From Combs to Comb-*g*-Comb Centipedes

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The construction of macromolecules of increasing complexity exhibiting a precise architecture, size, shape, and functionality is a challenging domain of rapidly growing interest. It found its incentives in the increasing needs for molecular devices which accompany the development of nanotechnologies. Three-dimensional, compact and shape persistent hyperbranched polymers are potential candidates for these applications since, in contrast to linear polymers, they tend to behave as individual entities in solution and in the bulk. As a consequence, an individual macromolecule is able to provide specific properties at the nanometer scale. Dendrimers, arborescent-graft polymers, molecular combs, and monodendron-jacketed chains are some examples of such new macromolecular devices.

A major support for the advancement in the design of functional molecular nanoobjects is our improving ability to control their macromolecular structure in great detail, thanks to the important progresses achieved in the control of polymerization reactions. The availability of new analytical tools that provide observation down to the nanometer scale is a second major reason.[1] It makes possible direct observation and visualization of single molecules, allowing confirmation of the targeted structures and of their behavior and properties as isolated nanoobject or as assemblies. Using high-resolution microscopy, the shape, conformation, contour length, and end-to-end distance of single chains of natural and synthetic branched polymers have been visualized.[2−11] These imaging techniques enable a detailed analysis of their internal characteristics such as the chemical architecture, the local conformation, and chain flexibility. Very recently, the direct vizualization of an internal organization of hyperbranched copolymers in chemically distinct subdomains has been presented.[12−14]

Indeed, the elaboration of precise macromolecular nanodevices often requires the use of strategies involving several building steps and necessitates the tuning and the combination of polymerization and functionalization methods first developed for the synthesis of linear polymers and copolymers. In line with this approach we have recently proposed a methodology based on the covalent assembly of polymer blocks prepared by anionic and cationic living polymerizations for the synthesis of hyperbranched polymers of increasing complexity.[5,15] PS combs and PS dendrigrafts of well-controlled dimensions and architecture were first prepared by the combination of grafting onto and grafting from approaches. The strategy involves (a) attachment of living end-functional polystyrene onto a poly(chloroethyl vinyl ether) (PCEVE) backbone and (b) initiation of the cationic polymerization of chloroethyl vinyl ether from the functional acetal termini of the attached PS blocks followed by repetition of steps (a) and (b) for the synthesis of dendrigraft of increasing generation. This approach was extended to the preparation of core−shell like architectures by connecting chemically different macromolecular blocks at the extremity of the last PS branches of the dendrigrafts.

Using this approach, we have investigated the synthesis, the molecular characteristics, and internal organization of a new series of hyperbranched polymers that we have called "comb centipedes". They are constituted of a comblike PS central backbone surrounded by randomly distributed, covalently attached, lateral comblike polymers of either identical or different chemical composition, as illustrated Scheme 1. The step-by-step synthesis, characterization, and visualization by AFM of these individual macromolecules are presented.

The preparation of comb centipedes was achieved in three distinct steps. The strategy is inspired from the previously described preparation of PS combs and PS dendrigrafts. In a first step a PS comb polymer is prepared by deactivation of polystyryllithium (PSLi) chains onto a PCEVE backbone. In the current synthesis two different types of living PSLi chains were added successively to the PCEVE backbone chain ($\overline{DP}_n$ = 845, noted $PCEVE_1$) in toluene: (a) an acetal-end functionalized PSLi (F-PS_1, $\overline{DP}_n$ = 200), in a small amount corresponding to about 3.5% of the total number of CEVE units of the backbone; (b) a nonfunctional PSLi (PS_2, $\overline{DP}_n$ = 60), in slight excess with respect to the total number of CEVE units (120%). The grafting results in the formation of wormlike PS comb cylinders with a cross-sectional diameter in direct relation to the size of the highly predominant PS_2 branches (see Scheme 1, step a). The low proportion of the longer end functional F-PS_1 branches aimed at introducing F anchoring sites at the periphery, far away from the central backbone, and randomly distributed along the comb structure.

Molar mass measurements of the PS grafted $PCEVE_1$ at the different stages of the synthesis allowed the determination of the proportion and number of F-PS_1 and PS_2 graft per chain. Data collected in Table 1 indicate that approximately 30 F-PS_1 and 620 PS_2 branches are attached to each $PCEVE_1$ backbone. This corresponds to the substitution of about 77% of CEVE units by a PS graft. An AFM image of $PCEVE_1$-*g*-(F-PS_1,PS_2) combs is presented Figure 1. As can be seen, the isolated comb macromolecules appear as wormlike structures. However, in contrast to PCEVE-*g*-PS combs, the molecules present protuberances at their surface attributed to longer F-PS_1 branches, which yield a local increase of the macromolecule section. This can be related to the very high packing density of the PS branches in the combs that forces the longer F-PS_1 to set partly outside of the comb cylinder and lay on the surface, as illustrated in Scheme 1. The average contour length of isolated macromolecules is about 250 nm. Considering the $PCEVE_1$ backbone ($\overline{DP}_n$ = 840) extended at each end by a PS branch ($2 \times \overline{DP}_n = 60$) this yields an average length per monomer units of 0.26 nm, in agreement with an almost fully stretched backbone

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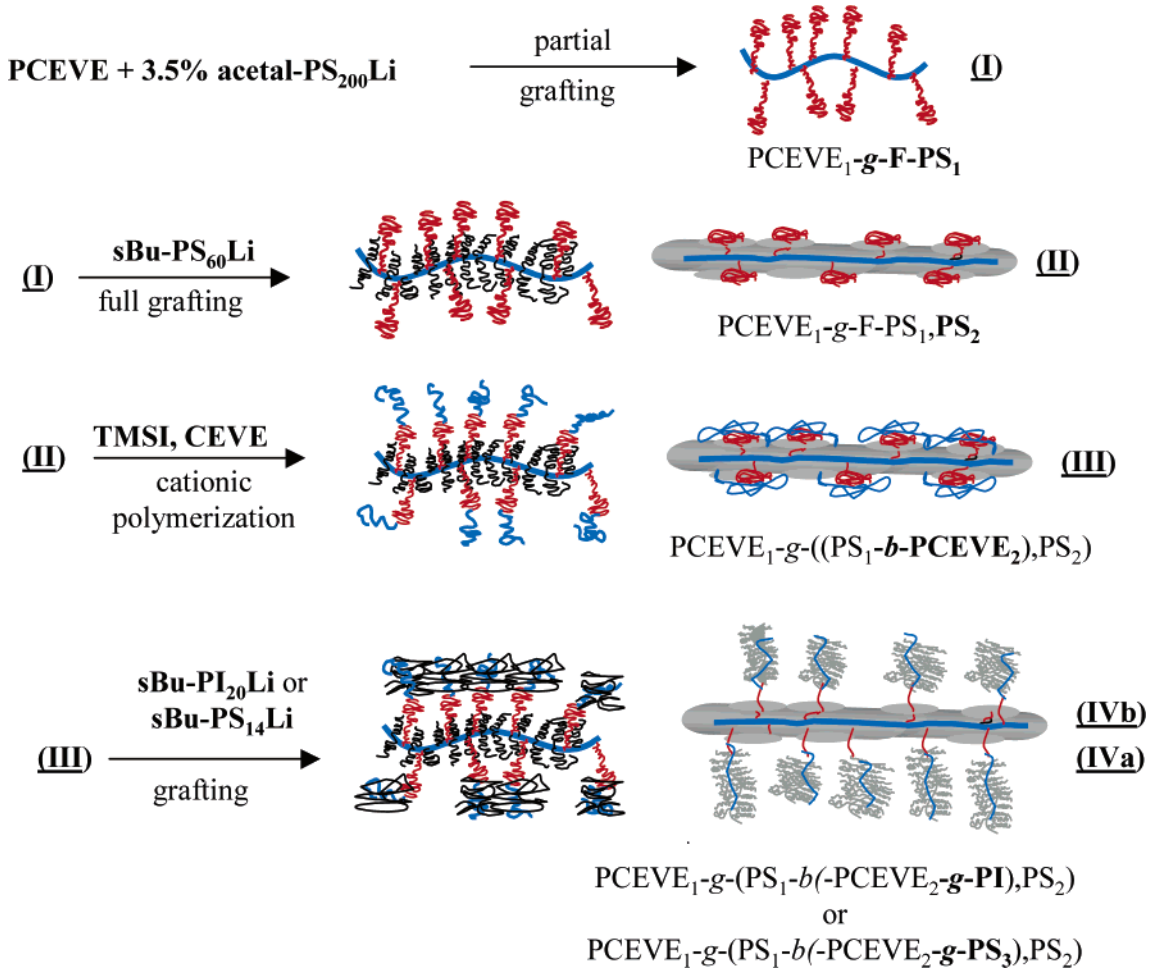
Scheme 1



chain. The average diameter of the brushes, around 24 nm, is also consistent with the PS branch $\overline{DP}_n$. However, it yields an average monomer unit length of only 0.20 nm, suggesting some chain folding likely at the periphery of the comb.

Extension of the diethylacetal-terminated F-PS_1 branches by a PCEVE block ($PCEVE_2$) yields PS combs with randomly distributed PS_1-*b*-$PCEVE_2$ branches. Their preparation was achieved as previously reported by transformation of the PS_1-acetal terminus into α-iodo ether by action of TMSI, followed by CEVE polymerization catalyzed by zinc chloride. As generally noticed in this step a small fraction of homo-PCEVE chains (homo-$PCEVE_2$) is also formed due to side initiation by hydrogen iodide formed by partial TMSI hydrolysis. The homo-$PCEVE_2$ ($\overline{DP}_n$ = 200), recovered by fractionation, was used as reference to estimate the dimensions of the $PCEVE_2$ blocks, assuming that the rate of CEVE polymerization was identical for the two initiation mechanisms. This assumption is corroborated by the relative proportion of $CEVE_2$ and S units, determined by ^{1}H NMR, in the comb copolymer, although this measure does not give access to the PCEVE block length which also depends on the initiation efficiency. The main

Table 1. Dimensions and Characteristic Parameters of the Successive Building Blocks and Final Comb Centipedes

building blocks and polymers	M_w[e] (g/mol)	I_p	R_g[f] (nm)	graft eff[g] (%)
$PCEVE_1$ backbone	9.0×10^4 ($\overline{DP}_n \approx 840$)	1.15		
F−PS_1 graft[a]	2.03×10^4 ($\overline{DP}_n \approx 200$)	1.02		
$PCEVE_1$-*g*-F-PS_1[b] (**I**)	6.15×10^5	1.10	19	$PS_1 = 3.5$
PS_2 graft[a]	6.35×10^3 ($\overline{DP}_n \approx 60$)	1.03		
$PCEVE_1$-*g*-(F-PS_1, PS_2)[b] (**II**)	4.57×10^6	1.13	43	$PS_1 = 3.5$, $PS_2 = 74$
$PCEVE_2$ lin	2.09×10^4 ($\overline{DP}_n = 200$)	1.02		
$PCEVE_1$-*g*-((PS_1-*b*-$PCEVE_2$), PS_2)[c] (**III**)	4.95×10^6 (5.20×10^6)[d]	1.16	45	$PCEVE_2 = 95$[h]
PS_3 graft	1.35×10^3 ($\overline{DP}_n \approx 13$)	1.10		
$PCEVE_1$-*g*-((PS_1-*b*-($PCEVE_2$-*g*-PS_3)), PS_2) (**IVa**)	11.70×10^6	1.11	59	$PS_3 = 80$
PI graft	1.30×10^3 ($\overline{DP}_n \approx 23$)	1.04		
$PCEVE_1$-*g*-((PS_1-*b*-($PCEVE_2$-*g*-PI)), PS_2) (**IVb**)	11.40×10^6	1.12	59	PI = 80

[a] Sampled from acetal-PS_1Li solution before grafting. [b] After elimination of residual ungrafted PS. [c] Recovered by fractionation of the crude PCEVE-*g*-((PS_1-*b*-$PCEVE_2$), PS_2)solution and elimination of the linear PCEVE. [d] M_{wth} calculated from $M_{w,PCEVE-g-(F-PS_1,PS_2)}$ + nbr of PS_1 branches(30) × (Dp_{PCEVE_2}(200) × 106.5). [e] Determined by SLS in THF at 20 °C. [f] Determined by SLS in THF at 25 °C. [g] Number of PS (or PI) branch/number of CEVE units of the $PCEVE_1$ backbone. [h] Calculated from the ratio $M_{w,th}/M_{w,SLS}$.

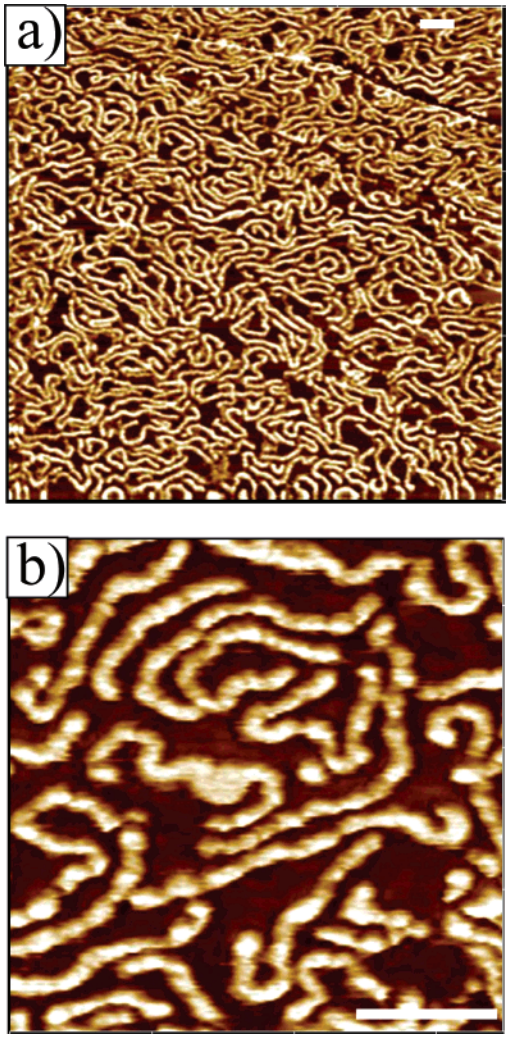


Figure 1. TMAFM images of $PCEVE_1$-*g*-((FPS_1, PS_2) combs (**II**) deposited on HOPG from dichloromethane solution. (a) Phase: 1 × 1 μm; data scale 20°; scale bar: 100 nm. (b) Phase 300 × 300 nm.

characteristics of the $PCEVE_1$-*g*-(PS_1-*b*-$PCEVE_2$,PS_2) comb copolymer are indicated in Table 1. The AFM images of the corresponding comb copolymers are shown Figure 2. The molecules appear as curved long cylinders with dimensions fully consistent with the comb precursor but with a quite different aspect attributed to partial coverage of their surface by the softer $PCEVE_2$ blocks attached to PS_1 branches.

Finally, the synthesis of comb centipedes, i.e., combs-on-PS combs, was achieved in a further step by grafting polystyryllithium (PS_3Li) or polyisoprenyllithium (PILi) onto the chloroethyl groups of the $PCEVE_2$ blocks of $PCEVE_1$-*g*-(PS_1-*b*-$PCEVE_2$,PS_2).

The molecular characteristics of the PS and PI comb centipedes are collected in Table 1. The values of the radius of gyration determined by SLS in THF show the increase in size of the macromolecules at each construction step. The final grafting step results in a strong increase, more than double, of the macromolecule molar mass and of its gyration radius despite the limited number of combs generated per macromolecules (about 30 if we refer to the number or $PCEVE_2$ blocks) and to the quite low molar mass of the PS_3 and PI grafts (1350 and 1300 g/mol, respectively). Indeed, the molar mass increase (about 6.5 × 10^6 g/mol for each) is not far from the one predicted by the calculation: $\bar{M}_n$ increase = nbre

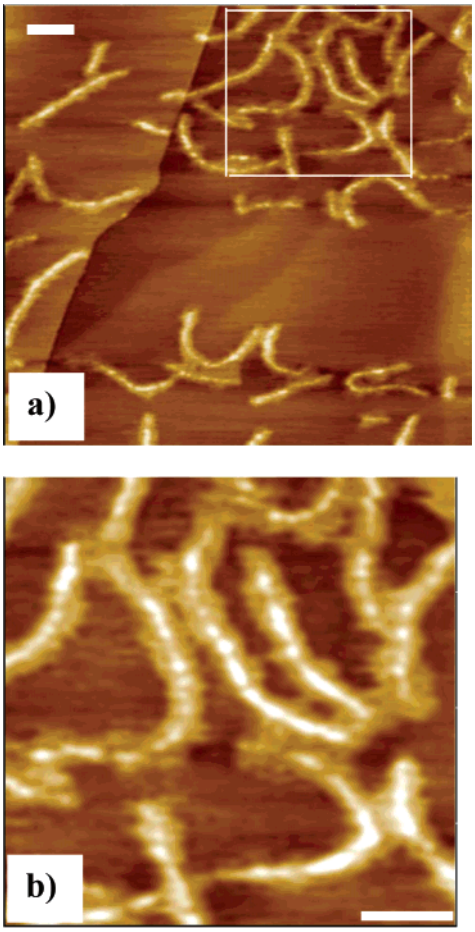


Figure 2. TMAFM height image (1 × 1 μm) of isolated $PCEVE_1$-*g*-((PS_1-*b*-$PCEVE_2$), PS_2) combs (**III**) deposited on HOPG from dichloromethane solution. (a) Data scale: 3 nm. Scale bar: 100 nm . (b) Enlarged section of (a) (×3).

$PCEVE_2$ blocks/comb × $\overline{DP}_{n,PCEVE_2}$ × $\bar{M}_{n,graft}$ = 30 × 200 × 1350 (or 1300) ≈ 8.1 × 10^6 (or 7.8 × 10^6). The experimental value corresponds to the substitution of about 80% of the CEVE units of $PCEVE_2$ blocks both for the PS and PI grafts, in good agreement with the targeted structures.

Direct vizualization of the macromolecules is a very attractive and straightforward technique for the characterization of such complex architectures. The AFM images of PS and PI centipedes are shown in Figures 3 and 4, respectively. Deposits on graphite (HOPG) obtained from evaporation of their dichloromethane solution yield the visualization of spatially arranged macromolecules. For PS comb centipedes (Figure 3a,b), despite the identical chemical composition of the central and attached peripheral combs, we can notice two distinct domains for each centipede molecule: a long white central part corresponding to the core cylindrical comb surrounded by a broad light brown nonuniform envelope constituted by the peripheral PS comb moieties. These results are consistent with the absence of interdiffusion between PS branches of central and lateral combs, in relation to the high density in branches and compactness. The presence of an internal organization in distinct subdomains in the PI centipedes is more clearly observed due to the incompatibility between the PS branches of the central comb and the PI ones constituting the peripheral combs (Figure 3c,d). The central comb backbone appears in the phase image as a thick white wormlike structure surrounded by a broad

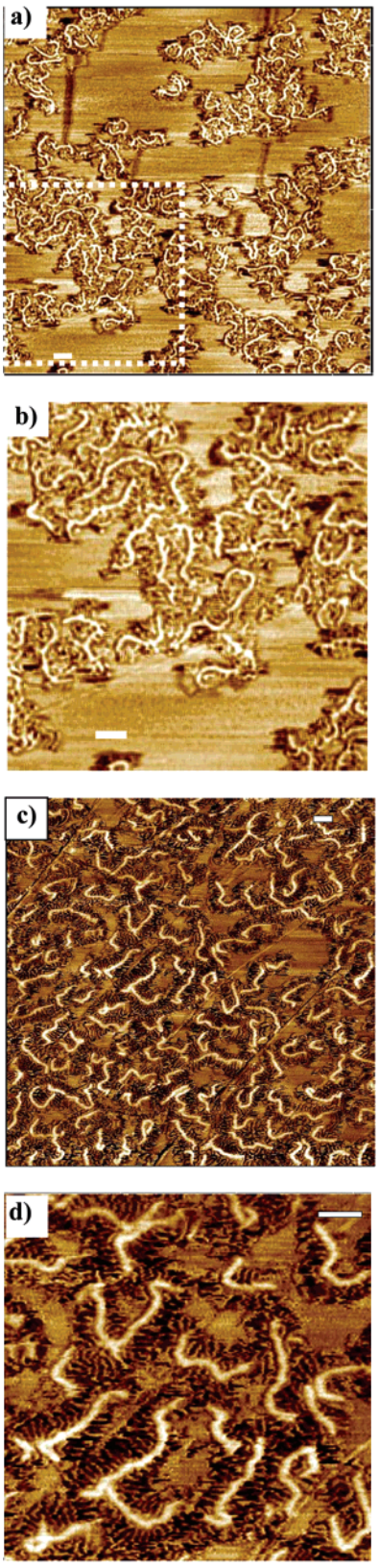


Figure 3. TMAFM images of PS and PI comb centipedes deposited on HOPG from dichloromethane solution: PCEVE$_1$-*g*-((PS$_1$-*b*-(PCEVE$_2$-*g*-PS$_3$)), PS$_2$) (**IVa**). (a) Phase: 2 × 2 μm. (b) Phase: 1.6 × 1.6 μm; data scale: 15°. PCEVE$_1$-*g*-((PS$_1$-*b*-(PCEVE$_2$-*g*-PI)), PS$_2$) (**IVb**). (c) Phase: 2 × 2 μm. (d) Phase: 800 × 800 nm; data scale: 30°. Scale bars: 100 nm.

envelope made by the alternance of dark brown and light brown bands corresponding to peripheral PI combs arranged perpendicular to the central backbone. De-

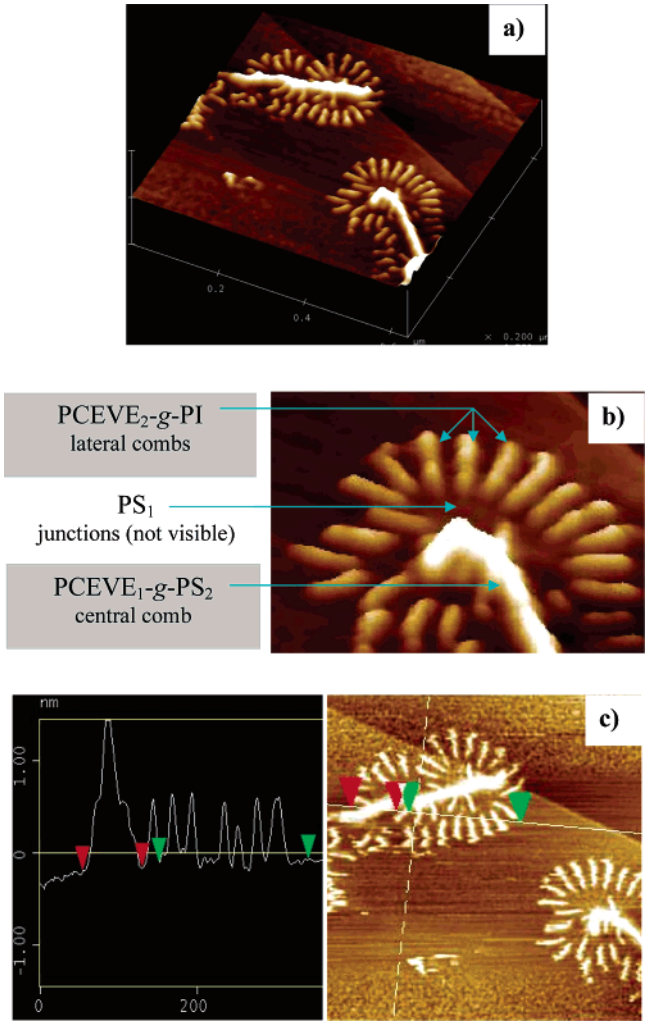


Figure 4. TMAFM of isolated PI comb centipedes PCEVE$_1$-*g*-((PS$_1$-*b*-(PCEVE$_2$-*g*-PI)), PS$_2$) (**IVb**): (a) phase image (600 × 600 nm); (b) enlarged section of (a); (c) height section analysis: 500 × 500 nm.

posits on the graphite surface obtained from more diluted solutions (10 times) allowed to observe centipedes as isolated nanoobjects (Figure 4). Their structure fully extended on graphite appears organized around a central backbone, average length 250 nm, diameter 24 nm, assigned to the central PCEVE$_1$-*g*-PS$_2$ comb. The latter is surrounded by a series of thinner brown sticks bearing a central lighter crest corresponding to PCEVE$_2$-*g*-PI combs, average length 60 and 15 nm diameter, which are arranged perpendicular to the central backbone. This yields for the lateral comb (PCEVE$_2$, $\overline{DP}_n$ = 200 extended by 2 PI $\overline{DP}_n$ = 23) an average dimension for each monomer units of about 0.24 nm, a slightly lower value than observed for the central comb. The average number of peripheral combs per macromolecule can be estimated to about 30, a value in very good agreement with the number of F-PS$_1$ grafted per PCEVE$_1$ chain. The distance between the central comb (PCEVE$_1$-*g*-PS$_2$, $\overline{DP}_n$ of PS$_2$ = 60) and the peripheral PI ones is about 30−35 nm. This closely corresponds to the F-PS$_1$ chain linkage ($\overline{DP}_n$ = 200) in almost complete extension: ($\overline{DP}_n$ F-PS$_1$ − $\overline{DP}_n$ PS$_2$) × 2.5 Å = (200 − 60) × 2.5 Å = 35 nm.

In conclusion, we have reported the synthesis of branched macromolecules constituted by the covalent

assembly of comb polymers forming new hyperbranched architectures called "comb centipedes". The step-by-step synthesis was monitored and checked by analytical and AFM techniques. Images of isolated macromolecular objects provide detailed information on the self-organization of chain segments inside each nanoobject and stress in particular the importance of packing density and compatibility between blocks of different chemical nature on the internal organization into separated compartments. The functionalization of branch termini by various organic groups and its influence on surface organization of centipedes are under investigation.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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