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Poly(styrene)comb-*b*-Poly(ethylene oxide)comb Copolymers: Synthesis and AFM Investigation of Intra- and Supramolecular Organization as Thin Deposits

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ABSTRACT: PScomb-*block*-PEOcomb copolymers having a poly(chloroethyl vinyl ether)-*b*-poly(hydroxy ethyl vinyl ether) backbone with polystyrene chains on one side and poly(ethylene oxide) chains on the other, i.e. (PCEVE-*g*-PS)-*b*-(POHEVE-*g*-PEO), were synthesized. The strategy is based on grafting of polystyryllithium onto the reactive chloro functions of the poly(chloroethyl vinyl ether) first block and on grafting polyethylene oxide from the hydroxyl functions of the second block. This procedure allows the preparation of densely grafted amphiphilic diblocklike, Janus-type, comblike copolymers with high molar masses and narrow polydispersity.The characteristics and dimensions of isolated (PCEVE-*g*-PS)-*b*-(POHEVE-*g*-PEO) macromolecules were studied by light scattering in THF, a good solvent of both PS and PEO branches, as well as using AFM imaging of highly diluted deposits. Unimolecular rodlike nano-objects with distinct PS and PEO domains were observed, in agreement with their diblocklike structure. In relation with their amphiphilic nature, the combs can self-assemble in different morphologies. When graphite deposits are made from more concentrated methylene dichloride solutions, the PScomb-*b*-PEOcomb copolymers self-assemble directly on the substrate, forming flowerlike molecular aggregates interconnected by their PEO moieties. When deposits are made from a selective solvent (methanol) of the PEO comb block, hyperbranched micelles formed in the solution retain their structure on the solid substrate, yielding well-defined spherical objects.

Introduction

Recently there has been an increasing interest in the synthesis and study of densely grafted copolymers. Different synthetic strategies have been developed to prepare comblike polymers of various chemical composition and architecture with controlled chain parameters. So far, three main methods have been used, often referred as the "grafting from"[1−6] (initiating the growth of side chains from the backbone), the "grafting through"[7−14] (polymerization of macromonomers), and the "grafting onto"[15−20] (attachment of side chains to the backbone) approaches. Various polymerization methods, including radical, cationic, and anionic mechanisms have been employed, but so far, a limited number of reports have dealt with a study of the behavior of comb polymers and copolymers in solution and in bulk.[21−29]

We have described recently the controlled synthesis of a series of densely grafted copolymers based on a "grafting onto" process. Comblike block copolymers having a poly(chloroethyl vinyl ether) backbone and poly(styrene-*b*-isoprene) side chains, i.e., PCEVE-*g*-(PS-*b*-PI), were synthesized via the coupling reaction of ω-acetal-polystyryllithium onto the reactive functions of a PCEVE backbone. This was followed in a second step by the grafting of living polyisoprenyllithium chains onto the acetal ends of PS branches activated by trimethyl silyl iodide.[30] These comblike copolymers were found to behave as isolated unimolecular micelles in selective solvents of the PI blocks.

In the present work we report the synthesis and investigate the characteristics in solution and as solid deposit of new "Janus"-type comblike copolymers constituted by PS and PEO combs covalent linked by one of their backbone end, i.e., (polychloroethyl vinyl ether-*g*-polystyrene)-*b*-(polyhydroxy ethyl vinyl ether-*g*-polyethylene oxide), (PCEVE-*g*-PS)-*b*-(POHEVE-*g*-PEO). Their behavior as isolated macromolecules and their nanoscale organization as thin deposits from various solutions based either from good solvents for both the PS and PEO or from selective solvent of the PEO blocks were examined by atomic force microscopy (AFM).

Experimental Section

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 and DMSO (99% J.T. Baker) were purified by distillation over molecular sieves. α-Chloroethyl vinyl ether (CEVE) (99%, ACROS, France) was washed with an aqueous NaOH solution (1 N) and distilled twice over calcium hydride. Styrene and ethylene oxide (99%, Sigma-Aldrich Chimie, Saint Quentin Fallavier, France) were purified by distillation over calcium hydride at reduced pressure. *s*-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. Zinc chloride (Sigma-Aldrich Chimie, Saint Quentin Fallavier, France) was dissolved in dry diethyl ether (solution at $0.155\ \mathrm{mol{\cdot}L^{-1}}$).

Polymerization Procedures. 1. Synthesis of the PCEVE-*b*-PAcEVE Backbone. The synthesis of acetoxyethyl vinyl ether (AcEVE) and of poly(chloroethyl vinyl ether)-*b*-poly(2-acetoxyethyl vinyl ether), (PCEVE-*b*-PAcEVE), diblock copolymer have been described in detail in a previous contribution.[31] Briefly, a PCEVE was first synthesized by living cationic polymerization of chloroethyl vinyl ether using hydrogen iodide as initiating system[32,33] and zinc chloride as catalyst at −15 °C for 24 h. Then, AcEVE was added to the solution and its polymerization was carried out at 0 °C for 12 h before $LiBH_4$ was added as terminating agent, thus yielding PCEVE-*b*-PAcEVE block copolymers (**1**) (Scheme 1a).

2. Synthesis of the (PCEVE-*g*-PS)-*b*-PpyranOEVE PScomb-*b*-tail Copolymers. The preparation of the diblock copolymer

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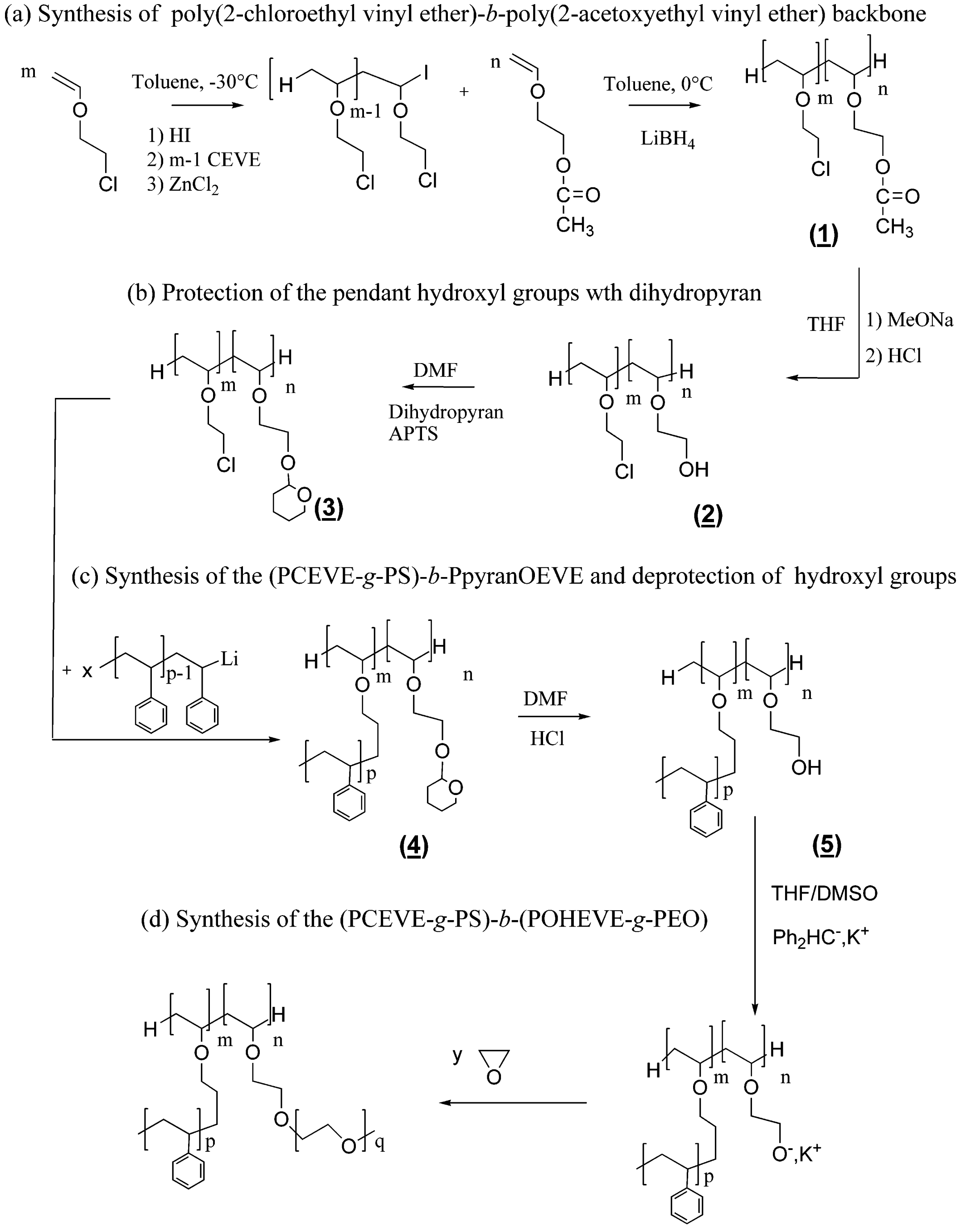
Scheme 1


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

(b) Protection of the pendant hydroxyl groups wth dihydropyran

(c) Synthesis of the (PCEVE-*g*-PS)-*b*-PpyranOEVE and deprotection of hydroxyl groups

(d) Synthesis of the (PCEVE-*g*-PS)-*b*-(POHEVE-*g*-PEO)

backbone has also been described in detail.[31] The acetoxy side groups of the PAcEVE **(1)** were first hydrolyzed by polymer treatment in THF with an excess of sodium methanolate at 20 °C for 2 h. HCl solution (0.1 N) was added to the system to neutralize the solution yielding poly(chloroethyl vinyl ether)-*b*-poly(2-hydroxyethyl vinyl ether) **(2)**. In a following step, the hydroxyl groups (Scheme 1b) were protected with 3,4-dihydro-2*H*-pyran to give the resulting linear block copolymer (**3**) that was characterized by SEC and ^{1}H NMR (see Table 1).

Finally, living polystyryllithium chains were incrementally added to a weighted amount of PCEVE-*b*-PpyranOEVE (**4**), as previously described,[32,33] to form a PScomb-*b*-tail copolymer with polystyrene branches, (PCEVE-*g*-PS)-*b*-PpyranOEVE (Scheme 1c). Selective precipitation of the polymer/cyclohexane solution by slow addition of heptane to the polymer solution allowed recovering the PS comb free of ungrafted linear PS.

3. Synthesis of the (PCEVE-*g*-PS)-*b*-(POHEVE-*g*-PEO), PScomb-*b*-PEOcomb Copolymers. The pendant pyran groups of the PpyranOEVE units of the graft copolymer **4** were first 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** was used after activation to grow PEO branches.

For example, 1 g of (PCEVE-*g*-PS)-*b*-POHEVE (**5a**) ($\bar{M}_n = 1.69 \times 10^6$ g·mol^{-1}, $\bar{M}_w/\bar{M}_n = 1.22$) corresponding to 4.7×10^{-5} mol of hydroxyl functions was placed in a 500 mL flame-dried glass reactor fitted with PTFE stopcocks and dissolved in 20 mL of dry THF. To remove any traces of moisture from the polymer, the solvent was evaporated under vacuum and replaced by a new volume of dry THF. This operation was repeated twice, and the polymer was finally redissolved into anhydrous THF (200 mL, 50:50, v/v). Diphenyl methyl potassium, DPMK (0.2 mL, 4.0×10^{-5} mol with [DPMK] = 0.2 mol·L^{-1}) was added and the mixture stirred for 1 h before introduction of ethylene oxide (EO) (0.21 mL, 7.1×10^{-3} mol). Upon addition of DPMK, the solution turned pale yellow and then dark blue after EO introduction. The solution

Table 1. Characteristics of the PCEVE-*b*-PAcEVE Block Copolymers (1a, 1b), (PCEVE-*g*-PS)-*b*-PpyranOEVE PScomb-*b*-tail Copolymers (4a, 4b), and (PCEVE-*g*-PS)-*b*-(POHEVE-*g*-PEO) PScomb-*b*-PEOcomb Copolymers (6a, 6b)

ref no.	constitutive blocks $\overline{DP}_n$ (PCEVE-PS)-*b*-(POHEVE-PEO)	$\bar{M}_{w,th}$ (g/mol) × 10^{-6}	$\bar{M}_{w,exp}$ (LS)^c (g/mol) × 10^{-6}	$\bar{M}_w/\bar{M}_n$	grafting eff.,%^{d}		$\Phi_{v\ PS/PEO}{}^e$
					PS	PEO	
1a	(230−0)-(80−0)	0.03^a	−	1.08	−	−	0/0
1b	(390−0)-(370−0)	0.15^a	−	1.11	−	−	0/0
4a	(230−79)-(80−0)	1.92^b	1.69	1.17	88	−	100/0
4b	(390−71)-(370−0)	2.96^b	2.52	1.20	85	−	100/0
6a	(230−79)-(80−60)	2.14^b	2.04	1.22	88	100	90/10
6b	(390−71)-(370−136)	5.17^b	n.d.	bimodal	85	low	

[a] Determined using SEC for the PCEVE block and NMR for the POHEVE block. [b] Calculated from $\overline{DP}_n$ (column 2) assuming one PS block grafted per CEVE unit $\bar{M}_{w,th} = \bar{M}_{w,PCEVE} + \bar{M}_{w,PAcEVE} + A\bar{M}_{w,PS} + B\bar{M}_{w,PEO}$ with *A* and *B* for, respectively, DP_{PCEVE} and DP_{PAcEVE}. [c] $\bar{M}_{w,exp}$ determined by light scattering (LS) in THF at 25 °C: d*n*/d*c* = 0.181 for (PCEVE-*g*-PS)-*b*-PpyranOEVE and d*n*/d*c* =0.171, 0.132 for, respectively, **6a** and **6b**. [d] Coupling efficiency based on the molar mass determined by SLS. [e] $\Phi_{v,PS/PEO}$ correspond to the volume fractions of PS and PEO; the volume of PCEVE-*b*-PAcEVE (<1%) and was neglected.

was stirred for 24 h at room temperature, and the polymerization was terminated by addition of 1 mL of methanol. The resulting polymer mixture was poured into water to solubilize the homoPEO formed by side initiation, and the PScomb-*b*-PEOcomb copolymer (PCEVE-*g*-PS)-*b*-(POHEVE-*g*-PEO) (**6a**) was recovered by centrifugation, free of ungrafted linear PEO, as confirmed by SEC. The chemical composition of **6a** was determined by ^{1}H NMR, and its molar mass and molar mass distribution by SEC and LS techniques (see data Table 1).

Analysis and Characterization techniques. 1. Static and Dynamic Scattering Measurements. They were performed using an ALV (Langen-FRG) apparatus consisting of an automatic goniometer table, a digital rate meter, and a temperature control of the sample cell within $T \pm 0.1$ °C. The scattered light of a vertically polarized $\lambda_0 = 4328$ Å argon laser was measured at different angles in the range of 40−150° The reduced elastic scattering $I(q)/kC$, with $K = 4\pi^2 n_0 (dn/dc)^2 (I_0^{90°}/R^{90°})/\lambda_0^4 N_A$, 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 $\theta = 90°$, respectively; d*n*/d*c* 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 where $q = (4\pi n/\lambda_0)\sin(\theta/2)$, θ is the scattering angle, and *n* is the refractive index of the medium. All elastic intensities were calculated according to standard procedures using toluene as the standard with known absolute scattering intensity.

The d*n*/d*c* values were determined for each polymer and copolymers at 633 nm in THF by differential refractometry. d*n*/d*c* =0.181 for (PCEVE-*g*-PS)-*b*-PpyranOEVE and d*n*/d*c* =0.171, 0.132 for, respectively, **6a** and **6b**.

For the dynamic properties, the experiments were carried out in steps of 20° in the scattering angle. The ALV 5000 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,[34] were analyzed by means of Contin analysis to give the effective diffusion coefficient $D = \Gamma(q)/q^2$ 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 conditions by spin-coating on substrates starting from solutions in dichloromethane. Practically, 20 μL of a dilute solution (0.01 wt %) were spin-cast on a 1 × 1 cm^2 highly oriented pyrolytic graphite (HOPG) or mica substrate. 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^{-1}, a resonance frequency lying in the 270−320 kHz range, and a radius of curvature of less than 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.

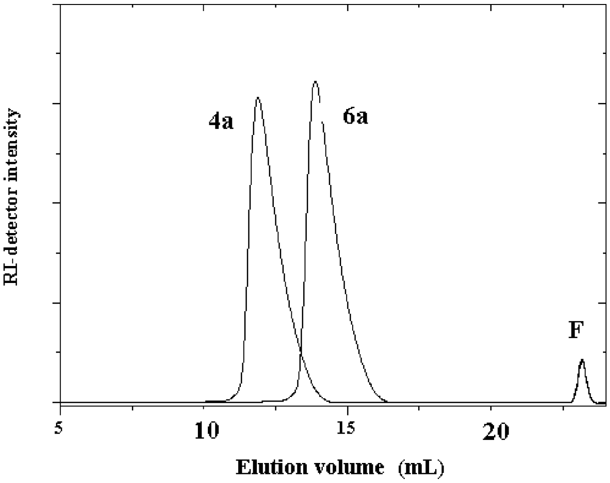


Figure 1. SEC chromatograms recorded at the different building stages of the synthesis of comblike copolymers: (PCEVE$_{230}$-*g*-PS$_{79}$)-*b*-PpyranOEVE$_{80}$ (**4a**) and (PCEVE$_{230}$-*g*-PS$_{79}$)-*b*-(POHEVE$_{80}$-*g*-PEO$_{60}$) (**6a**).

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 (distilled from CaH$_2$) was performed at 25 °C at a flow rate of 0.7 mL·min^{-1} 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 Å, 1500 Å, 10^4 Å, 10^5 Å).

Results and Discussion

The synthesis of PScomb-*b*-PEOcomb copolymers has been achieved using a multistep strategy illustrated in Scheme 1.

Synthesis of (PCEVE-*g*-PS)-*b*-(POHEVE-*g*-PEO). The preparation of PScomb-*b*-PEOcomb copolymers was achieved in three distinct steps. The strategy is inspired from the previously described preparation of PScomb-*b*-PIcomb copolymers.[31]

Step 1. A backbone of **1** was prepared by sequential living cationic polymerization of chloroethyl vinyl ether (CEVE) and 2-acetoxyethyl vinyl ether (AcEVE) monomers in toluene at −30 °C (Scheme 1a) using HI as initiator and zinc dichloride as catalysts. The characteristics of the diblock copolymers are given in Table 1. The molar mass of the PCEVE first block was determined by SEC after sampling the reaction mixture prior adding the second monomer. The chemical composition of the copolymers was determined by ^{1}H NMR analysis (spectrum of **1a** given as Supporting Information) and its final $\overline{DP}_n$ was calculated on the basis of its composition and $\overline{DP}_n$ of initial PCEVE block.

Table 2. Characteristics and Dimensions in THF at 25 °C of the (PCEVE-*g*-PS)-*b*-PpyranOEVE, PScomb-*b*-tail Copolymers (4a, 4b) and of the (PCEVE-*g*-PS)-*b*-(POHEVE-*g*-PEO) PScomb-*b*-PEOcomb Copolymer (6a)

ref no.	constitutive blocks, $\overline{DP}_n$ (PCEVE-PS)-*b*-(POHEVE-PEO)	$\bar{M}_{w,exp}$ (LS) (g/mol) × 10^{-6}	R_{H0} (nm)[a]	R_g (nm)[b]	R_g/R_{H0}
4a	(230−79)-(80−0)	1.69	21.0	24.7	1.18
4b	(390−71)-(370−0)	2.52	31.1	39.8	1.28
6a	(230−79)-(80−60)	2.04	24.2	30.2	1.25

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

In order to avoid side reactions during the grafting of polystyryllithium chains on the PCEVE block, the 2-acetoxy functional groups of the PAcEVE were hydrolyzed and the hydroxyl groups were substituted by 3,4-dihydro-2*H*-pyran, yielding a new diblock copolymer, **3** (Scheme 1b). The ^{1}H spectrum of **3a** is available as Supporting Information.

Step 2. The PCEVE block of **3** was used as reactive backbone to selectively graft living PSLi chains, yielding **4** (Scheme 1c). Two samples of different composition and block length were prepared. After fractionation to remove ungrafted PS chains by selective precipitation in a cyclohexane/heptane mixture, the (PCEVE-*g*-PS)-*b*-PpyranOEVE were characterized by ^{1}H NMR (spectrum of **4b** given as Supporting Information), SEC and light scattering (LS). The corresponding data are collected in Table 1. A Typical SEC chromatogram (**4a**) is shown Figure 1. The theoretical molar masses of **4a** and **4b** were calculated from the $\overline{DP}_n$ of the initial PCEVE-*b*-PpyranOEVE backbone and that of the PSLi grafts, assuming one PS branch 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 85% and 88%, respectively, for samples **4b** and **4a**, whereas their molar mass distribution remains narrow ($I_p < 1.2$).

Step 3. The hydroxyl pendant groups of the copolymers **4** were deprotected in the presence of acid and water (Scheme 1d) to yield the PScomb-*b*-tail copolymers **5**. The latter was dissolved in a 50:50 THF/DMSO mixture, and the pendant hydroxyl groups were deprotonated with DPMK, Scheme 1e, to allow EO polymerization. The use of this reacting medium limits aggregation phenomena of potassium alkoxides and avoids precipitation of the deprotonated comblike copolymers. After 24 h EO polymerization at 25 °C, the reaction was quenched by adding methanol yielding PScomb-*b*-PEOcomb copolymers, **6**. The later were freed from homopoly(ethylene oxide) chains formed by side initiation by dissolution in water and centrifugation, and then characterized by ^{1}H NMR and SEC using a SLS detector. The SEC chromatogram of **6a** and of its precursor **4a** are shown in Figure 1. They are consistent with a homogeneous growth of PEO branches over all the precursor chains (**4a**). In contrast for the PScomb-*b*-tail copolymers (PCEVE$_{390}$-*g*-PS$_{71}$)-*b*-POHEVE$_{370}$ with a longer POHEVE tail (**5b**), EO polymerization did proceed homogeneously and yield polymers with bimodal molar mass distribution, suggesting that some of the (PCEVE$_{390}$-*g*-PS$_{71}$)-*b*-POHEVE$_{370}$ chains are trapped into strong aggregates, making hydroxyl of POHEVE unable to contribute to initiation of EO polymerization. Attempts to use higher fractions of DMSO were unsuccessful and mixtures of PScomb-*b*-PEOcomb copolymers (**6b**) with PScomb-*b*-tail copolymers (**5b**) were obtained. A similar situation was reported by Ishizu et al.[35]

Further studies on the PScomb-*b*-PEOcomb copolymers were thus performed on **6a**. Its chemical composition was determined by ^{1}H NMR assuming the contribution of the backbone protons negligible, and the $\overline{DP}_n$ of the PEO branches was calculated assuming that all the hydroxyl groups of the POHEVE backbone were converted into PEO branches. The main characteristics of the corresponding **6a** are collected Table 1.

The solution properties of PScomb-*b*-tail copolymers **4a** and **4b** and of PScomb-*b*-PEOcombs **6a** were investigated in THF, a common good solvent for polystyrene and poly(ethylene oxide), using static and dynamic light scattering. The mass-average molar mass $\bar{M}_w$ and the radius of gyration R_g, were determined by static light scattering. The corresponding values are collected in Tables 1 and 2. A significant increase of $\bar{M}_w$ and R_g is observed after the PEO grafting step, see **4a** and **6a**, Table 2. The Zimm plot of the PScomb-*b*-PEOcomb copolymer **6a** is shown in Figure 3. Compared to AFM data given later in this article, the slightly smaller R_g value obtained by SLS for **6a** can be explained by the 3D conformation of macromolecules in THF solution as compared to the flattened, almost 2D conformation of adsorbed molecules deposited on graphite.

The autocorrelation functions $C(q, t)$ and the particle size distribution obtained by CONTIN analysis of DLS data for **4a** and **6a**, at 2.0 g·L^{-1}, are illustrated in Figure 4. The CONTIN analysis of the autocorrelation functions shows a monomodal decay time distribution at all scattering angles. A slight increase in the relaxation times is observed between systems **4a** and **6a** and is in agreement with the increase of the comb polymer size with PEO branches. The very narrow particle size distribution for both samples supports the presence of a single type of object corresponding to isolated macromolecules with low polydispersity as already observed by SEC. The hydrodynamic radius, R_H, for **4a** and **6a**, calculated using the Stokes−Einstein relation from the diffusion coefficients in dilute solution, are listed in Table 2. The low values obtained, respectively, 21 and 36.5 nm, are in agreement with a very compact structure of the comb copolymers while the values of the ratio R_g/R_{H0} are, respectively, 1.18 and 1.25 for **4a** and **6a**.

AFM Imaging. The shape and dimensions of individual PScomb-PEOcomb and their assemblies were investigated by AFM, which provides spatial resolution down to the subnanometer scale and strong contrast between soft and rigid phases of different chemical composition. To that end, highly diluted solutions of comb block copolymers (0.1 g·L^{-1}) were prepared in methylene dichloride, a good solvent of PS and PEO branches, and spin-casted on graphite (HOPG) to form deposits of individual macromolecules. Figure 5 shows the phase (a) and topographic (b, c) images of **6a**. Light brown cylindrical objects corresponding to the PS comb moiety are observed on the phase image. Most of the observed molecules are capped by a spherical black spot constituted by the softer PEO comb block. The higher magnification of topographic images Figure 5b,c also clearly displays isolated two-sided macromolecules. The latter appear as relatively uniform objects, which adopt an overall cylindrical conformation with an average length of 107 nm and a width of 34 nm. The polystyrene moiety, Figure 5b, corresponds to the brown domain of the object. They have an average length of 70 nm with a height of only 1.3 nm, indicating that the PS

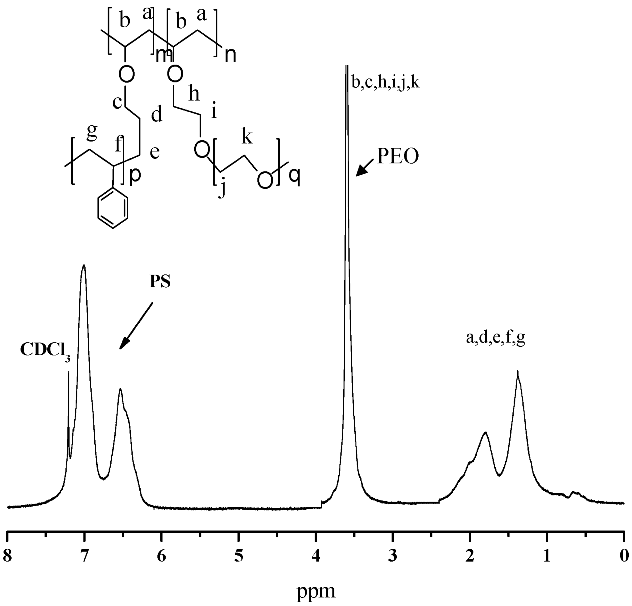


Figure 2. 400 MHz ^{1}H NMR spectrum of **6a** in $CDCl_3$.

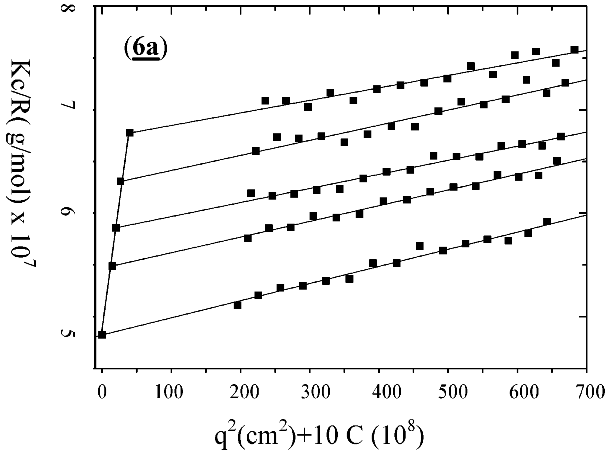


Figure 3. Zimm diagram obtained for **6a** in THF at 25 °C.

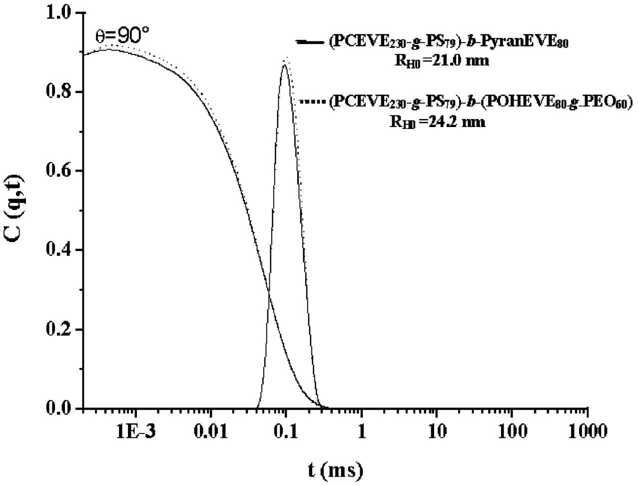


Figure 4. Normalized field correlation and corresponding relaxation times at $\theta = 90°$ for a concentration of 2.0 g•L^{-1} solution in THF, at 25 °C for (a) **4a** and (b) **6a**.

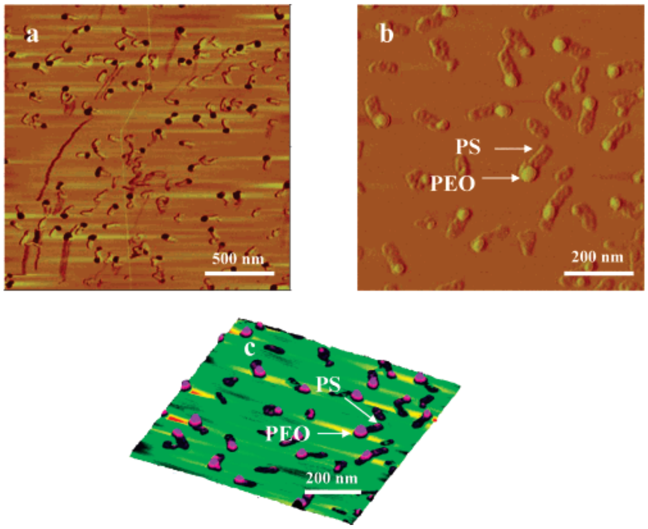


Figure 5. AFM tapping phase (a) and topographic (b, c) images of **6a** obtained from deposit of methylene dichloride solutions (0.1 g•L^{-1}) on graphite and showing isolated macromolecules with PS and PEO domains.

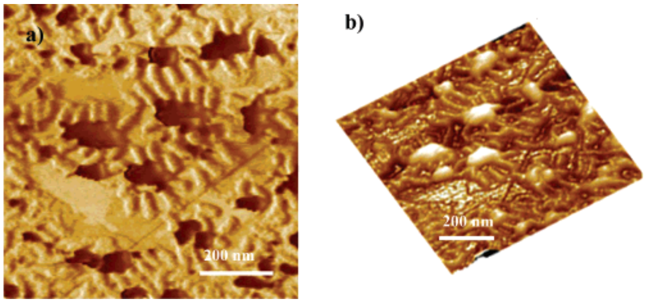


Figure 6. AFM tapping phase (a) and topographic images (b) of **6a** obtained from deposition of methylene dichloride solutions (0.5 g•L^{-1}) on graphite showing flowerlike aggregates with PEO domains forming the central core and PS comb blocks as petals.

branches are lying completely flat on the substrate due to their strong affinity toward graphite. The comb poly(ethylene oxide) moieties are observed as white circular domains with an average height of 4.1 nm, i.e., about 3 times higher than the PS ones. This is due to the lower affinity of the PEO grafts for the nonpolar graphite surface, which in response tend to reduce their surface of contact with the support. Changes in the image colors, Figure 5c, allow visualizing better the two constitutive moieties of the macromolecules.

Upon increasing the density of comb macromolecules on the HOPG substrate, starting from slightly more concentrated CH_2Cl_2 solution for deposits (0.5 g•mL^{-1}), the diblock combs were observe to self-assemble. This can be clearly visualized on the phase and topographic images, Figure 6 a,b. Flowerlike aggregates constituted by PScomb-*b*-PEOcomb molecules interconnected by their PEO domain are observed with PS comb located at the periphery. As estimated from the average number of PS branches per PEO core, the aggregates are constituted by the assembly of an average number of about 10 comb macromolecules. Since CH_2Cl_2 is a good solvent both for PEO and PS, it is believed that the assembly process takes place on the substrate, probably during solvent evaporation. The height profile of flowerlike aggregates is shown in Figure 7. The PEO cores present an average height of about 8 nm, while the surrounding PS combs are more flattened and exhibit a height of about 3 nm, in relation with the different affinity of PEO and PS with the HOPG substrate.

Micellization Behavior. The self-assembly properties of PScomb-*b*-PEOcomb copolymers **6a** were further investigated using methanol, a selective solvent for poly(ethylene oxide), for the preparation of macromolecule deposits. In this media, the amphiphilic diblock combs are expected to form micelles

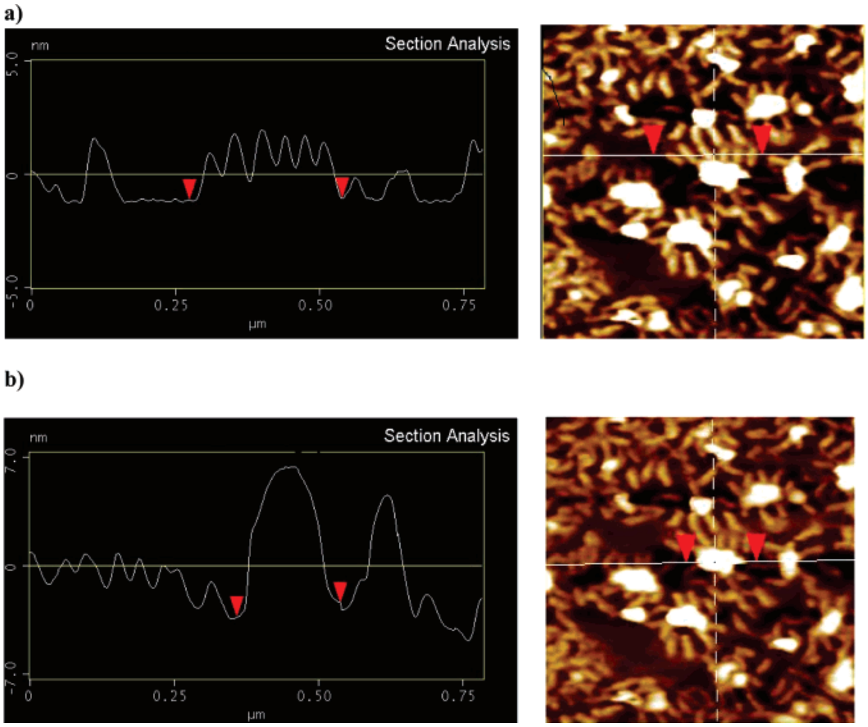


Figure 7. Section analysis of flowerlike aggregates of **6a** obtained from deposition of methylene dichloride solutions (0.5 g·L^{-1}) on graphite: (a) series of isolated PS combs, (b) PEO core.

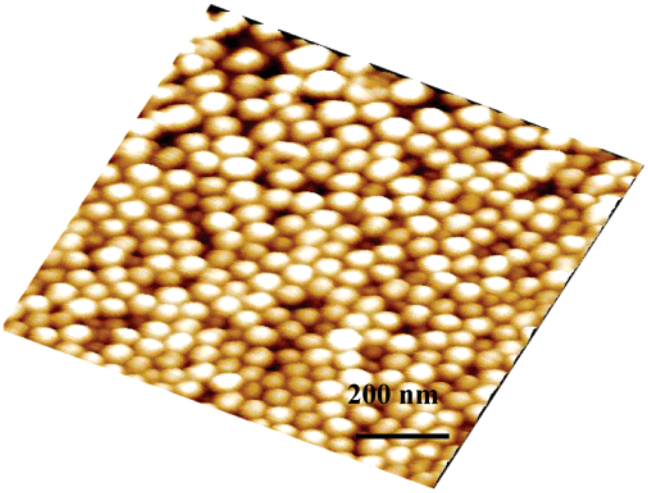


Figure 8. AFM tapping topographic image of hyperbranched micelles of **6a** obtained from deposit of methanol solution (0.1 g·L^{-1}) on a mica substrate.

with a PS core and PEO as corona. This was confirmed by SLS measurements, which indicates the presence of a single distribution of objects with R_{H0} whose size is 52 nm.

Diluted methanol solutions of **6a** were directly spin-cast on mica to preserve the micellar organization and analyzed by AFM, see Figure 8. The formation of spherical objects with a narrow and homogeneous size distribution withand an average radius of 37 nm is observed, a value slightly lower than measured by DLS but which is consistent with hyperbranched micelles with a core constituted by PS combs and a corona made of PEO combs.

Conclusion

The synthesis of PScomb-*b*-tail copolymers (PCEVE-g-PS)-b-PpyranOEVE and PScomb-*b*-PEOcomb copolymers (PCEVE-*g*-PS)-*b*-(POHEVE-*g*-PEO) with controlled chain parameters and high molar mass was successfully achieved using a multistage process. It is based on the preparation of diblock copolymers as reactive backbone followed by selective “grafting onto” and “grafting from” steps on each backbone block. The resulting densely branched diblocklike comb copolymers were further characterized in very dilute regime as single unimolecular objects using SLS/DLS and as highly diluted deposits by AFM. Besides, the PScomb-*b*-PEOcomb copolymers were shown to self-assemble into different micellar structures. When deposited from a methanol solution, selective solvent for PEO, the formation of spherical hyperbranched micelles with a corona constituted of PEO combs and a core made by the PS comb blocks was observed by AFM. Conversely, when the PScomb-*b*-PEOcomb were deposited from a good solvent at a concentration higher than a critical value allowing intermolecular interactions between the diblock comb copolymers, the macromolecules were observed to self-assemble directly on the graphite substrate by interconnecting their PEO domains, thus forming flowerlike objects with a core constituted by PEO domains surrounded by PS combs.

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