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Synthesis of (Poly(chloroethyl vinyl ether)-*g*-polystyrene)comb-*b*-(poly(chloropyran ethoxy vinyl ether)-*g*-polyisoprene)comb Copolymers and Study of Hyper-Branched Micelle Formation in Dilute Solutions

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ABSTRACT: Poly(styrene)comb-*b*-poly(isoprene)comb copolymers having a heterofunctional polyvinyl ether diblock backbone were synthesized by the grafting onto method. Their synthesis involves in a first step the selective coupling reaction of polystyryllithium chains onto the reactive chloroether functions of a poly(chloroethyl vinyl ether) first block while the second block poly(pyranethoxy vinyl ether) remains unchanged, yielding Poly(styrene)comb with a poly(pyranethoxy vinyl ether) tail. In a second step, living polyisoprenyllithium chains are grafted onto the second block previously modified to introduce reactive chlorobutyl functions. The obtained high molar masses PScomb-*b*-PIcomb copolymers exhibit a low polydispersity and a controlled number of branches. Their characteristics and behavior were further studied as isolated objects using imaging technique such as atomic force microscopy and using light scattering in a good solvent for PS and PI moieties, and in a selective solvent of PIcomb blocks. The PScomb-*b*-PIcomb copolymers adopt a cylindrical conformation in good solvent and self-assemble in micelles by association of the combPS blocks in heptane.

1. Introduction

Different types of organization and assembly of linear copolymers have been observed in solution and in bulk.[1,2] Besides other molecular parameters such as chemical composition, comonomer unit distribution, molar masses, polydispersity, etc., chain architecture plays an important role in the solution behavior of macromolecules and in their self-assembly process to form a variety of micelle morphology. Recently, regularly branched macromolecules such as comb type copolymers have attracted a growing interest because of their unique chain topology.[3−10] Although a large number of publications have been dedicated to the synthesis of comb-like block copolymers,[11−28] a limited number of studies have concerned a detailed investigation of their organization and behavior in solution and in bulk.[29−35]

In this paper we describe the synthesis and the characteristics in solution of a series of PScomb-*b*-PIcomb diblock-like copolymers, (polychloroethyl vinyl ether-*g*-polystyrene)-*b*-poly(chloropyranethoxy vinyl ether-*g*-polyisoprene), (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI). These multibranched copolymers can be visualized as two comb polymers of different chemical composition connected to each other by one end of their backbone. The solution properties of these PScomb-*b*-PIcomb copolymers and their capacity to self-assemble have been investigated using dynamic and static light scattering (DLS/SLS) in various solvents, either good for both the PS and PI moieties or selective of the PI blocks as well as in thin deposits by atomic force microscopy (AFM).

2. Experimental Section

2.1. Materials. Cyclohexane and toluene (99.5%, J. T. Baker, Deventer, The Netherlands) were purified by distillation over calcium hydride and stored over polystyryllithium seeds. DMF (99% J.T. Baker) was purified by distillation over molecular sieves. α-Chloroethyl vinyl ether (CEVE) (99%, Sigma-Aldrich Chimie, Saint Quentin Fallavier, France) was washed with an aqueous NaOH solution (1 N) and distilled twice over calcium hydride. Styrene and Isoprene (99%, Sigma-Aldrich Chimie, Saint Quentin Fallavier, France) were purified by distillation over calcium hydride at reduced pressure and stored over dibutyl magnesium. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) (99.5%, Sigma-Aldrich Chimie, Saint Quentin Fallavier, France) was dried and purified by distillation over sodium. *sec*-Butyllithium (1.3 M in cyclohexane, Sigma-Aldrich Chimie, Saint Quentin Fallavier, France) was used as received. All the reactants were stored under dry nitrogen in glass apparatus fitted with PTFE stopcocks.

HCl gas (Setic Labo France) was used as received. Zinc chloride (Sigma Aldrich Saint Quentin Fallavier, France) was dissolved in dry diethyl ether (solution at 0.155 mol L^{-1}).

2.2. Synthesis. 2-Acetoxyethyl Vinyl Ether (AcEVE). A 20 mL (0.20 mol) sample of chloroethyl vinyl ether was added to 36 g (0.38 mol) of potassium acetate in the presence of tetrabutylammonium bromide (10 g, 0.03 mol) and stirred at 80 °C in DMF for 24 h. The methylene dichloride mixture was then washed several times with water and AcEVE was recovered by solvent evaporation and distillation (yield: 17 g). It was finally characterized by ^{1}H NMR (δ in ppm): 6.18−6.28 ($=CH-O-$, 1H), 4.02−4.06 and 3.62−3.66 ($-O-CH_2-CH_2-O-$, 4H), 3.91−3.99 and 3.77−3.80 ($-H_2C=$, 2H).

3,4-Dihydro-2*H*-pyran-2-(4 chlorobutyl methyl ether). A 200 mL (1.83 mol) sample of dichlorobutane was added to 10 mL (0.097 mol) of 3,4-dihydro-2*H*-pyran-2-methanol) in the presence of tetrabutylammonium bromide (26 g, 0.08 mol) under basic conditions (100 mL of a 50% sodium hydroxide solution) for 24 h. The product solution was then washed several times with a NaOH solution, and the resulting chlorobutyl functionalized cyclic acetal was recovered by distilled over CaH_2 (yield: 8 g) and characterized by ^{1}H NMR (δ in ppm): 6.2 ($-CH{=}CH-O-$, 1H), 4.5 ($-CH{=}CH-O-$, 1H), 3.8 ($-O-CH-CH_2$, 2H), 3.3−3.5 ($-CH_2-O-$ and $-CH_2Cl$, 6H), 1,5−2 ($-CH_2-$, 8H).

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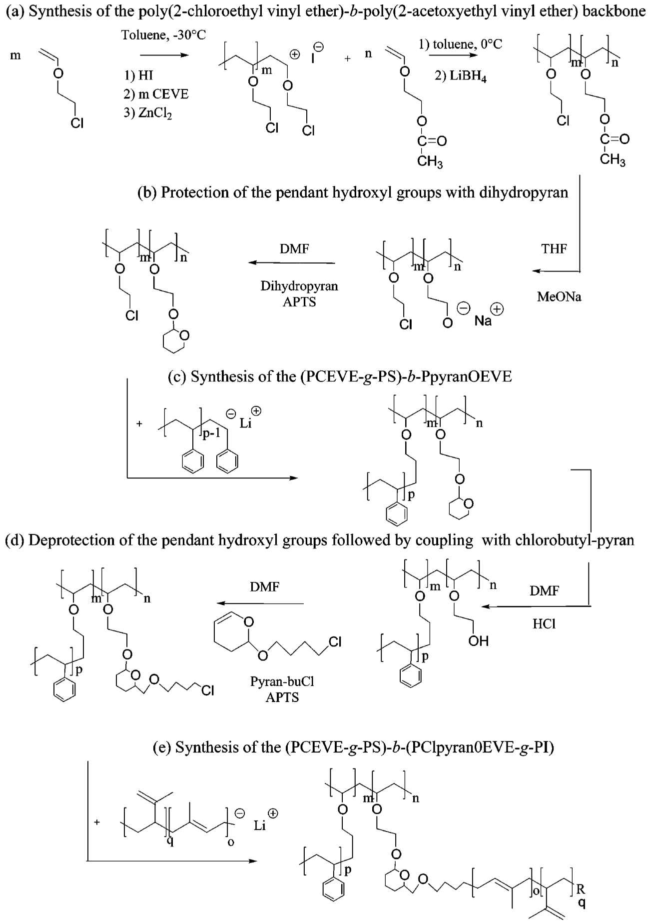
Scheme 1


(a) Synthesis of the poly(2-chloroethyl vinyl ether)-*b*-poly(2-acetoxyethyl vinyl ether) backbone

(b) Protection of the pendant hydroxyl groups with dihydropyran

(c) Synthesis of the (PCEVE-*g*-PS)-*b*-PpyranOEVE

(d) Deprotection of the pendant hydroxyl groups followed by coupling with chlorobutyl-pyran

(e) Synthesis of the (PCEVE-*g*-PS)-*b*-(PClpyran0EVE-*g*-PI)

2.3. Polymerization Procedures. Synthesis of the PCEVE-*b*-PAcEVE Backbone. PCEVE-*b*-PAcEVE (**1**), used as the central backbone diblock, was prepared by living cationic polymerization of chloroethyl vinyl ether (13 g, 0.122 mol) at −30 °C in toluene using hydrogen iodide, HI (0.31 mmol), as initiating system and zinc chloride in diethyl ether (2 mL solution, 0.1 mmol) as catalyst. The evolution of the PCEVE molar mass with time was followed by sampling the polymerization solution under high vacuum followed by SEC analysis. After quantitative CEVE conversion ($\bar{M}_n$(SEC) = 41000 g/mol, $\{\bar{M}_w\}/\{\bar{M}_n\}$ = 1.07, 2-acetoxyethyl vinyl ether (AcEVE) (16 g, 0.123 mol) was then added to the polymerization system to form the second polymer block and polymerization was carried out at 0 °C for 12 h. The polymerization was terminated by addition of $LiBH_4$ (2 M solution in THF) in excess, thus yielding poly(chloroethyl vinyl ether)-*b*-poly(2-acetoxyethyl vinyl ether) block copolymer (**1**) (Scheme 1a). The polymer solution was then washed several times with a solution of potassium thiosulfate and neutral water and the polymer was precipitated in methanol. **1** was finally recovered by solvent evaporation and characterized (yield 28 g, $\bar{M}_n$(diblock) = 89100 determined by ^{1}H NMR), .

Synthesis of (PCEVE-g-PS)-*b*-PpyranOEVE Copolymers. The acetoxy side groups of the PAcEVE (**1**) were hydrolyzed by polymer treatment in THF with an excess of sodium methanolate at 20 °C for 2 h. A HCl solution (0.1 N) was then added to the system to neutralize the solution and the polymer was precipitated several times in diethyl ether and dried to yield poly(chloroethyl vinyl ether)-*b*-poly(2-hydroxyethyl vinyl ether) (**2**) block copolymer. To protect hydroxyl groups (Scheme 1b) as the tetrahydropyranyl ether, the copolymer (1 g, 2.5 × 10^{-3} mol) was dissolved in dry DMF and reacted under stirring at room temperature with 3,4-dihydro-2*H*-pyran (10 mmol) in the presence of 50 mg (2.5 × 10^{-4} mol) of *p*-toluenesulfonic acid. After addition of dichloromethane, the resulting linear block copolymer **3** was washed several times with water, precipitated into methanol, and characterized by ^{1}H NMR.

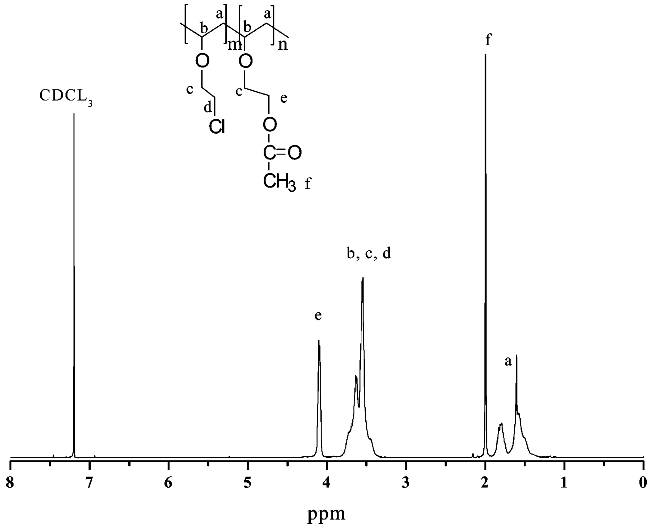


Figure 1. 400 MHz ^{1}H NMR spectrum of polychloroethyl vinyl ether-*b*-polyacetoxy ethyl vinyl ether diblock copolymer (**1a**). Solvent $CDCl_3$

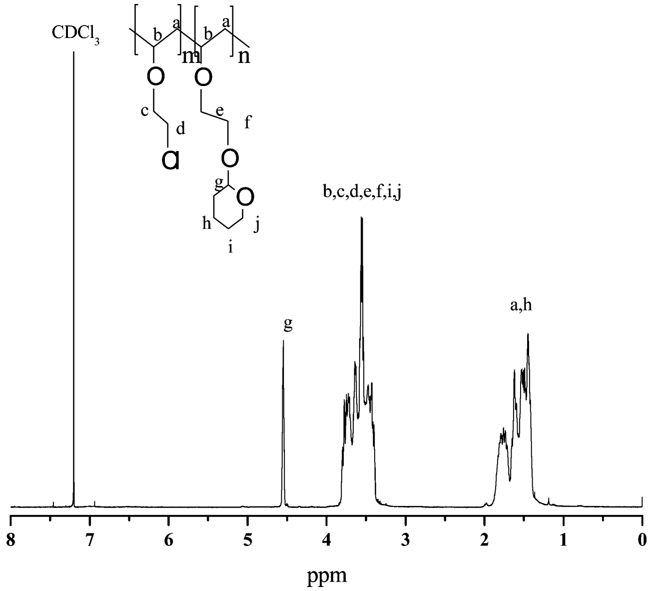


Figure 2. ^{1}H NMR spectrum of poly(chloroethyl vinyl ether)-*b*-poly(pyranethoxy vinyl ether) diblock copolymer (**3a**). Solvent: $CDCl_3$.

A cyclohexane solution of living polystyryllithium chains was then progressively added to a weighted amount of PCEVE-*b*-PpyranOEVE (**3**), previously degassed under vacuum and dissolved in dry THF, to form comb-like copolymer **4** (PCEVE-*g*-PS)-*b*-PpyranOEVE with polystyrene branches, (Scheme 1c). Selective precipitation of the polymer/cyclohexane solution by slow addition of heptane allows us to recover the PS comb free of ungrafted linear PS.

Synthesis of (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI), PScomb-*b*-PIcomb Copolymers. The pendant pyran groups of the pyranOEVE units of the (PCEVE-*g*-PS)-*b*-PpyranOEVE copolymer (**4**) were hydrolyzed in methylene dichloride at 20 °C in the presence of HCl/methanol solution for 4 h to yield (PCEVE-*g*-PS)-*b*-POHEVE (**5**). The latter was then precipitated into methanol and dried. Then copolymer **5** (1 g, 1.6 × 10^{-4} mol) was dissolved in dry DMF and reacted with 3,4-dihydro-2*H*-pyran-2-(4 chlorobutyl methyl ether) (1 mL, 5 × 10^{-3} mol) in the presence of 50 mg (2.5 × 10^{-4} mol) of *p*-toluenesulfonic acid for 24 h (Scheme 1d) to yield polymer **6**, which was recovered by precipitation into methanol, dried, and characterized by ^{1}H NMR and SEC.

Finally, a cyclohexane solution of living polyisoprenyllithium chains was incrementally added to a weighted amount of (PCEVE-*g*-PS)-*b*-PClpyranOEVE, previously degassed under vacuum and

Table 1. Characteristics of the PCEVE-*b*-PAcEVE (1a, 1b) Block Copolymers, (PCEVE-*g*-PS)-*b*-PpyranOEVE (4a, 4b) Comb-*b*-tail Copolymers and (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI) (7a, 7b) Comb-*b*-comb Copolymers[a]

ref no.	constitutive blocks $\overline{\mathrm{DP}}_n$ (PCEVE-*g*-PS)-*b*-(PXOEVE-*g*-PI)	$\bar{M}_{n,th}$[b] (g/mol) × 10^{-4}	$\bar{M}_{w,exp}$[c,d] (g/mol) × 10^{-4}	$\bar{M}_w/\bar{M}_n$	grafting eff,[e] % PS	grafting eff,[e] % PI	$\Phi_{v,PS/PI}$[f]
1a	(390[g]−0)−(370−0)		8.9	1.11			0/0
1b	(300[h]−0)−(474−0)		9.3	1.27			0/0
4a	(390−60)−(370−0)	259	222[b]	1.20	85		100/0
4b	(300−58)−(474−0)	198	149[b]	1.31	75		100/0
7a	(390−60)−(370−60)	410	317[b]	1.21	85	77	58/42
7b	(300−58)−(474−62)	398	350[b]	1.45	75	88	52/48
8a	(390−60)−(370−61)[i]	498	424[b]	1.18	85		100/0

[a] With X = acetoxy, or pyran or chloropyran. [b] Calculated from $\overline{\mathrm{DP}}_n$ (column 2) assuming one graft per vinyl ether unit of first block (PS) for **4** and of the two blocks (PS, PI) for **7** and (PS, PS) for **8**: $\bar{M}_{n,th} = \bar{M}_{n,PCEVE} + \bar{M}_{n,PAcEVE} + A \times \bar{M}_{n,PS} + B \times \bar{M}_{n,PI(orPS)}$ with A and B for, respectively, DP_{PCEVE} and DP_{PAcEVE}. [c] $\bar{M}_{n,exp}$ determined by SEC for the PCEVE block and ^{1}H NMR for the diblocks **1a** and **1b**. [d] $\bar{M}_{w,exp}$ determined by light scattering (LS)) in THF at 25 °C: dn/dc = 0.181 mL/g for (PCEVE-*g*-PS)-*b*-PpyranOEVE (**4**) and dn/dc = 0.150 and 0.146 mL/g for, respectively, (PCEVE-*g*-PS)-*g*-(PClpyranOEVE-*b*-PI) (**7a** and **7b**). [e] Coupling efficiency based on the molar mass determined by SLS. [f] $\Phi_{v\ PS/PI}$ corresponds to the volume fractions of PS and PI; the volume of PCEVE-*b*-PAcEVE (<1%) was neglected. [g] $\bar{M}_{n,exp}$SEC = 41 500, $\bar{M}_w/\bar{M}_n$ = 1.07. [h] $\bar{M}_{n,exp}$SEC = 32 000, $\bar{M}_w/\bar{M}_n$ = 1.07. [i] (PCEVE-*g*-PS$_1$)-*g*-(PClpyranOEVE-*b*-PS$_2$).

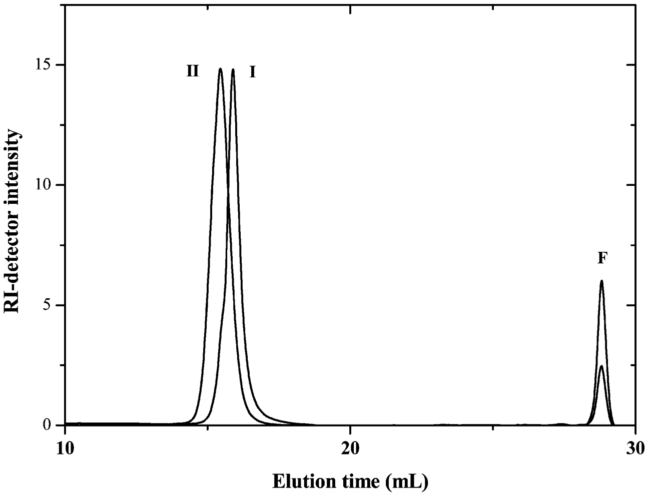


Figure 3. SEC traces recorded at the different building stages of the synthesis of comb-like block copolymers: (I) (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-PCpyranOEVE$_{370}$; (II) (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-(PCpyranOEVE$_{370}$-*g*-PI$_{60}$).

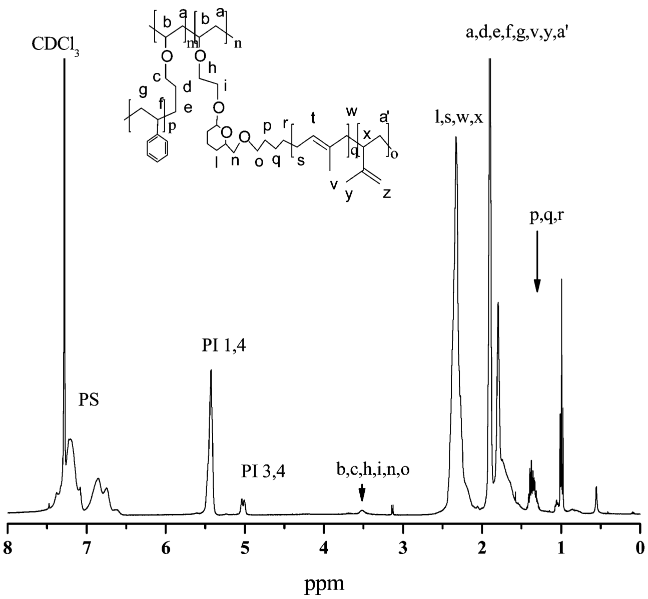


Figure 4. ^{1}H NMR spectrum of (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-(PClpyranOEVE$_{370}$-*g*-PI$_{60}$) comb-like-block copolymers. Solvent: CDCl$_3$.

dissolved in dry THF to form a PScomb-*b*-PIcomb copolymer with polystyrene and polyisoprene branches, (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI) (**7**) (Scheme 1e). Selective precipitation of the dichloromethane polymer solution with 2-butanol allows the recovery of the PS comb-*b*-comb free of ungrafted linear PI.

A very similar procedure was applied for the preparation of (PCEVE-*g*-PS$_1$)-*b*-(PClpyranOEVE-*g*-PS$_2$) (**8a**), except that PILi was replaced by PSLi. Selective precipitation to recover PS$_1$comb-*b*-PS$_2$comb, free of ungrafted PS, was performed in the cyclohexane/heptane mixture.

2.4. Analysis and Characterization. Static and Dynamic Light Scattering Measurements. The experiments were carried out using the ALV (Langen-FRG) apparatus consisting of an automatic goniometer table, a digital rate meter, and a temperature control of the sample cell within ± 0.1 °C. The scattered light of a vertically polarized λ_0 = 4328 Å laser was measured at different angles in the range of 40°-150° corresponding to $1.2 \times 10^{-3} < q/\text{Å} < 3.3 \times 10^{-3}$ where $q = (4\pi n/\lambda_0)\sin(\theta/2)$, θ is the scattering angle, and n is the refractive index of the medium. The reduced elastic scattering $I(q)/kC$, with $K = 4\pi^2 n_0(\mathrm{d}n/\mathrm{d}c)^2(I_0^{90°}/R^{90°})/\lambda_0^4 N_A$, was measured in steps of 5° in the scattering angle, where n_0 is the refractive index of the standard (toluene); $I_0^{90°}$ and $R^{90°}$ are the intensity and the Rayleigh ratio of the standard at θ = 90°, respectively; dn/dc is the increment of the refractive index; C is the concentration, expressed in g/cm^3, and $I(q)$ is the intensity scattered by the sample. All elastic intensities were calculated according to standard procedures using toluene as the standard with known absolute scattering intensity.

For the dynamic properties, the experiments were carried out in steps of 20° in the scattering angle. The ALV5000 autocorrelator (ALV, FRG) was used to compute the autocorrelation functions $I(q,t)$ from the scattered intensity data. The autocorrelation functions of the scattered intensity, deduced from the Siegert relation,[36] were analyzed by means of Contin analysis to give the effective diffusion coefficient $D_{eff} = \Gamma(q)/q^2$ as a function of the scattering angle and ultimately the hydrodynamic radius $R_H = k_B T/(6\pi\eta D)$; when η is the viscosity of the medium.

Atomic Force Microscopy (AFM). Samples for AFM analysis were prepared by solvent casting at ambient temperature by spin-coating on substrates starting from deposits of dichloromethane solutions. Practically, 20 μL of a dilute polymer solution (0.01 wt %) were spin-cast on a 1 × 1 cm^2 highly oriented pyrolytic graphite (HOPG). Samples were analyzed after complete evaporation of the solvent at room temperature. All AFM images were recorded in air with a Dimension microscope (Digital Instruments, Santa Barbara, CA), operated in tapping mode. The probes were commercially available silicon tips with a spring constant of 40 N/m, a resonance frequency lying in the 270−320 kHz range, and a radius of curvature of 10 nm. In this work, both the topography and the phase signal images were recorded with the highest sampling resolution available, i.e., 512 × 512 data points.

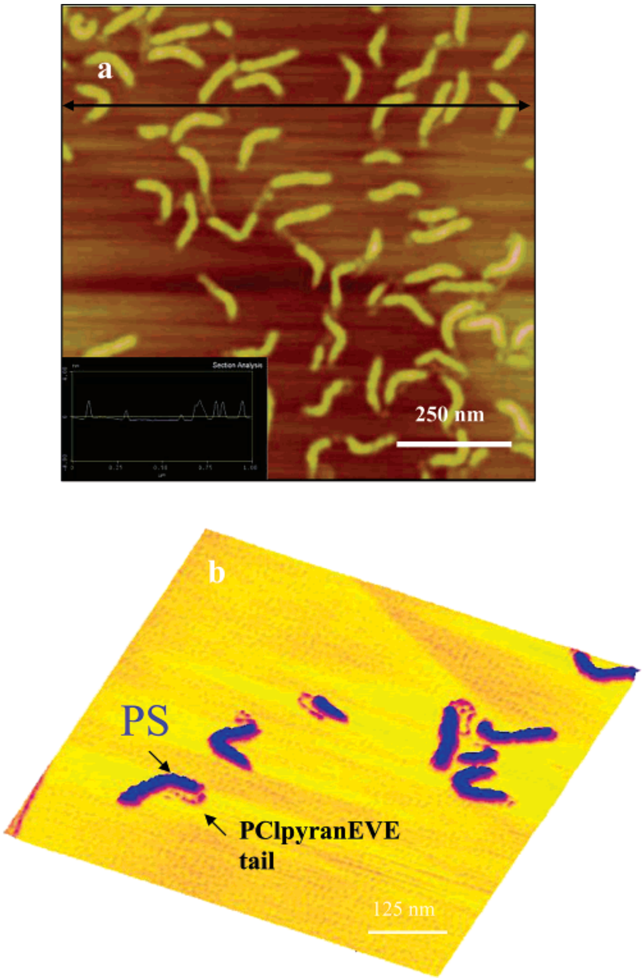


Figure 5. AFM tapping topographic image (a, b) of (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-PpyranOEVE$_{370}$ obtained from the deposit of methylene dichloride solutions on graphite.

Other Characterization Techniques and Measurements. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 400 MHz FT apparatus. Size exclusion chromatography (SEC) analysis in THF was performed at 25 °C at a flow rate of 0.7 mL/min using a Varian apparatus equipped with refractive index/laser light scattering (Wyatt technology) dual detection and fitted with four TSK columns (300 × 7.7 mm^2; 250, 1500, 10^4, and 10^5 Å) calibrated with linear polystyrene and poly(chloroethyl vinyl ether) standards.

3. Results and Discussion

We first report the synthesis by a two steps grafting onto approach of poly(chloroethyl vinyl ether-*g*-polystyrene)-*b*-poly(chloropyranethoxy vinyl ether-*g*-polyisoprene), PScomb-*b*-PIcomb copolymers, with different block composition and molar masses. The strategy used is illustrated in Scheme 1, and the step-by step synthesis is described below.

3.1. Synthesis of PScomb-*b*-PIcomb. A poly(chloroethyl vinyl ether)-*b*-poly(2-acetoxyethyl vinyl ether) PCEVE-*b*-PAcEVE diblock copolymer (**1**) used as precursor of the reactive backbone chain was first synthesized by living cationic polymerization of the corresponding functional vinyl ethers (Scheme 1a). The living polymerization of CEVE was initiated by addition of hydrogen iodide to the monomer in toluene at −30 °C followed by introduction of $ZnCl_2$ as catalyst.[37] Conversion was checked by polymer sampling with time. After quantitative CEVE polymerization, the molar mass and molar mass distribution of the PCEVE block were determined by SEC. After quantitative CEVE conversion, 2-acetoxyethyl vinyl ether (AcEVE) was added to the medium and the polymerization was carried out at 0 °C. The polymerization was finally quenched by addition of $LiBH_4$, thus yielding poly(CEVE)-*b*-poly(AcEVE) diblock copolymer (**1**). Copolymer composition was determined by ^{1}H NMR, see Figure 1, while $\overline{DP}_n$ of the PAcEVE block and copolymer molar masses were calculated on the basis of the copolymer composition and of the PCEVE block length determined by SEC (Figure A is given as Supporting Information). Characteristics of **1a** and **1b** are collected in Table 1.

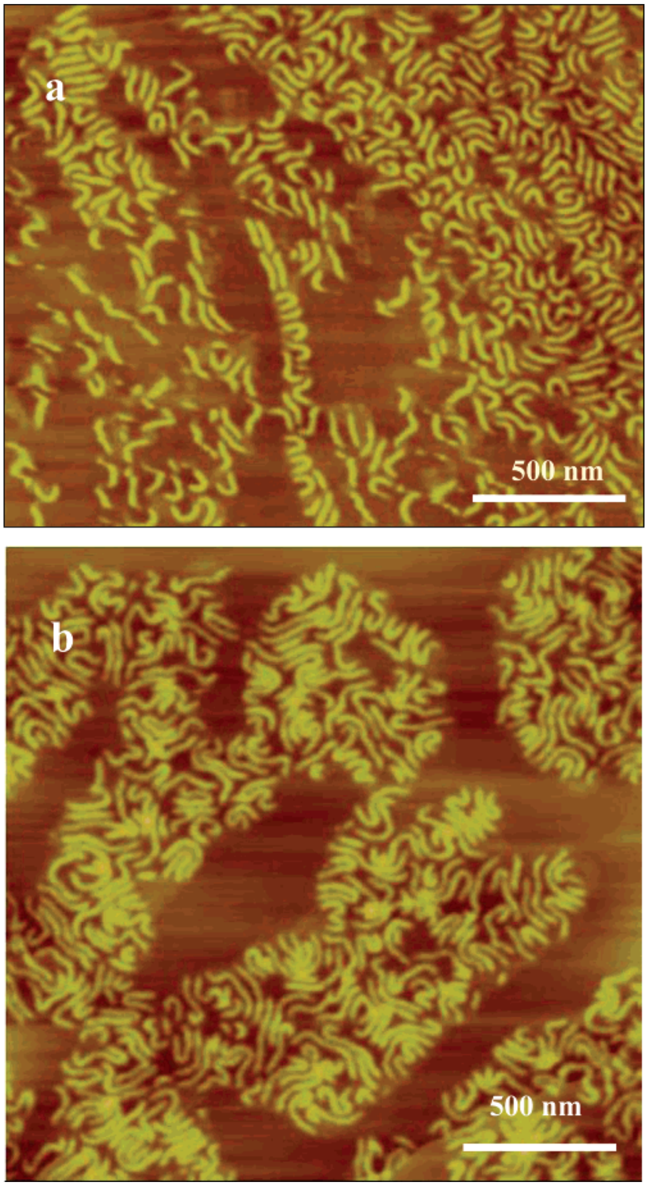


Figure 6. AFM tapping topographic image of (a) (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-(PClpyranOEVE$_{370}$-*g*-PI$_{60}$) and (b) (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-(PClpyranOEVE$_{370}$-*g*-PS$_{61}$) obtained from the deposit of methylene dichloride solutions on graphite.

To avoid side reactions during PSLi grafting onto CEVE units, the acetoxy groups of **1** were converted into more stable acetals. To that purpose the acetoxy groups were hydrolyzed to give polymer **2** and the pendant hydroxyles were transformed by 3,4-dihydro-2*H*-pyran (Scheme 1b) yielding PCEVE-*b*-PpyranOEVE diblock copolymer (**3**). The ^{1}H NMR spectrum of compound (**3a**) is shown in Figure 2.

Living polystyryllithium was then grafted onto the PCEVE block, as previously described[5,37] to form (PCEVE-*g*-PS)-*b*-

PpyranOEVE copolymer (**4**), a PS comb bearing a linear PpyranOEVE tail (Scheme 1c). After elimination of ungrafted PS chains by selective precipitation in a cyclohexane/heptane mixture, the comb-*b*-tail copolymer was characterized by SEC, SLS and DLS. A typical SEC chromatogram of a (PCEVE-*g*-PS)-*b*-PpyranOEVE is shown in Figure 3 (I). Theoretical molar masses of **4a** and **4b** were calculated from the $\overline{\mathrm{DP}}_\mathrm{n}$ of the initial PCEVE-*b*-PpyranOEVE backbone and of the PS grafts, assuming one PS graft per CEVE unit. Experimental molar masses determined using SLS are in good agreement with the calculated values and are consistent with a PS grafting efficiency of about 75 and 85% for samples **4b** and **4a**, respectively. The molar mass distributions remain narrow in the range 1.2−1.3 and the corresponding data are collected in Table 1.

In order to graft polyisoprene onto the second backbone block, the pyranyl groups of the PpyranOEVE block were removed in acidic media to generate copolymer **5** with hydroxyl functions. The later were used to anchor 3,4-dihydro-2*H*-pyran-2-(4 chlorobutyl methyl ether), Scheme 1d. The corresponding PScomb-*b*-tail (PCEVE-*g*-PS)-*b*-PClpyranOEVE copolymer (**6**), was used as reactive backbone to graft living polyisoprenyllithium chains, following the technique previously reported for PSLi grafting. To achieve maximal grafting, PILi was added in excess and reacted for 36 h at 20 °C. Ungrafted polyisoprene chains were removed by selective precipitation of the high molar mass PScomb-*b*-PIcomb copolymer into 2-butanol. The poly(chloroethyl vinyl ether-*g*-polystyrene)-*b*-poly(chloropyranethoxy vinyl ether-*g*-polyisoprene)s, (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI), **7a** and **7b**, were characterized by ^{1}H NMR (Figure 4), SEC (Figure 3, II) and light scattering techniques.

Theoretical molar masses of PScomb-*b*-PIcomb copolymers **7** were calculated from the $\overline{\mathrm{DP}}_\mathrm{n}$ of the PCEVE-*b*-PClpyranOEVE backbone and that of the PS and PI grafts, assuming one graft chain per CEVE unit and one graft chain per ClpyranOEVE unit. Results are in good agreement with experimental molar masses determined using SLS. On the basis of molar masses of samples **4a** and **4b**, they correspond to a PI grafting efficiency between 75 and 90%. These results suggest that only a few unreacted CEVE and ClpyranOEVE units remain in the final PScomb-*b*-PIcomb copolymers.

AFM Imaging. To further characterize the architecture, size and conformation of the comb copolymers, these systems were examined by AFM. Highly diluted solutions of the copolymers were prepared in methylene dichloride (0.1 g/L) and spin-cast on oriented graphite or mica to observe individual macromolecules.

Figure 5 shows the AFM images of the PScomb-*b*-tail copolymer (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-PpyranOEVE$_{370}$ (**4a**). They reveal individual macromolecules, which appear as long cylindrical objects with a homogeneous average contour length of about 115 nm and a width of 25 nm. The very low cylinder height of 1.5 nm indicates that the molecules are completely flattened due to the good affinity of PS with the substrate. Interestingly, even the linear PpyranOEVEtail located at one PS cylinder end can be visualized thanks to the high spatial resolution of tapping mode AFM, see Figure 5a,b.

Attempts to characterize the (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-PClpyranOEVE$_{370}$-*g*-PI$_{60}$) (**7a**) on graphite in similar conditions partially failed. Only the PCEVE$_{390}$-*g*-PS$_{60}$ block with dimensions identical to those observed for **4a** cylinders could be observed as illustrated in Figure 6a. It was not possible to visualize the polyisoprene comb block on the graphite surface, likely because the PI chains are lying flat onto the substrate. To verify if this behavior could be related to the PI nature, a PS$_1$comb-*b*-PS$_2$comb was prepared by grafting a second set of PS branches onto copolymer **6a**, yielding copolymer (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-(PClpyranOEVE$_{370}$-*g*-PS$_{61}$) (**8a**). As it may be seen on the AFM image illustrated in Figure 6b, the latter exhibits the same section and height as PScomb-*b*-tail cylinders **4a,** but twice their length, in agreement with quantitative PS grafting on the PClpyranOEVE block of structure **6**.

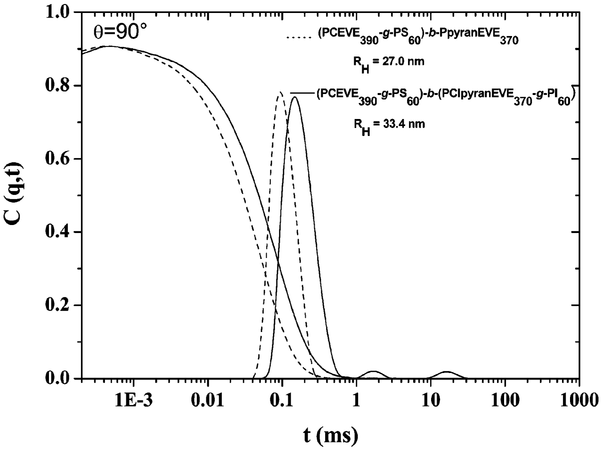


Figure 7. Normalized field correlation and corresponding relaxation times at $\theta = 90°$ for a concentration of 4.1 g/L solution in THF, at a temperature of 25 °C: (a) (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-PpyranOEVE$_{370}$ and (b) (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-(PClpyranOEVE$_{370}$-*g*-PI$_{60}$).

Table 2. Characteristics and Dimensions in THF at 25 °C of (PCEVE-*g*-PS)-*b*-PpyranOEVE (4a, 4b) Comb-*b*-tail Copolymers and (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI) (7a, 7b) Copolymers

ref no.	constitutive blocks, $\overline{\mathrm{DP}}_\mathrm{n}$ (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI)	R_{H0} (nm)^a	R_g (nm)^b	$R_\mathrm{g}/R_{\mathrm{H0}}$
4a	(390−60)−(370−0)	27.1	35.1	1.30
4b	(300−58)−(474−0)	30.8	38.7	1.26
7a	(390−60)−(370−60)	33.4	49.5	1.48
7b	(300−58)−(474−62)	34.1	46.8	1.37

[a] R_{H0} determined using DLS extrapolated to infinite dilution ($C \rightarrow 0$). [b] R_g determined using SLS from Zimm method.

Solution Properties. The characteristics and solution behavior of (PCEVE-*g*-PS)-*b*-PpyranOEVE comb-*b*-tail and of (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI) PScomb-*b*-PIcomb copolymers have been investigated using static and dynamic light scattering technique in THF, a good solvent for the backbone and the polystyrene and polyisoprene branches.

Figure 7 shows the normalized autocorrelation functions obtained for (PCEVE-*g*-PS)-*b*-PpyranOEVE (**4a**) and (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI) (**7a**) at $T = 25$ °C. The CONTIN analysis shows for both copolymers a monomodal decay time distribution at all scattering angles, indicating the presence of a single population of objects of very narrow size distribution. Their apparent hydrodynamic radius R_h, calculated according to the Stockes−Einstein relation under the assumption that the scattering particles have a spherical shape, are respectively 27 nm for **4a** and 33 nm for **7a**; see Table 2. These R_h values are in agreement with the presence in solution of isolated macromolecules and agree with SEC and AFM data. The radius of gyration of the isolated combs, measured in THF using SLS from Zimm plots (available as Supporting Information, Figure B) and the $R_\mathrm{g}/R_{\mathrm{H0}}$ ratio are collected in Table 2. $R_\mathrm{g}/R_{\mathrm{H0}}$, which ranges from 1.26 and 1.48, are slightly higher for the PScomb-*b*-PIcomb copolymers than for the PScomb-*b*-tail, in agreement with a more elongated structure for the former architecture.

Micellization Study. In the literature, only a little attention has been paid to the micellization of comb-like copolymers in

Table 3. Characteristics and Dimensions in Heptane at 25 °C of Micelles of (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI) Copolymers (7a), (7b)

ref no.	constitutive blocks, $\overline{\mathrm{DP}}_n$ (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI)	$\bar{M}_{\mathrm{w,\ exp}}$ (LS)[a] (g/mol) × 10^{-6}	$N_{\mathrm{agg}}^{\mathrm{app}}$ [b]	R_{H0} (nm)[c]	R_g (nm)[d]	R_g/R_{H0}
7a	(390−60)−(370−60)	26.2	8	69.8	46.3	0.66
7b	(300−58)−(474−62)	83.9	24	94.9	72.4	0.76

[a] $\bar{M}_{\mathrm{w,\ exp}}$ of micelles determined by light scattering (LS) in heptane at 25 °C: dn/dc = 0.177 mL/g for respectively (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI) **(*7a*)** and **(*7b*)** [b] $N_{\mathrm{agg}}^{\mathrm{app}}$ apparent aggregation numbers estimated from the ratio $\bar{M}_{\mathrm{w,exp}}$(micelle)/ $\bar{M}_{\mathrm{w,exp}}$((PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI)). [c] R_{H0} determined using DLS extrapolated to infinite dilution (C→0). [d] R_g determined using SLS from Zimm method.

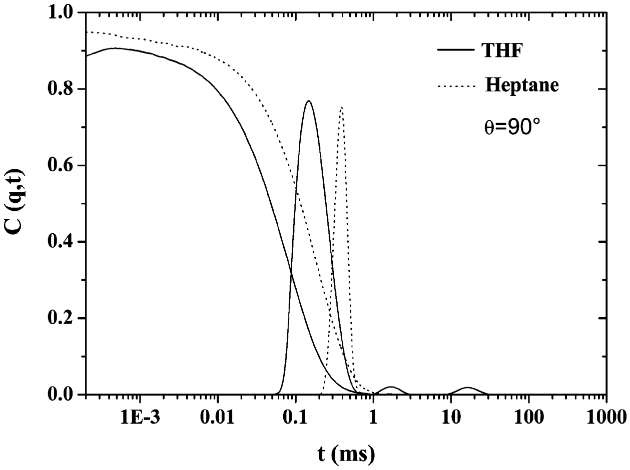


Figure 8. Normalized field correlation and corresponding relaxation times at $\theta = 90°$, at the temperature of 25 °C for (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-(PClpyranOEVE$_{370}$-*g*-PI$_{60}$): (a) in THF at 4.1 g/L solution; (b) in heptane at 0.5 g/L.

selective solvents.[29,30,35,38−44] In order to better understand the influence of the chain architecture on the self-assembly process of macromolecules, the behavior of (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI), PScomb-*b*-PIcomb copolymers (**7**), was investigated using static and dynamic light scattering in heptane, a selective solvent of the polyisoprene moieties. The results are collected in Table 3.

The autocorrelation functions of copolymer (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-(PClpyranEVE$_{370}$-*g*-PI$_{60}$) (**7a**) measured by DLS in THF and heptane are displayed in Figure 8. The significantly lower relaxation time observed in hydrocarbon reflects the association of macromolecules. Indeed the Contin analysis of the correlation functions in heptane indicates the presence of a single distribution with a narrow profile, in agreement with the formation of micelles with a narrow polydispersity. Similar results were observed with **7b**. Within the range of concentration examined in this study (0.1−4 mg/mL), we did not observed isolated macromolecules in selective solvent. The apparent micelle hydrodynamic radii, calculated according to Stokes−Einstein relation, varies from 70 to 95 nm for **7a** and **7b**, in agreement both with the highly branched structure of the polymers and the low aggregation numbers ($N_{\mathrm{agg}}^{\mathrm{app}}$), meaning that only few PScomb-*b*-PIcomb macromolecules are associated in a single hyperbranched micelle. The corresponding values are collected in Table 3. ($N_{\mathrm{agg}}^{\mathrm{app}}$) is higher for the PScomb-*b*-PIcomb constituted by the smaller PS moieties and the larger PI one, which constitute the micelle core and the corona respectively. The ratio R_g/R_{H0} close to 0.7 is consistent with the formation of spherical micelles with a highly compact structure.

To tentatively confirm the hyperbranched micellar morphology by AFM, highly diluted solutions of the PScomb-*b*-PIcomb copolymer (**7a**) were prepared in heptane (0.1 mg/mL) and directly spin-casted on graphite to preserve the micellar organization. Figure 9 shows AFM images of ovoidal objects uniform in shape and size with an average length of 120 nm and a section of 85 nm. These results fit nicely with the shape and size of the micelles observed in heptane using DLS.

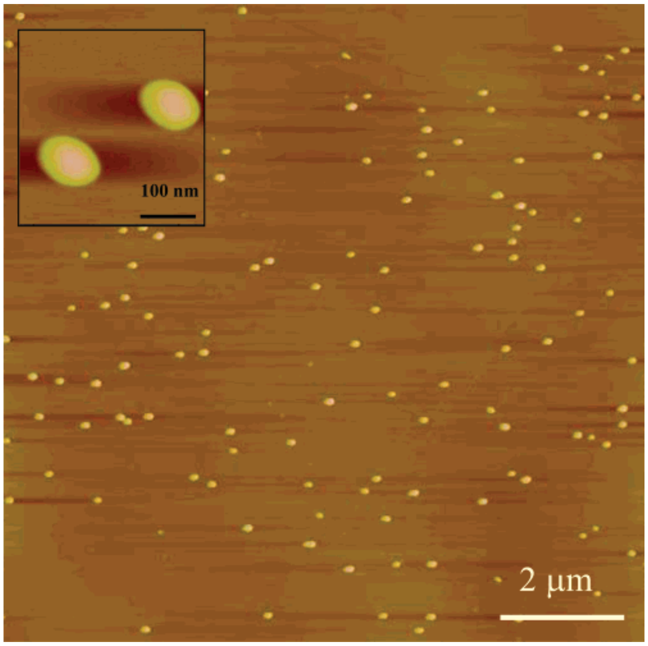
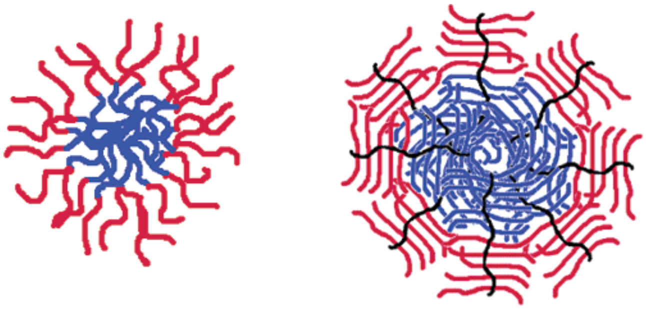


Figure 9. AFM tapping topographic image of hyperbranched micelles of (PCEVE$_{390}$-*g*-PS$_{60}$)-*b*-(PClpyranOEVE$_{370}$-*g*-PI$_{60}$) (**7a**) obtained from deposit of a heptane solution on graphite.

Scheme 2



4. Conclusion

The synthesis of comb-*b*-tail copolymers (PCEVE-*g*-PS)-*b*-PpyranOEVE and PScomb-*b*-PIcomb copolymers (PCEVE-*g*-PS)-*b*-(PClpyranOEVE-*g*-PI) with controlled chain parameters and high molar mass was successfully achieved by a two steps grafting onto approach. Thanks to the living polymerization techniques, a good control in the size, shape, and branching density of the macromolecular objects could be achieved. DLS was used to investigate the characteristics and behavior of the PScomb-*b*-PIcomb in a good solvent of the two comb-blocks and in a selective solvent of the PI moieties. Whereas they are present as isolated objects in good solvent for both blocks such as THF, in heptane the PScomb-*b*-PIcombs self-assemble into homogeneous and almost spherical object corresponding to hyperbranched micelles, illustrated in Scheme 2. AFM study allowed us to directly visualize the conformation, dimensions, and organization of the PScomb-*b*-tail and PScomb-*b*-PIcomb polymers as isolated objects and as hyperbranched micellar structure in agreement with the DLS results. Other investigations are under study on asymmetric systems with emphasis on hyperbranched vesicular morphology.

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Supporting Information Available: Figures showing SEC curves (A) and Zimm plots (B). This material is available free of charge via the Internet at http://pubs.acs.org.

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