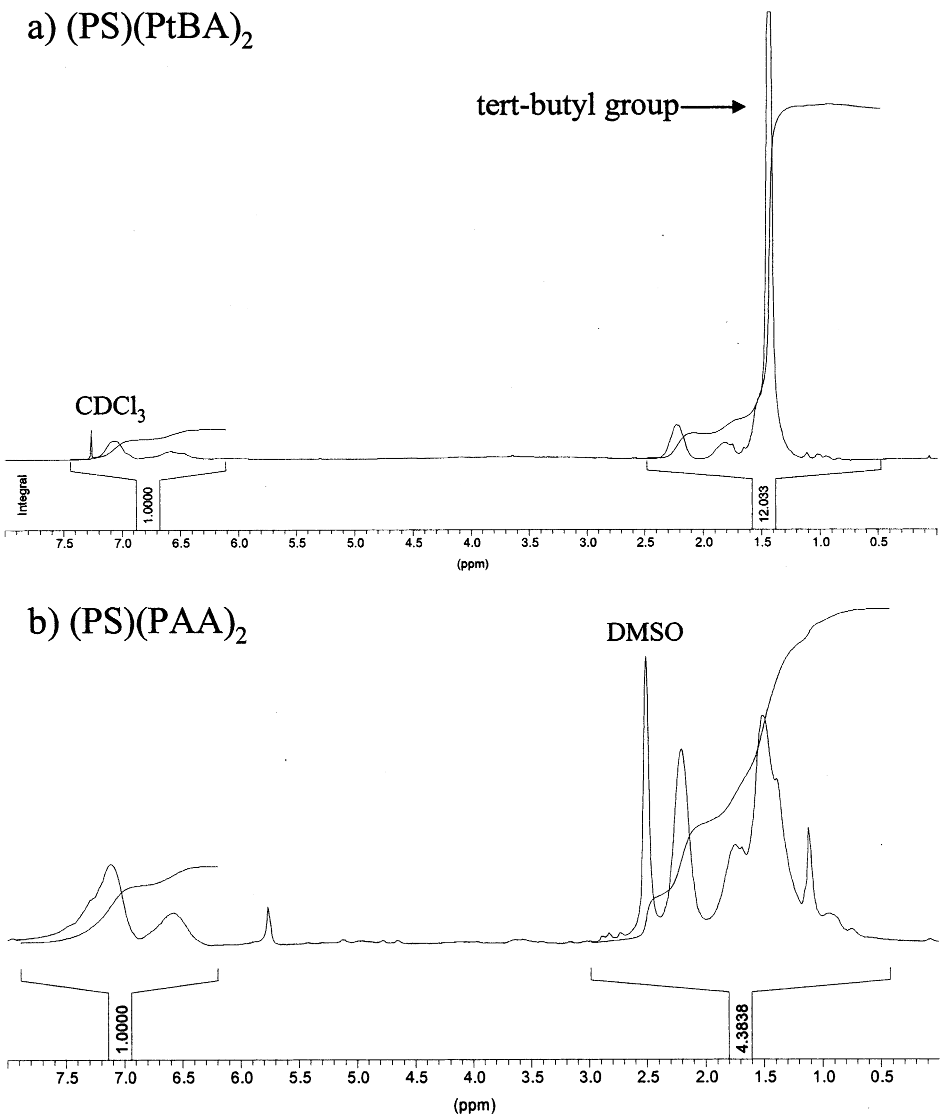


Figure 6. ^{1}H NMR of (a) PS(P*t*BA)$_2$ miktoarm star with a molar mass of 19 300 and (b) PS(PAA)$_2$ after hydrolysis under acidic conditions.

blocks. The evolution of the signals appearing in the 1.5−2 ppm region before and after reaction is indicative of a quantitative hydrolysis. In addition, IR spectroscopy analyses of such PS(PAA)$_2$ samples showed that *tert*-butyl ester functions of PS(P*t*BA)$_2$ were all removed upon hydrolysis (no band at 1728 cm^{-1}) and replaced by carboxylic acids as indicated by the broad band seen in the 3050−3500 cm^{-1} region. Solution properties of these new amphiphilic copolymers are currently under investigation.

Conclusion

This paper described a new methodology to synthesize AA′$_2$-type asymmetric and AB$_2$-type miktoarm stars. Atom transfer radical polymerization was followed with chemical transformation of the chain ends to obtain PS(PS′)$_2$ and PS(P*t*BA)$_2$ stars in a controlled and simple manner. Subsequent acidic treatment of PS(P*t*BA)$_2$ miktoarm stars to hydrolyze the *tert*-butyl ester groups afforded amphiphilic PS(PAA)$_2$ miktoarm stars carrying one polystyrene arm and two poly(acrylic acid) ones. This synthetic methodology can now be applied to assemble a wide range of polymeric chains in dendrimer-like topologies. In this case, multifunctional initiators would be required instead of monofunctional ones as described here. Such a synthetic pathway to dendritic polymers consisting of macromolecular generations is currently under investigation.

Acknowledgment. The authors thank CNRS and the Ministry of Education, Government of France, for the postdoctoral assistance to Raju Francis.

References and Notes

(1) (a) Matyjaszewski, K. *Chem.—Eur. J.* **1999**, *5*, 3095. (b) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (c) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3686.

(2) (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, G.; Hamer, G. K. *Macromolecules* **1993**, *26*, 5316. (b) Hawker, C. J. *Trends Polym. Sci.* **1994**, *4*, 183. (c) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661.

(3) (a) Chiefari, J.; Chong, Y. K.; Ercole, F.; Kristina, J.; Jeffrey, J.; Le, T. P.; Mayadunne, R. T.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559. (b) Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Ercole, F.; Kristina, J.; Jeffrey, J.; Le, T. P.; Mayadunne, R. T.; Meijs, G. F.; Moad, C. L.; Moad, G. *Macromol. Symp.* **1999**, *143*, 291.

(4) (a) Heise, A.; Hedrick, J. L.; Trollsas, M.; Miller, R. D.; Frank, C. W. *Macromolecules* **1999**, *32*, 231. (d) Haddleton, D. M.;

Waterson, C. *Macromolecules* **1999**, *32*, 8732. (e) Wu, X.; Fraser, C. L. *Macromolecules* **2000**, *33*, 4053. (f) Ueda, J.; Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 557. (g) Kasko, A. M.; Heintz, A. M.; Pugh, C. *Macromolecules* **1998**, *31*, 256. (h) Ueda, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6762.

(5) (a) Heise, A.; Hedrick, J. L.; Franck, C. W.; Miller, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 8647. (b) Heise, A.; Nguyen, C.; Malek, R.; Hedrick, J. L.; Franck, C. W.; Miller, R. D. *Macromolecules* **2000**, *33*, 2346.

(6) (a) Haddleton, D. M.; Waterson, C. *Macromolecules* **1999**, *32*, 8732. (b) Wu, X.; Fraser, C. L. *Macromolecules* **2000**, *33*, 4053. (c) Ueda, J.; Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 557. (d) Kasko, A. M.; Heintz, A. M.; Pugh, C. *Macromolecules* **1998**, *31*, 256. (e) Ueda, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6762.

(7) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.

(8) Matyjaszewski, K. In *Controlled/Living Radical Polymerization: Progress in ATRP, NMP and RAFT*; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000.

(9) (a) Matyjaszewski, K.; Miller, P. J.; Fossum, E.; Nagakawa, Y. *Appl. Organomet. Chem.* **1998**, *12*, 667. (b) Matyjaszewski, K.; Miller, P. J.; Pyun, J.; Kickelbick, G.; Diamanti, S. *Macromolecules* **1999**, *32*, 6526.

(10) (a) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. *Macromolecules* **1998**, *31*, 7218. (b) Angot, S.; Murthy, K. S.; Taton, D.; Gnanou, Y. *Macromolecules* **2000**, *33*, 7261.

(11) (a) Ueda, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 6762. (b) Percec, V.; Barboiu, B.; Bera, T. K.; Van der Sluis, Grubbs, R. B.; Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4776.

(12) Haddleton, D. M.; Edmonds, R.; Heming, A. M.; Kelly, E. J.; Kukulj, D. *New J. Chem.* **1999**, *23*, 477.

(13) Haddleton, D. M.; Heming, A. M.; Jarvis, A. P.; Khan, A.; Marsh, A.; Perrier, S.; Bon, S. A.; Jackson, S. G.; Edmonds, R.; Kelly, E.; Kukulj, D.; Waterson, C. *Macromol. Symp.* **2000**, *157*, 201.

(14) Hovestad, N. J.; Van Koten, G.; Bon, S. A. F.; Haddleton, D. M. *Macromolecules* **2000**, *33*, 4048.

(15) Percec, V.; Barboiu, B.; Bera, T. K.; Van der Sluis, Grubbs, R. B.; Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4776.

(16) (a) Collins, J. E.; Fraser, C. L. *Macromolecules* **1998**, *31*, 6715. (b) Fraser, C. L.; Davis, A. P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *33*, 4704. (c) Johnson, R. M.; Corbin, P. S.; Ng, C.; Fraser, C. L. *Macromolecules* **2000**, *33*, 7404. (d) Wu, X.; Fraser, C. L. *Macromolecules* **2000**, *33*, 7776. (e) Wu, X.; Collins, J. E.; McAlvin, J. E.; Cutts, R. W.; Fraser, C. L. *Macromolecules* **2001**, *34*, 2812.

(17) Hadjichristidis, N. J. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857.

(18) (a) Hadjichristidis, N. J. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 857. (b) Hadjichristidis, N. J.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747.

(19) Heise, A.; Trollsas, M.; Magbitang, T.; Hedrick, J. L.; Franck, C. W.; Miller, R. D. *Macromolecules* **2001**, *34*, 2798.

(20) (a) Guo, Y. M.; Pan, C. Y.; Wang, J. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2134. (b) Guo, Y. M.; Xu, J.; Pan, C. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 437.

(21) Coessens, V.; Nakagawa, Y.; Matyjaszewski, K. *Polym. Bull. (Berlin)* **1998**, *40*, 135.

(22) Coessens, V.; Matyjaszewski, K. *J. Macromol. Sci.* **1999**, *A36*, 667.

(23) Coessens, V.; Matyjaszewski, K. *Macromol. Rapid Commun.* **1999**, *20*, 127.

(24) Moon, B.; Hoye, T. R.; Macosko, C. W. *Macromolecules* **2001**, *34*, 7941.

(25) Pascual, S.; Coutin, B.; Tardi, M.; Polton, A.; Vairon, J. P.; Chiarelli, R. *Macromolecules* **2001**, *34*, 5752.

(26) Ma, Q.; Wooley, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4805.

MA020872G